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A new blue light-emitting terphenyl-bridged bisbenzimidazolium salts: Synthesis, crystal structure, and photophysical properties

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ABSTRACT

Eight novel terphenyl-bridged bisbenzimidazolium salts bearing *N*-alkyl side chains were synthesized by alkylation and quaternization of terphenyl-bridged bisbenzimidazoles with excess alkyl bromides, using sodium carbonate as the base in *N*,*N*-dimethylformamide solution. The bisbenzimidazolium salts showed good solubility in water and common organic solvents, such as dichloromethane, chloroform, methanol, acetonitrile, and *N*,*N*-dimethylformamide. They emitted violet–blue light ($\lambda_{max}^{Em} \approx 397$–$400$ nm) with fluorescence quantum yields of 0.65–0.78 in aqueous solution, whereas they emitted blue light ($\lambda_{max}^{Em} \approx 420$–$441$ nm) in thin films. The photoluminescent properties and crystal structure of the bisbenzimidazolium salts have been investigated.

1. Introduction

Research into multi-layered organic light-emitting diodes (OLEDs) has been actively pursued since their discovery by Tang et al. [1] because of their potential applications in flat-panel displays [2–8]. Efficient bright electroluminescence of the three primary colors-red, green, and blue is essential to achieve full color displays. After two decades of active research, many new blue-emitting materials, such as anthracene derivatives [9,10], fluorene derivatives [11,12], pyrazoloquinolines [13], pyrene derivatives [14], and others, have been exploited for the construction of blue OLEDs. However, these compounds often do not have good solubility in common organic solvents and easily aggregate in the solid state due to the strong intermolecular interactions [15–21]. The solubility and aggregation problems limit their synthesis, characterizations and applications. Thus, the synthesis of new blue-emitting materials with high solubility and low aggregating properties is essential.

Benzimidazole-based compounds have received much attention in the past few decades for their intense luminescence. They are widely used as fluorescent probes [22,23], fluorescent brightening agents [24], and nonlinear optical materials [25,26]. Various applications in OLED devices have recently been found for benzimidazole-based compounds [27,28]. A well-known example is the application of 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl)benzene (TPBI) as an electron transport and hole-blocking material. In addition to their capacity as electron transport materials (ETMs), benzimidazole-based compounds have also been used as luminescent materials in OLEDs [29,30].

In this study, a series of novel blue light-emitting bisbenzimidazolium salts (Fig. 1, 5a–5h) are designed and synthesized. The *p*-terphenyl group was preferred as the core because of its linearity, generally high fluorescence quantum yield, and high photo-stability [31–33]. Additionally, the four alkyl side chains within these molecules may lead to a large intermolecular distance, thus decreasing the tendency of aggregation and improving the solubility. These bisbenzimidazolium salts were tested for their solubility in water and common organic solvents. Then, the optical properties and crystal structures were determined by UV–vis absorption, fluorescence emission spectroscopy, and X-ray diffraction.

2. Experimental section

2.1. Measurements

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike) and remained uncorrected. Proton and carbon nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C

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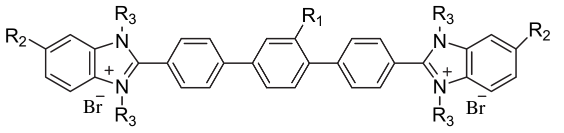


5a - 5h

5a: R_1= H, R_2= H, R_3= CH_3
5b: R_1= H, R_2= H, R_3= C_2H_5
5c: R_1= H, R_2= H, R_3= C_4H_9
5d: R_1= H, R_2= CH_3, R_3= CH_3
5e: R_1= H, R_2= CH_3, R_3= C_2H_5
5f: R_1= H, R_2= CH_3, R_3= C_4H_9
5g: R_1= CH_3, R_2= H, R_3= CH_3
5h: R_1= CH_3, R_2= H, R_3= C_2H_5

Fig. 1. Molecular structures of **5a–5h.**

NMR) were recoreded on either a Bruker AV-500 or AV-300 spectrometer using deuterated dimethylsulfoxide (DMSO–d_6) as the solvent with tetramethylsilane (TMS) as the internal standard. Electrospray ionization-mass spectroscopy (ESI-MS) measurements were carried out with an Agilent 1100 series LC/MSD Trap SL mass spectrometer. Elemental analyses were performed with a Vario EL III elemental analyzer. Optical absorption spectra were obtained using an HP-8453 UV/vis/near-IR spectrophotometer (Agilent). Photoluminescence spectroscopy was performed on an LS-55 spectrofluorometer (Perkin–Elmer). The fluorescence quantum yields (Φ_F) of these compounds in solution were determined by the standard method (using 9,10-diphenylanthracene as the standard). The X-ray crystallographic analysis was performed on a Nonius CAD4 single-crystal diffractometer (Enraf-Nonius).

