

Supporting Information

Chemical Syntheses and Compound Characterization

General

All experiments were carried out under standard Schlenk conditions and argon atmosphere. 1,1'-dibromoferrocene was synthesized by modified literature conditions; 1,1,2,2-tetrachlorodibromoethane was used instead of 1,2-dibromoethane.^[S1] Corannulene was obtained using an analogous procedure to that of Scott *et al.*^[S2]

THF was distilled from sodium-potassium alloy/benzophenone and 1,2-dichloroethane was distilled from phosphorus pentoxide. Both were stored over molecular sieves (3 Å).

Melting points were determined on a Gallenkamp Melting Point Apparatus and are not corrected. IR spectra were recorded on a Nicolet iS10 MFR FT-IR Sp spectrometer (signals are denoted as following, s (strong), m (medium) and w (weak)). ¹H and ¹³C NMR spectra were measured on a JEOL ECS 400 spectrometer or on a Bruker Instruments AVIII 700 at 23 °C. CDCl₃ and CD₂Cl₂ were used as solvents and the residual solvent peak was taken as an internal standard (¹H NMR: CDCl₃ 7.26, CD₂Cl₂ 5.30 ppm; ¹³C {¹H} NMR: CDCl₃ 77.0 ppm, CD₂Cl₂ 54.0 ppm;). Mass spectra were measured on a MAT CH7A (EI, 80 eV, 3 kV). High resolution masses were determined by peak match method against perfluorokerosene. TLC analysis was performed using Merck Silica gel 60 F254.

Gold(III) chloride and ferrocene were purchased from Alfa Aesar, *N*-iodosuccinimide from Molecular, decamethylferrocene from ABCR, *n*-butyllithium and *tert*-butyllithium from Acros, palladium(II) acetate from Chempur and tetrabutylammonium hexafluorophosphate from Fluka Analytical.

Moniodocorannulene (2)

Corannulene (120.0 mg, 0.48 mmol, 1.0 eq.), *N*-iodosuccinimide (108.0 mg, 0.48 mmol, 1.0 eq.) and gold(III) chloride (5.0 mol%) were dissolved in 1,2-dichloroethane (10 mL). The mixture immediately darkened. After stirring the mixture for 6 h at RT it was heated to reflux for 48 h. The solvent was removed and the crude product was purified by flash column chromatography on silica gel (*n*-pentane/ethyl acetate 20:1) to yield pure **2** (162.3 mg, 90 %) as a yellow amorphous powder.

Mp: 163 °C; **¹H NMR** (400 MHz, CDCl₃): δ = 7.70 (d, *J* = 8.8 Hz, 1 H), 7.75 – 7.84 (m, 6 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 8.32 (s, 1 H); **¹³C NMR** (101 MHz, CDCl₃): δ = 136.44 (C-H, 1 C), 135.64 (hub C, 1 C), 135.53 (hub C, 1 C), 135.32 (hub C, 1 C), 135.09 (hub C, 1 C), 134.97 (hub C, 1 C), 132.77 (flank C, 1 C), 132.36 (flank C, 1 C), 131.00 (flank C, 1 C), 130.98 (flank C, 1 C), 130.83 (flank C, 1 C), 129.90 (C-H, 1 C), 128.24 (C-H, 1 C), 127.72 (C-H, 1 C), 127.64 (C-H, 1 C), 127.39 (C-H, 1 C), 127.25 (C-H, 1 C), 126.99 (C-H, 1 C), 125.68 (C-H, 1 C), 125.68 (C-H, 1 C), 96.04 ppm (C-I, 1 C); **MS** (EI, 50 °C): *m/z* 375.9752 ([M]⁺, found), 375.9749 ([M]⁺, calc'd), 248 ([M]⁺ -HI, 100 %), 124 ([M-HI]²⁺, 43); **IR**: ν = 2919 (m), 2850 (m), 1601 (w), 1070 (m), 1011 (m), 821 (m), 669 cm⁻¹ (m).

