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Peripheral Substituents Effect on Redox-Isomerism in Ytterbium Bis-phthalocyaninates at the Interfaces

A. V. Arakcheev,[a] A. A. Sobolev,[a,b] M. A. Polovkova,[a] A. G. Martynov,[a] Yu. G. Gorbunova,[a,c] and S. L. Selektor[a@]

[a]*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia*
[b]*MIREA – Russian Technological University, M. V. Lomonosov Institute of Fine Chemical Technologies, 119454 Moscow, Russia*
[c]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russia*
[@]*Corresponding author E-mail: pcss_lab@mail.ru*

Nowadays, coordination compounds capable of redox isomeric transformations are intensively discussed by researchers around the world due to the promise of creating efficient molecular switches based on them. In this work, the redox isomerization of ytterbium bis-phthalocyaninates with different peripheral substitutions in Langmuir monolayers and Langmuir-Blodgett films was discovered and studied. We show the possibility of control over the tautomeric equilibrium established in ytterbium bis-phthalocyaninates at the air/water interface by varying the peripheral substituents in the studied complexes. In particular, photoinduced redox isomerization of homoleptic crown-substituted ytterbium bis-phthalocyaninate in ultrathin films on solid and liquid substrates has been demonstrated. It was found that the impact of certain substituents in the peripheral positions of phthalocyanine macrocycles on the tendency of the studied complexes to redox isomerization depends on the physical nature of inducing stimulus.

Keywords: Redox-isomerism, photochromism, molecular switches, phthalocyanines, lanthanides, Langmuir monolayers, Langmuir-Blodgett films.

Влияние периферийных заместителей на редокс-изомерию в бис-фталоцианинатах иттербия на межфазных границах

А. В. Аракчеев,[a] А. А. Соболев,[a,b] М. А. Половкова,[a] А. Г. Мартынов,[a] Ю. Г. Горбунова,[a,c] С. Л. Селектор[a]

[a]*Федеральное государственное бюджетное учреждение науки Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук, 119071 Москва, Россия*
[b]*«МИРЭА – Российский технологический университет», 119454 Москва, Россия*
[c]*Федеральное государственное бюджетное учреждение науки Институт общей и неорганической химии им. Н.С. Курнакова Российской академии наук, 119991 Москва, Россия*
[@]*E-mail: pcss_lab@mail.ru*

В настоящее время координационные соединения, способные к редокс-изомерным превращениям, привлекают внимание исследователей по всему миру из-за перспектив создания эффективных молекулярных переключателей на их основе. В данной работе обнаружена и изучена редокс-изомеризация бис-фталоцианинатов иттербия с различным периферийным замещением в монослоях Ленгмюра и плёнках Ленгмюра-Блоджетт. Показана возможность управления таутомерным равновесием, устанавливающимся в бис-фталоцианинатах иттербия на границе раздела воздух/вода, за счёт варьирования периферийных заместителей в исследуемых комплексах. В частности, продемонстрирована фотоиндуцированная редокс-изомеризация гомолептического краун-замещённого бис-фталоцианината иттербия в ультратонких плёнках на твёрдых и жидких подложках. Установлено, что влияние тех или иных заместителей в периферийных положениях фталоцианиновых макроциклов на склонность исследуемых комплексов к редокс-изомеризации зависит от индуцирующего её стимула.

Ключевые слова: Редокс-изомерия, фотохромизм, молекулярные переключатели, фталоцианины, лантаниды, монослои Ленгмюра, плёнки Ленгмюра-Блоджетт.

