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Molecular and ionic complexes of pyrrolidinofullerene bearing chelating 3-pyridyl units[†]

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Molecular and ionic complexes of *cis*-2',5'-di(pyridin-3-yl)pyrrolidino[3',4':1,9](C_{60} - I_h)[5,6]fullerene DP3FP with chlorobenzene (C_6H_3 Cl), manganese(II) tetraphenylporphyrin (Mn^{II} TPP) and tetrakis(dimethylamino)ethylene (TDAE) have been obtained for the first time. X-ray single crystal structure determination for the crystalline DP3FP· C_6H_5 Cl (1) solvate proved unambiguously its molecular structure with the *cis*-arrangement of chelating 3-pyridyl groups. It has been demonstrated that DP3FP easily forms self-assembled photoactive complexes with metallated porphyrins. For example, the formation of a 1 : 1 complex between DP3FP and zinc (II) tetraphenylporphyrin (Zn^{II} TPP) in cyclohexane solution (2) was evidenced using absorption spectroscopy. A successful X-ray single crystal structure determination was performed for a self-assembled triad composed of a DP3FP molecule linked with two Mn^{II}TPP molecules in {DP3FP·(Mn^{III}TPP)₂}·($C_6H_4Cl_2$)₃ (3). A strong organic donor TDAE reduces DP3FP to the radical anion state thus forming an ionic complex (TDAE⁺⁺)·(DP3FP⁻⁻)·($C_6H_4Cl_2$)_{1.6} (4). Optical, electronic and magnetic properties of 4 were investigated in detail. The performed studies strongly suggest that pyrrolidinofullerene DP3FP can be used as a building block in the design of various organic materials with advanced optoelectronic and/or magnetic properties.

Introduction

Fullerenes and their derivatives are three-dimensional electron acceptor materials widely used in research and technology. Fullerene derivatives are promising building blocks in the design of donor–acceptor dyads where fullerenes perform as electron acceptor units, while metalloporphyrins, phthalocyanines and other molecules perform as donor components.¹⁻⁴ The strongest advantage of fullerene-based acceptors is their small reorganization energy which provides the formation of long-lived charge separated states.

Self-assembled fullerene/porphyrin and fullerene/phthalocyanine systems are of particular interest since they mimic natural photosynthetic antenna.^{2,3} Fullerene/porphyrin architectures are widely applied for construction of different types of photovoltaic devices. The most intensely studied are photoelectrochemical solar cells based on metal oxide or gold electrodes covered with monolayers of fullerene/porphyrin dyads or triads.5 High light-power conversion efficiency was achieved using fullerene/porphyrin nanoclusters.⁶ Particularly exciting are self-assembled nanotubes and nanorodes composed of fullerene derivatives and porphyrins. These systems produce solar cells with promising efficiency of 0.63% that might be significantly increased after subsequent optimization.⁷ Planar p-n heterojunction devices were dramatically improved when pyrrolidinofullerenes bearing chelating pyridyl groups (PyFs) were used as electron acceptor materials in combination with zinc phthalocyanine as electron donor.8 The observed increase in device efficiency was attributed to complex formation at the interface between the *p*- and *n*-type materials.9 Photoactive fullerene-phthalocyanine systems were also successfully applied in the design of bulk heterojunction and mixed heterojunction solar cells.^{10,11}

The above examples illustrate the importance of pyridylappended fullerene derivatives for design of photoactive systems for solar energy conversion. Many self-assembled dyads composed of pyrrolidinofullerenes and metallated porphyrins (phthalocyanines) were investigated in solution. They were based on pyrrolidinofullerenes bearing one chelating pyridyl or imidazolyl group,¹²⁻¹⁴ or two chelating substituents at 2' and 5' positions of the pyrrolidine ring,¹⁵⁻¹⁷ or even three chelating pyridyl units at positions 1',2',5'.^{18,19} On the contrary, there are just few examples

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[†] Electronic supplementary information (ESI) available: Electronic supplementary information (ESI) available: IR spectra of starting compounds and complexes 1, 2 and 4. Crystallographic data in CIF format for complex 1 at 100 and 295R and complex 3 at 120 K. CCDC reference numbers 822362, 822364 and 822366. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11040c

of porphyrine–fullerene dyads characterized in solid state by X-ray single crystal diffraction. All such systems are non-covalently linked dyads composed of one pyrrolidinofullerene molecule and one $Zn^{II}TPP$ molecule.^{20–22}

In this work we report the preparation and X-ray single crystal structures of parent pyrrolidinofullerene DP3FP (1) and the first triad composed of DP3FP and two Mn^{II}TPP molecules (3) (Fig. 1). In addition, synthesis and spectroscopic characterization of 1:1 complexes of DP3FP with Zn^{II}TPP (2) and TDAE (4) are discussed.



