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Formation of Coordination Porphyrin Pentamers in New Supramolecular Complex of Fullerene: $\{(ZnTPP)_4{\cdot}4\text{-}TPyP\}{\cdot}(C_{60})_2{\cdot}(C_6H_5CN)_{3.5}$

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ABSTRACT: A new supramolecular complex of fullerene C_{60}, $\{(ZnTPP)_4{\cdot}(4\text{-}TPyP)\}{\cdot}(C_{60})_2{\cdot}(C_6H_5CN)_{3.5}$ (ZnTPP: zinc(II) tetraphenylporphyrin; 4-TPyP: tetra(4-pyridyl)porphyrin) involving unusual pentamers containing five porphyrin fragments, was obtained. The crystal structure, IR and UV−vis−NIR spectra of the complex, and the molecular structure of the pentamer are presented.

Fullerenes are promising components to be used in photovoltaic devices such as plastic solar cells and modeling of artificial photosynthesis.[1,2] Dyads and triads containing fullerenes and covalently or coordinatively attached porphyrins and phthalocyanines show effective charge transfer from chromophore to fullerenes, which results in relatively long-lived charge-separated states in both solution[3,4] and solid phase.[5]

Donor−acceptor complexes of fullerenes with porphyrins were intensively studied along with dyads and triads. It was shown that photoexcitation of zinc(II) tetraphenylporphyrin in the presence of C_{60} in solution results in effective charge transfer from porphyrin to the C_{60} molecule.[6] Photoinduced charge transfer between C_{60} and more complicated coordination porphyrin aggregates, namely, $(RuTPP{\cdot}CO)_4{\cdot}(3\text{-}TPyP)$, and $(RuTPP{\cdot}CO)_4{\cdot}(4\text{-}TPyP)$ pentamers (RuTPP·CO: ruthenium(II) carbonyl tetraphenylporphyrin; 4-TPyP: tetra(4-pyridyl)porphyrin); 3-TPyP: tetra(3-pyridyl)porphyrin), was studied in solution.[7] Up to now about several dozens of crystalline fullerene complexes with metal-containing octaethyl- and tetraarylporphyrins and metal-free tetraarylporphyrins were characterized.[8−12] Such complexes can also be promising photoactive materials.[3] Several approaches were used to develop porphyrin-fullerene architectures in the solid state. A multicomponent approach allows one to obtain ionic complexes of general formula: $[(D_1^{\bullet+}){\cdot}(Co^{II}TPP{\cdot}C_{60}^{-}){\cdot}solvent]$ (D_1: bis(benzene)chromium or tetrakis(dimethylamino)ethylene; Co^{II}TPP: cobalt(II) tetraphenylporphyrin).[13−15] Metal-bridged pyridyl-substituted porphyrins form another family of fullerene/porphyrin complexes.[16,17] We used N-containing ligands to obtain supramolecular fullerene C_{60} complexes with ZnTPP·Py and CoTPP·Py (Py: pyridine) monomeric units,[12] and $(ZnTPP)_2$Prz (Prz: pyrazine) dimers.[18]

