Triarylamine polymers by microwave-assisted polycondensation for use in organic field-effect transistors†

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Triarylamine polymers can be rapidly assembled by microwave-assisted amination of aryldibromides. A series of polymers are reported with backbones containing 4,4′-biphenyl, 2.9-fluorene and 3,6-carbazole repeating units. These polymers have been used to fabricate organic field-effect transistors. The devices show very stable operation under ambient conditions and p-type mobilities up to 2.3×10^{-3} cm^2 V^{-1} s^{-1}, close to the highest mobility reported to date for this class of amorphous semiconductors.

Introduction

The development of polymeric organic semiconductors has been attracting great interest in academia and industry, as these materials can be used to fabricate organic light-emitting diodes (OLEDs),[1] field-effect transistors (OFETs),[2–4] photovoltaic cells[5] and sensors.[6] One of the key benefits of polymeric semiconductors is the ability to use low-cost, solution-based deposition methods to fabricate devices under ambient conditions. Poly(arylamine)s are particularly interesting candidates for the semiconducting layer of an OFET because the polymers can be handled in air and the devices show very stable performance under ambient conditions with a mobility higher than 10^{-3} cm^2 V^{-1} s^{-1}.[7,8] In addition, thin films of most poly(arylamine)s are amorphous and this avoids the high temperature annealing required by most semi-crystalline polymers. Amorphous triarylamine polymers have been used successfully as charge transport layers in OLEDs, photocopiers and laser printers and more recently in OFETs for use as vapour sensors.[6b]

The simplest approach to prepare triarylamine polymers is to couple a dihalobenzene with an aniline by use of a palladium, copper or nickel catalyst in the presence of a base.[9] In these reactions high molecular weight triarylamine polymers are only obtained at high conversion of amine and halogen functional groups. Conventional heating and extended reaction times of several days are required to achieve the desired conversion.[10]

To avoid these extended reaction times, we recently communicated the synthesis of a triarylamine polymer by a microwave-assisted palladium-catalyzed cross-coupling reaction between 2,4-dimethylaniline and 4,4′-dibromobiphenyl.[11] The reaction

times were reduced to five minutes when the reactions were carried out at 100 °C. Microwave irradiation heats a solution homogeneously by direct coupling between the electromagnetic radiation and the molecular dipoles of the solvent(s)/reagent(s), and in some cases it can produce cleaner and faster reactions than those observed with conventional heating.[12] Microwave irradiation has only recently been exploited in polymer chemistry, where it appears that certain polymerizations can be accelerated significantly and side reactions avoided.[13]

In this paper we have extended our previous study to investigate the synthesis, characterisation and field-effect mobilities of a series of new triarylamine polymers (1–6), containing fused ring aromatic groups in the polymer backbone. These polymers were rapidly assembled by a microwave-assisted palladium-catalyzed cross-coupling reaction between a primary arylamine and an aryldibromide. The physical and electrochemical behaviour of the polymers were examined and polymers suitable for application as the semiconducting layer of an OFET were prepared.

Results and discussion

Synthesis

The synthetic route to the poly(triarylamine) 1–6 is shown in Scheme 1 and involves a microwave-assisted palladium-catalyzed cross-coupling reaction between 4-methoxy-2-methylaniline or 2,4-dimethylaniline and 9,9-di-(2′-ethylhexyl)-2,7-dibromofluorene, N-2′-ethylhexyl-3,7-dibromocarbazole or 4,4′-dibromobiphenyl. Reaction at 100 °C for five minutes was found to be an optimum from our earlier studies.[11] The initial polymerisation is expected to give polymers terminated by either amino or bromo groups by virtue of the reaction mechanism. These groups can act as traps for charge carriers or undergo chemical reaction during operation of organic electronic devices using these polymers. These end groups were removed by sequential reaction of the initial polymers with diethylamine and 4-bromoanisole (Scheme 1) to remove the terminal amino and bromo functionalities, respectively. The final polymers 1–6 were isolated by precipitation and extensively purified. Polymers 1–6 were obtained in good yield (82–89%) (Table 1), and were soluble in

