

Supporting Information

A Dendrons Modified Ruthenium Complex: Enhanced Open Circuit Voltage in Dye-Sensitized Solar Cells

Jing Xu, Hongwei Wu, Xinru Jia,* and Dechun Zou

Beijing National Laboratory for Molecular Sciences and Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing, China.

Materials

The $[\text{RuCl}_2(\text{p-cymene})]_2$, 4, 4'-dicarboxylic acid-2, 2'-bipyridine (dcbpy), NH_4NCS were purchased from Alfa Aesar and used as received. The BuG1 and DG1 were prepared according to the previous reference¹. The Z907 ($\text{RuLL}'(\text{NCS})_2$, L=4, 4'-dicarboxylic acid-2, 2'-bipyridine, L'=4, 4'-dinonyl-2, 2'-bipyridine) was obtained from Shanghai Materwin Technology Limited Company. The sephadex LH-20 filler was purchased from H&E Co., Ltd., Beijing, China.

The lithium perchlorate (LiClO_4 , 99%), 4-*tert*-butylpyridine (TBP) were purchased from Aldrich. The CH_3CN (AN) was purchased from Siyou Inc., Tianjin, China. The I_2 (AR) was purchased from the Beijing Chemical Reagent Company. The FTO, TiO_2 paste (DHS-TPP3, diameter: 20nm), 1-butyl-3-methylimidazolium iodide (BMII) were purchased from Heptachroma Inc., Dalian, China. The $\text{Co}(\text{phen})_3(\text{PF}_6)_2$ and $\text{Co}(\text{phen})_3(\text{PF}_6)_3$ were obtained as the previous literature.²

Synthesis and characterization

The synthetic procedures of the ligand Dcbpy-BuG1 and the dye sensitizer RG1 were displayed in Scheme S1. The detailed processes were described as follows.

Synthesis of the ligand Dcbpy-BuG1

(1) Synthesis of 4, 4'-dicarbonyl dichloride-2, 2'-bipyridine (Dcbpy-Cl)³

Compound 4, 4'-dicarboxylic acid-2, 2'-bipyridine (dcbpy) (528.5 mg, 2.166 mmol) was added into 30 mL thionyl chloride (SOCl_2). The mixture was stirred and refluxed until the solution became transparent. Then excess thionyl chloride was evaporated under vacuum and the obtained product Dcbpy-Cl was kept for the next step.

(2) Synthesis of the ligand Dcbpy-BuG1³

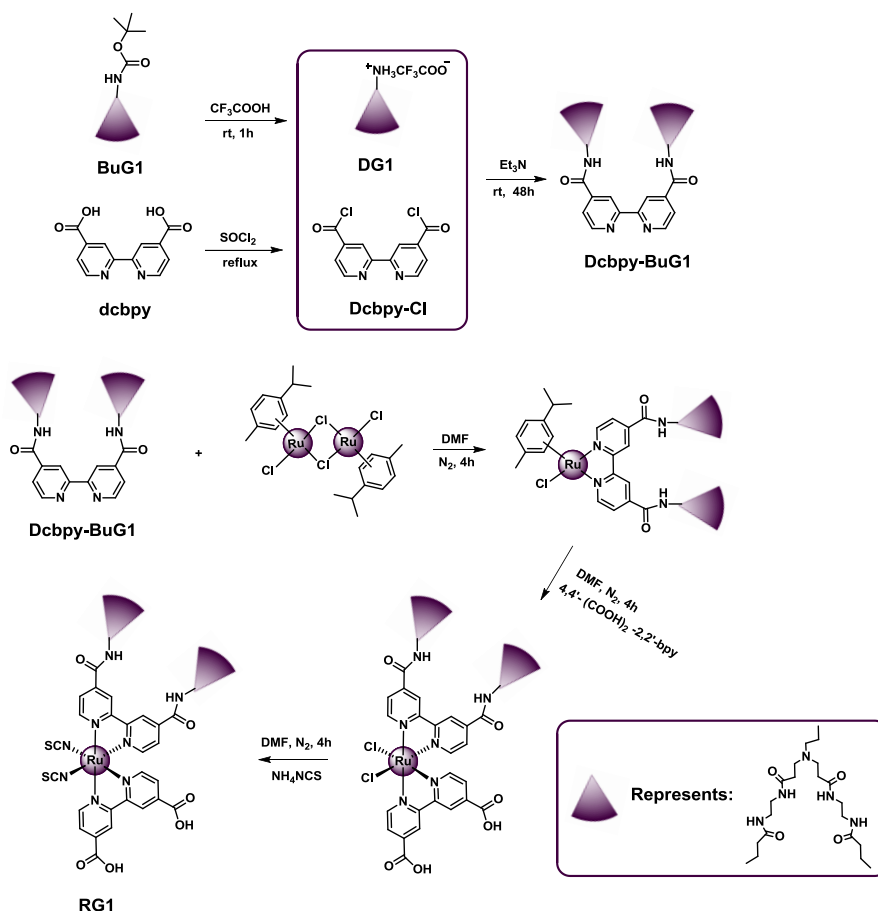
BuG1 and DG1 were prepared in accordance to the previous reference¹. DG1 (3.17 g, 5.848 mmol) and triethylamine (3.4 mL, 23.92 mmol) was dissolved into 30mL anhydrous CH₂Cl₂. Then a CH₂Cl₂ solution of the above prepared Dcbpy-Cl was dropwise added into the mixture solution under the ice-salt bath condition. After, the solution was stirred and reacted 48 h at room temperature. The generated precipitate was filtrated and washed with CH₂Cl₂. The crude product was purified by precipitation in THF and a silica column with CHCl₃ / MeOH (2:1) as the eluant to afford Dcbpy-BuG1 (1.61 g, yield: 70%).

