Synthesis of Photo-Crosslinkable Hole-Transport Polymers with Tunable Oxidation Potentials And Their Use In Organic Light-Emitting Diodes

Richard D. Hreha,[a] Ya-Dong Zhang,[a] Benoit Domercq,[b] Nathalie Larribeau,[b] Joshua N. Haddock,[b]
Bernard Kippelen,*[b] Seth R. Marder*[a,b]

[a] Department of Chemistry, The University of Arizona, Tucson, AZ 85721, USA
[b] Optical Sciences Center, The University of Arizona, Tucson, AZ 85721, USA
E-mail: smarder@u.arizona.edu

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Abstract: A series of photo-crosslinkable arylamine-based hole-transport copolymers has been synthesized. The synthetic methodology employed allows for the redox potential of the polymer to be tuned by the incorporation of electron-donating or -withdrawing moieties. Upon exposure to ultraviolet radiation, the polymers become insoluble, as evidenced by UV/Vis absorption spectroscopy, a feature that is useful for the fabrication of multilayer organic light-emitting diodes (OLEDs) by solution processing techniques. OLEDs based on these hole-transport polymers have been fabricated and the performance of the devices has been evaluated. The photo-crosslinking process has been optimized so that it no longer adversely impacts device performance.

Key words: hole-transport agents, photo-crosslinked polymers, organic light-emitting diodes, bis(diarylamino)biphenyls

Introduction

Light-emitting diodes (LEDs) based on organic small molecules[1,2] or polymeric materials[3,4] have recently attracted considerable interest due to their potential application in flat-panel displays.[5] To date, the most efficient devices are multilayer structures composed of hole-transport, emitting, and electron-transport layers sandwiched between an anode and a cathode.[6] Multilayer organic light-emitting diodes (OLEDs) based on small molecules can be fabricated by sequential vapor deposition of each layer in high vacuum. However, OLED fabrication using solution-based methods must be used for non-volatile polymeric materials. However, for solution-based fabrication of multilayer OLEDs it is necessary that the first layer is not dissolved during the deposition of a subsequent layer. One approach that has been employed to circumvent this problem is to render a material insoluble subsequent to application by using either photo-induced or thermal crosslinking reactions.[7] Recently, photo-crosslinkable polymers, as well as thermally crosslinkable oligomers, for OLEDs have been reported.[8–10] Recently, we reported on a series of photo-crosslinkable side-chain acrylate polymers containing a bis(diarylamino)biphenyl hole-transport agent and cinnamate[11,12] and chalcone[13,14] groups as photo-crosslinking groups.[15] In this earlier work, the efficiency of devices was impaired by the photo-crosslinking step. Here we report an extension of this work entailing the synthesis and characterization of a new set of variable-redox-potential photo-crosslinkable side-chain acrylate polymers. We also describe fabrication of OLED devices based upon these new polymers. The device fabrication conditions have been optimized using these new polymers to minimize the decrease in the device performance that had been previously reported.[15]

Results and Discussion

We designed a series of methacrylate-based photo-crosslinkable polymers in which bis(diarylamino)biphenyl moieties are the hole-transport agent. As in our previous work,[4,15] this group was chosen since such molecules are widely used in vapor-deposited small-molecule-based OLEDs due to their high hole mobilities and their tunable orbital energies. Since we have previously found the device characteristics of bis(diarylamino)biphenyl-styrene polymers to depend strongly on the orbital energies of the polymers,[4] we designed the new polymers to have a variety of redox potentials to allow tuning of the relative rates of injection of holes into the polymer. The new polymers also differ from those in reference[15] in the linker between the bis(diarylamino)biphenyl and the acrylate polymer backbone.

The syntheses and molecular structures of the hole-transport methacrylate-type monomers and the photo-crosslinkable monomers are shown in Schemes 1–3. The monomers **1-OMe**, **1-Me**, **1-F** and **1-F$_2$** were synthesized from hydroxyl-containing compounds by reaction with methacrylic acid using 1,3–dicyclohexylcarbodiimide (DCC) as a dehydrating agent and 4-dimethylaminopyridine (DMAP) as a catalyst. The monomers **1-Me**, **1-F$_2$**, and **12** were obtained in pure form by column chromatography on silica gel, eluting with a 7:3 ratio of dichloromethane–hexanes; monomer **1-OMe** was purified by column chromatography on silica gel, eluting with dichloromethane. Pure monomer **1-F** was obtained by reprecipitation of the crude product from tetrahydrofuran (THF) into methanol (purification on silica gel was initially avoided as similar compounds reportedly decompose on silica gel; however, this was not observed with compounds **1-OMe**, **1-Me**, and **1-F$_2$**).[15] The cores of the hole-

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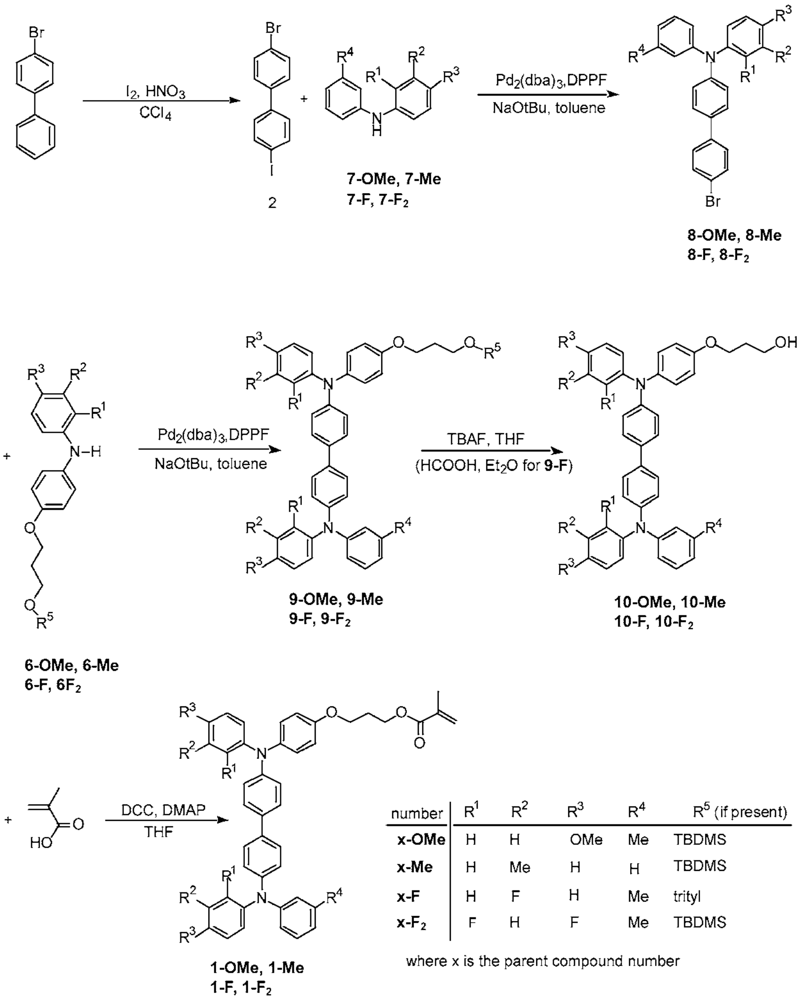
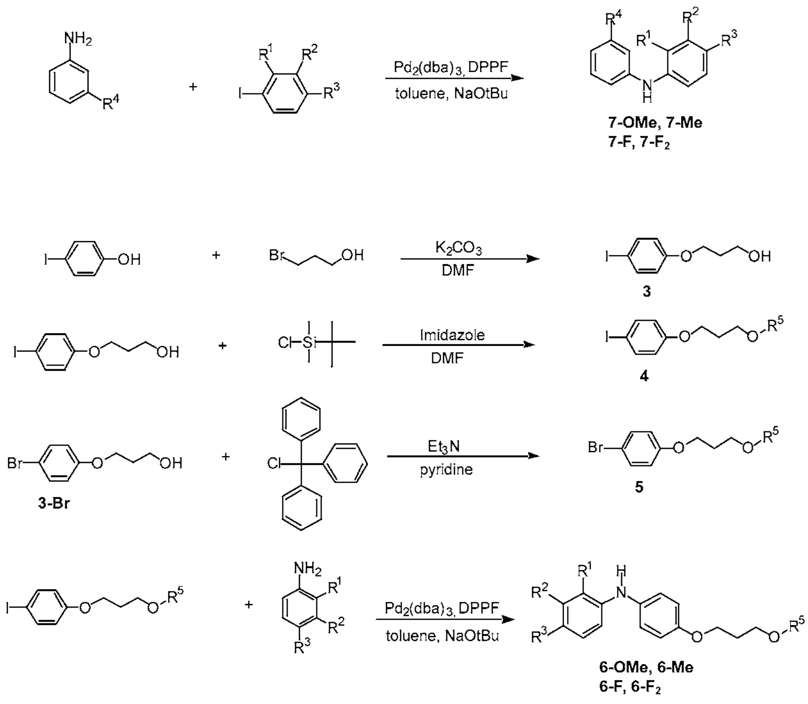
transport monomers were built up from compound **2**, which was obtained from the iodination of 4-bromobiphenyl using iodine and nitric acid. The amines **7-OMe**, **7-Me**, **7-F**, **7-F$_2$** were coupled to compound **2** selectively at the iodine functionality using tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) as the catalyst system in the presence of sodium *t*-butoxide.[16] In our previous work with 4,4′-dibromobiphenyl we observed coupling of primary amines at both bromine positions leading to *N*,*N*′-diphenyl-1,1′-biphenyl-3,4-diamine structures.[15] When compound **2** is coupled to one equivalent of an amine there appears to be complete selectivity for reaction at the iodine as none of the bromine-coupling product was seen. The amines **6-OMe**, **6-Me**, **6-F** and **6-F$_2$** were then coupled at the bromine using the same conditions. The secondary amines **6-OMe**, **6-Me**, **6-F**, **6-F$_2$**, **7-OMe**, **7-Me**, **7-F**, and **7-F$_2$** were themselves synthesized under the same conditions (as shown in Scheme 3). The alcohols **3** and **3-Br** were synthesized from 4-iodophenol or 4-bromophenol respectively, which was reacted with 3-bromopropanol under nucleophilic substitution conditions. The alcohol was then converted to the silyl ether **4** or the trityl ether **5**. The *tert*-butyldimethylsilyl (TBDMS) protecting group is preferred due to the ease which it can be installed and removed. Monomer **1-OMe**, was homopolymerized and monomers **1-OMe**, **1-Me**, **1-F** and **1-F$_2$** were copolymerized with 30% (mole ratio) of crosslinkable monomer **12** using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator under argon at 60 °C for 60 hours (as shown in Scheme 4). The polymers were obtained in pure form as white powders by precipitation three times, once from benzene into methanol and twice from THF into methanol. The structure of the compounds and polymers were confirmed by NMR spectroscopy and elemental analysis (as shown in the experimental section). The ^1H NMR spectra of the copolymers exhibited extensive broadening of the peaks leading to peak overlap and undiscernible multiplicities.



