

Global Aromaticity at the Nanoscale

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Aromaticity can be defined by the ability of a molecule to sustain a ring current when placed in a magnetic field. Hückel's rule states that molecular rings with $[4n+2]$ π -electrons are aromatic, with an induced magnetisation that opposes the external field inside the ring, whereas those with $4n$ π -electrons are antiaromatic, with the opposite magnetisation. This rule reliably predicts the behaviour of small molecules, typically with fewer than 22 π -electrons ($n = 5$). It is not clear whether aromaticity has a size limit, or whether Hückel's rule extends to much larger macrocycles. Here, we present evidence for global aromaticity in porphyrin nanorings with circuits of up to 162 π -electrons ($n = 40$); aromaticity is controlled by changing the constitution, oxidation state and conformation. Whenever a ring current is observed, its direction is correctly predicted by Hückel's rule. The largest ring currents occur when the porphyrins units have fractional oxidation states.

The extent of electronic delocalisation in linear molecules is limited by the onset of symmetry-breaking transitions, which can be viewed as Peierls-type electron-vibration interactions or as shifts in mixed-valence behaviour¹. For example, cyanine dyes feature a linear chain of C-C bonds with bond order 1.5 and negligible bond length alternation (like the C-C bonds in benzene) resulting in charge delocalisation, but if the chain exceeds a critical length, the symmetry collapses, localising the charge^{2,3}. It is not clear whether similar effects limit the size of an aromatic ring, or whether molecular ring currents can extend into the

domain of mesoscopic phenomena such as Aharonov-Bohm oscillations⁴. Many new globally aromatic macrocycles have been reported during the last few years⁵⁻¹⁸, but apart from the porphyrin nanorings discussed here, there are no reports of aromatic rings with more than 62 π -electrons⁷. Here we explore circuits of up to 162 π -electrons in a large family of nanorings in a wide range of oxidation states. In these nanorings, each porphyrin contributes 10 electrons to the Hückel π -electron count, and each linking alkyne contributes 2 electrons, so a nanoring cation **c-PN[b_xe_y]^{Q+}** has an electron count of $10N + 4x + 2y - Q$ (where N is the number of porphyrin units; x and y are the number of butadiyne and ethyne links respectively). Recently, we reported that the butadiyne-linked six-porphyrin nanoring **c-P6[b₆]** displays global aromaticity when oxidised⁸, reduced¹⁷ or electronically excited¹⁸. According to Schleyer's terminology¹⁹, all the nanorings discussed here are 'trannulenes' rather than 'annulenes', since the p-orbitals making up the aromatic π -system are oriented in the plane of the ring, whereas in annulenes the p-orbitals are perpendicular to the ring. Trannulenes follow Hückel's rule in the same way as annulenes, although Hückel did not anticipate this type of system.²⁰

The six-porphyrin nanoring complexes **c-P6[e₆]**·**T6***, **c-P6[be₅]**·**T6***, **c-P6[b₅e]**·**T6** and **c-P6[b₆]**·**T6** provide a homologous series of compounds in which we systematically vary the number of π -electrons by changing the number of -C≡C- units, while preserving the circular geometry (which is locked by the template, **T6*** or **T6**, Figure 1)^{21,22}. The ¹H NMR spectra of the 2+, 4+ and 6+ oxidation states of all four complexes reveal the presence of aromatic or antiaromatic ring currents, and the directions of these ring currents agree perfectly with Hückel's rule. Thus, **c-P6[e₆]**·**T6*** (neutral: 72 π e) and **c-P6[b₆]**·**T6** (neutral: 84 π e) are both aromatic in the 2+ and 6+ oxidation states and antiaromatic in the 4+ state, whereas **c-P6[be₅]**·**T6*** (neutral: 74 π e) and **c-P6[b₅e]**·**T6** (neutral: 82 π e) are both antiaromatic in the 2+ and 6+ states and aromatic in the 4+ state. The most obvious evidence for these ring currents comes from the chemical shifts of the template α and β pyridyl ¹H resonances; for example, these protons are strongly shielded ($\delta_H = -7.3$ and -3.6 ppm, vs. 8.7 and 7.5, respectively in the free template) in aromatic **c-P6[e₆]**·**T6***²⁺ and strongly deshielded ($\delta_H = 36.0$ and 30.1 ppm, respectively) in antiaromatic **c-P6[e₆]**·**T6***⁴⁺. Further evidence is provided by the trihexylsilyl (THS) ¹H and ¹³C signals. In each spectrum, we observe one group of THS signals that is essentially unshifted, at 0–2 ppm as in the neutral compounds (THS_{out}, coloured orange in Figure 1, near the zero-shielding cone of the nanoring), and one group of THS signals that is shielded or deshielded,

