Chem Soc Rev



REVIEW ARTICLE

View Article Online



Cite this: Chem. Soc. Rev., 2024, **53**, 1624

Organoboron-based multiple-resonance emitters: synthesis, structure-property correlations, and prospects†

Masashi Mamada, 🕩 ‡ Masahiro Hayakawa, 🕩 ‡ Junki Ochi 🕩 ‡ and Takuii Hatakevama 🕩 *

Boron-based multiple-resonance (MR) emitters exhibit the advantages of narrowband emission, high absolute photoluminescence quantum yield, thermally activated delayed fluorescence (TADF), and sufficient stability during the operation of organic light-emitting diodes (OLEDs). Thus, such MR emitters have been widely applied as blue emitters in triplet-triplet-annihilation-driven fluorescent devices used in smartphones and televisions. Moreover, they hold great promise as TADF or terminal emitters in TADF-assisted fluorescence or phosphor-sensitised fluorescent OLEDs. Herein we comprehensively review organoboron-based MR emitters based on their synthetic strategies, clarify structure-photophysical property correlations, and provide design quidelines and future development prospects.

Received 30th September 2023 DOI: 10.1039/d3cs00837a

rsc li/chem-soc-rev

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, E-mail: hatake@kuchem.kyoto-u.ac.ip

- † Electronic supplementary information (ESI) available: List of compounds. See DOI: https://doi.org/10.1039/d3cs00837a
- ‡ These authors equally contributed to this work.

1. Introduction

Given their advantageous optical and electrochemical properties, π -conjugated compounds featuring tricoordinated sp²-hybridised boron (B_{sp2}) atoms with empty p_z orbitals have attracted significant attention in the field of materials chemistry. 1-21 The inherent



Masashi Mamada

Masashi Mamada obtained his PhD degree in 2010 from Tokyo Institute of Technology under the supervision of Prof. Yoshiro Yamashita. After working as a postdoctoral researcher in Prof. Pavel Anzenbacher's group at Bowling Green State University, USA, until 2011, he joined Innovation Center for Organic Electronics (INOEL) of Yamagata University as an assistant professor. In 2016, he moved to Prof. Chihaya Adachi's group of

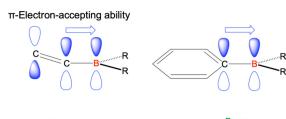
Center for Organic Photonics and Electronics Research (OPERA) at Kyushu University as an assistant professor to contribute to the Molecular Exciton Engineering Project. He is currently an associate professor in the Department of Chemistry, Graduate School of Science at Kyoto University. His research is focused on synthesis and photophysics of novel organic materials for optoelectronic applications such as OLEDs, OFETs, and organic lasers.



Masahiro Hayakawa

Masahiro Hayakawa received his BSc (2017), MSc (2019), and PhD (2022) degrees in Chemistry from Nagoya University under the supervision of Prof. Shigehiro Yamaguchi and Prof. Aiko Fukazawa. In 2022, he joined group of Prof. Takuji Hatakeyama and started his academic career as an assistant professor in the Department of Chemistry, Graduate School of Science at Kyoto University. His current research interest is the

development of unusual π -conjugated compounds.



Review Article



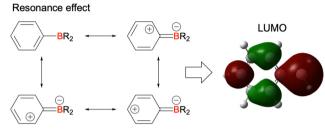


Fig. 1 Representative features of a tricoordinated sp²-hybridised boron (B_{sp2}) atom.

vulnerability of B_{sp2}-C bonds to moisture and oxygen necessitates the adoption of protective measures such as steric shielding²²⁻²⁴ (e.g., Mes₂B group (Mes = mesityl)), intramolecular π -electron donation²⁵⁻³⁴ (e.g., aza- and oxaborines), and planarity constraints335,36 (e.g., boron-doped polycyclic aromatic hydrocarbons (PAHs)) to achieve sufficient stability for use in, e.g., nonlinear optics, optoelectronics, stimuli-responsive systems, bioimaging, sensing, and catalysis. Although the observed functionalities mostly originate from the π -electron-accepting ability or Lewis acidity of B_{sp2}, the resonance effect of such

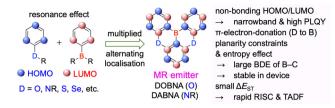


Fig. 2 Molecular design and physical properties of multiple-resonance (MR) emitters

centres has not been intentionally exploited in material design (Fig. 1).

In 2015 and 2016, a new molecular design utilising the opposite resonance effects of B_{sp2} and electron-donating atoms (e.g., oxygen³⁷ and nitrogen³⁸) at relative ortho-positions in a polycyclic aromatic skeleton was proposed by Hatakeyama et al. (Fig. 2). In such structures, the highest occupied molecular orbital (HOMO) is mainly localised on electron-donating atoms and carbons ortho/para relative to them, whereas the lowest unoccupied molecular orbital (LUMO) is mainly localised on the boron atom and carbons ortho/para relative to it in adjacent benzene rings. This alternating localisation of frontier molecular orbitals (FMOs) results in narrowband emission, high absolute photoluminescence (PL) quantum yield (Φ_{PL}), thermally activated delayed fluorescence (TADF), 39-41 and sufficient stability during the operation of organic light-emitting diodes (OLEDs). 42,43 Consequently, more than 400 organoboron-based multiple-resonance (MR) emitters have been developed 44-53 after the pioneering reports on 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (DOBNA)37 and 5,9-diaza-13b-boranaphtho[3,2,1-de]anthracene (DABNA).³⁸

For organic emitters, the full width at half maximum (FWHM) of the emission peak is generally correlated with the degree of structural relaxation in the first singlet excited state (S1).54,55



Junki Ochi

Junki Ochi received his BSc (2018), MSc (2020), and PhD (2023) degrees in Chemistry from Kyoto University under the supervision of Prof. Yoshiki Chujo and Prof. Kazuo Tanaka. In 2023, he joined of Prof. Takuji group Hatakeyama in the Department of Chemistry, Graduate School of Science at Kyoto University, as a Program-Specific Assistant Professor. His current research interest developing heteroatom-containing luminescent materials.



Takuji Hatakeyama

Takuji Hatakeyama received his PhD degree in 2005 from the University of Tokyo under the supervision of Prof. Eiichi Nakamura. After working as a postdoctoral researcher in Prof. Rustem F. Ismagilov's group at Chicago University, he joined the group of Prof. Masaharu Nakamura at Kyoto University as an assistant professor in 2006. In 2013, he initiated his independent research career as associate professor

Kwansei Gakuin University, and was promoted to a full professor in 2018. Since 2022, he has been a full professor in the Department of Chemistry, Graduate School of Science at Kyoto University. His research interests include the development of carbon-heteroatom bond formation reactions and synthesis of novel boron-based materials for optoelectronic applications.

Chem Soc Rev

номо

(L-SOMO)

LUMO

(H-SOMO)

structura >70 nn номо (L-SOMO) 400 450 500 550 600 LUMO (H-SOMO) (b) 35-50 nm номо LUMO n (L-SOMO) (H-SOMO) stretching vibration 400 450 500 550 600 ~1500 cm⁻¹ (c) <30 nm

Fig. 3 Typical vibronic spectra of (a) D–A-type, (b) LE, and (c) MR emitters.

scissoring/twisting vibration ⁰

<200 cm-

400 450 500 550 600

Wavelength /nm

The number of vibrational modes (stretching, bending, scissoring, rocking, wagging, twisting, etc.) and vibronic transitions (0-1, 0-2, 0-3, etc.) in each mode that can couple with electronic excitation and, hence, the extent of emission peak broadening, are positively correlated with the extent of structural differences between the ground (S_0) and S_1 states (Fig. 3a). This correlation is the underlying reason for the broad emission (FWHM > 70 nm) of donor-acceptor (D-A)-type emitters featuring intramolecular charge-transfer (ICT) excited states. For π -conjugated compounds with a rigid framework and no strong donor or acceptor groups (e.g., pyrene and perylene), locally excited (LE) character becomes dominant to result in narrower emission (FWHM < 50 nm). Moreover, LE emitters show small Stokes shifts (10-20 nm) because of their minimal structural relaxation in the S₁ state. However, in terms of colour purity, even LE emitters cannot compete with inorganic ones (e.g., GaN-based lightemitting diodes (LEDs)56 and CdS/ZnS quantum dots57,58) because of the unfavourable vibronic peaks with energy intervals of $\sim 1500 \text{ cm}^{-1}$ observed in the former case (Fig. 3b). 42,57,58 This behaviour indicates strong vibronic coupling between the S₁-S₀ electronic transition and stretching vibrations originating from the bonding/anti-bonding character of FMOs. 54,59 In contrast, MR emitters do not show obvious vibronic peaks because of the non-bonding character of their FMOs and feature S₁-S₀ electronic transition coupling with the scissoring/twisting vibrations at <200 cm⁻¹ and not with the stretching vibrations at $\sim 1500 \text{ cm}^{-1.60}$ As a result, all vibronic transitions with energy intervals of $< 200 \text{ cm}^{-1}$ are included in one emission peak with a FWHM of < 30 nm (Fig. 3c). Given the minimal vibronic coupling between the electronic transition and stretching vibrations, the non-radiative transition from S_1 to S_0 is efficiently suppressed, and most MR emitters therefore exhibit high Φ_{PL} (> 90%). $^{61-63}$

The pioneering work of Adachi et al. (2012)^{41,64,65} inspired numerous studies on organic TADF emitters for optoelectronic devices. Unlike conventional fluorescent emitters, which can harvest only singlet excitons, TADF emitters can harvest both singlet and triplet excitons via efficient reverse intersystem crossing (RISC) from the triplet excited (T₁) state to the S₁ state, which enables the realisation of OLEDs with internal quantum efficiencies (IQEs) of up to 100% (Fig. 4).41 According to firstorder perturbation theory, namely Fermi's golden rule, the rate constant for the RISC between two states (k_{RISC}) is proportional to the spin-orbit coupling (SOC) matrix element $(\langle S_n | \hat{H}_{SOC} | T_n \rangle)$ and inversely proportional to the exciton singlet-triplet energy gap $(\Delta E_{\rm ST})$, i.e., $k_{\rm RISC} \propto \langle S_n | \hat{H}_{\rm SOC} | T_n \rangle \exp(-\Delta E_{\rm ST} / k_{\rm B} T)$, where $k_{\rm B}$ is the Boltzmann constant and T is the absolute temperature. $^{66-69}$ To simultaneously realise a small ΔE_{ST} and sufficient transition oscillator strength (f) of conventional TADF emitters, twisted D-A structures with D and A units of variable electron-donating and -accepting abilities can be used to achieve an appropriate overlap of FMO wavefunctions. 70-73 The balance between $\Delta E_{\rm ST}$ and f can be also optimised by introducing π-spacer introduction. However, as mentioned above, D-A-type TADF emitters exhibit broad emission peaks because of their substantial structural relaxation in the S₁ state. In contrast, MR emitters feature both TADF properties and narrowband emission because their alternating HOMO-LUMO separation efficiently suppresses the exchange interaction between FMOs and vibronic coupling with stretching vibrations in excited states. Therefore, MR emitters are usually denoted as MR-TADF emitters to clearly distinguish them from D-A-type TADF emitters. From a theoretical viewpoint, MR-TADF emitters are characterised by short-range charge-transfer (CT) character and long-range electronic delocalisation in the excited state, which collectively result in a small $\Delta E_{\rm ST}$ + large f, which is ideal for TADF emitters.⁷⁴ These distinctive features enable light

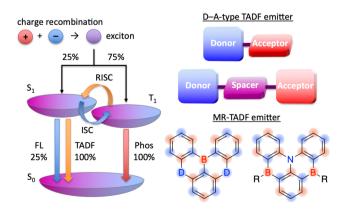


Fig. 4 HOMO-LUMO separation in D-A-type TADF and MR-TADF emitters (D = O, NR, S, Se, etc.; A = BR, CO, etc.).

amplification for solid-state laser applications despite the difficulty of lasing with most TADF materials. Table Moreover, because of their planar structures, MR-TADF emitters prefer a horizontal orientation in vacuum-deposited OLEDs, which results in high outcoupling efficiency and external quantum efficiency (EQE). Table 3-81 One drawback of MR-TADF emitters is their insufficiently fast RISC ($k_{\rm RISC} = 10^4 - 10^5 \ {\rm s}^{-1}$) due to the weak SOC between their S₁ and T_n states. Although state-of-the-art D-A-type TADF emitters exhibit strong SOC between their LE (T_n) and CT (S₁) states because of the twisted D-A structures, $^{67-74}$ the generation of sufficient SOC in the planar and rigid π -conjugated frameworks of MR emitters is challenging. $^{82-85}$

Over the last three decades, much effort has been dedicated to developing emitters based on $B_{\rm sp^2}$, $^{1-21}$ although their industrial applicability is questionable because of their rapid degradation via the cleavage of $B_{\rm sp^2}$ –C bonds during device operation (Fig. 5). This behaviour is due to the critically small bond dissociation energy (BDE)⁸⁶ of the radical-cation species that decomposes to produce a borinium ion and $C_{\rm sp^2}$ -centred radical species; the BDE (ΔH^{\ddagger}) of triphenylborane (Ph₃B) in radical-cation and neutral states is 51.1 and 116.9 kcal mol⁻¹, respectively. Although the incorporation of electron-donating atoms in phenoxaborin and phenazaborin increases the BDE (ΔH^{\ddagger}) of the radical-cation state by 35.7 and 39.0 kcal mol⁻¹, respectively, through the stabilisation of this state and destabilisation of borinium ions, the ΔG^{\ddagger} of bond dissociation is much smaller

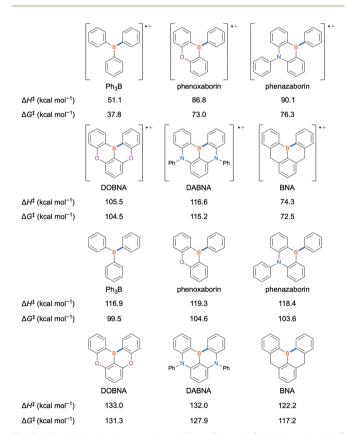


Fig. 5 Bond dissociation energies of $B_{sp^2}-C$ bonds (highlighted in blue) in representative compounds calculated at the B3LYP/6-31G(d) level of theory.

than the ΔH^{\dagger} because of the entropy gain due to the generation of two species from one. For MR emitters, the BDE (ΔH^{\dagger}) of the radical-cation state is even higher, equalling 105.5 kcal mol^{-1} for **DOBNA** and 116.6 kcal mol^{-1} for **DABNA**. Notably, the differences between the ΔH^{\dagger} and ΔG^{\dagger} BDE values of these MR emitters are negligibly small, suggesting a substantial contribution of the intramolecular (ring-fusion) effect to the suppression of bond dissociation. However, this effect alone is insufficient, as exemplified by the much smaller BDE (ΔG^{\dagger}) of 72.5 kcal mol^{-1} observed for 5,9-dihydro-13b-boranaphtho[3,2,1-de]anthracene (BNA).

These intrinsic features of MR emitters make them ideal for practical applications, as evidenced by the fact that patents have been filed for more than 3000 related molecules in the last few years. As a result, DABNA derivatives are now widely commercialised as blue emitters in triplet-triplet annihilation (TTA)-driven fluorescent devices for smartphones and televisions. 87-91 However, MR emitters have not been implemented as TADF emitters because of their rapid degradation through the long-lived T₁ state in TADF-OLEDs.⁸⁷ One of the most effective ways of realising reliable TADF devices is boosting the RISC of MR emitters. However, promising approaches such as the introduction of heavy atoms 92-95 lead to structural weakness (e.g., small BDE of heavy atoms and strain energy), which adversely affects the device lifetime despite the increased k_{RISC} . Another promising approach is the extension of the MR skeleton to enhance charge delocalisation and decrease $\Delta E_{\rm ST}$. 60,74 However, most large molecules suffer from poor synthetic efficiency or require solution-phase processing and are therefore difficult to commercialise. The use of MR emitters as terminal emitters (TEs) in TADF-assisted fluorescence (TAF, i.e., hyperfluorescence) 96-100 or phosphor-sensitised fluorescence (PSF) OLEDs 101,102 is a more promising approach, as in this case, all the intrinsic features of MR emitters (e.g., narrowband emission, high Φ_{PL} , small Stokes shift, high molar extinction coefficient, and horizontal dipole orientation) positively affect device properties. The precise adjustment of TE's ionisation potential and electron affinity of a TE is necessary to prevent carrier trapping in the emissive layer (comprising a sensitiser and host material), and thus maximise the characteristics of TAF- and PSF-based OLEDs, especially the device lifetime. However, adjustment based on the introduction of donor or acceptor groups leads to structural weakness. Establishing a molecular design that fulfils all of the requirements for practical applications requires an understanding of the available chemical space of MR emitters. Therefore, we herein comprehensively review organoboron-based MR emitters, highlight their synthetic strategies classified as one-pot borylation, one-shot borylation, and late-stage functionalisation, and establish material structure-photophysical property correlations to accelerate the practical application of these compounds in OLED displays and open up new applications that remain largely unexplored. 103,104

Given that some MR emitters have been named differently in different papers, we list all compound names in chronological order in the tables and schemes, and the earliest reported compound name is adopted as a representative one afterwards.

Table 1 List of abbreviations (general terms) used in the text

Chem Soc Rev

Abbreviations	Full meaning	Abbreviations	Full meaning
acac	Acetylacetonate	LE	Locally excited
ACQ	Aggregation caused quenching	3 LLCT	Ligand-to-ligand CT
AIE	Aggregation-induced emission	LUMO	Lowest unoccupied molecular orbital
ArLi	Aryl lithium species	MR	Multiple resonance
BDE	Bond dissociation energy	3 MLCT	Metal-to-ligand CT
Bpin	Boronic acid pinacol ester	NMR	Nuclear magnetic resonance
CT	Charge transfer	OLED	Organic light-emitting diode
CIE	Commission internationale de l'éclairage	PAH	Polycyclic aromatic hydrocarbons
CPL	Circularly polarised luminescence	$\Phi_{ m PL}$	Photoluminescence quantum yield, PLQY
D-A	Donor-acceptor	PL	Photoluminescence
$\Delta E_{ m ST}$	S_1 - T_1 energy gap	PSF	Phosphor-sensitised fluorescence
DFT	Density functional theory	RISC	Reverse intersystem crossing
EPR	Electron paramagnetic resonance	rt	Room temperature
EQE	External quantum efficiency	S _N Ar	Nucleophilic aromatic substitution reaction
equiv	Equivalent	SMe	Methylthio (group)
f	Oscillator strength	SOC	Spin-orbit coupling
FMOs	Frontier molecular orbitals	S_0	Singlet ground (state)
FWHM	Full width at half maximum	S_1	The first singlet excited (state)
$ g_{\rm PL} $	Dissymmetry values	TADF	Thermally activated delayed fluorescence
НОМО	Highest occupied molecular orbital	$\tau_{\mathbf{d}}$	Delayed fluorescence lifetime
Hyperfluorescence	TADF-assisted fluorescence (TAF)	TE	Terminal emitter
ICT	Intramolecular charge-transfer	ТТА	Triplet-triplet annihilation
³ ILCT	Intraligand CT	T_1	The first triplet excited (state)
IQE	Internal quantum efficiency	UV-Vis	Ultraviolet-visible
$k_{ m RISC}$	RISC rate constant		

If the earliest paper uses compound numbers and does not provide specific compound names, we use the earliest reported compound name instead of the number. MR emitters with no names established to date are newly named, and the name is enclosed in parentheses. In addition, we list the abbreviations for general terms (Table 1) and reagents and OLED materials (Table 2).

2. One-pot borylation

As the versatile methodology for the construction of cyclic π conjugated compounds with B_{sp2} atoms connected to aromatic residues, a "one-pot borylation" protocol has been developed in the past decade. This protocol consists of three tandem steps, namely the lithiation of carbon-hydrogen or carbonhalogen bonds by an alkyllithium reagent, transmetalation by boron tribromide (BBr3), and tandem intramolecular bora-Friedel-Crafts reaction (i.e., electrophilic C-H borylation) (Scheme 1). The final cyclisation step generally proceeds in the absence of Lewis acid additives, which are generally used as efficient promoters of electrophilic C-H borylation, 25,107-110 as the nucleophilicity of arene rings is increased by two electronrich atoms (X1 and X2 in Scheme 1). Moreover, these electrondonating atoms induce the MR effect and impart photophysical properties desirable for OLED fabrication, such as narrowband emission, high Φ_{PL} , TADF, and sufficient stability in the device. Given that the above development has inspired the design and synthesis of numerous MR-TADF optoelectronic materials, the present section overviews those prepared by one-pot borylation and classifies them according to their synthesis method. In particular, the synthesis route of one-pot borylation precursors has to be thoughtfully designed because an appropriate directing group for lithiation should be included.

2.1 DOBNA and its derivatives

2.1.1 Directed ortho-lithiation. The one-pot borylation method was first proposed by Hatakeyama et al. (2015) and relied on directed *ortho*-lithiation, *i.e.*, the ability of aromatic C-H bonds adjacent to coordinative functional groups to be lithiated in a regioselective manner.³⁷ Table 3 lists the conditions used to synthesise O,B,O-embedded DOBNA based on the selective lithiation of 1,3-diphenoxybenzene at the position between the two directing aryloxy groups. After the successive addition of n-butyllithium ("BuLi) and BBr3, the reaction mixture was supplemented with an amine and heated at 120 °C for 5 h. Screening of the reaction conditions identified the optimal amine loading as 2.0 equivalent (equiv.) (entries 1-4) and the optimal amines as N,N-diisopropylethylamine (NEt'Pr₂), 1,2,2,6,6-pentamethylpiperidine (PMP), and N,N-dimethyl-ptoluidine (entries 5-9). Under optimal conditions (entry 3), which are still regarded as the standard for one-pot borylation, DOBNA was obtained in an isolated yield of 62%.

A similar procedure was used to prepare DOBNA derivatives *via* directed *ortho*-lithiation (Fig. 6 and Table 4).^{37,111-113} In the first step, lithiation by alkyllithiums ("BuLi, *sec*-butyllithium ("BuLi), and *tert*-butyllithium ('BuLi)) proceeded at a relatively high temperature (room temperature (rt) – 90 °C) for several hours. Subsequent borylation with BBr₃ (1.2–2.0 equiv.) proceeded at rt – 50 °C, and the final intramolecular cyclisation was conducted in the presence of NEtⁱPr₂ upon heating at 100–120 °C to afford DOBNA derivatives, including those with phenoxazine (DOBNA-Phenox) and carbazole (TMCz-BO, TMCz-3P, and TDBA-Cz) functional groups, in moderate yields.

Table 2 List of abbreviations (reagents and OLED materials) used in the text

Review Article

Abbreviations	Full meaning	Abbreviations	Full meaning
AIBN	2-Azoisobutyronitrile	MeI	Iodomethane
$AlCl_3$	Aluminium chloride	MeOH	Methyl alcohol
BBr_3	Boron tribromide	2-MeTHF	2-Methyltetrahydrofuran
SCl_3	Boron trichloride	$MesB(OMe)_2$	Dimethyl mesitylboronate
BI_3	Boron triiodide	MesMgBr	Mesityl magnesium bromide
BCPO	Bis-4(<i>N</i> -carbazolyl)phenylphosphine oxide	mCPBA	3-Chloroperbenzoic acid
Bepp2	Bis[2-(2-hydroxyphenyl)-pyridine] beryllium	mCPBC	9-(3-(9 <i>H</i> -Carbazol-9-yl)phenyl)-9 <i>H</i> -3,9'-bicarbazole
BF ₃ ·Et ₂ O	Boron trifluoride diethyl ether complex	mCPCN	9-(3-(9 <i>H</i> -Carbazole-9-yl)phenyl)-9 <i>H</i> -carbazole-3-carbonitrile
Bpin) ₂	Bis(pinacolato)diboron	mMTDATA	4,4',4"-Tris(N-3-methylphenyl-N-phenylamino)triphenylamine
Bu₂O	Dibutyl ether	NaH	Sodium hydride
CBP	4,4'-Di(9 <i>H</i> -carbazol-9-yl)-1,1'-biphenyl	$NaHCO_3$	Sodium hydrogencarbonate
$\mathrm{Co_2(CO)_8}$	Octacarbonyldicobalt	NaOH	Sodium hydroxide
Cs ₂ CO ₃	Cesium carbonate	NaOAc	Sodium acetate
	Tetrakis(acetonitrile)copper(i) hexafluorophosphate	NaO ^t Bu	Sodium <i>tert</i> -butoxide
CuCl	Copper(i) chloride	Na_2CO_3	Sodium carbonate
	Copper(ii) perchlorate hexahydrate	NECO-296	Bis(di- <i>tert</i> -butyl(3-methyl-2-butenyl)phosphine)dichlo palladium
CuCN	Copper(i) cyanide	$NEt^{l}Pr_{2}$	<i>N,N</i> -Diisopropylethylamine
CuI	Copper(i) iodide	ⁿ BuLi	<i>n</i> -Butyllithium
BCTF	2,4,6-Tris(2-(3,6-di- <i>tert</i> -butyl-9 <i>H</i> -carbazol-9-yl)-5-(tri-fluoromethyl)phenyl)-1,3,5-triazine	NBS	N-Bromosuccinimide
DBFDPO	4,6-Bis(diphenylphosphoryl)dibenzofuran	NMP	N-Methyl-2-pyrrolidone
DBFPO (PPF)	Dibenzo[b , d]furan-2,8-diylbis(diphenylphosphine oxide)	NPB	N^4 , N^4 '-Di(naphthalen-1-yl)- N^4 , N^4 '-diphenyl-[1,1'-biphenyl]-4,4'-diamine
OBU	1,8-Diazabicyclo[5.4.0]undec-7-ene	PdCl ₂ (amphos) ₂	Bis[di-tert-butyl(4-dimethylaminophenyl)phosphine]dichloropalladium
26DCzPPy	$2,\!6\text{-Bis}(3\text{-}(9H\text{-}carbazol\text{-}9\text{-}yl)phenyl)pyridine$	$PdCl_2(dppf)$	[1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	PdCl ₂ (PPh ₃) ₂	Bis(triphenylphosphine)palladium(II) dichloride
DIC-TRz	11-(4,6-diphenyl-1,3,5-triazin-2-yl)-12-phenyl-11,12-dihydroindolo[2,3- <i>a</i>]carbazole	Pd(OAc) ₂	palladium(II) acetate
OMAc	<i>N,N</i> -Dimethylacetamide		Bis(tri-o-tolylphosphine)palladium(II) dichloride
OMAP	4-Dimethylaminopyridine	$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
OMF	<i>N,N</i> -Dimethylformamide	$Pd_2(dba)_3$	Tris(dibenzylideneacetone)dipalladium(0)
OMFBD-TRZ	2-(3'-(9,9-Dimethyl-9 <i>H</i> -fluoren-2-yl)-[1,1'-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine	PhBCl ₂	Dichlorophenylborane
OMMN	Dimethylmalononitrile	$PhB(OH)_2$	Phenylboronic acid
OMIC-TRZ	1,3-Dihydro-1,1-dimethyl-3-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)indeno-[2,1- <i>b</i>]-carbazole	PhCzBCz	9-(2-(9-Phenyl-9 <i>H</i> -carbazol-3-yl)phenyl)-9 <i>H</i> -3,9'-bicarbazole
OPEPO	Bis[2-(diphenylphosphino)phenyl]ether oxide	Ph_2PH	Diphenylphosphane
ltbpy	4,4'-Di- <i>tert</i> -butyl-2,2'-bipyridyl	Ph ₃ B	Triphenylborane
OTBPY	2,6-Di- <i>tert</i> -butylpyridine	PMMA	Polymethylmethacrylate
EtOH	Ethyl alcohol	PMP	1,2,2,6,6-Pentamethylpiperidine
NEt ₃	Triethylamine	P(OEt) ₃	Triethyl phosphite
eCl ₃	Iron(III) chloride	PO-T2T	2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazir
FF	Fluorenofluorene	PPF (DBFPO)	Dibenzo[b,d]furan-2,8-divlbis(diphenylphosphine
		,	oxide)
HBC	Hexabenzocoronene	PPh ₃	Triphenylphosphine
HBr	Hydrogen bromide/hydrobromic acid	PS	Polystyrene
HCl	Hydrogen chloride/hydrochloric acid	^s BuLi	sec-Butyllithium
ΗI	Hydrogen iodide/hydriodic acid	SF3TRZ	2-(9,9'-Spirobi[fluoren]-3-yl)-4,6-diphenyl-1,3,5-triazir
HOAc	Acetic acid	SiCzCz	9-(3-(Triphenylsilyl)phenyl)-9 <i>H</i> -3,9'-bicarbazole
F	Indenofluorene	SiTrzCz ₂	9,9'-(6-(3-(Triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9 <i>H</i> -carbazole)
PrOBpin rCl ₃	2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane Iridium trichloride	$SnCl_2$ $SOCl_2$	Tin(II) chloride Thionyl chloride
Ir(cod)(OCH ₃)] ₂	(1,5-Cyclooctadiene)(methoxy)iridium(ı) dimer	SPhos	2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl
(OAc	Potassium acetate	TBAF	Tetrabutylammonium fluoride
KO ^t Bu	Potassium <i>tert</i> -butoxide	^t Bu-Benzene	tert-Butylbenzene
CPF ₆	Potassium hyxafluorophosphate	^t BuLi	tert-Butyllithium
C_2CO_3	Potassium carbonate	[^t Bu ₃ PH]BF ₄	Tri- <i>tert</i> -butylphosphonium tetrafluoroborate
C_2CO_3 C_2PtCl_4	Potassium tetrachloroplatinate(II)	TBTA	Tris[(1-benzyl-1 <i>H</i> -1,2,3-triazol-4-yl)methyl]amine
C_2 P C_{14} C_3 P O_4	Tripotassium phosphate	TCTA	Tris(4-(9 <i>H</i> -carbazol-9-yl)phenyl)amine
ζ ₄ [Fe(CN) ₆]	Potassium ferrocyanide	TfOH	Trifluoromethanesulfonic acid
ALTE(CN)6] MADN	2-Methyl-9,10-bis(naphthalen-2-yl)anthracene	THF	Tetrahydrofuran
nCBP	3,3'-Di(9 <i>H</i> -carbazol-9-yl)-1,1'-biphenyl	TMS	Trimethylsilyl
порі	3′,5-Di(9 <i>H</i> -carbazol-9-yl)-[1,1′-biphenyl]-3-carbonitrile	TPSS	2,2',7,7'-Tetraphenyl-9,9'-spirobi[thioxanthene]
nCRP-CN			2.2 ././ Tenaphenyi-3.3 -Spirobilulloxallulelle
mCBP-CN mCP	1,3-Di(9 <i>H</i> -carbazol-9-yl)benzene	XPhos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbipheny

Chem Soc Rev **Review Article**

$$\begin{array}{c|c} X_1 & X_2 & RLi \\ \hline \end{array}$$

Scheme 1 General synthesis procedure of one-pot borylation.

Table 3 Synthesis of DOBNA via directed ortho-lithiation in ref. 37

1) "BuLi (1.2 equiv) 70 °C, 4 h 2) BBr ₃ (1.2 equiv) 1, 1, 1 h 0-xylene 120 °C, 5 h	DOBNA
--	-------

Entry ^a	Amine	X	$Yield^b$ [%]
1	None	0	16
2	NEt^iPr_2	1.0	62
3	$\mathrm{NEt}^i\mathrm{Pr}_2^-$	2.0	71 ^c
4	$\mathrm{NEt}^i\mathrm{Pr}_2$	3.0	44
5	NEt ₃	2.0	13
6	2,2,6,6-Tetramethylpiperidine	2.0	2
7	PMP	2.0	68
8	2,6-Lutidine	2.0	41
9	<i>N,N</i> -Dimethyl- <i>p</i> -toluidine	2.0	71 ^c

^a Reactions were carried out on a 1.0 mmol scale. ^b Yield determined by ¹H nuclear magnetic resonance (NMR) measurements using dibromomethane as an internal standard. ^c Average of two experiments.

DOBNA, DOBNA-Ph-2, DOBNA-Ph-3, and DOBNA-Phenox were later named in ref. 105.

In the case of DOBNA-Helix (Scheme 2, denoted as 4 in the original paper), which was the major product (33%) despite its sterically hindered [6]helicene substructure, borylation-cyclisation proceeded in a regioselective manner, with the less distorted isomer ("byproduct" in Scheme 2) formed in only 2%

yield. This result suggests that electronic effects (i.e. HOMO distribution) are more important than steric ones under the optimised conditions of one-pot borylation.

2.1.2 Lithium-halogen exchange. Although directed ortholithiation provides access to MR-TADF frameworks, its low reactivity and regioselectivity sometimes prevent effective borylation-cyclisation. Therefore, the development of an alternative methodology was required and borylation via lithium-halogen exchange is now widely adopted as a more practical route. This route requires the regioselective modification of 1,2,3trisubstituted benzenes to maintain a halogen atom between the two aryloxy groups. To achieve this selectivity, nucleophilic aromatic substitution (S_NAr), which proceeds preferentially on the fluorine substituent, plays an important role.

Commercially available 2-bromo-1,3-difluorobenzene is one of the most promising starting materials for one-pot borylation via lithium-halogen exchange. The first example of such synthesis was reported at the same time as the first directed ortholithiation method (Scheme 3).37 The double S_NAr reaction of 2-bromo-1,3-difluorobenzene with [1,1-biphenyl]-3-ol furnished the bromine-containing precursor in 87% yield, with subsequent one-pot borylation under standard conditions affording 2c (later named DOBNA-Ph-1, 105 or simply DOBNA-Ph 114) in 74% yield.

Fig. 7 and Table 5 summarise DOBNA derivatives synthesised using lithium-halogen exchange. 115-121 DOBNA-Ph, B1, B2-OH, BOS, BSS, and tBuAcBO were synthesised from 1bromo-2,6-difluorobenzene, while the other compounds in Fig. 7 were derived from 1,3-difluoro-2-iodobenzene.

Unlike directed ortho-lithiation, lithium-halogen exchange proceeded under mild conditions (-78 °C to rt). In addition to the oxygen-bridged precursor characteristic of DOBNA derivatives, sulphur-bridged ones could also be used (BOS and BSS). Although triazole functional groups were tolerated under

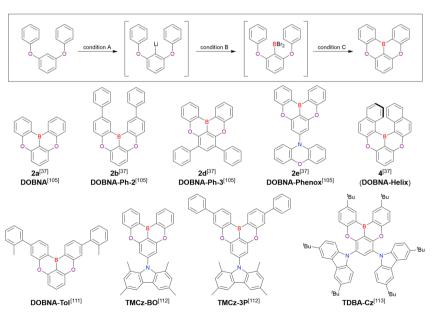


Fig. 6 DOBNA derivatives synthesised by directed ortho-lithiation

Conditions used to synthesise the compounds shown in Fig. 6

Compound	Condition A ^a	Condition B ^a	Condition C^a	Solvent	Yield [%]	Ref.
DOBNA	ⁿ BuLi (1.1)/70 °C, 4 h	BBr ₃ (1.2)/40 °C, 1 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 5 h	^t Bu-Benzene	62	37 and 105
DOBNA-Ph-2	ⁿ BuLi (1.1)/70 °C, 1 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 4 h	o-Xylene	54	37 and 105
DOBNA-Ph-3	^t BuLi (1.2)/rt, 12 h	BBr ₃ (1.5)/50 °C, 4 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 24 h	^t Bu-Benzene	42	37 and 105
DOBNA-Phenox	ⁿ BuLi (1.2)/50 °C, 12 h	BBr ₃ (1.5)/rt, 12 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 24 h	^t Bu-Benzene	56	37 and 105
DOBNA-Helix	ⁿ BuLi (1.5)/90 °C, 4 h	BBr ₃ (2.0)/rt, 13 h	NEt ⁱ Pr ₂ (2.0)/100 °C, 24 h	^t Bu-Benzene	33	37
DOBNA-Tol	^s BuLi (1.2)/70 °C, 3 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 3 h	Xylene	16	111
TMCz-BO	ⁿ BuLi (1.2)/50 °C, 4 h	BBr ₃ (1.5)/40 °C, 1 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 5 h	^t Bu-Benzene	15	112
TMCz-3P	ⁿ BuLi (1.2)/50 °C, 4 h	BBr ₃ (1.5)/40 °C, 1 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 5 h	^t Bu-Benzene	15	112
TDBA-Cz	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/140 °C, 20 h	^t Bu-Benzene	35	113

^a Numbers in parentheses refer to reagent loadings (equivalents).

Scheme 2 Regioselectivity of borylation-cyclisation reaction

Scheme 3 Synthesis of DOBNA-Ph via lithium-halogen exchange.

standard conditions, the related yields were rather low (5% for B1, 22% for B2-OH, and 6% for B3). This result suggests that the coordination of $N_{\rm sp^2}$ to boron atoms can inhibit intramolecular electrophilic C-H borylation. As discussed in the next subsection, bromine-containing products can be synthesised using the same methodology.

One indicative result is the synthesis of **B2-OH** (Scheme 4), in which the introduction of boron was accompanied by the removal of a methoxy group under the action of BBr3, and the resulting phenoxy group was used for subsequent chemical modification (Scheme 55 in Section 4). Given that the reagents used in one-pot borylation (aryllithium species (ArLi) and BBr₃) are highly reactive, one should consider functional group tolerance when designing the synthesis route.

2.1.3 Borvlation of tetrasubstituted precursors. As shown in the previous subsection, trisubstituted benzenes are the key starting materials for constructing DOBNA-based scaffolds.

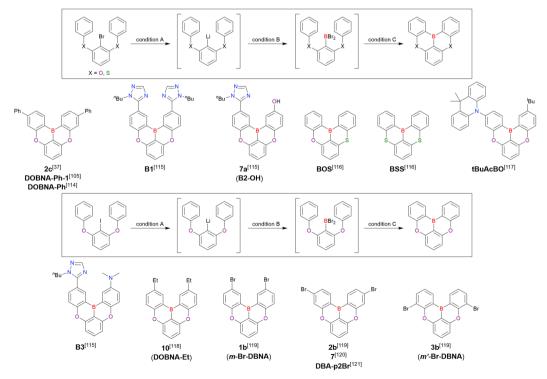


Fig. 7 DOBNA derivatives synthesised via lithium-halogen exchange.

Chem Soc Rev **Review Article**

Table 5 Conditions used to synthesise the compounds shown in Fig. 7

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
DOBNA-Ph	ⁿ BuLi (1.1)/−40 °C to rt	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/130 °C, 3 h	o-Xylene	74	37 and 105
B1	^t BuLi (2.0)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/150$ °C, 24 h	^t Bu-Benzene	5	115
B2-OH	ⁿ BuLi (1.2)/−30 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/140$ °C, 24 h	^t Bu-Benzene	22	115
BOS	ⁿ BuLi (1.1)/50 °C, 1 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/125$ °C, 12 h	<i>m</i> -Xylene	25	116
BSS	ⁿ BuLi (1.1)/50 °C, 1 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/125$ °C, 12 h	<i>m</i> -Xylene	40	116
tBuAcBO	ⁿ BuLi (2.0)/rt, 2 h	BBr ₃ (—)/rt, 2 h	NEt ⁱ Pr ₂ (—)/180 °C, 24 h	^t Bu-Benzene	16	117
B3	^t BuLi (2.0)/-30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/150$ °C, 24 h	^t Bu-Benzene	6	115
DOBNA-Et	ⁿ BuLi (1.1)/-78 °C, 10 min	BBr ₃ (1.2)/0 °C, 1 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 21 h	Toluene	30	118
m-Br-DBNA	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/140 °C, 24 h	<i>m</i> -Xylene	52	119
DBA-p2Br	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/140 °C, 24 h	<i>m</i> -Xylene	25	119
•	ⁿ BuLi (1.1)/−30 °C, 1 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/140 °C, 3 h	^t Bu-Benzene	37	120
	ⁿ BuLi (1.0)/−30 °C, 1 h	$BBr_3 (1.1)/-30$ °C to rt	$NEt^{i}Pr_{2}$ (5.0)/120 °C, 14 h	^t Bu-Benzene	72	121
m'-Br-DBNA	ⁿ BuLi (1.0)/−30 °C, 2 h	$BBr_3(1.2)/rt$, 1 h	$NEt^{i}Pr_{2}(2.0)/140$ °C, 24 h	<i>m</i> -Xylene	40	119
^a Numbers in	parentheses refer to reagent lo	adinos (equivalents)				

Scheme 4 Accompanying deprotection reaction (methoxy removal) induced by BBr₃.

Hence, tetrasubstituted benzenes were expected to be promising starting materials for accessing more diverse MR-TADF frameworks. In an early example reported by Kwon et al. (Scheme 5), 122 Br-TDBA was synthesised from 1,4-dibromo-2,6-difluorobenzene in two steps. The first step, a double S_NAr reaction, proceeded in high yield (80%) to afford the borylation precursor, and the second step involved one-pot borylation under standard conditions. Although the precursor contained two bromine atoms capable of reacting with ⁿBuLi, lithiumbromine exchange mainly proceeded at the ortho-position relative to the aryloxy groups because of their directing effect. As a result, Br-TDBA was obtained in 15% yield.

From the viewpoint of material chemistry, bromine groups are highly important because they allow for further functionalisation, as exemplified by the tuning of photophysical properties and the addition of various functionalities through the chemical modification of bromine-containing MR-TADF frameworks (see Section 4). Therefore, various bromine-containing DOBNA derivatives have been synthesised using selective lithium-halogen exchange (Fig. 8 and Table 6). 116,120,122-138

Scheme 5 Synthesis of Br-TDBA from a tetrasubstituted benzene.

The reaction temperature of the first lithium-halogen exchange was kept relatively low (-78 °C to rt), probably to suppress the undesired exchange at the remaining bromine atom. Although the yield of **Br-TDBA** was relatively low (15%) in Kwon's work, ¹²² the same product was synthesised later with up to 49% yield, 129 which suggests that lithium-halogen exchange proceeds with high selectivity. The variations in product yield probably originated from the actual concentration of alkyllithium reagents or the purity of BBr3. The effect of the halogen type (Br versus I) on the reaction yield was small, as the yields of Br-TDBA prepared from Br $(15-49\%)^{122,123,125-129}$ and I $(41\%)^{124}$ derivatives were similar. Interestingly, a pyridine-containing derivative, DOBNA-Pyr, could be synthesised in much higher yield (92%), although the detailed purification and characterisation data were not reported. 139

2.1.4 Photophysical properties. Unlike the MR effect of the recently reported MR-TADF frameworks, the MR effect of DOBNA derivatives has not been a research focus because of the low electron-donating ability of oxygen atoms. However, some reports investigated the photophysical properties of these derivatives in detail. Table 7 summarises $\lambda_{\rm PL}^{\rm max}$, FWHM, $\Phi_{\rm PL}$, $\Delta E_{\rm ST}$, and k_{RISC} values as representative photophysical parameters of the MR-TADF emitters presented in Fig. 6-8. Compounds whose photophysical data have not been reported are excluded from Table 7. Given that $\Delta E_{\rm ST}$ and $k_{\rm RISC}$ can be estimated in several ways, the values presented herein need to be compared with caution. When grafted with diarylamine and carbazolyl groups, the DOBNA scaffold acts as an electron acceptor and induces longrange D-A-type CT emission (DOBNA-Phenox, 37 TMCz-BO, 112 TMCz-3P, 112 TDBA-Cz, 113 B3, 115 and tBuAcBO117). As such emission does not fully reflect the photophysical properties derived from the MR effect, they are not discussed in this section (longrange D-A-type CT emission is reviewed in Section 4). In general, non-D-A-type DOBNA derivatives (DOBNA, 37,116 DOBNA-Ph, 37 **DOBNA-Ph-2**,³⁷ **DOBNA-Ph-3**,³⁷ **B1**,¹¹⁵ **BOS**,¹¹⁶ and **BSS**¹¹⁶) feature a high transition energy ($\lambda_{\rm PL}^{\rm max} \approx 400$ nm, T_1 = 2.9–3.0 eV), moderate Φ_{PL} (0.60–0.80), and moderate k_{RISC} (10³–10⁴ s⁻¹), and are therefore widely used as host materials for the emitting layers of OLEDs, benefiting from the high T_1 energy.

For example, OLEDs containing DOBNA-Ph and DOBNA-Ph-3 as host materials exhibited performances superior to that of

DOBNA derivatives synthesised from tetrasubstituted benzenes.

