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# Synthesis and photophysical properties of a series of thermally stable terphenyl-bridged bisbenzimidazoles

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ABSTRACT

Nine novel terphenyl-bridged bisbenzimidazoles were synthesized in high yield by the condensation of *o*-phenylenediamines and terphenyl dinitriles in the presence of polyphosphoric acid. The bisbenzimidazoles are thermally robust with high decomposition temperatures (>346 °C) and high melting transitions and emit blue light at ~410 nm with fluorescence quantum yield >0.4 in solution. Electrochemical studies indicate that the novel bisbenzimidazoles have a formal reduction potential in the range of −1.44 to −1.55 V and estimated electron affinities (lowest unoccupied molecular orbital levels) of 3.09–3.24 eV. The results indicate their potential use as blue-emitting materials in organic light-emitting diodes.

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## 1. Introduction

Ever since Tang and Vanslyke constructed electroluminescent (EL) devices using organic materials as emitters, the development of new EL materials has become an active area of research because of their potential use in displays [1–5]. For high-performance full-color displays, it is necessary to develop light-emitting materials with good color purity and high efficiency in the three elemental colors of red, green, and blue. The stability and efficiency of green and red emitters have approached commercially viable levels. The design and synthesis of blue emitters suitable for fabrication of stable organic light-emitting diode (OLED) devices, however, remain major challenges for researchers [6–10]. Due to a large band gap energy, blue light-emitting materials often have low electron affinities (EAs ≤ 2.5 eV), making it difficult to inject charges efficiently into them from the cathode [8,11]. In addition, the color purity and stability of blue emitters require improvement [12].

Benzimidazole-based compounds are known for their intense luminescence and are widely used in fluorescent probes [13,14], fluorescent brightening agents [15], non-linear optical materials [16,17], and phosphorescent OLEDs [18]. They also bear electron-withdrawing imine nitrogen (C=N) moieties, which behave as electron-accepting molecules that can facilitate electrochemical reduction, a feature that renders them suitable electron carriers [19]. In order to develop thermally stable blue emitters with good electron injection and transport abilities, a series of novel bisbenzimidazole compounds based on the terphenyl core (**4a**–**4i**, Fig. 1) were designed and synthesized in this study. The thermal stability, photophysical, and electrochemical properties of **4a**–**4i** were also investigated.

## 2. Experimental Section

### 2.1. Measurements

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike) and remained uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on either a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300 spectrometer at 300 MHz, using deuterated dimethylsulfoxide (DMSO-$d_6$) and trifluoroacetic acid (TFA) as the solvents, 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. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an AVARTE360 FTIR spectrometer (Thermo Nicolet). Elemental analyses were performed with a Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

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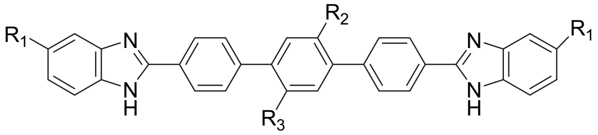


**4a:** $R_1$ = H, $R_2$ = H, $R_3$ = H **4b:** $R_1$ = Br, $R_2$ = H, $R_3$ = H **4c:** $R_1$ = $CH_3$, $R_2$ = H, $R_3$= H
**4d:** $R_1$ = H, $R_2$ = $CH_3$, $R_3$ = H **4e:** $R_1$ = H, $R_2$ = $CH_3$, $R_3$ = $CH_3$ **4f:** $R_1$ = $CH_3$, $R_2$ = $CH_3$, $R_3$= H
**4g:** $R_1$ = H, $R_2$ = F, $R_3$ = H **4h:** $R_1$ = Br, $R_2$ = F, $R_3$ = H **4i:** $R_1$ = $CH_3$, $R_2$ = F, $R_3$= H

**Fig. 1.** Molecular structures of **4a**–**4i**.

were conducted on a TA Instruments NETZSCH TG 209 and a DSC Instruments NETZSCH DSC 204, respectively. A heating rate of 10 °C/min from room temperature to 500 °C was applied under normal atmospheric conditions. Optical absorption spectra were obtained using an HP-8453 UV/vis/near-IR spectrophotometer (Agilent). Photoluminescence spectra were carried out on an LS-55 spectrofluorometer (Perkin–Elmer). The electrochemical analyses were carried out using a CHI600c electrochemical workstation.

### 2.2. Synthesis

*n*-Butyllithium and tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] were purchased from ABCR Chemical Ltd. 2,5-Dibromotoluene (**1b**) and 1,4-dibromo-2-fluorobenzene (**1d**) were purchased from J&K Chemical Ltd. 4-Bromo-1,2-benzenediamine (**3b**), 3,4-diaminotoluene (**3c**), ferrocene, and other reagents were purchased from Sinopharm Chemcial Reagent Co. Ltd. Tetra-*n*-butylammonium perchlorate (TBAP) and ferrocene were purified by double recrystallization from ethanol. Solvents were purified through conventional procedures prior to use.

