Dibenzothiophene-*S,S*-dioxide–fluorene co-oligomers. Stable, highly-efficient blue emitters with improved electron affinity†

Irene I. Perepichka,[a] Igor F. Perepichka,*[bc] Martin R. Bryce*[c] and Lars-Olof Pålsson[c]

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Incorporation of dibenzothiophene-*S,S*-dioxide units into conjugated fluorene oligomers changes the frontier orbital energy levels and presents an effective way to increase the electron affinity of these materials, which are highly fluorescent with bright blue emission in both solution and the solid state.

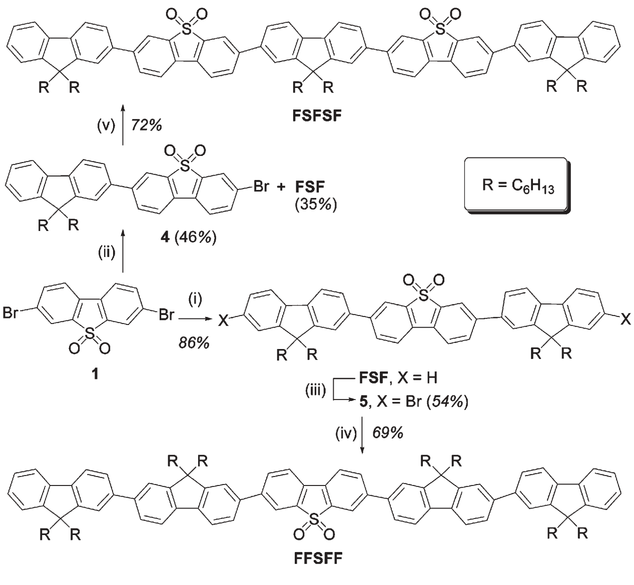
Monodisperse, well-defined π-conjugated oligomers offer many exciting prospects in materials science and organic nanoelectronics providing deep insights into the photophysics of conjugated systems and the supramolecular structure of conjugated polymers.[1] Over the last decade, polyfluorenes have emerged as leading electroluminescent materials with bright blue emission, high hole mobility and easily tunable properties through chemical modifications and copolymerisations.[2] Many linear oligofluorenes have been synthesised and studied as models for polyfluorenes.[3]

In the fluorene structure the two benzene rings are coplanarised by the bridging C9 atom, which increases the conjugation length and improves the luminescence efficiency of the materials (as compared to poly-*p*-phenylenes). Dibenzothiophene-*S,S*-dioxide (**S**) can be considered as an alternative structure with coplanar benzene rings. Additionally, the acceptor character of the SO_2 group should decrease the LUMO energy level thereby improving the electron transport properties of materials. Moreover, we expected that in contrast to structurally similar electron deficient 9-fluorenone units, which are known to quench the blue photo- and electroluminescence (PL, EL) when incorporated into oligo/polyfluorenes and result in the appearance of undesirable green emission,[4] **S** units would not alter the PL efficiency of the materials. Thus, Barbarella *et al.* recently showed that incorporation of thiophene-*S,S*-dioxide units into oligothiophenes results in easily-reduced thiophene-based materials with highly efficient and tunable photoluminescence (PL).[5] Light-emitting devices based on oligomers and polymers containing thiophene-*S,S*-dioxide units in the backbone have also been demonstrated.[6]

We now report the incorporation of dibenzothiophene-*S,S*-dioxide (**S**) units into the main chain of oligofluorenes and a study of the redox and photoluminescent properties of these new materials. Three 9,9-dihexylfluorene (**F**)–**S** co-oligomers (**FSF**, **FFSFF**, and **FSFSF**) were synthesised using a Suzuki cross-coupling protocol between dibenzothiophene-*S,S*-dioxide derivatives (**1**, **4**, or **5**) and 9,9-dihexylfluorene-2-boronic (**2**) or -2,7-diboronic acids (**3**) (Scheme 1).