4,4'-di(9H-carbazol-9-yl)-1,1'-biphenyl (CBP) in terms of driving voltage, current efficiency, power efficiency, and external quantum efficiency at 1000 cd m⁻².37 Currently, DOBNA-Ph and DOBNA-Tol are widely used as host materials for OLEDs. Importantly, the replacement of oxygen by sulphur (BOS and BSS) causes red-shifted emission (λ_{PL}^{max} = 434 nm for **BOO** and 457 nm for **BOS**) and accelerated RISC ($k_{RISC} = 6.1 \times 10^4 \text{ s}^{-1}$ for **BOO** and $1.18 \times 10^5 \text{ s}^{-1}$ for **BOS**) because of the heavy-atom effect. ¹¹⁶

2.2 DABNA and its derivatives

2.2.1 One-pot borylation of triarylamine precursors. The one-pot borylation-based synthesis of DOBNA proposed in 2015 highlights the potential of fully cyclised π -conjugated materials containing boron and electron-rich atoms. In addition to O,B,O-embedded DOBNA-type scaffolds, O,B,S- and S,B,Sembedded frameworks can be constructed using similar procedures, as shown above. The powerful route involving an S_NAr reaction is, however, not highly effective for the synthesis of triarylamine-based N,B,N-embedded scaffolds. In 2016, Hatakeyama et al. established an alternative strategy for accessing DABNA and its derivatives (Scheme 6).³⁸

The corresponding one-pot borylation precursors were synthesised from the commercially available 1-bromo-2,3dichlorobenzene by Buchwald-Hartwig coupling. The reaction of this starting material with diphenylamine (2.2 equiv.) afforded the key borylation precursor in 66% yield (Scheme 6, left). The chlorine atom for the subsequent lithium-halogen exchange was retained because of its sterically hindered environment. A non-symmetric intermediate could be synthesised by the sequential coupling of N^1, N^1, N^3 -triphenylbenzene-1,3-diamine and di([1,1'-biphenyl]-3-yl)amine based on the difference in reactivity between bromine and chlorine atoms (Scheme 6, right). The final one-pot borylation afforded N,B,Nembedded π -conjugated compounds, **DABNA-1** and **DABNA-2**, in yields of 32% and 31%, respectively. In the case of DABNA-2, tandem electrophilic C-H borylation occurred at the paraposition relative to the diphenylamine group, probably because of its electron-donating nature and bulkiness. These processes were robust and scalable, as confirmed by the synthesis of the target compounds in amounts of 6.0 g.

The chemical structures of derivatives possessing the DABNA skeleton and the related synthesis results are summarised in

Table 6 Conditions used to synthesise the compounds shown in Fig. 8

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
Br-TDBA	ⁿ BuLi (1.1)/rt, 1 h	BBr ₃ (1.2)/45 °C, 50 min	NEt ⁱ Pr ₂ (2.0)/120 °C, 20 h	<i>m</i> -Xylene	15	122
	ⁿ BuLi (1.1)/rt, 1 h	BBr ₃ (1.2)/50 °C, 1 h	NEt ⁱ Pr ₂ (2.0)/180 °C, 10 h	<i>m</i> -Xylene	41	123
	ⁿ BuLi (1.1)/−20 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.4)/120 °C, 12 h	<i>m</i> -Xylene	41	124
	ⁿ BuLi (1.1)/rt, 1 h	BBr ₃ (1.2)/50 °C, 1 h	NEt ⁱ Pr ₂ (2.0)/180 °C, 10 h	<i>m</i> -Xylene	38	125
	ⁿ BuLi (1.1)/0 °C, 2 h	BBr ₃ (1.2)/rt, 20 min	NEt ⁱ Pr ₂ (0.9)/180 °C, 12 h	o-Dichlorobenzene	27	126
	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.4)/120 °C, 12 h	<i>m</i> -Xylene	43	127
	ⁿ BuLi (1.1)/rt, 2 h	BBr ₃ (1.2)/50 °C, 50 min	NEt ⁱ Pr ₂ (6.0)/120 °C, 20 h	Xylene	19	128
	ⁿ BuLi (1.1)/rt, 2 h	BBr ₃ (1.2)/45 °C, 1 h	NEt ⁱ Pr ₂ (2.0)/135 °C, 20 h	Xylene	49	129
Br-TOSBA	ⁿ BuLi (0.7)/rt, 1 h	BBr ₃ (0.8)/45 °C, 50 min	NEt ⁱ Pr ₂ (1.3)/120 °C, 20 h	<i>m</i> -Xylene	19	130
Br-TSBA	ⁿ BuLi (0.7)/rt, 1 h	BBr ₃ (0.8)/45 °C, 50 min	NEt ⁱ Pr ₂ (1.3)/120 °C, 20 h	<i>m</i> -Xylene	19	131
Br-DBA	ⁿ BuLi (1.1)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (3.8)/130 °C, 20 h	<i>m</i> -Xylene	20	132
	ⁿ BuLi (1.1)/−30 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (3.8)/130 °C, 20 h	<i>m</i> -Xylene	49	116
	ⁿ BuLi (1.1)/−20 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.4)/120 °C, 12 h	^t Bu-Benzene	45	124
	ⁿ BuLi (1.1)/−30 °C, 1 h	BBr_3 (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/140 °C, 3 h	<i>m</i> -Xylene	42	120
BOSBr	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr_3 (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 20 h	<i>m</i> -Xylene	44	116
BSSBr	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr_3 (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/125 °C, 20 h	<i>m</i> -Xylene	40	116
	ⁿ BuLi (1.0)/−30 °C, 2 h	BBr ₃ (1.3)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/125 °C, 20 h	<i>m</i> -Xylene	68	133
BOO-F-Br	ⁿ BuLi (1.1)/−30 °C, 2 h	BBr_3 (1.2)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 20 h	<i>m</i> -Xylene	30	132
<i>p</i> MDBA-Br	ⁿ BuLi (1.1)/rt, 2 h	$BBr_3 (1.2)/50 ^{\circ}C$, 50 min	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 20 h	<i>m</i> -Xylene	64	134
mMDBA-Br	ⁿ BuLi (1.1)/rt, 2 h	$BBr_3 (1.2)/50 ^{\circ}C$, 50 min	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 20 h	<i>m</i> -Xylene	46	134
DOBNA-Et-Br	ⁿ BuLi (1.0)/−78 °C, 10 min	BBr ₃ (1.2)/0 °C, 0.5 h	$NEt^{i}Pr_{2}$ (2.0)/110 °C, 14 h	Toluene	43	135
DOBNA-C8-Br	ⁿ BuLi (1.1)/−78 °C, 10 min	BBr ₃ (1.2)/0 °C, 10 min	NEt ⁱ Pr ₂ (2.0)/110 °C, 14 h	Toluene	34	136
BO-Br	<u></u>	b	b	b	30	137
DOBNA-Br3	ⁿ BuLi (1.1)/25 °C, 1 h	BBr ₃ (1.2)/0 °C, 1 h	NEt ⁱ Pr ₂ (1.9)/130 °C, 12 h	Xylene	61	138
DOBNA-Pyr	ⁿ BuLi (1.3)/rt, 1 h	BBr ₃ (1.3)/rt, 1 h	NEt ⁱ Pr ₂ (2.1)/120 °C, 12 h	<i>m</i> -Xylene	92	139

^a Numbers in parentheses refer to reagent loadings (equivalents). ^b Not described.

Photophysical properties of the compounds shown in Fig. 6-8

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{\text{RISC}} [s^{-1}]$	Ref.
DOBNA	CH ₂ Cl ₂ /1 wt%-PMMA ^b	398/398	—/33	0.72/0.80	0.15/0.18	$-/1.7 \times 10^3$	37
	Toluene/1 wt%-PS ^b	396/—	30/—	/0.70	0.18/—	$-/1.1 \times 10^4$	116
DOBNA-Ph	CH ₂ Cl ₂	410	_	0.60	0.31	_	37
DOBNA-Ph-2	CH_2Cl_2	410	_	0.65	0.21	_	37
DOBNA-Ph-3	CH_2Cl_2	436	_	0.57	0.14	_	37
B1	$CH_2Cl_2/5$ wt%-PMMA ^b	409/407	—/—	/0.75	0.21/—	—/—	115
BOS	Toluene/1 wt%-PS ^b	434/—	29/—	/0.63	0.17/—	$-/6.1 \times 10^4$	116
BSS	Toluene/1 wt%-PS ^b	457/—	27/—	/0.58	0.15/—	$-/1.18 \times 10^5$	116
DOBNA-Phenox ^a	1 wt%-PMMA ^b	492	_	0.92	0.06	_	37
$TMCz-BO^a$	Toluene/30 wt%-PPF ^b	446/467	—/—	0.81/0.98	-/0.020	$-/1.9 \times 10^6$	112
$TMCz-3P^a$	Toluene/30 wt%-PPF ^b	455/477	_/_	0.56/0.76	-/0.134	$-/3.3 \times 10^4$	112
$TDBA-Cz^a$	Toluene/10 wt%-DPEPO ^b /neat-film	461/456/462	43/46/41	-/1.00/0.88	0.14/—/—	$-/-/1.40 \times 10^6$	113
$B3^a$	CH ₂ Cl ₂ /5 wt%-PMMA ^b	535/497	_/_	-/0.51	0.11/—	_/_	115
tBuAcBO ^a	Toluene/5 wt%-mCP ^b	464/468	 /61	/0.66	/0.10	$-/1.24 \times 10^6$	117
		7					

^a Compounds showing long-range D-A-type CT emission. ^b See Table 2 for the full compound name.

Fig. 9 and Table 8. 38,88,102,104,140-149 In addition to 1-bromo-2,3dichlorobenzene, some studies used 1,3-dibromo-2-chlorobenzene as a starting material. t-DABNA, TBE01, TBE02, and Tp-DABNA can be viewed as a straightforward expansion of DABNA-1 via functional group addition. The diarylamine group of the precursor was changed to the 9,10-dihydroacridine group to obtain carbon-bridged MR-TADF frameworks (BN-DMAC, BN-DPAC, BN2). Similarly, structures bridged by oxygen (2PXZBN), nitrogen (TCZ-F-DABNA and BNIP-tBuDPAC), sulphur (2PTZBN, BN4, BN5, and helicene-BN), and selenium atoms (BNSSe and BNSeSe) were obtained. Moreover, a triangulene analogue, BN3, was synthesised using the basic one-pot borylation protocol. Tetrasubstituted starting materials (M-tDABNA, TPXZBN, and

DPXZCZBN) were also used, as shown for DOBNA-type compounds. The first step (lithium-chlorine exchange) proceeded in the presence of ^tBuLi at high temperatures (50–80 °C), probably because of the low reactivity of chlorine groups. In most cases, the reaction yield was moderate (20-40%).

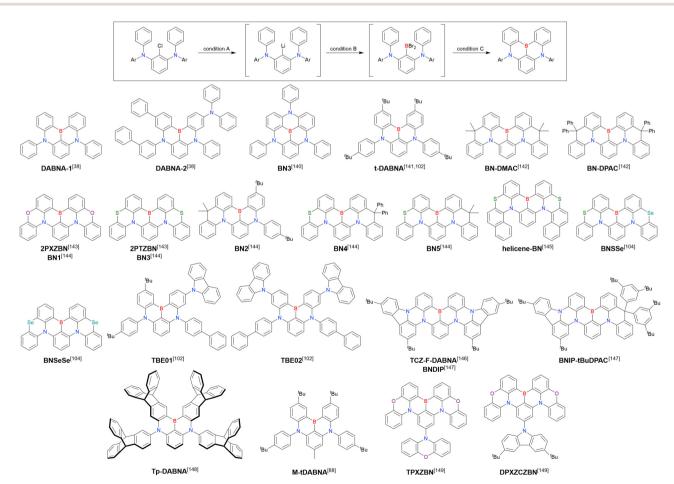
Although the replacement of chlorine with bromine is the most straightforward solution to the problem of sluggish lithium-chlorine exchange, this alternative route has been underexplored because of the commercial rarity of the corresponding starting materials. The few compounds successfully prepared from tribromobenzene are listed in Fig. 10 and Table 9. 150-152 The synthesis of these compounds, especially that of DTBA-BN2, is characterised by lithium-bromine exchange

Scheme 6 Synthesis of DABNA-1 and DABNA-2. (a) HNPh₂ (2.2 equiv.), ^tBuOK (2.5 equiv.), (AmPhos)₂PdCl₂ (1.0 mol%), o-xylene, 80 °C, 2 h then 120 °C, 3 h. (b) ^tBuLi (1.2 equiv.), ^tBu-benzene, 60 °C, 2 h; BBr₃ (1.2 equiv.), rt, 0.5 h; NEtⁱPr₂ (2.0 equiv.), 120 °C, 3 h. (c) HNPh(m-Ph₂N-C₆H₄) (1.0 equiv.), ^tBuOK (1.5 equiv.), (AmPhos)₂PdCl₂ (0.5 mol%), o-xylene, 90 °C, 2.5 h. (d) HN(m-Ph-C₆H₄)₂ (1.0 equiv.), ^tBuOK (1.5 equiv.), (AmPhos)₂PdCl₂ (1.0 mol%), o-xylene, 120 °C, 1 h. (e) ^tBuLi (2.0 equiv.), ^tBu-benzene, 60 °C, 3 h; BBr₃ (2.0 equiv.), rt, 0.5 h; NEtⁱPr₂ (2.0 equiv.), 120 °C, 1.5 h.

conditions ("BuLi, -60 °C, 1 h) that are milder than those of lithium-chlorine exchange. Thus, the choice of the halogen atom in one-pot borylation precursors should be carefully considered on the balance of reactivity and accessibility.

The one-pot borylation of a 1,3-diamino-5-carbazolylsubstituted precursor via directed ortho-lithiation was attempted as another route to synthesising DABNA derivatives (Scheme 7). 153 The resulting compound (TBN-TPA) was identified by Huang et al. as being borylated between the two diarylamine groups. This structure was later corrected (CzDABNA-NP-TB) by Hatakeyama et al., by showing that the boron atom is inserted at the carbon between the diarylamino and carbazolyl groups. 111 This behaviour can be ascribed to the less pronounced electron-donating character of carbazole groups than diarylamino groups, which can facilitate the nucleophilic reaction with ⁿBuLi at the adjacent position. Therefore, directed ortho-lithiation can suffer from unpredictable or poor regioselectivity. In particular, the directing effects of diarylamine and carbazole groups are inferior to that of aryloxy groups because of the delocalisation of the nitrogen lone pair.

2.2.2 Photophysical properties. Although DOBNA and its derivatives were the initial examples of MR-TADF emitters, the development of the one-pot borylation protocol for DABNA derivatives in 2016 enabled the development of numerous



DABNA-based MR-TADF emitters

Chem Soc Rev

Table 8 Conditions used to synthesise the compounds shown in Fig. 9

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
DABNA-1	^t BuLi (1.2)/60 °C, 2 h	BBr ₃ (1.2)/rt, 0.5 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 3 h	^t Bu-Benzene	32	38
DABNA-2	^t BuLi (2.0)/60 °C, 3 h	BBr ₃ (2.0)/rt, 0.5 h	NEt ⁱ Pr ₂ (2.0)/120 °C, 1.5 h	^t Bu-Benzene	31	38
BN3	^t BuLi (1.0)/50 °C, 0.5 h	BBr ₃ (2.1)/-45 °C	NEt ⁱ Pr ₂ (2.2)/reflux, 14 h	^t Bu-Benzene	45	140
t-DABNA	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.0)/100 ^{\circ}C, 2 h$	^t Bu-Benzene	31	141
	^t BuLi (1.2)/70 °C, 3 h	BBr ₃ (1.5)/rt, 2 h	NEt ⁱ Pr ₂ (2.0)/70 °C, 12 h	^t Bu-Benzene	21	102
BN-DMAC	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/reflux, overnight	Mesitylene	25	142
BN-DPAC	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/reflux, overnight	Mesitylene	13	142
2PXZBN	^t BuLi (2.2)/60 °C, 2 h	BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/160 °C, 24 h	Mesitylene	23	143
	^t BuLi (2.7)/60 °C, 2 h	BBr ₃ (2.8)/rt, 0.5 h	NEt ⁱ Pr ₂ (2.8)/120 °C, 3 h	^t Bu-Benzene	32	144
2PTZBN	^t BuLi (2.2)/60 °C, 2 h	BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/160 °C, 24 h	Mesitylene	25	143
	^t BuLi (2.5)/60 °C, 2 h	BBr ₃ (2.5)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.5)/120$ °C, 3 h	^t Bu-Benzene	39	144
BN2	^t BuLi (2.5)/60 °C, 2 h	BBr ₃ (2.5)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.5)/120$ °C, 3 h	^t Bu-Benzene	39	144
BN4	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.0)/120$ °C, 3 h	^t Bu-Benzene	41	144
BN5	^t BuLi (3.0)/60 °C, 2 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}(3.0)/120$ °C, 3 h	^t Bu-Benzene	39	144
helicene-BN	^t BuLi (2.2)/60 °C, 1 h	BBr ₃ (2.5)/rt, 1 h	NEt ⁱ Pr ₂ (1.2)/130 °C, 24 h	^t Bu-Benzene	15	145
BNSSe	^t BuLi (2.5)/60 °C, 5 h	BBr ₃ (2.5)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.5)/160$ °C, 14 h	Mesitylene	21	104
BNSeSe	^t BuLi (2.5)/60 °C, 5 h	BBr ₃ (2.5)/rt, 0.5 h	$NEt^{i}Pr_{2}(5.0)/160$ °C, 14 h	Mesitylene	30	104
TBE01	^t BuLi (2.0)/70 °C, 3 h	BBr ₃ (2.0)/rt, 2 h	$NEt^{i}Pr_{2}(2.4)/70$ °C, 12 h	^t Bu-Benzene	24	102
TBE02	^t BuLi (2.0)/70 °C, 3 h	$BBr_3(2.0)/rt, 2 h$	$NEt^{i}Pr_{2}(2.7)/70$ °C, 12 h	^t Bu-Benzene	21	102
TCZ-F-DABNA	^t BuLi (2.5)/60 °C, 3 h	BBr ₃ (1.5)/rt, 6 h	$NEt^{i}Pr_{2}(2.5)/130$ °C, 12 h	^t Bu-Benzene	82	146
	^t BuLi (2.2)/60 °C, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}(1.2)/130$ °C, 24 h	^t Bu-Benzene	48	147
BNIP-tBuDPAC	^t BuLi (2.2)/60 °C, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}(1.2)/130$ °C, 24 h	^t Bu-Benzene	38	147
Tp-DABNA	^t BuLi (3.0)/80 °C, 4 h	BBr ₃ (3.0)/60 °C, 1 h	$NEt^{i}Pr_{2}(3.0)/120$ °C, 12 h	^t Bu-Benzene	18	148
M-tDABNA	^t BuLi (1.2)/60 °C, 3 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/120$ °C, 12 h	^t Bu-Benzene	27	88
TPXZBN	^t BuLi (4.5)/60 °C, 2 h	$BBr_3(2.4)/rt, 0.5 h$	$NEt^{i}Pr_{2}(3.8)/120$ °C, 12 h	^t Bu-Benzene	19	149
DPXCZBN	^t BuLi (4.5)/60 °C, 2 h	BBr ₃ (2.4)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (3.8)/120 °C, 12 h	^t Bu-Benzene	15	149

^a Numbers in parentheses refer to reagent loadings (equivalents).

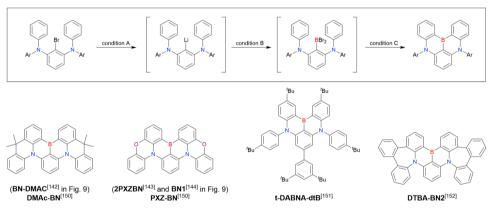


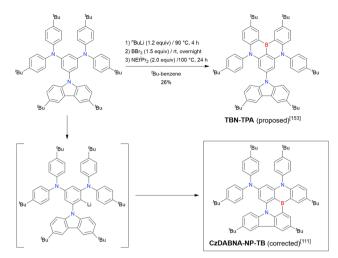
Fig. 10 DABNA derivatives synthesised by lithium-bromine exchange.

Table 9 Conditions used to synthesise the compounds shown in Fig. 10

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
DMAc-BN ^b PXZ-BN ^b t-DABNA-dtB DTBA-BN2	"BuLi (1.1)/60 °C, 0.5 h "BuLi (1.1)/60 °C, 0.5 h "BuLi (2.0)/rt, 0.5 h "BuLi (2.2)/-60 °C, 1 h	BBr ₃ (1.2)/rt, 0.5 h BBr ₃ (1.2)/rt, 0.5 h BBr ₃ (2.0)/rt, 6 h BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/110 °C, overnight NEt ⁱ Pr ₂ (2.0)/110 °C, overnight NEt ⁱ Pr ₂ (2.0)/120 °C, overnight NEt ⁱ Pr ₂ (4.0)/120 °C, 12 h	Toluene Toluene <i>o</i> -Xylene Toluene	38 41 38 40	150 150 151 152
a Numbers in pa	arentheses refer to reagent lo	adings (equivalents). ^b Sa	ame compound appeared in Fig. 9 an	d Table 8.		

MR-TADF emitters suitable for use in the emitting layers of OLEDs. In the original paper, 38 DABNA-1 and DABNA-2 were used as MR-TADF emitters in OLEDs for the first time and achieved pure blue emission at 459-467 nm with a narrow FWHM of 28 nm and an IQE of ~100%, thus achieving a record-setting performance for blue OLEDs.

Table 10 lists the photophysical properties of DABNA-based MR-TADF emitters. The most notable feature is the sharp PL



Scheme 7 Two possible chemical structures derived from the directed ortho-lithiation of a 1,3-diamino-5-carbazozyl substituted precursor.

band (FWHM = 20-40 nm) and small ΔE_{ST} (0.1-0.2 eV) due to the MR effect of boron and nitrogen atoms. Moreover, the corresponding $\Phi_{\rm PL}$ is above 0.90 in most cases, and the average λ_{PL}^{max} values (460-510 nm) are ~50 nm higher than those of DOBNA-based emitters. This spectral shift is attributed to the higher atomic orbital energies of nitrogen compared to those of oxygen, which enhances the conjugation between the lone pair of nitrogen and the π -orbitals of the benzene ring. Note that BN3, a triangulene analogue, showed relatively low Φ_{PL} , probably due to the small oscillator strength (0.1138). 140

Table 10 reveals some trends useful for designing DABNAbased emitters. BN-DMAC, DMAc-BN, BN-DPAC, and BN2 were constructed by inserting sp³-carbon into the DABNA skeleton. Compared to **DABNA-1**, the λ_{PL}^{max} bands of these materials were red-shifted (462 nm to 475-490 nm) because of the extended π -conjugation. The helical structures induced by intramolecular locking were beneficial for increasing k_{RISC} (9.9 × 10³ s⁻¹ to 2.4 × 10⁴-1.26 × 10⁵ s⁻¹).

The analysis of TCZ-F-DABNA, BNDIP, and BNIP-tBuDPAC shows that additional nitrogen atoms at ortho-positions relative to the original nitrogen atoms (i.e., at meta-positions relative to boron atoms) can extend π -conjugation and increase the bathochromic shift in PL spectra to 550 nm. 146,147 Although the k_{RISC} values are generally the same as those of DOBNA derivatives (10³-10⁴ s⁻¹), the heavy-atom effect can increase them to $> 1.0 \times 10^5 \text{ s}^{-1}$ when sulphur and/or selenium atoms are introduced, as exemplified by 2PTZBN, BN4, BNSSe, and BNSeSe. 104,143,144 The more distorted structures due to the long C-S or C-Se bonds can also increase the SOC to accelerate RISC.

Carbazole-based MR-TADF emitters 2.3

2.3.1 One-pot borylation of carbazole-based precursors. As summarised in this section, the synthesis of DOBNA and DABNA derivatives have inspired the preparation of numerous MR-TADF emitters. From a synthesis viewpoint, these two

Table 10 Photophysical properties of the compounds shown in Fig. 9 and 10

Compound	Condition	λ_{PL}^{max} [nm]	FWHM [nm]	$\Phi_{ ext{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} [\mathrm{eV}]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
DABNA-1	CH ₂ Cl ₂ /EtOH/1 wt%-mCBP ^a	462/458/460	33/36/30	0.89/0.84/0.88	/0.15/0.18	$-/-/9.9 \times 10^3$	38
DABNA-2	CH ₂ Cl ₂ /EtOH/1 wt%-mCBP ^a	470/463/469	34/34/28	0.85/0.90/0.90	-/0.15/0.14	$-/-/1.48 \times 10^4$	38
BN3	CH ₂ Cl ₂ /1 wt%-PMMA ^a	403/399	/26	0.362/0.54	/0.21	-/-	140
t-DABNA	Solution ^b /DPEPO ^a	443°/—	—/—	— /0 . 85	0.17/—	$-/2.44 \times 10^3$	141
t-DABNA	Toluene/SiCzCz:SiTrzCz ₂ ^a	456/—	21/—	0.993/—	0.21/—	$-/2.7 \times 10^3$	102
\mathbf{BN} - \mathbf{DMAC}^d	Toluene/1 wt%-mCBP ^a	485/489	29/39	— /0.63	0.14/—	$-/9.6 \times 10^4$	142
DMAc-BN ^d	2-MeTHF/3 wt%-mCBP ^a	484/—	33/—	/0.88	0.16/—	$-/2.4 \times 10^4$	150
BN-DPAC	Toluene/1 wt%-mCBP ^a	490/493	30/38	 /0 . 86	0.11/—	$-/1.26 \times 10^{5}$	142
2PXZBN ^e	Toluene/1 wt%-mCBP/PO-T2T ^a	504/515	34/40	0.78/0.84	0.19/0.18	$1.03 \times 10^5 / 0.56 \times 10^5$	143
$\mathbf{BN1}^e$	Toluene	502	41	0.61	0.20		144
PXZ-BN ^e	2-MeTHF/3 wt%-mCBP ^a	502/—	38/—	- /0 . 90	0.17/—	$-/0.9 \times 10^4$	150
2PTZBN ^f	Toluene/1 wt%-mCBP/PO-T2T ^a	510/519	39/44	0.58/0.80	0.15/0.14	$2.76 \times 10^{5}/1.17 \times 10^{5}$	143
$BN3^f$	Toluene	511	46	0.72	0.16	$1.0 imes 10^5$	144
BN2	Toluene	475	34	0.88	0.20		144
BN4	Toluene/3 wt%-mCPCN ^a	500/522	43/50	0.88/0.96	0.14/—	$1.6 \times 10^5/3.7 \times 10^4$	144
BN5	Toluene/3 wt%-mCPCN ^a	497/512	44/49	0.87/0.92	0.14/—	$7.4 \times 10^4/3.3 \times 10^4$	144
helicene-BN	Toluene/1 wt%-DMIC-TRZ ^a	520/525	46/48	/0.98	0.18/0.15	$-/4.6 \times 10^{4}$	145
BNSSe	Toluene/1 wt%-DMIC-TRZ ^a	505/520	39/—	— /0 . 99	0.17/0.12	$-/6.0 \times 10^{5}$	104
BNSeSe	Toluene/1 wt%-DMIC-TRZ ^a	502/514	38/—	/1.00	0.17/0.14	$-/2.0 \times 10^{6}$	104
TBE01	Toluene/0.4 wt%-SiCzCz:SiTrzCz ₂ ^a	459/—	21/—	0.911/—	0.16/—	$-/5.1 \times 10^{3}$	102
TBE02	Toluene/0.4 wt%-SiCzCz:SiTrzCz ₂ ^a	459/—	21/—	0.891/—	0.14/—	$-/1.03 \times 10^4$	102
TCZ-F-DABNA ^g	Toluene/8 wt%-PhCzBCz ^a	558/—	38/—	— /0 . 99	0.12/—	$-/7.80 \times 10^4$	146
$BNDIP^g$	Toluene/1 wt%-DMIC-TRZ ^a	558/584	38/61	— /0 . 96	0.13/0.09	$-/2.3 \times 10^4$	147
BNIP-tBuDPAC	Toluene/1 wt%-DMIC-TRZ ^a	544/557	43/53	/0.98	0.14/0.11	$-/1.2 \times 10^4$	147
Tp-DABNA	Toluene/2 wt%-mCBP:DPEPO ^a	458/463	19/24	0.96/0.99	0.17/0.15	$-/5.7 \times 10^3$	148
M-tDABNA	Toluene/3 wt%-MADN ^a	/461	/27	— /0 . 77	0.11/—	—/—	88
TPXZBN	Toluene/5 wt%-mCBP ^a	502/—	33/—	0.91/0.99	0.16/—	$-/4.8 \times 10^4$	149
DPXCZBN	Toluene/5 wt%-mCBP ^a	500/—	32/—	0.90/0.94	0.13/—	$-/1.11 \times 10^{5}$	149
t-DABNA-dtB	Toluene/3 wt%-mCBP ^a	465/473	22/30	— /0 . 97	0.19/—	$-/2.08 \times 10^4$	151
DTBA-BN2	Toluene/3 wt%-26DCzPPy ^a	490/496	41/—	0.96/0.97	0.13/—	$2.3 \times 10^5/4.8 \times 10^5$	152

a See Table 2 for the full compound name. b Solvent was not identified. Calculated from the reported S₁ energy in eV. d Same compound named differently. ^e Same compound named differently. ^f Same compound named differently. ^g Same compound named differently.

Chem Soc Rev **Review Article**

Synthesis of a carbazole-based MR-TADF emitter.

frameworks are complementary, with the oxygen atoms in DOBNA scaffolds inserted via an S_NAr reaction and the nitrogen atoms in DABNA scaffolds inserted via Buchwald-Hartwig coupling. Consequently, different methods of introducing nitrogen atoms are worth investigating to expand the chemical space of MR-TADF emitters. More importantly, almost all DABNA derivatives were obtained via lithium-chlorine exchange under harsh conditions because of the limited availability of starting materials. Thus, a general procedure providing access to N,B,Nembedded frameworks via lithium-bromine exchange is desired to improve functional group tolerance.

In 2020, Wang et al. reported the first MR-TADF emitter synthesised via an S_NAr reaction involving carbazolyl groups (Scheme 8). 154 The bis(di(tert-butyl)carbazolyl)phenylene parent skeleton was synthesised in 80% yield starting from 2-bromo-1,3-difluorobenzene, with the subsequent basic onepot borylation affording DtBuCzB (also known as BCzBN) in 26% yield. Similar to the case of the S_NAr substitution-based DOBNA skeleton construction, the carbazolyl group successfully and selectively substituted a fluorine atom, while the bromine atom was preserved for the subsequent one-pot borylation. Therefore, a bromine group could be easily introduced into the one-pot borylation precursor because of the commercial availability of 1-bromo-2,6-difluorobenzene.

Currently, the carbazole-based N,B,N-embedded framework (called CzBN in this review) is the one most widely used for the construction of MR-TADF emitters. The abundant methods for carbazolyl group pre-functionalisation allow numerous substructures to be attached to B,N,B-embedded frameworks (Fig. 11 and Table 11). 155-165 In most cases, the para-positions of the carbazole nitrogen atoms were pre-functionalised and used in the S_NAr-based one-pot borylation protocol. The highly functionalised carbazolyl subunits (e.g., those in BN-ICz-1, BN-ICz-2, and BN-DICz) were also completely constructed before

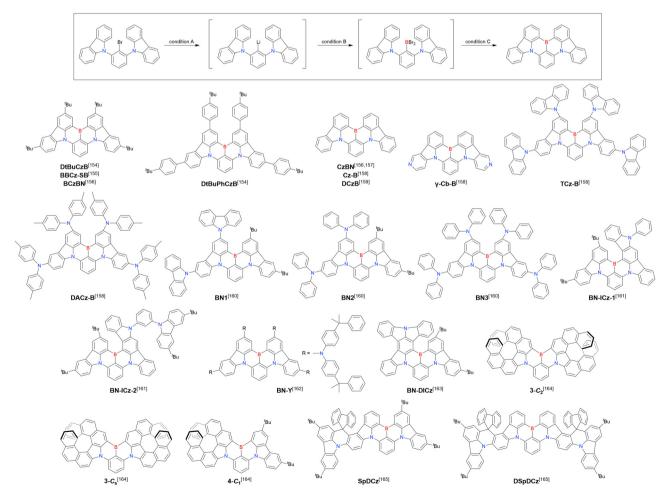


Fig. 11 Carbazole moiety-containing MR-TADF emitters.

Table 11 Conditions used to synthesise the compounds shown in Fig. 11

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref
DtBuCzB	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/130 °C, 5 h	^t Bu-Benzene	26	154
	ⁿ BuLi (1.7)/rt, 4 h	BBr ₃ (1.7)/rt, 12 h	$NEt^{i}Pr_{2}(2.7)/170$ °C, 24 h	^t Bu-Benzene	24	155
	ⁿ BuLi (1.2)/rt, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.0)/120$ °C, 3 h	^t Bu-Benzene	47	156
DtBuPhCzB	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/130$ °C, 5 h	^t Bu-Benzene	17	154
CzBN	ⁿ BuLi (1.2)/rt, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.0)/120$ °C, 3 h	^t Bu-Benzene	41	156
	ⁿ BuLi (1.2)/60 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	$NEt^{i}Pr_{2}(2.0)/110$ °C, 8 h	Toluene	29	157
	ⁿ BuLi (1.5)/rt, 2 h	BBr ₃ (1.5)/rt, 2 h	$NEt^{i}Pr_{2}(2.0)/110$ °C, 24 h	Toluene	37	158
	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	20	159
γ-Cb-B	ⁿ BuLi (2.0)/rt, 2 h	BBr ₃ (2.0)/rt, 2 h	PMP (3.0)/170 °C, 24 h	^t Bu-Benzene	12	158
TCz-B	ⁿ BuLi (1.1)/0 °C, 1 h	BBr ₃ (1.2)/rt, 2 h	$NEt^{i}Pr_{2}$ (2.0)/140 °C, 18 h	o-Xylene	56	158
DACz-B	ⁿ BuLi (1.1)/0 °C, 1 h	BBr ₃ (1.2)/rt, 2 h	$NEt^{i}Pr_{2}$ (2.0)/170 °C, 32 h	^t Bu-Benzene	12	158
BN1	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	21	160
BN2	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	41	160
BN3	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	35	160
BN-ICz-1	ⁿ BuLi (3.0)/60 °C, 24 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (4.5)/120 °C, 5 h	^t Bu-Benzene	23	161
BN-ICz-2	ⁿ BuLi (3.0)/60 °C, 24 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (4.5)/120 °C, 5 h	^t Bu-Benzene	22	161
BN-Y	^t BuLi (2.0)/40 °C, 2 h	BBr ₃ (1.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 8 h	^t Bu-Benzene	82	162
BN-DICz	ⁿ BuLi (3.0)/60 °C, 24 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (4.5)/120 °C, 5 h	^t Bu-Benzene	22	163
$3-C_2/3-C_s$	ⁿ BuLi (2.5)/rt, 4 h	BBr ₃ (3.0)/rt, 15 h	$NEt^{i}Pr_{2}$ (3.5)/175 °C, 24 h	o-Dichlorobenzene	18	164
$4-C_1$	ⁿ BuLi (2.3)/rt, 4 h	BBr ₃ (3.0)/rt, 15 h	$NEt^{i}Pr_{2}$ (3.5)/175 °C, 24 h	o-Dichlorobenzene	19	164
SpDCz	ⁿ BuLi (1.1)/40 °C, 1 h	BBr ₃ (3.1)/50 °C, 3 h	$NEt^{i}Pr_{2}$ (3.1)/125 °C, 20 h	<i>m</i> -Xylene	65	165
DSpDCz	ⁿ BuLi (1.1)/40 °C, 1 h	BBr ₃ (3.1)/50 °C, 3 h	$NEt^{i}Pr_{2}$ (3.1)/125 °C, 20 h	<i>m</i> -Xylene	58	165

^a Numbers in parentheses refer to reagent loadings (equivalents).

being merged into the central phenyl ring. Even an aza[7]helicene subunit could be introduced into the MR-TADF framework $(3-C_2, 3-C_5, 4-C_1)$.

In addition to di-carbazolyl frameworks, a combination of carbazolyl and chalcogen groups was easily achieved using sequential nucleophilic substitutions followed by basic one-pot borylation (Fig. 12, Table 12). 94,166-171 Oxygen-bridged (CzBO, BON-DO, BON-D1, BON-D2, CzBNO, and SOBN) and sulphur-bridged (CzBS and Cz-BSN) compounds were successfully prepared from 2-bromo-1,3-difluorobenzene. Additionally, selenium-bridged

compounds were demonstrated, which was not addressed in previous subsections. The corresponding precursors were synthesised from 2-bromo-3-fluoroaniline using a Sandmeyer-type reaction (CzBSe)94 or from 2-bromo-1,3-difluorobenzene using an S_NAr reaction (Cz-BSeN). 169

Carbazole-based MR-TADF emitters derived from tetrasubstituted benzene can be accessed in a similar manner as DOBNA- and DABNA-based ones (Fig. 13, 14 and Tables 13, 14). 172-187 Although a methoxy group was deprotected by BBr3 in the one-pot borylation procedure (Scheme 4), the methylthio (SMe)

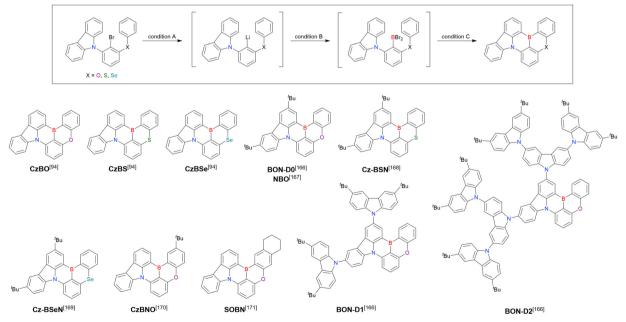


Fig. 12 MR-TADF emitters synthesised by sequential S_NAr reactions.

This journal is © The Royal Society of Chemistry 2024

Table 12 Conditions used to synthesise the compounds shown in Fig. 12

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
CzBO	ⁿ BuLi (1.1)/−30 °C, 1 h	BBr ₃ (1.2)/rt, 2 h	NEt ⁱ Pr ₂ (2.0)/140 °C, 12 h	^t Bu-Benzene	28	94
CzBS	ⁿ BuLi (1.1)/−30 °C, 1 h	BBr ₃ (1.2)/rt, 2 h	$NEt^{i}Pr_{2}(2.0)/140$ °C, 12 h	^t Bu-Benzene	36	94
CzBSe	ⁿ BuLi (1.1)/−30 °C, 1 h	BBr ₃ (1.2)/rt, 2 h	$NEt^{i}Pr_{2}(2.0)/140$ °C, 12 h	^t Bu-Benzene	32	94
BON-D0	ⁿ BuLi (1.1)/60 °C, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}(2.0)/120$ °C, 5 h	<i>m</i> -Xylene	31	166
	ⁿ BuLi (1.1)/60 °C, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (2.0)/110 °C, overnight	Toluene	17	167
Cz-BSN	ⁿ BuLi (1.1)/60 °C, 2 h	BBr ₃ (1.2)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/130 °C, 24 h	o-Xylene	20	168
Cz-BSeN	ⁿ BuLi (1.1)/50 °C, 2 h	$BBr_3 (1.2)/-30$ °C, 0.5 h	$NEt^{i}Pr_{2}(2.0)/130$ °C, 48 h	<i>o</i> -Xylene	15	169
CzBNO	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/140 °C, 24 h	^t Bu-Benzene	32	170
SOBN	ⁿ BuLi (4.0)/90 °C, 2 h	BBr ₃ (4.0)/rt, 1 h	NEt ⁱ Pr ₂ (11)/120 °C, 12 h	^t Bu-Benzene	20	171
BON-D1	ⁿ BuLi (1.0)/60 °C, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 5 h	<i>m</i> -Xylene	23	166
BON-D2	ⁿ BuLi (1.0)/60 °C, 2 h	BBr ₃ (1.2)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 5 h	<i>m</i> -Xylene	22	166
	, ,	, f	, ,	-		

^a Numbers in parentheses refer to reagent loadings (equivalents).

group was preserved under the same conditions (BN(p)SCH₃, Fig. 13). Bromine-containing compounds suitable for subsequent chemical modification were also obtained (BNCz-Br and BNCz-Br-Cz2, Fig. 14).

At this point, one should mention some indicative results. In 2023, the synthesis of indole-fused MR-TADF frameworks was reported (Scheme 9). The first attempt to obtain the nonsubstituted indole derivative **InBN** failed in the borylation part, probably because the reactive β -position of the indole unit inhibited the desired reaction during the electrophilic borylation step. Hence, methyl-protected precursors were prepared

and smoothly converted into indole-based MR-TADF emitters (TMInBN, Mes-InBN, Cz-InBN, and TCz-InBN) with yields of 8-12%.

As described in Section 2.1.3, the synthesis of bromine-substituted MR-TADF skeletons is an intriguing topic. In particular, sulphur- and selenium-containing compounds are favourable for improving the TADF character. **Br-Cz-BSN** and **Cz-BSeN-Br** were successfully synthesised as heavy-atom-containing MR-type building blocks (Scheme 10). Similar to the synthesis of bromo-containing DOBNA derivatives (Section 2.1.3), the commercial availability of the starting material,

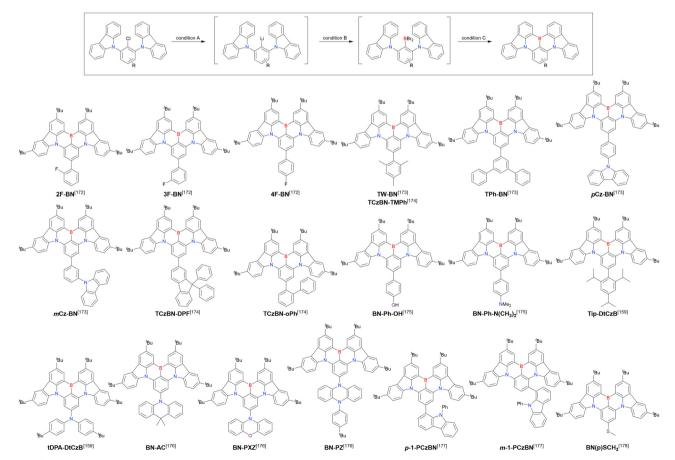


Fig. 13 Carbazole-based MR-TADF emitters synthesised from tetrasubstituted benzene (1).

Review Article

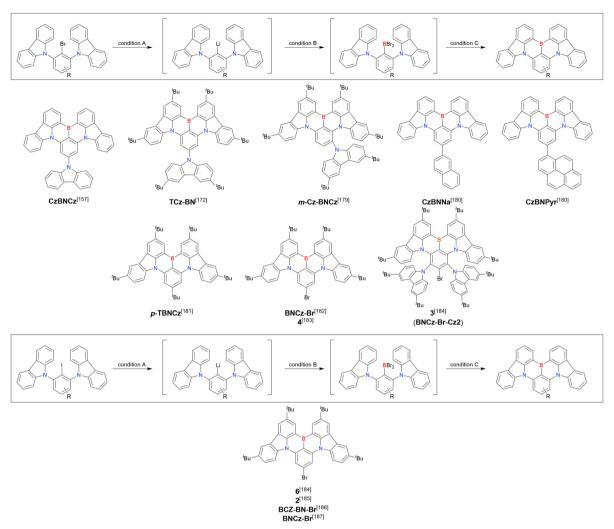


Fig. 14 Carbazole-based MR-TADF emitters synthesised from tetrasubstituted benzene (2).

Table 13 Conditions used to synthesise the compounds shown in Fig. 13

Compound	Condition A ^a	Condition B ^a	Condition C^a	Solvent	Yield [%]	Ref.
2F-BN	^t BuLi (3.0)/60 °C, 2 h	BBr ₃ (3.0)/rt, 0.5 h	NEt ⁱ Pr ₂ (4.8)/120 °C, 5 h	^t Bu-Benzene	25	172
3F-BN	^t BuLi (3.0)/60 °C, 2 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (4.8)/120 °C, 5 h	^t Bu-Benzene	31	172
4F-BN	^t BuLi (3.0)/60 °C, 2 h	BBr ₃ (3.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (4.8)/120 °C, 5 h	^t Bu-Benzene	26	172
TW-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	32	173
	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	35	174
TPh-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	25	173
pCz-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	22	173
mCz-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	20	173
TCzBN-DPF	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	34	174
TCzBN-oPh	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 5 h	^t Bu-Benzene	38	174
BN-Ph-OH	ⁿ BuLi (1.5)/70 °C, 2 h	BBr ₃ (1.8)/rt, 0.5 h	NEt ⁱ Pr ₂ (2.5)/120 °C, 10 h	^t Bu-Benzene	20	175
BN-PhN(CH3)2	ⁿ BuLi (1.5)/70 °C, 2 h	BBr ₃ (1.8)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (2.5)/120 °C, 10 h	^t Bu-Benzene	18	175
Tip-DtCzB	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	38	159
tDPA-DtCzB	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	$NEt^{i}Pr_{2}$ (2.0)/130 °C, 6 h	^t Bu-Benzene	25	159
BN-AC	^t BuLi (2.9)/90 °C, 2 h	BBr ₃ (2.9)/rt, 2 h	$NEt^{i}Pr_{2}$ (8.0)/130 °C, 24 h	^t Bu-Benzene	44	176
BN-PXZ	^t BuLi (2.9)/90 °C, 2 h	BBr ₃ (2.9)/rt, 2 h	$NEt^{i}Pr_{2}$ (8.0)/130 °C, 24 h	^t Bu-Benzene	59	176
BN-PZ	^t BuLi (2.9)/90 °C, 2 h	BBr ₃ (2.9)/rt, 2 h	NEt ⁱ Pr ₂ (8.0)/130 °C, 24 h	^t Bu-Benzene	34	176
p-1-PCzBN	^t BuLi (4.0)/80 °C, 2 h	BBr ₃ (4.5)/rt, 40 min	NEt ⁱ Pr ₂ (4.0)/125 °C, 17 h	^t Bu-Benzene	92	177
m-1-PCzBN	^t BuLi (4.0)/80 °C, 2 h	BBr ₃ (4.5)/rt, 40 min	NEt ⁱ Pr ₂ (4.0)/125 °C, 17 h	^t Bu-Benzene	45	177
BN(p)SCH ₃	^t BuLi (3.0)/60 °C, 2 h	$BBr_3 (3.0)/rt, 0.5 h$	$NEt^{i}Pr_{2}$ (5.0)/120 °C, 5 h	Mesitylene	21	178

^a Numbers in parentheses refer to reagent loadings (equivalents).

