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Synthesis of acrylate and norbornene polymers with pendant 2,7-bis(diarylamino)fluorene hole-transport groups

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Abstract—New hole-transport monomers have been synthesized in which a 2,7-(diarylamino)fluorene hole-transport functionality is linked through the 9-position of the fluorene bridge to a polymerizable acrylate or norbornene group; these monomers have been polymerized under free-radical and ring-opening metathesis polymerization (ROMP) conditions, respectively. The norbornene monomer has also been copolymerized with a cinnamate-functionalized norbornene; this copolymer can be rendered insoluble through photo-crosslinking of the cinnamate groups under UV irradiation, thus permitting the use of the polymer in organic electronic devices based upon multiple polymer layers. The norbornene monomer has also been copolymerized with dicyclopentadiene to afford insoluble crosslinked films. Time-of-flight studies indicate that the norbornene polymer has a higher hole mobility than the analogous acrylate material, consistent with the predictions of the disorder formalism.

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1. Introduction

Organic light-emitting diodes (OLEDs) are typically based upon vacuum-deposited small molecules or upon solutionprocessible conjugated polymers. We have been interested in a third strategy in which devices are based upon solutionprocessible side-chain polymers in which the side-chains are functionalized with small molecules with transport or luminescent properties.^{1–21} Here the ease of solution processing is retained, whilst the electronic properties of materials can be tuned through the choice of small molecule from among the wide range of well-studied examples. The rheological properties of the polymer may be tuned through the choice of polymer backbone, and through copolymerization with other monomers. In particular, we have focused on polyacrylates: copolymerization of monomers functionalized with 4,4'-bis(diarylamino)biphenyl ('TPD') hole-transport (HT) groups with those bearing photo-

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crosslinkable groups has led to polymers that can be rendered insoluble after processing from solution, thus permitting photo-patterning by UV irradiation through a photolithographic mask and fabrication of devices incorporating multiple solution-processible polymer layers.^{15–19,22} OLEDs based on small-molecule 2,7-bis(diarylamino)-9,9dimethylfluorenes as the HT material have recently been shown to have similar performance to those based upon TPD species with comparable ionization potential (the fluorene species are ca. 0.11-0.14 V more readily oxidized than their biphenyl analogues).²³ Here, we report on the synthesis of bis(diarylamino)fluorene HT polymers with backbones based on (i) radical-polymerized methacrylate groups and (ii) on the ring-opening metathesis polymerization (ROMP) of norbornene. We were particularly interested in norbornene-based polymers, since, according to the disorder formalism of Bässler, Borsenberger and co-workers,^{24–27} the relatively non-polar main chain should have less adverse effect on the hole mobilities of the material than polar ester groups of poly(acrylate)s, the dipole moments associated with which being anticipated to lead to increased energetic disorder in the HT manifold.²² Moreover, ROMP offers possibilities to obtain polymers with narrow molecular-weight distributions, to control the nature of the end groups, to obtain well-defined block

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Scheme 1. Synthesis of bis(diarylamino)fluorene-based monomers.

copolymers, and to incorporate a wide range of other chemical functionalities into polymers.^{28–32} We also report the incorporation of our norbornene HT monomer into a photocrosslinkable copolymer with a new cinnamatefunctionalized norbornene monomer, and into a crosslinked copolymer with dicyclopentadiene. Finally, we compare the hole mobilities of the acrylate and norbornene polymers measured using the time-of-flight technique.

2. Results and discussion

Our synthetic route to bis(diarylamino)fluorene monomers (Scheme 1) takes advantage of the ease with which fluorene may be alkylated in the 9-position. Thus, 2,7-dibromo-9methylfluorene, 1, was obtained by lithiation of 2,7-dibromofluorene with "BuLi, followed by treatment with methyl iodide (1 has previously been obtained by bromination of 9-methylfluorene³³). The protected-hydroxyl-functionalized 2,7-dibromofluorene, 3, was then obtained by alkylation with tert-butyldimethylsilyl-protected 3-bromopropanol using potassium hydroxide as a base. Alternatively, alkylation can be carried out using unprotected 3-bromopropanol under the same conditions, with subsequent protection of the hydroxy group using tert-butyldimethylchlorosilane. The fluorene core, 3, was then coupled with phenyl-m'-tolylamine using the palladium-catalyzed coupling reaction developed by Buchwald and Hartwig,^{34,35} specifically using tris(dibenzylideneacetone)dipalladium (Pd_2dba_3) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) as the catalyst system in the presence of sodium tertbutoxide.³⁶ After deprotection of the alcohol using tetra-nbutylammonium fluoride in tetrahydrofuran, the hydroxylfunctionalized bis(diarylamino)fluorene, **5**, can potentially be attached to a variety of polymerizable groups. The methacrylate monomer, **6**, was obtained by condensation of **5** with methacrylic acid using 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent and 4-(dimethylamino)pyridine (DMAP) as a catalyst. The norbornene monomer, **8**, was synthesized under Williamson ether synthesis conditions (Scheme 1); the norbornene tosylate used, **7**, was synthesized in a modification of a literature procedure (Scheme 2).³⁷ Compound **7** was also used to synthesize a cinnamate monomer, **9**, as a photocrosslinking group suitable for copolymerization with **8** (Scheme 2).

