Supporting Information

Water/alcohol soluble electron injection material containing azacrown ether groups: Synthesis, characterization and application to enhancement of electroluminescence

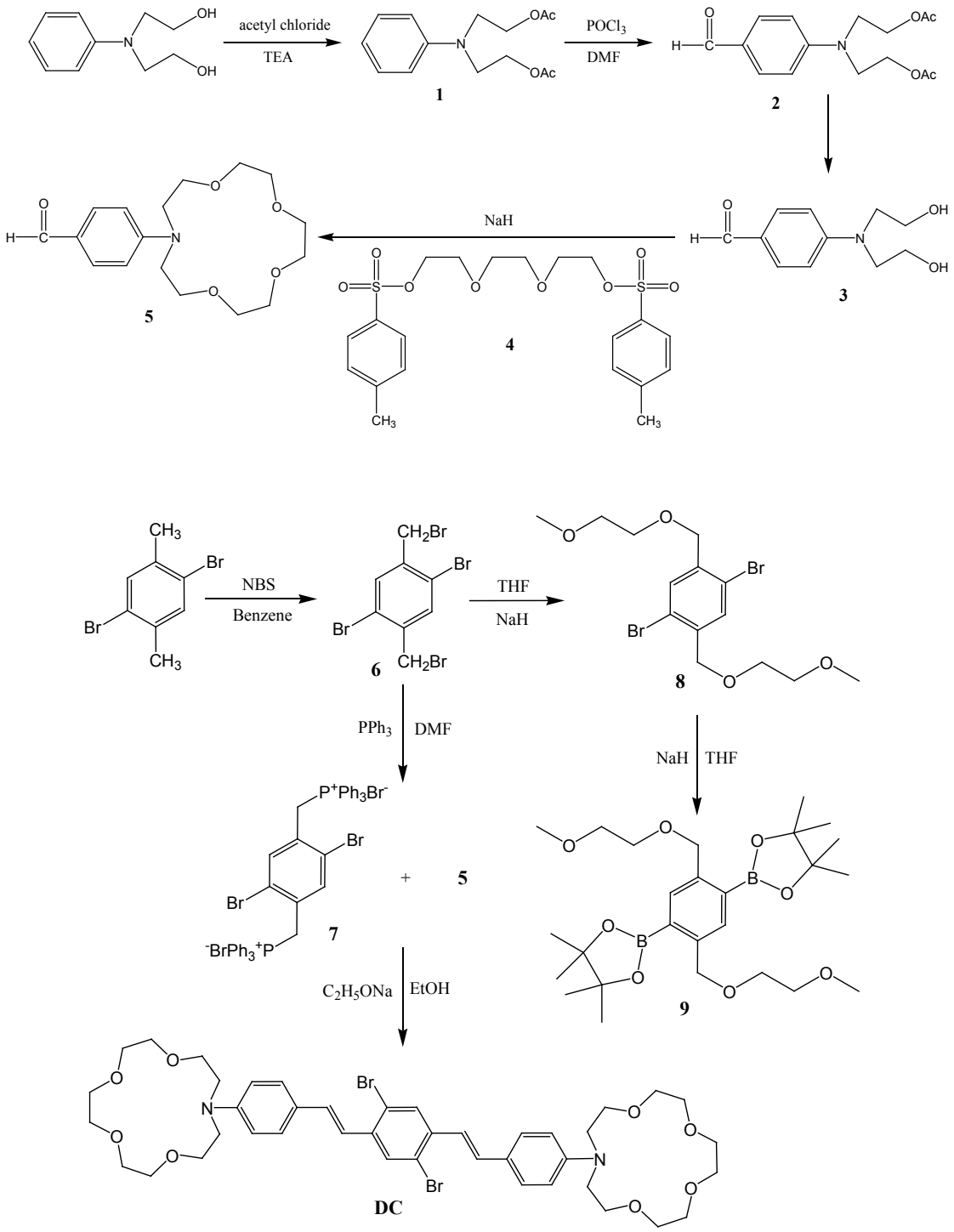
Chia-Shing Wu, Huai-An Lu, Chiao-Pei Chen, Tzung-Fang Guo[†] and Yun Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

