Dyes and Pigments 132 (2016) 282-290

Contents lists available at ScienceDirect

**Dyes and Pigments** 

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

### Triphenylethylene-based fluorophores: Facile preparation and fullcolor emission in both solution and solid states



PIĞMËNTS

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#### A R T I C L E I N F O

Article history: Received 1 February 2016 Accepted 6 April 2016 Available online 7 April 2016

Keywords: Fluorescence Full-color emission Materials science Solid-state luminescence Triphenylethylene

#### ABSTRACT

A series of triphenylethylene-based luminophoric molecules were efficiently synthesized. The substituent effect of the fluorophores on their photophysical properties was then investigated. Consequently, it was found that longer conjugated system and larger molecular dipole of the donor– $\pi$ –acceptor fluorophores could result in bathochromic shifts of UV–vis absorption and emission bands, so do the Stokes shifts. Especially, full-color fluorescent emissions in both solution and solid states could be achieved by changing conjugation length and substituents with different electron-donating or accepting abilities in the triphenylethylene skeleton. The density functional theory calculations further demonstrated that with the increase of the electron-donating or accepting abilities of the substituents, the energy gaps of the fluorophores gradually decreased, which elucidated the substituent effect of the organic fluorophores on their photophysical properties.

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#### 1. Introduction

Considerable interest about luminescent materials has been attracted to organic lighting-emitting diodes (OLEDs) because of their vast application in display and lighting in recent years [1-3]. However, many organic fluorophores with multiple aromatic rings suffer from the notorious aggregation-caused quenching (ACQ) effect in solid states [4–6]. In 2001, Tang's group discovered a novel and unusual phenomenon, termed aggregation-induced emission (AIE), which is an anti-ACQ effect [7]: Many molecules are weak or non-luminescent in the solution state but become highly emissive when in the aggregated states. It has technological implications to modulate solid-state optical properties of fluorophores due to their real world applications, which are commonly used as solid films in photonic and electronic devices [8–11]. Notably, motivated by the commercial potentials of full-color displays [12,13] and whitelighting emission [14–16], it has a urgent need to realize multicolor emission with molecular mixtures of similar chemical structures. However, a limited number of fluorophores was found to show admirable color-tunable AIE behaviors in the solid state. Most of the AIE-active molecules reported emit blue and green lights [17–20]. Triphenylethylene is also an AIE-type molecule [21–25]. It has a

twisted structure, and is relatively easily prepared. It can be transformed into its derivatives with donor $-\pi$ -acceptor (D $-\pi$ -A) system due to the asymmetric nature of its structure, which could modulate emission to longer wavelength more easily. Remarkably, the D $-\pi$ -A type molecules usually exhibit distinctive fluorescence properties owing to their intramolecular charge transfer (ICT) transitions, which endows them with tuned electronic states under various environments [26–29].

In this work, we designed and synthesized a series of triphenylethylene skeleton derivatives. Their max emission peaks could be tuned in full-color range both in solution and solid states by conjugation extension and introduction of the D $-\pi$ -A structure, from 383 nm to 643 nm in THF solution and from 458 nm to 687 nm in solid, respectively.

#### 2. Results and discussion

#### 2.1. Synthesis

Herein, we report a series of fluorophores 3a-c, 4a-c, 5a-c, and 7a-e based on a triphenylethylene skeleton consisting of various combinations of different substituent (Scheme 1). In the design of these compounds, we take the following factors into account. (i) As an AIE-type molecule, triphenylethylene can make its derivatives exhibit AIE properties [21–25]. (ii) Conjugation length extension can generate a significant bathochromic shift of fluorescent



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Scheme 1. Synthesis and structures of fluorophores 3a-c, 4a-c, 5a-c, and 7a-e.

emission [30]. (iii) Both electronic and steric effects of a cyano group affect the emission process of an AIE fluorophore [31–33]. (iv) The D $-\pi$ –A system is an attractive electronic structure for organic light-emitting materials because the photophysical and redox properties can be fine-tuned by the judicious combination of a donor and an acceptor [34–36]. By the combination of the conjugative effect, strong intramolecular push–pull electronic effect, and twisted structure, these fluorophores show fluorescence and large Stokes shifts in both solution and solid states.

By combining all the considerations above, the triphenylethylene derivatives 3a-c [37,38] were prepared through a Horner-Wadsworth-Emmons (HWE) olefination reaction from commercial substituted benzophenones 1a-c and phosphite ester 2 [39] in 70–80% vields in the presence of potassium *tert*-butoxide at 25 °C. The methoxyl  $(-OCH_3)$  and dimethylamino  $[-N(CH_3)_2]$  groups were employed as the electron donor (D) groups, because they had the different strength of the electron-donating ability which could be reflected from the molecular dipole moments (Table 1) and the substrates could be obtained directly from the commercial reagents. At the same time, a cyano (-CN) group was introduced as an electron acceptor (A) group in order to facilitate subsequent functional group transformation. Then, reduction of the -CN groups in compounds **3a-c** by DIBAL-H afforded the aldehydes **4a-c** [11,40,41] in 90–95% yields (another type fluorophores). With the aldehydes **4a**–**c** in hand, on one hand, the  $\pi$ -extended derivatives **5a–c** were obtained in 70–80% yields by the HWE olefination reaction of aldehydes **4a–c** with phosphite ester **2** under the same conditions as described above. On the other hand, in order to make the conjugated system more twisted for increasing AIE effect of the molecules, compounds **7a–c** were synthesized in 80–88% yields through the Knoevenagel condensation of aldehydes **4a–c** with phenylacetonitrile **6a**. Another two compounds **7d** and **7e** were also synthesized from aldehydes **4a** and **4b** with *p*-nitrobenzeneacetonitrile **6b** in 90–94% yields for the increasing of molecular polarity by the introduction of nitro (–NO<sub>2</sub>) group. The chemical structures of the new compounds were all characterized by <sup>1</sup>H and <sup>13</sup>C NMR, and high resolution mass spectra (see supporting information).

