† Electronic Supporting Information

A bright entry to improve the performance of DSSCs with the influence of novel optoelectronic acridinedione based macromolecules in I^-/I_3^- electrolytes

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General procedure for the synthesis of 1,3,5-tris{[9-(1-(1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-10-(alkyl/aryl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethylacridine -1,8(2*H*,5*H*,9*H*,10*H*)-dione]methyl}-2,4,6-trimethylbenzene, 13a-g.

To a stirred solution of 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene (1.0 mol) **(8)** and *O*-propargylacridinedione (3.3 mol) **(5a-g)** in THF:H_2O (50 mL:50 mL), $CuSO_4.5H_2O$ (20 mol %) and sodium ascorbate (20 mol %) were added. The mixture was stirred with catalytic amount of DMF at room temperature for 10 - 12 hours till the disappearance of the starting materials as evidenced by TLC. The crude product was dissolved in CH_2Cl_2 and extracted with H_2O (2 x 30 mL). The organic layer was dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The product was purified by column chromatography using $CHCl_3$:MeOH mixture (9:1) as eluent.

The structures of all the macromolecules were confirmed by their spectral analysis. Thus, in the IR spectrum of compound **13b** the carbonyl group of acridinedione exhibited a peak at 1636 cm^{-1}. The ^1H NMR spectrum of compound **13b** showed a singlet at δ 7.34 due to CH proton of triazole ring. The benzylic CH proton of acridinedione exhibited a singlet at δ 5.12 and the methyl groups of acridinedione resonated as two singlets in the region δ 0.71-0.85. The benzylic CH_2 proton appeared as a singlet at δ 5.05. ^{13}C NMR spectrum of **13b** showed a peak at 195.91 ppm for the carbonyl carbon of acridinedione and DEPT-135 studies showed four methylene carbons present at 41.72, 49.02, 50.17 and 61.90 ppm confirms the formation of macromolecular cycloadduct. In addition, the MALDI-TOF mass spectrum of **13b** showed a molecular ion peak at *m/z* 1726.19 (M^+), which also confirmed the structure of the product. The cycloadducts gave satisfactory elemental analysis.

Compound 13a: Pale yellow solid (1.15 g, 85 %), mp. 226-228 °C; IR (KBr): 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.93-0.99 (two singlets, 36H); 2.11 (s, 12H); 2.25 (s, 9H); 2.29-2.54 (m, 12H); 3.18 (s, 9H); 4.95 (s, 6H); 5.10 (s, 3H); 5.53 (s, 6H); 6.62-7.02 (dd, 12H, ArH); 7.27 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 15.64, 27.54, 27.76, 29.86, 32.48, 39.50,

48.01, 48.93, 60.90, 113.46, 115.13, 121.38, 128.83, 136.29, 139.31, 139.55, 144.06, 150.25, 156.28, 195.96 ppm. MALDI-TOF *m/z* 1537.89 (M^+); Anal. Calcd. for $C_{93}H_{108}N_{12}O_9$: C, 72.63; H, 7.08; N, 10.93 %. Found: C, 72.71; H, 7.16; N, 10.86 %.

Compound 13b: Pale yellow solid (1.30 g, 86 %), mp. 210-212 °C; IR (KBr): 1636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.71-0.85 (two singlets, 36H); 1.70-2.14 (m, 24H); 2.28 (s, 9H); 5.05 (s, 6H); 5.12 (s, 3H); 5.57 (s, 6H); 6.74-7.45 (m, 27H, ArH); 7.34 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.62, 26.72, 29.62, 31.75, 32.31, 41.72, 49.02, 50.17, 61.90, 114.45, 114.61, 122.41, 128.76, 129.36, 130.04, 130.51, 138.97, 139.33, 139.80, 144.38, 149.67, 156.21, 195.91 ppm. MALDI-TOF *m/z* 1726.19 (M^+); Anal. Calcd. for $C_{108}H_{114}N_{12}O_9$: C, 75.24; H, 6.66; N, 9.75 %. Found: C, 75.33; H, 6.57; N, 9.82 %.

Compound 13c: Pale yellow solid (1.32 g, 83 %), mp. 236-238 °C; IR (KBr): 1631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.70-0.86 (two singlets, 36H); 1.73-2.25 (m, 24H); 2.33 (s, 9H); 2.40 (s, 9H); 5.04 (s, 6H); 5.11 (s, 3H); 5.58 (s, 6H); 6.72-7.43 (m, 24H, ArH); 7.27 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.73, 21.26, 26.82, 29.66, 31.76, 32.37, 41.77, 49.57, 50.15, 61.47, 114.61, 114.65, 123.31, 128.81, 130.29, 136.26, 139.52, 139.54, 140.19, 143.82, 150.28, 156.01, 196.00 ppm. MALDI-TOF *m/z* 1766.31 (M^+); Anal. Calcd. for $C_{111}H_{120}N_{12}O_9$: C, 75.48; H, 6.85; N, 9.52 %. Found: C, 75.39; H, 6.96; N, 9.59 %.

Compound 13d: Pale yellow solid (1.40 g, 88 %), mp. 260-262 °C; IR (KBr): 1636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.72-0.86 (two singlets, 36H); 1.75-2.26 (m, 24H); 2.33 (s, 9H); 3.84 (s, 9H); 5.06 (s, 6H); 5.11 (s, 3H); 5.59 (s, 6H); 6.75-7.41 (m, 24H, ArH); 7.22 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.73, 26.83, 29.71, 31.76, 32.31, 41.78, 49.18, 50.22, 55.66, 61.95, 114.50, 114.63, 115.13, 122.61, 128.79, 130.23, 130.54, 130.90, 131.50, 139.45, 139.87, 144.39, 150.24, 156.21, 159.82, 195.91 ppm. MALDI-TOF *m/z* 1814.19 (M^+); Anal. Calcd. for $C_{111}H_{120}N_{12}O_{12}$: C, 73.49; H, 6.67; N, 9.26 %. Found: C, 73.58; H, 6.76; N, 9.18 %.

