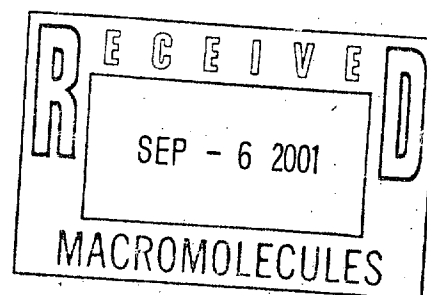


Highly Fluorescent Poly(arylene ethynylene)s Containing Quinoline and 3-Alkylthiophene

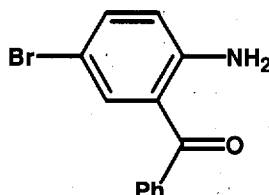
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Supporting Information



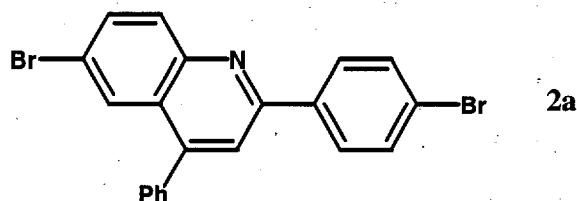
MONOMERS SYNTHESIS



1

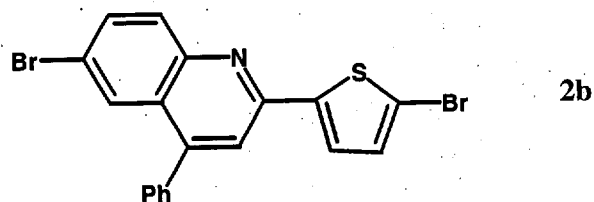
Synthesis of 5-bromo-2-aminobenzophenone (1). In an Erlenmeyer, 2-aminobenzophenone (5g, 25.3 mmol) was added into 50 mL of CHCl_3 . Then, a freshly prepared solution of tetrabutylammonium tribromide in 150 mL of CHCl_3 was quickly added under good agitation at room temperature. The mixture was stirred overnight. Under vigorous stirring, 200 mL of a 5% sodium thiosulfate solution was added. The mixture was maintained under vigorous stirring for 30 minutes. The CHCl_3 layer was separated and washed twice with 200 mL of water. After evaporation, the oil residue was worked up with 200 mL of diethylether, and washed with water, dried over sodium sulfate, filtered and dried. A flash chromatography (silica gel) with diethylether as eluent

afforded 6.5 g (93% yield) of **1** as a yellow powder. $^1\text{H-NMR}$ (200 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 7.65 (2H, d, $^3J_{\text{HH}} = 8.5$ Hz); 7.55 (s, 1H) ; 7.50 (t, 1H, $^3J_{\text{HH}} = 8.2$ Hz); 7.37 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz); 6.66 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz); 6.0 (s, 2H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 198.5, 150.2, 139.7, 137.3, 136.6, 132.0, 128.8, 119.8, 119.3, 118.9. FT-IR (KBr, cm^{-1}) : 3417 $\nu_{(\text{N-H asymmetric})}$; 3311 $\nu_{(\text{N-H symmetric})}$ 1613 $\nu_{(\text{C=O})}$.Elemental analysis (%) calculated for $\text{C}_{13}\text{H}_{10}\text{BrNO}$: C, 55.98; H, 3.45; N, 5.09. Found: C, 56.55; H, 3.65; N, 5.07

