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Submitted date: 04/03/2019 • Posted date: 04/03/2019
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Citation information: Peeks, Martin; Gong, Juliane; McLoughlin, Kirstie; Kobatake, Takayuki; Haver, Renee; Herz, Laura; et al. (2019): Aromaticity and Antiaromaticity in the Excited States of Porphyrin Nanorings. ChemRxiv. Preprint.

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Aromaticity and Antiaromaticity in the Excited States of Porphyrin Nanorings

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Supporting Information Placeholder

ABSTRACT: Aromaticity can be a useful concept for predicting the behavior of excited states. Here we show that π-conjugated porphyrin nanorings exhibit size-dependent excited-state global aromaticity and antiaromaticity, for rings containing up to eight porphyrin subunits, although they have no significant global aromaticity in their neutral singlet ground states. Applying Baird’s law, odd rings ([4n] π-electrons) are aromatic in their excited states, whereas the excited states of even rings ([4n+2] π-electrons) are antiaromatic. These predictions are borne out by density functional theory (DFT) studies of the nucleus-independent chemical shift (NICS) in the T1 triplet state of each ring, which reveal the critical importance of the triplet delocalization to the emergence of excited-state aromaticity. The singlet excited states (S1) are explored by measurements of the radiative rate and fluorescence peak wavelength, revealing a subtle odd-even alternation as a function of ring size, consistent with symmetry-breaking in antiaromatic excited states.

Carbocyclic π-systems with circuits of [4n+2] and [4n] π-electrons are expected to be aromatic and antiaromatic, respectively, according to modern formulations of Hückel’s rule.1 Introduction of a twist into the π-system reverses the mnemonic and [4n] π-electron systems become “Möbius aromatic”.2,3 In 1972, Baird predicted a further case in which Hückel’s rule would be reversed: in the lowest triplet state (T1) of a molecule, giving rise to excited-state aromaticity and antiaromaticity for annulenes with [4n] and [4n+2] π-electrons, respectively.4 Several experimental examples of T1 aromaticity have been presented, and the predictive power of Baird’s rule has been extended to the S1 excited state.5–7 The theory of excited-state aromaticity has been used to rationalize photochemical reactivity.8,9 More recently, it has been used to provide design principles for photoswitches10 and molecular motors,11 for energy-level tuning in fulvenes,12 and to explain photoinduced structural changes in a liquid crystal.13

The three main computational methods for investigating (anti)aromaticity involve calculating: (1) bond-length alternation using the harmonic oscillator model (HOMA); (2) aromatic stabilization energy (ASE); and (3) the magnetic effects of (anti)aromaticity using the nucleus-independent chemical shift (NICS).14–16 It is generally accepted that the magnetic criterion is the least ambiguous, particularly for large molecules comprising several potential (anti)aromatic electron pathways, for which HOMA and ASE can be unsuitable. Experimentally, aromatic character is most convincingly assessed by NMR measurements, which reveal the presence of a ring current. Excited-state (anti)aromaticity is more difficult to evaluate experimentally, because NMR is not practical for S1 or T1 excited states.

Kim and coworkers have assigned excited-state (anti)aromaticity on the basis of the shape of the excited-state absorption spectrum.6 They found that the antiaromatic excited (triplet) states of hexaphyrins and other expanded porphyrins exhibit broad and featureless absorption spectra, whereas the aromatic excited-state spectra are sharper and more structured, qualitatively resembling the ground-state absorption spectra of aromatic analogues. Kim’s group recently employed time-resolved infrared spectroscopy (TR-IR) to assess aromaticity in singlet excited states, on the basis that aromatic molecules are more symmetric (thus have fewer IR-active vibrations) than antiaromatic ones.17

Despite a recent surge of studies into excited-state aromaticity,13,15–21 the effect has rarely been investigated in macrocycles that can sustain multiple aromatic pathways.18,19 A prime example of a system with local (monomer-bound) and global ring currents is given by the series of cycloparaphenylenes.
In their electronically neutral ground states, these molecules exhibit no global aromaticity (the peripheral electron circuit would contain $[4\pi]$ π-electrons), and instead the local aromaticity of each 6 π-electron benzene circuit is apparent. However, when such rings are oxidized to the 2+ state, they exhibit global aromaticity about their circumference, determined by calculations, NMR, and magnetic circular dichroism (MCD).\textsuperscript{27,28} We reported a similar effect in a [6]-porphyrin nanoring (c-P6, Figure 1).\textsuperscript{1,29,30} In its neutral state, this molecule has $[4\pi]$ π-electrons but exhibits no global ring current: instead, the 18 π-electron circuit of each porphyrin contributes local aromaticity. However, when the ring is oxidized by removal of 4 or 6 π-electrons, global antiaromaticity (80 π) and aromaticity (78 π), respectively, results (Figure 2).\textsuperscript{31} This global aromaticity is demonstrated by characteristic NMR chemical shifts and by DFT calculations of magnetic shielding.

Figure 1: Examples of macrocyclic π-conjugated molecules which exhibit no ground-state global aromaticity in their neutral ground states; only local aromaticity: cycloparaphenylenes ([N]CPP) and porphyrin nanorings (c-PN).

