

β,β -Directly Linked Porphyrin Rings: Synthesis, Photophysical Properties, and Fullerene Binding

Qiang Chen, Amber L. Thompson, Kirsten E. Christensen, Peter N. Horton, Simon J. Coles, and Harry L. Anderson*



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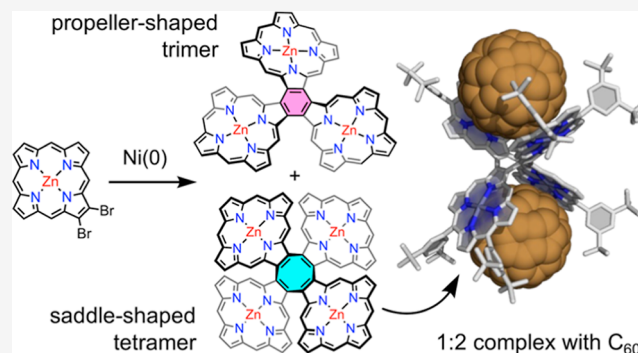
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ABSTRACT: Cyclic porphyrin oligomers have been studied as models for photosynthetic light-harvesting antenna complexes and as potential receptors for supramolecular chemistry. Here, we report the synthesis of unprecedented β,β -directly linked cyclic zinc porphyrin oligomers, the trimer (CP3) and tetramer (CP4), by Yamamoto coupling of a 2,3-dibromoporphyrin precursor. Their three-dimensional structures were confirmed by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analyses. The minimum-energy geometries of CP3 and CP4 have propeller and saddle shapes, respectively, as calculated using density functional theory. Their different geometries result in distinct photophysical and electrochemical properties. The smaller dihedral angles between the porphyrin units in CP3, compared with CP4, result in stronger π -conjugation, splitting the ultraviolet–vis absorption bands and shifting them to longer wavelengths. Analysis of the crystallographic bond lengths indicates that the central benzene ring of the CP3 is partially aromatic [harmonic oscillator model of aromaticity (HOMA) 0.52], whereas the central cyclooctatetraene ring of the CP4 is non-aromatic (HOMA -0.02). The saddle-shaped structure of CP4 makes it a ditopic receptor for fullerenes, with affinity constants of $(1.1 \pm 0.4) \times 10^5 \text{ M}^{-1}$ for C_{70} and $(2.2 \pm 0.1) \times 10^4 \text{ M}^{-1}$ for C_{60} , respectively, in toluene solution at 298 K. The formation of a 1:2 complex with C_{60} is confirmed by NMR titration and single-crystal X-ray diffraction.



INTRODUCTION

Covalent cyclic porphyrin oligomers have been widely studied since the 1970s as models for photosynthetic systems,^{1,2} as multitopic receptors for molecule recognition,^{3–6} as catalysts,⁷ and as models for exploring electronic delocalization and aromaticity.⁸ Most of these macrocycles have “spacers” bridging between the porphyrin units, such as alkynes,⁹ butadiynes,¹⁰ thiophenes,¹¹ or *para*-phenylenes.¹² Directly linked cyclic porphyrin oligomers (i.e., with no spacers) can exhibit fascinating cooperative behavior as a result of the tight proximity between neighboring porphyrin chromophores,¹³ but they are difficult to synthesize. Osuka and co-workers reported the first *meso,meso* (5,10) directly linked cyclic porphyrin oligomers, with various ring sizes, through an oxidative coupling strategy¹⁴ (Figure 1a). The same team also prepared β,β (2,12)-linked oligomers¹⁵ (Figure 1b), via the formation of Pt^{II} complexes followed by reductive elimination, as well as β,β (3,7)-linked rings, via Suzuki–Miyaura coupling.¹⁶ These porphyrin arrays show unusual photophysical properties, such as size-dependent excitation energy transfer.^{2,13,15} Here, we report the synthesis of two unprecedented β,β (2,3) directly linked cyclic porphyrin oligomers (Figure 1c), trimer CP3 and tetramer CP4, via

one-step Yamamoto coupling of a 2,3-dibromo-10,15-bis-(3,5-di-*tert*-butylphenyl)porphyrin(Zn) 1 (Figure 1c and Scheme 1). These two porphyrin oligomers feature a central aromatic benzene or nonaromatic cyclooctatetraene (COT) ring, respectively. Their structures have been unambiguously characterized by a combination of nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and X-ray single-crystal diffraction analysis.