Fig. 1 Molecular structures of the investigated compounds.

Results and discussion

1.1 Microwave-assisted synthesis of DP3FP

Efficient methods for the preparation of pyrrolidinofullerenes with the appended chelating pyridyl groups were reported.^{23,24} The synthesis of fullerene derivatives bearing 2-pyridyl or 4-pyridyl groups was straightforward and produced desired products in high yields within short reaction times (2–5 min to 1–2 h). On the contrary, the preparation of fullerene derivatives bearing 3-pyridyl groups required the application of some catalysts (organic

bases or acids) and continuous heating of the reagents at reflux in 1,2-dichlorobenzene (10–12 h).

Here we proposed the conduction of such reactions under microwave heating conditions. Indeed, irradiating a mixture of the [60]fullerene, 3-pyridinecarboxaldehyde, 3-picolylamine and butyric acid dissolved in 1,2-dichlorobenzene in a conventional microwave oven (600 W) produced the title product 1 in 15 min with 70% yield (Scheme 1). Similar results were achieved under conventional heating conditions only after 6–10 h. Therefore, there is an obvious accelerating effect of microwave irradiation on the formation of the title pyrrolidinofullerene. Thus, compound 1 (DP3FP) can easily and quickly be prepared under microwave conditions to be available on a multigram scale for various applications.



1.2 Molecular structure of DP3FP

The crystals of starting DP3FP were obtained as 1:1 solvate with chlorobenzene DP3FP·C₆H₅Cl (1) by slow concentration of the chlorobenzene solution of pyrrolidinofullerene in argon atmosphere. The crystal structure of 1 was studied at room temperature and 100 K. At both temperatures DP3FP is ordered, whereas solvent C₆H₅Cl molecules are disordered between three orientations. The top and side views of the DP3FP molecule are shown in Fig. 2. It is clearly seen that two 3-pyridyl groups are arranged in *cis*-configuration with respect to the pyrrolidine ring. This result unambiguously justifies indirect assignment of stereochemistry of pyrrolidinofullerene DP3FP made previously from the analysis of the NMR data.^{23,24} Pyridine nitrogens in DP3FP are arranged in the opposite directions.



Fig. 2 Top (a) and side (b) views of the DP3FP molecule in solvate 1. Carbon atoms of the pyrrolidine addend are marked with orange color for clarity.

The pyrrolidine ring is attached to the 6–6 bond of the fullerene cage which elongates from 1.380(4) Å in C₆₀ to 1.585(4) Å in DP3FP. The attachment of the pyrrolidine ring distorts significantly the fullerene cage. Thus, the length of the cage along the axis passing through the functionalized 6–6 bond is 0.3 Å greater than the dimensions of the carbon cage in the two other

Table 1 Association constants for complexes of different pyrrolidinofullerenes with metallated porphyrins

Compound	\mathbf{R}^{1}	\mathbb{R}^2	R ³	Porphyrin	Solvent	$K_{\rm a} \times 10^3 \text{ L mol}^{-1}$	Ref.
P2FP	2-Pv	Н	Н	ZnTPP	1,2-dichlorobenzene	no binding	14
P3FP	3-Py	Н	Н	ZnTPP	1,2-dichlorobenzene	7.74	14
P4FP	4-Py	Н	Н	ZnTPP	1,2-dichlorobenzene	7.66	14
ImPhFP	ImPh	Н	Н	ZnTPP	1,2-dichlorobenzene	11.6	14
2P4FP	Н	4-Py	Н	ZnTPP	1,2-dichlorobenzene	74	21
MP4FP	4-Pv	Me	Н	InClTPP	chloroform	69	13
MP4FP	4-Pv	Me	Н	ZnTPP	1,2-dichlorobenzene	7.2	14
DP2FP	2-Pv	Н	2-Pv	ZnTPP	cyclohexane	12.0	18
DP3FP	3-Pv	Н	3-Py	ZnTPP	cyclohexane	84	This work
DP4FP	4-Py	Н	4-Py	ZnTPP	1,2-dichlorobenzene	14.5	15

Definitions: R¹, R² and R³ are substituents in the pyrrolidine ring according to Fig. 3; K_a, association constant; ImPh, 4-(1*H*-imidazol-1-yl)phenyl.

orthogonal directions. This is a reasonable consequence of the appearance of two sp³-hybridized carbon atoms in the fullerene cage.