Compound 13e: Pale yellow solid (1.37 g, 86 %), mp. 218-220 °C; IR (KBr): 1638 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71-0.87 (two singlets, 36H); 1.71-2.21 (m, 24H); 2.28 (s, 9H); 5.01 (s, 6H); 5.10 (s, 3H); 5.55 (s, 6H); 6.72-7.48 (m, 24H, ArH); 7.45 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.66, 26.82, 29.66, 31.77, 32.18, 32.41, 41.83, 49.06, 50.17, 61.95, 114.53, 114.93, 122.45, 128.78, 130.39, 130.58, 131.04, 135.43, 137.57, 139.14, 139.84, 144.39, 149.21, 156.34, 195.81 ppm. MALDI-TOF *m/z* 1827.42 (M^+); Anal. Calcd. for $C_{108}H_{111}Cl_3N_{12}O_9$: C, 70.98; H, 6.12; N, 9.20 %. Found: C, 71.07; H, 6.20; N, 9.29 %.

Compound 13f: Pale yellow solid (1.46 g, 85 %), mp. 202-204 °C; IR (KBr): 1633 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72-0.86 (two singlets, 36H); 1.72-2.23 (m, 24H); 2.30 (s, 9H); 4.99 (s, 6H); 5.10 (s, 3H); 5.53 (s, 6H); 6.71-7.46 (m, 24H, ArH); 7.42 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.64, 26.79, 29.63, 31.76, 32.17, 32.41, 41.84, 49.10, 50.19, 61.97, 114.54, 114.95, 122.42, 128.76, 130.41, 130.57, 131.09, 135.45, 137.56, 139.15, 139.83, 144.39, 149.22, 156.34, 195.89 ppm. MALDI-TOF *m/z* 1960.79 (M^+); Anal. Calcd. for $C_{108}H_{111}Br_3N_{12}O_9$: C, 66.15; H, 5.71; N, 8.57 %. Found: C, 66.28; H, 5.62; N, 8.66 %.

Compound 13g: Pale yellow solid (1.27 g, 78 %), mp. 218-220 °C; IR (KBr): 1635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74-0.89 (two singlets, 36H); 1.76-2.26 (m, 24H); 2.33 (s, 9H); 5.08 (s, 6H); 5.13 (s, 3H); 5.54 (s, 6H); 6.74-7.48 (m, 24H, ArH); 7.46 (s, 3H). ^{13}C (75 MHz, $CDCl_3$) 16.67, 26.81, 29.61, 31.74, 32.19, 32.46, 41.88, 49.15, 50.21, 61.99, 114.56, 114.99, 122.46, 128.73, 130.39, 130.60, 131.13, 135.49, 137.57, 139.16, 140.11, 144.41, 149.19, 156.32, 195.93 ppm. MALDI-TOF *m/z* 1859.22 (M^+); Anal. Calcd. for $C_{108}H_{111}N_{15}O_{15}$: C, 69.77; H, 6.02; N, 11.30 %. Found: C, 69.85; H, 6.11; N, 11.19 %.

General procedure for the synthesis of 1,3-di{[9-(1-((1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-10-(alkyl/aryl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethylacridine -1,8(2*H*,5*H*,9*H*,10*H*)-dione]-2,2-bis[9-(1-((1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-10-(alkyl/aryl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethylacridine-1,8(2*H*,5*H*,9*H*,10*H*) -dione]methyl} propane, 14 a-g

To a stirred solution of 1,3-diazido-2,2-bis(azidomethyl)propane (1.0 mol) **(12)** and *O*-propargylacridinedione (4.4 mol) **(5a-g)** in THF:H_2O (50 mL:50 mL) were added $CuSO_4.5H_2O$ (20 mol %) and sodium ascorbate (20 mol %). The mixture was stirred with catalytic amount of DMF at room temperature for 10 - 12 hours till the disappearance of the starting materials as evidenced by TLC. The crude product was dissolved in CH_2Cl_2 and extracted with H_2O (2 x 30 mL). The organic layer was dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The product was purified by column chromatography using $CHCl_3$:MeOH mixture (9:1) as eluent.

^{1}H NMR spectrum of compound **14d** showed a singlet at δ 8.21 due to CH proton of triazole ring. The benzylic CH proton of acridinedione exhibited a singlet at δ 5.19 and the methyl groups of acridinedione resonated as two singlets in the region δ 0.78-0.93. A singlet appeared at δ 4.32 due to methylene proton in the core moiety. The ^{13}C NMR spectrum of **14d** showed a peak at 195.91 ppm for the carbonyl carbon of acridinedione and DEPT-135 studies showed four methylene carbons present at 41.77, 49.27, 50.22 and 61.64 ppm which confirmed the formation of macromolecule. Further more, COSY spectrums of cycloadduct confirmed the connectivity between the methylene carbons with corresponding methylene protons, thus, δ_H 1.67-2.20 with 41.77 and 50.22; δ_H 4.32 with 49.27; δ_H 5.16 with 61.64. The molecular weight of the cycloadducts was confirmed by MALDI-TOF mass spectrum of **14d** showed a molecular ion peak at *m/z* 2274.79 (M^+) and the compound gave satisfactory elemental analysis.

Compound 14a: Pale yellow solid (1.71 g, 85 %), mp.196-198 °C; IR (KBr): 1631 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91-0.98 (two singlets, 48H); 1.66-2.19 (s, 32H); 3.18 (s, 12H); 4.95 (s, 8H); 5.10 (s, 4H); 5.53 (s, 8H); 6.63-7.11 (dd, 16H, ArH); 7.17 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 26.59, 28.96, 31.48, 32.50, 42.01, 46.83, 49.61, 51.38, 60.90, 113.92, 115.13, 126.38, 128.82, 133.84, 144.05, 150.26, 156.23, 195.93 ppm. MALDI-TOF *m/z* 1906.38 (M^+); Anal. Calcd. for $C_{113}H_{132}N_{16}O_{12}$: C, 71.19; H, 6.98; N, 11.76 %; Found: C, 71.31; H, 6.89; N, 11.83 %.