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† Electronic supplementary information (ESI) available: UV-vis spectra of 1–6 in film. See DOI: 10.1039/b808840c
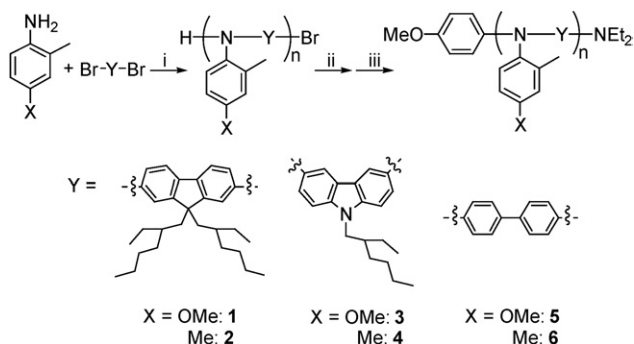
Scheme 1 Synthesis of poly(arylamine)s *via* microwave-assisted amination. *Reagents and conditions*: (i) Pd$_2$(dba)$_3$, P(*t*-Bu)$_3$, NaO-*t*-Bu, toluene, microwave, 100 °C, 5 min. (ii) 4-bromoanisole, Pd$_2$(dba)$_3$, P(*t*-Bu)$_3$, NaO-*t*-Bu, toluene, microwave, 100 °C, 1 min. (iii) diethylamine, Pd$_2$(dba)$_3$, P(*t*-Bu)$_3$, NaO-*t*-Bu, toluene, microwave, 100 °C, 1 min.

Table 1 Polymer molecular weights and reaction yield[a]

Polymer	Yield (%)	M_n	M_w	M_w/M_n
1	90	7200	20 500	2.84
1[b]	34	14 100	19 700	1.40
2	86	8300	23 500	2.81
2[b]	66	8500	19 700	2.30
3	89	4200	8100	1.92
4	85	8200	11 800	1.44
5	83	13 800	19 400	1.40
6	82	13 100	23 100	1.76

[a] Calculated from gel-permeation chromatography (GPC) measurements carried out using THF as the solvent and calibrated by polystyrene standards. [b] Isolated by Soxhlet extraction.

common organic solvents, such as dichloromethane, chlorobenzene, chloroform, tetrahydrofuran and toluene. The number-average molecular weight (M_n) of the polymers was in the range 4000 to 14 000. The polydispersity of as-synthesised **1** was high (2.84), subsequent Soxhlet extraction with dichloromethane and sequential washing with methanol, acetone and dichloromethane gave a lower dispersity (1.40) and higher molecular weight material (M_n = 14 100). A similar but less dramatic improvement in molecular weight and polydispersity can be seen for polymer **2**.

Optical and electrochemical properties

The optical and electrochemical properties of **1–6** were examined by UV-vis absorption spectroscopy, fluorimetry and cyclic voltammetry; the results are summarized in Table 2. The optical band gaps (E_g) were estimated from the onset of the solution absorption spectra. The biphenyl polymers (**5** and **6**) are the least conjugated, followed by the fluorene-containing polymers (**1** and **2**) with the carbazole polymers (**3** and **4**) showing the highest conjugation. This order is consistent with previous studies of small-molecule triarylamines.[14] The polymers were photoluminescent in solution and the quantum yields (ϕ in Table 2) of polymers **1**, **2** and **5** were found to be relatively high (ϕ = 0.43–0.58). The absorption spectra of the polymers containing a methoxy group (**1**, **3** and **5**) showed similar spectra to the corresponding polymer containing a methyl group (**2**, **4** and **6**).

Table 2 Optical and electrochemical properties of the polymers

Polymer	λ_{max}/ nm	λ_{em}/ nm	ϕ [a]	E_g/ eV [b]	$E_{1/2}$/ eV [c]	E_{HOMO}/ eV [d]	E_{LUMO}/ eV [e]
1	414	430	0.48	2.86	−0.08	−4.5	−1.6
2	413	428	0.43	2.87	−0.05	−4.5	−1.7
3	325	466	0.04	2.61	−0.14	−4.4	−1.8
4	328	461	0.04	2.63	−0.11	−4.5	−1.8
5	379	422	0.58	2.99	0.15	−4.8	−1.8
6	381	419	0.18	2.99	0.15	−4.8	−1.8

[a] PL quantum yields were calculated using quinine sulfate standards.[16] [b] From optical absorption/emission data in dichloromethane. E_g = optical band gap. [c] 0.1 M [(*n*-C$_4$H$_9$)$_4$N]PF$_6$ in CH$_2$Cl$_2$: *vs.* Fc$^+$/Fc. [d] Estimated *vs.* vacuum level from E_{HOMO} = −1.4 $E_{1/2}$ − 4.6 eV.[17] [e] Estimated from E_{LUMO} = E_{HOMO} + E_g.
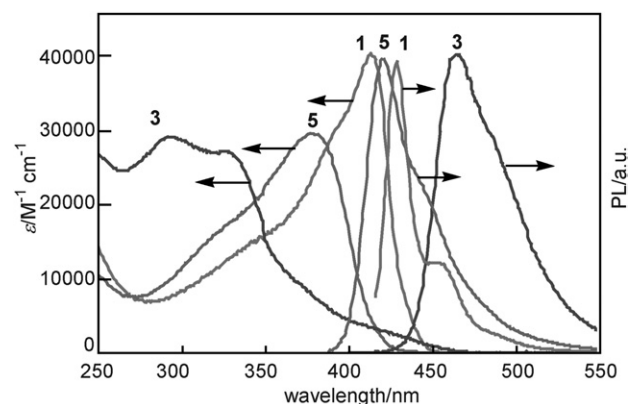

