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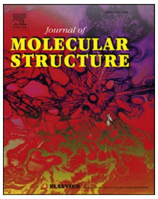

Hybrid multi-porphyrin supramolecular assemblies: Synthesis and structure elucidation by 2D DOSY NMR studies

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ABSTRACT

Design and synthesis of hybrid multi-metalloporphyrin assembles have been performed. The chemical structure of the synthesized complexes and their stability in solution were confirmed by the methods of 2D DOSY NMR spectroscopy, which have been specially adapted for these supramolecular architectures in solutions.

Tin(IV)-porphyrins are ideal scaffolds for the construction of axially bonded multi-porphyrin supramolecular assemblies. In the literature there are described multi-porphyrin arrays, in which porphyrin moieties of different nature are axially coordinated from both sides of the tin(IV)-porphyrin core [1–8] and multi-porphyrin supramolecular assemblies in which the porphyrin macrocycles are linked to the tin(IV)-porphyrin through polyfunctional organic ligands [9–12].

In continuation of our studies in the field of supramolecular chemistry of porphyrins [7,8,13–19], in this work synthesis and NMR studies of Ru(II) tetraphenylporphyrin [RuP(CO) (I)] and complexes of I and Sn(IV)porphyrin [$SnP(OH)_2$ (II)] with 3-hydroxypyridine [L] with one $SnP(L)_2$ (III)] and two [$SnP(OH)_2$-4RuP(CO) (IV), $SnP(L)_2$-6RuP(CO) (V)] centers of binding were carried out. Complexes (IV) and (V) were investigated by 2D NMR spectroscopy.

It was found that due to peculiarities of the chemical structure and to the low concentration of the complex in solution studies by 1H NMR, 2D 1H-1H ROESY, 2D 1H-1H COSY for this system are not sufficiently informative. In addition, the interpretation of results is complicated by the fact that NMR signals in the spectra of the molecules at the same time depend on two factors: a change in the shielding and a variation of the electron density distribution upon complex formation. Thus questions about the size and stability of the complexes formed remains open. Therefore, to obtain direct evidence of the fact of complex formation and information about their size, other approaches should be used.

We have applied an approach to elucidate the structures for complex that is based on the analysis of two-dimensional diffusion high-resolution spectroscopy (2D DOSY).

1. Experimental

1.1. Preparation of Ru(II)-[5,10,15,20-tetrakis(phenyl)porphyrin]

[$RuP(CO)(H_2O)$, I, Fig. 1] was obtained from 5,10,15,20-tetrakis(phenyl)porphyrin according with [6]. $R_f = 0.67$ (eluent: chloroform). UV–Vis (benzene, nm): λ_{max} (log ε) 411 (5.21), 490 (3.66), 529 (4.30). IR (KBr, cm^{-1}): ν_{CO} 1948. FAB Mass Spectrum: [m/z (rel. intens. %)]: 743.5 (79) (calc. 742.4). Anal. Calcd. for $C_{45}H_{32}N_4O_2Ru$: C, 66.09; H,3.92; N, 6.85. Found: C, 66.01; H, 3.89; N, 6.81.

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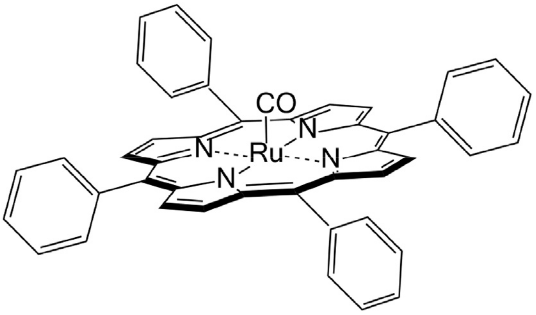

Fig. 1. Structure of the RuP(CO) (I).

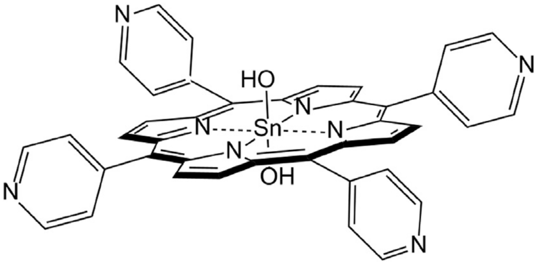

Fig. 2. Structure of the $SnP(OH)_2$ (II).

