

Neutral and ionic complexes of C₆₀ with (ZnOEP)₂·BPy coordination dimers†‡

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Coordination (ZnOEP)₂·BPy dimers formed by zinc octaethylporphyrin and 4,4'-bipyridine co-crystallize with neutral C₆₀ and the (TDAE^{·+})·(C₆₀^{·−}) ion-radical salt to form molecular and ionic multi-component complexes: {(ZnOEP)₂·BPy}·(C₆₀)₂·(CHCl₃)₂ (**1**) and (TDAE^{·+})₂·{(ZnOEP)₂·BPy}·(C₆₀^{·−})₂·(C₆H₆)_{0.75}·(C₆H₄Cl₂)_{0.25} (**2**). The C₆₀ molecules are arranged in layers in **1** with the interfullerene center-to-center distances of 10.04–10.17 Å and in linear chains in **2** with the uniform interfullerene center-to-center distance of 10.61 Å. EPR measurements show exchange interaction between C₆₀^{·−} and TDAE^{·+} ion-radicals in **2**, which results in the appearance of one signal with *g* = 2.0027 and Δ*H*_{pp} = 19.8 G at 295 K rather than two signals from individual ion-radicals. The EPR signal from **2** is split into two components below 30 K and its integral intensity decreases below 9.6 K, which is evidence of antiferromagnetic interactions of spins.

Introduction

Fullerene complexes evoked great interest due to promising magnetic, conducting and optical properties.^{1–3} Up to now a wide variety of organic and organometallic compounds were used for the preparation of these complexes, namely, aromatic hydrocarbons,^{4,5} amines,⁶ metallocenes,⁷ metalloporphyrins^{8–11} and metal dithiocarbamates.¹² The design of functional complexes based on fullerenes requires both the search for new classes of donor molecules able to form complexes with fullerenes and the development of synthetic approaches, which allow one to modify known molecular complexes (D₁·fullerene) and obtain multi-component neutral {(D₁·L)·fullerene} and ionic {(D₂⁺)·(D₁)·(fullerene[−])} complexes.^{13–19}

The first approach uses relatively weak coordination bonding and allows the design of fullerene complexes with coordination assemblies of metalloporphyrins and metal (II) dithiocarbamates. For example, zinc tetraphenylporphyrin forms monomers, dimers and pentamers {(ZnTPP)_x·L, *x* = 1, 2, and 4; L = pyridine, tetramethylethylenediamine, pyrazine, 4,4'-bipyridine, and tetrapyrildylporphyrin), which

co-crystallize with fullerenes to form complexes with one-dimensional, layered and paired arrangement of fullerene molecules.^{13,14} Similarly, coordination monomers and dimers of metal (II) dithiocarbamates with diazabicyclooctane, *N,N'*-dimethylpyperazine and hexamethylenetetramine as L form complexes with C₆₀, which have layered and 3D packing of fullerene molecules.¹⁵

The second approach uses D₁ molecules, which can produce large cavities when packing with spherical fullerene molecules to accommodate a third component, which can be either a strong donor or a cation (D₂⁺).^{16–19} This approach allows one to vary (D₂⁺) cations with different spin states within series of {(D₂⁺)·(D₁)·(fullerene[−])} complexes to affect their properties.^{18,19}

In this work we combined the two above mentioned approaches. We used bidentate 4,4'-bipyridine ligand to assemble coordination dimers with zinc octaethylporphyrin, (ZnOEP)₂·BPy, which were then co-crystallized with C₆₀ to form molecular complex **1**: {(ZnOEP)₂·BPy}·(C₆₀)₂·(CHCl₃)₂. The packing of (ZnOEP)₂·BPy dimers and C₆₀ can produce large cavities, which were used to accommodate a strong TDAE donor to form ionic multi-component complex **2**: (TDAE^{·+})₂·{(ZnOEP)₂·BPy}·(C₆₀^{·−})₂·(C₆H₆)_{0.75}·(C₆H₄Cl₂)_{0.25}. Crystal structures of both complexes were solved, their UV-vis-NIR and IR spectra were analyzed, and magnetic properties were studied.

