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УДК 546.824

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ASSESSING OF THE MIXED-VALENCE STATES IN ZINC MESO-FERROCENYLPORPHYRIN: EXPERIMENTAL AND THEORETICAL DATA

The formation of the stable at room temperature mixed-valence state in the zinc 5,10,15,20-tetra(ferrocenyl)porphyrin has been investigated by UV-VIS-NIR, Mössbauer, NMR, electrochemical, and theoretical (DFT) methods. On the basis of experimental and theoretical data it has been concluded that the first oxidation process involves

three-electron oxidation and thus, the long-range metal–metal coupling can be observed not only for the systems with rotationally hindered ferrocene substituents, but also for the porphyrins with the free rotation of the ferrocene moieties.

Multinuclear-containing compounds with strong long-range metal–metal coupling represent an important class of metallocomplexes. These molecules are interesting both from the fundamental (multiredox processes, magnetic coupling, and unpaired electron density migration) and from practical (opto-electronic materials for application in high-speed photonic or redox devices) point of view [1]. Polyferrocenyl-containing molecules are among the best candidates for the multimetal redox active groups because of their well-known metal–metal coupling properties and thermal stability [2—5]. The formation of mixed-valence complexes in bisferrocenes was discovered a long time ago and the influence of different factors on the formation and stability of mixed-valence states has been intensively investigated [6—14]. However, in spite of the large progress in understanding of different factors, which are playing dominant role in the metal-metal coupling process, such as the type of connection, length of connector, and orientation of ferrocenyl units, useful molecular devices have not been prepared yet. The outstanding thermal and chemical stabilities as well as the possibility to tune macrocyclic redox potentials make porphyrins and related compounds the best candidates for the ligand, which can connect several redox-active metallocenters, in particular ferrocenes [15, 16]. It is commonly accepted that the iron centers should be located at a distance of less than 5.4 Å for the effective oxidation metal–metal coupling between the ferrocene units in the same molecule [1—4]. Kadish showed that the metal–metal coupling between two ferrocenyl substituents could be achieved when these groups are axially coordinated to germanium porphyrins [17, 18]. Recently, Barrell et al. have shown a rare example of pure atropisomer formation for the α,α-5,15-bis(ferrocenyl)-28,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin, which demonstrated a long-range (>10 Å) metal–metal coupling between two ferrocenyl substituents [19]. The same long-range metal–metal coupling and macrocycle metal dependence have been later observed for the ethyl analog of Barrell's porphyrin [20]. Both authors reasonably concluded that the possible reason of the observed long-range metal–metal interactions in the investigated porphyrins is the rotational hindrance of ferrocenyl groups. The first meso-tetraferrocenylporphyrins were described in 1977 [21]. In spite of the low purity of the reported compounds, the forma-

tion of mixed-valence derivatives was clearly documented. The synthesis of pure meso-tetraferrocenyl porphyrin and its metal complexes, however, has not been published until recently and allows us to obtain these complexes in relatively high yield and purity [22]. However, as has been reported by some of us and very recently by other authors, the purity of published in 1977 free-base 5,10,15,20-tetra(ferrocenyl)porphyrin and respective copper complex, based on reported spectra, is very low. This fact stimulated us to reinvestigate the free-base 5,10,15,20-tetra(ferrocenyl)porphyrin and new zinc 5,10,15,20-tetra(ferrocenyl)porphyrin complex in order to confirm the hypothesis concerning important role of the steric fixation of ferrocenyl moieties in the long-range metal–metal coupling in these compounds, and the results for the zinc complex are presented in this paper.

