Geodesic-Planar Conjugates: Substituted Buckybowls—Synthesis, Photoluminescence and Electrochemistry

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Syntheses

Dichloromethane and ethyl acetate for column chromatography were distilled prior to use. All experiments requiring inert atmosphere were carried out under nitrogen using Schlenk techniques. All other solvents and all commercially available reagents were used without any prior purification. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Bruker Avance NEO 800, Bruker Avance III 600, Bruker Avance III 400 and JEOL Resonance ECZ 400S. Deuterated solvents were purchased in sealed ampules and dried where necessary according to standard procedures.$^{[1]}$ Structure assignments were done based on 2D-NMR (COSY, HSQC, HMBC, NOESY) experiments. $^1$H-NMR chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents ($C_2D_2Cl_4$ δ H = 5.91 ppm, δ C = 73.78 ppm; CDCl$_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). EI-MS spectra were recorded on a JEOL JMS-Q1500GC with direct insertion probe; HR-EI-MS were recorded on a Waters Micromass GCT TOF spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum 100 ATR unit using compounds in solid state. 4-Bromo-13,16-difluorobenzo[**s**]picene (4) was obtained by double photocyclization of the respective stilbenes according to the procedure described by Papaianina et al.$^{[2]}$ Resulting 4-bromo-13,16-difluorobenzo[**s**]picene (4) and 4-bromo-13,16-difluorobenzo[**s**]picene (4) were purified by repeated precipitation from cold methanol. All stilbene derivatives were used as cis/trans isomeric mixtures as received from the Wittig reaction since the isomers do interconvert under photocyclization conditions. For the aluminum oxide promoted dehydrofluorination reaction, typically 3.0 g of $\gamma$-Al$_2$O$_3$ (neutral, EcoChrom, MP Biomedicals) were activated in Duran glassware at 525 °C for 30 min in vacuum ($10^{-3}$ mbar). After cooling to 250 °C, fluoroarene (50 mg) was added and the reaction was carried out at 280 °C in vacuum ($10^{-3}$ mbar) until full consumption of starting material was evident by EI-MS. After cooling to room temperature, products were transferred to a Soxhlet thimble and extracted using CH$_2$Cl$_2$. Analytically pure products were obtained by precipitation with MeOH from the corresponding CH$_2$Cl$_2$ extract in typical yields of > 90%.
Scheme S1. Enhanced version of Scheme 1 (Synthesis of 1-bromoindacenopicene (Idpc-Br)) of the manuscript showing important synthetic intermediates.

**Suzuki coupling (general procedure A)**

A Schlenk flask purged with nitrogen was charged with Idpc-Br (1 eq.), Pd(PPh₃)₄ (0.01 eq.), sodium carbonate (3 eq.), and the corresponding phenylboronic acid (1.5 eq) in a 1,4-dioxane/H₂O solution. The reaction mixture was degassed by bubbling nitrogen via cannula through the mixture for 15 min. Then, the reaction mixture was heated under reflux conditions until full consumption of starting material was detected by TLC. The solvent was removed under reduced pressure and the residue was dissolved in CH₂Cl₂ (100 mL) and washed with saturated bicarbonate solution (100 mL) and brine (100 mL). The organic phase was dried over magnesium sulfate, filtered, and the residue was purified by silica gel chromatography using PE/CH₂Cl₂ (3:1) as eluent.

**Sonogashira coupling (general procedure B)**

A Schlenk flask purged with nitrogen was charged with Idpc-Br (1 eq.), CuI (0.025 eq.), PdCl₂(PPh₃)₂ (0.05 eq.), diisopropylamine (2 eq.), and the corresponding phenylacetylene (1.20 eq.). THF was added and the mixture was degassed by three freeze-pump-thaw cycles. Afterwards, the reaction mixture was heated to reflux until full consumption of starting material was detected by TLC. The volatiles were removed under reduced pressure and the residue was dissolved in CH₂Cl₂ (100 mL) and brine (100 mL) and washed with saturated bicarbonate solution (100 mL) and brine (100 mL). The organic phase was dried over magnesium sulfate, filtered, and the residue was purified by silica gel chromatography using a mixture of toluene/CH₂Cl₂ (5:2) as eluent.
8a was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh3)4 (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3 eq.) and phenylboronic acid (36.3 mg, 1.5 eq) in a 1,4-dioxan/H2O (14:1) solution (50 mL). Orange solid (67.0 mg, 0.17 mmol, 84%).

1H NMR (600 MHz, C2D2Cl4) δ = 8.05 (d, δJHH = 8.8 Hz, 1H, H10), 8.04 (d, δJHH = 8.9 Hz, 1H, H11), 7.86 (d, δJHH = 8.9 Hz, 1H, H12), 7.74 (d, δJHH = 8.7 Hz, 1H, H9), 7.73 (d, δJHH = 7.2 Hz, 1H, H3), 7.67 (d, δJHH = 6.9 Hz, 1H, H6), 7.64 (bs, 2H, H4 + H5), 7.63 – 7.58 (m, 3H, H8 + H2' + H6'), 7.50 – 7.45 (m, 2H, H3' + H5'), 7.43 – 7.40 (m, 1H, H4'), 7.38 (d, δJHH = 7.2 Hz, 1H, H2) 7.36 (dd, δJHH = 8.2, 7.0 Hz, 1H, H7); 13C NMR (150 MHz, C2D2Cl4) δ = 140.59 (C1), 138.85 (C1'), 138.71 (Cq), 138.54 (Cq), 138.17 (Cq), 138.14 (Cq), 138.02 (Cq), 138.00 (2C, Cq), 137.77 (Cq), 137.05 (Cq), 136.42 (Cq), 129.74 (C10b), 129.69 (C10a), 129.68 (2C, C2' + C6'), 129.00 (C2), 128.94 (C8a), 128.88 (C7), 128.55 (2C, C3' + C5'), 127.69 (C4'), 127.12 (C12a), 126.93 (C9), 126.74 (C8), 126.17 (C12), 125.67 (C5), 125.43 (C4), 124.19 (C10), 123.94 (C11), 123.82 (C3), 123.58 (C6); IR (cm⁻¹) 2891, 1856, 1547, 1480, 1392, 1254, 1137, 1100, 1071, 1011, 940, 799, 781, 752, 704; MS (EI): m/z (rel. int.) = 400 (100%), 323 (40 %); HRMS (EI) m/z Calcd for C32H16 [M⁺]: 400.1252. Found: 400.1256.

8b was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh3)4 (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3.00 eq.) and 4-methoxyphenylboronic acid (45.2 mg, 1.50 eq.) in a 1,4-dioxan/H2O (14:1) solution (50 mL). Orange solid (67.5 mg, 0.16 mmol, 79 %).

1H NMR (600 MHz, C2D2Cl4) δ = 8.03 (d, δJHH = 8.7 Hz, 1H, H10), 8.02 (d, δJHH = 9.0 Hz, 1H, H11), 7.86 (d, δJHH = 8.8 Hz, 1H, H12), 7.72 (d, δJHH = 8.7 Hz, 1H, H9), 7.70 (d, δJHH = 7.2 Hz, 1H, H3), 7.65 (d, δJHH = 6.9 Hz, 1H, H6), 7.61 (s, 2H, H4 + H5), 7.58 (d, δJHH = 8.1 Hz, 1H, H8), 7.55 (d, δJHH = 8.6 Hz, 2H, H2'), 7.34 (dd, δJHH = 8.0, 7.0 Hz, 2H, H2 + H7), 7.02 (d, δJHH = 8.6 Hz, 2H, H3'), 3.84 (s, 3H, OMe); 13C NMR (150 MHz, C2D2Cl4) δ = 159.15 (C4'), 140.26 (C1), 138.71 (Cq), 138.37 (Cq), 138.16 (Cq), 138.08 (Cq), 137.99 (Cq), 137.91 (Cq), 137.70 (Cq), 137.53 (Cq), 137.10 (Cq), 136.38 (Cq), 131.34 (C1'), 130.81 (2C, C2'), 129.66 (C10b), 29.64 (C10a), 128.90 (C8a), 128.83 (C7), 128.59 (C2), 127.19 (C12a), 126.86 (C9), 126.67 (C8), 126.24 (C12), 126.52 (C5), 125.27 (C4), 124.06 (C11), 123.91 (C10), 123.87 (C3), 123.50 (C6), 114.01 (2C, C3'), 55.39 (OMe); 1H NMR (400 MHz, CDCl3) δ = 8.09 (dd, J = 8.5 Hz, 2H, H10 + H11), 7.91 (d, J = 8.8 Hz, 1H, H12), 7.77 (d, J = 8.7 Hz, 1H, H9), 7.74 (d, J = 7.1 Hz, 1H, H3), 7.71 (dd, J = 6.9 Hz, 1H, H6), 7.67 (2H, H4 + H5), 7.64 (d, J = 8.1 Hz, 1H, H8), 7.61 (d,
8c was synthesized according to general procedure A using **Idpc-Br** (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh₃)₄ (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3 eq.) and 4-nitrophenylboronic acid (49.7 mg, 1.5 eq) in a 1,4-dioxane/H₂O (2:1) solution (50 mL). Red solid (73.3 mg, 0.16 mmol, 83 %).

**1H NMR** (600 MHz, C₂D₂Cl₄) δ = 8.31 (d, 3JHH = 8.2 Hz, 2H, H3*), 8.09 – 8.02 (m, 2H, H10 + H11), 7.76 - 7.71 (m, 5H, H3 + H9 + H12 + H2*), 7.68 (d, 3JHH = 6.9 Hz, 1H, H6), 7.65 (s, 2H), 7.61 (d, 3JHH = 8.0 Hz, 1H, H8), 7.38 (d, 3JHH = 7.1 Hz, 1H, H2), 7.37 (dd, 3JHH = 7.9, 6.9 Hz, 1H, H7); **13C NMR** (150 MHz, C₂D₂Cl₄) δ =146.98 (C4*), 145.80 (C1*), 139.44 (C11*), 138.97 (C9), 138.58 (Cq), 138.17 (Cq), 138.03 (Cq), 137.86 (Cq), 137.76 (Cq), 137.52 (Cq), 137.02 (Cq), 136.38 (Cq), 130.41 (C2, C3*), 129.97 (C10b), 129.54 (C2), 129.02 (C7), 129.00 (C10a), 128.19 (C8a), 127.08 (C3), 126.91 (C8), 126.49 (C12a), 125.84 (C2, C4 + C5), 125.11 (C10), 124.96 (C9), 123.91 (C12), 123.82 (C2, C2*), 123.77 (C11), 123.57 (C6); **IR** (cm⁻¹) 3035, 1922, 1730, 1593, 1509, 1421, 1341, 1107, 1012, 953, 861, 837, 823, 801, 782, 753, 702; **MS** (EI): m/z (rel. int.) = 445 (100 %), 399 (30 %), 323 (60 %).

8d was synthesized according to general procedure A using **Idpc-Br** (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh₃)₄ (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3.00 eq.) and 2-fluorophenylboronic acid (41.6 mg, 1.50 eq) in a 1,4-dioxane/H₂O (14:1) solution (50 mL). Orange solid (74.5 mg, 0.18 mmol, 89%)

**1H NMR** (600 MHz, C₂D₂Cl₄) δ = 8.01 (d, 3JHH = 8.7 Hz, 1H, H10), 8.00 (d, 3JHH = 8.9 Hz, 1H, H11), 7.73 - 7.70 (m, 2H, H3 + H9), 7.65 (d, 3JHH = 6.9 Hz, 1H, H6), 7.62 (dd, 3JHH = 8.9, 2.2 Hz, 1H, H12), 7.60 (bs, 2H, H4 + H5), 7.58 (d, 3JHH = 8.1 Hz, 1H, H8), 7.46 (dd, 3JHH = 7.5, 1.7 Hz, 1H, H6*), 7.41 (ddd, J = 9.9, 4.9, 2.3 Hz, 1H, H4*), 7.37 (d, 3JHH = 7.1 Hz, 1H, H2), 7.34 (dd, 3JHH = 8.1, 7.0 Hz, 1H, H7), 7.25 (m, 1H, H5*), 7.21 (m, 1H, H3*); **19F NMR** (375 MHz, C₂D₂Cl₄) δ = -113.88; **13C NMR** (150 MHz, C₂D₂Cl₄) δ = 159.61 (d, J = 247.5
Hz, C2'), 138.70 (Cq), 138.62 (Cq), 138.61 (Cq), 138.13 (Cq), 138.09 (Cq), 138.01 (Cq), 137.94 (Cq), 137.76 (Cq), 136.66 (Cq), 136.39 (Cq), 134.08 (C1), 132.17 (d, J = 3.3 Hz, C6*), 130.18 (C2), 129.79 (C10b), 129.74 (C7), 129.62 (C10a), 128.87 (d, J = 6.8 Hz, C4*), 128.85 (C8a), 127.60 (C12a), 126.90 (C9), 126.75 (C8), 126.27 (d, J = 15.3 Hz, C1*), 125.99 (d, J = 2.3 Hz, C12), 125.64 (C5), 125.57 (C4), 124.29 (d, J = 3.5 Hz, C5*), 124.16 (C11), 123.88 (C10), 123.59 (C6), 123.49 (C3), 115.93 (d, J = 22.2 Hz, C3*); IR (cm⁻¹) 2957, 2874, 1464, 1381, 1251, 1129, 1097, 1073, 1004, 943, 793, 779, 753, 739; MS (EI): m/z (rel. int.) = 418 (100 %), 399 (80 %), 323 (30 %).

8e was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh₃)₄ (2.30 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3.00 eq.) and 2-chlorophenylboronic acid (46.5 mg, 1.50 eq.) in a 1,4-dioxan/H₂O (14:1) solution (50 mL). Orange solid (75.0 mg, 0.17 mmol, 87 %).