Results and discussion

1. Synthesis

Both complexes were obtained by the diffusion method. For the preparation of **1**, a CHCl₃ solution containing ZnOEP and an excess of BPy diffused into a benzene solution of C₆₀. The crystals of **1** were formed after one month. For the preparation of **2**, a hexane solution diffused into a dichlorobenzene-benzene

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‡ Electronic supplementary information (ESI) available: IR spectra of starting compounds and complexes **1** and **2**, EPR spectra of **2** and temperature dependencies of the parameters of EPR signal in **2**. See DOI: 10.1039/b708100f

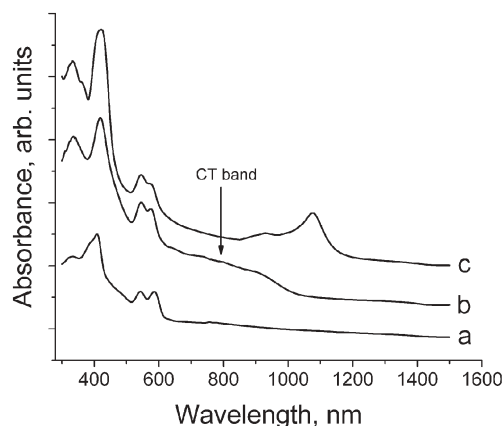


Fig. 1 UV-visible-NIR spectra of starting ZnOEP (a); complexes **1** (b) and **2** (c) in KBr pellets in the 300–1500 nm range.

solution containing $(\text{TDAE}^+)(\text{C}_{60}^{\cdot-})$ salt, ZnOEP and an excess of BPy. The crystals of **2** were formed after one month and were free of $(\text{TDAE}^+)(\text{C}_{60}^{\cdot-})$ admixture.

2. IR- and UV-vis-NIR spectra

The IR spectra of **1** and **2** are superpositions of the spectra of starting components: ZnOEP, BPy, C_{60} , TDAE and solvent molecules (see ESI†). There are four IR active bands from C_{60} at 527, 577, 1182 and 1429 cm^{-1} ($F_{1u}(1-4)$ modes, respectively). $F_{1u}(4)$ mode of C_{60} (which is most sensitive to charge transfer to the C_{60} molecule)²⁰ is positioned in the spectrum of **1** at 1424 cm^{-1} that can justify only weak charge transfer to C_{60} . In contrast to **1**, C_{60} has -1 charged state in **2** since the position of $F_{1u}(4)$ mode of C_{60} in the spectrum of **2** (1390 cm^{-1}) is very close to the position of this mode in the spectra of other ion-radical salts with approximate -1 charged state of C_{60} .^{20,21} The C–N stretching mode of TDAE is very sensitive to its charged state and shifts in the following order: 1340 cm^{-1} for neutral TDAE; 1518 cm^{-1} for $(\text{TDAE}^+)(\text{C}_{60}^{\cdot-})$ with approximate $+1$ charge on TDAE; and 1659, 1675 cm^{-1} for TDAE(Cl_2) with $+2$ charge on TDAE.²² The position of this mode in the spectrum of **2** at 1516 cm^{-1} clearly indicates the formation of $\text{TDAE}^{\cdot+}$ radical cations.

The UV-visible-NIR spectra of starting ZnOEP, **1** and **2** are shown in Fig. 1. The position of the Soret band for ZnOEP is at 409 nm and those of the Q-bands are at 542 and 586 nm (Fig. 1a). The formation of **1** and **2** noticeably shifts (by 9–10 nm) the position of the Soret band to the red side

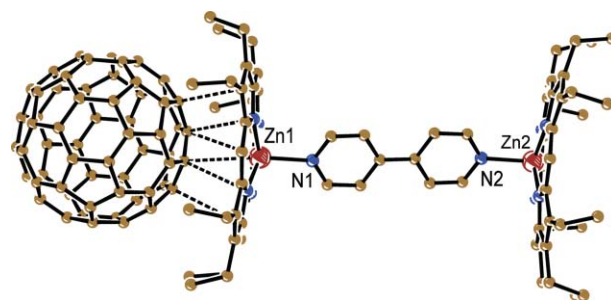


Fig. 2 Van der Waals contacts between C_{60} molecule and coordination $\text{ZnOEP}_2\cdot\text{BPy}$ dimers in **1** (dashed lines). Only one most occupied orientation was shown for disordered C_{60} .