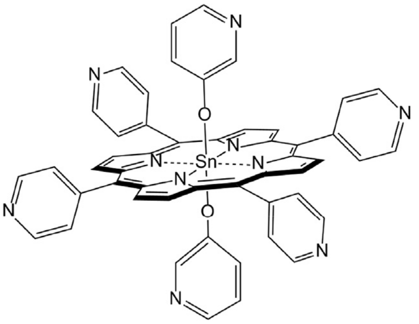

Fig. 3. Structure of the $SnP(L)_2$ (III).

1.2. *Preparation of Sn(IV)-Trans-Dihydroxy-[5,10,15,20-tetrakis(4-pyridyl)porphyrin]*

[$SnP(OH)_2$, II, Fig. 2] was obtained from *Sn(IV)-Trans*-dichloro [5,10,15,20-tetrakis(4-pyridyl)porphyrin] [$SnP(Cl)_2$] according with [13]. $R_f = 0.43$ (eluent: chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 9.12 (8H, d., CH $_{pyr.}$), 9.11 (8H, d., Ar-H_{ortho}), 8.30 (8H, d., Ar-H_{meta}), −6.06 (2H, s., OH). IR (KBr, cm^{-1}) ν_{OH} 3587; UV–Vis (benzene, nm): λ_{max} (log ε) 424 (4.93), 524 (3.34), 561 (3.78), 600 (3.59). FAB Mass Spectrum: [m/z (rel. intens. %)]: 751.2 (85) (calc. 750.1). Anal. Calcd. for $C_{40}H_{26}N_8O_2Sn\cdot 2H_2O$: C, 59.64; H.3.75; N, 13.91. Found: C, 59.28; H, 3.67; N, 13.59.

1.3. *Preparation of Sn(IV)-Trans-Di(3-oxypyridine)-[5,10,15,20-tetrakis(4-pyridyl)porphyrin]*

[$SnP(L)_2$, III, Fig. 3] was obtained by 1 h refluxing of $SnP(OH)_2$ (75 mg, 0.1 mmol) with 3-hydroxypyridine (24 mg, 0.25 mmol) in benzene. Yield: 85 mg (90%). $R_f = 0.54$ (eluent: chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 9.11 (8H, d., CH $_{pyr.}$), 9.09 (8H, d., Ar-H_{ortho}), 8.29 (8H, d., Ar-H_{meta}), 7.05 (2H, d., L-H), 5.45 (2H, t., L-H), 3.08 (2H, t., L-H), 2.13 (2H, s., L-H). UV–Vis (benzene, nm): λ_{max} (log ε) 426 (4.90), 526 (3.32), 563 (3.77), 602 (3.57). FAB Mass Spectrum: [m/z (rel. intens. %)]: 923.2 (67) (calc. 922.1). Anal. Calcd. (%) for $C_{50}H_{32}N_{10}O_2Sn$: C, 65.05; H,3.47; N, 15.17. Found: C, 64.81; H, 3.45; N, 15.09.

1.4. *Preparation of hybrid porphyrin pentamer (IV)*

[$SnP(OH)_2$-4RuP(CO), IV, Fig. 4] was obtained by 1 h stirring of RuP(CO) (I) with $SnP(OH)_2$ (II) in benzene in molar ratio of 4:1.

The solvent was evaporated, the resulting dark red residue was dissolved in 5 mL of $CHCl_3$ and subjected to chromatography on a silica gel column (eluent: $CHCl_3$-acetone (3:1) v/v). $R_f = 0.67$ (eluent: chloroform-acetone, 3:1). Yield: 82 mg (90%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.61 (32H, s, CH pyr.(Ru, eq.)), 8.22 (16H, d., Ar-ortho(Ru)), 7.91 (16H, d., Ar-ortho(Ru)), 7.69 (16H, t., Ar-meta(Ru)), 7.73 (16H, t., Ar-meta(Ru)), 7.64 (16H, t., Ar-para(Ru)), 6.98 (8H, s, CH pyr.(Sn)), 5.58 (8H, d., Ar-ortho(Sn)), 1.73 (8H, d., Ar-