Introduction

The creation of compact switchable materials based on macrocyclic compounds and their complexes is an important task on the way to miniaturizing electronic devices.[1] The prospects for using a certain molecule in a real device are determined primarily by the range of properties changed upon switching. Currently, the variety of organic switches allows for the development of sensor systems,[2] memory storage devices,[3] logic components,[4] and nonlinear optical materials[5,6] based on them. Since their discovery,[7] coordination compounds capable of redox isomeric transformations have attracted the attention of research groups around the world.[8,9] Remaining a unique phenomenon found in an extremely small collection of complex compounds of d- and f-elements,[10-13] controlled intramolecular electron transfer leads to changes in a wide range of physicochemical characteristics of the molecule.[14] The most studied physical stimuli inducing redox isomerization are changes in the local environment (solvent replacement),[15] thermal exposure,[16] application of external pressure,[17] and X-ray radiation.[18,19]

In this regard, the adjustment of chemical environment of the redox-active metal center to optimize the redox isomerization process acquires an extremely important issue. For example, in recent years, Kasper S. Pedersen's group is developing a new approach to obtaining redox-isomerizing complexes – the synthesis of 3D coordination polymers based on Sm, Yb and pyrazine linkers. Changing the pattern of exchange interactions in such systems by varying the Sm/Yb ratio upon synthesis allows for the fine tuning of the tautomerization parameters.[11,20] The most studied compounds capable of redox isomerism, cobalt dioxolen complexes, have been in the focus of researchers' attention for several decades. The predicting of ability of Co complexes to valence tautomerism is based on: firstly, varying the structure of two types of ligands (dioxolene ligand and bidentate/tetradentate N-donor ancillary ligand) and, secondly, choosing between the neutral or cationic form of the complex.[21] The use of a wide range of ligands of different structures, DFT calculations, and in situ measurements during the switching process allow for the fine tuning of the mutual arrangement of the ligands and metal center boundary orbitals for thermally induced redox isomerization. The most interesting phenomenon in the context of molecular switches in dioxolene-cobalt complexes is the photoinduced tautomerization discovered by Osamu Sato's group. However, such tautomerization only occurs at temperatures below 50 K.[22,23] It should be emphasized that the examples of redox-isomerizing complexes described in the literature refer to systems in which transformations take place upon heating/cooling (in the case of lanthanide complexes in an inert atmosphere), which is a significant limitation from a practical point of view. Consequently, a logical direction for development in this area is the search for new compounds in which the organic environment of the redox-active metal can be adjusted to reveal new, more convenient stimuli that induce redox isomerization.

Previously, in the works of our laboratory, examples of redox isomerization of lanthanide bis-phthalocyaninates upon the transition from solution to the air/water interface and during compression/expansion of a monolayer were described.[24-27] It was shown that the bistable equilibrium in planar supramolecular systems arises due to the asymmetry of the local environment in the Langmuir monolayer at the water surface.[26] Moreover, for monolayers of samarium and europium complexes, we have obtained evidence of reversible redox isomeric transformations under the irradiation by UV and red light,[27] as well as under the effect of X-ray radiation, the energy of which matches the ionization energy of the metal center cation.[28] However, the influence of peripheral substituents in macrocyclic ligands on the characteristic features of tautomeric transformations during compression/expansion and irradiation of a monolayer has not been studied yet.

Experimental

The studied compounds – bis(tetra-15-crown-5-phthalocyaninato)ytterbium(III) **Yb[C$_4$]$_2$** and bis(octa-*n*-butoxyphthalocyaninato)ytterbium(III) **Yb[B$_8$]$_2$** – were synthesized according to a previously described procedures.[26] Here **[B$_8$]** and **[C$_4$]** stand for octa-*n*-butoxy- and tetra-15-crown-5-substituted phthalocyanine ligands following the previously proposed notation[29] (Figure 1).

