



# Design and synthesis of triphenylamine-malonitrile derivatives as solvatochromic fluorescent dyes

Yang Yang<sup>a,b</sup>, Bin Li<sup>a,\*</sup>, Liming Zhang<sup>a</sup>

<sup>a</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, PR China

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## ABSTRACT

A series of intramolecular charge transfer (ICT) molecules with multiple dicyanovinyl substitutes on triphenylamine were synthesized in good yields by Knoevenagel condensation of corresponding triphenylamine aldehydes and malonodinitrile. Photophysical property of these triphenylamine malonitrile dyes were studied, along with their intriguing solvatochromic behavior. The fluorescence emission of most dyes was highly sensitive to solvent polarity, yielding blue to yellow and even red fluorescence in different organic solvents. Both the fluorescence and the Stokes shifts were linearly dependent on the orientation polarizability ( $\Delta f$ ) and empirical polarity parameter  $E_T(30)$  according to Reichardt–Dimroth equation. Further analysis suggested that the solvatochromic behavior of these dyes was caused by dipole moment change upon excitation from ground to excited state.

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## 1. Introduction

Fluorescent dyes capable of changing their color and brightness upon various environment polarity, which are the so-called solvatochromic dyes [1,2], have recently attracted much attention because of their applicability as probes for the determination of solvent polarity as well as volatile organic compounds [3,4]. In the past decades, a wide variety of organic solvent-sensitive probes displaying either negative or positive solvatochromism have been reported [5–10]. As solvatochromism is based on the interaction between solvent and fluorophore molecules, solvent-dependent changes in the spectra of these solvatochromic dyes provide a sensitive response to changes in the surrounding environment.

The most well-established solvatochromic dyes are those that undergo excited state charge transfer, showing red shift of their emission band with increasing solvent polarity [11–13]. Another promising class is dyes undergoing excited state intramolecular proton transfer, showing solvent-sensitive dual emission [14,15]. Most of the environment sensitive dyes exhibit strong changes in dipole moment upon electronic excitation due to intramolecular charge transfer (ICT) from an electron-donor to an electron-acceptor group [16,17].

It is well-known that cyano group is one of the strongest electron-withdrawing groups. Electron accepting effect can be

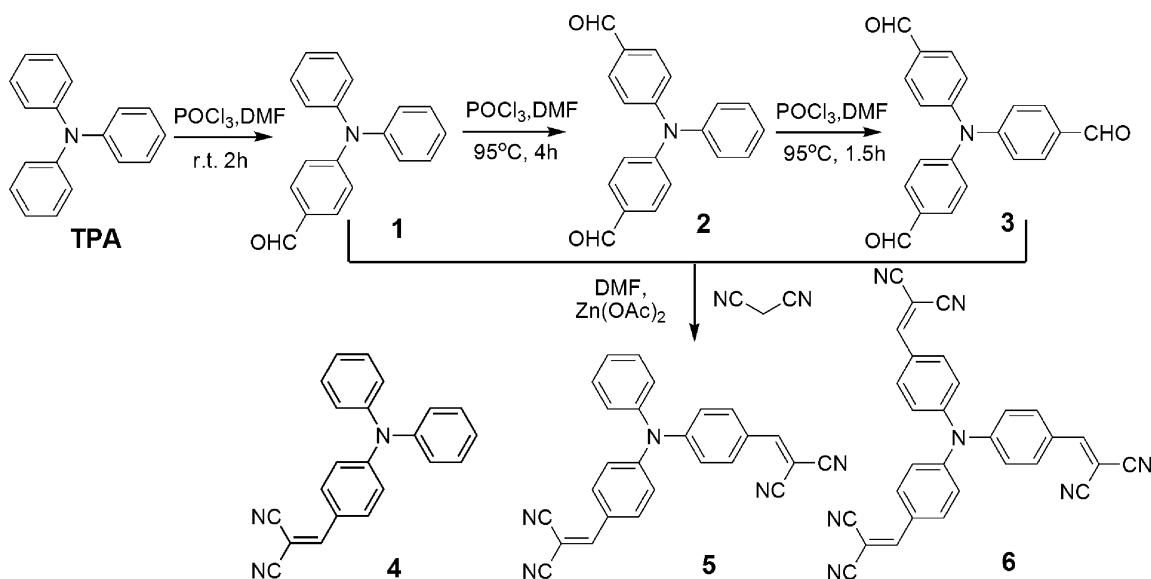
further enhanced by introducing several cyano groups into a conjugated system [18,19]. In this context, we have designed and synthesized a series of new multi-branched ICT compounds (4–6, Scheme 1), which contain different numbers of dicyanovinyl groups (electron acceptor), and the same triphenylamine core (electron donor) [20]. These chromophores have a common D– $\pi$ –A structural, especially for dye 6 which owns a tri-dendritic centrosymmetric D–( $\pi$ –A)<sub>3</sub> structural motif (where  $\pi$  is a  $\pi$ -conjugated bridge, D is a donor, and A is an acceptor) [21,22]. The novel chromophores possess potential application prospects due to their simple preparation and efficient initiating properties [23–27].