Corannulenylferrocene (3)

In a 100 mL Schlenk tube ferrocene (79 mg, 0.43 mmol, 2.0 eq.), potassium *tert*-butoxide (5 mg, 0.04 mmol, 0.2 eq.) were dissolved in THF (2 mL). The orange solution was cooled to -20 °C and *tert*-butyllithium in *n*-hexane (0.34 mL, 1.9 M, 3.5 eq.) was added drop-wise. After addition the reaction was stirred at -30 °C for one hour. A solution of anhydrous zinc chloride (103 mg, 0.75 mmol, 3.5 eq.) in THF (1 mL) was added via cannula and the solution was stirred for an additional hour at -30 °C, followed by one hour at room temperature. Palladium(II) acetate (1 mol%), triphenyl phosphane (2 mol%) and **2** (64 mg, 0.18 mmol, 1.0 eq.) were added in one portion and the reaction mixture was heated at 60 °C for 48 h. After addition of water (10 mL) the red reaction mixture is transferred to a separation funnel, DCM is added and the organic layer was washed with water (4 x 30 mL). After drying with anhydrous sodium sulfate and removal of the solvent the crude product was purified by column chromatography on neutral aluminiumoxide (pentane/toluene 3:1). The product was obtained as a red solid (33 mg, 42 %).

Mp: 216 °C; **¹H NMR** (700 MHz, CDCl₃): δ = 8.00 (½ AB, ³*J* = 8.6 Hz, 1H), 7.77-7.97 (m, 8H), , 5.00 (s, 2H), 4.54 (s, 2H), 4.25 ppm (s, 5H); **¹³C NMR** (175 MHz, CDCl₃): δ = 139.28 (C ipso, 1 C), 136.20 (C hub, 1 C), 136.00 (C hub), 135.79 (C hub, 1 C), 135.67 (C hub, 1 C), 134.78 (C hub,

1 C), 131.04 (C spoke, 1 C), 130.60 (CH spoke, 1 C), 130.59 (C spoke, 1 C), 130.54 (C spoke, 1 C), 129.81 (C spoke, 1 C), 127.49 (CH rim, 1 C), 127.48 (CH rim, 1 C), 127.45 (CH rim, 1 C), 127.32 (CH rim, 1 C), 127.17 (CH rim, 1 C), 126.97 (CH rim, 1 C), 126.93 (CH rim, 1 C), 126.82 (CH rim, 1 C), 124.88 (CH rim, 1 C), 70.56 (cp, 5 C), 69.91 (cp sub, 2 C), 69.66 ppm (cp sub, 2 C); **MS** (EI, 50 °C): m/z 434.0737 (found), 434.0758 (calc'd), 311 (37 %, $[C_{25}H_{11}]^+$), 121 (14 %, $[C_5H_5Fe]^+$), 56 (8 %, Fe^+), 217 (5 %, $[M]^{2+}$). **IR**: ν = 2956 (m), 2922 (m), 2852 (m), 1902 (w), 1771 (w), 1615 (w), 1481 (m), 1454 (m), 1427 (m), 1402 (m), 1386 (w), 1310 (m), 1258 (m), 1140 (w), 1099 (m), 1045 (m), 1029 (m), 995 (m), 950 (w), 826 (s), 787 (s), 762 (m), 695 (mid), 654 (m), 561 (m), 582 cm^{-1} (m).

1,1'-Dicorannulenylferrocene (4):

In a 25 mL Schlenk tube a solution of 1,1'-dibromoferrocene (50.2 mg, 0.15 mmol, 1.0 eq.) in THF (2 mL), degassed and after cooling to -70 °C *n*-butyl lithium in *n*-hexane (0.18 mL, 2.5 M, 3.0 eq.) was added drop-wise. After stirring for one hour at RT and then cooling to -30 °C dry zinc chloride (70.0 mg, 0.51 mmol, 3.5 eq.) was added in one portion. The mixture was stirred at RT for 1 h. Upon addition of **2** (121.2 mg, 0.32 mmol, 2.2 eq.), palladium(II) acetate (0.8 mg, 3.65 μ mol, 2.5 mol%) and triphenyl phosphane (1.9 mg, 7.30 μ mol, 5 mol%) the orange mixture undergoes a color change to deep red and was stirred for 12 h at 70 °C. The reaction mixture was transferred to a separation funnel using DCM (20 mL) and extracted with water (4 x 100 mL). After drying with anhydrous sodium sulfate and filtration the crude product was purified by column chromatography on silica gel (pentane/dichloromethane 3:1). The product was obtained as red solid (40 mg, 40 %).