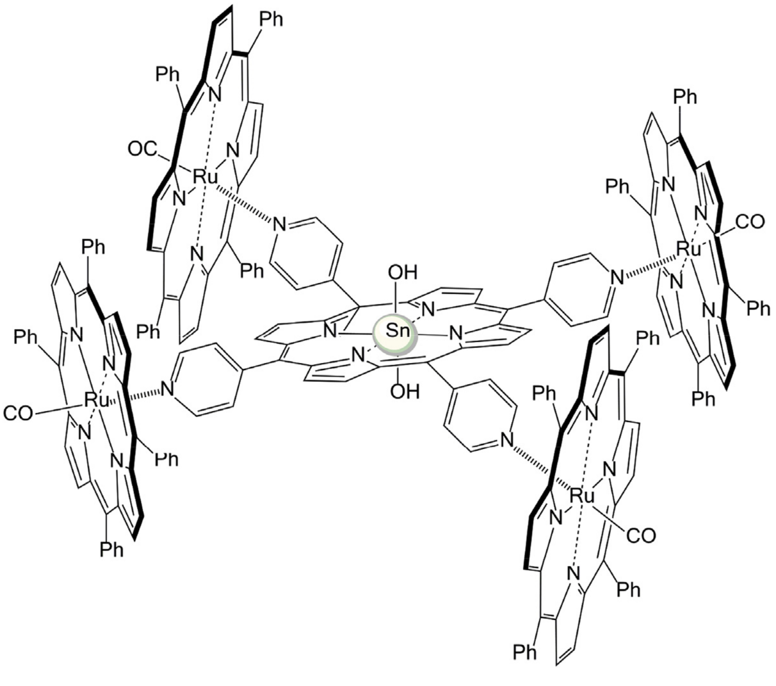

Fig. 4. Structure of the $SnP(OH)_2$-4RuP(CO) (IV).

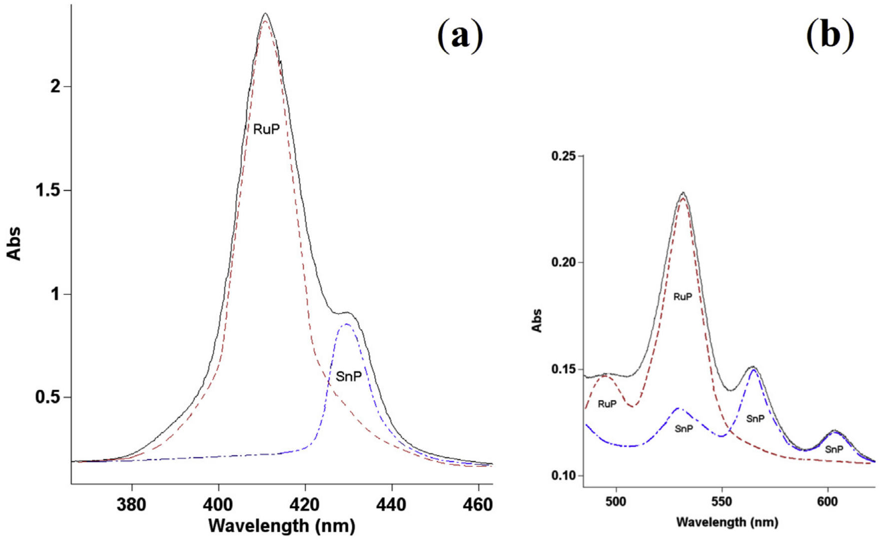

Fig. 5. UV–Vis spectra of (IV) in benzene in the Soret band (a) and visible (b) regions.

meta(Sn)), −6.09 (2H, s., OH). UV–Vis (benzene, nm, Fig. 5): λ_{max} (log ε) 411 (5.21) 429 (4.43), 429 (3.56) 532 (4.12), 564 (3.58), 603 (3.19). Anal. Calcd. for $C_{220}H_{154}N_{24}O_6SnRu_4$: C, 70.44; H, 4.10; N, 8.96. Found: C, 70.28; H, 4.07; N, 8.82.