## 2. Experimental

### 2.1. Materials and physical measurements

Solvents were dried and distilled according to standard procedures prior to use. All other compounds were commercially available and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance 300 spectrometer using tetramethylsilane as the internal standard. IR spectra were recorded in diffuse reflection with a Magna 560 FT-IR spectrophotometer. All the photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The UV/vis spectra of freshly prepared solutions were performed with a Shimadzu UV-3101 spectrophotometer.

\* Corresponding author. Tel.: +86 431 86176935; fax: +86 431 86176935.  
E-mail address: [lib020@yahoo.cn](mailto:lib020@yahoo.cn) (B. Li).



Scheme 1. Synthesis of TPA-malononitrile dyes 4–6.

## 2.2. Synthesis of triphenylamine-malonitrile derivatives 4–6

**2-(4-Diphenylamino-benzylidene)-malononitrile (4)** To a solution of 4-(diphenylamino)-benzaldehyde **1** (273 mg, 1.0 mmol) and malononitrile (66 mg, 1.0 mmol) in DMF (10 mL) was added  $Zn(OAc)_2 \cdot 2H_2O$  (220 mg, 1.0 mmol) at rt. The reaction was monitored by TLC. After 2 h the reaction mixture was washed with water ( $5 \times 150$  mL), extracted with  $CH_2Cl_2$  and dried over  $MgSO_4$ . After removal of the solvent under a reduced pressure, the residue was purified with column chromatography (silica gel, petroleum ether/EtOAc, 10:1, v/v). The product **4** was obtained as orange powder in 92% yield (295 mg):  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.73 (d,  $J=9.0$  Hz, 2H), 7.51 (s, 1H), 7.38 (dd,  $J=10.4, 4.9$  Hz, 4H), 7.31–7.15 (m, 5H), 7.14–7.03 (m, 1H), 6.98 (dd,  $J=20.7, 8.2$  Hz, 2H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  157.82, 153.50, 145.19, 132.94, 129.95, 129.17, 126.72, 126.12, 124.18, 122.75, 118.50, 115.13, 114.02, 75.72; IR (KBr,  $cm^{-1}$ ):  $\nu=2928, 2678, 2360, 2217, 1567, 1448, 1314, 1190, 1075, 826, 696$ . Anal. Calcd for  $C_{22}H_{15}N_3$ : C, 82.22; H, 4.70; N, 13.08. Found: C, 82.02; H, 4.82; N, 13.16.