Compound 14b: Pale yellow solid (1.87 g, 82 %), mp. 230-232 °C; IR (KBr): 1630 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76-0.93 (two singlets, 48H); 1.66-2.21 (m, 32H); 4.33 (s, 8H); 5.18 (s, 8H); 5.20 (s, 4H); 6.87-7.97 (m, 36H, ArH); 8.06 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 26.75, 29.64, 31.74, 32.33, 41.74, 46.44, 49.25, 50.19, 61.62, 114.62, 127.11, 128.75, 129.37, 130.86, 131.58, 139.34, 143.97, 149.68, 156.29, 159.85, 195.91 ppm. MALDI-TOF *m/z* 2154.66 (M^+); Anal. Calcd. for $C_{133}H_{140}N_{16}O_{12}$: C, 74.14; H, 6.55; N, 10.40 %; Found: C, 74.26; H, 6.63; N, 10.31 %.

Compound 14c: Pale yellow solid (1.89 g, 81 %), mp. 252-254 °C; IR (KBr): 1635 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78-0.93 (two singlets, 48H); 1.66-2.21 (m, 32H); 2.28 (s, 12H); 4.31 (s, 8H); 5.18 (s, 8H); 5.19 (s, 4H); 6.85-7.42 (m, 32H, ArH); 8.20 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 25.46, 26.87, 29.71, 31.76, 32.32, 41.76, 46.49, 49.28, 50.22, 61.70, 114.65, 115.13, 127.15, 128.82, 130.29, 130.91, 131.54, 139.45, 144.08, 150.26, 156.29, 159.82, 195.93 ppm. MALDI-TOF *m/z* 2210.74 (M^+); Anal. Calcd. for $C_{137}H_{148}N_{16}O_{12}$: C, 74.43; H, 6.75; N, 10.14 %; Found: C, 74.55; H, 6.67; N, 10.23 %.

Compound 14d: Pale yellow solid (2.14 g, 89 %), mp. 280-282 °C; IR (KBr): 1634 cm^{1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78-0.93 (two singlets, 48H); 1.67-2.20 (m, 32H); 3.91 (s, 12H); 4.32 (s, 8H); 5.16 (s, 8H); 5.19 (s, 4H); 6.84-7.32 (m, 32H, ArH); 8.21 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 26.83, 29.69, 31.74, 32.33, 41.77, 46.48, 49.27, 50.22, 55.61, 61.64, 114.63, 115.12, 127.07, 128.76, 130.18, 130.88, 131.54, 139.45, 144.04, 150.21, 156.27, 159.82, 195.91 ppm. MALDI-TOF *m/z* 2274.79 (M^+); Anal. Calcd. for $C_{137}H_{148}N_{16}O_{16}$: C, 72.34; H, 6.56; N, 9.85 %; Found: C, 72.42; H, 6.48; N, 9.91 %.

Compound 14e: Pale yellow solid (1.96 g, 81 %), mp. 268-270 °C; IR (KBr): 1636 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72-0.91 (two singlets, 48H); 1.59-2.19 (m, 32H); 4.30 (s, 8H); 5.14 (s, 8H); 5.16 (s, 4H); 6.81-7.32 (m, 32H, ArH); 7.46 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 26.76, 29.64, 31.71, 32.29, 41.71, 46.46, 49.23, 50.20, 55.59, 61.61, 114.61, 115.11, 127.01, 128.75, 130.20, 130.91, 131.52, 139.39, 144.00, 149.95, 156.24, 159.61, 195.93 ppm. MALDI-TOF *m/z* 2292.43 (M^+); Anal. Calcd. for $C_{133}H_{136}Cl_4N_{16}O_{12}$: C, 69.68; H, 5.98;N, 9.78 %; Found: C, 69.76; H, 5.88; N, 9.85 %.

Compound 14f: Pale yellow solid (2.16 g, 83 %), mp. 298-200 °C; IR (KBr): 1637 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.69-0.89 (two singlets, 48H); 1.52-2.03 (m, 32H); 4.29 (s, 8H); 5.11 (s, 8H); 5.14 (s, 4H); 6.79-7.28 (m, 32H, ArH); 7.39 (s, 4H). ^{13}C (75 MHz, $CDCl_3$) 26.73, 29.61, 31.69, 32.21, 41.70, 46.39, 49.20, 50.18, 55.51, 61.60, 114.56, 115.07, 127.00, 128.70, 130.16, 130.83, 131.46, 139.31, 144.13, 149.64, 156.22, 159.63, 195.86 ppm. MALDI-TOF *m/z* 2470.21 (M^+); Anal. Calcd. for $C_{133}H_{136}Br_4N_{16}O_{12}$: C, 64.67; H, 5.55;N, 9.07 %; Found: C, 64.59; H, 5.63; N, 9.13 %.

Compound 14g: Pale yellow solid (1.85 g, 75 %), mp. 286-288 °C; IR (KBr): 1636 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74-0.95 (two singlets, 48H); 1.71-2.29 (m, 32H); 4.72 (s, 8H); 5.28 (s, 8H); 5.36 (s, 4H); 6.92-8.13 (m, 32H, ArH); 8.23 (s, 4H). ^{13}C (100 MHz, $CDCl_3$) 26.94, 29.85, 31.76, 33.22, 41.96, 46.85, 49.68, 50.73, 56.33, 61.96, 115.13, 115.67, 127.87, 128.96, 130.38, 130.63, 131.75, 139.52, 144.21, 150.01, 156.62, 159.12, 196.00 ppm. MALDI-TOF *m/z* 2334.71 (M^+); Anal. Calcd. for $C_{133}H_{136}N_{20}O_{20}$: C, 68.42; H, 5.87; N, 12.00%; Found: C, 68.50; H, 5.93; N, 11.92 %.

