Synthesis of electron-accepting polymers containing phenanthra-9,10-quinone units[†]

Julien E. Gautrot, ** Philip Hodge, ** Madeleine Helliwell, * James Raftery * and Domenico Cupertino

Received 28th January 2009, Accepted 26th March 2009 First published as an Advance Article on the web 11th May 2009 DOI: 10.1039/b901853k

Polymers containing 9,10-phenanthraquinone moieties as part of an extended π -electron system have been prepared by Suzuki couplings between 2,7- or 3,6-dibromophenanthraquinone and 9,9dioctylfluorene-2,7-diboronic acid bispinacol ester. Closely related model compounds were prepared similarly. All the products were characterised by FT-IR, ¹H NMR and UV-vis/fluorescence spectroscopy and, where relevant, mass spectrometry. Cyclic voltammetry measurements indicate that these materials display electron affinities of up to 4.0 eV. This value is one of the highest reported for conjugated polymers.

Introduction

In recent years there has been great interest in polymers that have a π -electron system along the backbone.¹⁻³ Frequently studied examples include polyacetylenes,⁴ poly(phenylene vinylene)s,⁵ polypyrroles⁶ and polythiophenes.⁷ Polymers that have such π electron systems can, for example, function as light-emitting diodes (LEDs),^{5,8–10} field effect transistors (FETs),^{5,11-18} or key components in photovoltaic devices.^{19–21} Polymers which have the further feature that they are good electron acceptors are potentially useful for a variety of electronic applications. Thus far one of the more successful polymers of this type is poly(oxobenzimidazoquinoline).²² The present paper is concerned with a new type of electron-accepting material where the acceptor is a quinone unit.

In Nature a type of molecule widely used for accepting electrons is quinones. These, for example, play a key role in oxidative phosphorylation (derivatives of benzoquinone)²³ and photosynthesis (derivatives of benzoquinone and of naphthoquinone).²⁴ For electronic applications, however, derivatives of 9,10-anthraquinone (1) are a more obvious type to consider because apart from accepting electrons readily they generally have a higher chemical and thermal stability than benzoquinones and naphthoquinones. A few polymers containing anthraquinone units in the backbone have been synthesised.^{25–32} Ideally, however, for electronic applications the moieties that accept the electrons should be an integral part of a fully conjugated backbone π -electron system. Unfortunately the two aromatic rings in anthraquinone (1) are not fully conjugated to each other, though

^cAvecia, Blackley, Manchester, UK M9 8ZS

in reduced forms, such as the anion-radical or the dianion that are anthracene derivatives, these are conjugated.



One type of quinone moiety that can be fully conjugated with a backbone π -electron system is that present in 9,10-phenanthraquinone (2). Moreover, this quinone is a more powerful electron acceptor than 9,10-anthraquinone (1).³³ Another interesting feature of quinone 2 is the fact that the two carbonyl groups are on the same 'side' of the molecule with the result that it has a significant dipole. This is of interest because it is often crucial for the thin films used in electronic devices to be ordered. The dipoles are likely to cause derivatives containing these units to stack with the dipoles anti-parallel to each other. The stacking of the quinone units can be expected to facilitate electron transfers between polymer chains.

In this paper we describe the synthesis and characterisation of some polymers and closely related model compounds containing 9,10-phenanthraquinone moieties. In order to improve the solubility of the materials, the quinone monomers were copolymerised with a dioctylfluorene derivative. Since this work was completed³⁴ a group based in China has reported the synthesis and characterisation of one polymer that is closely related to the one described here.³⁵ However, the spectroscopic measurements and the interpretations of these differ significantly from ours. The analyses based on the X-ray studies are new.

Experimental

General methods

These are as given previously.³⁶ 9,9-Dioctylfluorene-2-boronic acid pinacol ester $(3)^{36,37}$ and 9,9-dioctylfluorene-2,7-diboronic acid bispinacol ester (4) were synthesised as described

^aOrganic Materials Innovation Centre, School of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: jeg45@ cam.ac.uk; Philip.Hodge@man.ac.uk

^bSchool of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL

[†] Electronic supplementary information (ESI) available: CCDC reference numbers 701642 and 701643. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b901853k

previously.³⁶ DCM = dichloromethane; THF = tetrahydrofuran. In SEC analyses solutions were filtered with 0.22 μ m filters prior to injection into the instrument.

Synthesis of materials

2,7-Dibromo-9,10-dihydrophenanthrene 9,10-Dihy-(5). drophenanthrene (6) (1.36 g, 7.54 mmol), DCM (30 mL) and iron filings (10 mg) were placed in a round-bottom flask (100 mL) fitted with a septum and wrapped in aluminium foil to exclude light. The mixture was stirred vigorously and cooled to 0 °C. Bromine (2.53 g, 15.8 mmol) in DCM (30 mL) was added via the septum over 2 h. The mixture was stirred for a further 12 h at 20 °C. It was then washed with aqueous sodium thiosulfate (0.1 M, 3×50 mL) and water (3×50 mL), and dried over magnesium sulfate. The organic solvent was evaporated off and the residue recrystallised from ethyl acetate. This gave compound 5 as white crystals (1.41 g, 55%), mp 160-162 °C (lit., 38 168 °C); IR (NaCl, cm⁻¹) 2947, 2906, 2836, 1588, 1569, 1469, 1428, 1388, 1293, 1185, 1076, 1001, 879 and 812; ¹H NMR (CDCl₃, ppm) δ 8.30 (2H, dd, J = 1 and 2 Hz, H-3), 7.88 (2H, d, J = 2 Hz, H-4) and 7.87 (2H, d, J = 1 Hz, H-1); ¹³C NMR (CDCl₃, ppm) δ 28.8, 121.8, 125.5, 130.4, 131.4, 132.9 and 139.4; MS (EI/CI) triplet 336/338/340 g mol^{-1} , $C_{14}H_{10}Br_2$ requires 338 g mol^{-1} for Br = 80.