**2,2'-(4,4'-(phenylazanediyldene)bis(4,1-phenylene)bis(methan-1-yl-1-ylidene))dimalononitrile (5)** **4,4'-(phenylazanediyldene)dibenzaldehyde 2** (301 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol) and  $Zn(OAc)_2 \cdot 2H_2O$  (220 mg, 1.0 mmol) were used in accordance with the general procedure given above. The product **5** was obtained as red powder in 86% yield (341 mg):  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.84 (d,  $J=8.9$  Hz, 4H),

7.63 (s, 2H), 7.45 (t,  $J=7.5$  Hz, 2H), 7.34 (t,  $J=7.4$  Hz, 1H), 7.18 (d,  $J=8.7$  Hz, 6H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  157.58, 151.20, 144.25, 132.54, 130.42, 127.33, 125.84, 122.73, 114.13, 113.08, 79.54; IR (KBr,  $cm^{-1}$ ):  $\nu=3027, 2221, 1573, 1497, 1438, 1374, 1330, 1292, 1183, 828, 693$ . Anal. Calcd for  $C_{26}H_{15}N_5$ : C, 78.57; H, 3.80; N, 17.62. Found: C, 78.37; H, 3.90; N, 17.50.

**2,2'-(4,4'-(nitrotrilobenzaldehyde)trimalononitrile (6)** **4,4'-(nitrotrilobenzaldehyde 3** (329 mg, 1.0 mmol), malononitrile (198 mg, 3.0 mmol) and  $Zn(OAc)_2 \cdot 2H_2O$  (220 mg, 1.0 mmol) were used in accordance with the general procedure given above. The product **6** was obtained as dark red powder in 81% yield (383 mg):  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.92 (d,  $J=8.7$  Hz, 6H), 7.70 (s, 3H), 7.26 (t,  $J=3.3$  Hz, 6H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  157.47, 150.01, 132.78, 127.66, 124.88, 113.77, 112.76, 81.59; IR (KBr,  $cm^{-1}$ ):  $\nu=2923, 2854, 2358, 2219, 1578, 1557, 1497, 1372, 1310, 1270, 1183, 826, 610$ . Anal. Calcd for  $C_{30}H_{15}N_7$ : C, 76.10; H, 3.19; N, 20.71. Found: C, 76.02; H, 3.39; N, 20.65

## 3. Results and discussion

### 3.1. Synthesis

Substituted triphenylamines 1–3 were synthesized via Vilsmeier-Haack reaction with different ratios of Vilsmeier reagent and triphenylamine according to known procedures

Table 1  
Spectroscopic properties of dyes 4–6 in different solvents.

Solvent	$E_T(30)$	Dye 4			Dye 5			Dye 6		
		$\lambda_{abs}$	$\lambda_{em}$	$\Phi_F^a$	$\lambda_{abs}$	$\lambda_{em}$	$\Phi_F$	$\lambda_{abs}$	$\lambda_{em}$	$\Phi_F$
Hexane	31.0	428	490	0.081	454	473	0.335 <sup>c</sup>	/	/	/ <sup>b</sup>
$CCl_4$	32.4	437	513	0.091	465	497	0.298	451	473	0.192 <sup>c</sup>
Toluene	33.9	439	532	0.106	467	516	0.225	454	497	0.153
Ether	34.5	431	548	0.132	459	516	0.241	447	503	0.185
THF	37.4	433	574	0.026	464	536	0.192	454	527	0.19
EtOAc	38.1	431	572	0.023	461	535	0.179	450	526	0.184
$CH_2Cl_2$	40.7	443	585	0.011	474	538	0.223	460	525	0.142
Acetone	42.2	432	587	0.003	463	563	0.013	454	553	0.078
MeCN	45.6	432	574	0.001	462	569	0.003	454	559	0.01

<sup>a</sup> Quantum yields were determined at 25 °C by using either Quinine Sulfate (for 4,  $\Phi_F=0.55$  in 0.5 M  $H_2SO_4$ ) or Fluorescein (for 5 and 6,  $\Phi_F=0.88$  in 0.1 M NaOH) as standards.