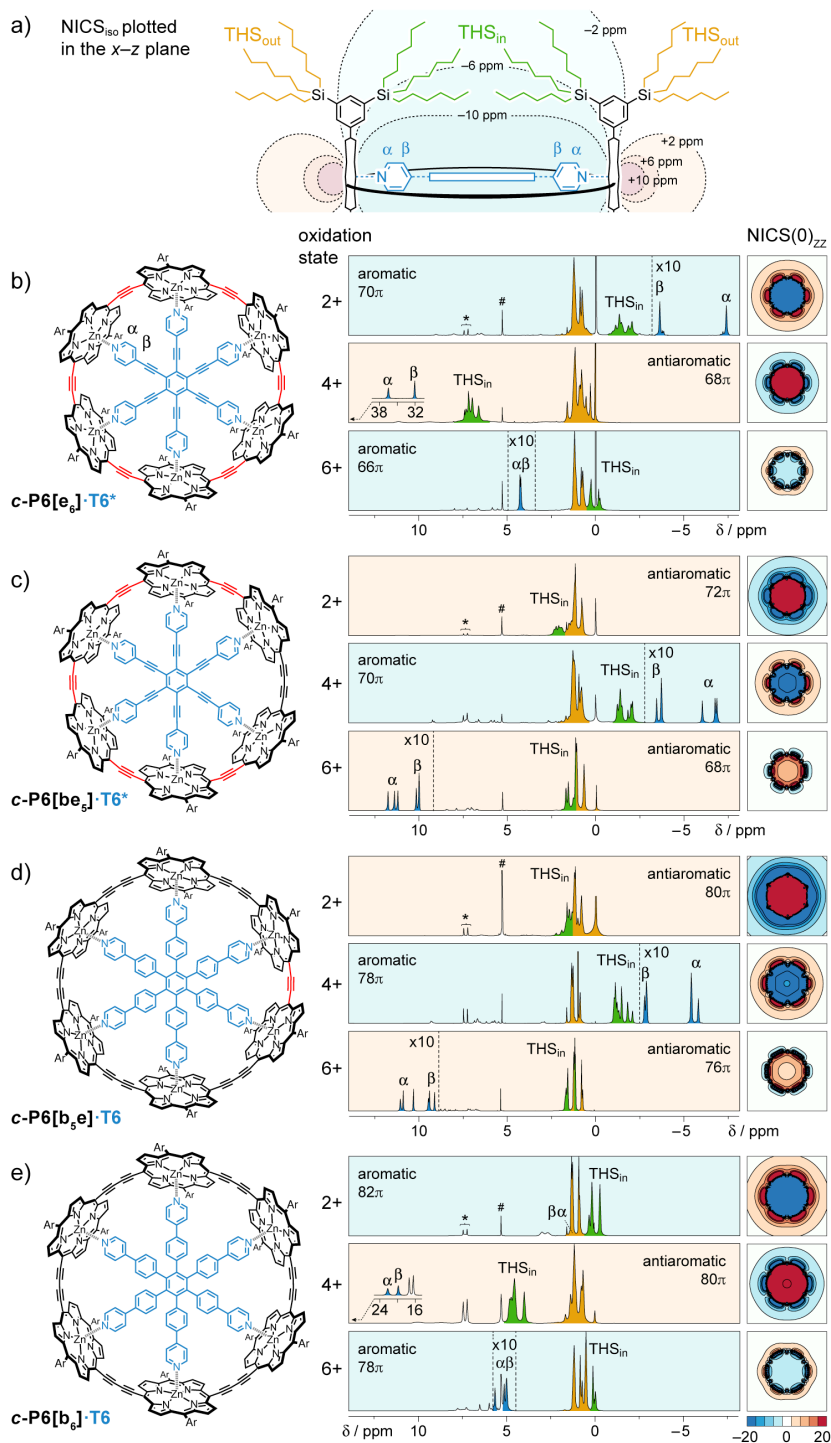


Figure 1. Aromatic and antiaromatic states of a family of oxidised six-porphyrin nanorings.

