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Note

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Synthesis of a Cyclophane Bearing Two Benz[*a*]anthracene Units Connected at 5 and 7 Positions with Two Naphth-1,4-diyl Groups

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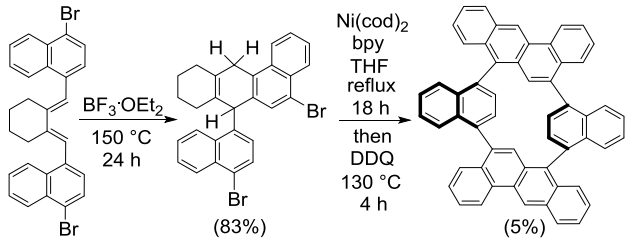
Supporting Information Placeholder

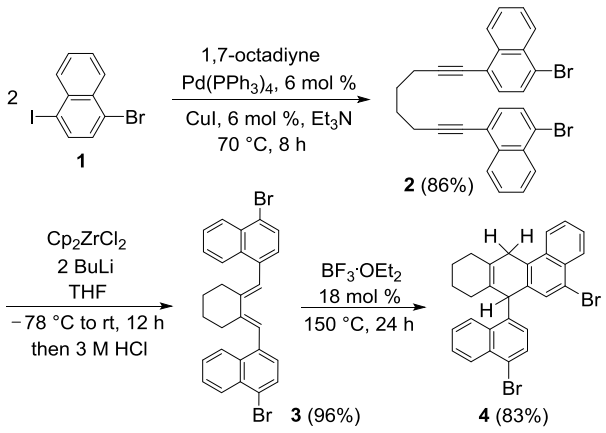


ABSTRACT: A synthetic pathway to a cyclophane bearing two benz[*a*]anthracene units connected at 5 and 7 positions through two naphth-1,4-diyl groups was developed and its structure was confirmed by X-ray structure analysis. Because of structural constraints, the two naphthyl groups are distorted from planarity and the bonds connecting them to the benz[*a*]anthracene units are bent significantly. The UV–vis and fluorescence spectra of the cyclophane are red-shifted from 7-(1-naphthalenyl)benz[*a*]anthracene, which is the corresponding monomeric polycyclic aromatic hydrocarbon.

Cyclophanes as bridged aromatic compounds have continued to attract considerable attention due in part to their unusual structural features, ability to form host-guest complexes, and interesting material properties.[1] Development of synthetic methods for strained cyclophanes faces the challenge of overcoming the developing strain energy along the synthetic pathways. Several synthetic strategies have been reported for cyclophanes, including systems containing unusually strained structures.[2] During our investigation of new synthetic pathways for cycloparaphenylenes,[3] a serendipitous discovery led to the formation of a strained cyclophane bearing two benz[*a*]anthracene units connected at 5 and 7 positions through two naphth-1,4-diyl groups

The synthetic sequence began with the Sonogashira reactions between 1-bromo-4-iodonaphthalene (**1**) and 1,7-octadiyne to give diyne **2** in 86% isolated yield (Scheme 1). Treatment of **2** with zirconocene, generated in situ from Cp_2ZrCl_2 and two equiv of BuLi, followed by hydrolysis with aqueous HCl produced 1,3-butadiene **3**.[4] Upon being exposed to a catalytic amount of $BF_3{\cdot}OEt_2$ (18 mol %) at 150 °C for 24 h, diene **3** was transformed to the rearranged isomer **4** in 83% isolated yield. The DFT-optimized structure of **4** is shown in Figure 1. The temperature-dependent ^1H NMR studies indicate that the rate of rotation around the bond attaching the 4-bromo-1-naphthyl group to the hydrogenated benz[*a*]anthracene unit is relatively slow on the NMR time scale at room temperature.