<sup>b</sup> Could not be estimated due to low solubility.

<sup>c</sup> Low solubility in corresponded solvents.

[25,26]. Dicyanovinyl derivative 4 was synthesized by condensation of 1 with malonodinitrile [20,27]. The reaction was carried out in *N,N*-dimethylformamide (DMF) at room temperature with  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  as catalyst (Scheme 1). All new compounds were isolated as red-colored solids and found to be stable under ambient conditions. Their identity and structures were confirmed with NMR and mass spectra.

### 3.2. Photophysical properties

The solvatochromism of the novel dyes was measured in a number of solvents varying in polarity for which the solvent parameters are available (see Table S4 in ESI). The spectroscopic property of dyes 4–6 should be solvent dependent owing to their donor–acceptor arrangement. In particular, both the absorption and the fluorescence of these compounds should undergo solvent induced changes. Spectral red shifts in the absorption and the fluorescence are expected in polar solvents due to the stabilization of the ICT occurring between the terminal donor–acceptor groups. To confirm this hypothesis, the absorption and the fluorescence spectra of dyes 4–6 were investigated in organic solvents owing varying polarities [28].

At first, the absorption property of the new dyes was characterized in different organic solvents (Fig. 1). A slightly positive solvatochromism is observed, as the absorption maxima in polar solvents are red shift compared to those in apolar solvents (Table 1). This result suggests that the electronic excitation increases the dipole moment of the molecules and that the directions of the ground and excited state dipoles are similar to each other [10]. In other words, the electron transition types do not change and the red shift is indeed caused by ICT process, which has been significantly influenced by the surrounding medium [29].

Next, the fluorescence spectra of dyes 4–6 were studied in solvents with different polarities. For all three dyes, the emission spectra shift dramatically to longer wavelengths with increasing solvent polarity (Fig. 2). For example, the emission maxima for dyes 4, 5, and 6 are 513, 497, and 473 nm in  $\text{CCl}_4$  and 574, 569, and 559 nm in acetonitrile, respectively. Since each of dyes 4–6 bear electron donor and acceptor groups, a charge transfer (CT) probably occurs in the excited state from the electron-donor to the electron-acceptor group through the conjugation core. The CT process is expected to strongly increase the dipole moment in the excited state, explaining the positive fluorescence solvatochromism in these compounds. The shape of the emission spectra undergoes a slight change, suggesting that the change of solvent polarity exerts an impact on the emissive center. However, no new emission peak appears, indicating that the ICT process remains in different solvents. And the change in full width half maximum (FWHM, becoming wider) proves that the emissive center is stabilized by polar solvent molecules and the excitation state could be stabilized, leading to the wider spectra.

The emission spectra of dyes 4–6 are highly solvent sensitive, demonstrating that the engineering strategy is valid. As illustrated in Fig. 2 for dye 6, a marked red shift of the emission band is observed with increasing solvent polarity (Fig. 3). In contrast, the absorption is little affected. This suggests that an ICT phenomenon takes place after excitation, prior to emission, and that the emission stems from a strongly dipolar emissive state. The stabilization of the ICT state by solvent molecules, refers as solvent relaxation, usually brings changes in the intensity and shape of emission bands. Generally speaking, the more the solvent polarizes the lower energy of the relaxed state and the larger red-shift in fluorescence spectra can be seen. This relaxation effect is the key for the polarity-dependent fluorescence of dyes 4–6.

