Received: 7 March 2013,

Revised: 8 July 2013,

(wileyonlinelibrary.com) DOI 10.1002/bio.2580

# Study on the synthesis and structure–effect relationship of multi-aryl imidazoles with their fluorescence properties

# Mi Tian, Chao Wang, LiGong Wang, Kai Luo, An Zhao and CanCheng Guo\*

ABSTRACT: In this paper, 23 multi-aryl imidazole derivatives were synthesized and identified by nuclear magnetic resonance, ultraviolet-visible and elemental analysis. At the same time, their ultraviolet-visible maximum absorption ( $\lambda_{ab}^{max}$ ), fluorescence emission maximum ( $\lambda_{em}^{max}$ ) and quantum yields ( $\Phi_f$ ) were measured. The relationships between the optical behaviors and structures for these compounds were assessed. The results show that the  $\lambda_{ab}^{max}$  and  $\lambda_{em}^{max}$  are red-shifted and the fluorescence  $\Phi_f$  are increased by the introduction of electron-withdrawing substituents and the increase in the planarity of multi-aryl imidazole molecules. The results also showed that the fluorescence quantum yields of the compounds containing two imidazole nuclei are double the corresponding mono-imidazole nucleus compounds. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: multi-aryl imidazole; fluorescent molecule; quantum yield; structure-activity; molecular planarity

## Introduction

The discovery and development of compounds containing a large conjugated system with specific properties is of great interest in a multitude of areas of chemical research (1-5). Among these compounds, derivatives based on imidazole have drawn considerable attention due to their unique attributes (6-11). They not only exhibit traditional fluorescent and phosphorescent characteristics, but also excellent two-photon absorption properties (12-21). These features have already stimulated research in a number of areas, including fundamental photophysical investigations, photographic materials, electroluminescent materials, optical materials, three-dimensional optical data storage, twophoton fluorescent microscopy and imaging (22-25). Meantime, it was found that these kinds of compounds are ubiquitous in various bioactive molecules having antiulcer, antiviral, anticancer and antihypertension properties (26,27). Although heterocyclic imidazole derivatives have been widely studied in chemistry, biology and materials science, the design and synthesis of compounds possessing a large conjugated system with high fluorescent performances is still highly desirable (28–35).

In this study, 23 multi-aryl imidazole derivatives were designed and synthesized as shown in Fig. 1. At the same time, their maximum absorption ( $\lambda_{ab}^{max}$ ), fluorescence emission maximum ( $\lambda_{em}^{max}$ ) and quantum yields ( $\Phi_f$ ) were measured. The relationship between the molecular structure and luminescence properties was investigated in three aspects: seven kinds of substituents were introduced on 2,4,5-triphenylimidazole (**1a–1h**) and 2phenyl-phenanthroimidazole (**2a–2h**) to examine the electronic effects of substituents. In addition to the mono-imidazole derivatives, some compounds containing two imidazole nuclei were also synthesized. It was discovered that the fluorescence quantum yields of these compounds actually more than doubled than those of the corresponding mono-imidazole derivatives. In view of the influence of molecular rigidity on optical performances, phenanthroimidazole compounds were also synthesized.

# Experimental

#### General

<sup>1</sup>H-NMR spectra were recorded using a Varian INOVA-400 spectrometer. Mass spectra were recorded with a Thermo-Finnigan LCQ-Advantage mass spectrometer. Elemental analyses were performed with an Elementar Vario-EL-III. The melt points were obtained using an RY-1 melting point apparatus were uncorrected. The ultravioletvisible (UV-vis) spectra and the fluorescence spectra were recorded with a Schimadu UV-3150 spectrophotometer and a Schimadu F-4500 fluorescence spectrophotometer respectively.

4-(diphenylamino)benzaldehyde was synthesized according to the literature (36), aldehyde was distilled before utilization and the other materials were commercially available AR grade chemicals.

#### Synthesis and characterization

1: In a 100 mL round-bottomed flask fitted with an efficient reflux condenser were placed 4 mmol of benzil, 12 mmol of aldehyde, 2.46 g of ammonium acetate and 30 mL acetic acid. The reactants were magnetically stirred and refluxed for 3 h. Then the mixture was poured into ice water and solid precipitated out, which was filtered, washed with water and ether and dried under reduce pressure. The crude product was purified by flash column chromatography on silica gel eluted with ethyl acetate/dichloromethane (1 : 10) to give the product **1a–1h**.

**1a**: White crystal (yield 87%) m.p. 280~282°C; <sup>1</sup>(400 MHz, CDCl<sub>3</sub>, TMS) δ: 7.31~7.37 (m, 6H), 7.54 (d, *J* = 7.2 Hz, 4H), 7.94

<sup>\*</sup> Correspondence to: CanCheng Guo, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, Hunan, China. E-mail: ccguo@hnu.edu.cn

College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, Hunan, China





Figure 1. The structure of compounds 1-8 and 10.

(d, J = 7.6 Hz, 2H), 8.09 (t, J = 8.0 Hz, 3H); MS (ESI) m/z: 296.1 (M<sup>+</sup>+1). Anal.calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>: C 85.11, H 5.44, N 9.45; found C 81.16, H 5.42, N 9.42.