Mp: 237 °C (decomposition); **1H NMR** (700 MHz, CD_2Cl_2): δ = 8.16 (d, $^3J=8.7$ Hz, 2H), 8.10 (s, 2H), 7.66-7.37 (m, 12H), 7.26 (d, $^3J=8.5$ Hz, 2H), 5.03-4.58 (m, 8H) ppm. **^{13}C NMR** (176 MHz, CD_2Cl_2): δ = 137.13 (C ipso, 2 C), 136.05 (C hub, 2 C), 135.54 (C hub, 2 C), 135.45 (C hub, 2 C), 135.31 (C hub, 2 C), 134.15 (C hub, 2 C), 130.62 (C spoke, 2 C), 130.53 (C spoke, 2 C), 130.30 (C spoke, 2 C), 130.23 (C spoke, 2 C), 129.60 (C spoke, 2 C), 127.51 (CH rim, 2 C), 127.45 (CH rim, 2 C), 127.44 (CH rim, 2 C), 127.31 (CH rim, 2 C), 127.09 (CH rim, 2 C), 127.05 (CH rim, 2 C), 126.99 (CH rim, 2 C), 126.60 (CH rim, 2 C), 125.10 (CH rim, 2 C), 71.37 (cp sub, 4 C), 71.12 (cp sub, 4 C), 63.34 ppm (cp ipso, 2 C); **MS** (EI, 250 °C): m/z = 682.1364 ($[M]^+$, found), 682.1385 ($[M]^+$, calc'd), 313 (35 %, $[C_{25}H_{13}]^+$), 341 (17 %, $[M]^{2+}$). **IR**: ν = 2918 (m), 2853 (m), 1892 (v), 1723 (m), 1620 (w), 1513 (m), 1462 (m), 1313 (m), 1258 (m), 1138 (m), 1020 (m), 863 (m), 814 (s), 739 (m), 690 (m), 659 (m), 538 (s) cm^{-1} .

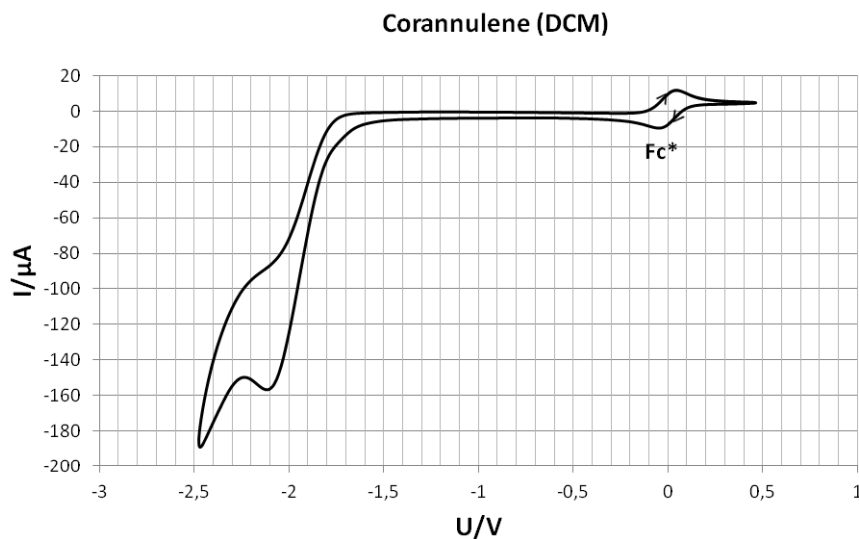
Cyclic voltammetry:

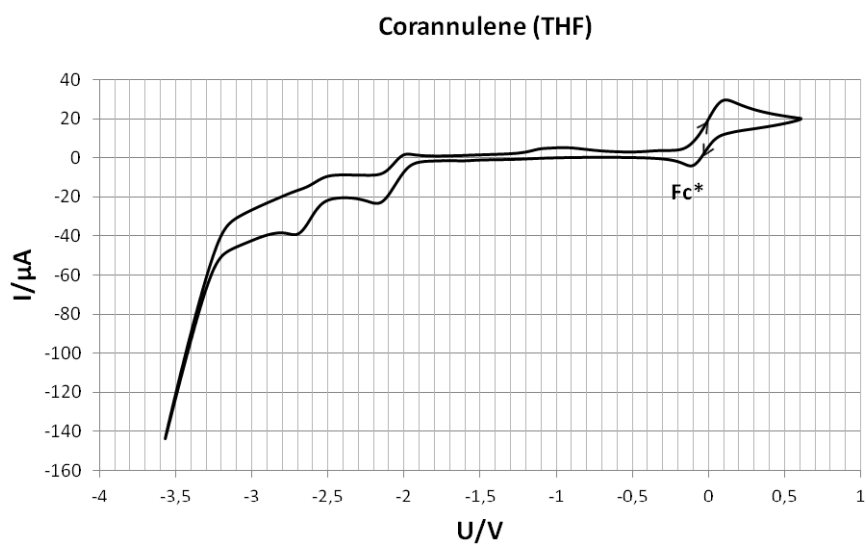
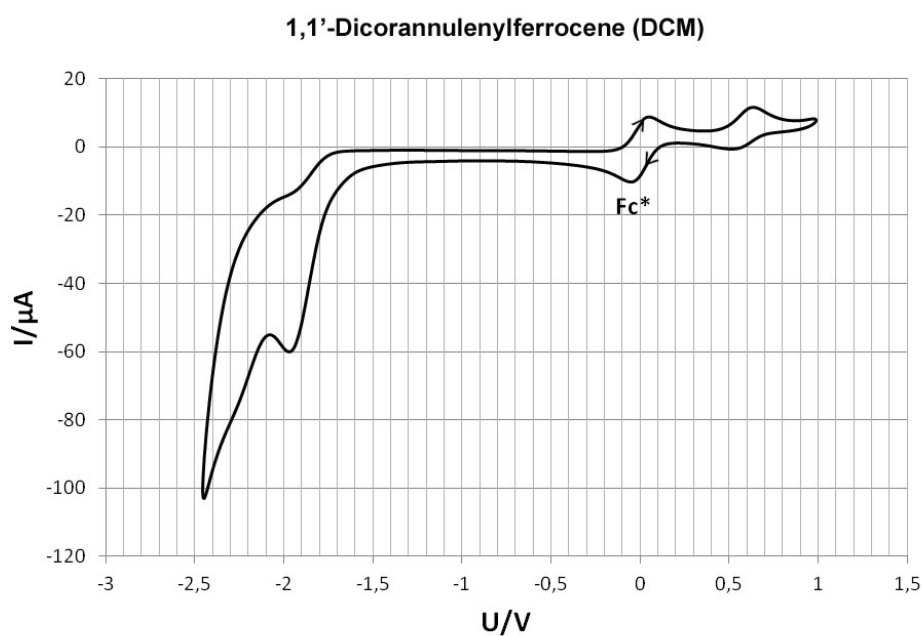
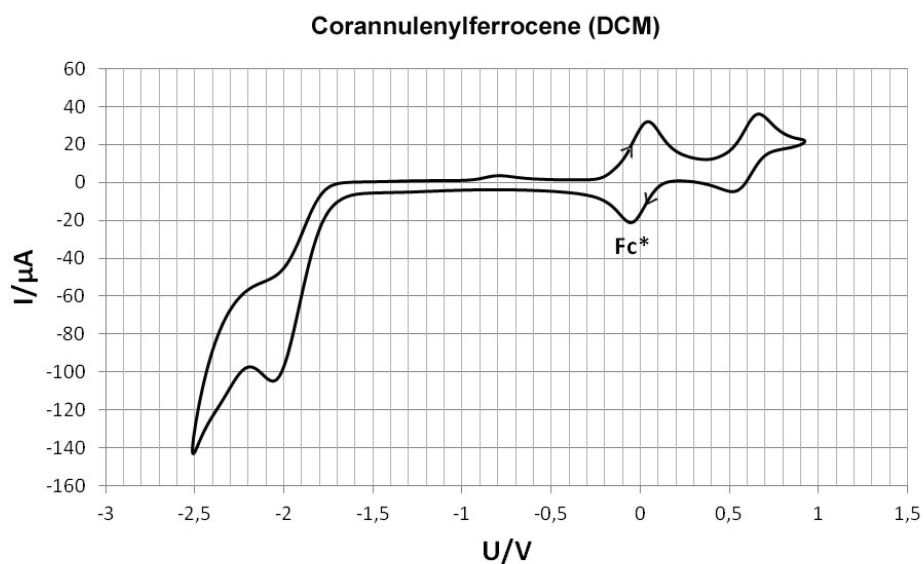
Electrochemical measurements were carried out on a MaterialsM 510 (20V/1A) potentiostat.

