

Supporting Information

Aromaticity and π -bond covalency: Prominent
intermolecular covalent bonding interaction of a Kekulé
hydrocarbon with very large singlet biradical character

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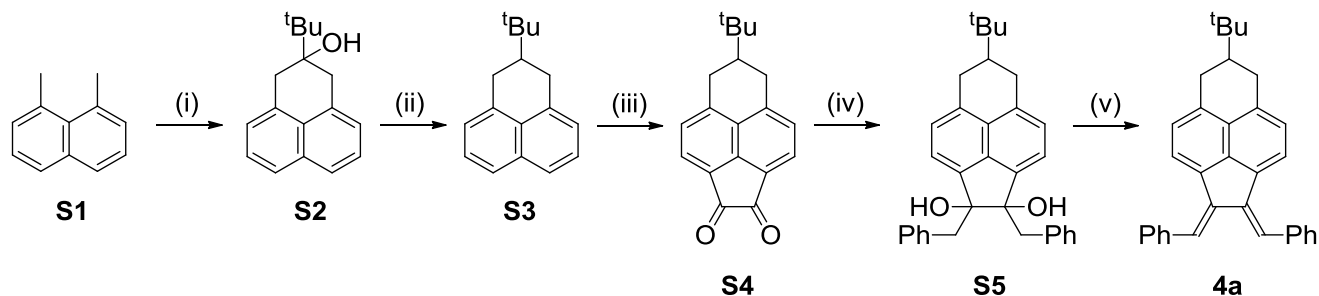
Experimental Section.

Material and Methods. All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under an argon atmosphere in well-dried glassware. Dried solvents were prepared by distillation under argon. Dichloromethane and toluene were dried and distilled over calcium hydride. Column chromatography was performed with silica gel [Wako gel C-200 (Wako)]. Infrared spectra were recorded on a JASCO FT/IR-660M spectrometer. Electronic spectra were measured by a Shimadzu UV-3100PC spectrometer. ^1H spectra were obtained on JEOL EX-270 spectrometers. FAB mass spectra were taken by using JEOL JMS SX-102 mass spectrometers. Data collection for X-ray crystal analysis was performed on Rigaku/Varimax diffractometer (Mo-K α , $\lambda = 0.71069 \text{ \AA}$). The structure was solved with direct methods and refined with full-matrix least squares. The temperature dependent polarized reflection spectra in infrared and visible region were observed using two spectrometers combined with a microscope: FT-IR spectrometer, Nicolet Magna 760 (600–12000 cm^{-1}) and multi-channel detection system, Atago Macs 320 (11000–30000 cm^{-1}). The absolute reflectivity was determined by comparing the reflected light from a gold mirror and silicon single crystal, respectively. The single crystal was fixed with silicon grease on a copper sample holder, and the crystal face was adjusted so as to be normal the incident light by use of goniometer head.

Computational methods. DFT calculation was performed with the Gaussian 03 program.^[1] Geometry optimization was carried out at the B3LYP level of density functional theory with the 6-31G** basis set.

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Synthesis of 1,2-Dibenzylidene-6-*tert*-butyl-2,5,6,7-tetrahydrocyclopenta[*cd*]phenalene (4a).



Scheme S1. Synthesis of **4a**. Reaction conditions: (i) BuLi, TMEDA, 65 °C, then ^tBuCO₂Et, -20 °C to rt, 47%. (ii) Et₃SiH, TFA, CH₂Cl₂, rt, 73%. (iii) (COCl)₂, AlCl₃, rt, 63%. (iv) PhCH₂MgCl, THF, rt, 69%. (v) TsOH•H₂O, toluene, 90 °C, quant.

2-(*tert*-Butyl)-2,3-dihydro-2-hydroxyphenalene (S2). To a solution of 1,8-dimethylnaphthalene (**S1**) (16.226 g, 103.9 mmol) in TMEDA (34.3 mL, 228.5 mmol) was added butyllithium (1.6 M in hexane, 142.8 mL, 228.5 mmol), and the reaction mixture was heated to 60 °C for 3 h. After cooling to -20 °C, ether (100 mL) and ethyl pivalate (23.7 mL, 156 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 12 h. After addition of water and 2N hydrochloric acid, the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layers were washed with saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, and filtered. After column chromatography on silica gel (dichloromethane), **S2** (11.719 g, 47%) was obtained as colorless powder. mp 146–147 °C. TLC *R_f* 0.42 (dichloromethane). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 3.32 (d, *J* = 15.5 Hz, 2H), 3.15 (d, *J* = 15.5, 2H), 1.16 (s, 9H). EI-MS *m/z* 240 (M⁺). IR (KBr) 3585 cm⁻¹. Anal. Calcd for C₁₇H₂₀O: C, 84.96; H, 8.39. Found: C, 84.84; H, 8.38.

