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Porphyrin "Flying-Saucers": Solid State and Solution Structure of a Novel Pentameric Array of Axially-Ligated Canted Porphyrins

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Introduction

Supramolecular arrays of porphyrins are actively investigated as models of the photosynthetic reaction center and as light-harvesting devices.[1,2] Synthetic models are required for understanding how photoinduced long-range electron or energy-transfer processes depend on the three-dimensional architecture of the pigments (number, distance, mutual orientation).

We previously described the orthogonal dimeric and pentameric arrays of porphyrins [Ru(TPP)(CO)(4′MPyP)] and (4′TPyP)$[Ru(TPP)(CO)]_4$,[3] derived by axial coordination of *meso* 4′-pyridylporphyrins (4′-PyPs) to Ru(TPP)(CO) units.[4] Recent experimental evidence suggested that some photophysical properties of the adducts might be due to the "side-to-face" arrangement of the pigments.[5] Hence, we decided to investigate whether such photophysical properties depend upon the dihedral angle between the porphyrin planes by using *meso* 3′-pyridylporphyrins (3′PyPs), instead of 4′PyPs, as building blocks.[6] Even though several side-to-face arrays of perpendicularly linked porphyrins have been described,[4,7] the examples of canted adducts are few and all very recent.[8,9] After describing the solution and solid-state structure of the canted dimeric adduct [Ru(TPP)(CO)(3′MPyP)],[9] we report herein a thorough NMR characterization of the corresponding pentameric array (3′TPyP)$[Ru(TPP)(CO)]_4$ (**1**), together with a well-defined X-ray structure of the corresponding zinc derivative (Zn•3′TPyP)$[Ru(TPP)(CO)]_4$ (**1Zn**). Well-defined structural characterization of conjugates of high nuclearity is rare[7b] and concerns exclusively perpendicular arrays.

Experimental Section

3′TPyP was prepared as described.[10] Characterization of 3′TPyP: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.46$ (s, 4H, 3′py H2), 9.08 (m, 4H, 3′py H6), 8.87 (s, 8H, pyrrole), 8.53 (m, 4H, 3′py H4), 7.79 (m, 4H, 3′py H5), −2.83 (s, 2H, NH); UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 417 (450 000), 482 (3600), 514 (19 300), 547 (7800), 588 (5800), 644 nm (4000).

(3′TPyP)$[Ru(TPP)(CO)]_4$ (1). Addition of 3′TPyP (11.7 mg, 1.8×10^{-2} mmol) to a chloroform suspension (15 mL) of [Ru(TPP)(CO)(EtOH)] (60 mg, 7.78×10^{-2} mmol) yielded a deep-purple solution within minutes. The system was allowed to react overnight at room temperature. The crude product precipitated from the concentrated solution upon addition of *n*-hexane and was collected on a filter, washed with cold methanol and *n*-hexane, and vacuum-dried; yielded 57.5 mg (84%). **1** was recrystallyzed from chloroform/*n*-hexane. Characterization of **1**. $C_{220}H_{138}N_{24}O_4Ru_4$ (3586): calcd C 73.7, H 3.85, N 9.38; found C 73.2, H 3.80, N 9.19. M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.44$ (s, 32H, pyrrole TPP), 8.11 (d, 16H, *exo* phenyl *o*-H), 7.57 (t, 16H, *exo* phenyl *m*-H), 7.42 (t, 16H, phenyl *p*-H), 7.32 (d, 16H, *endo* phenyl *o*-H), 6.89 (t, 16H, *endo* phenyl *m*-H), 6.50 (m, 4H, 3′py H4), 6.39 (s, br, 8H, pyrrole 3′TPyP), 5.70 (m, 4H, 3′py H5), 2.17 (s, 4H, 3′py H2), 1.98 (m, 4H, 3′py H6), −4.31 (s, 2H, NH). IR (Nujol): $\nu = 1950$ cm^{-1} (C═O). UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 407 (1 064 000), 531 (81 200), 564 (23 300), 594 (7700), 654 nm (4400).