(418 and 419 nm, respectively). The positions of the Q-bands are shifted insignificantly (542 and 576 nm for **1** and 545 and 574 nm for **2**). These shifts are a result of the coordination of the BPy ligand to ZnOEP. Similar shifts are observed at the formation of coordination dimers of ZnTPP with N-containing ligands in the complexes with C_{60} .^{13,14} Complex **1** manifests a relatively intense broad charge transfer (CT) band in the visible-NIR range with the maximum at about 800 nm (Fig. 1b). Such bands are characteristic of C_{60} complexes with metalloporphyrins, which acquire a concave shape as a result of coordination of additional ligands.¹⁴ Complexes of fullerenes with planar porphyrins manifest only weak or even no CT bands.¹¹ Absorption at 1070 nm characteristic of $\text{C}_{60}^{\cdot-}$ is not observed in the spectrum of **1** indicating its neutral ground state. Complex **2** manifests intense bands at 930 and 1076 nm characteristic of $\text{C}_{60}^{\cdot-}$ (Fig. 1c). It was shown that the charged state of C_{60} in $(\text{TDAE}^+)(\text{C}_{60}^{\cdot-})$ is also close to -1 .²²

3. Crystal structures

$\{(\text{ZnOEP}_2\cdot\text{BPy})\cdot(\text{C}_{60})_2\cdot(\text{CHCl}_3)_2$ (**1**). The complex crystallizes in a triclinic unit cell. Each $(\text{ZnOEP}_2)\cdot\text{BPy}$ dimer forms vdW contacts (Fig. 2) with two fullerene molecules, and two solvent CHCl_3 molecules occupy vacancies between the ZnOEP planes (Fig. 3). The length of the $\text{Zn}\cdots\text{N}(\text{BPy})$ coordination bond is 2.173(3) Å that is noticeably longer than the averaged length of the $\text{Zn}\cdots\text{N}(\text{OEP})$ bonds (2.080 Å). Porphyrin macrocycles in the dimer are arranged nearly parallel to each other and do not rotate. All ethyl substituents of ZnOEP are directed toward fullerene molecules. The ZnOEP macrocycle has a concave shape with the rms deviations of atoms by 0.176 Å from the mean porphyrin plane and the displacement of the zinc atom

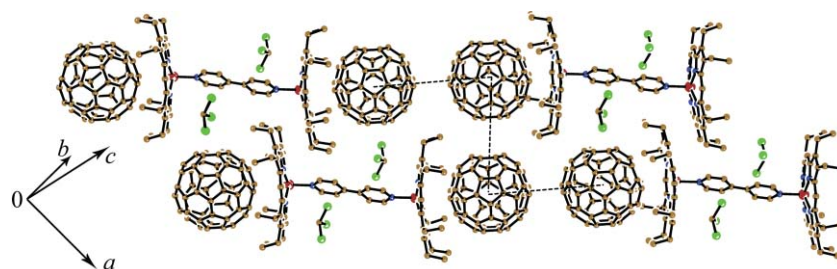


Fig. 3 Fragment of crystal structure of **1**. C_{60} layers are shown by dashed lines. Only one most occupied orientation was shown for disordered C_{60} and CHCl_3 molecules.

from this plane toward the BPy ligand by 0.539 Å. As a result, the shape of the ZnOEP macrocycle conforms well to the spherical shape of C_{60} and allows the formation of multiple vdW contacts between them (Fig. 2). The C $\cdots$ C contacts lie in the 3.28–3.39 Å range and the N $\cdots$ C contacts lie in the 3.09–3.21 Å range for both orientations of C_{60} . Though C_{60} is surrounded by eight ethyl groups of ZnOEP, no shortened H(ethyl of ZnOEP) $\cdots$ C(C_{60}) contacts are formed. This could be a reason for C_{60} disorder in this complex. In previously studied C_{60} complexes with metal (II) octaethylporphyrins the C_{60} molecules were usually ordered to form multiple H(MOEP) $\cdots$ C(C_{60}) contacts.⁸ The shortest Zn $\cdots$ C(C_{60}) contacts of 3.101 and 3.369 Å for one C_{60} orientation and 3.150 and 3.268 Å for the other C_{60} orientation are formed with the 6-6 bond of C_{60} (Fig. 2). The C_{60} molecules form layers in **1** (Fig. 3). The interfullerene center-to-center distances between C_{60} molecules in the layer are 10.041, 10.080 and 10.166 Å. These distances are rather close to the center-to-center distances in pure C_{60} at 153 K (9.94 Å²³).

