Cite this: Dalton Trans., 2012, 41, 10440



Syntheses of rod-shaped fluorescent 1,3,2-benzodiazaboroles with phosphonium, and phosphane chalcogenide acceptor functions[†]

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Received 23rd March 2012, Accepted 27th June 2012 DOI: 10.1039/c2dt30666b

A series of 1,4-phenylenes X-C₆H₄-BDB with a 1,3,2-benzodiazaborolyl (BDB) and a phosphorus based end group [X = PPh₂ (**2**), P(O)Ph₂ (**3**), P(S)Ph₂ (**4**), P(Se)Ph₂ (**5**), P(AuCl)Ph₂ (**6**) and P(Me)Ph₂ (**7**)] as well as 2-(2')thienyl-1,3,2-benzodiazaboroles with a second end group X [X = PPh₂ (**8**), P(S)Ph₂ (**9**), P(Se)Ph₂ (**10**) and P(Me)Ph₂ (**11**)] in the 5' position were synthesised using established methodologies. Molecular structures of **2–9** and **11** were determined by X-ray diffraction. Compounds **3**, **4**, **6**, **7**, **9** and **11** show intense blue luminescence in cyclohexane, toluene, chloroform, dichloromethane and tetrahydrofuran with pronounced solvatochromism. Thereby Stokes shifts in the range of 8950–10 440 cm⁻¹ and quantum yields up to 0.70 were observed in dichloromethane solutions. In contrast to this, for the selenides **5** and **10** quantum yields are small (<0.1). The absorption maxima (298–340 nm) are well reproduced by TD-DFT computations (B3LYB/G-311G(d,p)) and arise from strong HOMO–LUMO transitions. With the exception of **5** and **10** the HOMOs of the molecules under study are mainly located on the benzodiazaborole group. In **5** and **10** the HOMOs are on the selenium atoms. The LUMOs of all new neutral molecules are mainly represented by the phenylene or thiophene bridge. In the phosphonium cations the LUMOs have additional contributions from the phosphonium unit.

Introduction

Over the last two decades the development of fluorescent organic compounds for potential application in photonic devices has been the focus of significant interest. Among an infinite number of molecular structures with the desired character, three-coordinate organoboron compounds and polymers are of emerging importance.^{1,2} Their linear and non-linear optical and electronic properties make them particularly attractive for use in functional materials. Herein the three-coordinate boron centre usually behaves as a π -acceptor due to its vacant p-orbital. This field has been dominated by the use of dimesitylboryl (BMes₂, Mes = 2,4,6-Me₃C₆H₂) and related moieties as the unsaturated boron centre herein is sterically well shielded by methyl groups. The π -acceptor character of the BMes₂ unit is similar to NO₂ and CN based on UV³ and cyclovoltammetric data.⁴ Compounds

like these can display sizable second and third order non-linear optical (NLO) properties.^{5–10} Due to their low LUMO energies they are interesting as efficient electron-transporting or emitting layers in organic light emitting diodes (OLEDs).^{11–13} Organoboron containing species are often strongly colored and/or luminescent¹⁴ which renders them useful as colorimetric or luminescent sensors for anions such as fluoride^{15,16} and cyanide.¹⁷ Conjugated molecules with boryl substituents display very large Stokes shifts and high quantum yields in solution as well as in the solid state, which indicates the lack of close packing as a result of the sterically congesting mesityl groups.^{18,19}

In the past decade, the chemistry of 1,3,2-diazaboroles has been rapidly developed.²⁰⁻²⁵ Some of these compounds show strong luminescence as solids and in solution.^{26–34} For synthetic reasons the 1,3-diethyl-1,3,2-benzodiazaborolyl group (1,3-Et₂-1,3,2-N₂BC₆H₄) is frequently used and compounds having this function are moderately air-stable.^{22,28–33} Calculations on 2-arylethynyl-1,3,2-benzodiazaboroles showed a localisation of the HOMO on the diazaborole group, leading to the suggestion that this group could act as a π -donor.³³ This proposal was confirmed by the easy oxidation of diazaboroles in cyclic voltammetric experiments.^{24,31,34} In line with these observations it was obvious to study syntheses and photophysical properties of compounds containing different types of three-coordinate boron centers which may function as a π -donor on one end or as a π -acceptor on the other end of the molecule. Thereby it was disclosed that the π -electron donating capacity of the 1,3-diethyl-

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[†]Electronic supplementary information (ESI) available: Tables of atomic coordinates for [B3LYP/6-311G(d,p)] optimized geometries, values of total energies and ionization energies (IEs) of **2–11**. CCDC 873268–873276. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30666b

1,3,2-benzodiazaborolyl group towards the BMes₂-unit lies between that of methoxy- and dimethylamino-groups.³⁵

To improve the different photophysical properties of the fluorophor in terms of higher molar extinction coefficients, higher fluorescence quantum yields and better photo-, thermo- and electro-stabilities, we also looked at alternative acceptor systems. In a number of informative papers triarylphosphane-oxides and -sulfides were successfully employed as acceptor units in highly fluorescent push–pull chromophores in extended organic π -electron systems.^{36,37} Thus, it was obvious to also consider diarylphosphanes, their chalcogenides, phosphonium salts and related gold complexes as potential acceptors in our push–pull chromophores. *p*-Boryl-phenylene-phosphonium salts have been tested as fluoride and cyanide sensors before. In contrast to our approach these systems contain π -accepting diarylboryl units instead of donating functions.^{16,17}

Results and discussion

The new borolyl compounds **2** and **8** were formed by the established protocol of reacting 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole 1^{23} with suitable organolithiums which are available by treatment of either 4-bromophenyl-diphenylphosphane³⁸ or 2-bromo-5-diphenylphosphanyl-thiophene³⁹ with 2 equiv. of *tert*-butyllithium at low temperature (Scheme 1).

The oxidation of **2** to the corresponding triarylphosphane oxide **3** was effected with an excess of oxone (KHSO₅·KH-SO₄·K₂SO₄) in the presence of silica in boiling toluene (65% yield). The corresponding sulfide **4** and selenide **5** were formed in good yield from **2** by reaction with excess elemental sulfur in toluene or with grey selenium in dichloromethane, respectively (Scheme 1).

Reaction of equimolar amounts of **2** and tetrahydrothiophene gold(1)chloride⁴⁰ in dichloromethane gives rise to the formation of gold(i) complex **6** in 53% yield. Alkylation of compound **2** with a slight excess of dimethyl sulfate in CH_2Cl_2 at room temperature led to phosphonium salt **7**, which was isolated as a colourless solid in 83% yield (Scheme 1).

