Supporting Information
for
Global Aromaticity and Antiaromaticity in a Porphyrin Nanoring Anions

Martin D. Peeks\textsuperscript{1,2}, Michael Jirasek\textsuperscript{1}, Timothy D. W. Claridge\textsuperscript{1}, and Harry. L. Anderson\textsuperscript{1,*}

\textsuperscript{1}Department of Chemistry, University of Oxford, Chemistry Research Laboratory, OX1 3TA, UK
\textsuperscript{2}School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia
*harry.anderson@chem.ox.ac.uk
# Contents

S1 Computational Chemistry ................................................................. S3
  S1.1 Summary of NICS values ............................................................. S3
S2 Synthesis and sample preparation ....................................................... S4
  S2.1 Quantification of CoCp₂⁺ concentration ........................................ S7
S3 NMR assignments .............................................................................. S8
  S3.1 Summary of assignments ............................................................... S8
  S3.2 Full-scale ¹H spectra ................................................................. S9
  S3.3 Proof of reversibility ................................................................. S10
  S3.4 Additional spectra for hexa-anions ............................................ S10
  S3.5 Additional spectra for tetra-anions ............................................ S18
  S3.6 Dynamic NMR analyses ......................................................... S22
    S3.6.1 Neutral c-P6 ..................................................................... S23
    S3.6.2 c-P6⁶⁻ ............................................................................. S25
    S3.6.3 Summary ........................................................................ S26
S4 Cartesian coordinates ................................................................. S27
  S4.1 c-P6 (B3LYP/6-31+G*) ................................................................. S27
  S4.2 c-P6⁴⁻ (B3LYP/6-31+G*) ............................................................. S28
  S4.3 c-P6⁶⁻ (B3LYP/6-31+G*) ............................................................. S29
S1 Computational Chemistry

DFT geometry optimizations were performed using the B3LYP, ωB97X-D, and M06-2X functionals and the 6-31+G* all-electron basis set,[51–58] as implemented in Gaussian16/A.03.[59] The meso-aryl groups on the nanorings were truncated to –H. NICS surfaces were calculated with a 20 Å × 20 Å grid of ghost atoms with 1 Å spacing.

S1.1 Summary of NICS values

Table S1: NICS(0)iso and NICS(0)zz (all units ppm) at the centers of c-P6 as a function of oxidation state and DFT functional. The basis set was 6-31+G* in all cases.

|         | NICS(0)iso | NICS(0)zz | NICS(0)iso | NICS(0)zz | NICS(0)iso | NICS(0)zz |
|---------|------------|-----------|------------|-----------|------------|-----------|
| Neutral |           |           |            |           |            |           |
| B3LYP   | −1.51      | 1.00      | 88.69      | 267.85    | −12.95     | −39.53    |
| ωB97X//B3LYP | −1.82      | 0.58      | 6.98       | 23.84     | −15.10     | −43.78    |
| M06-2X//B3LYP | −1.81      | 0.64      | 11.46      | 37.07     | −14.72     | −43.69    |
| ωB97X//ωB97X-D | −1.85      | 0.57      | −0.65      | 1.20      | −14.89     | −43.20    |
| M06-2X//M06-2X | −1.88      | 0.58      | 4.48       | 16.24     | −14.34     | −42.73    |

Table S2: Ellipticity of c-P6 as a function of oxidation state as calculated by different functionals. The basis set was 6-31+G* in all cases. Ellipticity is calculated as the ratio of the lengths of the semi-minor and semi-major axes.

|         | Neutral | 4− | 6− |
|---------|---------|----|----|
| B3LYP   | 1.00    | 1.098 | 1.00 |
| ωB97X-D | 1.00    | 1.318 | 1.00 |
| M06-2X  | 1.00    | 1.185 | 1.00 |

Figure S1: NICS(0)zz for c-P6, c-P64−, and c-P66−. Level of theory: B3LYP/6-31+G*. White circles indicate the location of porphyrin subunits; the white ring indicates the approximate circumference of the porphyrin nanoring.
Figure S2: NICS(0)$_{iso}$ for (left–right) c-P6, c-P6$^{4-}$, and c-P6$^{6-}$, calculated in the yz plane (i.e. perpendicular to the ring plane). The approximate locations of the porphyrin subunits and their sidechains are shown. The white ovals denote the approximate region occupied by the solubilizing trihexylsilyl groups. In the 4$^-$ and 6$^-$ oxidation states, THS$_o$ is located in a region of no magnetic (de)shielding. Level of theory: B3LYP/6-31+G*.

