Supporting information

Heterocycle Containing Different Atoms as π-bridge effect on the Performance of Dye-Sensitized Solar Cells

Hailang Jia,a Xuehai Ju,b Mingdao Zhang,a Zemin Jua and Hegen Zheng*a

aState Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, P. R. China
bSchool of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China
General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. \(N, N\)-Dimethylformamide, toluene and tetrahydrofuran were dried and distilled from \(\text{CaH}_2\).

The \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra were recorded on a Bruker DRX (500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

Synthesis of the dye JP-O

Scheme S1 Reagents and conditions: a) Tris(4-bromophenyl)amine, \(\text{Pd(PPh}_3\rangle_4, \text{K}_2\text{CO}_3, \text{H}_2\text{O, 1, 4-dioxane, 90°C; b) Bis(pinacolato)diboron, Pd(dppf)Cl}_2, \text{KOAc, DMF, 80°C; c) \text{Pd(PPh}_3\rangle_4, \text{K}_2\text{CO}_3, \text{H}_2\text{O, 1, 4-dioxane, 90°C; d) i: TBAF, THF, rt; ii: 5-bromofuroic acid, Pd}_2(\text{dba})_3, \text{AsPh}_3, \text{TEA, THF, reflux.}##
**Experimental Details:**

**Synthesis of compound 2 to compound 5**

The compounds 2-5 were synthesized according to ref. 1.

**Synthesis of dye JP-O**

To a solution of compound 5 (300 mg, 0.167 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H2O and then extracted with CH2Cl2. The organic layer was dried over anhydrous MgSO4 and the solvent was removed under reduced pressure. The residue and 5-bromofuroic acid (127 mg, 0.668 mmol) were dissolved in a mixture of anhydrous THF (40 mL) and TEA (10 mL) underdinitrogen, then Pd2(dba)3 (46 mg, 0.050 mmol) and AsPh3 (102 mg, 0.334 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (CH2Cl2/MeOH = 20/1), recrystallization from MeOH/Ether to give dye JP-O (200 mg, 67%) as a green solid. 1HNMR (CDCl3, 500Hz) δH 9.67 (d, J = 4.5Hz, 2H), 8.96 (d, J = 4.5Hz, 2H), 8.93 (d, J = 4.5Hz, 2H), 8.85 (d, J = 4.5Hz, 2H), 8.07 (d, J = 8.0Hz, 2H), 7.73 (t, J = 8.5Hz, 2H), 7.61 (d, J = 8.0Hz, 4H), 7.48 (d, J = 8.0Hz, 2H), 7.41 (d, J = 8.0Hz, 4H), 7.13 (d, J = 3.0Hz, 2H), 7.05 (d, J = 8.5Hz, 6H), 6.77 (d, J = 3.5Hz, 2H), 3.88 (s, 8H), 2.86 (t, J = 7.5Hz, 4H), 1.72-1.78 (m, 4H), 6.77 (d, J = 3.5Hz, 2H), 3.88 (s, 8H), 2.86 (t, J = 7.5Hz, 4H), 1.72-1.78 (m, 4H), 1.42-1.48 (m, 4H), 1.31-1.38 (m, 8H), 0.83-1.01 (m, 30H), 0.64-0.71 (m, 8H), 0.53-0.57 (m, 20H), 0.45-0.49 (m, 8H). 13CNMR (CDCl3, 125Hz) δC 160.0, 152.0, 151.2, 150.3, 149.4, 146.6, 146.5, 145.2, 143.8, 141.5, 137.8, 135.6, 135.4, 132.5, 131.8, 130.9, 130.0, 129.7, 126.5, 125.0, 124.7, 122.0, 121.6, 116.1, 114.8, 105.2, 68.6, 31.6, 31.4, 30.3, 29.7, 28.7, 25.3, 22.6, 22.3, 14.1, 13.8. MS (ESI): Calcd for C109H127N5O7S2Zn, 1748.71; found, 1746.75.
**Fig. S1** Emission spectra of JP-S and JP-O in DCM

**Fig. S2** The normalized absorption spectra (solid lines) and emission spectra (broken lines) of JP-S (black) and JP-O (red) in DCM (the intersection of JP-S and JP-O is 613 nm and 601 nm, respectively, $E_{\text{o-o}} = 1240 / \lambda$).
**Fig. S3** Absorption spectrum of TiO\(_2\) film.

**Fig. S4** HOMO and LUMO frontier molecular orbitals of JP-S and JP-O calculated by density-functional theory (DFT) at the DFT-B3LYP/LanL2MB level with Gaussian 09 suite of programs.
Fig. S5 The geometry optimized ground state molecular structures of JP-S and JP-O.

Fig. S6 Absorption spectra of JP-S+TTR1 and JP-O+TTR1 anchoring on the 14 μm porous TiO$_2$ nanoparticle films.
References