

ARTICLE

Unexpected Supramolecular Induced Redox Switching in Sandwich Gd Bispthalocyaninate

Anna A. Sinelshchikova,^{a,b} Lyudmila A. Lapkina,^c Vladimir E. Larchenko,^d Pavel V. Dorovatovskii,^e Aslan Yu. Tsivadze,^{b, c} and Yulia G. Gorbunova^{*b, c}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The redox state of the phthalocyanine in sandwich lanthanide complexes is crucial for their applications. In this work, we demonstrate that the cation-induced supramolecular assembly of crown-substituted phthalocyanine lanthanide complexes **Ln[(15C5)₄Pc]₂** can be used to control the redox state of the ligand simultaneously with the coordination sphere of the central metal. We achieve unprecedented redox switching of phthalocyanine ligands in a double-decker Gd(III) complex, resulting from the intramolecular inclusion of potassium cations between the decks with simultaneous twisting of the ligands (the skew angle between them decreases from 44.61° to 0.21°). Such a structural change leads to an increase in the deck to deck distance and drastically facilitates ligand reduction. It was demonstrated that this process is anion dependent. Thus, only potassium salts of weak acids (KOPiv, KOAc) induce intramolecular inclusion of cations with redox switching in contrast to salts of strong acids (KBr, KOPic, KSCN and KPF₆), where such a redox process does not occur. This breakthrough opens new avenues for controlling the electrochromic properties of phthalocyanines, along with other properties, such as electrical conductivity, optics, etc.

Introduction

Phthalocyanines (Pcs) and their lanthanide complexes are π -conjugated electron-rich molecules, widely studied for various applications^{1–5}. Phthalocyanines possess numerous aromatic π -electrons, which determine their photo- and redox-activity^{6–9}, electrochromic^{10,11} and semiconducting properties¹². These properties are further enhanced in sandwich lanthanide complexes due to intramolecular π - π interactions and the intrinsic nature of the metal centres^{13–18}. The electrochromic behaviour of bispthalocyaninates is determined by the ligand-centred redox conversion of **M(Pc)₂** between at least three forms of trivalent metal complexes¹⁹ – anionic **[M³⁺(Pc²⁻)₂]⁻**, neutral **[(Pc⁻)M³⁺(Pc²⁻)]⁰** and cationic **[M³⁺(Pc⁻)₂]⁺** ones. In addition to the spectacular blue-green-red colour changes displayed by these three forms, switching between redox states in sandwich Pcs is also crucial to tune their electron conductivity²⁰, magnetic properties^{21–23} or nonlinear optical response²⁴. The electron-conducting properties of double-decker lanthanide complexes are determined by the unpaired π -electron of the neutral form, making them important organic semiconductors

first time reported in 1987¹². The interaction of double-deckers with oxidizing or reducing gases, such as NO₂ or NH₃, switches the redox state of ligands and drastically reduces the conductivity, which allows to use these complexes as semiconducting gas sensors^{25,26}. Sandwich phthalocyanines can also be employed to construct voltammetric sensors, known as electronic nose and tongue, to discriminate odours from a variety of foods, beverages or fumes^{27–29}. The introduction of substituents responsible for supramolecular assembly opens up new opportunities to organize phthalocyanine molecules in a specific way^{3,30–36}. One of the brightest examples of such substituents are crown ethers^{37–44}, which enable the cation-induced assembly of sandwich lanthanide complexes, leading to control of their functional properties^{45–55}. Alkali cations with an ionic radius larger than the crown ether cavity can connect two adjacent molecules forming dimers^{41,55–61} or longer oligomers^{62–65} (Fig. 1a, b). They can also integrate between decks of the same sandwich molecule, altering the coordination polyhedra of the lanthanide centre⁶⁶ (Fig. 1c), if the deck-to-deck distance is large enough. Late lanthanide complexes, including Lu with the smallest radius, do not allow *intramolecular* inclusion of alkali cations and form the extended nanowires through *intermolecular* connections of double-deckers by potassium cations^{62,63,65}. This leads to very high electron conductivity of the final material up to 11.4 S·cm⁻¹⁶⁵. In contrast, a similar strategy for the middle lanthanides results in an electron conductivity that is 8 orders of magnitude lower. The reason for this difference has not been studied in detail, but our work reveals an important factor for that. Here we report comprehensive solution and single crystal X-ray diffraction characterization of the product of *intramolecular* potassium ion inclusion in the double-decker gadolinium complex Gd[(15C5)₄Pc]₂. This is the first direct structural characterization of the alkali cations intercalation into double-decker lanthanide complexes with crown phthalocyanines. We demonstrate

