Supporting Information

for

Synthesis and Applications of Main-Chain Ru^{II} Metallo-Polymers Containing Bis-terpyridyl Ligands with Various Benzodiazole Cores for Solar Cells

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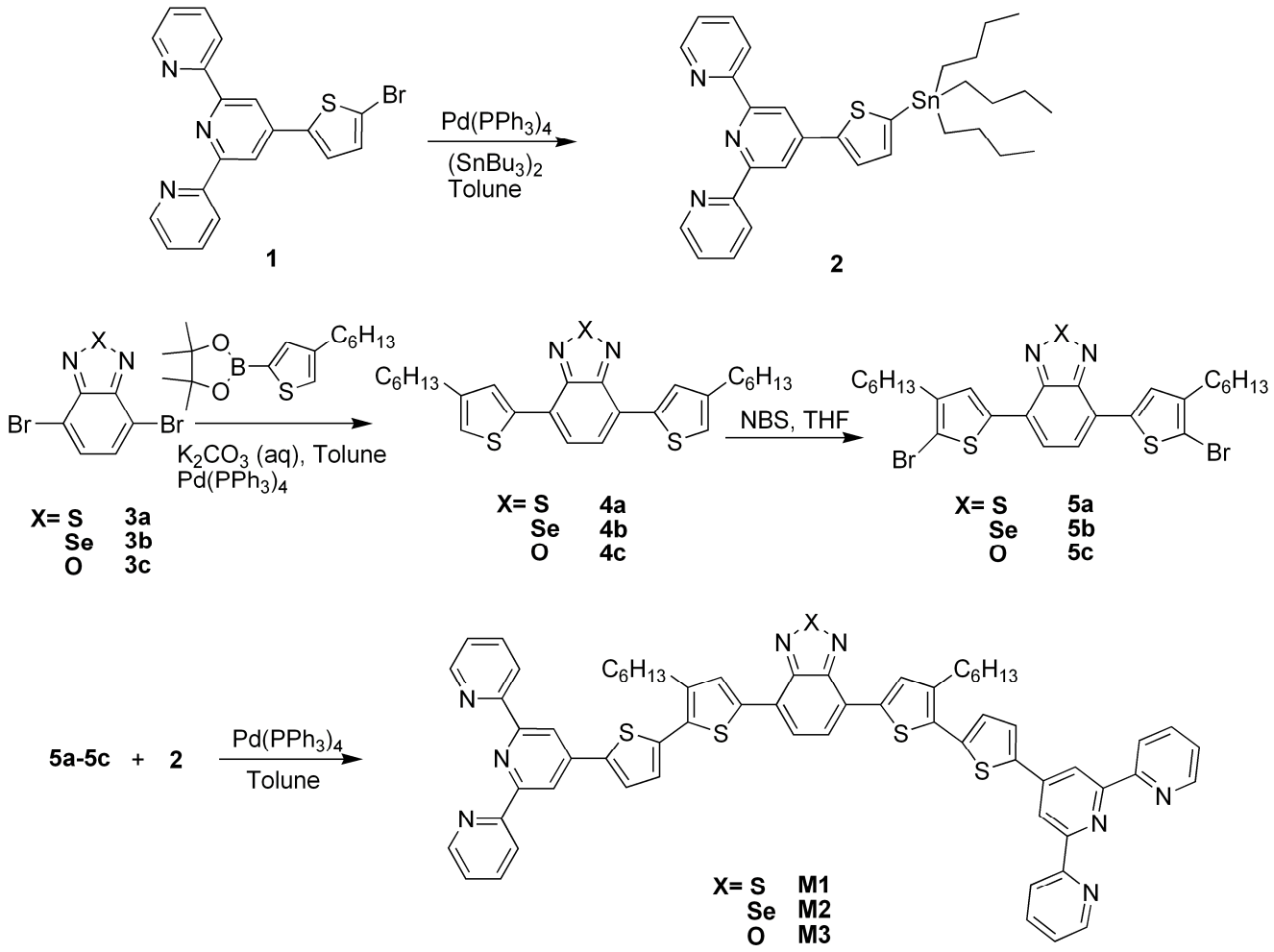
Materials. All chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, Fluka, TCI, TEDIA, and Lancaster Chemical Co. Toluene, tetrahydrofuran, and diethyl ether were distilled over sodium/benzophenone to keep anhydrous before use. Chloroform ($CHCl_3$) was purified by refluxing with calcium hydride and then distilled. If not otherwise specified, the other solvents were degassed by nitrogen 1 h prior to use. . Synthesis of 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**),[1] 4,7-dibromo-2,1,3-benzothiadiazole (**3a**),[2] 4,7-dibromo-2,1,3-benzoselenadiazole (**3b**),[3] and 4,7-dibromo-2,1,3-benzoxadiazole (**3c**)[4] were prepared by following the literature procedures. 4′-(2-Bromo-5-thienyl)-2,2′,6′,2″-terpyridine **(1)** was prepared by the modified method described in the literature.[5]

Instrumentation. ^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 solvents. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Thermogravimetric analyses (TGA) were conducted with a TA Instruments Q500 at a heating rate of 10°C/min under nitrogen. Viscosity measurements were proceeded by 10% weight of metallo-polymer solutions (in NMP) in contrast to that proceeded by bis-terpyridyl ligand solutions under the same condition (with viscosity η = 6 cp) on a BROOKFILEL DV-III+ RHEOMETER system at 25°C (100 RPM, Spindle number 4). UV-visible absorption were recorded in dilute chloroform (for **M1-M3**) and DMF (for **P1-P3**) solutions (10^{-6} M) on a HP G1103A spectrophotometer. Solid films of UV-vis measurements were spin-coated on quartz substrates from chloroform and DMF solutions with a concentration of 10 mg/mL for bis-terpyridyl ligands (**M1-M3**) and polymers (**P1-P3**), respectively. UV-vis titrations were performed by taking 10^{-5} M of bis-terpyridyl ligands (**M1-M3**) in the co-solvent of chlorofom: acetonitrile (8:2 v/v), and titrated with 50 μl aliquots of 3.9×10^{-4} M solutions containing metal salts $Zn(OAc)_2$ in the EtOH. Cyclic voltammetry (CV) measurements were performed using a BAS 100 electrochemical analyzer with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution (in acetonitrile) at room temperature with a scanning rate of 100 mV/s. During the CV measurements, the solutions were purged with

nitrogen for 30 s. In each case, a carbon working electrode coated with a thin layer of monomers or polymers, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode were used, and Ag/AgCl (3 M KCl) electrode was served as a reference electrode for all potentials quoted herein. The redox couple of ferrocene/ferrocenium ion (Fc/Fc^{+}) was used as an external standard. The corresponding HOMO and LUMO levels were calculated using $E_{ox/onset}$ and $E_{red/onset}$ for experiments in solid films, which were performed by drop-casting films with the similar thicknesses from THF or DMF solutions (ca. 5 mg/mL).