The difference in geometry between CP3 and CP4 has a striking effect on their optical properties, electronic structures, and affinities for fullerenes. Trimer CP3 is almost flat; its density functional theory (DFT)-calculated geometry is D_3 propeller-shaped (Figure 1c), with a small energy difference of 4.6 kJ/mol with respect to other conformers, making it conformationally dynamic. In contrast, CP4 has a saddle-shaped conformation with a high barrier to saddle inversion.

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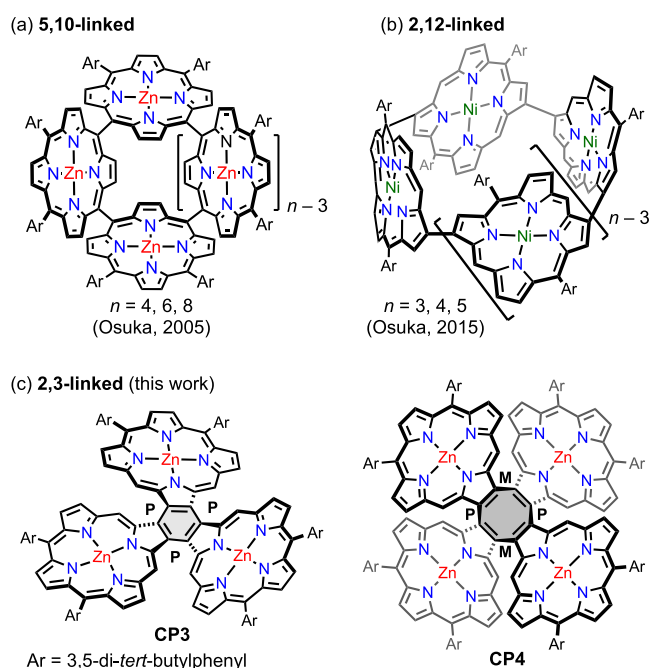
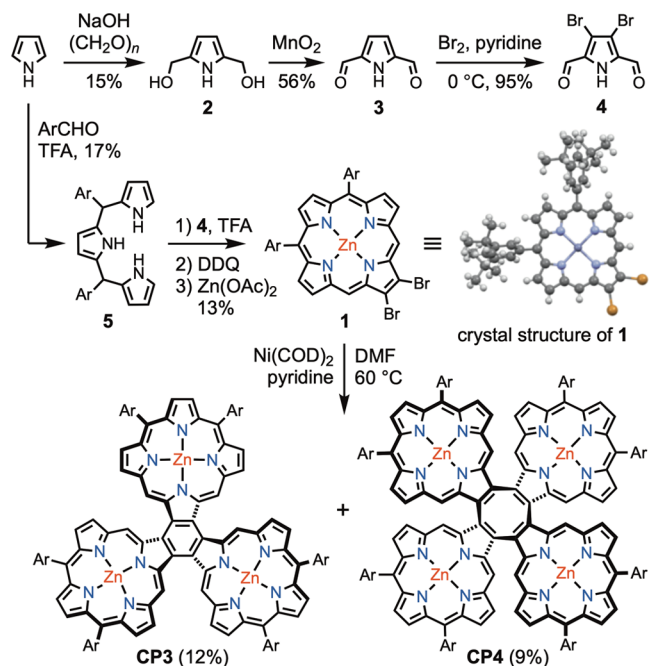


Figure 1. Representative examples of directly linked cyclic porphyrin oligomers: (a) *meso,meso* (5,10)-linked; (b) β,β (2,12)-linked; and (c) β,β (2,3)-linked trimer CP3 and tetramer CP4 in this work.

Scheme 1. Synthesis of β,β -Linked Cyclic Porphyrin Trimer (CP3) and Tetramer (CP4)^a



^aAr = 3,5-di-*tert*-butylphenyl; COD = 1,5-cyclooctadiene; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; TFA = CF₃CO₂H; and DMF = *N,N*-dimethylformamide.

The almost planar geometry of CP3 allows efficient π -conjugation, reducing the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and shifting the UV–vis absorption and fluorescence spectra to longer wavelengths, whereas absorption and fluorescence spectra of CP4 are more like those of a porphyrin monomer,

with weak electronic coupling between the porphyrin units. While CP3 shows no interaction with fullerenes, the saddle-shaped geometry of CP4 makes it a good ditopic receptor, with association constants of $(1.1 \pm 0.4) \times 10^5 \text{ M}^{-1}$ for C₇₀ and $(2.2 \pm 0.1) \times 10^4 \text{ M}^{-1}$ for C₆₀ in toluene solution at 298 K. This tetramer is the first directly linked cyclic porphyrin oligomer with a high affinity for fullerenes.