Similarly, diphenylphosphanyl-thiophene **8** was treated with S_8 to give sulfide **9** (34% yield), to an oxidation with grey selenium to furnish selenide **10** (90% yield) and to alkylation with dimethyl sulfate to afford phosphonium salt **11** in 92% yield (Scheme 1).

The compounds 2–11 are slightly air- and moisture sensitive due to the presence of the benzodiazaboryl group as well as the P(III) centre in derivatives 2 and 8. All new compounds are well soluble in common aprotic solvents such as toluene, ethers, CH_2Cl_2 , $CHcl_3$, CH_3CN and dimethyl sulfoxide.

Air-oxidation of **2** to form **3** was considerably accelerated under UV irradiation as proven by ${}^{31}P{}^{1}H$ NMR spectroscopy.

In the phenylene-bridged derivatives, ¹¹B{¹H]-NMR-resonances are observed in the narrow range of $\delta = 27.7$ to 29.7 ppm, whereas the corresponding signals of the thiophenes appear at slightly higher field ($\delta^{11}B = 25.4-26.6$ ppm). Known compounds with thienyl substituents at the boron atom of benzo-1,3,2-diazaboroles give rise to signals at $\delta = 26.0-26.6$ ppm in their ¹¹B{¹H}NMR spectra. Previously prepared 1,3,2-benzodiazaboroles with the boron atoms substituted by benzene rings reveal singlets in the range of $\delta = 28.6$ to 29.3 ppm. The singlet of the phosphorus atom in the ³¹P{¹H}NMR-spectrum of **2** ($\delta =$ -5.3 ppm) is significantly downfield shifted by oxidation (**3**: $\delta =$ 29.5 ppm), sulfide formation (**4**: $\delta = 43.4$ ppm) and selenation (**5**: $\delta = 35.4$ ppm). The latter resonance is accompanied by ⁷⁹Sesatellites (¹J_{P,Se} = 728.8 Hz). Coordination of **2** to the gold center in **6** gives rise to a singlet at 33.5 ppm, whereas phosphonium salt **7** displays a singlet at $\delta = 22.1$ ppm. In the thiophene-substituted derivative **8**, the ³¹P{¹H}NMR-resonance was observed at considerably higher field ($\delta = -20.4$ ppm). In the corresponding sulfide **9** (δ ³¹P = 33.2 ppm), selenide **10** (δ ³¹P = 21.6 ppm, ¹J_{P,Se} = 763.0 Hz) and phosphonium salt **11** (δ ³¹P = 15.3 ppm), the expected deshielding of the four-coordinate phosphorus atoms is registered.

 1 H and 13 C{ 1 H}NMR-spectra of the novel compounds are similar to those of numerous other benzodiazaboroles.

X-Ray crystallography

Molecular structures were determined for the *p*-phenylene-based benzodiazaboroles 2-7 (Fig. 1, Table 1) and the three thiophene-based derivatives **8**, **9**, **11** (Fig. 2, Table 2). Bond lengths and torsion angles of interest are listed in Tables 1 and 2. These experimental data are compared with the corresponding B3LYP/ 6-311(d,p) calculated values (given in italics in Tables 1 and 2).

The unit cell of compound **3** contains two independent molecules and one molecule of water, which is involved in hydrogen bonding to the oxygen atoms of the P=O-functions (O(1)···O(3) = 2.792 Å, O(2)···O(3) = 2.875 Å). Bonding parameters of the independent molecules are identical within 3 esd's.

The bond lengths within the 1,3-diethyl-1,3,2-benzodiazaborolyl fragments and the B–C lengths in all structures are virtually identical as reflected in the B–N, N–C(alkyl), N–C(aryl) and B– C-separations of *ca.* 1.42, 1.46, 1.40 and 1.57 Å (Tables 1 and 2).

The geometrical parameters of the *p*-phenylene- and the 2,5thienyl-units are not exceptional and in full agreement with other benzodiazaborolyl-arenes and -thiophenes.³² The P–C(Ph) distances in **2** [1.834(1) Å(av.)] as well as those in **3** [1.801(3) Å (av.)], **4**, **5** [1.814(1) Å(av.)], **6** [1.820(4) Å(av.)] and **7** [1.798(1) Å(av.)] are comparable with those in related PPh₃ derivatives.^{41–45} The agreement between experimental and calculated values for **2–7** is pretty good. For the bond lengths the difference does not exceed 0.065 Å while the biggest deviation from experimental of 12.9° is noted for the torsion angle C(13)– C(14)–P(1)–C(29) in **7**.

It is remarkable, however, that in the thiophene based benzodiazaboroles **8**, **9** and **11** the P–C(thiophene) links [1.820(1), 1.798(2), 1.775(1) Å)] are shorter than the remaining P–C (phenyl) distances within 3 esd's [1.834(1), 1.840(1), 1.813(2), 1.818(2), 1.797(1); 1.802(1) Å]. In contrast to this, all three arylic P–C bonds in the phenylene-based benzodiazaboroles do not differ significantly. The bond lengths P=O in **3** (1.489(2)), P=S in **4** and **9** (1.960(4); 1.957(1)), P=Se in **5** (2.115(4)), and P–Au in **6** (2.225(1)) are comparable to those in Ph₃P=E (E = O: 1.46(1) Å;⁴¹ S: 1.950(3) Å;⁴² Se: 2.106(1) Å⁴³), Ph₃PAuCl (2.235(3) Å),⁴⁴ and Ph₃P–CH₃⁺ (1.790(2) Å).⁴⁵

The orientations of the (hetero)-aromatic π -systems with respect to the benzodiazaborolyl group are important as an ideal π -correspondence between the orbitals of boron and of the



Scheme 1 Syntheses of 2–11.

adjacent organic scaffold is expected in the case of coplanarity of the involved rings. The related torsion angles in 2–7 range from 140.9° in the phosphonium ion 7 to 59.4° in the selenophosphoryl derivative 5. The respective torsion angles between the two heterocycles range from -51.4° in 8 to 133.2° in the selenophosphoryl derivative 10. The angles between the planes defined by the atoms C(14), P, the chalcogen atom or the AuCl- or methyl-substituents and the adjacent benzene plane in 3–7 range from 147.2° in 3 to 32.6° in 7. In the thiophene derivatives the corresponding torsion angles are -56.2° in 9 and -160.9° in 11. The smaller angles in the phosphonium salts 7 and 11 suggest an improved interaction between the π -orbitals on boron and on the carbon atom attached to the boron centre.

