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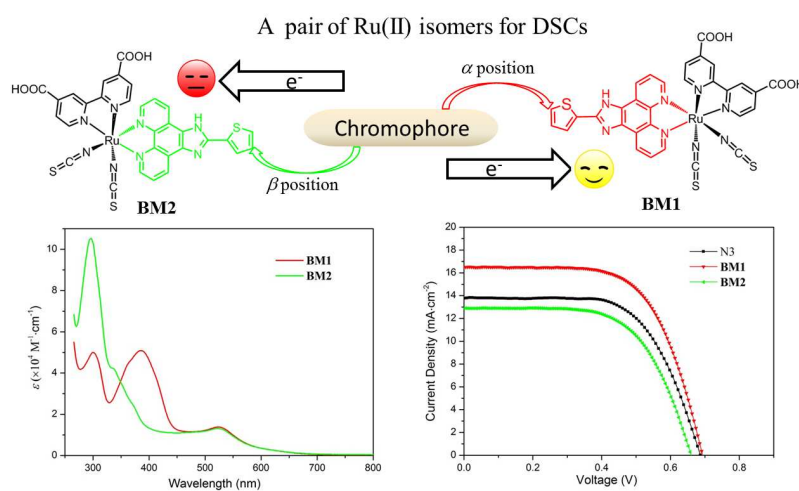
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Distinguishable photovoltaic performance on dye-sensitized solar cells by using ruthenium sensitizers with a pair of isomeric ancillary ligands

Binbin Ma, Yuxin Peng, Tao Tao and Wei Huang*

Graphic Abstract



A pair of isomeric ruthenium sensitizers **BM1** and **BM2**, having TIP based ancillary ligands with a 9-phenylcarbazole tail at α or β position of the thiophene unit, shows distinguishable photovoltaic performance on DSCs (PCEs: 7.33% and 5.33% for **BM1** and **BM2** as compared with 6.07% for standard N3-dye).

COMMUNICATION

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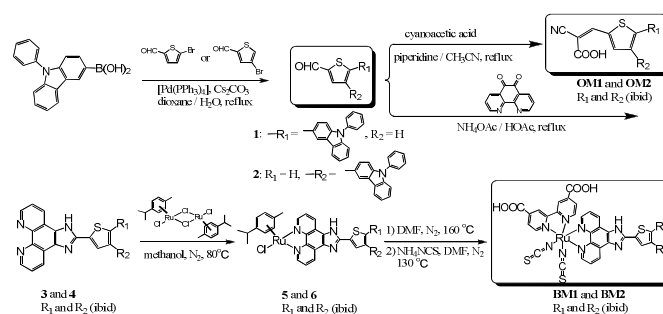
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A pair of isomeric ruthenium sensitizers BM1 and BM2, having TIP based ancillary ligands with a 9-phenylcarbazole tail at α or β position of the thiophene unit, shows distinguishable photovoltaic performance on DSCs (PCEs: 7.33% and 5.33% for BM1 and BM2 as compared with 6.07% for standard N3-dye).

Dye-sensitized solar cells (DSCs) have been extensively studied for photovoltaic applications because of their low cost and high power conversion efficiencies (PCEs) in the last two decades.¹ Since light-harvesting is the key process in the DSC device, many efforts have been devoted to increasing the absorptivity of the dyes.² Ruthenium polypyridine dyes have remarkable performance originating from their strong absorption in the visible region and long-lived charge-separated states such as N3- and N719-sensitized solar cells.³ Progress in optimizing the ruthenium based sensitizers for DSCs has been focused primarily on enhancing the light-harvesting ability and even exhibiting panchromatic light-harvesting band.⁴ Some research groups have achieved this goal by extending the conjugated lengths of the anchoring and/or ancillary ligands of ruthenium dyes,⁵ although it is still not very clear why the beneficial chromophores will improve the light-harvesting capability of complex dyes.

A few organic light-harvesting chromophores, such as thiophene and carbazole, have been employed for the synthesis of ruthenium dyes to enhance their PCEs,⁶ because they possess the common donor- π -acceptor structural arrangements and can act as the electron donors and π linkers.⁷ However, to our knowledge, there is only one report on two ruthenium dyes having bpy/thiophene/carbazole based ancillary ligands with one *tert*-C₄H₉ or *n*-C₇H₁₅ chain at 9 position of

the carbazole ring.⁸ In our previous reports, a series of 3,8 and 5,6 substituted 1,10-phenanthroline heterocyclic aromatic compounds have been synthesized and investigated on their photoresponsive properties.⁹ Herein we report the design and syntheses of two new isomeric ruthenium dyes (**BM1** and **BM2** depicted in Scheme 1) containing 2-thiophenimidazo[4,5-*f*][1,10]phenanthroline (TIP) based ancillary ligands with an electron-donating 9-phenylcarbazole tail at α or β position of the thiophene unit, where four types of heterocycles (1,10-phenanthroline, imidazole, thiophene and 9-phenylcarbazole) are incorporated into one molecule. The use of a pair of isomeric ancillary ligands **3** and **4** is to further reveal the influence of ligand conjugation on the ligand-to-metal charge-transfer by comparing their photovoltaic performance on DSCs.



