

Tetrahydroquinoline dyes with different spacers for organic dye-sensitized solar cells

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Abstract

Novel organic dyes (**C1-1**, **C1-5** and **C2-1**) with a tetrahydroquinoline moiety as the electron donor, different thiophene-containing electron spacers and a cyanoacrylic acid moiety as the electron acceptor have been designed and synthesized for the application in dye-sensitized solar cells (DSSCs). An interesting relationship between the dye structures, properties, and the performance of DSSCs based on these tetrahydroquinoline dyes is obtained. Although **C2-1** dye, which has a rigid electron spacer, has the narrowest action spectrum among these dyes, it gives the highest solar-to-electricity conversion efficiency (η) of 4.49% ($V_{oc} = 600$ mV, $J_{sc} = 11.20$ mA/cm², $ff = 0.67$) of a DSSC under simulated AM 1.5 irradiation (100 mW/cm²). Under the same conditions, the η value of a DSSC based on N3 dye is 6.16%.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have become one of the most promising low-cost alternatives for the photovoltaic conversion of solar energy compared with the conventional solid p–n junction photovoltaic devices [1,2]. The heart of a DSSC system is a mesoporous oxide layer composed of nanometer-sized particles anchored by a monolayer of the charge transfer dye such as Ru-polypyridyl-complex [2]. The most widely used sensitizer for the DSSCs application is *cis*-di-(thiocyanato)bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II), coded as N3 or N719 dye depending on whether it contains four or two protons [3,4]. High performance and good stability of DSSCs based on Ru dyes had been obtained in the literatures [5]. However, the Ru dyes are facing the problem of costs and environmental issues.

Metal-free dyes, which have many advantages such as large absorption coefficients (attributed to an intramolecular π – π^* transition), easily molecular design for desired photophysical and photochemical properties, inexpensive and environment friendly [6e,6g], are also adopted as sensitizers for DSSCs. But the efficiencies of DSSCs based on metal-free dyes are much lower than that of Ru dyes based solar cells. Recently, DSSCs performance based on metal-free organic dyes has been remarkably improved by several groups [6–14]. A much higher solar-to-electric power conversion efficiency of up to 9% in full sunlight has been achieved by Ito et al. using an indoline dye [14]. This result suggest that smart designed metal-free organic dyes are also highly competitive candidates for solar cells due to their low costs and easy synthesis.

Some electron donor acceptor π -conjugated (D- π -A) compounds have been found to possess photoinduced intramolecular charge transfer (PICT) properties [15]. The PICT character makes these compounds ideal dyes for DSSCs application. The charge transfer or separation between the electron donor and acceptor moieties in the molecule may facilitate the rapid electron injection from the dye molecule into the conduction band of the wide band semiconductor, e.g., TiO₂, which is required for efficient DSSCs. The cations formed after the electron injection are also in good match to the redox of the common used elec-

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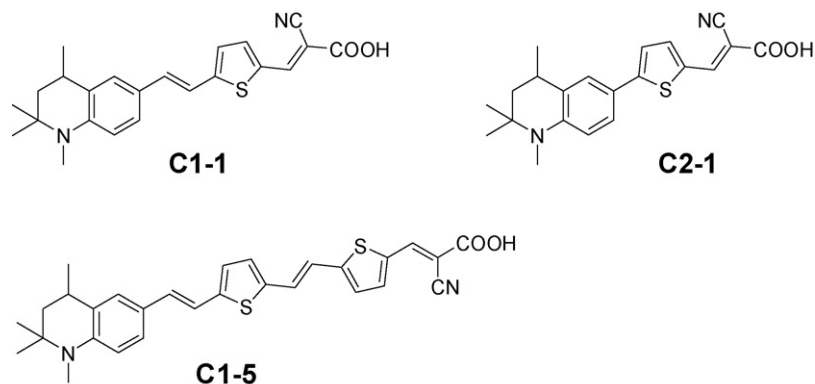


Fig. 1. Chemical structures of the tetrahydroquinoline dyes.

trolyte, I^-/I_3^- . In this paper, we report the design, synthesis and characterization of a series of organic dyes of this type aimed at providing a better understanding of the relationship between dye structures and performance of the DSSCs. The structures of these dyes are shown in Fig. 1. The same electron donor of 1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinoline, and the same electron acceptor, cyanoacrylic acid group are used in all these three dyes. However, different types of spacers containing thiophene moiety are adopted to the π -conjugating backbone for adjusting the absorption spectra, HOMO and LUMO levels of the dyes. Our results show that even a small change in the spacer of the dye can cause a significant change in the solar cell performance.

