Light-initiated reversible conversion of macrocyclic endoperoxides derived from half-sandwich rhodium-based metallarectangles†‡

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Although reversible photo-dimerization or oxygenation of anthracene and its derivatives is a common reaction, light-initiated reversible conversion of endoperoxide organometallic frameworks has only rarely been addressed. Herein, a series of tetranuclear organometallic macrocycles, \([\text{Cp}^*\text{Rh}_2(\mu-C_2O_4-\kappa\text{O})]_2(\text{BP4VA})_2(\text{OTf})_4\) (4), \([\text{Cp}^*\text{Rh}_2(\text{BiBzIm})_2](\text{BP4VA})_2(\text{OTf})_4\) (5), and \([\text{Cp}^*\text{Rh}_2(\text{DHBQ})_2](\text{BP4VA})_2(\text{OTf})_4\) (6), were obtained in good yields from the reactions of the binuclear half-sandwich rhodium precursors \([\text{Cp}^*\text{Rh}_2(\mu-C_2O_4-\kappa\text{O})]_2\) (1), \([\text{Cp}^*\text{Rh}_2(\text{BiBzIm})_2]\) (2), and \([\text{Cp}^*\text{Rh}_2(\text{DHBQ})\text{Cl}_2]\) (3) with the 9,10-bis((E)-2-(pyrid-4-yl)vinyl)anthracene (BP4VA) ligand. The photochemical reaction of these metallarectangles was investigated by NMR and UV/vis spectroscopy. We have demonstrated that complexes 4, 5, and 6 can be reversibly and nearly quantitatively converted to the macrocyclic endoperoxides \(4-\text{O}_2\), \(5-\text{O}_2\), and \(6-\text{O}_2\). Meanwhile, the structure of the endoperoxide photoproducts was unambiguously confirmed by \(^1\text{H}/^{13}\text{C}\) NMR spectroscopy, IR spectroscopy, elemental analyses, and X-ray crystallography.

Introduction

Photochemical reactions have attracted enormous attention of photochemists and spectroscopists due to their wide range of applications in biological, luminescent and semiconducting materials science.1 Among many known photochemical reaction systems, anthracene and its derivatives are of special interest, because such photochemical reactions will not only produce \([4 + 4]\) photodimerization products under ultraviolet irradiation at 360–370 nm,2 but also produce \([4 + 2]\) photooxygenation products (9,10-endoperoxides) in the presence of oxygen.3 The photooxygenation products play an important role in materials science and organic chemistry.4 However, unambiguous confirmation of the photoproducts is still a great challenge in a photochemical reaction. Most related reports only use UV/vis absorption spectroscopy to characterize the photoproducts at present; apparently this is not sufficiently rigorous.1,5,6

Half-sandwich organometallic \([\text{Cp}^*\text{M}]\) \([\text{M} = \text{Ir and Rh}; \text{Cp}^* = \eta^5\text{pentamethylcyclopentadienyl}]\) fragments are widely exploited as metal corners in the construction of metallosupra-

molecular macrocycles and cages, due to their advantageous properties such as solubility, thermal stability, and others needed for flexibility in fine-tuning processes.6 Recently, our group has developed a range of functional macrocyclic architectures from various half-sandwich organometallic units and appropriately functionalized ligands through rational design.7 We thus envisaged these stable, well-defined architectures as scaffolds for introducing anthracene groups and their derivatives into organometallic macrocycles for the rigorous study of their photochemical behavior.

Following this idea, we selected three types of binuclear half-sandwich rhodium precursors of different sizes, \([\text{Cp}^*\text{Rh}_2(\mu-C_2O_4-\kappa\text{O})\text{Cl}_2]\) (1), \([\text{Cp}^*\text{Rh}_2(\text{BiBzIm})\text{Cl}_2]\) (2), and \([\text{Cp}^*\text{Rh}_2(\text{DHBQ})\text{Cl}_2]\) (3), as well as 9,10-bis((E)-2-(pyrid-4-yl)vinyl)anthracene (BP4VA) as the bridging ligand, which contains a 9,10-functionalized anthracene moiety as the photoactive unit. Herein, we report on the synthesis and characterization of a series of organometallic tetranuclear rectangular macrocycles: \([\text{Cp}^*\text{Rh}_2(\mu-C_2O_4-\kappa\text{O})]_2(\text{BP4VA})_2(\text{OTf})_4\) (4), \([\text{Cp}^*\text{Rh}_2(\text{BiBzIm})_2](\text{BP4VA})_2(\text{OTf})_4\) (5), and \([\text{Cp}^*\text{Rh}_2(\text{DHBQ})_2](\text{BP4VA})_2(\text{OTf})_4\) (6). The photochemical reactions of these complexes in solution in the presence of oxygen gas were investigated by NMR spectroscopy and UV-vis absorption spectroscopy. The results reveal that complexes 4, 5, and 6 can reversibly be converted to the endoperoxide photoproducts \(4-\text{O}_2\), \(5-\text{O}_2\), and \(6-\text{O}_2\) under ultraviolet (365 nm and 254 nm) irradiation in the presence of oxygen, which is further confirmed by single-crystal X-ray crystallography.
Results and discussion

