## **Supporting information**

*Title:*  $\pi$ -Conjugated Polymer-Eu<sup>3+</sup> Complexes: A Versatile Luminescent Molecular Probe for Temperature Sensing

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## **Experimental section**



Scheme SS1. Synthesis of OPV-TEG.

**Materials:** 3-(4-Hydroxyphenyl)propionic acid, 2-ethylhexylbromide, triethylphosphite, 4hydroxybenzaldehyde, p-toluenesulfonylchloride, triethyleneglycol, hexaethyleneglycol, polyethyleneglycol ( $M_n = 400$ ), triethyleneglycol monomethylether, potassium-tert-butoxide, theonyltrifluoroacetylacetone, Gd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, Eu(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O were purchased from Aldrich chemicals. HBr in glacial acetic acid, paraformaldehyde, potassium carbonate and all other reagents and solvents were purchased locally and purified following the standard procedure. The compound 3-(3,5-bis ((diethoxyphosphoryl) methyl)-4-(2-ethylhexyloxy) phenyl) propanoic acid was synthesized by following the earlier our reported procedure.

General procedures: <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the monomers, oligomer and the polymers were recorded using 400-MHz Jeol NMR spectrophotometer in CDCl<sub>3</sub> containing small amount of TMS as internal standard. Infra-red spectra of the oligomer, polymers and their complexes were recorded using a Thermo-Scientific Nicolet 6700 FT-IR spectrometer with the solid state in KBr. The mass of all the monomers were confirmed by using the Applied Biosystems 4800 PLUS MALDI TOF/TOF analyzer. The molecular weight of the polymer and purity of the oligomers were determined by gel permeation chromatography (GPC) using a Viscotek VE 1122 pump, Viscotek VE 3580 RI detector, and Viscotek VE 3210 UV/Vis detector in tetrahydrofuran (THF) using polystyrene as standards. Thermal stability of the polymeric complexes was determined using Perkin Elmer thermal analyser STA 600 model at a heating rate of 10 °C/min in nitrogen atmosphere. The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Flurolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m Spex1680 monochromator and a 450W Xe lamp as the excitation source at room temperature. The excitation spectra are collected at 612 nm (Eu<sup>3+</sup> ion emission wavelength) and the emission spectra are recorded by exciting at the excitation maxima. The solution spectra were recorded in chlorobenzene and for solid state spectra polymers thin films were prepared by drop casting chlorobenzene on quartz substrates. The concentrations of the polymer and standard solution were adjusted in such a way to obtain the absorbance equal to 0.1 at 310 nm. The excitation and emission spectra of the complexes were corrected at instrumental function. The photoluminescence lifetime measurements were carried out at room temperature using a SPEX Flurolog HORIBA JOBIN VYON 1934 D phosphorimeter. The fluorescence quantum yields of the polymers were determined in water using quinine sulfate in 0.1N conc. H<sub>2</sub>SO<sub>4</sub> ( $\phi$ =0.53) as the standard by exciting at 310 nm. The concentration of the polymer solutions were adjusted in such a way to obtain the absorbance equal to 0.1 at 310 nm. The quantum yields of the samples are calculated by following the reported procedure. The XPS measurements were carried out using a multiprobe system (Omicron Nanotechnology, Germany) equipped with a dual Mg/Al X-ray

source and a hemispherical analyzer operating in constant analyzer energy (CAE) mode. The spectra were obtained with pass energy of 50 eV for survey scan and individual scans; a Mg K $\alpha$  X-ray source was operated at 300 W and 15 kV. The base pressure in the analyzing chamber was maintained at  $1 \times 10^{-10}$  mbar. For the quantification of the elements, relative sensitivity factors (RSF) provided by the manufacturer were used. For adventitious carbon, 284.9 eV was taken as the reference binding energy for charge correction.

**Synthesis** 2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4of methylbenzenesulfonate) (5a): The solution of sodium hydroxide (7.59g, 189.8 mmol) in water (40 mL) was added into the THF (60 mL) solution of triethyleneglycol (10.0 g, 66.6 mmol). The reaction mixture was cooled to 0 °C and stirred for 30 minutes. To this mixture, a THF (20 mL) solution of p-toluenesulfonylchloride (15.2 g, 79.9 mmol) was slowly added into the reaction mixture and stirring was continued for 3 h under ice cold conditions. The mixture was poured into water and the white precipitate was filtered, washed with excess water until the pH become neutral and dried in vacuum oven. The product was further purified by column chromatography using 20 % ethylacetate/ petether systm. Yield= 9.8 g (72 %). H<sup>1</sup>-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.77 (d, 4H, Ar - H), 7.30 (d, 4H, Ar - H), 4.11 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.63 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.50 (s, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>), 2.42 (s, 6H, Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 144.93 (2C), 132.99 (2C), 129.91 (4C), 128.01 (4C), 70.74 (2C), 69.25 (2C), 68.80 (2C) and 21.70 (2C). FT-IR (cm<sup>-1</sup>): 2950, 2890, 1590, 1450, 1360, 1180, 1130, 1100, 1010, 924, 812, 768, and 663. MALDI-TOF TOF: MW = 458.55 and m/z = 497.43 (M+ 39).

Synthesis of 3,6,9,12,15-pentaoxaheptadecane-1,17-diyl bis(4-methylbenzenesulfonate) (5b): Hexaethylene glycol hexaethyleneglycol (5 g, 17.7 mmol) was reacted with p-toluenesulfonyl chloride (6.7 g, 35.3 mmol) in the presence of sodium hydroxide (2.1 g, 53.0 mmol) as base in THF (24 mL) + water (12 mL) (2:1) mixture following the procedure described for **5a**. The product was further purified by column chromatography using 35 % ethylacetate/ petether systm. Yield= 4.1 g (40 %). H<sup>1</sup>-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.76 (d, 4H, Ar - H), 7.31 (d, 4H, Ar - H), 4.12 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.67 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.55-3.63 (m, 16H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>-), 2.42 (s, 6H, Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 144.93 (2C), 132.94 (2C), 129.92 (4C), 128.03 (4C), 70.75 (2C), 70.63, 70.55, 69.35 (2C), 68.71(2C) and 21.70 (2C). FT-IR (cm<sup>-1</sup>): 2910, 2890, 1740, 1600, 1450, 1350, 1180, 1120, 1100, 1010, 918, 814, 773 and 663. MALDI-TOF TOF: MW = 590.70 and m/z = 629.21 (M<sup>+</sup> + 39 (K<sup>+</sup>)).

