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Facile synthesis and photo-physical properties of cyano-substituted styryl derivatives based on carbazole/phenothiazine

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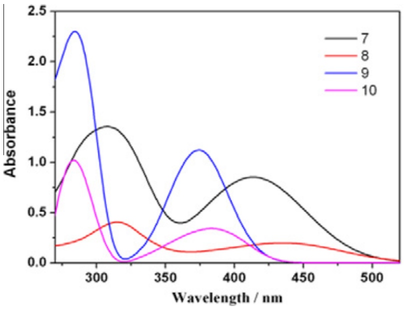
HIGHLIGHTS

- ▶ Four cyano-substituted styryl derivatives based on carbazole and phenothiazine were synthesized.
- ▶ The TGA results show these derivatives are thermally stable.
- ▶ These derivatives exhibited unusual large Stokes shifts.

GRAPHICAL ABSTRACT

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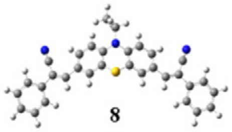
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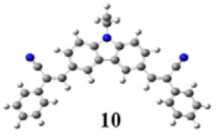
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ABSTRACT

Four new cyano-substituted styryl derivatives based on carbazole and phenothiazine were facilely synthesized by conventional Knoevenagel condensation and well characterized. The UV–vis spectra of these dyes showed the lowest-energy absorption bands were mainly caused by the HOMO–LUMO one-electron promotion as conformed by TD-DFT calculations. The thermogravimetric analysis showed these dyes were thermally stable up to 350 °C. The UV–vis absorption and fluorescence emission spectra were also studied in solvents of different polarity, these dyes exhibited unusual large Stokes shift.

Introduction

During the past few decades, donor–acceptor (D–A) organic materials have attracted considerable interests owing to their potential applications in electro/photoactive materials, such as nonlinear optical (NLO) materials [1–3], organic light-emitting diodes (OLEDs) [4], organic field-effect transistors (OFETs) [5,6], dye-sensitized solar cells (DSSCs) [7–9]. In such D–A dyads, the D and A moieties are often connected through a π-conjugated bridge to form D-π-A molecules. It is easy to modify their physical and chemical properties by tuning different donor or acceptor units. In most of the well-studied D-π-A architectures, carbazole has been widely used as electron–donor in opto- and electroactive materials, due to its good electron-donating and transporting capabilities [10,11]. With electron-rich sulfur and nitrogen heteroatoms, phenothiazine is also a well-known heterocyclic compound with high electron-donating ability. Its nonplanar butterfly conformation in the ground state can inhibit molecular aggregation and the formation of intermolecular excimers [12]. These advantages make phenothiazine and its derivatives suitable for diverse applications in organic devices [13–15]. Functional materials with carbazole and phenothiazine as basic building blocks have desirable photophysical and electron-transfer (ET) properties [16–18].

