Photonic materials derived from the [closo-B10H10]2-anion: Tuning photophysical properties in [closo-B10H8-1-X-10-(4-Y-NC5H5)]-

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Photonic materials derived from the \([\text{closo-B}_{10}H_{10}]^{2-}\) anion: Tuning photophysical properties in \([\text{closo-B}_{10}H_{10}-1-X-10-(4-Y-NC_5H_5)]^-\)

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The parent pyridine \([\text{closo-B}_{10}H_7-1-NC_5H_5]^-\) was substituted either at the antipodal B(10) position with CN, OAc, NO, I, Br, SCN, pyridine, OEt, and morpholine, or at the C(4) position of the pyridine ring with CN, COOEt, Me, and OMe groups. The substituent effects on electronic absorption and emission properties, and also on the boron cage geometry were investigated experimentally and with DFT (B3LYP/Def2TZVP) computational methods. Experimental and theoretical results were correlated with Hammett \(\sigma_p\) parameters. Fluorescence was also investigated in the solid state and from aggregates (AIE). Solvent effects on photophysical properties of \([\text{closo-B}_{10}H_7-1-NC_5H_5]^-\) were correlated with E,30 parameters, giving a slope of 0.71 for absorption and 0.17 for emission. Results demonstrated the substantial impact of the B(10) substituent on the HOMO and the C(4) substituent on the LUMO of the derivatives, which allows variation of the energy of the (\(\pi,\pi^*\)) intramolecular charge transfer band in the range of 330–450 nm, and the emission energy in the range of 530–580 nm in MeCN solutions. The substituent effect on excitation energy is 2.4 times greater for substitution at the pyridine ring (LUMO control) than for the B(10) position (HOMO control). Additivity of the substituent effect was tested on \([\text{closo-B}_{10}H_7-1-(NC_5H_5CN)-10-OEt]^-\) with \(\lambda_{max} = 501.5 \text{ nm in MeCN and } 560 \text{ nm in THF}\). These studies indicate that a substantial degree of control over photophysical properties is possible in derivatives of \([\text{closo-B}_{10}H_{10}]^{2-}\) through a combination of substituent and solvent (medium) effects.

Introduction

Photophysical properties of boron cluster derivatives continue to attract interest driven by fundamental science and applications in photonics and molecular electronics. They have also been explored as potential NLO materials. Current attention is focused on the \([\text{closo-1,2-C}_2B_{10}H_{12}]^-\) cluster (ortho-carborane), which acts as an effective enhancer of luminescent properties (both fluorescence and phosphorescence) of organic materials particularly in the solid-state and in aggregates (e.g. aggregate induced emission, AIE) photophysical properties of other clusters are rarely described in the literature.

Parent closo-boranes are poor chromophores due to their typically large HOMO–LUMO gaps, and, consequently, they exhibit only weak absorptions above 200 nm. Substitution of the clusters with either electron-rich groups (in carboranes) or electron-poor groups (in closo-borane anions) leads to the appearance of intense low energy photo-induced intramolecular charge transfer (CT) bands, and often fluorescence. This strategy is particularly effective in \(\pi\)-zwitterionic derivatives of closo-borane anions, such as \([\text{closo-B}_{10}H_{13}]^{2-}\),\(^{7,17-19}\) \([\text{closo-B}_{10}H_6O_2]^{3-}\),\(^{8,17,18}\) \([\text{closo-B}_{10}H_5C_1\text{I}]^{2-}\),\(^{13,20,21}\) and \([\text{closo-1,1-C}_2B_{10}H_{12}]^{2-}\),\(^{21-23}\) in which the relatively high-lying HOMO is localized on the \(\pi\) onium fragment. For example, the CT process in tropylium (ousenes)\(^{13,24,25}\) and pyridiniumzwitterion \(\pi\)-zwitterions involves a (\(\pi,\pi^*\)) excitation (HOMO–LUMO transition), which is schematically shown in Fig. 1. Relaxation of the excited state in the latter group of zwitterions also involves fluorescence with quantum yields up to 37%.\(^{8,19}\)

![Fig. 1. Schematic representation of (\(\pi,\pi^*\)) excitation and relaxation processes in \(\pi\)-zwitterionic derivatives of closo-boranes.](image-url)

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*Electronic Supplementary Information (ESI) available: full synthetic and compounds characterization details, NMR spectra, XRD, UV-vis, and computational details. See DOI: 10.1039/x0xx00000x*
The 10-vertex dianion [closo-B_{10}H_{10}]^{2-} (A, Fig. 2)\textsuperscript{27, 28} is exceptional among closo-boranes: its $D_{5h}$ symmetry allows for efficient interactions with $\pi$ substituents,\textsuperscript{29, 30} while the particularly high-lying HOMO\textsuperscript{31} allows relatively low energy ($\pi,\pi^*$) excitations in its zwitterionic derivatives. This is evident in [closo-B_{10}H_{10}-1-NC(H)_{2}] (1a)\textsuperscript{32} the CT band at 364.5 nm (3.39 eV, $\log \varepsilon = 3.85$)\textsuperscript{18} has the lowest energy among analogous derivatives of closo-borane anions,\textsuperscript{18, 20, 22, 23} and extends into the visible range. Moreover, pyridinium derivatives of cluster A are photoluminescent in the visible range with a quantum yield up to 7% and Stokes shifts of about 1.4 eV.\textsuperscript{8} Such compounds are of potential interest as photonic materials, especially if the absorption/emission energies can be tuned with substituents. To probe the extent of tunability of the excitations and emission energies in 1a, we focused on a series of pyridinium derivatives 1 and 2 (Fig. 2), which are accessible through the recently discovered\textsuperscript{22} selective functionalization of the apical positions in A.

Herein we report two series of pyridinium derivatives, 1 and 2, that contain a range of substituents either at the B(10) apex of the cluster or at the C(4) position of the pyridine ring, respectively. Substituent effects were investigated in the two series with structural (XRD), spectroscopic, and DFT methods. Photophysical properties were measured in MeCN solutions and in the solid state, while aggregation effects on emission were examined for two selected derivatives in the MeCN/H$_2$O mixtures. Solvent effects on the position and intensity of the CT band were studied for the prototype [closo-B_{10}H_{10}-1-NC(H)_{2}] (1a). Experimental data are augmented with DFT calculations, compared with theoretical geometry and excitation energies, and correlated with solvent and Hammett substituent parameters. Additivity of the substituent effects was tested on derivative [closo-B_{10}H_{10}-1-(NC(H)_{2}CN)-10-OEt] (3).

**Results**

**Synthesis**

Our previous work demonstrated that monoiodonium [closo-B_{10}H_{10}-1-IPh] (4[Et,N]) undergoes nuclophilic substitution with pyridine to give 1a[Et,N] and it also reacts with the CN anion giving [closo-B_{10}H_{10}-1-CN] (5a[Et,N]) in good yields.\textsuperscript{32} This suggests a 3-step method for the preparation of series 1 through the intermediate [closo-B_{10}H_{10}-1-IPh-10-X] (6, method A in Fig. 3). We also demonstrated that the reaction of bisiodonium [closo-B_{10}H_{10}-1,10-2(Ph)] (7) with AcO$^-$ gives monosubstituted product 6c with high selectivity,\textsuperscript{32} which indicates an alternative two-step process leading to 1 (method B, Fig. 3). Access to phenyliodonium derivative [closo-B_{10}H_{10}-1-IPh-10-NC(H)_{2}] (8) would provide a third method (method C, Fig. 3) to obtain products 1. Here we explore all three methods for preparation of pyridinium derivatives 1.

![Fig. 2](image1)

![Fig. 3](image2)

The initial synthesis of series 1 focused on the three-step method using 4[Bu,N], which is more readily available than the 4[Et,N] salt.\textsuperscript{33} To determine the scope of the method, the reactivity of 4[But,N] with several nucleophiles in MeCN at 60 °C was screened in NMR tube reactions. The progress of each reaction was monitored by $^1$H NMR spectroscopy as the rate of disappearance of the starting anion 4. Results demonstrated that the reactivity follows the order N$_2$ $>$ CN $>$ Br $>$ SCN $>$ AcO$^-$ $>$ morpholine. It was noted that only the N$_2$ anion gave a single product, [closo-B_{10}H_{10}-1-N$_2$] (5d). The reaction of 4 with the CN anion was slower and the expected product was contaminated with a side product resulting from independent decomposition of 4 (complete decomposition after 16 hr in MeCN at 55-60 °C in the absence of any nucleophile). Other nucleophiles, SCN, AcO, morpholine, pyridine, Br, and I, gave complex mixtures of products in which the desired product was either a minor component, or was not formed at all (pyridine, morpholine, Br, and I). Consequently, only the preparation of products 1b and 1d appear to be practical with method A.