[†]*Department of Photonics, National Cheng Kung University*

*Corresponding author: yunchen@mail.ncku.edu.tw

Synthesis of N,N-Bis(acetoxyethyl)phenylamine (1). A mixture of N-phenyldiethanolamine (8.0 g, 44 mmol), triethylamine (13.3 g, 132 mmol) and THF (40 mL) was added to a solution of acetyl chloride (9.3 mL, 132 mmol) in THF (40 mL). The mixture was stirred at 35 ^{o}C for 20 h. Then, 40 mL water was added dropwise to the mixture slowly. After removal of THF by rotary evaporation, the mixture was extracted with chloroform; the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was distilled in *vacuo* (210 ^{o}C, 7 torr) to obtain **1** (9.7 g , 82.9 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.20-7.24 (t, 2H, J = 16 Hz, Ar-H), 6.70-6.76 (m, 3H, Ar-H), 4.21-4.24 (t, 4H, J = 12.5 Hz , -CH_2-), 3.59-3.63 (t, 4H, J = 12.6 Hz, -CH_2-), 2.04 (s, 6H, -CH_3).Anal. Calcd. for $C_{14}H_{19}NO_4$ (%): C, 63.38; H, 7.22; N, 5.28. Found: C, 62.98 7.18; N, 5.22. FT-IR (KBr, cm^{-1}): ν 1735 (C=O stretch), 2963 (-CH stretch).



Scheme 1. Synthetic procedures of diborate monomer (**9**) and dibromo monomer (**DC**).

Synthesis of 4-(Bis(2-acetoxylethyl)amino)benzaldehyde (2). Phosphoryl trichloride (6.9 g, 45 mmol) was added slowly to N,N-dimethylformamide (13.8 g, 188 mmol) under ice bath and stirred at room temperature for 1 h, and then reacted at

75 °C for additional 12 h after adding compound **1**. Chloroform and sodium acetate solution (24.7 g, 0.3 mol) was added slowly under ice bath and stirred at room temperature overnight. The mixture was extracted with chloroform and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give **2** (12.2 g, 92.8 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 9.74 (s, H, -CHO) 6.81-6.83.(d, 2H, *J* = 8.6 Hz, Ar-H), 7.73-7.75 (d, 2H, *J* = 8.7 Hz, Ar-H), 4.26-4.29 (t, 4H, *J* = 12.2 Hz, -CH_2-), 3.71-3.74 (t, 4H, *J* = 12.3 Hz, -CH_2-), 2.04 (s, 6H, -CH_3). Anal. Calcd. for $C_{15}H_{19}NO_5$ (%): C, 61.42; H, 6.53; N, 4.78. Found: C, 61.09; H, 6.56; N, 4.65. FT-IR (KBr, cm^{-1}): ν 1676 (-CHO stretch), 1739 (C=O stretch), 2815 (-CH aldehyde), 2963 (-CH stretch).

Synthesis of 4-Bis(2-hydroxyethyl)amino)benzaldehyde (3). A mixture of **2** (10 g, 34 mmol), methanol (150 mL) and sodium carbonate solution (10.9 g, 102 mmol) was stirred at room temperature overnight. Few drops of 1N HCl were added to the mixture; and then the methanol was removed by rotary evaporation. The mixture was extracted with chloroform and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography eluted with ethyl acetate to give **3** (4.9 g, 69.5 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ 9.62 (s, H, -CHO) 7.63-7.66 (d, 2H, *J* = 8.7 Hz, Ar-H), 6.68-6.71 (d, 2H, *J* = 8.7 Hz, Ar-H), 3.86-3.89 (t, 4H, -CH_2-), 3.65-3.68 (t, 4H, -CH_2-), 3.40-3.45 (d, 2H, *J* = 16.4 Hz, -OH). Anal. Calcd. for $C_{11}H_{15}NO_3$ (%): C, 63.14; H, 7.23; N, 6.69. Found: C, 63.07; H, 7.28; N, 6.59. FT-IR (KBr, cm^{-1}): ν 1667 (-C=O stretch), 2753 (-CH aldehyde), 3352 (-OH stretch).

Synthesis of Triethyleneglycol Ditosylate (4). A mixture of *p*-toluenesulfonyl chloride (5.75 g, 0.03 mol), triethylene glycol (1.5 g, 0.01 mol) and THF (15 mL) was mechanically stirred at 0 °C. Aqueous solution of KOH (16 M, 4 mL) was added portionwise to the mixture within 1 h and then stirred at room temperature for 7 h.