Nuclear Magnetic Resonance Spectrum:

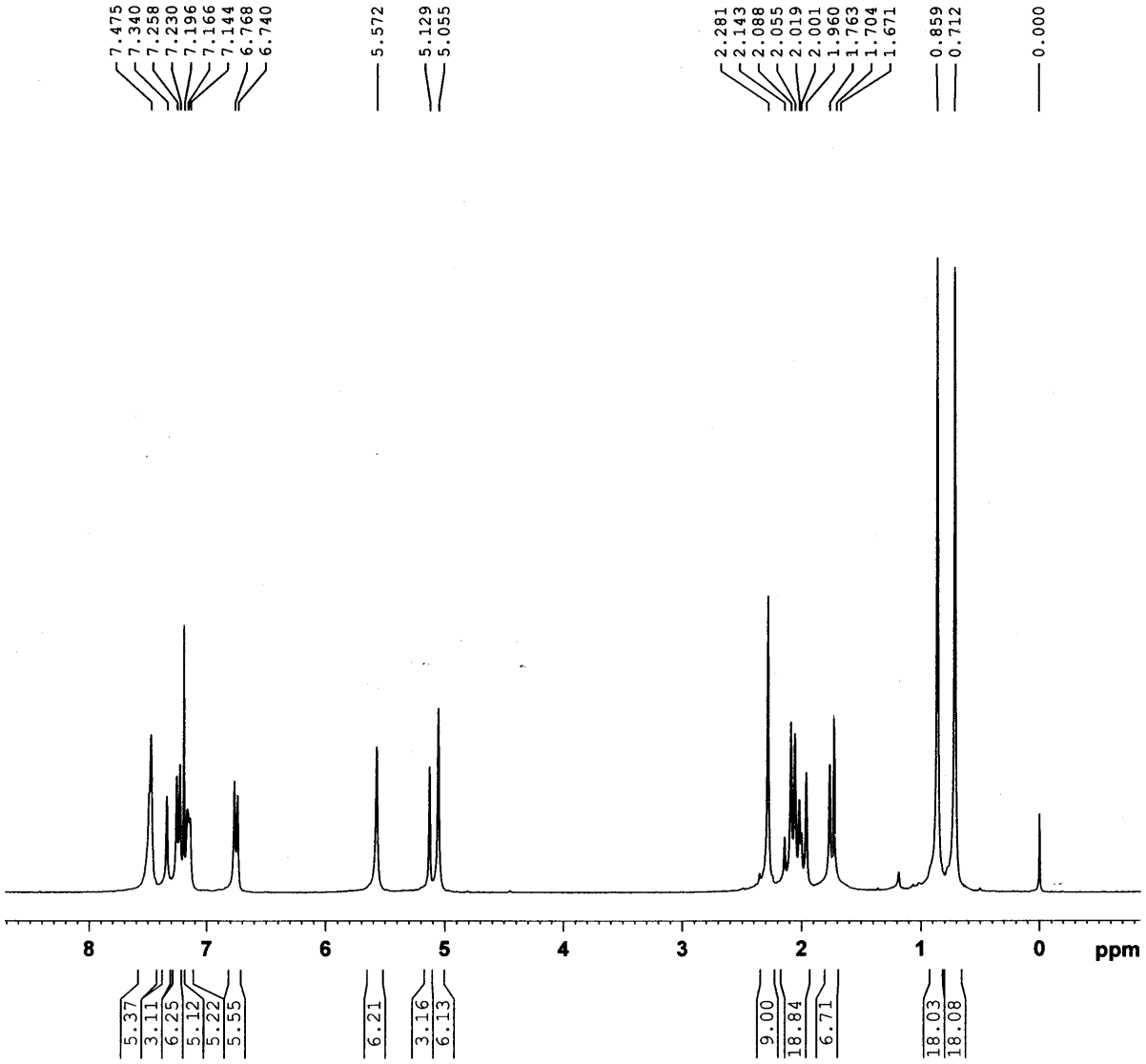

Figure 1a: ^{1}H NMR spectrum of **13b** in $CDCl_3$

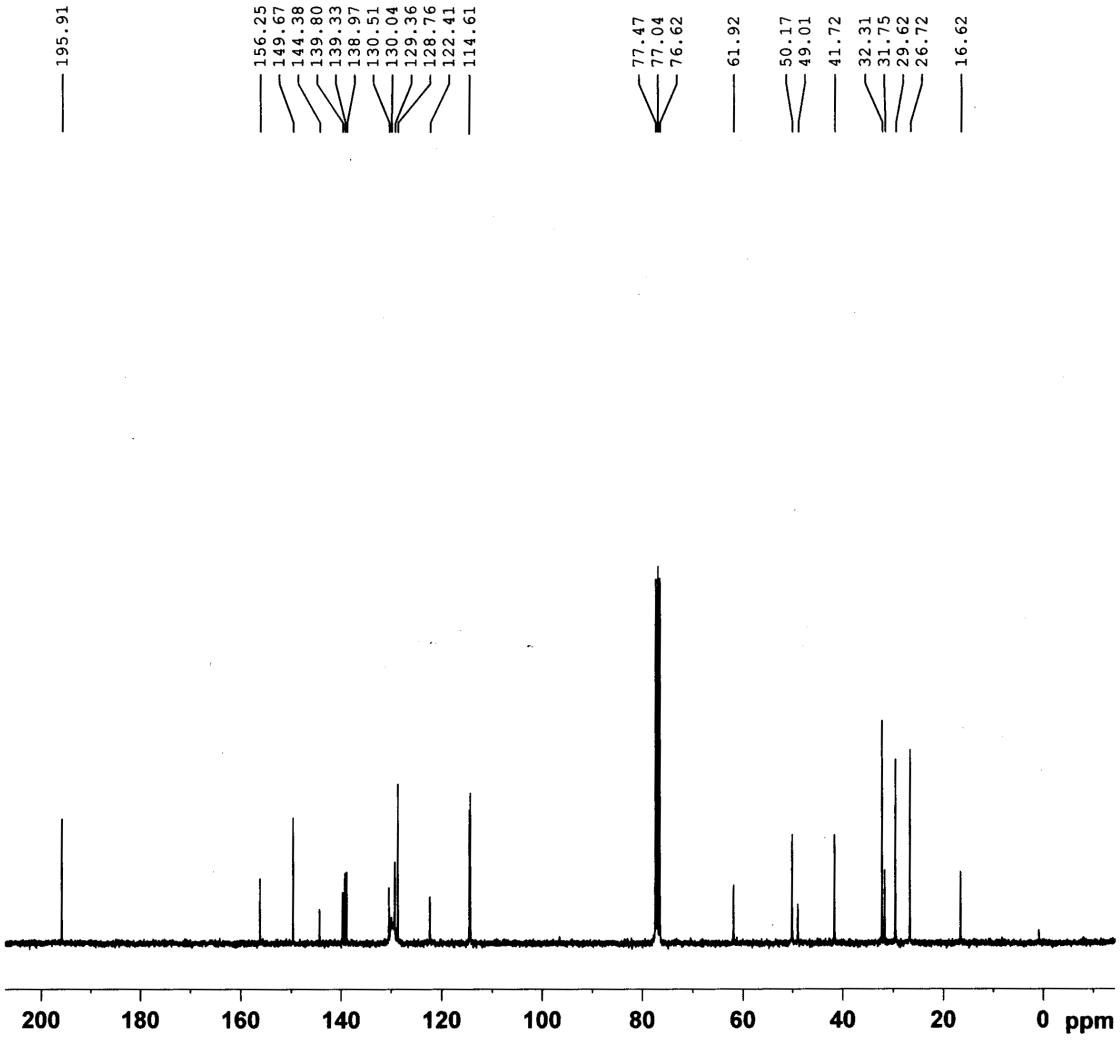

Figure 1b: ^{13}C NMR spectrum of **13b** in $CDCl_3$