1.3 Complex formation between DP3FP and Zn^{II}TPP in solution

Pyridyl substituted pyrrolidinofullerenes (Fig. 3) are strong enough ligands. They readily form self-assembled complexes with ZnTPP *via* axial coordination of pyridyl nitrogen to the metal atom in the macrocyclic ring. Binding constants published for various pyrrolidinofullerens bearing chelating groups and ZnTPP are listed in Table 1. It is seen that the complexes of 2P4FP with ZnTPP and MP3FP with indium(III) tetraphenylporphyrin chloride are characterized by the highest association constants.^{13,21}



Fig. 3 General formula of pyrrolidinofullerenes bearing pyridyl units at different positions. The definitions of R^1 , R^2 and R^3 for different compounds are shown in Table 1.

The association constant of the DP3FP–ZnTPP couple was determined using absorption spectroscopy. The absorption spectrum of ZnTPP in cyclohexane shows the intense Soret band at 416 nm and weaker Q-bands with the maxima at 547, 585 and 622 nm (Fig. 4, curve 0). In a typical spectroscopic titration experiment increasing amounts of DP3FP were added to the aliquot of ZnTPP dissolved in cyclohexane. Concentration of DP3FP in solution was varied from 4×10^{-6} to 2×10^{-5} mol L⁻¹. This corresponds to the changes in a DP3FP : ZnTPP ratio from 1:1 to 5:1. Evolution of the absorption spectrum of ZnTPP upon the addition of DP3FP is shown in Fig. 4

The increase in concentration of DP3FP results in the decrease in intensity of the Soret band of starting ZnTPP (416 nm) and the appearance of a new band at 430 nm which can be attributed to the Soret band of ZnTPP linked with the axially coordinated



Fig. 4 Evolution of the absorption spectrum of ZnTPP $(3.2 \times 10^{-6} \text{ mol } L^{-1})$ in cyclohexane upon the addition of 1–5 equivalents of DP3FP. The upper inset shows the Scatchard graph where the changes in absorbance (ΔA) at 416 nm are plotted against $\Delta A/[1]$, where [1] is concentration of DP3FP. The bottom inset illustrates the shift of the Q-bands of ZnTPP upon the addition of 0, 2, 3 and 5 equivalents of DP3FP.

DP3FP ligand. The Q-bands of ZnTPP are shifted to 563, 604 and 624 nm, which is also a consequence of complex formation (Fig. 4, bottom inset). The isobestic point located at 423 nm suggests the formation of a 1:1 complex.²⁵ The 1:1 stoichiometry of the complex was also determined from the Job's plot (ESI†).

The association constant K_a was determined from the slope of the Scatchard plot (Fig. 4, the upper inset). The obtained $K_{\rm a}$ value of 8.4 \pm 0.5 \times 10⁴ L mol⁻¹ indicates that DP3FP is a stronger ligand in cyclohexane than pyrrolidinofullerene DP2FP $(K_{\rm a} = 1.2 \times 10^4 \text{ L mol}^{-1})$.¹⁸ This difference can be due to different modes of coordination of DP2FP and DP3FP ligands with ZnTPP. In the case of pyrrolidinofullerene DP2FP, two 2-pyridyl groups are sterically hindered and cannot be involved in complex formation with ZnTPP. Therefore, a coordination bond is formed between the pyrrolidine nitrogen and zinc atom of ZnTPP. X-ray diffraction studies revealed that in this case the $N \cdots Zn$ bond is considerably longer (2.29 Å) than that in the dyads composed of MP4FP or 2P4FP ligands (the N···Zn bond length is 2.13-2.16 Å), which provides chelating 4-pyridyl groups coordination with ZnTPP. ^20-22 The longer $N \cdots Zn$ coordination bond suggests weaker association of DP2FP with ZnTPP. In the case of DP3FP 3-pyridyl units are not sterically hindered and can participate in complex formation with metallated porphyrins. This might be a reason why the association constant for DP3FP–Zn^{II}TPP system is larger than for the previously studied DP2FP–Zn^{II}TPP dyad.

The direct comparison of DP3FP with other ligands is problematic because the association constants are known to be strongly solvent dependent. For example, for a simple pyridine molecule used as a ligand for coordination with $Zn^{II}TPP$, the association constants of 610, 6900, 7750 and 25100 L mol⁻¹ were obtained in CHCl₃, CH₂Cl₂, C₆H₄Cl₂ and cyclohexane solvents, respectively.^{14,26} Nevertheless, the K_a value obtained in our experiments for DP3FP suggests that it is quite a strong ligand able to form complexes with a variety of metallated macrocycles.

