Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Design of Triphenylamine Appended Anthracene Derivatives: Electro-polymerization and their Electro-chromic Behaviours

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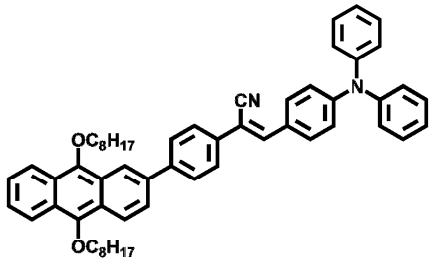
1. Synthesis of all monomers:

2. ***4-N,N-diphenylaminophenyl-2-(4-(9,10-bis(octyloxy)anthracen-6-yl)phenyl)acrylonitrile (2-TPACNANT):***

Dry and degassed EtOH (8 mL) and 2 M aqueous Na_2CO_3 (16 mL) were added to the solution of compound **1** (503.28 mg, 1.01 mmol), compound **B** (513.55 mg, 1.00 mmol) and $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) in 32 mL toluene under nitrogen atmosphere. After being refluxed at 110^0C for 48 h, the mixture was poured into water (100 mL). The organic layer was extracted with chloroform (3×40 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/$CHCl_3$ (v:v, 6:4) to afford compound **2-TPACNANT** as a yellow solid (510 mg, 63%).

^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 1H), 8.38 (d, 1H), 8.30 (d, 1H), 7.85 (d, 2H), 7.74-7.83 (m, 4H), 7.51 (s,1H), 7.49 (d, 2H), 7.33 (t, 4H), 7.18 (d, 3H7.12-7.15 (m, 3H), 7.06-7.12 (m, 2H), 4.20 (t, 4H), 2.04-2.09 (m, 4H), 1.66-1.71 (m, 4H), 1.32-1.49(m, 20H), 0.89-0.93 (m, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 150.20, 148.16, 147.75 146.79, 146.71, 141.50, 136.51, 134.31, 131.41, 130.88, 129.74,129.68, 129.63, 127.99, 127.91, 126.66, 126.37, 125.90, 125.68, 125.52, 125.45, 124.82, 124.57, 124.52, 124.49, 123.92, 122.99, 122.92. 121.08, 120.56, 118.86,107.49, 32.03, 30.90, 30.86, 29.76, 26.44, 22.86, 14.26; MALDI-TOF HRMS: **805.85** [M^+] (calcd for **$C_{57}H_{60}N_2O_2$** : **805.10**).



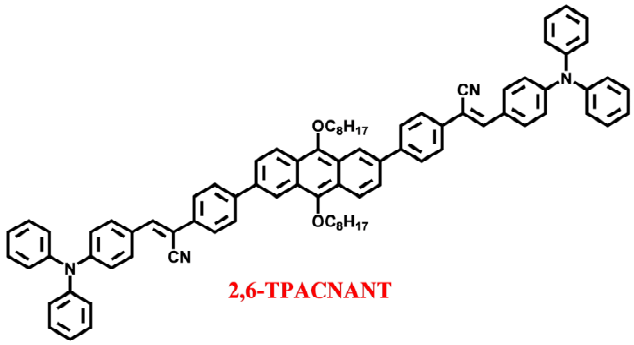
2-TPACNANT

3. **2,6-bis-[4-(N,N-diphenylamino)phenyl]-acrylonitrile-*(9,10-bis(octyloxy)anthracene***

(2,6-TPACNANT):

Dry and degassed EtOH (4 mL) and 2 M aqueous Na_2CO_3 (8 mL) were added to the solution of compound **1** (464 mg, 0.93 mmol), compound **A** (272 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in 16 mL toluene under nitrogen atmosphere. After being refluxed at 110^0C for 48 h, the mixture was poured into water (100 mL) and the organic layer was extracted with chloroform (3×40 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/$CHCl_3$ (v:v, 6:4) to afford compound **2,6-TPACNANT** as a yellow solid (280 mg, 51%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 2H), 8.39 (d, 2H), 7.86 (d, 4H), 7.78-7.83 (m, 8H), 7.52 (s, 2H), 7.32 (t, 8H), 7.11-7.7.18 (m, 12H), 7.07 (d, 4H), 4.25 (t, 4H), 2.07-2.10 (m, 4H), 1.60-1.73 (m, 4H), 1.32-1.49(m, 20H), 0.89-

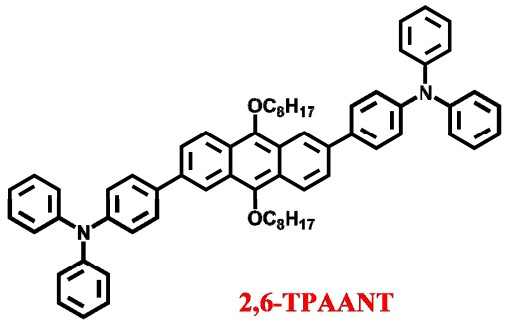
0.93 (m, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 150.20, 148.16, 147.75 146.79, 146.71, 141.50, 136.51, 134.31, 131.41, 130.88, 129.74,129.68, 129.63, 127.99, 127.91, 126.66, 126.37, 125.90, 125.68, 125.52, 125.45, 124.82, 124.57, 124.52, 124.49, 123.92, 122.99, 122.92. 121.08, 120.56, 118.86,107.49, 32.03, 30.90, 30.86, 29.76, 26.44, 22.86, 14.26; MALDI-TOF HRMS: **1176.52** [M^+] (calcd for **$C_{84}H_{78}N_2O_2$** : **1175.54**).