Ligand BP4VA\(^6\) and three binuclear half-sandwich rhodium precursors \([\text{Cp}\ast\text{Rh}_2(\mu-\text{C}_2\text{O}_4\kappa\text{O})\text{Cl}_2]\) \(^1,7\) \([\text{Cp}\ast\text{Rh}_2(\text{BiBzIm})\text{Cl}_2]\) \(\text{BiBzIm} = 2,2'\text{-bisbenzimidazole}\) \(^2,7\) and \([\text{Cp}\ast\text{Rh}_2(\text{DHBQ})\text{Cl}_2]\) \(\text{DHBQ} = 2,5\text{-dihydroxy-1,4-benzoquinonato}\) \(^3\) were prepared according to literature methods. The metallarectangles 4, 5, and 6 were obtained by reaction of the BP4VA ligand and the binuclear complexes following a two-step formation strategy. As shown in Scheme 1, firstly, the binuclear complex was treated with two equivalents of silver trifluoromethanesulfonate (AgOTf) in the dark, so that it can be connected to the bridging donor ligand. Followed by addition of the bidentate pyridine linker BP4VA ligand, the crystalline products 4, 5, and 6 were obtained after extraction with methanol/diethyl ether in yields of 83%, 85%, and 78%, respectively. Single crystals of 6 were characterized by \(^1\text{H}\) NMR, \(^13\text{C}\) NMR, \(^1\text{H}\) COSY NMR, IR, and UV-vis absorption spectroscopy, and their elemental analyses were in agreement with their compositions. The molecular structures of the complexes were further determined by single-crystal X-ray diffraction studies.

All of the new complexes were isolated as their triflate salts. They are soluble in most common polar organic solvents such as CH\(_2\)CN and CH\(_3\)OH. The new metallarectangles 4, 5, and 6 were characterized by \(^1\text{H}\) NMR, \(^1\text{H}\) COSY NMR, IR, and UV-vis absorption spectroscopy, and their elemental analyses were in agreement with their compositions. The molecular structures of the complexes were further determined by single-crystal X-ray diffraction studies.

The \(^1\text{H}\) NMR spectrum of metallarectangle 4 (Fig. S5, ESI†) in CD\(_3\)CN clearly showed a sharp singlet at 1.62 ppm due to the C-H protons. Four doublets were observed at 7.71, 8.02, 6.83, and 8.10 ppm for the pyridine ring and olefin proton signals, along with two signals at 7.20 and 7.79 ppm due to the protons of the central anthryl group of the BP4VA ligand. The intensity ratio of these peaks was 60 : 8 : 8 : 4 : 4 : 8 : 8, respectively. In addition, the IR spectrum of complex 4 exhibited a strong band at 1665 cm\(^{-1}\) owing to the C=O stretch of the oxalate\(^8,11\) and strong absorptions due to stretching vibrations of the OTf anions appeared at 1260, 1032, and 639 cm\(^{-1}\), respectively.\(^12\)

The detailed structure of metallarectangle 4 was confirmed by single-crystal X-ray analysis. The crystal crystallized in the triclinic system, space group \(\text{P}\bar{1}\). The thermal ellipsoid drawing of 4 with the atomic numbering scheme and selected bond lengths and angles is given in Fig. 1. Complex 4 is composed of \([\text{Cp}\ast\text{Rh}_2(\mu-\text{C}_2\text{O}_4\kappa\text{O})]_{\text{BP4VA}}\)\(^{4+}\) cations, OTf\(^-\) counter-anions, CH\(_3\)OH and water solvent molecules in the solid. The cation part of 4 displays a slightly distorted tetrancular rectangular structure bridged by two binuclear [\(\text{Cp}\ast\text{Rh}_2(\mu-\text{C}_2\text{O}_4\kappa\text{O})\)]\(^4\) building blocks and two bridging ligands BP4VA. In complex 4, the \{\text{Cp}\ast\text{Rh}\} fragments adopt a classical three-legged piano-stool geometry, in which Rh atoms are coordinated by one nitrogen atom from the BP4VA ligand and two oxygen atoms of the oxalate group. The distances of the adjacent Rh atoms along the edges are approximately 5.53 and 20.25 Å, and the diagonal length of the rectangular structure is approximately 21 Å. The average Rh–O and Rh–N bond distances are approximately 2.14 and 2.12 Å, respectively, which are compatible with the values of previously published rhodium-based tetrancularic metallarectangles.\(^12c,13\) In addition, the structure shows that the two central anthracene rings of the BP4VA ligands are partially parallel to each other with a distance of 3.4 Å, indicating the presence of \(\pi-\pi\) interaction in complex 4 (Fig. 2a).

