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Apical Functionalization of Chiral Heterohelicenes

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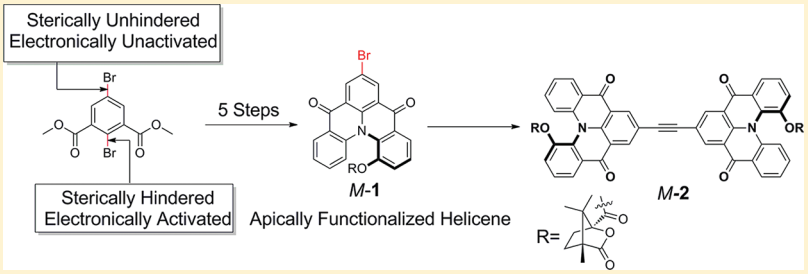
Supporting Information



ABSTRACT: We describe a synthetic protocol to selectively functionalize chiral bridged triarylamines at the apical position using regioselective copper-catalyzed amination reaction. This protocol allows the coupling of diphenylamines with a sterically hindered but electronically activated aryl−Br bond in the presence of a sterically unhindered but electronically unactivated aryl−Br bond. The unactivated aryl−Br bond was utilized further to synthesize a chiral heterohelicene homodimer using Stille coupling.

Bridged triarylamines are a class of π-conjugated molecules that exhibit axial chirality.[1−3] The combination of chirality and extended conjugation make these molecules interesting from the standpoints of fundamental science and technological applications.[4−13] For example, bridged triarylamines have been used as chromophores for single molecule chiroptical studies to understand the interaction between light and chiral molecules.[5−8] They have also been used as active materials in various optoelectronic devices.[9−13] However, in order to use bridged triarylamines as building blocks for functional materials, it is important that these molecules can be suitably functionalized at appropriate positions. Among the various positions, functional groups at the apical position can provide access to a broad range of molecules and macromolecules without compromising the symmetry of the building block. Selective apical functionalization of *achiral* bridge triarylamines have been reported by blocking the two nonapical positions *para* to the nitrogen with *tert*-butyl groups.[9,12] However, this method cannot be employed to obtain apically functionalized *chiral* bridged triarylamines from easily accessible starting materials.[14] To the best of our knowledge, there is no literature precedence to selectively obtain apically functionalized *chiral* bridged triarylamines. Here in we report a protocol, based on copper-catalyzed amination, to synthesize apically functionalized *chiral* bridged triarylamines by the selective coupling of a sterically hindered but electronically activated C−Br bond over a sterically unhindered, electronically unactivated C−Br bond.

Previously, we reported the synthesis of chiral bridged triarylamines with a *tert*-butyl group at the apical position.[14] We reasoned that installing a halogen moiety at the apical position instead of a *tert*-butyl group would allow us to perform metal-mediated cross-coupling reactions, which are often mild and tolerate a variety of functional groups, at this site, thereby vastly expanding the scope of chiral bridged triarylamines. Moreover, this would allow us to use resolved molecules, which bear a camphanate moiety such as (*M*)-**1** or (*P*)-**1** as building blocks for functional chiral materials. A straightforward way to install a halogen moiety at the apical position is to replace dimethyl 2-bromo-5-(*tert*-butyl)isophthalate with dimethyl 2,5-dibromoisophthalate in the synthetic scheme (Scheme 1). The key step is the first step, which involves the regioselective coupling of 2-methoxy-*N*-phenylaniline and dimethyl 2,5-dibromoisophthalate.

Synthesis of **1** began with Sandmeyer reaction of 4-bromo-2,6-dimethylaniline in the presence of CuBr to obtain 2,5-dibromo-1,3-dimethylbenzene (**3**) as reported previously.[15] **3** was oxidized in the presence of $KMnO_4$ to afford 2,5-dibromoisophthalic acid (**4**) in 70% yield. Esterification of **4** in the presence of methanol and sulfuric acid resulted in dimethyl 2,5-dibromoisophthalate (**5**) in 90% yield (Scheme 2).

2-Methoxy-*N*-phenylamine (**6**) was prepared using a previously reported synthetic procedure.[14] The regioselective coupling of **5** with **6** required a judicious choice of the catalyst and conditions, since the coupling was required to occur with a C−Br bond that was strerically hindered but electronically activated (due to the presence of two *ortho*-ester functionalities) instead of a C−Br bond that was sterically unhindered but electronically unactivated. On the basis of the work published previously by our group and others for the synthesis