¹H NMR (600 MHz, CDCl₃) δ = 8.11 (d, 3JHH = 8.7 Hz, 1H, H10), 8.07 (d, 3JHH = 8.8 Hz, 1H, H11), 7.79 (d, 3JHH = 8.7 Hz, 1H, H9), 7.78 (d, 3JHH = 7.1 Hz, 1H, H3), 7.73 (d, 3JHH = 6.9 Hz, 1H, H6), 7.72 – 7.68 (m, 2H, H4 + H5), 7.65 (d, 3JHH = 8.0 Hz, 1H, H8), 7.59 – 7.56 (m, 1H, H3*), 7.53 (d, 3JHH = 8.8 Hz, 1H, H12), 7.45 – 7.43 (m, 1H, H6*), 7.43 – 7.38 (m, 3H, H7 + H4* + H5*), 7.34 (d, 3JHH = 7.1 Hz, 1H, H2); ¹³C NMR (150 MHz, CDCl₃) δ = 139.17 (Cq), 139.07 (Cq), 139.00 (Cq), 138.80 (Cq), 138.68 (Cq), 138.67 (Cq), 138.60 (Cq), 138.37 (Cq), 138.03 (C1*), 137.91 (C1), 137.00 (Cq), 136.93 (Cq), 133.83 (C2*), 132.30 (C6*), 130.24 (C10b), 130.15 (C10a), 130.03 (C2), 129.99 (C3*), 129.33 (C4*), 129.26 (C8a), 128.94 (C7), 128.01 (C12a), 127.06 (C9), 126.88 (C8), 126.80 (C5*), 126.17 (C12), 125.75 (C5), 125.73 (C4), 124.32 (C11), 124.15 (C10), 123.58 (C6), 123.30 (C3); IR (cm⁻¹) 2923, 2360, 1511, 1412, 1241, 1134, 1015, 960, 821, 808, 756; MS (EI): m/z (rel. int.) = 434 (100 %), 399 (50 %), 323 (30 %).

8f was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh₃)₄ (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3.00 eq.) and 3,5-dimethoxyphenylboronic acid (54.1 mg, 1.5 eq.) in a 1,4-dioxan/H₂O (14:1) solution (50 mL). Orange solid (69.4 mg, 0.16 mmol, 76 %).

¹H NMR (600 MHz, C₂D₂Cl₄) δ = 8.03 (d, 3JHH = 8.8 Hz, 1H, H11), 8.03 (d, 3JHH = 8.8 Hz, 1H, H10) 7.91 (d, 3JHH = 8.9 Hz, 1H, H12), 7.72 (d, 3JHH = 8.7 Hz, 1H, H9), 7.71 (d, 3JHH = 7.3Hz, 1H, H3), 7.66 (d, 3JHH = 6.9 Hz, 1H, H6), 7.62 (s, 2H, H4 + H5), 7.59 (d, 3JHH = 8.1 Hz, 1H, H8), 7.38 (d, 3JHH = 7.2 Hz, 1H, H2), 7.34 (dd, 3JHH = 8.2, 7.0 Hz,
$^1$H, $H7$), 6.75 (d, $^4J_{HH} = 2.3$ Hz, 2H, $H2^*$), 6.52 (t, $^4J_{HH} = 2.3$ Hz, 1H, $H4^*$). 3.81 (s, 6H, $2x$ OMe); $^{13}$C NMR (150 MHz, C$_2$D$_2$Cl$_4$) δ = 160.53 (2C, C$^3$), 140.95 (C1$^*$), 140.38 (C1), 138.67 (Cq), 138.54 (Cq), 138.16 (Cq), 138.10 (2C, Cq), 137.97 (2C, Cq), 137.73 (Cq), 136.99 (Cq), 136.39 (Cq), 129.74 (C10b), 129.62 (C10a), 128.91 (C8a), 128.86 (C2), 128.79 (C7), 127.03 (C12a), 126.90 (C9), 126.73 (C8), 126.13 (C12), 125.64 (C5), 125.43 (C4), 124.20 (C11), 123.91 (C10), 123.69 (C3), 123.56 (C6), 107.91 (C2$^*$), 99.64 (C4$^*$), 55.50 (2C, $2x$ OMe); $^1$H NMR (400 MHz, CDC1$_3$) δ = 8.07 (d, $J = 8.8$ Hz, 2H, $H10 + H11$), 7.94 (d, $J = 8.9$ Hz, 1H, $H12$), 7.75 (d, $J = 8.7$ Hz, 1H, $H9$), 7.73 (d, $J = 7.1$ Hz, 1H, $H3$), 7.69 (d, $J = 6.9$ Hz, 1H, $H6$), 7.64 (s, 2H, $H4 + H5$), 7.62 (d, $J = 8.1$ Hz, 1H, $H8$), 7.42 (d, $J = 7.1$ Hz, 1H, $H2$), 7.38 (dd, $J = 8.1$, 6.9 Hz, 1H, $H7$), 6.81 (d, $J = 2.3$ Hz, 2H, $H2^*$), 6.58 (t, $J = 2.3$ Hz, 1H, $H4^*$), 3.89 (s, 6H, $2x$ OMe); $^{13}$C NMR (100 MHz, CDC1$_3$) δ = 160.94 (2C, C$^3$), 141.39 (C1$^*$), 140.70 (C1), 139.12 (Cq), 138.87 (Cq), 138.58 (Cq), 138.51 (Cq), 138.47 (Cq), 138.40 (Cq), 138.38 (Cq), 138.12 (Cq), 137.44 (Cq), 136.83 (Cq), 130.09 (C10b), 129.97 (C10a), 129.22 (C8a), 128.88 (C2), 128.83 (C7), 127.39 (C12a), 126.95 (C9), 126.80 (C8), 126.26 (C12), 125.67 (C5), 125.45 (C4), 124.40 (C11), 124.09 (C10), 123.61 (C3), 123.50 (C6), 108.13 (C2$^*$), 99.86 (C4$^*$), 55.66 (2C, $2x$ OMe); IR (cm$^{-1}$) 2956, 1592, 1455, 1421, 1264, 1204, 1155, 1066, 896, 810, 728; MS (EI): m/z (rel. int.) = 460 (100 %) 323 (40 %).

8g was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh$_3$)$_4$ (2.30 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3.00 eq.) and 3,5-methoxyphenylboronic acid (76.7 mg, 1.50 eq.) in a 1,4-dioxan/H$_2$O (14:1) solution (50 mL). Orange solid (67.5 mg, 0.16 mmol, 79 %).

$^1$H NMR (400 MHz, CDC1$_3$) δ = 8.12 – 8.09 (m, 3H, $H11 + H2^*$), 8.07 (d, $J = 8.7$ Hz, 1H, $H10$), 7.98 (bs, 1H, $H4^*$), 7.78 (d, $J = 8.7$ Hz, 1H, $H9$), 7.75 (d, $J = 7.1$ Hz, 1H, $H3$), 7.72 (d, $J = 6.9$ Hz, 1H, $H6$), 7.69 (d, $J = 8.8$ Hz, 1H, $H12$), 7.66 (s, 2H, $H4 + H5$), 7.65 (d, $J = 8.1$ Hz, 1H, $H8$), 7.41 (dd, $J = 8.1$, 6.9 Hz, 1H, $H7$), 7.40 (d, $J = 7.1$ Hz, 1H, $H2$); $^{19}$F NMR (375 MHz, C$_2$D$_2$Cl$_4$) δ = -62.22; $^{13}$C NMR (100 MHz, CDC1$_3$) δ = 141.48 (C1$^*$), 139.96 (Cq), 139.36 (Cq), 139.04 (Cq), 138.58 (Cq), 138.43 (Cq), 138.32 (Cq), 138.24 (Cq), 138.02 (Cq), 137.47 (Cq), 137.11 (Cq), 136.82 (C1), 132.13 (q, $^2J_{CF} = 33.3$ Hz, 2C, C$^3$), 130.31 (C10b), 129.82(C10a), 129.80 (m, 2C, C$^2$), 129.60 (C2), 129.34(C8a), 129.08 (C7), 127.16 (C9), 127.02 (C8), 126.69 (C12a), 125.89 (C5), 125.88 (C4), 125.37 (C11), 124.71 (C12), 124.07 (C10), 123.75 (C6), 123.47 (C3), 123.51 (q, $^1J_{CF} = 272.9$ Hz, C$^5$), 121.51-121.49 (hept, $^3J_{CF} = 3.6$ Hz, C$^4$); IR (cm$^{-1}$) 2957, 2875, 1464, 1421, 1382, 1215, 1149, 1065, 892, 807, 731; MS (EI): m/z (rel. int.) = 536 (100 %) 467 (30 %) 398 (20 %), 323 (50 %).
8h was synthesized according to general procedure A using Idpc-Br (80.0 mg, 0.20 mmol, 1.00 eq.), Pd(PPh3)4 (2.3 mg, 0.01 eq.), sodium carbonate (63.0 mg, 0.60 mmol, 3 eq.) and ferroceneboronic acid (68.4 mg, 1.5 eq) in a 1,4-dioxane/H2O (14:1) solution (50 mL). Red solid (84.7 mg, 0.17 mmol, 84 %). Crystals suitable for X-ray diffraction were grown by slow diffusion of n-hexane into a concentrated solution of 8h in CH2Cl2.

$^1$H NMR (600 MHz, C2D2Cl4): $\delta = 8.38$ (d, $^3J_{HH} = 8.9$ Hz, 1H, H12), 8.13 (d, $^3J_{HH} = 8.9$ Hz, 1H, H11), 8.11 (d, $^3J_{HH} = 8.8$ Hz, 1H, H10), 7.78 (d, $^3J_{HH} = 8.7$ Hz, 1H, H9), 7.69 (d, $^3J_{HH} = 6.9$ Hz, 1H, H6), 7.65 (d, $^3J_{HH} = 7.4$ Hz, 1H, H5), 7.62) (d, $^3J_{HH} = 7.7$ Hz, 2H, H8 + H4), 7.59 (d, $^3J_{HH} = 7.3$ Hz, 1H, H3), 7.48 (d, $^3J_{HH} = 7.4$ Hz, 1H, H2), 7.37 (t, $^3J_{HH} = 7.5$ Hz, 1H, H7), 4.82 (s, 2H, H2*), 4.46 (s, 2H, H3*), 4.13 (s, 5H, H4*); $^{13}$C NMR (150 MHz, C2D2Cl4) $\delta = 138.80$ (Cq), 138.45 (Cq), 138.29 (Cq), 138.21 (Cq), 138.09 (Cq), 138.07 (Cq), 137.81 (Cq), 137.61 (Cq), 137.08 (Cq), 136.44 (Cq), 129.61 (C10a), 129.50 (C10b), 128.96 (C8a), 128.90 (C7), 128.34 (C2), 127.33 (C12a), 126.93 (C9), 126.68 (C8), 126.41 (C12), 125.67 (C5), 125.07 (C4), 123.99 (C10), 123.61 (C3), 123.55 (C6), 123.50 (C11), 74.04 (C1*), 70.33 (5C, C4*), 69.73 (2C, C2*), 69.64 (2C, C3*); IR (cm$^{-1}$) 2958, 2875, 1463, 1382, 1251, 1151, 1073, 956, 817, 740; MS (EI): m/z (rel. int.) = 508 (100 %), 323 (60 %); HRMS (EI) m/z Calcd for C36H20Fe [M]+: 508.0914. Found: 508.0916. 

8i was synthesized according to general procedure B using Idpc-Br (0.1 g, 0.24 mmol, 1.00 eq.), Cul (1.2 mg, 0.025 eq.), PdCl2(PPh3)2 (8.4 mg, 0.05 eq.), diisopropylamine (0.1 mL, 2.00 eq.) and phenylacetylene (0.04 mL, 0.29 mmol, 1.20 eq.) dissolved in 20 ml THF. Red solid (90.4 mg, 0.21 mmol, 89 %).

$^1$H NMR (600 MHz, C2D2Cl4) $\delta = 8.12$ (d, $J = 8.8$ Hz, 1H, H11), 8.07 (d, $J = 8.7$ Hz, 1H, H10), 8.05 (d, $J = 8.7$ Hz, 1H, H12), 7.77 (d, $J = 8.7$ Hz, 1H, H9), 7.68 (d, $J = 6.9$ Hz, 1H, H6), 7.64 (d, $J = 7.2$ Hz, 1H, H3), 7.63 – 7.60 (m, 4H, H4 + H5 + H3*), 7.57 (d, $J = 7.2$ Hz, 1H, H2), 7.39 – 7.32 (m, 4H, H7 + H8, H2*), 7.28 – 7.22 (m, 1H, H4*); $^{13}$C NMR (150 MHz, C2D2Cl4) $\delta = 138.89$ (Cq), 138.71 (Cq), 138.57 (Cq), 138.19 (Cq), 138.07 (Cq), 138.05 (Cq), 138.01 (Cq), 137.84 (Cq), 136.44 (Cq), 136.33 (Cq), 132.83 (C2), 131.73 (2C, C2*), 130.23 (C10b), 129.73 (C10a), 129.06 (C12a), 128.99 (C7), 128.98 (C8a), 128.70 (C4*), 128.47 (2C, C3*), 127.07 (C9), 126.89 (C8), 125.85 (C5), 125.77 (C4), 125.55 (C12), 124.55 (C11), 123.97 (C10), 123.75 (C6), 123.34 (C3), 122.82 (C1*), 120.72 (C1), 95.31 (Cac2), 87.05 (Cac1); IR (cm$^{-1}$) 2957, 2873, 1463, 1380, 1209, 1138, 1067, 955, 836, 812, 741; MS (EI): m/z (rel. int.) = 424 (100 %), 323 (40 %).
8j was synthesized according to general procedure B using Idpc-Br (0.1 g, 0.24 mmol, 1.00 eq.), CuI (1.2 mg, 0.025 eq.), PdCl2(PPh3)2 (8.4 mg, 0.05 eq.), diisopropylamine (0.1 mL, 2.00 eq.) and 4-nitrophénylacétylène (43.0 mg, 0.29 mmol, 1.20 eq.) dissolved in 20 ml THF. Red solid (93.5 mg, 0.20 mmol, 83 %).