Scheme 1. Synthesis of Dibromide 4



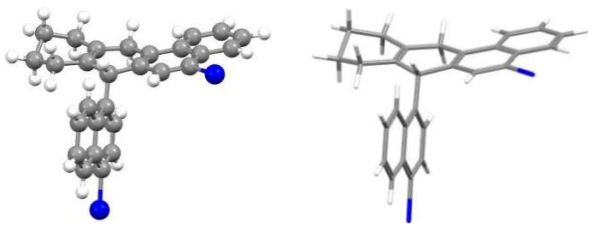
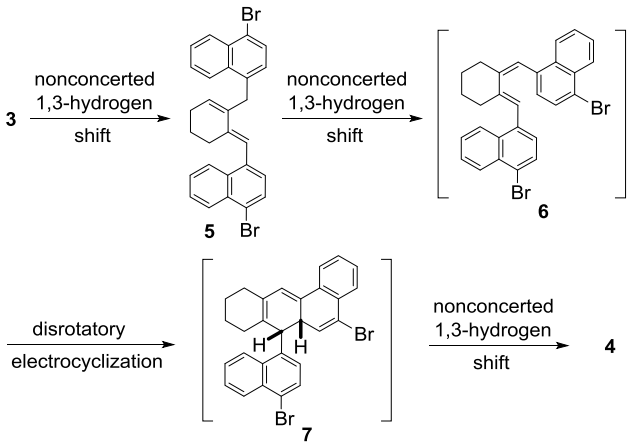


Figure 1. DFT-optimized structure of **4** with carbons (gray), hydrogens (white), and bromines (blue).

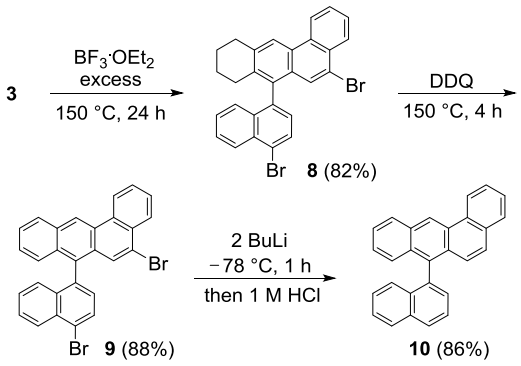
The formation of **4** was rather unexpected. Originally we were attempting to promote the Diels–Alder reaction between **3** and dimethyl acetylenedicarboxylate in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ for the preparation of a Diels–Alder adduct as a precursor leading to cycloparaphenylenes,[3b,e] but instead **4** was produced. A plausible reaction pathway from **3** to **4** could involve an initial nonconcerted 1,3-hydrogen shift to form **5** (Scheme 2). Compound **5** was found to be essentially the only initial product after heating at 150 °C for 2 h, and it was isolated for structural elucidation by NMR and HRMS spectroscopy. Heating the isolated **5** in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ at 150 °C for 24 h also gave **4**. It was also observed that heating **3** in the presence of a catalytic amount of acetic acid at 150 °C for 24 h also gave **4** in 92% isolated yield. A nonconcerted 1,3-hydrogen shift of **5** could produce **6** with one of the double bonds of the diene moiety having the *Z* geometry. A subsequent disrotatory electrocyclic reaction of **6**, which was not isolated and detected, to form **7** followed by a nonconcerted 1,3-hydrogen shift could then produce **4**.

Scheme 2. Plausible Reaction Mechanism for the Formation of 4



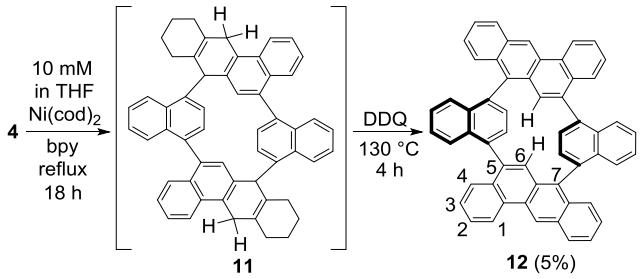
The connectivity of the carbon skeleton in **4** was further supported by the isolation of the aromatized product **8** when an excess of $BF_3{\cdot}OEt_2$ was used (Scheme 3). Oxidative aromatization of **8** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) produced **9** with its structure established by X-ray structure analysis. Treatment of **9** with BuLi for lithium–halogen exchange followed by protonation then gave 7-(1-naphthalenyl)benz[*a*]anthracene (**10**), which was prepared previously by an independent synthetic route.[5]

