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Bridged Triarylamines: A New Class of Heterohelicenes

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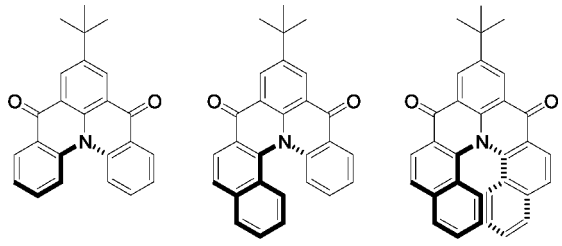
A series of bridged triarylamines, which constitute a new class of heterohelicenes, have been synthesized using a simple three-step procedure. These compounds are shown to be highly luminescent chromophores and are capable of being oxidized. The solid-state structures of these helicenes show a tendency for π-stacking interactions into an overall zigzag motif.

Since the pioneering work by Newman and Lednicer in 1955 on hexahelicene,[1] there have been numerous carbo- and heterohelicenes[2] developed in order to exploit the unique properties of these inherently helical molecules. A few potential applications of these compounds include asymmetric molecular recognition,[3] nonlinear optics,[4] liquid crystals,[5] and circularly polarized luminescence (CPL)[6] for back-lighting in LCD displays.[7] Recent advances in the area of helicenes have been made by Katz and co-workers,[4−6,8] Tanaka,[9] Rajca,[10] Branda,[11] Caronna,[12] and Rozen.[13] Despite the popularity of helicenes and their many potential applications, there has been little effort devoted to the design of an electroactive heterohelicene in which the heteroatom can be oxidized to a radical cation. Such a helicene would allow further study into how molecular helicity effects bulk electronic properties such as charge transport and conductance.[14] As a first step toward this goal, we set out to synthesize a heterohelicene based on triarylamine, a moiety that has been widely exploited in hole-transport materials for organic light-emitting diodes (OLEDs) due to its electronic, photochemical, and physical properties.[15] Here we report a series of novel helical molecules **1**−**3** that constitute a new class of electroactive heterohelicenes based on bridged triarylamines.



1 **2** **3**

The synthesis of an unfunctionalized derivative of the bridged triarlyamine **1** from an *ortho*-functionalized

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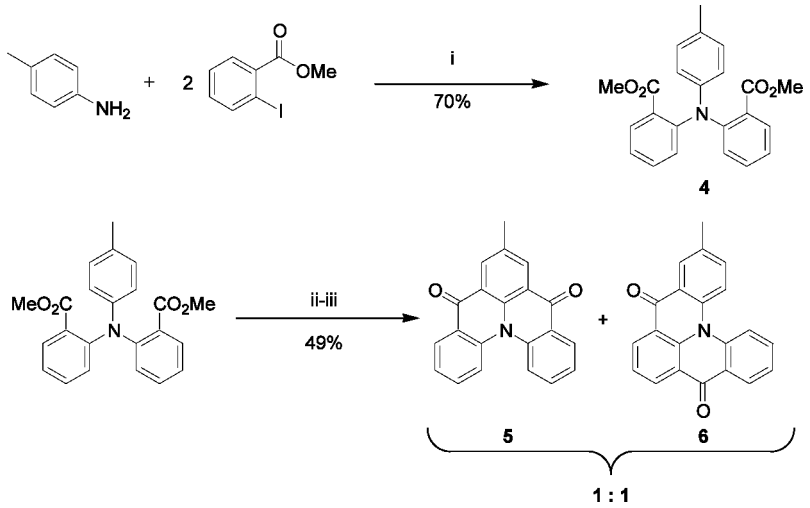
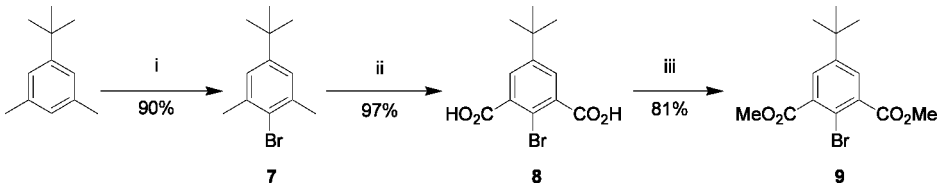
SCHEME 1. Synthesis of Mixed Symmetric and Unsymmetric Bridged Triarylamines[a]



[a] Reagents and conditions: (i) Cu/CuI, K_2CO_3, *n*-Bu_2O, 170 °C, 24 h; (ii) NaOH, H_2O/EtOH (1:1), reflux for 3 h and then HCl; (iii) $(COCl)_2$, CH_2Cl_2, DMF (cat.), reflux for 3 h and then $FeCl_3$, reflux 12 h.

SCHEME 2. Synthesis of 2-Bromo-5-*tert*-butyl-isophthalic Acid Dimethyl Ester 9[a]



[a] Reagents and conditions: (i) Br_2, Fe (cat.), CH_2Cl_2, 0−20 °C, 2 h; (ii) $KMnO_4$, *t*-BuOH/H_2O (1:1), reflux 19 h; (iii) MeOH, H_2SO_4 (cat.), reflux 18 h.

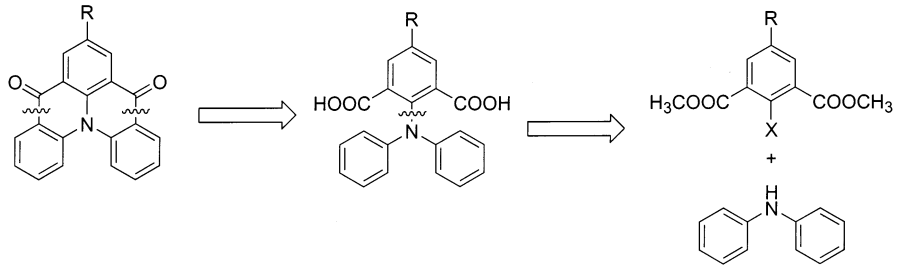


FIGURE 1. Synthetic strategy for the exclusive formation of the symmetric bridged triarylamine **1**.

triphenylamine was first developed by Hellwinkel and Melan[16] and later modified by our research group.[17] It was our goal to place a substituent at the top of the helicene, which would help to stabilize the radical cation.[18] To this end, we coupled *p*-toluidine to 2 equiv of methyl 2-iodobenzoate to make the functionalized triarylamine **4** in 70% yield (Scheme 1). Subsequent hydrolysis and cyclization gave a 1:1 mixture of the symmetric isomer **5** and the unsymmetric isomer **6**, which were inseparable by chromatography.[19] The formation of this unsymmetric isomer is problematic not only for isolation and purification but also for synthetic efficiency, decreasing the theoretical yield of our product by half.

