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Electronic Supplementary Information (ESI)

Cucurbit[7]uril-threaded fluorene-thiophene-based conjugated polyrotaxanes

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Experimental Section

In all the experiments commercial grade reagents and solvents were used without further purification unless noted. Silica gel (Kieselgel 60, 0.063-0.0200 mm) was used to carry out column chromatography. Thin layer chromatography was carried out on silica gel plates (Kieselgel 60 F254, 1 mm).The IR spectrum was recorded with Bruker Tensor 27 model FT-IR spectrometer. High sensitivity DLATGS detector with a resolution of up to1 cm^{-1} was used. All the samples were grinded very well to a fine powder before further grinding with KBr. The samples together with KBr were pressed under high pressure to form solid pellet disks. For hygroscopic samples, the pellets were first dried under oven before taking the measurement. The FT-IR of the samples was recorded in the range 400-4000 cm^{-1} for 64 scans. UV-Vis absorbance Spectrum was recorded with Cary 300 UV-Vis double beam spectrophotometer with spectral bandwidth down to 0.2 nm and Xenon Flash Lamp as the light source. The UV-Vis absorbance of the samples was recorded in solution using quartz cuvettes with 1cm length within the range 200-800 nm. The photoluminescence spectrum was recorded with Cary Eclipse Varian Spectrophotometer and Xenon lamp as the light source. The photoluminescence of the samples was recorded in solution using quartz cuvettes with 1cm length within the range 200-800 nm. Solid state photoluminescence of the samples was recorded on quartz. Slit width of 2.5 nm was used for fluorene based polymers. All the samples were excited at their respective excitation wavelength. The photoluminescence decay was measured with (Fluo Time 200, Pico Harp 300, Picoquant GMBH). The photoluminescence decay of all the samples was measured in both solution and solid state (on glass substrate). FluoFit software was used for decay analysis to obtain correlated life times of the samples. Both proton and carbon NMR were recorded with Bruker Avance DPX-400 MHz spectrometer. All the spectra were recorded in solution using different deuterated solvents. The chemical shift values were expressed relative to tetramethylsilane as an internal standard.The elemental composition of the samples was determined using FLASH 2000 Organic Elemental/ CHNS-O Analyzer. 2,5-(Bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT) was used as a standard and vanadium (V) pentaoxide (V_2O_5) was used as a catalyst. The mass of the monomers, oligomers and polymers were determined with Agilent 6224 High Resolution Mass Time-of-Flight (TOF) LC/MS with Electrospray Ionization method. Although the molecular weight of fluorene based polymers could not be determined, Agilent 1200 series SEC equipped with refractive index and UV-Vis detectors was used for molecular weight determination. Aqueous solution of 0.2-0.8 M $NaNO_3$, 0.01 M NaH_2PO_4 (pH= 2-7) was used as eluent on PL aquagel-OH MIXED-H column calibrated with poly(ethylene oxide) standards. In all the measurements 20 µL of mg/ml polymer solution was injected to the column and flows at a flow rate of 0.6 ml/min. Thermal Gravimetric Analysis (TGA) measurement was done on TGA Q500 at a heating rate of 20 ℃/min from 35 °C to 900 °C.

Synthesis of {6-[2,7-Dibromo-9-(6-trimethylamino-hexyl)-9H-fluoren-9-yl]-hexyl}-trimethyl-amine (M1)

2,7-Dibromo-9,9-bis(6-bromo-hexyl)-9H-fluorene[34-36] (1.00 g, 1.54 mmol) dissolved in dry THF (5 mL) and flushed with nitrogen. 25 % w/w solution of trimethylamine in THF (10 mL, 20 mmol) was added under nitrogen. The mixture was stirred at room temperature for 24 h. The reaction mixture was extracted with water/chloroform. The aqueous layer was collected and evaporated to dryness under reduced pressure; the residue was washed with cold acetone. White solid powder was obtained (0.99 g, 84%). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 0.43 (m, 4H), 0.99 (m, 4H), 1.00 (m, 4H), 1.47 (m, 4H), 1.98 (m, 4H), 2.90 (s, 18H), 3.19 (m, 4H), 7.47-7.59 (m, 6H); ^{13}C-NMR (100 MHz, D_2O, 25 °C) δ: 152.86, 139.21, 130.30, 126.10, 121.42, 121.22, 67.84, 55.72, 52.68, 48.89, 38.69, 27.58, 24.39, 22.38, 21.40.

ESI-MS m/z [M + H (-2Br)]$^+$ for $C_{31}H_{49}Br_2N_2$: calcd 607.23, found m/z 607.23 [M + H (-2Br)]$^+$

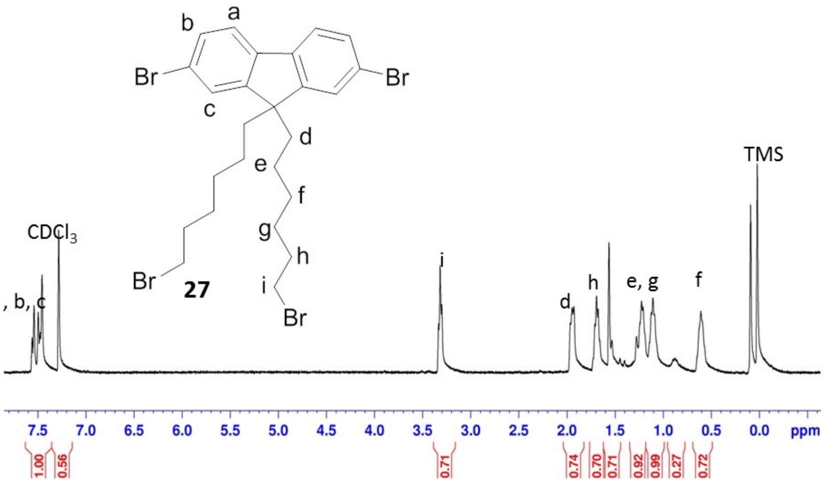

Fig. S1 ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of 2,7-Dibromo-9,9-bis(6-bromo-hexyl)-9H-fluorene.