### 2.2.1. Synthesis of 4-cyanophenyboronic acid

A 50 mL round-bottomed flask equipped with a temperature probe, magnetic stirrer, and septum was charged with tetrahydrofuran (16 mL) and 4-bromobenzonitrile (3.64 g, 20 mmol) under a nitrogen atmosphere. The mixture was cooled to −70 °C using a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane, 10.5 mL, 26 mmol) was added dropwise over 1 h *via* a syringe pump. After stirring at that temperature for 30 min, trimethyl borate (2.91 g, 28 mmol) was added to the mixture which was warmed to room temperature, stirred for an additional 1 h, then quenched with water (20 mL), acidified with 1 M aq HCl (40 mL), and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give a yellow solid. The solid was recrystallized from ethyl acetate-hexane (*v*/*v* = 1:4, 15 mL) to give 1.87 g (yield: 63%) of a colorless solid with the following properties: m.p. 300 °C (dec.); $^1H$ NMR (DMSO-$d_6$, 300 MHz): δ 7.77 (d, $J$ = 8.00 Hz, 2H), 7.92 (d, $J$ = 8.00, 2H), 8.37(s, 2H).

### 2.2.2. General procedure for the synthesis of 2a–2d

A tetrahydrofuran solution (50 mL) containing dibromobenzene derivatives **1a**–**1d** (5 mmol) was introduced under nitrogen into a Schlenk-type flask containing $Pd(PPh_3)_4$ (350 mg, 0.28 mmol) and $Na_2CO_3$ (2.12 g, 20 mmol). Solid 4-cyanophenylboronic acid (1.62 g, 11 mmol) was then added and the resulting mixture was heated at 65 °C while stirring continuously for 24 h. After the reaction mixture was allowed to cool to room temperature, the solvent was evaporated under vacuum. The residue was mixed with dichloromethane (30 mL), and then washed with water (50 mL) and brine (20 mL). The organic layer was collected and dried under $MgSO_4$. After filtration, the solvent was removed under vacuum. The crude product was purified by chromatography with petroleum ether/ethyl acetate 4:1 as the eluting solvent to give the desired products **2a**–**2d** with the following properties.

*2.2.2.1. 4′,4″-Bis-cyano[1,1′;4′,1″]terphenyl (**2a**).* Yield: 79%; white crystals; m.p. 297–299 °C (lit. [20]: 299–300 °C); $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.96–7.98 (m, 8H), 7.91 (brs, 4H); FTIR (KBr, $cm^{-1}$): 2223 (CN), 1598, 1483 (Ar C═C); Anal. Calcd. (%) for $C_{20}H_{12}N_2$: C, 85.69; H, 4.31. Found: C, 85.42; H, 4.51.

*2.2.2.2. 2′-Methyl-4,4″-bis-cyano[1,1′;4′,1″]terphenyl (**2b**).* Yield: 75%; white crystals; m.p. 254–255 °C; $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.77–7.70 (m, 6H), 7.52–7.45 (m, 4H), 7.31 (d, $J$ = 7.77, 1H), 2.34 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 300 MHz): δ 145.98, 145.02, 140.44, 139.20, 136.05, 132.69, 132.14, 130.30, 129.94, 129.54, 127.73, 124.97, 118.84, 118.79, 111.29, 111.22, 20.52; FTIR (KBr, $cm^{-1}$): 2223 (CN), 1597, 1482 (Ar C═C); ESI-MS: Calcd. for $C_{21}H_{14}N_2$, 294.4. Found: [$M-H^+$], 293.4; Anal. Calcd. (%) for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79. Found: C, 85.58; H, 4.82.

*2.2.2.3. 2′,5′-Dimethyl-4′,4″-bis-cyano[1,1′;4′,1″]terphenyl (**2c**).* Yield: 71%; white crystals; m.p. 301–303 °C; $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.94–7.91 (d, $J$ = 8.28, 4H), 7.62–7.59 (d, $J$ = 8.28, 4H), 7.21(s, 2H), 2.23 (s, 6H); $^{13}C$ NMR ($CDCl_3$, 300 MHz): δ 146.16, 139.98, 132.78, 132.04, 131.74, 129.92, 118.82, 111.01, 19.74; FTIR (KBr, $cm^{-1}$): 2221 (CN), 1601, 1482 (Ar C═C); ESI-MS: Calcd. for $C_{22}H_{16}N_2$, 308.4. Found: [$M-H^+$], 307.4; Anal. Calcd. (%) for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23. Found: C, 85.61; H, 5.26.

