Supporting Information

Facile Three-Step Synthesis and Photophysical Properties of [8]-, [9]-, and [12]Cyclo-1,4-naphthalene Nanorings via Platinum-Mediated Reductive Elimination

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**General.** All the air-sensitive reactions were carried out in a dry vessel under argon atmosphere. NMR spectra were collected on a Bruker BioSpin (\(^1\)H 400 MHz, \(^{13}\)C 100 MHz) spectrometer for CDCl\(_3\) solution of a sample. Chemical shift values were expressed in parts per million (ppm) relative to CDCl\(_3\) (\(\delta\) 7.26 ppm for \(^1\)H NMR). Flash chromatography was performed on silica gel (200~300 mesh) and preparative thin-layer chromatography (PTLC) were performed using silica gel GF254 precoated plates. High-resolution MALDI-TOF mass spectra were measured on a Bruker Daltonics Inc. LTQ Orbitrap XL hybrid Fourier Transform high-resolution Mass Spectrometer. UV-vis spectra were collected on a UNIC-3802 spectrophotometer in standard glass cuvettes.

**Materials.** All reagents such as 1-bromonaphthalene (C\(_{10}\)H\(_7\)Br, 96%), 2-methyl-1-(phenylmethyl)-1H-imidazole (C\(_{10}\)H\(_9\)BO\(_2\), 98%), triphenylphosphine (PPh\(_3\), 99%), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl\(_2\), 99%), potassium carbonate (K\(_2\)CO\(_3\), 99%), bis(pinacolato)diboron (C\(_{12}\)H\(_{24}\)B\(_2\)O\(_4\), 98%), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\(_3\))\(_4\), 99%), sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\), 99%), potassium acetate (C\(_2\)H\(_3\)KO\(_2\), 92%), cesium fluoride (CsF, 99%), and bromine (Br\(_2\), 99.5%) were obtained from Alfa Aesar or Sigma Aldrich and used without further purification. All organic solvents (THF, Toluene, CHCl\(_3\), MeOH, EtOH, Et\(_2\)O and 1,4-dioxane) were purchased from China Medicine Shanghai Chemical Reagent Co. and distilled under nitrogen prior to use. Dichloro(1,5-cyclooctadiene)platinum (Pt(COD)Cl\(_2\)) and 1,4-dibromonaphthalene (C\(_{10}\)H\(_6\)Br\(_2\)) were synthesized as reported. \(^{S1,2}\)
Synthesis of 1,1′-binaphthyl and 4,4′-dibromo-1,1′-binaphthyl. 1,1′-binaphthyl and 4,4′-dibromo-1,1′-binaphthyl were prepared according to the published procedures.\textsuperscript{S3}

Synthesis of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2). To a mixture of 1 (500 mg, 1.2 mmol), bis(pinacolato)diboron (925 mg, 3.6 mmol), Pd(dppf)Cl\textsubscript{2} (50 mg, 0.07 mmol) and anhydrous potassium acetate (600 mg, 6.1 mmol) in a round-bottom flask (50 ml) was added anhydrous 1, 4-dioxane (20 ml). The solution was bubbled with argon for 0.5 h before heated to 100 °C for 36 h. Upon cooling to room temperature, the solvent was removed under vacuum and the resulting product was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The organics was washed thoroughly with water, dried over anhydrous MgSO\textsubscript{4}, and then evaporated to dryness. The residue was purified by chromatography on a silica gel column with CH\textsubscript{2}Cl\textsubscript{2}/petroleum ether (1:5) as eluent. Yield 0.58 g (94%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) (ppm) 8.86 (d, \(J = 8\) Hz, 2H), 8.18 (d, \(J = 8\) Hz, 2H), 7.51 (t, 2H), 7.47 (d, \(J = 8\) Hz, 2H), 7.36 (d, \(J = 8\) Hz, 2H), 7.24 (d, \(J = 8\) Hz, 2H), 1.47 (s, 24H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 142.25, 137.12, 135.22, 132.64, 128.72, 127.03, 126.93, 126.40, 125.74, 83.95, 25.13 ppm; MS (ESI) \(m/z\) calcd. for C\textsubscript{32}H\textsubscript{36}B\textsubscript{2}O\textsubscript{4} [M+H]+: 507.2878, found: 507.2504.
Synthesis of [8]CN. 2 (100 mg, 0.20 mmol), CsF (120 mg, 0.86 mmol), and Pt(COD)Cl₂ (74 mg, 0.20 mmol) were dispersed in anhydrous THF (30 mL). Then, the mixture was heated and stirred for 24 h under an argon atmosphere. Thereafter, 20 mL of MeOH was added and a precipitate formed. Filtration was carried out and the resulting solid was dried in vacuum oven. This anhydrous solid material was transferred to a 50-mL oven dried Schlenk flask containing a magnetic stirring bar and triphenylphosphine (520 mg, 1.98 mmol), to which toluene (20 mL) was added. The mixture was bubbled with argon for 0.5 h before heated to reflux for another 36 h. Upon cooling to room temperature, the solvent was evaporated and the resulting product was redissolved in CH₂Cl₂ and passed through a short silica gel column, then further purified by preparative thin-layer chromatography using hexane/CH₂Cl₂ as the eluent (v/v, 4:1), giving [8]CN (1.3 mg) in 2.6% yield. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 6.92 (s, 16H), 7.52-7.60 (m, 16H), 8.47-8.55 (m, 16H) (Figure S11); HRMS (MALDI-TOF) m/z calcd. for C₈₀H₄₈[M]⁺: 1008.3756, found: 1008.3793 (Figure S7).