Interestingly, the three-dimen-
The red CD3CN solution was irradiated at 365 nm under an air atmosphere. However, when the solution was irradiated at 365 nm under a nitrogen atmosphere for 4 h, during which the color of the solution did not change. The metallarectangle is reactive toward O2 when irradiated at λ = 365 nm under air (free, 1 h, 2 h, 3 h, and 4 h).

As illustrated in Scheme 2, the photochemical reaction of complex 4 in solution was investigated. At room temperature, a red solution of complex 4 in degassed CD3CN was irradiated at λ = 365 nm under a nitrogen atmosphere for 4 h, during which the color of the solution did not change. However, when the red CD3CN solution was irradiated at 365 nm under an air or oxygen atmosphere, a yellow solution resulted. Moreover, when CD3OD was used as a solvent instead of CD3CN, the photochemical reaction phenomenon was not observed under the same reaction conditions. Preliminary studies showed that the metallarectangle 4 is reactive toward O2 when irradiated at λ = 365 nm, obtaining the macrocyclic endoperoxide 4-O2.

In addition, as shown in Fig. 3, the use of 1H NMR spectroscopy allowed the photochemical reaction of complex 4 to be investigated. At first, no detectable changes were observed in the 1H NMR spectra after irradiating the complex for 4 h under a nitrogen atmosphere. Then, a 1 mM solution of 4 in CD3CN was irradiated at λ = 365 nm under air. Upon irradiation, two new groups of proton signals gradually appeared, with a concomitant decrease in the concentration of metallarectangle 4. Two central anthracene moieties contained in each molecule of complex 4, which can act as photoactive units, are speculated to react with O2 stepwise to form an intermediate in which only one central anthracene moiety has been oxidized in the photochemical reaction process. As the 1H NMR signals of the central anthracene protons (δ = 7.20 and 7.95 ppm) gradually decreased, three sets of new signals of the anthracene proton resonances (δ = 7.00, 7.16, 7.54, 8.27 and 7.32, 7.48 ppm) gradually increased. Then the signals for the intermediate species (δ = 7.00, 7.16, 7.54 and 8.27 ppm) gradually decreased and finally disappeared, and the signals for endoperoxide 4-O2 (δ = 7.32 and 7.48 ppm) further increased and finally reached a maximum. A similar process was observed with the signals of the Cp* unit (Fig. S26†). After 4 h, nearly quantitative conversion was indicated by the disappearance of complex 4 proton resonances, and a new, unambiguous group of signals attributable to the endoperoxide photoproduction 4-O2 appeared. Compared with complex 4, the 1H NMR spectrum of 4-O2 exhibits similarly shaped signals for the protons of the Cp*, central anthracene, pyridyl, and olefin groups, and the intensity ratio of these peaks is equivalent to that of 4. However, significant changes take place in their chemical shift values owing to the loss of aromaticity of the central anthracene ring. For example, the signals of pyridine ring were found to be shifted from 7.71 and 8.02 ppm to 7.62 and 7.99 ppm, and the olefin proton signals were shifted from 6.83 and 8.10 ppm to 6.61 and 7.87 ppm. Additionally, the 1H diffusion-ordered spectroscopy (DOSY) NMR spectrum of 4-O2 (Fig. S17†) showed that the aromatic and Cp* signals displayed a single diffusion constant, suggesting that only one stoichiometry of assembly was present.

Another indication of the photochemical reaction process was the appearance of a new 13C NMR signal for the endoperoxide 4-O2 at δ = 81.81 ppm, corresponding to the bridgehead C9,10 carbons of the former central anthracene ring (Fig. S15†). In addition, as shown in Fig. 4, the resulting UV-vis absorption spectrum of 4 after irradiation also supported this conversion. No absorption was observed beyond λ = 300 nm, which indicated the formation of planar-symmetric photoproducts that involve only the central anthracene ring. In contrast, after irradiation of a 1 mM solution of free BP4VA in CDCl3 at λ = 365 nm under air for 2 h, no obvious changes were observed.

**Fig. 3** 1H NMR (CD3CN, 400 MHz, 25 °C) spectra of a 1 mM solution of 4; after irradiation at λ = 365 nm under air (free, 1 h, 2 h, 3 h, and 4 h).

