

Near-infrared quadrupolar chromophores combining three-coordinate boron-based superdonor and -acceptor units

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Abstract: In this work, two new quadrupolar A- π -D- π -A chromophores have been prepared featuring a strongly electron-donating diborene core and strongly electron-accepting dimesitylboryl (BMe₂) and bis(2,4,6-tris(trifluoromethyl)phenyl)boryl (B^FMe₂) end groups. Analysis of the compounds by NMR spectroscopy, X-ray crystallography, cyclic voltammetry and UV-vis-NIR absorption and emission spectroscopy indicated that the compounds possess extended conjugated π -systems spanning their B₄C₈ cores. The combination of exceptionally potent π -donor (diborene) and π -acceptor (diarylboryl) groups, both based on trigonal boron, leads to very small HOMO-LUMO gaps, resulting in strong absorption in the near-IR region with maxima in THF at 840 and 1092 nm, respectively, and very high extinction coefficients of ca. 120,000 M⁻¹cm⁻¹. Both molecules also display weak near-IR fluorescence with small Stokes shifts.

Luminescent materials are ubiquitous in modern life, with applications as diverse as lighting, telecommunications and biological imaging.^[1] Molecules that absorb and emit light in the visible range have generally dominated research as a result of applications that require detection by the human eye.^[2] Near-infrared (NIR) absorption and emission are much more difficult to achieve with molecular systems. Materials with sufficiently small band gaps for NIR absorption typically display extensive conjugation and/or contain metal ions, while the small energy differences between the ground and excited states promote non-radiative decay rather than emission.^[3] Nevertheless, emerging applications in biology and fibre optics have stimulated rapid progress in the development of NIR chromophores.^[4]

Three-coordinate organoboranes have been utilised extensively in the development of electronic and optical materials since the 1970s.^[5] The presence of an unoccupied p-orbital on boron allows it to function as an electron acceptor, which, in combination with a remote donor group and an appropriate π -conjugated linker, often leads to molecules and materials with

useful linear and nonlinear optical properties (Figure 1). The BMe₂ group is particularly popular, as it combines strong electron-accepting properties with steric protection of the empty p-orbital at boron.^[6] This prevents adduct formation between donor and acceptor moieties (i.e. forming frustrated Lewis pairs^[7]), as well as reducing sensitivity to hydrolysis. Fluorine-containing appendages provide even better acceptor ability; while the ubiquitous B(C₆F₅)₂ group is one of the most electron-poor boryl substituents,^[8] the bis(fluoromesityl)boryl group (fluoromesityl, ^FMes = 2,4,6-tris(trifluoromethyl)phenyl) retains this property while offering considerably improved shielding of the boron centre.^[9] Several molecules bearing this substituent as the acceptor have been found to display significant red shifts in their absorption and emission maxima, as well as much lower reduction potentials and higher stability than their non-fluorinated counterparts.^[10]

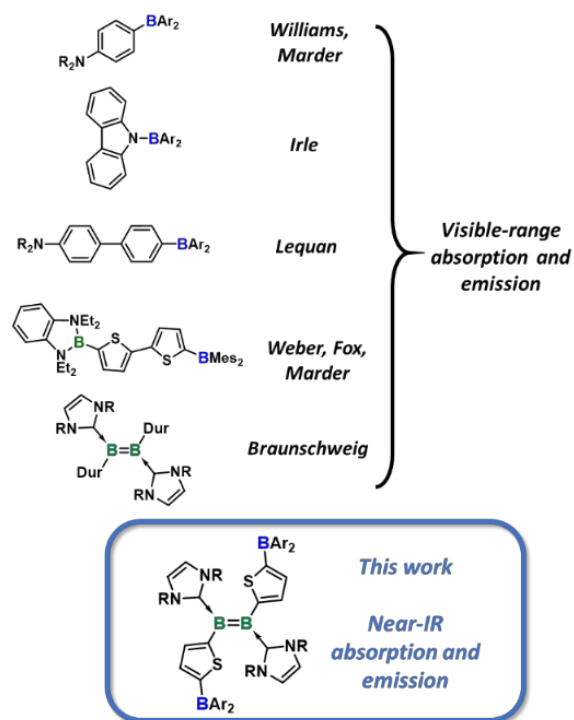


Figure 1. Selected donor-acceptor compounds containing three-coordinate boron (boron acceptor groups in blue, donor groups in green).