4-TPyP molecule containing four N atoms available for coordination to metals was proposed to be a good unit for molecular architecture. The attempt to obtain a coordination complex of ZnTPP with 4-TPyP results in the crystallization of $(ZnTPP)_2{\cdot}(4\text{-}TPyP)$ trimeric units.[19] The formation of $(ZnTPP)_4{\cdot}(4\text{-}TPyP)$ pentamers was supposed from the NMR measurements of the shifts of 4-TPyP protons in a chloroform solution of ZnTPP and 4-TPyP (at a 4:1 molar ratio); however, a 4:1 complex did not crystallize probably because of inefficient crystal packing of such pentamers in relation to the effective arrangement of the trimers.[19] Up to now, only $(RuTPP{\cdot}CO)_4{\cdot}(3\text{-}TPyP)$ and $(RuTPP{\cdot}CO)_4{\cdot}(3\text{-}ZnTPyP)$ pentamers,[20] coordination polymer $[\{(Mn^{III}TPP)_2{\cdot}4\text{-}TPyP\}(ClO_4)_2]_\infty$ containing “pentameric” connectivity[19] and the 4-TPyP complex with cyclic covalently bound ZnTPP tetramer[21] were structurally characterized in the solid state. In this work, we report a new supramolecular C_{60} complex with porphyrin pentamers: $\{(ZnTPP)_4{\cdot}(4\text{-}TPyP)\}{\cdot}(C_{60})_2{\cdot}(C_6H_5CN)_{3.5}$ (**1**). The crystal structure of **1** was determined, and the molecular structure of the $(ZnTPP)_4{\cdot}(4\text{-}TPyP)$ pentamer was described for the first time. The IR and UV−vis−NIR spectra of **1** are considered.

The crystals of **1** were prepared by the evaporation of chlorobenzene/benzonitrile solution (15:1 v/v) (16 mL)

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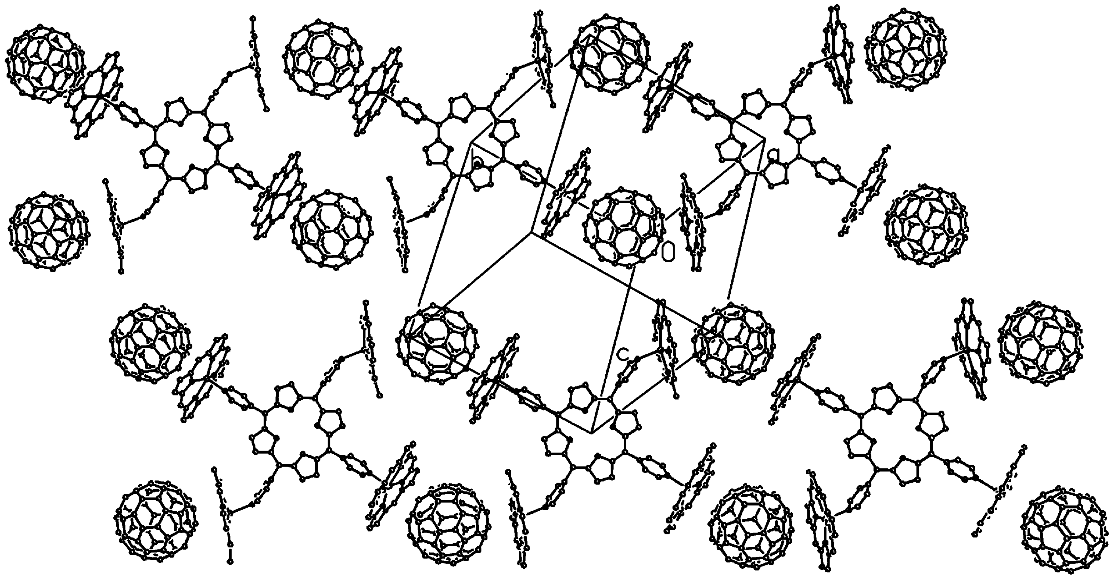

Figure 1. The view of the crystal structure of **1** on the $(ZnTPP)_4$·(4-TPyP) layer. Only one orientation is depicted for disordered C_{60} and ZnTPP (**B**) molecules. C_6H_5CN molecules and phenyl substituents of ZnTPP are omitted.

