Functional Group Introduction and Aromatic Unit Variation in a Set of π-Conjugated Macrocycles: Revealing the Central Role of Local and Global Aromaticity

Martina Rimmele, Wojciech Nogala, Maryam Seif-Eddine, Maxie M. Roessler, Martin Heeney, Felix Plasser, Florian Glöcklhofer

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π-Conjugated macrocycles are molecules with unique properties that are increasingly exploited for applications and the question of whether they can sustain global aromatic or antiaromatic ring currents is particularly intriguing. However, there are only a small number of experimental studies that investigate how the properties of π-conjugated macrocycles evolve with systematic structural changes. Here, we present such a systematic experimental study of a set of [2.2.2.2]cyclophanetetraenes, all with formally Hückel antiaromatic ground states, and combine it with an in-depth computational analysis. The study reveals the central role of local and global aromaticity for rationalizing the observed optoelectronic properties, ranging from extremely large Stokes shifts of up to 1.6 eV to reversible fourfold reduction, a highly useful feature for charge storage/accumulation applications. A recently developed method for the visualization of chemical shielding tensors (VIST) is applied to provide unique insight into local and global ring currents occurring in different planes along the macrocycle. Conformational changes as a result of the structural variations can further explain some of the observations. The study contributes to the development of structure–property relationships and molecular design guidelines and will help to understand, rationalize, and predict the properties of other π-conjugated macrocycles.

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Functional group introduction and aromatic unit variation in a set of \( \pi \)-conjugated macrocycles: revealing the central role of local and global aromaticity

Martina Rimmele, a,b Wojciech Nogala, c Maryam Seif-Eddine, a Maxie M. Roessler, a Martin Heeney, a,b Felix Plasser, d,* Florian Göcklhofer a,b,*

a Department of Chemistry, Imperial College London, London W12 0BZ, United Kingdom
b Centre for Processable Electronics, Imperial College London, London W12 0BZ, United Kingdom
c Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
d Department of Chemistry, Loughborough University, Loughborough LE11 3TU, United Kingdom

* E-mail: f.plasser@lboro.ac.uk, f.gocklhofer@imperial.ac.uk

Abstract

\( \pi \)-Conjugated macrocycles are molecules with unique properties that are increasingly exploited for applications and the question of whether they can sustain global aromatic or antiaromatic ring currents is particularly intriguing. However, there are only a small number of experimental studies that investigate how the properties of \( \pi \)-conjugated macrocycles evolve with systematic structural changes. Here, we present such a systematic experimental study of a set of [2.2.2.2]cyclophanetetraenes, all with formally Hückel antiaromatic ground states, and combine it with an in-depth computational analysis. The study reveals the central role of local and global aromaticity for rationalizing the observed optoelectronic properties, ranging from extremely large Stokes shifts of up to 1.6 eV to reversible fourfold reduction, a highly useful feature for charge storage/accumulation applications. A recently developed method for the visualization of chemical shielding tensors (VIST) is applied to provide unique insight into local and global ring currents occurring in different planes along the macrocycle. Conformational changes as a result of the structural variations can further explain some of the observations. The study contributes to the development of structure–property relationships and molecular design guidelines and will help to understand, rationalize, and predict the properties of other \( \pi \)-conjugated macrocycles.
Introduction

π-Conjugated macrocycles provide an exciting playing field for the discovery of effects and properties that cannot usually be attained with organic compounds. Their study began in the early 1960s and many π-conjugated macrocycles have been synthesized since.\(^1\) However, only recently the field has moved towards making use of the unique properties of these cyclic molecules for applications. π-Conjugated macrocycles are now being investigated in organic solar cells,\(^2\) photodetectors,\(^3\) field-effect transistors,\(^4,7\) and light-emitting diodes.\(^8\)\(^\text{-}11\) They can also be used in bioimaging,\(^12\) as templates for the growth of carbon nanotubes,\(^13\) and as molecular nanoreactors.\(^14\)

In our own research, we exploited the capability of [2.2.2]paracyclophane-1,9,17,25-tetraene, a [2.2.2]cyclophanetetraene with benzene units, denoted BCyc here, to switch between a locally aromatic neutral state and a globally aromatic doubly reduced state (Scheme 1).\(^{15,16}\) This switching enabled excellent redox properties and application as high-performance organic sodium-ion battery anode material. The macrocyclic geometry was further found to result in voids in the solid-state packing that can facilitate ion diffusion.

![Scheme 1](image)

**Scheme 1.** (a) Reversible two-electron reduction and aromaticity switching of the π-conjugated macrocycle [2.2.2]paracyclophane-1,9,17,25-tetraene, denoted BCyc here. (b) Visualization of chemical shielding tensors (VIST) with shielded (aromatic) contributions in blue and deshielded (antiaromatic) contributions in red. The VIST plots show that the neutral ground state is dominated by the local aromaticity of the phenylene units; the formally antiaromatic perimeter of \([4n]\) π-electrons only induces weak global antiaromaticity. The doubly reduced state, however, is dominated by the global aromaticity of the resulting \([4n+2]\) π-electron perimeter. Hydrogen atoms omitted for clarity.

Further applications of π-conjugated macrocycles are possible if the molecular structure is adapted accordingly. However, there are only a small number of experimental studies that investigate how the properties of π-conjugated macrocycles evolve with systematic structural changes, presumably due to
the difficulties of synthesizing sets of macrocycles that allow for such an investigation. Cycloparaphenylenes (CPPs) are probably the class of π-conjugated macrocycles for which the most extensive structural variations have been performed and several applications are now emerging. However, in contrast to BCyc, the π-system of these compounds, which have been synthesized over a period of more than a decade, is radially oriented, which makes it difficult to draw conclusions for other macrocyclic π-systems. We believe that further systematic studies of π-conjugated macrocycles are needed to gain a better understanding of the evolving properties. Such studies can also be expected to lead to the discovery and identification of unexpected effects and properties, which may ultimately result in the development of new materials and applications.

For the study presented here, we aimed to investigate how the introduction of electron-withdrawing groups at the vinylene bridges of BCyc can influence its properties. We were particularly interested in how this structural modification changes the redox properties of the compound. While the reduction of BCyc was found to be a two-electron process and the charges of BCyc²⁻ were delocalized, electron-withdrawing groups were expected to impact on this behavior, possibly enabling reduction beyond the dianion. Due to the availability of promising synthetic methods, we aimed to introduce ester groups as the electron-withdrawing groups to study these effects (Scheme 2, Functional group introduction).

In addition to the functional group introduction, we were curious how a variation of the aromatic units can affect the properties, replacing the benzene units of the ester-substituted macrocycle by naphthalene, anthracene, and pyrene units (Scheme 2, Aromatic unit variation). This variation gradually increases the size of the macrocycles, yielding a set of ester-substituted [2.2.2.2]cyclophanetetraenes (all with a formally aromatic macrocyclic system of [4n] π-electrons in the neutral ground state), and was expected to result in changes to the effective ring currents and the associated local and global (anti)aromaticity in the neutral and charged states. Nevertheless, our interest here was also to identify deviations from the expected trends to advance our understanding of the unique properties that can be attained with carefully designed π-conjugated macrocycles.

Scheme 2. Systematic structural changes to the π-conjugated macrocycle BCyc to study the evolving properties in a set of [2.2.2.2]cyclophanetetraenes: (i) introduction of electron-withdrawing ester groups and (ii) replacement of the benzene units by naphthalene, anthracene, and pyrene units.
Our aim was to combine this experimental investigation with an in-depth computational analysis to explain, understand, and confirm the experimental results and to evaluate computational tools and methods that can facilitate the study of $\pi$-conjugated macrocycles.

Results and Discussion

Synthesis. In contrast to the synthesis of the unsubstituted macrocycle BCyc (Scheme 1), which can be achieved by a Wittig reaction of terephthalaldehyde with $p$-xylylenebis(triphenylphosphonium bromide),15 the synthesis of the $\pi$-conjugated macrocycles with ester groups at the vinylene bridges requires $\alpha,\alpha'$-dioxoarylenediacetic acids (also known as arylendiglyoxylic acids) and arylendiacidic acids as the precursors.19,20 These precursors, such as compounds 2a and 3a in Scheme 3, can give ester-substituted macrocycles in a two-step reaction. In the first step, a Perkin-type condensation reaction of the precursors gives macrocyclic carboxylic anhydride intermediates, which are then converted into the ester-substituted macrocycles by addition of an alcohol and a bromoalkane in the second step. In this study, we either added ethanol and bromoethane or 1-hexanol and 1-bromohexane for the second step of the reaction, yielding ethyl or hexyl ester-substituted macrocycles, respectively.

For the synthesis of the macrocycles with benzene units, BCyc-Et and BCyc-Hx (Scheme 3), $\alpha,\alpha'$-dioxo-1,4-benzenediacidic acid 2a was obtained in two steps starting from 1,4-diodobenzene. In the first step, lithium-halogen exchange and quenching with an excess of diethyl oxalate gave compound 1a, which was then saponified to yield precursor 2a in an overall yield of 42%. An alternative one-step approach, Riley oxidation of 1,4-diacylbenzene under conditions previously used for the oxidation of acetophenone,21 also gave precursor 2a according to $^1$H NMR spectra. However, our attempts to separate the highly polar product from the by-products of this alternative approach were not successful. The second cyclisation precursor, 1,4-benzenediacidic acid 3a, is available from commercial suppliers.

Using precursors 2a and 3a, BCyc-Et and BCyc-Hx were obtained by adapting a protocol reported for the synthesis of the corresponding $\pi$-conjugated macrocycle with pyrene units.19 In contrast to the previous report, the macrocycles were purified by gel permeation chromatography (GPC) instead of silica gel column chromatography, enabling efficient separation of oligomeric by-products and, thus, helping to prevent an overestimation of the reaction yield. After purification, BCyc-Et was obtained as a yellow solid in a yield of 16%; the initially obtained oil slowly crystallized to give the yellow solid. A marginally higher yield of 17% was achieved when the precursors were dissolved and added to the reaction over a period of 10 hours using a syringe pump. Such slow addition can keep the concentration of the precursors in the reaction low, which is usually considered to favor cyclisation over the formation of linear oligomers, but the effect was negligible in our case. The macrocycle with hexyl ester groups, BCyc-Hx, was obtained as a dark oil in a lower yield of 8%. In contrast to BCyc-Et, this macrocycle did not crystallize, and the separation of the by-products was found to be more challenging, despite using GPC for purification.
Scheme 3. Synthesis of macrocycles BCyc-Et and BCyc-Hx with benzene units and ethyl/hexyl ester groups. Compound 1a was obtained from 1,4-diiodobenzene (Supporting Information section 1.3.1).

For the corresponding macrocycles with larger aromatic units, NCyc-Et, ACyc-Et, PCyc-Et and PCyc-Hx (Scheme 4 and Supporting Information Figure S1), the required α,α’-dioxoarylenediacetic acid precursors 2b-d were obtained in similar reactions as used for the synthesis of precursor 2a. However, dibrominated instead of diiodinated arenes were used as the starting materials for the synthesis of compounds 1b-d and the reaction conditions and reagents of both synthetic steps were adapted and optimized for each precursor. In contrast to precursor 3a, the arylenediacid acid precursors 3b-d are not commercially available but were synthesized by reduction of compounds 2b-d, adapting previously reported conditions.19,22 Interestingly, the corresponding reduction of substituents in the 9,10-positions of anthracene did not give the desired product (Supporting Information Figure S2).

The macrocycles were then prepared under the same conditions as BCyc-Et, yielding NCyc-Et as a pale yellow solid, ACyc-Et and PCyc-Et as orange solids, and PCyc-Hx as a red oil. No syringe pumps were used due to poor solubility of the precursors in the reaction solvent and the negligible effect on the reaction yield in the synthesis of BCyc-Et. As intended, the introduction of hexyl ester groups in PCyc-Hx, a reaction tested with the synthesis of BCyc-Hx, significantly improved the solubility of the compound compared to PCyc-Et, but the separation of the reaction by-products was again found to be tedious. The macrocycles were characterized by 1H and 13C NMR as well as by high-resolution mass spectrometry (HRMS) to confirm the molecular structure. Unfortunately, although we found the synthesis of all precursors and all other macrocycles to be reproducible, we struggled to re-synthesize ACyc-Et in later attempts. However, as highly interesting effects were observed for this macrocycle in both the computations and experiments, we do not want to omit the available data for this macrocycle here. The computational analysis also allows us to present a possible explanation for the difficulties with the synthesis of this compound related to its more flexible nature.
Scheme 4. (a) Synthesis of macrocycle NCyc-Et with naphthalene units and ethyl ester groups. Compound 1b was obtained from 2,6-dibromonaphthalene (Supporting Information section 1.3.2). (b) Macrocycles ACyc-Et, PCyc-Et, and PCyc-Hx with anthracene/pyrene units and ethyl/hexyl ester groups, obtained in analogous reactions using precursors 2c-d and 3c-d (Supporting Information sections 1.3 to 1.6, Figure S1).

**UV-vis absorption and photoluminescence.** UV-vis absorption spectra (Figure 1, solid lines) in CHCl₃ solution showed a peak at 315 nm for BCyc-Et and 313 nm for BCyc-Hx, both slightly redshifted compared to the unsubstituted macrocycle BCyc, which showed an absorption peak at 306 nm in the same solvent.¹⁵ In contrast to BCyc, an additional shoulder at approx. 262 nm was observed for both macrocycles. Considering that BCyc-Et and BCyc-Hx feature the same π-conjugated system, the similarity of their absorption spectra is not surprising. The photoluminescence (PL) spectra (Figure 1, dashed lines) also showed similar peak wavelengths, 526 nm for BCyc-Et and 530 nm for BCyc-Hx. The difference between the absorption and PL peak wavelengths corresponds to large Stokes shifts of 1.58 and 1.62 eV, respectively. Interestingly, despite featuring the same π-conjugated system, the PL was found to be significantly more intense for the hexyl-ester substituted macrocycle BCyc-Hx, possibly due to shielding of the chromophores by the hexyl chains.

With both NCyc-Et and ACyc-Et, a trend to further redshifted absorption is observed. NCyc-Et showed an absorption peak at 324 nm and a shoulder at 274 nm. The PL maximum was found to be at 486 nm, corresponding to a Stokes shift of 1.28 eV, smaller than for BCyc-Et/Hx. ACyc-Et showed an absorption peak at 264 nm and shoulders at longer wavelengths; PL data for ACyc-Et is not available.
The absorption spectrum of ACyc-Et has a markedly different shape compared to the other molecules studied and we assign this difference to its folded structure and the ensuing loss of symmetry that are discussed below.

