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LETTER

Photophysical property trends for a homologous series of bis-ethynyl-substituted benzochalcogendiazoles†

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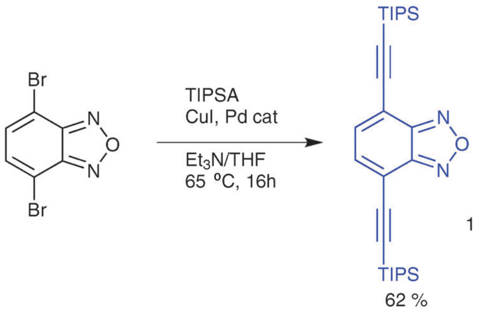
We report on the preparation and photophysical property study of three homologous benzoheteroarene–ethynylene systems. Significant differences in the series' optical properties indicate a change in the HOMO–LUMO energy as the chalcogen is altered (O, S and Se) which we have examined using TD-DFT methods and shown to be attributable to modification of the HOMO energy.

Highly conjugated linear organic compounds, based on the arylethynylene motif, have been studied extensively over recent decades. This is indubitably owing to their facile synthesis and interesting photophysical properties[1] which lends them to significant exploitation in the field of organic electronics and sensoring applications.[2]

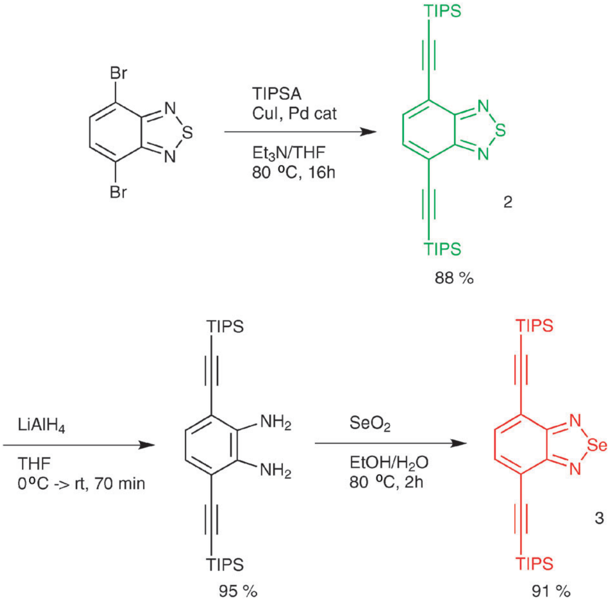
Indeed, numerous materials which feature extended acenes, functionalized with ethynyl substituents at various positions, have been reported by our group (ethynyl groups terminated with H, trimethylsilyl, triethylsilyl and triisopropylsilyl groups).[3]

In this work we present a systematic study on the change in photophysical properties as the chalcogenic heteroatom in the central ring is altered in a series of homologous structures (see compounds **1–3**, Schemes 1 and 2). The compounds conform to the arylethynylene motif, thus engendering them with potential as candidates in organic thin film transistors and OLEDs.

This work presents our first consideration of acenes featuring benzoselenadiazoles. In fact, comparison of effects caused by the heteroatom O, S and Se is becoming more common[4,5] and we are considering them due to the potential effects the heavy and large Se atom will have on the photophysical and structural properties, as well as for its touted ability to lower the bandgaps of its polymers, affording them potential in fabricated devices and applications.[6]



Scheme 1 Synthesis of compound **1**.



Scheme 2 Synthesis of compounds **2** and **3**.