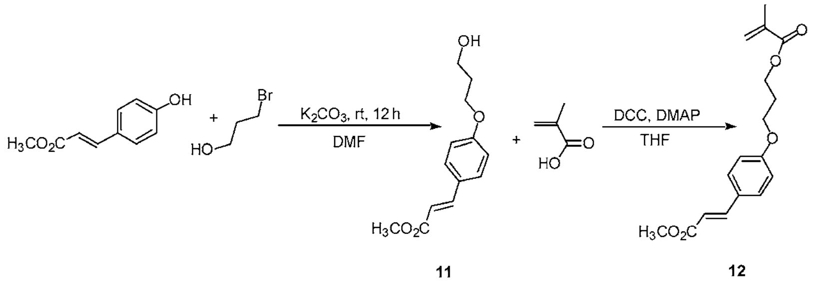
number	R^1	R^2	R^3	R^4	R^5 (if present)
x-OMe	H	H	OMe	Me	TBDMS
x-Me	H	Me	H	H	TBDMS
x-F	H	F	H	Me	trityl
x-F$_2$	F	H	F	Me	TBDMS

where x is the parent compound number

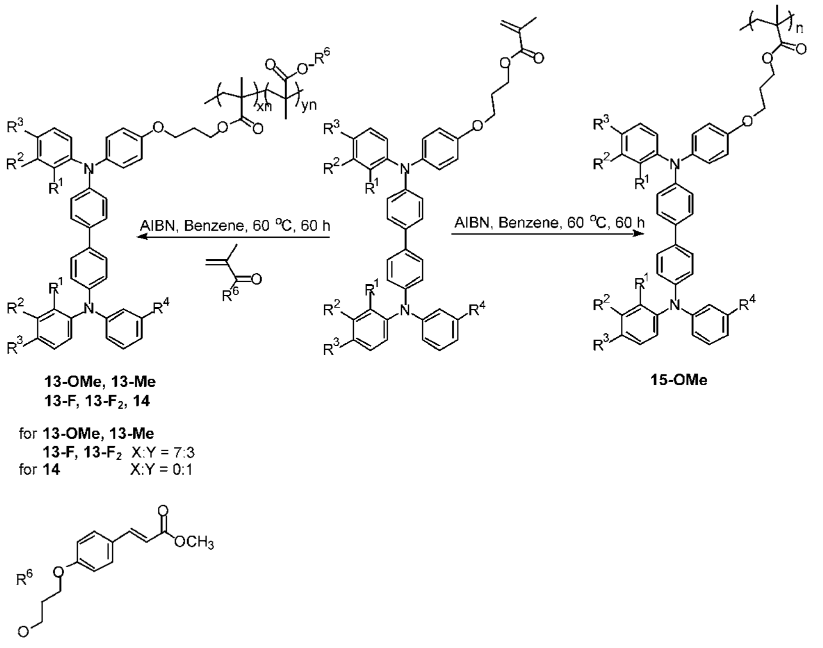
Scheme 1 Synthesis of monomers **1-OMe, 1-Me, 1-F, and 1-F$_2$**



Scheme 2 Synthesis of secondary amines



Scheme 3 Synthesis of monomer **12** with crosslinkable units



Scheme 4 Synthesis of the polymers

Each of the polymers was readily soluble in common organic solvents including THF, chloroform, toluene, benzene and dichloromethane. The glass-transition temperatures (T_g) of the polymers were determined by differential scanning calorimetry (DSC). The glass-transition temperatures of polymers **13-OMe**, **13-Me**, **13-F**, **13-F$_2$** and **15-OMe** are 97, 108, 99, 97, and 123 °C respectively. There was no evidence of other thermal process in the temperature range investigated (from 25 to 250 °C), suggesting that the polymers prepared are amorphous.

The redox potentials of the monomers **1-OMe**, **1-Me**, **1-F** and **1-F$_2$** versus ferrocenium/ferrocene were determined by cyclic voltammetry in dichloromethane (Table). The cyclic voltammograms show two sequential reversible one-electron processes corresponding to the successive removal of two electrons from the bis(diarylamino)biphenyl unit. The compounds **1-OMe**, **1-Me**, **1-F** and **1-F$_2$** demonstrate the expected trend of increasing redox potential as the electron-donating substituents on the bis(diarylamino)biphenyl moiety are replaced with electron-withdrawing substituents. The effects of the substituents parallel those seen in similarly substituted non-polymerizable molecular bis(diarylamino)biphenyls and bis(diarylamino)biphenyl-functionalized polyolefins.[4] However, the potentials in the present compounds are somewhat lower, presumably due to the electron-donating nature of the ether linkage to the polymerizable group.

Table Redox Potentials of Hole-Transport Monomers in CH_2Cl_2[a]

Monomer	$^1E_{1/2}$(mV)	$^2E_{1/2}$(mV)
1-OMe	105	360
1-Me	190	470
1-F	300	540
1-F$_2$	320	595

[a] Values are reported relative to the ferrocenium/ferrocene couple.

The crosslinking of the polymers upon UV-irradiation was monitored by UV spectroscopy. In initial experiments, thin films of polymers **13-OMe**, **13-Me**, **13-F**, **13-F$_2$**, **14** and **15-OMe** were obtained on a quartz substrate by spin-coating at 3000 rpm from THF solution (20 mg in 1 mL of THF). The polymer films were irradiated with an unfiltered handheld UV source (365 nm, 7 W, UVGL-25) for visualizing thin layer chromatography plates. The films were kept 1.7 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 353 nm, attributed to the bis(diarylamino)biphenyl moiety remained constant, suggesting that the cinnamate moieties undergo [2+2] cycloaddition without photo-induced damage to the hole-transport groups. To confirm these attributions and this hypothesis, and to remove complications in interpretation arising from some overlap between the 310 and 353 nm absorptions, homopolymer **15-OMe**, which has no crosslinkable units, and homopolymer **14**, which has no bis(diarylamino)biphenyl units, were synthesized for comparison with **13-OMe** and subjected to the same crosslinking conditions as **13-OMe**. The homopolymer **14** exhibited a decrease in absorbance at 310 nm similar to that seen for **13-OMe,** while there was no decrease in absorbance of **15-OMe**, confirming that the decrease in absorption is predominantly due to the [2+2] cycloaddition reaction and that the bis(diarylamino)biphenyl moieties are relatively stable under the crosslinking conditions.

The irradiated polymer **13-OMe**, **13-Me**, **13-F**, **13-F$_2$**, and **14** films on quartz substrates were used to demonstrate the insolubility of the polymers after UV irradiation. The UV absorption spectra were acquired after dipping the films in THF for increasing lengths of time. Even after soaking the films up to 80 minutes, no measurable decrease (<1% change in absorbance) in absorption was observed suggesting that the polymers were crosslinked. In comparison, for non-irradiated films of **13-OMe**, **13-Me**, **13-F**, **13-F$_2$**, and **14** on quartz, it was found that the absorption intensities dramatically decreased after dipping the films in THF for 1 minute. The same large decrease in absorption was found for an exposed film of **15-OMe** on a quartz substrate. These observations indicate that the crosslinked copolymers are insoluble in THF and that the insolubility is not a result of the exposure of the bis(diarylamino)biphenyl moiety to UV light, but due to the [2+2] cycloaddition reaction of the cinnamate moiety.

In subsequent studies, copolymers containing 70 mol% of these monomers and 30 mol% of cinnamate substituted acrylate monomer could be photo-crosslinked using the UV radiation (350 nm) provided by a standard UV-mask aligner. As was the case with the handheld UV source experiments (see above), the absorption band characteristic of the bis(diarylamino)biphenyl moiety at 353 nm does not vary upon UV exposure, whereas the cinnamate absorption band at 312 nm decreases as a function of UV exposure (Figure 1). To efficiently crosslink the polymer and make it insoluble, a minimum of 20 mJ/cm^2 of UV exposure was found to be required. We have been able to use standard lithographic techniques to pattern these materials. For instance, using a negative photolithography mask, we have been able to define features ranging from 50 to 10 μm as shown in Figure 1b.

Fabrication and Characterization of Light-Emitting Devices

To investigate the performance of the hole-transport polymers **13-OMe**, **13-Me**, **13-F**, and **13-F$_2$**, **15-OMe** in device geometry, we fabricated OLEDs with the following structure: ITO/polymer (**13-OMe** or **13-Me** or **13-F** or **13-F$_2$**,)/AlQ_3/Mg:Ag. AlQ_3 [aluminum tris(8-hydroxyquinolinate)] was chosen as an electron-transport and emitting material because its performance when combined with other hole-transport materials is well documented. The films of about 50 to 60 nm thickness were prepared by