$^1$H NMR (600 MHz, C$_2$D$_2$Cl$_4$) $\delta$ = 8.19 (d, $J$ = 8.7 Hz, 2H, $H10$), 8.00 (d, $J$ = 8.7 Hz, 1H, $H12$), 7.77 (d, $J$ = 8.7 Hz, 1H, $H9$), 7.73 (d, $J$ = 8.8 Hz, 2H, $H2'$), 7.69 (d, $J$ = 6.9 Hz, 1H, $H6$), 7.66 (d, $J$ = 7.2 Hz, 1H, $H3$), 7.64 – 7.59 (m, 4H, $H2 + H4 + H5 + H8$), 7.46 (dd, $J$ = 8.1, 6.9 Hz, 1H, $H7$); $^{13}$C NMR (150 MHz, C$_2$D$_2$Cl$_4$) $\delta$ = 146.81 (C4'), 139.75 (Cq), 139.20 (Cq), 138.50 (Cq), 138.22 (Cq), 138.10 (Cq), 138.02 (Cq), 137.89 (Cq), 137.83 (Cq), 136.44 (Cq), 136.33 (Cq), 133.69 (C2), 132.41(2C, C2'), 130.36 (C10b), 129.99 (C1'), 129.66 (C10a), 129.06 (C7), 129.03 (C8a), 128.90 (C12a), 127.16 (C9), 127.00 (C8), 126.11 (C5), 125.85 (C4), 125.22 (C12), 124.92 (C11), 123.94 (C10), 123.86 (C6), 123.65(2C, C3'), 123.20 (C3), 119.34 (C1), 93.13 (Cac2), 92.44 (Cac1); IR (cm$^{-1}$): 3046, 1902, 1859, 1547, 1480, 1421, 1392, 1194, 1136, 1099, 1071, 1010, 940, 890, 857, 816, 798, 778, 751, 704; MS (EI): m/z (rel. int.) = 469 (100 %), 323 (30 %); Anal. Calcd for C$_{34}$H$_{15}$NO$_2$: 86.98 % (C), 3.22 % (H), 2.98 % (N), Found: 86.69 % (C), 3.55 % (H), 3.09 % (N).

8k was synthesized according to general procedure B using Idpc-Br (0.1 g, 0.24 mmol, 1.00 eq.), Cul (1.2 mg, 0.025 eq.), PdCl$_2$(PPh$_3$)$_2$ (8.4 mg, 0.05 eq.), diisopropylamine (0.1 mL, 2.00 eq.) and 4-bromophénylacétylène (53.0 mg, 0.29 mmol, 1.20 eq.) dissolved in 20 ml THF. Red solid (102 mg, 0.20 mmol, 83 %).

$^1$H NMR (600 MHz, C$_2$D$_2$Cl$_4$) $\delta$ = 8.10 (d, $J$ = 8.8 Hz, 1H, $H11$), 8.06 (d, $J$ = 8.6 Hz, 1H, $H10$), 8.00 (d, $J$ = 8.7 Hz, 1H, $H12$), 7.76 (d, $J$ = 8.7 Hz, 1H, $H9$), 7.68 (d, $J$ = 6.8 Hz, 1H, $H6$), 7.64 – 7.58 (m, 4H, $H3 + H4 + H5 + H8$), 7.56 (d, $J$ = 7.2 Hz, 1H, $H2$), 7.52 – 7.44 (m, 4H, $H2' + H3'$), 7.37 (t, $J$ = 7.5 Hz, 1H, $H7$); $^{13}$C NMR (150 MHz, C$_2$D$_2$Cl$_4$) $\delta$ = 138.94 (2C, Cq), 138.56 (Cq), 138.18 (Cq), 138.05 (Cq), 137.98 (2C, Cq), 137.83 (Cq), 136.43 (Cq), 136.32 (Cq), 133.13 (2C, C2'), 132.96 (C2), 131.67 (2C, C3'), 130.24 (C10b), 129.68 (C10a), 129.00 (C7), 128.99 (8a), 128.95 (12a), 127.07 (C9), 126.91 (C8), 125.88 (C5), 125.77 (C4), 125.42 (C12), 124.61 (C11), 123.94 (C10), 123.76 (C6), 123.29 (C3), 122.78 (1'), 121.89 (4'), 120.31 (CI), 94.14 (Cac2), 88.20 (Cac1); IR (cm$^{-1}$) 3046, 2210, 1871,
8l was synthesized according to general procedure B using aryl Idpc-Br (83.0 mg, 0.21 mmol, 1.00 eq.), Cul (1.0 mg, 0.025 eq.), PdCl$_2$(PPh$_3$)$_2$ (7.4 mg, 0.05 eq.), diisopropylamine (0.1 mL, 2.00 eq.) and ethynylferrocene (52.0 mg, 0.25 mmol, 1.20 eq.) dissolved in 25 ml THF. Red solid (101 mg, 0.19 mmol, 92 %).

$^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$) $\delta = 8.12$ (d, $J = 8.8$ Hz, 1H, $H_{11}$), 8.06 (d, $J = 8.7$ Hz, 1H, $H_{10}$), 8.01 (d, $J = 8.8$ Hz, 1H, $H_{12}$), 7.76 (s, 5H, $H_2$), 7.51 (d, $J = 8.7$ Hz, 1H, $H_3$). $^{13}$C NMR (125 MHz, C$_2$D$_2$Cl$_4$) $\delta = 138.66$ (C$q$), 138.64(C$q$), 138.18 (C$q$), 138.16 (C$q$), 138.05(C$q$), 137.97 (C$q$), 137.94 (C$q$), 136.44 (C$q$), 132.21(C2), 130.14(C10b), 129.71(C10a), 129.08(C12a), 128.93(C7), 127.01(C9), 126.82(C8), 125.72(C5), 125.64(C4), 125.58(C12), 124.36(C11), 123.93(C10), 123.65(C6), 123.44(C3), 121.68(C1), 95.04(Cac2), 83.35(Cac1), 71.69(2C, C2$^*$), 70.13(5C, C4$^*$), 69.30(2C, C3$^*$), 64.74(C1$^*$); IR (cm$^{-1}$) 2958, 2875, 1463, 1382, 1149, 956, 801 752, 739; MS (EI): $m/z$ (rel. int.) = 532 (100 %), 323 (40 %); HRMS (EI) m/z Calcd for C$_{38}$H$_{20}$Fe [M]$^+$: 532.0914. Found: 532.0921.

4-Ferrocenyl-13,16-difluorobenzo[s]picene (5) was synthesized by adding to a solution of Pd(PPh$_3$)$_4$ (97.0 mg, 0.08 mmol, 0.05 eq.) and cesium fluoride (168 mg, 1.11 mmol, 2.2 eq.) in dry DMF (2 mL), tri-n-butylstannylferrocene (250 mg, 0.53 mmol, 1.0 eq.), a suspension of Idpc-Br (250 mg, 0.56 mmol, 1.1 eq.) in dry DMF (9 mL), and copper(I)iodide (45.0 mg, 0.24 mmol, 0.5 eq.). The reaction mixture was heated at 50 °C for 15 h whilst monitoring the reaction via EI-MS until full consumption of starting material. Upon cooling to room temperature the reaction mixture was filtered over a short celite plug with ethyl acetate (150 mL). The filtrate was washed with bicarbonate solution (2 x 30 mL), water (2 x 30 mL) and brine (30 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Column chromatography on silica using PE/ethyl acetate = 9:1 as eluent yielded a deep red powder. Repeated washing with copious amounts of n-pentane yielded title compound 5 as red powder (200 mg, 0.37 mmol, 65 %). Crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane into a concentrated solution of 5 in CH$_2$Cl$_2$. 

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$^1$H NMR (800 MHz, CDCl$_3$) $\delta$ = 8.75 (d, $^3$J$_{HH}$ = 9.1 Hz, 1H, H5), 8.52 (d, $^3$J$_{HH}$ = 8.8 Hz, 1H, H7), 8.47 (d, $^3$J$_{HH}$ = 9.1 Hz, 1H, H6), 8.23 (dd, $^6$J$_{HF}$ (through space) = 13.8 Hz, $^3$J$_{HH}$ = 8.2 Hz, 1H, H12), 8.11 (dd, $^6$J$_{HF}$ (through space) = 13.0 Hz, $^3$J$_{HH}$ = 7.7 Hz, 1H, H11), 7.97 (d, $^3$J$_{HH}$ = 7.9 Hz, 1H, H9), 7.93 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H, H3), 7.61 (dd, $^3$J$_{HH}$ = 8.2 Hz, 7.0 Hz, 1H, H10), 7.59 (dd, $^3$J$_{HH}$ = 7.9 Hz, 7.0 Hz, 1H, H11), 7.59 (dd, $^3$J$_{HH}$ = 7.9 Hz, 7.0 Hz, 1H, H10), 7.54 (dd, $^3$J$_{HH}$ = 9.1 Hz, 7.7 Hz, 1H, H12), 7.39 (d, $^3$J$_{HH}$ = 7.4 Hz, 1H, H14), 7.38 (d, $^3$J$_{HH}$ = 7.4 Hz, 1H, H15), 4.74 (s, 2H, H2' + H5'), 4.49 (s, 2H, H3' + H4'), 4.30 (s, 5H, H6'); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -104.07 (d, $^5$J$_{FF}$ = 17.7 Hz, 1F, F16), -104.20 (d, $^5$J$_{FF}$ = 17.7 Hz, 1F, F13); $^{13}$C NMR (200 MHz, CDCl$_3$) $\delta$ = 155.34 (dd, $^1$J$_{CF}$ = 246.2 Hz, $^4$J$_{CF}$ = 1.8 Hz, C13), 155.31 (dd, $^1$J$_{CF}$ = 250.2 Hz, $^4$J$_{CF}$ = 1.7 Hz, C16), 135.55 (C4), 132.47 (C8a), 131.03 (C4a), 130.77 (d, $^4$J$_{CF}$ = 3.2 Hz, C16c), 130.35 (d, $^4$J$_{CF}$ = 3.1 Hz, C12a), 130.06 (C6b), 129.83 (d, $^5$J$_{CF}$ (through space) = 14.4 Hz, C12), 129.82 (C6a), 129.51 (C8), 128.83 (d, $^5$J$_{CF}$ (through space) = 14.2 Hz, C1), 128.40 (C3), 127.64 (C5), 127.29 (C9), 126.26 (C10), 125.36 (C11), 124.54 (C3), 123.74 (d, $^3$J$_{CF}$ = 3.0 Hz, C12b), 123.53 (d, $^3$J$_{CF}$ = 3.1 Hz, C16b), 120.54 (dd, $^2$J$_{CF}$ = 13.7 Hz, 3JCF = 2.0 Hz, C12c), 120.27 (dd, $^2$J$_{CF}$ = 14.0 Hz, 3JCF = 2.5 Hz, C16a), 119.89 (C8), 119.37 (C6), 114.46 (dd, 2JCF = 11.8 Hz, $^3$J$_{CF}$ = 9.6 Hz, C14), 114.32 (dd, $^2$J$_{CF}$ = 12.2 Hz, $^3$J$_{CF}$ = 10.0 Hz, C15), 87.98 (C1'), 71.95 (C5'), 70.46 (C2'), 70.18 (5C, C6'), 68.69 (2C, C3'+4'); MS (EI): m/z (rel. int.) = 548. (100 %), 363 (80 %).

Idpc-B(pin) (10) was synthesized using Idpc-Br (100 mg, 0.25 mmol, 1.00 eq.), Pd(dpff)Cl$_2$ (10.0 mg, 0.01 mmol, 0.05 eq.), potassium acetate (73.0 mg, 0.74 mmol, 3.00 eq.), and bis(pinacolato)diboron (94.5 mg, 0.37 mmol, 1.50 eq.) dissolved in dry 1,4-dioxane (60 mL). The mixture was heated under reflux until full consumption of starting materials (TLC). The volatiles were removed under reduced pressure and water (200 mL) was added to the crude. The resulting mixture was extracted with CH$_2$Cl$_2$ (3 x 100 mL). The organic phases were dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica using a gradient system consisting of initially PE/CH$_2$Cl$_2$ = 3:1 gradually changed to CH$_2$Cl$_2$ as eluent to obtain boronic acid pinacol ester 10 as an orange solid (101 mg, 0.22 mmol, 90 %).
1341, 1143, 1106, 1061, 954, 807, 783, 753, 703; **MS (EI):** *m/z* (*rel. int.*) = 450 (100%), 323 (60%)

1,1’-Bisindacenopicene (Idpc)₂ (9) was synthesized according to general procedure A using **Idpc-Br** (23.0 mg, 0.06 mmol, 1.00 eq.), **Pd(PPh₃)₄** (1.0 mg, 0.01 eq.), sodium carbonate (24.0 mg, 0.22 mmol, 3.00 eq.) and **10** (30.0 mg, 0.07 mmol, 1.2 eq.) in a 1,4-dioxane/H₂O (14:1) solution (50 mL). Red solid (21.5 mg, 0.03 mmol, 60%).

**1H NMR** (600 MHz, C₂D₂Cl₄): δ = 8.05 (d, 3 *J*HH = 8.6 Hz, 1H, H10), 7.99 (d, 3 *J*HH = 8.8 Hz, 1H, H11), 7.83 (d, 3 *J*HH = 6.9 Hz, 2H, H3), 7.75 (d, 3 *J*HH = 8.6 Hz, 2H, H9), 7.73 – 7.67 (m, 8H, H4 + H5 + H6 + H12), 7.62 (d, 3 *J*HH = 8.1 Hz, 2H, H8), 7.52 (d, 3 *J*HH = 6.9 Hz, 2H, H2), 7.38 (t, 3 *J*HH = 7.5 Hz, 2H, H7), **13C NMR** (150 MHz, C₂D₂Cl₄) δ = 138.79 (Cq), 138.67 (Cq), 138.54 (Cq), 138.29 (Cq), 138.25 (Cq), 138.13 (Cq), 138.07 (Cq), 137.95 (Cq), 137.46 (C1'), 136.94 (Cq), 136.48 (Cq), 136.29 (Cq), 136.95 (Cq), 136.28 (C7), 129.96 (C8a), 128.98 (C7), 128.28 (C12a), 127.02 (C9), 126.83 (C8), 126.50 (C12), 125.80 (C5), 125.69 (C4), 124.21 (C11), 123.84 (C10), 123.68 (C6), 123.67 (C3); **IR (cm⁻¹)** 3029, 2891, 2202, 1869, 1591, 1504, 1415, 1375, 1339, 1250, 1136, 1107, 951, 892, 852, 801, 780, 757, 704, 667; **MS (EI):** *m/z* (*rel. int.*) = 646 (100%), 323 (50%).
X-ray Data Collection

Data collection for X-ray structure-determination was performed at a **STOE IPDS-II** diffractometer equipped with a graphite monochromated radiation source ($\lambda = 0.71073$ Å), an image plate detection system and an **Oxford Cryostream 700** with nitrogen as coolant gas. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell by a least-squares fit of the $2\Theta$ values, data reduction, LP correction, and the space group determination were performed using the **X-Area** software package delivered with the diffractometer.\[^3\] A semiempirical absorption correction method was performed after indexing of the crystal faces. The structures were solved by direct methods (**SHELXT-2014**\[^4\]) and refined by standard Fourier techniques against $F^2$ with a full-matrix least-squares algorithm using **SHELXL-2018**\[^5\]** and the **WinGX** (2018.3)\[^6\]** software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined with a riding model. Graphical representations were prepared with **ORTEP-III**\[^6\]** Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 2013240 (**Idpc-Fc**), 2013241 1,4-difluoro-6-methylbenzo[c]phenanthrene 3 and 2013242 13,16-difluoro-4-ferrocenylbenzo[s]picene 4. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk or [https://www.ccdc.cam.ac.uk](https://www.ccdc.cam.ac.uk)).
**Figure S1:** X-ray crystal structure of Idpc-Fc. Thermal ellipsoids are drawn at the 50% probability level, only one enantiomer shown. Hydrogen atoms are omitted for clarity.