Scheme S1. Synthetic Route for Bis-terpyridyl Ligands (M1-M3).

4′-(2-Bromo-5-thienyl)-2,2′,6′,2″-terpyridine (1). Aqueous potassium hydroxide (8.4 g, 150 mmol

in 40 mL water) was added to a solution of 2-Acetylpyridine in 400 mL of methanol. The reaction mixture was stirred for 30 min and then 9.55 g (50 mmol) of 2-bromothiophene carboxaldehyde in 50 mL of methanol was added dropwise. The solution was stirred overnight at room temperature. The solvent was then evaporated off under vacuum and extracted with dichloromethane. Then the crude was taken for the next step without further purifications. To the above crude an excess amount (50 gm) ammonium acetate in 200 mL of ethanol/acetic acid (2/1) was added. The mixture was heated to reflux for 6 h. The reaction mixture was cooled to room temperature, poured onto ice and water (1 liter) to give a pale yellow precipitate that was recrystallized with ethanol to yield the title compound as a white solid. (9.25 g, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.72 (d, J = 3.2 Hz, 2H), 8.61 (d, J = 7.8 Hz, 2H), 8.58 (s, 2H), 7.88 (ddd, J = 1.8 Hz, J = 7.5 Hz, J = 7.5 Hz, 2H), 7.51 (d, J = 4.2 Hz, 1H), 7.35 (ddd, J = 1 Hz, J = 4.8 Hz, J =7.8 Hz, 2H), 7.11 (d, J = 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 156.5, 156.1, 149.5, 143.6, 142.8, 137.3, 131.6, 126.3, 124.4, 121.7, 116.6, 114.6.

4'-(5-Tributylstannanyl-thiophen-2-yl)-[2,2';6',2'']terpyridine (2). To a solution of 4′-(2-Bromo-5-thienyl)-2,2′,6′,2″-terpyridine (4.00 g, 10.15 mmol) in toluene (20 mL), bis(tributyltin) (13 mL, 25 mmol, 2.5 equiv) was added in one portion, and the mixture was degassed with argon. $(PPh_3)_4Pd(0)$ (400 mg, 0.34 mmol) was added, and the mixture was refluxed overnight. The reaction mixture was cooled to room temperature, filtered and solvents were removed by reduced pressure. The residue was purified by column chromatography on alumina with 3:1 hexane/ ethyl acetate to give product as slightly yellowish oil, (3.2 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.74 (d, J = 3.2 Hz, 2H), 8.69 (s, 2H), 8.63 (d, J = 7.8 Hz, 2H), 7.88 (ddd, J = 1.8 Hz, J = 7.5 Hz, J = 7.5 Hz, 2H), 7.81 (d, J = 4.2 Hz, 1H), 7.36 (ddd, J = 1 Hz, J = 4.8 Hz, J = 7.8 Hz, 2H), 7.21 (d, J = 3.9 Hz, 1H), 1.55−1.63 (m, 6H), 1.30−1.44 (m, 6H), 1.09−1.15 (m, 6H),. 0.92 (t, J = 7.3 Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 157.5, 155.1, 149.5, 147.6, 141.8, 137.3, 131.6, 127.3, 124.4, 121.7, 117.6, 114.6, 29.8, 28.0, 14.4, 10.4.

General Procedure for 4a-4c. In a 100 mL flame-dried two-neck flask fitted with a condenser, 1.00 eq of dibromoarene (**3a-3c**), 2.2 eq of 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (**2**) and 0.03 eq. of tetrakis(triphenylphosphine)palladium was added. The mixture was degassed and purged nitrogen. Then 40 mL of anhydrous toluene and 2M aqueous potassium carbonate solution (8 mL) was added. The reaction mixture was heated to 90 °C with vigorous stirring until reaction completion by TLC analyses (~ 24 hours). The mixture was poured into water (100 mL) and extracted with methylene chloride. The organic layer was washed thrice with water, once with brine and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica gel with 20:1 hexane/ ethyl acetate to give product.

4, 7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (4a). Orange needles (yield: 88%); mp 75−77 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.97 (dd, 2H), 7.82 (d, *J*=1.8 Hz 2H), 7.04 (dd, 2H), 2.66 (t, *J*=7.5 Hz, 4H), 1.70 (m, 4H), 1.25-1.53 (m, 12H), 0.90 (t, *J*=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 153.02, 139.75, 128.42, 127.90, 127.21, 126.38,126.15,. 31.68, 29.70, 29.65, 29.03, 22.67, 14.14.

4, 7-bis(4-hexylthiophen-2-yl)- 2,1,3-benzoselenadiazole (4b). Purple solid (yield: 87%); mp 82−83 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.87 (d, *J*= 1.2 Hz, 2H), 7.71 (s, 2H), 7.04 (d, *J*=1.5 Hz, 2H), 2.68 (t, *J*=7.8 Hz, 4H), 1.68 (m, 4H), 1.20−1.43 (m, 12H), 0.90 (t, *J*=6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 158.19, 143.98, 139.29, 128.87, 127.42, 125.75,121.83,. 31.68, 30.56, 30.45, 29.04, 22.62, 14.10.

4,7-bis(4-hexylthiophen-2-yl)- 2,1,3-benzoxadiazole (4c). Yellow solid (yield: 92%); mp 78−79 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.95 (d, J= 1.2 Hz, 2H), 7.57 (s, 2H), 7.02 (d, *J*=1.2 Hz, 2H), 2.67 (t, *J*=7.6 Hz, 4H), 1.70 (m, 4H), 1.20−1.43 (m, 12H), 0.89 (t, *J*=7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 148.08, 145.28, 137.77, 30.40, 126.32, 122.31, 121.88, 31.90, 30.83, 30.65, 29.24, 22.85, 14.34.

General Bromination Procedure for 5a-5c. In a 100 mL flask, 1.00 eq of 4,7-di(4-hexyl-2-thienyl)-arene (**4a-4c**) was added into THF in nitrogen flow. After the solid dissolved completely, 2.10 eq N-bromosuccinimide (NBS) was added in portion wise. The reaction mixture was stirred at a room temperature for 5 hours. Then, hexane was added into the mixture, the white precipitate formed was

filtered off, the filtrate was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. Then residue was purified by column chromatography on silica gel with 1:2 hexane/ methylene chloride to give product.