Chem Soc Rev

Table 14 Conditions used to synthesise the compounds shown in Fig. 14

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref
CzBNCz	ⁿ BuLi (1.2)/60 °C, 2 h	BBr ₃ (1.2)/rt, 2 h	NEt ⁱ Pr ₂ (2.4)/110 °C, 10 h	Toluene	34	157
TCz-BN	^t BuLi (3.0)/60 °C, 2 h	$BBr_3 (3.0)/rt, 0.5 h$	$NEt^{i}Pr_{2}(4.8)/120$ °C, 5 h	^t Bu-Benzene	22	172
m-Cz-BNCz	^t BuLi (2.0)/60 °C, 2 h	$BBr_3(2.0)/rt$, 1 h	$NEt^{i}Pr_{2}(2.0)/130$ °C, 6 h	^t Bu-Benzene	15	179
CzBNNa	ⁿ BuLi (1.2)/60 °C, 2 h	BBr ₃ (1.5)/rt, 2 h	$NEt^{i}Pr_{2}(2.2)/110$ °C, 10 h	Toluene	28	180
CzBNpyr	ⁿ BuLi (1.2)/60 °C, 2 h	BBr ₃ (1.5)/rt, 2 h	$NEt^{i}Pr_{2}$ (2.3)/110 °C, 10 h	Xylene	35	180
p-TBNCz	^t BuLi (2.0)/60 °C, 4 h	$BBr_3(2.0)/rt, 6 h$	$NEt^{i}Pr_{2}(4.0)/120$ °C, 24 h	^t Bu-Benzene	52	181
BNCz-Br	ⁿ BuLi $(1.1)/-0$ °C to rt	$BBr_3 (2.0)/rt, 0.5 h$	$NEt^{i}Pr_{2}(2.0)/180$ °C, 12 h	Mesitylene	74	182
	ⁿ BuLi (1.1)/60 °C, 2 h	$BBr_3 (1.2)/rt, 0.5 h$	$NEt^{i}Pr_{2}$ (2.0)/120 °C, 5 h	<i>m</i> -Xylene	55	183
	ⁿ BuLi (1.1)/−60 °C, 1 h	$BBr_3 (1.5)/rt, 1 h$	$NEt^{i}Pr_{2}(4.0)/120$ °C, 8 h	Toluene	42	184
	ⁿ BuLi (1.1)/rt, 3 h	$BBr_3 (1.5)/rt, 3 h$	$NEt^{i}Pr_{2}$ (2.3)/160 °C, 24 h	^t Bu-Benzene	31	185
	ⁿ BuLi (1.1)/−78 °C, 3 h	$BBr_3 (1.5)/rt, 1 h$	$NEt^{i}Pr_{2}(4.0)/130$ °C, 8 h	Toluene	20	186
	ⁿ BuLi (1.2)/rt, 1 h	$BBr_3 (1.5)/rt, 1 h$	$NEt^{i}Pr_{2}(4.0)/130$ °C, 10 h	Xylene	16	187
BNCz-Br-Cz2	ⁿ BuLi (1.1)/−60 °C, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}(4.0)/120$ °C, 8 h	Toluene	45	184

^a Numbers in parentheses refer to reagent loadings (equivalents).

Synthesis of indole-based MR-TADF emitters reported in ref. 188.

1,4-dibromo-2,6-difluorobenzene, and the regioselectivity of aryloxy group-directed lithium-halogen exchange make these

Scheme 10 Synthesis of sulphur- and selenium-containing MR-TADF emitters.

compounds easily accessible. Given that the remaining bromo group facilitates subsequent chemical modification, these compounds can be versatile platforms for the synthesis of various types of functional emitters.

A one-pot multiple cyclisation method for synthesising highly substituted MR-TADF molecules via a combination of imino nitrogen-centred radical-based cyclisation and borylation-cyclisation was proposed in 2020 (Scheme 11). 189 The cyano-substituted starting material was prepared by Suzuki-Miyaura coupling, and AZA-BN was obtained in 20% yield under optimal conditions (3.0 equiv. of n BuLi and 4.8 equiv. of BBr₃). Lower reagent ratios resulted in failed boron introduction, which indicated that the addition of ⁿBuLi to the CN group occurred prior to the substitution of the chlorine atom. In addition, other lithium reagents such as phenyllithium and ^tBuLi did not give the desired product.

Recently, a novel boron-bridged compound, DBCz-Mes, was synthesised from a dibrominated precursor (Scheme 12). 91 Two boron atoms were simultaneously introduced using 2.4 equiv. of "BuLi and BBr3, and the reactive B-Br site remaining after intramolecular cyclisation was trapped by a mesityl Grignard reagent (MesMgBr) to afford DBCz-Mes in a total yield of 23%,

Scheme 11 Synthesis of aza-fused MR-TADF emitters reported in ref. 189.

Scheme 12 Synthesis of the boron-bridged compound reported in ref. 91.

which is as high as those of other general one-pot borylation protocols.

Although tri- and tetrasubstituted MR-TADF emitters can be easily accessed from commercially available starting materials, the synthesis of penta- and hexa-substituted N,B,N-embedded frameworks require multi-step chemical modification towards borylation precursors (Scheme 13 and Table 15). 155,190-194 BBCz-Y, BBCz-G, and BN-2Cz were conveniently obtained through the simultaneous introduction of multiple carbazolyl groups. Highly cyclised compounds, NBNP, VTCzBN, TCz-VTCzBN, and PPZ-BN, were synthesised in a stepwise manner using intramolecular cyclisation. Finally, the synthesis of TRZCzPh-BNCz, TRZTPh-BNCz, and TPh-BNCz involved iodination after the introduction of carbazolyl groups via a substitution reaction. The final one-pot borylation step was achieved via directed ortho-lithiation or lithium-halogen exchange under standard conditions.

2.3.2 Photophysical properties. As summarised above, the construction of MR-TADF frameworks via S_NAr reactions is currently the most common procedure because of their uncomplicated nature and the ready availability of the starting materials (1-bromo-2,6-difluorobenzene and its family). Additionally, coupling partners with carbazole- and chalcogen-containing substituents can also be endowed with diverse structures through pre-functionalisation. Therefore, the resulting MR-TADF emitters show diverse photophysical properties (Tables 16 and 17). As discussions of specific examples are outside the scope of this review, we briefly summarise the overall trends.

First, compared to that of DABNA derivatives, λ_{PL}^{max} shifts to longer wavelengths. For example, the simplest carbazole-based MR-TADF compound, CzBN, exhibits a PL maximum at 479 nm in CH₂Cl₂ solution, which is red-shifted by 17 nm relative to that of DABNA-1. 156 This change is attributed to the extension of π -conjugation and the increase in the ICT localisation area for a more efficient MR effect. Overall, simple carbazole-based MR-TADF emitters cover the PL colour range of sky-blue, green, and yellow, with blue emission remaining difficult to achieve, except for examples utilising pyridine units (γ-CB-B¹⁵⁸) or oxygen bridges (CzBO, 94 BON-D0, 166 and CzBNO 170). The carbazole unit is more rigid and planar than carbon-, oxygen-, sulphur-, and selenium-bridged diarylamino units, which are included in some compounds listed in Fig. 9 and 10. This is

Scheme 13 Penta- and hexa-substituted MR-TADF emitters

Chem Soc Rev **Review Article**

Table 15 Conditions used to synthesise the compounds shown in Scheme 13

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
BBCz-Y	ⁿ BuLi (1.5)/rt, 4 h	BBr ₃ (1.5)/rt, 12 h	NEt ⁱ Pr ₂ (2.4)/170 °C, 24 h	^t Bu-Benzene	28	155
	ⁿ BuLi (2.1)/rt, 4 h	BBr ₃ (2.1)/rt, 2 h	$NEt^{i}Pr_{2}$ (2.1)/160 °C, 6 h	^t Bu-Benzene	15	190
BBCz-G	ⁿ BuLi (1.5)/rt, 4 h	BBr ₃ (1.5)/rt, 12 h	$NEt^{i}Pr_{2}$ (2.4)/170 °C, 24 h	^t Bu-Benzene	23	155
BN-2Cz-tBu	ⁿ BuLi (2.1)/rt, 4 h	BBr ₃ (2.1)/rt, 2 h	$NEt^{i}Pr_{2}$ (2.1)/160 °C, 6 h	^t Bu-Benzene	17	190
NBNP	ⁿ BuLi (3.0)/70 °C, 1 h	BBr ₃ (4.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (2.9)/130 °C, 20 h	^t Bu-Benzene	14	191
TPh-BNCz	ⁿ BuLi (1.5)/rt, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}$ (4.0)/180 °C, 12 h	o-Dichlorobenzene	37	192
TRZCzPh-BNCz	ⁿ BuLi (1.5)/rt, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}(4.0)/180$ °C, 12 h	o-Dichlorobenzene	35	192
TRZTPh-BNCz	ⁿ BuLi (1.5)/rt, 1 h	BBr ₃ (1.5)/rt, 1 h	$NEt^{i}Pr_{2}(4.0)/180$ °C, 12 h	o-Dichlorobenzene	43	192
VTCzBN	^t BuLi (4.0)/70 °C, 1 h	BBr ₃ (4.4)/rt, 0.5 h	$NEt^{i}Pr_{2}(3.7)/130$ °C, 24 h	^t Bu-Benzene	15	193
TCz-VTCzBN	^t BuLi (4.0)/70 °C, 1 h	BBr ₃ (4.4)/rt, 0.5 h	$NEt^{i}Pr_{2}(3.7)/130$ °C, 24 h	^t Bu-Benzene	10	193
PPZ-BN	ⁿ BuLi (3.0)/rt, 1 h	$BBr_3 (3.0)/rt, 5 h$	NEt ⁱ Pr ₂ (4.5)/120 °C, 12 h	Xylene	21	194

^a Numbers in parentheses refer to reagent loadings (equivalents).

beneficial for obtaining small FWHMs (generally 20-30 nm) in the solution state. On the other hand, planarity often induces intermolecular interactions with the host material and causes PL spectrum broadening (10-20 nm). To overcome this drawback, peripheral bulky substituents have been introduced. For example, dicarbazole-based symmetric compounds, TCzBN-DPF, 174 TCzBN-oPh, 174 p-1-PCzBN, 177 m-1-PCzBN, 177 DBCz-Mes, 91 and TRZCzPh-BNCz, 192 successfully suppressed spectral broadening within 3 nm, even in host materials. In addition, the highly planar carbazole-based MR skeleton is disadvantageous for accelerating RISC (k_{RISC} typically below 1.0 \times 10⁵ s⁻¹). Thus, TAF and PSF OLEDs are often fabricated to achieve high EL performance. 97-100,102

Second, electron-donating groups at the para-position of nitrogen (also the meta-position of boron) cause a drastic bathochromic shift in the PL spectra. Tables 16 and 17 list numerous examples of PL wavelength tuning; generally, $\lambda_{\rm PL}^{\rm max}$ can be increased to >500 nm by introducing one or more electron-donating groups. In some cases, PL wavelengths

exceeding 550 nm (572 nm for DACz-B, 158 562 nm for BN3, 160 567 nm for BN-Y, 162 and 613 nm for PPZ-BN 194) were realised through peripheral functionalisation. The other photophysical parameters, namely FWHM, Φ_{PL} , ΔE_{ST} , and k_{RISC} , are comparable to those of DABNA-type MR-TADF emitters.

2.4 Other routes to MR-TADF emitters based on one-pot borylation

2.4.1 Combination of two complementary reactions. Previous subsections overviewed the synthetic routes to DOBNA, DABNA, and CzBN frameworks. The merging of S_NAr and Buchwald-Hartwig coupling reactions is another powerful route used to access other MR-TADF skeletons. In 2021, Yang et al. reported the sequential construction of a carbazoletriarylamine-fused compound, DPACzBN1, starting from 1bromo-2-chloro-3-fluorobenzene (Scheme 14). 195 The successive introduction of 9H-carbazole and diphenylamine moieties afforded the key intermediate in 49% yield (two steps). Although the following one-pot borylation required harsh

Table 16 Photophysical properties of the compounds shown in Fig. 11

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{ m PL}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
DtBuCzB ^a	Toluene/1 wt%-mCBP ^b	481/493	22/35	0.91/0.88	0.13/—	—/—	154
$BBCz-SB^a$	Toluene/2 wt%-mCBP ^b	489/490	23/25	0.98/0.98	0.15/—	$1.4 \times 10^4/2.0 \times 10^4$	155
\mathbf{BCzBN}^a	CH ₂ Cl ₂ /EtOH/toluene/neat film	497/—/—/517·571	—/—/—/—	—/—/0.863/—	/0.11//-	$-/-/1.48 \times 10^4/-$	156
DtBuPhCzB	Toluene/1 wt%-mCBP ^b	496/508	21/43	0.97/0.90	0.09/—	—/—	154
\mathbf{CzBN}^c	CH ₂ Cl ₂ /EtOH/toluene/neat film	479/—/—/502·570	—/—/—/—	—/—/0 . 871/—	/0.12//-	$-/-/1.69 \times 10^4/-$	156
\mathbf{CzBN}^c	Toluene/1 wt%-mCBP	473/485	25/32	0.91/0.99	0.15/—	$-/1.24 \times 10^4$	157
\mathbf{Cz} - \mathbf{B}^c	Toluene/1 wt%-mCBP ^b	477/484	25/30	0.98/0.97	0.14/—	$1.2 \times 10^4/2.7 \times 10^4$	158
\mathbf{DCzB}^{c}	Toluene/1 wt%-PhCzBCz ^b	474/484	24/36	0.81/0.78	0.13/—	$-/5.0 \times 10^3$	159
γ-Cb-B	Toluene/1 wt%-oCBP ^b	460/461	23/30	0.83/0.89	0.12/—	$3.1 \times 10^4 / 5.8 \times 10^4$	158
TCz-B	Toluene/1 wt%-mCBP	512/517	27/31	1.00/0.89	0.09/—	$2.0 \times 10^4/1.3 \times 10^4$	158
DACz-B	Toluene/1 wt%-mCBP	572/576	34/44	0.87/0.87	0.14/—	$1.8 \times 10^4 / 1.0 \times 10^4$	158
BN1	Toluene/1 wt%-mCBP	496/499	23/38	0.99/0.93	0.11/—	$-/1.9 \times 10^{5}$	160
BN2	Toluene/1 wt%-mCBP	534/538	30/41	0.98/0.89	0.13/—	$-/1.5 \times 10^{5}$	160
BN3	Toluene/1 wt%-mCBP	562/563	30/44	0.98/0.86	0.09/—	$-/1.4 \times 10^{5}$	160
BN-ICz-1	Toluene/3 wt%-3CTF:mCBP	521/522	21/24	0.992/0.98	0.22/—	$2.9 \times 10^4/-$	161
BN-ICz-2	Toluene/3 wt%-3CTF:mCBP ^b	521/522	22/24	0.983/0.97	0.18/—	$6.4 \times 10^4 / -$	161
BN-Y	Toluene	567	34	0.95	0.12	_	162
BN-DICz	Toluene/3 wt%-mCBP ^b	533/534	20/32	0.994/—	0.26/—	$7.8 \times 10^4/$ —	163
$3-C_2$	Toluene/2-MeTHF	543/544	23/—	0.72/—	 /0.35	—/—	164
$3-C_{\rm s}$	Toluene/2-MeTHF	546/546	23/—	0.78/—	 /0.35	—/—	164
$4-C_1$	Toluene/2-MeTHF	520/523	28/—	0.85/—	/0.32	_/_	164
SpDCz	Toluene/1 wt%-mCP ^b	498/498	26/29	/0.97	0.14/—	$-/3.1 \times 10^{5}$	165
DSpDCz	Toluene/1 wt%-mCP ^b	505/505	25/31	— /0 . 99	0.12/—	$-/3.0 \times 10^{5}$	165

^a Same compound named differently. ^b See Table 2 for the full compound name. ^c Same compound named differently.

Review Article

Table 17 Photophysical properties of the compounds shown in Fig. 12-14 and Schemes 9, 11-13

Compound	Condition	$\lambda_{PL}^{max} \left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\rm ST}$ [eV]	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
CzBO	Toluene/1 wt%-mCBP ^a	445/448	26/29	0.98/0.99	0.15/0.16	$-/9.0 \times 10^{3}$	94
CzBS	Toluene/1 wt%-mCBP ^a	471/472	28/30	0.99/0.98	0.11/0.14	$4.0 \times 10^5/2.2 \times 10^5$	94
CzBSe	Toluene/1 wt%-mCBP ^a	477/479	33/34	0.98/0.98	0.12/0.15	$1.5 \times 10^8/1.8 \times 10^8$	94
$\mathbf{BON} ext{-}\mathbf{D0}^{b}$	Toluene/5 wt%-mCP ^a	450/—	23/—	 /0 . 85	0.18/—	$-/6.73 \times 10^4$	166
\mathbf{NBO}^b	Toluene/3 wt%-mCBP ^a	448/458	25/45	— /0 . 99	/0.103	$-/1.2 \times 10^4$	167
BON-D1	Toluene/5 wt%-mCP ^a	476/—	28/—	/0.94	0.14/—	$-/7.72 \times 10^4$	166
BON-D2	Toluene/5 wt%-mCP ^a	472/—	31/—	 /0 . 98	0.10/—	$-/9.81 \times 10^4$	166
Cz-BSN	Toluene/1 wt%-PS ^a	476/—	24/—	/0.82	0.13/—	$-/9.6 \times 10^4$	168
Cz-BSeN	Toluene/1 wt%-PS ^a	479/—	30/—	 /0 . 87	0.15/—	$-/7.5 \times 10^6$	169
CzBNO	Toluene/3 wt%-26DCzPPy ^a	443/450	23/30	— /0 . 96	0.21/—	$-/3.47 \times 10^4$	170
SOBN	Toluene/5 wt%-26DCzPPy ^a	449/—	22/—	0.78/0.82	0.19/—	$-/1.4 \times 10^4$	171
2F-BN	Toluene/6 wt%-mCPBC ^a	494/—	24/—	 /0 . 887	0.16/—	$-/2.2 \times 10^4$	172
3F-BN	Toluene/6 wt%-mCPBC ^a	499/—	24/—	/0.834	0.08/—	$-/3.9 \times 10^4$	172
4F-BN	Toluene/6 wt%-mCPBC ^a	496/—	25/—	/0.914	0.11/—	$-/4.4 \times 10^4$	172
$TW-BN^c$	Toluene/3 wt%-mCBP ^a	486/485	20/25	0.86/0.92	0.12/—	$-/7.56 \times 10^3$	173
TCzBN-TMPh ^c	Toluene/1 wt%-SF3TRZ ^a	486/487	23/25	/0.94	0.12/—	$-/1.83 \times 10^4$	174
TPh-BN	Toluene/3 wt%-mCBP ^a	492/495	21/28	0.91/0.94	0.09/—	$-/1.43 \times 10^4$	173
pCz-BN	Toluene/3 wt%-mCBP ^a	491/496	21/30	0.90/0.95	0.15/—	$-/6.42 \times 10^3$	173
mCz-BN	Toluene/3 wt%-mCBP ^a	495/494	21/29	0.85/0.88	0.14/—	$-/1.64 \times 10^4$	173
TCzBN-DPF	Toluene/1 wt%-SF3TRZ ^a	491/495	24/26	/0.969	0.13/—	$-/3.92 \times 10^4$	174
TCzBN-oPh	Toluene/1 wt%-SF3TRZ ^a	489/491	23/24	-/0.961	0.14/—	$-/1.62 \times 10^4$	174
BN-Ph-OH	Toluene/3 wt%-mCBP ^a	485/494	26/—	/0.80	0.14/—	$-/2.85 \times 10^4$	175
BN-PhN(CH3)2	Toluene/3 wt%-mCBP ^a	486/500	24/—	/0.71	0.14/—	$-/8.10 \times 10^4$	175
Tip-DtCzB	Toluene/1 wt%-PhCzBCz ^a	477/486	19/29	0.96/0.95	0.13/—	$-/9.2 \times 10^3$	159
tDPA-DtCzB	Toluene/1 wt%-PhCzBCz ^a	470/484	21/30	0.86/0.85	0.11/—	$-/2.45 \times 10^4$	159
BN-AC	Toluene/15 wt%-mCBP ^a	479/484	26/—	—/0.94	0.14/—	$-/1.1 \times 10^{5}$	176
BN-PXZ	Toluene/15 wt%-mCBP ^a	480/486	28/—	—/0.97	0.12/—	$-/7.5 \times 10^{5}$	176
BN-PZ	Toluene/15 wt%-mCBP ^a	634/610	82/—	/0.98	0.03/—	$-/1.85 \times 10^6$	176
p-1-PCzBN	Toluene/4 wt%-26DCzPPy ^a	$489/495^{d}$	$25/26^d$	—/0.92	0.14/—	$-/7.0 \times 10^4$	177
m-1-PCzBN	Toluene/4 wt% 26DCzPPy ^a	$502/500^d$	$27/30^d$	—/0.95	0.09/—	$-/6.3 \times 10^4$	177
CzBNCz	Toluene/1 wt%-mCBP ^a	465/470	22/26	0.92/0.95	0.18/—	$-/7.6 \times 10^3$	157
TCz-BN	Toluene	477	22/20		0.1 0/	/7.0 × 10	172
m-Cz-BNCz	Toluene/solid/1 wt%-PhCzBCz ^a	519/521/520	38/39/47	0.97/—/0.92	0.08/—/—	$-/-/8.6 \times 10^5$	179
CzBNNa	Toluene/1 wt%-mCBP ^a	483/487	25/29	0.78/0.98	0.15/—	$-/3.07 \times 10^4$	180
CzBNpyr	Toluene/1 wt% mCBP ^a	480/485	25/29	0.85/0.90	0.15/—	_/	180
p-TBNCz	Toluene/1 wt%-PhCzBCz ^a	484/490	23/29	0.92/0.92	0.13/—	$-/ -/1.4 \times 10^4$	181
TMInBN	Toluene/1 wt%-FIGZBGZ Toluene/1 wt%-mCPBC ^a	$475/480^d$	$23/29$ $23/31^d$	0.66/—	0.39/—	4.6×10^4 /—	188
Mes-InBN	Toluene/1 wt% mCPBC ^a	475/479 ^d	$23/31$ $23/40^d$	0.70/—	0.40/—	$4.6 \times 10^{4}/-$	188
Cz-InBN	Toluene/1 wt%-mCPBC ^a	$470/479$ $470/470^d$	$\frac{23}{40}$ $\frac{22}{30}^d$	0.66/—	0.41/—	$5.9 \times 10^4/$ —	188
TCz-InBN	Toluene/1 wt%-mCPBC ^a	$470/470$ $470/473^d$	$\frac{22}{30}$ $\frac{22}{45}^d$	0.69/—	0.41/—	$5.4 \times 10^4/-$	188
AZA-BN	Toluene/4 wt%-mCBP ^a	522/526	28/36	0.69/—	0.42/—	$5.4 \times 10 / -/7.53 \times 10^3$	189
AZA-BN DBCz-Mes	Toluene/1 wt%-mCBP	452/452	28/36 14/16	0.99/0.94	0.18/—	$\frac{-7.53 \times 10}{2.9 \times 10^4/-}$	91
BBCz-Wes	Toluene/2 wt%-mCBP ^a	452/452 549/549	42/48	0.85/0.90	0.14/—	$2.9 \times 10 / -$ $1.0 \times 10^{5} / 1.1 \times 10^{5}$	155
BN-2Cz- <i>t</i> Bu ^e	Toluene	543	42/40	0.84	0.14/—	$1.0 \times 10 / 1.1 \times 10$ 1.39×10^5	190
BBCz-G	Toluene/2 wt%-mCBP ^a	543 517/519	34/50	0.90/0.99		$1.8 \times 10^{5}/1.9 \times 10^{5}$	155
BN-2Cz- <i>t</i> Bu	Toluene	522	34/30	0.70	0.14/— —	$1.8 \times 10 / 1.9 \times 10$ 1.83×10^5	190
			$\frac{-}{29/33^d}$		0.09/—	$-/3.0 \times 10^5$	190
NBNP	Toluene/4 wt%-mCBP ^a	500/502 ^d	49/33 24/27 ^d	—/0.93			
TRZCzPh-BNCz	Toluene/3 wt%-CBP ^a	514/516	$34/37^d$	0.930/0.976	0.13/—	$2.13 \times 10^6/8.8 \times 10^5$	192
TRZTPh-BNCz	Toluene/3 wt%-CBP ^a	513/516	29/33 ^d	0.947/0.990	0.11/—	$1.55 \times 10^6 / 7.5 \times 10^5$	192
TPh-BNCz	Toluene	509	33				192
VTCzBN	Toluene/4 wt%-26DCzPPy ^a	496/—	34/—	/0.98	0.06/—	$-/1.0 \times 10^6$	193
TCz-VTCzBN	Toluene/4 wt%-26DCzPPy ^a Toluene/0.5 wt%-CBP ^a	521/— 613/619	29/— 48/59	/0.98 0.88/0.82	<0.01/— 0.25/—	$-/0.9 \times 10^6$ $2.2 \times 10^4/-$	193 194
PPZ-BN							

^a See Table 2 for the full compound name. ^b Same compound named differently. ^c Same compound named differently. ^d Taken from the EL spectrum. ^e Same compound named differently.

conditions because of the sluggishness of lithium-chlorine exchange, the N,B,N-embedded skeleton, DPACzBN1, was formed in 13% yield.

MR-TADF emitters synthesised by similar protocols are summarised in Fig. 15 and Table 18. 103,147,170,195-199 As all compounds were derived from 1-bromo-2-chloro-3-fluorobenzene, the final borylation step was conducted under harsh conditions. The phenothiazine group could be introduced using both S_NAr (PTZBN1)196 and Buchwald-Hartwig coupling (Cz-PTZ-BN)197,198 reactions.

2.4.2 Late-stage bromination. The first DOBNA framework was synthesised via directed ortho-lithiation (see Section 2.1.1). Subsequently, borylation via lithium-halogen exchange became the most common one-pot borylation procedure. In this case, the halogen atom required for borylation is already contained in the starting material, and electron-rich substituents are sequentially introduced using the remaining key halogen atoms. As an alternative route, bromination just before borylation was attempted in some reports (Scheme 15 and Table 19). 191,200,201 The ortho-position of the two carbazolyl groups was easily

Chem Soc Rev Review Article

Scheme 14 Example of sequential MR-TADF precursor construction reported in ref. 195.

brominated by $\mathrm{Br_2}$ or *N*-bromosuccinimide (NBS), probably because of the directing effect of these electron-donating groups. In the synthesis of **NBO** and **LTCz-BN**, bromination and subsequent one-pot borylation were conducted without purification. Although the synthesis of **tCzphB-ph** and **tCzphB-Fl** consisted of two independent steps, the first bromination by NBS proceeded in an almost quantitative yield. This late-stage bromination

procedure can facilitate the synthesis of complex structures, as it helps to avoid the use of difficult-to-obtain starting materials such as highly substituted benzenes.

2.4.3 Stepwise borylation and cyclisation. MR-TADF frameworks are generally constructed by one-pot methods with BBr₃ as a boron source. In some reports, an alternative stepwise procedure was applied (Fig. 16 and Table 20).^{202–204} In this procedure, the key intermediate possessing a boronic acid pinacol ester (Bpin) group is synthesised in high or moderate yield by the sequential addition of ⁿBuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ⁱPrOBpin) to a bromine-containing precursor, with the subsequent intramolecular bora-Friedel–Crafts reaction affording fully cyclised target compounds.

The intermediate can be either isolated (**B-O-dpa**, **B-O-Cz**, **B-O-dmAc**, **B-dpa-Cz**, **B-dpa-dmAc**, and **B-dpa-SpiroAc**) or used without purification (**Br-DBA** and **B-O-dpAc**). Notably, **Br-DBA** was also synthesised by the basic one-pot borylation method (Fig. 8 and Table 6) with a comparable total yield ($\sim 40\%$). 120,124

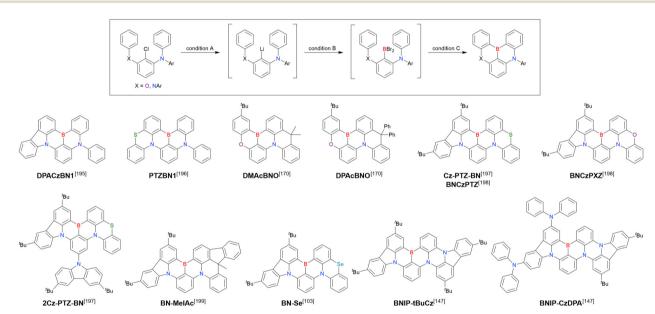
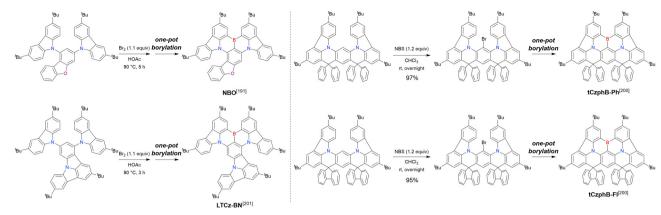


Fig. 15 MR-TADF emitters synthesised by sequential electrophilic aromatic substitution and Buchwald-Hartwig coupling reactions.

Table 18 Conditions used to synthesise the compounds shown in Fig. 15

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
DPACzBN1	^t BuLi (2.0)/80 °C, 3 h	BBr ₃ (2.0)/rt, 3 h	NEt ⁱ Pr ₂ (2.0)/180 °C, 24 h	Mesitylene	13	195
PTZBN1	^t BuLi (2.4)/60 °C, 2 h	BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/160 °C, 24 h	Mesitylene	25	196
DMAcBNO	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/140 °C, 24 h	^t Bu-Benzene	25	170
DPAcBNO	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/140 °C, 24 h	^t Bu-Benzene	32	170
Cz-PTZ-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 6 h	^t Bu-Benzene	22	197
	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 8 h	^t Bu-Benzene	20	198
BNCzPXZ	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 8 h	^t Bu-Benzene	18	198
2Cz-PTZ-BN	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 6 h	^t Bu-Benzene	16	197
BN-MelAc	^t BuLi (2.0)/60 °C, 2 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 24 h	Mesitylene	35	199
BN-Se	^t BuLi (2.0)/60 °C, 3 h	BBr ₃ (2.0)/rt, 1 h	NEt ⁱ Pr ₂ (2.0)/150 °C, 12 h	^t Bu-Benzene	34	103
BNIP-tBuCz	^t BuLi (2.2)/60 °C, 1 h	BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (1.2)/130 °C, 24 h	^t Bu-Benzene	54	147
BNIP-CzDPA	^t BuLi (2.2)/60 °C, 1 h	BBr ₃ (1.5)/rt, 1 h	NEt ⁱ Pr ₂ (1.2)/130 °C, 24 h	^t Bu-Benzene	40	147

^a Numbers in parentheses refer to reagent loadings (equivalents).



Scheme 15 MR-TADF emitters synthesised via late-stage bromination

Table 19 Conditions used to synthesise the compounds shown in Scheme 15

Compound	Condition A ^a	Condition B ^a	Condition C^a	Solvent	Yield [%]	Ref.
NBO	ⁿ BuLi (3.0)/70 °C, 1 h	BBr ₃ (4.0)/rt, 0.5 h	NEt ⁱ Pr ₂ (2.9)/130 °C, 18 h	^t Bu-Benzene	12 (2 steps)	191
tCzphB-Ph	ⁿ BuLi (1.5)/-40 °C, 2 h	BBr ₃ (2.9)/rt, overnight	NEt ⁱ Pr ₂ (2.9)/130 °C, 4 h	^t Bu-Benzene	61	200
tCzphB-Fl	ⁿ BuLi (1.5)/-40 °C, 2 h	BBr ₃ (2.9)/rt, overnight	NEt ⁱ Pr ₂ (2.9)/130 °C, 4 h	^t Bu-Benzene	55	200
LTCz-BN	^t BuLi (4.0)/70 °C, 1 h	BBr ₃ (4.2)/rt, 0.5 h	NEt ⁱ Pr ₂ (3.2)/130 °C, 24 h	^t Bu-Benzene	10 (2 steps)	201

^a Numbers in parentheses refer to reagent loadings (equivalents).

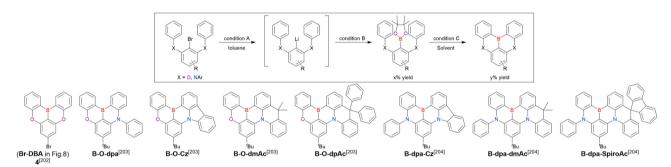


Fig. 16 MR-TADF emitters synthesised by stepwise borylation-cyclisation.

2.4.4 Photophysical properties. The photophysical properties of the compounds discussed in Section 2.4 are summarised in Table 21. Although a wide variety of structures are included, their properties are in line with previous discussions in Sections 2.1.4, 2.2.2, and 2.3.2.

2.5 Simultaneous introduction of two boron atoms

2.5.1 One nitrogen and two boron atoms. In 2019, Hatakeyama et al. developed a boron-enriched MR-TADF material, azadiboranaphthoanthracene (ADBNA), which contains two boron atoms and one nitrogen atom and corresponds to

Table 20 Conditions used to synthesise the compounds shown in Fig. 16

Compound	Condition A ^a	Condition B ^a	x [%]	Condition C ^a	Solvent	y [%]	Ref.
Br-DBA	ⁿ BuLi (—)/rt, 2 h	ⁱ PrOBpin (1.2)/rt, 2 h	_	AlCl ₃ (4.8)/100 °C, 3 h	Toluene	37 (2 steps)	202
B-O-dpa	ⁿ BuLi (1.2)/−20 °C, 1 h	ⁱ PrOBpin (3.0)/rt, 1 h	65	$AlCl_3$ (4.0), $NEt^i Pr_2$ (5.0)/110 °C, 2 h	Chlorobenzene	43	203
B-O-Cz	ⁿ BuLi (1.5)/−20 °C, 1 h	ⁱ PrOBpin (3.9)/rt, 1 h	76	$AlCl_3$ (4.0), $NEt^i Pr_2$ (5.0)/110 °C, 2 h	Chlorobenzene	47	203
B-O-dmAc	ⁿ BuLi (2.5)/−20 °C, 1 h	ⁱ PrOBpin (4.5)/rt, 1 h	49	AlCl ₃ (4.0), NEt ⁱ Pr ₂ (5.0)/110 °C, 2 h	Chlorobenzene	36	203
B-O-dpAc	ⁿ BuLi (2.5)/−20 °C, 1 h	ⁱ PrOBpin (5.0)/rt, 1 h	_	AlCl ₃ (6.0), NEt ⁱ Pr ₂ (2.4)/110 °C, 2 h	Chlorobenzene	33 (2 steps)	203
B-dpa-Cz	ⁿ BuLi (2.0)/−20 °C, 1 h	ⁱ PrOBpin (4.0)/rt, 1 h	65	AlCl ₃ (5.0), NEt ⁱ Pr ₂ (2.0)/110 $^{\circ}$ C, 2 h	Chlorobenzene	57	204
B-dpa-dmAc	ⁿ BuLi (2.5)/−20 °C, 1 h	ⁱ PrOBpin (4.5)/rt, 1 h	84	AlCl ₃ (3.0), NEt ⁱ Pr ₂ (1.0)/110 $^{\circ}$ C, 2 h	Toluene	25	204
B-dpa-SpiroAc	ⁿ BuLi (2.8)/−20 °C, 1 h	ⁱ PrOBpin (5.0)/rt, 1 h	44	$AlCl_3$ (5.0), $NEt^i Pr_2$ (2.0)/110 °C, 2 h	Toluene	50	204

^a Numbers in parentheses refer to reagent loadings (equivalents).

Chem Soc Rev **Review Article**

Table 21 Photophysical properties of the compounds shown in Fig. 15, 16 and Scheme 15

Compound	Condition	$\lambda_{PL}^{max} \left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\rm ST}$ [eV]	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
DPACzBN1	Toluene/3 wt%-26DCzPPy ^a	469/479	23/31	- /0.98	-/0.11	$-/1.2 \times 10^4$	195
PTZBN1	Toluene/2 wt%-26DCzPPy ^a	490/497	41/44	/0.98	/0.16	$-/1.11 \times 10^5$	196
DMAcBNO	Toluene/3 wt%-26DCzPPy ^a	462/470	34/41	— /0 . 99	0.23/—	$-/1.40 \times 10^4$	170
DPAcBNO	Toluene/3 wt%-26DCzPPy ^a	462/468	33/39	/0.98	0.19/—	$-/1.75 \times 10^4$	170
Cz -PTZ-BN b	Toluene/3 wt%-PhCzBCz ^a	510/524	37/50	0.84/0.91	0.11/—	$-/8.1 \times 10^4$	197
$BNCzPTZ^b$	Toluene/15 wt%-PhCzBCz ^a	509/—	42/—	0.84/0.91	0.09/—	$/1.54 \times 10^5$	198
BNCzPXZ	Toluene/7 wt%-PhCzBCz ^a	508/—	36/—	0.88/0.94	0.13/—	$-/2.31 \times 10^4$	198
2Cz-PTZ-BN	Toluene/3 wt%-PhCzBCz ^a	505/512	38/48	0.87/0.96	0.09/—	$/1.05 \times 10^5$	197
BN-MelAc	Toluene/2-MeTHF/1 wt%-DMIC-TRZ ^a	497/—/503	30/30/33	—/—/0.96	—/0.11/—	$//6.3 \times 10^4$	199
BN-Se	Toluene/1 wt%-DMIC-TRZ ^a	502/505	42/44	0.99/0.98	0.08/—	$1.6 \times 10^6/1.2 \times 10^6$	103
BNIP-tBuCz	Toluene/1 wt%-DMIC-TRZ ^a	564/570	60/61	 /0 . 96	0.08/0.13	$/0.9 \times 10^4$	147
BNIP-CzDPA	Toluene/1 wt%-DMIC-TRZ ^a	583/585	49/57	 /0 . 95	0.06/0.12	$/0.9 \times 10^4$	147
NBO	Toluene/4 wt%-mCBP ^a	487/—	27/—	/0.92	0.12/—	$/9.3 \times 10^5$	191
tCzphB-Ph	Toluene/2 wt%-TPSS ^a	523/527	21/23	/0.98	/0.04	—/—	200
tCzphB-Fl	Toluene/2 wt%-TPSS ^a	531/535	21/25	 /0 . 93	/0.04	—/—	200
LTCz-BN	Toluene/5 wt%-mCBP ^a	497/—	27/—	 /0 . 93	0.10/—	$/8.3 \times 10^5$	201
B-O-dpa	Toluene/10 wt%-DPEPO ^a	433/—	28/—	/0.86	0.18/—	$-/0.83 \times 10^4$	203
B-O-Cz	Toluene/10 wt%-DPEPO ^a	441/—	27/—	/0.94	0.15/—	-4.02×10^4	203
B-O-dmAc	Toluene/10 wt%-DPEPO ^a	461/—	38/—	/0.91	0.11/—	$-/1.82 \times 10^4$	203
B-O-dpAc	Toluene/10 wt%-DPEPO ^a	463/—	38/—	/0.94	0.06/—	$-/3.12 \times 10^4$	203
B-dpa-Cz	Toluene/3 wt%-mCPB ^a	466/469	27/33	/0.94	0.15/—	$-/2.74 \times 10^4$	204
B-dpa-dmAc	Toluene/3 wt%-mCPB ^a	472/476	31/38	/0.98	0.16/—	$-/4.48 \times 10^4$	204
B-dpa-SpiroAc	Toluene/3 wt%-mCPB ^a	472/476	31/38	/0.92	0.14/—	$-/4.97 \times 10^4$	204

^a See Table 2 for the full compound name. ^b Same compound named differently.

DABNA-1 inverted through the interchange of boron and nitrogen positions (Fig. 17a).²⁰⁵ The one-pot borylation of the tribrominated starting material afforded an intermediate possessing two B-Br bonds, which was then reacted with the desired Grignard reagents to afford ADBNA derivatives. One year later, Wang et al. reported a different route to synthesise ADBNA-based frameworks (Fig. 17b). 206 The key intermediate, Pre-ADBNA, was prepared in 65% yield by treating the lithiated starting material with dimethyl mesitylboronate (MesB(OMe)₂) (2.0 equiv.) and subsequently reacted with BBr3 and ArLi to afford cyclised B,N,B-embedded compounds. Notably, both symmetric and non-symmetric products were obtained by controlling the reagent amounts. When 1.0 equiv. of BBr₃ and 1.2 equiv. of ArLi were used, the B-Ar group was introduced only at the acyclic site of Pre-ADBNA. However, treatment with 5.0 equiv. of BBr₃ for a longer time and the use of 2.4 equiv. of ArLi resulted in the replacement of the remaining B-Mes site of Pre-ADBNA with an additional B-Ar group.

2.5.2 One-pot double borylation. Finally, the simultaneous introduction of two fully cyclised boron atoms using the basic one-pot borylation procedure are discussed. In 2020, Yasuda et al. reported the synthesis of a doubly borylated compound, BBCz-R (Scheme 16), starting from 1-bromo-2,6-difluorobenzene. ¹⁵⁵ One equivalent of 3,6-di-tert-butylcarbazole was introduced by the standard S_NAr reaction. Subsequently, a similar type of reaction with 2,8-di-tert-butyl-5,11-dihydroindolo[3,2-b]carbazole was conducted at the remaining fluorine group to form the dibrominated precursor. The final one-pot borylation step did not proceed regioselectively, i.e., a regioisomer (BBCz-Y-II, 7% yield) was obtained in addition to the desired BBCz-R (5% yield).

The procedure proposed by Yasuda et al. is now one of the most common strategies for one-pot double borylation (Fig. 18 and Table 22). $^{117,155,\bar{1}63,167,207,208}$ The sequential S_NAr reactions

of 2-bromo-1,6-difluorobenzene (first mono-substitution, then dimerisation) afforded diverse doubly borylated compounds. The data presented in ref. 207 (SBON and SBSN) suggest that protonation after lithium-bromine exchange is a common side reaction and can affect the yield of the final product. The possible proton sources are residual water in the solvents, HBr contained in BBr3, protons generated during C-H borylation, and so on.

Scheme 17 presents another versatile route to synthesise doubly borylated MR-TADF emitters.209 This procedure starts from 1,4-dibromo-2,3,5,6-tetrafluorobenzene and affords the dibrominated precursor through multiple S_NAr reactions. A hexasubstituted doubly N,B,N-embedded framework is then constructed by subsequent one-pot borylation. This protocol was adopted in some studies to prepare the desired MR-TADF frameworks (Fig. 19 and Table 23). 210-214 In addition to tetra-carbazolyl substituted compounds (R-BN, R-TBN, R-TPhBN, and BNS), the combination of a carbazolyl group and chalcogen bridge (BNO1, BNO2, BNO3, DBNS, DBNS-tBu, and BNNO) was also achieved. As mentioned in the following subsection, these species possess para-positioned boron and electron-donating atoms, which is beneficial for obtaining long-wavelength fluorescence.

Other synthesis routes for doubly borylated compounds are summarised in Fig. 20 and Table 24. 92,155,181,215,216 Overall, the reaction yields are lower than those observed for single borylation. Regioselectivity in electrophilic C-H borylation should be considered because poor selectivity causes the formation of undesired isomers after one-pot borylation. For example, the precursors of m-DBCz and DBTN-2 have similar chemical structures except for 'Bu groups on the central two benzene rings, which results in different regioselectivity in one-pot borylation. Although double lithiation at the same benzene ring is a good way to avoid the regioselectivity problem, the

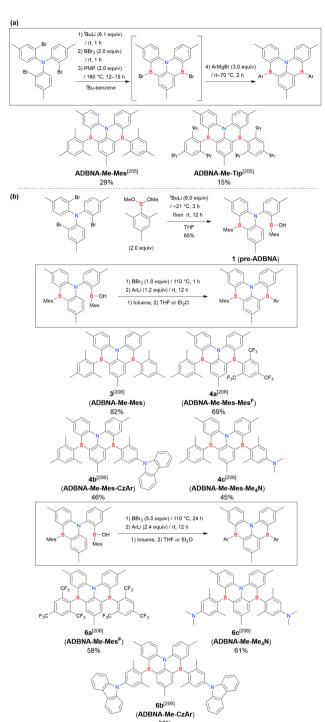


Fig. 17 Synthesis of boron-bridged compounds reported in ref. 205 and 206.

reaction yields remain low (BBCz-DB, 155 BSBS-N1, 92 BOBO-Z, 215 BOBS-Z,²¹⁵ and BSBS-Z²¹⁵). Moreover, the simultaneous introduction of three or more boron atoms has not been achieved to date.