The calculated geometrical parameters of 8, 9 and 11 fit also very well with the experimentally determined values of bond lengths (this difference does not exceed 0.03 Å). For the torsion angles the deviation is more significant and probably should be due to the difference between crystal and gas phase structure.

This experimental and theoretical geometry comparison is our starting point to the electronic structure study.

UV-visible and luminescence spectroscopy

Table 3 lists selected photophysical data for all new compounds shown in Scheme 1 along with related D– π –A systems for comparison. The lowest UV-absorption maxima (in CH₂Cl₂) (Fig. 3) decrease in energy on going from 2 ($\lambda_{max} = 298$ nm) > 3 (299 nm) > 4 \approx 5 (303 nm) > 6 (307 nm) > 8 \approx 9 (311 nm) > 10 (318 nm) > 7 (329 nm) to 11 (340 nm).

Within the series of molecules based on the *p*-phenylene linker the absorption maxima are not significantly influenced by the change from $P(O)Ph_2$ via the $P(E)Ph_2$ (E = S, Se) to the PPh₂(AuCl)-substituents, whereas the introduction of the phosphonium unit into the ring in 7 causes a marked increase to 329 nm. Similar observations were made with the thiophene derivatives. The replacement of the phenylene unit by the



Fig. 1 Molecular structures of compounds 2–7.

thiophene bridge in corresponding systems, *e.g.* **4** *vs.* **9**, **5** *vs.* **10** or **7** *vs.* **11**, causes a red-shift of the absorption (of 11, 15 and 11 nm, respectively), which reflects an improved delocalization of π -electrons along the rod-like scaffold of the thiophene based benzodiazaborole derivatives. It is also obvious that within the here designed push–pull molecules featuring a benzodiazaborole donor the methyl-diphenylphosphonium group is the best π -electron acceptor. The negligible solvatochromism of the absorptions agrees with a small dipole moment in the ground state.

All the compounds 3–7 and 9–11 are luminescent; the diphenyloxophosphanyl derivative 3 ($\Phi_{\rm f} = 0.70$), the diphenylthiophosphanyl derivatives 4 ($\Phi_{\rm f} = 0.56$) and 9 ($\Phi_{\rm f} = 0.69$) have acceptable quantum yields in CH₂Cl₂ solution.

In contrast to this, the quantum yields of the selenium containing compounds 5 and 10 in CH_2Cl_2 are only 0.01, respectively.

The Stokes shifts for these compounds are large with values from $5800-7040 \text{ cm}^{-1}$ in cyclohexane. They are even larger in the more polar solvent dichloromethane ranging from 8950 cm^{-1} in 5 to $10\,440 \text{ cm}^{-1}$ in 7.

In keeping with this, solvatochromic shifts of $2750-3630 \text{ cm}^{-1}$ are observed in the emission maxima by changing the solvent from cyclohexane to CH₂Cl₂ (Fig. 4). These observations are consistent with relatively large dipole moments of **3–7**, **9–11** in their singlet excited states.

The photophysical data for compounds 2 and 8 deserve a comment. Due to the fact that the absorption and emission spectra of 2 and 3 are nearly identical and that the quantum yields of 2 and 8 are very small, it was suspected that these emissions are caused by oxide impurities (see also ESI[†]).

Indeed, a CH_2Cl_2 solution of **8** which was irradiated for 2 h with UV light shows improved luminescence and signals in the ${}^{31}P{}^{1}H{}NMR$ spectrum for the related phosphane oxide. This observation also agrees with a report on quenching the emission of a photosensitized dye through single electron transfer from trivalent phosphorus compounds.⁴⁶ In a different paper the non-fluorescent nature of tris(9-anthryl)phosphane is reported. It is further mentioned that phosphanes Ph_2PAr (Ar = naphthyl, anthryl) have no fluorescence, whereas their phosphine oxides show intense fluorescence.⁴⁷

It is instructive to compare the photophysical data of 3–7 and 9–11 with those of $C_6H_4(NEt)_2$ -B $C_6H_4BMes_2$ (12) and $C_6H_4(NEt)_2B(C_4H_2S)BMes_2$ (13) in order to estimate the π -acceptor capacity of phosphorus containing functions with regard to the strong π -accepting dimesitylboryl group. The absorption maxima in these compounds suggest that the best P-containing acceptor in this study, namely PPh₂Me, is still not as effective as the BMes₂ group.

DFT electronic structure calculations

The TD-DFT calculated absorption maxima on compounds **2–6** and **8–10** are displayed in Table 6. The lowest energy absorption is calculated for **2** at the $\lambda_{\text{max}} = 308$ nm; all other absorption maxima are red-shifted and range from 319 to 324 nm for phenylene spacers containing compounds **3–5**, for **6** at the $\lambda_{\text{max}} = 340$ nm, and from 327 to 337 nm for thiophene spacers containing analogues **8–10**.

The most intense absorption is for thiophene bridged compounds calculated for 8 at 327 nm and corresponds to the energy of the HOMO \rightarrow LUMO transition. This band is observed in the UV/Vis spectrum also as one of the most intense bands at λ = 311 nm. In comparison to the experiment, the calculated absorption maxima for 2-5 and 8-10 (in CH₂Cl₂) are red-shifted by 10 to 26 nm. The ground state dipole moments μ_{g} , molecular polarizabilities α and the static first-order molecular hyperpolarizabilities β of compounds 2–5 and 8–10 have been calculated and are listed in Table 8. The magnitudes of μ_g are all found to be rather small, for phenylene containing series they range from 1.5 D for the unsubstituted derivative 2, via 3.9 D for the oxygen containing 3 to 4.9 D for 5, while the highest value is obtained for sulfur containing 4 (5.0 D). For thiophene bridged compounds, the same tendency is noted with slightly bigger values of the ground state dipole moments μ_{g} (8: 2.3 D; 9: 5.6 D; 10: 5.5 D).

