Electronic supplementary information

Photoinduced electron transfer in a supramolecular triad produced by prophyrin anion-induced electron transfer from tetrathiafulvalene calix[4]pyrrole to $Li^+@C_{60}$

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Synthetic experimental. General chemicals were purchased from commercial sources and used without further purification. Benzonitrile was distilled over phosphorous pentaoxide prior to use unless otherwise noted. The benzoannulated tetrathiafulvalene calix[4]pyrrole used in this study was synthesized as previously reported.[1] The porphyrin used to prepare salt **1**, 4-(10,15,20-triphenylporphyrin-5-yl) benzoic acid, was prepared by use of modified literature procedures.[2] First, benzoic acid, 4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)-, methyl ester was prepared by modifying a previously reported synthesis.[2a] Briefly, 1,9-*bis*-benzoyl-5-phenyldipyrromethane (430 mg, 1 mmol) was dissolved in 15 mL THF:MeOH (10:1). $NaBH_4$ was added, and solution was stirred for 30 min at room temperature. The solution was then poured into sat. NH_4Cl and extracted with 80 mL CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was dissolved in 360 mL MeCN. 4-Methylcarboxyphenyldipyrromethane (190 mg, 1 equiv) was added, followed by 1 mL of TFA added drop-wise. The resulting solution was stirred for 5 min. DDQ (60 mg) was added and the solution was stirred for an hour. The solution was concentrated under vacuum, and the resulting residue was purified by column chromatography over silica gel to give the desired product in 11% yield. NMR, MS, and UV data matched the literature values. From the ester, benzoic acid, 4-(10, 15, 20-triphenyl-21*H*,23*H*-porphin-5-yl was prepared using conditions detailed in the litrature.[2b] The desired compound was isolated in 74% yield and analysis gave values that matched the reported specroscopic data. The carboxylic acid proton was exchanged for the tetrahexylammonium cation by partitioining between a dichloromethane layer containing tetrahexylammonium chloride and an aqueous sodium hydroxide layer. This gave **1**.

Laser flash photolysis measurements. Nanosecond transient absorption spectral measurements were made according to the following procedure. A deaerated solution of **1**, TTF-C4P and $Li^+@C_{60}$ was excited by an Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at 532 nm. The resulting time resolved transient absorption spectra were measured by using a continuous Xe-lamp (150 W) and a photodiode (Hamamatsu 2949) as the probe light and detector, respectively. The output from the photodiode and the photomultiplier tube was recorded using a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The solutions were deoxygenated by N_2 purging for 10 min prior to making the measurements. Rates of photoinduced electron-transfer reactions were monitored by the rise and decay of the absorption band due to the TTF-C4P radical anion. First-order rate constants were determined by a least-squares curve fit. All experiments were performed at 298 K.

References

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