¹H NMR (300 MHz, DMSO, ppm): δ = 8.86-8.84 (d, 2H), 8.79 (s, 2H), 7.95 (br, 3H), 7.87-7.84 (m, 2H), 7.80 (br, 4H), 3.38 (m, 4H), 3.04 (m, 16H), 2.72-2.68 (t, 8H), 2.59 (t, 4H), 2.24-2.19 (t, 8H), 2.03-1.98 (t, 8H), 1.51-1.44 (m, 8H), 0.84-0.79 (t, 12H). ESI MS: calcd for C₅₂H₈₄N₁₄O₁₀, 1064; found, 1065 (M+H)⁺, 1087 (M+Na)⁺.

Synthesis of Ru[(dcbpy)(Dcbpy-BuG1)(NCS)₂] (RG1)

The synthesis of RG1 employed reliable one-pot assembly protocol^{4, 5}. [RuCl₂(p-cymene)]₂ (57.5 mg, 0.094 mmol) and Dcbpy-BuG1 (200 mg, 0.188 mmol) was dissolved in 40 mL anhydrous DMF. Under the protection of N₂, the solution was stirred at 90 °C for 4 h in the dark condition. Then, 4, 4'-dicarboxylic acid-2, 2'-bipyridine (dcbpy) (45.9 mg, 0.188 mmol) was added into the reaction solution. The reaction was continued at 160 °C for 4 h. After that, excess NH₄NCS (570 mg, 7.52 mmol) was added and the reaction mixture was stirred at 140 °C for another 4 h. After the solution cooling, DMF was evaporated under vacuum. The crude product was precipitated in acetone three times and then purified by sephedex LH-20 column with methanol as eluant to afford RG1(30 mg, yied: 10.5%).

¹H NMR (300 MHz, CD₃OD, ppm): δ = 9.56-9.55 (d, 1H), 9.45-9.44 (d, 1H), 9.02 (br, 2H), 8.84 (m, 2H), 8.26 (m, 2H), 7.78-7.76 (d, 1H), 7.61-7.59 (d, 1H), 7.55 (d, 1H), 7.45 (d, 1H), 3.67-3.52 (d, 4H), 3.26-3.16 (d, 16H), 2.95-2.76 (m, 12H), 2.48-2.39 (d, 8H), 2.16-2.08 (dt, 8H), 1.61-1.52 (dt, 8H), 0.91-0.84 (m, 12H). FTIR (KBr, cm⁻¹): 3418 (br), 3299 (br), 3081, 2962, 2928, 2873, 2111, 1649, 1544, 1467, 1432, 1375, 1326, 1236, 1129, 1022, 789, 764, 702, 668. ESI MS: calcd for C₆₆H₉₂N₁₈O₁₄RuS₂, 1526; Found, 1527(M+H)⁺, 1549(M+Na)⁺.