**1b**: White crystal (yield 73%) m.p. 233~235°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ: 2.32 (s, 3H)7.30 (d, J = 7.2 2H), 7.92 (d, J = 7.6 Hz, 4H), 8.07~8.11 (m, 6H), 8.17 (d, J =7.0 Hz, 2H); MS (ESI) *m/z*: 311.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>: C 85.13, H 5.85, N9.03; found C 84.98, H 5.70, N 9.33.

**1c**: White crystal (yield 73%), m.p. 227~228°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ: 3.76 (s, 3H), 6.88 (d, J = 8.4 Hz, 2H),7.29~7.35(m, 6H), 7.58 (d, J = 7.4 Hz, 4H), 7.81 (d, J = 8.9 Hz, 2 H); MS (ESI) m/z: 327.3 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O: C 80.55, H 5.84, N 8.70; found C 80.96, H 5.56, N 8.58.

**1d**: Yellow crystal (yield 82%), m.p. 240~242°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.29~7.32 (m, 6H), 7.60 (d, J = 7.6 Hz, 4H), 8.31~8.33 (d, J =7.8 Hz 2H), 8.42 (d, J =8.0 Hz, 2H); MS (ESI) m/z: 342.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C 73.89, H 4.43, N12.31; found C 73.69, H4.23, N 12.70.

**1e**: Yellow crystal (yield 55%) ; m.p. 245~247°C; <sup>1</sup>H-NMR (400 MHz, CDCl3, TMS)  $\delta$ : 7.46 (d, *J* =8.0 Hz, 4H), 7.54 (dd, *J*<sub>1</sub> =7.2 Hz, *J*<sub>2</sub> =15.2 Hz, 4H), 7.83 (d, *J* =7.6 Hz, 2H), 7.90 (dd, *J*<sub>1</sub> =7.4 Hz, *J*<sub>2</sub> =16 Hz, 2H), 8.21 (d, *J* = 7.8 Hz, 2H), 8.96 (s, 1H); MS (ESI) *m/z*: 341.1 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C 77.63, H 4.74, N 8.23; found C 77.02, H 5.03, N 9.58.

**1f**: White crystal (yield 63%) m.p. 295~297°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ: 7.29 (d, J = 7.2 Hz, 2H), 7.42 (d, J = 8.0 Hz, 4H), 8.22~8.29 (m, 6H), 8.42 (d, J = 8.0 Hz, 2H); MS (ESI) m/z: 321.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>: C 82.22, H 4.70, N 13.08, N 13.20; found C 81.82, H 4.98.

**1g**: White crystal (yield 84%). m.p. 240~242°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.27~7.40 (m, 6H), 7.54 (d, J = 7.2 Hz, 4H), 7.94 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 10.02 (s, 1H); MS (ESI) *m/z*: 325.1 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O: C 81.46, H 4.97, N 8.64, O 4.93; found C 81.43, H 4.50, N 8.66 O 4.94.

**1h**: White crystal (yield 75%) m.p. 258~259°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.04 (t, J = 8.4 Hz, 4H), 7.10 (t, J = 7.2 Hz, 4H), 7.30~7.42 (m, 10H), 7.50 (d, J = 7.2 Hz, 4H), 7.97 (d, J = 8.4 Hz, 2H); MS (ESI) *m/z*: 462.1 (M<sup>+</sup>–1). Anal.calcd for C<sub>33</sub>H<sub>25</sub>N<sub>3</sub>: C 85.50, H 5.44, N 9.06; found C 85.46, H 5.43, N 9.11.

**2**: Compounds **2a–2h** were prepared with the same procedures as **1** by reacting 4 mmol of phenanthraquinone with 12 mmol of aldehyde.

**2a**: White crystal (yield 90%) m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.52 (t, *J* = 8.0, 1H), 7.56~7.72 (m, 4H), 7.75 (t, *J* = 7.8 2H), 8.32 (d, *J* = 8.4 Hz, 2H); 8.55 (d, *J* = 8.0 Hz, 2H); 8.85 (d, *J* = 7.8 Hz, 2H); 13.4 (s, 1H); MS (ESI) *m/z*: 294.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>21</sub>H<sub>14</sub>N<sub>2</sub>: C 85.69, H 4.79, N 9.52; found C 85.48, H 4.47, N 10.05.

**2b**: White crystal (yield 82%) m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 2.19 (s, 3H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.60~7.71 (m, 4H), 8.17 (d, *J* = 7.0 Hz, 2H), 8.22 (d, *J* = 7.8 Hz, 2H), 8.81 (d, *J* = 7.4 Hz, 2H); MS (ESI) *m/z*: 309.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>: C 85.98, H5.52, N 9.50; found C 85.69, H 5.23, N 9.08.

**2c**: White crystal (yield 73%); m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 3.73 (s, 3H), 7.38 (t, *J* =8.4 Hz, 2H), 7.49~7.55 (m, 4H), 8.46~8.50 (m, 4H), 8.71 (d, *J* =8.4 Hz, 2H); MS (ESI) *m/z*: 325.1 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O: C 81.46, H 4.97, N 8.64; found C 81.61, H 5.24, N 8.70.

**2d**: Pink crystal (yield 62%); m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.65 (d, J =7.6 Hz, 2H), 7.75 (t, J =8.4, 2H), 8.35~8.42 (m, 6H), 8.62 (d, J =8.0 Hz, 2H); MS (ESI) *m/z*: 340.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>21</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C 73.65, H 4.23, N 12.60; found C 74.33, H 3.86, N12.38.

