

Design and Synthesis of a Novel Anchoring Ligand for Highly Efficient Thin Film Dye-Sensitized Solar Cells

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Experimental

NMR spectra were recorded on a *Bruker AMX 500* (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz) or an *Avance 400* spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz), at 25 °C. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (DMSO-d₆: ¹H δ = 2.5 ppm and ¹³C δ = 39.4 ppm) as internal standard. Melting points were determined using a *Büchi B-545* apparatus. Elemental analyses were performed on an *Elementar Vario EL* (University of Ulm). ESI and EI mass spectra were recorded on a *micromass ZMD* or a *Varian Saturn 2000 GC-MS*, MALDI-TOF on a *Bruker Daltonics Reflex III*. Optical measurements were carried out in 1 cm cuvettes with *Merck* spectroscopic grade solvents, absorption spectra recorded on a *Perkin Elmer Lambda 19* spectrometer and fluorescence spectra on a *Perkin Elmer LS 55* spectrometer. The emission spectra are fully corrected for the photodetector response. Cyclic voltammetry experiments were performed with a computer-controlled *EG&G PAR 273* potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag / AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple.

Synthesis:

4,4'-Di(thien-2-yl)-2,2'-bipyridine (1)

4,4'-Dibromo-2,2'-bipyridine (1.0 g, 3.18 mmol, 1.0 eq.), 2-tributylstannylthiophene (2.97 g, 7.96 mmol, 2.5 eq.), [Pd(PPh)₃Cl₂] (67 mg, 95.5 μmol, 0.03 eq.) and CsF (1.93 mg, 12.7 μmol, 4.0 eq.) were dissolved in a mixture of degassed toluene:THF (8:4). The reaction was performed in a microwave at 110 °C for 2 h. After completion, the mixture was poured into methanol and the precipitate was filtered off, washed with methanol, dichloromethane and finally diethyl ether to obtain compound **1**

(1.0 g, 3.12 mmol) in 98% yield as colorless solid. The purification of **1** can also be performed by column chromatography (Al_2O_3) using a hexane/dichloromethane solvent mixture in a 1:1 (v/v) ratio. M.p.: 219-220 °C; ^1H NMR: (DMSO-d_6 , 400 MHz) δ ppm: 7.25 (t, $^3J = 4.3$ Hz, 1H, ThH), 7.78 (d, $^3J = 4.97$ Hz, 2H, ThH+BpyH), 7.89 (s, $J = 3.32$ Hz, 1H, ThH), 8.59 (s, 1H, BpyH), 8.72 (d, $^3J = 5.13$ Hz, 1H, BpyH). ^{13}C NMR: (DMSO-d_6 , 100 MHz) δ ppm: 115.9, 119.8, 126.6, 128.4, 128.9, 140.2, 141.7, 150.1, 155.6. Elemental analysis: calc. for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{S}_2$ C: 67.47; H: 3.77; N: 8.74 %; found: C: 67.51; H: 3.79; N: 8.70 %.

5,5'-[2,2'-Bipyridin-4,4'-diyl]-bis[thiophene-2-carboxylic acid](2). To a solution of *n*-BuLi (2.14 mL, 3.43 mmol, 1.6 M, 2.2 eq.) in 10 mL THF diisopropylamine (0.53 mL, 3.75 mmol, 2.4 eq.) was added dropwise at -78 °C. The resulting mixture was stirred for 0.5 h at the same temperature and subsequently stirred at room temperature for another 10 min. The resulting lithium diisopropylamide solution was cooled to -78 °C and a solution of **1** (500 mg, 1.56 mmol, 1 eq.) in 100 mL dry tetrahydrofuran was added dropwise. The resulting mixture was stirred for 1 h at this temperature and then gaseous CO_2 was bubbled through the solution. The white precipitate of the carboxylate salt was acidified with 6M HCl (20 mL). The precipitate was filtered off and washed with methanol and diethyl ether. The crude product was further recrystallized from hot DMSO to obtain **2** (574 mg, 1.4 mmol, 90%) as colorless solid. M.p.: >300 °C; ^1H NMR: (DMSO-d_6 , 400 MHz) δ ppm: 7.81 (d, $^3J = 3.89$ Hz, 1H, ThH), 7.88 (dd, $^3J = 5.02$, 1.69 Hz, 1H, BpyH), 7.95 (d, $J = 3.93$ Hz, 1H, ThH), 8.66 (s, 1H, BpyH), 8.81 (d, $J = 5.20$ Hz, 1H, BpyH). ^{13}C NMR: (DMSO-d_6 , 100 MHz) δ ppm: 116.3, 120.4, 127.3, 134.2, 140.9, 146.0, 147.5, 150.4, 155.6, 162.4. Elemental analysis: calc. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$ C: 58.81; H: 2.96; N: 6.86 %; found: C: 58.87; H: 2.94; N: 6.80 %.