As for BCyc-Et and BCyc-Hx, the absorption spectra of PCyc-Et and PCyc-Hx were found to be very similar, showing peaks at 283 nm and 362/360 nm. The PL was again significantly more intense for the hexyl-ester substituted compound, while the peak wavelengths were similar, 588 nm for PCyc-Et and 593 nm for PCyc-Hx. This corresponds to Stokes shifts of 1.32 eV and 1.35 eV, respectively, similar to the Stokes shift observed for NCyc-Et.

Beside the experimental results discussed so far, Table 1 presents results computed at the time-dependent density functional theory level. The first computed singlet state of BCyc-Et, located at 353 nm, is symmetry forbidden within the four-fold symmetry of this molecule. This state may be tentatively assigned to the red tail between 350 and 400 nm observed in the experimental spectrum. A degenerate pair of bright states (oscillator strength of 0.77) follows at 315 nm, in good agreement with the experimentally observed absorption maximum. These three states, along with the dark S1 state (not listed in Table 1), are characterized by an excitation from a π-orbital delocalized over the whole system into the π*-orbitals on the vinylene units, with some contributions by the ester groups. Next, a degenerate pair of bright states (oscillator strength of 0.40) at 294 nm is found, which is consistent with the higher-energy shoulder in the spectrum.

Proceeding to NCyc-Et and PCyc-Et, both of which retain the four-fold symmetry, one finds the same structure with a dark low-energy state and a pair of bright degenerate states giving rise to the main peak in the spectrum. In agreement with the experiments, we find a consecutive red shift when going to NCyc-Et and further to PCyc-Et, but this shift is somewhat overestimated by the computations. For the bright pair of states in NCyc-Et and PCyc-Et we find oscillator strengths of 0.61 and 1.20, respectively, showing that the computed oscillator strengths are in good agreement with the relative experimental intensities. A discussion of ACyc-Et is more challenging considering that more states are involved due to the loss of symmetry in this molecule (as a result of the folded structure discussed below). We find two dark states (496 and 476 nm) before the first bright state located at 451 nm. Due to the lack of symmetry, this state is not degenerate, and we find a second bright state at a slightly higher energy (438 nm). We tentatively assign these two states to the extended red tail found between 400 and 500 nm in the absorption spectrum of ACyc-Et.
Figure 1. UV-vis absorption (solid lines) and photoluminescence spectra (dashed lines) of the macrocycles in CHCl₃ solution (5 µM). The excitation wavelengths for recording the photoluminescence (PL) spectra are shown in brackets; spectra obtained at other excitation wavelengths are available (Supporting Information Figure S43).

Table 1. Experimental and theoretical UV-vis absorption and photoluminescence bands of the macrocycles in solution and the experimental Stokes shifts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{abs,exp.} [nm]</th>
<th>λ_{abs,th.} [nm]</th>
<th>λ_{PL,exp.} [nm]</th>
<th>λ_{PL,th.} [nm]</th>
<th>Stokes shift [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCyc-Et</td>
<td>262/315</td>
<td>294/315/353</td>
<td>526</td>
<td>648</td>
<td>1.58</td>
</tr>
<tr>
<td>BCyc-Hx</td>
<td>262/313</td>
<td>n/a</td>
<td>530</td>
<td>n/a</td>
<td>1.62</td>
</tr>
<tr>
<td>NCyc-Et</td>
<td>274/324</td>
<td>342/353/379</td>
<td>486</td>
<td>450</td>
<td>1.28</td>
</tr>
<tr>
<td>ACyc-Et</td>
<td>264/307/387</td>
<td>451/476/496</td>
<td>n/a</td>
<td>592</td>
<td>n/a</td>
</tr>
<tr>
<td>PCyc-Et</td>
<td>275/283/362</td>
<td>398/431</td>
<td>588</td>
<td>580</td>
<td>1.32</td>
</tr>
<tr>
<td>PCyc-Hx</td>
<td>275/283/360</td>
<td>n/a</td>
<td>593(b)</td>
<td>n/a</td>
<td>1.35</td>
</tr>
</tbody>
</table>

(a) Wavelength of maxima shown in bold, wavelength of shoulders estimated. (b) Determined from the photoluminescence spectrum recorded with the detector voltage set to ‘medium’ (Supporting information Figure S44). (c) Computed at the optimized triplet geometry in dichloroethane (DCE).

Electrochemistry. π-Conjugated macrocycles are potentially interesting compounds for battery electrodes and other electrochemical applications, as we have shown in our investigation of BCyc.¹⁵ Cyclic voltammetry (CV) measurements (Figure 2) were expected to give insights into how the electrochemical properties evolve with the structural changes in our set of macrocycles. These measurements revealed a large shift of the first reduction wave upon introduction of the electron-withdrawing ester groups, from -2.29 V vs. ferrocene/ferrocene⁺ (Fc/Fc⁺) for BCyc to -1.65 V for BCyc-Et. In both cases, the reduction was found to be chemically reversible. However, in contrast to BCyc,
a second reduction wave was observed for BCyc-Et within the electrochemical window of the electrolyte solution, at a potential of -2.15 V.

Measuring cyclic voltammograms for BCyc-Et at defined concentrations in different solvents, we aimed to determine the stoichiometry of the observed reduction steps (as we did previously for BCyc). However, due to sluggish kinetics of electron transfer to the ester-substituted macrocycles, the analysis of the voltammograms could neither confirm that the reduction proceeds in two one-electron steps nor exclude the presence of two two-electron steps (see Supporting Information 4.2).

**Figure 2.** Cyclic voltammograms and redox potentials for the reduction of the macrocycles in dichloroethane (DCE), recorded on 2 mm diameter platinum disk electrodes at a scan rate of 0.1 V s$^{-1}$ with 0.1 M NBu$_4$PF$_6$ as the supporting electrolyte. Dotted lines show the measurement of the electrolyte solution without macrocycle. Previously reported redox potential of BCyc in DCE for comparison: -2.29 V vs. ferrocene/ferrocene$^+$ (Fc/Fc$^+$).

Upon variation of the aromatic units, a shift of the reduction to lower potential was observed for NCyc-Et; a redox potential of -1.92 V was determined for this compound. The voltammogram (and more clearly its 1st derivative, see Supporting Information Figure S45) indicates that there may be a second reduction step at -2.17 V. In contrast to BCyc-Et, the reduction was found to be chemically irreversible. The lower redox potential for the reduction of NCyc-Et compared to BCyc-Et may be explained by its weaker global antiaromaticity in the neutral state and weaker global aromaticity in the doubly reduced state, discussed further in the section on ring currents and chemical shielding below. Interestingly, further variation of the aromatic units led to unexpected effects. Chemically reversible
reduction at a significantly higher potential of -1.31 V was observed for ACyc-Et, while for PCyc-Et and PCyc-Hx the reduction remained at a similar potential as for NCyc-Et (at -1.84 V and -1.83 V, respectively), albeit being chemically reversible. For ACyc-Et, a second reduction wave was observed at -1.86 V.

Considering the relatively small structural differences between ACyc-Et and the most similar other macrocycles, NCyc-Et and PCyc-Et, as well as the absence of a general trend to serve as an explanation, rationalizing the observed redox potentials was difficult. Ruling out impurities as an explanation, we were curious if a computational investigation of the electrochemical properties could validate the results. Hence, we computed the redox potentials by optimizing the molecular geometries for the individual charged states using density functional theory and computing their Gibbs free energies in DCE solution (see computational details). Indeed, the computations showed a dip in the redox potential for the first reduction wave of ACyc-Et (Figure 3, top), but the dip was smaller than in the experiments.

The computations also showed very small differences in redox potential between the first and second reduction of all ester-substituted macrocycles, except for ACyc-Et. Furthermore, they revealed that the introduction of ester groups significantly facilitates the fourfold and sixfold reduction of the macrocycles; the redox potentials for the reduction to the tetra-/hexaanions shifted from -4.01/-5.43 V for BCyc to -2.48/-3.74 V for BCyc-Et. These results strongly support that the reduction steps of BCyc-Et observed in the CV measurements are two consecutive two-electron processes, corresponding to a reversible reduction to the dianion in the first step and to the tetraanion in the second step. For NCyc-Et, the potential differences were found to be even smaller, with the calculations indicating a potential of -1.82 V for the first reduction, -1.96 V for the second reduction, and -2.16 V for the reduction to the tetraanion. As all calculated potentials (Supporting Information Table S2), these values corresponded well with the experimentally determined redox potentials.

![Figure 3](image_url)

**Figure 3.** Calculated redox potentials vs. Fc/Fc⁺ for the reduction to the mono-, di-, tetra- and hexaanions (top) and oxidation to the corresponding cations (bottom) of the macrocycles in 1,2-dichloroethane (DCE). Data available in the Supporting Information Table S2.
While the introduction of the ester groups has its most pronounced effect on the reduction to the tetra- and hexa-anions, the variation of the aromatic units most significantly affects the oxidation to the tetra-/hexacations (Figure 3, bottom), shifting the corresponding potentials from 3.00/4.83 V for BCyc-Et to 1.68/3.28 V for ACyc-Et. In line with the calculations, the experimentally determined redox potentials for the first oxidation wave showed a similar, albeit smaller shift from 1.47 V for BCyc-Et to 0.85 V for ACyc-Et (Supporting Information Figure S45). For all ester-substituted macrocycles, the oxidation was found to be chemically irreversible in the CV measurements. In contrast, the two-electron oxidation of BCyc at 0.77 V was shown to be chemically reversible.\textsuperscript{15}

In addition to the redox potentials for the singlet states of the macrocycles discussed so far, we also calculated the redox potentials for the reduction and oxidation to the tetra-anions and -cations in the triplet state (Figure 3, dashed lines). These calculations showed surprisingly small differences between the singlet and triplet states, which are discussed further below in the section on the ring currents and chemical shielding.

**Conformation.** π-Conjugated macrocycles are often shape-persistent, meaning they are non-collapsible, geometrically well-defined, and conformationally restricted. We also expected the macrocycles from this study to be shape-persistent, but – when looking into the origin of the higher redox potential for the first reduction and the lower redox potential for the first oxidation of ACyc-Et compared to the other macrocycles (an effect observed in the calculations and experiments) – enhanced structural flexibility of the macrocycle was found to provide an explanation for the effect. As our calculations show, the macrocycle features a collapsed conformation in the neutral as well as in the first charged states (Figure 4a), enabling increased stabilization of the injected charges and resulting in the observed shift of the redox potentials. Figure 4a also shows electron density difference plots for the singly charged states of ACyc-Et, highlighting that the excess electron in the anion is predominantly located in the vicinity of the electron-withdrawing ester groups, whereas the hole in the cation is distributed over the aromatic units. The collapsed conformation also helps to explain the UV-vis absorption spectrum of the macrocycle as it reduces the symmetry, enabling lower energy transitions. In contrast to ACyc-Et, the more rigid nature of the other macrocycles seems to prevent a collapse (Figure 4b).

Interestingly, the more flexible nature of ACyc-Et can also provide an explanation for the difficulties with its synthesis. Conformation plays a crucial role in cyclization reactions, as it has a strong impact on the degree of competing oligomerization and polymerization reactions; an unfavorable conformation of the intermediates can impede the formation of macrocycles. Greater flexibility will make the conformation of the intermediates more prone to subtle changes in reaction conditions or impurities, explaining our results for the synthesis of ACyc-Et.
**Figure 4.** Calculated conformation of (a) ACyc-Et in the neutral and singly charged states and (b) BCyc-Et, NCyc-Et, and PCyc-Et in the neutral state. Panel (a) shows electron density differences between the neutral and charged states (isovalue -0.0015 e for ACyc-Et⁻ and +0.0015 e for ACyc-Et⁺). Hydrogen atoms omitted for clarity.

**EPR spectroelectrochemistry.** In order to clarify whether the two reduction steps observed in the CV measurements of BCyc-Et are one-electron steps (as cannot be excluded based on the measured voltammograms) or two-electron steps (as supported by the calculation of the redox potentials), electron paramagnetic resonance (EPR) spectroelectrochemical measurements were performed (see Supporting Information section 5). A reduction proceeding in two one-electron steps would result in the formation of a paramagnetic species and, consequently, in an EPR signal after the first reduction step. The signal would disappear again in the second step. If the reduction proceeds in two two-electron steps, no paramagnetic species is formed at any point of the reduction cycle and no EPR signal is expected.

Indeed, no EPR signal was observed at any point in the measurement of BCyc-Et (Supporting Information Figure S51), corroborating the reduction to the dianion in the first step and to the tetraanion in the second step. In contrast, measurements of the paramagnetic compound 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl (4-amino-TEMPO) showed an EPR signal (Supporting Information Figure S50), confirming that the absence of a signal in the measurements of BCyc-Et cannot be attributed to issues with the measurement set-up.

**Ring currents and chemical shielding.** The systematic structural changes of the macrocycles as well as the changes in redox and spin state were also expected to lead to changes in magnetic properties (ring currents and chemical shielding) and the associated global (anti)aromaticity, providing a powerful framework for explaining the observed properties. To assess the local and global (anti)aromaticity, we
carried out nucleus-independent chemical shift (NICS) calculations for the different states of the macrocycles. The NICS tensors were then represented graphically using the visualization of chemical shielding tensors (VIST) method (Figure 5, further VIST plots are provided in the Supporting Information section 6.3). VIST allows the visualization of local variations in aromaticity and antiaromaticity in the context of the molecular structure by showing the tensor components as blue (shielded, aromatic) or red (deshielded, antiaromatic) dumbbells. Each tensor component relates to ring currents in a plane perpendicular to it. The method provides insights into the anisotropy of the chemical shielding, a highly valuable feature when studying multi-ring systems such as our macrocycles, where several ring currents in different planes can interact, leading to strong magnetic anisotropy.