*2.2.2.4. 2′-Fluoro-4,4″-bis-cyano[1,1′;4′,1″]terphenyl (**2d**).* Yield: 81%; white solid; m.p. 292–294 °C (lit. [20]: 289–291 °C); $^1H$ NMR ($CDCl_3$, 500 MHz): δ 8.02–7.96 (m, 6H), 7.85–7.82 (m, 3H), 7.78–7.73 (m, 2H); FTIR (KBr, $cm^{-1}$): 2221 (CN), 1609, 1479 (Ar C═C); Anal. Calcd. (%) for $C_{20}H_{11}FN_2$: C, 80.52; H, 3.72. Found: C, 80.38; H, 3.79.

### 2.2.3. Procedures for the synthesis of 4a–4i

*2.2.3.1. 4,4″-Bis(benzimidazol-2-yl)-p-terphenyl (**4a**).* 1,2-Phenylene diamine (2.16 g, 20 mmol) and compound **2a** (10 mmol) were mixed with PPA (20 g) to give a stirrable paste. The mixture was heated slowly to 180 °C, after which the resulting solution was stirred at the same temperature for 6 h, permitted to cool to about 80 °C, and then poured into water (500 mL). The insoluble residue was collected by filtration, washed with a small amount of water (20 mL) and reslurried in an excess of 10% sodium carbonate solution (50 mL). The alkaline slurry was filtered and the product was washed thoroughly with water (3 × 200 mL) and dried at 60 °C. The crude product was purified by recrystallization from methanol (60 mL) to obtain pure **4a**. Yield: 85%; white powder; m.p. 448.2 °C; $^1H$ NMR (DMSO-$d_6$, 300 MHz): δ 12.97 (s, 2H), 8.31 (d, $J$ = 8.43, 4H), 7.98–7.89 (m, 8H), 7.70 (d, $J$ = 6.69, 2H), 7.56 (d, $J$ = 6.69, 2H), 7.24–7.18 (m, 4H); $^{13}C$ NMR (TFA:DMSO-$d_6$ = 1:5, 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.

*2.2.3.2. 4,4″-Bis(5-bromobenzimidazol-2-yl)-p-terphenyl (**4b**).* Following the same procedure described for the synthesis of **4a**, 4-bromo-1,2-benzenediamine and **2a** were used to obtained product **4b**. Yield: 81%; red powder; m.p. 342.6 °C; $^1$H NMR (DMSO-$d_6$ , 300 MHz): δ 13.14 (s, 2H), 8.31 (d, $J$ = 8.25, 4H), 7.98–7.88 (m, 8H), 7.62 (m, 2H), 7.45 (d, $J$ = 7.75, 2H), 7.19 (s, 2H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 149.97, 143.91, 138.46, 133.87, 131.85, 128.84, 127.83, 126.33, 122.39, 121.01, 118.13, 116.91, 116.02; FTIR (KBr, cm$^{-1}$): 3062 (N–H), 1618 (C=N), 1591, 1475 (Ar C=C); ESI-MS: Calcd. for $C_{32}H_{20}Br_2N_4$, 620.3. Found: $[M-H^+]$, 618.9; Anal. Calcd. (%) for $C_{32}H_{20}Br_2N_4$: C, 61.96; H, 3.25; N, 9.03. Found: C, 61.58; H, 3.33; N, 8.89.

*2.2.3.3. 4,4″-Bis(5-methylbenzimidazol-2-yl)-p-terphenyl (**4c**).* Compound **4c** was obtained from 3,4-diaminotoluene and **2a**. Yield: 87%; 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 (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 148.25, 143.75, 138.49, 136.46, 132.10, 129.93, 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, 10.89.

*2.2.3.4. 2′-Methyl-4,4″-bis(benzimidazol-2-yl)-p-terphenyl (**4d**).* Compound **4d** 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 (TFA:DMSO-$d_6$ = 1:5, 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.

*2.2.3.5. 2′,5′-Dimethyl-4,4″-bis(benzimidazol-2-yl)-p-terphenyl (**4e**).* Compound **4e** was obtained from 1,2-phenylene diamine and **2c**. Yield: 85%; orange powder; m.p. 344.5 °C; $^1$H NMR (DMSO-$d_6$, 300 MHz): δ 12.96 (s, 2H), 8.29 (d, $J$ = 8.28, 4H), 7.93 (d, $J$ = 8.43, 2H), 7.68–7.54 (m, 6H), 7.40 (d, $J$ = 8.26, 2H), 7.21 (brs, 4H), 2.23 (s, 6H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 149.27, 145.93, 145.02, 138.04, 136.57,, 132.15, 130.80, 128.91, 128.27, 126.57, 121.19, 20.84; FTIR (KBr, cm$^{-1}$): 3057 (N–H), 1620 (C=N), 1595, 1480 (Ar C=C); ESI-MS: Calcd. for $C_{34}H_{26}N_4$, 490.2. Found: $[M-H^+]$, 489.2, $[M+H^+]$, 491.3; Anal. Calcd. (%) for $C_{34}H_{26}N_4$: C, 83.24; H, 5.34; N, 11.42. Found: C, 83.18; H, 5.31; N, 11.29.