Synthesis and characterization of TFcPZn complex. Following Lindsey procedure for synthesis of meso-substituted porphyrins, the room temperature reaction between pyrrole and ferrocenecarbaldehyde leads to formation of porphyrinogen, which is readily oxidized by chloranil with the formation of desired TFcPH$_2$ complex with a 40 % yield. Free-base porphy-
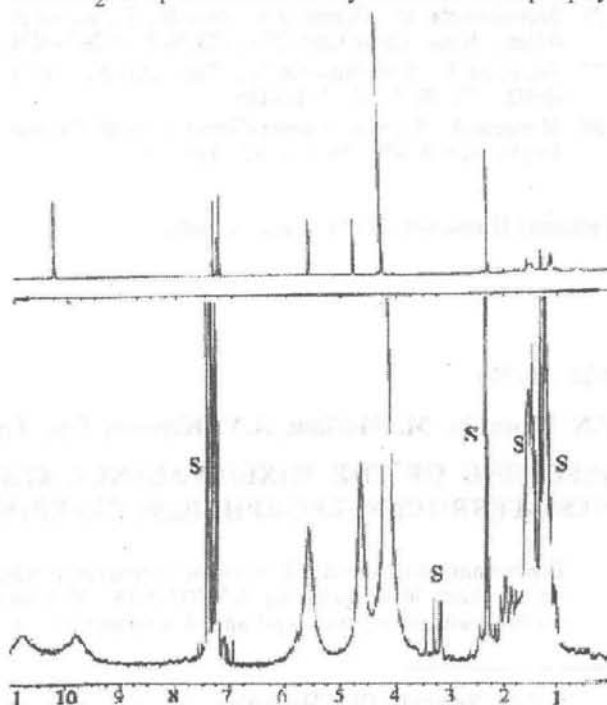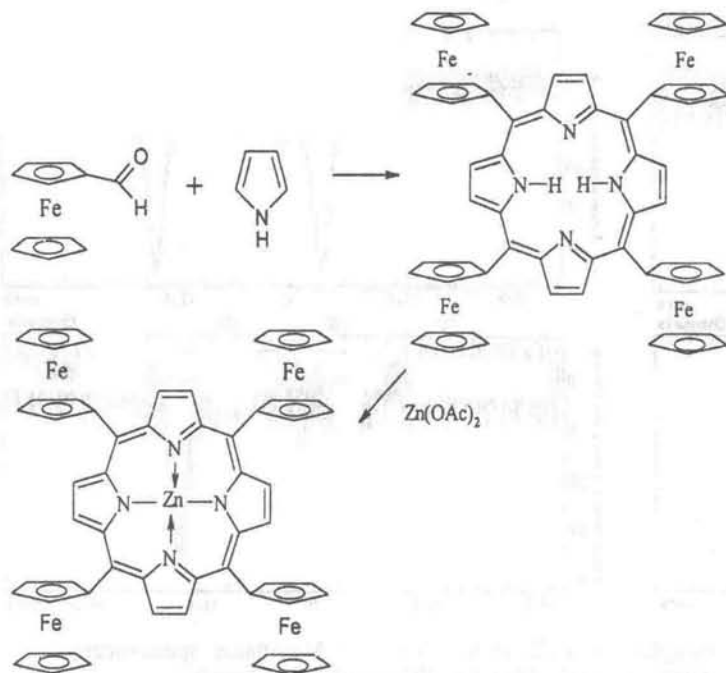

Fig. 1. Room-temperature (top) and low-temperature (210 K, bottom) ^{1}H NMR spectra of TFcPZn complex.

Scheme (reaction of ferrocenecarbaldehyde + pyrrole → TFcPH₂ → TFcPZn with Zn(OAc)₂)

rin can be easily converted to the TFcPZn complex by the reaction with zinc acetate at 80 °C in benzene (scheme). In the ¹H NMR spectra of TFcPZn complex, three clear peaks corresponding to the protons in α-Cp (5.37 ppm, Cp ring A), β-Cp (4.80 ppm, Cp ring A), and Cp-H (4.07, Cp ring B) positions have been observed along with β-pyrrolic protons, they show clear narrow peak at 9.84 ppm (fig. 1). As was shown recently [19], the rotation of ferrocenyl moieties in a free-base α,α-5,15-bis-(ferrocenyl)-2,8, 12,18-tetrabutyl-3,7,13,17-tetramethyl-porphyrin and its nickel complex is strictly limited because of the steric interaction between ferrocenyl moieties and alkyl chains attached to β-pyrrolic carbon atoms of porphyrin core. On the other hand, the variable-temperature ¹H NMR spectra of TFcPZn complex clearly indicate a free rotation of ferrocenyl moieties at room temperature. Thus, as can be expected, the initial sharp room-temperature signal of β-pyrrolic protons, located at 9.84 ppm for TFcPZn complex, splits into two broad singlets at 210 K with integral ratio of 1:1 (fig. 1). It is possible to estimate the rotational barriers for the ferrocenyl moieties in the TFcPZn complex from these spectral data using coalescent point temperature standard procedures. The activation energy ($\Delta G^{\neq}$) for the observed dynamic process was estimated to be 11.7 kcal/mol for the rotation of the ferrocenyl moieties in TFcPZn complex.

