Synthesis and crystal structure of a new supramolecular complex: $[(ZnTPP)_2Prz] \cdot C_{60} \cdot 5.34C_7H_8 \cdot 0.66C_6H_5CN^{\dagger}$

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A new supramolecular C_{60} complex containing $[(ZnTPP)_2Prz$ coordination dimers, $[(ZnTPP)_2Prz] \cdot C_{60} \cdot 5.34C_7H_8 \cdot 0.66C_6H_5CN$ (Prz: pyrazine), has been obtained; its synthesis, crystal structure and optical properties are described.

Fullerenes form a wide variety of molecular complexes¹ including those with porphyrins and metalloporphyrins.^{2–6} The latter complexes attract much attention as promising photoactive compounds,⁷ building blocks in the design of ionic multi-component complexes⁸ and useful tools for the structural investigation of endohedral⁹ and chemically modified fullerenes.² With the exception of the simple co-crystallization of fullerenes with metal octaethyl-^{2,6} and tetraphenyl-porphyrins,^{3–5} several more complicated porphyrin molecules have been co-crystallized with fullerenes.^{10,11} Some of these molecules show a very high affinity for fullerenes.¹¹

N-Containing ligands can coordinate to metals bonded to porphyrin macrocycles to form coordination oligomers or polymers in solution and the solid state.^{12,13} Pyrazine (Prz), 4,4'-bipyridine, tetrapyridylporphyrin and other compounds are used as bridging ligands in such systems.^{12,13} The different bridging ligands allow interplanar distances between metalloporphyrins, the conformation of oligomers and polymers formed, and the size of channels or cavities in the supramolecular structures to be varied.¹³ Because of this, the coordination oligomers can be viewed as new promising building blocks in various multi-component supramolecular fullerene– porphyrin architectures.

This work reports the supramolecular C_{60} complex with $[(ZnTPP)_2Prz]$ coordination dimers, in which two ZnTPP moieties are linked by pyrazine: $[(ZnTPP)_2Prz]\cdot C_{60}\cdot 5.34C_7H_8 \cdot 0.66C_6H_5CN$ (1). The synthesis, crystal structure and optical properties of this new solid are discussed. The molecular structure of the $[(ZnTPP)_2Prz]$ coordination dimer is presented for the first time.

Crystals of **1** were prepared by evaporation of a toluene/ benzonitrile (10 : 1 v/v) solution (22 mL) containing ZnTPP, Prz and C₆₀ at a 2 : 1 : 1 molar ratio under argon over 5–10 days. The solvent was decanted from the crystals precipitated, which were then washed with dry hexane to yield black prisms in 90% yield (see ESI†). The composition of the complex was determined from X–ray diffraction on a single crystal.‡

In contrast to six-coordinated Mn and four-coordinated Cu, the affinity of zinc for a five-coordinate environment provides an axial addition of only one bi- or tetra-dentate ligand to

ZnTPP that results in the formation of different coordination oligomers based on ZnTPP.¹³ In this study we used the bridging ligand pyrazine (Prz) capable of coordinating axially to two ZnTPP molecules to form the coordination dimer, $[(ZnTPP)_2Prz]$. The other axially directed site in ZnTPP is occupied by the C₆₀ molecule.

1 crystallizes in the triclinic lattice (Fig. 1) with ordered $(ZnTPP)_2Prz$ and C_{60} . $(ZnTPP)_2Prz$ forms a honeycomb framework (Fig. 1). The framework is strongly distorted from a hexagonal one and has the distances between the centres of the pyrazine molecules in the dimers in the 12.43–17.96 Å range. The C_{60} molecules form one-dimensional columns along the *a* direction, in which pairs of C_{60} with a centre-to-centre distance of 9.936 Å and a shortest van der Waals C···C contact of 2.899 Å (the sum of the van der Waals radii of carbon atoms of 3.420 Å¹⁴) alternate with the solvent molecules in a column (Fig. 2). Fullerene pairs separated by solvent molecules have no shortened contacts to each other (the centre-to-centre distance between the fullerenes from two adjacent pairs is 13.37 Å).

A peculiarity of the (ZnTPP)₂Prz geometry is that the porphyrin planes in the dimer are inclined at an angle of 30.3° and do not rotate with respect to each other (the dihedral angle is -0.3°) (Fig. 3). This geometry differs from that previously described for metalloporphyrin dimers linked by bidentate bridging pyrazine¹² or 4,4'-bipyridine¹³ ligands in which the porphyrin planes are essentially coplanar. The dimer in 1 is specified by the fact that one of the pyrazine nitrogen atoms is linearly bound to Zn(2) (the angle between the Prz plane and Zn(2)–N(Prz) bond is 2.3°). The other nitrogen atom forms a bent Zn(1)–N(Prz) bond (the corresponding angle is 18.6°). This makes the N atom environment close to trigonal pyramid (the sum of bond angles is 357.0(6)°). The Zn-N(Prz) distances are 2.179(2) and 2.211(2) Å for the nitrogen atoms with linear and bent bonds, respectively. These values are close to the corresponding Zn-N(Py) distances (2.151(4) and 2.133(6) Å) in fullerene containing complexes of $ZnTPP \cdot Py$ (Py = pyridine).⁵ The porphyrin macrocycles are planar in 1 with the zinc atoms displaced by 0.254 and 0.263 Å towards pyrazine from the mean plane of the porphyrin macrocycle. These values are noticeably smaller than those in the C60 and C70 complexes of ZnTPP·Py (0.435 and 0.433 Å).⁵