1.4 Preparation and X-ray single crystal structure characterization of the self-assembled triad composed of DP3FP and two Mn^{II}TPP units

We prepared complexes of DP3FP with tetraphenylporphyrinates of different metals such as cobalt(II), zinc(II) and manganese(II). In the case of Co^{II}TPP and Zn^{II}TPP, dark polycrystalline precipitates were formed in quantitative yields within several days. The obtained crystals were found to be very small and not suitable for the X-ray diffraction analysis. On the contrary, in the case of Mn^{II}TPP, the product does not precipitate so readily. Diffusion of hexane into the solution containing both DP3FP and Mn^{II}TPP in 1,2-dichlorobenzene during one month produced large black prisms with characteristic blue luster. These crystals rapidly degraded after isolation from mother solution. Therefore, a crystal taken from the solution was immediately cooled down to 100 K in nitrogen flow at the diffractometer and then successful measurements and the structure determination were preformed.

Structure of complex **3** was solved with relatively high *R*-factor (12.14%). The reason for this is the presence of large voids in this complex (calc. volume of 958 Å³) which are occupied by strongly disordered solvent molecules (those are $C_6H_4Cl_2$ molecules). Moreover solvent molecules can partially leave these cavities during transportation of a crystal from solution to diffractometer. That makes impossible qualitative analysis of disordered components in these voids. Thus the presented composition {DP3FP·(Mn^{II}TPP)₂}·(C₆H₄Cl₂)₃ takes in account only solvent molecules whose position was resolved correctly from X-ray diffraction data. In spite of a relatively high *R*-factor the geometry of DP3FP·(Mn^{II}TPP)₂ triads was solved with good precision since they are well ordered in the complex.

Geometry of DP3FP·($Mn^{II}TPP$)₂ triad is shown in Fig. 5. It is notable that pyridine nitrogens in DP3FP are arranged in the same direction in contrast to parent pyrrolidinofullerene whose molecular structure is shown in Fig. 2. The lengths of axial coordination Mn–N(DP3FP) bonds in triad for both Mn^{II}TPP is equal to 2.199(5) Å. These bonds are slightly longer than the Zn–N bonds in the dyads comprising chelating 4-pyridyl groups coordinated to Zn^{II}TPP. The average lengths of the equatorial Mn– N(TPP) bonds in Mn^{II}TPP is 2.110(5) Å. Relatively large lengths of these bonds strongly suggest the high spin state of Mn^{II}TPP in 3.²⁷ The porphyrin rings are distorted and have an umbrella shape with manganese atoms displaced by 0.415 Å out of the porphyrin plane (defined by four porphyrin ring nitrogen atoms) towards pyridine nitrogens. The planes of the two porphyrin molecules



Fig. 5 Top (a) and side (b) views of the molecular structure of coordination triad 3. The carbon atoms of the pyrrolidine ring are shown with orange color for clarity.

coordinated to the DP3FP unit form an angle of 61.4° (Fig. 5). This angle is defined by geometry of two 3-pyridyl substituents in the DP3FP molecule.

The projection of the crystal packing of 3 along the lattice *c* axis is shown in Fig. 6. The molecular arrangement is characterized by a zigzag of pyrrolidinofullerene chains and large continuous channels filled with disordered solvent molecules both parallel to



Fig. 6 The projection of the crystal packing of triad 3 along the lattice c axis which shows cross-sections of the zigzag fullerene chains and large channels occupied by solvent molecules (a); the projection of the chain of triad molecules along the lattice a axis (b). Green ellipses define the channels occupied by disordered solvent molecules. Green dashed lines show short VdW C···C contacts between fullerenes. Solvent molecules are not shown for clarity.

the lattice *c* axis. The pyrrolidinofullerene molecules are separated by porphyrin layers lying in the *ac* plane. Most probably, solvent molecules are weakly bonded in the channels and can easily leave the crystal. This results in rapid crystal degradation which was observed when the crystals were stored without solvent. The distances between the fullerene cages in the zigzag chains are not equal. One centre-to-centre distance is shorter (10.098 Å) than another (10.132 Å). There is a short Van der Waals (VdW) C ··· C contact with the length of 3.085 Å formed between two fullerene cages that are arranged in the close proximity to each other (Fig. 6b).