#### 2.2. Photophysical properties

With all the synthetic compounds in hand, UV–vis absorption spectra was first investigated in diluted THF solution (Table 1 and Fig. S1). The spectra of the fluorophores **3a**, **4a**, **5a**, and **7a** show a single absorption band corresponding to a  $\pi$ – $\pi$ \* transition with  $\lambda_{max}$  at 321 nm (**3a**), 333 nm (**4a**), 366 nm (**5a**), and 366 nm (**7a**), respectively. The introduction of electron-donating (D) groups in the benzene ring of triphenylethylene skeleton produces the emergence of a new transition from 350 nm (**3b**) to 436 nm (**7c**) assigned to an intramolecular charge transfer (ICT) between the

Table 1	
Photophysical properties of fluorophores 3a-c, 4a-c, 5a-c, and 7a-e in solution and	powder.

Samp	les Band gap	o (eV) <sup>c</sup> Band gap (e	eV) <sup>d</sup> Dipole moment (D) <sup>d</sup>	Solution <sup>a</sup>						Solid <sup>b</sup>				
				$\lambda_{abs} (nm)^{a}$	λ <sub>em</sub> (n	nm) Stokes s	hift (nm) $\Phi$	e <sub>f</sub> (%) <sup>e</sup>	$\tau (\text{ns})^{\text{f}}$	$\lambda_{abs}$ (n	$(m)^{g} \lambda_{em} (nm)$	) Stokes	shift (nm) $\Phi_{\rm f}$ (%)	$r^{\rm e} \tau (\rm ns)^{\rm f}$
3a	3.46	3.94	5.8	321	390	69		4.6	31.0	343	467	124	38.2	2.5
3b	2.97	3.71	8.2	291, 350	395	45		4.5	6.9	388	485	97	10.7	_h
3c	2.77	3.33	9.4	267, 364	412	48	-	5.6	7.1	415	550	135	0.6	_h
4a	3.31	3.77	4.1	333	383	50		3.9	25.4	347	458	111	5.5	0.5
4b	3.08	3.51	6.1	292, 356	396	40		6.6	6.7	375	525	150	1.2	_h
4c	2.65	3.16	7.4	271, 407	401	_		5.9	7.0	445	578	133	0.4	_h
5a	3.01	3.25	6.6	366	456	90	1	6.6	0.5	395	482	87	36.0	1.5
5b	2.88	3.07	9.1	298, 379	467	88		3.0	1.9	395	524	129	43.0	1.1
5c	2.58	2.75	10.8	328, 415	481	66		4.2	1.0	437	592	155	9.1	0.4
7a	2.96	3.22	4.4	366	468	102		4.5	1.0	339	499	160	34.4	1.5
7b	2.79	3.09	7.0	290, 388	510	122	:	2.8	0.5	410	519	109	26.5	0.3
7c	2.43	2.77	7.8	324, 436	616	180	-	5.3	0.3	449	636	187	5.3	1.0
7d	2.75	2.95	8.5	313, 381	552	171		4.6	_h	413	619	206	46.1	11.7
7e	2.48	2.68	11.6	421	643	222		4.5	1.4	450	687	237	1.4	2.4

 $^a\,$  Measured in THF (10  $\mu M).$ 

<sup>b</sup> Measured using powder.

<sup>c</sup> Calculated from UV-vis absorption.

<sup>d</sup> Calculated from DFT calculations [B3LYP/6-31G(d) level] by Gaussian 09 program.

<sup>e</sup> Absolute fluorescence quantum yield determined with a calibrated integrating sphere system.

<sup>f</sup> Averaged fluorescence lifetimes.

<sup>g</sup> Measured using thin film prepared from CH<sub>2</sub>Cl<sub>2</sub> solution.

<sup>h</sup> Fluorescence lifetimes were too short to detected

electron donor of the molecules and the electron acceptor groups. Comparison of the UV–vis absorption spectra of fluorophores **3b–c** and **4b–c** showed that the replacement of the –CN group by the –CHO group induces a bathochromic shift of the  $\pi$ – $\pi^*$  transition (**3b**: 291 nm, **4b**: 292 nm, **3c**: 267 nm, **4c**: 271 nm) and ICT bands (**3b**: 350 nm, **4b**: 356 nm, **3c**: 364 nm, **4c**: 407 nm). For the fluorophores **5b**, **5c**, **7b**, and **7c**, the bathochromic shifts for ICT bands (**5b**: 379 nm, **7b**: 388 nm, **5c**: 415 nm, **7c**: 436 nm) were observed with the transfer of –CN group from benzene to olefin, while the hypsochromic shift for the  $\pi$ – $\pi^*$  transition (**5b**: 298 nm, **7b**: 290 nm, **5c**: 328 nm, **7c**: 324 nm). Compared to fluorophores **7a** and **7b**, the ICT bands of fluorophores **7d** and **7e** were observed at longer wavelengths (**7d**: 381 nm, **7e**: 421 nm) when the stronger electron accepting –NO<sub>2</sub> groups were introduced.

For all the synthetic fluorophores, as UV-vis absorption tuned from 321 nm (**3a**) to 436 nm (**7c**) by the extension of conjugation length with additional phenylethylene unit and incorporation of electron-donating (D) and electron-accepting (A) groups, the maximum emission of the selected fluorophores range from 383 nm (4a) to 643 nm (7e) with the absolute fluorescence quantum yields (FQYs) around 2.8-16.6% in THF solution. It can be attributed to the intramolecular rotation of benzene rings in dilute solutions and the non-radiant energy consumption resulting in low quantum yields (most  $\Phi_{\rm f}$  < 10%). Then fluorescence lifetimes of the fluorophores were measured. The fluorescence decay of fluorophore 5c obeyed mono-exponential function with fluorescence lifetime of 1.0 ns. The other fluorophores obeyed bi-exponential or tri-exponential function with averaged fluorescence lifetimes around 0.3-31.0 ns (Fig. S5 and Table S1). They all fell into the nanosecond region. And the solution emission color ranging from blue to red covered the whole visible region (Fig. 1). Accordingly, the band gap energy became narrower with additional conjugation units or introducing electron-donating (D) and electron-accepting (A) groups (Table 1). The fluorophores of  $D-\pi-A$  substituted pattern exhibited the larger bathochromic emission and smaller band gap energy.