Synthesis of polyethyleneglycol bis(4-methylbenzenesulfonate) terminated (5c): Polyethyleneglycol (5.0 g, 12.5 mmol) was reacted with p-toluenesulfonyl chloride (6.1 g, 32.0 mmol) in the presence of sodium hydroxide (1.5 g, 38.5 mmol) as base in THF (12.5 mL) + water (12.5 mL) mixture (2:1) following the procedure described for **5a**. The product was further purified by column chromatography using 50 % ethylacetate/ petether systm. Yield= 6.6 g (75 %). H<sup>1</sup>-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.74 (d, 4H, Ar - H), 7.30 (d, 4H, Ar - H), 4.10 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.69 (t, 4H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>), 3.52-3.63 (m, 32H, Ar-SO<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>-), 2.42 (s, 6H, Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 144.88 (2C), 132.98 (2C), 129.90 (4C), 128.02 (4C), 70.74 (2C), 70.54 (2C), 69.50, 68.70 (2C) and 21.69 (2C). FT-IR (cm<sup>-1</sup>): 2880, 1730, 1600, 1460, 1360, 1180, 1120, 1020, 920, 816, 715 and 669. MALDI-TOF TOF: M<sub>n</sub> = 590.70 and the repeating unit mass m/z = 629.21(n x 44+326) +39 (K+), n = 8.

Synthesis of 4,4'-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde (6a): 4-Hydroxybenzaldehyde (6.70 g, 54.4 mmol) and anhyd. $K_2CO_3$  (7.5 g, 65.4 mmol) were taken in flask containing dry acetonitrile (80 mL) and stirred well at 80 °C under nitrogen atmosphere about 1 h. The catalytic amount of KI and TEG-OTs (10.0 g, 21.9 mmol) were added into the reaction mixture. The reaction was continued about 24 hours at 80 °C under nitrogen

atmosphere. The reaction mixture was poured into the water and then extracted with ethylacetate. The organic layer was washed with 5 % NaOH, brine solution, water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to get white solid product. It was further purified by column chromatography using 25 % ethylacetate/ petether systm. Yield= 4.1 g (79 %). H<sup>1</sup>-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.85 (s, 2H, Ar - CHO), 7.79 (d, 4H, Ar - H), 6.97 (d, 4H, Ar - H), 4.17- 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.86-3.88 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.74 (s, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 190.97, 163.86, 132.04, 130.12, 114.91, 71.00, 69.61, and 67.78. FT-IR (cm<sup>-1</sup>): 2920, 2870, 1690, 1600, 1520, 1480, 1310, 1270, 1210, 1160, 1120, 1030, 991, 823 and 609. MALDI-TOF TOF: MW = 358.39 and m/z = 397.11 (M<sup>+</sup> + 39 (K<sup>+</sup>)).

**4,4'-(3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(oxy))dibenzaldehyde** (6b): 4-Hydroxybenzaldehyde (2.9 g, 23.7 mmol) was reacted with compound **6b** (5.6 g, 94.9 mmol) using anhyd.K<sub>2</sub>CO<sub>3</sub> (3.3 g, 23.7 mmol) in dry acetonitrile (60 mL) following the procedure described for **6a**. It was further purified by column chromatography using 40 % ethylacetate/ petether systm. Yield= 2.3 g (50 %). H<sup>1</sup>-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.86 (s, 2H, Ar - CHO), 7.81 (d, 4H, Ar - H), 7.00 (d, 4H, Ar - H), 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.86 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.63-3.73 (m, 16H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 191.06, 163.89, 132.05, 130.08, 114.93, 70.93, 69.51, and 67.79. FT-IR (cm<sup>-1</sup>): 2870, 2740, 1690, 1600, 1590, 1510, 1450, 1430, 1390, 1350, 1310, 1260, 1220, 1160, 1100, 1050, 951, 835 and 615. MALDI-TOF TOF: MW = 490.76 and m/z = 529.22 (M<sup>+</sup> + K<sup>+</sup>).

Synthesis of of polyethylenegylycol bis(oxy)dibenzaldehyde terminated (6c): 4-Hydroxybenzaldehyde (3.5 g, 28.2 mmol) was reacted with compound 5c (8 g, 11.3 mmol) using anhyd.K<sub>2</sub>CO<sub>3</sub> (4.7 g, 33.9 mmol) in dry acetonitrile (60 mL) following the procedure described for 6a. The product was further purified by column chromatography using 55 % ethylacetate/ petether systm. Yield= 4.9 g (66 %). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.86 (s, 2H, Ar - CHO), 7.81 (d, 4H, Ar - H), 7.01 (d, 4H, Ar - H), 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.86 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.61-3.71 (m, 32H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 191.07, 163.88, 132.02, 130.03, 114.91, 70.89, 70.55, 69.47, and 67.80. FT-IR (cm<sup>-1</sup>): 2880,1690, 1600, 1580, 1510, 1450, 1350, 1310, 1260, 1110, 1050, 949, 835 and 773. MALDI-TOF TOF: M<sub>n</sub> = 666.75 and repeating unit mass m/z = 705.35 (n x 44+226) + 39 (K<sup>+</sup>)), n = 10.

## Synthesis of segmented $\pi$ -conjugated polymers

Typical procedure is explained for **Poly(OPV-TEG**) and other polymers were synthesized following similar procedure.