Scheme 3. Synthesis of Hydrocarbon 10



The Ni(cod)$_2$-mediated (cod being 1,5-cyclooctadiene) homocoupling reactions of **4** in the presence of 2,2'-bipyridyl (bpy)[6] most likely produced **11**, which was not isolated and characterized (Scheme 4). Oxidative aromatization of **11** with DDQ[3] at 150 °C for 4 h then produced cyclophane **12** in 5% yield over two steps from **4**.

Scheme 4. Synthesis of Cyclophane 12



The structure of **12** bearing two benz[*a*]anthracene units connected at 5 and 7 positions through two naphth-1,4-diyl groups was confirmed by X-ray structure analysis (Figure 2). The two naphthyl groups are essentially parallel to each other but perpendicular to the benz[*a*]anthracene units. They point in opposite directions and are distorted from planarity. The bonds connecting them to the C5 and C7 carbons of the benz[*a*]anthracene units are bent toward each other with bond angles of 114.5° and 115.1°, respectively, as indicated. The ^{1}H NMR signal of the hydrogens attached to C6 occurred at δ 4.87, which was shifted significantly upfield by the magnetic ring currents of the naphthyl groups.

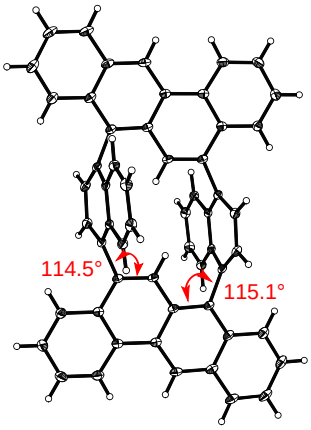


Figure 2. ORTEP drawing of cyclophane **12**. The molecule lies on a crystallographic center of inversion. The thermal ellipsoids are scaled to enclose 50% probability.

We also investigated the optical and electrochemical properties of cyclophane **12** and compared them with those of **10**. The UV–vis and fluorescence spectra were recorded in degassed dichloromethane as the solvent. Cyclophane **12** showed absorption maxima at 290 and 300 nm and absorption bands between 320 and 410 nm (Figure 3). They were red-shifted from those of **10**, which showed absorption maxima at 283 and 294 nm and absorption bands between 310 and 395 nm. The fluorescence maxima also showed red-shift from 396 and 417 nm in **10** to 402 and 429 nm in cyclophane **12**.

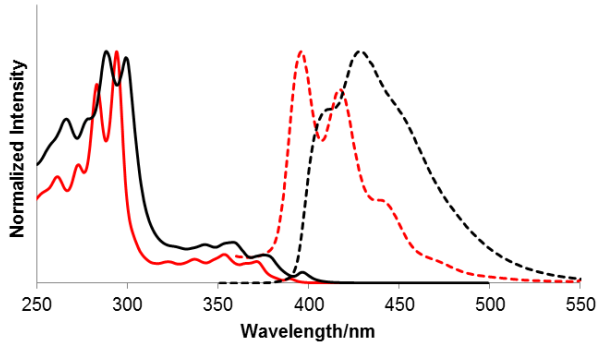


Figure 3. UV–vis (solid lines) and fluorescence (dashed lines) spectra of **10** (red) and **12** (black) in dichloromethane.

Electrochemical properties of **10** and cyclophane **12** were investigated by cyclic voltammetry in tetrahydrofuran with 0.1 M $[N(n\text{-}Bu)_4][PF_6]$ and referenced to ferrocene/ferrocenium (Fc/Fc^+) couple as an internal standard. Compound **10** showed a reversible reduction with $E_{1/2} = -2.59$ V and three irreversible oxidation events at $E_{pa} = 0.63$, 1.14, and 1.41 V. A similar redox behavior was also observed for cyclophane **12** with an irreversible redox couple at $E_{pa} = -2.42$ V and $E_{pc} = -2.73$ V. Again, no reversible oxidation events were observed for **12**.