2.5.3 Photophysical properties. Table 25 lists the photophysical properties of doubly borylated MR-TADF emitters, showing that compounds possessing one nitrogen and two boron atoms (ADBNA derivatives) exhibit photophysical parameters comparable to those of DABNA derivatives, except for the

Scheme 16 Synthesis of doubly borylated compound from 1-bromo-2,6-difluorobenzene reported in ref. 155

red-shifted emission wavelength. This difference in $\lambda_{\text{PL}}^{\text{max}}$ was attributed to the FMO energy levels. Although both HOMO and LUMO energy levels of ADBNA are lower than those of DABNA-1, the larger decrease in the LUMO energy level of ADBNA results in a smaller HOMO-LUMO energy gap.²⁰⁵ In the case of compounds obtained by one-pot double borylation, λ_{PL}^{max} largely depends on the relative position of boron and electron-donating atoms (or groups). If two electron-donating atoms are placed in the paraposition, λ_{PL}^{max} substantially increases to >600 nm (e.g., 615 nm for BBCz-R). 155 In particular, given that the compounds in Fig. 19 were obtained from 1,4-dibromo-2,3,5,6-tetrafluorobenzene, paratype substitution was inevitable and led to orange or red emission with $\lambda_{\rm PL}^{\rm max} > 600$ nm (660–662 nm for **R-BN**, 209,210 684–692 nm for **R-TBN**, ^{209,210} 696 nm for **R-TPhBN**, ²¹⁰ 605 nm for **BNO1**, ²¹¹ 609 nm for **BNO2**, ²¹¹ 616 nm for **BNO3**, ²¹¹ 631 nm for **DBNS**, ²¹² 641 nm for **DBNS-tBu**, 212 737 nm for **BNS**, 213 and 637 nm for BNNO²¹⁴). On the other hand, two electron-donating atoms in a meta-relationship had a smaller effect on the PL wavelength, resulting in $\lambda_{PL}^{max} = 440-520$ nm.

The relative position of the two boron atoms strongly influences the TADF properties. When two boron atoms are placed in a *meta*-position, a decrease in $\Delta E_{\rm ST}$ and an increase in $k_{\rm RISC}$ can be expected because the enlarged π -plane enhances long-range electronic delocalisation.⁷⁴ Wang et al. evaluated the effect of double borylation by comparing p-TBNCz and m-DBCz (Fig. 21)181 and showed that with an increase in the number of boron atoms, $\Delta E_{\rm ST}$ decreased, whereas k_{RISC} increased. On the other hand, two parapositioned boron atoms do not improve the TADF properties because the MR effect is partially broken by the undesired π extension. In this case, the positive effect of enhanced long-range electronic delocalisation is negated, and $\Delta E_{\rm ST}$ (0.1-0.2 eV) and

Chem Soc Rev Review Article

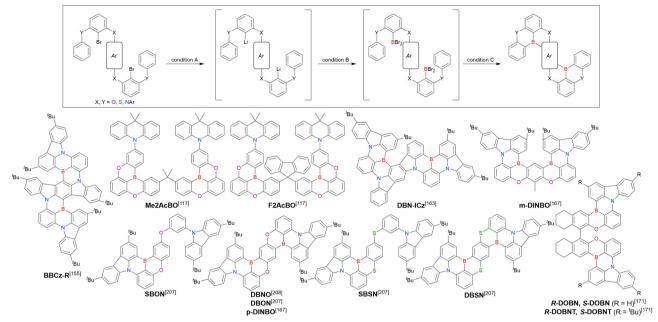
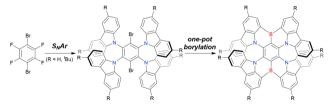


Fig. 18 MR-TADF emitters synthesised by one-pot double borylation.

Table 22 Conditions used to synthesise the compounds shown in Fig. 18

Compound	Condition A ^a	Condition B ^a	Condition C^a	Solvent	Yield [%]	Ref.
BBCz-R	ⁿ BuLi (3.0)/rt, 4 h	BBr ₃ (3.0)/rt, 12 h	NEt ⁱ Pr ₂ (4.6)/170 °C, 24 h	^t Bu-Benzene	5	155
Me2AcBO	^t BuLi (4.0)/rt, 2 h	BBr ₃ (—)/rt, 2 h	$NEt^{i}Pr_{2}$ (—)/180 °C, 24 h	^t Bu-Benzene	8	117
F2AcBO	^t BuLi (4.0)/rt, 2 h	BBr ₃ (—)/rt, 2 h	$NEt^{i}Pr_{2}$ (—)/180 °C, 24 h	^t Bu-Benzene	16	117
DBN-ICz	ⁿ BuLi (6.0)/60 °C, 24 h	BBr ₃ (6.0)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (9.0)/120 °C, 5 h	^t Bu-Benzene	36	163
m-DINBO	ⁿ BuLi (2.3)/60 °C, 2 h	$BBr_3 (3.1)/rt, 2 h$	$NEt^{i}Pr_{2}(4.1)/170$ °C, 24 h	^t Bu-Benzene	22	167
SBON	ⁿ BuLi (3.9)/80 °C, 5 h	BBr ₃ (7.8)/rt, 3 h	$NEt^{i}Pr_{2}$ (6.1)/190 °C, 16 h	^t Bu-Benzene	16	207
DBNO	^t BuLi (4.0)/0 °C, 6 h	$BBr_3(2.1)/rt$, 2 h	$NEt^{i}Pr_{2}(5.0)/120$ °C, 24 h	^t Bu-Benzene	16	208
	ⁿ BuLi (3.9)/80 °C, 5 h	BBr ₃ (7.8)/rt, 3 h	$NEt^{i}Pr_{2}$ (6.1)/190 °C, 16 h	^t Bu-Benzene	10	207
	ⁿ BuLi (2.3)/60 °C, 2 h	BBr ₃ (3.1)/rt, 2 h	$NEt^{i}Pr_{2}(4.1)/170$ °C, 48 h	^t Bu-Benzene	2	167
SBSN	ⁿ BuLi (4.0)/80 °C, 5 h	BBr ₃ (8.1)/rt, 3 h	$NEt^{i}Pr_{2}$ (6.4)/190 °C, 16 h	^t Bu-Benzene	24	207
DBSN	ⁿ BuLi (4.0)/80 °C, 5 h	BBr ₃ (8.1)/rt, 3 h	$NEt^{i}Pr_{2}$ (6.4)/190 °C, 16 h	^t Bu-Benzene	12	207
S-DOBN	ⁿ BuLi (4.0)/90 °C, 2 h	$BBr_3 (4.0)/rt$, 1 h	$NEt^{i}Pr_{2}$ (11)/120 °C, 12 h	^t Bu-Benzene	10	171
S-DOBNT	ⁿ BuLi (4.0)/90 °C, 2 h	$BBr_3 (4.0)/rt$, 1 h	$NEt^{i}Pr_{2}(11)/120$ °C, 12 h	^t Bu-Benzene	12	171

^a Numbers in parentheses refer to reagent loadings (equivalents).



Scheme 17 Synthesis of a doubly borylated compound from 1,4-dibromo-2,3,5,6-tetrafluorobenzene.

 $k_{\rm RISC}$ (<1.0 \times 10⁵ s⁻¹) remain moderate. In particular, **BNO1**, **BNO2**, and **BNO3** showed a very weak TADF character owing to the *para*-positioned boron atoms and highly planar structures.²¹¹

2.6 Summary

Numerous MR-TADF compounds have been synthesised since the first report of one-pot borylation in 2015. Although the basic protocol for one-pot borylation has been established, the synthesis route for borylation precursors needs to be tailored according to their structures. The obtained compounds usually show TADF properties and small FWHMs, benefiting from the MR effect. In addition, the results shown in Fig. 21 induce strong interest in introducing two or more boron atoms into MR-TADF frameworks. However, as discussed above, the simultaneous introduction of multiple boron atoms using one-pot protocols remains challenging. The further development of multiple borylation methodologies should enable the development of superior materials with MR-TADF characteristics.

3. One-shot borylation

Since Hatakeyama *et al.* proposed the molecular design of boron-embedded MR compounds with DOBNA and DABNA frameworks and their synthesis protocol (one-pot borylation),

Double-borylated MR-TADF emitters synthesised from hexa-substituted benzene

Table 23 Conditions used to synthesise the compounds shown in Fig. 19

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
R-BN	ⁿ BuLi (6.1)/60 °C, 24 h	BBr ₃ (12)/rt, 0.5 h	NEt ⁱ Pr ₂ (18)/120 °C, 5 h	^t Bu-Benzene	38	209
	ⁿ BuLi (4.0)/rt, 12 h	BBr ₃ (4.0)/rt, 24 h	$NEt^{i}Pr_{2}$ (4.0)/180 °C, 72 h	o-Dichlorobenzene	53	210
R-TBN	ⁿ BuLi (6.1)/60 °C, 24 h	BBr ₃ (12)/rt, 0.5 h	$NEt^{i}Pr_{2}$ (18)/120 °C, 5 h	^t Bu-Benzene	40	209
	ⁿ BuLi (4.0)/rt, 12 h	BBr ₃ (4.0)/rt, 24 h	$NEt^{i}Pr_{2}$ (4.0)/180 °C, 72 h	o-Dichlorobenzene	25	210
R-TPhBN	ⁿ BuLi (4.0)/rt, 12 h	BBr ₃ (4.0)/rt, 24 h	$NEt^{i}Pr_{2}$ (4.0)/180 °C, 72 h	o-Dichlorobenzene	23	210
BNO1	ⁿ BuLi (—)/60 °C, 8 h	BBr ₃ (—)/rt, 1 h	NEt ⁱ Pr ₂ (—)/170 °C, 24 h	Mesitylene	34	211
BNO2	ⁿ BuLi (—)/60 °C, 8 h	BBr ₃ (—)/rt, 1 h	NEt ⁱ Pr ₂ (—)/170 °C, 24 h	Mesitylene	38	211
BNO3	ⁿ BuLi (—)/60 °C, 8 h	BBr ₃ (—)/rt, 1 h	$NEt^{i}Pr_{2}$ (—)/170 °C, 24 h	Mesitylene	31	211
DBNS	ⁿ BuLi (2.5)/rt, 4 h	BBr ₃ (2.5)/rt, 2 h	$NEt^{i}Pr_{2}$ (3.9)/170 °C, 24 h	^t Bu-Benzene	30	212
DBNS-tBu	ⁿ BuLi (2.5)/rt, 4 h	$BBr_3 (2.5)/rt, 2 h$	$NEt^{i}Pr_{2}$ (3.5)/170 °C, 24 h	^t Bu-Benzene	16	212
BNS	ⁿ BuLi (4.0)/60 °C, 2 h	BBr ₃ (4.0)/rt, 6 h	$NEt^{i}Pr_{2}(4.0)/180$ °C, 48 h	o-Dichlorobenzene	22	213
BNNO	ⁿ BuLi (6.0)/60 °C, 2 h	BBr ₃ (6.0)/rt, 0.5 h	$NEt^{i}Pr_{2}(10)/135$ °C, 8 h	Xylene	30	214
				-		

^a Numbers in parentheses refer to reagent loadings (equivalents).

numerous corresponding derivatives have been prepared using the same methodology, as described in Section 2. One-pot borylation generally relies on metal-boron exchange followed by intramolecular tandem bora-Friedel-Crafts reactions. Therefore, in many cases, the borylation precursor should possess a halogen (Cl, Br, or I) atom at the desired borylation position to provide a scaffold for metal-halogen exchange. However, the ability of halogen groups to engage in cross-couplings often interferes with the desired reactions or increases the number of steps in precursor synthesis. In addition, molecules with multiple boron atoms are difficult to synthesise because one-pot borylation proceeds via organometallic species. Indeed, MR compounds containing more than three boron atoms have not been synthesised by one-pot borylation. Thus, despite its power for the synthesis of boron-embedded MR compounds, one-pot borylation is by no means a panacea.

This section focuses on one-shot borylation, which has been established in the last five years as a complementary method to one-pot borylation and involves successive intra- and intermolecular bora-Friedel-Crafts reactions converting multiple C-H bonds into C-B bonds in one shot. Unlike the one-pot borylation protocol, the one-shot borylation does not require functional groups such as halogens and features easier precursor synthesis, enabling the synthesis of MR compounds containing multiple (up to eight) boron atoms. This section overviews the one-shot borylation protocol and discusses its selectivity and the optical properties of Chem Soc Rev Review Article

Fig. 20 Double-borylated MR-TADF emitters not included in Fig. 18 and 19.

Table 24 Conditions used to synthesise the compounds shown in Fig. 20

Compound	Condition A ^a	Condition B ^a	Condition C ^a	Solvent	Yield [%]	Ref.
BBCz-DB	ⁿ BuLi (2.5)/rt, 4 h	BBr ₃ (2.5)/rt, 12 h	NEt ⁱ Pr ₂ (3.8)/170 °C, 24 h	^t Bu-Benzene	36	155
m-DBCz	^t BuLi (4.0)/0 °C, 12 h	BBr ₃ (3.0)/rt, 6 h	PMP (6.0)/160 °C, 24 h	^t Bu-Benzene	13	181
BSBS-N1	^t BuLi (4.8)/rt, 4 h	BBr ₃ (3.0)/rt, 12 h	PMP (4.0)/170 °C, 24 h	^t Bu-Benzene	18	92
BOBO-Z	ⁿ BuLi (3.0)/60 °C, 2 h	BBr ₃ (3.0)/rt, 2 h	PMP (4.5)/160 °C, 24 h	^t Bu-Benzene	20	215
BOBS-Z	ⁿ BuLi (4.4)/60 °C, 2 h	BBr ₃ (2.4)/rt, 2 h	PMP (4.0)/160 °C, 24 h	^t Bu-Benzene	20	215
BSBS-Z	ⁿ BuLi (4.4)/60 °C, 2 h	$BBr_3(2.4)/rt, 2 h$	PMP (4.0)/160 °C, 24 h	^t Bu-Benzene	14	215
DBTN-2	^t BuLi (2.5)/60 °C, 6 h	BBr ₃ (2.5)/rt, 6 h	$NEt^{i}Pr_{2}$ (2.5)/120 °C, 12 h	^t Bu-Benzene	5	216

^a Numbers in parentheses refer to reagent loadings (equivalents).

the resulting compounds. In addition, synthesis protocols involving not only C–H but also N–H borylation and a recently reported sequential one-pot/one-shot borylation protocol are presented.

3.1 One-shot (C-H) borylation

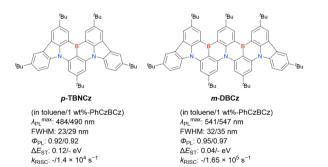
In 2018, Hatakeyama et al. demonstrated the potential utility of one-shot borylation protocols.²¹⁷ In the two-step synthesis of B₄N₃-doped nanographene **B4**, the crucial step is the quadruple borylation of triarylamines that converts 11 C-H bonds into C-B bonds in one shot. In addition, the judicious choice of the Brønsted base enables the selective double and triple borylation of triarylamines. The borylation precursor, N^1, N^1, N^3 , N^3 , N^5 , N^5 -hexakis (4-methylphenyl)-1,3,5-benzenetriamine, was obtained from 1,3,5-tribromobenzene by Buchwald-Hartwig coupling in 98% yield, and the subsequent one-shot quadruple borylation proceeded in the presence of 12 equiv. of boron triiodide (BI₃) under reflux conditions (bath temperature = 200 °C) to afford the target compound B4 in 35% isolated yield and a small amount of B3 as a byproduct (Scheme 18). Notably, B4 was synthesised using only the highly reactive BI₃ and not other boron sources such as boron trichloride (BCl₃) and BBr₃. Selective double and triple borylations were also achieved under optimal conditions. In the presence of 5.0 equiv. of BI₃ and 2.0 equiv. of Ph₃B, selective double borylation occurred under reflux conditions (bath temperature = 190 $^{\circ}$ C) to afford **B2** in 76% yield.

In contrast, triple borylation occurred at elevated temperatures (bath temperature = 200 °C) in 1,2,4-trichlorobenzene as a highboiling-point solvent to afford B3 in 45% yield. In addition, the double one-shot borylation of a fluorine-bearing triarylamine proceeded under similar conditions to afford B2-F in 58% yield (Scheme 18). Notably, the use of Ph₃B as a Brønsted base was crucial for B3 formation. The addition of Ph3B reduced the concentration of HI via its retro-Friedel-Crafts reaction. As a result, adequate HI concentrations were maintained in situ, and the Friedel-Crafts/retro-Friedel-Crafts reaction of the products was not inhibited to selectively give the thermodynamic product, i.e., B3. The reduction in HI concentration simultaneously increased the yield by suppressing competitive C-N bond cleavage. Indeed, the reaction in the absence of Ph₃B selectively afforded B3 in significantly reduced yield (13%). In contrast, other Brønsted bases such as NEtⁱPr₂ and N,N-dimethyltoluidine did not induce the formation of **B3**. Amine-type Brønsted bases effectively captured HI and therefore hindered the Friedel-Crafts/retro-Friedel-Crafts reaction of the products to afford only B2 as the kinetic product (44-54%). Hence, the trapping of Brønsted acids (e.g., HBr and HI) generated during the reaction is one of the general strategies for suppressing side reactions and controlling the selectivity of one-shot borylation. The resulting B,N-doped nanographenes (B2-B4 and B2-F) showed pure deep blue fluorescence and small $\Delta E_{\rm ST}$ values (0.14–0.18 eV) (Table 26).

Table 25 Photophysical properties of the compounds shown in Fig. 17–20

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{ ext{PL}}\left[ight]$	$\Delta E_{\rm ST}$ [eV]	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
ADBNA-Me-Mes	CH ₂ Cl ₂ /1 wt%-DOBNA-OAr ^b	484/482	38/33	0.79/0.89	-/0.19	$-/7.58 \times 10^3$	205
	CH ₂ Cl ₂ /1 wt%-PMMA ^a	482/485	—/—	0.71/0.84	/0.18	—/—	206
ADBNA-Me-Tip	CH ₂ Cl ₂ /1 wt%-DOBNA-OAr ^b	482/479	36/34	0.76/0.88	/0.20	$-/8.98 \times 10^3$	205
ADBNA-Me-Mes-Mes ^F	CH ₂ Cl ₂ /1 wt%-PMMA ^a	485/488	—/—	0.88/0.91	 /0 . 19	—/—	206
ADBNA-Me-Mes-CzAr	CH ₂ Cl ₂ /1 wt%-PMMA ^a	483/485	—/—	0.82/0.91	/0.18	—/—	206
ADBNA-Me-Mes-Me ₄ N	CH ₂ Cl ₂ /1 wt%-PMMA ^a	477.609/487	—/—	0.19/0.26	 /0 .1 7	—/—	206
ADBNA-Me-Mes ^F	CH ₂ Cl ₂ /1 wt%-PMMA ^a	487/491	—/—	0.85/0.93	/0.19	—/—	206
ADBNA-Me-CzAr	CH ₂ Cl ₂ /1 wt%-PMMA ^a	486/487	—/—	0.81/0.86	/0.17	—/—	206
ADBNA-Me-Me ₄ N	CH ₂ Cl ₂ /1 wt%-PMMA ^a	481.601/495	—/—	0.18/0.24	/0.13	—/—	206
BBCz-R	Toluene/2 wt%-mCBP ^a	615/619	21/27	0.89/0.79	0.19/—	$1.2 \times 10^4/1.2 \times 10^4$	155
Me2AcBO	Toluene/5 wt%-mCP ^a	474/470	/57	— /0 . 99	/0.05	$-/1.13 \times 10^6$	117
F2AcBO	Toluene/5 wt%-mCP ^a	478/467	/59	 /0 . 97	/0.05	$-/1.38 \times 10^6$	117
DBN-ICz	Toluene/3 wt%-mCBP ^a	542/545	18/23	0.986/—	0.20/—	$0.7 \times 10^4/$ —	163
m-DINBO	Toluene/3 wt%-mCBP ^a	456/466	17/22	/0.94	/0.060	$-/3.1 \times 10^4$	167
p-DINBO ^c	Toluene/3 wt%-mCBP ^a	500/512	19/45	- -/0 . 96	/0.061	$-/1.4 \times 10^4$	167
\mathbf{DBON}^{c}	Toluene/4 wt%-mCBP ^a	505/—	20/—	/0.98	0.13/—	$/0.8 \times 10^5$	207
\mathbf{DBNO}^{c}	Toluene/1 wt%-PhCzBCz ^a	500/508	19/28	0.96/0.84	0.17/—	$-/3.0 \times 10^4$	208
SBON	Toluene/4 wt%-mCBP ^a	463/—	24/—	/0.74	0.16/—	$-/0.5 \times 10^5$	207
SBSN	Toluene/4 wt%-mCBP ^a	489/—	27/—	 /0 . 76	0.10/—	$-/1.5 \times 10^5$	207
DBSN	Toluene/4 wt%-mCBP ^a	553/—	28/—	/0.98	0.13/—	$/1.9 \times 10^5$	207
R-DOBN	Toluene/5 wt%-26DCzPPya	453/—	21/—	0.83/0.91	0.14/—	$-/1.6 \times 10^4$	171
R-DOBNT	Toluene/5 wt%-26DCzPPy ^a	459/—	21/—	0.89/0.96	0.12/—	$/0.8 \times 10^4$	171
R-BN	Toluene	662	38	1.00	0.18	6.7×10^{4}	209
	Toluene	660	_	1.00	0.22	7.3×10^4	210
R-TBN	Toluene	692	38	1.00	0.16	$2.5 imes 10^4$	209
	Toluene	684	_	0.99	0.21	2.3×10^4	210
R-TPhBN	Toluene	696	_	0.90	0.18	3.0×10^{4}	210
BNO1	Toluene/1 wt%-DMIC-TRZ ^a	605/610	32/35	0.96/—	/0.25	—/—	211
BNO2	Toluene/1 wt%-DMIC-TRZ ^a	609/618	32/37	0.95/—	/0.27	—/—	211
BNO3	Toluene/1 wt%-DMIC-TRZ ^a	616/624	33/38	0.96/—	/0.26	—/—	211
DBNS	CH ₂ Cl ₂	631	40	0.80	0.20	$2.1 imes 10^5$	212
DBNS-tBu	CH_2Cl_2	641	39	0.85	0.19	$2.2 imes 10^5$	212
BNS	Toluene	737	_	0.82	0.14	8.1×10^3	213
BNNO	Toluene	637	32	0.95	0.09	$1.4 imes 10^4$	214
BBCz-DB	Toluene/2 wt%-mCBP ^a	466/471	16/26	0.93/0.91	0.15/—	$1.9 \times 10^4/2.2 \times 10^4$	155
m-DBCz	Toluene/1 wt%- PhCzBCz ^a	541/547	32/35	0.95/0.97	0.04/—	$-/1.65 \times 10^{5}$	181
BSBS-N1	Toluene/2 wt%-mCBP ^a	473/478	21/24	0.59/0.89	0.13/0.14	$1.5 \times 10^6/1.9 \times 10^6$	92
BOBO-Z	Toluene/3 wt%-mCBP ^a	441/445	15/18	0.76/0.64	0.15/0.10	$0.7 \times 10^5 / 0.7 \times 10^5$	215
BOBS-Z	Toluene/3 wt%-mCBP ^a	453/457	21/24	0.94/0.93	0.16/0.12	$4.3 \times 10^5/8.6 \times 10^5$	215
BSBS-Z	Toluene/3 wt%-mCBP ^a	460/464	20/22	0.93/0.88	0.14/0.12	$8.8 \times 10^5/1.6 \times 10^6$	215
DBTN-2	Toluene/2.5 wt%-SF3TRZ ^a	512/—	20/—	-/1.00	/0.06	$-/1.7 \times 10^{5}$	216

^a See Table 2 for the full compound name. ^b See Scheme 27. ^c Same compound named differently.

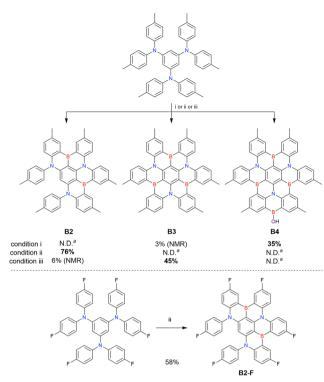


Photophysical parameters of **p-TBNCz** and **m-DBCz** reported in ref 181

The selectivity of one-shot borylation can be attributed to several factors, as discussed below. Hatakeyama et al. reported the synthesis of carbazole-based DABNA analogues using oneshot borylation (Scheme 19).111 The one-shot borylation of the

precursor bearing one carbazolyl and two di-p-tolylamino groups proceeded at 120 °C in the presence of 2.0 equiv. of BBr₃ to afford CzDABNA-NP-M/TB in 63% yield. Notably, no regioisomers were observed. Moreover, the double borylation of the same substrate was achieved at 140 °C using 4.0 equiv. of BBr₃. Two boron atoms were selectively introduced at orthopositions with respect to the carbazolyl group to afford CzB2-M/ **TB** in 72% yield. According to density functional theory (DFT) calculations, the HOMO energy levels of the borylation precursor, CzDABNA-NP-M/TB, and CzB2-M/TB (-4.84, -4.77, and -4.73 eV, respectively) are sufficiently high for electrophilic C-H borylation. The HOMO of the borylation precursor is mostly localised at para-positions relative to the di-p-tolylamino groups (red circles, Fig. 22), which is attributed to their stronger electron-donating nature compared to that of the carbazolyl group. This indicates that the initial borylation predominantly occurs at the carbon atom between the 9-carbazolyl and di-ptolylamino groups to afford CzDABNA-NP-M/TB. In other

Chem Soc Rev **Review Article**

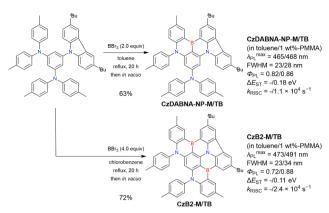


Scheme 18 Synthesis of B2, B3, B4, and B2-F. Conditions and reagents: (i) BI₃ (12 equiv.), o-dichlorobenzene, reflux (bath temperature: 200 °C), 12 h, (ii) Bl₃ (5.0 equiv.), Ph₃B (2.0 equiv.), o-dichlorobenzene, reflux (bath temperature: 190 °C), 20 h, (iii) BI₃ (5.0 equiv.), Ph₃B (2.0 equiv.), 1,2,4trichlorobenzene, 200 °C, 20 h. a Not detected in ref. 217.

words, the initial borylation of the one-shot borylation protocol occurs at the para-position with respect to the most electrondonating substituent and is followed by tandem bora-Friedel-Crafts reactions affording the kinetic product. The second borylation of CzDABNA-NP-M/TB can proceed at two sites, namely the ortho-positions relative to the di-p-tolylamino group. However, the *p*-tolyl groups (blue circles, Fig. 22) perpendicular to the central benzene ring prevent BBr3 from approaching the reactive carbon owing to steric hindrance.

In contrast, the carbazolyl group is positioned horizontally relative to the central benzene ring, allowing for easy access by BBr₃. Consequently, the second borylation predominantly occurs at the carbon atom located between the 9-carbazolyl and di-p-tolylamino groups to afford CzB2-M/TB. In brief, the selectivity of one-shot borylation is determined by both electronic and steric factors.

The synthesis of narrowband deep-blue emissive compounds BN1-BN3 by Yang et al. are a good example illustrating the kinetic and thermodynamic selectivity of one-shot borylation (Scheme 20



Scheme 19 Synthesis of CzDABNA-NP-M/TB and CzB2-M/TB reported in ref 111

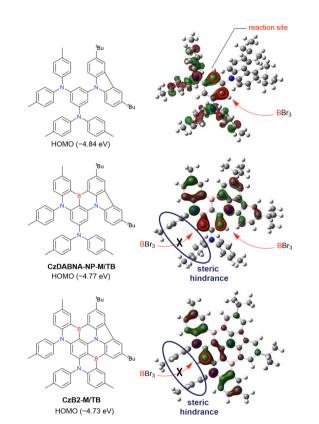


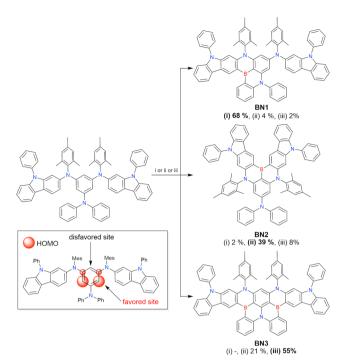
Fig. 22 Highest occupied Kohn-Sham orbitals (HOMOs) of the compounds shown in Scheme 19 calculated at the B3LYP/6-31G(d) level of theory.

and Table 27).218 The one-shot borylation was performed with 12 equiv. of BBr₃ at 180 °C and mainly occurred at the carbon

Table 26 Photophysical properties of the compounds shown in Scheme 18

Compound	Condition	$\lambda_{\mathrm{PL}}^{\mathrm{max}}\left[\mathrm{nm}\right]$	FWHM [nm]	$\Phi_{ m PL}$	$\Delta E_{ m ST} [{ m eV}]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$
B2	CH ₂ Cl ₂ /1 wt%-PMMA ^a	461/455	39/32	0.19/0.68	0.12/0.18	$-/4.1 \times 10^4$
B3	CH ₂ Cl ₂ /1 wt%-PMMA ^a	442/441	50/34	0.13/0.47	0.31/0.15	—/—
B4	CH ₂ Cl ₂ /1 wt%-PMMA ^a	449/450	22/38	0.21/0.61	0.19/0.15	—/—
B2-F	1 wt%-PMMA ^a	467	44	0.57	0.15	—/—

^a See Table 2 for the full compound name.

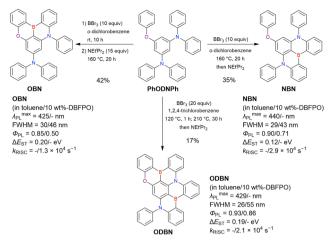


Scheme 20 Synthesis of BN1-BN3. Conditions and reagents: (i) BBr₃ (12 equiv.), o-dichlorobenzene, 180 °C, 20 h; then NEtⁱPr₂, (ii) BBr₃ (12 equiv.), o-dichlorobenzene, 210 °C, 20 h; then NEtⁱPr₂, (iii) BBr₃ (24 equiv.), o-dichlorobenzene, 210 °C, 20 h; then NEtⁱPr₂ (ref. 218).

atom in the central benzene ring at the para-position with respect to the 2-carbazolylmesitylamino group (where the HOMO was primarily localised) to afford mono-borylated BN1 in 68% yield. In contrast, the mono-borylated regioisomer BN2 was obtained in 39% yield as the major product at a higher reaction temperature (210 °C).

Although the borylated position of BN2 does not contribute to the precursor HOMO and is therefore a disfavoured site, DFT calculations suggest that BN2 is 2.2 kcal mol⁻¹ more stable than BN1. Hence, initial borylation is assumed to occur at the same position as in the case of BN1, with a subsequent retro-Friedel-Crafts reaction involving in situ generated HBr affording BN2 as the thermodynamic product. In addition, double one-shot borylation proceeded in the presence of an elevated amount of BBr₃ (24 equiv.) at 210 °C to give BN3 in 55% yield as the kinetic product.

The synthesis of O,B,N-embedded MR compounds by Wong et al. also describe the selectivity of one-shot borylation (Scheme 21).219 Based on the above description, initial borylation should occur at the para-position relative to the diphenylamino group. Indeed, the one-shot borylation performed using 10 equiv. of BBr₃ at room temperature occurred at this position,



Scheme 21 Synthesis of OBN, NBN, and ODBN in ref. 219

and the subsequent intramolecular bora-Friedel-Crafts reaction in the presence of NEtⁱPr₂ as a Brønsted base afforded **OBN** in 42% yield. The base reduced the concentration of in situ generated HBr and prevented the retro-Friedel-Crafts reaction to promote the formation of the kinetic product **OBN**. In contrast, one-shot borylation performed at higher temperature (160 °C) using 10 equiv. of BBr₃ selectively furnished NBN in 35% yield, i.e., boron was introduced at the para-position with respect to the phenoxy group. Given that this group is a weaker electron donor than the diphenylamine group and the paraposition relative to this group is therefore unfavourable for borvlation, NBN was concluded to be the thermodynamic product. In addition, double one-shot borylation affording ODBN in 17% yield was achieved by increasing the amount of BBr₃ (to 20 equiv.) and the reaction temperature (to 210 $^{\circ}$ C). Importantly, controlling the borylation temperature, number of boron equivalents, and/or Brønsted base addition enables the highly selective synthesis of kinetic/thermodynamic products.

Various MR emitters have been synthesised based on the abovementioned selectivity. One-shot borylation has also been applied to the synthesis of DABNA-type compounds (Scheme 22).111,220-223 An overview of these compounds and their borylation precursors shows that 1,3,5-trisubstituted benzenes are the preferred substrates, as they help to prevent undesired reactions. As mentioned above, one-shot borylation prefers to proceed at carbons where the HOMO is localised (ortho- and para-positions relative to the electron-donating group). However, in the case of 1,3-disubstituted benzene-type substrates, the borylation proceeds at the 4- or 6-positions rather than the sterically hindered 2-position. BBr₃ is the preferred boron source for their one-shot borylation, with no

Table 27 Photophysical properties of the compounds shown in Scheme 20

Compound	Condition	$\lambda_{\mathrm{PL}}^{\mathrm{max}}\left[\mathrm{nm}\right]$	FWHM [nm]	$\Phi_{ ext{PL}}$	$\Delta E_{\mathrm{ST}} [\mathrm{eV}]$	$k_{\rm RISC} \left[{ m s}^{-1} ight]$
BN1	Toluene/1 wt%-DBFPO ^a	454/458	18/22	/0.91	0.20/0.15	$-/1.3 \times 10^4$
BN2	Toluene/1 wt%-DBFPO ^a	464/467	15/22	/0.93	0.16/0.13	$-/2.6 \times 10^4$
BN3	Toluene/1 wt%-DBFPO ^a	456/458	17/21	/0.98	0.15/0.12	$-/2.55 \times 10^5$

^a See Table 2 for the full compound name.

Chem Soc Rev Review Article

Scheme 22 Synthesis of DABNA analogues by one-shot borylation.

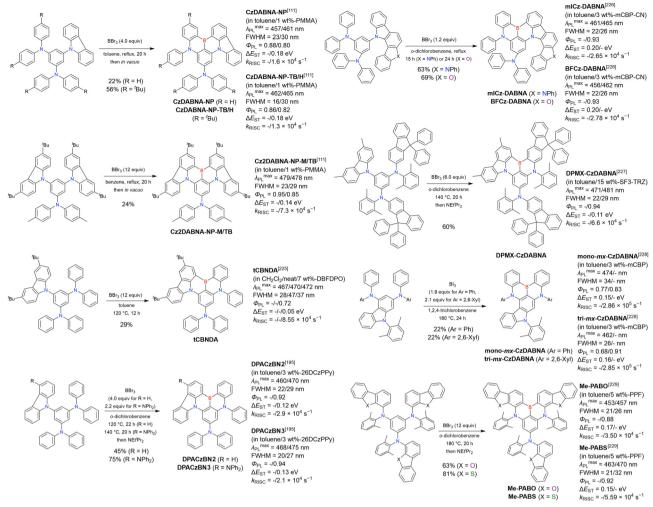
Scheme 23 Synthesis of the perylene-fused BN compounds by one-shot borylation reported in ref. 224.

uses of BCl₃ and BI₃ reported to date. The synthesis of hexa-^tBusubstituted DABNA (DABNA-NP-TB, t-DAB-DPA, or 3tPAB) has been independently reported by Hatakeyama et al., 111 Lee et al., 220 and Wang et al. 221 However, the corresponding yields varied widely. In the last two reports, the high reaction temperature was believed to facilitate the retro-Friedel-Crafts reaction involving the in situ generated HBr and induce deborylation and ^tBu group cleavage. In addition, all three substituents on the central benzene ring need not be electron-donating (e.g., amino and phenoxy) groups; for example, one of them can be a PAH.

The MR compounds BP-2DPA and DBP-4DPA, which have a perylene moiety instead of one diphenylamino group in the DABNA-NP core, were synthesised by Kwon et al. in yields of 39% and 37%, respectively, using one-shot borylation

(Scheme 23).²²⁴ Although many DABNA derivatives exhibit blue MR-TADF (e.g., **PAB**: λ_{PL}^{max} = 449 nm in toluene), ²²¹ **BP-2DPA** and **DBP-4DPA** feature significantly red-shifted emission (λ_{PL}^{max} = 599 nm and 605 nm in toluene, respectively), as perylene is a highly conjugated planar polycyclic aromatic system. On the other hand, BP-2DPA and DBP-4DPA do not exhibit TADF character due to the weak MR effect attributed to the non-MR perylene skeleton. Hence, BP-2DPA and DBP-4DPA were utilised as TEs for hyperfluorescence devices. The bonding/anti-bonding character of the FMOs of perylene remained, although weakened due to the fusion with the DABNA skeleton, and the shoulder peaks originating from the vibronic coupling between the S_1 - S_0 electronic transition and stretching vibrations were observed in the PL and EL spectra.

Electron-donating groups other than diarylamino moieties are also available, including carbazolyl, acridyl, azetidyl, and



Scheme 24 Synthesis of carbazole-based DABNA analogues by one-shot borylation.

ether groups. In particular, numerous carbazole-fused CzDABNA analogues were synthesised by one-shot borylation (Scheme 24). 111, 195, 225-229 When the 9-carbazolyl group is used as an electron-donating group, one-shot borylation proceeds based on the selectivity described above, as this group is a weaker electron donor than the diarylamino group. BBr₃ is used as the boron source in most cases, but BI₃ is also available. Carbazole ring incorporation is often used for emission wavelength tuning, as it results in the extension of the π -conjugated system and, hence, in red-shifted emission.

According to Wang et al., the one-shot borylation of a 9,10dihydro-9,9-dimethylacridine-substituted substrate with 4.0 equiv. of BBr₃ proceeded at the para-position relative to the diarylamino group to give tDMAC-BN in 32% yield, whereas that of a 9,10-dihydro-9,9-diphenylacridine-substituted substrate proceeded at the para-position relative to the acridine moiety to afford tDPAC-BN in 41% yield (Scheme 25). 230 Similarly, Wang et al. reported that the 9,10-dihydro-9,9-dimethylacridine moietycontaining borylated compound Ph-DMAC-BN was obtained in 44% yield and with similar selectivity under almost identical conditions. 231 When the 9,10-dihydroacridine moiety is used as an electron-donating group, the substituent at its 9-position seems to determine the selectivity of one-shot borylation.

Yang et al. attempted the one-shot borylation of the phenothiazine 5,5-dioxide-substituted substrate. 196 The one-shot borylation proceeded in the presence of 5.0 equiv. of BBr₃ to afford the borylation product PTZBN3 in 11% yield and the deoxygenated product PTZBN2 was obtained in 15% yield (Scheme 26). Although some S=O bond cleavage was observed, the sulfone moiety was found to be tolerant to one-shot borylation conditions to some extent.

One-shot borylation is also feasible for precursors bearing oxygenated electron-donating groups (e.g., aryloxy). In most cases, DOBNA derivatives are synthesised by one-pot borylation, but can also be prepared using the one-shot borylation of 1,3,5-trisubstituted benzene-type substrates. Hatakeyama et al. synthesised DOBNA-OAr in 91% yield as a host material for blue OLEDs by the one-shot borylation of three-fold symmetric 1,3,5-triaryloxybenzene in the presence of 4.0 equiv. of BI₃ followed by heat treatment in acetic acid (HOAc) (Scheme 27).⁶⁰

Heat treatment in acetic acid is an important procedure for increasing the yield of borylation reactions, especially when Chem Soc Rev Review Article

Scheme 25 Synthesis of acridine-based DABNA analogues by one-shot borylation.

Scheme 26 Synthesis of the phenothiazine-based DABNA analogues by one-shot borylation.

using a large excess of the boron source. As one-shot borylation proceeds at carbons contributing to the HOMO (often at the *para*-position relative to the electron-donating group), borylation at undesired peripheral positions may occur as a side reaction. Heat treatment in acetic acid removes the non-fused boron introduced at the periphery by excess BI₃. This technique was used to synthesise **2B-DTACrs** by Zysman-Colman *et al.*²³² In contrast to the mono-borylated **1B-DTACrs**, which was synthesised using 4.1 equiv. of BBr₃, the di-borylated **2B-DTACrs** was synthesised using 10 equiv. of BBr₃ followed by acetic acid treatment (Scheme 28).

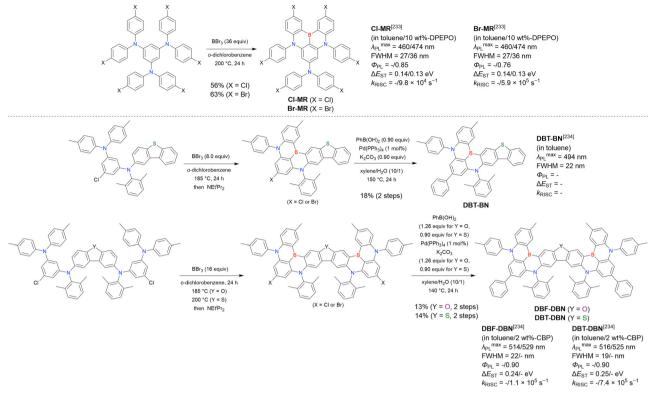
Furthermore, the conditions of one-shot borylation allow for the retention of convertible halogens such as chlorine and bromine as well as for late modification (Scheme 29). Lee and Hong reported that six chlorine or bromine atoms were maintained even upon treatment with 36 equiv. of BBr₃ in *o*-dichlorobenzene at 200 °C, which afforded mono-borylated

Scheme 27 Synthesis of DOBNA-OAr by one-shot borylation in ref. 60.

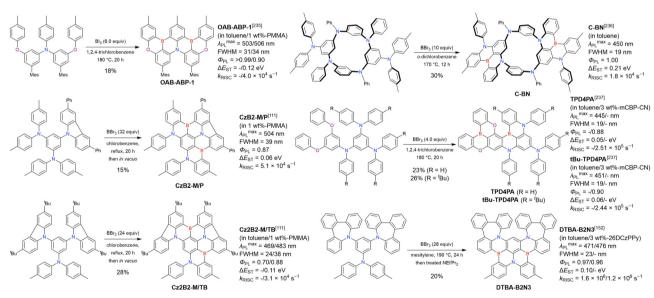
Scheme 28 Synthesis of 1B-DTACrs and 2B-DTACrs reported in ref. 232.

compounds **Cl-MR** and **Br-MR** in yields of 56% and 63%, respectively.²³³ In the synthesis of **DBT-BN**, **DBF-DBN**, and **DBT-DBN** by Wu and Lan *et al.*, the chlorine atoms in the borylation precursor were partially exchanged for bromine during one-shot borylation with BBr₃. However, this did not present a problem, as these halogen atoms were consumed in the subsequent Suzuki–Miyaura coupling.²³⁴

One-shot borylation is also a powerful method for achieving double borylation (Scheme 30). For example, the one-shot double borylation of a precursor synthesised from a commercially available compound in three steps was carried out in the presence of 6.0 equiv. of BI₃ at 180 °C to afford the sterically protected OAB-ABP-1 in 18% yield. 235 Note that the mesityl and methyl groups suppressed the undesirable borylation at the carbon atom contributing to the HOMO. Duan et al. used oneshot double borylation to prepare DABNA-incorporated calix[4]arene C-BN in 30% yield.236 Furthermore, You et al. used one-shot double borylation at 190 °C in the presence of 26 equiv. of BBr₃ to synthesise DTBA-B2N3 in 26% yield as an MR emitter by introducing a medium (azepine) ring to suppress aggregation-caused quenching (ACQ).152 Kwon et al. amalgamated the conventional DOBNA and DABNA structures, synthesising TPD4PA and tBu-TPD4PA in yields of 23% and 26%, respectively, via one-shot double borylation in the presence of



Scheme 29 Synthesis of BN compounds bearing halogen atoms by one-shot borylation.

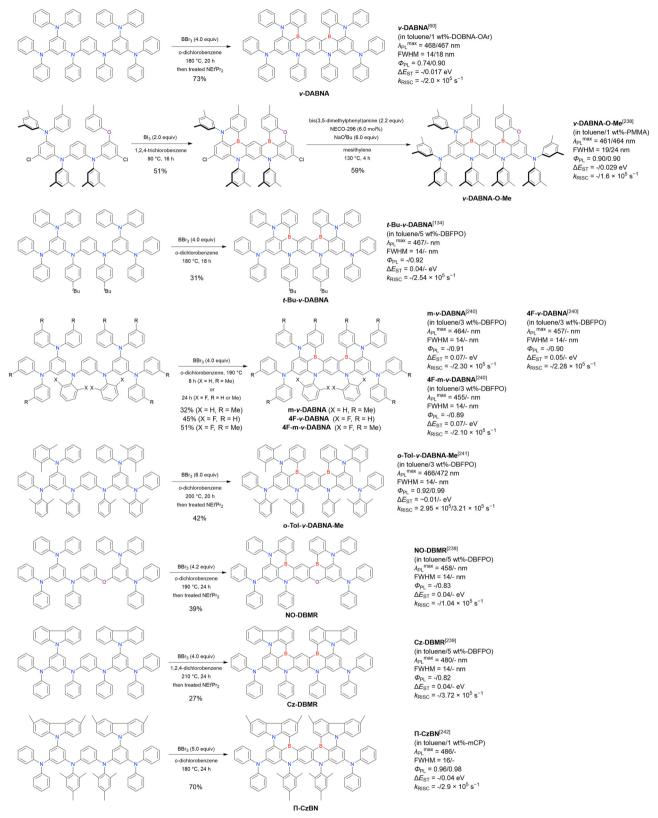


Scheme 30 Double one-shot borylation reactions.