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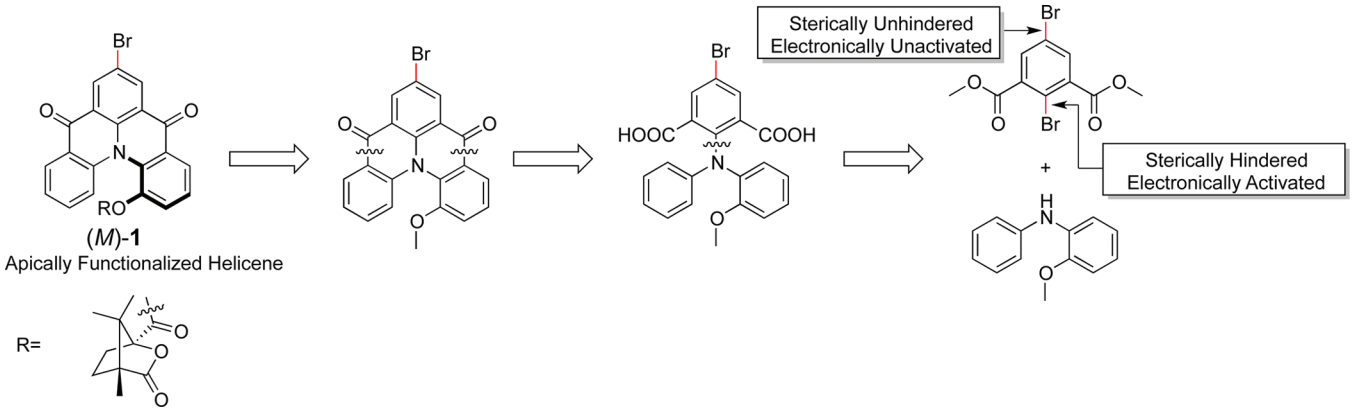
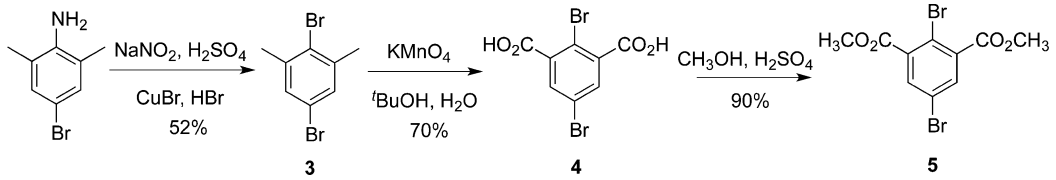
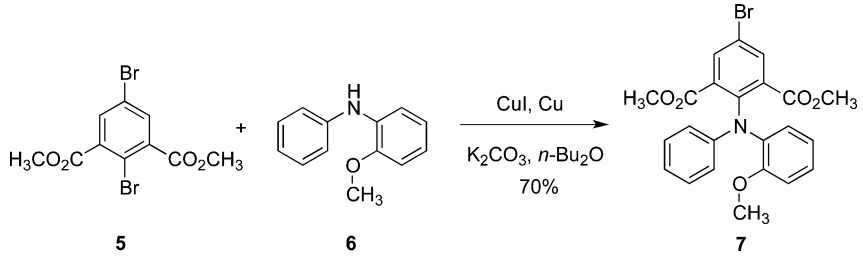
Scheme 1. Synthetic Strategy for the Exclusive Formation of Apically Functionalized Chiral Bridged Triarylamine



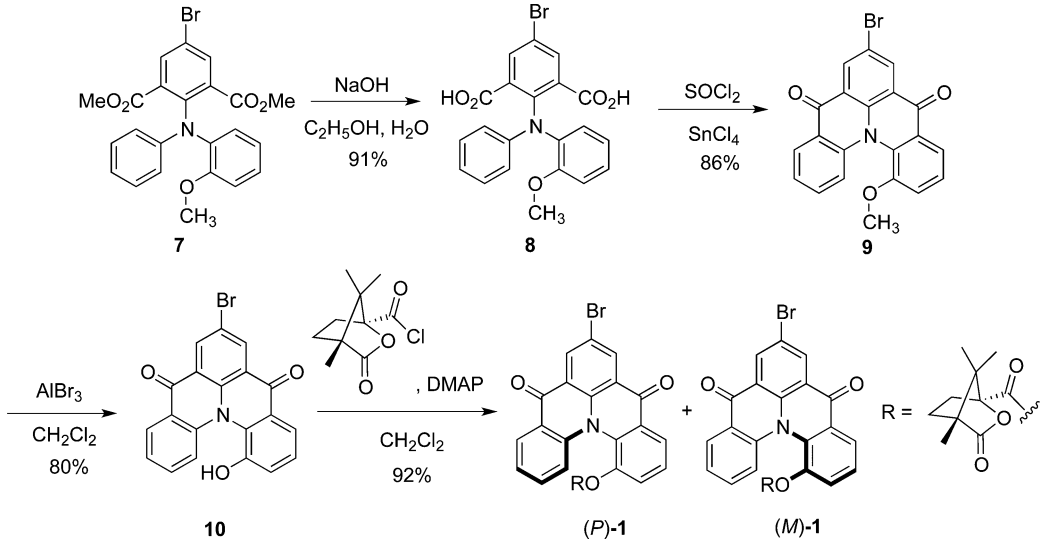
Scheme 2. Synthesis of Dimethyl 2,5-dibromoisophthalate 5