2-(*tert*-Butyl)-2,3-dihydrophenalene (S3). To a solution of **S2** (11.719 g, 48.76 mmol) in dichloromethane (200 mL) and trifluoroacetic acid (20 mL), triethylsilane (8.57 mL, 53.64 mmol) was added, and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was washed with water, saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, and filtered. After column chromatography on silica gel (hexane), **S3** (8.018 g, 73%) was obtained as light greenish yellow powder. mp 84–85 °C. TLC *R_f* 0.30 (hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.22 (d, *J* = 6.9 Hz, 2H), 3.14 (dd, *J* = 15.6, 3.4 Hz, 2H), 2.86 (dd, *J* = 15.6, 12.7, 2H), 1.80 (tt, *J* = 12.7, 3.4, 2H), 1.05 (s, 9H). EI-MS *m/z* 224 (M⁺). Anal. Calcd for C₁₇H₂₀: C, 91.01; H, 8.99. Found: C, 90.91; H, 9.00.

6-(tert-Butyl)-6,7-dihydro-1,2-dioxo-5H-cyclopenta[cd]phenalene (S4). To a solution of **S3** (8.018 g, 35.74 mmol) in oxalyl dichloride (4.60 mL, 53.6 mmol) and dichloromethane (80 mL) cooled to $-20\text{ }^{\circ}\text{C}$, aluminum chloride (11.411 g, 85.58 mmol) was added and the reaction mixture was allowed to warm to room temperature over 6 h. After the reaction mixture was poured into ice-cold water, 2N hydrochloric acid was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered. After column chromatography on silica gel (dichloromethane), **S4** (4.764 g, 63%) was obtained as a strong yellow powder. mp $288\text{ }^{\circ}\text{C}$ (dec.). TLC R_f 0.24 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.2$ Hz, 2H), 7.54 (d, $J = 7.2$ Hz, 2H), 3.30 (dd, $J = 16.3, 3.4$ Hz, 2H), 2.97 (dd, $J = 16.3, 12.5$ Hz, 2H), 1.91 (tt, $J = 12.5, 3.4$ Hz, 1H), 1.11 (s, 9H). EI-MS m/z 278 (M^+). IR (KBr) 1717 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52. Found: C, 81.73; H, 6.47.

1,2-Dibenzyl-6-tert-butyl-2,5,6,7-tetrahydro-1,2-dihydroxycyclopenta[cd]phenalene (S5). To a solution of benzyl magnesium chloride in tetrahydrofuran (100 mL), freshly prepared from magnesium (972 mg, 40.0 mmol) and benzyl chloride (3.45 mL, 30.0 mmol), **S4** (2.784 g, 10.00 mmol) was added, and the reaction mixture was stirred at room temperature for 14 h. After addition of water and 2N hydrochloric acid, the reaction mixture was extracted with ether. The organic layers were washed with saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered and concentrated *in vacuo*. The resulting solid was washed with dichloromethane–hexane to give **S5** (3.188 g, 69%) as a colorless powder. mp $212\text{--}215\text{ }^{\circ}\text{C}$. TLC R_f 0.12 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.21 (m, 6H), 7.09–7.03 (m, 6H), 6.49 (d, $J = 6.8$ Hz, 1H), 6.47 (d, $J = 7.1$ Hz, 1H), 3.484 (d, $J = 13.7$ Hz, 1H), 3.477 (d, $J = 13.7$ Hz, 1H), 3.15–3.06 (m, 2H), 2.87–2.74 (m, 2H), 2.804 (d, $J = 13.7$ Hz, 1H), 2.796 (d, $J = 13.7$ Hz, 1H), 1.82 (tt, $J = 12.4, 3.0$ Hz, 1H), 1.06 (s, 9H). EI-MS m/z 462 (M^+). IR (KBr) 3417 cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{O}_2$: C, 85.68; H, 7.41. Found: C, 85.33; H, 7.40.

1,2-Dibenzylidene-6-tert-butyl-2,5,6,7-tetrahydrocyclopenta[cd]phenalene (4a). To a solution of **S5** (3.188 g, 6.891 mmol) in toluene (700 mL) was added catalytic amount of *p*-toluenesulfonic acid, and the reaction mixture was heated to reflux for 12 h. After column chromatography on silica gel (toluene), **4a** (3.188 g, 100%) was obtained as a yellow powder. TLC R_f 0.30 (dichloromethane:hexane=1:5(v/v)). ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, 7.6 Hz, 4H), 7.44 (t, 7.6 Hz, 4H), 7.39 (d, 7.6 Hz, 2H) 7.36 (s, 2H), 7.31 (d, $J = 7.3$ Hz, 2H), 7.00 (d, $J = 7.3$ Hz, 2H), 3.06 (dd, $J = 16.2, 3.3$ Hz, 2H), 2.75 (dd, $J = 16.2, 12.3$ Hz, 2H), 1.76 (tt, $J = 12.3, 3.3$ Hz, 1H), 1.02 (s, 9H). EI-MS m/z 426 (M^+).

Synthesis of 2,12-Di-*tert*-butyl-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (3a).