**2e**: Yellow crystal (yield 55%) m.p.  $>300^{\circ}$ C; m.p. 238~240°C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.70 (d, J = 7.2 Hz, 2H), 7.82~8.12 (m, 6H), 8.19 (d, J = 8.0 Hz, 2H), 8.91 (d, J = 8.0 Hz, 2H), 11.04 (s, 1H); MS (ESI) m/z: 339.1 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C 78.09, H 4.17, N8.28; found C 71.22, H 4.68, N 8.01.

**2f**: Yellow crystal (yield 63%) m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 7.57 (d, *J* =7.2 Hz, 2H), 7.66 (d, *J* =8.4 Hz, 2H), 7.83~7.89 (m, 6H), 8.95 (d, *J* =7.6 Hz, 2H); MS (ESI) *m/z*: 320.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>22</sub>H<sub>13</sub>N<sub>3</sub>: C 82.94, H 4.10, N 13.16; found C 82.31, H 4.92, N 12.77.

**2g**: Yellow crystal (yield 82%). m.p. 268~270°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.69 (t, J = 8.4, 2H), 7.78 (t, J = 7.2 Hz, 2H), 8.14 (d, J = 8.4 Hz, 2H), 8.53 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 7.2 Hz, 2H), 8.88 (d, J = 8.0 Hz, 2H), 10.10 (s, 1H); MS (ESI) m/z: 321.1 (M<sup>+</sup>–1). Anal.calcd for C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O: C 81.97, H 4.38, N 8.69, O 4.96, found C 82.00, H 4.36, N 8.70, O 4.90.

**2h**: White crystal (yield 63%) m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.12~7.16 (m, 8H), 7.39 (t, *J* =7.2 Hz, 4H), 7.64~7.66 (m, 2H), 7.73(d, *J* = 8.0 Hz 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.52 (d, *J* = 8.0 Hz, 2H), 8.86 (dd, *J*<sub>1</sub> = 8.4Hz, *J*<sub>2</sub> = 8.8 Hz, 2H); MS (ESI) *m/z*: 462.4 (M<sup>+</sup>+1). Anal.calcd for C<sub>33</sub>H<sub>23</sub>N<sub>3</sub>: C 85.87, H 5.02, N 9.11; found C 85.85, H 5.07, N 9.08.

3: In a 100 mL round-bottomed flask fitted with an efficient reflux condenser were placed 1.26 g of benzil (6 mmol), 0.27 g of 1,4-benzenedicarboxaldehyde (2 mmol), 2.46 g of ammonium acetate and 30 mL acetic acid. The reactants were magnetically stirred and refluxed for 6 h. The reaction was monitored by the thin-layer chromatogaphy analysis. After the reaction was complete, the mixture was poured into ice water and solid precipitated out, which was filtered, washed with water and ether, dried under reduced pressure. The crude was purified by flash column chromatography on silica gel and eluted with ethyl acetate/dichloromethane (1 : 10) to give a yellow crystal (yield 71%). m.p. >300°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS) δ: 7.33 (t, J = 7.2 Hz, 4H), 7.44~7.48 (m, 8H), 7.52 (d, J = 7.2 Hz, 4H), 7.57 (d, J = 7.2 Hz, 8H), ,12.75 (s, 2H); MS (ESI) *m/z*: 515.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>: C 84.02, H 5.09, N 10.89; found C 84.04, H 5.10, N 10.86.

**4**: Compound 4 was prepared with the same procedures as 3 by reacting 6 mmol of phenanthraquinone with 2 mmol of 1,4-benzenedicarboxaldehyde. Yellow crystal (yield 60%). m.p. >300°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.67~7.78 (m, 8H), 8.52 (t, J = 7.2Hz, 4H), 8.60 (d, J = 7.9 Hz, 4H), 8.90 (d, J = 8.2 Hz 4H), 10.59 (s, 2H); MS (ESI) *m/z*: 510.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>36</sub>H<sub>22</sub>N<sub>4</sub>: C 84.68, H 4.34, N 10.98; found C 84.62, H 4.37, N 11.01.

**5**: Method A: Compound 5 was prepared by refluxing 4 mmol of phenanthraquinone with 2 mmol of 1 h and 2.46 g of ammonium acetate in 30 mL acetic acid for 6 h (yield 67%). Method B: Compound **5** was prepared by refluxing 4 mmol benzil with 2 mmol of 2 h and 2.46 g of ammonium acetate in 30 mL acetic acid for 6 h (yield 72%). Yellow crystal m.p.  $>300^{\circ}$ C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.33~7.43 (m, 6H), 7.48 (t, J = 7.6 Hz, 2H) 7.55 (d, J = 6.8 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.6, 2H), 7.78 (t, J = 7.8, 2H), 8.31 (d, J = 8.4, 2H), 8.42 (d, J = 8.4, 2H), 8.88 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 8.0$  Hz, 2H); MS (ESI) *m/z*: 513.2 (M<sup>+</sup>+1). Anal.Calcd for C<sub>36</sub>H<sub>24</sub>N<sub>4</sub>: C 84.35, H 4.72, N 10.93; found C 84.29, H 4.74, N 13.97.