a) Side view of a nanoring. Internal trihexylsilyl groups (THS_{in}, green) are sensitive to the global ring current whereas external ones (THS_{out}, orange-brown) are not. NICS_{iso} contours are drawn for (*c*-P6[e₆]·T6*)²⁺ from –10 to 10 ppm. ¹H NMR spectra of the template complexes: (b) *c*-P6[e₆]·T6*, (c) *c*-P6[b_{e5}]·T6*, (d) *c*-P6[b₅e]·T6 and (e) *c*-P6[b₆]·T6 in oxidation states 2+, 4+ and 6+; and corresponding NICS(0)_{zz} grids (5 × 5 nm) in the plane of the nanoring without template (LC-ωhPBE/6-31G*, ω = 0.1; colour axis is truncated above 20 and below –20 ppm; contours are drawn every 5 ppm). ¹H NMR spectra recorded at 500 MHz in CD₂Cl₂; oxidised states are generated by titration with thianthrenium hexafluoroantimonate. # and ‡ denote CHDCl₂ and thianthrene, respectively. Detailed spectra for each state are shown in Supplementary Figures S9–S12 and S19–S34. Dashed vertical lines indicate 10-fold magnifications.

depending on the direction of the ring current (THS_{in}, coloured green in Figure 1). Interconversion of THS_{in} and THS_{out} is slow on the NMR timescale, and the assignment of THS_{in} signals is confirmed by the observation of NOEs to protons of the template (**T6** or **T6***). There is an excellent linear correlation between changes in the chemical shift of the α -pyridyl template ¹H and ¹³C signals and the THS CH₂-Si and CH₃ ¹H and ¹³C signals, showing that all six signals report on the same global ring currents (Supplementary Figures S70–S73). The observed ring currents in this set of 12 species (four nanorings in three oxidation states) were compared with the results of nucleus-independent chemical shift (NICS) calculations^{23,24}. We screened a range of density functional theory (DFT) functionals for these NICS calculations (see Supplementary Figures S80 and S83). The B3LYP functional²⁵ gave good agreement with the NMR results for most species, but it failed to reproduce the anti-aromaticity of the dications **c-P6[bes]²⁺** and **c-P6[b₅e]²⁺**. The LC- ω hPBE ($\omega = 0.1$) functional²⁶ gave the best agreement with the observed NMR shifts (Figure 1b–e) and we chose this functional for all the NICS calculations shown in this article.

The evolution of the ring current with increasing ring size is illustrated by the ¹H NMR spectra of the 8-porphyrin nanoring complex **c-P8[e₈](T4*)₂**, which has a circuit of 96 π e when neutral (Figure 2)²¹. The THS and template protons show clear evidence for aromaticity in the 2+ and 6+ oxidation states, whereas the 4+ and 8+ oxidation states are antiaromatic. These results match the predictions of Hückel's rule and agree with calculated NICS values (Figure 2b). The magnitude of the ring current varies substantially between different oxidation states; thus the mean change in the chemical shift of the α -protons of the template (relative to unbound **T4***, $\delta_{\alpha} = 8.67$ ppm) is $\Delta\delta_{\alpha} = +11.8$ ppm in the 4+ state, and -15.6 ppm in the 6+ state, but it dwindles to $+1.9$ ppm in the 8+ state.