Bis(tetrabutylammonium)-cis-Dithiocyanato-di[5-(4'-(5-carboxythiophen-2-yl)-2,2'-bipyridin-4-yl)thiophene-2-carboxylate]ruthenium(II) (BTC-1). Dichloro(*p*-cymene)ruthenium(II) dimer (75.0 mg, 122 μmol , 1.0 eq.) and ligand **2** (200 mg, 489 μmol , 4.0 eq.) were added to a 50 mL dry Schlenk tube purged with argon. Then, the solid was suspended in 30 mL dry DMF and heated at 145 °C for 5 h in the dark to avoid light-induced *cis* to *trans* isomerization. Finally, ammonium thiocyanate (745 mg, 9.8 mmol, 20 eq.) was added and the mixture was stirred for 4 h at 135 °C.

After cooling to room temperature, the solvent was removed with a rotary evaporator. Ice water (100 mL) was added to the flask, and kept overnight in the refrigerator to complete the precipitation. The insoluble solid was collected on a sintered glass crucible by suction filtration. The solid was washed with distilled water and diethyl ether and then dried under vacuum. The crude complex was dissolved in basic methanol (tetra-*n*-butylammonium hydroxide) and purified on a Sephadex LH-20 column using methanol as eluent. The collected main band was concentrated and titrated with dilute acidic methanol solution (0.3 M HNO₃) to pH 5.6. The precipitate was collected on a sintered glass crucible by suction filtration and dried under high vacuum to provide complex **BTC-1**. ¹H NMR: (DMSO-*d*₆, 500 MHz) δppm: 0.9 (t, ³*J* = 7.36 Hz, 24H, CH₃), 1.3 (m, 16H, CH₂), 1.5 (m, 16H, CH₂), 3.1 (m, 16H, CH₂), 7.38 (dd, ³*J* = 6.11, 1.88 Hz, 2H, BpyH), 7.57 (d, *J* = 3.76 Hz, 2H, ThH), 7.61 (d, *J* = 6.13 Hz, 2H, BpyH), 7.70 (d, *J* = 3.63 Hz, 2H, ThH), 7.84 (d, *J* = 3.94 Hz, 2H, ThH), 8.05 (d, *J* = 3.87 Hz, 2H, ThH), 8.08 (dd, ³*J* = 5.97, ⁴*J* = 1.77 Hz, 2H, BpyH), 8.85 (d, ⁴*J* = 1.60 Hz, 2H, BpyH), 9.00 (d, ⁴*J* = 1.60 Hz, 2H, BpyH), 9.31 (d, ³*J* = 5.96 Hz, 2H, BpyH). Elemental Analysis (for C₄₂H₂₂N₆O₈RuS₆·2(C₄H₉)₄N: calcd. C: 58.59; H: 6.25; N: 7.39; found C:58.86; H:5.77; N:7.16.

Device Fabrication: The cells consisted of a mesoscopic TiO₂ film composed of a 7 μm thick transparent layer of 20 nm sized TiO₂anatase nanoparticles onto which a second 5 μm thick scattering layer of 400 nm sized TiO₂ was superimposed. The double layer films were heated to 520 °C and sintered for 30 min, then cooled to 80 °C. The electrode was immersed for 16 hours into the dye solution (150 μM) containing 10% DMSO in a acetonitrile/*tert*-butyl alcohol-mixture (volume ratio:1:1). The devices were fabricated with the low-volatile electrolyte coded Z946. The Z946 electrolyte contains 3-methoxypropionitrile as a solvent and 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.15 M I₂, 0.5 M *n*-butylbenzimidazole as well as 0.1 M guanidiniumthiocyanate (GuNCS) as solutes. The cell was sealed with a 25 μm-thick transparent Surlynring (from DuPont) at 130 °C for 15 seconds to the counter electrode (FTO glass, 15 Ω cm⁻², coated with a platinum solution chemically deposited at 450 °C for 15 min). The cells were filled with the electrolyte through a pre-drilled hole in the counter electrode. The hole was then sealed with a Bynel disc and a thin glass to avoid leakage of the electrolyte.