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# Red fluorescence thin film based on a strong push-pull dicyanoisophorone system

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**Abstract**: Dicyanoisophorone derivatives (1-3), which contain a strong push-pull chromophores system, have been prepared by a two-step condensation reaction, and their fluorescence in solution, polymeric thin film and pure solid state are measured. It is found that 1-3 exhibit no or weak fluorescence in both solution and pure solid state, but strong red fluorescence in polymeric thin film. Mechanism study implies that the enhanced fluorescence of 1-3 in polymeric thin film results from the restriction of intramolecular vibrational and rotational motions. In addition, it is also found that the polarity of polymeric matrix has influence over the fluorescence of dicyanoisophorone derivatives, using PMMA as polymeric matrix, a fluorescent thin film with a strong red emission is obtained.

*Keywords:* dicyanoisophorone derivatives, red fluorescence, polymeric matrix, thin film, push-pull chromophores system, synthesis.

#### 1. Introduction

Solid-state fluorescent dyes have created considerable interest in recent years owing to their wide potentials in material science [1-6] and biology [7-12]. From the standpoint of practical application, highly efficient solid-state emission is desired. However, most organic fluorophores exhibit strong fluorescence in dilute solutions but no or weak fluorescence in the solid state as a consequence of the tight molecular packing in the pure microcrystalline state or amorphous solid phase (thin film) [13, 14]. It has been revealed that strong intermolecular  $\pi$ - $\pi$  interaction is a principal factor of fluorescence quenching in the solid state [15,16].

Dicyanoisophorone derivatives with a push-pull chromophores system have attracted considerable attention due to their red fluorescence in both solution and in solid-state [17-21]. It has reported that dicyanoisophorone derivatives show unique enhanced emission rather than a fluorescence quenching upon aggregation in the solid state, the enhanced emission results from the impressive aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) in which the mechanisms include the effects of intramolecular planarization or restricted intramolecular vibrational and rotational motions in the solid state or of specific aggregation (H- or J-aggregation) or certainly a combination of all those effects depended on different structures and substituents [18,21]. Recently, we have found that the fluorescence of dicyanoisophorone derivatives with a push-pull chromophores system depend strongly not only on the chromophore used, but also on its environment [22]. Organic fluorescent dyes, which can exhibit fluorescence changes

upon the change of environment such as the formation of aggregates in pure solid state or doped in polymeric thin film, can be one of the most promising materials for the construction of desirable solid state fluorescent system [23-25]. To further understand the fluorescence behavior of dicyanoisophorone derivatives and to develop dicyanoisophorone-based solid state fluorescence system, we herein examine the fluorescence of dicyanoisophorone derivatives in polymeric thin film. Three dicyanoisophorone derivatives **1-3** (Scheme 1) are prepared, it is found that **1-3** show strong red emission in polymeric thin film, moreover, both emission wavelength and intensity are increased with the increase of the polarity of media. The mechanism implied that enhanced emission resulted from the inhibition of intramolecular vibrational and rotational motions of **1-3** in polymeric thin film.

## <Scheme 1>

## 2. Experimental

## 2.1. General

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

## 2.2. Chemical

The synthetic routes for target compounds 1-3 were presented in Scheme 2, and the detailed procedures were as follows: (a) To a solution of isophorone (3.8g, 27.6 mmol) and malononitrile (1.82g, 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. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 6.60 (s, 1H), 2.53 (s, 2H), 2.14 (s, 2H), 2.01 (s, 3H), 1.32 (s, 6H).  $^{13}$ C NMR (CDCl<sub>3</sub>): δ (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 (1.0 equiv.) and corresponding aromatic aldehydes (1.0 equiv.) were dissolved in dry acetonitrile (100 mL). Piperidine (0.01 equiv) was added and the solution was stirred at 40 °C till starting material disappeared (detected by TLC plate). The solution was concentrated and the product was purified by flash column chromatography (elute: petroleum ether / ethyl acetate = 10 / 1, v/v).

**1.** Yield: 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 16 Hz, 1H), 6.76 (d, J = 16 Hz, 1H), 6.73 (s, 1H), 6.64 (d, J = 8.9 Hz, 2H), 3.12 (s,

6H), 2.74 (s, 2H), 2.65 (s, 2H), 1.06 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl3):  $\delta$  = 169.2, 155.3, 151.2, 138.3, 129.5, 129.4, 124.4, 121.4, 114.1, 113.4, 112.3, 75.7, 42.9, 40.3, 39.2, 31.8, 28.1. HRMS (EI) calcd for C<sub>21</sub>H<sub>24</sub>N<sub>3</sub> (M<sup>+</sup>+1): 318.1970. Found: 318.1889. Anal. Calcd. For C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>: C, 79.46; H, 7.30. Found: C, 79.65; H, 7.18.