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (5a). Red solid (yield: 94%); mp 101-103 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.75 (s, 2H), 7.71 (s, 2H), 2.63 (t, *J*=7.2 Hz, 4H), 1.67 (m, 4H), 1.33−1.40 (m, 12H), 0.89 (t, *J*=7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 152.19, 143.01, 138.46, 128.03, 125.25, 124.80, 111.59, 31.62, 29.74, 29.67, 28.96, 22.64, 14.11. MS (FAB): m/z [M+] 626; calcd m/z [M+] 626.53. Element Anal. Calcd for $C_{26}H_{30}Br_2N_2S_3$: C, 49.84; H, 4.83; N, 4.47. Found: C, 49.62; H, 5.02; N, 4.62.

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3- benzoselenadiazole (5b). Purple solid (yield: 96%); mp 92-94 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.65 (s, 2H), 7.64 (s, 2H), 2.62 (t, *J*=7.2 Hz, 4H), 1.67 (m, 4H), 1.33−1.42 (m, 12H), 0.90 (t, *J*=6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 157.71, 142.62, 138.73, 127.63, 126.75, 124.93, 112.19, 31.62, 29.74, 29.67, 28.96, 22.64, 14.11. MS (FAB): m/z [M+] 674; calcd m/z [M+] 673.43.Element Anal. Calcd for $C_{26}H_{30}Br_2N_2S_2Se$: C, 46.37; H, 4.49; N, 4.16. Found: C, 46.78; H, 5.14; N, 4.33.

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3- benzoxadiazole (5c). Orange solid (yield: 93%); mp 108−110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.77 (s, 2H), 7.38 (s, 2H), 2.60 (t, *J*=7.2 Hz, 4H), 1.62 (m, 4H), 1.33−1.42 (m, 12H), 0.90 (t, *J*=6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 147.42, 143.88, 137.08, 129.71, 125.68, 121.35, 111.56, 31.59, 29.66, 29.64, 28.94, 22.60, 14.10. MS (FAB): m/z [M+] 610; calcd m/z [M+] 610.47.Element Anal. Calcd for $C_{26}H_{30}Br_2N_2OS_2$: C, 51.15; H, 4.95; N, 4.59. Found: C, 51.30; H, 5.22; N, 4.27.

General Synthetic Procedure for Bis-terpyridyl Ligands (M1-M3). M1-M3 were prepared via Stille coupling reaction using tetrakis(triphenylphosphine)palladium as a catalyst. In a flame dried two-neck flask, 1.00 eq of dibromo compounds (**5a-5c**) and 2.50 eq of compound **2** in toluene were degassed

with Argon. Then, 0.03 eq $Pd(PPh_3)_4$ were added and refluxed for 2 days. The reaction mixtures were cooled to room temperature, and solvents were removed by reduced pressure. After removal of the solvents, the product was precipitated from methanol. Further purification was achieved by column chromatography on alumina with chloroform as an eluant to give the products.

M1. According to the above-mentioned general procedure, **M1** was obtained as a purple solid (yield: 68%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.77 (d, *J*=4.2 Hz, 4H), 8.63 (m, 8H), 7.91 (s, 2H), 7.85 (dd, *J*=7.8 Hz, *J*=1.8Hz, 4H), 7.72 (S, 2H), 7.69 (d, *J*= 3.9 Hz, 2H), 7.35 (dd, *J*=7.8 Hz, *J*=1.8Hz, 4H), 7.22 (d, *J*=3.9 Hz, 2H), 2.87(t, *J*=6.9 Hz, 4H), 1.75 (m, 4H), 1.40-1.29 (m, 12H), 0.93(t, *J*=5.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 156.29, 149.43, 149.35, 143.29, 141.28, 138.26, 137.10, 132.95, 132.09, 130.91, 129.51, 128.83, 126.60, 125.47, 124.16, 121.54, 117.84, 116.94, 31.96, 30.69, 29.98, 29.55, 22.90, 14.36. MS (FAB): m/z [M+] 1096; calcd m/z [M+] 1095.49. Element Anal. Calcd for $C_{64}H_{54}N_8S_5$: C, 70.17; H, 4.97; N, 10.23; Found: C, 69.51; H, 5.26; N, 10.15.

M2. According to the above-mentioned general procedure, **M2** was obtained as a black solid (yield: 63%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.74 (d, *J* = 4.2 Hz, 4H), 8.61 (m, 8H), 7.85 (dd, *J* = 7.8 Hz, *J* =1.8Hz, 4H), 7.78 (s, 2H), 7.67 (d, *J* = 3.9 Hz, 2H), 7.62 (S, 2H), 7.35 (dd, *J* = 7.8 Hz, *J* =1.8Hz, 4H), 7.19 (d, *J* =3.6 Hz, 2H), 2.84 (t, *J* =6.9 Hz, 4H), 1.74 (m, 4H), 1.40-1.29 (m, 12H), 0.93(t, *J* = 5.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 158.41, 156.22, 149.31, 143.22, 141.15, 140.79, 138.44, 137.83, 137.05, 132.93, 130.51, 127.98, 126.54, 125.44, 124.11, 121.67, 117.84, 116.88, 31.99, 30.63, 29.98, 29.61, 22.93, 14.39. MS (FAB): m/z [M+] 1143; calcd m/z [M+] 1142.39. Element Anal. Calcd for $C_{64}H_{54}N_8S_4Se$: C, 67.29; H, 4.76; N, 9.81. Found: C, 66.77; H, 5.30; N, 9.63.

M3. According to the above-mentioned general procedure, **M3** was obtained as a dark purple solid (yield: 76%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.75 (d, *J* =4.2 Hz, 4H), 8.69 (m, 8H), 7.96 (s, 2H), 7.87 (dd, *J* = 7.2 Hz, *J* = 1.8Hz, 4H), 7.73 (d, *J* = 3.6 Hz, 2H), 7.50 (S, 2H), 7.37 (dd, *J* = 6.9 Hz, *J* = 1.2 Hz, 4H), 7.25 (d, *J* =3.9 Hz, 2H), 2.88(t, *J* =7.2 Hz, 4H), 1.78 (m, 4H), 1.40-1.29 (m, 12H), 0.93 (t, *J* =6.9

Hz, 6H), ^{13}C NMR ($CDCl_3$, 75 MHz, δ): 155.72, 148.96, 148.35, 143.10, 141.16, 138.10, 137.36, 133.05, 132.09, 130.68, 129.41, 128.63, 126.85, 125.28, 122.94, 121.61, 117.69, 116.97, 31.98, 30.60, 30.03, 29.60, 22.94, 14.38. MS (FAB): m/z [M+] 1078; calcd m/z [M+] 1078.33. Element Anal. Calcd for $C_{64}H_{54}N_8S_4O$: C, 71.21; H, 5.04; N, 10.38. Found: C, 70.75; H, 5.21; N, 10.11.