Synthesis of Poly(OPV-TEG): Compound 4 (1.0 g, 1.7 mmol) and compound 6a (0.23 g, 1.7 mmol) were dissolved in dry THF (15 mL). The mixture was stirred well under nitrogen atmosphere about 15 minutes at room temperature. Potassium tert-butoxide (10.4 mL in 1 M THF) was added drop wise and stirred for further 12 h at room temperature under nitrogen atmosphere. After 5 minutes the yellow precipitates were formed and accumulated as viscous beads. It was poured into water and neutralised with 10 % HCL, the product was washed with excess of water. The polymer was purified by re-dissolving in THF and precipitated methanol. It was dried in a vacuum oven at 40 °C for 5 h prior to further analysis. Yield = 0.34g (54 %). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>)  $\delta$ : 7.47-6.95 (m, 14H, Ar-H and vinylic H), 4.18 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.90 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.81 (s, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>), 2.97 (t, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 2.74 (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>COOH), 1.92-0.90 (m, 32H, aliphatic H). FT-IR (cm<sup>-1</sup>): 3538, 2921, 2860, 1731, 1605, 1564, 1372, 1219, 1013, 906, and 774. Molecular weight (GPC, in THF): M<sub>n</sub> = 8300 and M<sub>w</sub> = 24200.

Synthesis of Poly(OPV-HEG): Compound 4 (0.57 g, 1.0 mmol) was reacted with compound **6b** (0.49 g, 1.0 mmol) using potassium tert-butoxide (15 mL in 1 M THF) in dry THF (15 mL) following the procedure described for **Poly(OPV-TEG)**. The polymer was purified by re-

dissolving in THF and precipitated methanol. It was dried in a vacuum oven at 40 °C for 5 h prior to further analysis. Yield = 0.49 g (65 %). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>)  $\delta$ : 7.41-6.87 (m, 14H, Ar-H and vinylic H), 4.10 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.81 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.79-3.64 (m, 16H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>), 2.92 (t, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 2.68 (t,2H, CH<sub>2</sub>-CH<sub>2</sub>COOH), 1.84-0.83 (m, 32H, aliphatic H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 176.30, 158.73, 143.41, 136.25, 131.71, 130.01, 129.28, 121.97, 124.90, 121.39, 115.09, 114.53, 71.06, 70.86, 69.98, 67.70, 41.21, 36.03, 31.10, 29.67, 24.07, 23.44, 14.42, and 11.70. FT-IR (cm<sup>-1</sup>): 3662, 2926, 2860, 1742, 1598, 1511, 1460, 1376, 1249, 1178, 1131, 960, 775, 718 and 584. Molecular weight (GPC, in THF): M<sub>n</sub> = 12400 and M<sub>w</sub> = 18600.

**Synthesis of Poly(OPV-PEG400):** Compound **4** (0.57 g, 1.0 mmol) was reacted with compound **6c** (0.66 g, 1.0 mmol) using potassium tert-butoxide (6 mL in 1 M THF) in dry THF (15 mL) following the procedure described for **Poly(OPV-TEG)**. The polymer was purified by redissolving in THF and precipitated in methanol. It was dried in a vacuum oven at 40 °C for 5 h prior to further analysis. Yield = 0.59 g (62 %). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>)  $\delta$ : 7.41-6.87 (m, 14H, Ar-H and vinylic H), 4.10 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.81 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.79-3.64 (m, 16H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>), 2.92 (t, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 2.68 (t,2H, CH<sub>2</sub>-CH<sub>2</sub>COOH), 1.84-0.83 (m, 32H, aliphatic H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 176.34, 158.52, 153.18, 136.20, 132.15, 131.47, 130.06, 129.28, 127.74, 124.71, 121.16, 114.88, 114.29, 107.67, 106.41, 70.84, 70.55, 69.76, 69.76, 67.49, 66.98, 61.60, 40.99, 35.82, 32.33, 30.88, 29.55, 29.45, 27.86, 23.89, 23.20, 22.23, 14.19, 11.47, and 11.36. FT-IR (cm<sup>-1</sup>): 3664, 2926, 2860, 1742, 1592, 1508, 1462, 1358, 1249, 1104, 935, 778, 683 and 583. Molecular weight (GPC, in THF): M<sub>n</sub> = 3400 and M<sub>w</sub> = 6400.

Synthesis of Poly (OPV-DD): Compound 4 (0.55 g, 0.9 mmol) was reacted with compound 7 (0.39 g, 0.9 mmol) using potassium tert-butoxide (6 mL in 1 M THF) in dry THF (15 mL) following the procedure described for **Poly(OPV-TEG)**. The polymer was purified by redissolving in THF and precipitated in methanol. It was dried in a vacuum oven at 40 °C for 5 h prior to further analysis. Yield = 0.44 g (68 %). FT-IR (cm<sup>-1</sup>): 3689, 2931, 2848, 1744, 1598, 1460, 1376, 1300, 1246, 1137, 1009, 903, 774, 689 and 579. Molecular weight (GPC, in THF):  $M_n = 17500$  and  $M_w = 90000$ .

3-(4-((2-ethylhexyl)oxy)-3,5-bis((E)-4-(2-(2-(2-methoxyethoxy)ethoxy) **Synthesis** of )ethoxy)styryl)phenyl)propanoic acid (OPV-TEG): Compound 5 (0.57 g, 1.0 mmol) was reacted with compound 9 (0.53 g, 2.0 mmol) using potassium tert-butoxide dry THF (15 mL) following the procedure described for Poly(OPV-TEG). The product was purified by column chromatography using 25% ethyl acetate and petroleum ether. It was dried in a vacuum oven at 40 °C for 5 h prior to further analysis. Yield = 0.65 g (75 %). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>)  $\delta$ : 7.45-6.89 (m, 14H, Ar-H and vinylic H), 4.19 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 4.10 (d, 2H, Ar-OCH<sub>2</sub>CH) 3.86 (t, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>), 3.74-3.64 (m, 12H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>), 3.38 (s, 6H, OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>3</sub>), 2.96 (t, 2H, Ar-CH<sub>2</sub>CH<sub>2</sub>), 2.72 (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>COOH), 1.75-0.84 (m, 32H, aliphatic H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.35, 158.55, 153.24, 138.02, 132.29, 129.10, 127.76, 124.70, 121.19, 114.88, 114.32, 71.98, 70.72, 70.62, 62.88, 69.80, 67.51, 61.77, 59.11, 41.02, 35.90, 30.90, 29.48, 23.87, 23.23, 16.54, 14.21 and 11.49. FT-IR (cm<sup>-1</sup>): 3435, 2926, 2861, 1731, 1603, 1511, 1457, 1378, 1250, 1171, 1108, 1032, 972, 821, 771, and 674. MALDI-TOF TOF: MW = 807.45 and  $m/z = 845.51 (M^+ + K^+)$ .