To solve this problem, we devised a strategy to synthesize a triarylamine in which the two carboxyl moieties to be cyclized would be on the same ring (Figure 1), thus ensuring only one mode of cyclization, that of the desired symmetric heterohelicene. There were two major concerns to this strategy: first, the functionalized aryl halide must be synthesized and, second, the added steric bulk of two *ortho*-esters may hinder the coupling reaction.

By using a combination of literature procedures,[20] we prepared a large quantity of 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester (**9**) in high yield and without

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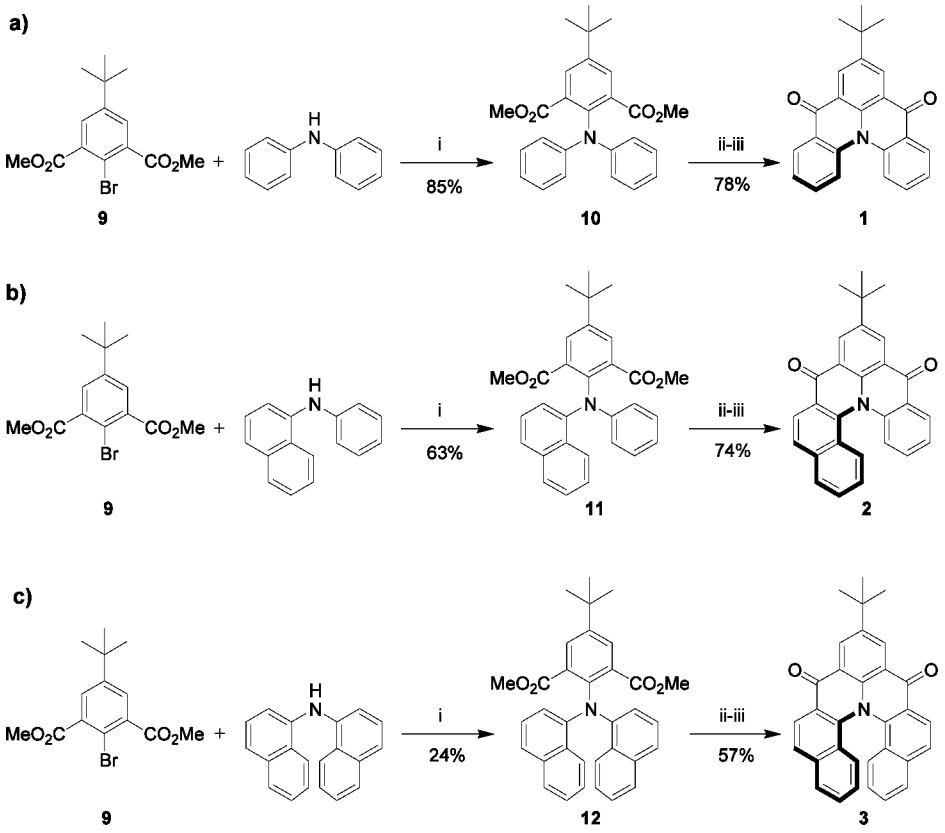
(19) See Supporting Information for details.

SCHEME 3. Three-Step Synthesis of Bridged Triarylamine Heterohelicenes[a]



[a] Reagents and conditions: (i) Cu or CuI, K_2CO_3, Ph_2O or nBu_2O, 150−190 °C, 2−5 days; (ii) NaOH, H_2O/EtOH (1:1), reflux for 1−3 days and then HCl; (iii) $(COCl)_2$, CH_2Cl_2, reflux for 0.5 h and then $SnCl_4$, reflux for 2−3 h.

the need for column chromatography (Scheme 2). We initially attempted to couple **9** to diphenylamine using the palladium(0)-catalyzed reactions reported by Buchwald[21] and Hartwig;[22] however, we were unable to obtain the desired product using these methodologies. The coupling of **9** to diphenylamine was eventually obtained using the copper-catalyzed Ullmann conditions (Scheme 3a). The yield (85%) was remarkably high considering the bulky reactants. We hypothesize that although the *ortho*-esters introduce some steric hindrance, the carbon−bromine bond may be activated by the electron-withdrawing effect of these substituents. It is not until the size of the diarylamine is increased that we see a significant reduction in the yield of the Ullman coupling. For example, *N*-phenyl-1-naphthylamine (Scheme 3b) and dinaphthylamine[23] (Scheme 3c) are coupled to **9** in 63 and 24% yields, respectively.

Each coupled product was hydrolyzed to the respective carboxylic acid derivative in near quantitative (95−97%) yield. We then converted the acids to the acid chlorides with oxalyl chloride in CH_2Cl_2, followed by an in situ cyclization with $SnCl_4$ to yield **1**, **2**, and **3** in 80, 78, and 60% yields, respectively. In our previously reported cyclization,[17] we employed thionyl chloride with $FeCl_3$ as the Lewis acid; however, the functionalized helicenes are susceptible to chlorination under these conditions. Our overall yields of **1**, **2**, and **3** are 66, 47, and 14%, respectively, and unlike many helicene syntheses,[11,12a,24] our method requires no photochemical or radical reactions.