Although three-coordinate boron is typically considered electron deficient, examples exist where it acts as an electron donor. For example, the 1,3,2-benzodiazaborolyl group has been used effectively by Weber, Fox, Marder and co-workers as the donor in conjugated donor-acceptor systems (see Figure 1).^[11] The group of Braunschweig has been heavily involved in the development of subvalent boron compounds, namely borylenes^[12] and diborenes,^[13] which are formally B(I) species, and thus highly electron rich. Indeed, the high-energy highest occupied molecular orbitals (HOMO) of these molecules typically lead to small HOMO-LUMO gaps and visible light absorption (and sometimes emission) in the absence of explicit acceptor moieties.^[14] We therefore set out to combine some of the strongest known donors and acceptors among three-coordinate

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boron compounds to produce quadrupolar molecules with unusual optical and electronic properties.

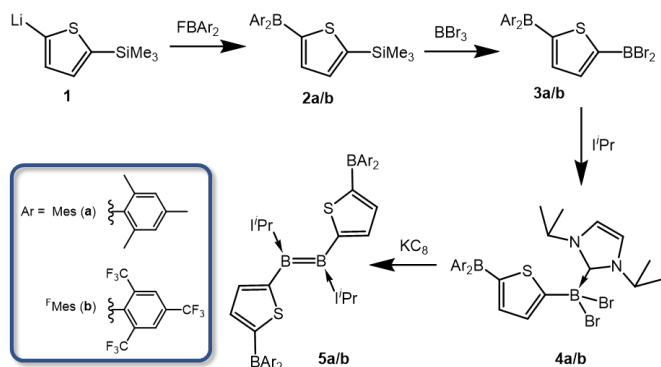


Figure 2. Synthesis of quadrupolar chromophores **5a** and **5b**.

We have recently reported the synthesis of a number of thiophene- and furan-substituted diborenes by the reductive coupling of two *N*-heterocyclic carbene (NHC)-stabilised aryldihaloboranes.^[15] An interesting feature that sets these heteroaryl-substituted diborenes apart from the majority of their aryl counterparts is that the thiophene (or furan) ring adopts a coplanar orientation with respect to the B=B bond, forming a well-conjugated π -system. Furthermore, substituents can be readily installed at the 5-position of the heteroarene prior to the coupling step, allowing modification of the electronic properties of the compounds. We targeted compounds **5a** and **5b** (Scheme 1), bearing the electron-accepting boryl substituents BMe₂ and B^FMe₂. Bis(boryl)thiophenes **3a** and **3b** were prepared by a similar protocol to that recently published for **3a** by Weber and co-workers.^[16] We subsequently synthesised diborenes **5a** and **5b** using the established strategy^[15] of coordination of 1,3-

diisopropylimidazol-2-ylidene (I'Pr) to the BBr₂ fragment followed by reductive coupling with KC₈ (Figure 2). Compound **5a** was isolated as a dark green crystalline solid, whereas crystals of **5b** were deep purple in colour.

The crystal structures of compounds **5a** and **5b** are shown in Figure 3. Selected parameters are given in Table 1 alongside those of previously published diborenes featuring electronically neutral (SiMe₃) and donating (NPh₂) groups for comparison.^[17] While the thiophene groups in **5a** are slightly twisted out of the B=B plane (C1-B1-B2-S1 = 23.5(3)°), the entire central B₄C₈ unit of **5b** is essentially planar. The dihedral angles between the BC₃ planes and the thiophene plane (**5a**: 13.9°; **5b**: 12.1, 16.5°) indicate that the (fluoro-)mesityl substituents on the outer boron atoms are aligned in such a way as to allow overlap of the formally empty boryl p_z orbital with the conjugated system, which is comparable to previously reported, related compounds.^[18] One would expect that, in a conjugated system, increasing π -electron-accepting ability of the substituent on the thiophene linker should lead to increases in the B1-B2, C1-C2 and C3-C4 bond lengths, with concomitant shortening of the B1-C1, C2-C3 and C4-B3 bonds. Although the variations are small (in most cases the differences between **5a** and **5b** fall within experimental error), over the series a clear trend becomes apparent, with systematic increases/decreases in the appropriate distances as the substituent in the 5-position changes from NPh₂ > SiMe₃ > BMe₂ > B^FMe₂, indicating significant conjugation in the boryl-substituted compounds in their ground state structures. The B-B bond lengths of **5a** (1.607(3) Å) and **5b** (1.618(6) Å) are at the upper range of those observed for diborenes, with the latter approaching that of a diborene radical cation (e.g. [(I'Pr)BDur]₂[B(3,5-(CF₃)₂C₆H₃)₄] (I'Pr = 1,3-dimethylimidazol-2-ylidene), B-B = 1.636(4) Å).^[19] This suggests significant delocalisation of the B=B electron density throughout the π -system.