4.0 equiv. of BBr₃.²³⁷ One-shot double borylation is often performed using a large excess of BBr3 or BI3. The thus obtained B2 compounds are expected to exhibit enhanced MR effects and smaller $\Delta E_{\rm ST}$ than B1 MR compounds because of the highly extended π -skeleton of the former.

In 2019, Hatakeyama et al. reported ν-DABNA as a new scaffold for narrowband MR-TADF emitters. 60 v-DABNA was

synthesised from commercially available compounds in three steps including palladium-catalysed C-N coupling and oneshot borylation. The one-shot borylation of the precursor with 4.0 equiv. of BBr₃ at 180 °C afforded ν-DABNA in 36% yield (Scheme 31). According to DFT calculations, the boron atoms were selectively introduced at the carbon atoms primarily contributing to the HOMO. Additionally, the small number of Chem Soc Rev **Review Article**



Scheme 31 Synthesis of ν -DABNA and its analogues by one-shot borylation.

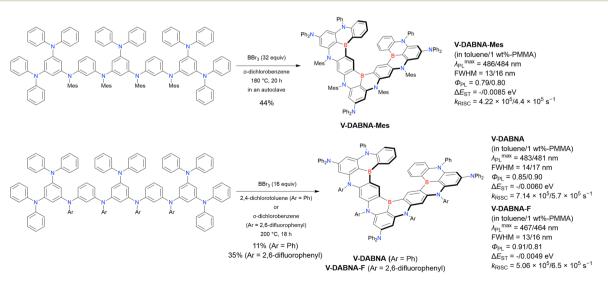
substituents at the central benzene ring and its steric accessibility are important for achieving highly selective borylation. Compared to DABNA-1,³⁸ v-DABNA exhibited a substantially higher $k_{\rm RISC}$ (2.0 \times 10⁵ s⁻¹) and was used to realise an OLED with an excellent EQE, minimum efficiency roll-off (34.4/32.8/ 26.0% at 15/100/1000 cd m⁻², respectively), and ultrapure blue

emission (FWHM = 18 nm). Therefore, ν -DABNA would replace DABNA as the benchmark for MR compounds. Following the success of v-DABNA, various related derivatives have been synthesised. Hatakeyama et al. reported ν -DABNA-O-Me, which can be viewed as ν -DABNA with an oxygen atom instead of the nitrogen atom. 238 The one-shot double borylation of a chlorinebearing precursor was carried out with a stoichiometric amount of BI₂ at 90 °C to obtain the desired intermediate in 51% yield. and the subsequent cross-coupling with bis(3,5-dimethylphenyl)amine at 130 $^{\circ}$ C afforded ν -DABNA-O-Me in 59% yield. In view of its lower atomic orbital energy, the oxygen atom restricts the π -conjugation of the HOMO rather than that of the LUMO. The replacement of nitrogen with oxygen affects the HOMO energy level more than it does the LUMO energy level. As a result, ν-DABNA-O-Me exhibits a larger HOMO-LUMO gap and displays a deeper blue emission (465 nm) than ν -DABNA. The emission maximum of v-DABNA (469 nm) is slightly redshifted relative to that of DABNA-1 (459 nm) because of π -extension. As a result, the Commission Internationale de l'Eclairage (CIE) coordinates (0.12, 0.11) deviated from the requirements defined by the National Television System Committee (0.14, 0.08). Therefore, the replacement of nitrogen by oxygen is a powerful strategy for achieving optimal emission wavelengths. Kwon et al. used a similar concept to synthesise NO-DBMR, where the different nitrogen position in ν -DABNA was replaced by oxygen.²³⁹ The final double one-shot borylation was carried out using 4.2 equiv. of BBr3 to afford NO-DBMR in 39% yield. Fluorination and methylation are also used to realise blue-shifted emission. Kwon et al. also obtained m-v-DABNA, 4F-v-DABNA, and 4F-m-v-DABNA in yields of 32%, 45%, and 51%, respectively, by one-shot borylation with 4.0 equiv. of BBr₃ from a substrate with a fluorinated or methylated benzene ringsubstituted nitrogen.240 Other approaches to derivative design involve the introduction of bulky substituents to prevent luminescence peak broadening due to excimer formation in the aggregated state and enhance the horizontal orientation. Based

on this strategy, Kwon et al. synthesised tBu-v-DABNA in 31% yield by introducing ^tBu groups into ν-DABNA, ¹³⁴ while Yoo et al. synthesised o-Tol-v-DABNA-Me in 42% yield via one-shot borylation with BBr3 by changing the substituent on the nitrogen to o-tolyl or xylyl. 241 As mentioned above, the introduction of the carbazole scaffold extends the π -conjugated system and leads to red-shifted emission. The same is true for ν -DABNA derivatives, as exemplified by carbazole-fused Cz-DBMR and Π-CzBN synthesised by Kwon et al. and Zhang et al., respectively. 239,242

In 2022, Hatakeyama et al. synthesised an expanded B,Nembedded heterohelicene, V-DABNA-Mes, as a representative new member of the DABNA series by triple one-shot borylation. 243 The one-shot triple borylation was achieved using 32 equiv. of BBr₃ in an autoclave at 180 °C to afford V-DABNA-Mes in 44% yield (Scheme 32). The steric protection provided by the mesityl groups suppresses both overborylation and borylation at undesired reactive sites. Notably, a significant drop in the yield of V-DABNA-Mes (3%) was observed under standard reflux conditions in a flask because of the decreased concentration of BBr₃ in the reaction mixture. The one-step construction of such giant helix structures is not only synthetically useful but also an important as a design strategy for the emitters of high-performance OLEDs, as the enhanced MR effect and extended π -helix structure led to small FWHM (13 nm) and large $k_{\rm RISC}$ (4.22 \times 10⁵ s⁻¹) in toluene. This facile and scalable method was applied to unsubstituted and fluorine-substituted compounds, and triple one-shot borylation with 16 equiv. of BBr3 gave V-DABNA and V-DABNA-F in 11% and 35% yields, respectively.244

Hatakeyama et al. achieved quadruple, sextuple, and octuple borylation to construct the largest MR-core structures, which comprised B,N-embedded nonacene (CzB4), tridecacene (CzB6), and heptadecacene (CzB8) frameworks, respectively. 245 The key to success was the judicious choice of the borylating reagent, namely BI3 combined with 2,6-di-tert-butylpyridine (DTBPY), and



Scheme 32 Synthesis of the V-DABNA series reported in ref. 243 and 244.

Chem Soc Rev **Review Article**

long alkyl-substituted carbazolyl groups as boron-trapping groups, which suppressed the decrease in HOMO energy and insolubilisation associated with borylation. The one-shot multiple borylation with 16-32 equiv. of BI₃ and 12-24 equiv. of DTBPY (as a bulky Brønsted base) proceeded at 150 °C to afford CzB4, CzB6, and CzB8 in yields of 90%, 86%, and 83%, respectively. Thus, each electrophilic C-H borylation proceeded in >99% yield, which is the highest efficiency reported to date for C-H borylation reactions (Scheme 33). The thus obtained large MR compounds exhibited ultra-narrowband green TADF with FWHM = 12–16 nm. This achievement suggests that carbazolyl groups may enable the construction of larger acene frameworks by multiple borylation.

Thus, one-shot borylation is a powerful synthesis method for developing boron-embedded MR compounds, especially for the introduction of multiple boron atoms, and is complementary to one-pot borylation. The selectivity of this reaction is mainly determined by electronic and steric requirements; therefore, a deep understanding of these requirements is useful for MR emitter design. It should be noted that one-shot borylation is not a panacea, allowing the synthesis of only a small fraction of the vast chemical space of MR compounds.

3.2 One-shot (N-H) borylation

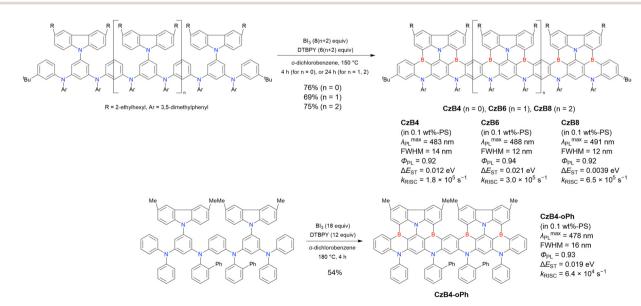
This subsection focuses on MR compounds with B-N bonds synthesised by amine-directed one-shot borylation (N-H borylation). B-N covalent bonds were first used to formally replace the isoelectronic C=C bonds by Dewar in 1958. 25 Although the corresponding B,N-doped PAHs are being intensively researched because of the unique optical and electronic properties imparted by dipole B-N bonds, 26-33 highly B-N-doped PAHs do not exhibit MR-TADF and exhibit relatively large FWHMs. 246,247 In 2022, Duan et al. used the amine-directed formation of B-N bonds to demonstrate the preparation of MR compounds m[B-N]N1 and m[B-N]N2.²⁴⁸ Amine-directed

$$\begin{array}{c} R^1 \\ R^2 \\ R^2 \\ R^1 \\ R^2 \\$$

Scheme 34 Synthesis of m[B-N]N1 and m[B-N]N2 by the amine-directed one-shot borylation reported in ref. 248.

double borylation 106 occurred in chlorobenzene at 150 °C in the presence of 4.0 equiv. of BBr₃ and 4.0 equiv. of base to produce m[B-N]N1 and m[B-N]N2 in yields of 90% and 92%, respectively (Scheme 34). Notably, the two boron atoms were introduced at ortho-positions relative to the nitrogen atoms, and other byproducts including regioisomers and monoborylated compounds were not detected. While m[B-N]N1 and m[B-N]N2 displayed narrowband pure emission with FWHM = 26–32 nm and $\Phi_{\rm PL} > 90\%$ but exhibited slightly larger $\Delta E_{\rm ST}$ (0.13-0.15 eV) and smaller $k_{\rm RISC}$ compared with other B2 compounds. This indicated that the MR effect was weakened because of carbazole moieties connecting the central benzene ring via C-C bonds.

The same group used this facile and scalable amine-directed double borylation method to prepare a standard para-B-π-B skeleton modified by the stepwise replacement of nitrogen atoms with oxygen atoms (Scheme 35).249 The resulting compounds featured a wide λ_{PL}^{max} range of 442-545 nm while maintaining narrow FWHM (19-26 nm) and high luminescence efficiency ($\Phi > 0.84$). On the other hand, these para-B- π -B



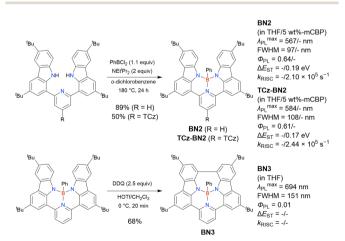
Scheme 33 Synthesis of CzB4-CzB8 and CzB4-oPh by one-shot quadruple, sextuple, and octuple borylation reported in ref. 245.

Review Article

Synthesis of B-N bond-embedded MR compounds reported Scheme 35 in ref 249

compounds exhibited large $\Delta E_{\rm ST}$ (0.26–0.44 eV) among the B2 compounds and did not show TADF behaviour because the MR effect is weakened when the two boron atoms are in the paraposition with respect to each other, and also because the carbazole moiety, which forms a C-C bond with the central benzene ring, has a weak MR effect.

Not only the synthesis of tricoordinate boron-based MR-TADF compounds, but also those of tetracoordinate boronbased MR-TADF compounds containing B-N bonds have been achieved using amine-directed one-shot borylation. Wang et al. reported tetracoordinate boron-containing MR-TADF emitters



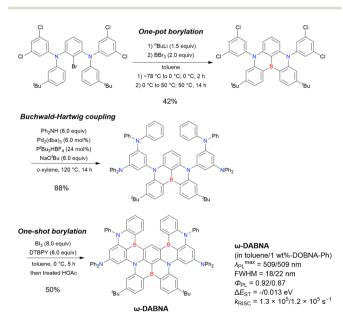
Scheme 36 Synthesis of tetracoordinate boron-containing MR compounds by one-shot borylation reported in ref. 250.

based on a C,N,C- or N,N,N-chelating pincer ligand.²⁵⁰ Among them, N,N,N-chelating compounds BN2, Tcz-BN2, and BN3 were synthesised using amine-directed one-shot borylation (Scheme 36). The amine-directed one-shot borylation of the N,N,N-ligand bearing one pyridine moiety and two N-H bonds occurred in the presence of dichlorophenylborane (PhBCl₂) as a boron source to afford BN2 and TCz-BN2, while the subsequent Scholl reaction of BN2 gave BN3. Unlike the emission spectra of conventional MR-compounds, the emission spectra of BN2 and TCz-BN2 were broad (FWHM = 97 and 108 nm, respectively) because of the large structural differences between the ground and excited states derived from tetracoordinate boron. In addition, BN2 and TCz-BN2 exhibited TADF character, although the boron orbitals are not involved in the MR structure and the MR effect is derived from the pyridine-containing skeleton.

In brief, amine-directed borylation is a facile and scalable method for synthesising B-N bond-bearing PAHs, although they often display no MR effects. The study of MR compounds bearing B-N bonds is currently in its early stage.

3.3 Sequential multiple borylation

One-shot borylation is a facile method for developing π extended MR compounds containing multiple boron atoms. However, because this reaction proceeds at the most sterically accessible carbon atom contributing to the HOMO, 251 the chemical space of boron-based MR compounds remains largely unexplored. To address this issue, Hatakeyama et al. proposed a new synthesis method for boron-based MR compounds, namely sequential multiple borylation, which involves one-pot borylation, Buchwald-Hartwig coupling, and one-shot borylation. 252 This method was used to synthesise an ultrapure green MR emitter (ω-DABNA) as a proof-of-concept (Scheme 37). The omega-shaped MR framework containing



Scheme 37 Synthesis of ω -DABNA by sequential multiple borylation reported in ref. 252

Chem Soc Rev Review Article

three boron atoms and four nitrogen atoms could not be accessed using conventional borylation protocols such as onepot or one-shot borylation. This structure, featuring three boron atoms introduced into the same benzene ring, could not be synthesised by one-pot borylation because electron repulsion destabilises the trilithiated intermediate formed in the course of this reaction. In the case of one-shot borylation, triple borvlation could not proceed because the HOMO is not localised at the third borylation position after the introduction of two boron atoms. The initial precursor, which has four chlorine atoms and one bromine atom, was prepared in two steps from a commercially available compound through iterative Buchwald-Hartwig coupling. The first key step in sequential multiple borylation, i.e., the one-pot borylation of the initial precursor, was the construction of a DABNA skeleton retaining four chlorine atoms. Lithium-bromine exchange was followed by a bora-Friedel-Crafts reaction in the presence of 2.0 equiv. of BBr₃, which afforded a DABNA derivative bearing four chlorine atoms in 42% yield. The second key step, i.e., the introduction of four diphenylamino groups into the DABNA derivative, was achieved by Buchwald-Hartwig coupling with diphenylamine, which afforded the final borylation precursor in 88% yield. The third key step was the one-shot borylation. Importantly, the HOMO of the final borylation precursor was mainly localised on the DABNA skeleton, and regioselective borylation reactions were therefore expected. Indeed, in the presence of DTBPY, the one-shot double borylation with 8.0 equiv. of BI3 afforded ω-DABNA in 50% yield. In the absence of DTBPY, a significant drop in yield (4%) was observed, and a considerable amount of the precursor (80%) was recovered. This indicated that the sterically hindered DTBPY selectively captured the in situ generated HI to promote borylation and suppress deborylation via the retro-bora-Friedel-Crafts reaction. In addition, the final one-shot borylation with BBr3 was carried out at 180 °C to afford ω-DABNA in a yield of 23%, which is lower than that obtained with BI₃ as the boron source (50%) because of the lower reactivity of BBr₃.

At about the same time as Hatakeyama *et al.*, Zysman-Calman *et al.* independently reported the synthesis of ladder-type deep-blue MR compounds **NBONacene** and **MesBDIDOBNA-N** using a protocol which can be categorized as sequential multiple borylations (Scheme 38).^{253,254} One-pot borylation afforded *pMDBA-Br* in 73% yield, with subsequent coupling giving the final borylation precursors in 47% and 57% yields, respectively. One-shot borylation was performed with excess BBr₃, and the R2BBr species generated *in situ* were trapped with a Grignard reagent to afford the target compounds, **NBONacene** and **MesB-DIDOBNA-N**, in 45% and 74% yields, respectively. Although the final borylation step does not construct a fully fused structure around the introduced boron atom, these synthesis methods also seem to be sequential multiple borylation protocols.

Sequential multiple borylation can be useful for the synthesising MR-TADF materials, especially those bearing multiple boron atoms at the same aromatic ring, and thus has the potential to become a new standard protocol for MR emitter synthesis.

Scheme 38 Synthesis of **NOBNacene** and **MesB-DIDOBNA-N** by sequential multiple borylation.

3.4 Summary

One-shot borylation converts multiple C-H/N-H bonds into C-B/N-B bonds to construct the boron-embedded π -conjugated skeletons in one shot. This is a powerful synthesis method for producing π-extended MR compounds. Furthermore, a sequential multiple borylation protocol that elaborately combines oneshot borylation and one-pot borylation was recently developed to expand the chemical space of MR compounds. Since detailed discussion of the photophysical properties of each obtained compound is beyond the scope of this review, we summarise the photophysical data for the related compounds in Table 28, and provide brief structure-property correlations. Basic relationships, such as the dependence of the maximum emission wavelength on the electron-donating abilities of the substituents, can be explained in a similar way to that of compounds obtained by one-pot borylation (see Sections 2.2.2 and 2.3.2). Most π -extended MR compounds with multiple boron atoms obtained by one-shot borylation show a small $\Delta E_{\rm ST}$ and large k_{RISC} because of enhanced short-range CT and long-range electronic delocalisation in the excited states.⁷⁴ Although π -extensions with 1,2-azaborine, heterole, and perylene result in materials with poor TADF properties because of the partial cancelation of the MR effect, the rigid and π -extended

Review Article

Table 28 Photophysical properties of the compounds shown in Section 3

Condition $\lambda_{\rm PL}^{\rm max}$ [nm] FWHM [nm] $\Delta E_{\rm ST}$ [eV] $k_{\rm RISC} \left[{\rm s}^{-1} \right]$ Ref. Compound $\Phi_{\mathrm{PL}}\left[-ight]$ **B2** CH₂Cl₂/1 wt%-PMMA^a 461/455 39/32 0.19/0.68 0.12/0.18 $-/4.1 \times 10^4$ 217 В3 CH2Cl2/1 wt%-PMMAa 442/441 50/34 0.13/0.47 0.31/0.15217 CH₂Cl₂/1 wt%-PMMA^a _/_ **B4** 449/450 22/38 0.21/0.610.19/0.15217 1 wt%-PMMAa 0.15 B2-F 467 44 0.57 217 CzDABNA-NP-M/TB Toluene/1 wt%-PMMAa 465/468 23/28 0.82/0.86-/0.18 $-/1.1 \times 10^4$ 111 CzB2-M/TB Toluene/1 wt%-PMMA^a 473/491 23/34 0.72/0.88 -/0.11 $-/2.4 \times 10^4$ 111 Toluene/1 wt%-DBFPO BN1 454/458 18/22 -/0.910.20/0.15 $-/1.3 \times 10^4$ 218 BN2 Toluene/1 wt%-DBFPOa 464/467 15/22 -/0.930.16/0.13 $-/2.6 \times 10^4$ 218 $-/2.55 \times 10^5$ BN₃ Toluene/1 wt%-DBFPOa 456/458 17/21 -/0.980.15/0.12218 OBN Toluene/10 wt%-DBFPO^a 425/-30/46 0.85/0.500.20/-- $-/1.3 \times 10^4$ 219 **NBN** Toluene/10 wt%-DBFPOa 440/-29/43 0.90/0.710.12/-- $-/2.9 \times 10^4$ 219 0.19/— $--/2.1 \times 10^4$ ODBN Toluene/10 wt%-DBFPOa 429/-26/55 0.93/0.86 219 DABNA-NP-M 1 wt%-PMMA^a 29 0.17 $1.4\,\times\,10^4$ 460 0.88 111 DABNA-NP-TB^b 1.4×10^4 1 wt%-PMMA^a 453 26 0.83 0.17 111 t-DAB-DPA^b 3 wt%-mCBP:mCBP-CN^a 0.94 3.97×10^4 220 449/453 23/— -/0.06 $-/6.95 \times 10^4$ PAB Toluene/3 wt%-mCP^a -/0.61221 2tPAB Toluene/3 wt%-mCP^a 456/457 26/--/0.67-/0.08 $-/6.34 \times 10^4$ 221 3tPAB^b 23/----/0.10 Toluene/3 wt%-mCP 456/458 -/0.75 $-/5.74 \times 10^4$ 221 $-/1.95 \times 10^4$ mBP-DABNA-Me Toluene/5 wt%-mCP:DPEPO^a 464/467 __/__ --/0.970.12/0.13222 pBP-DABNA-Me Toluene/5 wt%-mCP:DPEPOa 458/462 15/22 -/0.980.11/0.18 $-/6.85 \times 10^4$ 223 BP-2DPA Toluene/1 wt%-DIC-TRz^a 599/601 34/37 -/0.91224 DBP-4DPA _/_ Toluene/1 wt%-DIC-TRza 605/612 34/35 -/0.96224 CzDABNA-NP -/0.18 $-/1.6 \times 10^4$ Toluene/1 wt%-PMMA^a 457/461 23/30 0.88/0.80111 CzDABNA-NP-TB/H Toluene/1 wt%-PMMAa 462/465 16/30 0.86/0.82 -/0.18 $-/1.3 \times 10^4$ 111 Cz2DABNA-NP-M/TB $--/7.3 \times 10^4$ Toluene/1 wt%-PMMAa 479/478 23/29 0.95/0.85--/0.14111 tCBNDA CH₂Cl₂/neat/7 wt%-DBFDPO^a 467/470/472 28/47/37 --/--/0.72 --/--/0.05 $-/-/8.55 \times 10^4$ 225 $-/2.9 \times 10^4$ DPACzBN2 Toluene/3 wt%-26DCzPPya 460/470 22/29 -/0.92-/0.12195 Toluene/3 wt%-26DCzPPy^a DPACzBN3 468/475 20/27 -/0.94--/0.13 $-/2.1 \times 10^4$ 195

DEACEDING	TOTUCHE/3 Wt70-20DCZFFY	400/4/3	20/27	-/0.94	-/0.13	—/2.1 ∧ 10	193
mICz-DABNA	Toluene/3 wt%-mCBP-CN ^a	461/465	22/26	 /0 . 93	0.20/—	$-/2.65 \times 10^4$	226
BFCz-DABNA	Toluene/3 wt%-mCBP-CN ^a	456/462	22/26	 /0 . 93	0.20/—	$-/2.78 \times 10^4$	226
DPMX-CzDABNA	Toluene/15 wt%-SF3-TRZ ^a	471/481	22/29	/0.94	/0.11	$-/6.6 \times 10^4$	227
mono-mx-CzDABNA	Toluene/3 wt%-mCBP ^a	474/—	34/—	0.77/0.83	0.15/—	$-/2.86 \times 10^5$	228
tri-mx-CzDABNA	Toluene/3 wt%-mCBP ^a	462/—	26/—	0.68/0.91	0.16/—	$/2.85 \times 10^5$	228
Me-PABO	Toluene/5 wt%-PPF ^a	453/457	21/26	/0.88	0.17/—	$-/3.50 \times 10^4$	229
Me-PABS	Toluene/5 wt%-PPF ^a	463/470	21/32	/0.92	0.15/—	$-/5.59 \times 10^4$	229
tDMAC-BN	Toluene/1 wt%-PMMA ^a	468/—	26/—	/0.90	0.15/—	$/4.80 \times 10^4$	230
tDPAC-BN	Toluene/1 wt%-PMMA ^a	454/—	19/—	/0.94	0.17/—	$-/1.16 \times 10^4$	230
PhDMAC-BN	Toluene/5 wt%-PPF ^a	473/483	27/34	/0.86	0.14/—	$/5.04 \times 10^4$	231
PTZBN3	Toluene/26DCzPPy ^a	468/473	30/36	/0.98	0.17/—	-1.08×10^5	196
PTZBN2	Toluene/26DCzPPy ^a	483/487	41/42	/0.95	0.15/—	$-/4.51 \times 10^4$	196
DOBNA-Oar	Toluene/neat	388/433	34/—	0.65/—	0.16/—	—/—	60
1B-DTACrs	Toluene/5 wt%-mCBP ^a	438/443	27/28	0.99/0.83	0.22/0.21	—/—	232
2B-DTACrs	Toluene/5 wt%-mCBP ^a	443/448	21/24	0.64/0.74	0.16/0.16	$/1.3 \times 10^5$	232
Cl-MR	Toluene/10 wt%-DPEPO ^a	460/474	27/36	 /0 . 85	0.14/0.13	$/9.8 \times 10^4$	233
Br-MR	Toluene/10 wt%-DPEPO ^a	460/474	27/36	 /0 . 76	0.14/0.13	$/5.9 \times 10^5$	233
DBT-BN	Toluene	494	22	_	_	_	234
DBF-DBN	Toluene/2 wt%-CBP ^a	514/529	22/—	/0.90	0.24/—	$/1.1 \times 10^5$	234
DBT-DBN	Toluene/2 wt%-CBP ^a	516/525	19/—	/0.90	0.25/—	$/7.4 \times 10^5$	234
OAB-ABP-1	Toluene/1 wt%-PMMA ^a	503/506	31/34	>0.99/0.90	/0.12	$/4.0 \times 10^4$	235
CzB2-M/P	1 wt%-PMMA ^a	504	39	0.87	0.06	5.1×10^4	111
Cz2B2-M/TB	Toluene/1 wt%-PMMA ^a	469/483	24/38	0.70/0.88	/0.11	$-/3.1 \times 10^4$	111
C-BN	Toluene	450	19	1.00	0.21	1.8×10^{4}	236
TPD4PA	Toluene/3 wt%-mCBP-CN ^a	445/—	19/—	/0.88	0.05/—	$/2.51 \times 10^5$	237
tBu-TPD4PA	Toluene/3 wt%-mCBP-CN ^a	451/—	19/—	/0.90	0.06/—	$/2.44 \times 10^5$	237
DTBN-B2N3	Toluene/3 wt%-26DCzPPy ^a	471/475	23/—	0.97/0.96	0.10/—	$1.6 \times 10^6 / 1.2 \times 10^6$	152
ν-DABNA	Toluene/1 wt%-DOBNA-Oar	468/467	14/18	0.74/0.90	/0.017	$/2.0 \times 10^5$	60
ν-DABNA-O-Me	Toluene/1 wt%-PMMA ^a	461/464	19/24	0.90/0.90	/0.029	$-/1.6 \times 10^5$	238
t-Bu-ν-DABNA	Toluene/5 wt%-DBFPO ^a	467/—	14/—	/0.92	0.04/—	$-/2.54 \times 10^5$	134
m-ν-DABNA	Toluene/3 wt%-DBFPO ^a	464/—	14/—	/0.91	0.07/—	$-/2.30 \times 10^5$	240
4F-ν-DABNA	Toluene/3 wt%-DBFPO ^a	457/—	14/—	/0.90	0.05/—	$/2.28 \times 10^5$	240
4F-m-ν-DABNA	Toluene/3 wt%-DBFPO ^a	455/—	14/—	 /0 . 89	0.07/—	$-/2.10 \times 10^5$	240
o-Tol-ν-DABNA-Me	Toluene/3 wt%-DBFPO ^a	466/472	14/—	0.92/0.99	~ 0.01/—	$2.95 \times 10^5/3.21 \times 10^5$	241
NO-DBMR	Toluene/5 wt%-DBFPO ^a	458/—	14/—	/0.83	0.04/—	$-/1.04 \times 10^5$	239
Cz-DBMR	Toluene/5 wt%-DBFPO ^a	480/—	14/—	/0.82	0.04/—	$-/3.72 \times 10^5$	239
Π-CzBN	Toluene/1 wt%-mCP ^a	486/—	16/—	0.96/0.98	/0.04	$/2.9 \times 10^5$	242
V-DABNA-Mes	Toluene/1 wt%-PMMA ^a	486/484	13/16	0.79/0.80	/0.0085	$4.22 \times 10^5 / 4.4 \times 10^5$	243
V-DABNA	Toluene/1 wt%-PMMA ^a	483/481	14/17	0.85/0.90	/0.0060	$7.14 \times 10^5 / 5.7 \times 10^5$	244
V-DABNA-F	Toluene/1 wt%-PMMA ^a	467/464	13/16	0.91/0.81	/0.0049	$5.06 \times 10^5/6.5 \times 10^5$	244
CzB4	0.1 wt%-PS ^a	483	14	0.92	0.012	1.8×10^{5}	245
CzB6	0.1 wt%-PS ^a	488	12	0.94	0.021	$3.0 imes 10^5$	245

Table 28 (continued)

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
CzB8	0.1 wt%-PS ^a	491	12	0.92	0.0039	6.5×10^{5}	245
CzB4-oPh	0.1 wt%-PS ^a	478	16	0.93	0.019	6.4×10^{4}	245
m[B-N]N1	Toluene/2 wt%-mCPBC ^a	481/483	29/28	0.93/0.91	0.15/0.15	$3.8 \times 10^3 / 1.59 \times 10^4$	248
m[B-N]N2	Toluene/2 wt%-mCPBC ^a	491/491	34/33	0.91/0.90	0.10/0.13	$2.4 \times 10^3 / 1.44 \times 10^4$	248
p[B-N]O	Toluene/1 wt%-mCPBC ^a	488/497	19/23	0.93/0.91	0.43/0.44	—/—	249
p[B-N]NO	Toluene/1 wt%-mCPBC ^a	522/529	28/30	0.90/0.89	0.40/0.37	_/_	249
p[B-N]N	Toluene/1 wt%-mCPBC ^a	442/450	19/25	0.84/0.83	0.28/0.26	—/—	249
BN2	THF/5 wt%-mCBP ^a	567/—	97/—	0.64/—	/0.19	$/2.10 \times 10^5$	250
TCz-BN2	THF/5 wt%-mCBP ^a	584/—	108/—	0.61/—	/0.17	$/2.44 \times 10^5$	250
BN3	THF	694	151	0.01	—/—	—/—	250
ω-DABNA	Toluene/1 wt%-DOBNA-Ph ^c	509/509	18/22	0.92/0.87	/0.013	$1.3 \times 10^5/1.2 \times 10^5$	252
NBONacene	THF/1.5 wt%-TSPO1 ^a	305 427/410 430	40/38	0.33/0.71	0.31/0.30	$-/3.74 \times 10^3$	254
MesB-DIDOBNA-N	THF/1.5 wt%-TSPO1 ^a	399/402	23/19	0.33/0.75	0.24/0.24	$-/9.81 \times 10^3$	253

^a See Table 2 for the full compound name. ^b Same compound named differently. ^c See Scheme 3.

framework provides a narrow FWHM, which is suitable for use as a TE for hyperfluorescence or PSF OLEDs. Thus, one-shot borylation has contributed significantly to the development of excellent emitters for OLEDs. However, the accessible chemical space is still limited because this reaction can only proceed at sterically unhindered carbons with a certain HOMO distributions. Therefore, it is desirable to develop new methodologies to further expand the chemical space.

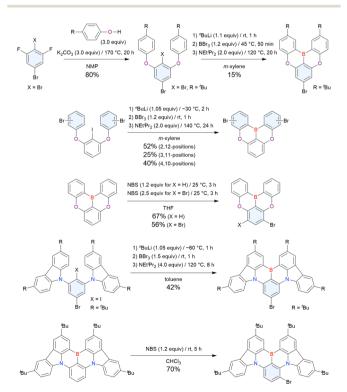
4. Late-stage functionalisation

As shown in previous sections, the photophysical properties of MR compounds, including their TADF characteristics, can be tuned over a wide range through the introduction of appropriate substituents. The routes to compounds with planar tricoordinate boron can be classified into those with earlyand late-stage functionalisation relative to borylation-cyclisation. The embedded boron centre sometimes limits certain types of post-reactions, e.g., some nucleophiles form tetracoordinated species while strongly acidic conditions promote retro-Friedel-Crafts reactions. Moreover, certain functional groups inhibit borylation, e.g., Lewis bases such as pyridyl groups can coordinate borylation reagents such as BBr₃, especially in the case of one-shot borylation. Thus, compounds with certain functional groups require appropriate synthesis approaches. In addition, late-stage functionalisation is advantageous for developing a series of derivatives and comparing their properties, even if these compounds can be synthesised using both schemes. Indeed, the first example of donorfunctionalised DOBNA (DOBNA-Phenox) was synthesised by one-pot borylation (Fig. 6), 37,105 while a wide variety of donor units have recently been developed using late-stage functionalisation. This section discusses compounds prepared using postborylation functionalisation to understand the factors determining the success of a given approach and therefore covers a wide variety of properties and structures. In particular, the DOBNA scaffold, which holds some distinct merits besides the MR effect with shortrange CT, is frequently incorporated as an acceptor unit into D-Atype TADF molecules showing long-range CT. Furthermore, this relatively stable scaffold can be used to synthesise B-doped PAHs

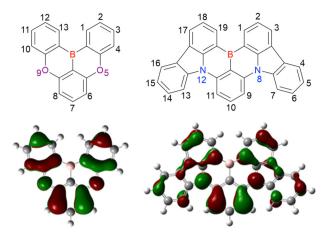
with electronic structures largely modulated by heterocycle fusion. In contrast, the functionalisation of the N,B,N-embedded CzBN structure mainly aims to improve the MR effect and OLED performances. The general synthesis procedures are summarised in Schemes 39–41 and 45, which cover most of the compounds appearing in this section. Thus, the structures and properties of these compounds are separately summarised in the following figures and tables. Meanwhile, certain reaction types such as nucleophilic addition and oxidation are discussed in additional schemes in each case.

4.1 Preparation of key intermediates bearing Br and Bpin groups

In the case of DOBNA, late-stage substitution is possible at 2, 3, 4, 6, and 7-positions *via* bromo-functionalisation (Fig. 23). In

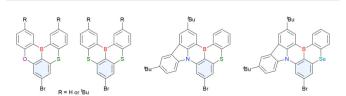


Scheme 39 Synthesis of bromo-substituted DOBNA and CzBN. The reaction conditions are reported in ref. 122, 119, 256, 184 and 258.



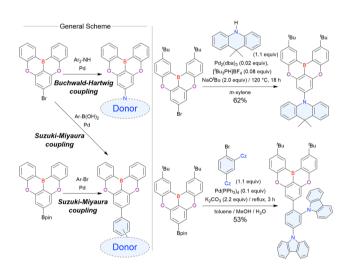
Atomic position numbers and HOMO distribution for DOBNA and CzBN.

particular, 7-bromo DOBNA derivatives, which can be prepared as shown in Scheme 39, are often subjected to Buchwald-Hartwig coupling to introduce arylamine electron donors. 122 The ^tBu groups at the peripheral 2,12-positions of the terminal phenyl rings reduce aggregation in the solid state. In addition, alkyl groups result in acceptor strengths lower than that of the unsubstituted DOBNA core (R = H), thus inducing a blue shift of the emission spectrum while increasing ΔE_{ST} when a donor unit is connected to 7-position. 202,255 Regarding borylation, lithium-halogen exchange might preferentially occur at the ortho-bromo atom with respect to the oxygen atoms despite the presence of two bromo atoms. Compounds prepared via lithium-bromine exchange were obtained in yields of up to $\sim 50\%$, ^{127,129} and the yields were not improved with lithiumiodine exchange using iodine compounds (X = I).120,124 Dibromo derivatives substituted at the terminal phenyl rings were synthesised in a similar manner in moderate yields. ¹¹⁹ On the other hand, 6-monobromo and 6,8-dibromo derivatives were prepared by the bromination of **DOBNA** with NBS because of the large HOMO coefficients at 6- and 8-positions (Fig. 23). 256 The HOMO distribution also indicated the difficulty of brominating DOBNA at 7-position after borylation, which explains the different synthesis strategy depicted in Scheme 39. Most CzBN derivatives used for late-stage reactions bear four ^tBu groups at 2,5,15,18-positions except for a very limited number of examples because these substituents hinder side reactions and increase the solubility of products. 162,257 CzBN derivatives mono-brominated at 10- and 9-positions were obtained using the approach employed to access brominated DOBNA derivatives. 184,258 Similarly, intermediates with various cyclised



Brominated derivatives with S- and Se-bridged structures.

Scheme 40 Synthesis of Bpin-substituted DOBNA and CzBN. The reaction conditions are reported in ref. 259, 260, and 185.



Scheme 41 Late-stage introduction of donor groups into DOBNA. The right panel shows the specific reaction conditions appearing in ref. 122 and 259

configurations and heteroatom bridges used for late-stage reactions were obtained by essentially identical methods (Fig. 24). 116,130,131,133,168,169 DOBNA and CzBN derivatives bearing boronic ester groups, which engage in Suzuki-Miyaura coupling with aryl halides, can be synthesised from brominated derivatives via Miyaura-Ishiyama borylation or iridiumcatalysed direct aromatic C-H (Hartwig-Miyaura) borylation (Scheme 40). 118,135,185,259-261 An asymmetric bridge with N and O atoms was also demonstrated.95

4.2 Donor-functionalised DOBNA-based materials

The DOBNA structure is useful for developing OLED host materials with high triplet energies as well as D-A-type TADF molecules with efficient spin-flip processes.^{37,112} The introduction of arylamine (e.g., carbazole-, diphenylamine-, 9,10-dihydroacridine- and Chem Soc Rev Review Article

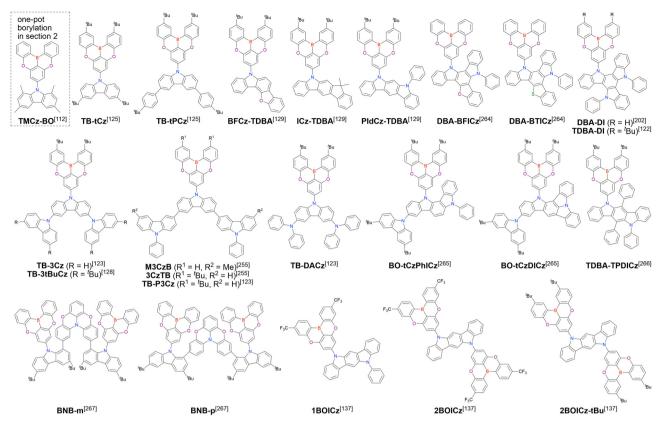


Fig. 25 DOBNA-based D-A-type TADF materials with carbazole-based donors at 7-position synthesised by late-stage functionalisation except **TMCz-BO**.

phenoxazine-based) donors by Buchwald–Hartwig coupling affords highly efficient D–A-type TADF emitters (Scheme 41). We emphasise that one-pot borylation is also useful for developing simple donor-functionalised DOBNA derivatives (Fig. 25 and 26). As mentioned above, the advantages of utilising DOBNA structures are the easy derivation of deep blue and relatively sharp emission owing to the high excited-state energies and rigid structures compared to those of acceptors such as sulfones used

in other deep blue emitters, although the emission colour can be tuned to orange-red by changing donor strength. The combination of the DOBNA structure and donors featuring spacers, such as the phenyl group, synthesised by Suzuki-Miyaura coupling leads to weak D–A interactions including through-space CT interactions and results in ultradeep blue (<450 nm) emitter and host materials. ^{259,262,263} The Buchwald-Hartwig amination of DOBNA derivatives typically proceeds in the presence of Pd₂(dba)₃

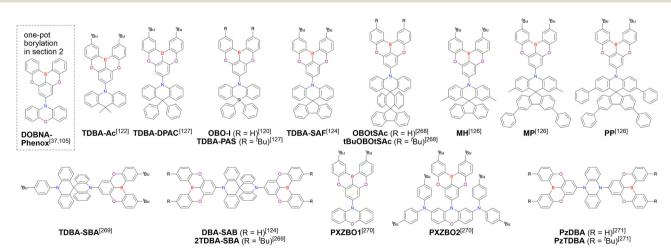


Fig. 26 DOBNA-based D-A-type TADF materials with 9,10-dihydroacridine-, phenoxazine- and 5,10-dihydrophenazine-based donors at 7-position synthesised by late-stage functionalisation except **DOBNA-Phenox**.

Review Article

Table 29 Photophysical properties of the materials shown in Fig. 25

Compound	Condition	$\lambda_{\mathrm{PL}}^{\mathrm{max}}\left[\mathrm{nm}\right]$	FWHM [nm]	$\Phi_{ ext{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
TMCz-BO	Toluene/30 wt%-PPF ^b	446/467	—/—	0.81/0.98	/0.020	$-/1.9 \times 10^{6}$	112
TB-tCz	Toluene/neat-film	415/433	$45/44^{b}$	0.53/0.41	0.23/0.20	$-/0.85 \times 10^6$	125
TB-tPCz	Toluene/neat-film	422/445	$46/42^{b}$	0.56/0.52	0.17/0.15	$-/1.05 \times 10^6$	125
BFCz-TDBA	Toluene/20 wt%-mCP ^a	$393/424^{b}$	$36/41^{b}$	0.84/0.58	0.24/—	$-/0.91 \times 10^6$	129
ICz-TDBA	Toluene/20 wt%-mCP ^a	$416/431^{b}$	$49/45^{b}$	0.84/0.63	0.19/—	$-/1.27 \times 10^6$	129
PIdCz-TDBA	Toluene/20 wt%-mCP ^a	$424/433^{b}$	$43/43^{b}$	0.88/0.55	0.20/—	$-/1.14 \times 10^6$	129
DBA-BFICz	Toluene/25 wt%-DBFPO ^a	$446/476^{b}$	$/64^{b}$	— /0 . 97	0.17/—	$-/3.50 \times 10^5$	264
DBA-BTICz	Toluene/25 wt%-DBFPO ^a	$445/476^{b}$	$/64^{b}$	 /0 . 95	0.29/—	$-/6.30 \times 10^5$	264
DBA-DI	Toluene/30 wt%-mCBP-can	467/—	—/—	 /0 . 95	0.03/—	$-/6.21 \times 10^6$	202
TDBA-DI	Toluene/20 wt%-DBFPO ^a	456/—	$55/65^{b}$	— /0 . 99	0.11/0.05	$-/1.08 \times 10^6$	122
TB-3Cz	Toluene/neat-film	413/433	—/—	0.52/0.97	—/—	$-/2.54 \times 10^5$	123
TB-3tBuCz	Toluene/10 wt%-26DCzPPy ^a	$425/425^{b}$	$46/46^{b}$	/1.00	0.05/—	$-/2.70 \times 10^5$	128
M3CzB	Toluene/20 wt%-DBFPO ^a	$445/478^{b}$	—/—	/0.93	0.14/—	$-/1.40 \times 10^5$	255
3CzTB	Toluene/20 wt%-DBFPO ^a	$433/470^{b}$	—/—	 /0 . 88	0.23/—	$-/1.02 \times 10^5$	255
TB-P3Cz	Toluene/neat-film	433/460	—/—	0.51/0.92	—/—	$-/2.46 \times 10^{5}$	123
TB-DACz	Toluene/neat-film	493/494	—/—	0.52/0.89	—/—	$-/1.35 \times 10^5$	123
BO-tCzPhICz	Toluene/30 wt%-mCP ^a	440/444	52/54	— /0 . 93	/0.08	$-/3.44 \times 10^6$	265
BO-tCzDICz	Toluene/30 wt%-mCP ^a	438/451	50/50	— /0 . 77	/0.15	$-/2.09 \times 10^6$	265
TDBA-TPDICz	Toluene/20 wt%-DBFPO ^a	$447/462^{b}$	$/58^{b}$	— /0 . 86	0.41/—	$-/1.15 \times 10^5$	266
BNB-m	Toluene/10 wt%-mCP ^a	504/502	$60/72^{b}$	— /1.00	/0.03	$-/1.60 \times 10^5$	267
BNB-p	Toluene/10 wt%-mCP ^a	529/518	$64/74^{b}$	 /0 . 86	/0.11	$-/9.88 \times 10^4$	267
1BOICz	Toluene/20 wt%-mCPBC ^a	527/534	$85/101^{b}$	0.90/1.00	/0.05	$-/1.12 \times 10^6$	137
2BOICz	Toluene/20 wt%-mCPBC ^a	518/528	83/91 ^b	0.89/1.00	/0.06	$-/1.18 \times 10^6$	137
2BOICz-tBu	Toluene/20 wt%-mCPBC ^a	$/467^{b}$	—/—	—/—	/0.25	—/—	137

^a See Table 2 for the full compound name. ^b Taken from the EL spectrum.