Figure S3: Top, middle: Anisotropy of the induced current density (AICD) for c-P6, c-P6$^{4-}$, and c-P6$^{6-}$; bottom: AICD and induced current vectors, for an applied magnetic field threading the ring from bottom-to-top. Level of theory: B3LYP/6-31+G*.

S2 Synthesis and sample preparation

c-P6 and c-P6-T6 were prepared as described previously.$^{[510]}$ The porphyrin subunits bore bulky trihexylsilyl (THS) solubilizing groups on their meso-aryl groups, to inhibit aggregation.

D$_8$-THF was purchased from Fluorochem (Eurisotop product) and was purified and dried by passage over freshly activated basic alumina, then degassed using the freeze-pump-thaw method, and finally stored over 4 Å molecular sieves. D$_8$-Pyridine ampoules were purchased from Fluorochem (Eurisotop product) and used without further purification, except freeze-pump-thaw degassing. D$_8$-Acetone was purchased from Sigma-Aldrich and used without further purification. CoCp$_2^*$ was purchased from Sigma-Aldrich and was purified by sublimation (200-250 °C under dynamic vacuum (ca. 2 × 10$^{-1}$ mbar)), using a specialist piece of glassware (Figure S4). CoCp$_2^*$ was handled exclusively under argon.
Samples of c-P6-T6 and c-P6 were weighed out and transferred to J. Young tap Schlenk ampoules. The tube atmosphere was evacuated (< 2 x 10^{-1} mbar) and refilled with argon three times, and the nanoring samples were then dissolved in d8-THF (+5% d5-pyridine) to a concentration of, typically, 2.5 mg/mL and degassed by the freeze-pump-thaw method. A disposable Injekt syringe was used to transfer nanoring stock solution (500 µL) to a clean, dry, air-free J. Young NMR tube, situated in an NMR tube filler capped with a rubber Subaseal (Figure S4f). The freshly-sublimated CoCp₂⁺ was dissolved in d8-THF and its concentration was determined as described below. For a single-shot reduction, an aliquot of CoCp₂⁺ was added to the nanoring solution in the NMR tube, at −78°C (dry ice/acetone bath), using a Hamilton or SGE Trajan syringe. We used long needles (>23 cm, e.g. ga26s/230mm/pst3 from Hamilton) to enable liquid transfer without tilting glassware. In general we have found that even 'non-coring' microsyringe needles have a tendency to introduce fragments of rubber from subaseals to solutions. We found it preferable to use a disposable 20G (or wider) needle to penetrate the septa, and then pass the microsyringe needle through the bore of this needle. This approach also avoided the inherent difficulties in penetrating a subaseal with a fine microsyringe needle. After addition of reducing agent, the J. Young NMR tube was capped under a strong flow of argon and its contents were freeze-pump-thaw degassed. CAUTION: argon condenses at liquid nitrogen temperatures. It is important to ensure that no condensed argon is present before an NMR tube is sealed and warmed to room temperature. This hazard can be avoided by using dry nitrogen instead of argon.

We also occasionally conducted reductions by addition of reducing agent to a frozen solution of nanoring in the NMR tube, then replacing the J. Young cap and applying vacuum to evaporate any condensed argon, and then continuing with the freeze-pump-thaw process. We emphasise, again, the inherent risks of using argon with liquid nitrogen.