In summary, a synthetic pathway to cyclophane **12** has been developed. Isomerization of 1,3-butadiene **3** to the hydrogenated benz[*a*]anthracene **4** followed by the $Ni(cod)_2$-mediated macrocyclization and oxidative aromatization with DDQ are the key steps of the synthetic pathway. The structure of **12** was established by X-ray structure analysis. Because of structural constraints, the two naphthyl groups are distorted from planarity and the bonds connecting them to the benz[*a*]anthracene units are bent significantly. The ^{1}H NMR signal of the hydrogens on the C6 carbons of the benz[*a*]anthracene units is shifted significantly upfield to δ 4.87. The UV–vis and fluorescence spectra of **10** and **12** were recorded, and their electrochemical properties in THF were probed by cyclic voltammetry.

EXPERIMENTAL SECTION

General Experimental Methods.

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere unless otherwise indicated. Chemicals, including 1,4-dibromonaphthalene, 1,7-octadiyne, tetrakis(triphenylphosphine)palladium $[Pd(PPh_3)_4]$, Cp_2ZrCl_2, $BF_3{\cdot}OEt_2$, bis(1,5-cyclooctadiene)nickel $[Ni(cod)_2]$, 2,2′-bipyridyl (bpy), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), were purchased from chemical suppliers and were used as received. Treatment of 1,4-dibromonaphthalene in THF with butyllithium at −78 °C followed by iodine produced 1-bromo-4-iodonaphthalene (**1**).[7] UV–vis absorption spectra were recorded on a spectrophotometer with a 1 nm resolution, and the baseline was corrected with a solvent filled square quartz cell. Fluorescence spectra were recorded on a spectrofluorophotometer with a 2 nm resolution. Infrared (IR) spectra of solid samples were recorded on a Fourier transform infrared system equipped with a diamond crystal attenuated total reflectance sampling interface. HRMS spectra were obtained on an FT-ICR or an Orbitrap mass analyzer coupled with electrospray ionization (ESI).

Preparation of ***2***. To a degassed solution of 1-bromo-4-iodonaphthalene (**1**, 6.20 g, 18.6 mmol), $Pd(PPh_3)_4$ (1.30 g, 1.12 mmol), and CuI (0.213 g, 1.12 mmol) in 200 mL of triethylamine was added 1,7-octadiyne (0.970 g, 9.15 mmol), and the mixture was stirred at 70 °C for 8 h. After the solution was cooled to rt, triethylamine was removed in vacuo, and then CH_2Cl_2 (400 mL) and water (200 mL) were added. The resulting mixture was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo to yield a pale-yellow solid. The pale yellow solid was purified by silica gel column chromatography using ethyl acetate/hexanes (1:9) as eluent to obtain **2** (4.05 g, 7.84 mmol, 86% yield) as a pale yellow solid: IR 1381, 834, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (2 H, dd, J = 8.0, 1.6 Hz), 8.24 (2 H, dd, J = 8.0, 2.0 Hz), 7.70 (2 H, d, J = 7.8 Hz), 7.63–7.53 (4 H, m), 7.46 (2 H, d, J = 7.8 Hz), 2.68 (4 H, m), 1.98 (4 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.5, 131.7, 130.1, 129.4, 127.6, 127.4, 127.3, 126.8, 122.7, 121.7, 95.9, 78.5, 28.0, 19.4; HRMS (ESI/FT-ICR) m/z $[M + H]^+$ calcd for $C_{28}H_{21}Br_2$ 515.0005, 516.9984, 518.9964; found 515.0010, 516.9989, 518.9969.