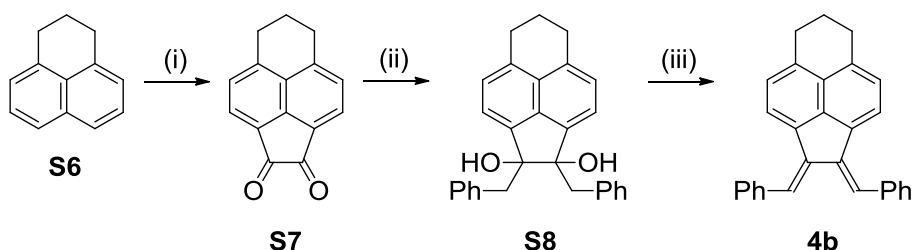
2,12-Di-*tert*-butyl-1,2,3,11,12,13-hexahydro-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthracene[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (5). To a solution of **4a** (3.188 g, 7.473 mmol) and 1,2,4,5-tetrabromobenzene (981 mg, 2.491 mmol) in toluene (200 mL) was added dropwise *n*-Butyl lithium (1.6 M in hexane, 6.23 mL, 9.97 mmol) over 2 h, and the reaction mixture was stirred at room temperature for 12 h. The resulting solid was separated, and the solution was washed with water, 2N hydrochloric acid, saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, and filtered, and the solvent was removed *in vacuo*. The combined solids were added *p*-benzoquinone (673 mg, 6.23 mmol) and toluene (200 mL), and the reaction mixture was refluxed for 2 h. After column chromatography on silica gel (toluene), **5** (924 g, 40%) was obtained as a strong yellow powder. mp > 300 °C. TLC *R_f* 0.78 (dichloromethane:hexane=1:1(v/v)). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 2H) 7.48–7.39 (m, 20H), 7.02 (d, *J* = 7.0 Hz, 4H), 6.65 (d, *J* = 7.0 Hz, 4H), 3.06 (dd, *J* = 15.9, 3.0 Hz, 4H), 2.77 (dd, *J* = 15.9, 12.3 Hz, 4H), 1.80 (tt, *J* = 12.3, 3.0 Hz, 2H), 1.01 (s, 18H). MALDI-TOF MS *m/z* 923 ([M+H]⁺). Anal. Calcd for C₃₃H₃₄O₂: C, 93.67; H, 6.33. Found: C, 93.51; H, 6.18.

2,12-Di-*tert*-butyl-1,2,3,11,12,13-hexahydro-1,3,11-trihydroxy-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (6). To a solution of **5** (540 mg, 0.585 mmol) in acetic acid (75 mL) and benzene (150 mL), Pb₃O₄ (377 mg, 0.550 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was washed with water, saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, and filtered, and the solvent was removed *in vacuo*. The resulting solids were added lithium aluminum hydride (111 mg, 2.92 mmol) and tetrahydrofuran (100 mL), and the reaction mixture was stirred at room temperature for 1 h. After addition of water and 2N hydrochloric acid, the reaction mixture was extracted with dichloromethane. The organic layers were washed with saturated aqueous NaHCO₃ and brine, dried over Na₂SO₄, and filtered. After column chromatography on silica gel [dichloromethane/ethyl acetate (10:1, v/v)], **6** (281 mg, 49%) was obtained as a strong yellowish orange powder. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 2H) 7.52–7.21 (m, 24H), 6.81–6.68 (m, 4H), 5.18–5.11 (m, 3H), 3.10–2.90 (m, 2H), 2.10–2.04 (m, 2H), 1.26 (s, 18H). MALDI-TOF MS *m/z* 971 ([M+H]⁺).

2,12-Di-*tert*-butyl-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (3a). To a solution of **6** (208 mg, 0.214 mmol) in toluene (20 mL) was added catalytic amount of *p*-toluenesulfonic acid, and the reaction mixture was heated to 90 °C for 30 min. After

column chromatography on silica gel (toluene), **3a** (80 mg, 41%) was obtained as a dark grayish purple powder. TLC R_f 0.73 [dichloromethane:hexane (1:1, v/v)],. MALDI-TOF MS m/z 917 ($[M+H]^+$).

Synthesis of 1,2-Dibenzylidene-2,5,6,7-tetrahydrocyclopenta[cd]phenalene (**4b**).



Scheme S2. Synthesis of **4b**. Reaction conditions: (i) $(\text{COCl})_2$, AlCl_3 , rt, 79%; (ii) PhCH_2MgCl , THF, rt, 66%; (iii) $\text{TsOH}\cdot\text{H}_2\text{O}$, toluene, 90 °C, 97%.

6,7-Dihydro-1,2-dioxo-5H-cyclopenta[cd]phenalene (S7). To a solution of 2,3-dihydro-1H-phenalene (**S6**) (8.490 g, 50.47 mmol) in oxalyl dichloride (15.2 mL, 177 mmol) and dichloromethane (85 mL) cooled to -78 °C, aluminum chloride (20.19 g, 151.4 mmol) was added and the reaction mixture was allowed to warm to room temperature over 19 h. After the reaction mixture was poured into ice-cold water, 2N hydrochloric acid was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered. After column chromatography on silica gel (dichloromethane), **S7** (8.88 g, 79%) was obtained as a vivid yellow powder. mp 256 °C (dec.). TLC R_f 0.24 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.2$ Hz, 2H), 7.54 (d, $J = 7.2$ Hz, 2H), 3.23 (d, $J = 6.0$ Hz, 2H), 2.23 (quintet, $J = 6.0$, 2H). EI-MS m/z 222 (M^+). IR (KBr) 1719 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_2$: C, 81.07; H, 4.54. Found: C, 80.91; H, 4.56.

