

Five different colours solid-state fluorescence of azastilbenes: a new push–pull π -conjugated system

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Abstract. Five push–pull azastilbene derivatives [R = –OH (1), –OCH₃ (2), –OCH₂CH₃ (3), –N(CH₃)₂ (4) and –N(CH₂CH₃)₂ (5)] have been synthesized and successfully characterized by ¹H NMR, ultraviolet–visible (UV–Vis) and Fourier-transform infrared (FT-IR) spectroscopy. Compounds 1–5 possess solid-state fluorescence in five different colours ranging from blue to orange (λ_{ex} at 400 nm) in which blue (λ_{em} at 474 nm) for 1, bright-blue (λ_{em} at 469 nm) for 2, green (λ_{em} at 537 nm) for 3, yellow (λ_{em} at 568 nm) for 4 and orange (λ_{em} at 540, 630 nm) for 5. Compounds 4 and 5 exhibited strong fluorescence with quantum yield values 0.61 and 0.84, respectively, higher than those of 1–3. Moreover, liquid-state fluorescence performed in non-polar solvent in order to investigate the effect of dipolar intermolecular interactions on their fluorescence properties, the results revealed that the emission spectra of 1–5 in liquid state are similar to those of solid state, indicating that no significant dipolar interactions were observed. Therefore, the substituent with electron-donating group as N- or O-donor and electron-withdrawing group as –SO₃H, on the azastilbene skeleton play a major role on their solid-state fluorescence.

Keywords. Dipole interaction; multi-colour fluorescence; push–pull azastilbene; quantum yield; solid-state fluorescence.

1. Introduction

Organic solid-state fluorescence materials have been attracted a great deal of interest in various electronic and photonic applications such as semiconductor lasers,¹ fluorescence sensors,² fluorescent technology,³ nonlinear optics,⁴ organic light-emitting diodes (OLEDs)⁵ and optoelectronic devices.^{6,7} One of the advantages of the organic solid-state fluorescence materials is the ability to tune and control of fluorescence colours. Many extensive studies have shown that organic materials exhibit a variety of fluorescent colours in the solid state (scheme 1) such as triphenylamine styryl dye (TMS1);⁸ 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl]anthracene derivatives (FLA-Cn)⁹ and diphenylamino-carbazole pyridinium dyes (OD).¹⁰ From these studies, it indicated that π -conjugated system influences the photonic properties of the compounds.

Stilbenes and azastilbenes are types of compounds which comprise the π -conjugated system in their molecules. Several of them exhibit interesting electronic and photonic properties.^{11–14} In addition, the previous report by Shirai and co-workers¹⁵ found that the substituents affect the photonic properties of the compounds. From the above mentioned, it led us to develop a new push–pull azastilbene fluorophore

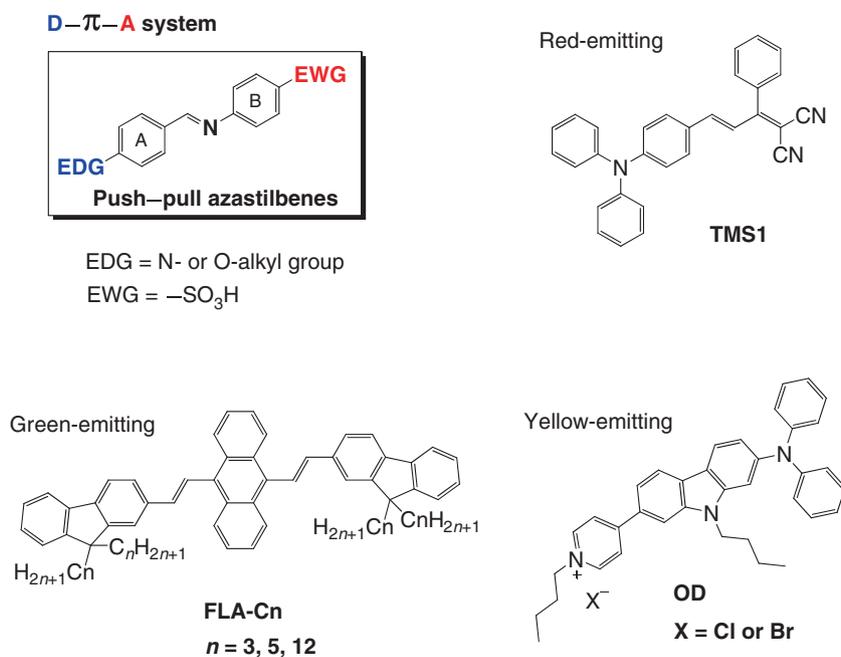
(D– π –A system) exhibiting multi-colour fluorescence by introducing electron-donating group (EDG) on ring A and electron-withdrawing group (EWG) on ring B of azastilbene skeleton (see scheme 1). Herein, we report the synthesis of five push–pull azastilbenes with two kinds of EDGs in which N-alkyl and O-alkyl groups and sulphonic acid as EWG. Their solid-state fluorescence properties were evaluated.

