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The Fingerprint of Aromaticity and Molecular Topology on the Photophysical Properties of Octaphyrins

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Abstract

Expanded porphyrins are currently recognized as the ideal test bed to explore the correlation between molecular properties and (anti)aromaticity since they can adopt different $\pi$-conjugation topologies and change easily the number of $\pi$-electrons along the conjugation pathway. From recent studies, aromaticity indeed emerges as the guiding concept to rationalize the spectroscopic features and the two-photon absorption cross-sections in expanded porphyrins. However, from the theoretical point of view, the complex structure-property relationship between aromaticity, $\pi$-conjugation topology and photophysical properties is not fully understood yet. To unravel such structure-property relationships, we focused on octaphyrin(1.1.1.1.1.1.1.1) macrocycles since they are flexible enough to provide twisted-Hückel, Möbius and Hückel untwisted topologies with distinct aromaticity character. In this work, the (anti)aromaticity of the different states was first quantified using different aromaticity criteria. Second, the fingerprints of aromaticity on the UV/vis were elucidated. Importantly, we found that the absorption spectra of certain antiaromatic Hückel structures are characterized by more intense absorption bands than its aromatic homologues, contrary to the general statement that antiaromatic expanded porphyrins exhibit significantly attenuated absorption bands as compared to aromatic ones. Finally, the role of aromaticity and $\pi$-conjugation topology on linear and nonlinear optical properties was scrutinized and our results pinpoint the importance of molecular topology and symmetry on the first and second hyperpolarizability. Overall, we demonstrate that expanded porphyrins upon topology interconversions can act as efficient nonlinear optical switches.
Introduction

Molecular switches are based on molecules able to interconvert between two or more stable states in response to external stimuli. These external stimuli correspond to a change in pH, redox reactions, light or metal complexation, among others. Owing to their tunable properties, molecular switches can be employed in a broad field of applications ranging from catalysis and imaging technologies to molecular electronics and single-molecule sensors. In the field of nonlinear optics, materials with commutable optical properties are sought for optoelectronic applications, including molecular-scale memory devices with multiple storage and non-destructive reading capacity. These switches are called optical switches and the variation of optical properties can involve the linear part (absorption) or the nonlinear optical properties (NLO), such as second harmonic generation (SHG), two-photon absorption (TPA) and third-harmonic generation (THG).

A large variety of molecular building blocks can be used as molecular switches, ranging from organometallics, polymers or highly conjugated π-systems. Among conjugated π-systems, expanded porphyrins have recently emerged as a promising platform to develop molecular switches due to their exceptional photophysical properties and versatile topology and aromaticity. Expanded porphyrins are the larger homologues of porphyrins, consisting of heterocyclic five-membered rings connected either directly or by bridging atoms in such a way that the internal ring pathway contains a minimum of 17 atoms. An appealing feature of expanded porphyrins is their ability to switch between different π-conjugation topologies (Möbius, Hückel and twisted-Hückel) under different external stimuli, such as solvent, temperature, (de)protonation and redox reactions as well as metalation. Those topological switches involve a reversal of the macrocyclic aromaticity and are coupled to dramatic variations of optoelectronic and photophysical properties. Even more recently, we have demonstrated that conductance switching in molecular junctions based on expanded porphyrins is triggered by aromaticity and topology changes.
Strong structure-property relationships between aromaticity, topology and number of π electrons are found in expanded porphyrins.\textsuperscript{23,24} The macrocyclic aromaticity is indeed closely determined by the molecular topology and the number of π-electrons in the annulene-type conjugation pathway.\textsuperscript{25} In macrocycles with Hückel and twisted-Hückel topologies, Hückel rule for aromaticity applies and therefore those macrocycles containing \([4n+2]\) π-electrons are expected to be aromatic. By contrast, \([4n]\) π-electron systems lying in a single-sided Möbius band follows the Möbius aromaticity rule.\textsuperscript{26–29} As a result, Möbius topologies with \([4n]\) π-electrons display aromaticity, while \([4n+2]\) π-electron Möbius systems are antiaromatic. Besides Hückel and Möbius aromaticity rules, expanded porphyrins were employed recently to verify experimentally Baird’s aromaticity rule,\textsuperscript{30} which states that the aromaticity of singlet ground state is reversed upon excitation to the first triplet excited state.\textsuperscript{31–38} As such, expanded porphyrins are currently recognized as the ideal test bed to explore the correlation between molecular properties and (anti)aromaticity.\textsuperscript{17}

Regarding the NLO properties, aromaticity was shown to be a guiding concept for the two-photon absorption (TPA) cross-sections in expanded porphyrins.\textsuperscript{39} The TPA cross-section characterizes the capacity for simultaneous absorption of two photons and corresponds to a third-order NLO process. At present, there is a strong demand for efficient TPA dyes for biomedical and technological applications.\textsuperscript{40} Appealingly, expanded porphyrins exhibit spectacularly high two-photon cross sections as compared to the parent porphyrin.\textsuperscript{41} Through extensive research, aromatic expanded porphyrins were shown to display TPA cross-sections larger than the antiaromatic counterparts.\textsuperscript{15,42,43} Due to the dependence of the NLO properties on aromaticity, it was recently demonstrated that Hückel-to-Möbius topological switches behave as efficient molecular optical switches.\textsuperscript{44,45} The efficiency of those novel switches is linked to high NLO contrasts between Hückel and Möbius structures.\textsuperscript{10} Importantly, the NLO contrasts of expanded porphyrins can be modulated by varying the nature and the
number of meso-substituents. More specifically, efficient NLO switches could be designed from push-pull hexaphyrins with strong electron-withdrawing and electron-releasing groups located on opposite sides of the skeleton ring.

Despite the computational and experimental studies reported on NLO properties in expanded porphyrins, the complex structure-property relationship between aromaticity, π-conjugation topology, and NLO properties is not fully understood yet. Our recent study on Hückel untwisted porphyrinoids pointed out that the influence of aromaticity on the first and second hyperpolarizabilities (β and γ, respectively) is significantly more complex than for the experimental TPA-cross sections. On one side, these NLO quantities are frequency-dependent and their magnitude is determined by the interplay between asymmetry, planarity and aromaticity. On the other side, aromaticity is not an observable and its evaluation is challenging. Due to the absence of a universal descriptor, aromaticity should be quantified using a set of descriptors based on different criteria (energetic, magnetic, structural, reactivity, and electronic). As a consequence, it is challenging to assess which factor controls the NLO properties of expanded porphyrins.

In order to expand our research towards the design of optical switches from expanded porphyrins, we examined here the structure-property relationships between topology, aromaticity and photophysical properties in octaphyrin(1.1.1.1.1.1.1) macrocycles. These specific expanded porphyrins were selected based on their ability to provide Hückel aromatic, Hückel antiaromatic and Möbius aromatic structures upon (de)protonation and redox reactions. Based on previous studies on the conformational preferences of octaphyrin macrocycles, five octaphyrins with varying number of π-electrons and distinct molecular topology were selected (Figure 1).
In the neutral state, meso-octakis(pentafluorophenyl)octaphyrin with 36–π electrons exhibits a nonaromatic twisted- Huckel, also known as figure-eight conformation (36F). Upon deprotonation, the figure-eight structure unfolds in a planar Huckel topology (36H2−), whereas protonation triggers a topological switch towards a Möbius topology (36M2+). The reduction of the neutral macrocycle induces the inversion of two pyrrole rings while keeping a twisted-Hückel topology (38F). Finally, the combination of reduction and protonation results in a Hückel untwisted topology (38H2+). Since the number of π-electrons and topology is different, the selected porphyrinoids provide an optimum test for investigating the correlation between (anti)aromaticity and nonlinear optical properties as well as spectroscopic features.

Figure 1. The lowest-energy conformations of octaphyrins upon reduction and (de)protonation reactions. Aromatic octaphyrins are colored in red, while green and grey are indicative for antiaromatic and nonaromatic systems, respectively.
In order to disentangle the effect of the topology and the charge of the macrocycle, additional conformations were considered, which are the neutral equivalents of protonated and deprotonated [36] and [38]octaphyrins (Figure 2).

Our main goal is to establish the role of aromaticity in determining both the photophysical and NLO properties of octaphyrin macrocycles. First, the aromaticity of the selected octaphyrins has been quantified using a large set of aromaticity descriptors based on magnetic, structural and reactivity criteria. Secondly, we investigate the fingerprints of (anti)aromaticity on the absorption spectra. In this regard, the absorption spectra of expanded porphyrins have been shown to be highly dependent on their aromaticity and, indeed, spectroscopical features are widely used to assess indirectly the (anti)aromaticity of porphyrinoids experimentally. As such, it is important to assess if the defining photophysical features for determining (anti)aromaticity in Hückel untwisted porphyrinoids still hold for flexible macrocycles, such as octaphyrins. Finally, the complex structure-property relationship between aromaticity and several linear and nonlinear optical properties has been established for this set of macrocycles.

