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D-D-π-A organic dye containing rhodanine-3-acetic acid moiety for dye-sensitized solar cells

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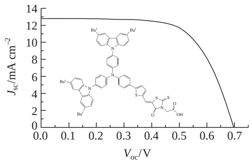
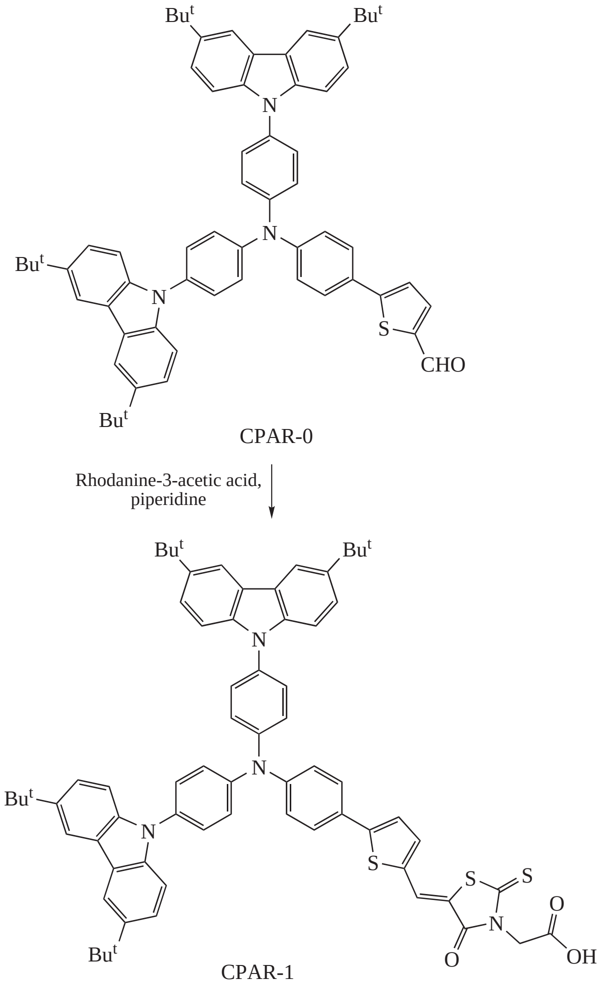
A new D-D-π-A organic dye has been prepared, whose energy conversion efficiency of dye-sensitized solar cell based on CPAR-1 reaches 5.9% under air mass 1.5 global irradiation.



In contemporary world, thin-film solar cells, such as organic solar cells,[1,2] perovskite solar cells,[3] and dye-sensitized solar cells (DSSCs)[4,5] are under intense academic and industrial investigations because of their environmentally-friendly, efficient, and low-cost features. In the process of photon to current in a DSSC device, photosensitizer plays a key role in determining the solar-cell performance.[6–8] Enormous sensitizers with high performance were developed. For example, Ru-based sensitizers like N719,[6] and black dye[7] achieved overall solar-to-electrical energy conversion efficiency (η) over 11%. Notably, porphyrin dye SM315 got $\eta > 13\%$.[8] Metal-free organic dyes, such as indoline,[9] triarylamine,[10] merocyanine[11] dyes *etc*., are useful in many fields including cost-effective environmentally-friendly photovoltaic systems like DSSCs. Double electron-donating group can provide higher electron donating ability and wider light response range of DSSC,[12] whereas rhodanine-3-acetic acid has been proved as an excellent electron-withdrawing anchoring group giving high stability of cell devices.[13]

Herein, we report a new organic dye (*Z*)-2-(5-{[5-(4-{bis-[4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl]amino}phenyl)-thiophen-2-yl]methylidene}-4-oxo-2-thioxothiazolidin-3-yl)-acetic acid (CPAR-1, Scheme 1),[†] which may be regarded as a D-D-π-A sensitizer. CPAR-0 was synthesized according to our published procedure.[14] CPAR-1 was obtained *via* Knoevenagel condensations between CPAR-0 and rhodanine-3-acetic acid.[13]



Scheme 1

The electronic absorption spectrum of CPAR-1 in chloroform solution is shown in Figure 1.[†] CPAR-1 has two absorption peaks in the ranges of 300–400 and 420–600 nm, which are due to the π–π interaction of internal CPAR-1 molecule and intramolecular

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[†] Commercially available reagents and solvents were used as received. UV-VIS absorption spectroscopy was performed on a Shimadzu UV-3600 spectrometer for liquid phase. Electron spray mass spectra were measured on a Thermo LCQ Fleet electro-spray mass spectrometer.