2,7-Dibromophenanthraquinone (7). Chromium trioxide (0.50 g, 5 mmol), acetic acid (18 mL) and water (2 mL) were placed in a round-bottom flask equipped with a thermometer and dropping funnel. The mixture was stirred magnetically and cooled in an ice bath. A solution of 2,7-dibromo-9,10-dihydrophenanthrene (5) (0.50 g, 1.48 mmol) in acetic acid (10 mL) was added dropwise whilst keeping the temperature below 15 °C. The dark brown mixture was stirred overnight at 20 °C and then poured over crushed ice (250 mL). The precipitate was filtered off, washed with water (3 \times 10 mL) and then with methanol (3 \times 10 mL). Recrystallisation of the dried product from nitrobenzene gave quinone 7 as orange needles (0.37 g, 68%) with mp 327–328 °C (lit., 39 323 °C); IR (NaCl, cm⁻¹) 1674, 1581, 1463, 1398, 1263, 1223, 1203, 1145, 1080, 1037, 905 and 832; ¹H NMR (CDCl₃ and d-TFA, ppm) δ 8.31 (2H, m, H-4), 7.89 (2H, s, H-1) and 7.88 (2H, m, H-3); ¹³C NMR (CDCl₃ and d-TFA, ppm) δ 125.1, 126.2, 130.4, 131.2, 134.2, 140.7 and 179.9; MS (EI/CI) triplet 364/366/ 368 g mol⁻¹, C₁₄H₆O₂Br₂ requires 366 g mol⁻¹. By HPLC analysis the final product obtained was >99.9% pure.

3,6-Dibromophenanthraquinone (8). Phenanthraquinone (2) (7.00 g, 33.7 mmol) and acetic acid (100 mL) were charged into a round-bottom flask (250 mL) fitted with a condenser and a hydrogen bromide trap. The mixture was heated to reflux and bromine (24.00 g, 134.8 mmol) was added in eight portions over 8 days (before each addition, the mixture was allowed to cool down to 20 °C to avoid bromine emissions) and the reaction followed by HPLC. After 8 days no starting material could be detected and the reaction had stopped. The reaction was deemed to be complete. The mixture was poured into water (400 mL). The yellow precipitate was filtered off, washed with aqueous sodium thiosulfate (0.1 M, 3×50 mL), water (3×50 mL) and methanol (3×50 mL). The solid remaining was recrystallised three times from xylene and dried under vacuum for 48 h. This

gave quinone **8** as yellow needles (8.53 g, 69%). It had mp 286–287 °C (lit.,⁴⁰ 286 °C); IR (NaCl, cm⁻¹) 1676, 1581, 1545, 1467, 1390, 1326, 1282, 1222, 1099, 1079, 1020, 919, 896 and 820; ¹H NMR (CDCl₃ and d-TFA, ppm) δ 8.13 (2H, d, J = 2 Hz, H-4), 8.07 (2H, d, J = 8 Hz, H-1) and 7.69 (2H, dd, J = 2 and 8 Hz, H-2); ¹³C NMR (CDCl₃ and d-TFA, ppm) δ 128.0, 129.1, 132.7, 134.0, 134.1, 136.6 and 180.0; MS (EI/CI) triplet 364/366/368 g mol⁻¹, C₁₄H₆O₂Br₂ requires 366 g mol⁻¹. By HPLC analysis the final product was >98% pure.

2,7-Bis(9',9'-dioctylfluoren-2'-yl)-9,10-phenanthraquinone (9). 2,7-Dibromophenanthraquinone (7) (161 mg, 0.44 mmol), 9,9dioctylfluorene-2-boronic acid pinacol ester (3) (500 mg, 0.97 mmol), and palladium[0] tetrakis(triphenylphosphine) (51 mg, 50 µmol) were placed in a round-bottom flask (3-neck, 100 mL). THF (20 mL, degassed with argon) and aqueous sodium carbonate (1.0 M, 5 mL, degassed with argon) were added via a septum. The mixture was heated under reflux for 28 h and then poured onto aqueous hydrochloric acid (0.1 M, 200 mL). The aqueous phase was extracted with DCM (3 \times 50 mL), the extracts washed with water $(3 \times 50 \text{ mL})$, and the organic solution dried. Evaporation of the solvent gave the crude product. Chromatography over a column of silica with a mixture of petroleum ether-DCM (9:1 v/v) gave compound 9 as a violet solid (193 mg, 45%). It had mp (DSC) 133 °C; IR (KBr, cm⁻¹) 2926, 2854, 1676, 1596, 1466, 1451, 1353, 1316, 1154, 1000, 969, 889, 823, 739 and 719; ¹H NMR (CDCl₃, ppm) δ 8.53 (2H, d, J =2 Hz, H-1), 8.14 (2H, d, J = 8 Hz, H-4), 8.05 (2H, dd, J = 2 and 8 Hz, H-3), 7.86–7.61 (8H, bm, Ar-H), 7.44–7.29 (6H, bm, Ar-H), 2.10-1.92 (8H, bm, aliphatic C-H), 1.26-0.96 (40H, bm, aliphatic C-H), 0.85-0.75 (12H, bm, aliphatic C-H) and 0.72-0.51 (8H, bm, aliphatic C-H); ¹³C NMR (CDCl₃, ppm) δ 14.3, 22.8, 23.9, 29.4, 30.2, 32.0, 40.5, 55.6, 119.2, 120.2, 120.5, 121.2, 123.2, 124.8, 126.0, 126.9, 127.1, 128.9, 129.1, 131.4, 133.9, 134.6, 137.5, 140.6, 141.1, 141.9, 142.9, 144.3, 150.1, 151.3, 151.5 and 180.9; MS (MALDI) 987 g mol⁻¹, C₇₂H₈₈O₂ requires 985 g mol⁻¹; microanalysis: calc: C, 87.7%, H, 9.0%; found: C, 87.6%, H, 9.2%; UV-vis spectrum (chloroform, nm) λ_{max} (ϵ/L mol⁻¹ cm⁻¹) 334 (26 100), 494 (2100) and 525 (2100). See text for CV results. By TGA it had T_{dec} 276 °C.

