New 3D Supramolecular Zn(II)–Coordinated Self-Assembled Organic Networks

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Experimental Section

General

All starting materials (chemicals) used in this project were purchased from commercial sources, e.g. Sigma Aldrich, Alfa Aesar et al. All reactions were carried out under inert N_2 atmosphere, unless otherwise stated. Analytical Thin Layer Chromatography (TLC) was performed on aluminum or Polyethylene terephthalate (PET) sheets pre-coated with silica gel or Aluminum Oxide (with fluorescent indicator 254 nm). Visualization was accomplished with UV light. Purification of reaction mixture using column chromatography was done on the silica gel 60.0 Geduran (Merck) or neutral Aluminum oxide (Brockmann Grade I, 58.0 angstroms).

Nuclear Magnetic Resonance (NMR) spectra (^{1}H and ^{13}C) were recorded on a Bruker Advance 400 spectrometer. The solvent used in the NMR characterization was deuterated-chloroform ($CDCl_3$), unless otherwise stated. Chemical shifts are given δ in units of ppm referenced to residual proton signals in $CDCl_3$. Coupling constants (J) are reported Hertz (Hz). NMR splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet;

AB, pair of doublet which is mirror image to each other; m, multiplet; and br, broad.

Mass spectra were recorded using Shimadzu Axima Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF) mass spectrometer. Molecular weight of polymers was determined by Gel Permeation Chromatography (GPC) method in chloroform, which was performed on Agilent GPC 1100 series model G1311A. In this method, column of PL gel 5.00 micron, MIXED-C was used and polystyrene was used as a standard.

Absorption spectra were taken on a UV-Vis recording spectrophotometer (Shimadzu UV-2501PC). Fluorescent measurements were taken on a spectrofluorophotometer (Shimadzu RF-5301PC).

Thermogravimetric Analysis (TGA) experiments were performed on TA TGA-Q500 with a dynamic heat rate (10 °C/min) under N_2 atmosphere (50.0 ml/min) in the temperature range 25–900 °C. Differential Scanning Calorimetry (DSC) measurements were performed on TA DSC-Q10 with dynamic heating and cooling rate (5 °C/min) under N_2 atmosphere (50.0 ml/min) in the temperature range 0–300 °C.

The electrochemical Cyclic Voltammetry (CV) was conducted on a frequency response analyzer (Solartron 1255B) with a sweep rate 100 mV/s by a platinum working electrode. Gold was used as counter electrode. Ag/Ag^+ was used as reference electrode and DCM or Acetonitrile containing $1.00 x 10^{-1}$ M tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6) was used as electrolyte in electrochemical measurements. Thin films were made by Spin Coater model P6700 series with 1.25 $x10^3$ rpm for 1.50 min.

XRD scanning (5° to 120°) was studied by Bruker AXS D8 Advance X-Ray diffractometer. Elemental Analysis and High Resolution $Electrospray^+$-Time-Of-Flight

Mass Spectra (HR ES^+-TOF MS) were done by Mr. Yang Yifan and Asst. Prof. So Cheuk Wai from School of Physical and Mathematical Sciences (Division of Chemistry & Biological Chemistry), Nanyang Technological University. Elemental Analysis was done on the EuroEA Elemental Analyser with calibration type of K-Factor. HR ES^+-TOF MS was done on the Water Q-TOF Premier Mass Spectrometer.

The porous properties of the networks were investigated by nitrogen adsorption at 77.3 K using ASAP Chemisorption Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corporation). Samples were degassed at 100 °C for 6 h under vacuum (1.00×10^{-5} bar) before analysis.

Synthesis and characterization

List of abbreviations

DCM = Dichloromethane

DI = Deionized

DMSO = Dimethyl sulfoxide

EA = Ethyl acetate

EtOH = Ethanol

MeOH = Methanol

NBS = N-Bromosuccinimide

NMP = N-Methyl-2-pyrrolidone

RBF = Round bottom flask

RT = Room temperature

$PdCl_2$(dppf) = [1,1-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)

$Pd(PPh_3)_4$ = Tetrakis(triphenylphosphine)palladium

$(Ph_3P)_2PdCl_2$ = Bis(triphenylphosphine)palladium(II) dichloride

THF = Tetrahydrofuran

Compounds **7** and **14** were made by literature procedure[1] whereas compounds **8** and **13** were made by literature procedure.[2]

Tetrakis(4-iodophenyl)methane (4). Tetraphenylmethane **3** (0.500 g, 1.56 mmol), I_2 (0.840 g, 3.30 mmol) and bis[(trifluoroacetoxy)iodo]benzene (1.55 g, 3.60 mmol) were dissolved in $CHCl_3$ (10.0 ml) in a RBF and the reaction mixture was heated at 55 °C until the colour of iodine disappeared. The reaction mixture was then concentrated under reduced pressure to remove solvent. Residual solid was washed with EtOH and acetone and purified by recrystallization from THF to give **4** as a white solid (0.430 g, 33.3%). **^{1}H NMR ($CDCl_3$):** δ 7.58 (d, *J* = 4.40 Hz, 2 H), 6.88 (d, *J* = 4.40 Hz, 2 H). **^{13}C NMR ($CDCl_3$):** δ 145.05, 137.08, 132.60, 92.44, 64.02.

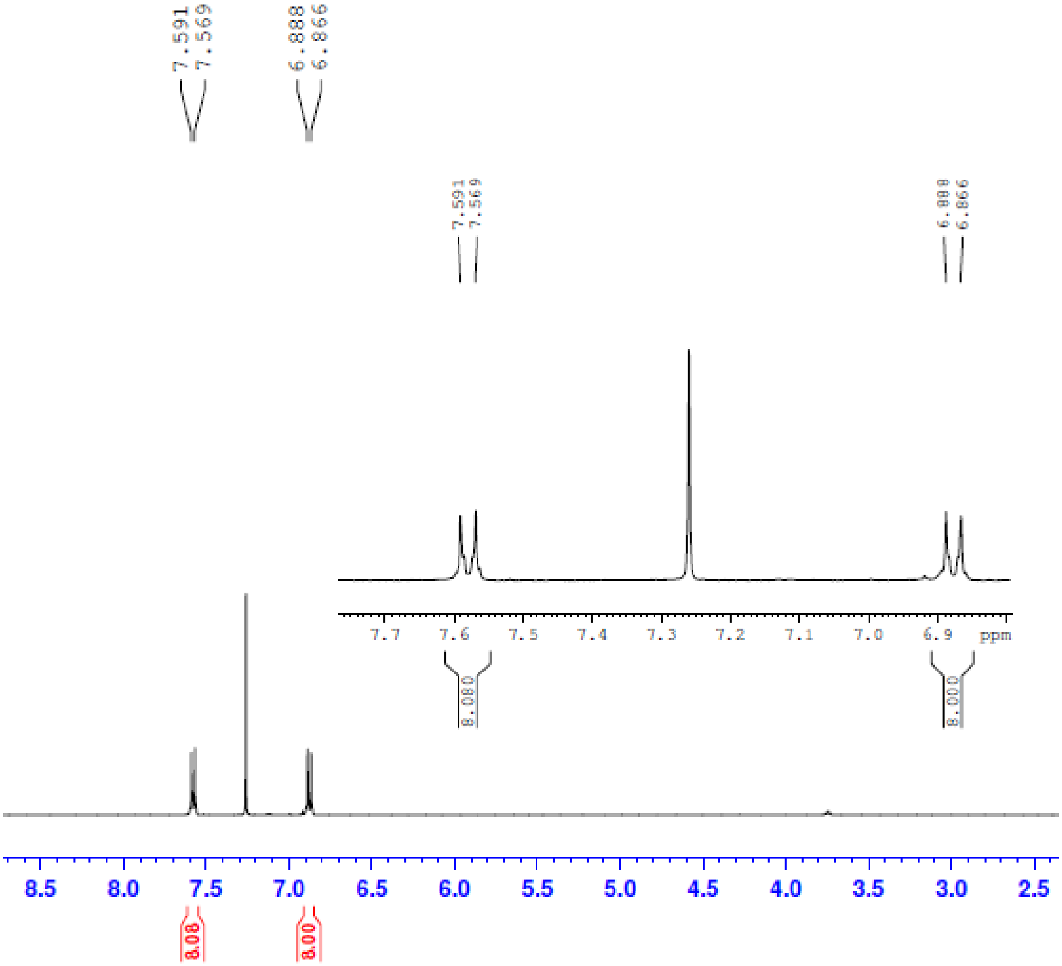


Figure A1 ^{1}H NMR spectrum of tetrakis(4-iodophenyl)methane **(4)**

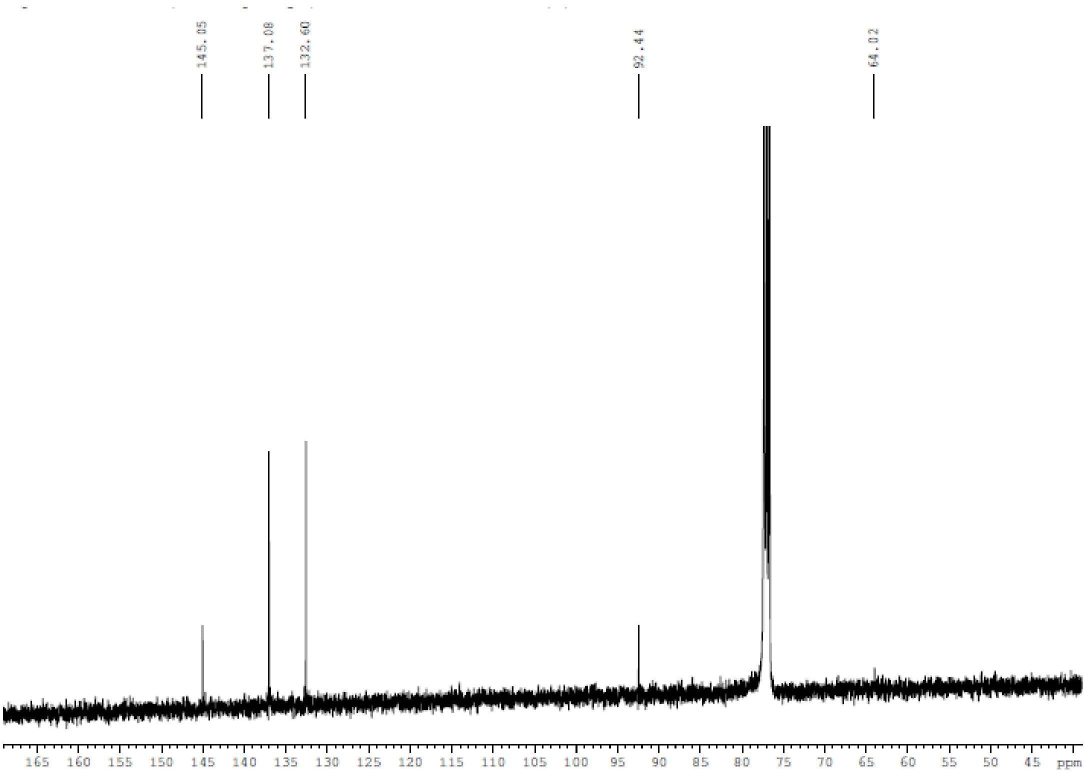


Figure A2 ^{13}C NMR spectrum of tetrakis(4-iodophenyl)methane **(4)**

Tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-phenyl)]methane (5). 4 (0.412 g, 0.500 mmol), bis(pinacolato)diborane (0.770 g, 3.00 mmol), potassium acetate (0.75 g, 7.50 mmol) and $PdCl_2$(dppf) (50.0 mg, 6.00×10^{-2} mmol) were dissolved in anhydrous DMSO (10.0 ml) and the reaction mixture was degassed. Reaction mixture was stirred at 80 °C for 12 h, cooled to RT, and then poured into ice water. The mixture was then extracted with $CHCl_3$ and water. The combined organic layers were dried over anhydrous $MgSO_4$. After the solvent was evaporated, the residue was washed with cold hexane. The solid residue was then recrystallized from MeOH-THF to afford **5** as a white solid (0.230 g, 60.0%). **^{1}H NMR ($CDCl_3$):** δ 7.65 (d, *J* = 8.40 Hz, 8 H), 7.27 (d, *J* = 8.40 Hz, 8 H), 1.31 (s, 48 H). **^{13}C NMR ($CDCl_3$):** δ 149.48, 134.14, 130.30, 83.72, 67.69, 24.86.

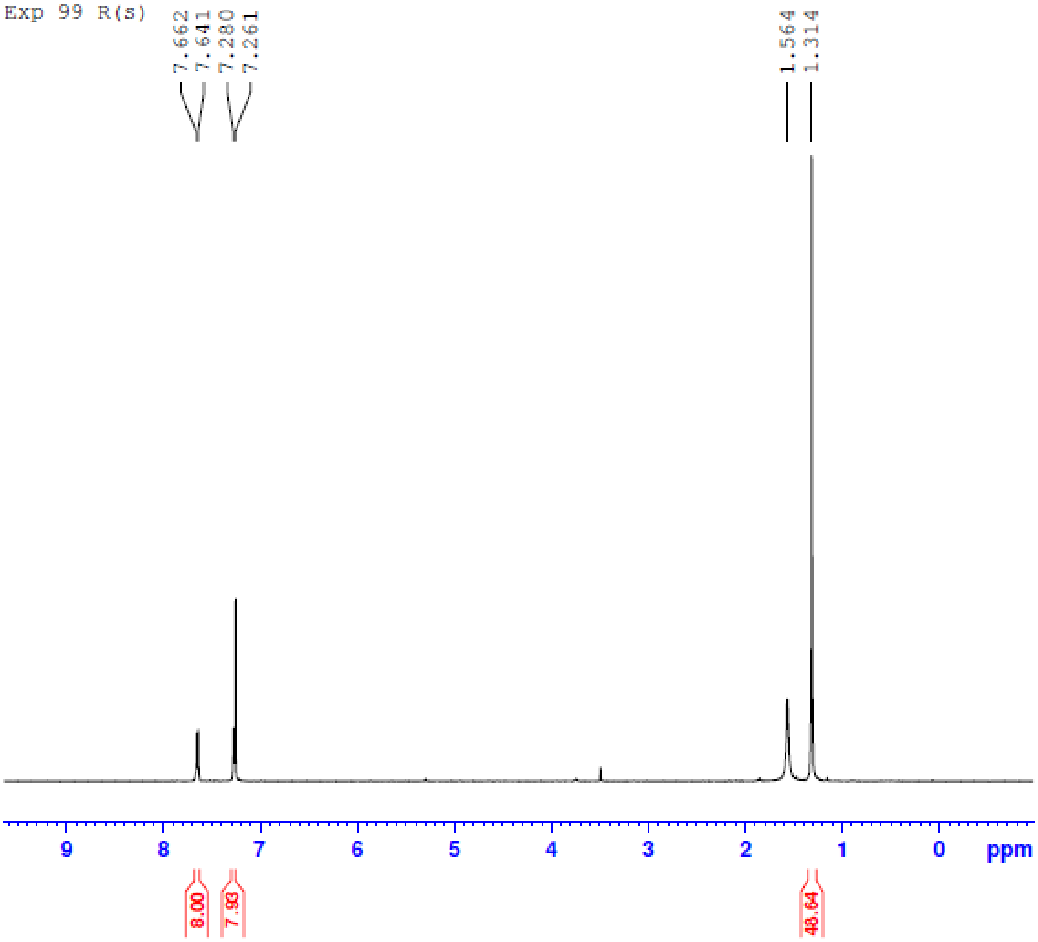


Figure A3 ^{1}H NMR of Tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-phenyl)]methane **(5)**