Scheme S1. The synthetic procedures of the ligand Dcbpy-BuG1 and the dye RG1.

Preparation of TiO₂ electrodes and the fabrication of DSSCs⁶

Photoanodes were prepared by making TiO₂ (DHS-TPP3, diameter: 20 nm) on FTO glass through screen-printing. After completing one screen-printing, the thickness of TiO₂ film was about 3.5 μm. The TiO₂ electrodes were sintered at 150 °C for 15 min, and then at 450 °C for 30 min. The above operation was repeated three times and the final thickness of TiO₂ film came up to 10.5 μm. After finished the last heating, the photoanodes (test area: ca. 0.254 cm²) were cooled to 100 °C and then immersed into the RG1 and Z907 methanol solution (Concentration: 3×10⁻⁴ M) respectively at room temperature for 24 h. For co-sensitized devices, the TiO₂ electrodes were fostered in Z907 methanol solution (Concentration: 3×10⁻⁴ M) for 12 h at first, and then immersed into the mixture of RG1 and Z907 (1:1) methanol solution (Concentration: 3×10⁻⁴ M) for another 12 h. The dye sensitized electrodes were rinsed with ethanol and used for photovoltaic measurement.

Counter electrodes employed an approximately 50 nm Pt film on the FTO glass by magnetic sputtering. DSSCs were fabricated by assembling dye-sensitized electrode and counter electrode to form a sandwich-type cell, the middle of which was separated by a 25 μm thick hot-melt ionomer film (Surlyn, Dupont). Solar cells were filled with electrolytes through the preset pore in

the hot-melt ionomer film and finally were sealed by Surlyn .

Four different electrolytes were used and the compositions of them were as follows. Electrolyte A contained 0.05 M iodine, 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M lithium perchlorate (LiClO_4), 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile. Electrolyte B has the same compositions with Electrolyte A except TBP. Electrolyte C was the acetonitrile solution of 0.2 M $\text{Co}(\text{phen})_3(\text{PF}_6)_2$, 0.2 M $\text{Co}(\text{phen})_3(\text{PF}_6)_3$, 0.05 M lithium perchlorate (LiClO_4), 0.5 M 4-*tert*-butylpyridine (TBP). Electrolyte D has the same compositions with Electrolyte C except TBP.

Methods and measurement

^1H NMR spectra were measured on 300 MHz (Varian mercury) spectrometers at room temperature, with $\text{DMSO-}d_6$ or $\text{CD}_3\text{OD-}d_4$ as the solvents. The electrospray ionization mass spectra (ESI-MS) were measured by an APEX IV Fourier transform ion cyclotron resonance mass spectrometer (Bruker). UV-Vis absorption spectra were scanned at a lambda 35 UV/Vis Spectrometer (Perkin Elmer). The MM2 computed structures were obtained using software ChemBio3D Ultra 12.0. FTIR spectra were obtained using a VECTOR 22 Fourier transform IR spectrometer (Bruker). Differential scanning calorimetry (DSC) measurements were carried out on TA Instruments DSC Q100 with a scan rate of 10 °C/min.

The performance of all solar cells was measured under AM1.5 simulated sunlight illumination. The simulated sunlight source was YSS-50A (Yamashita DESO). The intensity of simulated sunlight was 100 mw cm^{-2} . The electrochemical impedance spectra were obtained on the Autolab (The frequency range is from 100 kHz to 10 mHz). The chemical capacitance (C_μ), recombination resistance (R_{rec}) and electron lifetime (τ) were obtained upon fitting the electrochemical impedance spectra with the Z-view software according to an appropriate equivalent circuit.

