

Appendix A.

Supplementary data

**Self-assembly, optical, thermal and electrochemical properties of bis-N-benzyl
perylene diimide dye**

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Experimental

Materials

The chemicals, perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PDA), benzylamine, *m*-cresol and isoquinoline were reagent grade commercial products, purchased from Aldrich and used without further purification. PDA was dried overnight at 100 °C under vacuum. *M-Cresol* and isoquinoline were pre-dried over activated 4 Å molecular sieves and were distilled freshly prior to use. Spectroscopic grade solvents from Aldrich were used for all spectroscopic analyses.

Methods

Fourier transform infrared spectra (FTIR) were obtained in KBr pellets with high resolution using a JASCO FT/IR-6200 spectrometer. ¹H NMR spectra were recorded on a Bruker/XWIN spectrometer (400 MHz) in CDCl₃ using the residual solvent resonance of CHCl₃ at 7.24 ppm relative to SiMe₄ as internal reference. UV-vis absorption spectra in various solutions were recorded on a Varian-Cary 100 spectrometer. Solid-state absorption spectra were recorded on Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer. Fluorescence spectra at the excitation wavelength (λ_{exc}) of 485 nm were measured using a Varian-Cary Eclipse Fluorescence spectrophotometer. The relative fluorescence quantum yields (Φ_f) were determined using a solution of N,N'-didodecyl-3,4,9,10-perylenebis(dicarboximide) in chloroform as a standard whose quantum yield is unity. Mass spectrum was measured on MS/MS System 3200 QTRAP instruments as Fragmentor 50 eV ionization energy. Elemental analysis was performed on a Thermo Finnigan Flash EA 1112 C, H, and N analyzer. The morphology of self-assembled

hollow tubes, **T-1** and **1** were examined and imaged by scanning electron microscopy (SEM) using a JEOL-JSM6610LV analyzer equipped with Back-Scatter detector. The Acceleration Voltage used was 20 kV. EMITECH SC7620 sputtering machine was used to coat **1** sample for 120 s with gold at 5 mA current. Initially, the powdered **T-1** and **1** samples were directly casted onto a carbon-coated grid bands. Later, the specimens were gold sputter coated and analyzed. The average pore and diameter of **T-1** and **1** samples were determined by using ImageJ1.41 software. Thermal analyses, differential scanning calorimetry (DSC) curves in nitrogen and thermogravimetric analysis (TGA) thermograms in oxygen were determined on a Perkin Elmer/Pyris 1 instrument at a heating rate of 10 °C min⁻¹. Electrochemical measurements were carried out in solutions of NaBF₄ (0.1 M) in DMSO (1.5×10⁻⁴ M) and in solid-state (1 M HCl) by cyclic voltammetry (CV) and squarewave voltammetry (SQWV) experiments under argon employing a computer-controlled REFERENCE 600 Potentiostat/Galvanostat/ZRA workstation. A three-electrode cell with the glassy carbon working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode was used to measure the potentials. Reproducible surfaces are induced on working electrode and confirmed the reproducibility of resulting redox peak potentials. The technique of immobilized microparticles voltammetry is used to record the peak potentials in solid-state. The samples were deaerated thoroughly by bubbling pure argon gas at room temperature.

Synthesis of N,N'-bis-(benzyl)-3,4,9,10-perylenebis(dicarboximide), **1**

Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) (1.00 g, 2.55 mmol), benzylamine (0.82 mL, 7.65 mmol) were heated in a pre-dried solvent mixture of *m*-cresol (60 mL) and isoquinoline (8 mL) under argon atmosphere at 120 °C for 2 h, 160 °C for 2 h and at 200 °C for 6 h. The

solution was allowed to cool and the warm solution was poured into 300 mL acetone. The precipitate was filtered off and dried at 100 °C under vacuum. The crude product was treated with ethanol (EtOH) in a Soxhlet apparatus for 2 day in order to get rid of unreacted amine and solvents. The solid was dried in vacuum at 100 °C, giving a black powder (1.16 g, 80% yield). The crude product was sublimed under vacuum to produce a black crystalline solid.