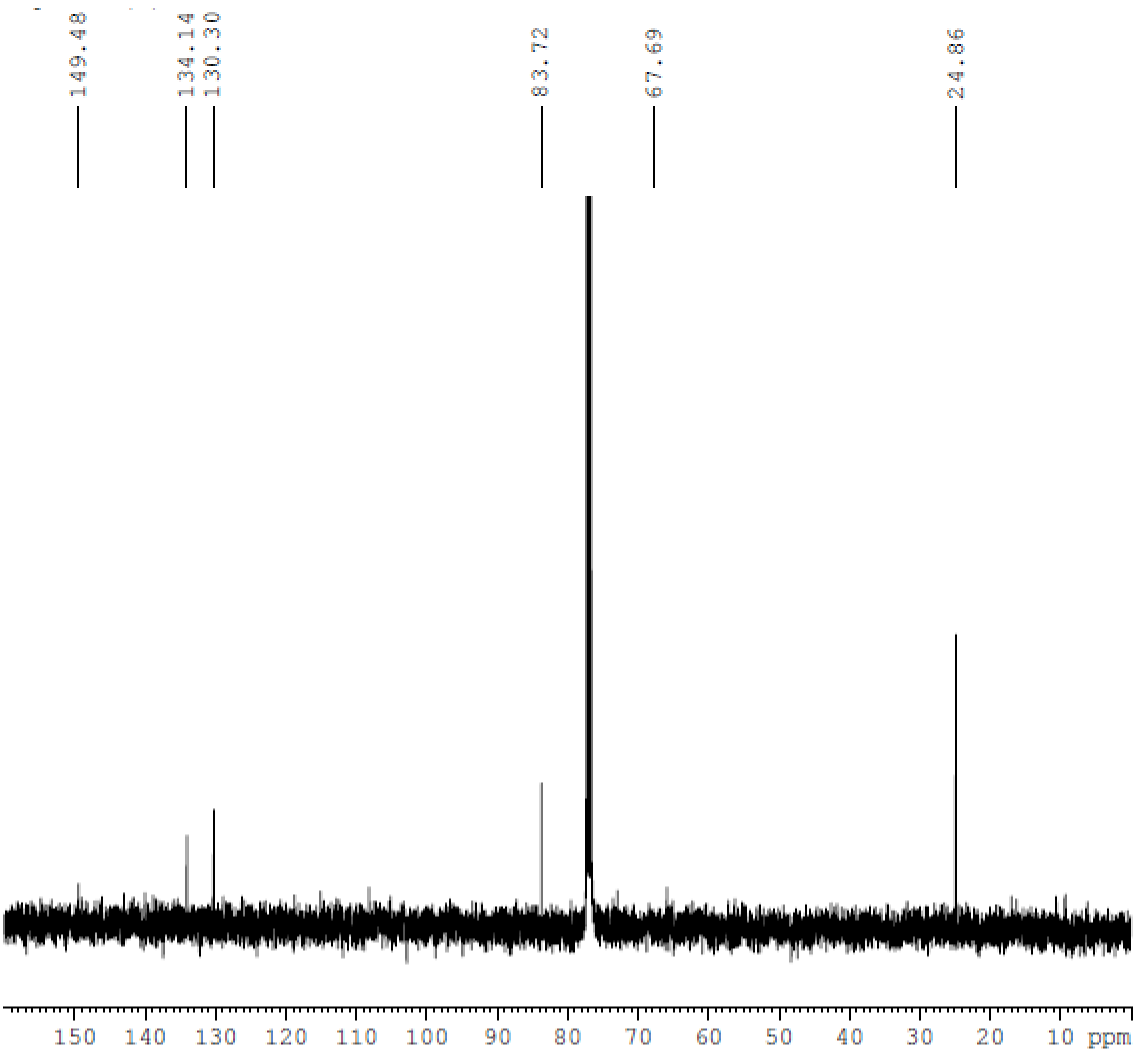


Figure A4 ^{13}C NMR of Tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-phenyl)]methane **(5)**

4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine (6). A RBF which contained Pd(dppf)Cl$_2$ (2.10 g, 2.58 mmol), potassium acetate (7.60 g, 77.4 mmol), bis(pinacolato)diboron (7.20 g, 28.4 mmol) and 4'-(4-bromophenyl)-2,2':6'2''-terpyridine[3] (10.0 g, 25.8 mmol) was degassed thoroughly with N$_2$ before adding DMSO (250 ml). The reaction mixture was then stirred at 80 °C overnight. After cooling down to RT, the reaction mixture was poured into ice water to form precipitate. The solid of precipitate was collected through filtration, followed by extraction in DCM and water. The aqueous layer was purple at this stage, presumably due to complexation of some terpyridine to ions released on decomposition of the catalyst. The DCM layer was then dried over $MgSO_4$ and concentrated using a rotary evaporator. Through column chromatography on silica gel with 30% EA in hexane followed by recrystallization in MeOH–THF, **6** was obtained as a white solid (6.27 g, 60.0%). **^{1}H NMR ($CDCl_3$):** δ 8.80 (s, 2 H), 8.77 (d, *J* = 4.40 Hz, 2 H), 8.72 (d, *J* = 4.00 Hz, 2 H), 7.95–7.91 (m, 6 H), 7.40 (t, *J* = 6.00 Hz, 2 H), 1.38 (s, 12 H). **^{13}C NMR ($CDCl_3$):** δ 155.52, 155.28, 150.39, 148.53, 140.60, 137.74, 135.43, 126.62, 124.10,121.86, 119.42, 83.99, 24.92. **MALDI TOF MS:** m/z 436 (M+1H).

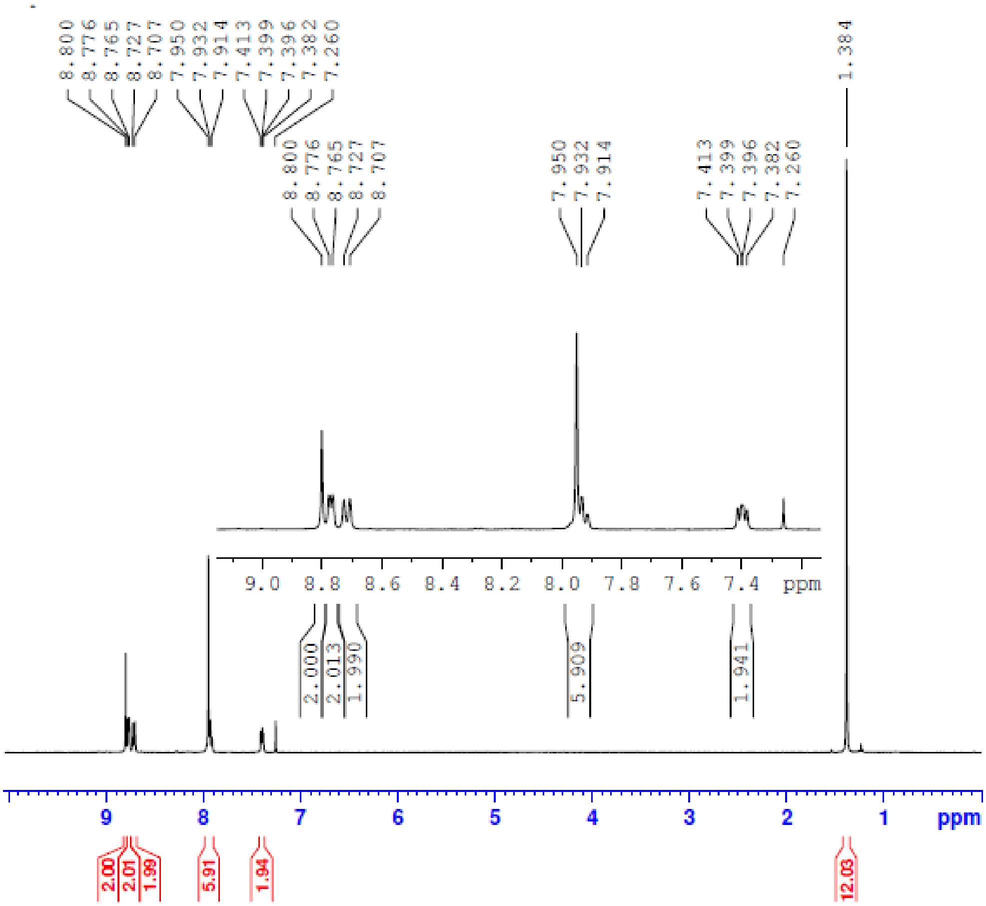


Figure A5 ^{1}H NMR of 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine **(6)**

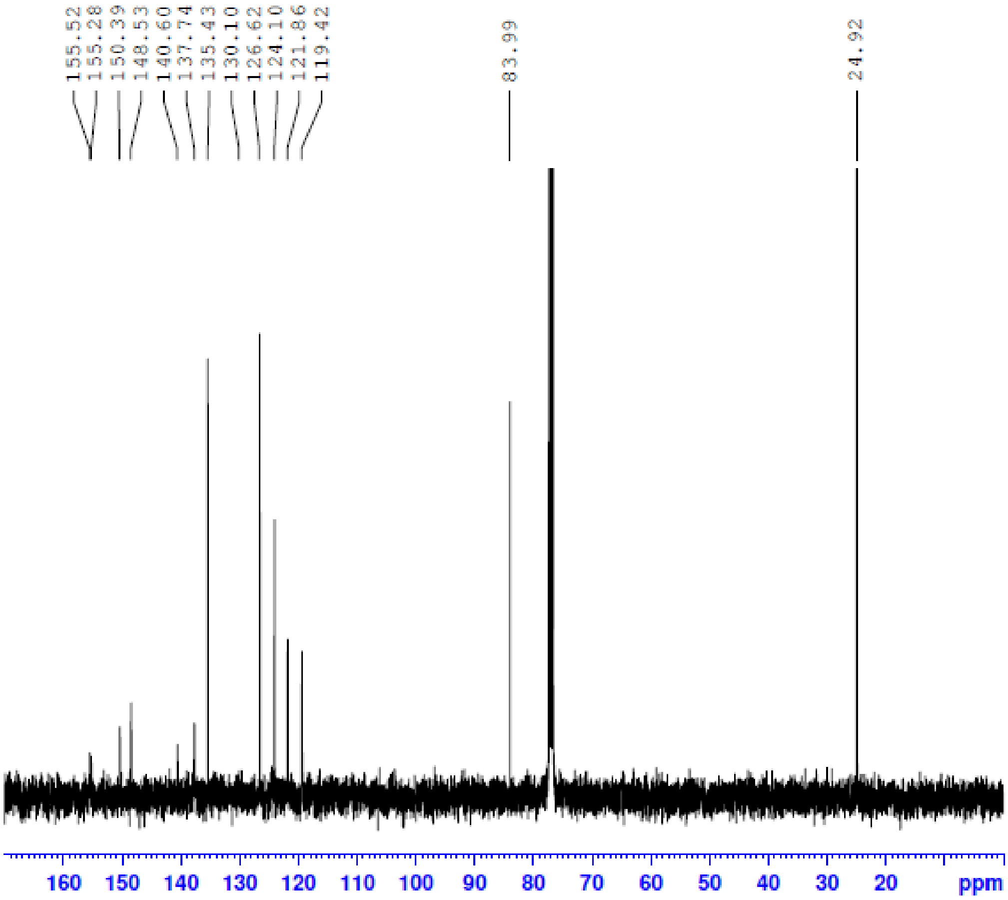
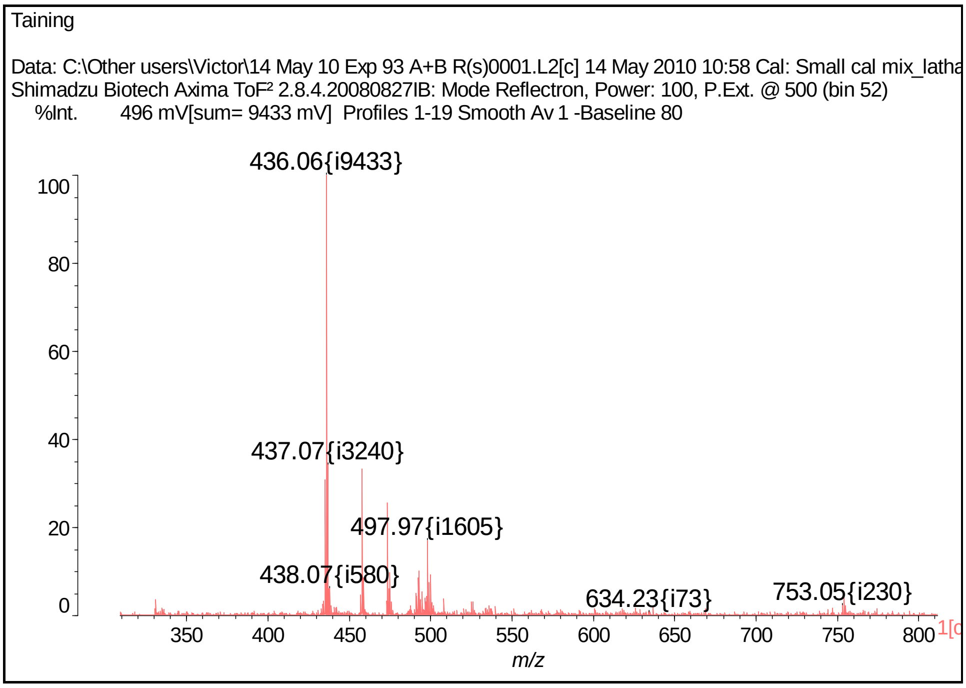


Figure A6 ^{13}C NMR of 4'-(4-Pinacolatoboronphenyl)-2,2':6',2"-terpyridine **(6)**


Taining

Data: C:\Other users\Victor\14 May 10 Exp 93 A+B R(s)0001.L2[c] 14 May 2010 10:58 Cal: Small cal mix_latha
Shimadzu Biotech Axima ToF² 2.8.4.20080827IB: Mode Reflectron, Power: 100, P.Ext. @ 500 (bin 52)
%Int. 496 mV[sum= 9433 mV] Profiles 1-19 Smooth Av 1 -Baseline 80

Figure A7 MALDI-TOF mass spectra of 4'-(4-Pinacolatoboronphenyl)-2,2':6',2"-terpyridine **(6)**

Monoadduct of 4’-(4-Pinacolatoboronphenyl)-2,2’:6’,2”-terpyridine with 4,7-dibromo-5,6-bis(dodecyloxy)benzo[c]thiadiazole (9). **7** (0.300 g, 0.460 mmol), **6** (8.00×10^{-2} g, 0.180 mmol) and $Pd(PPh_3)_4$ (2.10×10^{-2} g, 1.80×10^{-2} mmol) were put into a RBF and degassed using N_2. Aqueous K_2CO_3 (2.00 M, 10.0 ml) and THF (30.0 ml) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 80 °C overnight. The reaction mixture was cooled to RT and THF was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on alumina eluting with 10% EA in hexane. **9** was obtained as a light purple solid (80.0 mg, 50.0%). **^{1}H NMR ($CDCl_3$):** δ 8.92 (s, 2 H), 8.80–8.79 (m, 4 H), 8.13 (d, *J* = 8.00 Hz, 2 H), 7.99 (t, *J* = 7.60 Hz, 2 H), 7.85 (d, *J* = 8.00 Hz, 2 H), 7.44 (t, *J* = 6.40 Hz, 2 H), 4.26 (t, *J* = 6.80 Hz, 2 H), 3.85 (t, *J* = 6.80 Hz, 2 H), 1.62–1.51 (m, 4 H), 1.62–1.12 (br, 36 H), 0.880 (t, *J* = 7.20 Hz, 3 H), 0.820 (t, *J* = 7.20 Hz, 3 H). **^{13}C NMR ($CDCl_3$):** δ 155.96, 155.77, 154.63, 153.34, 151.32, 151.24, 149.86, 148.93, 138.18, 137.17, 134.00, 131.31, 127.09, 124.32, 123.94, 121.52, 119.02, 105.75, 75.01, 74.91, 31.95, 31.88, 29.65, 29.39, 29.32, 26.10, 25.91, 22.71, 22.67, 14.15, 14.11. **MALDI TOF MS**: m/z 896.45 (M+5). **HR ES$^+$-TOF MS**: calculated m/z: 890.4042 (M^+), found: m/z 890.4017 (M^+).

