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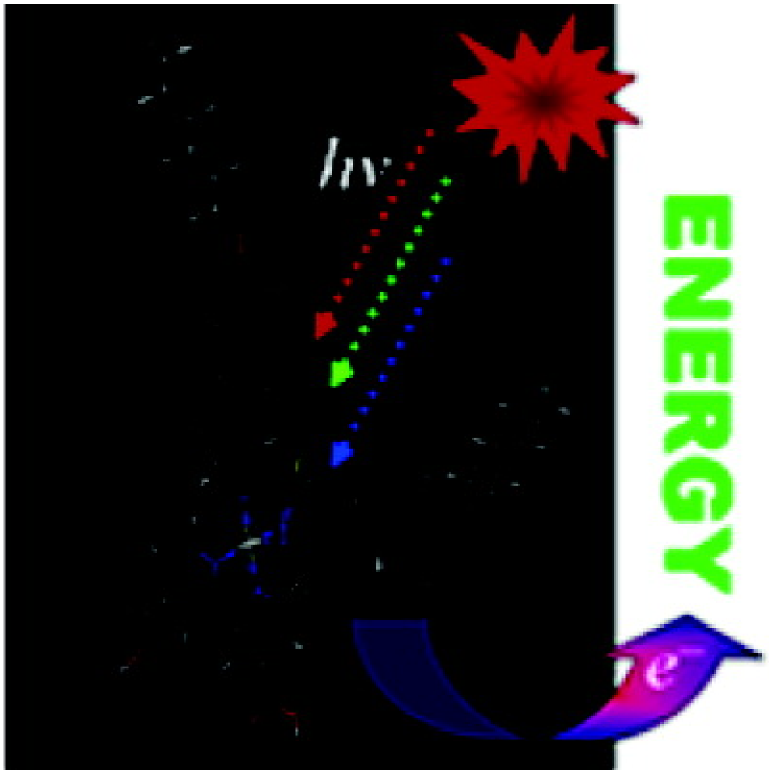

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A High Molar Extinction Coefficient Sensitizer for Stable Dye-Sensitized Solar Cells

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The sensitizer is a critical component in nanocrystalline dye-sensitized solar cells (DSCs) that have great potential for future photovoltaic applications owing to their high efficiency and low production cost.[1,2] Until now only three polypyridyl ruthenium(II) complexes[3−5] have achieved power conversion efficiencies over 10% in standard air mass 1.5 sunlight, although recently impressive photovoltaic performance has been obtained with some organic coumarin[6] and indoline[7] dyes having very high molar extinction coefficients. More critically, only one amphiphilic heteroleptic ruthenium complex[8] referred to as Z-907 has yielded devices that are stable under prolonged thermal stress at 80 °C. However, the molar extinction coefficient of this sensitizer is somewhat lower than that of the standard N-719 dye. Meanwhile, a compromise between efficiency and high-temperature stability has been noted for the Z-907 system.[9] Thus it is very important to develop transition-metal based sensitizers with improved molar extinction coefficients which maintain the desirable stability under thermal stress and light soaking. Here we report a novel amphiphilic ruthenium complex coded as K-19 (Figure 1) which accomplishes this goal. The enhanced absorption is expected by extending the conjugated system[5,10] of the hydrophobic spectator ligand.

The one-pot synthetic procedure[8] developed for heteroleptic polypyridyl ruthenium complexes was employed for the preparation of this new sensitizer. The 4,4′-bis(*p*-hexyloxystyryl)-2,2′-bipyridine ligand was synthesized from 4,4′-bis(diethylmethylphosphonate)-2,2′-bipyridine[11] and 4-hexyloxybenzaldehyde using the Horner−Emmons−Wadsworth reaction.[12] Further synthetic details and analytical data are provided in the Supporting Information.

Square-wave voltammetry in combination with the ultramicroelectrode technique[13] was used to measure the redox potential of the sensitizer. As shown in Figure S2, the anodic and cathodic peaks for the K-19 dye in DMF solution both appear at 0.95 V vs normal hydrogen electrode (NHE). The redox potential is 0.41 V higher than that[13] of the iodide electron donor providing ample driving force for efficient dye regeneration and thus net charge separation.