1.5. Preparation of hybrid porphyrin heptamer (V)

[SnP(L)$_2$-6RuP(CO), V, Fig. 6] was obtained by 1 h stirring of SnP(L)$_2$ (III) with RuP(CO) (I) in benzene in molar ratio of 1:6. The solvent was evaporated, the resulting dark red residue, dissolved in 5 mL of $CHCl_3$ and subjected to chromatography on a silica gel column (eluent - $CHCl_3$-acetone (3:2) v/v). $R_f = 0.54$ (eluent: chloroform-acetone, 3:2). Yield: 76 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70–8.60 (48H, m., CH pyr.(Ru, eq.) + pyr.(Ru, ax.)), 8.30 (24H, m., Ar-ortho(Ru)), 8.03 (24H, m., Ar-ortho(Ru)), 7.70 (48H, m., Ar-meta(Ru)), 7.57 (24H, t., Ar-para(Ru)), 7.27 (8H, s, CH pyr.(Sn)), 6.30 (2H, d., L-H), 5.66 (8H, d., Ar-ortho(Sn)), 5.61 (2H, d., L-H), 4.9 (2H, t., L-H), 1.81 (8H, d., Ar-meta(Sn)), 1.54 (2H, s., L-H). UV–Vis (benzene, nm, Fig. 7): λ_{max} (log ε) 411 (5.25) 429 (4.35), 429 (3.62) 532 (4.29), 564 (3.47), 603 (3.12). Anal. Calcd. for $C_{320}H_{230}N_{34}O_8SnRu_6$: C, 71.17; H, 4.26; N, 8.81. Found: C, 71.12; H, 4.23; N, 8.99.

2. Spectroscopy

5,10,15,20-tetrakis(4-pyridyl)porphyrin, *trans*-dichloro

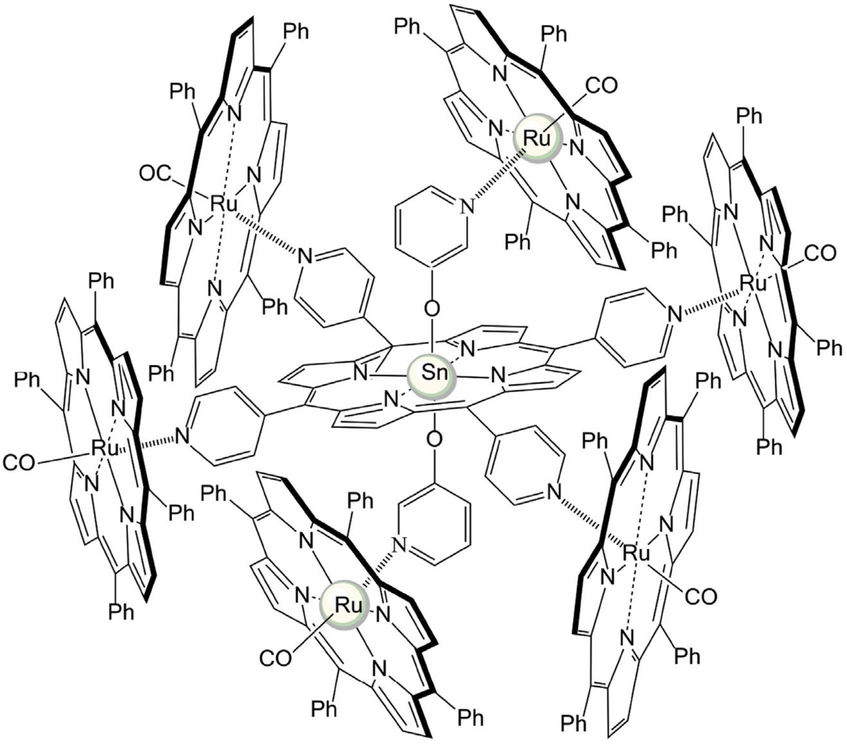

Fig. 6. Structure of the SnP(L)$_2$-6RuP(CO) (V).

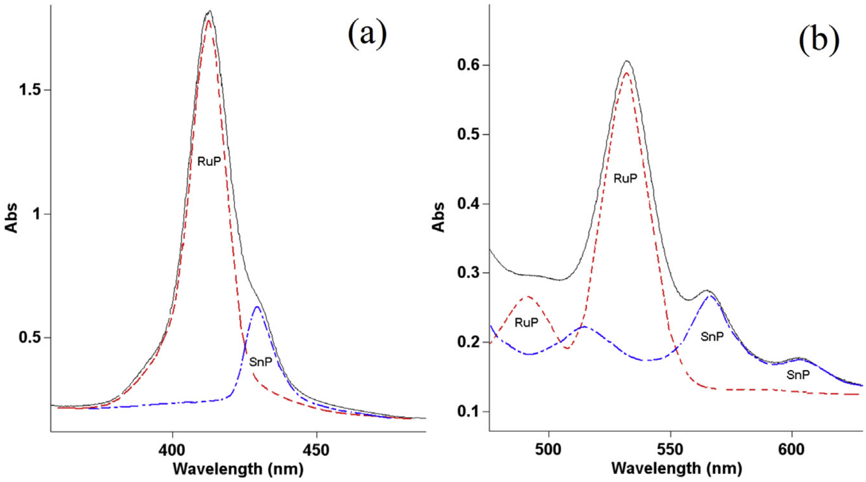

Fig. 7. UV–Vis spectra of (V) in benzene in the Soret band (a) and visible (b) regions.