(0.01-0.2 equiv.), [${}^{t}Bu_{3}PH$]BF₄ (0.015-0.3 equiv.), and NaO ${}^{t}Bu$ (1-4)equiv.) in aromatic solvents at >100 °C, although SPhos and XPhos are sometimes used as ligands. Suzuki-Miyaura coupling typically proceeds under the standard conditions of Pd(PPh₃)₄ (0.02-0.1 equiv.) and aqueous K2CO3 (2-3 equiv.). The yields of these reactions are generally sufficiently high (40-80%).

The HOMO and LUMO energies of DOBNA (about −6.0 and -3.0 eV, respectively) are deeper than those of standard donor units such as di-tBu-carbazole and 9,10-dihydro-9,9dimethylacridine. Hence, the functionalised DOBNA derivatives in Fig. 25 and 26 show CT excited states where the HOMO and LUMO are well separated in the substituted donor and DOBNA moieties, respectively, as is commonly supported by DFT calculations. However, according to Tables 29 and 30, the FWHMs of these compounds are smaller than those typically observed for D-A-type TADF materials, probably because of a certain contribution of the MR effect. In addition, a markedly high Φ_{PL} small $\Delta E_{\rm ST}$, and high $k_{\rm RISC}$ were simultaneously achieved.

The seminal work on this series of compounds was reported by Kwon et al. in 2019,122 and numerous following papers described a wide variety of donor units. The emission wavelengths seemed to be linearly correlated with the strength of the D-A interactions. For example, the emission of DBA-BFICz was blue-shifted relative to that of DBA-DI with a stronger

Table 30 Photophysical properties of the materials shown in Fig. 26

Compound	Condition	$\lambda_{PL}^{max} \left[nm \right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
DOBNA-Phenox	1 wt%-PMMA b /20 wt%-CBP a	$492/504^{b}$	/—	0.92/—	0.06/—	—/—	37
TDBA-Ac	Toluene/20 wt%-DBFPO ^a	458/—	$50/55^{b}$	 /0 . 93	0.06/—	$-/0.99 \times 10^6$	122
TDBA-DPAC	Toluene/20 wt%-DPEPO ^a	$444/450^{b}$	$52/60^{b}$	0.88/0.88	0.04/0.02	$-/1.23 \times 10^6$	127
OBO-I	Toluene/20 wt%-PPF ^a	439/451	$51/60^{b}$	0.47/0.81	—/—	$-/1.1 \times 10^6$	120
DTBA-PAS	Toluene/20 wt%-DPEPO ^a	$427/435^{b}$	50/54	0.35/0.92	—/—	-1.70×10^6	127
TDBA-SAF	Toluene/20 wt%-DPEPO ^a	$450/456^{b}$	$47/55^{b}$	/0.90	/0.11	$-/2.1 \times 10^6$	124
OBOtSAc	Toluene/10 wt%-DPEPO ^a	452/454	$50/50^{b}$	 /0 . 97	/0.06	$-/5.59 \times 10^5$	268
tBuOBOtSAc	Toluene/10 wt%-DPEPO ^a	446/450	$48/48^{b}$	/0.90	/0.08	-4.74×10^5	268
MH	Toluene/10 wt%-PPF ^a	$477/473^{b}$	$/58^{b}$	/0.99	$-0.01/\!-\!$	$-/1.52 \times 10^6$	126
MP	Toluene/10 wt%-PPF ^a	$472/470^{b}$	$/57^{b}$	/0.98	0.02/—	$-/0.58 \times 10^6$	126
PP	Toluene/10 wt%-PPF ^a	$475/471^{b}$	$/57^{b}$	/0.80	0.20/—	—/—	126
TDBA-SBA	Toluene/20 wt%-DBFPO ^a	$450/467^{b}$	$/55^{b}$	/0.89	0.01/—	$-/1.37 \times 10^6$	269
DBA-SAB	Toluene/20 wt%-DPEPO ^a	$460/472^{b}$	$52/62^{b}$	/0.87	/0.07	$-/1.9 \times 10^6$	124
2TDBA-SBA	Toluene/20 wt%-DBFPO ^a	$448/475^{b}$	$/56^{b}$	/0.87	0.01/—	$-/1.35 \times 10^6$	269
PXZBO1	Toluene/20 wt%-DBFPO ^a	506/507	—/—	/0.94	0.01/—	$-/2.42 \times 10^6$	270
PXZBO2	Toluene/20 wt%-DBFPO ^a	572/552	—/—	/0.97	0.01/—	$-/1.49 \times 10^6$	270
PzDBA	Toluene/5 wt%-TCTA ^a :Bepp ₂ ^a	$610/595^{b}$	—/—	/0.85	/0.05	$-/0.84 \times 10^6$	271
PzTDBA	Toluene/5 wt%-TCTA ^a :Bepp ₂ ^a	599/576 ^b	—/—	/1.00	/0.06	$-/1.19 \times 10^6$	271

^a See Table 2 for the full compound name. ^b Taken from the EL spectrum.

Chem Soc Rev **Review Article**

donor, 202,264 which enabled the fabrication of hyperfluorescence devices using v-DABNA.60 In addition, the emission of di-tBu-substituted DOBNA derivatives was blue-shifted by ~10 nm relative to that of unsubstituted DOBNA derivatives, as represented by the TDBA-DI versus DBA-DI case in Table 29 and the OBO-I versus DTBA-PAS case in Table 30 despite the reports from different research groups. 120,122,127,202 Stronger D-A interactions also seem to reduce ΔE_{ST} , as shown by the comparison between M3CzB and 3CzTB, 255 although comparing materials reported by different research groups may be more difficult because of the different criteria used to extract S₁ and T₁ energies from the spectra. Compounds having relatively strong donors with phenoxazine subunits (DOBNA-Phenox, BNB-m, BNB-p, PXZBO1, and PXZBO2) or strong electronwithdrawing CF3 groups attached to the DOBNA structure (1BOICz and 2BOICz) showed emission peaks >500 nm, ^{137,267,270} i.e., in the region where the hyperfluorescence system using green MR emitters is also operational. 163 In addition, A-D-A-type TADF compounds, PzDBA and PzTDBA, which represent a very rare configuration in the TADF family of materials, were developed using a 5,10-dihydrophenazine unit and showed orange to red emission.²⁷¹ However, these green to red emitters have relatively large FWHM values.

The distinct photophysical features of these materials are their quite short delayed-fluorescence lifetime (τ_d), weak concentration quenching, good solubility, and high molecular orientational factor. For D-A-type TADF materials, τ_d typically ranges from several to a few hundred microseconds and is generally shorter than that of MR-type TADF materials. In contrast, some of the materials in Fig. 25 and 26, e.g., TMCz-BO, ICz-TDBA, DBA-BFICz, TDBA-DI, DBA-DI, BOtCzPhICz, BO-tCzDICz, 1BOICz, 2BOICz, TDBA-Ac, TDBA-SBA, **DBA-SAB**, and **2TDBA-SBA**, showed nanosecond-scale τ_d values. 112,122,124,129,137,202,264,265,269 As shown in Tables 29 and 30, relatively high doping concentrations are generally selected for these compounds. In particular, TB-3Cz, TB-P3Cz, and TB-**DACz** showed very high Φ_{PL} values of >80% in the neat-film state. 123 As a result, aggregation-induced emission (AIE) properties were also investigated for these compounds as well as for TB-tCz and TB-tPCz. 123,125 Meanwhile, the introduction of silicon suppressed the broadening of the emission spectra at high doping concentrations.127 The solubility was also good despite the relatively planar nature of the DOBNA structure. For some compounds, namely TB-tCz, TB-tPCz, BFCz-TDBA, ICz-TDBA, PIdCz-TDBA, TB-3Cz, TB-3tBuCz, TB-P3Cz, TB-DACz, BO-tCzPhICz, and BO-tCzDICz, solution-processed OLEDs were fabricated, and high EQEs (>10%) and excellent CIE_v values (<0.1) were achieved. ^{123,125,128,129,265} The high EQEs of these compounds were ascribed to not only the high $\Phi_{\rm PL}$ but also high degree of horizontal dipole orientation. In general, rigid and linear molecular shapes are favourable for increasing horizontal molecular orientation during vacuum deposition.²⁷² Therefore, linear molecules such as TDBA-DI, 3CzTB, BNB-m, 1BOICz, 2BOICz, TDBA-SAF, DBA-SAB, OBOtSAc, tBuOBOtSAc, TDBA-SBA, 2TDBA-SBA, PzDBA, and PzTDBA are oriented horizontally, as the high aspect ratios of the molecular-shape result in high orientation factors, which follow the order of TDBA-SAF < DBA-SAB, 1BOICz < 2BOICz, OBOtSAc < tBuOBOtSAc, and $\textbf{TDBA-SBA} \, < \, \textbf{2TDBA-SBA}.^{122,124,137,255,267-269,271}$

The compounds shown in Fig. 27 are slightly different from those in Fig. 25 and 26. Although BCz, BBFCz, and BICz have CT excited states between donor and acceptor units, BCz also has an LE feature within the MR core according to the calculated S_1 , while the emission spectrum of **BICz** has a vibrational shoulder.²⁵⁹ Although the donor strength is higher for BICz than for BBFCz, the related emission maxima are similar (Table 31). This behaviour is different from that in the BFCz-TDBA versus ICz-TDBA case (Fig. 25), indicating a different nature of D-A interactions. However, these compounds also have the advantages of short τ_d (~1 μ s), weak concentration quenching with high Φ_{PL} in the neat film, AIE, and solution processability. BCzTC features a D-A interaction through a σ -linker, which results in a very weak CT interaction. Therefore, this compound was used as a bipolar host for a basic TADF material (t4CzIPN), with BDTC adopted as a reference unipolar host. 262 AC-BO, QAC-BO, and Cz-BO were synthesised as shown in Scheme 42.263 Although the organoboron atom generally acts as a Lewis acid, the Lewis acidity of the boron centre in the

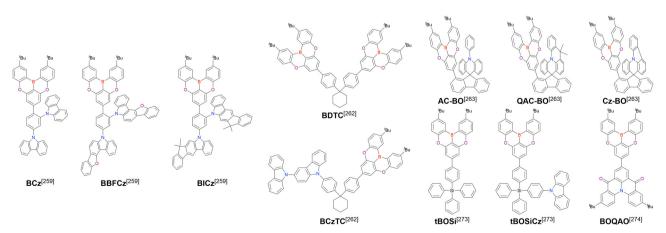


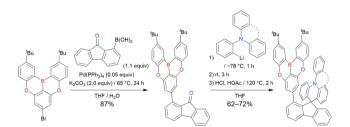
Fig. 27 DOBNA derivatives with substituents at 7-position synthesised by late-stage functionalisation.

Review Article

Table 31 Photophysical properties of the materials shown in Fig. 27

Compound	Condition	$\lambda_{\mathrm{PL}}^{\mathrm{max}}\left[\mathrm{nm}\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\rm ST}$ [eV]	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
BCz	Toluene/neat-film	405/414	25/37	0.26/0.61	/0.40	—/—	259
BBFCz	Toluene/neat-film	405/423	25/51	0.44/0.86	0.26/0.32	$-/0.90 \times 10^6$	259
BICz	Toluene/neat-film	407/431	49/53	0.21/0.76	0.15/0.18	$-/1.10 \times 10^6$	259
BDTC	Toluene/neat-film	403/416, 439	—/—	—/—	0.28/—	—/—	262
BCzTC	Toluene/neat-film	368, 404/414	—/—	—/—	0.24/—	—/—	262
AC-BO	Toluene/10 wt%-PMMA ^a	/446	/57	— /0 . 77	0.13/—	$-/0.23 \times 10^6$	263
QAC-BO	Toluene/10 wt%-PMMA ^a	/428	/49	— /0 . 83	0.20/—	$-/1.61 \times 10^{7}$	263
Cz-BO	Toluene/10 wt%-PMMA ^a	/411	/35	— /0 . 89	0.29/—	—/—	263
tBOSi	Toluene/5 wt%-mCPCN ^a	408/414	28/28	0.51/0.81	0.26/—	—/—	273
tBOSiCz	Toluene/5 wt%-mCPCN ^a	408/414	28/28	0.52/0.85	0.21/—	—/—	273
BOQAO	Toluene/5 wt%-CBP ^a	474/487	28/33	/0.99	0.22/—	$-/2.4 \times 10^4$	274
=							

^a See Table 2 for the full compound name.



Scheme 42 Late-stage introduction of donor groups for throughspace CT.

DOBNA scaffold might be decreased by the π -electrons of coplanar oxygen and become weaker than that of the carbonyl group. These compounds have through-space CT and thus exhibit deep blue emission. The emission properties of tBOSi and tBOSiCz should be similar to that of 7-phenyl-substituted DOBNA; moreover, the triphenylsilane moiety inhibits intermolecular interactions and thus helps to preserve the deep blue emission in the solid state.²⁷³ The combination of a carbonylbased MR structure (QAO) and DOBNA, named BOQAO and synthesised by Suzuki-Miyaura coupling (Scheme 41), should be critically different from the other abovementioned compounds because the DOBNA structure does not function as an acceptor owing to its LUMO level being shallower than that of QAO.²⁷⁴ Thus, the photophysical properties of BOQAO are similar to those of QAO, although a weak long-range intramolecular CT is involved.

DOBNA derivatives substituted at positions other than 7-position are summarised in Fig. 28 and Table 32. The molecules described by Wang et al. and Wu et al. were developed in 2019. The emission of compounds with two donors at the terminal phenyl rings was red-shifted relative to that of 7-substituted compounds (m-Ac-DBNA versus TDBA-Ac; DBA-Cz versus TB-tCz). 113,119,122,125 This class of compounds also showed high $\Phi_{ ext{PL}}$ in the aggregated states including neat films (>90% for **p-AC-DBNA**), short τ_d (920 ns for **DBA-DTMCz**), and highly oriented alignment (>0.8 for DBA-DTMCz and OBO-II). 119-121 Notably, the EQE of the device with a neat OBO-II-based emissive layer reached 23.1%. In addition, the hyperfluorescence device with v-DABNA doped into a DBA-DTMCz-based emissive layer showed an EOE of 43.9%, which is the highest value reported to date for such devices. Meanwhile, the three isomers of AC-DBNA display temperature-dependent emission and mechanochromism. In a series of OBA derivatives, phenoxazine derivatives (OBA-O and OBA-BrO) showed better Φ_{PL} and EQE values as well as emission maxima at shorter wavelengths than phenothiazine derivatives (OBA-S and OBA-BrS).256 However, **OBA-BrS** showed the shortest τ_d of 810 ns. Bromosubstituted derivatives showed elevated k_{RISC} values owing to the heavy-atom effect.

The synthesis and properties of DOBNA-based polymers are summarised in Scheme 43 and Table 33. After the introduction of the vinyl group by the Stille coupling of 7-brominated DOBNA derivatives with tributylvinylstannane or by their Suzuki-Miyaura coupling with (para-vinylphenyl)boronic acid

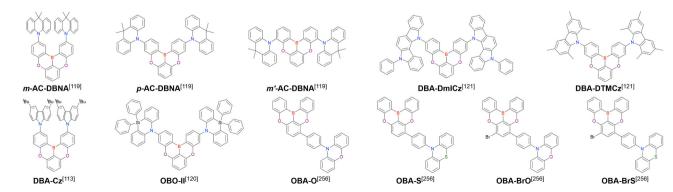
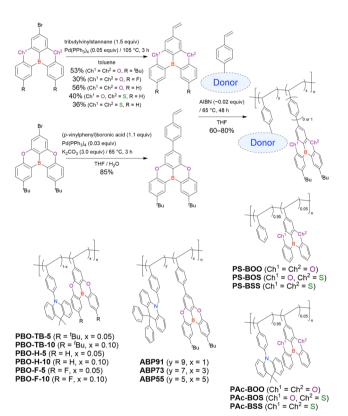


Fig. 28 DOBNA-based D-A-type TADF materials with substituents at 2, 3, 4 and 6-positions synthesised by late-stage functionalisation.

Table 32 Photophysical properties of the materials shown in Fig. 28

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
m-AC-DBNA	CH ₂ Cl ₂ /5 wt%-BCPO ^a /neat-film	569/492/514	—/—/—	0.58/0.89/0.73	-/0.01/	$-/2.61 \times 10^5/3.03 \times 10^5$	119
p-AC-DBNA	CH ₂ Cl ₂ /5 wt%-BCPO ^a /neat-film	557/496/516	—/—/—	0.96/0.96/0.94	/0.01/	$-1.7 \times 10^5 / 8.33 \times 10^5$	119
m'-AC-DBNA	CH ₂ Cl ₂ /5 wt%-BCPO ^a /neat-film	568/498/518	—/—/—	0.51/0.87/0.70	— /0.03/ —	$-/8.44 \times 10^5/3.98 \times 10^5$	119
DBA-DmICz	Toluene/30 wt%-DBFPO ^a /neat-film	$448/485^{b}/$ —	58/68 ^b /—	/0.95/0.83	0.12/—/—	$-/0.62 \times 10^6/-$	121
DBA-DTMCz	Toluene/30 wt%-DBFPO ^a /neat-film	$455/479^{b}/$	53/58 ^b /—	/0.99/0.86	0.02/—/—	$-/2.10 \times 10^6/-$	121
DBA-Cz	Toluene/10 wt%-DPEPO ^a /neat-film	447/450/494	38/47/75	/0.90/0.52	0.03/—/—	$-/-/4.6 \times 10^5$	113
OBO-II	Toluene/20 wt%-PPF ^a /neat-film	450/465/476	53/58 ^b /—	0.48/0.98/0.73	—/—/—	$-/9.2 \times 10^5/5.0 \times 10^5$	120
OBA-O	Toluene/10 wt%-mCP ^a	444/450	—/—	0.76/0.84	/0.09	$-/4.28 \times 10^5$	256
OBA-S	Toluene/10 wt%-mCP ^a	456/470	—/—	0.63/0.75	/0.09	$-/2.76 \times 10^5$	256
OBA-BrO	Toluene/10 wt%-mCP ^a	470/476	—/—	0.84/0.92	/0.04	$-/8.97 \times 10^5$	256
OBA-BrS	Toluene/10 wt%-mCP ^a	478/470	—/—	0.53/0.55	 /0 . 07	$-/8.41 \times 10^5$	256

^a See Table 2 for the full compound name. ^b Taken from the EL spectrum.



Scheme 43 Synthesis of DOBNA-based polymers reported in ref. 132. 275, and 116

under palladium catalysis, co-polymers with donor units were synthesised by free radical polymerisation using 2,2'azobis(isobutyronitrile) (AIBN) as an initiator. 116,132,275 Compounds of the PBO series showed through-space D-A interactions, which resulted in PBO-TB-5 and AC-BO showing similar emission maxima (Fig. 27). 132,263 Although the Φ_{PL} values of the polymers were lower than those of small molecules, sufficiently small $\Delta E_{\rm ST}$ values were achieved. The electron-donating ^tBu and electron-withdrawing F groups attached to the DOBNA scaffold modulated D-A interactions in a similar manner to that observed for small molecules in Fig. 25 and 26. The emission maxima of PBO derivatives shifted to longer

Table 33 Photophysical properties of the materials shown in Scheme 43^a

Compound	Condition	$\lambda_{PL}^{max} [nm]$	FWHM [nm]	$\Phi_{\rm PL}\left[\right]$	$\Delta E_{\rm ST}$ [eV]	Ref.
PBO-TB-5	Neat-film	444	_	0.32	0.09	132
PBO-TB-10	Neat-film	453	_	0.37	0.09	132
PBO-H-5	Neat-film	448	_	0.44	0.06	132
PBO-H-10	Neat-film	455	_	0.48	0.07	132
PBO-F-5	Neat-film	471	_	0.65	0.01	132
PBO-F-10	Neat-film	480	_	0.70	0.02	132
ABP91	Neat-film	407	_	_	0.30	275
ABP73	Neat-film	412, 436	_	_	0.29	275
ABP55	Neat-film	414, 442	_	_	0.29	275
PS-BOO	Toluene	398 (LE)	33	0.73	_	116
PS-BOS	Toluene	435 (LE)	31	0.65	_	116
PS-BSS	Toluene	456 (LE)	30	0.59	_	116
PAc-BOO	Toluene	457 (CT)	63	0.44	_	116
PAc-BOS	Toluene	434 (LE),	62	0.56	_	116
		475 (CT)				
PAc-BSS	Toluene	455 (LE)	30	0.60	_	116
$a k_{RISC}$ value	es were not	reported.				

wavelengths (by ~10 nm) with increasing DOBNA molar fraction. On the other hand, the effect of this parameter on the emission spectra is more obvious for the ABP series. 275 In view of the absence of intramolecular through-space CT, which was confirmed in solution-phase emission spectra, the intermolecular D-A interactions in the film state caused the appearance of a new CT emission peak, resulting in a large variation of the CT/LE ratio upon going from ABP91 to ABP55. Solutionprocessed OLEDs were fabricated using PBO derivatives as the emitter or ABP derivatives as the host for t4CzIPN, and EQEs of up to 15.0 and 22.2%, respectively, were achieved.

Wang et al. developed S-bridged DOBNA analogues (BOS and BSS) and investigated the photophysical properties of the parent structures and their polymers. 116 The introduction of sulphur reduced the energy gap by increasing HOMO and decreasing LUMO energies, thus resulting in deep blue emission with emission maxima of 434 nm (BOS) and 457 nm (BSS) without any substitutions. These maxima were red-shifted by 38-61 nm relative to that of unsubstituted DOBNA (BOO) at 396 nm. Importantly, the S-bridged structure preserved the narrow FWHMs (30, 29, and 27 nm for BOO, BOS and BSS, respectively). Moreover, k_{RISC} increased by one order of magnitude because of the enhancement of SOC via the heavy-atom



Fig. 29 S-Bridged DOBNA analogues synthesised by late-stage functionalisation.

effect of sulphur. 55 As a result, the delayed fluorescence ratio in total emission increased from 4% for BOO to 81% and 90% for BOS and BSS, respectively. Polystyrene (PS)-based polymers (PS-BOO, PS-BOS, and PS-BSS) showed emission similar to that of their parent DOBNA analogues. Interestingly, donor-based polymers showed different emission profiles because of the formation of CT excited states. The emission of PAc-BOO was broad, dependent on solvent polarity, and red-shifted by 59 nm compared to that of **PS-BOO**, which was assigned to long-range CT. In contrast, PAc-BSS showed only one narrow emission peak corresponding to the LE emission of MR BSS with shortrange CT. PAc-BOS showed two (LE and CT) emission bands. This feature was clearly correlated with the increase in the HOMO energy of BOO, BOS, and BSS, and the small offset of HOMO levels between donor and acceptor units hindered CT formation. The OLED with PAc-BSS showed the highest EQE of 13.1% for blue TADF polymers with a CIE, of < 0.15.

Small molecules with S-bridged DOBNA analogues and donor units connected at 7-position were subsequently developed (Fig. 29 and Table 34). Similar to the polymer case mentioned above, the higher HOMO levels of S-bridged structures resulted in red-shifted and LE-dominated emission. PhCz-TOSBA and TPA-TOSBA showed similar emission spectra in toluene, whereas the emission of TPA-TOSBA with a stronger donor exhibited partial long-range CT character. 130 For TSBA-Cz and TSBA-PhCz, both S₁ and T₁ states were LE-dominant, resulting in substantially similar photophysical properties based on the MR effect. 131 In BSS-Cz, BSS-PA, BSS-SpAc, and BSS-Ac, the HOMO levels of donor units become shallower in the order of Cz < PA < SpAc < Ac.¹³³ Similar to **TSBA-Cz**, **BSS-**Cz showed LE-dominated emission with a narrow FWHM of 28 nm because of the small HOMO offset. Notably, the emission wavelength was red-shifted by the incorporation of ^tBu

groups, which differed from the CT emission in D-A-type molecules in Fig. 25 and 26, suggesting pure MR emission. Although no CT between BSS and 9,10-dihydro-9,9-dimethylacridine was observed in the PAc-BSS polymer, BSS-SpAc and BSS-Ac showed long-range CT emission in addition to LE emission.

Scheme 44 shows some examples of the fused π -extension of DOBNA derivatives. The synthesis of Ph-OBNA involved Suzuki-Miyaura coupling followed by cyclisation and N-aryl coupling reactions.²⁷⁶ Although Ph-OBNA showed TADF properties, its planar structure led to excimer formation at high concentrations and ACO. Another fused DOBNA derivative, DOBDiKTa, has a carbonyl-based MR structure (QAO, here called DiKTa) composed of two merged MR fragments.²⁷⁷ Although DOB-DiKTa is composed of the same units as BOQAO in Fig. 27, the fused benzene is substituted by the electron-withdrawing boron atom and carbonyl group in a meta relationship as well as the electron-donating nitrogen and oxygen atoms in the same relationship, effectively merging the MR effect. The synthesis of DOBDiKTa involved two coupling reactions followed by saponification and two-fold intramolecular Friedel-Crafts acrylation promoted by SnCl2 as a Lewis acid. The emission maximum of DOBDiKTa was slightly blue-shifted relative to that of QAO. In addition, the TADF properties including Φ_{PL} , ΔE_{ST} , and k_{RISC} were superior to those of each individual MR unit.

4.3 Functionalised CzBN

The late-stage synthesis strategies for CzBN derivatives are fundamentally identical to those for DOBNA derivatives, as shown in Scheme 45 corresponding to Scheme 41. Similar to the DOBNA case, one-pot borylation is seldom selected for synthesising some donor-substituted CzBN derivatives but may still be useful given the reports of exactly the same

Table 34 Photophysical properties of the materials shown in Fig. 29

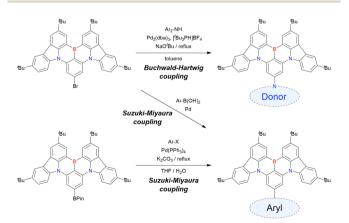
Compound	Condition	λ ^{max} _{PL} [nm]	FWHM [nm]	$\Phi_{ ext{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
PhCz-TOSBA	Toluene/10 wt%-26DCzPPy ^a	444/454	32/41	/0.61	0.23/—	$-/4.08 \times 10^4$	130
TPA-TOSBA	Toluene/10 wt%-26DCzPPy ^a	447/467	34/67	/0.62	0.36/—	$-/1.91 \times 10^4$	130
TSBA-Cz	Toluene/10 wt%-26DCzPPy ^a	463/469	30/40	/0.80	0.21/—	$-/5.29 \times 10^4$	131
TSBA-PhCz	Toluene/10 wt%-26DCzPPy ^a	470/478	36/40	/0.80	0.18/—	$-/7.62 \times 10^4$	131
BSS-Cz	Toluene/1 wt%-PS ^a	455/457	28/29	0.86/—	0.14/—	$-/1.5 \times 10^5$	133
BSS-PA	Toluene/1 wt%-PS ^a	454/—	35/—	0.66/—	0.13/—	$-/1.6 \times 10^5$	133
BSS-SpAc	Toluene/1 wt%-PS ^a	456, 505/—	101/—	0.89/—	0.07/—	$-/1.5 \times 10^5, 3.0 \times 10^5$	133
BSS-Ac	Toluene/1 wt%-PS ^a	456, 513/—	105/—	0.90/—	0.04/—	$-/1.5 \times 10^5$, 5.2×10^5	133

^a See Table 2 for the full compound name.

Chem Soc Rev **Review Article**

Scheme 44 Late-stage ring-fusion of DOBNA derivatives.

compounds prepared by both methods (vide infra). The standard reaction conditions for the Buchwald-Hartwig amination of CzBN derivatives are Pd₂(dba)₃ (0.02-0.08 equiv.), [tBu_3PH]BF₄ (0.08–0.32 equiv.), and NaO tBu (2–4 equiv.) in aromatic solvents at >80 °C. The Suzuki-Miyaura coupling conditions are broadly variable, with a representative example being Pd(PPh₃)₄ (~ 0.05 equiv.) and K₂CO₃ (~ 2 equiv.) in THF/ H₂O at reflux. As most materials discussed here are based on 3,6-di-tert-butyl-9H-carbazole, the photophysical properties of the tetra-^tBu CzBN skeleton (originally named **DtBuCzB**, but referred to here as BCzBN to correspond to the substituted CzBN) are the basis for evaluating substitution effects. Typical



Scheme 45 General scheme for the late-stage functionalisation of CzBN by Buchwald-Hartwig and Suzuki-Miyaura couplings

emission maximum, FWHM, $\Phi_{\rm PL}$, $\Delta E_{\rm ST}$, and $k_{\rm RISC}$ values for BCzBN in toluene are 481-484 nm, 22-23 nm, 91-98%, 0.13-0.15 eV, and 1.4–3.0 \times 10 4 s $^{-1}$, respectively. 154,257,278 In general. the MR effect with narrow emission is maintained even for relatively strong donor substituents because the HOMO of CzBN is shallower than that of DOBNA. Changes in the excited-state nature upon going from MR with short-range CT to long-range D-A-type CT could be observed by comparing phenoxazine-substituted derivatives, with the HOMO levels of the CzBN moiety slightly decreasing upon going from CzBN3 to CzBN1 (Fig. 30 and Table 35).²⁵⁷ Thus, CzBN1 showed two emission bands, namely a sharp band at 471 nm and a broad band at 533 nm. Although CzBN3 (aka BN-PXZ¹⁷⁶ in Section 2 and BNCz-PXZ) exhibited a small FWHM comparable to that of **BCzBN** in toluene, a new broad band at ~ 600 nm emerged in polar solvents. 187 In contrast, BNCz-DMAC (aka BN-AC in Section 2)176 and BNCz-SAF with weaker donors showed a single narrow emission band even in polar solvents with a small positive solvatochromic effect, which is a common feature of MR materials. These results indicate that the HOMO of **BCzBN** was very slightly shallower than that of the phenoxazine moiety. Despite the negligible change in the shape of the emission spectrum upon the introduction of diarylamine donors, these substituents affected the HOMO-LUMO gap of the CzBN core and the electronic properties of the related derivatives. The HOMO of CzBN has no coefficient on the atom in 10-position (Fig. 23), unlike the corresponding LUMO. The opposite HOMO-LUMO behaviour is observed at 9- and 11positions. Thus, the introduction of electron-donating substituents such as arylamines directly at 10-position, which is paraposition with respect to the B atom, increases the energy gap. In fact, the emission spectra of CzBN3, BNCz-DMAC, BNCz-SAF, and SPBAC-tCzBN were slightly blue-shifted relative to that of BCzBN. 187,257,279 In contrast, the emission spectra were slightly red-shifted upon the introduction of electron-withdrawing substituents (Fig. 31 and Table 36). Note that the introduction of electron-donating arylamines with a phenyl spacer caused a red shift because of the contribution of long-range CT characteristics (vide infra, e.g., o-SPAC-tCzBN).²⁷⁹ The important advantage of introducing substituents is the incorporation of intersegmental CT triplet states such as the T₂ level, which accelerates RISC. This level is silently induced without perturbing the lowest excited singlet states. Thus, the emission properties of, e.g., CzBN3 and SPAC-tCzBN are substantially similar to those of BCzBN, while the k_{RISC} values of these two compounds exceed that of BCzBN by about one order of magnitude. The emission of a heptagonal tribenzo[b,d,f]azepine derivative, TBA-BCz-BN, is further blueshifted relative to that of carbazole and diphenylamine derivatives. 111,172,186 DCz-BSN and DCz-BSeN synthesised based on this strategy and featuring asymmetric S- and Se-bridged CzBN structures, respectively, exhibit high-colour-purity emission in the deep blue region and large k_{risc} . ^{168,169} Compounds bearing electron-donating groups with a phenyl spacer, namely BNCzpTPA, BNCz-mTPA, o-SPAC-tCzBN, S-Cz-BN, D-Cz-BN, BN-CP1, BN-CP2, BN-PhOH, and BN-PhOCH3, showed slightly red-shifted emission, while some compounds with relatively strong donors,

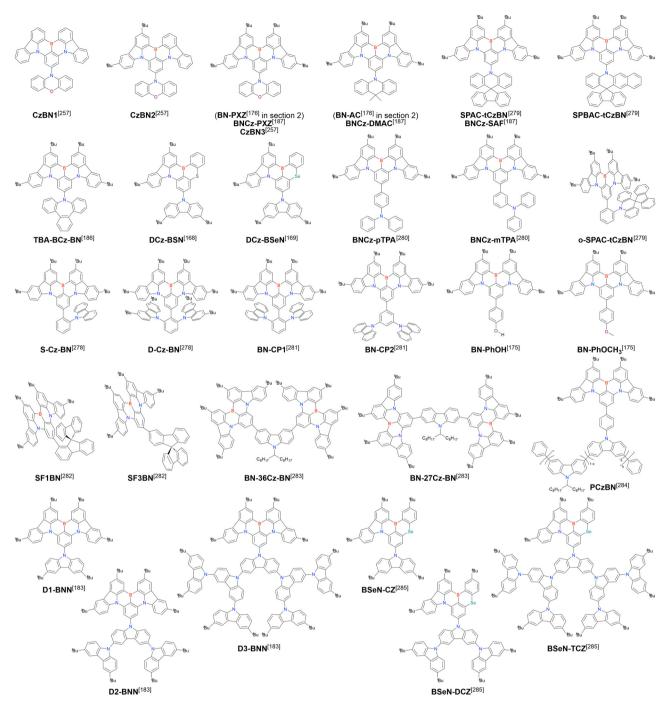


Fig. 30 CzBN derivatives with donor substituents at the 10-position and related chalcogen-bridged compounds synthesised by late-stage functionalisation.

namely BNCz-pTPA, BNCz-mTPA, and o-SPAC-tCzBN, exhibited higher k_{RISC} because of the distinct contribution of the long-range CT triplet state. 175,278-281 Although the basic photophysical properties of BN-PhOH and BN-PhOCH3 are not significantly different, the synthesis of methoxy-substituted compounds might not be straightforward because of demethylation by BBr₃; however, the SMe group can be preserved. 175,178 Thus, the methoxy derivative was synthesised using the Williamson ether synthesis in the presence of sodium hydride (Scheme 46). 175

MR emitters generally suffer from strong molecular aggregation owing to their planar structures and thus experience substantial deterioration of emission properties at high doping concentrations. In particular, concentration quenchinginduced decreases in Φ_{PL} and Dexter energy transfer-induced triplet loss are serious issues in the corresponding OLEDs. Thus, MR emitter-based OLEDs are usually fabricated using very low doping concentrations such as 1 wt%. The structural modifications of MR emitters also aim to suppress aggregation.

Chem Soc Rev

Table 35 Photophysical properties of the compounds shown in Fig. 30

Compound	Condition	λ _{PL} ^{max} [nm]	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
CzBN1	Toluene/5 wt%-DMIC-TRZ ^a	471, 533/523 ^b	78/75 ^b	0.95/0.95	0.13/—	$2.06 \times 10^6 / 1.3 \times 10^6$	257
CzBN2	Toluene/5 wt%-DMIC-TRZ ^a	$477, 522/481^b$	$75/75^{b}$	0.97/0.97	0.14/—	$7.82 \times 10^5/4.4 \times 10^5$	257
CzBN3	Toluene/5 wt%-DMIC-TRZ ^a	478/487 ^b	$21/27^{b}$	0.99/0.98	0.15/—	$3.27 \times 10^5/2.8 \times 10^5$	257
BNCz-PXZ	Toluene/3 wt%-mCBP ^a	477/482	23/34	/0.84	0.12/—	$-/3.11 \times 10^5$	187
BNCz-DMAC	Toluene/3 wt%-mCBP ^a	478/484	22/26	/0.83	0.13/—	$-/1.20 \times 10^6$	187
BNCz-SAF	Toluene/3 wt%-mCBP ^a	478/484	23/25	 /0.86	0.15/—	$-/7.4 \times 10^{5}$	187
SPAC-tCzBN	Toluene/10 wt%-PhCzBCz ^a	$481/480^{b}$	$20/24^{b}$	/0.83	0.13/—	$-/0.9 \times 10^{5}$	279
SPBAC-tCzBN	Toluene/10 wt%-PhCzBCz ^a	$480/480^{b}$	$20/25^{b}$	/0.89	0.13/—	$/1.2 \times 10^5$	279
TBA-BCz-BN	Toluene/3 wt%-mCBP ^a	468/472	22/28	 /0.86	0.14/	—/—	186
DCz-BSN	Toluene/1 wt%-PS ^a	463/462	26/—	/0.88	0.12/—	$-/1.04 \times 10^5$	168
DCz-BSeN	Toluene/1 wt%-PS ^a	472/467	28/—	— /0 . 93	0.14/—	$-/8.8 \times 10^6$	169
BNCz-pTPA	Toluene/1 wt%-mCBP ^a	$487/490^{b}$	$22/29^{b}$	0.95/—	0.11/—	-4.45×10^5	280
BNCz-mTPA	Toluene/1 wt%-mCBP ^a	$489/490^{b}$	$22/30^{b}$	0.92/—	0.12/—	$-/2.29 \times 10^5$	280
o-SPAC-tCzBN	Toluene/10 wt%-PhCzBCz ^a	$490/492^{b}$	$21/26^{b}$	 /0.86	0.11/—	$-/1.1 \times 10^5$	279
S-Cz-BN	Toluene/1 wt%-mCBP ^a /neat-film	490/488 ^b /—	$23/26^{b}/40$	0.94/0.95/0.47	0.16/—/—	$1.8 \times 10^4/2.9 \times 10^4/$	278
D-Cz-BN	Toluene/1 wt%-mCBP ^a /neat-film	490/488 ^b /—	$22/24^b/26$	0.98/0.98/0.54		$1.8 \times 10^4/3.0 \times 10^4/$	278
BN-CP1	Toluene/1 wt%-mCBP ^a /neat-film	490/496/502	23/25/28	/0.93/0.40	0.12/—/—	$-/1.56 \times 10^4/-$	281
BN-CP2	Toluene/1 wt%-mCBP ^a /neat-film	490/496/521	23/26/48	/0.91/0.25	0.13/—/—	$-/1.43 \times 10^4/-$	281
BN-PhOH	Toluene/3 wt%-mCBP ^a	485/494	$26/32^{b}$	0.80/—	0.14/—	$-/2.85 \times 10^4$	175
BN-PhOCH ₃	Toluene/3 wt%-mCBP ^a	485/494	$26/29^{b}$	0.78/—	0.15/—	$-/2.98 \times 10^4$	175
SF1BN	Toluene/2 wt%-mCBP ^a	$493/492^{b}$	$23/28^{b}$	0.90/0.93	0.13/—	$-/9.12 \times 10^4$	282
SF3BN	Toluene/2 wt%-mCBP ^a	$493/492^b$	$25/28^{b}$	0.86/0.90	0.15/—	$-/3.31 \times 10^4$	282
BN-36Cz-BN	Toluene/5 wt%-DMIC-TRZ ^a	488/497	22/33	— /0.65	0.125/—	$-/1.6 \times 10^{5}$	283
BN-27Cz-BN	Toluene/5 wt%-DMIC-TRZ ^a	489/499	22/32	— /0.66	0.124/—	$-/0.80 \times 10^5$	283
PCzBN1	Toluene/neat-film	421, 487/430, 452, 491	25/33	 /0.58	/0.14	$-/8.2 \times 10^4$	284
PCzBN3	Toluene/neat-film	421, 487/423, 451, 496	25/42	 /0.51	 /0 . 13	$-/8.6 \times 10^4$	284
PCzBN5	Toluene/neat-film	421, 488/501	25/43	 /0.43	 /0 . 13	$-/2.18 \times 10^{5}$	284
D1-BNN	Toluene/10 wt%-mCP ^a	474/483 ^b	21/26	/0.68	0.15/—	$-/1.55 \times 10^{3}$	183
D2-BNN	Toluene/10 wt%-mCP ^a	473/478 ^b	21/24	 /0 . 80	0.16/—	$-/2.35 \times 10^{3}$	183
D3-BNN	Toluene/10 wt%-mCP ^a	$473/477^b$	21/24	/0.92	0.17/—	$-/3.94 \times 10^{3}$	183
BSeN-CZ	Toluene/1 wt%-PS ^a	476/—	26/30	/0.76	0.12/—	$-/8.5 \times 10^6$	285
BSeN-DCZ	Toluene/1 wt%-PS ^a	475/—	26/29	/0.79	0.12/—	$-/9.0 \times 10^6$	285
BSeN-TCZ	Toluene/1 wt%-PS ^a	474/—	26/30	/0.85	0.12/—	$-/9.1 \times 10^6$	285

^a See Table 2 for the full compound name. ^b Taken from the EL spectrum.

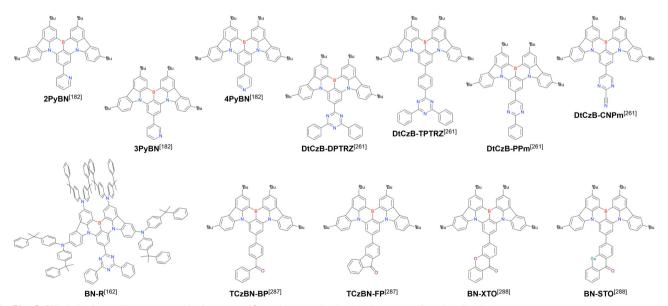


Fig. 31 CzBN derivatives with acceptor substituents at 10-position synthesised by late-stage functionalisation.

Among the available methods, the steric wrapping strategy is particularly efficient. For example, the $\Phi_{\rm PL}$ of a 30 wt% BCzBNdoped film was less than 50%, while doping with 30 wt% S-CzBN and D-Cz-BN maintained high $\Phi_{\rm PL}$ values of > 80–90%. 278 In addition, spectral broadening was found to be negligible for D-Cz-BN even in the neat-film. This trend was also confirmed by

Review Article Chem Soc Rev

Table 36	Photophysical	properties of the	e materials shown	in Fig. 31

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{\mathrm{RISC}} \left[\mathrm{s}^{-1} \right]$	Ref.
2PyBN	Toluene/1 wt%-DMIC-TRZ ^a	499/507	$21/26^{b}$	/0.94	/0.02	$-/7.7 \times 10^4$	182
3PyBN	Toluene/1 wt%-DMIC-TRZ ^a	490/497	$23/27^{b}$	- /0 . 90	/0.03	$-/8.7 \times 10^4$	182
4PyBN	Toluene/1 wt%-DMIC-TRZ ^a	495/506	$24/27^{b}$	/0.86	/0.02	$-/9.5 \times 10^4$	182
DtCzB-DPTRZ	Toluene/3 wt%-PhCzBCz ^a	521/536	24/43	0.94/0.87	0.18/—	$-/0.10 \times 10^4$	261
DtCzB-TPTRZ	Toluene/3 wt%-PhCzBCz ^a	501/520	27/41	0.97/0.95	0.11/—	$-/1.08 \times 10^4$	261
DtCzB-PPm	Toluene/3 wt%-PhCzBCz ^a	499/510	25/36	0.96/0.94	0.11/—	$-/1.02 \times 10^4$	261
DtCzB-CNPm	Toluene/3 wt%-PhCzBCz ^a	515/540	36/45	0.93/0.87	0.15/—	$-/0.14 \times 10^4$	261
BN-R	Toluene/1 wt%-NPB ^a :DMFBD-TRZ ^a	624/620	46/49	0.94/0.90	0.11/—	$-/1.1 \times 10^4$	162
TCzBN-BP	Toluene/3 wt%-SF3TRZ ^a	497/508	29/33	/0.98	0.14/0.09	$-/7.7 \times 10^4$	287
TCzBN-FP	Toluene/5 wt%-SF3TRZ ^a	516/542	37/56	 /0 . 75	0.17/0.14	$-/5.1 \times 10^4$	287
BN-XTO	Toluene/5 wt%-DMIC-TRZ ^a	/515	26/33	- -/0 . 93	/0.08	$-/3.0 \times 10^4$	288
BN-STO	Toluene/5 wt%-DMIC-TRZ ^a	/517	29/34	 /0 . 96	/0.13	$/1.2 \times 10^5$	288

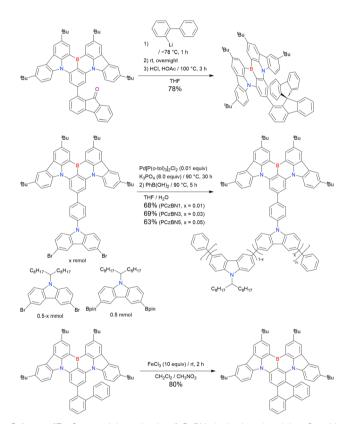
^a See Table 2 for the full compound name. ^b Taken from the EL spectrum.

Scheme 46 Synthesis of a methoxy-substituted compound

the comparison between BN-CP1 and BN-CP2 simultaneously reported by different groups.²⁸¹ Two derivatives with the more electrically neutral spiro-9,9'-bifluorene moiety, namely SF1BN and SF3BN, were examined to prove the influence of steric hindrance on photophysical properties.²⁸² Although SF3BN, D-Cz-BN, and BN-CP1 were synthesised by routine Suzuki-Miyaura coupling (Scheme 45), SF1BN had to be synthesised by a different method (Scheme 47) because the bulky fluorene moiety prevented the catalytic cycle of this coupling.