Synthesis of 1,1’:4’,1″-ternaphthalene and 4,4″-dibromo-1,1’:4’,1″-ternaphthalene. The general procedure above was used to synthesis 1,1’:4’,1″-ternaphthalene and 4,4″-dibromo-1,1’:4’,1″-ternaphthalene.²³
Synthesis of 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1′′-ternaphthalene (5). To a mixture of 4 (830 mg, 1.5 mmol), bis(pinacolato)diboron (940 mg, 3.7 mmol), Pd(dppf)Cl$_2$ (60 mg, 0.08 mmol) and anhydrous potassium acetate (900 mg, 9.2 mmol) in a round-bottom flask (50 ml) was added dried DMF (15 ml). The solution was bubbled with argon for 0.5 h before heated to 120 °C for 36 h. Upon cooling to room temperature, the solvent was removed under vacuum and the resulting product was extracted with CH$_2$Cl$_2$. The organics was washed thoroughly with water, dried over anhydrous MgSO$_4$, and then evaporated to dryness. The residue was purified by chromatography on a silica gel column with CH$_2$Cl$_2$/petroleum ether (1:5) as eluent. Yield 0.93 g (95%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.91 (d, $J$ = 8 Hz, 2H), 8.25 (d, $J$ = 8 Hz, 2H), 7.64 (d, $J$ = 8 Hz, 2H), 7.60-7.52 (m, 6H), 7.47-7.42 (m, 2H), 7.34 (t, 2H), 7.20-7.26 (m, 2H), 1.49 (s, 24H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 142.19, 138.64, 137.21, 135.31, 132.91, 132.85, 128.80, 127.37, 127.21, 127.12, 126.97, 126.46, 125.97, 125.82, 84.00, 25.17 ppm; HRMS (ESI) m/z calcd. for C$_{42}$H$_{42}$B$_2$O$_4$ [M+H]$^+$: 633.3347, found: 633.3345.

Synthesis of [9]CN and [12]CN. The general procedure above for [8]CN was used with the exception that 5 (125 mg, 0.20 mmol) was used in place of 2 to afford [9]CN (2.1 mg) in 2.9% yield and [12]CN (2.6 mg) in 3.5% yield. [9]CN: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ (ppm) 6.23 (s, 2H), 7.00 (s, 2H), 7.03 (d, $J$ = 8 Hz, 2H), 7.08-7.13 (m, 4H), 7.20 (d, $J$ = 8 Hz, 2H), 7.35 (d, $J$ = 8 Hz, 2H), 7.40 (d, $J$ = 8 Hz, 2H), 7.44 (d, $J$ = 8 Hz, 2H), 7.56-7.62 (m, 4H), 7.66-7.72 (m, 10H), 7.74-7.80 (m, 6H), 8.21-8.25 (m, 2H), 8.40-8.45 (m, 4H), 8.46-8.50 (m, 2H), 8.51-8.55 (m, 4H), 8.57 (d, $J$ = 8 Hz, 2H),
8.72 (d, J = 8 Hz, 2H) (Figure S12); HRMS (MALDI-TOF) m/z calcd. for C_{90}H_{54} [M]^+: 1134.4226, found: 1134.4204 (Figure S8). [12] CN: \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 400 MHz): δ (ppm) 7.27 (s, 24H), 7.58-7.65 (m, 24H), 8.44-8.52 (m, 24H) (Figure S13); HRMS (MALDI-TOF) m/z calcd. for C\textsubscript{120}H\textsubscript{72} [M]^+: 1513.5668, found: 1513.5630 (Figure S9).

References.

Figure S1. $^1$H NMR spectrum of 4,4'$\text{-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-}$$1,1'$-binaphthalene (2) in CDCl$_3$. 
Figure S2. $^{13}$C NMR spectrum of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2) in CDCl$_3$. 
Figure S3. HR-MS (ESI) data for 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2).
Figure S4. $^1$H NMR spectrum of 4,4″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1″-terphenyl (5) in CDCl$_3$. *: signals of residue DMF.
Figure S5. $^{13}$C NMR spectrum of 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1′′-ternaphthalene (5) in CDCl$_3$. 

![NMR spectrum of 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1′′-ternaphthalene (5) in CDCl$_3$.](image)
Figure S6. HR-MS (ESI) data for 4,4″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1″-terphenyl (5).
Figure S7. HRMS (MALDI-TOF) data for [8]CN.
Figure S8. HRMS (MALDI-TOF) data for [9]CN.
Figure S9. HRMS (MALDI-TOF) data for [12]CN.
Figure S10. HRMS (MALDI-TOF) data for [10]CN.
Figure S11. $^1$H NMR spectrum of [8]CN in CDCl$_3$. 
**Figure S12.** $^1$H NMR spectrum of [9]CN in DMSO-$d_6$. 
Figure S13. $^1$H NMR spectrum of [12]CN in CD$_2$Cl$_2$. 

![NMR spectrum](image)

Figure S13. $^1$H NMR spectrum of [12]CN in CD$_2$Cl$_2$. 

![NMR spectrum](image)