The methacrylate monomer, 6, was polymerized to give P6 under free-radical conditions using 2,2'-azobisisobutyronitrile (AIBN) as an initiator (Scheme 3); GPC analysis in THF was used to estimate the molecular weight distribution of P6 and suggested $M_{\rm p}=17,000$ and $M_{\rm w}=59,000$, corresponding to PDI=3.5. The norbornene monomer, 8, was polymerized to give P8 using the Grubbs catalyst, Ru1 (Scheme 3). As expected, the ROMP process gave polymer with a much lower polydispersity than the radical polymerization; GPC suggested M_n=13,000 M_w=16,000 and PDI=1.2. A copolymer, P8-9, was synthesized from a 7:3 ratio of 8 and 9 using the Grubbs' second-generation catalyst, Ru2 (Scheme 3). All three polymers were readily soluble in a range of organic solvents including THF, chloroform, toluene, benzene and dichloromethane. Differential scanning calorimetry (DSC) showed the glasstransition temperatures (T_g) of P8 and P8-9 to be 97 and 120 °C, respectively, with no evidence of other thermal



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Scheme 3. Polymerization reactions of the bis(diarylamino)fluorene monomers, 6 and 8, and structures of the ROMP initiators used (mes=2,4,6-trimethylphenyl; Cy=cyclohexyl).

process in the temperature range investigated (25-250 °C), suggesting these polymers are amorphous.

Crosslinking of **P8–9** under UV irradiation was monitored by UV spectroscopy. In initial experiments, thin films of **P8–9** were obtained on a glass substrate by spin-coating at 1600 rpm from THF solution (20.0 mg in 1 ml). The polymer films were irradiated using an unfiltered handheld UV source (365 nm, 7 W, UVGL-25, for visualizing thin-layer chromatography plates). The films were kept 6.1 cm from the UV lamp. The progress of the crosslinking was monitored by UV–vis spectroscopy; the absorbance at 310 nm, attributed to the cinnamate group, was found to decrease, whilst that at 377 nm, attributed to the bis(diarylamino)fluorene moiety, remained constant, consistent with the cinnamate groups undergoing 2+2 cycloaddition reactions without photo-induced damage to the HT groups occurring.

The insolubility of the UV-irradiated **P8–9** films on glass substrates was demonstrated by dipping the films in THF for increasing lengths of time and monitoring the UV spectra of the films. For the films that were exposed to 365 nm light from 3 to 6 min, only a small decrease (<5% change) in absorbance was observed, even after soaking the films for up to 120 min, suggesting that the polymers were largely crosslinked. In comparison, the bis(diarylamino)fluorene absorbances of non-irradiated films of **P8–9** on glass were found to decrease dramatically, even after soaking the films in THF for less than 1 min. These findings are entirely analogous to those we have previously reported for bis(diarylamino)biphenyl/cinnamate acrylate-based copolymers,¹⁵ clearly showing the general applicability of the photocrosslinking of cinnamate side chains as a means to render polymer films insoluble, and suggesting that it should be possible to incorporate norbornene HT polymers into devices based on the processing of more than one layer from solution.

Whilst **P8–9** contains considerably fewer polar groups than our previous crosslinkable acrylate polymers, there are still polar ester groups associated with the crosslinking groups. To further reduce the polarity of our crosslinked polymers, we investigated the copolymerization of 8 with dicyclopentadiene (Scheme 3). At room temperature this copolymerization resulted in the formation of an insoluble, presumably crosslinked, material. To create films of the insoluble material, we first initiated the polymerization of 8 using Ru1 and allowed it to proceed for 2.5 h to obtain active oligomers; these were then spin-cast with dicyclopentadiene and the polymerization allowed to proceed to form insoluble films. The film-forming properties of these solutions rapidly deteriorated as the viscosity of the solution increased and the solution eventually gelled. The films that were applied to a glass substrate were soaked in THF and the UV absorption was monitored. Initially a large decrease in the UV absorption was observed in all the films indicating that a large fraction of the material was not incorporated in a crosslinked film. The film that remained after the first soaking was found to be completely insoluble indicating that a portion of the material was crosslinked.