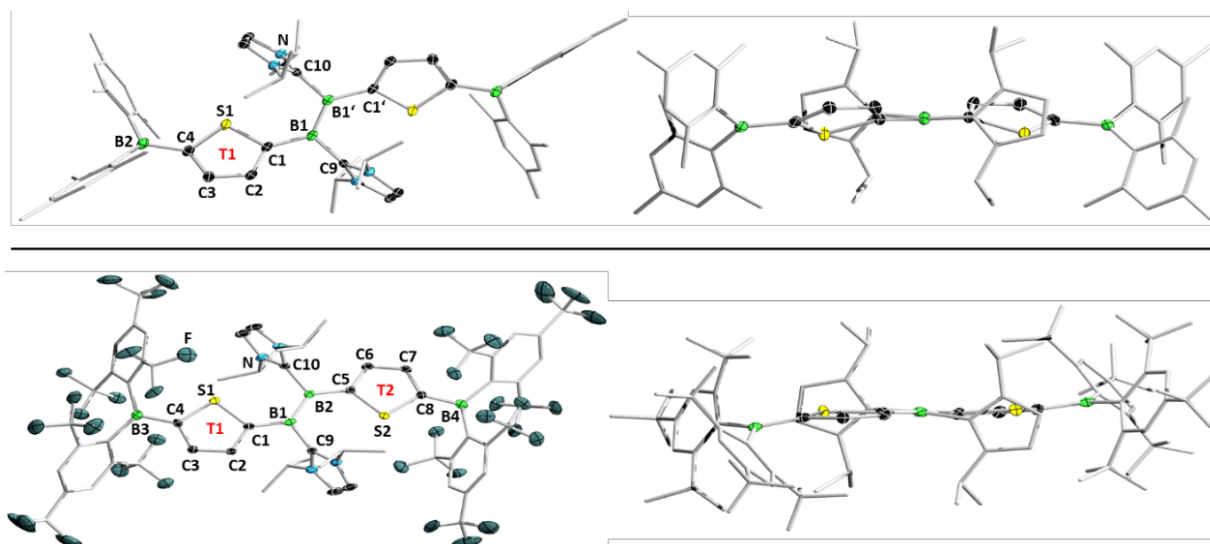


Figure 3. Crystal structures of **5a** (top) and **5b** (bottom) viewed perpendicular to (left) or in line with (right) the boron-boron double bond. Selected atomic displacement ellipsoids are displayed at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths, torsion angles and dihedral angles of thienyl-substituted diborenes with variation of the substituent at the 5-position of the thienyl group.

Thiophene Subst.	NPh ₂ *	SiMe ₃	BMe ₂ (5a)	B ^F Me ₂ (5b)	Trend L-R
B1-B2 (B1-B1')	1.592(2)	1.587(7)	1.607(3)	1.618(6)	Increase
B1-C1 (B2-C5)	1.560(2), 1.559(2)	1.557(5)	1.549(3)	1.527(6), 1.534(6)	Decrease
C1-C2 (C5-C6)	1.387(2), 1.384(2)	1.397(6)	1.402(3)	1.414(6), 1.411(5)	Increase
C2-C3 (C6-C7)	1.416(2), 1.416(2)	1.412(4)	1.393(3)	1.381(6), 1.389(6)	Decrease
C3-C4 (C7-C8)	1.354(2), 1.355(2)	1.362(7)	1.397(3)	1.393(5), 1.397(5)	Increase
C4-B3 (C8-B4)	-	-	1.516(3)	1.502(7), 1.504(7)	-
C1-B1-B2-C5 (C1-B1-B1'-C1')	172.6(1)	180.0(4)	179.9(2)	178.5(4)	-
B2-B1-C1-S1 (B1-B2-C5-S2)	5.1(2), 22.7(2)	6.4(4)	23.5(3)	0.1(6), 6.9(6)	-
C1-B1-B2-C10 (C5-B2-B1-C9)	3.7(2), 5.0(2)	0.9(7)	4.6(4)	9.3(6), 4.2(6)	-
BC ₃ plane-T1 (T2)	-	-	13.9	12.1, 16.5	-

The stabilising NHC is 1,3-di-*iso*-propylimidazol-2-ylidene unless otherwise stated. * NHC is 1,3,4,5-tetramethylimidazol-2-ylidene. Single values are given where a crystallographic inversion center is present.