2,6-TPACNANT

4. ***2,6-bis-[4-(N,N-diphenylamino)phenyl]-(9,10-bis(octyloxy)anthracene (2,6-TPAANT):***

Dry and degassed EtOH (8 mL) and 2 M aqueous Na_2CO_3 (16 mL) were added to the solution of compound **2** (560 mg, 1.5 mmol), compound **A** (355 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (34 mg, 0.03 mmol) in 32 mL toluene under nitrogen atmosphere. After being refluxed at 110^{0}C for 48 h, the mixture was poured into water (100 mL) and the organic layer was extracted with chloroform (3×40 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/$CHCI_3$ (v:v, 6:4) to afford compound **2,6-TPACNANT** as a bright yellow solid (344 mg, 62%).
^{1}H-NMR ($CDCl_3$, ppm): δ 8.45 (s, 2H), 8.33 (d, 2H), 7.76 (d, 2H), 7.69 (d, 4H), 7.31 (t, 8H), 7.17-7.21 (m,12H), 7.06 (t, 4H), 4.21 (t, 4H), 2.05-2.08 (m, 4H), 1.68-1.71 (m, 4H), 1.28-1.49(m, 20H), 0.89 (t, 6H). ^{13}C-NMR (500 MHz, $CDCl_3$,ppm)δ 147.81, 136.92, 134.98, 129.48, 128.03, 125.63, 125.15, 124.77, 123.93, 123.24, 119.44, 32.00, 30.92, 29.75, 29.52, 26.59, 22.81, 14.25. MALDI-TOF HRMS: 920.90 [M^+] (calcd for $C_{66}H_{68}N_2O_2$: **921.26**).



2,6-TPAANT

2. ^{1}H-NMR and ^{13}C-NMR and MALDI-TOF HRMS spectra:

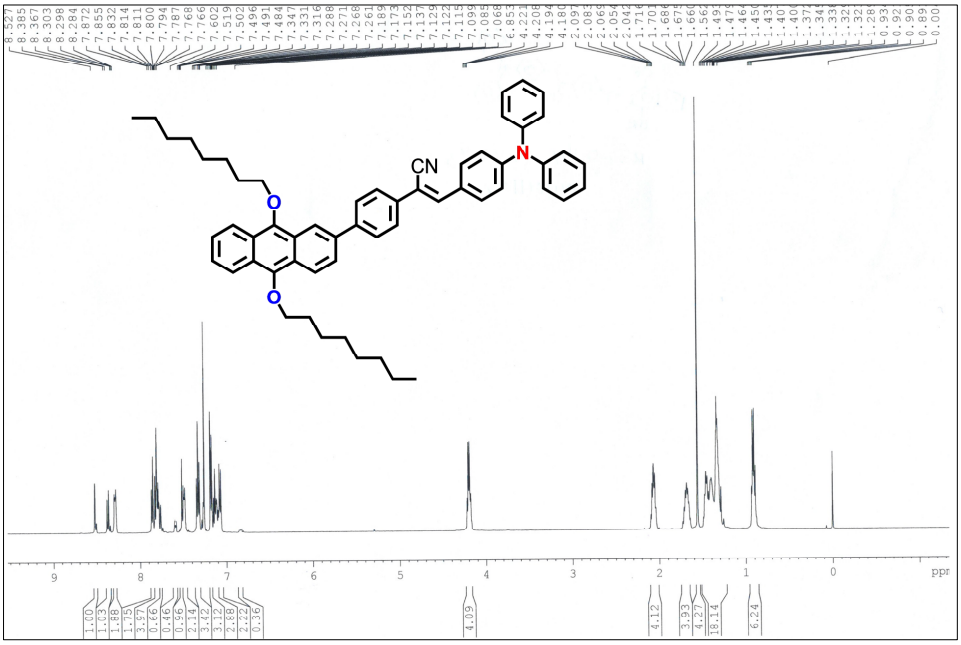


Figure Sa. ^{1}H-NMR spectrum of **2-TPACNANT.**

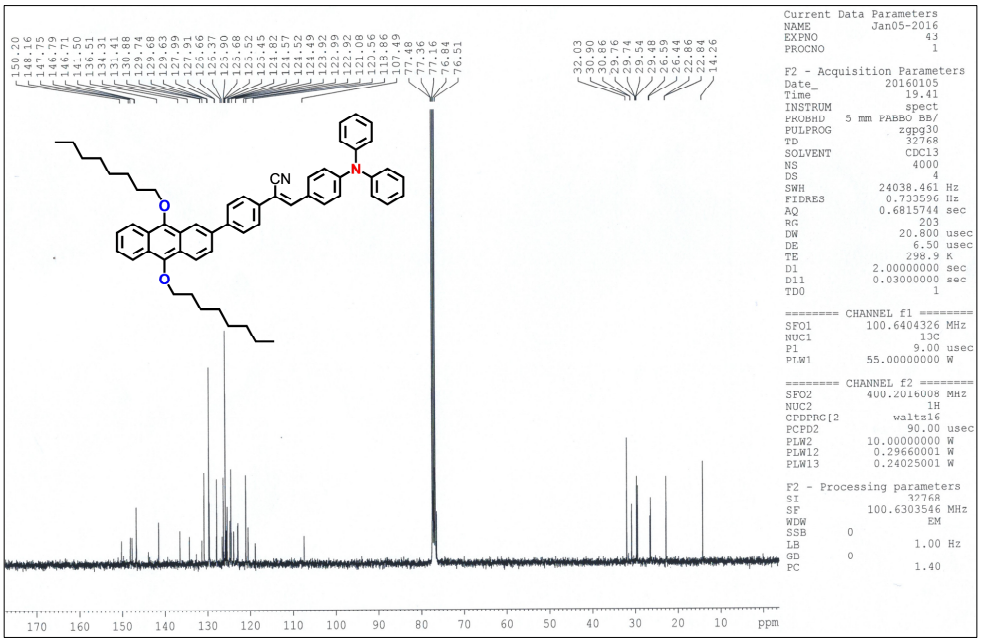


Figure Sb. ^{13}C-NMR spectrum of **2-TPACNANT**

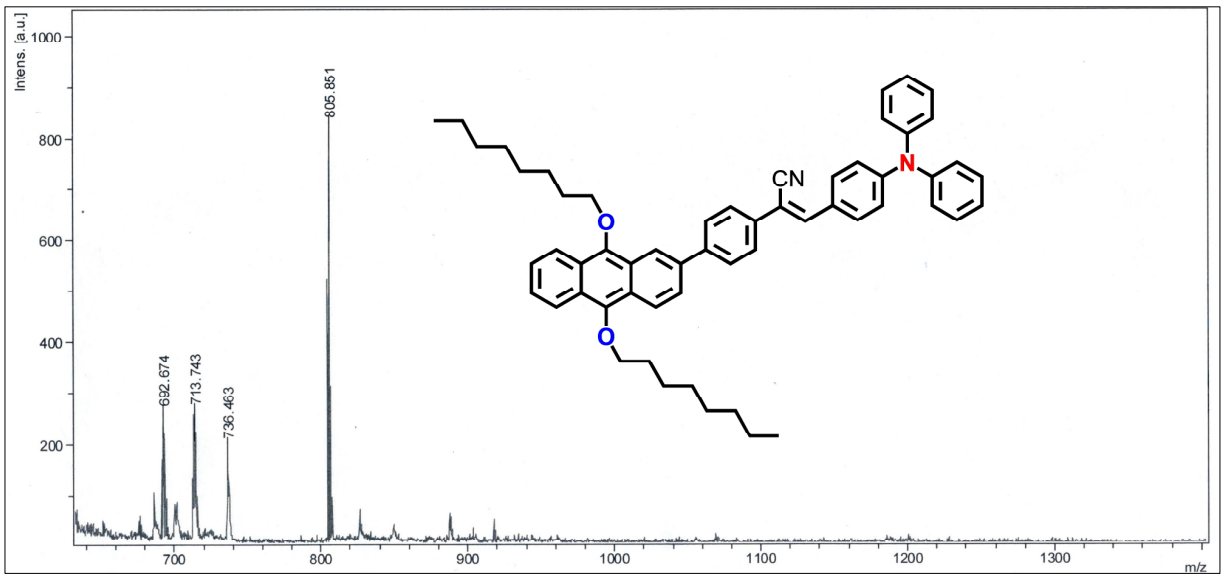