All three oligomers are yellowish, highly fluorescent materials with bright blue emission in both solution (λ_{PL} = 430–450 nm, Φ_{PL} = 65–67%) and the solid state (λ_{PL} = 447–462 nm, Φ_{PL} = 44–63%) (Table 1). They have good solubility in non-polar solvents (chloroform, toluene, tetrahydrofuran). Whereas there are minor red shifts of 10–16 nm in both absorption and PL spectra from trimer **FSF** to pentamers **FFSFF** or **FSFSF**, both pentamers show near identical PL emission (~460 nm) and longest wavelength absorption maxima (~385 nm) (Fig. 1). An important feature of the **F–S** oligomers is that their high PL efficiency is maintained in the solid state (44–63%), in contrast to fluorene–thiophene-*S,S*-dioxide copolymers, where the PL efficiency is drastically reduced in films compared to solution (0.5–0.8% and 16–19%, respectively).[6b,c]

The oligomers are thermally stable compounds with decomposition temperatures T_d > 300 °C; no mass loss was observed below this temperature in TGA experiments (see ESI†). The films were annealed at 180 °C for 24 h in air and then re-dissolved for NMR and MS characterisation, which showed no signature of decomposition/oxidation processes. FTIR spectra of the annealed



Scheme 1 (i) **1** + **2** (2 mole equiv.), $Pd(PPh_3)_2Cl_2$, dioxane–2M K_2CO_3–H_2O, reflux, 24 h; (ii) **1** (3 mole equiv.) + **2**, $Pd(PPh_3)_2Cl_2$, dioxane–2M K_2CO_3–H_2O, reflux, 20 h; (iii) Br_2–$CHCl_3$, rt, 40 h; (iv) **2**, $Pd(PPh_3)_2Cl_2$, dioxane–2 M K_2CO_3–H_2O, 95 °C, 18 h; (v) **3**, $Pd(PPh_3)_2Cl_2$, dioxane–2 M K_2CO_3–H_2O, 100 °C, 40 h.

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† Electronic supplementary information (ESI) available: experimental and calculation details, synthetic procedures and characterisation for intermediates and **F–S** co-oligomers, including ^1H and ^{13}C NMR spectra, MS, electron absorption and PL spectra, CV, TGA and DSC. See http://www.rsc.org/suppdata/cc/b4/b417717g/

*i_perepichka@yahoo.com; i.f.perepichka@durham.ac.uk (Igor F. Perepichka)
m.r.bryce@durham.ac.uk (Martin R. Bryce)

Table 1 Spectral and electrochemical data for oligomers **FSF**, **FFSFF**, **FSFSF**, and **FFFFF**

	λ_{abs}/nm CHCl$_3$	λ_{abs}/nm film	λ_{PL}/nm CHCl$_3$	λ_{PL}/nm film	Φ_{PL} (%)[b] CHCl$_3$	Φ_{PL} (%) film[c]	$E_{1/2}^{ox}$/V[d]	$E_{1/2}^{red}$/V[e]	E_g^{opt}/eV[f]	E_g^{CV}/eV[g]
FSF	344, 369	352, 372	430, 442sh	447	67	63 (44)	1.28, 1.35	−2.02, −2.34	3.01	3.12
FFSFF	360sh,[a] 384	360sh, 384	449	457	67	46 (28)	1.04, 1.35	−2.01, −2.29	2.90	2.91
FSFSF	360sh, 385	360sh, 383	430, 450sh	462	65	44 (21)	1.22, 1.32	−2.00, −2.34, −2.44	2.94	2.98
FFFFF	371	370					0.91, 1.02, 1.22	−2.53, −2.62	3.05	3.27

[a] Shoulder. [b] PL quantum yields. [c] In parentheses for annealed films (150 °C, 3 h). [d] In DCM; ref. Ag/Ag$^+$. [e] In THF, ref. Ag/Ag$^+$. [f] From the red edge of the absorption in CHCl$_3$. [g] From the difference between the onsets of the oxidation and reduction processes.

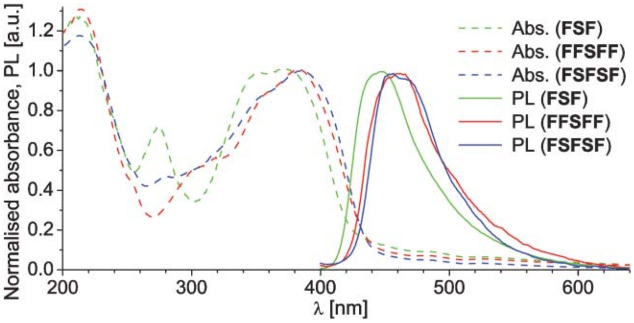

Fig. 1 Normalised UV-Vis absorption and photoluminescence spectra of **FFF**, **FFSFF** and **FSFSF** co-oligomers in films (λ_{exc} = 390 nm).