All solvents and reagents were handled using standard Schlenk line techniques. Subaseals were used on all vessels wherever possible in order to avoid ingress of oxygen and water. A glove-box was not required for this work.

NMR spectra were recorded on a Bruker AvII 500 MHz, a Bruker AvIII 700 MHz, and a Bruker AVIII 950 MHz. The spectrum of the 4− oxidation state of c-P6-T6 is extremely sensitive to the amount of reducing agent added: when a slight excess or deficit of reducing agent is introduced (e.g., we estimate, 3.8 eq or 4.2 eq), broader THS resonances are observed and the "inner" THS resonances are more strongly deshielded and reduced in intensity. The spectra of both the 6− and 4− oxidation states are very sensitive to temperature: the sharpest ¹H spectrum of c-P6-T6⁶⁻ is observed around 273 K, whereas the sharpest spectrum of c-P6-T6⁴⁻ is observed around 288 K. Below these temperatures, there are signs of aggregation; above, spectra are broadened, presumably due to electron exchange. For the ring without template, the sharpest spectra are observed at much lower temperatures: 223 K for 6− and 213 K for 4−.

The 6− oxidation state is stable in solution for 2 to 3 days at moderately reduced temperature (~273 K), or up to 1 day at room temperature. The 4− oxidation state is noticeably less stable: the sample corresponding to the NMR spectrum shown in main text Figure 3 exhibited signs of decomposition over the course of hours at 288 K (the temperature of NMR analysis, at which the sharpest spectra are observed). Samples of the reduced rings without templates are much more stable during NMR analyses, probably owing to the lower temperature used.

1The NMR tube filler is a cylindrical piece of glass (i.d. approx 22 mm) equipped with a side arm tap and tapered glass tube (for attachment to the Schlenk line), and featuring at the upper part of the cylinder a female B24/29 joint (for insertion of a subaseal) and at the lower part of the cylinder a 5 mm thermometer adapter with a compression O-ring. Typically, NMR tubes can be evacuated to at least 5 x 10⁻² mbar with this setup; small leaks in the O-ring part can be avoided by the application of a thin film of vacuum grease, or PTFE tape.
Figure S4: (a) Solid CoCp₂⁺ is loaded into the left arm of the sublimation apparatus and is sublimated under vacuum using a heat gun; (b) after sublimation, pure CoCp₂⁺ is deposited on the wall of the right arm of the apparatus, but some powder has also transferred to the right arm without sublimation. A Pasteur pipette is used to deliver a stream of dry nitrogen to remove the loose powder; (c) the right arm now only contains sublimated material; (d) addition of d₈-THF affords the stock solution of reducing agent; (e) a Hamilton syringe with a long needle is used to extract an aliquot of reducing agent. Note that the Hamilton needle is threaded through a pink (18G) needle; (f) the reducing agent is then added to the NMR tube in the NMR tube filler, with cooling. Note the presence of a cream (19G) needle in the subbaseal, through which the Hamilton needle will pass.
S2.1 Quantification of CoCp₂⁺ concentration

The concentration of CoCp₂⁺ solutions was estimated by quenching an aliquot (typically 20 µL) of CoCp₂⁺ stock solution (in d₈-THF) by addition to an excess of solid ferrocenium hexafluorophosphosphate in a dry, air-free, NMR tube. The addition was conducted under an atmosphere of argon, using the NMR tube filler. The d₈-THF was removed by application of dynamic vacuum and the residue was redissolved in d₆-acetone (500 µL), to ensure complete dissolution of the mixture. An aliquot of tert-butyl benzene (2.5 µL, Alfa Aesar) was added as an internal reference. The ¹H NMR spectrum was recorded with sufficiently long delay time for quantitation (d₁ = 5 sec) and the relative integrals of the internal reference and the CH₃ peak of decamethylcobaltocenium were determined by deconvolution of the relevant resonances.

The typical concentration of CoCp₂⁺ was 1 mM when used for stoichiometric reduction (i.e. to reach the 4− oxidation state). Higher concentrations (ca 18 mM) were used when addition of excess reducing agent was desired (i.e. to reach the 6− oxidation state).