3.6-Bis(9',9'-dioctylfluoren-2'-vl)-9,10-phenanthraquinone (10). Compound 10 was prepared, using a procedure similar to that described for compound 9, from 3,6-dibromophenanthraquinone (8) (500 mg, 1.37 mmol), 9,9-dioctylfluorene-2-boronic acid pinacol ester (3) (1.77 g, 3.42 mmol), palladium[0] tetrakis(triphenylphosphine) (162 mg, 140 µmol), THF (40 mL, degassed with argon) and aqueous sodium carbonate (1.0 M, 5 mL, degassed with argon). Chromatography of the crude product over silica with a mixture of petroleum ether (bp 40-60 °C)–DCM (9 : 1 v/v) afforded compound 10 as an amorphous orange solid (872 mg, 88%). By TGA it had T_{dec} 309 °C. It had IR (KBr, cm⁻¹) 2926, 2854, 1676, 1594, 1465, 1453, 1396, 1314, 1292, 1234, 1134, 1004, 926, 885, 826 and 740; ¹H NMR (CDCl₃, ppm) $\delta 8.39 (2H, d, J = 1 Hz, H-4), 8.33 (2H, d, J = 8 Hz, H-1), 7.85 (2H, d, J = 8 Hz, H-1), 7.85 (2H, d, J = 1 Hz, H-1)$ d, J = 8 Hz, H-2), 7.82–7.64 (8H, bm, Ar-H), 7.44–7.33 (6H, bm, Ar-H), 2.06 (8H, bm, aliphatic C-H), 1.20-0.99 (40H, bm, aliphatic C-H), 0.78 (12H, t, J = 6.7 Hz, aliphatic C-H) and 0.69 (8H, bm, aliphatic C-H); ¹³C NMR (CDCl₃, ppm) δ 14.3, 21.4,

22.9, 24.1, 29.5, 30.3, 32.0, 40.6, 55.6, 120.4, 121.8, 122.9, 123.3, 126.6, 127.3, 128.0, 128.6, 130.0, 131.5, 136.5, 138.4, 140.4, 142.7, 149.5, 151.4, 152.2 and 180.4; MS (MALDI) 989 g mol⁻¹, $C_{72}H_{88}O_2$ requires 985 g mol⁻¹; microanalysis: calc: C, 87.7%, H, 9.0%; found: C, 87.8%, H, 8.7%; UV-vis spectrum (chloroform, nm) λ_{max} (ϵ/L mol⁻¹ cm⁻¹) 301 (57 200), and 414 (23 500). See text for CV results.

Poly(9,10-phenanthraquinone-2,7-diyl-alt-9,9-dioctylfluorene-2',7'-diyl) (11). Polymer 11 was prepared, using a procedure similar to that described above for the preparation of compound 9, from 2,7-dibromophenanthraquinone (7) (250 mg, 0.68 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bispinacol ester (4) (439 mg, 0.68 mmol), palladium[0] tetrakis(triphenylphosphine) (81 mg, 70 µmol), THF (20 mL, degassed with argon) and aqueous sodium carbonate (1.0 M, 5 mL, degassed with argon). This afforded polymer 11 as a vellow solid (373 mg, 92%). IR (NaCl, cm⁻¹) 2926, 2853, 2679, 1676, 1598, 1461, 1436, 1312, 1256, 1148, 1098, 998, 971, 889, 817 and 756; ¹H NMR (CDCl₃, ppm) δ 8.53 (2H, m, H-1), 8.13 (2H, m, H-4), 8.05 (2H, m, H-3), 7.93-7.28 (6H, bm, Ar-H), 2.12 (4H, bm, aliphatic C-H), 1.11 (20H, bm, aliphatic C-H) and 0.79 (10H, bm, aliphatic C-H); ¹³C NMR (CDCl₃, ppm) δ 14.1, 22.6, 23.9, 29.2, 30.0, 30.7, 31.7, 40.4, 55.7, 120.6, 121.1, 124.7, 126.0, 127.2, 128.7, 128.8, 131.2, 132.1, 134.4, 137.6, 140.9, 142.5, 152.2 and 180.6; SEC (THF, g mol⁻¹) $M_{\rm n}$ 6200, M_w 16 000; (CHCl₃) M_n 153 000, M_w 438 000; UV-vis spectrum (chloroform, nm) λ_{max} (ϵ/L mol⁻¹ cm⁻¹) 364 (43 700), 493 (3900) and 526 (4100). See text for CV results. By DSC no thermal transitions could be observed between -50 °C and 120 °C. By TGA it had T_{dec} 303 °C.

Poly(9,10-phenanthraquinone-3,6-diyl-alt-9,9-dioctylfluorene-2',7'-diyl) (12). Polymer 12 was prepared, using a procedure similar to that described for polymer 11, from 3,6-dibromophenanthraquinone (8) (400 mg, 0.63 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bispinacol ester (4) (232 mg, 0.63 mmol), palladium[0] tetrakis(triphenylphosphine) (44 mg, 38 µmol), THF (20 mL, degassed with argon) and aqueous sodium carbonate (1.0 M, 5 mL, degassed with argon). This afforded polymer 12 as an orange powder (245 mg, 65%). It had IR (NaCl, cm⁻¹) 2926, 2853, 1677, 1594, 1465, 1399, 1313, 1291, 1233, 1135, 925, 885, 818 and 755; ¹H NMR (CDCl₃, ppm) δ 8.34 (4H, bm, H-1 and H-4), 7.92 (2H, bs, H-2), 7.85-7.53 (6H, bm, Ar-H), 2.17 (4H, bm, aliphatic C-H), 1.09 (20H, bm, aliphatic C-H) and 0.86-0.61 (10H, bm, aliphatic C-H); ¹³C NMR (CDCl₃, ppm) δ 14.3, 22.8, 24.2, 29.5, 30.3, 32.0, 40.6, 56.0, 121.1, 122.0, 122.7, 122.9, 126.9, 128.7, 130.2, 131.6, 136.3, 136.4, 139.2, 141.7, 149.2, 152.6 and 180.3; (THF, g mol⁻¹) M_n 3500, M_w 5300; UV-vis spectrum (chloroform, nm) λ_{max} (ϵ/L mol⁻¹ cm⁻¹) 309 (37 100) and 424 (22 700). See text for CV results. DSC: no thermal transition could be observed between 0 °C and 250 °C; TGA: T_{dec} , 379 °C.