Scheme 1 Synthetic route for two isomeric ruthenium sensitizers **BM1** and **BM2**, together with two organic ones **OM1** and **OM2**.

Unlike the traditional one-pot synthetic approach, a stepwise method is used to synthesize the ruthenium complexes where every intermediate is isolated and characterized including two single crystals of **1** and **2** (Fig. 1a and 1b). The reaction of [RuCl₂(*p*-cymene)]₂ with the ancillary ligands **3** and **4** in a 1:2 stoichiometry in dry methanol resulted in the formation of mononuclear Ru(II) complexes **5** and **6**. After the chromatographic column purification, DMF solution of the anchoring ligand dcby (4,4'-dicarboxylic acid-2,2'-bipyridine) was then added, together with excess ammonium thiocyanate, to produce the desired ruthenium sensitizers **BM1** and **BM2**, respectively.

State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093 (P.R. China). Fax: 86 25 8331 4502; Tel: 86 25 8368 6526; E-mail: whuang@nju.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details. CCDC reference numbers 993165-993167 for **1-3**. For ESI and crystallographic data in CIF or other electronic format See DOI:10.1039/b000000x/

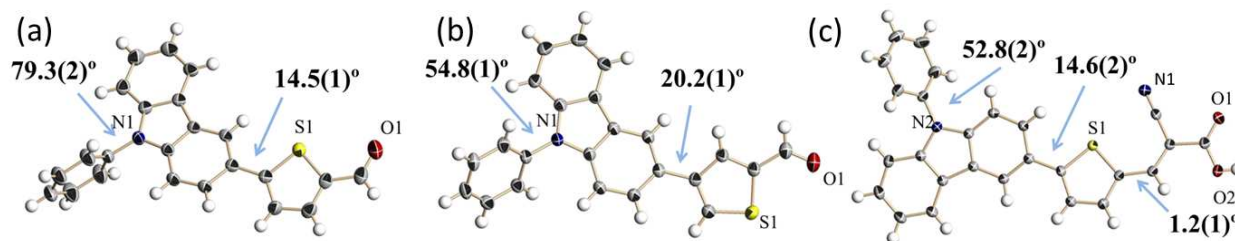


Fig. 1 ORTEP drawings of intermediates **1**, **2** and **OM1** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the protons are shown as small spheres of arbitrary radii.

Table 1 Optical, electrochemical data, and cell performance of five sensitizers.

Sensitizer	$\epsilon / \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ($\lambda_{\text{max}}/\text{nm}$) $\pi-\pi^*$, $\pi-\pi^*$ or $4d-\pi^*$, $4d-\pi^*$	E_{ox}^b of Ru ^{III/II} (V vs Fc/Fc ⁺)	E_{HOMO}^c (eV)	E_{LUMO}^c (eV)	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF ^e	η (%)
BM1	5.00 (301) ^a ; 5.09 (385); 1.38 (525)	0.30	-5.40	-3.68	16.50 ^d	0.69	64.1	7.34 ¹
BM2	10.5 (296); 4.18(338); 1.31 (525)	0.30	-5.40	-3.67	12.90	0.66	62.6	5.33
OM1	2.16 (292); 3.83 (391)	0.55	-5.65	-3.40	5.85	0.66	62.3	2.40
OM2	6.41 (300); 1.52 (339)	0.60	-5.70	-2.67	0.80	0.59	0.72	0.34
N3	4.42 (411); 1.39 (385); 1.35 (530)		-5.15 ¹²	-3.47	13.82	0.69	64.0	6.07

^a Absorption maxima. ^b The values of E_{HOMO} and E_{LUMO} were calculated with the following formula: HOMO (eV) = $E_{\text{ox}} - E_{\text{Fc/Fc}^+} + 5.1$; LUMO (eV) = HOMO - E_{g} . E_{g} is the absorption onset estimated from the electronic absorption spectra of the sensitizers; ^c The values in parentheses were calculated by integration of the IPCE with the AM1.5G solar spectrum; ^d FF = fill factor; ^e The power conversion efficiency of N3-sensitized solar cell (where N3 is [Ru(dcbpy)₂(NCS)₂]) measured by the same device fabrication process is 6.07%.