1,2-Dibenzyl-2,5,6,7-tetrahydro-1,2-dihydroxycyclopenta[cd]phenalene (S8). To a solution of benzyl magnesium chloride in tetrahydrofuran (80 mL), freshly prepared from magnesium (1.108 g, 45.59 mmol) and benzyl chloride (3.93 mL, 34.19 mmol), **S7** (2.533 g, 11.40 mmol) was added, and the reaction mixture was stirred at room temperature for 1.5 h. After addition of water and saturated aqueous NH_4Cl , the reaction mixture was extracted with dichloromethane. The organic layers were washed with saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered and concentrated *in vacuo*. The resulting solid was washed with ether–hexane to give **S8** (3.055 g, 66%) as a pale yellow powder. mp 199–204 °C. TLC R_f 0.12 (dichloromethane). ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.22 (m,

6H), 7.10–7.03 (m, 6H), 6.49 (d, $J = 7.0$ Hz, 2H), 3.47 (d, $J = 13.7$ Hz, 2H), 3.11–2.98 (m, 4H), 2.81 (d, $J = 13.7$ Hz, 2H), 2.11 (quintet, $J = 6.0$, 2H). EI-MS m/z 406 (M^+). IR (KBr) 3388 cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2$: C, 85.68; H, 6.45. Found: C, 85.37; H, 6.46.

1,2-Dibenzylidene-2,5,6,7-tetrahydrocyclopenta[*cd*]phenalene (4b). To a solution of **S8** (1.500 g, 3.690 mmol) in toluene (600 mL) was added catalytic amount of *p*-toluenesulfonic acid, and the reaction mixture was heated to reflux for 10 h. After column chromatography on silica gel (toluene), **4b** (1.328 g, 97%) was obtained as a vivid yellow powder. mp 139–141 °C. TLC R_f 0.27 (dichloromethane:hexane=1:5(v/v)). ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 7.6$ Hz, 4H), 7.45 (t, $J = 7.6$ Hz, 4H), 7.40 (s, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.30 (d, $J = 7.3$ Hz, 2H), 7.00 (d, $J = 7.3$ Hz, 2H), 3.01 (t, $J = 5.9$ Hz, 4H), 2.06 (quintet, $J = 5.9$, 2H). EI-MS m/z 370 (M^+). Anal. Calcd for $\text{C}_{29}\text{H}_{22}$: C, 94.01; H, 5.99. Found: C, 94.20; H, 6.05.

Synthesis of 6,8,16,18-Tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (3b).

1,2,3,11,12,13-Hexahydro-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (7). To a solution of **4b** (1.328 g, 3.533 mmol) and 1,2,4,5-tetrabromobenzene (564.5 mg, 1.434 mmol) in toluene (130 mL) was added dropwise butyl lithium (1.6 M in hexane, 1.97 mL, 3.15 mmol) over 2 h, and the reaction mixture was stirred at room temperature for 11 h. The resulting solid was separated, and the solution was washed with water, 2N hydrochloric acid, saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered and concentrated *in vacuo*. The combined solids were added *p*-benzoquinone (673 mg, 6.23 mmol) and toluene (200 mL), and the reaction mixture was refluxed for 2 h. After column chromatography on silica gel (toluene), **7** (924 mg, 40%) was obtained as a vivid yellowish orange powder. mp > 300 °C. TLC R_f 0.75 (dichloromethane:hexane=1:1(v/v)). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 2H), 7.52–7.38 (m, 20H), 7.01 (d, $J = 7.2$ Hz, 4H), 6.64 (d, $J = 7.2$ Hz, 4H), 3.01 (t, $J = 5.7$ Hz, 8H), 2.08 (quintet, $J = 5.7$, 4H). MALDI-TOF MS m/z 811 ($[\text{M}+\text{H}]^+$).

1,11-/1,13-Diacetoxy-1,2,3,11,12,13-hexahydro-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthracene [1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (8). To a solution of **7** (204 mg, 0.250 mmol) in acetic acid (35 mL) and benzene (100 mL) heated to 60 °C, Pb_3O_4 (377 mg, 0.550 mmol) was added, and the reaction mixture was heated to 60 °C for 3.5 h. The reaction mixture was washed with water, saturated aqueous NaHCO_3 and brine, dried over Na_2SO_4 , and filtered. After column chromatography on silica gel

(dichloromethane), **8** (62 mg, 27%) was obtained as a strong yellowish orange powder. TLC R_f 0.26 (dichloromethane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (s, 2H), 7.52–7.36 (m, 20H), 7.29 (d, $J = 7.6$ Hz, 2H), 7.09 (d, $J = 7.3$ Hz, 2H), 6.69 (d, $J = 7.6$ Hz, 2H), 6.66 (d, $J = 7.3$ Hz, 2H), 6.23–6.18 (m, 2H), 3.28–3.21 (m, 2H), 3.05–2.99 (m, 2H), 2.28–2.24 (m, 4H), 2.03 (s, 6H). MALDI-TOF MS m/z 927 ($[\text{M}+\text{H}]^+$). IR (KBr) 1737, 1237 cm^{-1} .