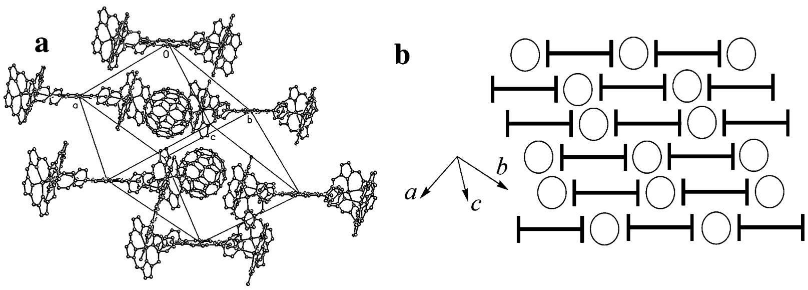

Figure 2. The view of the crystal structure of **1** along the planes of 4-TPyP macrocycles. (a) The fragment of the crystal structure of **1**. (b) The schematic presentation of the packing of C_{60} and $(ZnTPP)_4$·(4-TPyP) pentamers.

containing ZnTPP, 4-TPyP, and C_{60} at a 4:1:2 molar ratio under argon over 6 days. The solvent was decanted from the crystals, which were then washed with dry hexane (black plates with blue luster, yield 70%). The composition of the complex was determined from single-crystal X-ray diffraction.[22]

The complex crystallizes in the triclinic lattice with ZnTPP, C_{60}, and partially occupied solvent C_6H_5CN molecules in general positions and 4-TPyP molecule at an inversion center. The C_{60} molecules are statistically disordered between two orientations with a 35:65 occupancy ratio linked to each other by rotation of the fullerene molecule by 90° about a noncrystallographic 2-fold axis passing through the midpoints of two oppositely located 6/6 bonds. One of ZnTPP molecules (molecule **B**) is also statistically disordered between two orientations with a 40:60 occupancy ratio. The disordered orientations are linked by a small shift and bending of the TPP macrocycle.

The most interesting peculiarity of **1** is the formation of large $(ZnTPP)_4$·(4-TPyP) pentamers stabilized in the solid state by the van der Waals conformance to bulky C_{60} molecules. Each pentamer forms short van der Waals contacts with four C_{60} molecules via the ZnTPP macrocycles. These aggregates are packed in layers as shown in Figure 1. The neighboring $(ZnTPP)_4$·(4-TPyP) pentamers have two common C_{60} molecules in the layer, and consequently each C_{60} molecule forms van der Waals contacts with two ZnTPP molecules belonging to neighboring pentamers. Each fullerene molecule has only one C_{60} neighbor (Figure 2a,b) belonging to another layer and located at a center-to-center distance of 9.95 Å, which corresponds to the shortest intermolecular C···C distance of 3.27 Å.

The view of the crystal structure of **1** along the planes of 4-TPyP macrocycles is shown in Figure 2a,b. It was calculated that C_{60} molecule can fit perfectly to the "basket" of the $(RuTPP·CO)_4$·(4-ZnTPyP) pentamer in solution being placed near the central 4-ZnTPyP porphyrin fragment with the closest Zn···C(C_{60}) distance of about 3.0 Å.[7] In the case of **1**, another stable configuration is reached in which the C_{60} molecule is surrounded by two ZnTPP fragments. $(ZnTPP)_2C_{60}$ units are located over $(ZnTPP)_4$·(4-TPyP) box from the other layer (Figure 2a); however, the C_{60} molecule is placed too far from the 4-TPyP plane to form van der Waals contacts (C, N(4-TPyP)···C(C_{60}) > 6 Å).

The molecular structure of the $(ZnTPP)_4$·(4-TPyP) pentamer is shown in Figure 3. The macrocycles of oppositely located ZnTPP molecules are parallel due to crystallographic symmetry, while the ZnTPP moieties in the $(ZnTPP)_2$·Prz dimer in the complex with C_{60} are inclined at 30.3° with respect to each other.[18] The pentamer in **1** is formed by bent Zn−N(Py) coordination for molecule **A** (the dihedral angle between the Py plane and the Zn···N(Py) bond is 33°) and almost linear Zn−N(Py) coordination for molecule **B** (the corresponding dihedral angle is 4.5°). The Zn···N(Py) distances are 2.13 and 2.21 Å for the nitrogen atoms with linear and bent bonds, respectively. On the contrary, $(ZnTPP)_2$·(4-TPyP) trimers without C_{60} contain only bent Zn···N(Py) bonds with the Zn···N(Py) distance of 2.197 Å.[19] The porphyrin macrocycle in ZnTPP is almost planar with small saddle-like deviations (the r.m.s. devia-

