

# Synthesis and crystal structure of a wheel-shaped supramolecular coordination complex

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**Abstract.** Supramolecular coordination complex (SCC) possessing spatially arranged three anthraquinone dimers in a slipped-cofacial orientation was achieved by the treatment of  $\text{Re}_2(\text{CO})_{10}$ , 2-hydroxymethylanthraquinone and tritopic N-donor *via fac*- $\text{Re}(\text{CO})_3$ -directed one pot approach. The off-set  $\pi$ -stacking and  $\text{C}\equiv\text{O}\cdots\text{H}$  bonding interactions stabilize the ring structure.

**Keywords.** Rhenium; molecular ring; anthraquinone; non-covalent interactions; supramolecules; X-ray structure.

## 1. Introduction

The metal-directed self-assembly methods and crystal X-ray crystallography have been collectively providing supramolecular coordination complexes from aesthetically pleasing small to unimaginably big molecular architectures.<sup>1</sup> The crystallographic analysis has become the most powerful analytical technique for the elucidation of the structure of the final product. The details of the structural parameters and the non-covalent interactions existing in the supramolecular coordination complexes (SCCs) provide motivation to create interesting and potential new molecules as well as mimics of naturally existing molecules.

A variety of metal-directed synthetic methods have been applied to design and synthesize distorted cycles and platonic solid shaped metallacycles e.g., rectangles, prisms and octahedron; modulating the size and properties of the final structure by changing either the organic building unit or metal cores.<sup>2</sup> No attention has been paid to achieve wheel-shaped structures possessing spatially arranged  $\pi$ -dimers in a cyclic manner. However, owing to the poor-directionality of the  $\pi$ - $\pi$  interactions, the construction of non-covalently bound  $\pi$ -stacked dimers is challenging.<sup>3</sup> Moreover, a cyclic arrangement of close lying, non-covalently linked chromophores is an important feature of the photosynthetic antenna and reaction centre proteins where a slipped-cofacial orientation (SCO) of *bacteriochlorophyll*-*a*

dimers in the light harvesting complexes (LHCs) plays a crucial role in photosynthetic bacteria.<sup>3</sup> Keeping these under consideration, efforts are still being expanded on the design and synthesis of macrocyclic ring-like functional assemblies possessing non-covalently linked  $\pi$ -stacked dimers of porphyrin or other chromophores using metal-directed strategy. In this paper we report a one-step synthesis and crystal structure of a wheel-shaped supramolecule possessing cyclic arrangement of slipped-cofacial dimers of anthraquinone units.

## 2. Experimental

### 2.1 General experimental methods

$\text{Re}_2(\text{CO})_{10}$ , 2-hydroxymethylanthraquinone (H-mAq) and 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (tpt) were purchased from commercial sources and used as received. Toluene was purified by conventional procedures and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer.  $^1\text{H}$  NMR spectra for **1** and the bulk product were recorded on a Bruker AMX-400 FT-NMR spectrometer. ICPMS was recorded on a Perkin-Elmer ICP Mass Spectrometer. X-ray data for complex **1** was collected using an OXFORD XCALIBUR-S CCD single crystal X-ray diffractometer. The structure was solved and refined by full-matrix least-squares techniques on  $F^2$  using the SHELX-97 program.<sup>10</sup> The absorption corrections were done by multiscan (SHELXTL program package), and all the data was corrected for Lorentz, polarization effects.