**Computational Details**

All the calculations were performed using the Gaussian 09.D01 software package with the M06, B3LYP and CAM-B3LYP functionals together with the split-valence basis sets [6-31G(d,p) and 6-311+G(d,p)]. Geometry optimization and frequency calculations were carried out at the M06/6-31G(d,p) level of theory. As shown by previous benchmarks
towards experiment, the M06 functional provides realistic geometries and conformational energies for octaphyrins in good agreement with the experimental data. All the structures are minima on the potential energy surface with no imaginary frequencies. The harmonic oscillator model of aromaticity (HOMA) was computed as structural descriptor of the aromaticity:

\[ HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} (R_{opt} - R_i)^2 \]

where \( \alpha \) denotes an empirical constant fixed for each type of bond (with the dimension of Å\(^{-2} \)) and \( n \) corresponds to the number of bonds taken into account in the summation. \( R_i \) is the running bond length along the annulene-type conjugation pathway. Nonaromatic systems present ideally HOMA values close to zero, whereas HOMA = 1 for fully aromatic ones with all bonds equal to the optimal value \( R_{opt} \). For C-C bonds, \( \alpha = 257.7 \) and \( R_{opt} = 1.388 \) Å, whereas \( \alpha = 93.52 \) and \( R_{opt} = 1.334 \) Å for C-N bonds.

Magnetic susceptibilities exaltation (\( \Lambda \)) and relative hardness (\( \Delta \eta \)) of unsubstituted species were computed using the isomerization scheme (ISE) (Figure 3). The magnetic susceptibilities were evaluated using the CGST method with both B3LYP and CAM-B3LYP functionals in combination with the 6-31+G(d,p) basis set. Even though the susceptibility exaltation evolves significantly with the amount of exact exchange (Table S1), the \( \Lambda \) values computed at both levels of theory are correlated linearly to each other (Figure S1). HOMO and LUMO energies of the methyl and methylene derivatives were employed to evaluate the relative hardness (\( \Delta \eta \)) in the frame of the isomerization scheme.

Nucleus-independent chemical shift (NICS) values were calculated at the geometrical center of the heavy atoms of the macrocycle and at 1 Å above and below the ring center, together with its out-of-plane tensor component, using the GIAO method with CAM-
Figure 3. Reaction used to evaluate several aromaticity descriptors in octaphyrins. \( \Delta \eta \) are given in kcal mol\(^{-1}\) and \( \Lambda \) in ppm cgs.

B3LYP and B3LYP functionals combined with the 6-311+G(d,p) basis set. Similar to \( \Lambda \), an excellent linear correlation is found for the NICS\(_{zz}\)(1) values computed at both levels of theory (Figure S1). For nonplanar structures, the reference plane was found by least-square fitting considering all the coordinates of the heavy atoms of the macrocycles.\(^{71}\) However, for twisted-Hückel topologies, the molecule was oriented in such a way that the 2D projection exhibits the largest macrocyclic area, leading to the topology of a ring and the external magnetic field was applied to such projection (Figure 4). In addition, we computed the anisotropy of the induced current density (AICD) plots to get an insight of the induced delocalization of \( \pi \)-electrons.\(^{72,73}\) In AICD plots, the current density vectors are plotted into the AICD isosurfaces to distinguish between anisotropies caused by diatropic and paratropic ring currents. For AICD calculations, the external magnetic field is applied perpendicular to the least-square molecular plane.

Figure 4. Orientation of the twisted-Hückel and Hückel structures employed in the calculation of the NICS-based indices. The magnetic field is oriented along the z axis.
As additional geometrical descriptors, the average dihedral angle between neighboring pyrrole rings ($\Phi_p$) were evaluated as a measure of the torsional ring strain,\textsuperscript{23} together with the $\pi$-conjugation index ($\Pi$) quantifying the extent of the effective overlap of neighboring p orbitals. $\Pi$ equals 1 for a completely planar system, it is positive for any Hückel (double-sided) conformation and negative for any Möbius (single-sided) surface. Normally, macrocyclic aromaticity is associated with porphyrinoids having $\Pi$ values higher than 0.3.\textsuperscript{19}

As the molecular orbitals H, H-1 and L, L+1 are quasi-degenerate orbitals in aromatic systems, we investigated whether our systems required multireference methods. Two methods were applied to assess whether some of our systems exhibit diradical character. First, the spin projected diradical character was computed, as defined by Yamaguchi ($y^{SP}_i$).\textsuperscript{74} This diradical character is based on the unrestricted occupation number of natural frontier orbitals ($n^u_{HONO-i}/n^u_{LUNO+i}$) and the overlap between the corresponding natural orbitals ($S^u_i$). The spin projected diradical character is a measure for the instability of the chemical bond and can vary between 0 (closed-shell) and 1 (pure diradical).\textsuperscript{75,76} As none of the macrocycles is characterized by a value larger than 0.1 (Table S2), those systems present hardly any diradical character and single-reference methods can be used to evaluate the photophysical and NLO properties of octaphyrins

\begin{equation}
S^SP_i = \frac{n^u_{HONO-i} - n^u_{LUNO+i}}{2}
\end{equation}

\begin{equation}
y^{SP}_i = 2 - \frac{(n^u_{HONO-i})^2}{1 + (S^u_i)^2}
\end{equation}

\begin{equation}
y^{SP}_i = \frac{(n^u_{LUNO+i})^2}{1 + (S^u_i)^2}
\end{equation}

We also used an alternative way to check the diradical character of the systems by computing
the relative energy of the triplet and the singlet states at the unrestricted CAM-B3LYP/6-311+G(d,p) level of theory. In the case of a diradical system with interacting unpaired electrons, the energy of the triplet state is expected to be lower than the open-shell singlet state in the absence of dynamic spin polarization.\textsuperscript{77–79} In all the investigated octaphyrins, the singlet state yields the lower energy (Table S3).

Time-dependent DFT (TD-DFT) calculations were carried out at the CAM-B3LYP/6-311+G(d,p) level of theory to evaluate excitation energies and corresponding oscillator strengths (\(f_{osc}\)) of main low-energy electronic transitions.\textsuperscript{80} For time-dependent DFT calculations, thirty excited states have been calculated. CAM-B3LYP was selected on the basis of several TD-DFT benchmark studies concerning excited state calculations, in particular oscillator strengths.\textsuperscript{81,82} Furthermore, we have investigated the effect of the exchange in DFT functionals on the evaluation of the oscillator strengths in octaphyrins with varying topology (Table S4). Importantly, no large discrepancies are found in terms of the shape and intensities of the most relevant absorption bands between M06-2X, CAM-B3LYP and M11. On the other side, B3LYP absorption bands are red-shifted with respect to the other functionals leading to systematically reduced oscillator strengths (Figure S8).

Polarizabilities and hyperpolarizabilities were evaluated at the coupled-perturbed Kohn-Sham (CPKS) and TD-DFT levels to obtain their static and dynamic NLO responses, respectively. Several benchmark studies assessed the reliable performance of the long-range corrected CAM-B3LYP functional in the evaluation of NLO properties of organic molecules, including expanded porphyrins.\textsuperscript{44,45,83,84} Electric dipole polarizability (\(\alpha\)), first (\(\beta\)) and second (\(\gamma\)) hyperpolarizabilities, are defined by an equation describing the change in the components of the electric dipole moment \(\Delta \mu_\zeta (\zeta=x,y,z)\), arising from the application of external electric fields \(\mathbf{F}\):
\[ \Delta \mu_\kappa = \sum_{\eta=x,y,z} \alpha_{\eta}(\omega_\sigma; \omega_1) F_\eta(\omega_1) + \frac{1}{2!} \sum_{\eta \xi = x,y,z} \beta_{\eta \xi}(\omega_\sigma; \omega_1, \omega_2) F_\eta(\omega_1) F_\xi(\omega_2) \]
\[ + \frac{1}{3!} \sum_{\eta \xi \zeta = x,y,z} \gamma_{\eta \xi \zeta}(\omega_\sigma; \omega_1, \omega_2, \omega_3) F_\eta(\omega_1) F_\xi(\omega_2) F_\zeta(\omega_3) + \ldots \] (5)

where \( F_\eta(\omega_1) \) is the amplitude of the field oscillating at pulsation \( \omega_1 \) and applied in the \( \eta \) direction and \( \omega_\sigma = \sum_i \omega_i \).

The intrinsic nature of the polarizability tensor \( \alpha_{ii} \) resides in the average polarizability \( \overline{\alpha} \) and its anisotropy \( \Delta \alpha \), defined as:

\[ \overline{\alpha} = \frac{1}{3} \sum_{i=x,y,z} \alpha_{ii} \] (6)

\[ \Delta \alpha^2 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6\alpha_{xz}^2 + 6\alpha_{yz}^2 + 6\alpha_{xy}^2 \right] \] (7)

The longitudinal component of \( \beta \) is connected to the second harmonic generation (SHG) and its electric-field induced analogue (EFISHG). EFISHG measurements provide insight in the projection of the vector part of \( \beta \) on the dipole moment vector \( \mu \):

\[ \beta_{ij}(\pm 2\omega, \omega, \omega) = \frac{1}{5} \sum_{i=x,y,z} \frac{\mu_i}{||\mu||} \sum_j (\beta_{ijj} + \beta_{jji} + \beta_{jij}) = \frac{3}{5} \sum_{i=x,y,z} \frac{\mu_i \beta_i}{||\mu||} \] (8)

where \( ||\mu|| \) denotes the norm of the dipole moment and \( \mu_i \) and \( \beta_i \) the components of the \( \mu \) vector and \( \beta \) vector part, respectively. \( \beta_{ij} \) is not defined for charged species since it depends on the dipole moment, which is undefined for charged species. In addition, we considered the \( \gamma_{ij} \) quantity because it is also related to EFISHG measurements.
\[ \gamma_{//}(-2\omega; \omega, \omega, 0) = \frac{1}{15} \sum_{i,j=x,y,z} (\gamma_{ijj} + \gamma_{ij} + \gamma_{ijji}) \] (9)

Unlike \( \beta_{//} \), Hyper Rayleigh scattering first hyperpolarizability (\( \beta_{HRS} \)) and depolarization ratio (DR) are both defined for neutral and charged systems. \( \beta_{HRS} \) is related to the orientational average of the first hyperpolarizability over all molecular orientations. Experimentally, \( \beta_{HRS} \) denotes the second-order NLO response that can be extracted from Hyper-Rayleigh scattering, namely the intensity of the incoherent scattering at frequency \( 2\omega \) on incidence of a laser with frequency \( \omega \). DR provides insight over the geometry of the part of the molecule responsible for the NLO response.\(^{85}\)

\[ \beta_{HRS} = \sqrt{\langle \beta^2_{ZZZ} \rangle + \langle \beta^2_{ZXX} \rangle} \] (10)

\[ DR = \frac{\langle \beta^2_{ZZZ} \rangle}{\langle \beta^2_{ZXX} \rangle} \] (11)

where \( \langle \beta^2_{ZZZ} \rangle \) and \( \langle \beta^2_{ZXX} \rangle \) correspond to the orientational averages of the \( \beta \).