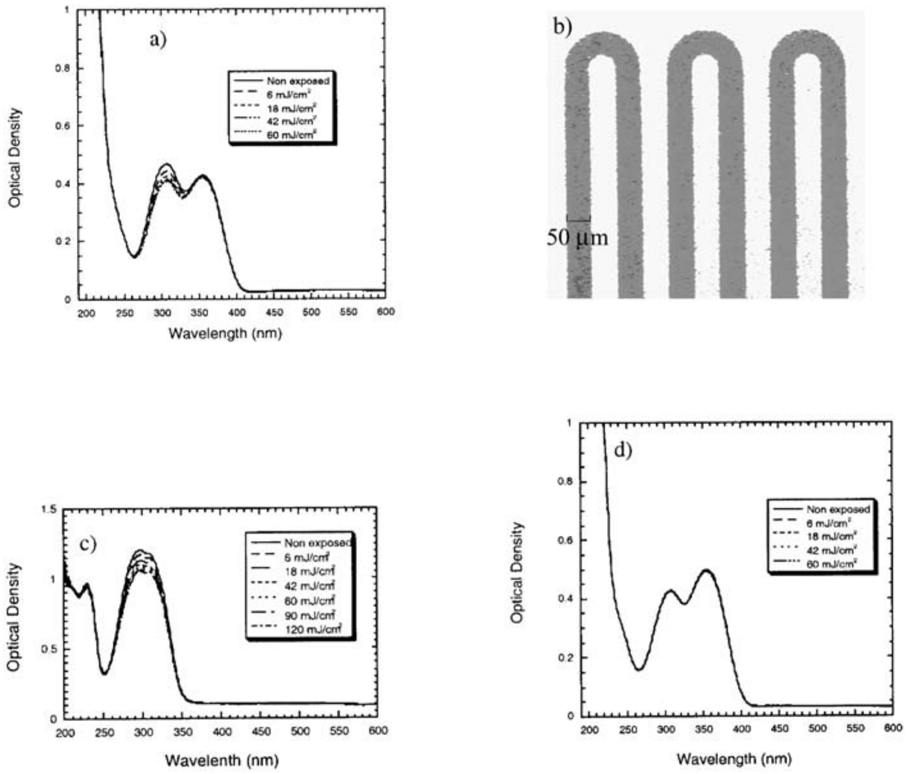


Figure 1 (a) Evolution of the absorption spectra of a 50 nm thick film of **13-OMe** under UV exposure. (b) Photograph of 50 µm sized features obtained after photo-crosslinking (25 mJ/cm^2) of a 60 nm thin film of **13-OMe**. (c) Evolution of the absorption spectra of a film of **14** under UV exposure. (d) Evolution of the absorption spectra of a film of **15** under UV exposure.

spin coating polymers **13-OMe**, **13-Me**, **13-F** and **13-F$_2$** onto O$_2$-plasma-treated ITO with sheet resistance of 20 Ω/□ (Colorado Concept Coatings, L.L.C.) from toluene solutions. Then, 60 nm-thick AlQ$_3$ films were vapor deposited at a rate of 1 Å/s under a pressure of 1×10^{-6} Torr on top of the hole-transport layer. The metal cathode, a 1:10 alloy of silver and magnesium, was deposited through a mask to define five devices, each with an emissive area of 0.1 cm^2.

OLED devices using these new polymers exhibit performances comparable to those of their wholly vapor-deposited equivalents. The light emission of all the devices corresponds to the typical AlQ$_3$ emission spectrum. Figure 2 shows the typical characteristic of an ITO/ **13-F** /AlQ$_3$/Mg:Ag device. The current density exhibits a typical diode behavior with a strong rectification above 2 V. The light is first detected around 3 V. The external quantum efficiency for **13-F**-based devices reaches a maximum value of 1.2% at around 8 V with a luminance of 1320 cd/m^2.

Upon crosslinking, we have previously reported that the performance of OLEDs devices decreases significantly.[15] Optimization of UV exposure to minimize any adverse effects is, therefore, critical for device performance. We have investigated the dependence of the device performance as a function of the UV exposure for devices with

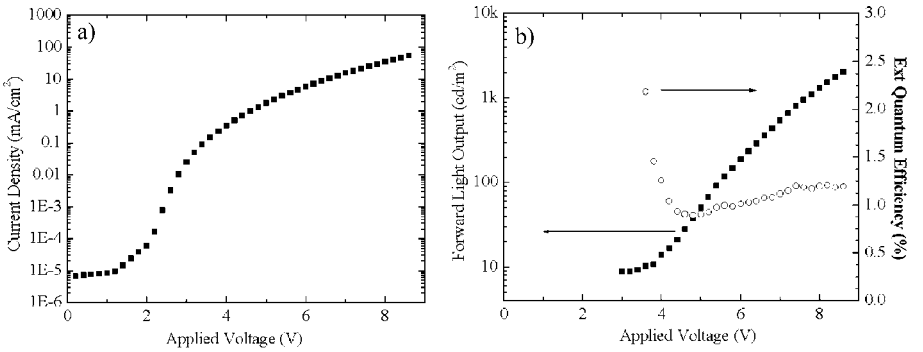


Figure 2 (a) Current density, and (b) luminance and external quantum efficiency as a function of applied voltage for a ITO/**13-F** /AlQ$_3$/Mg:Ag [50 nm/50 nm/300 nm (10:1)] device.

structure ITO/**13-F**/AlQ_3/Mg:Ag. For each device, the hole-transport polymer was spin-coated and crosslinked using different UV energy densities ranging from 0 mJ/cm^2 to 180 mJ/cm^2. The AlQ_3 layer was then deposited on all the samples during the same deposition run. We found that for UV exposure energies of up to 30 mJ/cm^2, which are adequate to render the films insoluble; there is no measurable decrease in the performance of the devices relative to the uncrosslinked material. Presumably this level of UV dosage leads to sufficient cross-linking to confer insolubility, yet insufficient decomposition of the bis(diarylamino)biphenyl moities to adversely affect factors governing device performance, such as charge mobility. Detailed device fabrication and characterization studies are currently in progress, and will be published in due course.

Chemicals received from commercial sources were used without further purification. The synthesis of compound **11** was reported previously.[15] NMR spectra were recorded with a Varian Unity Plus spectrometer at 500 MHz (^{1}H) and 126 MHz (^{13}C) in $CDCl_3$ or acetone-d_6 unless otherwise stated. Spectra were internally referenced relative to TMS [δ (^{1}H) = 0; δ (^{13}C) = 0] using either the TMS ^{1}H resonance or the ^{13}C resonance of the solvent. UV/Vis spectra were recorded as thin films on quartz substrates with a Hewlett Packard 8453 spectrometer. GC-MS spectra were run on a Hewlett Packard HP6890 GC with a Hewlett Packard 5973 mass spectrometer. The glass-transition temperatures were determined by thermal analysis using a Shimadzu DSC-50 differential scanning calorimeter run at 10°/min. Cyclic voltammetry was performed under argon using ca. 10^{-4} M solutions in sample and 0.1 M in $Bu_4N^+PF_6^-$ using a glassy-carbon working electrode, a platinum auxiliary electrode, a AgCl/Ag pseudo-reference electrode, and a BAS 100B potentiostat. Potentials were referenced by the addition of ferrocene to the cell, and are quoted to the nearest 5 mV relative to the ferrocenium/ferrocene couple at 0 V.

4-Bromo-4′-iodo-1,1′-biphenyl (2)[17]

4-Bromobiphenyl (49.83 g, 214 mmol), I_2 (32.5 g, 128.4 mmol) and CCl_4 (100 mL) were added to a 500 mL round bottom flask equipped with an efficient reflux condenser. The mixture was heated to 50 °C and was stirred while concd HNO_3 (24.0 g, 385 mmol, 17.0 mL) was added over 30 min. After all the HNO_3 was added, the mixture was gently refluxed until GC-MS showed none of the 4-bromobiphenyl. The mixture was extracted with toluene and the oily layer was washed with conc. HNO_3 (3 × 10 mL). The material was washed with 10% aq NaOH (50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the pale brown crystals were recrystallized from hot hexanes. The purified product was isolated as white crystals (58.61 g, 77%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.0 Hz, 2 H), 7.42 (d, J = 8.0 Hz, 2 H), 7.57 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.0 Hz, 2 H).

GC-MS: m/z (rel. int., %) = 358, 360 (1:1, 100, M$^+$).

3-(4-Iodophenoxy)propan-1-ol (3)[18]

To a 500 mL round bottom flask was added 4-iodophenol (24.9 g, 113 mmol), 3-bromopropanol (18.9 g, 136 mmol), DMF (100 mL) and K_2CO_3 (31.2 g, 226 mmol). The reaction mixture was stirred at r.t. and the reaction was followed by TLC. Upon the disappearance of 4-iodophenol, the mixture was poured into a separatory funnel containing H_2O (100 mL). The product was extracted with EtOAc and the organic layer was washed with cold water (3 × 50 mL) and brine (50 mL). The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with EtOAc–CH_2Cl_2 (1:49). The solvent was removed under reduced pressure and the residual solvent was removed in vacuo. The yield of the desired product, isolated as white crystals, was 26.30 g (84%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.69 (s, 1 H), 2.04 (quint, J = 6.0 Hz, 2 H), 3.86 (t, J = 6.0 Hz, 2 H), 4.09 (t, J = 6.0 Hz, 2 H), 6.69 (d, J = 7.0 Hz, 2 H), 7.56 (d, J = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.8, 60.2, 65.6, 82.9, 116.8, 138.2, 158.56.

3-(4-Bromophenoxy)propan-1-ol (3-Br)[19]

To a 500 mL round bottom flask was added 4-bromophenol (32.22 g, 186 mmol), 3-bromopropanol (31.06 g, 224 mmol), DMF (50 mL) and K_2CO_3 (43.2 g, 313 mmol). The reaction mixture was stirred at r.t. and the reaction was followed by TLC. Upon the disappearance of 4-iodophenol, the mixture was poured into a separatory funnel containing H_2O (100 mL). The product was extracted with EtOAc and the organic layer was washed with cold water (3 × 50 mL) and brine (50 mL). The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel, eluting with CH_2Cl_2. The solvent was removed under reduced pressure and the residual solvent was removed in vacuo. The yield of the desired product, isolated as white crystals, was 37.2 g (93%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.01 (quint, J = 6.0 Hz, 2 H), 2.25 (s, 1 H), 3.82 (t, J = 6.0 Hz, 2 H), 4.05 (t, J = 6.0 Hz, 2 H), 6.77 (d, J = 9.0 Hz, 2 H), 7.35 (d, J = 9.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.9, 59.9, 65.6, 112.9, 116.2, 132.2, 157.8.

tert-Butyl[3-(4-iodophenoxy)propoxy]dimethylsilane (4)

To a dry 250 mL round bottom flask under N_2 was added **3** (26.3 g, 94.5 mmol), *tert*-butyldimethylsilyl chloride (17.82 g, 118.2 mmol), imidazole (8.1 g, 118.2 mmol) and DMF (50 mL). The reaction mixture was stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was poured into a separatory funnel containing cold water (100 mL). The product was extracted with Et_2O (3 × 50 mL). The Et_2O layers were combined and washed with cold water (3 × 100 mL) and brine (3 × 45 mL). The solvent was removed under reduced pressure and the residue was purified by flash chromatography eluting with 1:4 CH_2Cl_2–hexanes. The solvent was removed under reduced pressure and the residual solvent was removed in vacuo. The mass of the purified product isolated as colorless oil was 37.08 g (~100%). The purity of the product was estimated to be greater than 95% by ^{1}H NMR and was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.58 (s, 6 H), 0.88 (s, 9 H), 1.97 (quint, J = 6.0 Hz, 2 H), 3.79 (t, J = 6.0 Hz, 2 H), 4.03 (t, J = 6.0 Hz, 2 H), 6.69 (d, J = 9.0 Hz, 2 H), 7.54 (d, J = 9.0 Hz, 2 H).