Cyclic voltammetry studies on THF solutions of compounds **5a** and **5b** (see Supporting Information) revealed oxidation waves; the oxidation of **5a** occurs at -1.19 V (all values vs. Fc/Fc⁺), indicating that it is significantly more difficult to oxidise than previously studied NHC-stabilised diborenes ($E_{1/2} = -1.53$ to -1.56 V),^[20] whereas the oxidation wave of **5b** is found at -0.80 V, a value surpassed only by a diborene stabilised by the relatively poor donor bis(diphenylphosphino)methane ($E_{1/2} = -0.51$ V). The HOMO energy is thus markedly affected by the thienyl substituent. The presence of the BMe₂ and B^FMe₂ groups also allows the species to be reduced; **5a** displays a reduction wave at -2.60 V, whereas for **5b** this occurs at -1.73 V, showing the profound effect of fluorination of the aryl substituents. Indeed, the similarity of these values to the reduction potentials of related B^FMe₂- and BMe₂-substituted compounds, 4-*t*BuC₆H₄B^FMe₂ ($E_{1/2} = -1.63$ V), 4-Ph₂NC₆H₄B^FMe₂ ($E_{1/2} = -1.66$ V) and 4-Ph₂NC₆H₄BMe₂ ($E_{1/2} = -2.60$ V),^[21] indicates that the effect of the donor on the reduction potential is relatively small. All of the redox processes are fully reversible, suggesting the existence of stable radical cations and radical anions of both compounds.

In order to obtain more information about the electronic structures of **5a** and **5b**, we carried out Density Functional Theory (DFT) calculations at the def2-TZVP level of theory, the results of which are summarised in Figure 4. The HOMOs of the diborenes lie well above the other occupied frontier orbitals in energy and are mainly located on the B=B bonds, with smaller contributions from the thiophene units and the boron atoms of the BMe₂ or B^FMe₂ groups. In both cases, the LUMO is more delocalised over the whole π -system, with C_{thiophene}-BAR₂ bonding and B=B antibonding character. The electron-withdrawing CF₃ groups on the aryl rings of the triarylborane moiety of **5b** stabilise the unoccupied frontier orbitals significantly more than the occupied ones, leading to a much smaller HOMO-LUMO gap of 1.52 eV compared to 1.95 eV in **5a**. It is also important to note that the LUMO of **5b** is much more polarised towards the triarylborane units, with significant delocalisation into the ^FMe groups, as this can be expected to affect the photophysical properties strongly (see below). The very small HOMO-LUMO gap of **5b** led us to consider the possibility that a triplet biradical state may be accessible either thermally or via photoexcitation. We therefore performed continuous wave and transient EPR spectroscopy on the compound, but no signal attributable to such a state was observed (see supporting information).

Given the conjugation in **5a**, and especially **5b**, we were optimistic that the compounds would display interesting optical properties. As a consequence of the small HOMO-LUMO gap and the energetic isolation of these two frontier orbitals, **5a** displayed very low energy absorption maxima in THF or toluene at $\lambda = 840$ and 828 nm, respectively, with an exceptionally high extinction coefficient of $\epsilon_{\text{THF}} = 120,000 \text{ M}^{-1} \text{ cm}^{-1}$ for the S₁ ← S₀ absorption, which has HOMO(π) → LUMO(π^*) character based on TD-DFT calculations (Figure 5). The absorption band is narrow; its full width at half maximum (fwhm) value of 970 cm^{-1} (THF) is comparable to that of BODIPY and squaraine dyes.^[22] For comparison, diborenes typically display a λ_{max} value of between 330 and 570 nm in their solution UV-vis absorption spectra.^[23] Likewise, the low energy absorption of **5a** is shifted several hundred nanometres into the red

compared with typical quadrupolar chromophores bearing BMe₂ acceptors.^[6]

