Synthesis and Characterization of Fluorene-Based Oligomers and Polymers Incorporating *N*-Arylphenothiazine-*S,S*-dioxide Units

KIRAN T. KAMTEKAR,¹ KATJA DAHMS,² ANDREI S. BATSANOV,² VYGINTAS JANKUS,³ HELEN L. VAUGHAN,³ ANDREW P. MONKMAN,³ MARTIN R. BRYCE²

¹Zumtobel LED Division, Green Lane Industrial Estate, Spennymoor, Durham, DL16 6HL, United Kingdom ²Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom ³Department of Physics, Durham University, South Road, Durham, DH1 3LE, United Kingdom

Received 28 October 2010; accepted 29 November 2010 DOI: 10.1002/pola.24527 Published online 3 January 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of 3,7-bis(9,9-di-*n*-hexylfluoren-2-yl)-*N*-arylphenothiazine-*S*,*S*-dioxide trimers and (9,9-di-*n*-octylfluorene-2,7-diyl-co-*N*-arylphenothiazine-*S*,*S*-dioxide) co-polymers, with varying ratios of phenothiazine-*S*,*S*-dioxide units, have been prepared in good yields by palladium-catalyzed cross-coupling reactions. The materials are deep blue emitters and show no solvatochromism or evidence for an intramolecular chargetransfer state. The photoluminescence quantum yields of the trimers are Φ_{PL} 15–30% in solution and 14–25% in films. The polymers demonstrated very high values in solution (Φ_{PL} 74– 84%) and Φ_{PL} values in films of 28–47%. The estimated HOMO

INTRODUCTION Following intense worldwide academic and industrial investigations over the last 20 years, organic/polymer light-emitting diode (O/PLED) displays are making their way into the marketplace.1 However, the majority of commercial OLED displays are fabricated by vacuum processing techniques which limit the size of the display that can be manufactured at commercially acceptable yields and costs. Solution processing techniques offer a much more scalable method for fabricating displays and lighting panels.² Hence, there is continued interest in soluble-processable conjugated polymers. Polyfluorenes (PFs) are among the most widely studied light-emitting polymers due to their facile chemical modifications, high quantum yields and large band gap which allows for the insertion of co-monomers or dopants to tune the emitted color over the full gamut of the visible spectrum.³ However, PFs suffer from several problems: there is a large barrier to hole injection into PFs from the common hole injection layer (HIL) poly(ethylenedioxythiophene) PEDOT: poly(styrenesulfonate) PSS, and PF devices are prone to degradation over time leading to a broad green emission band and reduced efficiency. This emission has been attributed to the formation of aggregates and defects in the chain or at the end groups.⁴ Thus, the use of PFs to achieve highefficiency blue OLEDs with acceptable lifetimes has not yet been accomplished.

energy levels are between -5.64 and -5.62 eV for the polymers with 15% incorporation of the phenothiazine-*S*,*S*-dioxide units. An analogous *N*-arylphenothiazine co-polymer shows significantly red shifted absorption and emission. Solution electrochemical data and density functional theory calculations are also presented. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1129–1137, 2011

KEYWORDS: conjugated polymers; fluorescence; fluorene; luminescence; oligomers; phenothiazine

We⁵ and other groups⁶ have shown that the incorporation of electron deficient dibenzothiophene-*S*,*S*-dioxide-3,7-diyl (S) units into a PF backbone can stabilize the blue emission against the onset of green emission. This occurs via formation of an intramolecular charge-transfer (ICT) state in the $p(F-S)_n$ co-polymers which acts as a competing trap to any fluorenone units in the polymer chain. However, the emission from $p(F-S)_n$ co-polymers is slightly red-shifted compared with PF. It is, therefore, intriguing to further investigate the properties of sulfone-containing polyfluorenes.⁷ In the present work we incorporate N-arylphenothiazine-S,S-dioxide (S_N) units into fluorene trimers and polymers. The S_N units reduce the conjugation in the backbone compared to the S analog, as shown in Figure 1. Additionally, the folded structure of the S_N ring system should hinder aggregation and interchain excimer formation which lead to red-shifted emission.

Phenothiazines have been studied as electron donor units and hole-transport materials.⁸ Oxidation of phenothiazine to the SO or SO₂ derivatives will impart electron accepting properties to the system. Poly(*p*-phenylene vinylene)-based co-polymers containing phenothiazine-*S*-oxide and phenothiazine-*S*,*S*-dioxide moieties were reported with low molecular weights.⁹ BASF reported small molecules based on

Additional Supporting Information may be found in the online version of this article. Correspondence to: M. R. Bryce (E-mail: m.r.bryce@durham.ac. uk)

Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 1129–1137 (2011) © 2011 Wiley Periodicals, Inc.



FIGURE 1 Reducing the backbone conjugation in \boldsymbol{S}_{N} compared with $\boldsymbol{S}.$

phenothiazine-*S*,*S*-dioxides, for example, the bis-sulfone **1** as a hole- and exciton-blocking layer (Fig. 2).¹⁰ To our knowledge, Shim and coworkers¹¹ are the only group to report the insertion of *N*-alkylphenothiazine-*S*,*S*-dioxides into PF derivatives.

