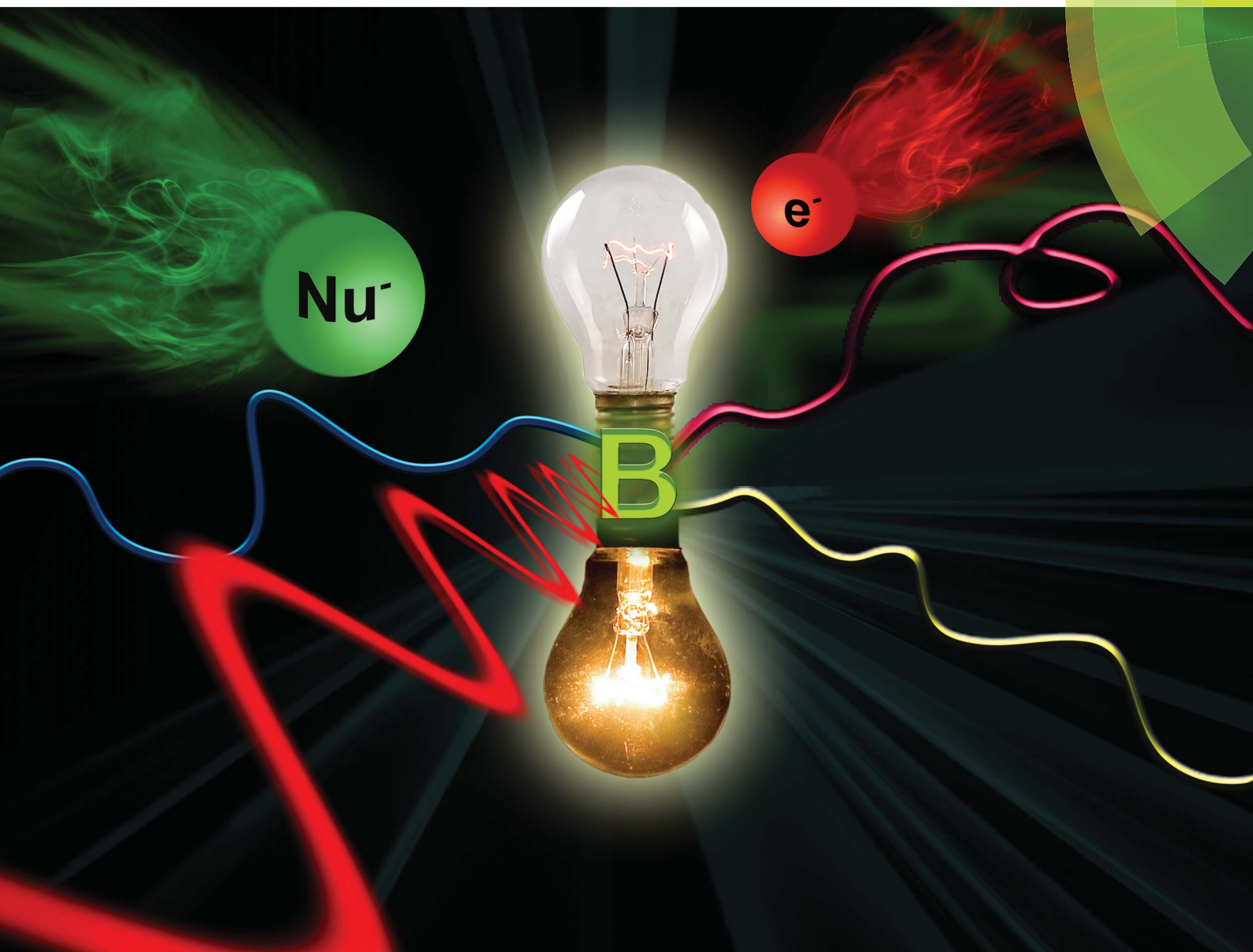


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