Figure 2 shows the proton spectra of racemic **1**−**3**. The characteristic effect of the increasing helical overlap from molecules **1** to **2** is an upfield shift of proton "e". Similarly, the chemical shifts of protons "g′/g" and "f′/f" are also shifted upfield from molecules **2** to **3**. Such a shielding effect by ring-current on the increasingly overlapping aromatic rings is a common phenomenon observed in carbohelicenes.[2a]

Single-crystal X-ray diffraction of **1**−**3** shows that the helical twist of these compounds is indeed sterically driven by the increasing overlap of the terminal aryl rings (Figure 3). Looking at the packing motif (Figure 4), it can be seen these molecules exist as racemic mixtures of atropisomers that π-stack in a zigzag motif, similar to that observed in hydrogen-bonded *ortho*-substituted diphenylamines.[26] This is yet another example of helically

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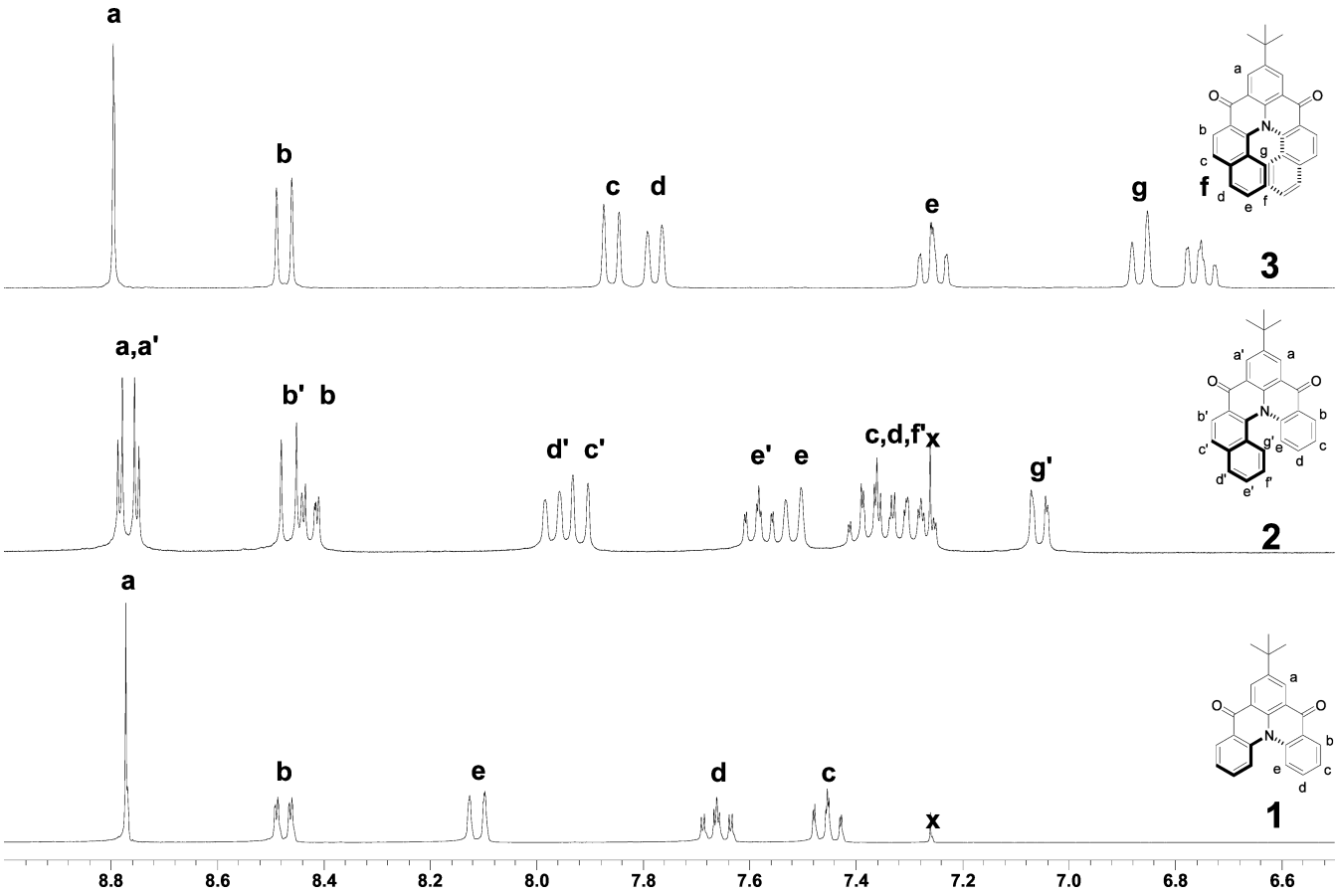

FIGURE 2. Aromatic region of the ^{1}H NMR spectra of **1**−**3**. The $CDCl_3$ solvent peaks are denoted by "x". Chemical shift assignments are supported by two-dimensional COSY experiments.

biased molecules that prefer to adopt the zigzag supramolecular structure over a helical one, at least when present as a racemic mixture. The interplanar angles (θ) between the terminal rings of **1**, **2**, and **3** are 43.4, 58.8, and 60.1°, respectively. In comparison, this angle is 58.5° in hexahelicene and ∼70° in binaphthyl. The slope (ϕ) of the zigzag in **1**, **2**, and **3** is 21.6, 79.0, and 61.0°. The repeat distances (d_1) for **1**, **2**, and **3** are 12.0, 14.5, and 14.1 Å with the distance between atropisomers (d_2) being 6.0, 4.7, and 7.1 Å. It should be noted that for **2**, d_2 is not half of d_1, which denotes a dimeric-type stacking in which terminal phenyl−phenyl and naphthyl−naphthyl π-interactions preferentially form between the unsymmetrical atropisomers.

The absorption and emission spectra (Figure 5) of these molecules were obtained from chloroform solutions at concentrations of 2×10^{-5} and $\sim 1 \times 10^{-6}$ M, respectively. The absorption maxima (λ_{max}) of **1**, **2**, and **3** are 442, 446, and 460 nm, with extinction coefficients (ϵ) of 22.6×10^3, 17.7×10^3, and 14.4×10^3 cm^{-1} M^{-1}, respectively. These absorption maxima are much higher than those observed for carbo- and thiahelicenes of the same size.[2a] When excited at these wavelengths, **1**, **2**, and **3** emit at 460, 468, and 486 nm, respectively. The observed red shift in the absorption and emission spectra are consistent with increasing conjugation of the chromophore. It is interesting to note that the absorption maxima of **3** coincides with the emission maxima of **1**, suggesting that energy transfer between these molecules may be possible. No phosphorescence was visually noted for any of these molecules; however, no experiments were conducted to confirm the complete absence of phosphorescence.