FTIR (KBr, cm^{-1}): $\nu = 3031, 2970, 1694, 1646, 1593, 1497, 1436, 1321, 1239, 1165, 955, 812, 744$. $^1\text{H NMR}$, δ_{H} (ppm) (400 MHz, CDCl_3): 8.81 (d, 4Ar-H, C(1), C(6), C(7), C(12)), 8.74 (d, 4Ar-H, C(2), C(5), C(8), C(11)), 7.59 (d, 4Ar-H, C(19), C(23), C(19'), C(23')), 7.28 (m, 6Ar-H, C(20), C(21), C(22), C(20'), C(21'), C(22')), 5.41 (s, 4H, C(17), C(17')). UV-vis (CHCl_3): λ_{max} , nm (ϵ_{max} , $\text{cm}^{-1}\text{M}^{-1}$) = 459 (1500), 490 (3700), 527 (5900). Fluorescence (CHCl_3) λ_{max} , nm: 538, 576, 628. Fluorescence quantum yield (CHCl_3 , reference, dodecyldiimide (CHCl_3) with $\Phi_{\text{f}} = 100\%$): 98%. MS (EI): m/z: 569.50. Anal. calcd. for $\text{C}_{38}\text{H}_{22}\text{N}_2\text{O}_4$ (M_{w} , 570.58); C, 79.99; H, 3.89; N, 4.91. Found: C, 80.07; H, 3.93; N, 4.92.

Self-assembled bis-N-benzyl perylene diimide structures fabrication, T-1

The self-assembly of **T-1** into hollow tubes microstructures were produced by the solution mixture method according to the literature.⁸ A homogeneous solution of **1** in DMF (1 mL, 1×10^{-5} M) was quickly injected into an equal amount of water (1 mL) and kept at room temperature for overnight. The solvent was evaporated and the self-assembled microstructures were obtained. The experimental technique reported was consistent with reproducible results under the given conditions.

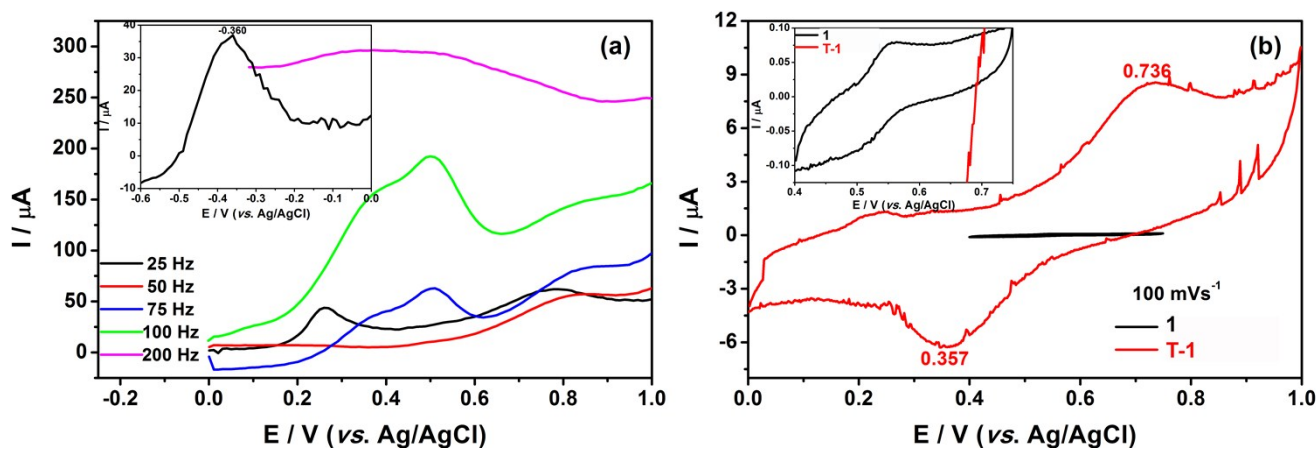


Fig. S1. (a) Frequency dependent squarewave voltammograms of **T-1** and the inset infers the weak reduction at 25 Hz; (b) Comparison of cyclic voltammograms of **1** (black) and **T-1** (red) particles at 100 mVs^{-1} , inset shows the enlarged cyclic voltammogram of **1** for clarity.

As can be seen clearly, The weak reduction peak potential for self-assembled **T-1** (inset of Figure S1a) was apparent. The shift in peak potentials upon increase in frequency was also obvious for **T-1** from SQWVs (Figure S1a). Figure S1b indicates the overlap CVs of **1** and **T-1** in solid-state. The predominant CV of **T-1** is apparent when compared to the CV of **1** (inset of Figure S1b). Obviously, self-assembled **T-1** hollow tubes make them more conductive when compared to **1**.