Supporting Information

Ferrocenyl substituted calixarenes: synthesis, structure, and properties

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Table of Contents

I. Experimental details ................................................................. S2

II. Crystallographic data ................................................................. S4

III. Electrochemical Data for 5b-5c .................................................. S7

IV. Copies of ¹H NMR, ¹³C NMR and HRMS Spectra of the New Compounds ................................... S8

V. TGA plots for compounds 5a-5c ................................................ S17

VI. References .................................................................................. S17
General: Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. Triethylamine (TEA) was received from commercial source, and distilled on KOH prior to use. \(^1\)H NMR (400 MHz), and \(^{13}\)C NMR (100MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using CDCl\(_3\) as solvent. Tetramethylsilane (TMS) was used as reference for recording \(^1\)H (of residual proton; \(\delta = 7.26\) ppm), and \(^{13}\)C (\(\delta = 77.0\) ppm) spectra in CDCl\(_3\). UV-visible absorption spectra of all compounds in Dichloromethane were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using Platinum as a working electrode, Pt wire as the counter electrode, and Ag/Ag\(^+\) as the reference electrode. HRMS was recorded on Brucker-Daltonics, micro TOF-Q II mass spectrometer.

Synthesis and Characterization

The reactant 5a was purchased from Sigma-Aldrich, and the reactants 5b-5c were synthesized via diazotization of 4-ethynylaniline, and 3-ethynylaniline respectively, according to known methods.\(^1\)

General procedure for synthesis of 5a-5c.

5,11,17,23-Tetraiodo-25,26,27,28-tetra-(n-propoxy)calix[4]arene 4 (160 mg, 0.14 mmol) was stirred together with Pd(PPh\(_3\))\(_2\)Cl\(_2\) (40 mg, 0.05 mmol) and CuI (0.09 mg, 0.05 mmol) in degassed diisopropylamine (20 mL) and THF (20ml) for 30 min at room temperature before the corresponding ethynyl ferrocene (6 equivalent, 0.875mmol) was added. The mixture was heated at 80 °C for 48 h. The solvent was removed; the remaining residue was suspended in water (50 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (MgSO\(_4\)) and concentrated in vacuum. The resulting crude product was purified by column chromatography on silica gel eluting with CH\(_2\)Cl\(_2\)/hexane (2:3). The desired compound obtained
from the column was recrystallized from chloroform/methanol to give compounds S3 in 70-
80% yield.

Compound 5a: Orange solid (164 mg, 79%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 6.93 (s, 8H),
4.40-4.43 (m, 12H), 4.19 (s, 20H), 4.11 (t, 8H), 3.88 (t, 8H), 3.16 (d, 4H, $J = 12.23$ Hz), 1.94
(m, 8H), 0.99 (t, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 156.57$, 134.74, 131.19, 117.18,
86.88, 86.25, 71.59, 70.02, 68.58, 66.23, 31.03, 23.36, 10.49. HRMS (ESI) m/z, calcd for MH$^+$
(C$_{88}$H$_{80}$Fe$_4$O$_4$): 1424.3462; found: 1424.3516.

Compound 5b: Orange solid (176 mg, 70%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.36 (d, 8H, $J$
= 8.55 Hz), 7.27 (d, 8H, $J = 8.29$ Hz), 6.99 (s, 8H), 4.57 (m, 8H), 4.45 (d, 4H, $J = 13.31$ Hz),
4.27 (m, 8H), 3.97 (s, 20H), 3.91 (t, 8H), 3.20 (d, 4H, $J = 13.31$ Hz), 1.99-1.93 (m, 8H), 1.00 (t,
12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 156.96$, 139.21, 134.88, 132.06, 131.84, 125.77,
121.09, 117.50, 90.17, 88.61, 84.61, 69.86, 69.38, 66.69, 31.05, 23.43, 10.52. HRMS (ESI) m/z,
calcd for MH$^+$ (C$_{112}$H$_{96}$Fe$_4$O$_4$): 1729.4740; found: 1729.4737.