The UV-VIS spectrum of TFcPZn complex consists of a Soret band at 435 nm with a small shoulder at ca 490 nm and Q-band at 679 nm with a shoulder at 618 nm (fig. 2). In general, the Soret and Q-bands in TFcPZn complex are significantly red-shifted as compared to zinc meso-tetraphenylporphyrin (TPPZn), revealing strong electronic coupling between the porphyrin π-system and the ferrocenyl moieties [16]. The Mössbauer spectrum of neutral TFcPZn complex is shown in fig. 3 with the parameters presented in table, clearly supporting the presence of only Fe^{2+} centers in the molecule [3, 4, 23]. The isomer shifts and quadrupole splitting in TFcPZn complex are close to those of ferrocene itself (isomer shift is 0.7, and quadrupole splitting is 2.37 mm/s) [23]. These data show that the porphyrin core does not affect significantly the electronic structure of the iron ions in TFcPZn complex.

Formation of the mixed-valence state in the TFcPZn complex by chemical oxidation. The electrochemical behavior of the TFcPZn complex was investigated by CV and DPV methods and will be published elsewhere. Briefly, the voltammogram of the TFcPZn complex in o-dichlorobenzene (DCB) shows a first quasi-reversible oxidation at 450 mV along with second irreversible oxidation wave at higher potential. The nature of the first prominent oxidation couple, namely, Ox_1, observed at 450 mV (average values) for the TFcPZn complex was probed by chemical oxidation with tetracyanoethylene (TCE) at room temperature in order to determine the number of the oxidized ferrocenyl substituents. As has been pointed out recently [24], the Ox_1 process for $TFcPH_2$ complex can be defined as four-electron oxidation involving four ferrocenyl moieties. This assignment, however, was based only on electrochemical data and thus cannot be inadequately supportive. Therefore, we in-
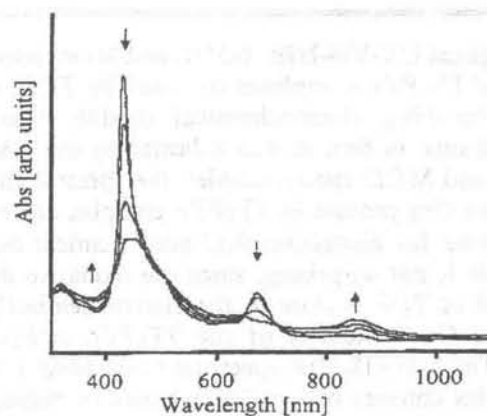