Preparation of ***3***. To a solution of Cp_2ZrCl_2 (2.68 g, 9.17 mmol) in THF (70 mL) at −78 °C under an argon atmosphere was added *n*-butyllithium (7.0 mL of a 2.5 M solution in hexanes, 17.5 mmol). After 1 h at −78 °C, **2** (3.75 g, 7.26 mmol) in 30 mL of THF under argon was added slowly via cannula. The reaction mixture was then warmed to rt. After 12 h, the reaction mixture was poured into 300 mL of a 3 M aqueous HCl solution. After 30 min of stirring, the reaction mixture was extracted with dichloromethane (2 × 100 mL). The combined organic layers were washed with a saturated Na_2CO_3 solution and dried over $MgSO_4$. After passing through a silica gel column (9.0 cm high, 2.5 cm in diameter), the solvent was evaporated in vacuo, and the residue was washed with cold ethanol to give **3** (3.60 g, 6.98 mmol, 96% yield) as a white solid: IR 1503, 1377, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (2 H, dd, J = 7.8, 1.6 Hz), 8.14 (2 H, dd, J = 7.4, 1.6 Hz), 7.80 (2 H, d, J = 7.4 Hz), 7.66–7.57 (4 H, m), 7.26 (2 H, d, J = 7 Hz), 7.07 (2 H, s), 2.45 (4 H, m), 1.63 (4 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5, 135.1, 133.6, 132.0, 129.4, 127.6, 127.3, 127.2, 126.6, 125.7, 121.8, 120.9, 30.8, 26.7; HRMS (ESI/Orbitrap) m/z $[M]^+$ calcd for $C_{28}H_{22}Br_2$ 516.0083, 518.0062, 520.0042; found 516.0091, 518.0068, 520.0040.

Preparation of ***4***. To a 25 mL pressure vessel were added **3** (0.700 g, 1.35 mmol), $BF_3{\cdot}OEt_2$ (0.03 mL, 0.2 mmol) and 1 mL of dry toluene under an argon atmosphere. The reaction mixture was stirred at 150 °C for 24 h before it was cooled to rt. Toluene was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 5:95) to afford **4** (0.585 g, 1.13 mmol, 83% yield) as a white solid: IR 1595, 1378, 750 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 8.31 (1 H, d, J = 8.2 Hz), 8.17 (1 H, d, J = 8.2 Hz), 8.09 (1 H, d, J = 8.8 Hz), 7.71–7.66 (1 H, br), 7.63–7.55 (4 H, m), 7.28 (1 H, s), 7.15 (1 H, br), 5.22 (1 H, br), 3.86 (1 H, d, J = 22.6 Hz), 3.78 (1 H, d, J = 21.7 Hz), 2.26 (2 H, m), 1.90 (1 H, m), 1.74 (1 H, m), 1.62–1.48 (4 H, m); ^{1}H NMR (600 MHz, $CDCl_3$, 60 °C) δ 8.32 (1 H, d, J = 8.6 Hz), 8.31–8.23 (1 H, br), 8.18 (1 H, d, J = 8.2 Hz), 8.09 (1 H, d, J = 8.2 Hz), 7.69 (1 H, d, J = 7.8 Hz), 7.61 (1 H, t, J = 7.6 Hz), 7.57 (1 H, t, J = 7.9 Hz), 7.56 (1 H, t, J = 7.5 Hz), 7.53–7.46 (1 H, br), 7.31 (1 H, s), 7.16 (1 H, d, J = 7.6 Hz), 5.25 (1 H, s), 3.88 (1 H, d, J = 21.2 Hz), 3.79 (1 H, d, J = 21.5 Hz), 2.29 (2 H, m), 1.93 (1 H, m), 1.76 (1 H, m), 1.62–1.50 (3 H, m), 1.43 (1 H, br); ^{13}C NMR ($CDCl_3$, 150 MHz, 25 °C) δ 132.7, 130.6, 130.5, 129.9, 129.87, 128.1, 128.0, 127.7, 126.9, 126.5, 125.6, 124.1, 123.6, 121.2,

32.6, 30.3, 28.1, 23.1, 22.7; ^{13}C NMR ($CDCl_3$, 150 MHz, –40 °C) δ 142.8, 142.6, 138.6, 136.6, 135.2, 133.3, 132.3, 132.2, 132.1, 131.3, 130.6, 130.2, 130.1, 129.93, 129.88, 129.3, 129.0, 128.0, 127.9, 127.6, 127.4, 127.2, 127.0, 126.8, 126.7, 126.4, 126.3, 52.1, 43.6, 32.3, 32.2, 31.6, 29.96, 29.89, 28.1, 27.6, 22.8, 22.7, 22.5; HRMS (ESI/Orbitrap) *m*/*z* $[M]^+$ calcd for $C_{28}H_{22}Br_2$ 516.0083, 518.0062, 520.0042; found 516.0097, 518.0087, 520.0030.