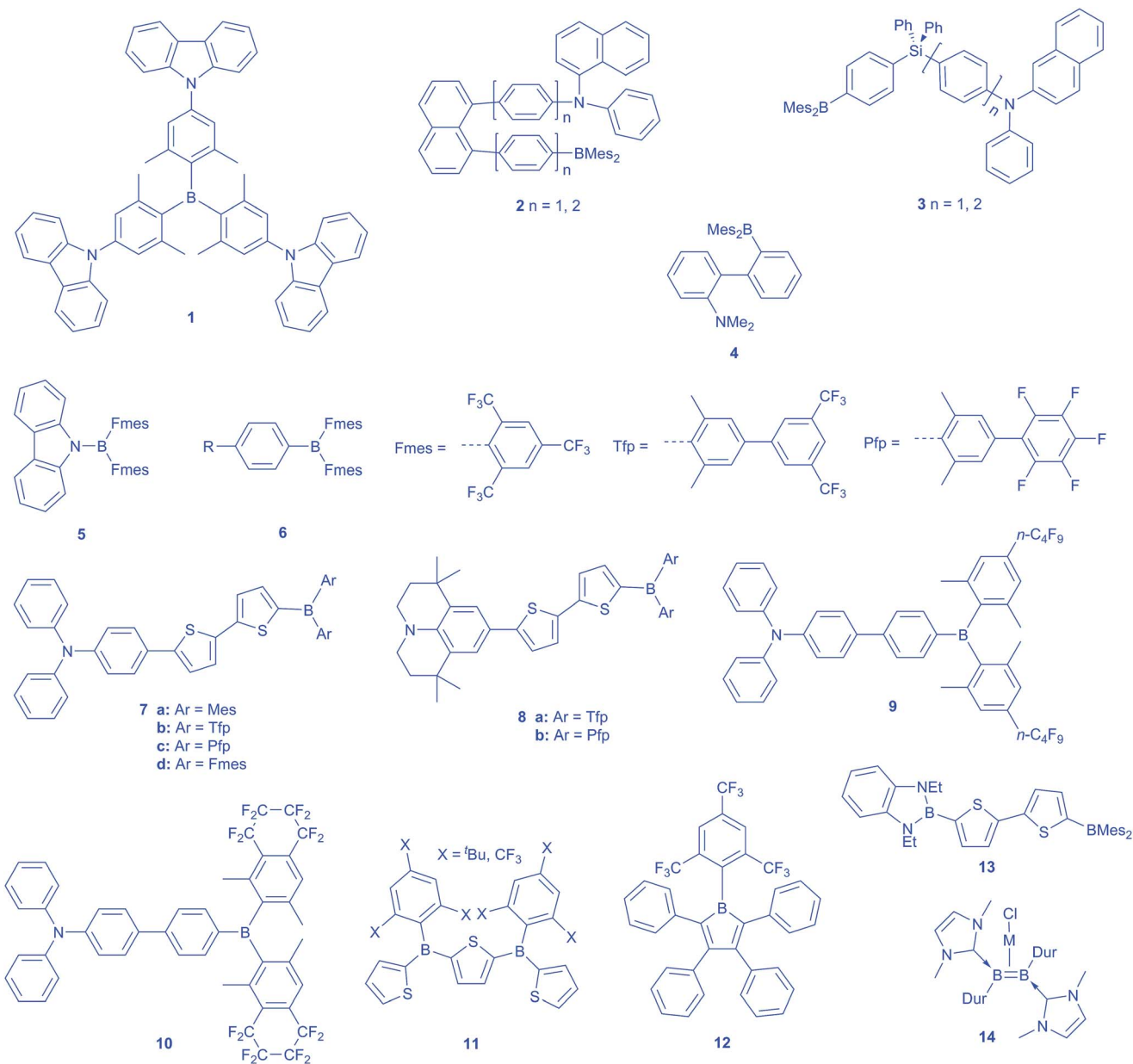
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PERSPECTIVE