We have previously investigated the electronic delocalization in the singlet and triplet excited states of linear butadiyne-linked porphyrin oligomers, the nanoring c-P6, and, for singlet excited states, much larger rings (c-PN up to $N = 40$). The singlet excited state delocalizes around the entire nanoring within 200 fs for nanorings up to c-P24.\textsuperscript{31,32} c-P6 emits from a delocalized singlet state, whereas partial localization probably occurs prior to emission in c-P10 and larger nanorings, as indicated by an increase in the radiative rate.\textsuperscript{32} EPR measurements of triplet states indicate uniform triplet delocalization (or fast hopping, at 20 K, on the timescale of the EPR hyperfine coupling, ca. 100 ns) for c-P6, and show that the spin density is mainly localized over 2–3 units in linear oligomers,\textsuperscript{33} which is consistent with the presence of a coherent triplet exciton extended over at least six units.\textsuperscript{34} With most functionals, our DFT results do not predict uniform delocalization of the triplet state of the nanorings \textit{(vide infra)}, resulting in different spin densities on each porphyrin subunit.

Figure 2: The porphyrin nanoring c-P6 contains both a global conjugated circuit (84 π-electrons) and six local porphyrin aromatic circuits (6 × 18π). (a) In its ground state, local circuits dominate and there is no global aromaticity. (b and c) In the 4+ and 6+ oxidation states, local aromaticity is lost and global antiaromaticity and aromaticity, respectively, arise. (d) In part of this work, we show that the T\textsubscript{1} state exhibits global excited-state aromaticity in addition to local (anti)aromaticity.

Here we present DFT results predicting excited-state (T\textsubscript{1}) aromaticity and antiaromaticity in small porphyrin nanorings, consistent with Baird’s rule. We then present experimental measurements of fluorescence quantum yields, emission spectra, and radiative rates, which indicate the presence of excited-state aromaticity in the S\textsubscript{1} state of small porphyrin nanorings (c-P5 to c-P9). Experimental measurements of the triplet state lifetimes were not possible due to the low triplet yields of porphyrin nanorings, also encountered for longer oligomers.\textsuperscript{33,35}

We used DFT to calculate NICS values in the S\textsubscript{0} and T\textsubscript{1} states of nanorings from c-P5 to c-P8. Larger nanorings are computationally intractable owing to their size and the loss of symmetry in excited states. The NICS value gives the NMR shielding at a point in space, from which the presence and nature of (anti)aromatic ring-currents can be readily deduced. The parenthetical number (d in NICS(d)) corresponds to the distance above the molecular plane at which the NICS probe atom is placed, in Å. The NICS(0) value is the most suitable for these systems; use of NICS(1) is not justified because there is no spurious electron density (such as from σ-bonds in the case of benzene) at the center of the nanorings. A negative NICS value inside the ring indicates aromaticity; positive indicates antiaromaticity. We calculated NICS(0) values across a grid of points through each nanoring in their S\textsubscript{0} and T\textsubscript{1} states, at the B3LYP/6-31G* level of theory\textsuperscript{36–40} using Gaussian16/A.03\textsuperscript{41} and Gaussian09/D.01.\textsuperscript{42} Here we report two NICS values: the isotropic NICS (NICS(0)\textsubscript{iso}) and the zz component of the shielding tensor (NICS(0)\textsubscript{zz}), where the z-axis is the N-fold rotation axis of the c-PN nanoring. The latter is more sensitive to global aromatic ring-current effects, whereas the former is more analogous to chemical shieldings measured through solution NMR chemical shifts. The NICS(0)\textsubscript{zz} values in the S\textsubscript{0} states were approximately zero for all rings (Table 1 and Figure S1), confirming their ground-state global non-aromaticity, whereas the NICS(0)\textsubscript{iso} depicts shielding above and below the plane of each porphyrin subunit, consistent with
c-P5, and c-P8. In the same

local aromaticity. The NICS(0)iso and NICS(0)zz for each ring in the T1 state (Figure 3, Table 1 and SI Figure S2) reveal an alternation between aromaticity and antiaromaticity as a function of ring size, consistent with Baird’s rule and the π-electron count: each monomer subunit in the nanorings contributes 14 π-electrons; thus c-P5 has 70 π-electrons [4n + 2]; c-P6 has 84 [4n]; c-P7 has 98 [4n + 2] and c-P8 has 112 [4n]. The NICS values indicate the presence of substantial global aromatic and antiaromatic ring currents in the triplet states of c-P6 and c-P5, respectively, whereas the effect is more subtle in c-P7 and c-P8.

We used the following functionals: M06 and the consequent effect on NICS values for the choice of functional with the degree of triplet delocalization in the 31G* level of theory. Perhaps as a consequence of the larger rings are essentially non-aromatic at the B3LYP/6-31G* level of theory.

Table 1: NICS(0)iso and NICS(0)zz (all units ppm) at the B3LYP/6-31G* level of theory.

|          | S0 ground state | T1 excited state |
|----------|-----------------|------------------|
|          | iso  | zz  | iso  | zz  |
| c-P5     | 2.5  | 0.1 | 1.6  | 10.3 |
| c-P6     | 1.4  | 1.1 | 5.4  | 12.2 |
| c-P7     | 1.2  | 0.5 | 0.4  | 2.1  |
| c-P8     | 0.9  | 0.5 | 1.3  | 1.5  |

In our previous studies of c-P6 in its oxidized states, we found that oxidation to the 4+ or 6+ state results in the loss of local porphyrin aromaticity and the emergence of a global ring current.39 Surprisingly, the NICS(0)iso calculations (Figure 4 and SI Figure S2) suggest that the local aromaticity of each porphyrin subunit persists in the triplet states (cf. negative NICS above and below each porphyrin), except in the case of the porphyrin unit with the greatest spin density. For this porphyrin, the NICS(0)iso is consistent with weak local antiaromaticity. This change is paralleled in the NICS of reduced porphyrin monomers (P1+), where addition of an electron changes the ring from aromatic to antiaromatic (SI Figure S6). Analogously, porphyrin monomer dications and dianions are antiaromatic, with 16 π-electrons and 20 π-electrons, respectively.43,44

Figure 4: (a) NICS(0)iso for c-P5 in its T1 excited state; (b) spin density distribution for c-P5 in its T1 excited state, in the same orientation, both calculated at the B3LYP/6-31G* level of theory. Arrows in part (a) use the same convention as in Figure 2: red arrows correspond to antiaromatic (paratropic) ring currents; blue arrows to aromatic (diatropic). The porphyrin bearing the most spin density (calc. 1.26 spins) has a mildly antiaromatic local ring current.

