



# Two-photon induced excimer emission of dicyanoisophorone derivative in crystal state



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## ABSTRACT

In this work, two-photon induced excimer up-conversion emission of dicyanoisophorone derivative (**1**) in crystal state is described. **1** shows crystal emission, with one-photon excitation both monomer and excimer emission are detected. An enhanced excimer emission of **1** in crystal state has been observed with a 800 nm Ti-sapphire femtosecond pulse laser, mechanism reveals that the enhanced excimer emission may result from the two-photon absorption. X-ray single crystal analysis demonstrates that the molecules of **1** adopt a face-to-face offset stacking mode in crystals, which benefits the excimers formation and emission.

## 1. Introduction

Two-photon pumped lasers have been regarded as a promising strategy [1,2] to accomplish frequency up-conversion of coherent light without phase-matching requirements. The early reported materials which exhibit up-conversion emission are usually from inorganic rare earth [3–5] or metal oxides semiconductors [6–8], and few are based on organic material due to the quench of emission of organic dye in solid state. Recently, with the development of the aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE), up-conversion based on organic materials has been developed [9–12].

Organic conjugated emitters have attracted considerable attention due to their various opto-functional applications. Early studies focused on the design and synthesis of organic molecules that exhibit active optoelectronic properties when they doped in polymeric thin film [13–16]. Since then, researchers have worked to enhance the properties of the molecules in crystal state [17–20], especially in organic nonlinear optical crystals [21–23] due to their potential application in the field of nanophotonics and biological imaging as the nonlinear probes in the near-field multiphoton fluorescence excitation imaging. Well-defined organic crystals, typically as single crystals, can provide not only high carrier mobility but also a visualized model to investigate basic intermolecular interactions and thus may precisely disclose the relationship between molecular packing modes and optoelectronic properties. Therefore, understanding and controlling molecular packing modes or conformation and the consequent intermolecular interactions

are very important for obtaining solid-state material with the desired chemical and physical properties [24–26].

In this paper we report the up-conversion emission of excimers in crystal based on a conjugated dicyanoisophorone derivative **1** (Scheme 1). The interest in fluorescence measurements was stimulated by the observation of an intense reddish luminescence emerging from the crystalline sample of **1** when illuminated with Ti-sapphire femtosecond pulse laser working at 800 nm wavelength. Preliminary study suggested that the up-conversion reddish emission resulted from the excimers of **1** in crystal with two-photon excitation.

## 2. Experimental

### 2.1. Materials and equipment

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 and 100 MHz, respectively, with TMS as an internal reference. MS spectra were recorded with TOC-MS spectrometer, respectively. UV absorption spectra and fluorescence spectra in solution were measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. Fluorescence quantum yields in solid state were measured with a fluorescence spectrophotometer (Edinburgh Instruments FLS-920). Solid absorption spectra were measured with UV-VIS-NIR spectrophotometer (Cray 50000, Varian). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reaction was

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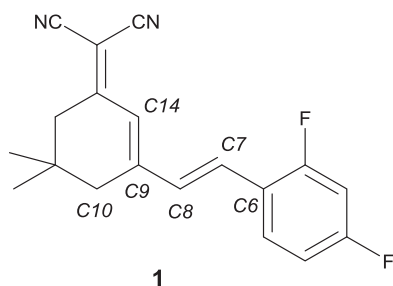
E-mail address: [yichen@mail.ipc.ac.cn](mailto:yichen@mail.ipc.ac.cn) (Y. Chen).

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Scheme 1. Chemical structure of 1.

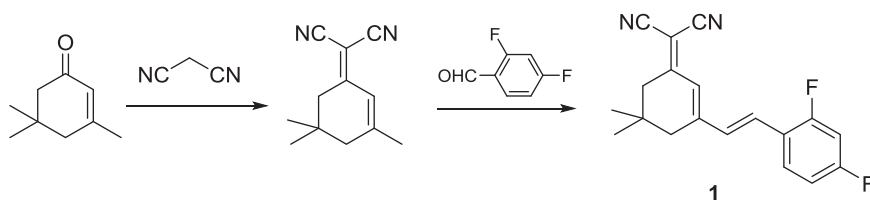
monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (70–230 mesh).

## 2.2. Experiment for two-photon pumped emission

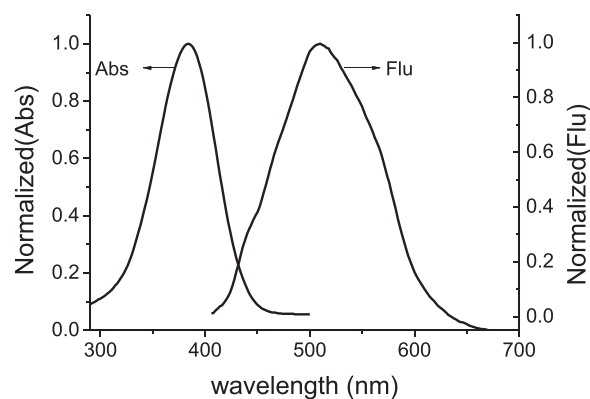
In two-photon pumped emission experiment, a Ti-sapphire laser system (Mai Tai HP, Spectra-Physics) with a pulse width of 120 fs and a repetition rate of 82 MHz was employed as an excitation light source. The energy of excited pulse can be controlled by neutral density filters, and the beam of excite laser was focused into the central of the cuvette with a plan-convex lens (focal length = 100 mm) under experiment. The fluorescence emitted from the sample was collected by a fiber spectrometer (SD 2000, Ocean Optics) and the detect direction is perpendicular to the laser transmission direction.