6,8,16,18-Tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (3b). To a solution of **9** (62.0 mg, 0.067 mmol) in toluene (30 mL) heated to 90 °C, catalytic amount of *p*-toluenesulfonic acid monohydrate was added and the reaction mixture was heated at 90 °C for 10 min. The mixture was cooled on ice-bath. The crude product was purified by column chromatography on silica gel (toluene) to give 1,11-/1,13-Dihydro-6,8,16,18-tetraphenyldicyclopenta[*b,i*]anthraceno[1,2,3-*cd*:7,8,9-*c'd'*]diphenalene (**9**) (46.4 mg, 87%) as an air-sensitive dark yellowish brown powder. TLC R_f 0.59 (dichloromethane:hexane=1:1(v/v)). MALDI-TOF MS m/z 807 ($[\text{M}+\text{H}]^+$).

To a solution of **9** (25.7 mg, 0.0318 mmol) in toluene (39 mL) heated at 90 °C, a solution of *p*-benzoquinone (4.8 mg, 0.044 mmol) in toluene (3 mL) was added. The reaction mixture was slowly cooled to room temperature and the resulting crystal was collected and washed with acetone to give **3b** (17.2 mg, 55%) as a black plate. mp >300 °C in a sealed tube. MALDI-TOF MS m/z 804 (M^+).

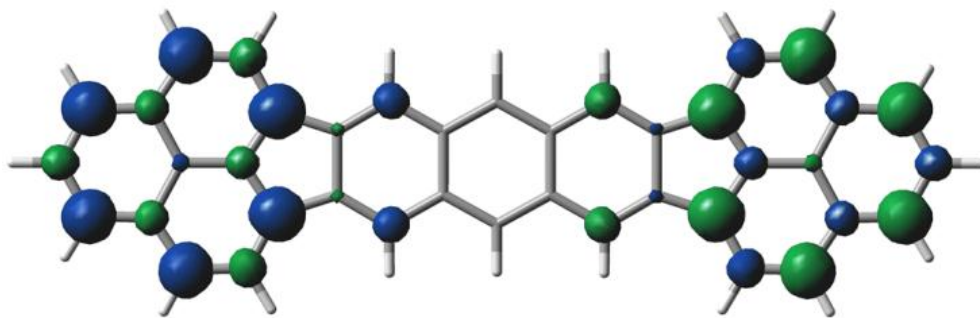


Figure S1. Spin density map for the unsubstituted compound of **3** calculated with a broken-symmetry UB3LYP/6-31G** method. Blue and green surfaces of the spin density maps represent α and β spin densities drawn at 0.004 e/au³ level, respectively.

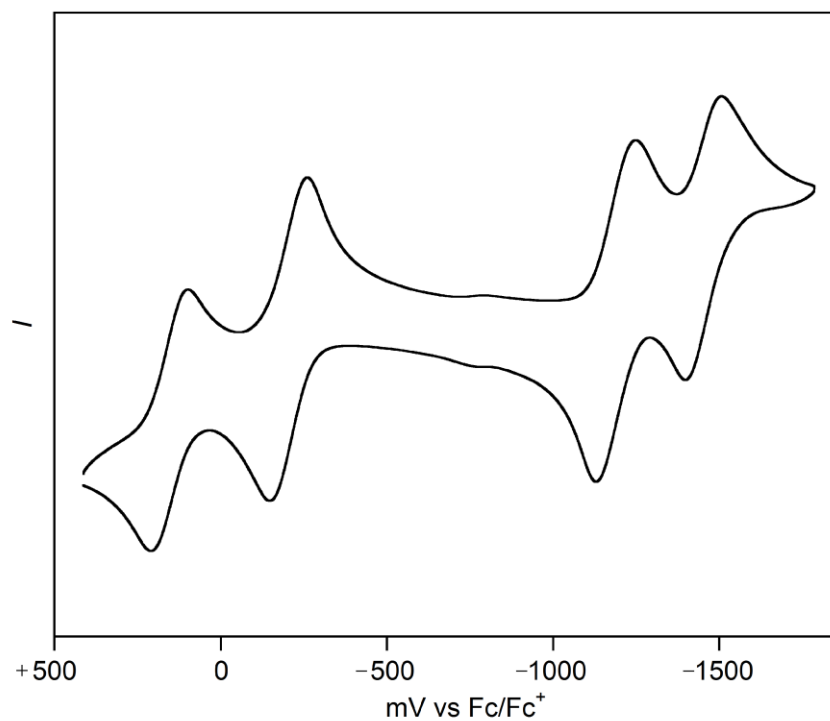


Figure S2. Cyclic voltammogram of **3a**. Conditions; in CH₂Cl₂ at rt, 0.1 M Bu₄NClO₄, working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgNO₃, scan rate = 0.1 V/s.