For each macrocycle and state, the NICS tensors were computed and visualized at two different positions: (i) 1 Å off the plane of a ring of the aromatic units, denoted NICS(1)\textsubscript{a} here, and (ii) at the center of the macrocycle, denoted NICS(0). The NICS(1)\textsubscript{a} tensor can tell us how strongly the local aromaticity of the aromatic units is perturbed by macrocyclic currents, while the NICS(0) tensor is best suited to provide information about the macrocyclic currents themselves. The VIST plots for BCyc and BCyc\textsuperscript{2} (Scheme 1b) illustrate the expected changes: In the neutral state, the main component of the NICS(1)\textsubscript{a} tensor is shielded and perpendicular to the plane of the aromatic unit. In the doubly reduced state, however, it is tilted and almost perpendicular to the plane of the macrocycle, indicating strong perturbation of the local aromaticity by macrocyclic currents, as described previously. In contrast, the main component of the central NICS(0) tensor is slightly deshielded (+11.0 ppm) in the neutral state (due to the macrocyclic 4n \(\pi\)-electron system) but strongly shielded (-38.7 ppm) in the doubly reduced state (due to the resulting 4n+2 \(\pi\)-electron system), indicating a transition from weak antiaromatic (paratropic) to strong aromatic (diatropic) macrocyclic currents. A similar, but somewhat less pronounced, effect was observed in the VIST plots for BCyc-Et and BCyc-Et\textsuperscript{2} (Figure 5a).

The VIST plots for BCyc and BCyc-Et in the triplet excited state as well as BCyc\textsuperscript{2} and BCyc-Et\textsuperscript{2} in the singlet ground state (Figure 5d and b) showed similar NICS tensors as their dianions, indicating similarly strong aromatic macrocyclic currents (Baird aromaticity in the triplet excited state, Hückel aromaticity in the doubly charged ground states). Moving to the tetraanions, the VIST plots indicate strong antiaromatic macrocyclic currents in the singlet state (Hückel antiaromaticity) and strong aromatic currents in the triplet state of BCyc\textsuperscript{4} (Baird aromaticity) (Figure 5e). The currents are considerably weaker in the corresponding states of BCyc-Et\textsuperscript{4} (Figure 5c) and the reduction in current is particularly pronounced in the singlet state. Notwithstanding the weaker currents, the aromaticity in the triplet state and the antiaromaticity in the singlet state of the tetraanions provide an explanation for the unusually small difference in energy between the two states and the ensuing small difference in computed redox potentials (see Figure 3).
Figure 5. (a) to (c) VIST plots for BCyc-Et in different charge and spin states. (d) and (e) VIST plots for BCyc for comparison (see also Scheme 1b). Shielded (aromatic) tensor components are shown in blue, deshielded (antiaromatic) tensor components in red. Each tensor component relates to ring currents in a plane perpendicular to it. In all VIST plots, hydrogen atoms were omitted for clarity.

Further VIST plots are provided in the Supporting Information section 6.3.

To understand the weaker currents in the ester-substituted compound, we computed electron density difference plots (Supporting information section 6.4). In these plots, BCyc-Et is shown to be able to place positive as well as negative charge on the ester groups, whereas for BCyc the changes in electron density are largely concentrated on the π-electron perimeter. As a consequence, BCyc acts more like an idealised [24]annulene in its charged states, switching between aromatic and antiaromatic states with the addition or subtraction of two electrons. This effect is alleviated for BCyc-Et, as other orbitals aside from the π-orbitals on the perimeter also play a significant role. The difference between the two macrocycles is particularly pronounced for the tetraanions. BCyc\textsuperscript{4−} has no option aside from placing the additional electrons along the macrocyclic π-conjugated pathway, which induces strong antiaromaticity, as seen by the pronounced deshielding in the VIST plots as well as the strongly negative redox potential for the reduction to the tetraanion. By contrast, BCyc-Et\textsuperscript{4−} is able to place the additional electron density into the ester groups, thus avoiding the formation of a strongly antiaromatic state, causing a dramatic shift in the computed redox potential for the reduction by about 1.5 V when compared to BCyc\textsuperscript{4−}. 
For comparing the full set of macrocycles in the different states, the component of the NICS(0) tensor perpendicular to the plane of the macrocycle, denoted NICS(0)zz, is most instructive, as it can serve as an indicator of the diatropic (aromatic) or paratropic (antiaromatic) macrocyclic currents. Shielded tensor components correspond to negative NICS(0)zz values and indicate global aromaticity, deshielded tensor components correspond to positive values and indicate global antiaromaticity. Figure 6 provides an overview of the NICS(0)zz values of the macrocycles in the different states. Almost without exception, the signs of the NICS(0)zz values agree with the predictions of (anti)aromaticity following Hückel’s and Baird’s rule, highlighting the consistency between these approaches. In all states, the values indicate a decrease of the macrocyclic currents with the introduction of the ester groups, as can be seen when comparing the values of BCyc and BCyc-Et, but the magnitude of the decrease depends on the state. In the neutral singlet state, the NICS(0)zz values indicate only a small decrease (by about one third) in paratropic currents upon introduction of the ester groups, whereas the decrease is somewhat larger for the mono- and dianions. A further stepwise decrease can be observed when increasing the size of the aromatic units, moving to NCyc-Et and PCyc-Et. Only ACyc-Et deviates from this general trend, a result of its folded conformation. In the neutral triplet state, the NICS(0)zz values indicate macrocyclic currents that are significantly stronger than the currents in the neutral singlet state, suggesting that the excited-state Baird aromaticity is more pronounced than the ground-state Hückel antiaromaticity in the neutral macrocycles.

Figure 6. Comparison of NICS(0)zz values of the macrocycles in different charge and spin states (singlet states: filled bars, triplet states: unfilled bars). Negative values indicate diatropic (aromatic) macrocyclic currents, positive values indicate paratropic (antiaromatic) macrocyclic currents. The corresponding data is available in the Supporting Information Table S3.
To interpret the data from Figure 6 in some more detail, it is important to note that the diamagnetic shielding is approximately proportional to the number of electrons contributing to the ring current divided by the radius of the ring. In line with this, we find that due to the enhanced number of electrons the shielding for the anionic systems is slightly more negative than for the cationic systems. This is particularly true when comparing the dianions with the dications, a trend that is also seen for smaller annulenes. Looking at the radii, we find that going from BCyc-Et to PCyc-Et the radius increases by about 50% (from 4 Å to 6 Å). All else equal, one would expect the NICS(0)zz values to decrease by a third. However, the NICS(0)zz values of the dianion and dication decrease by more than half (despite the increased number of electrons), highlighting that the aromaticity of these states in PCyc-Et is clearly reduced when compared to BCyc-Et.

To understand the reduced aromaticity for the macrocycles containing larger aromatic systems, it is instructive to view their VIST plots, as exemplified in Figure 7 for the dianions. BCyc-Et$^2$, shown on the left, exhibits the expected behavior for a globally aromatic system, as the dominant contributions for both, the NICS(0) and NICS(1)zz tensors, are approximately perpendicular to the plane of the macrocycle. A similar behavior but slightly less pronounced is found for NCyc-Et$^2$. The two larger macrocycles, ACyc-Et$^2$ and PCyc-Et$^2$, show an entirely different behavior; the NICS(1)zz tensor stands perpendicular to the aromatic unit and the NICS(0) tensor almost vanishes. This discussion supports the interpretation that the dianions of the smaller molecules become globally aromatic at the expense of local aromaticity of the individual units, whereas the local aromaticity is maintained at the cost of weaker global aromaticity for the larger macrocycles.

Figure 7. VIST plots for the dianions of the macrocycles, highlighting that global aromaticity dominates for BCyc-Et$^2$ and NCyc-Et$^2$ whereas local aromaticity remains for ACyc-Et$^2$ and PCyc-Et$^2$. Hydrogen atoms omitted for clarity.

Stokes shifts. As shown in Table 1, all the molecules studied possess strong Stokes shifts of more than 1 eV and this effect is particularly pronounced for BCyc-Et. In this section, we consider excited-state energies and shielding tensors to examine if these Stokes shifts can be seen as a consequence of excited-state aromaticity (see also Ref. 25). For this discussion, one would ideally compute shielding tensors for the $S_1$ state at the relaxed $S_1$ geometry. However, neither a geometry optimisation nor a
computation of shielding tensors in the $S_1$ state is routinely possible for molecules of the size considered here. A TDDFT optimisation of $S_1$ is not only computationally demanding but is also sensitive to spurious charge transfer problems\textsuperscript{26,27} in systems of the size considered here. Therefore, we optimised the triplet geometry instead, using unrestricted Kohn-Sham theory (UKS) as a computationally efficient and numerically stable alternative. At the UKS level, it is also straightforward to compute the shielding tensors relevant to the $T_1$ state. For the following analysis, it is worth noting that $S_1$ and $T_1$ are both dominated by the HOMO/LUMO transition and, thus, we expect that any statement made about the $T_1$ in terms of molecular geometry and electronic structure is also transferable to the $S_1$ (see Refs 23,28-30 for more information on the similarities of excited-state aromaticity in singlet and triplet excited states).

In the centre of Figure 8, we present the total energies of the $S_0$, $T_1$, $S_1$, $S_2$, and $S_3$ states computed at the $S_0$ and $T_1$ geometries. As discussed above, the transition to the $S_1$ state is symmetry-forbidden and the first band in the absorption spectrum relates to the degenerate $S_2/S_3$ states. These are located at 3.94 eV at the $S_0$ geometry, which corresponds to a computed absorption wavelength ($\lambda_{abs}$) of 315 nm. The photoluminescence wavelength ($\lambda_{PL}$) is approximated here via the energy difference of $S_1$ and $S_0$ at the $T_1$ geometry, obtaining a value of 1.91 eV or 648 nm. The computed photoluminescence energy is about 0.4 eV lower than the experimental value but, importantly, reflects the large Stokes shift and we are confident that the following discussion based on $T_1$ correctly captures the underlying physics related to the strong Stokes shifts observed. Figure 8 highlights that the large Stokes shift is obtained via a combination of three effects: (i) internal conversion from $S_2/S_3$ to $S_1$ according to Kasha’s rule, (ii) destabilization of $S_0$, and (iii) stabilization of $S_1$ as the excited-state geometry is relaxed. The first effect amounts to about 0.4 eV while the latter two contribute about 0.8 eV each. It should be noted that emission from the $S_1$ state is also symmetry forbidden at the excited-state geometry, highlighting that only rather weak luminescence is expected.

**Figure 8.** Comparison of energetic and magnetic properties of the electronic states of BCyc-Et optimized for the lowest singlet ($S_0$) and triplet ($T_1$). Energies relative to the $S_0$ minimum and the associated absorption ($\lambda_{abs}$) and photoluminescence ($\lambda_{PL}$) wavelengths to/from the $S_1$ states are shown in the center. VIST plots for the $S_0$ and $T_1$ states, each for the $S_0$ and $T_1$ geometries, are shown on the sides.
Interestingly, the total energy of the $S_2/S_3$ states is almost unaffected by the structure optimization. Within the MO picture, this difference can be explained by the fact that the structural relaxation strongly stabilizes the LUMO (from -2.4 to -4.8 eV at the PBE0/def2-SV(P) level), leaving the other orbitals largely unaffected. Therefore, only the $T_1$ and $S_1$, which are dominated by the HOMO/LUMO transition, are notably affected.

Moving beyond the MO picture, we can endeavor to explain the effects within the framework of excited-state aromaticity. Specifically, we propose that the geometry relaxation in the excited state produces enhanced excited-state aromaticity for $T_1/S_1$ in connection with enhanced ground-state antiaromaticity for $S_0$. To examine this hypothesis, we have computed chemical shielding tensors related to the $S_0$ and $T_1$ states at the $S_0$ (Figure 8, left) and $T_1$ (Figure 8, right) geometries. Starting with the chemical shielding of the $S_0$ state computed at the $S_0$ geometry, shown on the lower left in Figure 8, we find a slightly deshielded out-of-plane component for the NICS(0) tensor (NICS(0)$_{zz}$, +7.5 ppm). The NICS(1)$_{ax}$ tensor, on the other hand, shows one strongly shielded component perpendicular to the benzene unit, indicating its local aromaticity. The formal vertical excitation to $T_1$, represented in the upper left panel, induces only modest Baird aromaticity and the NICS(0)$_{zz}$ component only becomes slightly shielded (-6.3 ppm) along with minor variations of NICS(1)$_{ax}$. The situation changes dramatically once the triplet geometry is allowed to relax, as seen on the upper right in Figure 8. For the relaxed $T_1$ state one finds strong indications of global aromaticity for both the NICS(0) and NICS(1)$_{az}$ positions (-23.6 and -29.2 ppm). Staying at the $T_1$ geometry but performing computations for the $S_0$ state, we find notably enhanced antiaromaticity when compared to the $S_0$ geometry, yielding a dominant NICS(0) component of +14.9 ppm. However, the dominant component of NICS(1)$_{ax}$ (-20.4 ppm) keeps pointing away from the phenylene ring, highlighting that much of its local aromaticity is restored.

From the viewpoint of molecular structures, it is observed that the bond length alternation changes significantly when going from the ground- to excited-state optimized structure. In the ground state, there is a clear difference between the length of the vinylene double bond (1.35 Å) and that of the single bond connecting vinylene and phenylene (1.48 Å), whereas this difference is significantly reduced at the $T_1$ geometry (1.39 / 1.44 Å). The reduction in bond-length alternation is similar to what is observed in the open-chain analogue, poly($p$-phenylene vinylene) (PPV). However, the consequences are much more pronounced in the cyclic system presented here, noting that the stabilization of $S_1$ upon geometry relaxation in open-chain PPV amounts to only about 0.2 eV, as opposed to the 0.8 eV found here.

**Conclusions**

The results of this detailed experimental and computational study of a set of $[2.2.2.2]$cyclophane-tetraenes show that systematic variations of the molecular structure can indeed produce pronounced
variations in terms of their redox- and photochemistry. The study advances our fundamental understanding of such systems, helping to develop structure–property relationships and molecular design guidelines for π-conjugated macrocycles, paving the way to the development of macrocycles for new applications. The structural variations investigated, the introduction of electron-withdrawing ethyl or hexyl ester groups and the variation of the aromatic units, yielded a set of six ester-substituted π-conjugated macrocycles and were found to have drastic effects on some of the properties but also on the synthesis.

While the synthesis of some cyclization precursors required considerable optimization, the synthesis of the macrocycles themselves was generally found to be straightforward when adapting previously reported conditions, except for the synthesis of the ester-substituted macrocycle with anthracene units, ACyc-Et, which suffered from poor reproducibility. In contrast to the other macrocycles, the computations indicated a folded conformation for ACyc-Et, leading us to conclude that small structural variations can result in significant differences in conformation that may affect the synthesis. The folded conformation also resulted in a markedly different shape of the absorption spectrum due to the entailing loss of symmetry.