Cyclic voltametry of **1**−**3** was conducted in dichloromethane solutions at concentrations of 1×10^{-3} M (Figure 6). Compound **1** shows a quasireversible, one-electron oxidation at $E_{1/2} = 1.57$ V (vs SCE), which is similar to some substituted phenyl acridones.[27] Compounds **2** and **3** show oxidation potentials at $E_{1/2} = 1.44$ V and $= 1.49$ V, respectively. In comparison, triphenylamine forms an unstable monocation radical at ∼0.98 V, which rapidly dimerizes to form tetraphenylbenzidine.[18] There is no evidence of a dimerization or any other chemical process taking place when these bridged triarylamines are oxidized. This is a good indication of the stability of the radical cation formed upon oxidation. This stabilization may in part be attributed to the presence of the *tert*-butyl substituent that blocks the top *para* position where dimerization would be most likely to occur. Also, the carbonyl bridges may stabilize the radical cation by contributing additional resonance pathways.

In summary, we have reported the synthesis, solid-state structure, and photochemical and electrochemical

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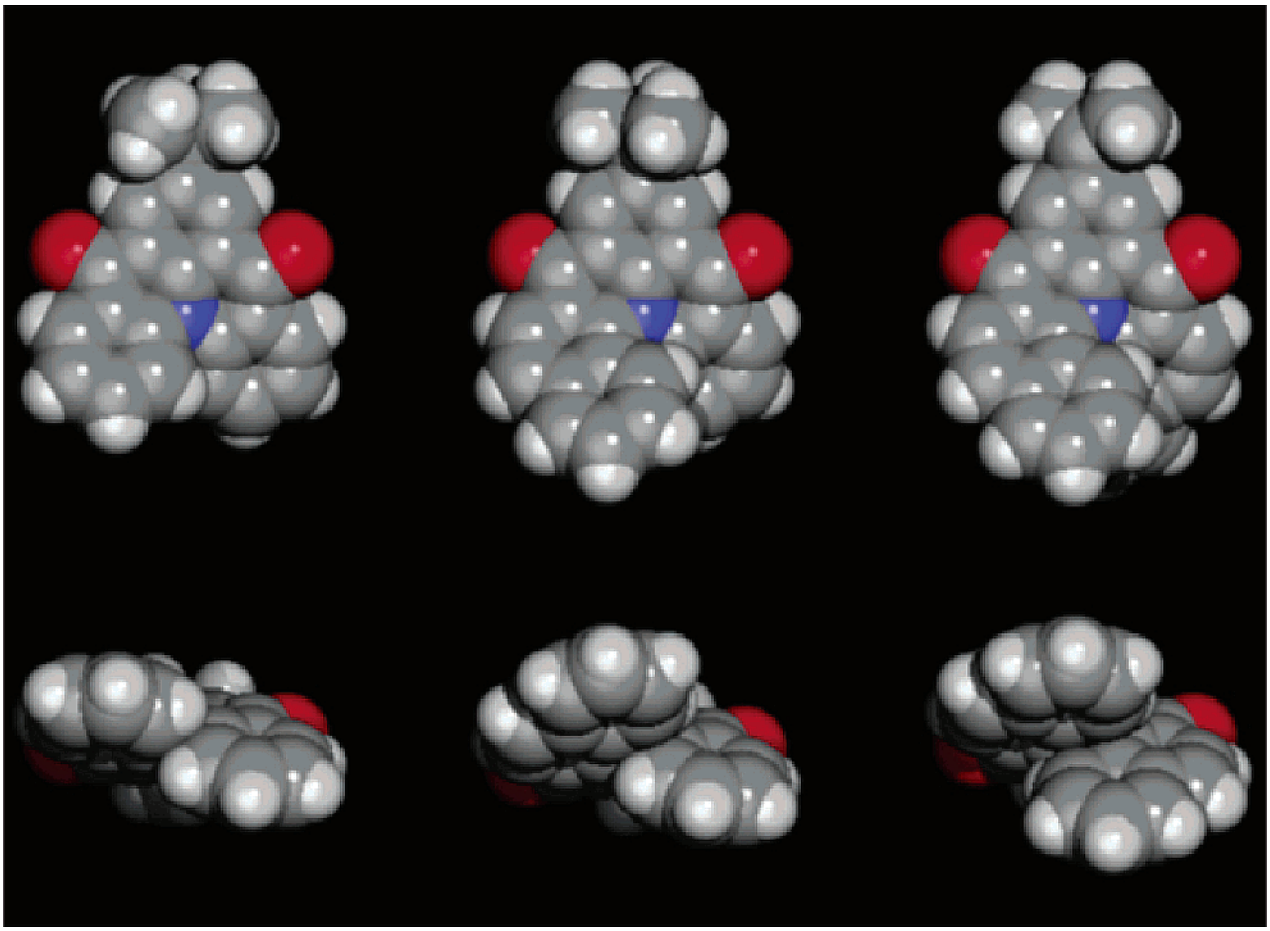

FIGURE 3. Space-filling renderings from the single-crystal X-ray diffraction data of **1**−**3** (from left to right) as viewed from above (top) and side (bottom).

properties of **1**−**3**. These molecules constitute a new class of electroactive heterohelicenes based on bridged triarylamines. Our efforts are now focused on the resolution of the atropisomers of these compounds in order to study the barriers of racemization[28] and other properties of the enantiomerically pure electroactive helicenes. These results will be reported in due course.

Experimental Section

2,2′-[(4-Methylphenyl)imino]bisbenzoicacid-dimethylester (4). *p*-Toluidine (5.36 g, 50 mmol) was coupled with methyl 2-iodobenzoate (22.4 mL, 105 mmol) in 50 mL of *n*-butyl ether, with K_2CO_3 (14.51 g, 105 mmol), Cu (0.75 g, 12 mmol), and CuI (0.50 g, 2.6 mmol), heated to 170 °C for 120 h. The reaction was filtered and the solvent removed by vacuum distillation. The crude product was purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent and then recrystallized from ethanol to give 12.99 g (70% yield) of **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J = 1.7, 7.7 Hz, 2H), 7.38 (dt, J = 1.7, 8.1 Hz, 2H), 7.12 (m, 4H), 6.98 (d, J = 8.1, 2H), 6.71 (d, J = 8.7, 2H), 3.39 (s, 6H), 2.24 (s, 3H). Anal. Calcd for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.29; H, 5.55; N, 3.69. Crystal data: $C_{23}H_{21}NO_4$, M = 375.42, triclinic, *P*-1, a = 10.1343(2) Å, b = 10.1351(2) Å, c = 11.8738(3) Å, α = 111.00(10)°, β = 113.43(10)°, γ = 96.55(9)°, V = 996.63(4) Å^3, Z = 2, m = 0.086 mm^{-1}, T = 298 K, data/parameters = 3470/254, converging to R_1 = 0.0547, wR_2 = 0.1307 (on 2638, $I > 2\sigma$(I) observed data); R_1 = 0.0798, wR_2 = 0.1685 (all data), residual electron density = 0.480 e/Å^3.