The mixture was poured into ice water, the appearing white precipitate was collected by filtration and re-crystallized from methanol/water to afford white crystal of **4** (4.05 g, 88.6 %, m.p. 83.5-84 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): 7.25-7.79 (m, 8H, aromatic region), 4.1 (m, 4H), 3.6 (m, 4H), 3.5 (s, 4H), 2.4 (s, 6H). FT-IR (KBr, cm^{-1}): 1600 (aromatic ring), 1129 (C-O-C), 1175 (sulfonate). Anal. Calc. for $C_{20}H_{26}O_8S_2$ (%): C, 52.39; H, 5.72. Found: C, 52.37; H, 5.72.

Synthesis of 4-(monoaza-15-crown-5)benzaldehyde (5). A mixture of compound **3** (0.4 g, 2.09 mmol) and NaH (0.8 g, 60% in mineral oil, 20 mmol) in dried THF (300 mL) was refluxed for 30 min under nitrogen atmosphere. The mixture was added dropwise with a solution of compound **4** (1.0 g, 2.1 mmol) in THF (200 mL) and then stirred at 70 ^{o}C for 2 days. After adding an aqueous solution of H_2SO_4 (2 M, 50 mL), the THF was removed by rotary evaporation. The mixture was then extracted with chloroform and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: acetone/*n*-hexane = 3/2) to give **5** (0.3 g, 44.5%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 9.73 (s, H, -C<u>H</u>O) 7.70-7.73 (d, 2H, *J* = 8.8 Hz, Ar-<u>H</u>), 6.71-6.74 (d, 2H, *J* = 8.7 Hz), 3.52 (m, 4H, crown ether), 3.77-3.80 (m, 16H, crown ether). Anal. Calcd. for $C_{17}H_{25}NO_5$ (%): C, 63.14; H, 7.79; N, 4.33. Found: C, 62.68; H, 7.77; N, 4.14. FT-IR (KBr, cm^{-1}): ν 2798 (-CH aldehyde), 1667 (-C=O stretch), 1124 (C-O stretch).

Synthesis of 1,4-dibromo-2,5-bis(bromomethyl)benzene (6). A mixture of 2,5-dibromo-*p*-xylene (6 g, 22.73 mmol) and N-bromosuccinimide (8.9 g, 50 mmol) in benzene (60 mL) was refluxed under nitrogen atmosphere. And then 1,1'-azobis(cyclohexane carbonitrile) was added to the mixture. The mixture was stirred at 80 ^{o}C for 1 day under nitrogen atmosphere. The mixture was extracted with chloroform and the organic layer was dried ($MgSO_4$) and concentrated under reduced

pressure. After removal of $CHCl_3$ by a rotary evaporator, it was re-crystallized from ethanol to afford white crystal of **6** (4.32 g, 43.7 %, m.p. 157.5-158 ℃). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.66 (s, 2H, Ar-H), 4.51 (s, 4H, -CH_2-). Anal. Calcd. for $C_8H_6Br_4$ (%): C, 22.78; H, 1.43. Found: C, 22.84; H, 1.52.

