Chemical Science

ROYAL SOCIETY
OF **CHEMISTRY**

PERSPECTIVE
Todd B. Marder *et al.*
Recent developments in and perspectives on three-coordinate boron
materials: a bright future

PERSPECTIVE

Recent developments in and perspectives on three-coordinate boron materials: a bright future

Lei Ji,† Stefanie Griesbeck† and Todd B. Marder*

The empty p_z-orbital of a three-coordinate organoboron compound leads to its electron-deficient properties, which make it an excellent π-acceptor in conjugated organic chromophores. The empty p-orbital in such Lewis acids can be attacked by nucleophiles, so bulky groups are often employed to provide air-stable materials. However, many of these can still bind fluoride and cyanide anions leading to applications as anion-selective sensors. One electron reduction generates radical anions. The π-acceptor strength can be easily tuned by varying the organic substituents. Many of these compounds show strong two-photon absorption (TPA) and two-photon excited fluorescence (TPEF) behaviour, which can be applied for *e.g.* biological imaging. Furthermore, these chromophores can be used as emitters and electron transporters in OLEDs, and examples have recently been found to exhibit efficient thermally activated delayed fluorescence (TADF). The three-coordinate organoboron unit can also be incorporated into polycyclic aromatic hydrocarbons. Such boron-doped compounds exhibit very interesting properties, distinct from their all-carbon analogues. Significant developments have been made in all of these areas in recent years and new applications are rapidly emerging for this class of boron compounds.

Introduction

Three-coordinate boron has a trigonal-planar geometry with an empty p_z-orbital and is isoelectronic with a carbonium ion.

Institut für Anorganische Chemie and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: todd.marder@uni-wuerzburg.de

† These authors contributed equally to this work.

While such compounds are well-known as Lewis acids, binding Lewis bases *via* the empty orbital, suitable steric hindrance can inhibit such interactions leading to what are now termed "Frustrated Lewis Pairs" or FLPs.[1–11] Interest in FLPs has grown rapidly with their demonstrated ability to activate small molecules such as H_2. However, what is often overlooked is the fact that steric hindrance around the boron centre was recognized several decades ago as providing a useful way to prepare air-stable triarylboranes in which the protected empty p_z-orbital

Lei Ji began his studies at Liaoning University (Shenyang, China), where he obtained his bachelor's degree in Chemistry in 2006. He then moved to Shandong University (Jinan, China), where his research focused on the two-photon absorption properties of three-coordinate boron-containing materials and he obtained his PhD degree at the end of 2011. He was an exchange student at the University of Durham (Durham, UK) for 1 year during his PhD, supported by the China Scholarship Council. From 2012, he has been a postdoctoral researcher in the group of Prof. Dr Todd Marder at the Universität Würzburg (Würzburg, Germany). He currently works on boron-based radicals and the photophysical properties of triarylborane and pyrene derivatives.

Stefanie Griesbeck studied chemistry at the Julius-Maximilians-Universität Würzburg and did her Bachelor's Thesis with Prof. Dr Christoph Lambert at the Institute of Organic Chemistry. For her Master's Thesis, she joined the group of Prof. Dr Todd B. Marder at the Institute of Inorganic Chemistry of the Universität Würzburg. Stefanie is currently working towards her PhD with Prof. Marder, carrying out research on the synthesis and photophysical properties of triarylborane chromophores for two-photon excited fluorescence imaging of live cells.

on boron can act as a strong π-acceptor (A) in conjugated organic π-systems.[12] Thus, in the 1970's, a group at Kodak first examined the solvatochromic emission properties of compounds of the form $4\text{-D-}C_6H_4\text{-BMes}_2$ where D is a π-donor, such as Me_2N, and Mes is the bulky mesityl group, 2,4,6-$Me_3C_6H_2$.[13] In fact, these were indeed FLPs insofar as the Lewis basic Me_2N-group was inhibited by the bulk of the $BMes_2$ moiety from forming N–B dative bonds. Thus, the propeller arrangements of the *ortho*-methyl substituted benzenes generally shields the boron p_z-orbital from attack by Lewis bases or nucleophiles with the exception of very small anions such as F^- and CN^-. As such, compounds of this type have been developed recently as selective anion sensors.[14–17] In fact, $4\text{-D-}C_6H_4\text{-BMes}_2$ represents an excellent and simple example of a compound exhibiting intramolecular charge transfer (ICT) behaviour upon photoexcitation, as illustrated by its strongly solvatochromic fluorescence emission. Historically, we and Lequan's group recognized the ability of aryl $BMes_2$ systems to exhibit interesting second order nonlinear optical properties as early as 1990,[18–23] and we reported on the 2nd order NLO behaviour of a series of D–π–A (A = $BMes_2$ acceptor) compounds then, with more detailed experimental and theoretical studies following sometime later.[24] We also prepared a series of compounds incorporating diarylphosphino π-donor groups, namely *trans*-$Ph_2P\text{-CH}=\text{CH-BMes}_2$, $Ph_2P\text{-C}\equiv\text{C-BMes}_2$ and 1,4-$Ph_2P\text{-}C_6H_4\text{-}$$BMes_2$ in the early 1990's,[18,23] setting the stage for the fascinating 1,4-$Ar_2P\text{-}C_6F_4\text{-B}(C_6F_5)_2$ FLPs developed by Welch and Stephan *et al.* in 2006.[1] Early on, we also recognized the potential of centrosymmetric compounds containing two terminal $BMes_2$

moieties linked by an extended organic π-system to function as third order NLO materials.[25] Subsequently, we and many research groups have reported a wide range of interesting electronic and optical properties of 3-coordinate boron and related compounds and polymers, and we reviewed the early work in this field in 2002 and 2004.[26,27] The applications of 3-coordinate boron compounds in electronic and optical materials have expanded very rapidly over the past 2 decades.[17,28–32] We highlight below a few recent contributions using $BMes_2$ moieties along with the development of alternative strong B-based π-acceptors by us and others, focusing on systems which retain or enhance the air-stability of such species, a property which is most desirable for ease of preparation and handling, and thus for use in electronic or optical devices and other applications.

Modifying the electronic properties of 3-coordinate boron

The solvatochromic behaviour of many D–π–A compounds using dimesitylboryl or related 3-coordinate boron moieties as the electron accepting group has been widely explored. Below, we highlight the most important recent examples. Lambert reported a very interesting octupolar trigonal compound **1** with tris(2,6-xylyl)boron as the core, attached to three carbazole donors at the 4-positions (Scheme 1).[33] They showed in solution, using polarized steady-state fluorescence spectroscopy, a symmetry-broken ground state. Upon photoexcitation, an inversion of the dipole moment takes place, leading to a negative solvatochromism for the charge transfer absorption band, while the emission spectrum is positively affected. Furthermore, they proposed a dynamic dipole moment in the excited state, which can hop between the branches of the otherwise symmetric molecule.[34] Thereby, the dipole moment can respond to the solvent relaxation and change its direction according to the local field of the solvation shell, thus leading to a faster energy relaxation compared to a model compound with just one donor moiety.

By employing $BMes_2$ as the acceptor, Wang and co-workers have reported the first few examples of through-space ICT in such compounds, which included the U-shaped 1,8-naphthylenediyl and V-shaped silylene-spaced donor acceptor compounds **2–3**.[35,36] These compounds are strongly emissive and can be used as F^- sensors. More recently, Zhao and co-workers reported a simpler compound exhibiting through-space ICT, with a dimesitylborane and a dimethylamine incorporated at the o,o'-positions of a biphenyl framework **4**.[37] The Lambert group reported a hexaarylbenzene with three triarylamine donors and three triarylborane acceptors with weak donor–acceptor interactions due to through-space charge transfer.[38] Additionally, the excitation energy can be redistributed between the aryl substituents within the fluorescence lifetime. Highly fluorescent *N*-borylated 2,5-diarylpyrroles with dimesitylborane as the acceptor moiety were reported by Yamaguchi in 2013.[39] These molecules show a twisted conformation in the ground state, which is planarised in the excited state, leading to an increased electron-donating ability of the nitrogen by enhanced π-delocalisation. Therefore,

Todd Marder obtained his BSc from M.I.T. and his PhD from UCLA (Regents Intern Fellow). He was a postdoc at the University of Bristol (UK), and a Visiting Research Scientist at DuPont Central Research before joining the faculty at the University of Waterloo, Canada. He moved to the University of Durham, (UK) in 1997 as Chair of Inorganic Chemistry and then to the University of Würzburg, Germany in 2012, also as Chair of Inorganic Chemistry. Honors include: the Rutherford Memorial Medal for Chemistry (Royal Society of Canada), RSC (UK) Awards in Main Group Element Chemistry and in Organometallic Chemistry, JSPS Fellowship, Humboldt Research Award, Royal Society Wolfson Research Merit Award, membership in the Bavarian Academy of Sciences, Visiting/Honorary/Distinguished/Guest Professorships in the UK, France, Hong Kong, mainland China, Japan, India and the Craig Lectureship in Australia. He has served on the editorial boards of Organometallics, Inorganic Chemistry, JOMC, Polyhedron, Inorganica Chimica Acta, Applied Organometallic Chemistry, Canadian Journal of Chemistry, etc. and has published over 300 papers, and presented over 375 invited lectures.

Scheme 1   3-Coordinate boron compounds with different electronic properties.

the ICT character is increased by stronger donors, resulting in a more red-shifted emission. Müllen reported boron–nitrogen containing 'dendrimers,' the optical properties of which can be controlled by the donor/acceptor ratio. A ratio of 1 : 1 exhibits a more efficient charge transfer than the 1 : 2 analogue, and therefore a stronger solvent dependence.[40]

In 2003, working with K. Dillon, we reported the synthesis of FB(Fmes)$_2$ (Fmes = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$), the trifluoromethyl analogue of FBMes$_2$, and this is a useful precursor to a series of compounds containing the B(Fmes)$_2$ group.[41] In addition, we decided to explore, theoretically, the electronic effect of substituents, X, on boron on the HOMO and LUMO in a consistent series of compounds of the form 2,5'-(BX$_2$)$_2$-(C$_4$H$_2$S)$_2$, i.e., related to and including 2,5'-(BMes$_2$)$_2$-dithiophene

previously employed by Shirota as an electron transporter in OLEDs (vide infra).[42] Examination of X = C$_6$F$_5$ and 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, i.e., Fmes, showed that these two fluorinated arenes had fairly similar electronic effects, dropping the LUMO by ca. 1 eV with respect to X = Mes. While Jäkle had used B(C$_6$F$_5$)$_2$ moieties successfully to provide strong Lewis acidity, these systems are not stable to water.[43,44] In contrast, we felt that electronically similar but sterically very demanding Fmes would provide new air-stable, readily reducible boron compounds with strongly enhanced π-acceptor character.

With this in mind, we and Yamaguchi began to explore the optical properties of donor-substituted B(Fmes)$_2$ compounds. While our work was in progress, Yamaguchi thus reported the synthesis of carbazole directly bonded to a B(Fmes)$_2$ group via

its N-atom **5**.[45] They observed a strong red shift in emission compared with the BMes$_2$ analogue, and also noted evidence for a twisted intramolecular charge transfer (TICT) excited state, with their calculations suggesting that this state maintained 2-fold rotational symmetry. Recently, Thilagar and co-workers have reported the TICT behaviour of 4-BMes$_2$ aniline.[46] We prepared two compounds of the form 4-R–C$_6$H$_4$–B(Fmes)$_2$ **6**, wherein R = ^{t}Bu or the strong π-donor Ph$_2$N.[47] For comparison, we also prepared the known 4-Ph$_2$N–C$_6$H$_4$–BMes$_2$ analogue. In addition, Stephan's group had simultaneously prepared PhB(Fmes)$_2$ and had shown that it was so sterically hindered at the boron centre that it did not form FLPs with phosphines that were capable of activating even the smallest molecule, H$_2$. In contrast, the less hindered compound HB(Fmes)$_2$ was shown to exhibit interesting chemical reactivity.[48]

We first measured the redox properties of our aryl-B(Fmes)$_2$ compounds and, as expected, these showed reduction potentials which were *ca.* 1 V lower than that of 1,4-Ph$_2$N–C$_6$H$_4$–BMes$_2$, consistent with our previous calculations on the thienyl-bridged 3-coordinate boron compounds, *vide supra*. We then explored the photophysical behaviour of the new ArB(Fmes)$_2$ compounds. Having shown that B(Fmes)$_2$ is an exceptional π-acceptor, we also noted that this led to quenching of emission in more polar solvents due to TICT behaviour, in which, in contrast to the study by Yamaguchi,[45] it appears that one Fmes group rotates into the BC$_3$ plane in the excited state.[47]

We thus decided to prepare analogues with acceptor strengths lying between those of BMes$_2$ and B(Fmes)$_2$ in order to tune the properties of our systems, as the BMes$_2$ compounds we had examined thus far did not show signs of TICT behaviour.[49] A straightforward approach was to make use of the steric selectively of the Ir-catalysed C–H borylation methodology.[50] Thus, direct borylation of 1-Br-2,6-Me$_2$-C$_6$H$_3$ gave 1-Br-2,6-Me$_2$-4-Bpin-C$_6$H$_2$ which was then coupled with either 1-Br-3,5-(CF$_3$)$_2$C$_6$H$_3$ or BrC$_6$F$_5$ yielding the two respective 1-Br-2,6-Me$_2$-4-Arf-C$_6$H$_2$ derivatives Tfp-Br and Pfp-Br (for the structures of Tfp and Pfp, see Scheme 1) *via* Pd-catalysed Suzuki–Miyaura reactions. Thus, we synthesised two series of D–π–A compounds, each with triphenylamine (**7**) or julolidine (**8**) as the donor, where A is BAr$_2$ (Ar = Mes, Tfp, Pfp, Fmes). These compounds show high quantum yields up to unity. By comparing their photophysical properties and cyclic voltammetry, we established the order of acceptor strength as BMes$_2$ < B(Pfp)$_2$ $\approx$ B(Tfp)$_2$ $\ll$ B(Fmes)$_2$.[49] In contrast to the B(Fmes)$_2$ compounds, these systems showed strong emission in the red-NIR region in polar solvents. Wakamiya and Yamaguchi recently reported compounds **9** and **10**, which bear n-C$_4$F$_9$ at the 4-position or a –CF$_2$CF$_2$CF$_2$CF$_2$– loop at the 3,4-positions of 2,6-xylyl group.[51] Both systems show enhanced strong acceptor properties, while maintaining high fluorescence quantum yields in polar solvents.