In addition, another pair of organic isomers (**OM1** and **OM2**), having similar extended 9-phenylcarbazole moiety at α or β position of the thiophene ring, has been prepared¹⁰ and used for the determination of PCE for comparison. By checking the latest version of CCDC databases (ConQuest Version 1.14 (Build RC5), CSD Version 5.34 updated to November 2013), it is found that there are only two examples on thiophene substituted 2-cyano-acrylic acid derivatives in literature.¹¹ So **OM1** is structurally characterized in this work, as shown in Fig. 1c.

X-ray single-crystal structural analyses for compounds **1**, **2** and DMF solvate of **OM1** reveal that the carbazole and thiophene rings are essentially coplanar with the dihedral angles between them of 14.5(1)° in **1**, 20.2(1)° in **2** and 14.6(2)° in **OM1**·DMF. In contrast, the dihedral angles between carbazole and phenyl rings are much larger as 79.3(2)° in **1**, 54.8(1)° in **2** and 52.8(2)° in **OM1**·DMF.

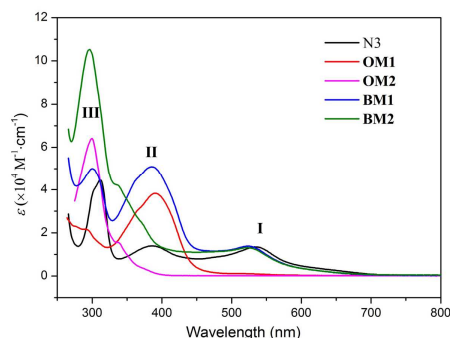


Fig. 2 UV-vis absorption spectra of five sensitizers in their DMF solutions with the same concentration of 1.00×10^{-5} M.

The electronic absorption spectra of three dyes and N3 measured in DMF are displayed in Fig. 2, and the optical data are summarized in Table 1. The absorption spectrum of the **BM1** shows a metal-to-ligand charge transfer (MLCT) peak centered at 525 nm (band I), which is a little blue-shifted in comparison with that of N3. However, the absorption centered at 385 nm (band II), which is assigned as the ancillary ligand localized transition, is much stronger than that of N3 because of incorporating the 9-phenylcarbazole substituted

thiophene moiety at α position in the ancillary ligand. Actually, band II of **BM1** is stronger than those reported bpy/thiophene/carbazole system,⁸ and the molar extinction coefficient (ϵ) can reach as high as $5.09 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ at 385 nm. In contrast, band II of **BM2** is much weaker since the 9-phenylcarbazole substitution at β position of the thiophene ring in the ancillary ligand. Instead, **BM2** exhibits a very strong absorption peak at 296 nm (band III) with a high ϵ value of $1.05 \times 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$, which is similar to a previously reported two ruthenium dyes containing phenothiazine or *N,N*-diphenylamino substituted group at β position of the thiophene unit.^{6a} The alteration of UV-vis spectra on absorption bands II and III in the cases of **BM1** and **BM2** is suggested to be a reflection of their different π conjugation system, which means that α 9-phenylcarbazole substituted TIP has much better delocalized π electron system than corresponding β substituted one. In addition, similar variations on the absorption bands II and III for **OM1** and **OM2** can be observed.

The electrochemical data in Table 1 show that **BM1** and **BM2** have the same oxidation potential, and the energy levels of the lowest-unoccupied molecular orbitals (LUMOs) for two sensitizers are almost the same since they have close absorption onset (Fig. 2). Therefore, it is suggested that the driving force for electron injection from the excited dye into TiO₂ conduction band for two sensitizers is similar.

With regard to two pairs of isomeric compounds **BM1/BM2** and **OM1/OM2**, considering the great discrepancy of their UV-vis absorptions, distinguishable photovoltaic performance on DSCs could be expected. So we have carried out the corresponding DSC determination. The DSCs in our experiments consist of a transparent FTO conducting glass electrode, a Pt count electrode and a liquid electrolyte. The electrolyte is composed of 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.5 M lithium iodide, 0.05 M 4-*tert*-butylpyridine and 0.05 M iodine in acetonitrile.