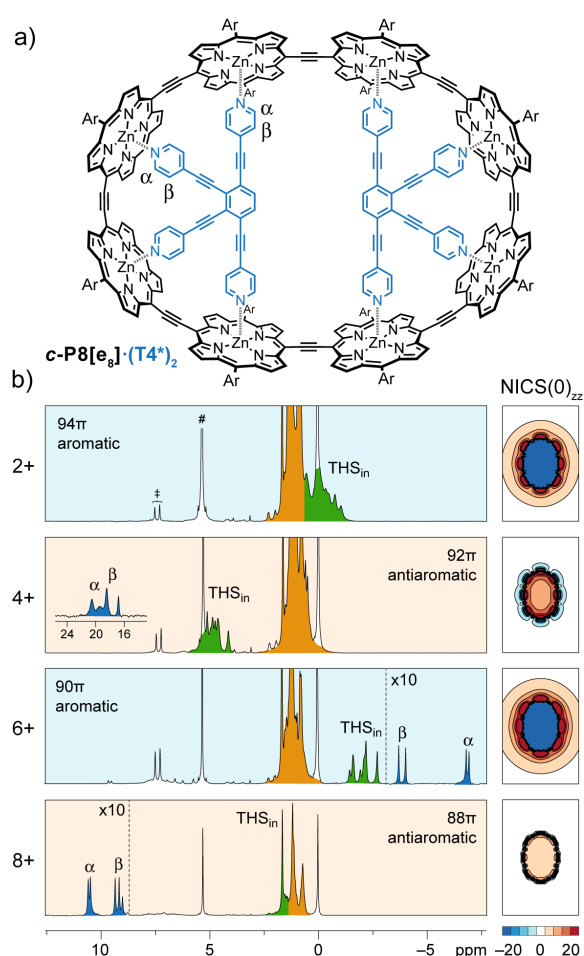


Figure 2. Hückel behaviour in a template-bound eight-porphyrin ring.

a) Molecular structure of $c\text{-P8}[\text{e}_8] \cdot (\text{T4}^*)_2$. Ar = 3,5-bis(trihexylsilyl)phenyl. b) ^1H NMR spectra of oxidised $c\text{-P8}[\text{e}_8] \cdot (\text{T4}^*)_2$. Labels denote the most important resonances THS_{in} (green), THS_{out} (orange), and template (α , β). # and ‡ denote CH_2Cl_2 and thianthrene, respectively. Detailed spectra for each state are shown in Supplementary Figures S14 and S45–S47. NICS(0)_{zz} grids (LC- ω hPBE/6-31G*, $\omega = 0.1$) in the xy plane for each state (without template).

Fluorinated templates allow the aromaticity of nanorings to be evaluated using ^{19}F NMR, as exemplified by the extended six-legged template **T6ef** (Figure 3). Two molecules of this template stack to form a stable 2:1 complex with the nanoring, $c\text{-P12}[\text{b}_{12}] \cdot (\text{T6ef})_2$ (circuit electron count: 168 π when neutral²⁷), in which the CF_3 groups are positioned to probe the global ring current. The CF_3 ^{19}F resonance is shielded in the aromatic 6+ and 10+ oxidation states, but deshielded in the antiaromatic 8+ oxidation state (Figure 3a). These shifts of the CF_3 ^{19}F resonance are fully consistent with shifts of the THS_{in} ^1H signals (shaded green, Figure 3a) and they agree with the predictions of NICS calculations (a range of functionals were tested for $c\text{-P12}[\text{b}_{12}]^{n+}$ and, as for the 6-porphyrin rings, LC- ω hPBE ($\omega = 0.1$) was found to give the best agreement with experimental ring current shifts; see Supplementary Figures S88–S90, and Tables S7 and S8). No aromatic or antiaromatic ring current was detected for the 12+ oxidation state, and this result is reproduced by the NICS calculations, although this 12+ state is expected to be antiaromatic (156 π ; $4n$; $n = 39$). The ^{19}F NMR titrations also show CF_3 signals attributed to the open-shell 7+, 9+ and 11+ oxidation states, at similar chemical shifts to the neutral compound — thus the shielding or deshielding effects in the open-shell cations are small compared

with those in closed-shell species. EXSY NMR experiments show that the odd-electron oxidation states are in chemical exchange with the even-electron states, on a timescale of seconds. It is not surprising that mixtures of oxidation states are formed during these titrations, because the oxidation potentials are closely spaced (for calculated speciation curves, see Supplementary Figure S79), but it is remarkable that these open-shell species give spectra that are sharp enough to be observed.