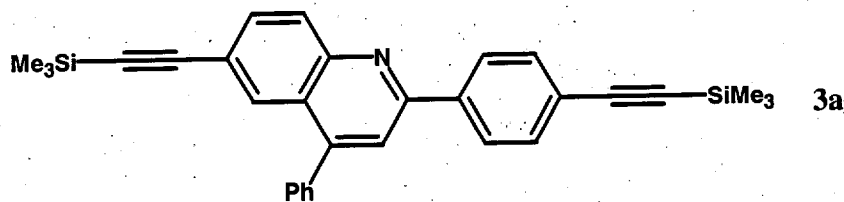


Synthesis of 6-bromo-2-(p-bromophenyl)-4-phenylquinoline (2a). In a dry two-neck flask equipped with an argon inlet, 15 g of diphenylphosphate (DPP) was mixed with **1** (4.0 g, 14.4 mmol) and 4-acetyl bromobenzene (3.2g, 16 mmol) and 3 mL of toluene. The temperature was gradually increased until 120°C and held for 24 hours. After cooling, 400 mL of CH_2Cl_2 was added to the reaction mixture followed by 400 mL NaOH aqueous 10% solution. After decantation, the dichloromethane layer was washed five times with 500 mL of water, dried over sodium sulfate, filtered and dried. An off-white crude product was obtained and purified by re-crystallization in MeOH/THF (9v/1v). This procedure afforded 7.3 g of white product **2a** (86% yield). $^1\text{H-NMR}$ (200 MHz, CD_2Cl_2 , 298K) $\delta(\text{ppm})$: 7.56 (m, 5H); 7.66 (m, 2H); 7.80 (m, 2H); 8.08(m, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2 , 298K) $\delta(\text{ppm})$: 156.2, 149.0, 147.7, 138.4, 137.9, 132.6, 132.3, 129.9, 129.5, 129.4, 128.3, 127.5, 124.7, 121.4, 120.9, 120.3. FT-IR (KBr, cm^{-1}) : 1586 $\nu_{(\text{C=N})}$.

Elemental analysis (%) calculated for $C_{21}H_{13}Br_2N$: C , 57.44; H, 2.98; N, 3.19. Found: C, 57.39; H, 2.92; N, 3.11.

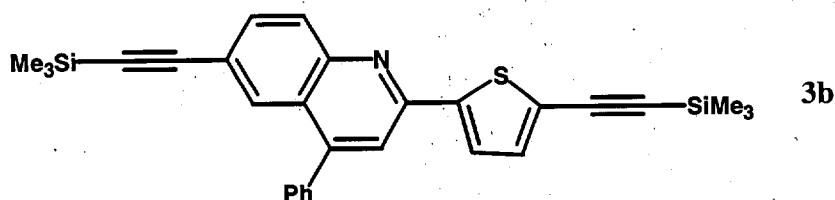


Synthesis of 6-bromo-2-(5-bromothiophene)-4-phenylquinoline (2b). A similar procedure as described for **2a** was used with 2-acetyl-5-bromothiophene (3.34g, 16.3 mmol) 2-aminobenzophenone (3g, 18.7 mmol), 15 g of DPP, and 3 mL of toluene. An off-white product was obtained in 80% yield (5.2g). 1H -NMR (200 MHz, $CDCl_3$, 298K) δ (ppm) : 7.13-8.20 (m, Ar) ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ (ppm): 151.7, 148.9, 147.6, 137.7, 133.7, 131.7, 131.5, 129.8, 129.3, 128.9, 128.3, 127.6, 126.5, 120.8, 118.1, 117.2. FT-IR (KBr, cm^{-1}) : 1580 $\nu_{(C=N)}$. Elemental analysis (%) calculated for $C_{19}H_{11}Br_2NS$: C, 51.26; H, 2.49; N, 3.15. Found : C, 49.04; H, 2.38; N, 3.13.



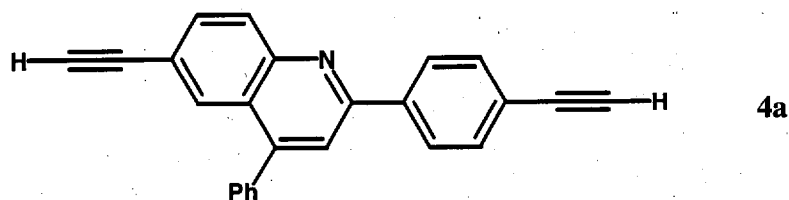
Synthesis of 4-phenyl-6-trimethylsilylethynyl-2-trimethylsilylethynylphenyl quinoline (3a). In a Schlenk type flask, **2a** (4.7g, 10.7 mmol) was introduced and degassed. Then, 20 mL and 30 mL of degassed diisopropylamine and THF respectively