For the larger c-P7 and c-P8 rings, the magnitude of NICS(0)iso in the T1 state is significantly reduced compared to that for c-P5 and c-P6 (~2 ppm vs. ~10 ppm), indicating that the larger rings are essentially non-aromatic at the B3LYP/6-31G* level of theory, perhaps as a consequence of the finite delocalization of the triplet state (over 5–6 porphyrin units).

The predicted triplet delocalization is strongly affected by the choice of density functional. We decided to compare the choice of functional with the degree of triplet delocalization and the consequent effect on NICS values for c-P5 and c-P6. We used the following functionals: M06-L, M06-2X, CAM-B3LYP, and LC-oHPBE (ω = 0.05, 0.1, 0.2).45–48 The B3LYP/6-31G* geometry was used in all cases. The results (Figure 3 (b), SI Tables S2 and S3 and Figures S3 and S4)
show that the NICS(0), value is extremely sensitive to the degree of triplet delocalization: those functionals that tend to over-delocalize, such as M06-L and B3LYP, afford a larger NICS than those that tend to under-delocalize. Most calculations of excited-state aromaticity, to date, have employed B3LYP. As the molecules of interest become larger, it becomes important to carefully consider whether the DFT model accurately describes the electron delocalization. For c-P6, the triplet state is believed to be either fully delocalized around the ring, or hopping rapidly on the EPR spectroscopic timescale. Our B3LYP calculations are consistent with delocalization of spin density over all six porphyrin units in triplet c-P6, albeit not evenly. Previous B3LYP calculations of triplet density in linear oligomers were consistent with those determined by ENDOR measurements.

Singlet excited states are generally more delocalized than triplet states, As mentioned above, Kim and coworkers have employed TR-IR to assess the (anti)aromatic character of singlet excited states on the basis that an antiaromatic state will undergo a pseudo-Jahn Teller distortion, thus adopting a lower-symmetry excited state and so exhibiting more IR-active bands than an analogous aromatic excited state of high symmetry. We reasoned that this effect should also result in a perturbation of the emission properties of porphyrin nanorings. Emission quantum yields for small nanorings are low (<5%), due to the dipole-forbidden nature of the S → S transition. The reason is best explained by reference to c-P6: in the point-dipole approximation, the transition dipole moments of the six porphyrin monomers around the ring (directed along the butadiyne axis of each monomer) cancel, leaving no net transition dipole moment. A similar S → S forbiddenness has been reported in small cyclopaphylenes, where introduction of a symmetry-breaking element to the molecular structure leads to enhanced emission. For both the c-PN and [N]CPP series, fluorescence quantum yield increases with ring size, as a consequence of increased structural flexibility and the loss of excited-state symmetry. For antiaromatic rings, pseudo-Jahn Teller distortion in the excited-state would lead to reduced excited-state symmetry and thus an increase in emission quantum yield for excited-state antiaromatic rings, whereas emission from excited-state aromatic rings will remain largely forbidden. It is important to remember that the porphyrin nanorings have, in their ground states, no global aromaticity and are highly symmetric.

We measured the radiative rates (Figure 5) and fluorescence quantum yields (Φ) of c-P5 to c-P16 (see SI for experimental details). Radiative rates were recovered from measurements of the total excited-state lifetimes by time-correlated single photon counting (TCSPC). The results show that as ring size increases, the radiative rate and Φ also increase, from 0.05 ns⁻¹/1% for c-P6 to 0.4 ns⁻¹/20% for c-P16, consistent with previous reports on larger rings. For the smaller rings (c-P5 to c-P9) there is a subtle odd-even variation in radiative rate: odd rings tend to have a higher radiative rate, and even rings lower. We used a linear model to determine whether the data are best described by a model based only on oligomer length (model A), or a model also incorporating the odd/even porphyrin count of the ring, taking account of the extra degree of freedom (model B; see SI for full details). For the full data set (c-P5 to c-P16), model A describes the data better than model B. However for the dataset including only c-P5 to c-P9, model B provides a better description of the data (see SI Figure S12). Analysis of Φ gives similar results (see SI Figure S13 and Table S4). Thus we conclude that there is an odd-even effect in the Φ and radiative rates of small porphyrin nanorings, consistent with excited-state symmetry breaking in antiaromatic odd-numbered rings. A similar effect is apparent in the photoluminescence peak energy (Figure 5b, SI Figures S10, S11 and S14, Table S4), which is consistent with a slight odd-even alternation of the HOMO-LUMO gaps as a function of ring size (SI Figure S7).

Figure 5: (a) Radiative rates, and (b) Energy of PL peak maximum, measured in toluene containing 1% pyridine, referenced to l-P6 (1.47 eV), as a function of ring size N for c-P5–c-P9. Lines connect measurements from the same experimental replicate. λex = 500 nm. See SI Figure S11 for the full range.

In conclusion, DFT predicts that porphyrin nanorings will exhibit excited-state aromaticity in their triplet (T) states, though the computational result is very sensitive to the extent of triplet delocalization and thus to the choice of DFT functional. We also present spectroscopic evidence for singlet excited-state (S) (anti)aromaticity in nanorings containing 5–9 porphyrin subunits, comprising 70–126 π-electrons, consistent with Baird’s rule based on their π-electron counts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of computational, synthetic, photophysical and statistical methods, Cartesian coordinates for calculated geometries, and supplementary results figures (PDF).