Synthesis and characterization of CPAR-1. A MeCN (15 ml) solution of CPAR-0 (0.910 g, 1.0 mmol), cyanoacetic acid (0.170 g, 2.0 mmol), and a few drops of piperidine were heated to reflux for 2 h. After cooling to room temperature, solvents were removed by rotary evaporation. The residue was purified by silica gel column chromatography with CH_2Cl_2–MeOH (10 : 1, v/v) as eluent to afford the dye CPAR-1 as a red solid (0.747 g, 69%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 8.28 (s, 4H), 8.05 (s, 1H), 7.75–7.84 (m, 3H), 7.70 (s, 1H), 7.62 (d, 4H, *J* 7.5 Hz), 7.48 (d, 4H, *J* 8.0 Hz), 7.42 (d, 4H, *J* 7.5 Hz), 7.37 (d, 4H, *J* 8.0 Hz), 7.27 (d, 2H, *J* 6.5 Hz), 4.45 (s, 2H), 1.41 (s, 36H). MS (ESI-MS), *m*/*z*: 1081.90 $[M-H]^-$ (calc. for $C_{68}H_{66}N_4O_3S_3$, *m*/*z*: 1083.47).

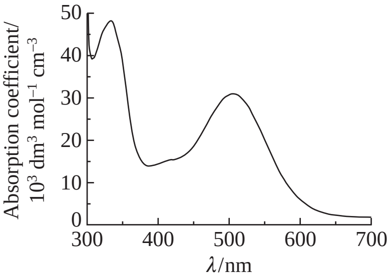

Figure 1 Electronic absorption spectrum of CPAR-1 in $CHCl_3$ solution.

charge transfer (ICT) transition from triarylamine units to the rhodanine-3-acetic acid acceptor moiety,[15] respectively. Absorption maxima (λ_{max}) are observed at 340 nm (ε = 48163 dm^3 mol^{-1} cm^{-1}) and 507 nm (ε = 30879 dm^3 mol^{-1} cm^{-1}).

To gain more insight into the electronic structure of CPAR-1, density function theory (DFT) calculations were performed by B3LYP method for the geometry optimization.[16] The observed two bands in absorption spectrum of CPAR-1 are caused by several kinds of electron excitation. The low-energy band located in the range of 420–600 nm is ascribed to HOMO / LUMO and HOMO–1/LUMO transition, while the UV band in the range of 300–400 nm is composed of HOMO/LUMO+1 and HOMO–1/LUMO+1. The electron distributions of the four regular energy levels of CPAR-1 are shown in Figure 2. The HOMO–1 of CPAR-1 is mainly delocalized across the two carbazole groups, while the HOMO of CPAR-1 is populated in the whole molecule except the rhodanine-3-acetic acid and *tert*-butyl groups. Both the LUMO and LUMO+1 are delocalized across the π-A moiety with a large composition on the anchoring group (see Figure 2), where the electron is close to the TiO_2 surface and can be smoothly injected into the CB of the TiO_2 semiconductor. Therefore, photons from each of the two absorption bands at 300–400 nm and 420–600 nm are useful for electron injection and photovoltaic conversion. Thus, distributions on HOMO and LUMO levels are separated in all three compounds indicating that the HOMO–LUMO transition can be considered as a charge-transfer transition.