^{13}C NMR (125 MHz, ($CDCl_3$)): δ = –2.98, 18.29, 25.89, 32.18, 59.28, 64.47, 82.48, 116.85, 139.11, 158.89.

HRMS: m/z calcd for $C_{15}H_{26}IO_2Si$ 393.0747, found 393.0754.

1-Bromo-4-[3-(trityloxy)propoxy]benzene (5)

To a solution of **3-Br** (18.0 g, 78.0 mmol) and triphenylmethylchloride (21.77 g, 78 mmol) in pyridine (40 mL) under N_2, was added 4-dimethylaminopyridine (150 mg, 1.2 mmol). The solution was stirred at 70 °C for 32 h and the progress of the reaction was monitored by TLC. The pyridine was removed under reduced pressure and the material was dissolved in CH_2Cl_2 (100 mL) and the CH_2Cl_2 layer was washed with cold water (3 × 50 mL). The crude material was purified by flash chromatography on silica gel, eluting with CH_2Cl_2. The material was further purified by column chromatography on silica gel, eluting with hexanes–EtOAc (3:1). The solvent was removed under reduced pressure and the residual solvent was removed in vacuo. The yield of product isolated as a viscous oil was 37.1 g (~100%). The purity of the product was estimated greater than 95% by ^{1}H NMR and was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (quint J = 6 Hz, 2 H), 3.28 (t, J = 6 Hz, 2 H), 4.10 (t, J = 6 Hz, 2 H), 6.76 (d, J = 9 Hz, 2 H), 7.26 (m, 9 H), 7.37 (d, J = 9 Hz, 6 H), 7.43 (m, 6 H).

^{13}C NMR (75 MHz, ($CDCl_3$): δ = 29.76, 59.73, 65.02, 86.45, 112.59, 116.27, 126.88, 127.21, 127.70, 127.88, 128.58, 132.11,144.11, 157.96.

HRMS: *m*/*z* calcd for $C_{28}H_{25}BrO_2$ 472.1038, found 472.1034.

N-[4-(3-{*tert*-Butyl(dimethyl)silyl]oxy}propoxy)phenyl]-3-methylaniline (6-Me)

To a dry 500 mL round bottom flask under argon were added **4** (13.64 g, 35.8 mmol), *m*-toluidine (4.5 g, 41.2 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.4 g, 0.44 mmol) and DPPF (0.5 g, 0.88 mmol) were added. After stirring for 10 min, *t*-BuONa (3.9 g, 41.2 mmol) was added. The reaction mixture was heated to 90 °C and stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel eluting with CH_2Cl_2. The product was purified by flash chromatography eluting with CH_2Cl_2–hexanes (1:1). The solvent was removed in vacuo to give 10.26 g (77%) of the desired product as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70 (s, 6 H), 0.91 (s, 9 H), 2.00 (quint, J = 6 Hz, 2 H), 2.29 (s, 3 H), 3.82 (t, J = 6 Hz, 2 H), 4.06 (t, J = 6 Hz, 2 H), 5.46 (s, 1 H), 6.67 (d, J = 7 Hz, 1 H), 6.73 (d, J = 7 Hz, 2 H), 6.87 (d, J = 9 Hz, 2 H), 7.06 (d, J = 8 Hz, 2 H), 7.11 (t, J = 8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.15, 18.55, 21.77, 26.14, 32.70, 59.80, 65.05, 112.91, 115.47, 116.43, 120.58, 122.44, 129.33, 135.87, 145.39,154.89.

Anal. Calcd for $C_{22}H_{33}NO_2Si$ Found: C, 70.84; H, 8.84; N, 3.80.

HRMS: *m*/*z* calcd for $C_{22}H_{33}NO_2Si$ 372.2359, found 372.2348.

N-[4-(3-{*tert*-Butyl(dimethyl)silyl]oxy}propoxy)phenyl]-4-methoxyaniline (6-OMe)

To a dry 500 mL round bottom flask under argon, were added **4** (13.84 g, 35.3 mmol), 4-methoxyaniline (5.1 g, 41.0 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.61 g, 0.56 mmol) and DPPF (0.7 g, 1.12 mmol) were added. After stirring for 10 min, *t*-BuONa (4.3 g, 45.0 mmol) was added. The reaction mixture was heated to 90 °C and was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel eluting with CH_2Cl_2. The product was purified by flash chromatography eluting with CH_2Cl_2–hexanes (7:3). The solvent was removed in vacuo to afford 8.50 g (62%) of the product as a brown oil.

^{1}H NMR (500 MHz, acetone-d_6): δ = 0.07 (s, 6 H), 0.90 (s, 9 H), 1.94 (quint, J = 6 Hz, 2 H), 3.74 (s, 3 H), 3.83 (t, J = 6 Hz, 2 H), 4.04 (t, J = 6 Hz, 2 H), 6.79 (s, 1 H), 6.84 (m, 4 H), 6.97 (m, 4 H).

^{13}C NMR (125 MHz, acetone-d_6): δ = –2.88, 21.11, 28.60, 35.66, 57.99, 62.45, 67.64, 117.61, 118.35, 121.75, 121.82, 125.71, 141.56, 156.29, 156.93.

Anal. Calcd for $C_{22}H_{33}NO_3Si$: C, 68.17; H, 8.58; N, 3.61. Found: C, 68.19; H, 8.38; N, 3.63.

HRMS: *m*/*z* calcd for $C_{22}H_{33}NO_3Si$ 387.2230, found 387.2231.

3-Fluoro-*N*-{4-[3-(trityloxy)propoxy]phenyl}aniline (6-F)

To a dry 250 mL round bottom flask under argon, were added 3-fluoroaniline (4.3 g, 38 mmol), **5** (14.58 g, 31 mmol) and toluene (50 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.6 g, 0.7 mmol) and DPPF (0.6 g, 1.1 mmol) were added. After stirring for 10 min, *t*-BuONa (4.8 g, 50 mmol) was added. The temperature was increased to 90 °C using an oil bath and the reaction mixture was stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material the mixture was filtered through a plug of silica gel eluting with CH_2Cl_2. The product was purified by column chromatography on silica gel, eluting with toluene. The solvent was removed under reduced pressure. The residual solvent was removed in vacuo; pale yellow glass; yield: 12.71 g (83%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (quint, J = 6.0 Hz, 2 H), 3.32 (t, J = 6.5 Hz, 2 H), 4.15 (t, J = 6.5 Hz, 2 H), 5.58 (s, 1 H), 6.51 (dt, J = 2.5 Hz, 9.0 Hz, 1 H), 6.20 (m, 2 H), 6.88 (d, J = 7.5 Hz, 2 H), 7.10 (d, J = 8.5 Hz, 2 H), 7.14 (q, J = 8.0 Hz, 1 H), 7.26 (m, 9 H), 7.46 (d, J = 7.0 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.94, 59.94, 65.18, 86.48, 101.45, 101.65, 105.50, 105.67, 110.67, 115.37, 123.40, 126.90, 127.74, 128.66, 130.34, 130.41, 134.34, 144.21, 147.41, 147.48, 155.31, 162.95, 164.88.

Anal. Calcd for $C_{34}H_{30}FNO_2$: C, 81.09; H, 6.00; N, 2.76. Found: C, 81.42; H, 6.12; N, 2.98.

HRMS: *m*/*z* calcd for $C_{34}H_{30}FNO_2$ 503.2261, found 503.2245.

N-[4-(3-{*tert*-Butyl(dimethyl)silyl]oxy}propoxy)phenyl]-2,4-difluoroaniline (6-F_2)

To a dry 500 mL round bottom flask under argon, were added **4** (18.44 g, 47.0 mmol), 2,4-difluoroaniline (6.5 g, 51.0 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.65 g, 0.71 mmol) and DPPF (0.8 g, 1.40 mmol) were added. After stirring for 10 min, *t*-BuONa (5.1 g, 54.0 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel eluting with CH_2Cl_2. The product was purified by column chromatography eluting with CH_2Cl_2–hexanes (1:4). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to furnish 5.09 g (28%) of the desired product as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.88 (s, 9 H), 1.99 (quint, J = 6 Hz, 2 H), 3.81 (t, J = 6 Hz, 2 H), 4.05 (t, J = 6 Hz, 2 H), 5.43 (s, 1 H), 6.72 (tq, J = 8.5 Hz, 1.5 Hz, 1H), 6.87 (m, 3 H), 7.01 (m, 3 H).

^{13}C NMR (125 MHz, ($CDCl_3$): δ = –5.18, 18.52, 26.12, 32.64, 59.71, 65.02, 103.88, 104.06, 104.26, 110.76, 110.79, 110.94, 110.96, 115.59, 116.26, 116.29, 116.33, 116.36, 122.41, 130.22, 130.31, 135.00, 151.09, 151.18, 153.03, 153.11, 154.79, 154.88, 155.29, 156.71, 156.80.

HRMS: *m*/*z* calcd for $C_{21}H_{29}F_2NO_2Si$ 393.1936, found 393.1939.

Anal. Calcd for $C_{21}H_{29}F_2NO_2Si$: C, 64.09; H, 7.43; N, 3.56. Found: C, 64.22; H, 7.52; N, 3.58.

N-(4-Methoxyphenyl)-3-methylaniline (7-OMe)[20]

To a dry 500 mL round bottom flask under argon were added 4-iodoanisole (14.7 g, 67.1 mmol), *m*-toluidine (7.5 g, 70.0 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (1.2 g, 1.3 mmol) and DPPF (1.5 g, 2.7 mmol) were added. After stirring for 10 min, *t*-BuONa (12.5 g, 127 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material, the reaction mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by flash chromatography eluting, with CH_2Cl_2–hexanes (3:7). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 7.80 g (59%) of the desired product as a pale yellow oil.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 3.81 (s, 3 H), 5.47 (s, 1 H), 6.68 (m, 2 H) 6.87 (d, *J* = 7.5 Hz, 2 H), 7.12 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.56, 55.54, 112.72, 114.60, 116.26, 120.43, 122.18, 129.13, 139.14.