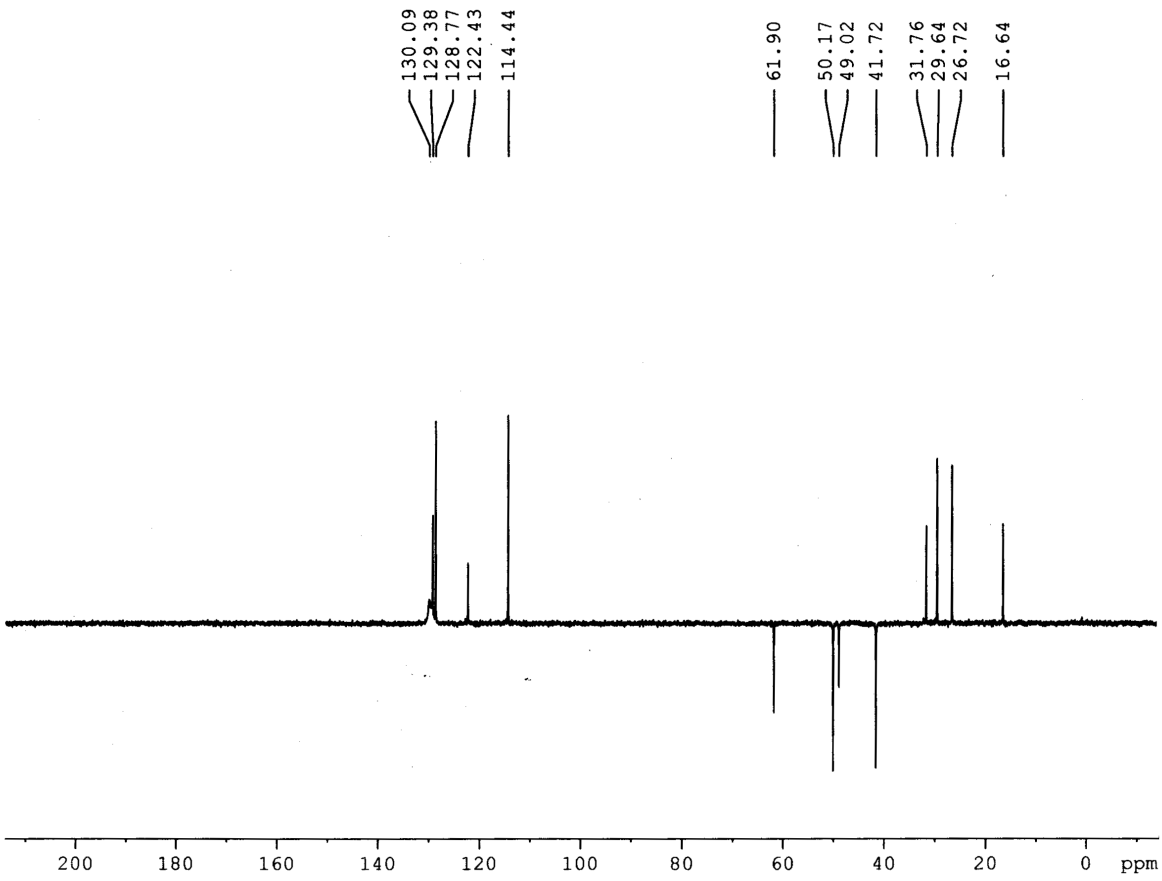

Figure 1c: DEPT-135 spectrum of **13b** in $CDCl_3$

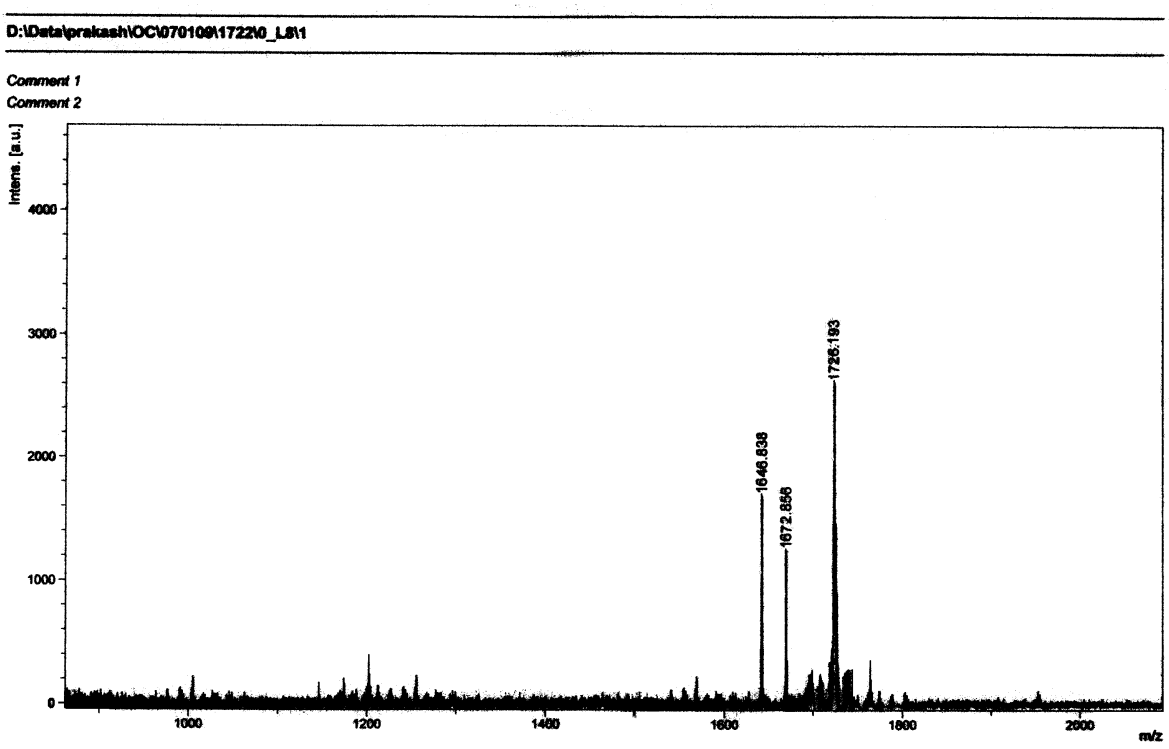

Figure 1d: MALDI-TOF mass spectrum of **13b**

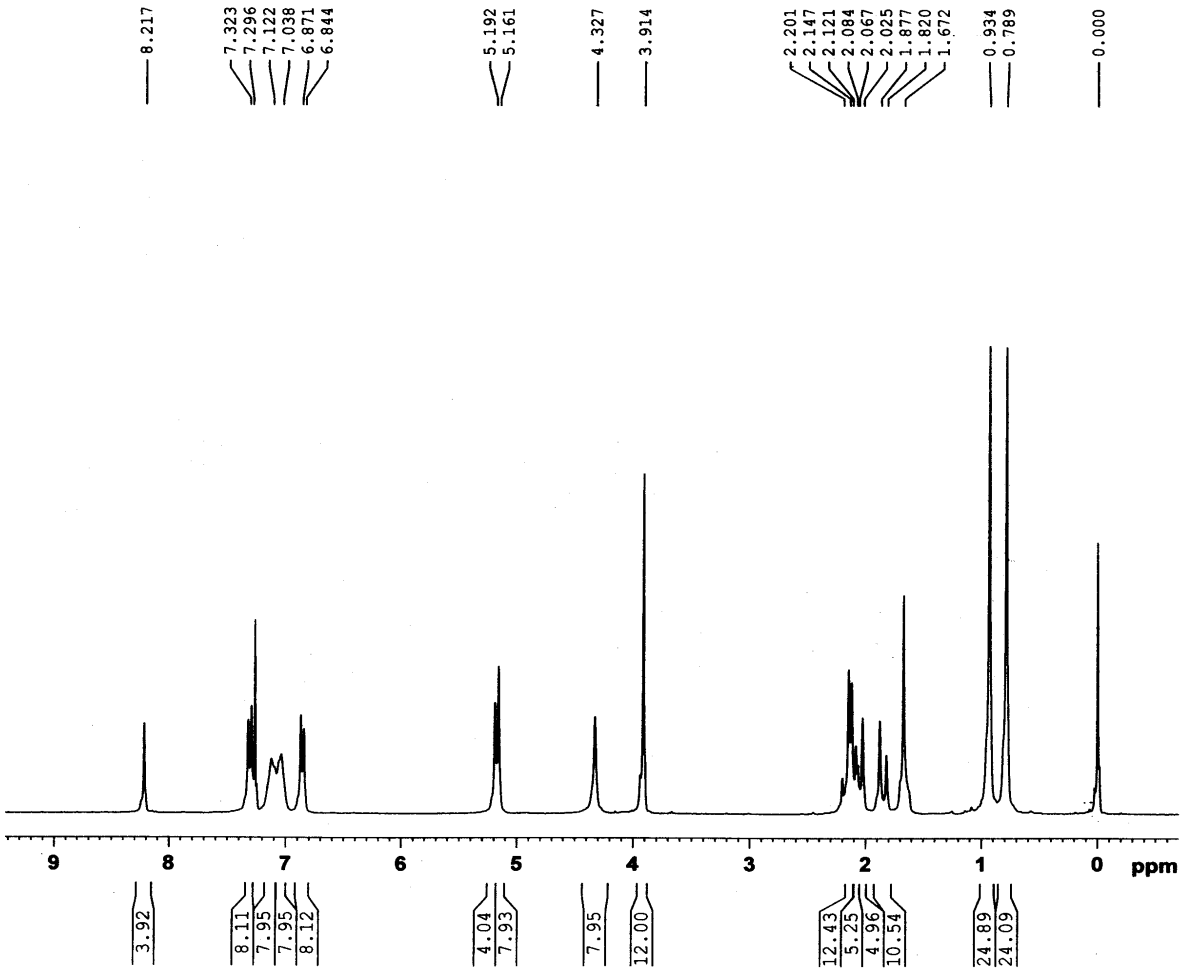

