Supporting Information

Oligothiophene Nanoparticles: Photophysical and Electrogenerated Chemiluminescence Studies


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1. General Considerations

1.1. Chemicals: **Hexamer-1** and **Hexamer-2** were synthesized according to procedure described previously [1]; tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$), anhydrous acetonitrile (99.93%) and benzene (99%) were purchased from Sigma-Aldrich (Milwaukee, WI) and used without further purification. All other solvents (dichloromethane, chlorobenzene and ethanol) were obtained from Fisher Sci. (Fair Lawn, NJ) and used as received.

1.2. Apparatus and Methods

Absorbance and fluorescence measurements were carried out in air. UV-Vis measurements were made using a DU 640 spectrophotometer (Beckman, Fullerton, CA). Fluorescence measurements were carried out using Fluorolog-3 Spectrophotometer (Jobin Yvon Inc., NJ) with a 450-W xenon lamp as a source. Absorbance and fluorescence measurements were performed immediately after preparing solutions. Solutions for electrochemical measurements were prepared inside an Ar atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). Upon preparation, the solutions were sealed in a glass tube with a cap. Three metallic rods were drilled inside the cap for the electrical connections. A Pt L-shaped electrode with an area of 0.0314 cm$^2$, Pt wire and Ag wire were used as working, counter and reference electrodes, respectively. The working electrode was polished with 0.3 µM alumina prior to every experiment. Glassware was dried in an oven at 120 ºC prior to use. Electrochemical measurements were carried out using a CHI 660 (CH Instruments, Austin, TX). ECL signals were produced by pulsing at about 80 mV from the oxidation and reduction peaks. The slit width was set at 0.5 cm. Spectra were collected with a Princeton Instruments Spec-10 CCD camera (Trenton, NJ) with an Acton SpectraPr-150
monochromator (Acton, MA). ECL experiments were carried out under the same conditions as the fluorescence experiments using a Pt wire as a working electrode and slit width of 1 mm. DLS measurements were done using a Model Zetasizer nano ZS ((Malvern Instruments), Worcestershire, UK) at 90° for for several concentrations. TEM experiments were carried out using a FEI Tecnai instrument (Hillsboro, Oregon). Samples of around 5 µM were deposited on a 400 mesh carbon coated copper TEM grid.

2. Fluorescence data.

(a)
Figure S1. Images of (a) Hexamer-1 and (b) Hexamer-2 in different ratios of water:THF; from top to bottom: 90% THF: 10% water; 60% THF: 40% water; 50% THF: 50% water; 40% THF: 60% water; 20% THF: 80% water; 10% THF: 90% water; (b) 90% THF: 10% water; 10% THF: 90% water (v/v). The concentration was varied from 0.016 mM to 0.1 mM: from right to left (0.1 mM, 0.05 mM, 0.025 mM, 0.013 mM, 0.065 m, 0.032 mM, 0.016 mM). The solutions were irradiated with a handheld UV lamp.
Figure 2. Fluorescence spectra for the different concentration and ratios of (a) 40 % THF: 60 % water; (b,c) difference between fluorescence in a range of solvents for 0.01 mM solution of (b) Hexamer-1 and (c) Hexamer-2: hexane (blue), THF-ethanol (magenta), benzene (red), THF (green), chlorobenzene (black).

3. Dynamic light scattering (DLS) characterization.
Figure S3. DLS data for the thiophene **Hexamer-1** (a,b) and **Hexamer-2** (c,d); data for (a) and (c) was collected prior usage of the 500 nm filter and b and d after usage of the filter.