The aims of the present work were: (i) To exploit *N*-aryl substituents on the phenothiazine-*S*,*S*-dioxide moiety to provide additional versatility by varying the electronic properties of the aryl group. (ii) To prepare \mathbf{F} - $\mathbf{S}_{\mathbf{N}}$ oligomers and study their photophysical and solution electrochemical properties. (iii) To prepare $(\mathbf{F}$ - $\mathbf{S}_{\mathbf{N}})_n$ co-polymers incorporating *N*-arylphenothiazine-*S*,*S*-dioxide units. An analogous *N*-arylphenothiazine co-polymer is also reported to probe the effect of the sulfone unit. Oligomers incorporating both \mathbf{F} and $\mathbf{S}_{\mathbf{N}}$ units have not been reported previously: oligomers provide a good model for the properties of analogous polymers.¹² The results are supported by density functional theory (DFT) calculations.

EXPERIMENTAL

General experimental details and characterization data for compounds **7a-f**, **8a-f**, **9a-f**, **11b-f**, **14a-d**, and **15** are in the Supporting Information. Compounds **12**, **13a**, and **13b** were synthesized by the literature procedures and were purified by recrystallization from ethanol then hexane (**12**) or acetonitrile then hexane (**13a**, **13b**).

For the photophysical measurements, the trimers and polymers were dissolved in toluene or chlorobenzene. Films were spin-coated at 2500 rpm for 1 min from 10 mg/mL (polymers) or 20 mg/mL (trimers) toluene solutions. Steady state absorption and luminescence emission spectra of the solutions and films were recorded using a UV/VIS spectrophotometer (UV-VIS 3600 from Shimadzu) and a commercial spectrofluorimeter (Fluoromax from Jobin Yvon), respectively. Triplet spectra of spin-coated films were recorded using a home-made system consisting of an excitation source, a pulsed YAG laser emitting at 355 nm, a spectrograph, collection optics and a gated iCCD camera. Samples were excited at a 45° angle to the substrate plane. For low temperature triplet spectral measurements (from 14 to 30 K) spin-coated films were placed in a cryostat and spectra were recorded tens of milliseconds after excitation to gate the fluorescence emission. Quantum efficiencies in toluene solutions were determined using quinine sulfate in 1M H_2SO_4 solution as a standard, which was cross-calibrated with 9,10-diphenylanthracene in cyclohexane.¹³ The solution Representative synthetic procedures are reported below.

3,7-Bis(9,9-di-*n*-hexylfluoren-2-yl)-*N*-(4-*n*-butylphenyl)-phenothiazine-*S*,*S*-dioxide (11a)

3,7-Dibromo-N-(n-butylphenyl)phenothiazine-S,S-dioxide (9a) (205 mg, 0.4 mmol), 9,9-di-n-hexylfluoren-2-yl boronic acid (10) (320 mg, 0.85 mol), toluene (8 mL), 1,4-dioxane (32 mL), and a solution of potassium phosphate (750 mg in 5 mL water) were combined in a flask and degassed with argon for 0.5 h before bis(triphenylphosphine)palladium dichloride (20 mg, 6 mol %) was added and the mixture was stirred at 90 °C for 16 h. After cooling, the layers were separated and the aqueous layer was extracted with toluene and the combined organic extracts were washed with brine, dried, filtered and concentrated to yield a white solid which was purified by column chromatography on silica gel eluting with a gradient from 2:1 to 1:1 v/v petroleum ether 40-60:dichloromethane. The product 11a was isolated as a white solid after recrystallization from ethanol (216 mg, 55%). M.p. 254.3–254.8 °C; ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.48 ppm (d, I = 2.2 Hz, 2H), 7.79–7.65 (m, 6H), 7.61–7.46 (m, 6H), 7.38-7.25 (m, 9H), 6.74 (d, J = 9.0 Hz, 2H), 2.85-2.74 (m, 2H), 1.99 (dd, J = 9.7 Hz, J = 6.9 Hz, 8H), 1.74 (t, J = 7.8 Hz, 2H), 1.46 (dd, J = 15.0 Hz, J = 7.4 Hz, 2H), 1.16-0.91 (m, 29H), 0.78-0.51 (m, 22H); ¹³C NMR (101 MHz, $CDCl_3$): $\delta = 151.95$ ppm, 151.25, 145.19, 141.11, 140.76, 139.80, 137.82, 136.67, 136.01, 131.81, 131.50, 130.23, 127.42, 127.03, 125.76, 123.12, 122.93, 121.44, 121.28, 120.36, 120.03, 118.15, 55.50, 40.68, 35.69, 33.75, 31.71, 29.92, 24.01, 22.79, 22.69, 14.19; MALDI: m/z 1028 (M⁺); Anal. Calcd. for C₇₂H₈₅NO₂S: C 84.08; H 8.33; N 1.36; Found: C 83.94; H 8.34; N 1.53.