Fig. 2. Changes in the UV-VIS-NIT spectra of TFcPZn complex as a function of oxidation.
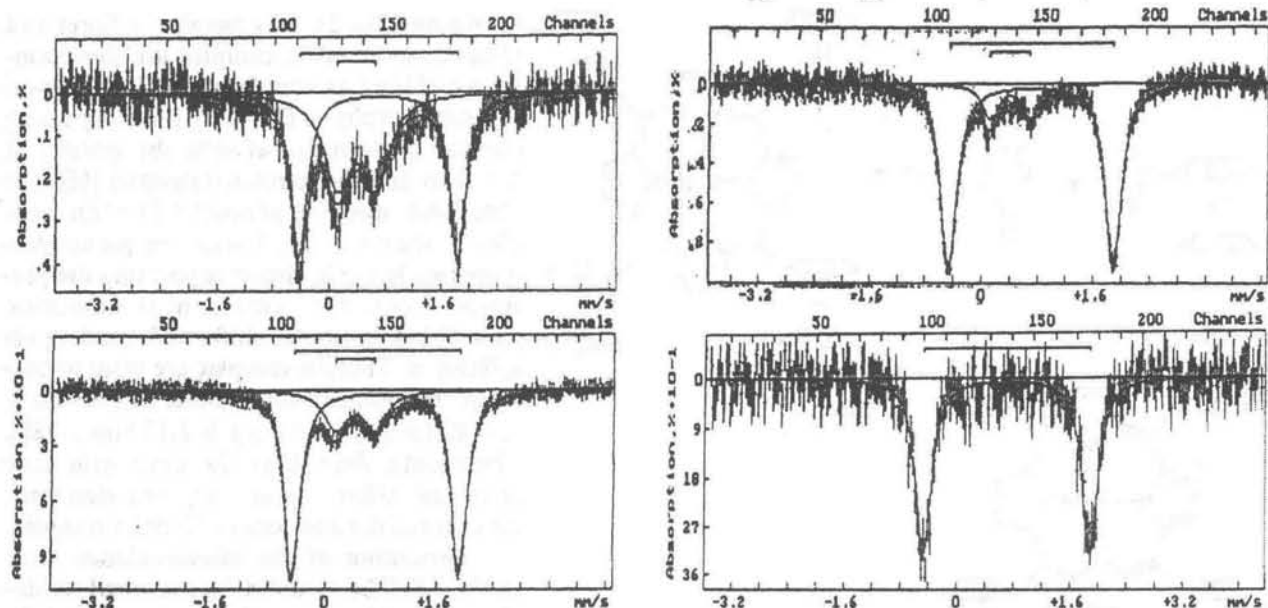
Fig. 3. Dynamics of oxidation of TFcPZn complex by TCE as monitored by Mossbauer spectroscopy
(from the bottom to the top): starting material; TFcPZn : TCE = 1:0.5 (mol/mol);
TFcPZn : TCE = 1:1 (mol/mol); TFcPH$_2$: TCE= = 1:3 (mol/mol).

^{57}Fe Mossbauer room-temperature spectral parameters
of TFcPZn complex

Compound	Compo-und : oxidant	δ *	ΔE$_Q$	Relative area
		mm/s		
TFcPZn		0.71	2.37	1.00
TFcPZn : TCE	1:0.5	0.71; 0.40	2.35; 0.60	0.86; 0.14
TFcPZn : TCE	1:1	0.71; 0.41	2.34; 0.61	0.72; 0.28
TFcPZn : TCE	1:2	0.71; 0.40	2.32; 0.60	0.65; 0.35
TFcPZn : TCE	1:3	0.70; 0.39	2.28; 0.56	0.51; 0.49

* Relative to sodium nitroprusside.

vestigated UV-VIS-NIR, NMR, and Mossbauer spectra of TFcPZn complexes oxidized by TCE, which is mimicking electrochemical oxidation at Ox$_1$ conditions. In fact, as was indicated by the UV-VIS-NIR and MCD spectroscopies, the spectral changes for the Ox$_1$ process in TFcPZn complex are exactly the same for electrochemical and chemical oxidations. It is not surprising, since the oxidative on potential of TCE is close to the electrochemically observed Ox$_1$ potential of the TFcPZn complex.

The UV-VIS-NIR spectrum of oxidized TFcPZn complex consists of two Soret bands of reduced intensity with the one component having a small blue shift and the other component having a small red shift as compared to neutral molecule. The Q-band intensity decreases, and three new bands located at 633, 677, and 862 nm appear (fig. 2). The band located at 633 nm can be attributed to the ferricinium charge-transfer band, while the band at 862 nm to the intravalence charge-transfer transitions [1—4]. The position and intensity of 862 nm band is very close to intravalence charge-transfer band in the one-electron oxidized free-base α,α-5,15-bis(ferrocenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin recently reported by Burrell et al. [19]. Moreover, such an intensive near-IR band is a spectroscopic signature of most of the known mixed-valence (trapped valence state) poly(ferrocenyl)-containing systems [1—4]. The blue shift and decreased intensity of Soret band in oxidized TFcPZn complex is in good agreement with the formation of porphyrin cation-radical, which was observed for the other d-metal porphyrins [16].