**Fig. 4** UV/vis spectra of a 1 × 10−5 M solution of 4 and 4-O2 in CH3CN.
in the $^1$H NMR spectra (Fig. S27†). Meanwhile, the photoreaction of a binuclear complex of [Cp*Rh$_2$(BP4VA)]$^{4+}$ (see the ESI†) in a CD$_2$CN solution was also investigated by NMR spectroscopy. The $^1$H NMR spectra showed that the signals had no detectable change after the solution was irradiated at $\lambda = 365$ nm both under a nitrogen atmosphere and under air for 4 hours. This indicated that the {Cp*Rh} fragment in macrocycles may play an important role in the photochemical reaction.

A solution of 4 in acetonitrile was irradiated at 365 nm under an air or oxygen atmosphere, and the mixture was stirred at room temperature for 4 h. The volatiles were removed and the solid powder was recrystallized from acetonitrile/diethyl ether to give yellow crystals of 4-O$_2$. Single-crystal X-ray structure determination confirmed the structure of this photoproduct.

Single crystals suitable for X-ray structure determination were obtained by slow vapor diffusion of diethyl ether into a acetonitrile solution of macrocyclic endoperoxide 4-O$_2$. Single-crystal X-ray structure determination confirmed that 4-O$_2$ possesses a tetranuclear rectangle structure similar to complex 4. The thermal ellipsoid drawing with the atomic numbering of 4-O$_2$ is shown in Fig. 5. The structures of 4-O$_2$ clearly show that both central anthracene ring moieties of the complex 4 molecule have been oxidized, rather than linking to the opposite anthracene ring. These results confirmed that there is no [4 + 4] photodimerization reaction in the process, but rather a [4 + 2] photooxygénation reaction occurred, involving the cycloaddition of O$_2$ (singlet oxygen, generated from ambient air by direct irradiation of UV light$^{15}$) with the electron-rich carbon atoms of the anthracene ring.$^{15,16}$ In the structure of 4-O$_2$, the rhodium atom adopts a typical three-legged piano-stool conformation and is coordinated by one nitrogen atom from the oxidized BP4VA ligand and two oxygen atoms of oxalate group, resulting in a slightly distorted tetranuclear rectangle structure with dimensions of $5.48 \times 19.50$ Å as defined by the rhodium centers. The O–O distances of the newly formed peroxide groups of the intramolecular endoperoxide 4-O$_2$ are 1.521(13) Å. Additionally, the three-dimensional packing of 4-O$_2$ shows the formation of stacked channels when viewed from the y-axis, analogous to complex 4 (Fig. 5b).

To further investigate [4 + 2] photooxygénation reactions in half-sandwich rhodium-based metallarectangle systems, two binuclear rhodium precursors of different sizes and structures ([Cp*Rh$_2$(BiBzIm)]$^+$(2) and [Cp*Rh$_2$(DHBQ)Cl$_2$] (3)) were introduced (Scheme 1). The Rh⋯Rh distance of 2 is approximately 5.6 Å,$^{17}$ almost equivalent to complex 1, but this building block is significantly wider than 1. For complex 3, the Rh⋯Rh distance is much larger than that of complex 1 (approximately 8.0 Å).$^{10}$ By using complexes 2 and 3 in the place of complex 1 as building blocks with the BP4VA ligand under the same reaction conditions, complexes 5 and 6 were obtained as bright red and dark brown crystals, respectively. The structures of the two complexes were also confirmed by $^1$H NMR, $^{13}$C NMR, and IR spectroscopy, in addition to elemental analysis and X-ray crystallography. Compared with complex 4, the $^1$H NMR spectra of 5 and 6 show similar signals for the protons of the Cp*, central anthracene, pyridyl, and olefin units, with equivalent intensity ratios to those of 4. How, the spectra show significant differences due to the different binuclear building blocks used in 5 and 6. For example, the $^1$H NMR spectrum of 5 shows two distinct signals at 7.52 and 8.09 ppm for the aromatic protons of the BiBzIm ligand, and a sharp singlet was noted at 5.65 ppm due to the protons of the benzene ring of the DHBQ ligand in metallarectangle 6. Similarly, the IR spectra of complexes 5 and 6 also have some clear differences compared to that of 4 due to the disparate building blocks. The spectrum of 5 clearly showed a C≡N stretching frequency at ca. 1355 cm$^{-1}$ due to the BiBzIm ligand,$^{17,18}$ and two strong bands were observed at 1376 and 1259 cm$^{-1}$ for the DHBQ ligand of 6.$^{10}$ Strong absorptions attributed to the stretching vibrations of the OTf$^-$ anions were observed in the IR spectra of both complexes, as in that of complex 4, suggesting that these complexes have similar backbone structures.