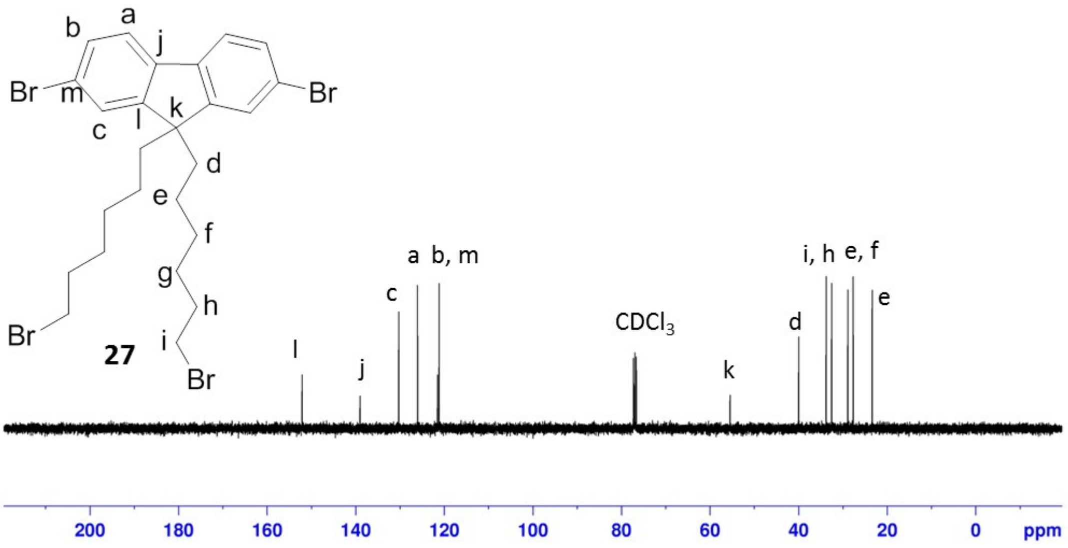

Fig. S2 ^{13}C-NMR (100 MHz, CDCl$_3$, 25 °C) spectrum of 2,7-Dibromo-9,9-bis(6-bromo-hexyl)-9H-fluorene.

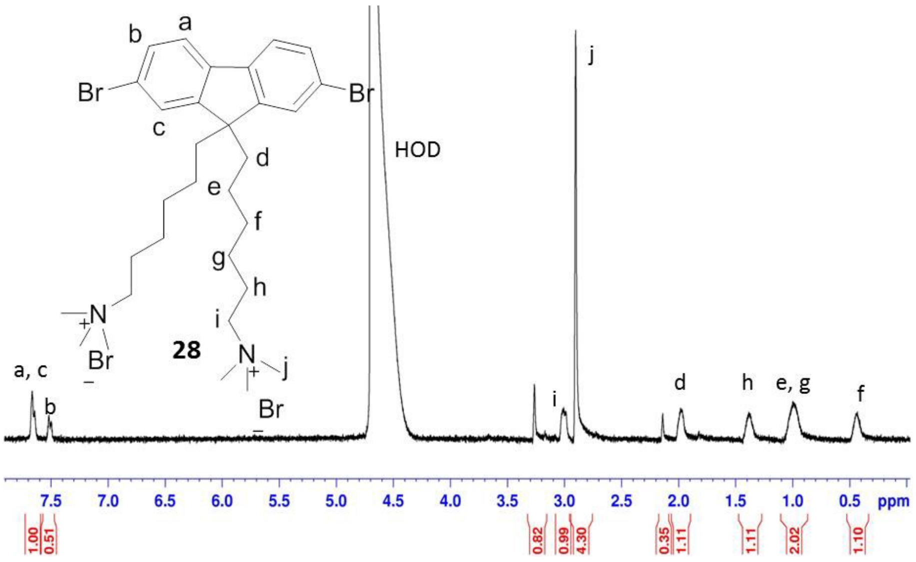

Fig. S3 ^{1}H-NMR (400 MHz, D$_2$O, 25 °C) spectrum of {6-[2,7-Dibromo-9-(6-trimethylamino-hexyl)-9H-fluoren-9-yl]-hexyl}-trimethyl-amine (**M1**).