Optical IR (see ESI[†]) and NIR spectra of 3 in KBr pellet provided some information on the nature of electronic interactions between the pyrolidinofullerene and the Mn^{II}TPP units in the triad. First of all, very small shift of the characteristic IR band of starting DP3FP at 1427 cm⁻¹ to 1432 cm⁻¹ in triad 3 suggests that there is no noticeable charge transfer from porphyrin to pyrrolidinofullerene.²⁸ A solid state absorption spectrum of triad 3 in the NIR range shows no bands that can be attributed to the DP3FP⁻⁻ radical anion, which is further evidence of the absence of charge transfer in this system. The Soret and Q-bands of the Mn^{II}TPP units in triad 3 were observed at 444, 571 and 616 nm, respectively. These positions are almost equal to those in the spectrum of uncomplexed Mn^{II}TPP in which the Soret band appears at 443 nm, while Q-bands are manifested at 572 and 611 nm. A small shift of these bands upon complex formation of Mn^{II}TPP with DP3FP suggests weak electronic interactions between these components. Much stronger shifts of the Mn^{II}TPP absorption bands (up to 10 nm) were observed in the ionic fullerene $\{(Cation^+)_2 \cdot Mn^{II}TPP\} \cdot (C_{60}^{-})_2$ complexes when Mn^{II}TPP coordinates nitrogen containing N-methyldiazabicyclooctane or N, N'N'-trimethylpiperazinium (MDABCO⁺) (TMP^{+}) cations.29-31

Thus, triad **3** is a molecular architecture which shows no noticeable charge transfer from the porphyrin to the pyrrolidinofullerene unit. Similarly, no charge transfer was observed previously for supramolecular complexes of Mn^{II}TPP with fullerenes C_{60} and C_{70} .^{32,33}

1.5 The formation of ionic complex of D3PFP with tetrakis(dimethylamino)ethylene TDAE·D3P-FP·($C_6H_4Cl_2$)_{1.6} (4)

Tetrakis(dimethylamino)ethylene is a stronger donor than $Mn^{II}TPP$ with the first oxidation potential $E^{+/0}$ of -0.75 V vs. SCE.³⁴ To prepare the complex, parent DP3FP (30 mg) was dissolved together with an excess of TDAE (0.5 mL) in 1,2-dichlorobenzene. Slow diffusion of hexane into the prepared solution results in the formation of dark crystals of complex 4, which has the TDAE·DP3FP·(C₆H₄Cl₂)_{1.6} formula according to the chemical analysis data. The FTIR spectrum of 4 showed strongly shifted absorption bands of the DP3FP unit (ESI†). The characteristic band of parent DP3FP at 1427 cm⁻¹ was shifted to 1386 cm⁻¹ in the spectrum of 4 as compared to the spectrum of parent DP3FP.

The TDAE molecule also has one characteristic band which changes its position from 1340 cm⁻¹ in the neutral state³⁵ to 1518 cm⁻¹ in the radical cation state in $(TDAE^{++}) \cdot (C_{60}^{+-})^{35}$ or

 $(TDAE^{+}) \cdot (C_{70}^{-}) \cdot (C_6H_4Cl_2) \cdot (C_6H_{14})_{0.5}^{36}$ and to 1667–1672 cm⁻¹ in the dication state.³⁵ The TDAE characteristic band was observed at 1521 cm⁻¹ in the spectrum of 4 thus indicating the formation of the TDAE⁺⁺ cation.

The optical absorption spectrum of **4** in KBr pellet in the visible and NIR ranges is shown in Fig. 7. New absorption bands appear in the spectrum of **4** at 792 and 998 nm. These bands can be attributed to the D3PFP⁻⁻ radical anion. Similar bands appear in the NIR spectrum of C_{60}^{--} at 930–950 and 1070–1090 nm.³⁷⁻³⁹ Thus, the obtained spectroscopic data prove unambiguously that complex **4** has ionic ground state and can be presented as (TDAE⁺⁺)·(DP3FP⁻⁻)·(C₆H₄Cl₂)_{1.6}.



Fig. 7 The absorption spectrum of 4 in KBr pellet in the visible–NIR range.

The ESR spectrum of polycrystalline **4** manifested an intense asymmetric signal at room temperature which can be well fitted by two narrow lines ($g_1 = 2.0030$, $\Delta H = 0.7$ G and $g_2 = 2.0035$, $\Delta H = 0.5$ G, Fig. 8). It is known that TDAE⁺⁺ shows a narrow signal with $g = 2.0035^{36}$ whereas anion radicals of pyrrolidinofullerenes manifest narrow ESR signals with g = 2.0001-2.0002.⁴⁰ Narrow ESR signals with *g*-factors larger than 2.0000 are also characteristic of radical anions of other fullerene derivatives.^{41,42}



Fig. 8 The experimental ESR spectrum of polycrystalline **4** at 260 K (top). The fitting of the signal by two Lorentzian curves (bottom).