The solid-state structures of complexes 5 and 6 were determined by single-crystal X-ray diffraction analysis, and confirmed that they have similar tetranuclear rectangle structures consistent with the metallarectangle 4. The thermal ellipsoid drawings of the two complexes with the atomic numbering scheme and selected bond lengths and angles are given in Fig. 6. The crystal structure of 5 is composed of [Cp*Rh$_2$(BiBzIm)]$^+$(BP4VA)$_2$$^{4+}$ cations, OTf$^-$ counterions, and CH$_3$CN molecules, while that of complex 6 is composed of [Cp*Rh$_2$(DHBQ)]$^+$(BP4VA)$_2$$^{4+}$ cations, OTf$^-$ counterions,
and some solvent molecules. Similarly to 4, the cation part of the complexes adopts a slightly distorted tetranuclear rectangular structure bridged by two dipyridyl BP4VA donor ligands and two binuclear building blocks ([Cp*2Rh2(BisZIm)]<sup>+</sup> in 5 or [Cp*<sup>+</sup>Rh2(DHBQ)]<sup>+</sup> in 6). The dimensions of the rectangular structures are 5.61 × 20.22 Å for 5 and 7.94 × 19.95 Å for 6, while the diagonal lengths are approximately 21 Å for 5 and 22 Å for 6. In addition, the structures of metallarectangles 5 and 6 also show the presence of parallel-displaced π–π stacking similar to complex 4 (Fig. S1†), and the face to face distances are 3.5 Å for 5 and 3.4 Å for 6, respectively. Furthermore, the three-dimensional packing of the two complexes shows the formation of stacked channels when viewed from the y axis, analogous to the metallarectangle 4 (Fig. S2†).

As illustrated in Scheme 2, the photochemical reactions of complexes 5 and 6 were also investigated by NMR spectroscopy and UV absorption spectroscopy. As expected, all of the results were similar to those obtained with complex 4. Complexes 5 and 6 were converted into the macrocyclic endoperoxides 5-O<sub>2</sub> and 6-O<sub>2</sub> by irradiation at λ = 365 nm under air. The <sup>1</sup>H NMR spectra (Fig. S28 and S30†) showed all proton resonances of 5 and 6 to be replaced by a new, unambiguous group of signals after irradiation for 4 and 5 h, respectively. During the reaction, the color of complex 5 in CD<sub>3</sub>CN solution changed from red to yellow and that of complex 6 in the same solvent was little changed and was slightly lighter. Similarly, the use of <sup>1</sup>H NMR spectroscopy allowed the photochemical reaction process of complexes 5 and 6 to be elucidated (Fig. S29 and S31†). The results indicated the presence of an intermediate during the reaction of both complexes. The <sup>13</sup>C NMR spectrum of the resulting endoperoxides 5-O<sub>2</sub> and 6-O<sub>2</sub> also supported this conversion, and new signals for the bridgehead C<sub>9,10</sub> carbon nuclei of the former central anthracene ring were found at 82.12 and 82.55 ppm, respectively (Fig. S19 and S23†). Additionally, the UV-vis absorption spectra of 5-O<sub>2</sub> and 6-O<sub>2</sub> also supported this conversion through distinct quenching of the anthryl bands after irradiation (Fig. S33 and S34†). The macrocyclic endoperoxides were formed during these photochemical reactions of 5 and 6, which was strongly supported by all the observed results. In other words, the size of the binuclear rhodium precursors has little effect on the photochemical reactions. X-ray crystallographic analysis further confirmed the molecular structure of the two macrocyclic endoperoxides.

Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into solutions of the macrocyclic endoperoxides in methanol/acetonitrile. Single-crystal X-ray structural analysis revealed similarly deformed tetranuclear rectangle structures of the macrocyclic endoperoxides 5-O<sub>2</sub> and 6-O<sub>2</sub>, and the thermal ellipsoid drawings with the atomic numbering scheme and selected bond lengths and angles are given in Fig. 7a (5-O<sub>2</sub>) and Fig. 7b (6-O<sub>2</sub>). Similar to endoperoxide 4-O<sub>2</sub>, the structures of the two endoperoxides revealed that the central anthracene ring moieties of complexes 5 and 6 had been oxidized rather than linked to the opposite anthracene ring. In both complexes, each rhodium...
atom adopts a typical three-legged piano-stool conformation and was coordinated by three oxygen or nitrogen atoms and a Cp* ring. The dimensions of the oxidised rectangular structures were found to be $5.59 \times 19.44 \text{ Å}$ for $5\text{O}_2$ and $7.97 \times 19.60 \text{ Å}$ for $6\text{O}_2$. The newly formed O–O bond lengths of the endoperoxide photoproducts are $1.480(7) \text{ Å}$ for $5\text{O}_2$ and $1.497(6) \text{ Å}$ for $6\text{O}_2$, respectively. In addition, the three-dimensional packing of these complexes shows the formation of stacked channels when viewed from the y-axis analogous to their initial structures (Fig. S3\textsuperscript{3}).