Figure S5: ¹H NMR (500 MHz, 298 K, d₆-acetone) spectrum of a mixture of CoCp₂⁺, FcPF₆, and tBuPh.
### S3 NMR assignments

#### S3.1 Summary of assignments

Table S3: Summary of $^1$H NMR chemical shifts (ppm) for c-P6-T6 in its neutral (500 MHz, 298 K, $d_8$-THF + 5% pyridine), 4− (500 MHz, 288 K, $d_8$-THF + 5% pyridine), and 6− (950 MHz, 273 K, $d_8$-THF + 5% pyridine) oxidation states. $^{13}$C chemical shifts for the adjacent carbon are given in parentheses where available. The chemical shift difference between inner ($\delta_i$) and outer ($\delta_o$) protons is given by: $\Delta \delta = \delta_i - \delta_o$

| Proton(s) | $\delta_H$ neutral | $\delta_H$ 4− | $\delta_H$ 6− |
|-----------|---------------------|----------------|----------------|
| $\alpha$  | 2.35                | 12.8–15.5      | 5.80           |
| $\beta$   | 5.19                | 12.8–15.5      | 4.4–4.1        |
| $\gamma$  | 5.57                | 12.8–15.5      | 4.4–4.1        |
| $\delta$  | 5.63                | 12.8–15.5      | 4.4–4.1        |
| a         | 9.59                |                | 3.02?          |
| b         | 8.78                | 17.64          | 3.75           |
| $o_o$     | 8.16                | 6.77           | 7.79           |
| $o_i$     | 8.36                | 12.18          | 4.44           |
| p         | 8.09                | 9.17           | 6.73 (137.4)   |
| TTHS CH3  | 0.8–1.6             | 0.7–1.9        | 0.80 (14.2)    |
| TTHS CH3  | 0.8–1.6             | 2.5–3.9        | −0.38 (13.1)   |
| TTHS SiCH2| 0.8–1.6             | 0.7–1.9        | 0.72 (12.5)    |
| TTHS SiCH2| 0.8–1.6             | 2.5–3.9        | −0.87 (10.9)   |
| $\Delta \delta_{\text{TTHS CH3}}$ | ca. 0 | ca. 2 | −1.18 (−1.1) |
| $\Delta \delta_{\text{TTHS SiCH2}}$ | ca. 0 | ca. 2 | −1.59 (−1.6) |
| $\Delta \delta_{\text{ortho}}$ | 0.20 | 5.41 | −3.35 |
S3.2 Full-scale $^1$H spectra

Figure S6: Full-scale versions of the spectra shown in main text Figure 3. c-P6-T6$^{4–}$ (500 MHz, 288 K, $d_8$-THF + 5% $d_5$-pyridine); c-P6-T6$^{6–}$ (950 MHz, 273 K, $d_8$-THF + 5% $d_5$-pyridine). In the expansions shown in grey, tall peaks are truncated. Impurities are denoted by symbols: * is pyridine; † is THF; # is grease.
S3.3 Proof of reversibility

Figure S7: c-P6-T6 (500 MHz, 298 K, CDCl₃) after reduction to the 6− oxidation state and subsequent re-oxidation using FcPF₆, and passage through an alumina plug (CHCl₃), and then through a size-exclusion column (Biobeads SX-1, toluene).