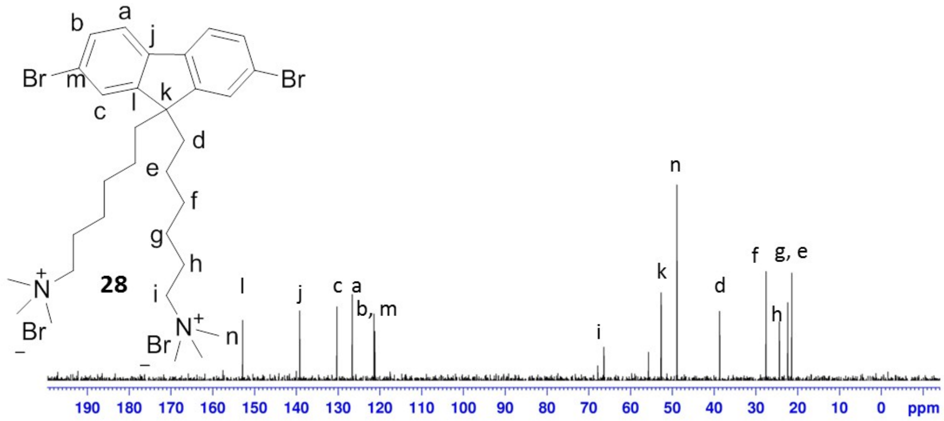

Fig. S4 ^{13}C-NMR (100 MHz, D_2O, 25 °C) spectrum of {6-[2,7-Dibromo-9-(6-trimethylamino-hexyl)-9H-fluoren-9-yl]-hexyl}-trimethyl-amine (**M1**).

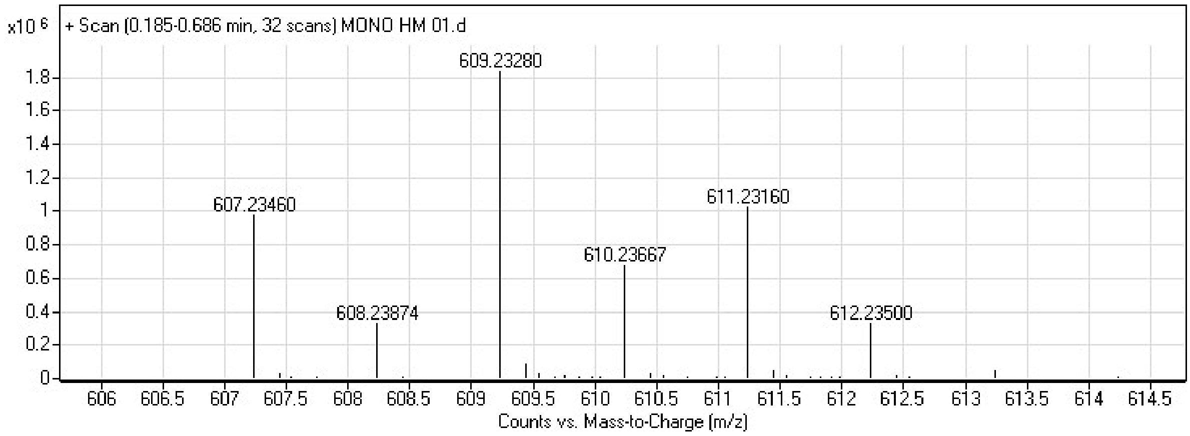

Fig. S5 ESI-Mass spectrum of {6-[2,7-Dibromo-9-(6-trimethylamino-hexyl)-9H-fluoren-9-yl]-hexyl}-trimethyl-amine (**M1**). ESI-MS m/z [M + H (-2Br)]$^+$ for $C_{31}H_{49}Br_2N_2$: calcd 607.23, found m/z 607.23 [M + H (-2Br)]$^+$

Synthesis of {3-[2,7-Dibromo-9-(3-trimethylamino-propyl)-9H-fluoren-9-yl]-propyl}-trimethyl-amine (M2)

2,7-Dibromo-9,9-bis(3-bromo-propyl)-9H-fluorene[34-36] (1.00g, 1.77 mmol) dissolved in dry THF (5 mL) and flushed with nitrogen. 25%wt solution of trimethylamine in THF (10 mL, 20 mmol) was added under nitrogen. The mixture was stirred at room temperature for 24 h. The reaction mixture was extracted with water/chloroform. The aqueous layer was collected and evaporated to dryness under reduced pressure; the residue was washed with cold acetone. White solid powder was obtained (1.05 g, 87%). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 0.90 (m, 4H), 2.06 (m, 4H), 2.71 (s, 18), 2.96 (m, 4H), 7.47-7.59 (m, 6H); ^{13}C-NMR (100 MHz, D_2O, 25 °C) δ: 160.84, 150.04, 139.27, 131.43, 126.68, 122.06, 66.13, 52.59, 35.05, 17.37.

ESI-MS m/z [M -Br)]$^+$ for $C_{25}H_{36}Br_3N_2$: calcd 601.04, found m/z 601.05 [M - Br)]$^+$

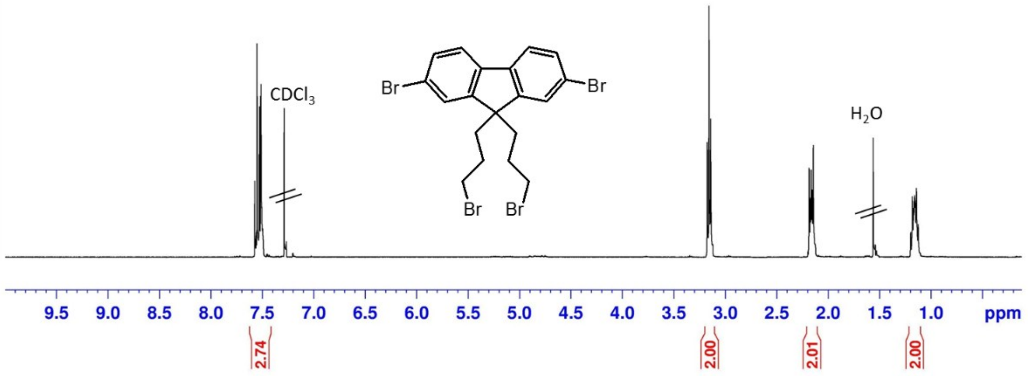

Fig. S6 ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C) spectrum of 2,7-Dibromo-9,9-bis(3-bromo-propyl)-9H-fluorene.