2-Bromo-5-*tert*-butyl-1,3-dimethylbenzene (7).[20a] In a 250 mL round-bottom flask equipped with a magnetic stir bar and an addition funnel were added 5-*tert*-butyl-*m*-xylene (91.0 mL, 0.48 mol) and 1 large spatula scoop (∼1 g) of iron powder to 75 mL of chloroform. The solution was cooled to 0 °C. A solution of bromine (27.3 mL, 0.53 mol) in 22.7 mL of chloroform was added dropwise via the addition funnel. The reaction was stirred for 2 h at room temperature and then poured into a cold solution of dilute aqueous NaOH (∼1 M). The mixture was separated, and the aqueous layer was washed several times with ether. The combined organic layers were dried with sodium sulfate, filtered, and concentrated to a clear oil, which became a white solid upon standing. The crude solid was recrystallized from ethanol (several crops) to give 104.52 g (90% yield,) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H), 2.41 (s, 6H), 1.29 (s, 9H). Crystal data: $C_{12}H_{17}Br$, M = 241.177, 0rthorhombic, *Pnma*, a = 9.6439(4) Å, b = 7.3388(2) Å, c = 16.8992(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1196.04(8) Å^3, Z = 4, m = 3.394 mm^{-1}, T = 298 K, data/parameters = 1127/77, converging to R_1 = 0.0427, wR_2 = 0.1137 (on 912, $I > 2\sigma$(I) observed data); R_1 = 0.0550, wR_2 = 0.1247 (all data), residual electron density = 0.542 e/Å^3.

2-Bromo-5-*tert*-butyl-isophthalic Acid (8).[20b] In a 2 L three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was added 2-bromo-5-*tert*-butyl-1,3-dimethylbenzene **7** (104.5 g, 0.43 mol), dispersed in 800 mL of a 1:1 mixture of *tert*-butyl alcohol and water. $KMnO_4$ (143.8 g, 0.91 mol) was added, and the reaction mixture was heated to reflux for 1 h. After the mixture was cooled to room temperature, more $KMnO_4$ (143.8 g, 0.91 mol) was added and

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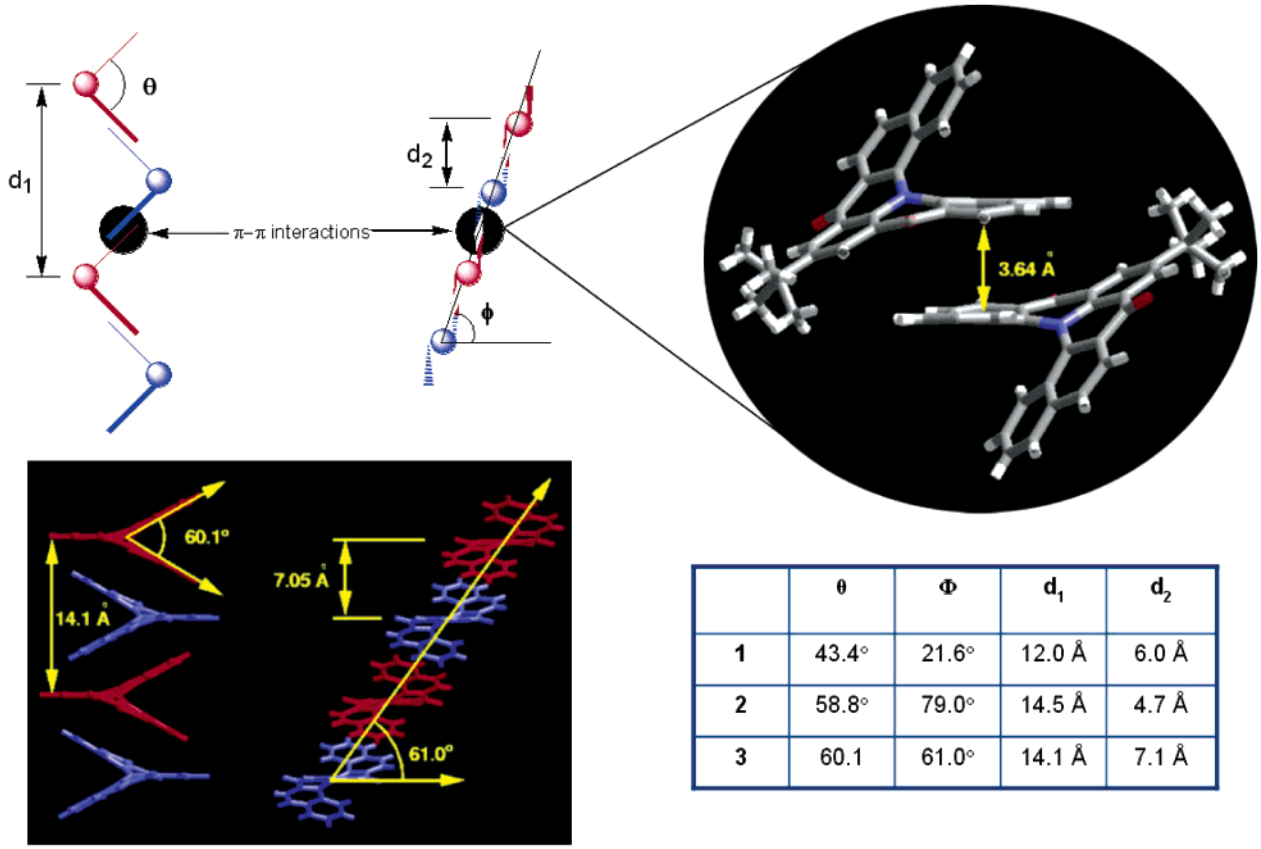

	θ	Φ	d_1	d_2
1	43.4°	21.6°	12.0 Å	6.0 Å
2	58.8°	79.0°	14.5 Å	4.7 Å
3	60.1	61.0°	14.1 Å	7.1 Å

FIGURE 4. Schematic of the zigzag packing motif observed in **1**−**3** (top left) as seen from the side and rotated 90°. The analogous image from the single-crystal X-ray diffraction of **3** is shown (bottom left) with the π-stacking interactions magnified (top right). *P*-isomers (blue) and *M*-isomers (red) are shown with the methyl groups of the *tert*-butyl moiety removed for clarity. A summary of the packing distances and angles is given as a table (bottom right).

the reaction mixture was refluxed for an additional 18 h. After the mixture was cooled to 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 precipitate collected and oven-dried (~80 °C) overnight to give 125.8 g (97% yield) of the title compound: ^{1}H NMR (300 MHz, CD_3OD) δ 8.61 (s, 2H), 2.19 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ 170.30, 152.22, 137.53, 129.81, 115.37, 35.66, 31.29.