Reference

1. Gautrot, J. E.; Hodge, P.; Cupertio, D.; Helliwell, M. *New. J. Chem*. **2007**, 31, 1585-1593.
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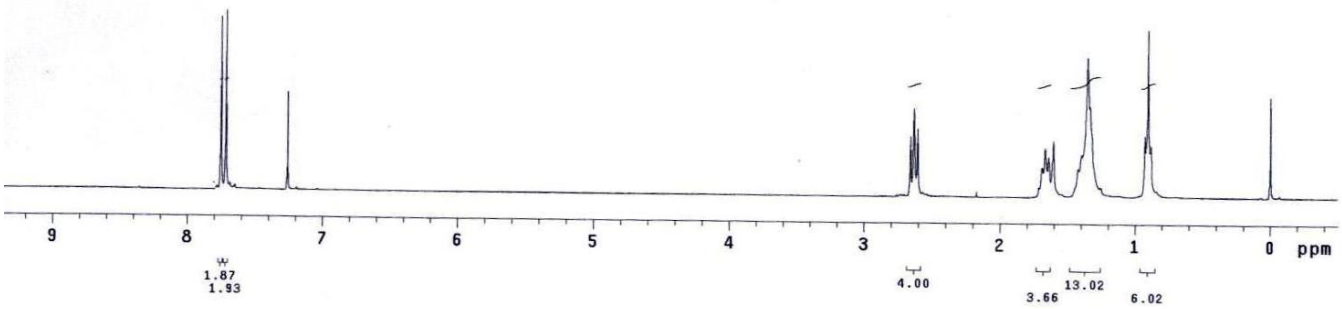


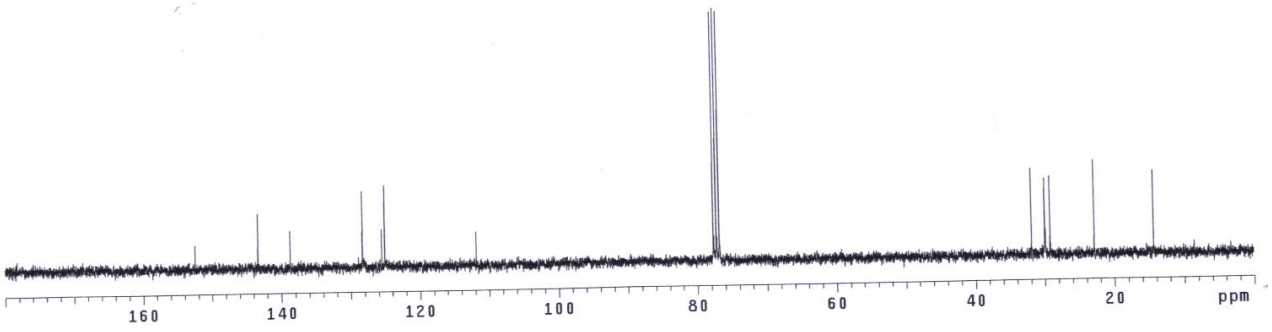


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of **5a**.

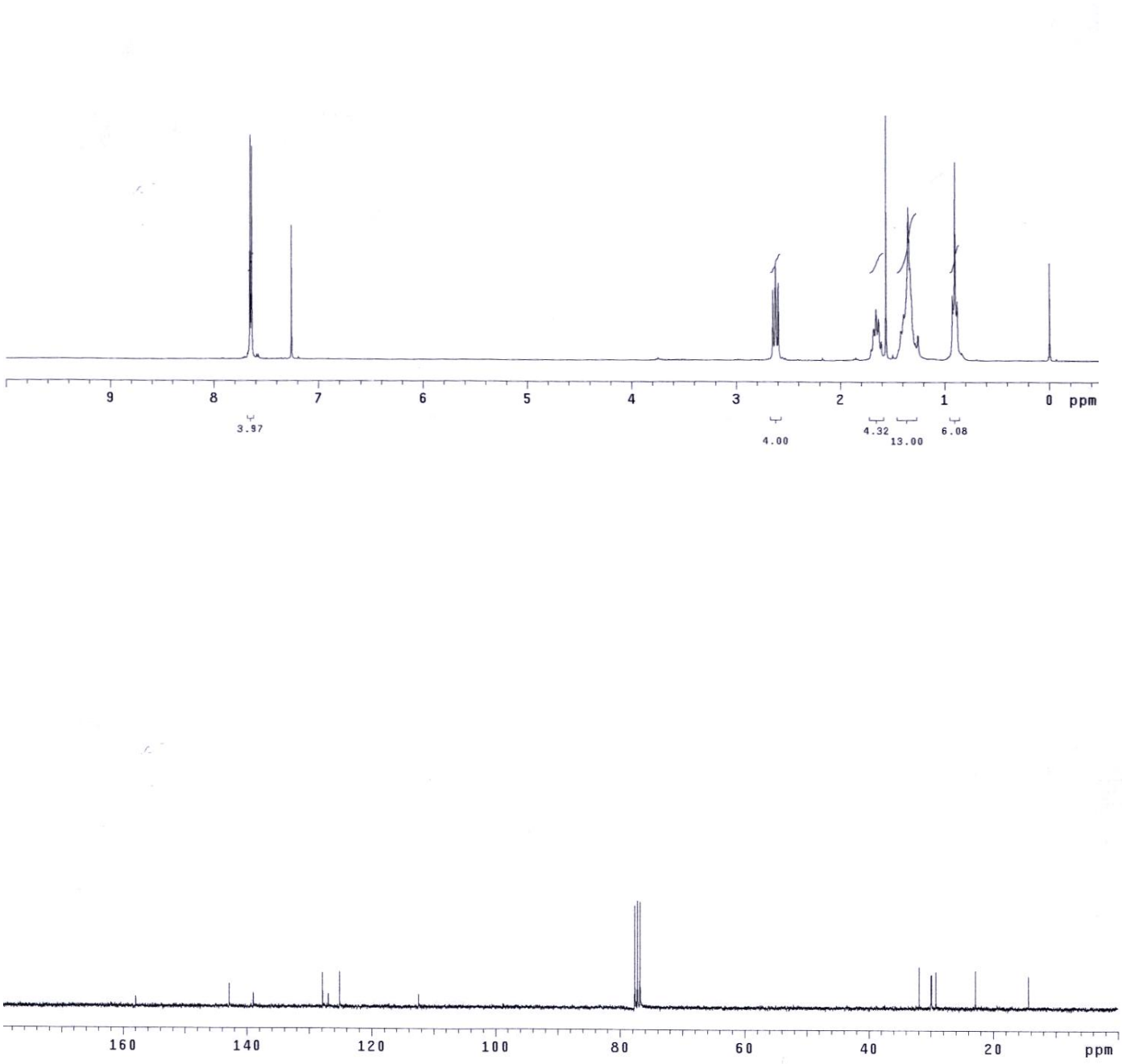


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **5b**.