We can further conclude that the introduction of hexyl instead of ethyl ester groups can give π-conjugated macrocycles that are viscous oils. Even with large aromatic pyrene units, these macrocycles did not crystallize during prolonged storage and dissolved well in organic solvents. The hexyl ester-substituted macrocycles also showed a significantly more intense photoluminescence than their ethyl ester analogs, which we attributed to enhanced shielding of the chromophores by the larger hexyl ester groups, enabling emission from the formally symmetry-forbidden lowest singlet excited state. In contrast to the photoluminescence spectra, the absorption spectra of the ethyl and hexyl ester analogs were almost identical.

Regarding the electrochemical properties, the introduction of the ester groups was found to drastically shift the first reduction wave to higher potential in the cyclic voltammetry measurements (compared to the previously reported unsubstituted macrocycle [2.2.2.2]paracyclophane-1,9,17,25-tetraene, denoted BCyc in this work). Computations showed that even more pronounced shifts occur for the reduction to the tetra- and hexaanions. In contrast, increasing the size of the aromatic units was found to have its most pronounced effect on the oxidation to the tetra- and hexacations. From EPR spectroelectrochemical measurements, we conclude that the two reversible reduction steps observed in the cyclic voltammogram of BCyc-Et are two consecutive two-electron processes. This reversible fourfold reduction, in combination with the commercial availability of one of the cyclisation precursors and the lower molecular weight compared to the other macrocycles, renders BCyc-Et the most interesting macrocycle to be used, for example, as a building block for battery electrode materials or as component of a multielectron photoredox catalyst.
A detailed investigation of the ring currents and chemical shielding allowed us to rationalize many of the observed optoelectronic properties in the context of local and global aromaticity in different planes. The recently developed method for the visualization of chemical shielding tensors (VIST) was found to provide particularly useful insights in this regard. Most importantly, the method provided an intuitive explanation of the large Stokes shifts of up to 1.6 eV, showing that emission occurs at a geometry where excited-state aromaticity and ground-state antiaromaticity are both significantly increased, thus, narrowing the gap between the states. A more detailed analysis of excited-state energies was presented to substantiate this viewpoint.

From the weaker global aromaticity and antiaromaticity in the different charge and spin states after introduction of the ester groups, it can be concluded that the ester-substituted macrocycles have additional flexibility of placing positive as well as negative charge on the ester groups, largely explaining the observed redox properties; the effect was further confirmed by electron density difference plots. It can further be concluded that, as a general trend, increasing the size of the aromatic units results in weaker global aromaticity but stronger local aromaticity.

In summary, we have shown that [2.2.2.2]cyclophanetetraenes provide versatile scaffolds for applications as molecular materials due to their unusual optoelectronic properties along with their high tunability. Their remarkable properties, in particular their large Stokes shifts and the accessibility of a variety of charged states, were traced back to their formal ground state antiaromaticity – illustrated via VIST plots – along with high structural flexibility. We have shown that their properties can be effectively tuned via two independent strategies: (i) introduction of electron-withdrawing groups to allow for easier reduction and (ii) variation of the aromatic groups to alter the balance between local and global aromaticity, indicating that a wide range of target properties can be achieved using this remarkable class of molecules as basis for molecular design.

**Methods**

Experimental details for the synthesis and purification of all compounds as well as characterization results confirming their identity and purity are provided in the Supporting Information (see section 1.3 for compounds 1a-e, section 1.4 for precursors 2a-e, section 1.5 for precursors 3b-d, and section 1.6 for macrocycles BCyc-Et to PCyc-Hx).

UV-vis absorption spectra were recorded on an Agilent Cary 60 UV-vis spectrophotometer at room temperature. The measurements were carried out with 5 μM solutions in CHCl₃ at a scan rate of 300 nm min⁻¹ and a data interval of 0.5 nm. Photoluminescence (PL) spectra were acquired on an Agilent Cary Eclipse fluorescence spectrophotometer with 5 μM solutions in CHCl₃ at a scan rate of 120 nm min⁻¹ and a data interval of 1 nm. The excitation and emission slits were set to 5 nm, the emission and excitation filters were set to ‘auto’ setting, and the detector voltage was set to ‘high’ (800 V). For PCyc-
Et and PCyc-Hx additional spectra were recorded using ‘medium’ (600 V) detector voltage (Supporting Information Figure S44), due to the peak exceeding the maximum of 1000 counts with the ‘high’ setting.

Cyclic voltammetry measurements were performed in an argon atmosphere glovebox (LabStar, MBraun) using a PalmSens4 potentiostat controlled via Bluetooth connection in a standard three-electrode setup. Platinum disk electrodes of 2 mm diameter, a silver wire, and a platinum wire served as working, quasi-reference, and auxiliary electrodes, respectively. Small glass test tube vessels were used as open electrochemical cells. The electrolyte volume was below 0.4 mL. After the measurements, an arbitrary amount of ferrocene (internal reference) was added to the solution to evaluate the redox potentials of the studied compounds (Supporting Information Figure S45 and Figure S48). Cyclic voltammograms were fitted to simulated voltammograms using the DigiSim 3.03b software (Bioanalytical Systems). For steady-state voltammetry (Supporting Information Figure S47), platinum disk ultramicroelectrodes of 25 μm diameter were used as the working electrode. Details for the EPR spectroelectrochemical measurements are provided in the Supporting Information section 5.

Computations considered singlet states of charge -6, -4, -2, -1, 0, +1, +2, +4, +6 as well as triplet states of charge -4, 0, +4. Geometries for these electronic states were optimized in vacuum using the PBE0 functional along with the def2-SV(P) basis set and the D3 dispersion correction in its optimized power parameterization. The nature of the stationary points as minima was verified using a finite difference Davidson procedure to avoid computation of the full ab initio Hessian.

Redox potentials were determined via single-point computations using PBE0-D3 along with the def2-SV(P) basis set (possessing additional diffuse basis functions) and including solvation effects using a conductor-like polarizable continuum model considering a dielectric constant ε of 10.125 to represent 1,2-dichloroethane. First, the ionization potential (IP) of a state of molecular charge (z) was computed according to

$$\text{IP}(z) = G(z) - G(0)$$

where G(z) corresponds to the total free energy in solution at the PBE0-D3/def2-SVPD level. No vibrational effects were included considering that a vibrational analysis was unfeasible for the largest systems considered and noting that vibrational effects are generally expected to play a minor role for redox potentials. Subsequently the redox potential for any given redox couple $z_1/z_2$ was computed as

$$E(z_1/z_2) = \frac{\text{IP}(z_2) - \text{IP}(z_1)}{e \times (z_2 - z_1)} - E_{\text{ref}}$$

where $e$ is the unit charge and $E_{\text{ref}}$ is the absolute potential of the reference electrode (cf. Ref. 39). A value of 4.70 V was used for $E_{\text{ref}}$. Redox potentials for the reductions were computed in complete analogy, only using the electron affinity instead of the IP. The values reported pertain to the redox couples (-6/-4), (-4/-2), (-2/-1), (-1/0), (0/+1), (+1/+2), (+2/+4), (+4/+6). These calculations were carried out in Q-Chem.

40,41
Absorption wavelengths were computed using time-dependent DFT (TDDFT) with the \( \omega \text{PBEh} \) functional\(^{32,42} \) (using 20\% global Hartree-Fock exchange and \( \omega = 0.1 \) a.u.) and the \text{def2-SV(P)} basis set and considering solvation in 1,2-dichloroethane (\( \varepsilon = 10.125, \varepsilon_\infty = 2.087 \)). Approximate photoluminescence energies were computed at the triplet geometries, optimized via unrestricted Kohn-Sham (UKS) theory, considering that TDDFT geometry optimizations are not feasible for the largest systems considered here.

Nucleus independent chemical shifts (NICS)\(^{43} \) were computed at the PBE0/\text{def2-SVP} level using gauge including atomic orbitals\(^{44} \) as implemented in Gaussian 09.\(^{45} \) NICS tensors were represented graphically using the VIST (visualization of chemical shielding tensors) method\(^{16} \) as implemented in a developmental version of TheoDORE 2.3\(^{46} \) and using VMD as a graphical backend.\(^{47} \)

**Supporting Information**

The available Supporting Information for this article contains the synthetic procedures and essential compound characterization, the \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra, further photoluminescence spectra and cyclic voltammograms (including the voltammograms at defined concentrations and the corresponding data), details for the EPR spectroelectrochemistry, and further computational data and plots (including anisotropy of the induced current density (ACID) plots for comparison).

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Supporting Information

Functional group introduction and aromatic unit variation in a set of π-conjugated macrocycles: revealing the central role of local and global aromaticity

Martina Rimmele, a,b Wojciech Nogala, c Maryam Seif-Eddine, a Maxie M. Roessler, a Martin Heeney, a,b Felix Plasser, d,* Florian Glöcklhofer a,b,*

a Department of Chemistry, Imperial College London, London W12 0BZ, United Kingdom
b Centre for Processable Electronics, Imperial College London, London W12 0BZ, United Kingdom
c Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
d Department of Chemistry, Loughborough University, Loughborough LE11 3TU, United Kingdom
* E-mail: f.plasser@lboro.ac.uk, f.glocklhofer@imperial.ac.uk

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1 Synthesis

Reagents and solvents were purchased from commercial suppliers and used without further purification, including compound 3a and the halogenated precursors for the synthesis of compounds 1a-e, with the exception of 2,6-dibromoanthracene for the synthesis of compound 1c, which was obtained from 2,6-dibromoanthraquinone following a previously reported procedure.¹

1.1 Overview of synthetic routes

![Chemical structures and reactions](image)

Figure S1. Synthetic routes to π-conjugated macrocycles with ethyl ester groups (BCyc-Et, NCyc-Et, ACyc-Et, PCyc-Et) or hexyl ester groups (BCyc-Hx, PCyc-Hx) and different aromatic units. Compounds 1a-d were obtained from halogenated starting materials.
Figure S2. Synthetic route to compound 2e (including the halogenated starting material) and unsuccessful conversion into compound 3e.

1.2 Instrumentation

Purification by preparative GPC was carried out on a LaboACE LC-5060 (Japan Analytical Industry Co., Tokyo, JAPAN) recycling GPC system equipped with a JAIGEL-2HR column and a TOYDAD800-S detector. CHCl₃ was used as the eluent at a flow rate of 10 mL min⁻¹.

NMR spectra were recorded at 400 MHz for ¹H and 101 MHz for ¹³C on a Bruker AV-400 spectrometer. High-resolution mass spectrometry was carried out on systems from Thermo Scientific for atmospheric pressure chemical ionization (APCI) and Waters for electrospray ionization (ESI). While the Thermo Scientific system gives the actual mass of the ionized compounds, the Waters system is calibrated to give the mass of the neutral compounds. This was considered when calculating the m/z values for comparison with the measurements.

1.3 Synthesis of compounds 1a-e

The procedures for synthesis of compounds 1a-e were inspired and adapted from previous reports.²⁻⁴

1.3.1 α₁,α₄-Dioxo-1,4-benzenedicarboxylic acid, 1,4-diethyl ester (1a)

1,4-Diodobenzene (3.50 g, 10.6 mmol, 1.0 equiv.) was dissolved in 150 mL dry degassed THF under nitrogen and cooled to -78 °C with an acetone/dry ice bath. t-BuLi (1.7 M in pentane, 25 mL, 42.5 mmol, 4.0 equiv.) was then added slowly by cannula transfer under vigorous stirring. The resulting mixture was kept at -78 °C for 2 h and was then cooled to -94 °C with an acetone/N₂(liq.) bath for the quick addition of diethyl oxalate (14 mL, 105 mmol, 9.9 equiv.). The reaction was kept at -94 °C for 1 h and was then allowed to slowly warm to r.t. After stirring at r.t. for 1 h, the reaction was poured into 2 M aqueous HCl (200 mL) and extracted three times with CH₂Cl₂. The combined organic phases were extracted with 2 x 150 mL sat. aqu. Na₂SO₃ solution and dried over MgSO₄. The solvent was evaporated
under reduced pressure and the remaining diethyl oxalate was distilled off under high vacuum. The compound was purified by column chromatography on silica gel using CH$_2$Cl$_2$/petroleum ether (1:1) as eluent. For removing trace amounts of diethyl oxalate, the now crystalline product was suspended in hexane and filtered off, yielding compound 1a as pure, slightly yellow crystals (1.30 g, 4.67 mmol, 44%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.16 (s, 4H), 4.47 (q, $J = 7.1$ Hz, 4H), 1.44 (t, $J = 7.2$ Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 185.3, 162.9, 136.9, 130.4, 63.0, 14.2 ppm. HRMS (ESI): $m/z$ calcd for C$_{12}$H$_9$O$_6$: 249.0399 [M–C$_2$H$_5$]; found 249.0390.

1.3.2 $\alpha^2,\alpha^6$-Dioxo-2,6-naphthalenediacetic acid, 2,6-diethyl ester (1b)

2,6-Dibromonaphthalene (3.04 g, 10.6 mmol, 1.0 equiv.) was dissolved in 150 mL dry degassed Et$_2$O under nitrogen and cooled to -78 °C with an acetone/dry ice bath. t-BuLi (1.7 M in pentane, 25 mL, 42.5 mmol, 4.0 equiv.) was then added slowly by cannula transfer under vigorous stirring. The resulting mixture was kept at -78 °C for 2 h and was then cooled to -94 °C with an acetone/N$_2$(liq.) bath for the quick addition of diethyl oxalate (14 mL, 105 mmol, 9.9 equiv.). The reaction was kept at -94 °C for 1 h and was then allowed to slowly warm to r.t. After stirring at r.t. for 1 h, the reaction was poured into 2 M aqueous HCl (200 mL) and extracted three times with CH$_2$Cl$_2$. The combined organic phases were dried over MgSO$_4$, the solvent was evaporated under reduced pressure, and the remaining diethyl oxalate was distilled off under high vacuum. The compound was purified by column chromatography on silica gel using CH$_2$Cl$_2$/petroleum ether (1:1) as eluent. For removing trace amounts of diethyl oxalate, the now crystalline product was suspended in hexane and filtered off, yielding compound 1b as pure white powder (2.24 g, 6.82 mmol, 64%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.62 (m, 2H), 8.15 (dd, $J = 8.6$, 1.6 Hz, 2H), 8.10 (d, $J = 8.6$ Hz, 2H), 4.52 (q, $J = 7.1$ Hz, 4H), 1.47 (t, $J = 7.1$ Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 185.8, 163.4, 135.4, 132.8, 132.7, 131.0, 125.5, 62.8, 14.3 ppm. HRMS (APCI): $m/z$ calcd for C$_{18}$H$_{17}$O$_6$: 329.1020 [M+H]$^+$; found 329.1020.