(Zn·3′TPyP)$[Ru(TPP)(CO)]_4$ (1Zn). A methanol solution (5 mL) of zinc acetate (22 mg, 9.8×10^{-2} mmol) was added to the deep-purple chloroform solution (50 mL) of **1** (70 mg, 2.0×10^{-2} mmol). The system was allowed to react overnight at room temperature. The crude product precipitated from the concentrated solution upon addition of *n*-hexane and was collected on a filter, thoroughly washed with water, methanol, and then with *n*-hexane, and vacuum-dried; yielded 54 mg (76%). Recrystallization from chloroform/*n*-hexane yielded crystals suitable for X-ray analysis. Characterization of **1Zn**: $C_{220}H_{136}N_{24}O_4Ru_4Zn$ (3651.36): calcd C 72.3, H 3.73, N 9.20; found C 72.6, H 3.76, N 9.15. m.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.42$ (s, 32H, pyrrole TPP), 8.10 (d, 16H, *exo* phenyl *o*-H), 7.56 (t, 16H, *exo* phenyl *m*-H), 7.42 (t, 16H, phenyl *p*-H), 7.28 (d, 16H, *endo* phenyl *o*-H), 6.87 (t, 16H, *endo* phenyl *m*-H), 6.62 (m, 4H, 3′py H4), 6.51 (s, 8H, pyrrole 3′TPyP), 5.70 (m, 4H, 3′py H5), 2.14 (s, 4H, 3′py H2), 1.98 (m, 4H, 3′py H6); IR (Nujol): $\nu = 1949$ cm^{-1} (C═O); UV−vis (CH_2Cl_2): λ_{max} (ϵ) = 407 (1 110 000), 432 (326 700), 533 (76 000), 564 (29 200), 595 (6700), 655 nm (1000).

Crystallographic Study. $C_{220}H_{136}N_{24}O_4Ru_4Zn\cdot CHCl_3\cdot 13C_6H_{14}$, $M = 4889$, tetragonal, space group $P4_2/n$, $a = 31.551$ Å, $b = 31.551$ Å, $c = 12.900$ Å, $Z = 2$, $V = 12\,841$ Å^3, $\rho_{calcd} = 1.27$ g cm^{-3}, final R1, wR2, and S are 0.083, 0.237, and 1.0637, respectively, for 576 parameters and 4040 independent reflections with $I > 2\sigma(I)$. Crystals (dark red needles, approximately $0.3 \times 0.08 \times 0.05$ mm) outside the

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(3) Abbreviations: *meso*-tetraphenylporphyrin (TPP); 5-(4′-pyridyl)-10,-15,20-triphenylporphyrin (4′MPyP); 5,10,15,20-tetra(4′-pyridyl)porphyrin (4′TPyP); 5-(3′-pyridyl)-10,15,20-triphenylporphyrin (3′MPyP); 5,10,15,20-tetra(3′-pyridyl)porphyrin (3′TPyP); octaethylporphyrin (OEP).

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(6) Assuming that the 3′N(py) rings lie perpendicularly to the mean plane of 3′PyP and that the Ru−3′N bond is perpendicular to the TPP plane, a 30° dihedral angle between 3′PyP and TPP planes would be expected (see top of Figure 3).

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mother liquor, from the release of the crystallization solvent, started to degrade in seconds. A few crystals with the mother liquor were transferred to a large amount of one component of an epoxy-glue. In this dense solution, the crystals were stable. A selected crystal was fixed on the glass fiber by means of the second glue component and flash frozen to 100 K. Data were collected at the X-ray diffraction beamline of the Elettra Synchrotron (Trieste, Italy), using the rotating crystal method with 0.8 Å monochromatic wavelength and a MAR 345 mm image plate with a crystal-detector distance of 140 mm giving 1.00 Å resolution at the edge. The data were integrated using the program DENZO[11] and reflections subsequently were scaled and merged using the program SCALEPACK,[11] giving a final R_{merge} of 0.102 for 5090 independent reflections. The structure was solved by a heavy atom method, using SHELXL-97.[12] The complex was located on a $\bar{4}$ crystallographic symmetry center. After an anisotropic refinement (R1 = 0.19), the difference Fourier maps showed many uninterpretable weak peaks in the regions above the Zn atom and behind the Ru(TPP)(CO) moiety from solvent molecules, $CHCl_3$ and *n*-hexane, used during crystallization. Disordered solvent correction was made using PLATON-SQUEEZE software,[13] and 1396 electrons per unit cell of solvent were recognized. The new electron density maps showed a chlorine atom of a disordered chloroform bound to the zinc. The Zn atom was found to be shifted in the direction of $\bar{4}$ axis toward Cl with the Zn−Cl fragment disordered in two equivalent positions below and above the central porphyrin ring. The 1396 electrons of the disordered solvent were assigned to the remaining fragment of chloroform and to 26 *n*-hexane molecules per unit cell. Refinements were carried out by full-matrix least squares of F^2 for all data using SHELXL-97.[12]