Fig. 1 UV-vis and PL spectra of **1**, **3** and **5** in dichloromethane solution. The molar absorption coefficient ε is based on the repeat unit of the polymers.

The optical absorption and emission spectra of the fluorene polymer **1** recorded in dichloromethane solution (λ_{max} = 414 nm and λ_{em} = 430 nm) are shown in Fig. 1. The small Stokes shift and vibronic structure observed for **1** suggests that incorporation of the fluorene unit, connected at the 2,7-positions, into the polymer backbone leads to a very rigid chromophore structure. Similar results have been reported previously for related π-conjugated polymers.[15] By contrast, carbazole polymer **3** (λ_{max} = 325 nm and λ_{em} = 466 nm) and biphenyl polymer **5** (λ_{max} = 379 nm and λ_{em} = 422 nm) showed broad unstructured emissions, consistent with a high degree of rotational freedom between individual carbazole units connected in the 3,6-positions of **3** and the individual phenyl rings of **5**. The optical absorption spectra of all of these polymers in the solid state were very similar to those in solution, and these results support the view that the polymers are amorphous solids (see ESI†). Films of polymer **1** deposited on SiO$_2$ appear amorphous by AFM, with a surface roughness that is very similar to that of the underlying substrate. The morphology of these films was not changed by annealing at 100 °C.

The cyclic voltammograms (CVs) of **1**, **3** and **5**, recorded in a dichloromethane solution of [(C$_4$H$_9$)$_4$N]PF$_6$ (0.10 M), are shown in Fig. 2. The electrochemical data for all polymers are summarized in Table 2. Solutions of **1** exhibited two reversible oxidations at $E_{1/2}$ = −0.08 and 0.58 V against ferrocene/ferrocenium. Solutions of **3** and **5** showed three and two oxidation
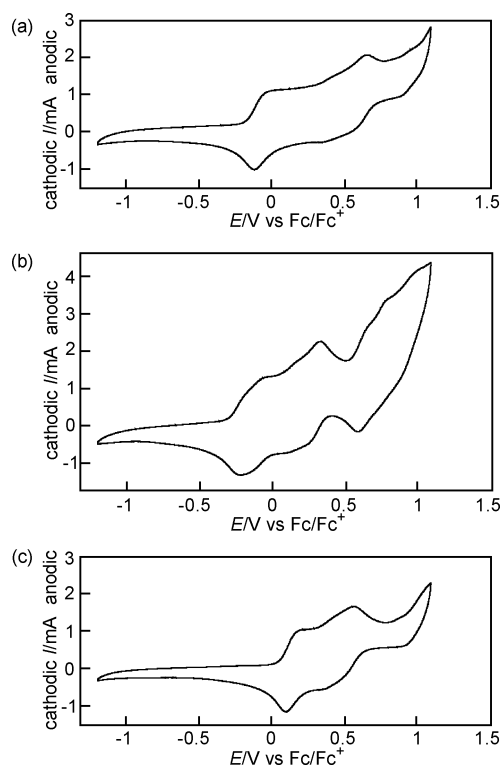
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J. Mater. Chem., 2008, **18**, 5230–5236 | 5231

Fig. 2 Cyclic voltammograms of (a) **1**, (b) **3** and (c) **5** in dichloromethane containing 0.1 M [(C₄H₉)₄N]PF₆, scan rate 100 mV s⁻¹.

peaks, respectively. In all cases repeated scanning gave essentially the same trace, highlighting the oxidative stability of these polymers. Polyaniline,[18] poly(diphenylamine)[19] and oligo(aryl)-amines[20] show similar behaviour in cyclic voltammetry, with two oxidation peaks in aqueous and organic media. The close resemblance of the voltammograms of polymers **1–6** with those of polyaniline and poly(diphenylamine) suggests that the electro-chemical oxidation of **1–6** involves the oxidation of the polymer to form a poly(emeraldine)-type struture[18,19] which contains ammonium radical cations. The third oxidation of **3** between 0.5 V and 1.0 V is due to oxidation of the carbazole nitrogen.[21]