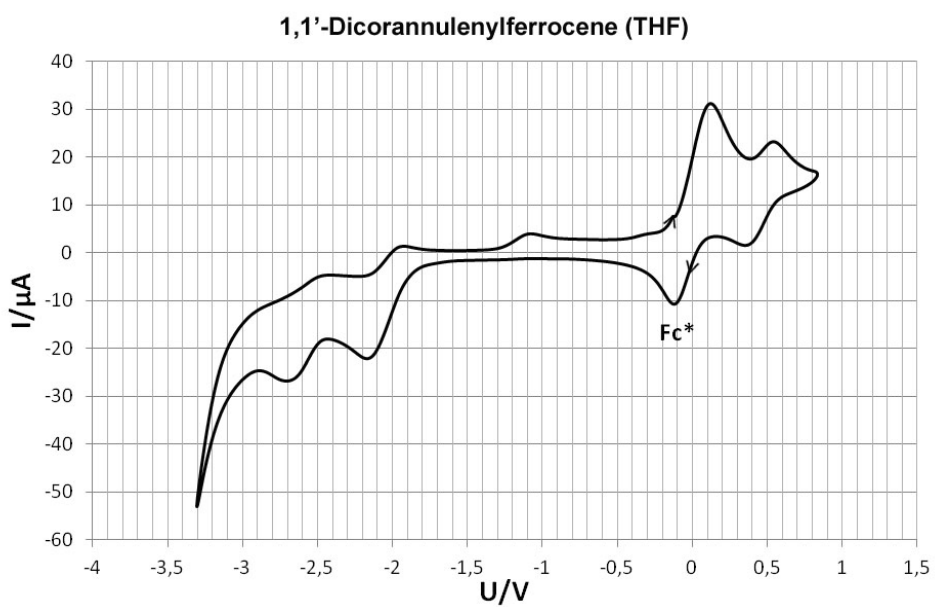
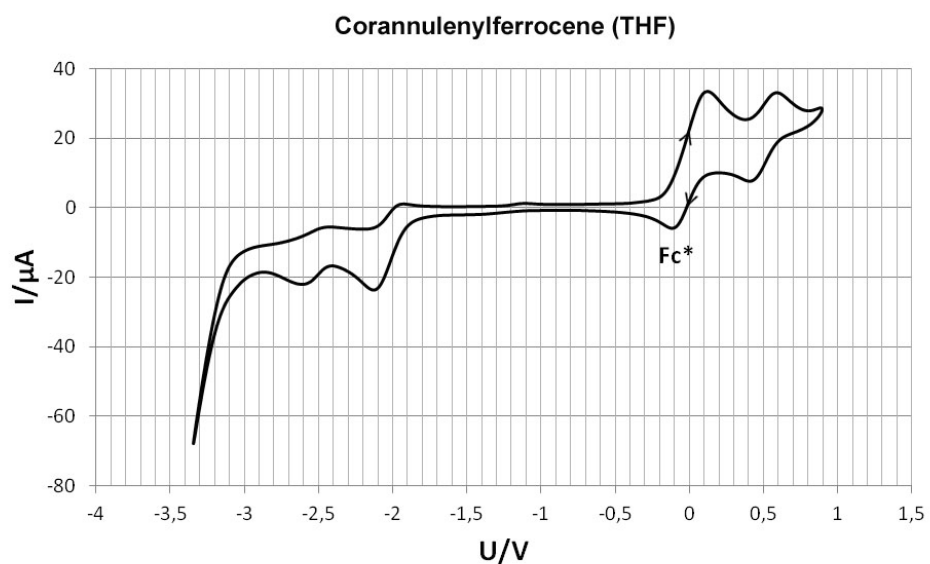
Table S1: Half-wave potentials of **1**, **3**, **4** vs. Fc*.

Compound	$E_{1/2} = (E_{pk} + E_{pa})/2$	$E_{1/2} = (E_{pk} + E_{pa})/2$
	[V], [(ⁿ Bu) ₄ N]PF ₆ , DCM	[V], [(ⁿ Bu) ₄ N]PF ₆ , THF
ferrocene	0.56 [§]	0.48 [§]
1	ca. -1.88 [§]	-2.08, ca. -2.58 [#]
3	0.58, ca. -1.87 [§]	0.50, -2.03, -2.51 [§]
4	0.57, ca. -1.85 [§]	0.45, -2.05, -2.56 [§]

Working electrode: Platinum, auxiliary electrode: Platinum internal reference: Fc* (10⁻³ M), substance concentration: 5·10⁻⁴ M, conducting salt concentration: 0.1 M, measuring error: ± 0.03 V. All measured values are referenced against Fc*/Fc⁺. [§] 0.2 V scan rate, [#] 0.05 V scan rate. Measurement temperature 298 K.