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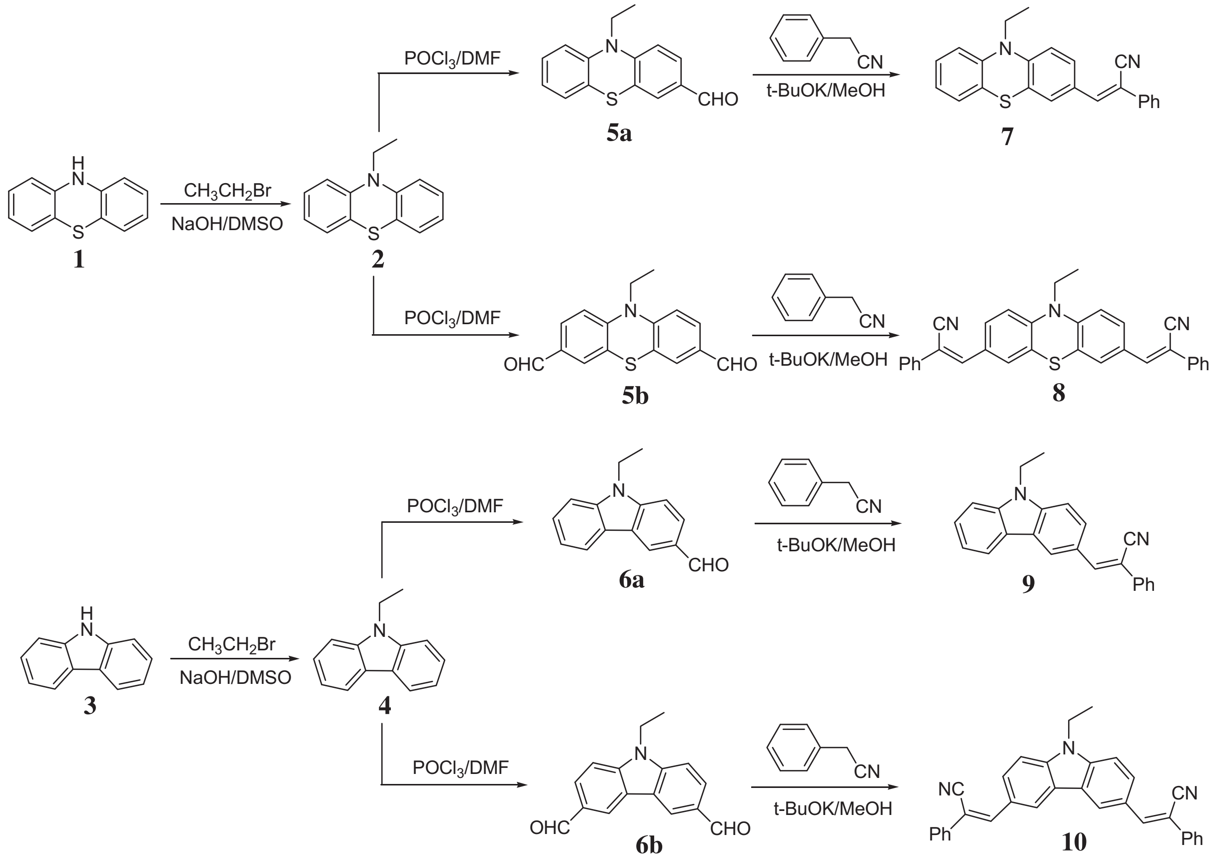

Scheme 1. Synthetic route of compounds **7–10**.

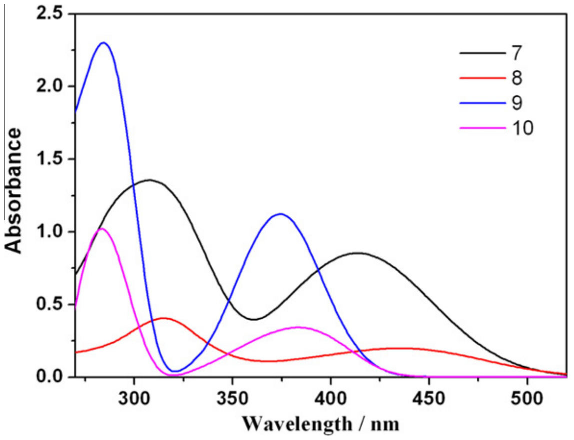

Fig. 1. UV–vis absorption of **7–10** in dichloromethane.

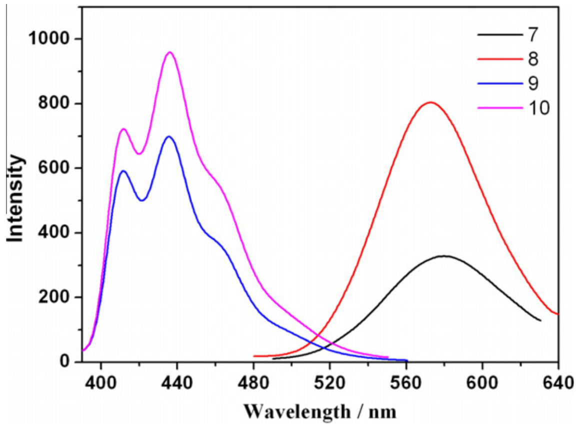

Fig. 2. Emission spectra of **7–10** in dichloromethane.

On the other hand, the cyano group is well-known for its electron-withdrawing characteristic which is beneficial to enhance electron affinity of the chromophores. Thus, cyano-substituted styryl derivatives also have increasing interests because of their more and more applications in fluorescent organic nanoparticles (FONs) [19,20], heterojunction solar cells [21,22], two-photon absorption (TPA) materials [23,24] and aggregation-induced emission enhancement (AIEE) materials [25–28]. However, there have been always efforts to design and synthesize novel and well-defined cyano-substituted styryl derivatives with prospective applications. To the best of our knowledge, cyano-substituted styryl derivatives based on carbazole/phenothiazine have not been reported previously. Herein, we presented the facile synthesis and characterization of cyano-substituted styryl derivatives based on carbazole and phenothiazine. Their thermal stability, UV–vis absorption and fluorescence emission characteristics in different solvents were studied. DFT calculations were also presented, in order to investigate the electronic structures and properties of these dyes.