The energy levels of the highest occupied molecular orbital (HOMO) for **1–6** were calculated using the equation reported by Forrest and co-workers.[17] The energy of the corresponding lowest unoccupied molecular orbitals (LUMO) were estimated by addition of the optical E_g values (Table 2) to the respective HOMO energy. The ionisation potentials of polymers **1–4** are lower than those of the biphenyl polymers **5** and **6**. The incorporation of a fused aromatic ring of fluorene or carbazole increases the degree of conjugation and hence decreases the ionisation potential. The E_{HOMO} values for **1–6** can also be compared with those of the homopolymers of substituted fluo-rene (E_{HOMO} = −5.5 eV)[22] and carbazole (E_{HOMO} = −5.3 eV) units.[23] The ionisation potentials of polymers **1–6** are all lower than these values due to the presence of an electron-donating nitrogen atom in the polymer main chain.

OFET characteristics

The charge transport properties of the amorphous polymers **1–6** were assessed by solution processing of OFET devices. Initial

efforts focussed on determining the influence of the solvent on the performance of the OFET devices.[24] Films of **1** were spin-coated on a poly(methylmethacrylate) (PMMA)/SiO₂ insulating layer[25] from solutions of the polymer in five different solvents, dichloromethane (CH₂Cl₂), chlorobenzene (CB), chloroform (CHCl₃), tetrahydrofuran (THF) and toluene. Polymer **1** per-formed as a p-type semiconductor and the mobility of the devices was determined in the saturation regime by the equation:

$$I_{DS} = \mu C_i \frac{W}{2L}(V_G - V_T)^2 \qquad (1)$$

where I_{DS} is the drain-source current, μ is the field-effect mobility, C_i is the capacitance of the gate dielectric per unit area, W is the channel width, L is the channel length and V_T is the threshold voltage. The hysteresis voltage was also estimated from the difference in potential between forward and backward scans in the plots of square root of drain current *versus* gate voltage.

The relationship between the FET mobility and the solvent solubility parameter is shown in Fig. 3a.[26] The interactions between the solvent and the polymer are important in deter-mining the final film morphology. The devices showed FET mobilities between 2.7 × 10⁻⁵ and 1.8 × 10⁻⁴ cm² V⁻¹ s⁻¹, depending on the solvents used for the film deposition on PMM-treated SiO₂/Si substrate. The mobilities tend to increase with increasing solubility parameter, the exception being films deposited from THF, which show lower mobilities than expec-ted. Devices deposited from CH₂Cl₂ and CHCl₃ showed higher hysteresis (Fig. 3b) than those deposited from other solvents; this may be due to the presence of trace acids in these solvents. Chlorobenzene showed much lower hysteresis and appreciable hole mobility, hence this solvent was chosen for the fabrication of FET devices using the other five polymers.

The dependence of the charge mobility on dielectric surface properties was also evaluated. Thin films of **1** were deposited on SiO₂/Si, PMMA-SiO₂/Si and octadecyltrichlorosilane (OTS)-treated SiO₂/Si[27] substrates at ambient conditions. For the devices on pristine SiO₂/Si substrates, the hole mobility was 5.2 × 10⁻⁶ cm² V⁻¹ s⁻¹ and the on/off ratio was higher than 10². When the SiO₂/Si substrate was treated with PMMA a large improve-ment in the performance was observed, with the mobility increasing to 1.3 × 10⁻⁴ cm² V⁻¹ s⁻¹ and the on/off ratio being higher than 10³. When the SiO₂/Si substrate was treated with OTS a further improvement in the performance was observed, with the mobility increasing to 2.4 × 10⁻³ cm² V⁻¹ s⁻¹ which is
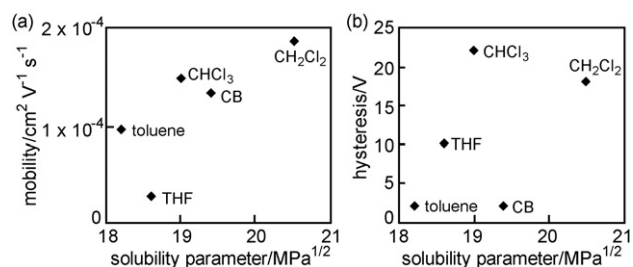

