Electronic Supplementary Information

A new ruthenium sensitizer enhances the absorptivity of mesoporous titania film for high efficiency dye-sensitized solar cell

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1. Synthesis of 5-octylthieno[3,2-*b*]thiophene

To a stirred solution of thieno[3,2-*b*]thiophene (10.7 mmol) in anhydrous CH_2Cl_2 (200 mL) was added octanoyl chloride (11.0 mmol). The mixture was stirred for 30 min at room temperature, cooled to 0 °C, and $AlCl_3$ (12.0 mmol) was added portionwise. The mixture was then warmed to 25 °C and stirred overnight. The reaction was quenched by the addition of water and acidified with a 2 M HCl aqueous solution. The mixture was extracted with CH_2Cl_2. The organic layers were washed with water and dried over $MgSO_4$. After the removal of solvent, the crude product was purified by column chromatography (CH_2Cl_2/*n*-hexane: 1/1) on silica gel to afford 1-(thieno[3,2-*b*]thiophen-2-yl)octan-1-one (2.08 g) as milk white solid. Yield: 72%. ^1H NMR (400 MHz, $CDCl_3$, δ_H): 7.90 (s, 1H), 7.61 (d, 1H), 7.30 (d, 1H), 2.92 (t, 2H), 1.81–1.74 (m, 2H), 1.37–1.30 (m, 8H), 0.88 (t, 3H). Cold anhydrous ether (100 mL) was added to separate batches of $LiAlH_4$ (58.0 mmol) and $AlCl_3$ (13.5 mmol) and the resulting suspended solutions were carefully mixed. To this mixture was added 1-(thieno[3,2-*b*]thiophen-2-yl)octan-1-one (6.0 mmol) in dry ether at 0 °C. The mixture was warmed to room temperature and then stirred for 3 h. The reaction was quenched by the careful addition of ether and a 2 M HCl aqueous solution. The gray precipitate was filtrated and washed with ether. The combined filtrate was extracted, washed with water, and dried over $MgSO_4$. After rotary evaporation of solvent, the crude product was purified with column chromatography (*n*-hexane) on silica gel to afford white solid. (1.46 g). Yield: 96%. ^1H NMR (400 MHz, $CDCl_3$, δ_H): 7.27 (d, 1H), 7.18 (d, 1H), 6.95 (s, 1H), 2.87 (t, 2H), 1.73–1.53 (m, 2H), 1.39–1.27 (m, 10H), 0.88 (t, 3H).

2. Synthesis of 4,4'-bis(5-octylthieno[3,2-b]thiophen-2-yl)-2,2'-bipyridine

n-Butyllithium (6.94 mmol) was slowly added dropwise to a solution of 5-octylthieno[3,2-*b*]thiophene (5.94 mmol) in anhydrous THF at −78 °C under Ar. The mixture was stirred at this temperature for 30 min and then for 1.5 h at room temperature followed, after cooling to −78 °C, by the addition of tributylstannyl chloride (7.52 mmol). After stirring for 4 h at room temperature, the reaction was terminated by adding a saturated NH_4Cl aqueous solution. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After the removal of solvent, the crude tributyl(5-octylthieno[3,2-*b*]thiophen-2-yl)stannane (5.2 mmol) was mixed with 4,4'-dibromo-2,2'-bipyridine (1.72 mmol) in 150 mL DMF. The catalyst $Pd(PPh_3)_2Cl_2$ (0.08 mmol) was added to the solution and the mixture was heated at 85 °C under Ar overnight. After the removal of DMF, the resulting solid was purified by column chromatography on silica gel using $CHCl_3$ as eluent to afford an ivory white solid. Yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 8.73 (s, 2H), 8.67 (d, 2H), 7.84 (s, 2H), 7.52 (d, 2H), 6.99 (s, 2H), 2.90 (t, 4H), 1.76–1.72 (m, 4H), 1.41–1.28 (m, 20H), 0.89 (t, 6H). MS (EI) *m/z* calcd. for $C_{38}H_{44}N_2S_4$: 657.03. Found: 657.24.