General Procedure for the Preparation of $F-S_N$ co-polymers 14a-d

The respective dibromophenothiazine-*S*,*S*-dioxide derivative (**9a-f**), 2,7-dibromo-9,9-di-*n*-octylfluorene (**12**)¹⁶ and 9,9-di*n*-octylfluorene-2,7-bis boronic ester (**13a** or **13b**)¹⁷ were



FIGURE 2 Bis-sulfone derivative 1.



SCHEME 1 The synthesis of the arylamine pendant group.

dissolved in dry toluene (16 mL) and degassed for 0.5 h. Bis(tri-o-tolylphosphine)palladium dichloride (6 mg) and trio-tolylphosphine (11 mg) were added and degassing was continued for 10 min. A degassed solution of tetraethylammonium hydroxide (20 wt % in water, 4 mL) was added, and the mixture was vigorously stirred at 115 °C in the dark for 18-20 h. Bromobenzene (0.1 mL) was added, and the mixture was stirred at 115 °C for a further 1 h before benzeneboronic acid (100 mg) was added and the mixture stirred at 115 °C for a further 1 h. After cooling, the viscous mixture was slowly poured into vigorously stirred methanol (300 mL). The crude polymer fibers were isolated by filtration and washed with methanol, water and more methanol. After drying the polymer was dissolved in toluene (20 mL) and stirred with an aqueous solution of sodium diethyldithiocarbamate at 65 °C overnight. The layers were separated and the organic layer was washed with dilute HCl solution, sodium acetate solution and water before being filtered through celite (545 grade). The polymer solution was concentrated until it became viscous, transferred to a dropping funnel and dropped slowly into vigorously stirred methanol (300 mL). The polymer fibers were filtered and washed with methanol, acetone and more methanol before being oven dried (70 °C) overnight.

X-Ray Crystallography

Crystals of **8a** and **9a** suitable for X-ray analysis were grown from ethanol. X-ray diffraction experiments (Table S1) were carried out on a Siemens 3-circle diffractometer with a SMART 1000 CCD area detector, using graphite-monochromated Mo- K_{α} radiation ($\overline{\lambda} = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N₂ cryostat. Data were corrected for absorption by Gaussian integration based on crystal face-indexing.¹⁸ The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL 6.14 software.¹⁹ Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre: **8a** (795031), **9a** (795032).

RESULTS AND DISCUSSION

Synthesis

The synthesis of the arylamine pendant group **5** is shown in Scheme 1 and was completed in two high-yielding palladium-catalyzed C-N cross-coupling steps from aniline **2** and 1-bromo-4-n-butylbenzene **3**.

1-Bromo-4-ethylhexyloxybenzene was prepared by the alkylation of 4-bromophenol in the presence of carbonate.²⁰ Scheme 2 displays the route to the functionalized phenothiazine-*S*,*S*-dioxides. Following a palladium-catalyzed C-N cross-coupling, bromination of the *N*-arylphenothiazines with *N*-bromosuccinimide occurred exclusively at the 3 and 7 positions, with the exception of compound **7d**, where a mixture of 3,7-dibromo and 2,8-dibromo regioisomers (1:1 ratio) were observed and separately isolated. This is due to the extra electron-withdrawing nature of the two trifluoromethyl groups in this compound. Finally, the dibromophenothiazines **8a–f** were oxidized with either hydrogen peroxide or *m*CPBA. The *N*-phenyl substituents were chosen to include alkyl (**9a** and **9b**), electron withdrawing (**9c** and **9d**) and electron donating (**9e** and **9f**) groups.

Single crystal X-ray diffraction studies gave insights into the conformations of **8a** and **9a** (Fig. 3, Table 1). Similar molecular conformations were observed for both structures. The phenothiazine ring system is folded along the S...N vector; planar rings *i* and *ii* form a dihedral angle (θ) of 155.6° (**8a**) and 160.8° (**9a**) while ring *iii* is inclined to the bisectral plane of this angle by 11° and 2°, respectively. The nitrogen atom is sp² hybridized, π -conjugated with rings *i* and *ii* but not *iii*, as reflected also in C–N distances. A similar conformation was observed in unsubstituted phenothiazine ($\theta = 158.5^\circ$),²¹ *N*-phenylphenothiazine ($\theta = 154.5^\circ$ and 148.1°)²³ and *N*-(4-bromophenyl)-phenothiazine ($\theta = 144.9^\circ$ and



SCHEME 2 The three step synthesis of the phenothiazine-S, S-dioxide derivatives **9** and the structures of the different aryl units **a**-**f**.



FIGURE 3 X-ray molecular structures of **8a** (left) and **9a** at 120 K. Thermal ellipsoids are drawn at the 50% probability level.