X-Ray crystal structure determination

Crystals were mounted in the inert oil fomblin (perfluoropolymethylisopropyl ether) in a Hamilton Cryoloop. The data were collected on a Bruker SMART APEX diffractometer,⁴¹ and the crystals were cryocooled to 100 K, using an Oxford Cryosystems 700 Series Cryostream Cooler. Absorption corrections were applied using the program SADABS.⁴¹ The structures were solved and refined using SHELX97.⁴¹ The nonhydrogen atoms were refined anisotropically and the hydrogen atoms were placed in idealised positions (C–H = 0.95 Å) and assigned isotropic thermal parameters of 1.2 times those of the parent atoms. Computations were carried out using the SHELXTL program package.⁴²

Crystal data for compound 7. $C_{14}H_6Br_2O_2$, M_w 366.01, triclinic, space group $P\bar{1}$, a = 7.307(2), b = 7.976(2), c = 11.348(2) Å, $\alpha = 73.870(3)$, $\beta = 77.321(4)$, $\gamma = 64.943(3)^\circ$, V = 571.5(2) Å³, Z = 2, $D_c = 2.127$ g cm⁻³, μ (MoK α) = 7.079 mm⁻¹, F(000) = 352, T = 100 K. Crystal dimensions were $0.3 \times 0.2 \times 0.01$ mm. 2875 reflections measured, 1987 independent reflections ($R_{int} = 0.094$), $R_1 = 0.084$ for the 858 reflections with $I > 2\sigma(I)$, w $R(F^2) = 0.185$ (all data).

Crystal data for compound 8. $C_{14}H_6Br_2O_2$, M_w 366.01, monoclinic, space group $P2_1/n$, a = 11.683(6), b = 7.257(4), c = 14.885(8) Å, $\beta = 109.542(8)^\circ$, V = 1189.2(10) Å³, Z = 4, $D_c = 2.044$ g cm⁻³, σ (MoK α) = 6.805 mm⁻¹, F(000) = 704, T = 100 K. Crystal dimensions were $0.2 \times 0.1 \times 0.01$ mm. 6392 reflections measured, 2426 independent reflections ($R_{int} = 0.068$), $R_1 = 0.053$ for the 1711 reflections with $I > 2\sigma(I)$, w $R(F^2) = 0.104$ (all data).

Results and discussion

Synthesis of 2,7-dibromophenanthraquinone (7) and 3,6dibromophenanthraquinone (8)

Structural isomers 7 and 8 were chosen as the starting point for the synthesis of the present polymers and model compounds. The syntheses are outlined in Scheme 1. Various attempts to synthesise 2,7-dibromophenanthraquinone (7) by the direct bromination of phenanthraquinone (2), following procedures described in the literature, gave, by TLC analysis, complex mixtures.40,43 The quinone was, however, prepared successfully by a two-step method. First, 9,10-dihydrophenanthrene (6) in DCM at 20 °C was brominated by treatment with bromine in the presence of iron filings, then the product 5 was oxidised with chromium trioxide in aqueous acetic acid. 3.6-Dibromoanthraquinone (8), on the other hand, was successfully prepared directly by reaction of 9,10-phenanthraquinone (2) with bromine in aqueous acetic acid.44 All the products were characterised by FT-IR and ¹H NMR spectroscopy and mass spectrometry. Both quinones had mps that are in agreement with the literature values.



Scheme 1 Synthesis of 2,7-dibromophenanthraquinone (7) and 3,6-dibromophenanthraquinone (8).



Fig. 1 ORTEP plots of the X-ray crystal structure of (A) **8** and (B) **7**, with ellipsoids drawn at 50% probability level.

To confirm the structures of the dibromoquinones and to determine how the molecules pack in the crystal, single crystal X-ray crystal structures were determined. The structures, shown in Fig. 1A and B, indicate that the isomers obtained were indeed the expected ones based on the mps and ¹H NMR spectra. Inspection of the overall arrangement of the molecules in the crystals additionally shows that, as expected on the basis of the dipole moments, the molecules are stacked with alternate molecules having their dipoles anti-parallel: see Fig. 2A and B. The perpendicular spacings between the quinone layers were 3.24 Å for **7** and 3.41 Å for **8**. Full details of the X-ray results are given in the ESI.†

Synthesis of model compounds 9 and 10

Since the polymers were to be synthesised by Suzuki couplings between the dibromoquinones and 9,9-dioctylfluorene-2,7diboronic acid bispinacol ester (4), model compounds 9 and 10 were prepared by similar couplings with 9,9-dioctylfluorene-2boronic acid pinacol ester (3):³⁶ see Scheme 2. The products were characterised by FT-IR and ¹H NMR spectroscopy, mass spectrometry and elemental analysis. Differential scanning calorimetry (DSC) measurements revealed that 9 melts at 133 °C, while 10 is amorphous. Thus, the "linear" compound 9 has a greater tendency to organise and pack regularly than the "angular" isomer 10. Thermogravimetric analyses (TGA) revealed that 9 and 10 are thermally stable up to 276 and 309 °C, respectively. The ultraviolet-visible (UV-vis) spectra and the cyclic voltametry (CV) results are discussed below together with those of other materials.

Both 9 and 10 were stable in the *solid* state, that is the state in which materials of this general type would be used in devices, but



Fig. 2 Packing of molecules (A) 8 and (B) 7 in the crystals, with hydrogen atoms omitted for clarity. It is evident that in each case the molecules stack with the dipoles of neighbouring molecules anti-parallel.

solutions in chloroform partially decolourised when left in sunlight for several days and solutions in THF decolourised completely. In this latter solvent, photochemical hydrogen abstraction by 9,10-phenanthraquinone (2) is a well-documented phenomenon.⁴⁵ Because of this, the solutions prepared for the various measurements were stored in the dark.