Anion 5b was obtained using a modification of our literature procedure (Scheme 1). Thus, the reaction of 4[But,N] with [Bu,N]CN at 55 °C in MeCN gave a crude product containing about 60–65% of the expected 5b and some unknown side products, from which pure 5b[But,N] was isolated in 50–55% yield by column chromatography followed
by recrystallization. The subsequent reaction of 5b[Bu4N] with PhI(OAc)2 in MeCN solutions gave 6b[Bu4N], which after purification with column chromatography was reacted with excess pyridine to give the expected product 1b[Bu4N] (Scheme 2). Synthesis of azide 1d[Bu4N] was more straightforward. Thus, 4[Bu4N] was smoothly reacted with 1.1 eq of [Bu4N]+N3 and the resulting azide 5d[Na4N] was isolated by column chromatography in 95% yield (Scheme 1). The azide subsequently converted to phenyliodination 6d[Na4N] and reacted with pyridine to give 1d[Na4N] in 55% yield for the two-step process (Scheme 2).

Iodo derivative 1e[Na4N] was obtained in 38% overall yield by reacting iodoide 5e[Na4N], obtained from 4[Na4N] according to the literature method (Scheme 1),33 with PhI(OAc)2 in MeCN followed by reaction of the resulting [closo-B10H8-1-1-10-1Ph]- (6e[Na4N]) with pyridine (Scheme 2). An alternative method of obtaining 6e[Na4N] directly from bisiodonium 7 (method B) with controlled amounts of BuLi was much less efficient, and the desired product was isolated in 25% yield from a complex mixture of products using column chromatography. To facilitate crystal growth for XRD analyses, the cation in 1e[Na4N] and in 1b[Na4N] was exchanged for [Et4N]+ using Dowex-50 exchange resin followed by treatment of the eluent with [Et4N]+OH-

The preparation of acetoxy, thiocyanato, and bromo derivatives (1c[Et4N], 1f[Et4N] and 1g[Et4N]) was accomplished using bisiodonium derivative 7 according to method B (Fig. 3). Thus, acetate 6c[Et4N], prepared as described before from 7,32 was reacted with excess pyridine to yield the desired product 1c[Et4N] in 74% yield. A similar reaction of 7 with 1.5 eq of [Et4N]+SCN in MeCN at 60 °C gave a mixture of products, from which 6f[Et4N] was isolated by column chromatography in 16% yield. The subsequent thermolysis of 6f[Et4N] in pyridine solutions gave 1f[Et4N] in 78% yield. Bromide 1g[Et4N] was obtained in 56% overall yield from 7 in the same two step sequence reaction with 75% yield for each 6g[Et4N] and 1g[Et4N]

Finally, dipyridinium derivative [closo-B10H8-1,10-2(NC6H4)] (1h) was obtained directly from bisiodonium 7 upon reaction with neat pyridine.

In an attempt to simplify the preparation of 1b[Na4N], bisiodonium 7 was reacted with 1.1 eq of the [Na4N]+CN in MeCN at 55 °C. The resulting mixture contained the desired 6b[Na4N] as the main component, which was isolated by column chromatography in 53% yield. This process turned out to be more convenient than method A, although poor solubility of bisiodonium 7 in the reaction medium complicated the reaction progress and product isolation.

Method B was also tested as one-pot preparation of the azide 1d[Na4N] and bromide 1g[Et4N] without purification of the intermediate monoiiodonium derivatives 6d and 6g. In this case the final products were obtained in 64% (1d[Na4N]), and 68% (1g[Et4N]) overall yields based on bisiodonium 7.

Results with 4 and 7 indicate that the presence of an onium substituent in the antipodal position facilitates substitution of the PhI group in derivatives of A. In an effort to improve the yield for the preparation of the thiocyano derivative 1f[Et4N], pyridinium derivative 8 was obtained by phenyliodination of 1a[Na4N] in MeCN and isolated in 69% yield (method C, Scheme 3). The subsequent reaction of 8 with [Na4N]+SCN in MeCN gave relatively clean conversion to product 1f[Et4N], which was isolated in 55% yield.

The demonstrated high reactivity of 8 towards SCN− suggests the possibility of its reaction with other nucleophiles even as weak as EtOH to obtain anion [closo-B10H8-1-NC6H4-10-OEt] (1i). Indeed, heating EtOH solutions of 8 at reflux demonstrated very slow progress towards a single product over several days. Heating of the reaction mixture at 110 °C in

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a pressure tube for 2 days led to the complete conversion of 8 to the protonated product tentatively assigned as structure 9 and isolated by chromatography in 69% yield (Scheme 3). A more accurate structure for the product might be 1i with an associated hydronium ion ([1i][H₃O]⁺), which is consistent with the waxy and sticky constitution of the product. Treatment with [Me₄N]⁺·OH·5H₂O in MeCN gave 1f[Me₄N], isolated in 53% yield as orange microcrystals.

Preparation of the morpholine derivative 1j required a different approach. Since 4[Bu₄N] did not react with morpholine in MeCN solutions, it was reacted with neat morpholine at 85 °C (Scheme 4). The resulting complex mixture of products was reacted with PhI(OAc)₂ in AcOH and the bis-zwitterion 6k was isolated in 30% yield by column chromatography. The subsequent reaction of 6k with neat pyridine gave the morpholium derivative 1k in 76% yield. Deprotonation of the morpholium group in 1k with [Et₄N]⁺·OH⁻ in MeCN solutions presumably led to the formation of the desired anion 1j, which was golden yellow, but unstable under the reaction conditions, and 1j[Et₄N] could not be isolated.

The same method was not successful for the preparation of the ethoxy derivative 1i, and pure phenyldonium 6i could not be isolated from complex reaction mixtures. Derivatives 2[Bu₄N] were obtained by reacting 4[Bu₄N] in neat liquid 4-substituted pyridines (Y = COEt, Me, OMe) at 80 °C (Scheme 5). For solid 4-cyanopyridine the reaction was conducted in concentrated solutions of 4[Bu₄N] in MeCN (0.55 M) in the presence of 5 eq of the nucleophile.

Finally, ion pair 3[Bu₄N] was prepared using an adaptation of method C shown in Scheme 3. Thus, 2b[Bu₄N] was converted to phenyldonium derivative 10, which was solvolyzed in EtOH at 120 °C and the resulting crude protonated product was treated with aqueous [Bu₄N]⁺·HSO₄⁻ and NaHCO₃ in CH₂Cl₂ (Scheme 6). The desired 3[Bu₄N] was isolated by column chromatography passivated with [Bu₄N]⁺·HCO₃⁻ in 22% overall yield based on 2b[Bu₄N].

Crystal and molecular structures

Yellow-greenish triclinic crystals of 1b[Et₄N] and 1g[Et₄N] and monoclinic crystals of 1c[Et₄N] and 1k were obtained from MeCN/EtOH solutions on cooling. Monoclinic crystals of 1d[Bu₄N] and 1e[Et₄N] were grown from MeCN/EtOAc solutions, while 1h crystallized from EtOH solutions on slow cooling. Orthorhombic crystals of 1f[Et₄N] were obtained by slow evaporation of MeCN/CH₂Cl₂ solutions. Crystals of 1j[Me₄N] suitable for XRD analysis could not be obtained. Selected bond lengths and angles are collected in Table 1. Molecular structures for all eight new derivatives are shown in Fig. 4.