Fig. 3 (a) Plot of field-effect mobility of **1** on PMMA-treated SiO₂/Si substrates *versus* the solubility parameters of the solvents used for spin-coating. (b) Plot of hysteresis voltage of **1** on PMMA-treated SiO₂/Si substrates *versus* the solvents used for spin-coating.
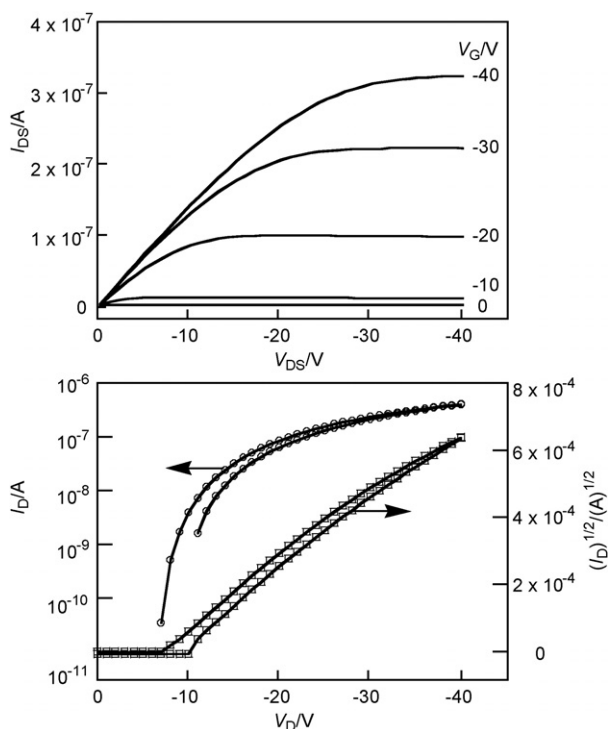
Fig. 4 The output (top) and transfer (bottom) characteristics of FET devices of **1** on OTS-treated SiO$_2$/Si substrates.

close to the highest mobility reported to date for amorphous poly(arylamine) transistors (Fig. 4).[6b,7] The on/off ratio was above 10^4, as shown in the I_D vs. V_D plots in Fig. 4 (bottom). These results indicate that the interface between the semi-conducting polymer and the insulating layer strongly affects the carrier mobility in these devices. Similar improvements have been reported in the literature.[7] Veres and co-workers concluded that low polarity gate insulators such as PMMA and OTS can decrease the energetic disorder and carrier localization, which act as a carrier trap at the interface with amorphous organic semi-conductors.[7a,b] Consequently, higher performances are shown in the OFET devices using PMMA and OTS insulating layers rather than polar pristine SiO$_2$ insulating layers.[27]

FET devices for all polymers (**1–6**) were therefore fabricated on OTS-treated SiO$_2$/Si substrates from chlorobenzene solution, and the results are summarized in Table 3. Devices fabricated from polymer **1** showed the best performance of this series as they have an extended π-conjugation and a rigid structural

Table 3 OFET properties of the polymers on OTS-SiO$_2$/Si substrate

Polymer	Mobility/ cm^2 V^{-1} s^{-1}	Threshold voltage/V	$I_{on/off}$	Hysteresis/V [a]
1	2.4×10^{-3}	−7	1.0×10^4	3
2	9.2×10^{-4}	−2	1.3×10^3	6
3	1.1×10^{-5}	−5	1.2×10^3	14
4	7.6×10^{-5}	−6	1.3×10^2	6
5	5.1×10^{-4}	−8	4.3×10^5	12
6	2.2×10^{-3}	−10	5.7×10^4	8

[a] Difference in potential between forward and backward scan.

element in the polymer main chain. This structural rigidity is consistent with the small Stokes shift observed in photo-luminescence (Fig. 1). When deposited under similar conditions, polymer **2** showed slightly lower performance, and the performances of polymers **3** and **4** were lower still ($\mu = 10^{-5}$–10^{-6} cm^2 V^{-1} s^{-1}). It appears that the 3,6-connectivity of the carbazole ring is detrimental to charge transport as the main chain is not effectively conjugated when linked in this fashion. It can also be noticed that the molecular weight of **3** and **4** are lower than those of the other polymers; this may also have a negative impact on the charge mobility in thin films of polymers **3** and **4**.[28] The biphenyl-based polymers **5** and **6** exhibited good performance, with charge mobilities in the range 10^{-4}–10^{-3} cm^2 V^{-1} s^{-1}, these values being similar to literature values for poly(triarylamine)s measured on OTS insulating layers.[7]

Conclusions

A variety of poly(arylamine)s (*e.g.* **1–6**) can be prepared by the microwave-assisted palladium-catalyzed amination of primary arylamines and aryldibromides. Reaction times can be reduced to a few minutes when the reaction is carried out at 100 °C, making the route attractive for generating libraries of electro-active materials based on a polyarylamine backbone. Polymers **1–6** were used to fabricate OFET devices, and the best perfor-mance was observed for devices fabricated on OTS-treated SiO$_2$/Si substrates using a chlorobenzene solution of **1** under ambient conditions, with a hole mobility of 2.4×10^{-3} cm^2 V^{-1} s^{-1} and an on/off ratio above 10^4. The performance of these amorphous semiconductors do not reach those of the best crystalline mate-rials or indeed those of amorphous cyclopentadithiophene–benzothiadiazole polymers reported recently.[29] However, they are readily processable from solution under ambient conditions, and the device performance is extremely reproducible and stable under ambient operation and storage. Polymers **1–6** are under investigation for use as charge transport layers in hybrid photovoltaic devices and the active layer of OFET-based sensors.