**Results and Discussion**

**Structure-aromaticity relationship in octaphyrins**

The three-dimensional structures of the lowest-energy conformations of unsubstituted octaphyrins are shown in Figure 5. The labelling of each structure consists of the oxidation state, followed by a symbol representing the most stable topology together with the charge of the macrocycle. In this regard, it is noteworthy that the number of \( \pi \)-electrons along the conjugation pathway is referred as the oxidation state of the macrocycle. As such, \( 38H^{2+} \) stands for a diprotonated octaphyrin with 38 \( \pi \)-electrons displaying a Hückel topology.
Except $36\text{H}^2-$, most of the macrocycles do not present high molecular symmetry. For instance, the point group of $36\text{M}^2+$ and $38\text{H}^2+$ equals $C_1$ while $36\text{F}$ and $38\text{F}$ exhibit a $C_2$ symmetry. By contrast, the planar $36\text{H}^2-$ is characterized by a $D_{2h}$ symmetry and is ring-strain free ($\Phi_p=0$, $\Pi=0.99$). In comparison to neutral species, diprotonated octaphyrins present enhanced torsional ring strain and reduced $\Pi$ values, what is related to the reduced planarity caused by the introduction of the half-twist into the Möbius structure and the inversion of five pyrrole rings in the Hückel structure.

![Figure 5. 3D structures of the lowest-energy conformations of the main unsubstituted octaphyrins with varying topology, oxidation state and protonation state. Red five-membered rings are linked to aromatic structures, whereas green and grey ones to antiaromatic and nonaromatic configurations, respectively.](image)

To describe quantitatively the aromaticity of these systems, we have used aromaticity descriptors based on different criteria, namely structural, reactivity and magnetic indices. The aromaticity indices are collected in Table 1. The majority of our aromaticity descriptors provide a straightforward distinction between aromatic and antiaromatic octaphyrins. On the one hand, $36\text{M}^2+$, $38\text{H}^2+$ and $38\text{F}$ are characterized by positive relative hardness $\Delta\eta$, negative diamagnetic susceptibility exaltation $\Lambda$ and negative NICS indices, which are indicative for aromaticity. On the other hand, $36\text{H}^2-$ exhibits negative $\Delta\eta$ and highly positive $\Lambda$ and NICS-based indices, thus demonstrating the paratropicity of this system. As shown
by the reduced values of $\Lambda$, $\Delta \eta$ and NICS$_{zz}(1)$, 36F can be classified as nonaromatic. Such structure-aromaticity relationships are in agreement with the qualitative predictions of the annulene model and different spectroscopical techniques.$^{46,86}$

It is important to note that the structural index HOMA should be applied with caution to assess the aromaticity of expanded porphyrins.$^{23,25,27,87}$ Although aromatic macrocycles are characterized by larger HOMA values than 36F and 36H$^{2-}$, the differences between aromatic and antiaromatic counterparts are rather small. According to the magnitude of the energy gap $\Delta E_{HL}$, we observed a straightforward distinction between aromatic and antiaromatic systems: $36M^{2+} \sim 38F > 36F > 38H^{2+} >> 36H^{2-}$. As observed previously,$^{47}$ the energy gap is larger in aromatic species. Nevertheless, as indicated by the previous sequence, the difference between nonaromatic and aromatic is less clear-cut.

Table 1. Reactivity, magnetic, structural and electronic properties of unsubstituted octaphyrins$^a$

<table>
<thead>
<tr>
<th>system</th>
<th>$\Delta \eta$</th>
<th>$\Lambda$</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
<th>NICS$_{zz}(1)$</th>
<th>HOMA</th>
<th>$\Pi^b$</th>
<th>$\Phi_p^c$</th>
<th>$\Delta E_{HL}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>36F</td>
<td>-3.8</td>
<td>22</td>
<td>-5.4$^e$</td>
<td>-5.5$^e$</td>
<td>1.3</td>
<td>0.75</td>
<td>0.78</td>
<td>15.0</td>
<td>2.99</td>
</tr>
<tr>
<td>38F</td>
<td>4.9</td>
<td>-158</td>
<td>-14.0</td>
<td>-11.8</td>
<td>-28.3</td>
<td>0.87</td>
<td>0.81</td>
<td>14.9</td>
<td>3.05</td>
</tr>
<tr>
<td>36M$^{2+}$</td>
<td>10.8</td>
<td>-559</td>
<td>-10.4</td>
<td>-10.0</td>
<td>-26.0</td>
<td>0.80</td>
<td>-0.39</td>
<td>33.8</td>
<td>3.06</td>
</tr>
<tr>
<td>38H$^{2+}$</td>
<td>9.6</td>
<td>-1081</td>
<td>-12.4</td>
<td>-11.8</td>
<td>-32.2</td>
<td>0.84</td>
<td>0.56</td>
<td>25.1</td>
<td>2.92</td>
</tr>
<tr>
<td>36H$^{2-}$</td>
<td>-8.5</td>
<td>1024</td>
<td>18.0</td>
<td>17.2</td>
<td>54.1</td>
<td>0.69</td>
<td>0.99</td>
<td>0.0</td>
<td>2.74</td>
</tr>
</tbody>
</table>

[a] $\Delta \eta$ given in kcal mol$^{-1}$, $\Lambda$ in ppm cgs, NICS indices in ppm and they were computed with the B3LYP functional. [b] $\Pi$ is unitless. [c] The unit of $\Phi_p$ is degrees. [d] HOMO-LUMO energy difference (eV) calculated at CAM-B3LYP/6-311+G(d,p) level of theory. [e] The ”probe atoms” in the twisted-Hückel structures are located near the stacked pyrrole rings reflecting its local diatropicity.

To acquire more insight on the aromaticity of these unsubstituted octaphyrins, anisotropy of the induced current density (AICD) plots were computed, together with magnetic field-induced current densities, obtained for external magnetic field perpendicular to the $\pi$-system (see Computational Details).$^{72,73}$ The direction of the current density vector enables to distinguish between diatropic and paratropic ring currents. In Figure 6, 36M$^{2+}$ and 38H$^{2+}$ clearly exhibit clockwise density current vectors, indicative for aromaticity. By contrast, it
is difficult to assess whether the nonaromatic \( {36F} \) present diatropic current or paratropic ring currents. In addition, the AICD plot of \( {38F} \) is more similar to that of \( {36F} \) in shape and pattern than to \( {36M}^{2+} \) and \( {38H}^{2+} \), but the direction of the ring currents is slightly clockwise (Figure S5). With its counterclockwise induced current density, \( {36H}^{-2} \) is clearly antiaromatic and displays a strong paratropic induced ring current.

![AICD plots of octaphyrins.](image)

**Figure 6.** AICD plots of octaphyrins. The large arrow denotes the direction of the induced ring current: clockwise for diatropic ring currents and anticlockwise for paratropic ring currents (isosurface value of 0.05 a.u.).

**Influence of aromaticity on the photophysical properties of octaphyrins**

In agreement with experimental studies,\(^{46,57}\) aromatic and antiaromatic octaphyrins are characterized by very distinct photophysical properties, resulting from the different arrangement of the molecular frontier orbitals in aromatic and anti/nonaromatic systems (Figure 7). In aromatic systems (\( {36M}^{2+}, {38F}, {38H}^{2+} \)), H/H-1 and L/L+1 are quasi-degenerated two by two. By contrast, antiaromatic and nonaromatic systems are characterized by H-1 and H (L and L+1) with distinct energy, whereas H-1 and H-2 (L+1 and L+2) present similar energy. When going from aromatic to antiaromatic, H-1 and L+1 evolve from quasi-degenerated in energy with H and L orbitals,\(^{42}\) to become close in energy with H-2 and L+2 orbitals,
respectively.\textsuperscript{88} Regarding the arrangement of its MOs, the nonaromatic 36F corresponds to an intermediate situation between aromatic and antiaromatic systems. It is worth noting that the orbital energies shift to lower and lower energies when going from anionic to cationic macrocycles. In order to assess whether our systems can be treated as single reference systems, we have investigated the diradical character of the macrocycles using the spin projected diradical character (see Tables S2 and S3).\textsuperscript{89} Importantly, the selected macrocycles present hardly any diradical character and, accordingly, single-reference methods can be used to evaluate the photophysical and NLO properties of octaphyrins.

