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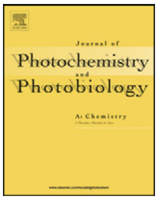

Diarylethene-based imines and amines: Synthesis, photochromic properties and effects of substitution

Ziyong Li, Jun Yin *, Xianghua Wu, Yan Lin, Qingbin Zeng, Fangying Fan, Sheng Hua Liu *

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan 430079, PR China

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ABSTRACT

Condensation of dialdehyde 1 with different aromatic amines gave a series of symmetrical diarylethenes containing Schiff-base moieties, which were reduced with $NaBH_4$ to give the corresponding diarylethene amines. The structures of all new compounds were confirmed by NMR spectroscopy, mass spectrometry, X-ray diffraction and elemental analysis. Their photochromic properties were also investigated, revealing that diarylethene imines displayed better photochromic properties in solution than their amine analogues. Furthermore, we found that by varying the aromatic amine precursor, diarylethenes with different polychromic behavior could be obtained. A number of different aromatic amines were investigated, including different carbon skeletons and substitution with different halogens in various positions, to tune the polychromic behavior.

1. Introduction

Photochromism is the reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. The design and synthesis of novel photochromic molecules has attracted significant interest due to their potential application in photonic devices such as memory media and optical switching [1,2]. Recently, photochromic compounds such as spiropyrans [3], azobenzene [4], fulgides [5] and diarylethenes [6–8] have been extensively investigated. Among these compounds, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene or benzothiophene rings, are considered the most promising candidates for technological applications because of their excellent thermal stability, remarkable fatigue resistance, and high sensitivity [9–24]. Photochromic diarylethenes have therefore attracted much attention, and previous studies have shown that their properties can be tuned by variation of the size and nature of substituent groups. For example, Irie et al. [25] and Uchida et al. [26], Pu et al. [27–30] and Fan et al. [31,32] reported that variation of the terminal substituted phenyl groups affected the photochromic properties and the photochemical reactivity of diarylethenes. Morimitsu et al. [33], and Takami and Irie [34] demonstrated that bulky alkoxy substituents at the 2- and 2′-positions of the thiophene rings can strongly suppress cycloreversion quantum yields. Recently, Yamaguchi and Irie [35,36] reported that bulky alkyl chains at the 2-positions of benzothiophene and benzofuran rings can increase the cyclization quantum yields.

Imines act as an excellent ligand and are widely used in coordination chemistry [37–42], macrocyclic chemistry [43–47] and biochemistry [48,49]. When part of a conjugated π-system, imines have also been used in optoelectronic materials. Therefore it was anticipated that the incorporation of an imine into a photochromic diarylethene system would impart novel photochemical properties on the system. Herein, we report the synthesis of a series of diarylethene imines and amines bearing different substituents. Their structures were confirmed by NMR spectroscopy, mass spectrometry, X-ray diffraction and elemental analysis. The photochromic properties of these compounds were studied, and we discuss here the effects of different substituents, substitution sites and the size of the substituted groups on the photochromic properties of the compounds.

2. Results and discussion

2.1. Synthesis, structure and characterization

The target diarylethene imines **2a–h** were obtained by condensation of different substituted aromatic amines with 1,2-bis(5-formyl-2-methylthien-3-yl)cyclopentene **1** in the presence of excess anhydrous magnesium sulfate in yields of 21–89%. The

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* Corresponding authors. Tel.: +86 27 67867725.
E-mail addresses: yinj@mail.ccnu.edu.cn (J. Yin), chshliu@mail.ccnu.edu.cn (S.H. Liu).

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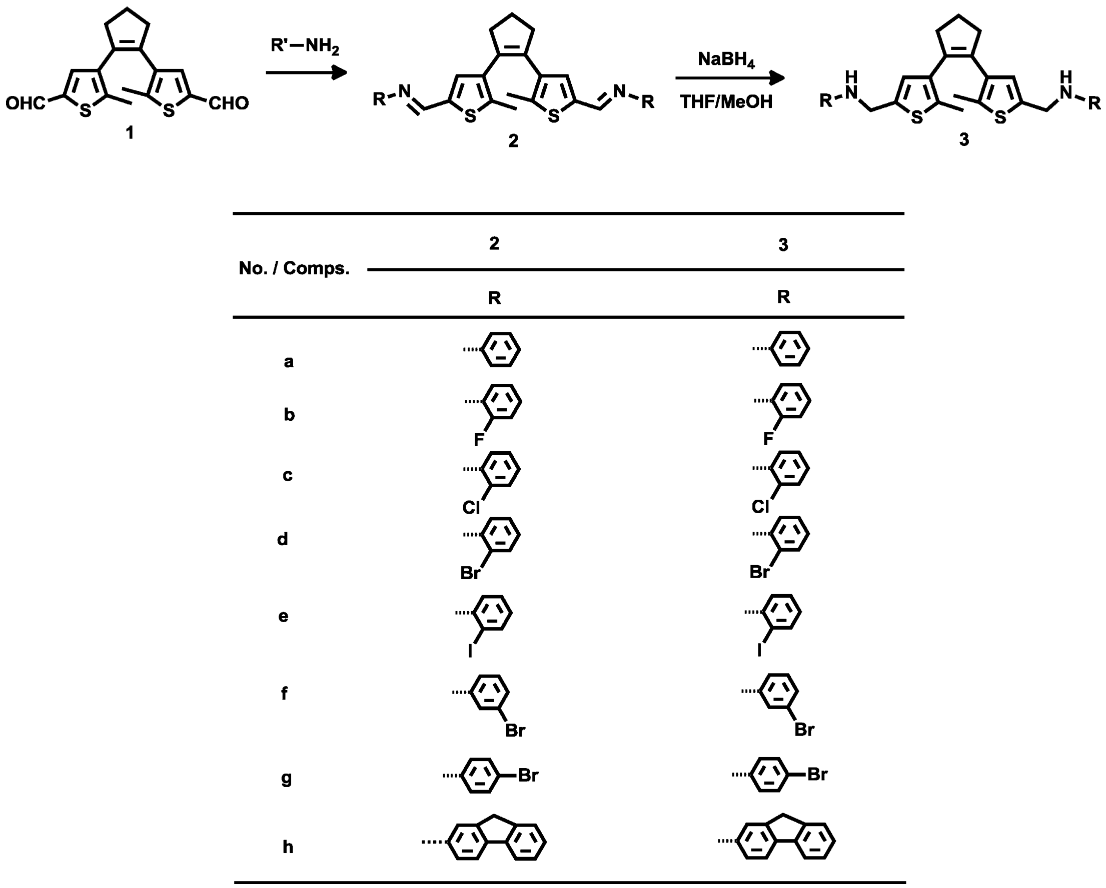