**Table S1:** Crystal data and structure refinement parameters for Idpc-Fc (CCDC2013240)

| Parameter | Idpc-Fc (CCDC2013240) |
|-----------|------------------------|
| Empirical formula | C$_{36}$H$_{20}$Fe |
| Formula weight | 508.37 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | P b c a |
| Unit cell dimensions | $a = 10.4054(16)$ Å  
$b = 7.4277(11)$ Å  
$c = 57.662(11)$ Å |
| Volume | 4456.6(13) Å$^3$ |
| Z | 8 |
| Density (calculated) | 1.515 Mg/m$^3$ |
| Absorption coefficient | 0.703 mm$^{-1}$ |
| $F(000)$ | 2096 |
| Crystal size | 0.100 x 0.070 x 0.010 mm$^3$ |
| Theta range for data collection | 1.413 to 26.999°. |
| Index ranges | -13$\leq$|h|$\leq$12, -9$\leq$|k|$\leq$9, -71$\leq$|l|$\leq$73 |
| Reflections collected | 18678 |
| Independent reflections | 4815 [R(int) = 0.1940] |
| Completeness to theta = 25.242° | 98.7 % |
| Absorption correction | Integration |
| Max. and min. transmission | 0.9821 and 0.9272 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4815 / 0 / 335 |
| Goodness-of-fit on $F^2$ | 0.854 |
| Final R indices [$I>2\sigma(I)$] | $R_f = 0.0680$, $wR_2 = 0.1086$ |
| $R$ indices (all data) | $R_f = 0.2133$, $wR_2 = 0.1533$ |
| Largest diff. peak and hole | 0.303 and -0.467 e.Å$^{-3}$ |
Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for Idpc-Fc. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Fe(1)| -140(1) | 6852(1) | 4569(1) | 42(1) |
| C(1) | 1049(6) | 6280(8) | 4071(1) | 36(2) |
| C(1') | 1011(6) | 5707(9) | 4319(1) | 41(2) |
| C(2) | -68(7) | 6436(8) | 3938(1) | 43(2) |
| C(2') | 1765(6) | 6394(9) | 4504(1) | 45(2) |
| C(3) | -79(6) | 6942(9) | 3699(1) | 40(1) |
| C(3') | 1374(7) | 5559(9) | 4711(1) | 44(2) |
| C(3A) | 1026(6) | 7434(8) | 3595(1) | 39(2) |
| C(3B) | 1765(6) | 6394(9) | 4504(1) | 45(2) |
| C(3C) | 3289(7) | 7640(8) | 3600(1) | 34(2) |
| C(3D) | 2831(6) | 8003(8) | 3371(1) | 36(1) |
| C(3E) | 1492(7) | 7812(8) | 3348(1) | 39(2) |
| C(4) | 1073(7) | 7596(8) | 3120(1) | 41(2) |
| C(4') | 373(7) | 4317(9) | 4656(1) | 44(2) |
| C(5) | 1983(6) | 7404(9) | 2931(1) | 42(2) |
| C(5') | 138(7) | 4423(9) | 4415(1) | 47(2) |
| C(5A) | 3298(6) | 7464(9) | 2965(1) | 39(2) |
| C(5B) | 3663(6) | 7835(8) | 3196(1) | 35(2) |
| C(5C) | 4945(6) | 7279(7) | 3246(1) | 36(1) |
| C(5D) | 5461(6) | 6654(9) | 3035(1) | 38(2) |
| C(5E) | 4527(6) | 6730(9) | 3054(1) | 40(2) |
| C(6) | 4860(8) | 5950(8) | 2648(1) | 45(2) |
| C(6') | -1016(7) | 8974(9) | 4414(1) | 49(2) |
| C(7) | 6104(7) | 5097(9) | 2630(1) | 48(2) |
| C(7') | -367(7) | 9530(9) | 4615(1) | 50(2) |
| C(8) | 6930(7) | 4932(9) | 2814(1) | 44(2) |
| C(8') | -880(7) | 8578(10) | 4807(1) | 49(2) |
| C(8A) | 6611(7) | 5685(9) | 3033(1) | 41(2) |
| C(9) | 7207(7) | 5399(9) | 3256(1) | 42(2) |
| C(9') | -1847(7) | 7432(10) | 4725(1) | 52(2) |
| C(10) | 6617(6) | 5919(8) | 3460(1) | 39(2) |
| C(10') | -1934(7) | 7669(10) | 4481(1) | 50(2) |
| C(10A) | 5411(6) | 6866(9) | 3465(1) | 38(2) |
| C(10B) | 4494(6) | 7063(8) | 3659(1) | 35(2) |
| C(11) | 4596(6) | 6412(8) | 3893(1) | 39(2) |
| C(12) | 3530(6) | 6269(8) | 4036(1) | 37(2) |
| C(12A) | 2250(6) | 6673(9) | 3960(1) | 36(1) |
Table S3. Bond lengths [Å] for Idpc-Fc.

| Bond                  | Length 1 (Å) | Bond                  | Length 2 (Å) | Bond                  | Length 3 (Å) |
|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|
| Fe(1)-C(3’)           | 2.019(7)    | C(3’)-C(4’)           | 1.427(9)    | C(5D)-C(8A)           | 1.396(9)    |
| Fe(1)-C(4’)           | 2.020(7)    | C(3A)-C(3B)           | 1.454(9)    | C(5D)-C(5E)           | 1.427(8)    |
| Fe(1)-C(7’)           | 2.021(7)    | C(3A)-C(3E)           | 1.529(9)    | C(5E)-C(6)            | 1.367(8)    |
| Fe(1)-C(10’)          | 2.027(7)    | C(3B)-C(12A)          | 1.395(8)    | C(6)-C(7)             | 1.444(10)   |
| Fe(1)-C(6’)           | 2.029(7)    | C(3B)-C(3C)           | 1.399(9)    | C(6’)-C(7)            | 1.406(9)    |
| Fe(1)-C(8’)           | 2.030(7)    | C(3C)-C(10B)          | 1.368(8)    | C(6’)-C(10’)          | 1.416(10)   |
| Fe(1)-C(5’)           | 2.031(7)    | C(3C)-C(3D)           | 1.431(8)    | C(7)-C(8)             | 1.369(9)    |
| Fe(1)-C(9’)           | 2.038(7)    | C(3D)-C(5B)           | 1.338(8)    | C(7’)-C(8’)           | 1.417(9)    |
| Fe(1)-C(2’)           | 2.046(7)    | C(3D)-C(3E)           | 1.406(8)    | C(8)-C(8A)            | 1.419(9)    |
| Fe(1)-C(1’)           | 2.059(7)    | C(3E)-C(4)            | 1.394(8)    | C(8’)-C(9’)           | 1.400(10)   |
| C(1)-C(2)             | 1.398(9)    | C(4)-C(5)             | 1.453(9)    | C(8A)-C(9)            | 1.444(9)    |
| C(1)-C(12A)           | 1.433(8)    | C(4’)-C(5’)           | 1.414(8)    | C(9)-C(10)            | 1.383(9)    |
| C(1)-C(1’)            | 1.491(9)    | C(5)-C(5A)            | 1.383(8)    | C(9’)-C(10’)          | 1.421(10)   |
| C(1’)-C(2’)           | 1.419(9)    | C(5A)-C(5B)           | 1.408(8)    | C(10)-C(10A)          | 1.440(9)    |
| C(1’)-C(5’)           | 1.429(9)    | C(5A)-C(5E)           | 1.531(9)    | C(10A)-C(10B)         | 1.479(8)    |
| C(2)-C(3)             | 1.426(8)    | C(5B)-C(5C)           | 1.426(8)    | C(10B)-C(11)          | 1.434(8)    |
| C(2’)-C(3’)           | 1.408(9)    | C(5C)-C(10A)          | 1.386(8)    | C(11)-C(12)           | 1.385(8)    |
| C(3)-C(3A)            | 1.347(8)    | C(5C)-C(5D)           | 1.411(8)    | C(12)-C(12A)          | 1.433(8)    |
| Bond Angles[^°] for 1dpc-Fe. |
|--------------------------------|
| C(3')-Fe(1)-C(4')  41.4(3)   | C(2')-C(1')-C(12A)  117.6(6) |
| C(3')-Fe(1)-C(7)   120.4(3)  | C(2')-C(1)-C(12A)   117.6(6) |
| C(4')-Fe(1)-C(7)   156.2(3)  | C(2A)-C(1)-C(1')    121.8(6) |
| C(3')-Fe(1)-C(10') 164.2(3) | C(2')-C(1')-C(5')   120.5(6) |
| C(4')-Fe(1)-C(10') 125.8(3) | C(2')-C(1')-C(5')   107.5(6) |
| C(7')-Fe(1)-C(10') 68.3(3)  | C(5')-C(1')-C(1')  125.4(6) |
| C(3')-Fe(1)-C(6')  154.0(3) | C(2')-C(1')-Fe(1)   69.3(4) |
| C(4')-Fe(1)-C(6')  162.2(3) | C(5')-C(1')-Fe(1)   68.5(4) |
| C(7')-Fe(1)-C(6')  40.6(3)  | C(1')-C(1')-Fe(1)  124.7(5) |
| C(10')-Fe(1)-C(6') 40.9(3)  | C(1')-C(2')-Fe(1)  119.7(6) |
| C(6')-Fe(1)-C(8')  68.7(3)  | C(3')-C(2')-C(3')  110.9(6) |
| C(3')-Fe(1)-C(5')  69.1(3)  | C(2')-C(3')-Fe(1)  107.9(6) |
| C(4')-Fe(1)-C(5')  40.9(2)  | C(4')-C(3')-Fe(1)  70.8(4) |
| C(7')-Fe(1)-C(5')  161.5(3) | C(5')-C(3')-C(3B)  116.7(6) |
| C(10')-Fe(1)-C(5') 106.8(3) | C(3')-C(3A)-C(3E)  137.4(6) |
| C(6')-Fe(1)-C(9')  124.1(3) | C(3B)-C(3A)-C(3E)  105.0(5) |
| C(3')-Fe(1)-C(9')  156.6(3) | C(12A)-C(3B)-C(3C) 122.3(6) |
| C(4')-Fe(1)-C(9')  40.3(3)  | C(12A)-C(3B)-C(3A) 124.9(6) |
| C(5')-Fe(1)-C(9')  120.4(3) | C(3C)-C(3B)-C(3A)  111.6(5) |
| C(7')-Fe(1)-C(9')  68.4(3)  | C(3C)-C(3B)-C(3)   124.2(6) |
| C(10')-Fe(1)-C(9') 40.9(3)  | C(5B)-C(3D)-C(3E)  117.7(6) |
| C(6')-Fe(1)-C(12)  40.5(3)  | C(3E)-C(3D)-C(3C)  113.4(6) |
| C(3')-Fe(1)-C(12)  68.6(3)  | C(4)-C(3E)-C(3A)   139.2(6) |
| C(4')-Fe(1)-C(12)  107.5(3) | C(5B)-C(3D)-C(3C)  104.2(5) |
| C(7')-Fe(1)-C(12)  153.6(3) | C(3D)-C(3E)-C(3A)  118.9(3) |
| C(10')-Fe(1)-C(12) 118.9(3) | C(3E)-C(4)-C(5)   121.1(6) |
| C(6')-Fe(1)-C(14)  126.6(3) | C(5')-C(4)-C(3)   108.0(6) |
| C(3')-Fe(1)-C(14)  68.5(3)  | C(5')-C(4)-C(5')  70.0(4) |
| C(4')-Fe(1)-C(14)  163.9(3) | C(5')-C(4')-C(1')  69.3(4) |
| C(7')-Fe(1)-C(14)  68.5(3)  | C(5A)-C(5)-C(4)  122.3(6) |
| C(10')-Fe(1)-C(14) 68.6(3)  | C(4')-C(5')-C(1')  108.0(6) |
| C(6')-Fe(1)-C(16)  124.5(3) | C(4')-C(5')-Fe(1)  69.1(4) |
| C(3')-Fe(1)-C(16)  119.0(3) | C(1')-C(5')-Fe(1)  70.6(4) |
| C(4')-Fe(1)-C(16)  105.8(3) | C(5)-C(5A)-C(5B)  114.1(6) |
| C(7')-Fe(1)-C(16)  162.8(3) | C(5)-C(5A)-C(5E)  139.0(6) |
| C(10')-Fe(1)-C(16) 40.9(3)  | C(5B)-C(5A)-C(5E)  103.8(5) |
| C(6')-Fe(1)-C(18)  154.7(3) | C(3D)-C(5B)-C(5A) 123.8(6) |
| C(3')-Fe(1)-C(18)  40.4(2)  | C(3D)-C(5B)-C(5C)  118.5(5) |

