Supplementary Information

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

Reji Varghese, Subi J. George and Ayyappanpillai Ajayaghosh*

Photosciences and Photonics Division, Regional Research Laboratory (CSIR), Trivandrum-695019, India.



Fig.S1. Changes in the absorption spectra of **BU-OPV1** (1.1×10^{-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-OPV**s is shown in Scheme 1. The starting bisaldehyde derivative 1 was synthesized as per reported procedures.¹ 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 isocyante resulted in **BU-OPV1** and **BU-OPV2** respectively.



Scheme S1. Syntheis of BU-OPVs. Reagents and conditions: (a) diethyl(4-nitrobenzyl) phosphonate, THF, NaH, room temperature, 8 h. (b) $SnCl_2$. $2H_2O$, EtOH/EtOAc, 70 ^{0}C , 7 h. (c) alkyl isocyanate, toluene, 100 ^{0}C , 12 h.

Compound 2: Diethyl (4-nitobenzyl) phosphonate² (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 CHCl₃, the collected organic fractions were washed with 3N HCl and dried over anhydrous Na₂SO₄. Evaporation of the solvent gave compound **2** as a deep red powder. Yield: 78%. m.p. 150-152 °C. ¹H NMR (300 MHz, CDCl₃,

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. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.92–0.97 (t, 6H, -CH₃), 1.30–1.56 (m, 36H, -CH₂), 1.89–1.91 (m, 4H, -CH₂), 3.78 (s, br., 4H, -NCH₂), 4.06–4.10 (t, *J* = 6.3 Hz, 4H, -OCH₂), 6.75 (s, 2H, aromatic), 6.72–6.75 (d, *J* = 8 Hz, 4H, aromatic), 7.05–7.11 (d, *J* = 17 Hz, 2H, vinylic), 7.39–7.42 (d, *J* = 8.5 Hz, 4H, aromatic), 7.37–7.43 (d, *J* = 17 Hz, 2H, vinylic) ppm. MALDI–TOF MS (MW=680.53): *m/z* = 680.53.

BU-OPV1: A solution of butyl isocyante (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 0 C; FT-IR (KBr): v = 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 = 6.2 Hz, 6H, -CH₃), 0.91-0.96 (t, J = 7.2 Hz, 6H, $-CH_3$), 1.27-1.80 (m, $16H_3$, $-CH_2$), 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 0 C; FT–IR (KBr): v = 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 ($\Phi_f = 0.546$). The experiments were done using optically matching solutions and the quantum yield is calculated using Equation 1.

where, A_s and A_r are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r 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.

$$\frac{1}{(\Phi_{\rm f} - \Phi_{\rm ob})} = \frac{1}{(\Phi_{\rm f} - \Phi_{\rm fc})} + \frac{1}{K(\Phi_{\rm f} - \Phi_{\rm fc})[X]} \qquad (2)$$
$$\frac{1}{(\Phi_{\rm f} - \Phi_{\rm ob})} = \frac{1}{(\Phi_{\rm f} - \Phi_{\rm fc})} + \frac{1}{K(\Phi_{\rm f} - \Phi_{\rm fc})[X]^2} \qquad (3)$$

where, K is the association constant, Φ_f is the quantum yield of emission of free host, Φ_{ob} is the observed quantum yield and Φ_{fc} is the quantum yield of emission of host-guest complex.

References

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