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Interaction of Octopus−like Cobalt(II) Phthalocyaninate with Fullerene C_{70} Studied by ESR Spectroscopy

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*This work reports on synthesis and characterizations of cobalt(II) complex **1Co** with octopus-like phthalocyanine ligand bearing eight peripheral O-benzyl-diethyleneglycol substituents. Concentration-dependent investigation of UV-Vis spectra of **1Co** in chloroform evidenced of its aggregation at high concentrations (0.3 mM) with the formation of dimers with dimerization constant $(4.8\pm0.2)\cdot10^{3}$ M^{-1}. Supramolecular assembling of **1Co** with fullerene $\mathbf{C_{70}}$ was studied by UV-Vis titration and by ESR spectroscopy. Both methods suggest the absence of notable interactions between electronic systems of **1Co** and $\mathbf{C_{70}}$ in ground state, the formation of the assembly **1Co•**$\mathbf{C_{70}}$ occurs via noncovalent interactions.*

Keywords: Phthalocyanine, cobalt, fullerene, electronic spin resonance, supramolecular assembling.

Исследование взаимодействия осьминогоподобного фталоцианината кобальта(II) с фуллереном C_{70} методом спектроскопии ЭПР

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*Синтезирован фталоцианинат кобальта(II) **1Co**, содержащий восемь фрагментов О-бензилдиэтиленгликоля. Методом ЭСП изучена агрегация комплекса в концентрированных растворах (до 0.3 мМ в хлороформе). С использованием регрессионного анализа установлено, что в концентрированных растворах происходит димеризация молекул **1Co**, константа димеризации составляет $(4.8\pm0.2)\cdot10^{3}$ M^{-1}. Взаимодействие **1Co** с фуллереном $\mathbf{C_{70}}$ исследовано с использованием методов спектрофотометрического титрования и спектроскопии ЭПР. Показано, что образование супрамолекулярного ансамбля **1Co•**$\mathbf{C_{70}}$ происходит за счет нековалентных взаимодействий и не сопровождается заметным взаимодействием между электронными системами **1Co** и $\mathbf{C_{70}}$.*

Ключевые слова: Фталоцианин, кобальт, фуллерен, ЭПР, супрамолекулярная сборка.

Introduction

Donor-acceptor assemblies based on tetrapyrrolic macrocycles and nanocarbon materials – fullerenes, graphenes, nanotubes, *etc.*, are promising conductive materials and photoactive components of photovoltaic devices.[1–7] Such hybrid materials can be formed either by covalent bonding of tetrapyrroles to nanocarbons, or by their supramolecular assembling. The former method results in transformation of sp^2-carbon atoms in intact nanocarbons into sp^3-C, which cannot participate in electronic conjugation. Supramolecular approach does not have this disadvantage, it is widely used to form co-crystals of fullerenes with porphyrins and phthalocyanines,[8–11] however assembling of fullerenes with tetrapyrroles in solution requires accurate design of receptor groups providing efficient and controllable binding and selectivity.[12–15]

Previously, we have synthesized new fullerene-binding receptors – zinc and magnesium phthalocyaninates bearing eight peripheral *O*-benzyldiethyleneglycol substituents starting from [2'-(2''-benzylethoxy)ethoxy]phthalonitrile[16] (Figure 1). These molecules resemble octopuses, which capture fullerenes with their eight "limbs" *via* noncovalent hydrophobic and π-π interactions. Using UV-Vis and fluorescence spectroscopy we demonstrated high affinity of receptors for $\mathbf{C_{60}}$ and $\mathbf{C_{70}}$, with selectivity to $\mathbf{C_{70}}$: binding constants for $\mathbf{C_{70}}$ were almost two times higher than for $\mathbf{C_{60}}$. This result was rationalized using semi-empirical calculations at PM6-DH2 level.

In the present work we have synthesized cobalt(II) complex **1Co** with octopus-like phthalocyanine ligand, investigated aggregation of **1Co** in chloroform and studied its interaction with $\mathbf{C_{70}}$ by spectrophotometric titration. Due to the presence of one unpaired electron in Co^{2+} ion with d^7-configuration this interaction could be studied by ESR spectroscopy. It let us draw a conclusion about assembling of **1Co** and $\mathbf{C_{70}}$ molecules *via* noncovalent dipole-dipole interactions.