![Figure 7](image_url)

\textbf{Figure 7.} Molecular orbital diagrams of unsubstituted octaphyrins computed at the CAM-B3LYP/6-311+G(d,p) level of theory.

Figure 8 exhibits the absorption spectrum of 36H\textsuperscript{2−}, 36M\textsuperscript{2+}, 38H\textsuperscript{2+}, 38F and 36F evaluated at the CAM-B3LYP/6-311G+(d,p) level of theory. According to the magnitude of the molar extinction coefficient of the most intense absorption band, we observe the following sequence: 36H\textsuperscript{2−} \textasciitilde 38H\textsuperscript{2+} \textasciitilde 36M\textsuperscript{2+} \textasciitilde 38F \textasciitilde 36F. Surprisingly, the absorption spectrum of the highly antiaromatic 36H\textsuperscript{2−} is characterized by more intense absorption bands than its aromatic homologues. Similarly, Higashino et al observed very recently intense B bands in the spectrum of an antiaromatic [28]hexaphyrin.\textsuperscript{90} This observation contradicts the general statement that antiaromatic expanded porphyrins exhibit significantly attenuated absorption bands as compared to aromatic ones\textsuperscript{17} and further analysis is needed to unveil the factors
leading to intense B-like bands in certain antiaromatic expanded porphyrins (vide infra).

![Figure 8. Calculated UV/vis spectra for unsubstituted octaphyrins. The spectra were simulated with a full width at half maximum (FWHM) of 0.333 eV. The absorption peaks of aromatic and anti/nonaromatic systems are represented by full/dashed line.](image)

Excluding $36H^2^-$, large differences in the UV/vis spectra are found for aromatic and nonaromatic octaphyrins. Whereas intense peaks are found for aromatic octaphyrins, much weaker absorption bands are observed in the nonaromatic $36F$. In addition, the intensity of the main absorption band seems to be correlated with the aromatic character. Thus, those macrocycles with higher aromatic character according to $\Lambda$ exhibit more intense B bands (Figure 8). Beside the intensity, the absorption spectrum of antiaromatic and nonaromatic octaphyrins is blue-shifted and the main absorption bands correspond to electronic transitions involving different molecular orbitals as compared to aromatic species.

As highlighted in Figure S9, the UV/vis spectrum of aromatic $36M^{2+}$, $38H^{2+}$ and $38F$ consists of three type of bands: intense B bands, less intense absorption bands associated to high-energy transitions and very weak Q bands. Moreover, the spectrum of $36M^{2+}$ and $38H^{2+}$ presents split B and Q bands, which is indicative for aromaticity. By contrast, the absorption spectrum of $38F$ exhibits unsplit B and Q bands.
Table 2. Properties of the most relevant electronic transitions of with varying total charge and oxidation state.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Bands</th>
<th>36H\textsuperscript{2−}</th>
<th>36F</th>
<th>36M\textsuperscript{2+}</th>
<th>38F</th>
<th>38H\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q\textsubscript{1}</td>
<td>1451\textsuperscript{b} (0.000\textsuperscript{c})</td>
<td>1306\textsuperscript{b} (0.001\textsuperscript{c})</td>
<td>1092\textsuperscript{b} (0.008\textsuperscript{c})</td>
<td>1213.1\textsuperscript{b} (0.001\textsuperscript{c})</td>
<td>1223\textsuperscript{b} (0.002\textsuperscript{c})</td>
</tr>
<tr>
<td>H→L (92%)</td>
<td>H→L (96%)</td>
<td>H→L+1 (45%)</td>
<td>H→L+1 (47%)</td>
<td>H→L+1 (46%)</td>
<td>H→L+1 (41%)</td>
</tr>
<tr>
<td>Q\textsubscript{2}</td>
<td></td>
<td>777 (0.052\textsuperscript{c})</td>
<td>1087 (0.004\textsuperscript{c})</td>
<td>887 (0.007\textsuperscript{c})</td>
<td>1223\textsuperscript{b} (0.002\textsuperscript{c})</td>
</tr>
<tr>
<td></td>
<td>H-1→L (70%)</td>
<td>H→L+1 (54%)</td>
<td>H→L+1 (43%)</td>
<td>H→L+1 (43%)</td>
<td>H→L+1 (39%)</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td></td>
<td>517\textsuperscript{b} (2.205\textsuperscript{c})</td>
<td>488\textsuperscript{b} (1.041\textsuperscript{c})</td>
<td>572\textsuperscript{b} (1.421\textsuperscript{c})</td>
<td>572\textsuperscript{b} (1.376\textsuperscript{c})</td>
</tr>
<tr>
<td></td>
<td>H→L+2 (82%)</td>
<td>H→L+2 (75%)</td>
<td>H→L+1 (43%)</td>
<td>H→L+1 (46%)</td>
<td>H→L+1 (43%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H→L+1 (38%)</td>
<td>H→L+1 (45%)</td>
<td>H→L+1 (39%)</td>
<td>H→L+1 (39%)</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td></td>
<td>537\textsuperscript{b} (2.152\textsuperscript{c})</td>
<td>546\textsuperscript{b} (2.209\textsuperscript{c})</td>
<td>572\textsuperscript{b} (1.376\textsuperscript{c})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H→L+1 (53%)</td>
<td>H→L+3 (32%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H→L (22%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High energy</td>
<td>489\textsuperscript{b} (0.814\textsuperscript{c})</td>
<td>353\textsuperscript{b} (0.491\textsuperscript{c})</td>
<td>379\textsuperscript{b} (0.209\textsuperscript{c})</td>
<td>363\textsuperscript{b} (0.767\textsuperscript{c})</td>
<td>488\textsuperscript{b} (0.418\textsuperscript{c})</td>
</tr>
<tr>
<td></td>
<td>H-1→L (94%)</td>
<td>H-2→L+2 (58.3 %)</td>
<td>H-2→L+1 (20%)</td>
<td>H-2→L+1 (42%)</td>
<td>H→L+2 (37%)</td>
</tr>
<tr>
<td></td>
<td>H-4→L (15.6%)</td>
<td>H-2→L+2 (17%)</td>
<td>H-3→L (25%)</td>
<td>H-1→L+2 (24%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-5→L (18%)</td>
<td>H-3→L+1 (12%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Computed at the TD-DFT CAM-B3LYP level of theory using the IEFPCM scheme (solvent = CH\textsubscript{2}Cl\textsubscript{2}) on ground state geometries optimized in vacuum. \textsuperscript{b} Absorption wavelength (λ in nm). \textsuperscript{c} Oscillator strength (f\textsubscript{osc}).

In aromatic systems, the most intense absorption bands, also known as Soret or B bands (f\textsubscript{osc} > 2.0), result from the electronic transitions involving H, H-1, L and L+1 molecular orbitals (Table 2 and S5-S9). Even though 36M\textsuperscript{2+}, 38H\textsuperscript{2+} and 38F are all aromatic systems, their high-energy transitions have distinct contributions in their absorption spectra and different intensities. For instance, absorption bands associated to the high-energy transitions in 36M\textsuperscript{2+} and 38H\textsuperscript{2+} present significantly lower intensity and oscillator strengths (f\textsubscript{osc} < 0.5) than in 38F (f\textsubscript{osc} = 0.8). As compared to aromatic homologues, the UV/vis spectrum of nonaromatic 36F exhibit significantly weaker absorption bands (Figure 8 and Table S8). In 36F, the main absorption bands are associated to high-energy transitions H→L+2 (f\textsubscript{osc}=1.04) and H-2→L+2 (f\textsubscript{osc}=0.49). Interestingly, the electronic transition involving HOMO and LUMO in 36F is extremely weak in contrast to aromatic systems.
One striking feature is that the intensity of some high-energy transitions of antiaromatic systems can exceed those of the B bands in aromatic systems. In our test set, the antiaromatic 36H$_2^-$ was found to have a more intense absorption bands than the aromatic analogues (Figure 10 and Table 2). This increased absorbance of the B-like band in 36H$_2^-$ was also observed experimentally and attributed to its high molecular symmetry. Similarly, we recently found that the intensity of the B-like band is quite significant in antiaromatic doubly oxidized and reduced congeners of the regular porphyrins with 16 $\pi$- and 20 $\pi$-electronic structures. As such, it becomes important to investigate the electronic and structural features leading to intense B-like absorption bands in certain antiaromatic expanded porphyrins. In order to unveil these factors, we have investigated the photophysical properties of different antiaromatic conformations of neutral [36]octaphyrins to avoid the influence of the macrocycle charge. More specifically, we have considered three additional conformations (36F$_b$, 36H$_a$ and 36H$_b$), which are the neutral equivalents to 38F, 36H$_2^-$ and 38H$_2^+$ (Figure 9), respectively. Taking into account that those macrocycles contain 36 $\pi$-electrons and an even number of half-twists, all are expected to be antiaromatic according to the Hückel rule. Indeed, the aromaticity descriptors confirm their antiaromaticity.