Figure Sc. MALDI-TOF spectrum of **2-TPACNANT**

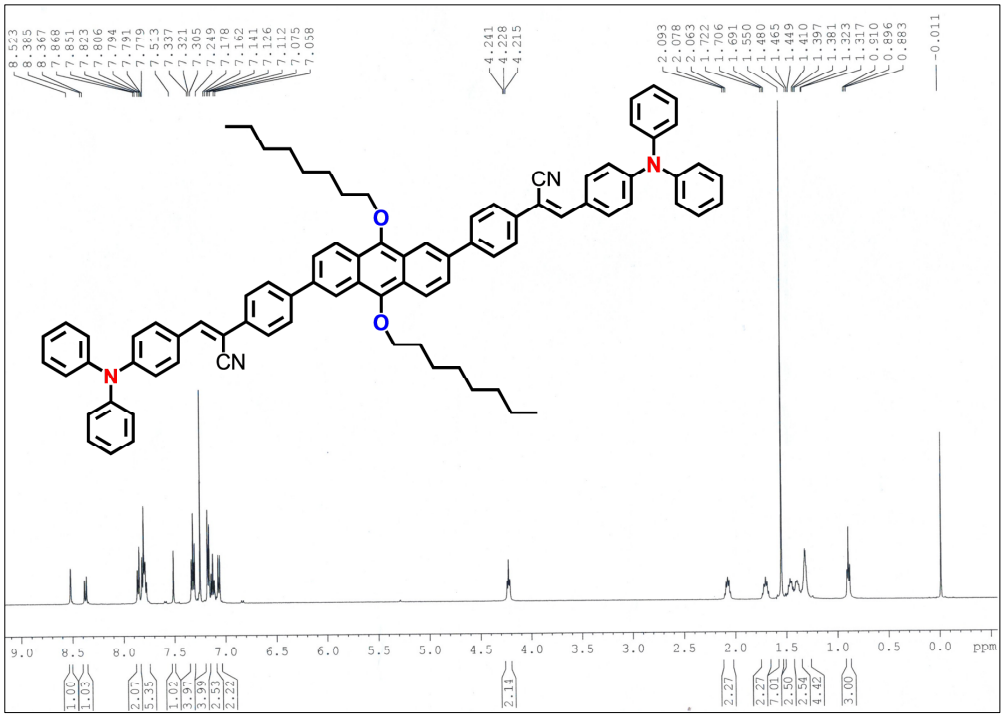


Figure Sd.[1]H NMR spectrum of **2,6-TPACNANT**

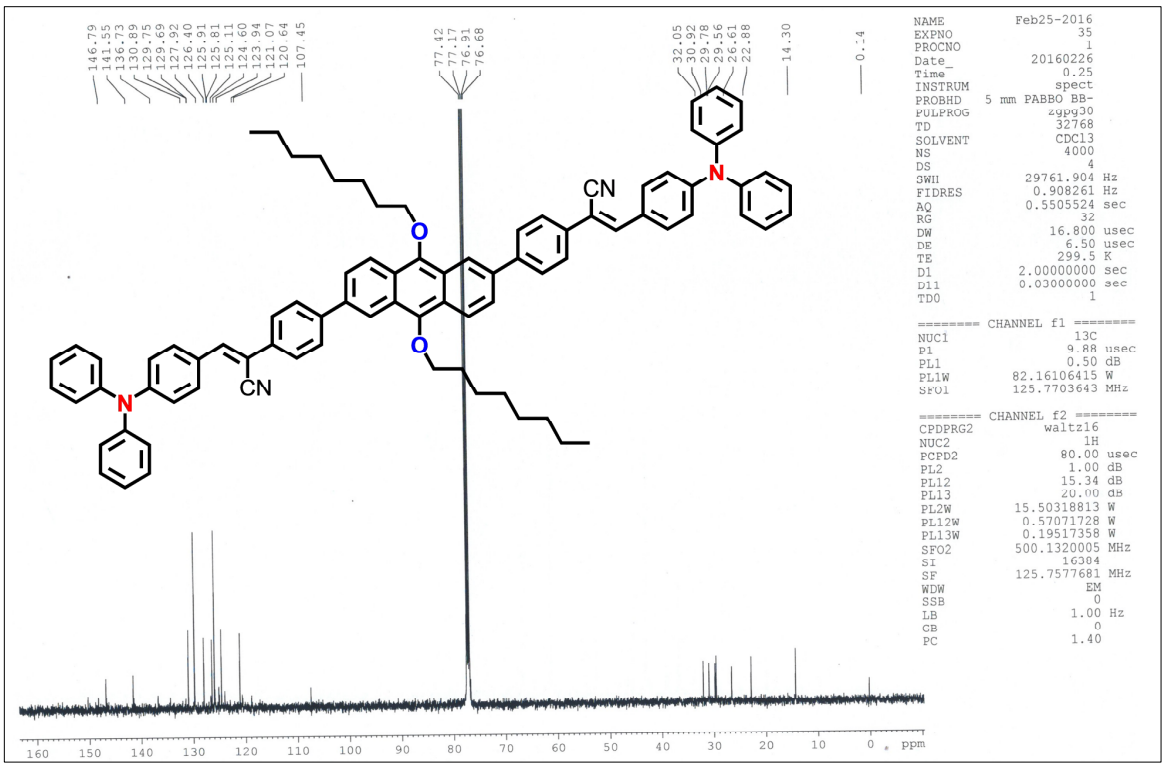


Figure Se. ^{13}C-NMR spectrum of **2,6-TPACNANT**