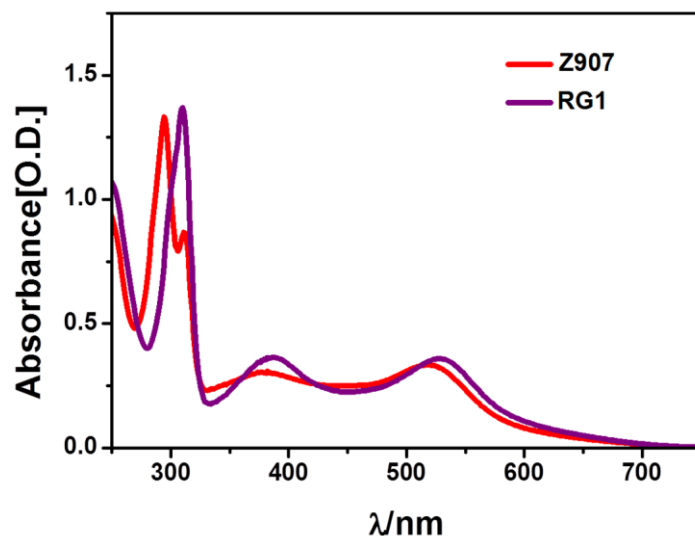


Figure S1. The UV-Vis absorption spectra of RG1 and Z907 in methanol solution (Concentration: $3 \times 10^{-5} \text{M}$).

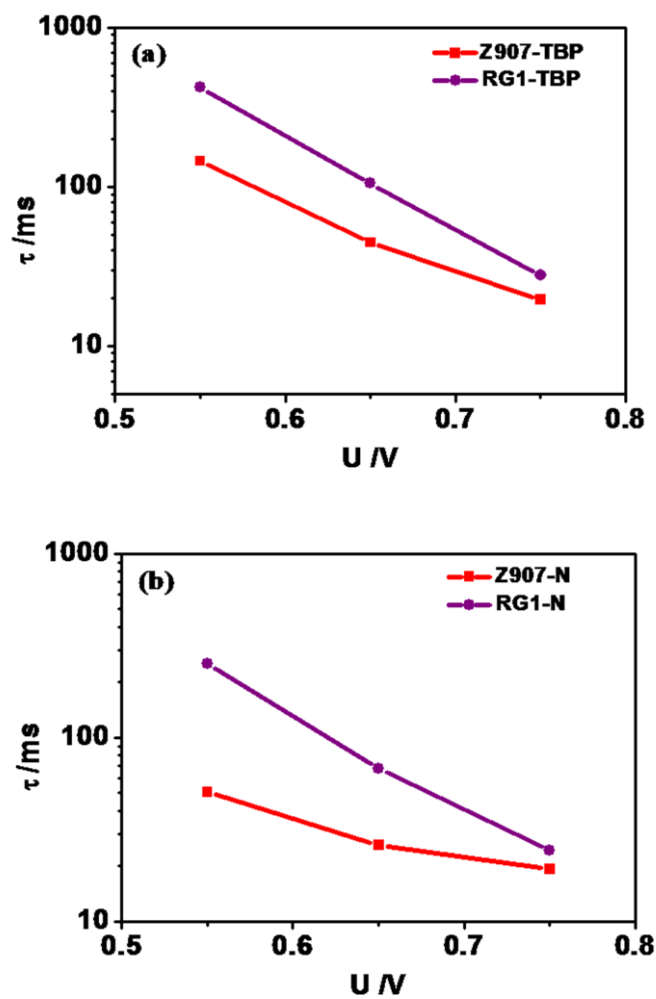


Figure S2. The electron lifetime plots of RG1 and Z907 devices using I_3^-/I^- as the electrolyte (a) with and (b) without TBP under different reverse bias in the dark condition.

