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Synthesis and photophysical properties of 1,4-bis(4,5-diarylimidazol) benzene dyes

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Abstract

A class of π-conjugated 1,4-bis(4,5-diarylimidazol)benzene dyes (**1**–**5**) are synthesized, and all dyes exhibit strong fluorescence in solution ($\phi_f = 0.96$–0.45, in DMSO). It is found that both absorption and fluorescence of dyes are influenced by molecular structures and electronic properties of substitute groups, but little influenced by the polarity of solvents and pH value. Besides, two-photon properties of dyes are also investigated. The largest two-photon absorption cross-section ($\sigma = 98$ GM) for dye **4** is obtained with 700 nm in DMSO, and two-photon fluorescence emission is also observed with 740 nm excitation in solution.

Keywords: 1,4-Bis(4,5-diarylimidazol)benzenes; Fluorescence; Two-photon absorption; Two-photon fluorescence

1. Introduction

The development of new molecular fluorophores for biologic analysis [1] and optical application [2] has emerged as an actively investigated research in recent years. Despite the multitude of available fluorophores [3], new fluorophoric systems with easy preparation and strong fluorescence are hotly sought for more challenging applications including two-photon fluorescence imaging [4], fluorescence sensor [5], fluorescence switching [6] and nondestructive readout [7]. Herein, we report a family of π-conjugated 1,4-bis(4,5-diarylimidazol)benzenes (**1**–**5**) (Scheme 1), which are obtained easily and exhibit very strong fluorescence in solution. Although some of them have been reported alone on synthesis and properties [8], That the photophysical properties of these dyes influenced by both molecular structures and electronic properties of substitute groups as well as the solvent polarity and pH value is, for the first time, reported in this paper. Beside, both two-photon absorption cross-section and two-photon fluorescence emission of these dyes are investigated for the first time, and the results are also presented in this paper.

2. Experimental

2.1. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz with TMS as an internal reference and DMSO-d_6 as solvent. UV absorption spectra and fluorescence spectra were measured on an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. Two-photon induced excited fluorescence spectra were recorded on SD2000 spectrometer (Ocean Optical), excited by mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics) which oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively.

2.2. Chemicals

All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Compounds **1**–**5** were prepared as following: a vigorously stirred mixture of terephthaladehyde (40 mg, 0.3 mmol), phenanthrenequinone (140 mg, 0.67 mmol), and ammonium acetate (300 mg, 3.9 mmol) in ethanol (50 ml) was refluxed for 10 h. During this time, the color gradually changed, and bright yellow precipitate was produced. The reaction mixture

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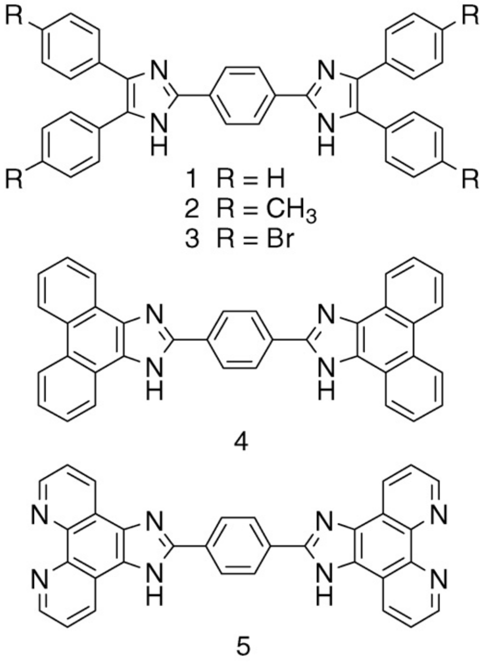

Scheme 1. Chemical structures of 1,4-bis(4,5-diarylimidazol)benzenes.

was cooled, and the yellow product was filtered off, washed with water and EtOH, pure **4** was obtained after vacuum-dried. Compounds **1**–**3** and **5** were prepared by the same procedures except that the starting material was replaced by benzil, benzil derivatives and 1,10-phenanthroline-5,6-dione, respectively.