2-Bromo-5-*tert*-butyl-isophthalic Acid Dimethyl Ester (9).[20c] In a 2 L round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added 2-bromo-5-*tert*-butyl-isophthalic acid **8** (104.6 g, 0.35 mol), in 750 mL of methanol and 80 mL of H_2SO_4. The reaction mixture was heated to reflux for 18 h and poured into water (~500 mL). The reaction was neutralized with $NaHCO_3$, and the aqueous solution was washed several times with ether. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Recrystallization from hexane gave 93.8 g (81% yield) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 2H), 3.95 (s, 6H), 1.33 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.32, 150.67, 134.91, 129.42, 115.56, 52.65, 34.70, 30.84. Anal. Calcd for $C_{14}H_{17}BrO_4$: C, 51.08; H, 5.21; Found: C, 50.58; H, 5.27.

General Procedure for Ullmann Coupling. The diarylamine (1.0 equiv), 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **9** (1.1 equiv), potassium carbonate (1.2 equiv), and copper bronze (15 mol %) were combined with diphenyl ether in a round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was heated to ~190 °C for 48−96 h under argon. The reaction was filtered, the solvent removed by vacuum distillation, and the residue purified by column chromatography.

5-*tert*-Butyl-2-diphenylamino-isophthalic Acid Dimethyl Ester (10). Diphenylamine (0.85 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **9** (1.81 g, 5.5 mmol) according to the above Ullmann procedure for 48 h. The crude product was purified by flash chromatography using a 5:1 solution of hexane/ethyl acetate as the eluent to give 1.77 g (85% yield) of the title compound as a yellow crystalline solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.18 (m, 4H), 6.95 (m, 6H), 3.47 (s, 6H), 1.35 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.4, 148.9, 147.4, 142.0, 132.3, 131.1, 129.1, 122.5, 122.3, 52.5, 31.4. Anal. Calcd for $C_{26}H_{27}NO_4$: C, 74.80; H, 6.52; N, 3.35. Found: C, 74.60; H, 6.73; N, 3.34. Crystal data: $C_{26}H_{27}NO_4$, M = 417.505, monoclinic, $P2_1/c$, a = 12.1636(4) Å, b = 17.4913(6) Å, c = 11.8633(3) Å, α = 90.00°, β = 110.62(13)°, γ = 90.00°, V = 2362.26(13) Å^3, Z = 4, m = 0.079 mm^{-1}, T = 298 K, data/parameters = 4082/280, converging to R_1 = 0.0788, wR_2 = 0.1896 (on 2395, $I > 2\sigma(I)$ observed data); R_1 = 0.1397, wR_2 = 0.2252 (all data), residual electron density = 0.423 e/Å^3.

5-*tert*-Butyl-2-(naphthalen-1-yl-phenyl-amino)-isophthalic Acid Dimethyl Ester (11). *N*-Phenyl-1-naphthylamine (1.10 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **9** (1.81 g, 5.5 mmol) according to the above Ullmann procedure for 96 h. The crude product was purified by flash chromatography using a 3:1 solution of dichloromethane/hexane as the eluent to give 1.48 g (63% yield) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.63 (s, 2H), 7.63 (d, J = 8.1 Hz, 1H), 7.38 (t, J = 8.1 Hz, 2H), 7.25 (dt, J = 7.4, 1.0 Hz, 2H), 7.12 (t, J = 8.3 Hz, 2H), 6.87 (dt, J = 7.4, 1.0 Hz, 1H), 6.74 (br d, J = 8.2 Hz, 2H), 3.14 (br

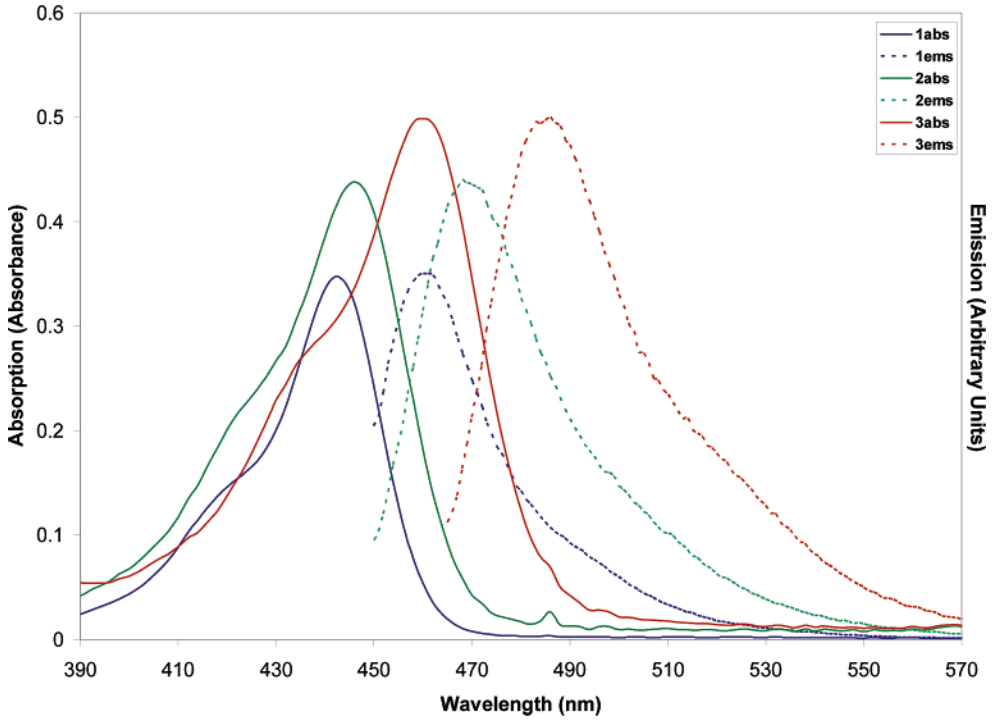

FIGURE 5. Absorption (solid) spectra of 2×10^{-5} M and emission (dashed) spectra of $\sim 1 \times 10^{-6}$ M solutions of **1** (blue), **2** (green), and **3** (red) in $CHCl_3$. For each sample, the emission spectrum was normalized with respect to the absorption spectrum.