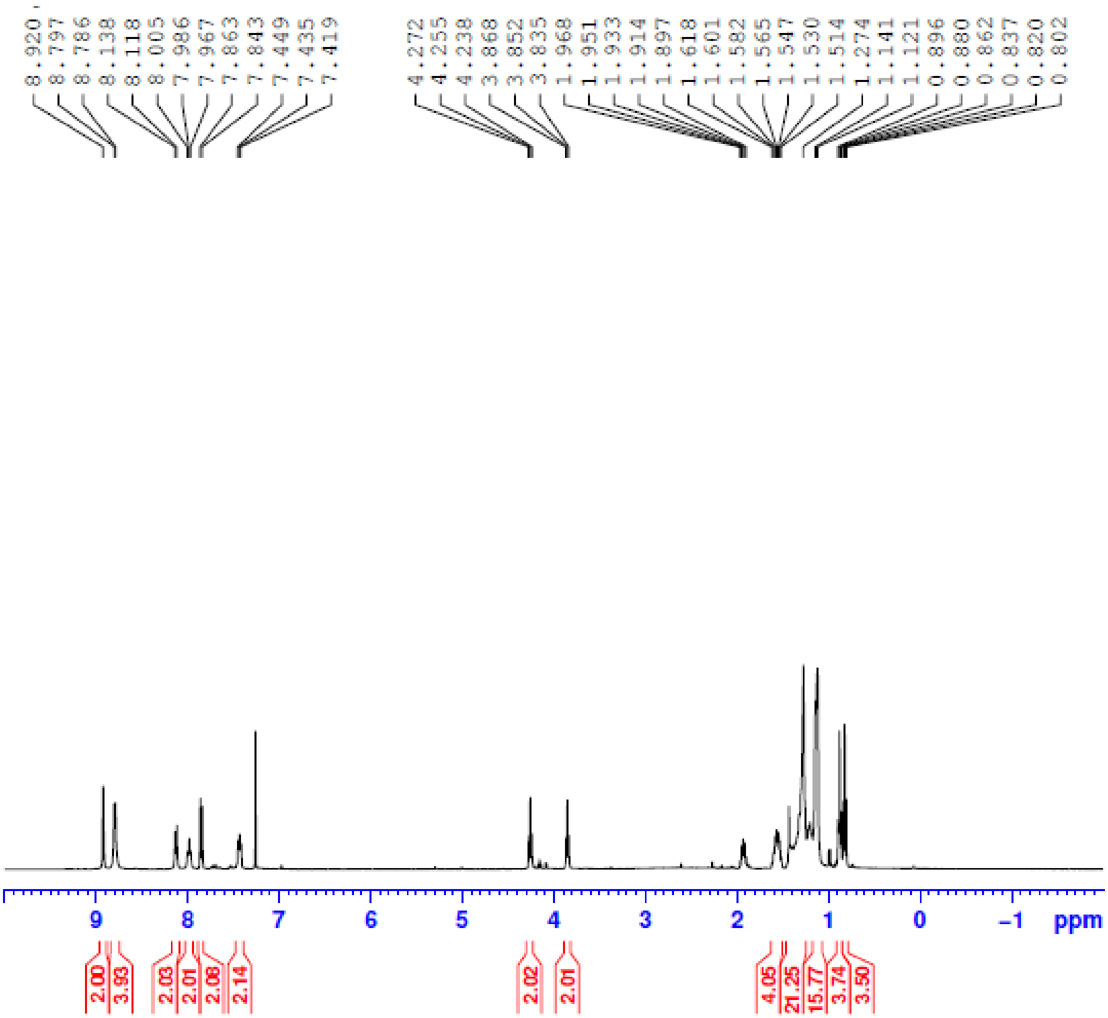


Figure A8 ^{1}H NMR spectrum of **9**

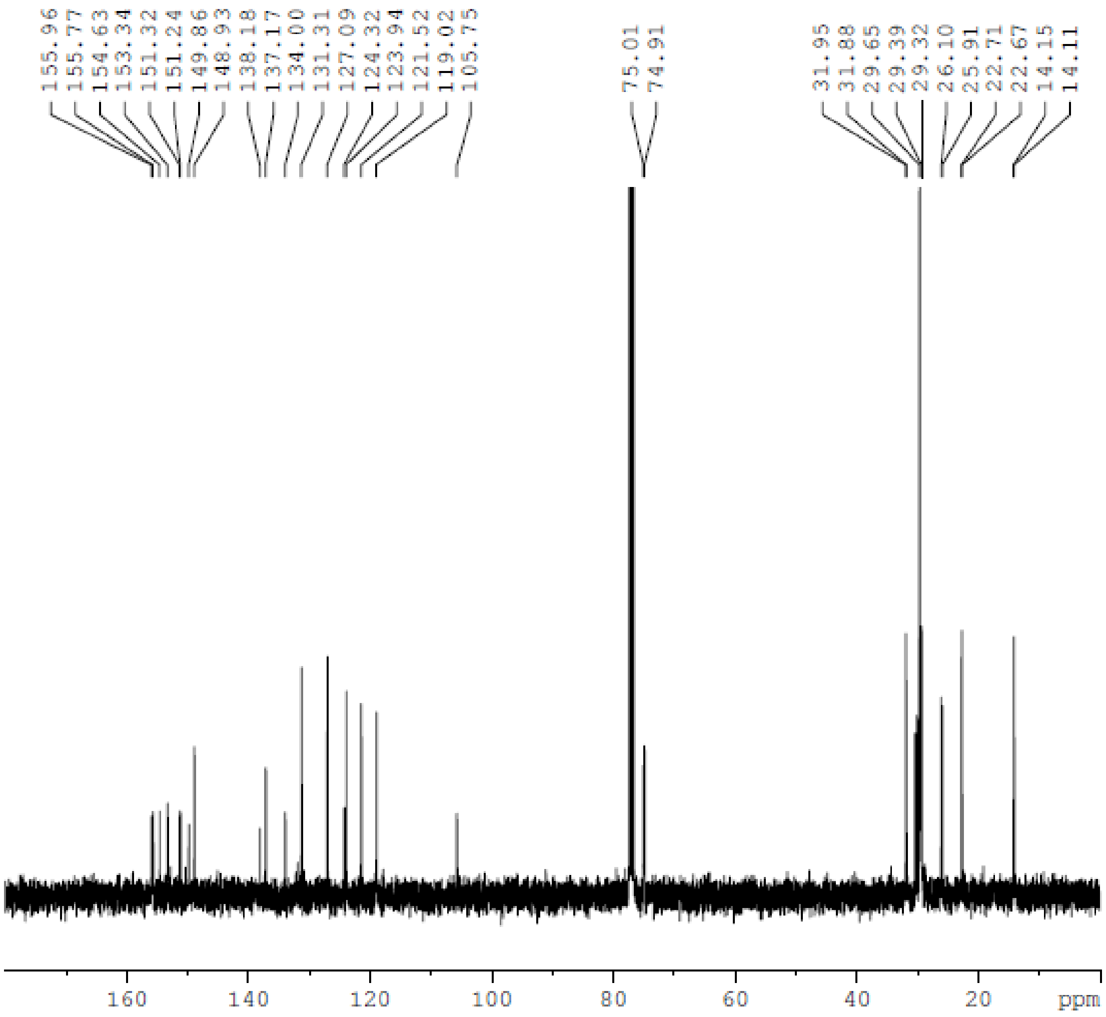


Figure A9 ^{13}C NMR spectrum of **9**

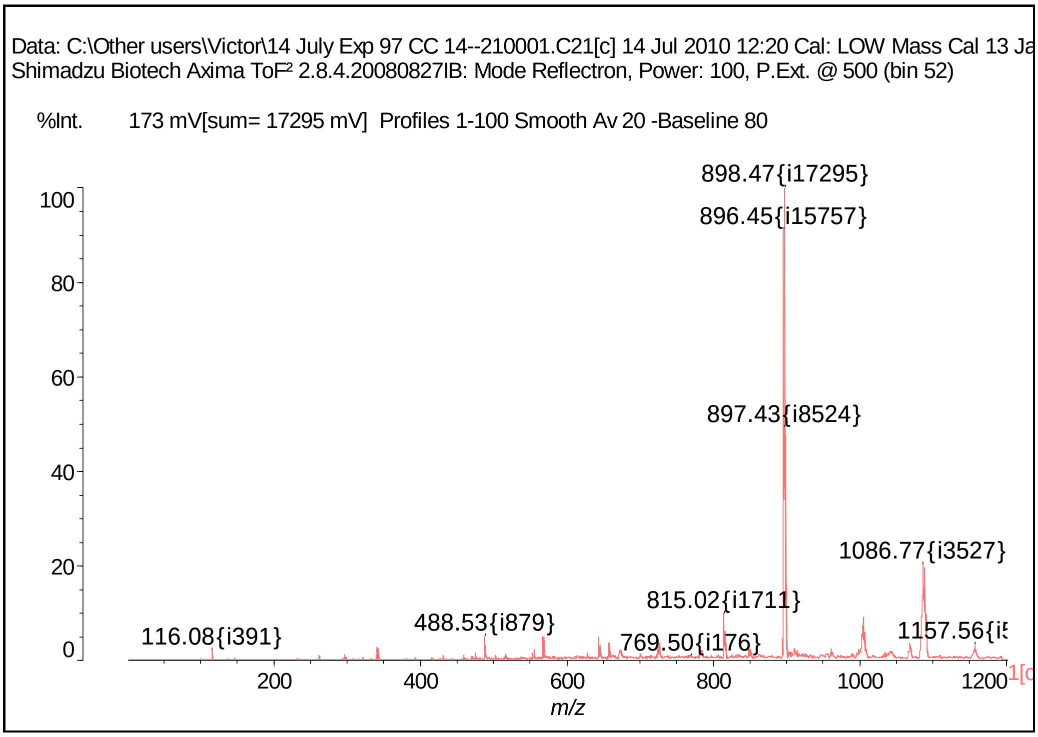


Figure A10 MALDI MS of **9**

Monoadduct of 4’-(4-Pinacolatoboronphenyl)-2,2’:6’,2”-terpyridine with 1,4-dibromo-2,5-bis(dodecyloxy)benzene (10). **8** (0.420 g, 0.690 mmol), **6** (0.100 g, 0.230 mmol), and $Pd(PPh_3)_4$ (1.60×10^{-2} g, 1.40×10^{-2} mmol) were put into RBF and degassed using N_2. Aqueous K_2CO_3 (2.00 M, 10.0 ml) and THF (30.0 ml) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 80 °C overnight. The reaction mixture was cooled to RT and THF was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on alumina eluting with 10% EA in hexane. **10** was obtained as a white solid (140 mg, 50.0%). **^{1}H NMR ($CDCl_3$):** δ 8.91 (s, 2 H), 8.80 (d, *J* = 4.40 Hz, 2 H), 8.77 (d, *J* = 4.00 Hz, 2 H), 8.04–7.98 (m, 4 H), 7.70 (d, *J* = 8.40 Hz, 2 H), 7.45 (t, *J* = 6.80 Hz, 2 H), 4.04 (t, *J* = 6.40 Hz, 2 H), 3.90 (t, *J* = 6.40 Hz, 2 H), 1.74–1.67 (m, 2 H), 1.55–1.47 (m, 2 H), 1.47–1.20 (br, 36 H), 0.877 (m, 6 H). **^{13}C NMR ($CDCl_3$):** δ 155.19, 150.51, 150.28, 149.99, 148.19, 139.05, 138.24, 136.44, 130.13, 130.06, 127.02, 125.53, 124.22, 122.07, 119.46, 118.48, 116.28, 111.77, 70.38, 69.78, 31.93, 31.88, 29.66, 29.61, 29.37, 29.33, 29.26, 29.19, 26.03, 22.70, 22.67, 14.13, 14.11. **MALDI TOF MS**: m/z 832.19 (M), 755.06 (M-Br). **HR ES$^+$-TOF MS**: calculated m/z: 832.4417 (M^+), found: m/z 832.4398 (M^+).