150.8°).²⁴ Although substantial differences of θ between symmetrically independent molecules in the last three structures indicate its "softness" towards crystal packing effects, phenothiazine folding mainly depends on the bond geometry at the S and N atoms.²⁵ Thus, an electron-withdrawing substituent in ring *iii* causes the latter to turn perpendicularly to the bisectral plane of θ and thus engage into π -conjugation with the nitrogen atom at the expense of weaker endocyclic C–N bonding. Consequently, the θ angle narrows to 136.0° or 136.9° in *N*-(4-cyanophenyl)-phenothiazine²¹ and to 124.5° or 120.8° in *N*-(4-nitrophenyl)phenothiazine.²⁶

Compound **9a** is only the second phenothiazine-*S,S*-dioxide characterized crystallographically, after the cationic *N*-(2-dimethylammonium-propyl) derivative (dioxopromethazinium), studied as terephthalate and picrate salts,²⁷ with θ ranging from 139° to 148°.

Bis-3,7-(9,9-di-*n*-hexylfluoren-2-yl)phenothiazine-*S*,*S*-dioxide **F-S**_N-**F** trimers **11a**-**f**, analogous to the trimers we reported previously with dibenzothiophene-*S*,*S*-dioxide (**S**) units, ^{5(c)} were prepared by Suzuki-Miyaura cross-coupling with 9,9-di-*n*-hexylfluoren-2-yl boronic acid **10** as illustrated in Scheme 3.

For the polymer synthesis monomers were repeatedly recrystallized until their purity was >99% as established by high performance liquid chromatography (HPLC) before undergoing Suzuki polycondensation with **12** and **13a** or **13b** in toluene with tetraethylammonium hydroxide as an

TABLE 1 Selected Bond Distances (Å) and Angles (°)

Compound	8a	9a
S-C(9)	1.7592(15)	1.7408(16)
S-C(11)	1.7602(16)	1.7350(15)
N-C(10)	1.416(2)	1.400(2)
N-C(12)	1.415(2)	1.401(2)
N-C(13)	1.444(2)	1.453(2)
mean C-N-C	118.6(1)	119.5(1)
C(9)-S-C(11)	99.84(7)	100.93(7)

emulsifying base, followed by end-capping with phenyl groups, as shown in Scheme 4. This was followed by dissolving the precipitated polymer fibers in toluene and stirring with a palladium scavenging diethyl dithiocarbamic acid solution before washing with acid, base and water. Subsequently, the polymers were re-precipitated into methanol and isolated as pale fibers.

The $F\text{-}S_N$ polymers 14a-d displayed weight-average molecular weights between 80 and 210 kDa as measured by gel permeation chromatography (GPC) and were soluble in common organic solvents such as THF, chloroform, and toluene. The S_N unit was incorporated into the polyfluorene backbone in up to 15% ratio; a higher percentage of the S_N unit resulted in insoluble, low molecular weight co-polymers. The data are shown in Table 2.

For comparison, the phenothiazine co-polymer **15** (with a sulfide unit replacing the sulfone unit; Fig. 4) was obtained via the same Suzuki polycondensation route using monomers **8e**, **12**, and **13b**.

Optical Properties

The photophysical properties of the trimers and co-polymers were investigated and spectral data, photoluminescence quantum yields (PLQYs) and triplet energies are summarized in Table 3. The λ_{max} of emission for trimers **11a–f** in both toluene and chloroform is observed at approximately 390 nm, except for **11d** with two trifluoromethyl groups for which λ_{max} is 408 and 387 nm in toluene and chloroform, respectively.

In Figure 5, the absorption and emission spectra in solution of compound **11e** and 3,7-bis(9,9-di-*n*-hexylfluorene-2-yl)dibenzothiophene-*S*,*S*-dioxide, **F-S-F**^{5(c)} are displayed. By incorporating the S_N unit into the trimer, instead of the **S** unit, no solvatochromism or ICT state is observed. This demonstrates that the formation of the ICT state in **FSF** is not the result of the presence of the sulfone group alone. This observation provides valuable information for the design of co-polymers which display ICT.



SCHEME 3 The synthesis of F-S_N-F trimers (Substituents a-f are defined in Scheme 2).



SCHEME 4 The synthesis of F-S_N polymers 14a-d.

To further understand the impact of the *S*,*S*-dioxide group, Figure 6 shows the comparison of the absorption and emission spectra of co-polymers 14d and 15. The absorbance spectra for both compounds are very similar with λ_{max} 387 nm and 385 nm in toluene, and at $\lambda_{\rm max}$ 386 nm and 384 nm in chloroform for 14d and 15, respectively, which is consist ent with the data for pure poly(9,9-di-n-octylfluorene) (PF8).²⁸ The two co-polymers show no distinct solvato chromism. However, there is a clear bathochromic shift of approximately 65 nm in the emission spectra from $\lambda_{\rm max}$ 414 and 416 nm in toluene and chloroform for polymer 14d (which are comparable with data for pure PF8)²⁹ to λ_{max} 478 and 482 nm in toluene and chloroform for polymer 15, implying a smaller highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap for the sulfide 15 compared with the sulfone 14d. This red shift can be attributed to an increase of conjugation resulting from the sulfur lone pairs in 15, and the change from the electron-withdrawing sulfone in 14d to the electron-donating sulfide in 15. A conformational effect is unlikely to contribute significantly to this red shift; as discussed above, the building blocks 8a and 9a possess similar folding of the phenothiazine and phenothiazine-S,S-dioxide units in their crystal structures (Fig. 3).