Scheme 1. Synthesis of diarylethene imines **2a–h** and amines **3a–h**.

imines **2a–h** were reduced using sodium borohydride ($NaBH_4$) in a solution of MeOH and THF to give the corresponding amines in 67–91% yields (Scheme 1). All of the target compounds were fully characterized by standard spectroscopic techniques such as NMR, X-ray, MS and elemental analysis. For example, in the ^{1}H NMR spectra, the resonance of the imine protons in **2a–h** (CH=N) appeared as a singlet at 8.24–8.51 ppm, and after reduction, the resonance of amine protons (NH) in diarylethenes **3a–h** were observed at 4.01–4.67 ppm.

2.2. *Single X-crystal diffraction*

Single crystals of **2d** and **3g** were obtained from a mixed dichloromethane and hexane solution. The molecular structures of **2d** and **3g** were determined by X-ray crystallography. Fig. 1 shows ORTEP drawings of the ring-opened isomers **2d** and **3g** and crystallographic details are listed in Table 1. The diarylethenes **2d** and **3g** crystallized with an approximate C_2 symmetry with the photoactive antiparallel conformation in the crystalline phase, which can undergo photocyclization [50]. The molecules feature three types of planar ring system, and two dihedral angles between each of the adjacent planar rings. The dihedral angles between the cyclopentene ring and the thiophene ring were found to be 54.64° for diarylethene **2d** and 47.23° for diarylethene **3g**, and those between the thiophene ring and the benzene ring (attached via carbon–nitrogen double or single bonds) were 61.03° and 84.78°, respectively. For diarylethene **2d**, the C9–N1 bond distance was 1.268 Å, indicating that this bond was a double bond, being significantly shorter than the carbon–nitrogen single bond (1.399 Å). The C9–N1 bond distance was longer in **3g** (1.459 Å), where the imine had been reduced to an amine. The crystal structures also revealed that the intramolecular distance between the two reactive carbons (C5–C5a and C7–C7a) were 3.555 Å and 3.572 Å, respectively. This distance is considered sufficiently small to allow cyclization to take place (less than 4.2 Å [51,52]). However the color changes were not obvious when the crystal were irradiated with UV light.

Table 1
Crystal data and structure refinement parameters for **2d** and **3g**.

	2d	**3g**
Formula	$C_{29}H_{24}Br_2N_2S_2$	$C_{29}H_{28}Br_2N_2S_2$
Formula weight	624.44	628.47
Temperature (K)	292 (2)	298 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2
a (Å)	15.2572 (19)	20.506 (3)
b (Å)	20.257 (2)	8.0332 (11)
c (Å)	9.2415 (11)	8.6121 (12)
β (°)	109.438 (2)	96.690 (2)
Volume (Å^{-3})	2693.4 (6)	1409.0 (3)
Z	4	2
D_{cal} (Mg/m^3)	1.540	1.481
F(0 0 0)	1256	636
Crystal size (mm^3)	0.40 × 0.20 × 0.10	0.20 × 0.19 × 0.18
Goodness-of-fit on F^2	1.073	1.060
Final R indices [$I > 2\sigma(I)$]		
R_1	0.0512	0.0485
wR_2	0.1274	0.1354
R indices (all data)		
R_1	0.0928	0.0607
wR_2	0.1417	0.1419