Experimental

Materials and equipments

All chemicals and solvents were purchased from commercial supplies and used without further purification. Flash column

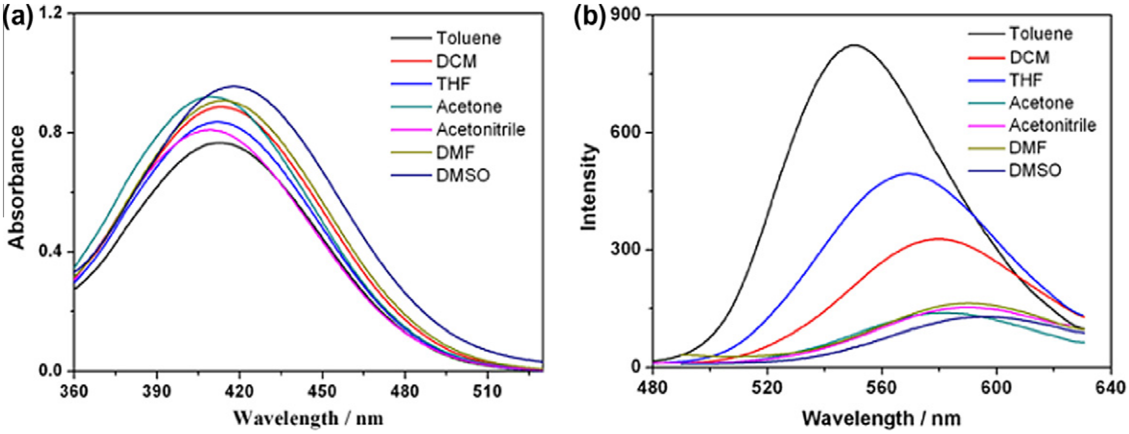

Fig. 3. (a) Absorption spectra of **7** in different solvents with the same concentration of 1×10^{-5} M. (b) fluorescence spectra of **7** in different solvents with the same concentration of 1×10^{-6} M.

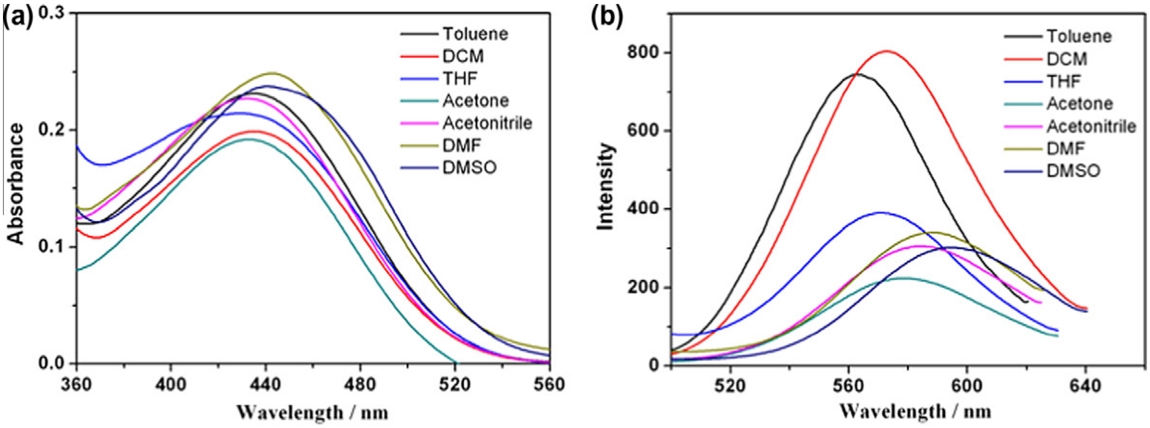

Fig. 4. (a) Absorption spectra of **8** in different solvents with the same concentration of 1×10^{-5} M. (b) fluorescence spectra of **8** in different solvents with the same concentration of 1×10^{-6} M.