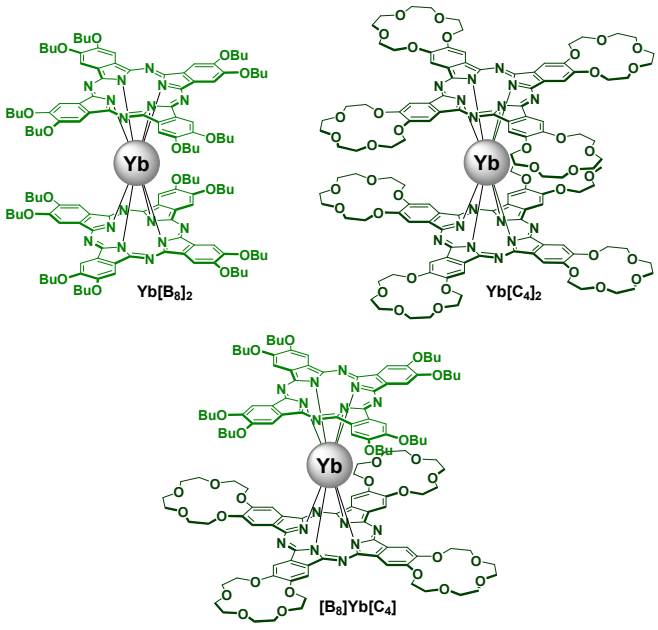

Figure 1. Chemical structure of studied compounds: **Yb[B$_8$]$_2$**, **[B$_8$]Yb[C$_4$]** and **Yb[C$_4$]**.

Synthesis of (octa-n-butoxyphthalocyaninato)(tetra-15-crown-5-phthalocyaninato)ytterbium(III), ***[B$_8$]Yb[C$_4$]***. A solution of octa-*n*-butoxyphthalocyanine **H$_2$[B$_8$]** (36.0 mg; 0.033 mmol), tetra-15-crown-5-phthalocyanine **H$_2$[C$_4$]** (42.4 mg; 0.033 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (99.4 μL; 0.665 mmol) in mixture of 3 mL of 1-chloronaphthalene : *n*-octanol (2:1) mixture was heated to reflux under a stream of argon, and solid $Yb(OAc)_3{\times}4H_2O$ (0.0491 g; 0.116 mmol) was added. After 2.5 h, the reaction mixture was cooled to ambient temperature and precipitated from hexane. The target heteroleptic complex **[B$_8$]Yb[C$_4$]** was isolated by column chromatography on neutral Al_2O_3 with gradient elution with a mixture of $CHCl_3$: MeOH (1.5 vol.% MeOH). The yield of the target complex was 33 mg (39%). MALDI TOF *m/z*: calculated for $C_{128}H_{152}N_{16}O_{28}Yb$ 2535.0 found 2535.0 [M$^+$] (Figure S1). ^{1}H NMR (600 MHz, chloroform-*d*) δ ppm: 7.31 (s, 8H, α-CH_2), 7.14 (s, 8H, 1-CH_2), 6.44 (s, 8H, α′-CH_2), 5.92 (s, 8H, 1′-CH_2), 4.98 (m, 8H, β-CH_2), 4.76 (m, 8H, β′-CH_2), 4.50 (m, 8H, γ-CH_2), 4.35 (m, 16H, δ,δ′-CH_2), 4.27 (m, 8H, γ′-CH_2), 2.96 (s, 8H, 2-CH_2), 2.85 (s, 8H, 2′-CH_2), 2.43 (m, 16H, 3,3′-CH_2), 1.56 (t, *J* = 6.9 Hz, 24H, CH_3), -9.07 and -11.08 (2s, 2×8H, H_{Ar}^{CR} and H_{Ar}^{OBu}) (Figure S2). UV-Vis ($CHCl_3$) λ_{max} nm (lg ε): 1415 (4.69), 916 (4.17), 668 (5.71), 603 (5.06), 478 (4.90), 367 (5.16), 292 (5.62).

Langmuir-Blodgett device Kibron Microtrough G2 with a trough area of 280 cm^2 with PTFE and moveable barriers made of hydrophilic polyacetal was used for Langmuir monolayer formation. Compression isotherms were recorded using automated Langmuir balance and platinum Wilhelmi plate. The monolayers were formed by spreading the studied solutions onto the air/water interface using a chromatographic syringe. Then, the system was left undisturbed for 15−20 min in order for the solvent to evaporate from the interface. After that, monolayer compression at the rate of 5 mm min^{-1} commenced. Transfer of Langmuir monolayers onto solid substrates was carried out by the Langmuir-Blodgett (LB) technique (vertical transfer) using an automated dipper device at surface pressures of around 10 (LBF10) and 20 (LBF20) mN/m in case of monolayers containing divalent and trivalent lanthanide complexes, respectively, as described in the Results and Discussion section. All studied LB films were single-layered. Ultrapure water (18 MΩ cm) deionized by the Millipore Milli-Q water purification system was used as a subphase in Langmuir monolayer studies.