A single Fmes on boron is sufficient to provide a dramatic enhancement of stability and greatly improved acceptor ability with respect to Mes. Thus, Jäkle and Marder reported a series of air- and moisture-stable conjugated thienylboranes **11**, which are inert even to acids and strong bases, due to their bulky Fmes or 2,4,6-tri-*tert*-butylphenyl (Mes*) groups.[52] In contrast to the

Mes* groups, the Fmes compounds also exhibit a high Lewis acidity toward very small anions, because of their highly electron-withdrawing character.

Boroles (RBC$_4$R$'_4$) represent another interesting class of electron-deficient 3-coordinate boron compounds, being 4π-antiaromatic analogues of [C$_5$H$_5$]$^+$.[53–56] They are, however, notoriously sensitive to air, water and various dimerisation processes.[57] We recently demonstrated a *ca.* 600-fold improvement in stability towards water for pentaarylborole **12**, with a bulky Fmes group on the boron, compared to its mesityl analogue, whilst at the same time enhancing the electron-deficient character of the borole.[58] This borole was prepared through a new and general method for borole synthesis, by reaction of Li[(Fmes)BF$_3$] with 1,4-dilithio-1,3-butadiene reagents,[59] and it shows good thermal stability without dimerising or isomerising as reported for some other boroles. Thus, an air-stable ArBF$_3$ salt can serve as the electrophile in place of more sensitive ArBX$_2$ compounds.[60] Meanwhile, Wagner and co-workers reported the preparation of triarylboranes by nucleophilic reaction of aryl-lithium reagents with ArBF$_3$K salts.[61] A few days before this perspective was submitted, Dixon, Rupar and co-workers reported the stability of dibenzoboroles (borafluorenes) with various substituents on the boron atom. They disclosed that Fmes is an outstanding protecting group comparable with the Tip group (Tip = 2,4,6-iPr$_3$C$_6$H$_2$). The Fmes-protected dibenzoborole could be isolated by silica column chromatography in air and only 5% decomposition after 24 hours in solution under air occurred.

In 2009, as part of an experimental and theoretical study of the optical properties of another type of 3-coordinate boron centre, namely the benzodiazaboroles of L. Weber *et al.*, we noted that these species could unexpectedly serve as π-donors, a novel observation for a 3-coordinate boron moiety.[42,62–65] This allowed the development of a series, *e.g.* **13**, of π-linked dipolar compounds featuring 3-coordinate boron centres in the role of both π-donor and π-acceptor.[63–65] A new group of 3-coordinate boron compounds in which the very electron-rich B=B double bond can serve as a strong π-donor **14** has been reported by the Braunschweig group. Neutral NHC-stabilised diborenes coordinate to Ag(I) and Cu(I) in an olefin-like η^2 mode, which is mostly of electrostatic nature due to the high electron density on the B=B double bond.[66,67] These metal complexes are highly luminescent compared to their olefin analogues.

3-Coordinate boron-based radicals

As a consequence of the strong π-acceptor properties of the 3-coordinate boron unit, triarylboranes have been demonstrated to be good negative-charge and spin carriers.[68] Most of the boron-containing radical anions can be prepared by reduction with alkali metals or other strong reducing agents. Bulky groups are needed to protect the boron radical centre from the formation of diamagnetic clusters. The BMes$_3$ radical anion has been studied in detail since the 1950s, demonstrating that the negative charge resides mostly on the boron centre, but is also delocalised into the mesityl groups to some extent.[69–71] Its lithium salt was isolated and characterised by single crystal

X-ray diffraction in 1986 by Power and co-workers.[72] They reported that the geometry of the radical anion of BMes$_3$ is very similar to that of the neutral BMes$_3$, with a slight elongation of the B–C bonds. Subsequently, the study of boron-based radicals, the formation of boron–boron one-electron bonds, and arene-bridged mixed valent diboranes has attracted much attention.[73–77]

Early on, Kaim also recognised the π-acceptor ability of the BMes$_2$ group, examining the electrochemical reduction of, for example, 1,4-Mes$_2$B–C$_6$H$_4$–BMes$_2$ (**15**) and 4,4'-Mes$_2$B–(C$_6$H$_4$)$_2$–BMes$_2$ (**16**), showing that the extra electron in the radical anion was completely delocalised over the two boron centres as well as the bridging phenylene or biphenylene group, resulting in what has been referred to as a boron mixed-valence compound, analogous to widely studied transition metal mixed-valence-species (Scheme 2).[78–83] Indeed, compounds such as **16** are the inverse of the 4,4'-Ar$_2$N–(C$_6$H$_4$)$_2$–NAr$_2$ systems, which are widely used as hole transport materials in OLEDs due to their ease of oxidation to their respective radical cations.[84,85] Shirota has employed thienyl-bridged Mes$_2$B–(C$_4$H$_2$S)$_n$–BMes$_2$ compounds (n = 2, 3) as electron transporters in OLEDs.[86,87] We have recently confirmed, by isolation of its anion salt and determination of its molecular structure by single-crystal X-ray diffraction, that in the radical anion of **15** the unpaired electron is fully delocalised between the two BMes$_2$ group and the phenylene bridge.[88]

Pyrene is a prototypical luminescent polycyclic aromatic compound which exhibits highly efficient fluorescence and an unusually long singlet lifetime.[89,90] Thus, pyrene and its derivatives have been widely employed in numerous applications. Interestingly, however, both the HOMO and the LUMO of pyrene possess a nodal plane perpendicular to the molecular plane and passing through carbon atoms 2 and 7 (Scheme 2) lying along the long molecular 2-fold axis. As such, neither electrophilic nor nucleophilic aromatic substitutions typically take place at C$_2$ or C$_7$. However, as these are the least sterically demanding sites, iridium-catalysed direct C–H borylation of pyrene with B$_2$pin$_2$ (pin = OCMe$_2$CMe$_2$O) takes place exactly at these positions, as steric effects dominate over electronic ones.[50,91–93] This has allowed us to prepare 2,7-bis(Bpin)pyrene in excellent yield and on a large scale directly from pyrene, and the product can also be readily converted to 2,7-dibromopyrene in the same pot.[94] This has opened up a new avenue in pyrene chemistry by providing an efficient, rapid route to a wide variety of desirable 2,7-pyrene derivatives *via* simple pyrene reagents which can act as formal nucleophilic or electrophilic partners, respectively, in cross-coupling reactions as well as being useful precursors for classical organic reactions.

Normally, substituting the 2- or 2,7-positions with odd-electron substituents does not cause strong communication between the substituents and pyrene, which would generate high spin radicals at room temperature.[95] This is due to the lack of mixing between the HOMO and LUMO of pyrene and those of the substituents. In fact, we have reported the electronic structure and photophysical properties of 2-(BMes$_2$) pyrene in 2011.[96] In that paper, we noted that the introduction of the strong π-acceptor BMes$_2$ groups allows mixing of the empty p$_z$-orbital of the boron with the LUMO+1 orbital of pyrene (it cannot mix with the LUMO due to its nodal properties, *vide supra*).[96] This stabilises what was the pyrene LUMO+1 sufficiently to drop it below the "pyrene-LUMO" in energy, reversing the order of these two virtual frontier orbitals. This is
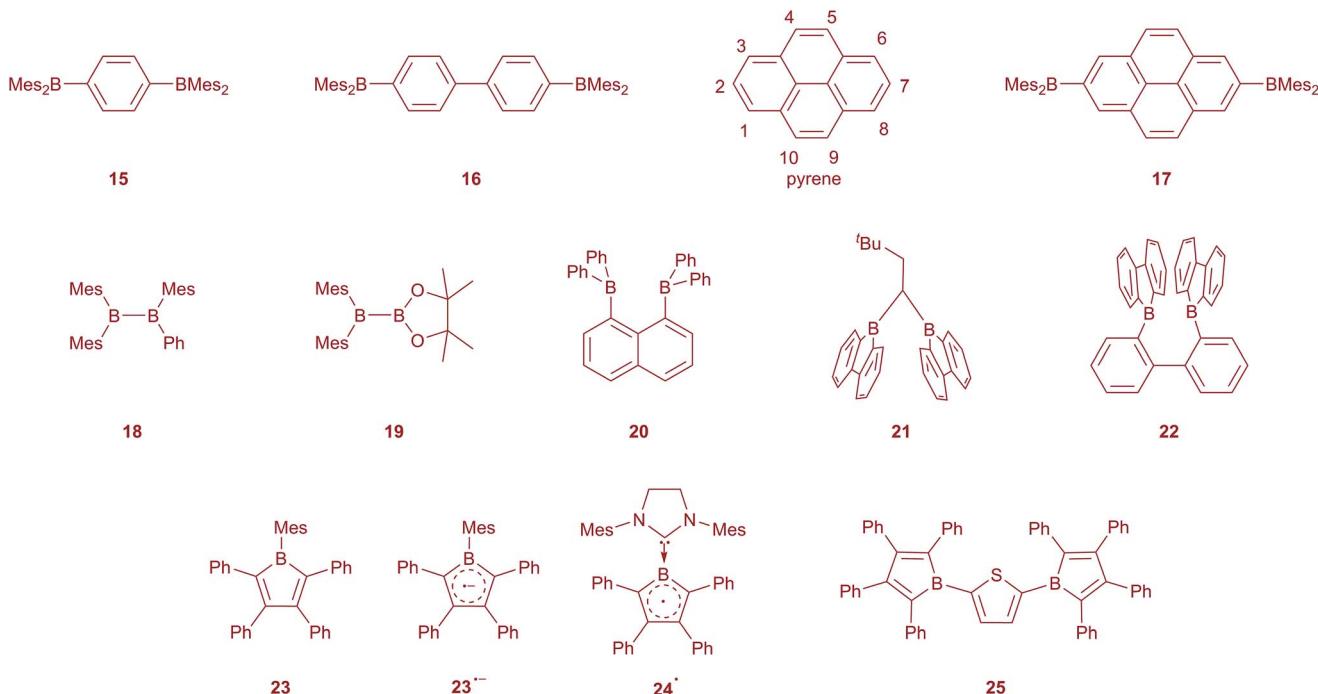
Scheme 2 3-Coordinate boron radicals and their precursors.

a particularly nice illustration of the excellent π-acceptor properties of BMes$_2$ and its ability to conjugate with organic π-systems. As a result, reduction of 2- and 2,7-BMes$_2$-substituted pyrenes would be expected to show electron delocalisation between the boron and pyrene. Thus, we prepared **17**, which can be readily reduced to its radical monoanion and its diamagnetic dianion, all of which have been characterised by single-crystal X-ray diffraction.[88] All three compounds are crystallographically centrosymmetric, and experimental and theoretical studies confirm the full delocalisation of the "extra" 1 and 2 electrons in the radical anion and the dianion over the pyrenylene bridge as well as the two boron centres. As an aside, we note that the introduction of strong π-donors (*e.g.*, R$_2$N) at the 2- or 2,7-positions allows mixing with the HOMO−1 of pyrene (recall that mixing with the pyrene HOMO is also excluded due to its nodal properties) raising it in energy above what was the pyrene HOMO.[97–100] Thus, not only can we reverse the order of LUMO and LUMO+1, but also that of HOMO and HOMO−1 by judicious choice of substituents.