*2.2.3.6. 2′-Methyl-4,4″-bis(5-methylbenzimidazol-2-yl)-p-terphenyl (**4f**).* Compound **4f** was obtained from 3,4-diaminotoluene and **2b**. Yield: 87%; yellow powder; m.p. 323.9 °C; $^1$H NMR (DMSO-$d_6$, 300 MHz): δ 12.83 (s, 2H), 8.27 (d, $J$ = 8.45, 2H), 8.25 (d, $J$ = 8.40, 2H), 7.92 (d, $J$ = 8.45, 2H), 7.77–7.54 (m, 5H), 7.47–7.40 (m, 2H), 7.33 (s, 2H), 7.06 (d, $J$ = 8.40, 1H), 7.04 (d, $J$ = 8.20, 1H), 2.43 (s, 6H), 2.41 (s, 3H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 148.45, 148.33, 145.65, 144.09, 140.20, 138.10, 136.47, 136.02, 132.15, 130.42, 129.98, 129.36, 128.61, 128.03, 127.82, 124.88, 122.08, 121.94, 121.01, 113.50, 21.25, 20.36; FTIR (KBr, cm$^{-1}$): 3031 (N–H), 1616 (C=N), 1593, 1477 (Ar C=C); ESI-MS: Calcd. for $C_{35}H_{28}N_4$, 504.23. Found: $[M-H^+]$, 503.2; Anal. Calcd. (%) for $C_{35}H_{28}N_4$: C, 83.30; H, 5.59; N, 11.10. Found: C, 83.18; H, 5.49; N, 11.15.

*2.2.3.7. 2′-Fluoro-4,4″-bis(benzimidazol-2-yl)-p-terphenyl (**4g**).* Compound **4g** was obtained from 1,2-Phenylene diamine and **2d**. Yield: 83%; white powder; m.p. 462.7 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz): δ 12.99 (s, 2H), 8.32 (d, $J$ = 6.45, 4H), 8.02 (d, $J$ = 8.15, 2H), 7.84–7.75 (m, 5H), 7.69 (s, 2H), 7.57 (s, 2H), 7.23 (brs, 4H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 161.57 (d, $^1J_{CF}$ = 247.6 Hz), 148.73, 148.68, 142.64, 140.88, 139.47, 131.95, 131.64, 130.10, 128.81, 128.46, 128.07, 126.37, 123.74. 122.76, 122.65, 120.91, 114.94 (d, $^2J_{CF}$ = 24.2 Hz); FTIR (KBr, cm$^{-1}$): 3055 (N–H), 1619 (C=N), 1591, 1483 (Ar C=C), 1186 (Ar–F); ESI-MS: Calcd. for $C_{32}H_{21}FN_4$, 480.1. Found: $[M-H^+]$, 479.1; Anal. Calcd. (%) for $C_{32}H_{21}FN_4$: C, 79.98; H, 4.40; N, 11.66. Found: C, 79.67; H, 4.31; N, 12.09.