Arylethynylene materials containing the benzothiadiazole unit are relatively simple to prepare, due to the ease of preparing the key intermediate 4,7-dibromobenzothiadiazole,[7] and were reported recently to display high fluorescence quantum yields.[8] Furthermore, incorporation of the benzothiadiazole moiety into oligomeric and polymeric systems has resulted in materials with promising application as OPVs and OLEDs.[9]

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† Electronic supplementary information (ESI) available: Detailed preparation of intermediates and molecular structures. CCDC 846082 (**1**), 846083 (**2**), and 846084 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2nj20847d

The oxygen-containing analogue benzofurazan is less well known in this field. However it is commonly used as a "fluorescent handle" for labelling of biological species.[10] Furthermore, recent work has found benzofurazan-containing arylethynylenes to exhibit very high quantum yields (up to 96%).[11] 4,7-Dibromobenzofurazan was made following a literature method[9] by bromination of commercially available benzofurazan. This was isolated in good yield (78%).

Sonogashira cross coupling of 4,7-dibromobenzofurazan with triisopropylsilylacetylene afforded the target 4,7-bis-(triisopropylsilylethynyl) benzofurazan (**1**, Scheme 1).

Various analogues of **2** (Scheme 2) have been reported previously, as mentioned above. However, the formation of small acetylene-coupled benzofurazan and benzoselenadiazole systems is hitherto unknown.

Preparation of benzoselenadiazole is possible *via* the diamine used to prepare the sulfur analogue (see ESI†),[12] however coupling of 4,7-dibromobenzoselenadiazole with triisopropylsilyl-acetylene under Sonogashira conditions was unsuccessful. A second method (Scheme 2) was attempted *via* the sulfur analogue, resulting in successful isolation of **3** in 91% yield.

The photophysical properties of these systems have been determined and the results are displayed in Table 1. Examination of the absorption λ_{max} illustrates a clear trend for the progression of the HOMO energies, attributable to the group VI atom. As shown in Fig. 1, the absorption maxima exhibit a bathochromic shift as the heteroatom is changed from O (372 nm) → S (384 nm) → Se (412 nm) which indicates a decrease in the $S_1 \leftarrow S_0$ gap. The emission maxima also exhibit a bathochromic shift upon substitution of the heteroatom: O (425 nm) → S (441 nm) → Se (480 nm). The compounds' absorption spectra display similar profiles, with a red-shifted shoulder on the lowest energy absorption band, assigned as the $S_1 \leftarrow S_0$ transition.

Compounds **2** and **3** display higher energy absorption bands ($S_2 \leftarrow S_0$), with some evidence of vibronic structure; such detailed fine structure is not observed in the lower energy absorption bands, attributed to charge transfer (from the alkynyl-substituents to the central, electron-deficient, heterocycle) broadening this band. Selenium derivative **3** exhibits an absorption maximum significantly more red-shifted to compound **2** than compound **2** is to **1** (1770 cm^{-1} *cf.* 840 cm^{-1}). The emission spectra (Fig. 1) for the three compounds are also similar in profile, with a single high energy shoulder on the broad emission bands. Additionally they are mirror images of the lowest energy absorption bands. The ordering of the emission maxima follows the trend displayed by the absorption maxima, with the difference between compounds **2** and **3** more than double that between compounds **1** and **2** (1843 cm^{-1} *cf.* 853 cm^{-1}). Also, upon dissolution in increasing polarity solvents, a small red shift of approximately 30 nm has been observed in the emission of all these compounds, although no change was observed in the absorption maxima.