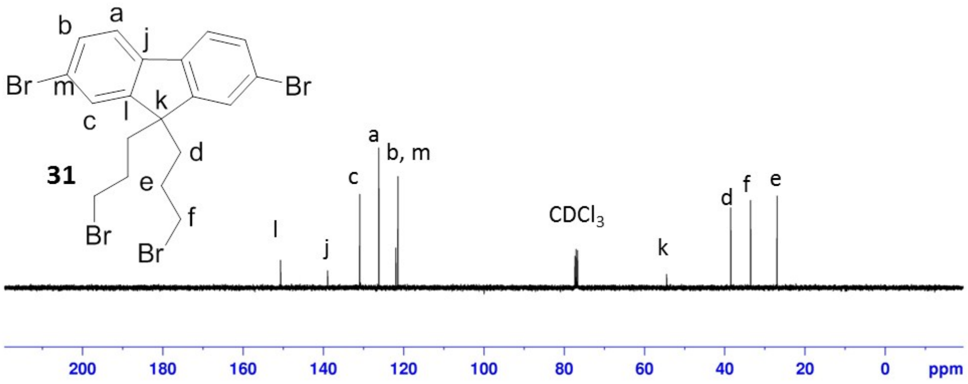

Fig. S7 ^{13}C-NMR (100 MHz, CDCl$_3$, 25 °C) spectrum of 2,7-Dibromo-9,9-bis(3-bromo-propyl)-9H-fluorene.

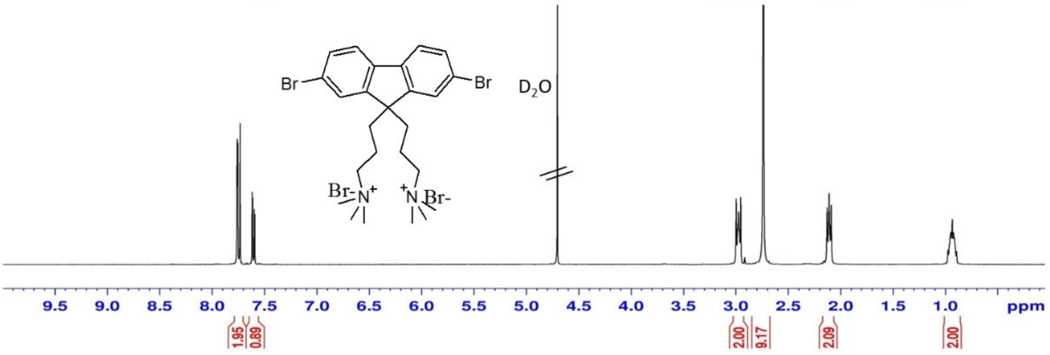

Fig. S8 ^{1}H-NMR (400 MHz, D$_2$O, 25 °C) spectrum of {3-[2,7-Dibromo-9-(3-trimethylamino-propyl)-9H-fluoren-9-yl]-propyl}-trimethyl-amine (**M2**).

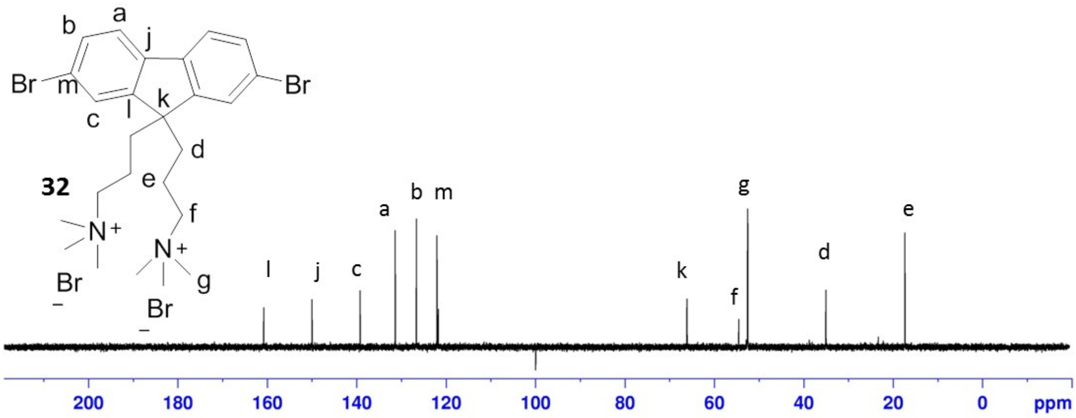

Fig. S9 ^{13}C-NMR (100 MHz, D_2O, 25 °C) spectrum of {3-[2,7-Dibromo-9-(3-trimethylamino-propyl)-9H-fluoren-9-yl]-propyl}-trimethyl-amine (**M2**).