The low energy metal-to-ligand transition (MLCT) absorption band at 543 nm of the K-19 dye has a molar extinction coefficient of 18.2×10^3 M^{-1} cm^{-1}, which is higher than the corresponding values of the Z-907 (12.2×10^3 M^{-1} cm^{-1}) and even the standard N-719 dye (14.0×10^3 M^{-1} cm^{-1}).[14] Shown in Figure S3 is the absorption and emission spectrum of the K-19 dye in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1). The emission is centered at 818 nm, and the E_{0-0} transition energy was estimated to be 1.7 eV. Thus the excited-state redox potential, $\phi^0(S^+/S^*)$, of the K-19 sensitizer is calculated to be −0.75 V vs NHE which is more negative than that of the TiO_2 conduction band edge, providing thermodynamic driving force for electron injection. The enhanced light harvesting in the 400−750 nm region due to the extension of the π conjugated system can be clearly seen from Figure S4, which compares the visible absorption spectra of K-19 and Z-907 anchored on a 8 μm thick transparent nanocrystalline TiO_2 film. Semiempirical calculations confirm that the extension of the π conjugation of the ligand increases the absorption cross section while lowering its π^* level. Nevertheless, the lowest unoccupied molecular orbital (LUMO) remains still on the 4,4′-dicarboxylic acid-2,2′-bipyridine anchoring ligand.

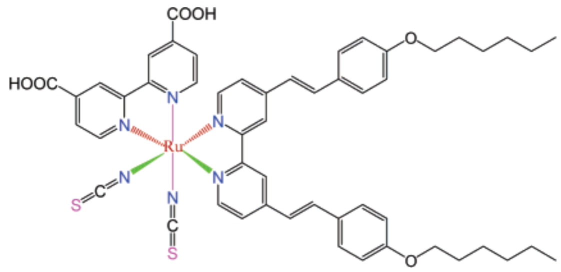

Figure 1. Molecular structure of the K-19 sensitizer.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum of the K-19 powder exhibits prominent bands at 2099 cm^{-1} (NCS), 1717 cm^{-1} (COOH), and 1244 cm^{-1} (C−O). The spectrum of K-19 anchored on TiO_2 film (Figure S5) clearly shows the bands at 1624 cm^{-1} and 1379 cm^{-1} for the asymmetric and symmetric stretching modes of the carboxylate group and the complete loss of the 1717 cm^{-1} peak. From these ATR-FTIR data it can be inferred that the dye is anchored on the surface through the two carboxylate groups via a bidentate chelation or a bridging of surface titanium ions rather than an ester type linkage.[15] The NCS signal remains at 2104 cm^{-1} indicating that the NCS coordinated to the ruthenium center through the N atom is unaffected by the adsorption process. The other peaks at 2955 cm^{-1}, 2931 cm^{-1}, and 2854 cm^{-1} correspond to the stretching modes of the aliphatic chains, while the sp^2 C−H stretching mode is observed at 3065 cm^{-1}. The sharp peaks located at 1541 cm^{-1} and 1431 cm^{-1} arise from aromatic ring modes.

The photovoltaic performance of N-719, Z-907, and K-19 sensitizers was compared using the previously introduced low vapor pressure and thermally stable electrolyte[8] composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M I_2, and 0.5 M *N*-methylbenzimidazole in 3-methoxypropionitrile. State of the art mesoporous titania films[16] were employed, whose fabrication and the assembly of complete, hot-melt sealed cells have been described previously.[16] A 10 μm thick film of 20-nm-sized TiO_2 particles was first screen-printed on a fluorine-doped SnO_2 (FTO) conducting glass electrode, and a second 4 μm thick second layer of 400-nm-sized light scattering anatase particles was subsequently coated onto the first one. The surface of the TiO_2 electrode was derivatized with the sensitizer by immersing it into a 300 μM dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) at room temperature for 12 h. A platinized FTO conducting glass was used as counter electrode.