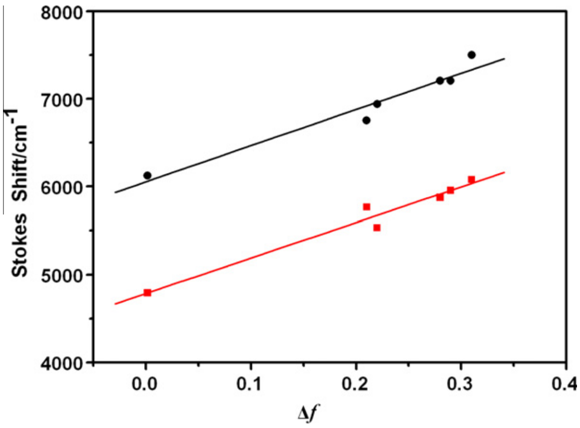

Fig. 5. Mataga–Lippert plots observed for **7** (black) and **8** (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

chromatography was performed employing 200–300 mesh silica gel. IR spectra were obtained on an AVATA 360 infrared spectrometer in the 400–4000 cm^{-1} region. The UV–visible spectra were recorded on an Australia GBC UV/Vis 916 spectrophotometer in the range of 250–700 nm. The fluorescence spectra were obtained on a Horiba Fluorolog 3. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 NMR spectrometer operating at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. MS spectra were measured on LCQ Advantage instrument and MALDI AXIMA-CFR(PLUS). The thermal gravimetric analyses (TG-DSC) were carried out with a NETZSCH STA 449F3 thermal analyzer with a heating rate of 10 K min^{-1} under N_2 atmosphere. All reactions were performed under a nitrogen atmosphere.

Synthesis and characterization

*Synthesis of 10-ethyl-10H-phenotiazine **2**, 9-ethyl-9H-carbazole **4**, 10-ethyl-10H-3-phenotiazine carbaldehyde **5a**, 10-ethyl-10H-3,7-phenotiazine dicarbaldehyde **5b**, 9-ethyl-9H-carbazole-3-carboxaldehyde **6a**, 9-ethyl-9H-carbazole-3,6-dicarboxaldehyde **6b**.*

Compounds **2**, **4**, **5a–b**, **6a–b** were synthesized according to the published literature [29,30].

*Synthesis of 3-[2-phenyl-2-cyanovinyl]-10-ethyl-10H-phenothiazine **7***

10-Ethyl-10H-3-phenotiazine carbaldehyde (0.31 g, 1.2 mmol) **5a**, 2-phenylacetonitrile (0.29 g, 2.5 mmol) and potassium tert-butoxide (1.22 g, 10 mmol) were dissolved in methanol (50 mL). The mixture was heated to reflux and stirred for 12 h under an atmosphere of N_2. After cooling to room temperature, the mixture was poured into water (200 mL), neutralized to pH 7 with 1 M HCl aqueous solution, and then extracted with dichloromethane. The extract was washed with plenty of brine and dried over Na_2SO_4,