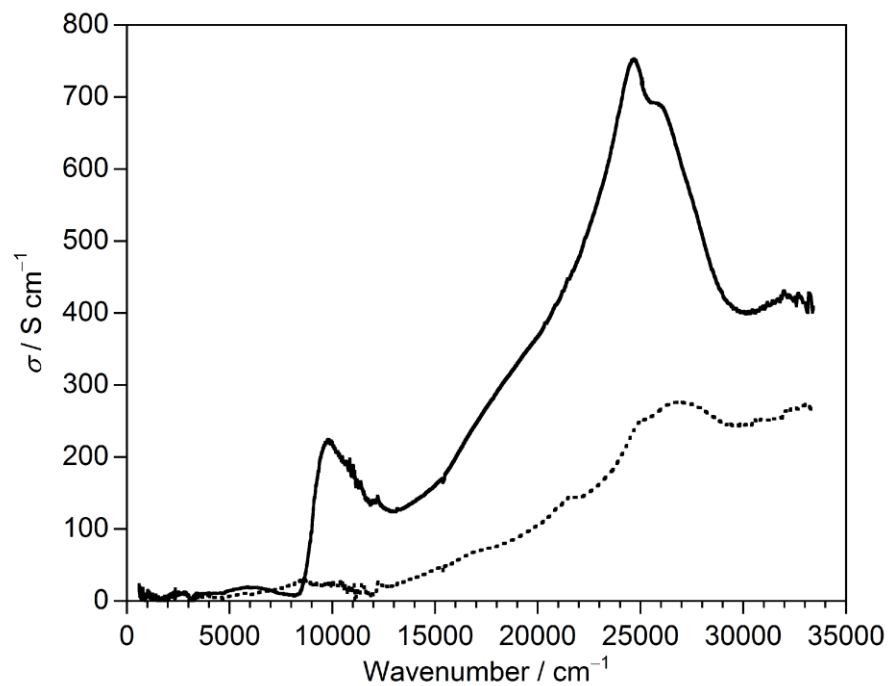


Figure S3. Optical conductivity of **3b** with the light polarized along (solid line) and perpendicular (dashed line) to the *c*-axis.

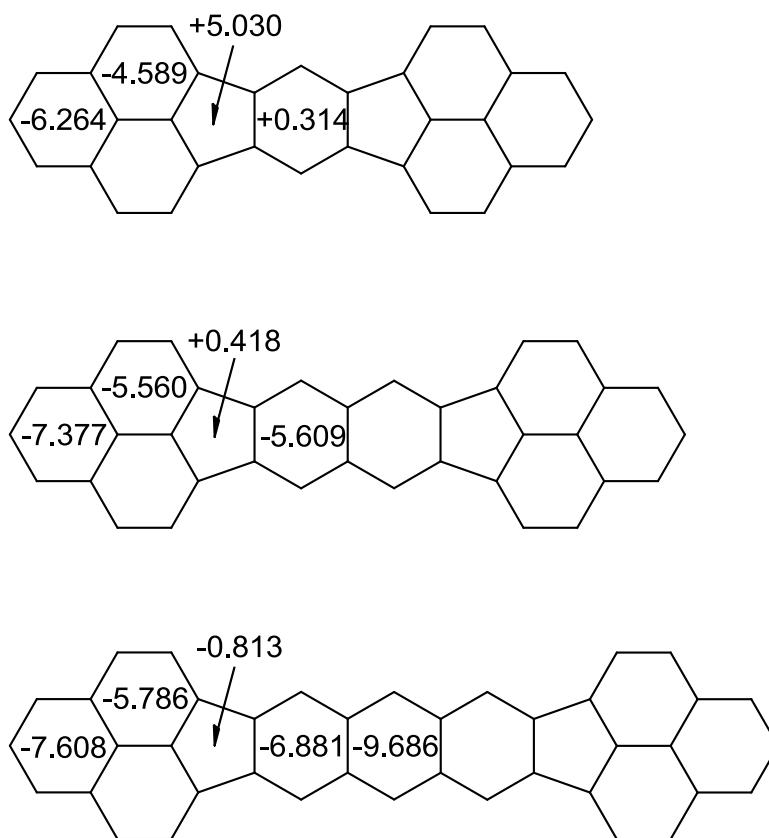


Figure S4. NICS(1) values for unsubstituted compounds of **1** (top), **2** (middle) and **3** (bottom) calculated with the GIAO (gauge-including atomic orbital)-UB3LYP/6-31G** method.

Gaussian Input data

1) RB3LYP/6-31G** calculation for the unsubstituted compound of **3**

#P RB3LYP/6-31G(d,p) opt FormCheck=All Pop=(Reg) SCF=(MaxCycle=200) SCF=Tight

Singlet, closed-shell

	0	1	
C	0.00000	-1.43651	0.00000
C	0.00000	1.43651	0.00000
C	-1.20238	-0.72688	0.00000
C	1.20238	0.72688	0.00000
C	-1.20238	0.72688	0.00000
C	1.20238	-0.72688	0.00000
C	-3.62725	-0.72688	0.00000
C	3.62725	0.72688	0.00000
C	-3.62725	0.72688	0.00000
C	3.62725	-0.72688	0.00000
C	-2.42487	-1.43651	0.00000
C	2.42487	1.43651	0.00000
C	-2.42487	1.43651	0.00000
C	2.42487	-1.43651	0.00000
C	-5.00177	-1.17356	0.00000
C	5.00177	1.17356	0.00000
C	-5.00177	1.17356	0.00000
C	5.00177	-1.17356	0.00000
C	-5.67753	-2.41754	0.00000
C	5.67753	2.41754	0.00000
C	-5.67753	2.41754	0.00000
C	5.67753	-2.41754	0.00000
C	-7.06337	-2.44474	0.00000
C	7.06337	2.44474	0.00000
C	-7.06337	2.44474	0.00000
C	7.06337	-2.44474	0.00000
C	-7.86567	-1.25300	0.00000
C	7.86567	1.25300	0.00000
C	-7.86567	1.25300	0.00000
C	7.86567	-1.25300	0.00000
C	-9.27434	-1.22218	0.00000
C	9.27434	1.22218	0.00000
C	-9.27434	1.22218	0.00000
C	9.27434	-1.22218	0.00000
C	-9.95470	0.00000	0.00000
C	9.95470	0.00000	0.00000
C	-5.79547	0.00000	0.00000
C	5.79547	0.00000	0.00000
C	-7.18819	0.00000	0.00000
C	7.18819	0.00000	0.00000
H	0.00000	-2.52418	0.00000
H	0.00000	2.52418	0.00000
H	-2.42487	-2.52418	0.00000
H	2.42487	2.52418	0.00000
H	-2.42487	2.52418	0.00000
H	2.42487	-2.52418	0.00000
H	-5.12426	-3.35264	0.00000
H	5.12426	3.35264	0.00000
H	-5.12426	3.35264	0.00000
H	5.12426	-3.35264	0.00000
H	-7.57473	-3.40369	0.00000
H	7.57473	3.40369	0.00000
H	-7.57473	3.40369	0.00000
H	7.57473	-3.40369	0.00000
H	-9.83583	-2.15241	0.00000
H	9.83583	2.15241	0.00000
H	-9.83583	2.15241	0.00000
H	9.83583	-2.15241	0.00000
H	-11.04048	0.00000	0.00000
H	11.04048	0.00000	0.00000