A number of studies have revealed that the decomposition of endoperoxide photoproducts occurs either by irradiation with deep UV light ($\lambda < 300 \text{ nm}$) or thermally (about 60 °C).\textsuperscript{18} In this study, we sought to investigate the deep UV light cycloreversion of the macrocyclic endoperoxides by NMR spectroscopy and UV-vis absorption spectroscopy. When a yellow Cd$_2$CN solution of endoperoxide $4\text{O}_2$ was irradiated with shorter wavelength light ($\lambda = 254 \text{ nm}$) for 8 hours at room temperature in a quartz tube reactor, the color reverted back to red. The $^1\text{H}$ NMR spectrum of the solution indicated a nearly quantitative conversion of the macrocyclic endoperoxide $4\text{O}_2$ due to the disappearance of endoperoxide $4\text{O}_2$ proton resonances and the restored signals of complex 4 after irradiation (Fig. 8). The UV-vis absorption spectrum also supported this reversible conversion for the absorption bands of the central anthracene ring were restored after irradiation (Fig. S3\textsuperscript{3}). The other typical cycloreversion method was also employed by heating a Cd$_2$CN solution of $4\text{O}_2$. However, even after heating the solution to 60 °C for 12 hours, the color of the solution remained unchanged and no changes in the $^1\text{H}$ NMR spectra and UV-vis absorption spectra were observed. The decomposition reactions of macrocyclic endoperoxides $5\text{O}_2$ and $6\text{O}_2$ were also investigated by the same techniques. The experimental results of $^1\text{H}$ NMR spectroscopy and UV-vis absorption spectroscopy indicated that these endoperoxides could also be reversibly converted to the original anthracene structures after irradiation at $\lambda = 254 \text{ nm}$ for 8 hours (Fig. S28, S30, S34, and S35) and no change was observed after heating to 60 °C for 12 hours. This indicated that the endoperoxide photoproducts $5\text{O}_2$ and $6\text{O}_2$ can only reversibly be converted to the organometallic macrocycles 5 and 6 under irradiation at $\lambda = 254 \text{ nm}$.

**Conclusions**

In summary, a series of discrete organometallic macrocycles with tetranuclear rectangle structures were synthesized by using the anthracene-containing BP4VA ligand together with half-sandwich rhodium building blocks. We found that the metallaractangles 4, 5, and 6 were nearly quantitatively converted into the macrocyclic endoperoxides $4\text{O}_2$, $5\text{O}_2$, and $6\text{O}_2$ under irradiation at 365 nm. The structures of the endoperoxide photoproducts have been unambiguously confirmed by $^1\text{H}/^1\text{C}$ NMR and IR spectroscopy, as well as elemental analysis and X-ray crystallography. Further studies found that the endoperoxides undergo reversible conversion to the original anthracene structures under irradiation at 254 nm. These results will be useful for further work on the design and synthesis of macrocyclic endoperoxide frameworks.

**Experimental section**

**General considerations**

All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise mentioned. All reactions were carried out using a Matrix-10 reactor with sixteen ultraviolet lamps (10 W per lamp) as the irradiation source. NMR spectra were recorded on Bruker AVANCE I 400 spectrometers at room temperature and referenced to the residual protonated solvent. Proton chemical shifts are reported relative to the residual solvent peak ($\delta \text{H} = 1.94$ (CD$_3$CN), $\delta \text{H} = 3.31$ (CD$_3$OD), and $\delta \text{H} = 7.26$ (CDCl$_3$)). Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra of the solid samples (KBr tablets) in the range of 400–4000 cm$^{-1}$ were recorded on a Nicolet AVATAR-360IR spectrometer. UV/vis absorption spectra were recorded on a Lambda 20 UV/vis spectrometer.

**Synthesis of complex 4**

Ag(OTf) $[51.4 \text{ mg, } 0.2 \text{ mmol}]$ was added to a solution of $[\text{Cp}^*\text{Rh}_2(\mu-C_2\text{O}_4\cdot\text{κO})\text{Cl}_2]$ (1) [63.9 mg, 0.1 mmol] in CH$_3$OH (20 mL) at room temperature. The mixture was sheltered from light and stirred for 3 h, followed by filtration to remove AgCl, at which point the BP4VA ligand (38.5 mg, 0.1 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 12 h. The solvent was then concentrated to about 3 mL. Upon the addition of diethyl ether, a dark red solid of 4 precipitated and was collected and dried under vacuum after washing with diethyl ether. Yield: 106 mg, 83%.