^a BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, Leioa 48940, Spain, E-mail: anna.sinelshchikova@bcmaterials.net

^b Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr., 31, bldg. 4, 119071, Moscow, Russia.

^c Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr., 31, 119991, Moscow, Russia, E-mail: yulia@igic.ras.ru

^d JSC Fine Chemicals R&D Center, Krasnobogatyrskaya 42, Building 1, Moscow, 107258, Russia.

^e National Research Center "Kurchatov Institute", Kurchatov Square 1, Moscow 123182, Russia.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

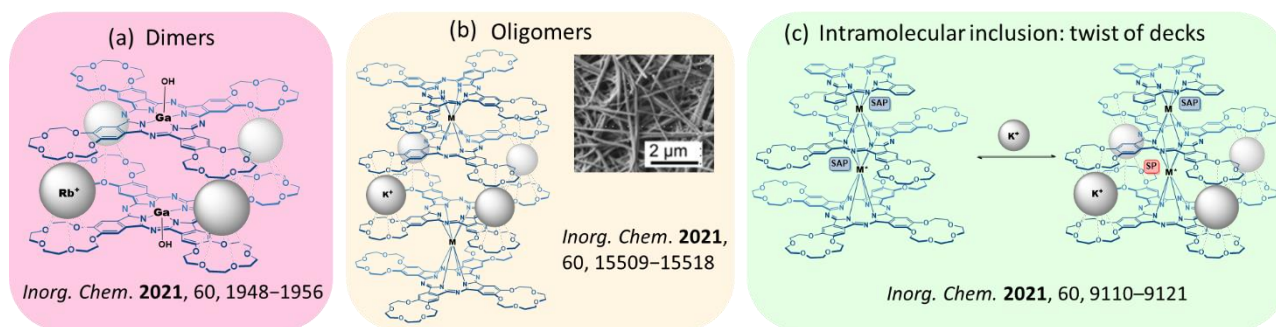


Fig. 1 Examples of cation-induced supramolecular assembly of crown-substituted sandwich lanthanide phthalocyanines.

that for the middle lanthanide double-deckers, supramolecular assembly can additionally control the redox state of the ligand which is crucial for the electron conductivity³⁷.

Results and discussion

Supramolecular assembly of Gd[(15C5)₄Pc]₂ (I) in solution

The neutral form of the double-decker complexes [(15C5)₄Pc²⁻]₂Ln³⁺[(15C5)₄Pc^{•-}]⁰ possess characteristic spectra corresponding to $\pi-\pi^*$ transitions in macrocyclic ligands, including a high-intensity Q band in the range of 660–690 nm; a radical band in the range of 480–510 nm, assigned to the presence of one unpaired electron distributed between two phthalocyanines, as well as B (Soret) bands at 350–400 nm (Fig. 2, Fig. S1). Owing to macrocyclic substituents, the bis(tetra-15-crown-5)-phthalocyaninate Ln[(15C5)₄Pc]₂ can form sandwich complexes with alkali cations such as potassium or rubidium. It is known that for the double-decker complexes of the middle lanthanides it results in two possible processes: *intramolecular* binding of the alkali cations with the formation of inclusion complex (Fig. 1c) or *intermolecular* cofacial binding of adjacent molecules with the formation of 1D oligomers (Fig. 1b)^{51,67}. Each kind of interaction leads to characteristic changes in UV-vis spectra. *Intramolecular* binding leads to a red shift of the Q-band of the complex⁶⁷. When assembling into 1D structures, a significant broadening and decrease in the Q-band intensity, along with a slight blue-shift, are observed⁶⁵. It is important to emphasize that none of these structures for double-deckers were characterized by crystallographic data.