Synthesis of polymers 11 and 12

Polymers 11 and 12 were prepared by treating dibromoquinones 7 and 8, respectively, with 9,9-dioctylfluorene-2,7-diboronic acid bispinacol ester 4,³⁶ under similar reaction conditions to those used to prepare the model compounds. The syntheses are summarised in Scheme 3. The FT-IR and ¹H NMR spectra of the products closely resembled those of the model compounds but, as expected, the signals in the NMR spectra of the polymers were broader and less well defined.

The SEC results obtained for polymer 11 using THF as the eluent indicated that the polymer had $M_{\rm n}$ of 6200 and $M_{\rm w}$ of 16 000. The trace displayed some features in its tail that are



Scheme 2 Synthesis of model compounds 9 and 10: (i) Pd(PPh₃)₄, Na₂CO₃, THF.



Scheme 3 Synthesis of polymers 11 and 12: (i) Pd(PPh₃)₄, Na₂CO₃, THF.

typical of the presence of some low molecular weight oligomers: see Fig. 3. When, however, chloroform was used as the eluent the trace showed just one broad featureless peak and the $M_{\rm p}$ value was 153 000 and $M_{\rm w}$ 438 000: see Fig. 3. These observations strongly suggest that polymer 11 does not aggregate in THF but does aggregate in chloroform. The SEC results obtained for polymer 12 in THF showed that it had M_n 3500 and M_w 5300. Similar results were obtained using chloroform as the eluent. Thus, polymer 12 does not appear to aggregate in either THF or chloroform. These observations are consistent with the fact that polymer 11 has a more "linear" structure than polymer 12, and with the fact that the "linear" model compound 9 is crystalline, whilst the "angular" model compound 10 is amorphous. Further evidence of aggregation phenomena is given below in the discussion of the UV-vis and fluorescence spectra of these materials.

The DSC traces for both polymers do not display any clear transitions, which suggests that they are amorphous. Glass transitions are, however, often weak and may not always be detected by DSC measurements. The TGA measurements reveal that polymers **11** and **12** are thermally stable up to 303 and 379 $^{\circ}$ C, respectively.

After the above syntheses had been completed a research group based in China reported the synthesis of polymer 13.³⁵ This only differs from polymer 11 in the length of the alkyl side chains: polymer 13 has *n*-hexyl chains whereas polymer 11 has *n*-octyl chains. However, as discussed below, the UV spectroscopic data and the CV data reported for polymer 13 and some of the interpretations of these data differ from the data we report for polymer 11.

Photophysical properties

The UV-vis data obtained for compounds 2, 9 and 10 and polymers 11–13 are summarised in Table 1. This includes proven or suggested assignments.

The UV-vis spectroscopy of *ortho*-quinones, especially 9,10phenanthraquinone (**2**), has been studied many times.^{46–48} Fig. 4 displays the spectra obtained for 9,10-phenanthraquinone (**2**) in chloroform obtained in the present work. The spectrum displays



Fig. 3 SEC traces obtained for polymer **11** in THF (solid line) and chloroform (dashed line). Marker is *n*-dodecane.



transitions at 268, 324 and 418 nm. These can all be assigned to $\pi - \pi^*$ transitions: see Table 1, entry 1.^{45–48} The n- π^* is known to be present around 500 nm,⁴⁶ and can be observed as a shoulder when a logarithmic scale is used.

The spectra of model compounds 9 and 10 are also shown in Fig. 4 and summarised in Table 1, entries 2 and 3. These compounds each display just two π - π * bands. If there is a third band it is not apparent at >260 nm. In both cases the weak n- π * band is believed to be hidden beneath the main bands. When going from 10 to 9 it is interesting to note that both of the observed transitions are shifted to longer wavelengths. This is consistent with the more extended conjugation in the "linear" model 9 as compared to the "angular" 10. Thus, in 9 all the linkages between the aromatic rings are *para*-linkages, whereas in 10 there are two *meta*- and two *para*-linkages. It is not clear why the extinction coefficients for compound 10 are so much higher than those for compound 9.

Finally on the UV-vis spectra of the model compounds, it is of interest to consider the nature of the longest wavelength band of compound 9, *i.e.* the band at 525 nm. This broad transition is thought to be a combination of two peaks. One is the expected long wavelength π - π * transition (the bathochromic shift compared to 10 and 2 is believed to be due to a charge-transfer phenomenon between the electron-rich fluorene and the electron-

Table 1Summary of UV-vis spectra of compounds 2, 9 and 10 andpolymers 11–13 with suggested assignments

Entry	Compound/ polymer	π - π * Bands ^{<i>a</i>} λ_{\max} /nm	n– π^* Band ^{<i>a</i>} λ_{\max} /nm	Band due to aggregation ^{<i>a</i>} λ_{max}/nm		
1	2^b	268 (29 000), 324 (4900),	500 (sh) ^e	_		
2	9 ^b	418 (1700) 334 (26 100), na 494 (2100)	nd	525 (2100)		
3	10 ^b	301 (57 200), na, 414 (23 500)	nd	nd		
4	11 ^b	364 (37 000), na, 493 (39 000)	nd	526 (4100)		
5	12 ^b	309 (37 100), na, 424 (22 700)	nd	nd		
6 ^{<i>c</i>}	13 ^d	370 (51 600), na, na	465 (4920)	nd		

^{*a*} Numbers in brackets are extinction coefficients measured for the corresponding transition, expressed in L mol⁻¹ cm⁻¹; na = not available. nd = not detected. ^{*b*} Determined for solution in chloroform. ^{*c*} Data taken from reference 34. ^{*d*} Determined for solution in tetrahydrofuran. ^{*e*} sh = shoulder.

poor quinone moieties) whilst the other arises from an aggregation phenomenon. Fig. 5A shows the spectra of **9** in chloroform and in toluene. As noted above, chloroform favours aggregation of polymer **11**, toluene does not. Consequently in the UV-vis spectrum the intensity of the aggregation peak decreases on going from chloroform solution to toluene. Further evidence of this phenomenon is given by the fluorescence spectra in these solvents. Thus, compound **9** does not display fluorescence in chloroform, whereas it does in toluene solutions: see Fig. 5B. This is consistent with the fact that aggregation can quench fluorescence.