Hole mobilities have been measured for **P6** and **P8** using the time-of-flight method according to methods we have previously described.^{15,23,38} Figure 1 compares the room-temperature hole mobilities of the two polymers as a

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Figure 1. Electric-field dependence of the hole mobilities measured for P6 and P8 measured as a function of electric field at 299 K; symbols represent experimental data, lines are linear fits according to the disorder formalism.

function of electric field; the mobilities are comparable to those of blends composed of TPD or bis(diarylamino)fluorene small molecules and polystyrene. The norbornene polymer, **P8**, does indeed show higher hole mobility than its polyacrylate analogue, **P6**, consistent with a reduction in the energetic disorder due to use of a non-polar backbone.^{24–27} We have also demonstrated that OLEDs can be fabricated based upon **P8**. Details of the device work, along with a detailed study of the hole mobilities of **P6**, **P8** and related compounds, will be published elsewhere.

3. Summary

Bis(diarylamino)fluorene hole-transport groups can readily be attached to polymerizable groups through the 9-position of the fluorene. We have synthesized both acrylate and norbornene-based polymers, and have found a higher hole mobility in the latter material, consistent with the disorder formalism, which predicts polar polymer backbones should adversely affect the mobility. Cross-linked films based upon the norbornene-bis(diarylamino)fluorene monomer can be obtained either through photocrosslinking a copolymer with a cinnamate – norbornene monomer, or through copolymerizing active norbornene-bis(diarylamino)fluorene oligomers with dicyclopentadiene.

4. Experimental

4.1. General

Chemicals received from commercial sources were used without further purification. Norbornene-based materials are all derived from (5-norbornen-2-yl)methanol obtained from Aldrich as a mixture (ca. 1:1) of *endo* and *exo* isomers; no attempt was made to separate the isomers for any of our norbornene compounds and so the reported data, therefore, represents the isomeric mixture. Column chromatography was performed using silica gel (200–400 mesh, 60 Å); columns were typically ca. 15–25 cm in length and with a cross-sectional area ca. 10 cm² per 1 g of material to be purified. NMR spectra were internally referenced relative to tetramethylsilane (TMS; $\delta(^{1}H)=0$ ppm; $\delta(^{13}C)=0$ ppm)

using either the TMS ¹H resonance or the ¹³C resonance of the solvent. UV–vis spectra of thin films on quartz substrates were recorded with a Hewlett Packard 8453 spectrometer. GC-MS data were acquired on a Hewlett Packard HP6890 GC with a Hewlett Packard 5973 mass spectrometer. Glass-transition temperatures were determined using a Shimadzu DSC-50 differential scanning calorimeter run at 10 °C min⁻¹. Gel-permeation chromatography (GPC) was performed at 30 °C in THF using American Polymer Standards columns (100 Å, 1000 Å, 10^5 Å, 5 µm), a Waters WAT038040 column heater, and a Waters 410 RI detector. Calibration was performed using Polymer Laboratories narrow polystyrene standards (580–350×10⁶).

4.2. 2,7-Dibromo-9-methylfluorene, 1³³

To a dry 250 ml round-bottomed flask containing a magnetic stir bar was added 2,7-dibromofluorene (19.03 g, 58.7 mmol) and 100 ml of dry THF under argon. The solid was dissolved and the temperature of the reaction mixture was lowered to -78 °C in a dry ice/acetone bath. A 1.6 M solution of "BuLi (40 ml, 64.0 mmol) in hexanes was added over a period of 5 min. The reaction was stirred for 5 min and methyl iodide (9.1 g, 64.0 mmol) was added. The reaction mixture was stirred for 2 h and then carefully poured into a 1000 ml separatory funnel containing 200 ml of dichloromethane and 100 ml of water. The organic layer was collected and the water layer was extracted with dichloromethane (3×50 ml). The organic layers were combined and the solvent was removed under reduced pressure to yield the crude product as a white powder. The product was obtained in pure form as white crystals after recrystallization from hot hexanes (14.0 g, 39.1 mmol, 70.4%). ¹H NMR (500 MHz, CDCl₃) δ 1.50 (d, J=8 Hz, 3H), 3.92 (q, J=8 Hz, 1H), 7.49 (d, J=8 Hz, 2H), 7.57 (d, J=8 Hz, 2H), 7.62 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 17.9, 42.4, 121.9, 121.2, 127.4, 130.3, 138.5, 150.6. The ¹H NMR data are consistent with the literature.³³

