Highly Improved Photocurrents of Dye-Sensitized Solar Cells containing Ultrathin 3D Inverse Opal Electrodes sensitized with a Dithienothiophene-based Organic dye

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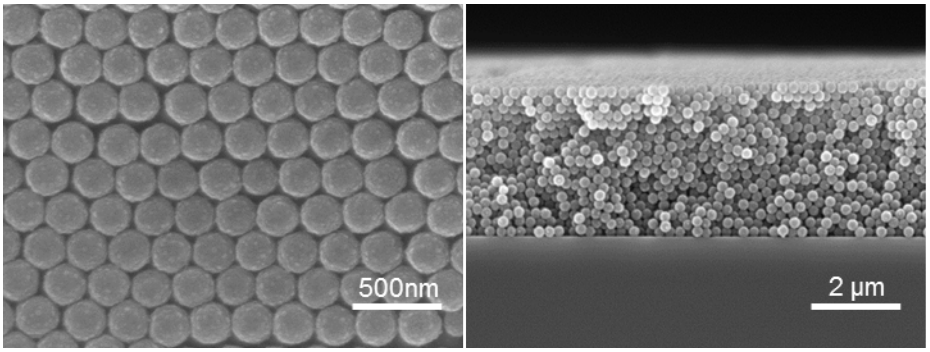

Figure S1. Surface and cross-section SEM image of PS opals

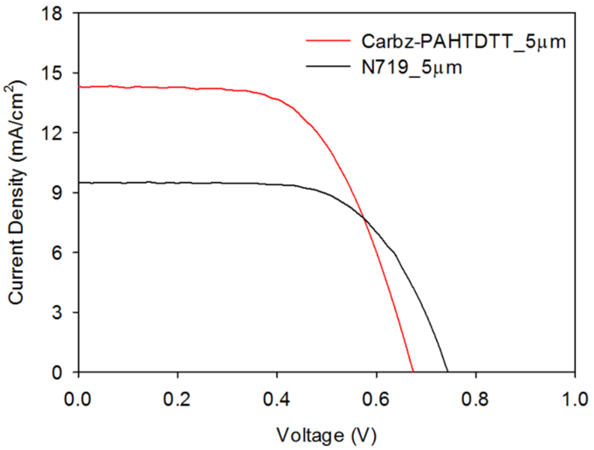

Figure S2. Photocurrent density-Voltage (*J-V*) curves for DSCs sensitized using Carbz-PAHTDTT and N719 dyes.

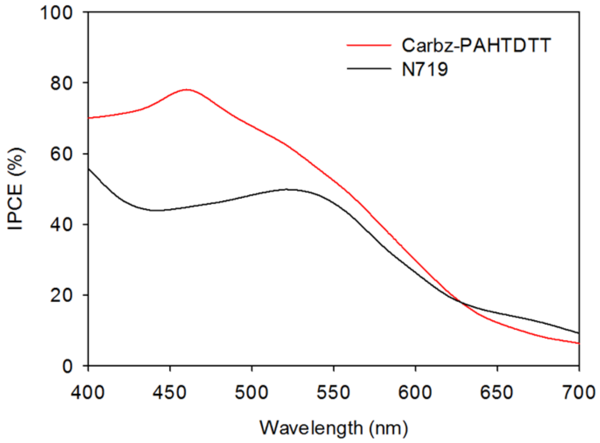

Figure S3. IPCE spectra of DSCs prepared using Carbz-PAHTDTT and N719 dyes. The IPCE peak values for the DSCs prepared with Carbz-PAHTDTT and N719 dye were 80% at 460 nm and 52% at 520 nm, respectively. Thus, the maximum IPCE wavelength corresponded to the wavelength of the maximum absorbance.