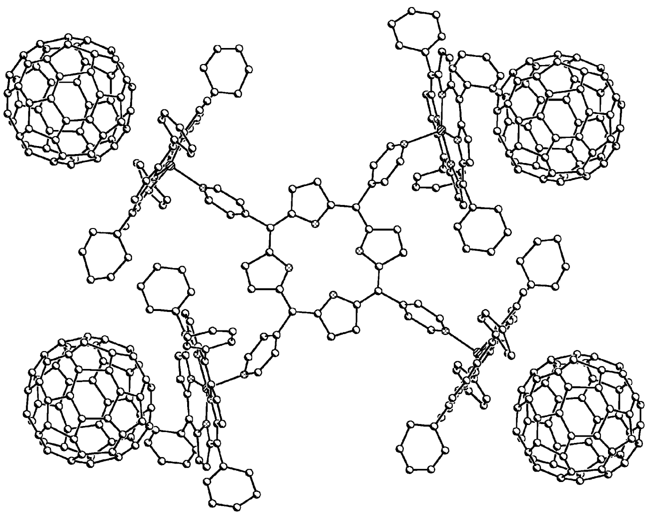

Figure 3. The molecular structure of $(ZnTPP)_4$·(4-TPyP) pentamer forming short van der Waals contacts with four C_{60} molecules via ZnTPP macrocycles. Only one orientation is depicted for disordered C_{60} and ZnTPP (**B**) molecules.

tions of the atoms from the mean plane in the porphyrin macrocycle are 0.116 Å for **A** molecule and 0.0107−0.057 Å for different orientations of the disordered **B** molecule). These deviations are similar to those for saddle-shaped metal(II) tetraphenylporphyrins in the solvent-free complexes with fullerene: 0.263 Å in $(CuTPP)_2$·C_{60} (CuTPP: copper(II) tetraphenylporphyrin)[11] or 0.216 Å in CoTMPP·C_{60} (CoTMPP: cobalt(II) tetrakis(*p*-methoxyphenyl)porphyrin).[12] Zinc atoms are displaced from the mean plane of the porphyrin macrocycle toward the pyridine ligand by 0.430 (molecule **A**), and 0.314 and 0.334 Å (two orientations of molecule **B**). These values are close to those for pyridine-coordinated ZnTPP in the complexes with C_{60} and C_{70} (0.435 and 0.433 Å, respectively),[12] and slightly larger than in $(ZnTPP)_2$·(4-TPyP) trimer (0.27 Å).[19]

The shortest ZnTPP···C(C_{60}) distances lie in the range of 2.96−3.23 (N···C) and 3.22−3.39 Å (C···C), whereas Zn···C(C_{60}) distances are in the range of 3.16−2.23 Å. Such distances are typical for other N-coordinated ZnTPP molecular complexes with fullerenes and indicate the absence of noticeable metal···C_{60} interaction and the presence of the weak interaction between π-systems of ZnTPP macrocycle and C_{60}.