Crystal systems of most salts 1[R₄N] contain a single ion pair in the asymmetric unit, while 1f[Et₄N] and the previously reported 1a[Et₄N] contain two anions and two cations. The thiocyanato derivative 1f exhibits positional disorder of the SCN group in both unique molecules. In contrast, the [R₄N]⁺ cation is positionally disordered in most salts with the exception of 1b[Et₄N] and 1e[Et₄N] and 1g[Et₄N]. Additionally, 1g[Et₄N] co-crystallizes with an acetonirole molecule highly disordered around the special position. Therefore, the solvent molecule was removed from the model using the SQUEEZE tool in PLATON program. 34

The intragro dimensions of the anions, such as B–B bond distances and angles, are typical for (closo-B₁₀) derivatives. 28, 35 (Table 1). In general, the more electron withdrawing the substituent, the more contracted the B₁₀ cage, 35 although there is no linear correlation of the B(1)–B(10) distance with Hammett 36 parameters σₘ. 35 The substituent effect is evident from a comparison of the B(1)–B(10) distance in the parent anion [closo-B₁₀H₁₀]²⁻ (A, 3.717(4) Å), 38 monopyridinium 1b–1g (avg 3.636(14) Å) and bis-zwitterion 1h (3.620(3) Å) and 1k (3.611(2) Å). The response to the substituent is largely localized at the substitution apex, which results in contraction of the square pyramid (distance from the equatorial belt). Thus, substitution of the parent anion A with pyridinium results in a contraction of the pyramid from 1.100 Å to 1.056 Å in 1a, which remains nearly constant in the series (Table 1). The pyramid height of the opposite apex is barely affected by substitution with a pyridinium group, but it does respond to the presence of substituent X. For example, the
pyramid height ranges from 1.095 Å for 1a (X = H) to 1.060 for 1e (X = I).

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<th>1d[BuN]</th>
<th>1e[EtN]</th>
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<th>1g[EtN]</th>
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* Deviation in ° from the ideal staggered orientation of pyridine.

The pyridine–B(1) distance of 1.527(3) Å is essentially the same in the entire series, within experimental error, for all 9 derivatives. The orientation of the pyridine ring varies from nearly ideally staggered in 1b to more than half way between staggered and eclipsed (34° off the staggered conformation in 1a, Table 1). Orientation of the functional groups, OAc, N3 and SCN is about half way between the staggered and eclipsed conformations, while the morpholinum group adopts a nearly ideal staggered orientation with respect to the [closo-B10] cage (7.1° off the ideal staggered).

Fig. 4 Atomic displacement ellipsoid representation of 1b–1h and 1k. For geometrical dimensions see Table 1 and the text. In 1b–1g counterions are omitted for clarity and in 1f only one unique molecule is shown. The corresponding ellipsoids are at the 50% probability level and the numbering system corresponds to the chemical structure.

The B(10)–X distances in derivatives 1i are typical for other derivatives of the [closo-B10H10]+ cation containing B(1)–CN,35 B(1)–OCOR,36 B(1)–I,33,39 B(1)–SCN,40 B(2)–Br,41 and B(1)–NH2 substituents. The structure of compound 1d represents the first example of azido derivative of a closo-borane. The azido group is nearly linear with the angles α.N.N = 175.6(2)° and α.B.N = 120.9(1)°. Interestingly, the N(1)–N(2) and N(2)–N(3) distances are similar (1.185(2) and 1.154(2) Å, respectively) and much different from those in typical organic azides (e.g. 1.229(3) and 1.128(3) Å in 1,6-diazidodiadamantane;43 1.242(3) and 1.130(3) Å in 4-Me2NPHN3).44 This is consistent with a shift in negative charge to the terminal nitrogen atom (N3) and significant contribution from the second resonance structure (R–N≡N=N → R–N=N=N) [Et].

The supramolecular assembly of the cyano derivative 1b[EtN] appears to be isostructural with that observed in the bromo derivative 1g[EtN] (Fig. 5). The unit cell dimensions c are nearly the same for 1b[EtN] and 1g[EtN], while dimensions a and b are slightly different in the two structures. The unit cell identity parameter π = 0.0006 indicates a close resemblance between these two unit cells. Moreover, their crystal structures adopt similar molecular packing. In both of them, molecules of 1b and 1g are assembled in infinite chains running along the [100] direction. These chains are stabilized by C−H−B interactions between the pyridine C−H fragment and the boron cluster. The respective intermolecular contacts in 1b[EtN] and 1g[EtN] are 0.337 Å and 0.274 Å shorter than the sum of the van der Waals radii, respectively. Additionally, neighbouring chains are associated through B−C interactions between the boron moiety and the pyridine ring. These contacts for 1b[EtN] and 1g[EtN] are -0.181 Å and -0.127 Å, respectively, inside the van der Waals separation. The resulting double chains running along [100] direction are separated from each other by counterion molecules. Although iodine is regarded as an isomorphous substituent with bromine, the crystal packing of 1e[EtN] is completely different from those observed in 1b[EtN] and 1g[EtN]. In this case the molecular assembly in 1e[EtN] is affected by the presence of the solvent molecule in the crystal lattice.
**Molecular modelling**

For a better understanding of properties of the investigated compounds, their electronic structures and excitation energies were modelled using the TD-DFT method at the CAM-B3LYP/Def2TZVP // B3LYP/Def2TZVP level of theory in MeCN dielectric medium. Optimizations in series 1 performed with the B3LYP/Def2TZVP method in a weak dielectric medium of PhCl gave accurate molecular geometries, as determined by comparison with selected experimental dimensions: the B(1)–B(10) distance was overestimated by 0.012(4) Å, and B–pyridine and B–X distances were underestimated by –0.006(13) and –0.004(3) Å, respectively. The necessity for inclusion of a weak dielectric medium in geometry optimization of boron zwitterions was demonstrated previously. Other basis sets (e.g., TZVP and M06-2x) or lack of dielectric medium give significantly less accurate results.

**Photophysical properties**

Absorption and emission properties were investigated for all compounds in series 1 and 2 in MeCN solutions, while solvent effects on photophysical properties were studied for the prototypical 1a[Bu4N], a representative for both series. Photoluminescent properties in series 1 and 2 were also investigated in the solid state and for two selected derivatives in aggregates.

**Solution spectroscopy in MeCN.** Electronic absorption spectra measured in MeCN solutions revealed two distinct bands above 200 nm in all compounds in series 1 and 2: a weak, higher energy band and a broad, medium intensity, lower energy band (Figs. 6 and 7). The former band can be attributed to a π–π* transition in the pyridine ring, since it shows essentially no dependence on substituent X in series 1 and weak dependence on Y in series 2. In contrast, the position of the lower energy band exhibits a strong substituent dependence in the boron cluster (X in series 1, Fig. 6, Table 2) and in the pyridine ring (Y in series 2, Fig. 7). In addition, there is a significant solvatochromic effect (*vide infra*), consistent with assignment as an intramolecular charge transfer (CT) excitation. This assignment is supported with results from TD-DFT calculations: the lowest energy absorption band in 1 and 2 is a (π,π*) excitation involving a transition from the HOMO, localized primarily on the boron cluster, to the LUMO, localized on the pyridinium fragment, as shown for 1b in Fig. 8.

Analysis of the data in Table 2 indicates that the energy of the CT band decreases in series 1 with decreasing electron-withdrawing character of the substituent X from 3.769 eV for 1k (X=NR2) to 3.151 eV for 1i (X=OEt). Data for 1j with the most electron-donating NR2 substituent is uncertain due to its chemical instability. In series 2 the substituent effect is opposite and the energy decreases with increasing electron-withdrawing character of the substituent Y from 3.652 eV for 2n (Y=OMe) to 2.743 eV for 2b (Y=CN). These results lead to the conclusion that X primarily affects the energy of the HOMO, while Y impacts the energy of the LUMO in derivatives of 1a.

Finally, anion 3, which combines the most electron donating substituent X in series 1 and most withdrawing group in series 2 shows an intense absorption at 501.5 nm. This is in agreement with expectations.
Table 2. Experimental and DFT calculated energies of the CT excitation, and emission energies in MeCN solutions and solid state.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption $\lambda_{max} \rightarrow \pi^*$</th>
<th>Emission $\lambda_{em}$ (Stokes Shift)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experimental $\lambda$ (nm)</td>
<td>theoretical $\lambda$ (nm)</td>
</tr>
<tr>
<td>1a</td>
<td>365.0 (3.85)</td>
<td>312.5 (0.291)</td>
</tr>
<tr>
<td>1b</td>
<td>339.0 (3.85)</td>
<td>295.7 (0.334)</td>
</tr>
<tr>
<td>1c</td>
<td>368.5 (3.88)</td>
<td>316.1 (0.278)</td>
</tr>
<tr>
<td>1d</td>
<td>365.0 (3.90)</td>
<td>322.6 (0.328)</td>
</tr>
<tr>
<td>1e</td>
<td>357.0 (3.92)</td>
<td>305.3 (0.332)</td>
</tr>
<tr>
<td>1f</td>
<td>344.5 (3.81)</td>
<td>306.6 (0.324)</td>
</tr>
<tr>
<td>1g</td>
<td>358.0 (3.91)</td>
<td>306.8 (0.314)</td>
</tr>
<tr>
<td>1h</td>
<td>335.0 (4.20)</td>
<td>298.8 (0.550)</td>
</tr>
<tr>
<td>1i</td>
<td>393.5 (3.84)</td>
<td>345.2 (0.293)</td>
</tr>
<tr>
<td>1j</td>
<td>f</td>
<td>370.0 (0.279)</td>
</tr>
<tr>
<td>1k</td>
<td>329.0 (3.84)</td>
<td>287.4 (0.323)</td>
</tr>
<tr>
<td>2b</td>
<td>452.0 (3.98)</td>
<td>390.3 (0.417)</td>
</tr>
<tr>
<td>2l</td>
<td>431.0 (3.95)</td>
<td>368.5 (0.403)</td>
</tr>
<tr>
<td>2m</td>
<td>357.5 (3.93)</td>
<td>302.9 (0.336)</td>
</tr>
<tr>
<td>2n</td>
<td>339.5 (3.79)</td>
<td>288.4 (0.370)</td>
</tr>
<tr>
<td>3</td>
<td>501.5 (3.94)</td>
<td>448.8 (0.436)</td>
</tr>
</tbody>
</table>

