Supplementary Information

Anion Induced Modulation of Self-Assembly and Optical Properties in Urea End-capped Oligo(\(p\)-phenylenevinylene)

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Fig. S1. Changes in the absorption spectra of BU-OPV1 (1.1 x 10^{-5} M) in cyclohexane-chloroform (16:1) solvent mixture upon the addition of (a) 0-2 equivalents of TBAF (indicating the absence of any significant changes) and (b) 2-32 equivalents of TBAF (showing the increase in the extinction coefficient and disappearance of the shoulder band at 450 nm at higher concentrations of TBAF).

Fig. S2. Excitation spectra of BU-OPV1 (1.1 x 10^{-5} M) in cyclohexane-chloroform (16:1) solvent mixture (——) and upon the addition 32 equivalents of TBAF (……..).
Fig. S3. Benesi-Hildebrand plot of $1/(\Phi_f - \Phi_{obs})$ versus $1/[X]$ for BU-OPV1 on titration upto 2 equivalents of TBAF. (The linear fit showed a 1:1 complexation between BU-OPV1 and fluoride ions).

Fig. S4. Benesi-Hildebrand plot of $1/(\Phi_f - \Phi_{obs})$ versus $1/[X]^2$ for BU-OPV1 upon titration with TBAF (2-32 equivalents). (The linear fit showed a 1:2 complexation between BU-OPV1 and fluoride ions.)
Experimental Section

Synthesis

The synthetic route of BU-OPVs is shown in Scheme 1. The starting bisaldehyde derivative 1 was synthesized as per reported procedures. Detailed procedures for the synthesis of compounds 2, 3 and BU-OPV1-2 are described below. Reaction of the bisaniline derivative 3 with butyl isocyanate or dodecyl isocyanate resulted in BU-OPV1 and BU-OPV2 respectively.

Scheme S1. Synthesis of BU-OPVs. Reagents and conditions: (a) diethyl(4-nitrobenzyl) phosphonate, THF, NaH, room temperature, 8 h. (b) SnCl 2. 2H2O, EtOH/EtOAc, 70 °C, 7 h. (c) alkyl isocyanate, toluene, 100 °C, 12 h.

Compound 2: Diethyl (4-nitobenzyl) phosphonate 2 (0.546 g, 2.0 mmol) was dissolved in anhydrous THF (15 mL) under an argon atmosphere and NaH (0.092 g, 4 mmol) was added to the solution at room temperature. After stirring for 10 min, a solution of the aldehyde 1 (0.502 g, 1 mmol) in anhydrous THF (30 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred for an additional 4 h at room temperature and subsequently poured into a mixture of crushed ice containing 30 mL of 6 N HCl. The mixture was extracted several times with CHCl 3, the collected organic fractions were washed with 3N HCl and dried over anhydrous Na 2SO 4. Evaporation of the solvent gave compound 2 as a deep red powder. Yield: 78%. m.p. 150-152 °C. $^1$H NMR (300 MHz, CDCl 3,
TMS): δ 0.952–0.908 (t, 6H, −CH3), 0.9–1.6 (m, 36H, −CH2), 1.928–1.932 (m, 4H, −CH2), 4.12–4.16 (t, J = 6.6 Hz, 4H, −OCH2), 7.19 (s, 2H, aromatic), 7.25–7.30 (d, J = 16.5 Hz, 2H, vinylic), 7.66–7.71 (d, J = 15.6 Hz, 2H, vinylic), 7.69–7.71 (d, J = 8.95 Hz, 4H, aromatic), 8.27–8.30 (d, J = 9 Hz, 4H, aromatic) ppm. MALDI-TOF MS (MW= 740.48): m/z= 740.45.

**Compound 3**: Under an argon atmosphere, 2 (0.74 g, 1 mmol) was suspended in a mixture of 15 mL ethanol and 30 mL ethyl acetate. 1.42 g (10 mmol) of SnCl2.2H2O was added to the suspension. The reaction mixture was heated to 70 °C, stirred for 7 h and subsequently poured onto crushed ice. The aqueous phase was extracted several times with diethyl ether. The collected organic fractions were dried over anhydrous Na2SO4 and the solvent was removed in vacuo to give 0.408 g of 3 (60 %) as a dark solid. Compound 3 was used for the next step without further purification.