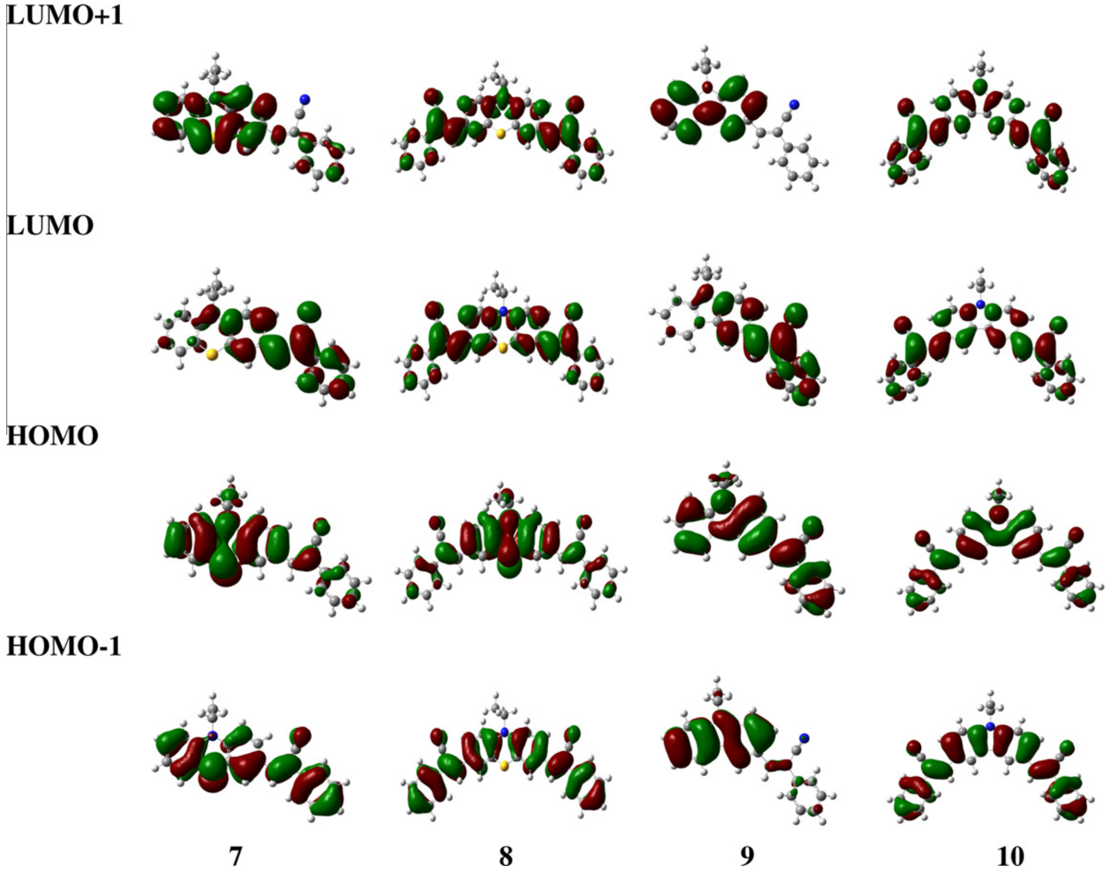

Fig. 6. HOMO and LUMO distributions obtained from DFT calculations of **7**–**10**.

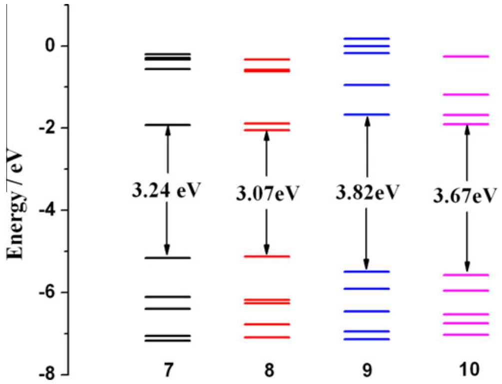

Fig. 7. Schematic representation of the frontier orbital energy levels of **7**–**10**.

the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:4) as eluent. Yield: 0.38 g (89%) of orange-red oil. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 1.44 (t, J = 6.8 Hz, 3H), 3.95 (q, J = 6.8 Hz, 2H), 6.86–6.89 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 7.09–7.16 (m, 2H), 7.34–7.44 (m, 4H), 7.54 (s, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.80 (dd, J = 8.4, 1.6 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 146.71, 143.58, 140.81, 134.79, 130.03, 129.16, 129.05, 128.80, 128.25, 128.06, 127.95, 127.55, 127.43, 125.79, 124.25, 123.08, 118.49, 117.94, 115.30, 114.76, 108.57, 42.18, 12.88; IR (NaCl): 3061, 3031, 2981, 2935, 2208, 1590, 1572, 1497, 1467, 1406, 1368, 1330, 1286, 1251, 1206, 1137, 1111; MS (ESI): m/z 355.0 [M+H]$^+$.

Table 1
Electronic spectral data of **7**–**10** calculated with TDDFT at the B3LYP/6-31G∗ level.

Compounds	f	Composition	E (eV, nm)	Exp. (eV, nm)
7	0.4796	H → L (98%)	2.63 (474)	3.02 (413)
	0.5418	H-1 → L (88%)	3.59 (346)	4.02 (309)
8	0.8406	H → L (99%)	2.58 (481)	2.86 (435)
	0.1897	H-1 → L (97%)	3.62 (343)	3.94 (315)
9	0.9970	H → L (99%)	3.20 (388)	3.32 (374)
	0.2351	H-2 → L (79%) H → L + 1 (13%)	4.20 (296)	4.30 (289)
10	1.2929	H → L (99%)	2.94 (422)	3.23 (384)
	0.2309	H-2 → L + 1 (74%) H-3 → L (18%)	4.26 (292)	4.39 (283)

