Sensors and Actuators B 183 (2013) 46–51

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

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

Yang Yang[a,b], Bin Li[a,*], Liming Zhang[a]

[a] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China
[b] University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 5 January 2013
Received in revised form 25 March 2013
Accepted 25 March 2013
Available online 3 April 2013

Keywords:
Triphenylamine
Malononitrile
Solvatochromic
ICT
Knoevenagel condensation

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 (Δf) 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.

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–π–A structural, especially for dye 6 which owns a tri-dendritic centrosymmetric D–(π–A)$_3$ structural motif (where π is a π-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

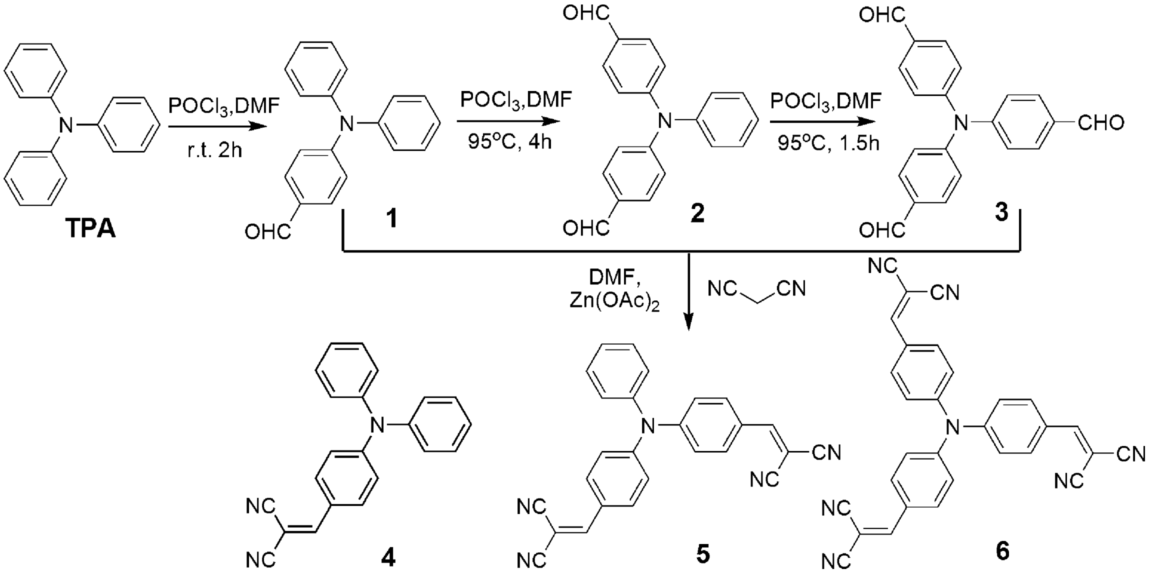
2.1. Materials and physical measurements

Solvents were dried and distilled according to standard procedures prior to use. All other compounds were commercially available and used as received. ^{1}H and ^{13}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 (B. Li).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.03.108



Scheme 1. Synthesis of TPA-malonitrile 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 × 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 power in 92% yield (295 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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}): ν = 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′-(phenylazanediyl)bis(4,1-phenylene)bis(methan-1-yl-1-ylidene))dimalononitrile (**5**).* 4,4′-(phenylazanediyl)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 power in 86% yield (341 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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}): ν = 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′,2″-(4,4′,4″-nitrilotris(benzene-4,1-diyl)tris(methan-1-yl-1-ylidene))trimalononitrile (**6**).* 4,4′,4″-nitrilotribenzaldehyde **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 power in 81% yield (383 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 157.47, 150.01, 132.78, 127.66, 124.88, 113.77, 112.76, 81.59; IR (KBr, cm^{-1}): ν = 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		
		λ_{abs}	λ_{em}	Φ_F [a]	λ_{abs}	λ_{em}	Φ_F	λ_{abs}	λ_{em}	Φ_F
Hexane	31.0	428	490	0.081	454	473	0.335[c]	/	/	/[b]
CCl_4	32.4	437	513	0.091	465	497	0.298	451	473	0.192[c]
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

[a] Quantum yields were determined at 25 °C by using either Quinine Sulfate (for 4, Φ_F = 0.55 in 0.5 M H_2SO_4) or Fluorescein (for 5 and 6, Φ_F = 0.88 in 0.1 M NaOH) as standards.
[b] Could not be estimated due to low solubility.
[c] Low solubility in corresponded solvents.