Compound 5c: Orange solid (170 mg, 70%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.56 (s, 4H),
7.29 (d, 4H, $J = 8.88$ Hz), 7.24 (d, 4H, $J = 8.68$ Hz), 6.97-7.01 (m, 12H), 4.60 (m, 8H), 4.48 (d,
4H, $J = 12.87$ Hz), 4.24 (m, 8H), 3.99 (s, 20H), 3.92 (t, 8H), 3.22 (d, 4H, $J = 13.79$ Hz), 1.91-
2.01 (m, 8H), 1.02 (t, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 156.94$, 139.28, 134.77, 132.00,
129.25, 128.79, 128.21, 125.55, 123.57, 117.14, 89.65, 88.50, 84.60, 69.64, 69.01, 66.51, 30.92,
23.26, 10.36. HRMS (ESI) m/z, calcd for MH$^+$ (C$_{112}$H$_{96}$Fe$_4$O$_4$): 1729.4740; found: 1729.4737.
Single crystal X-ray diffraction Studies

Single crystal X-ray structural studies of 5a were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo Kα radiation (\(\lambda_α = 0.71073 \text{ Å}\)). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on \(F^2\). The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen
atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. The crystal and refinement data are summarized in Table 2. The CCDC number 903776 contains the supplementary crystallographic data for 5a. This data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement parameter for compound 5a.

<table>
<thead>
<tr>
<th>Compound</th>
<th>5a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{88}$ H$</em>{80}$ Fe$_4$ O$_4$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1424.92</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength/A</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, $P$ cab</td>
</tr>
</tbody>
</table>
| Unit cell dimensions | a = 15.7383(4) Å  alpha = 90 deg.  
                         b = 50.6519(11) Å  beta = 90 deg.  
                         c = 18.0535(4) Å  gamma = 90 deg. |
| Volume      | 14391.8(6) Å$^3$ |
| Z, Calculated density | 8, 1.315 Mg/m$^3$ |
| Absorption coefficient | 0.842 mm$^{-1}$ |
| F(000)      | 5952        |
| Crystal size | 0.34 x 0.28 x 0.22 mm |
| Theta range for data collection/(°) | 2.96 to 25.00 |
| Limiting indices | -18≤h≤18, -48≤k≤60, -21≤l≤21 |
**Reflections collected / unique**: 111276 / 12648 \( [R(int) = 0.0597] \)

**Completeness to theta = 25.00**: 99.8 %

**Absorption correction**: Semi-empirical from equivalents

**Max. and min. transmission**: 0.8364 and 0.7627

**Refinement method**: Full-matrix least-squares on \( F^2 \)

**Data / restraints / parameters**: 12648 / 0 / 869

**Goodness-of-fit on \( F^2 \)**: 1.066

**Final R indices [I>2sigma(I)]**: \( R_1 = 0.0672, \text{wR}_2 = 0.1628 \)

**R indices (all data)**: \( R_1 = 0.0788, \text{wR}_2 = 0.1715 \)

**Largest diff. peak and hole**: 0.954 and -0.667 e.Å\(^{-3} \)

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**Table S2**: Selected bond length of intermolecular interactions in the crystal structure 5a.

<table>
<thead>
<tr>
<th>C-H-π Interactions</th>
<th>Bond length Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H83----C18, C13, C14, C16, C17, C15</td>
<td>2.675</td>
</tr>
<tr>
<td>H56----C66, C67, C68, C65, C64</td>
<td>3.026</td>
</tr>
<tr>
<td>H26----C80, C81, C82, C83, C79</td>
<td>3.19</td>
</tr>
<tr>
<td>H51----C86, C87, C88, C84, C85</td>
<td>3.597</td>
</tr>
</tbody>
</table>
Electrochemical Data for 5b, 5c.

**Figure S2.** Cyclic voltammogram of calixarene 5b.

**Figure S3.** Cyclic voltammogram of calixarene 5c.
Copies of $^1$H NMR, $^{13}$C NMR and HRMS Spectra of the Compounds 5a-5c.

Figure S4. $^1$H NMR Spectra of 5a.
Figure S5. $^{13}$C NMR Spectra of 5a.
Figure S6. HRMS Spectra of 5a.
Figure S7. $^1$H NMR Spectra of 5b.
Figure S8. $^{13}$C NMR Spectra of 5b.
Figure S9. HRMS Spectra of 5b.
Figure S10. $^1$H NMR Spectra of 5c.
Figure S11. $^{13}$C NMR Spectra of 5c.
**Figure S12. HRMS Spectra of 5c.**
Figure S13. TGA plots of compounds 5a–5c.

References