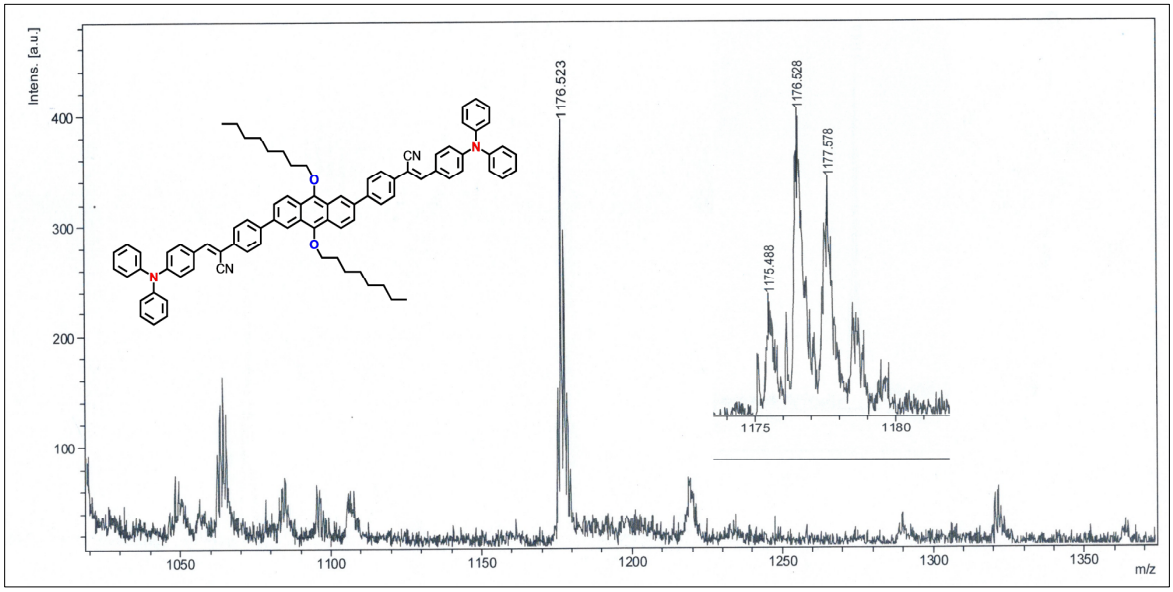


Figure Sf. MALDI-TOF spectrum of **2,6-TPACNANT**

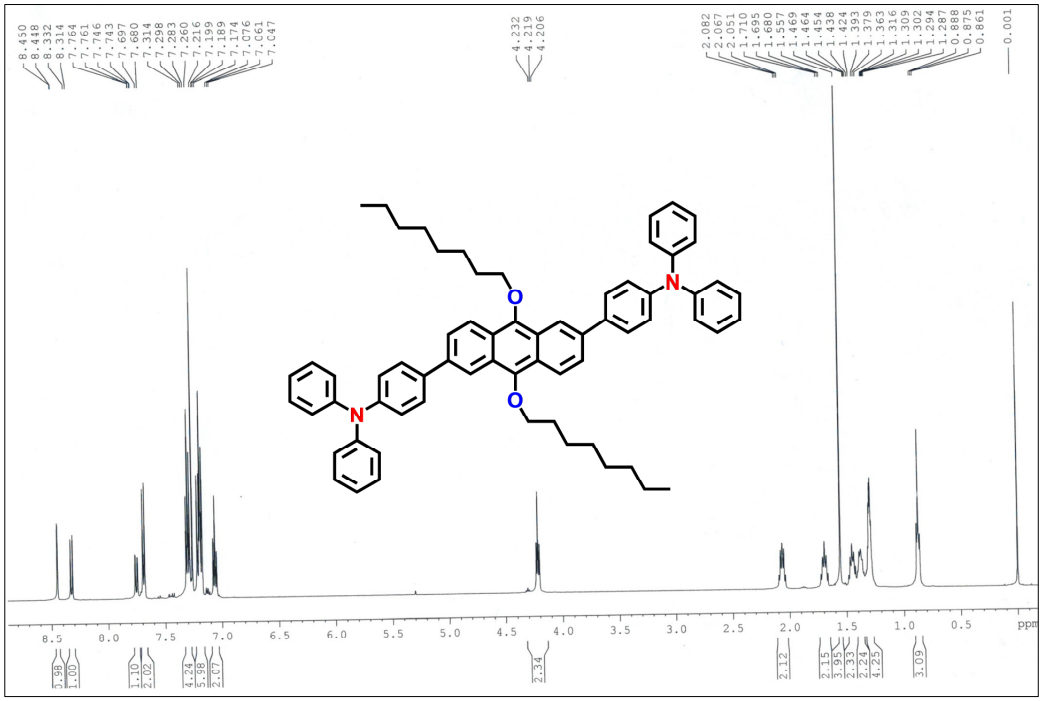


Figure Sg.[1]H NMR spectrum of **2,6-TPAANT**

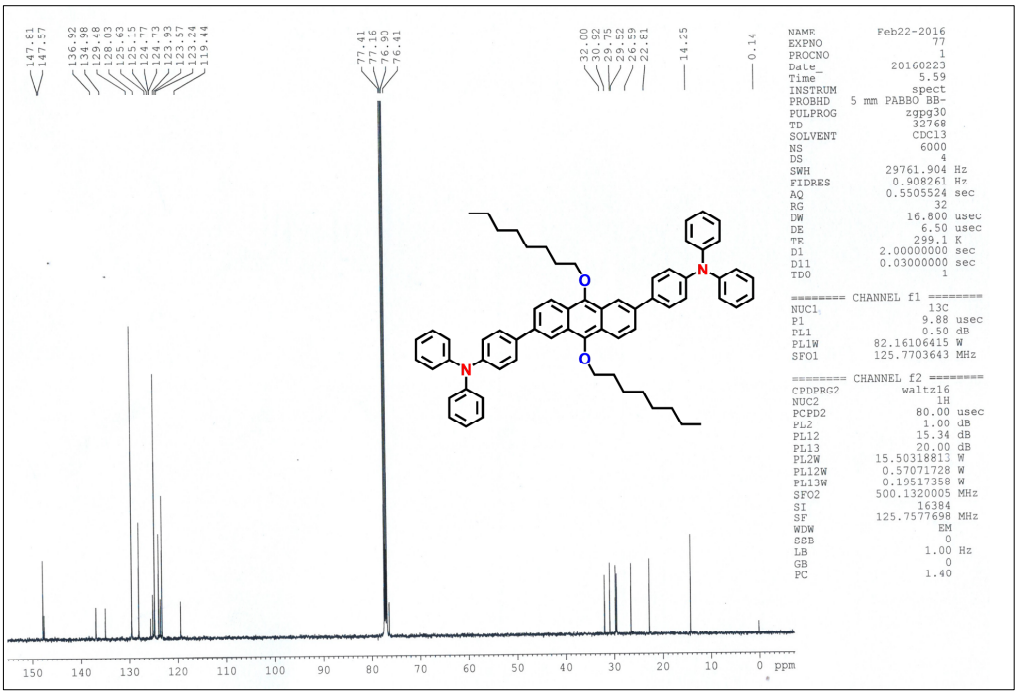