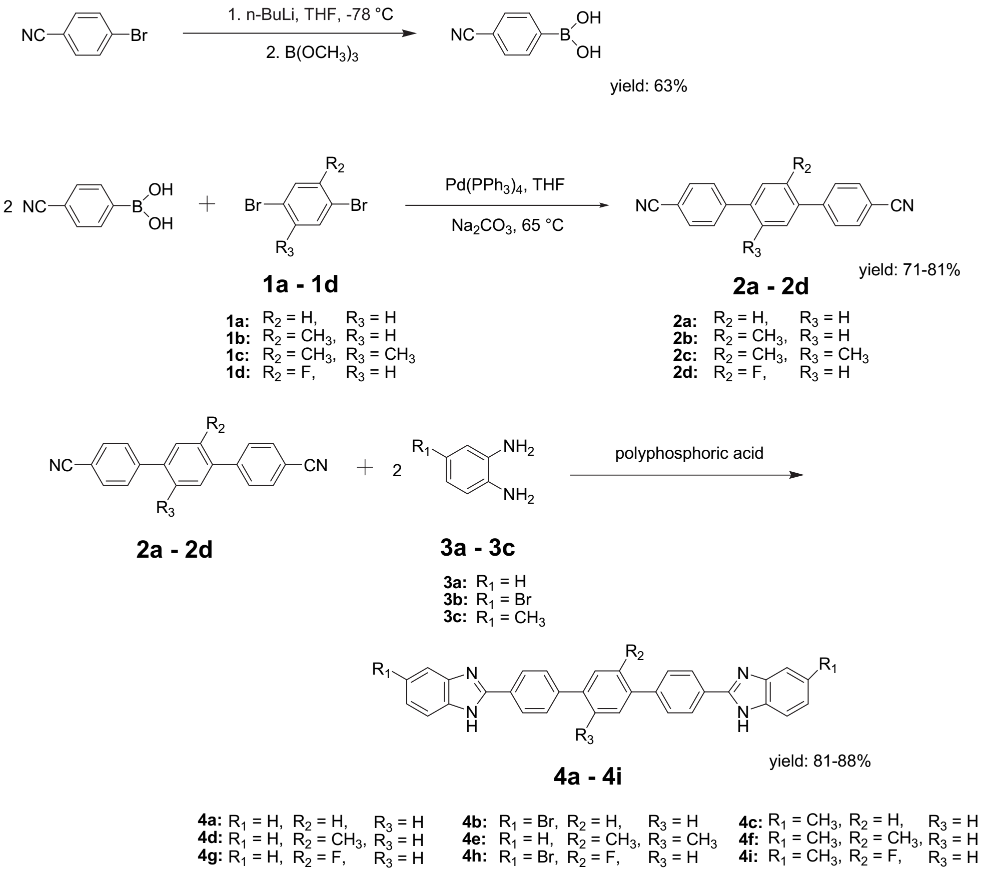
*2.2.3.8. 2′-Fluoro-4,4″-bis(5-bromobenzimidazol-2-yl)-p-terphenyl (**4h**).* Compound **4h** was obtained from 4-bromo-1,2-benzenediamine and **2d**. Yield: 81%; red powder; m.p. 327.3 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz): δ 13.36 (s, 2H), 8.31 (d, $J$ = 6.45, 4H), 8.01–7.55 (m, 10H), 7.44–7.18(m, 3H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 161.59 (d, $^1J_{CF}$ = 242.8 Hz), 149.84, 149.76, 142.51, 140.75, 139.42, 133.83, 131.99, 131.78, 131.50, 130.01, 129.71, 129.10, 128.77, 128.41 127.92, 127.63, 126.57, 126.41, 124.34, 123.61, 122.78, 121.12, 118.33, 117.01, 116.11, 114.88 (d, $^2J_{CF}$ = 24.2 Hz); FTIR (KBr, cm$^{-1}$): 3060 (N-H), 1617 (C=N), 1589, 1481 (Ar C=C), 1185 (Ar–F); ESI-MS: Calcd. for $C_{32}H_{19}Br_2FN_4$, 638.3. Found: $[M-H^+]$, 637.2; Anal. Calcd. (%) for $C_{32}H_{19}Br_2FN_4$: C, 60.21; H, 3.00; N, 8.78. Found: C, 60.42; H, 3.11; N, 8.59.

*2.2.3.9. 2′-Fluoro-4,4′-bis(5-methylbenzimidazol-2-yl)-p-terphenyl (**4i**).* Compound **4i** was obtained from 3,4-diaminotoluene and **2d**. Yield: 88%; yellow powder; m.p. 362.9 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz): δ 12.84 (s, 2H), 8.29 (d, $J$ = 7.20, 4H), 7.99 (d, $J$ = 7.95, 2H), 7.81–7.75 (m, 5H), 7.55–7.35 (m, 4H), 7.05 (s, 2H), 2.44 (s, 6H); $^{13}$C NMR (TFA:DMSO-$d_6$ = 1:5, 300 MHz): δ 161.51 (d, $^1J_{CF}$ = 248.2 Hz), 148.17, 148.11, 142.43, 140.81, 140.71, 139.28, 136.58, 132.17, 131.58, 130.01, 128.63, 128.29, 127.98, 127.89, 126.66, 123.67, 122.71, 122.60, 121.01, 114.89 (d, $^2J_{CF}$ = 23.6 Hz), 113.53, 21.26; FTIR (KBr, cm$^{-1}$): 3034 (N-H), 1621 (C=N), 1588, 1481 (Ar C=C), 1192 (Ar–F); ESI-MS: Calcd. for $C_{34}H_{25}FN_4$, 508.2. Found: $[M-H^+]$, 507.1; Anal. Calcd. (%) for $C_{34}H_{25}FN_4$: C, 80.29; H, 4.95; N, 11.02. Found: C, 80.34; H, 5.01; N, 10.86.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis of the bisbenzimidazoles **4a**–**4i** is outlined in Scheme 1. 4-Cyanophenylboronic acid was prepared with a 63% yield from the lithium-halogen exchange reaction of 4-bromobenzonitrile with *n*-butyllithium, followed by treatment with trimethyl borate and then dilute acid [21]. The terphenyl dinitriles **2a**–**2d** were synthesized by the Suzuki coupling reaction of one equivalent of the dibromobenzene derivatives **1a**–**1d** with 2.2 equivalents of 4-cyanophenylboronic acid, using $Pd(PPh_3)_4$ as the catalyst and $Na_2CO_3$ as the base in tetrahydrofuran solution at 65 °C. The yields ranged from 71 to 81% [20]. Compounds **4a**–**4i** were synthesized by the condensation of *o*-phenylenediamines **3a**–**3c** with terphenyl dinitriles **2a**–**2d** using PPA as the activator [22,23]. The yields ranged from 81 to 88%. $^1$H NMR spectra, mass spectra and elemental analyses on **4a**–**4i** confirmed the proposed structures and their purity. The $^{13}$C NMR spectra were not as complex as expected perhaps due to dynamic features such as slow rotation