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## 2.2 Synthesis of hexanuclear complex 1

A mixture of  $\text{Re}_2(\text{CO})_{10}$  (98.4 mg, 0.15 mol), tpt (32 mg, 0.10 mmol), and H-mAq (71.5 mg, 0.30 mmol) in toluene (15 mL) was placed in a Teflon inliner which was placed in a stainless steel autoclave. The autoclave was placed in an oven maintained at  $150^\circ\text{C}$  for 25 h and then cooled to room temperature. Good quality single crystals of **1** were separated from the resulting product and washed with pet-ether. Yield: 68.1 mg. FTIR ( $\text{KBr}/\text{cm}^{-1}$ ): 2023 ( $\text{C}\equiv\text{O}$ ), 2018 ( $\text{C}\equiv\text{O}$ ), 1809 ( $\text{C}\equiv\text{O}$ ), 1674 ( $\text{C}=\text{O}$ ).  $^1\text{H}$ NMR ( $d_6$ -DMSO):  $\delta$  8.95 (12 H, d,  $^3J_{\text{H,H}} = 6$  Hz,  $\text{H}^{\text{a}}$ , tpt), 8.64 (12 H, d,  $^3J_{\text{H,H}} = 6$  Hz,  $\text{H}^{\text{b}}$ , tpt), 8.22–8.19 (12 H, m,  $\text{H}^{8,5}$ , -mAq), 8.18 (6 H, s,  $\text{H}^1$ , -mAq), 7.94–7.91 (12 H, m,  $\text{H}^{7,6}$ , -mAq), 7.85 (6 H, d,  $\text{H}^3$ , -mAq), 5.6 (6H, t, -OH, mAq), 4.7 (12 H, d,  $^2J_{\text{H,H}} = 6$  Hz,  $-\text{CH}_2-$ , -mAq).

## 2.3 Crystal diffraction data

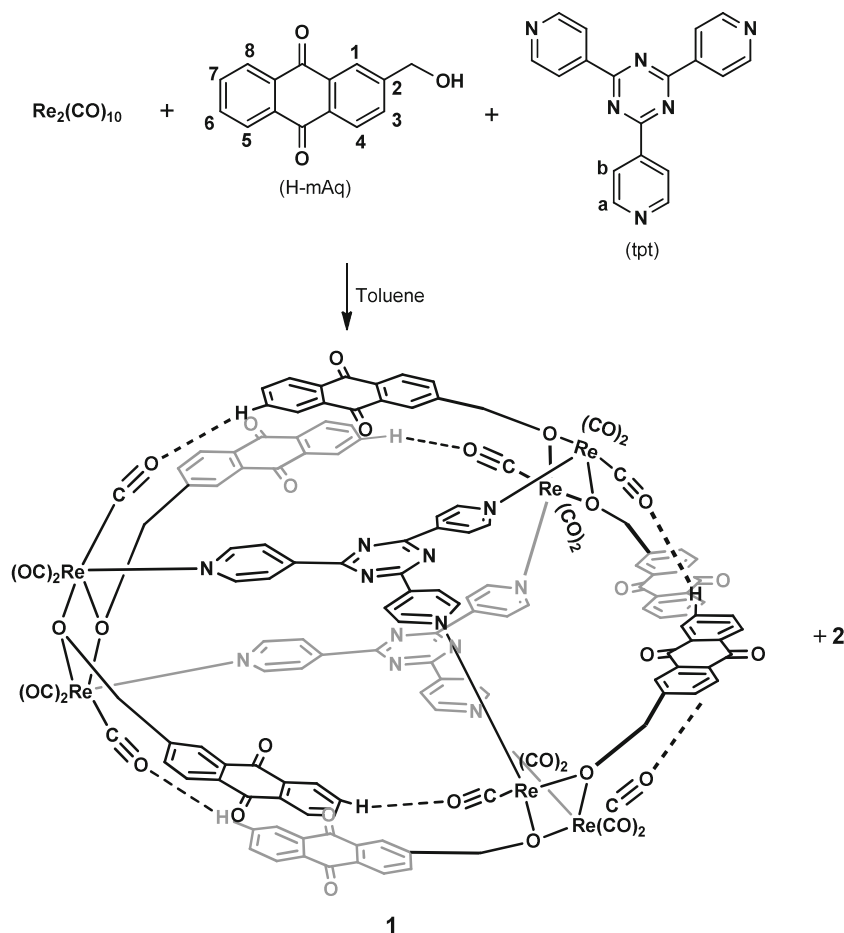
$\text{C}_{144}\text{H}_{78}\text{N}_{12}\text{O}_{37}\text{Re}_6$ ,  $M = 3685.45$ , hexagonal,  $a = 24.1039(6)$ ,  $b = 24.1039(6)$ ,  $c = 13.1545(3)$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 120^\circ$ ,  $V = 6618.8(3)$  Å<sup>3</sup>,  $T = 183(2)$  K,