Scheme 3. Synthesis of 7 by Regioselective Copper-Catalyzed Coupling



Scheme 4. Synthesis of Apically Functionalized (*M*)-1 and (*P*)-1



of triphenylamines from diphenylamines, copper was chosen as the choice of catalyst for the coupling.[16,17] Furthermore, it is known that coupling of *ortho*-bromobenzoic acids with aniline proceeds with high regioselectivity due to the accelerating effect of the *ortho*-carboxylate group in homogeneous copper-catalyzed reactions.[18] Therefore, we hypothesized that copper-mediated coupling of **5** with **6** may proceed regioselectively because of the presence of two *ortho*-carboxylate ester groups in **5**. Gratifyingly, regioselective coupling of **5** with **6** was achieved in the presence of Cu/CuI

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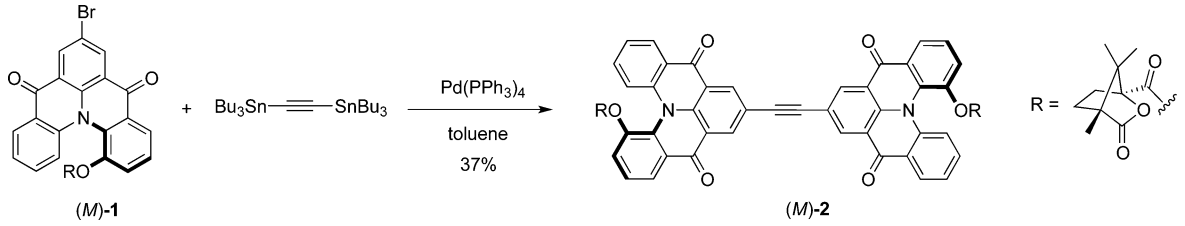
Scheme 5. Synthesis of Acetylene Bridged Homodimer (*M*)-2



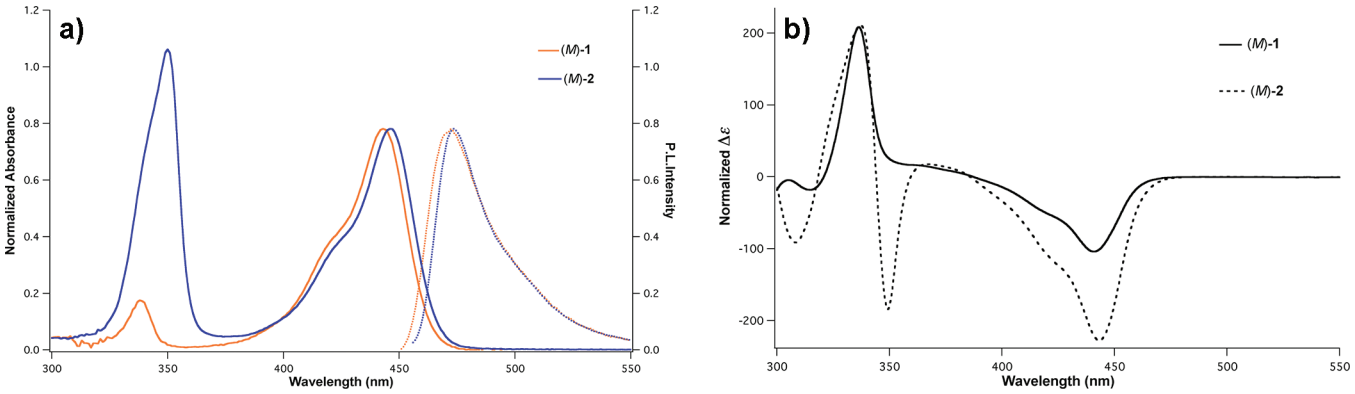


Figure 1. (a) Normalized UV−vis absorption spectra (solid line) and emission spectra (dotted line) of (*M*)-**1** and (*M*)-**2** in dichloromethane. (b) Normalized CD spectra of (*M*)-**1** and (*M*)-**2** in dichloromethane.

to afford triarylamine **7** in 70% yield (Scheme 3). In addition to ^{1}H and ^{13}C NMR, the key evidence for the formation of the regioisomer **7** was obtained from the single crystal X-ray diffraction analysis (Figure S1 in the Supporting Information).