Results and Discussion

Reaction of 3′TPyP with a slight excess of [Ru(TPP)(CO)(EtOH)] in $CHCl_3$ at room temperature, followed by precipitation with *n*-hexane, yielded selectively and almost quantitatively the pentameric compound (3′TPyP)[Ru(TPP)(CO)]$_4$ (**1**). The corresponding zinc adduct (Zn·3′TPyP)[Ru(TPP)(CO)]$_4$ (**1Zn**) was prepared by treatment of **1** with an excess of zinc acetate in $CHCl_3$/MeOH. Recrystallization of **1Zn** from $CHCl_3$/*n*-hexane yielded crystals suitable for X-ray analysis (data collected at the X-ray diffraction beamline of the Elettra Synchrotron of Trieste, Italy), which established the molecular structure shown in Figure 1. The pentameric adduct has a very compact structure; the ruthenium porphyrin rings lie alternatively above and below the mean plane of the central 3′TPyP, thus giving a global “flying-saucer” shape to the assembly when side-viewed (see graphical abstract). The 3′N(py) six-membered rings have a propeller-like arrangement and form dihedral angles of about 65° with the mean plane of 3′TPyP. Accordingly, the pairs of ruthenium porphyrins that face each other on the same side of the 3′TPyP plane and that are bonded almost orthogonally to the 3′N(py)’s are tilted away by approximately 50°. The dihedral angle between the mean plane of 3′TPyP and that of TPP is very close to 40° (compared to ca. 43° in [Ru(TPP)(CO)(3′MPyP)][9] and ca. 81° in [Ru(OEP)(CO)(4′MPyP)][7c]). Moreover, the mutal orientation of opposite Ru(TPP)(CO) units is such that the phenyl groups pointing toward each other are staggered, thus allowing the two porphyrin rings to mesh together like two gears (Figure 2). Bond distances within both porphyrin rings are average for these systems.[7c,9,14] The Ru−3′N(py) bond length (2.179(9) Å) is comparable to that found in the canted dimeric adduct [Ru(TPP)(CO)(3′MPyP)] (2.189(2) Å)[9] and in [Ru(TPP)(CO)(py)] (2.193(4) Å),[14] but significantly shorter than that found for the 4′N(py) compound [Ru(OEP)(CO)(4′MPyP)] (2.237(4) Å),[7c] suggesting that coordination of Zn·3′TPyP to the four Ru(TPP)(CO) units is not strained. The central zinc porphyrin is bent; the Zn atom was found displaced from the site of $\bar{4}$ symmetry along the *c* axis by 0.426(3) Å. Furthermore, it is involved in an axial coordination with a chlorine atom of a disordered chloroform. The ruthenium porphyrin macrocycle is slightly puckered, and the Ru atom lies 0.132(2) Å out of the plane toward the CO group.