**Synthesis of Eu<sup>3+</sup> complexes:** The segmented polymers and oligomer were converted into their corresponding sodium salts in THF/MeOH mixture with NaOH (1.1 mole equivalents) in water solution and the mixture was heated at 70 °C for 1h. Theonyltrifluoroacetylacetone (TTA) (0.05

g, 0.22 mmol) in ethanol (5 mL) and NaOH (0.012 g, 0.29 mmol) in water were added into the in-situ prepared sodium salt of polymer (0.073 mmol). The whole mixture stirred well about 30 minutes and  $Eu(NO_3)_3.6H_2O$  (0.03 g, 0.07 mmol) in ethanol (1 mL) was slowly added into the mixture. The complex was concentrated and precipitated in water. The precipitates were filtered and washed with water, hot ethanol and dried in vacuum oven.

**Poly(OPV-DD)** -**Eu**<sup>3+</sup>: Yield = 0.072 g (66%). FT-IR (cm<sup>-1</sup>): 3730, 3625, 2966, 2918, 2872, 2363, 1690, 1595, 1517, 1450, 1301, 1240, 1140, 955, 843, 774, 710, and 630.

**Poly(OPV-TEG)** -**Eu**<sup>3+</sup>: Yield = 0.056 g (53%). FT-IR (cm<sup>-1</sup>): 3614, 2954, 2861, 2350, 1607, 1511, 1451, 1408, 1290, 1240, 1192, 1134, 1068, 938, 853, 788, 723, 648, and 575.

**Poly(OPV-HEG)-Eu<sup>3+</sup>:** Yield = 0.07 g (63%). FT-IR (cm<sup>-1</sup>): 3675, 2911, 2350, 1702, 1613, 1508, 1464, 1400, 1287, 1426, 1130, 1050, 947, 784, 670 and 604.

**Poly(OPV-PEG)-Eu<sup>3+</sup>:** Yield = 0.03 g (29%). FT-IR (cm<sup>-1</sup>): 3688, 2988, 2854, 1593, 1501, 1464, 1358, 1250, 1097, 950, 781, 670 and 577.

**OPV-TEG -Eu<sup>3+</sup>:** Yield = 0.4 g (59%). FT-IR (cm<sup>-1</sup>): 3418, 2922, 2868, 1605, 1540, 1510, 1450, 1415, 1352, 1300, 1249, 1186, 1140, 1062, 972, 959, 934, 859, 781, 718, 684, 640 and 582.

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GPC and Thermal Data



Figure SF1. GPC chromatogram of the segmented polymers.

**Note:** The GPC chromatograms of the polymers were appeared as single peak which indicated the formation of uniformly dispersed polymers. The  $M_n$  decreased with the increase PEG chain length (especially PEG-400) which was attributed to the availability of little aldehyde functionality for polymerization in the bis-aldehyde derivatives at longer PEG chains.

**Table ST1**.  $M_n$ ,  $M_w$ , Thermal decomposition temperature (T<sub>D</sub>), glass transition temperature (T<sub>g</sub>),  $\lambda_{max}$  and quantum yield ( $\phi$ ) of the segmented polymers.

Compound	M <sub>n</sub>	$\mathbf{M}_{\mathbf{w}}$	T <sub>D</sub>	Tg	λ	φ	
			(°C)	(°Č)	Abs	FL	
Poly(OPV-DD)	17800	37500	389	83.7	310 (311)	409 (438)	0.27
Poly(OPV-TEG)	8300	24200	391	69.9	310 (310)	412 (462)	0.13
Poly(OPV-HEG)	12400	18600	381	12.3	310 (310)	409 (415)	0.18
Poly(OPV-PEG)	3400	6400	351	8.3	311(310)	412 (440)	0.17



**Figure SF2**. TGA plot of segmented polymers (a) and their Eu<sup>3+</sup> complexes (b).

**Note:** TGA analysis confirmed that all polymers and their  $Eu^{3+}$  complexes were thermally more stable up to 300 °C.



Figure SF3. DSC analysis of segmented conjugated polymers.

**Note:** The glass transition temperature of the segmented polymers was decreased with increase of PEG chain length in the polymer backbone. The glass transition temperature of the fully hydrophobic chain containing polymer is higher than PEG unit containing polymers which indicate that the rigidity of the segmented polymers is decreases with increasing of flexible PEG content in the polymeric chain.

Photophysical studies of Polymer and Eu<sup>3+</sup> complexes



**Figure SF4**. Absorption and emission spectra of segmented  $\pi$ -conjugated polymers in chlorobenzene solution (*a*) and solid state (drop casted films) (*b*).



## **Figure SF5**. *FT-IR spectra of the segmented Poly-(OPV-TEG),OPV and their Eu^{3+} complexes.*

**Note:** The carbonyl stretching frequency of the polymers and oligomer at 1735 cm<sup>-1</sup> was completely vanished and new peaks corresponding to antisymmetric and symmetric vibration of the M-C=O carboxylate group were appeared approximately at 1615 cm<sup>-1</sup> and 1450 cm<sup>-1</sup> in the polymeric Eu<sup>3+</sup> complexes.