Cartesian coordinates for calculated geometries (XYZ files in a ZIP archive, and in the PDF).

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ACKNOWLEDGMENT

We thank the Oxford Advanced Research Computing facility for computational support and the EPSRC (grants EP/M016110/1 and EP/J007161/1) and ERC (grant 320969)
Supporting Information
for
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S1 Computational Chemistry

DFT geometry optimizations were performed using the B3LYP functional and the 6-31G* all-electron basis set, as implemented in Gaussian09/D.01 and Gaussian16/A.03. The meso-aryl groups on the nanorings were truncated to –H. Nanorings c-P5, c-P6, c-P7 and c-P8 were optimized in their $S_0$ state with the highest possible symmetry ($D_{nv}$). The geometries converged as follows: c-P5 ($D_{5h}$), c-P6 ($D_{6h}$), c-P7 ($C_{7v}$) and c-P8 ($C_{8v}$). Triplet states were then optimized and converged to non-symmetric ($C_1$) geometries. The stability of the triplet wavefunctions was checked, confirming that they corresponded to the $T_1$ state and not some higher energy state. There was no excessive spin contamination ($\langle S^2 \rangle = 2$). NICS shieldings were calculated using the GIAO method using either B3LYP, LC-wHPBE ($w = 0.05, 0.1$ or $0.2$), M06-L, M06-2X, or CAM-B3LYP, at the B3LYP/6-31G* geometry. Additionally, M06-2X NMR shieldings were calculated at the M06-2X/6-31G*//M06-2X/6-31G* level. NICS surfaces were calculated with a $20 \text{ Å} \times 20 \text{ Å}$ grid of ghost atoms with $1 \text{ Å}$ spacing.

S1.1 Summary of NICS values, and discussion of spin densities

Table S1: NICS(0)$_{iso}$ and NICS(0)$_{zz}$ (all units ppm) at the centers of porphyrin nanorings in their $S_0$ and $T_1$ states. Level of theory: B3LYP/6-31G*.

| π-electron count | $S_0$ | | | $T_1$ |
|------------------|-------|---|---|---|
|                  | NICS(0)$_{iso}$ | NICS(0)$_{zz}$ | NICS(0)$_{iso}$ | NICS(0)$_{zz}$ |
| c-P5             | 70    | -2.5 | -0.1 | 1.6 | 10.3 |
| c-P6             | 84    | -1.4 | 1.1  | -5.4 | -12.2 |
| c-P7             | 98    | -1.2 | 0.5  | 0.4  | 2.1  |
| c-P8             | 112   | -0.9 | 0.5  | -1.3 | -1.5 |

The Mulliken spin populations of the constituent atoms for each porphyrin were summed, affording the spin per porphyrin subunit. These spin densities were then represented as $N$ equally spaced radial vectors ($r_i$) around a circle, with length (weight) proportional to their spin density. The spin density delocalization was quantified as the angular deviation of these vectors, calculated using the CircStat toolbox in MATLAB. The total spin density is normalized to 1.

The angular deviation ($\Gamma_{\text{trip}}$) takes a range of values from 0 to $\sqrt{2}$, where a higher value corresponds to increased delocalization. It is calculated from the length of the normalized mean resultant vector ($R = ||\tau||$, where $\tau = \sum r_i$) of the distribution, using:

$$\Gamma_{\text{trip}} = \sqrt{2(1 - R)}$$  \hspace{1cm} (S1)
**Table S2:** NICS(0)\textsubscript{iso} and NICS(0)\textsubscript{zz} (all units ppm) at the center of c-P5 in its T\textsubscript{1} state for different DFT functionals.

| Functional            | $\Gamma_{\text{trip}}$ | NICS(0)\textsubscript{iso} | NICS(0)\textsubscript{zz} |
|-----------------------|-------------------------|------------------------------|----------------------------|
| B3LYP//B3LYP          | 0.777                   | 1.6                          | 10.3                       |
| M06-2X//M06-2X        | 0.572                   | -1.5                         | 1.7                        |
| M06-L//B3LYP          | 0.926                   | 11.1                         | 38.3                       |
| M06-2X//B3LYP         | 0.655                   | -1.2                         | 2.5                        |
| CAM-B3LYP//B3LYP      | 0.609                   | -1.4                         | 1.6                        |
| LC-\omega HPBE//B3LYP ($\omega = 0.05$) | 0.834         | 2.7                          | 13.3                       |
| LC-\omega HPBE//B3LYP ($\omega = 0.1$) | 0.671         | -0.6                         | 3.4                        |
| LC-\omega HPBE//B3LYP ($\omega = 0.2$) | 0.579         | -1.4                         | 1.5                        |

**Table S3:** NICS(0)\textsubscript{iso} and NICS(0)\textsubscript{zz} (all units ppm) at the center of c-P6 in its T\textsubscript{1} state for different DFT functionals.

| Functional            | $\Gamma_{\text{trip}}$ | NICS(0)\textsubscript{iso} | NICS(0)\textsubscript{zz} |
|-----------------------|-------------------------|------------------------------|----------------------------|
| B3LYP//B3LYP          | 0.941                   | -5.4                         | -12.2                      |
| M06-2X//M06-2X        | 0.490                   | -1.3                         | 0.4                        |
| M06-L//B3LYP          | 1.414                   | -9.2                         | -23.6                      |
| M06-2X//B3LYP         | 0.548                   | -1.4                         | 0.1                        |
| CAM-B3LYP//B3LYP      | 0.540                   | -1.1                         | 0.6                        |
| LC-\omega HPBE//B3LYP ($\omega = 0.05$) | 0.873        | -4.2                         | -8.9                       |
| LC-\omega HPBE//B3LYP ($\omega = 0.1$) | 0.573        | -1.3                         | -0.3                       |
| LC-\omega HPBE//B3LYP ($\omega = 0.2$) | 0.487        | -1.1                         | 0.6                        |
S1.2 NICS grids for $S_0$ ground states