Subsequent ester hydrolysis of **7** in the presence of NaOH gave diacid **8** in 91% yield. The diacid **8** was converted to the corresponding acid chloride with $SOCl_2$ in dichloromethane, followed by an in situ intramolecular cyclization in the presence of $SnCl_4$ to yield racemic bridged triarylamine **9** in 86% yield. The methyl ether in **9** was then cleaved in the presence of $AlBr_3$/NaI in dichloromethane to give phenol **10** in 80% yield. As reported previously by our group, esterification of racemic phenol **10** with (1*S*)-camphanic chloride and 4-dimethylaminopyridine (DMAP) resulted in atropdiastereomers (*M*)-**1** and (*P*)-**1** in 92% combined yield (Scheme 4).[14]

^{1}H NMR spectra of both (*M*)-**1** and (*P*)-**1** showed the presence of two doublets at 8.76 and 8.72 ppm with a coupling constant J = 2.4 Hz, consistent with a meta coupling, which indicates the presence of apical functionality. High-resolution ESI mass spectra of (*M*)-**1** and (*P*)-**1** showed the presence of two M + H ion peaks with a ratio of 1:1 at m/z 572.1 and 574.1, consistent with the presence of bromine at the apical position. The ^{1}H NMR spectra of (*M*)-**1** and (*P*)-**1** differ in the chemical shifts of camphanate methyl protons H_a and aromatic proton H_j (Figure S2 in the Supporting Information). As reported previously, this is due to the difference in ring currents caused by a change in the preferred conformation of the camphanate group in (*M*)-**1** and (*P*)-**1**.[14,19] The circular dichroism (CD) spectra of (*M*)-**1** and (*P*)-**1** showed an identical peak pattern with opposite sign, thus confirming the enantiomeric nature of the bridged triarylamine helicene chromophore, since the configuration of the camphanate group is identical in both the diastereomers (Figure S3 in the Supporting Information). Once we had accomplished the synthesis of (*M*)-**1** and (*P*)-**1**, we wanted to further study if a significant change is caused in the optical and electronic properties of (*M*)-**1** by extending the conjugation. This led us to the synthesis of acetylene bridged chiral bridged triarylamine homodimer (*M*)-**2** from (*M*)-**1** via palladium(0)-catalyzed Stille coupling reaction. Two equivalents of (*M*)-**1** were coupled to bis(tributylstannyl)acetylene in the presence of $Pd(PPh_3)_4$ in toluene to yield homodimer (*M*)-**2** in 37% yield (Scheme 5). The low yield of (*M*)-**2** is consistent with previously reported palladium(0)-catalyzed Stille coupling of similar bridged triarylamines with bis(tributylstannyl)acetylene.[9] ^{1}H NMR spectrum of (*M*)-**2** showed a similar peak pattern with respect to (*M*)-**1**, which indicates the presence of a homodimer. ^{13}C NMR spectrum of (*M*)-**2** showed an additional peak at δ 89.03 with respect to (*M*)-**1**, which is attributed to the additional acetylenic carbons in (*M*)-**2**.

Single crystals suitable for X-ray diffraction of (*M*)-**1** and (*M*)-**2** were obtained in a binary solvent mixture of hexanes and ethylacetate. The structures displayed in Figure S1 in the Supporting Information show the absolute stereochemistry of (*M*)-**1** and (*M*)-**2**. Both (*M*)-**1** (168.53°) and (*M*)-**2** (167.03° and 170.99°) showed O═C—C—O camphanate dihedral angles similar to previously reported camphanate dihedral angles for (*M*)-[7]helicenes, consistent with an *M*-configuration (Figure S1 in the Supporting Information).[20]

Diastereomers (*M*)-**1** and (*P*)-**1** showed identical UV−vis absorption and emission spectra with absorption maxima at 443 nm, and the emission maxima at 472 nm (when excited at 443 nm). However, the absorption spectrum of (*M*)-**2** showed an additional peak at 350 nm. The emission spectra (*M*)-**2** showed no significant change compared to (*M*)-**1**, with the emission maxima occurring at 473 nm (when excited at 446 nm) (Figure 1a). The CD spectrum of (*M*)-**2** showed a similar sign and peak pattern with respect to (*M*)-**1**, confirming the *M*-configuration in (*M*)-**2** (Figure 1b). Furthermore, the CD spectrum of (*M*)-**2** also showed the presence of an additional peak at 350 nm, similar to its absorption spectrum.