**Data for complex 4:**

$^1\text{H}$ NMR (400 MHz, Cd$_2$CN, ppm): $\delta = 1.62$ (s, 60H, $\text{Cp}^*\text{H}$), 6.83 (d, $J = 16.4$ Hz, 4H, $-\text{CH} = \text{CH} = \text{CH} = \text{CH}$), 7.20 (dd, $J = 6.8, 2.8$ Hz, 8H, anthracene–H), 7.71 (d, $J = 6$ Hz, 8H, pyridyl–H), 7.95 (dd, $J = 6.4, 3.2$ Hz, 8H, anthracene–H), 8.02 (d, $J = 6$ Hz, 8H, pyridyl–H), 8.10 (d, $J = 16.8$ Hz, 4H, 8H, pyridyl–H).
Synthesis of complex 4-O₂

A solution of 4 (132 mg, 0.05 mmol) in CH₃CN (20 mL) was irradiated at 365 nm under air, and the mixture was stirred at room temperature for 4 h. The volatiles were removed and the solid powder was recrystallized from CH₃CN/ether to give yellow crystals of 4-O₂. Yield: 128 mg, 93%. *Data for complex 4-O₂*: ¹H NMR (400 MHz, CD₃CN, ppm): δ = 1.59 (s, 60H, Cp⁺-H), 6.61 (d, J = 16.4 Hz, 4H, -CH=CH-), 7.32 (dd, J = 5.2, 3.2 Hz, 8H, anthracene-H), 7.48 (dd, J = 5.2, 3.2 Hz, 8H, anthracene-H), 7.62 (d, J = 5.6 Hz, 8H, pyridyl-H), 7.87 (d, J = 16.4 Hz, 4H, -CH=CH-), 7.99 (d, J = 6 Hz, 8H, pyridyl-H). ¹³C{¹H} NMR (101 MHz, CD₃CN, ppm): δ = 9.01, 81.81, 96.53, 96.62, 123.34, 125.03, 128.69, 130.29, 132.18, 140.94, 147.74, 151.99, 171.49. IR (KBr disk, cm⁻¹): ν = 3455 (s), 1663 (m), 1619 (s), 1460 (w), 1426 (w), 1384 (w), 1260 (m), 1066 (w), 1032 (s), 979 (w), 855 (w), 765 (w), 639 (m), 574 (w), 518 (w), 459 (w). Elemental analysis calcld (%) for C₁₅₅H₁₁₁₂O₂₅₅N₂₁₅F₁₁₁₂Rh₄S₄: C: 51.14, H: 4.51, N: 2.12; found C: 49.27, H: 4.74, N: 2.09.

Synthesis of complex 5-O₂

A solution of 5 (160 mg, 0.05 mmol) in CH₂CN (20 mL) was irradiated at 365 nm under air, and the mixture was stirred at room temperature for 4 h. The volatiles were removed and the solid powder was recrystallized from CH₂CN/ether to give yellow crystals of 5-O₂. Yield: 151 mg, 95%. *Data for complex 5-O₂*: ¹H NMR (400 MHz, CD₂CN, ppm): δ = 1.75 (s, 60H, Cp⁺-H), 6.56 (d, J = 16.8 Hz, 4H, -CH=CH-), 7.01 (dd, J = 5.2, 3.2 Hz, 8H, anthracene-H), 7.13 (dd, J = 5.2, 3.2 Hz, 8H, anthracene-H), 7.34 (d, J = 6.4 Hz, 8H, pyridyl-H), 7.45-7.52 (m, J = 6.4, 3.6 Hz, 12H, -CH=CH- and Ar-H), 8.04 (dd, J = 6.4, 3.2 Hz, 8H, Ar-H), 8.27 (d, J = 6.8 Hz, 8H, pyridyl-H). ¹³C{¹H} NMR (101 MHz, CD₂CN, ppm): δ = 10.36, 82.12, 98.15, 98.23, 117.32, 123.19, 124.19, 124.82, 128.77, 130.58, 130.89, 140.21, 144.56, 147.38, 153.73, 157.41. IR (KBr disk, cm⁻¹): ν = 3451 (s), 1606 (m), 1449 (m), 1380 (w), 1355 (w), 1257 (s), 1224 (w), 1159 (m), 1066 (w), 1031 (s), 978 (w), 911 (w), 849 (w), 750 (m), 638 (s), 573 (w), 518 (w), 495 (w), 443 (w). Elemental analysis calcld (%) for C₁₅₃H₁₁₂O₂₁₅N₂₁₁₂F₁₁₁₂Rh₄S₄: C: 51.88, H: 4.80, N: 5.26; found C: 52.05, H: 4.51, N: 5.09.