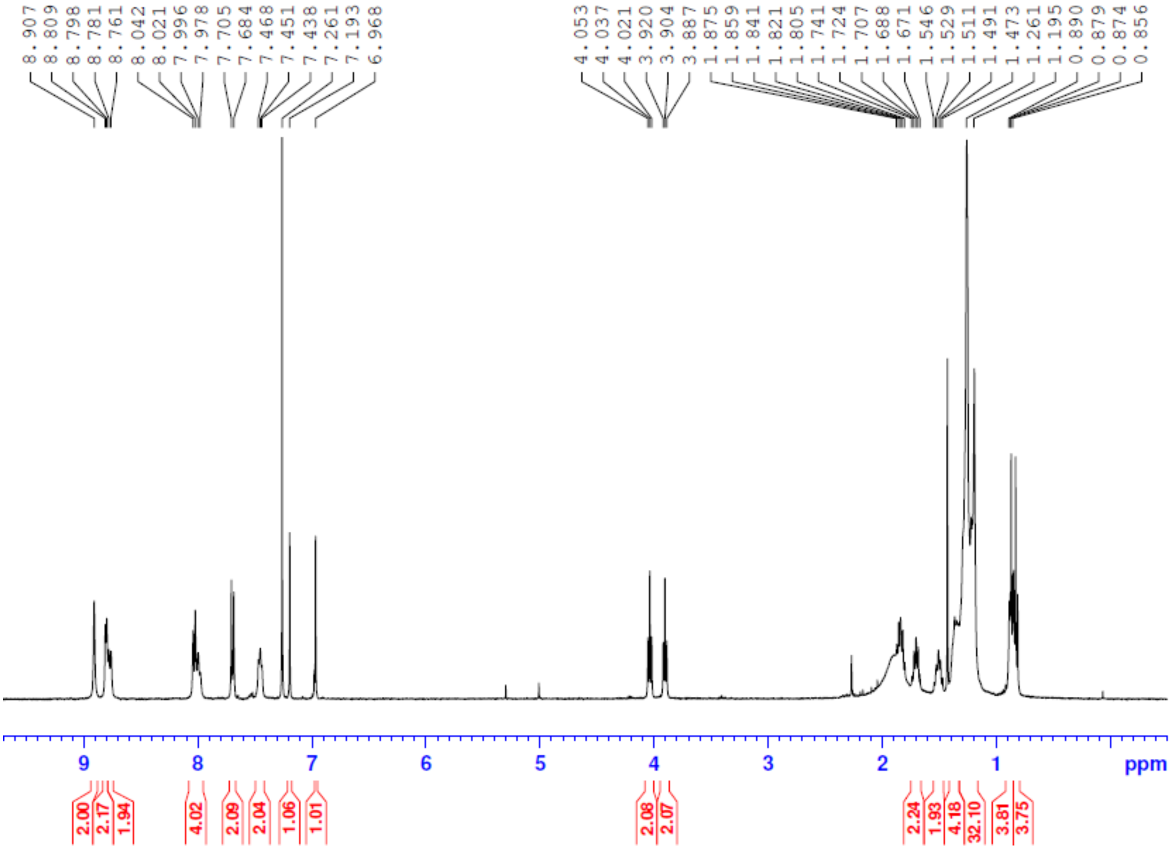


Figure A11 ^{1}H NMR spectrum of **10**

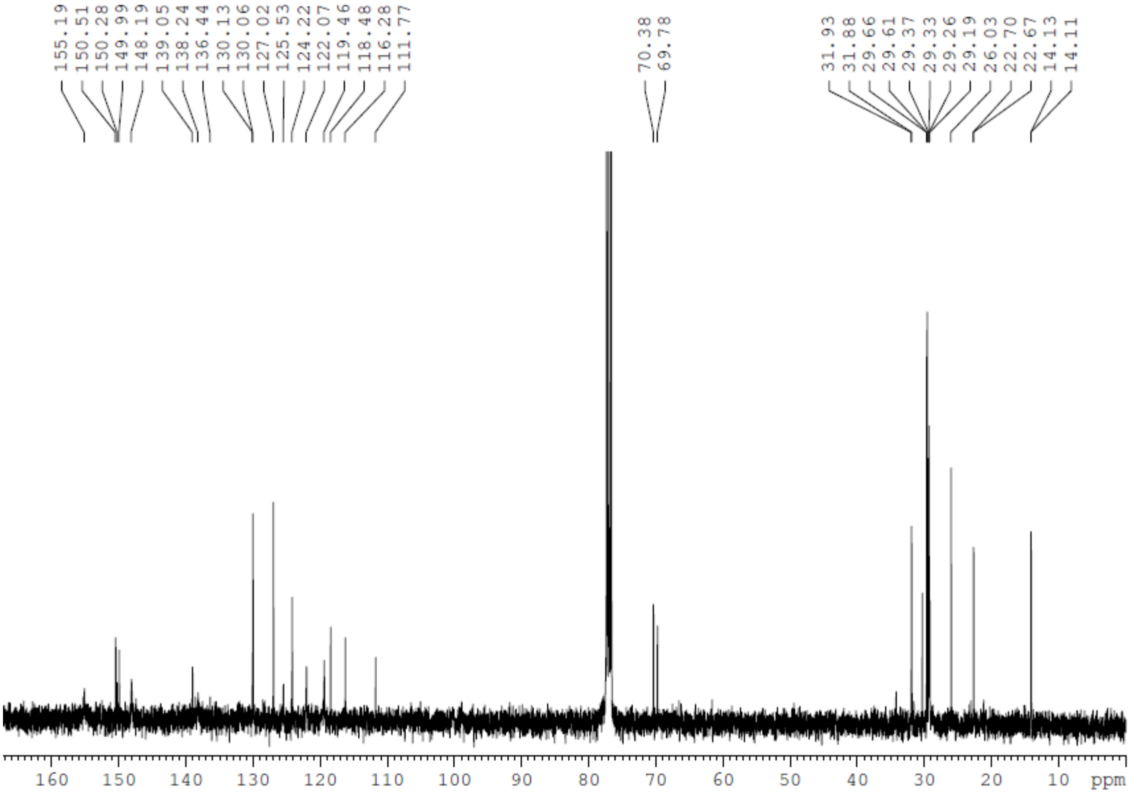


Figure A12 ^{13}C NMR spectrum of **10**

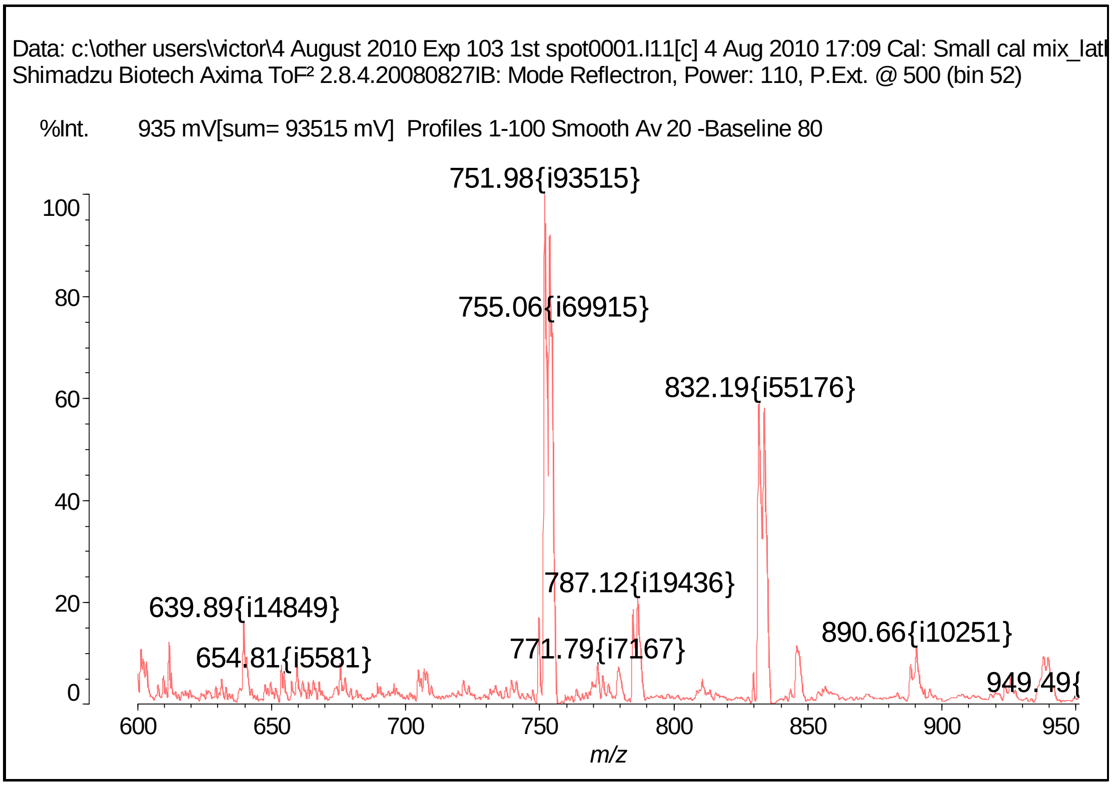


Figure A13 MALDI MS of **10**

Tetraadduct of (Monoadduct of 4’-(4-Pinacolatoboronphenyl)-2,2’:6’,2”-terpyridine with 4,7-dibromo-5,6-bis(dodecyloxy)benzo[c]thiadiazole) with Tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-phenyl)]methane (1). **5** (0.450 g, 0.540 mmol), **9** (2.90 g, 3.29 mmol), $Pd(PPh_3)_4$ ($6.30x10^{-2}$ g, $5.40x10^{-2}$ mmol) were put into RBF and degassed using N_2. Aqueous K_2CO_3 (2.00 M, 60.0 ml) and toluene (100 ml) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 88 °C for 3 days. The reaction mixture was cooled to RT and toluene was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on alumina eluting with 20% EA in hexane. **1** was obtained as a light purple glassy solid (550 mg, 30.0%). **^{1}H NMR ($CDCl_3$):** δ 8.96 (s, 8 H), 8.83–8.82 (m, 16 H), 8.18 (d, *J* = 7.60 Hz, 8 H), 8.03 (s, 8 H), 7.95 (d, *J* = 8 Hz, 8 H), 7.81 (d, *J* = 8.40 Hz, 8 H), 7.66 (d, *J* = 8.00 Hz, 8 H), 7.47 (s, 8 H), 3.95 (s, 16 H), 1.65–1.58 (m, 16 H), 1.25–1.12 (br, 144 H), 0.82–0.79 (m, 24 H). **^{13}C NMR ($CDCl_3$):** δ 155.20, 153.47, 153.44, 152.15, 150.16, 148.41, 146.34, 137.88, 135.04, 131.83, 131.54, 131.28, 129.99, 127.06, 124.58, 124.15, 123.87, 121.95, 119.35, 74.78, 74.68, 65.11, 31.91, 31.87, 30.30, 29.70, 29.67, 29.56, 29.46, 29.36, 29.31, 26.03, 22.67, 22.65, 14.11, 14.09. **Anal. Calcd.** for $C_{229}H_{272}N_{20}O_8S_4$: C, 77.2; H, 7.70; N, 7.87; O, 3.59; S, 3.60. Found: C, 77.2; H, 7.83; N, 7.56; S, 1.88.