Then the substituent and the regioisomeric effects on the photophysical properties of the fluorophores were investigated. The maximum emission of **3b** (395 nm) and **4b** (396 nm) with two  $-OCH_3$  groups exhibited 5 nm and 13 nm bathochromic shifts



**Fig. 1.** Fluorescent emission spectra of fluorophores 3a-c, 4a-c, 5a-c, and 7a-e in tetrahydrofuran at 10  $\mu$ M.

compared with 3a (390 nm) and 4a (383 nm), respectively. However, the maximum emission of 4c (401 nm) exhibited significantly hypsochromic shift compared to 3c (412 nm) when the stronger electron-donating ability group -N(CH<sub>3</sub>)<sub>2</sub> was introduced in the benzene rings of the triphenylethylene skeleton. But for the two types of longer  $\pi$ -conjugated molecules (**5a**-**c** and **7a**-**c**), the maximum emission of **7a** (468 nm), **7b** (510 nm), and **7c** (616 nm) exhibited 12 nm, 43 nm, and 135 nm bathochromic shifts compared with **5a** (456 nm), **5b** (467 nm), and **5c** (481 nm) when -CN groups transformed from the benzene groups to the olefins, respectively (Table 1 and Fig. S2). Compared to fluorophores **7a**–**b**, when the stronger electron-accepting ability groups -NO<sub>2</sub> were introduced, fluorophores 7d (552 nm) and 7e (643 nm) exhibited more significantly bathochromic shifts. It is very interesting that fluorophores 7a-e exhibited large Stokes shifts (102-222 nm). Especially, fluorophores 7c (180 nm), 7d (171 nm), and 7e (222 nm) showed larger Stokes shifts, which will be vital to their real world applications [42,43]. Thus, the enhancement of the molecular dipole of the D $-\pi$ -A fluorophores resulted in the bathochromic shift of the UV–vis absorption, so do the fluorescent emission.

The photophysical properties of the fluorophores in the solid state were also further investigated. All these fluorophores showed broad solid-state absorption in the UV–visible region ranged from 339 nm (**7a**) to 450 nm (**7e**) (Table 1 and Fig. S3). As shown in Fig. 2(a), the emissions of fluorophores **3a–c**, **4a–c**, **5a–c**, and **7a–e** covered the whole visible region in the solid state and had further bathochromic shifts compared with those in solution. The maximum emission ranged from 458 nm (**4a**) to 687 nm (**7e**).

As most of these AIE molecules, the non-planar structure of the triphenylethylene skeleton was effective to avoid the intermolecular  $\pi - \pi$  stacking in solid states, and subsequently prevent the fluorescence quenching of the fluorophores. Consequently, by changing the substituents with different electron-donating or electron-accepting abilities in the skeleton, a series of triphenylethylene-based fluorophores with full-color fluorescent emissions in the solid state could be obtained with the absolute fluorescence quantum yields (FQYs) around 0.4-46.1%. As shown in Table 1, among the synthesized fluorophores, the emission intensity of these compounds was dependent on the introduced electron-donating (D) or electron-accepting (A) groups. For the same conjugation structure, when the donor groups [-OCH<sub>3</sub> and -N(CH<sub>3</sub>)<sub>2</sub>] were attached to the benzene rings of the triphenylethylene skeleton, the FQYs were decreased. Even, the FQYs of fluorophores with the substitution of  $-N(CH_3)_2$  in solid state were decreased much more (3c: 0.6%, 4c: 0.4%, 5c: 9.1%, 7c: 5.3%). We speculated that it might be owing to the lone electron pairs of the nitrogen atoms  $[in -N(CH_3)_2]$  partially quenched the fluorescence of the four fluorophores. While the -CHO group as an acceptor group connected to triphenylethylene, the FQYs of fluorophores 4a-c were below 10% and lower than those in solutions. Compared to fluorophores 4a-c, the emission intensity of fluorophores 5a-c which submitted by -CN group was obviously enhanced in solid state. However, the FQYs of the fluorophores with  $-NO_2$  group as acceptor were dependent on the introduced donor group, such as fluorophores 7d and 7e. The fluorescence decay of fluorophore 4a obeyed mono-exponential function with fluorescence lifetime of 0.5 ns. The other fluorophores obeyed bi-exponential or tri-



**Fig. 2.** (a) Fluorescent emission spectra of fluorophores **3a–c**, **4a–c**, **5a–c**, and **7a–e** in powder. (b) Photographs of the powder of selected fluorophores **3a**, **4a**, **5a–c**, and **7a–e** under 365 nm UV light.

exponential function with averaged fluorescence lifetimes around 0.3–11.7 ns, but the fluorescence lifetimes of fluorophores **3b–c** and **4b–c** were too short to be detected (Table 1, Fig. S6, and Table S2). As shown in Fig. 2(b), the fluorescence photos of the selected fluorophores **3a**, **4a**, **5a–c**, and **7a–e** in powder under 365 nm irradiation unambiguously demonstrated their panchromatic properties. In addition, all the fluorophores **3a–c**, **4a–c**, **5a–c**, and **7a–e** (except **3b** and **5a**) exhibited the large Stokes shifts of more than 100 nm in the solid state as well (Table 1 and Fig. S4). Especially for fluorophore **7e**, the Stokes shift is even up to 237 nm, which could effectively avoid imaging interference of absorption bands to the emission bands.

#### 2.3. Analysis of structure-property relation

To confirm the molecular structures of these species and understand the above emission features of these fluorophores. X-ray single crystal analysis has been conducted for compounds 3a, 3c, and **7b**. The crystals suitable for X-ray analysis were obtained from petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> [44]. The crystal structures of compounds 3a and 3c were shown in Fig. 3. It was found that the triphenylethylene skeleton displayed a twisted framework as the dihedral angles between three benzene rings and the central ethylene moiety are 6.7°, 69.9°, 26.7° (3a) and 40.7°, 60.8°, 13.9° (3c), respectively (Fig. S7 and Fig. S8). These non-planar structure could restrain the intermolecular face-to-face packing. The 3a molecules are arranged in a loose manner, and  $\pi - \pi$  intermolecular interactions are hampered, owing to steric hindrance imposed by one of the benzene rings without CN-substituted, which can effectively minimize the quenching of fluorescence caused by solid aggregation to give a 38.2% absolute fluorescence quantum yield in the solid state [Fig. 3(a,b)]. However, compared with compound 3a, the 3c molecules appeared closer arrangement in crystal packing, where the distance between the carbon atom of benzene connected with  $-N(CH_3)_2$  group and the plane of the benzene ring with CNsubstituted in adjacent molecule is 3.47 Å [Fig. 3(c,d)]. This allowed a certain degree of overlap of conjugated system between adjacent molecules, and then resulted in a certain  $\pi - \pi$  stacking interactions. which led to fluorescence quenching. So compound 3c gave only a 0.6% absolute fluorescence quantum yield in the solid state.