Fig. 4 shows the UV-vis spectra for solutions of polymers 11 and 12 in chloroform: Table 1, entries 4 and 5. The shapes of the spectra are very similar to those of the corresponding models, the



Fig. 4 UV-vis spectra of 9,10-phenanthraquinones 2 (solid line), 9 (dashed line) and 10 (squares) and polymers 11 (dotted line) and 12 (triangles) for solutions in chloroform.



Fig. 5 (A) UV-vis spectra of model **9** in chloroform (solid line) and in toluene (dotted line); (B) fluorescence spectrum of model **9** in toluene ($\lambda_{\text{excitation}}$: 350 nm).

main difference being that the peaks are red-shifted by up to 30 nm on going from the model compound to the corresponding polymer. This is consistent with an increase in the length of the conjugated system. As expected, this shift is larger in the case of "linear" polymer 11 and this is consistent with what has been discussed above concerning the *meta-* and *para-*linkages. In other words, the small shift observed when going from model 10 to polymer 12 is due to the *meta-*linkages, which do not allow full conjugation of the polymer backbone.⁵ In contrast, the longer wavelength peaks (at 494 nm and 414 nm for 9 and 10, respectively) are almost unchanged in the UV-vis spectra of polymers 11 and 12, compared to those of compounds 9 and 10. This observation is consistent with the charge-transfer nature of the 493 nm transition in the case of 11 and to the lack of conjugation typical of *meta-*aryls in the case of 12.

The UV-vis spectrum for polymer **13** as a solution in *THF* is summarised in Table 1, entry $6.^{35}$ Assignments are those of the group based in China. The spectrum differs significantly from those of the present models **9** and **10** and polymers **11** and **12** measured for solutions in *chloroform*. The transition that is present in the spectrum of **9** at 493 nm is shifted in the spectrum of **13** to 465 nm. This is possibly due to the fact that chloroform, a protic solvent, stabilises charge-transfer transitions from electron-rich aromatic systems to quinones (owing to the stronger nucleophilic behaviour of their ketones).⁴⁷ Given the intensity of the band at 465 nm ($\varepsilon = 4920$ L mol⁻¹ cm⁻¹), it seems unlikely that it is due to an $n-\pi^*$ transition.

Electrochemical properties

The electrochemical behaviour of *ortho*-quinones is very similar to that of the more extensively studied *para*-quinones. Phenan-thraquinone (**2**) is known to display two successive one-electron reduction steps in aprotic solutions, similarly to what can be observed for 9,10-anthraquinone (**1**).^{49,50} However, the difference in resonance energy between the quinone and the dianion is higher in the case of 9,10-anthraquinone (**1**).⁵¹ so the half-wave potential of 9,10-phenanthraquinone (**2**) is shifted to more positive potentials relative to 9,10-anthraquinone (**1**). Fig. 6 shows the CV of 9,10-phenanthraquinone (**2**) in dichloromethane. It can be seen that some of the phenomena that

distorted the shape of the CVs of 9,10-anthraquinones, such as the formation of dimers and the influence of trace amounts of water or other protic donors, have similar effects in the case of the *ortho*-quinones.^{47,48,51} These effects have been reported previously.⁵¹

The results obtained for the cyclic voltammetry of models 9 and 10, together with 9,10-phenanthraquinone (2), for *solutions in dichloromethane* are gathered in Table 2. The shapes of the CVs for the two model compounds are very similar to what was observed for compound 2. However, the gap between the cathodic and anodic peaks of the first reduction step $\Delta E^{(1)}$ was much larger in the case of the models (550 and 570 mV) than for phenanthraquinone (2) (120 mV). This phenomenon could be related to interactions between molecules occurring during the electrochemical processes, or to significant electronic and structural reorganisation upon reduction. The latter is more likely because the gap between the first and second reduction steps increases significantly when going from 9,10-phenanthraquinone (2) to both models: see Table 2. This increase corresponds to a stabilisation of the semiquinone state compared to the dianion state.

The shift in the half-wave potential when going from 9,10-phenanthraquinone (2) to both models is easier to rationalise. As for the parent anthraquinone-based derivatives,⁴⁷ the



Fig. 6 Cyclic voltammogram of 9,10-phenanthraquinone (2) (3 mmol L^{-1}) in dichloromethane; electrolyte: TBAPF₆ (0.1 mol L^{-1}); scan rate: 0.1 V s⁻¹; reference Ag/AgCl.

Table 2 Electrochemical data from cyclic voltammetry

Model/polymer	$E_{\rm red1}$ ^(I) /mV	$\Delta E^{(I)}/mV$	$E_{\rm red2}^{(II)}/\rm mV$	$\Delta E^{(II)}/mV$	EA ^d /eV	HOMO ^e /eV	LUMO ^e /eV	Eg CV ^f /eV	Eg Opt ^g /eV
2 ^{<i>a</i>}	-490	120	-1090	400					
9 ^a	-610	570	-1780	200	3.8	-6.2	-4.2	2	2.30
10 ^b	-600	550	-1820	500	3.9	-6.3	-4.3	2	2.30
11 ^b	-550	240	-1160	с	4.0	-6.2	-4.3	1.9	2.00
12^b	-570	260	-880	240	4.0	-6.3	-4.3	2	2.10

^{*a*} Measurements performed in degassed DCM. ^{*b*} Measurements performed in acetonitrile. ^{*c*} Only the cathodic peak was observed. ^{*d*} Electron affinities were calculated from the onset potentials for reduction E_{onred} according to the equation $EA = 4.4 + E_{onred}$.^{52,53 *e*} HOMO and LUMO levels determined from the onset of reduction E_{onset} .^{54 *f*} Electrochemical band gap determined from the HOMO and LUMO levels. ^{*g*} Optical band gap determined from the onset of adsorption. Electrolyte: TBAPF₆, 0.1 mol L⁻¹. Scan rate: 0.1 V s⁻¹. Reference: Ag/AgCl. (I) First reduction step; (II) second reduction step.

strong electron-donor nature of the two aryl substituents in the 2,7- or 3,6-position has the effect of shifting the first reduction peak cathodically.