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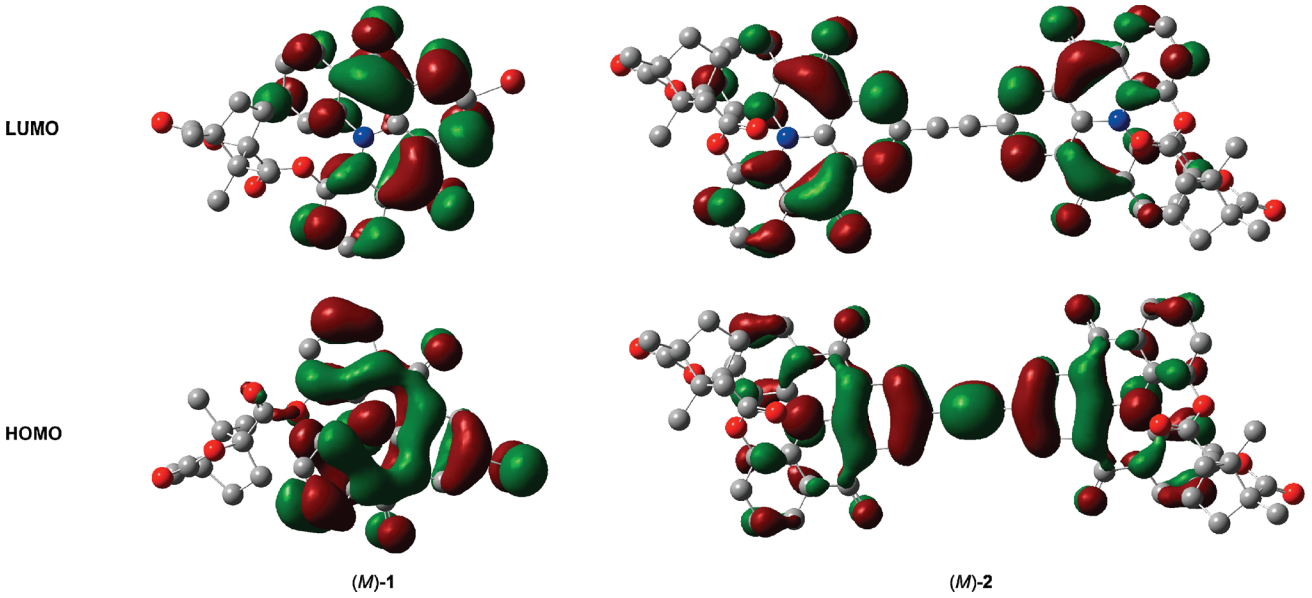

Figure 2. HOMO and LUMO surface plots for (*M*)-**1** and (*M*)-**2**.

Cyclic voltammograms (CV) of (*M*)-**1** and (*M*)-**2** were recorded in acetonitrile solutions at 1×10^{-3} M concentrations. (*M*)-**1** shows quasireversible oxidation and reduction peaks at 1.48, −1.43 V (vs Ag/Ag^+), respectively,[21] whereas (*M*)-**2** shows two quasireversible oxidation peaks at 1.33 and 1.54 V and a reduction peak at −1.41 V (vs Ag/Ag^+) (Figure S4 in the Supporting Information). Lower oxidation potential for (*M*)-**2** compared to (*M*)-**1** might be because of the enhanced conjugation via ethyne linker. The redox values for (*M*)-**1** are consistent for three repeated cycles, indicating that (*M*)-**1** dimerization was hindered because of the presence of bromine functionality at the apical position.[22] Frontier orbital energies were obtained using established procedures from CV.[23] The calculated HOMO and LUMO energy levels are −6.19 and −3.28 eV for (*M*)-**1** and −6.04 and −3.3 eV for (*M*)-**2**. Frontier orbital surface plots for (*M*)-**1** and (*M*)-**2** were estimated from optimized geometry using B3LYP level of theory with 6-311g(d,p) as the basis set. The frontier molecular orbitals (FMO) of (*M*)-**2** are evenly distributed on both the helicenes (Figure 2).