Experimental

General methods

All materials were purchased from commercial sources. The reactions were conducted in sealed 10 mL tubes by microwave dielectric heating in a CEM Explorer or CEM Discover with a maximum power output of 300 W. The reaction temperature (100 °C) was reached in 100 s for all reactions and the time recorded is the time at which the reaction was held at 100 °C. Polymer molecular weight was determined by GPC in tetra-hydrofuran (THF) solution using a Viscotek GPCmax VE2001 and a Viscotek VE3580 RI detector (referenced to polystyrene standards). ^{1}H NMR spectra were obtained using a Bruker 300 MHz spectrometer and elemental analysis using a Carlo Erba Instruments EA1108 elemental analyzer. UV-Vis absorp-tion spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and fluorescence spectra on a Varian Cary Eclipse fluorimeter. CV was performed at 100 mV s^{-1} in a BASI Epsilon electrochemical workstation with a three-electrode cell, Ag/AgNO$_3$ as reference electrode, platinum wire as counter-electrode and working electrode, in argon-purged, anhydrous

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0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane at room temperature.

Synthesis of poly[[(2-methyl-4-methoxyphenyl)imino]-9,9-di-(2′-ethylhexyl)fluorene-2,7-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (1)

4-Methoxy-2-methylaniline (0.110 g, 0.80 mmol), 9,9-di-(2′-ethylhexyl)-2,7-dibromofluorene (0.439 g, 0.80 mmol), NaO-t-Bu (0.232 g, 2.4 mmol), $Pd_2(dba)_3$ (0.015 g, 0.016 mmol) and toluene (3 mL) were combined in a 10 mL microwave reactor tube in a Schlenk tube and degassed with N_2(g). Then, 1.0 M of P(t-Bu)$_3$ (0.10 mL, 0.10 mmol) in toluene solution was added into the reaction mixture and sealed. The reaction mixture was heated in a microwave reactor at 100 °C for the specified reaction time. After cooling to room temperature, any sediment in the crude mixture was dispersed by ultrasonication. Then, diethylamine (0.100 mL, 0.97 mmol) was added into the crude mixture to quench the bromide terminal group and the mixture was heated in a microwave reactor (100 °C, 1 min). Subsequently, 4-bromoanisole (1.00 mL, 7.99 mmol) was added into the mixture to quench the amine terminal groups and again the mixture was heated in a microwave reactor (100 °C, 1 min). The crude product mixture was cooled to room temperature, poured into methanol and the precipitate was collected by filtration. The precipitate was dissolved in dichloromethane, loaded onto a silica gel column (3 cm) and eluted with dichloromethane. The eluent was concentrated under reduced pressure and then reprecipitated into methanol. The precipitate was collected by filtration and dried *in vacuo* to obtain the crude product (0.378 g, 90% mass recovery). Further purification was carried out by Soxhlet extraction using methanol, acetone and dichloromethane as solvents. The dichloromethane fraction was reprecipitated into methanol, the precipitate was collected by filtration and dried *in vacuo* to give **1** (0.142 g, 34%) as a light yellow powder. ¹H NMR (300 MHz, C_6D_6, δ): 7.49 (s, 2H, fluorene), 7.25 (broad, 4H, fluorene), 6.88 (s, 1H, phenyl), 6.84 (m, 2H, phenyl), 6.74 (m, 0.07H, C_6H_4OMe), 3.38 (s, 3H, OCH$_3$), 3.33 (s, 0.10H, OCH$_3$), 3.13 (broad, 0.02H, NCH$_2$CH$_3$), 2.29 (s, 3H, CH$_3$), 1.84 (broad, 4H, -CH$_2$-), 1.34 (broad, 2H, -CH-), 1.25 (m, 4H, -CH$_2$-), 1.08 (broad, 12H, -(CH$_2$)$_3$-), 0.93 (t, J = 6.8 Hz, 6H, CH$_3$), 0.76 (t, J = 6.6 Hz, 6H, CH$_3$); Anal. calcd for C$_{37}$H$_{49}$NO: C 84.84, H 9.78, N 2.67; found: C 82.76, H 9.39, N 2.46.