1.3.3 $\alpha^2,\alpha^6$-Dioxo-2,6-anthracenediacetic acid, 2,6-diethyl ester (1c)

2,6-Dibromoanthracene (2.00 g, 5.95 mmol, 1.0 equiv.) was dissolved in dry Et$_2$O (120 mL) under nitrogen and cooled to -78 °C with an acetone/dry ice bath. n-BuLi (2.5 M in hexanes, 9.5 mL, 23.8 mmol, 4.0 equiv.) was then added slowly under vigorous stirring. The resulting mixture was kept
at -78 °C for 1 h and was then allowed to warm to r.t. After 2 h at r.t., the reaction was cooled to -94 °C with an acetone/N₂(liq.) bath for the quick addition of diethyl oxalate (8.0 mL, 58.9 mmol, 9.9 equiv.). The reaction was kept at -94 °C for 1 h and was then allowed to slowly warm to r.t. After stirring at r.t. for 1 h, the reaction was poured into 2 M aqueous HCl (200 mL) and extracted three times with CH₂Cl₂. The combined organic phases were dried over MgSO₄ and the solvent was evaporated under reduced pressure. The resulting crude product was filtered over a thick pad of silica using petroleum ether/CH₂Cl₂ (1:1) to elute diethyl oxalate and other impurities before eluting the pure product with CH₂Cl₂. After evaporation of the solvent, compound 1c was obtained as pure yellow powder (0.69 g, 1.82 mmol, 31%).

1H NMR (400 MHz, CDCl₃): δ = 8.81 (d, J = 1.8 Hz, 2H), 8.65 (s, 2H), 8.14 (d, J = 8.9 Hz, 2H), 8.07 (dd, J = 8.9, 1.7 Hz, 2H), 4.54 (q, J = 7.2 Hz, 4H), 1.49 (t, J = 7.2 Hz, 6H) ppm.

13C NMR (101 MHz, CDCl₃): δ = 186.0, 163.7, 135.3, 133.7, 132.3, 131.1, 130.1, 129.9, 123.4, 62.8, 14.3 ppm. HRMS (APCI): m/z calcd for C₃₂H₂₁O₆+: 379.1176 [M+H]+; found: 379.1167.

1.3.4 α₁,α₆-Dioxo-1,6-pyrenediacetic acid, 1,6-diethyl ester (1d)

1,6-Dibromopyrene (3.00 g, 8.33 mmol, 1.0 equiv.) was dissolved in dry THF (150 mL) under nitrogen and cooled to -78 °C with an acetone/dry ice bath. n-BuLi (1.6 M in hexanes, 20.3 mL, 32.5 mmol, 3.9 equiv.) was then added slowly under vigorous stirring. The resulting mixture was kept at -78 °C for 1 h and was then allowed to warm to r.t. After 2 h at r.t., the reaction was cooled to -94 °C with an acetone/N₂(liq.) bath for the quick addition of diethyl oxalate (11 mL, 82.5 mmol, 9.9 equiv.). The reaction was kept at -94 °C for 1 h and was then allowed to slowly warm to r.t. After stirring at r.t. for 1 h, the reaction was poured into 2 M aqueous HCl (100 mL) and extracted three times with CH₂Cl₂. The combined organic phases were dried over MgSO₄ and the solvent was evaporated under reduced pressure. The resulting crude product was recrystallized from EtOH, yielding compound 1d as pure, bright orange powder (2.02 g, 5.02 mmol, 60%). 1H NMR (400 MHz, CDCl₃): δ = 9.39 (d, J = 9.3 Hz, 2H), 8.43 (d, J = 8.1 Hz, 2H), 8.34 (d, J = 8.2 Hz, 2H), 8.31 (d, J = 9.4 Hz, 2H), 4.56 (q, J = 7.1 Hz, 4H), 1.50 (t, J = 7.2 Hz, 6H) ppm. 13C NMR (101 MHz, CDCl₃): δ = 189.1, 164.7, 134.6, 131.5, 130.67, 130.64, 127.8, 126.7, 126.0, 124.5, 62.9, 14.4 ppm. NMR spectra in good agreement with the literature.

1.3.5 \( \alpha^9,\alpha^{10}\)-Dioxo-9,10-anthracenediacetic acid, 9,10-diethyl ester (1e)

9,10-Dibromoanthracene (1.50 g, 4.46 mmol, 1.0 equiv.) was dissolved in dry \( \text{Et}_2\text{O} \) (80 mL) under nitrogen and cooled to -78 °C with an acetone/dry ice bath. \( n\)-BuLi (2.5 M in hexanes, 11 mL, 26.8 mmol, 6.0 equiv.) was then added slowly under vigorous stirring. The resulting mixture was kept at -78 °C for 1 h and was then allowed to warm to r.t. After 2 h at r.t., the reaction was cooled to -94 °C with an acetone/\( \text{N}_2\) (liq.) bath for the quick addition of diethyl oxalate (6.0 mL, 44.2 mmol, 9.9 equiv.). The reaction was kept at -94 °C for 1 h and was then allowed to slowly warm to r.t. After stirring at r.t. for 1 h, the reaction was poured into 2 M aqueous HCl (200 mL) and extracted three times with \( \text{CH}_2\text{Cl}_2 \). The combined organic phases were dried over MgSO₄ and the solvent was evaporated under reduced pressure. The resulting crude product was recrystallized from EtOH, yielding compound 1e as pure, bright yellow powder (0.93 g, 2.46 mmol, 55%). \(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.98 - 7.87 \) (m, 4H), 7.64 - 7.56 (m, 4H), 4.38 (q, \( J = 7.1 \) Hz, 4H), 1.32 (t, \( J = 7.1 \) Hz, 6H) ppm. \(^{13}\)C NMR (101 MHz, CDCl₃): \( \delta = 192.3, 162.3, 134.1, 128.3, 127.8, 124.9, 63.4, 14.1 \) ppm. HRMS (APCI): \( m/z \) calcd for \( \text{C}_{22}\text{H}_{19}\text{O}_6^+ \): 379.1176 [M+H]; found: 379.1174.

1.4 Synthesis of compounds 2a-e

The synthesis of compounds 2a-e was carried out using standard procedures for the saponification of carboxylic esters. The procedure for the synthesis of 2c-e was further inspired by previous reports.⁴

1.4.1 \( \alpha^1,\alpha^4\)-Dioxo-1,4-benzenedicarboxylic acid (2a)

2 M aqueous NaOH (4.0 mL) was added to compound 1a (0.40 g, 1.44 mmol, 1.0 equiv.) and the mixture stirred at r.t. overnight. The mixture was acidified to pH 1 with 4 M aqueous HCl and extracted three times with \( \text{Et}_2\text{O} \). The combined organic layers were dried over MgSO₄ and the solvent was evaporated under reduced pressure to give compound 2a as a white powder (0.30 g, 1.35 mmol, 94%).
1H NMR (400 MHz, DMSO-d$_6$): $\delta = 8.14$ (s, 4H) ppm. 13C NMR (101 MHz, DMSO-d$_6$): $\delta = 187.8$, 165.0, 136.3, 130.1 ppm. HRMS (ESI): $m/z$ calc'd for C$_{10}$H$_5$O$_6$: 221.0086 [M-H]; found: 221.0093.

1.4.2 $\alpha^2,\alpha^6$-Dioxo-2,6-naphthalenediacetic acid (2b)

![Chemical structure of 2b](image)

Molecular Weight: 328.32

2 M aqueous NaOH (30 mL) was added to compound 1b (1.50 g, 4.57 mmol, 1.0 equiv.) and the mixture stirred at r.t. overnight. The mixture was acidified to pH 1 with 4 M aqueous HCl and extracted three times with Et$_2$O. The combined organic layers were dried over MgSO$_4$ and the solvent was evaporated under reduced pressure to give compound 2b as a white powder (1.20 g, 4.41 mmol, 96%). 1H NMR (400 MHz, DMSO-d$_6$): $\delta = 8.72$ (d, $J = 2.0$ Hz, 2H), 8.42 (d, $J = 8.5$ Hz, 2H), 8.08 (dd, $J = 8.5, 1.7$ Hz, 2H) ppm. 13C NMR (101 MHz, DMSO-d$_6$): $\delta = 188.4$, 165.6, 134.8, 132.2, 132.0, 131.2, 124.8 ppm. HRMS (ESI): $m/z$ calc'd for C$_{14}$H$_7$O$_6$: 271.0243 [M-H]; found: 271.0236.

1.4.3 $\alpha^2,\alpha^6$-Dioxo-2,6-anthracenediacetic acid (2c)

![Chemical structure of 2c](image)

Molecular Weight: 378.38

Compound 1c (0.44 g, 1.16 mmol, 1.0 equiv.) was suspended in 30 mL EtOH. NaHCO$_3$ (2.63 g, 31.3 mmol, 27 equiv.) dissolved in 15 mL H$_2$O was then added and the reaction was heated to reflux overnight. The reaction was then allowed to cool to r.t., poured into 150 mL 2 M aqueous HCl, and extracted three times with Et$_2$O. The combined organic phases were dried over MgSO$_4$ and the solvent was evaporated under reduced pressure. For removing residues of H$_2$O, the compound was redissolved in acetone and the solvent was evaporated again under reduced pressure to give compound 2c as a red powder (0.36 g, 1.12 mmol, 97%). 1H NMR (400 MHz, DMSO-d$_6$): $\delta = 9.07$ (s, 2H), 8.88 (d, $J = 1.7$ Hz, 2H), 8.31 (d, $J = 9.0$ Hz, 2H), 7.99 (dd, $J = 8.9, 1.7$ Hz, 2H) ppm. 13C NMR (101 MHz, DMSO-d$_6$): $\delta = 188.5$, 165.9, 134.7, 133.0, 131.7, 130.2, 130.1 (two C according to HSQC spectrum), 122.6 ppm. HRMS (ESI): $m/z$ calc'd for C$_{18}$H$_9$O$_6$: 321.0399 [M-H]; found: 321.0405.
1.4.4 \( \alpha^1,\alpha^6 \)-Dioxo-1,6-pyrenediacetic acid (2d)

![Chemical structure](image)

Compound 1d (2.30 g, 5.72 mmol, 1.0 equiv.) was suspended in 60 mL EtOH. NaHCO\(_3\) (13.0 g, 154 mmol, 27 equiv.) dissolved in 160 mL H\(_2\)O was then added and the reaction was heated to reflux overnight. The reaction was then allowed to cool to r.t., poured into 200 mL 2 M aqueous HCl, and the resulting precipitate was filtered off using a sintered glass funnel. For removing residues of H\(_2\)O, the compound was dissolved in acetone and the solvent was evaporated under reduced pressure to give compound 2d as a red powder (1.78 g, 5.14 mmol, 90%). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 9.24\) (d, \(J = 9.3\) Hz, 2H), 8.58 (d, \(J = 8.1\) Hz, 2H), 8.56 – 8.49 (m, 4H) ppm. \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta = 191.2, 166.2, 133.7, 130.6\) (two C according to HSQC spectrum), 130.1, 126.7, 126.5, 126.4, 123.4 ppm. NMR spectra in accordance with the literature. \(^4\) HRMS (ESI): \(m/z\) calcd for C\(_{20}\)H\(_9\)O\(_6\)\(-\): 345.0399 \([M-H]^{-}\); found: 345.0405.

1.4.5 \( \alpha^9,\alpha^{10} \)-Dioxo-9,10-anthracenediacetic acid (2e)

![Chemical structure](image)

Compound 1e (1.83 g, 4.84 mmol, 1.0 equiv.) was suspended in 100 mL EtOH. NaHCO\(_3\) (11.0 g, 131 mmol, 27 equiv.) dissolved in 270 mL H\(_2\)O was then added and the reaction was heated to reflux overnight. The reaction was then allowed to cool to r.t., poured into 200 mL 2 M aqueous HCl, and extracted three times with Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\) and the solvent was evaporated under reduced pressure to give compound 2e as a yellow powder (1.44 g, 4.47 mmol, 92%). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.97 – 7.88\) (m, 4H), 7.81 – 7.65 (m, 4H) ppm. \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta = 194.4, 163.6, 134.3, 128.0, 127.1, 124.6\). HRMS (ESI): \(m/z\) calcd for C\(_{17}\)H\(_9\)O\(_4\): 277.0501 \([M-COOH]^{-}\); found: 277.0510.
1.5 Synthesis of compounds 3b-d

The synthesis of compounds 3b-d was carried out by adapting previously reported procedures.\textsuperscript{5,6}

Notes: (i) Compound 3a was obtained from commercial suppliers. (ii) The synthesis of compound 3e was not successful following the procedure used for the synthesis of compounds 3b-d.

1.5.1 2,6-Naphthalenediacetic acid (3b)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{2b} & \quad \text{3b}
\end{align*}
\]

Molecular Weight: 272.21

Compound 2b (0.50 g, 1.84 mmol, 1.0 equiv.) and NaI (0.33 g, 2.20 mmol, 1.2 equiv.) were dissolved in 10 mL acetic acid in a reaction vial equipped with a septum. H\textsubscript{3}PO\textsubscript{4} (50 wt\% in H\textsubscript{2}O, 0.5 mL, 4.78 mmol, 2.6 equiv.) was added and the mixture was degassed with nitrogen for 15 min and subsequently heated to reflux under nitrogen for 4 days. After cooling to r.t., water (2 mL) was added and the precipitate was filtered off and dried in vacuo, yielding compound 3b (0.24 g, 0.98 mmol, 53\%) as a white powder. \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}): \(\delta = 12.35\) (bs, 2H), 7.81 (d, \(J = 8.4\) Hz, 2H), 7.74 (m, 2H), 7.41 (dd, \(J = 8.4, 1.6\) Hz, 2H), 3.73 (s, 4H) ppm. \textsuperscript{13}C NMR (101 MHz, DMSO-d\textsubscript{6}): \(\delta = 172.7, 132.4, 131.8, 128.1, 127.4, 127.3, 40.8\) ppm. HRMS (ESI): \(m/z\) calcd for C\textsubscript{14}H\textsubscript{11}O\textsubscript{4}: 243.0657 \([M-H]^-\), found: 243.0661.