**6**: In a 250 mL round-bottomed flask fitted with an efficient reflux condenser were placed 0.44 g of 1,2-diaminobenzene (4 mmol), 1.09 g of 4-(diphenylamino)benzaldehyde (4 mmol) and 100 mL methanol. The reactants were magnetically stirred and refluxed overnight. Then the mixture was poured into ice water, and solid precipitated out, which was filtered, washed with water and ether, dried under reduce pressure. The crude was purified by flash column chromatography on silica gel and eluted with ethyl acetate/dichloromethane (1 : 3) to give a white crystal (yield 77%). m.p. 278~280°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.06 (d, *J* = 7.6, 2H), 7.15 (m, 8H), 7.36 (t, *J* = 8 Hz, 4H), 7.56 (s, 2H), 8.07 (d, 2H), 12.78 (s, 1H); MS (ESI) *m/z*: 362.3 (M<sup>+</sup>+1). Anal. calcd for C<sub>25</sub>H<sub>19</sub>N<sub>3</sub>: C 83.07, H 5.30, N 11.63; found C 83.10, H 5.26, N 11.64.

**7**: Compound **7** was prepared with the same procedures as **6** by reacting 0.44 g of 1,2-diaminobenzene (4 mmol) with 1.30 g of 1 h (4 mmol). After regular work-up, a yellow crystal was obtained (yield 68%). m.p. >300°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.23 (dd,  $J_1 = 2.8$  Hz,  $J_2 = 3.2$  Hz, 2H), 7.75 (m, 6H), 7.59 (m, 6H), 8.31 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 12.4$  Hz, 4H), 12.9 (s, 1H), 13.0

(s, 1H); MS (ESI) m/z: 413.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>28</sub>H<sub>20</sub>N<sub>4</sub>: C 81.53, H 4.89, N 13.58; found C 81.52, H 4.86, N 13.62.

**8**: Compound **8** was prepared with the same procedures as **6** by reacting 0.44 g of 1,2-diaminobenzene (4 mmol) reacted with 1.29 g of 2 h (4 mmol). After regular work-up, a yellow crystal was obtained (yield 61%). m.p. >300°C; <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.26 (d, J = 5.2 Hz, 2H), 7.68~7.79 (m, 6H), 8.42 (d, J = 8.4, 2H), 8.51 (d, J = 8.4 Hz 2H), 8.63 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 16$  Hz 2H), 8.89 (t, J = 7.6 Hz, 2H), 13.11 (s, 1H), 13.63 (s, 1H); MS (ESI) *m/z*: 411.2 (M<sup>+</sup>+1). Anal.calcd for C<sub>28</sub>H<sub>18</sub>N<sub>4</sub>: C 81.93, H 4.42, N 13.65; found C 81.98, H 4.40, N 13.62.

**10**: In a 250 mL round-bottomed flask with a reflux condenser, 0.7 g of carbazole (4 mmol), 1.1 g of potassium tert-butoxide (10 mmol) and 100 mL dry DMF were placed. The reactants were magnetically stirred and heated to 110°C for half an hour. Then 0.5 g of 4-fluoro-benzaldehyde was added to the mixture. The reaction continued for 36 h and then the mixture was poured into ice water, and extracted with dichloromethane. The crude was purified by flash column chromatography on silica gel, and eluted with dichloromethane/n-hexane (1 : 2) to obtain the 4-*N*-carbazolylbenzaldehyde (yield 84%). Yellow crystal, m. p. 278~281°C, <sup>1</sup>H-NMR (400 MHz, DMSO, TMS)  $\delta$ : 7.25 (m, 4H), 7.49 (m, 4H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 7.6 Hz, 2H) 8.48 (d, *J* = 8.4 Hz, 2H); 13.14 (s, 1H) MS (ESI) *m/z*: 360 (M<sup>+</sup>+1). Anal.calcd for C<sub>25</sub>H<sub>17</sub>N<sub>3</sub>: C 83.18, H 5.161, N 11.73; found C 83.54, H 4.77, N 11.69.

#### Spectra measurements

The fluorescence quantum yield was measured by a simple method. One  $\mu$ g/mL quinine sulfate was dissolved in 0.05 mol/L H<sub>2</sub>SO<sub>4</sub> solution as the standard solution ( $\Phi_{fstd} = 0.55$ ), the sample concentration was 2 × 10<sup>-6</sup> mol/L.

The fluorescence quantum yield can be calculated in accordance with the following formula:

$$\varPhi_{fx} = \frac{n^2_x}{n^2_{std}} \cdot \frac{F_x}{F_{std}} \cdot \frac{A_{std}}{A_x} \cdot \varPhi_{fstd}$$

where *n* is the refractive index of the solution, *F* is a fluorescent integral area, *A* is the absorbance;  $n_x$  is 1.44 as chloroform,  $n_{std}$  using 1.34 as the literature values (37). As the fluorescence excitation wavelength is the cross-point of the UV-vis absorption curves of the sample solution and standard solution,  $A_{std}$  and  $A_x$  can be ignored.

### **Results and discussion**

#### Synthesis

The condensation *o*-dicarbonyl compounds with aldehydes and ammonia or ammonium acetate in acetic acid is commonly used for the formation of the imidazole ring (9), we chose this strategy for the preparation of the 19 imidazoles. Benzil and benzaldehydes were condensed to provide multi-aryl imidazoles **1a–1h** in good yields. As for the phenanthroimidazole derivatives, we substituted benzil with phenanthraquinone, and using the same procedure, the multi-aryl imidazoles **2a–2h** were obtained (Fig. 2).

However, the reaction of benzil with 1,4-benzenedicarboxaldehyde under the standard reaction condition afforded a mixture of



Figure 2. Preparation of compounds 1 and 2.

compound **1g** and **3** as competitive products. Two analogous competitive products **2g** and **4** were also observed in the reaction of phenanthraquinone and 1,4-benzenedicarboxaldehyde (Fig. 3).