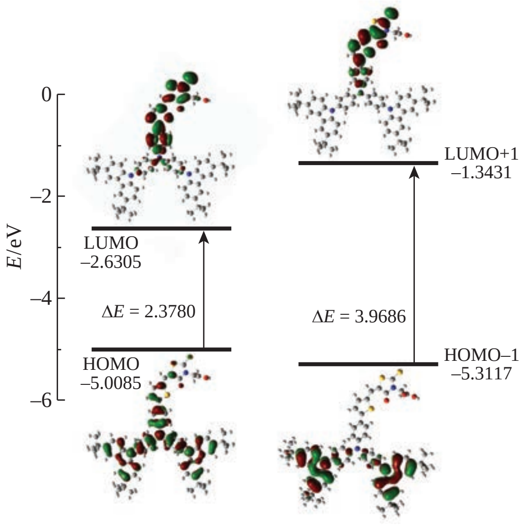

Figure 2 Calculated HOMO–1, HOMO, LUMO and LUMO+1 levels (eV) for CPAR-1.

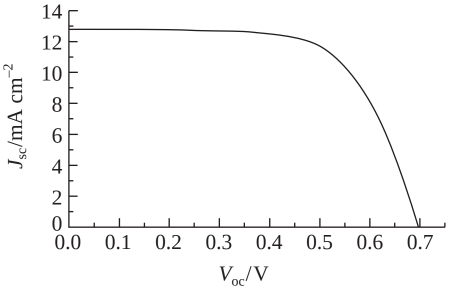

Figure 3 Photocurrent density–voltage curve for the DSSC based on CPAR-1 under AM 1.5G full sunlight irradiation.

CPAR-1 was used to manufacture dye-sensitized solar cells.[‡,17–19] The size of the active surface of the DSSC devices was 6 × 6 mm. The devices employed FTO glass anchored dye-loaded TiO_2 nanoparticle film as positive electrode, platinum-coated glass as counter electrode, and a solution of 0.6 M DMII, 50 mM LiI, 30 mM I_2, 0.5 M *tert*-butylpyridine and 0.1 M GuNCS in acetonitrile and valeronitrile (85 : 15) as the electrolyte.[14] Photocurrent–voltage (J–V) curve for the DSSCs recorded under air mass 1.5 global (AM 1.5G) full sunlight irradiation (100 mW cm^{-2}) is presented in Figure 3. The overall conversion efficiency η of CPAR-1 reaches 5.90% (J_{sc} = 12.79 mA cm^{-2}, V_{oc} = 0.698 V and FF = 66.00%), which is in the reasonable range of efficiencies of metal-free organic dyes.[20,21]

In summary, a new D-D-π-A sensitizer CPAR-1 was designed and synthesized. CPAR-1 has a wide absorption band of 300–650 nm. The DSSC device based on CPAR-1 was fabricated, and its overall solar-to-electrical energy conversion efficiency reaches 5.9%. In addition, the electronic structure of CPAR-1 was examined using DFT calculations.

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[‡] *Fabrication and characterization of the DSSC devices*. A paste composed of 22-nm-sized TiO_2 nanoparticles was coated on a $TiCl_4$-treated FTO glass substrate to obtain the required thickness on repetitive screen printing.[17,18] Crystallization of TiO_2 films was performed with a programmed procedure: (1) 80 °C for 15 min; (2) 135 °C for 10 min; (3) 325 °C for 30 min; (4) 375 °C for 5 min; (5) 450 °C for 15 min, and (6) 500 °C for 15 min. The resulting material had a transparent layer (thickness ~17 μm), which was treated again with $TiCl_4$ at 70 °C for 30 min and sintered at 500 °C for 30 min. The electrode was then immersed into a dye solution (0.2 mM) in EtOH – toluene (1:1) at 25 °C for 2 h for dye loading onto the TiO_2 film. The dye-adsorbed TiO_2 electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating with a Surlyn film as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell *via* vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). An Al foil was taped at the back side of each counter electrode to reflect unabsorbed light back to the photoanode. A Xenon light source (Oriel) was used to give an irradiance of 100 mW cm^{-2} at the surface of a testing cell using a Keithley 2400 source meter. The measurement delay time was fixed to 40 ms with 100 measurement points scanning from V_{oc} to J_{sc}.[19] For the setup used in our measurements, there was no hysteresis in the I–V curves when reversing the scan direction.

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