In conclusion, we have established a straightforward route for the synthesis of apically functionalized chiral bridged triarylamines (*M*)-**1** and (*P*)-**1**. The chemistry allowed us to synthesize a chiral helicene homodimer (*M*)-**2** via palladium(0)-catalyzed Stille coupling. The single crystal X-ray diffraction analysis and CD of both (*M*)-**1** and (*M*)-**2** show a chiral signature consistent with an *M*-configuration. FMO of (*M*)-**2** is symmetrically distributed on both the helicenes. (*M*)-**2** was easier to oxidize and also has an additional absorption peak at 350 nm compared to the (*M*)-**1**. This might be because of the extended conjugation in (*M*)-**2** compared to (*M*)-**1**. Single molecule spectroscopy measurements on these molecules will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out in oven-dried glassware (160 °C). The chemicals were purchased from major chemical suppliers and were used without further purification unless otherwise noted. Dichloromethane was redistilled over calcium hydride under argon atmosphere and stored over 4 Å molecular sieves. Toluene was redistilled under argon atmosphere over sodium-benzophenone ketyl. Flash chromatography was performed using silica gel (standard grade, 60 Å, 230−400 mesh). Analytical thin layer chromatography was performed on precoated silica gel glass plates with visualization under UV light. Chemical shifts (δ) and coupling constants are reported in parts per million and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; and combinations therein (i.e., dd, doublet of doublets). X-ray data were collected with Mo Kα (λ = 0.71072 Å) as the incident radiation. Diffraction data were collected at ambient temperature unless otherwise stated. The raw data were integrated, refined, scaled, and corrected for Lorentz polarization and absorption effects, if necessary, using the programs DENZO and SCALEPAK. Structure solutions and refinements were done (on F_o^2) using a suite of crystal structure solution and refinement programs. Data scans for CD were taken from 300 to 550 nm at a rate of 50 nm/min, with a 0.2 nm data pitch and a 4 s response. Two scans were taken for each sample at a constant temperature of 23 °C. Data obtained with a high tension voltage over 600 V were not included in the analysis. Fluorescence spectra were recorded with excitation and emission bandwidth kept at 1 nm. Scanning speed was set at 50 nm/min. CV was recorded with tetrabutylammonium hexafluorophosphate as a supporting electrolyte (0.1 M) in acetonitrile with platinum as the working electrode. The redox potentials were determined versus an Ag/Ag^+ reference electrode. The working and auxiliary electrodes were cleaned after each run. In these conditions, the redox potential of Fc/Fc+ (Fc = ferrocene) was +0.09 V versus Ag/Ag^+. It is assumed that the redox potential of Fc/Fc+ has an absolute energy level of −4.80 eV to vacuum. HOMO and LUMO values were calculated using Fc/Fc^+ as a reference.

Experimental Procedures. 2,5-Dibromoisophthalic Acid (4). In a 100 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added 2,5-dibromo-1,3-dimethylbenzene (**3**) (6.45 g, 24.44 mmol), dispersed in 80 mL of a 1:1 mixture of *t*-butanol and water. $KMnO_4$ (8.5 g, 53.76 mmol) was added, and the reaction mixture was heated to reflux for 1 h. After cooling to room temperature, more $KMnO_4$ (8.5 g, 53.76 mmol) was added, and the reaction mixture was refluxed for an additional 18 h. After cooling to room temperature, the reaction was filtered through Celite, and the filtrate was reduced by 1/3. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and dissolved in aqueous $NaHCO_3$. The aqueous layer was washed with ether to remove any residual organics. The aqueous layer was then acidified with concentrated HCl, and the

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precipitate was collected and oven-dried (~80 °C) overnight to give 5.5 g (70% yield) of the title compound: ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.88 (br s, 2H), 7.91 (s, 2H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 166.9, 139.1, 133.4, 121.1, 115.9; HRMS (ESI) m/z For $C_8H_4O_4Br_2Na$ calculated 344.8374, found 344.8380.

Dimethyl 2,5-Dibromoisophthalate (5). In a 100 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added **4** (5.5 g, 17 mmol), in 60 mL of methanol and 4.5 mL of H_2SO_4. The reaction mixture was heated to reflux for 18 h and poured into water (~20 mL). The reaction was neutralized with $NaHCO_3$, and aqueous solution was washed several times with ether. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography using 4:1 hexane/ethyl acetate as the eluent to give 5.3 g (90% yield) of **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 3.95 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.6, 136.7, 135.1, 120.9, 118.1, 53.1; HRMS (ESI) m/z For $C_{10}H_9Br_2O_4$ $[M + H]^+$ calculated 350.8868, found 350.8867.

Synthesis of (7). 2-Methoxy-*N*-phenylaniline (**6**) (2.0 g, 10.00 mmol), dimethyl 2,5-dibromoisophthalate (**5**) (3.50 g, 10.0 mmol), copper (0.064 g, 1.0 mmol), copper(I) iodide (0.133 g, 0.7 mmol), and potassium carbonate (2.06 g, 15.0 mmol) were combined in a 50 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. Thirty milliliters of di-*n*-butylether was added, and the reaction was heated to 150 °C under argon for 60 h. The solvent was removed under dynamic vacuum, and the residue was filtered using dichloromethane as a wash solvent. The filtrate was reduced by rotary evaporation, and the residue was then purified by flash chromatography using 4:1 hexane/ethyl acetate as the eluent to give 3.2 g (70% yield) of **7**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.40 (s, 6H), 3.55 (s, 3H), 6.81 (d, J = 8 Hz, 2H), 6.84−6.91 (m, 3H), 7.00 (d, J = 8 Hz, 1H), 7.06 (t, J = 8 Hz, 1H), 7.15 (t, J = 8 Hz, 2H), 7.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 166.5, 153.5, 147.60, 144.0, 135.7, 134.7, 133.0, 128.5, 127.1, 125.2, 121.7, 121.1, 121.0, 116.5, 113.0, 55.7, 52.2; HRMS (ESI) m/z For $C_{23}H_{21}BrNO_5$ $[M + H]^+$ calculated 470.0603, found 470.0598.