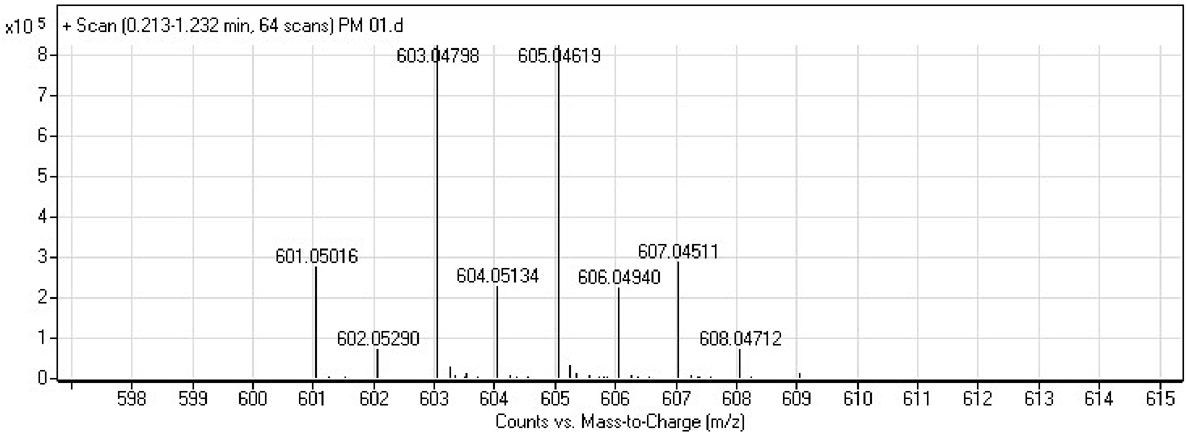

Fig. S10 ESI-Mass spectrum of {3-[2,7-Dibromo-9-(3-trimethylamino-propyl)-9H-fluoren-9-yl]-propyl}-trimethyl-amine (**M2**). ESI-MS m/z $[M - Br]^+$ for $C_{25}H_{36}Br_3N_2$: calcd 601.04, found m/z 601.05 $[M - Br]^+$

Poly[9,9-bis{6(N,N,N-trimethylamino)hexyl}fluorene-*co*-2,5-thienylene (P1) :

M1 (300 mg, 0.390 mmol), 2,5-thiophenediboronicester (98 mg, 0.390 mmol), $Pd(OAc)_2$ (10 mg, 0.01 mmol), and potassium carbonate (500 mg, 3.61 mmol) were placed in a 25-mL round-bottom flask. Water (10 mL) was added to the flask and the reaction vessel was degassed. The mixture was stirred at 80 °C for 48 h under nitrogen. Water (250 mL) was added to the reaction mixture and filtered under suction. The filtrate was concentrated to 120 mL and then put under ultrafiltration with 5000 Da cut-off polyethersulfone membrane filter at 5 bar and 1ml/min flow rate. The filtration was stopped after 5 L of water was collected. Retantate solution was concentrated to a minimum volume and the remaining viscous solution was precipitated in excess acetone. Shiny dark greenish solid flakes were obtained (247 mg, 62%). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 0.4-1.5 (br, 20 H), 2.5-3.2 (br, 22H), 7.0-8.5 (br, 8H).

Poly[9,9-bis{6(N,N,N-trimethylamino)hexyl}fluorene-co-2,5-thienylene with Cucurbit[7]uril (P1CB7) :

Cucurbit[7]uril (300 mg, 0.301 mmol) and 2,5-thiophenediboronic ester (62 mg, 0.247 mmol) were placed in a 25-mL round-bottom flask. Water (10 mL) was added to the flask and the reaction vessel was degassed. The mixture was stirred for 2 h at 50 °C. **M1** (150 mg, 0.195 mmol), $Pd(OAc)_2$ (10 mg, 0.01 mmol), and potassium carbonate (500 mg, 3.61 mmol) were added to the reaction mixture. The mixture was stirred at 80 °C for 48 h under nitrogen. Water (250 mL) was added to the reaction mixture and filtered under suction. The filtrate was concentrated to 120 mL and put under ultrafiltration with 5000 Da cut-off polyethersulfone membrane at 5 bar and 1ml/min flow rate. The filtration was stopped after 5 L of water was collected. Retentate solution was concentrated to a minimum volume and the remaining viscous solution was precipitated into excess acetone. Brownish yellow solid powder was obtained (187 mg). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 0.4-1.5 (br, 20 H), 2.5-3.2 (br, 22H), 4.07 (br, 14H), 5.34 (br, 14H), 4.07 (br, 14H), 6.24 (br, 1H), 6.54 (br, 1H), 7.0-8.5 (br, 8H).

FT-IR (KBr, ν_{max}/cm^{-1}): 1735 (C = O)

Poly[9,9-bis{3(N,N,N-trimethylamino)propyl}fluorene-*co*-2,5-thienylene (P2).

M4 (325 mg, 0.476 mmol), 2,5-thiophenediboronicester (119 mg, 0.476 mmol), $Pd(OAc)_2$ (10 mg, 0.01 mmol), and potassium carbonate (500 mg, 3.61 mmol) were placed in a 25-mL round-bottom flask. Water (10 mL) was added to the flask and the reaction vessel was degassed. The mixture was stirred at 80 °C for 48 h under nitrogen. Water (250 mL) was added to the reaction mixture and filtered under suction. The filtrate was concentrated to 120 mL and then put under ultrafiltration with 5000 Da cut-off polyethersulfone membrane at 5 bar and 1mL/min flow rate. The filtration was stopped after 5 L of water was collected. Retentate solution was concentrated to a minimum volume and the remaining viscous solution was precipitated into excess acetone. Dark greenish solid powder was obtained (205 mg, 47%) ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 0.96 (m, 4H), 2.21 (m, 4H), 2.68 (s, 18), 2.91 (m, 4H), 7.12-7.89 (m, 8H).