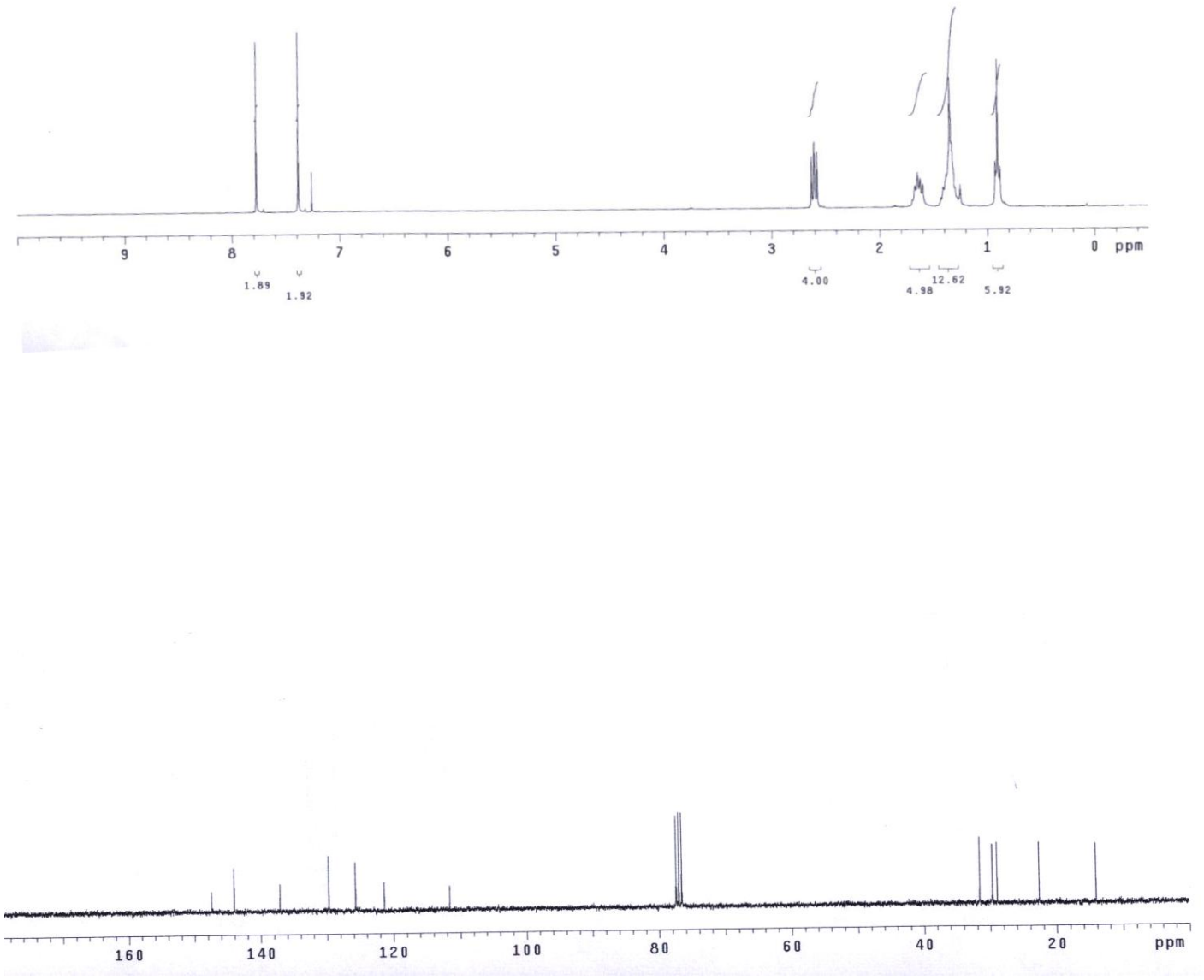
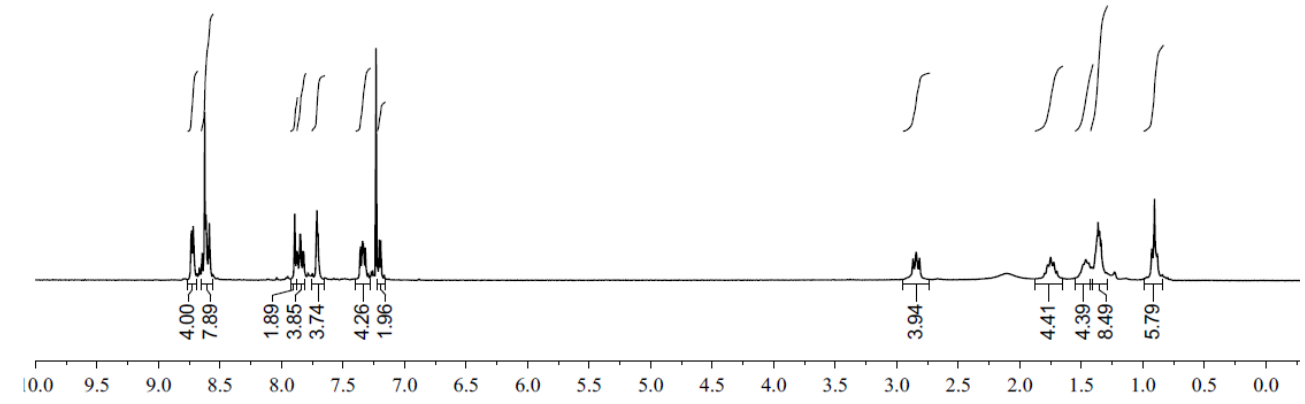
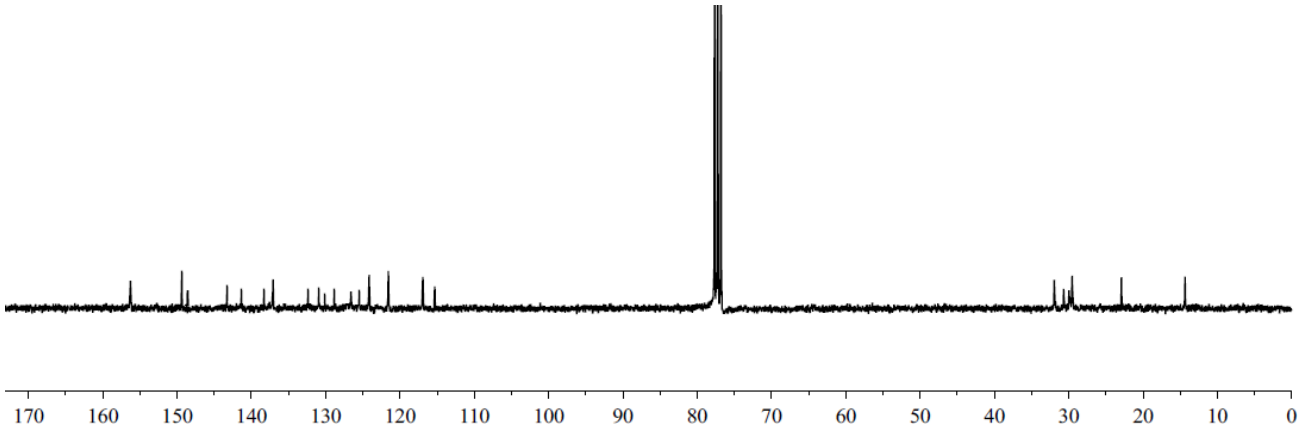