2) CASSCF(2,2)/6-31G//RB3LYP/6-31G** calculation for the unsubstituted compound of 3

#P CASSCF(2,2,NRoot=1)/6-31G NOSYMM FormCheck=All Pop=(Reg)
SCF=Tight Guess=(Read)

CASSCF(2,2), Ground State

	0	1	
C	-0.000000	1.400431	0.000000
C	-0.000000	-1.400431	0.000000
C	0.000000	0.727190	1.228418
C	-0.000000	-0.727190	-1.228418
C	-0.000000	-0.727190	1.228418
C	0.000000	0.727190	-1.228418
C	0.000000	0.736245	3.657921
C	-0.000000	-0.736245	-3.657921
C	-0.000000	-0.736245	3.657921
C	0.000000	0.736245	-3.657921
C	0.000000	1.426438	2.466011
C	-0.000000	-1.426438	-2.466011
C	-0.000000	-1.426438	2.466011
C	0.000000	1.426438	-2.466011
C	0.000000	1.177622	5.035174
C	-0.000000	-1.177622	-5.035174
C	-0.000000	-1.177622	5.035174
C	0.000000	1.177622	-5.035174
C	0.000000	2.419671	5.709537
C	-0.000000	-2.419671	-5.709537
C	-0.000000	-2.419671	5.709537
C	0.000000	2.419671	-5.709537
C	0.000000	2.447332	7.095554
C	-0.000000	-2.447332	-7.095554
C	-0.000000	-2.447332	7.095554
C	0.000000	2.447332	-7.095554
C	0.000000	1.253830	7.895842
C	-0.000000	-1.253830	-7.895842
C	-0.000000	-1.253830	7.895842
C	0.000000	1.253830	-7.895842
C	0.000000	1.222546	9.305277
C	-0.000000	-1.222546	-9.305277
C	-0.000000	-1.222546	9.305277
C	0.000000	1.222546	-9.305277
C	0.000000	-0.000000	9.983265
C	0.000000	-0.000000	-9.983265
C	0.000000	-0.000000	5.821954
C	0.000000	-0.000000	-5.821954
C	0.000000	-0.000000	7.218447
C	0.000000	-0.000000	-7.218447
H	-0.000000	2.488607	0.000000
H	-0.000000	-2.488607	0.000000
H	0.000000	2.513909	2.451508
H	-0.000000	-2.513909	-2.451508
H	-0.000000	-2.513909	2.451508
H	0.000000	2.513909	-2.451508
H	0.000000	3.355009	5.156417
H	-0.000000	-3.355009	-5.156417
H	-0.000000	-3.355009	5.156417
H	0.000000	3.355009	-5.156417
H	0.000000	3.405953	7.607516
H	-0.000000	-3.405953	-7.607516
H	-0.000000	-3.405953	7.607516
H	0.000000	3.405953	-7.607516
H	0.000000	2.153159	9.866333
H	-0.000000	-2.153159	-9.866333
H	-0.000000	-2.153159	9.866333
H	0.000000	2.153159	-9.866333
H	0.000000	-0.000000	11.069540
H	0.000000	-0.000000	-11.069540

3) Broken-symmetry UB3LYP/6-31G** calculation for the unsubstituted compound of 3

#P UB3LYP/6-31G(d,p) opt FormCheck=All Pop=(Reg) SCF=(MaxCycle=200)
SCF=Tight Guess=(mix)