Poly[9,9-bis{3(N,N,N-trimethylamino)propyl}fluorene-co-2,5-thienylene with Cucurbit[7]uril (P2CB7)

Cucurbit[7]uril (300 mg, 0.301 mmol) and 2,5-thiophenediboronic ester (62 mg, 0.247 mmol) were placed in a 25-mL two necked round-bottom flask. Water (10 mL) was added to the flask and the reaction vessel was degassed. The mixture was stirred for 2 h at 50 ˚C. **M2** (169 mg, 0.247 mmol), $Pd(OAc)_2$ (10 mg, 0.01 mmol), and potassium carbonate (500 mg, 3.61 mmol) were added to the reaction mixture. The mixture was stirred at 80 ˚C for 48 h under nitrogen. Water (250 mL) was added to the reaction mixture and filtered under suction. The filtrate was concentrated to 120 mL and put under ultrafiltration with polyethersulfone 5000 Da cut-off membrane filter at 5 bar and 1 ml/min flow rate. The filtration was stopped after 5 L of water was collected. Retentate solution was concentrated to a minimum volume and the remaining viscous solution was precipitated into excess acetone. Brownish yellow solid powder was obtained (80 mg). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 1.03 (m, 4H), 2.23 (m, 4H), 2.69 (s, 18), 2.96 (m, 4H), 4.17 (br, 12H), 5.44 (br, 12H), 5.85 (br, 12H), 7.17-7.91 (m, 8H).

FT-IR (KBr, ν_{max}/cm^{-1}): 1735 (C = O).

Synthesis of 2,5-thiophenediboronic ester:

2,5-thiophenediboronic acid (2.00 g, 11.6 mmol) was placed in a 50-ml two-necked round bottom flask. Toluene (25 mL) was added to the flask and the solution was stirred for 10 min. To the solution, 1,3-propanediol (1.76 g, 23.2 mmol) was added and the mixture was heated to 130 °C. The reaction mixture was refluxed for overnight. The reaction mixture is transferred into one-necked round bottom flask and the solvent is removed under reduced pressure. A white precipitate is observed in the flask and ethanol is used to wash the product under suction. The product was further purified by washing with n-hexane. A white solid powder was obtained (1.89 g, 64%). ^{1}H-NMR (400 MHz, D_2O, 25 °C) δ: 1.73 (m, 4H), 3.62 (t, 8H), 7.66 (s, 2H) ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C) δ: 136.03, 62.09, 27.40.

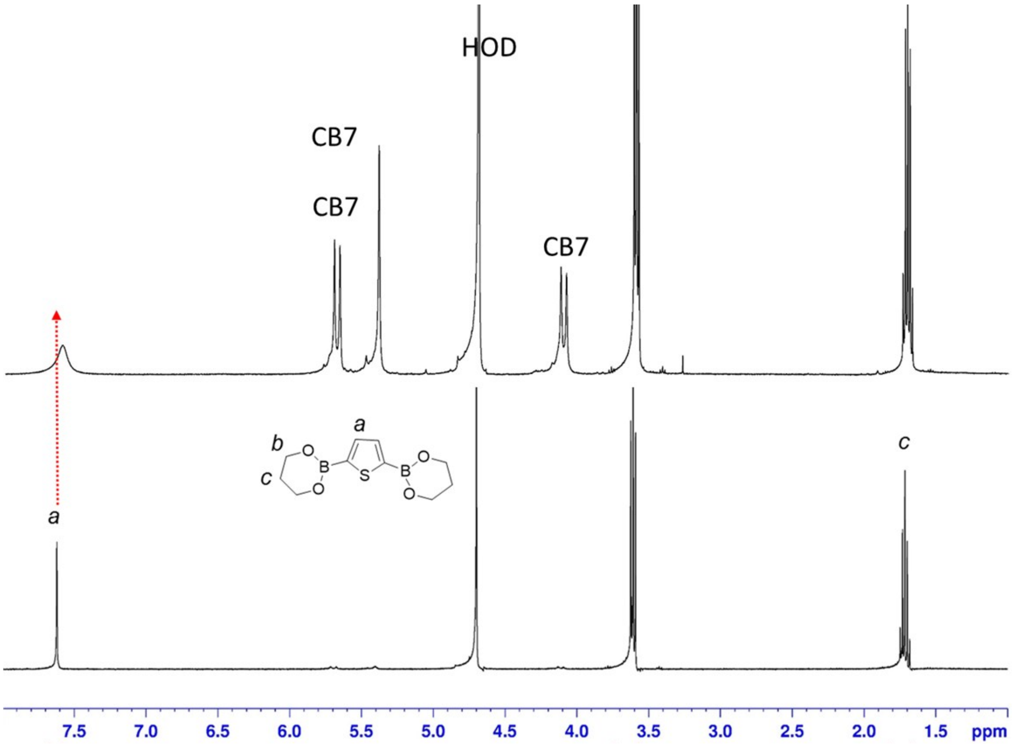

Fig. S11 ^{1}H-NMR (400 MHz, D_2O, 25 °C) spectra of 2,5-thiophenediboronic ester in the presence (3 folds excess of 2,5-thiophenediboronic ester) and in the absence of CB7.

Fabrication and characterization of all solution processed OLEDs:

ITO coated (15 Ohm/Sq) glass substrates were partially etched and cleaned by solvent cleaning (water, acetone, and isopropyl alcohol). Then, UV-Ozone treatment was performed. PEDOT:PSS (Clevios PVP AI 4083) is spin coated at 4000 rpm for 1 min and annealed at 150°C for 30 min. Poly-TPD (American Dye Source, ADS 254BE) is dissolved in cholorobenzene (10 mg/ml) and spin coated on the film at 2000 rpm for 1 min and annealed at 120 °C for 30 min. Polymers (**P1**, **P1CB7**) dissolved in methanol are spin coated on the poly-TPD layer at 1500 rpm for 1 min. Subsequently, our own synthesized ZnO nanoparticles (2-4 nm in size) are spin coated at 2000 rpm for 1 min and annealed at 80 °C. Finally, the samples are loaded into a thermal evaporator with a hard-mask defining the device area as 2 by 2 mm. 100 nm thick Aluminum is deposited at the base pressure of $2x10^{-6}$ Torr. The devices are tested using Agilent B1500A parameter analyzer and electroluminescence spectra is collected via fiber connected spectrometer (Ocean Optics, Maya2000).