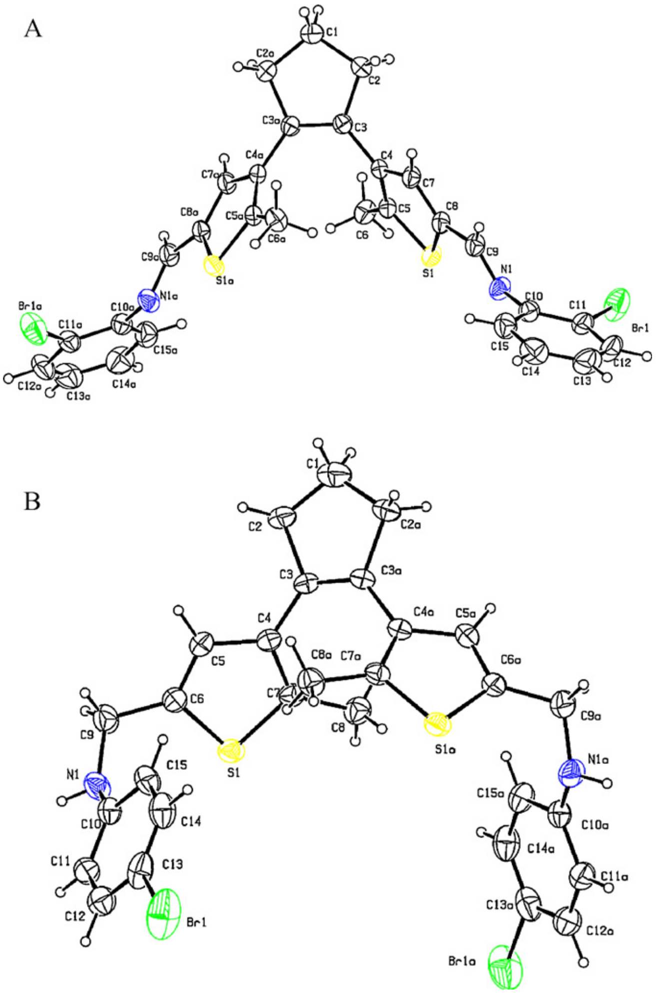

Fig. 1. ORTEP drawing of molecular structures of open-ring isomers **2d** (A) and **3g** (B).

Table 2
Absorption characteristics and photochromic quantum yields of **2a–h** in CH_2Cl_2 (3.0×10^{-5} mol/L).

Compound	$\lambda_{max}{}^{Abs}$/nm[a] ($\varepsilon \times 10^4$)	$\lambda_{max}{}^{Abs}$/nm[b] ($\varepsilon \times 10^4$)	Φ[c]	
	(Open)	(PSS)	$\varphi_{o\text{-}c}$ (λ/nm)	$\varphi_{c\text{-}o}$ (λ/nm)
2a	348 (2.36) 282 (2.52)	598 (0.68)	0.218 (598)	0.0070 (348)
2b	350 (2.97) 282 (3.37)	600 (0.86)	0.027 (600)	0.0006 (350)
2c	348 (2.28) 282 (3.03)	594 (0.44)	0.080 (594)	0.0090 (348)
2d	348 (2.38) 282 (3.25)	606 (0.63)	0.050 (606)	0.0080 (348)
2e	352 (2.37) 288 (3.27)	588 (0.27)	0.016 (588)	0.0003 (352)
2f	350 (3.64) 282 (3.53)	608 (1.33)	0.023 (608)	0.0013 (350)
2g	352 (2.99) 282 (3.07)	602 (0.57)	0.062 (602)	0.0040 (352)
2h	368 (3.79) 284 (3.38)	610 (0.18)	0.237 (610)	0.0059 (368)

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.

2.3. Photochromic properties

The UV/Vis absorption spectra of the diarylethenes were measured in dichloromethane solution. Table 2 shows the absorption spectra of diarylethene imines **2a–h**. The results indicated that the substituted groups and substitution positions on the benzene rings did not significantly change the UV/Vis absorption spectra in imines **2a–g**. However, compared with **2a–g**, the maximum absorption wavelength of imine **2h**, which has a fluorene moiety rather than a benzene, showed a 15 nm red shift. The similar absorption spectra for **2a–g** and different spectrum for **2h** indicates that the UV/Vis absorption is more significantly affected by the extent of the conjugated system than the substituents attached.

The photochromic behaviors of the diarylethene imines **2a–h** were measured using photo irradiation in dichloromethane solution at room temperature. Upon irradiation with UV light, a new absorption band at 588–610 nm appeared for all compounds, as shown in Table 2, due to the formation of the ring-closed isomer (Fig. 2). For example, Fig. 3A shows the changes observed in **2f**, where upon irradiation with UV light ($\lambda = 302$ nm) the appearance of a new absorption band at 608 nm was observed, along with a decrease in the absorption band in the UV region. Furthermore, the pale yellow dichloromethane solution was observed to turn pale blue immediately upon irradiation (Fig. 4). In addition, a well-defined isosbestic point was observed at 368 nm, which clearly indicated that the diarylethene imine **2f** was converted to a photocyclized isomer. Moreover, upon irradiation with visible light ($\lambda > 402$ nm), the pale blue solution reverted to pale yellow. The other diarylethene imines with halogen substituted benzene rings also exhibited similar photochromic behaviors. From these data, shown in Table 2, it was found that the effects of different substituents and substitution sites on the absorption maxima of the closed-ring isomers of diarylethene imines **2a–h** were not significant. However, compared with the starting material diarylethene dialdehyde **1**, these imines displayed 8–30 nm red-shifts due to more extended π-conjugation systems. [53]