S3.4 Additional spectra for hexa-anions

Figure S8: Comparison of ¹H NMR spectra of c-P6⁶⁻ (top, 228 K) and c-P6-T6⁶⁻ (bottom, 248 K) (both 500 MHz, d₈-THF). In these spectra, the resonance labelled b overlaps with the THF resonance at 3.58 ppm.
Figure S9: $^1$H TOCSY spectrum of c-P6•T6$^6$ (500 MHz, 248 K, $d_8$-THF). This region shows the correlations between the $\alpha$, $\alpha_0$, and $\rho$ resonances, which confirms their assignment since there is no other AXY spin system in the molecule. $t_{mix} = 80$ ms.
Figure S10: $^1$H TOCSY spectrum of c-P6-T6$^{5+}$ (500 MHz, 248 K, $d_8$-THF). This region shows the correlations within the THS$^i$ and THS$^o$ multiplets, respectively. $t_{mix} = 80$ ms.
Figure S11: $^1$H NOESY spectrum of c-P6-T6$^{b*}$ (950 MHz, 273 K, $d_8$-THF + 5% $d_5$-pyridine). There are no visible cross-peaks outside the region shown. $t_{mix} = 300$ ms. No reliable cross-peaks are observed to the resonance tentatively labelled $a?$, probably as a result of its extreme linewidth.
Figure S12: $^1$H–$^{13}$C HSQC of c-P6-T6$^6$ (500 MHz, 248 K, $d_8$-THF). There are no visible cross-peaks outside the region shown.
Figure S13: Diffusion edited spectrum of c-P6·T6° (700 MHz, 273 K, d8-THF). Top: normal 1H spectrum; middle: spectrum measured using diffusion-editing pulse sequence (double stimulated echo (DSTE) with $\Delta = 75$ ms and $\delta = 2000$ µs), with 2% gradient power; bottom: spectrum measured using diffusion-editing pulse sequence (as above) with 90% gradient power. Resonances corresponding to slowly-diffusing components, consistent with c-P6·T6, are highlighted in red. Very broad resonances are attenuated by the diffusion sequence and are therefore absent from both the diffusion reference spectrum and the diffusion-edited spectrum.
Figure S14: Diffusion edited spectrum of c-P66+ (500 MHz, 228 K, d8-THF). Top: normal 1H spectrum; middle: spectrum measured using diffusion-editing pulse sequence (double stimulated echo (DSTE) with $\Delta = 125$ ms and $\delta = 3200$ µs), with 2% gradient power; bottom: spectrum measured using diffusion-editing pulse sequence (as above) with 90% gradient power. Resonances corresponding to slowly-diffusing components, consistent with c-P6, are highlighted in red. Very broad resonances are attenuated by the diffusion sequence and are therefore absent from both the diffusion reference spectrum and the diffusion-edited spectrum.
Figure S15: Comparison of the $^1$H NMR spectra of c-P6-T6$^{6+}$ (CD$_2$Cl$_2$) and c-P6-T6$^{6-}$ (d$_8$-THF + 5% pyridine). The spectrum for c-P6-T6$^{6+}$ has previously been reported.$^{[S11]}$
S3.5 Additional spectra for tetra-anions

Figure S16: Comparison of $^1$H NMR spectra of $c$-P6$^-$-T6$^{4-}$ (top, 288 K) and $c$-P6$^{4-}$ (bottom, 233 K) (both 500 MHz, $d_8$-THF + 5% $d_5$-pyridine). The large chemical shift differences for assigned resonances between the spectra with and without template are attributed to (a) temperature effects, since the spectra are measured at very different temperatures; (b) exchange with the 3$^-$ and 5$^-$ oxidation states, owing to slightly different extents of reduction in each sample.
Figure S17: $^1$H NOESY spectrum of c-P6$^{4+}$ (500 MHz, 288 K, $d_8$-THF + 5% $d_5$-pyridine). There are no visible cross-peaks outside the region shown. $t_{\text{mix}} = 350$ ms. Assignments are shown. The cross-peaks indicated by the grey oval box correspond to impurities.
Figure S18: $^1$H NOESY spectrum of c-P6$^{4+}$ (500 MHz, 233 K, $d_8$-THF + 5% $d_5$-pyridine). There are no visible cross-peaks outside the region shown. $t_{\text{mix}} = 300$ ms. Assignments are shown. Due to the absence of template, there is exchange between the inner and outer environments (i.e. o$_o$ $\leftrightarrow$ o$_i$ and THS$_o$ $\leftrightarrow$ THS$_i$), hence correlations appear between (for example) THS$_i$ and o$_o$, and between THS$_i$ and THS$_o$. 
Figure S19: Diffusion edited spectrum of c-P6-T6$^{4+}$ (500 MHz, 288 K, d$_8$-THF + 5% d$_5$-pyridine). Top: normal $^1$H spectrum; middle: spectrum measured using diffusion-editing pulse sequence (double stimulated echo (DSTE) with $\Delta = 75$ ms and $\delta = 2000 \mu$s), with 5% gradient power; bottom: spectrum measured using diffusion-editing pulse sequence (as above) with 90% gradient power. Resonances corresponding to slowly-diffusing components, consistent with c-P6-T6, are highlighted in red. Very broad resonances are attenuated by the diffusion sequence and are therefore absent from both the diffusion reference spectrum and the diffusion-edited spectrum.
S3.6 Dynamic NMR analyses