Structure elucidation:

Structure determination by single-crystal X-ray diffraction was carried out by selecting an appropriate crystal under the microscope.

a) The data set was collected with a Bruker-AXS SMART CCD.

b) The data set was collected on a MAR225 (Bruker) CCD image plate detector with synchrotron radiation ($\lambda = 0.9050 \text{ \AA}$) on the BL 14.1 beamline at the BESSY storage ring (the laboratory site of the Protein Structure Factory at the Free University of Berlin, Germany) by Prof. Dr. S. I. Troyanov (Humboldt University Berlin). Crystallographic data and parameters of the structure solution and refinement for the compounds studied are summarized in table **S2** and **S3**.

The structures were solved using direct methods (SHELXS-97) and refined by full-matrix least squares procedures (SHELXL-97) ^[S3]. Multi-scan absorption corrections were applied (SADABS). Hydrogen atoms were included in the refinement at calculated positions using a riding model.

Visualization was done with Mercury 2.4 using the Ortep display mode; POV Ray 3.6 was used for rendering.

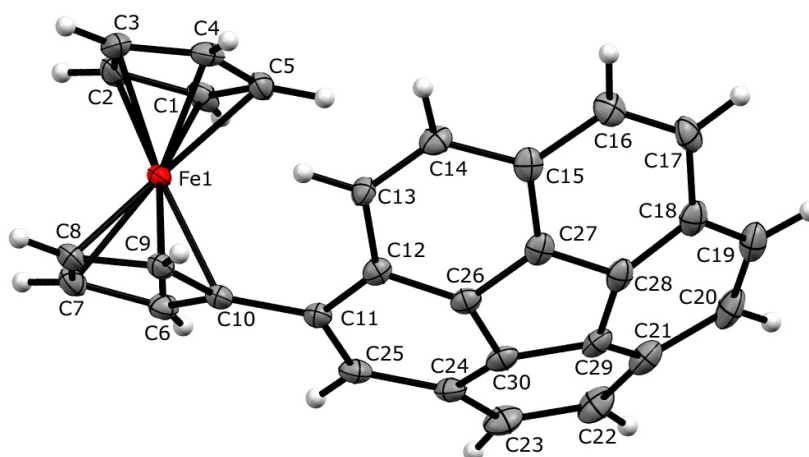


Fig. S1: Mercury view of the asymmetric unit of **3**, rendered with POV-Ray.

Table S2: Crystallographic details of **3**.

Compound reference	3
Chemical formula	C ₃₀ H ₁₈ Fe
Formula Mass	434.29
Crystal system	Orthorhombic
<i>a</i> /Å	22.011(5)
<i>b</i> /Å	43.742(9)
<i>c</i> /Å	8.1622(17)
α /°	90.00
β /°	90.00
γ /°	90.00
Unit cell volume/Å ³	7858(3)
Temperature/K	133(2)
Space group	<i>Fdd2</i>
No. of formula units per unit cell, <i>Z</i>	16
Radiation type	MoK α
Absorption coefficient, μ /mm ⁻¹	0.783
No. of reflections measured	25166
No. of independent reflections	5905
<i>R</i> _{int}	0.0455
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2 σ (<i>I</i>))	0.0429
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0925
Final <i>R</i> _{<i>I</i>} values (all data)	0.0554
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0978
Goodness of fit on <i>F</i> ²	1.081
Flack parameter	-0.045(13)