2. Experimental

2.1 General experimental procedures

All the chemical reagents and solvents were of analytical grade, purchased commercially and used without further purification. Melting points were determined on a Fisher–John melting point apparatus. Ultraviolet–visible (UV–Vis) absorption spectra were measured on a Shimadzu UV-2450. Fourier-transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer FTS 165 Fourier-transform infrared spectrometer. The ¹H NMR spectra were recorded on 300 MHz Bruker NMR Ultra Shield spectrometer in DMSO-*d*₆ with TMS as the internal standard. Chemical shifts reported in ppm are expressed in Hertz. Both solid- and liquid-states fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS 55 Luminescence Spectrometer.

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Scheme 1. The designed structure of push-pull azastilbenes and other π -conjugated compounds.

2.2 Method of solid- and liquid-states fluorescence measurement

The powder samples of each azastilbene compounds (0.72 mmol) were heaped in the tray, covered with a quartz plate and then the solid-state fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS 55 Luminescence Spectrometer with slit width of 10 nm at the ambient temperature. Liquid-state fluorescence excitation and emission spectra of the clear solution of each azastilbene compound (1.0 mmol) in tetrahydrofuran (THF) were performed on Perkin-Elmer LS 55 Luminescence Spectrometer with slit width of 10 nm at the ambient temperature. For emission spectra study, the excitation wavelength of both solid and liquid states was set at 400 nm, as selected from their maximum UV-Vis absorption bands. The difference of relative intensities in reflection between the sample and MgO powder was calibrated using diffusion reflection in a non-absorbed wavelength, in the present case it is 650 nm. Finally, fluorescence quantum yield (Φ_f) was determined by Wrighton's method and calculated according to the below equation¹⁶

$$\Phi_f = j_f / (\gamma j_0 - j) \quad (1)$$

where j_f is the fluorescence intensity of the sample, γ the calibration factor (ranging over 0.85–0.97), j_0 the back-scattered intensity of excitation light from a blank (in the present case it is MgO) and j the back-scattered intensity of a loaded sample.

2.3 Synthesis of azastilbene derivatives (1–5)

A mixture of sulphanilic acid (2.8 mmol) and each benzaldehyde derivative (2.8 mmol), in which 4-hydroxybenzaldehyde

for **1**, 4-methoxybenzaldehyde for **2**, 4-ethoxybenzaldehyde for **3**, 4-dimethylaminobenzaldehyde for **4** and 4-diethylaminobenzaldehyde for **5**, was dissolved in 3:1 water-methanol and stirred at 100°C, and the reaction mixture was monitored by TLC. After 2 h, the reaction was completed to give the azastilbene products as a precipitate, which was then filtrated and washed with distilled water. The obtained precipitate was further purified by recrystallization in ethanol to afford the desired azastilbene products **1–5**.

(*E*)-4-sulphonic-4'-hydroxyazastilbene (**1**): Yellow solid (92% yield); mp >300°C; UV-Vis (solid state) λ_{max} : 249, 418 nm; IR (KBr) ν_{max} : 3430 (O-H stretching), 3008 (C-H stretching), 1666 (C=N stretching), 1379 (S=O stretching) cm^{-1} . ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.79 (s, 1H, N=CH), 7.76 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.65 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.19 (d, $J = 8.4$ Hz, 2H, Ar-H) and 6.93 (d, $J = 8.4$ Hz, 2H, Ar-H).

(*E*)-4-sulphonic-4'-methoxyazastilbene (**2**): Yellow solid (86% yield); mp > 300°C; UV-Vis (solid state) λ_{max} : 285, 410 nm; IR (KBr) ν_{max} : 3397 (O-H stretching), 2965 (C-H stretching), 1671 (C=N stretching), 1348 (S=O stretching), 1004 (C-O stretching) cm^{-1} . ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.87 (s, 1H, N=CH), 7.88 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.67 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.27 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.7$ Hz, 2H, Ar-H) and 3.87 (s, 3H, $-\text{OCH}_3$).