Solution-processable BCzBN derivatives were developed using N-branched-alkyl carbazoles. Small molecules with two BCzBN moieties, BN-36Cz-BN and BN-27Cz-BN, showed relatively weak ACQ. 283 A polycarbazole-based MR polymer (PCzBN) was prepared by grafting the BCzBN moiety as a pendant (Scheme 47).²⁸⁴ MR dendrimers were also developed by introducing up to third-generation carbazole dendrons at the periphery of the BCzBN skeleton. 183,285 Compounds based on a thirdgeneration carbazole dendron (D3-BNN and BSeN-TCZ) showed higher $\Phi_{\rm PL}$ than those based on a first-generation dendron (D1-BNN and BSeN-Cz). Concentration quenching and emission spectrum broadening were also suppressed when the thirdgeneration dendron was used at high doping concentrations.

Compounds with acceptor moieties at 10-position are summarised in Fig. 31 and Table 36. The presence of pyridine-type substructures may disorder the tandem lithiation-borylationannulation and one-shot electrophilic C-H borylation. Some works also reported these attempts and the failure of the corresponding reactions. 182,261 Thus, compounds 2PyBN, 3PyBN, 4PyBN, DtCzB-DPTRZ, DtCzB-TPTRZ, DtCzB-PPm, and DtCzB-CNPm were prepared by late-stage reactions, with the



Scheme 47 Sequential synthesis of CzBN derivatives involving Suzuki-Miyaura coupling in Scheme 45. Top: Nucleophilic addition of 2-lithio-1,1'-biphenyl to a carbonyl group followed by intramolecular condensation-cyclisation. Middle: Polymerisation reaction. The dibromo precursor was prepared from CzBN-Bpin and 3,6-dibromo-9-(4iodophenyl)-9H-carbazole. Bottom: Oxidative Scholl coupling.

synthesis of the PyBN series involving CuCl-assisted Suzuki-Miyaura coupling. 286 Note that in pyridyl DOBNA synthesis, the pyridine-functionalised precursor underwent lithiationborylation to afford the desired product in good yield. 139 Although all of these pyridine-based BCzBN derivatives exhibited red-shifted emission compared to that of the parent BCzBN, the intramolecular hydrogen-bonding in 2PyBN and DtCzB-DPTRZ caused molecular rigidity, enhanced

Chem Soc Rev Review Article

Fig. 32 CzBN derivatives with substituents at 9-position synthesised by late-stage functionalisation.

conjugation, and more strongly red-shifted emission. The replacement of the 'Bu group by a bis[4-(2-phenyl-2-propyl)phenyl]amine unit in BN-R substantially increased the HOMO energy, affording a red emitter with a narrow spectrum. The bulky donor moiety also helps to suppress aggregation and enhance solubility. The carbonyl moiety may also cause unpredictable side reactions during borylation. Thus, some compounds have been developed using late-stage reactions. Similar to the case of relatively strong donors as substituents, 187 long-range CT became dominant with relatively strong acceptors (TCzBN-BP *versus* TCzBN-FP). In addition to the management of intersegmental CT triplet states, the heavy-atom effect further increased $k_{\rm RISC}$ in BN-STO. 288

BCzBN derivatives with donors and acceptors at 9-position (Fig. 32 and Table 37) were synthesised through bromination using NBS (Scheme 39) followed by Suzuki–Miyaura coupling.²⁵⁸ Polycyclisation extended at 9- and 10-positions formed a triphenylene core in **BN-TP** (Fig. 33 and Table 38), which was difficult to obtain from triphenylene as the starting material. Alternatively, this species could be synthesised from **BCzBN** *via* a threestep process including the Hartwig-Miyaura C–H borylation, Suzuki–Miyaura coupling, and the Scholl reaction in the presence of FeCl₃ (Scheme 47).²⁸⁹ The large HOMO coefficient at 9-position was conducive to intramolecular cyclisation. Nitrogen-containing compounds **BN-TP-N1-4** were synthesised using the same approach, with the construction of phenyl-pyridine moieties in **BT-TP-N2** and **BT-TP-N3** performed using a different sequence.²⁹⁰

The HOMO and LUMO of **BN-TP** extend to each benzene ring connected to 9- and 10-positions, respectively, and the whole molecular orbital preserves the alternating distribution characteristic of MR materials. Thus, the conventional HOMO and LUMO distributions of PAHs including triphenylene showing uniform bonding and anti-bonding between carbon atoms were effectively modulated with the help of the MR fragment. The extension of π -conjugation onto the triphenylene part in

BN-TP resulted in an emission peak that was red-shifted relative to that of BN-DP. In addition, nitrogen atoms anchored at positions contributing to the LUMO afforded further red-shifted emission in BN-TP-N1 and BN-TP-N2. In contrast, blue-shifted (ultrapure green) emission was observed for BN-TP-N3 and BN-TP-N4. The dimerisation of BCzBN also extended the conjugation of MR cores, resulting in green emitters. ¹⁸⁵ As shown in Scheme 48, the synthesis of *p*-CzB involved the frequently used standard Suzuki–Miyaura coupling, while *m*-CzB was synthesised in moderate yield by oxidative coupling using Cu(ClO₄)₂·6H₂O as the oxidant, as this type of reaction was favoured by the large HOMO distribution at 9- and 11-positions.

The introduction of cyano groups at the para-position of boron resulted in a bathochromic shift to give MR materials with green to red emission (Table 39). Interestingly, several methods have been used to introduce cyano groups by substituting halogen atoms in late-stage functionalisation (Scheme 49). Treatment with CuCN in refluxing DMF (Rosenmund-von Braun reaction) is the most simple and widely used method, and has been applied for the synthesis of CN-BCz-BN. 184 Meanwhile, CNCz-BNCz, which has two additional carbazole rings, was synthesised through lithiation with "BuLi followed by transnitrilation with dimethylmalononitrile (DMMN).291 Lithiation after the introduction of boron might cause relatively low yields. Palladium-catalysed cyanation with K₄[Fe(CN)₆] as an environmentally benign reagent was used to synthesise a DABNA derivative, where the MR core was prepared by one-shot borylation. 114 The combination of oneshot borylation and late-stage cyanation through the substitution of halogen atoms enables the further development of MR emitters over the full colour range.

The late-stage synthesis of oxidised sulphur and phosphorus species are summarised in Scheme 50. As mentioned above, **BN(p)SCH**₃ was synthesised *via* tandem lithiation-borylation-

Table 37 Photophysical properties of the materials shown in Fig. 32

Compound	Condition	λ ^{max} _{PL} [nm]	FWHM [nm]	$\Phi_{ m PL}\left[ight]$	$\Delta E_{\mathrm{ST}} \left[\mathrm{eV} \right]$	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
m-PCz-BNCz	Toluene/3 wt%-PhCzBCz ^a	494/500	25/33	0.97/0.98	0.15/—	$-/1.29 \times 10^4$	258
m-DPAcP-BNCz	Toluene/3 wt%-PhCzBCz ^a	491/498	26/34	0.97/0.97	0.14/—	$-/1.16 \times 10^4$	258
m-BN-BNCz	Toluene/3 wt%-PhCzBCz ^a	488/496	25/32	0.93/0.95	0.16/—	$-/0.93 \times 10^4$	258
m-SF-BNCz	Toluene/3 wt%-PhCzBCz ^a	491/498	25/32	0.96/0.98	0.16/—	$-/1.16 \times 10^4$	258

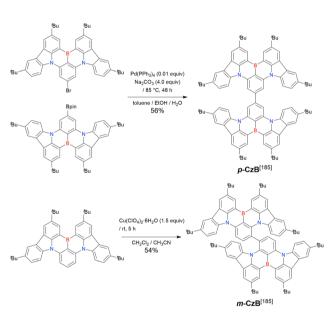
^a See Table 2 for the full compound name.

Fig. 33 CzBN derivatives with fused π -extension synthesised by late-stage functionalisation.

Table 38 Photophysical properties of the compounds shown in Fig. 33

Compound Co	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\varPhi_{\rm PL}\left[-\!-\!\right]$	$\Delta E_{\rm ST}$ [eV]	$k_{\rm RISC} \left[{ m s}^{-1} \right]$	Ref.
BN-TP TO BN-TP-N1 TO BN-TP-N2 TO BN-TP-N3 TO	oluene oluene/3 wt%-/10 wt%-PhCzBCz ^a oluene/3 wt%-PhCzBCz ^a	490/— 523/529/537 526/534 528/535 519/526 520/530	23/— 34/36/39 33/43 33/43 32/39 32/42	0.94/— 0.96/0.96/0.92 0.94/0.95 0.92/0.91 0.99/0.97 0.98/0.97	0.16/— 0.14/—/— 0.17/— 0.19/— 0.15/— 0.14/—	$-/ -/2.09 \times 10^4/2.26 \times 10^4$ $-/1.01 \times 10^4$ $-/0.83 \times 10^4$ $-/1.70 \times 10^4$ $-/1.90 \times 10^4$	289 289 290 290 290 290

^a See Table 2 for the full compound name.



Scheme 48 Synthesis of a CzBN dimer by oxidative coupling.

annulation from a BCzBN precursor with a pre-installed SMe group¹⁷⁸ and then treated with 3-chloroperbenzoic acid (mCPBA) to afford the corresponding sulfoxide (BN(p)SOCH₃) and sulfone (BN(p)SO₂CH₃). Diphenyl sulphide and diphenyl sulfone derivatives (TCzBN-S and TCzBN-SO, respectively) were prepared by Suzuki-Miyaura coupling with the corresponding bromide.292 The electron-donating SMe group caused blueshifted emission, while electron-withdrawing sulfoxide and sulfone moieties yielded red-shifted emission. The k_{RISC} values of BN(p)SCH3 and TCzBN-S exceeded those of the oxidised compounds because of the differences in ΔE_{ST} . A phosphine oxide derivative, tCBNDADPO, was designed as an ambipolar self-host.²⁹³ The host segments were integrated into the MR core without involving a CT excited state. The synthesis of this

compound included bromination by NBS on the diphenylamine unit, palladium-catalysed P-C coupling, and oxidation with H_2O_2 . The Φ_{PL} of **tCBNDADPO** with a high doping concentration of 30 wt% was 99% in the doped film. The comparison of compounds with/without phosphorylation was reported in a different paper.225

Late-stage reactions allow for the introduction of various functionalities. The chiral MR compounds shown in Fig. 34 were synthesised using the coupling reactions presented in Scheme 45. 260,294 The effects of π -framework extension on the MR properties were basically same as those for the materials mentioned above. Additional chiral units of [2.2]paracyclo(1,4)carbazolophane (Czp) and octahydro-binaphthol (OBN) participated in the circularly polarised luminescence (CPL) process. Thus, the $|g_{\rm PL}|$ factors of Czp-tBuCzB (1.6 \times 10⁻³) and Czp-POAB (1.4 \times 10⁻³) were similar to those of other CP-TADF molecules with the Czp moiety. 295 Similarly, the CPL properties of OBN-2CN-BN and **OBN-4CN-BN** were similar to those reported in the literature. ²⁹⁶

Metal complexes

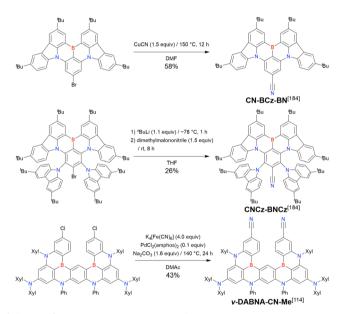
Phosphorescent metal complexes based on the DOBNA scaffold have been reported; e.g., a ligand based on DOBNA-pyridine was synthesised by the borylation of 2-(4-bromo-3,5-diphenoxyphenyl)pyridine (Scheme 51 and Table 40). Phosphorescent iridium(III) complexes with the acetylacetonate (acac) ligand, [Ir(C^N)2(acac)], were prepared by well-established methods. 139 The emission maximum of IrBBacac having two DOBNA-based ligands (638 nm) was largely red-shifted relative to that of the corresponding complex without boron atoms (544 nm). The good rigidity and planarity of the DOBNA-based ligand contributed to the small FWHM. The combination with a N-embedded ligand (IrBNacac) showed a slightly blue-shifted emission maximum at 523 nm and a narrower FWHM.²⁹⁷ The different types of ligands led to the T1 level with several characters including a metal-to-ligand CT transition (3MLCT),

Table 39 Photophysical properties of the materials shown in Schemes 48–50

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\rm ST}$ [eV]	$k_{ m RISC} \left[{ m s}^{-1} ight]$	Ref.
p-CzB	Toluene/1 wt%-mCBP-can	505/513	34/41	0.85/0.80	0.17/0.14	$4.2 \times 10^4 / 4.6 \times 10^4$	185
m-CzB	Toluene/1 wt%-mCBP-can	515/517	35/40	0.90/0.85	0.13/0.09	$1.2 \times 10^5/2.3 \times 10^5$	185
CN-BCz-BN	Toluene	496	21		_	_	184
CNCz-BNCz	Toluene/3 wt%-CBP ^a	581/582	42/45	0.90/0.96	0.18/—	$4.2 \times 10^{5}/$ —	184
ν-DABNA-CN-Me	Toluene/1 wt%-PMMA ^a	496/503	17/27	0.86/0.74	/0.1	$1.0 \times 10^{5}/\!-\!$	114
BN(p)SCH ₃	Toluene/3 wt%-26DCzppy ^a	479/488	24/38	 /0 . 92	0.12/—	$-/6.4 \times 10^4$	178
BN(p)SOCH ₃	Toluene/3 wt%-26DCzppy ^a	482/490	22/33	 /0.71	0.16/—	$-/3.0 \times 10^4$	178
BN(p)SO ₂ CH ₃	Toluene/3 wt%-26DCzppy ^a	490/496	21/29	— /0 . 99	0.20/—	$-/3.5 \times 10^4$	178
TCzBN-S	Toluene/8 wt%-SF3TRZ ^a	488/498	25/32	 /0 . 98	0.14/0.13	$-/1.4 \times 10^5$	292
TCzBN-SO	Toluene/8 wt%-SF3TRZ ^a	494/508	27/31	 /0 . 98	0.14/0.14	$-/5.6 \times 10^4$	292
tCBNDADPO	$CH_2Cl_2/10$ wt%-/30 wt%-DBFDPO ^a	466/472/472	26/38/44	/0.79/0.99	//0.04	$-/1.75 \times 10^4/2.43 \times 10^4$	293
tCBNDASPO	CH ₂ Cl ₂ /20 wt%-/30 wt%-DBFDPO ^a	467/472/472	28/32/32	/0.92/0.79	/0.04/	$-4.55 \times 10^4/3.82 \times 10^4$	225

^a See Table 2 for the full compound name.

Chem Soc Rev

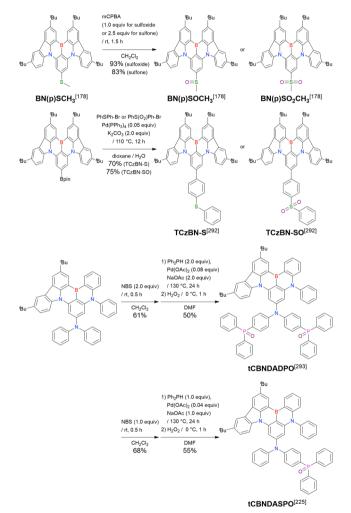


Scheme 49 Late-stage introduction of cyano groups.

CT transition from the N-embedded ligand to the B-embedded ligand (3 LLCT), and intraligand CT (3 ILCT). Platinum(II) complexes, **PtBacac** and **PtBbpy**, were also synthesised by standard methods using the same ligand. 298 The gold(I) coordination strategy aimed to enhance the RISC efficiency for MR emission because of the large spin–orbit coupling constant. The MR structure of **BCzBN** for green emission and that of the newly developed BNO for blue emission were covalently linked to Aucontaining N-heterocyclic carbene (Au-NHC) via a Au-C_{aryl} bond. Five bulky NHC ancillary ligands strongly bonded to gold(I). The complexes were synthesised by a coupling reaction between Bpinfunctionalised MR cores and (NHC)AuCl (Scheme 51). 95,299 The emission wavelengths of gold complexes were slightly red-shifted compared to those without the Au-NHC functionality. The high $\Phi_{\rm PL}$ and narrow FWHM were maintained despite the large $k_{\rm RISC}$.

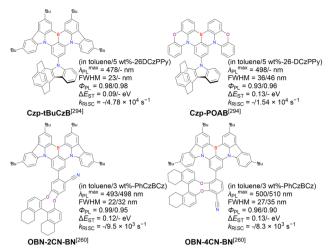
4.5 B-doped fused PAHs

The introduction of heteroatoms, especially boron, oxygen, and nitrogen, into fused PAHs affords novel π -conjugated systems



Scheme 50 Late-stage introduction of sulfoxide, sulfone, and phosphine oxide groups.

showing dramatically different optoelectronic properties despite their structural similarities. Recent progress in the development of the bottom-up synthesis of nanographenes using solution-based techniques holds great promise for accelerating the evolution of heteroatom incorporation. Late-stage



CzBN derivatives showing CPL

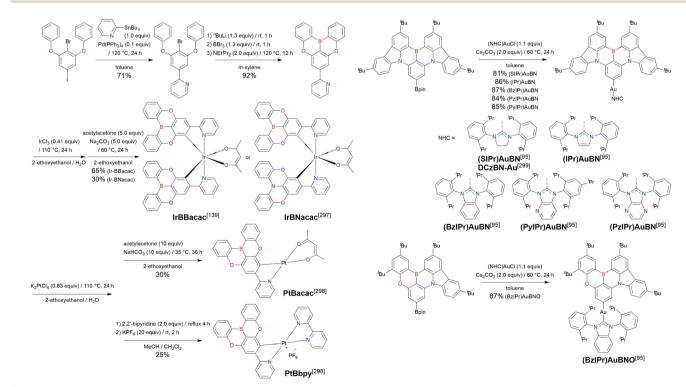
synthesis using pre-prepared MR structures such as DOBNA and BCzBN is advantageous for constructing extended π conjugation in a short number of steps. We have not summarised photophysical properties for the following compounds described in Schemes 52-56 since they do not show any TADF characteristics.

Hexabenzocoronene-based molecules are examples of DOBNA-fused systems (Scheme 52). 136 Chemical structures having multiple helical regions and distorted configurations affect the electronic properties. Intermediates with alkyne moieties were synthesised by Sonogashira-Hagihara coupling using DOBNA derivatives. The subsequent cyclotrimerisation of

these alkyne derivatives catalysed by Co₂(CO)₈ vielded hexa-aryl precursors.

Intramolecular cyclodehydrogenation was performed using FeCl₃ for HBC-3BO and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoromethanesulfonic acid (TfOH) for HBC-6BO to complete the reaction. For HBC-6BO, the branched alkyl chains were used to enhance solubility. The absorption/ emission maxima of tBu-HBC. HBC-3BO, and HBC-6BO were located at 360/493, 438/529 and 514/602 nm, respectively, showing that the introduction of the DOBNA scaffold resulted in a substantial red-shift. $\Phi_{\rm PL}$ also increased after the incorporation of the DOBNA moiety (from 5.8% to 18-20%).

Certain PAHs have a unique open-shell singlet biradical character. Indenofluorenes (IFs) and their π -extended derivatives show moderate-to-high biradical characters, while Bcontaining biradicaloids might be more challenging to synthesise because of their high reactivities. Therefore, rigid and stable DOBNA and CzBN structures were merged with IFs to afford, e.g., DOBNA and CzBN-fused s- and as-indacenes. The central core structures are based on indeno[1,2-b]fluorene, indeno[2,1-b]fluorene, and fluoreno[1,2-b]fluorene, which are herein referred to as [1,2-b]IF, [2,1-b]IF, and [1,2-b]FF, respectively (Scheme 53). The corresponding synthesis process involved three steps including Suzuki-Miyaura coupling, nucleophilic addition of mesityl magnesium bromide to yield a diol, intramolecular Friedel-Crafts alkylation induced by treatment with BF3·Et2O, and oxidative dehydrogenation with DDO. 118,135,300 The characterisation of [1,2-b]IF-α-DOBNA and [2,1-b]IF-α-DOBNA using NMR, X-ray single-crystal analysis, electron paramagnetic resonance (EPR), ultraviolet-visible



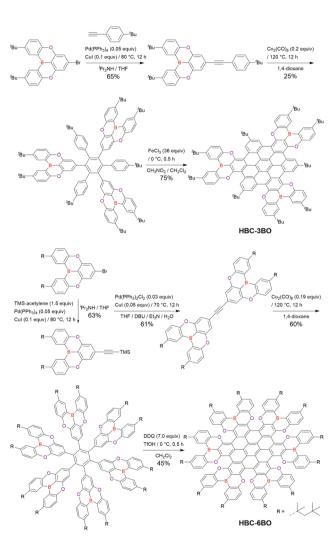
Scheme 51 Synthesis of DOBNA- and CzBN-based metal complexes

Chem Soc Rev

Table 40 Photophysical properties of the compounds shown in Scheme 51

Compound	Condition	$\lambda_{PL}^{max}\left[nm\right]$	FWHM [nm]	$\Phi_{\mathrm{PL}}\left[ight]$	$\Delta E_{\mathrm{ST}} [\mathrm{eV}]$	$k_{ m RISC} \left[{ m s^{-1}} ight]$	Ref.
IrBBacac	CH ₂ Cl ₂ /10 wt%-CBP ^a :mMTDATA ^a	638/639	— /53	0.21/0.34	NA ^b /NA ^b	NA ^b /NA ^b	139
IrBNacac	$CH_2Cl_2/1$ wt%-PS ^a	625/623	/50	— /0 . 35	NA^b/NA^b	NA^b/NA^b	297
PtBacac	$CH_2Cl_2/1$ wt%-PS ^a	578/578	—/—	0.30/0.45	NA^b/NA^b	NA^b/NA^b	298
PtBbpy	$CH_2Cl_2/1$ wt%- PS^a	 /588	—/—	/0.12	NA^b/NA^b	NA^b/NA^b	298
(SIPr)AuBN	THF/2 wt%-PMMA ^a	511/515	30/37	0.88/0.92	—/—	—/—	95
DCzBN-Au	Toluene/1 wt%-mCP ^a	514/508	28/39	 /0 . 95	0.09/0.13	$-/2.3 \times 10^{7}$	299
(IPr)AuBN	THF/MeCN/2 wt%-PMMA ^a	511/—/514	31/—/37	0.83/—/0.90	—/—/—	$-/3.3 \times 10^4/-$	95
(BzIPr)AuBN	THF/MeCN/2 wt%-PMMA ^a	511/—/513	30/—/37	0.86/—/0.91	—/—/—	$-/5.0 \times 10^4/-$	95
(PyIPr)AuBN	THF/MeCN/2 wt%-PMMA ^a	511/—/514	30/—/37	0.93/—/0.88	—/—/—	$-/3.2 \times 10^4/-$	95
(PzIPr)AuBN	THF/2 wt%-PMMA ^a	510/514	30/37	0.78/0.87	—/—	—/—	95
(BzIPr)AuBNO	THF/MeCN/2 wt%-PMMA ^a	471/—/473	30/—/37	0.89/—/0.84	-/-/-	$/1.1 \times 10^4/$	95

^a See Table 2 for the full compound name. ^b Not applicable because of phosphorescent materials.



Scheme 52 Synthesis of DOBNA-based nanographene reported in ref. 136

(UV-vis) absorption, and cyclic voltammetry measurements confirmed the significant contributions of the open-shell biradical form, which exceeded those for the corresponding indenofluorenes. The isomeric compound [1,2-b]IF-β-DOBNA showed clearly resolved NMR signals, a very weak EPR signal,

and a wider energy gap, which indicated a much smaller biradical character. N,B,N-substituted species showed a higher biradical character than O,B,O-substituted ones according to theoretical calculations. Thus, [1,2-b]IF- α -BCzBN and [1,2-b]FFα-BCzBN showed significantly red-shifted absorption maxima at 803 and 876 nm, respectively, as well as small energy gaps. These results demonstrate that MR structures greatly influence the open-shell biradical nature of PAHs.

Lewis acid-base adducts

The vacant p-orbital of boron is responsible for Lewis acidity, although the structural constraint of boron atoms in the planar π -conjugated systems with N,O heteroatom bridges in MR structures lowers this acidity. Indeed, DOBNA and CzBN derivatives can interact with Lewis bases such as pyridine, 4-dimethylaminopyridine (DMAP), and fluoride (Scheme 54). A compound with a DOBNA and N-embedded dioxygen-bridged structure, BO-NO, showed yellow emission in the polar CH₂Cl₂. ³⁰¹ The emission intensity decreased upon the addition of pyridine, while the addition of DMAP induced the emergence of a new emission band in the blue region and decreased the intensity of the emission band in the yellow region. The binding constants of BO-NO towards pyridine and DMAP were estimated as 27 and $4.2 \times 10^4 \text{ M}^{-1}$, respectively, which are much lower than those of planar fused trinaphthylboranes.302 The phosphorescence of IrBBacac showed a similar behaviour. 139 The emission peak lost intensity and shifted to longer wavelengths (from 647 to 667 nm) upon the addition of pyridine. In contrast, DMAP addition caused an emission blue shift and intensity increase.

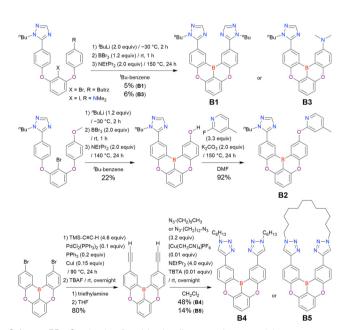
The two Lewis bases, pyridine and DMAP, coordinated at different positions, and π - π interactions between two DMAP molecules were observed in the crystal structure. As BCzBN shows intense emission with a narrow FWHM and high Φ_{PL} as well as good chemical and thermal stability, it is well suited for the construction of turn-off-type fluorescent probes. The interactions between the boron centre and the fluoride ion upon the addition of tetrabutylammonium fluoride (TBAF) resulted in the formation of a non-fluorescent complex and, hence, substantial emission quenching.303 Consequently, boron-based MR materials hold great promise for the highly sensitive, selective, and reversible sensing of fluoride ions.

Scheme 53 Synthesis of DOBNA-based biradicaloids.

Lewis acid-base coordination not only changed optical properties, but also enhanced the open-shell biradical character^{118,135}

N-Heterocycle-tethered DOBNA structures were investigated as stimuli-responsive materials. 115 Although compounds B1 and B3 were synthesised by one-pot borylation, the synthesis of B2 involved an additional S_NAr reaction. The syntheses of B4 and B5 involved Sonogashira-Hagihara cross-coupling followed by a click reaction (Scheme 55). Compounds **B1–B3** having an *n*butyl-1H-1,2,4-triazole scaffold exhibited emission intensity enhancement at elevated temperatures in solution, while compounds **B4** and **B5** containing an *n*-hexyl-1*H*-1,2,3-triazole scaffold showed fluorescence quenching under the same conditions. The thermally responsive emission of B1-B3 was

Scheme 54 Lewis acid-base adducts of DOBNA and CzBN structures.



Scheme 55 Synthesis of multi-stimuli responsive materials.

caused by the dynamic switching of intermolecular B-N interactions. In addition, these compounds exhibited remarkable mechanochromism in the solid state. The formation of B-N pairs was also used to develop supramolecular copolymers. 138 The peripheries of the DOBNA core accommodated three amide units as H-bonding supramolecular motifs, which were Chem Soc Rev **Review Article**

Scheme 56 Late-stage introduction of peripheral gallic amides with (S)-3,7-dimethyloctyl chains for supramolecular copolymers.

introduced by late-stage coupling to give S-B1 (Scheme 56). Cofacial B-N contacts in the copolymer with S-N1 facilitated the formation of an exciplex with TADF properties, followed by circularly polarised emission. Overall, the high stability of bridged triarylboranes is of key importance, enabling a wide variety of applications.

4.7 Summary

Late-stage functionalisation is a useful method for developing a wide variety of structures, as photophysical properties can be finely tuned by the attachment of appropriate donor and acceptor moieties. Moreover, this method enables the utilisation of MR fragments as building blocks and thus allows one to expand the application scope of MR materials by gaining additional functionality and incorporation into systems with extended π -conjugation.

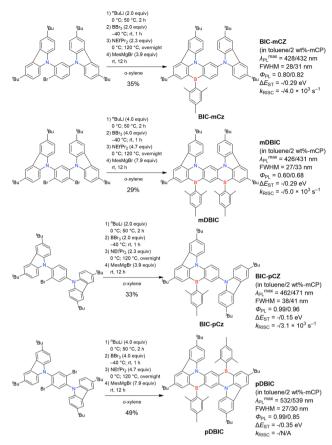
5. Ladder-type boron-based MR compounds

Most boron-based MR-TADF compounds introduced in the previous sections possess boron atoms at the ring junction, featuring planarity constraints, i.e., planarised triaryl boronbased compounds.³⁷ On the other hand, some B,N-based PAHs, in which boron atoms are not fully constrained, also exhibit MR effects. These compounds are synthesised using methods closely resembling one-pot or one-shot borylation, as discussed in the present section. The incorporation of tricoordinate boron atoms into the framework of linear acenes is an effective strategy for achieving the properties of the parent π conjugated systems, which are inaccessible in carbon-only acenes. In 2006, Kawashima et al. reported a series of laddertype fused azaborines in which the boron and nitrogen atoms are located in para-positions with respect to each other.³⁰⁴ Zysman-Colman et al. reported B,N-doped heptacene α-3BNOH, where the boron and nitrogen atoms are located in para-positions with respect to each other. 305 The triple electrophilic C-H borylation of N^1 -(3-(di-p-tolylamino)phenyl)- N^1 , N^3 ,-N³-tri-p-tolylbenzene-1,3-diamine occurred in the presence of

Scheme 57 Synthesis of α -3BNOH and α -3BNMes by triple electrophilic C-H borylation

18 equiv. of BBr3 and afforded a tri-B-Br intermediate that was subsequently hydrolysed to give α-3BNOH in 68% yield (Scheme 57, top). Note that the process up to the point of hydrolysis is the same as that of one-shot borylation. The thus obtained α-3BNOH exhibited narrow deep blue emission with CIE coordinates of (0.17, 0.01) and presented an attractive combination of TADF and TTA in a single material. α-3BNMes was also synthesized by trapping the tri-B-Br intermediate with a Grignard reagent instead of hydrolysing the former (Scheme 57, bottom). 306 α-3BNMes showed a narrow blue emission at 442 nm (FWHM = 30 nm) that was red-shifted compared with that of α-3BNOH because of the replacement of the strongly mesomerically electron-donating hydroxyl groups with inductively electron-withdrawing mesityl substituents. It is noteworthy that BN-doped heptacene α-3BNMes exhibited TADF behaviour in contrast to BN-doped pentacene reported by Kawashima et al.³⁰⁴ due to the small ΔE_{ST} (0.28 eV) attributed to the highly π -extended structure.

Duan et al. prepared carbazole-fused 1,4-diazaborine type MR-TADF compounds with nonplanar boron atoms on the periphery.³⁰⁷ Starting with mono-brominated bis(*N*-carbazolyl)benzene, the one-pot sequence of lithium-bromine exchange, borylation, intramolecular bora-Friedel-Crafts reaction, and trapping with a Grignard reagent afforded mono-borylated BIC-mCz and BIC-pCz in yields of 35% and 33%, respectively (Scheme 58). In the same manner, double-borylated mDBIC and pDBIC were obtained from a dibrominated precursor in 29% and 49% yields, respectively. Notably, the process up to trapping with the Grignard reagent is identical to the one-pot borylation protocol, the only difference being the presence of a non-condensed substituent on the boron centre. The above borylated compounds displayed deep blue to pure green MR



Scheme 58 Synthesis of BIC-mCz, BIC-pCz, mDBIC, and pDBIC.

emission at 426-532 nm with a FWHM of 27-38 nm. These ladder-type boron-based MR compounds exhibit larger $\Delta E_{\rm ST}$ and smaller k_{RISC} due to their relatively small MR effects.

6. Conclusions

This review summarises the synthetic routes for boron-based MR emitters. For single or double borylation, one-pot borylation is the first choice because of its high regioselectivity. Commercially available polyhalobenzenes containing fluorine, chlorine, bromine, and iodine atoms are efficiently converted to one-pot borylation precursors via S_NAr reactions and Buchwald-Hartwig couplings with complementary site (halogen) selectivity. However, diarylamines cannot be introduced via S_NAr reactions, which has severely limited the chemical space of MR emitters. Moreover, double borylation is generally lowyielding and therefore impractical. For multiple borylation, one-shot borylation is an advantageous method but requires a judicious choice of precursors and reaction conditions to achieve kinetic or thermodynamic regioselectivity control. The combination of one-pot and one-shot borylations, i.e., sequential multiple borylation, is a promising method for constructing novel MR skeletons with multiple boron atoms. The late-stage functionalisation of MR emitters is useful for tuning their emission wavelengths, increasing their k_{RISC} values, or imparting new functions (e.g., chiroptical, sensing, and stimuli-responsive

properties). Although these protocols have achieved impressive results for the last several years, the practical application of MR emitters is still limited to their use as blue-fluorescent emitters in OLED displays. Therefore, to design MR emitters not only exhibiting specific properties but also complying with all practical requirements, especially high stability during device operation, the current chemical space needs to be well understood and further expanded by developing new synthetic protocols. Furthermore, the expansion of the chemical space will break through unconscious limits of one's imagination and pave the way for practical applications beyond OLEDs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by JST CREST (Grant Number JPMJCR22B3), JSPS Grants-in-Aid for Transformative Research Areas (Condensed Conjugation, 20H05863), Grants-in-Aid for Scientific Research(B) (21H02019), Grants-in-Aid for Scientific Research(C) (23K04879), and Grant-in-Aid for Research Activity Start-up (23K19243 and 23K19245).

Notes and references

- 1 F. Jäkle, Coord. Chem. Rev., 2006, 250, 1107-1121.
- 2 A. Wakamiya and S. Yamaguchi, Pure Appl. Chem., 2006, 78, 1413-1424.
- 3 Z. M. Hudson and S. Wang, Acc. Chem. Res., 2009, 42, 1584-1596.
- 4 C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbai, Chem. Rev., 2010, 110, 3958-3984.
- 5 F. Jäkle, Chem. Rev., 2010, 110, 3985-4022.
- 6 A. Escande and M. J. Ingleson, Chem. Commun., 2015, 51,
- 7 A. Wakamiya and S. Yamaguchi, Bull. Chem. Soc. Ipn., 2015, 88, 1357-1377.
- 8 Y. Ren and F. Jäkle, Dalton Trans., 2016, 45, 13996-14007.
- 9 L. Ji, S. Griesbeck and T. B. Marder, Chem. Sci., 2017, 8, 846-863.
- 10 G. Turkoglu, M. E. Cinar and T. Ozturk, Molecules, 2017, 22, 1522.
- 11 E. von Grotthuss, A. John, T. Kaese and M. Wagner, Asian J. Org. Chem., 2018, 7, 37-53.
- 12 S. K. Mellerup and S. Wang, Chem. Soc. Rev., 2019, 48, 3537-3549.
- 13 H. Helten, Chem. Asian J., 2019, 14, 919-935.
- 14 J. Huo, H. Wang, S. Li, H. Shi, Y. Tang and B. Z. Tang, Chem. Rec., 2020, 20, 556-569.
- 15 X. Yin, J. Liu and F. Jäkle, Chem. Eur. J., 2021, 27, 2973-2986.
- 16 S. M. Berger, M. Ferger and T. B. Marder, Chem. Eur. J., 2021, 27, 7043-7058.

17 J. Shi, Z. Ran, F. Peng, M. Chen, L. Li, L. Ji and W. Huang, I. Mater. Chem. C. 2022. 10, 9165–9191.

Chem Soc Rev

112-120.

- J. Mater. Chem. C, 2022, 10, 9165-9191.18 S. M. Berger and T. B. Marder, Mater. Horiz., 2022, 9,
- 19 M. Wang and C.-H. Zhao, Chem. Rec., 2022, 22, e202100199.
- 20 J. Han, Y. Chen, N. Li, Z. Huang and C. Yang, *Aggregate*, 2022, 3, e182.
- 21 R. Wang, C.-S. Lee and Z. Lu, *J. Organomet. Chem.*, 2023, **984**, 122564.
- 22 J. Doty, B. Babb, P. Grisdale, M. Glogowski and J. Williams, J. Organomet. Chem., 1972, 38, 229–236.
- 23 C. D. Entwistle and T. B. Marder, *Angew. Chem.*, *Int. Ed.*, 2002, 41, 2927–2931.
- 24 C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, 16, 4574–4585.
- 25 M. J. S. Dewar, V. P. Kubba and R. Pettit, J. Chem. Soc., 1958, 3073–3076.
- 26 Z. Liu and T. B. Marder, *Angew. Chem., Int. Ed.*, 2008, 47, 242–244.
- 27 M. J. D. Bosdet and W. E. Piers, *Can. J. Chem.*, 2009, **87**, 8–29.
- 28 P. G. Campbell, A. J. V. Marwitz and S.-Y. Liu, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 6074–6092.
- 29 M. M. Morgan and W. E. Piers, *Dalton Trans.*, 2016, 45, 5920–5924.
- 30 J.-Y. Wang and J. Pei, *Chin. Chem. Lett.*, 2016, 27, 1139–1146.
- 31 G. Belanger-Chabot, H. Braunschweig and D. K. Roy, *Eur. J. Inorg. Chem.*, 2017, 4353–4368.
- 32 Z. X. Giustra and S.-Y. Liu, J. Am. Chem. Soc., 2018, 140, 1184–1194.
- 33 X. Chen, D. Tan and D.-T. Yang, *J. Mater. Chem. C*, 2022, **10**, 13499–13532.
- 34 I. Shin, H. N. Lim and W. P. Hong, *Synthesis*, 2022, 570–588.
- 35 Z. Zhou, A. Wakamiya, T. Kushida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2012, **134**, 4529–4532.
- 36 M. Hirai, N. Tanaka, M. Sakai and S. Yamaguchi, *Chem. Rev.*, 2019, **119**, 8291–8331.
- 37 H. Hirai, K. Nakajima, S. Nakatsuka, K. Siren, J. Ni, S. Nomura, T. Ikuta and T. Hatakeyama, *Angew. Chem.*, *Int. Ed.*, 2015, 54, 13581–13585.
- 38 T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono and T. Ikuta, *Adv. Mater.*, 2016, **28**, 2777–2781.
- 39 C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, 1961, 57, 1894–1904.
- 40 A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato and C. Adachi, *Adv. Mater.*, 2009, 21, 4802–4806.
- 41 H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234–238.
- 42 C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1987, **51**, 913–915.
- 43 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151–154.

- 44 S. M. Suresh, D. Hall, D. Beljonne, Y. Olivier and E. Zysman-Colman, *Adv. Funct. Mater.*, 2020, **30**, 1908677.
- 45 H. J. Kim and T. Yasuda, *Adv. Opt. Mater.*, 2022, **10**, 2201714.
- 46 R. K. Konidena and K. R. Naveen, *Adv. Photonics Res.*, 2022, 3, 2200201.
- 47 T. Fan, Y. Zhang, D. Zhang and L. Duan, *Chem. Eur. J.*, 2022, **28**, e202104624.
- 48 K. R. Naveen, H. I. Yang and J. H. Kwon, *Commun. Chem.*, 2022, 5, 149.
- 49 K. R. Naveen, P. Palanisamy, M. Y. Chae and J. H. Kwon, *Chem. Commun.*, 2023, **59**, 3685–3702.
- 50 Y. Xu, Q. Wang, X. Song, Y. Wang and C. Li, *Chem. Eur. J.*, 2023, **29**, e202203414.
- 51 L. Xiaofeng, Z. Dongdong, D. Lian and Z. Yuewei, *Front. Chem.*, 2023, **11**, 1198404.
- 52 H.-Z. Li, F.-M. Xie, Y.-Q. Li and J.-X. Tang, *J. Mater. Chem. C*, 2023, **11**, 6471–6511.
- 53 C. Lv, X. Wang, Q. Zhang and Y. Zhang, *Mater. Chem. Front.*, 2023, 7, 2809–2827.
- 54 F. Santoro, A. Lami, R. Improta, J. Bloino and V. Barone, J. Chem. Phys., 2008, 128, 224311.
- 55 I. S. Park, K. Matsuo, N. Aizawa and T. Yasuda, *Adv. Funct. Mater.*, 2018, 28, 1802031.
- 56 S. Park, Y. Xiong, R.-H. Kim, P. Elvikis, M. Meitl, D.-H. Kim, J. Wu, J. Yoon, C.-J. Yu, Z. Liu, Y. Huang, K.-C. Hwang, P. Ferreira, X. Li, K. Choquette and J. A. Rogers, *Science*, 2009, 325, 977–981.
- 57 V. L. Colvin, M. C. Schlamp and A. P. Alivisatos, *Nature*, 1994, 370, 354–357.
- 58 S. Coe, W. K. Woo, M. Bawendi and V. Bulovic, *Nature*, 2002, **420**, 800–803.
- 59 T. Sato, K. Tokunaga, N. Iwahara, K. Shizu and K. Tanaka, in *The Jahn–Teller Effect*, ed. H. Koppel, D. Yarkony and H. Barentzen, Springer, Springer Series in Chemical Physics, 2009, vol. 97, pp. 99–129.
- 60 Y. Kondo, K. Yoshiura, S. Kitera, H. Nishi, S. Oda, H. Gotoh, Y. Sasada, M. Yanai and T. Hatakeyama, *Nat. Photonics*, 2019, 13, 678–682.
- 61 M. G. Prais, D. F. Heller and K. F. Freed, *Chem. Phys.*, 1974,6, 331–352.
- 62 Y. Lei, H. Guo, J. Wang and R. Jia, *Dalton Trans.*, 2019, 48, 5064–5071.
- 63 L. Liu, Q. Wei, Y. Cheng, H. Ma, S. Xiong and X. Zhang, J. Mater. Chem. C, 2020, 8, 5839–5846.
- 64 K. Goushi, K. Yoshida, K. Sato and C. Adachi, *Nat. Photonics*, 2012, **6**, 253–258.
- 65 Q. Zhang, J. Li, J. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, J. Am. Chem. Soc., 2012, 134, 14706–14709.
- 66 J.-L. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, Chem. Rev., 2004, 104, 4971–5004.
- 67 M. K. Etherington, J. Gibson, H. F. Higginbotham, T. J. Penfold and A. P. Monkman, *Nat. Commun.*, 2016, 7, 13680.
- 68 P. K. Samanta, D. Kim, V. Coropceanu and J.-L. Brédas, J. Am. Chem. Soc., 2017, 139, 4042–4051.

69 H. Noda, X.-K. Chen, H. Nakanotani, T. Hosokai, M. Miyajima, N. Notsuka, Y. Kashima, J.-L. Brédas and C. Adachi, Nat. Mater., 2019, 18, 1084-1090.

Review Article

- 70 B. Wex and B. R. Kaafarani, J. Mater. Chem. C, 2017, 5, 8622-8653.
- 71 X.-K. Chen, D. Kim and J.-L. Brédas, Acc. Chem. Res., 2018, **51**, 2215-2224.
- 72 J. Eng and T. J. Penfold, Chem. Rec., 2020, 20, 831-856.
- 73 H. Nakanotani, Y. Tsuchiya and C. Adachi, Chem. Lett., 2021, 50, 938-948.
- 74 A. Pershin, D. Hall, V. Lemaur, J.-C. Sancho-Garcia, L. Muccio-li, E. Zysman-Colman, D. Beljonne and Y. Olivier, Nat. Commun., 2019, 10, 597.
- 75 H. Nakanotani, T. Furukawa, T. Hosogai, T. Hatakeyama and C. Adachi, Adv. Opt. Mater., 2017, 5, 1700051.
- 76 C.-C. Yan, X.-D. Wang and L.-S. Liao, Adv. Sci., 2022, 9, 2200525.
- 77 M. Mamada, S. Maedera, S. Oda, T. B. Nguyen, H. Nakanotani, T. Hatakeyama and C. Adachi, Mater. Chem. Front., 2023, 7, 259-266.
- 78 D. Yokoyama, J. Mater. Chem., 2011, 21, 19187-19202.
- 79 J. Frischeisen, D. Yokoyama, A. Endo, C. Adachi and W. Brütting, Org. Electron., 2011, 12, 809-817.
- 80 W. Brütting, J. Frischeisen, T. D. Schmidt, B. J. Scholz and C. Mayr, Phys. Status Solidi A, 2013, 210, 44-65.
- 81 T. D. Schmidt, T. Lampe, M. R. D. Sylvinson, P. I. Djurovich, M. E. Thompson and W. Brütting, Phys. Rev. Applied., 2017, 8, 037001.
- 82 T. Northey and T. J. Penfold, Org. Electron., 2018, 59, 45-48.
- 83 I. Kim, K. H. Cho, S. O. Jeon, W.-J. Son, D. Kim, Y. M. Rhee, I. Jang, H. Choi and D. S. Kim, *JACS Au*, 2021, 1, 987–997.
- 84 X. Wu, B.-K. Su, D.-G. Chen, D. Liu, C.-C. Wu, Z.-X. Huang, T.-C. Lin, C.-H. Wu, M. Zhu, E. Y. Li, W.-Y. Hung, W. Zhu and P.-T. Chou, Nat. Photonics, 2021, 15, 780-786.
- 85 K. Shizu and H. Kaji, Commun. Chem., 2022, 5, 53.
- 86 S. Schmidbauer, A. Hohenleutner and B. König, Adv. Mater., 2013, 25, 2114-2129.
- 87 J. Lee, C. Jeong, T. Batagoda, C. Coburn, M. E. Thompson and S. R. Forrest, Nat. Commun., 2017, 8, 15566.
- 88 H. Lim, S.-J. Woo, Y. H. Ha, Y.-H. Kim and J.-J. Kim, Adv. Mater., 2022, 34, 2100161.
- 89 T. B. Nguyen, H. Nakanotani and C. Adachi, Adv. Opt. Mater., 2022, 10, 2200704.
- 90 H. Jiang, P. Tao and W.-Y. Wong, ACS Mater. Lett., 2023, 5, 822-845.
- 91 X. Wang, L. Wang, G. Meng, X. Zeng, D. Zhang and L. Duan, *Sci. Adv.*, 2023, **9**, eadh1434.
- 92 M. Nagata, H. Min, E. Watanabe, H. Fukumoto, Y. Mizuhata, N. Tokitoh, T. Agou and T. Yasuda, Angew. Chem., Int. Ed., 2021, 60, 20280-20285.
- 93 S. M. Pratik, V. Coropceanu and J.-L. Brédas, ACS Mater. Lett., 2022, 4, 440-447.
- 94 I. S. Park, H. Min and T. Yasuda, Angew. Chem., Int. Ed., 2022, 61, e202205684.
- 95 S. Cai, G. S. M. Tong, L. Du, G. K.-M. So, F.-F. Hung, T.-L. Lam, G. Cheng, H. Xiao, X. Chang, Z.-X. Xu and C.-M. Che, Angew. Chem., Int. Ed., 2022, 61, e202213392.