4.3. 2,7-Dibromo-9-(3-hydroxypropyl)-9-methyl-fluorene, 2

To a 500 ml round-bottomed flask equipped a magnetic stir bar was added 1 (33.17 g, 98.1 mmol) and 150 ml of DMSO. After the solid had dissolved, potassium hydroxide (12.8 g, 119 mmol), 18-crown-6 (0.1 g), water (5 ml), and 3-bromopropan-1-ol (16.3 g, 117.0 mmol) were added and the reaction was stirred while the progress of the reaction was followed by GC/MS. Upon disappearance of the starting material, the reaction mixture was carefully poured into a 1000 ml separatory funnel containing 300 ml of dichloromethane and the solution was washed a saturated aqueous solution of sodium chloride (3×50 ml) and with distilled water (2×100 ml). The organic layer was collected and the solvent was removed under reduced pressure. The resulting material was purified by column chromatography eluting with dichloromethane to give a pale yellow oil (28.9 g, 73.4 mmol, 74.8%). ¹H NMR (300 MHz, CDCl₃) δ 0.88 (m, 2H), 1.24 (s, 1H), 1.46 (s, 3H), 2.02 (dt, J=3.9 Hz, 2H), 3.39 (t, J=6.6 Hz, 2H), 7.45 (dd, J=2.1, 7.8 Hz, 2H), 7.50 (d, J=2.1 Hz, 2H), 7.53 (d, J=7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 26.72, 27.77, 36.73, 51.18, 62.98,

121.63, 121.85, 126.45, 130.70, 138.35, 153.63. Anal. Calcd for $C_{17}H_{16}Br_2O$: C, 51.55; H, 4.07. Found: C, 51.56; H, 4.03. HRMS: Calcd for $C_{17}H_{16}Br_2O$ 393.9548, found 393.9574.

4.4. 2,7-Dibromo-9-[3-(*tert*-butyldimethylsilyloxy)-propyl]-9-methylfluorene, 3

To a 500 ml round-bottomed flask equipped a magnetic stir bar was added 2 (28.9 g, 73.1 mmol) and 50 ml of DMF. After the solid had dissolved, tert-butyldimethylchlorosilane (14.4 g, 95.6 mmol) and imidazole (6.5 g, 95.6 mmol) were added and the reaction mixture was stirred while the progress of the reaction was followed by thin-layer chromatography (TLC). Upon the disappearance of the starting material, the reaction mixture was poured into a 1000 ml separatory funnel containing 100 ml of diethyl ether and 100 ml of ice-cold water and the solution was extracted with diethyl ether (3×50 ml). The organic layer was collected and the solvent was removed under reduced pressure. The product was isolated as a pale yellow oil by column chromatography, eluting with 4:1 hexanes/dichloromethane (30.4 g, 59.5 mmol, 81.4%). ¹H NMR (500 MHz, $CDCl_3$) $\delta = 0.05$ (s, 6H), 0.82 (m, 2H), 0.85 (s, 9H), 1.46 (s, 3H), 2.03 (dt, J=5 Hz, 2H), 3.36 (t, J=6 Hz, 2H), 7.46 (dd, J=2, 8 Hz, 2H), 7.49 (d, J=2 Hz, 2H), 7.54 (d, J=8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ -1.42, 22.23, 29.87, 30.62, 31.55, 40.41, 54.94, 66.78, 125.25, 125.48, 130.20, 134.28, 142.05, 157.52. Anal. Calcd for C₂₃H₃₀Br₂OSi: C, 54.13; H, 5.92. Found: C, 54.30; H, 5.80. HRMS: Calcd for C₂₃H₃₀Br₂OSi 509.0511, found 509.0503.