*Synthesis of 3,7-bis[2-phenyl-2-cyanovinyl]-10-ethyl-10H-phenothiazine **8***

10-Ethyl-10H-3,7-phenotiazine dicarbaldehyde (0.28 g, 1 mmol) **5b**, 2-phenylacetonitrile (0.35 g, 3 mmol) and potassium tert-butoxide (1.22 g, 10 mmol) were dissolved in methanol (50 mL). The mixture was heated to reflux and stirred for 12 h under an atmosphere of N$_2$. After cooling to room temperature, an orange solid precipitate was filtered off, washed with cold methanol, and purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:6) as eluent. Yield: 0.32 g (67%) of orange powder. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 1.48 (t, J = 6.8 Hz, 3H), 4.00 (q, J = 6.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 7.36–7.39 (m, 4H), 7.42–7.46 (m, 4H), 7.52 (s, 2H), 7.64–7.66 (d, J = 7.2 Hz, 4H), 7.82–7.82 (d, J = 7.2 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 145.29, 145.20, 144.84, 142.57, 140.41, 134.63, 132.89, 129.77, 129.35, 129.24, 129.05, 128.93, 128.81, 128.68, 128.66, 128.61, 128.42, 128.31, 128.16, 125.83, 123.40, 123.34, 123.04, 120.41, 118.28, 114.98, 114.92, 114.52, 112.41, 109.35, 42.54, 12.72; IR (KBr): 3127, 2926, 2208, 1574, 1473, 1404, 1369, 1253, 1205, 1176, 1133, 1113; MS (TOF): *m*/*z* 481.10 [M$^+$].

Synthesis of 3-[2-phenyl-2-cyanovinyl]-9-ethyl-9H-carbazole ***9***

9-Ethyl-9H-carbazole-3-carboxaldehyde (0.34 g, 1.5 mmol) **6a**, 2-phenylacetonitrile (0.23 g, 2 mmol) and potassium tert-butoxide (1.22 g, 10 mmol) were dissolved in methanol (50 mL). The mixture was heated to reflux and stirred for 12 h under an atmosphere of N_2. After cooling to room temperature, the mixture was poured into water (200 mL), neutralized to pH 7 with 1 M HCl aqueous solution, and then extracted with dichloromethane. The extract was washed with plenty of brine and dried over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane/hexane (1:1) as eluent. Yield: 0.38 g (76%) of yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 1.42 (t, *J* = 7.2 Hz, 3H), 4.33 (q, *J* = 6.8 Hz, 2H), 7.27–7.52 (m, 7H), 7.68–7.70 (m, 3H), 8.09–8.14 (m, 2H), 8.61 (s, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 143.51, 141.15, 140.56, 135.33, 129.22, 129.02, 128.48, 127.93, 127.19, 126.47, 125.75, 124.84, 123.35, 122.93, 122.54, 120.80, 119.85, 119.17, 108.97, 108.82, 107.36, 37.78, 13.85; IR (NaCl): 3057, 2976, 2932, 2206, 1627, 1586, 1496, 1471, 1448, 1387, 1346, 1234, 1159, 1132; MS (ESI): *m*/*z* 323.2 [M+H]$^+$.

Synthesis of 3,6-bis[2-phenyl-2-cyanovinyl]-9-ethyl-9H-carbazole ***10***

9-Ethyl-9H-carbazole-3,6-dicarboxaldehyde (0.15 g, 0.6 mmol) **6b**, 2-phenylacetonitrile (0.29 g, 2.5 mmol) and potassium tert-butoxide (1.22 g, 10 mmol) were dissolved in methanol (50 mL). The mixture was heated to reflux and stirred for 12 h under an atmosphere of N_2. After cooling to room temperature, yellow solid precipitate was filtered off, washed with cold methanol, and purified by column chromatography on silica gel using dichloromethane/hexane (1:1) as eluent. Yield: 0.17 g (63%) of yellow powder. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) δ: 1.51 (t, *J* = 7.2 Hz, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 7.37–7.51 (m, 8H), 7.72–7.74 (d, 6H), 8.21–8.23 (d, *J* = 8.8 Hz, 2H), 8.65 (s, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 142.99, 141.62, 135.07, 129.04, 128.67, 127.92, 127.52, 125.83, 125.80, 123.27, 122.95, 118.93, 109.37, 108.38, 38.14, 13.93; IR (KBr): 3126, 2976, 2924, 2206, 1629, 1586, 1490, 1446, 1392, 1348, 1239, 1160, 1130; MS (ESI): *m*/*z* 472.2 [M+Na]$^+$.