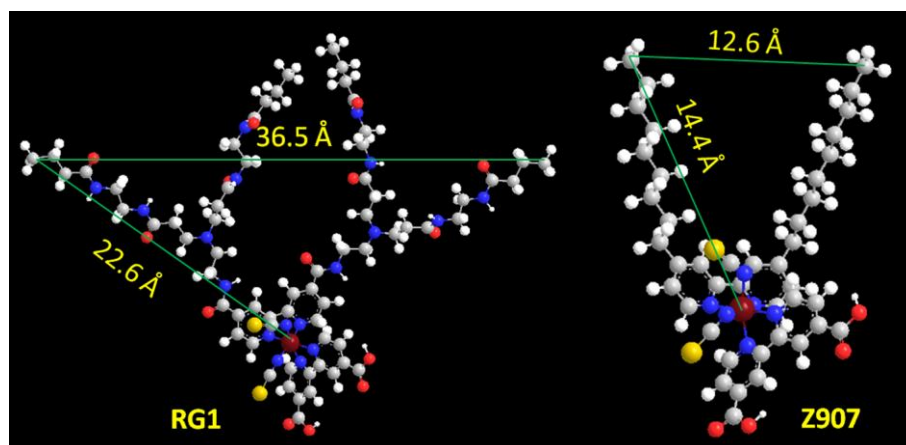


Figure S3. MM2 computed structures of RG1 and Z907 in Ball and Stick Type.

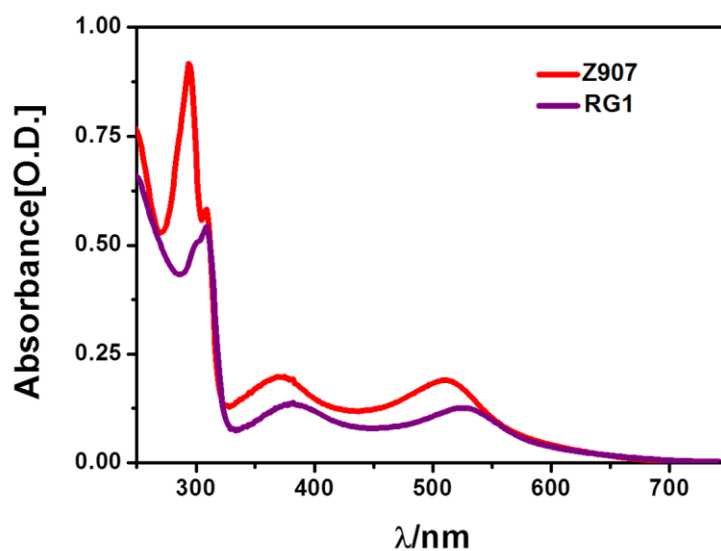


Figure S4. The UV-Vis absorption spectra of the desorption solution of RG1 and Z907 coated photoanodes.

RG1 and Z907 coated photoanodes were immersed and desorbed in 4ml NaOH/methanol solution (Concentration: 0.1 M). We calculated the loading amount of dyes in mesoporous TiO₂ based on λ_{\max} and the molar extinction coefficient of RG1 and Z907, as a result, the adsorption amount of RG1 (0.67×10^{17} molecules cm⁻²) was 63% relative to that of Z907 (1.07×10^{17} molecules cm⁻²).

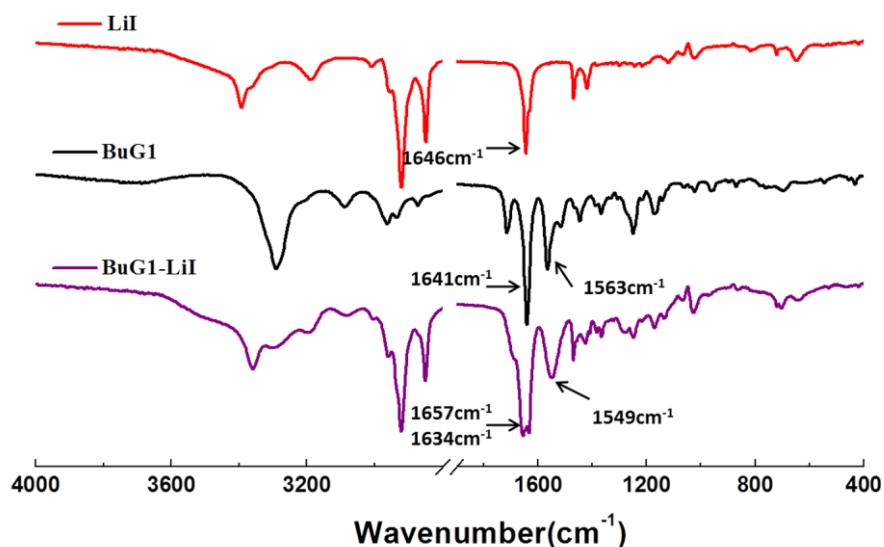


Figure S5. The FT-IR spectra of LiI, BuG1, and BuG1 with LiI (5:1).