**Scheme 1.** Synthesis of bisbenzimidazoles (**4a**–**4i**).

about the various biphenyl and phenyl-benzimidazole linkages, slow relaxation times associated with several quaternary C atoms and some accidental equivalence of signals. The series **4a**–**4i** were, to varying degrees, soluble in MeOH, THF, DMF and formic acid.

The thermal properties of the synthesized compounds, including the melting and decomposition temperatures of these molecules, are shown in Table 1. All the compounds had melting transitions ranging from 323.9 to 462.7 °C, with the trimethyl-substituted compound **4f** melting at the lowest temperature, 323.9 °C and the fluoro analogue **4g** melting at the highest temperature, 462.7 °C. The decomposition temperatures determined by TGA were all above 346 °C, demonstrating that the series of bisbenzimidazoles **4a**–**4i** were very robust molecules.

### 3.2. Optical properties

The UV–vis absorption spectra of the bisbenzimidazoles in dilute DMF solution ($10^{-5}$ mol $L^{-1}$) are displayed in Fig. 2, and their photophysical properties are summarized in Table 1. All nine compounds showed strong absorptions, with maximum wavelengths in the range of 323–351 nm. Unsubstituted **4a**, bromo-substituted **4b** and methyl-substituted **4c** had nearly identical absorption maxima ($\lambda_{max}^{Abs}$) at 349, 350, and 351 nm, respectively. Compared to **4a**–**4c**, the absorption $\lambda_{max}^{Abs}$ of the bisbenzimidazoles

**Table 1**
Physical properties of **4a**–**4i**.

| Compound | $T_m/T_d$ (°C) | ε ($10^4$ $M^{-1}$ $cm^{-1}$) | $\lambda_{max}^{Abs}$ (nm) | $\lambda_{max}^{Em}$ (nm) | Stokes shift (nm) | $E_g^{opt}$ (eV)[a] | $\Phi_F$[b] |
|---|---|---|---|---|---|---|---|
| **4a** | 448.2/463 | 5.79 | 349 | 409 | 60 | 3.17 | 0.88 |
| **4b** | 342.6/346 | 3.31 | 350 | 410 | 60 | 3.14 | 0.42 |
| **4c** | 354.3/462 | 5.73 | 351 | 416 | 65 | 3.15 | 0.94 |
| **4d** | 339.1/438 | 3.82 | 330 | 403 | 73 | 3.25 | 0.82 |
| **4e** | 344.5/425 | 3.65 | 323 | 401 | 78 | 3.30 | 0.78 |
| **4f** | 323.9/440 | 4.18 | 333 | 408 | 75 | 3.24 | 0.86 |
| **4g** | 462.7/478 | 4.36 | 343 | 414 | 71 | 3.13 | 0.91 |
| **4h** | 327.3/362 | 3.67 | 342 | 417 | 75 | 3.12 | 0.48 |
| **4i** | 362.9/445 | 5.82 | 344 | 423 | 79 | 3.10 | 0.98 |

[a] Estimated from the onset of absorption spectra ($E_g^{opt} = 1240/\lambda_{onset}$).

[b] Determined in DMF solution ($A < 0.1$) at room temperature using 9,10-diphenylanthracene ($\Phi_F = 0.90$ in hexane) as standard.