RESULTS AND DISCUSSION

Synthesis and NMR Spectroscopy. The key intermediate in the synthesis of CP3 and CP4 is the 2,3-dibromo-10,15-diarylporphyrin 1. This monomer was synthesized via [3 + 1] condensation of tripyrrane 5 and 3,4-dibromopyrrole 4 (Scheme 1). First, twofold hydroxymethylation of pyrrole with paraformaldehyde gave 2,5-bis(hydroxymethyl)pyrrole 2 in 15% yield.¹⁷ Then, oxidation of 2 with activated MnO₂ gave 2,5-diformylpyrrole 3 in 56% yield.¹⁸ Treatment with bromine in the presence of pyridine converts 3 to 3,4-dibromo-2,5-diformylpyrrole (4) in 95% yield.¹⁹ Meanwhile, tripyrrane 5 was synthesized in 17% yield by condensation of pyrrole and 3,5-di-*tert*-butylbenzaldehyde catalyzed by trifluoroacetic acid.²⁰ Condensation of tripyrrane 5 and 3,4-dibromo-2,5-diformylpyrrole (4), followed by oxidation with DDQ and metalation with zinc acetate, provided porphyrin 1 in 13% yield over two steps.²¹ The structure of this dibromoporphyrin was confirmed by X-ray crystallography (Scheme 1, CCDC: 2253581). Finally, Yamamoto coupling of 1 using Ni(COD)₂ in DMF gave a mixture of linear and cyclic porphyrin oligomers. After silica gel column chromatography, CP3 and CP4 were isolated in 12 and 9% yields, respectively. Molecular ions were observed at m/z : 2238.92 for CP3 (calcd for C₁₄₄H₁₅₀N₁₂Zn₃, 2239.00 [M]⁺) and m/z : 2985.88 for CP4 (calcd for C₁₉₂H₂₀₀N₁₆Zn₄, 2985.33 [M]⁺) by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and the isotopic distribution patterns agree well with simulations (Figures S52 and S53). We also detected larger oligomeric byproducts by MS (Figure S48), but they were not isolated or fully characterized.

¹H NMR spectra of CP3 and CP4 exhibit simple patterns, reflecting their high symmetries (Figure 2). Distinct sets of signals can be recognized consisting of one singlet associated with the *meso*-protons (H^a), two doublets coupled to each other corresponding to the β -positions (H^b and H^c), and one singlet from the other β -positions (H^d), similar to that of precursor porphyrin 1 (Figure 2c). The *meso*-protons (H^a) of CP3 resonate at an extremely high chemical shift (δ = 12.9 ppm) compared with that of 1 (δ = 9.7 ppm), reflecting the proximity between the porphyrin units that puts H^a in the deshielding region of two porphyrins. However, the *meso*-protons (H^a) of CP4 is only slightly downfield shifted to 11.0 ppm. ¹H NMR signals of the 3,5-di-*tert*-butylphenyl groups show that desymmetrization occurs for H^c and H^g, which appear as two triplets (Figure 2b). The splitting of these signals implies CP4 adopts a stable D_{2d} symmetric saddle shape, which cannot convert to other conformers (Figure 3). In contrast, the simple spectrum of CP3 implies either that the three porphyrin units are coplanar or that the different conformers interconvert rapidly on the NMR time scale. Even when the ¹H NMR spectrum of CP3 was recorded at −90 °C (Figure S46), no splitting of ¹H NMR signals of H^c could be seen, reflecting the low barrier to conformation exchange. By contrast, for CP4, no coalescence of ¹H NMR peaks H^c and H^g was observed, even