		2	3	4	5	6	7
BC	B(1)–C(11)	1.566(2)	1.574(4)	1.567(2)	1.570(2)	1.570(5)	1.566(2)
B–N	B(1)–N(1)	1.566 1.432(2)	1.567 1.426(4)	1.567 1.438(2)	1.567 1.431(2)	1.568 1.431(5)	1.572 1.434(2)
	B(1)–N(2)	1.440 1.433(2)	1.441 1.438(4)	1.441 1.432(2) 1.441	1.441 1.434(2) 1.441	1.440 1.421(5)	1.437 1.440(2)
Р–С	P(1)-C(14)	1.837(1) 1.853	1.441 1.808(3) 1.833	1.441 1.816(1) 1.841	1.441 1.820(1) 1.842	1.816(4) 1.837	1.790(1)
	P(1)-C(17)	1.832(1) 1.854	1.801(3) 1.833	1.815(1) 1.843	1.814(1) 1.844	1.818(4) 1.839	1.798(1) 1.812
	P(1)-C(23)	1.836(1) 1.854	1.802(3) 1.834	1.813(1) 1.843	1.814(1) 1.844	1.822(4) 1.839	1.798(1) 1.812
P=X		1100 /	P(1)–O(1) 1.489(2) 1.499	P(1)–S(1) 1.9595(4) 1.978	P(1)–Se(1) 2.1145(4) 2.138	P(1)–Au(1) 2.225(1) 2.290	P(1)–C(29) 1.793(1) 1.823
Aryl-links	C(11)-C(12)	1.405(2) 1.406	1.403(4) 1.406	1.406(2) 1.405	1.402(2) 1.407	1.397(5) 1.405	1.403(2) 1.409
C–C	C(12)–C(13)	1.389(2) 1.391	1.395(4) 1.393	1.387(2) 1.393	1.396(2) 1.390	1.395(5) 1.392	1.391(2) 1.388
	C(13)-C(14)	1.400(2) 1.402	1.391(4) 1.399	1.398(2) 1.399	1.400(2) 1.399	1.397(5) 1.399	1.398(2) 1.404
	C(14)–C(15)	1.402(2) 1.399	1.394(4) <i>1.399</i>	1.400(2) 1.399	1.398(2) 1.398	1.403(5) 1.400	1.397(2) 1.401
	C(15)-C(16)	1.388(2) 1.394	1.386(4) <i>1.391</i>	1.392(2) 1.390	1.384(2) <i>1.393</i>	1.394(5) <i>1.391</i>	1.384(2) <i>1.391</i>
	C(11)–C(16)	1.406(2) 1.404	1.396(4) 1.406	1.402(2) <i>1.406</i>	1.404(2) 1.405	1.399(5) 1.406	1.405(2) 1.406
Borolyl unit	N(1)–C(7)	1.461(2) 1.458	1.452(4) 1.459	1.458(1) 1.459	1.461(2) <i>1.459</i>	1.440(7) 1.459	1.462(1) 1.460
N–(Et)	N(2)–C(9)	1.460(2) 1.459	1.455(4) <i>1.459</i>	1.460(1) 1.459	1.463(2) 1.459	1.450(4) 1.459	1.464(2) 1.461
N–C(aryl)	N(1)–C(1)	1.398(2) 1.397	1.405(4) 1.397	1.399(1) 1.397	1.395(2) 1.397	1.398(4) 1.440	1.399(1) 1.400
	N(2)–C(2)	1.401(2) 1.397	1.406(4) 1.397	1.395(1) 1.397	1.399(2) 1.397	1.394(4) <i>1.440</i>	1.396(2) 1.399
C–C	C(1)–C(2)	1.408(2) 1.415	1.394(4) <i>1.415</i>	1.407(2) 1.414	1.410(2) 1.414	1.408(5) <i>1.414</i>	1.413(2) <i>1.412</i>
Torsion angles	N(1)–B(1)–C(11)–C(12)	-128.1 -121.4	-62.5 -52.9	-57.0 -51.2	-58.2 128.1	-125.0 51.3	-42.9 -46.4
	N(1)-B(1)-C(11)-C(16)	50.7 59.1	118.4 <i>126.2</i>	121.6 <i>128.4</i>	123.0 -51.4	59.4 -128.3	140.9 133.9
	C(13)-C(14)-P(1)-C(17)	4.6 9.5	25.0 28.8	88.8 89.9	22.0 17.7	-165.20 -158.6	-88.84 73.4
	C(13)-C(14)-P(1)-C(23)	101.1 96.4	-90.16 -84.0	-158.6 20.7	-91.07 -92.9	83.70 89.8	152.76 164.6
	C(13)-C(14)-P(1)-X		147.2 152.2	-34.96 -34.7	145.4 <i>142.4</i>	-41.3° 34.2	32.64° 45.5
a X = Au(1). b X =	= C(29).						

Table 1	Experimental and B3LM	P/6-311G(d,p) selected be	and lengths [Å] and torsic	on angles [°] for 2–7	(calculated values in italics)
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These low values are consistent with the absence of solvatochromism for these compounds. The situation is a little bit different in the case of **6** and two cations **7** and **11** for which the ground state dipole moments are bigger (**6**: 10.2; **7**: 12.6; **11**: 11.3 D). The molecular polarizabilities α of compounds **2–11** vary little in the range 5.8–6.6 × 10⁻²³ esu.

Donor–acceptor substituted π -conjugated organic molecules having low-lying charge transfer excited states exhibit large firstorder non-linear properties. The molecular hyperpolarizabilities β of **2–11** were computed as analytical third derivatives of the energy and correspond to the static hyperpolarizabilities (frequency = 0). An increase in the range $\beta = 4.6 \times 10^{-30}$ esu (**2**) < 13.8×10^{-30} esu (**8**) < 16.0×10^{-30} esu (**3**) < 19.4×10^{-30} esu (**4**) $\leq 19.6 \times 10^{-30}$ esu (**10**) < 20.0×10^{-30} esu (**9**) $\leq 20.1 \times$ 10^{-30} esu (5) $\leq 25.7 \times 10^{-30}$ esu (6) was calculated. For two cations 7 and 11 very big values of static first-order molecular hyperpolarizabilities (β) in comparison with 2–6 and 8–10 are calculated (120.2×10^{-30} and 96.8×10^{-30} esu, respectively). These data were computed on the basis of the two state model,⁴⁸ whereby β is proportional to the dipole moment change between the ground and the excited state $\Delta\mu$ and the square of the transition moment integral for the optical transition between two states (oscillator strength).

The hyperpolarizability is inversely proportional to the square of the energy of the respective transition and its magnitude of β may also be dominated by the size of the HOMO–LUMO gaps. In keeping with this, the small β -value of **2** (4.6 × 10⁻³⁰ esu) would agree with the largest HOMO–LUMO gap (4.558 eV)



Fig. 2 Molecular structures of compounds 8, 9 and 11.

and the very big β -values of 7 and 11 are very nicely correlated with the smallest HOMO–LUMO gaps (3.075 and 3.099 eV, respectively).