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **5c**.

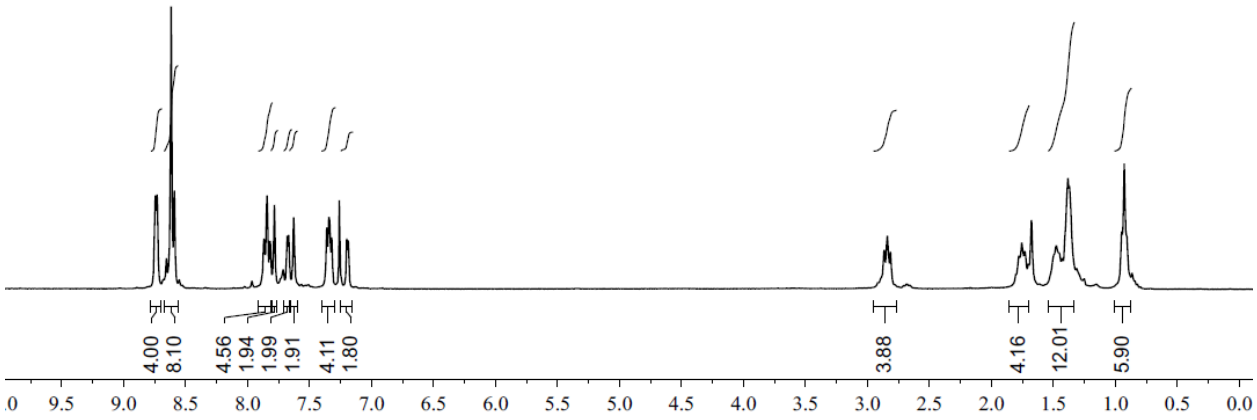


δ (ppm)



δ (ppm)

Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **M1**.



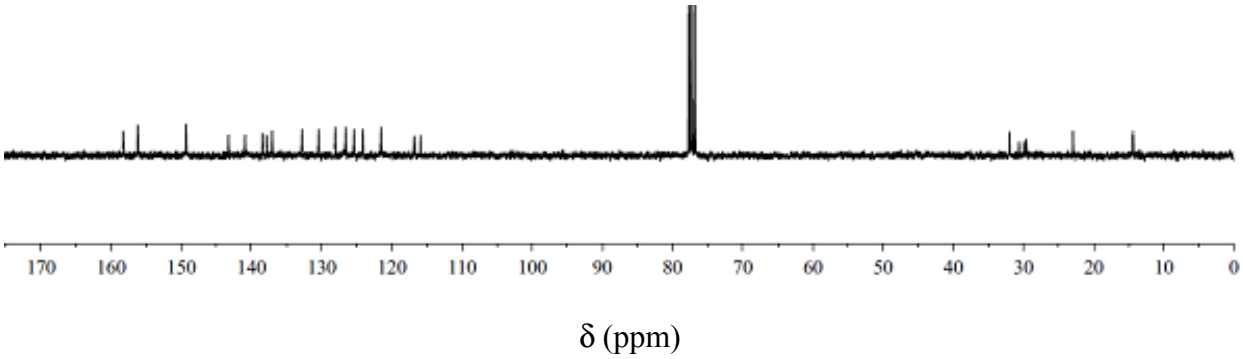
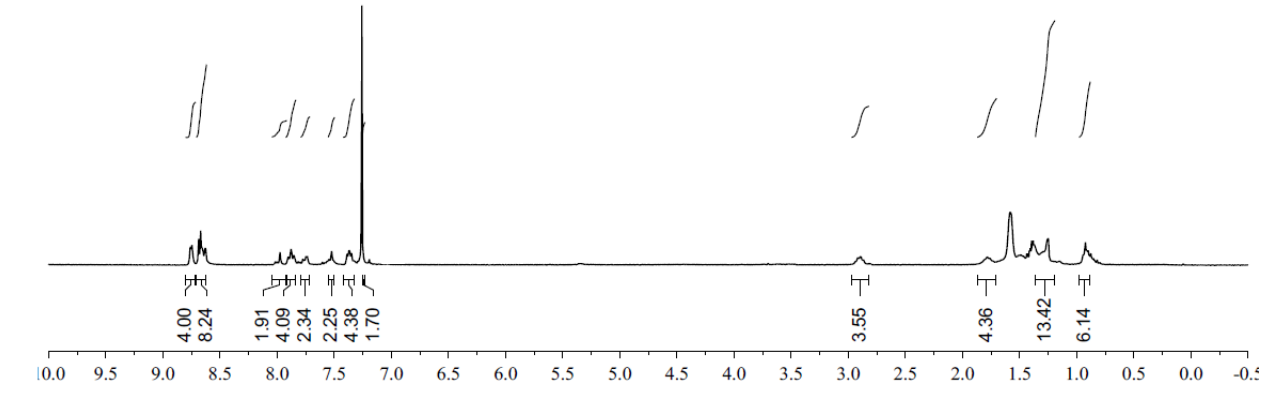