The T6 template plays an important role in restricting inter-porphyrin rotation in c-P6-T6. In its absence, the neutral ring exhibits rapid inter-porphyrin rotation (ϕ_A in Figure S21), such that only one resonance for the o_o and o_i protons, in fast exchange, is observed in the 1H NMR.

Evaluating the barrier to the ϕ_A exchange process permits its comparison between neutral and charged (aromatic) rings. An increase in torsion barrier could arise from increased aromatic stabilization energy.

In these analyses, it is important to separate the contribution of a second o_o ⇄ o_i exchange process, which occurs even in the presence of T6. This exchange occurs as a result of the meso-aryl rotation, which is expected to be relatively hindered (ϕ_B in Figure S21). In the results below, the meso-aryl rotation ϕ_B is fully characterized by VT-NMR and EXSY for neutral c-P6-T6, explored by EXSY for c-P6-T6^6–, and the interporphyrin torsion ϕ_A is explored by VT-NMR for neutral c-P6, and by EXSY for c-P6^6–.

Figure S21: Schematic for the two mechanisms for exchange of o_o and o_i considered in this section. ϕ_A corresponds to rotation of the entire porphyrin subunit, thus exchanging o_o and o_i, whereas ϕ_B corresponds to rotation of the meso-aryl group, with the same result. The latter process occurs much more slowly.
S3.6.1 Neutral c-P6

At coalescence temperature $T_c = 200 - 203$ K (Figure S22), the chemical exchange rate constant for the exchange between $o_o$ and $o_i$ $k_{chem} = 577 \text{ s}^{-1}$, according to:[S12]

$$k_{chem} = 2 \cdot \frac{\pi \delta \nu}{\sqrt{2}}$$  \hspace{1cm} (S1)

where $\delta \nu = 130$ Hz, based on the chemical shift difference between $o_o$ and $o_i$ in c-P6-T6 (0.26 ppm). Using the Eyring equation, $\Delta G^{\ddagger}_{200 - 203 \text{K}} = (38.0 \pm 0.3) \text{ kJ mol}^{-1}$.

The exchange of $o_o$ and $o_i$ arises through rotation of the entire porphyrin subunit, not through rotation of the meso-aryl group. We were able to confirm this by performing EXSY experiments on c-P6-T6 at 298 K, which revealed negligible exchange between the $o_o$ and $o_i$ resonances. Upon heating a sample of c-P6-T6 in $d_8$-toluene to 373 K, some line-broadening of the $o_i$ and $o_o$ resonances was observed but coalescence was not reached (Figure S23). EXSY

Figure S22: VT-NMR (500 MHz, $d_8$-THF) of c-P6. The coalescence point for the inner and outer ortho protons is indicated with $T_c$, 200 K.
experiments at 353 K revealed $k_{chem} = 13 \text{s}^{-1}$, corresponding to $\Delta G^\ddagger_{353 \text{K}} = 79.4 \text{kJ mol}^{-1}$ (Figure S24). Therefore we can safely conclude that the meso-aryl rotation does not affect the data shown in Figure S22.