Tables 4 and 5 display [B3LYP/6-311G(d, p)] calculated MO energies of 2-5 and 8-10, as well as HOMO-LUMO gaps and the first four Δ SCF/TD-DFT ionization energies (IE). The LUMOs are located at π^* of phenyl in 2–5, or thiophene in 8–10 units with slight contribution of the vacant $2p_{z}$ orbital of boron, whereas the HOMOs in 2-4 and 8-9 correspond to the benzodiazaborole unit (π_3 - π_{NBN}). In 5 and 10 the HOMOs are located on the selenium atom. The lowest energies of the HOMOs are noted for 2 and 5 (-5.536 and -5.553 eV, respectively) and the highest value is obtained for 4 (-5.670 eV). The energetical position of the HOMOs (and consequently that of IE₁ which ranged from 6.82 to 7.18 eV) is very insensitive towards structural modification, but the nature of HOMOs is different in 5 and 10 compared to 2-4 and 8-9. For the latter ones (2-4 and 8-9), the calculated $(\pi_3 - \pi_{NBN})$ ionization energies are slightly influenced by the other part of the molecule in comparison with unsubstituted 2 (IE₁ = 6.83 eV) and 8 (IE₁ = 6.78 eV); the oxygen withdrawing effect is noted in the case of 3 (IE₁ = 7.18 eV) and, surprisingly, the strongest stabilizing effect of selenium in 10 $(IE_3 = 7.24 \text{ eV})$. The influence of the sulfur atom seems less significant in this case. For sulfur and selenium containing compounds (4-5, 9-10), the ionization energies of their lone pairs correspond to the HOMO -1 and HOMO -2 in 4 (IE₂ = 7.03 eV, $IE_3 = 7.31 \text{ eV}$) and 9 ($IE_2 = 7.05 \text{ eV}$, $IE_3 = 7.40 \text{ eV}$), or to the HOMO and HOMO - 1 in 5 (IE₁ = 6.82 eV, IE₂ = 6.84 eV) and 10 (IE₁ = 6.82 eV, IE₂ = 6.86 eV), and are computed at nearly the same value for sulfur (4, 9) or selenium (5, 10) derivatives, independently of phenylene or thiophene bridging. The HOMO-LUMO gap decreases continuously from 2 via 3, 4 to 5, and then from 8 via 9 to 10, and mirrors the increasing red shift in the whole series. As can be seen from Table 7, the most important one is observed for cations 7 and 11, since it goes to the visible region.

Experimental

All experiments were performed under an atmosphere of dry oxygen-free argon using Schlenk techniques. All solvents were dried with the usual drying agents and freshly distilled prior to use. The compounds 4-bromophenyl-diphenylphosphane,³⁸ 5-bromo-2-diphenylphosphanyl-thiophene,³⁹ 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole 1^{23} and tetrahydrothiophene-gold(1) chloride⁴⁰ were prepared according to literature methods.

Oxone (2KHSO₅·KHSO₄·K₂SO₄) was purchased from Alfa Aeser Johnson Matthey Comp., Karlsruhe (Germany). A 1.6 M pentane solution of *tert*-butyllithium and a 1.6 M hexane solution of *n*-butyllithium were obtained from Aldrich.

NMR spectra were recorded in C_6D_6 or CDCl₃ at room temperature on a Bruker AM Avance DRX500 spectrometer (¹H, ¹¹B, ¹³C) with SiMe₄ (¹H, ¹³C) and BF₃·OEt₂ (¹¹B) as external standards. Some expected ¹³C peaks corresponding to the boronbound carbon atoms were not detected above the noise levels.

The poor values of C and N in elemental analysis may be a result of incomplete combustion due to formation of ceramic boron carbides or nitrides. In keeping with this, varying amounts of solid residues were found after combustion. No significant impurities could be detected in the NMR/MS and EES-spectra, which can be seen as a typical fingerprint of the molecules and would show any other fluorescent species.

Absorption spectra were measured with a UV/VIS doublebeam spectrometer (Shimadzu UV-2550). The quantum yields were determined against POPOP (p-bis-5-phenyl-oxazolyl(2)benzene) ($\Phi = 0.93$) as the standard. Single crystals were coated with a layer of hydrocarbon oil and attached to a glass fiber. Crystallographic data were collected with a Nonius KappaCCD diffractometer with Mo-Ka radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 100 K for 2, 4, 5, 6, 7, 8, 9 and 11 and 200 K for 3. Mass spectra were obtained with a VG Autospec sector field mass spectrometer (Micromass). Crystallographic programs used for structure solution and refinement were from SHELX-97.54 The structures were solved by direct methods and were refined by using full-matrix least squares on F^2 of all unique reflections and anisotropic thermal parameters for all non-hydrogen atoms, except disordered atoms in 8 and 12. All hydrogen atoms were refined using a riding model with U(H) = 1.5 U_{eq} for CH₃ groups and U(H) = 1.2 U_{eq} for all others.

Disordered *n*-pentane in **6** was treated by SQUEEZE/ PLATON.⁵⁵ CCDC 873268–873276 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4-(Diphenylphosphanyl)-1-(1',3'-diethyl-1',3',2'benzodiazaborol-2'yl)-benzene (2)

An ethereal solution (30 mL) of 4-bromophenyl-diphenylphosphane (1.24 g, 3.63 mmol) was added to a cold solution (-78 °C) of 7.63 mmol *tert*-butyllithium (4.77 mL) in a mixture of diethyl ether (30 mL) and *n*-hexane (30 mL). The mixture was stirred at -60 °C for 3 h, then re-chilled to -78 °C before a sample of 1.01 g (3.99 mmol) of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole (1) was added. The orange solution was allowed to slowly warm up to ambient temperature, whereby a colourless