Herein we used the neutral radical complex Gd[(15C5)₄Pc]₂^{0•} (I) for titration with potassium salts. The titration of I solution in CHCl₃-CH₃OH by KOiPr methanol solution in the conditions similar to⁶⁶ allowed to register two parallel processes (Fig. 2): the unexpected formation of specie II with drastically blue-shifted Q-band from 674 nm to 646 nm and the formation of the expected *intramolecular* inclusion complex III with Q-band at 698 nm. The second process of *intramolecular* cations inclusion agrees well with previous experience⁶⁷: by inclusion of K⁺ the distance between decks increases due to the large ionic radius of K⁺ and all different lanthanide complexes independent from ion radius have similar spectra with Q-band around 698 nm. However, the appearance of sharp new bands of an unknown species II is different from both that we could expect – *intramolecular* K⁺ inclusion or *intermolecular* oligomers formation.

Interestingly, once the titration is complete with a high excess of KOiPr (50 eq), the spectra change with time, shifting the equilibrium

further towards the formation of the unknown species II (Fig. S2), indicating a slow kinetics of II formation. We decided to study the process in detail and determine the structure of the previously unknown complex II.

The same spectral changes were observed when using another potassium salt, KOAc (Fig. S3). However, when testing potassium salts of strong acids like KBr (see Fig. 3), KOPic (Fig. S4), KSCN (Fig. S5), and KPF₆ (Fig. S6), only the formation of the *intramolecular* inclusion complex III with a stable Q-band at 698 nm was observed. This confirms the anionic selectivity in the electrochromic properties of Gd[(15C5)₄Pc]₂, as previously found in⁶⁷ for other lanthanides: titration by potassium salts of strong acids results in red-shift and the color of solution changes from green to purple, with the potassium salts of weak acids blue-shift occurs and the color changes from green to blue (Fig. S7).

The fact that the formation of the new complex II is detected only when using salts of weak acids suggests that the hydrolysis of potassium salts plays a crucial role. In all titration experiments we used methanol as solvent for potassium salts, which can contain traces of water. Salts of strong acids and strong bases yield a neutral pH when they hydrolyze, while salts of weak acids and strong bases result in a basic pH.

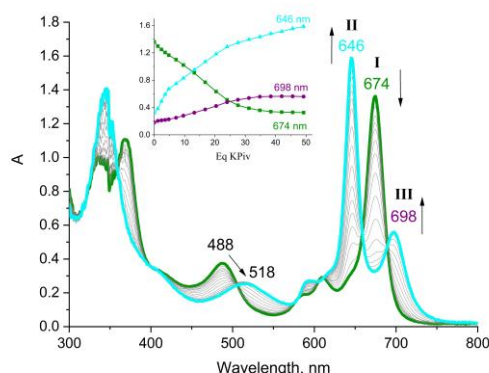


Fig. 2 Spectrophotometric titration of the solution of complex I in CHCl₃:CH₃OH = 4 : 1 (c = 11.4 μM) with the solution of KOiPr in CH₃OH (c = 2.85 mM). The inset shows the titration curves.