Complex **2** has an orthorhombic unit cell. The $C_{60}^{\cdot-}$ radical anions rotate even at 90 K. Probably this rotation is not free because of the non-uniform distribution of 120 carbon atoms over the fullerene sphere. However, the attempts to approximate fullerene disorder by several orientations showed that there are more than three orientations of $C_{60}^{\cdot-}$. The TDAE $^+$ radical cations are disordered between two orientations, whereas the BPy ligand is disordered between four orientations. In **2** there is one crystallographically independent (ZnOEP) $_2$ -BPy dimer, two $C_{60}^{\cdot-}$ and TDAE $^+$ ion-radicals and one vacancy, which is shared by solvent C_6H_6 and $C_6H_4Cl_2$ molecules.

TDAE $^+$ and $C_{60}^{\cdot-}$ ion-radicals form ionic TDAE $^+$ - $C_{60}^{\cdot-}$ layers. Fig. 4a shows the projection on this layer and Fig. 4b shows the view along these layers. The ionic layers alternate with the neutral layers composed of closely packed ZnOEP molecules. Within ionic layers one-dimensional chains formed by $C_{60}^{\cdot-}$ can be outlined along the *b* axis with a uniform interfullerene center-to-center distance of 10.61 Å. This distance is longer than that in the antiferromagnetic phase of (TDAE $^+$)($C_{60}^{\cdot-}$) (9.915 Å, the shortened vdW C $\cdots$ C contacts are 3.081–3.379 Å²⁵) and prevents the formation of shortened vdW C $\cdots$ C contacts between $C_{60}^{\cdot-}$ in **2** (all C $\cdots$ C contacts are longer than 3.45 Å). The chains of $C_{60}^{\cdot-}$ are separated by the chains formed by alternating (solvent-TDAE $^+$ -BPy-TDAE $^+$) units (Fig. 4a). The TDAE $^+$ radical cations are isolated in the chains but form vdW contacts with solvent molecules (Cl $\cdots$ C contacts), BPy (C and N $\cdots$ C contacts) and $C_{60}^{\cdot-}$. Therefore, TDAE $^+$ and $C_{60}^{\cdot-}$ ion-radicals have rather loose packing in **2**.

The geometry of the (ZnOEP) $_2$ -BPy dimer in **2** is slightly different from that in **1**. Porphyrin macrocycles are arranged parallel to each other and rotate by an angle of 3.38°. The length of the Zn $\cdots$ N(BPy) coordination bond is noticeably shorter in **2** (2.112(1) Å) than in **1** and even close to the length of the averaged Zn $\cdots$ N(OEP) bonds (2.0705 Å). The ZnOEP macrocycles have the rms deviations of atoms 0.1477 Å from the mean porphyrin plane and the displacement of zinc atom by 0.462 Å from this plane toward the BPy ligand. One of two $C_{60}^{\cdot-}$ is located in the cage formed by two bowl-shaped ZnOEP molecules (Fig. 4b), which conform well with the