Beyond the arene bridged diboranes, the formation of B–B bonds during reduction is very important for the development of bonding theory. In organic diboron compounds such as **18** and **19**,[101] one- and two-electron reductions lead to the formation of one-electron B–B π-bonds and B=B double bonds, respectively.[102–106] Recently, the formation of a one-electron σ-bond by reduction of bis(organoboron) compounds, when appropriately spatially separated, has been disclosed. In 2000, Gabbaï and co-workers reported the one-electron reduction of 1,8-bis(diphenylboryl)naphthalene (**20**), in which the two boron centres are spatially close to one another.[107] The EPR spectrum of the radical anion of **20** reveals the delocalisation of the unpaired electron between the two boron centres. DFT calculations show that there is a strong one-electron σ-bond between the two boron centres, with a slight decrease of the B–B distance and pyramidalisation of the BC$_3$ moieties. The formation of another B–B one-electron σ-bond was recently reported by Wagner *et al.*[108,109] The X-ray crystal structures of the radical anions of **21** and **22** reveal a decrease of the B–B distance compared to the neutral compounds. EPR spectroscopy and DFT calculations further confirmed the formation of a B–B one-electron σ-bond.

Another interesting boron radical system is the one-electron reduced anti-aromatic free borole **23**. The hyperfine coupling constant of its boron (3.44 G) is much smaller than that of triarylborane radical anions, indicating a much stronger delocalisation of the unpaired electron into the borole ring.[60] The change in bond length alternation confirms the delocalisation of the unpaired electron. However, trapping of the radical anion with dibenzoyl peroxide reveals that the spin is still largely populated on the boron atom. Recently, Braunschweig and co-workers reported a neutral borole radical **24˙**, in which the boron was stabilised by an NHC.[110] The EPR spectrum of this borole radical ($A(^{11}B) = 3.02$ G) shows more delocalisation of the unpaired electron within the five-membered ring compared to the aforementioned pentaryl borole radical anion.[110,111]

Interestingly, the dianion of 2,5-diborolylthiophene **25** also shows complete delocalisation of the unpaired electron. The single-crystal X-ray structure and theoretical studies of the dianion of the diborolylthiophene reveal its quinoidal structure with singlet biradical character.[112]

Boron-containing polycyclic π-systems

Polycyclic aromatic hydrocarbons (PAHs) are very important in organic electronics, for example, as hole/charge transporters in organic field-effect transistors (OFETs). Depending on the demands of the device, different heteroatoms are introduced into the π-systems, to adjust the HOMO and LUMO levels of PAHs and thus their photophysical and electrochemical properties. Although many hetero PAHs with electron-rich sulphur and nitrogen have been reported, compounds with electron-deficient boron atoms, which have empty p$_z$-orbitals,[113] have rarely been studied, although BN-containing systems have received considerable attention.[114,115] Fundamental studies of the aromatic/anti-aromatic, chemical, and photophysical properties of the fused 5-membered boroles[116–123] and the 7-membered borepin[124–128] have been discussed in the last decade, and they have recently been reviewed in detail.[28,51,113,129]

In 2012, Yamaguchi and co-workers found that planarised triarylboranes can be stabilised by structural constraints.[130,131] They found that planar triarylboron compounds **26** and **27** are stable to water and air without the steric protection usually required in the vertical direction (Scheme 3). The B–C bonds in **27** are much shorter than those in BPh$_3$, as a result of structural constraints. Compound **27** can, however, bind fluoride with a similar binding affinity as BMes$_3$, and thus is still a good Lewis acid. Interestingly, the reduction potential of **27** does not differ from that of BMes$_3$, and reduction is still reversible, indicating no dimer formation, in contrast to the unprotected BPh$_3$.[71] This demonstrates that these compounds are especially useful as potential electron-transporting materials. Indeed, the radical anion of **27** has been isolated and the EPR spectrum, X-ray structure, and DFT calculations reveal a stronger delocalisation of the spin compared to the BPh$_3$ radical anion.[132] This demonstrates more mixing of the boron p$_z$-orbital with the π*-orbitals of the aromatic system in **27**. The hyperfine coupling constants for the protons in the EPR spectrum of the radical anion of **27** are similar to those of its neutral, isoelectronic carbon radical species, demonstrating an effective delocalisation of the unpaired electron over the whole planar molecule.

Interestingly, the radical anion of **27** can change between bowl-shaped and coplanar conformations at room temperature. This suggested that there could be two conformations in the excited state of the constrained triarylborane. Recent studies reveal that photoexcited **26** and **27** both show dual emission at room temperature, with different ratios in THF and 3-methylpentane.[133] Transient absorption, fluorescence lifetime measurements, and DFT calculations reveal a higher energy planar and a lower energy bowl-shaped excited state. At room temperature, the lower energy emission dominates the fluorescence spectra. However, because the lowest energy ground state structure is planar, the planar excited state is more easily formed. The ratio of
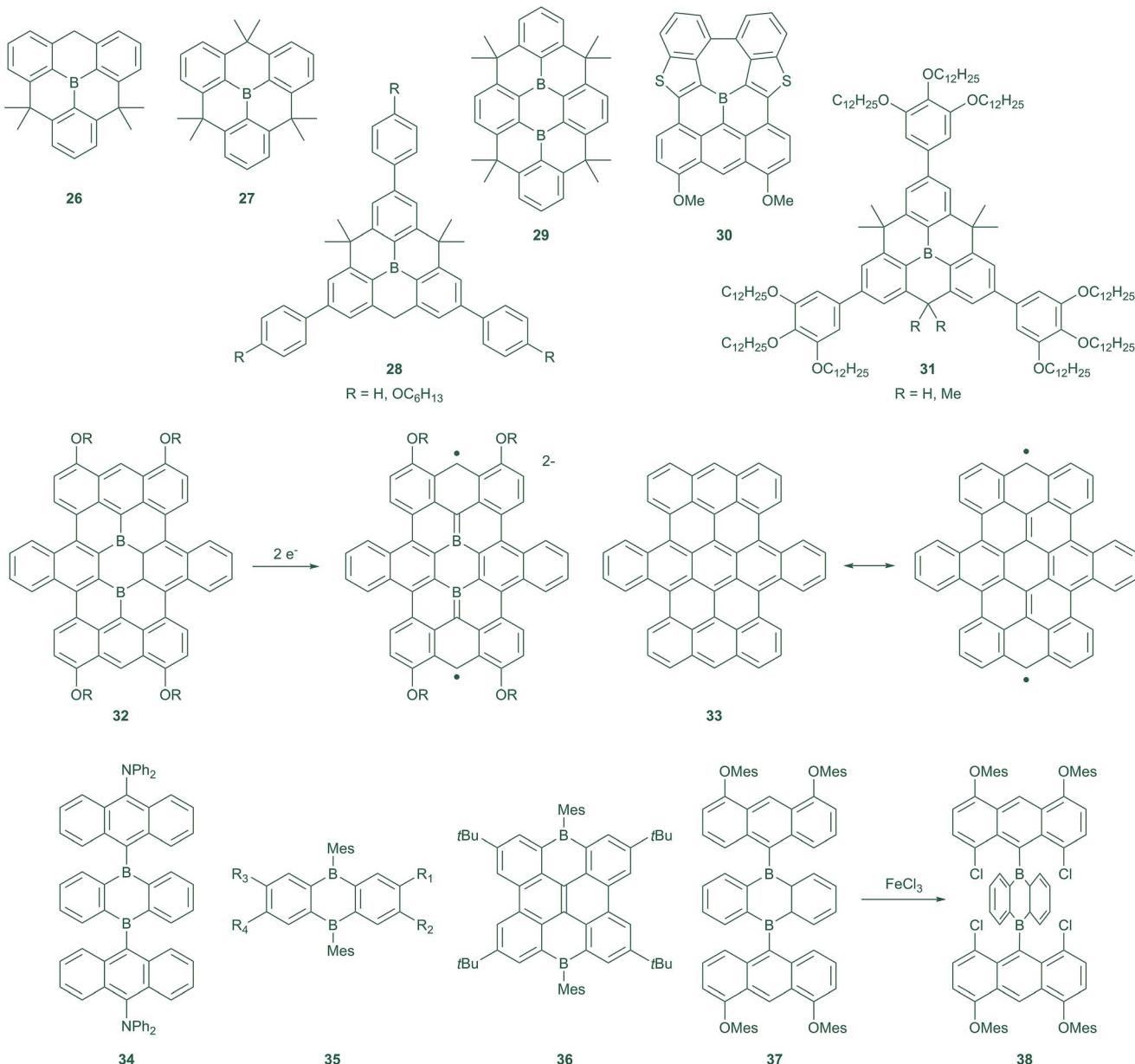
Scheme 3 Boron-containing polycyclic π-systems.

the two emission bands from the planar and the bowl-shaped excited states are thus dependent on temperature in 3-methylpentane. With decreasing temperature (in most cases, below 100 K), fluorescence is observed only from the higher energy planarised excited state. This is possibly the consequence of the fact that the activation energy for the transformation from the planarised to the bowl-shaped excited state cannot be overcome at very low temperatures. This is the case for the π-extended compound **28**.[133]

Since 2012, a considerable number of large boron-doped PAHs, such as **29–32**, have been synthesised,[45,130–140] many of which have been examined for use as electron-transporting materials,[138] liquid crystals,[139] battery electrodes,[140] *etc.* The planarisation of the triarylborane makes π–π stacking

easier, thus, *e.g.* **31** (R = H) forms discotic liquid crystals at room temperature, with an electron mobility value of *ca.* 10^{-3} cm^2 V^{-1} s^{-1}.[139]

An enlarged, boron-doped graphene **32**, containing two boron centres, has also been reported.[135,140] The X-ray crystal structure shows the molecule to be planar, except for the two side phenyl rings in the middle row, which twist out of the plane due to H–H repulsions. These compounds are very Lewis acidic and can be used as amine sensors, as binding of an amine causes fluorescence "turn-on". These compounds show two reversible reduction waves by cyclic voltammetry. While their full hydrocarbon analogue **33** has open-shell singlet character in its ground state, due to Clar's sextets rule, **32** has a closed-shell ground state. The two-electron reduced [**32**]$^{2-}$,

species isoelectronic with **33**, has a triplet ground state with a triplet–singlet energy gap of 0.45 kJ mol^{-1} (estimated by temperature-dependent EPR spectroscopy). Compound **32** (R = *n*-butyl) has also been used as a battery electrode material, instead of graphene, and it shows excellent performance.[140]

One of the most important series of PAHs, the acenes (anthracene, tetracene, pentacene, *etc.*), are not stable when there are more than six rings in a row, because the molecules tend to split into Clar's sextets, thus generating biradical character. Introducing heteroatoms could enhance the stability of large acenes.[141–144] Recently, a stable *N*-heteroacene with 13 rings in a row has been synthesised and its structure has been confirmed by single crystal X-ray diffraction.[145] However, insertion of two sp^2 boron atoms in place of the two *para* carbon atoms of a benzene ring has not been well studied. Wagner and co-workers have recently reported many compounds based on 9,10-diboraanthracene.[146–156] The 9,10-diboraanthracenes have been successfully applied as catalysts for dihydrogen activation[157] and the inverse-electron-demand Diels–Alder reaction.[158,159] When the boron atoms are protected by bulky substituents, such as 9-anthrancenyl or 2-mesityl, the diboraanthracenes **34–36** are stable in air for several hours or days, and could be isolated following chromatography on a silica column. However, degradation was observed in dilute solutions (10^{-5} M) of **37** during photophysical measurements.[160] Yamaguchi and co-workers found that the introduction of two chloro atoms at the 1,8-positions of the 9-naphthalenyl substituent could stabilise the boron *via* Cl–B interactions. This results in a weak Cl–B–Cl three-centre, four-electron bond and a nominally five-coordinate boron centre. This compound could be worked up with water and isolated following chromatography on silica without any precautions. Interestingly, the S$_0$–S$_1$ transition in **38** is simply a π–π* transition, while **37** shows an ICT transition. Indeed, the LUMOs of most of the diboraanthracene-containing compounds are located on the diboraanthracene core, while the HOMOs are located on the bulky boron substituents. The S$_0$–S$_1$ transition (absorption/emission) thus involves charge transfer from the boron substituents to the diboraanthracene core.