2. Yield: 55%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.39$  (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.72 (s, 1H), 6.31 (d, J = 8.0 Hz, 1H), 6.02 (d, J = 2.0 Hz, 1H), 3.40-3.35 (q, 4H), 2.56 (s, 2H), 2.50 (s, 1H), 2.47 (s, 2H), 1.19 (t, J<sub>1</sub> = 8.2 Hz, J<sub>2</sub> = 7.2 Hz, 6H), 1.06 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.8$ , 156.3, 149.2, 136.9, 135.3, 131.1, 130.5, 128.4, 124.4, 116.4, 113.6, 112.7, 78.4, 42.1, 41.3, 40.5, 37.8, 31.8, 28.2. HRMS (EI) calcd for C<sub>23</sub>H<sub>27</sub>N<sub>3</sub>O: 361.2154. Found: 361.2168.

**3**. Yield: 60%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.41 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 16.0 Hz, 1H), 6.70 (s, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.01 (d, J = 2.0 Hz, 1H), 4.38-4.32 (q, 2H), 3.39-3.34 (q, 4H), 2.57 (s, 2H), 2.49 (s, 2H), 1.42 (t, J<sub>1</sub> = 7.2 Hz, J<sub>2</sub> = 6.8 Hz, 3H), 1.18 (t, J<sub>1</sub> = 8.2 Hz, J<sub>2</sub> = 7.2 Hz, 6H), 1.05 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.8, 155.3, 151.0, 136.9, 134.5, 131.1, 129.8, 128.4, 124.3, 115.4, 113.6, 112.2, 78.8, 78.2, 65.0, 41.3, 40.8, 37.3, 31.7, 28.2, 14.8. HRMS (EI) calcd for C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>O: 389.2467. Found: 389.2471.

#### <Scheme 2>

## 2.3 The preparation of polymeric-fluorescent dye thin film.

PMMA and PS thin films were prepared as follows: **1-3** (1.0 mg, 0.5 mg, 0.25 mg) was dissolved in 2.0 mL of a PMMA–cyclohexanone solution (13%, w/w) or 2.0 ml

of a PS-toluene solution (5%, w/w). A film was obtained by spin coating a 0.35 ml PMMA-cyclohexanone solution or a 0.35 ml of a PS-toluene solution on quartz glass (size:  $2.5 \text{ cm} \times 1.2 \text{ cm}$ ), and dried in air at room temperature. The concentration of **1-3** in PMMA thin film is *ca* 0.1%, 0.2% and 0.4% (w/w), and in PS thin film is *ca* 0.25%, 0.5% and 1.0% (w/w).

#### 3. Results and discussion

#### 3.1. Optical properties of dicyanoisophorone derivatives 1-3 in solution

The optical properties of dicyanoisophorone derivatives 1-3 are measured in different solution (20 µM) and photophysical data are reported in Table 1. Absorbance and fluorescence spectra of compound 3 measured at room temperature in different solvents are shown in Fig. 1 and Fig. 2, respectively. Absorption data are characteristic of induced charge transfer transitions in push-pull dipolar molecules. It was found that the maximum absorption shifted from 480 nm to 504 nm when electron-donating substituent in benzene ring changed from H (1) to OCH<sub>3</sub>(3) in cyclohexane solution, which is in agreement with the assumption of intramolecular charge transfer (ICT), and an ICT enhancement results in the bathochromic shift of the absorption bands. In addition, a positive solvatochromism was observed for 1-3 in different solvent. As presented in Fig. 1, the maximum absorption shifted from 504 nm to 554 nm (3) when solvent changed from cyclohexane to DMSO. The solvatochromism is characteristic of induced charge transfer transitions in push-pull dipolar molecules, which is in agreement with this attribution and in agreement with reported in this type of molecules [18].

<Table 1> < Fig. 1>

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<Fig. 2>
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The fluorescence investigation of 1-3 in solvents exhibits that 1-3 show very weak fluorescence in solution, and small quantum yields ( $\phi_f$ ) are obtained using rubrene ( $\phi_f$ = 0.27, in MeOH) as reference [26] (Table 1). Further examination finds that 1-3show prominent solvent polarity dependent changes in their emission characteristics. It was found that the emission bands of 1-3 were significant bathochromic shift with increasing the polarity of solvents, the maximum emission shifted from 518 nm to 659 nm when solvent changed from cyclohexane to DMSO (Fig. 2). Moreover, a significant dependence of quantum yield with the polarity of solvent was observed, as presented in Table 1, the quantum yields of 1-3 were increased with the increase of the polarity of solvents, which is different from the common results in which the emission intensity of ICT compounds such as styryl dyes (comprised by strong donor and acceptor moieties joined by  $\pi$ -conjugation in a single molecule) is usually decreased with increase of polarity of solvents [27-29]. A possible explanation is that the styryl dyes with strong ICT character are much more polar in nature in excited states than that in ground states, the dye molecules in the excited state adopt a planar or quasi-planar conformation in large polarity solvent such that a large extent of charge is transferred from the strong electron donating moiety to the strong electron acceptor via the participation of the styryl  $\pi$ -conjugation, resulting in the enhancement

of emission intensity [30].