(*E*)-4-sulphonic-4'-ethoxyazastilbene (**3**): Yellow solid (93% yield); mp > 300°C; UV-Vis (solid state) λ_{max} : 275, 434 nm; IR (KBr) ν_{max} : 3403 (O-H stretching), 2987 (C-H stretching), 1654 (C=N stretching), 1368 (S=O stretching), 1140 (C-O stretching) cm^{-1} . ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.86 (s, 1H, N=CH), 7.86 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.68 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.23 (d, $J = 8.7$ Hz, 2H,

Ar-H), 7.11 (d, $J = 8.7$ Hz, 2H, Ar-H), 4.15 (q, $J = 6.9$ Hz, 2H, $-\text{OCH}_2-$) and 1.36 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$).

(*E*)-4-sulphonic-4'-dimethylaminoazastilbene (**4**): Orange solid (95% yield); mp $> 300^\circ\text{C}$; UV-Vis (solid state) λ_{max} : 280, 443 nm; IR (KBr) ν_{max} : 3435 (O-H stretching), 2912 (C-H stretching), 1655 (C=N stretching), 1371 (S=O stretching) cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6): δ 9.67 (s, 1H, N=CH), 7.69 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.57 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.04 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.79 (d, $J = 8.7$ Hz, 2H, Ar-H) and 3.05 (s, 6H, $-\text{N}(\text{CH}_3)_2$).

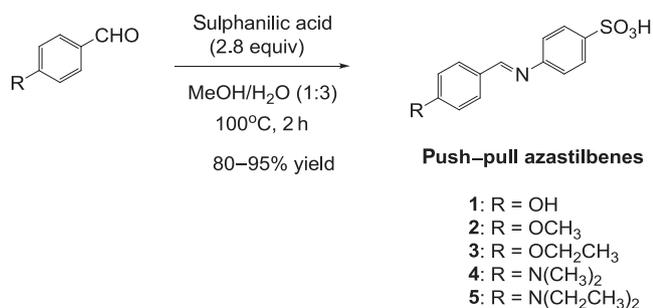
(*E*)-4-sulphonic-4'-diethylaminoazastilbene (**5**): Orange solid (80% yield); mp $267\text{--}268^\circ\text{C}$ (decomposed); UV-Vis (solid state) λ_{max} : 286, 461 nm; IR (KBr) ν_{max} : 3414 (O-H stretching), 2977 (C-H stretching), 1654 (C=N stretching), 1346 (S=O stretching) cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6): δ 9.63 (s, 1H, N=CH), 7.66 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.57 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.05 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.76 (d, $J = 8.4$ Hz, 2H, Ar-H), 3.44 (q, $J = 6.9$ Hz, 4H, $-\text{N}(\text{CH}_2-)_2$) and 1.13 (t, $J = 6.9$ Hz, 6H, $-\text{CH}_3)_2$).

3. Results and discussion

We reported the successful synthesis of push-pull azastilbene derivatives **1–5**, which were formed by condensation of benzaldehyde derivatives and sulphanilic acid as illustrated in scheme 2.

FT-IR spectra of **1–5** exhibited a key vibration signal of the C=N stretching at $1654\text{--}1671$ cm^{-1} (see section 2). The ^1H NMR (300 MHz, DMSO- d_6) spectra of **1–5** also exhibited a singlet signal of an olefinic proton at δ 9.63–9.87 ppm (see section 2) responsible for a signal of an imine part on the azastilbene skeleton, which indicated that the formation of desired azastilbene skeleton was successfully formed *via* condensation reaction.

The solid-state UV-Vis absorption spectra of **1–5** exhibited two key electronic transitions of $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ at 249–286 and 410–461 nm, respectively (see section 2 and figure 1a). The solid-state UV-Vis spectra of **4** and **5** also showed strong red-shifted absorption bands than **1–3**. It could be suggested that N-substituent group as $\text{N}(\text{CH}_3)_2$ and $\text{N}(\text{CH}_2\text{CH}_3)_2$ for **4** and **5** posses electron donating ability than O-substituent group as OH, OCH_3 and OCH_2CH_3 for **1–3**, respectively, which caused the red-shift of the absorption



Scheme 2. Synthesis of the push-pull azastilbenes **1–5**.

spectra. From the maximum absorbance of solid-state UV-Vis spectral data, the excitation wavelength was then set at 400 nm in order to study the solid-state fluorescence emission spectra.