Solvent-dependent spectral shift is usually interpreted by the orientation polarizability ( $\Delta f$ ), according to the Lippert–Mataga

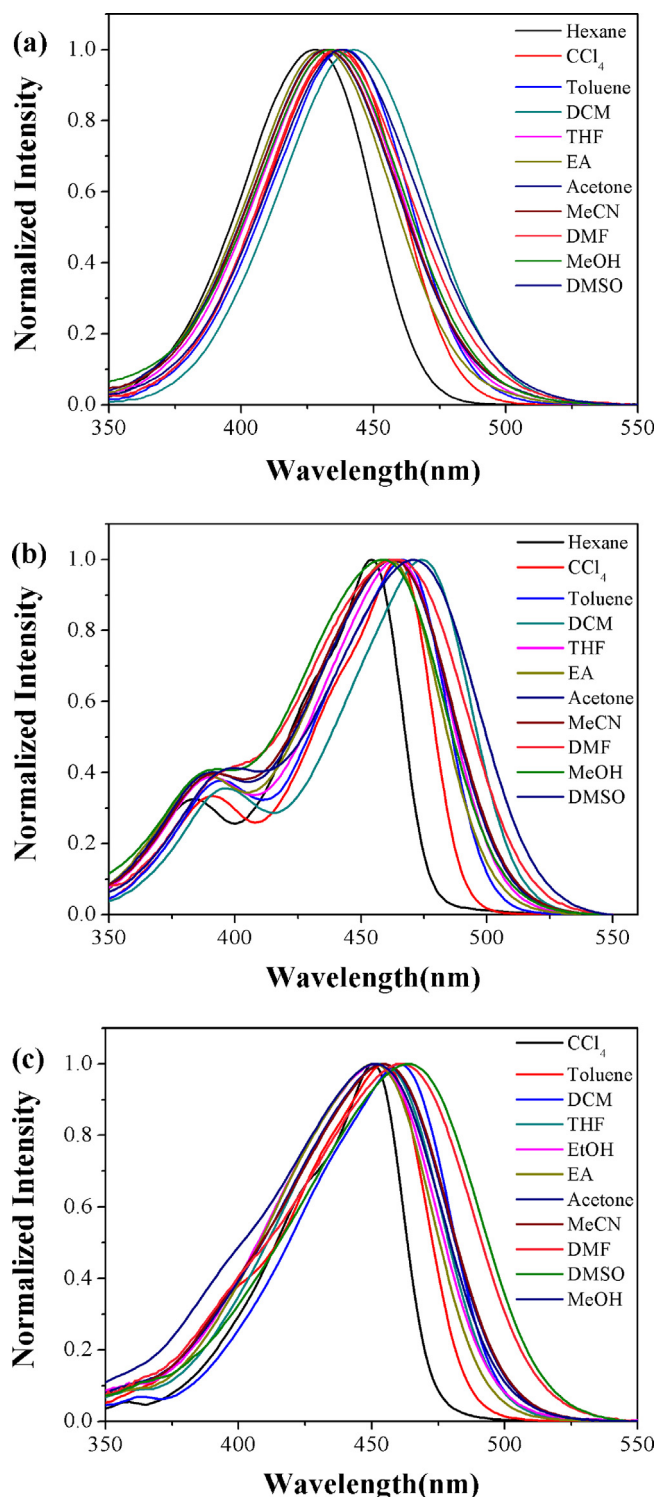
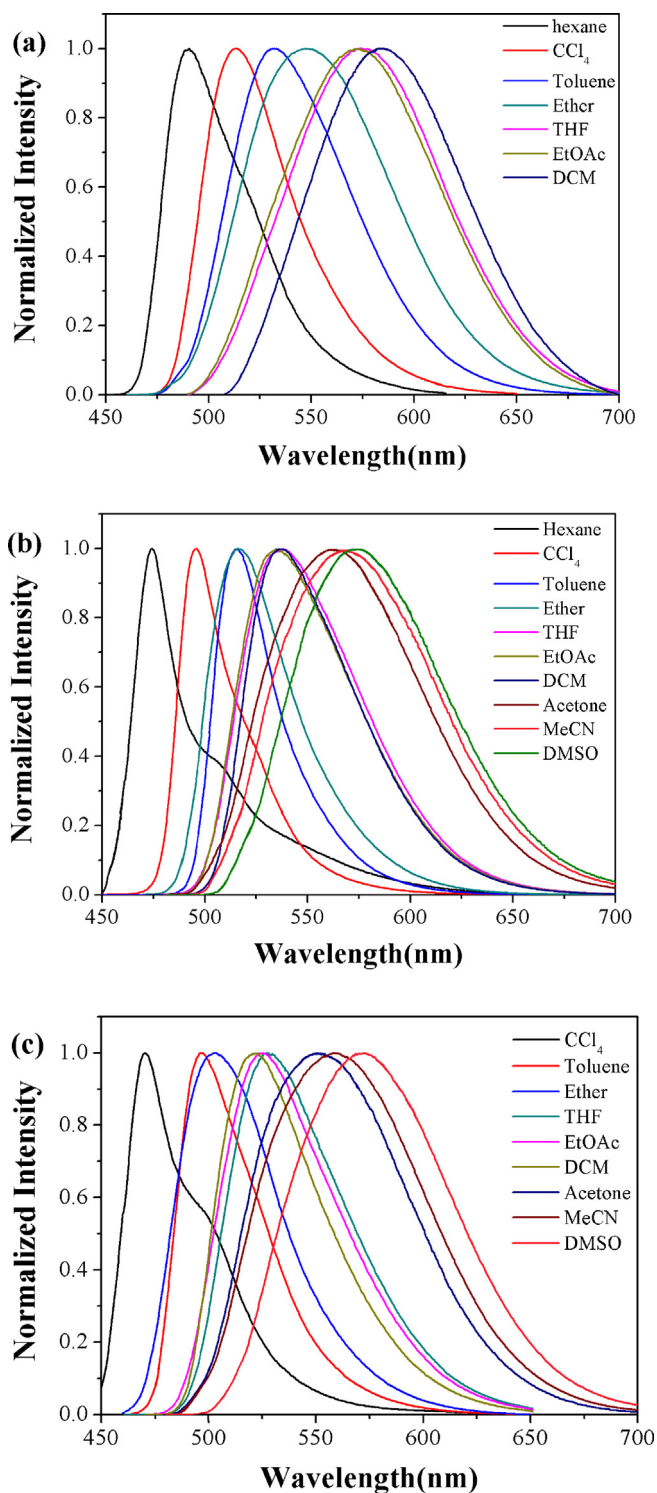