The UV−vis−NIR spectrum of a single crystal of **1** derived from the Kramers-Kroning transformation of the reflectance spectrum is shown in Figure 4. The band at 334 nm is attributed to C_{60} and its position is blue shifted relative to that in parent C_{60} (346 nm). The presence of two chromophore molecules is justified by two Soret bands with the maxima at 440 and 454 mn. The first weaker band is ascribed to 4-TPyP, whereas the second one is attributed to ZnTPP. The latter band is red shifted relative to starting ZnTPP (431 nm) due to 4-TPyP coordination. The bands at 573 and 610 nm are also attributed to porphyrin chromophores. The $(ZnTPP)_2$·Prz dimer in the complex with C_{60} has close positions of the bands at 442, 566, and 605 nm.[18] An additional absorption band with the maximum at 820 nm can be ascribed to a charge-transfer band (Figure 4) due to electron transfer from ZnTPP to the C_{60} molecule at the absorption of light quantum. The IR spectrum of **1**[23] is a superposition of the spectra of the starting components. The position of $F_{1u}(4)$ mode of C_{60} (at 1429 cm^{-1}), which is sensitive to charge transfer to the C_{60} molecule, remains unchanged in the complex, indicating the absence of noticeable charge transfer in the ground state. Thus, **1** can be classified as a neutral charge-transfer complex.

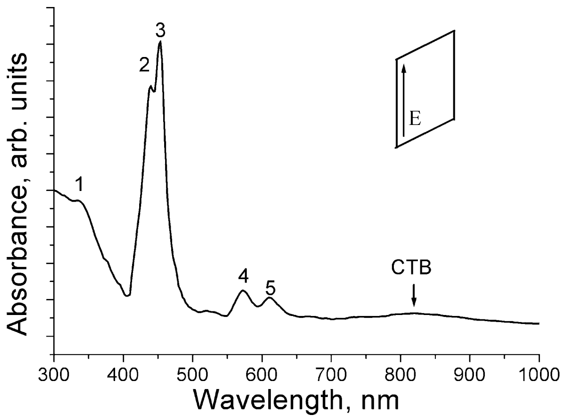

Figure 4. The UV−visible spectrum of a single crystal of **1** for one polarization of light.

The resulting crystalline fullerene complex with porphyrin pentamers can be an interesting photoactive compound. This prediction is based on the observation of rapid singlet energy transfer in toluene solution containing fullerene C_{60} and similar (RuTPP·CO)$_4$·(4-TPyP) pentamer with the box structure.[7] The use of fullerene allows for the first time the stabilization of bulky $(ZnTPP)_4$·(4-TPyP) pentamers in the solid state. Zinc in ZnTPP has preferentially a five-coordinative environment[24] providing an axial addition of only one of bi- or tetradentate ligands. Such an addition protrudes the zinc atom toward the N-containing ligand and produces a slightly concave surface of ZnTPP macrocycle, which becomes suitable for a closer approach of a spherical fullerene molecule. As a result, fullerene is located in the capsule formed by two slightly concave ZnTPP molecules providing the efficient packing of fullerenes with ZnTPP oligomers bonded by N-containing ligands. Indeed, ZnTPP does not form a complex with C_{60}, whereas five-coordinated ZnTPP·Py monomers,[12] $(ZnTPP)_2$·Prz dimers,[18] and even $(ZnTPP)_4$·(4-TPyP) pentamers cocrystallize with C_{60}. Thus, fullerenes can be used to stabilize some coordination oligomers of metalloporphyrins unstable in the solid state.

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Supporting Information Available: X-ray crystallographic information file (CIF) for complex **1**, the Experimental Section, and IR data for the starting compounds and the complex **1**. These materials are available free of charge via the Internet at http://pubs.asc.org.

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(22) Crystallographic data for **1**: $C_{180.25}H_{77.75}N_{13.75}Zn_2$, M_r = 2566.55.80 g mol^{-1}, black, triclinic, $P\bar{1}$, $a = 16.6488(10)$, $b = 19.0749(11)$, $c = 21.5917(13)$ Å, $\alpha = 90.344(2)$, $\beta = 105.864(2)$, $\gamma = 96.447(2)°$, $V = 6549.3(7)$ Å^3, $Z = 2$, $d_{calc} = 1.301$ g/cm^3, $\mu = 0.431$ mm^{-1}, $T = 110(2)$ K, data/parameters 27934/1319, $R_1 = 0.0842$ $[I > 2\sigma(I)]$, $wR_2 = 0.1959$, GOF = 1.251.

(23) See Supporting Information.

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