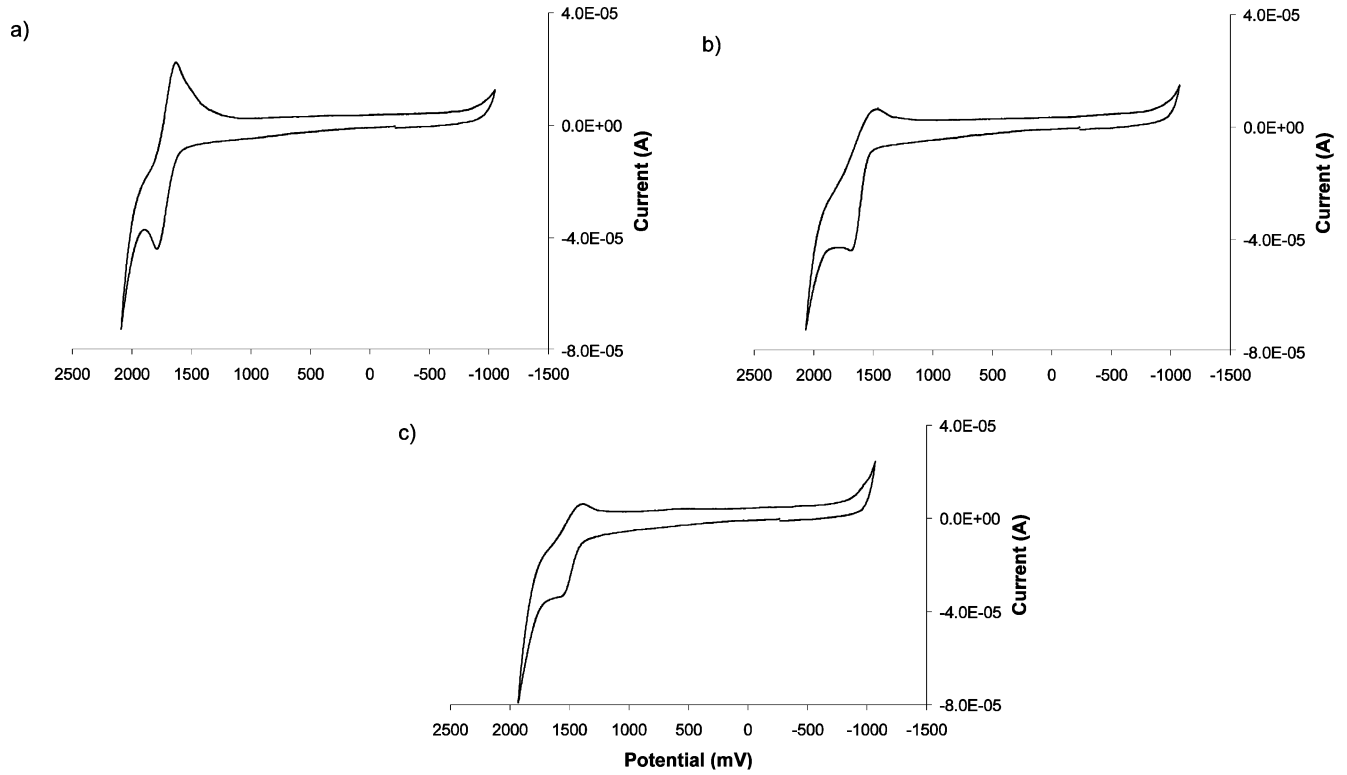

FIGURE 6. Cyclic voltammograms of (a) **1**, (b) **2**, and (c) **3** in CH_2Cl_2.

s, 6H), 1.35 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.3, 148.6, 147.8, 142.7, 142.7, 134.8, 131.7, 129.8, 128.6, 128.2, 126.1, 125.9, 125.5, 125.3, 125.0, 124.9, 121.21, 120.64, 52.0, 34.6, 31.08; HRMS calcd for $C_{30}H_{29}NO_4$ 467.2097, found 467.2061; mp = 220−222 °C.

5-*tert*-Butyl-2-(di-naphthalen-1-yl-amino)-isophthalic Acid Dimethyl Ester (12). Dinaphthylamine (1.34 g, 5.0 mmol) was coupled with 2-bromo-5-*tert*-butyl-isophthalic acid dimethyl ester **9** (6.0 g, 17.93 mmol) in 25 mL of *n*-butyl ether, with K_2CO_3 (1.382 g, 10 mmol) and CuI (1.143 g, 6.0 mmol),

heated to 150 °C for 120 h. The reaction was filtered and the solvent removed by vacuum distillation. The crude product was purified by flash chromatography using 3:1 dichloromethane/hexane as the eluent to give 0.61 g (24% yield) of the title compound. NMR spectra were difficult to interpret precisely due to large peak broadening; however, further conformation of structure can be made by HRMS and X-ray crystallography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (br s), 7.80 (d, J = 8.1 Hz), 7.59 (br s), 7.36 (br s), 6.75 (br s), {aromatic region 6.6−8.4, 16H}, 2.6−3.3 (br d, 6H), 1.30 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 31.0, 34.5, 51.7, 125.5, 125.6, 128.1, 128.2, 135.0, 143.6, 144.6, 146.5, 168.6; HRMS calcd for $C_{34}H_{31}NO_4$ 517.2253, found 517.2252. mp = 194−196 °C. Crystal data: $C_{34}H_{31}NO_4$, M = 517.652, triclinic, P-1, a = 10.9431(3) Å, b = 11.7705(3) Å, c = 12.3238(3) Å, α = 99.21(14)°, β = 92.74(13)°, γ = 115.08(11)°, V = 1407.17(6) Å^3, Z = 2, m = 0.080 mm^{-1}, T = 298 K, data/parameters = 4892/352, converging to R_1 = 0.0498, wR_2 = 0.1119 (on 3474, $I > 2\sigma$(I) observed data); R_1 = 0.0788, wR_2 = 0.1282 (all data), residual electron density = 0.184 e/Å^3.