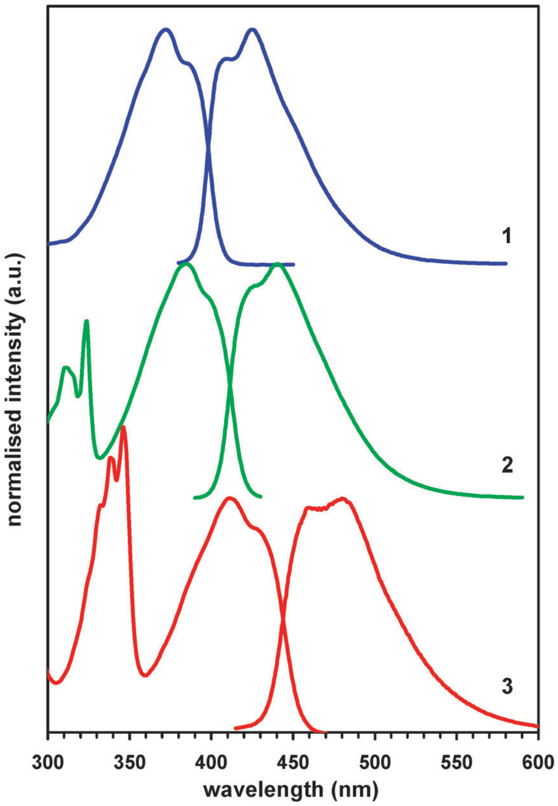


Fig. 1 Absorption and emission spectra of compounds **1–3**, measured in *n*-hexane.

Stoke's shifts increase slightly through the series, with a greater increase for compound **3**. The presence of the selenium atom drastically diminishes the oscillator strength for the $S_1 \leftrightarrow S_0$ transition in the diazole, resulting in both attenuated extinction coefficient (ε = 12 500 mol^{-1} dm^3 cm^{-1}) and pure radiative lifetime (τ_0 = 27.5 ns) relative to the oxygen and sulfur analogues ($\varepsilon \approx$ 20 000 mol^{-1} dm^3 cm^{-1}; $\varphi_f \approx 0.8$; $\tau_0 \approx 5$ ns).

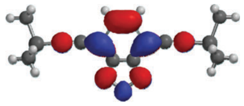
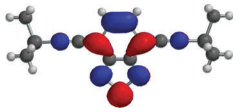
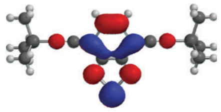
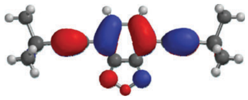
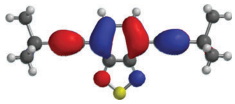
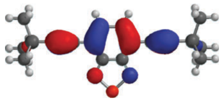
DFT calculations have been performed (Spartan '10,[13] gas-phase, B3LYP using 6-311++G(d) basis set) to afford optimised geometries of these systems, which exhibit similar structures to those determined using X-ray crystallographic analysis (see ESI†). TD-DFT energy calculations (Gaussian '09,[14] B3LYP and CAM-B3LYP using 6-311++G(d)) have afforded predictions of the HOMO–LUMO energies and frequency calculations have afforded predicted Raman vibrational modes.

From the energy calculations it is shown that the HOMO–LUMO gap is attributable to the $S_1 \leftarrow S_0$ transition for all three systems. According to the calculations (see Table 2), the greatest effect upon switching the chalcogen is observed in the energy of the HOMO, which shows a greater overall change than the LUMO experiences (0.28 eV *cf.* 0.14 eV). Furthermore, the trend exhibited for the change in the HOMO energy calculated

Table 1 Photophysical properties of compounds **1–3**, obtained in *n*-hexane

Compound	Abs λ_{max}/nm	Em λ_{max}/nm	ε/mol^{-1} dm^3 cm^{-1}	Stoke's shift/cm^{-1}	Φ_f (±10%)	τ_f/ns (±10%)	k_f^a/ns^{-1} (±0.14%)	k_{nr}^b/ns^{-1} (±10%)
1	372	435	19 900	3350	0.76	3.4	0.22	0.07
2	384	441	20 600	3370	0.83	5.1	0.16	0.03
3	412	480	12 500	3440	0.04	1.1	0.04	0.96

Table 2 Molecular orbitals visualised using Spartan '10 and Gaussian '09 (B3LYP/6-311++G(d) and CAM-B3LYP/6-311++G(d))