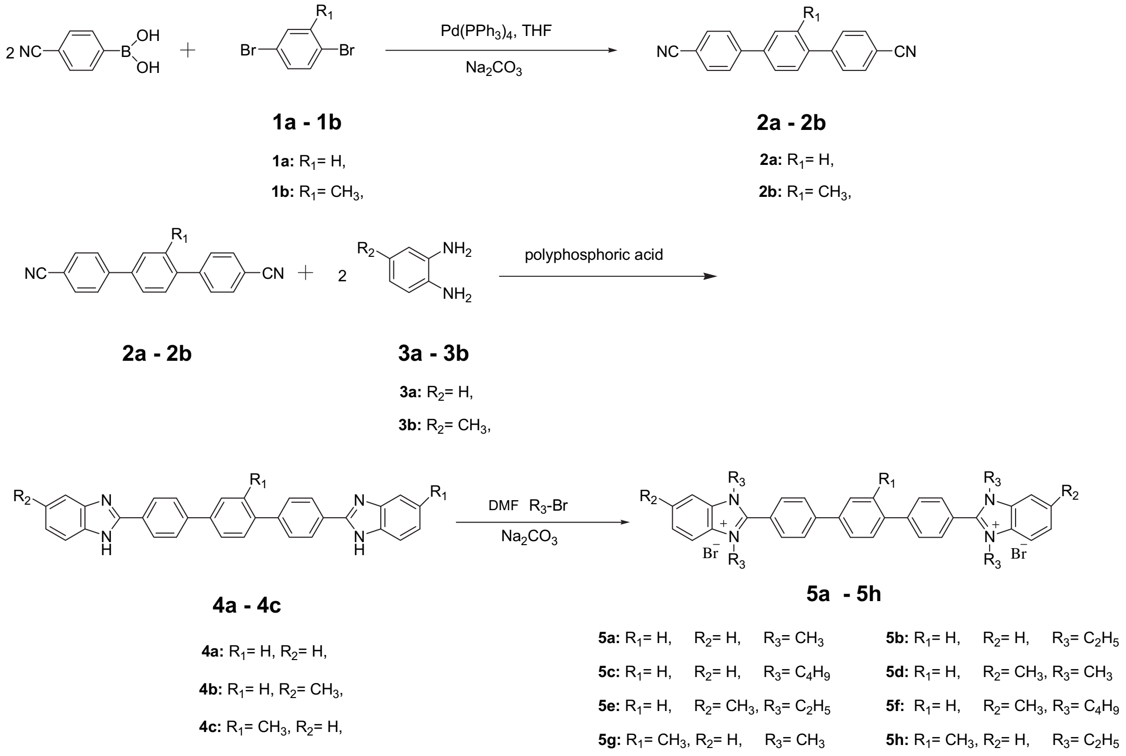
2.2. *Synthesis*

Tetrakis(triphenylphosphine)palladium(0) was purchased from ABCR Chemical Ltd. 1,4-Dibromobenzene (**1a**) and 2,5-dibromotoluene (**1b**) were purchased from J&K Chemical Ltd. 1,2-Benzenediamine (**3a**), 3,4-diaminotoluene (**3b**), and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. 4-Cyanophenylboronic acid was synthesized according to methods described in the literature [34]. Solvents were purified through conventional procedures prior to use.

2.2.1. *Procedures for the synthesis of **4a–4c***

*2.2.1.1. 4,4″-bis(benzimidazol-2-yl)-p-terphenyl (**4a**).* 1,2-Phenylene diamine (10.8 g, 100 mmol) and compound **2a** (14.1 g, 50 mmol) were added into polyphosphoric acid (PPA) (120 g) to obtain a stirrable paste. The mixture was then immediately heated at 200 °C while stirring for 4 h. After cooling to about 70 °C, it was poured into water (1200 mL). Insoluble residue was collected by filtration, washed with a small amount of water (80 mL), and reslurried in an excess of 10% sodium carbonate solution (250 mL). The alkaline slurry was filtered, and the product was washed thoroughly with water (3 × 500 mL) and dried at 60 °C. The crude product was purified by recrystallization from methanol (300 mL) to obtain pure **4a**. Yield: 87%; white powder; m.p. 448.2 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 12.97 (s, 2H), 8.31 (d, J = 8.43 Hz, 4H), 7.98–7.89 (m, 8H), 7.70 (d, J = 6.69 Hz, 2H), 7.56 (d, J = 6.69 Hz, 2H), 7.24–7.18 (m, 4H); ^{13}C NMR (DMSO–d_6 and TFA, 300 MHz): δ 148.99, 144.27, 138.83, 132.04, 128.99, 128.08, 126.50, 122.30, 121.05; FTIR (KBr, cm^{-1}): 3057 (N–H), 1621 (C═N), 1597, 1480 (Ar C═C); ESI-MS: Calcd. for $C_{32}H_{22}N_4$, 462.2. Found: [M − H$^+$], 461.1; Anal. Calcd. (%) for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.18; H, 4.83; N, 11.89.

*2.2.1.2. 4,4″-bis(5-methylbenzimidazol-2-yl)-p-terphenyl (**4b**).* Compound **4b** was obtained from 3,4-diaminotoluene and **2a**. Yield: 88%; yellow powder; m.p. 354.3 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 12.84 (s, 2H), 8.28 (d, J = 8.28, 4H), 7.96–7.87 (m, 8H), 7.54–7.39 (m, 4H), 7.05 (s, 2H), 2.45 (s, 6H); ^{13}C NMR (DMSO–d_6 and TFA, 300 MHz): δ 148.25, 143.75, 138.49, 136.46, 132.10, 129.93,



Scheme 1. Synthesis of terphenyl-bridged bisbenzimidazolium salts (**5a–5h**).