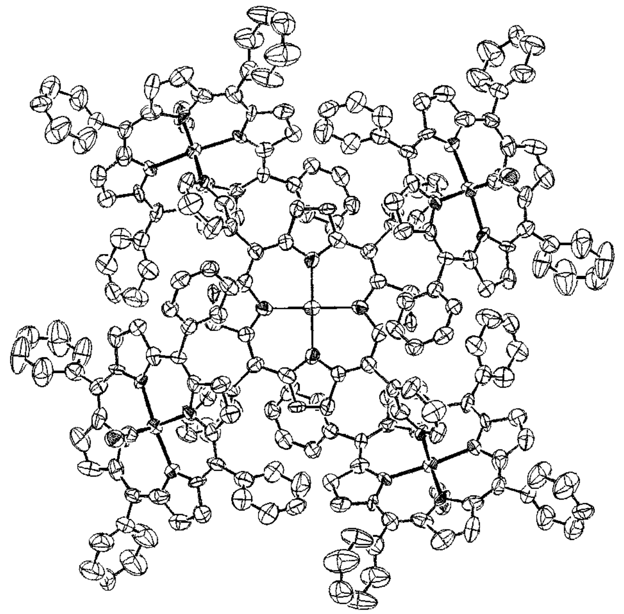

Figure 1. ORTEP view (thermal ellipsoids at 20% probability) of (Zn·3′TPyP)[Ru(TPP)(CO)]$_4$ (**1Zn**) with the atom-labeling scheme of the asymmetric unit. Selected bond lengths [Å] and angles [deg]: Ru−N1 2.041(7), Ru−N2 2.024(7), Ru−N3 2.047(7), Ru−N4 2.035(8), Ru−N6 2.179(9), Ru−C1(CO) 1.815(12), C1(CO)−O1(CO) 1.167(11), Zn−N5 2.097(8); Ru−C1(CO)−O1(CO) 175.6(9), C1(CO)−Ru−N6 177.5(4).

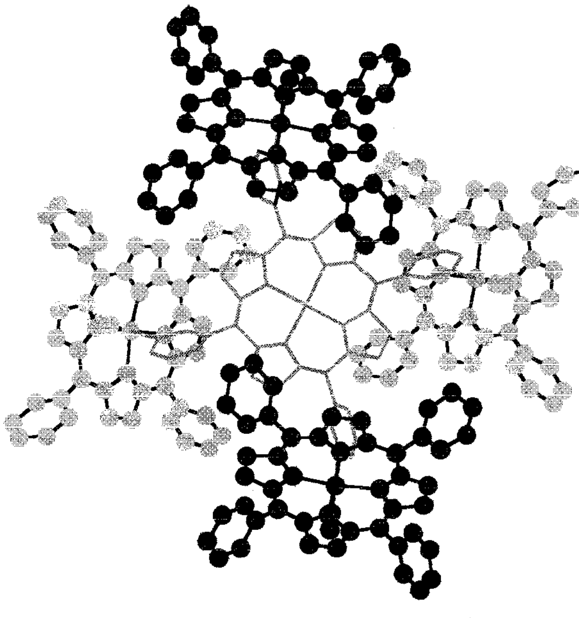

Figure 2. A view of the molecular structure of (Zn·3′TPyP)[Ru(TPP)(CO)]$_4$ (**1Zn**) perpendicular to the central porphyrin plane; Ru(TPP)(CO) units laying above the mean plane of Zn·3′TPyP are darker.

Both **1** and **1Zn** are soluble and stable (according to ^{1}H NMR) in chloroform solution. The electronic absorption spectrum of **1** matched very closely to the sum of the spectra of the monomeric components, suggesting weak mutual perturbation

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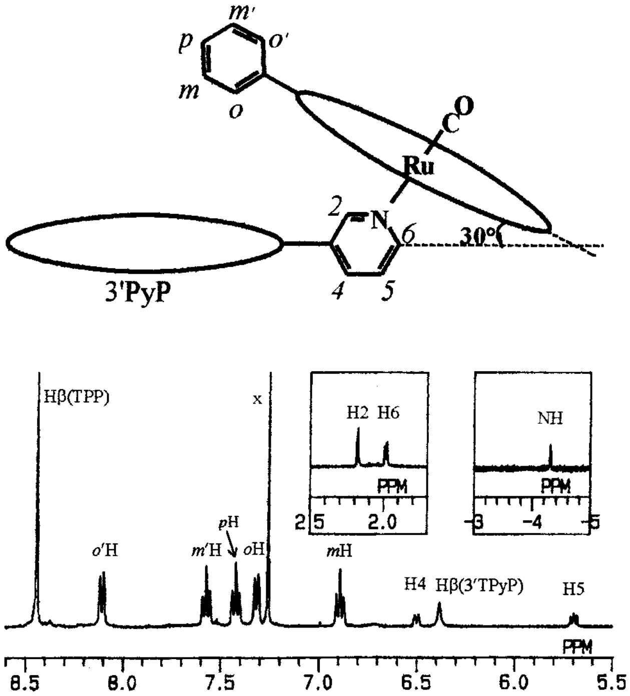