Compound	**1**: NON	**2**: NSN	**3**: NSeN
LUMO/eV	 −3.14	 −3.00	 −3.09
HOMO/eV	 −6.42	 −6.22	 −6.15
DFT ΔE/eV	3.28	3.22	3.06
TD-DFT ΔE/eV (oscillator strength)	3.29 (0.51)	3.23 (0.35)	3.06 (0.27)
Cam-TD DFT ΔE/eV (oscillator strength)	3.36 (0.65)	3.28 (0.50)	3.06 (0.39)
Observed band-gap/eV	3.32	3.21	3.01

using *ab initio* methods mirrors that of the absorption and emission maxima. Predicted molecular orbital plots for these systems indicate great similarity for the HOMOs. Less similarity between the homologues is observed for the LUMOs, with greater electron density being drawn towards the large selenium atom on the central ring. The linear trend of the HOMO energies (Se > S > O) is not maintained in the LUMO energies (S > Se > O). However, we are pleased to see excellent agreement between the predicted band-gap energies and those determined experimentally.

The predicted Raman spectra indicate excellent agreement with those obtained experimentally (see Fig. 2), further validating the computed structures. Compound **1** features a higher energy vibration (1418 cm^{-1}) compared to equivalent vibrational modes at approximately 1352 cm^{-1} for **2** and 1362 cm^{-1} for **3**. These vibrational modes correspond to a stretch in the central ring system, so is thus clearly an effect of the chalcogen.

In conclusion we have shown that in otherwise identical systems, the group VI heteroatom exhibits substantial control over its host molecules' photophysical properties by modification of the HOMO energy. Calculations have confirmed this assessment, also predicting band gaps in excellent agreement with those determined experimentally. The oxygen and sulfur derivatives (**1** and **2**) behave quite differently to compound **3**, displaying similar quantum yields and lifetimes and thus rates of radiative decay (k_f), implying essentially the same mechanism of decay. The selenium derivative displays the lowest energy absorption and emission maxima, as well as an attenuation of the fluorescence quantum yields and lifetimes. The selenium derivative exhibits a much lower rate of radiative decay (k_f), indicating potentially a different decay pathway.

The properties of compounds **1** and **2** are so alike that we question the lack of research into the oxygen-containing derivatives for material-based applications, echoing Swager's earlier comments,[9] especially considering their facile preparation.

This work has demonstrated the significant control the chalcogen has over its parent molecule's HOMO energy, and as such research is being continued into larger heteroacene systems incorporating selenium. This will enable further comparisons with sulfur-containing analogues from the group's earlier work.[3]

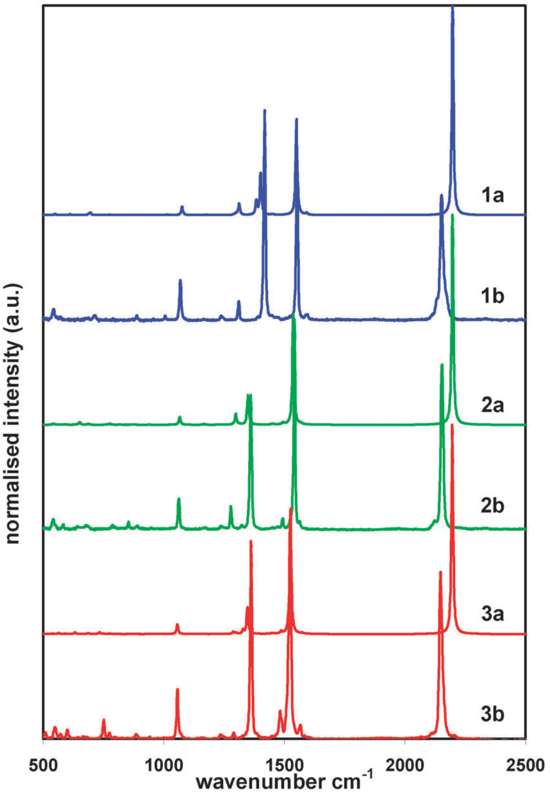


Fig. 2 Simulated (a) and experimental (b) Raman spectra for compounds **1–3**.