4.5. 2,7-Bis(phenyl-*m*'-tolylamino)-9-(3-hydroxypropyl)-9-methylfluorene, 5

To a 250 ml round-bottomed flask equipped with a magnetic stir bar was added phenyl-m'-tolylamine (12.5 g, 68.2 mmol), Pd₂(dba)₃ (0.94 g, 1.0 mmol), dppf (1.1 g, 2.0 mmol), 3 (14.5 g, 28.4 mmol), and 100 ml of toluene under argon. The reaction mixture was allowed to stir for 10 min and sodium tert-butoxide (8.5 g, 88.0 mmol) was added. The reaction was stirred at 110 °C, while the progress of the reaction was monitored by TLC. Upon the disappearance of 3 the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel eluting with 4:1 hexanes/ dichloromethane. The solvent was removed under reduced pressure and the material (4) was deprotected without further characterization: to the 250 ml round-bottomed flask containing the material and a magnetic stir bar were added THF (30 ml) and a solution of tetra-n-butylammonium fluoride (1.0 M in THF, 100 ml). The mixture was stirred while the reaction was followed by TLC. Upon the disappearance of the protected alcohol, the solution was poured into a 500 ml separatory funnel containing 100 ml of water. The product was extracted with diethyl ether $(3 \times 50 \text{ ml})$. The organic layers were combined and the solvent was removed under reduced pressure. The product was isolated as a pale yellow glassy solid after flash chromatography, eluting with dichloromethane (9.31 g, 54.6%). ¹H NMR (300 MHz, (CD₃)₂CO) δ 0.94 (quint, J=4.5 Hz, 2H), 1.33 (s, 3H), 1.87 (t, J=8.1 Hz, 2H), 2.22 (s, 6H), 3.28 (t, J=5.1 Hz, 2H), 3.29 (s 1H), 6.85 (m, 4H), 6.97

(m, 6H), 7.07 (dd, J=1.2, 8.1 Hz, 4H), 7.14 (t, J=7.5 Hz, 2H), 7.19 (d, J=2.1 Hz, 2H), 7.25 (m, 4H), 7.58 (d, J=8.1 Hz, 2H). ¹³C NMR (75 MHz, (CD₃)₂CO) δ 22.35, 27.74, 29.90, 38.32, 51.96, 63.60, 119.59, 120.82, 121.74, 123.22, 124.12, 124.24, 124.45, 125.14, 129.84, 129.95, 135.76, 139.63, 147.49, 148.69, 148.78, 153.92. HRMS: Calcd for C₄₃H₄₀N₂O 600.3141, found 600.3137. Anal. Calcd for C₄₃H₄₀N₂O: C, 85.96; H, 6.71; N, 4.66. Found: C, 85.54; H, 6.69; N, 4.62.

4.6. 2,7-Bis(phenyl-*m*[']**-tolylamino)-9-[3-(methacryloyl-oxy)propyl]-9-methylfluorene**, **6**

To a dry 250 ml round-bottomed flask under argon were added 5 (1.69 g, 2.8 mmol), dicyclohexylcarbodiimide (1.22 g, 5.9 mmol), methacrylic acid (0.31 g, 3.6 mmol), and 50 ml of THF. The solution was cooled to 0 °C and 4-(dimethyl-amino)pyridine (0.2 g, 1.7 mmol) was added. The temperature was allowed to rise to room temperature while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material the solvent was removed under reduced pressure. The brown solid was dissolved in 100 ml of dichloromethane and washed with 3×50 ml portions of water. The solvent was removed under reduced pressure. The product was purified by flash chromatography, eluting with 7:3 hexanes/dichloromethane. The solvent was removed under reduced pressure to give a pale yellow glassy solid (1.42 g, 2.12 mmol, 75.7%). ¹H NMR (300 MHz, (CD₃)₂CO) δ 1.09 (quint., J=7.2 Hz, 2H), 1.84 (s, 3H), 1.96 (t, J=7.8 Hz, 2H), 2.23 (s, 6H), 3.85 (t, J=6.6 Hz, 2H), 5.53 (d, J=1.8 Hz, 1H), 5.96 (d, J=1 Hz, 1H), 6.85 (d, J=8.4 Hz, 3H), 6.91 (d, J=7.5 Hz, 3H), 7.00 (m, 4H), 7.08 (d, J=7.8 Hz, 4H), 7.16 (t, J=7.8 Hz, 2H), 7.20 (s, 2H), 7.27 (t, J=7.5 Hz, 4H), 7.62 (d, J=7.8 Hz, 2H). ¹³C NMR (75 MHz, (CD₃)₂CO) δ 18.42, 21.39, 24.87, 26.97, 36.98, 50.98, 65.13, 119.71, 121.05, 121.89, 123.34, 124.37, 124.43, 124.54, 125.28, 125.42, 129.95, 130.06, 135.85, 137.32, 139.75, 147.81, 148.82, 148.91, 153.60, 167.21. Anal. Calcd for C47H44N2O2: C, 84.40; H, 6.63; N, 4.19. Found: C, 84.44; H, 6.68; N, 4.17. HRMS: Calcd for C₄₇H₄₄N₂O₂ 668.3403, found 668.3395.