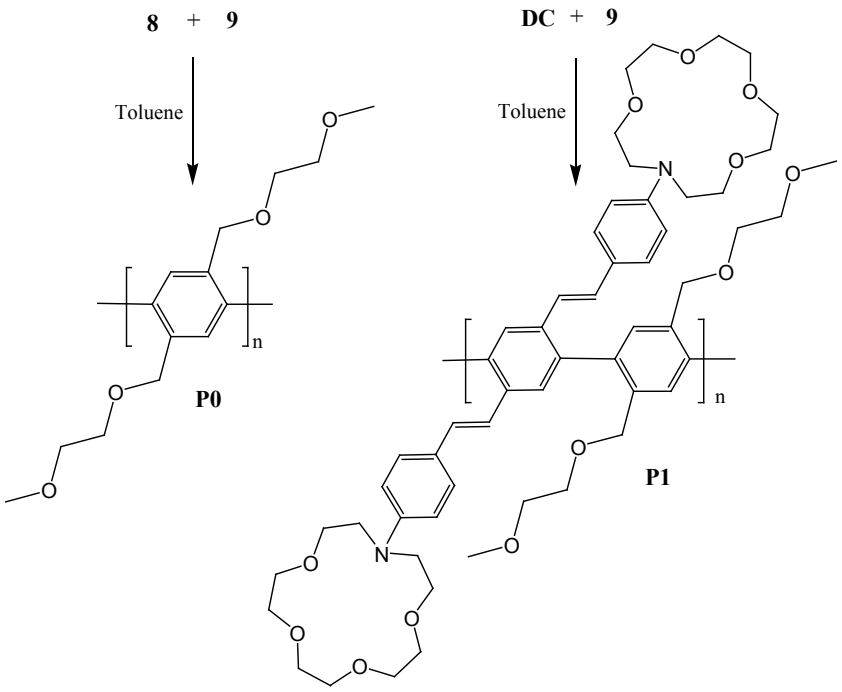
Synthesis of 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)] (7). To a mixture of compound **6** (5 g, 11.8 mmol) and triphenylphosphine (9.32 g, 35.4 mmol) and DMF (100 mL) was stirred at 100 ^{o}C for 18 h under nitrogen atmosphere. The mixture was poured into an excess of ethyl ether, the appearing solid was collected by filtration and re-crystallized from methanol to afford white crystal of **7** (7.1 g, 63.4 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.64-7.81 (m, 30H, Ar-H), 7.37 (s, 2H, J = 8.7 Hz, Ar-H), 5.67-5.69 (m, 4H), 3.52 (m, 4H, crown ether), 3.77-3.80 (m, 16H, crown ether). Anal. Calcd. for $C_{44}H_{36}Br_4P_2$ (%): C, 54.8; H, 3.97. Found: C, 54.78; H, 4.08.

Synthesis of 1,4-dibromo-2,5-bis[(2-methoxyethoxy)methyl]benzene (8). A mixture of compound **6** (3.7 g, 8.8 mmol), 2-methoxyethanol (4 g, 52.6 mmol) and NaH (2.11 g, 60 % in mineral oil, 52.6 mmol) in dried THF (50 mL) was refluxed for 1 day under nitrogen atmosphere. The mixture was then extracted with chloroform and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. It was re-crystallized from ethanol to afford light yellow crystal of **8** (2.2 g, 61.1 %, m.p. 73.5-74 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.68 (s, 2H, Ar-H), 4.58 (s, 4H, -CH_2-), 3.71-3.73 (m, 4H), 3.61-3.63 (m, 4H), 3.42 (s, 6H, -CH_3). Anal. Calcd. for $C_{14}H_{20}Br_2O_4$ (%): C, 54.8; H, 3.97. Found: C, 54.88; H, 4.08. FT-IR (KBr, cm^{-1}): ν 1105 (C-O stretch), 2877 (O-CH_2).

Synthesis of 2,2'-[2,5-bis(2-methoxyethoxy)methyl]-1,4-phenylene-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9). To a 50-mL glass reactor was added with compound **8** (2.2 g,

5.3 mmol) and dried THF (35 ml). The mixture was cooled to -78 ^{o}C, added dropwise with *tert*-BuLi (10 mL, 1.9 M in pentane, 19 mmol) and stirred for 4 hour. And then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.3 mL, 16 mmol) was added to the reaction mixture and stirred for 1 h. The mixture was extracted using ether and water, dried over $MgSO_4$, and dried by rotary evaporation. The residue was recrystallized from *n*-hexane to afford light yellow crystal of **9** (0.9 g, 33.5 %, m.p. 74-75 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.60 (s, 2H, Ar-H), 4.77 (s, 4H, -CH_2-), 3.59-3.61 (m, 4H), 3.53-3.56 (m, 4H), 3.37 (s, 6H, -CH_3), 1.34 (s, 24H, -CH_3). Anal. Calcd. for $C_{26}H_{44}B_2O_8$ (%): C, 40.80; H, 4.89. Found: C, 40.93; H, 5.03. FT-IR (KBr, cm^{-1}): ν 1105 (C-O stretch), 2877 (O-CH_2).