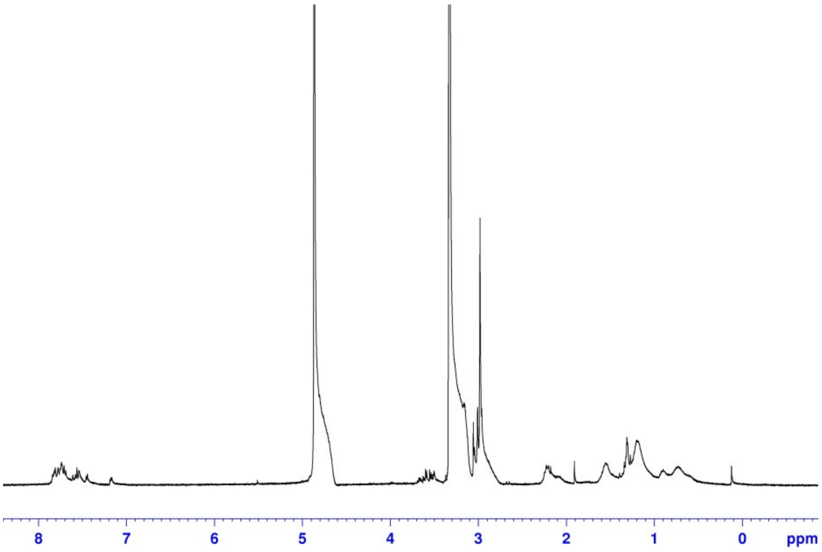

Fig. S12 ^{1}H-NMR (400 MHz, MeOD, 25 °C) spectrum of **P2.**

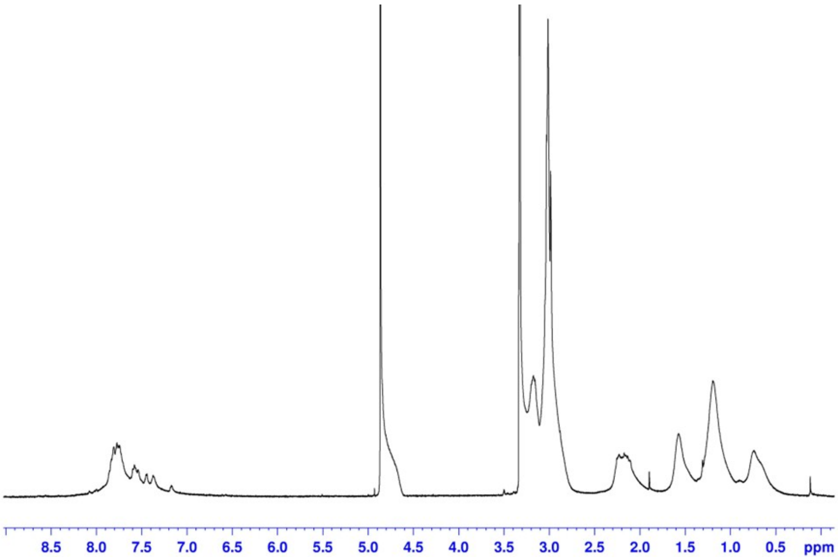

Fig. S13 ^{1}H-NMR (400 MHz, MeOD, 25 °C) spectrum of **P1.**

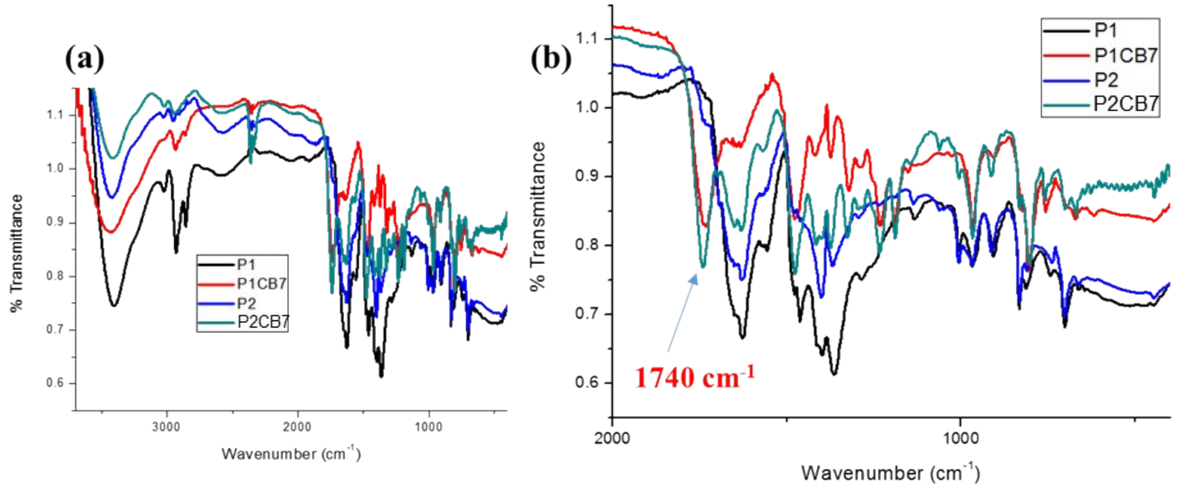

Fig. S14 (a) IR Spectra of **P1**, **P1CB7**, **P2** and **P2CB7; (b)** Expanded area of IR Spectra of **P1**, **P1CB7**, **P2** and **P2CB6**.