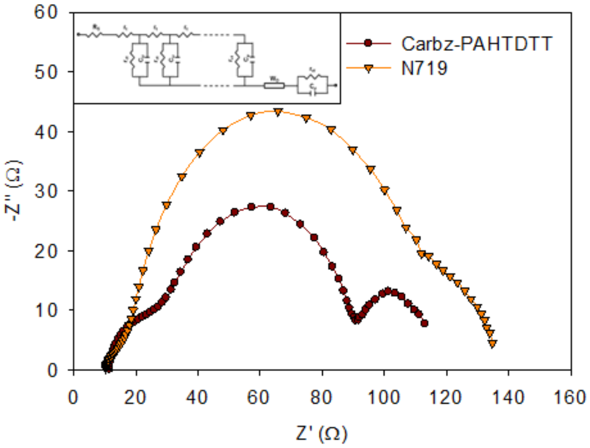

Figure S4. Nyquist plot of the EIS measurement for the DSCs sensitized with Carbz-PAHTDTT or N719 dyes. The resistances for various interfaces within the DSCs were estimated by fitting with an equivalent circuit (inset). The electron collection efficiency can then be calculated from the following equation: $\eta_{cc} = 1- (r_t/r_{ct})L^2$ The η_{cc} was 95.9% for the Carbz-PHATDTT TiO_2 IO electrode and 97.5% for N719 IO TiO_2 electrode.

Synthesis of Carbz-PAHTDTT

The synthesis of triphenylamine (TPA): The synthesis of TPA was previously reported by A. Kelkar et al.[2] 4 mmol of arylhalide, 0.08 mmol of CuI and potassium tert-butoxide were added in toluene (20 mL). The solution was stirred and heated at 115 ^{o}C for 3.5 h. After cooling to temperature, the reaction solution was filtered to remove the precipitated potassium tert-butoxide and washed with toluene. The products were concentrated and purified by column chromatography with silica gel using hexane and CH_2Cl_2 as eluent to yield to give TPA.

The synthesis of 4-formytriphenylamine (S2): The synthesis of S2 was previously reported by Lai et el.[3] To mixture of 12.23 mmol of Ph_3N and dimethylformaldehyde (DMF, 40 mL) at 0 ^{o}C was added 12.87 mmol of $POCl_3$ dropwisely with stirring. The mixture was stirred at 95 ^{o}C under nitrogen for 20 hr. The mixture was poured into ice-water and neutralized with 4 M NaOH solution. The solution was concentrated and purified by column chromatography with silica gel using hexane and CH_2Cl_2 as eluent to give the S2.

The synthesis of {4-[bis(4-iodophenyl)amino]benz}-aldehyde (S3) and {4-[bis(4-carbazol-9--yl-phenyl)amino]phenyl}-aldehyde (S4) were previously reported by Z. Ning et al.

Synthesis of 4-(bis(4-iodophenyl)amino)benz-aldehyde (S3): 18.2 mmol of S2 (4.96 g), 24.6 mol of potassium iodide and, acetic acid (60 mL), and water (6 ml) was stirred in one reactor. The 18.2 mmol potassium iodate was added in the mixture and was stirred for 12 h at 80 ^{o}C. After reaction finished and then, the acetic acid was removed by rotary evaporation. The black residue was dissolved in ethyl acetate and washed with water and sodium bicarbonate repeatedly. The organic layer was dried over $MgSO_4$, and concentrated to give yellow solid (S3).

Synthesis of {4-[bis(4-carbazol-9-yl-phenyl)amino]phenyl}-aldehyde (S4): 18.7 mmol of diphenylamine (3.15 g), 4.6 mmol of copper powder (0.30 g), 0.05 mol potassium carbonate (6.93 g), and 1.25 mmol 18-crown-6 (0.33 g) in 1,2-dichlorobenzene (40 mL) were heated to reflux. 12.5 mmol of S3 (4.98 g) in 1,2-dichlorobenzene (10 mL) was added slowly and the mixture was heated to react at 190 °C for 24 h. After the inorganic components were filtered off while hot, the product was precipitated into methanol and purified by column chromatography with silica gel using hexane and CH_2Cl_2 as eluent to yield 3.5 g of a yellow solid.