The photocurrent density-voltage curves and incident photon-to-current efficiency (IPCE) spectra of the DSCs based on these dyes and N3 under the AM1.5 sunlight illumination are shown in Fig. 3. It is noted that the DSC based on **BM1** reaches a PCE value of 7.33%, which is 21% higher than that of the N3-sensitized solar cell (6.07%) under the same cell fabrication and efficiency measuring procedures. The efficiency of **BM2** based cell (5.33%) is lower than that of the cell based on **BM1**, which is consistent with the results of their UV-

vis absorption and IPCE spectra. The efficiency of **OM1** sensitized solar cell (2.40%) is much lower than **BM1**, and **OM2** sensitized solar cell (0.34%) is also much lower than **OM1** mainly originating from their different UV-vis absorptions. That means we find a way to alter the PCEs of traditional ruthenium and organic dyes by introducing the same electron donors and π linkers into the ancillary ligands at different substituted positions.

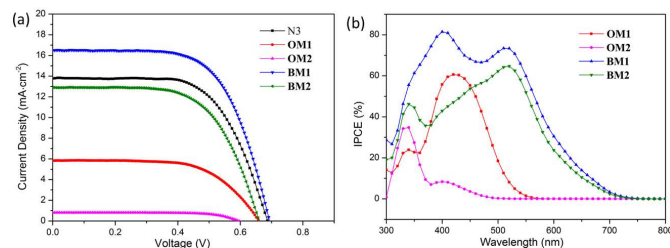


Fig. 3 (a) Current density-voltage characteristics of the photovoltaic devices with different photosensitizers under the AM1.5 simulated sunlight (100 mW·cm⁻²) illumination (thickness of TiO₂ = 12 μm; cell active area = 0.16 cm²). (b) IPCE spectra of the photovoltaic devices with different photosensitizers.

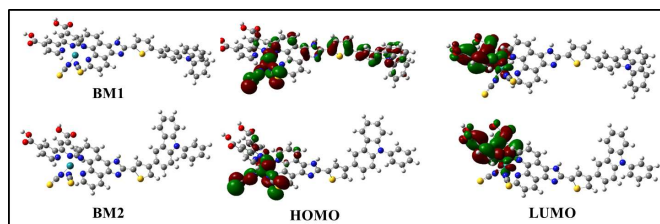


Fig. 4 Frontier orbitals of **BM1** and **BM2**.

It is known that the energy levels of the frontier orbitals of dye molecules play important roles in the electron-transfer processes in DSC cells. To further reveal the characteristics of π -conjugated dyes, the optimized molecular structures for **BM1** and **BM2**, as well as the frontier molecular orbitals of their calculated highest-occupied molecular orbitals (HOMOs) and LUMOs energy levels are shown in Fig. 4. All calculations were carried out with Gaussian 09 programs.¹³ The resultant HOMO-LUMO gaps for TIP-incorporated ligands **3** and **4** are 3.52 and 3.81 eV, respectively, while those for complexes **BM1** and **BM2** are much smaller at 2.49 and 2.50 eV, respectively, which are in good agreement with their UV-vis absorptions. The LUMOs of **BM1** and **BM2** are delocalized homogeneously on the anchoring ligand as expected. However, different from **BM2**, the HOMO of **BM1** is populated among Ru-*t*_{2g}, NCS⁻ and π orbital of the ancillary ligand. That means the ligand-to-metal charge transfer transition may preferentially occur between the ancillary ligand and the ruthenium center in **BM1**, which makes the electron transfer and injection process to the anchoring ligand and even TiO₂ more effective, and finally gives rise to the improvement of its PCE.

In summary, we prepared two new ruthenium based dyes (**BM1** and **BM2**) in which 9-phenylcarbazole tail was introduced at α or β position of the thiophene unit in the TIP skeleton, respectively, forming two isomeric ancillary ligands with four heterocycles (1,10-phenanthroline, imidazole, thiophene and 9-phenylcarbazole). Distinguishable photovoltaic performance on DSCs has been achieved with the PCEs of 7.33% and 5.33% for **BM1** and **BM2** in comparison with 6.07% for standard N3-dye, which is believed to originate from their π conjugated structures of isomeric ancillary ligands evidenced by their different UV-vis

absorption spectra. Analogous phenomena can also be found for another pair of organic isomers (**OM1** and **OM2**) having similar extended 9-phenylcarbazole moiety at α or β position of the thiophene ring. We believe **BM1** and **BM2** are good model molecules for investigations on the DSC performance of ancillary ligands in ruthenium sensitizers. The current comparative study not only reports a ruthenium complex (**BM1**) with high performance on DSCs, but also demonstrates an effective approach to improve the PCEs for ruthenium dyes merely by introducing the same electron donors and π linkers into the ancillary ligands at different substituted positions.

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