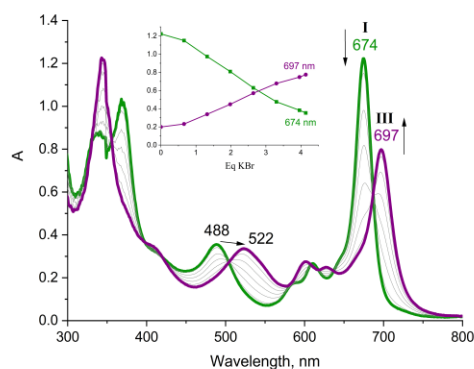
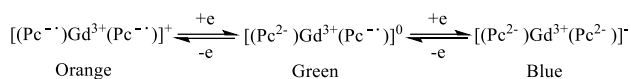


Fig. 3 Spectrophotometric titration of the solution of complex I in CHCl_3 ($c = 10.0 \mu\text{M}$) with the solution of KBr in CH_3OH ($c = 1.52 \text{ mM}$). The inset shows the titration curves.

Phthalocyanine double-deckers are known to be reduced in basic conditions⁶⁸. Therefore, our suggestion is that when using KO piv or KOAc, we observe inclusion of K^+ cations and subsequent reduction of ligand in basic conditions.

Verification of supramolecular induced reduction of I

Indeed, double-decker Gd complex with phthalocyanines can exist in three redox forms and each form has its characteristic spectra (Fig. 4, Scheme 1, Table S1): neutral radical form $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^{0\bullet}$ (I), reduced anionic form $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^-$ (I⁻) and oxidized cationic form $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^+$ (I⁺). The switching between the forms can be easily achieved by use of corresponding reducing (hydrazine hydrate N_2H_4) or oxidizing agent (traces of Br_2 in N-bromosuccinimide NBS).



Scheme 1 Three redox forms of complex I.

The reduction of the complex I results in the disappearance of characteristic band of unpaired electron at 480 nm and the blue-shift of Q-bands – similar changes to what we observe during the formation of II. However, the value of blue-shift and final spectra of I⁻ differs from II.

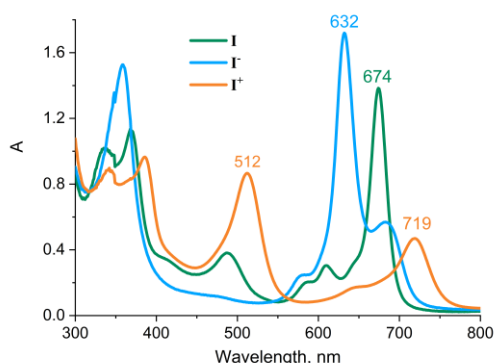


Fig. 4 UV-vis absorption spectra of Gd(III) complexes with $(15\text{C}5)_4\text{Pc}$ in CHCl_3 . Three electronic forms: neutral radical $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^{0\bullet} = \text{I}$ (green), reduced anionic $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- = \text{I}^-$ (blue) and oxidized cationic $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^+ = \text{I}^+$ (orange).

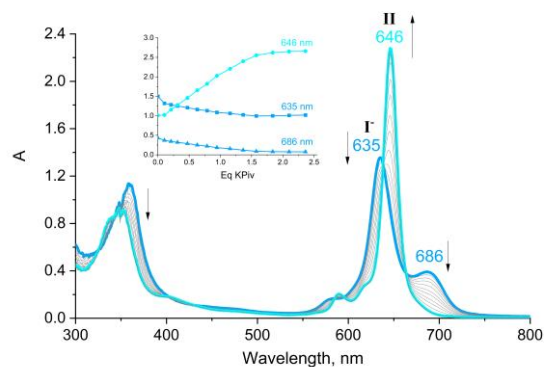


Fig. 5 Spectrophotometric titration of the solution of complex $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- = \text{I}^-$ in $\text{CHCl}_3 : \text{CH}_3\text{OH} = 10 : 1$ ($c = 8.20 \mu\text{M}$) with the solution of KO piv in CH_3OH ($c = 0.2 \text{ mM}$). The inset shows the titration curves.