The synthesis of {4-[bis(4-carbazol-9-yl-phenyl)amino]phenyl}methanol (S5), {4-[bis(4--carbazol-9-yl-phenyl)amino]benzyl}triphenylphosphonium bromide (S6), 5-{6[5(2{4[bis(4--carbazol-9-yl-phenyl)amino]phenyl}vinyl)3-hexyl-thien-2-yl]dithieno[3,2-b;2',3'-d]thiophen--2-

yl}4-hexyl-thien-2-carbaldehyde (S8), 3-(5{6[5(2{4[bis(4-carbazol-9-yl-phenyl)amino]-phenyl}vinyl)3-hexyl-thien-2yl]dithieno[3,2-b;2',3'-d]thiophen-2-yl}4-hexyl-thien-2-yl)2--cyano-acrylic acid (Carbz-PAHTDTT) were previously reported by Daeneke et al.[1]

The synthesis of {4-[bis(4-carbazol-9-yl-phenyl)amino]phenyl}methanol (S5): 3.6 mmol of $NaBH_4$ (136 mg) was added in dry dichloromethane (30 mL) and anhydrous ethanol (10 mL), the S4 was added rapidly, and was stirred at room temperature for 2 h. The solution was added into water (50 mL) with vigorous stirring and the aqueous layer was extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and solvent was removed to give the pale yellow solid by rotary evaporated and was concentrated to give pale yellow solid.

The synthesis of The {4-[bis(4-carbazol-9-yl-phenyl)amino]benzyl}triphenylphosphonium bromide (S6): 2.5 mmol of S5 (1.5 g) and 2.7 mmol of PPh_3.HBr (0.93 g) was dissolved in chloroform (20 mL) and the mixture was heated to reflux for 3 h. After solvent was evaporated, the residue was triturated with hexane and CH_2Cl_2 and filter to yield 2.2 g of pale yellow solid.

The synthesis of 5-{6[5(2{4[bis(4-carbazol-9-yl-phenyl)amino]phenyl}vinyl)3-hexyl-thien--2-yl]dithieno[3,2-b;2',3'-d]thiophen-2-yl}4-hexyl-thien-2-carbaldehyde (S8): 0.50 mmol of 5,5'-(dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl)bis(4-hexylthiophene-2-carbaldehyde) (S7, 292 mg) and 1 mmol of anhydrous K_2CO_3 (138 mg), 0.025 mmol of 18-crown-6 (7 mg) in DMF (10 mL) at 70 ^oC. The solution was added in a DMF (10 mL) solution of 0.05 mmol S6 (465 mg) dropwisely over 3 h and then, the mixture was stirred for 3 h at 70 ^oC. The residue was extracted with CH_2Cl_2. The organic layers were washed with water and brine solution. The organic layer was dried over $MgSO_4$, and purified by column chromatography on silica gel eluting with hexane/dichloromethane (v/v 4:1 to 1/4) to give the 241 mg of S8 as red solid.

The synthesis of 3-(5{6[5(2{4[bis(4-carbazol-9-yl-phenyl)amino]phenyl}vinyl)3-hexyl--thien-2yl]dithieno[3,2-b;2',3'-d]thiophen-2-yl}4-hexyl-thien-2-yl)2-cyano-acrylic acid (Carbz-PAHTDTT): A solution of the 0.14 mmol of S8 (70 mg) in a mixture of acetonitrile (10 mL) and chloroform (10 mL) with an excess of 1.2 mmol of cyanoacetic acid (102 mg) and piperidine (0.1 mL) extracted with CH_2Cl_2. The organic extracts were washed with 1 M HCl, water, and brine solution. The organic layer was dried over $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography on silica gel eluting with dichloromethane / methanol / acetic acid (volume proportions, 10/1/0 to 10/1/0.1) to give the Carbz-PAHTDTT as dark solid.

The dye-adsorbed films were washed in anhydrous ethanol to remove the physically attached dye. The counter electrodes were prepared by dropping a 0.7 mM H_2PtCl_6 ethanol solution onto the FTO substrate, followed by annealing for 20 min at 450 °C. The TiO_2 electrode and counter electrode were assembled using a 60 µm polymer spacer (Surlyn, DuPont). The electrolyte was introduced between the TiO_2 electrode and the counter electrode. The electrolyte contained 25 mM LiI (Aldrich), 55 mM I_2 (Yakuri), 0.6 M dimethyl-propyl imidazole iodide (DMPII, Solaronix), and guanidinium thiocyanate (GuSCN) in a 8.5:1.5 (v/v) mixture of acetonitrile (Aldrich) and valeronitrile (Aldrich).

Reference

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2. A. A. Kelkar, N. M. Patil and R. V. Chaudhari, Tetrahedron Lett, 2002, **43**, 7143-7146.
3. G. F. Lai, X. R. Bu, J. Santos and E. A. Mintz, Synlett, 1997, 1275-1276.