space group  $P6_32_2$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 5.552$  mm<sup>-1</sup>, 36038 reflections measured, 4214 unique ( $R_{\text{int}} = 0.0926$ ) which were used in all calculations. GOF on  $F^2$ : 0.650.  $R^{\text{a}} [I > 2\sigma(I)]$ : 0.0364.  $R_w^{\text{b}}$  (all data): 0.0837. The final  $wR(F_2)$  was 0.1057 (all data).

## 3. Results and discussion

### 3.1 Characterization

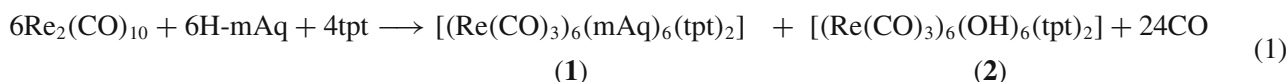
A combination of  $\text{Re}_2(\text{CO})_{10}$ , 2-hydroxymethyl-9,10-anthraquinone (H-mAq) and 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (tpt) in toluene under solvothermal conditions leads to a mixture of products as brown crystals and light-brown powder (scheme 1 and eq. 1). Few bigger crystals out of the bulk product were hand-picked under a microscope and used for structural analysis. The crystalline product  $[(\text{Re}(\text{CO})_3)_6(\text{mAq})_6(\text{tpt})_2]$  (**1**) and powder  $[(\text{Re}(\text{CO})_3)_6(\text{OH})_6(\text{tpt})_2]$  (**2**) are air- and moisture-stable and poorly soluble in most of the organic solvents. The FT-IR spectrum of **1** exhibits strong bands at 2023, 2018, and 1809 cm<sup>-1</sup>,



**Scheme 1.** Multicomponent assembly of metallomacroring **1**.

characteristic of *fac*-Re(CO)<sub>3</sub> moiety in an asymmetric environment.<sup>4</sup> The absorption band at 1674 cm<sup>-1</sup> is attributed to the stretching vibrations of C=O bond of the anthraquinone fragments (figure S2).<sup>5</sup> The <sup>1</sup>HNMR spectrum of **1** dissolved in *d*<sub>6</sub>-DMSO by heating shows a pair of doublets (8.95, 8.64 ppm)

for the pyridyl protons of the tpt units. No significant chemical shifts were observed for the protons of anthraquinone unit in **1** as compared to anthraquinone protons of the free ligand which indicated towards the poor stability of complex **1** in solution (figure S3 in ESI<sup>†</sup>).