* Recorded in MeCN. For full-range absorption spectra see the ESI. † Obtained with the TD-CAM-B3LYP/Def2TZVP // B3LYP/Def2TZVP method in MeCN dielectric medium. ‡ Excitation at the wavelength of maximum absorption. ‡ Ref. ‡ No emission. †† Unreliable data.

Derivatives 1, except for 1e (X=I), 1g (X=Br) and 1i (X=OEt), and also derivatives 2m (Y=Me), 2n (Y=OMe) and 3, fluoresce weakly in MeCN solutions at substantially lower energies (Table 2, Fig. 6 and 7). The most fluorescent in these series appear to be 1h, 1k and 2n, which are structurally similar to pyridinium derivatives that have measured quantum yields of 2-4% in MeCN solutions. Excitation at the wavelength of maximum absorption. Excitation at the wavelength of maximum absorption.

Solvatochromism. To determine the effect of the medium on photophysical processes in series 1 and 2, absorption and emission spectra were recorded for the parent derivative 1a[BuN]$_2$, a representative of both series, in eight solvents covering the full range of polarity. Results shown in Fig. 9 demonstrate a negative solvatochromatic effect on the CT and emission bands: the energies increase with increasing polarity of the solvent. Thus, $\lambda_{max}$ of the CT band decreased from 401.5 nm for THF solution to 338.5 nm for formamide solution ($\DeltaE$= 0.575 eV), while the emission spectra changed from 582.0 nm to 338.0 nm in the same solvents ($\DeltaE$=0.157 eV). It is notable that the order of solvents effects is not the same for absorption and emission. Also, the Stokes shift diminishes with decreasing solvent polarity from 1.375 eV for formamide to 0.957 eV for THF. These observations are consistent with strong solvation of the anionic $S_0$ state (GS) and weaker solvent effects on the zwitterionic $S_1$ state.

Comparison of the experimental excitation energies for 1a[BuN]$_2$ with solvent E$_{30}$ parameters demonstrates a linear correlation for all data points except for those obtained in CH$_2$Cl$_2$ (Fig. 10). The slope of the best-fit line indicates that the solvent affects the electronic absorption of 1a less than it does the reference pyridinium N-phenolate betaine dyes by about 30%. Similar analysis of the emission energy shows poorer correlation with the E$_{30}$ parameters and a significantly smaller solvatochromic effect of about a quarter of that observed for the absorption energies.

Fig. 9. Normalized absorption (top) and emission (bottom) spectra for 1a[BuN]$_2$ in selected solvents plotted to show the top of the absorption peak.

Fig. 10. Correlation of absorption (blue) and emission (black) energies and the Stokes shift (green) for 1a[BuN]$_2$ with solvent parameter E$_{30}$. The best-fit lines (excluding the datapoint for CH$_2$Cl$_2$ in red): $E_a$ = 45.2(26)+0.716(45)×E$_{30}$, $r^2 = 0.967$; $E_em$ = 42.9(20)+0.174(45)×E$_{30}$, $r^2 = 0.975$; $E_{em,max}$= 58.47(24)+E$_{30}$, $r^2 = 0.943$.

Solid-state and aggregation-induced emission (AIE). Most polycrystalline samples of 1 and 2 fluoresce when irradiated with UV light (Table 2). Interestingly, even 1e and 1g are photoluminescent in the solid-state despite the presence of a heavy halogen and lack of emission in MeCN solutions. Compound 1i exhibits solid-state fluorescence at $\lambda_{max}$ = 572 nm, the lowest energy emission of the series. However, derivative 1d (X=NH$_2$), which fluoresce, and two pyridinium derivatives, 2b (Y=CN) and 2l (Y=COOEt), which do not fluoresce in solution, are not photoluminescent in the solid-
state. The emission energy in the solid state is higher than that in MeCN solutions, as shown for 1b in Fig. 11. Consequently the Stokes shifts are lower by an average of 0.275(38) eV in all derivatives.

![Graph showing emission energy comparison between MeCN solution, solid-state, and different concentrations of MeCN solution in water.](image)

**Fig. 11.** Emission of 1b [X=CN] in solution (black), solid-state (green), 10% MeCN solution in H2O (red) and 1% MeCN solution in H2O (blue). The intensity in arbitrary units expected for relative 10% (red) and 1% (blue) solutions. The arrow shows a 13 times relative increase.

Finally, aggregation induced emission (AIE) was briefly investigated for two representative derivatives: 1b[Bu3N] and 1e[Et3N]. In the former case, a mixture of MeCN solution with H2O (1:10 ratio) showed emission at 517 nm, which is an intermediate energy between that in MeCN solution (538.5 nm) and that in solid-state (486.5 nm, Fig. 11). In contrast, a blue shift of 1:100 and 1:10 times relative increase.

Data analysis. Analysis of experimental photophysical data is enriched by comparison with calculated excitation energies and by correlation analysis with substituent parameters.36 Hammett σp parameters, often used in such analyses, are not available for all substituents X, or they have uncertain values. For the purpose of the present work they were derived from a correlation analysis of 1H NMR data for 20 monosubstituted benzene derivatives Ph–X in acetone-d6: N-morpholinyl (–0.58), acetoxy (0.00), and N-morpholinium (0.48).17 Particularly noteworthy is the revised σp value for the OAc group, which is significantly lower than that originally reported,17 (0.31) and fits the trends for σp values for related substituents (e.g. σp = 0.13 for OCOPh) and other correlations.35

Correlation of the substituent effect with the position of the CT band reveals an excellent linear dependence on the σp values in both series of derivatives with r² > 0.98 (Fig. 12). The correlation does not include the data for morpholine derivatives 1j and 1k and for 1l (X = OEt). For anion 1j, the σp value for the morpholinium group derived from the protonated N-phenylmorpholine is significantly underestimated (σp = 0.48 vs σp = 0.82 for the NMe3 group). This is presumably related to the high basicity of the amino group in {closo-B10} derivatives46,50 and the lack of dissociation in acetone solutions. In contrast, the reference compound for 1H NMR analysis, the N-phenylmorpholinium cation, can exist in equilibrium with the free amine, resulting in a lower-than-expected σp value. Using the correlation for the remaining seven data points in series 1, the expected energy of absorption for 1j was estimated at 3.13(1) eV (396 nm), which is consistent with a shoulder band in the absorption spectrum of 1j generated in situ.17 Using the same correlation, the expected value σp for the morpholinium group was determined to be 0.92(1), which is reasonable considering the accepted Hammett value of 0.82 for the NMe3 group36 and the electron withdrawing character of the oxygen atom in morpholine (e.g. σp = –0.72 for the NMe3 group and –0.58 for N-morpholine).

![Graph showing Hammett correlation of the CT energy in series 1 (black diamonds) and 2 (red dots) with σp substituent parameters. The magenta diamonds indicate the data points for morpholine derivatives 1j and 1k, and the blue diamond for 1l. Best-fit functions excluding morpholine and 1j derivatives: for series 1 (black) E_{CT} = 3.377(9) + 0.424(26) \times \sigma_p, r^2 = 0.981 and for series 2 (red) E_{CT} = 3.36(2) + 0.97(6) \times \sigma_p, r^2 = 0.987.](image)

**Fig. 12.** Hammet correlation of the CT energy in series 1 (black diamonds) and 2 (red dots) with σp substituent parameters. The magenta diamonds indicate the data points for morpholine derivatives 1j and 1k, and the blue diamond for 1l. Best-fit functions excluding morpholine and 1j derivatives: for series 1 (black) E_{CT} = 3.377(9)+0.424(26)\times\sigma_p, r^2 = 0.981 and for series 2 (red) E_{CT} = 3.36(2) − 0.97(6)\times\sigma_p, r^2 = 0.987.