Exact attribution of these signals is not possible. Spectrum can belong to one common spin having axial symmetry with the g_{\perp}



Fig. 9 Temperature dependence of g-factor (a) and linewidth (b) for the two components of the ESR spectrum of polycrystalline 4 in the 4–295 K range.

and g_{II} components or to different spins ($g_2 = 2.0035$ is close to the g-factor of EPR signal from TDAE⁺⁺ whereas $g_1 = 2.0030$ is shifted closer to DP3FP⁻⁻ and can belong to both TDAE⁺⁺ and DP3FP⁻⁻ species having exchange interaction. The remarkable ferromagnetic phase of (TDAE⁺⁺)·(C_{60}^{--}) is also characterized only by one broad EPR signal with g = 2.0003.⁴² This value lies between the characteristic positions of the TDAE⁺⁺ and C_{60}^{--} ESR signals. The appearance of only one broad signal can be a consequence of strong exchange interactions between the paramagnetic TDAE⁺⁺ and C_{60}^{--} units.

The temperature dependences of g-factors and linewidths of the components of the ESR spectrum of 4 are shown in Fig. 9. Both components can be observed in the spectrum down to 80 K with nearly temperature independent parameters. Broadening of these signals and their shifting towards larger g-factors is observed below 60 K. We also analyzed the temperature dependence of total integral intensity of the ESR signal in the the spectrum of 4 (Fig. 10). It can be well fitted by the Curie-Weiss law with the negative Weiss temperature of -10 K in the whole temperature range (4–295 K). SQUID measurments for the sample of 4 support ESR data. Reciprocal magnetic susceptibility can be fitted well by the Curie-Weiss expression with negative Weiss temperature of -9 K in the 10-300 K range. Therefore, the observed broadening of the ESR signals and increasing g-factors below 60 K might be attributed to antiferromagnertic interactions of TDAE⁺⁺ and DP3FP⁻⁻ spins in 4. It should be noted for comparison that

200000 still 160000 40000 0 50 100 150 200 250 300 Temperature, K

Fig. 10 Temperature dependence of integral intensity of both components of the ESR spectrum of 4 fitted by the Curie–Weiss law with the Weiss temperature of -10 K.

broadening of the EPR signal and increasing *g*-factor were also observed for ferromagnetic (TDAE⁺⁺)·(C_{60}^{-}) complex below 20 K. These changes were associated with a ferromagnetic transition.⁴³

Conclusions

We have presented for the first time the improved microwaveassisted synthesis of pyrrolidinofullerene DP3FP (1) bearing two chelating 3-pyridyl groups at 2' and 5' positions of the pyrrolidine ring. The molecular structure of DP3FP was determined by the X-ray single crystal structure analysis for its 1:1 solvate with chlorobenzene. It was proved unambiguously that two 3-pyridyl groups in the DP3FP molecule are arranged in *cis*-configuration with respect to the pyrrolidine ring.

It was shown that DP3FP is a strong ligand capable of complex formation with a variety of metallated macrocycles. In particular, the formation of a 1:1 complex between DP3FP and ZnTPP was evidenced in solution. The association constant of $8.4 \pm 0.5 \times 10^4$ L mol⁻¹ determined for this complex in cyclohexane exceeds the binding constants reported previously for other complexes of pyrrolidinofullerenes with porphyrins in cyclohexane, chloroform and 1,2-dichlorobenzene.

Self-assembled triad **3** composed of one DP3FP unit and two $Mn^{II}TPP$ molecules was prepared and characterized by X-ray single crystal diffraction. It was revealed that both $Mn^{II}TPP$ molecules form coordination bonds with the nitrogen atoms of two 3-pyridyl groups of the DP3FP molecule. Optical spectra showed weak electronic interactions between the porphyrin and pyrrolidinofullerene units in triad **3** and the absence of charge transfer in the ground state.