While the effects of substitution were not obvious from the absorption wavelength, the effect of substitution on the quantum yields and the molar absorption coefficients was striking. Among the diarylethene imines containing halogen substituted benzene rings, **2b–g**, the cyclization quantum yield of *ortho*-chloro substituted **2c** was the largest ($\varphi_{o\text{-}c} = 0.08$), while that of *ortho*-iodo substituted **2e** was the smallest ($\varphi_{o\text{-}c} = 0.016$). In dichloromethane solution, the molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of *meta*-bromo substituted **2f** were the largest, while the open-ring isomer of *ortho*-chloro substituted **2c** and the closed-ring isomer of *ortho*-iodo substituted **2e** were the smallest. As the cyclization quantum yields showed, the *ortho*-chloro substituted **2c** and the *ortho*-iodo substituted **2e** exhibited the largest and the smallest cycloreversion quantum yields, respectively. In addition, compared with the

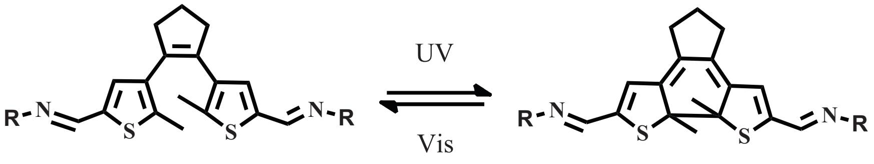

Fig. 2. Photochromism of diarylethenes imines.

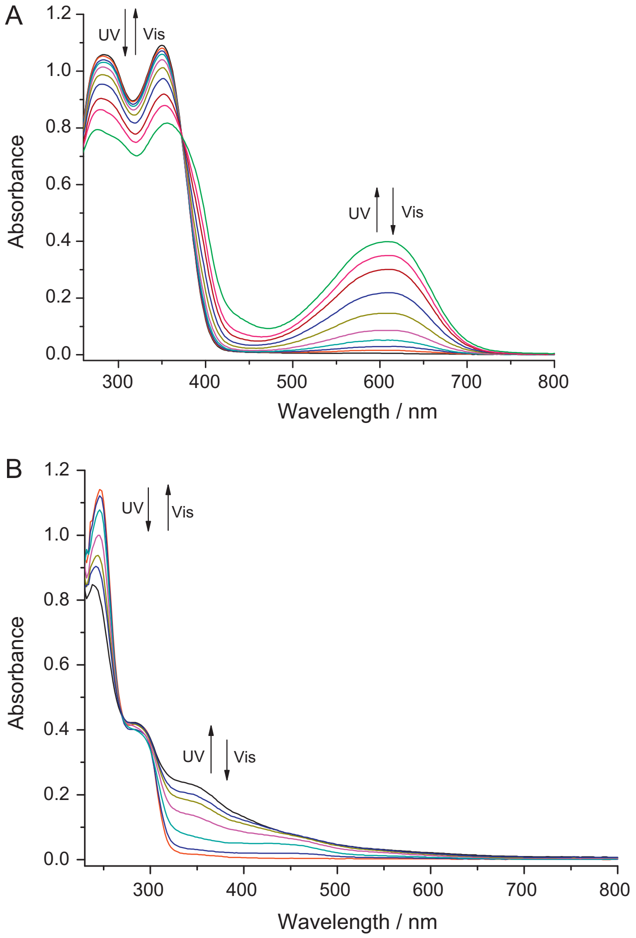

Fig. 3. Absorption spectral changes of diarylethene imine **2f** (A) and amine **3d** (B) by photoirradiation in CH_2Cl_2 (3.0×10^{-5} mol/L) at room temperature.

chloro-, bromo- and iodo-substituted diarylethene imines, we found that the introduction of strongly electron-deficient fluorine atoms did not significantly affect photochromic behavior. While the more extended conjugated system of the fluorene containing diarylethene imine **2h** did not enhance this compound's photochromic behavior, the cyclization quantum yield of **2h** was larger than that of the halogen substituted diarylethene imines. According to the Table 2, such low quantum yields may attribute to the heavy atom effect of dichloromethane as solvent.

After reduction using $NaBH_4$, the UV/Vis absorption spectra of diarylethene amines, **3a–h**, exhibited significant blue-shifts when compared with their imine analogues, due to a decrease in the length of the conjugated system (Fig. 5). Their photochromic properties were investigated under the same conditions as above for **2a–h**. For example, upon irradiation with UV light (λ = 302 nm) of amine **3d**, a new absorption band due to the formation of the closed-ring isomer was observed in the region of 315–540 nm along with a decrease in the absorption band at 250 nm (Fig. 3B) and the colorless solution became pale yellow (Fig. 4). Upon irradiation with visible light (λ > 402 nm), the pale yellow solution reverted to colorless. Similar results were obtained for the photochromic reaction of all other diarylethene amines (**3a–c** and **3e–h**) in dichloromethane.

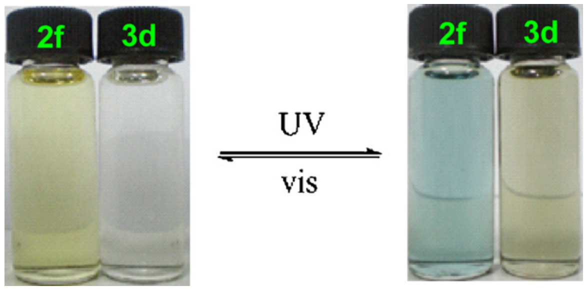

Fig. 4. Photograph of the color change of compounds **2f** and **3d**.