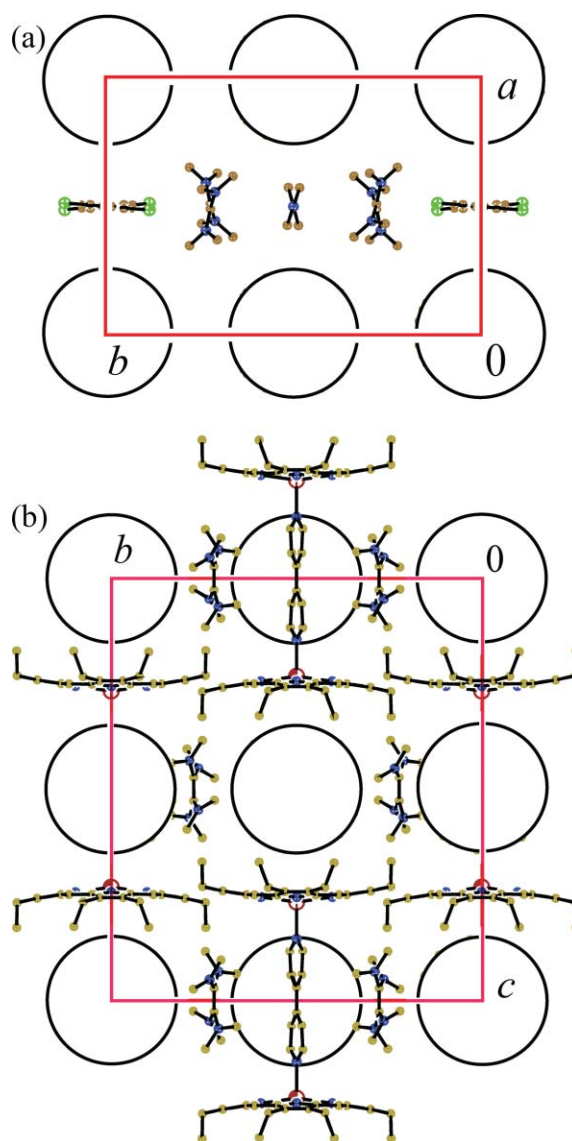


Fig. 4 View of the crystal structure of **2** along crystallographic *c*- (a) and *a*-axes (b). $C_{60}^{\cdot-}$ are shown by circles. Only one most occupied orientation is shown for TDAE $^+$. In (b) only one orientation of BPy is shown and solvent molecules are not depicted for clarity.

spherical shape of C_{60} to provide the formation of vdW N, C(ZnOEP) $\cdots$ C($C_{60}^{\cdot-}$) and Zn $\cdots$ C($C_{60}^{\cdot-}$) contacts, the Zn $\cdots$ C($C_{60}^{\cdot-}$) distances being longer than 3 Å. The other $C_{60}^{\cdot-}$ radical anion is positioned in the voids formed by two (ZnOEP) $_2$ -BPy dimers (this space is limited by planes of the four ZnOEP macrocycles and two BPy ligands) (Fig. 4b). Though there is the essential difference in the environment of two crystallographically independent $C_{60}^{\cdot-}$ in **2**, they are disordered in both positions. To understand why $C_{60}^{\cdot-}$ is disordered in the cage formed by ZnOEP molecules one should take into account that neither shortened H(ZnOEP) $\cdots$ C($C_{60}^{\cdot-}$) contacts nor the coordination of zinc atom to the fullerene cage are found in this case (similarly to **1**). Most probably good complementarity between the shapes of ZnOEP macrocycles and C_{60} spheres and the formation of shortened N, C(ZnOEP) $\cdots$ C($C_{60}^{\cdot-}$) contacts is still not enough to fix C_{60} rotation.

4. Magnetic properties of **2**

The two-component $(\text{TDAE}^+)(\text{C}_{60}^-)$ complex is a well-known ferromagnet with the highest transition temperature ($T_c = 16$ K) for metal free compounds.²⁴ The antiferromagnetic phase of $(\text{TDAE}^+)(\text{C}_{60}^-)$ is also known.²⁵ In both antiferro- and ferromagnetic phases the C_{60}^- radical anions form closely packed one-dimensional chains and the difference between the two phases is only in the orientation of C_{60}^- .²⁶ We studied the $(\text{TDAE}^+)(\text{TBPDA})_2(\text{C}_{60}^-)$ complex, in which TDAE^+ and C_{60}^- ion-radicals were isolated by bulky TBPDA molecules. Nevertheless, antiferromagnetic interaction of spins found in this complex resulted in the decrease in magnetic moment of the complex even below 100 K.^{18,19} In **2** we constructed one-dimensional chains from C_{60}^- , which are similar to the C_{60}^- chains in $(\text{TDAE}^+)(\text{C}_{60}^-)$, but have longer distances between C_{60}^- .