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **M2.**



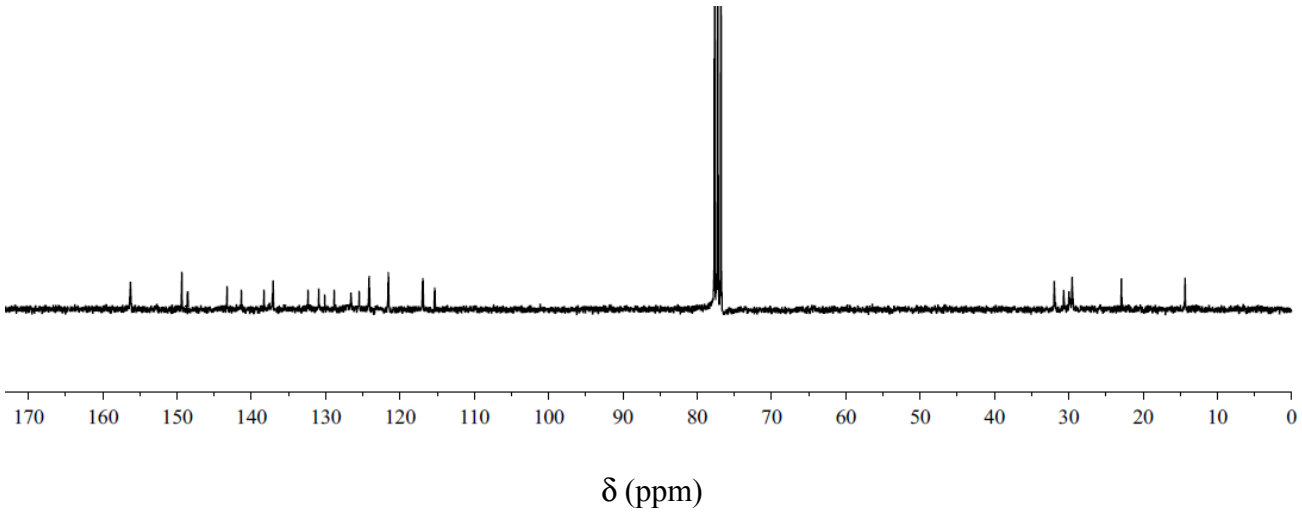


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **M3.**

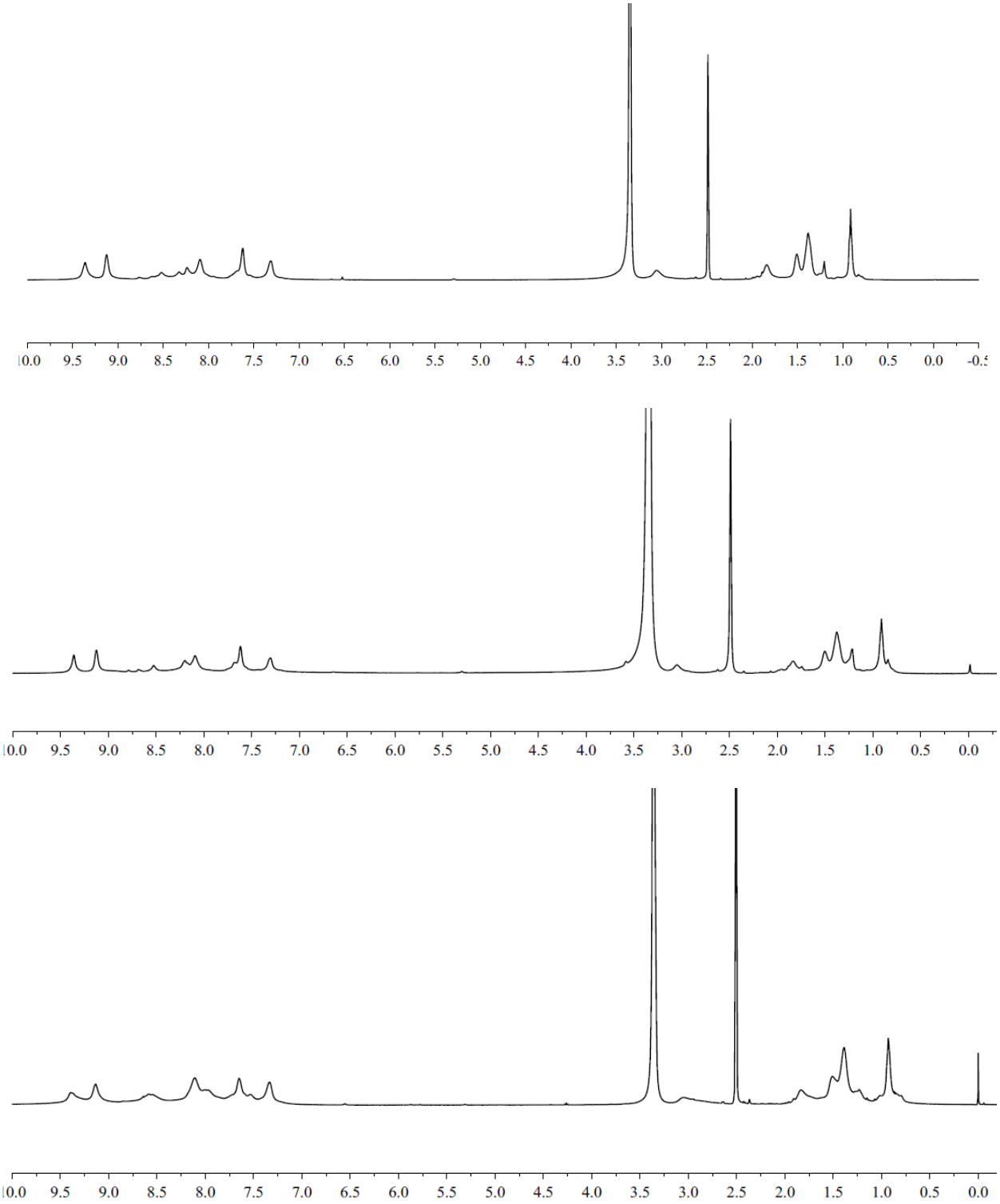


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **P1-P3.**

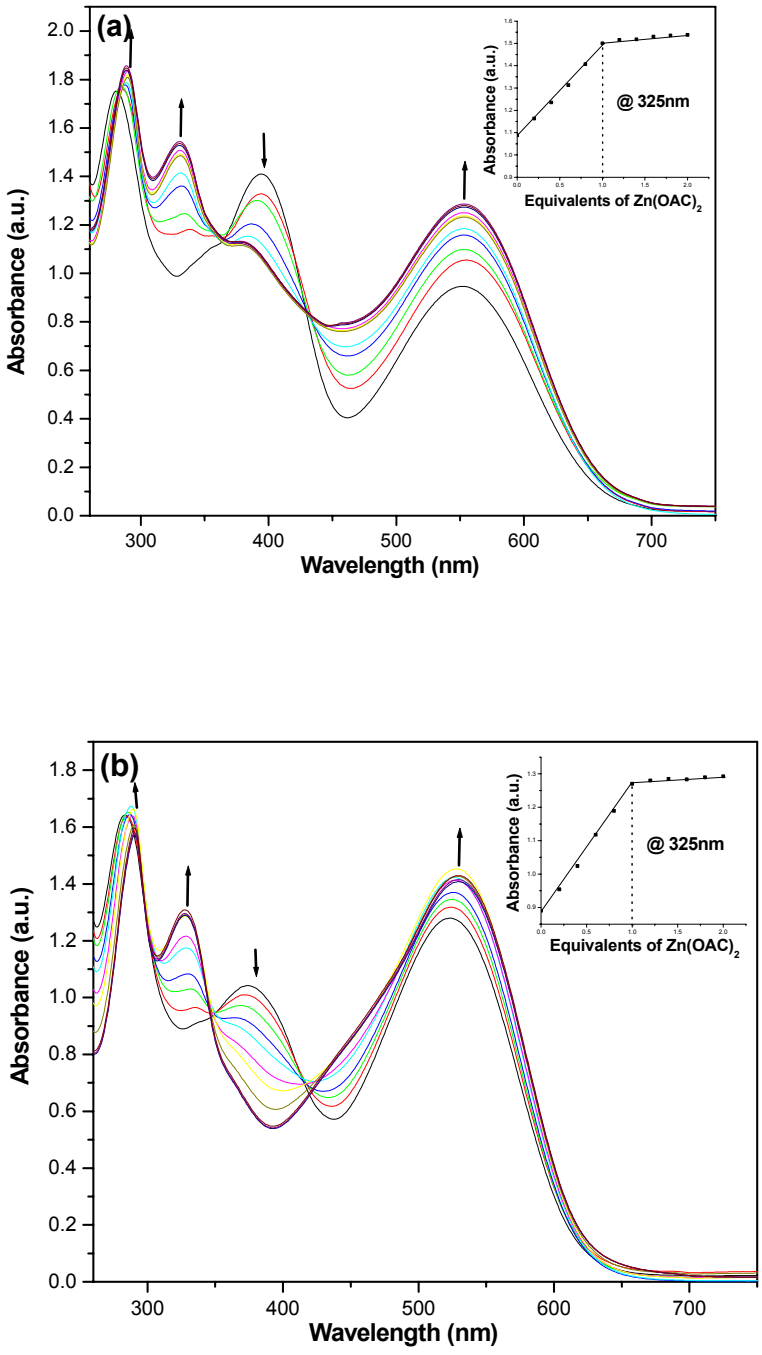


Figure S8. UV-vis absorption spectra acquired upon the titration of (a) **M2**, (b) **M3**, (in 2:8 