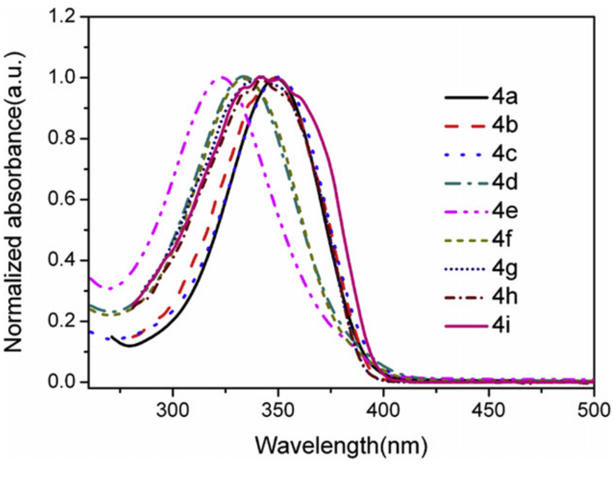


**Fig. 2.** UV–vis absorption spectra of **4a**–**4i** in DMF solution ($10^{-5}$ mol $L^{-1}$).

with substituents at the terphenyl core, **4d**–**4i**, showed varying degrees of blue-shift. Methyl-substituted **4d** and **4f** were blue-shifted by 19 and 18 nm, respectively, compared to the corresponding unsubstituted **4a** and **4c**. Compared to **4a**, **4b**, and **4c**, fluoro-substituted **4g**, **4h**, and **4i** were blue-shifted by 6 nm, 8 nm, and 7 nm, respectively. Compound **4e**, having two methyl groups substituted at the 2′ and 5′ positions of its terphenyl core, had an absorption $\lambda_{max}^{Abs}$ showing a larger blue-shift (26 nm) compared to **4a**. This blue-shift may be attributed to steric effects due to the methyl group and fluorine atom at the central benzene ring in the terphenylene system, which results in lack of planarity of the molecule and an increase in the electronic transition energy [24,25]. Optical band gaps ($E_g^{opt}$) determined from the absorption edge of the solution spectra [26] are also given in Table 1, and varied from 3.10 eV in **4i** to 3.30 eV in **4e**.

The emission spectra of the nine bisbenzimidazoles in DMF solution ($10^{-7}$ mol L$^{-1}$) are shown in Fig. 3. All nine compounds emit blue light with emission maxima in the 401–423 nm range. The bisbenzimidazoles that have methyl groups on the benzimidazole moieties (**4c**, **4f**, and **4i**) show red-shifted fluorescence relative to those that have no methyl groups (**4a, 4d**, and **4g**). Compared to **4a**–**4c**, the maximum emission wavelengths of fluoro-substituted **4g**, **4h**, and **4i** are red-shifted by 5, 7, and 6 nm respectively. Compound **4i** showed the longest emission wavelength (423 nm) and was red-shifted by 14 nm compared to **4a**. These observations may be due to the electron-donating effect of the methyl group substituted at the benzimidazole moiety and the electron-withdrawing effect of the fluoro atom substituted at the terphenyl core [27,28].

The fluorescence quantum yields ($\Phi_F$) of these compounds in DMF solution were determined by the standard method (using 9,10-diphenylanthracene as the standard) [29]. The fluorescence quantum yields were in the range from 0.42 for **4b** to 0.98 for **4i**. As can be seen from Table 1, the $\Phi_F$ of **4d**–**4f** were lower than that of compounds **4a**–**4c**, which may be attributed to a loss of planarity in the excited state provided by the steric hindrance of the methyl groups at the terphenyl core [30,31]. Compounds **4b** and **4h** have the lowest quantum yields, which are likely the result of competing $S_1 \rightarrow T_1$ intersystem crossing because of the “internal heavy-atom effect” [32].

### 3.3. Electrochemical properties

The electrochemical properties of compounds **4a**–**4i**, were determined by cyclic voltammetry in dry DMF ($10^{-3}$ mol L$^{-1}$) solutions, using 0.1 M TBAP as the supporting electrolyte. Platinum wire electrodes were used as both counter and working electrodes and silver/silver ions (Ag in 0.1 M $AgNO_3$ solution) were used as the reference electrode. The Ag/Ag$^+$ ($AgNO_3$) reference electrode was calibrated at the beginning of the experiments by running cyclic voltammetry on ferrocene as the internal standard. The ferrocene oxidation potential was located at +100 mV relative to the Ag/$AgNO_3$ reference electrode. The potential values obtained versus Fc$^+$/Fc were converted to versus saturated calomel electrode (SCE) by adding a constant of 0.1588 V to them [33,34].