The CVs for polymers **11** and **12** were obtained *for cast films* on a glassy carbon electrode. They were measured as films partly due to their poor solubility in suitable solvents for CV studies and partly because in an electronic device they would usually be present as films. As is common for the CVs of polymer films, due to slow diffusion effects, changes in solvation and aggregation of the polymer chains, as well as disproportionation, the CVs of the two polymers are quite distorted: see Fig. 7.^{36,47,55} Interestingly, polymer **11** displays not the expected two reduction steps, but three. This may be due to interactions between the phenanthraquinone units in aggregates. Polymer **12**, however, does not display any anodic peak for the second reduction step, which suggests the occurrence of a side reaction.

The results obtained for the CVs of the two polymers are summarised in Table 2. It is interesting to see that in each case the first half-wave potential is shifted to slightly higher potentials, compared to the models, suggesting that the effect of the fluorene moieties on CT phenomena is split between two phenan-thraquinone units. The reduction potential measured for polymer **11** compares well with that reported in the literature for its *n*-hexyl parent **13**.³⁵ However, the relative positions of the two polymers' first reduction peaks, with respect to that of **2**, are opposite. Indeed, the reduction of **13** is shifted anodically compared to that of **2**. As the electrochemical potential measured by Hanif *et al.* was not placed in the context of other

diaryl-phenanthraquinones,³⁵ this observation is difficult to rationalise and could be due to the differences in the conditions used to perform our measurements.

The electron affinities (EAs) that were measured using a ferrocene internal reference, for both polymers, are near 4.0 eV, which lies amongst the highest electron affinities reported for conjugated polymers. Table 2 displays the position of the HOMO and LUMO levels for the different materials, as well as their electrochemical and optical band gap. Given the high first reduction potential measured for 9-12, the EAs measured and the position of the LUMO level determined for these materials are in good agreement with the results obtained for related anthraguinone derivatives, which displayed EAs near 3.6 eV and first reduction potential near -0.85 V (against Ag/AgCl).47,48 Notably, the electrochemical band gap closely matches the optical band gap determined from the onset of adsorption of the different materials. These EAs and LUMO levels range amongst the highest reported in the literature: for example, benzimidazobenzophenanthroline ladder type polymer⁵⁶ has a LUMO at -4.4 eV (using -4.8 eV as the level of the SCE reference, as in the present study) and fullerene C₆₀ has an EA of 3.9-4.1 eV.⁵⁷

Conclusions

The synthesis of copolymers using Suzuki couplings between 2,7-dibromophenanthraquinone (7) and fluorene derivative 4 and between 3,6-dibromophenanthraquinone (8) and fluorene derivative 4 is described. Model compounds 9 and 10 were



Fig. 7 Cyclic voltammogram of polymer (A) 11 and (B) 12 films on glassy carbon electrode in acetonitrile; electrolyte: TBAPF₆ (0.1 mol L^{-1}); scan rate: 0.1 V s⁻¹; reference Ag/AgCl.

prepared similarly from the same quinones but in combination with fluorene derivative 3. The structures of these new materials were confirmed by FT-IR and ¹H NMR spectroscopy. The UVvis spectroscopy of the polymers and their model compounds clearly showed that a linear structure, such as that found in polymer 11, favours aggregation. Aggregation is in part thought to be due to the fact that the carbonyl groups of each quinone mojety are pointing in the same direction. This results in the phenanthraquinone moieties having significant dipoles. They are expected to pack with neighbouring dipoles anti-parallel, as shown in the X-ray crystal structures shown in Fig. 2. The antiparallel packing also reduces the steric interactions between neighbouring molecules or polymer chains. Such aggregation phenomenon, which indicates strong overlapping of the molecular orbitals of adjacent molecules or polymer chains, together with the high electron affinities measured for polymers 11 and 12, suggests that materials of this general type may be useful for organic electronics applications.

Acknowledgements

We thank Avecia for a PhD Studentship (JEG) and EPSRC for financial support under the Carbon Based Electronics Programme.

References

- 1 W. J. Feast, J. Tsibouklis, K. L. Power, L. Groenendal and E. W. Meijer, Polymer, 1996, 37, 5015.
- 2 A. G. MacDiarmid, Angew. Chem., Int. Ed., 2001, 40, 2581.
- 3 J. Jagur-Grodzinski, Polym. Adv. Technol., 2002, 13, 615.
- 4 (a) W. J. Feast and R. H. Friend, J. Mater. Sci., 1990, 25, 3796; (b) J. W. Y. Lam and B. Z. Tang, Acc. Chem. Res., 2005, 38, 745.
- 5 A. Kraft, A. C. Grimsdale and A. B. Holmes, Angew. Chem., Int. Ed., 1998, 37, 403.
- 6 L.-X. Wang, X.-G. Li and Y.-L. Yang, React. Funct. Polym., 2001, 47, 125.
- 7 R. D. McCullough, Adv. Mater., 1998, 10, 93.
- 8 R. H. Friend, R. W. Gymer and A. B. Holmes, Nature, 1999, 397, 121.
- 9 U. Scherf and E. J. W. List, Adv. Mater., 2002, 14, 477.
- 10 H.-G. Nothofer, A. Meisel, T. Miteva, D. Neher, M. Forster, M. Oda, G. Lieser, D. Sainova, A. Yasuda, D. Lupo, W. Knoll and U. Scherf, Macromol. Symp., 2000, 154, 139.
- 11 L. Rothberg, Nature, 1990, 347, 518.
- A. Pron and P. Rannou, Prog. Polym. Sci., 2001, 27, 135.
- 13 H. Fuchigami, A. Tsumura and H. Koezuka, Appl. Phys. Lett., 1993, 63, 1372.
- 14 C. D. Dimitrakopoulos and D. J. Mascaro, IBM J. Res. Dev., 2001, 45.11.
- 15 D. J. Sandman, Trends Polym. Sci. (Cambridge, UK), 1994, 2, 44.
- 16 F. Wurthner, Angew. Chem., Int. Ed., 2001, 40, 1037.
- 17 P. J. Brown, H. Sirringhaus and R. H. Friend, Synth. Met., 1999, 101, 557
- 18 H. Sirringhaus, R. J. Wilson, R. H. Friend, M. Inbasekaran, W. Wu, W. P. Woo, M. Grell and D. C. C. Bradley, Appl. Phys. Lett., 2000, 77.406.
- 19 R. N. Marks, J. J. M. Halls, D. C. C. Bradley, R. H. Friend and A. B. Holmes, J. Phys.: Condens. Matter, 1994, 6, 1379.