The ratio of these two competitive products was affected by the ratio of substrates and reaction time evidently. When benzil was treated with 3 equiv of 1,4-benzenedicarboxaldehyde for 3 h, **1g** was isolated as the main product. However, **3** became the major product when the ratio of benzil and 1,4-benzenedicarboxaldehyde was inversed and the reaction time was extended to 6 h. Similarly, either compound **2g** or **4** could be isolated as the main product by varying the reactant ratio through the condensation of phenanthraquinone and 1,4-benzenedicarboxaldehyde under similar conditions.

With **1g** and **2g** in hand, subsequent reaction of **1g** with benzil provided pure compound **3**, and the reaction of **2g** with phenanthraquinone gave compound **4**. In addition, condensation of **1g** with phenanthraquinone or **2g** with benzil provided compound **5** (Fig. 4).

As benzimidazole derivatives are extensively prepared by the reactions of organic acids or aldehydes with 1,2-diaminobenzene (7,13), 2-(4-diphenylaminophenyl)benzimidazole **6** was prepared by

refluxing 4-(diphenylamino)benzaldehyde with 1,2-diaminobenzene in methanol. In a similar fashion, **1g** and **2g** were treated with 1,2-diaminobenzene to produce **7** and **8**, respectively. By using 4-*N*-carbazolylbenzaldehyde (9) as the aldehyde intermediate, compound **10** was also prepared by the same strategy (Fig. 5).

#### The optical properties

UV-vis absorption and fluorescence spectra for compounds **1–8**, **10** were measured. Their maximum absorption wavelength  $(\lambda_{ab}^{max})$ , maximum emission wavelength  $(\lambda_{em}^{max})$  Stokes shift  $(\triangle \lambda)$ and fluorescence quantum yield  $(\Phi_f)$  are shown in Table 1.

The optical properties of substituted multi-aryl imidazole compounds. The UV-vis absorption and fluorescence spectra of 1 and 2 were shown in Fig. 6. From this figure, we can see that the impact of electron-donating substituents such as  $-CH_3$ ,  $-OCH_3$  on the UV-vis and fluorescence spectra was not significant. However, with electron-withdrawing substituents such as  $-NO_2$ , -COOH and -CHO, the  $\lambda_{ab}^{max}$  and the  $\lambda_{em}^{max}$  of compounds 1 and 2 were red-shifted and the  $\Phi_f$  increased too. Impressively, the nitro-substituted multi-aryl imidazole compounds such as 1d and 2d



Figure 3. Preparation of compounds 1g, 2g, 3 and 4.





Figure 4. Preparation of 3-5.



Figure 5. Preparation of compounds 6–8 and 10.

can even absorb visible light and emit red fluorescence with  $\lambda_{ab}^{max}$  red-shifted by 82 and 91 nm respectively and  $\lambda_{em}^{max}$  red-shifted by 154 and 162 nm respectively. As for the formyl substituted compounds such as **1g** and **2g**, the  $\lambda_{ab}^{max}$ s were red-shifted by 53 and 60 nm, respectively and the  $\lambda_{em}^{max}$ s were red-shifted by 68 and 64 nm, respectively, whereas the  $\Phi_f$  increased by 103% and 78% respectively when compared with non-substituted multi-aryl imidazole compounds.

To explain the effect of electron-donating substituents and electron-withdrawing substituents on the multi-aryl imidazoles, we carried out calculations on the energy levels of the frontier orbitals. We have done the theoretical calculation for **1–10** using Kohn–Sham density functional theory with the 6-31G basis set and RID-B3LYP-FC functional. The orbital energy values are shown in Fig. 7. From the figure, we can see that  $-CH_3$ ,  $-OCH_3$  substituents raise the energy levels of the HOMO orbital and

# Table 1. The spectroscopic data of 1-8 and 10



1a   308   3     1b   306   3     1c   301   3     1d   390   5     1e   344   4     1f   342   4	99     0.32       885     0.38       995     0.40       553     0.25       132     0.38       119     0.42	2a 2b 2c 2d 2e 2f	313 317 311 404 369	402 395 405 564 437	0.40 0.40 0.45 0.21 0.33
1b     306     3       1c     301     3       1d     390     5       1e     344     4       1f     342     4	885     0.38       995     0.40       553     0.25       132     0.38       119     0.42	2b 2c 2d 2e	317 311 404 369	395 405 564 437	0.40 0.45 0.21 0.33
1c     301     3       1d     390     5       1e     344     4       1f     342     4	995 0.40   553 0.25   32 0.38   119 0.42	2c 2d 2e	311 404 369	405 564 437	0.45 0.21 0.33
1d     390     5       1e     344     4       1f     342     4       1a     261     4	5530.251320.381190.42	2d 2e 26	404 369	564 437	0.21 0.33
1e     344     4       1f     342     4       1a     261     4	0.38 0.42	2e	369	437	0.33
<b>1f</b> 342 4	0.42	26			
<b>1a</b> 261 /		21	368	435	0.55
ig 301 4	67 0.65	2g	373	466	0.71
<b>1h</b> 355 4	0.57	2h	369	419	0.68
<b>3</b> 356 4	26 0.69	4	364	445	0.81
<b>5</b> 352 4	36 0.82	6	357	426	0.65
<b>7</b> 353 4	26 0.71	8	372	434	0.80
10 331 3	0.74				



Figure 6. The ultraviolet-visible absorption (2  $\times$  10<sup>-6</sup> mol/L; CHCl<sub>3</sub> solution) and fluorescence spectra (2  $\times$  10<sup>-7</sup> mol/L CHCl<sub>3</sub> solution) of 1 and 2.