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



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 $\text{B}(\text{Fmes})_2$ ($\text{Fmes} = 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$), the trifluoromethyl analogue of $\text{B}(\text{Mes})_2$, and this is a useful precursor to a series of compounds containing the $\text{B}(\text{Fmes})_2$ 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 $2,5'\text{-(BX}_2)_2\text{-(C}_4\text{H}_2\text{S)}_2$, *i.e.*, related to and including $2,5'\text{-(B}(\text{Mes})_2)_2\text{-dithiophene}$

previously employed by Shirota as an electron transporter in OLEDs (*vide infra*).⁴² Examination of $\text{X} = \text{C}_6\text{F}_5$ and $2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$, *i.e.*, Fmes, showed that these two fluorinated arenes had fairly similar electronic effects, dropping the LUMO by *ca.* 1 eV with respect to $\text{X} = \text{Mes}$. While Jäkle had used $\text{B}(\text{C}_6\text{F}_5)_2$ 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 $\text{B}(\text{Fmes})_2$ compounds. While our work was in progress, Yamaguchi thus reported the synthesis of carbazole directly bonded to a $\text{B}(\text{Fmes})_2$ group *via*



a particularly nice illustration of the excellent π -acceptor properties of BMe_2 and its ability to conjugate with organic π -systems. As a result, reduction of 2- and 2,7- BMe_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_2N) 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, Gabbai 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 ($A(^{11}\text{B}) = 3.02$ 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-diborolythiophene **25** also shows complete delocalisation of the unpaired electron. The

single-crystal X-ray structure and theoretical studies of the dianion of the diborolythiophene reveal its quinoidal structure with singlet biradical character.¹¹²