**Figure SF6**. *MALDI-TOF spectra of the OPV-TEG-*  $Eu^{3+}$  *complex*.

**Note:** The MALDI-TOF spectrum of OPV-TEG-Eu<sup>3+</sup> complex showed peak at 1434.21 amu which is molecular ion peak of Eu(TTA)<sub>2</sub>.OPV-TEG with two water molecules. MALDI-TOF MS spectra of the complex showed a mass peak at 1434.21 amu with respect to  $(OPVTEG)(TTA)_2 Eu^{3+}(H_2O)_2$ . The Eu<sup>3+</sup> ion complex was constituted by two TTA carboxylic units and one OPV carboxylic unit for the charge neutralization at the metal center. Further, the eight coordination of the Eu<sup>3+</sup> ion was satisfied by the coordination of two water molecules from the solvent. Hence, both the carboxylic acid units from TTA and OPV units indeed participated in the Eu<sup>3+</sup> ion complex formation.



**Figure SF7**. XPS spectra of the Poly(OPV-TEG)-  $Eu^{3+}$  complex; **a**) Eu3d core level spectra, **b**) Eu4d core level spectra, **c**) C1s spectra and **d**) O1s spectra.

**Note:** Among the all polymer- $Eu^{3+}$  complexes, Poly(OPV-TEG)-  $Eu^{3+}$  complex was subjected for detailed XPS measurement to determine the metal coordination environment and elements in the complex. The peaks corresoponds to the  $Eu3d_{5/2}$  and  $Eu3d_{3/2}$  binding energy values were appeared at 1136.4 and 1166.2 eV repectively. Similarly, the Eu4d core level XPS spectra showed two peaks at 139.3 and 144.6 eV which are accordance with binding energy values of reported Eu4d level. The different nature of carbon atoms present in the polymer-Eu<sup>3+</sup> complexes were identified by C1s XPS spectra in figure SF7c. The broad C1s peak was fitted with Guassian multiple programms and the peak values were appeared at 287.2 eV, 289.9 eV and 291.1 eV. The strong peak at 287.2 eV was assigned to C-C and C-H carbon atoms and broad weak peak at 289.9 eV was assigned to carbon bonded to oxygen atoms (TTA) in the conjugated system respectively. The peak corresponds to carboxylate group carbon atom coordinated to  $Eu^{3+}$  ion were appeared at 289.9 eV. The actual binding energies of COOH group carbon atom in the present system were almost similar to the polyacrylic systems which was attributed to similarity of aliphatic COOH group in the conjugated OPV chromophore. The binding energy value at 533.1 is corresponding to ether oxygen atom (C-O) of polymeric unit. The oxygen atom of carboxylate and diketone groups coordinated with Eu atom showed binding energy values at 534.5 and 535.8 eV respectively. These results are clearly confirmed that the  $Eu^{3+}$  metal ion is coordinated with both carboxylate of polymeric chain and  $\beta$ -diketone group.



**Figure SF8**. Absorbance (solution (a)) and excitation (solid state (b)) state spectra of segmented polymers and oligomer-Eu<sup>3+</sup> complexes.

**Note:** The absorbance spectra of the polymers and oligomer  $-Eu^{3+}$  complexes showed almost same absorption maxima in the chlorobenzene solution which is almost to similar their excitation spectra (in figure 2a). It is clearly indicating that resulted emission is arising from kind species. The excitation spectra of polymer complexes in the film state showed excitation maxima at 365 nm which is almost similar to excitation spectra in chlorobenzene solution.



**Figure SF9**. Absorption and emission spectra of the  $Eu^{3+}$  complexes of segmented polymers in *THF* solutions.

<u>Note:</u> The photophysical characteristics of the segmented polymer- $Eu^{3+}$  complexes were studied also in THF solution to comparing the role of solvent (see supporting information). In THF solution, there was no self emission observed in both emission spectra of the  $Eu^{3+}$  complexes as like in chlorobenzene solution. It suggested that polarity of the solvents is not influencing on the photoexcitation energy transfer process in the  $Eu^{3+}$  complexes.

Complexes	A <sub>RAD</sub> (S <sup>-1</sup> )		A <sub>NR</sub> (S <sup>-1</sup> )		τ <sub>obs</sub> (μs)		Φ <sub>Ln</sub> (%)	
	Film	Soln	Film	Soln	Film	soln	Film	Soln
Poly(OPV-DD)-Eu <sup>3+</sup>	860	922	3847	681	212	384	18	35
Poly(OPV-TEG)-Eu <sup>3+</sup>	898	986	2397	664	303	274	27	27
Poly(OPV-HEG)-Eu <sup>3+</sup>	849	846	2391	368	308	311	26	38
Poly(OPV-PEG)-Eu <sup>3+</sup>	862	909	2364	300	309	312	26	28

**Table ST2**. Lifetime, radiative ( $A_{RAD}$ ), non- radiative ( $A_{NR}$ ) and intrinsic quantum yield ( $\phi_{Ln}$ ) of polymer-Eu<sup>3+</sup> complexes.

<u>Note</u>: On the basis of the room-temperature emission spectra and on the lifetime measurements, radiative ( $A_{RAD}$ ), non- radiative ( $A_{NR}$ ) and intrinsic quantum yield ( $\phi_{Ln}$ ) of the  ${}^{5}D_{0}$  Eu<sup>3+</sup> ion excited state were calculated for segmented polymer-Eu<sup>3+</sup> complexes by following the earlier reported procedures. The luminescence decay lifetime ( $\tau$ ) is directly related to the radiative and non-radiative decay rates of the lanthanide ion. The radiative lifetime ( $\tau_{rad}$ ) can be calculated using eq. 1, assuming that the energy of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition (MD) and its oscillator strength are constant.