Figure S1: NICS(0)$_{\text{iso}}$ (left column) and NICS(0)$_{zz}$ (right column) for c-P5, c-P6, c-P7, and c-P8, in their $S_0$ singlet ground states, calculated at the B3LYP/6-31G* level of theory. White circles indicate the positions of porphyrin units.
S1.3 NICS grids for $T_1$ excited states

Figure S2: NICS(0)$_{iso}$ (left column) and NICS(0)$_{zz}$ (right column) for c-P5, c-P6, c-P7, and c-P8, in their $T_1$ states, calculated at the B3LYP/6-31G* level of theory. White circles indicate the positions of porphyrin units.
Figure S3: NICS(0)$_{iso}$ (left column) and NICS(0)$_{zz}$ (right column) for $c$-$P5$ in its $T_1$ state, calculated using the functionals M06-L and LC-$\omega$HPBE ($\omega = 0.05$, $\omega = 0.1$, and $\omega = 0.2$), and the 6-31G* basis set. White circles indicate the positions of porphyrin units.
Figure S4: NICS(0)_{iso} (left column) and NICS(0)_{zz} (right column) for c-P6 in its T\textsubscript{1} state, calculated using the functionals M06-L and LC-ωHPBE (ω = 0.05, ω = 0.1, and ω = 0.2), and the 6-31G* basis set. White circles indicate the positions of porphyrin units.
S1.4 Spin densities for T\textsubscript{1} excited states

Figure S5: Calculated spin densities (\(\alpha - \beta\)) for (a) c-P5, (b) c-P6, (c) c-P7, and (d) c-P8 in their T\textsubscript{1} states at the B3LYP/6-31G* level of theory.
S1.5 NICS grids for a porphyrin monomer in neutral and −1 oxidation states

Figure S6: NICS(0)_{iso} (left column) and NICS(0)_{zz} (right column) for P1 in its neutral and radical anion states, calculated using at the B3LYP/6-31G* level of theory.
S1.6 HOMO–LUMO gaps of porphyrin nanorings

Figure S7: (a) Frontier molecular orbital energies for c-P5–c-P8 (B3LYP/6-31G*) in the S0 state. (b) HOMO–LUMO gaps for c-P5–c-P8 in the S0 state (B3LYP/6-31G*).

S2 Synthesis

Unless stated otherwise, all reagents were obtained from commercial sources and used as received without further purification. Diethyl ether (Et2O), chloroform (CHCl3), tetrahydrofuran (THF), and toluene were dried by passing through activated alumina columns using a positive pressure of dry N2 in an MBraun MB-SPS-5 benchtop solvent purification system (H2O content < 20 ppm, determined by Karl-Fischer titration). Diisopropylamine (DIPA) was dried by distillation from CaH2. Analytical gel permeation chromatography (GPC) was performed on a JAIGEL H-P precolumn, a JAIGEL 3H-A (8 mm × 500 mm) and a JAIGEL 4H-A column (8 mm × 500 mm) in series with THF:pyridine 100:1 as eluent. Preparative recycling gel permeation chromatography was performed on a JAIGEL H-P precolumn, a JAIGEL 3H (20 mm × 600 mm) and a JAIGEL 4H column (20 mm × 600 mm) in series with toluene:pyridine 100:1 as eluent. Flash column chromatography was performed on Merck silica gel 60 (40–63 μm). Alumina columns were performed using aluminium oxide (activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å) from Sigma Aldrich (purchased before 2017). For TLC, Merck silica gel 60 F254 aluminium-backed sheets were used. Size exclusion chromatography (SEC) was carried out using Bio-Beads SX-1, 200–400 mesh (Bio Rad).

NMR spectra were recorded on Bruker AVIII400, Bruker AVIII400, Bruker AVIII500 and Bruker AVIII500 spectrometers. The residual solvent peak was used as internal reference. Multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constant(s) are reported wherever possible. MALDI-TOF-MS spectra were measured using a Waters MALDI Micro MX. UV-vis absorption spectra were recorded at ambient temperature with a Perkin-Elmer Lambda 20 using quartz 1 cm cuvettes.

All porphyrin oligomers bore bulky trihexysilyl (THS) solubilizing groups on the meso-aryl groups, to inhibit aggregation. c-P5, c-P6, and c-P7 were prepared using template-directed synthesis followed by removal of the template (see below and refs). c-P8 was the larger nanorings were all produced as side-products in the large-scale synthesis of c-P6 and were isolated by recycling GPC. Notably, the yield of c-P10 (2.3%) is much higher than that of c-P12 (0.1%), presumably because the bulky THS sidechains disfavour the formation of the c-P12·T62 figure-of-eight complex, instead favoring a less-crowded c-P10·T62 complex in which two pyridine units (one per template) are unbound.
S2.1  \textit{c-P6-T6}