4.7. (5-Norbornen-2-yl)methyl p-toluenesulfonate, 737,39,40

To a 250 ml round-bottomed flask equipped with a magnetic stir bar was added *p*-toluenesulfonyl chloride (33.7 g, (5-norbornen-2-yl)methanol 177 mmol), (20.0 g, 161 mmol) and 80 ml of dichloromethane. After the solid had dissolved, the temperature of the solution was lowered to 0 °C in an ice bath and triethylamine (18.0 g, 177 mmol) was added. The reaction was stirred, and its progress was monitored by TLC. Upon the disappearance of the *p*-toluenesulfonyl chloride, the reaction mixture was poured into a 1000 ml separatory funnel containing 200 ml of dichloromethane and 100 ml of water. The organic layer was collected and subsequently washed with distilled water $(3 \times 50 \text{ ml})$. The solvent was removed under reduced pressure and the product was isolated as a colorless oil after purification by flash chromatography eluting with 8:2 hexanes/dichloromethane (33.0 g, 118.6 mmol, 73.7%). ¹H NMR (300 MHz, CDCl₃) δ 0.42 (ddd, J=2.4, 4.5, 11.7 Hz, 0.5H), 1.05 (dt, J=4.5, 11.7 Hz, 0.5H), 1.14 (d, J=9.0 Hz, 0.5H), 1.21 (d, J=8.4 Hz, 1H), 1.28 (m, 0.5H), 1.42 (dd,

J=2.1, 8.1 Hz, 0.5H), 1.77 (m, 1H), 2.38 (m, 0.5H), 2.44 (s, 3H), 2.68 (s, 0.5H), 2.78 (s, 1H), 2.87 (s, 0.5H), 3.55 (t, *J*=9.6 Hz, 0.5H), 3.79 (dd, *J*=6.3, 9.3 Hz, 0.5H), 3.90 (t, *J*=9.3 Hz, 0.5H), 4.07 (dd, *J*=6.3, 9.6 Hz, 0.5H), 5.67 (dd, *J*=3.0, 6.0 Hz, 0.5H), 6.04 (s, 0.5H), 6.08 (dd, *J*=3.0, 5.7 Hz, 0.5 Hz) 7.34 (d, *J*=8.1 Hz, 2H), 7.77 (d, *J*=5.4, 8.4 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 21.59, 28.59, 29.28, 37.95, 38.13, 41.51, 42.11, 43.29, 43.56, 44.76, 49.23, 73.72, 74.34, 127.82, 129.74, 129.79, 131.71, 133.91, 135.92, 137.01, 137.92, 144.57, 144.64. Anal. Calcd for C₁₅H₁₉O₃S: C, 64.72; H, 6.52. Found: C, 64.88; H, 6.37. HRMS: Calcd for C₁₅H₁₉O₃S 279.1055, found 279.1049. The ¹H NMR data are consistent with the literature.³⁹

4.8. 2,7-Bis(phenyl-*m*'-tolylamino)-9-{**3**-[(**5**-norbornen-2-yl)methoxy]propyl}-9-methylfluorene, 8

To a 250 ml round-bottomed flask equipped with a reflux condenser and a magnetic stir bar was added 60% sodium hydride in mineral oil (0.7 g, 17.6 mmol) and 50 ml of dry THF under a nitrogen atmosphere. The mixture was heated to 60 °C and a solution of 7 (7.0 g, 11.7 mmol) and 5 (4.90 g, 7.6 mmol) in 50 ml of THF was added over 20 min. The reaction was stirred, while its progress was monitored by TLC. Upon the disappearance of 5, the reaction was quenched with 10 ml of water. The reaction mixture was poured into a separatory funnel containing 50 ml of dichloromethane and 50 ml of water. The organic layers were combined and the solvent was removed under reduced pressure. The product was obtained as a white powder (7.22 g, 10.2 mmol, 87.2%) after column chromatography eluting with 7:3 hexanes/dichloromethane, followed by reprecipitation in methanol from THF. ¹H NMR (300 MHz, CDCl₃) δ 0.44 (m, 0.5H), 0.91 (t, J=7.2 Hz, 0.5H), 1.04 (m, 2.5H), 1.30 (m, 3H), 1.37 (s, 3H), 1.60 (m, 1H), 1.82 (m, 2H), 2.28 (s, 6H), 2.68 (s, 0.5H), 2.78 (s, 1H), 2.85 (s, 0.5H), 2.89 (t, J=9.0 Hz, 0.5H), 3.02 (dd, J=6.6, 9.3 Hz, 0.5H), 3.16 (m, 2H), 3.35 (dd, J=6.6, 9.3 Hz, 0.5H), 5.88 (dd, J=2.4, 5.7 Hz, 0.5H), 6.08 (m, 1.5H), 6.84 (d, J=7.2 Hz, 2H), 6.97 (m, 8H), 7.15 (m, 6H), 7.26 (t, J=7.0 Hz, 4H), 7.49 (d, J=7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 21.40, 24.89, 26.48, 29.13, 29.69, 36.80, 38.69, 38.77, 41.47, 42.13, 43.62, 43.90, 44.93, 49.36, 50.33, 71.22, 71.31, 74.36, 75.29, 118.99, 119.85, 121.12, 122.29, 123.37, 123.59, 124.59, 128.92, 129.07, 132.43, 135.02, 136.53, 136.60, 137.03, 138.92, 146.65, 147.76, 152.97. HRMS: Calcd for C₅₁H₅₀N₂O 706.3923, found 706.3937. Anal. Calcd for C₅₁H₅₀N₂O: C, 86.65; H, 7.13; N, 3.96. Found: C, 86.39; H, 6.97; N, 4.30.