Synthesis of (8). Compound **7** (4.40 g, 9.36 mmol) and NaOH (3.75 g, 93.6 mmol) was heated to reflux in 50 mL of 1:1 ethanol/water for 24 h. Ethanol was removed by rotary evaporation, diluted with 10 mL of water, and acidified with concentrated hydrochloric acid. The resulting precipitate was collected by vacuum filtration and washed with copious portions of distilled water. The solid was dried in an 80 °C oven for 12 h to give 3.7 g (91% yield) of the diacid of **8**. Recrystallization from ethanol/water mixture gave crystals suitable for single crystal X-ray diffraction: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.47 (s, 3H), 6.57 (d, J = 8.6 Hz, 2H), 6.77−6.82 (m, 2H), 6.9−6.97 (m, 2H), 7.07−7.1 (m, 3H), 7.81 (s, 2H), 12.84 (br s, 2H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 166.8, 153.8, 147.8, 143.4, 135.9, 135.2, 134.5, 128.4, 127.3, 125.3, 121.0, 120.8, 120.2, 117.2, 113.6, 56.0; HRMS (ESI) m/z For $C_{21}H_{17}BrNO_5$ $[M + H]^+$ calculated 442.0290, found 442.0287.

Synthesis of (9). The diacid **8** (1.2 g, 2.71 mmol) was dispersed in 25 mL of dry dichloromethane in a 50 mL, 3-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser. Under an argon atmosphere, a few drops of DMF were added, followed by thionyl chloride (1.2 mL, 16.3 mmol). The reaction was heated to reflux for 2 h and cooled slightly, and $SnCl_4$ (2.0 mL, 16.3 mmol) was added. The reaction was heated to reflux for an additional 18 h, cooled to room temperature, and added dropwise to 50 mL of a 1 M aqueous solution of NaOH. The aqueous layer was washed with several portions of dichloromethane. The combined organic layers were dried over sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The residue was then purified by flash chromatography using dichloromethane as the eluent to give 0.940 g of **9** (86% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.74 (s, 3H), 7.23 (d, J = 8.35 Hz, 1H), 7.32 (dd, J = 8 and 1.3 Hz, 1H), 7.4 (t, J = 7.9 Hz, 1H), 7.51−7.6 (m, 2H), 8.1 (dd, J = 8 and 1.4 Hz, 1H), 8.34 (dd, J = 7.9 and 1.6 Hz, 1H), 8.7 (d, J = 2.5 Hz, 1H), 8.76 (d, J = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 178.5, 178.2, 150.9, 140.7, 139.3, 135.1, 134.6, 131.6, 129.0, 128.9, 126.5, 126.4, 125.8, 125.0, 124.8, 124.6, 121.0, 119.6, 117.3, 116.6, 55.6; HRMS (ESI) m/z For $C_{21}H_{13}BrNO_3$ $[M + H]^+$ calculated 406.0079, found 406.0080.

Synthesis of (10). **9** (0.580 g, 1.43 mmol) and NaI (0.215 g, 1.43 mmol) were dispersed in 25 mL of dry dichloromethane in a 50 mL, 3-neck round-bottom flask equipped with a magnetic stir bar. The reaction mixture was then cooled in an ice bath. $AlBr_3$ (2.3 g. 8.6 mmol) was then added in one portion to the reaction mixture. After 20 min, the ice bath was removed, and the reaction was stirred for 16 h at room temperature. The reaction mixture was then cooled in an ice bath; methanol, 1 M HCl, and water were added. The aqueous layer was washed with several portions of dichloromethane, the combined organic layers were dried over sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The residue was then purified by flash chromatography using 9:1 dichloromethane/diethylether as the eluent to give 0.450 g of **10** (80% yield): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.35−7.4 (m, 2H), 7.44- 7.52 (m, 2H), 7.7−7.75 (m, 1H), 7.8 (dd, J = 7.7 and 1.4 Hz, 1H), 8.17 (dd, J = 8 and 1.4 Hz, 1H), 8.52 (d, J = 2.5 Hz, 1H), 8.58 (d, J = 2.5 Hz, 1H), 10.89 (br s, 1H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 177.9, 177.8, 149.5, 140.0, 139.4, 134.0, 133.9, 132.7, 128.9, 127.4, 127.2, 125.7, 125.2, 125.0, 124.8, 124.3, 122.8, 122.1, 117.5, 116.3; HRMS (ESI) m/z For $C_{20}H_{11}BrNO_3$ $[M + H]^+$ calculated 391.9922, found 391.9921.