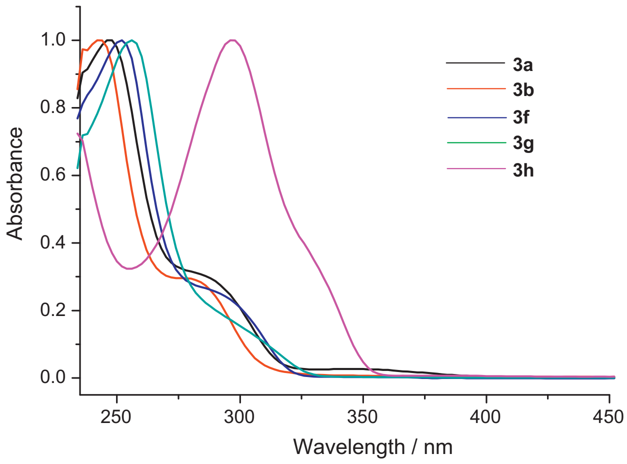

Fig. 5. The UV/Vis absorption spectra of diarylethene amines **3a** and **b**, **f–h** in CH_2Cl_2 (3.0×10^{-5} mol/L) at room temperature.

3. Conclusion

A series of symmetrical diarylethenes containing carbon–nitrogen double and single bonds have been synthesized and their photochromic properties in solution investigated. The results indicated that substitution (F, Cl, Br, I) and the substituent position of the precursor amine can affect the cyclization and cycloreversion quantum yields of the diarylethene imines and amines produced, however, they do not affect the UV/Vis absorption spectra observed upon irradiation with UV or visible light. Compared with the diarylethene amines, the diarylethene imines displayed better photoswitching properties in solution. Further research efforts will focus on utilizing the excellent coordinative ability of the Schiff base to investigate the effect of metal ions on the photochromic properties of these ligands.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium-benzophenone. EtOH and MeOH were distilled under drying pipe from magnesium–iodine. 1, 2-Bis(5-formyl-2-methylthien-3-yl)cyclopentene **(1)** was prepared by the previous literature [53]. Amines and other starting materials were obtained commercially as analytical-grade and used without further purification. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [54]. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ^1H and ^{13}C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or 600 MHz. The chemical shifts are relative to TMS. UV–Vis absorption spectra were recorded on U-3310 UV Spectrophotometer.

4.2. General synthetic procedure of **2a–h**

Synthesis of **2**: To a solution of **1** (1.0 mmol) in anhydrous EtOH (80 mL) was added amines (2.0 mmol) with anhydrous magnesium sulfate acting as drying agent under argon atmosphere. The mixture was refluxed for 24 h. After removing the solvent, the compound was recrystallized from the mixture solution of dichloromethane and hexane to give diarylethene imines in 21–89% yields.

Compound **2a**: Yield, 83%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.06 (s, 6H, CH$_3$), 1.98–2.09 (m, 2H, CH$_2$), 2.83 (t, J = 7.2 Hz, 4H, CH$_2$), 7.15 (s, 2H, thiophene-H), 7.17–7.37 (m, 10H, Ar), 8.28 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.10 (s, CH$_3$), 22.89 (s, CH$_2$), 38.33 (s, CH$_2$), 120.99, 125.81, 129.05, 133.51, 134.63, 136.45, 138.70, 140.89, 151.44 (s, Ar, ethene, thiophene), 154.87 (s, CH=N). MS (m/z): 466 [M]$^+$. Anal. Calcd for C$_{29}$H$_{26}$N$_2$S$_2$: C, 74.64; H, 5.62; N, 6.00. Found: C, 74.46; H, 5.80; N, 5.87.

Compound **2b**: Yield, 58%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.07 (s, 6H, CH$_3$), 2.16–2.18 (m, 2H, CH$_2$), 2.83 (t, J = 7.2 Hz, 4H, CH$_2$), 7.18 (s, 2H, thiophene-H), 7.10–7.13 (m, 8H, Ar), 8.46 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.12 (s, CH$_3$), 22.85 (s, CH$_2$), 38.30 (s, CH$_2$), 116.13,(d, Ar), 122.31, 1124.36, 126.44, 134.02, 134.59, 136.49, 138.50, 139.34, 141.63, 153.99, 155.30, (s, Ar, ethene, thiophene), 156.47 (s, CH=N). MS (m/z): 502 [M]$^+$. Anal. Calcd for C$_{29}$H$_{24}$F$_2$N$_2$S$_2$: C, 69.30; H, 4.81; N, 5.57. Found: C, 69.47; H, 4.52; N, 5.78.

Compound **2c**: Yield, 47%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.07 (s, 6H, CH$_3$), 2.04–2.09 (m, 2H, CH$_2$), 2.83 (t, J = 7.6 Hz, 4H, CH$_2$), 7.01 (d, J = 7.6 Hz, 2H, Ar), 7.07–7.25 (m, 4H, Ar), 7.18 (s, 2H, thiophene-H), 7.40 (d, J = 8.0 Hz, 2H, Ar), 8.32 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.14 (s, CH$_3$), 22.84 (s, CH$_2$), 38.31 (s, CH$_2$), 120.07, 126.20, 127.45, 128.03, 129.82, 134.10, 134.58, 136.49, 138.30, 141.80, 148.84, (s, Ar, ethene, thiophene), 154.32 (s, CH=N). MS (m/z): 534 [M]$^+$.Anal. Calcd for C$_{29}$H$_{24}$Cl$_2$N$_2$S$_2$: C, 65.04; H, 4.52; N, 5.23. Found: C, 65.21; H, 4.26; N, 5.08.