Figure Sh. [13]C NMR spectrum of **2,6-TPAANT**

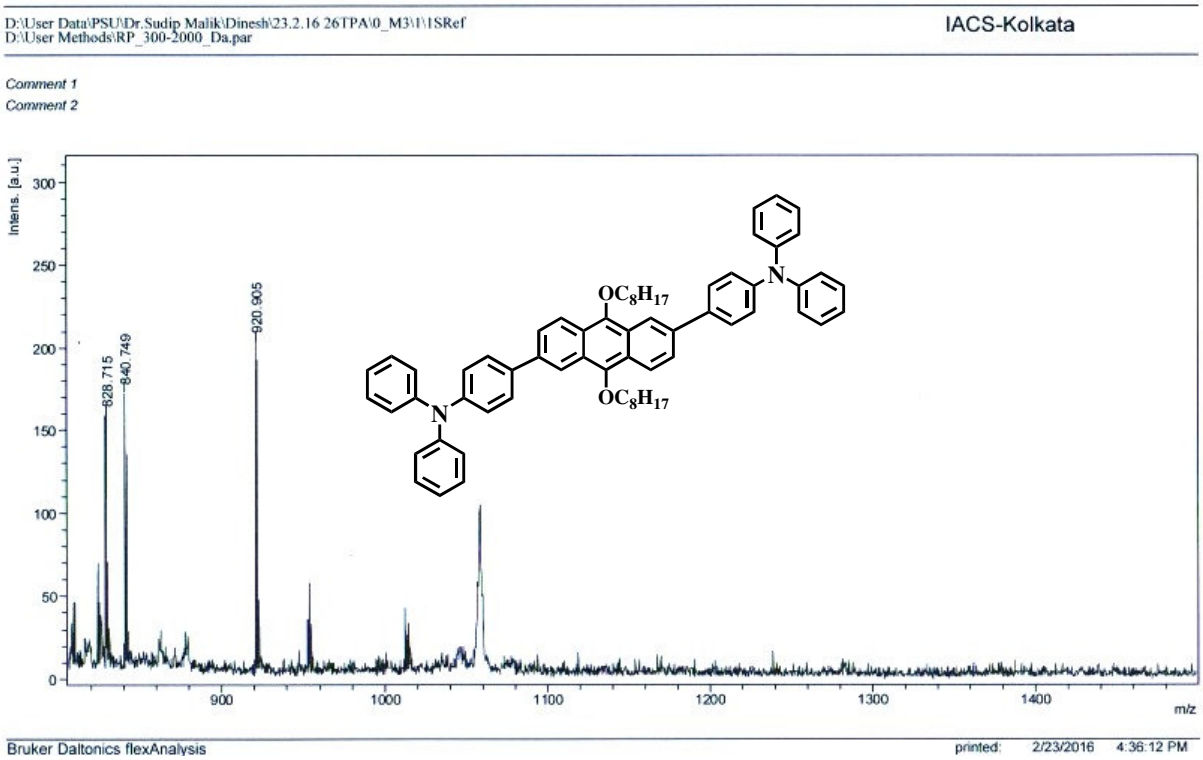
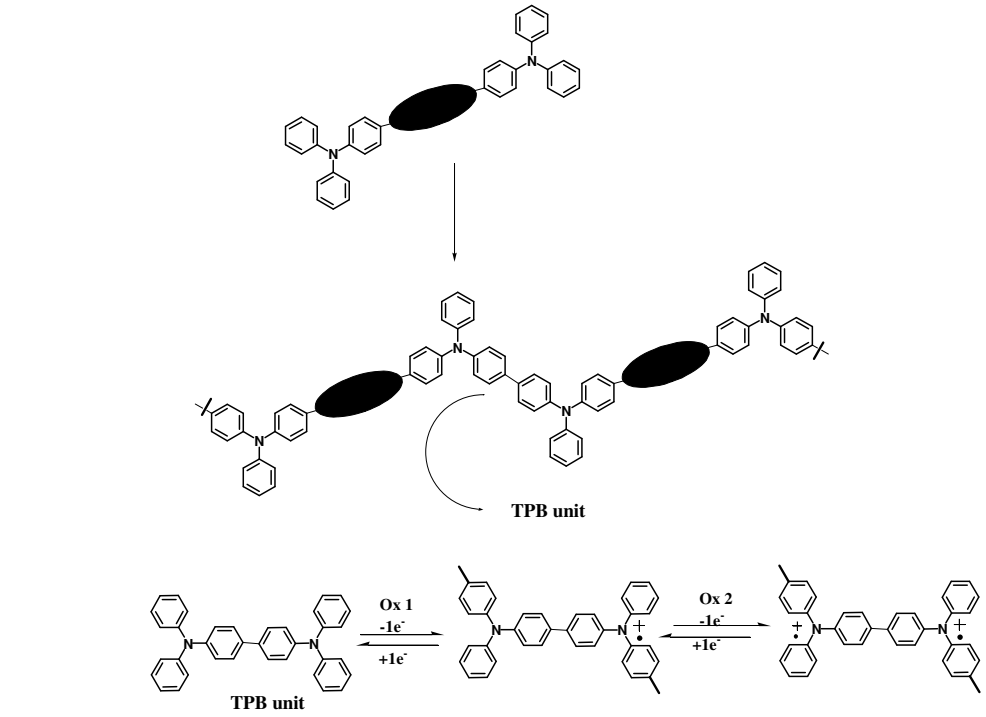


Figure Si. MALDI-TOF spectrum of **2,6-TPAANT**



Scheme S1. Electropolymerization and the possible path of oxidation process.