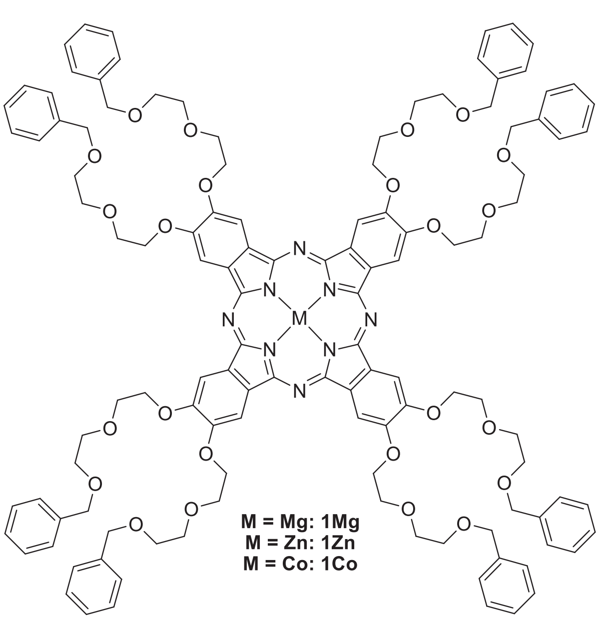


Figure 1. Octopus-like fullerene receptors **1M**. M=Zn and Mg (Ref.[16]), Co (this work).

Experimental

[2'-(2''-Benzylethoxy)ethoxy]phthalonitrile **2** was synthesized according to previously reported procedures.[17,18] Cobalt acetate tetrahydrate (Aldrich) was dried at 90 °C in vacuum to obtain anhydrous salt. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Merck) was distilled over CaH_2 in vacuum and stored under argon. Isoamyl alcohol (Sigma-Aldrich) was distilled over sodium and stored under argon. Chloroform was distilled over $NaHCO_3$ to remove acidic impurities. Neutral alumina (Macherey Nagel) was used for chromatography. Other reagents and solvents were purchased from commercial suppliers and were used without additional purification.

UV-Vis spectra were recorded at room temperature on Cary-100 and Thermo Evolution 210 spectrophotometers in 0.1-1 cm pathlength cuvettes. MALDI TOF mass-spectra were measured on Ultraflex spectrometer (Bruker Daltonics) with 2,5-dihydroxybenzoic acid (DHB), used as a matrix.

X-Band ESR spectra were measured at 9.8 GHz microwave frequency on Bruker Elexsys E-680X radiospectrometer in the temperature range of 300-100 K. Since low-spin cobalt(II) complexes tend to form adducts with molecular oxygen, we paid particular attention to sample preparation. Samples of **1Co** were dissolved under vacuum in solvents, which were previously deoxygenated by repeated freeze-pump-thaw cycles. Resulting solutions were transferred into cells for ESR measurements. The spectra were measured below the melting points of solvents.

Resulting ESR spectra were described using rhombic spin Hamiltonian with S=1/2 spin, Zeeman and hyperfine interactions:

$$H_{glass} = g_z\beta H_z\hat{S}_z + g_x\beta H_x\hat{S}_x + g_y\beta H\hat{S}_y + A\hat{I}_z\hat{S}_z + B\hat{I}_x\hat{S}_x + C\hat{I}_y\hat{S}_y \quad (1)$$

Here g_z, g_x, g_y – *z, x, y* – components of *g*-tensor, *A*, *B*, *C* – *z, x, y* – components of HFS tensor, $\hat{S}_z$, $\hat{S}_x$, $\hat{S}_y$ – projections of spin operator onto coordination axes, S=1/2, $\hat{I}_z$, $\hat{I}_x$, $\hat{I}_y$ – projections of nuclear spin operator onto coordination axes, I=3.5.