The experimental absorption wavelength for anion 1l was 15 nm higher than expected from the correlation (Fig. 12). This discrepancy might be due to a different type of interaction of the alkoxy group with the 3-D aromatic {closo-B10} cluster than with the π-system of benzene, from which the σp values were derived. Only one of the two lone pairs of the oxygen atom interacts with the benzene π-system, whereas both unshared electron pairs interact simultaneously with the π-system of the {closo-B10} cluster (Fig. 13), presumably resulting in the strong
substituent effect of the OEt group. This conclusion is consistent with the fact that the calculated and experimental (π,π*) CT energies for 1I fit the trend for other derivatives.

Analysis of the slopes of the two correlation lines in Fig. 12 indicates that the substituent Y (on the pyridine ring) has greater than twice the impact on the excitation energy than substituent X in the boron cluster derivatives of 1a (slopes 0.97 vs 0.42, respectively).

TD-DFT calculations in a MeCN dielectric medium at the CAM-B3LYP/Def2TZVP // B3LYP/Def2TZVP level of theory reproduced the trends in the experimental CT energies in both series of compounds (Fig. 14). The data show better correlation in series p (r² = 0.999), in which substituent Y is varied on the pyridine ring (slope 1.23±0.02). In contrast, the correlation data for series o is somewhat scattered (r² = 0.89, slope 1.145±0.006), presumably due to the conformational properties of {closo-B10H10} derivatives. Combined datapoints for both series give a good overall linear correlation with a slope of 1.154(5).

Discussion

The present work demonstrates extensive functionalization of the apical position of the {closo-B10H10}2– anion (A) with a diverse set of substituents. Three general approaches to heterodisubstituted derivatives of A revealed significant differences in reactivity of aryliodonium intermediates towards nucleophiles. Thus, the presence of an onium substituent in the antipodal position of the {closo-B10H10} cluster increases reactivity towards nucleophilic substitution, presumably through withdrawing of electron density from the iodine center. Consequently, phenyliodonium derivatives 7 and 8 are more reactive than mono-phenyliodonium derivatives 4 and 6. The latter can be obtained with significant selectivity by monosubstitution of 7 with a more reactive nucleophile.

The order of reactivity revealed in the synthetic work is much different from that expected based on standard nucleophilicities.51 Thus, the observed reactivity towards 4 in MeCN followed the order: N3– > CN– > pyridine > amines, OAc, Br, SCN > EtOH, while the nucleophilicity parameter N follows a different order OAc > N3– > CN– > R3NH > Br > SCN > pyridine > EtOH for reactions in MeCN.52 The surprising lack of reactivity between the phenyliodonium zwitterions of boron clusters and amines was noted previously for derivatives of the {closo-1-CB11H11}2– anion.22 Thus, the observed reactivity dictates
the method of installation of functional groups in the \([\text{closo-B}_\text{lo}H_{10}]^2\) anion and the preparation of heterodisubstituted derivatives of A.

Using the first method (method A), 4 reacts stoichiometrically with highly reactive nucleophiles (e.g., CN\(^{-}\) and \(\text{N}_2\)) and also reacts with an excess (e.g. 2b) or neat (e.g. 1a, 2i–2n) pyridines to give relatively clean monosubstitution products. On the other hand, thermolysis of 4 in neat morpholine, a secondary amine, gives a complex mixture of products containing about 50% of the expected derivative 5k. The pure product is isolated as bis-zwitterion 6k after installation of the PhI\(^{+}\) group.

Using the second method (method B) 7 reacts with moderately reactive nucleophiles to substitute one of the two phenyliodonium groups with high selectivity giving 6. Loss of the onium fragment (PhI\(^{+}\)) deactivates the second phenyliodonium towards substitution. In a variation of this method (method C), the pyridinium substituent is used to activate the phenyliodonium leaving group in 8, which reacts smoothly with weak nucleophiles including EtOH, giving an alternative approach to series 1. The process is, however, limited to nucleophiles that do not attack the pyridinium substituents causing ring-opening. The reaction with EtOH is particularly noteworthy. It represents a convenient alternative to the preparation of 1-alkoxy derivatives of anion A, which were obtained before from \([\text{closo-B}_\text{lo}H_{10}]-1-\text{OH}\)^2, or attempted direct 1-alkoxylation.\(^{52, 53}\)

Substitution of the \([\text{closo-B}_\text{lo}H_{10}]^2\) anion through aryliodonium intermediates can be complicated by several types of side processes. The most important pathway is the formation of B–I instead of B–Nu derivatives through single electron transfer from the Nu to the iodine center. The second factor affecting isolation of pure products is the enhanced chemical stability), the LUMO presumably could be lowered and at least partial loss of the \([\text{R}_2\text{N}]^+\) counterion. For instance, X=OH was recently shown to be a fully protonated oxonium ion.\(^{35}\) Morpholinium 1k was fully protonated and all attempts to remove the proton to obtain 1l resulted in decomposition. Also acetate 1c, azide 1d and ethoxide 1l tend to partially protonate. Protonation can be avoided by treatment with \([\text{R}_2\text{N}]^+\text{OH}\) and by using \([\text{R}_2\text{N}]^+\text{HCO}_3\) for chromatography. A desirable substituent that is electron-donating but lacks basic centers available for protonation is the alkyl group (\(\sigma_p \approx -0.15\)).\(^{36}\) but unfortunately there is currently no synthetic access to alkyl derivatives of the \([\text{closo-B}_\text{lo}]^2\) cluster.

Another source of impurities is facile halogenation with electrophiles that may be formed during reactions with PhI(OAc)_2, if the solution contains any halide anion (e.g. from the \([\text{R}_2\text{N}]^+\text{X}\)). For example, 11 was identified by XRD analysis as a contaminant in a batch of 1g, prepared using excess \([\text{Et}_4\text{N}]^+\text{Br}\).

Photophysical results demonstrate that the judicious choice of X and Y in the derivatives of \([\text{closo-B}_\text{lo}H_{10}-1-\text{NC}_3\text{H}_2]^{-}\) (1a) allows the tuning of the \([\text{closo-B}_\text{lo}]^2\) photophysical properties through strategic adjustment of the HOMO and the LUMO energies. While most derivatives 1 and 2 absorb in the range 300–450 nm, pushing the electronic absorption to lower energies requires a strongly electron donating substituent X and a strongly electron withdrawing Y. Among the substituents X, the most electron donating substituent X that gives chemically stable derivatives is ethoxy, while the most electron withdrawing substituent Y reported here is cyano. To test the additivity of substituent effects established for individual series of derivatives, compound 3 was synthesized and characterized (Fig. 16). Using the TD-DFT calculated excitation energy and the correlation in Fig. 14, the predicted electronic absorption in 3 is at \(\lambda_{\text{max}} = 518±2\) nm, which compares favorably to the value observed experimentally (\(\lambda_{\text{max}} = 501.5\) nm).

Although an alkoxy group appears to be the limit for a substituent effect X to increase the HOMO energy (due to chemical stability), the LUMO presumably could be lowered further by using substituents such as NO2 (\(\sigma_p = 0.78\)) and SO2CF3 (\(\sigma_p = 0.98\))\(^{36}\) that are more strongly electron withdrawing than CN (\(\sigma_p = 0.66\)).

**Conclusions**

The synthetic work reported here has demonstrated that an extensive set of functional groups at the apical position of the \([\text{closo-B}_\text{lo}H_{10}]^2\) anion is accessible through four general approaches and two phenyliodonium zwitterions, 4 and 7. Structural analysis confirmed the dependence of the \([\text{closo-B}_\text{lo}]^2\) cluster geometry on the electronic nature of the apical
substituent, while DFT calculations confirmed the need for a weak dielectric medium for proper geometry optimization.