N-(3-Fluorophenyl)-*N*-(3-methylphenyl)amine (7-F)

To a dry 500 mL round bottom flask under argon were added 1-fluoro-3-iodobenzene (22.1 g, 100 mmol), *m*-toluidine (12.5 g, 116 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (1.2 g, 1.3 mmol) and DPPF (1.5 g, 2.7 mmol) were added. After stirring for 10 min, *t*-BuONa (12.5 g, 127 mmol) was added. The reaction mixture was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by flash chromatography, eluting with CH_2Cl_2–hexanes (3:2). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo and 18.62 g (93%) of the product was isolated as a pale yellow oil.

^1H NMR (500 MHz, ($CDCl_3$): δ = 2.35 (s, 3 H), 5.74 (s, 1 H), 6.59 (t, *J* = 9.0 Hz, 1 H), 6.78 (d, *J* = 7.0 Hz, 2 H), 6.84 (d, *J* = 7.5 Hz, 1 H), 6.94 (s, 2 H), 7.22 (m, 2 H).

^{13}C NMR (125 MHz, ($CDCl_3$): δ = 21.50, 103.36, 103.56, 106.77, 106.94, 112.46, 116.09, 119.70, 122.94, 129.25 130.38, 130.45, 139.37, 141.85, 145.39, 145.47, 162.79, 164.72.

HRMS: *m*/*z* calcd for $C_{13}H_{12}FN$ 201.0954, found 201.0957.

Anal. Calcd for $C_{13}H_{12}FN$: C, 77.59; H, 6.01; N, 6.96. Found: C, 77.70; H, 6.11; N, 7.10.

2,4-Difluoro-*N*-(3-methylphenyl)aniline (7-F_2)

To a dry 500 mL round bottom flask under argon were added difluoro-1-iodobenzene (14.15 g, 59 mmol), *m*-toluidine (8.03 g, 75 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and $Pd_2(dba)_3$ (0.73 g, 0.8 mmol) and DPPF (0.87 g, 1.5 mmol) were added. After stirring for 10 min, *t*-BuONa (7.4 g, 77 mmol) was added. The reaction mixture was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of starting material, the reaction mixture was carefully poured into a separatory funnel containing H_2O (50 mL). The product was extracted with toluene (3 × 50 mL). The solvent was removed under reduced pressure and the material was purified by flash chromatography on silica gel, eluting with hexane–CH_2Cl_2 (7:3). The solvent was removed under reduced pressure and the residual solvent was removed in vacuo. The yield of the desired product isolated as a yellow oil was 11.46 g (88%).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 5.55 (s, 1 H), 6.85 (m, 5 H), 7.18 (t, *J* = 8.5 Hz, 1 H), 7.27 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.50, 103.98, 104.16, 104.19. 104.38, 110.74, 110.89, 110.91, 114.61, 118.28, 119.30, 119.33, 119.37, 119.40, 122.28, 127.77, 129.23, 139.37, 142.61, 152.35, 154.20, 155.69, 155.78, 157.61.

HRMS: *m*/*z* calcd for $C_{13}H_{11}F_2N$ 443.0885, found 443.0882.

Anal. Calcd for $C_{13}H_{11}F_2N$: C, 71.22; H, 5.06; N, 6.39. Found: C, 71.35; H, 4.88; N, 6.44.

N-(3-Methylphenyl)-*N*-phenyl-4-bromo-1,1′-biphenyl-4′-amine (8-Me)[21]

To a dry 250 mL round bottom flask under argon were added 3-methyldiphenylamine (8.41 g 47.0 mmol), **2** (20.0 g, 55.9 mmol) and toluene (50 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.77 g, 0.8 mmol) and DPPF (0.93 g, 1.6 mmol) were added. After stirring for 10 min, *t*-BuONa (5.6 g, 58 mmol) was added. The temperature of the reaction was raised to 90 °C while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by flash chromatography, eluting with a solution of hexanes–CH_2Cl_2 (1:1). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to afford 6.76 g (35%) of the desired product as white crystals.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 6.88 (d, *J* = 7.5 Hz, 1 H), 6.93 (m, 2 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 7.12 (m, 4 H), 7.17 (t, 7.5 Hz, 1 H), 7.28 (m, 2 H), 7.44 (m, 4 H), 7.54 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.40, 120.80, 121.88, 122.91, 123.53, 124.10, 124.43, 127.46, 125.32, 127.46, 128.14, 129.10, 129.23, 131.76, 133.36, 139.19, 139.54, 147.39, 147.57.

N-(4′-Bromo-1,1′-biphenyl-4-yl)-*N*-(4-methoxyphenyl)-*N*-(3-methylphenyl)amine (8-OMe)

To a dry 250 mL round bottom flask under argon were added **7-OMe** (7.78 g 36.5 mmol), **2** (14.3 g, 40.0 mmol) and toluene (50 mL). The mixture was deoxygenated for 10 min and $Pd_2(dba)_3$ (0.55 g, 0.6 mmol) and DPPF (0.6 g, 1.2 mmol) were added. After stirring for 10 min, *t*-BuONa (3.9 g, 40 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by flash chromatography, eluting with hexanes–CH_2Cl_2 (7:3). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 9.82 g (61%) of the desired product as white crystals.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 3.82 (s, 3 H), 6.82 (d, *J* = 7.0 Hz, 1 H), 6.90 (m, 4 H), 7.05 (d, *J* = 9.0 Hz, 2 H), 7.12 (m, 3 H), 7.41 (q, *J* = 3 Hz, 4 H), 7.52 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.43, 55.44, 114.74, 120.63, 120.76, 122.17, 123.37, 124.20, 127.34, 127.44, 128.06, 128.97, 131.73, 132.46, 139.04, 139.62, 140.43, 147.64, 147.97, 156.25.

HRMS: *m*/*z* calcd for $C_{26}H_{22}BrNO$ 443.0885 found 443.0882.

Anal. Calcd for $C_{26}H_{22}BrNO$: C, 70.28; H, 4.99; N, 3.15. Found: C, 70.39; H, 5.04; N, 3.31.

N-(4′-Bromo-1,1′-biphenyl-4-yl)-*N*-(3-fluorophenyl)-*N*-(3-methylphenyl)amine (8-F)

To a dry 250 mL round bottom flask under argon were added **7-F** (5.5 g, 27.5 mmol), **2** (8.5 g, 23.7 mmol) and toluene (50 mL). The mixture was deoxygenated for 10 min and $Pd_2(dba)_3$ (0.4 g, 0.4 mmol) and DPPF (0.4 g, 0.7 mmol) were added. After stirring for 10 min, *t*-BuONa (3.4 g, 35 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by column chromatography, eluting with hexanes–toluene (93:7). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to afford 6.88 g (67%) of the desired product was isolated as a pale yellow glassy solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 6.90 (dt, *J* = 2.5 Hz, 5 Hz, 1 H), 6.78 (dt, *J* = 2.0 Hz, 9 Hz, 1 H), 6.86 (dd, *J* = 2.5 Hz, 8.5

Hz, 1 H), 6.95 (dd, $J = 7.5$ Hz, 16.5 Hz, 3 H), 7.17 (m, 4 H), 7.46 (m, 4 H), 7.50 (d, $J = 7.5$ Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.40$, 108.84, 109.01, 109.90, 110.01, 118.54, 121.05, 122.48, 124.40, 124.89, 125.95, 127.67, 128.23, 129.29, 130.05, 130.12, 131.81, 134.35, 139.40, 139.44, 146.85, 146.95, 149.33, 162.46, 164.41.

GC-MS: *m*/*z* (rel. int., %) = 431, 433 (1:1, 100, M^+).

Anal. Calcd for $C_{25}H_{19}BrFN$: C, 69.45; H, 4.43; N, 3.24. Found: C, 69.42; H, 4.25; N, 3.25.

N-(4′-Bromo-1,1′-biphenyl-4-yl)-*N*-(2,4-difluorophenyl)-*N*-(3-methylphenyl)amine (8-F_2)

To a dry 250 mL round bottom flask under argon were added **7-F_2** (9.5 g 43.4 mmol), **2** (16.8 g, 47.7 mmol) and toluene (50 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.7 g, 0.7 mmol) and DPPF (0.8 g, 1.4 mmol) were added. After stirring for 10 min, *t*-BuONa (3.4 g, 35 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by column chromatography, eluting with a solution of hexanes–CH_2Cl_2 (95:5). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 12.19 g (63%) of the desired product was isolated as a pale yellow glass.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.31$ (s, 3 H), 6.90 (m, 5 H), 7.02 (d, $J = 9$ Hz, 2 H), 7.22 (m, 2 H), 7.44 (d, $J = 9.0$ Hz, 4 H), 7.54 (d, $J = 8.0$ Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.49$, 105.31, 105.51, 105.71, 112.05, 112.02, 112.23, 120.02, 120.85, 121.26, 123.47, 124.04, 127.53, 128.17, 129.13, 130.44, 130.51, 131.80, 133.19, 139.25, 139.52, 146.61, 146.94, 157.63, 159.18, 159.26, 159.65, 161.24.

HRMS: *m*/*z* calcd for $C_{25}H_{18}F_2BrN$: 451.0574, found 451.0577.

Anal. Calcd for $C_{25}H_{18}F_2BrN$: C, 66.68; H, 4.03; N, 3.11. Found: C, 67.07; H, 3.98; N, 3.15.

N,*N*′-Bis(3-fluorophenyl)-*N*-(3-methylphenyl)-*N*′-{4-[3-(trityloxy)propoxy]phenyl}-1,1′-biphenyl-4,4′-diamine (9-F)

To a dry 500 mL round bottom flask under argon was added **6-F** (12.34 g, 24.51 mmol), **8-F** (11.40 g, 26.4 mmol), and toluene (100 mL). The mixture was deoxygenated for 10 min and then $Pd_2(dba)_3$ (0.2 g, 0.2 mmol) and DPPF (0.2 g, 0.3 mmol) were added. After stirring for 10 min, *t*-BuONa (3.1 g, 32 mmol) was added. The temperature was raised to 90 °C and the reaction mixture was stirred while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material the mixture was filtered through a plug of silica gel, eluting with CH_2Cl_2. The product was purified by column chromatography, eluting with hexanes–CH_2Cl_2 (70:30). The solvent was removed under reduced pressure and the residual solvent was removed in vacuo to give 19.31 g (92%) of the desired product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, acetone-d_6): $\delta = 2.06$ (quint, $J = 7.0$ Hz, 2 H), 2.26 (s, 3 H), 3.29 (t, $J = 6.0$ Hz, 2 H), 4.18 (t, $J = 6.0$ Hz, 2 H), 6.70 (m, 4 H), 6.80 (dd, $J = 3.0$ Hz, 8.5 Hz, 2 H), 6.94 (m, 5 H), 7.11 (m, 6 H), 7.25 (m, 12 H), 7.46 (d, $J = 8.0$ Hz, 6 H), 7.57 (m, 4 H).