The parameters of ESR spectra were found using best approximation method, which minimizes the error function

$$F = \sum_i \left(Y_i^T - Y_t^E\right)^2 / N \quad (2)$$

Here Y_i^E – the array of the observed intensities of ESR signals at different values of magnetic field, Y_i^T – theoretical values of intensities at the same values of magnetic field, N – number of points. Theoretical spectra were plotted according to the previously reported procedure.[19] Line shapes were described using Gaussian and Lorentzian functions.[20] The line widths were parameterized using relaxation theory:[21]

$$\sigma_k = \alpha_k + \beta_k m_I + \gamma_k m_I^2 \quad (3)$$

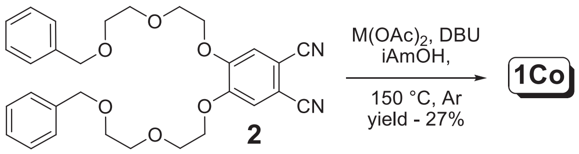
Here m_I – projection of nuclear spin on the magnetic field direction, k=*x, y, z*, α_k, β_k, γ_k – broadening parameters in corresponding orientations. Minimization of error function (Eq. 2) implied variation of g-factors, HFS constants, line widths and shapes.

*Cobalt(II) 2,3,9,10,16,17,23,24-octakis[2'-(2''-benzylethoxy)ethoxy]phthalocyaninate (**1Co**).* The mixture of phthalonitrile **2** (118 mg, 0.23 mmol), $Co(OAc)_2$ (21 mg, 0.12 mmol) and DBU (35 mg, 0.23 mmol) in 3 mL of isoamyl alcohol was refluxed under argon for 24 h. After cooling to room temperature the dark-green reaction mixture was diluted with hexane, the formed precipitate was filtered, the filtrate was discarded and the solid was washed off the filter with chloroform. After column chromatography on neutral alumina (elution with $CHCl_3$+(0–5)vol.% MeOH) followed by size-exclusion chromatography (Bio-Beads S-X1, elution with $CHCl_3$+2.5vol.% MeOH) the complex **1Co** was isolated as a dark-green sticky solid (33 mg, yield 27 %). *m/z* (MALDI-TOF) found 2124.8 $[M]^+$, calculated for $C_{120}H_{128}CoN_8O_{24}$ 2125.0. UV-Vis ($CHCl_3$) λ (lg ε) nm: 297 (4.87), 606 (4.39), 670 (5.04).

Results and Discussion

Synthesis and Spectral Characterization of 1Co

Synthesis of complex **1Co** was performed starting from the previously reported phthalonitrile **2** using its DBU-promoted template condensation in the presence of anhydrous Co(OAc)$_2$ in refluxing isoamyl alcohol (Scheme 1).



Scheme 1.

The synthesized complex was characterized by MALDI-TOF mass-spectrometry and UV-Vis spectroscopy. The presence of paramagnetic Co^{2+} ion in the molecule precluded application of NMR spectroscopy for characterization because of strong broadening and shifting of resonance signals in spectra.

The investigation of concentration-dependent UV-Vis spectra of **1Co** in CHCl$_3$ evidenced that the increase of the complex concentration resulted in decrease of the efficient extinction coefficient (ε_{eff}) with simultaneous broadening of the *Q*-band and its vibrational satellite. For example, lgε_{eff} changed from 5.04 to 4.87 upon increase of $C_{\mathbf{1Co}}$ from $4{\cdot}10^{-6}$ M to $3{\cdot}10^{-4}$ M (Figures 2, 3). This spectral behavior evidenced of phthalocyanine aggregating in solution.[22]

Analysis of nonlinear ranges of plots in Figure 3 was performed using approach, proposed by Mataga,[23] which was widely used for the analysis of phthalocyanine aggregation.[24–26] In accordance with this approach, the solution with total concentration of dissolved chromophore C_0 is characterized by efficient extinction coefficient $\varepsilon_{eff}=Al^{-1}C_0^{-1}$, which is different from extinction of monomeric compound ε_M in the case if the molecules of chromophor are aggregating. Putting n as an aggregation number in the equilibrium $nM \leftrightarrow M_n$ and K as a constant of this equilibrium, the following relation between all these values was proposed:

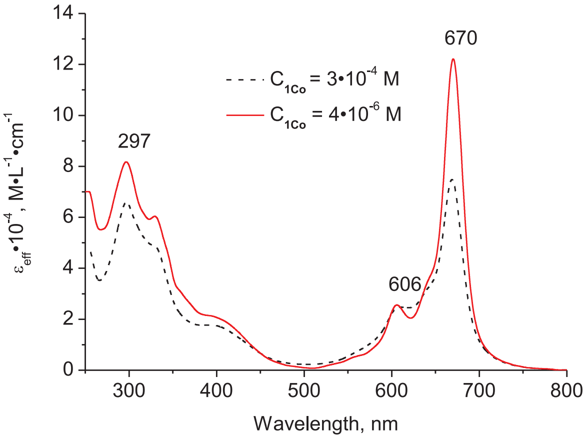


Figure 2. UV-Vis spectra of **1Co** in CHCl$_3$ at different concentrations.

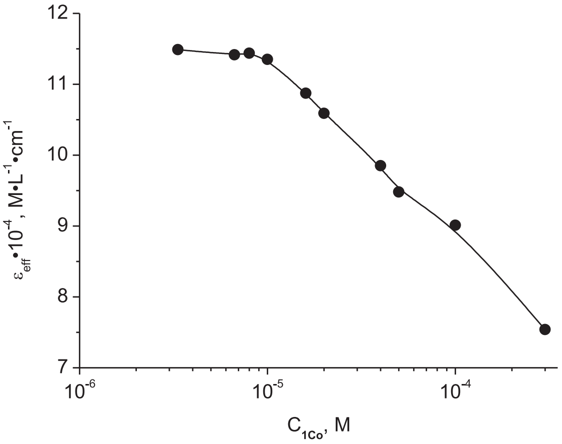


Figure 3. Dependence of efficient extinction coefficient $\varepsilon_{eff}=Al^{-1}C_0^{-1}$ at 670 nm on concentration for **1Co** in CHCl$_3$.

$$lg\left[C_0\cdot\left(1-\frac{\varepsilon_{eff}}{\varepsilon_M}\right)\right]=lg\left(n\cdot K\right)+n\cdot lg\left[C_0\cdot\left(\frac{\varepsilon_{eff}}{\varepsilon_M}\right)\right] \qquad (4)$$

Thus, plotting lg[$C_0(1-\varepsilon_{eff}{\cdot}\varepsilon_M^{-1})$] *vs.* lg[$C_0{\cdot}\varepsilon_{eff}{\cdot}\varepsilon_M^{-1}$] should give a straight line with the slope, equal to n. Indeed, plotting the corresponding values for **1Co** gave linear dependency with the slope n=1.7 (Figure 4), suggesting that mainly dimerization of phthalocyanine molecules occurs upon aggregation.

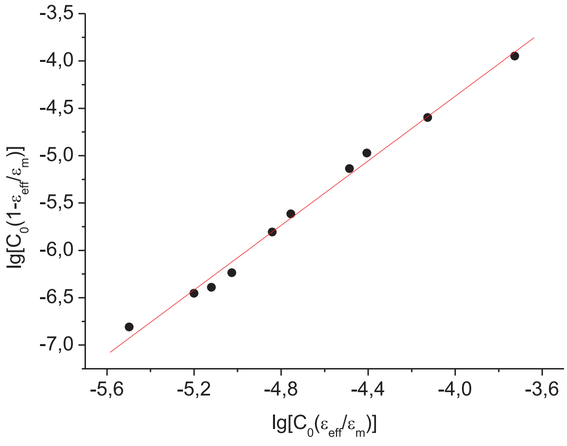


Figure 4. Graphical analysis of ε_{eff} values for determination of aggregation number n in accordance with Eq. (4), obtained for *Q*-band of **1Co** at 670 nm (n=1.70±0.05, R^2=0.993).