(**1**) Yield 73%. mp > 300 °C. ^{1}H NMR: 12.76 (s, 2H), 8.19 (s, 4H), 7.58 (d, J = 7.4 Hz, 4H), 7.54 (d, J = 7.4 Hz, 4H), 7.46 (t, 4H), 7.39 (t, 2H), 7.32 (t, 4H), 7.24 (t, 2H). ^{13}C NMR: 145.1, 137.4, 135.1, 131.0, 129.8, 128.7, 128.4, 128.3, 127.9, 127.2, 126.7, 125.4. FAB MS (*m/z*): $[M+\mathrm{H}]^+$ calcd. for $C_{36}H_{26}N_4$: 514.63. Found: 515. Anal. Calcd. for $C_{36}H_{26}N_4$: C, 84.02; H, 5.09; N, 10.89. Found: C, 84.04; H, 5.07; N, 10.92. (**2**) Yield 70%. mp > 300 °C. ^{1}H NMR: 12.63 (s, 2H), 8.15 (s, 4H), 7.46 (d, J = 8.0 Hz, 4H), 7.40 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 8.0 Hz, 4H), 2.36 (s, 6H), 2.19 (s, 6H). ^{13}C NMR: 144.8, 137.1, 135.7, 132.4, 129.8, 129.3, 128.8, 128.2, 127.1, 125.3, 20.8. FAB MS (*m/z*): $[M+\mathrm{H}]^+$ calcd. for $C_{40}H_{34}N_4$: 570.74, Found: 571. Anal. Calcd. for $C_{38}H_{34}N_4$: C, 84.18; H, 6.00; N, 9.82. Found: C, 84.21; H, 5.58; N, 9.86. (**3**) Yield 65%. mp > 300 °C. ^{1}H NMR: 12.91 (s, 2H), 8.17 (s, 4H), 7.86 (d, J = 2.2 Hz, 4H), 7.68 (d, J = 8.0 Hz, 4H), 7.55–7.46 (m, 8H). ^{13}C NMR: 192.9, 136.7, 134.1, 132.6, 131.8, 131.7, 131.4, 131.2, 130.4, 130.1, 129.8, 129.2, 125.6, 119.9. FAB MS (*m/z*): $[M+\mathrm{H}]^+$ calcd. for $C_{36}H_{22}Br_4N_4$: 830.21, Found: 831. Anal. Calcd. for $C_{36}H_{22}Br_4N_4$: C, 52.08; H, 2.67; N, 6.75. Found: C, 52.11; H, 2.64; N, 6.78. (**4**) Yield 80%. mp > 300 °C. ^{1}H NMR: 13.61 (s, 2H), 8.91 (d, J = 8.4 Hz, 2H), 8.87 (d, J = 8.3 Hz, 2H), 8.66 (d, J = 7.8 Hz, 2H), 8.62 (d, J = 8.0 Hz, 2H), 8.54 (s, 4H), 7.81–7.74 (m, 4H), 7.69–7.65 (m, 4H). ^{13}C NMR: 148.5, 137.3, 130.7, 127.9, 127.8, 127.7, 127.3, 127.2, 126.9, 126.6, 125.6, 125.4, 124.2, 123.8, 122.4, 122.1, 122.0. FAB MS (*m/z*): $[M+\mathrm{H}]^+$ calcd. for $C_{36}H_{22}N_4$: 510.60, Found: 511. Anal. Calcd. for $C_{36}H_{22}N_4$: C, 84.68; H, 4.34; N, 10.97. Found: C, 84.68; H, 4.31; N, 10.99. (**5**) Yield 78%. mp > 300 °C. ^{1}H NMR: 13.99 (s, 2H), 9.07 (d, J = 4.2 Hz, 4H), 8.99 (d, J = 8.0 Hz, 4H), 8.53 (s, 4H), 7.88–7.84 (m, 4H). FAB MS (*m/z*): $[M+\mathrm{H}]^+$ calcd. for $C_{32}H_{18}N_8$: 514.5502, Found: 515. Anal. Calcd. for $C_{32}H_{18}N_8$: C, 74.70; H, 3.52; N, 21.78. Found: C, 74.74; H, 3.50; N, 21.82.

3. Results and discussion

The absorption spectra of **1** and **4** in DMSO solution were presented in Fig. 1. The absorption peaks of **1** were at $\lambda = 380$ nm (should) ($\varepsilon = 3.2 \times 10^4$), 363 nm ($\varepsilon = 4.2 \times 10^4$), and 300 nm ($\varepsilon = 2.0 \times 10^4$), respectively. By comparison of the absorption spectrum of **1** with that of benzil, it is found that the longer peaks (380 and 363 nm) attribute to the absorption of the whole molecule **1**, while the shorter peak at 300 nm corresponds to the absorption of benzil group. Similar results were obtained when the absorption spectra of **4** was measured. As shown in Fig. 1 (down), The two longer absorption bands at $\lambda_{\max} = 410$ nm ($\varepsilon = 3.5 \times 10^4$) and $\lambda_{\max} = 386$ nm ($\varepsilon = 4.4 \times 10^4$), respectively, attribute to the absorption of the whole molecule **4**, while the absorption at $\lambda_{\max} = 272$ nm ($\varepsilon = 8.0 \times 10^4$) corresponds to the absorption of phenanthrenequinone group. Investigating other dyes **2**, **3**, and **5** found that the results were similar to that of the above. The UV data of dyes **1**–**5** are listed in Table 1.

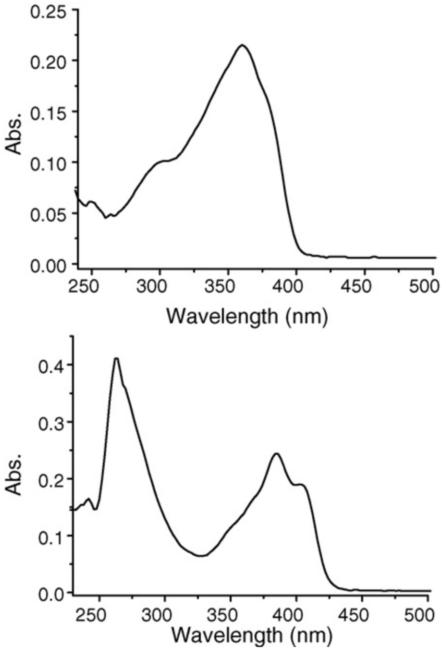

Fig. 1. Absorption spectra of **1** (up) and **4** (down) in DMSO ($c = 5 \times 10^{-6}$ M).

Table 1
The UV data of dyes **1**–**5** in DMSO (5×10^{-6} M)

Dye	λ (nm)/ε ($\times 10^4$)	λ (nm)/ε ($\times 10^4$)	λ (nm)/ε ($\times 10^4$)
1	380 (3.2)	363 (4.2)	300 (2.0)
2	395 (3.1)	370 (4.0)	305 (2.1)
3	289 (2.4)	368 (3.6)	287 (2.5)
4	410 (3.5)	386 (4.4)	272 (8.0)
5	398 (3.6)	378 (4.4)	284 (3.8)