Table 1
Physical properties of **5a**–**5h.**

Comp.	Solubility (mg ml^{-1})[a]			ε (10^4 M^{-1} cm^{-1})	λ_{max}^{Abs} (nm)	λ_{max}^{Em} (nm)	λ_{max}^{Em} [b] (nm) film	Φ_F[c]	E_g^{opt}[d] (eV)
	H_2O	CH_3OH	CH_2Cl_2						
5a	19.7	129.5	17.2	6.21	312	397	440	0.71	3.52
5b	9.2	132.1	98.6	6.08	305	397	426	0.75	3.59
5c	5.0	141.4	162.3	6.05	303	397	421	0.77	3.59
5d	16.5	117.9	19.7	6.67	315	397	441	0.68	3.51
5e	7.6	126.0	112.0	6.51	307	397	427	0.72	3.59
5f	6.4	118.6	177.8	6.32	304	397	420	0.78	3.57
5g	17.3	135.5	22.3	4.78	299	399	438	0.65	3.56
5h	5.8	148.7	106.1	4.80	290	400	423	0.71	3.63

[a] solubility test at room temperature.
[b] The thin film for PL measurements was prepared by spin-coating a dichloromethane solution on a quartz plate, followed by drying for 5 h at room temperature.
[c] Determined in an aqueous solution ($A < 0.1$) at room temperature using 9,10-diphenyl-anthracene ($\Phi_f = 0.90$ in cyclohexane) as standard [45].
[d] Estimated from onset of the absorption spectra ($E_g^{opt} = 1240/\lambda_{onset}$).

128.61, 127.81, 122.16, 120.91, 113.43, 21.22; FTIR (KBr, cm^{-1}): 3034 (N–H), 1619 (C=N), 1595, 1478 (Ar C=C); ESI-MS: Calcd. for $C_{34}H_{26}N_4$, 490.2. Found: [M − H$^+$], 489.3, [M + H$^+$], 491.5; Anal. Calcd. (%) for $C_{34}H_{26}N_4$: C, 83.24; H, 5.34; N, 11.42. Found: C, 83.18; H, 5.37; N, 11.29.

2.2.1.3. 2′-methyl-4,4″-bis(benzimidazol-2-yl)-p-terphenyl (***4c***). Compound **4c** was obtained from 1,2-phenylene diamine and **2b**. Yield: 88%; orange powder; m.p. 339.1 °C; ^{1}H NMR (DMSO–d_6, 500 MHz): δ 12.97 (s, 2H), 8.30 (d, J = 8.45, 2H), 8.28 (d, J = 8.40, 2H), 7.95 (d, J = 8.45, 2H), 7.78 (s, 1H), 7.72–7.65 (m, 3H), 7.60 (d, J = 8.40, 2H), 7.56 (d, J = 8.00, 2H), 7.42 (d, J = 7.95, 1H), 7.22 (brs, 4H), 2.42 (s, 3H); ^{13}C NMR (DMSO–d_6 and TFA, 300 MHz): δ 149.12, 148.99, 146.06, 144.51, 140.40, 138.33, 136.21, 132.07, 130.62, 129.55, 128.91, 128.34, 128.02, 126.45, 125.06, 122.13, 122.01, 121.19, 114.28, 20.47; FTIR (KBr, cm^{-1}): 3054 (N–H), 1616 (C=N), 1589, 1477 (Ar C=C); ESI-MS: Calcd. for $C_{33}H_{24}N_4$, 476.2. Found: [M − H$^+$], 475.2, [M + H$^+$], 477.2; Anal. Calcd. (%) for $C_{33}H_{24}N_4$: C, 83.17; H, 5.08; N, 11.76. Found: C, 83.28; H, 5.13; N, 11.39.

2.2.2. Procedures for the synthesis of *5a*–*5h*

2.2.2.1. [1,1′;4′,1″]-terphenyl-4,4″-bis(1,3-dimethyl-2-benzimidazolium bromide) ***5a***. A 100 mL autoclave with a magnetic spin bar was charged with **4a** (2.31 g, 5 mmol) dissolved in *N*,*N*-dimethylformamide (DMF) (40 mL). Bromomethane (2.85 g, 30 mmol) and Na_2CO_3 (1.06 g, 10 mmol) were added to this solution. The mixture was heated at 110 °C for 24 h while stirring. After the reaction mixture was allowed to cool to 60 °C, the solvent and extra bromomethane were evaporated under vacuum. The residue was dissolved in chloroform (50 mL), and the insoluble residue was removed by filtration. Chloroform was removed under vacuum. The crude product was purified by chromatography (dichloromethane/methanol 8:1 as the elution) to obtain pure **5a**. Yield: 85%; white crystals; m.p. 371–373 °C; ^{1}H NMR (DMSO–d_6, 500 MHz): δ 8.25–8.21 (m, 8H), 8.06 (d, J = 7.55 Hz, 8H), 7.81–7.78 (m, 4H), 4.09 (s, 12H); ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.68, 143.15, 138.37, 130.92, 130.87, 127.76, 127.55, 126.62, 120.26, 113.39, 32.86; FTIR (KBr, cm^{-1}): 1602 (C=N), 1545, 1469 (Ar C=C); MS (ES) m/z: 260.2 [M − 2Br$^-$]$^{2+}$; Anal. Calcd. (%) for $C_{36}H_{32}Br_2N_4$: C, 63.54; H, 4.74; N, 8.23. Found: C, 63.48; H, 4.83; N, 8.29.