were added under argon. Trimethylsilylacetylene (3.8 mL, 25 mmol) was added and followed by $\text{PdCl}_2(\text{PPh}_3)_2$ (150mg, 0.21mmol) and CuI (40mg, 0.21mmol). The mixture was heated at 60°C for 24 hours. After cooling, the solvents were removed under vacuum. Then, 300 mL of ether was added and washed with water (500 mL) twice. The ether layer was dried with sodium sulfate, filtered and dried. This procedure afforded **3a** as a crude brown product with 95% yield (4.8g). $^1\text{H-NMR}$ (200 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 8.19 (m, 3H); 8.05(m, 1H) ; 7.90(s, 1H); 7.82 (m,1H); 7.59 (m, 5H); 7.67 (m,2H); 0.34 (s, 9H) ;0.31 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 156.6, 149.5, 148.8, 139.4, 138.4, 133.2, 132.9, 130.6, 130.0, 129.9, 129.2, 129.1, 127.7, 125.9, 124.8, 121.7, 120.97, 108.5, 105.4, 96.5, 96.3. FT-IR (KBr, cm^{-1}) : 1583, $\nu(\text{C}=\text{N})$; 2145, $\nu(\text{C}\equiv\text{C})$; 2952 $\nu(\text{CH}, \text{SiMe}_3)$. Elemental analysis (%) calculated for $\text{C}_{31}\text{H}_{31}\text{NSi}_2$: C, 78.59; H, 6.60; N, 2.96. Found : C, 77.74; H, 6.66; N, 2.69.



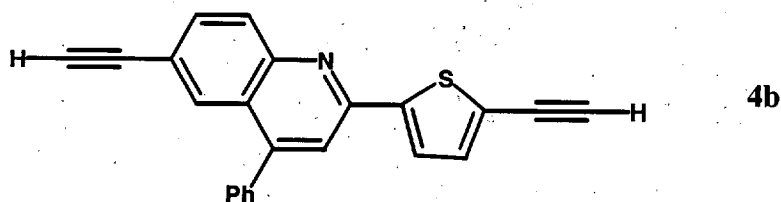
Synthesis of 4-phenyl-6-trimethylsilylethynyl-2-trimethylsilylethynylphenyl quinoline (3b). A similar procedure as described above for **3a** was used with **2b** (5.5g, 12.4 mmol), trimethylsilylacetylene TMSA (5.2mL, 37 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (130mg, 0.18 mmol), CuI (35mg, 0.18 mmol), 50 mL of diisopropylamine, and 30 mL of THF.

The procedure afforded **3b** as a crude brown product with 89% yield (5.2 g). ^1H -NMR (200 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 7.5-8.0 (m, 11H); 0.31 (s, 9H); 0.29 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 152.0, 149.4, 148.6, 138.1, 134.1, 133.4, 130.1, 129.9, 129.3, 129.2, 126.7, 126.3, 126.1, 121.5, 118.7, 100.4, 98.2, 96.30, 0.247. FT-IR (KBr, cm^{-1}) : 1586 $\nu_{(\text{C}=\text{N})}$; 2142, $\nu_{(\text{C}\equiv\text{C})}$; 2955, $\nu_{(\text{CH}, \text{SiMe}_3)}$. Elemental analysis (%) calculated for $\text{C}_{29}\text{H}_{29}\text{NSSi}_2$: C, 72.60; H, 6.09; N, 2.92; S, 6.68. Found : C, 72.12; H, 5.84; N, 2.88; S, 6.38.



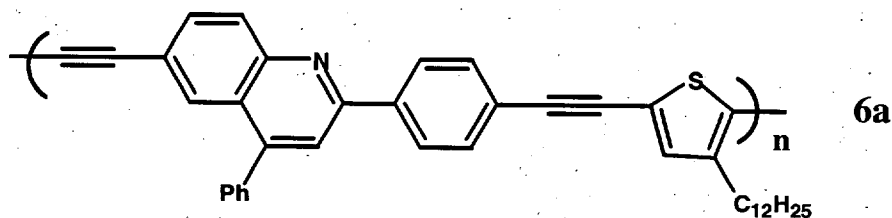
Synthesis of 6-ethynyl-2-(p-ethynylphenyl)-4-phenylquinoline (4a). To a solution of **3a** (4g, 8.5 mmol) in THF (25 mL) and MeOH (25 mL) was added dropwise a solution of NaOH (1g, 25 mmol) in 25 mL of water. The mixture was stirred at room temperature for one hour. After evaporation of THF and MeOH under vacuum, 300 mL of CH_2Cl_2 was added and the product was extracted and washed with water several times. The dichloromethane was dried over sodium sulfate, filtered and dried to afford a crude brown product which was chromatographed with silica gel and ether as eluent. A pale brown product was obtained with 82 % yield (2.2g). ^1H NMR (200 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 7.5-8.3 (m, 13H); 3.24 (s, 1H); 3.20 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3 , 298K)