[^°]: degrees
Table S5. Anisotropic displacement parameters (Å²x 10³) for Idpc-Fc. The anisotropic displacement factor exponent takes the form: -2π²[ h²a*²U₁₁ + ... + 2 h k a* b* U₁₂ ]

|       | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| Fe(1) | 39(1)| 43(1)| 45(1)| 1(1) | 5(1) | 2(1) |
| C(1)  | 33(4)| 33(4)| 43(4)| -10(3)| 2(3)| -2(3)|
| C(1') | 41(4)| 37(4)| 45(4)| 2(3) | 1(3) | -2(3)|
| C(2)  | 43(4)| 38(4)| 49(3)| -4(3)| 1(4) | 2(4) |
| C(2') | 35(4)| 50(5)| 51(4)| -5(3)| 5(3) | -6(3)|
| C(3)  | 27(4)| 43(3)| 49(3)| -8(3)| -4(3)| 3(4) |
| C(3') | 45(5)| 52(5)| 34(4)| 2(3) | 0(3) | 2(4) |
| C(3A) | 38(4)| 35(4)| 42(4)| -3(3)| 4(3) | 0(3) |
| C(3B) | 41(4)| 30(4)| 35(3)| -8(3)| -4(3)| 1(3) |
| C(3C) | 42(4)| 25(3)| 35(3)| 1(3) | 6(3) | -8(3)|
| C(3D) | 43(4)| 30(3)| 36(3)| 0(3) | -2(3)| -1(3)|
| C(3E) | 48(4)| 28(4)| 41(4)| -3(3)| -5(3)| 7(3) |
| C(4)  | 43(4)| 33(4)| 48(4)| -1(3)| -11(3)| 9(3) |
| C(4') | 47(5)| 42(4)| 44(4)| 5(3) | 5(3) | 9(4) |
| C(5)  | 45(4)| 40(4)| 41(3)| 3(3) | -15(4)| 5(3) |
| C(5') | 45(4)| 47(4)| 48(4)| 3(3) | 4(4) | 8(4) |
| C(5A) | 42(4)| 34(3)| 41(4)| 11(3)| -3(3)| 4(3) |
| C(5B) | 42(4)| 25(4)| 37(3)| 1(3) | 1(3) | 6(3) |
| C(5C) | 32(4)| 31(3)| 46(3)| -1(3)| 2(3) | -13(3)|
| C(5D) | 41(4)| 33(4)| 39(3)| 1(3) | -1(3)| -1(3)|
| C(5E) | 48(4)| 31(3)| 40(3)| 3(3) | 2(3) | -7(3)|
| C(6)  | 60(5)| 40(4)| 36(3)| 4(3) | 1(4) | 0(4) |
| C(6') | 50(5)| 42(4)| 54(4)| 1(4) | 15(4)| 5(4) |
| C(7)  | 55(5)| 39(4)| 48(4)| 2(3) | 10(4)| -3(4)|
| C(7') | 51(5)| 48(4)| 50(4)| -5(3)| 6(4) | 7(4) |
| C(8)  | 46(5)| 36(4)| 49(4)| 6(3) | 4(3) | -4(3)|
| C(8') | 61(5)| 47(5)| 40(4)| 3(3) | 5(4) | 9(4) |
| C(8A) | 48(5)| 35(4)| 40(4)| 2(3) | 0(3) | -6(3)|
| C(9)  | 35(4)| 44(4)| 48(4)| 5(3) | 3(3) | 3(3) |
| C(9') | 48(5)| 45(5)| 64(5)| 3(4) | 10(4)| 5(4) |
| C(10) | 36(4)| 37(4)| 42(4)| 2(3) | -3(3)| -9(3)|
| C(10')| 39(5)| 47(5)| 62(5)| -6(4)| -4(3)| 5(3) |
| C(10A)| 39(4)| 36(3)| 38(3)| -2(3)| 0(3) | -4(3)|
| C(10B)| 37(4)| 28(3)| 40(3)| 4(3) | -2(3)| -2(3)|
| C(11) | 34(4)| 37(4)| 45(4)| 1(3) | -9(3)| 5(3) |
| C(12) | 40(4)| 42(4)| 30(3)| -2(3)| -5(3)| 2(3) |
| C(12A)| 35(4)| 31(4)| 40(3)| -6(3)| 4(3) | -1(3)|
Figure S2: X-ray crystal structure of 1,4-difluoro-6-methylbenzo[c]phenanthrene (3). Thermal ellipsoids are drawn at the 50 % probability level; only one enantiomer shown. Hydrogen atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for 1,4-difluoro-6-methylbenzo[c]phenanthrene (3) (CCDC2013241).

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                            | C_{19}H_{12}F_{2}                          |
| Formula weight                                | 278.29                                     |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | P 21/n                                     |
| Unit cell dimensions                          | a = 10.8868(4) Å                          |
|                                              | b = 8.0267(4) Å                           |
|                                              | β = 94.842(3)°                             |
|                                              | c = 14.6183(5) Å                          |
| Volume                                        | 1272.86(9) Å                               |
| Z                                             | 4                                          |
| Density (calculated)                         | 1.452 Mg/m³                                |
| Absorption coefficient                       | 0.103 mm⁻¹                                 |
| F(000)                                        | 576                                        |
| Crystal size                                  | 0.500 x 0.283 x 0.050 mm³                  |
| Theta range for data collection              | 2.244 to 26.806°                          |
| Index ranges                                  | -13<=h<=12, -10<=k<=10, -17<=l<=18        |
| Reflections collected                        | 9168                                       |
| Independent reflections                      | 2675 [R_{int} = 0.0268]                    |
| Completeness to theta = 25.242°              | 99.1 %                                     |
| Absorption correction                        | Integration                                |
| Max. and min. transmission                   | 0.9871 and 0.9513                         |
| Refinement method                            | Full-matrix least-squares on F²           |
| Data / restraints / parameters                | 2675 / 0 / 191                             |
| Goodness-of-fit on F²                         | 1.052                                      |
| Final R indices [I>2σ(I)]                    | R_f = 0.0418, wR_f = 0.1091               |
|                                              | R indices (all data)                       | R_f = 0.0471, wR_f = 0.1151               |
| Largest diff. peak and hole                   | 0.176 and -0.237 e.Å⁻³                    |
Table S7. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1,4-difluoro-6-methylbenzo[c]phenanthrene (3). $U(eq)$ is defined as one third of the trace of the orthogonalized $U^0$ tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| F1  | 7222(1)| 1594(1)| 5989(1)| 28(1) |
| F2  | 2676(1)| 3784(1)| 4743(1)| 33(1) |
| C8  | 5867(1)| 585(2) | 3220(1)| 24(1) |
| C4  | 3846(1)| 3322(2)| 5041(1)| 27(1) |
| C7  | 4593(1)| 999(2) | 2970(1)| 26(1) |
| C5  | 4533(1)| 2487(2)| 4409(1)| 25(1) |
| C2  | 5448(1)| 3079(2)| 6224(1)| 28(1) |
| C17 | 6500(1)| 1271(2)| 4013(1)| 23(1) |
| C10 | 7746(1)| -743(2)| 2811(1)| 28(1) |
| C16 | 7835(1)| 1272(2)| 4078(1)| 23(1) |
| C15 | 8562(1)| 2431(2)| 4615(1)| 25(1) |
| C1  | 6148(1)| 2282(2)| 5628(1)| 25(1) |
| C3  | 4269(1)| 3651(2)| 5921(1)| 29(1) |
| C12 | 9756(1)| 174(2) | 3547(1)| 28(1) |
| C18 | 5774(1)| 2040(2)| 4688(1)| 23(1) |
| C13 | 10435(1)| 1248(2)| 4112(1)| 29(1) |
| C9  | 6518(1)| -481(2)| 2644(1)| 27(1) |
| C11 | 8449(1)| 198(2) | 3491(1)| 25(1) |
| C6  | 3990(1)| 2016(2)| 3527(1)| 27(1) |
| C14 | 9828(1)| 2422(2)| 4629(1)| 27(1) |
| C19 | 3959(1)| 382(2) | 2082(1)| 32(1) |
Table S8. Bond lengths [Å] for 1,4-difluoro-6-methylbenzo[c]phenanthrene (3).

| Bond Lengths | Value   |
|--------------|---------|
| C(1)-C(2)    | 1.3588(15) |
| C(1)-C(8)    | 1.4092(19)  |
| C(2)-C(3)    | 1.356(2)    |
| C(3)-C(4)    | 1.3425(18)  |
| C(4)-C(5)    | 1.4293(19)  |
| C(5)-C(6)    | 1.356(2)    |
| C(6)-C(7)    | 1.360(2)    |
| C(7)-C(8)    | 1.4425(18)  |
| C(8)-C(9)    | 1.4293(19)  |
| C(9)-C(10)   | 1.3557(19)  |
| C(10)-C(11)  | 1.4300(12)  |
| C(11)-C(12)  | 1.365(2)    |
| C(12)-C(13)  | 1.4493(18)  |
| C(13)-C(14)  | 1.3425(18)  |
| C(14)-C(15)  | 1.356(2)    |
| C(15)-C(16)  | 1.356(2)    |
| C(16)-C(17)  | 1.4493(18)  |
| C(17)-C(18)  | 1.356(2)    |
| C(18)-C(19)  | 1.4293(19)  |
| C(19)-C(20)  | 1.356(2)    |

Table S9. Bond angles [°] for 1,4-difluoro-6-methylbenzo[c]phenanthrene (3).

| Bond Angles  | Value   |
|--------------|---------|
| C(1)-C(2)-C(3) | 119.04(12) |
| C(1)-C(3)-C(4) | 117.72(13) |
| C(2)-C(3)-C(4) | 119.95(13) |
| C(3)-C(4)-C(5) | 119.23(13) |
| C(4)-C(5)-C(6) | 118.67(13) |
| C(5)-C(6)-C(7) | 118.64(13) |
| C(6)-C(7)-C(8) | 118.23(12) |
| C(7)-C(8)-C(9) | 117.95(12) |
| C(8)-C(9)-C(10) | 119.54(13) |
| C(9)-C(10)-C(11) | 120.54(13) |
| C(10)-C(11)-C(12) | 120.77(13) |
| C(11)-C(12)-C(13) | 120.77(13) |
| C(12)-C(13)-C(14) | 120.77(13) |
| C(13)-C(14)-C(15) | 120.77(13) |
| C(14)-C(15)-C(16) | 120.77(13) |
| C(15)-C(16)-C(17) | 120.77(13) |
| C(16)-C(17)-C(18) | 120.77(13) |
| C(17)-C(18)-C(19) | 120.77(13) |
| C(18)-C(19)-C(20) | 120.77(13) |

| Bond Angles  | Value   |
|--------------|---------|
| F(1)-C(1)-C(2) | 116.82(12) |
| F(1)-C(1)-C(18) | 118.65(12) |
| C(2)-C(1)-C(18) | 118.65(12) |
| C(3)-C(2)-C(3) | 119.92(13) |
| C(4)-C(3)-C(2) | 120.72(12) |
| C(5)-C(4)-C(5) | 120.99(13) |
| C(6)-C(5)-C(6) | 120.99(13) |
| C(7)-C(6)-C(7) | 120.99(13) |
| C(8)-C(7)-C(8) | 120.99(13) |
| C(9)-C(8)-C(9) | 120.99(13) |
| C(10)-C(9)-C(10) | 120.99(13) |
| C(11)-C(10)-C(11) | 120.99(13) |
| C(12)-C(11)-C(12) | 120.99(13) |
| C(13)-C(12)-C(13) | 120.99(13) |
| C(14)-C(13)-C(14) | 120.99(13) |
| C(15)-C(14)-C(15) | 120.99(13) |
| C(16)-C(15)-C(16) | 120.99(13) |
| C(17)-C(16)-C(17) | 120.99(13) |
| C(18)-C(17)-C(18) | 120.99(13) |
| C(19)-C(18)-C(19) | 120.99(13) |
| C(20)-C(19)-C(20) | 120.99(13) |
Table S10. Anisotropic displacement parameters (Å² x 10³) for 1,4-difluoro-6-methylbenzo[c]phenanthrene (3). The anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁ + ... + 2hk a* b* U₁₂]

|       | U₁₁   | U₁₂   | U₁₃   | U₂₂   | U₂₃   | U₃₃   |
|-------|-------|-------|-------|-------|-------|-------|
| F(1)  | 28(1) | 33(1) | 24(1) | 2(1)  | 1(1)  | 3(1)  |
| F(2)  | 24(1) | 34(1) | 42(1) | -4(1) | 4(1)  | 4(1)  |
| C(8)  | 27(1) | 23(1) | 23(1) | 3(1)  | 2(1)  | -1(1) |
| C(4)  | 23(1) | 24(1) | 35(1) | 1(1)  | 4(1)  | 0(1)  |
| C(7)  | 28(1) | 25(1) | 25(1) | 3(1)  | 0(1)  | -3(1) |
| C(5)  | 25(1) | 22(1) | 28(1) | 2(1)  | 4(1)  | -1(1) |
| C(2)  | 33(1) | 28(1) | 24(1) | 0(1)  | 6(1)  | -2(1) |
| C(17) | 25(1) | 22(1) | 23(1) | 2(1)  | 3(1)  | -1(1) |
| C(10) | 33(1) | 26(1) | 25(1) | -1(1) | 7(1)  | 2(1)  |
| C(16) | 26(1) | 23(1) | 21(1) | 4(1)  | 2(1)  | 1(1)  |
| C(15) | 28(1) | 26(1) | 22(1) | 2(1)  | 4(1)  | 1(1)  |
| C(1)  | 25(1) | 24(1) | 26(1) | 2(1)  | 3(1)  | -1(1) |
| C(3)  | 31(1) | 26(1) | 31(1) | -2(1) | 11(1) | 0(1)  |
| C(12) | 29(1) | 28(1) | 27(1) | 3(1)  | 8(1)  | 5(1)  |
| C(18) | 25(1) | 21(1) | 24(1) | 2(1)  | 4(1)  | -2(1) |
| C(13) | 24(1) | 32(1) | 30(1) | 7(1)  | 5(1)  | 2(1)  |
| C(9)  | 33(1) | 26(1) | 22(1) | -1(1) | 2(1)  | -1(1) |
| C(11) | 29(1) | 24(1) | 23(1) | 4(1)  | 5(1)  | 2(1)  |
| C(6)  | 25(1) | 25(1) | 31(1) | 3(1)  | 1(1)  | -1(1) |
| C(14) | 27(1) | 30(1) | 25(1) | 3(1)  | 1(1)  | -2(1) |
| C(19) | 33(1) | 33(1) | 30(1) | -1(1) | -2(1) | 1(1)  |
**Figure S3:** X-ray crystal structure of 13,16-difluoro-4-ferrocenylbenzo[s] picene (5). Thermal ellipsoids are drawn at the 50% probability level; only one enantiomer shown. Hydrogen atoms are omitted for clarity.