Figure 3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of (3′TPyP)[Ru(TPP)(CO)]$_4$ (**1**). See top drawing for labeling scheme; pyrrole resonances are marked with β, solvent peak with x.

of the chromophoric units. The particularly simple ^{1}H NMR spectrum of the pentamer (Figure 3) indicated that a symmetrical arrangement of the four Ru(TPP)(CO) units around 3′TPyP (very likely similar to that found in the solid state and resulting from rapidly, on the NMR time-scale, equilibrating conformers) is preserved also in solution; no exchange between coordinated and free 3′TPyP was observed. All resonances of 3′TPyP were dramatically shifted upfield by the cumulative shielding effect of the four anisotropic ruthenium porphyrins. The upfield shift is highest for H2 and H6 ($\Delta\delta$ = ca. −7 ppm),[15] thus establishing unambiguously the coordination site of ruthenium, and gradually decreases as the Ru porphyrin−proton distance increases. For geometrical reasons, because of the canting of the porphyrin planes, the shielding effect on the inner NH protons ($\Delta\delta = -1.48$ ppm) in **1** is lower compared to that observed in the corresponding orthogonal array (4′TPyP)[Ru(TPP)(CO)]$_4$ ($\Delta\delta = -1.95$ ppm).[4] All 16 phenyl rings are equivalent, indicating free rotation of Ru(TPP) about the Ru-3′N(py) bond; however, the pairs of ortho- and meta-protons on each ring are clearly nonequivalent, suggesting that rotation about the C(*meso*)−C(phenyl) bond is slow on the NMR time-scale. Five well-resolved multiplets for the aromatic protons were in fact observed, with COSY connections between *o*H−*m*H−*p*H−*m*′H−*o*′H. In virtue of the mutual orientation of porphyrin planes, which brings the phenyl rings into the anisotropic region of 3′TPyP (Figure 3), the shielding effect on *endo* protons (*o*H 7.32 ppm, *m*H 6.89 ppm) is much larger than that of *exo* protons (*o*′H 8.11 ppm, *m*′H 7.57 ppm) and considerably more pronounced than in the (4′TPyP)[Ru(TPP)(CO)]$_4$ adduct.[4] Overall, the NMR data, through chemical shift and symmetry arguments, indicated that at room temperature all six-membered rings experience hindered rotation about the C(*meso*)−C(ring) bond and lie essentially perpendicular to the mean plane of the corresponding porphyrin. Therefore, in solution the dihedral angle between 3′TPyP and TPP planes, as an average, is very likely closer to the ideal value of 30°. In CD_2Cl_2, a progressive broadening of all resonances was observed for $T < -20$ °C (beginning with the singlet of eight 3′TPyP pyrrole protons), very likely because of the decreased rate of rotation of the Ru(TPP)(CO) units about the Ru-3′N(py) bonds.

Conclusions

The pentameric arrays of canted porphyrins **1** and **1Zn** represent new entries in the class of metal-mediated supramolecular assemblies of chromophores, thus allowing comparisons with previously studied perpendicular and canted side-to-face arrays. This is also the first case in which a well-defined X-ray structure of a canted adduct of axially ligated porphyrins of high nuclearity is reported. The photophysical properties of **1** and of the corresponding perpendicular pentamer are described in detail in a forthcoming paper.[5]

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, calculated hydrogen atomic coordinates, interatomic distances and angles, anisotropic displacement parameters, and torsion angles for **1Zn**, and figures illustrating dihedral and torsion angles, two porphyrins with atomic numbering scheme and plane labels, nonplanarity of porphyrin skeletons, and COSY spectrum of **1**, and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] The chemical shift difference $\Delta\delta$ is defined as δ(pentamer) − δ(parent porphyrin).