$$A_{RAD} = 1/\tau_{rad} = A_{MD,0} n^3 (I_{tot}/I_{MD})$$
(1)

where,  $A_{\text{MD},0}$  (14.65 s<sup>-1</sup>) is the spontaneous emission probability of the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$  transition in vacuo,  $I_{\text{tot}}/I_{\text{MD}}$  is the ratio of the total area of the corrected Eu<sup>3+</sup> emission spectrum to the area of the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$  band, and *n* is the refractive index of the medium. An average index of refraction equal to 1.5 was considered. Lifetime ( $\tau$ ), radiative (A<sub>RAD</sub>) and nonradiative (A<sub>NR</sub>) transition rates are related to through the following eq 2

$$1/\tau_{obs} = A_T = A_{RAD} + A_{NR}$$

(2)

Where  $A_{RAD}$  can be obtained by summing over the radiative rates  $A_{0,J}$  for each  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  transition. Assuming that nonradiative and radiative processes are essentially involved in the depopulation of  ${}^{5}D_{0}$  state, the intrinsic quantum yield  $\eta$  can be expressed as

 $\phi_{\text{Ln}} = (A_{\text{RAD}} / A_{\text{RAD}} + A_{\text{NR}})$ (3)

The parameters  $A_{RAD}$ ,  $A_{NR}$  and the intrinsic quantum yield values ( $\eta$ ) for the Eu<sup>3+</sup> complexes are shown in the Table 2.



**Figure SF10.** *Phosphrescence spectra of segmented polymers and oligomer-Gd*<sup>3+</sup> *complexes at* 77*K* 

**Note:** The triplet energy levels  $({}^{3}\pi\pi^{*})$  of the ligands were calculated by reference to the lower wavelength emission edges from the low-temperature phosphorescence spectra of the Gd<sup>3+</sup> complexes of the pertinent ligands.



**Figure SF11**. Schematic diagram for the energy transfer pathways in segmented polymer- $Eu^{3+}$  complexes.

**Note:** The energy transfer mechanism and trace the role TTA moiety in the complexes, singlet and triplet energy levels of polymeric and oligomeric ligands were calculated and schematic energy transfer diagrams for polymers and oligomer are shown in the SF11. According to Latva's empirical rule, energy transfer from ligand to excited state of  $Eu^{3+}$  metal ion is more effective when  $\Delta E ({}^{3}\pi\pi^{*}{}^{-5}D_{0})$  is equal to 2500 - 4000 cm<sup>-1</sup>. As shown in figure SF11, energy gap  $\Delta E ({}^{3}\pi\pi^{*}{}^{-5}D_{0})$  between the triplet excited state of the polymers or oligomer and excited state of  $Eu^{3+}$  ion is obtained as approximately 5755-5880 cm<sup>-1</sup>. Therefore, according to Latva's rule, the direct energy transfer from the polymer ligand to  $Eu^{3+}$  ion is not possible. The triplet state energy level of TTA was much lower than that of the triplet state of polymer (or oligomer) and the same time the difference in the energy levels of TTA to the excited state of  $Eu^{3+}$  ion was only 2910 cm<sup>-1</sup>. It is expected that initially energy was transfered from triplet state of polymers or oligomer to triplet state of the TTA and subsequently it was transfered to  $Eu^{3+}$  ion metal centre.



**Figure SF12**. *FT-IR and TGA analysis of Poly(OPV-TEG)-Eu3+ complexes with(1, 2 and three equvalent) and with out using of TTA.* 

**Note:** Upon complexation with Eu<sup>3+</sup> ion (absence of TTA), the carbonyl stretching frequency of carboxyl group of the polymer at 1705 cm<sup>-1</sup> was completely vanished and new peaks were appeared at 1605 and 1550 cm<sup>-1</sup> corresponding to carbonyl stretching frquency of Eu-C=O group.Further, the FT-IR spectra of Eu<sup>3+</sup> complex of Poly(OPV-TEG) and TTA unit, the new peaks were appeared at 787, 712, 675, 632 and 579 cm<sup>-1</sup> along with polymer stretching frequencies of C-H and carbonyl group. These results are clearly indicated that both of polymers and TTA units were participated in the metal complexation during the insitu metal complexation reaction with polymer and TTA unit. Similarly, the TGA thermogram of polymer-Eu complex and Polymer-Eu-TTA complexes are more stable upto 280°C which indicated the presence of polymer group in thecomplexes.



**Figure SF13**. Absorption and emission spectra of  $Poly(OPV-TEG)-Eu^{3+}$  complexes with (1, 2 and three equivalents) and with out using of TTA in chlorobenzene solution.

**Note:** The absorption spectra of Polymer-Eu-TTA and Polymer-Eu complexes have broad absorption maxima from 390-380 nm. The absorption spectra of of Polymer-Eu-TTA complexes were showed 20 nm red shift compared to Poly-Eu<sup>3+</sup> complex due to presence of TTA absorption bands. The emission spectra of the Eu<sup>3+</sup> complexes were recorded by exciting at their absorption maxima and shown in figure SF13. The emission spectra of Polymer-Eu complexes showed only self emission of conjugated chromophore at 410 nm. Upon complexation of polymer and one equvalent of TTA with Eu metal ion, the new emission peaks were appeared at 613 nm corresponds to Eu metal centered emission and there was no self emission occured. Further increasing of TTA component in the Polymer-Eu complex, the emission intensity increased as compared to one equivalent of TTA with polymer-Eu complex and there was no self emission observed. Tese results are clearly indicate that minimun one TTA unit is required for complete harvesting of energy from the OPV unit to metal center and both TTA and polymer unit are involving in the energy transfer process.