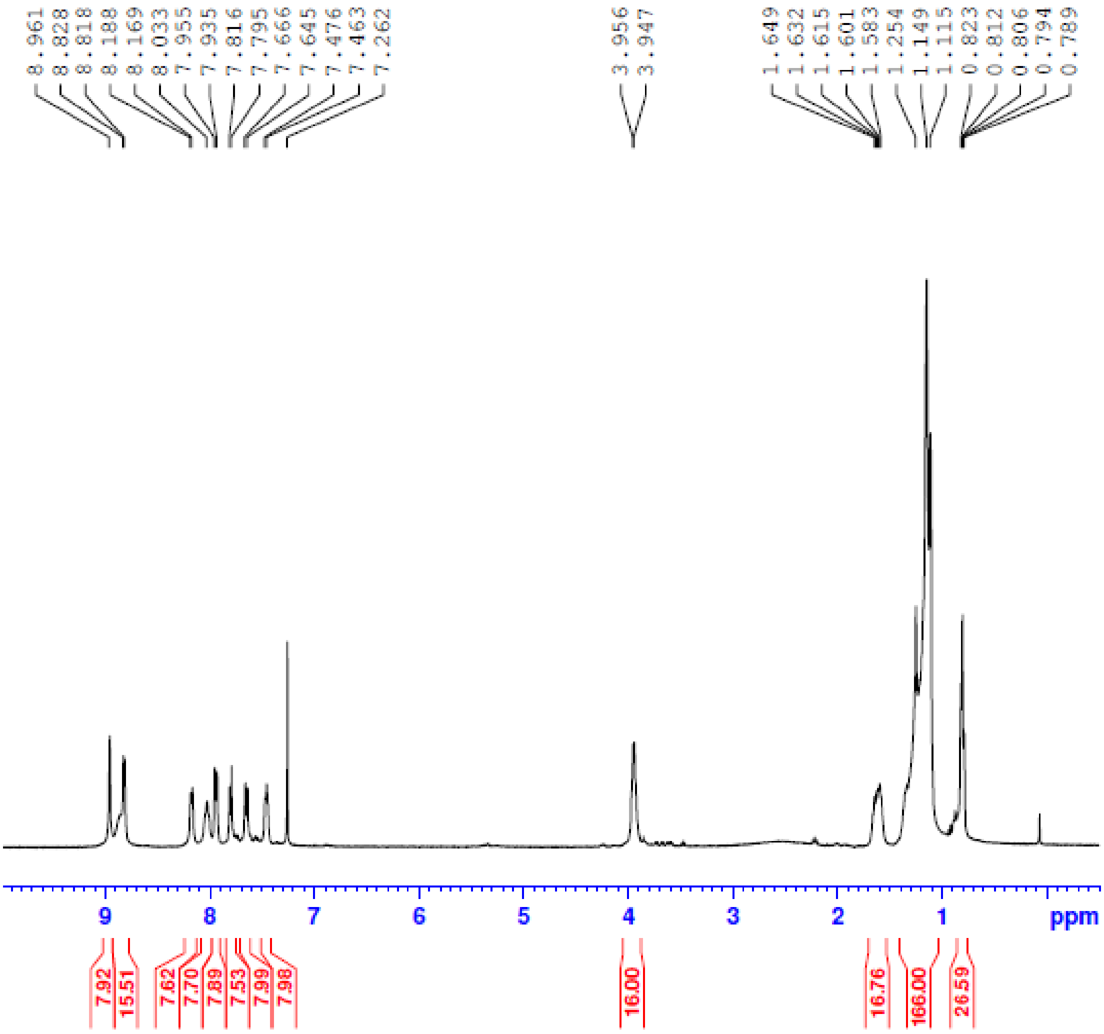


Figure A14 ^{1}H NMR spectrum of **1**

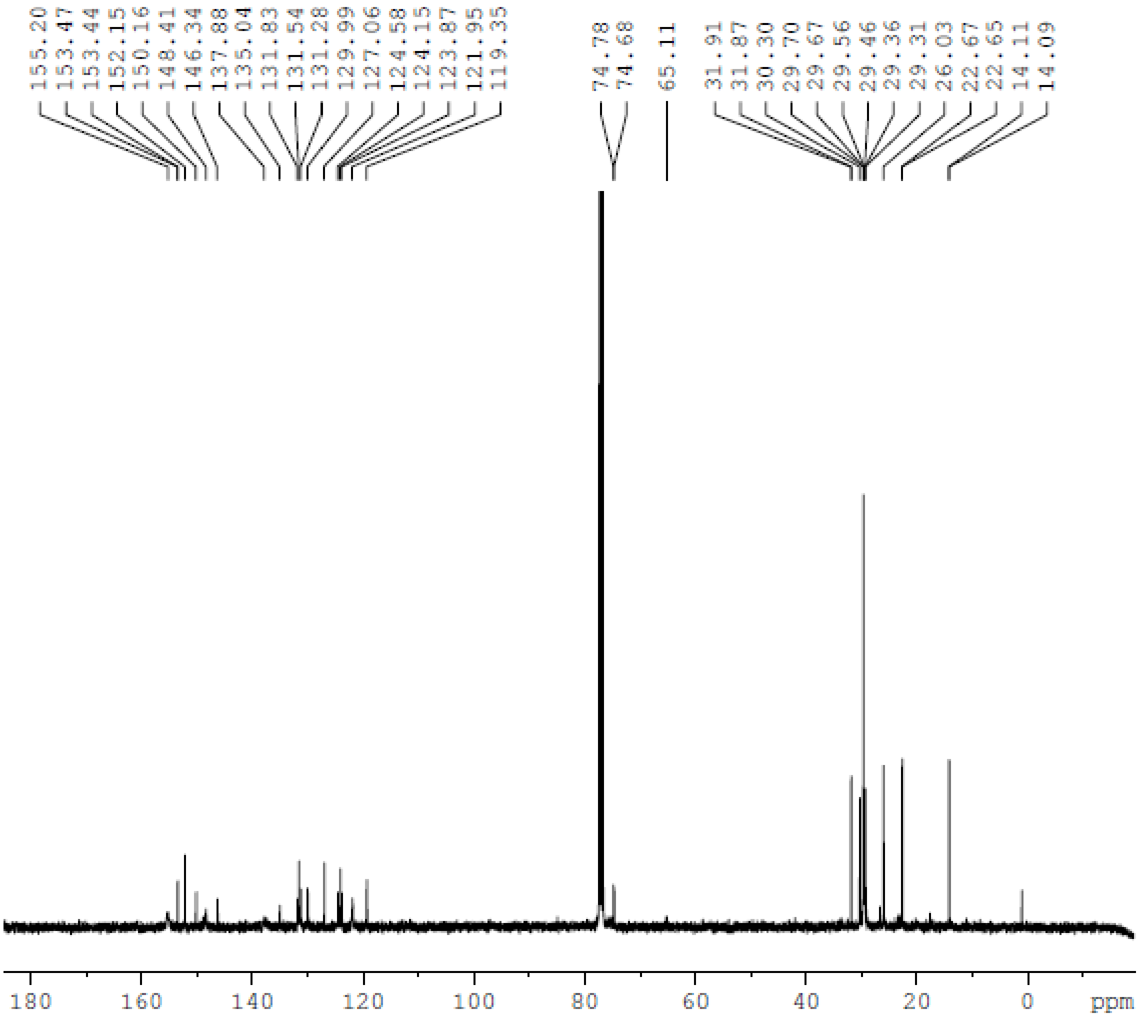


Figure A15 ^{13}C NMR spectrum of **1**

Tetraadduct of (Monoadduct of 4'-(4-Pinacolatoboronphenyl)-2,2':6',2"-terpyridine with 1,4-dibromo-2,5-bis(dodecyloxy)benzene) with Tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane-phenyl)]methane (2). **5** (0.450 g, 0.540 mmol), **10** (2.80 g, 3.35 mmol) and Pd(PPh$_3$)$_4$ (6.30x10^{-2} g, 5.40x10^{-2} mmol) were put into RBF and degassed using N$_2$. Aqueous K$_2$CO$_3$ (2.00 M, 60.0 ml) and toluene (100 ml) were degassed using N$_2$ and then injected into the RBF. The reaction mixture was then stirred in the dark at 88 °C for 3 days. The reaction mixture was cooled to RT and toluene was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on alumina eluting with 20% EA in hexane. **2** was obtained as an off-white glassy solid (700 mg, 40.0%). **^{1}H NMR ($CDCl_3$):** δ 8.89 (s, 8 H), 8.80–8.75 (m, 16 H), 8.4 (d, *J* = 8.00 Hz, 8 H), 7.96 (t, *J* =8.00 Hz, 8 H), 7.81 (d, *J* = 8.00 Hz, 8 H), 7.63 (d, *J* = 8.00 Hz, 8 H), 7.49 (d, *J* = 8.00 Hz, 8 H), 7.42 (t, *J* =8.00 Hz, 8 H), 7.11 (s, 4 H), 7.09 (s, 4 H), 3.99 (t, *J* = 9.60 Hz, 16 H), 1.77–1.73 (m, 16 H), 1.42–1.40 (m, 16 H), 1.26–1.19 (br, 128 H), 0.84–0.81 (m, 24 H). **^{13}C NMR ($CDCl_3$):** δ 155.56, 155.13, 150.53, 150.49, 150.30, 148.46, 145.71, 143.27, 139.60, 137.80, 136.29, 135.84, 130.92, 129.80, 128.81, 128.60, 126.92, 124.08, 121.89, 119.25, 116.30, 116.21, 69.80, 69.74, 68.17, 31.93, 31.88, 29.71, 29.68, 29.64, 29.47, 29.38, 29.34, 26.17, 26.08, 22.70, 22.67, 14.13, 14.10. **MALDI TOF MS**: m/z 3328.6 (M). **Anal. Calcd.** for $C_{229}H_{280}N_{12}O_8$: C, 82.6; H, 8.48; N, 5.05; O, 3.85. Found: C, 82.2; H, 11.7; N, 5.17.

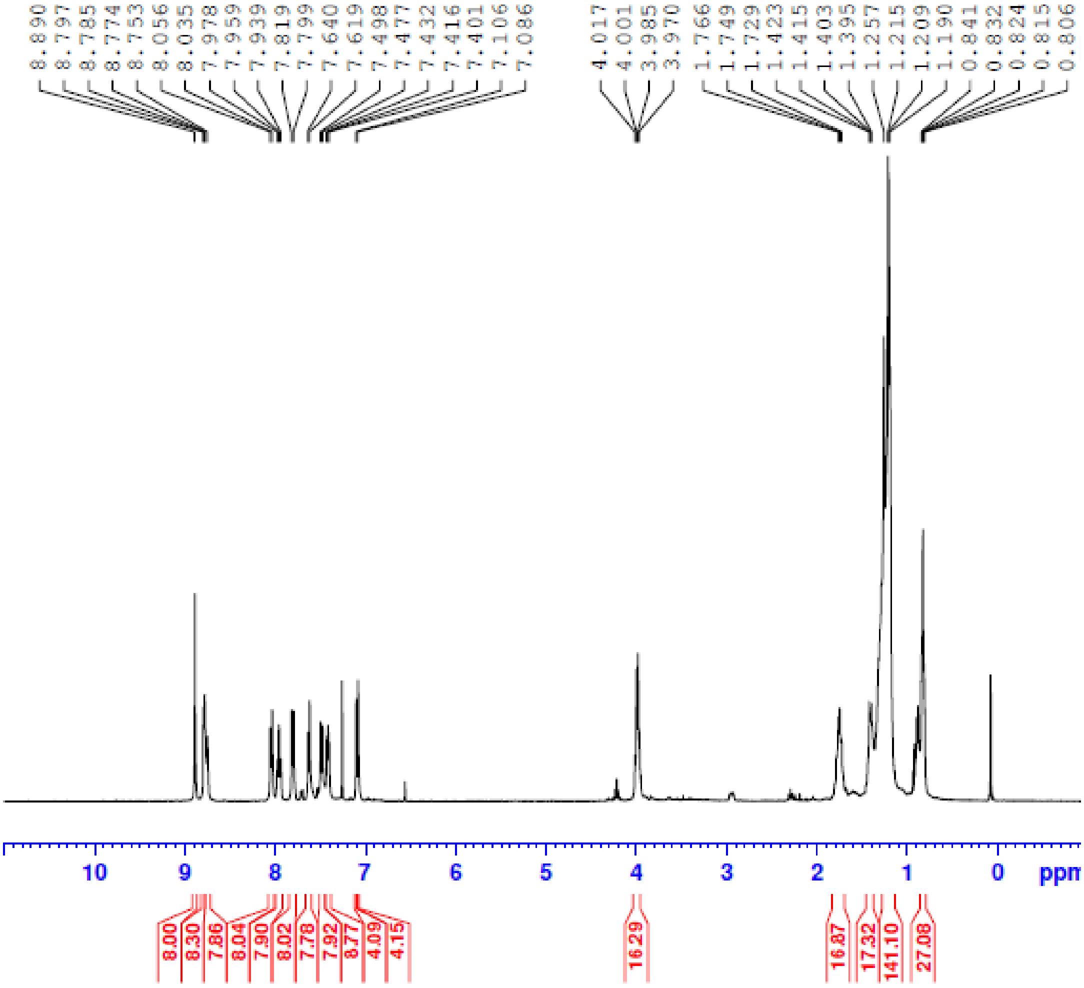


Figure A16 ^{1}H NMR spectrum of **2**

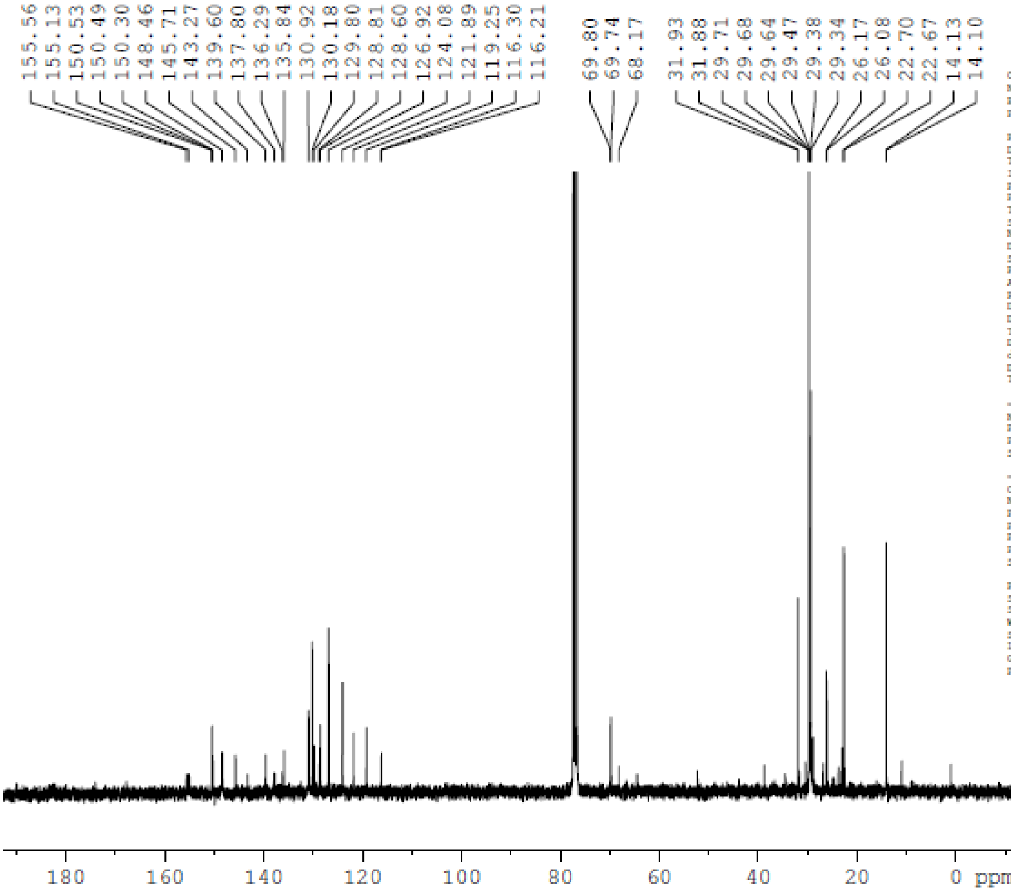
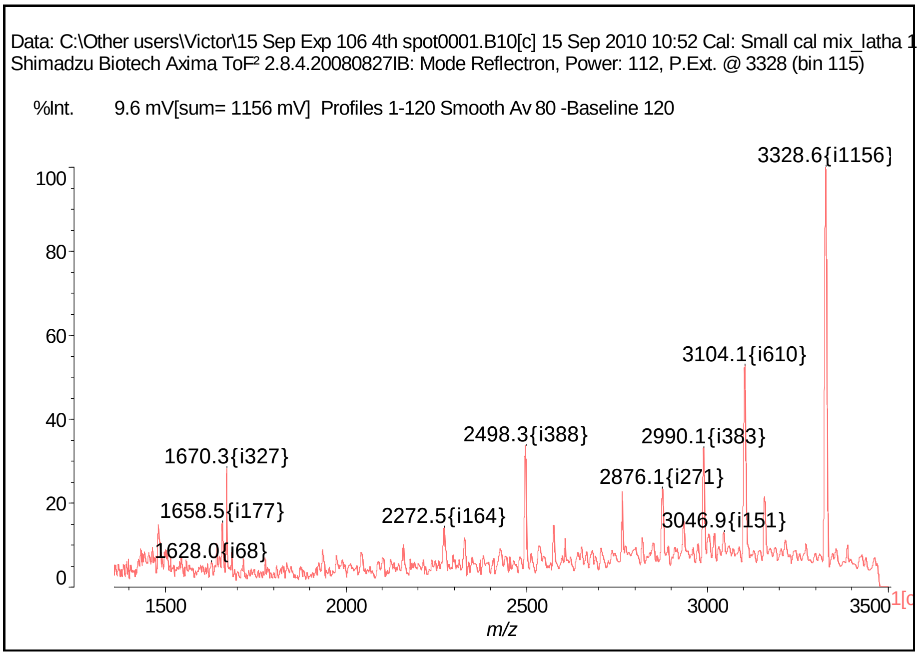


Figure A17 ^{13}C NMR spectrum of **2**



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%Int. 9.6 mV[sum= 1156 mV] Profiles 1-120 Smooth Av 80 -Baseline 120

Figure A18 MALDI MS of **2**

Diadduct of 1,4-dibromo-2,5-bis(2-ethyhexyloxy)benzene with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine (11). **13** (0.500 g, 1.02 mmol), **6** (1.11 g, 2.54 mmol) and $Pd(PPh_3)_4$ (0.120 g, 0.102 mmol) were put into RBF and degassed using N_2. Aqeuous K_2CO_3 (2.00 M, 20.0 ml) and THF (50.0 ml) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 80 °C for 2 days. The reaction mixture was cooled to RT and THF was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$ and concentrated using a rotary evaporator. Recrystallization from MeOH–THF gave **11** as a faint yellow solid (0.630 g, 65.0%). **^{1}H NMR (CD_2Cl_2):** δ 8.87 (s, 4 H), 8.76 (d, *J* = 4.80 Hz, 4 H), 8.73 (d, *J* = 8.00 Hz, 4 H), 8.02 (d, *J* = 8.00 Hz, 4 H), 7.96–7.92 (m, 4 H), 7.85 (d, *J* = 8.00 Hz, 4 H), 7.43–7.40 (m, 4 H), 3.94 (t, *J* = 5.60 Hz, 4 H), 1.74–1.68 (m, 2 H), 1.51–1.43 (m, 8 H), 1.31–1.29 (m, 8 H), 0.926–0.879 (m, 12 H). **^{13}C NMR (CD_2Cl_2):** δ 156.17, 156.05, 150.55, 149.79, 149.18, 139.42, 136.91, 136.84, 130.24, 130.16, 126.67, 123.88, 112.11, 118.50, 115.64, 71.76, 39.63, 30.60, 29.02, 23.96, 23.06, 13.85, 10.87. **MALDI TOF MS**: m/z 949.18 (M). **HR ES$^+$-TOF MS**: calculated m/z: 949.5169 (M^+), found: m/z 949.5167 (M^+).

