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The photophysics, crystal and electronic structures of some novel benzene-linked bisimidazole compounds

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ABSTRACT

Several novel disubstituted benzene-bridged bisimidazole derivatives (**3a–3h**) were prepared and characterized. Their optical properties, crystal structures and quantum chemical calculations were also investigated. The UV–vis spectra observed ($\lambda_{\text{max}}^{\text{Abs}}$: 325–348 nm) in acetonitrile showed low optical band gaps ($E_{\text{g}}^{\text{opt}}$: 2.89–3.25 eV). All these compounds display strong fluorescence in solution with emission spectra ($\lambda_{\text{max}}^{\text{Em}}$: 389.5–418 nm) (fluorescence quantum yield in the range 0.46–0.95) and significant Stokes shift (3670–5490 cm^{-1}). The single crystal structures of **3h** solvates were presented and discussed. The space groups of **3h** solvates (**3h1**: **3h** · 2H₂O and **3h2**: **3h** · DMSO · 2H₂O) were *C*₂/*c* and *P*₂₁/*c*, respectively. Quantum chemical calculations using DFT B3LYP/6-31G(d) showed obvious difference in LUMO (−1.273 to −1.715 eV) and HOMO (−4.838 to −5.296 eV) while they were similar in $E_{\text{g}}^{\text{cal}}$ (3.393–3.599 eV) values of these compounds. These results demonstrate that these novel disubstituted benzene-bridged bisimidazole derivatives are promising electron-transporting electro luminescent materials and blue-light emitting materials for OLED.

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1. Introduction

During the past few decades, new molecules and polymeric semiconducting materials based on conjugated aromatic rings are of wide interest as electronic and optoelectronic devices including organic light-emitting diodes (OLED) [1–4], photovoltaic cell [5–7,9,10], field-effect transistors [8,11–14], and other elements of “plastic electronics” [15–18]. Among these materials, conjugated imidazoles and their metal complexes have been extensively investigated as n-type (electron transport) organic semiconductors over the past 20 years [19–23]. Although there are several reports for synthesis, physical properties, crystal structures [24–28] and intramolecular proton transfer (ESIPT) phenomenon [27–32] of these imidazole compounds, investigations on electronic structures and crystal structures of benzene-linked bisimidazole which may serve as structurally well-defined model systems of OLED are surprisingly limited. The studies on the structure–property relationships of electron transport materials [33], hole-transporting materials [34] and blue emitting material [35] for OLED have indicated that the substituent, topological and dipole structure of molecules would obviously influence the performance of OLED. Thus the structure–property relationship of benzene-linked bisimidazole, which would be used as a new potential OLED, is still an interesting challenge.

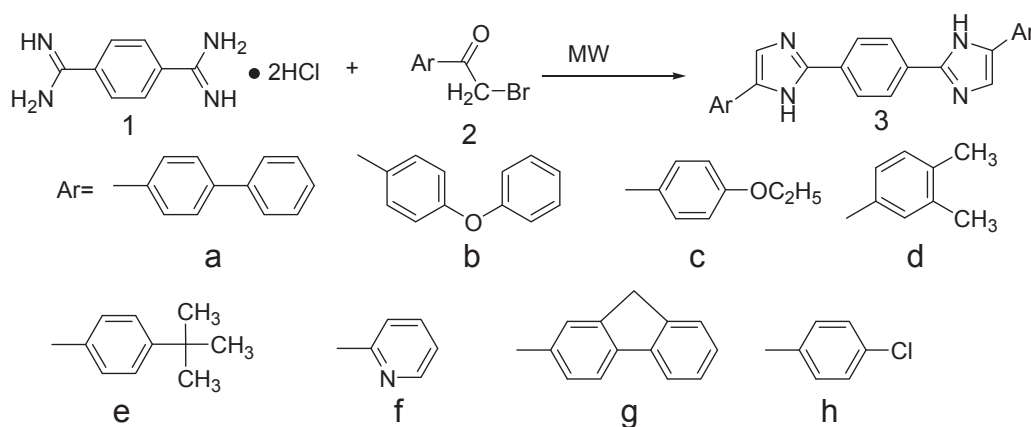
Recently, a series of disubstituted benzene-linked bisimidazole compounds reported by our group [36] showed the lowest energy absorption bands ($\lambda_{\text{max}}^{\text{Abs}}$: 339–348 nm) originated from π – π^* transitions and low optical band gaps ($E_{\text{g}}^{\text{opt}}$: 3.06–3.25 eV). These compounds all emitted strong blue fluorescence with emitting maxima wavelength ($\lambda_{\text{max}}^{\text{Em}}$) ranging from 389.5 to 415.5 nm in diluted acetonitrile solution. The results suggested that benzene-linked bisimidazole compounds have a potential application as blue electroluminescent materials, which motivated us to further investigate the structure–property relationship of these bisimidazole derivatives. In order to investigate the influence of substituent and conjugated structure on the photophysical properties, seven novel disubstituted benzene-linked bisimidazole compounds were prepared and characterized in this paper. The crystal structures and optical properties in solvents as well as the quantum chemical calculations were also performed to help us look into the electronic properties, the geometries and the structure–property relationship of these compounds. The structure–property relationship of benzene-linked bisimidazole compounds would be some benefit to the design of these potential OLED materials.