2.2.2.2. [1,1′;4′,1″]-terphenyl-4,4″-bis(1,3-diethy-2-benzimidazolium bromide) ***5b***. Compound **5b** was obtained from bromoethane and **4a**. Yield: 82%; white crystals; m.p. 267–269 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 8.25–8.21 (m, 8H), 8.06 (d, J = 7.62 Hz, 8H), 7.80–7.77 (m, 4H), 4.36 (q, 8H), 1.40 (t, 12H). ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.59, 143.25, 138.40, 130.82, 130.80, 127.78, 127.61, 126.59, 120.38, 113.59, 41.26, 14.27; FTIR (KBr, cm^{-1}): 1607 (C=N), 1545, 1470 (Ar C=C); MS (ES) m/z: 288.3 [M – 2Br$^-$]$^{2+}$ Anal. Calcd. (%) for $C_{40}H_{40}Br_2N_4$: C, 65.22; H, 5.47; N, 7.61. Found: C, 65.27; H, 5.43; N, 7.59.

2.2.2.3. [1,1′;4′,1″]-terphenyl-4,4″-(1,3-dibutyl-2-benzimidazolium bromide) ***5c***. Compound **5c** was obtained from 1-bromobutane and **4a**. Yield: 64%; white crystals; m.p. 304–306 °C; ^{1}H NMR (DMSO–d_6, 500 MHz): δ 8.25–8.22 (m, 8H), 8.05 (d, J = 7.49 Hz, 8H), 7.80–7.76 (m, 4H), 4.34 (t, 8H), 1.78–1.68 (m, 8H), 1.24–1.19 (m, 8H), 0.75 (t, 12H). ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.74, 143.10, 138.31, 131.07, 130.99, 127.75, 127.50, 126.61, 120.41, 113.52, 45.58, 32.69, 18.90, 13.08; FTIR (KBr, cm^{-1}): 1605 (C=N), 1549, 1462 (Ar C=C); MS (ES) m/z: 344.6 [M – 2Br$^-$]$^{2+}$ Anal. Calcd. (%) for $C_{48}H_{56}Br_2N_4$: C, 67.92; H, 6.65; N, 6.60. Found: C, 67.89; H, 6.62; N, 6.67.

2.2.2.4. [1,1′;4′,1″]-terphenyll-4,4″-bis(1,3,5-trimethyl-2-benzimidazolium bromide) ***5d***. Compound **5d** was obtained from bromomethane and **4b**. Yield: 88%; white crystals; m.p. 352–353 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 8.21(d, J = 8.43 Hz, 4H), 8.04 (d, J = 8.52 Hz,10H), 7.99 (s, 2H), 7.60 (d, J = 8.52 Hz, 2H), 3.95 (s, 12H), 2.61 (s, 6H); ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.62, 143.26, 138.52, 136.88, 131.98, 131.54, 129.98, 127.99, 127.85, 127.43, 120.14, 112.96, 112.76, 32.82, 21.20; FTIR (KBr, cm^{-1}): 1603 (C=N), 1549, 1464 (Ar C=C); MS (ES) m/z: 274.5 [M – 2Br$^-$]$^{2+}$ Anal. Calcd. (%) for $C_{38}H_{36}Br_2N_4$: C, 64.42; H, 5.12; N, 7.91. Found: C, 64.38; H, 5.13; N, 7.89.

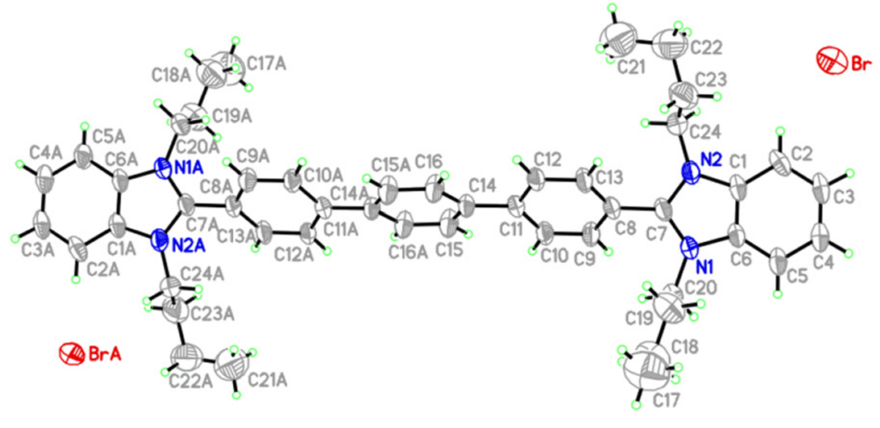


Fig. 2. Single crystal structure of **5c**.