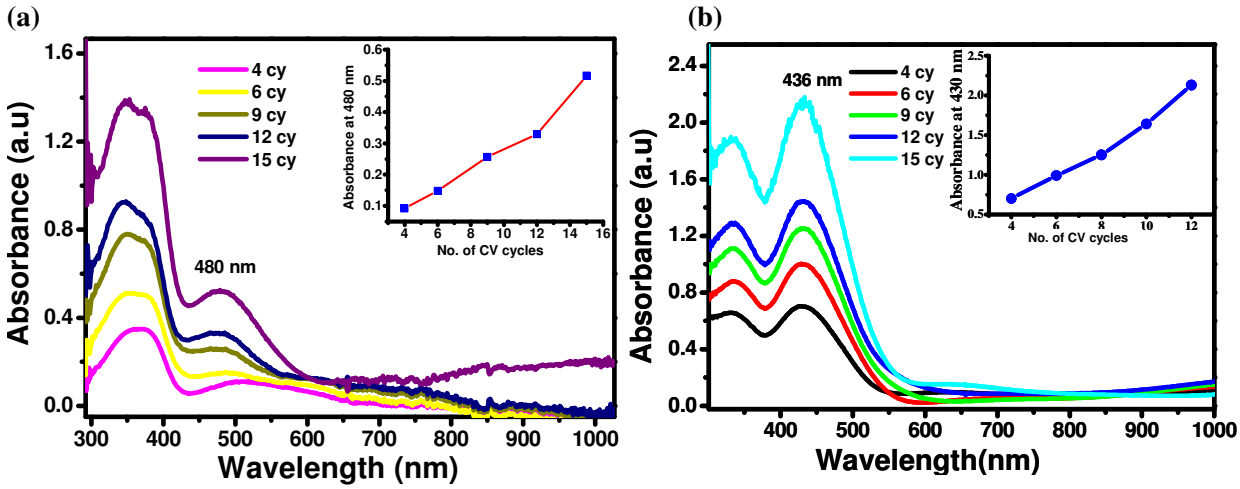


Figure S1. Absorption spectra of (a) ***p*-2,6-TPAANT** and (b) ***p*-2,6-TPACNANT** on ITO electrodes obtained after 4, 6, 9, and 12 CV and 15 scan cycles in electro-polymerization process. (Inset) Relationship between the absorbance of **p-2,6-TPAANT** electrodes at 480 nm and **p-2,6-TPAANT** at 436 nm vs the number of CV cycles.

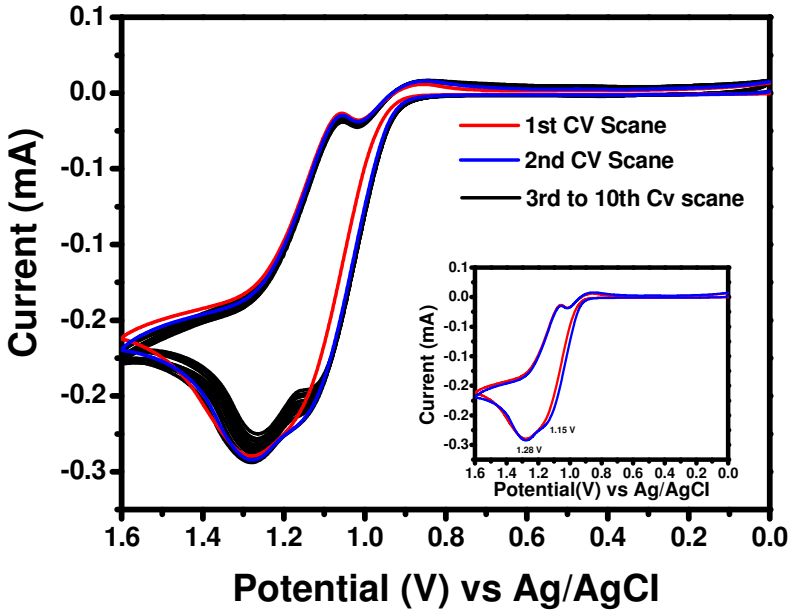


Figure S2. Repeated CV scanning of (a) **2-TPACNANT** between 0 and 1.6 V in 0.1 M Bu_4NClO_4/ DCM with a scan rate of 50 mV/s. The inset in displays the first and second scan.

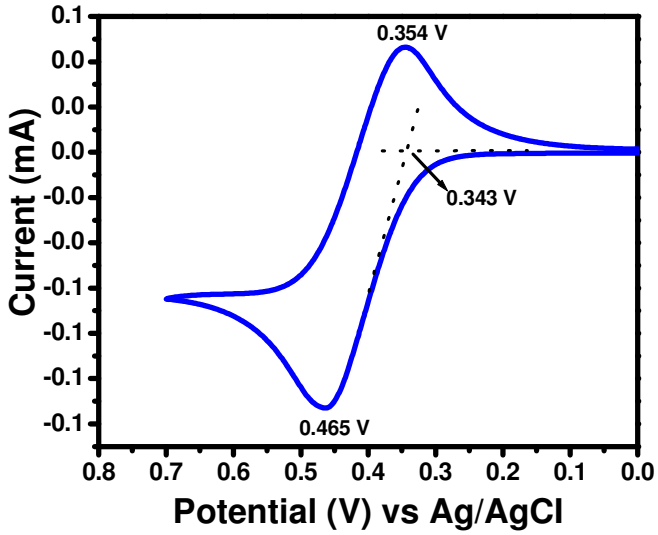


Figure S3.The CV diagram of 1mM ferrocene standard in 0.1 M Bu_4NClO_4/MeCN with a scan rate of 50 mV/s.

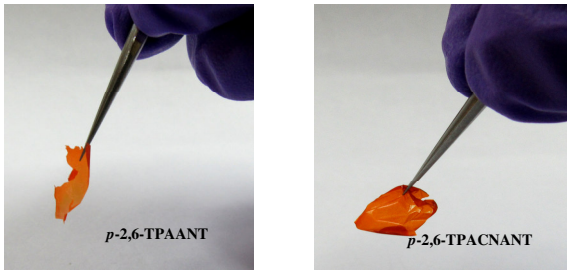


Figure S4. The polymer film removed from ITO glass.