Alternatively, compound **3** (0.100 g, 0.193 mmol) was taken up in 2 mL of toluene and heated at 150 °C for 24 h in the presence of a catalytic amount of acetic acid (4 drops) to produce **4** (0.092 g, 0.18 mmol, 92% yield) as a white solid.

*Isolation of **5***. From the reaction mixture for the preparation of **4**, an aliquot of 0.1 mL was removed within 2 h and concentrated in vacuo. The resulting product without further purification was identified as **5**: IR 1377, 1261, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.33 (1 H, dd, *J* = 8.8, 1.5 Hz), 8.22 (1 H, d, *J* = 8.4 Hz), 8.09 (1 H, d, *J* = 8.2 Hz), 7.79 (1 H, d, *J* = 7.6 Hz), 7.73 (1 H, d, *J* = 7.6 Hz), 7.63–7.52 (4 H, m), 7.40 (1 H, ddd, *J* = 8.2, 6.8, 1.2 Hz), 7.33 (1 H, d, *J* = 7.6 Hz), 7.16 (1 H, dd, *J* = 7.6, 0.9 Hz), 6.76 (1 H, s), 5.68 (1 H, t, *J* = 4.2 Hz), 4.17 (2 H, s), 2.46 (2 H, m), 2.20 (2 H, m), 1.69 (2 H, quintet, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 139.0, 136.6, 135.3, 135.1, 133.6, 133.4, 132.0, 131.8, 129.6, 129.2, 127.9, 127.5, 127.09, 127.07, 127.0, 126.9, 126.8, 126.5, 125.6, 124.4, 121.4, 121.3, 120.5, 36.3, 27.8, 26.4, 23.0; HRMS (ESI/Orbitrap) *m*/*z* $[M]^+$ calcd for $C_{28}H_{22}Br_2$ 516.0083, 518.0062, 520.0042; found 516.0090, 518.0069, 520.0033.

Compound **5** was taken up in dry toluene and heated in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ at 150 °C for 24 h to produce **4**.

*Preparation of **8***. To a 25 mL pressure vessel was added a solution of **3** (2.44 g, 4.71 mmol) and $BF_3{\cdot}OEt_2$ (1.0 mL, 8.1 mmol) in 2 mL of dry toluene under an argon atmosphere. The reaction mixture was stirred at 150 °C for 24 h before it was cooled to rt. Toluene was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 5:95) to afford **8** (2.00 g, 3.87 mmol, 82% yield) as a brown solid: IR 1727, 1444, 1252, 756 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (1 H, dd, *J* = 8.6, 0.7 Hz), 8.53 (1 H, s), 8.39 (1 H, dd, *J* = 8.0, 1.9 Hz), 8.27 (1 H, dd, *J* = 7.4, 1.3 Hz), 7.95 (1 H, d, *J* = 7.5 Hz), 7.71 (1 H, ddd, *J* = 8.3, 7.0, 1.5 Hz), 7.66 (1 H, ddd, *J* = 8.2, 7.0, 1.3 Hz), 7.61 (1 H, ddd, *J* = 8.1, 6.8, 1.2 Hz), 7.36 (1 H, s), 7.34 (1 H, ddd, *J* = 8.3, 6.7, 1.1 Hz), 7.23–7.20 (2 H, m), 3.16 (2 H, t, *J* = 6.5 Hz), 2.48 (1 H, dt, *J* = 17.3, 6.5 Hz), 2.21 (1 H, dt, *J* = 17.3, 6.2 Hz), 1.87 (2 H, quintet, *J* = 6.2 Hz), 1.76–1.64 (2 H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.1, 137.0, 136.3, 135.5, 133.7, 132.3, 131.0, 129.99, 129.93, 129.90, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.3, 127.23, 127.22, 126.2, 122.8, 122.7, 121.2, 30.9, 28.0, 23.2, 22.9; HRMS (ESI/FT-ICR) *m*/*z* $[M]^+$ calcd for $C_{28}H_{20}Br_2$ 513.9926, 515.9906, 517.9885; found 513.9934, 515.9914, 517.9891.