2.2.2.5. [1,1′;4′,1″]-terphenyl-4,4″-bis(5-methyl-1,3-diethyl-2-benzimidazolium bromide) ***5e***. Compound **5e** was obtained from bromoethane and **4b.** Yield: 83%; white crystals; m.p. 269–271 °C; ^{1}H NMR (DMSO–d_6, 500 MHz): δ 8.21(d, $J = 8.40$ Hz, 4H), 8.10 (d, $J = 8.55$ Hz 2H), 8.06–8.03(m, 10H), 7.61(d, $J = 8.60$ Hz, 2H), 4.31(q, 8H), 2.61(s, 6H), 1.38 (t, 12H); ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.05, 143.18, 138.40, 136.93, 131.03, 130.88, 128.97, 127.98, 127.80, 127.61, 120.47, 113.21, 112.98, 41.24, 21.17, 14.28; FTIR (KBr, cm^{-1}): 1605 (C=N), 1549, 1462 (Ar C=C); MS (ES) m/z: 302.3 $[M - 2Br^-]^{2+}$; Anal. Calcd. (%) for $C_{42}H_{44}Br_2N_4$: C, 65.97; H, 5.80; N, 7.33. Found: C, 65.88; H, 5.84; N, 7.35.

2.2.2.6. [1,1′;4′,1″]-terphenyl-4,4″-bis(5-methyl-1,3-dibutyl-2-benzimidazolium bromide) ***5f***. Compound **5f** was obtained from 1-bromobutane and **4b**. Yield: 67%; white crystals; m.p. 285–287 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 8.20 (d, $J = 8.42$ Hz, 4H), 8.11–8.01 (m, 12H), 7.62 (d, $J = 8.58$ Hz, 2H), 4.30 (t, 8H), 2.60 (s, 6H), 1.73–1.70 (m, 8H), 1.22–1.20 (m, 8H), 0.74 (t, 12H); ^{13}C NMR (DMSO–d_6, 300 MHz): δ 149.43, 143.21, 138.88, 136.99, 131.30, 130.22, 130.13, 127.80, 127.70, 124.29, 120.40, 113.34, 113.01, 45.58, 30.54, 21.22, 18.94, 13.15; FTIR (KBr, cm^{-1}): 1607 (C=N), 1545, 1469 (Ar C=C); MS (ES) m/z: 358.7 $[M - 2Br^-]^{2+}$ Anal. Calcd. (%) for $C_{50}H_{60}Br_2N_4$: C, 68.49; H, 6.90; N, 6.39. Found: C, 68.48; H, 6.93; N, 6.41.

2.2.2.7. 2′-methyl-[1,1′;4′,1″]-terphenyl-4,4″-bis(1,3,-dimethyl-2-benzimidazolium bromide) ***5g***. Compound **5g** was obtained from bromomethane and **4c**. Yield: 89%; white crystals; m.p. 263–265 °C; ^{1}H NMR (DMSO–d_6, 300 MHz): δ 8.24–8.19(m, 4H), 8.18 (d, $J = 8.35$ Hz, 2H), 8.06–8.02 (m, 4H), 7.88–7.84 (m, 4H), 7.81–7.78 (m, 4H), 7.53 (d, $J = 7.87$ Hz, 1H), 3.98(s, 12H), 2.49 (s, 3H); ^{13}C NMR (DMSO–d_6, 500 MHz): δ 150.17, 150.04, 144.96, 143.69, 140.04, 138.19, 135.91, 131.75, 131.51, 131.45, 130.86, 130.38, 129.03, 129.37, 127.79, 127.48, 126.59, 124.88, 119.95, 119.90, 119.70, 113.37, 32.85, 20.32; FTIR (KBr, cm^{-1}): 1602 (C=N), 1546, 1462 (Ar C=C); MS (ES) m/z: 267.7 $[M - 2Br^-]^{2+}$ Anal. Calcd. (%) for $C_{37}H_{34}Br_2N_4$: C, 63.99; H, 4.93; N, 8.07. Found: C, 63.92; H, 4.97; N, 8.11.

Table 2
Crystal and structural refinement data of **5c**.

Empirical formula	$C_{48}H_{56}Br_2N_4$
Formula weight	848.77
Temperature (K)	296 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n (no. 14)
a (Å)	9.556 (3)
b (Å)	12.740 (4)
c (Å)	17.839 (6)
α (°)	90.00
β (°)	91.512 (5)
γ (°)	90.00
Volume (Å^3)	2171.0 (13)
Z	33
D_{calc} (g/cm^3)	1.298
μ (mm^{-1})	1.904
F (000)	884
Crystal dimensions (mm)	0.20 × 0.10 × 0.10
Color of crystal	colorless
Shape of crystal	needle
$2\theta_{max}$ (°)	54.98
No. of reflections measured	18570
No. of reflections observed [$I > 2\sigma(I)$]	4986
No. of variables	244
R	0.0605
R_w	0.1742
Largest diff. peak and hole (e Å^{-3})	0.411 and −0.415
Maximum shift in final cycles	0.000

Table 3
Selected bond lengths (Å), bond angles, and torsional angles (°) for **5c**.