We used the 12-porphyrin nanoring **c-P12[b₁₂]** to explore the relationship between 3D conformation and aromaticity. The magnitude of the ring current induced in a macroscopic ring of metal wire depends on the total magnetic flux passing through the ring. If the ring has a figure-of-eight shape, with two equal lobes such that the magnetic flux passing through each loop induces equal and opposite currents, then there will be no net ring current. We sought to test whether this principle applies on the molecular scale, so we synthesised a small six-legged template, **T6f**, which forms a figure-of-eight shaped²⁷ 1:2 complex **c-P12[b₁₂]·(T6f)₂** (note that this system is doubly twisted, not Möbius^{28,29}, Figure 3b) and investigated the ring currents in this system by ¹H and ¹⁹F NMR as a function of oxidation state, under identical conditions to those used for the circular **c-P12[b₁₂]·(T6ef)₂**. The resulting ¹H, ¹³C and ¹⁹F NMR spectra show the absence of any detectable ring currents ($\Delta\delta < 0.1$ ppm) in the figure-of-eight nanoring, confirming that aromaticity can be switched on/off by geometry. This result is reproduced by the NICS calculations (Supplementary Figure S91). The suppression of ring currents in figure-of-eight shaped annulenes has been predicted theoretically^{28,30}, but it has not been observed experimentally in other figure-of-eight shaped aromatic systems^{6,7,14,28,29,31}, probably because they were not the right shape to achieve cancellation of the ring current. The topology of a closed ribbon can be described by the linking number L_k , the writhe W_r and the twist T_w (ref. 32–34). Total cancellation of the ring current is expected for a geometry with $W_r = 2$, $T_w = 0$ and $L_k = 2$ with D_2 symmetry²⁸, which is close to the geometry of **c-P12[b₁₂]·(T6f)₂** ($W_r = 1.8$, $T_w = 0.2$ and $L_k = 2$, from the crystal structure of **c-P12[b₁₂]·(T6)₂**, ref: 35). The **c-P12[b₁₂]·(T6ef)₂** ring has a large cross sectional area ($A_{xy} = 22$ nm²; $A_{xz} = A_{yz} = 0$; Figure 3a) resulting in a substantial ring current, whereas the **c-P12[b₁₂]·(T6f)₂** lemniscate has a small net cross section ($A_{xy} = 0$, $A_{xz} = 2.3$ nm², $A_{yz} = 0.4$ nm²; Figure 3b and Supplementary Figure S93) resulting in a weak response to magnetic field. The ring current in **c-P12[b₁₂]·(T6f)₂** is blocked by the global topology ($T_w \approx 0$ and $W_r \approx 2$), not by any local break in π -conjugation.