**Figure SF14**. Luminescent decay profiles of segmented polymer- $Eu^{3+}$  complexes in chlorobenzene solution.



*Figure SF15. Temperature dependent emission spectra for Poly(OPV-DD) and Poly(OPV-TEG-)*  $Eu^{3+}$  *complexes in chlorobenzene in both heating and cooling cycle.* 

**Note:** In the temperature dependent emission spectra of Poly(OPV-DD)-Eu<sup>3+</sup> and Poly(OPV-TEG)-Eu<sup>3+</sup> complexes, the emission intensity at 615 nm decreased slowly with increase of temperature and the emission intensity at higher temperature is almost vanished. This temperature dependent emission is increased when sample was cooled and decrease or increase of emission intensity with changing in temperature (heating or cooling) followed non-linear trend. It is clearly indicating that Poly(OPV-DD)-Eu<sup>3+</sup> and Poly(OPV-TEG)-Eu<sup>3+</sup> complexes showed reversible temperature dependent emission and also the complexes are stable at higher temperature.



*Figure SF16*. *Temperature dependent emission spectra for* **Poly(OPV-PEG-)**  $Eu^{3+}$  *complexes in chlorobenzene in both heating and cooling cycle..* 

**Note:** In the temperature dependent emission spectra of Poly(OPV-PEG-)  $Eu^{3+}$  complex, the emission intensity at 615 nm decreased slowly with increase of temperature and the emission intensity at higher temperature is almost vanished. This temperature dependent emission is increased when sample was cooled and decrease or increase of emission intensity with changing in temperature (heating or cooling) followed non- linear trend with break point 62°C. It is clearly indicating that the Poly(OPV-PEG-)  $Eu^{3+}$  complex showed reversible temperature dependent emission and also the complex is stable at higher temperature.



**Figure SF17**. Temperature dependent emission spectra for **Poly(OPV-TEG)-**  $Eu^{3+}$  complexes in various solvents (a) chlrobenzene (b) 1,4-dichlorobenzene (ODCB), (c) 1,4-xylene, (d)dimethyl sulfoxide(DMSO), (e) N,N-dimethylformamide (DMF), (f) tetrahedrafuran (THF) in both heating and cooling cycle..

**Note:** The temperature dependent emission spectra was recorded for Poly(OPV-TEG-) Eu<sup>3+</sup> complex in various solvents and shown in above. For all solvents, the emission intensity at 615 nm decreased slowly with increase of temperature and the emission intensity at higher temperature is almost vanished. This temperature dependent emission is increased when sample was cooled and decrease or increase of emission intensity with changing in temperature (heating or cooling) followed non- linear trend. However, the self emission of the OPV chromophore was appeared at 410 nm along with the temperature dependent luminescent behaviors in dimethyl sulfoxide(DMSO), N,N-dimethylformamide (DMF), and tetrahedrafuran (THF) solvents. On the other hand, ODCB, chlorobenzene and xylene did not show any chromophore self-emission and only the temperature dependent emission behaviors were observed from the metal center. Though, the self emission is exhibited in the polymer-Eu<sup>3+</sup> complex for DMSO, DMF and THF solvents, the temperature sensing ability is retained in all the solvents.



*Figure SF18.* Absorbance and Temperature dependent emission spectra for Poly(OPV-TEG)- $Eu^{3+}$  complexe in various concentrations in both heating and cooling cycle.

**Note:** The absorbance spectra of **Poly(OPV-TEG)-**  $Eu^{3+}$  complex was recorded in various concentrations. The temperature dependent emission spectra was recorded for Poly(OPV-TEG-)  $Eu^{3+}$  complex with various cocnetrations and shown in above. For all concentrations, the emission intensity at 615 nm decreased slowly with increase of temperature and the emission intensity at higher temperature is almost vanished. This temperature dependent emission is increased when sample was cooled and decrease or increase of emission intensity with changing in temperature (heating or cooling) followed non- linear trend. These results are clearly indicated that temperature sensing properties of polymer-Eu<sup>3+</sup> complex is retained even at low concentration also.



*Figure SF19* The plot of emission intensity Vs temperature for *Poly(OPV-HEG)-Eu*<sup>3+</sup> complex in chlorobenzene solution and film.

**Note:** In this figure, emission intensity with various temperatures compared in both solution and film for **Poly(OPV-HEG)-Eu<sup>3+</sup>** complex. The solid state emission spectra were also showed similar trend as like in solution state upon changing the temperature. However, in the solid state, the emission intensity at 100°C is not completely vanished which indicated that the isolation of the polymeric chain in the solid state is restricted.

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Figure SF20. Temperature dependent luminescent decay profiles of Poly(OPV-DD)- $Eu^{3+}$ , Poly(OPV-TEG-)  $Eu^{3+}$  and Poly(OPV-PEG-)  $Eu^{3+}$  complexes in solution.

**Note:** The luminescent decay profiles of the polymer- $Eu^{3+}$  complexes were dropped slowly with increase of temperature and the polymer complexes showed reversibility in the luminescence decay profiles when the solution was cooled. It suggested that all the polymer complexes highly sensitive to temperature and they are showing reversibility in cooling process.

Temperature	Hea	ting	Cooling		
(° C)	$\tau_1$ (ms)	$\mathbb{R}^2$	$\tau_1$ (ms)	$\mathbb{R}^2$	
20	0.312	0.998	0.325	0.999	
30	0.296	0.999	0.300	0.999	
40	0.262	0.999	0.261	0.998	
50	0.206	0.998	0.208	0.998	
60	0.163	0.998	0.154	0.997	
70	0.132	0.997	0.111	0.997	
80	0.041	0.998	0.037	0.998	
90	0.042	0.997	0.016	0.998	
100	0.029	0.995	0.029	0.995	

Table ST3.	Luminescent decay lifetime values $(\tau_1)$ of <b>Poly(OPV-HEG)-Eu<sup>3</sup></b>	+with various	5
	temperature.		

<u>Note:</u> Luminescent decay lifetime  $\tau_1$  values were obtained by the fitting the luminescent decay profiles of Eu<sup>3+</sup> complexes with mono-exponential upto 70°C and after 70°C the decay profiles were fitted with bi-exponential decay. These values were plotted with various temperature and shown in figure 5.

