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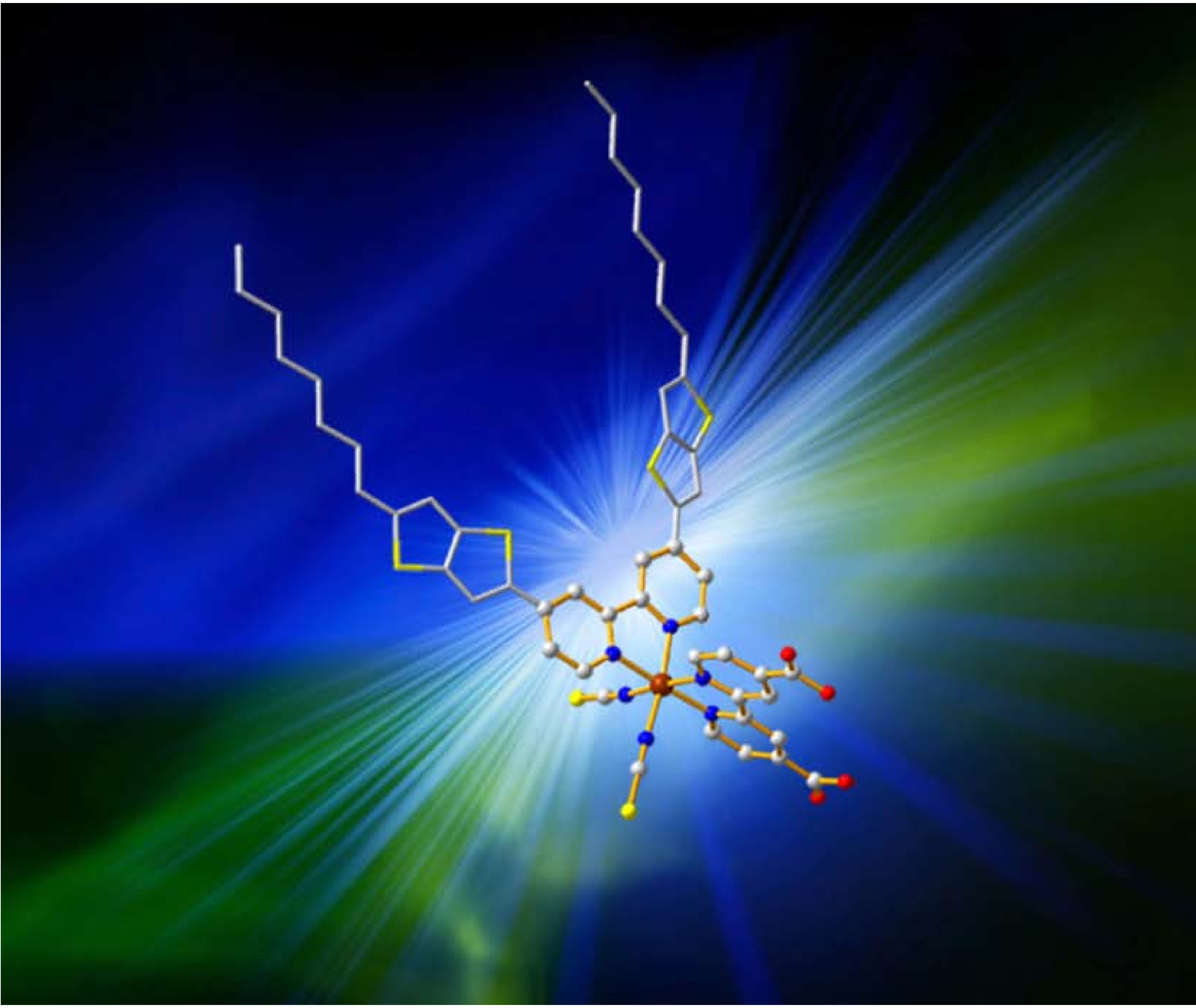

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A new heteroleptic ruthenium sensitizer enhances the absorptivity of mesoporous titania film for a high efficiency dye-sensitized solar cell†

Feifei Gao,[a] Yuan Wang,[a] Jing Zhang,[a] Dong Shi,[a] Mingkui Wang,[b] Robin Humphry-Baker,[b] Peng Wang,*[a] Shaik M. Zakeeruddin*[b] and Michael Grätzel*[b]

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A heteroleptic polypyridyl ruthenium complex, *cis*-Ru(4,4′-bis(5-octylthieno[3,2-*b*]thiophen-2-yl)-2,2′-bipyridine)(4,4′-dicarboxyl-2,2′-bipyridine)(NCS)$_2$, with a high molar extinction coefficient of 20.5 × 10^3 M^{-1} cm^{-1} at 553 nm has been synthesized and demonstrated as a highly efficient sensitizer for a dye-sensitized solar cell, giving a power conversion efficiency of 10.53% measured under an irradiation of air mass 1.5 global (AM 1.5G) full sunlight.