All experiments related to the formation of monolayers and films of the studied lanthanide bis-phthalocyaninates were carried out under ambient conditions: air, and subphase temperature of 21 ± 0.1 °C.

UV-Vis spectra of Yb(III) bis-phthalocyaninates monolayers on aqueous subphase were recorded in the wavelength range of 370−800 nm using an AvaSpec-2048 optic fiber spectrophotometer equipped with halogen light source AvaLight HAL (Avantes, The Netherlands). According to the previously described technique,[30] a reflectometric probe with a fiber diameter of 400 μm combined with a six-fiber irradiating cable was placed perpendicularly to the subphase surface at a distance of 2−3 mm from the monolayer. The signal obtained upon light reflection from the aqueous subphase surface immediately before the monolayer spreading was used as a baseline. UV-irradiation of the monolayer was carried out using a mercury UV-lamp (the lamp spectrum is shown in SM (Figure S3)) after stopping the barriers of the Langmuir trough when a target value of surface pressure (10 mN/m) was reached. UV-Vis absorption spectra of the monolayer were recorded before, after, and in parallel with irradiation.

UV-Vis spectra of **Yb[B$_8$]$_2$**, **Yb[C$_4$]$_2$**, **[B$_8$]Yb[C$_4$]** solutions and ultrathin films were measured in the wavelength range of 220−900 nm using a Shimadzu 2450 PC spectrophotometer (Japan).

Results and Discussion

Redox-isomeric transformations at the air/water interface

Earlier[26] we have shown that the UV-Vis absorption spectra of a monolayer of octa-butoxy substituted ytterbium bis-phthalocyaninate undergo dramatically changes upon the transition from solution to the air/water interface (Figure 2a). The bathochromic shift of the Q-band indicates the one-electron oxidation of the phthalocyanine ligand and, accordingly, the redox isomerization of the complex $[L^{\bullet-}Yb^{3+}L^{2-}]^0 \rightarrow [Yb^{2+}L^{\bullet-}{}_2]^0$ (Figure 2a – 1, 2). The tautomeric transformation is induced by a change in the molecule local environment with a violation of symmetry: one phthalocyanine macrocycle is in water, the other is in air. In turn, lateral compression causes reverse changes in the Q band, indicating a shift in the redox isomeric equilibrium in the ytterbium bis-phthalocyaninate monomolecular film towards a state that is stable in solution $[Yb^{2+}L^{\bullet-}{}_2]^0 \rightarrow [L^{\bullet-}Yb^{3+}L^{2-}]^0$ (Figure 2a – 2, 3). When the monolayer is compressed, the discotic molecule is reorientated on the edge and the symmetry of the local environment of the phthalocyanines is partially restored – both macrocycles are partially immersed in the aqueous subphase. These facts