## 3.2. Fluorescence of dicyanoisophorone derivatives 1-3 in polymeric thin film

Both absorption and fluorescence of dicyanoisophorone derivatives 1-3 in polymeric thin film are measured. Relevant photophysical data are summarized in Table 2, and absorption and fluorescence spectral of dicyanoisophorone derivative 3 are shown in Figs. 3 and 4. It was found that the maximum absorption of 3 shifted from 524 nm to 540 nm when polymeric matrix changed from polystyrene (PS) to poly methyl methacrylate (PMMA), which suggested that ICT of 3 was increased with the increase of the polarity of polymeric matrix, that is in agreement with the result in solution. Similar results were obtained with 2 and 3 in polymeric thin film. Solid-state fluorescence of 1-3 showed that all compounds exhibited strong fluorescence emission in polymeric thin film. The quantum yields of 1-3 in different polymeric thin film were measured by an integrating sphere and the largest quantum yield of  $\phi = 0.64$  was obtained (Table 2). As compared to solution, the quantum yields of 1-3 in polymeric thin film are much larger than these in solution. Moreover, the emission bands of 1-3 were also significant bathochromic shift with increasing the polarity of polymeric matrix, the maximum emission of 3 shifted from 605 nm to 630 nm when polymeric matrix changed from PS to PMMA.

## <Table 2>

## <Fig. 3>

#### <Fig. 4>

## 3.3. A possible mechanism for enhanced fluorescence of 1-3 in polymeric thin film

To insight into a possible mechanism for the enhancement of fluorescence of dicyanoisophorone derivatives 1-3 in polymeric thin film, the aggregation-induced emission behaviors of 1-3 in polymeric thin film are investigated. It was found that the emission wavelength was red-shifted, but the fluorescence intensity was decreased when the concentration of 1-3 was increased. As presented in Figs. 5 and 6, upon increasing the concentration of 3 from 0.1% to 0.4% (w/w) in PMMA film or from 0.25% to 1.0% (w/w) in PS film, the emission wavelength had 10 nm red-shift for PMMA film or 8 nm for PS film, and at the same time, the fluorescence intensity was decreased about 35% in PMMA film and 74% in PS film, respectively. Similar results were obtained when 3 was replaced by 1 and 2. Red-shift in emission wavelength and decrease in fluorescence intensity with the increase of concentration implied that the aggregation of 1-3 in polymeric thin film did not increase the fluorescence but decrease the fluorescence, the quenched fluorescence probably resulted from the significant molecular interactions and self-absorption. In addition, control experiment showed that no or a very weak fluorescence ( $\phi_f \leq 0.005$ ) was detected upon excitation 1-3 in pure solid state (amorphous powder) due to the self-absorption resulted from the aggregation in the solid state. As shown in Fig. 7, the absorption of 3 in pure solid state red-shifted to near infrared region (~1000 nm), such a long absorption wavelength covered the emission band of 3, and caused strong re-absorption which resulted in the fluorescence quench.

## <Fig. 5>

<Fig. 6>

#### <Fig. 7>

The enhanced emission of 1-3 in polymeric thin film probably results from the restriction of intramolecular vibrational and rotational motions. To confirm the suggestion, the fluorescence of 1-3 in solution with different viscosity and different temperature are conducted. Control experiments showed that the fluorescence intensity of 1-3 in mixed EtOH-glycerol solution was increased when the viscosity of solution was increased. It was found that the fluorescence intensity of 3 was increased with increase of ratio of glycerol. As shown in Fig. 8, the fluorescent intensity of 3 was enhanced by 12% with a slight red-shift when added glycerol in mixed solvent was up to 10% (volume ratio). Similar results were obtained with 1 and 2. Besides, the effect of temperature on the fluorescence of 1-3 in solution revealed that a significant decrease in fluorescence when the temperature of solution was more than 30 °C. As shown in Fig. 9, the fluorescence of 1 was decreased by 28% when the temperature was increased from 30 °C (ambient temperature) to 50 °C. On the contrary, the fluorescence was increased by 17% when the temperature was dropped to 10 °C. Both viscosity-depended emission and temperature-depended emission suggested that the enhancement of fluorescence was probably from the restriction of intramolecular vibrational and rotational motions.