When we started the titration by KO piv from reduced anionic I⁻ complex we obtained absolutely the same specie II with Q-band at 646 nm (Fig. 5). The formation of specie II is much faster compared to initial titrations of neutral form I, which can be explain by the slow kinetics of the reduction step in slightly basic conditions.

It is known that switching between redox states causes modulation of near-IR absorbance, and the nature of the NIR bands of neutral green complexes is determined by unpaired electron and has been previously discussed^{69–70}. We measured NIR spectra for initial complex I and supramolecular complexes II and III. The complex I has a broad band around 1600 cm^{-1} . When a KBr solution is added to the complex, we observe a redshift in this band, indicating the formation of an inclusion complex. However, when KO piv is added, the intensity of the band decreases over time, suggesting that the complex loses an unpaired electron on the ligand (Fig. S8).

It is known that the lanthanide double-decker complexes with larger ion size reduces easier than the complexes with small ion radius^{71–73}. Our hypothesis is that inclusion of K^+ cations in double-decker results in two main structural changes: *i*) twist of ligands and change of coordination polyhedron of Gd(III), *ii*) increase of distance between ligands due to the large size of potassium cations. As a result, double-decker of middle lanthanide becomes similar to complexes of early lanthanides with larger size and can be reduced easier in slightly basic conditions. In order to verify the structural changes during K^+ inclusion, the single crystals of I and II were grown.

Single crystal XRD of I and II

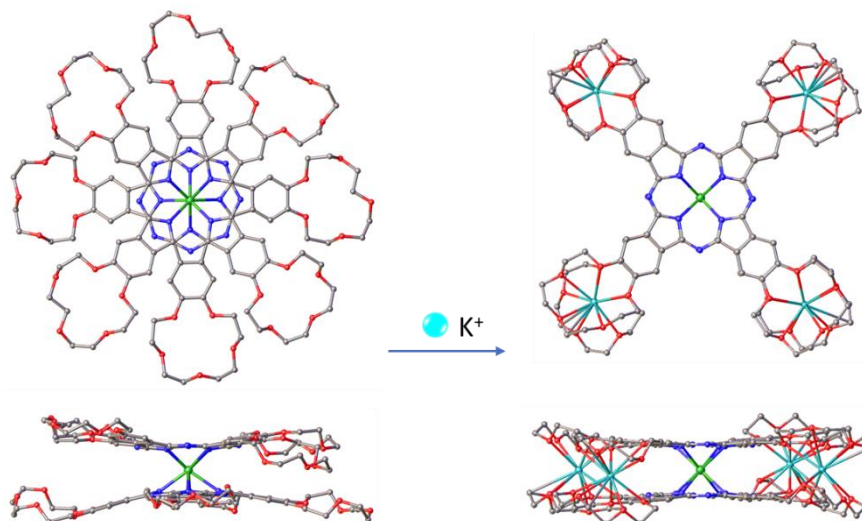


Fig. 6 Top and side views of the single-crystal X-ray diffraction structures of the complexes I and II: $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2 \cdot 6\text{Ph}_2\text{O}$ and $\{[\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- \cdot 4\text{K}^+]^{3+} \cdot \text{PivO}^- \cdot \text{PivOH} \cdot 2\text{Cl}^-] \cdot 13\text{CHCl}_3 \cdot 2\text{H}_2\text{O}$. The H atoms, solvent molecules, and counterions are not shown for clarity.

We succeeded in growing the single crystals of both – initial double-decker I and the product of its interaction with KOPIV complex II. Single crystal XRD (SCXRD) allowed for the first time and unambiguously prove the formation of *intramolecular* inclusion complex for double-decker of middle lanthanide and showed that using KOPIV methanol solution we obtain reduced form of ligand (Fig. 6). The crystallographic data, refinement parameters, bond lengths and angles, asymmetric units, and location of the charge-compensating anions in $\text{Gd}[(15\text{C}5)_4\text{Pc}]_2 \cdot 6\text{Ph}_2\text{O}$ and $\{[\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- \cdot 4\text{K}^+]^{3+} \cdot \text{PivO}^- \cdot \text{PivOH} \cdot 2\text{Cl}^-] \cdot 13\text{CHCl}_3 \cdot 2\text{H}_2\text{O}$ are represented in Fig. S9–S11 and Tables S2–S7. The reduced form of the double-decker is determined from the charge balance of observed anions and the complex (see ESI for details, SCXRD section).