Synthesis of complex 6

Ag(OTf) (51.4 mg, 0.2 mmol) was added to a solution of [Cp²Rh₂(DBHQB)[C]₃] (3) (68.5 mg, 0.1 mmol) in CH₂OH (20 mL) at room temperature. The mixture was sheltered from light and stirred for 3 h, followed by filtration to remove AgCl, and then the BP4VA ligand (38.5 mg, 0.1 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 12 h. The solvent was concentrated to about 3 mL. Upon the addition of diethyl ether, a dark brown solid of 6 precipitated and was collected and dried under vacuum after washing with diethyl ether. Yield: 115 mg, 78%. *Data for complex 6*: ¹H NMR (400 MHz, CD₂CN, ppm): δ = 1.67 (s, 60H, Cp⁺-H), 5.65 (s, 4H, Ar-H), 6.85 (d, J = 16.4 Hz, 4H, -CH=CH-). 10.0 (dd, J = 6.8, 2.8 Hz, 8H, anthracene-H), 7.77 (d, J = 5.2 Hz, 8H, pyridyl-H), 8.02 (dd, J = 6.8, 2.8 Hz, 8H, anthracene-H), 8.19-8.25 (m, 12H, pyridyl-H and -CH=CH-). ¹³C{¹H} NMR (101 MHz, CD₂CN, ppm): δ = 9.03, 96.71, 96.80, 124.80, 126.66, 126.81, 129.75, 132.46, 134.10, 143.73, 147.86, 152.37, 184.54. IR (KBr disk, cm⁻¹): ν = 3445 (s), 1608 (m), 1531 (s), 1427 (w), 1376 (m), 1259 (s), 1225 (w), 1161 (m), 1066 (w), 1031 (m), 824 (w), 765 (w), 639 (m), 580 (w), 519 (w). Elemental analysis calcld (%) for C₁₃₃H₁₁₅O₂₅₅N₂₁₁₂F₁₁₁₂Rh₄S₄: C: 50.62, H: 5.07, N: 1.90; found C: 51.09, H: 4.62, N: 2.15.

Synthesis of complex 6-O₂

A solution of 6 (147 mg, 0.05 mmol) in CH₂CN (20 mL) was irradiated at 365 nm under air, and the mixture was stirred at room temperature for 5 h. The volatiles were removed and the solid powder was recrystallized from CH₂CN/ether to give yellow crystals of 6-O₂. Yield: 144 mg, 92%. *Data for complex 6-O₂*: ¹H NMR (400 MHz, CD₂CN, ppm): δ = 1.64 (s, 60H, Cp⁺-H), 5.64 (s, 4H, Ar-H), 6.99 (d, J = 16.4 Hz, 4H, -CH=CH-), 7.07 (m, 8H, anthracene-H), 7.28 (m, 8H, anthracene-H), 7.84 (d, J = 16.4 Hz, 4H, -CH=CH-), 7.78 (d, J = 5.6 Hz, 8H,
pyridyl–H), 8.28 (d, J = 5.6 Hz, 8H, pyridyl–H). $^{13}$C(1H) NMR (101 MHz, CD$_3$CN, ppm): δ = 8.99, 82.55, 96.70, 96.79, 102.64, 123.32, 125.26, 128.97, 130.85, 131.32, 140.25, 148.01, 152.50, 184.70. IR (KBr disk, cm$^{-1}$): ν = 3451 (s), 1614 (m), 1523 (s), 1460 (w), 1427 (w), 1375 (m), 1258 (s), 1224 (w), 1160 (m), 1061 (w), 1031 (m), 977 (w), 821 (w), 763 (w), 639 (m), 588 (w), 518 (w). Elemental analysis calcd (%) for C$_{136}$H$_{148}$O$_{26}$N$_{12}$F$_{12}$Rh$_{4}$S$_{4}$: C: 52.11, H: 4.76, N: 5.36; found C: 51.89, H: 4.34, N: 4.98.

X-ray crystallography details

Single crystals of 4, 5, 6, 4-O$_2$, 5-O$_2$ and 6-O$_2$ suitable for X-ray diffraction study were obtained at room temperature. X-ray intensity data of 4, 6, 4-O$_2$, and 5-O$_2$ were collected on a Bruker D8 VENTURE system at 173 K, and data of 5 and 6-O$_2$ were collected on a CCD-Bruker SMART APEX system at 202 K and 173 K, respectively. These structures were solved by direct methods, using Fourier techniques, and refined on $F^2$ by a full matrix-least-squares method. All calculations were carried out using the SHELXTL program.$^{19}$ Crystal data, data collection parameters, and the results of the analysis of these complexes are listed in Tables S1–S6 in the ESI.$^†$ CCDC: 1575529 (4), 1575532 (5), 1575533 (6), 1575530 (4-O$_2$), 1575531 (5-O$_2$), and 1575534 (6-O$_2$)$^2_2$ contain the supplementary crystallographic data for this paper.

Conflicts of interest

There are no conflicts to declare.

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References