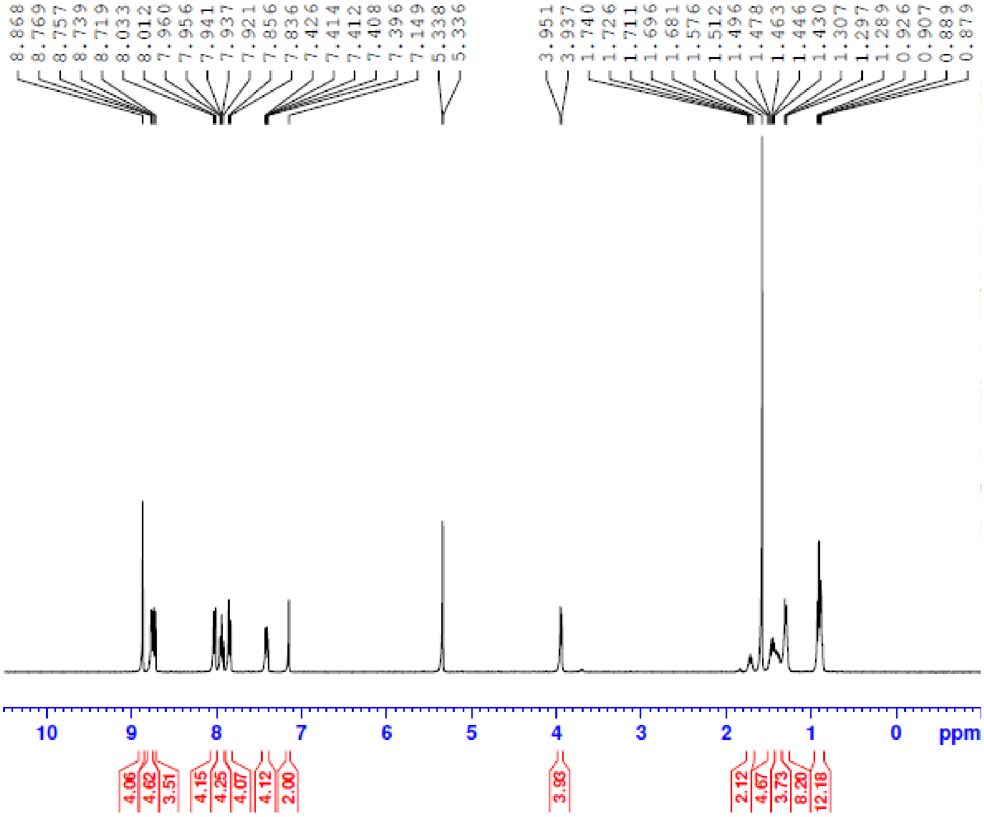


Figure A19 ^{1}H NMR spectrum of **11**

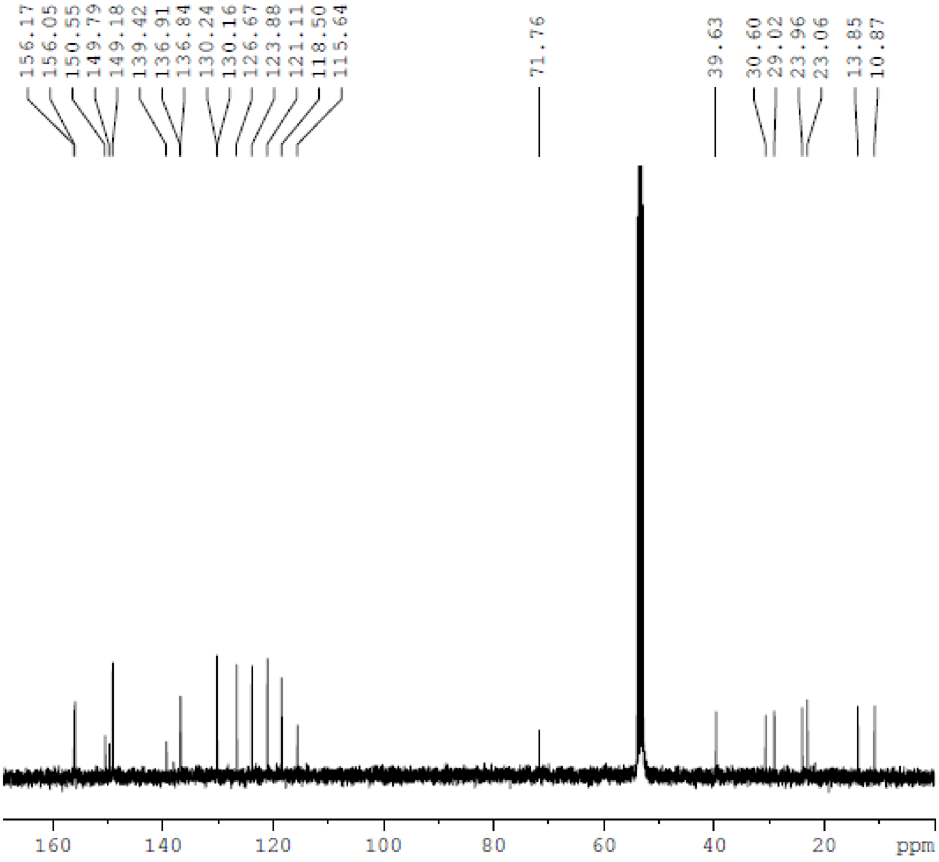


Figure A20 ^{13}C NMR spectrum of **11**

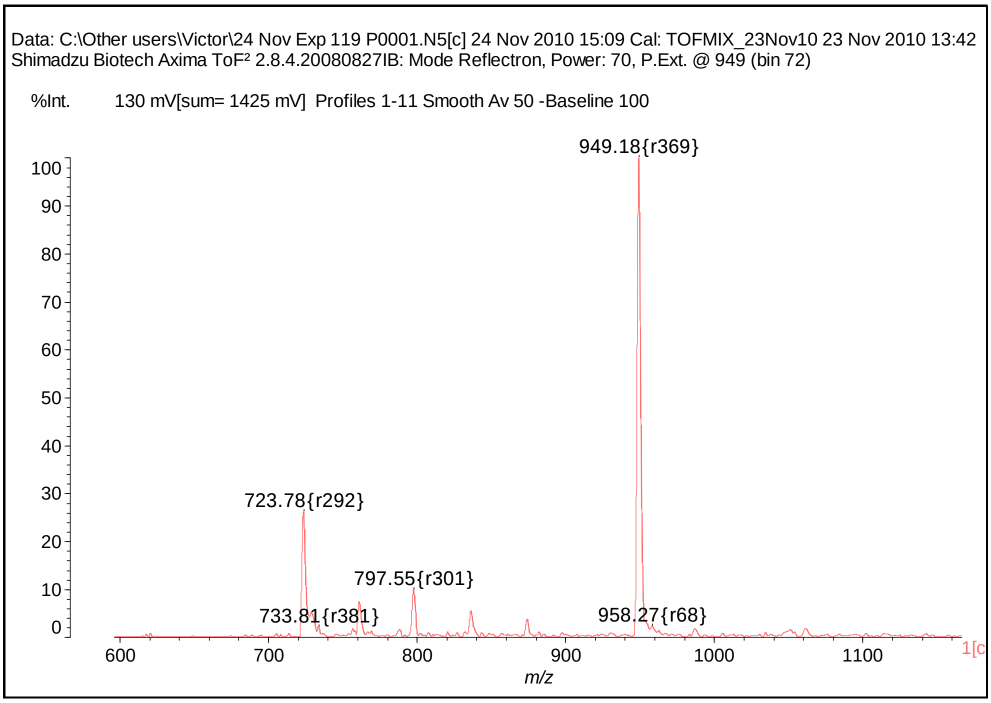


Figure A21 MALDI MS of **11**

Diadduct of 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine (12). 14 (0.200 g, 0.240 mmol), **6** (0.220 g, 0.500 mmol) and $Pd(PPh_3)_4$ (3.00×10^{-2} g, 2.40×10^{-2} mmol) were put into RBF and degassed using N_2. Aqueous K_2CO_3 (2.00 M, 20.0 ml) and THF (35.0 ml) were degassed using N_2 and then injected into the RBF. The reaction mixture was then stirred in the dark at 80 °C for 2 days. The reaction mixture was then cooled to RT and THF was removed using a rotary evaporator. The reaction mixture was then extracted with DCM and water. The DCM layer was dried over $MgSO_4$, concentrated and subjected to column chromatography on silica gel eluting with a solvent mixture of 3% triethylamine in DCM to give **12** as a red solid (0.250 g, 81.0%). **^{1}H NMR ($CDCl_3$):** δ 8.80 (s, 4 H), 8.76 (d, *J* = 4.00 Hz, 4 H), 8.70 (d, *J* = 8.00 Hz, 4 H), 8.57 (d, *J* = 4.00 Hz, 2 H), 7.99 (d, *J* = 4.00 Hz, 4 H), 7.92–7.86 (m, 8 H), 7.56 (d, *J* = 3.60 Hz, 2 H), 7.37 (t, *J* = 6.40 Hz, 4 H), 4.22 (t, *J* = 6.80 Hz, 4 H), 2.06–1.99 (m, 4 H), 1.43–1.23 (br, 36 H), 0.830 (t, *J* = 6.40 Hz, 6 H). **^{13}C NMR ($CDCl_3$):** δ 156.28, 156.04, 151.93, 150.91, 149.17, 144.84, 136.90, 135.16, 134.29, 132.06, 127.86, 126.23, 123.86, 123.62, 121.40, 118.51, 117.56, 74.62, 31.93, 29.75, 29.70, 29.38, 22.67, 14.10. **MALDI TOF MS**: m/z 1283.38 (M). **HR ES$^+$-TOF MS**: calculated m/z: 1283.5801 (M$^+$), found: m/z 1283.5780 (M$^+$).

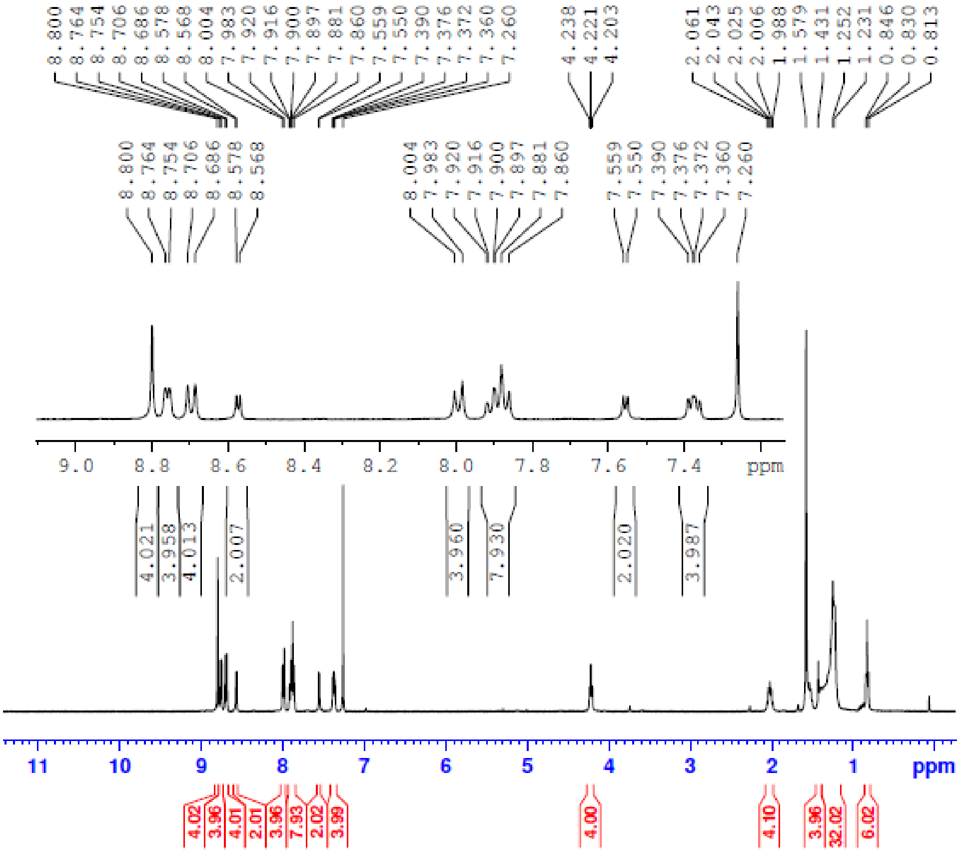


Figure A22 ^{1}H NMR spectrum of **12**

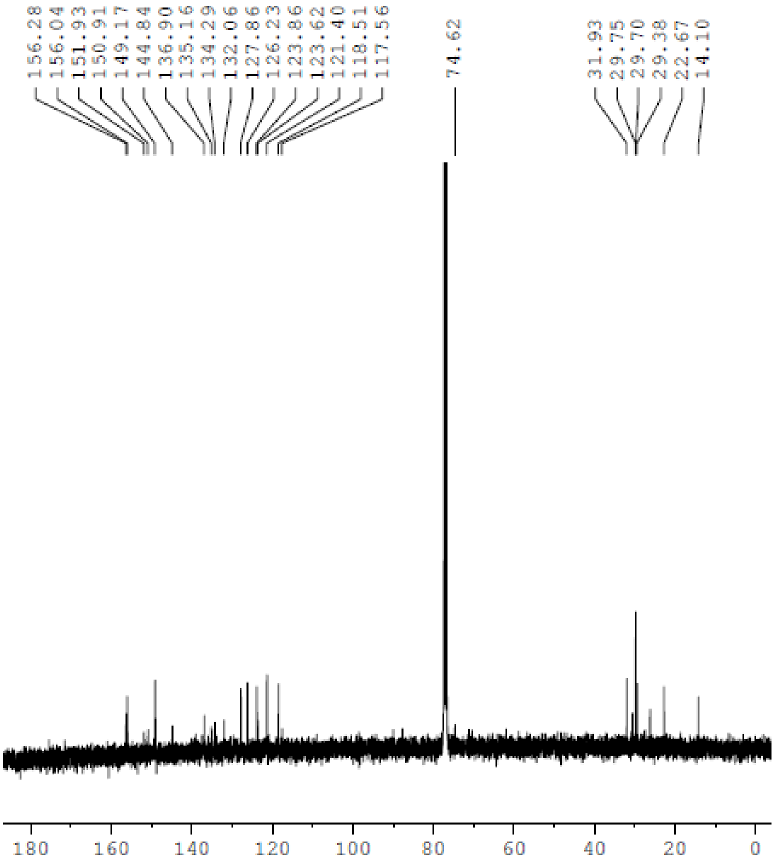
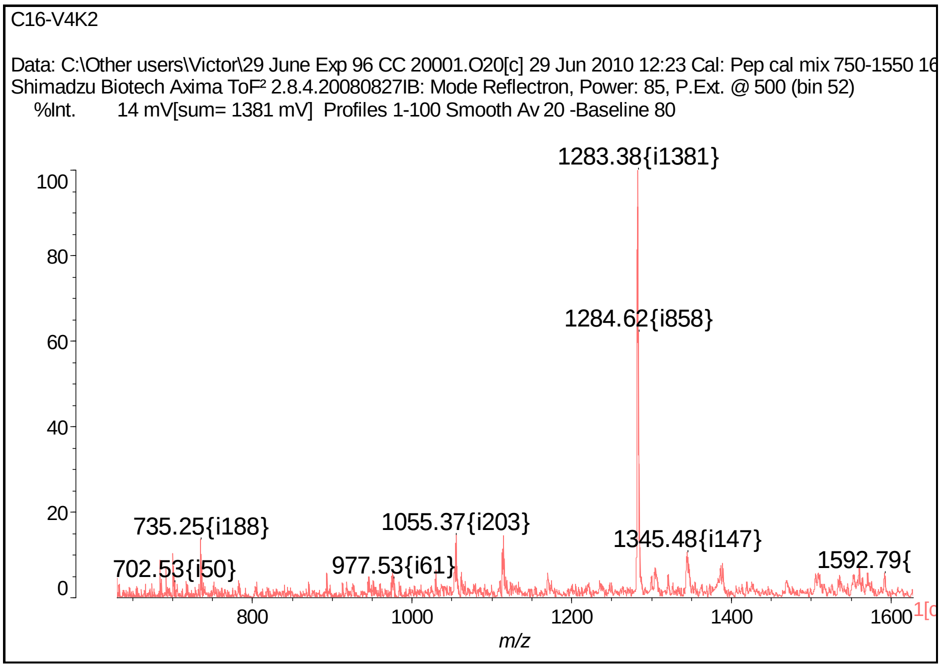


Figure A23 ^{13}C NMR spectrum of **12**


C16-V4K2

Data: C:\Other users\Victor\29 June Exp 96 CC 20001.O20[c] 29 Jun 2010 12:23 Cal: Pep cal mix 750-1550 16
Shimadzu Biotech Axima ToF² 2.8.4.20080827IB: Mode Reflectron, Power: 85, P.Ext. @ 500 (bin 52)
%Int. 14 mV[sum= 1381 mV] Profiles 1-100 Smooth Av 20 -Baseline 80

Figure A24 MALDI MS of **12**

Poly {Diadduct of 1,4-dibromo-2,5-bis(2-ethyhexyloxy)benzene with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine} (P1). Zinc(II) acetate dihydrate (12.0 mg, 5.30×10^{-2} mmol) in NMP (2.00 ml) was added dropwise into a solution of **11** (50.0 mg, 5.30×10^{-2} mmol) in NMP (10.0 ml). The reaction mixture was then stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was added into the hot solution and the stirring was continued for 30 min. After cooling down to RT, the reaction mixture was poured into MeOH. The precipitate was filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **P1** as a yellow solid (30.0 mg, 43.0%).