1.5.2 2,6-Anthracenediacetic acid (3c)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{2c} & \quad \text{3c}
\end{align*}
\]

Molecular Weight: 322.27

Compound 2c (0.50 g, 1.55 mmol, 1.0 equiv.) and NaI (0.22 g, 1.47 mmol, 0.95 equiv.) were dissolved in 12.5 mL acetic acid in a reaction vial equipped with a septum. H\textsubscript{3}PO\textsubscript{4} (50 wt\% in H\textsubscript{2}O, 0.5 mL, 4.8 mmol, 3.1 equiv.) was added and the mixture was degassed with nitrogen for 15 min and subsequently heated to reflux under nitrogen for 4 days. After cooling to r.t., water (5 mL) was added and the precipitate was filtered off and dried in vacuo, yielding compound 3c (0.35 g, 1.19 mmol, 77\%) as an off-white powder. \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}): \(\delta = 12.41\) (bs, 2H), 8.48 (s, 2H), 8.03 (d, \(J = 8.7\) Hz, 2H), 7.92 (d, \(J = 1.6\) Hz, 2H), 7.42 (dd, \(J = 8.7, 1.7\) Hz, 2H), 3.79 (s, 4H) ppm. \textsuperscript{13}C NMR (101 MHz, DMSO-d\textsubscript{6}): \(\delta = 172.6, 132.4, 131.8, 128.1, 127.4, 127.3, 40.8\) ppm. HRMS (APCI): \(m/z\) calcd for C\textsubscript{18}H\textsubscript{15}O\textsubscript{4}\textsuperscript{+}: 295.0965 \([M+H]^+\); found: 295.0960.
1.5.3 1,6-Pyrenediacetic acid (3d)

Compound 2d (0.45 g, 1.30 mmol, 1.0 equiv.) and NaI (0.19 g, 1.27 mmol, 0.98 equiv.) were dissolved in 5.7 mL acetic acid in a reaction vial equipped with a septum. H₃PO₄ (50 wt% in H₂O, 0.44 mL, 4.0 mmol, 3.1 equiv.) was added and the mixture was degassed with nitrogen for 15 min and subsequently heated to reflux under nitrogen for 4 days. After cooling to r.t., THF (17 mL) was added and the precipitate was filtered off and dried in vacuo, yielding compound 3d (0.39 g, 1.23 mmol, 94%) as a pale-yellow powder. ¹H NMR (400 MHz, DMSO-d₆): δ = 12.51 (bs, 2H), 8.30 – 8.18 (m, 6H), 8.01 (d, J = 7.9 Hz, 2H), 4.35 (s, 4H) ppm. ¹³C NMR (101 MHz, DMSO-d₆): δ = 172.8, 129.8, 129.6, 128.9, 127.5, 124.8, 123.3 ppm (note: methylene carbon signal hidden by solvent signal). NMR spectra in accordance with the literature. HRMS (APCI): m/z calcd. for C₂₀H₁₅O₄⁺: 319.0965 [M+H]+; found: 319.0962.

1.6 Synthesis of the π-conjugated macrocycles

The macrocycles were prepared adapting a previously reported procedure.

1.6.1 General procedure

To a mixture of the respective dioxodiacetic acid 2a-d (1.0 equiv.) and diacetic acid 3a-d (1.0 equiv.) in varying amounts of dry degassed THF under nitrogen, triethylamine (9.5 equiv., Et₃N) and acetic anhydride (15 equiv., Ac₂O) were added. The reaction mixture was heated to reflux under nitrogen for 3 days before the respective alkyl bromide (44 equiv., RBr), the respective alcohol (82 equiv., ROH), and 1,8-diazabicyclo[5.4.0]undec-7-ene (21 equiv., DBU) were added. After refluxing for another 24 h, the reaction was allowed to cool to r.t., poured into 1 M aqueous HCl (350 mL), extracted three times with CHCl₃, and dried over MgSO₄. Evaporation of the solvent under reduced pressure gave the crude product, which was split into two fractions for purification by gel permeation chromatography (GPC).
Each fraction was dissolved in CHCl₃ and filtered through a 0.2 µm syringe filter before loading the GPC column with the resulting solution (CHCl₃ was used as eluent for the GPC).

**Alternative procedure using a syringe pump for the addition of the dioxodiacetic and diacetic acid:**
To a refluxing mixture of Et₃N (9.5 equiv.) and Ac₂O (15 equiv.) in dry degassed THF (400 mL) under nitrogen, the respective dioxodiacetic acid (1.0 equiv.) and diacetic acid (1.0 equiv.) dissolved in 20 mL dry degassed THF were added over 10 h (2 mL h⁻¹) using a syringe pump. The reaction was refluxed for 3 days (starting with the addition of the reactants) before adding the respective alkyl bromide (44 equiv., RBr), the respective alcohol (82 equiv., ROH) and DBU (21 equiv.) and proceeding with next steps in accordance with the general procedure described above.

### 1.6.2 Macrocycle BCyc-Et

![Chemical structure of BCyc-Et](image)

**Synthesis of macrocycle BCyc-Et following the general procedure:**
α¹,α⁴-Dioxo-1,4-benzenediacetic acid 2a (250 mg, 1.13 mmol, 1.0 equiv.), 1,4-benzenediacetic acid 3a (219 mg, 1.13 mmol, 1.0 equiv.), dry degassed THF (400 mL), Et₃N (1.5 mL, 10.7 mmol, 9.5 equiv.), Ac₂O (1.6 mL, 16.9 mmol, 15 equiv.), EtBr (3.7 mL, 49.5 mmol, 44 equiv.), EtOH (5.4 mL, 92.3 mmol, 82 equiv.) and DBU (3.5 mL, 23.6 mmol, 21 equiv.) were used. Purification by GPC and evaporation of the solvent afforded macrocycle BCyc-Et as a dark yellow oil (87.9 mg, 0.089 mmol, 16%), which slowly crystallised over time and upon further drying in vacuo to give a yellow powder.

1H NMR (400 MHz, CDCl₃): δ = 6.93 (s, 16H), 4.31 (q, J = 7.1 Hz, 16H), 1.31 (t, J = 7.2 Hz, 24H) ppm. 13C NMR (101 MHz, CDCl₃): δ = 167.8, 137.5, 134.6, 129.9, 62.1, 14.2 ppm. HRMS (APCI): m/z calcd. for C₅₆H₅₆O₁₆⁺: 984.3563 [M⁺]; found: 984.3525. HRMS (ESI): m/z calcd. for C₅₆H₅₆O₁₆Na⁺: 1007.3466 [M⁺Na⁺]; found: 1007.3480.

**Synthesis of macrocycle BCyc-Et following the alternative procedure (using a syringe pump):**
The same amounts of reagents and reactants as for the synthesis following the general procedure were used. Purification by GPC and evaporation of the solvent afforded macrocycle BCyc-Et (93.6 mg, 0.095 mmol, 17%) as a dark yellow oil, which slowly crystallised over time to give a yellow powder.
1.6.3 Macrocycle BCyc-Hx

\[
\begin{align*}
\text{Molecular Weight:} & \quad 222.15 \\
\text{Molecular Weight:} & \quad 194.19
\end{align*}
\]

Synthesis of macrocycle BCyc-Hx following the alternative procedure (using a syringe pump):
\(\alpha^1,\alpha^4\)-dioxo-1,4-benzenediacetic acid 2a (250 mg, 1.13 mmol, 1.0 equiv.), 1,4-benzenediacetic acid 3a (219 mg, 1.13 mmol, 1.0 equiv.), dry degassed THF (400 mL), Et\(\text{3}N\) (1.5 mL, 10.7 mmol, 9.5 equiv.), Ac\(\text{2}O\) (1.6 mL, 16.9 mmol, 15 equiv.), 1-bromohexane (7.0 mL, 49.5 mmol, 44 equiv.), 1-hexanol (11.6 mL, 92.3 mmol, 82 equiv.) and DBU (3.5 mL, 23.7 mmol, 21 equiv.) were used.

Purification by GPC and evaporation of the solvent afforded macrocycle BCyc-Hx (68.4 mg, 0.0477 mmol, 8%) as a brown oil. \(\text{H NMR (400 MHz, CDCl}_3\):} \(\delta = 6.92 (s, 16\text{H}), 4.23 (t, J = 6.8 \text{ Hz, } 16\text{H}), 1.66 (p, J = 7.0 \text{ Hz, } 16\text{H}), 1.35 - 1.22 (m, 48\text{H}), 0.86 (t, J = 6.7 \text{ Hz, } 24\text{H}) \text{ppm.} \)

\(\text{C NMR (101 MHz, CDCl}_3\):} \(\delta = 167.8, 137.5, 134.6, 129.9, 66.3, 31.5, 28.4, 25.6, 22.6, 14.1 \text{ ppm.} \)

HRMS (APCI): \(m/z\) calcd. for \(\text{C}_{98}\text{H}_{120}\text{O}_{16}\): 1432.8571 \([\text{M}]^+\), found: 1432.8540.

1.6.4 Macrocycle NCyc-Et

\[
\begin{align*}
\text{Molecular Weight:} & \quad 272.21 \\
\text{Molecular Weight:} & \quad 244.25
\end{align*}
\]

Synthesis of macrocycle NCyc-Et following the general procedure:
\(\alpha^2,\alpha^6\)-Dioxo-2,6-naphthalenediacetic acid 2b (268 mg, 0.985 mmol, 1.0 equiv.), 2,6-naphthalenediacetic acid 3b (240 mg, 0.985 mmol, 1.0 equiv.), dry degassed THF (400 mL), Et\(\text{3}N\) (1.3 mL, 9.35 mmol, 9.5 equiv.), Ac\(\text{2}O\) (1.4 mL, 14.8 mmol, 15 equiv.), EtBr (3.2 mL, 43.3 mmol, 44 equiv.), EtOH (4.7 mL, 80.7 mmol, 82 equiv.) and DBU (3.1 mL, 20.7 mmol, 21 equiv.) were used.

Purification by GPC and evaporation of the solvent afforded macrocycle NCyc-Et (46.1 mg, 0.0389 mmol, 8%) as a pale-yellow powder. \(\text{H NMR (400 MHz, CDCl}_3\):} \(\delta = 7.51 (d, J = 1.6 \text{ Hz, } 8\text{H}), 7.24 (d, J = 8.6 \text{ Hz, } 8\text{H}), 6.88 (dd, J = 8.6, 1.7 \text{ Hz, } 8\text{H}), 4.35 (q, J = 7.2 \text{ Hz, } 16\text{H}), 1.32 (t, J = 7.2 \text{ Hz, } 24\text{H}) \text{ppm.} \)

\(\text{C NMR (101 MHz, CDCl}_3\):} \(\delta = \ldots \text{ppm.} \)
(101 MHz, CDCl$_3$): $\delta = 168.0, 138.4, 133.0, 132.3, 129.7, 128.1, 127.8, 62.1, 14.2$ ppm. HRMS (APCI): $m/z$ calcd. for C$_{72}$H$_{64}$O$_{16}$: 1184.4189 [M]$^+$, found: 1184.4194.

1.6.5 Macrocycle ACyc-Et

![Diagram of ACyc-Et synthesis]

_Synthesis of macrocycle ACyc-Et following the general procedure:_

$\alpha^2,\alpha^6$-Dioxo-2,6-anthracenediacetic acid 2c (250 mg, 0.776 mmol, 1.0 equiv.), 2,6-anthracenediacetic acid 3c (228 mg, 0.776 mmol, 1.0 equiv.), dry degassed THF (400 mL), Et$_3$N (1.0 mL, 7.37 mmol, 9.5 equiv.), Ac$_2$O (1.1 mL, 11.6 mmol, 15 equiv.), EtBr (2.5 mL, 34.1 mmol, 44 equiv.), EtOH (3.7 mL, 63.6 mmol, 82 equiv.) and DBU (2.4 mL, 16.3 mmol, 21 equiv.) were used. Purification by GPC and evaporation of the solvent afforded macrocycle ACyc-Et (36.0 mg, 0.0260 mmol, 7%) as a dark orange powder. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.08$ (s, 8H), 7.87 (d, $J = 1.7$ Hz, 8H), 7.61 (d, $J = 8.9$ Hz, 8H), 7.06 (dd, $J = 8.9$, 1.8 Hz, 8H), 4.37 (q, 16H), 1.32 (t, $J = 7.2$ Hz, 24H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 168.3, 138.2, 132.1, 131.7, 131.1, 130.4, 128.2, 127.0, 126.95, 62.0, 14.2$ ppm.

**Important note:** Although we found the synthesis of all precursors and all other macrocycles to be reproducible, we struggled to re-synthesize ACyc-Et in later attempts. However, as highly interesting effects were observed for this macrocycle in both the computations and experiments, we decided not to omit the available data here.

1.6.6 Macrocycle PCyc-Et

![Diagram of PCyc-Et synthesis]
Synthesis of macrocycle PCyc-Et following the general procedure:

α¹,α⁶-Dioxo-1,6-pyrenedicarboxylic acid 2d (235 mg, 0.679 mmol, 1.0 equiv.), 1,6-pyrenedicarboxylic acid 3d (216 mg, 0.679 mmol, 1.0 equiv.), dry degassed THF (350 mL), Et₃N (0.90 mL, 6.45 mmol, 9.5 equiv.), Ac₂O (0.96 mL, 10.2 mmol, 15 equiv.), EtBr (2.2 mL, 29.9 mmol, 44 equiv.), EtOH (3.2 mL, 55.6 mmol, 82 equiv.) and DBU (2.1 mL, 14.3 mmol, 21 equiv.) were used. Purification by GPC and evaporation of the solvent afforded macrocycle PCyc-Et (37.9 mg, 0.0256 mmol, 8%) as an orange powder. ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (d, J = 9.2 Hz, 8H), 7.86 (d, J = 8.0 Hz, 8H), 7.77 (d, J = 8.0 Hz, 8H), 7.70 (d, J = 9.2 Hz, 8H), 4.21 – 4.13 (m, 16H), 1.13 (t, J = 7.1 Hz, 24H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.2, 139.8, 130.9, 129.7, 129.0, 127.9, 127.7, 124.9, 124.7, 124.6, 62.0, 14.0 ppm. NMR spectra in good agreement with the spectra in CD₂Cl₂ in the literature. HRMS (APCI): m/z calcd. for C₁₂₆H₇₃O₁₆⁺: 1481.4848 [M+H]⁺; found: 1481.4835.