The equilibrium between the monomer M and the dimer D is described by the dimerization constant K_d (Eq. 5) and the material balance (Eq. 6):

$$K_d=\frac{[D]}{[M]^2} \qquad (5)$$

$$C_0=[M]+2[D] \qquad (6)$$

These equations can be used to evaluate the equilibrium concentration of the monomer:

$$\left[M\right]=\frac{\sqrt{1+8C_0K_d}-1}{4K_d} \tag{7}$$

The optical density at certain wavelength is an additive value, which is determined by absorptions of both monomer and dimer depending on their equilibrium concentrations and characteristic extinction coefficients. Taking into account the equation of material balance (Eq. 6), it can be expressed in the following way:

$$A=\varepsilon_M\cdot\left[M\right]+\varepsilon_D\cdot\left[D\right]=\left(\varepsilon_M-\frac{\varepsilon_D}{2}\right)\cdot\left[M\right]+\frac{C_0\cdot\varepsilon_D}{2} \tag{8}$$

Combination of Eqs. (7) and (8) gives nonlinear equation (9), which expresses optical density as a function of concentration of dissolved compound. Other terms of this equation, namely equilibrium constant K_d as well as extinction coefficients of monomer and dimer (ε_M and ε_D, respectively) are unknown, but they can be found by nonlinear regression analysis, therefore, we can reveal the UV-Vis spectra of monomer and dimer. Since changes in UV-Vis spectra caused by aggregation depend on mutual arrangement of chromophores within the dimer, its architecture can be proposed.

$$A=\left(\varepsilon_M-\frac{\varepsilon_D}{2}\right)\cdot\frac{\sqrt{1+8C_0K_d}-1}{4K_d}+\frac{C_0\cdot\varepsilon_D}{2} \tag{9}$$

To perform this analysis, we have used the *Q*-band region. The array of UV-Vis data for 35 wavelengths (from 550 to 720 nm with 5 nm step) was chosen. The data was taken for 11 solutions with concentrations in the range of $4\cdot10^{-6}\div3\cdot10^{-4}$ M (altogether 35×11=385 data points). The values of ε_M for 670 nm was fixed at the value of $1.10\cdot10^5$ $\text{L}\cdot\text{M}^{-1}\cdot\text{cm}^{-1}$ and all other parameters were varied until convergence was achieved. The value of found equilibrium constant K_d was $(4.8\pm0.2)\cdot10^3$ M^{-1}. The calculated UV-Vis spectra of both monomer and dimer are given in Figure 5. In accordance with the excitonic model of chromophore interaction, the blue-shifted maximum of the aggregate *Q*-band suggests significant overlap of stacked phthalocyanine π-systems (H-dimer).[27]

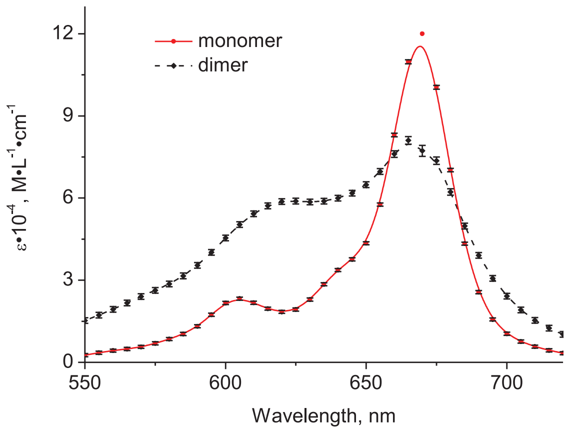


Figure 5. Calculated UV-Vis spectra of monomeric and dimeric forms of **1Co** in CHCl_3.

Studies of Interaction between **1Co** and $\mathbf{C_{70}}$

The interaction of $\mathbf{C_{70}}$ with the **1Co** was studied by UV-Vis titration of its solution in CHCl_3 with the solution of fullerene in toluene. This titration did not result in any notable shift of the Pcs *Q*-band (Figure 6) suggesting the absence of significant ground state interaction between molecular orbitals of **1Co** and $\mathbf{C_{70}}$.