On the contrary, complex 4 formed by DP3FP with the strong organic donor TDAE has ionic ground state and its composition can be represented by the formula (TDAE⁺⁺)·(DP3FP⁻⁻)·(C₆H₄Cl₂)_{1.6}. The formation of the radical anion and cation was proved by the optical absorption spectra in the visible, NIR and IR ranges. The EPR spectrum of 4 was considered as a superposition of two narrow signals ($g_1 = 2.0030$, $\Delta H = 0.7$ G and $g_2 = 2.0035$, $\Delta H = 0.5$ G). Noticeable broadening of the signals and their shift towards higher *g*-factors observed below 60 K strongly suggests antiferromagnertic interactions between the TDAE⁺⁺ and DP3FP⁻⁻ units. This conclusion is supported by the temperature dependence of integral intensity of the EPR signal in the 4–295 K range and by the temperature dependence of reciprocal magnetic susceptibility in the 10–300 K range which were fitted by the

Curie–Weiss law with negative Weiss temperatures of -10 and -9 K, respectively.

Experimental

Materials

Mn^{III}TPPCl, Co^{II}TPP, Zn^{II}TPP and tetrakis(dimethylamino)ethylene (TDAE) were purchased from Aldrich. Mn^{II}TPP was synthesized by the reduction of Mn^{III}TPPCl with an excess of NaBH₄ in ethanol.⁴⁴ Solvents were purified in argon atmosphere. Chlorobenzene (Aldrich) was used as received. 1,2-Dichlorobenzene (Aldrich) was distilled over CaH₂ under reduced pressure and hexane was distilled over Na/benzophenone under argon. Solvents for preparation of **3** and **4** were degassed and stored in a glove box. All manipulations for the synthesis of **3** and **4** were carried out in a MBraun 150B-G glove box with controlled atmosphere. The crystals were stored in a glove box and put in anaerobic conditions in 5 mm quartz tubes for EPR measurements under argon. KBr pellets for IR and visible–NIR measurements were prepared in a glovebox.

Synthesis

Pyrrolidinofullerene DP3FP was synthesized as follows. Fullerene C_{60} (230 mg) was dissolved in 12 mL of 1,2-dichlorobenzene together with 80 mg of 3-pyridinecarboxaldehyde and 80 mg of 3-picolylamine. The reaction mixture was closed in a 100 mL teflon reactor and heated inside a conventional microwave oven at 600 W for 15 min. (Caution: the conditions should be carefully adjusted to prevent overheating of dichlorobenzene up to and above the boiling temperature and explosive opening of the reactor). After heating, the teflon container was cooled down to room temperature. The reaction mixture was diluted by 3–4 volumes of toluene/methanol mixtures as eluent. The product yield was 70%. Column chromatography isolation of DP3FP and spectroscopic characteristics of this compound were previously reported in detail.²³

For the preparation of the crystals of DP3FP·C₆H₅Cl (1), starting fulleropyrrolidine (30 mg, 0.033 mmol) was dissolved in chlorobenzene (15 mL). Slow evaporation of the solution under argon produces the crystals of 1 whose composition was determined from X-ray analysis on single crystal. Unit cell parameters for several crystals tested from one synthesis are the same showing that crystals belong to one crystal phase. The prisms of 1 were of brown–black color and were obtained with 60% yield.

The crystals of $\{DP3FP\cdot(Mn^{II}TPP)_2\}\cdot(C_6H_4Cl_2)_3$ (3) were obtained in anaerobic conditions since $Mn^{II}TPP$ is sensitive to oxygen. DP3FP (30 mg, 0.033 mmol) and a slight excess of $Mn^{II}TPP$ (24 mg, 0.036 mmol) were dissolved in 14 mL of 1,2-dichlorobenzene at 60 °C for 6 h. The resulting dark green solution was filtered into a 50 mL tube for diffusion and hexane was layered over the obtained solution. After one month well-shaped crystals were formed on the walls of the tube in the hexane part of the solution. The crystal for X-ray diffraction measurements was taken directly from the solution and immediately cooled down to 100 K in the nitrogen flow. Therefore, the composition of **3** was determined from the X-ray diffraction data. The composition

of the fresh crystal of **3** was additionally tested by the Energy Dispersive X-ray analysis (EDX) using a SUPRA-50UP electron microscope to show a Cl to Mn ratio in a crystal to be close to 6:1. Therefore the real composition of complex 3 should be close to $\{DP3FP \cdot (Mn^{II}TPP)_2\} \cdot (C_6H_4Cl_2)_6$. The difference between the compositions determined from EDX and X-ray diffraction analyses is three solvent C6H4Cl2 molecules. Most probably these molecules occupy large voids in the structure of 3 where they are strongly disordered. The crystals were decanted from the solution, washed with hexane to yield black prisms with characteristic blue luster (25% yield). The IR and visible-NIR spectra were measured on fresh crystals. Testing the crystals by X-ray diffraction one day later showed that they completely lost crystallinity (most probably due to the loss of solvent). Similarly, Co^{II}TPP and ZnTPP were used in the synthesis instead of Mn^{II}TPP. However, in this case a nearly quantitatively polycrystalline precipitate was formed after several days.