Spectroscopic investigation of series 1 and 2, supported with TD-DFT calculations, revealed significant substituent and solvent effects on the position of the (π,π*) CT band in the prototypical chromophore \([\text{closo-B}_{10}\text{H}_{10}-1-\text{NC}_{2}\text{H}_{5}] (1\text{a})\), which allows the CT absorption band to be tuned in the visible range. Substituents on the pyridine ring (series 2) affect the LUMO 2.4 times more strongly than substituents on the (\text{closo-B}_{10}) cluster impact the HOMO (series 1). The most electron donating substituent that is available to increase the level of the HOMO in chemically stable derivatives of anion \(\text{A}\) is the \(\text{EtO}\) group, and its effect is significantly stronger than might be expected from the \(\sigma_p\) parameter. Greater latitude in substituent choice is observed in controlling the LUMO. A combination of the \(\text{EtO}\) and CN (\(\sigma_p = 0.66\)) substituents increased the \(\lambda_{\text{max}}\) from 365 nm in 1a to 501.5 nm in 3. Further contraction of the HOMO–LUMO gap to access the low energy range of the visible spectrum is likely possible through more strongly electron withdrawing substituents such as \(\text{NO}_2\) (\(\sigma_p = 0.78\)).

About two thirds of the compounds in series 1 and 2 exhibit weak or moderate solution fluorescence, with a smaller substituent impact on the energy range (0.21 eV). Substituents \(X\) that quench solution fluorescence of the parent 1a are halogens (\(\text{Br}, \text{I}\)) or OEt connected directly to the (\text{closo-B}_{10}) cluster (series 1), and COOEt and CN groups on the pyridine ring (series 2). The Stokes shift in these derivatives is substituent-dependent and ranges from 1.084–1.432 eV. Many compounds, even the \(\text{Br}\) and \(\text{I}\) derivatives, but not the \(\text{N}_3\) derivative, exhibit solid-state emission with a smaller Stokes shift (~1 eV) than solutions. Two selected derivatives containing CN (1b) and I (1e) substituents, also demonstrated aggregation-induced emission (AIE) in highly dilute MeCN/\text{H}_2\text{O} solutions.

The substantial solvatochromatic effects observed for 1a offer additional means to manipulate the position of the absorption band in the range of \(\Delta E = 0.575\) eV for solvents ranging from THF (\(E_1 = 37.5\)) to formamide (\(E_1 = 55.9\)). The solvatochromatic effect for 1a is about 70% of that observed for the reference pyridinium betaines that define the \(E_1\) scale. A solvent effect is also observed for emission, although the magnitude is much smaller, about one quarter of that in the absorption spectra. The additivity of the established correlations for series 1 and 2 was demonstrated on anion 3, which allows the prediction of the CT band energy in other derivatives in selected media.

The results presented here demonstrate synthetic access to a broad range of substituents at the apical position of the \([\text{closo-B}_{10}\text{H}_{10}]^2\) anion and describe basic relationships between the structure and photophysical properties of these derivatives. Photophysical effects and behaviour observed in series 1 and 2 demonstrate the potential for the \([\text{closo-B}_{10}\text{H}_{10}]^2\) anion to serve as the key building block for a new class of photonic materials with substituent- and medium-tunable intramolecular CT absorption and emission.

**Computational Details**

Quantum-mechanical calculations were carried out using the Gaussian 09 suite of programs. Geometry optimizations were performed with the B3LYP method and Def2TZVP basis set using tight convergence limits and appropriate symmetry constraints. All calculations were performed in PhCl dielectric medium (arbitrarily chosen) with the PCM model supplied in the Gaussian package. The equilibrium geometry for each compound was obtained in a PhCl dielectric medium (vide supra). The solvation model was implemented with the PCM model using the SCRF(solvent= name) keyword.

**Experimental section**

**General.** Reagents and solvents were obtained commercially. Anion \([\text{closo-B}_{10}\text{H}_{10}]^2\) was obtained from \(\text{B}_{10}\text{H}_{12}\) according to a literature procedure. Reactions were conducted in an argon atmosphere and subsequent manipulations in air. TLC analyses were conducted on silica gel plates 60-F254. Column chromatography was performed using 70-230 mesh silica gel (Merck). Melting points were recorded uncorrected in capillary tubes or by DSC. NMR spectra were obtained at 500 MHz (\(\text{H}\)), 126 MHz (\(\text{C}\)) and 160 MHz (\(\text{N}\)) in acetonitrile-\(d_6\) unless specified otherwise. Chemical shifts were referenced to the solvent (acetonitrile-\(d_6\)). NMR spectra were obtained at 500 MHz (\(\text{H}\)) and 126 MHz (\(\text{C}\)) and 160 MHz (\(\text{N}\)) in acetonitrile-\(d_6\). NMR chemical shifts were taken from the H-decoupled spectra. IR spectra were recorded for neat samples using an ATR attachment. HR mass spectrometry was conducted with the TOF-MS ES method most often in the negative mode.

Preparation of 6[RnN] and other intermediates is provided in the ESI.

**General procedure for the preparation of [closo-B_{10}H_{10}-1-X-10-NC_{2}H_{5}] (RnN).** Iodonium derivative 6[RnN] was obtained from \(\text{B}_{10}\text{H}_{12}\) and to an external sample of neat BF\(_3\)•Et\(_2\)O in acetonitrile-\(d_6\) and to an external sample of neat BF\(_3\)•Et\(_2\)O in acetonitrile-\(d_6\). 11B NMR chemical shifts were taken from the H-decoupled spectra. IR spectra were recorded for neat samples using an ATR attachment. HR mass spectrometry was conducted with the TOF-MS ES method most often in the negative mode.

**Method A/B from [closo-B_{10}H_{10}-1-Ph-10-X] (6[RnN]).** Iodonium derivative 6[RnN] was obtained from \(\text{B}_{10}\text{H}_{12}\) and to an external sample of neat BF\(_3\)•Et\(_2\)O in acetonitrile-\(d_6\) and to an external sample of neat BF\(_3\)•Et\(_2\)O in acetonitrile-\(d_6\). 11B NMR chemical shifts were taken from the H-decoupled spectra. IR spectra were recorded for neat samples using an ATR attachment. HR mass spectrometry was conducted with the TOF-MS ES method most often in the negative mode.

**Method C from [closo-B_{10}H_{10}-1-Ph-10-(NC_{2}H_{5})] (8).** Iodonium derivative 8 was obtained from \(\text{B}_{10}\text{H}_{12}\) and to an external sample of neat BF\(_3\)•Et\(_2\)O in acetonitrile-\(d_6\). 11B NMR chemical shifts were taken from the H-decoupled spectra. IR spectra were recorded for neat samples using an ATR attachment. HR mass spectrometry was conducted with the TOF-MS ES method most often in the negative mode.
at 110 °C for 2 days. Volatiles were removed under vacuum, the semi-solid residue was washed with hexanes and then with dilute HCl (except when EtOH was used), dried and purified by column chromatography (SiO₂, MeCN/CH₂Cl₂) giving the desired product 1[R(N)] as the first main fraction. The product was further purified by recrystallization, usually from EtOH/CH₂Cl₂.

**[closob-B₂H₂₋1-NC₅H₄][Bu₂N⁺]** (1a[Bu₂N]). Starting with 6a made with method A: 35 mg (50% yield); yellow powder, Rᵣ = 0.2 (MeCN/CH₂Cl₂ 1:15); mp 167 °C; ¹H NMR (500 MHz, acetone-d₆) δ 0.03–1.22 (m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (s, J = 7.4 Hz, 8H), 1.76 – 1.85 (m, 8H), 3.34 – 3.51 (m, 8H), 3.88 (br q, J = 14.5 Hz, 1H), 7.90 (t, J = 7.2 Hz, 2H), 8.35 (tt, J₁ = 7.7 Hz, J₂ = 1.1 Hz 1H), 9.57 (d, J = 5.4 Hz, 2H); ¹³C NMR (126 MHz, acetone-d₆) δ 13.9, 20.4, 24.5, 59.5, 126.5, 141.4, 148.8; ¹⁹F NMR (160 MHz, acetone-d₆) δ -27.4 (d, J = 135 Hz, 4B), -23.4 (d, J = 130 Hz, 4B), 4.7 (d, J = 146 Hz, 18), 13.9 (s, 1B); UV (MeCN) λₘₐₓ (log ε) 365.0 nm (3.85); IR, ν 2487 (1H), 1470, 1007, 778, 692 cm⁻¹; HRMS (ESI-) m/z calc. for C₁₂H₂₂F₂N₂O₃: 256.2117, found: 256.2141. Anal. Calcld. for C₁₂H₂₂F₂N₂O₃: C, 64.68; H, 9.44; N, 7.28. Found: C, 64.78; H, 9.34; N, 7.17.