The overall route to \textit{c-P6-T6} is shown in Scheme S1. Steps (i) to (v) are described elsewhere.\textsuperscript{515}

\begin{scheme}
(i) TF, CH\textsubscript{2}Cl\textsubscript{2}, then DDQ, then Et\textsubscript{3}N; (ii) Zn(OAc)\textsubscript{2} \cdot 2H\textsubscript{2}O, CHCl\textsubscript{3}, MeOH; (iii) \textit{N}-bromosuccinimide, CH\textsubscript{2}Cl\textsubscript{2}; (iv) CPDIPS-acetylene, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, THF, DIPA; (v) TBAF, CH\textsubscript{2}Cl\textsubscript{2}; (vi) T6, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, 1,4-benzoquinone, CHCl\textsubscript{3}, DIPA, 20 °C, 16 h, 20–36%. Yields and full experimental procedures for steps (i)–(v) reported in ref. \textsuperscript{[S15].}

\textit{\{H,H\}-P1} (200 mg, 0.12 mmol) and template T6 (26 mg, 29 µmol) were dissolved in CHCl\textsubscript{3} (133 mL) by sonication for 2 h. A solution of Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (27 mg, 39 µmol), copper(I) iodide (37 mg, 0.19 mmol) and 1,4-benzoquinone (89 mg, 0.80 mmol) in CHCl\textsubscript{3} (18 mL) and DIPA (0.25 mL) was added to the porphyrin mixture at 20 °C. The mixture was stirred at 20 °C overnight, open to air. The reaction mixture was partially concentrated and passed over a plug of alumina (CHCl\textsubscript{3}). Purification by SEC (toluene) and preparative recycling GPC (toluene + 1% pyridine) afforded \textit{c-P6-T6} (78 mg, 36%) as a brown solid. On a larger scale (800 mg \textit{\{H,H\}-P1}), the yield was only 20% due to apparent co-absorption of polymer and product to alumina and glass frits during purification, and consequent mechanical losses. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \textit{δ}, ppm: 9.54 (d, J = 4.2 Hz, 24H), 8.72 (d, J = 4.2 Hz, 24H), 8.30 (bs, 12H), 7.98 (bs, 12H), 7.97 (bs, 12H), 5.52 (d, J = 8.5 Hz, 12H), 5.45 (d, J = 8.5 Hz, 12H), 4.98 (d, J = 6.1 Hz, 12H), 2.41 (d, J = 5.8 Hz, 12H), 1.54–1.41 (m, 144H), 1.41–1.17 (m, 144H), 0.98–0.77 (m, 360H); MS (MALDI-TOF) \textit{m/z}: calcd. M\textsuperscript{+} for C\textsubscript{720}H\textsubscript{1068}N\textsubscript{30}Si\textsubscript{24}Zn\textsubscript{6}: 11211; found: 11207. UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \textit{λ}_{\text{max}} [nm] (log \textit{ε} [M\textsuperscript{-1} cm\textsuperscript{-1}]): 850 (5.61), 808 (5.70), 772 (5.57), 612 (4.59), 482 (5.76).
S2.2 Free-base c-P6 [H₂]₆-c-P6

Trifluoroacetic acid (95 µL, 1.24 mmol) was added to a solution of c-P6-T6 (23 mg, 2.078 µmol) in CHCl₃ (2 mL). The mixture was stirred at 20 °C until UV-vis indicated complete conversion of starting material (typically 5 min), then pyridine (0.2 mL) was added and the mixture was immediately filtered over a short column of silica gel (CHCl₃ + 1% pyridine). Removing the solvent yielded FB-c-P6 (16 mg, 79%) as a green solid. Yields varied from 79% to 100%. ¹H (400 MHz, CDCl₃) δH, ppm: 9.56 (d, J = 4.7 Hz, 24H), 8.71 (d, J = 4.7 Hz, 24H), 8.15 (bs, 24H), 7.96 (bs, 12H), 1.52–1.36 (m, 144H), 1.36–1.14 (m, 432H), 1.07–0.94 (m, 144H), 0.94–0.85 (m, 216H), −1.29 (s, 12H); MS (MALDI-TOF) m/z: calcd. M⁺ for C₆₄H₁₀₃₂N₂₄Si₂₄: 9834; found: 9836; UV-vis (CH₂Cl₂) λ_max [nm] (log ε [M⁻¹ cm⁻¹]): 791 (5.47), 771 (5.49), 659 (5.30), 466 (5.72).
S2.3  \( c\)-P6

\[
[H_2]_6\cdot c\text{-P6} (43.9 \text{ mg, } 4.5 \mu\text{mol}) \text{ was dissolved in CHCl}_3 (6 \text{ mL}) \text{ and a solution of } Zn(OAc)_2 \cdot 2\text{H}_2\text{O} \text{ (8.8 mg, } 219 \mu\text{mol) in methanol (0.6 mL) was added. The mixture was stirred at 40 } ^\circ\text{C for 70 min, at which time UV-vis indicated reaction completion. The mixture was then filtered through a short column of silica gel (CH}_2\text{Cl}_2 + 1\% \text{pyridine}) \text{ to afford } c\text{-P6 (46 mg, quant.) as a brown solid.}
\]

\[
\begin{align*}
\text{Scheme S3: (i) } & Zn(OAc)_2 \cdot 2\text{H}_2\text{O, CHCl}_3, \text{ MeOH, } 40 \, ^\circ\text{C}, 70 \, \text{min, quant. Over two steps (with Scheme S2), 73%.}
\end{align*}
\]

S2.4 Removal of templates from larger rings

The template, \( T_6 \), was removed from rings larger than \( c\)-P6 by displacement with pyridine. A sample of ring was dissolved in CHCl3 + 20% pyridine, and passed through a SEC column (eluting with CHCl3 + 20% pyridine). The absence of template was confirmed by \(^1\)H NMR spectroscopy. Residual pyridine could be removed by washing a CH2Cl2 solution of nanoring with a saturated aqueous solution of potassium hydrogen phthalate (three times), then with water (twice) before passage over a SiO2 plug (CHCl3) to remove water and phthalate residues. An alternative method of removing pyridine is to repeatedly dissolve the sample in tetrahydrofuran, and remove the solvents by evaporation. The phthalate wash is much more reliable.