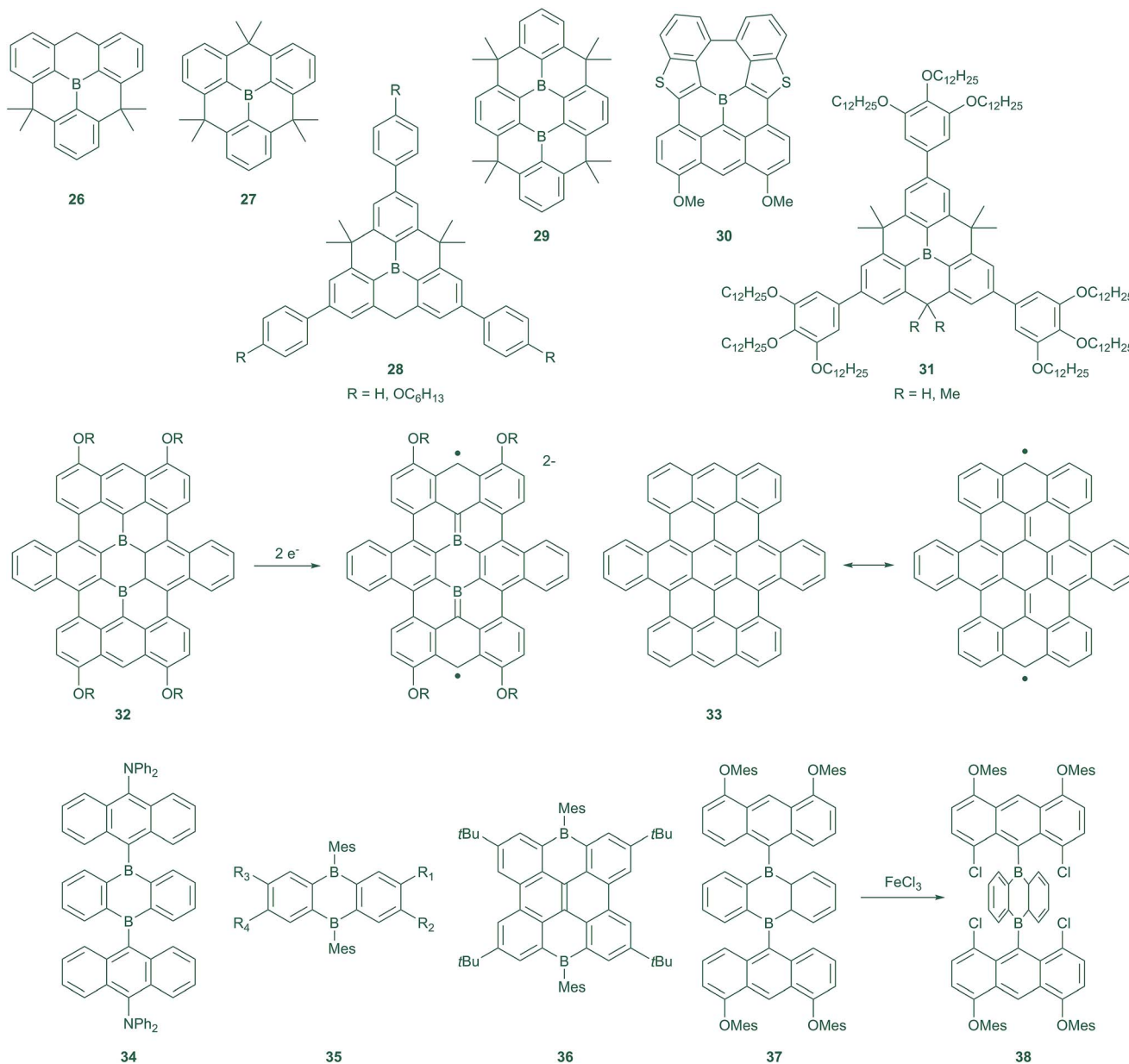
Boron-containing polycyclic π -systems

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 BMe_3 , and thus is still a good Lewis acid. Interestingly, the reduction potential of **27** does not differ from that of BMe_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.* $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.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 $[\mathbf{32}]^{2-}$,



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** ($R = n\text{-butyl}$) 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 activation¹⁵⁷ and the inverse-electron-demand Diels–Alder reaction.^{158,159} When the boron atoms are protected by bulky substituents, such as 9-anthracenyl 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 $\text{S}_0\text{--}\text{S}_1$ transition in **38** is simply a $\pi\text{--}\pi^*$ 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 $\text{S}_0\text{--}\text{S}_1$ transition (absorption/emission) thus involves charge transfer from the boron substituents to the diboraanthracene core.

Anion sensors^{14–17}

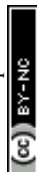
As mentioned above, typically only small anions such as F^- and CN^- can overcome the steric bulk of BMes_2 and attack the free p_z -orbital at the boron. Thus, aryl BMes_2 compounds can act as selective sensors for these specific anions. The absorption and emission spectra change upon the addition of 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