**[closob-B₂H₂₋1-NT₄₋10-NC₅H₄][Bu₂N⁺]** (1d[Bu₂N]). Starting with 6d made with method A: 80 mg (83% yield) and 123.5 mg (64%) overall yield with method B: pale yellow-green crystals from MeCN/EtOAc; Rᵣ = 0.90 (9% MeCN in CH₂Cl₂); mp 156 °C; ¹H NMR (500 MHz, acetone-d₆) δ 0.52–1.25 (m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (s, J = 7.4 Hz, 8H), 1.82 (qu, J = 7.7 Hz, 2H), 3.34–3.51 (m, 8H), 3.88 (br q, J = 14.5 Hz, 1H), 7.90 (t, J = 7.2 Hz, 2H), 8.35 (tt, J₁ = 7.7 Hz, J₂ = 1.1 Hz 1H), 9.57 (d, J = 5.4 Hz, 2H); ¹³C NMR (126 MHz, acetone-d₆) δ 13.9, 20.4, 24.5, 59.5, 126.4, 141.9, 149.3; ¹⁹F NMR (160 MHz, acetone-d₆) δ -27.8 (d, J = 132 Hz, 4B), -25.6 (d, J = 131 Hz, 4B), 12.0 (s, 18), 18.4 (s, 1B); IR, ν 2478 (1H), 2112 (N₂), 1470, 1425, 998, 773, 692 cm⁻¹; UV (MeCN) λₘₐₓ (log ε) 365.0 (3.90); HRMS (ESI-) calc. for C₁₄H₂₄F₂N₄O₃: m/z = 239.2076, found: 239.2084. Anal. Calcld. for C₁₄H₂₄F₂N₄O₃: C, 52.57; H, 10.30; N, 14.60. Found: C, 52.34; H, 10.16; N, 12.91.

**[closob-B₂H₂₋1-1-I-10-NC₅H₄][Bu₂N⁺]** (1e[Bu₂N]). Method A. Starting with 6e: 52 mg (46% yield); pale yellow-green crystals from ACN/EtOAc; Rᵣ = 0.93 (9% MeCN in CH₂Cl₂); mp 192 °C; ¹H NMR (500 MHz, acetone-d₆) δ 0.40–1.20 (br m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (s, J = 7.2 Hz, 8H), 1.82 (qu, J = 7.7 Hz, 2H), 3.34–3.51 (m, 8H), 3.88 (br q, J = 14.5 Hz, 1H), 7.90 (t, J = 7.2 Hz, 2H), 8.35 (tt, J₁ = 7.7 Hz, J₂ = 1.5 Hz 1H), 9.57 (d, J = 6.5 Hz, 2H); UV (MeCN) λₘₐₓ (log ε) 366.0 nm.

**[closob-B₂H₂₋1-1-CN-10-NC₅H₄][Bu₂N⁺]** (1b[Bu₂N]). Starting with 6b made with method B: 83 mg (60% yield) pale yellow-green crystals from MeCN/CH₂Cl₂; Rᵣ = 0.71 (9% MeCN in CH₂Cl₂); mp 180 °C; ¹H NMR (500 MHz, acetone-d₆) δ 0.44–1.24 (br m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (s, J = 7.4 Hz, 8H), 1.82 (qu, J = 8.0 Hz, 8H), 3.42 (m, 8H), 7.99 (t, J = 7.1 Hz, 2H), 8.45 (t, J = 7.7 Hz, 1H), 9.53 (d, J = 5.3 Hz, 2H); ¹³C NMR (126 MHz, acetone-d₆) δ 13.9, 20.4, 24.5, 59.5, 127.0, 142.6, 148.7; ¹⁹F NMR (160 MHz, acetone-d₆) δ -24.5 (d, J = 151 Hz, 4B), -23.4 (d, J = 142 Hz, 4B), -4.9 (s, 1B), 19.0 (s, 1B); IR ν 2481 (1H), 2189 (CN), 1460, 989, 782, 688 cm⁻¹; UV (MeCN) λₘₐₓ (log ε) 339.0 (3.85); HRMS (ESI-) m/z calc. for C₁₄H₁₃F₂N₃O: 223.2015, found: 223.2038. Anal. Calcld. for C₁₄H₁₃F₂N₃O: C, 56.98; H, 10.65; N, 9.06. Found: C, 56.90; H, 10.63; N, 8.90.

**[closob-B₂H₂₋1-OAc-10-NC₅H₄][Et⁺]** (1c[Et⁺]). The product isolated from column chromatography was washed with a diluted solution of [Et⁺]OH: To balance the cation, solutions of 1[R(N)] in CH₂Cl₂ was washed with an aqueous solution of [R(N)]OH and recrystallized, typically from MeCN/THF. Starting with 6c made with method B: 50 mg (74% yield); pale yellow-green crystals from MeCN/THF; Rᵣ = 0.32 (30% MeCN in CH₂Cl₂); mp 253 °C; ¹H NMR (500 MHz, acetone-d₆) δ 0.44 – 1.10 (br m, 8H), 1.38 (tt, J₁ = 7.2 Hz, J₂ = 1.9 Hz, 12H), 2.31 (s, 3H), 3.48 (q, J = 7.3 Hz, 8H), 7.88 – 7.92 (m, 2H), 8.37 (tt, J₁ = 7.7 Hz, J₂ = 1.4 Hz, 1H), 9.57 (d, J = 5.3 Hz, 2H); ¹¹C NMR (126 MHz, acetone-d₆) δ 7.8, 53.1, 126.8, 142.2, 148.7; ¹⁹F NMR (160 MHz, acetone-d₆) δ -23.1 (d, J = 96 Hz, 8B), -1.5 (s, 1B), 17.4 (s, 1B); IR, ν 3400 cm⁻¹.
Definitions: 275.2328, found: 275.2344. Anal. Calcd. for C\textsubscript{d}H\textsubscript{7}N\textsubscript{4}O:\ C, 7.7 Hz, J\textsubscript{d} = 6.5 Hz, J\textsubscript{h} = 1.5 Hz, 2H). 8.44 (tt, J\textsubscript{d} = 7.7 Hz, J\textsubscript{h} = 1.5 Hz). 9.53 (dd, J\textsubscript{d} = 6.5 Hz, J\textsubscript{h} = 1.5 Hz, 2H). 1\textsuperscript{13}C NMR (162 MHz, acetone-d\textsubscript{6}): 7.8, 53.2, 126.7, 140.2, 148.9; 1\textsuperscript{18}B NMR (160 MHz, acetone-d\textsubscript{6}) δ -24.8 (d, J = 113 Hz, 4B), -24.2 (d, J = 108 Hz, 4B), 13.7 (s, 1B), 14.3 (s, 1B); IR, ν = 2481 (BH), 2139 (CN), 1465, 876, 769, 692 cm\textsuperscript{-1}; UV (MeCN) λ\textsubscript{max} (log ε) 344.5 (3.81); HRMS (ESI-) m/z calcd. for C\textsubscript{d}H\textsubscript{7}B\textsubscript{4}N\textsubscript{5}: 255.1735, found: 255.1749. Anal. Calcd. for C\textsubscript{d}H\textsubscript{7}B\textsubscript{4}N\textsubscript{5}: C, 43.84; H, 8.67; N, 10.95. Found: C, 43.83; H, 8.54; N, 10.76.

Preparation of [closo-B\textsubscript{2}H\textsubscript{2}(1-NC\textsubscript{4}H\textsubscript{4}-4-Y)]\textsuperscript{+} [Bu\textsubscript{4}N\textsuperscript{+}] (2[Bu\textsubscript{4}N\textsuperscript{+}]): A solution of monophenylidionium derivative [4[Bu\textsubscript{4}N\textsuperscript{+}]] (60.0 mg, 0.106 mmol) was dissolved in neat 4-substituted pyridine (0.5 mL) and the reaction mixture was stirred overnight at 80 °C. For solid 4-cyanopyridine (55 mg, 0.5 eq) was used and all reagents were dissolved in small amount of dry MeCN (0.2 mL). Unreacted pyridine was removed under high vacuum and the remaining oily residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) and washed twice with 5% aqueous HCl, then with water. The solvent was evaporated and purified on silica gel (CH\textsubscript{2}Cl\textsubscript{2} 100% gradient to 10% MeCN in CH\textsubscript{2}Cl\textsubscript{2}), then recrystallized from EtOH with small amount of CH\textsubscript{2}Cl\textsubscript{2} cooled to give pure product in 50 – 67% yield.