Results and discussion

Synthesis

The preparation of the target compound was synthesized in three synthetic steps from commercially available phenotiazine and carbazole (Scheme 1). The first step was the alkylation of phenotiazine and carbazole in the presence of sodium hydroxide followed by the formylation of 10-ethyl-10H-phenotiazine, **2** and 9-ethyl-9H-carbazole **4** using the Vilsmeier-Haack condition (POCl$_3$/DMF) to get mono- and diformyl compounds **5a**–**b** and **6a**–**b**, respectively. In the last stage of the synthesis, the four target compounds were prepared by classical Knoevenagel condensation, aldehyde **5a**–**b**, **6a**–**b** and 2-phenylacetonitrile were refluxed in absolute ethanol in the presence of potassium tert-butoxide as the strong base under an atmosphere of N_2 to obtain the desired compounds in moderate yields. All the newly synthesized compounds **7**–**10** were easily separated and purified by column chromatography and fully characterized and verified by FT-IR, ^{1}H NMR, ^{13}C NMR and Mass spectra.

Photophysical properties

The photophysical properties of these dyes were investigated in dilute dichloromethane solution. The comparison of UV–vis absorption spectra of **7**–**10** in dichloromethane solution (1×10^{-5} M) at room temperature were shown in Fig. 1. The UV–vis absorptions of these compounds have two absorption maxima ($\lambda_{max} \sim 280$–310 nm and $\lambda_{max} \sim 370$–430 nm). The low energy absorption band which can be assigned to an intramolecular charge-transfer (ICT) transition has lower absorption coefficient at λ_{max} than the high energy absorption band for all of these four compounds, and the absorptions of **7** and **9** which have only one electron-withdraw group have higher absorption coefficient than **8** and **10**, respectively, which have two electron-withdraw groups (Table S1). On the other hand, **7** and **8** with phenothiazine as the donor group have lower energy absorption band both of the two absorption maxima than that of **9** and **10** with carbazole as the donor group, respectively, which could be attributed to the lower HOMO of phenothiazine than that of carbazole. The emission spectra for **7**–**10** in dilute dichloromethane (1×10^{-6} M) at room temperature are displayed in Fig. 2. Overall, the emission spectrum for **7** displays a maximum at 579 nm without significant red-shift comparing with that of **8** (λ_{max} = 573 nm). This reinforces that both 3 and 7 positions-substituted phenothiazine by electron-withdraw group imparts a negligible effect on the emission when compared with only 3 position-subsitituded phenothiazine. However, the fluorescence spectra for **9** and **10** show nearly identical fluorescence emission with a maximum at 436 nm and a shoulder at 411 nm (Table S1), indicating that substitution of carbazole with withdraw group at 3 and 6 positions causes no significant red-shift. Nevertheless, it is interesting to note that **7** and **9** which have only one electron-withdraw group have higher absorption intensities but lower fluorescence emission intensities than **8** and **10**, respectively (Fig. 2).

In order to investigate the solvent effect on photophysical behaviors of these dyes, we also examined their photophysical spectra of **7** and **8** in different solvents varying from toluene to DMSO in sequence of dielectric constants. The UV–vis absorption and fluorescence emission data of **7**–**8** were shown in Table S2. Although the UV–vis absorption bands of **7** and **8** roughly remained the same in all of these solvents, the emission spectra were significantly red-shifted and weakened in intensity with increasing solvent polarity (as shown in Figs. 3 and 4). For example, the emission maximum of **7** in DMSO (598 nm) is about 47 nm red-shifted from that in toluene (551 nm) (Table S2). Similarly the emission maxima of **8** gradually red-shifts from toluene (562 nm) to DMSO (595 nm). Generally, a fluorophore has a larger dipole moment in the excited state than that in the ground state. After excitation, solvent dipoles can reorient or relax lowering the energy of the excited state. Therefore, this strong solvent effect can be attributed to a decrease in the energy of the singlet excited states when the polarity of the solvent increases. When compared the absorption spectra with the emission spectra in different solvents, both **7** and **8** showed large Stokes shifts, which are significantly larger than other simple styryl compounds [31]. For a given donor–acceptor compound, the Stokes shift increase was associated with the conjugation length increase. Compound **7**, however, showed a larger Stokes shift (from 139 to 181 nm) than that of **8** (from 122 to 154 nm) despite its shorter conjugation. To obtain further insight into the observed positive solvent effect on fluorescence emission, by plotting the Stokes shifts of **7** and **8** as a function of the solvent orientation polarizability, the corresponding Mataga–Lippert plots [32] of **7** and **8** based on different solvents were constructed and shown in Fig. 5. These plots illustrated the typical behavior of these compounds in the excited states with the variation of orientation polarizability of the solvent. The linear relationship suggested that only one excited state was present upon excitation. The slope of the Mataga-Lippert plots of both **7** and **8** seen from the Mataga–Lippert equation suggested that the excited-state dipole moment was larger than the ground-state dipole moment. However, the similar slope of the Lippert plots of **7** and **8** indicated that the intramolecular charge-transfer (ICT) features of **7** and **8** were equally significant.