[5,10,15,20-tetrakis(4-pyridyl)porphyrin, 3-hydroxypyridine and solvents from Sigma–Aldrich were used without further purification. The reactions course was controlled by the results of a TLC on UV-254 Silufol plates. The individual compounds were isolated by column chromatography on a silica gel column with chloroform-acetone mixture as eluent. UV–Vis spectra of the porphyrins were measured on a Varian spectrophotometer Cary 100. FAB Mass Spectra were measured on a MX-1310 spectrometer at the energy of electrons ionization 70 eV and ionization cell temperature 150–200 °C. The IR spectra were recorded on an Avatar 360-FT-IR-ESP in KBr pellets. Elemental analysis was carried out on a Flash EA 1112 analyser.

All NMR experiments were performed on a Bruker Avance III-500 NMR spectrometer equipped with a 5 mm probe using standard Bruker TOPSPIN Software. Temperature control was performed using a Bruker variable temperature unit (BVT-2000) in combination with a Bruker cooling unit (BCU-05) to provide chilled air. Experiments were performed at 298 K without sample spinning.

^{1}H NMR (500 MHz) spectra were recorded using 90° pulses and

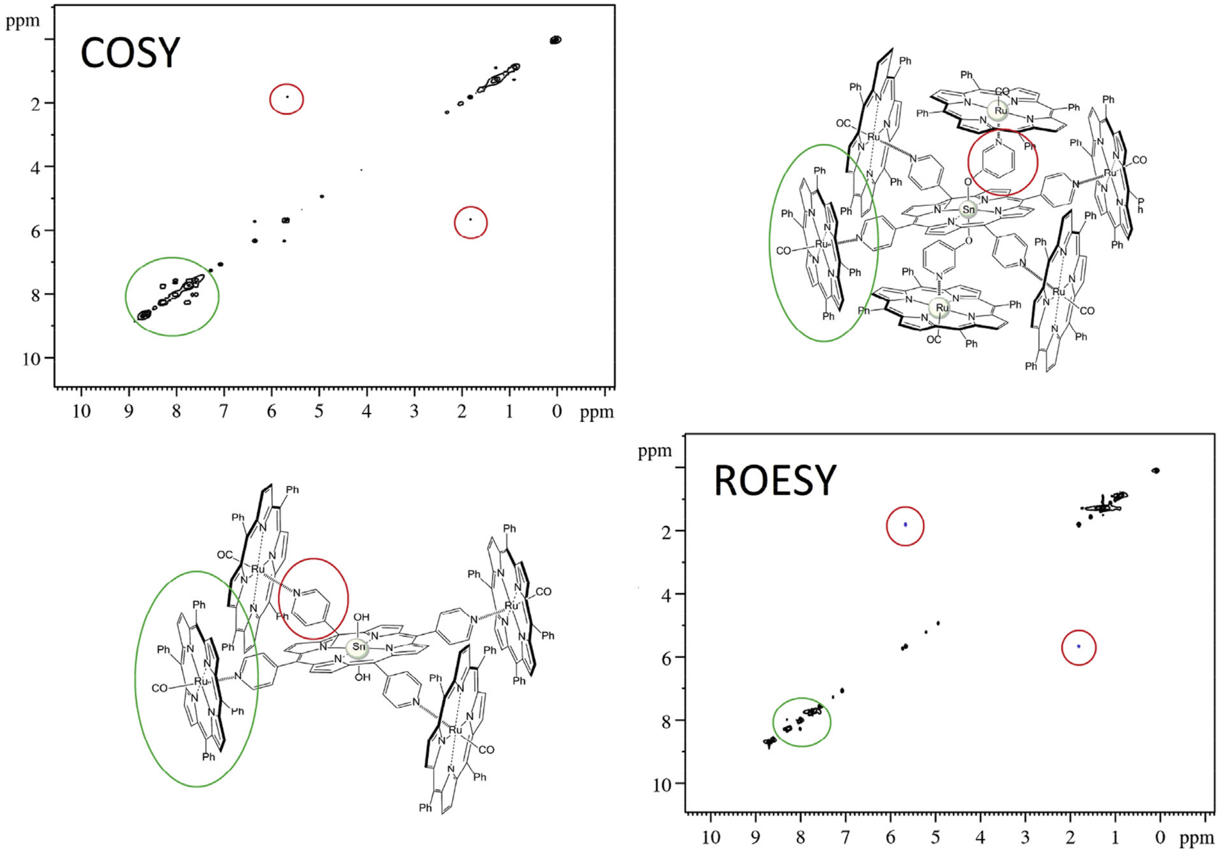

Fig. 8. ^{1}H-^{1}H 2D COSY and ^{1}H-^{1}H 2D ROESY NMR spectra of the complex (IV) and (V) in chloroform.

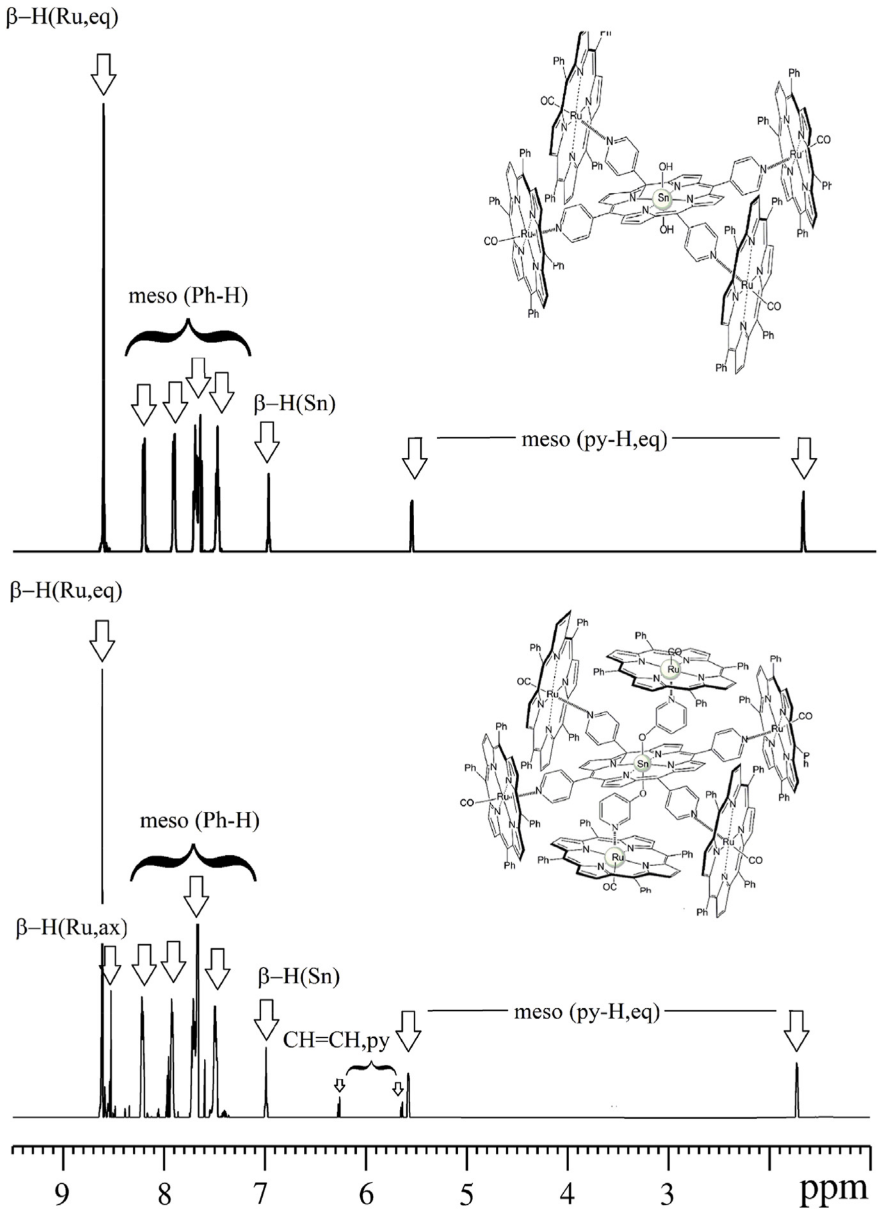

Fig. 9. 1D sections from 2D DOSY spectra of the complexes (IV) and (V) in chloroform corresponding to characteristic self-diffusion coefficients for these complexes.

relaxation delay of 1 s; spectral width was 19.13 ppm; 128 scans were acquired. Proton NMR is relative to deuterium solvent peaks.