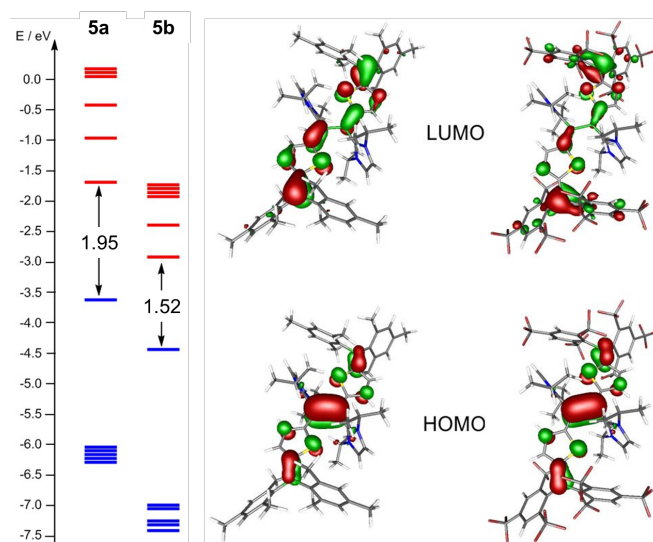


Figure 4. Molecular orbital diagrams of the frontier orbital region (occupied orbitals: blue; unoccupied orbitals: red) and depiction of the HOMO and LUMO of **5a** (left) and **5b** (right).

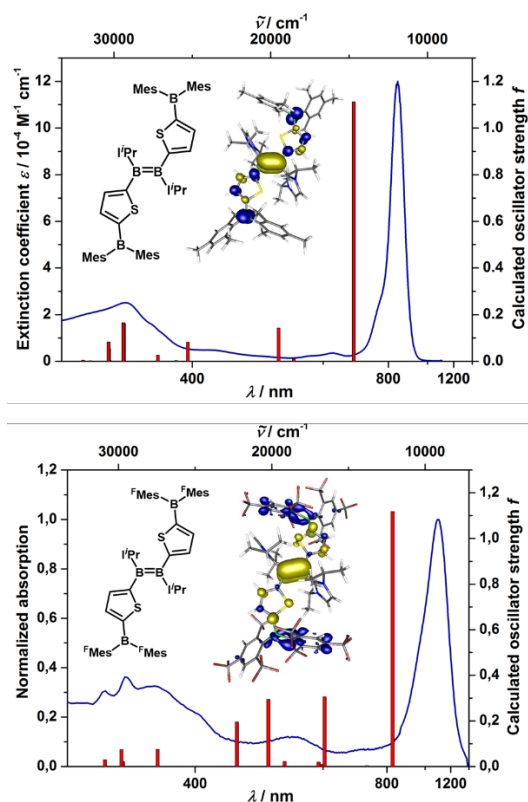


Figure 5. Experimental absorption spectra in THF, calculated oscillator strengths f and transition density difference for $S_1 \leftarrow S_0$ of **5a** (top) and **5b** (bottom). Compound **5b** was too sensitive for reliable determination of the extinction coefficient ϵ ; note that the calculated oscillator strength of the $S_1 \leftarrow S_0$ transition is similar to that of **5a**. Full width at half maximum values: 970 cm^{-1} (**5a**); 2030 cm^{-1} (**5b**).

In addition, **5a** shows unusual near-IR fluorescence in THF and toluene solutions at room temperature at $\lambda = 884$ and 863 nm, respectively, albeit very weakly, precluding the determination of lifetimes and quantum yields (Figure 6, top). A vibrational progression of the emission of ca. 650 cm^{-1} is observed at 77 K in an optical glass of 2-MeTHF (Figure 6, bottom, $\lambda_{\text{max}} = 920$ nm), which corresponds to the calculated out-of-plane vibration of the trigonal boron centres, but may also involve distortions of the thiophene rings and the B=B unit (see Supporting Information). The very small Stokes shift of ca. 600-700 cm^{-1} indicates that the overall charge transfer character and the geometrical distortion in the excited state are small, giving rise to the assumption that S_0 and S_1 are so-called nested states, and that non-radiative decay occurs according to the energy-gap law. Compound **5a** shows only a very small degree of solvatochromism in its absorption spectra, while the effect in the emission spectra is only marginally greater. This slight red shift in the more polar solvent THF is consistent with the small Stokes shift, suggesting minimal structural rearrangement in the excited state. The λ_{max} of emission of both **5a** and **5b** shifts bathochromically at higher optical densities, presumably due to the increasing significance of self-absorption at high concentration. Interestingly, in the solid state the fluorescence is absent, indicating an additional efficient non-radiative decay channel due to intermolecular interactions. The electron-withdrawing CF_3 groups at the aryl substituents of **5b** not only shift the absorption bathochromically further into the near-IR, to $\lambda = 1092$ nm in THF (Figure 5, bottom), but also lead to enhanced non-radiative decay in solution either following the energy-gap law or due to additional vibrational modes as a result of electron density delocalisation into the aryl rings upon

excitation (see Figure 5), such that no emission can be observed at room temperature. The emission at 77 K in 2-MeTHF is very weak, with a maximum at 1234 nm and a vibrational progression of ca. 650 cm^{-1} (Figure 6, bottom).