Each (ZnTPP)₂Prz moiety has two fullerene neighbours (Fig. 1). The 6–6 bond of C₆₀, which is common to two fused six-membered rings, is arranged close to the Zn atom forming shortened Zn…C(C₆₀) contacts in the 3.094–3.399 Å range. These distances are characteristic of ZnTPP complexes with fullerenes (2.89–3.08 Å).^{3,5}

Solvent molecules occupy cavities in the $(\mbox{ZnTPP})_2\mbox{Prz}$ and



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[†] Electronic supplementary information (ESI) available: charaterisation for compound **1**. See http://www.rsc.org/suppdata/ce/b3/b303415a/



Fig. 1 Honeycomb supramolecular structure of 1. Click here to access a 3D representation.



Fig. 2 View of the one-dimensional columns of alternating C_{60} and solvent molecules parallel to the *a*-direction. The shortened van der Waals contacts are shown by dashed lines.

 C_{60} packing. C_{60} forms several shortened van der Waals C···C contacts with solvent molecules in the 3.303–3.324 Å range (Fig. 2).

The UV-VIS-NIR spectrum of **1** is shown in Fig. 4. The bands at 263 and 330 nm (the bands 1 and 2 in Fig. 4) are ascribed to neutral C_{60} . These bands are blue shifted by 5 and 16 nm, respectively, relative to those of parent C_{60} (267 and 346 nm). The bands at 442, 566 and 605 nm (the bands 3, 4 and 5, respectively in Fig. 4) are attributed to the ZnTPP chromophore. These bands are red shifted relative to those of starting ZnTPP as a result of pyrazine and fullerene coordination to ZnTPP.

Additional absorption in the visible range with a maximum at 760 nm can be ascribed to a charge transfer band (CTB) (Fig. 4, arrow) resulting from electron transfer from ZnTPP to the C_{60} molecule with the absorption of a light

quantum. The presence of the fairly intense CTB indicates an efficient overlapping of the π -systems of ZnTPP and C₆₀ in 1 in contrast to other complexes of metal-containing tetraphenyl-porphyrins with fullerenes (in which a CTB is either absent or very weak^{4,5}).

It was shown earlier that photoinduced charge transfer in fullerene complexes is realized mainly by direct charge transfer from donor to fullerene molecule.¹⁵ Because of this, photoinduced charge transfer is also possible in **1**. Luminescence characteristic of the parent ZnTPP is not observed at photoexcitation of **1**. This is associated probably with its quenching as a result of charge transfer from the excited porphyrin molecule to C_{60} .

Thus, the coordination dimers co-crystallize with fullerene C_{60} . This can be used for the development of new supramolecular fullerene–porphyrin complexes and the study of molecular



Fig. 3 Coordination of pyrazine to two ZnTPP molecules (full lines) and shortened van der Waals contacts of C_{60} with $[(ZnTPP)_2Prz]$ dimer (dashed lines) in 1.



Fig. 4 UV-VIS-NIR spectra of 1 (a) and C_{60} (b). The arrow shows the position of the charge transfer band (CTB).

structures of different coordination dimers. The obtained complexes can be interesting as photoactive compounds.

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Notes and references

‡ Crystal data for 1: C_{190.5}H_{98.02}N_{10.66}Zn₂, *M*_r=2666.80 g mol⁻¹, black prisms, triclinic, *P*1, *a* = 13.3658(2), *b* = 19.5386(3), *c* = 24.7121(4) Å, α = 85.6754(3), β = 84.5849(3), γ = 88.3817(3)°, *V* = 6405.0(2) Å³, *Z* = 2, *d*_{calc} = 1.383 g cm⁻³, μ = 0.443 mm⁻¹, *T* = 90.0(1) K, max. 2φ = 59.4°, reflections measured = 115208, unique reflections (*R*_{int}) = 33340 (0.043), reflections *I* > 2σ (*I*) = 26069, parameters refined = 1821, *R*₁ = 0.062, *wR*₂ = 0.183, G.O.F. = 1.050. CCDC reference number 196176. See http:// www.rsc.org/suppdata/ce/b3/b303415a/ for crystallographic data in CIF or other electronic format.

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