The crystal structure of compound **7b** was shown in Fig. 4. The triphenylethylene framework is distorted as the dihedral angles between three benzene rings and the central ethylene moiety are  $36.8^{\circ}$ ,  $66.3^{\circ}$ , and  $20.1^{\circ}$ , respectively (Fig. S9). It was noted that two hydrogen atoms (in  $-OCH_3$ ) interact with -CN group (neighboring molecule) and one of the benzene rings of the triphenylethylene



Fig. 3. Single crystal structures of compounds 3a (a,b) and 3c (c,d) from the packing view.



**Fig. 4.** Single crystal structure of compound **7b** from the (a) b axis view and (b) packing view.

framework (neighboring molecule) to form one OCH2-H···N hydrogen bond (2.73 Å) and one OCH<sub>2</sub>-H··· $\pi$  bond (2.82 Å), respectively. Then a network is formed in the crystal as shown in Fig. 4(a), the oxygen atom  $(in - OCH_3)$  interacts with one hydrogen atom of the benzene ring of the triphenylethylene framework (neighboring molecule) to form one  $C-H\cdots O$  hydrogen bond (2.70 Å). The molecules arranged in two layers with two opposite directions [Fig. 4(b)]. The two layers were induced by two CH···C interactions with distances 2.87 Å and 2.78 Å, respectively. It is the OCH<sub>2</sub>-H···N hydrogen bond that fix the double bonds, and prevent the free twisting motions around the double bonds. Assisted by the strong supramolecular interactions, the molecule becomes more rigid. The twisted structure of compound **7b** prevents  $\pi - \pi$ stacking interactions along the long molecular axis by the bulky -CN and phenyl substituents. Thus the strong supramolecular interactions induce tight packing and rigid molecules, without parallel stacking, making compound **7b** show strong fluorescence with 26.5% absolute fluorescence quantum yield in the solid state.

To gain insight into the influence of the  $\pi$ -conjugted system in the ground state and electronic effect of substituents on the aromatic rings of the skeleton, density functional theory (DFT) calculations [B3LYP/6-31G(d) level] of fluorophores **3a–c**, **4a–c**, **5a–c**, and **7a–e** were further carried out by Gaussian 09 program, and the optimized geometries and HOMO/LUMO plots of the fluorophores are illustrated in Fig. 5. All of the molecules adopt twisted nonplanar conformations at the terminal aromatic rings, which is favorable for active intramolecular rotations of the aromatic rings in solution. Obviously, the electron density of the LUMOs are mainly localized over the electron-accepting moieties, but the electron density of the HOMOs are mainly distributed on the substituted tristyl moieties. Compared with compounds **3a** and **4a**, the HOMOs of compounds 3c and 4c with the strong electron-donating -N(CH<sub>3</sub>)<sub>2</sub> group showed upshift more seriously than their LUMOs, respectively. Therefore, the energy gaps of compounds 3c (3.33 eV) and **4c** (3.16 eV) were smaller than that of compounds **3a** (3.94 eV) and **4a** (3.77 eV), which well explained that the absorption and emission bands of compounds **3c** and **4c** were longer than those of compounds **3a** and **4a**. Fluorophores **5a–c** and **7a–c** have similar results compared with fluorophores **3a**–**c** and **4a**–**c**, but the HOMOs of compounds 7d and 7e with the strong electronaccepting -NO<sub>2</sub> group moved to downshift, while their LUMOs showed downshift more seriously. Hence, the energy gaps of compounds **7d** (2.95 eV) and **7e** (2.68 eV) were smaller than that of compounds **7a** (3.22 eV) and **7b** (3.09 eV), which well explained that the absorption and emission bands of compounds 7d and 7e were longer than those of compounds 7a and 7b. Thus, the panchromatic emissive properties of the triphenylethylene-based fluorophores could be theoretically explained.

#### 3. Conclusions

In summary, we have obtained a series of triphenylethylenebased fluorophores exhibiting fluorescent emission in the region ranging from blue to red in both solution and solid states. By changing the conjugation length and the substituents on the triphenylethylene skeleton, the fluorescent emission wavelength could cover the entire visible spectral region with maxima wavelengths ranging from 390 nm to 643 nm in solution and 458 nm-687 nm in solid state. Some structure-property relationships were rationalized by a combination of X-ray crystallographic analysis and DFT calculations. It showed that with the increase of the electron-donating abilities or electron-accepting abilities of the substituents, the energy gaps of the fluorophores gradually decreased, which theoretically elucidated the substituent effect of the fluorophores on their photophysical properties. Comparing to other reported fluorophores, the synthetic triphenylethylene-based fluorophores mentioned above enjoy the advantages of facile synthesis and tunable full-color fluorescent emission, which would provide more opportunity for their real world applications.

#### 4. Experimental section

#### 4.1. General information

All reactions that required anhydrous conditions were carried out by standard procedures under argon atmosphere. Commercially available reagents **1a**–**c** and **6a**–**b** were used as received. The



Fig. 5. Calculated molecular orbitals and energy levels of fluorophores 3a-c, 4a-c, 5a-c, and 7a-e.

solvents were dried by distillation over appropriate drying reagents. Petroleum ether used had a boiling range of 60-90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was performed through silica gel (200-300 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM 400 MHz spectrometer, as were the DEPT 135 experiments. Chemical shift values ( $\delta$ )are given in ppm and coupling constants (1) in Hz. Residual solvent signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra were used as an internal reference (CDCl<sub>3</sub>:  $\delta_{\rm H} = 7.26$ ,  $\delta_{\rm C} = 77.0$  ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), m (multiplet). Melting points were determined by use of a microscope apparatus and are uncorrected. Mass spectra were obtained using electrospray ionization (ESI), as indicated, on a Thermo Orbitrap Elite mass spectrometer. Single crystal X-ray diffraction measurements were made on a Bruker X8 APEX diffractometer working with graphite monochromated Mo Ka radiation. UV-vis absorptions were carried out on a UV-Cary100 spectrophotometer. The fluorescence spectra and the absolute fluorescence quantum yields were measured from the solution and powder form using the Edinburgh Instruments (FLS920). Phosphite ester 2 was synthesized as previously reported [39].