Experimental

Syntheses

4,7-Bis(triisopropylethynyl)-benzofurazan (1). 4,7-Dibromobenzofurazan (370 mg, 1.33 mmol) was dissolved in a mixture of THF (15 mL) and Et_3N (10 mL) and the solution degassed by 4 freeze–pump–thaw cycles. Under a flow of nitrogen triisopropylsilyl acetylene (0.75 mL, 3.33 mmol), $Pd(PPh_3)_4$ (46 mg, 5 mol%) and CuI (5 mg, 2 mol%) were added and the mixture stirred at 65 °C for 16 h, during which time the solution turned fluorescent yellow/green under illumination by a long wave (365 nm) UV lamp, and a large amount of precipitate had formed. The mixture was filtered through a short silica plug, eluting with hexanes and diethylether. The collected fraction was reduced *in vacuo* and the crude product (orange/brown solid) was chromatographed on a silica gel column. Using gradient elution of petroleum ether : diethylether (100 → 75 : 25) the compound was isolated as a yellow, slightly tacky solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 42H), 7.46 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 11.41, 18.79, 100.47, 103.00, 113.07, 134.63, 149.78; MS (EI): *m*/*z*: calcd for $C_{28}H_{44}N_2SSi_2$ 480.2963, found: 480.2992.

4,7-Bis(triisopropylsilylethynyl)-benzothiadiazole (2). 4,7-Dibromobenzothiadiazole (310 mg, 1.05 mmol) was dissolved in a Et_3N/THF (1 : 4, 15 mL) solvent mixture and the solution degassed *via* three freeze–pump–thaw cycles. TIPS-acetylene (0.5 mL, 2.2 mmol) was added *via* a syringe and $PdCl_2(PPh_3)_2$ (40 mg, 5 mol%) and CuI (10 mg, 2 mol%) added under a flow of nitrogen. The mixture was stirred at 75 °C for 48 h. The resulting mixture was filtered through a silica plug, eluting with pet. ether/ethyl acetate. The solvent was reduced *in vacuo* and the residue chromatographed on a silica gel column, eluting with petroleum ether. The product was isolated as a lightly yellow solid (460 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.24 (m, 42H), 7.67 (s, 2H); 13C{1H} NMR (75 MHz, $CDCl_3$): 11.49, 18.85, 100.40, 102.40, 117.61, 132.82, 154.79; MS (EI): *m*/*z*: calcd for $C_{28}H_{44}N_2SSi_2$ 496.31, found: 496.28; elemental analysis calcd for $C_{28}H_{44}N_2SSi_2$ C 67.68, H 8.93, N 5.64%, found: C 67.78, H 9.04, N 5.69%.

4,7-Bis(triisopropylsilylethynyl)-benzoselenadiazole (3). To a solution of 3,6-bis(triisopropylsilyl ethynyl)benzene-1,2-diamine (0.70 g, 1.48 mmol) in EtOH (13 mL) at 60 °C was added a solution of selenium dioxide (0.49 g, 4.45 mmol) in hot water (4 mL). After 2 h the suspension was filtered through a Büchner funnel and the collected yellow precipitate was washed with water. Purification by flash column chromatography gave a deep yellow solid (silica gel, petroleum ether (100) to petroleum ether/ethyl acetate, 99 : 1) in good yields (730 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.23 (m, 42H), 7.57 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 11.53, 18.87, 100.10, 103.05, 119.40, 133.10, 159.65. IR: υ = 2942, 2863, 2148, 1460, 994, 881, 801; MS (ESI): *m*/*z* calcd for $C_{28}H_{45}N_2SeSi_2$ $[M + H]^+$: 545.22823, found: 545.22838, correct isotope distribution; calcd for $C_{28}H_{44}N_2SeSi_2$ C 61.84, H 8.16, N 5.15%, found: C 61.95, H 8.26, N 5.18%.

Acknowledgements

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