N(1)–C(6)	1.386 (5)	N(2)–C(1)	1.410 (5)
N(1)–C(7)	1.343 (5)	N(2)–C(7)	1.340 (5)
N(1)–C(20)	1.463 (5)	N(2)–C(24)	1.489 (5)
C(6)–N(1)–C(7)	108.7 (3)	N(1)–C(6)–C(1)	107.4 (3)
C(6)–N(1)–C(20)	124.6 (3)	N(1)–C(6)–C(5)	131.6 (4)
C(7)–N(1)–C(20)	126.4 (3)	N(1)–C(7)–N(2)	109.1 (3)
C(1)–N(2)–C(7)	108.1 (3)	N(1)–C(7)–C(8)	126.4 (3)
C(1)–N(2)–C(24)	124.0 (3)	N(2)–C(7)–C(8)	124.2 (3)
C(7)–N(2)–C(24)	127.9 (3)	N(1)–C(20)–C(19)	113.4 (4)
N(2)–C(1)–C(2)	130.2 (4)	N(2)–C(24)–C(23)	108.4 (4)
N(2)–C(1)–C(6)	106.6 (3)		
C(6)–N(1)–C(7)–N(2)	0.7 (4)	C(24)–N(2)–C(7)–N(1)	177.4 (3)
C(20)–N(1)–C(7)–N(2)	174.1 (3)	N(2)–C(1)–C(6)–N(1)	−0.3 (4)
C(1)–N(2)–C(7)–N(1)	−0.8 (4)		

2.2.2.8. 2′-methyl-[1,1′;4′,1″]-terphenyl-4,4″-bis(1,3-diethyl-2-benzimidazolium bromide) ***5h***. Compound **5h** was obtained from bromoethane and **4c**. Yield: 81%; white crystals; m.p. 266–268 °C; ^{1}H NMR (DMSO–d_6, 500 MHz): δ 8.24–8.20 (m, 4H), 8.18 (d, $J = 8.50$ Hz, 2H), 8.06–8.03 (m, 4H), 7.89–7.82 (m, 4H), 7.80–7.78 (m, 4H), 7.55 (d, $J = 7.91$ Hz, 1H), 4.35 (q, 8H), 2.48 (s, 3H), 1.41 (t, 12H). ^{13}C NMR (DMSO–d_6, 500 MHz): δ 149.71, 149.65, 144.90, 143.69, 139.98, 138.17, 135.88, 131.54, 130.82, 130.42, 130.67, 130.16, 130.12, 129.43, 127.72, 127.46, 126.62, 124.88, 120.27, 120.04, 119.83 113.66, 41.30, 20.31, 14.33; FTIR (KBr, cm^{-1}): 1604 (C=N), 1547, 1468 (Ar C=C); MS (ES) m/z: 295.6 $[M - 2Br^-]^{2+}$; Anal. Calcd. (%) for $C_{41}H_{42}Br_2N_4$: C, 65.61; H, 5.64; N, 7.46. Found: C, 65.57; H, 5.67; N, 7.43.

2.3. X-ray diffraction crystallography

Compound **5c** was prepared for single crystal X-ray diffraction by dissolving 0.2 g **5c** in acetonitrile (5 mL). This solution was then allowed to evaporate at room temperature over 30 days. A very thin colorless crystal with approximate dimensions of 0.20 mm × 0.10 mm × 0.10 mm was placed on a glass fiber. Diffraction data were collected on a Nonius CAD4 single crystal diffractometer equipped with a graphite-monochromated MoKα radiation source ($\lambda = 0.71073$ Å) and operated at a $\omega/2\theta$ scan mode at 296 K. Crystal structures were solved by a direct method and refined by a full-matrix least-squares procedure on F^2 using the SHELXL-97 program [35]. Positions of hydrogen atoms were located by geometrical calculation and were then refined (x, y, z, and U_{iso} fixed to 1.2 times U_{iso} of atom they are bound to). The final refinement converged at $R1 = 0.0605$ and $wR2 = 0.1742$ for 2322 reflections [$I > 2\sigma(I)$] with 244 variable parameters and no restraint.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of compounds **5a**–**5h** is outlined in Scheme 1. The terphenyl dinitriles **2a**–**2b** were synthesized by a Suzuki coupling reaction of the dibromobenzene derivatives **1a**–**1b** with 4-cyanophenylboronic acid in tetrahydrofuran solution at 65 °C

Table 4
Intermolecular hydrogen bond geometry (Å, °) for **5c**.

D–H···A	D–H	H···A	D···A	D–H···A
C9–H9A^{i}···Br	0.9300	2.9100	3.604 (4)	132.00
C24–H24B^{ii}···Br	0.9700	2.9000	3.861 (5)	171.00

Symmetry transformations used to generate equivalent atoms: (i) $1 + x, -1 + y, z$; (ii) $x, -1 + y, z$.