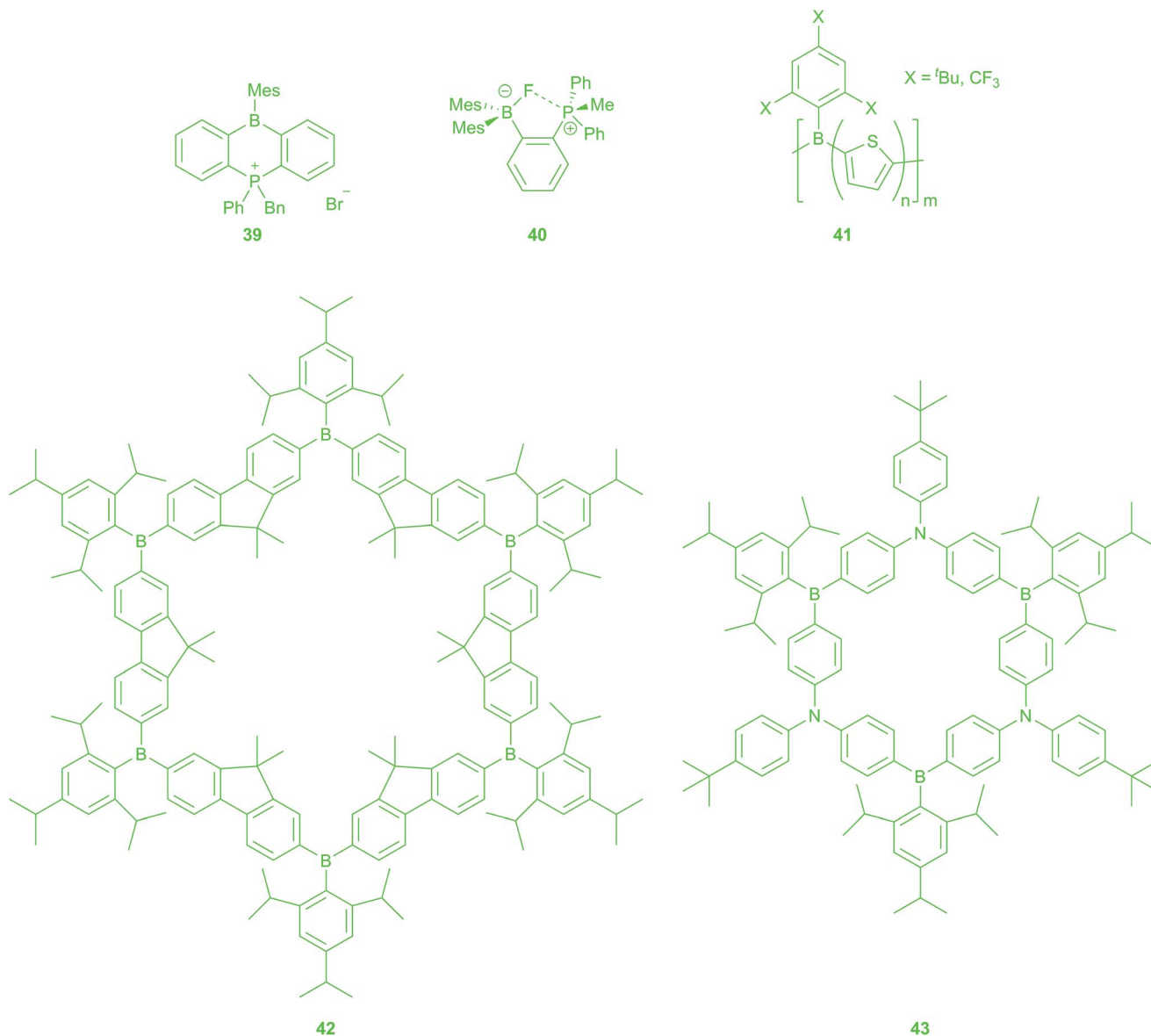
after the addition of F^-) and “turn-on” (emission colour changes with complexation of F^-) sensors by investigating the aforementioned U- and V-shaped bridges between triarylborane acceptors and triarylamine donors.^{35,36} Furthermore, they reported metal complexes as “turn-on” sensors, especially Pt(II) complexes with bipy ligands with triarylborane and triarylamine substituents,^{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 boracyclopentane **42**. Whereas the emission from CT states of the partially complexed species $[\text{43}(\text{CN})]^-$ and $[\text{43}(\text{CN})_2]_2^-$ remains strong, $[\text{42}(\text{CN})]^-$ 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** ($\text{R}_1, \text{R}_4 = \text{Br}$ and $\text{R}_2, \text{R}_3 = \text{H}$ or $\text{R}_1, \text{R}_3 = \text{Br}$ and $\text{R}_2, \text{R}_4 = \text{H}$) (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.