## 2.3. Synthesis of 1

The synthetic route for 1 was outlined in Scheme 2, and the detailed procedures were presented as follows: (a) To a solution of isophorone (3.8 g, 27.6 mmol) and malononitrile (1.82 g, 27.6 mmol) in dry ethanol (150 mL) was added piperidine (23 mg, 0.276 mmol). The solution was stirred at 60 °C till starting material disappeared (detected by TLC plate). After cooling to room temperature, the solution was slowly poured into water (200 mL) and the precipitated solid was filtered. Recrystallization from heptane afforded 2-(3,5,5-trimethylcyclohex-2-enylidene) malononitrile as a brown solid. Yield: 4.5 g (90%). M.p. 73–75 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.60 (s, 1 H), 2.53 (s, 2 H), 2.14 (s, 2 H), 2.01 (s, 3 H), 1.32 (s, 6 H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 170.3, 161, 120.2, 113.1, 76.4, 45.6, 42.3, 32.4, 27.5, 25.1. (b) Under argon, 2-(3,5,5-trimethylcyclohex-2-enylidene) malononitrile (1.86 g, 10 mmol) and 2,4-difluorobenzaldehydes (1.42 g, 10 mmol) are dissolved in dry acetonitrile (100 mL). Piperidine (0.85 g, 0.1 mmol) is added and the solution is stirred at 40 °C till starting material disappeared (detected by TLC plate). The solution is concentrated and the product is purified by flash column chromatography (elute: petroleum ether/ethyl acetate = 10 / 1, v/v). 1. Yield: 82%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53–7.47 (m, 1H), 7.08–7.04 (d,  $J$  = 16 Hz, 1H), 6.93–6.89 (d,  $J$  = 16 Hz, 1H), 6.86–6.76 (m, 3H), 2.54 (s, 2H), 2.39 (s, 2H), 1.01 (s, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 179.2, 159.3, 158.2, 136.5, 135.1, 129.5, 128.8, 126.3, 119.1, 114.0, 112.5, 110.4, 78.4, 42.0, 39.2, 35.3, 28.1. HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_2\text{N}_2$  ( $\text{M}^+$ ): 310.1282. Found: 310.1284.



Scheme 2. Synthesis of 1.

Fig. 1. Absorption and fluorescence of 1 in DCM solution (10  $\mu\text{M}$ ),  $\lambda_{\text{ex}}$  = 390 nm.

## 3. Results and discussion

### 3.1. Absorption and fluorescence of 1 in solution

Absorption of 1 in dichloromethane (DCM) dilute solution (10  $\mu\text{M}$ ) was measured. The linear absorption of 1 in DCM with a maximum at 384 nm ( $\epsilon = 4.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and the low-energy tail extended to  $\sim 450$  nm (Fig. 1). The polarity of solvents has a little influenced on the absorption of 1, and only 6 nm of red-shift was detected when the solvent was changed from DCM to DMSO. The small solvatochromism suggested that a weak intramolecular charge transfer existed in the molecules.

Upon excitation the solution of 1 with 390 nm light, nearly no fluorescence was observed by naked eye. With a large slit window ( $10 \times 10$  mm), one structureless emission peak at  $\lambda_{\text{em}} = 505$  nm with a shoulder at  $\sim 540$  nm was detected (Fig. 1). As shown in Fig. 1, no significant emission peak was detected wavelength beyond 600 nm. By using rhodamine B ( $\phi_{\text{r}} = 0.31$  in  $\text{H}_2\text{O}$ ) as reference, less than 0.1% of fluorescence quantum yield was obtained.

### 3.2. Emission properties of 1 in crystal state

Fig. 2 displays absorption and emission spectral of 1 in crystal state. The absorption of 1 in crystal state covered a wide range of 200–600 nm with two large peaks around 320 nm and 450 nm, respectively, which is quite different from that in solution. The wide and red-shifted absorption resulted from the aggregation of 1 at crystal state. One main emission maximum appeared at  $\lambda_{\text{max}} = 515$  nm with two significant shoulders around at 540 nm and 620 nm, respectively, were observed, and a small absolute fluorescent quantum yield of 4.5% was obtained. As compared to the solution, the original peaks at 510 nm and 540 nm, respectively, corresponded to the monomers emission. The small red-shift ( $\Delta \lambda_{\text{em}} = 10$  nm) may be due to a higher planarity of the molecule or more probably to aggregation in solid state. It is worth noting that a significant red emission at  $\sim 620$  nm was detected, which was not observed in the solution. Such a large red-shifted emission probably attributed to the excimer emission of 1 due to the molecules aggregation and a high planarity of the molecule in solid state [27].

To further confirm the excimer emission of 1 at  $\sim 620$  nm,

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