Single crystal diffraction analysis confirmed that the *intramolecular* binding of K^+ ions induced significant molecular motion by twisting of the decks and simultaneously changed the redox state of the ligand. Phthalocyanines twist changes the skew angle between them from 44.61° to 0.21° and switches the coordination polyhedron of Gd(III) from SAP (square antiprismatic) to SP (square prismatic) (Fig. 6) in analogy to previously reported triple-decker complexes⁶⁶. The inclusion of K^+ ions causes a significant change in geometry, affecting specific bond lengths and distances, as shown in Table 1. This includes an increase in the interligand distance between the N_4 planes of crown-substituted ligands from $2.805(10)$ to $3.016(8)$ Å and an elongation of Gd–N(Pc) distances from $2.423(2)$ to $2.480(2)$ Å. The increase in distance between ligands can be attributed to a combination of three factors: the π – π repulsion of forced eclipsed crown-Pc decks, as demonstrated by DFT calculations⁶⁶, the inclusion of large size potassium cations, and the one-electron reduction of phthalocyanines. The reduction is known to increase the deck-to-deck distance, as previously observed in variously substituted tetrapyrrole Gd double-decker crystal structures in distinct redox states^{74–76}. The distance between ligands in $\{\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- \cdot 4\text{K}^+\}^{3+}$ is closer to

those in tetrapyrrole triple-decker Gd complexes^{75,77} (Table S3), which typically exceeds the distances in double-deckers. In contrast to inclusion complex of triple-decker $[\text{Y}^*,\text{Y}] \cdot 4\text{KBPh}_4$ ⁶⁶ where the forced eclipsing of the crown-Pc ligands resulted in their deviation from planarity, in this case, we observe that the phthalocyanine rings become flatter after potassium intercalation (Fig. 6, Table 1). This is due to the one-electron reduction of the ligand, which reduces the repulsion between decks and increases the deck-to-deck distance. Thus, the addition of KOPIV to I results in the *intramolecular* inclusion of K^+ with subsequent one-electron reduction of phthalocyanine. This is a completely new observation, never reported before.

Table 1 Selected Structural Characteristics of I and II According to Single-Crystal X-ray Diffraction Studies

crystal	I	II
formula	$\text{Gd}[(15\text{C}5)_4\text{Pc}]_2 \cdot 6\text{Ph}_2\text{O}$	$\{[\text{Gd}[(15\text{C}5)_4\text{Pc}]_2^- \cdot 4\text{K}^+]^{3+} \cdot \text{PivO}^- \cdot \text{PivOH} \cdot 2\text{Cl}^-] \cdot 13\text{CHCl}_3 \cdot 2\text{H}_2\text{O}$
Bond Length (Å)		
M–N _{iso} , Å	2.4032(17) – 2.4318(17)	2.466(11) – 2.496(11)
M–N _{iso} , Å, av.	2.423(2)	2.480(2)
Plane distances (Å)		
N ₄ – N ₄ , Å	2.805(10)	3.016(8)
M–N ₄ , Å	1.401 – 1.404	1.508
Skew Angle (deg) ^a		
	44.61	0.21
Deviation from Planarity		
(deg) ^b	5.0 – 13.8	2.7 – 8.9
Å ^c	0.135, 0.137	0.085

^a Average torsion angle N1–Cg1–Cg2–N2, where Cg1 and Cg2 are the centroids of the corresponding N_4 planes, ^b Dihedral angles between the isoindoline rings and the corresponding N_4 plane, ^c RMSD of atoms from the plane of 24 atoms