^{13}C NMR (125 MHz, acetone-d_6): $\delta = 11.65$, 11.78, 20.50, 26.51, 59.81, 64.80, 86.36, 100.28, 107.43,m 107.60, 107.76, 108.23, 108.41, 108.82, 109.02, 115.63, 116.88, 118.11, 122.47, 123.87, 124.72, 124.96, 125.88, 126.88, 127.33, 127.35, 127.70, 127.99, 128.56, 129.43, 130.36, 130.45, 134.66, 135.27, 139.39, 139.48, 144.37, 146.19, 146.43, 146.95, 149.70, 150.06, 156.51, 162.40, 164.32.

HRMS: *m*/*z* calcd for $C_{59}H_{48}F_2N_2O_2$ 854.3684, found 854.3693.

Anal. Calcd for $C_{59}H_{48}F_2N_2O_2$: C, 82.88; H, 5.66; N, 3.28. Found: C, 83.18; H, 5.51; N, 3.36.

3-[4-(3-Methyl{4′-[3-methyl(phenyl)anilino][1,1′-biphenyl]-4-yl}anilino)phenoxy]propan-1-ol (10-Me)

To a dry 250 mL round bottom flask under argon were added **6-Me** (6.10 g 16.2 mmol), **8-Me** (6.71 g, 16.3 mmol) and toluene (50 mL). The mixture was deoxygenated by bubbling argon through the solution for 10 min, and then $Pd_2(dba)_3$ (0.22 g, 0.25 mmol) and DPPF (0.27 g, 0.5 mmol) were added. After stirring for 10 min, *t*-BuONa (2.0 g, 20 mmol) was added. The temperature of the reaction mixture was raised to 100 °C while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a fritted glass funnel. The solvent was removed under reduced pressure to yield a brown viscous oil. The material was dissolved in THF (30 mL) and a solution of 1 M Bu_4NF in THF was added. The mixture was allowed to stir while being followed by TLC. Upon the disappearance of the TBDMS-protected alcohol, the solution was poured into a 500 mL separatory funnel containing H_2O (100 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by flash chromatography, eluting with a solution of CH_2Cl_2–EtOAc (9:1). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to yield 9.13 g (95%) of the product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.61$ (s, 1 H), 2.06 (quint, $J = 3.5$ Hz, 2 H), 2.65 (d, $J = 5.5$ Hz, 6 H), 3.90 (t, $J = 6.0$ Hz, 2 H), 4.12 (t, $J = 6.5$ Hz, 2 H), 6.80 (d, $J = 7.0$ Hz, 1 H), 6.90 (m, 7 H), 7.04 (t, $J = 7.0$ Hz, 1 H), 7.12 (m, 10 H), 7.27 (m, 2 H), 7.43 (t, $J = 8.5$ Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.44$, 21.49, 31.99, 60.57, 66.02, 115.30, 120.47, 121.61, 122.58, 122.78, 123.06, 123.79, 123.90, 124.06, 124.14, 125.05, 127.13, 127.15, 127.23, 128.95, 129.06, 129.19, 133.75, 134.68, 138.97, 139.09, 140.91, 146.66, 147.11, 147.64, 147.81, 147.88, 155.21.

HRMS: *m*/*z* calcd for $C_{41}H_{38}N_2O_2$: 590.2933, found 590.2933.

Anal. Calcd for $C_{41}H_{38}N_2O_2$: C, 83.36; H, 6.48; N, 4.74. Found: C, 83.35; H, 6.66; N, 4.90.

3-[4-(4-Methoxy{4′-[4-methoxy(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl}anilino)phenoxy]propan-1-ol (10-OMe)

To a dry 250 mL round bottom flask under argon were added **6-OMe** (7.95 g 20.5 mmol), **8-OMe** (9.59 g, 21.6 mmol) and toluene (50 mL). The mixture was deoxygenated and then $Pd_2(dba)_3$ (0.30 g, 0.32 mmol) and DPPF (0.40 g, 0.64 mmol) were added. After stirring for 10 min, *t*-BuONa (1.4 g, 25 mmol) was added The temperature of the reaction mixture was raised to 100 °C while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material the mixture was filtered through a fritted glass funnel. The solvent was removed under reduced pressure to yield a brown viscous oil. The material was dissolved in THF (30 mL) and a 1 M solution of Bu_4NF in THF (20 mL) was added. The mixture was allowed to stir while the reaction was followed by TLC. Upon the disappearance of the TBDMS protected alcohol, the solution was poured into a 500 mL separatory funnel containing H_2O (100 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by flash chromatography, eluting with a solution of CH_2Cl_2–EtOAc (19:1). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 11.27 g (86%) of the product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, acetone-d_6): $\delta = 1.98$ (quint, 6 Hz, 2 H), 2.35 (s, 3 H), 2.86 (s, 1 H), 3.75 (t, $J = 6$ Hz, 2 H), 3.79 (s, 3 H), 3.80 (s, 3 H), 4.11 (t, $J = 6$ Hz, 2 H), 6.82 (t, $J = 6.5$ Hz, 2 H), 6.94 (m, 9 H), 7.00 (d, $J = 8.5$ Hz, 2 H), 7.06 (m, 6 H), 7.15 (t, $J = 8.0$ Hz, 1 H), 7.47 (dd, $J = 3.5$ Hz, 9.0 Hz, 4 H).

^{13}C NMR (125 MHz, acetone-d_6): δ = 20.59, 32.48, 54.80, 64.85, 114.67, 114.76, 115.26, 120.17, 120.43, 122.57, 122.93, 123.54, 126.54, 126.72, 127.28, 128.99, 132.31, 133.79, 138.75, 140.48, 140.64, 140.74, 146.95, 147.78, 148.04, 155.62, 156.12, 156.47.

HRMS: *m*/*z* calcd for $C_{42}H_{40}N_2O_4$: 636.2988, found 636.2992.

Anal Calcd for $C_{42}H_{40}N_2O_4$: C, 79.22; H, 6.33; N, 4.40. Found: C, 79.12; H, 6.15; N, 4.43.

3-[4-(3-Fluoro{4′-[3-fluoro(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl}anilino)phenoxy]propan-1-ol (10-F)

To a 1000 mL round bottom flask, was added **9-F** (18.69, 21.86 mmol), Et_2O (360 mL) and 95% formic acid (190 mL). The solution was stirred for 4 h while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was carefully poured into a separatory funnel containing H_2O (50 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and washed with aq sat. $NaHCO_3$ (5 × 50 mL). The excess solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel, eluting with CH_2Cl_2. The solvent was removed under reduced pressure and the residual solvent was removed in vacuo to afford 5.43 g (41%) of the desired product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, acetone-d_6): δ = 1.98 (quint, 6 Hz, 2 H), 2.26 (s, 3 H), 3.70 (s, 1 H), 3.75 (t, $J = 6$ Hz, 2 H), 4.11 (t, $J = 6$ Hz, 2 H), 6.69 (m, 4 H), 6.80 (m, 2 H), 6.95 (m, 5 H), 7.11 (m, 6 H), 7.22 (m, 3 H), 7.59 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.51, 32.42, 58.11, 64.87, 107.43, 107.57, 107.60, 107.76, 108.25, 108.42, 108.85, 109.04, 115.57, 116.88, 118.14, 122.47, 123.84, 124.72, 124.95, 125.86, 127.31, 127.35, 128.01, 129.45, 130.36, 130.44, 130.46, 130.55, 134.65, 135.27, 139.39, 146.19, 146.43, 146.95, 149.70, 149.77, 149.99, 150.06, 156.70, 162.40, 162.37, 164.32.

HRMS: *m*/*z* calcd for $C_{40}H_{34}F_2N_2O_5$ 613.2667, found 613.2697

Anal. Calcd for $C_{40}H_{34}F_2N_2O_5$: C, 78.41; H, 5.59; N, 4.57. Found: C, 78.20; H, 5.62; N, 4.52.

3-[4-({4′-[2,4-Difluoro(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl}-2,4-difluoroanilino)phenoxy]propan-1-ol (10-F$_2$)

To a dry 250 mL round bottom flask under argon were added **6-F$_2$** (4.52 g 11.49 mmol), **8-F$_2$** (6.21 g, 13.8 mmol) and toluene (50 mL). The mixture was deoxygenated and then $Pd_2(dba)_3$ (0.19 g, 0.2 mmol) and DPPF (0.23 g, 0.4 mmol) were added. After stirring for 10 min, *t*-BuONa (1.4 g, 15 mmol) was added. The temperature of the reaction was raised to 100 °C while the progress of the reaction was monitored by TLC. Upon the disappearance of the starting material, the mixture was filtered through a fritted glass funnel. The solvent was removed under reduced pressure to yield a brown viscous oil. The material was dissolved in THF (30 mL) and a 1 M solution of Bu_4NF in THF (20 mL) was added. The mixture was allowed to stir while the progress of the reaction was followed by TLC. Upon the disappearance of the TBDMS protected alcohol, the solution was poured into a 500 mL separatory funnel containing H_2O (100 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by flash chromatography, eluting with CH_2Cl_2. The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 5.93 g (80%) of the product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.67 (s, 1 H), 2.06 (quint, $J = 6.0$ Hz, 2 H), 3.28 (s, 3 H), 3.87 (t, $J = 6.0$ Hz, 2 H), 4.13 (t, $J = 6.0$ Hz, 2 H), 6.80 (m, 11 H), 7.01 (d, $J = 8.5$ Hz, 2 H), 7.08 (d, $J = 8.5$ Hz, 2 H), 7.19 (m, 3 H), 7.41 (t, $J = 9.0$ Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.46, 31.94, 60.57, 66.04, 105.21, 105.40, 105.61, 111.92, 112.03, 115.24, 119.36, 119.61, 121.85, 122.81, 123.49, 125.78, 127.11, 128.99, 129.91, 130.35, 133.19, 134.45, 139.08, 139.95, 145.90, 146.73, 146.88, 155.26.