When comparing the UV/vis spectra of nonaromatic 36F to those of antiaromatic neutral [36]octaphyrins (Figure 10), we observe the following sequence according to the molar absorbance of the most intense band: 36H$_a$ ($C_{2v}$) > 36H$_b$ ($C_1$) > 36F$_b$ ($C_2$) > 36F ($C_2$). As can be inferred from Figure 9, the previous sequence is correlated to the antiaromatic charac-
ter of the systems in such a way that octaphyrins with higher antiaromatic character exhibit more intense B-like band. Despite having a similar topology and non-degenerated HOMO and LUMO orbitals, the spectra of $36\text{F}$ and $36\text{F}_b$ differ significantly in terms of intensity of the Soret-like band.

![Figure 10](image-url)

**Figure 10.** Evolution of the contribution of H-2→L transition to the Soret-like band in the UV/vis spectra of antiaromatic octaphyrins.

Regarding the molecular orbital diagram, we observe that the energy gap between HOMO-1/HOMO-2 and LUMO+1/LUMO+2 is reduced in $36\text{F}_b$ as compared with those of $36\text{F}$. This minor change in the MO distribution results in a different contribution and nature of the electronic transitions associated to the Soret band in the figure-eight structure (Figure 11). Even though the Soret band is mainly associated to H→L+2 in both twisted-Hückel topologies, the contribution is different: 75% for $36\text{F}$ and 50% for $36\text{F}_b$. Besides, the contribution of H-2→L transition to the Soret band is larger in $36\text{F}_b$: 15.4% vs 3% ($36\text{F}$).

When looking to the neutral Hückel antiaromatic macrocycles ($36\text{H}_a$ and $36\text{H}_b$), we notice that the contribution of H→L+2 transition diminishes or even vanishes, while the Soret-like band becomes significantly more intense in both untwisted systems. On the other hand, the contribution of H-2→L and H-1→L transitions increases significantly in the Soret band in $36\text{H}_b$ and $36\text{H}_a$, respectively, which might be coupled to the large increase of the intensity
of the Soret band. As such, the intensity of the Soret-like band in antiaromatic systems seems to increase with the degree of contribution of H-2/H-1→L transitions. Indeed, the highly intense Soret-like band in the deprotonated antiaromatic $36H^2-$ mainly arises from a H-2→L transitions (82.7%).

Figure 11. Evolution of the molecular orbital diagram and most important electronic transitions associated to the Soret band in antiaromatic neutral octaphyrins computed at the CAM-B3LYP/6-311+G(d,p) level of theory.

To gain more insight on the nature of the most intense electronic transitions, we applied the perimeter model. The perimeter model or free electron model (FMO) is a qualitative model used to predict whether electronic transitions between orbitals are allowed or forbidden based on the number of nodal planes in the corresponding orbitals. According to this model, a transition is allowed when the difference in the number of nodal planes between the two orbitals ($\Delta k$) is zero or one. Based on the number of nodal planes, we observe that the perimeter model works quite well for aromatic octaphyrins, where the main transitions involve H-1, H, L and L+1 molecular orbitals (Figure 12). However, this model is not valid for the nonaromatic $36F$ where high-energy transitions become important (Figure S10). Due to the large difference in number of nodal planes, the perimeter model predicts that the electronic transition between H and L+2 orbitals in $36F$ is forbidden, whereas it is
allowed by symmetry and $f_{osc}$ is large (1.04). In addition, it is remarkable that the perimeter model correctly predicts that the electronic transitions $H \rightarrow L+2$ and $H-2 \rightarrow L$ are allowed for the antiaromatic $36H^{2-}$, but also the H-L transition which is forbidden by symmetry. In conclusion, the perimeter model is fully valid for assessing the allowed and forbidden electronic transitions in aromatic octaphyrins, but is unable to rationalize the viable electronic transitions in antiaromatic nonaromatic octaphyrins.

Figure 12. Molecular orbitals together with the number of nodal planes for different orbitals of selected Hückel octaphyrins: a) aromatic $38H^{2+}$ and b) antiaromatic $36H^{2-}$. 
Polarizability and nonlinear optical properties

For molecules, the relevant optical quantities correspond to the polarizability ($\alpha$), first ($\beta$) and second hyperpolarizability ($\gamma$), associated with second- and third-order nonlinear effects, respectively. Accordingly, we computed the average polarizability and its anisotropy together with the first and second hyperpolarizability in the five unsubstituted octaphyrins (Figure 1), for which the meso-substituted homologues have been synthesized. Such quantities are collected in Tables 3-4. Besides the isolated octaphyrins, we also evaluated four additional conformations of the neutral [36]octaphyrin ($36F_b$, $36H_a$, $36H_b$, $36M$) and one [38]octaphyrin ($38H_b$) (Figure 2). These additional systems are the neutral equivalents of protonated and deprotonated octaphyrins. As such they will help to disentangle the effect of the molecular topology, the charge of the macrocycle and reduction separately on the NLO properties.

Regarding the average polarizability ($\overline{\alpha}$) and its anisotropy ($\Delta\alpha$) computed at different frequencies (Table 3), it is clear that these quantities do not evolve significantly with the incident wavelength in the selected frequency range. As can be inferred from Table 3, the following order is observed for the decrease of the static average polarizability: $38H^{2+} \geq 36H^- > 36M^{2+} > 38F > 36F$. As such, the molecular topology together with the aromaticity appears to be the key factors governing polarizability. In general, Hückel untwisted topologies are characterized by larger $\overline{\alpha}$ than Möbius singly-twisted topologies and these, in turn, larger than figure-eight structures (Figure 13). Within the same topology, aromaticity seems to be important for determining $\overline{\alpha}$, in such a way that aromatic systems are characterized by larger average polarizability in both static and dynamic regime than antiaromatic homologues with similar topology (e.g. $38F/36F$, $38H^{2+}/36H^{2-}$ and $38H_b/36H_b$). The same trends are observed for the variations of the anisotropy across octaphyrin macrocycles, but slightly larger differences in $\Delta\alpha$ are induced by aromaticity. As such, the nonaromatic $36F$ exhibits the lowest $\overline{\alpha}$ and $\Delta\alpha$ value. Regarding the charge of the macrocycle, we
observe from the comparison of the neutral to the (de)protonated analogues (e.g. $36H_a/36H^2−$, $38H_b/38H^{2+}$ and $36M/36M^{2+}$), that (de)protonation enhances the magnitude of both $\bar{\alpha}$ and $\Delta\alpha$. Similarly, solvation enhances the magnitude of average polarizability and its anisotropy, but it does not alter the trends in the gas phase (Table S10). Overall, among octaphyrin macrocycles, $\pi$-conjugation topology and aromaticity emerge as the main factors to tune the polarizability and its anisotropy, together with the charge state of the macrocycle.

Table 3. Average static polarizability $\bar{\alpha}$ and $\Delta\alpha$ (a.u.) of unsubstituted octaphyrins computed at different frequencies ($\omega$ in eV) in gas-phase.

<table>
<thead>
<tr>
<th>System</th>
<th>$\bar{\alpha}$ ($\omega=0$)</th>
<th>$\bar{\alpha}$ ($\omega=0.413$)</th>
<th>$\bar{\alpha}$ ($\omega=0.583$)</th>
<th>$\bar{\alpha}$ ($\omega=0.653$)</th>
<th>$\Delta\alpha$ ($\omega=0$)</th>
<th>$\Delta\alpha$ ($\omega=0.413$)</th>
<th>$\Delta\alpha$ ($\omega=0.583$)</th>
<th>$\Delta\alpha$ ($\omega=0.653$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$36H^2−$ ($D_{2h}$)</td>
<td>1098</td>
<td>1118</td>
<td>1138</td>
<td>1150</td>
<td>1271</td>
<td>1301</td>
<td>1334</td>
<td>1351</td>
</tr>
<tr>
<td>$36F$ ($C_2$)</td>
<td>769</td>
<td>779</td>
<td>788</td>
<td>794</td>
<td>753</td>
<td>768</td>
<td>785</td>
<td>794</td>
</tr>
<tr>
<td>$38F$ ($C_2$)</td>
<td>989</td>
<td>1008</td>
<td>1028</td>
<td>1039</td>
<td>1321</td>
<td>1360</td>
<td>1402</td>
<td>1425</td>
</tr>
<tr>
<td>$36M^{2+}$ ($C_1$)</td>
<td>1018</td>
<td>1039</td>
<td>1062</td>
<td>1074</td>
<td>1078</td>
<td>1110</td>
<td>1145</td>
<td>1164</td>
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<tr>
<td>$38H^{2+}$ ($C_1$)</td>
<td>1104</td>
<td>1129</td>
<td>1156</td>
<td>1170</td>
<td>1330</td>
<td>1370</td>
<td>1413</td>
<td>1436</td>
</tr>
<tr>
<td>$36F_b$ ($C_2$)</td>
<td>859</td>
<td>870</td>
<td>882</td>
<td>889</td>
<td>1066</td>
<td>1089</td>
<td>1111</td>
<td>1124</td>
</tr>
<tr>
<td>$36H_a$ ($C_{2v}$)</td>
<td>1020</td>
<td>1037</td>
<td>1055</td>
<td>1064</td>
<td>1160</td>
<td>1185</td>
<td>1212</td>
<td>1226</td>
</tr>
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<td>971</td>
<td>979</td>
<td>1041</td>
<td>1062</td>
<td>1084</td>
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</tr>
<tr>
<td>$36M$ ($C_1$)</td>
<td>965</td>
<td>982</td>
<td>999</td>
<td>1008</td>
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<td>1027</td>
<td>1054</td>
<td>1069</td>
</tr>
<tr>
<td>$38H_b$ ($C_1$)</td>
<td>1053</td>
<td>1074</td>
<td>1097</td>
<td>1110</td>
<td>1197</td>
<td>1230</td>
<td>1264</td>
<td>1284</td>
</tr>
</tbody>
</table>

[a] $\bar{\alpha}$ and $\Delta\alpha$ were evaluated at the CAM-B3LYP/6-311+G(d,p) level of theory, in the gas-phase. [b] $\lambda=1900$ nm ($\omega=0.653$ eV) is close to the 1907 nm laser excitation, commonly employed for scattering experiments. [c] To study the frequency-dispersion of the NLO properties, additional energies were selected which lie out of the resonance region associated to the first excitation energy.