3. Synthesis of C104

Dichloro(*p*-cymene)ruthenium(II) dimer (0.32 mmol) and 4,4'-bis(5-octylthieno[3,2-*b*]thiophen-2-yl)-2,2'-bipyridine (0.64 mmol) were dissolved in DMF. The reaction mixture was heated with stirring at 80 °C for 4 h under argon in the dark. Subsequently, 4,4'-dicarboxylic acid-2,2'-bipyridine (0.64 mmol) was added into the flask and the reaction mixture was heated to 140 °C for 4 h. In excess of NH_4NCS (26.50 mmol) was added to the resulting dark solution and the stirring continued for another 4 h at the same temperature. Then, the reaction mixture was cooled down to room temperature and the solvent was removed on a rotary evaporator under vacuum. Water was added to get the precipitate. The solid was collected on a sintered glass crucible by suction filtration, washed with water and Et_2O, and dried under vacuum. The crude complex was dissolved in basic methanol (NaOH) and purified on a Sephadex LH-20 column with methanol as eluent. The collected main band was concentrated and slowly dropped with an acidic methanol solution (HNO_3) to pH 5.5. The precipitate was collected on a sintered glass crucible by suction filtration and dried. Yield: 62%. ^{1}H NMR (200 MHz, CD_3OD+NaOD, δ_H): 9.65 (d, 1H), 9.10 (d, 1H), 9.00 (s, 1H), 8.85 (s, 1H), 8.40 (s, 1H), 8.30 (d, 1H), 8.25 (s, 2H), 8.10 (s, 1H), 7.85 (d,1H), 7.60 (d, 1H), 7.30 (d, 1H), 7.20 (s, 2H), 7.10 (d,1H), 6.85 (d,1H), 3.05 (t, 2H), 2.95 (t, 2H), 1.80 (m, 4H), 1.40 (m, 20H), 0.95 (m, 6H). Anal. Calcd for $NaRu_2C_{104}H_{103}N_{12}O_8S_{12}\cdot 4H_2O$: C, 53.59; H, 4.80; N, 7.21%. Found: C, 53.65; H, 5.11; N, 7.15%.

4. Calculation

We optimized the geometrical structure of C104 with density functional theory (DFT) employing the Gaussian03 program package, with B3LYP/3-21G* functional and basis set. By using the same method, we further carried out time dependent density functional theory (TDDFT) calculation in combination with the Polarizable Continuum Model (PCM) for the solvent effect of acetonitrile.

