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Supporting Information

1,3,5-Triferrocenyl-2,4,6-tris(ethynylferrocenyl)-

benzene – A new Member of the Family of

Multiferrocenyl-functionalized Cyclic Systems

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Table of Contents

Figure SI1	<i>T</i> -shaped π - π interactions in 6a	2
Figure SI2	ORTEP diagram of 4b	3
Figure SI3	ORTEP diagram of 4b	3
Figure SI4	Deconvolution of the square wave voltammogram of 6a	4
Figure SI5	UV-Vis/NIR spectra of 6a	4
Figure SI6	UV-Vis/NIR spectra of 6b	5
Figure SI7	Cyclic and square wave voltammogram of 7	5
Figure SI8	Cyclic and square wave voltammogram of 8	6
Figure SI9	UV-Vis/NIR spectra of 8	6



Figure SI1. ORTEP diagram (50 % probability level) of the molecular structure of **6a** showing two molecules. Hydrogen atoms are omitted for clarity. Orange: iron; green: chlorine; blue: distances between two centroids of the benzenes (Å): CT1–CT13/CT10–CT6 4.673(8), CT1–CT9 5.048(8).

Refinement details for 6a: The compound consists of rather small plates (0.02 mm height), thus the intensity of the reflection intensity, also at high exposure times, is rather low. The cell was found with only 47 % of the overall reflections. Attempts to find a next component in wrong peaks still resulted in 46 % unindexed reflections, which is too low for a treatment as a twinned crystal. For the molecule, some anisotropic displacement ellipsoids of the cyclopentadienyls were rather elongated and hence the SIMU/ISOR restraints were applied¹ which explains the number of restraints. Although, using the AFIX 66 command on the central 6-memberd Ring, on atoms C2, C3, C5 and C6, but also C7, C11, C31 and C44 a further EADP instruction was applied for an anisotropic refinement. Furthermore, some reflections exhibiting an Error/esd greater 4 were omitted to improve the R1 and the wR2 values.



Figure SI2. ORTEP diagram (50 % probability level) of the molecular structure of **4b** showing the main and the disordered part (*) of the molecule. Further disordered Cl and hydrogen atoms are omitted for clarity.



Figure SI3. ORTEP diagram (50 % probability level) of the molecular structure of **4b** showing two molecules. Hydrogen atoms are omitted for clarity. The highlighted (#) molecule was generated by the following symmetry operation: -x, 1-y, -z. The disordered part of **4b** (Figure SI1) can be converted by the equal symmetry operation resulting in an equal stacking, which is omitted for clarity as well as further disordered Cl atoms.

Refinement details for 4b: The structure exhibits a large disordering including the benzene core and Cl3 and Cl1' atoms. A possible twinning and thus another space group required, was checked during the cell search and for the refined structure², but a twinning component or a twinning law could not be detected. For the molecule, some anisotropic displacement ellipsoids of the cyclopentadienyls were rather elongated and hence the SIMU/ISOR restraints were applied¹ which explains the number of restraints. On the central C6 core and its disordered part the AFIX 66 command was applied. Further EADP instructions were required for an anisotropic refinement of Cl3/Cl3A, C26/C26' and Cl1'/Cl1A/Cl1. Furthermore, some reflections exhibiting an Error/esd greater 4 were omitted to improve the R1 and the wR2 values.



Figure SI4. Deconvolution of the square wave voltammogram of **6a** giving an integrated peak area of 1:2:1. The redox separation between the two ferrocenyl-related redox processes is $\Delta E_2^{\circ} = 60$ mV.



Figure SI5. UV-Vis/NIR spectra of **6a** at rising potentials *vs* Ag/AgCl: -200 to 1000 mV. Inset: enlarged illustration. Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L⁻¹ [N^{*n*}Bu₄][B(C₆F₅)₄] as supporting electrolyte.



Figure SI6. UV-Vis/NIR spectra of **6b** at rising potentials *vs* Ag/AgCl: -200 to 1000. Inset: enlarged illustration. Measurement conditions: 25 °C, dichloromethane, 0.1 mol·L⁻¹ [N^{*n*}Bu₄][B(C₆F₅)₄] as supporting electrolyte.



Figure SI7. Voltammograms of dichloromethane solutions containing 1.0 mmol· L⁻¹ of 1bromo-2-ethynylferrocenyl benzene (**8**) at 25 °C. Supporting electrolyte $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$ (0.1 mol· L⁻¹). Cyclic voltammogram (top; scan rate: 100 mV· s⁻¹ at a glassy-carbon electrode); square-wave voltammogram (bottom; scan rate: 1 mV· s⁻¹). Decamethylferrocene was used as an internal reference (event marked with *). $E^{\circ'}(\Delta E_{p})$ in mV: 102 (59).



Figure SI8. Voltammograms of dichloromethane solutions containing 1.0 mmol· L⁻¹ of 1ethynylferrocenyl-2-ferrocenyl benzene (**9**) at 25 °C. Supporting electrolyte $[N(^{n}Bu)_{4}][B(C_{6}F_{5})_{4}]$ (0.1 mol· L⁻¹). Cyclic voltammogram (top; scan rate: 100 mV· s⁻¹ at a glassy-carbon electrode); square-wave voltammogram (bottom; scan rate: 1 mV· s⁻¹). Decamethylferrocene was used as an internal reference (event marked with *). $E_{1}^{\circ\prime}$ (ΔE_{p}) in mV: -77 (64); $E_{2}^{\circ\prime}$ (ΔE_{p}) in mV: 323 (64); $\Delta E^{\circ\prime}$ in mV: 400.



Figure SI9. UV-Vis/NIR spectra of **9** at rising potentials *vs* Ag/AgCl: -200 to 500. Measurement conditions: 25 °C, 3.3 mmol·L⁻¹ of the analyte in dichloromethane, 0.1 mol·L⁻¹ $[N^n Bu_4][B(C_6F_5)_4]$ as supporting electrolyte.

¹ a) P. McArdle, J. Appl. Cryst. 1995, **28**, 65; b) G. M. Sheldrick, Acta Cryst. 2008, **A64**, 112.

² A. L. Spek, J.Appl.Cryst. 2003, 36, 7–13.