Complexes	$k_0(S^{-1})$	$A(S^{-1})$	$E_a (KJmol_{1})$	$\mathbf{R}^2$	Sensitivity
Eu(TTA) <sub>3</sub> .Poly(OPV-DD)	2603	$4.14 \times 10^{13}$	$6.28 \times 10^2$	0.99	$1.63\pm0.02$ K <sup>-1</sup>
Eu(TTA) <sub>3</sub> .Poly(OPV-TEG	3650	$6.31 \times 10^{13}$	$6.37 \times 10^{2}$	0.99	$1.54\pm0.03$ K <sup>-1</sup>
Eu(TTA) <sub>3</sub> .Poly(OPV-HEG	3210	$6.95 \times 10^{11}$	$6.62 \times 10^2$	0.99	$1.52\pm0.01 \text{K}^{-1}$
Eu(TTA) <sub>3</sub> .Poly(OPV-PEG	3931	$3.56 \times 10^{13}$	$6.14 \times 10^2$	0.99	$1.67 \pm 0.01 \text{K}^{-1}$

 Table ST4. Calculated parameters for Arrhenius type equation and sensitivity.



*Figure SF21*. Temperature dependent absorption spectra for *Poly(OPV-DD)*(*a* and *b*), *Poly(OPV-TEG)* (*c* and *d*), and *Poly(OPV-HEG)* (*e* and *f*), in chlorobenzene solution in both heating and cooling cycle.

**Note:** Upon variation of temperature, there were no changes observed in the absorption spectra of the segmented polymers in both heating and cooling cycles. It is clearly indicating that the segmented polymers underwent any topology changes with changing of temperatures.



Figure SF22. Temperature dependent emission spectra for Poly(OPV-DD)(a and b), Poly(OPV-TEG) (c and d), and Poly(OPV-HEG) (e and f), in chlorobenzene solution in heating and cooling cycle.

**Note:** In the emission spectra of polymers, the emission intensity at 410 nm was decreased very slowly upon heating and no significant quenching was observed after  $60^{\circ}$ C which is clearly reflected in photograph. Furthermore there was no aggregation peak observed as cooling of the samples which clearly indicated that polymers did not go any topology change with changing of temperature.



**Figure SF23**. Temperature dependent emission spectra of **Poly(OPV-HEG)-Eu<sup>3+</sup>** complexes in chlorobenzene solution in heating (**a**) and cooling (**b**). The plot of emission intensity at 425 nm Versus temperature for all segmented polymer-Eu<sup>3+</sup> complexes (right side inset).

**Note:** The residual emission corresponds to OPV chromophore did not change much in the emission spectra of the polymer- $Eu^{3+}$  complexes and the plot of emission intensity at 420 nm versus various temperatures showed straight line in both heating and cooling which suggested that the residual emission corresponds to OPV chromophore did not undergo any changes. Other complexes also showed similar trend in their emission spectra.

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<sup>1</sup>H-NMR,<sup>13</sup>-NMR and MALDI-TOF data



Figure SF24. 1H-NMR spectra of Poly(OPV-TEG) and OPV-TEG.



Figure SF25. MALDI-TOF spectra of 5C and 6C.

**Note:** Since the purity of monomeric reactants are more sensitive and important for formation of high molecular weight polymers in the Wittig-Horner polycondensation reactions, the purity of the monomers and intermediates were confirmed by MALDI -TOF analysis. It is well known that MALDI- TOF analysis is very useful tool for confirming the post derivatization of mono dispersed polymers by end group analysis as compared to NMR spectroscopic techniques. Here, derivatization of polyethylene glycol ( $M_n = 400$ ) into dialdehyde was confirmed by MALDI-TOF via end group analysis. The MALDI-TOF spectra of the PEG derivatives are shown in figure S11. The MALDI- TOF spectra of PEG-OTs exhibited the monomodel distribution with maximum intense peak at 717.29 amu corresponds to molecular weight of single polymer chain with repeating unit  $(n \times 44 + 326) + 39$  (n = 8) which is terminated with tosylated group. The mass difference between the two adjacent peaks in the distribution is 44 which is repeating unit (-CH<sub>2</sub>CH<sub>2</sub>O-) mass of PEG. The conversion of tosylated compound to dialdhyde is clearly reflected in the MALDI-TOF spectrum of the PEG-CHO. In figure S11, the molecular ion peak with high intensity was appeared at 705.35 amu which belongs to the mass of repeating unit of PEG-CHO (n x 44 + 226) + 39 with terminal unit, here n is 10. It is clearly confirmed that the terminal unit of PEG-400 is undergone with dialdehyde derivatization.



**Figure SF26**. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI spectra of (ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) (**5a**).



**Figure SF27**. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI spectra of 3,6,9,12,15-pentaoxaheptadecane-1,17-diyl bis(4-methylbenzenesulfonate) (**5b**).



**Figure SF28**. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI spectra of 3,6,9,12,15,18,21,24,27nonaoxanonacosane-1,29-diyl bis(4-methylbenzenesulfonate) (**5c**).



**Figure SF29**. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI spectra of 4,4'-(((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))dibenzaldehyde (**6a**).







**Figure SF31**. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI spectra of 4,4'-(3,6,9,12,15,18,21,24,27-nonaoxanonacosane-1,29-diylbis(oxy))dibenzaldehyde (**6c**).



**Figure S31**. <sup>1</sup>H-NMR spectra of poly(3-(3-(4-(2-(2-ethoxyethoxy)ethoxy)styryl)-4-(2-ethylhexyloxy)-5-styrylphenyl)propanoic acid) (**Poly(OPV-TEG**)).



**Figure SF32**. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of poly(3-(3-(4-(3,6,9,12,15-pentaoxaheptadecyloxy)styryl)-4-(2-ethyl hexyloxy)-5-styrylphenyl)propanoic acid) (**Poly(OPV-HEG)**).



**Figure SF33**. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of poly(3-(3-(4-(3,6,9,12,15,18,21,24,27-nonaoxanonacosyloxy)styryl)-4-(2-ethylhexyloxy)-5-styryl phenyl)propanoic acid) (**Poly(OPV-PEG**)).