## 4.2. The preparation and characterization data of fluorophores 3a-c

#### 4.2.1. 4-(2,2-Diphenylethenyl)benzonitrile (3a)

Potassium tert-butoxide (1.18 g. 10.54 mmol) was added to a solution of benzophenone 1a (956 mg, 5.25 mmol) and phosphite ester 2 (1.97 g. 7.79 mmol) in anhydrous THF (100 mL) at 0 °C under argon atmosphere, then the reaction mixture was stirred at 25 °C for 5 h. A color change from colorless to yellow was observed. Upon completion of the reaction, the solvent was concentrated under reduced pressure. The resulting residue was diluted with water (20 mL) and then extracted with ethyl acetate (3  $\times$  20 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel afforded compound 3a as a white amorphous solid (1.18 g, 80%).  $R_f = 0.35$  (petroleum ether/ ethyl acetate 15:1). m.p.: 110-111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.40 (d, J = 8.4 Hz, 2H; Ar–H), 7.37–7.34 (m, 8H; Ar-H), 7.18-7.16 (m, 2H; Ar-H), 7.09 (d, J = 8.0 Hz, 2H; Ar-H), 6.95 (s, 1H; CH). MS (ESI-TOF): m/z 282.1 ([M + H]<sup>+</sup>, calcd for  $C_{21}H_{16}N$  282.1). The data were identical with those in the reference. [37].

#### 4.2.2. 4-[2,2-Bis(4-methoxy-phenyl)ethenyl]benzonitrile (3b)

The preparation procedure was the same as that used for compound **3a**. Starting with bis(4-methoxyphenyl)methanone **1b** (1.27 g, 5.25 mmol), phosphite ester **2** (1.97 g, 7.79 mmol) and potassium *tert*-butoxide (1.18 g, 10.54 mmol), compound **3b** was obtained as a white amorphous solid (1.38 g, 77%). R<sub>f</sub> = 0.50 (petroleum ether/ethyl acetate 4:1). m.p.: 112–113 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.37 (d, J = 8.0 Hz, 2H; Ar–H), 7.25 (d, J = 9.0 Hz, 2H; Ar–H), 7.08 (d, J = 8.4 Hz, 2H; Ar–H), 6.86 (d, J = 8.0 Hz, 2H; Ar–H), 6.85 (d, J = 9.0 Hz, 2H; Ar–H), 6.79 (s, 1H; CH), 3.82 (s, 3H; OCH<sub>3</sub>). MS (ESI-TOF): m/z 341.1 ([M]<sup>+</sup>, calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub> 341.1). The data were identical with those in the reference. [38].

#### 4.2.3. 4-[2,2-Bis(4-dimethylamino-phenyl)ethenyl]benzonitrile (3c)

The preparation procedure was the same as that used for compound **3a**. Starting with 4,4'-bis(dimethylamino)benzophenone **1c** (1.41 g, 5.26 mmol), phosphite ester **2** (1.97 g, 7.79 mmol) and potassium *tert*-butoxide (1.18 g, 10.54 mmol), compound **3c** was obtained as a yellow amorphous solid (1.35 g, 70%).  $R_f = 0.55$  (petroleum ether/ethyl acetate 3:1). m.p.: 156–157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.37 (d, J = 8.4 Hz, 2H; Ar–H), 7.25 (d, J = 9.6 Hz, 2H; Ar–H), 7.11 (d, J = 8.8 Hz, 2H; Ar–H), 7.03 (d, J = 8.8 Hz, 2H; Ar–H), 6.69 (s, 1H; CH), 6.67 (d, J = 8.0 Hz, 4H; Ar–H), 3.00 (s, 6H; NCH<sub>3</sub>), 2.99 (s, 6H; NCH<sub>3</sub>). MS (ESI-TOF): m/z 368.2 ([M + H]<sup>+</sup>, calcd for C<sub>25</sub>H<sub>26</sub>N<sub>3</sub> 368.2). The data were identical with those in the reference. [38].

### 4.3. The preparation and characterization data of fluorophores 4a-c

#### 4.3.1. 4-(2,2-Diphenylethenyl)benzaldehyde (4a)

A solution of DIBAL-H (7.3 mL, 1.5 M in toluene, 10.95 mmol) was added dropwise to a stirred solution of compound **3a** (1.55 g, 5.52 mmol) in anhydrous toluene (50 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 5 h and quenched by CH<sub>3</sub>OH (20 mL). Then the aqueous solution of saturated seignette salt (20 mL) was added into the resulting mixture and the stirring continuously at 25 °C for 2 h until the solution was divided into two layers. The organic layer was dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel afforded compound **4a** as a white amorphous solid (1.49 g, 95%).  $R_f = 0.38$  (petroleum ether/ethyl acetate 15:1). m.p.: 97–99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 9.91 (s, 1H; CHO), 7.65 (d, *J* = 8.4 Hz, 2H; Ar–H), 7.37–7.35 (m, 8H; Ar–H), 7.21–7.19 (m, 2H; Ar–H), 7.17 (d, J = 8.4 Hz, 2H; Ar–H), 7.01 (s, 1H; CH). MS (ESI-TOF): m/z 285.1 ([M+H]<sup>+</sup>, calcd for C<sub>21</sub>H<sub>17</sub>O 285.1). The data were identical with those in the reference. [25].