Anion sensors[14–17]

As mentioned above, typically only small anions such as F$^-$ and CN$^-$ can overcome the steric bulk of BMes$_2$ and attack the free p$_z$-orbital at the boron. Thus, aryl BMes$_2$ compounds can act as selective sensors for these specific anions. The absorption and emission spectra change upon the addition of F$^-$ and CN$^-$ due to interruption of the π-conjugation. Interestingly, at temperatures below 253 K, coordination of bromide ion to dibenzopnictogenborin **39** (Scheme 4) was observed by Kawashima.[161] The complexation of anions can be followed stepwise by incorporating more than one trigonal boron moiety into a compound.[162] Furthermore, ratiometric sensing is observed for compounds where the binding of an anion inhibits an energy transfer resulting in a new emission band.[163] The Wang group developed "turn-off" (emission is completely quenched

after the addition of F$^-$) and "turn-on" (emission colour changes with complexation of F$^-$) sensors by investigating the aforementioned U- and V-shaped bridges between triarylborane acceptors and triarylamine donors.[35,36] Furthermore, they reported metal complexes as "turn-on" sensors, especially Pt(II) complexes with bipy ligands with triarylborane and triarylamine substitutents,[164–166] as well as some lanthanide complexes.[167] Recently, compounds with a triarylborane as well as a dicyanovinyl acceptor were reported for colourimetric discrimination, by the naked eye, between the two interfering anions, F$^-$ and CN$^-$.[168–170]

Gabbaï and co-workers enhanced the fluoride binding affinity by incorporation of a hydrogen-bond donor near to the triarylborane,[171] as well as by using bidentate Lewis acids. For other studies of bidentate boron Lewis acids and their role in olefin polymerization catalysis, see: ref. 172. The proximity of two neutral Lewis acidic centres, one or two of them being triarylboranes, enforced by the 1,8-naphthalenediyl backbone, promotes F$^-$ binding by chelation and leads to very high binding constants.[173–175] Incorporation of one cationic binding site, *e.g.* **40**, at the bidentate ligand results in cooperative, favourable coulombic effects which enhance the binding affinity.[176,177] They also reported linear cationic compounds for fluoride sensing in water, in which the Lewis acidity at the boron is enhanced sufficiently to overcome the large hydration enthalpy of fluoride.[178,179]

Jäkle and co-workers synthesised oligomers and polymers with BMes$_2$ groups in the side-chain, and observed remarkable "turn-on" fluorescence by anion complexation, in contrast to polymers with boron in the main-chain.[180,181] Yamaguchi previously reported side-chain BMes$_2$-containing systems to be very efficient solid-state fluorescent materials.[182,183] Enhanced anion binding strength by introduction of cationic groups was also reported for the side-chain polymers.[184] Interestingly, Jäkle and co-workers also reported a polymer with BTip(OH) in the side-chain with tunable properties stimulated by F$^-$ and temperature.[185] A new approach for air- and moisture-stable polythiophenes with boron in the main chain was reported 2016.[186] The Jäkle group used Mes* or Fmes for steric protection of the boron atom against hydrolysis. Polymers of the type **41** showed unusually intense luminescence in the solid state favoured by the rigid, planar structure enforced by the bulky pendent groups.

A highly luminescent conjugated organoboron macrocycle with six Lewis acidic boron centres **42** was also used as "turn-off" sensor for F$^-$ and CN$^-$. Interestingly, reversible reductions occur at more negative potentials than those for the linear oligomeric analogue due to larger coulombic repulsion within the cyclic framework.[187,188] Comparison with the first ambipolar π-conjugated B–N macrocycle **43** shows a smaller HOMO–LUMO gap for the latter one.[189] The CN$^-$ sensing by this "π-expanded borazine" is very different from that of the respective boracyclophane **42**. Whereas the emission from CT states of the partially complexed species [**43**(CN)]$^-$ and [**43**(CN)$_2$]$_2$$^-$ remains strong, [**42**(CN)]$^-$ shows a very weakly emissive low-energy CT state. New design strategies utilising carbazoles as donors gave access to unstrained
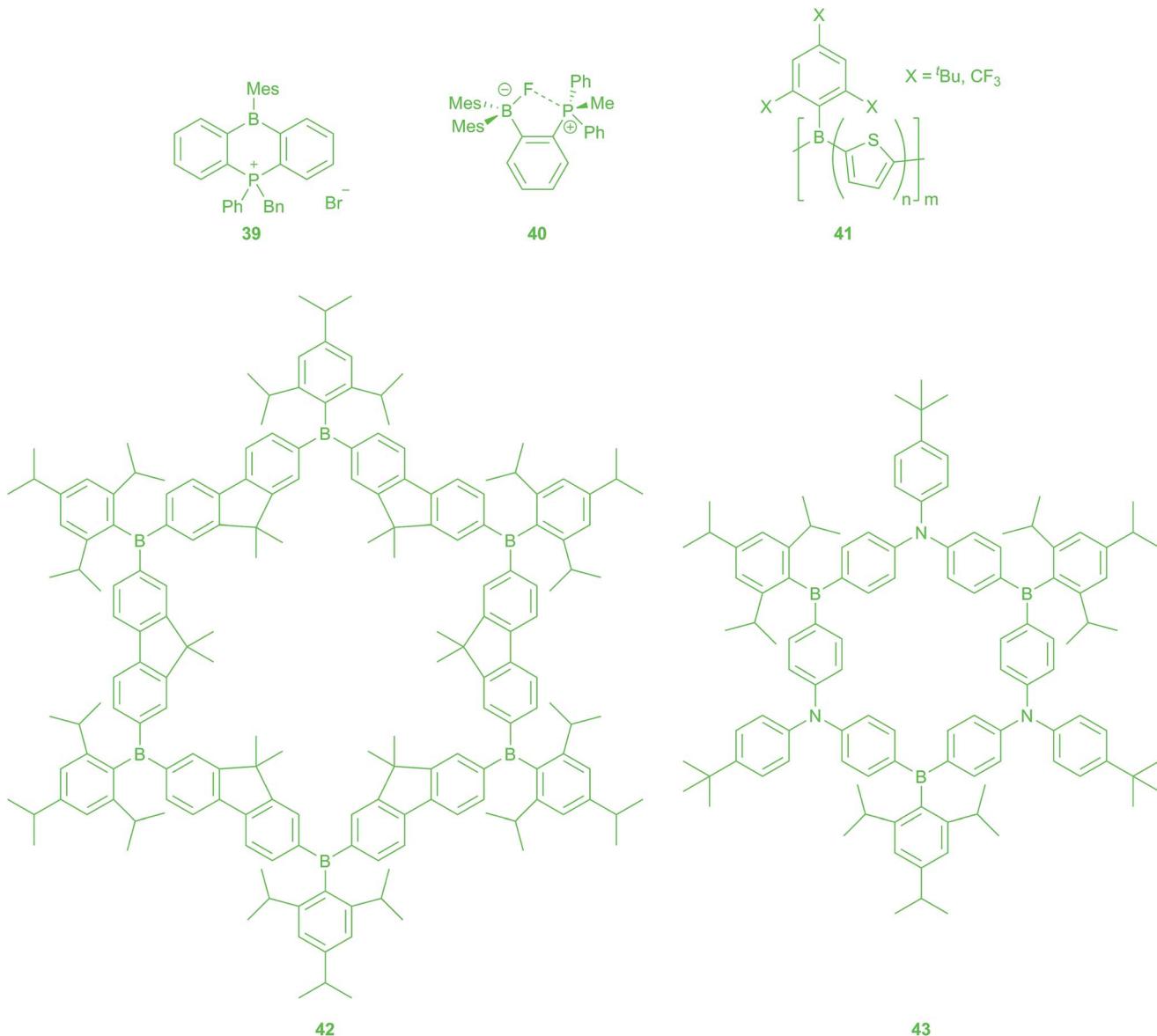
Scheme 4 Triarylboranes as anion sensors.

ambipolar macrocycles. Electronic communication between the boron centres is influenced by the π-bridge in the cycle. Complexation of CN^- changes the geometry of the macrocycle and leads to the appearance of strong CT emission bands for the bis(cyanide) complex.[190]

A completely different building block is a diboraanthracene **35** (R_1, R_4 = Br and R_2, R_3 = H or R_1, R_3 = Br and R_2, R_4 = H) (Scheme 3), which was used to prepare air- and water-stable oligomers,[153] after earlier polymers formed by hydroboration polymerisation of 9,10-dihydro-9,10-diboraanthracene were found to be sensitive towards air and moisture.[146] The new oligomers were prepared by Stille-type C–C coupling reactions with thiophenes. Polymers are not necessary, because the oligomers have already reached the limit of conjugation length and form free-standing thin films.

3-Coordinate boron in chromophores exhibiting strong two-photon absorption

Two-photon absorption (TPA) is a phenomenon in which a molecule absorbs two photons, to reach the S_n excited state.[191–194] In particular, we are interested in those cases in which the absorption of two photons occurs essentially simultaneously, via a virtual state, with each photon having less energy than the S_0–S_1 gap (S_0–S_2 gap for quadrupolar symmetry molecules). An indication of TPA is emission at higher energy than that of either of the two absorbed photons, a phenomenon known as two-photon excited fluorescence (TPEF). TPA is proportional to the square of the light intensity and the intrinsic TPA coefficient of the organic dye, the latter being known as its

two-photon cross-section (σ_2). The units of σ_2 are cm^4 per s per photon, which is too large for most TPA dyes. Thus, units of Göppert-Mayer (GM), named for the person who first predicted TPA theoretically, are used, where 1 GM is 10^{-50} cm^4 per s per photon. Compounds with $\sigma_{2,max} > 50$ GM are considered to be excellent TPA dyes. Compared to one-photon absorption, TPA has the advantages of long-wavelength absorption and squared light intensity dependence leading to excellent 3D resolution (*i.e.*, especially depth resolution at the focus of a laser beam). Thus, it can be used effectively in bio-imaging (which will be discussed below), 3D optical data storage, microfabrication, optical power-limiting, photodynamic therapy, *etc.* Thus, designing organic molecules with large σ_2 values is highly desirable. Due to the fact that the two-photon cross-section is proportional to the square of the transition dipole moment (ΔM_{01}) and the square of the dipole moment change between S_0 and S_1 ($\Delta\mu_{01}$) for dipolar molecules, for example, compounds bearing strong donors and acceptors with strong ICT transitions normally have large σ_2 values. Also important is the structural design of the chromophore. Quadrupolar and octupolar compounds have also been studied in detail and show very strong TPA, both theoretically and experimentally.[195–197] Within the context of the aforementioned electron-deficient and excitation-induced charge transfer properties of the 3-coordinate boron compounds, Fang, Liu and coworkers as well as our group have developed various dipolar, quadrupolar
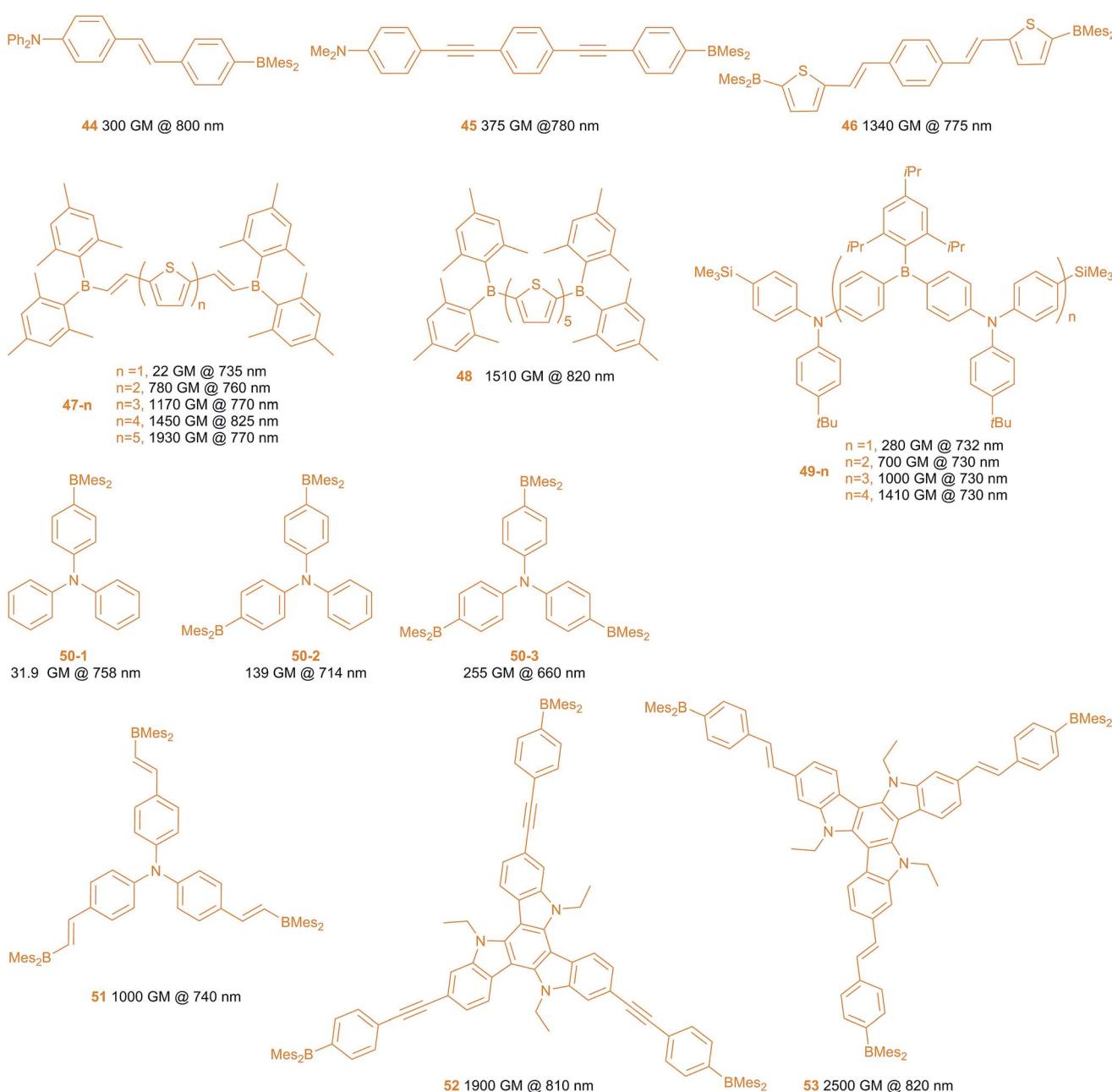
Scheme 5 3-Coordinate boron compounds with large TPA cross-sections.