From the solid-state fluorescence emission spectra of **1–5** in figure 1b and table 1, it showed that the push-pull azastilbenes **1–5** exhibited five different emission wavelengths (λ_{em}) in which 474 nm for **1**, 469 nm for **2**, 537 nm for **3**, 568 nm for **4** and 540 and 630 nm for **5**. In figure 1c, the appearance of fluorescence colours of **1–5** were performed under UV irradiation (λ_{ex} at 365 nm), the results showed that push-pull azastilbenes **1–5** emitted five different

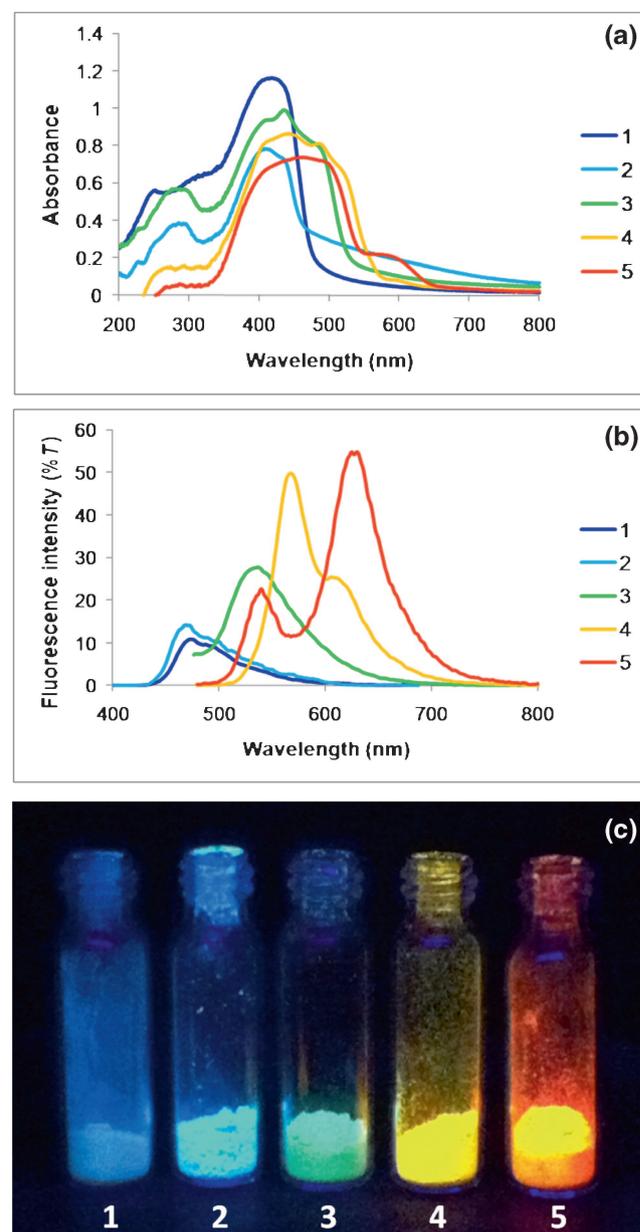


Figure 1. Photophysical properties of **1–5**. (a) Solid-state UV-Vis absorption spectra. (b) Solid-state fluorescence emission spectra (λ_{ex} at 400 nm). (c) The appearance fluorescence colour images under UV irradiation.

Table 1. Solid-state photophysical data for **1–5**.

No.	R	λ_{abs} (nm)	λ_{em} (nm)	Fluorescence intensity	Stokes shift (nm)	Fluorescence colours	Φ_f
1	–OH	418	474	10.87	56	Blue	0.12
2	–OCH ₃	410	469	14.08	59	Bright-blue	0.18
3	–OCH ₂ CH ₃	434	537	27.62	103	Green	0.32
4	–N(CH ₃) ₂	443	568	49.83	125	Yellow	0.61
5	–N(CH ₂ CH ₃) ₂	461	540, 630*	54.80	169	Orange	0.84

* Selected emission wavelength for Stoke shift calculation.

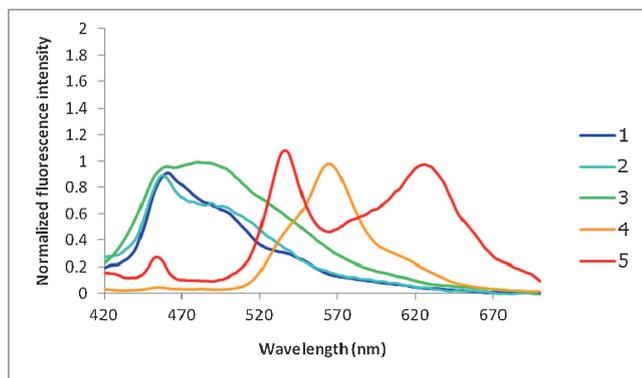


Figure 2. Liquid-state fluorescence emission spectra of **1–5** in THF (λ_{ex} at 400 nm).

fluorescence colours ranging from blue to orange in which blue for **1**, bright-blue for **2**, green for **3**, yellow for **4** and orange for **5**, which corresponded to each of their emission wavelengths. The various fluorescence colours of **1–5** could be finely tuned by varying the donor substituent groups.