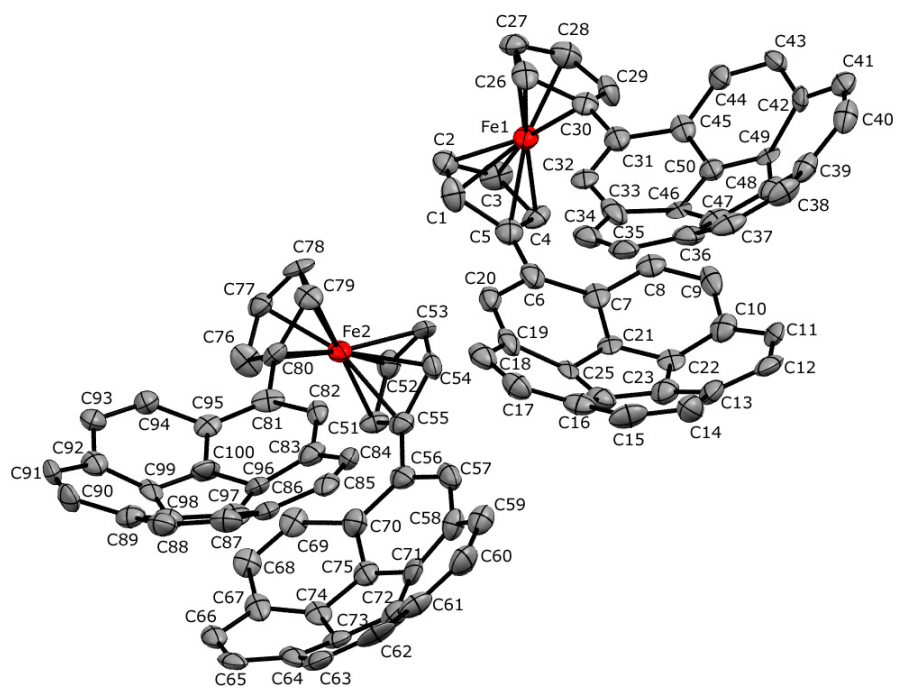


Fig S2: Mercury view of the asymmetric unit, rendered with POV-Ray.

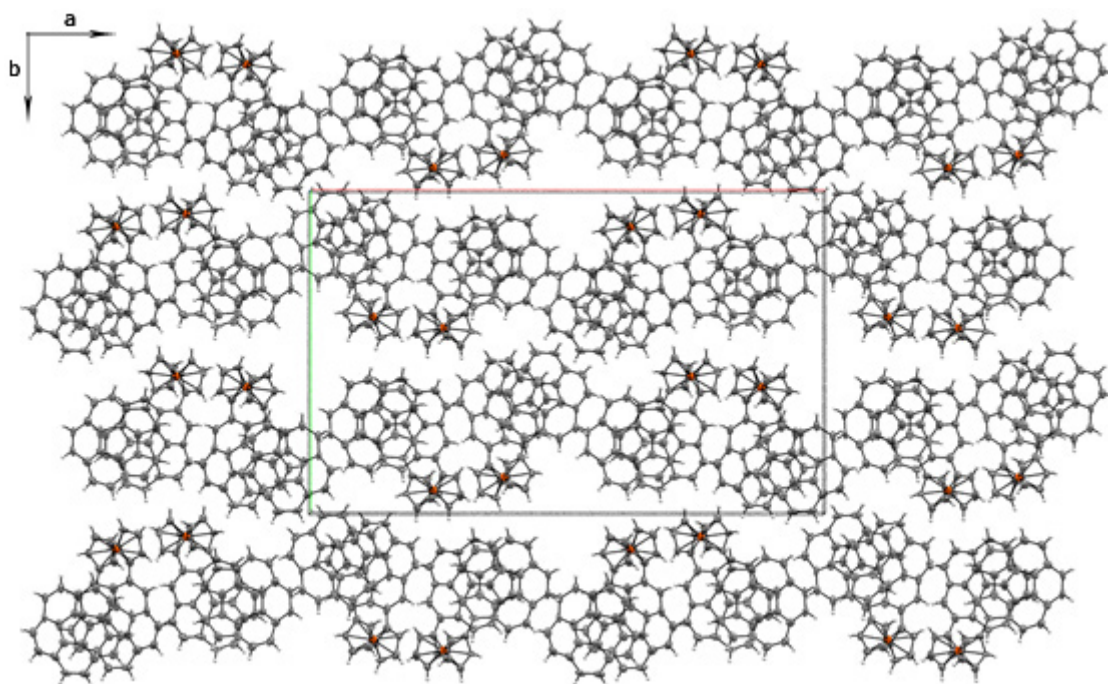


Fig S3: View along the c-axis.

Table S3: Crystallographic details of **4**.

Compound reference	4
Chemical formula	C ₅₀ H ₂₆ Fe
Formula Mass	682.56
Crystal system	Orthorhombic
<i>a</i> /Å	38.198(8)
<i>b</i> /Å	23.938(5)
<i>c</i> /Å	7.6480(15)
α /°	90.00
β /°	90.00
γ /°	90.00
Unit cell volume/Å ³	6993(2)
Temperature/K	100(2)
Space group	<i>Pna</i> 2(1)
No. of formula units per unit cell, <i>Z</i>	8
Radiation type	Synchrotron
Absorption coefficient, μ /mm ⁻¹	0.467
No. of reflections measured	70718
No. of independent reflections	13727
<i>R</i> _{int}	0.0519
Final <i>R</i> _I values (<i>I</i> > 2σ(<i>I</i>))	0.1001
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.2561
Final <i>R</i> _I values (all data)	0.1130
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.2643
Goodness of fit on <i>F</i> ²	1.039
Flack parameter	-0.09(3)

Table S4. Comparison of C-C bond lengths of **1** and **3**:

	1 ^[S4] bond length in Å	3 bond length in Å
Hub	1.4119(5)-1.4161(3)	1.406(3)-1.428(3)
Spoke	1.3768(4)-1.3812(4)	1.379(3)-1.387(3)
Flank	1.4430(5)-1.4466(5)	1.388(4)-1.404(3)
Rim	1.3868(3)-1.3905(3)	1.430(3)-1.468(3)

A comparison to the bond lengths of **4** is not appropriate due to the quality of the data set.