- View Article Online
- 20 R. Pacios and D. C. C. Bradley, Synth. Met., 2002, 127, 261.
- 21 D. Gebeyehu, C. J. Brabec and S. Sariciftci, Thin Solid Films, 2002, 403-404. 271.
- 22 X. L. Chen and S. A. Jenekhe, Macromolecules, 1997, 30, 1728; F. E. Arnold and R. L. Van Deusen, Macromolecules, 1969, 2, 497
- 23 G. Zubay, Biochemistry, Brown WC Publishers, Dubuque, Iowa, 1998, ch. 16, pp. 347-358.
- 24 G. Zubay, Biochemistry, Brown WC Publishers, Dubuque, Iowa, 1998, Chapter 17, pp. 377-382.
- 25 H. Etori, T. Kanbara and T. Yamamoto, Chem. Lett., 1994, 461.
- 26 T. Yamamoto and H. Etori, Macromolecules, 1995, 28, 3371.
- 27 P. Hodge, G. A. Power and M. A. Rabjohns, Chem. Commun., 1997, 73
- 28 G. A. Power, P. Hodge, I. D. Clarke, M. A. Rabjohns and I. Goodbody, Chem. Commun., 1998, 873.
- 29 Y. Muramatsu and T. Yamamoto, Polymer, 1999, 40, 6607.
- 30 Y. Muramatsu, T. Yamamoto, M. Hasegawa, T. Yagi and H. Koinuma, Polymer, 2001, 42, 6673.
- 31 I. Goodbody, P. Hodge and A. Ben-Haida, React. Funct. Polym., 2008, 68, 414.
- 32 P. Hodge and J. E. Gautrot, Polym. Int., 2009, 58, 261.
- 33 G. J. Gleicher, in The Chemistry of Quinonoid Compounds, ed. S. Patai, Wiley, London, 1974, p. 18.
- 34 J. E. Gautrot, Synthesis of Novel Conjugated Polymers with High electron Affinities for Applications in Electronic Devices, PhD thesis, University of Manchester, 2004.
- 35 M. Hanif, P. Lu, M. Li, Y. Zheng, Z. Xie, Y. Ma, D. Li and J. Li, Polym. Int., 2007, 56, 1507.
- 36 J. E. Gautrot and P. Hodge, Polymer, 2007, 48, 7065.
- 37 M. Belletête, S. Beaupre, J. Bouchard, P. Blondin, M. Leclerc and G. Durocher, J. Phys. Chem. B, 2000, 104, 9118.
- 38 J. C. Miller, J. S. Meek and S. J. Strickler, J. Am. Chem. Soc., 1977, 99 8175
- 39 J. Schmidt and E. Junghans, Chem. Ber., 1904, 37, 3558.
- 40 M. V. Bhatt, Tetrahedron, 1964, 20, 803.
- 41 SMART (Version 5.625), SADABS (Version 2.03a) and SHELXTL Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- 42 G. M. Sheldrick, SHELX97, Program for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
- 43 H. Lee and R. G. Harvey, J. Org. Chem., 1986, **51**, 2847. 44 K. Paruch, T. J. Katz, C. Incarvito, K.-C. Lam, B. Rhatigan and A. L. Rheingold, J. Org. Chem., 2000, 65, 7602.
- 45 M. R. Rubin, J. Org. Chem., 1963, 28, 1949.
- 46 A. Kuboyama, F. Kobayashi and S. Morokuma, Bull. Chem. Soc. Jpn., 1975, 48, 2145.
- 47 J. E. Gautrot, P. Hodge, D. Cupertino and M. Helliwell, New J. Chem., 2007, 31, 1585.
- 48 J. E. Gautrot, P. Hodge, D. Cupertino and M. Helliwell, New J. Chem., 2006, 30, 1801.
- 49 J. Q. Chambers, Electrochemistry of quinones, in The Chemistry of Quinonoid Compounds, ed. S. Patai and Z. Rappoport, John Wiley and Sons, Chichester, 1988, 719.
- 50 M. W. Lehman and D. H. Evans, J. Electroanal. Chem., 2001, 500, 12
- 51 N. Gupta and H. Linschitz, J. Am. Chem. Soc., 1997, 119, 6384
- 52 S. Janietz, J. Barche, A. Wedel and D. Sainova, Macromol. Chem. Phys., 2004, 205, 187.
- 53 S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran and E. P. Woo, Appl. Phys. Lett., 1998, 73, 2453.
- 54 B. C. Thompson, Y.-G. Kim and J. R. Reynolds, Macromolecules, 2005, 38, 5359.
- 55 A. Iraqi, J. A. Crayston and J. C. Walton, J. Mater. Chem., 1998, 8, 31
- 56 M. M. Alam and S. A. Jenekhe, Chem. Mater., 2004, 16, 4647.
- 57 P. Peumans and S. R. Forrest, Appl. Phys. Lett., 2001, 79, 126.