The sensitizer is a pivotal element in the nanocrystalline dye-sensitized solar cell[1] (DSC) which is very promising for future photovoltaic applications due to its high efficiency and low production cost. While an impressive device efficiency has been reached with a metal-free organic dye possessing a very high molar extinction coefficient,[2] it is fair to note that the DSC efficiency record of ~11.1%[3] measured under the irradiance of AM 1.5G sunlight is held by the well-known N719 or black dye in combination with a thick mesoscopic titania film. However, stability under prolonged heating at 80 °C proved too hard to reach with the high efficiency N719 or black dye based cells. In 2003, a thermally stable, ~7% efficiency DSC[4] was disclosed employing the amphiphilic Z907 sensitizer.[5] However, the molar extinction coefficient of this sensitizer is somewhat lower than that of the standard N719 dye. Meanwhile, a compromise between efficiency and high temperature stability has been noted for the Z907 sensitizer.[6] Subsequently, we initiated the concept of developing a high molar extinction coefficient, amphiphilic ruthenium sensitizer,[7] followed by other groups,[8] with a motivation to enhance device efficiency. In this context, Chen *et al.*[8c] reported a noteworthy sensitizer with a high molar extinction coefficient of 21.2 × 10^3 M^{-1} cm^{-1}, showing a power conversion efficiency of 8.54%. However, in view of their reported photocurrent action spectrum, it appears that the 23.92 mA cm^{-2} short-circuit photocurrent density reported in this work may not have been corrected for spectral mismatch.

Here we report a very promising sensitizer, coded C104 and shown in Fig. 1, which even under preliminary testing has already achieved a strikingly high efficiency of 10.53% under illumination with AM 1.5G full sunlight. The 4,4′-bis(5-octylthieno[3,2-*b*]thiophen-2-yl)-2,2′-bipyridine antenna ligand was synthesized *via* the Stille coupling reaction of 4,4′-dibromo-2,2′-bipyridine and tributyl(5-octylthieno[3,2-*b*]thiophen-2-yl)stannane.† The one-pot synthetic procedure developed for heteroleptic polypyridyl ruthenium complexes[5] was employed for the preparation of this new sensitizer at a good yield.†

As shown in Fig. 2, the electronic absorption spectrum of the C104 dye has two intense absorption bands at 312 nm and 368 nm in the UV region and the characteristic metal-to-ligand charge-transfer transition (MLCT) absorption bands in the visible region like other heteroleptic polypyridyl ruthenium complexes.[7] In DMF, the low energy MLCT transition absorption peaks at 553 nm, which is 30 nm red-shifted compared to that of Z907 or its analogues. The measured peak molar extinction coefficient (ε) is 20.5 × 10^3 M^{-1} cm^{-1}, which is very close to our calculated value and significantly higher than the corresponding values for the standard Z907 (12.2 × 10^3 M^{-1} cm^{-1}) and N719 (14.0 × 10^3 M^{-1} cm^{-1}) sensitizers.[9,10] As presented in the Electronic Supplementary Information (ESI), we detailed the origins of these transitions by calculating the electronic states of C104 with the time-dependent density functional theory (TDDFT).† The impressive improvement of extending the π conjugated system of the ancillary ligands in heteroleptic ruthenium complexes such as C104 is apparent from Fig. 2B, which depicts the absorption spectra in the visible region of Z907Na, N719 and C104

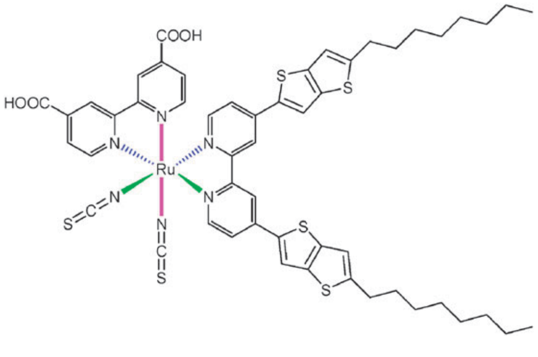

Fig. 1 Molecular structure of the C104 sensitizer.