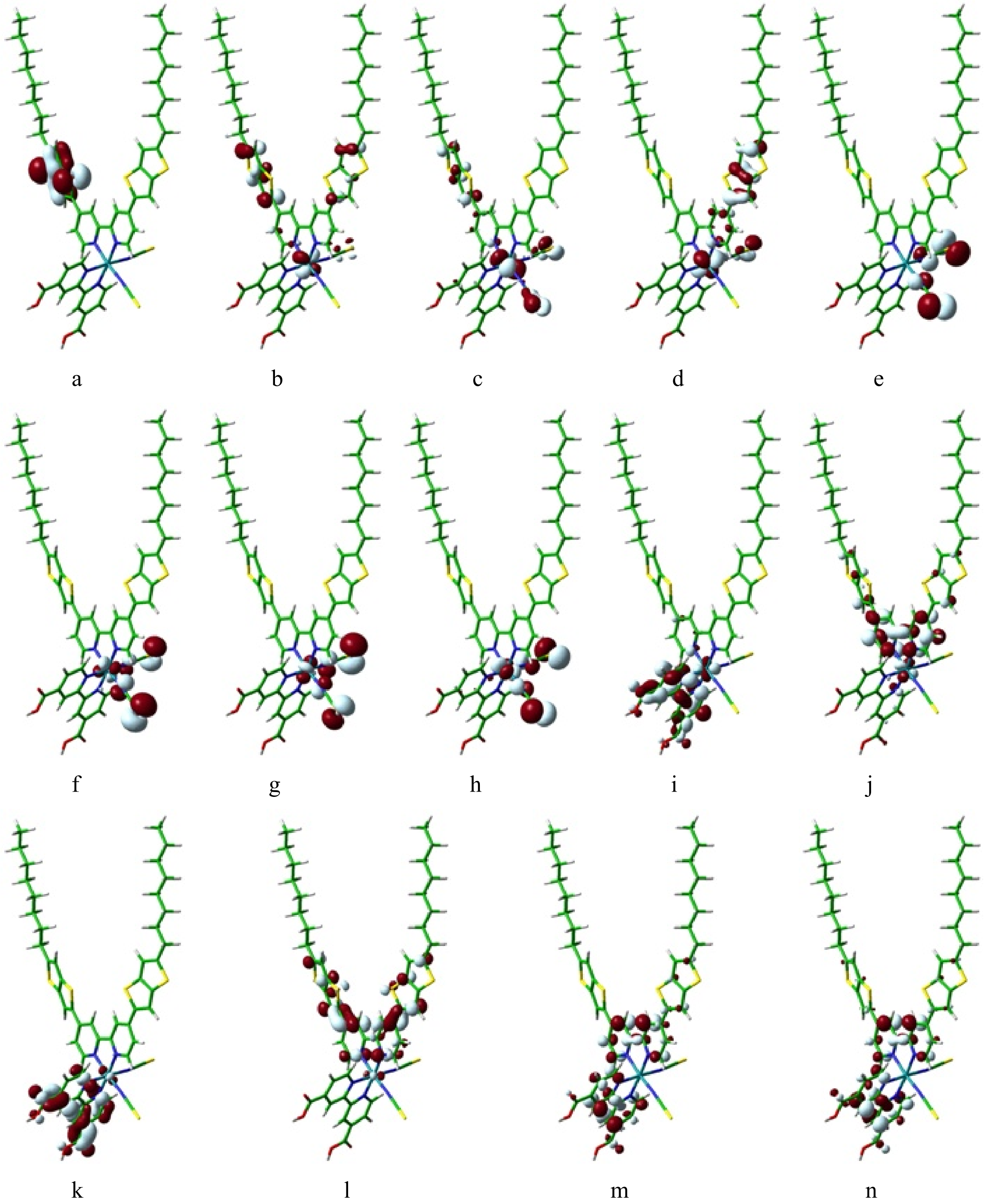

Fig. S1 Calculated molecular orbitals of the C104 sensitizer. *a*) HOMO-10; *b*) HOMO–8; *c*) HOMO–5; *d*) HOMO–4; *e*) HOMO–3; *f*) HOMO–2; *g*) HOMO–1; *h*) HOMO; *i*) LUMO; *j*) LUMO+1; *k*) LUMO+2; *l*) LUMO+3; *m*) LUMO+4; *n*) LUMO+5.

Table 1 Properties of electronic transitions with the relative oscillator strengths larger than 0.05.

Transition energy/nm	Oscillator strength	Excitation assignment
624.7	0.0582	HOMO→LUMO+1 (85%)
577.1	0.1356	HOMO–2→LUMO (71%) HOMO–1→LUMO+1 (9%) HOMO→LUMO+2 (8%)
530.9	0.1387	HOMO–1→ LUMO+1 (50%) HOMO–2→ LUMO+1 (22%) HOMO→ LUMO+2 (12%) HOMO→ LUMO+1 (5%)
491.2	0.0878	HOMO→LUMO+2 (68%) HOMO→LUMO+3 (6%) HOMO–2→LUMO (5%)
459.6	0.1161	HOMO→ LUMO+3 (55%) HOMO–2→ LUMO+2 (11%) HOMO–1→ LUMO+2 (10%) HOMO–3→ LUMO (7%)
444.9	0.0652	HOMO →LUMO+4 (55%) HOMO–2→LUMO+2 (39%)
426.7	0.1484	HOMO–1→ LUMO+3 (87%)
416.3	0.0757	HOMO–2→LUMO+3 (51%) HOMO–3→LUMO+1 (36%)
404.9	0.2834	HOMO–4→LUMO+1 (84%)
396.6	0.2240	HOMO–5→ LUMO+1 (78%) HOMO–8→ LUMO (8%) HOMO–3→ LUMO+1 (5%)
391.0	0.0590	HOMO–1→LUMO+5 (83%) HOMO–8→LUMO (12%)
349.7	0.0830	HOMO–5→LUMO+2 (49%) HOMO–3→LUMO+3 (22%) HOMO–3→LUMO+2 (11%)
348.0	0.1081	HOMO–3→ LUMO+3 (55%) HOMO–5→ LUMO+2 (19%) HOMO–4→ LUMO+3 (13%)
341.8	0.3794	HOMO–4→ LUMO+3 (41%) HOMO–5→ LUMO+3 (33%) HOMO–3→ LUMO+3 (6%)
335.4	0.3360	HOMO–5→ LUMO+3 (46%) HOMO–4→ LUMO+3 (17%)
334.3	0.0989	HOMO–3→LUMO+4 (66%) HOMO–5→LUMO+4 (11%) HOMO–10→LUMO+1 (6%)
327.3	0.1107	HOMO–4→ LUMO+4 (57%)

		HOMO–4→ LUMO+5 (17%) HOMO–3→ LUMO+5 (10%)
325.5	0.1236	HOMO–5→ LUMO+4 (39%) HOMO–3→ LUMO+5 (36%) HOMO–4→ LUMO+5 (7%) HOMO–4→ LUMO+4 (6%)
312.6	0.0677	HOMO–5→LUMO+5 (74%) HOMO–5→LUMO+4 (9%)