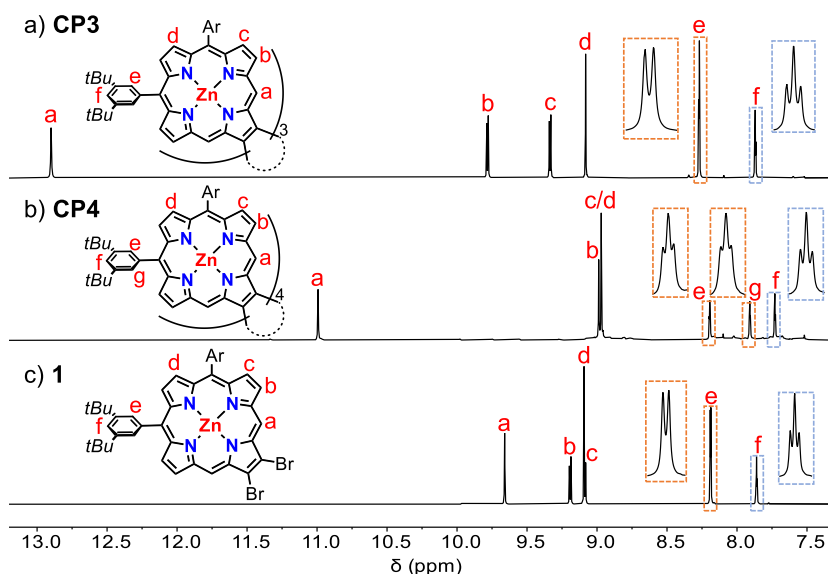


Figure 2. Aromatic regions of the ^1H NMR spectra of (a) CP3, (b) CP4 and (c) 2,3-dibromo-10,15-bis-(3,5-di-*tert*-butylphenyl)porphyrin(Zn) (1) recorded in CDCl_3 (1% v/v of pyridine- d_5 was added for CP3 to suppress aggregation, see Figure S47 for spectra without pyridine- d_5) at 298 K, 400 MHz.

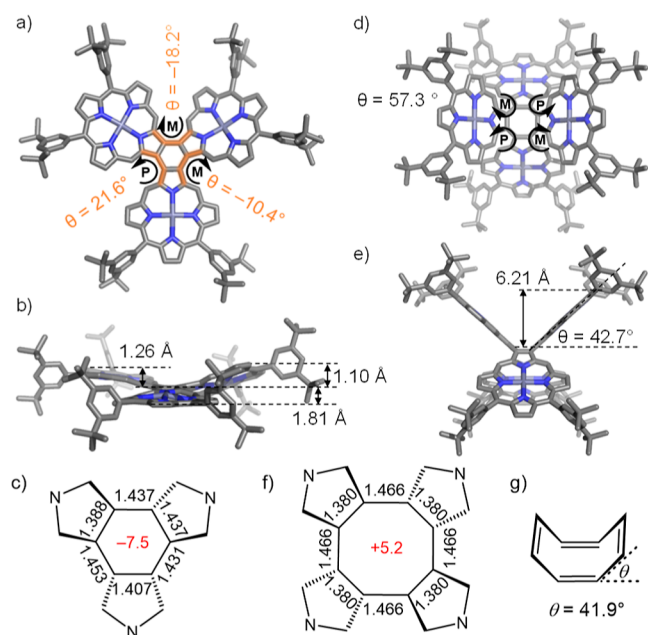


Figure 3. Structure of CP3 from single-crystal X-ray diffraction studies (only one enantiomer is shown, hydrogen atoms and solvent molecules are omitted for clarity): (a) top view; (b) front view; (c) bond lengths in the central benzene ring and NICS(1) (in red); (d,e) optimized structure of CP4 by DFT on the B3LYP/6-31G(d,p) level of theory; (f) bond lengths of central COT and NICS(1) (in red); and (g) dihedral angle of unsubstituted COT reported in the literature (CCDC 1320377).²²

at 100 °C (Figure S46), demonstrating the high barrier to saddle inversion.

Crystallography and Computational Modeling. Crystals of CP3 suitable for X-ray analysis were grown by diffusion of methanol vapor into a solution in 1,2-dichloroethane at room temperature. The structure determination revealed a star-shaped geometry (Figure 3a,b). The dihedral angles around the central benzene ring (measured $\text{C}_\alpha\text{--C}_\beta\text{--C}_{\beta'}\text{--C}_{\alpha'}$) are 21.8(19), $-18.1(18)$, and $-10.4(17)^\circ$ (Figure 3a);

two of the porphyrin units are twisted, relative to the central benzene, whereas the third is slightly folded. In contrast, DFT calculations predicted that the D_3 -symmetric propeller-shaped conformation has the lowest energy in the gas phase. (All DFT calculations in this study were performed with B3LYP/6-31G(d,p), Gaussian 16/A.03; see the Supporting Information for details). The calculated energy difference between the conformation in the crystal and the DFT-optimized geometry of CP3 is only 4.6 kJ/mol, and coordination of solvent molecules (methanol) to the zinc centers may influence the preferred conformation. In the crystals, two enantiomers were found (P,M,M and P,P,M, where P and M denote right-handed and left-handed helices, respectively), which form homochiral dimers and these dimers pack alternatively along the *c*-axis (Figure S26).