*Preparation of **9***. To a 25 mL flask containing **8** (0.100 g, 0.194 mmol) in chlorobenzene (2 mL) was added DDQ (0.265 g, 1.17 mmol). The reaction mixture was heated at 150 °C for 4 h before it was cooled to rt. Dichloromethane (100 mL) was added, and the solution was immediately passed through a basic alumina column (7.0 cm high, 2.5 cm in diameter), and the column was further eluted with 100 mL of dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 1:9) to produce **9** (0.085 g, 0.17 mmol, 88% yield) as a yellow solid: IR 1503, 1374, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (1 H, s), 8.95 (1 H, d, *J* = 8.2 Hz), 8.44 (1 H, d, *J* = 8.7 Hz), 8.31 (1 H, d, *J* = 7.8 Hz), 8.20 (1 H, d, *J* = 8.2 Hz), 8.03 (1 H, d, *J* = 7.8 Hz), 7.79 (1 H, t, *J* = 7.8 Hz), 7.72 (1 H, t, *J* = 7.6 Hz), 7.64–7.54 (3 H, m), 7.39 (1 H, d, *J* = 7.8 Hz), 7.36–7.24 (3 H, m), 7.09 (1 H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 134.5, 133.8, 132.2, 131.7, 131.6, 131.4, 130.1, 129.7, 129.6, 129.4, 128.79, 128.76, 128.4, 128.0, 127.9, 127.62, 127.58, 127.3, 126.9, 126.58, 126.56, 126.1, 123.3, 123.1, 122.9, 122.5; HRMS (ESI/Orbitrap) *m*/*z* $[M]^+$ calcd for $C_{28}H_{16}Br_2$ 509.9613, 511.9593, 513.9572; found 509.9629, 511.9600, 513.9565.

Recrystallization of **9** from a mixture of chloroform and hexanes produced a single crystal suitable for X-ray structure analysis.

*Preparation of **10***.[5] To a 25 mL flask containing **9** (0.070 g, 0.14 mmol) in THF (2 mL) at –78 °C was added butyllithium (0.13 mL, 2.5 M in hexanes, 0.33 mmol). The reaction mixture was stirred at –78 °C for 1 h and then treated with 0.5 mL of a 1.0 M aqueous HCl solution before it was warmed to rt. The reaction mixture was extracted with ethyl acetate (2 × 25 mL). The combined organic layers were washed with a saturated aqueous Na_2CO_3 solution and dried over $MgSO_4$. After passing through a short silica gel column, the solvent was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 5:9.5) to produce **10** (0.043 g, 0.12 mmol, 86% yield) as a pale yellow solid: IR 1734, 1505, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (1 H, s), 8.96 (1 H, d, *J* = 8.2 Hz), 8.22 (1 H, d, *J* = 8.4 Hz), 8.07 (1 H, d, *J* = 8.2 Hz), 8.01 (1 H, d, *J* = 8.3 Hz), 7.79 (1 H, dd, *J* = 7.6, 1.3 Hz), 7.75–7.68 (2 H, m), 7.62 (1 H, ddd, *J* = 8.2, 7.2, 1.2 Hz), 7.57–7.52 (2 H, m), 7.48 (1 H, ddd, *J* = 8.2, 6.7, 1.3 Hz), 7.43–7.38 (2 H, m), 7.32 (1 H, ddd, *J* = 8.7, 6.5, 1.2 Hz), 7.24–7.19 (2 H, m), 7.11 (1 H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.6, 135.4, 133.7, 133.5, 131.60, 131.56, 131.54, 130.6, 129.6, 129.1, 128.63, 128.58, 128.55, 128.2, 128.1, 127.2, 127.1, 127.0, 126.7, 126.5, 126.3, 126.0, 125.9, 125.63, 125.58, 125.56, 123.1, 121.9; HRMS (ESI/FT-ICR) *m*/*z* $[M]^+$ calcd for $C_{28}H_{18}$ 354.1403; found 354.1413.