**BU-OPV1**: A solution of butyl isocyanate (0.248 g, 2.5 mmol) in toluene (20 mL) was slowly added to a solution of compound 3 (0.68 g, 1 mmol) in toluene (60 mL). The reaction mixture was heated to 100 °C, stirred for 12 h, cooled to room temperature and subsequently the solvent was evaporated. Purification by column chromatography (silica gel,100-200 mesh, chloroform/hexane 3 : 1) yielded 0.79 g (90 %) of BU-OPV1 as a yellow solid. m.p. 235-237 °C; FT-IR (KBr): ν = 658, 720, 808, 855, 968, 1046, 1206, 1243, 1424, 1470, 1558, 1646, 2851, 2918, 3332 cm⁻¹. 1H NMR (300 MHz, CDCl3, TMS): δ 0.85–0.90 (t, J = 6.8 Hz, −CH3), 0.88–0.95 (t, J = 7.2 Hz, −CH3), 1.27–1.80 (m, 16H, −CH2), 1.38–1.56 (m, 28H, −CH2), 1.59–1.62 (m, 4H, −CH2), 1.84–1.87 (m, 4H, −CH2), 3.26–3.29 (m, 4H, −NCH2), 4.04–4.07 (m, 4H, −OCH2), 4.64 (s, br., 2H, −NH), 6.02 (s, br., 2H, −NH), 7.02 (s, 2H, aromatic), 7.09–7.15 (d, J = 16.8 Hz, 2H, vinylic), 7.18–7.24 (d, J = 16.5 Hz, 2H, vinylic), 7.45–7.47 (d, J = 6 Hz, 4H, aromatic), 7.54–7.57 (d, J = 9 Hz, 4H, aromatic) ppm. 13C NMR (300 MHz, THF) δ 13.99, 14.28, 19.16, 20.76, 23.44, 24.60, 24.90, 25.18, 25.44, 25.71, 27.03, 30.27, 33.39, 67.23, 110.81, 111.17, 112.28, 114.61, 115.01, 116.55, 118.51, 118.57, 127.64, 131.99, 141.40, 151.82 ppm. MALDI-TOF MS (MW=878.66): m/z= 878.62.

**BU-OPV2**: Yield 85 %; m.p. 215–218 °C; FT–IR (KBr): ν = 656, 721, 808, 845, 964, 1034, 1200, 1238, 1425, 1476, 1563, 1650, 2855, 2923, 3329 cm⁻¹. 1H NMR (300MHz, CDCl3, TMS): δ 0.80–0.87 (t, 4H, J = 6.8 Hz, −CH3), 0.88–0.95 (t, J =
7.0 Hz, 4H, −CH3), 1.26–1.89 (m, 32H, −CH2), 1.27–1.36 (m, 44H, −CH2), 1.59–1.62 (m, 4H, −CH2), 1.84–1.87 (m, 4H, −CH2), 3.21–3.39 (m, 4H, −NCH2), 3.96–3.99 (m, 4H, −OCH2), 5.02 (s, br., 2H, −NH), 6.5 (s, br., 2H, −NH), 6.99 (s, 2H, aromatic), 7.02–7.07 (d, J=16.8 Hz, 2H, vinylic), 7.11–7.17 (d, J=16.8 Hz, 2H, vinylic), 7.38–7.35 (d, J=8.5 Hz, 4H, aromatic), 7.54–7.57 (d, J=9 Hz, 4H, aromatic) ppm. 13C NMR (300 MHz, THF): δ 12.87, 16.29, 19.45, 20.63, 21.72, 23.52, 24.01, 24.56, 24.98, 25.98, 26.36, 27.66, 31.22, 32.38, 67.78, 111.33, 112.17, 112.77, 113.62, 115.99, 116.11, 116.45, 117.53, 127.89, 130.99, 138.40, 149.82.

Optical Measurements. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. Temperature dependent studies were carried out either in a 1 cm quartz cuvette with a thermistor directly attached to the wall of the cuvette holder. Fluorescence spectra of optically dilute solutions were recorded from 390-700 nm at the excitation wavelengths of 380 nm.

Quantum Yield Measurements. Fluorescence quantum yields of BU-OPVs in cyclohexane and chloroform upon excitation at 380 nm is reported relative to quinine sulfate (Φf = 0.546). The experiments were done using optically matching solutions and the quantum yield is calculated using Equation 1.

Φf = Φr (As/Fs) (η2s/η2r) …………………   (1)

where, As and Ar are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength, Fs and Fr are the corresponding relative integrated fluorescence intensities and η is the refractive index.

Calculation of Association Constants. The association constants were determined by the fluorescence spectral changes using Benesi-Hildebrand equation.3

The Benesi-Hildebrand equations for 1:1 and 2:1 complex formation are given by Equation (2) and Equation (3) respectively.
\[
\frac{1}{(\Phi_f - \Phi_{ob})} = \frac{1}{(\Phi_f - \Phi_{fc})} + \frac{1}{K(\Phi_f - \Phi_{fc})[X]} \quad \text{---------- (2)}
\]
\[
\frac{1}{(\Phi_f - \Phi_{ob})} = \frac{1}{(\Phi_f - \Phi_{fc})} + \frac{1}{K(\Phi_f - \Phi_{fc})[X]^2} \quad \text{---------- (3)}
\]

where, \( K \) is the association constant, \( \Phi_f \) is the quantum yield of emission of free host, \( \Phi_{ob} \) is the observed quantum yield and \( \Phi_{fc} \) is the quantum yield of emission of host-guest complex.

References