The peaks at 1641cm^{-1} $\nu(\text{C}=\text{O})$ and 1563cm^{-1} $\delta(\text{N}-\text{H})$ corresponding to amide groups were splitted and red shifted respectively after adding LiI in the system, demonstrating the interactions of amide groups in PAMAM dendrons with lithium ($\text{C}=\text{O}\cdots\text{Li}^+$)⁸ and iodide ($\text{NH}\cdots\text{I}^-$) ions.

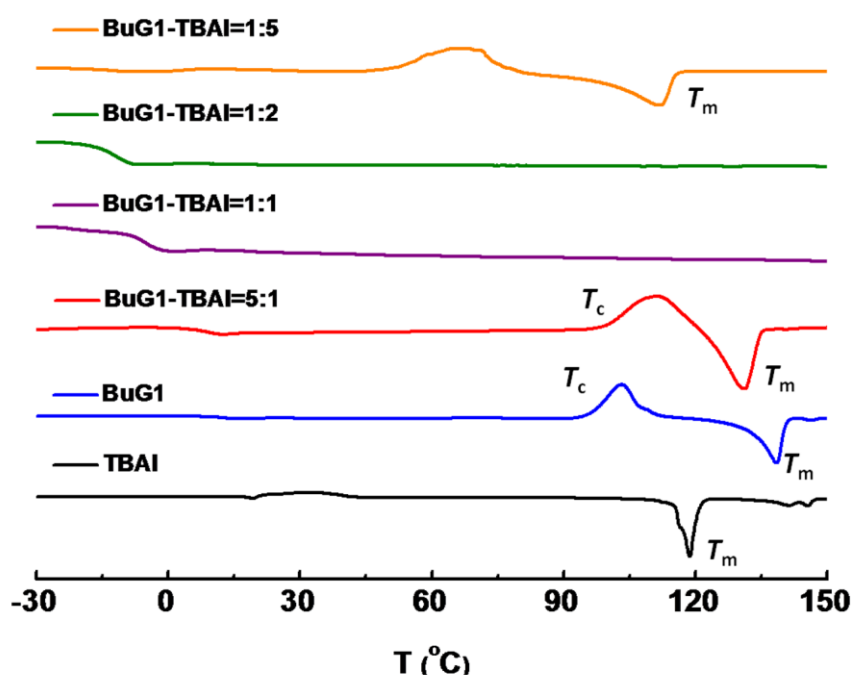


Figure S6. DSC curves of tetrabutylammonium iodide (TBAI), BuG1 and mixtures of the two in different molar ratios.

As shown in Figure S6, BuG1 and TBAI exhibit clear T_m in DSC curves. For mixed samples with either component in a large excess (BuG1: TBAI = 5:1 or 1:5), T_m s broaden and shift to lower temperature. When the ratio of the two components is 1:1 or 1:2, T_m s are depressed and only glass transition can be observed. This indicates the existence of non-covalent interaction between

iodide ions and amide groups in dendrons and the formation of homogeneous complexes at the ratio of 1:1 and 1:2.^{7,8}

