

Supplementary Material (ESI) for:

A new tunable light-emitting and pi-stacked hexa-ethyleneglycol naphthalene-bisimide oligomer: Synthesis, photophysics and electrochemical properties

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Materials

Tetrabutylammonium hexafluorophosphate (TBAPF6) and ferrocene were used as purchased from Fluka. All other chemical reagents and solvents used were purchased from Aldrich. 1,4,5,8-naphthalenetetracarboxylic dianhydride (**1**) was dried in a vacuum oven at 100 °C overnight. *m*-Cresol was pre-dried over activated 4 Å molecular sieves in order to eliminate any residual water and distilled immediately prior to use. The solvents chloroform (CHCl₃), dichloromethane (DCM) and methanol (MeOH) were obtained from Aldrich and purified by distillation. Organic solvent solutions were dried over Na₂SO₄ and evaporated on a rotary evaporator under reduced pressure. All reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60 F₂₅₄ precoated aluminum plates, which were developed with UV light followed by spraying with acidic vanillin solution. All the other chemicals used were of reagent grade and used without further purification, unless otherwise stated.

Characterizations

¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ on a Bruker/XWIN spectrometer, and tetramethylsilane (TMS) was used as internal standard. The infrared spectrum of **3** was recorded from pressed KBr pellets using a FTIR-Satellite spectrometer (Mattson, USA). UV absorption and emission spectra of solutions were measured with a Varian-Cary 100 spectrophotometer and spectra of solid state were obtained in thin films with a Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer, equipped with solid state accessories. Carbon, nitrogen and hydrogen contents were determined using a Carlo-Erba 1106 elemental analyzer. Thermogravimetric analyses (TGA) were carried out on a TG-MS: Simultane TG-DTA/DSC apparatus STA 449 Jupiter from Netzsch, equipped with Balzers Quadstar 422V at a heating rate

of $10\text{ }^{\circ}\text{C min}^{-1}$ in oxygen. Thermal analyses were obtained from a PerkinElmer Diamond type DSC instrument at a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen. Cyclic voltammeteries (CV) in solution were performed using a three-electrode cell with separate compartments for the reference electrode (Ag, AgCl (sat) in acetonitrile/saturated calomel) and the counter electrode (Pt wire). The working electrode for the cyclic voltammetric studies, which was cleaned by polishing with an Al_2O_3 slurry, was an Au disc with an area of 0.078 cm^2 ; solutions were $1 \times 10^{-4}\text{ M}$ in electroactive material and 0.1 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF6). Data were recorded on an EG&G PAR 273A computer-controlled potentiostat. Ferrocene was used as an internal reference. The scan rate of $5 - 500\text{ mV s}^{-1}$ was employed for cyclic voltammeteries in DCM and MeOH: CH_3CN (50:50) binary solvent mixture. All the electrolyte solutions were degassed with N_2 prior to the electrochemical measurements.

The weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity ($\text{PDI} = M_w/M_n$) were determined by gel permeation chromatography (GPC) with a high performance liquid chromatography (HPLC) system from ThermoSeparation Products using two columns (PSS-PFG, $7\mu\text{m } 10^2$ and 10^3 \AA), with isocratic pump, autosampler, in combination with a detector Shodex RI71. The samples were to run in hexafluoroisopropanol (HFIP) with 0.05 M potassiumtrifluoroacetate (KTFAc) and calibrated with polymethylmethacrylate (12 narrow PMMA) standard at $23\text{ }^{\circ}\text{C}$. The oligomer was completely soluble in HFIP. The solution was filtered through a $1\text{ }\mu\text{m}$ filter unit and $50\text{ }\mu\text{m}$ was injected for the GPC measurement. The calculation of the average molecular weight and the molecular weight distribution of the sample were done by the so called slice by slice method based on the PMMA calibration. Intrinsic viscosity was measured at $25\text{ }^{\circ}\text{C}$ in *m*-cresol, using an Ubbelohde

viscometer. The intrinsic viscosity value $[\eta]$ was obtained by measuring specific viscosity $\eta_{sp} = \eta/\eta_o - 1$ and reduced viscosity $\eta_{red} = \eta_{sp}/c$ at five different concentrations, plotting η_{sp}/c vs c and extrapolating to zero concentration.