Compound **2d**: Yield, 64%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.09 (s, 6H, CH$_3$), 2.08–2.11 (m, 2H, CH$_2$), 2.83 (t, J = 7.2 Hz, 4H, CH$_2$), 6.99–7.05 (m, 4H, Ar), 7.18 (s, 2H, thiophene-H), 7.25–7.58 (m, 2H, Ar), 7.59 (d, J = 8.0 Hz, 2H, Ar), 8.28 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.40 (s, CH$_3$), 22.92 (s, CH$_2$), 38.37 (s, CH$_2$), 118.43, 119.82, 126.50, 128.20, 132.96, 134.01, 134.70, 136.59, 138.40, 141.88, 150.21 (s, Ar, ethene, thiophene), 154.02 (s, CH=N). MS (m/z): 624 [M]$^+$.Anal. Calcd for C$_{29}$H$_{24}$Br$_2$N$_2$S$_2$: C, 55.78; H, 3.87; N, 4.49. Found: C, 55.59; H, 4.15; N, 4.50.

Compound **2e**: Yield, 71%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.10 (s, 6H, CH$_3$), 2.08–2.12 (m, 2H, CH$_2$), 2.83 (t, J = 7.2 Hz, 4H, CH$_2$), 7.88 (t, J = 7.6 Hz, 2H, Ar), 6.98 (d, J = 7.6 Hz, 2H, Ar), 7.19 (s, 2H, thiophene-H), 7.31 (t, J = 7.2 Hz, 2H, Ar), 7.85 (d, J = 7.6 Hz, 2H, Ar), 8.24 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.18 (s, CH$_3$), 22.86 (s, CH$_2$), 38.31 (s, CH$_2$), 95.34, 118.34, 126.87, 129.18, 133.89, 134.58, 136.57, 138.31, 138.93, 141.83, 152.34 (s, Ar, ethene, thiophene), 153.25 (s, CH=N). MS (m/z): 718 [M]$^+$. Anal. Calcd for C$_{29}$H$_{24}$I$_2$N$_2$S$_2$: C, 48.48; H, 3.37; N, 3.90. Found: C, 48.19; H, 3.55; N, 3.66.

Compound **2f**: Yield, 73%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.06 (s, 6H, CH$_3$), 2.06–2.10 (m, 2H, CH$_2$), 2.82 (t, J = 7.2 Hz, 4H, CH$_2$), 7.11 (d, J = 7.2 Hz, 2H, Ar), 7.17 (s, 2H, thiophene-H), 7.21 (t, J = 7.2 Hz, 2H, Ar), 7.31 (d, J = 6.4 Hz, 4H, Ar), 8.35 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.12 (s, CH$_3$), 22.88 (s, CH$_2$), 38.30 (s, CH$_2$), 120.16, 122.67, 123.73, 128.58, 130.34, 134.16, 134.68, 136.58, 138.29, 141.64, 152.81 (s, Ar, ethene, thiophene), 153.65 (s, CH=N). MS (m/z): 624 [M]$^+$. Anal. Calcd for C$_{29}$H$_{24}$Br$_2$N$_2$S$_2$: C, 55.78; H, 3.87; N, 4.49. Found: C, 55.91; H, 4.07; N, 4.53.

Compound **2g**: Yield, 21%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.06 (s, 6H, CH$_3$), 2.02–2.11 (m, 2H, CH$_2$), 2.82 (t, J = 7.6 Hz, 4H, CH$_2$), 7.05 (d, J = 8.4 Hz, 4H, Ar), 7.16 (s, 2H, thiophene-H), 7.45 (d, J = 8.4 Hz, 4H, Ar), 8.35 (s, 2H, CH=N), ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.08 (s, CH$_3$), 22.87 (s, CH$_2$), 38.30 (s, CH$_2$), 119.12, 122.66, 132.07, 133.88, 134.66, 136.56, 138.44, 141.38, 150.32 (s, Ar, ethene, thiophene), 153.07 (s, CH=N). MS (m/z): 624 [M]$^+$. Anal. Calcd for C$_{29}$H$_{24}$Br$_2$N$_2$S$_2$: C, 55.78; H, 3.87; N, 4.49. Found: C, 55.53; H, 3.59; N, 4.68.

