

## Synthesis, characterization and crystal structures of new organic compounds containing cyanoacrylic acid



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### ABSTRACT

New organic compounds, cin-aa (**1**) and mecin-aa (**2**), containing cyanoacrylic acid as an acceptor were synthesized by the reaction of cinnamaldehyde or  $\alpha$ -methylcinnamaldehyde with cyanoacetic acid in acetonitrile. The compounds **1** and **2** were characterized by elemental analyses (CHN), FT-IR, UV–Vis and <sup>1</sup>H NMR spectroscopy, and their monoclinic centrosymmetric structures were determined by single crystal X-ray diffraction. In addition, they were tested for their potential use as photosensitizers in dye-sensitized solar cells (DSSC). Overall conversion efficiencies of **1** and **2** were determined as 0.04 and 0.09, respectively, under full sunlight irradiation. To get further insight into the molecular structure of **1** and **2**, their geometry and energies of HOMO and LUMO were optimized by density functional theory calculation at the B3LYP/6-31G(d) level with Gaussian 03.

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## 1. Introduction

Organic compounds containing cyanoacrylic acid have been extensively studied as organic dyes in dye-sensitized solar cells due to their power conversion efficiency ( $\eta$ ), ease of preparation, high structural flexibility, high extinction coefficients in the visible region and relatively low cost [1–10]. Until now, many kinds of organic compounds containing cyanoacrylic acid group as acceptor have been developed for DSSCs, such as coumarin, indoline, triphenylamine and rhodanine [1–10], but there is rare report on their crystal structure determination [11]. In this study, we have synthesized new organic compounds containing cyanoacrylic acid (Scheme 1); characterized them by using elemental analysis (CHN), FT-IR, <sup>1</sup>H NMR and UV–Vis spectroscopy; investigated their atomic and electronic structure by single crystal X-ray diffraction and theoretical studies; and measured their photovoltaic properties.

## 2. Experimental

### 2.1. Materials and characterization

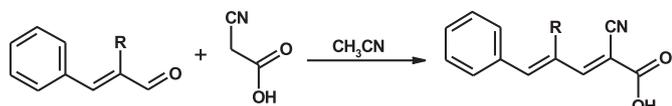
All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on an FT-IR Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN–O–Rapid analyzer. <sup>1</sup>H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in  $\delta$  units downfield from TMS. Absorption spectra were measured with Perkin–Elmer UV–Vis spectrophotometer.

### 2.2. Fabrication and characterization of DSSCs

The FTO conducting glass, titania oxide pastes of Ti nanoxide T/SP and Tinanoxide R/SP were purchased from Solaronix. A thin film of TiO<sub>2</sub> (16–18 mm) was coated on a 0.25 cm<sup>2</sup> FTO glass substrate. It was immersed in a THF solution containing  $3 \times 10^{-4}$  M dye sensitizers for at least 12 h, then rinsed with anhydrous acetonitrile

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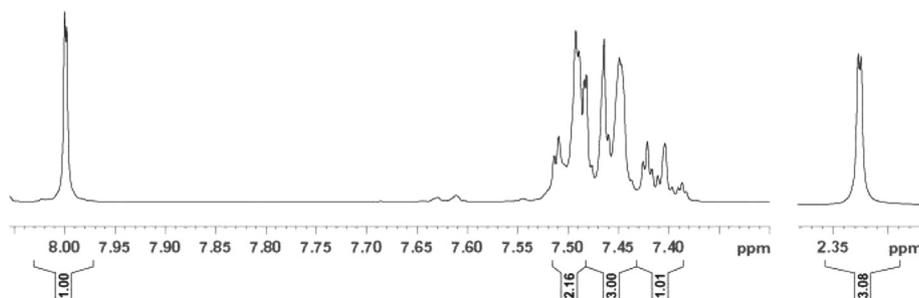