4.9. Methyl 4-[(5-norbornen-2-yl)methoxy]cinnamate, 9

To a 500 ml round-bottomed flask was added methyl 4-hydroxycinnamate (5.66 g, 38.2 mmol), 7 (10.6 g, 38.2 mmol), acetone (50 ml), 18-crown-6 (0.10 g) and potassium carbonate (5.80 g, 42.1 mmol). The reaction was stirred at reflux while being followed by TLC. Upon the disappearance of methyl 4-hydroxycinnamate, the mixture was poured into a separatory funnel containing 100 ml of water. The product was extracted into diethyl ether (3×50 ml) and the organic layer was washed with cold water (3×50 ml) and 1 M NaOH (50 ml). The solvent was removed under reduced pressure. The material was obtained

as a white powder after three reprecipitations into methanol from THF (4.50 g, 15.8 mmol, 49.8%). ¹H NMR (300 MHz, CDCl₃) δ 0.58 (ddd, J=2.4, 11.7 Hz, 0.5H), 1.24 (m, 3H), 1.45 (dd, J=2.1, 7.8 Hz, 0.5H), 1.87 (m, 1H), 2.51 (m, 0.5H), 2.82 (s, 1.5H), 3.20 (s, 0.5H), 3.51 (t, J=9.0 Hz, 0.5H), 3.67 (dd, J=3.0, 6.3 Hz, 0.5H), 3.74 (s, 3H), 3.80 (t, J=9.0 Hz, 0.5H), 3.97 (dd, J=3.0, 6.3 Hz, 0.5H), 5.96 (dd, J=2.4, 3.0 Hz, 0.5H), 6.10 (m, 1.5H), 6.26 (dd, J=2.4, 15.9 Hz, 1H), 6.84 (dd, J=2.4, 8.7 Hz, 2H), 7.40 (dd, J=4.2, 8.7 Hz, 2H), 7.60 (dd, J=2.1, 15.6 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 28.84, 29.45, 38.10, 38.32, 41.43, 42.07, 43.51, 43.70, 44.86, 49.25, 51.31, 71.36, 72.15, 114.66, 114.84, 114.92, 126.64, 126.74, 129.49, 129.53, 132.06, 136.19, 136.69, 137.45, 144.36, 1454.39, 160.82, 160.85, 167.51. HRMS: Calcd for C₁₈H₂₀O₃ 284.1412, found 284.1417. Anal. Calcd for C₁₈H₂₀O₃: C, 76.05; H, 7.09. Found: C, 75.73; H, 7.04.

4.10. Poly{2,7-bis(phenyl-*m*′-tolylamino)-9-[3-(meth-acryloyloxy)propyl]-9-methylfluorene}, P6

To a thick-walled glass tube containing an argon atmosphere and a stir bar was added 0.35 g (0.75 mmol) of **6** and 0.0006 g (0.0075 mmol) of AIBN. The tube was pump-filled with argon and 5 ml of deoxygenated dry benzene was added. The tube was sealed and heated at 60 °C for 60 h. The reaction mixture was allowed to cool and was poured into 100 ml of methanol. The white solid was collected by vacuum filtration and was dissolved in THF followed by reprecipitation in methanol. The process was repeated three times. The product isolated as a white powder was collected vacuum filtration (0.27 g, 77.1%). ¹H NMR (300 MHz, CDCl₃) δ 1.05 (m, broad overlapping, 10H), 2.06 (s, broad, 8H), 3.36 (m, broad overlapping, 2H), 6.97 (m, broad overlapping, 24H). Anal. Calcd for poly(C₄₇H₄₄N₂O₂): C, 84.40; H, 6.63; N, 4.19. Found: C, 84.22; H, 6.64; N, 4.17.