Fig. 1. Normalized absorption spectra of dyes 4–6 in different solvents. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

method [30]. This involves plotting the observed Stokes shift ( $\Delta\nu$ ) as a function of the solvent's orientation polarizability ( $\Delta f$ ), which is described by solvent's refractive index ( $n$ ) and its dielectric constant ( $\epsilon$ ), according to Eq. (1).

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$



**Fig. 2.** Fluorescence emission spectra of dyes 4–6 in different solvents (normalized emission spectra). The emission peak showed red shift with increasing polarity of solvents. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

Therefore, the Lippert–Mataga plot should be linear, provided the solvent–solute interactions are exclusively dipolar. However, as seen in Fig. 4, there is a poor linear correlation between the Stokes shift of 4 and the solvent orientation polarizability. Poor linear correlations are also observed for 5 and 6, implying that strong solute–solvent interaction other than dipole–dipole interaction occurs in the excited states of dyes 4–6.

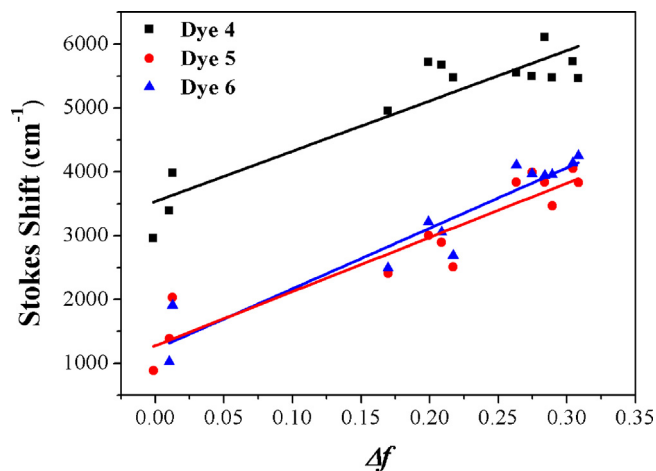


**Fig. 3.** Photographs of the solution of (a) 4 TPA-M, (b) 5 TPA-DM and (c) 6 TPA-TM 100  $\mu\text{M}$  under UV irradiation (365 nm) in different organic solvents. The successive solvents (left to right) corresponded to hexane,  $\text{CCl}_4$ , toluene, diethyl ether, THF, dichloromethane, ethyl acetate, acetone, acetonitrile and DMSO.

In order to get a deep understanding on the solvatochromism behavior of dyes 4–6, the Reichardt–Dimroth equation is introduced to describe the dependence of solvent induced fluorescence changes [31]. The empirical parameter  $E_T(30)$  is a measure of both polarity and acidity together, but is not dependent on polarizability. It is calculated from the maximum absorbance of pyridinium-Nphenolate betaine dye (RD) according to Eq. (2).

$$E_T(30)(\text{kal mol}^{-1}) = \frac{28591}{\lambda_{\text{max, RD}}} \quad (2)$$

A fine linear correlation between the position of the emission maximum and  $E_T(30)$  is observed for all three chromophores in aprotic solvents (Fig. 5), indicating the involvement of solvent polarity dependent ICT emissive states. The solvent-dependent red shift of the emission maximum grows in the following order: 6  $\rightarrow$  5  $\rightarrow$  4. For dye 4, the emission band shifts by 2770  $\text{cm}^{-1}$  from hexane to acetonitrile, and the corresponding shifts are 3169 and 3113  $\text{cm}^{-1}$  for 5 and 6, respectively. Moreover, the slope of the curves in Fig. 5 increases in the same order: 6  $\rightarrow$  5  $\rightarrow$  4, confirming the increase in solvent sensitivity. These differences in solvent sensitivity perfectly correlates with the length of  $\pi$ -conjugated system of the dyes and the differences in the electron polarizability which likely increase the dipole moment difference in the following order: 6  $\rightarrow$  5  $\rightarrow$  4.