$\delta(\text{ppm})$: 156.8, 149.6, 148.9, 139.8, 138.2, 133.1, 132.9, 131.3, 130.7, 130.5, 129.3, 129.2, 127.8, 125.9, 123.8, 120.7, 120.1, 8, 84.0, 83.9, 79.27, 78.92. FT-IR (KBr, cm^{-1}): 1588, $\nu_{(\text{C}=\text{N})}$, 2095 $\nu_{(\text{C}=\text{C})}$; 3297 $\nu_{(\text{C}=\text{H})}$. Elemental analysis (%) calculated for $\text{C}_{25}\text{H}_{15}\text{N}$: C, 91.16; H, 4.59; N, 4.25. Found: C, 90.83; H, 5.06; N, 4.06. MS (EI): m/z 330 (M^+).

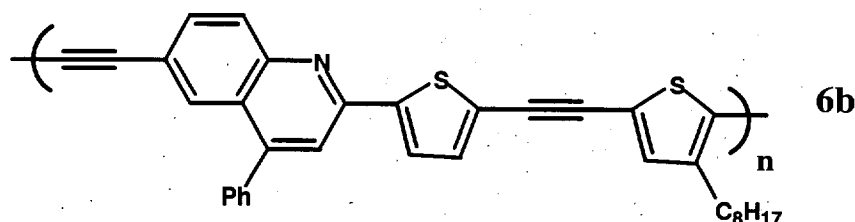


Synthesis of 6-ethynyl-2-(5-ethynylthiophene)-4-phenylquinoline (4b). A similar procedure as described above for **4a** was used for **3b** (3g, 6.4 mmol) in 30 mL THF, 30 mL MeOH and NaOH (0.5 g, 12.5 mmol). A yellow product was obtained, 76 % yield (1.6 g). ^1H -NMR (200 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 7.30-8.0 (m, 13H); 3.52 (s, 1H); 3.2(s, 1H). ^{13}C -NMR (125 MHz, CDCl_3 , 298K) $\delta(\text{ppm})$: 152.0, 149.4, 148.7, 146.9, 137.9, 134.6, 133.1, 130.5, 130.3, 129.9, 127.2 126.1, 126.0, 125.5, 120.5, 118.6, 84.0, 83.5, 79.0, 78.1. FT-IR (KBr, cm^{-1}) : 1588, $\nu_{(\text{C}=\text{N})}$; 2095, $\nu_{(\text{C}=\text{C})}$; 3297, $\nu_{(\text{C}=\text{H})}$. Elemental analysis (%) calculated for $\text{C}_{23}\text{H}_{13}\text{NS}$ (Calc., %) C, 82.36; H, 3.91; N, 4.18; S, 9.56. Found: C, 83.56; H, 4.0 3; N, 3.82; S, 8.84. MS(EI): m/z 336 (M^+).

POLYMER SYNTHESIS



Synthesis of polymer 6a (PQEPDT). Under an atmosphere of argon, degassed diisopropylamine/THF (10 mL/10 mL) was added to a 50 mL Schlenk flask containing **4a** (320 mg, 0.97 mmol) and **5a** (397 mg, 0.97 mmol), CuI (8 mg, 0.04 mmol) and PdCl₂(PPh₃)₂ (30 mg, 0.04 mmol). The mixture was heated at 60°C for 72 hours, cooled and then the solvents were removed. The residue was reprecipitated from THF into methanol, washed with hot methanol and *n*-hexane. A reddish powder was obtained with 83 % yield. ¹H-NMR (200 MHz, tetrachloroethane-*d*₄, 298K) δ(ppm) : 0.90 (s, 3H, CH₃), 1.30 (s, 12H, CH₂), 1.65 (s, 8H, CH₂), 2.5-2.7 (m, 2H, Th-CH₂), 7.6-7.84 (m, Ar-H, Th-H). FT-IR (KBr, cm⁻¹): 2919 ν_(CH, CH₃), 2805 ν_(CH, CH₂), 1584 ν_(C=N), 2183 ν_(C≡C). Anal. Calc. for C₄₂H₄₃NS: C, 84.93; H, 7.13; N, 2.42; found: C, 77.98; H, 7.27; N, 2.41. GPC (Pst standards, Toluene, 30°C): *M_n*, 5150; *M_w*, 9725; *M_z*, 17700.