		8	9	11
В-С	B(1)-C(11)	1.557(2)	1.561(3)	1.5316(2)
B–N	B(1)–N(1)	1.554 1.436(2)	1.557 1.429(3)	1.563 1.433(2)
	B(1)–N(2)	1.442 1.430(2) 1.442	1.440 1.435(3) 1.440	1.430 1.4314(2) 1.435
Р–С	P(1)-C(14)	1.442 1.820(1) 1.834	1.798(2) 1.817	1.435 1.775(1) 1.778
	P(1)-C(15)	1.840(1) 1.854	1.818(2) 1.842	1.797(1) 1.812
	P(1)-C(21)	1.834(1)	1.813(2) 1.842	1.802(1) 1.811
P=X		1.000	P(1)=S(2) 1.957(1)	P(1)-C(27) 1.792(1)
A ryl-links			1.9/4	1.021
S–C	S(1)–C(11)	1.726(1) 1.748	1.727(2) 1.745	1.723(1) 1.742
	S(1)–C(14)	1.724(1) 1.745	1.728(2) 1.740	1.723(1) 1.747
C–C	C(11)-C(12)	1.375(2) 1.379	1.373(3) 1.379	1.381(2) 1.383
	C(12)-C(13)	1.423(2) 1.420	1.418(3) 1.418	1.410(2) 1.412
	C(13)-C(14)	1.378(2) 1.378	1.373(3) 1.375	1.378(2)
Borolyl unit	N(1)-C(7)	1.461(2) 1.459	1.465(3) 1.458	1.470(2) 1.461
N-(Et)	N(2)-C(9)	1.455(2) 1.458	1.468(3) 1.460	1.459(2) 1.461
N–C(aryl)	N(1)-C(1)	1.393(2) 1.396	1.399(3) 1.396	1.401(2) 1.399
	N(2)-C(2)	1.396(2) 1.396	1.400(3) 1.397	1.396(2) 1.398
С–С	C(1)–C(2)	1.410(2) 1.414	1.409(3) 1.414	1.408(2) 1.412
Torsion angles	N(1)-B(1)-C(11)-C(12)	131.7 40.7	-48.9 41.9	-139.9 -141.0
	N(1)-B(1)-C(11)-S(1)	-51.4 -42.2	133.2 136.0	33.7
	S(1)-C(14)-P(1)-C(15)	-18.4 92.0	179.4 11.6	-75.3 77.3
	S(1)-C(14)-P(1)-C(21)	-121.3 -162.4	68.1 <i>81 2</i>	46.3 -160.9
	S(1)-C(14)-P(1)-X	102.7	S(1)-C(14)-P(1)-S(2) -56.2 -44.0	S(1)–C(14)–P(1)–C(27) 164.8 –42.0

Table 2 Experimental and B3LYP/6-311G(d,p) selected bond lengths [Å] and torsion angles [°] for 8, 9 and 11 (calculated values in italics)

precipitate separated. It was filtered, and the filtrate was concentrated to a volume of *ca*. 2 mL. A crude product was precipitated by the addition of *n*-pentane (100 mL). The slurry was stirred for 12 h at room temperature. Then the supernatant solvent was decanted and the solid was crystallised from a 1:1 mixture of dichloromethane and *n*-hexane to afford 1.14 g (72%) of colourless microcrystalline **2**. Found C 77.52, H 6.78, N 6.18%. $C_{28}H_{28}BN_2P$ (434.32) requires: C 77.43, H 6.50, N 6.45%.

4-(Diphenyl-oxophosphanyl)-1-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-benzene (3)

Samples of solid oxone (3.14 g, 5.18 mmol) and silica (3.14 g, 51.0 mmol) were added to a solution of **2** (0.37 g, 0.85 mmol) in toluene (30 mL). The mixture was heated for 3 d at 110 °C. The re-cooled slurry was filtered, and solvent and volatile components were subsequently removed *in vacuo*. Dichloromethane (20 mL) was added to the residue and the mixture was washed

with water (3 \times 10 mL). The organic phase was separated and evaporated to dryness. The crude product was purified by crystallisation from a 1 : 10 mixture of CH₂Cl₂ and *n*-hexane to yield 0.25 g (65%) of **3** as a colourless solid.

Found C 73.69, H 6.34, N 6.10%. $C_{28}H_{28}BN_2OP$ (450.32) requires: C 74.68, H 6.27, N 6.22%.

4-(Diphenyl-thiophosphanyl)-1-(1',3',-diethyl-1',3',2'benzodiazaborol-2'-yl)-benzene (4)

A solution of **2** (0.40 g, 0.92 mmol) and elemental sulfur (0.01 g, 3 mmol) in 30 mL of toluene was stirred for 1 d at room temperature. It was filtered and the filtrate was freed from solvent *in vacuo*. The crude product was washed with *n*-pentane (3×20 mL) and then crystallised from a 1 : 1 mixture of CH₂Cl₂ and *n*-hexane. Product **3** was obtained as colourless crystals. Yield 0.23 g (53%).

Found C 71.09, H 6.01, N 6.62%. C₂₈H₂₈BN₂PS (466.39) requires: C 72.11, H 6.05, N 6.01%.

Compound	Solvent	$\lambda_{\max, abs.} [nm]$	$E [\mathrm{L} \mathrm{mol}^{-1} \mathrm{cm}^{-1}]$	$\lambda_{\rm max, \ em.} \ [nm]$	Stokes shift [cm ⁻¹]	$arPsi_{ m f}$
2	$c - C_6 H_{12}$	295	17 981	_	_	
2	CH ₂ Cl ₂	298	13 802			_
3	$c - C_6 H_{12}$	298		384	6880	0.70
3	PhCH ₃	292		399	7680	0.72
3	CHCl ₃	300		412	8940	0.20
3	THF	299		416	9080	0.74
3	CH ₂ Cl ₂	299		426	9630	0.70
4	$c - C_6 H_{12}$	300	9850	370	6090	0.04
4	CH ₂ Cl ₂	300	13 884	431	9590	0.56
5	$c - C_6 H_{12}$	303	10 634	369	5700	0.05
5	CH ₂ Cl ₂	303	5664	429	8950	0.01
6	$c - C_6 H_{12}$	308		385	7040	
6	PhCH ₃	310	11 470	414	7990	0.68
6	CHCl ₃	308	12 580	430	10 870	0.09
6	THF	307	11 570	436	9500	0.33
6	CH_2Cl_2	307	12 900	442	10 220	0.54
6	MeCN	297	11 690	425	10 600	0.21
7	THF	315	5878	469	11 000	0.03
7	CH_2Cl_2	329	18 950	496	10 440	0.57
8	$c - C_6 H_{12}$	310	16 740			
8	CH_2Cl_2	311	18 050			
9	CH_2Cl_2	311		445	9680	0.85
10	$c - C_6 H_{12}$	318	9196	389	6110	0.10
10	CH_2Cl_2	318	8490	442	9740	0.01
11	PhCH ₃	332	9080	476	8400	0.15
11	CHCl ₃	337	9460	493	9100	0.34
11	THF	328	8120	488	9130	0.03
11	CH_2Cl_2	340	8390	504	9060	0.69
11	MeCN	325	6050	517	11 150	0.09
11	DMSO	328	9170	526	6780	
12	$c - C_6 H_{12}$	327	29 600	408	6070	0.99
12	THF	329	31 600	477	9440	0.09
13	$c - C_6 H_{12}$	345	19 400	439	6210	0.81
13	THF	350	20 100	482	7820	0.46

 Table 3
 Selected photophysical data of compounds 2–13



Fig. 3 UV/Vis-spectra of 3-7 in CH_2Cl_2 .