Compound **2h**: Yield, 87%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.09 (s, 6H, CH$_3$), 2.04–2.11 (m, 2H, CH$_2$), 2.84 (t, J = 7.2 Hz, 4H, CH$_2$), 3.90 (s, 4H, CH$_2$), 7.17 (s, 2H, thiophene-H), 7.23–7.39 (m, 8H, fluorene), 7.52 (d, J = 7.6 Hz, 2H, fluorene), 7.75 (d, J = 8.0 Hz, 4H, fluorene), 8.49 (s, 2H, CH=N). ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.12 (s, CH$_3$), 22.96 (s, CH$_2$), 36.92 (s, CH$_2$), 38.36 (s, CH$_2$), 117.66, 119.68, 120.28, 124.97, 126.42, 126.80, 133.31, 134.72, 136.53, 138.98, 139.78, 140.85, 141.40, 143.33, 144.37, 150.34 (s, fluorene, ethene, thiophene). MS (m/z): 642 [M]$^+$. Anal. Calcd for C$_{43}$H$_{34}$N$_2$S$_2$: C, 80.34; H, 5.33; N, 4.36. Found: C, 80.50; H, 5.15; N, 4.52.

4.3. General synthetic procedure of **3a–h**

Synthesis of **3**: To a solution of **2** (1.0 mmol) in anhydrous MeOH (8 mL) and THF (10 mL) was added sodium borohydride (10 mmol) under a argon atmosphere. The mixture was reacted under dark conditions for 12 h at room temperature. The product was extracted with absolute ethyl ether, then dried over sodium sulfate, upon removed of solvent under reduced pressure and purified on a silica gel column using petroleum ether/ethyl acetate (9:1) as the eluent to give diarylethene amines in 67–91% yields.

Compound **3a**: Yield, 85%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.87 (s, 6H, CH$_3$), 1.98–2.02 (m, 2H, CH$_2$), 2.73 (t, J = 7.6 Hz, 4H, CH$_2$), 4.02 (s, 2H, N–H), 4.34 (s, 4H, N–CH$_2$), 6.60 (s, 4H, Ar), 6.62 (s, 2H, thiophene-H), 6.71 (t, J = 7.6 Hz, 2H, Ar), 7.15 (t, J = 8.4 Hz, 4H, Ar). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.19 (s, CH$_3$), 29.66 (s, CH$_2$), 38.24 (s, CH$_2$), 43.53 (s, N–CH$_2$) 113.12, 117.88, 126.09, 129.15, 133.70, 134.47, 135.21, 138.26, 147.57 (s, Ar, ethene, thiophene). MS (m/z): 470 [M]$^+$. Anal. Calcd for C$_{29}$H$_{30}$N$_2$S$_2$: C, 74.00; H, 6.42; N, 5.95. Found: C, 74.30; H, 6.24; N, 5.64.

Compound **3b**: Yield, 80%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.87 (s, 6H, CH$_3$), 2.00–2.02 (m, 2H, CH$_2$), 2.74 (t, J = 7.2 Hz, 4H, CH$_2$), 4.22 (s, 2H, N–H), 4.37 (s, 4H, N–CH$_2$), 6.63 (s, 2H, thiophene-H), 6.65 (s, 2H, Ar), 6.70 (t, J = 7.8 Hz, 2H, Ar), 6.96 (t, J = 9.0 Hz, 4H, Ar). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.19 (s, CH$_3$), 22.93 (s, CH$_2$), 38.24 (s, CH$_2$), 43.12 (s, N–CH$_2$), 112.58 (s), 114.42 (d), 117.19 (d), 124.46 (s), 126.21 (s), 133.90 (s), 134.48 (s), 135.24 (s), 135.99 (s), 137.80 (s), 150.77 (s), 152.36 (s), (Ar, ethene, thiophene). MS (m/z): 506 [M]$^+$. Anal. Calcd for C$_{29}$H$_{28}$F$_2$N$_2$S$_2$: C, 68.74; H, 5.57; N, 5.53. Found: C, 69.02; H, 5.34; N, 5.29.

Compound **3c**: Yield, 67%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.87 (s, 6H, CH$_3$), 1.93–2.02 (m, 2H, CH$_2$), 2.73 (t, J = 6.6 Hz, 4H, CH$_2$), 4.38 (s, 4H, N–CH$_2$), 4.65 (s, 2H, N–H), 6.62 (s, 2H, thiophene-H), 6.65 (d, J = 8.4 Hz, 4H, Ar), 7.08 (t, J = 7.2 Hz, 2H, Ar), 7.23 (d, J = 7.8 Hz, 2H, Ar). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.16 (s, CH$_3$), 22.90 (s, CH$_2$), 38.20 (s, CH$_2$), 43.12 (s, N–CH$_2$), 111.63, 117.68, 119.25, 126.13, 127.62, 129.03, 133.84, 134.47, 135.22, 137.60, 143.33 (s, Ar, ethene, thiophene). MS (m/z): 538 [M]$^+$. Anal. Calcd for C$_{29}$H$_{28}$Cl$_2$N$_2$S$_2$: C, 64.55; H, 5.23; N, 5.19. Found: C, 64.81; H, 5.01; N, 4.99.

Compound **3d**: Yield, 85%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.87 (s, 6H, CH$_3$), 1.93–2.02 (m, 2H, CH$_2$), 2.74 (t, J = 6.6 Hz, 4H, CH$_2$), 4.38 (s, 4H, N–CH$_2$), 4.67 (s, 2H, N–H), 6.57 (d, J = 7.2 Hz, 4H, Ar), 6.63 (s, 2H, thiophene-H), 7.13 (d, J = 7.2 Hz, 2H, Ar), 7.40 (d, J = 6.6 Hz, 2H, Ar). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.21 (s, CH$_3$), 22.93 (s, CH$_2$), 38.21 (s, CH$_2$), 43.32 (s, N–CH$_2$), 109.86, 111.75, 118.25, 126.16, 128.34, 132.34, 133.87, 134.50, 135.25, 137.55, 144.31 (s, Ar, ethene, thiophene). MS (m/z): 626 [M]$^+$. Anal. Calcd for C$_{29}$H$_{28}$Br$_2$N$_2$S$_2$: C, 55.42; H, 4.49; N, 4.46. Found: C, 55.43; H, 4.26; N, 4.17.