2. Experimental details

2.1. Synthesis

The synthesis of the dyes was carried out under classical procedures and is shown in Scheme 1. The electron donor, 1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinoline (**1**), was synthesized using improved literature procedures and served as starting compound [16,17]. The synthetic details will be published elsewhere. The characterization data of these dyes are listed below.

2-Cyano-3-[5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)-vinyl]-thiophen-2-yl]-acrylic acid (**C1-1**). Black solid (yield 80%). Mp: 208–210 °C. $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz, ppm): δ 1.17 (s, 3H), 1.27 (s, 3H), 1.33 (d, $J=6.6$ Hz, 3H), 1.41 (dd, $J_1=12.6$ Hz, $J_2=12.9$ Hz, 1H), 1.83 (dd, $J_1=4.2$ Hz, $J_2=13.0$ Hz, 1H), 2.77–2.80 (m, 4H), 6.54 (d, $J=8.7$ Hz, 1H), 7.00 (d, $J=16.1$ Hz, 1H), 7.18 (d, $J=3.9$ Hz, 1H), 7.21 (d, $J=16.0$ Hz, 1H), 7.30 (d, $J=8.5$ Hz, 1H), 7.34 (s, 1H), 7.59 (d, $J=3.9$ Hz, 1H), 8.06 (s, 1H). HRMS-EI (m/z): $[M-\text{CO}_2]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{S}$, 348.1660; found, 348.1656.

2-Cyano-3-[5-(2-[5-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)-vinyl]-thiophen-2-yl)-vinyl]-thiophen-2-yl]-acrylic acid (**C1-5**). Black solid (yield 64%). Mp: >260 °C. $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz, ppm): δ 1.17 (s, 3H), 1.26 (s, 3H), 1.33 (d, $J=6.6$ Hz, 3H), 1.41 (dd, $J_1=12.8$ Hz, $J_2=13.4$ Hz, 1H), 1.83 (dd, $J_1=4.1$ Hz, $J_2=12.8$ Hz, 1H), 2.79 (m, 4H), 6.53 (d, $J=9.0$ Hz, 1H), 6.84 (d, $J=16.3$ Hz, 1H), 7.04 (d, $J=3.5$ Hz, 1H), 7.09–7.17 (m, 2H), 7.23–7.35 (m, 5H),

7.75 (s, 1H), 8.20 (s, 1H). HRMS-EI (m/z): $[M-\text{CO}_2]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{S}_2$, 456.1694; found, 456.1693.

2-Cyano-3-[5-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)-thiophen-2-yl]-acrylic acid (**C2-1**). Red brown solid (yield 83%). Mp: 185–190 °C. $^1\text{H NMR}$ (DMSO- d_6 , 400 MHz, ppm): δ 1.19 (s, 3H), 1.29 (s, 3H), 1.34 (d, $J=6.5$ Hz, 3H), 1.43 (dd, $J_1=12.4$ Hz, $J_2=13.3$ Hz, 1H), 1.86 (dd, $J_1=4.2$ Hz, $J_2=13.0$ Hz, 1H), 2.82–2.84 (m, 4H), 6.61 (d, $J=8.4$ Hz, 1H), 7.42–7.45 (m, 2H), 7.49 (d, $J=3.7$ Hz, 1H), 7.82 (d, $J=3.6$ Hz, 1H), 8.27 (s, 1H). HRMS-EI (m/z): $[M-\text{CO}_2]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{S}$, 322.1504; found, 322.1498.

2.2. Analytical measurements

The absorption and emission spectra were measured on a HP-8453 spectrophotometer and PTI-C-700 fluorescence spectrometer, respectively. The $^1\text{H NMR}$ spectra were recorded on a VARIAN INOVA 400 MHz NMR spectrometer. High resolution mass spectral determinations were made on a Micro-mass GC-Tof MS instrument. Melting-points were measured with a X-4 melting-point apparatus with microscope. Electrochemical redox potentials were obtained by cyclic voltammetry using a three-electrode cell and an electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon electrode; the auxiliary electrode was a Pt wire and Ag/Ag^+ was used as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF_6 , 0.1 M) was used as supporting electrolyte in DMF. Ferrocene was added to each sample solution at the end of the experiments and the ferrocenium/ferrocene (Fc/Fc^+) redox couple was used as an internal potential reference. The potentials versus NHE are calibrated by addition of 630 mV to the potentials versus Fc/Fc^+ [11].

2.3. Fabrication of the nanocrystalline TiO_2 solar cells

Titania paste was prepared from P25 (Degussa, Germany) following literature procedure [3] and deposited onto the F-doped tin oxide conducting glass (TEC8, sheet resistance of $8 \Omega/\text{square}$, Pilkington, USA) by doctor-blading. The resulted layer photoelectrode of 10 μm thickness, was sintered at 500 °C for 30 min in air. The sintered film was further treated with

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