Thermal gravimetric analysis

The thermal stability is one of the key requirements for some practical applications. In order to gain more insight into these dyes, **8** and **10** were subjected to the thermogravimetric analysis to investigate their thermal stabilities. The thermal stability studies were performed under nitrogen gas at a heating rate of 10 °C/min, and the results were shown in Fig. S1. Above 350 °C the thermogravimetric curves of **8** and **10** show a major loss in weight, with decomposition temperatures at 352, 373 °C for **8** and **10**, respectively. These results confirm that both of them are thermally stable.

Quantum chemistry calculations

To visualize geometries and electronic structures of these four compounds, all these dyes have been subjected to quantum chemical analysis by density functional theory (DFT). DFT calculations were performed using the B3LYP method with 6-31G* basis set implemented in Gaussian 03 program package [33,34]. We optimized the molecular structures of these compounds without symmetry constraints. Fig. 6 shows the molecular geometries and HOMO–LUMO surfaces of all these dyes synthesized in this study. Generally, the HOMOs are expected to lie on the electron-rich groups while the LUMOs are localized on the electron-poor groups. As expected, DFT studies of these dyes clearly indicated that the HOMOs of compounds **7** and **8** were primarily localized on center phenothiazine core, and in contrast the LUMOs mostly existed on the cyano moiety, while the HOMOs of compounds **9** and **10** were nearly delocalized throughout the entire π-framework and LUMOs mainly existed on the peripheral electron-poor moiety. The HOMO–LUMO excitation moves the electron density distribution from the center phenothiazine (carbazole) core to the outer cyano moiety**.** Fig. 7 demonstrated the calculated frontier orbital energy levels of **7**–**10**. The calculated HOMO–LUMO gaps for **7** and **8** are 3.24 and 3.07 eV, while those for carbazole derivatives **9** and **10** are 3.82 and 3.67 eV, respectively. The lower energy gap values (3.07 and 3.67 eV) of **8** and **10**, compared to those (3.24 and 3.82 eV) of **7** and **9**, mainly due to the reducing of the LUMO energy of **8** and **10** as the result of the introduction of another electron-withdrawing group. On the other hand, the lower energy gap values (3.24 and 3.07 eV) of **7** and **8**, compared to those of the corresponding counterparts **9** and **10** (3.82 and 3.67 eV, respectively), indicated that phenothiazine possesses higher electron-donating ability than carbazole. All this trends obtained by DFT calculations are agreement with experimental absorption spectra results.

It is well-known that the HOMOs, LUMOs, and energy gaps are directly related to the optical properties, while the calculation of the excited states carried out by the time-dependent density functional theory (TD-DFT) provides a convenient method to link the results of electronic structure calculations with experimental data. To investigate the nature of electronic transitions of these dyes, the UV–vis absorption spectra in dichloromethane by TD-DFT calculation were also performed. The strong absorption wavelength λ, oscillator strength f, and main configuration are listed in Table 1. The results indicate that the lowest energy transition for compounds **7**–**10** are in general corresponding to a charge transfer excitation from the HOMO to the LUMO. Compared with the experimental data, the considerable blue-shift of the absorption maximum from the calculations is related to the self-interaction error in TD-DFT arising from the electron transfer in the extended charge-transfer state [35].

Conclusions

In conclusion, we have demonstrated an efficient and facile synthesis of cyano-substituted styryl derivatives based on carbazole and phenothiazine. They were soluble in common organic solvents, showing broad absorption curves. The solvent effect on photophysical behaviors of these dyes was also investigated, and the results showed that the maximal emission displayed a large wavelength shifted and the unusual large Stokes shift increased with the increase of the solvent polarity. DFT calculation results confirmed these dyes based on phenothiazine had narrower energy gaps than that of carbazole, and the lowest-energy absorption bands were mainly due to the HOMO–LUMO one-electron promotion. The thermogravimetric analysis results showed that they were thermally stable hence these dyes may have various application. Further investigations of these dyes on various applications are currently underway.

Acknowledgements

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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.saa.2012.04.090.

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