Figure 2a: ^{1}H NMR spectrum of **14d** in $CDCl_3$

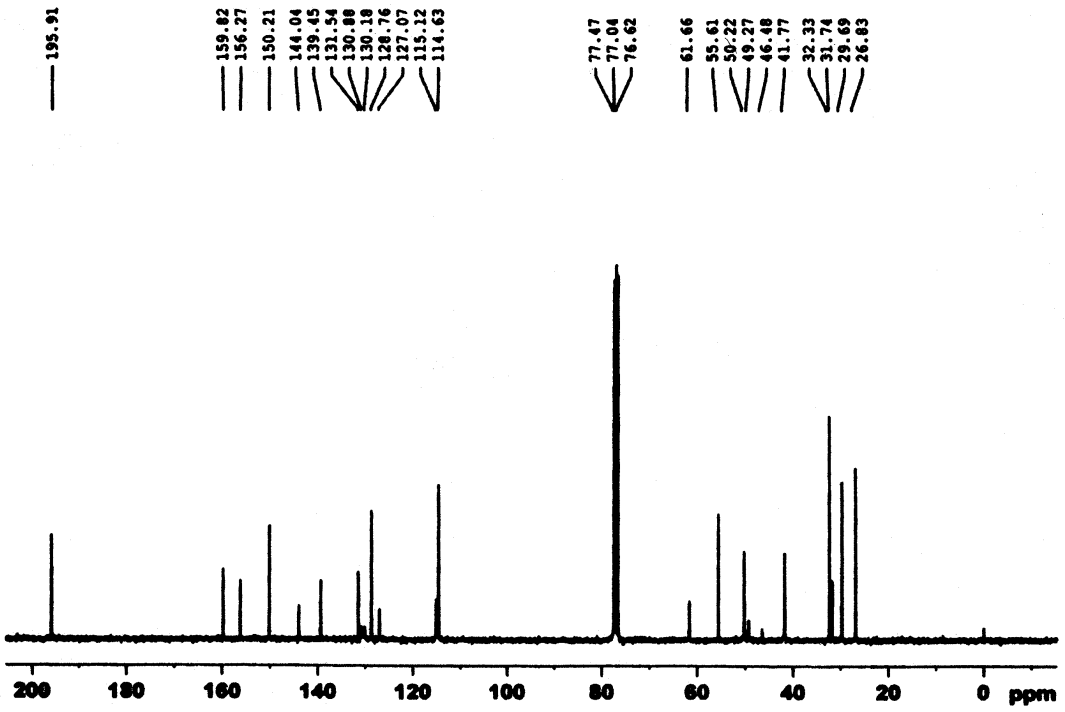

Figure 2b: ^{13}C NMR spectrum of **14d** in $CDCl_3$

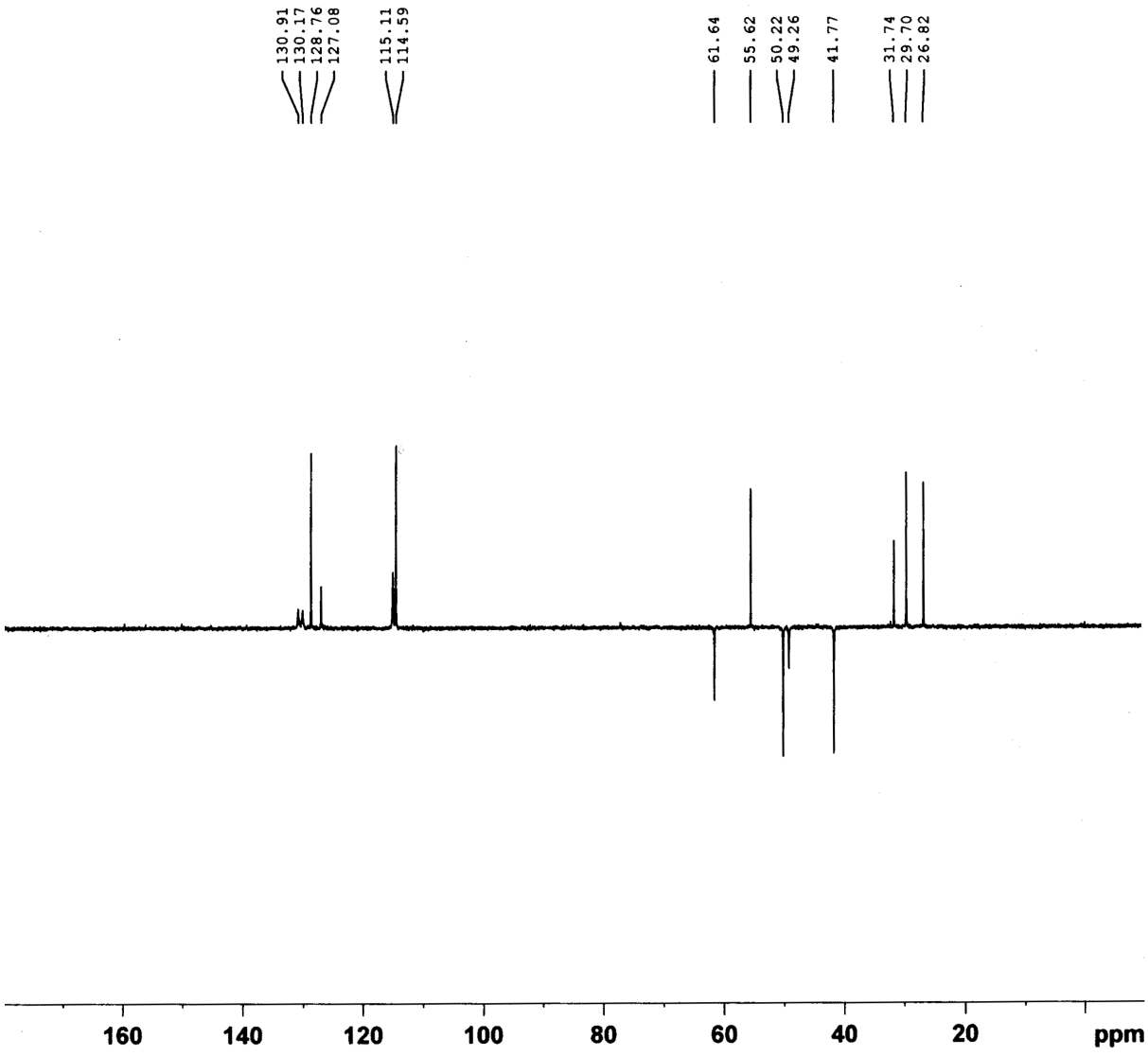

Figure 2c: DEPT-135 spectrum of **14d** in $CDCl_3$