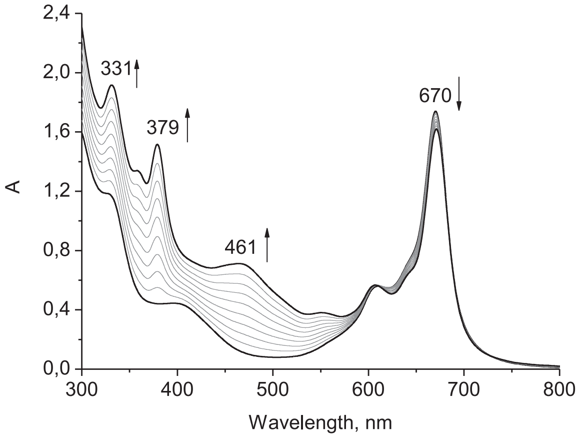


Figure 6. Spectrophotometric titration of solution of **1Co** in CHCl_3 ($C_{\text{1Co}}=1.5\cdot10^{-5}$ M) with the solution of $\mathbf{C_{70}}$ in toluene ($C_{\text{C70}}=8.9\cdot10^{-4}$ M). Each step corresponds to addition of 0.2 equivalents of fullerene.

The interaction of **1Co** with $\mathbf{C_{70}}$ could be studied by ESR due to the presence of one unpaired electron in low-spin Co^{2+} ion. Figure 7 shows the spectrum of **1Co** solution in CHCl_3 deoxygenated by repeated freeze-pump-thaw cycles. The complex was ESR silent at room temperature; therefore, its spectrum was measured at 100 K.

The components of hyperfine splitting are superimposed with the broad band, which cannot be compensated by the correction of the baseline. We suppose that this line originates from the aggregation of **1Co** in the solution at the applied concentration (~10^{-3} M), which is needed for acquisition of informative spectrum. Moreover, we expected that the spectrum would have axial symmetry; however, good match between the experimental and calculated spectra could be obtained only in rhombic approximation. This might be due to some deformation of the macrocycle because of the flexibility of bulky substituents.[28] The ESR spectrum of **1Co** reveals well resolved hyperfine structure containing eight lines in parallel orientation of *g*-tensor and poorly resolved structure in perpendicular orientation, which arises from magnetic interaction between unpaired electron spin and nuclear spin (I=7/2) of Co^{2+} ion. The spin Hamiltonian parameters are listed in Table 1.

To show the sensitivity of ESR spectra of **1Co** to rearrangement of spin density, we have also measured ESR spectrum of **1Co** in aerobic conditions. To enhance interaction of **1Co** with molecular oxygen pyridine was added to the sample which coordinates to cobalt ion in *trans*-position to O_2 molecule.[29,30] The appearance of spectrum is given in Figure 8, and the spin Hamiltonian parameters of the resulting spectrum are given in the Table 1. These

Table 1. Parameters of spin Hamiltonian for the cobalt phthalocyaninates **1Co** and its adducts with fullerene **C_{70}** and molecular oxygen.

	g_z	g_x	g_y	A, ×10^3 cm^{-1}	B, ×10^3 cm^{-1}	C, ×10^3 cm^{-1}
1Co	1.991	2.119	2.390	11.41	4.10	6.58
1Co•O_2	1.991	2.065	2.008	0.76	1.61	1.02
1Co•C_{70}	1.986	2.118	2.388	11.34	4.15	6.60

parameters evidence that in the formed adduct of **1Co** with molecular oxygen almost 80 % of spin density is localized on the dioxygen group and it can be formally described as **PcCo(III)O_2^-**. This experiment evidences of high sensitivity of low-spin cobalt complex with one electron at d_{z^2} orbital to addition of molecules with uncompensated spin density.

Finally, Figure 9 shows ESR spectrum of **1Co** in the presence of fullerene **C_{70}** measured under anaerobic conditions. The parameters of spin Hamiltonian of **1Co•C_{70}** are similar to those of starting **1Co** (Table 1), however, the HFS lines in parallel orientation of *g*-tensor almost vanish. The significant broadening of lines in parallel orientation is characterized by α, β and γ values, which are found by computational modeling. They are assigned to relaxation behavior of systems – rotations, vibrations, *etc.* In the case of **1Co** these values are equal to α_z=25.12 G, β_z=2.18 G, γ_z=3.11 G, while in the case of **1Co•C_{70}** these values are equal to α_z=46.18 G, β_z=5.01 G, γ_z=3.82 G. Upon formation of the complex with fullerene, the most notable change is observed in the case of α_z term, which characterizes the rate of molecular rotation. Therefore, it can be concluded that **1Co** interacts with **C_{70}** *via* dipole-dipole interactions significant additional delocalization of spin density, which is in line with the previous studies,[31] although further theoretical work is required for complete description of CoPc-C_{70} interaction which might also include σ-donor and π-acceptor interactions between the fullerene and the CoPc unit. Such type of interaction was proposed previously to describe properties of the covalent CoPor-C_{60} diad.[32]

Conclusions

In the present work, we have synthesized and investigated novel octopus-like cobalt(II) phthalocyaninate **1Co**, studied its aggregation in solution by concentration-dependent UV-Vis spectroscopy and investigated interaction between **1Co** with **C_{70}** by ESR spectroscopy.