The two-dimension Diffusion Order Spectroscopy (2D DOSY) spectra were recorded with PGSTE pulse sequence using a bipolar gradient pulses and the insertion of a supplementary delay (LED) [20]. The PGSTE sequence was used with a diffusion delay of 0.1 s, a total diffusion-encoding pulse width of 5 ms. For each of 32 gradient amplitudes, 64 transients of 16384 complex data points were acquired.

3. Results and discussion

Absorption spectra of the pentamer (see, Fig. 5) and heptamer (see, Fig. 7) obtained in benzene solution over the range 300–700 nm are the sum of the individual components indicating little or no molecular interaction between the porphyrin units in the ground state, consistent with the results obtained on the same systems [21]. Chemical shift differences between pentamer and heptamer in $CDCl_3$ are shown in Fig. 9 and the availability of β-pyrrolic for axial hydrogens (β-H(Ru,ax)) provide evidence for the complex formation (Fig. 10).

Both chemical (COSY) and through-space correlations (ROESY), which were experimentally observed only for the substrate of 3-hydroxypyridine (red circle in Fig. 8) and for meso-protons of porphyrins (green circle in Fig. 8), give no direct evidence for the existence of the complex. Because of the symmetry of the complex (IV) we observed similar spectra for (V). The ROESY measurements allowed us to assign the individual proton signals and to determine through-space interactions specific to the hybrid multi-porphyrin supramolecular assemblies. Difference between characteristic peaks at $\delta = 8.61$ ppm, $\delta = 8.52$ ppm corresponding to the β-pyrrolic protons on β-H(Ru,eq) and β-H(Ru,ax) porphyrins, respectively (Fig. 9), is small and hampers interpretation of the ROESY and COSY spectra. All cross-peaks obtained in the ROESY and COSY experiments are intra-component peaks showing a correlation between β-pyrrolic protons and ortho meso-pyridyl(meso(Ph-H) in

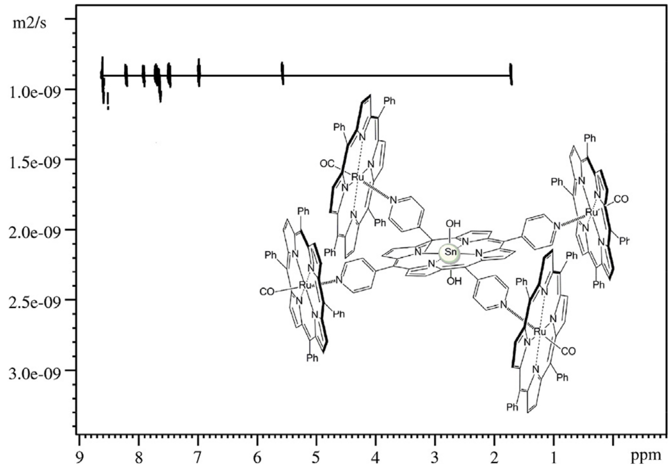

Fig. 10. ^{1}H 2D DOSY NMR spectrum of the complex (IV) in chloroform.

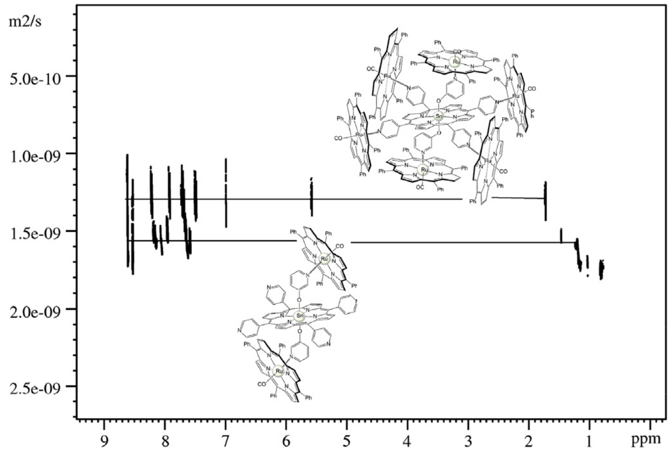

Fig. 11. 2D DOSY NMR spectrum of the complex (V) in chloroform.