Singlet Biradical, Broken Symmetry

	0	1	
C	-0.000000	1.400431	0.000000
C	-0.000000	-1.400431	0.000000
C	0.000000	0.727190	1.228418
C	-0.000000	-0.727190	-1.228418
C	-0.000000	-0.727190	1.228418
C	0.000000	0.727190	-1.228418
C	0.000000	0.736245	3.657921
C	-0.000000	-0.736245	-3.657921
C	-0.000000	-0.736245	3.657921
C	0.000000	0.736245	-3.657921
C	0.000000	1.426438	2.466011
C	-0.000000	-1.426438	-2.466011
C	-0.000000	-1.426438	2.466011
C	0.000000	1.426438	-2.466011
C	0.000000	1.177622	5.035174
C	-0.000000	-1.177622	-5.035174
C	-0.000000	-1.177622	5.035174
C	0.000000	1.177622	-5.035174
C	0.000000	2.419671	5.709537
C	-0.000000	-2.419671	-5.709537
C	-0.000000	-2.419671	5.709537
C	0.000000	2.419671	-5.709537
C	0.000000	2.447332	7.095554
C	-0.000000	-2.447332	-7.095554
C	-0.000000	-2.447332	7.095554
C	0.000000	2.447332	-7.095554
C	0.000000	1.253830	7.895842
C	-0.000000	-1.253830	-7.895842
C	-0.000000	-1.253830	7.895842
C	0.000000	1.253830	-7.895842
C	0.000000	1.222546	9.305277
C	-0.000000	-1.222546	-9.305277
C	-0.000000	-1.222546	9.305277
C	0.000000	1.222546	-9.305277
C	0.000000	-0.000000	9.983265
C	0.000000	-0.000000	-9.983265
C	0.000000	-0.000000	5.821954
C	0.000000	-0.000000	-5.821954
C	0.000000	-0.000000	7.218447
C	0.000000	-0.000000	-7.218447
H	-0.000000	2.488607	0.000000
H	-0.000000	-2.488607	0.000000
H	0.000000	2.513909	2.451508
H	-0.000000	-2.513909	-2.451508
H	-0.000000	-2.513909	2.451508
H	0.000000	2.513909	-2.451508
H	0.000000	3.355009	5.156417
H	-0.000000	-3.355009	-5.156417
H	-0.000000	-3.355009	5.156417
H	0.000000	3.355009	-5.156417
H	0.000000	3.405953	7.607516
H	-0.000000	-3.405953	-7.607516
H	-0.000000	-3.405953	7.607516
H	0.000000	3.405953	-7.607516
H	0.000000	2.153159	9.866333
H	-0.000000	-2.153159	-9.866333
H	-0.000000	-2.153159	9.866333
H	0.000000	2.153159	-9.866333
H	0.000000	-0.000000	11.069540
H	0.000000	-0.000000	-11.069540

4) Triplet UB3LYP/6-31G** calculation for the unsubstituted compound of 3

#P UB3LYP/6-31G(d,p) opt FormCheck=All Pop=(Reg) SCF=(MaxCycle=200)
SCF=Tight

Triplet Biradical

	0	3	
C	-0.000000	1.400431	0.000000
C	-0.000000	-1.400431	0.000000
C	0.000000	0.727190	1.228418
C	-0.000000	-0.727190	-1.228418
C	-0.000000	-0.727190	1.228418
C	0.000000	0.727190	-1.228418
C	0.000000	0.736245	3.657921
C	-0.000000	-0.736245	-3.657921
C	-0.000000	-0.736245	3.657921
C	0.000000	0.736245	-3.657921
C	0.000000	1.426438	2.466011
C	-0.000000	-1.426438	-2.466011
C	-0.000000	-1.426438	2.466011
C	0.000000	1.426438	-2.466011
C	0.000000	1.177622	5.035174
C	-0.000000	-1.177622	-5.035174
C	-0.000000	-1.177622	5.035174
C	0.000000	1.177622	-5.035174
C	0.000000	2.419671	5.709537
C	-0.000000	-2.419671	-5.709537
C	-0.000000	-2.419671	5.709537
C	0.000000	2.419671	-5.709537
C	0.000000	2.447332	7.095554
C	-0.000000	-2.447332	-7.095554
C	-0.000000	-2.447332	7.095554
C	0.000000	2.447332	-7.095554
C	0.000000	1.253830	7.895842
C	-0.000000	-1.253830	-7.895842
C	-0.000000	-1.253830	7.895842
C	0.000000	1.253830	-7.895842
C	0.000000	1.222546	9.305277
C	-0.000000	-1.222546	-9.305277
C	-0.000000	-1.222546	9.305277
C	0.000000	1.222546	-9.305277
C	0.000000	-0.000000	9.983265
C	0.000000	-0.000000	-9.983265
C	0.000000	-0.000000	5.821954
C	0.000000	-0.000000	-5.821954
C	0.000000	-0.000000	7.218447
C	0.000000	-0.000000	-7.218447
H	-0.000000	2.488607	0.000000
H	-0.000000	-2.488607	0.000000
H	0.000000	2.513909	2.451508
H	-0.000000	-2.513909	-2.451508
H	-0.000000	-2.513909	2.451508
H	0.000000	2.513909	-2.451508
H	0.000000	3.355009	5.156417
H	-0.000000	-3.355009	-5.156417
H	-0.000000	-3.355009	5.156417
H	0.000000	3.355009	-5.156417
H	0.000000	3.405953	7.607516
H	-0.000000	-3.405953	-7.607516
H	-0.000000	-3.405953	7.607516
H	0.000000	3.405953	-7.607516
H	0.000000	2.153159	9.866333
H	-0.000000	-2.153159	-9.866333
H	-0.000000	-2.153159	9.866333
H	0.000000	2.153159	-9.866333
H	0.000000	-0.000000	11.069540
H	0.000000	-0.000000	-11.069540