**Table S11.** Crystal data and structure refinement for 13,16-difluoro-4-ferrocenylbenzo[s] picene (5) (CCDC2013242).

| Property                                               | Value                          |
|--------------------------------------------------------|--------------------------------|
| Empirical formula                                      | C_{36}H_{22}F_{2}Fe             |
| Formula weight                                         | 548.38                         |
| Temperature                                            | 100(2) K                       |
| Wavelength                                             | 0.71073 Å                      |
| Crystal system                                         | monoclinic                     |
| Space group                                            | P2_1/n                         |
| Unit cell dimensions                                   | a = 11.354(3) Å, b = 7.2776(11) Å, c = 29.406(7) Å |
| Volume                                                 | 2425.8(9) Å                    |
| Z                                                       | 4                              |
| Density (calculated)                                   | 1.502                          |
| Absorption coefficient                                 | 0.663                          |
| F(000)                                                 | 1128                           |
| Crystal size                                           | 0.02 × 0.20 × 0.30 mm^3        |
| Theta range for data collection                        | 2.244 to 26.806°               |
| Index ranges                                           | -13 <= h <= 13, -8 <= k <= 8, -34 <= l <= 34 |
| Reflections collected                                  | 29912                          |
| Independent reflections                                | 4266 [R_{int} = 0.0739]         |
| Completeness to theta                                  | 100%                           |
| Absorption correction                                  | Integration                    |
| Max. and min. transmission                             | 0.9903 and 0.8604              |
| Refinement method                                      | Full-matrix least-squares on F^2 |
| Data / restraints / parameters                          | 4266 / 0 / 353                 |
| Goodness-of-fit on F^2                                  | 1.063                          |
| Final R indices [I>2sigma(I)]                          | R_1 = 0.0639, wR_2 = 0.1544    |
| R indices (all data)                                   | R_1 = 0.0829, wR_2 = 0.1642    |
| Largest diff. peak and hole                            | 0.90 and -0.75 e Å^3           |
Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 13,16-difluoro-4-ferrocenylbenzo[s] picene (5). U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| Fe(1)| 6091(1)| -84(1)| 877(1)| 31(1) |
| F(1) | 5201(2)| 7856(3)| 2657(1)| 32(1) |
| F(2) | 3581(2)| 6600(3)| 4311(1)| 34(1) |
| C(1) | 5662(3)| 2631(5)| 1723(1)| 27(1) |
| C(2) | 6773(4)| 3418(5)| 1767(1)| 27(1) |
| C(3) | 7139(3)| 4453(6)| 2157(1)| 27(1) |
| C(4) | 6390(3)| 4738(5)| 2493(1)| 25(1) |
| C(5) | 5254(3)| 3957(5)| 2471(1)| 25(1) |
| C(6) | 4474(3)| 4153(5)| 2835(1)| 23(1) |
| C(7) | 4596(3)| 5599(5)| 3185(1)| 24(1) |
| C(8) | 4965(3)| 7398(6)| 3092(1)| 27(1) |
| C(9) | 5024(4)| 8791(6)| 3407(2)| 31(1) |
| C(10)| 4615(4)| 8470(5)| 3835(2)| 29(1) |
| C(11)| 4140(3)| 6768(6)| 3920(1)| 27(1) |
| C(12)| 4135(3)| 5269(5)| 3615(1)| 23(1) |
| C(13)| 3518(3)| 3535(5)| 3689(1)| 24(1) |
| C(14)| 3379(4)| 2736(5)| 4130(1)| 26(1) |
| C(15)| 4155(4)| 3122(6)| 4514(1)| 30(1) |
| C(16)| 4032(4)| 2236(6)| 4921(2)| 37(1) |
| C(17)| 3131(5)| 957(7)| 4969(2)| 41(1) |
| C(18)| 2388(4)| 512(6)| 4601(2)| 35(1) |
| C(19)| 2513(4)| 1344(6)| 4175(2)| 29(1) |
| C(20)| 1856(4)| 709(6)| 3772(2)| 30(1) |
| C(21)| 2138(3)| 1264(5)| 3356(2)| 28(1) |
| C(22)| 3025(3)| 2635(5)| 3301(1)| 25(1) |
| C(23)| 3523(3)| 2936(5)| 2866(1)| 24(1) |
| C(24)| 3173(3)| 1889(6)| 2470(1)| 28(1) |
| C(25)| 3787(4)| 1909(6)| 2090(2)| 30(1) |
| C(26)| 4896(3)| 2828(5)| 2087(1)| 25(1) |
| C(27)| 5266(4)| 1825(6)| 1268(2)| 31(1) |
| C(28)| 4513(4)| 285(7)| 1155(2)| 39(1) |
| C(29)| 4329(4)| 181(7)| 676(2)| 40(1) |
| C(30)| 5016(4)| 1609(7)| 482(2)| 37(1) |
| C(31)| 5575(4)| 2617(6)| 846(2)| 35(1) |
| C(32)| 7493(5)| -1146(8)| 1261(2)| 54(2) |
| C(33)| 6708(6)| -2574(7)| 1108(2)| 52(1) |
| C(34)| 6640(5)| -2541(7)| 623(2)| 45(1) |
| C(35)| 7375(4)| -1086(7)| 480(2)| 45(1) |
| C(36)| 7879(4)| -223(8)| 876(2)| 53(1) |
Table S13. Bond lengths [Å] for 13,16-difluoro-4-ferrocenylbenzo[5] picene (5).

|          |          |          |          |          |
|----------|----------|----------|----------|----------|
| Fe(1)-C28 | 2.030(5) | C(5)-C(6) | 1.434(6) | C(18)-C(19) | 1.405(6) |
| Fe(1)-C36 | 2.033(5) | C(5)-C(26) | 1.437(6) | C(19)-C(20) | 1.438(6) |
| Fe(1)-C33 | 2.045(5) | C(6)-C(23) | 1.403(5) | C(20)-C(21) | 1.344(6) |
| Fe(1)-C34 | 2.048(5) | C(6)-C(7) | 1.473(5) | C(21)-C(22) | 1.433(6) |
| Fe(1)-C30 | 2.048(5) | C(7)-C(8) | 1.407(6) | C(22)-C(23) | 1.446(6) |
| Fe(1)-C32 | 2.049(5) | C(7)-C(12) | 1.416(6) | C(23)-C(24) | 1.428(6) |
| Fe(1)-C31 | 2.052(5) | C(8)-C(9) | 1.373(6) | C(24)-C(25) | 1.350(6) |
| Fe(1)-C35 | 2.052(5) | C(9)-C(10) | 1.386(6) | C(25)-C(26) | 1.426(6) |
| Fe(1)-C29 | 2.062(5) | C(10)-C(11) | 1.380(6) | C(27)-C(31) | 1.431(6) |
| Fe(1)-C27 | 2.063(4) | C(11)-C(12) | 1.413(6) | C(27)-C(28) | 1.437(6) |
| F(1)-C8  | 1.362(5) | C(12)-C(13) | 1.466(5) | C(28)-C(29) | 1.414(7) |
| F(2)-C11 | 1.349(5) | C(13)-C(22) | 1.405(6) | C(29)-C(30) | 1.438(7) |
| C(1)-C2  | 1.385(6) | C(13)-C(14) | 1.437(6) | C(30)-C(31) | 1.418(7) |
| C(1)-C26 | 1.423(6) | C(14)-C(15) | 1.422(6) | C(32)-C(36) | 1.407(9) |
| C(1)-C27 | 1.506(6) | C(14)-C(19) | 1.423(6) | C(32)-C(33) | 1.424(8) |
| C(2)-C3  | 1.414(6) | C(15)-C(16) | 1.372(6) | C(33)-C(34) | 1.424(7) |
| C(3)-C4  | 1.356(6) | C(16)-C(17) | 1.396(7) | C(34)-C(35) | 1.427(8) |
| C(4)-C5  | 1.408(6) | C(17)-C(18) | 1.373(7) | C(35)-C(36) | 1.415(7) |
Table S14. Bond angles [°] for 13,16-difluoro-4-ferrocenylbenzo[6]picene (5).

| Bond                  | Angle 1 | Angle 2 | Angle 3 |
|-----------------------|---------|---------|---------|
| C(28)-Fe(1)-C(36)    | 155.7(2)| C(29)-Fe(1)-C(27) | 68.43(17) |
| C(28)-Fe(1)-C(33)    | 106.0(2)| C(2)-C(1)-C(26)   | 118.7(4)  |
| C(36)-Fe(1)-C(33)    | 68.5(3) | C(2)-C(1)-C(27)   | 117.9(4)  |
| C(28)-Fe(1)-C(34)    | 123.8(2)| C(26)-C(1)-C(27)  | 122.9(4)  |
| C(36)-Fe(1)-C(34)    | 68.4(2) | C(1)-C(2)-C(3)    | 121.3(4)  |
| C(33)-Fe(1)-C(34)    | 40.7(2) | C(4)-C(3)-C(2)    | 120.3(4)  |
| C(28)-Fe(1)-C(30)    | 68.8(2) | C(3)-C(4)-C(5)    | 121.1(4)  |
| C(36)-Fe(1)-C(30)    | 126.3(2)| C(4)-C(5)-C(6)    | 121.9(4)  |
| C(33)-Fe(1)-C(30)    | 154.6(2)| C(4)-C(5)-C(26)   | 119.0(4)  |
| C(34)-Fe(1)-C(30)    | 120.20(19)| C(6)-C(5)-C(26)  | 119.0(4)  |
| C(28)-Fe(1)-C(32)    | 120.2(2)| C(23)-C(6)-C(5)   | 119.7(4)  |
| C(36)-Fe(1)-C(32)    | 40.3(3) | C(23)-C(6)-C(7)   | 116.6(4)  |
| C(33)-Fe(1)-C(32)    | 40.7(2) | C(5)-C(6)-C(7)    | 123.7(4)  |
| C(34)-Fe(1)-C(32)    | 68.1(2) | C(8)-C(7)-C(12)   | 121.4(4)  |
| C(30)-Fe(1)-C(32)    | 163.4(2)| C(8)-C(7)-C(6)    | 123.1(4)  |
| C(28)-Fe(1)-C(31)    | 68.6(2) | C(12)-C(7)-C(6)   | 118.3(3)  |
| C(36)-Fe(1)-C(31)    | 109.3(2)| F(1)-C(8)-C(9)    | 116.7(4)  |
| C(33)-Fe(1)-C(31)    | 162.74(19)| F(1)-C(8)-C(7)  | 119.1(4)  |
| C(34)-Fe(1)-C(31)    | 155.9(2)| C(9)-C(8)-C(7)    | 124.0(4)  |
| C(30)-Fe(1)-C(31)    | 40.47(18)| C(8)-C(9)-C(10)  | 118.9(4)  |
| C(32)-Fe(1)-C(31)    | 126.6(2)| C(11)-C(10)-C(9)  | 118.1(4)  |
| C(28)-Fe(1)-C(35)    | 161.5(2)| F(2)-C(11)-C(10)  | 116.4(4)  |
| C(36)-Fe(1)-C(35)    | 40.5(2) | F(2)-C(11)-C(12)  | 119.1(4)  |
| C(33)-Fe(1)-C(35)    | 68.5(2) | C(10)-C(11)-C(12)| 124.4(4)  |
| C(34)-Fe(1)-C(35)    | 40.7(2) | C(11)-C(12)-C(7)  | 116.6(4)  |
| C(30)-Fe(1)-C(35)    | 108.1(2)| C(11)-C(12)-C(13)| 123.6(4)  |
| C(32)-Fe(1)-C(35)    | 67.9(2) | C(7)-C(12)-C(13)  | 118.9(3)  |
| C(31)-Fe(1)-C(35)    | 121.7(2)| C(22)-C(13)-C(14)| 119.0(4)  |
| C(28)-Fe(1)-C(29)    | 40.43(19)| C(22)-C(13)-C(12)| 116.8(4)  |
| C(36)-Fe(1)-C(29)    | 163.2(2)| C(14)-C(13)-C(12)| 124.2(4)  |
| C(33)-Fe(1)-C(29)    | 119.1(2)| C(15)-C(14)-C(19)| 117.8(4)  |
| C(34)-Fe(1)-C(29)    | 106.8(2)| C(15)-C(14)-C(13)| 122.8(4)  |
| C(32)-Fe(1)-C(29)    | 41.0(2) | C(19)-C(14)-C(13)| 119.0(4)  |
| C(31)-Fe(1)-C(29)    | 154.5(2)| C(16)-C(15)-C(14)| 120.7(4)  |
| C(35)-Fe(1)-C(29)    | 68.17(19)| C(15)-C(16)-C(17)| 120.9(4)  |
| C(35)-Fe(1)-C(29)    | 125.46(19)| C(18)-C(17)-C(16)| 119.8(4)  |
| C(36)-Fe(1)-C(27)    | 41.09(18)| C(17)-C(18)-C(19)| 120.9(4)  |
| C(36)-Fe(1)-C(27)    | 121.28(19)| C(18)-C(19)-C(14)| 119.7(4)  |
| C(33)-Fe(1)-C(27)    | 124.7(2) | C(18)-C(19)-C(20)| 121.4(4)  |
| C(34)-Fe(1)-C(27)    | 161.5(2)| C(14)-C(19)-C(20)| 118.7(4)  |
| C(30)-Fe(1)-C(27)    | 68.68(18)| C(21)-C(20)-C(19)| 120.9(4)  |
| C(32)-Fe(1)-C(27)    | 108.05(19)| C(20)-C(21)-C(22)| 121.2(4)  |
| C(31)-Fe(1)-C(27)    | 40.70(18)| C(13)-C(22)-C(21)| 118.9(4)  |
| C(35)-Fe(1)-C(27)    | 156.4(2) | C(13)-C(22)-C(23)| 119.4(4)  |
Table S15. Anisotropic displacement parameters (Å² x 10³) for 13,16-difluoro-4-ferrocenylbenzo[s] picene (5).
The anisotropic displacement factor exponent takes the form: $-2\pi^2 \left[ h^2 a^* a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} \right]$.