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[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 130022 Changchun, China. E-mail: peng.wang@ciac.jl.cn; Fax: +86 431 852 629 53; Tel: +86 431 852 629 52*

[b] *Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH 1015 Lausanne, Switzerland*

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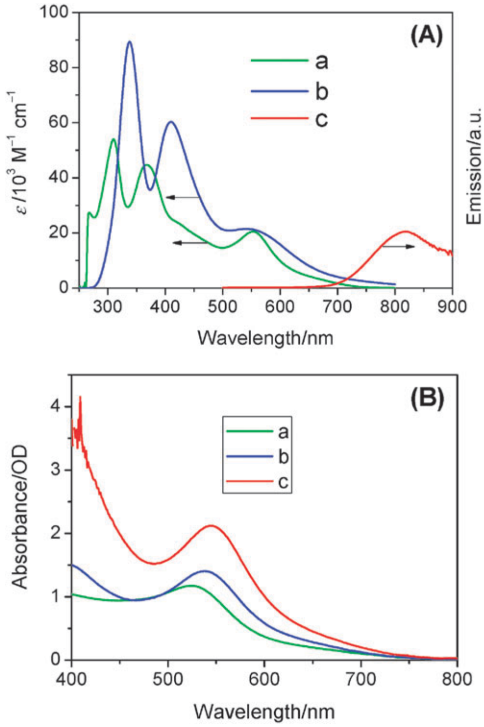

Fig. 2 (A) Experimental (a) and calculated (b) electronic absorption spectra and (c) emission spectrum of C104 sensitizer in DMF. (B) Absorption spectra of (a) Z907Na, (b) N719 and (c) C104 anchored on a 7 μm-thick mesoporous titania film.

anchored on a 7 μm thick transparent nanocrystalline TiO_2 film. The shortening of the light absorption length of mesoporous titania film endowed by the C104 sensitizer is highly desirable to achieve a good charge collection yield for a high efficiency DSC. Also decreasing the film thickness augments the open-circuit photovoltage of the cell due to lowering of the dark current. Excitation of the low energy MLCT transition of the C104 sensitizer in DMF produces an emission centered at 817 nm. The emission spectrum was further analyzed by applying a Gaussian reconvolution method, which made it possible to determine the integral under emission peak devoid of Raman and other instrumental artefacts.[11] The excitation transition energy (E_{0-0}) of C104 was estimated to be 1.56 eV.

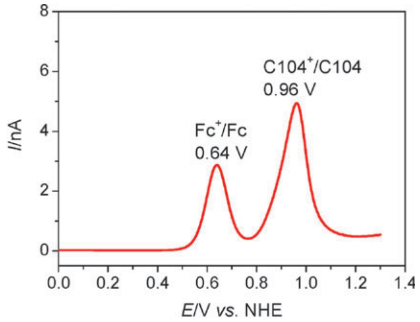

Fig. 3 Square-wave voltammogram of the C104 sensitizer dissolved in DMF with 0.1 M *n*-tetrabutylammonium hexafluorophosphate as supporting electrolyte. Working electrode: Pt ultramicroelectrode; Counter electrode: Pt mesh; Reference electrode: Ag wire. Ferrocene was used as internal reference.

As presented in Fig. 3, the formal redox potential ($\phi^0(S^+/S)$) of C104 sensitizer determined by ultramicroelectrode square-wave voltammetry is 0.96 V *vs.* NHE, which is 0.42 V higher than that of the triiodide/iodide couple employed in the electrolyte, providing the ample driving force for efficient dye regeneration and thus net charge separation. Note that the corresponding $\phi^0(S^+/S)$ of N719 and Z907Na dyes are 1.04 V and 0.87 V *vs.* NHE. Furthermore, its excited-state formal redox potential ($\phi^0(S^+/S^*)$) was calculated to be −0.6 V *vs.* NHE. The negative offset of $\phi^0(S^+/S^*)$ relative to the conduction band edge of TiO_2 provides the thermodynamic driving force for electron injection.

The ATR-FTIR spectrum (Fig. 4) of C104 anchored on TiO_2 film clearly shows the bands at 1607 cm^{-1} and 1381 cm^{-1} for the asymmetric and symmetric stretching modes of the carboxylate group, indicating that the carboxylic acid is deprotonated and involved in the adsorption of the dye on the surface of TiO_2. From the ATR-FTIR data we infer that the dye is anchored on the surface through the carboxylate group *via* a bidentate chelation or a bridging of surface titanium ions rather than an ester type linkage.[12] The sharp pyridine and thieno[3,2-*b*]thiophene ring modes are at 1535 cm^{-1}, 1462 cm^{-1}, 1422 cm^{-1}, 1234 cm^{-1} and 1020 cm^{-1}. The NCS signal remains at 2100 cm^{-1}, indicating that NCS coordinated to the ruthenium centre through the N atom is unaffected by the adsorption process. The saturated hydrocarbon chain of the ancillary ligand is easily identified from their C–H stretch modes in the 2800–3000 cm^{-1} region. Peaks at 2852 cm^{-1} and 2924 cm^{-1} are due to the symmetric and asymmetric $-CH_2-$ stretch vibrations. The corresponding CH_3- peak is observed at 2956 cm^{-1}, while the C–H stretching mode of aromatic units is at 3075 cm^{-1}.

