

Supramolecular porphyrin-fullerene complexes as potential photoactive materials

A. L. Litvinov,^a D. V. Konarev,^a A. Yu. Kovalevsky,^b
P. Coppens,^b R. N. Lyubovskaya^a

^a Institute of Problems of Chemical Physics RAS,
Chernogolovka, Moscow region 142432, Russia

^b Department of Chemistry, State University of New York
at Buffalo, Buffalo, New York, 14214 USA
E-mail: litvin@cat.icp.ac.ru

Now supramolecular chemistry of metalloporphyrins as promising photoactive systems, electron and energy transfer mediators, and redox catalysts is rapidly developed. Fullerenes form a wide variety of molecular complexes including those with metalloporphyrins. Fullerenes can also be used as guest molecules in various supramolecular systems. Since fullerenes are known to manifest unique photoacceptor properties, their insertion in supramolecular porphyrin complexes can result in the design of new promising photoactive systems.

In this report, we communicated the insertion of fullerene in a supramolecular framework formed by the [(ZnTPP)₂Prz] dimers (Prz: pyrazine), in which two ZnTPP moieties are linked by the pyrazine molecule. [(ZnTPP)₂Prz]•C₆₀•5.34C₇H₈•0.66C₆H₅CN (**1**) is an unusual example of the cage structure with large channels accommodating the C₆₀ molecules. Crystal structure and UV-VIS-NIR spectra of **1** are described below.

1 crystallizes in the triclinic lattice (Fig. 1). (ZnTPP)₂Prz and C₆₀ are ordered. (ZnTPP)₂Prz forms a honeycomb framework with large channels (up to ~10 × 20 Å in size) arranged along the crystallographic *a*-axis. The framework is strongly distorted from a hexagonal one and has the distances between the centres of pyrazine molecules in the dimers in the 12.43-17.96 Å range. Each channel is occupied by fullerene and solvent molecules. The C₆₀ molecules form pairs with the centre-to-centre distances of 9.936 Å and the shortest van der Waals C...C contacts of 2.899 Å (the sum of the van der Waals radii of carbon atoms is 3.420 Å). Fullerene pairs alternate with solvent molecules along the channel and have no shortened contacts to each other.

Each (ZnTPP)₂Prz moiety has two fullerene neighbours. The 6-6 bond of C₆₀ arranges close to 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).

The UV-VIS-NIR spectrum of **1** is shown in Fig. 2. The bands at 263 and 330 nm (the bands 1 and 2 in Fig. 2) are ascribed to neutral C₆₀. These bands are blue shifted by 5 and 16 nm, respectively, relative to those of parent C₆₀ (267 and 346 nm). The bands at 442, 566 and 605 nm (the bands 3, 4 and 5, respectively in Fig. 2) are attributed to the ZnTPP chromophore (Fig. 2a). These bands are red shifted relative to those of starting ZnTPP. These changes may be a result of pyrazine and fullerene coordination to ZnTPP.

Additional absorption in the visible range with a maximum at 740 nm can be ascribed to a charge transfer band (CTB) resulting from charge transfer from ZnTPP to the C₆₀ molecule at absorption of light quantum (Fig. 2, arrow). The presence of intense enough CTB indicates the efficient overlapping of π -systems of ZnTPP and C₆₀ in **1** in contrast to other complexes of metal-containing porphyrins with fullerenes (in which CTB is either absent or very weak).

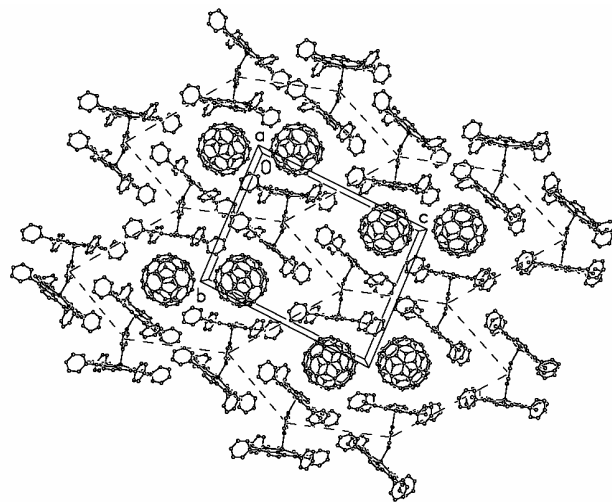


Fig. 1. Honeycomb supramolecular structure of **1**.

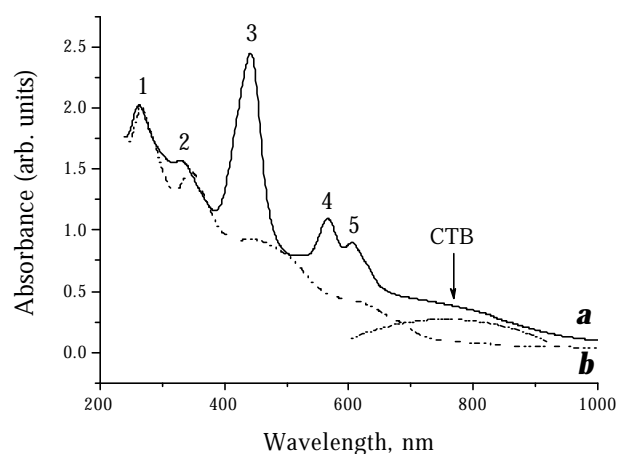


Fig. 2. UV-VIS-NIR spectra of **1** (a) and C₆₀ (b). The arrow shows the position of charge transfer band (CTB).

It was shown earlier that photoinduced charge transfer in fullerene complexes is realized mainly due to direct charge transfer from donor to fullerene molecule. Supramolecular porphyrin systems involving fullerene can possess better photophysical characteristics as a result of higher efficiency of the overlapping chromophore π -systems than fullerene complexes with metalloporphyrins.

Luminescence characteristic of parent ZnTPP is not observed at photoexcitation of **1** in similar conditions. This is associated probably with its quenching as a result of charge transfer from the excited porphyrin molecule to \dot{N}_{60} . The unique structure of **1** and the presence of CTB makes it possible to use fullerene containing supramolecular porphyrin systems in the design of photoactive materials.

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