Fig. 4 Emission spectra of 3 in different solvents (l. t. r.) (c-C₆H₁₂, toluene, THF, CHCl₃, CH₂Cl₂).

4-(Diphenyl-selenophosphanyl)-1-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-benzene (5)

Samples of **2** (0.075 g, 0.17 mmol) and grey selenium (0.0136 g, 0.17 mmol) were stirred in CH_2Cl_2 (15 mL) for 1 d at room temperature. It was filtered, the filtrate freed from solvent and the colourless solid residue was washed with *n*-pentane (2 × 10 mL). Product **5** was isolated as a colourless powder (0.085 g, 96.5% yield).

Found C 65.34, H 5.75, N 5.34%. $C_{28}H_{28}BN_2PSe$ (513.28) requires: C 65.52, H 5.50, N 4.46%.

[κ-P{4-(diphenylphosphanyl)-1-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-benzene}-gold(1) chloride] (6)

A mixture of **2** (0.027 g, 62.4 mmol) and 0.020 g (62.4 mmol) of tetrahydrothiophene-gold(1) chloride in 5 mL of CH_2Cl_2 was



Table 4 B3LYP/6-311G(d, p) calculated MO's (LUMO, HOMO, HOMO – 1, HOMO – 2, HOMO – 3) energies [eV] of **2**, **3**, **4** and **5**, as well as the HOMO–LUMO gap [eV–nm] and first four Δ SCF/TD-DFT ionization energies [eV], contour values are plotted at ± 0.04 (e bohr⁻³)^{1/2}

stirred for 20 min at room temperature. Concentrating the mixture was followed by the addition of 10 mL of *n*-pentane, whereby a colourless solid precipitated. It was filtered and the filter-cake was washed with *n*-pentane (2×10 mL). After drying *in vacuo* at 60 °C overnight, 0.022 g of product **6** (53%) was obtained. Single crystals of **6** were grown from a 1 : 2 mixture of CH₂Cl₂ and *n*-pentane.

Found C 50.68, H 4.26, N 4.38%. C₂₈H₂₈AuBClN₂P (667.75) requires: C 50.36, H 4.38, N 4.20%.

[4-(Methyl-diphenylphosphonio)-1-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-benzene]-monomethylsulfate (7)

A sample of dimethyl sulfate (0.67 g, 5.27 mmol) was added dropwise to a well-stirred solution of **2** (1.91 g, 4.4 mmol) in 50 mL of CH₂Cl₂. Stirring was continued overnight before solvent and volatiles were removed *in vacuo*. The residue was dissolved in CH₂Cl₂ (5 mL) and layered with *n*-hexane (5 mL). Then the vessel was stored at -7 °C for 10 h. Colourless solid 7 (2.03 g, 83%) was isolated by filtration and drying *in vacuo*. Single crystals of 7 were grown from a concentrated CH₂Cl₂solution which was layered with the five-fold volume of *n*-pentane and stored at -7 °C. Found C 63.32, H 6.48, N 4.50%. C₃₀H₃₅BN₂O₄PS (561.46) requires: C 64.18, H 6.28, N 4.99%.

5-(Diphenylphosphanyl)-2-(1',3'diethyl-1',3',2'-benzodiazaborol-2'-yl)-thiophene (8)

solution of 5-(diphenylphosphanyl)-2-bromothiophene Α (2.45 g, 7.17 mmol) in diethyl ether (20 mL) was added dropwise to a chilled (-78 °C) solution of tert-butyllithium (15.1 mmol) in 20 mL of diethyl ether, before a sample of 2-bromo-1,3-diethyl-1,3,2-benzodiazaborole 1 (1.99 g, 7.89 mmol) was added. The mixture was allowed to warm to room temperature and filtered. The filter-cake was washed with diethyl ether (50 mL). Solvent and volatile components were removed in vacuo, and the residue was triturated with 100 mL of CHCl₃. A colourless solid was filtered off, and the filtrate was freed from the solvent. The solid residue was continuously extracted with *n*-pentane during a period of 2 d. Product 8 (1.14 g, 35%) was isolated from the filtrate as a colourless solid. Crystallisation of 8 was effected from a CH₂Cl₂-n-pentane mixture during 2 d at -7 °C.

Found C 70.51, H 6.11, N 6.29%. C₂₆H₂₆BN₂PS (440.35) requires: C 70.92, H 5.95, N 6.36%.



Table 5 B3LYP/6-311G(d, p) calculated MO's (LUMO, HOMO, HOMO – 1, HOMO – 2, HOMO – 3) energies [eV] of **8**, **9** and **10**, as well as the HOMO–LUMO gap [eV–nm] and first four Δ SCF/TD-DFT ionization energies [eV], contour values are plotted at ±0.04 (e bohr⁻³)^{1/2}

Table 6 Comparison of calculated [B3LYP/6-311G(d,p)] data for optimized geometries of 2, 3, 4, 5, 6, 8, 9 and 10, and observed UV absorption maxima

Compound	Calc. λ_{\max} [nm]	Oscillator strength (<i>f</i>)	Exp. λ_{max} (abs, nm)	$\Delta \lambda_{max}$ (calc - exp)
2	308	0.32	298	10
3	319	0.24	299	20
4	325	0.28	303	22
5	324.5	0.22	303	21.5
6	340	0.24	308	32
8	327	0.45	311	16
9	337	0.33	311	26
10	336	0.22	318	18

5-(Diphenyl-thiophosphanyl)-2-(1',3',diethyl-1',3',2'benzodiazaborol-2'-yl)-thiophene 9

A slurry of **8** (1.81 g, 4.1 mmol) and 1.32 g (41.1 mmol) of sulfur in CH_2Cl_2 (30 mL) was stirred for 24 h at room temperature. After filtration the filtrate was evaporated to dryness. The solid residue was continuously extracted with *n*-pentane during 2 d, then dissolved in CH_2Cl_2 (10 mL) and the solution was covered with a layer of *n*-pentane (20 mL). Storing at -30 °C for

2 d afforded 0.66 g (34%) of colourless solid **8**. The generation of single crystals required storing a CH_2Cl_2 –*n*-pentane solution for three months at 20 °C.