Synthesis of 6b (PQETOT). By using a similar procedure, **6b** was obtained starting from **4b** (324 mg, 0.968 mmol) and **5b** (342 mg, 0.968 mmol), PdCl₂(PPh₃)₂ (27mg, 0.04 mmol) and CuI (7 mg, 0.04 mmol). A yellow-brown powder was obtained with 78 % yield. ¹H-NMR (200 MHz, Tetrachloroethane-*d*₄, 298K) δ(ppm) : 0.89 (s, 3H, CH₃), 1.35 (s, 8H, CH₂), 1.65 (s, 4H, CH₂), 2.6-2.8 (m, 2H, CH₂-Th), 7.1-8.3 (m, 11H, Ar-H,

Th-H). FT-IR (KBr, cm^{-1}): 2919 $\nu_{(\text{CH}, \text{CH}_3)}$, 2850 $\nu_{(\text{CH}, \text{CH}_2)}$, 1584 $\nu_{(\text{C}=\text{N})}$, 2188 $\nu_{(\text{C}\equiv\text{C})}$. Anal. calc. for $\text{C}_{36}\text{H}_{33}\text{NS}_2$: C, 79.51; H, 6.12; N, 2.58; found C, 79.55; H, 6.07; N, 2.22. GPC (Pst standards, Toluene, 30°C): M_n , 7500; M_w , 14600; M_z , 23300.

General Methods

FT-IR spectra were recorded KBr pellets on a Perkin Elmer spectrophotometer. A Bruker DPX 200 instrument at 200 MHz was used for obtaining NMR measurements. Deuterated CDCl_3 , CD_2Cl_2 , (1, 1', 2, 2')-tetrachloroethane were used as solvents. All chemical shifts were listed in ppm downfield from tetramethylsilane or the deuterated solvents for ^{13}C NMR. GPC analysis of the polymers was performed on a Waters 150C (64/25) equipped with AM GPC columns Gel (1000 Å+500 Å+100 Å) using toluene as the elution solvent. DSC analysis was carried out on a TA Instrument at a heating rate of 10°C/min and TGA analysis was done on TA Instrument at a heating rate of 10°C/min under nitrogen gas. UV-Vis spectra were recorded on a Perkin Elmer UV/VIS/NIR Lambda 900 and photoluminescence spectra were obtained using a SPEX Fluorolog fluorimeter (model 1680). Polymer thin film spectra were recorded by using a front face 22.5° detection. Films were spin coated on a microscope cover glass (20x20 mm) from a 5 mg/mL solution of polymer in a THF/ Toluene mixture (1v/1v). Quantum yield of THF solutions were measured relative to dichloroanthracene in hexane as a standards ($\phi = 0.54$ at 365 nm). Quantum yields of polymers thin films were determined relative to a film of 10^{-3}M 9,10-diphenylanthracene in poly(methylmethacrylate) ($\phi = 0.83$). All solvents were spectral grade. Silica Gel was purchased from Aldrich (Davisil, grade 633, 200-425 Mesh 60 Å). All commercially available reagents were used without further purification.

Highly Fluorescent Poly(arylene ethynylene)s Containing Quinoline and 3-Alkylthiophene

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351750, University of Washington, Seattle, Washington, 98195-1750.

Supporting Information

List of figures

Figure S1. Cyclic voltamograms of the reduction and oxidation of the polymers **6a** and **6b**.

Figure S2. Thermograms analysis of the polymers **6a** and **6b**.

Figure S3. FT-IR spectra of the polymers **6a** and **6b**.

Table 1. Properties of polymers

Polymer	Yield (%)	M_n^a	M_w^a	M_z^a	T_o (°C) ^{b)}	$\lambda_{\max}^{\text{abs}}$ (nm)	Log (ϵ)	$\lambda_{\max}^{\text{em}}$ (nm)	$\lambda_{\max}^{\text{abs c)}$ (nm)	$\lambda_{\max}^{\text{em c)}$ (nm)
PQEPDT	83	5150	9725	17700	200	430	4.1	508	449	605
PQETOT	78	7500	14600	23300	250	412	4.5	470	424	560

^{a)} Estimated from GPC (Toluene, Pst). ^{b)} Onset temperature of weight loss; heating rate of 10 °C/min under N₂. ^{c)} Thin film.