#### 4.3.2. 4-[2,2-Bis(4-methoxy-phenyl)ethenyl]benzaldehyde (4b)

The preparation procedure was the same as that used for compound **4a**. Starting with compound **3b** (1.87 g, 5.48 mmol), DIBAL-H (7.3 mL, 1.5 M in toluene, 10.95 mmol), compound **4b** was obtained as a green amorphous solid (1.74 g, 92%).  $R_f = 0.50$  (petroleum ether/ethyl acetate 4:1). m.p.: 116–118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 9.89 (s, 1H; CHO), 7.64 (d, J = 8.4 Hz, 2H; Ar–H), 7.28 (d, J = 8.8 Hz, 2H; Ar–H), 7.17 (d, J = 8.4 Hz, 2H; Ar–H), 7.10 (d, J = 8.8 Hz, 2H; Ar–H), 6.87 (d, J = 8.4 Hz, 4H; Ar–H), 6.86 (s, 1H; CH), 3.84 (s, 3H; OCH<sub>3</sub>), 3.83 (s, 3H; OCH<sub>3</sub>). MS (ESI-TOF): m/z 345.1 ([M + H]<sup>+</sup>, calcd for C<sub>23</sub>H<sub>21</sub>O<sub>3</sub> 345.1). The data were identical with those in the reference. [41].

## 4.3.3. 4-[2,2-Bis(4-dimethylamino-phenyl)ethenyl]benzaldehyde (**4c**)

The preparation procedure was the same as that used for compound **4a**. Starting with compound **3c** (2.02 g, 5.50 mmol), DIBAL-H (7.3 mL, 1.5 M in toluene, 10.95 mmol), compound **4c** was obtained as a yellow amorphous solid (1.84 g, 90%).  $R_f = 0.65$  (petroleum ether/ethyl acetate 3:1). m.p.: 178–179 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 9.87 (s, 1H; CHO), 7.62 (d, J = 8.0 Hz, 2H; Ar–H), 7.27 (d, J = 8.0 Hz, 2H; Ar–H), 7.19 (d, J = 8.4 Hz, 2H; Ar–H), 7.06 (d, J = 8.4 Hz, 2H; Ar–H), 6.67 (d, J = 8.4 Hz, 2H; Ar–H), 3.00 (s, 6H; NCH<sub>3</sub>), 2.99 (s, 6H; NCH<sub>3</sub>). MS (ESI-TOF): m/z 371.2 ([M + H]<sup>+</sup>, calcd for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O 371.2). The data were identical with those in the reference. [40].

### 4.4. The preparation and characterization data of fluorophores **5a–c**

#### 4.4.1. (E)-4-[4-(2,2-Diphenylvinyl)styryl]benzonitrile (5a)

The preparation procedure was the same as that used for compound **3a**. Starting with aldehyde **4a** (148 mg, 0.52 mmol), phosphite ester **2** (197 mg, 0.78 mmol), compound **5a** was obtained as a green amorphous solid (159 mg, 80%).  $R_f = 0.73$  (petroleum ether/ ethyl acetate 4:1). m.p.: 153–155 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.61 (d, J = 8.0 Hz, 2H; Ar–H), 7.53 (d, J = 8.4 Hz, 2H; Ar–H), 7.37–7.30 (m, 10H; Ar–H), 7.25–7.23 (m, 2H; Ar–H), 7.12 (d, J = 16.6 Hz, 1H; CH), 7.04 (d, J = 8.4 Hz, 2H; Ar–H), 7.01 (d, J = 16.6 Hz, 1H; CH), 6.98 (s, 1H; CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 143.3 (C), 143.2 (C), 141.8 (C), 140.3 (C), 137.9 (C), 134.6 (C), 132.4 (CH), 131.9 (CH), 130.3 (CH), 130.0 (CH), 128.7 (CH), 128.2 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 119.0 (C), 110.4 (C), one Ar–CH resonance was not resolved. HRMS (ESI-TOF): m/z 383.1664 ([M]<sup>+</sup>, calcd for C<sub>29</sub>H<sub>21</sub>N 383.1669).

### *4.4.2.* (*E*)-4-{4-[2,2-Bis(4-methoxy-phenyl)vinyl]styryl}benzonitrile (**5b**)

The preparation procedure was the same as that used for compound 3a. Starting with compound 4b (179 mg, 0.52 mmol), phosphite ester 2 (197 mg, 0.78 mmol), compound 5b was obtained as a greenish yellow amorphous solid (179 mg, 78%).  $R_{f}=\,0.54$ (petroleum ether/ethyl acetate 3:1). m.p.: 189–190 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.61 (d, J = 8.4 Hz, 2H; Ar–H), 7.53 (d, J = 8.4 Hz, 2H; Ar–H), 7.30 (d, J = 8.4 Hz, 2H; Ar–H), 7.27 (d, J = 8.8 Hz, 2H; Ar–H), 7.14 (d, J = 8.8 Hz, 2H; Ar–H), 7.08 (d, J = 17.0 Hz, 1H; CH), 7.05 (d, J = 8.0 Hz, 2H; Ar–H), 7.01 (d, J = 17.0 Hz, 1H; CH), 6.89 (d, J = 8.8 Hz, 2H; Ar–H), 6.86 (d, I = 8.8 Hz, 2H; Ar-H), 6.83 (s, 1H; CH), 3.85 (s, 3H; OCH<sub>3</sub>), 3.83 (s, 3H; OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 159.4 (C), 159.1 (C), 142.6 (C), 141.9 (C), 138.5 (C), 136.1 (C), 134.1 (C), 132.6 (C), 132.4 (CH), 132.1 (CH), 131.6 (CH), 129.8 (CH), 128.9 (CH), 126.7 (CH), 126.6 (CH), 126.1 (CH), 125.5 (CH), 119.0 (C), 114.1 (CH), 113.6 (CH), 110.3 (C), 55.3 (CH<sub>3</sub>), 55.2 (CH<sub>3</sub>). HRMS (ESI-TOF): m/z 443.1873 ([M]<sup>+</sup>, calcd for C<sub>31</sub>H<sub>25</sub>NO<sub>2</sub> 443.1879).