S2.5  \( c\)-P8

\( c\)-P8 was isolated as a by-product in the synthesis of \( c\text{-P6}\cdot T_6 \) (from 0.8 g \{H,H\}-P1) as a brown solid (3.2 mg, 0.4%). \(^1\)H (400 MHz, CDCl3) \( \delta_h \), ppm: 9.74 (d, \( J = 4.5 \text{ Hz, } 32\)H), 8.85 (d, \( J = 4.5 \text{ Hz, } 32\)H), 8.21 (s, 32H), 7.97 (s, 16H), 1.76–0.72 (m, 1248H); MS (MALDI-TOF) \( m/z \): calcd. \( M^+ \) for \( C_{864}H_{1360}N_{32}Si_{32}Zn_8 \): 13615; found: 13786; UV-vis (CH2Cl2) \( \lambda_{\text{max}} \) [nm] (log \( \epsilon \) [M\(^{-1}\) cm\(^{-1}\)]): 818 (5.54), 597 (4.62), 495 (5.74), 469 (5.68).
S2.6  c-P9

c-P9 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (2.9 mg, 0.4%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 9.83 (d, \(J = 4.6\) Hz, 36H), 8.93 (d, \(J = 4.6\) Hz, 36H), 8.26 (s, 36H), 8.00 (s, 18H), 1.52–0.80 (m, 1404H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{972}\)H\(_{1530}\)N\(_{36}\)Si\(_{36}\)Zn\(_{9}\): 15317; found: 15550; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 821 (5.60), 600 (4.66), 487 (5.78), 472 (5.77).

S2.7  c-P10

c-P10 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (19.2 mg, 2.3%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 9.80 (d, \(J = 4.6\) Hz, 40H), 8.88 (d, \(J = 4.6\) Hz, 40H), 8.25 (s, 40H), 7.99 (s, 20H), 1.60–0.79 (m, 1560H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{1080}\)H\(_{1700}\)N\(_{40}\)Si\(_{40}\)Zn\(_{10}\): 17019; found: 17241; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 821 (5.73), 598 (4.81), 495 (5.89, sh.), 471 (5.92).

S2.8  c-P11

c-P11 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (2.1 mg, 0.3%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 9.90 (d, \(J = 4.7\) Hz, 44H), 8.98 (d, \(J = 4.6\) Hz, 40H), 8.31 (s, 40H) 8.02 (s, 20H), 1.74–0.63 (m, 1872H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{1188}\)H\(_{1870}\)N\(_{48}\)Si\(_{48}\)Zn\(_{11}\): 18721; found: 19016; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 820 (5.70), 596 (4.79), 493 (5.88), 471 (5.89).

S2.9  c-P12

c-P12 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (1.2 mg, 0.1%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 9.68 (d, \(J = 4.5\) Hz, 48H), 8.80 (d, \(J = 4.5\) Hz, 48H), 8.17 (s, 48H), 7.95 (s, 24H), 1.74–0.63 (m, 1872H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{1296}\)H\(_{2040}\)N\(_{48}\)Si\(_{48}\)Zn\(_{12}\): 20423; found: 20657; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 821 (5.88), 596 (4.88), 488 (6.06), 472 (6.07).

S2.10  c-P13

c-P13 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (1.9 mg, 0.2%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 9.93 (d, \(J = 0.45\) Hz, 52H), 9.00 (d, \(J = 0.45\) Hz, 52H), 8.33 (s, 52H), 8.04 (s, 52H), 1.62–0.82 (m, 2028H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{1404}\)H\(_{2210}\)N\(_{52}\)Si\(_{52}\)Zn\(_{13}\): 22125; found: 22530; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 821 (5.75), 595 (4.83), 490 (5.91), 472 (5.93).

S2.11  c-P16

c-P16 was isolated as a by-product in the synthesis of c-P6-T6 (from 0.8 g \{H,H\}-P1) as a brown solid (2.4 mg, 0.3%). \(^1\)H (400 MHz, CDCl\(_3\)) \(\delta\) ppm: 10.00 (d, \(J = 4.4\) Hz, 64H), 9.07 (d, \(J = 4.4\) Hz, 64H), 8.39 (s, 64H), 8.08 (s, 32H), 1.60–0.86 (m, 2496H); MS (MALDI-TOF) \(m/z\) calcld. \(M^+\) for C\(_{1728}\)H\(_{2720}\)N\(_{64}\)Si\(_{64}\)Zn\(_{16}\): 27230; found: 27686; UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) [nm] (log \(\epsilon\) [M\(^{-1}\) cm\(^{-1}\)]): 829 (5.89), 594 (4.97), 491 (6.03), 473 (6.05).
**S2.12 GPC retention times of THS porphyrin oligomers**

![Graph showing GPC retention times of THS porphyrin oligomers](image)

**Figure S8:** Analytical GPC retention times for THS porphyrin oligomers. Using two JIAGEL-H columns in series (3H-A then 4H-A), with THF:1% pyridine eluent and a 1 mL min\(^{-1}\) flow rate. The lines show linear regression fits: \(RT = m \cdot N + c\) where \(RT\) is retention time and \(N\) is oligomer length. For cyclic oligomers, \(m = -0.373\) min and \(c = 34.54\) min. For linear oligomers, \(m = -0.625\) min and \(c = 34.37\) min. For both fits, \(R^2 = 0.989\).