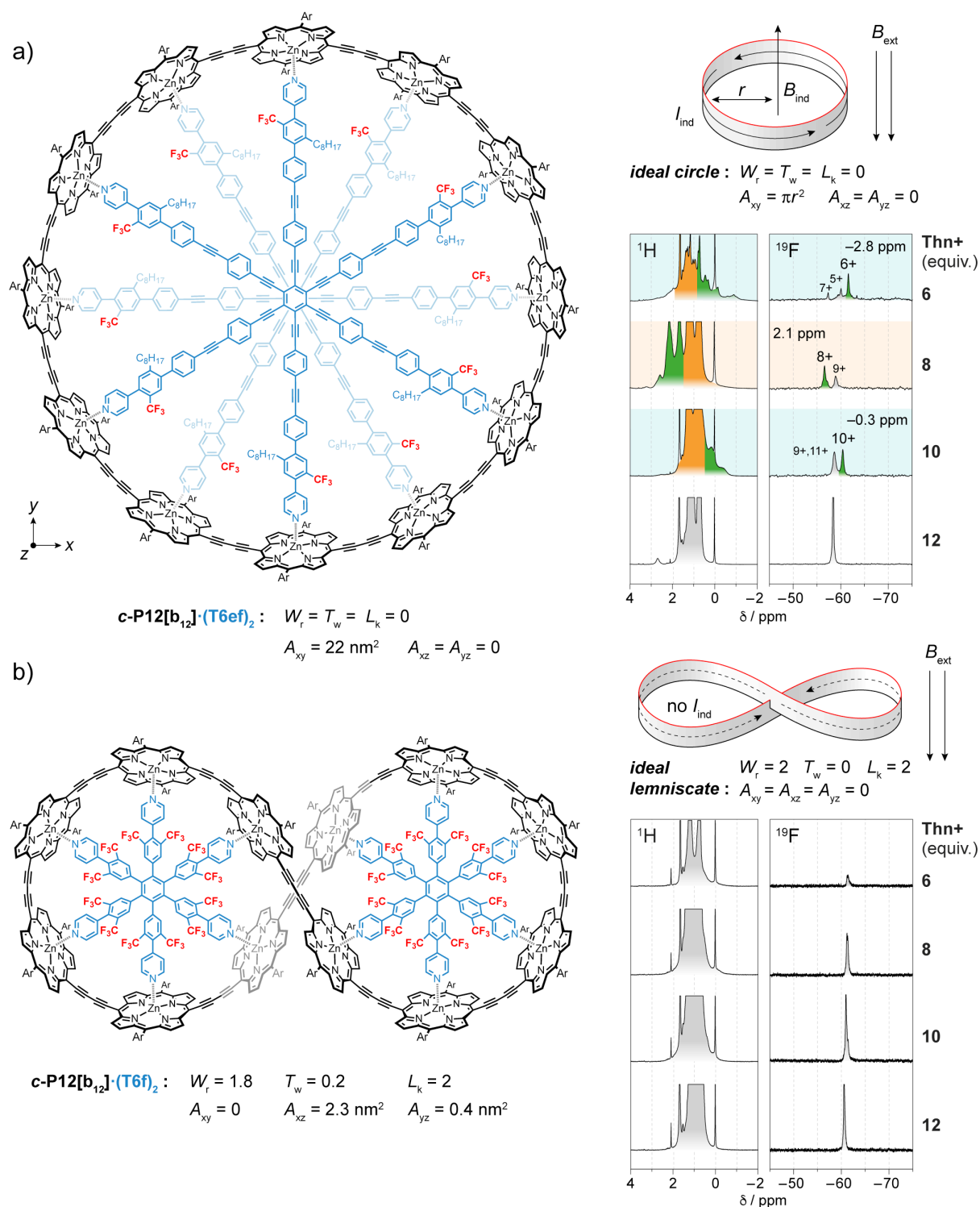


Figure 3. Ring currents in topologically distinct twelve-porphyrin ring complexes.

Left: Schematic representation of two **c-P12[b₁₂]** complexes forming either a circle (a): **c-P12[b₁₂] \cdot (T6ef)₂, or a lemniscate (b): **c-P12[b₁₂] \cdot (T6f)₂. Both templates feature fluorine probes. Right: A circular conformation is predicted to exhibit ring currents and thus an induced magnetic moment upon the application of an external magnetic field. In the lemniscate, the two loops induce opposite currents which cancel, and no ring current is expected. ¹H and ¹⁹F-NMR spectra of oxidised **c-P12[b₁₂] \cdot (T6ef)₂ and **c-P12[b₁₂] \cdot (T6f)₂. Green shading indicates the interior THS_{in} resonance. Backgrounds indicate a global aromatic (blue) or antiaromatic (orange) state. Detailed spectra for each state are shown in Supplementary Figures S17, S18 and S58–S67. L_k , W_r and T_w are the linking number, writhe and twist that specify the topology of the loop^{32–34}. A_{xy} , A_{xz} and A_{yz} are the net cross section areas; $A_{xy} = 0$ for **c-P12[b₁₂] \cdot (T6f)₂ because it has D_2 symmetry and the areas of the two loops cancel.**********

The ring currents observed in this whole family of nanorings are summarised in Figure 4, which plots the shift in the THS_{in} resonances ($\Delta\delta_{\text{THS in}}$) as a function of oxidation state. Whenever a ring current is observed, its direction (aromatic or antiaromatic) matches the prediction from Hückel's rule. The magnitude of the ring current varies with the average oxidation state of the porphyrin units ($\overline{P_{\text{OX}}} = Q/N$). The largest ring currents are observed in mixed-valence systems, where $\overline{P_{\text{OX}}} \approx +0.5$ to $+0.7$. Global ring currents are not observed in the neutral rings ($\overline{P_{\text{OX}}} = 0$), where the local porphyrin ring current dominates; in the larger rings, the ring current also vanishes when $\overline{P_{\text{OX}}} = 1$ (see square points for *c*-P8[b₈](T4)₂⁸⁺, *c*-P10[b₁₀](T5)₂¹⁰⁺ and *c*-P12[b₁₂](T6ef)₂¹²⁺ in Figure 4). The formation of a mixed valence state appears to be essential for efficient nanoscale charge delocalisation, just as the presence of a partially filled band is essential for conductance in an extended lattice³⁶.