Syntheses of **2**–**6** were carried out analogously as shown in Scheme 1. Reactants, yield and characterization data of the polymers are shown below.

Poly[[(2,4-dimethylphenyl)imino]-9,9-di-(2′-ethylhexyl)fluorene-2,7-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (2)

2,4-Dimethylaniline (0.097 g, 0.80 mmol), 9,9-di-(2′-ethylhexyl)-2,7-dibromofluorene (0.439 g, 0.80 mmol). Light yellow power, crude (0.349 g, 86%) and product after Soxhlet extraction (0.268 g, 66%): ¹H NMR (300 MHz, C_6D_6, δ): 7.46 (s, 2H, fluorene), 7.22 (broad, 4H, fluorene), 7.01 (broad, 3H, phenyl), 6.82 (broad, 0.09H, C_6H_4OMe), 3.32 (s, 0.10H, OCH$_3$), 2.28 (s, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$), 1.78 (m, 4H, -CH$_2$-), 1.34 (broad, 2H, -CH-), 1.25 (m, 4H, -CH$_2$-), 1.06 (broad, 12H, -(CH$_2$)$_3$-), 0.93 (t, J = 6.8 Hz, 6H, CH$_3$), 0.75 (broad, 6H, CH$_3$); Anal. calcd for (C$_{37}$H$_{49}$N)(C$_7$H$_7$O)$_{0.25}$(C$_4$H$_{10}$N)$_{0.1}$: C 86.79, H 9.63, N 2.84; found: C 86.47, H 9.94, N 2.51.

Poly[[(2-methyl-4-methoxyphenyl)imino]-9-(2′-ethylhexyl)carbazole-3,6-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (3)

4-Methoxy-2-methylaniline (0.110 g, 0.80 mmol), N-2′-ethylhexyl-3,7-dibromocarbazole (0.350 g, 0.80 mmol). Light green powder (0.295 g, 89%): ¹H NMR (300 MHz, C_6D_6, δ): 8.17 (s, 2H, carbazole), 7.83 (m, 2H, carbazole), 7.39 (m, 2H, carbazole), 7.08 (m, 1H, phenyl), 6.84–6.51 (m, 2H, phenyl), 3.57 (d, J = 6.2, 2H, N-CH$_2$-), 3.29 (s, 3H, OCH$_3$), 2.25 (s, 3H, CH$_3$), 2.17–1.91 (m, 3H, -CH- and -CH$_2$-), 1.13 (broad, 6H, -(CH$_2$)$_3$-), 0.80 (m, 3H, CH$_3$), 0.72 (m, 3H, CH$_3$); Anal. calcd for (C$_{20}$H$_{32}$N$_2$O)(C$_7$H$_7$O)$_{0.1}$(C$_4$H$_{10}$N)$_{0.1}$: C 81.19, H 7.89, N 6.83; found: C 81.51, H 8.21, N 6.48.

Poly[[(2,4-dimethylphenyl)imino]-9-(2′-ethylhexyl)-carbazole-3,6-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (4)

2,4-Dimethylaniline (0.097 g, 0.80 mmol), N-2′-ethylhexyl-3,7-dibromocarbazole (0.350 g, 0.80 mmol). Light green powder (0.270 g, 85%): ¹H NMR (300 MHz, C_6D_6, δ): 8.11 (s, 2H, carbazole), 7.80 (m, 2H, carbazole), 7.37 (m, 2H, carbazole), 7.06–6.80 (m, 2H, phenyl), 6.72 (s, 1H, phenyl), 3.68 (broad, 2H, N-CH$_2$-), 3.29 (s, 0.14H, OCH$_3$), 2.24 (s, 3H, CH$_3$), 2.18 (s, 3H, CH$_3$), 2.10–1.90 (m, 3H, -CH- and -CH$_2$-), 1.12 (broad, 6H, -(CH$_2$)$_3$-), 0.79 (broad, 3H, CH$_3$), 0.71 (broad, 3H, CH$_3$); Anal. calcd for (C$_{28}$H$_{32}$N$_2$)(C$_7$H$_7$O)$_{0.26}$(C$_4$H$_{10}$N)$_{0.1}$: C 84.09, H 8.13, N 6.81; found: C 83.99, H 8.18, N 6.53.