and octupolar compounds featuring BMes$_2$ π-acceptor moieties, which show strong TPA and TPEF behaviour.[198–206] Scheme 5 shows several typical 3-coordinate boron compounds which have large σ$_2$ values.[198–208]

Compound **44** is a very typical dipolar compound, which has a very strong electron acceptor (BMes$_2$) and donor (NPh$_2$). The emission is strongly solvent-dependent, indicating a large dipole moment in the excited states, and thus a large Δμ$_{01}$. This compound has σ$_{2,max}$ of 300 GM at 800 nm, which is much larger than most dipolar dyes of similar size.[199] The energy of the lowest TPA-allowed transition of this compound is the same as its S$_0$–S$_1$ transition in the one-photon absorption spectrum. Thus, λ$_{max}$ for TPA = 2λ$_{max}$ for one-photon absorption. By using longer bridges between the donor and the acceptor, compound **45** shows a larger σ$_{2,max}$ of 375 GM, despite the fact that alkynyl moieties are typically not as good as alkenyl ones in the π-bridge for TPA dyes.[203]

Quadrupolar molecules have been reported to have considerably enhanced TPA compared to their dipolar counterparts.[195] Due to the fact that the parity selection rule is different for one- vs. two-photon absorption in quadrupoles, the S$_0$–S$_1$ transition is allowed for one-photon absorption but forbidden for TPA, while the S$_0$–S$_2$ transition is allowed for TPA but forbidden for one-photon absorption.[195] Thus, the energy of the TPA maximum is higher than half of the energy of the one-photon absorption. Compound **46** is a representative quadrupolar molecule.[200] The σ$_{2,max}$ of **46** is 1340 GM (at 775 nm), which is about four times that of the similar size dipolar compound **45**. Recently, we have reported a series of thiophene- and thiophene-vinyl-bridged dyes **47-n** and **48**. In the case of **47-n**, as the number of thiophenes increases from one to four, the σ$_{2,max}$ of the S$_0$–S$_2$ TPA increases from 22 to 1450 GM with a concomitant red shifting of the TPA band. However, the increase in TPA plateaus around four thienyl units. Although **47-5** displays a σ$_{2,max}$ of 1930 GM at 770 nm, it seems likely that this is due to a higher energy transition than the S$_0$–S$_2$ one. Thus, the S$_0$–S$_2$ TPA band of **47-5** only red-shifts from **47-4** without obvious enhancement. With the same conjugated bridge length, **48** shows a similar two-photon absorption band and intensity as **47-4**. More recently, Jäkle and co-workers have reported a series of quadrupolar molecules **49-n**. The σ$_2$ values increase linearly with increasing number n of the D–A subunits, but σ$_2$/n is not enhanced in these compounds with rising n.[208]

Another important series of TPA dyes are octupolar compounds. Their lowest one-photon allowed transition, S$_0$–S$_1$, is also two-photon allowed. In addition, octupolar compounds can have a much stronger, higher energy two-photon allowed band which is forbidden for one-photon transitions.[196] The mono-, bis- and tris-BMes$_2$ substituted triphenylamines have been compared recently.[207] Compound **50-1** has a two-photon excited S$_0$–S$_1$ transition band with σ$_{2,max}$ = 32 GM (758 nm). However, the two-photon absorption of this transition (S$_0$–S$_1$) in the bis-substituted compound (quasi-quadrupolar) **50-2** is very weak (σ$_2$ = 2.9 GM, 808 nm), but it has a very strong TPA band at 714 nm (σ$_{2,max}$ = 139 GM), for the S$_0$–S$_2$ transition. In comparison, the S$_0$–S$_2$ two-photon absorption band of the three-branched octupolar compound **50-3** has a large σ$_{2,max}$ of 255 GM at 660 nm. These strongly suggest that the octupolar compounds have much larger TPA cross sections. Another factor that affects the TPA cross section is the size of the
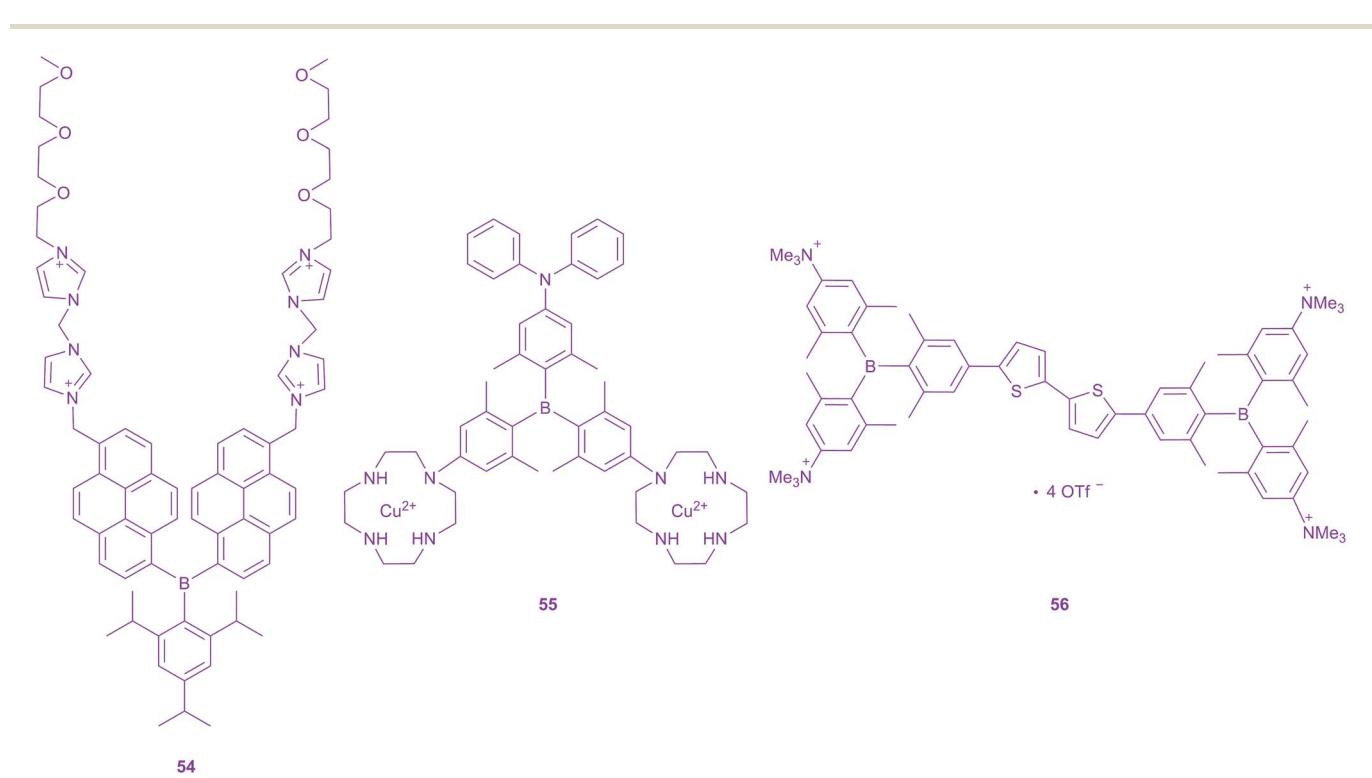
Scheme 6 Triarylboranes used as biological imaging agents.

molecule. By introduction of one more ethylene bridge, the $\sigma_{2,max}$ of **51** increases to 200 GM (880 nm) for the S_0–S_1 transition and 1000 GM (740 nm) for the S_0–S_2 transition.[203] With three nitrogen π-donors and larger π-systems, **52** (1900 GM at 810 nm) and **53** (2500 GM at 820 nm) bear the largest two-photon cross sections among the octupolar triarylboranes reported to date.[205] Due to the fact that the wavelength window of the measurement was very narrow and the TPA maximum is very close to the one-photon absorption maximum, another much stronger higher energy TPA absorption band is also possible in the shorter wavelength region.

Bioimaging

Very recently, a new application of triarylboranes in cell imaging has emerged. Yang and co-workers reported the water-soluble, non-ionic triarylborane **54**, incorporating polyethylene glycol chains as the hydrophilic groups, as an efficient fluorescence indicator for ATP in the cytoplasm and cell membrane (Scheme 6).[209] Furthermore, they could sense hydrogen sulphide release in mitochondria with another water-soluble triarylborane **55**.[210] By addition of hydrogen sulphide, **55** acts as a two-photon excited "turn-on" fluorescence sensor as the emission is quenched in the absence of H₂S. They demonstrate cell-membrane permeability and a preferential distribution in mitochondria. They utilised their chromophore for fluorescence lifetime imaging and TPEF imaging of live cells and found moderate TPA cross sections with a maximum of 60 GM in DMSO. Very recently, we reported a quadrupolar tetracationic chromophore with triarylboranes as the acceptors **56**.[211] This compound is found to be water-soluble, still very emissive in water ($\Phi_f = 0.10$) and exhibits a large TPA cross section of 268 GM in water at 800 nm. Furthermore, it localises in the mitochondria and is non-toxic to cells in the required concentration range. Therefore, we demonstrated its use as a TPEF imaging agent for mitochondrial microscopy.[211]

OLEDs

Organic light-emitting diodes (OLEDs) are very important in lighting applications and in flat panel display screens with high energy efficiency and resolution. In the organic emitting layer of OLEDs, the recombination of holes and electrons populates the excited states of the molecules. These excited molecules then emit photons and generate light. During the formation of excitons, the singlet : triplet ratio is expected to be 1 : 3. Thus, there should be two ways of emitting: fluorescence and phosphorescence to the singlet ground state. In an organic molecule without any heavy atom, fluorescence is usually very fast and the lack of spin–orbit coupling leads to slower, inefficient inter-system crossing between singlet and triplet manifolds. Thus, phosphorescence, which would arise from the T_1–S_0 transition, is forbidden because of the spin-selection rule. Traditional OLEDs using pure organic boron-containing materials as the emitting layer present very low external quantum efficiencies (η_{EQE}) because only a quarter at most of the electrochemically generated excitons can be converted to light. After introducing

3-coordinate boranes into OLEDs as very efficient electron transporters,[86,87] Shirota and co-workers examined several pure organic boranes for use as the electroluminescent layer.[212–214] Many pure organic boranes have been reported by Wang and others for use in electroluminescent layers, mostly based on fluorescence.[215–219] However, their η_{EQE} are limited to a few percent.

One way of utilising the triplet excitons is to introduce heavy atoms into the system to relax the spin selection rule and
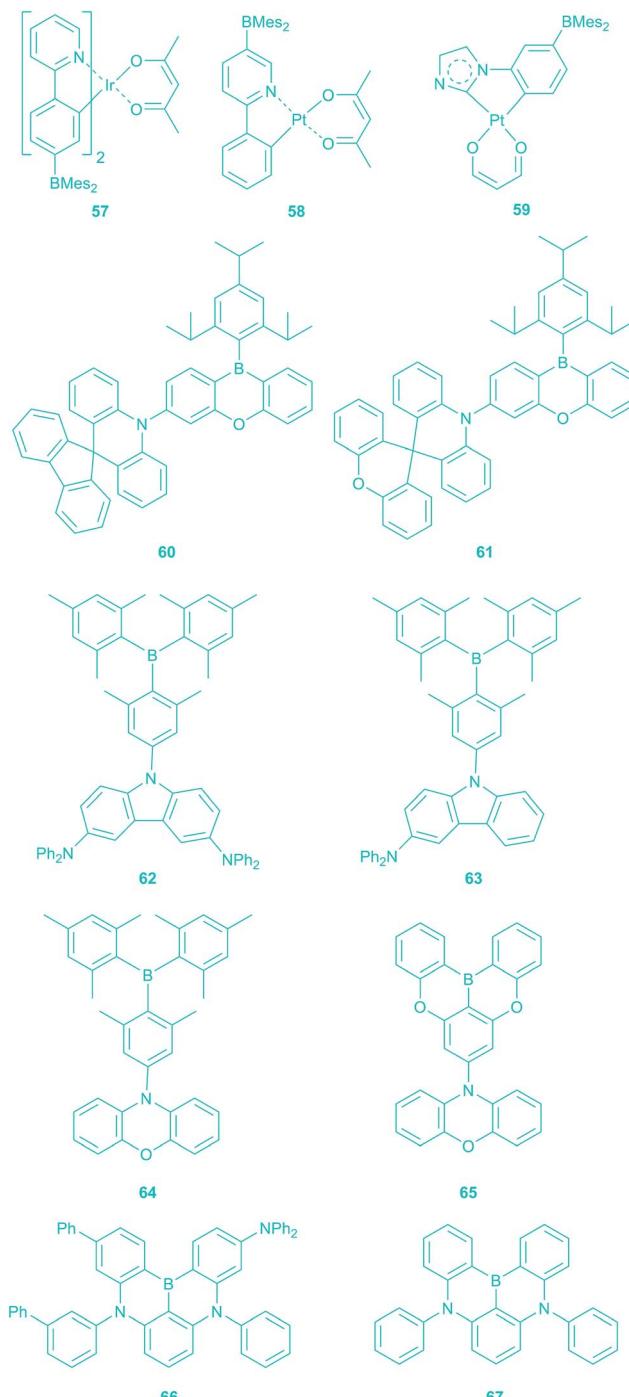
Scheme 7 Triarylboranes used in OLEDs.