HRMS: *m*/*z* calcd for $C_{40}H_{32}FN_2O_2$: 648.2400, found 648.2400.

Anal. Calcd for $C_{40}H_{32}F_4N_2O_2$: C, 74.06; H, 4.97; N, 4.32. Found: C, 73.83; H, 4.81; N, 4.50.

3-[4-(3-Methyl{4′-[3-methyl(phenyl)anilino][1,1′-biphenyl]-4-yl}anilino)phenoxy]propyl 2-Methacrylate (1-Me)

To a dry 250 mL round bottom flask under argon were added **10-Me** (7.72 g, 13.1 mmol), dicyclohexylcarbodiimide (4.20 g, 20.0 mmol), methacrylic acid (1.50 g, 17.0 mmol), and THF (50 mL). The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.2 g, 1.7 mmol) was added. The temperature was allowed to rise to r.t. while the progress of the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was poured into cold water (200 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel, eluting with CH_2Cl_2–hexanes (7:3). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to furnish 8.07 g (94%) of the desired product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.21 (quint, $J = 6.5$ Hz, 2 H), 2.29 (s, 3 H), 2.30 (s, 3 H), 4.10 (t, $J = 6.0$ Hz, 2 H), 4.40 (t, $J = 6.0$ Hz, 2 H), 5.61 (s, 1 H), 6.16 (s, 1 H), 6.83 (d, $J = 7.5$ Hz, 1 H), 6.88 (d, $J = 9.5$ Hz, 3 H), 6.94 (m, 4 H), 7.03 (t, $J = 7.5$ Hz, 1 H), 7.14 (m, 10 H), 7.28 (t, $J = 8.0$ Hz, 2 H), 7.46 (t, $J = 8.0$ Hz, 4 H).

^{13}C NMR (125 Hz, $CDCl_3$): δ = 18.37, 21.44, 28.74, 55.36, 61.56, 64.59, 115.29, 120.46, 121.61, 122.58, 122.77, 123.04, 123.79, 123.89, 124.06, 124.14, 125.05, 125.58, 127.11, 127.15, 127.24, 128.95, 129.05, 129.18, 133.73, 134.68, 136.30, 138.95, 139.09, 140.84, 146.65, 147.14, 147.64, 147.81, 147.90, 155.26, 167.39.

HRMS: *m*/*z* calcd for $C_{45}H_{42}N_2O_3$: 658.3195, found 658.3190.

Anal. Calcd for $C_{45}H_{42}N_2O_3$: C, 82.04; H, 6.43; N, 4.25. Found: C, 82.05; H, 6.40; N, 4.32.

3-[4-(4-Methoxy{4′-4[4-methoxy(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl)anilino)phenoxy]propyl 2-Methacrylate (1-OMe)

To a dry 250 mL round bottom flask under argon were added **10-OMe** (11.22 g, 17.6 mmol), dicyclohexylcarbodiimide (5.09 g, 24.7 mmol), methacrylic acid (1.82 g, 21.1 mmol), and THF (50 mL). The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.2g, 1.7 mmol) was added. The temperature was allowed to raise to r.t. while the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was poured into cold water (200 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel, eluting with CH_2Cl_2. The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to afford 11.21 g (90%) of the desired product as a pale yellow glassy solid.

^{1}H NMR (500 MHz, acetone-d_6): δ = 1.93 (s, 3 H), 2.17 (quint, $J = 6.5$ Hz, 2 H), 2.24 (s, 3 H), 3.8 (d, $J = 5.5$ Hz, 6 H), 4.14 (t, $J = 6.0$ Hz, 2 H), 4.34 (t, $J = 6.0$ Hz, 2 H), 5.63 (s, 1 H), 6.10 (s, 1 H), 6.83 (m, 2 H), 6.93 (m, 9 H), 7.00 (d, $J = 8.5$ Hz, 2 H), 7.08 (m, 6 H), 7.16 (t, $J = 8.0$ Hz, 1 H), 7.49 (dd, $J = 11.5$ Hz, 8.5 Hz, 4 H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ = 18.05, 21.11, 28.65, 55.36, 61.41, 64.72, 114.60, 115.17, 120.25, 122.64, 122.88, 123.69, 125.02, 126.74, 127.28, 127.70, 128.80, 133.78, 136.49, 138.98, 146.93, 156.25, 167.10.

HRMS: *m*/*z* calcd for $C_{46}H_{44}N_2O_5$: 705.3328, found 705.3346.

Anal. Calcd for $C_{46}H_{44}N_2O_5$: C, 78.38; H, 6.29; N, 3.97. Found: C, 78.41; H, 6.12; N, 4.03.

3-[4-(3-Fluoro{4′-[3-fluoro(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl}anilino)phenoxy]propyl 2-Methacrylate (1-F)

To a dry 250 mL round bottom flask under argon were added **10-F** (5.01 g, 8.18 mmol), dicyclohexylcarbodiimide (2.0 g, 9.8 mmol), methacrylic acid (0.9 g, 9.8 mmol), and THF (50 mL). The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.3 g, 2.5 mmol) was added. The temperature was allowed to raise to r.t. while the reaction was followed by TLC. Upon the disappearance of the starting material, the mixture was poured into cold MeOH (200 mL). The white crystals were collected by vacuum filtration and recrystallized from a mixture of THF and MeOH. The white powder was dried under vacuum; yield: 4.75 g (85%).

^{1}H NMR (500 MHz, acetone-d_6): δ = 1.93 (s, 3 H), 2.17 (quint, *J* = 6.5 Hz, 2 H), 2.27 (s, 3 H), 4.15 (t, *J* = 6.0 Hz, 2 H), 4.34 (t, *J* = 6.0 Hz, 2 H), 5.63 (quint, *J* = 2.0 Hz, 1 H), 6.09 (q, *J* = 1 Hz, 1 H), 6.73 (m, 6 H), 6.95 (m, 5 H), 7.12 (m, 6 H), 7.24 (quint, *J* = 6.5 Hz, 3 H), 7.59 (m, 4 H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ = 17.53, 20.48, 61.25, 64.62, 107.46, 107.59, 107.63, 107.79, 108.23, 108.41, 108.81, 109.01. 115.62, 116.89, 118.12, 118.09, 122.47, 123.90, 124.72, 124.96, 125.88, 127.33, 127.35, 127.99, 129.43, 130.38, 130.45, 130.55, 134.71, 135.28, 136.51, 139.41, 139.65, 146.20, 146.42, 146.95, 149.70, 149.79, 150.04, 156.41, 162.40, 164.32, 166.51.

HRMS: *m*/*z* calcd for $C_{44}H_{38}F_4N_2O_3$: 680.2850, found 680.2856.

Anal. Calcd for $C_{44}H_{38}F_2N_2O_3$: C, 77.63; H, 5.63; N, 4.11. Found: C, 77.57; H, 5.46; N, 4.03.

3-[4-{4′-[2,4-difluoro(3-methylphenyl)anilino][1,1′-biphenyl]-4-yl}-2,4-difluoroanilino)phenoxy]propyl 2-Methacrylate (1-F_2)

To a dry 250 mL round bottom flask under argon were **10-F_2** (2.88 g, 14 mmol), methacrylic acid (1.00 g, 11.1 mmol), and THF (50 mL). The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.2 g, 1.7 mmol) was added. The temperature was allowed to raise to r.t. while the reaction was followed by TLC. Upon the disappearance of the starting material the mixture was poured into cold water (200 mL). The product was extracted with Et_2O (3 × 50 mL). The organic layers were combined and the solvent was removed under reduced pressure. The product was purified by flash chromatography on silica gel, eluting with CH_2Cl_2–hexanes (7:3). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to yield 11.21 g (90%) of the desired product as a pale yellow glass.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.96 (s, 3 H), 2.18 (quint, *J* = 6.5 Hz, 2 H), 2.23 (s, 3 H), 4.05 (t, *J* = 6.0 Hz, 2 H), 4.37 (t, *J* = 6.0 Hz, 2 H), 5.58 (s, 1 H), 6.76 (t, *J* = 8.0 Hz, 1 H), 6.87 (m, 11 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 7.23 (m, 3 H), 7.41 (t, *J* = 9.0 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.36, 21.49, 28.71, 61.52, 64.60, 105.21, 105.42, 105.63, 111.95, 112.12, 115.26, 119.39, 119.60, 121.88. 122.84, 123.53, 125.58, 125.85, 127.14, 129.02, 129.88, 130.44, 130.82, 133.17, 134.49, 136.29, 139.09, 139.90, 145.92, 148.79, 146.92, 155.35, 167.36.

HRMS: *m*/*z* calcd for $C_{44}H_{36}F_4N_2O_3$: 716.2662, found 716.2665.

Anal. Calcd for $C_{46}H_{36}F_4N_2O_3$: C, 73.73; H, 5.06; N, 3.91. Found: C, 73.78; H, 5.11; N, 3.96.

3-{4-[(*E*)-3-Methoxy-3-oxoprop-1-enyl]phenoxy}propyl 2-Methacrylate (12)[15]

To a dry 250 mL round bottom flask under argon were added **11** (9.18 g, 39.0 mmol), dicyclohexylcarbodiimide (9.6 g, 46.8 mmol), methacrylic acid (4.02 g, 46.8 mmol), and THF (50 mL). The solution was cooled to 0 °C in an ice-bath and 4-dimethylaminopyridine (0.2 g, 1.7 mmol) was added. The temperature was allowed to increase to r.t. while the reaction was followed by TLC. Upon the disappearance of the starting material the mixture was filtered through a fritted glass funnel. The solid was rinsed with THF (3 × 10 mL) and the solution was transferred to a round bottom flask and the solvent was removed under reduced pressure. The product was purified by flash chromatography over silica gel, eluting with CH_2Cl_2–hexanes (7:3). The solvent was removed under reduced pressure. The residual solvent was removed in vacuo to give 7.81 g (66%) of the desired product as white crystals.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3 H), 2.18 (quint, *J* = 6.0 Hz, 2 H), 3.79 (s, 3 H), 4.09 (t, *J* = 6.5 Hz, 2 H), 4.34 (t, *J* = 6.5 Hz, 2 H), 5.57 (s, 1 H), 6.10 (s, 1 H), 6.30 (d, *J* = 16 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 7.46 (d, *J* = 9.0 Hz, 2 H), 7.64 (d, *J* = 16 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.28, 28.51, 51.56, 61.32, 64.49, 114.73, 115.26, 125.58, 127.15, 129.69, 136.18, 144.44, 160.51, 167.29, 167.72.