Synthesis of (*M*)-1 and (*P*)-1. Compound **10** (0.365 g, 0.93 mmol) and DMAP (0.171 g, 1.4 mmol) were dissolved in 20 mL of dry dichloromethane. (1*S*)-camphanic chloride (0.405 g, 1.9 mmol) was added, and the reaction was heated to reflux under argon for 12 h. Dichloromethane was then removed under vacuum, and the residue was purified by flash chromatography using 1:1 hexane/ethyl acetate as the eluent to give 0.250 g of (*M*)-**1** and 0.240 g of (*P*)-**1** (92% combined yield).

For (*M*)-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.79 (s, 3H), 0.89−0.92 (m, 1H), 0.94 (s, 3H), 1.04 (s, 3H), 1.45−1.51 (m, 1H), 1.62−1.75 (m, 2H), 7.42−7.55 (m, 3H), 7.6 (t, J = 7.8 Hz, 1H), 7.72−7.76 (m, 1H), 8.35 (dd, J = 7.8 and 1.6 Hz, 1H), 8.44 (dd, J = 7.8 and 1.6 Hz, 1H), 8.72 (d, J = 2.4 Hz, 1H), 8.76 (d, J = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 177.9, 177.4, 177.4, 164.2, 140.3, 139.1, 138.7, 135.3, 134.8, 133.6, 132.0, 129.2, 128.2, 127.0, 126.3, 125.6, 125.1, 124.9, 120.4, 117.9, 89.9, 54.9, 54.6, 29.9, 28.7, 16.6, 16.5, 9.5; HRMS (ESI) m/z For $C_{30}H_{23}BrNO_6$ $[M + H]^+$ calculated 572.0709, found 572.0714.

For (*P*)-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.62 (s, 3H), 0.95 (s, 3H), 1.02 (s, 3H), 1.62−1.65 (m, 2H), 1.75−1.9 (m, 2H), 7.45−7.53 (m, 3H), 7.61 (t, J = 7.8, 1H), 7.65−7.7 (m, 1H), 8.33 (dd, J = 7.8 and 1.6 Hz, 1H), 8.43 (dd, J = 7.8 and 1.6 Hz, 1H), 8.71 (d, J = 2.4 Hz, 1H), 8.75 (d, J = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 177.7, 177.3, 176.8, 164.9, 140.7, 139.8, 138.9, 135.4, 134.7, 133.6, 133.1, 132.0, 129.3, 128.4, 127.3, 127.0, 126.2, 125.7, 125.5, 125.3, 124.9, 120.4, 120.4, 119.9, 117.9, 89.9, 54.5, 54.4, 30.5, 28.7, 16.7, 16.5, 9.5; HRMS (ESI) m/z For $C_{30}H_{23}BrNO_6$ $[M + H]^+$ calculated 572.0709, found 572.0710.

Synthesis of (*M*)-2. In a 50 mL Schlenk flask equipped with a magnetic stir bar, a solution of (*M*)-**1** (250 mg, 0.44 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.044 mmol) in dry toluene (15 mL) was bubbled with argon for 1 h. 1,2-Bis(tributylstannyl)ethyne (0.132 mg, 0.22 mmol) was added, and the reaction was heated to 100 °C for a period of 12 h. Toluene was then removed under vacuum to yield a black residue, which was purified by flash chromatography using 3:7 hexane/ethyl acetate as the eluent to give 80 mg of (*M*)-**2** (37% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.81 (s, 3H), 0.88−0.92 (m, 1H), 0.95 (s, 3H), 1.05 (s, 3H), 1.47−1.51 (m, 1H), 1.67−1.74 (m, 2H), 7.45−7.56 (m, 3H), 7.63 (t, J = 7.7 Hz, 1H), 7.73−7.77 (m, 1H), 8.39 (dd, J = 7.8 and 1.5 Hz, 1H), 8.48 (dd, J = 7.8 and 1.6 Hz, 1H), 8.81 (d, J = 2 Hz, 1H), 8.85 (d, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 178.3, 177.7, 177.5, 164.3, 140.4, 139.5, 139.2, 135.6, 135.2, 133.5, 131.9, 129.4, 128.1, 127.9, 127.0, 126.3, 125.7, 125.2, 124.3, 123.7, 120.4, 119.0, 90.0, 89.0, 54.9, 54.6, 29.6, 28.7, 16.7, 16.5, 9.6; HRMS m/z For $C_{62}H_{45}N_2O_{12}$ $[M + H]^+$ calculated 1009.2972, found 1009.2986.

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■ ASSOCIATED CONTENT

Supporting Information

Characterization data and copies of ^{1}H and ^{13}C NMR spectra of all compounds synthesized and crystallographic information files (CIF) for **4**, **7**, **8**, (*M*)-**1**, and (*M*)-**2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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