**Fig. 4.** Dependence of the Stokes shifts of dyes 4–6 as a function of the Lippert parameter ( $\Delta f$ ).

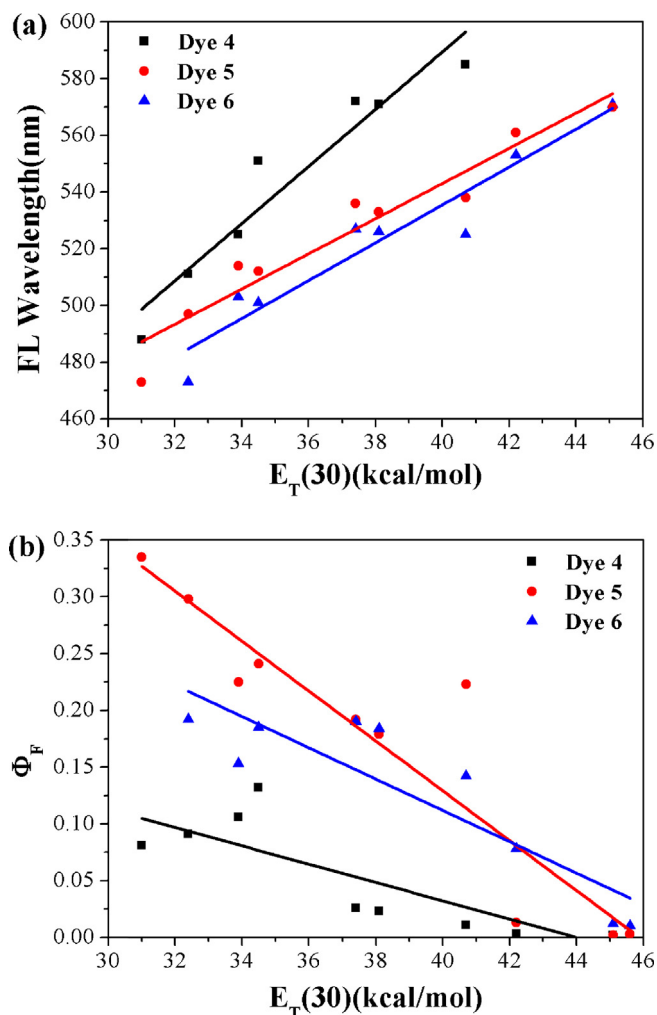


Fig. 5. Plot of the fluorescence maximum and quantum yields ( $\Phi_F$ ) of dyes 4–6 versus the  $E_T(30)$  polarity parameter of different solvents.

Fluorescence quantum yields ( $\Phi_F$ ) of dye 4 are observed as high as 0.132 in organic solvents of medium and low polarity (Table 1). The quantum yields of dyes 5 and 6 are generally higher in apolar solvents, but not in polar solvents. For dyes 5 and 6, a clear decrease in the  $\Phi_F$  is observed with the increase in the polarity index  $E_T(30)$  (Fig. 5). Noticeably, the decrease in  $\Phi_F$  with polarity is faster for 5 than that for 6, indicating that stronger dipolar moments favor the quenching by polar solvents [32,33]. In contrast, for the less dipolar dye 6, the solute–solvent and dipole–dipole interactions are more complex as QY is higher for solvents of medium polarity.

#### 4. Conclusion

In this work, a series of multi-branched chromophores with the same core and dicyanovinyl acceptors have been synthesized by Knoevenagel condensation reaction. The chromophores show outstanding solvatochromic behavior. Their emissions are tunable in visible region with large Stokes shift up to 20–90 nm. Their solvatochromism increases with the fluorophore conjugation length, providing extremely large spectral shifts, which according to the Lippert–Mataga expression is due to the large dipole moment difference. The considerable long-wavelength shift of the fluorescence spectra of the studied compounds with increase in solvent polarity is caused by the solvent relaxation. Due to their large red-shifted emission compared with that of Prodan and large Stokes shifts, the synthesized TPA-Malononitrile dyes have the potential to be

applied as probes in the investigation of binary solvent mixtures and monitor changes in solvent relaxation in low-polar media.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2013.03.108>.

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## Biographies

**Yang Yang** obtained his B.Sc. degree in 2005 and M.Sc. degree in organic chemistry from Northeast Normal University in 2008. He is currently carrying out his graduate work for PhD degree under the supervising of Professor Bin Li in condensed state physics in Changchun Institute of Optics Fine Mechanics and Physics of Chinese Academy of Sciences (CIOMP). His research focuses on the synthesis and application of fluorescent functional material in environmental and biological fields.

**Bin Li** received his PhD in 1997 in Inorganic Chemistry from Changchun Institute of Applied Chemistry of Chinese Academy of Sciences (CAS), and then he became a postdoc at the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University from 1997 to 1999. He joined the research group of Prof. V.W.W. Yam as a research assistant at Department of Chemistry of Hong Kong University in February 2000. He has been an associate professor since 1999 at NNU and a professor since 2003 at CIOMP of CAS. His current research interests are the study of application of transition metal complex as gas sensors, and the organic light emitting devices (OLED).

**Liming Zhang** received his B.Sc. degree in 2005 from Northeast Normal University and PhD in 2010 in condensed state physics in Changchun Institute of Optics Fine Mechanics and Physics of Chinese Academy of Sciences (CIOMP), and then he became a research assistant at CIOMP. His research interest is luminescent materials.