UV-Vis:

UV-Vis spectra were measured on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer using Hellma Analytics 111-QS cuvettes. Dichloromethane was used as solvent; with a $1 \cdot 10^{-5}$ M compound concentration.

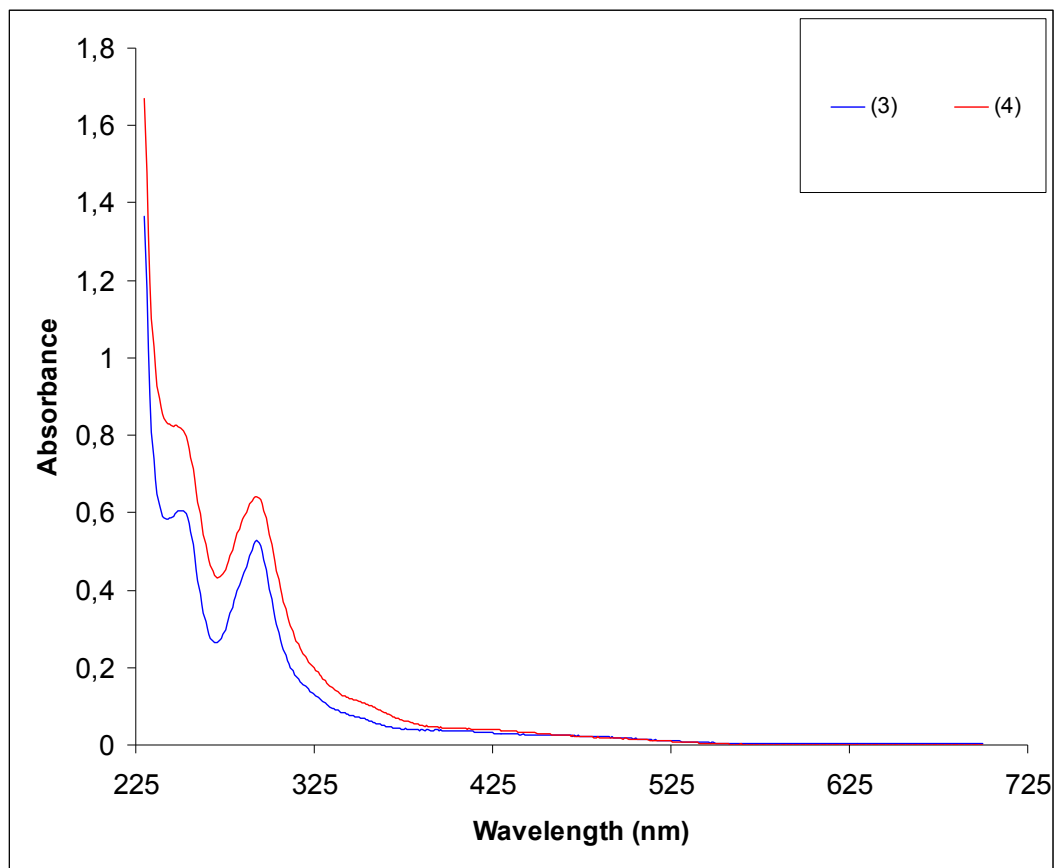


Table S5: Absorption maxima

compound	λ_{\max}
3	251
	294
4	248
	292

Literature:

- [S1] A. Shafir, M. P. Power, G. D. Whitener and J. Arnold, *Organometallics*, 2000, **19**, 3978.
- [S2] L. T. Scott, P. Cheng, N. N. Hashemi, M. S. Bratcher, D. T. Meyer and H. B. Warren, *J. Am. Chem. Soc.* 1997, **119**, 10963.
- [S3] SHELX - G. M. Sheldrick, *Acta Cryst A*, 2008, A64, 112-122.
- [S4] S. Grabowsky, M. Weber, Y.-S. Chen, D. Lentz, B. M. Schmidt, M. Hesse and P. Luger, *Z. Naturforsch.*, 2010, **65b**, 452. (Structure: CCDC755910)