Fig. 9) protons within the same porphyrin (green circle in Fig. 8). Cross-peaks indicated by the red circle (Fig. 8) show a correlation only between meso-protons (meso(py-H,eq)) within the same pyridine fragment.

As previously reported [13,14,22–25] 2D DOSY NMR has proven to be an extremely powerful tool to observe self-assembled porphyrin systems in solution that were difficult to characterize by traditional spectroscopic techniques [26–28].

Self-diffusion coefficients differ significantly depending on the molecular size. For further analysis of these data, it was necessary to clarify the relationship between the molecular weight ($M_{i,j}$) and the self-diffusion coefficients of the complex ($D_{i,j}$). Shapes of molecular components affect this relationship, which complicates the numerical analysis of the data. In this case, extended shape of the complex for the studied compounds can be expected. However, taking into account the fact that the ratio of the self-diffusion coefficients of two spherical-shape particles is inversely proportional to the cube root of the ratio of their molecular masses, and in the case of elongated shape, to the square root, the following relationship was used for estimating the molecular weight of the complexes [29]:

$$\sqrt[3]{\frac{M_j}{M_i}} \le \frac{D_i}{D_j} \le \sqrt{\frac{M_j}{M_i}} \qquad (1)$$

Using this simple relation, the calculation of limits of experimental diffusion coefficients is straightforward. Thus, the ratio of the self-diffusion coefficients of complexes (IV) and (V) should lie within the range from 0.833 to 0.886. In order to determine the values of self-diffusion coefficients D_i and D_j from an experiment on a quantitative level, viscosity of the solvent should be taken into account. It follows from the Stokes–Einstein equation $D = k_BT/(6\pi\eta r_H)$ (where T is the absolute temperature, k_B is the Boltzmann constant, r_H is the hydrodynamic radius of the solute, and η is the viscosity of the solvent) that the ratio of the self-diffusion coefficients of a complex ($D_\mathrm{i,j}^\mathrm{complex}$) and the reference compound ($D_\mathrm{i,j}^\mathrm{ref}$) is independent of the viscosity: $D_\mathrm{i,j} = D_\mathrm{i,j}^\mathrm{complex}/D_\mathrm{i,j}^\mathrm{ref}$. In our experiment chloroform was used as an internal diffusion reference because its molecules presumably do not take part in H-bonding (standard such as TMS may also be used for this purpose) [30]. Thus, ratio $D_\mathrm{i}/D_\mathrm{j}$ for the pentamer ($D_\mathrm{i}^\mathrm{IV} = 0.86 \times 10^{-9}$ m^2/s, $D_\mathrm{i}^\mathrm{ref} = 3.64 \times 10^{-9}$ m^2/s) and the heptamer ($D_\mathrm{j}^\mathrm{IV} = 1.05 \times 10^{-9}$ m^2/s, $D_\mathrm{j}^\mathrm{ref} = 3.89 \times 10^{-9}$ m^2/s) can be calculated as follows: $D_\mathrm{i}/D_\mathrm{j} = (0.86/3.64)/(1.05/3.89) = 0.875$ $\approx$0.88. The experimental value of the ratio of the self-diffusion coefficients is 0.88, which agrees quite well with the theoretical prediction and proves the formation of the complex. It is also evident from Fig. 11 that an intermediate component is present in solution. The trimers are formed upon a partial decomposition of the heptamer due to its low stability. In turn, when the triads bind the ligand molecules, their transformation back to the heptamer occurs. This is a dynamical process, and the balance is strongly shifted towards formation of the heptamer. In addition, we calculated diffusion coefficients for triads and their values (0.76) were in the expected range 0.669–0.765. The ratio of the self-diffusion coefficient of the intermediate component to that of (V) also corresponds well to their molecular weights according to Eq. (1), which gives another evidence for the proposed complex structure.

Thus, the chemical structure of the synthesized complexes and their stability in solution are confirmed by modern methods of two-dimensional NMR spectroscopy, which have been specially adapted for the solution of such problems. We believe that our proposed approach can be used for unambiguous proof of the chemical structure of this class of compounds.

Acknowledgements

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