Being intrigued by the presence of both IVCT band and porphyrin cation-radical, we recorded Mossbauer and NMR spectra of TFcPZn complex with different TCE to TFcPZn ratio. The Mossbauer spectroscopic changes are shown in fig. 3 and table. The Mossbauer spectra clearly indicate that only two ferrocenyl moieties in TFcPZn complex are oxidized in Ox$_1$ process at room temperature even if a large excess (up to 1:100) of TCE has been applied. Thus, when TCE was added, a new doublet with parame-

ters close to the ferricinium salts appears, and the final spectrum consists of two doublets with equivalent areas (table). The observed final spectrum is clearly indicated by so-called trapped valence situation in the oxidized TFcPZn complex. It has been shown that Mössbauer spectroscopy can be used to monitor the intramolecular electron-transfer rate in mixed-valence systems [26]. Indeed, when the electron-transfer rate is slower than ca $10^7 \, s^{-1}$, then the Mössbauer spectrum consists of a superposition of two quadrupole-splitted doublets with characteristics typical of Fe^{II} and Fe^{III}, metallocenes [4, 26], as observed in the case of TFcPZn complex.

The results obtained from the NMR experiments support Mössbauer spectroscopy observations. For instance, the signals of starting α- and β-protons assigned to A–Cp ring directly attached to the porphyrin core become split when the starting TFcPZn complex is titrated by TCE. Again, the final product contains two singlets for ferrocene protons from A-rings and two singlets from ferricinium A-rings with the ratio 1:1 in excellent agreement with the Mössbauer data (fig. 1). The possibility of $TFc(Fe^{2+})P(2-)Zn / [TFc(Fe^{3+})P(2-)Zn]^{4+}$ mixture formation in TCE titration experiments can be almost excluded on the basis of Mössbauer spectra. In fact, as was discussed earlier for a large number of bis-(ferrocenyl)-containing compounds, having metal—metal coupling, the quadrupole splittings in the ferrocene site of the one-electron oxidized species are lower as compared to starting materials because of electron donation from the non-oxidized ferrocene site to the oxidized ferricinium moiety [4, 23]. The Mössbauer spectra of TFcPZn complex in TCE titration experiments are in excellent agreement with the above observation. Thus, the quadrupole splitting for the ferrocenyl-containing sites in complex oxidized by TCE TFcPZn reduced significantly from 2.37 to 2.28 mm/s. Again, the clearly resolved doublet for the ferricinium-containing sites is in much better agreement with the proposed $2Fe^{2+}/2Fe^{3+}$-containing structure than with possible $TFc(Fe^{2+})-P(2-)Zn / [TFc(Fe^{3+})P(2-)Zn]^{4+}$ mixture formation, for which doublet for ferrocene-containing sites with quadrupole splitting 2.37—2.36 mm/s and poorly resolved doublet for ferricinium sites can be expected [4, 23]. Finally, if we suppose a $TFc(Fe^{2+})-P(2-)Zn / [TFc(Fe^{3+})P(2-)Zn]^{4+}$ mixture formation in oxidative titration experiments, it is impossible to explain why all ferrocene moieties do not oxidize even if a large excess of TCE to porphyrin has been applied (up to 100:1). Thus, on the basis of Mössbauer and NMR spectra of oxidized TFcPZn com-