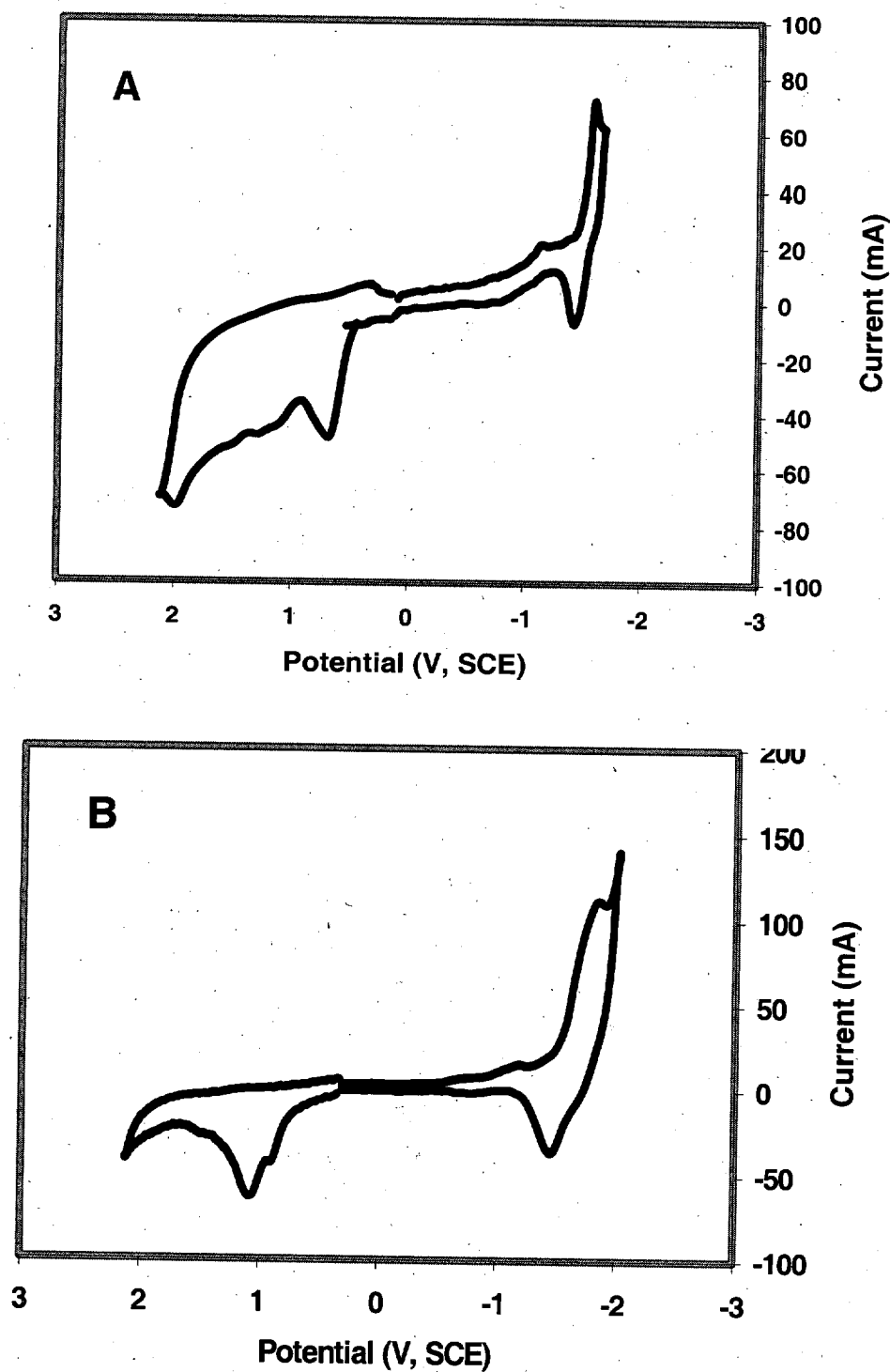
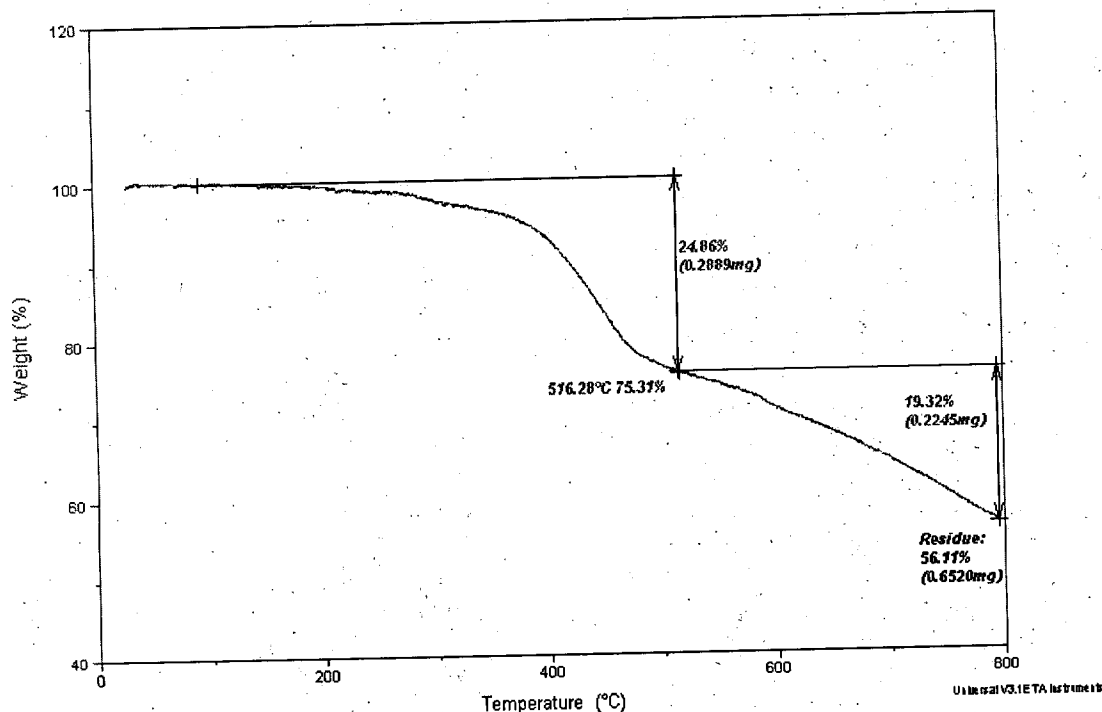