We were not able to grow suitable single crystals of CP4 for X-ray analysis, despite screening many solvent systems, although the crystal structure of fullerene complex CP4-2C₆₀ was determined, as discussed below. According to the DFT calculations, the most stable conformation of CP4 is saddle-shaped having stereochemistry of P,M,P,M. The lowest energy geometry has a C_1 symmetry, but it is only 0.09 kJ/mol below the idealized D_{2d} saddle conformation, and these two conformers are more stable than the other diastereoisomers by over 252 kJ/mol (Figure S7). In the lowest energy C_1 symmetric geometry of CP4, the angles between the planes of neighboring porphyrin cores (planes each calculated for 24 core C and N atoms) are $\sim 57.3^\circ$, as shown in Figure 3d,e. The angle between the mean plane of each porphyrin and that of the COT ring is 42.7° (Figure 3e). The distance of the outermost β carbon atoms from the mean plane of the central COT is 6.21 Å. The folding angle of the COT unit, defined as the angle between the mean plane of one C=C=C unit and the mean plane of the whole COT is 42.2° , which is similar to that in unsubstituted COT (mean 41.9°).²²

The local aromaticity of the benzene ring at the core of CP3 can be evaluated from the C–C bond lengths using the harmonic oscillator model of aromaticity (HOMA), which compares the bond lengths around a ring to those in benzene

($R_{\text{opt}} = 1.388 \text{ \AA}$).²³ This analysis gives HOMA values of 0.52(11) and 0.81, from the crystallographic and DFT coordinates, respectively, which indicates that this benzene core has partial aromatic characters (see the [Supporting Information](#) for details). The nucleus-independent chemical shift calculated at a position of 1.0 Å above the center of this ring is NICS(1) = −7.5 ppm (for the D_3 geometry of **CP3**), which should be compared with a value of −10.2 ppm for benzene, confirming the partial aromatic character.²⁴ The central COT ring in **CP4** has strong bond-length alternation (Figure 3f), giving HOMA values of +0.21 and −0.02(18), from the DFT coordinates and the crystal structure of **CP4**·2C₆₀, respectively. This shows that there is no significant aromatic or antiaromatic delocalization in this core, as found in COT [HOMOA = −0.18(3)].²² The NICS(1) for the center of **CP4** is +5.2 ppm, which confirms that it is nonaromatic.

Photophysics and Electrochemistry. UV–vis absorption and fluorescence spectra of **CP3** and **CP4** are compared with those of monomer **P1**, as shown in Figure 4 (all spectra

recorded in toluene). Absorption spectra of both **CP3** and **CP4** show broader Soret bands and red-shifted Q-bands, compared with **P1**. The absorption bands of **CP3** are broader and more red-shifted than those of **CP4**, reflecting stronger electronic coupling and π -conjugation between the porphyrin units in **CP3**. Fluorescence spectra of **CP3** and **CP4** also red shift with respect to **P1** and their predominant emission peaks appear at 681 and 600 nm, respectively. Fluorescence quantum yields are 0.040 and 0.068 in non-deaerated toluene using zinc tetraphenylporphyrin ($\Phi = 0.029$ in toluene) as a standard²⁵ and are slightly higher than **P1** ($\Phi = 0.031$).

The electrochemistry of **P1**, **CP3**, and **CP4** was investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV). The CV trace of **P1** exhibits two reversible oxidation peaks at half-wave potentials of 0.41 and 0.71 V and two reduction peaks with half-wave potentials of −1.89 and −2.13 V versus Fc/Fc⁺. **CP3** shows three reversible oxidation peaks at 0.30, 0.46, and 0.71 V as well as one observable reduction peak at −1.84 V. The narrower HOMO–LUMO energy gap of **CP3** reflects the strong π -conjugation between the constituted porphyrins. Two reversible oxidation and reduction peaks located at 0.50, 0.91, −1.66, and −1.93 V were observed for **CP4** within the measured potential range. The fact that the measured redox potentials of **CP4** are close to **P1** reflects the weak electronic communication between the porphyrin units. It is surprising that the first oxidation potential of **CP4** (0.50 V) is higher than that of **P1** (0.41 V); a possible explanation for this effect is that the more sterically congested environment around each porphyrin unit in **CP4** hinders solvation of the positive charge when one of the four porphyrin units becomes oxidized to the radical cation.