Similar behavior is observed in the film absorption and emission spectra of 14d and 15, Figure 7. The absorbance is again similar at $\lambda_{\rm max}$ 384 and 385 nm, respectively. However, a shoulder at 290 nm can be seen in the spectrum of polymer 15 which is due to the $n-\pi^*$ transition and this is not

0	enneeren Allida varaee at 120 min fer 21a ana 160 min fer 20
7	again demonstrate a significant bathochromic shift of $58\ \mathrm{nm}.$
1	PLQYs were measured both in toluene solutions and films
-	for all the trimers and polymers studied. The trimers 11a-f
)	showed quantum yields between 15–30% in solution and

on and between 14-25% in film. Polymers 14a-d demonstrated very high PLQYs in solution (Φ_{PL} 74–84%) and respectable PLQYs in films (Φ_{PL} 28–47%). The quantum yields for 15 were 37% in solution and 29% in film. The lower PLQY values for 15 may be due to the sulfide units acting as traps via energy migration from the polyfluorene segments.

seen in the spectrum of 14d. The introduction of the sulfone

group removes the free electrons on the sulfur atom. The emission λ_{max} values at 425 nm for $\mathbf{14d}$ and 483 nm for $\mathbf{15}$

In addition, triplet energies were determined. The trimers exhibited triplet levels of ET 2.48 eV (onset of phosphorescence), while for co-polymers $14a-d E_T = 2.23$ eV, and for **15** $E_{\rm T} = 2.19$ eV were observed. These values are similar to those of PF8 implying that the triplet excited state is predominantly localized on the fluorene segments.

Solution Electrochemical Properties

To obtain the energy levels of the HOMO and LUMO, the electrochemical redox properties were investigated by cyclic voltammetry (CV). All measurements were calibrated using ferrocene (Fc) as a standard. The CVs of the $F-S_N-F$ trimers typically showed three sequential quasi-reversible oxidation waves in dry dichloromethane electrolyte solution. Each wave is ascribed to a one-electron process. For 11a-e the

			~		~ .	.	
IABL	.E 2	Data	tor	the	CO-I	Polvmei	îS.

Polymer	Feed Ratio ^a F:S_N	Mn	M _w
14a	95:5	47,000	150,000
14b	85:15	57,000	207,000
14c	85:15	45,000	165,000
14d	85:15	33,000	81,000
15	85:15	33,000	82,000

^{a 1}H NMR analysis confirmed that the incorporation rate of the S_N units is in very good agreement with the monomer feed ratios.



FIGURE 4 Structure of co-polymer 15.

TABLE 3 Photo	physical	Data for	Oligomers	and Poly	vmers
---------------	----------	----------	-----------	----------	-------

Trimer/Polymer	Solvent/Film	λ_{\max}^{abs}/nm	λ_{\max}^{PL}/nm	PLQY, Φ_{PL}	Triplet Energy in Films/eV
11a	PhMe	353	387 (407)	0.37 ± 0.05	
	CHCl ₃	353	388 (408)		
	Film	355	399 (414)	0.25 ± 0.05	Peak 2.40; onset 2.48
11b	PhMe	353 (317)	389 (407)	0.40 ± 0.03	
	CHCI ₃	353 (317)	391 (410)		
	Film	355 (319)	399 (414)	0.17 ± 0.05	Peak 2.38; onset 2.47
11c	PhMe	352	385 (405)	0.36 ± 0.04	
	CHCI ₃	351	387 (405)		
	Film	352	397	0.24 ± 0.05	Peak 2.43; onset 2.50
11d	PhMe	341	408	0.15 ± 0.03	
	CHCI ₃	335	387 (404)		
	Film	344	406	0.14 ± 0.05	Peak 2.40; onset 2.48
11e	PhMe	353 (317)	390 (407)	0.39 ± 0.03	
	CHCI ₃	353 (317)	391 (409)		
	Film	355 (319)	399 (414)	0.22 ± 0.05	Peak 2.39; onset 2.47
11f	PhMe	353 (321)	389 (411)	0.30 ± 0.05	
	CHCI ₃	353 (321)	392 (409)		
	Film	355 (322)	404 (416)	0.21 ± 0.05	Peak 2.39; onset 2.48
14a	PhMe	387	414 (439)	0.82 ± 0.04	
	CHCl ₃	389	416 (440)		
	Film	387	426 (444)	0.46 ± 0.05	Peak 2.15; onset 2.23
14b	PhMe	386	414 (438)	0.74 ± 0.04	
	CHCI ₃	386	416 (440)		
	Film	384	428 (447)	0.28 ± 0.05	Peak 2.16; onset 2.23
14c	PhMe	386	414 (438)	0.84 ± 0.04	
	CHCI ₃	387	416 (440)		
	Film	384	426 (446)	0.36 ± 0.05	Peak 2.16; onset 2.23
14d	PhMe	386	414 (439)	0.82 ± 0.10	
	CHCI ₃	387	416 (440)		
	Film	384	425 (445)	0.47 ± 0.05	Peak 2.16; onset 2.25
15	PhMe	384	478	0.37 ± 0.04	
	CHCI ₃	385	482		
	Film	382	/83	0.29 + 0.05	Peak 2 09: onset 2 19



FIGURE 5 Absorption and emission spectra of FSF and 11e.