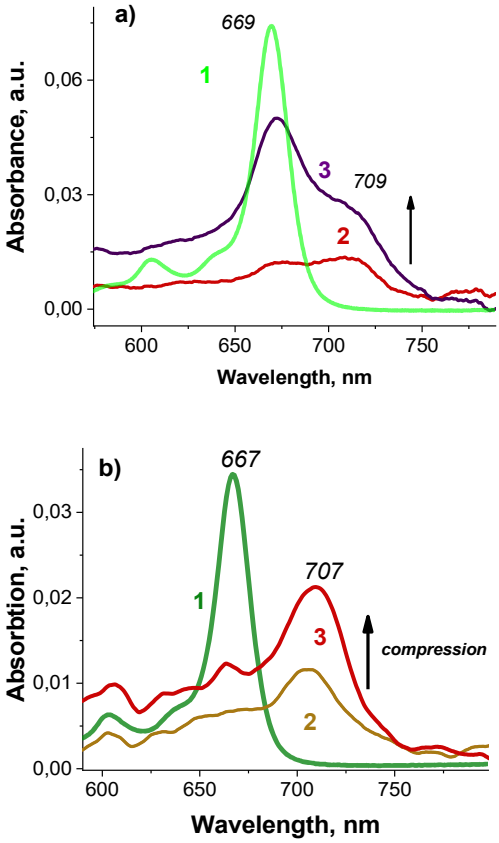

Figure 2. a) 1 – UV-Vis spectra of **Yb[B$_8$]$_2$** solution, 2 and 3 – UV-Vis spectra of the **Yb[B$_8$]$_2$** monolayer at the 5 and 25 mN/m, respectively; b) 1 – UV-Vis spectra of **Yb[C$_4$]$_2$** solution, 2 and 3 – evolution of the UV-Vis spectra of the **Yb[C$_4$]$_2$** monolayer at lateral compression from the 5 to 25 mN/m, respectively.

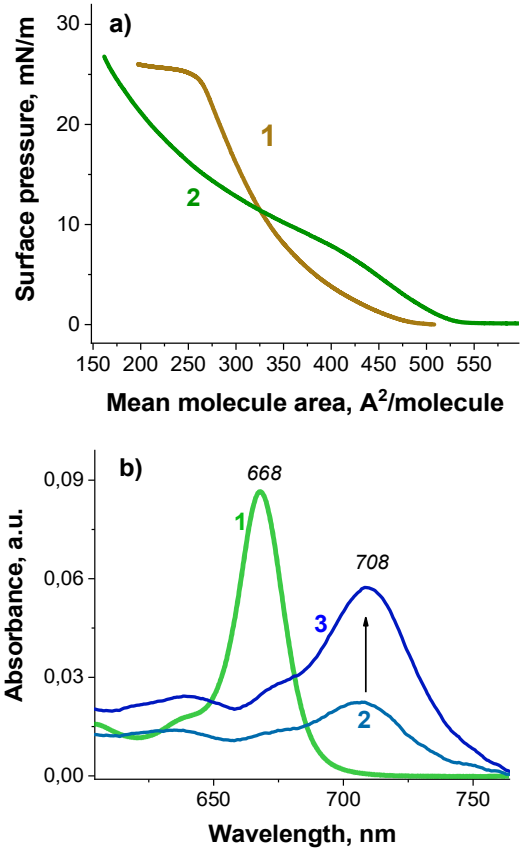

Figure 3. a) Compression isotherms for Langmuir monolayers of (1) **Yb[B$_8$]$_2$** and (2) **Yb[C$_4$]$_2$** at the air/water interface; b) – UV-Vis spectra of **[B$_8$]Yb[C$_4$]** solution, 2 and 3 – evolution of the UV-Vis spectra of the **[B$_8$]Yb[C$_4$]** monolayer at lateral compression from the 5 to 25 mN/m, respectively.

indicate the presence of two redox isomeric forms and the possibility of controlled switching, achieved by reorientation of the molecule relative to the air/water interface. In the context of searching ways to control tautomer equilibrium and factors affecting the stability of the divalent metal center state, complexes with a different peripheral substitution were synthesized: **Yb[C$_4$]$_2$** and **[B$_8$]Yb[C$_4$]**. The UV-Vis absorption spectra of the new compounds were found to be almost identical, with only a small hypsochromic shift of the main maxima in the row **Yb[B$_8$]$_2$** – **[B$_8$]Yb[C$_4$]** – **Yb[C$_4$]$_2$**, associated with a decrease in the donor ability of the peripheral substituents (Figure S4).