LUMO orbital. However, the energy level of LUMO orbital is raised more than the HOMO orbital, thus actually making the energy gap larger than before. In sharp contrast, electron withdrawing groups such as  $-NO_2$ , -COOH and -CHO substituents actually lower the energy levels of both orbitals. As the energy level of LUMO is lowered more, the energy gap

between the HOMO and LUMO orbitals becomes smaller, making the electronic transition much easier; hence, the  $\lambda_{ab}^{max}$  is red-shifted. Others who have carried out quantum chemical calculations on many large  $\pi$ -conjugated compounds also concluded that the introduction of electron-withdrawing substituent is in favor of electronic transitions because of the

# LUMINESCENCE The Journal of Biological and Chemical Luminescence



Figure 7. Orbitals energy values of (a) 1, 3 and 7, and (b) 2, 4 and 8.

reduction of the HOMO and LUMO energy gap (38). For **1h** and **2h**, the bond length of C–N between the –NPh<sub>2</sub> and benzene is calculated to be 0.142 nm, which suggests the existence of a hyperconjugation effect (standard bond length: C–N: 0.147 nm, C=N: 0.127 nm (38)). The resultant electron delocalization can raise the HOMO and lower the LUMO, which leads to the redshift of  $\lambda_{ab}^{max}$ .

The optical properties of multi-aryl imidazole and multi-aryl double imidazole compounds. The UV-vis absorption and fluorescence spectra of **1a**, **2a**, **3–8** are shown in Fig. 8. When **3**, **4**, **5**, **7** and **8** were compared with mono-imidazole compounds, the double imidazole compounds have a red-shift of  $\lambda_{ab}^{max}$  by more than 44 nm and  $\lambda_{em}^{max}$  by more than 27 nm. Furthermore, the introduction of imidazoles on the phenyl ring of multi-aryl imidazoles leads to a double increase of  $\Phi_{f.}$  In particular, compounds **4**, **5** and **8**, which have the 9,10-phenanthroimidazole structure, show excellent fluorescent properties with  $\Phi_{f}$  of more than 0.8. The calculation result indicated that the larger  $\pi$  conjugated system can decrease the LUMO energy level substantially (Fig. 7).

The influence of multi-aryl imidazole molecular planarity on the spectroscopic properties. For all the synthesized imidazoles, density functional theory was used to simulate and optimize their structures. The adjacent phenyl rings in the **4**, **5** positions of imidazole deviate from the imidazole ring plane in the aryl-imidazole compounds due to the steric effects. The C–C bond connecting the two adjacent phenyl rings was designed to form a rigid structure to increase the multi-aryl imidazole planarity. The dihedral agles  $\alpha$ ,  $\beta$  between each benzene ring and imidazole ring, the  $\lambda_{ab}^{max}$ ,  $\lambda_{em}^{max}$ ,  $\Phi_{f}$  and energy gap are shown in Table 2.

As shown in Table 2 the dihedral angles  $\alpha$ ,  $\beta$  are between 25.78 and 40.69° in free rotatable phenyl imidazole compounds such as **1**, **3**, **7**, but they are only 0~0.17° in the bonded phenyl



**Figure 8.** The ultraviolet-visible absorption  $(2 \times 10^{-6} \text{ mol/L}; \text{CHCl}_3 \text{ solution})$  and fluorescence spectra  $(2 \times 10^{-7} \text{ mol/L CHCl}_3 \text{ solution})$  of **1a**, **2a** and **3–8**.

imidazole compounds as **2**, **4**, **8**. This enhancement of the planarity and rigidity of aryl-imidazole compounds can lead to expansion of the  $\pi$  electron delocalization conjugation and decrease of the energy gap between HOMO and LUMO, thus resulting in the increase of  $\Phi_f$  and the red-shifts of  $\lambda_{ab}^{max}$  and  $\lambda_{em}^{max}$ . Therefore, it can be concluded that the introduction of chemical bonds to prevent the substituents' rotation can increase the planarity of the conjugated system and improve the efficiency of luminescence.

However, the data of **10** is somewhat unexpected. Compared with **6**,  $\lambda_{ab}^{max}$  and  $\lambda_{em}^{max}$  of **10** were blue-shifted by 26 nm and 35 nm, respectively. Quantum chemical calculation results indicate that the introduction of C–C bond to combine the two benzenes as a carbazole subunit actually reduces the two benzene dihedral angle from 67.7° to 0.01°, but the dihedral angle of the carbazole and benzene ring is actually increased from 38.9° to 52.7°. The C–N bond length from carbazole to benzene is 1.42 nm, which is closer to the value of the C–N bond rather than C=N. It means the steric effect is the major influence in **10** rather than the  $\sigma$ – $\pi$  hyperconjugation. The enhanced distortion results in the increased energy gap between the HOMO



Table 2. The dihedral angles and spectroscopy data										
Compounds	$\angle \alpha$	∠β	$\lambda_{ab}^{max}/nm$	$\lambda_{em}^{max}/nm$	$\Phi_{\rm f}$	ΔE				
1a	27.95	35.3	308	399	0.32	3.42				
2a	0.8	0.9	313	402	0.40	3.36				
3	56.7	52.2	356	426	0.69	2.96				
4	0.6	0.6	364	445	0.81	2.84				
7	31.4	38.6	353	426	0.71	2.98				
8	0.9	0.1	372	434	0.80	2.93				
б	38.9	29.2	357	426	0.65	3.11				
10	52.7	52.7	331	391	0.74	3.21				



Figure 9. The molecular structure of (a) 6 and (b) 10. (c) The ultraviolet-visible absorption and fluorescence spectra of 6 and 10.

and LUMO and the blue-shift of the spectrum. The molecular structures, UV-vis absorption and fluorescence spectra of **6** and **10** are shown in Fig. 9.