Figure 13. Evolution of the average static polarizability as a function of the topology, aromaticity and charge of selected octaphyrins. The aromaticity of each structure is indicated by the dot color: green (antiaromatic), red (aromatic) and grey (nonaromatic).
The first ($\beta$) and second hyperpolarizability ($\gamma$), both in static and dynamic regime, are reported in Table 4 for our set of octaphyrins. Regarding first hyperpolarizabilities, we focus on two measurable second-order NLO responses: the hyper-Rayleigh scattering (HRS) response ($\beta_{\text{HRS}}$) and the electric-field-induced second harmonic generation (EFISHG) response ($\beta_{//}$).\textsuperscript{10,85} The parallel first hyperpolarizability ($\beta_{//}$) is only reported for neutral systems because ionic species are not susceptible of electric-field induced orientations since they would rather migrate than orient.\textsuperscript{85} We also computed the depolarization ratio (DR), which provides information on the geometry of the chromophore.\textsuperscript{93}

Table 4. Static and dynamic Hyper-Rayleigh scattering first hyperpolarizability, depolarization ratio and longitudinal component of first and second hyperpolarizability of unsubstituted octaphyrins. \textsuperscript{a}

<table>
<thead>
<tr>
<th>system</th>
<th>$\beta_{\text{HRS}}$</th>
<th>DR</th>
<th>$\beta_{//}$</th>
<th>$\gamma_{//}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>36F$(C_2)$</td>
<td>1014 1660</td>
<td>1.62 1.49</td>
<td>407 334</td>
<td>632 1081</td>
</tr>
<tr>
<td>36H$^2-(D_{2h})$</td>
<td>~0 ~0</td>
<td>$b$ $b$</td>
<td>$c$ $c$</td>
<td>1359 2239</td>
</tr>
<tr>
<td>36M$^2+(C_1)$</td>
<td>3535 15035</td>
<td>4.70 4.30</td>
<td>$c$ $c$</td>
<td>1463 3191</td>
</tr>
<tr>
<td>38F$(C_2)$</td>
<td>897 1042</td>
<td>1.61 1.04</td>
<td>-342 27</td>
<td>533 870</td>
</tr>
<tr>
<td>38H$^2+(C_1)$</td>
<td>2836 9360</td>
<td>1.81 1.78</td>
<td>$c$ $c$</td>
<td>863 4349</td>
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<td>36F$_b(C_2)$</td>
<td>2922 3850</td>
<td>1.69 1.71</td>
<td>-1467 -2127</td>
<td>1219 1906</td>
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<tr>
<td>36H$<em>a(C</em>{2v})$</td>
<td>252 351</td>
<td>3.64 4.32</td>
<td>324 460</td>
<td>2199 3555</td>
</tr>
<tr>
<td>36H$_b(C_1)$</td>
<td>1593 2707</td>
<td>1.69 1.06</td>
<td>574 -485</td>
<td>2408 3400</td>
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<tr>
<td>36M$(C_1)$</td>
<td>2547 9665</td>
<td>3.50 2.05</td>
<td>2825 8591</td>
<td>2780 7032</td>
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<td>38H$_a(C_1)$</td>
<td>4154 39285</td>
<td>5.15 3.17</td>
<td>4346 45966</td>
<td>3334 135</td>
</tr>
</tbody>
</table>

\[a\] $\beta_{\text{HRS}}$, $\beta_{//}$ (in a.u.) and $\gamma_{//}$ (in $10^3$ a.u.) were evaluated at the restricted CAM-B3LYP/6-311+G(d,p) level of theory in gas-phase. \[b\] $\beta_{\text{HRS}}$ of 36H$^2-$ is not zero due to round-off errors in the coordinates and DR is not reported for 36H$^2-$ because $\beta_{\text{HRS}}$ is close to zero. \[c\] $\beta_{//}$ is not reported for charged systems.

As expected, centrosymmetric structures as 36H$^2-$ display a $\beta_{\text{HRS}}$ equal zero. As displayed in Figure 14, the topology switches induce dramatic changes in the $\beta_{\text{HRS}}$, considerably larger than variations in polarizability. Among the isolated octaphyrins, the diprotonated Möbius topology 36M$^2+$ exhibits the largest $\beta_{\text{HRS}}$ response, followed by the diprotonated Hückel topology 38H$^2+$. Figure-eight conformations (36F and 38F) exhibit significantly lower $\beta_{\text{HRS}}$ values than non-centrosymmetric Hückel and Möbius topologies. Indeed, our results point out that the larger $\beta_{\text{HRS}}$ responses are linked to the less symmetric structures. Overall,
variations in the molecular topology induced by (de)protonation trigger large changes in $\beta_{HRS}$ providing a proof-of-principle of the potential applicability of topology switches for optoelectronic applications.

Figure 14. Evolution of average polarizability (in a.u.) and Hyper-Rayleigh scattering first hyperpolarizability (in a.u.) upon the topology switches induced by (de)protonation and redox interconversions.

The change of topology involves a significant variation in torsional ring strain, which was found to be intrinsically correlated to the $\beta_{HRS}$ values in Hückel porphyrinoids. As shown in Figure 14, a similar correlation between $\beta_{HRS}$ values and torsional ring strain ($\Phi_p$) is found for unsubstituted octaphyrins, in such a way that the least planar macrocycles exhibit large second-order optical nonlinearities. Similar to $\beta_{HRS}$, the magnitude of $\beta_{//}$ is enhanced by larger ring strain, while symmetric and planar macrocycles exhibit reduced EFISHG responses. Hence, torsional strain provides a guiding principle for the design of NLO switches based on expanded porphyrins. Overall, the magnitude of the first hyperpolarizability is determined by the symmetry and planarity, whereas no clear role of the aromaticity is found.
Figure 15. Evolution of the HRS first hyperpolarizability as a function of the torsional ring strain of unsubstituted octaphyrins. The aromaticity of each structure is indicated by the dot color: green (antiaromatic), red (aromatic) and grey (nonaromatic).

The switching efficiency is determined by the first-hyperpolarizability contrasts, i.e. the ratio between the $\beta_{HRS}$ responses of the different states involved in the switching. Since the neutral octaphyrin adopts a nonaromatic figure-eight conformation in the neutral state, the $\beta_{HRS}$ contrasts are evaluated with respect to $36F$. According to the $\beta_{HRS}$ contrasts (Table 5), we observe the following sequence: $36F \rightarrow 36H^{2-} > 36F \rightarrow 36M^{2+} > 36F \rightarrow 38H^{2+} > 36F \rightarrow 38F$. Hence, the largest contrasts are linked to those switches involving drastic changes in the topology and the molecular symmetry. As can be inferred from Table 5, the $\beta_{HRS}$ contrasts can be substantially enhanced by solvation and by frequency-dispersion effects.

To further understand the effect of topological switches on the first hyperpolarizability contrasts, we have considered separately the topology and (de)protonation effect on the $\beta_{HRS}$ responses. Figure 16 illustrates the changes in the NLO responses of the switches induced by...
(de)protonation: \(36F \rightarrow 36H^2^-\) and \(36F \rightarrow 36M^{2+}\). For the first switch, the neutral Hückel octaphyrin \(36H_a\) having a similar conformation to \(36H^2^-\) constitutes an intermediate step for the \(36F \rightarrow 36H^2^-\) interconversion. However, \(36H_a\) is neither centrosymmetric \((C_{2v})\) nor fully ring-strain free \((\Phi_p = 3.0^\circ)\) and consequently, it is characterized by a relatively small but non-zero \(\beta_{HRS}\) of 252 a.u. As such, the change in the \(\beta_{HRS}\) response from \(36H_a\) to \(36H^2^-\) is still important due to the existence of an inversion center in the deprotonated structure. Regarding the Hückel-to-Möbius interconversion \(36F \rightarrow 36M^{2+}\), the intermediate neutral structure with a Möbius topology \(36M\) was considered \((\Phi_p = 30.5^\circ)\). In this case, the largest variation in \(\beta_{HRS}\) is observed for the topology interconversion of the neutral octaphyrin, while protonation enhances the first hyperpolarizability of the Möbius topology in a lesser extent.

Table 5. NLO contrasts\(^a\) for the different interconversions based on Hyper-Rayleigh scattering first hyperpolarizability\(^b\) in gas and in solvent phase computed at different frequencies \((\omega \text{ in eV})\)

<table>
<thead>
<tr>
<th>interconversion</th>
<th>gas-phase</th>
<th>DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.413</td>
</tr>
<tr>
<td>(36F \rightarrow 36H^2^-)</td>
<td>(\infty^c)</td>
<td>(\infty^c)</td>
</tr>
<tr>
<td>(36F \rightarrow 36M^{2+})</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>(36F \rightarrow 38F)</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>(36F \rightarrow 38H^{2+})</td>
<td>2.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\(^{a}\) The contrast are defined as the largest \(\beta_{HRS}\) value divided by the smallest \(\beta_{HRS}\) value. \(^b\) \(\beta_{HRS}\) (in \(10^3\) a.u.) were evaluated at the restricted CAM-B3LYP/6-311+G(d,p) level of theory in gas-phase and in DCM. \(^{c}\) \(\beta_{HRS}\) of \(36H^2^-\) is zero due to symmetry.