2. Experimental section

2.1. Measurements

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike China). ¹H NMR and ¹³C NMR spectra

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Scheme 1. Synthesis of disubstituted benzene-linked bisimidazole compounds (**3a–3h**).

were recorded on a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300 spectrometer at 300 MHz using CDCl_3 or $\text{DMSO-}d_6$ as the solvent, with tetramethylsilane as an internal standard. Electron impact (EI) mass spectrometry was investigated on an autospec premier instrument with isobutene as carrier gas. Optical absorption spectra were obtained by using an HP-8453 UV/Vis/near-IR spectrophotometer (Agilent). Photoluminescence spectra were carried out on LS-55 spectrofluorometer (Perkin-Elmer). Microwave synthesis was carried out on system of WBFY-201 apparatus (Yiheng China). The elemental analyses were performed with a Vario EL III elemental analyzer.

2.2. Synthesis

Compounds **2a** [37], **2b** [38], **2c** [37], **2d** [39], **2e** [37], **2f** [40] and **2g** [41] were prepared according to the published procedures. The synthesis of **3a–3h** is shown in the Scheme 1 and they were prepared according to our published procedures [36], in which, **3h** was prepared as a reference.

2.2.1. 2-Bromo-1-(4-phenylphenyl)ethanone (**2a**)

The yield was 85%, which was a white acicular crystal; m.p. 125–126 °C (Ref. [37]: 125 °C). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 8.07 (m, 2H), 7.77 (m, 2H), 7.63 (m, 2H), 7.45 (m, 3H), 4.48 (s, 2H, $-\text{CH}_2\text{Br}$).

2.2.2. 2-Bromo-1-(4-phenoxyphenyl)ethanone (**2b**)

The yield was 85%, which was a colorless liquid; b.p. 213–215 °C/5 mmHg (Ref. [38]: 197–198 °C/4 mmHg). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 8.06 (d, 2H, $J=5.1$ Hz), 7.71 (d, 2H, $J=5.2$ Hz), 7.63 (d, $J=7.2$ Hz, 2H), 7.48 (m, 2H), 7.41 (m, 2H), 4.47 (s, 1H, $-\text{CH}_2\text{Br}$).

2.2.3. 2-Bromo-1-(4-ethoxyphenyl)ethanone (**2c**)

The yield was 85%, which was a white powder; m.p. 58–60 °C (Ref. [37]: 58–60 °C). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 7.90 (d, $J=8.9$ Hz, 2H), 6.89 (d, $J=8.9$ Hz, 2H), 4.48 (s, 2H, $-\text{CH}_2\text{Br}$), 4.07 (q, 2H, $J=7.0$ Hz), 1.43 (t, 3H, $J=7.0$ Hz).

2.2.4. 2-Bromo-1-(3,4-dimethylphenyl)ethanone (**2d**)

The yield was 75%, which was a white powder; m.p. 61–63 °C (Ref. [39]: 61 °C). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 7.76 (s, 1H), 7.71 (m, 1H), 7.25 (m, 1H), 4.42 (s, 2H, $-\text{CH}_2\text{Br}$), 2.32 (m, 6H).