Poly[[(2-methyl-4-methoxyphenyl)imino][1,1′-biphenyl]-4,4′-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (5)

4-Methoxy-2-methylaniline (0.110 g, 0.80 mmol), 4,4′-dibromobiphenyl (0.250 g, 0.80 mmol). Light yellow powder (0.190 g, 83%): ¹H NMR (300 MHz, C_6D_6, δ): 7.47 (d, J = 8.6 Hz, 4H, phenyl), 7.16 (d, J = 8.3 Hz, 4H, phenyl), 7.10 (d, J = 8.5 Hz, 1H, phenyl), 6.79 (d, J = 2.5 Hz, 1H, phenyl), 6.74 (m, 0.1H, C_6H_4OMe), 6.68 (dd, J = 8.5 and 2.5 Hz, 1H, phenyl), 3.35 (s, 3H, OCH$_3$), 3.32 (s, 0.14H, OCH$_3$), 3.01 (q, J = 6.8 Hz, 0.09H, NCH$_2$CH$_3$), 2.07 (s, 3H, CH$_3$), 0.92 (t, J = 6.8 Hz, 0.11H, NCH$_2$CH$_3$); Anal. calcd for C$_{20}$H$_{17}$NO: C 83.59, H 5.96, N 4.87; found: C 83.33, H 6.09, N 4.62.

Poly[[(2,4-dimethylphenyl)imino][1,1′-biphenyl]-4,4′-diyl], α-(4-methoxyphenyl)-ω-(diethylamino)- (6)

2,4-Dimethylaniline (0.097 g, 0.80 mmol), 4,4′-dibromobiphenyl (0.250 g, 0.80 mmol). Light yellow powder (0.180 g, 82%); ¹H NMR (300 MHz, C_6D_6, δ): 7.44 (d, J = 8.3 Hz, 4H, phenyl), 7.14 (d, J = 8.5 Hz, 4H, phenyl), 7.08 (s, 1H, phenyl), 7.10 (d, J = 9.0 Hz, 1H, phenyl), 6.91 (s, 1H, phenyl), 6.89 (d, J = 9.0 Hz, 1H, phenyl), 6.85 (d, J = 8.8 Hz, 0.19H, C_6H_4OMe), 6.71 (d, J = 8.8 Hz, 0.20H, C_6H_4OMe), 3.30 (s, 3H, OCH$_3$), 2.99 (weak, 0.006H, NCH$_2$CH$_3$), 2.15 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 0.91 (very weak, 0.02H, NCH$_2$CH$_3$); Anal. calcd for (C$_{20}$H$_{17}$N)(C$_7$H$_7$O)$_{0.2}$(C$_4$H$_{10}$N)$_{0.1}$: C 87.28, H 6.52, N 5.14; found: C 87.43, H 6.29, N 4.87.

Fabrication of OFETs

A solution of 5 wt% of poly(methylmethacrylate) (PMMA) in n-butyl acetate was spin-coated (3000 rpm) onto pieces (6 × 6 mm^2) of highly doped n-type silicon on which a 300 nm thick oxide layerr had been thermally grown. The PMMA was then baked at 180 °C for 2 h giving a film thickness 400–500 nm. The capacitance of PMMA/SiO$_2$ insulating layer was measured as 4 nF cm^{-2}. A solution of 1 wt% of polymer **1** in five different solvents – dichloromethane, chlorobenzene, chloroform, tetrahydrofuran or toluene – was spin-coated (3000 rpm) onto the PMMA-coated Si/SiO$_2$. To remove the solvent completely, the fabricated devices were annealed at 80 °C for 2 hours under nitrogen. Gold source and drain electrodes were thermally evaporated under high vacuum conditions (<10^{-6} Torr) on the organic semiconductor layer through a shadow mask with a channel width (W) of 2000 µm and a channel length (L) of 60 µm. Finally, the FET properties were measured by an Agilent E5270B precision measurement mainframe at room temperature in air.

Octadecyltrichlorosilane (OTS) was deposited onto pieces (6 × 6 mm^2) of highly doped n-type silicon on which a 300 nm thick oxide layer had been thermally grown by immersing films in 10^{-3} M of OTS in cyclohexane. The capacitance of the OTS-treated SiO$_2$ insulating layer was measured as 11 nF cm^{-2}. A solution of 1 wt% of polymer **1–6** in chlorobenzene was spin-coated (3000 rpm) onto the OTS-coated Si/SiO$_2$. To remove the solvent completely, the fabricated devices were annealed at 80 °C for 2 hours under nitrogen. Gold source and drain electrodes were thermally evaporated under high vacuum conditions (<10^{-6} Torr) on the organic semiconductor layer through a shadow mask with a channel width (W) of 2000 µm and a channel length (L) of 60 µm. Finally, the FET properties were measured by an Agilent E5270B precision measurement mainframe at room temperature in air.

Acknowledgements

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