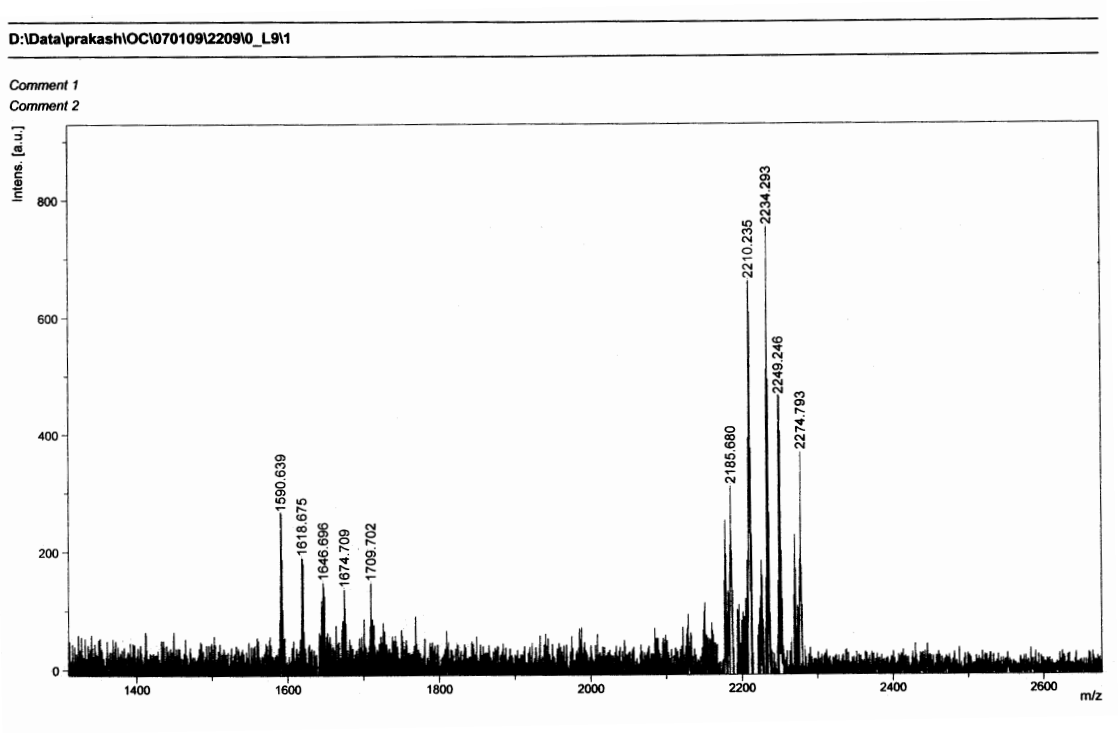

Figure 2d: MALDI-TOF mass spectrum **14d**

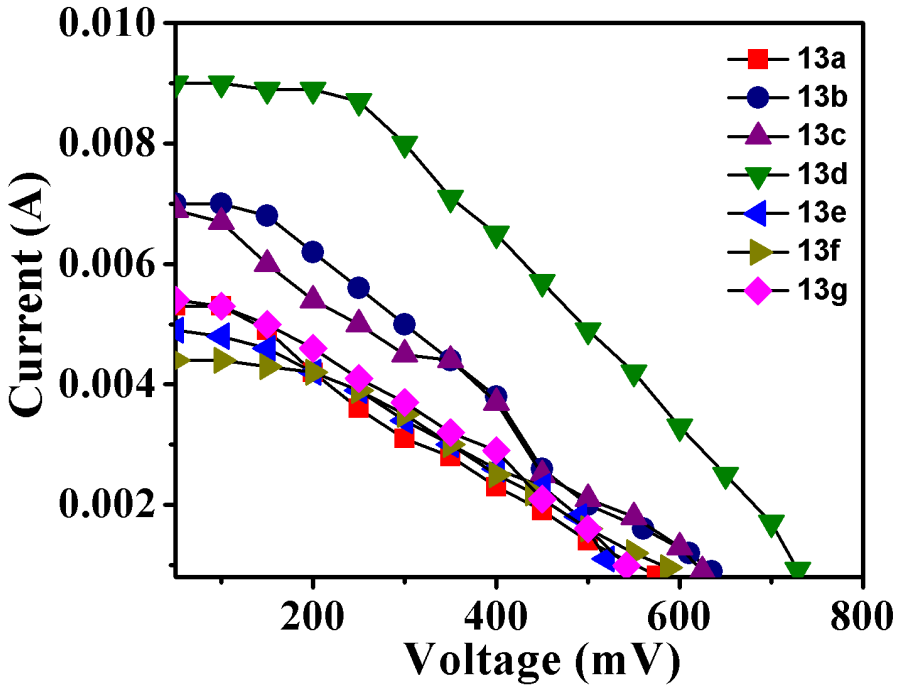

Figure 3a: J-V curves of DSSCs made of [Ru(mttpy)$_2$](N3) with macromolecular cycloadducts **13a-g** in KI/I$_2$ electrolyte at 100 mW/cm^2.

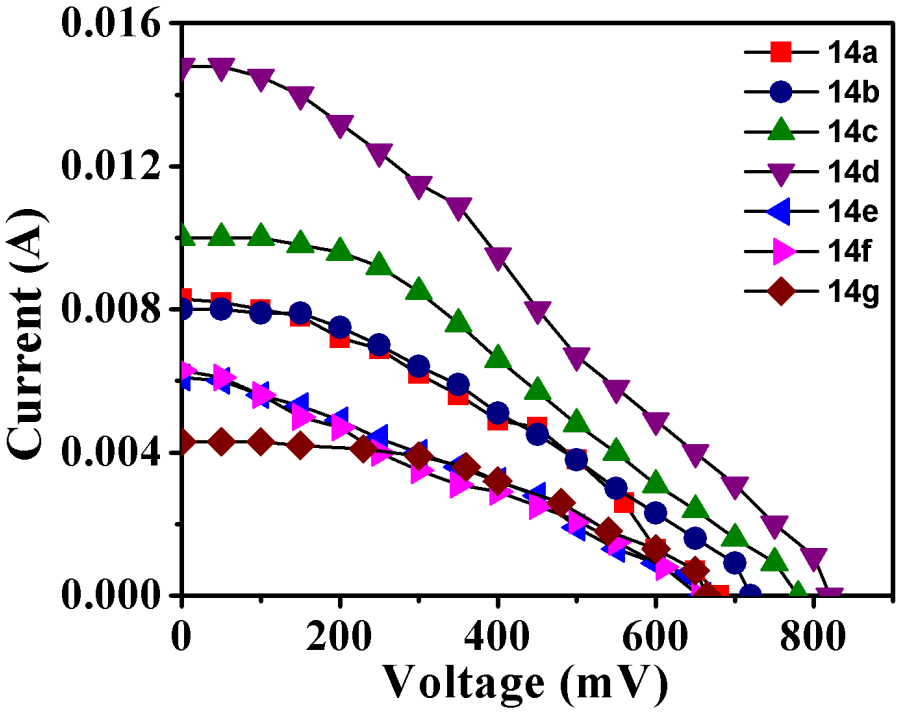

Figure 3b: J-V curves of DSSCs made of [Ru(mttpy)$_2$](N3) with macromolecular cycloadducts **14a-g** in KI/I$_2$ electrolyte at 100 mW/cm^2.