After replacing the peripheral substituents of both phthalocyanine macrocycles with 15-crown-5 the transition from solution to interface, as in the first case, is accompanied by the change in the absorption spectrum, which is interpreted as the result of intramolecular electron transfer from the ligand to the metal (Figure 2b – 1, 2). However, the passage to more bulky peripheral substituents leads to the change in the of monolayer behaviour under compression. While the isotherm of **Yb[B$_8$]$_2$** (Figure 3a – 1) shows a smooth rise, indicating a process of molecular reorientation in the range of 400–450 Å^2/molecule, the compression curve of **Yb[C$_4$]$_2$** (Figure 3a – 2) displays an increase in the pressure onset area and a pronounced plateau in the range of 300–400 Å^2/molecule. Such changes are apparently due to the bulkiness of 15-crown-5 ethers and the greater hydrophilicity of the new substituents. During lateral compression, the absorption spectra of **Yb[C$_4$]$_2$** show only an increase in the intensity of the Q-band and the appearance of only a small shoulder in the 667 nm region. This indicates greater stability of the $[Yb^{2+}L^{\bullet-}{}_2]^0$ redox-isomeric form of the crown substituted complex to lateral compression and reorientation at the interface (Figure 2b – 2, 3). On the other hand, upon heteroleptic substitution of phthalocyanine macrocycles, the UV-Vis spectra of the monolayer under compression demonstrate only an increase in the main absorption band without the appearance of any signs of the $[L^{\bullet-}Yb^{3+}L^{2-}]^0$ form (Figure 3b). Despite the intermediate electron-donating abilities of the substituents in the complex **[B$_8$]Yb[C$_4$]** compared to homoleptic analogues, the $[Yb^{2+}L^{\bullet-}{}_2]^0$ form in the heteroleptic complex remains much more stable, suggesting a contribution of the intrinsic asymmetry of the complex to the divalent ytterbium form stability.

Photoinduced redox-isomerization in Langmuir monolayers

Previously we have shown that in Langmuir monolayers of crown-substituted samarium and europium bis-phthalocyaninates control of redox isomerization can be realized not only by lateral compression, but also by irradiation.[27] Under UV irradiation of monolayers of Sm and Eu complexes, a spectral evolution was observed that is specific for the transition $[Yb^{2+}L^{\bullet-}{}_2]^0 \rightarrow [L^{\bullet-}\ Yb^{3+}L^{2-}]^0$. To our surprise, octa-butoxy-substituted ytterbium bis-phthalocyaninate **Yb[B$_8$]$_2$**, which is characterized by a labile equilibrium at the air/water interface during compression-expansion of the monolayer, did not show a significant response to prolonged irradiation with a UV lamp. In contrast, in the **Yb[C$_4$]$_2$** monolayer, which demonstrates the stability of the $[Yb^{2+}L^{\bullet-}{}_2]^0$ form to lateral compression, photoinduced redox isomerization is observed (Figure 4), similar to the evolution of the spectra of samarium and europium complexes upon irradiation. Thus, the $[Yb^{2+}L^{\bullet-}{}_2]^0$ state in the **Yb[B$_8$]$_2$** complex, which is unstable to lateral compression, is immune to photoionization; in turn, the mechanically stable form $[Yb^{2+}L^{\bullet-}{}_2]^0$ in **Yb[C$_4$]$_2$** transforms into $[L^{\bullet-}Yb^{3+}L^{2-}]^0$ within a short time under irradiation (Figure 4, insert).

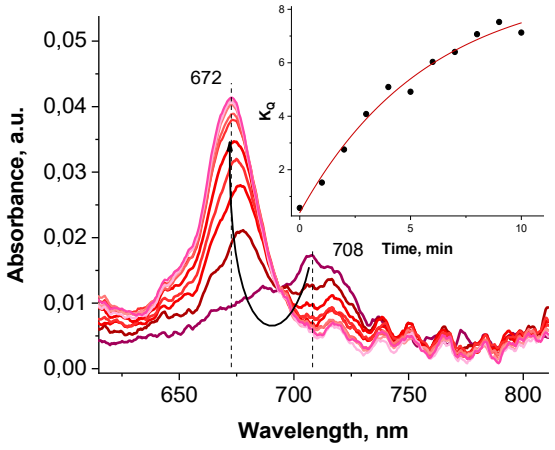

Figure 4. The evolution of **Yb[C$_4$]$_2$** monolayer UV-Vis absorption spectra under UV irradiation at the surface pressure of 10 mN/m.