Figure S23: VT-NMR of c-P6-T6 (500 MHz, $d_8$-toluene).
S3.6.2 \textit{c-P6}^6^- 

The rate constant for exchange of the \( \text{o}_o \) and \( \text{o}_i \) protons in \textit{c-P6}^6^- was measured using a series of 1D-EXSY experiments with variable mixing times \( t_{\text{mix}} \) from 5 ms to 100 ms. Spectra were measured at 228 K on an Avance AV/500 MHz spectrometer. The \( \text{o}_o \) resonance was selectively excited (7.7 ppm).

The system was modelled as a two-state exchanging system:

\[
A \quad \xrightarrow{k_{\text{chem}}} \quad B
\]

with equal populations of A and B (i.e. outer and inner \textit{ortho} protons, respectively). The intensities can be expressed as follows:

\[
I_A = \frac{1}{4} \exp \left( \frac{-t_{\text{mix}}}{T_1} \right) (1 + \exp (-k_{\text{obs}} t_{\text{mix}})) M^0 \tag{S2}
\]

and

\[
I_B = \frac{1}{4} \exp \left( \frac{-t_{\text{mix}}}{T_1} \right) (1 - \exp (-k_{\text{obs}} t_{\text{mix}})) M^0 \tag{S3}
\]

where \( t_{\text{mix}} \) is the exchange mixing time (\( d_8 \)), \( T_1 \) is the relaxation time constant (assumed equal for A and B), \( k_{\text{obs}} \) is the exchange rate constant, where \( k_{\text{chem}} = 2k_{\text{obs}} \), and \( M^0 \) is the initial magnetization. Taking the ratio of the intensities:

\[
r = \frac{I_B}{I_A} \tag{S4}
\]

\[
r = \frac{1 - \exp (-k_{\text{obs}} t_{\text{mix}})}{1 + \exp (-k_{\text{obs}} t_{\text{mix}})} \tag{S5}
\]

Fitting the experimental intensities (determined by deconvolution of the \( \text{o}_o \) and \( \text{o}_i \) resonances) to Equation S5 affords \( k_{\text{chem}} = 15 \text{ s}^{-1} \) (Figure S25).
Figure S25: Experimental ratio of exchange intensities for the $o_o$ and $o_i$ resonances as a function of mixing time $t_{\text{mix}}$. The $o_o$ resonance was selectively excited. \textit{c-P6}$^6^-$ (500 MHz, 228 K, $d_8$-THF). The line represents the fit of Equation S5, with $k_{\text{chem}} = 15 \text{s}^{-1}$.

We attempted EXSY experiments on \textit{c-P6-T6}$^6^-$, in which the inter-porphyrin rotation is restricted by the presence of the template. Any $o_o$ to $o_i$ EXSY would then arise from rotation of the meso-aryl group. EXSY measurements at 268 K revealed no reliable exchange peak between $o_o$ and $o_i$, with any signal (either exchange or relayed nOe) only appearing at long mixing times. Accordingly, we conclude that the meso-aryl rotation does not contribute in the lower-temperature EXSY experiments on \textit{c-P6}$^6^-$ described above.

S3.6.3 Summary

In preference to using the error in the fit, we have applied an estimated error of 25% to the $k_{\text{chem}}$ determined by EXSY for \textit{c-P6}$^6^-$.

| Oxidation state | $T_{\text{meas}}$ (K) | $k_{\text{chem}}$ at $T_{\text{meas}}$ (s$^{-1}$) | $\Delta G^\ddagger_{\text{meas}}$ (kJ/mol) | Estimated $T_c$ (K) |
|----------------|-----------------------|-----------------------------------------------|-----------------------------------------|---------------------|
| Neutral        | 202–203               | 577                                           | 38.0 ± 0.3                              | 200–203             |
| 6$^-$          | 228                   | $15.1 \pm 3.8$                                | $50.2 \pm 0.5$                           | $295 \pm 3$         |
| 6$^+$          | 213                   | $3.5 \pm 0.9$                                 | $49.5 \pm 0.4$                           | $282 \pm 2$         |
| 12$^+$         | 213                   | $172 \pm 43$                                 | $42.6 \pm 0.4$                           | $234 \pm 2$         |
### Cartesian coordinates

The Cartesian coordinates listed below are also available in the native XYZ file format in a separate ZIP archive, with the Supporting Information online.