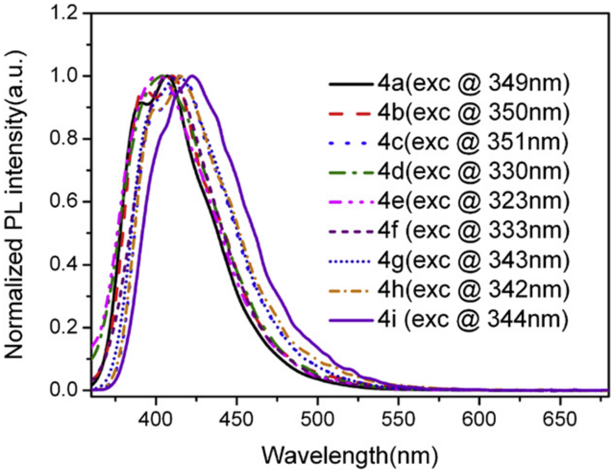


**Fig. 3.** PL spectra of **4a**–**4i** in DMF solution ($10^{-7}$ mol L$^{-1}$).

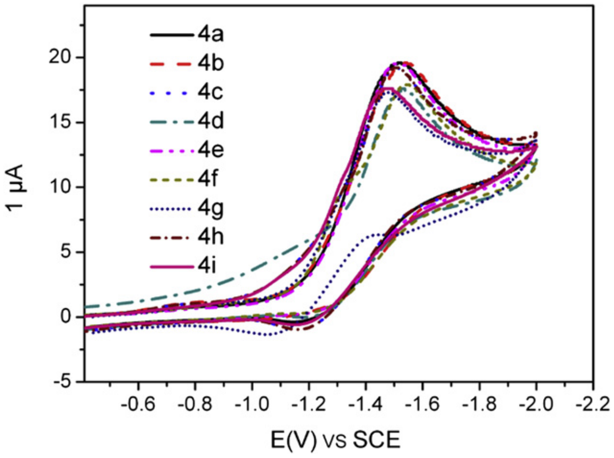


**Fig. 4.** Cyclic voltammograms of **4a**–**4i**. Scan rate = 40 mV/s.

The cyclic voltammograms (CVs) for the cathodic reductions of these nine bisbenzimidazoles are shown in Fig. 4. All these compounds exhibited a notable reduction peak in their CV curve, which originates from the reduction of the benzimidazole moiety [35]. The formal reduction potentials ($E_{red}^{peak}$, versus SCE) vary from −1.44 V for **4h** to −1.55 V for **4f**. The electron-withdrawing fluoro substitution of the bisbenzimidazoles slightly shifts the formal reduction potential to more positive values. Electron affinities (lowest unoccupied molecular orbital, LUMO) were estimated from the onset of the reduction wave ($EA = E_{red}^{onset} + 4.4$) by using an SCE energy level of 4.4 eV versus a vacuum [36]. The highest occupied molecular orbital (HOMO) level can be estimated by subtracting the optical band gaps ($E_g^{opt}$) from the LUMO level [3,37]. The LUMO and HOMO levels of **4a** were calculated to be −3.13 eV and −6.30 eV, respectively. Detailed data for the CV and energy level parameters are listed in Table 2. All nine bisbenzimidazoles have electron affinities between 3.09 and 3.24 eV (below vacuum), revealing low energy barriers to electron injection from the cathode.

**Table 2**
Electrochemical Properties of **4a**–**4i**[a].

| Compound | $E_{red}^{peak}$ (V) | $E_{red}^{onset}$ (V) | LUMO (eV)[b] | HOMO (eV)[b] |
|---|---|---|---|---|
| **4a** | −1.52 | −1.27 | −3.13 | −6.30 |
| **4b** | −1.54 | −1.26 | −3.14 | −6.28 |
| **4c** | −1.51 | −1.23 | −3.17 | −6.32 |
| **4d** | −1.53 | −1.25 | −3.15 | −6.40 |
| **4e** | −1.50 | −1.31 | −3.09 | −6.33 |
| **4f** | −1.55 | −1.29 | −3.11 | −6.41 |
| **4g** | −1.48 | −1.19 | −3.21 | −6.34 |
| **4h** | −1.44 | −1.16 | −3.24 | −6.36 |
| **4i** | −1.49 | −1.21 | −3.19 | −6.29 |

[a] All potentials versus SCE reference.

[b] EA (LUMO) = $E_{red}^{onset} + 4.4$ eV; the HOMO energies are estimated according to the optical band gap and the LUMO energy values from electrochemical experimental results.

## 4. Conclusions

A series of terphenyl-bridged bisbenzimidazoles were synthesized and characterized. Their thermal stabilities, photophysical, and electrochemical properties were investigated. Results of TGA and DSC measurements indicated that all these compounds are thermally robust with high decomposition temperatures ($>346$ °C) and high melting transitions (323.9–462.7 °C). Compared to **4a**–**4c**, the UV–Vis absorption maximum peaks of **4d**–**4i** were blue-shifted probably because of the steric effects of substitution at the central benzene ring of terphenyl. These maximum peaks ranged from 323 nm to 351 nm. Compounds **4a**–**4i** emitted blue light with fluorescence quantum yields of 0.42–0.98 in dilute DMF solution. Cyclic voltammetry indicated that the electrochemical properties of these compounds are little affected by substitution neither in the terphenyl core nor in the benzimidazole moiety which open opportunities to tune the optical properties without the loss of electrochemical properties. Formal reduction potentials for **4a**–**4i** in the range of $-1.44$ to $-1.55$ V (versus SCE) with estimated electron affinities (LUMO levels) of 3.09–3.24 eV were also established. These bisbenzimidazoles show promise for future applications as efficient blue emitters in OLEDs.

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