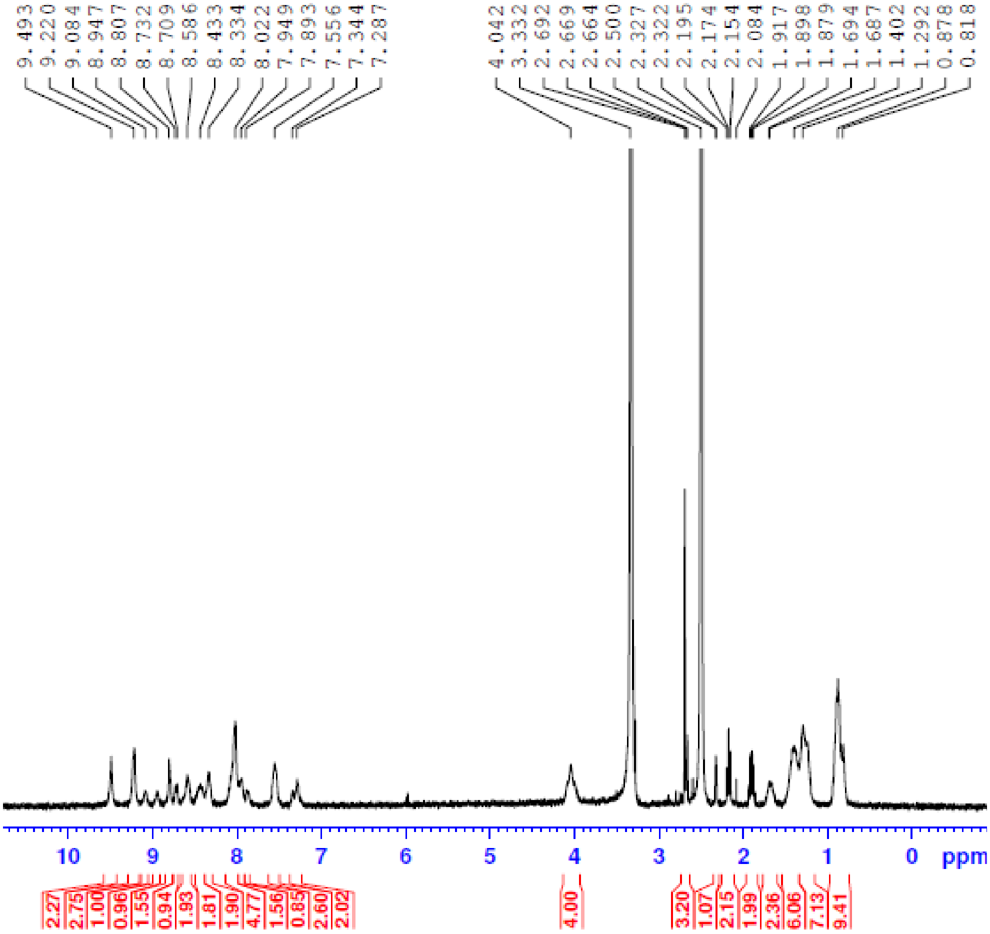


Figure A25 ^{1}H NMR spectrum (in DMSO-d_6) of **P1**

Poly {Diadduct of 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine} (P2). Zinc(II) acetate dihydrate (8.60 mg, 3.90x10^{-2} mmol) in NMP (2.00 ml) was added dropwise into a solution of **12** (50.0 mg, 3.90x10^{-2} mmol) in NMP (10.0 ml). The reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was added into the hot solution and the stirring was continued for 30 min. After cooling down to RT, reaction mixture was poured into MeOH. The precipitate was filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **P2** as a red solid (41.0 mg, 43.0%).

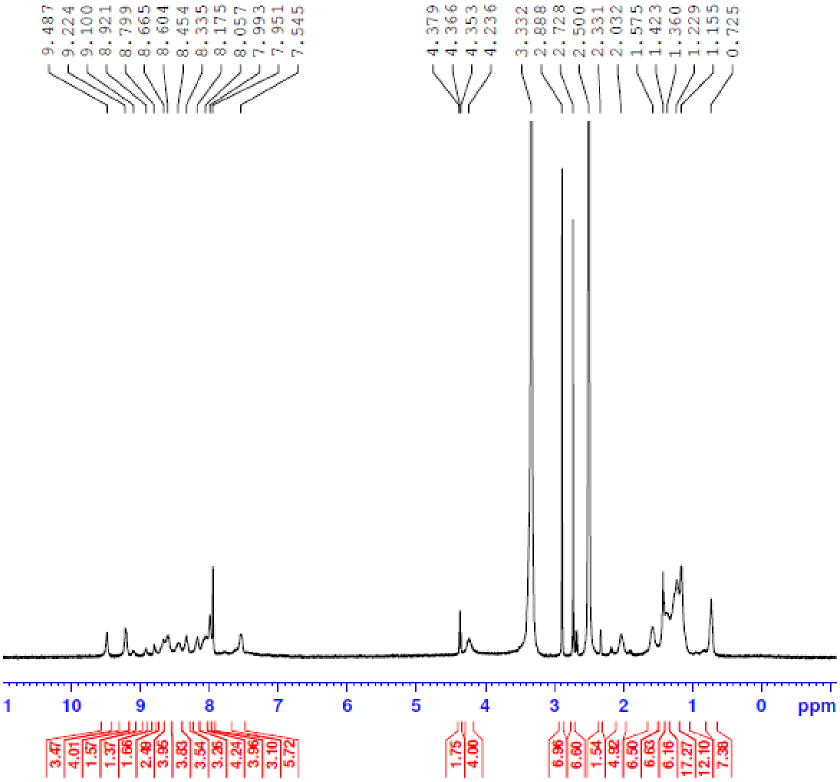


Figure A26 ^{1}H NMR spectrum (in DMSO-d_6) of **P2**

Poly {{Diadduct of 1,4-dibromo-2,5-bis(2-ethyhexyloxy)benzene with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine}-*alt*-{Diadduct of 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole with 4'-(4-Pinacolatoboronphenyl)-2,2':6',2''-terpyridine}} (P3). 11 (50.0 mg, 5.30×10^{-2} mmol) in NMP (10.0 ml) was added dropwise into a solution of zinc(II) acetate dihydrate (24.0 mg, 0.110 mmol) in NMP (5.00 ml). The reaction mixture was then stirred at RT for 2 h, and a solution of **12** (68.0 mg, 5.30×10^{-2} mmol) in NMP (10.0 ml) was added dropwise into the reaction mixture. The reaction mixture was then heated at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was added into the hot solution and the stirring was continued for 30 min. After cooling down to RT, the reaction mixture was poured into MeOH. The precipitate was filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **P3** as a red solid (115 mg, 74.0%).

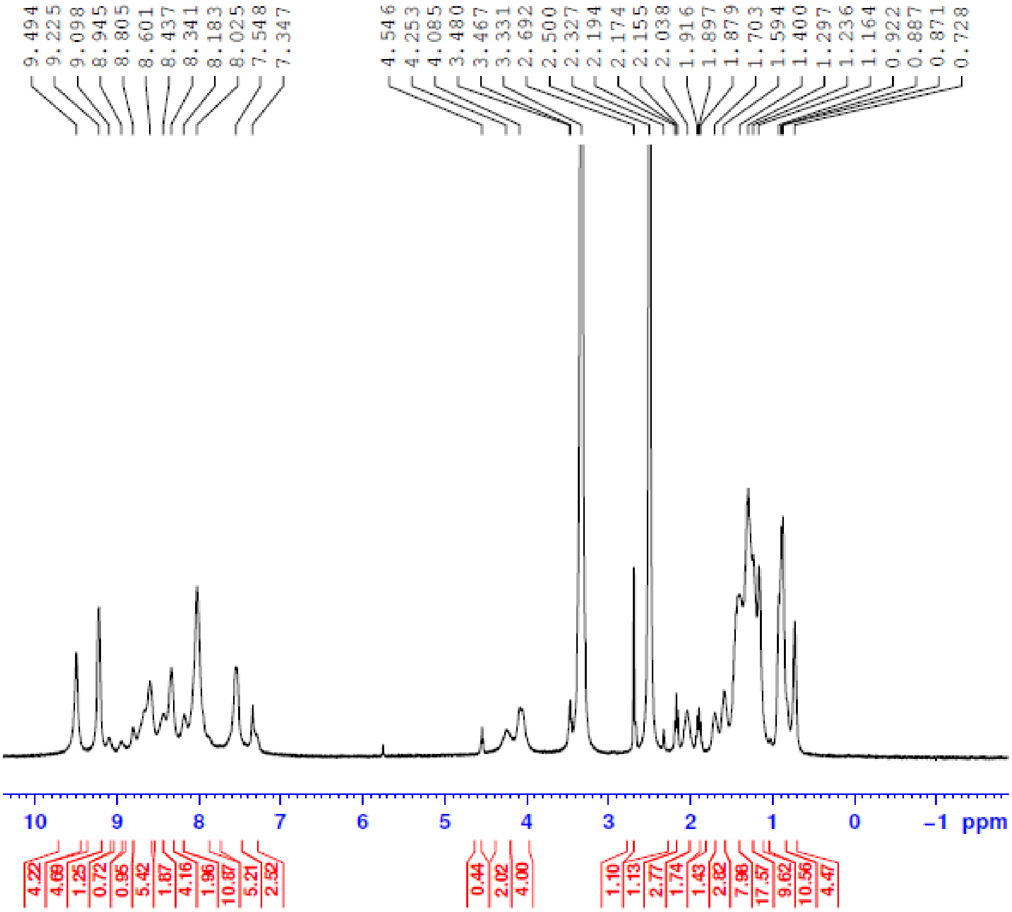


Figure A27 ^{1}H NMR spectrum (in DMSO-d$_6$) of **P3**

Zn(II)-self-assembled network of 2 (S1). Zinc(II) acetate dihydrate (6.60 mg, 3.00x10^{-2} mmol) in NMP (2.00 ml) was added dropwise into a solution of **2** (50.0 mg, 1.50x10^{-2} mmol) in NMP (10.0 ml). The reaction mixture was then stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S1** as a yellow solid (55.0 mg, 92.0%).

Zn(II)-self-assembled network of 1 (S2). Zinc(II) acetate dihydrate (6.20 mg, 2.80x10^{-2}

mmol) in NMP (2.00 ml) was added dropwise into a solution of **1** (50.0 mg, 1.40x10^{-2} mmol) in NMP (10.0 ml). The reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S2** as a light yellow solid (35.0 mg, 58.0%).

Zn(II)-self-assembled network of 2 with 11 (S3). S1 (55.0 mg, 1.40x10^{-2} mmol) in NMP (10.0 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (6.20 mg, 2.80x10^{-2} mmol) in NMP (2.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. **11** (26.6 mg, 2.80x10^{-2} mmol) in NMP (10.0 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S3** as a yellow solid (84.0 mg, 90.0%).

Zn(II)-self-assembled network of 2 with 12 (S4). S1 (55.0 mg, 1.40x10^{-2} mmol) in NMP (10.0 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (6.20 mg, 2.80x10^{-2} mmol) in NMP (2.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. **12** (36.0 mg, 2.80x10^{-2} mmol) in NMP (10.0 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S4** as a red solid (64.0 mg, 63.0%).

Zn(II)-self-assembled network of 1 with 11 (S5). **S2** (45.0 mg, 1.05x10^{-2} mmol) in NMP (10.0 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (4.61 mg, 2.10x10^{-2} mmol) in NMP (2.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. **11** (20.0 mg, 2.10x10^{-2} mmol) in NMP (10.0 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S5** as a yellow solid (50.0 mg, 70.0%).

Zn(II)-self-assembled network of 1 with 12 (S6). **S2** (45.0 mg, 1.05x10^{-2} mmol) in NMP (10.0 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (4.61 mg, 2.10x10^{-2}

mmol) in NMP (2.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. **12** (27.0 mg, 2.1x10^{-2} mmol) in NMP (10.0 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S6** as a red solid (50.0 mg, 63.0%).

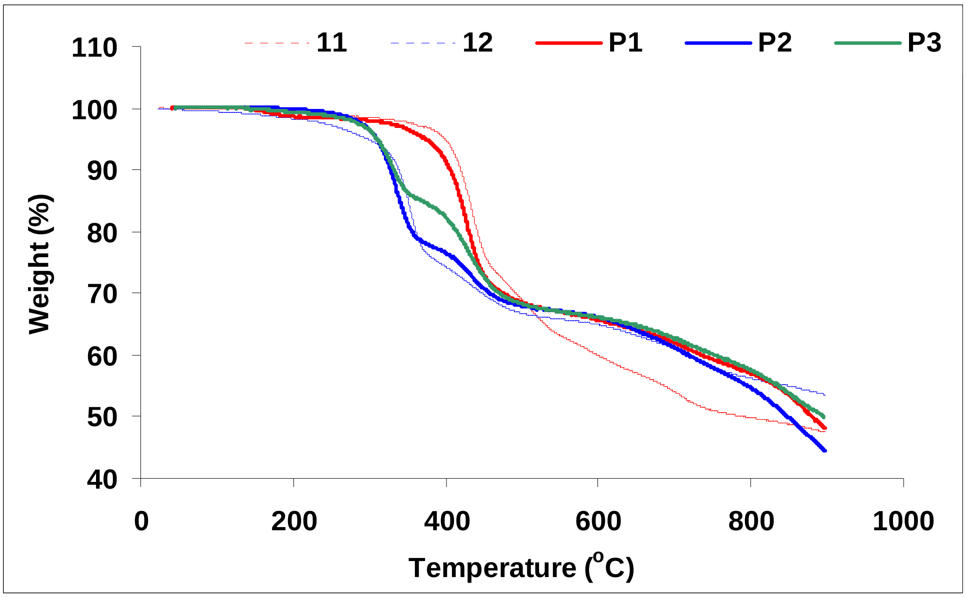


Figure A28 TGA scans of bis(tpys) monomers **11**–**12** and metallopolymers **P1**–**3**