Fullerene Binding. The design and synthesis of molecular receptors for fullerenes has been a focus of research because of their application in the separation and regioselective functionalization of fullerenes.^{4,26} Although many porphyrin-based fullerene receptors have been reported, all of them have spacers linking the porphyrin units.^{4–6} The saddle-shaped geometry of **CP4** and the cavity between two cofacial porphyrins inspired us to investigate its application as a host for fullerenes. The formation of a **CP4**·2C₆₀ complex was first detected by UV–vis titrations in toluene solution (Figure 5a). The Soret band absorption maxima of **CP4** red-shifted from 415 to 424 nm with the addition of C₆₀. The binding constant was measured to be $(2.2 \pm 0.1) \times 10^4 \text{ M}^{-1}$ by fitting the titration data to a 1:1 binding isotherm (Table S3). Similar behavior was observed for C₇₀, which shows a higher binding constant of $(1.1 \pm 0.4) \times 10^5 \text{ M}^{-1}$. Most porphyrin-based fullerene receptors bind C₇₀ more strongly than C₆₀ and this selectivity has been used for separating fullerenes.^{4,27} The strong binding of **CP4** with fullerenes was also confirmed by MALDI-TOF MS measurements using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix, which show peaks of the complexes with C₆₀ (Figure S23).

The stoichiometry of binding was checked by the ¹H NMR titration of **CP4** with C₆₀. As shown in Figure 5b, the protons (H^a) on the *meso*-positions of porphyrin and the ortho-position of the aryl groups (H^e) all shifted to the lower field region, while the protons on the other ortho-position of the aryl groups (H^g) shifted to the high-magnetic field region with the addition of C₆₀. The chemical shift changes approach saturation at around [C₆₀]/**CP4** = 2:1. ¹H NMR titration data fitted well to a 1:1 binding isotherm with a concentration of

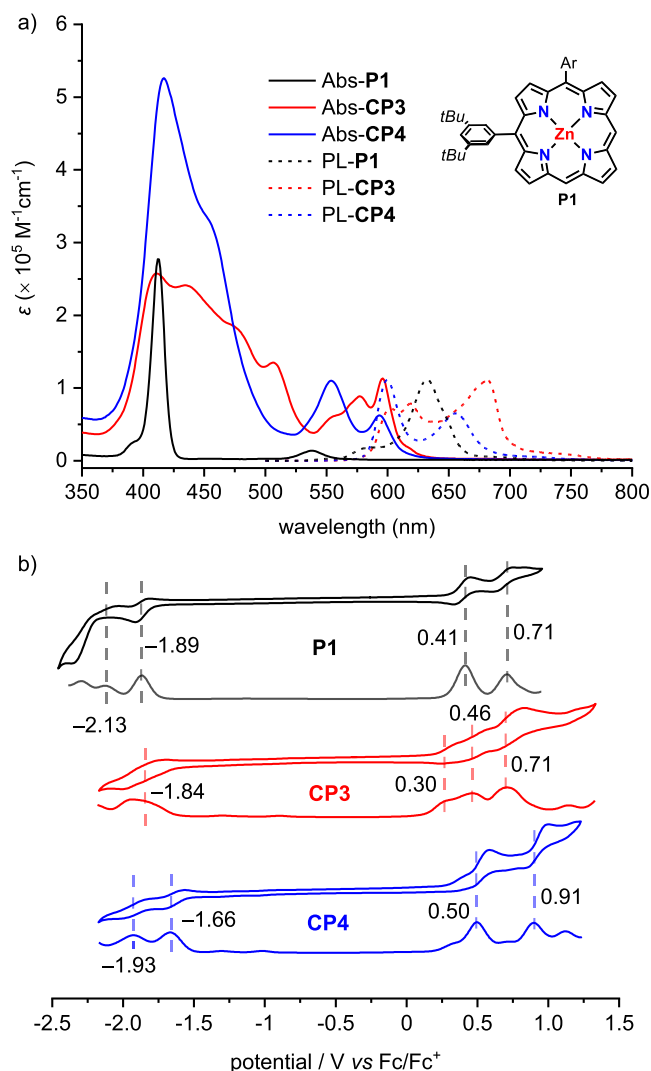


Figure 4. (a) UV–vis absorption and normalized fluorescence spectra of **P1**, **CP3**, and **CP4** measured in toluene (concentration 1 μM); for fluorescence measurements, excitation wavelengths are 417 nm (**P1**), 416 nm (**CP3**), and 415 nm (**CP4**); (b) cyclic and square wave voltammograms of **P1**, **CP3**, and **CP4** measured in dichloromethane with 0.1 M *n*-Bu₄NPF₆ at 298 K, scan rate 50 mV/s.