The magnetic behaviour of **2** was studied on a polycrystalline sample by EPR spectroscopy from room temperature ($\text{RT} = 295$ K) down to 4 K. At RT the complex manifests a single Lorentzian line with g -factor equal to 2.0027 and a linewidth (ΔH_{pp}) of 19.8 G. The g -factor value is an intermediate one between those characteristic of TDAE^+ ($g = 2.0035$)²⁷ and C_{60}^- (1.9996–2.0000)²⁸. The appearance of one signal instead of two signals from individual ion-radicals indicates the existence of exchange interaction between TDAE^+ and C_{60}^- in **2**. It should be noted that only one signal was found in other TDAE containing fullerene complexes ($g = 2.0003$ and $\Delta H_{\text{pp}} = 22$ G in $(\text{TDAE}^+)(\text{C}_{60}^-)$ ²⁹ and $g = 2.0009$ and $\Delta H_{\text{pp}} = 29.3$ G in $(\text{TDAE}^+)(\text{TBPDA})_2(\text{C}_{60}^-)$ ^{18,19}). Magnetic exchange can be realized either by direct interaction between two ion-radicals as in $(\text{TDAE}^+)(\text{C}_{60}^-)$ or indirectly through the diamagnetic TBPDA molecules as in $(\text{TDAE}^+)(\text{TBPDA})_2(\text{C}_{60}^-)$ ¹⁹. Most probably, exchange interaction is realized in **2** in both ways: directly due to the presence of vdW contacts between TDAE^+ and C_{60}^- and indirectly through the diamagnetic solvent molecules and BPy.

The EPR signal noticeably narrows with the temperature decrease (Fig. 5, inset) that is characteristic of the EPR signal from C_{60}^- .²⁸ Below 30 K the signal splits into two

components, which become slightly wider with the temperature decrease and the drop in integral intensity below 9.6 K (Fig. 5) is evidence for the antiferromagnetic interaction of the spins. Similar splitting of the EPR signal into two components was observed previously in several ionic C_{60} complexes, which also manifest antiferromagnetic interaction of spins.^{18,19,30} The magnetic behaviour of **2** is similar to that of the antiferromagnetic phase of $(\text{TDAE}^+)(\text{C}_{60}^-)$.³¹ However, due to more loose packing of C_{60}^- in the chains of **2**, the antiferromagnetic ordering manifests itself at lower temperatures. The $(\text{intensity} \times T)$ value decreases in $(\text{TDAE}^+)(\text{C}_{60}^-)$ even below 60 K,³¹ whereas in **2** the decrease in the $(\text{intensity} \times T)$ value is observed only below 20 K.

Conclusion

The multi-component approach allows one to design neutral and ionic complexes of ZnOEP with C_{60} . Bidentate BPy coordinates to two ZnOEP molecules to form coordination dimers with the $\text{Zn} \cdots \text{N}(\text{BPy})$ bonds in the 2.11–2.17 Å range. These dimers efficiently pack with C_{60} molecules to form molecular complex **1**: $\{(\text{ZnOEP})_2\text{BPy}\}(\text{C}_{60})_2(\text{CHCl}_3)_2$. The reason for this is the slightly concave shape of the ZnOEP macrocycles, which conforms well with the spherical shape of C_{60} .

The packing of the $(\text{ZnOEP})_2\text{BPy}$ dimers and C_{60} has large cavities. Such packing allows additional donors or cations of small size to be introduced to form multi-component ionic complexes. In this work TDAE was used as an additional donor. Since TDAE reduces C_{60} to an anion-radical state, $(\text{TDAE}^+)_2\{(\text{ZnOEP})_2\text{BPy}\}(\text{C}_{60}^-)_2(\text{C}_6\text{H}_6)_{0.75}(\text{C}_6\text{H}_4\text{Cl}_2)_{0.25}$ (**2**) with an ionic ground state is formed. In **2** the ionic $\text{TDAE}^+ - \text{C}_{60}^-$ layers alternate with the neutral ZnOEP layers. Complex **2** manifests antiferromagnetic interaction of spins at low temperatures (below 30 K), similarly to the antiferromagnetic phase of $(\text{TDAE}^+)(\text{C}_{60}^-)$. However, the magnetic interactions in **2** are weaker due to longer distances between C_{60}^- in one-dimensional chains and between TDAE^+ and C_{60}^- ion-radicals. Nevertheless, the multi-component approach is a useful tool to trace how changes in the crystal structure can affect magnetic properties. It also makes it possible to vary cations (D_2^+) or neutral metalloporphyrin molecules (for example, using $\text{Mn}^{\text{II}}\text{OEP}$ or $\text{Co}^{\text{II}}\text{OEP}$) within a series of $\{(\text{D}_2^+)_2\{(\text{M}^{\text{II}}\text{OEP})_2\text{BPy}\}(\text{C}_{60}^-)_2\text{solvent}\}$ complexes. Such variations can essentially affect magnetic properties of the complexes. This work is now in progress.