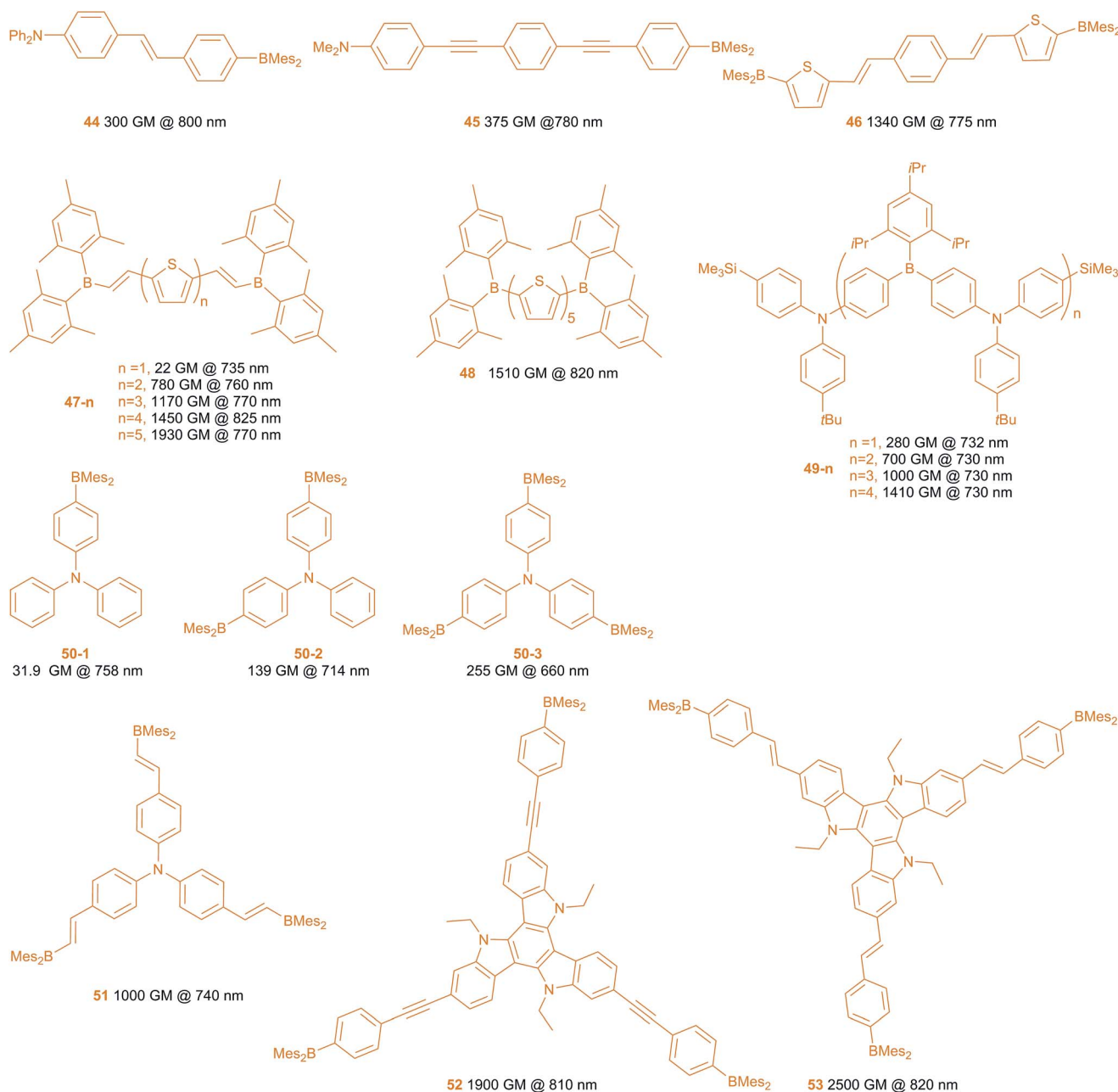
3-Coordinate boron in chromophores exhibiting strong two-photon absorption

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 $\sigma_{2,\text{max}} > 50 \text{ GM}$ 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.