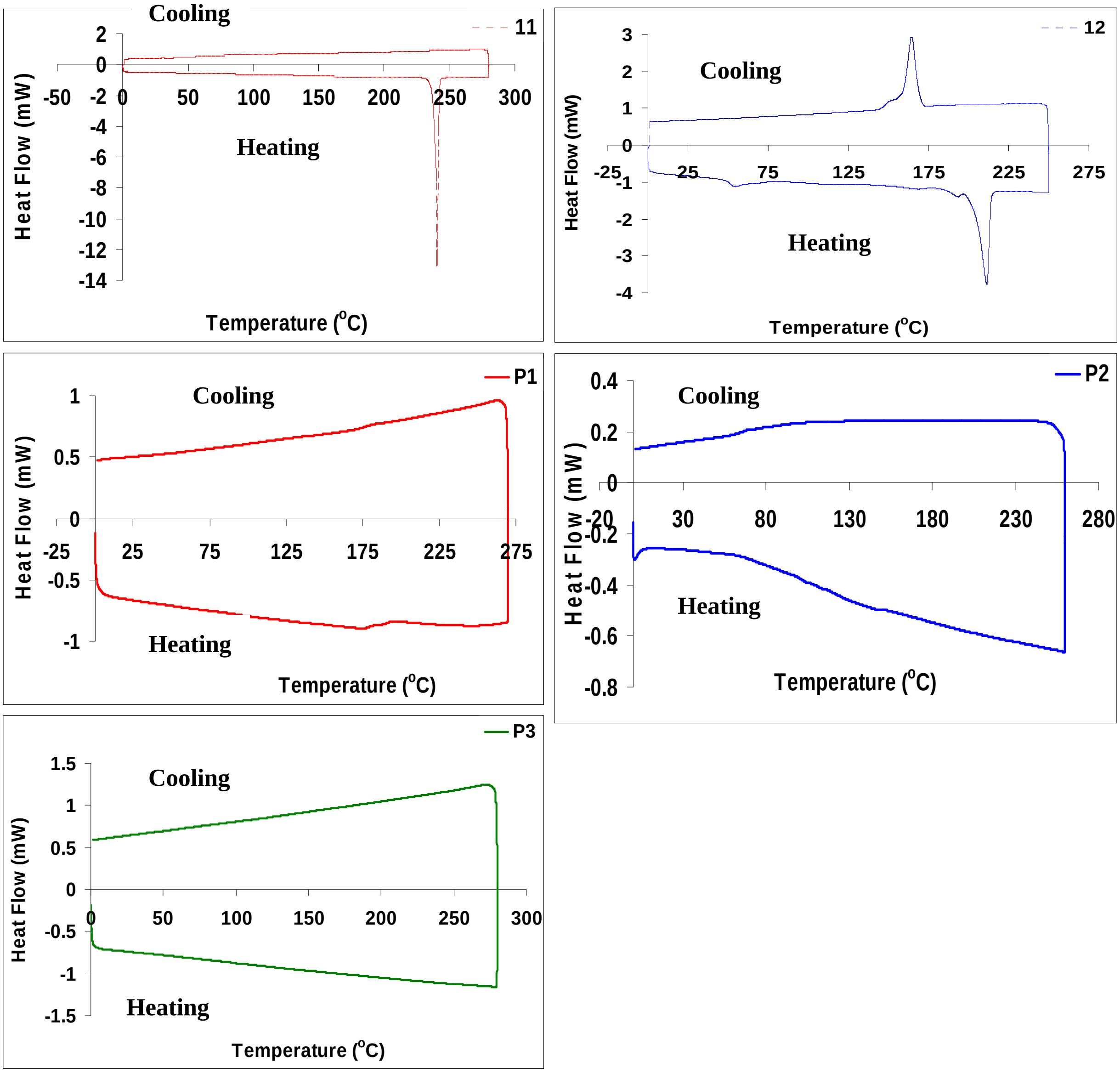


Figure A29 DSC scans of bis(tpys) monomers **11**–**12** and metallopolymers **P1**–**3**

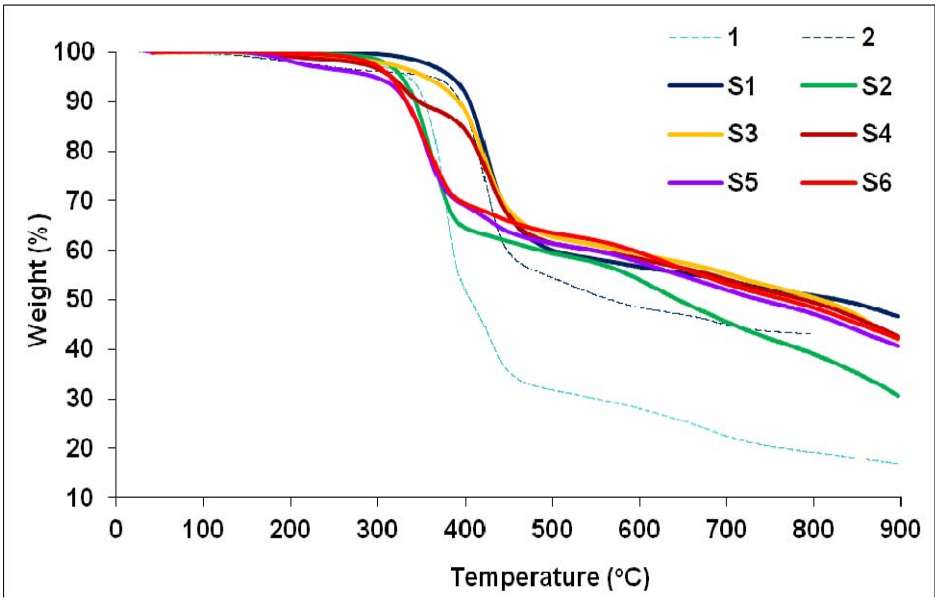


Figure A30 TGA scans of 3D conjugated cores **1–2** and 3D metal-coordinated self-assembled supramolecular networks **S1–6**

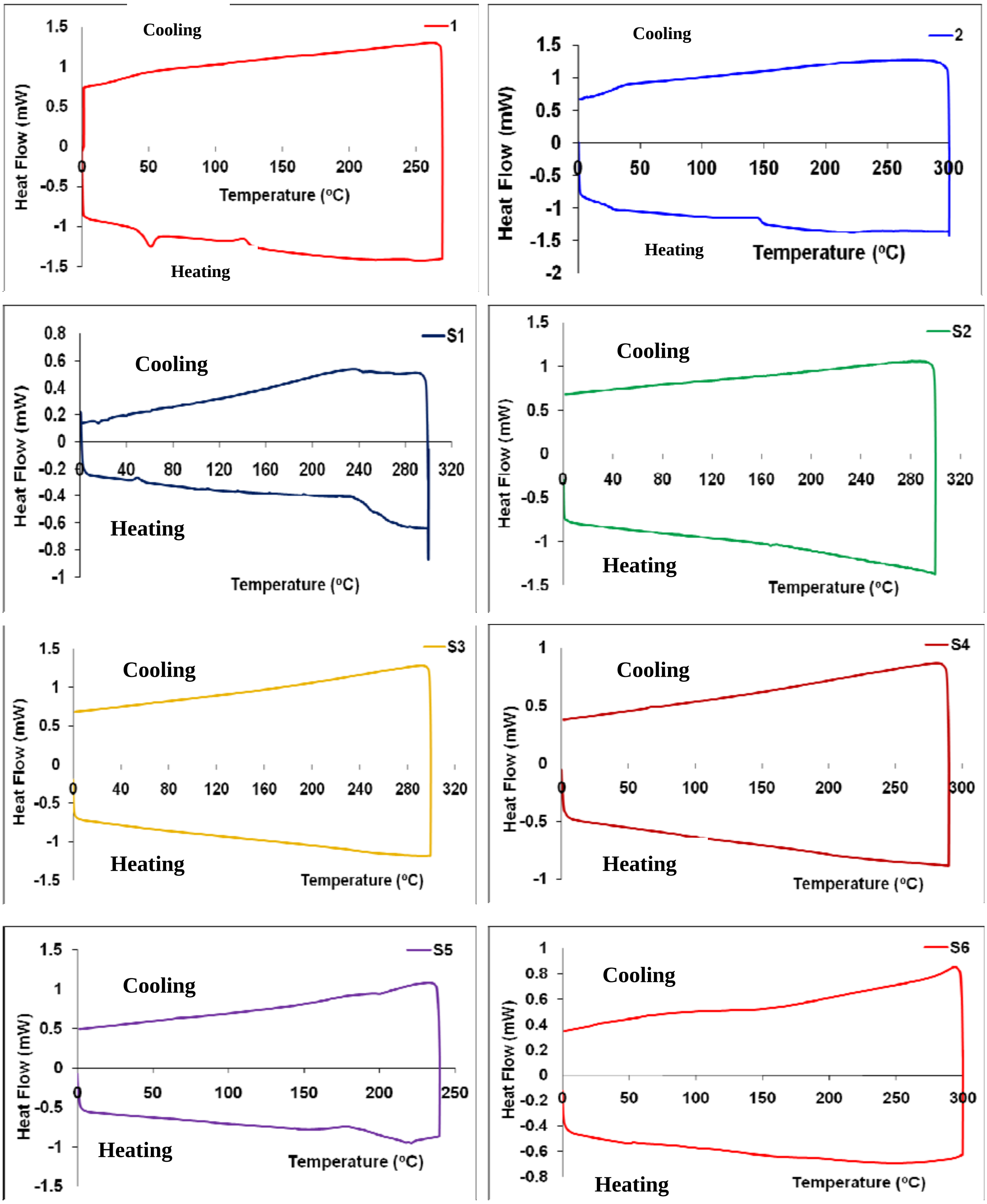


Figure A31 DSC scans (2nd cycle) of 3D conjugated cores **1–2** and 3D metal-coordinated self-assembled supramolecular networks **S1–6**

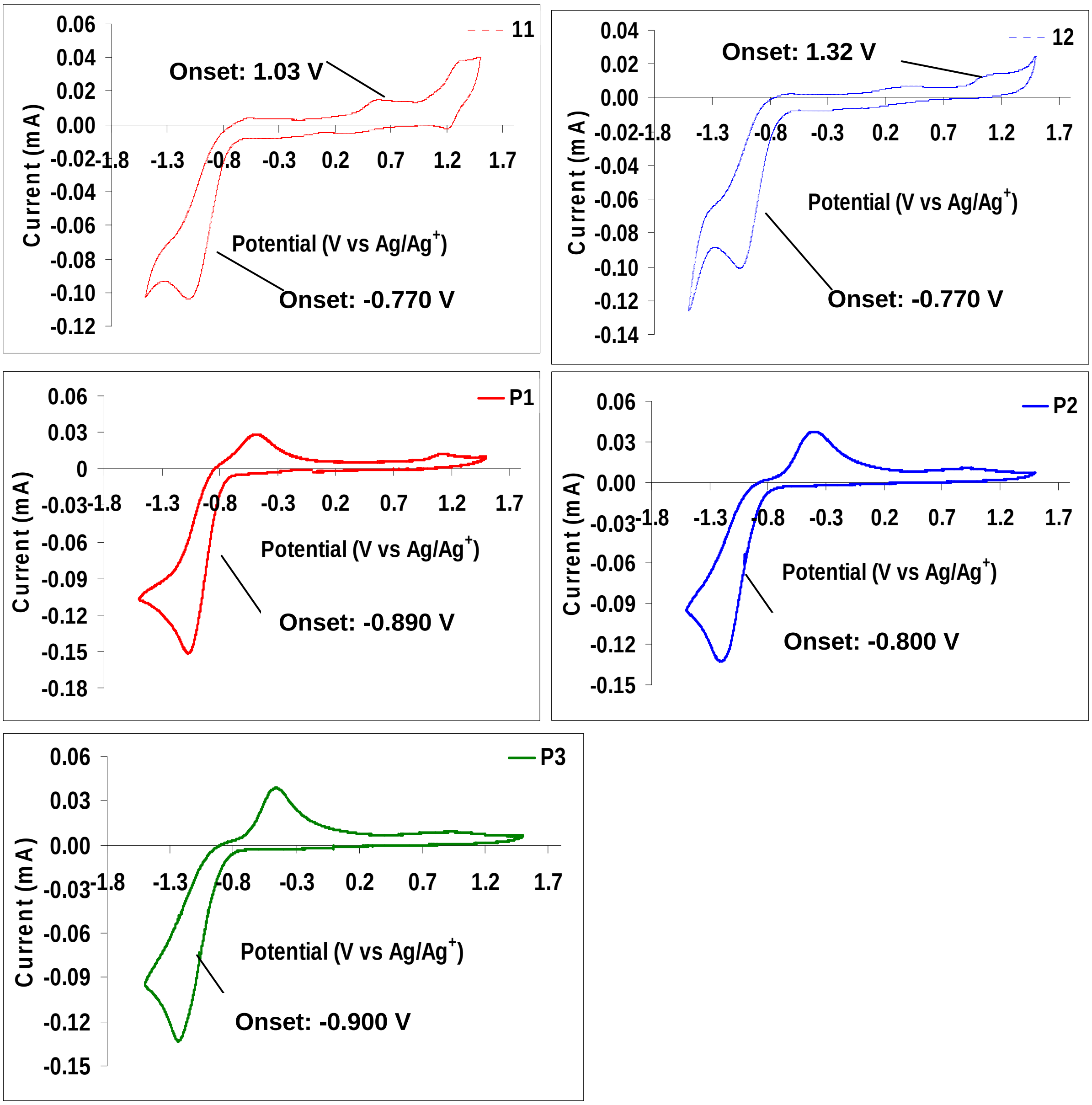


Figure A32 Cyclic voltammograms of **11–12** on a platinum electrode (wire) in 0.100 M Bu4NPF6, DCM solution with a sweep rate of 100 mV/s and **P1–3** on a platinum electrode (wire) in 0.100 M Bu4NPF6, acetonitrile solution with a sweep rate of 100 mV/s

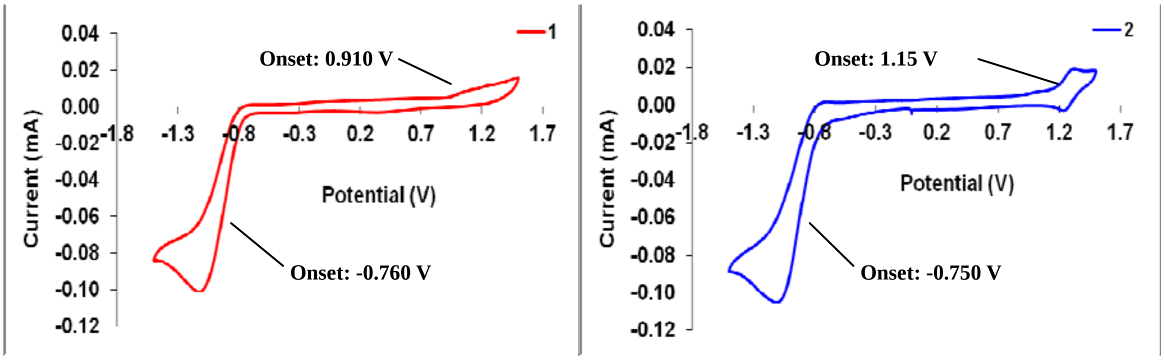


Figure A33 Cyclic voltammograms of **1** and **2** on a platinum electrode (wire) in 0.100 M Bu_4NPF_6, DCM solution with a sweep rate of 100 mV/s

Nanocomposite (S3 (with CdSe)). S1 (27.0 mg, $7.00x10^{-3}$ mmol) in NMP (5.00 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (3.10 mg, $1.40x10^{-2}$ mmol) in NMP (1.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. CdSe in excess (50.0 mg) was added into the reaction mixture followed by injection of NMP (5.00 ml). **11** (13.3 mg, $1.40x10^{-2}$ mmol) in NMP (5.00 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S3 (with CdSe)** as a dark orange solid (48.0 mg).

Nanocomposite (S4 (with CdSe)). S1 (27.0 mg, $7.00x10^{-3}$ mmol) in NMP (5.00 ml) was heated to 105 °C. Zinc(II) acetate dihydrate (3.10 mg, $1.40x10^{-2}$ mmol) in NMP (1.00 ml) was added dropwise into the reaction mixture. The reaction mixture was stirred at 105 °C under N_2 for 1 h. CdSe in excess (50.0 mg) was added into the reaction mixture followed by injection of NMP (5.00 ml). **12** (18.0 mg, 1.40x10^{-2} mmol) in NMP (5.00 ml) was then added dropwise and the resulting reaction mixture was stirred at 105 °C under N_2 for 24 h. An excess of NH_4PF_6 was then added into the hot reaction mixture and it was continued stirring for 30 min. The reaction mixture was then poured into MeOH. The precipitate was then filtered off and washed with MeOH. Precipitate was redissolved with NMP followed by reprecipitation of the solid by adding ether. The precipitate was dried at 50 °C under vacuum for 24 h to give **S4 (with CdSe)** as a red solid (38.0 mg).

References:

(1) Lim, Z. B.; Xue, B.; Bomma, S.; Li, H.; Sun, S.; Lam, Y. M.; Belcher, W. J.; Dastoor, P. C.; Grimsdale, A. C. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49*, 4387.

(2) Vahlenkamp, T.; Wegner, G. *Macromolecular Chemistry and Physics* **1994**, *195*, 1933.

(3) Wang, J. J. *Synlett* **2005**, 1251.