To determine the fluorescence efficiency, therefore fluorescence quantum yields of **1–5** were carried out as shown in table 1. It was found that N-substituted azastilbenes **4** and **5** showed higher Φ_f values with 0.61 and 0.84, respectively, in comparison to those of O-substituted azastilbenes **1–3**, indicating that N-substituted groups could enhance the fluorescent intensity.

The presence of the sulphonic and imine parts on this class of molecules was expected that the dipolar intermolecular interactions could be formed self-organized architectures, which may cause their exhibited solid-state fluorescences. To investigate this interaction, the liquid-state fluorescence in non-polar solvent as THF was further performed. In figure 2, the liquid-state fluorescence spectra of **1–5** showed similar emission spectra to those observed in solid-state fluorescence, indicating that no significant dipolar interactions affect the solid-state fluorescence properties of **1–5**.¹⁷

In addition, the crystal packing of **5**¹⁸ as shown in figure 3 is clearly seen that no π – π interaction was observed in the solid state indicating by the centroid–centroid distances (Cg–Cg) between the amino- and sulphonic-substituted

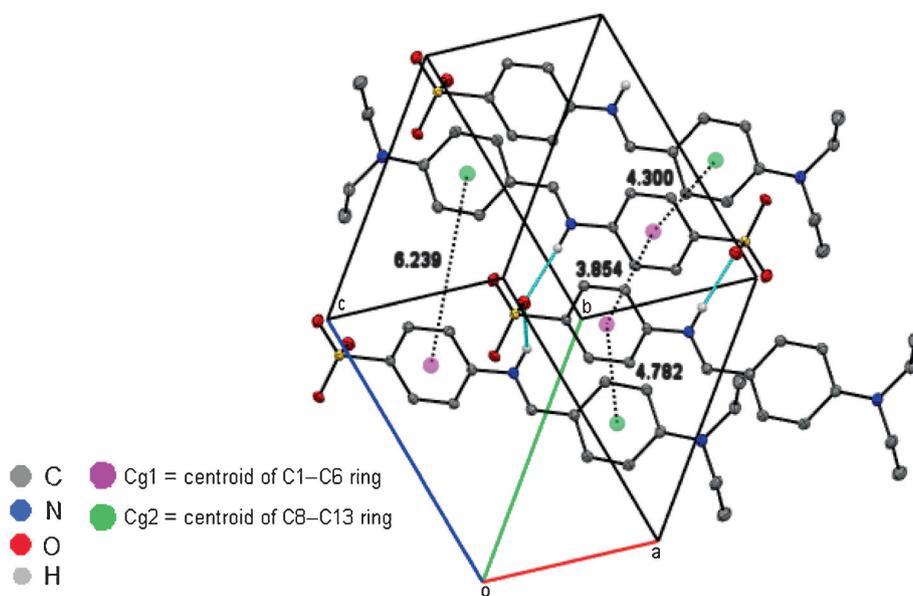


Figure 3. Cg–Cg distances in the solid state of **5**. Only H atom involved in hydrogen bonding was shown for clarity.

phenyl rings (Cg–Cg distances = 3.854(6), 4.300(6), 4.782(6) and 6.239(6) Å) are out of ranges of the π – π interaction (3.3–3.8 Å).¹⁹

From the above mention, it showed that substituents with electron-donating group as N- or O-donor and electron-withdrawing group as –SO₃H, on the azastilbene skeleton responsible for their solid-state fluorescence properties.

4. Conclusion

We have successfully synthesized and developed the five push–pull azastilbenes **1–5**, which emit various fluorescence colours with promising quantum yields. Compounds **1–5** were synthesized in the quantitative yields (80–95% yield) by condensation of sulphanilic acid and benzaldehyde derivatives. Interestingly that the solid-state fluorescence of **1–5** showed five different colours in range of blue to orange in which blue for **1**, bright-blue for **2**, green for **3**, yellow for **4** and orange for **5**. The results suggested that N-substituted group on the azastilbene skeleton has a strong influence on their solid-state fluorescence. Therefore, electron-donating and electron-withdrawing groups on the azastilbene skeleton play a major role on their solid-state fluorescence properties. These synthesized push–pull azastilbenes could be good candidates for various photonic applications.

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