Experimental

Materials

Zinc octaethylporphyrin (ZnTPP), 4,4'-bipyridine (BPy) and tetrakis(dimethylamino)ethylene (TDAE) were purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. Chloroform (CHCl_3) was used as received. Other solvents were purified in an argon atmosphere. *o*-Dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$) was distilled over CaH_2 under reduced pressure, benzene (C_6H_6) and hexane were distilled over Na/benzophenone. The solvents were degassed and stored in a glove box.

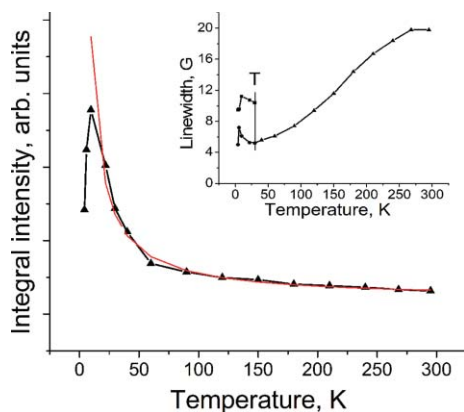


Fig. 5 Temperature dependence of integral intensity of the EPR signal in **2**. Red line shows the Curie curve calculated for **2**. Inset shows the temperature dependence of linewidth of the EPR signals. “T” marks the temperature of the splitting of the EPR signal into two components.

All manipulations for the synthesis of **2** were carried out in a MBraun 150B-G glove box with controlled atmosphere and the content of H₂O and O₂ was less than 1 ppm. The crystals were stored in a glove box and sealed in 2 mm quartz tubes for EPR measurements under 10^{−5} Torr. KBr pellets for IR- and UV-visible-NIR measurements were prepared in a glove box.

Synthesis

The crystals of (ZnOEP₂·BPy)·(C₆₀)₂·(CHCl₃)₂ (**1**) were obtained by diffusion. The CHCl₃ solution (20 mL) containing ZnOEP (20 mg, 0.0335 mmol) and an excess of BPy (80 mg, 0.51 mmol) diffused in the C₆H₆ solution (20 mL) containing C₆₀ (20 mg, 0.0277 mmol). After 1 month the crystals were formed on the walls of the diffusion tube. The solvent was decanted and the crystals were washed with acetone to give black prisms with characteristic blue luster (20 mg, 48% yield).

The crystals of (TDAE⁺)₂·{(ZnOEP)₂·BPy}·(C₆₀[−])₂·(C₆H₆)_{0.75}·(C₆H₄Cl₂)_{0.25} (**2**) were obtained by diffusion. ZnOEP (20 mg, 0.0335 mmol), an excess of BPy (80 mg, 0.51 mmol) and C₆₀ (25 mg, 0.0347 mmol) were dissolved upon stirring in 20 mL of the C₆H₄Cl₂–C₆H₆ (4 : 1) mixture during 2 h at 60 °C. The solution was cooled down to room temperature and 1 mL of TDAE was added. The solution was stirred for one more hour, filtered in the tube for diffusion (45 mL volume), and hexane (22 mL) was carefully layered over. After 1 month the solvent was decanted from the crystals precipitated and they were washed with hexane to give 14 mg (25% yield) of black prisms with characteristic blue luster.

The composition of **1** and **2** was determined from X-ray diffraction data for a single crystal. The unit cell parameters of several selected crystals from one synthesis were the same.

General

FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrometer (400–7800 cm^{−1}). UV-visible-NIR spectra were measured in KBr pellets on a Shimadzu-3100 spectrometer in the 220–1600 nm range. EPR spectra of **2** were recorded from 295 down to 4 K with a JEOL JES-TE 200 X-band ESR spectrometer.