4.11. Poly{2,7-bis(phenyl-m'-tolylamino)-9-[3-(5-norbornen-2-yl)methoxypropyl]-9-methylfluorene}, P8

To a Kontes tube containing an nitrogen atmosphere and a stir bar was added 1.00 g 8 in 1.5 ml of dichloromethane and 0.023 g (0.0028 mmol) of [Ru(PCy₃)₂(=CHPh)Cl₂] {Cy= cyclohexyl}, Ru1. The tube was sealed and the reaction was stirred for 35 min. The reaction mixture was quenched by stirring for 1 h with 5 ml of ethyl vinyl ether. The reaction mixture was poured into 100 ml of methanol. The white solid was collected by vacuum filtration and was dissolved in THF and then precipitated into methanol. The process was repeated twice. The product was collected as a white powder by vacuum filtration (0.76 g, 74.3%). ¹H NMR (300 MHz, THF- d_8) δ 0.93 (s, broad, 4H), 1.23 (m, broad overlapping, 6H), 1.73 (m, broad overlapping, 4H), 2.15 (s, broad, 5H), 2.44 (m, broad overlapping, 1H), 3.02 (m, broad overlapping, 5H), 5.12 (m, broad overlapping, 2H), 6.89 (m, broad overlapping, 22H), 7.44 (s, broad, 2H). Anal. Calcd for poly(C₅₁H₅₀N₂O): C, 86.65; H, 7.13; N, 3.96. Found: C, 86.39; H, 6.93; N, 4.26.

4.12. Copolymer (7:3) of 8 and 9, P8-9

To a Kontes tube containing an nitrogen atmosphere and a stir bar was added 0.25 g (0.35 mmol) 8 in 4.0 ml of

dichloromethane, 0.059 g (0.0069 mmol) of [RuL(PCy₃)- $(=CHPh)Cl_2$] {L=1,3-bis(mesityl)-2-imidazolidinylidene, Cy=cyclohexyl}, **Ru2**, and 0.04 g (0.15 mmol) of **9**. The tube was sealed and the reaction was stirred for 6 h. The reaction mixture was quenched with 5 ml of ethyl vinyl ether and was poured into 100 ml of methanol. The white solid was collected by vacuum filtration and was dissolved in THF and then precipitated in methanol. The process was repeated twice. The product was collected as a white powder by vacuum filtration (0.17 g, 58.0%). $T_g = 113$ °C. ¹H NMR $(300 \text{ MHz}, \text{THF-}d_8) \delta 0.42 \text{ (m, broad overlapping 3H)}, 1.25$ (m, broad overlapping, 6H), 1.78 (m, broad overlapping, 6H), 2.16 (m, broad overlapping, 4H), 2.44 (m, broad overlapping, 6H), 3.16 (m, broad overlapping, 3H), 5.24 (m, broad overlapping, 3H), 6.28 (m, broad overlapping, 26H). Anal. Calcd: C, 85.08; H, 7.12; N, 3.38. Found: C, 84.34; H, 7.01; N, 3.32.

4.13. Copolymerization of 8 and dicyclopentadiene

To a Kontes tube containing an nitrogen atmosphere and a stir bar was added 0.21 g (0.30 mmol) of **8** in 25.0 ml of 1,2-dichloroethane and 0.005 g (0.006 mmol) of $[\text{Ru}(\text{PCy}_3)_2$ -(=CHPh)Cl₂] {Cy=cyclohexyl}, **Ru1**. The tube was sealed and stirred for 2.5 h at 60 °C. 1 ml of this oligomer solution was mixed with 1 ml of a crosslinker solution composed of 0.48 g (3.6 mmol) of dicyclopentadiene dissolved in 20 ml of 1,2-dichloroethane. The solution was mixed for either 90, 150 or 180 s, and then applied by spin-coating at 1000 rpm to glass slides. At times longer than 3 min the viscosity had increased too much for the solution to be spin-coated.

4.14. Time-of-flight mobility measurements

Samples were prepared by melting a small amount of material between two ITO-coated glass slides at a temperature between 130 and 140 °C. Calibrated glass spacers (20 μ m) were used to ensure a uniform sample thickness. Finally samples were sealed with quick-setting epoxy adhesive. The measurements were conducted as described elsewhere.³⁸

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