# Conclusion

Twenty-three multi-aryl imidazoles were synthesized and the relationship between the imidazole structure and fluorescent properties was investigated. The effects of electronic properties of substituents, molecular planarity and double imidazole structure on the  $\lambda_{ab}^{max}$ ,  $\lambda_{em}^{max}$  and the  $\Phi_f$  were explored. The results show that multi-aryl imidazoles with the strong electron-absorbing group – NO<sub>2</sub> can absorb visible light and emit red fluorescent light, and the  $\Phi_f$  can be more than doubled with the strong electron-absorbing group –CHO or by the introduction of the double imidazole structure. The multi-aryl imidazoles with 9,10-phenanthroimidazole structure give high fluorescent quantum yields above 0.8. These structure–activity relationship studies for the fluorescent performances of multi-aryl imidazoles could be helpful for further development of highly efficient luminous devices.

#### Acknowledgments

We gratefully thank the financial support of the National Natural Science Fund of China (grants 21372068).

## References

- Huang J-W, Hu S-G, Li T, Fan L-F, Ji L-N. A fluorescence study of tetraphenylporphyrinatozinc (ii)/imidazolyl-linked porphyrinatoiron (iii) systems. Spectrochim Acta A 2003;59:2585–91.
- Lupton JM. Chromophores in conjugated polymers-all straight? Chem Phys Chem 2012;13:901–7.
- Zhang Y, Cai X, Bian Y, Jiang J. Organic semiconductors of phthalocyanine compounds for field effect transistors (fets). Struct Bonding 2010;135:275–322.
- 4. Kwon JE, Park SY. Advanced organic optoelectronic materials: Harnessing excited-state intramolecular proton transfer (esipt) process. Adv Mater 2011;23:3615–42.
- Shimizu M, Hiyama T. Organic fluorophores exhibiting highly efficient photoluminescence in the solid state. Chem Asian J 2010;5:1516–31.
- Wu L, Burgess K. Syntheses of highly fluorescent gfp-chromophore analogues. J Am Chem Soc 2008;130:4089–96.
- Das B, Holla H, Srinivas Y. Efficient (bromodimethyl) sulfonium bromide mediated synthesis of benzimidazoles. Tetra Lett 2007;48:61–4.
- Matschke M, Blumhoff J, Beckert R. 4h-imidazoles as functional dyes: Synthesis of bichromophores and extension of the merocyanine system. Tetrahedron 2008;64:7815–21.
- Pan W-L, Tan H-B, Chen Y, Mu D-H, Liu H-B, Wan Y-Q, Song H-C. The synthesis and preliminary optical study of 1-alkyl-2,4,5-triphenylimidazole derivatives. Dyes Pigments 2008;76:17–23.
- Bu L, Sawada T, Shosenji H, Yoshida K, Mataka S. Crystallographic structures and solid fluorescence behaviors of crystals of a 2-(9-anthryl)phenanthroimidazole-type clathrate host. Dyes Pigments 2003;57:181–95.