v/v CH_3CN:$CHCl_3$) with $Zn(OAc)_2$ (in EtOH). The insets show the normalized absorption at 325 nm as a

function of Zn^{2+}:**M2-M3**, respectively.

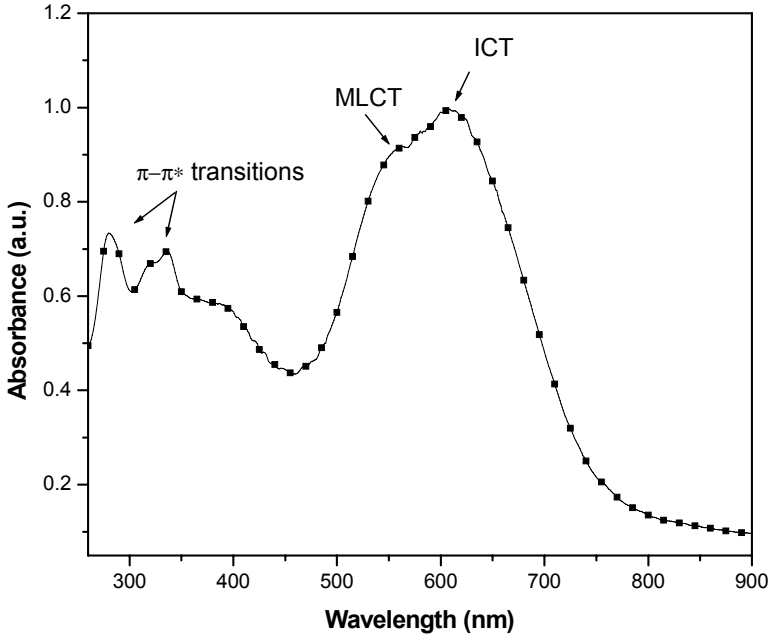


Figure S9. Representation of peaks in the normalized UV-vis spectra of metallo-polymer **P2**.

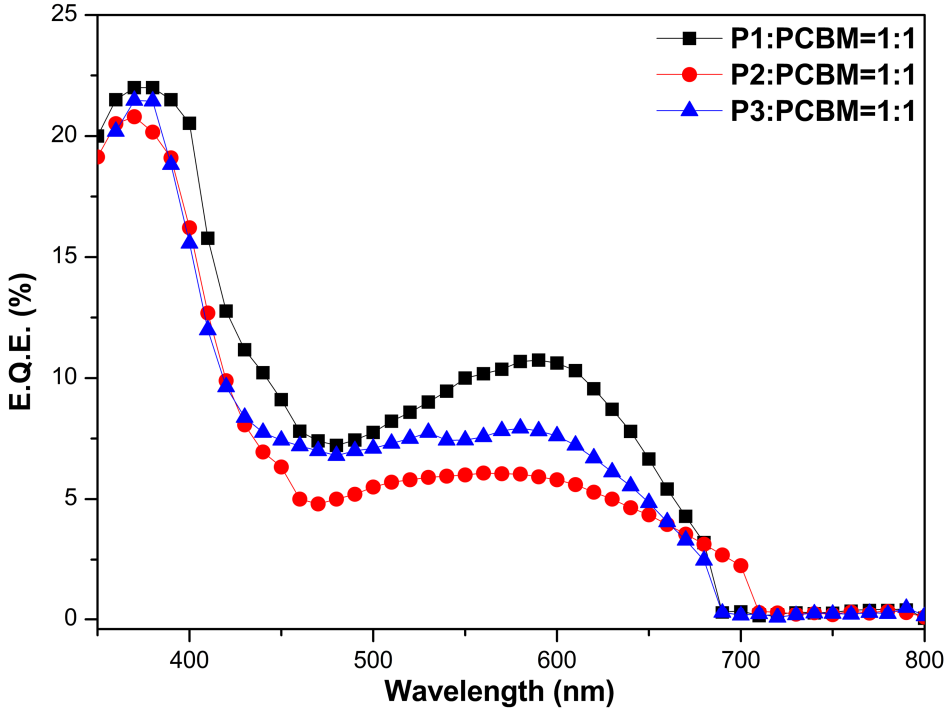


Figure S10. EQE curves of the PSC devices based on polymers **P1-P3**: PCBM (1:1 wt%).