FIGURE 6 Absorption and emission spectra of 14d and 15 in toluene and chloroform.



FIGURE 7 Absorption and emission spectra of 14d and 15 films.

 $E_{\rm ox}$ values for these three waves are approximately 0.9–1.0, 1.2-1.3, and 1.4-1.5 V, depending on the N-aryl substituent. The CV of 11e is shown in Figure 8. For 11f, the oxidation waves are shifted to significantly lower potentials (E_{ox} 0.55, 0.86 V) due to the strongly electron-donating triarylamine substituent on nitrogen stabilizing the cationic species. For all the trimers, the reductive waves are irreversible and poorly defined. The onset oxidation potentials are closely related to the HOMO levels and were calculated using the value for ferrocene of -4.8 eV with respect to the vacuum level which is defined as zero.³⁰ According to the correlation: HOMO = $-(E_{ox}^{onset} - E_{Fc} + 4.8)$ (eV), where E_{ox}^{onset} is the onset potential of oxidation, the HOMO level was calculated. The LUMO levels were determined according to: LUMO =HOMO $- Eg^{opt}$, where Eg^{opt} is the optically measured HOMO-LUMO gap. The results are summarized in Table 4.

For the trimers, the HOMO levels ranged from -5.75 to -5.24 eV and the LUMO levels from -2.51 to -2.03 eV, respectively. These values correlate well with the different *N*-aryl substituents: trimer **11d**, with the strongly electron-



FIGURE 8 Oxidative cyclic voltammogram of trimer **11e** in CH_2CI_2 versus ferrocene; electrolyte *n*-Bu₄NPF₆ (0.1 M); scan rate 100 mV s⁻¹.

 TABLE 4 Optical and Solution Electrochemical Data of the

 Trimers and Polymers

	$\textit{Eg}^{ ext{opt}}$ (eV)	$E_{\rm ox}^{\rm onset}$ vs. $E_{\rm Fc}$ (V)	HOMO (eV)	LUMO (eV)
11a	3.24	0.79	-5.59	-2.35
11b	3.23	0.80	-5.60	-2.37
11c	3.25	0.83	-5.63	-2.38
11d	3.24	0.95	-5.75	-2.51
11e	3.23	0.78	-5.58	-2.35
11f	3.21	0.44	-5.24	-2.03
14a	3.00	0.88	-5.96	-2.68
14b	3.01	0.82	-5.62	-2.61
14c	3.01	0.84	-5.64	-2.63
14d	3.00	0.84	-5.64	-2.64
15	2.94	0.88	-5.56	-2.62

withdrawing 3,5-bis(trifluoromethyl)phenyl group, demonstrated the lowest HOMO and LUMO levels, whereas the trimer 11f, with the strongly electron-donating triarylamine group, showed the highest HOMO and LUMO levels. The influence of the pendant group disperses in the polymers. For polymer **14a** with only 5% incorporation of the S_N group the lowest HOMO and LUMO energy levels were found at -5.96 and -2.68 eV, respectively. For polymers 14b-d the energy levels were located at -5.64 to -5.62 eV for the HOMO and -2.64 to -2.61 eV for the LUMO. Compound 15 displayed the HOMO at -5.56 eV and the LUMO at -2.62 eV. The optically measured HOMO-LUMO gaps were found to be approximately 3.2 eV for oligomers 11a-f, 3.0 eV for the phenothiazine-S,S-dioxide polymers 14a-d and 2.94 eV for the phenothiazine polymer **15**. Thus, $(F-S_N)_n$ co-polymers possess a higher HOMO than polyfluorene homo-polymers (5.8 eV).³¹ The higher HOMO level of the $(\mathbf{F}-\mathbf{S}_{N})_{n}$ co-polymers offers the advantage of a smaller energy barrier with respect to indium tin oxide (ITO)/PEDOT (5.0-5.2 eV) which is a standard HIL in OLEDs, a factor which should improve hole injection and lower driving voltages.³²



FIGURE 9 HOMO and LUMO energy distribution maps for sulfone **11e**' (left) and its sulfide analog (i.e., with a central phenothiazine unit) (right).