Figure S1. Cyclic voltammograms of **6a** (PQEPDT) (B, bottom) and **6b** (PQETOT) (A, top) at a scan rate of 40 mV/sec in 0.1 M TBAPF₆ / acetonitrile

Sample: UW C8TQ1
Size: 1.1620 mg
Method: Ramp

TGA

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Instrument: TGA Q500 V2.27 Build 112



Sample: UW C12BQ
Size: 2.4460 mg
Method: Ramp

TGA

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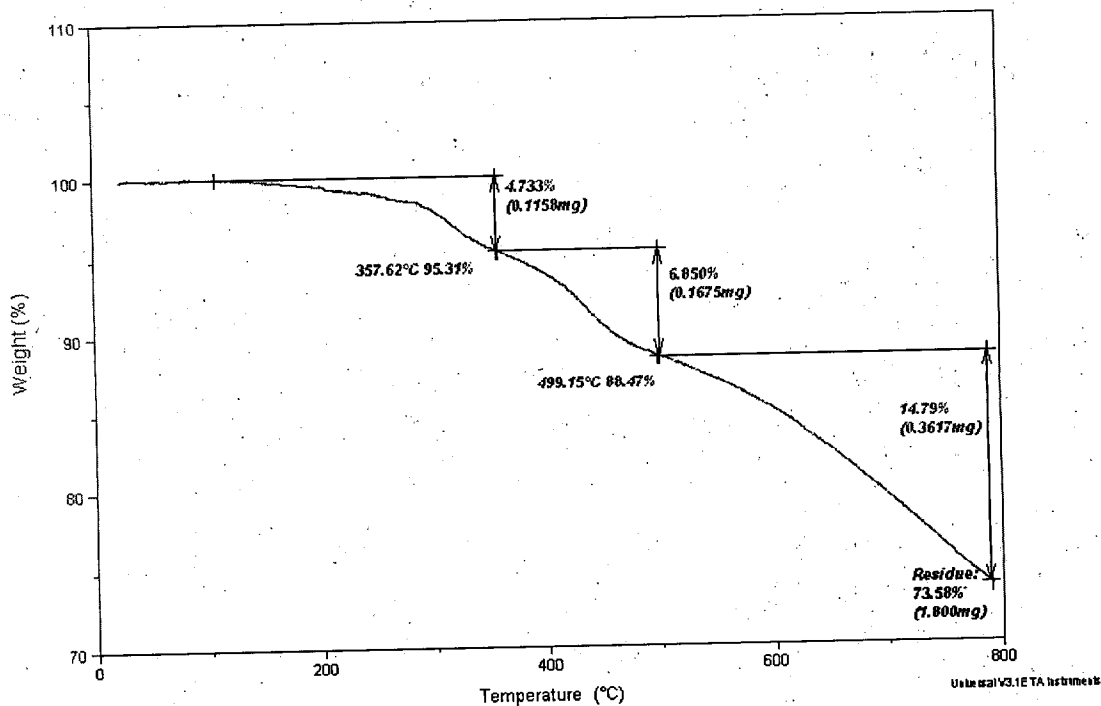