*Preparation of **12***. A 500 mL flask containing **4** (0.575 g, 1.11 mmol) and 2,2′-bipyridyl (0.423 g, 2.71 mmol) was flushed with nitrogen. The flask was then placed in a glovebox before $Ni(cod)_2$ (0.739 g, 2.69 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox. THF (110 mL) was introduced via cannula, and the reaction mixture was heated at reflux for 24 h before it was cooled to rt. The reaction mixture was passed through a silica gel column (10 cm high, 1.5 cm in diameter), and the column was further eluted with ethyl acetate (150 mL) and dichloromethane (150 mL). The combined eluates were concentrated, and the residue was used in the next step without further purification. To the flask containing the residue was added DDQ (0.500 g, 2.20 mmol). The flask was flushed with nitrogen, and chlorobenzene (3 mL) was added by using a syringe. The reaction mixture was heated at 130 °C for 4 h before it was cooled to rt. Dichloromethane (100 mL) was added, and the solution was immediately passed through a basic alumina column (7.0 cm high, 2.5 cm in diameter), and the column was further eluted with dichloromethane (100 mL). The combined eluates were concentrated, and the residue was purified by flash column

chromatography (silica gel/ethyl acetate:hexanes = 1:9) to produce **12** (0.020 g, 0.028 mmol, 5% yield) as a white solid: mp >230 °C; IR 1725, 1459, 1263, 762 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.38 (2 H, s), 9.08 (2 H, dd, J = 8.3, 1.0 Hz), 8.42 (2 H, dd, J = 8.5, 1.3 Hz), 8.34 (2 H, dd, J = 8.4, 1.3 Hz), 8.21 (2 H, dd, J = 7.8, 1.3 Hz), 7.82 (2 H, ddd, J = 8.3, 7.0, 1.3 Hz), 7.72 (2 H, ddd, J = 7.8, 7.0, 1.0 Hz), 7.70 (2 H, ddd, J = 8.4, 6.6, 1.3 Hz), 7.66 (2 H, ddd, J = 8.5, 6.6, 1.3 Hz), 7.42 (2 H, dd, J = 8.6, 1.3 Hz), 7.31 (2 H, d, J = 7.2 Hz), 7.27 (2 H, dd, J = 8.3, 1.4 Hz), 7.15 (2 H, ddd, J = 8.3, 6.8, 1.4 Hz), 7.14 (2 H, d, J = 7.2 Hz), 7.10 (2 H, ddd, J = 8.3, 6.8, 1.3 Hz), 4.87 (2 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.9, 138.1, 137.3, 136.3, 135.44, 135.39, 131.7, 131.3, 130.7, 130.5, 130.4, 130.3, 129.7, 129.1, 128.8, 127.74, 127.69, 127.3, 127.1, 126.9, 126.50, 126.45, 126.1, 125.90, 125.83, 125.81, 123.6, 121.7; HRMS (ESI/FT-ICR) m/z $[M]^+$ calcd for $C_{56}H_{32}$ 704.2499; found 704.2504.

Recrystallization of **12** from a mixture of chloroform and hexanes produced a single crystal suitable for X-ray structure analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Tables listing crystal data and structure refinement for **9** and **12**; UV–visible and fluorescence spectra of **10** and **12**; cyclic voltammograms of **10** and **12**; ^1H and ^{13}C NMR spectra of all new compounds (PDF)
X-ray crystallographic file for **9** (CIF)
X-ray crystallographic file for **12** (CIF)

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Notes

The authors declare no competing financial interest.

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