plex it can be clearly concluded that only two ferrocene units are oxidized with Ox_1 process. Taking this fact into consideration, it becomes understandable that the near-IR band centered at 868 nm can be assigned to intravalence charge-transfer band, as in the case of monooxidized α,α-5,15-bis(ferrocenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin [19]. However, as was pointed out above, in the case of TFcPZn complex, the ferrocene units show free rotation, at least at room temperature, as was clearly indicated by NMR spectroscopy. On the other hand, one of the reasonable postulates for strong long-range metal–metal coupling (steric fixation of the ferrocene units) now becomes to be an unnecessary condition. This is a very promising and important result, which opens a lot of interesting possibilities for the synthesis of other porphyrin-like systems having long-range metal–metal coupling. For instance, the main difference between 5,15-bis(ferrocenyl)-10,20-bis(tolyl)porphyrin [19] and TFcPZn complex (for which free rotation of ferrocenyl moieties is postulated) is the presence of cis-ferrocenyl moieties in the latter case. Thus, it can be expected that 5,10- bis(ferrocenyl)porphyrin will have a strong long-range metal–metal coupling (some of such compounds are now under investigation). Now we still have to discuss the following question: how many electrons withdraw in Ox_1 process from the starting TFcPZn complex? As was mentioned above, from the electrochemical data, the Ox_1 process can be assigned as a nearly three-electron process. From the Mossbauer and NMR data it can be clearly concluded that only two ferrocenyl moieties are oxidized under Ox_1 process conditions. Thus, if the Ox_1 process is three-electron, then the third electron should be withdrawn from the porphyrin core with the formation of respective porphyrin cation-radical species.

In order to confirm our experimental assignments, the electronic structure of neutral and oxidized TFcPZn complex as calculated at density functional theory level. Since the X-ray determined geometry of neutral and oxidized TFcPZn complex is unavailable, the starting geometry has been obtained by full geometry optimization at B3LYP//6-31G(d) level with the borders of S_4 and C_2 point groups for the neutral and oxidized compounds, respectively. The calculated spin densities of the oxidized TFcPZn complex indicate electrons withdrawal from two ferrocene substituents and porphyrin core with a good agreement with the experimental observations. In addition, Mulliken population analysis assigns iron center as Fe^{II}, while the other two as Fe^{III}. Finally, the DFT calculations on the oxidized TFcPZn

complex predict a large quadrupole splitting in Mössbauer spectrum for Fe^{II} centers and small quadrupole splitting for the Fe^{III} one. As expected, the calculated quadrupole splittings for the Fe^{II} centers are close for the neutral and oxidized compounds. The most intriguing result of the DFT calculation on oxidized TFcPZn complex is that the Fe^{III} centers are predicted to be at 5 and 10 positions. In other words, ferrocene to ferricinium oxidation takes place in the *cis*, not *trans* positions of *meso*-tetraferrocenyl porphyrin.

We have characterized the neutral and oxidized forms of zinc 5,10,15,20-tetra(ferrocenyl)porphyrin using UV-VIS-NIR, NMR, and Mossbauer spectroscopic methods as well as DFT calculations. The first oxidation process includes both oxidation of porphyrin core as well as two ferrocenyl moieties. For the chemically oxidized species a characteristic intravalence charge-transfer band was observed in UV-VIS spectra in the near-IR region. Finally, we have shown that steric fixation of the ferrocene units is not the necessary condition for the long-range metal-metal coupling in the polyferrocene-containing systems.

Details on the synthesis of zinc 5,10,15,20-tetra(ferrocenyl)porphyrin will be published elsewhere. Characterization data: Yield 0.028 g (83 %). UV-VIS (λ_{max}/nm, CH_2Cl_2, $\varepsilon \times 10^{-4}$): 436 (148), 489 sh, 618 sh, 679 (28.3). ^{1}H NMR ($CDCl_3$, tms, δ): 9.84 (s, 8H, β-pyrr), 5.37 (m, 8H, α-Cp), 4.80 (m, 8H, β-Cp), 4.07 (s, 20H, CpH). MS (FAB, m-NBA, *m/z*): 1108 $[M]^+$. Found, %: C 64.29; H 4.31; N 5.13; Zn 5.42; Anal Calcd for $C_{60}H_{44}N_4Fe_4Zn \cdot H_2O$, %: C 63.89; H 4.08; N 4.97; Zn 5.77.