## 4.4.3. (E)-4-{4-[2,2-Bis(4-dimethylamino-phenyl)vinyl]styryl} benzonitrile (**5c**)

The preparation procedure was the same as that used for compound **3a**. Starting with compound **4c** (192 mg, 0.52 mmol), phosphite ester 2 (197 mg, 0.78 mmol), compound 5c was obtained as an orange amorphous solid (171 mg, 70%).  $R_f = 0.56$  (petroleum ether/ethyl acetate 3:1). m.p.: 152–153 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 7.60 (d, *J* = 8.4 Hz, 2H; Ar–H), 7.53 (d, J = 8.4 Hz, 2H; Ar-H), 7.29 (d, J = 8.4 Hz, 2H; Ar-H), 7.26 (d, J = 8.8 Hz, 2H; Ar–H), 7.12 (d, J = 16.2 Hz, 1H; CH), 7.10 (d, J = 8.4 Hz, 2H; Ar–H), 7.08 (d, *J* = 8.0 Hz, 2H; Ar–H), 6.99 (d, *J* = 16.2 Hz, 1H; CH), 6.75 (s, 1H; CH), 6.70 (d, J = 7.2 Hz, 2H; Ar-H), 6.68 (d, *J* = 7.6 Hz, 2H; Ar–H), 3.00 (s, 6H; NCH<sub>3</sub>), 2.98 ppm (s, 6H; NCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 150.1 (C), 149.8 (C), 143.7 (C), 142.1 (C), 139.5 (C), 133.4 (C), 132.4 (CH), 132.3 (CH), 131.4 (CH), 129.6 (CH), 128.8 (CH), 126.6 (CH), 126.5 (CH), 125.6 (CH), 123.2 (CH), 119.1 (C), 112.3 (CH), 111.9 (CH), 110.1 (C), 40.5 (CH<sub>3</sub>), two Ar-C and one CH<sub>3</sub> resonances were not resolved. HRMS (ESI-TOF): m/z 470.2583 ([M + H]<sup>+</sup>, calcd for C<sub>33</sub>H<sub>32</sub>N<sub>3</sub> 470.2589).

# 4.5. The preparation and characterization data of fluorophores **7a–e**

### 4.5.1. (Z)-2-Phenyl-3-[4-(2,2-diphenylvinyl)phenyl]acrylonitrile (7a)

A freshly prepared sodium methoxide solution in anhydrous  $CH_3OH$  (0.05 mL, 1 M in  $CH_3OH$ ) was added dropwise to a solution of aldehyde **4a** (150 mg, 0.53 mmol) and phenylacetonitrile **6a** (64 mg, 0.55 mmol) in EtOH (100 mL) at 25 °C. Then the reaction mixture was stirred for 5 h at the same temperature. A color change from colorless to yellow was observed. Upon completion of the reaction, the solvent was concentrated under reduced pressure. The

resulting residue was diluted with water (10 mL) and then extracted with ethyl acetate (3  $\times$  10 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel afforded **7a** as a greenish vellow amorphous solid (179 mg, 88%).  $R_f = 0.38$  (petroleum ether/ethyl acetate 20:1). m.p.: 135–137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 7.70 (d, *J* = 8.4 Hz, 2H; Ar–H), 7.65 (d, *J* = 7.2 Hz, 2H; Ar–H), 7.46–7.32 (m, 12H; Ar-H, CH), 7.24–7.22 (m, 2H; Ar-H), 7.11 (d, *J* = 8.4 Hz, 2H; Ar-H), 7.00 (s, 1H; CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 144.6 (C), 143.0 (C), 141.7 (CH), 140.0 (C), 139.9 (C), 134.7 (C), 131.9 (C), 130.2 (CH), 130.0 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.3 (CH), 127.91 (CH), 127.87 (CH), 127.7 (CH), 127.1 (CH), 125.9 (CH), 118.2 (C), 110.6 (C), one Ar–CH resonance was not resolved. HRMS (ESI-TOF): m/z 384.1743 ([M + H]<sup>+</sup>, calcd for C<sub>29</sub>H<sub>22</sub>N 384.1747).

### 4.5.2. (Z)-2-Phenyl-3-{4-[2,2-bis(4-methoxy-phenyl)vinyl]phenyl} acrylonitrile (**7b**)

The preparation procedure was the same as that used for compound 7a. Starting with aldehyde 4b (182 mg, 0.53 mmol), phenylacetonitrile 6a (64 mg, 0.55 mmol) and sodium methoxide solution in anhydrous CH<sub>3</sub>OH (0.05 mL, 1 M in CH<sub>3</sub>OH), compound 7b was obtained as a yellow amorphous solid (200 mg, 85%).  $R_f = 0.50$  (petroleum ether/ethyl acetate 4:1). m.p.: 145–147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.70 (d, J = 8.0 Hz, 2H; Ar-H), 7.65 (d, J = 7.2 Hz, 2H; Ar-H), 7.45-7.36 (m, 4H; Ar-H, CH), 7.28 (d, I = 8.4 Hz, 2H; Ar-H), 7.14 (d, I = 7.2 Hz, 2H; Ar-H), 7.12 (d, I = 6.8 Hz, 2H; Ar-H), 6.90 (d, I = 8.8 Hz, 2H; Ar-H), 6.87 (d, *J* = 8.8 Hz, 2H; Ar–H), 6.85 (s, 1H; CH), 3.86 (s, 3H; OCH<sub>3</sub>), 3.83 (s, 3H; OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 159.6 (C), 159.3 (C), 143.9 (C), 141.8 (CH), 140.5 (C), 135.9 (C), 134.7 (C), 132.2 (C), 131.5 (CH), 131.4 (C), 129.8 (CH), 129.1 (CH), 129.01 (CH), 128.99 (CH), 128.9 (CH), 125.8 (CH), 125.1 (CH), 118.2 (C), 114.2 (CH), 113.6 (CH), 110.1 (C), 55.3 (CH<sub>3</sub>), 55.2 (CH<sub>3</sub>). HRMS (ESI-TOF): m/z 443.1874 ([M]<sup>+</sup>, calcd for C<sub>31</sub>H<sub>25</sub>NO<sub>2</sub> 443.1879).