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Fe(1) | 33(1)    | 28(1)    | 32(1)    | -2(1)    | 1(1)     | 0(1)     |
| F(1)  | 37(1)    | 25(1)    | 35(1)    | 5(1)     | 3(1)     | -3(1)    |
| F(2)  | 38(1)    | 28(1)    | 39(1)    | -7(1)    | 11(1)    | -2(1)    |
| C(1)  | 26(2)    | 24(2)    | 30(2)    | 0(2)     | 2(2)     | 2(2)     |
| C(2)  | 28(2)    | 23(2)    | 30(2)    | 1(2)     | 5(2)     | 0(2)     |
| C(3)  | 22(2)    | 25(2)    | 35(2)    | 2(2)     | -1(2)    | -1(2)    |
| C(4)  | 25(2)    | 20(2)    | 29(2)    | 1(2)     | -1(2)    | -1(2)    |
| C(5)  | 24(2)    | 24(2)    | 27(2)    | 4(2)     | -1(2)    | 2(2)     |
| C(6)  | 23(2)    | 19(2)    | 26(2)    | 0(2)     | -4(2)    | 3(2)     |
| C(7)  | 19(2)    | 19(2)    | 32(2)    | -1(2)    | -1(2)    | 2(2)     |
| C(8)  | 22(2)    | 26(2)    | 34(2)    | 1(2)     | 1(2)     | 1(2)     |
| C(9)  | 26(2)    | 19(2)    | 47(3)    | -3(2)    | 4(2)     | -1(2)    |
| C(10) | 26(2)    | 21(2)    | 41(2)    | -7(2)    | 1(2)     | 2(2)     |
| C(11) | 24(2)    | 26(2)    | 33(2)    | -2(2)    | 6(2)     | 1(2)     |
| C(12) | 20(2)    | 18(2)    | 32(2)    | -1(2)    | -1(2)    | 3(2)     |
| C(13) | 18(2)    | 22(2)    | 33(2)    | -3(2)    | 3(2)     | 2(2)     |
| C(14) | 27(2)    | 22(2)    | 30(2)    | -3(2)    | 4(2)     | 2(2)     |
| C(15) | 31(2)    | 25(2)    | 32(2)    | -2(2)    | 2(2)     | -3(2)    |
| C(16) | 47(3)    | 34(2)    | 32(2)    | -4(2)    | 2(2)     | -10(2)   |
| C(17) | 55(3)    | 37(3)    | 30(2)    | 2(2)     | 8(2)     | -10(2)   |
| C(18) | 40(2)    | 29(2)    | 37(2)    | -3(2)    | 9(2)     | -9(2)    |
| C(19) | 27(2)    | 25(2)    | 35(2)    | -2(2)    | 6(2)     | -1(2)    |
| C(20) | 26(2)    | 25(2)    | 38(2)    | -2(2)    | 6(2)     | -5(2)    |
| C(21) | 25(2)    | 23(2)    | 35(2)    | -4(2)    | 0(2)     | -3(2)    |
| C(22) | 21(2)    | 22(2)    | 33(2)    | -1(2)    | 1(2)     | 2(2)     |
| C(23) | 22(2)    | 21(2)    | 30(2)    | 0(2)     | 2(2)     | 3(2)     |
| C(24) | 23(2)    | 27(2)    | 34(2)    | -2(2)    | 1(2)     | -2(2)    |
| C(25) | 27(2)    | 30(2)    | 33(2)    | -7(2)    | -1(2)    | -5(2)    |
| C(26) | 24(2)    | 19(2)    | 33(2)    | 1(2)     | 0(2)     | -1(2)    |
| C(27) | 27(2)    | 33(2)    | 34(2)    | -3(2)    | 2(2)     | 2(2)     |
| C(28) | 37(2)    | 40(3)    | 41(3)    | -6(2)    | 6(2)     | -7(2)    |
| C(29) | 37(2)    | 44(3)    | 36(2)    | -10(2)   | -6(2)    | -7(2)    |
| C(30) | 38(2)    | 42(3)    | 31(2)    | -2(2)    | 1(2)     | 11(2)    |
| C(31) | 38(2)    | 32(2)    | 36(2)    | 2(2)     | 4(2)     | 5(2)     |
| C(32) | 60(3)    | 54(3)    | 46(3)    | -17(3)   | -17(3)   | 24(3)    |
| C(33) | 83(4)    | 30(2)    | 41(3)    | -1(2)    | -12(3)   | 12(3)    |
| C(34) | 61(3)    | 32(2)    | 41(3)    | -7(2)    | -3(2)    | 12(2)    |
| C(35) | 41(3)    | 49(3)    | 45(3)    | -9(2)    | -3(2)    | 14(2)    |
| C(36) | 34(2)    | 52(3)    | 72(4)    | -22(3)   | 2(2)     | 7(2)     |
Packing Diagrams and Other Visualization

**Figure S4**: Packing diagram of 1,4-difluoro-6-methylbenzo[c]phenanthrene (3) in the crystal. View along $b$-axis, enantiomers are shown in different color, elementary cell shown in black.

**Figure S5**: Packing diagram of 1,4-difluoro-6-methylbenzo[c]phenanthrene (3) in the crystal. View along $c$-axis, enantiomers are shown in different color, elementary cell shown in black.
**Figure S6.** Wire representation of 4-ferrocenyl-13,16-difluorobenzos[\textgreek{e}]picene (5) showing distance between C4H⋯F1 and C15H⋯F2; other hydrogen atoms are omitted for clarity; distances and structure from X-ray diffraction data.

**Figure S7.** Packing diagram of \textit{Idpc-Fc} (8h) in the crystal. View along \textit{a}-axis, enantiomers are shown in different color, elementary cell shown in black.

**Figure S8.** Packing diagram of \textit{Idpc-Fc} (8h) in the crystal. View along \textit{b}-axis.
Figure S9. Packing diagram of Idpc-Fc (8h) in the crystal. Stacked view along b-axis.

Figure S10. Packing diagram of Idpc-Fc (8h) in the crystal showing partial bowl-in-bowl stacking of the fluoranthene-part; top view; centroid-centroid distances given in Å.

Figure S11. Packing diagram of Idpc-Fc (8h) in the crystal showing partial bowl-in-bowl stacking of the fluoranthene-part; side view; centroid-centroid distances given in Å.
Figure S12. Calculated pyramidalization angle $\theta_p$ of central carbon atoms based on X-ray data of IdPc-Fc and [IdPc].
Quantum Chemistry

The ground state electronic structures of the full models of the studied compounds were calculated by density functional theory (DFT) methods using the Gaussian 16 program packages. Geometry optimization followed by vibrational analysis was performed in solvent media. Solvent effects were described by the polarizable continuum model (PCM) with standard parameters for dichloromethane. For Fe, the ten-electron quasirelativistic effective core potential (ECP) MDF10 was used and 6-31G(d) polarized double-ζ basis sets for the remaining atoms were employed together with the Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0). The GaussSum program package was used to analyze the results, while the visualization of the results was performed with the Avogadro program package. Graphical representations of molecular orbitals were generated with the help of GNU Parallel and plotted using the vmd program package in combination with POV-Ray.

Figure S 13. Molecular orbital scheme displaying the effect of various substituents on the frontier orbitals. – From top to bottom: LUMO+1, LUMO, HOMO and HOMO-1.
Table S 16. Assignment of the electronic transitions of the studied indacenopicene derivatives.

| Substance | $\lambda_{ex}$ in nm | $\lambda_{calc}$ in nm | $f$  | Major contribution | Assignment            |
|-----------|----------------------|------------------------|------|--------------------|----------------------|
| Idpc      | 491                  | 450                    | 0.021| HOMO->LUMO (98%)   | $\pi\pi^*$           |
|           | 449                  | 415                    | 0.043| H-1->LUMO (93%)    | $\pi\pi^*$, weak ICT |
|           | 384                  | 360                    | 0.119| H-2->LUMO (90%)   | $\pi\pi^*$           |
|           | 318                  | 319                    | 0.042| HOMO->L+1 (83%)   | $\pi\pi^*$, weak ICT |
|           | 286                  | 273                    | 1.348| HOMO->L+2 (78%)   | $\pi\pi^*$, weak ICT |
| Idpc-Br   | 492                  | 455                    | 0.0446| HOMO->LUMO (97%)  | $\pi\pi^*$           |
|           | 451                  | 419                    | 0.0457| H-1->LUMO (92%)    | $\pi\pi^*$, weak ICT |
|           | 386                  | 364                    | 0.1403| H-2->LUMO (91%)   | $\pi\pi^*$           |
|           | 318                  | 324                    | 0.0574| HOMO->L+1 (79%)   | $\pi\pi^*$, weak ICT |
|           | 286                  | 280                    | 1.1153| HOMO->L+2 (71%)   | $\pi\pi^*$, weak ICT |
| Idpc-Ph (8a) | 498             | 462                    | 0.0865| HOMO->LUMO (95%)  | $\pi\pi^*$, weak ICT |
|           | 449                  | 419                    | 0.0468| H-1->LUMO (90%)    | $\pi\pi^*$           |
|           | 387                  | 365                    | 0.1995| H-2->LUMO (92%)   | $\pi\pi^*$           |
|           | 336                  | 312                    | 0.1512| H-1->L+1 (80%)   | $\pi\pi^*$           |
|           | 293                  | 286                    | 1.1137| H-6->LUMO (13%),  | $\pi\pi^*$, (weak) ICT |
|           |                      |                        |      | HOMO->L+2 (55%)   |                      |
| Idpc-Ph-OMe(8b) | 501           | 471                    | 0.1433| HOMO->LUMO (90%)  | $\pi\pi^*$, (weak) ICT |
|           | 447                  | 417                    | 0.05  | H-1->LUMO (87%)   | $\pi\pi^*$           |
|           | 389                  | 374                    | 0.3315| H-2->LUMO (89%)   | $\pi\pi^*$, (weak) ICT |
|           | 321                  | 311                    | 0.141 | H-1->L+1 (78%)   | $\pi\pi^*$           |
|           | 294                  | 289                    | 0.7747| HOMO->L+2 (50%)   | $\pi\pi^*$, weak ICT |
| Idpc-Ph-NO2 (8c) | 496           | 467                    | 0.1443| HOMO->LUMO (82%)  | $\pi\pi^*$, ICT      |
|           | 457                  | 433                    | 0.0599| H-1->LUMO (84%)    | $\pi\pi^*$, ICT      |
|           | 390                  | 387                    | 0.2645| HOMO->L+1 (74%)   | $\pi\pi^*$, ICT      |
|           | 329                  | 309                    | 0.1134| H-1->L+2 (74%)   | $\pi\pi^*$, (weak) ICT |
|           | 290                  | 278                    | 0.9535| HOMO->L+3 (54%)   | $\pi\pi^*$, (weak) ICT |
| Idpc-Ph-o-F (8d) | 494           | 491                    | 0.0776| HOMO->LUMO (95%)  | $\pi\pi^*$, weak ICT |
|           | 451                  | 420                    | 0.0464| H-1->LUMO (90%)    | $\pi\pi^*$           |
|           | 387                  | 365                    | 0.1876| H-2->LUMO (92%)   | $\pi\pi^*$           |
|           | 335                  | 312                    | 0.1533| H-1->L+1 (80%)   | $\pi\pi^*$           |
|           | 292                  | 284                    | 1.2134| HOMO->L+2 (63%)   | $\pi\pi^*$, (weak) ICT |
| Idpc-Ph-o-Cl (8e) | 492           | 458                    | 0.0561| HOMO->LUMO (97%)  | $\pi\pi^*$, weak ICT |
|           | 451                  | 420                    | 0.0458| H-1->LUMO (91%)    | $\pi\pi^*$           |
|           | 387                  | 364                    | 0.1597| H-2->LUMO (91%)   | $\pi\pi^*$           |
|           | 336                  | 311                    | 0.1588| H-1->L+1 (81%)   | $\pi\pi^*$           |
|           | 294                  | 282                    | 1.2234| HOMO->L+2 (61%)   | $\pi\pi^*$, (weak) ICT |
| Idpc-Ph-(m-OMe)2 (8f) | 499           | 461                    | 0.0869| HOMO->LUMO (94%)  | $\pi\pi^*$, (weak) ICT |
|           | 451                  | 419                    | 0.0475| H-2->LUMO (81%)    | $\pi\pi^*$, weak ICT |
|           | 388                  | 365                    | 0.2074| H-3->LUMO (92%)   | $\pi\pi^*$           |
|           | 334                  | 311                    | 0.1593| H-2->L+1 (72%)   | $\pi\pi^*$, weak ICT |
|           | 299                  | 282                    | 1.1047| HOMO->L+2 (62%)   | $\pi\pi^*$, (weak) ICT |
| Substance                  | λ_{exp} in nm | λ_{calc} in nm | f   | Major contribution                        | Assignment                  |
|---------------------------|--------------|----------------|-----|------------------------------------------|-----------------------------|
| Idpc-Ph-(m-CF₃)₂(8g)      | 493          | 459            | 0.073 | HOMO→LUMO (96%)                         | ππ*                         |
|                           | 455          | 423            | 0.0479 | H-1→LUMO (92%)                          | ππ*, (weak) ICT             |
|                           | 388          | 367            | 0.1693 | H-2→LUMO (91%)                          | ππ*, (weak) ICT             |
|                           | 338          | 328            | 0.122  | HOMO→L+1 (76%)                          | ππ*, (weak) ICT             |
|                           | 294          | 287            | 0.8942 | HOMO→L+3 (72%)                          | ππ*, ICT                    |
| Idpc-Fc (8h)              | 532          | 481            | 0.0703 | H-1→L+6 (26%), HOMO→LUMO (40%)         | ππ*, MLCT                   |
|                           | 501          | 419            | 0.0453 | H-3→LUMO (88%)                          | ππ*, (ICT), dd*             |
|                           | 452          | 364            | 0.1923 | H-4→LUMO (90%)                          | ππ*, (ICT), dd*             |
|                           | 389          | 324            | 0.0279 | H-7→LUMO (58%)                          | ππ*, (ICT), dd*             |
|                           | 346          | 312            | 0.1316 | H-3→L+1 (62%), H-4→L+1 (14%)            | ππ*, (ICT)                  |
|                           | 290          | 290            | 0.8402 | H-4→L+2 (48%)                           |                             |
| Idpc≡Ph (8i)              | 508          | 483            | 0.283  | HOMO→LUMO (90%)                         | ππ*                         |
|                           | 449          | 432            | 0.0664 | H-1→LUMO (88%)                          | ππ*, weak ICT               |
|                           | 397          | 384            | 0.529  | H-2→LUMO (91%)                          | ππ*                         |
|                           | 352          | 344            | 0.1997 | HOMO→L+1 (82%)                          | ππ*, weak ICT               |
|                           | 292          | 301            | 0.8318 | HOMO→L+2 (71%)                          | ππ*, weak ICT               |
| Idpc≡Ph-NO₂ (8j)          | 507          | 492            | 0.4465 | HOMO→LUMO (83%)                         | ππ*, (weak) ICT             |
|                           | 464          | 452            | 0.1287 | H-1→LUMO (83%)                          | ππ*, ICT                    |
|                           | 399          | 407            | 0.714  | H-2→LUMO (56%)                          | ππ*, (weak) ICT             |
|                           | 339          | 393            | 0.0723 | H-3→LUMO (66%)                          | ππ*, weak ICT               |
|                           | 292          | 328            | 0.0159 | HOMO→L+2 (81%)                          | ππ*, (weak) ICT             |
| Idpc≡Ph-Br (8k)           | 504          | 484            | 0.3188 | HOMO→LUMO (90%)                         | ππ*, (weak) ICT             |
|                           | 460          | 434            | 0.0756 | H-1→LUMO (88%)                          | ππ*                         |
|                           | 397          | 386            | 0.6161 | H-2→LUMO (91%)                          | ππ*                         |
|                           | 353          | 345            | 0.2418 | HOMO→L+1 (81%)                          | ππ*, weak ICT               |
|                           | 293          | 304            | 0.5564 | HOMO→L+2 (63%)                          | ππ*, weak ICT               |
| Idpc≡Fc (8l)              | 519          | 490            | 0.2312 | HOMO→LUMO (65%)                         | ππ*, MLCT                   |
|                           | 485          | 428            | 0.0636 | H-3→LUMO (81%)                          | ππ*, (ICT), dd*             |
|                           | 459          | 380            | 0.2887 | H-4→LUMO (80%)                          | ππ*, (ICT), dd*             |
|                           | 394          | 331            | 0.0716 | H-7→LUMO (66%)                          | ππ*, (ICT), dd*             |
|                           | 350          | 316            | 0.1082 | H-3→L+1 (66%)                           | ππ*, (ICT), dd*             |
|                           | 290          | 302            | 0.3742 | H-5→L+1 (18%), H-4→L+1 (18%), H-2→L+1   | ππ*, (ICT),                  |
|                           |              |                |       | (10%), HOMO→L+2 (34%)                   | (MLCT)                      |
| (Idpc)₂ (9)               | 504          | 478            | 0.3242 | HOMO→LUMO (85%)                         | ππ*, weak ICT               |
|                           | 474          | 455            | 0.006  | HOMO→L+1 (51%)                          | ππ*, weak ICT               |
|                           | 391          | 396            | 0.0024 | H-3→LUMO (39%)                          | ππ*, weak ICT               |
|                           | 322          | 330            | 0.0673 | HOMO→L+1 (41%)                          | ππ*, weak ICT               |
|                           | 296          | 283            | 1.2121 | H-3→L+3 (21%), HOMO→L+5 (38%)           | ππ*, weak ICT               |
Figure S 14. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc.