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1.5); mp 170 °C; 1H NMR (500 MHz, acetone-d$_6$) δ 0.08 – 1.21 (m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (sext, J = 7.2 Hz, 8H), 1.46 (t, J = 7.1 Hz, 3H), 1.81 (quin, J = 8.0 Hz, 8H), 3.40 – 3.45 (m, 4H), 4.03 (br q, J = 148 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.83 (br q, J = 6.8 Hz, 2H), 9.72 (d, J = 6.8 Hz, 2H); 13C NMR (126 MHz, acetone-d$_6$) δ 13.9, 14.4, 20.4, 24.5, 59.5, 63.3, 125.6, 141.3, 149.6, 164.0; 18B NMR (160 MHz, acetone-d$_6$) δ -26.7 (d, J = 131 Hz, 4B), -22.3 (d, J = 130 Hz, 4B), 7.1 (d, J = 144 Hz, 1B), 14.1 (s, 1B); UV (MeCN) λ$_{max}$ (log ε) 331.0 (3.95); IR, ν 2467 (BH), 1425, 1245, 1208, 1008, 768; HRMS (ESI-) m/z calcd. for C$_2$H$_6$B$_6$O$_3$N$: 270.2274, found: 270.2299. Anal. Calcd. for C$_2$H$_6$B$_6$O$_3$N$: C, 56.43; H, 10.66; N, 5.54. Found: C, 56.48; H, 10.36; N, 5.29.

[closo-B$_2$H$_2$-1-(NC$_3$H$_4$-4-Me)]$^+$ [Bu$_4$N]$^-$ (2m[Bu$_4$N]). Obtained 30.0 mg (63% yield); yellow powder, R$_f$ = 0.2 (MeCN/CH$_2$Cl$_2$: 1:15); mp 170 °C; 1H NMR (500 MHz, acetone-d$_6$) δ 0.04 – 0.90 (m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (sext, J = 7.4 Hz, 8H), 1.81 (quin, J = 8.0 Hz, 8H), 2.65 (s, 3H), 3.39 – 3.45 (m, 8H), 3.82 (br q, J = 145 Hz, 1H), 7.70 (d, J = 6.0 Hz, 2H), 9.38 (d, J = 5.9 Hz, 2H); 13C NMR (126 MHz, acetone-d$_6$) δ 13.9, 20.4, 21.4, 24.56, 59.5, 127.0, 148.0, 154.3; 18B NMR (160 MHz, acetone-d$_6$) δ -27.7 (d, J = 133 Hz, 4B), -23.8 (d, J = 129 Hz, 4B), 4.0 (d, J = 144 Hz, 1B), 13.7 (s, 1B); UV (MeCN) λ$_{max}$ (log ε) 357.5 (3.93); IR, ν 2467 (BH), 1488, 1447, 1209, 998, 836; HRMS (ESI-) m/z calcd. for C$_2$H$_6$B$_6$O$_3$N$: 212.2219, found: 212.2227. Anal. Calcd. for C$_2$H$_6$B$_6$O$_3$N$: C, 58.36; H, 11.58; N, 6.19. Found: C, 58.28; H, 11.52; N, 6.00.

[closo-B$_2$H$_2$-1-(NC$_4$H$_4$-4-O-Me)]$^+$ [Bu$_4$N]$^-$ (2n[Bu$_4$N]). Obtained 25.0 mg (50% yield); light yellow powder, R$_f$ = 0.2 (MeCN/CH$_2$Cl$_2$: 1:15); mp 170 °C; 1H NMR (500 MHz, acetone-d$_6$) δ 0.04 – 1.31 (br m, 8H), 0.97 (t, J = 7.4 Hz, 12H), 1.43 (sext, J = 7.4 Hz, 8H), 1.81 (quin, J = 8.0 Hz, 8H), 3.37 – 3.47 (m, 8H), 3.75 (br q, J = 154 Hz, 1H), 4.16 (s, 3H), 7.39 (d, J = 7.3 Hz, 2H), 9.33 (d, J = 7.3 Hz, 2H); 13C NMR (126 MHz, acetone-d$_6$) δ 13.9, 20.4, 24.6, 57.5, 59.5, 112.1, 150.1, 169.6; 18B NMR (160 MHz, acetone-d$_6$) δ -28.0 (d, J = 127 Hz, 4B), -24.3 (d, J = 125 Hz, 4B), 2.9 (d, J = 141 Hz, 1B), 13.7 (s, 1B); UV (MeCN) λ$_{max}$ (log ε) 339.5 (3.79); IR, ν 2463 (BH), 1631, 1506, 1308, 1196, 1002, 867, 575; HRMS (ESI-) m/z calcd. for C$_2$H$_6$B$_6$O$_3$N$: 228.2168, found: 228.2177. Anal. Calcd. for C$_2$H$_6$B$_6$O$_3$N$: C, 56.77; H, 10.52; N, 8.27. Found: C, 56.47; H, 10.36; N, 7.97.

Synthetic details of the intermediates and precursors are available in the ESI.

X-ray data collection
Single-crystal X-ray diffraction measurements for derivatives 1 were conducted at low temperature (100.0(1) K) using the CuK$_\alpha$ radiation ($\lambda$=1.54184 Å). The data were collected and processed using CrystAlisPro program. All structures were solved with the ShelXT $^{46}$, 6 structure solution program using Intrinsic Phasing and refined in the ShelXle by the full-matrix least-squares minimization on $F^2$ with the ShelXL refinement package. All non-hydrogen atoms were refined anisotropically. The C–H and B–H hydrogen atoms were generated geometrically and refined isotropically using a riding model. Full crystallographic data collection and refinement details are provided in the Electronic Supplementary Information (ESI).

CDCDC files 1995610-1995617 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.ukstructures/

Electronic spectroscopy
Electronic absorption spectra were measured for 3 concentrations in spectrophotometric grade MeCN and molar extinction coefficients $\varepsilon$ were obtained from the Beer’s Law plot with typical $r^2$ > 0.99 for each compound. Solvatochromic studies of 1a were conducted similarly recording spectra for a single dilute solution.

Fluorescence spectra were recorded for diluted MeCN solutions using a Hitachi F-4500 Fluorescence Spectrophotometer. The excitation wavelength was set to the absorbance max and $\lambda_{em}$ was scanned from $\lambda_{max}$ +50 nm to 900 nm. Relative intensity and $\lambda_{em}$ of fluorescence were somewhat concentration-dependent in weakly fluorescent compounds.

Solid-state fluorescence was measured for polycrystalline samples in a borosilicate glass capillary. The sample was excited at the wavelength on maximum absorption obtained in MeCN solutions. The normalized emission spectra are shown in ESI.
For AIE measurements, aliquots of a 2.45 x 10^{-4} M solution of 1b[Bu4N] in MeCN and a 1.22 x 10^{-5} M solution of 1e[Et4N] in MeCN were added to 3.0 mL distilled water in a quartz cuvette and mixed by pipette. Solutions of 1%, 9.1%, and 16.7% of MeCN in H2O were prepared from the addition of 30, 300, and 600 μL of stock solution, respectively, to 3.0 mL of H2O. The resulting concentrations of 1b[Bu4N] were: 8.09 x 10^{-5} M (1%), 2.23 x 10^{-5} M (9.1%), and 4.08 x 10^{-5} M (16.7%). The excitation wavelength was set to the absorbance 5 max and 5 was scanned from λmax +50 nm to 900 nm. Selected data are collected in Table 2 and all spectra and details of data analysis are shown in the ESI.

Conflicts of interest
There are no conflicts to declare.

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Notes and references


22. R. Żurawski, R. Jakubowski, S. Domagała, P. Kasznyski and K. Woźniak, Regioselective functionalization of the


37. For details see the ESI.


63. W. H. Knoth, Chemistry of boranes. XXVI. Inner diazonium salts 1,10-B_{10}H_{8}(N_{2})_{2} ·B_{10}Cl_{4}(N_{2})_{2}, and ·B_{10}I_{4}(N_{2})_{2}, *J. Am. Chem. Soc.*, 1966, 88, 935-939.


Graphical TOC

\[ \text{X} = \text{H, CN, OAc, N}_2, \text{I}, \text{SCN, Br, Pyridine, EtO, morpholine} \]

\[ \text{Y} = \text{H, CN, COOEI, Me, OMe} \]

TF, MeCN, formamide