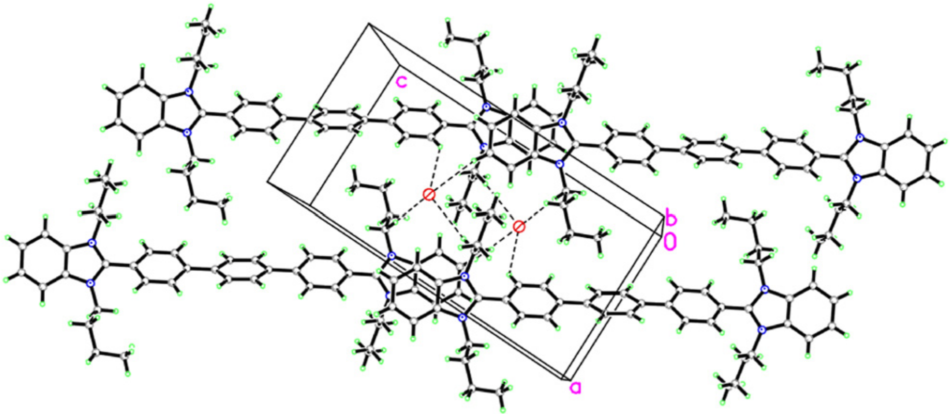


Fig. 3. Representation of intermolecular hydrogen bonds (dashed lines) and interlayer π–π stacking (dashed arrow, Å) [symmetry codes: (i) 1 + *x*, −1 + *y*, *z*; (ii) *x*, −1 + *y*, *z*].

using $Pd(PPh_3)_4$ as the catalyst and Na_2CO_3 as the base [36]. Compounds **4a**–**4c** were synthesized by the condensation of *o*-phenylenediamines **3a**–**3b** with terphenyl dinitriles **2a**–**2b** using PPA as the catalyst [33,37–39]. Compounds **5a**–**5h** were synthesized by alkylation and quaternization of compounds **4a**–**4c** with excess alkyl bromides in DMF at 110 °C [40,41]. The ^1H NMR spectra, ^{13}C NMR spectra, MS spectra, and elemental analysis of **5a**–**5h** confirmed the proposed structures. The crystal structure of compound **5c** was revealed by X-ray crystallography.

Compounds **5a**–**5h** are colourless crystals, stable in air and have melting points higher than 260 °C. They can dissolve in water, dichloromethane, chloroform, methanol, acetonitrile, 1,4-dioxane, and DMF. The solubilities of **5a**–**5h** in different solvents are listed in Table 1 for a comparative study. The solubility of these compounds in water and dichloromethane is largely dependent on the length of the *N*-alkyl side chains. The solubility increased in dichloromethane but decreased in water as the chain length increased. All compounds exhibited excellent solubility in methanol.

3.2. *X-ray diffraction crystallography of compound* **5c**

The molecular structure of compound **5c** is shown in Fig. 2. Compound **5c** crystallizes in the monoclinic P21/n space group without the presence of any solvent molecule. All non-hydrogen atoms were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters. Details of the structural determination and refinement results for **5c** are given in Table 2. Selected bond lengths (Å), bond angles, and torsional angles are listed in Table 3, and the hydrogen bonding interactions are shown in Table 4. The dihedral angle between the N2/C1/C6/N1/C7 ring and the C8 ring is 55.65°, and the dihedral angle between the C8 ring and the C14 ring is 15.66°. Due to molecular centrosymmetry, the dihedral angle between N2A/C1A/C6A/N1A/C7A and the C8A ring is also 55.65°, and the dihedral angle between the C8A ring and the C14A ring is 15.66°. The structure is supported by two weak intermolecular C–H···Br hydrogen bonds (Fig. 3), which gives support to molecular packing stability in the unit cell.

3.3. *Optical properties*

The UV–vis absorption spectra of compounds **5a**–**5h** diluted in water (10^{-5} M) are displayed in Fig. 4. Their photophysical properties are summarized in Table 1. All compounds show strong absorptions, with maximum wavelengths in the range of 290–315 nm. The molar absorption coefficients of these compounds are reasonably high, ranging from 4.80 to 6.67 (10^4 M^{-1} cm^{-1}). The absorption λ_{max}^{Abs} of *N*-methyl-substituted **5a** and **5d** are at 312 and 315 nm, respectively. Compared to **5a** and **5d**, the absorption λ_{max}^{Abs} of the *N*-ethyl-substituted **5b** and **5e** are

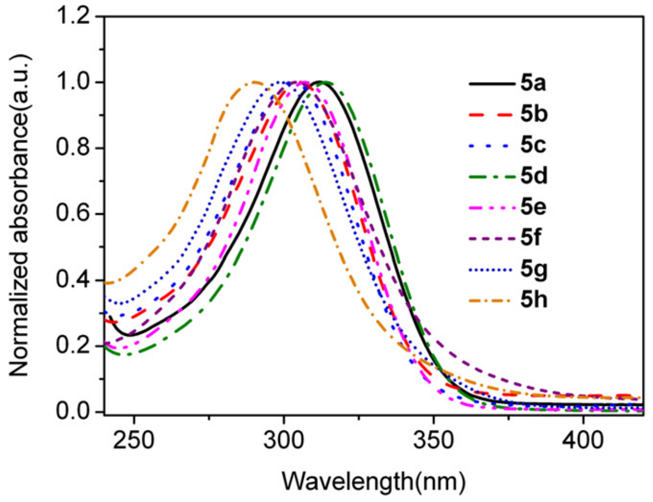


Fig. 4. UV–vis absorption spectra of **5a**–**5h** in water (10^{-5} M).