#### S4.1 c-P6 (B3LYP/6-31+G*)

| C  | C -8.203260000 | -12.150027000 | 0.000000000 |
| C  | C -9.121925000 | -9.260903000 | 0.000000000 |
| C  | C -3.459215000 | -12.507300000 | -0.000000000 |
| C  | C -9.560959000 | -8.770128000 | -1.259715000 |
| C  | C -2.814674000 | -12.665098000 | 1.259715000 |
| C  | C -9.214572000 | -12.360507000 | 0.000000000 |
| C  | C -7.264382000 | -7.674128000 | 1.439160000 |
| C  | C -9.438899000 | -8.586600000 | 3.412831000 |
| C  | C -9.511580000 | -8.203260000 | 2.539754000 |
| C  | C -9.511580000 | -9.121925000 | -0.000000000 |
| C  | C -3.483889000 | -12.665098000 | 1.259715000 |
| C  | C -3.483889000 | -12.665098000 | -3.491424000 |
| C  | C -2.814674000 | -12.665098000 | -3.491424000 |
| C  | C -1.252507000 | -12.886655000 | 2.539754000 |
| C  | C -9.511580000 | -8.203260000 | -3.491424000 |
| C  | C -1.252507000 | -12.886655000 | -2.682395000 |
| C  | C -2.158220000 | -12.897890000 | 2.539754000 |
| C  | C -11.771140000 | -12.897890000 | -2.682395000 |
| C  | C -9.844351000 | -8.588600000 | 3.412831000 |

---

**ZIP archive, with the Supporting Information online.**
H  9.988420000  8.8088690000  -4.5689710000  H  11.4362580000  -6.6027270000  4.4907680000
C  7.1169740000  10.9794600000  -0.0000000000  H  -0.0000000000  -13.2054530000  4.4907680000
H  -11.4362580000  6.6027270000  -4.4907680000  H  -11.4362580000  -6.6027270000  4.4907680000
H  -11.4362580000  -6.6027270000  -4.4907680000  H  -11.4362580000  6.6027270000  4.4907680000
H  -0.0000000000  -13.2054530000  4.4907680000  H  0.0000000000  13.2054530000  4.4907680000
H  11.4362580000  -6.6027270000  -4.4907680000  H  11.4362580000  6.6027270000  4.4907680000
H  11.4362580000  6.6027270000  4.4907680000  H  0.0000000000  13.2054530000  -4.4907680000
H  0.0000000000  13.2054530000  4.4907680000

S31
References

[S1] A. D. Becke, *J. Chem. Phys.* 1993, 98, 5648–5652.

[S2] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* 1972, 56, 2257–2261.

[S3] V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, *J. Chem. Phys.* 1998, 109, 1223–1229.

[S4] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* 1971, 54, 724–728.

[S5] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* 1973, 28, 213–222.

[S6] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *Journal of Computational Chemistry* 1983, 4, 294–301.

[S7] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2008, 10, 6615–6620.

[S8] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* 2008, 120, 215–241.

[S9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Revision A.03, Gaussian Inc. Wallingford CT, 2016.

[S10] C. E. Tait, P. Neuhaus, M. D. Peaks, H. L. Anderson, C. R. Timmel, *J. Am. Chem. Soc.* 2015, 137, 8284–8293.

[S11] M. D. Peaks, T. D. W. Claridge, H. L. Anderson, *Nature* 2017, 541, 200–203.

[S12] M. L. H. Green, L. L. Wong, A. Sella, *Organometallics* 1992, 11, 2660–2668.