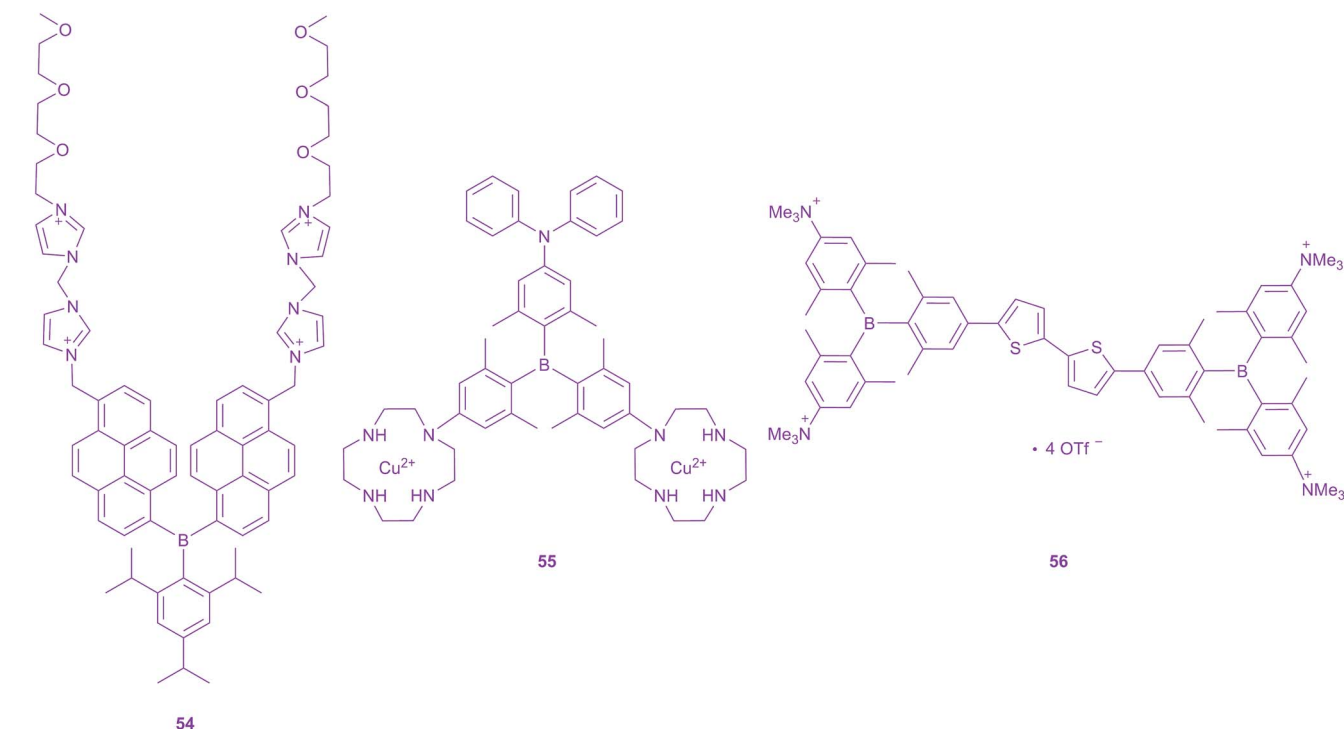
and octupolar compounds featuring BMe₂ π-acceptor moieties, which show strong TPA and TPEF behaviour.¹⁹⁸⁻²⁰⁶ Scheme 5 shows several typical 3-coordinate boron compounds which have large σ₂ values.¹⁹⁸⁻²⁰⁸

Compound **44** is a very typical dipolar compound, which has a very strong electron acceptor (BMe₂) and donor (NPh₂). The emission is strongly solvent-dependent, indicating a large dipole moment in the excited states, and thus a large Δμ₀₁. 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 S₀–S₁ 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 S₀–S₁ transition is allowed for one-photon absorption but forbidden for TPA, while the S₀–S₂ 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 S₀–S₂ 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 S₀–S₂ one. Thus, the S₀–S₂ 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 σ₂ values increase linearly with increasing number *n* of the D–A subunits, but σ₂/*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, S₀–S₁, 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-BMe₂ substituted triphenylamines have been compared recently.²⁰⁷ Compound **50-1** has a two-photon excited S₀–S₁ transition band with σ_{2,max} = 32 GM (758 nm). However, the two-photon absorption of this transition (S₀–S₁) in the bis-substituted compound (quasi-quadrupolar) **50-2** is very weak (σ₂ = 2.9 GM, 808 nm), but it has a very strong TPA band at 714 nm (σ_{2,max} = 139 GM), for the S₀–S₂ transition. In comparison, the S₀–S₂ 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