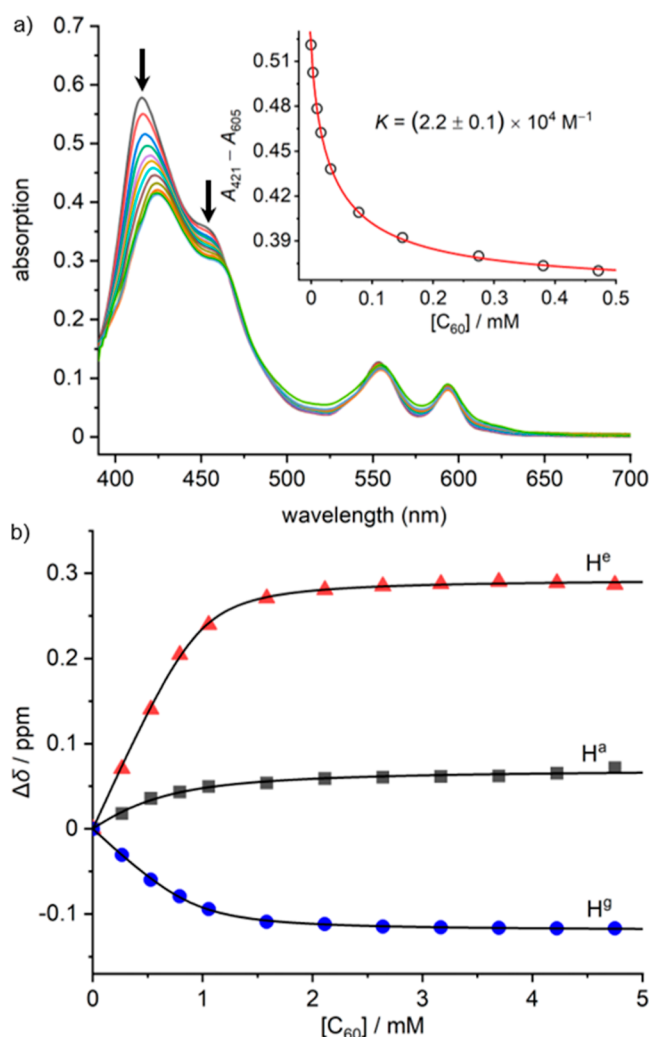


Figure 5. (a) UV-vis absorption spectra change of **CP4** ($c = 1.65 \mu\text{M}$) with the addition of C_{60} ($c = 0\text{--}0.47 \text{ mM}$) in toluene at 298 K, 10 mm path length. Spectra were corrected by subtracting C_{60} absorption; the inset shows plots of $A_{421} - A_{605}$ against the concentration of C_{60} , circles indicate the experimental data; (b) plots of chemical shift changes of protons (H^a , H^e , and H^g) on **CP4** ($c = 0.49 \text{ mM}$) with the addition of C_{60} (400 MHz, d_8 -toluene, 298 K).

receptor of 0.98 mM, which is exactly twice the actual concentration of **CP4**, implying that both sides of the receptor bind C_{60} independent of each other, i.e., with no cooperativity.

Single crystals of complex **CP4**· 2C_{60} were obtained by slow diffusion of methanol vapor into a solution of **CP4** and excess C_{60} in *o*-dichlorobenzene. Single-crystal X-ray diffraction studies revealed the 1:2 complex (**Figure 6**), which crystallized in the triclinic space group $P1$. The asymmetric unit was found to contain two molecules of **CP4** and four molecules of C_{60} . Examination of the structure suggested the presence of pseudo symmetry, which was thought to potentially be caused by a phase transition. For this reason, the sample was re-examined to explore whether data collected on a high temperature phase would give better results. Despite numerous attempts, the original triclinic phase was not seen again, instead a new orthorhombic phase was repeatedly found. This also revealed a 1:2 complex of **CP4** with C_{60} . The data and refinement for this new polymorph were markedly better than the first triclinic phase so this is the one primarily discussed here (though the