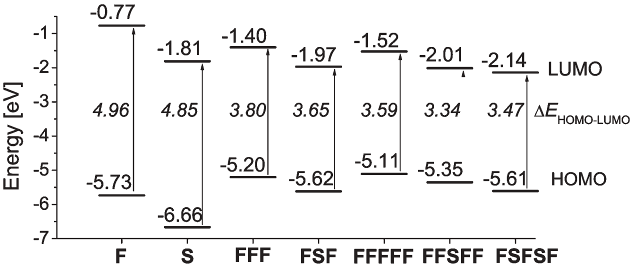

Fig. 2 B3LYP/6-31G(d) energy levels diagram for oligofluorenes and fluorene–dibenzothiophene-*S,S*-dioxide co-oligomers (in these calculations **F** denotes 9,9-diethylfluorene, see ESI†).

films (180 °C, 24 h) did not show the appearance of the C=O stretching mode of the fluorenone moiety (1720 cm^{-1}), which is generally observed on annealing polyfluorenes[4a,d] (ESI†). PL spectroscopy indicated that on annealing the films at 150 °C structural ordering of these short oligomers occurs: the initially broad featureless PL spectra became well-structured with clear vibronic bands (Fig. S6, ESI†). This ordering is accompanied by some decrease in PL efficiency (Table 1). It should be noted, however, that because of the independence of the PL efficiency and the shape of the PL spectra of **FFSFF** films with annealing time (1, 2 or 3 h) we attribute this to the film reorganisation and exclude the possibility that the decrease in PL efficiency was the result of thermal decomposition (see ESI†). Moreover, no additional band in the green region of the PL spectra was observed after annealing, which typically occurs with polyfluorenes as a result of the oxidative formation of fluorenone defects and fast energy transfer to these sites.[4] Thus, although **FFSFF** has a melting point above 200 °C (226 °C in capillary; 219 °C in DSC experiments at a heating rate of 10 °C min^{-1}, ΔH = 16 kcal mol^{-1}), differential scanning calorimetry of freshly prepared material, which is amorphous, shows a glass transition at 117 °C (ΔH = 0.70 kcal mol^{-1}). Obviously, heating above this temperature should lead to reorganisation of the film, which will affect the PL spectra and the PL efficiency after annealing. Re-dissolving the film, which was annealed at 150 °C for 3 h and then kept at ambient temperature in air for 6 months in chloroform, showed the same value of Φ_{PL} as for pristine material (Fig. S7, ESI†).

DFT calculations reveal that both HOMO and LUMO energies of **S** are *ca.* 1 eV lower than those of **F** (Fig. 2). A comparison of the HOMO/LUMO levels for oligofluorenes **FFF** and **FFFFF** with those for the co-oligomers which incorporate **S** units, shows that for the latter systems the decrease in LUMO energy levels is pronounced as well. Thus, for pentamers **FFSFF** and **FSFSF** the LUMO levels are 0.49 eV and 0.62 eV lower than that of **FFFFF**, indicating that these co-oligomers possess much better electron accepting properties. Nonetheless, **FFSFF** is still a good donor: its HOMO level is only 0.24 eV lower than that for pentafluorene **FFFFF**, so one could expect both p- and n-doping processes for **F–S** co-oligomers.

To study the p- and n-doping ability of the oligomers we studied their electrochemical properties. Cyclic voltammetry of all the **F–S** oligomers showed reversible or quasi-reversible oxidation peaks similar to the corresponding oligofluorenes (Table 1). Moreover, on reduction they showed two reversible well-separated waves, with the reduction potentials significantly positively shifted compared to oligofluorenes (Fig. 3, Table 1).[7] For comparison we performed CV experiments for pentafluorene oligomer **(FFFFF)** under the same conditions (Table 1, ESI†). The first oxidation potentials of **FFSFF** (1.04 V) and **FSFSF** oligomers (1.22 V) are negatively shifted compared to **FFFFF** by 0.13 and 0.31 V, respectively, indicating their moderately reduced donor

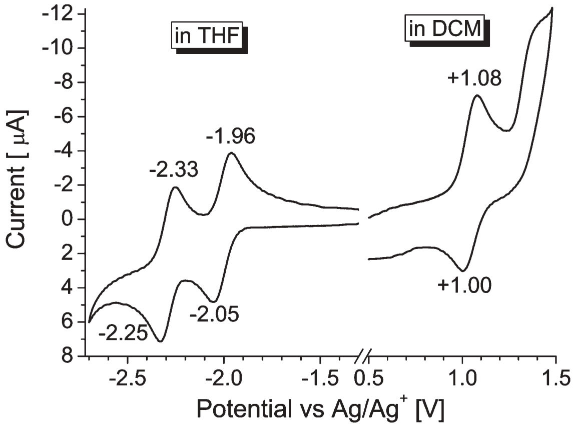

Fig. 3 Cyclic voltammetry of **FFSFF**; electrolyte 0.2 M Bu$_4$NPF$_6$, scan rate 100 mV s^{-1}, 20 °C.