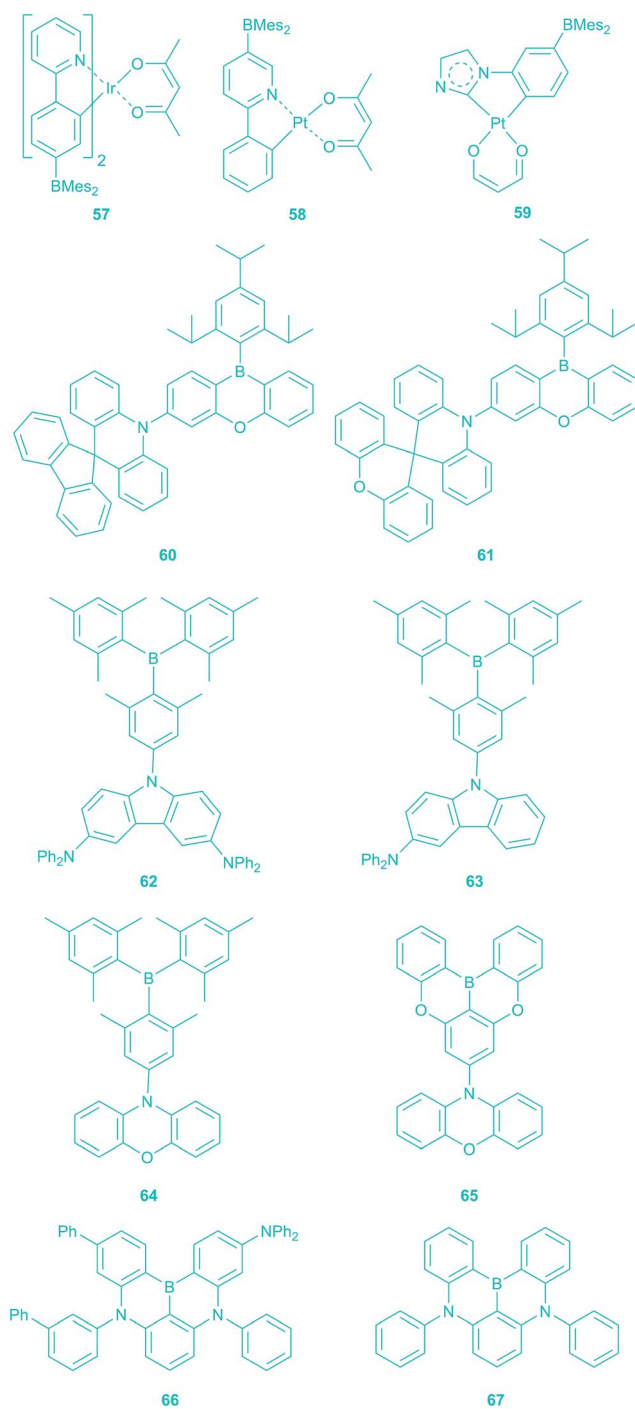
Very recently, a new application of triarylboranes in cell imaging has emerged. Yang and co-workers reported the water-soluble, non-ionic triarylborane **54**, incorporating polyethylene glycol chains as the hydrophilic groups, as an efficient fluorescence indicator for ATP in the cytoplasm and cell 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 H_2S . 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 BMes₂-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 BMes₂ 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** ($R = \textit{tert}$ -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** ($R = \textit{tert}$ -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-aryl₂ 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 bio-imaging 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 boracenes 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!

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