facilitate the T_1–S_0 transition because of their strong spin–orbital coupling. Due to the fact that the energy of the S_1 state is higher than that of the T_1 state in most cases, the S_1 state can relax to the T_1 state *via* intersystem crossing, often within femtoseconds. Thus, in theory, the excited state could be populated to give 100% triplets, and the external quantum efficiency of phosphorescent OLEDs (PHOLEDs) could be much higher than that of fluorescent OLEDs. Several boron-containing transition metal complexes have been designed as PHOLED emitters with high η_{EQE}. In collaboration with Wong and co-workers, we have reported a red-emitting BMes$_2$-substituted Ir-2-phenylpyridine complex (**57**) with a high η_{EQE} of 9.4%.[220] The external quantum efficiency of a Pt(II) complex (**58**) reported by Wang and co-workers reached 21%.[221–224] However, most of the organometallic PHOLEDs emit at lower energy in the colour range from yellow to red.[17] The design of PHOLEDs with a larger band-gap is challenging. By employing BMes$_2$ as a substituent to decrease the energy of the HOMO of phenylimidazole as the ligand (compound **59**), Wang and co-workers reported high energy blue emitting OLEDs with high η_{EQE}.[225]

Most PHOLEDs utilize expensive third-row transition metals to achieve efficient phosphorescence. However, another way of making use of the triplet state was recently reported by Adachi and co-workers.[226] In some highly twisted compounds, the triplet state energy is not much lower than that of the singlet excited state. This is due to the lack of efficient spatial overlap of the HOMO and LUMO as a result of the large dihedral angle between the donor and acceptor moieties. Thus, it appears possible for the singlet excited state to be repopulated from the triplet state at room temperature by thermally activated reverse intersystem-crossing (RISC) and then it can relax to the ground state by fluorescence. This process is termed thermally-activated delayed fluorescence (TADF). The speed and efficiency of TADF are affected by the temperature and the S_1–T_1 gap. Indeed, Marder and Wang have both reported long-lived emissions, presumably from the triplet excited states of triarylboranes, including **6** (R = *tert*-butyl).[47,227] The energy difference between the singlet and triplet excited state (as indicated by the emission spectra measured at 77 K) of **6** (R = *tert*-butyl) is very small.

In the last one- and a half years, Hatakeyama, Adachi, and Kaji reported TADF-based OLEDs which use twisted 3-coordinate organoboranes (**60–67**) as emitters.[228–231] The highest η_{EQE} of the first TADF-based OLED device using triarylborane **61** as the luminescence layer was *ca.* 20%, which is comparable to the most efficient PHOLEDs (Scheme 7).[229] The blue emitters **62** and **64** show the highest η_{EQE} (21.6% and 22.8%) among the TADF-based OLEDs. The recent interest in 3-coordinate organoboranes as the emitting layer of OLEDs again demonstrates the wide array of applications of triarylboranes in material science.

Conclusions and perspectives

Studies of the synthesis and applications of 3-coordinate boron compounds in material science have increased dramatically in the last few decades. Triarylboranes are efficient acceptors in

chromophores with strong absorptivities and high fluorescence quantum yields. The process of exciting a D–π–boron chromophore results in a charge transfer from the donor to the electron-deficient 3-coordinate boron group. The 3-coordinate boron atom can also lower the energy of an unoccupied orbital of a molecule by mixing the empty boron p_z-orbital with the unoccupied molecule orbital, thus generating a lower-lying excited state and a red-shifted emission. When the empty p_z-orbital mixes with a higher unoccupied molecular orbital efficiently, such as in the case of pyrene derivative **17**, a switching of the energy ordering of the unoccupied molecular orbitals can occur. By introducing stronger electron-withdrawing substituents in B-aryl$_2$ groups, such as changing Mes to Fmes or other electron-acceptor, the LUMO of the molecule is further lowered, the ICT is enhanced, and the fluorescence is further red-shifted. It should be noted that the strong ICT of these D–π–A triarylboranes makes them efficient TPA materials. Bearing in mind the red-shifted emissions and high fluorescence quantum yields of triarylboranes, these compounds can be applied as two-photon excited fluorescence sensors in bioimaging as long as they are water-soluble and water-stable. Triarylboranes modified to be water-soluble and water-stable, red-emissive and strongly two-photon absorbing could be very interesting for bioimaging in the future.

Due to the empty p_z-orbital, the 3-coordinate boron compounds are also efficient electron and spin carriers. Thus, such compounds can be used as electron-transporting materials both in devices and liquid crystals. For this aspect, planarised, constrained triarylboranes are highly promising as the intermolecular stacking is easier than for the sterically-protected triarylboranes. Although acenes and azaacenes have been studied as semiconductors for many years, the study of boraacences has just begun. Exchanging some of the sp^2 carbons by boron atoms could stabilise the LUMO of acenes and strongly enhance their electron-transporting properties. The spin-carrier character of the 3-coordinate boron also makes boron radicals intrinsic magnetic materials.

Although the application of triarylboranes as TADF emitters is a very new field, the external quantum efficiencies reported for several devices using new triarylboranes are the highest among the TADF-based OLEDs. One can anticipate that this area will attract much attention as TADF emitters based on triarylboranes could be employed in the next generation of OLEDs. Clearly, 3-coordinate boron chemistry has a bright future!

Acknowledgements

References

1 G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126.

2 D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032.

3 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881.

4 D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625.

5 D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441.

6 D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76.

7 D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306–316.

8 G. Erker and D. W. Stephan, *Frustrated Lewis Pairs I: Uncovering and Understanding*, Springer-Verlag, Heidelberg, Berlin, 2013.

9 D. W. Stephan and G. Erker, *Frustrated Lewis Pairs II: Expanding the Scope Preface*, Springer-Verlag, Heidelberg, Berlin, 2013.

10 S. Mukherjee and P. Thilagar, *J. Chem. Sci.*, 2015, **127**, 241–255.

11 S. Mukherjee and P. Thilagar, *Resonance*, 2014, **19**, 1017–1027.

12 P. J. Grisdale, J. L. Williams, M. Glogowski and B. Babb, *J. Org. Chem.*, 1971, **36**, 544–549.

13 J. Doty, B. Babb, P. Grisdale, M. Glogowski and J. Williams, *J. Organomet. Chem.*, 1972, **38**, 229–236.

14 T. W. Hudnall, C. W. Chiu and F. P. Gabbaï, *Acc. Chem. Res.*, 2009, **42**, 388–397.

15 C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, *Chem. Rev.*, 2010, **110**, 3958–3984.

16 F. Jäkle, *Chem. Rev.*, 2010, **110**, 3985–4022.

17 Z. M. Hudson and S. Wang, *Acc. Chem. Res.*, 2009, **42**, 1584–1596.

18 Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz and L.-T. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1489–1492.

19 M. Lequan, R. M. Lequan and K. C. Ching, *J. Mater. Chem.*, 1991, **1**, 997–999.

20 M. Lequan, R. M. Lequan, K. C. Ching, M. Barzoukas, A. Fort, H. Lahoucine, G. Bravic, D. Chasseau and J. Gaultier, *J. Mater. Chem.*, 1992, **2**, 719–725.

21 M. Lequan, R. M. Lequan, K. Chane-Ching, A.-C. Callier, M. Barzoukas and A. Fort, *Adv. Mater. Opt. Electron.*, 1992, **1**, 243–247.

22 C. Branger, M. Lequan, R. M. Lequan, M. Barzoukas and A. Fort, *J. Mater. Chem.*, 1996, **6**, 555–558.

23 Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams and L.-T. Cheng, *J. Organomet. Chem.*, 1993, **449**, 27–37.

24 Z. Yuan, C. D. Entwistle, J. C. Collings, D. Albesa-Jové, A. S. Batsanov, J. A. Howard, N. J. Taylor, H. M. Kaiser, D. E. Kaufmann, S. Y. Poon, W. Y. Wong, C. Jardin, S. Fathallah, A. Boucekkine, J. F. Halet and T. B. Marder, *Chem.–Eur. J.*, 2006, **12**, 2758–2771.

25 Z. Yuan, N. J. Taylor, R. Ramachandran and T. B. Marder, *Appl. Organomet. Chem.*, 1996, **10**, 305–316.

26 C. D. Entwistle and T. B. Marder, *Angew. Chem., Int. Ed.*, 2002, **41**, 2927–2931.

27 C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574–4585.

28 S. Yamaguchi and A. Wakamiya, *Pure Appl. Chem.*, 2006, **78**, 1413–1424.

29 F. Jäkle, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, ed. R. B. King, John Wiley & Sons, Ltd, Chichester, UK, 2nd edn, 2011.

30 F. Jäkle, *Coord. Chem. Rev.*, 2006, **250**, 1107–1121.

31 M. Elbing and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2008, **47**, 834–838.

32 Y. Ren and F. Jäkle, *Dalton Trans.*, 2016, **45**, 13996–14007.

33 R. Stahl, C. Lambert, C. Kaiser, R. Wortmann and R. Jakober, *Chem.–Eur. J.*, 2006, **12**, 2358–2370.

34 U. Megerle, F. Selmaier, C. Lambert, E. Riedle and S. Lochbrunner, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6245–6251.

35 X. Y. Liu, D. R. Bai and S. Wang, *Angew. Chem., Int. Ed.*, 2006, **45**, 5475–5478.

36 D. R. Bai, X. Y. Liu and S. Wang, *Chem.–Eur. J.*, 2007, **13**, 5713–5723.

37 H. Pan, G. L. Fu, Y. H. Zhao and C. H. Zhao, *Org. Lett.*, 2011, **13**, 4830–4833.

38 M. Steeger and C. Lambert, *Chem.–Eur. J.*, 2012, **18**, 11937–11948.

39 T. Taniguchi, J. Wang, S. Irle and S. Yamaguchi, *Dalton Trans.*, 2013, **42**, 620–624.

40 A. Proń, M. Baumgarten and K. Müllen, *Org. Lett.*, 2010, **12**, 4236–4239.

41 S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder and A. L. Thompson, *Dalton Trans.*, 2003, **32**, 4395–4405.

42 L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H.-G. Stammler and B. Neumann, *Dalton Trans.*, 2009, **38**, 1339.

43 Y. Qin, G. Cheng, A. Sundararaman and F. Jäkle, *J. Am. Chem. Soc.*, 2002, **124**, 12672–12673.

44 A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *J. Am. Chem. Soc.*, 2006, **128**, 16554–16565.

45 J. Wang, Y. Wang, T. Taniguchi, S. Yamaguchi and S. Irle, *J. Phys. Chem. A*, 2012, **116**, 1151–1158.

46 P. Sudhakar, S. Mukherjee and P. Thilagar, *Organometallics*, 2013, **32**, 3129–3133.

47 Z. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Steffen, L. E. Longobardi, D. W. Stephan, C. Lambert and T. B. Marder, *Chem. Sci.*, 2015, **6**, 308–321.

48 Z. Lu, Z. Cheng, Z. Chen, L. Weng, Z. H. Li and H. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 12227–12231.

49 Z. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Eichhorn, A. Steffen, Y. Wang and T. B. Marder, *Chem.–Eur. J.*, 2015, **21**, 177–190.

50 I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890–931.

51 A. Wakamiya and S. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1357–1377.

52 X. Yin, J. Chen, R. A. Lalancette, T. B. Marder and F. Jäkle, *Angew. Chem., Int. Ed.*, 2014, **53**, 9761–9765.

53 A. Steffen, R. M. Ward, W. D. Jones and T. B. Marder, *Coord. Chem. Rev.*, 2010, **254**, 1950–1976.

54 H. Braunschweig and I. Krummenacher, in *Organic Redox Systems: Synthesis, Properties, and Applications*, ed. T. Nishinaga, John Wiley & Sons, Inc, Hoboken, NJ, 2016, pp. 503–522.

55 H. Braunschweig, I. Krummenacher and J. Wahler, *Adv. Organomet. Chem.*, 2013, **61**, 1–53.

56 H. Braunschweig and T. Kupfer, *Chem. Commun.*, 2011, **47**, 10903–10914.

57 Z. Zhang, Z. Wang, M. Haehnel, A. Eichhorn, R. M. Edkins, A. Steffen, A. Krueger, Z. Lin and T. B. Marder, *Chem. Commun.*, 2016, **52**, 9707–9710.