Compound **3e**: Yield, 90%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.88 (s, 6H, CH$_3$), 1.94–2.02 (m, 2H, CH$_2$), 2.75 (t, J = 6.6 Hz, 4H, CH$_2$), 4.38 (s, 4H, N–CH$_2$), 4.53 (s, 2H, N–H), 6.45–6.58 (m, 4H, Ar), 6.63 (s, 2H, thiophene-H), 7.17 (d, J = 6.6 Hz, 2H, Ar), 7.65 (d, J = 7.2 Hz, 2H, Ar). ^{13}C NMR (150 MHz, CDCl$_3$): δ 14.24 (s, CH$_3$), 22.94 (s, CH$_2$), 38.21

(s, CH_2), 43.70 (s, N–CH_2), 85.58, 111.09, 119.12, 126.21, 129.29, 133.89, 134.52, 135.27, 137.46, 138.96, 146.61 (s, Ar, ethene, thiophene). MS (*m*/*z*): 722 $[M]^+$.Anal. Calcd for $C_{29}H_{28}I_2N_2S_2$: C, 48.21; H, 3.91; N, 3.88. Found: C, 48.91; H, 3.65; N, 3.69.

Compound **3f**: Yield, 82%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 6H, CH_3), 1.97–2.05 (m, 2H, CH_2), 2.73 (t, J = 7.2 Hz, 4H, CH_2), 4.04 (s, 2H, N–H), 4.29 (s, 4H, N–CH_2), 6.49–7.00 (m, 8H, Ar), 6.49–6.51 (m, 2H, Ar), 6.61 (s, 2H, thiophene-H), 6.73 (t, J = 1.6 Hz, 2H, Ar), 6.81 (d, J = 8.0 Hz, 2H, Ar), 6.98 (t, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.23 (s, CH_3), 22.91 (s, CH_2), 38.23 (s, CH_2), 43.23 (s, N–CH_2), 111.79, 115.62, 120.57, 123.13, 123.20, 130.38, 133.91, 134.45, 135.25, 137.51, 144.74 (s, Ar, ethene, thiophene). MS (*m*/*z*): 626 $[M]^+$.Anal. Calcd for $C_{29}H_{28}Br_2N_2S_2$: C, 55.42; H, 4.49; N, 4.46. Found: C, 55.60; H, 4.19; N, 4.51.

Compound **3g**: Yield, 91%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 6H, CH_3), 1.99–2.03 (m, 2H, CH_2), 2.73 (t, J = 7.6 Hz, 4H, CH_2), 4.01 (s, 2H, N–H), 4.29 (s, 4H, N–CH_2), 6.46–6.48 (m, 4H, Ar), 6.58 (s, 2H, thiophene-H), 7.20–7.24 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.20 (s, CH_3), 22.91 (s, CH_2), 38.17 (s, CH_2), 43.41 (s, N–CH_2), 109.47, 114.67, 126.20, 131.80, 133.81, 134.48, 135.22, 137.73, 146.45 (s, Ar, ethene, thiophene). MS (*m*/*z*): 626 $[M]^+$. Anal. Calcd for $C_{29}H_{28}Br_2N_2S_2$: C, 55.42; H, 4.49; N, 4.46. Found: C, 55.13; H, 4.21; N, 4.57.

Compound **3h**: Yield, 84%. ^1H NMR (600 MHz, $CDCl_3$): δ 1.88 (s, 6H, CH_3), 1.99–2.03 (m, 2H, CH_2), 2.73 (t, J = 6.6 Hz, 4H, CH_2), 3.75 (s, 4H, CH_2), 4.01 (s, 2H, N–H), 4.34 (s, 4H, N–CH_2), 6.59–6.63 (m, 4H, fluorene), 6.76 (s, 2H, thiophene-H), 7.15 (t, 2H, J = 7.2 Hz, fluorene), 7.27 (t, 2H, J = 7.2 Hz, fluorene), 7.42 (d, 2H, J = 7.2 Hz, fluorene), 7.53 (d, 2H, J = 7.8 Hz, fluorene), 7.58 (d, 2H, J = 7.8 Hz, fluorene), ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.23 (s, CH_3), 22.91 (s, CH_2), 36.88 (s, CH_2), 38.21 (s, CH_2), 43.73 (s, N–CH_2), 109.54, 112.18, 118.43, 120.52, 124.64, 124.83, 126.05, 126.54, 132.29, 133.67, 134.47, 135.22, 138.27, 142.14, 144.99, 147.03 (s, fluorene, ethene, thiophene). MS (*m*/*z*): 646 $[M]^+$. Anal. Calcd for $C_{43}H_{38}N_2S_2$: C, 49.84; H, 5.92; N, 4.33. Found: C, 49.65; H, 5.80; N, 4.60.

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