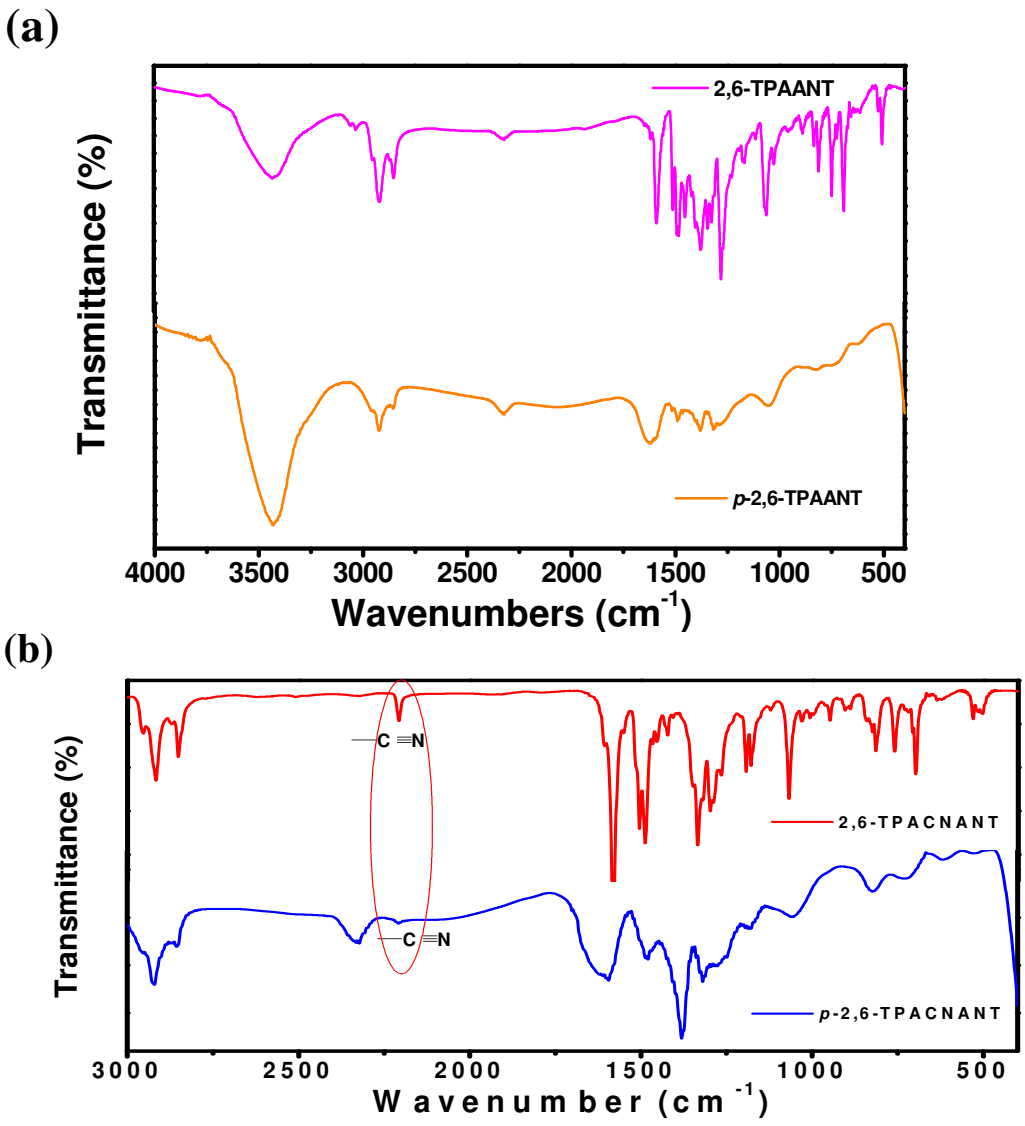


Figure S5. IR spectra of the monomer and polymer of (a) **2,6-TPAANT** and ***p*-2.6-TPAANT** (b) **2,6-TPACNANT** and ***p*-2,6-TPACNANT .**

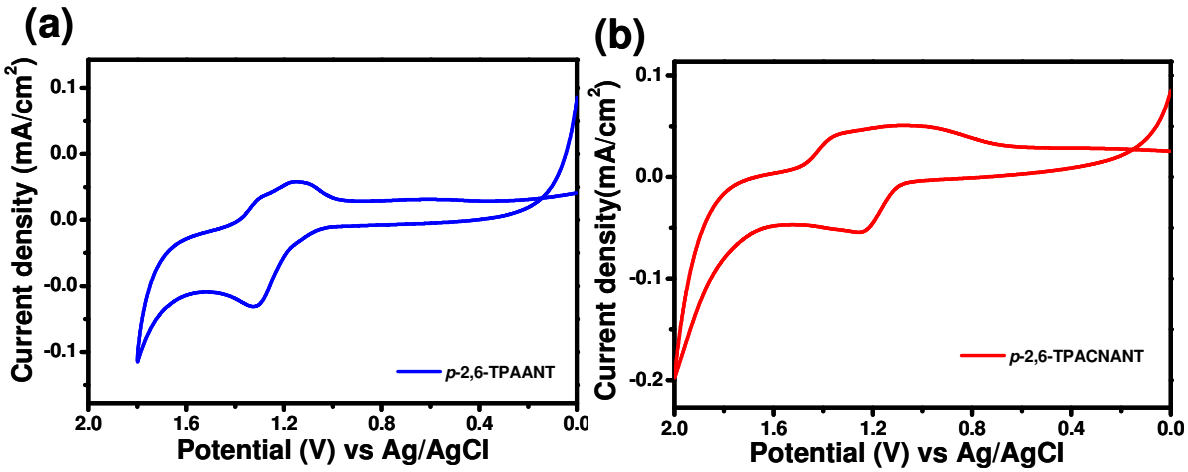


Figure S6. Cyclic voltammograms of the fabricated electrochromic device based on polymer film for (a) ***p*-2,6-TPAANT** and (b) ***p*-2,6-TPACNANT**.