The emerging contradiction indicates the fundamentally different nature of redox isomeric transitions $[Yb^{2+}L^{\bullet-}{}_2]^0 \rightarrow [L^{\bullet-}Yb^{3+}L^{2-}]^0$ upon the compression and under UV irradiation. Most interestingly, the influence of substituents on the characteristic features of redox-isomeric equilibrium in monolayers of ytterbium bis-phthalocyaninates has a dual nature – it affects redox-isomeric transformations induced by different stimuli in different manner. Finally, the state $[Yb^{2+}L^{\bullet-}{}_2]^0$ in the heteroleptic substituted complex **[B$_8$]Yb[C$_4$]** (which, recall, is intermediate in terms of the donor-acceptor properties of the substituents) proved to be the most stable, with no changes in the absorption spectrum under either lateral compression or UV irradiation.

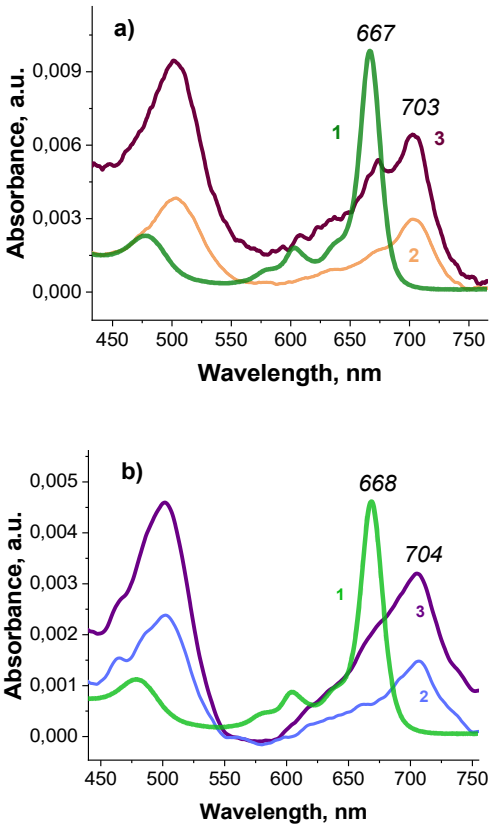

Figure 5. UV-Vis spectra of **Yb[C$_4$]$_2$** (a) and **[B$_8$]Yb[C$_4$]** (b): 1 – solutions; 2 and 3 – LBF10 and LBF20, respectively.

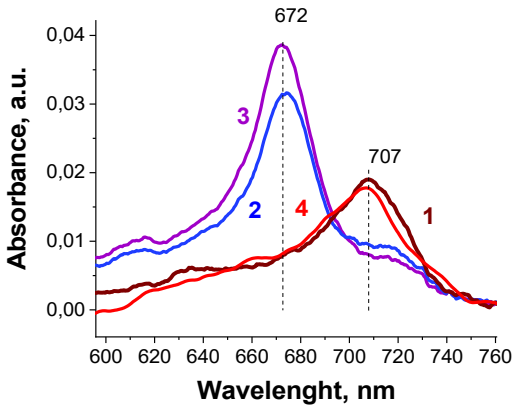

Figure 6. UV-Vis spectra of LBF10 **Yb[C$_4$]$_2$**: 1 – initial film, 2 and 3 – LBF10 **Yb[C$_4$]$_2$** after 5 and 15 min of UV-irradiation respectively, 4 – UV-irradiated LBF10 after 15 min exposure under the red light.