General Procedure for Cyclization with $SnCl_4$. The triarylamine diester derivative was hydrolyzed with sodium hydroxide (10 equiv) in a solution of 1:1 ethanol/water heated to reflux for 12−72 h. Acidification with concentrated hydrochloric acid precipitated the triarylamine diacid, which was collected by vacuum filtration and oven-dried (~80 °C) overnight. Yields were nearly quantitative (95−97%), and the material was used in the next step without further purification. The triarylamine diacid (1 equiv) was dispersed in dry dichloromethane in a three-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser with a drying tube. A few drops of *N*,*N*-dimethylformamide was added followed by oxalyl chloride (2.2 equiv). The reaction was heated to reflux for 0.5 h. Tin(IV) chloride (2.2 equiv) was added and the reaction refluxed for an additional 2−3 h. The reaction mixture was added dropwise to an aqueous solution of sodium hydroxide (~1 M) and extracted with dichloromethane. The organic layer was collected and dried over sodium sulfate, filtered, and concentrated. The crude product was then purified by flash chromatography.

7-*tert*-Butyl-13b-aza-naphtho[3,2,1-de]anthracene-5,9-dione (1). Following the above general cyclization procedure, 5-*tert*-butyl-2-diphenylamino-isophthalic acid (0.20 g, 0.5 mmol) was cyclized and then purified by flash chromatography (using 3:1 hexane/ethyl acetate as the eluent) to give 0.14 g (80% yield) of **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.48 (dd, J = 1.7, 7.9 Hz, 2H), 8.12 (d, J = 8.6 Hz, 2H), 7.67 (dt, J = 1.7, 8.6 Hz, 2H), 7.46 (dt, J = 0.9, 7.9 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 178.75, 147.09, 139.62, 137.43, 132.53, 129.84, 127.80, 126.35, 124.95, 123.16, 120.03, 35.00, 31.30; HRMS calcd for $C_{24}H_{19}NO_2$ 353.1416, found 353.1411; mp = 247−249 °C. Crystal data: $C_{20}H_{11}NO_2$, M = 353.1416, orthorhombic, *Pbcn*, a = 12.2443(13) Å, b = 12.454(2) Å, c = 11.9541(13) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1822.9(4) Å^3, Z = 4, m = 0.080 mm^{-1}, T = 298 K, data/parameters = 1571/138, converging to R_1 = 0.1638, wR_2 = 0.3901 (on 1043, $I > 2\sigma$(I) observed data); R_1 = 0.2089, wR_2 = 0.4183 (all data), residual electron density = 0.493 e/Å^3.

Compound 2. Following the above general cyclization procedure, 5-*tert*-butyl-2-(naphthalen-1-yl-phenyl-amino)isophthalic acid (1.34 g, 3.26 mmol) was cyclized and then purified by flash chromatography (using 5:1 dichlormethane/hexane as the eluent) to give 0.95 g (78% yield) of **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, J = 2.4, 9.2 Hz 2H), 8.48 (d, J = 8.7 Hz, 1H), 8.43 (dd, J = 2.1, 7.5 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.59 (dt, J = 1.1, 8.1 Hz, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.37 (m, 3H), 7.07 (d, J = 9.2 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 179.76, 178.89, 147.56, 142.08, 138.76, 137.70, 136.35, 131.84, 129.53, 129.06, 128.95, 128.54, 127.49, 127.11, 126.60, 125.60, 125.56, 124.79, 124.73, 124.71, 124.04, 123.66, 122.16, 121.30, 35.10, 31.34; HRMS calcd for $C_{28}H_{21}NO_2$ 403.1572, found 403.1597; mp = 319−321 °C. Crystal data: $C_{28}H_{21}NO_2$, M = 403.481, monoclinic, $P2_1/c$ (no. 14), a = 8.8628(2) Å, b = 11.4131(3) Å, c = 20.4548-(7) Å, α = 90.00°, β = 93.29 (1)°, γ = 90.00°, V = 2065.63(10) Å^3, Z = 4, μ = 0.081 mm^{-1}, T = 298 K, data/parameters = 3608/280, converging to R_1 = 0.0680, wR_2 = 0.1927 (on 2484, $I > 2\sigma$(I) observed data); R_1 = 0.1004, wR_2 = 0.2092 (all data), residual electron density = 0.479 e/Å^3.

Compound 3. Following the above general cyclization procedure, 5-*tert*-butyl-2-(di-naphthalen-1-yl-amino)isophthalic acid (0.98 g, 2.0 mmol) was cyclized and then purified by flash chromatography using dichloromethane as the eluent to give 0.55 g (60% yield) of **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 2H), 8.48 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 8.1 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.76 (t, J = 8.6, 2H), 1.52 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 179.51, 147.95, 141.01, 138.91, 135.86, 128.83, 128.50, 128.10, 126.26, 125.71, 125.48, 124.83, 124.34, 124.05, 122.00, 35.18, 31.39; HRMS calcd for $C_{32}H_{23}NO_2$ 453.1729; found 453.1718. Crystal data: $C_{32}H_{23}NO_2$, M = 453.541, monoclinic, $C2/c$, a = 17.986(2) Å, b = 13.832(2) Å, c = 11.967(2) Å, α = 90.00°, β = 128.57(6)°, γ = 90.00°, V = 2327.7(5) Å^3, Z = 4, m = 0.080 mm^{-1}, T = 298 K, data/parameters = 1156/165, converging to R_1 = 0.1242, wR_2 = 0.3322 (on 696, $I > 2\sigma$(I) observed data); R_1 = 0.1827, wR_2 = 0.3715 (all data), residual electron density = 0.580 e/Å^3.

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Supporting Information Available: Experimental procedures and characterization data for **5**, **6**, and dinaphthylamine, crystallographic information files (CIF) for **1**−**5**, **7**, **10**, **12**, and dinaphthylamine, and two-dimensional NMR spectra for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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