**S3 Photophysical measurements**

Nanoring samples were prepared at a concentration of \(\sim 1 \mu\text{M}\) in toluene + 1% pyridine (the latter to suppress aggregation). Fluorescence quantum yields (\(\Phi_F\)) were measured relative to that of l-P6, using the technique reported previously, with excitation at 500 nm.\(^{S18,S19}\) Excited state lifetimes (\(\tau\)) were measured by time-correlated single-photon counting (TCSPC) spectroscopy, and the radiative rate (\(k_R\)) was calculated.

\[
\tau = \frac{1}{k_{\text{tot}}} \tag{S2}
\]

\[
k_{\text{tot}} = k_R + k_{NR} \tag{S3}
\]

\[
\Phi = \frac{k_R}{k_R + k_{NR}} \tag{S4}
\]

\[
k_R = \Phi k_{\text{tot}} \tag{S5}
\]

![UV-Vis spectra of nanorings in toluene/1% pyridine](image)

**Figure S9:** UV-Vis spectra of nanorings in toluene/1% pyridine.
**Figure S10:** Normalized photoluminescence spectra of porphyrin nanorings, $\lambda_{ex}$ 500 nm, in toluene/1% pyridine.

**Figure S11:** (a) Radiative rates; (b) quantum yields and (c) energy of maximum intensity peak in PL spectra, for c-P5 to c-P16, $\lambda_{ex}$ = 500 nm, in toluene/1% pyridine. Lines connect measurements from the same experimental replicate. The PL maxima are calibrated based on measurements of I-P6, for which PL$_{max}$ is taken as 1.47 eV.

### S3.1 Statistical analysis

We compare two linear models in their ability to describe the experimental data for c-P5 to c-P9, inclusive.$^{520}$

Model A, $Y \sim N$, states that $Y$ (radiative rate, PL$_{max}$, or quantum yield) only depends on oligomer length ($N$).

In model B, $Y \sim N + O$, $Y$ also depends on whether the oligomer is odd ($O = 1$) or even ($O = -1$).

Model A: \[ Y \sim N \]

Model B: \[ Y \sim N + O \]
The R package (v. 3.2.1)\textsuperscript{S21} was used to compare the fits of the model. A linear model was employed, assuming Gaussian distribution of errors in measurements. The data from all four runs was analyzed together. The AIC (Akaike information criterion) statistic was used to evaluate the best model. Essentially, AIC tests (and compares) the suitability of models. A lower AIC score (hence a negative $\Delta$AIC, where $\Delta$AIC = AIC\textsubscript{model B} - AIC\textsubscript{model A}) corresponds to a better model. The AIC score is increased by the presence of additional parameters, and by a poor fit to the data.

The AIC revealed that model B (including odd-even effects) fit the data better (Table S4) for nanorings from \textit{c-P5} to \textit{c-P9}. When the whole dataset was fit (i.e. \textit{c-P5} to \textit{c-P16}), model B was no better than model A for both radiative rates and quantum yields.

Table S4: Comparison of calculated $\Delta$AIC (defined as $\Delta$AIC = AIC\textsubscript{model B} - AIC\textsubscript{model A}) for different experimental measurements ($Y$).

| $Y$         | $\Delta$AIC for $5 \leq N \leq 16$ | $\Delta$AIC for $5 \leq N \leq 9$ |
|-------------|----------------------------------|----------------------------------|
| Radiative rates | 2                                | -16                               |
| Quantum yield ($\Phi_F$) | 1                                | -17                               |
| PL\textsubscript{max} | -12                              | -15                               |

The difference between models A and B is clearly illustrated by plots of the fits to all three experimental datasets (Figures S12 to S14).

In conclusion, a model including odd-even behaviour is better able to describe the experimental photophysical data than a model without, but only for nanorings smaller than \textit{c-P10}.

\[ RR = 0.02092 \cdot N + 0.03992 \cdot \text{odd} - 0.10627 \]

Figure S12: Comparison of fit (red line and open circles) and data (filled black circles) for radiative rates of \textit{c-P5} to \textit{c-P9}. (a) model A, which depends only on \textit{N}; (b) model B, which depends on \textit{N} and whether the ring is odd or even. In model B, RR = 0.02092 \cdot \textit{N} + 0.03992 \cdot \text{odd} - 0.10627.
Figure S13: Comparison of fit (red line and open circles) and data (filled black circles) for QY of c-P5 to c-P9. (a) model A, which depends only on $N$; (b) model B, which depends on $N$ and whether the ring is odd or even. In model B, $\Phi_F = 0.1388 \cdot N + 0.2686 \cdot \text{odd} - 0.7659$.

Figure S14: Comparison of fit (red line and open circles) and data (filled black circles) for $\text{PL}_{\text{max}}$ of c-P5 to c-P9. (a) model A, which depends only on $N$; (b) model B, which depends on $N$ and whether the ring is odd or even. In model B, $\text{PL}_{\text{max}} = 0.006945 \cdot N + 0.010057 \cdot \text{odd} + 1.338092$. 

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 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-P5 5n**

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**S20**

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C 3.49133110091 0.00000000000 0.000000000000 0.000000000000 4.507960562295 0.000000000000
C -4.911957240195 0.00000000000 0.000000000000 0.000000000000 -4.507960562295 0.000000000000
C -6.128681699253 0.00000000000 0.000000000000 0.000000000000 -7.193289518343 0.000000000000
C 4.911957240195 0.00000000000 0.000000000000 0.000000000000 7.193289518343 0.000000000000
C 6.128681699253 0.00000000000 0.000000000000 0.000000000000 7.193289518343 0.000000000000
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