## <Fig. 8>

<Fig. 9>

## 4. Conclusions

In summary, red fluorescence thin film based on dicyanoisophorone derivatives with a strong push-pull chromophores system has been developed. It has demonstrated that dicyanoisophorone derivatives with a strong push-pull chromophores system exhibit strong red fluorescence in polymeric thin film due to the restricted intramolecular vibrational and rotational motions. It has also demonstrated that the polarity of polymeric matrix affects the fluorescence of dicyanoisophorone derivatives, with large polar polymeric matrix, strong and red-shifted emission is obtained.

Red fluorescence thin film with  $\lambda_{em} = 630 \sim 650$  nm is potential application in light-conversion for plants growing-up. Light ecology research shows that blue light region of 400 ~ 480 nm and red light region of 630 ~ 680 nm are good for photosynthesis. Organic fluorescence dyes have good compatibility with polymer medium and are easy processing. Fluorescent polymeric thin film with high photo-stable and strong red emission is desired. Further photo-stable studies as well as applications of the present fluorescent dyes to light-conversion for photosynthesis are in progress.

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11

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Compds	Solvent	$\lambda_{max}(nm)$	ε (l cm <sup>-1</sup> mol <sup>-1</sup> )	$\lambda_{em}(nm)$	$\phi_{f}$	$\Delta\lambda(nm)$
1	cyclohexane	480	31800	576	0.04	95
	CH <sub>3</sub> CN	494	27400	644	0.08	150
	DMSO	518	26000	659	0.10	141
2	cyclohexane	506	29900	578	0.02	72
	CH <sub>3</sub> CN	522	26900	645	0.04	123
	DMSO	558	31000	666	0.05	108
3	cyclohexane	504	41200	576	0.04	72
	CH <sub>3</sub> CN	526	39200	651	0.08	125
	DMSO	554	37200	666	0.09	112

Table 1. Spectroscopic data of compounds 1-3 in solution <sup>a</sup>

<sup>a</sup>  $\lambda_{abs}$ : maximum absorption wavelength,  $\lambda_{em}$ : maximum emission wavelength at ambient temperature,  $\epsilon$ : molar absorption coefficients at maximum absorption wavelength,  $\phi_f$ : fluorescence quantum yield using rubrene ( $\phi_f = 0.27$ , in MeOH) as reference.  $\Delta\lambda$ : Stoke's shifte calculated by ( $\Delta\lambda = \lambda_{em} - \lambda_{abs}$  nm).

Compds	polymer	$\lambda_{abs}(nm)$	$\lambda_{em}(nm)$	$\phi_f$	$\Delta\lambda(nm)$	
1	PMMA	506	610	0.64	104	
	PS	500	580	0.34	80	
2	PMMA	538	628	0.54	90	
	PS	524	604	0.28	80	
3	PMMA	540	630	0.49	90	
	PS	524	605	0.33	81	

Table 2. Spectroscopic data of compounds 1-3 in different polymeric thin film<sup>a</sup>

<sup>a</sup>  $\lambda_{abs}$ : maximum absorption wavelength,  $\lambda_{em}$ : maximum emission wavelength at ambient temperature,  $\phi_{f}$ : measured by an integrating sphere at ambient temperature.  $\Delta\lambda$ : Stoke's shifte calculated by ( $\Delta\lambda = \lambda_{em} - \lambda_{abs}$  nm).

17

## **Figures captions**

- Scheme 1. Chemical structure of target compound.
- Scheme 2. General synthetic route for dicyanoisophorone derivatives 1-3.
- Fig. 1. The absorption of 3 (20  $\mu$ M) in different solution.
- Fig. 2. The fluorescence of 3 in  $(20 \ \mu M)$  in different solution.
- Fig. 3. The absorption of 3 in different polymeric thin film.
- Fig. 4. The fluorescence of 3 in different polymeric thin film.
- Fig. 5. The fluorescence of 3 in PMMA thin film with different concentration
- (**3**/PMMA: 0.1%; 0.2%; 0.4% w/w).
- Fig. 6. The fluorescence of 3 in PS thin film with different concentration (3/PS: 0.25%; 0.5%; 1.0% w/w).
- Fig. 7. Absorption spectral of 3 in pure solid state (amorphous powder).
- Fig. 8. Fluorescence spectral change of 3 in mixed solvent (EtOH-glycerol).
- Fig. 9. Fluorescence spectral change of 3 in EtOH at different temperature.

# Scheme 1



Scheme 2







































## Highlight

- Dicyanoisophorone derivatives with a strong push-pull chromophores system is prepared.
- Strong red fluorescence thin film based on dicyanoisophorone derivatives is obtained.
- The enhanced fluorescence results from the restriction of intramolecular vibrational and rotational motions.