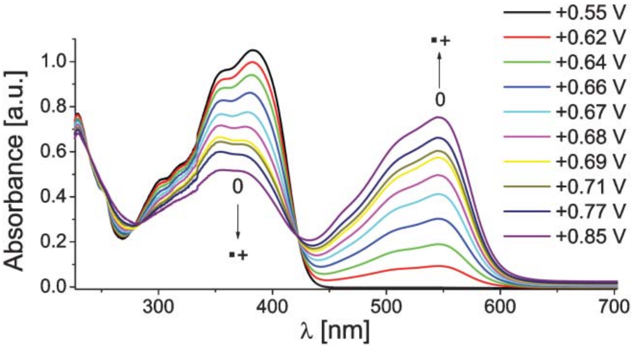

Fig. 4 Spectroelectrochemistry of **FFSFF** oxidation in 0.2 M Bu_4NPF_6–DCM, 20 °C; potentials are *vs.* Pt wire reference electrode.

properties. On the other hand, positive shifts of the first reduction potentials for **FFSFF** (0.52 V) and **FSFSF** (0.53 V) compared to **FFFFF** are more pronounced, thus confirming their substantially improved acceptor properties (Fig. 3). These experimental results are in reasonably good agreement with theoretical calculations, which predict a decrease in the LUMO (by 0.49 eV for **FFSFF** and by 0.62 eV for **FSFSF**) and HOMO (by 0.24 eV for **FFSFF** and by 0.50 eV for **FSFSF**) energy levels for **F–S** pentamers compared to **FFFFF** (Fig. 2).

An increase in the difference between the first and the second single-electron reduction processes for the **F–S** oligomers ($\Delta E_{1/2}^{\mathrm{red1-2}}$ = 0.28–0.34 V) compared to the corresponding oligofluorenes ($\Delta E_{1/2}^{\mathrm{red1-2}}$ = 0.09 V for **FFFFF**) indicates an increase in the thermodynamic stability of the derived radical anions, thus confirming the good electrochemical stability of the **F–S** oligomers for both p- and n-doping.

Spectroelectrochemical studies on **FFSFF** established the reversible generation of radical cation species with a characteristic absorption at 545 nm, typical for oligofluorene derivatives (Fig. 4).[7a] This oxidation is a fully reversible process and on sweeping the potential the absorption of neutral **FFSFF** was completely restored.

In summary, well-defined fluorene–dibenzothiophene-*S,S*-dioxide oligomers have been synthesised, which show high luminescence efficiency in both solution and the solid state. The results demonstrate that dibenzothiophene-*S,S*-dioxide is a promising electron-deficient unit for light-emitting oligomers and polymers, allowing tuning of frontier orbital energies, such that the materials can be reversibly both p- and n-doped. Whereas the alternating **F–S** copolymer is highly fluorescent but with very low solubility, random **F–S** copolymers (up to 30% of **S** units) are soluble in common solvents and demonstrate bright blue fluorescence with high Φ_{PL}. Preliminary results on random **F–S** copolymers for PLED applications have demonstrated an increase in the external EL efficiency (Φ_{EL}^{ex}) of the devices with an increasing content of **S** units in the co-polymers, reaching values of Φ_{EL}^{ex} for single-layer ITO/PEDOT/polymer/Ca/Al devices as high as 3% for the **F–S** co-polymer containing 30 mol% of **S** units. Detailed device studies will be reported elsewhere.[8]

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Irene I. Perepichka,[a] **Igor F. Perepichka,***[bc] **Martin R. Bryce***[c] **and Lars-Olof Pålsson**[c]
[a]*Department of Chemistry, Donetsk National University, Donetsk 83055, Ukraine*
[b]*L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk 83114, Ukraine. E-mail: i_perepichka@yahoo.com*
[c]*Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: i.f.perepichka@durham.ac.uk; m.r.bryce@durham.ac.uk; Fax: +44-191-3844737*

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