X-Ray crystal structure determination

Crystal data of **1** at 110(2) K: C₂₀₄H₉₈Cl₆N₁₀Zn₂, *M_r* = 3032.36 g mol^{−1}, black prisms, triclinic, *P* $\bar{1}$, *a* = 13.847(9), *b* = 14.011(11), *c* = 19.795(16) Å, α = 78.50(3), β = 76.35(3), γ = 63.27(2)°, *V* = 3314(4) Å³, *Z* = 2, *d*_{calc} = 1.519 g cm^{−3}, μ = 0.555 mm^{−1}, *F*(000) = 1554, max. 2 θ _{max} = 60.08°. In total, 26 298 reflections were measured, 18 271 of which were independent. The least-squares refinement on *F*² was done to *R*₁ [*F* > 2σ(*F*)] = 0.0917 for 10 828 observed reflections, *wR*₂ = 0.2453 (all data), *R*₁ = 0.1366 for all 18 271 observed reflections with 1238 parameters and 8840 restraints; final GoF = 0.951. CCDC reference number is 648658.

Crystal data of **2** at 90(2) K: C₂₂₈H_{149.5}Cl_{0.5}N₁₈Zn₂, *M_r* = 3289.6 g mol^{−1}, black prisms, orthorhombic, *I* 222, *a* = 14.8555(4), *b* = 21.2150(7), *c* = 24.2022(6) Å, *V* = 7627.6(4) Å³, *Z* = 2, *d*_{calc} = 1.436 g cm^{−3}, μ = 0.397 mm^{−1}, *F*(000) = 3440, max. 2 θ _{max} = 69°. In total, 124 312 reflections were measured,

15 596 of which were independent. The least-squares refinement on *F*² was done to *R*₁ [*F* > 2σ(*F*)] = 0.0496 for 13 620 observed reflections, *wR*₂ = 0.1466 (all data), *R*₁ = 0.0571 for all 15 605 observed reflections with 930 parameters and 1934 restraints; final GoF = 1.077. CCDC reference number is 648659.

X-Ray diffraction data for **1** were collected using a Bruker SMART CCD diffractometer (sealed tube, Mo K α radiation, λ = 0.71073 Å, μ = 0.08 mm^{−1}) and for **2** using a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo K α radiation, λ = 0.71073 Å). Both diffractometers were equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. For **1** a series of three ω scans with a 0.3° frame width was collected. For **2** the data were collected by the rotation method with 0.3° frame-width (ω scan) and 10 s exposure time per frame. Four sets of data (600 frames in each set) were collected, nominally covering half of the reciprocal space. Both structures were solved by direct methods using the SHELXTL program package³² and refined by full-matrix least squares on *F*². The ordered non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the “riding” model with *U*_{iso} = 1.2*U*_{eq} of the connected non-hydrogen atom or as ideal CH₃ groups with *U*_{iso} = 1.5*U*_{eq}.

Disorder

Fullerenes are disordered in **1** between two orientations with the 0.512/0.488 occupancies. These orientations are linked by the rotation of fullerene molecules about threefold non-crystallographic axis. Chloroform molecules are disordered between three positions with the 0.658/0.237/0.105 occupancies.

Both crystallographically independent fullerene molecules rotate almost freely in **2**. The attempts to approximate them by several orientations show that there are more than three orientations for each C₆₀[−]. In this case disordered fullerene molecules were approximated with 120 carbon atoms with the 0.5 occupancy assigned to electron density peaks after using direct method and consequent Fourier syntheses. Atomic coordinates and anisotropic thermal parameters for fullerene atoms were refined by a SHELXL conjugate-gradient least square procedure at the early stages and full-matrix least square procedure in final refinement, with thermal parameters fixed. The BPy ligand is disordered between four orientations with the 0.30/0.26/0.22/0.22 occupancies, which are linked by its rotation about the axis passing through two nitrogen atoms. The TDAE⁺ radical cations are disordered between two positions with 0.698/0.302 occupancies. The position of solvent molecules is shared by benzene and dichlorobenzene molecules with the 0.75/0.25 occupancies.

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