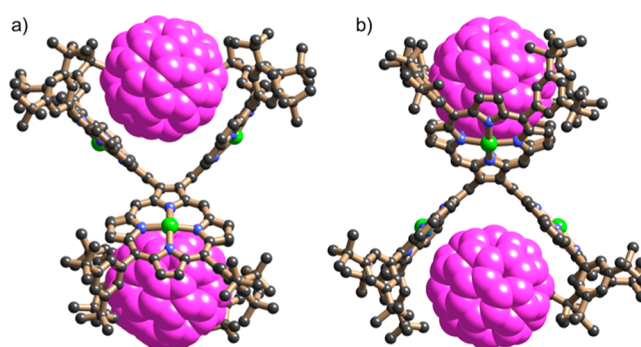


Figure 6. X-ray structure of **CP4**· 2C_{60} (orthorhombic phase). Two orthogonal views of the molecular unit; solvent molecules, hydrogen atoms, and disorder omitted for clarity.

triclinic polymorph is included in the [Supporting Information](#)).²⁸

All three crystallographically distinct **CP4**· 2C_{60} complexes seen in both crystal structure determinations have essentially the same geometry with methanol molecules coordinated to the central zinc atoms from the side that does not interact with fullerenes. Two fullerene molecules are captured by the cavity between two porphyrins located above and below the central COT ring. The shortest fullerene carbon to zinc distances are in the range of 3.15–3.29 Å, which is shorter than the sum of the van der Waals radii,²⁹ indicating an attractive interaction between fullerene and porphyrins. Each porphyrin skeleton adopts a saddle distortion, with a concave face towards a bound C_{60} molecule. The geometry of the **CP4** unit in this crystal of the C_{60} complex is similar to the DFT-calculated structure of **CP4** (**Figure 3**), which is consistent with the non-cooperative binding behavior deduced from UV-vis absorption and ^1H NMR titration data.

CONCLUSIONS

We have reported the synthesis of two 2,3-linked cyclic porphyrin oligomers **CP3** and **CP4**, with benzene and COT cores, via Yamamoto coupling of 2,3-dibromoporphyrin. The Yamamoto coupling of vicinal dibromides has previously been applied to link together various other conjugated π -systems, such as helicenes,³⁰ acepleiadylene,³¹ and tetracenes,³² but in most cases, this reaction gives just the benzene-centered cyclic trimer, not the COT-centered cyclic tetramer. The different numbers of porphyrin units in **CP3** and **CP4** result in different 3D geometries, leading to distinct optoelectronic properties. Although the minimum-energy geometry of **CP3** has a D_3 propeller-shaped structure, its crystal structure adopts a lower symmetry P,M,M/M,P,P configuration, whereas **CP4** exists in a stable saddle-shaped conformation with stereochemistry of P,M,P,M. π -Conjugation in **CP3** results in splitting and red shift of the absorption bands. By contrast, the saddle-shaped **CP4** shows similar optical and electrochemical properties to the monomer, due to the large dihedral angles between porphyrin units. The saddle-shaped geometry of **CP4** makes it a good receptor for fullerene and high binding constants of $(1.1 \pm 0.4) \times 10^5$ and $(2.2 \pm 0.1) \times 10^4 \text{ M}^{-1}$ were obtained for C_{70} and C_{60} , respectively, in toluene solution at 298 K. The 1:2 fullerene binding mode of **CP4** could be useful for holding two paramagnetic endohedral fullerenes at a fixed distance for quantum information processing.^{5b,33} This work also provides new insights into the design and synthesis of directly linked

cyclic porphyrin arrays with applications in photophysics and supramolecular chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c03549>.

Experimental details, characterization data, ^1H NMR, ^{13}C NMR, and MS spectra, and calculation details (PDF)

Accession Codes

CCDC 2223433 and 2253581–2253583 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Harry L. Anderson – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0002-1801-8132; Email: harry.anderson@chem.ox.ac.uk

Authors

Qiang Chen – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0001-5612-1504

Amber L. Thompson – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.; orcid.org/0000-0001-8258-860X

Kirsten E. Christensen – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.

Peter N. Horton – National Crystallography Service, School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

Simon J. Coles – National Crystallography Service, School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.; orcid.org/0000-0001-8414-9272

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.3c03549>

Notes

The authors declare no competing financial interest.

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