The photocurrent action spectrum of the K-19 dye is presented in the inset of Figure 2. The incident photon to current conversion

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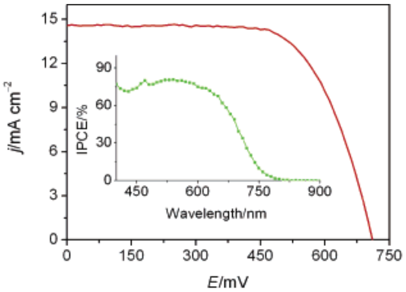

Figure 2. Photocurrent density−voltage characteristics under AM 1.5 full sunlight (100 mW cm^{-2}). The inset is the photocurrent action spectrum. Cell active area tested with mask: 0.158 cm^2.

Table 1. Photovoltaic Performance of DSCs with Different Sensitizers under the AM 1.5 Full Sunlight (100 mW cm^{-2})

sensitizer	V_{oc}/mV	J_{sc}/mA cm^{-2}	*ff*	η/%
N-719	726	12.95	0.709	6.7
Z-907	701	12.16	0.699	6.0
K-19	711	14.61	0.671	7.0

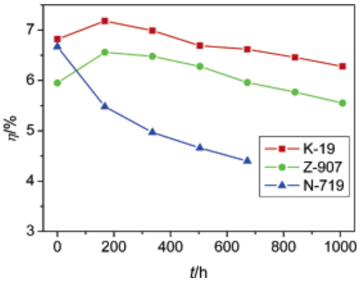

Figure 3. Evolution of device efficiencies with different sensitizers during thermal aging at 80 °C.

efficiency (IPCE) exceeds 70% in a broad spectral range from 400 to 650 nm, reaching a maximum of about 80% at 540 nm. The short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (*ff*) under air mass (AM) 1.5 full sunlight are 14.61 mA cm^{-2}, 711 mV, and 0.671, respectively, yielding an overall conversion efficiency (η) of 7.0%. Table 1 shows that the N-719 and Z-907 sensitizers give lower conversion efficiencies under these conditions. Note that cells with the N-719 sensitizer exhibit 11% conversion efficiency, employing a thicker film and a volatile acetonitrile based electrolyte.[17] We also noted that the K-19 maintained its conversion efficiency even when a 20% thinner TiO_2 film was used in contrast to the two other sensitizer.

Figure 3 compares the evolution of device efficiencies using N-719, Z-907, and K-19 as sensitizers during thermal aging at 80 °C. As reported in our previous work[8] devices with the N-719 dye showed poor stability, which is probably caused by the sensitizer desorption at high temperature. In contrast the two amphiphilic sensitizers Z-907 and K-19 both retained over 92% of their initial performances under the thermal stress at 80 °C for 1000 h. The efficiency increase observed during the initial stage of the thermal aging is due to a rise in the short circuit photocurrent (Figure S6). The likely cause for this effect is faster dye regeneration as previously observed for the Z-907 sensitizer.[8] The V_{oc} did drop ∼90 mV during the thermal aging. However, by using 1-decylphosphonic acid as a coadsorbent at a molar ratio of 1:4 in the K-19 sensitizer solution, the photovoltage drop was attenuated to 40 mV while maintaining a 92% stability in device efficiency (Figure S7).

Cells based on the K-19 sensitizer also showed an excellent photochemical stability when submitted to accelerated testing in a solar simulator at 100 mW cm^{-2} intensity. After 1000 h of light soaking at 60 °C, no drop in efficiency (Figure S8) was observed for cells covered with an ultraviolet absorbing polymer film. A 74 mV drop in V_{oc} was compensated by an increase of J_{sc}, while the fill factor was very stable. It therefore appears that the styryl unit attached to the bipyridly ligand remains intact after prolonged visible light soaking.

In conclusion, an amphiphilic heteroleptic polypyridyl ruthenium complex accomplishing enhanced harvesting of visible light has been synthesized and demonstrated as an efficient, stable sensitizer for nanocrystalline dye-sensitized solar cells. Further optimization of the cell parameters to take the full potential of this new and promising sensitizer is underway.

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Supporting Information Available: Synthesis of K-19 and the evolutions of detailed device parameters during aging tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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