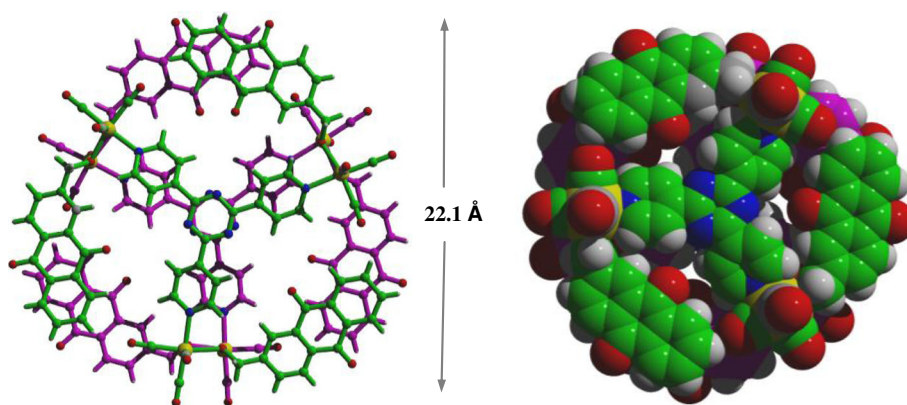


However, the <sup>1</sup>HNMR spectrum of the powder sample shows two types of resonance patterns; one of the patterns match exactly with that of the crystalline product (1), while the other indicates the formation of a hydroxyl-bridged trigonal prism (2) (figure S3). The observation of the molecular ion peak at 2371.87 m/z for (2) in the ICPMS spectrum confirmed the presence of 2 (figure S4). Several attempts to procure pure **1** by varying the concentration of starting materials and reaction conditions were fruitless. The complete separation of **1** from the bulk was extremely difficult due to the poor solubility and tininess of the crystals. Based on the integration ratios of the <sup>1</sup>HNMR resonances, the yield of complex **1** was estimated to be above 30%. Therefore, it can be proposed that the bulk product consists of a mixture of **1** and **2**.

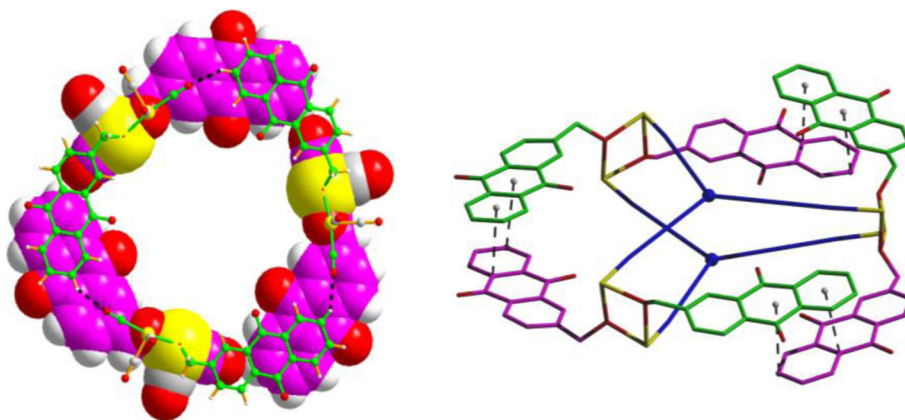
### 3.2 X-ray crystal structure

Compound **1** crystallizes in a chiral space group *P*6<sub>3</sub>2<sub>2</sub> and adopts a spoked-wheel structure (figure 1). The ring

in **1** is composed of alternatively arranged three rigid modules of anthraquinone dimers (mAq)<sub>2</sub> and three ((CO)<sub>3</sub>Re-(μ<sub>2</sub>-O)<sub>2</sub>-Re(CO)<sub>3</sub>) units having a diameter of about 2.2 nm including the van der Waals radii. The two tpt units act as spokes to support the ring structure. Several intramolecular non-covalent interactions such as C-H···O≡C and π-π stacking stabilize the ring framework. The slipped-cofacial head-to-head orientation, planarity and tilted angle favours the strong electrostatic self-complimentary π-π interactions of electron rich arene portions to electron poor quinone portions of Aq units in (mAq)<sub>2</sub> dimer units in **1** (figure 1). The distance between the two anthraquinone moieties in a anthraquinone dimer is in the range of 3.6 to 3.8 Å (figure 2). Complex **1** has three anthraquinone dimer sets and the distance between the two mAq duplexes is *ca.* 7.27 Å. The hydrogen atom of the sixth carbon of anthraquinone unit bridges to a nearby carbonyl unit (C-H···O≡C (D = 3.11 Å, d = 2.32 Å, θ = 143°)) in a concerted fashion to complete the ring structure (figure 2).<sup>6</sup> Examples of metal-based trigonal-prisms were reported



**Figure 1.** Structure of **1** (ball and stick and space-filling representations, Green = rose = C, white = H, blue = N, red = O, yellow = Re).