58 Z. Zhang, R. M. Edkins, M. Haehnel, M. Wehner, A. Eichhorn, L. Mailänder, M. Meier, J. Brand, F. Brede, K. Müller-Buschbaum, H. Braunschweig and T. B. Marder, *Chem. Sci.*, 2015, **6**, 5922–5927.

59 Z. Xi, *Acc. Chem. Res.*, 2010, **43**, 1342–1351.

60 H. Braunschweig, V. Dyakonov, J. O. C. Jimenez-Halla, K. Kraft, I. Krummenacher, K. Radacki, A. Sperlich and J. Wahler, *Angew. Chem., Int. Ed.*, 2012, **51**, 2977–2980.

61 K. Schickedanz, T. Trageser, M. Bolte, H. W. Lerner and M. Wagner, *Chem. Commun.*, 2015, **51**, 15808–15810.

62 L. Weber, V. Werner, M. A. Fox, T. B. Marder, S. Schwedler, A. Brockhinke, H. G. Stammler and B. Neumann, *Dalton Trans.*, 2009, **38**, 2823–2831.

63 L. Weber, D. Eickhoff, T. B. Marder, M. A. Fox, P. J. Low, A. D. Dwyer, D. J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stammler and B. Neumann, *Chem.–Eur. J.*, 2012, **18**, 1369–1382.

64 L. Weber, D. Eickhoff, J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann and M. A. Fox, *Dalton Trans.*, 2012, **41**, 10328–10346.

65 L. Weber, J. Halama, L. Böhling, A. Chrostowska, A. Dargelos, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2011, **2011**, 3091–3101.

66 P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer and A. Vargas, *Angew. Chem., Int. Ed.*, 2012, **51**, 9931–9934.

67 H. Braunschweig, A. Damme, R. D. Dewhurst and A. Vargas, *Nat. Chem.*, 2013, **5**, 115–121.

68 J. E. Leffler, G. Watts, T. Tanigaki, E. Dolan and D. S. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 6825–6830.

69 H. C. Brown and V. H. Dodson, *J. Am. Chem. Soc.*, 1957, **79**, 2302–2306.

70 S. I. Weissman and H. v. Willigen, *J. Am. Chem. Soc.*, 1965, **87**, 2285–2286.

71 T. J. DuPont and J. L. Mills, *J. Am. Chem. Soc.*, 1975, **97**, 6375–6382.

72 M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1986, **108**, 4235–4236.

73 P. Y. Feng, Y. H. Liu, T. S. Lin, S. M. Peng and C. W. Chiu, *Angew. Chem., Int. Ed.*, 2014, **53**, 6237–6240.

74 Y. Zheng, J. Xiong, Y. Sun, X. Pan and J. Wu, *Angew. Chem., Int. Ed.*, 2015, **54**, 12933–12936.

75 L. E. Longobardi, L. Liu, S. Grimme and D. W. Stephan, *J. Am. Chem. Soc.*, 2016, **138**, 2500–2503.

76 C. W. Chiu and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2007, **46**, 1723–1725.

77 D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou and G. Bertrand, *Science*, 2002, **295**, 1880–1881.

78 W. Kaim and A. Schulz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 615–616.

79 A. Schulz and W. Kaim, *Chem. Ber.*, 1989, **122**, 1863–1868.

80 A. Lichtblau, W. Kaim, A. Schulz and T. Stahl, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1497–1501.

81 J. Fiedler, S. Zališ, A. Klein, F. M. Hornung and W. Kaim, *Inorg. Chem.*, 1996, **35**, 3039–3043.

82 S. Záliš and W. Kaim, *Main Group Chem.*, 2007, **5**, 267–276.

83 W. Kaim, N. S. Hosmane, S. Záliš, J. A. Maguire and W. N. Lipscomb, *Angew. Chem., Int. Ed.*, 2009, **48**, 5082–5091.

84 A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556–4573.

85 P. J. Low, M. A. J. Paterson, H. Puschmann, A. E. Goeta, J. A. K. Howard, C. Lambert, J. C. Cherryman, D. R. Tackley, S. Leeming and B. Brown, *Chem.–Eur. J.*, 2004, **10**, 83–91.

86 T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, 1998, **120**, 9714–9715.

87 M. Kinoshita and Y. Shirota, *Chem. Lett.*, 2001, 614–615.

88 L. Ji, R. M. Edkins, A. Lorbach, I. Krummenacher, C. Brückner, A. Eichhorn, H. Braunschweig, B. Engels, P. J. Low and T. B. Marder, *J. Am. Chem. Soc.*, 2015, **137**, 6750–6753.

89 T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, 2011, **111**, 7260–7314.

90 J. M. Casas-Solvas, J. D. Howgego and A. P. Davis, *Org. Biomol. Chem.*, 2014, **12**, 212–232.

91 D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder and R. N. Perutz, *Chem. Commun.*, 2005, **41**, 2172–2174.

92 A. S. Batsanov, J. A. K. Howard, D. Albesa-Jové, J. C. Collings, Z. Liu, I. A. I. Mkhalid, M.-H. Thibault and T. B. Marder, *Cryst. Growth Des.*, 2012, **12**, 2794–2802.

93 Z. Liu, Y. Wang, Y. Chen, J. Liu, Q. Fang, C. Kleeberg and T. B. Marder, *J. Org. Chem.*, 2012, **77**, 7124–7128.

94 A. G. Crawford, Z. Liu, I. A. I. Mkhalid, M.-H. Thibault, N. Schwarz, G. Alcaraz, A. Steffen, J. C. Collings, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Chem.–Eur. J.*, 2012, **18**, 5022–5035.

95 M. Kreyenschmidt, M. Baumgarten, N. Tyutyulkov and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1957–1959.

96 A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L.-O. Pålsson, D. J. Tozer and T. B. Marder, *J. Am. Chem. Soc.*, 2011, **133**, 13349–13362.

97 L. Ji, A. Lorbach, R. M. Edkins and T. B. Marder, *J. Org. Chem.*, 2015, **80**, 5658–5665.

98 R. Kurata, K. Tanaka and A. Ito, *J. Org. Chem.*, 2016, **81**, 137–145.

99 B. R. Kaafarani, C. Risko, T. H. El-Assaad, A. a. O. El-Ballouli, S. R. Marder and S. Barlow, *J. Phys. Chem. C*, 2016, **120**, 3156–3166.

100 B. R. Kaafarani, A. a. O. El-Ballouli, R. Trattnig, A. Fonari, S. Sax, B. Wex, C. Risko, R. S. Khnayzer, S. Barlow,

D. Patra, T. V. Timofeeva, E. J. W. List, J.-L. Brédas and S. R. Marder, *J. Mater. Chem. C*, 2013, **1**, 1638.

101 E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott and T. B. Marder, *Chem. Rev.*, 2016, **116**, 9091–9161.

102 W. J. Grigsby and P. P. Power, *Chem. Commun.*, 1996, **32**, 2235–2236.

103 W. J. Grigsby and P. Power, *Chem.–Eur. J.*, 1997, **3**, 368–375.

104 H. Asakawa, K.-H. Lee, K. Furukawa, Z. Lin and M. Yamashita, *Chem.–Eur. J.*, 2015, **21**, 4267–4271.

105 A. Moezzi, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1992, **114**, 2715–2717.

106 T. Kaese, A. Hübner, M. Bolte, H.-W. Lerner and M. Wagner, *J. Am. Chem. Soc.*, 2016, **138**, 6224–6233.

107 J. D. Hoefelmeyer and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2000, **122**, 9054–9055.

108 A. Hubner, A. M. Diehl, M. Diefenbach, B. Endeward, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2014, **53**, 4832–4835.

109 A. Hubner, T. Kaese, M. Diefenbach, B. Endeward, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *J. Am. Chem. Soc.*, 2015, **137**, 3705–3714.

110 R. Bertermann, H. Braunschweig, R. D. Dewhurst, C. Hörl, T. Kramer and I. Krummenacher, *Angew. Chem., Int. Ed.*, 2014, **53**, 5453–5457.

111 P. Bissinger, H. Braunschweig, A. Damme, I. Krummenacher, A. K. Phukan, K. Radacki and S. Sugawara, *Angew. Chem., Int. Ed.*, 2014, **53**, 7360–7363.

112 H. Braunschweig, V. Dyakonov, B. Engels, Z. Falk, C. Hörl, J. H. Klein, T. Kramer, H. Kraus, I. Krummenacher, C. Lambert and C. Walter, *Angew. Chem., Int. Ed.*, 2013, **52**, 12852–12855.

113 A. Escande and M. J. Ingleson, *Chem. Commun.*, 2015, **51**, 6257–6274.

114 M. J. Bosdet and W. E. Piers, *Can. J. Chem.*, 2009, **87**, 8–29.

115 Z. Liu and T. B. Marder, *Angew. Chem., Int. Ed.*, 2008, **47**, 242–244.

116 A. Hubner, M. Diefenbach, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2012, **51**, 12514–12518.

117 A. Hubner, Z. W. Qu, U. Englert, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *J. Am. Chem. Soc.*, 2011, **133**, 4596–4609.

118 S. Yamaguchi, T. Shirasaka, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2002, **124**, 8816–8817.

119 A. Wakamiya, K. Mishima, K. Ekawa and S. Yamaguchi, *Chem. Commun.*, 2008, **44**, 579–581.

120 A. Iida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2011, **133**, 6952–6955.

121 A. Iida, A. Sekioka and S. Yamaguchi, *Chem. Sci.*, 2012, **3**, 1461.

122 D. M. Chen, Q. Qin, Z. B. Sun, Q. Peng and C. H. Zhao, *Chem. Commun.*, 2014, **50**, 782–784.

123 M. F. Smith, S. J. Cassidy, I. A. Adams, M. Vasiliu, D. L. Gerlach, D. A. Dixon and P. A. Rupar, *Organometallics*, 2016, **35**, 3182–3191.

124 A. Caruso Jr, M. A. Siegler and J. D. Tovar, *Angew. Chem., Int. Ed.*, 2010, **49**, 4213–4217.

125 A. Caruso Jr and J. D. Tovar, *J. Org. Chem.*, 2011, **76**, 2227–2239.

126 A. Caruso Jr and J. D. Tovar, *Org. Lett.*, 2011, **13**, 3106–3109.

127 D. R. Levine, A. Caruso Jr, M. A. Siegler and J. D. Tovar, *Chem. Commun.*, 2012, **48**, 6256–6258.

128 D. R. Levine, M. A. Siegler and J. D. Tovar, *J. Am. Chem. Soc.*, 2014, **136**, 7132–7139.

129 R. E. Messersmith and J. D. Tovar, *J. Phys. Org. Chem.*, 2015, **28**, 378–387.

130 S. Saito, K. Matsuo and S. Yamaguchi, *J. Am. Chem. Soc.*, 2012, **134**, 9130–9133.

131 Z. Zhou, A. Wakamiya, T. Kushida and S. Yamaguchi, *J. Am. Chem. Soc.*, 2012, **134**, 4529–4532.

132 T. Kushida and S. Yamaguchi, *Organometallics*, 2013, **32**, 6654–6657.

133 T. Kushida, C. Camacho, A. Shuto, S. Irle, M. Muramatsu, T. Katayama, S. Ito, Y. Nagasawa, H. Miyasaka, E. Sakuda, N. Kitamura, Z. Zhou, A. Wakamiya and S. Yamaguchi, *Chem. Sci.*, 2014, **5**, 1296–1304.

134 J. F. Araneda, B. Neue and W. E. Piers, *Angew. Chem., Int. Ed.*, 2012, **51**, 9977–9979.

135 C. Dou, S. Saito, K. Matsuo, I. Hisaki and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2012, **51**, 12206–12210.

136 T. Kushida, Z. Zhou, A. Wakamiya and S. Yamaguchi, *Chem. Commun.*, 2012, **48**, 10715–10717.

137 T. Kushida and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2013, **52**, 8054–8058.

138 A. Shuto, T. Kushida, T. Fukushima, H. Kaji and S. Yamaguchi, *Org. Lett.*, 2013, **15**, 6234–6237.

139 T. Kushida, A. Shuto, M. Yoshio, T. Kato and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2015, **54**, 6922–6925.

140 S. Osumi, S. Saito, C. Dou, K. Matsuo, K. Kume, H. Yoshikawa, K. Awaga and S. Yamaguchi, *Chem. Sci.*, 2016, **7**, 219–227.

141 U. H. F. Bunz, *Acc. Chem. Res.*, 2015, **48**, 1676–1686.

142 U. H. F. Bunz, J. U. Engelhart, B. D. Lindner and M. Schaffroth, *Angew. Chem., Int. Ed.*, 2013, **52**, 3810–3821.

143 U. H. F. Bunz, *Chem.–Eur. J.*, 2009, **15**, 6780–6789.

144 L. Ji, M. Haehnel, I. Krummenacher, P. Biegger, F. L. Geyer, O. Tverskoy, M. Schaffroth, J. Han, A. Dreuw, T. B. Marder and U. H. Bunz, *Angew. Chem., Int. Ed.*, 2016, **55**, 10498–10501.