Figure S2- Thermograms analysis (TGA) of (A, Top) PQETOT (6b) and (B, Bottom) PQEPDT (6a)

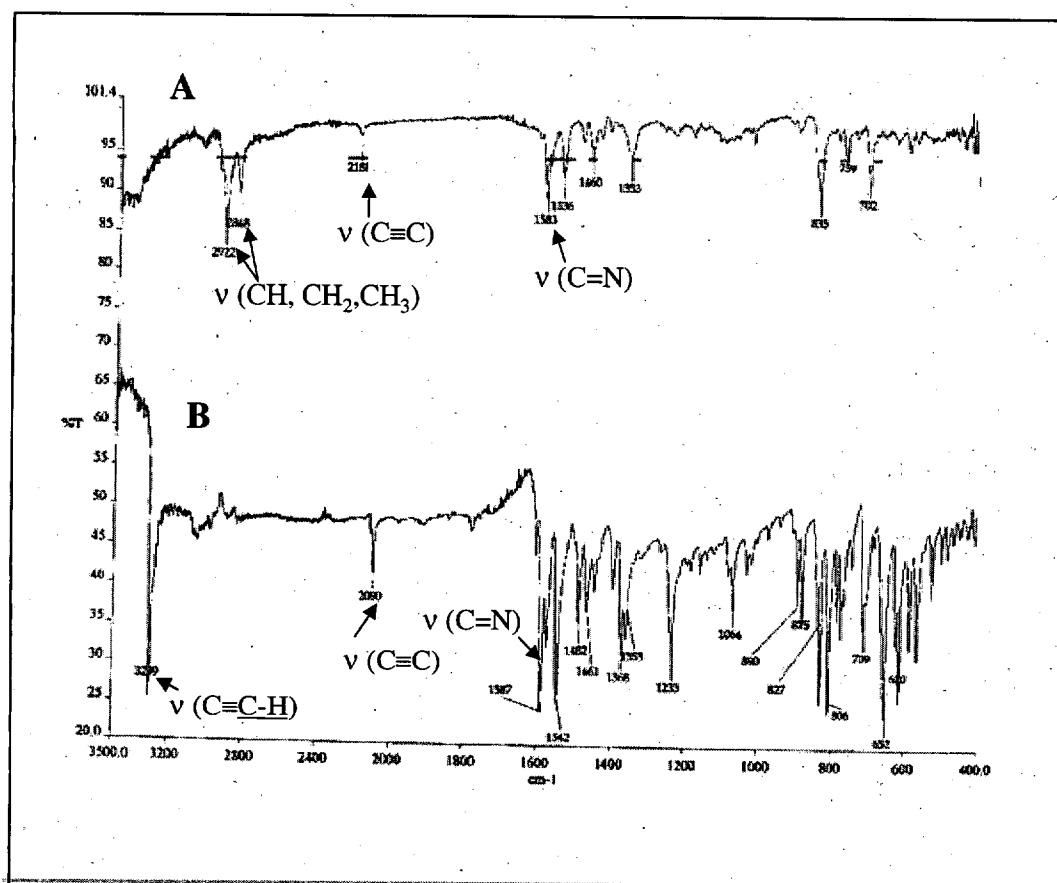


Figure S3. FT-IR spectra of **6b** (A, top) and **4b** (B, bottom).