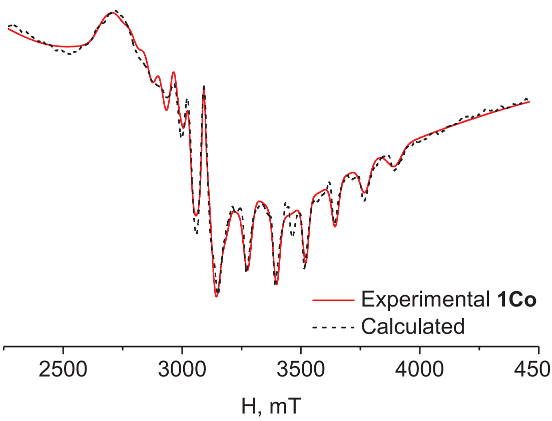


Figure 7. Experimental (solid line) and calculated (dashed line) ESR spectra of **1Co** in deoxygenated $CHCl_3$ at 100 K.

We have shown the absence of notable coupling between electronic systems of Co(II) complex and fullerene, their interaction occurs *via* noncovalent dipole-dipole interactions, which manifests in changes of line shapes in ESR spectra without significant alteration of spin Hamiltonian parameters.

Previous theoretical studies of complexes of CoPc with fullerene suggest that such assemblies can act as bidirectional switches with tuneable direction of electron transport which can be achieved by oxidation of reduction of CoPc molecules.[33] Our study proposes the approach to con-

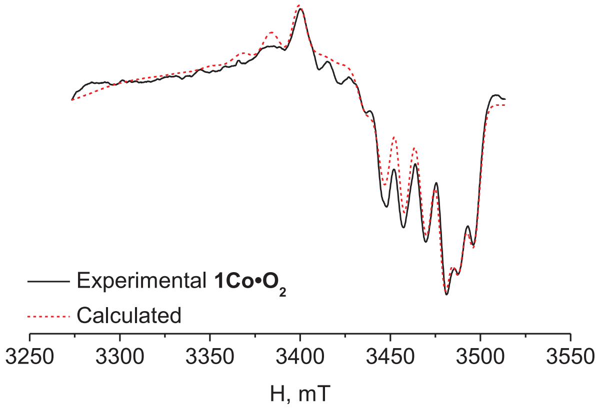


Figure 8. Experimental (solid line) and calculated (dashed line) ESR spectra of **1Co** in the mixture of $CHCl_3$ and pyridine (1:1 vol.) in the presence of air at 100 K.

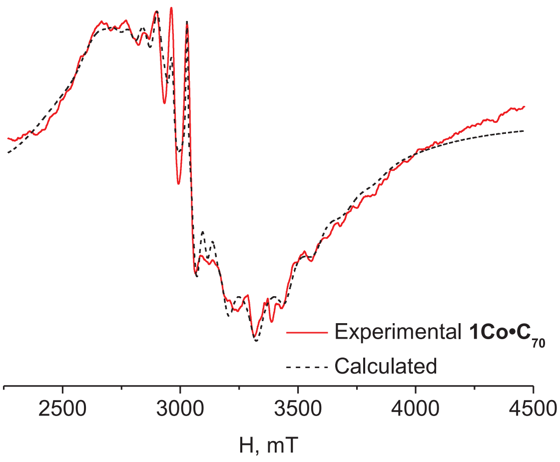


Figure 9. Experimental (solid line) and calculated (dashed line) ESR spectra of **1Co** in deoxygenated $CHCl_3$ after addition of excess of **C_{70}** in toluene at 100 K.

struction of such assemblies suggesting the perspectives of further development of octopus-like phthalocyanines and studies of their receptor properties.

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