- Boydston AJ, Pecinovsky CS, Chao ST, Bielawski CW. Phase-tunable fluorophores based upon benzobis (imidazolium) salts. J Am Chem Soc 2007;129:14550–1.
- 12. Xie N, Chen Y. Synthesis and photophysical properties of 1,4-bis(4,5diarylimidazol) benzene dyes. J Photochem Photobiol A 2007;189:253–7.
- Yan Y-N, Lin D-Y, Pan W-L, Li X-L, Wan Y-Q, Mai Y-L, Song H-C. Synthesis and optical behaviors of 2-(9-phenanthrenyl)-, 2-(9-anthryl)-, and 2-(1-pyrenyl)-1-alkylimidazole homologues. Spectrochim Acta A 2009;74:233–42.
- Bu L, Sawada T, Kuwahara Y, Shosenji H, Yoshida K. Crystallographic structure and solid-state fluorescence enhancement behavior of a 2-(9-anthryl)phenanthroimidazole-type clathrate host upon inclusion of amine molecules. Dyes Pigments 2003;59:43–52.
- Guo J-G, Cui Y-M, Lin H-X, Xie X-Z, Chen H-F. New fluorene derivatives based on 3,9-dihydrofluoreno[3,2-d]imidazole (fi):Characterization and influence of substituents on photoluminescence. J Photochem Photobiol A 2011;219:42–9.
- Ooyama Y, Kumaoka H, Uwada K, Yoshida K. Photophysical properties of phenanthro [9, 10-< i> d</i>] imidazole-type fluorescent hosts upon inclusion of organic solvent molecules. Tetrahedron 2009;65:8336–43.
- Fridman N, Kaftory M, Speiser S. Structures and photophysics of lophine and double lophine derivatives. Sensors Actuators B 2007;126:107–15.
- Boydston AJ, Vu PD, Dykhno OL, Chang V, Wyatt AR, Stockett AS, Ritschdorff ET, Jason B, Bielawski CW. Modular fluorescent benzobis (imidazolium) salts: Syntheses, photophysical analyses, and applications. J Am Chem Soc 2008;130:3143–56.
- Tanaka K, Kurushima T, Iwata S, Shimada S. Fluorescent behavior of 2-(3,4,5,6-tetrafluoro-2-hydroxyphenyl) imidazo-[1,2-a] pyridine in the presence of metal perchlorate. J Heterocyclic Chem 2009;44:303–7.
- Fridman N, Kaftory M, Eichen Y, Speiser S. Spectroscopy, photophysical and photochemical properties of bisimidazole derivatives. J Photochem Photobiol A 2007;188:25–33.
- 21. Sun T, Pan YL, Wu JY, Zhou HP, Zhao ZZ, Tian YP. Synthesis, luminescence and cyclic voltammetric studies of several novel carboxylato diruthenium complexes. Transition Met Chem 2007;32:449–55.
- 22. Shin RY, Sonar P, Siew PS, Chen Z-K, Sellinger A. Electron-accepting conjugated materials based on 2-vinyl-4, 5-dicyanoimidazoles for application in organic electronics. J Org Chem 2009;74:3293–8.
- Jayabharathi J, Thanikachalam V, Devi KB, Srinivasan N. Physicochemical studies of some novel y-shaped imidazole derivatives – a sensitive chemisensor. Spectrochim Acta A 2011;82:513–20.
- 24. Lin W, Long L, Yuan L, Cao Z, Chen B, Tan W. A ratiometric fluorescent probe for cysteine and homocysteine displaying a large emission shift. Org Lett 2008;10:5577–80.

- Lin W, Yuan L, Tan W, Feng J, Long L. Construction of fluorescent probes via protection/deprotection of functional groups:A ratiometric fluorescent probe for cu2+. Chem Eur J 2008;15:1030–5.
- Sarshar S, Zhang C, Moran EJ, Krane S, Rodarte JC, Benbatoul KD, Dixon R, Mjalli AMM. 2,4,5-trisubstituted imidazoles: Novel nontoxic modulators of p-glycoprotein mediated multidrug resistance. Part 1. Bioorg Med Chem Lett 2000;10:2599–601.
- Zhang Q, Tu T, d'Avignon DA, Gross ML. Balance of beneficial and deleterious health effects of quinones: A case study of the chemical properties of genistein and estrone quinones. J Am Chem Soc 2008;131:1067–76.
- Henary MM, Wu, CJ, Sumalekshmy S, Li J, Mandal S, Fahrni CJ. Excited-state intramolecular proton transfer in 2-(2'arylsulfonamidophenyl)benzimidazole derivatives: The effect of donor and acceptor substituents. J Org Chem 2007;72:4784–97.
- Angelova SE, Spassova MI, Deneva VV, Rogojerov MI, Antonov LM. Aggregation of 2-aminobenzimidazole – a combined experimental and theoretical investigation. Chem Phys Chem 2011;12:1747–55.
- Feng K, Hsu F-L, Van DerVeer D, Bota K, Bu XR. Tuning fluorescence properties of imidazole derivatives with thiophene and thiazole. J Photochem Photobiol A 2004;165:223–8.
- Liao W-X, Peng Y-W, Yu L, Ning X-Q, Zeng H-P. (e)-ethyl 2-cyano-3-[4-(4,5-diphenyl-1h-imidazol-2-yl)phenyl]acrylate dihydrate. Acta Crystallographica Section E 2011;67:o707.
- Nayak MK, Dogra SK. Spectral characteristics of various prototropic species of 2-(3'-aminophenyl)pyrido[3,4-d]imidazole. J Photochem Photobiol A 2005;171:9–20.
- Gostev FE, Kol'tsova LS, Petrukhin AN, Titov AA, Shiyonok AI, Zaichenko NL, Marevtsev VS, Sarkisov OM. Spectral luminescent properties and dynamics of intramolecular processes in 2,4,5triarylimidazoles. J Photochem Photobiol A 2003;156:15–22.
- Yamaguchi E, Shibahara F, Murai T. 1-alkynyl- and 1-alkenyl-3arylimidazo[1,5-a]pyridines: Synthesis, photophysical properties, and observation of a linear correlation between the fluorescent wavelength and hammett substituent constants. J Org Chem 2011;76:6146–58.
- Ryazanova O, Zozulya V, Voloshin I, Karachevtsev V, Makitruk V, Stepanian S. Absorption and fluorescent spectral studies of imidazophenazine derivatives. Spectrochim Acta A 2004;60:2005–11.
- Ji L, Fang Q, Yuan M-S, Liu Z-Q, Shen Y-X, Chen H-F. Switching high two-photon efficiency: From 3,8,13-substituted triindole derivatives to their 2,7,12-isomers. Org Lett 2010;12:5192–5.
- 37. Ci Y, Jia X. A simple method to measure fluorescence quantum yield. Chin J Anal Chem 1986;14:616–18.
- 38. Jena B, Manoharan SS, Prakash S. Specificity and selectivity in photoluminescent properties of  $\pi$ -conjugated benzheterazole molecules. J Phys Chem C 2009;113:20942–8.