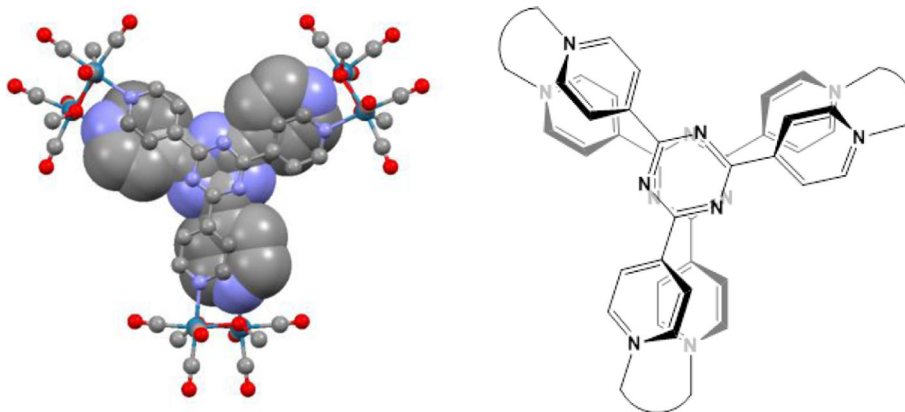
**Figure 2.** Left: space-filling and ball and stick view of **1** showing intramolecular H-bonds (two tpt units are omitted). Right: stick view of **1** showing dimeric unit (two tpt units are shown as blue sticks, H atoms and carbonyl groups are omitted for clarity).

previously by us and others.<sup>4</sup> To the best of our knowledge, this is the first report on SCC with more than one slipped-cofacially arranged organic dimers in a cyclic manner.<sup>1,4</sup>

Interestingly, the tpt units are found to be twisted in the trigonal prismatic framework of SCC **1**. The cofacial pyridyl subunits are out of the plane of the triazine rings by an angle of  $21.5^\circ$  and are not perfectly eclipsed; inducing chirality to **1** (triazines, dihedral angle =  $0^\circ$ ,  $d$  (centroid  $\cdots$  centroid distance) =  $3.4 \text{ \AA}$ ; pyridines, tilted angle =  $21.5^\circ$ , dihedral angle =  $2.3^\circ$ ,  $d$  =  $3.4\text{--}3.5 \text{ \AA}$ ) (figure 3). A variety of tpt based metalloprisms having the eclipsed pyridyl units are known to be achiral.<sup>4</sup> The degree of deviation from the trigonal prismatic geometry is measured by the Bailar Twist Angles which is  $18.29^\circ$  for all the three pyridyl dimers.<sup>7</sup> A very few