Hückel's rule was originally formulated to explain the unusual properties of benzene, and other molecules with 6 π -electrons³⁷. It is remarkable that this simple rule correctly predicts the magnetic response of large oxidised nanorings with circuits of up to 162 π -electrons. This work shows that electronic delocalisation can extend coherently around molecular rings with circumferences of 16 nm. These supramolecular rings allow the magnitude of the ring current to be controlled by topology in a way that has not yet been demonstrated for small molecules.

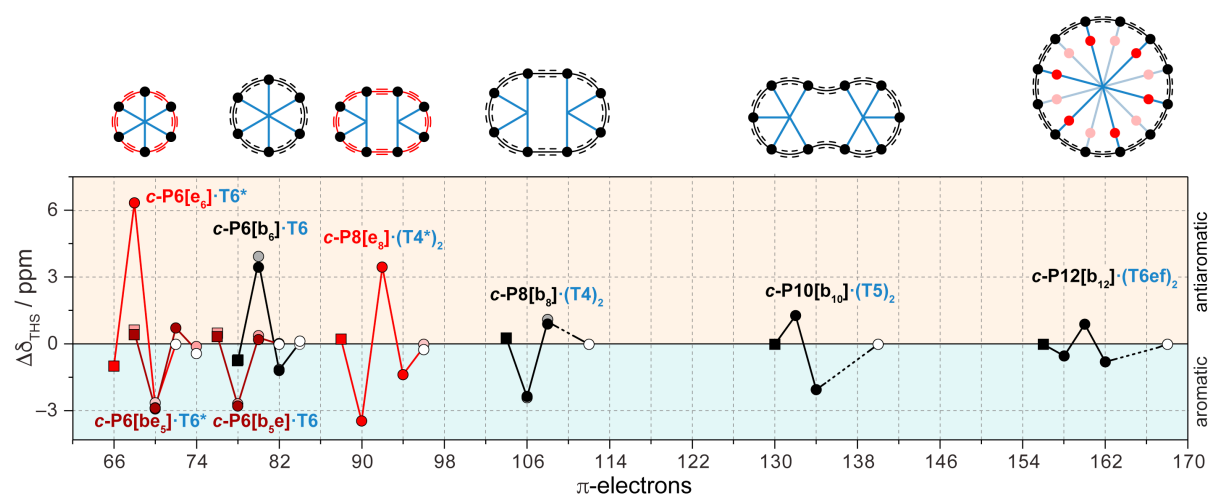


Figure 4. Variation in shielding and deshielding of the THS groups across eight different nanorings.

Top: Schematic representation of a family of related porphyrin rings with increasing number of porphyrins. Red indicates ethyne, black indicates butadiyne linkers. Black dots indicate zinc-porphyrins. Templates are represented in blue. *Bottom:* Plot of the observed ¹H chemical shift difference $\Delta\delta_{\text{THS}} = \delta_{\text{THS(in)}} - \delta_{\text{THS(out)}}$ between inner and outer THS probe for each oxidation state of the nanoring. A positive or negative shift indicates a global antiaromatic or aromatic current, respectively. Empty circles indicate the corresponding neutral species. Squares indicate oxidation states with $\overline{P_{\text{OX}}} = 1$. Vertical dashed lines denote oxidation states with $4n+2$ π -electrons. Lines connecting dots are for visual guidance only. $\Delta\delta_{\text{THS}}$ values are shown for both the CH₃ signals (dark points) and SiCH₂ signals (faded points) of the THS chains.

Methods

All ^1H NMR oxidation titrations were carried out by adding thianthrenium hexafluoroantimonate to a solution of the porphyrin nanoring in CD_2Cl_2 at $-60\text{ }^\circ\text{C}$ to $-20\text{ }^\circ\text{C}$ (see SI for details). At the end of the titration, decamethylferrocene (FeCp_2^*) was added to reduce the porphyrin nanoring back to its neutral form; this process is highly reversible.

Data availability

The raw NMR spectra and computational data are available from the corresponding author on request. All other data that support these findings are available within the paper or Supplementary Information.

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