Some preliminary photovoltaic experiments were conducted to compare the performance of C104 with the Z907Na sensitizer using an acetonitrile based electrolyte composed of 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 30 mM I_2, 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85/15, *v*/*v*). State of the art mesoporous titania film was employed, whose fabrication and assembly to complete, hot-melt sealed cells have been described previously.[13] A 7 μm thick film of 20 nm-sized TiO_2 particles was first screen-printed on a fluorine-doped SnO_2

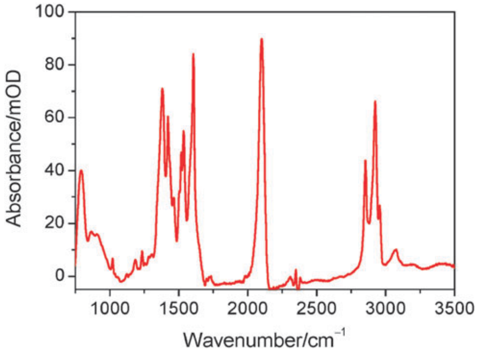

Fig. 4 ATR-FTIR spectrum of a mesoporous TiO_2 film coated with the C104 sensitizer. The spectrum of a TiO_2 reference film heated at 500 °C to remove surface-adsorbed water was subtracted for clarity of presentation.

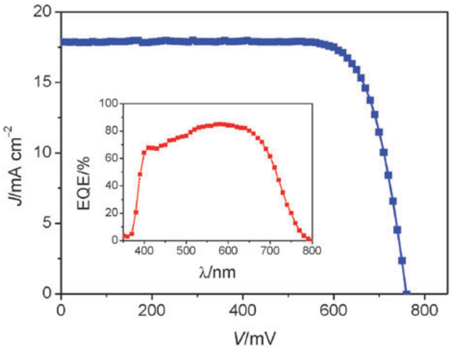

Fig. 5 *J–V* characteristic of a DSC with the C104 sensitizer under the illumination of AM 1.5G full sunlight (100 mW cm^{-2}). The inset is its photocurrent action spectrum. Cell active area tested with a mask: 0.158 cm^2.

(FTO) conducting glass electrode and a 4 μm thick second layer of 400 nm-sized light scattering anatase particles was subsequently coated onto the first one. The TiO_2 electrode was derivatized by immersing it in a dye solution containing 300 μM C104 and 300 μM 3α,7α-dihydroxy-5β-cholanic acid in a mixture of acetonitrile and *tert*-butyl alcohol (1 : 1, *v*/*v*) at room temperature for 12 h. A platinized FTO conducting glass was used as counter electrode. The two electrodes were separated by a 25 μm thick Surlyn hot-melt gasket and sealed up by heating. The internal space was carefully filled with the above mentioned electrolyte using a vacuum back filling system. The electrolyte-injecting hole was made by an ultrafine sandblaster on the counter electrode glass substrate. It was sealed with a Bynel sheet and a thin glass cover by heating.

The photocurrent action spectrum of a DSC with C104 as sensitizer is shown in the inset of Fig. 5. The incident photon-to-collected electron conversion efficiency (IPCE or EQE) exceeds 60% in the whole visible spectral region, with a broad plateau of over 80% from 520 to 650 nm, reaching the maximum of 85% at 580 nm. Considering the light absorption and scattering loss by the conducting glass, the maximum efficiency for absorbed photon-to-collected electron conversion efficiency (APCE or IQE) is close to unity over a broad spectral range. From the overlap integral of this curve with the standard global AM 1.5G solar emission spectrum, a short-circuit photocurrent density of 17.89 mA cm^{-2} is calculated, which is in excellent agreement with the measured photocurrent density. Therefore there is negligible spectral mismatch between our solar simulator and the standard AM 1.5G sunlight. As shown in Fig. 5, its short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (*FF*) of a DSC with the C104 dye under AM 1.5G full sunlight are 17.87 mA cm^{-2}, 760 mV, and 0.776, respectively, yielding an overall conversion efficiency (η) of 10.53%. At various lower incident light intensities, overall power conversion efficiencies are even higher than 10.7%. Obtaining such a high conversion efficiency with a relatively thin double layer film (total thickness of 12 μm) is impressive compared to Z907Na dye showing a ~9.0% efficiency. In addition, our preliminary tests with a solvent-free ionic liquid electrolyte have shown that this new sensitizer is very stable under prolonged thermal and light-soaking stress, proving the success of introducing a thienothiophene unit in heteroleptic sensitizers for DSC.

In summary, we have developed a novel heteroleptic ruthenium sensitizer with a high molar extinction coefficient to considerably enhance the optical absorptivity of mesoporous titania film. For a newly developed dye, the achievement of over 10.5% power conversion efficiencies is very encouraging. We are now systematically optimizing the cell parameters to explore the full potential of this promising sensitizer.

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