All calculations were conducted using Gaussian 03 software [27] running under Windows and UNIX OS. The geometry optimizations were done using B3LYP exchange-correlation functional [28] and 6-31G(d) basis set in the borders of S_4 and C_2 point groups for the neutral and oxidized complexes, respectively. Single point calculations were conducted using the same exchange-correlation functional, Wachter's full electron basis set for iron and zinc atoms, 6-311G(d) basis set for nitrogen and carbon atoms, and 6-31G(d) basis set for hydrogen atoms.

РЕЗЮМЕ. Изучено образование смешановалентных состояний 5,10,15,20-тетра(ферроценил)порфирина цинка, устойчивых при комнатной температуре. На основании данных ЭСП, Мессбауэровской, ЯМР-спектроскопии, а также электрохимических и теоретических методов исследований сделан вывод, что первый процесс окисления включает трехэлектронный переход и, таким образом, дальнейшее взаимодействие металл—металл может наблюдаться не только для систем с затрудненным вращением ферроценовых заместителей, но и для порфиринов со свободным вращением ферроценовых групп.

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УДК 546.831:667.287

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ПРИКЛАДНЫЕ АСПЕКТЫ ХИМИИ ФТАЛОЦИАНИНОВЫХ КОМПЛЕКСОВ МЕТАЛЛОВ

Рассмотрены возможности применения фталоцианиновых систем в качестве новых функциональных материалов — электрохромных, нелинейно-оптических, сенсорных, жидкокристаллических, а также использование их в биологии и медицине.

В 1928 году химики шотландской фирмы Scottish Dyes Ltd в процессе производства фталимида из фталевого ангидрида и аммиака нашли на стенках реактора темно-синее, чрезвычайно устойчивое по отношению к кислотам и основаниям, содержащее в себе железо вещество. Детальное изучение его свойств и строения привело к открытию нового класса макроциклических тетрапиррольных соединений — фталоцианинов (Pc) [1]. Исчерпывающий синтез фталоцианина железа (PcFe) был впервые описан в классических работах Р. Линстеда с сотрудниками [1—3].

Фталоцианины оказались не только новым, но и чрезвычайно перспективным практически классом макроциклических соединений благодаря их уникальным свойствам. Традиционно их используют в качестве светопрочных пигментов и красителей. В настоящее время в мире фталоцианиновые соединения выпускаются в больших объемах для удовлетворения потребностей в синих и зеленых пигментах и красителях для полиграфии, легкой промышленности, промышленности фотографических материалов, покрытий автомобилей, пластмасс. Например, фталоцианина меди производится около 50 000 т в год [4].

Наряду с высокой термической и химической стабильностью, способностью к сублимации, фталоцианины обладают замечательными оптическими, фотофизическими, электрохимическими и биологическими свойствами, что обеспечивает их использование не только в научных целях, но и в высокотехнологических отраслях производства [5—7]. Поэтому цель настоящего обзора — привлечь внимание исследователей из различных областей науки и техники к именно этим, интересным в практическом смысле соединениям.

Это не означает, что в литературе отсутствуют обзоры по химии фталоцианиновых соединений; первый обзор был сделан Moser F.H., Thomas A.L. уже через несколько лет после открытия фталоцианиновых комплексов [8], что свидетельствует об интересе к ним с первых дней их существования. Дальнейшие достижения в области химии фталоцианиновых красителей были обобщены Booth G. [9] и Leznoff C.C., Lever A.B.P. [10]. В 1989 г. под редакцией Е.А. Лукьянца был издан атлас спектров фталоцианиновых, нафталоцианиновых и других родственных соединений [11]. В 2002—2004 гг. вышел в свет справочник по химии порфиринов и родственных соединений, в котором несколько томов посвящено фталоцианиновым соединениям [12].

Методы синтеза фталоцианиновых комплексов. Основные методы синтеза Pc-систем были разработаны Р. Линстедом. Он показал, что фталоцианины можно получить исходя из различных производных фталевой кислоты, но ключевой всегда является стадия образования фталодинитри-

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