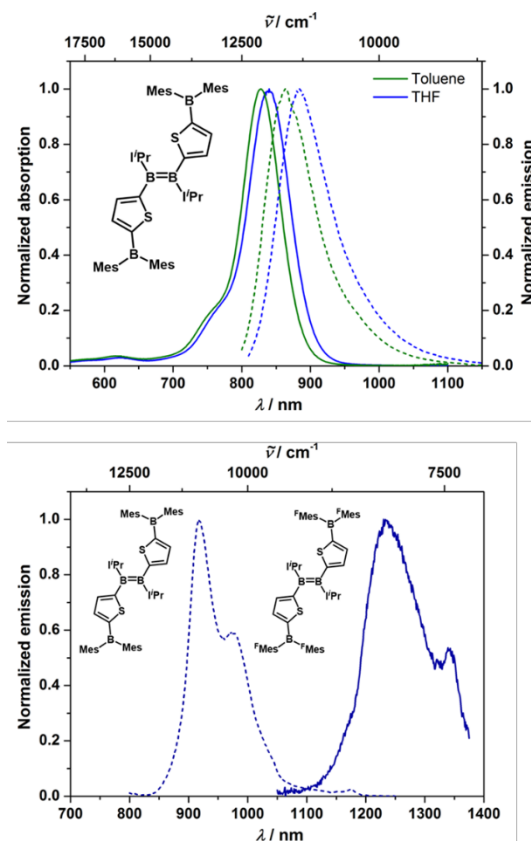


Figure 6. Top: normalized absorption (solid line) and emission (dashed line) of **5a** in toluene (green) and THF (blue), respectively, recorded at an optical density of 0.1 at room temperature. Bottom: emission spectra of **5a** (dashed line) and **5b** (solid line) in a frozen 2-MeTHF glass at 77 K.

In conclusion, we have reported novel quadrupolar A- π -D- π -A chromophores featuring superdonor and superacceptor units based on three-coordinate boron atoms. Combining strongly π -donating diborenes with strongly π -accepting boryl moieties by the use of a conjugated thieryl linker provides efficient conjugation and exceptionally small HOMO-LUMO gaps, leading to a remarkable red shift of the absorption and emission wavelengths into the near-IR region. The superiority of the $\text{B}^{\text{F}}\text{Mes}_2$ group over $\text{B}^{\text{Me}}\text{Mes}_2$ as an acceptor is underlined by the extremely long wavelength absorption (1092 nm) and emission (1234 nm) of its diborene compound compared to those of the mesityl derivative (840 and 920 nm, respectively). Unusually for diborenes, the compounds can be reduced electrochemically to their radical anions, with the fluorinated derivative showing a significantly more facile reduction. Our current focuses are structural modification of the compounds and improvement of their tolerance to atmospheric conditions.

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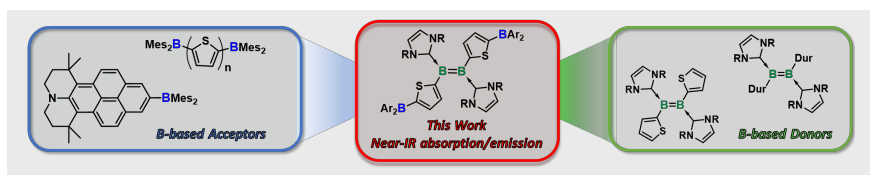
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Keywords: boron • near-IR chromophores • conjugation • low-valent compounds • synthesis

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COMMUNICATION



Double B-side: Combination of extremely potent boron-based donor and acceptor moieties in a conjugated system leads to quadrupolar chromophores with extremely small HOMO-LUMO gaps, displaying highly unusual near-IR absorption and emission.

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Page No. – Page No.

Near-infrared quadrupolar chromophores combining three-coordinate boron-based superdonor and -acceptor units