Synthesis of 2,5-dibromo-1,4-bis[ethene-bis(monoaza-15-crown-5)styryl] (DC). A mixture of compound **5** (3.76 g, 11.64 mmol) and compound **7** (2.21 g, 2.33 mmol) in dried ethanol (5 mL) was added dropwise with sodium ethoxide (3.77 mL, 11.64 mmol) and stirred at room temperature overnight under nitrogen atmosphere. The mixture was extracted with chloroform, the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: acetone/*n*-hexane = 1/1) to give **DC** (0.8 g, 39 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.82 (s, H, Ar-H), 7.41-7.43 (d, 2H, *J* =8.8 Hz, Ar-H), 7.11-7.15 (d, 2H, -C=CH-), 6.94-6.98 (d, 2H, -HC=C-), 6.66-6.68 (d, 2H, *J*=8.7 Hz, Ar-H), 3.76-3.79 (m, 8H, crown ether), 3.64-3.67 (m, 32H, crown ether). Anal. Calcd. for $C_{42}H_{54}Br_2N_2O_8$ (%): C, 57.67; H, 6.22; N, 3.20. Found: C, 57.50; H, 6.22; N, 3.19. FT-IR (KBr, cm^{-1}): ν 1138 (C-O stretch), 2883 (O-CH_2).



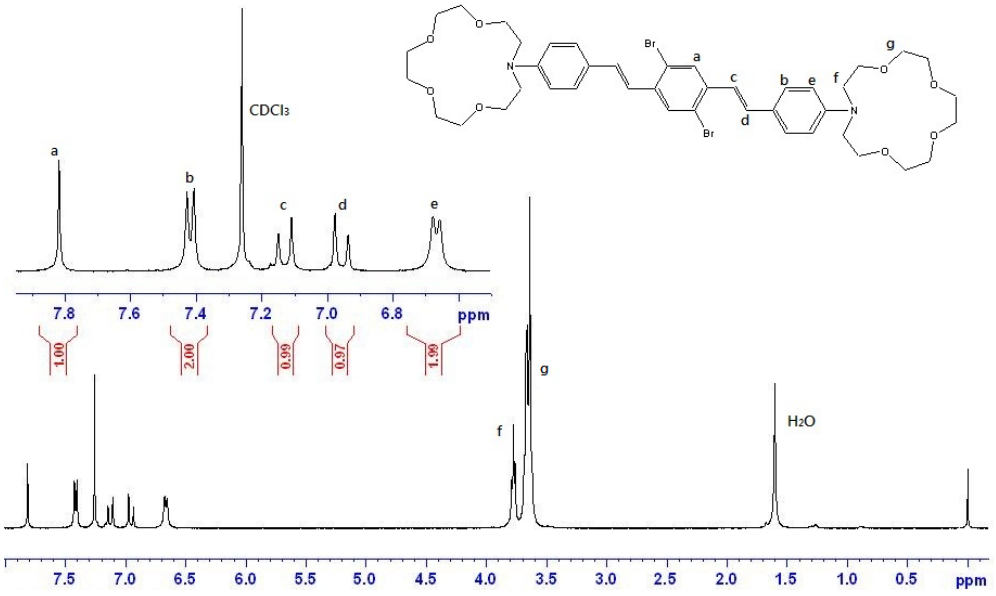
Scheme 2. Synthetic procedures of homopolymer **P0** and copoly(*p*-phenylene) **P1**.

Synthesis of Polymers P0 and P1. To a 25-mL glass reactor was added with compound **9** (0.116 g, 0.23 mmol), **DC** (0.2 g, 0.23 mmol), aqueous solution of 2 M K_2CO_3 (5 mL), $Pd(PPh_3)_4$, and toluene (10 mL) under nitrogen. The mixture was stirred at 80 ^oC for 2 days after adding Aliquat 336. The polymerization proceeded for additional 12 hours after adding bromobenzene (0.018 g, 0.115 mmol) as end-capping agent. The mixture was extracted with distilled water three times after adding chloroform. It was then poured into a lot of amount of *n*-hexane and the appearing precipitate was collected by filtration. The precipitate was purified by extracting with *n*-hexane for 2 days using a Soxhlet extractor to provide **P1** (0.1 g, 45.5 %). The synthesis procedures of homopolymer (**P0**) were similar to those used in the preparation of **P1** except that compound **8** was used instead of **DC**. The yield was 60 % (0.12 g).