Found C 66.08, H 5.58, N 5.92, S 13.84%. $C_{26}H_{26}BN_2PS_2$ (472.41) requires: C 66.10, H 5.55, N 5.93, S 13.57%.

5-(Diphenyl-selenophosphanyl)-2-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-thiophene (10)

A mixture of **8** (0.57 g, 1.29 mmol) and 0.15 g (1.94 mmol) of grey selenium in 20 mL CH₂Cl₂ was stirred for 48 h at 20 °C. Product **10** (0.60 g, 90%) was isolated from the filtrate by evaporating the solvent and washing the colourless solid residue with *n*-pentane.

Found C 59.87, H 5.33, N 5.09%. C₂₆H₂₆BN₂PSSe (519.31) requires: C 60.13, H 5.05, N 5.39%.

[5-(Methyl-diphenylphosphonio)-2-(1',3'-diethyl-1',3',2'benzodiazaborol-2'-yl)-thiophene]-monomethylsulfate (11)

Similar to the preparation of 7 a combination of 8 (0.05 g, 0.135 mmol) and 0.036 g (0.3 mmol) of dimethyl sulfate in

Table 7 B3LYP/6-311G(d,p) calculated MO's (LUMO, HOMO, HOMO – 1, HOMO – 2, HOMO – 3) energies [eV], Δ (HOMO – LUMO) [eV–nm] and first HOMO \rightarrow LUMO UV transition for compounds 7 and 11, contour values are plotted at ±0.04 (e bohr⁻³)^{1/2}

7 11 LUMO 4.624 4 501 номо 8 122 HOMO - 1HOMO - 2HOMO - 33.099-400.53 A(HOMO-LUMO) 3.075-403.66 First HOMO \rightarrow 2.6802-462.59 2.6760-463.31 LUMO UV transition

CH₂Cl₂ (10 mL) afforded 0.07 g (92%) of colourless crystalline 11 from CH₂Cl₂–*n*-hexane (1 : 2) at -30 °C.

Found C 58.68, H 5.62, N 4.84%. C₂₈H₃₃BN₂O₄PS₂ (567.49) requires: C 59.26, H 5.86, N 4.94%.

Computational methods

All calculations were performed by using the Gaussian 0949 program package with the 6-311G(d,p) basis set. DFT has been shown to predict various molecular properties successfully.50 All geometry optimizations were carried out with the B3LYP⁵¹ functional and were followed by frequency calculations to verify that the stationary points obtained are true energy minima. Ionization energies (IE) were calculated by using the B3LYP functional with Δ SCF/TD-DFT, which means that separate SCF calculations were performed to optimize the orbitals of the ground state and the appropriate ionic state (IE = $E_{\text{cation}} - E_{\text{neutral}}$). The advantages of the most frequently employed Δ SCF/TD-DFT method of calculations of the first ionization energies have been demonstrated previously.⁵² The TD-DFT⁵³ approach provides a first principle method for the calculation of excitation energies within a density functional context taking into account the low-lying ion calculated by the Δ SCF method.

Table 8 B3LYP/6-311G+(d,p) calculated ground state (μ_g) dipole moments, molecular polarizabilities (α), static first-order molecular hyperpolarizabilities (β) and the change of dipole moments ($\Delta \mu$) of compounds 2–11

Compound	$\mu_{\rm g}$ [D]	α [10 ⁻²³ esu]	β [10 ⁻³⁰ esu]	Δμ [D]
2	1.5	5.9	4.6	14.2
3	3.9	5.8	16.0	18.6
4	5.0	6.2	19.4	16.9
5	4.9	6.3	20.1	12.4
6	10.2	6.6	25.7	20.0
7	12.6	6.1	120.2	20.7
8	2.3	5.9	13.8	12.6
9	5.6	6.1	20.0	13.2
10	5.5	6.1	19.6	10.9
11	11.3	5.8	96.8	15.5

Conclusions

We have presented the synthesis of new molecules containing 1,3,2-benzodiazaborole moieties connected to diphenyl-phosphino groups *via p*-phenylene- or 2,5-thiophene-diyl linkers using known methodologies.

Modification of the phosphorus atom to Ph₂P(X) (X = O, S, AuCl) functionalities leads to highly luminescent materials with quantum yields in the range of $\Phi_{\rm f} = 0.70$ to $\Phi_{\rm f} = 0.56$, while for X = Se only weak luminescence was detected ($\Phi_{\rm f} = 0.01$). This is presumably due to dissimilarities in the frontier orbital situation of the molecules.

With the exception of the selenium derivatives **5** and **10** the HOMOs of the new compounds are located on the benzodiazaborole part. In **5** and **10** the HOMOs are represented by the lone pair on selenium. The LUMOs are of π^* character and are located at the phenylene-/thiophene-bridge with slight contributions of the vacant $2p_z$ orbital on boron.

For all molecules under study, the most intense transition (between 200 and 400 nm) corresponds to a charge transfer from the benzodiazaborole group to the phenylene or thiophene bridge, respectively. Additionally, unlike the absorption maxima, emission maxima show large solvatochromic shifts in solvents of increasing polarity. This is in agreement with essentially nonpolar ground states for the compounds 2-5, 8-10 with calculated dipolar moments μ_g of 1.5–5.6 D, much more pronounced polarity is conferred to compound 6 (10.2 D) and two cations 7 (12.6 D) and 11 (11.3 D). Changes of the dipole moments between the ground state and excited state $\Delta \mu$ are in the range of 10.9 D in 10 to 20.7 D in 7. The strong change of the dipole moment between the ground state and excited state is characteristic of a charge transfer. The formal insertion of a thiophene in place of a phenylene unit as a linker does not provide any significant changes of the corresponding IEs of 2-6, 8-10 which means that the electronic structure seems practically unperturbed by the substitution pattern of these compounds.

None of these modifications showed a notable influence on the absorption and emission bands, whereas the spectra of phosphonium salts (X = CH_3^+) 7 and 11 showed significant red shifts. In contrast to the other materials the LUMOs of these compounds are lower in energy and exhibit considerable contributions of the phosphonium unit. According to increased dipolar

moments μ_g 12.6 D and $\Delta \mu$ 20.7. The phosphonium compound 7 is characterized by the lowest HOMO–LUMO gap (3.075 eV) and displays the most pronounced donor–acceptor behaviour in the series of compounds presented here.

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