Figure S 15. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Br.
Figure S 16. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Ph (8a).

Figure S 17. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Ph-OMe (8b).
Figure S 18. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Ph-NO$_2$ (8c).

Figure S 19. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Ph-o-F (8d).
Figure S 20. Superposition of experimental and calculated spectra and corresponding oscillator strengths of Idpc-Ph-o-Cl (8e).

Figure S 21. Superposition of experimental and calculated spectra and corresponding oscillator strengths of Idpc-Ph-(m-OMe)₂ (8f).
Figure S 22. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Ph-(m-CF₃)$_2$ (8g).

Figure S 23. Superposition of experimental and calculated spectra and corresponding oscillator strengths of 1dpc-Fe (8h).
Figure S 24. Superposition of experimental and calculated spectra and corresponding oscillator strengths of \( \text{1dpc-Ph} \) (8i).

Figure S 25. Superposition of experimental and calculated spectra and corresponding oscillator strengths of \( \text{1dpc-Ph-NO}_2 \) (8j).
Figure S 26. Superposition of experimental and calculated spectra and corresponding oscillator strengths of $\text{1dpc-Br-Ph}$ (8k).

Figure S 27. Superposition of experimental and calculated spectra and corresponding oscillator strengths of $\text{1dpc-Fc}$ (8l).
Figure S 28. Superposition of experimental and calculated spectra and corresponding oscillator strengths of (Idpc)$_2$(9).
**Figure S 29.** MO diagram and electron difference density maps of Idpc-Br.

**Figure S 30.** MO diagram and electron difference density maps of Idpc-Ph (8a).
Figure S 31. MO diagram and electron difference density maps of Idpc-Ph-OMe (8b).

Figure S 32. MO diagram and electron difference density maps of Idpc-Ph-NO₂ (8c).
Figure S 33. MO diagram and electron difference density maps of Idpc-Ph-o-F (8d).

Figure S 34. MO diagram and electron difference density maps of Idpc-Ph-o-Cl (8e).
Figure S 35. MO diagram and electron difference density maps of Idpc-Ph(m-OMe)$_2$ (8f).

Figure S 36. MO diagram and electron difference density maps of Idpc-Ph(m-CF$_3$)$_2$ (8g).
Figure S 37. MO diagram and electron difference density maps of Idpc-Fc (8h).

Figure S 38. MO diagram and electron difference density maps of Idpc≡Ph (8i).
Figure S 39. MO diagram and electron difference density maps of 1dpc-≡-Ph-NO2 (8j).

Figure S 40. MO diagram and electron difference density maps of 1dpc-≡-Ph-Br (8k).
Figure S 41. MO diagram and electron difference density maps of Idpc≡Fe (8).

Figure S 42. MO diagram and electron difference density maps of (Idpc)$_2$ (9).
Electronic Absorption Spectra for Solvatochromism experiments

Figure S 43. Superimposed electronic absorption spectra of ortho-substituted phenyl derivatives of indacenopine in dichloromethane.

Figure S 44. Solvatochromism experiment for 1dpc.
Figure S 45. Solvatochromism experiment for 1dpe-PhOMe (8b).

Figure S 46. Solvatochromism experiment for 1dpe-PhNO2 (8c).
Figure S 47. Solvatochromism experiment for 1dp-Fe (8h).

Figure S 48. Solvatochromism experiment for 1dp-PhNO₂ (8j).
**Luminescence Spectroscopy**

UV/vis/NIR spectra in CH$_2$Cl$_2$ solutions of the respective compounds were recorded on a TIDAS fiber optic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from J&M in HELLMAN quartz cuvettes with 0.1 cm optical path lengths. Luminescence spectra and lifetimes as well as quantum yields were measured in CH$_2$Cl$_2$ solutions on a PicoQuant FluoTime 300 spectrometer. Absolute quantum yields were determined with an integrating sphere within the PicoQuant FluoTime 300 spectrometer.
Figure S 49. Superimposed absorption, excitation and emission spectrum of Idpc-Br.

Figure S 50. Superimposed absorption, excitation and emission spectrum of Idpc-Ph (8a).
Figure S 51. Superimposed absorption, excitation and emission spectrum of 1dpc-Ph-OMe (8b).

Figure S 52. Superimposed absorption, excitation and emission spectrum of 1dpc-Ph-NO₂ (8c).
Figure S 53. Superimposed absorption, excitation and emission spectrum of 1dpc-Ph-\(\alpha\)-F(8d).

Figure S 54. Superimposed absorption, excitation and emission spectrum of 1dpc-Ph-\(\alpha\)-Cl(8e).
Figure S 55. Superimposed absorption, excitation and emission spectrum of Idpc-Ph-(m-OMe)₂ (8f).

Figure S 56. Superimposed absorption, excitation and emission spectrum of Idpc-Ph-(m-CF₃)₂ (8g).
Figure S 57. Superimposed absorption, excitation and emission spectrum of 1dpc-Fc (8h).

Figure S 58. Superimposed absorption, excitation and emission spectrum of 1dpc≡Ph (8i).
Figure S 59. Superimposed absorption, excitation and emission spectrum of Idpc≡Ph-NO₂ (8j).

Figure S 60. Superimposed absorption, excitation and emission spectrum of Idpc≡Ph-Br (8k).
Figure S 61. Superimposed absorption, excitation and emission spectrum of Idpc≡Fc (81).

Figure S 62. Superimposed absorption, excitation and emission spectrum of (Idpc)$_2$ (9).
Electrochemistry

Cyclic voltammetry analysis was performed in a one-compartment cell with 5–7 mL of 1,2-dichlorobenzene as the solvent and NBu₄PF₆ (0.1 M) as the supporting electrolyte. A platinum electrode (Ø = 1.1 mm, BASI) was used as the working electrode. It was polished with diamond pastes (1.5 and 1 μm particle size) from Buehler and Wirtz before measurements. A computer-controlled BASi EPSILON potentiostat was used for recording the voltammograms. An Ag/AgCl wire pseudo reference electrode and a Pt-wire as auxiliary electrode were used in the measurements. The cell was connected to an argon-gas cylinder. Potential calibration was performed by adding appropriate quantities of decamethylferrocene (Cp*₂Fe) after all scans of interest had been acquired. Potentials are reported against the ferrocene/ferrocnium (Cp₂Fe⁰⁺) couple, which is 550 mV positive of the Cp*₂Fe⁰⁺ couple under our conditions. Decamethylferrocene had to be used because of a too small separation between the oxidation wave of ferrocene derivatives 8h and 8i and the usual ferrocene standard.

The OTTLE cell was also home-built and comprises of a Pt-mesh working and counter electrode and a thin silver wire as a pseudoreference electrode sandwiched between the CaF₂ windows of a conventional liquid IR cell. Its design follows that of Hartl et al.[18] The working electrode is positioned in the center of the spectrometer beam. For every measurement, a Wenking POS 2 potentiostat by Bank Elektronik - Intelligent Controls GmbH was used. FT-IR spectra were recorded using a Bruker Tensor II FT-IR spectrometer. UV/Vis/NIR spectra were obtained on a TIDAS fiberoptic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from j&m Analytik AG.
Figure S 63. Cyclic voltammogram of Idpe recorded in 1,2-dichlorobenzene at room temperature.

Figure S 64. Cyclic voltammogram of Idpe-Br recorded in 1,2-dichlorobenzene at room temperature.
Figure S 65. Cyclic voltammogram of \textit{Idpc-Ph} (8a) recorded in 1,2-dichlorobenzene at room temperature.

Figure S 66. Cyclic voltammogram of \textit{Idpc-Ph-OMe} (8b) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 67. Cyclic voltammogram of Idpc-Ph-NO₂ (8c) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 68. Cyclic voltammogram (left) and square wave (right) of Idpc-Ph-o-F (8d) recorded in 1,2-dichlorobenzene at room temperature.

Figure S 69. Cyclic voltammogram (left) and square wave (right) of Idpc-Ph-o-Cl (8e) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 70. Cyclic voltammogram of Idpe-Ph-(m-OMe)\(_2\) (8f) recorded in 1,2-dichlorobenzene at room temperature.

Figure S 71. Cyclic voltammogram of Idpe-Ph-(m-CF\(_3\))\(_2\) (8g) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 72. Cyclic voltammogram of Idpc-Fe (8h) recorded in 1,2-dichlorobenzene at room temperature. – left: oxidation; right: reduction with superimposed square wave.

Figure S 73. Cyclic voltammogram of Idpc-≡Ph (8i) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 74. Cyclic voltammogram of Idpc≡Ph-NO$_2$ (8j) recorded in 1,2-dichlorobenzene at room temperature.

Figure S 75. Cyclic voltammogram of Idpc≡Ph-Br (8k) recorded in 1,2-dichlorobenzene at room temperature.
Figure S 76. Cyclic voltammograms of Idpc≡-Fc (8l) recorded in 1,2-dichlorobenzene at room temperature. – left: oxidation; right: reduction.
Figure S 77. Cyclic voltammogram of (Idpc)$_2$(9) recorded in 1,2-dichlorobenzene at room temperature.
NMR-Spectra

Spectrum S 1. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8a

Spectrum S 2. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8a
Spectrum S 3. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8b

Spectrum S 4. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8b
Spectrum S 5. $^1$H-NMR spectrum (600 MHz, CDCl$_3$) of 8b

Spectrum S 6. $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of 8b
Spectrum S 7. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8c

Spectrum S 8. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8c
Spectrum S 9. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8d

Spectrum S 10. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8d
Spectrum S 11. $^{19}$F-NMR spectrum (375 MHz, C$_2$D$_2$Cl$_4$) of 8d

Spectrum S 12. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8e
Spectrum S 13. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8e

Spectrum S 14. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8f
Spectrum S 15. $^{13}$C-NMR spectrum (150 MHz, $C_2D_2Cl_4$) of 8f

Spectrum S 16. $^1$H-NMR spectrum (600 MHz, CDCl$_3$) of 8f
Spectrum S 17. $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of $8f$

Spectrum S 18. $^1$H-NMR spectrum (600 MHz, CDCl$_3$) of $8g$
Spectrum S 19. $^{13}$C-NMR spectrum (150 MHz, CDCl$_3$) of 8g

Spectrum S 20. $^{19}$F-NMR spectrum (375 MHz, CDCl$_3$) of 8g
Spectrum S 21. \(^1\)H-NMR spectrum (600 MHz, C\(_2\)D\(_2\)Cl\(_4\)) of 8h

Spectrum S 22. \(^{13}\)C-NMR spectrum (150 MHz, C\(_2\)D\(_2\)Cl\(_4\)) of 8h
Spectrum S 23. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of $8i$

Spectrum S 24. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of $8i$
Spectrum S 25. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8j

Spectrum S 26. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8j
Spectrum S 27. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8k

Spectrum S 28. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8k
Spectrum S 29. $^1$H-NMR spectrum (600 MHz, C$_2$D$_2$Cl$_4$) of 8l

Spectrum S 30. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 8l
Spectrum S 31. $^1$H-NMR spectrum (800 MHz, CDCl$_3$) of 5

Spectrum S 32. $^{13}$C-NMR spectrum (200 MHz, CDCl$_3$) of 5
Spectrum S 33. $^{19}$F-NMR spectrum (375 MHz, CDCl$_3$) of 5

Spectrum S 34. $^1$H-NMR spectrum (400 MHz, CDCl$_3$) of 10
Spectrum S 37. $^{13}$C-NMR spectrum (150 MHz, C$_2$D$_2$Cl$_4$) of 9
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