Table 4 also collects the longitudinal component of the second hyperpolarizability in static and dynamic field. Unlike \(\beta_{HRS}\) and \(\beta_{//}\) values, the magnitude of \(\gamma_{//}\) values is mainly influenced by the topology of the system and the charge state (Figure 17). In neutral octaphyrins, twisted-Hückel topologies are characterized by significantly reduced \(\gamma_{//}\) values than Möbius and Hückel topologies. Within neutral untwisted topologies, aromatic systems exhibit larger \(\gamma_{//}\) values than antiaromatic homologues. However, the global charge also influence the magnitude of \(\gamma_{//}\) values in both static and dynamic regime. For instance, \(36M^{2+}\) and \(36H^2^-\) are characterized by significantly lower \(\gamma_{//}\) values than their neutral homologues.
Figure 16. Evolution of average polarizability and Hyper-Rayleigh scattering first hyperpolarizability along the topology switches $36F \rightarrow 36H^2^-$ and $36F \rightarrow 36M^{2+}$, disentangling the effects of the topology switch and de(protonation).

As can be inferred by Table 4, the exalted magnitude of $\beta_{HRS}$ in $36M$, $36M^{2+}$, $38H$ and $38H^{2+}$ at 1900 nm (0.653 eV) indicate that those systems are close to resonance. The first resonance energy corresponds to half of the first excitation energy, namely the Q band ($36M$: 1.4 eV, $36M^{2+}$: 1.14 eV, $38H$: 1.22 eV and $38H^{2+}$: 1.01 eV, $36F$: 0.95 eV, $38F$:1.02 eV, $36H^2-$: 0.85 eV). In general, aromatic octaphyrins display larger first resonance energy than antiaromatic and nonaromatic homologues. Since $36M^{2+}$ and $38H^{2+}$ are close to resonance, the contrast in $\beta_{HRS}$ values drastically increases for the interconversions $36F \rightarrow 36M^{2+}$ and $36F \rightarrow 38H^{2+}$ when going from the static regime to 1900 nm (Table S12 and Figure S15). Therefore, the contrast in $\beta_{HRS}$ values can be fine-tuned with the wavelength of the incident light (Table 5). The dispersion-frequency plots for $\beta_{HRS}$ in gas and DCM are reported in Figures S13-S14. In comparison to the isotropic polarizability, the magnitude of $\beta_{HRS}$ evolves largely with the wavelength of the incident light, especially in aromatic systems. Finally, all NLO properties are enhanced upon solvation except DR values. Nevertheless, all the trends regarding NLO are similar in gas and solvent-phase.
Figure 17. Evolution of the static longitudinal component of the second hyperpolarizability (in $10^3$ a.u.) in neutral and (de)protonated octaphyrins.

Effects of meso-substitution on the structure-property relationships

Since nonlinear optical and photophysical properties can be tuned with meso-substitution, we investigated the effect of adding substituents on optoelectronic properties of the five octaphyrins shown in Figure 18. In this section, it is important to note that our goal is to assess if the devised structure-property relationships hold for real-world meso-substituted octaphyrins. In particular, we have selected the pentafluorophenyl groups since the experimental absorption spectra of these meso-aryl substituted octaphyrins is currently available, being certainly appropriate to test our computational findings. A detailed investigation of the effect of peripheral substituents on the NLO properties is out of the scope of the present article, although it is expected that the presence of strong electron–withdrawing and electron–releasing groups located on opposite sides of the octaphyrin skeleton will led to a dramatic increase of the NLO responses of the topological switches.
It is noteworthy that there is an important effect of dispersion in twisted-Hückel topologies, especially for the $\pi - \pi$ stacking between the central pyrroles. A decreased in the $\pi - \pi$ stacking distance in such topologies is observed upon adding dispersion in the order B3LYP $>$ M06 $>$ B3LYP-D3 (see Table S13). Again, the best agreement with the experimental structure is provided by M06 (Figure S16), which contains indirectly dispersion through the parametrization.\textsuperscript{59}

Table 6 reports the magnetic, structural and electronic properties of meso-substituted octaphyrins together with the torsional descriptors. Although some indices present reduced values as compare to unsubstituted hologues, the trend for aromaticity remains unchanged. In comparison to unsubstituted species, the trend for aromaticity remains unchanged. Based on the NICS\textsubscript{zz}(1) values, \textbf{36M}^2+, \textbf{38H}^2+ and \textbf{38F} are clearly aromatic, \textbf{36H}^{2}\textsuperscript{−} is highly antiaromatic and \textbf{36F} is nonaromatic. Similarly, the energy gap of meso-substituted species is slightly reduced, but still the antiaromatic \textbf{36H}^{2}\textsuperscript{−} exhibits the smallest HOMO-LUMO gap.
In comparison to unsubstituted octaphyrins, the presence of meso-pentafluorophenyl groups enhances the intensity of the absorption bands while inducing a redshift (Figure 19 and S17). But importantly, the fingerprints of aromaticity on the absorption spectra are conserved upon meso-substitution. With respect to the nonaromatic 36F, the UV/vis spectra of aromatic meso-substituted octaphyrins present more intense B bands, while their molar absorbance decays more slowly in the near-infrared region. In agreement with the experimental observations, meso-substituted 36H\(^{2-}\) and 38H\(^{2+}\) are characterized by a similar intensity while the difference in wavelength is larger than in unsubstituted homologues. Even though the composition of the absorption bands is more complex, the B bands of aromatic meso-substituted octaphyrins correspond to electronic transitions involving H-1, H, L and L+1 orbitals. By contrast, the intense B band in 36H\(^{2-}\) is associated to a combination of H-2/H-1→L and H→L+1/L+2 electronic transitions.

In general, the overall features of the experimental UV/vis spectra of meso-octakis(pentafluorophenyl) octaphyrins are well reproduced.\(^{46,57}\) In Table 7, the calculated and experimental data are reported for 36F, 36M\(^{2+}\), 38F, 38H\(^{2+}\) and 36H\(^{2-}\). Although there are discrepancies between experimental and theoretical wavelengths, simulated B bands are in qualitative agreement with experimental data with exception of the variation of \(\lambda\) for 38F to 36H\(^{2-}\), for which the use of an explicit solvation model might be invoked.

\begin{table}[h]
\centering
\caption{Magnetic, structural and electronic properties of meso-substituted octaphyrins}
\begin{tabular}{lcccccc}
\hline
systems & NICS(0)\(^{a}\) & NICS(1)\(^{a}\) & NICS\(_{zz}(1)\)^{a} & HOMA & \(\Pi\)^{b} & \(\Phi_{p}\) & \(\Delta E_{HL}\)^{d} \\
\hline
36F(C\(_{6}\)F\(_{5}\)) & -4.2 & -3.2 & 5.1 & 0.74 & 0.66 & 21.6 & 2.96 \\
38F(C\(_{6}\)F\(_{5}\)) & -11.3 & -9.7 & -19.3 & 0.85 & 0.60 & 24.1 & 2.82 \\
36M\(^{2+}\)(C\(_{6}\)F\(_{5}\)) & -8.0 & -7.6 & -18.3 & 0.78 & -0.31 & 35.5 & 2.95 \\
38H\(^{2+}\)(C\(_{6}\)F\(_{5}\)) & -11.0 & -10.4 & -27.5 & 0.83 & 0.40 & 31.9 & 2.83 \\
36H\(^{2-}\)(C\(_{6}\)F\(_{5}\)) & 15.1 & 14.5 & 46.6 & 0.66 & 0.79 & 18.7 & 2.71 \\
\hline
\end{tabular}
\end{table}

\(^{a}\) NICS indices were computed at the B3LYP/6-311+G(d,p) level of theory. \(^{b}\) \(\Pi\) is unitless. \(^{c}\) \(\Phi_{p}\) in degrees. \(^{d}\) HOMO-LUMO energy difference (eV) calculated at the CAM-B3LYP/6-311+G(d,p) level of theory.
Figure 19. Calculated UV/vis spectra for meso-substituted octaphyrins. The spectra were simulated with a FHWM of 0.333 eV.

For instance, the B bands become more intense and red-shifted when going from $36\text{F}$ to $36\text{M}^{2+}$, whereas the intensity of high energy transitions decreases. In reduced species such as $38\text{F}$ to $38\text{H}^{2+}$, protonation barely affects the intensity of the B bands or induces any large displacement of the absorption wavelength in line with the fact that both structures are clearly aromatic.

Table 7. Experimental and calculated properties associated to the main electronic transitions of meso-susbstituted octaphyrins with various oxidation state.