1.6.7 Macrocycle PCyc-Hx

Synthesis of macrocycle PCyc-Hx following the general procedure:

α¹,α⁶-Dioxo-1,6-pyrenedicarboxylic acid 2d (250 mg, 0.722 mmol, 1.0 equiv.), 1,6-pyrenedicarboxylic acid 3d (230 mg, 0.722 mmol, 1.0 equiv.), dry degassed THF (300 mL), Et₃N (0.96 mL, 6.86 mmol, 9.5 equiv.), Ac₂O (1.0 mL, 10.8 mmol, 15 equiv.), 1-bromohexane (4.5 mL, 31.8 mmol, 44 equiv.), 1-hexanol (7.4 mL, 59.2 mmol, 82 equiv.) and DBU (2.3 mL, 15.2 mmol, 21 equiv.) were used. Purification by GPC and evaporation of the solvent afforded macrocycle PCyc-Hx (37.5 mg, 0.0194 mmol, 5%) as a red oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 (d, J = 9.2 Hz, 8H), 7.86 (d, J = 8.0 Hz, 8H), 7.77 (d, J = 9.3 Hz, 8H), 4.13 – 4.00 (m, 16H), 1.45 – 1.38 (m, 16H), 1.04 – 0.88 (m, 48H), 0.69 – 0.61 (m, 24H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 168.2, 139.9, 130.8, 129.7, 129.0, 127.9, 127.6, 124.9, 124.6, 124.5, 66.0, 31.2, 28.3, 25.4, 22.4, 13.9 ppm. HRMS (APCI): m/z calcd. for C₁₂₈H₁₃₇O₁₆⁺: 1929.9856 [M+H]⁺; found: 1929.9817.
1. **1H and 13C NMR spectra**

**Figure S3.** 1H NMR (400 MHz, CDCl3) of compound 1a.

**Figure S4.** 13C NMR (101 MHz, CDCl3) of compound 1a.
**Figure S5.** $^1$H NMR (400 MHz, CDCl$_3$) of compound 1b.

**Figure S6.** $^{13}$C NMR (101 MHz, CDCl$_3$) of compound 1b.
Figure S7. $^1$H NMR (400 MHz, CDCl$_3$) of compound 1c.

Figure S8. $^{13}$C NMR (101 MHz, CDCl$_3$) of compound 1c.
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) of compound 1d.

Figure S10. $^{13}$C NMR (101 MHz, CDCl$_3$) of compound 1d.
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) of compound 1e.

Figure S12. $^{13}$C NMR (101 MHz, CDCl$_3$) of compound 1e.
Figure S13. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 2a.

Figure S14. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 2a.
Figure S15. $^1$H NMR (400 MHz, DMSO-d6) of compound 2b.

Figure S16. $^{13}$C NMR (101 MHz, DMSO-d6) of compound 2b.
Figure S17. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 2c.

Figure S18. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 2c.
**Figure S19.** $^1$H-$^{13}$C HSQC spectrum (400 MHz, 101 MHz, DMSO-$d_6$) of compound 2c.

**Figure S20.** $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 2d.
Figure S21. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 2d.

Figure S22. $^1$H-$^{13}$C HSQC spectrum (400 MHz, 101 MHz, DMSO-$d_6$) of compound 2d.
Figure S23. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 2e.

Figure S24. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 2e.
Figure S25. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 3b.

Figure S26. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 3b.
Figure S27. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 3c.

Figure S28. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 3c.
Figure S29. $^1$H NMR (400 MHz, DMSO-$d_6$) of compound 3d.

Figure S30. $^{13}$C NMR (101 MHz, DMSO-$d_6$) of compound 3d.
Figure S31. $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle BCyc-Et.

Figure S32. $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle BCyc-Et.
**Figure S33.** $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle BCye-Hx.

**Figure S34.** $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle BCye-Hx.
Figure S35. $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle NCyc-Et.

Figure S36. $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle NCyc-Et.
Figure S37. $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle ACyc-Et.

Figure S38. $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle ACyc-Et.
Figure S39. $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle PCyc-Et.

Figure S40. $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle PCyc-Et.
Figure S41. $^1$H NMR (400 MHz, CDCl$_3$) of macrocycle PCyc-Hx.

Figure S42. $^{13}$C NMR (101 MHz, CDCl$_3$) of macrocycle PCyc-Hx.
3 Photoluminescence spectra

Figure S43. Photoluminescence spectra of the macrocycles recorded at different excitation wavelengths (shown in brackets) in CHCl₃ solution (5 µM) with the detector voltage set to ‘high’ (800 V). The dashed lines show the spectra provided in Figure 1.

Figure S44. Photoluminescence spectra of PCyc-Et and PCyc-Hx recorded at two different excitation wavelengths in CHCl₃ solution (5 µM) with the detector voltage set to ‘high’ (800 V) or ‘medium’ (600 V).

4 Cyclic voltammetry (CV) in solution

Chemicals and materials
Ferrocene (Fc, 98%) was obtained from Aldrich. 1,2-Dichloroethane (DCE, anhydrous, 99.8%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), propylene carbonate (PC, anhydrous, 99.7%), and
tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$, >98%) were from Sigma-Aldrich. Silver wire (0.5 mm dia.), platinum wires (0.5 mm, 0.1 mm and 0.025 mm diameter) were from Mint of Poland. 2 mm diameter disk platinum electrode (CHI303) was from CHi Instruments.

**Voltammetric measurements**

Details provided in the methods section of the paper.

4.1 Electroreduction and -oxidation of the macrocycles at arbitrary concentration in 1,2-dichloroethane

**Electroreduction:** For BCyc-Et, PCyc-Et, and PCyc-Hx, the mid-peak potential vs. Fc/Fc$^+$ (the midpoints between the anodic and cathodic peak potentials) were determined and are provided in the main part of the paper. For NCyc-Et and ACyc-Et, where the peak potentials could not be determined, the inflection-point potentials were determined by differentiating the cyclic voltammograms (Figure S45).

**Electrooxidation:** As the electrooxidation was chemically irreversible for all macrocycles, the inflection-point potentials were determined by differentiating the cyclic voltammograms (Figure S45).

The measurements were carried out at arbitrary concentration as the small amounts available for some of the macrocycles prevented the preparation of solutions with defined concentration. While the concentration has an impact on the current, the redox potential does not depend on the concentration.

**Figure S45.** Cyclic voltammograms of (a) BCyc-Et, (b) NCyc-Et, (c) ACyc-Et, and (d) PCyc-Et and their first derivatives (with ferrocene as the internal reference), recorded in 1,2-dichloroethane (DCE) on platinum disk electrodes of 2 mm diameter. Scan rate $v = 0.1$ V s$^{-1}$, supporting electrolyte: 0.1 M NBu$_4$PF$_6$.  

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4.2 Electroreduction of BCyc-Et at defined concentrations

Cyclic voltammetry of BCyc-Et solutions in 1,2-dichloroethane (DCE), N,N-dimethylformamide (DMF), and propylene carbonate (PC), all containing 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, were performed with 2 mm diameter platinum disk electrode. The obtained voltammograms (Figure S46) suggest two quasi-reversible electroreduction steps. With the intention of getting an indication of the stoichiometry and kinetic parameters of these steps, simulated voltammograms were fitted to the obtained voltammograms using DigiSim 3.03b software, assuming two consecutive one-electron reductions steps:

\[
\begin{align*}
\text{BCyc-Et} + e^- & \rightleftharpoons \text{BCyc-Et}^- & E^{0'}(1), k_0(1), \alpha(1) \\
\text{BCyc-Et}^- + e^- & \rightleftharpoons \text{BCyc-Et}^{2-} & E^{0'}(2), k_0(2), \alpha(2)
\end{align*}
\]

Similarly to non-substituted BCyc (also known as PCT),$^7$ the most reduced form in the assumed process (BCyc-Et$^{2-}$) is considered to be a reductant strong enough to be oxidized homogeneously, most probably by H$_2$O and O$_2$ traces in solvents:

\[
\text{BCyc-Et}^{2-} + \text{(oxidant)} \rightarrow \text{BCyc-Et}^- + \text{(reduced oxidant)}
\]

\[ k \]

**Figure S46.** Cyclic voltammograms of BCyc-Et in (a) DCE, (b) DMF, and (c) PC recorded on platinum disk electrodes of 2 mm diameter (solid lines). Scan rate $v = 0.1$ V s$^{-1}$, supporting electrolyte: 0.1 M NBu$_4$PF$_6$. Simulated cyclic voltammograms assuming two one-electron reduction steps (dotted lines) with fitted kinetic parameters, formal potentials, and diffusion coefficients. All parameters for the simulations are listed in Table S1. Other parameters for the simulations:

(a) uncompensated resistance ($R_u$): 1 kΩ, double layer capacitance ($C_{dl}$): 10 μF; (b) $R_u = 0$ Ω, $C_{dl} = 15$ μF; (c) $R_u = 0$ Ω, $C_{dl} = 10$ μF. Temperature: 298.2 K.

The recorded cyclic voltammograms of BCyc-Et in the different solvents (DCE, DMF, PC) are shown in Figure S46 (solid lines), together with the simulated voltammograms (dotted lines) assuming two consecutive one-electron reduction steps with fitted thermodynamic ($E^{0'}(1,2)$ – formal potentials of reactions (1 and 2)), kinetic ($k_0(1,2)$ – standard electron transfer (ET) rate constants, $\alpha(1,2)$ – ET coefficients, $k$ – rate constant of pseudo-1$^\text{st}$ order reaction of homogeneous regeneration of B-Et-Cycle$^-$
(eq. 3)) and hydrodynamic ($D$ – diffusion coefficient, $r_H$ – effective hydrodynamic radius of BCyc-Et) parameters according to the abovementioned mechanism. The parameters found by fitting are listed in gray cells in Table S1. Hydrodynamic radii ($r_H$) were calculated from fitted diffusion coefficients and solvent viscosities using the Stokes-Einstein equation. Additional peaks of low current magnitude that are visible in the recorded voltammograms can be caused by adsorption of BCyc-Et on the platinum electrode.

Contrary to the previous approach used for the analysis of the voltammograms of BCyc, where diffusion coefficients were obtained from steady-state voltammograms recorded with an ultramicroelectrode (UME), here the diffusion limiting current could not be unambiguously read from voltammograms recorded with a 25 μm diameter UME (Figure S47). This is due to the slower kinetics of the electron transfer for BCyc-Et than for BCyc. Therefore, diffusion coefficients ($D$) of BCyc-Et were obtained by fitting to voltammograms recorded with a bigger (2 mm diameter) electrode. To verify the procedure of finding $D$ by fitting cyclic voltammograms recorded at a larger disk electrode, we applied the procedure to the voltammograms of BCyc. Diffusion coefficients of BCyc obtained this way differ less than 10% from the values obtained from the UME measurements.

**Table S1.** Physicochemical parameters of the electroreduction of BCyc-Et assuming two one-electron reduction steps (diffusion coefficient, $D$; concentration, $c$; hydrodynamic radius, $r_H$; formal potentials, $E^0$; standard electron transfer rate constants, $k_0$; electron transfer coefficients, $\alpha$) in three different solvents (dynamic viscosity, $\eta$; dipole moment, $\mu$) at 298.15 K. Parameters from fitting simulated voltammograms to voltammograms obtained using platinum disk electrodes of 2 mm diameter highlighted in gray. Hydrodynamic radii were calculated using the Stokes-Einstein equation and viscosities from literature.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$ (mPa·s)</th>
<th>$\mu$ (D)</th>
<th>$D$ (cm$^2$·s$^{-1}$)</th>
<th>$c$ (mmol·dm$^{-3}$)</th>
<th>$r_H$ (nm)</th>
<th>$E^0$(1) (V)</th>
<th>$k_0$(1) (cm·s$^{-1}$)</th>
<th>$\alpha$(1)</th>
<th>$E^0$(2) (V)</th>
<th>$k_0$(2) (cm·s$^{-1}$)</th>
<th>$\alpha$(2)</th>
<th>$k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloro-ethane (DCE)</td>
<td>0.7644 (Ref. 5)</td>
<td>2.94</td>
<td>5.0 × 10$^{-6}$</td>
<td>14.5</td>
<td>0.56</td>
<td>-1.66</td>
<td>3.1 × 10$^{-4}$</td>
<td>0.49</td>
<td>-2.12</td>
<td>1.6 × 10$^{-5}$</td>
<td>0.4</td>
<td>0.67</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>0.864 (Ref. 7)</td>
<td>3.82</td>
<td>4.2 × 10$^{-6}$</td>
<td>6.2</td>
<td>0.59</td>
<td>-1.52</td>
<td>6.5 × 10$^{-4}$</td>
<td>0.58</td>
<td>-2.11</td>
<td>1.1 × 10$^{-5}$</td>
<td>0.48</td>
<td>0.4</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td>2.4711 (Ref. 11)</td>
<td>5.36</td>
<td>1.4 × 10$^{-6}$</td>
<td>5.2</td>
<td>0.62</td>
<td>-1.48</td>
<td>4.8 × 10$^{-4}$</td>
<td>0.55</td>
<td>-2.03</td>
<td>10$^{-5}$</td>
<td>0.32</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Discussion of the simulation results**

The hydrodynamic radii obtained from fitting voltammograms simulated under the assumption of two one-electron reduction steps ($r_H$ in Table S1) roughly correspond to the size of the macrocycle. However, estimating the hydrodynamic radius from the molecular geometry is difficult and neglects that interactions with solvent molecules can increase the actual hydrodynamic radius. Such interactions can be expected particularly for molecules with polar functional groups, such as ester groups.
Under the assumption of two two-electron reduction steps, larger hydrodynamic radii would be obtained from the simulations, which do not correspond well with the bare macrocycle but may in line with an increased hydrodynamic radius because of interactions with solvent molecules.