P1: ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 ^oC): δ 7.74, 7.35-7.59, 7.15, 6.55-6.60, 6.34 (m, 16H, Ar-H and –HC=CH-), 4.42-4.45 (m, 4H, Ar-CH_2-O), 3.63, 3.49, 3,37

(m, 48H, crown ether and O-C<u>H</u>$_2$-), 3.15-3.17 (m, 6H, -C<u>H</u>$_3$). Anal. Calcd. for $C_{56}H_{74}N_2O_{12}$ (%): C, 69.54; H, 7.71; N, 2.90. Found: C, 68.55; H, 7.61; N, 2.74.

P0: ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ 7.47 (s, 2H, Ar-<u>H</u>), 4.36-4.39 (m, 4H, Ar-C<u>H</u>$_2$-O), 3.64-3.68 (m, 8H,-C<u>H</u>$_2$-), 3.32-3.36 (m, 6H, -C<u>H</u>$_3$). Anal. Calcd. for $C_{14}H_{20}O_4$ (%): C, 66.65; H, 7.99. Found: C, 65.54; H, 7.86.



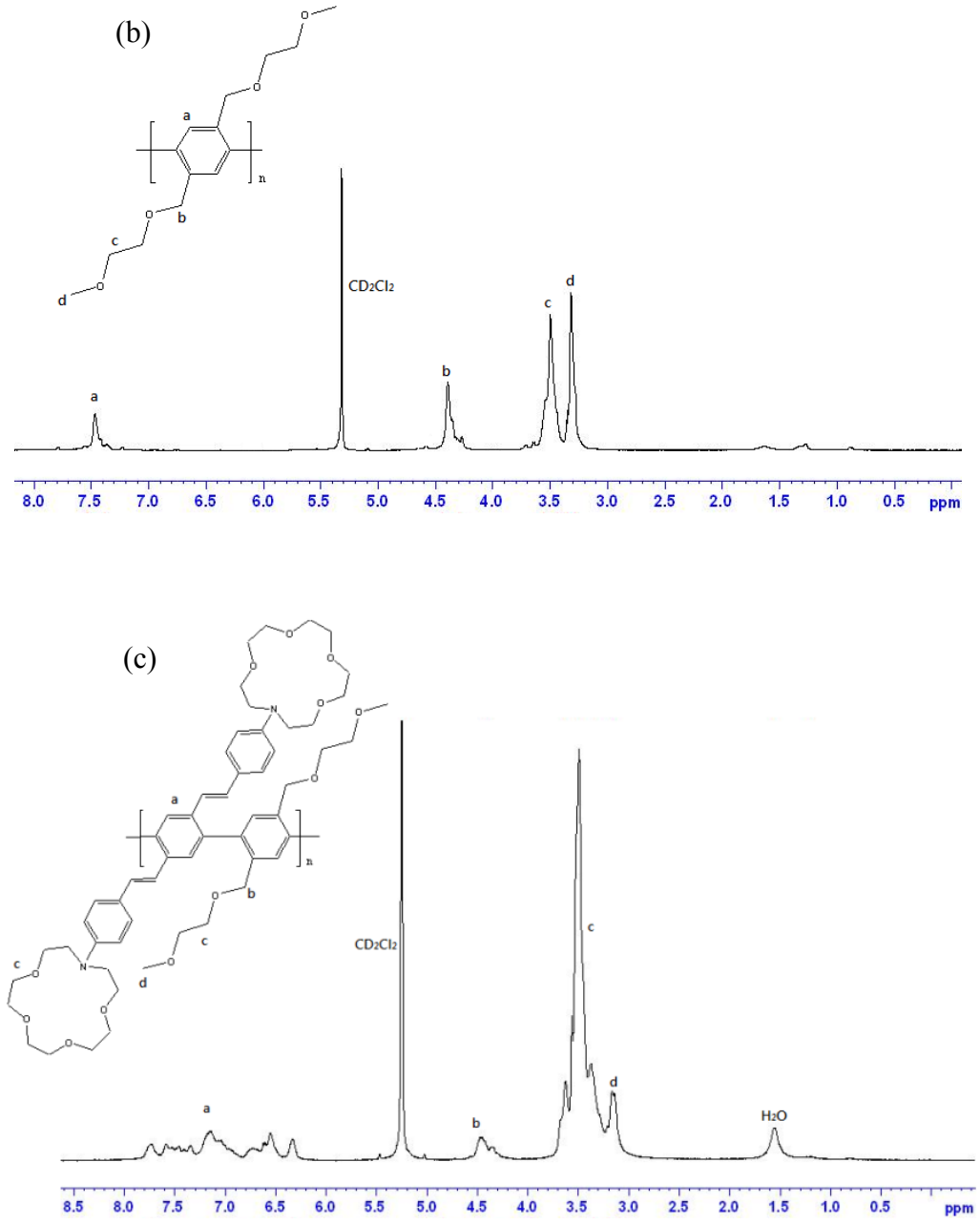


Figure S1. ^{1}H NMR spectra of **(a)** compound **DC** and polymers (b) **P0** and (c) **P1**.

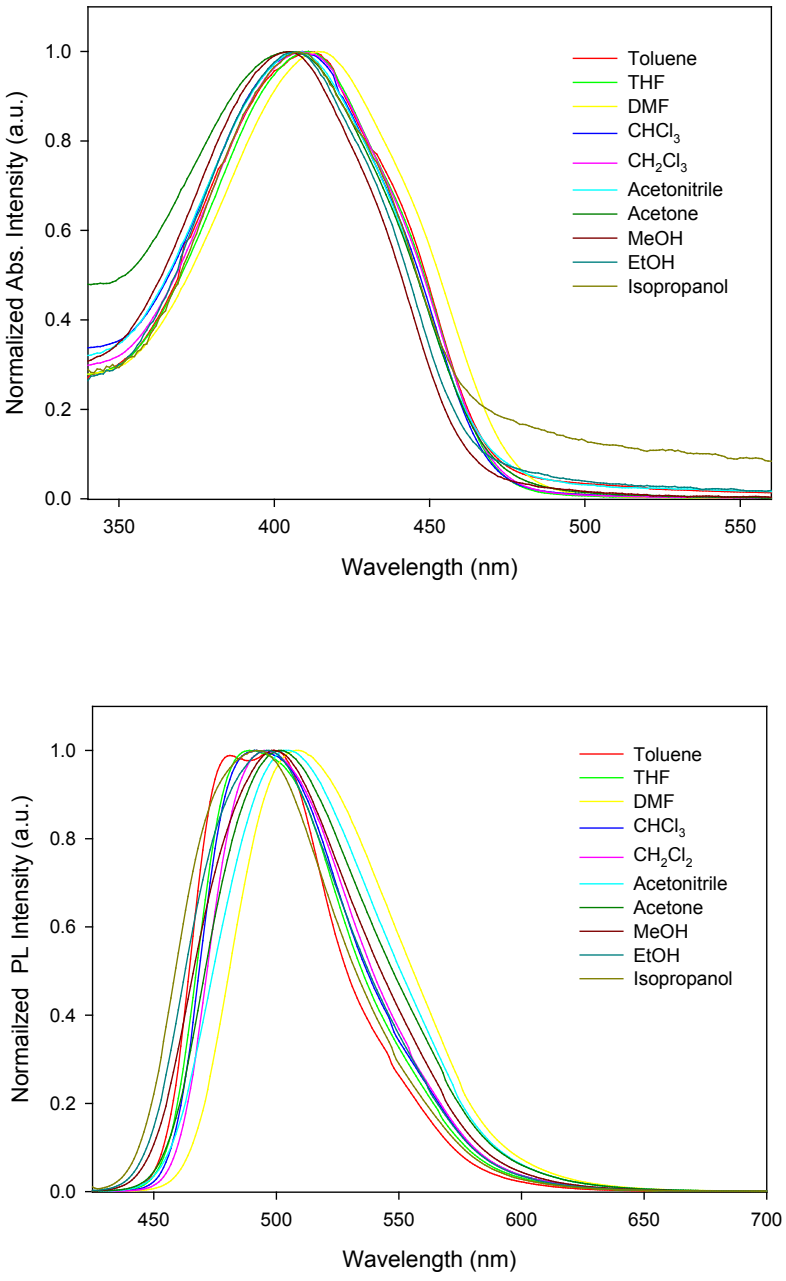


Figure S2. Absorption spectra and photoluminescence emission spectra of **P1** in various solvents (1.0×10^{-5} M).