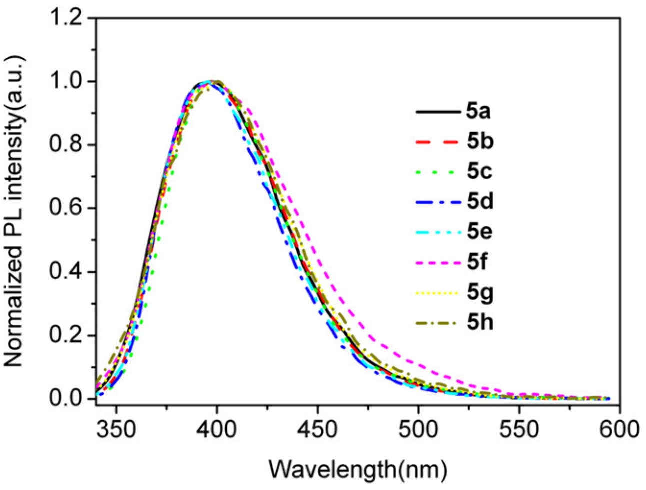


Fig. 5. Fluorescence emission spectra of **5a**–**5h** in water (10^{-7} M).

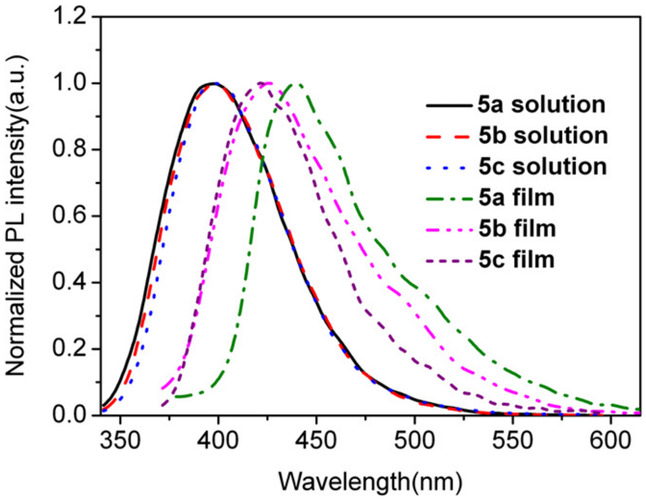


Fig. 6. Fluorescence emission spectra of **5a**–**5c** in the aqueous solution and in the film.

blue-shifted by 7 and 8 nm, respectively, and *N*-butyl-substituted **5c** and **5f** are blue-shifted by 9 and 11 nm, respectively. This blue shift may be due to the steric effect of the *N*-alkyl chain. As the length of the *N*-alkyl chain increases, the dihedral angle between the benzimidazole ring and the terphenyl ring becomes bigger, leading to a lower coplanarity of the molecule. On the other hand, the bisbenzimidazolium salts that have methyl groups on the terphenylene core (**5g** and **5h**) are blue-shifted by 13 and 15 nm, respectively, compared to the corresponding unsubstituted **5a** and **5b**. This blue-shift may be attributed to the steric effect of the methyl group at the central benzene ring in the terphenylene system, which results in less coplanarity of the molecule [42]. Optical band gaps ($\boldsymbol{E}_g^{opt}$) determined from the absorption edge of the solution spectra [43] are also given in Table 1. The $\boldsymbol{E}_g^{opt}$ varies from 3.51 eV in **5d**–3.63 eV in **5h**.

The emission spectra of compounds **5a**–**5h** in water (10^{-7} M) are shown in Fig. 5. All compounds emit violet–blue light with a maximum emission in the 397–400 nm range. Different *N*-alkyl side chains do not have any significant effects on the emission maximum, indicating that fluorescence emissions originate from the bisbenzimidazolium backbone. However, a dependence of fluorescence quantum yields (Φ_F) on the *N*-alkyl side chains can be observed. The Φ_F of these compounds increase with the increase of carbon atoms in the *N*-alkyl side chains. The results indicated that large side chains provide the bisbenzimidazolium backbone better protection from the effects of the solvent molecules or other bisbenzimidazolium molecules [44].

The fluorescence emission spectra of **5a**, **5b**, and **5c** in the solution and the film are shown in Fig. 6. Compared with the emission spectra in the solution, the emission bands in the film are not only broad but also significantly red-shifted, indicating an increased intermolecular interaction in the film state. The degree of red-shift occurs in the order of **5c** < **5b** < **5a**. This supports the assumption in this study that large side groups can increase the distance of molecules, which leads to the decrease of intermolecular interaction in the solid state.

4. Conclusions

In summary, a new series of bisbenzimidazolium salt-based blue-emitting materials was synthesized and characterized by UV–vis absorption and fluorescence emission spectroscopy. The bisbenzimidazolium salts showed good solubility in water and common organic solvents. Fluorescence measurements indicated that the aggregation tendency of the molecule in the thin films was reduced as the number of carbon atoms in the *N*-alkyl side chains increased. The compounds emitted violet–blue light ($\lambda_{max}^{Em} \approx 397$–$400$ nm) with fluorescence quantum yields of 0.65–0.78 when diluted in water, whereas they emitted blue light ($\lambda_{max}^{Em} \approx 420$–$441$ nm) in thin films. Thus, these new compounds have potential applications as blue light emitters in OLEDs. Further studies of their application are underway in our laboratory.

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