2.2.5. 2-Bromo-1-(4-tert-butylphenyl)ethanone (**2e**)

The yield was 69%, which was a colorless liquid; b.p. 172–175 °C/5 mmHg (Ref. [37]: 127 °C/0.5 mmHg) $^1\text{H NMR}$ (CDCl_3 ,

300 MHz): δ ppm 7.98 (m, 2H), 7.47 (m, 2H), 4.56 (s, 2H, $-\text{CH}_2\text{Br}$), 1.34 (s, 9H).

2.2.6. 2-Bromo-1-(2-pyridinyl)-1-ethanone hydrobromide (**2f**)

The yield was 75%, which was a white solid; m.p. 202–204 °C (Ref. [40]: 203–205 °C) $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 11.68 (s, 1H), 8.77 (m, 1H), 8.11 (m, 2H), 7.76 (m, 1H), 5.04 (s, 2H, $-\text{CH}_2\text{Br}$).

2.2.7. 2-Bromo-1-(9H-fluoren-2-yl)ethanone (**2g**)

The yield was 96%, which was a white solid; m.p. 143–145 °C (Ref. [41]: 142–143 °C) $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ ppm 8.17 (s, 1H), 8.03 (d, 1H, $J=8.0$ Hz), 7.85 (m, 2H), 7.60 (d, 1H, $J=7.0$ Hz), 7.42 (m, 2H), 4.51 (s, 2H, $-\text{CH}_2\text{Br}$), 3.98 (s, 2H).

General procedure for synthesis of benzene-bridged bisimidazole derivatives (**3**). Benzene-1,4-dicarboxamidium dichloride (**1**) (1.18 g, 5 mmol), α -bromo arylketones **2** (10–12 mmol), KHCO_3 (2 g, 20 mmol) and NaCl (5.85 g, 100 mmol) were mixed thoroughly in a mortar. The reaction mixture was transferred into a beaker and irradiated with microwaves for 2 min (300 W). Then the mixture was cooled down to the room temperature, mixed and irradiated for 2 min again. This procedure was repeated until the completion of this reaction, which was monitored by TLC (eluent: pure ethyl acetate). The crude product was washed with hot brine and recrystallized from methanol/tetrahydrofuran (1:1).

2.2.8. 5-(4-Phenylphenyl)-2-(4-(5-(4-phenylphenyl)-1H-imidazol-2-yl)phenyl)-1H-imidazole (**3a**)

The yield was 58%, which was a white solid; m.p. > 310 °C. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ ppm 12.68 (br, 2H, $-\text{NH}$), 8.14 (s, 4H, $\delta\text{Ar-H}$), 7.97 (s, 4H, Ar-H), 7.72 (m, 10H, Ar-H), 7.47 (d, 4H, $J=7.6$ Hz, $\delta\text{Ar-H}$), 7.36 (s, 2H, Ar-H). $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$, 300 MHz): δ ppm 145.5, 141.4, 138.2, 134.8, 129.8, 129.1, 125.7, 125.3, 124.3, 123.6, 118.8, 114.3. $\delta\text{EI-MS}$ (70 eV, m/z): Calcd. For $\text{C}_{36}\text{H}_{26}\text{N}_4$: 514.22. Found: $[\text{M}+\text{H}^+]$, 515.2. The analytical calculation (%) for $\text{C}_{36}\text{H}_{26}\text{N}_4\cdot 2\text{H}_2\text{O}$: C, 78.52; H, 5.49; N, 10.17. resulted in C, 77.42; H, 5.78; N, 10.22, respectively.

2.2.9. 5-(4-Phenoxyphenyl)-2-(4-(5-(4-phenoxyphenyl)-1H-imidazol-2-yl)phenyl)-1H-imidazole (**3b**)

The yield was 69%, which was a white solid; m.p. > 310 °C. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ ppm 12.68 (br, 2H, $-\text{NH}$), 8.10 (s, 4H, Ar-H), 7.89 (d, 4H, $J=8.5$ Hz, Ar-H), 7.72 (s, 2H, Ar-H), 7.41 (d, 4H, $J=8.5$ Hz, Ar-H), 7.14 (d, 2H, $J=7.5$ Hz, Ar-H), 7.05 (m, 8H, Ar-H). $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$, 300 MHz): δ ppm 158.7, 157.4, 145.6, 142.1, 130.5, 127.4, 125.7, 125.1, 123.1, 118.2, 113.9, 113.2. EI-MS (70 eV, m/z): Calcd. For $\text{C}_{36}\text{H}_{26}\text{N}_4\text{O}_2$: 546.21. Found: $[\text{M}+\text{H}^+]$, 547.2. The analytical

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