HOMO and LUMO distribution maps for the sulfone oligomer **11e'** (the structures were simplified by replacing the hexyl and octyl chains with methyl groups to reduce the calculation time) and its sulfide analog were calculated at the B3LYP/6-31G* level and are shown in Figure 9. For the sulfide trimer, substantial localization of the HOMO on the sulfur atom of the phenothiazine unit is observed, whereas the LUMO is delocalized over the whole trimer. In contrast, for sulfone trimer **11e'** the HOMO is delocalized over more of the trimer, while the LUMO is less delocalized than is the case with the sulfide.

CONCLUSIONS

A series of new fluorene trimers and polymers incorporating N-arylphenothiazine-S,S-dioxide units have been prepared in good yields following a facile multi-step route involving palladium-catalyzed cross-coupling methodology. The materials are deep blue emitters which show no solvatochromism or ICT state. Comparing the solution and film emission spectra of polymer 14d with the sulfide analog 15, a distinct bathochromic shift was observed for 15, which can be attributed to the increase of conjugation through the phenothiazine system (15) due to the presence of lone pairs of electrons on sulfur, compared to the sulfone unit (14d). PLQYs are 15-30% in solution and between 14-25% in film for trimers 11a-f. Polymers 14a-d demonstrated very high PLQYs in solution (Φ_{PL} 74–84%) and good PLQYs in film (Φ_{PL} 28–47%). Triplet energies were E_T 2.48 eV for trimers and 2.23 eV and 2.19 eV for co-polymers 14a-d and 15, respectively. For the trimers, the pendant N-aryl group influences the HOMO levels, which range from -5.75 to -5.24 eV (based on solution electrochemical data). The LUMO levels were observed accordingly at -2.51 to -2.03 eV. This influence of the pendant group is absent in the co-polymers with 15% incorporation of phenothiazine-S,S-dioxide units. The optical band gaps were 3.2 eV for the oligomers and 3.0 eV for the phenothiazine-*S*,*S*-dioxide polymers **14a–d**. Hence, $(\mathbf{F-S}_N)_n$ co-polymers possess a higher HOMO than polyfluorene homo-polymers. The HOMO and LUMO distribution maps for trimer 11e' and its sulfide (phenothiazine) derivative were calculated at the B3LYP/6-31G* level and show that the HOMO for the sulfide trimer is more localized on the sulfur atom of the phenothiazine unit, whereas the HOMO of trimer **11e** is more delocalized over the whole π -system. These results establish that N-arylphenothiazine-S,S-dioxide and N-arylphenothiazine units are versatile units for incorporation into fluorene-based polymers which may be applicable in PLED applications.

This work was funded by the TSB as part of the TOPLESS project and by EPSRC. We thank Dr. G. Williams (Zumtobel LED Division) for supporting this work.

REFERENCES AND NOTES

1 (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. Nature 1990, 347, 539–541; (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. Nature 1999, 397, 121–128; (c) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. Nature 1993, 365, 628–630; (d) Müllen, K.; Scherf, U. Organic Light Emitting Devices: Synthesis, Properties and Applications; Wiley-VCH: Weinheim, 2006.

2 (a) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. Adv Mater 2010, 22, 572–582; (b) Beaupre, S.; Bourdreault, P.-L. T.; Leclerc, M. Adv Mater 2010, 22, E6–E27.

3 (a) Leclerc, M. J Polym Sci Part A: Polym Chem 2001, 39, 2867–2873; (b) Scherf, U.; List, E. J. W. Adv Mater 2002, 14, 477–487; (c) Polyfluorenes, Adv Polym Sci 212; Scherf, U., Neher, D., Eds; Springer-Verlag: Berlin, 2008.

4 (a) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. J Am Chem Soc 2007, 129, 11910–11911; (b) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. Adv Funct Mater 2003, 13, 525–530; (c) Kappaun, S.; Scheiber, H.; Trattnig, R.; Zojer, E.; List, E. J. W.; Slugovc, C. Chem Commun 2008, 5170–5172; (d) List, E. J. W.; Guentner, R.; de Freitas, P. S.; Scherf, U. Adv Mater 2002, 14, 374–378.

5 (a) Kamtekar, K. T.; Vaughan, H. L.; Lyons, B. P.; Monkman, A. P.; Pandya, S. U.; Bryce, M. R. Macromolecules 2010, 43, 4481–4488; (b) King, S. M.; Perepichka, I. I.; Perepichka, I. F.; Dias, F. B.; Bryce, M. R.; Monkman, A. P. Adv Funct Mater 2009, 19, 586–591; (c) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Palsson, L.-O. Chem Commun 2005, 3397–3399.

6 (a) Grisorio, R.; Piliego, C.; Cosma, P.; Fini, P.; Mastrorilli, P.; Gigli, G.; Suranna, G. P.; Nobile, C. F. J Polym Sci Part A: Polym Chem 2009, 47, 2093–2104; 6 (b) Li, Y.; Wu, H.; Zou, J.; Ying, L.; Yang, W.; Cao, Y. Org Electron 2009, 10, 901–909; 6 (c) Liu, J.; Zou, J.; Yang, W.; Wu, H.; Li, C.; Zhang, B.; Peng, J.; Cao, Y. Chem Mater 2008, 20, 4499–4506.