The TDAE·DP3FP·($C_6H_4Cl_2$)_{1.6} (4) was prepared by dissolving DP3FP (30 mg, 0.033 mmol) in 14 mL of 1,2-dichlorobenzene with an excess of TDAE (0.5 mL) upon stirring at 60 °C for a night. Brown solution was formed. The solution was cooled down to room temperature, filtered in a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. Diffusion was carried out during 1 month to yield the crystals of 4 on the wall of the tube. The solvent was decanted from the crystals, which were washed with hexane to give black plates up to $0.3 \times 0.3 \times 0.5$ mm³ in size with 40% yield. The composition of 4 was determined by elemental analysis: TDAE·DP3FP·($C_6H_4Cl_2$)_{1.6} ($C_{91.6}H_{39.4}N_7Cl_{3.2}$, 1350.8); found, %: C = 80.85, H = 2.93, N = 7.48; Cl = 8.33; calc., %: C = 81.43, H = 2.92, N = 7.25; Cl = 8.40.

General

FT-IR spectra were measured in KBr pellets with a Perkin-Elmer Spectrum BX spectrometer (400–4000 cm⁻¹). The UVvisible spectrum was measured in KBr pellet on a Shimadzu-3100 spectrometer in the 400–1600 nm range. Solution spectra in visible range were measured on Specord M40. ESR spectra were recorded with a Radiopan SE/X-2547 spectrometer at room temperature and with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat in the 295–4 K range. Magnetic susceptibility measurements were carried out with a Quantum Design MPMS-XL SQUID magnetometer at a magnetic field of 1000 G between 2 and 300 K.

X-ray crystal structure determination

Crystal data for 1 at 100(2) K. $C_{78}H_{16}CIN_3$, $M_r = 1030.39$ g mol⁻¹, dark brown prism, monoclinic, $P 2_1/c$, a = 10.0579(10), b = 41.578(5), c = 9.9818(9) Å, $\beta = 102.202(9)^\circ$, V = 4079.9(7) Å³, Z = 4, $d_{calc} = 1.677$ g cm⁻³, $\mu = 0.161$ mm⁻¹, $F(000) = 2088, 2\theta_{max} = 52.80^\circ$, reflections measured 30736, unique reflections 8353, reflections with $I > 2\sigma(I) = 5371$, parameters refined 838, restraints 391, $R_1 = 0.0768$, w $R_2 = 0.1550$, G.O.F. = 1.064, CCDC reference number is 822365.

Crystal data for 1 at 293(2) K. $C_{78}H_{16}CIN_3$, $M_r = 1030.39$ g mol⁻¹, dark brown prism, monoclinic, $P 2_1/c$, a = 10.1250(12), b = 42.021(5), c = 10.0152(10) Å, $\beta = 101.937(11)^\circ$, V = 4169.0(8) Å³, Z = 4, $d_{calc} = 1.642$ g cm⁻³, $\mu = 0.158$ mm⁻¹, F(000) = 2088,

 $2\theta_{\text{max}} = 52.74^{\circ}$, reflections measured 31698, unique reflections 8495, reflections with $I > 2\sigma(I) = 4550$, parameters refined 838, restraints 385, $R_1 = 0.0711$, w $R_2 = 0.2225$, G.O.F. = 1.018, CCDC reference number is 822362.

Crystal data for 3 at 120(2) K. $C_{178}H_{79}Cl_6Mn_2N_{11}$, $M_r = 2694.10 \text{ g mol}^{-1}$, black prism, monoclinic, C 2/m, a = 28.6483(15), b = 26.2811(16), c = 19.8784(12) Å, $\beta = 101.854(5)^\circ$, V = 14647.4(15) Å³, Z = 4, $d_{calc} = 1.222 \text{ g cm}^{-3}$, $\mu = 0.339 \text{ mm}^{-1}$, F(000) = 5504, $2\theta_{max} = 52.74^\circ$, reflections measured 52022, unique reflections 15269, reflections with $I > 2\sigma(I) = 6503$, parameters refined 1104, restraints 1212, $R_1 = 0.1214$, $wR_2 = 0.3658$, G.O.F. = 1.081, CCDC reference number is 822366.

X-ray diffraction data for 1 and 3 were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated MoK_{α} radiation using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97.⁴⁵ Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the "riding" model with $U_{iso} = 1.2U_{eq}$ of the connected non-hydrogen atom.

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