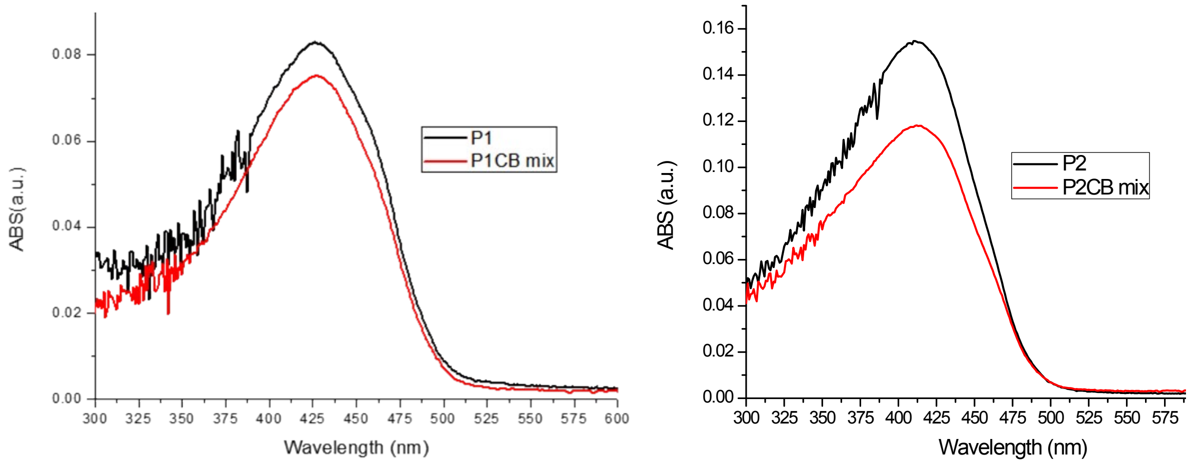

Fig. S15 UV-vis absorption spectra of **P1, P2** and 1:1 mixture of **CB7/P1** (per repeat unit) and **CB7/P2** in aqueous media.

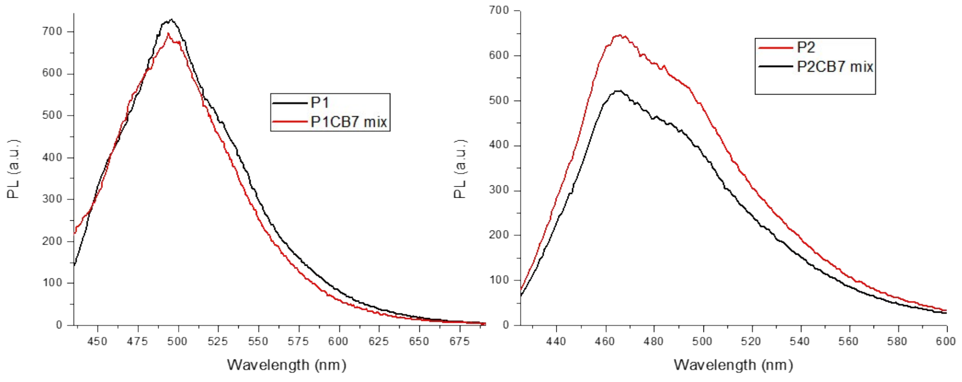

Fig. S16 PL spectra of **P1, P2** and 1:1 mixture of **CB7/P1** (per repeat unit) and **CB7/P2** in aqueous media.

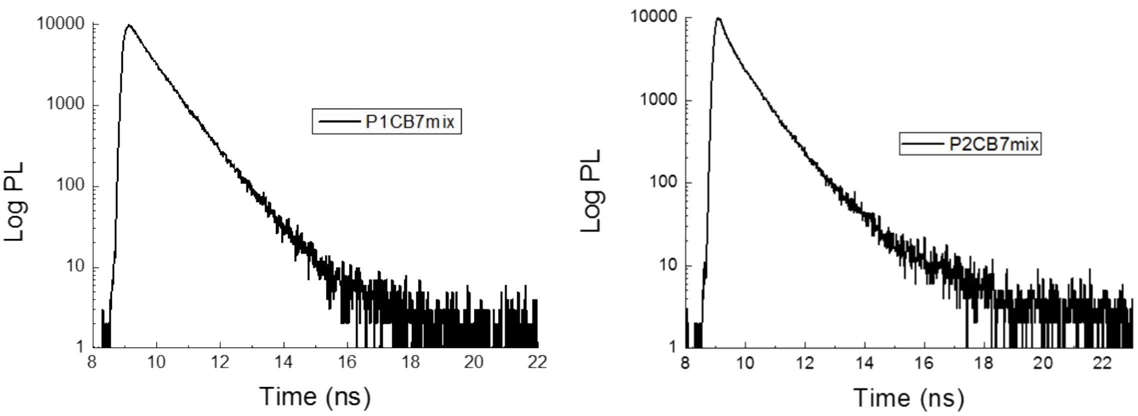

Fig. S17 Biexponentially fitted fluorescence lifetime decay curves of 1:1 mixture of **CB7**/**P1** (per repeat unit) and **CB7**/**P2** in aqueous media.