Polymer 13-OMe

To a thick-walled glass tube containing argon and a stir bar was added **1-OMe** (2.00 g, 23.04 mmol), **12 (**0.40 g, 1.30 mmol), and AIBN (0.007 g, 0.04 mmol). The tube was again pump-filled with argon and deoxygenated anhyd benzene (10 mL) was added. The tube was sealed and heated at 60 °C for 72 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF, followed by precipitation in MeOH. The process was repeated three times. The product was collected as a white powder by vacuum filtration; yield: 1.90 g (79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (s, 2 H), 1.02 (s, 2 H), 1.26 (s, 1 H), 1.56 (s, 2 H), 1.99 (s, 6H), 2.13 (s, 3 H), 2.19 (s, 6 H), 3.66 (s, 2 H), 3.89 (s, 4 H), 4.07 (s, 4 H), 6.21 (s, *J* = 1.5 Hz, 1 H), 6.88 (m, 33 H), 7.16 (s, 3 H), 7.27 (s, 8 H) 7.54, (d, *J* = 1.5 Hz, 1 H).

Anal. Calcd: C, 79.54; H, 6.46; N, 3.54. Found: C, 79.18; H, 6.27; N, 3.45.

Polymer 13-Me

To a thick-walled glass tube containing argon and a stir bar was added **1-Me** (1.20 g, 1.70 mmol), **12 (**0.22 g, 0.73 mmol) and AIBN (0.0039 g, 0.024 mmol). The tube was pump-filled with argon and deoxygenated anhyd benzene (10 mL) was added. The tube was sealed and heated at 60 °C for 82 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF followed by reprecipitation in MeOH. The process was repeated three times. The product isolated as a white powder was collected vacuum filtration; yield: 0.95 g (67%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (s, 3 H), 1.02 (s, 3 H), 1.26 (s, 1 H), 1.57 (s, 5 H), 1.98 (s, 8H), 2.18 (s, 5 H), 3.69 (m, 15 H), 3.86 (m, 9 H), 6.22 (d, *J* = 15.5 Hz 1 H), 6.83 (m, 4 H), 7.42 (m, 10 H), 7.55 (d, *J* = 16.0 Hz, 1 H).

Anal. Calcd: C, 76.63; H, 6.34; N, 3.35. Found: C, 76.33; H, 6.36; N, 3.38.

Polymer 13-F

To a thick-walled glass tube containing argon and a stir bar was added **1-F** (1.50 g, 2.2 mmol), **12** (0.29 g, 0.94 mmol) and AIBN (0.005 g, 0.031 mmol). The tube was pump-filled with argon and deoxygenated anhyd benzene (10 mL) was added. The tube was sealed and heated at 60 °C for 72 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF and then reprecipitated from MeOH. The process was repeated three times. The product isolated as a white powder was collected by vacuum filtration; yield: 1.41 g (79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89–2.21 (br overlapping peaks 36 H), 3.67–4.09 (br overlapping peaks 18 H), 6.22 (d, *J* = 15.5 Hz, 1 H), 6.69–7.30 (br overlapping peaks, 55 H), 7.56 (d, *J* = 15.5 Hz, 1 H).

Anal. Calcd: C, 75.96; H, 5.79; N, 3.44. Found: C, 75.68; H, 5.57; N, 3.39.

Polymer (13-F_2)

To a thick-walled glass tube containing argon and a stir bar was added **1-F_2** (1.70 g, 2.37 mmol), **12** (0.32 g, 1.02 mmol) and AIBN (0.0056 g, 0.034 mmol). The tube was again pump filled with argon and deoxygenated anhyd benzene (10 mL) was added. The tube was sealed and heated at 60 °C for 82 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF followed by precipitation from MeOH. The process was repeated twice followed by reprecipitation from THF into MeOH. The product was collected as a white powder by vacuum filtration; yield: 1.82 g (90%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (s, 3 H), 0.99 (s, 3 H), 1.56 (s, 2 H), 1.98 (s, 9 H), 2.20 (s, 6H), 3.67 (s, 3 H), 3.88 (s, 6 H), 4.05 (s, 6 H), 6.20 (d, *J* = 1.5 Hz, 1 H), 6.78 (s, 23 H), 6.92 (s, 8 H), 7.07 (s, 6 H), 7.27 (s, 11 H), 7.54 (d, *J* = 1.5 Hz, 1 H).

Anal. Calcd: C, 72.68; H, 5.31; N, 3.29. Found: C, 72.43; H, 5.26; N, 3.29.

Polymer 14

To a thick-walled glass tube containing argon and a stir bar was added **12 (**0.50 g, 1.64 mmol) and AIBN (0.0021 g, 0.0014 mmol). The tube was pump-filled with argon and deoxygenated anhyd benzene (10 mL) was added. The tube was sealed and heated at 60 °C for 82 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF and then precipitated from MeOH. The process was repeated twice followed by reprecipitation in acetone from THF. The product was collected as a white powder by vacuum filtration; yield: 0.42 g (84%).

^{1}H NMR (500 MHz, ($CDCl_3$): δ = 0.84 (m, 2 H), 1.88 (m, 3 H), 1.99 (s, 3 H), 3.76 (s, 3 H), 3.94 (s, 2 H), 4.04 (s, 2 H), 6.25 (d, *J* = 27 Hz 1 H), 6.81 (d, *J* = 13.0 Hz, 4 H), 7.39 (d, *J* = 13.5 Hz, 2 H), 7.58 (d, *J* = 26.0 Hz, 1 H).

Anal. Calcd: C, 67.09; H, 6.62. Found: C, 66.81; H, 6.40.

Polymer 15-OMe

To a thick-walled glass tube containing argon and a stir bar was added **1-OMe** (1.00 g, 1.41 mmol) and AIBN (0.0023 g, 0.0014 mmol). The tube was pump-filled with argon and deoxygenated anhyd benzene (10 mL). The tube was sealed and heated at 60 °C for 82 h. The reaction mixture was allowed to cool and was poured into MeOH (100 mL). The white solid was collected by vacuum filtration and was dissolved in THF and then precipitated in MeOH. The process was repeated twice followed by reprecipitation in acetone from THF. The product was collected as a white powder by vacuum filtration; yield: 0.80 g (80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (s, 2 H), 1.65 (s, 1 H), 1.99 (s, 3 H), 2.19 (s, 3 H), 3.62 (s, 3H), 3.71 (s, 3 H), 3.90 (m, 4 H), 6.83 (m, 20 H), 7.02 (m, 4 H).

^{13}C NMR (125 MHz, C_4D_8O): δ = 21.64, 55.67, 115.54, 116.16, 121.19, 121.89, 123.63, 123.70, 124.53, 127.36, 127.66, 128.07, 129.75, 133.63, 134.94, 139.55, 141.62, 141.83, 141.99, 147.88, 148.58, 149.11, 155.98, 157.00, 157.37.

Anal. Calcd: C, 78.38; H, 6.29; N, 3.97. Found: C, 78.03; H, 6.30; N, 4.06.

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References

(1) Adachi, C.; Nagai, K.; Tamoto, N. *App. Phys. Lett.* **1995**, *66*, 2679.

(2) Tang, C. W.; VanSlyke, S. A. *App. Phys. Lett.* **1987**, *51*, 913.

(3) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burna, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(4) Bellmann, E.; Shaheen, S. E.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1999**, *11*, 399.

(5) Burrows, P. E.; Gu, G.; Bulovic, V.; Shen, Z.; Forrest, S. R.; Thompson, M. E. *IEEE Trans. Electron Devices* **1997**, *44*, 1188.

(6) Bulovic, V.; Gu, G.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Nature* **1996**, *318*, 29.

(7) Allcock, H. R. *Chem. Mater.* **1994**, *6*, 1476.

(8) Li, X.-C.; Yong, T.-M.; Gruner, J.; Holmes, A. B.; Moratti, S. C.; Cacialli, F.; Friend, R. H. *Synth. Met.* **1997**, *84*, 437.

(9) Bayerl, M. S.; Braig, T.; Nuyken, O.; Muller, D. C.; Grob, M.; Meerholz, K. *Macromol. Rapid Commun.* **1999**, *20*, 224.

(10) Li, W.; Wang, Q.; Cui, J.; Chou, H.; Shaheen, S. E.; Jabbour, G. E.; Anderson, J.; Lee, P.; Kippelen, B.; Peyghambarian, N.; Armstrong, N. R.; Marks, T. J. *Adv. Mater.* **1999**, *11*, 730.

(11) Langer, E. M.; Liberti, P. *Polym. Commun.* **1991**, *32*, 453.

(12) Watanabe, S.; Harachima, S.; Tsukada, N. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *22*, 1033.

(13) Rami Reddy, A. V.; Subramanian, K.; Krishnasamy, V.; Ravichandran, J. *Eur. Polym. J.* **1996**, *32*, 916.

(14) Subramanian, K.; Krishnasamy, V.; Nanjundan, S.; Rami Reddy, A. V. *Eur. Polym. J.* **2000**, *36*, 2343.

(15) Zhang, Y. D.; Hreha, R. D.; Marder, S. R.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N. *J. Mater. Chem.* **2002**, *12*, 1703.

(16) Hartwig, J. F. *Angew. Chem. Int. Ed.* **1998**, *37*, 2046.

(17) Hu, N. X.; Ong, B. S.; Xie, S.; Popovic, Z. D.; Hor, A. M. Eur. Pat. Appl. 827367, **1998**; *Chem. Abstr.* **1998**, *128*, 223711.

(18) Hansen, H. C.; Olsson, R.; Croston, G.; Andersson, C. M. *Bioorg. Med. Chem. Lett.* **2000**, *21*, 2435.

(19) Hsieh, C. J.; Wu, S. H.; Hsiue, G. H.; Hsu, C. S.; Chain, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1077.

(20) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.

(21) Goodbrand, H. B.; Hu, N. X. *J. Org. Chem.* **1999**, *64*, 670.