7 Li, J. Y.; Ziegler, A.; Wegner, G. Chem Eur J 2005, 11, 4450-4457.

8 (a) Hsieh, B.-Y.; Chen, Y. J Polym Sci Part A: Polym Chem 2009, 47, 833–844; (b) Padhy, H.; Huang, J.-H.; Sahu, D.; Patra, D.; Kekuda, D.; Chu, C.-W.; Lin, H.-C. J Polym Sci Part A: Polym Chem 2010, 48, 4823–4834.

9 Yang, L. Y.; Wang, C.; Li, L. Q.; Janietz, S.; Wedel, A.; Hua, Y. L.; Yin, S. G. J Polym Sci Part A: Polym Chem 2007, 45, 4291–4299.

10 Gessner, T.; Schmidt, H.-W.; Thelakkat, M.; Baete, M. Patent Applications 2005-EP12647, 2006056465, 25.11.2005, 2006.

11 (a) Lee, J.; Lee, J.-I.; Park, M.-J.; Jung, Y. K.; Cho, N. S.; Cho, H. J.; Hwang, D.-H.; Lee, S.-K.; Park, J.-H.; Hong, J.; Chu, H. Y.; Shim, H.-K. J Polym Sci Part A: Polym Chem 2007, 45, 1236–1246; (b) Park, M.-J.; Lee, J.; Jung, I. H.; Park, J.-H.; Hwang, D.-H.; Shim, H.-K. Macromolecules 2008, 41, 9643–9649.

12 Pasini, M.; Giovanella, U.; Betti, P.; Bolognesi, A.; Botta, C.; Destri, S.; Porzio, W.; Vercelli, B.; Zotti, G. ChemPhysChem 2009, 10, 2143–2149.

13 (a) Lakowitz, J. R., Principles of Fluorescence Spectroscopy; Kluwer Academic/Plenum Publishers: New York, 1999; (b) Mardelli, M.; Olmsted, J. J Photochem 1977, 7, 277–285. 14 Palsson, L. O.; Monkman, A. P. Adv Mater 2002, 14, 757–758.

15 (a) Kawamura, Y.; Sasabe, H.; Adachi, C. Jpn J Appl Phys Part 1 2004, 43, 7729–7730; (b) Kawamura, Y; Yamamoto, H.; Goushi, K.; Sasabe, H.; Adachi, C. Appl Phys Lett 2004, 84, 2724–2726.

16 Ranger, M., Rondeau, D., Leclerc, M. Macromolecules 1997, 30, 7686–7691.

17 Hou, Q.; Xu, X.; Wang, W.; Yuan, M.; Pengs, J.; Cao, Y. J Mater Chem 2002, 12, 2887–2892.

18 Sheldrick G. M. SADABS 2006/1, Bruker AXS, Madison, Wisconsin, USA, 2006.

19 Sheldrick, G. M. Acta Crystallogr 2008, A64, 112-122.

20 Tang, C.; Liu, F.; Xia, Y.-J.; Xie, L.-H.; Wei, A.; Li, S.-B.; Fan, Q.-L.; Huang, W. J Mater Chem 2006, 16, 4074–4080.

21 McDowell, J. J. H. Acta Crystallogr 1976, B32, 5-10.

22 Klein, C. L.; Conrad, J. M. III; Morris, S. A. Acta Crystallogr 1985, C41, 1202–1204.

23 McKeown, N. B.; Badriya, S.; Helliwell, M.; Shkunov, M. J Mater Chem 2007, 17, 2088–2094.

24 Chu, S. S. C.; Yang, H. T. Acta Crystallogr 1977, B33, 1892–1896.

25 Borowicz, P.; Herbich, J.; Kapturkiewicz, A.; Anulewicz-Ostrowska, R.; Nowacki, J.; Grampp, G. Phys Chem Chem Phys 2000, 2, 4275–4280.

26 Jovanovic, M. V.; Biehl, E. R.; de Meester, P.; Chu, S. S. C. J Heterocycl Chem 1984, 21, 1793–1800.

27 (a) Harrison, W. T. A.; Ashok, M. A.; Yathirajan, H. S.; Achar, B. N. Acta Crystallogr 2007, E63, o3277; (b) Zhu, D.-X.; Sun, W.; Yang, G.-F.; Ng, S. W. Acta Crystallogr 2007, E63, o4830.

28 Bright, D. W.; Dias, F. B.; Galbrecht, F.; Scherf, U.; Monkman, A. P. Adv Funct Mater 2009, 19, 67–73.

29 Dias, F. B.; King, S.; Monkman, A. P.; Perepichka, I. I.; Kryuchkov, M. A.; Perepichka, I. F.; Bryce, M. R. J Phys Chem B 2008, 112, 6557–6566.

30 Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. Adv Mater 1995, 7, 551–554.

31 Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. Appl Phys Lett 1998, 73, 2453–2455.

32 Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. Adv Mater 2002, 14, 809–811.