- 96 H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda and C. Adachi, Nat. Commun., 2014, 5, 4016.
- 97 D. Zhang, X. Song, A. J. Gillett, B. H. Drummond, S. T. E. Jones, G. Li, H. He, M. Cai, D. Credgington and L. Duan, Adv. Mater., 2020, 32, 1908355.
- 98 C.-Y. Chan, M. Tanaka, Y.-T. Lee, Y.-W. Wong, H. Nakanotani, T. Hatakeyama and C. Adachi, Nat. Photonics, 2021, 15, 203-207.
- 99 S. O. Jeon, K. H. Lee, J. S. Kim, S.-G. Ihn, Y. S. Chung, J. W. Kim, H. Lee, S. Kim, H. Choi and J. Y. Lee, Nat. Photonics, 2021, 15, 208-215.
- 100 M. Mamada, H. Katagiri, C.-Y. Chan, Y.-T. Lee, K. Goushi, H. Nakanotani, T. Hatakeyama and C. Adachi, Adv. Funct. Mater., 2022, 32, 2204352.
- 101 P. Heimel, A. Mondal, F. May, W. Kowalsky, C. Lennartz, D. Andrienko and R. Lovrincic, Nat. Commun., 2018, 9, 4990.
- 102 E. Kim, J. Park, M. Jun, H. Shin, J. Baek, T. Kim, S. Kim, J. Lee, H. Ahn and S. Kim, Sci. Adv., 2022, 8, eabq1641.
- 103 X. Cao, K. Pan, J. Miao, X. Lv, Z. Huang, F. Ni, X. Yin, Y. Wei and C. Yang, J. Am. Chem. Soc., 2022, 144, 22976-22984.
- 104 Y. X. Hu, J. Miao, T. Hua, Z. Huang, Y. Qi, Y. Zou, Y. Qiu, H. Xia, H. Liu, X. Cao and C. Yang, Nat. Photonics, 2022, 16, 803-810.
- 105 S. Oda and T. Hatakeyama, Bull. Chem. Soc. Ipn., 2021, 94, 950-960.
- 106 T. Hatakeyama, S. Hashimoto, S. Seki and M. Nakamura, J. Am. Chem. Soc., 2011, 133, 18614-18617.
- 107 A. D. Grosso, R. G. Pritchard, C. A. Muryn and M. J. Ingleson, Organometallics, 2010, 29, 241–249.
- 108 N. Ishida, T. Moriya, T. Goya and M. Murakami, J. Org. Chem., 2010, 75, 8709-8712.
- 109 S. A. Iqbal, J. Pahl, K. Yuan and M. J. Ingleson, Chem. Soc. Rev., 2020, 49, 4564-4591.
- 110 S. Rej and N. Chatani, Angew. Chem., Int. Ed., 2022, 61, e202209539.
- 111 S. Oda, W. Kumano, T. Hama, R. Kawasumi, K. Yoshiura and T. Hatakeyama, Angew. Chem., Int. Ed., 2021, 60, 2882-2886.
- 112 J. U. Kim, I. S. Park, C.-Y. Chan, M. Tanaka, Y. Tsuchiya, H. Nakanotani and C. Adachi, Nat. Commun., 2020, 11, 1765.
- 113 J. Han, Z. Huang, J. Miao, Y. Qiu, Z. Xie and C. Yang, Chem. Sci., 2022, 13, 3402-3408.
- 114 S. Oda, T. Sugitani, H. Tanaka, K. Tabata, R. Kawasumi and T. Hatakeyama, Adv. Mater., 2022, 34, 2201778.
- 115 G. Meng, T. Peng, Y. Shi, H. Li, X. Wang, X. Yin, D.-T. Yang, S. Wang and N. Wang, J. Mater. Chem. C, 2020, 8, 7749-7754.
- 116 F. Chen, L. Zhao, X. Wang, Q. Yang, W. Li, H. Tian, S. Shao, L. Wang, X. Jing and F. Wang, Sci. China: Chem., 2021, 64, 547-551.
- 117 Y. Chen, N. Li, Z. Huang, G. Xie and C. Yang, Chem. Eng. J., 2022, 430, 133078.
- 118 X. Tian, J. Guo, W. Sun, L. Yuan, C. Dou and Y. Wang, Chem. - Eur. J., 2022, 28, e202200045.

119 G. Meng, X. Chen, X. Wang, N. Wang, T. Peng and S. Wang, *Adv. Opt. Mater.*, 2019, 7, 1900130.

Chem Soc Rev

- 120 I. S. Park, H. Min, J. U. Kim and T. Yasuda, Adv. Opt. Mater., 2021, 9, 2101282.
- 121 H. Lee, R. Braveenth, S. Muruganantham, C. Y. Jeon, H. S. Lee and J. H. Kwon, *Nat. Commun.*, 2023, 14, 419.
- 122 D. H. Ahn, S. W. Kim, H. Lee, I. J. Ko, D. Karthik, J. Y. Lee and J. H. Kwon, *Nat. Photonics*, 2019, **13**, 540–546.
- 123 H. J. Kim, M. Godumala, S. K. Kim, J. Yoon, C. Y. Kim, H. Park, J. H. Kwon, M. J. Cho and D. H. Choi, *Adv. Opt. Mater.*, 2020, 8, 1902175.
- 124 H. Lim, H. J. Cheon, S.-J. Woo, S.-K. Kwon, Y.-H. Kim and J.-J. Kim, *Adv. Mater.*, 2020, **32**, 2004083.
- 125 H. J. Kim, H. Kang, J.-E. Jeong, S. H. Park, C. W. Koh, C. W. Kim, H. Y. Woo, M. J. Cho, S. Park and D. H. Choi, Adv. Funct. Mater., 2021, 31, 2102588.
- 126 R. Pei, H. Liu, C. Zhou, J. Miao and C. Yang, *J. Mater. Chem. C*, 2021, **9**, 17136–17142.
- 127 H.-J. Tan, G.-X. Yang, Y.-L. Deng, C. Cao, J.-H. Tan, Z.-L. Zhu, W.-C. Chen, Y. Xiong, J.-X. Jian, C.-S. Lee and Q.-X. Tong, *Adv. Mater.*, 2022, **34**, 2200537.
- 128 Y. Xie, L. Hua, Z. Wang, Y. Liu, S. Ying, Y. Liu, Z. Ren and S. Yan, *Sci. China: Chem.*, 2023, **66**, 826–836.
- 129 B. Chen, C. Liao, D. Li, H. Liu and S. Wang, *J. Mater. Chem. C*, 2023, **11**, 8767–8775.
- 130 H. Gao, S. Shen, Y. Qin, G. Liu, T. Gao, X. Dong, Z. Pang, X. Xie, P. Wang and Y. Wang, J. Phys. Chem. Lett., 2022, 13, 7561–7567.
- 131 H. Gao, Z. Li, Z. Pang, Y. Qin, G. Liu, T. Gao, X. Dong, S. Shen, X. Xie, P. Wang, C.-S. Lee and Y. Wang, ACS Appl. Mater. Interfaces, 2023, 15, 5529–5537.
- 132 F. Chen, J. Hu, X. Wang, S. Shao, L. Wang, X. Jing and F. Wang, *Sci. China: Chem.*, 2020, **63**, 1112–1120.
- 133 Y. Chang, Y. Wu, X. Wang, W. Li, Q. Yang, S. Wang, S. Shao and L. Wang, *Chem. Eng. J.*, 2023, 451, 138545.
- 134 K. R. Naveen, H. Lee, R. Braveenth, D. Karthik, K. J. Yang, S. J. Hwang and J. H. Kwon, *Adv. Funct. Mater.*, 2021, 32, 2110356.
- 135 J. Guo, Y. Yang, C. Dou and Y. Wang, J. Am. Chem. Soc., 2021, 143, 18272–18279.
- 136 J. Guo, T. Zhang, Z. Li, K. Ye, Y. Wang and C. Dou, *Chem. Commun.*, 2023, **59**, 2644–2647.
- 137 G. Meng, H. Dai, Q. Wang, J. Zhou, T. Fan, X. Zeng, X. Wang, Y. Zhang, D. Yang, D. Ma, D. Zhang and L. Duan, *Nat. Commun.*, 2023, 14, 2394.
- 138 B. Adelizzi, P. Chidchob, N. Tanaka, B. A. G. Lamers, S. C. J. Meskers, S. Ogi, A. R. A. Palmans, S. Yamaguchi and E. W. Meijer, *J. Am. Chem. Soc.*, 2020, 142, 16681–16689.
- 139 Q. Li, C. Shi, M. Huang, X. Wei, H. Yan, C. Yang and A. Yuan, *Chem. Sci.*, 2019, **10**, 3257–3263.
- 140 S. Nakatsuka, H. Gotoh, K. Kinoshita, N. Yasuda and T. Hatakeyama, *Angew. Chem., Int. Ed.*, 2017, **56**, 5087–5090.
- 141 S. H. Han, J. H. Jeong, J. W. Yoo and J. Y. Lee, *J. Mater. Chem. C*, 2019, 7, 3082–3089.

- 142 P. Jiang, L. Zhan, X. Cao, X. Lv, S. Gong, Z. Chen, C. Zhou, Z. Huang, F. Ni, Y. Zou and C. Yang, *Adv. Opt. Mater.*, 2021, 9, 2100825.
- 143 T. Hua, L. Zhan, N. Li, Z. Huang, X. Cao, Z. Xiao, S. Gong, C. Zhou, C. Zhong and C. Yang, *Chem. Eng. J.*, 2021, 426, 131169.
- 144 X. Wu, J.-W. Huang, B.-K. Su, S. Wang, L. Yuan, W.-Q. Zheng, H. Zhang, Y.-X. Zheng, W. Zhu and P.-T. Chou, Adv. Mater., 2022, 34, 2105080.
- 145 W. Yang, N. Li, J. Miao, L. Zhan, S. Gong, Z. Huang and C. Yang, *CCS Chem.*, 2022, **4**, 3463–3471.
- 146 Y.-C. Cheng, X.-C. Fan, F. Huang, X. Xiong, J. Yu, K. Wang, C.-S. Lee and X.-H. Zhang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212575.
- 147 W. Yang, J. Miao, F. Hu, Y. Zou, C. Zhong, S. Gong and C. Yang, Adv. Funct. Mater., 2023, 33, 2213056.
- 148 H. Mubarok, A. Amin, T. Lee, J. Jung, J.-H. Lee and M. H. Lee, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306879.
- 149 J.-J. Hu, X.-F. Luo, Y.-P. Zhang, M.-X. Mao, H.-X. Ni, X. Liang and Y.-X. Zheng, J. Mater. Chem. C, 2022, 10, 768–773.
- 150 G. Liu, H. Sasabe, K. Kumada, A. Matsunaga, H. Katagiri and J. Kido, *J. Mater. Chem. C*, 2021, **9**, 8308–8313.
- 151 J. Park, K. J. Kim, J. Lim, T. Kim and J. Y. Lee, *Adv. Mater.*, 2022, 34, 2108581.
- 152 B. Lei, Z. Huang, S. Li, J. Liu, Z. Bin and J. You, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218405.
- 153 X. Liang, Z.-P. Yan, H.-B. Han, Z.-G. Wu, Y.-X. Zheng, H. Meng, J.-L. Zuo and W. Huang, *Angew. Chem.*, *Int. Ed.*, 2018, 57, 11316–11320.
- 154 Y. Xu, Z. Cheng, Z. Li, B. Liang, J. Wang, J. Wei, Z. Zhang and Y. Wang, *Adv. Opt. Mater.*, 2020, **8**, 1902142.
- 155 M. Yang, I. S. Park and T. Yasuda, *J. Am. Chem. Soc.*, 2020, **142**, 19468–19472.
- 156 S. Xu, Q. Yang, Y. Zhang, H. Li, Q. Xue, G. Xie, M. Gu, J. Jin,L. Huang and R. Chen, *Chin. Chem. Lett.*, 2021, 32, 1372–1376.
- 157 Y.-T. Lee, C.-Y. Chan, M. Tanaka, M. Mamada, U. Balijapalli, Y. Tsuchiya, H. Nakanotani, T. Hatakeyama and C. Adachi, *Adv. Electron. Mater.*, 2021, 7, 2001090.
- 158 M. Yang, S. Shikita, H. Min, I. S. Park, H. Shibata, N. Amanokura and T. Yasuda, *Angew. Chem., Int. Ed.*, 2021, **60**, 23142–23147.
- 159 X. Yan, Z. Li, Q. Wang, Y. Qu, Y. Xu and Y. Wang, *J. Mater. Chem. C*, 2022, **10**, 15408–15415.
- 160 Y. Qi, W. Ning, Y. Zou, X. Cao, S. Gong and C. Yang, Adv. Funct. Mater., 2021, 31, 2102017.
- 161 Y. Zhang, G. Li, L. Wang, T. Huang, J. Wei, G. Meng, X. Wang, X. Zeng, D. Zhang and L. Duan, *Angew. Chem.*, Int. Ed., 2022, 61, e202202380.
- 162 X. Cai, Y. Xu, Y. Pan, L. Li, Y. Pu, X. Zhuang, C. Li and Y. Wang, Angew. Chem., Int. Ed., 2023, 62, e202216473.
- 163 Y. Zhang, J. Wei, L. Wang, T. Huang, G. Meng, X. Wang, X. Zeng, M. Du, T. Fan, C. Yin, D. Zhang and L. Duan, *Adv. Mater.*, 2023, 35, 2209396.

164 F. Zhang, F. Rauch, A. Swain, T. B. Marder and P. Ravat, Angew. Chem., Int. Ed., 2023, 62, e202218965.

Review Article

- 165 B. Du, K. Zhang, P. Wang, X. Wang, S. Wang, S. Shao and L. Wang, J. Mater. Chem. C, 2023, 11, 9578-9585.
- 166 J. Liu, L. Chen, X. Wang, Q. Yang, L. Zhao, C. Tong, S. Wang, S. Shao and L. Wang, Macromol. Rapid Commun., 2022, 43, e2200079.
- 167 G. Liu, H. Sasabe, K. Kumada, H. Arai and J. Kido, Chem. -Eur. J., 2022, 28, e202201605.
- 168 Q. Li, Y. Wu, X. Wang, Q. Yang, J. Hu, R. Zhong, S. Shao and L. Wang, *Chem. – Eur. J.*, 2022, **28**, e202104214.
- 169 Q. Li, Y. Wu, Q. Yang, S. Wang, S. Shao and L. Wang, ACS Appl. Mater. Interfaces, 2022, 14, 49995-50003.
- 170 J. Han, Z. Huang, X. Lv, J. Miao, Y. Qiu, X. Cao and C. Yang, Adv. Opt. Mater., 2022, 10, 2102092.
- 171 Z.-P. Yan, L. Yuan, Y. Zhang, M.-X. Mao, X.-J. Liao, H.-X. Ni, Z.-H. Wang, Z. An, Y.-X. Zheng and J.-L. Zuo, Adv. Mater., 2022, 34, 2204253.
- 172 Y. Zhang, D. Zhang, J. Wei, Z. Liu, Y. Lu and L. Duan, Angew. Chem., Int. Ed., 2019, 58, 16912-16917.
- 173 F. Liu, Z. Cheng, L. Wan, Z. Feng, H. Liu, H. Jin, L. Gao, P. Lu and W. Yang, Small, 2022, 18, e2106462.
- 174 F. Huang, X.-C. Fan, Y.-C. Cheng, H. Wu, Y.-Z. Shi, J. Yu, K. Wang, C.-S. Lee and X.-H. Zhang, Mater. Horiz., 2022, 9, 2226–2232.
- 175 W. Xue, H. Yan, Y. He, L. Wu, X. Zhang, Y. Wu, J. Xu, J. He, C. Yan and H. Meng, Chem. - Eur. J., 2022, 28, e202201006.
- 176 Y.-H. He, F.-M. Xie, H.-Z. Li, K. Zhang, Y. Shen, F. Ding, C.-Y. Wang, Y.-Q. Li and J.-X. Tang, Mater. Chem. Front., 2023, 7, 2454-2463.
- 177 X.-F. Luo, H.-X. Ni, X. Liang, D. Yang, D. Ma, Y.-X. Zheng and J.-L. Zuo, Adv. Opt. Mater., 2023, 11, 2203002.
- 178 Y. Li, W. Li, J. Hu, X. Yao, L. Hua, W. Cai, S. Shi, C. Zhang, Z. Liu, S. Li, X. Chen, Z. Sun, Z. Ren, M.-C. Tang, G. Wei and Z. Fei, Adv. Opt. Mater., 2023, 11, 2300298.
- 179 Y. Xu, C. Li, Z. Li, Q. Wang, X. Cai, J. Wei and Y. Wang, Angew. Chem., Int. Ed., 2020, 59, 17442-17446.
- 180 Y.-T. Lee, C.-Y. Chan, M. Tanaka, M. Mamada, K. Goushi, X. Tang, Y. Tsuchiya, H. Nakanotani and C. Adachi, Adv. Opt. Mater., 2022, 10, 2200682.
- 181 X. Cai, Y. Pu, C. Li, Z. Wang and Y. Wang, Angew. Chem., Int. Ed., 2023, 62, e202304104.
- 182 Y. Zou, M. Yu, J. Miao, T. Huang, S. Liao, X. Cao and C. Yang, Chem. Sci., 2023, 14, 3326-3331.
- 183 J.-P. Liu, L. Chen, L. Zhao, C.-Y. Tong, S.-M. Wang, S.-Y. Shao and L.-X. Wang, Chin. J. Polym. Sci., 2023, 41, 802-810.
- 184 Y. Liu, X. Xiao, Y. Ran, Z. Bin and J. You, Chem. Sci., 2021, 12, 9408-9412.
- 185 M. Yang, R. K. Konidena, S. Shikita and T. Yasuda, J. Mater. Chem. C, 2023, 11, 917-922.
- 186 X. Xiao, B. Lei, D. Wu and Z. Bin, Chem. Commun., 2023, 59, 6556-6559.
- 187 Q. Wu, J. Li, D. Liu, Y. Mei, B. Liu, J. Wang, M. Xu and Y. Li, Dyes Pigm., 2023, 217, 111421.
- 188 C.-Z. Du, Y. Lv, H. Dai, X. Hong, J. Zhou, J.-K. Li, R.-R. Gao, D. Zhang, L. Duan and X.-Y. Wang, J. Mater. Chem. C, 2023, 11, 2469-2474.

- 189 Y. Zhang, D. Zhang, J. Wei, X. Hong, Y. Lu, D. Hu, G. Li, Z. Liu, Y. Chen and L. Duan, Angew. Chem., Int. Ed., 2020, **59**, 17499-17503.
- 190 Y. Wei, K. Pan, X. Cao, Y. Li, X. Zhou and C. Yang, CCS Chem., 2022, 4, 3852-3863.
- 191 X.-F. Luo, H.-X. Ni, H.-L. Ma, Z.-Z. Qu, J. Wang, Y.-X. Zheng and J.-L. Zuo, Adv. Opt. Mater., 2022, 10, 2102513.
- 192 Y. Liu, X. Xiao, Z. Huang, D. Yang, D. Ma, J. Liu, B. Lei, Z. Bin and J. You, Angew. Chem., Int. Ed., 2022, 61, e202210210.
- 193 X.-F. Luo, S.-Q. Song, H.-X. Ni, H. Ma, D. Yang, D. Ma, Y.-X. Zheng and J.-L. Zuo, Angew. Chem., Int. Ed., 2022, 61, e202209984.
- 194 H. Chen, T. Fan, G. Zhao, D. Zhang, G. Li, W. Jiang, L. Duan and Y. Zhang, Angew. Chem., Int. Ed., 2023, 62, e202300934.
- 195 Y. Qiu, H. Xia, J. Miao, Z. Huang, N. Li, X. Cao, J. Han, C. Zhou, C. Zhong and C. Yang, ACS Appl. Mater. Interfaces, 2021, 13, 59035-59042.
- 196 T. Hua, J. Miao, H. Xia, Z. Huang, X. Cao, N. Li and C. Yang, Adv. Funct. Mater., 2022, 32, 2201032.
- 197 F. Liu, Z. Cheng, Y. Jiang, L. Gao, H. Liu, H. Liu, Z. Feng, P. Lu and W. Yang, Angew. Chem., Int. Ed., 2022, 61, e202116927.
- 198 X. Xiong, Y.-C. Cheng, K. Wang, J. Yu and X.-H. Zhang, Mater. Chem. Front., 2023, 7, 929-936.
- 199 Y. Yang, N. Li, J. Miao, X. Cao, A. Ying, K. Pan, X. Lv, F. Ni, Z. Huang, S. Gong and C. Yang, Angew. Chem., Int. Ed., 2022, 61, e202202227.
- 200 J. Liu, Y. Zhu, T. Tsuboi, C. Deng, W. Lou, D. Wang, T. Liu and Q. Zhang, Nat. Commun., 2022, 13, 4876.
- 201 X.-F. Luo, H.-X. Ni, L. Shen, L. Wang, X. Xiao and Y.-X. Zheng, Chem. Commun., 2023, 59, 2489-2492.
- 202 D. H. Ahn, J. H. Maeng, H. Lee, H. Yoo, R. Lampande, J. Y. Lee and J. H. Kwon, Adv. Opt. Mater., 2020, 8, 2000102.
- 203 J. Park, J. Lim, J. H. Lee, B. Jang, J. H. Han, S. S. Yoon and J. Y. Lee, ACS Appl. Mater. Interfaces, 2021, 13, 45798-45805.
- 204 J. Park, J. Moon, J. Lim, J. Woo, S. S. Yoon and J. Y. Lee, J. Mater. Chem. C, 2022, 10, 12300-12306.
- 205 S. Oda, B. Kawakami, R. Kawasumi, R. Okita and T. Hatakeyama, Org. Lett., 2019, 21, 9311-9314.
- 206 J. A. Knöller, G. Meng, X. Wang, D. Hall, A. Pershin, D. Beljonne, Y. Olivier, S. Laschat, E. Zysman-Colman and S. Wang, Angew. Chem., Int. Ed., 2020, 59, 3156-3160.
- 207 X.-F. Luo, H.-X. Ni, A.-Q. Lv, X.-K. Yao, H.-L. Ma and Y.-X. Zheng, Adv. Opt. Mater., 2022, 10, 2200504.
- 208 X. Cai, J. Xue, C. Li, B. Liang, A. Ying, Y. Tan, S. Gong and Y. Wang, Angew. Chem., Int. Ed., 2022, 61, e202200337.
- 209 Y. Zhang, D. Zhang, T. Huang, A. J. Gillett, Y. Liu, D. Hu, L. Cui, Z. Bin, G. Li, J. Wei and L. Duan, Angew. Chem., Int. Ed., 2021, 60, 20498-20503.
- 210 J.-K. Li, X.-Y. Chen, Y.-L. Guo, X.-C. Wang, A. C.-H. Sue, X.-Y. Cao and X.-Y. Wang, J. Am. Chem. Soc., 2021, 143, 17958-17963.
- 211 Y. Zou, J. Hu, M. Yu, J. Miao, Z. Xie, Y. Qiu, X. Cao and C. Yang, Adv. Mater., 2022, 34, 2201442.

212 Y. Wang, K. Zhang, F. Chen, X. Wang, Q. Yang, S. Wang,

Chem Soc Rev

- S. Shao and L. Wang, Chin. J. Chem., 2022, 40, 2671-2677.
- 213 J.-K. Li, M.-Y. Zhang, L. Zeng, L. Huang and X.-Y. Wang, Angew. Chem., Int. Ed., 2023, 62, e202303093.
- 214 T. Fan, M. Du, X. Jia, L. Wang, Z. Yin, Y. Shu, Y. Zhang, J. Wei, D. Zhang and L. Duan, Adv. Mater., 2023, 35, 2301018.
- 215 I. S. Park, M. Yang, H. Shibata, N. Amanokura and T. Yasuda, Adv. Mater., 2022, 34, 2107951.
- 216 X.-C. Fan, K. Wang, Y.-Z. Shi, Y.-C. Cheng, Y.-T. Lee, J. Yu, X.-K. Chen, C. Adachi and X.-H. Zhang, Nat. Photonics, 2023, 17, 280-285.
- 217 K. Matsui, S. Oda, K. Yoshiura, K. Nakajima, N. Yasuda and T. Hatakeyama, J. Am. Chem. Soc., 2018, 140, 1195-1198.
- 218 X. Lv, J. Miao, M. Liu, Q. Peng, C. Zhong, Y. Hu, X. Cao, H. Wu, Y. Yang, C. Zhou, J. Ma, Y. Zou and C. Yang, Angew. Chem., Int. Ed., 2022, 61, e202201588.
- 219 J. Jin, C. Duan, H. Jiang, P. Tao, H. Xu and W.-Y. Wong, Angew. Chem., Int. Ed., 2023, 62, e202218947.
- 220 J. H. Kim, W. J. Chung, J. Kim and J. Y. Lee, Mater. Today Energy, 2021, 21, 100792.
- 221 Y. Wang, Y. Duan, R. Guo, S. Ye, K. Di, W. Zhang, S. Zhuang and L. Wang, Org. Electron., 2021, 97, 106275.
- 222 H. J. Cheon, Y.-S. Shin, N.-H. Park, J.-H. Lee and Y.-H. Kim, Small, 2022, 18, e2107574.
- 223 H.-J. Cheon, S.-J. Woo, S.-H. Baek, J.-H. Lee and Y.-H. Kim, Adv. Mater., 2022, 34, 2207416.
- 224 K. R. Naveen, S. J. Hwang, H. Lee and J. H. Kwon, Adv. Electron. Mater., 2022, 8, 2101114.
- 225 J. Bian, S. Chen, L. Qiu, N. Zhang, J. Zhang, C. Duan, C. Han and H. Xu, Research, 2022, 2022, 9838120.
- 226 H. Lee, R. Braveenth, J. D. Park, C. Y. Jeon, H. S. Lee and J. H. Kwon, ACS Appl. Mater. Interfaces, 2022, 14, 36927-36935.
- 227 Y.-N. Hu, X.-C. Fan, F. Huang, Y.-Z. Shi, H. Wang, Y.-C. Cheng, M.-Y. Chen, K. Wang, J. Yu and X.-H. Zhang, Adv. Opt. Mater., 2023, 11, 2202267.
- 228 E. Ravindran, H. E. Baek, H. W. Son, J. H. Park, Y.-H. Kim and M. C. Suh, Adv. Funct. Mater., 2023, 33, 2213461.
- 229 K. Di, R. Guo, Y. Wang, Y. Lv, H. Su, Q. Zhang, B. Yang and L. Wang, J. Mater. Chem. C, 2023, 11, 6429-6437.
- 230 Y. Wang, K. Di, Y. Duan, R. Guo, L. Lian, W. Zhang and W. L. Wang, Chem. Eng. J., 2022, 431, 133221.
- 231 Y. Wang, R. Guo, A. Ying, K. Di, L. Chen, H. Gu, S. Liu, Y. Duan, H. Su, S. Gong and L. Wang, Adv. Opt. Mater., 2023, 11, 2202034.
- 232 C.-Y. Chan, S. Madayanad Suresh, Y.-T. Lee, Y. Tsuchiya, T. Matulaitis, D. Hall, A. M. Z. Slawin, S. Warriner, D. Beljonne, Y. Olivier, C. Adachi and E. Zysman-Colman, Chem. Commun., 2022, 58, 9377-9380.
- 233 Y. Lee and J.-I. Hong, *J. Mater. Chem. C*, 2022, **10**, 11855–11861.
- 234 M. Wang, Z. Fu, R. Cheng, J. Du, T. Wu, Z. Bin, D. Wu, Y. Yang and J. Lan, Chem. Commun., 2023, 59, 5126-5129.
- 235 N. Ikeda, S. Oda, R. Matsumoto, M. Yoshioka, D. Fukushima, K. Yoshiura, N. Yasuda and T. Hatakeyama, Adv. Mater., 2020, 32, 2004072.

- 236 T. Fan, Y. Zhang, L. Wang, Q. Wang, C. Yin, M. Du, X. Jia, G. Li and L. Duan, Angew. Chem., Int. Ed., 2022, 61, e202213585.
- 237 K. R. Naveen, H. Lee, L. H. Seung, Y. H. Jung, C. P. Keshavananda Prabhu, S. Muruganantham and J. H. Kwon, Chem. Eng. J., 2023, 451, 138498.
- 238 H. Tanaka, S. Oda, G. Ricci, H. Gotoh, K. Tabata, R. Kawasumi, D. Beljonne, Y. Olivier and T. Hatakeyama, Angew. Chem., Int. Ed., 2021, 60, 17910-17914.
- 239 K. R. Naveen, J. H. Oh, H. Lee and J. H. Kwon, Angew. Chem., Int. Ed., 2023, 62, e202306768.
- 240 K. Rayappa Naveen, H. Lee, R. Braveenth, K. Joon Yang, S. Jae Hwang and J. Hyuk Kwon, Chem. Eng. J., 2022, 432, 134381.
- 241 H. S. Kim, H. J. Cheon, D. Lee, W. Lee, J. Kim, Y.-H. Kim and S. Yoo, Sci. Adv., 2023, 9, eadf1388.
- 242 F. Huang, X.-C. Fan, Y.-C. Cheng, H. Wu, X. Xiong, J. Yu, K. Wang and X.-H. Zhang, Angew. Chem., Int. Ed., 2023, 62, e202306413.
- 243 S. Oda, B. Kawakami, Y. Yamasaki, R. Matsumoto, M. Yoshioka, D. Fukushima, S. Nakatsuka and T. Hatakeyama, J. Am. Chem. Soc., 2022, 144, 106-112.
- 244 S. Oda, B. Kawakami, M. Horiuchi, Y. Yamasaki, R. Kawasumi and T. Hatakeyama, Adv. Sci., 2023, 10, 2205070.
- 245 Y. Sano, T. Shintani, M. Hayakawa, S. Oda, M. Kondo, T. Matsushita and T. Hatakeyama, J. Am. Chem. Soc., 2023, 145, 11504-11511.
- 246 S. Nakatsuka, N. Yasuda and T. Hatakeyama, J. Am. Chem. Soc., 2018, 140, 13562-13565.
- 247 D. T. Yang, T. Nakamura, Z. He, X. Wang, A. Wakamiya, T. Peng and S. Wang, Org. Lett., 2018, 20, 6741-6745.
- 248 G. Meng, H. Dai, T. Huang, J. Wei, J. Zhou, X. Li, X. Wang, X. Hong, C. Yin, X. Zeng, Y. Zhang, D. Yang, D. Ma, G. Li, D. Zhang and L. Duan, Angew. Chem., Int. Ed., 2022, 61, e202207293.
- 249 G. Meng, H. Dai, J. Zhou, T. Huang, X. Zeng, Q. Wang, X. Wang, Y. Zhang, T. Fan, D. Yang, D. Ma, D. Zhang and L. Duan, Chem. Sci., 2023, 14, 979-986.
- 250 G. Meng, L. Liu, Z. He, D. Hall, X. Wang, T. Peng, X. Yin, P. Chen, D. Beljonne, Y. Olivier, E. Zysman-Colman, N. Wang and S. Wang, Chem. Sci., 2022, 13, 1665-1674.
- 251 S. Oda, K. Ueura, B. Kawakami and T. Hatakeyama, Org. Lett., 2020, 22, 700-704.
- 252 S. Uemura, S. Oda, M. Hayakawa, R. Kawasumi, N. Ikeda, Y.-T. Lee, C.-Y. Chan, Y. Tsuchiya, C. Adachi and T. Hatakeyama, J. Am. Chem. Soc., 2023, 145, 1505-1511.
- 253 S. Madayanad Suresh, L. Zhang, T. Matulaitis, D. Hall, C. Si, G. Ricci, A. M. Z. Slawin, S. Warriner, D. Beljonne, Y. Olivier, I. D. W. Samuel and E. Zysman-Colman, Adv. Mater., 2023, 35, 2300997.
- 254 S. Madayanad Suresh, L. Zhang, D. Hall, C. Si, G. Ricci, T. Matulaitis, A. M. Z. Slawin, S. Warriner, Y. Olivier, I. D. W. Samuel and E. Zysman-Colman, Angew. Chem., *Int. Ed.*, 2023, **62**, e202215522.
- 255 D. Karthik, D. H. Ahn, J. H. Ryu, H. Lee, J. H. Maeng, J. Y. Lee and J. H. Kwon, J. Mater. Chem. C, 2020, 8, 2272-2279.

256 D. Song, Y. Yu, L. Yue, D. Zhong, Y. Zhang, X. Yang, Y. Sun, G. Zhou and Z. Wu, J. Mater. Chem. C, 2019, 7, 11953-11963.

Review Article

- 257 Z. Huang, H. Xie, J. Miao, Y. Wei, Y. Zou, T. Hua, X. Cao and C. Yang, J. Am. Chem. Soc., 2023, 145, 12550-12560.
- 258 Q. Wang, Y. Xu, T. Yang, J. Xue and Y. Wang, Adv. Mater., 2023, 35, 2205166.
- 259 J. Hwang, H. Kang, J.-E. Jeong, H. Y. Woo, M. J. Cho, S. Park and D. H. Choi, Chem. Eng. J., 2021, 416, 129185.
- 260 Y. Xu, Q. Wang, X. Cai, C. Li and Y. Wang, Adv. Mater., 2021, 33, 2100652.
- 261 Y. Xu, C. Li, Z. Li, J. Wang, J. Xue, Q. Wang, X. Cai and Y. Wang, CCS Chem., 2022, 4, 2065-2079. (Previous citation CCS Chem., 2021, 3, 2077).
- 262 D. W. Lee, J. Hwang, H. J. Kim, H. Lee, J. M. Ha, H. Y. Woo, S. Park, M. J. Cho and D. H. Choi, ACS Appl. Mater. Interfaces, 2021, 13, 49076-49084.
- 263 Z. Zhao, C. Zeng, X. Peng, Y. Liu, H. Zhao, L. Hua, S.-J. Su, S. Yan and Z. Ren, Angew. Chem., Int. Ed., 2022, 61, e202210864.
- 264 R. Braveenth, H. Lee, J. D. Park, K. J. Yang, S. J. Hwang, K. R. Naveen, R. Lampande and J. H. Kwon, Adv. Funct. Mater., 2021, 31, 2105805.
- 265 J. Hwang, C. W. Koh, J. M. Ha, H. Y. Woo, S. Park, M. J. Cho and D. H. Choi, ACS Appl. Mater. Interfaces, 2021, 13, 61454-61462.
- 266 J. H. Maeng, D. H. Ahn, H. Lee, Y. H. Jung, D. Karthik, J. Y. Lee and J. H. Kwon, Dyes Pigm., 2020, 180, 108485.
- 267 J. Wang, J. Miao, C. Jiang, S. Luo, C. Yang and K. Li, Adv. Opt. Mater., 2022, 10, 2201071.
- 268 Y. Lee and J.-I. Hong, Adv. Opt. Mater., 2021, 9, 2100406.
- 269 T. Hua, Y.-C. Liu, C.-W. Huang, N. Li, C. Zhou, Z. Huang, X. Cao, C.-C. Wu and C. Yang, Chem. Eng. J., 2022, 433, 133598.
- 270 H. Xie, Z. Huang, N. Li, T. Hua, J. Miao and C. Yang, J. Mater. Chem. C, 2022, 10, 11239-11245.
- 271 D. Karthik, Y. H. Jung, H. Lee, S. Hwang, B.-M. Seo, J.-Y. Kim, C. W. Han and J. H. Kwon, Adv. Mater., 2021, 33, 2007724.
- 272 Y. Watanabe, H. Sasabe and J. Kido, Bull. Chem. Soc. Jpn., 2019, 92, 716-728.
- 273 X.-Q. Gan, Z.-M. Ding, D.-H. Liu, W.-Q. Zheng, B. Ma, H. Zhang, X. Chang, L. Wang, Y. Liu, X. Wu, S.-J. Su and W. Zhu, Adv. Opt. Mater., 2023, 11, 2300195.
- 274 Y.-J. Yu, S.-N. Zou, C.-C. Peng, Z.-Q. Feng, Y.-K. Qu, S.-Y. Yang, Z.-Q. Jiang and L.-S. Liao, J. Mater. Chem. C, 2022, 10, 4941-4946.
- 275 M. Godumala, J. Hwang, H. Kang, J.-E. Jeong, A. K. Harit, M. J. Cho, H. Y. Woo, S. Park and D. H. Choi, ACS Appl. Mater. Interfaces, 2020, 12, 35300-35310.
- 276 E. Y. Park, J. H. Park, Y.-H. Kim and M. C. Suh, J. Mater. *Chem. C*, 2022, **10**, 4705–4716.
- 277 S. Wu, L. Zhang, J. Wang, A. Kumar Gupta, I. D. W. Samuel and E. Zysman-Colman, Angew. Chem., Int. Ed., 2023, 62, e202305182.

- 278 Y. Zhang, J. Wei, D. Zhang, C. Yin, G. Li, Z. Liu, X. Jia, J. Qiao and L. Duan, Angew. Chem., Int. Ed., 2022, 61, e202113206.
- 279 X. Song, S. Shen, S. Zou, F. Guo, Y. Wang, S. Gao and Y. Zhang, Chem. Eng. J., 2023, 467, 143557.
- 280 G. Chen, J. Wang, W.-C. Chen, Y. Gong, N. Zhuang, H. Liang, L. Xing, Y. Liu, S. Ji, H.-L. Zhang, Z. Zhao, Y. Huo and B. Z. Tang, Adv. Funct. Mater., 2023, 2211893.
- 281 P. Jiang, J. Miao, X. Cao, H. Xia, K. Pan, T. Hua, X. Lv, Z. Huang, Y. Zou and C. Yang, Adv. Mater., 2022, 34, 2106954.
- 282 Y.-K. Qu, D.-Y. Zhou, F.-C. Kong, Q. Zheng, X. Tang, Y.-H. Zhu, C.-C. Huang, Z.-Q. Feng, J. Fan, C. Adachi, L.-S. Liao and Z.-Q. Jiang, Angew. Chem., Int. Ed., 2022, 61, e202201886.
- 283 T. Wang, X. Yin, X. Cao and C. Yang, Angew. Chem., Int. Ed., 2023, **62**, e202301988.
- 284 T. Wang, Y. Zou, Z. Huang, N. Li, J. Miao and C. Yang, Angew. Chem., Int. Ed., 2022, 61, e202211172.
- 285 L. Yang, P. Wang, K. Zhang, S. Wang, S. Shao and L. Wang, Dyes Pigm., 2023, 216, 111371.
- 286 J. Z. Deng, D. V. Paone, A. T. Ginnetti, H. Kurihara, S. D. Dreher, S. A. Weissman, S. R. Stauffer and C. S. Burgey, Org. Lett., 2009, 11, 345-347.
- 287 F. Huang, X.-C. Fan, Y.-C. Cheng, Y. Xie, S. Luo, T. Zhang, H. Wu, X. Xiong, J. Yu, D.-D. Zhang, X.-K. Chen, K. Wang and X.-H. Zhang, Adv. Opt. Mater., 2023, 11, 2202950.
- 288 Y. Hu, J. Miao, C. Zhong, Y. Zeng, S. Gong, X. Cao, X. Zhou, Y. Gu and C. Yang, Angew. Chem., Int. Ed., 2023, 62, e202302478.
- 289 Y. Xu, Q. Wang, J. Wei, X. Peng, J. Xue, Z. Wang, S.-J. Su and Y. Wang, Angew. Chem., Int. Ed., 2022, 61, e202204652.
- 290 Q. Wang, Y. Xu, T. Huang, Y. Qu, J. Xue, B. Liang and Y. Wang, Angew. Chem., Int. Ed., 2023, 62, e202301930.
- 291 J. T. Reeves, C. A. Malapit, F. G. Buono, K. P. Sidhu, M. A. Marsini, C. A. Sader, K. R. Fandrick, C. A. Busacca and C. H. Senanayake, J. Am. Chem. Soc., 2015, 137, 9481-9488.
- 292 F. Huang, Y.-C. Cheng, H. Wu, X. Xiong, J. Yu, X.-C. Fan, K. Wang and X.-H. Zhang, Chem. Eng. J., 2023, 465, 142900.
- 293 J. Bian, S. Chen, L. Qiu, R. Tian, Y. Man, Y. Wang, S. Chen, J. Zhang, C. Duan, C. Han and H. Xu, Adv. Mater., 2022, 34, 2110547.
- 294 X.-J. Liao, D. Pu, L. Yuan, J. Tong, S. Xing, Z.-L. Tu, J.-L. Zuo, W.-H. Zheng and Y.-X. Zheng, Angew. Chem., *Int. Ed.*, 2023, **62**, e202217045.
- 295 N. Sharma, E. Spuling, C. Mattern, W. Li, O. Fuhr, Y. Tsuchiya, C. Adachi, S. Brase, I. Samuel and E. Zysman-Colman, Chem. Sci., 2019, 10, 6689-6696.
- 296 Z.-G. Wu, H.-B. Han, Z.-P. Yan, X.-F. Luo, Y. Wang, Y.-X. Zheng, J.-L. Zuo and Y. Pan, Adv. Mater., 2019, 31, 1900524.
- 297 M. Wu, N. Li, C. Shi, J. Song, R. Zeng, F. Li, Q. Li, A. Yuan and C. Yang, Inorg. Chem. Front., 2023, 10, 1262-1269.
- 298 C. Shi, F. Li, Q. Li, W. Zhao, Y. Cao, Q. Zhao and A. Yuan, Inorg. Chem., 2021, 60, 525-534.

Chem Soc Rev **Review Article**

- 299 J. Wang, N. Li, C. Zhong, J. Miao, Z. Huang, M. Yu, Y. X. Hu, S. Luo, Y. Zou, K. Li and C. Yang, Adv. Mater., 2023, 35, 2208378.
- 300 J. Guo, Z. Li, X. Tian, T. Zhang, Y. Wang and C. Dou, Angew. Chem., Int. Ed., 2023, 62, e202217470.
- 301 G. Li, X. Liu, M. Wu, R. Zeng, Q. Li, A. Yuan and C. Shi, Dyes Pigm., 2022, 208, 110805.
- 302 K. Matsuo, S. Saito and S. Yamaguchi, J. Am. Chem. Soc., 2014, 136, 12580-12583.
- 303 Y. Qi, X. Cao, Y. Zou and C. Yang, J. Mater. Chem. C, 2021, 9, 1567-1571.
- 304 T. Agou, J. Kobayashi and T. Kawashima, Org. Lett., 2006, 8, 2241-2244.
- 305 S. M. Suresh, E. Duda, D. Hall, Z. Yao, S. Bagnich, A. M. Z. Slawin, H. Bässler, D. Beljonne, M. Buck, Y. Olivier, A. Köhler and E. Zysman-Colman, J. Am. Chem. Soc., 2020, 142, 6588-6599.
- 306 K. Stavrou, S. Madayanad Suresh, D. Hall, A. Danos, N. A. Kukhta, A. M. Z. Slawin, S. Warriner, D. Beljonne, Y. Olivier, A. Monkman and E. Zysman-Colman, Adv. Opt. Mater., 2022, 10, 2200688.
- 307 X. Wang, Y. Zhang, H. Dai, G. Li, M. Liu, G. Meng, X. Zeng, T. Huang, L. Wang, Q. Peng, D. Yang, D. Ma, D. Zhang and L. Duan, Angew. Chem., Int. Ed., 2022, 61, e202206916.