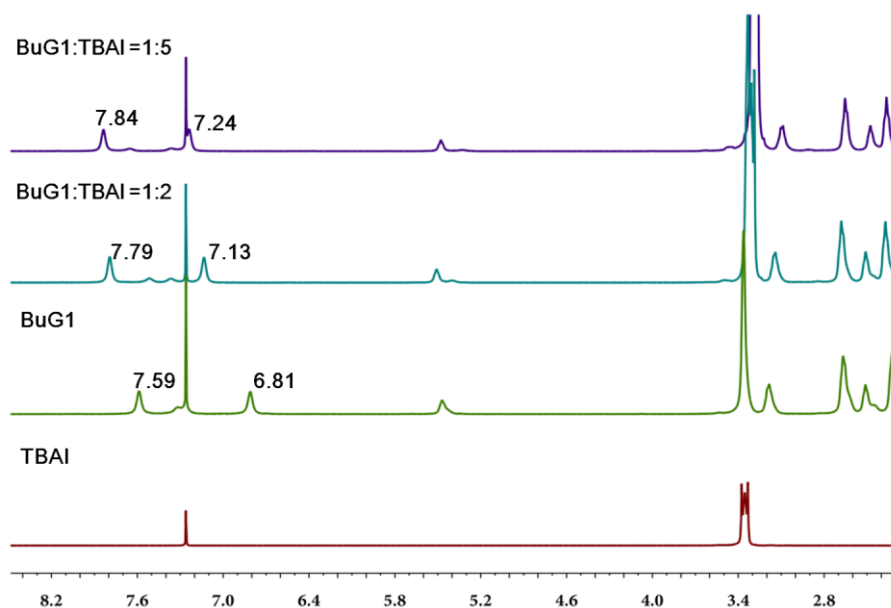


Figure S7. ^1H NMR spectra of TBAI, BuG1 and mixtures of the two in different molar ratios (Solvent: CDCl_3).

The signals at 6.81 and 7.59 ppm are assigned to the protons of amide groups in BuG1. When BuG1 is mixed with TBAI, these signals shift to lower field. This is ascribed to the formation of hydrogen bonds between amide groups and iodide ions,⁹ which implies and mimics the similar interaction of RG1 dye with iodide ions in the electrolyte in DSSCs.

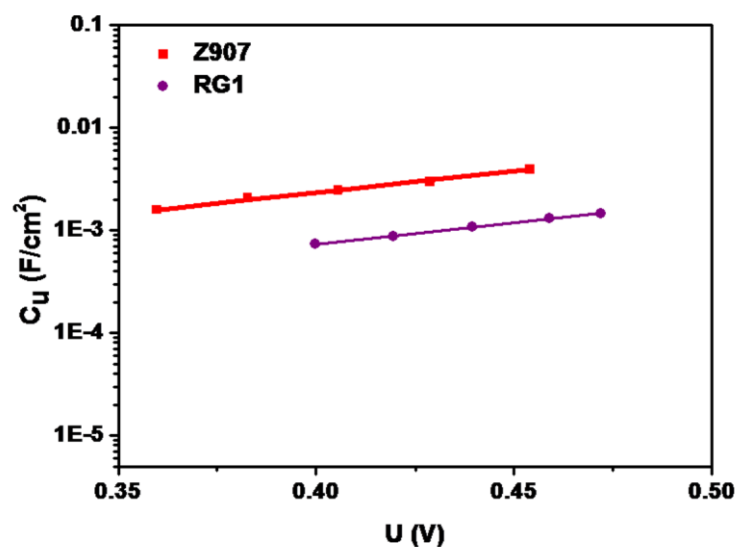


Figure S8. Chemical capacitance (C_μ) of mesoporous TiO_2 films using I^-/I_3^- as the electrolyte without TBP under different reverse bias in the dark condition.

Chemical capacitance (C_μ) is a key factor to manifest the shift of the conduction band and it is usually given by the following equation:¹⁰

$$C_{\mu} = \frac{e^2 N_t d(1-p)}{K_B T_C} \exp \left[\frac{E_{F,\text{redox}} - E_{\text{CB}}}{K_B T_C} \right] \exp \left[\frac{eV}{K_B T_C} \right] \quad (1)$$

where e is the elementary charge, N_t is the total density of surface states (taken as a constant), d is the thickness of the titania film, p is the film porosity, K_B is the Boltzmann constant, T_C is a parameter depicting the distribution profile of interband states, $E_{F,\text{redox}}$ is the chemical redox potential of the redox couples in the electrolyte, and V is the potential bias in impedance measurements. Supposing $E_{F,\text{redox}}$ as a constant, C_{μ} is determined by the potential bias (V) and E_{CB} . As shown in Figure S8, RG1 device displays lower C_{μ} than Z907 device at the same potential bias (V), indicating a positive shift of the conduction band. This can be ascribed to the fact that the interaction of dendritic branches with Li^+ and the highly packed structures of RG1 prevent the cations accessing to the TiO_2 surface, such leading to the shift of the conduction band toward vacuum level.

Reference

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