# 4.5.3. (Z)-2-Phenyl-3-{4-[2,2-bis(4-dimethylamino-phenyl)vinyl] phenyl}acrylonitrile (**7c**)

The preparation procedure was the same as that used for compound 7a. Starting with aldehyde 4c (196 mg, 0.53 mmol), phenylacetonitrile 6a (64 mg, 0.55 mmol) and sodium methoxide solution in CH<sub>3</sub>OH (0.05 mL, 1 M in CH<sub>3</sub>OH), compound 7c was obtained as a red amorphous solid (199 mg, 80%).  $R_{f}=0.55$  (petroleum ether/ethyl acetate 3:1). m.p.: 171–173 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 7.70 (d, J = 8.4 Hz, 2H; Ar–H), 7.64 (d, *J* = 7.2 Hz, 2H; Ar–H), 7.45–7.35 (m, 4H; Ar–H, CH), 7.27 (d, J = 8.8 Hz, 2H; Ar-H), 7.15 (d, J = 8.4 Hz, 2H; Ar-H), 7.09 (d, J = 8.8 Hz, 2H; Ar-H), 6.76 (s, 1H; CH), 6.70 (d, J = 8.8 Hz, 2H; Ar-H), 6.68 (d, J = 8.8 Hz, 2H; Ar-H), 3.02 (s, 6H; NCH<sub>3</sub>), 2.99 (s, 6H; NCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 150.3 (C), 149.9 (C), 145.3 (C), 142.1 (CH), 141.6 (C), 134.9 (C), 131.8 (C), 131.3 (CH), 130.7 (C), 129.6 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 127.8 (C), 125.8 (CH), 122.7 (CH), 118.5 (C), 112.2 (CH), 111.8 (CH), 109.3 (C), 40.42 (CH<sub>3</sub>), 40.38 (CH<sub>3</sub>), one Ar–CH resonance was not resolved. HRMS (ESI-TOF): m/z 470.2586 ([M+H]<sup>+</sup>, calcd for C33H32N3 470.2589).

### 4.5.4. (*Z*)-2-(4-Nitrophenyl)-3-[4-(2,2-diphenylvinyl)phenyl] acrylonitrile (**7d**)

The preparation procedure was the same as that used for compound **7a**. Starting with aldehyde **4a** (150 mg, 0.53 mmol), *p*nitrobenzeneacetonitrile **6b** (89 mg, 0.55 mmol) and sodium methoxide solution in CH<sub>3</sub>OH (0.05 mL, 1 M in CH<sub>3</sub>OH), compound **7d** was obtained as a red amorphous solid (213 mg, 94%).  $R_f = 0.75$  (petroleum ether/ethyl acetate 3:1). m.p.:  $153-154 \, ^{\circ}C$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25  $^{\circ}C$ , TMS):  $\delta$  (ppm) 8.29 (d,  $J = 9.2 \, \text{Hz}$ , 2H; Ar–H), 7.81 (d,  $J = 9.2 \, \text{Hz}$ , 2H; Ar–H), 7.74 (d,  $J = 8.4 \, \text{Hz}$ , 2H; Ar–H), 7.55 (s, 1H; CH), 7.39–7.34 (m, 8H; Ar–H), 7.23–7.21 (m, 2H; Ar–H), 7.14 (d,  $J = 8.4 \, \text{Hz}$ , 2H; Ar–H), 7.00 (s, 1H; CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25  $^{\circ}C$ , TMS):  $\delta$  (ppm) 147.8 (C), 145.5 (C), 144.9 (CH), 142.8 (C), 141.3 (C), 140.8 (C), 139.8 (C), 131.0 (C), 130.20 (CH), 130.16 (CH), 129.6 (CH), 128.9 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 126.8 (CH), 126.6 (CH), 124.4 (CH), 117.4 (C), 108.2 (C). HRMS (ESI-TOF): m/z 428.1514 ([M]<sup>+</sup>, calcd for C<sub>29</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> 428.1520).

# 4.5.5. (Z)-2-(4-Nitrophenyl)-3-{4-[2,2-bis(4-methoxy-phenyl) vinyl]phenyl} acrylonitrile (7e)

The preparation procedure was the same as that used for compound 7a. Starting with aldehyde 4b (182 mg, 0.53 mmol), pnitrobenzeneacetonitrile 6b (89 mg, 0.55 mmol) and sodium methoxide solution in CH<sub>3</sub>OH (0.05 mL, 1 M in CH<sub>3</sub>OH), compound **7e** was obtained as a red amorphous solid (233 mg, 90%).  $R_f = 0.58$ (petroleum ether/ethyl acetate 4:1). m.p.: 77–79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  (ppm) 8.29 (d, J = 9.2 Hz, 2H; Ar–H), 7.81 (d, J = 8.8 Hz, 2H; Ar–H), 7.74 (d, J = 8.4 Hz, 2H; Ar–H), 7.55 (s, 1H; CH), 7.28 (d, J = 8.8 Hz, 2H; Ar–H), 7.15 (d, J = 7.2 Hz, 2H; Ar-H), 7.13 (d, I = 8.8 Hz, 2H; Ar-H), 6.89 (d, I = 8.8 Hz, 2H; Ar-H), 6.87 (d, J = 8.8 Hz, 2H; Ar–H), 6.85 (s, 1H; CH), 3.86 (s, 3H; OCH<sub>3</sub>), 3.83 (s, 3H; OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ (ppm) 159.7 (C), 159.4 (C), 147.7 (C), 145.0 (CH), 144.9 (C), 141.9 (C), 140.9 (C), 135.8 (C), 132.1 (C), 131.5 (CH), 130.5 (C), 130.0 (CH), 129.7 (CH), 129.1 (CH), 126.5 (CH), 124.8 (CH), 124.3 (CH), 117.5 (C), 114.2 (CH), 113.7 (CH), 107.7 (C), 55.3 (CH<sub>3</sub>), 55.2 (CH<sub>3</sub>). HRMS (ESI-TOF): m/z 488.1725 ([M]<sup>+</sup>, calcd for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> 488.1730).

#### Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (Grant Nos. 21572085, 21272098, 21572086, and 21190034), the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT: IRT\_15R28), and the 111 Project for financial support. We gratefully acknowledge Yong-Liang Shao in Lanzhou University for X-ray crystallographic analyses.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.04.014.

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