**Scheme 1.** Synthesis and structures of the title compounds, R = H (**1**) and R = Me (**2**).

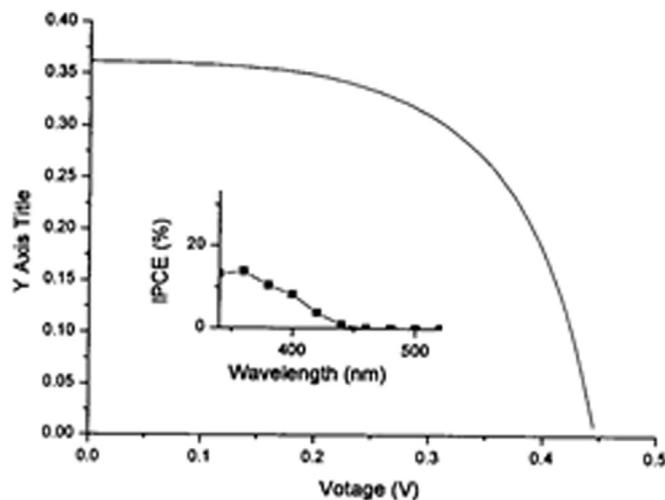
and dried. Another piece of FTO sputtered with 100 nm thick Pt was used as a counter electrode. The active area was kept of 0.25 cm<sup>2</sup> by adhering a 6 mm thick polyester tape on the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between the two electrodes. Two electrolytes were used, coded E1 and E2. E1 was an acetonitrile solution containing LiI (0.5 M), I<sub>2</sub> (0.05 M) and 4-tert-butylpyridine (TBP) (0.5 M), while E2 consisted of a solution of 3-dimethylimidazolium iodide (1.0 M), LiI (0.05 M), I<sub>2</sub> (0.03 M), guanidinium thiocyanate (0.1 M), and TBP (0.5 M) in MeCN: valeronitrile (85: 15, v/v). Devices made of a commercial dye N719 under the same conditions (3<sub>10</sub>4 M, Solaronix S.A., Switzerland) were used as a reference. The cell parameters were obtained under incident light with an intensity of 100 mW cm<sup>-2</sup> measured by a thermopile probe (Oriol 71964), which was generated by a 300 W (Oriol Class A Solar Simulator 91160A-1000, Newport) passing through an AM 1.5 filter (Oriol 74110). The light intensity was further calibrated by an Oriol reference solar cell (Oriol 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriol 74100) under short-circuit conditions. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/Gain-Phase analyzer (SI 1260, Solartron).

### 2.3. X-ray crystallography

Single crystals of the dimension 0.53 mm × 0.45 mm × 0.27 mm (**1**) and 0.40 mm × 0.27 mm × 0.14 mm (**2**) were chosen for X-ray diffraction study. Crystallographic measurements were done at 120 K with a four circle CCD diffractometer Gemini of Oxford Diffraction, Ltd., with mirrors-collimated Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Crystal structures were solved by charge flipping with program SUPERFLIP [12] and refined with the Jana2006 program package [13] by full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by ORTEP III [14]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, H atoms bonded to C were kept at ideal positions with C–H = 0.96 Å while positions of H atom bonded to O were refined freely. In both cases  $U_{\text{iso}}(\text{H})$  was set to 1.2  $U_{\text{eq}}(\text{C})$  or 1.5  $U_{\text{eq}}(\text{O})$ . All non-hydrogen atoms were refined using harmonic refinement.



**Fig. 1.** <sup>1</sup>H NMR spectrum of **2**.



**Fig. 2.** IPCE spectrum and  $J$ - $V$  curve of DSSCs based on **1**.

### 2.4. Theoretical study

The geometries of **1** and **2** were optimized by using Hartree-Fock (HF) and density functional method (B3LYP) with 6-31G basis set. All calculations were performed using the Gaussian 98 R-A.9 package [15].

### 2.5. Preparation of cin-aa (**1**)

Trans-cinnamaldehyde (0.4 mmol) and cyanoacetic acid (0.4 mmol) were dissolved in a mixture of methanol:acetonitrile (1:1 v/v, 20 ml) in the presence of piperidine (0.4 mmol). The mixture was stirred and refluxed for 1.5 h to give a clear yellow solution. The mixture was cooled and the product was allowed to crystallize by slow evaporation technique at room temperature. After 5 days, the formed yellow crystals of **1** were collected by filtration and dried at room temperature. *Anal.* Calc. for C<sub>12</sub>H<sub>9</sub>N<sub>1</sub>O<sub>2</sub>: C, 72.35; H, 4.55; N, 7.03%. Found: C, 72.43; H, 4.61; N, 6.98%. FT-IR (KBr, cm<sup>-1</sup>): 2221 (C≡N), 1678 (C=O), 1608, 1573 (C=C). UV-Vis, (CHCl<sub>3</sub>,  $\lambda_{\text{max}}$  (nm)); 393, 350. <sup>1</sup>H NMR (DMSO-*d*<sup>6</sup>,  $\delta$  (ppm)): 7.18 (dd, 1H), 7.45 (m, 3H), 7.60 (d, 1H), 7.67–7.70 (m, 2H), 8.08 (d, 1H), 13.25 (b s, 1H).

### 2.6. Preparation of mecin-aa (**2**)

Compound **2** was synthesized using the same procedure as that for **1**, except that alpha-methylcinnamaldehyde was used instead of trans-cinnamaldehyde. Yellow crystals of **2** were obtained. *Anal.*

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