<table>
<thead>
<tr>
<th></th>
<th>B bands</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$36\text{H}^{2-}(\text{C}_6\text{F}_5)$</td>
</tr>
<tr>
<td>$\lambda_{\text{calc}}$</td>
<td>680.9</td>
</tr>
<tr>
<td></td>
<td>652.2</td>
</tr>
<tr>
<td>$f_{\text{osc,calc}}$</td>
<td>$3.71^b$</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
</tr>
<tr>
<td>$\lambda_{\text{exp}}$</td>
<td>761.0</td>
</tr>
<tr>
<td></td>
<td>728.0</td>
</tr>
</tbody>
</table>

[a] Experimental absorption wavelength.$^{46,57}$ [b] The maximum absorbance of $36\text{H}^{2-}$ equals $3 \times 10^5$ L mol$^{-1}$ cm$^{-1}$.$^{57}$ [c] The maximum absorbance for $36\text{F}$ and $38\text{F}$ are $1.1 \times 10^5$ and $3.45 \times 10^5$ L mol$^{-1}$ cm$^{-1}$, respectively.$^{46}$
Table 8 collects the average polarizability and NLO properties related to the first and second hyperpolarizability of *meso*-substituted octaphyrins. The magnitude of the NLO properties are enhanced upon *meso*-substitution, but the general trends remains unaltered. As such, twisted-Hückel topologies still present reduced values of $\bar{\alpha}$ and $\Delta\alpha$ as compared to Hückel and Möbius topologies. Within the same topology, aromatic macrocycles are characterized by larger $\bar{\alpha}$ and $\Delta\alpha$ than the antiaromatic counterparts in both the static and dynamic regime. Therefore, the topology still remains a key parameter to tune the magnitude in $\bar{\alpha}$ in *meso*-substituted systems.

Table 8. Average polarizability and HRS first hyperpolarizability, depolarization ratio and longitudinal component of first and second hyperpolarizability of *meso*-substituted octaphyrins computed at different frequencies ($\omega$ in eV).$^a$

<table>
<thead>
<tr>
<th>system</th>
<th>$\bar{\alpha}$ 0</th>
<th>$\beta_{HRS}$ 0</th>
<th>$\beta_{//}$ 0</th>
<th>$\gamma_{//}$ 0</th>
<th>$\beta_{//}$ 0.653</th>
<th>$\gamma_{//}$ 0.653</th>
</tr>
</thead>
<tbody>
<tr>
<td>36F(C₆F₅)(C₂)</td>
<td>1407</td>
<td>1443</td>
<td>1163</td>
<td>2291</td>
<td>79</td>
<td>-695</td>
</tr>
<tr>
<td>36H²⁻(C₆F₅)(C₁)</td>
<td>1802</td>
<td>1881</td>
<td>1554</td>
<td>2989</td>
<td>$^b$</td>
<td>$^b$</td>
</tr>
<tr>
<td>36M²⁺(C₆F₅)(C₁)</td>
<td>1809</td>
<td>1913</td>
<td>7146</td>
<td>21795</td>
<td>$^b$</td>
<td>$^b$</td>
</tr>
<tr>
<td>38F(C₆F₅)(C₂)</td>
<td>1650</td>
<td>1733</td>
<td>1767</td>
<td>4443</td>
<td>1709</td>
<td>2998</td>
</tr>
<tr>
<td>38H²⁺(C₆F₅)(C₁)</td>
<td>1969</td>
<td>2089</td>
<td>10454</td>
<td>25947</td>
<td>$^b$</td>
<td>$^b$</td>
</tr>
</tbody>
</table>

$^a$ $\bar{\alpha}$, $\beta_{HRS}$, $\beta_{//}$ (in a.u.) and $\gamma_{//}$ (in $10^3$ a.u.) were evaluated at the CAM-B3LYP/6-311+G(d,p) level of theory in gas-phase. $^b$ $\beta_{//}$ is not reported for charged systems.

Regarding $\beta_{HRS}$ and $\beta_{//}$, *meso*-octaphyrins with larger ring strain (38H²⁺ and 36M²⁺) present significantly larger $\beta_{HRS}(0,0,0)$ values than twisted-Hückel conformations (36F and 38F). As indicated by their exalted $\beta_{HRS}$ values, 38H²⁺ and 36M²⁺ are close to resonance at 1900 nm. Interestingly, the presence of bulky *meso*-substituents distorts 36H²⁻ leading to a non-planar and non-centrosymmetric macrocycle. The transition from $D_{2h}$ to $C_1$ symmetry point group induces a tremendous increases of $\beta_{HRS}$ values when going from unsubstituted to *meso*-substituted 36H²⁻. Again, much larger first hyperpolarizability contrasts are observed for the interconversions inducing a change of topology (36F $\rightarrow$ 36M²⁺ and 36F $\rightarrow$ 38H²⁺) as compared to the redox interconversion 36F $\rightarrow$ 38F, in which the twisted topology remains unchanged. Importantly, the contrast in $\beta_{HRS}$ for the different switches induced by (de)protonation and redox reactions are increased for substituted macrocycles.
These observations are in line with the work of M. Torrent et co-workers, who demonstrate that NLO contrasts in Hückel-Möbius switches in expanded porphyrins can be tuned by the nature of meso-substituents. Similar to $\beta_{HRS}$, meso-substituted octaphyrins are characterized by significantly larger longitudinal second hyperpolarizabilities in static and dynamic field as compared to unsubstituted species. Nevertheless, the topology and the charge of the macrocycle still play a key role in determining the magnitude of $\gamma_{//}$. For instance, Hückel and Möbius topologies display significantly larger second hyperpolarizability than twisted-Hückel topologies. Although the main trends for the second hyperpolarizability are conserved upon meso-substitution, $38F$ exhibits slightly larger $\gamma_{//}$ than $36F$, as opposed to their unsubstituted counterparts.

**Conclusions**

In this work, we have examined the aromaticity, UV/vis spectra and nonlinear optical properties of several unsubstituted and meso-substituted octaphyrins with distinct topology, oxidation state and protonation state. This test bed was selected based on the ability of octaphyrin macrocycles to adopt different $\pi$-conjugation topology upon redox and (de)protonation reactions. In order to establish the link between aromaticity and photophysical properties, the (anti)aromaticity of the octaphyrins was established first using an extensive set of aromaticity descriptors. Then, the UV/vis absorption spectra and NLO properties were rationalized in terms of aromaticity and molecular topology.

The majority of the aromaticity indices provide a straightforward distinction between aromatic and antiaromatic octaphyrins, while the difference between nonaromatic and antiaromatic configurations is less clear-cut. Importantly, macrocyclic aromaticity reverses upon redox reactions and topology interconversions and accordingly, the selected macrocycles provide an optimum test bed for investigating the correlation between (anti)aromaticity and
Regarding spectroscopic properties, we found that the UV/vis spectra of aromatic octaphyrins exhibit a very singular fingerprint, corresponding to the presence of Q bands and very intense B bands. In aromatic octaphyrins, such intense B bands are associated to electronic transitions involving the H, H-1 and L, L+1 molecular orbitals, which are nearly degenerated two by two. This degeneracy is broken in nonaromatic and antiaromatic octaphyrins, in which the orbital pairs H-1/H-2 and L+1/L+2 become close in energy. Remarkably, the UV/vis spectra of antiaromatic octaphyrins can display even more intense B bands than aromatic ones. More specifically, the intensity of the B-like bands in antiaromatic [36]octaphyrins increases as the contribution of the of H-2/H-1→L electronic transition to the B-band rises. By contrast, when the electronic transition mainly corresponds to the H→L+2 transition, the B bands of antiaromatic octaphyrins exhibit a reduced intensity as compared to their aromatic octaphyrins. Such enhanced B-band intensity in certain antiaromatic octaphyrins agrees with the experimental spectra, implying that the general statement “antiaromatic expanded porphyrins exhibit significantly attenuated absorption bands as compared to aromatic ones” needs to be apply with caution. These new findings are very important, specially taking into account that the UV/vis spectra are commonly used as an experimental measure of the aromaticity in expanded porphyrins.

The relationship between optical properties, aromaticity and topology in octaphyrins is more complex. On one side, molecular topology and aromaticity appears to be key factors governing polarizability. On the other side, the magnitude of both $\beta_{HRS}$ and $\beta_{//}$ are both enhanced in macrocycles with significant ring strain and reduced symmetry, while aromaticity itself has not a clear incidence on those quantities. Consequently, topology interconversions involving Möbius and Hückel topologies trigger dramatic changes in the first hyperpolarizability, demonstrating their potential as a novel type of nonlinear optical switches. Our findings
also pinpoint that the magnitude of the second hyperpolarizability is significantly reduced in
twisted-Hückel topologies and enhanced in aromatic systems within the same topology. In
addition, first and second order NLO properties are significantly more frequency-dependent
than polarizability and accordingly, $\beta_{HRS}$ contrasts can be fine-tuned with the wavelength
of the incident light.

Finally, it is important to emphasize that the devised structure-property relationships also
hold for real-world meso-substituted octaphyrins, for which the experimental absorption
spectra is currently available. As such, the fingerprints of aromaticity and topology on the
photophysical properties are conversed upon meso-substitution, although the $\beta_{HRS}$ contrasts
can be significantly enhanced by introducing electron-withdrawing and electron-releasing
groups on the opposite side of the macrocycle.

**Supporting information**

Aromaticity descriptors computed at different levels of theory, ACID plots, $^1$H NMR chemical
shifts, diradical character indices, detailed description of the main electronic transitions,
molecular orbitals, NLO properties and its frequency dispersion, together with the effect
of meso-substitution on the UV/vis spectra of octaphyrins can be found in the supporting
information.

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