Photochromic switches in Langmuir-Blodgett films

The next stage of the work was the study of the behaviour of ytterbium bis-phthalocyaninates with various substituents on a solid substrate. A comparison of Langmuir-Blodgett films LBF10 and LBF20, transferred at pressures of 10 and 20 mN/m, respectively, provided a slightly deeper insight into the stability of the $[Yb^{2+}L^{\bullet-}{}_2]^0$ form in **Yb[C$_4$]$_2$** and **[B$_8$]Yb[C$_4$]** monolayers. The UV-Vis absorption spectra of the LBF20 of homoleptic crown-substituted complex show the appearance of a shoulder in the 667 nm region, which indicates partial reverse redox isomerization during the transfer of the monolayer to a solid substrate at relatively high pressure (Figure 5a – 3). Mechanical disturbances arising at the three-phase interface during substrate movement through the monolayer can lead to structural rearrangements,[31] and in our case, this effect manifests as reverse redox isomerization into the $[L^{\bullet-}Yb^{3+}L^{2-}]^0$ form. In turn, the UV-Vis absorption spectra of LBF10 and LBF20 **[B$_8$]Yb[C$_4$]** demonstrate significantly greater stability of the $[Yb^{2+}L^{\bullet-}{}_2]^0$ form to mechanical stress (Figure 5b).

Under UV irradiation, LBF10 **Yb[C$_4$]$_2$** demonstrates a spectral change similar to the evolution observed upon irradiation of a monolayer at the air/water interface. Photoinduced redox isomerization in an ultrathin film on a quartz substrate proceeds completely within 15 minutes (Figure 6 – 1, 2, 3). As in the case of the previously described samarium and europium complexes,[27] photoinduced redox isomerization in **Yb[C$_4$]$_2$** is reversible: a direct transition $[Yb^{2+}L^{\bullet-}{}_2]^0 \rightarrow [L^{\bullet-}Yb^{3+}L^{2-}]^0$ occurs under UV irradiation, and the reverse transition $[L^{\bullet-}Yb^{3+}L^{2-}]^0 \rightarrow [Yb^{2+}L^{\bullet-}{}_2]^0$ takes place under red light (670 nm) (Figure 5 – 4). In contrast, for Langmuir-Blodgett films of octabutoxy substituted and heteroleptically substituted complexes, as it was in Langmuir monolayers, UV irradiation does not lead to significant spectral changes.

Conclusions and prospects

Thus, this work has demonstrated redox isomeric transformations in monomolecular films of ytterbium bis-phthalocyaninates with different peripheral substitutions. It has been shown that slight variations in the properties of substituents lead to significant changes in the characteristic features of redox isomeric equilibrium in monolayers of the studied complexes. It was revealed for the first time, that the replacement of butoxyl substituents with 15-crown-5 affects redox isomerization induced by different stimuli in different ways. Particularly, in **Yb[C$_4$]$_2$** monolayers the ability to undergo redox isomerization under lateral compression disappears, but a propensity towards photoinduced tautomerization arises, which is unavailable for **Yb[B$_8$]$_2$**. In turn, a heteroleptic complex, whose peripheral substituents exhibit intermediate donor abilities, demonstrates the greatest stability in Langmuir monolayers and Langmuir-Blodgett films to both lateral compression and long-term UV irradiation. This confirms our hypothesis about the key role of asymmetry in providing conditions for redox isomeric transformations in 2D systems.

The results of the work indicate not only different mechanisms of redox isomerization induced by different

stimuli, but also the surprising sensitivity of the ligand and metal center boundary orbitals to changes in peripheral substituents. In this regard, the most interesting fact is the stabilization of the $[Yb^{2+}L^{\bullet-}{}_2]^0$ form in heteroleptically substituted ytterbium bis-phthalocyanine, apparently due to the intrinsic asymmetry of the complex.

Although the chemistry of coordination compounds capable of redox isomerization has been around for 45 years, the most pressing question remains: what factors determine the ability of a particular stimulus to induce a transformation in a molecule? In our work, we found that in monolayers of lanthanide bis-phthalocyaninates redox isomerization induced by lateral compression or irradiation proceeds differently. Moreover, the effect of substituent changes on these processes is multidirectional. We hope that further research using more sophisticated physical methods will allow us, first, to unambiguously establish the mechanisms of transformations induced by different stimuli and, second, to effectively control the parameters of these transformations by varying the peripheral substituents and metal centers.

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