**Further measurements**

![Cyclic voltammograms](image)

**Figure S47.** Steady-state cyclic voltammograms of BCyc-Et in (a) DCE, (b) DMF, and (c) PC recorded on platinum disk ultramicroelectrodes of 25 μm diameter. Scan rate \( v = 10 \text{ mV s}^{-1} \), supporting electrolyte: 0.1 M NBu$_4$PF$_6$.

![Cyclic voltammograms](image)

**Figure S48.** Cyclic voltammograms of BCyc-Et with ferrocene in (a) DCE, (b) DMF, and (c) PC recorded on platinum disk electrodes of 2 mm diameter. Scan rate \( v = 0.1 \text{ V s}^{-1} \), supporting electrolyte: 0.1 M NBu$_4$PF$_6$.

5 **Electron paramagnetic resonance (EPR) spectroelectrochemistry**

**Chemicals**

All chemicals were purchased from Sigma-Aldrich: 1,2-dichloroethane (DCE, 99.8%), tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$, ≥99.0%), ferrocene (Fc, 98%), 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl (4-amino-TEMPO, 97%).

**Electrochemical measurement set-up**

A three-electrode set-up was used for all electrochemical measurements. All electrochemical measurements were carried out in a quartz EPR tube (Wilmad, outer diameter 4 mm), sealed with a suba-seal rubber septum (Figure S49). The working (WE) and counter electrodes (CE) were two Teflon-coated Pt wires (ADVENT, purity 99.99%, bare wire diameter = 0.125 mm), coiled to enhance their surface area. The working electrode was encased in a glass capillary to avoid short-circuiting and
maintain the wire at the bottom of the EPR tube that is inserted into the EPR cavity. An Ag/AgCl reference electrode (RE, calibrated using a master saturated calomel electrode SCE) was used for aqueous electrochemical measurements. Teflon-coated silver wire (ADVENT, purity 99.99\%, bare wire diameter = 0.125 mm) was used as a pseudo-reference electrode (pseudo-RE) for the measurements in DCE, with 5 mM ferrocene (Fc) added to calibrate the potential. The EPR tube was purged with nitrogen gas prior to electrochemical measurements performed with a µAutolabIII potentiostat in combination with NOVA software.

**Figure S49.** Spectroelectrochemical cell assembled in an EPR tube. The tube is inserted into the EPR setup, but only the bottom 2 mm of the tube are placed in the actual EPR cavity.

**EPR measurement set-up**

Continuous wave X-band EPR measurements were performed at room temperature in an X-band Super High Sensitivity Probehead ER 4122SHQE and an EMX-T-DU/L Bruker spectrometer. The bottom 2 mm of the EPR tube containing the electrochemical cell, i.e. only the working electrode (see Figure S49), was placed inside the EPR cavity (resulting in Q values of approx. 1300-4500 due to the conductivity of the sample). After insertion of the EPR tube into the cavity and optimisation of its position, the electrodes were connected to the potentiostat and the electrochemical and EPR measurements were carried out simultaneously.
Sample preparation

**BCyc-Et** or 4-amino-TEMPO was dissolved in 0.4 ml DCE to a final concentration of 5 mM and supplemented with 0.1 M nBu$_4$PF$_6$. Aqueous electrochemical measurements with 4-amino-TEMPO (5 mM) were carried out in 0.5 M Na$_2$CO$_3$ in milliQ water, adjusted to pH 8.0.

### 5.1 EPR spectroelectrochemical measurements of 4-amino-TEMPO

To test the measurement set-up, electrochemical EPR measurements were first carried out on the EPR active compound 4-amino-TEMPO under aqueous conditions. As can be seen in **Figure S50A**, the cyclic voltammogram showed a redox potential $E_{\text{m}, \text{pH 8.0}} = 0.631$ V vs. Ag/AgCl (0.836 V vs. SHE) that is consistent with previously reported values ($E_{\text{m}, \text{pH 7.0}} = 0.874$ V vs. SHE). The in operando EPR measurements show that the nitroxide EPR signal changes upon the redox reaction, but it does not disappear completely (Figure S50B), which is expected given that the redox reaction occurs just at the electrode.

**Figure S50.** Spectroelectrochemical measurements of 5 mM 4-amino-TEMPO in aq. 0.5 M Na$_2$CO$_3$ at pH 8.0: (A) Cyclic voltammogram recorded at a scan rate of 5 mV s$^{-1}$ and (B) set of incremented EPR spectra registered while cycling the applied potential at 5 mV s$^{-1}$. (C) Spectroelectrochemical measurements of 5 mM 4-amino-TEMPO in 0.4 ml DCE with 0.1 M nBu$_4$PF$_6$: set of incremented EPR spectra registered while cycling the applied potential at a scan rate of 5 mV s$^{-1}$.

Experimental conditions (EPR): microwave power = 20 mW, microwave frequency = 9.863 GHz (B), 9.844 GHz (C), modulation amplitude = 0.1 mT, sweep time = 5 s per scan, quality factor of the resonator as reported by the built-in Q indicator in the Xepr program = 1300 (B), 4800 (C).

The corresponding experiment under non-aqueous conditions (in DCE) showed more sluggish electron transfer, but redox cycling is nonetheless evident from the in operando electrochemical EPR measurements (**Figure S50C**).
5.2 EPR spectroelectrochemical measurements of BCyc-Et

In contrast to the measurements of 4-amino-TEMPO, in operando electrochemical EPR measurements with the BCyc-Et only gave EPR spectra with flat lines (Figure S51). Although the CV (Figure S51A) and the control measurements with 4-amino-TEMPO (Figure S50) suggest that the set-up needs to be further improved for optimal in-operando measurements, they enable us to conclude that it is highly unlikely that a paramagnetic intermediate is formed during redox cycling of BCyc-Et, corroborating that it does not proceed in single electron transfer steps.

Measurements at various scan rates including 5 mV s\(^{-1}\) (the scan rate used for the measurements shown in Figure S50) were carried out, with no EPR signal appearing in any of these measurements. In situ chronoamperometry coupled to EPR measurements was also carried out. A potential range of -2.5 V to -1.0 V (vs. Fe/Fc\(^+\)) was investigated by holding the potential for more than 300 seconds at different values while recording EPR spectra. In agreement with the result obtained from in situ CV-EPR measurements, no EPR signal was observed over the scanned potential range.

![Figure S51](image_url)

**Figure S51.** Spectroelectrochemical measurements of 5 mM BCyc-Et in 0.4 ml DCE with 0.1 M NBu\(_4\)PF\(_6\). (A) Cyclic voltammogram recorded at a scan rate of 0.1 V s\(^{-1}\) after subtraction of the blank measurement. (B) Set of incremented EPR spectra registered while cycling the applied potential at a scan rate of 0.1 V s\(^{-1}\). Experimental conditions: microwave power = 100 mW, microwave frequency = 9.854 GHz, modulation amplitude = 0.1 mT, sweep time = 5 s, quality factor of the resonator as reported by the built-in Q indicator in the Xepr program = 3900.
6 Computational analysis

6.1 Redox potentials

Table S2. Calculated redox potentials vs. Fe/Fe⁺ for the different redox couples of the macrocycles.

<table>
<thead>
<tr>
<th></th>
<th>-6/-4</th>
<th>-4/-2</th>
<th>-2/-1</th>
<th>-1/0</th>
<th>0/+1</th>
<th>+1/+2</th>
<th>+2/+4</th>
<th>+4/+6</th>
<th>-2/-4 (trip.)</th>
<th>+2/+4 (trip.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCyc</td>
<td>-5.43</td>
<td>-4.01</td>
<td>-2.47</td>
<td>-2.08</td>
<td>0.64</td>
<td>1.14</td>
<td>2.65</td>
<td>4.50</td>
<td>-4.10</td>
<td>2.80</td>
</tr>
<tr>
<td>BCyc-Et</td>
<td>-3.74</td>
<td>-2.48</td>
<td>-1.78</td>
<td>-1.66</td>
<td>1.52</td>
<td>1.91</td>
<td>3.00</td>
<td>4.83</td>
<td>-2.62</td>
<td>3.15</td>
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<tr>
<td>NCyc-Et</td>
<td>-3.15</td>
<td>-2.16</td>
<td>-1.96</td>
<td>-1.82</td>
<td>1.41</td>
<td>1.72</td>
<td>2.37</td>
<td>3.66</td>
<td>-2.33</td>
<td>2.43</td>
</tr>
<tr>
<td>ACyc-Et</td>
<td>-3.27</td>
<td>-2.22</td>
<td>-1.90</td>
<td>-1.62</td>
<td>0.72</td>
<td>1.19</td>
<td>1.68</td>
<td>3.28</td>
<td>-2.40</td>
<td>1.87</td>
</tr>
<tr>
<td>PCyc-Et</td>
<td>-2.97</td>
<td>-2.17</td>
<td>-1.84</td>
<td>-1.68</td>
<td>1.01</td>
<td>1.45</td>
<td>1.83</td>
<td>3.10</td>
<td>-2.20</td>
<td>2.02</td>
</tr>
</tbody>
</table>

6.2 Nucleus-independent chemical shifts (NICS)

Table S3. NICS(0)zz values of the macrocycles in the different charge and spin states.

<table>
<thead>
<tr>
<th>Charge state</th>
<th>BCyc</th>
<th>BCyc-Et</th>
<th>NCyc-Et</th>
<th>ACyc-Et</th>
<th>PCyc-Et</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NICS(0)zz (ppm)</td>
<td>NICS(0)zz (ppm)</td>
<td>NICS(0)zz (ppm)</td>
<td>NICS(0)zz (ppm)</td>
<td>NICS(0)zz (ppm)</td>
</tr>
<tr>
<td>-6</td>
<td>-45.95</td>
<td>-2.46</td>
<td>-8.07</td>
<td>-3.55</td>
<td>-13.68</td>
</tr>
<tr>
<td>-2</td>
<td>-38.65</td>
<td>-23.68</td>
<td>-16.75</td>
<td>-6.09</td>
<td>-10.98</td>
</tr>
<tr>
<td>-1</td>
<td>-8.32</td>
<td>-3.87</td>
<td>-3.07</td>
<td>-2.12</td>
<td>-1.67</td>
</tr>
<tr>
<td>0</td>
<td>10.98</td>
<td>-35.79</td>
<td>7.51</td>
<td>-23.57</td>
<td>5.49</td>
</tr>
<tr>
<td>+1</td>
<td>-6.90</td>
<td>-3.57</td>
<td>-2.06</td>
<td>-0.89</td>
<td>1.28</td>
</tr>
<tr>
<td>+2</td>
<td>-33.48</td>
<td>-20.87</td>
<td>-13.31</td>
<td>-3.02</td>
<td>-2.80</td>
</tr>
<tr>
<td>+4</td>
<td>34.63</td>
<td>-32.34</td>
<td>5.99</td>
<td>-17.67</td>
<td>3.93</td>
</tr>
<tr>
<td>+6</td>
<td>-27.72</td>
<td>4.69</td>
<td>-17.96</td>
<td>-15.18</td>
<td>3.43</td>
</tr>
</tbody>
</table>

Table S4. Isotropic NICS(0) values of the macrocycles in the different charge and spin states.

<table>
<thead>
<tr>
<th>Charge state</th>
<th>BCyc</th>
<th>BCyc-Et</th>
<th>NCyc-Et</th>
<th>ACyc-Et</th>
<th>PCyc-Et</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NICS(0) (ppm)</td>
<td>NICS(0) (ppm)</td>
<td>NICS(0) (ppm)</td>
<td>NICS(0) (ppm)</td>
<td>NICS(0) (ppm)</td>
</tr>
<tr>
<td>-6</td>
<td>-16.75</td>
<td>-5.26</td>
<td>-5.89</td>
<td>-2.97</td>
<td>-9.13</td>
</tr>
<tr>
<td>-4</td>
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<td>-16.23</td>
<td>-0.53</td>
<td>-9.09</td>
<td>-1.04</td>
</tr>
<tr>
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<td>-11.97</td>
<td>-8.36</td>
<td>-2.61</td>
<td>-8.74</td>
</tr>
<tr>
<td>-1</td>
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<td>-5.79</td>
<td>-4.23</td>
<td>-1.32</td>
<td>-5.91</td>
</tr>
<tr>
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<td>-2.75</td>
<td>-12.22</td>
<td>-0.90</td>
</tr>
<tr>
<td>+1</td>
<td>-5.33</td>
<td>-6.16</td>
<td>-4.40</td>
<td>-1.37</td>
<td>-4.98</td>
</tr>
<tr>
<td>+2</td>
<td>-14.11</td>
<td>-11.69</td>
<td>-7.87</td>
<td>-2.31</td>
<td>-5.83</td>
</tr>
<tr>
<td>+4</td>
<td>8.35</td>
<td>-13.77</td>
<td>-2.16</td>
<td>-10.32</td>
<td>0.36</td>
</tr>
<tr>
<td>+6</td>
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<td>-2.49</td>
<td>-8.86</td>
<td>-7.02</td>
<td>-3.84</td>
</tr>
</tbody>
</table>
6.3 Visualization of chemical shielding tensors (VIST)

6.3.1 VIST plots of BCyc in different charge and spin states

<table>
<thead>
<tr>
<th>BCyc</th>
<th>BCyc (triplet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCyc$^{2-}$</td>
<td>BCyc$^{2+}$</td>
</tr>
<tr>
<td>BCyc$^+$</td>
<td>BCyc$^{4+}$</td>
</tr>
<tr>
<td>BCyc$^+$ (triplet)</td>
<td>BCyc$^{4+}$ (triplet)</td>
</tr>
</tbody>
</table>
6.3.2 VIST plots of BCyc-Et in different charge and spin states
6.3.3 VIST plots of NCyc-Et in different charge and spin states
6.3.4 VIST plots of ACyc-Et in different charge states

6.3.5 VIST plots of PCyc-Et in different charge states
6.4 Electron density difference

6.4.1 Electron density difference plots of BCyc

Isovalues: -0.003 e for anions, +0.003 e for cations.
6.4.2 Electron density difference plots of BCyc-Et

Isovalues: -0.003 e for anions, +0.003 e for cations.
6.5 Anisotropy of the induced current density (ACID)

6.5.1 ACID plots of BCyc in different charge and spin states
6.5.2 ACID plots of BCyc-Et in different charge and spin states

BCyc-Et

BCyc-Et (triplet)

BCyc-Et$^2^-$

BCyc-Et$^{2+}$

BCyc-Et$^4^-$

BCyc-Et$^{4+}$
7 References