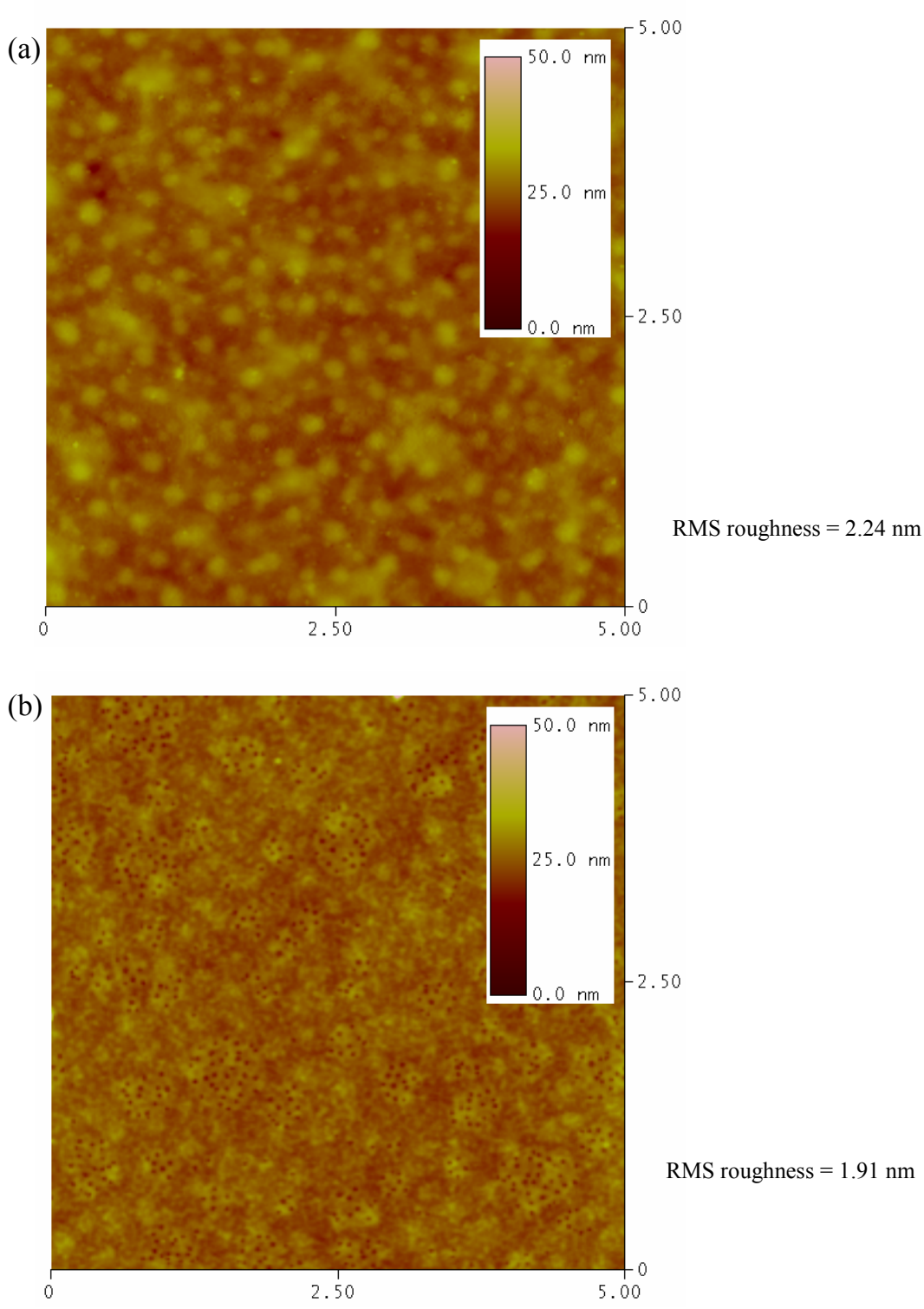


Figure S3. (a) AFM images of PF-Green-B film on top of PEDOT:PSS layer. (b) AFM images of **P1** film on top of PF-Green-B layer.