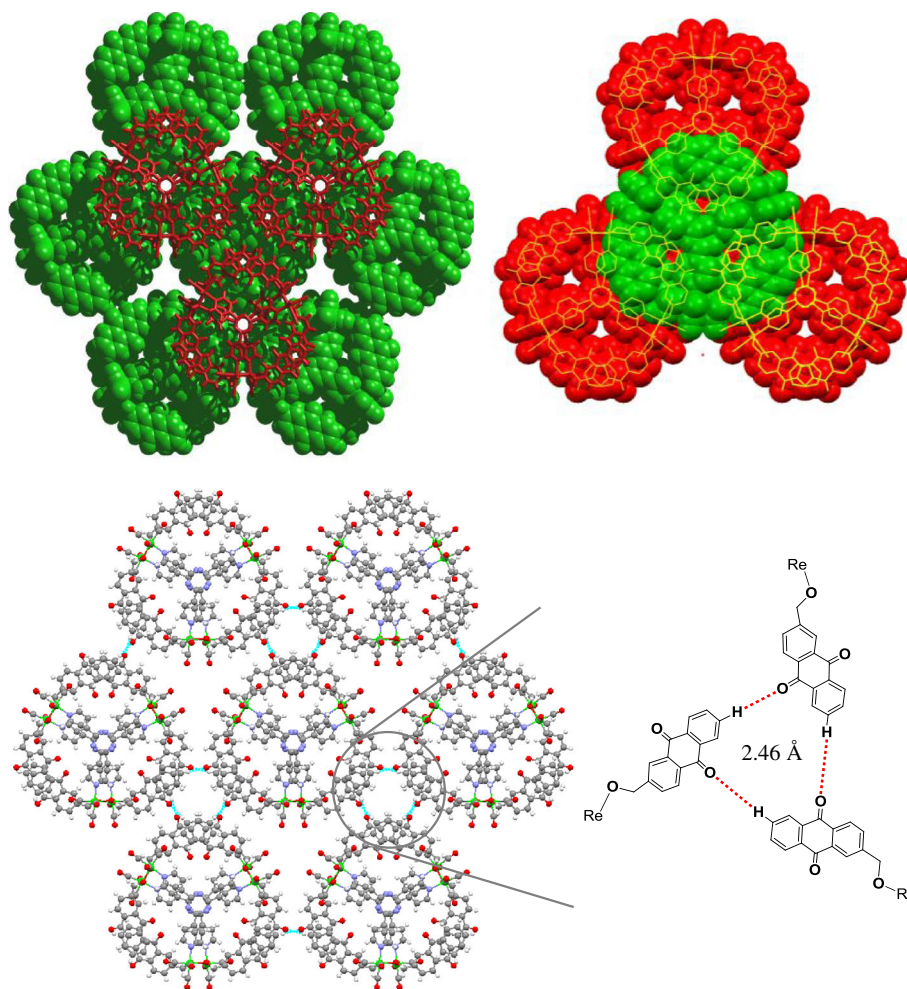
chiral self-assembled metalloprisms are known in the literature.<sup>8</sup>

Another feature of complex **1** is its packing arrangement. It extends as 2D hexagonal layered structure along the *ab* direction, stabilized by intermolecular  $\text{C-H} \cdots \text{O}$  interactions between anthraquinone units ( $\text{C-H} \cdots \text{O}=\text{C}$ ,  $D = 3.37 \text{ \AA}$ ,  $d = 2.46 \text{ \AA}$ ,  $\theta = 165.7^\circ$ ). Each anthraquinone in the ring interacts with anthraquinone units of the two neighbouring rings; hence, overall each macrocyclic ring interacts with six others (figure 4). A similar type of self-assembled H-bonded trimer of anthraquinone molecules was observed on a Cu(111) surface.<sup>9</sup> In addition, the sheets are stacked in an ABAB layered pattern along the *c*-axis, resulting in 3D supramolecular network through extensive intermolecular  $\pi \cdots \pi$  stacking interactions.



**Figure 3.** The Bailar Twist between the two tpt frameworks in the macrocycle **1**. All the three staggered pyridyl units show equal twist of  $18.29^\circ$ . The Aq dimers and hydrogens have been removed for clarity.





**Figure 4.** Top: space-filling and ball and stick view of portion of layers of molecules of **1**. Down: one layer containing six SCCs showing H-bonding interactions.

#### 4. Conclusion

These findings proffer a one-step design strategy to achieve nanocyclic ring structure consisting of organic chromophores positioned as slipped-cofacial dimers. We believe this metal-directed building principle would provide a new direction to assemble wheel-shaped supramolecules with photoactive units. Current research in our laboratory is directed to replace anthraquinone unit by porphyrin and other light harvesting units in similar systems as complex **1**.

#### Supplementary Information

The electronic supplementary information can be seen at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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