145 A. H. Endres, M. Schaffroth, F. Paulus, H. Reiss, H. Wadepohl, F. Rominger, R. Krämer and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2016, **138**, 1792–1795.

146 A. Lorbach, M. Bolte, H. Li, H. W. Lerner, M. C. Holthausen, F. Jäkle and M. Wagner, *Angew. Chem., Int. Ed.*, 2009, **48**, 4584–4588.

147 E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H. W. Lerner and M. Wagner, *Chem.–Eur. J.*, 2011, **17**, 12696–12705.

148 C. Hoffend, F. Schodel, M. Bolte, H. W. Lerner and M. Wagner, *Chem.–Eur. J.*, 2012, **18**, 15394–15405.

149 E. Januszewski, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2012, **31**, 8420–8425.

150 C. Hoffend, M. Diefenbach, E. Januszewski, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *Dalton Trans.*, 2013, **42**, 13826–13837.

151 C. Hoffend, K. Schickedanz, M. Bolte, H.-W. Lerner and M. Wagner, *Tetrahedron*, 2013, **69**, 7073–7081.

152 C. Reus, S. Weidlich, M. Bolte, H. W. Lerner and M. Wagner, *J. Am. Chem. Soc.*, 2013, **135**, 12892–12907.

153 C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle and M. Wagner, *Macromolecules*, 2014, **47**, 3727–3735.

154 V. M. Hertz, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2015, **54**, 8800–8804.

155 V. M. Hertz, H. W. Lerner and M. Wagner, *Org. Lett.*, 2015, **17**, 5240–5243.

156 V. M. Hertz, J. G. Massoth, M. Bolte, H. W. Lerner and M. Wagner, *Chem.–Eur. J.*, 2016, **22**, 13181–13188.

157 E. von Grotthuss, M. Diefenbach, M. Bolte, H. W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem., Int. Ed.*, 2016, **55**, 14067–14071.

158 S. N. Kessler, M. Neuburger and H. A. Wegner, *Eur. J. Org. Chem.*, 2011, **2011**, 3238–3245.

159 S. N. Kessler, M. Neuburger and H. A. Wegner, *J. Am. Chem. Soc.*, 2012, **134**, 17885–17888.

160 C. Dou, S. Saito and S. Yamaguchi, *J. Am. Chem. Soc.*, 2013, **135**, 9346–9349.

161 T. Agou, J. Kobayashi and T. Kawashima, *Inorg. Chem.*, 2006, **45**, 9137–9144.

162 S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372–11375.

163 S. K. Sarkar, S. Mukherjee and P. Thilagar, *Inorg. Chem.*, 2014, **53**, 2343–2345.

164 Y. Sun, N. Ross, S.-B. Zhao, K. Huszarik, W.-L. Jia, R.-Y. Wang, D. Macartney and S. Wang, *J. Am. Chem. Soc.*, 2007, **129**, 7510–7511.

165 Y. Sun and S. Wang, *Inorg. Chem.*, 2009, **48**, 3755–3767.

166 Y. Li, Y. Kang, J.-S. Lu, I. Wyman, S.-B. Ko and S. Wang, *Organometallics*, 2014, **33**, 964–973.

167 M. Varlan, B. A. Blight and S. Wang, *Chem. Commun.*, 2012, **48**, 12059–12061.

168 G. R. Kumar, S. K. Sarkar and P. Thilagar, *Phys. Chem. Chem. Phys.*, 2015, **17**, 30424–30432.

169 C. Wang, J. Jia, W. N. Zhang, H. Y. Zhang and C. H. Zhao, *Chem.–Eur. J.*, 2014, **20**, 16590–16601.

170 G. R. Kumar, S. K. Sarkar and P. Thilagar, *Chem.–Eur. J.*, 2016, DOI: 10.1002/chem.201603349.

171 T. W. Hudnall, M. Melaimi and F. P. Gabbaï, *Org. Lett.*, 2006, **8**, 2747–27499.

172 W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, **2000**, 2131–2142.

173 S. Solé and F. P. Gabbaï, *Chem. Commun.*, 2004, **40**, 1284–1285.

174 M. Melaïmi, S. Solé, C.-W. Chiu, H. Wang and F. P. Gabbaï, *Inorg. Chem.*, 2006, **45**, 8136–8143.

175 M. Melaimi and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2005, **127**, 9680–9681.

176 M. H. Lee and F. P. Gabbaï, *Inorg. Chem.*, 2007, **46**, 8132–8138.

177 T. W. Hudnall, Y. M. Kim, M. W. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, **130**, 10890–10891.

178 M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbaï, *Chem. Commun.*, 2007, **43**, 1133–1135.

179 Y. Kim and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 3363–3369.

180 H. Li, R. A. Lalancette and F. Jäkle, *Chem. Commun.*, 2011, **47**, 9378–9380.

181 F. Pammer and F. Jäkle, *Chem. Sci.*, 2012, **3**, 2598.

182 C.-H. Zhao, A. Wakamiya, Y. Inukai and S. Yamaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 15934–15935.

183 A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4273–4276.

184 F. Cheng, E. M. Bonder and F. Jäkle, *J. Am. Chem. Soc.*, 2013, **135**, 17286–17289.

185 W. M. Wan, F. Cheng and F. Jäkle, *Angew. Chem., Int. Ed.*, 2014, **53**, 8934–8938.

186 X. Yin, F. Guo, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2016, **49**, 537–546.

187 P. Chen, R. A. Lalancette and F. Jäkle, *J. Am. Chem. Soc.*, 2011, **133**, 8802–8805.

188 P. Chen and F. Jäkle, *J. Am. Chem. Soc.*, 2011, **133**, 20142–20145.

189 P. Chen, R. A. Lalancette and F. Jäkle, *Angew. Chem., Int. Ed.*, 2012, **51**, 7994–7998.

190 P. Chen, X. Yin, N. Baser-Kirazli and F. Jäkle, *Angew. Chem., Int. Ed.*, 2015, **54**, 10768–10772.

191 B. Strehmel and V. Strehmel, *Adv. Photochem.*, 2007, **29**, 111–354.

192 G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330.

193 M. Rumi, S. Barlow, J. Wang, J. W. Perry and S. R. Marder, in *Photoresponsive Polymers I*, ed. S. R. Marder and K.-S. Lee, Springer, Berlin, 2008, vol. 213, pp. 1–95.

194 F. Terenziani, C. Katan, E. Badaeva, S. Tretiak and M. Blanchard-Desce, *Adv. Mater.*, 2008, **20**, 4641–4678.

195 M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653–1656.

196 D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder and J. L. Brédas, *Adv. Funct. Mater.*, 2002, **12**, 631–641.

197 Q. Zheng, G. S. He and P. N. Prasad, *Chem. Mater.*, 2005, **17**, 6004–6011.

198 Z. Liu, Q. Fang, D. Wang, G. Xue, W. Yu, Z. Shao and M. Jiang, *Chem. Commun.*, 2002, **38**, 2900–2901.

199 Z. Liu, Q. Fang, D. Wang, D. Cao, G. Xue, W. Yu and H. Lei, *Chem.–Eur. J.*, 2003, **9**, 5074–5084.

200 Z. Liu, Q. Fang, D. Cao, D. Wang and G. Xu, *Org. Lett.*, 2004, **6**, 2933–2936.

201 M. Charlot, L. Porrés, C. D. Entwistle, A. Beeby, T. B. Marder and M. Blanchard-Desce, *Phys. Chem. Chem. Phys.*, 2005, **7**, 600.

202 Z. Liu, M. Shi, F. Li, Q. Fang, Z. Chen, T. Yi and C. Huang, *Org. Lett.*, 2005, **7**, 5481–5484.

203 J. C. Collings, S. Y. Poon, C. Le Droumaguet, M. Charlot, C. Katan, L. O. Pålsson, A. Beeby, J. A. Mosely, H. M. Kaiser, D. Kaufmann, W. Y. Wong, M. Blanchard-Desce and T. B. Marder, *Chem.–Eur. J.*, 2009, **15**, 198–208.

204 C. D. Entwistle, J. C. Collings, A. Steffen, L.-O. Pålsson, A. Beeby, D. Albesa-Jové, J. M. Burke, A. S. Batsanov, J. A. K. Howard, J. A. Mosely, S.-Y. Poon, W.-Y. Wong, F. Ibersiene, S. Fathallah, A. Boucekkine, J.-F. Halet and T. B. Marder, *J. Mater. Chem.*, 2009, **19**, 7532.

205 L. Ji, Q. Fang, M. Yuan, Z. Liu, Y. Shen and H. Chen, *Org. Lett.*, 2010, **12**, 5192–5195.

206 L. Ji, R. M. Edkins, L. J. Sewell, A. Beeby, A. S. Batsanov, K. Fucke, M. Drafz, J. A. K. Howard, O. Moutounet, F. Ibersiene, A. Boucekkine, E. Furet, Z. Liu, J.-F. Halet, C. Katan and T. B. Marder, *Chem.–Eur. J.*, 2014, **20**, 13618–13635.

207 N. S. Makarov, S. Mukhopadhyay, K. Yesudas, J.-L. Brédas, J. W. Perry, A. Pron, M. Kivala and K. Müllen, *J. Phys. Chem. A*, 2012, **116**, 3781–3793.

208 P. Chen, A. S. Marshall, S. H. Chi, X. Yin, J. W. Perry and F. Jäkle, *Chem.–Eur. J.*, 2015, **21**, 18237–18247.

209 X. Li, X. Guo, L. Cao, Z. Xun, S. Wang, S. Li, Y. Li and G. Yang, *Angew. Chem., Int. Ed.*, 2014, **53**, 7809–7813.

210 J. Liu, X. Guo, R. Hu, X. Liu, S. Wang, S. Li, Y. Li and G. Yang, *Anal. Chem.*, 2016, **88**, 1052–1057.

211 S. Griesbeck, Z. Zhang, M. Gutmann, T. Lühmann, R. M. Edkins, G. Clermont, A. N. Lazar, M. Haehnel, K. Edkins, A. Eichhorn, M. Blanchard-Desce, L. Meinel and T. B. Marder, *Chem.–Eur. J.*, 2016, **22**, 14701–14706.

212 Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto and T. Ohara, *J. Am. Chem. Soc.*, 2000, **122**, 11021–11022.

213 H. Doi, M. Kinoshita, K. Okumoto and Y. Shirota, *Chem. Mater.*, 2003, **15**, 1080–1089.

214 D. Mutaguchi, K. Okumoto, Y. Ohsedo, K. Moriwaki and Y. Shirota, *Org. Electron.*, 2003, **4**, 49–59.

215 W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao and S. Wang, *Chem.–Eur. J.*, 2004, **10**, 994–1006.

216 W. L. Jia, X. D. Feng, D. R. Bai, Z. H. Lu, S. Wang and G. Vamvounis, *Chem. Mater.*, 2005, **17**, 164–170.

217 W. L. Jia, M. J. Moran, Y.-Y. Yuan, Z. H. Lu and S. Wang, *J. Mater. Chem.*, 2005, **15**, 3326.

218 F. Li, W. Jia, S. Wang, Y. Zhao and Z.-H. Lu, *J. Appl. Phys.*, 2008, **103**, 034509.

219 F. Miyamoto, S. Nakatsuka, K. Yamada, K. Nakayama and T. Hatakeyama, *Org. Lett.*, 2015, **17**, 6158–6161.

220 G. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder and A. Beeby, *Adv. Funct. Mater.*, 2008, **18**, 499–511.

221 Z. M. Hudson, C. Sun, M. G. Helander, H. Amarne, Z.-H. Lu and S. Wang, *Adv. Funct. Mater.*, 2010, **20**, 3426–3439.

222 Z. B. Wang, M. G. Helander, Z. M. Hudson, J. Qiu, S. Wang and Z. H. Lu, *Appl. Phys. Lett.*, 2011, **98**, 213301.

223 Z. B. Wang, M. G. Helander, J. Qiu, D. P. Puzzo, M. T. Greiner, Z. M. Hudson, S. Wang, Z. W. Liu and Z. H. Lu, *Nat. Photonics*, 2011, **5**, 753–757.

224 X. Wang, Y.-L. Chang, J.-S. Lu, T. Zhang, Z.-H. Lu and S. Wang, *Adv. Funct. Mater.*, 2014, **24**, 1911–1927.

225 Z. M. Hudson, C. Sun, M. G. Helander, Y. L. Chang, Z. H. Lu and S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 13930–13933.

226 H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234–238.

227 W.-L. Jia, D. Song and S. Wang, *J. Org. Chem.*, 2003, **68**, 701–705.

228 H. Hirai, K. Nakajima, S. Nakatsuka, K. Shiren, J. Ni, S. Nomura, T. Ikuta and T. Hatakeyama, *Angew. Chem., Int. Ed.*, 2015, **54**, 13581–13585.

229 M. Numata, T. Yasuda and C. Adachi, *Chem. Commun.*, 2015, **51**, 9443–9446.

230 K. Suzuki, S. Kubo, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi and H. Kaji, *Angew. Chem., Int. Ed.*, 2015, **54**, 15231–15235.

231 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.