Conclusions

Summarizing obtained results, it was demonstrated the supramolecular controlled ligand reduction of double-decker Gd phthalocyaninate. The increased distance between ligands resulting from the supramolecular inclusion of potassium cations facilitates switching of redox state. The case reported here is a rare example of dynamic control simultaneously over the coordination environment of the Ln ion and the redox state of the ligand, achieved through large-amplitude molecular motion in the context of supramolecular self-assembly.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

AS thank the Human Frontier Science Program (HFSP) for their support (RGP0047/2022). Synthesis, XRD and spectral experiments were performed with support of Ministry of Science and Higher Education of the Russian Federation (grant agreement No. 075-15-2020-779) using the Center for Shared Use of Physical Methods of Investigation at the Frumkin Institute of Physical Chemistry and Electrochemistry, RAS (CKP FMI IPCE RAS), and at the Center for Shared Equipment of Kurnakov Institute of General and Inorganic Chemistry, RAS.

Notes and references

‡ CCDC 2323888 and 2323889 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

- Jiang, J.; Ng, D. K. P. A Decade Journey in the Chemistry of Sandwich-Type Tetrapyrrolo-Rare Earth Complexes. *Acc. Chem. Res.* **2009**, *42* (1), 79–88. <https://doi.org/10.1021/ar800097s>.
- Wöhrlé, D.; Schnurpfeil, G.; Makarov, S. G.; Kazarin, A.; Suvorova, O. N. Practical Applications of Phthalocyanines – from Dyes and Pigments to Materials for Optical, Electronic and Photo-Electronic Devices. *MHC* **2012**, *5* (3), 191–202. <https://doi.org/10.6060/mhc2012.120990w>.
- Martynov, A. G.; Safonova, E. A.; Tsvadze, A. Yu.; Gorbunova, Y. G. Functional Molecular Switches Involving Tetrapyrrolic Macrocycles. *Coordination Chemistry Reviews* **2019**, *387*, 325–347. <https://doi.org/10.1016/j.ccr.2019.02.004>.
- Martynov, A. G.; Horii, Y.; Katoh, K.; Bian, Y.; Jiang, J.; Yamashita, M.; Gorbunova, Y. G. Rare-Earth Based Tetrapyrrolic Sandwiches: Chemistry, Materials and Applications. *Chem. Soc. Rev.* **2022**, *51* (22), 9262–9339. <https://doi.org/10.1039/D2CS00559J>.
- Kobayashi, N.; Fukuda, T. Recent Progress in Phthalocyanine Chemistry: Synthesis and Characterization. In *Functional Dyes*; Elsevier, 2006; pp 1–45. <https://doi.org/10.1016/B978-044452176-7/50002-4>.
- Li, R.; Zhang, X.; Zhu, P.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Electron-Donating or -Withdrawing Nature of Substituents Revealed by the Electrochemistry of Metal-Free Phthalocyanines. *Inorg. Chem.* **2006**, *45* (5), 2327–2334. <https://doi.org/10.1021/ic051931k>.
- Zhu, P.; Lu, F.; Pan, N.; Arnold, D. P.; Zhang, S.; Jiang, J. Comparative Electrochemical Study of Unsubstituted and Substituted Bis(Phthalocyaninato) Rare Earth (III) Complexes. *Eur J Inorg Chem* **2004**, *2004* (3), 510–517. <https://doi.org/10.1002/ejic.200300509>.
- Alessio, P.; Rodríguez-Méndez, M. L.; De Saja Saez, J. A.; Constantino, C. J. L. Iron Phthalocyanine in Non-Aqueous Medium Forming Layer-by-Layer Films: Growth Mechanism, Molecular Architecture and Applications. *Phys. Chem. Chem. Phys.* **2010**, *12* (16), 3972. <https://doi.org/10.1039/b922242c>.
- Shokurov, A. V.; Yagodin, A. V.; Martynov, A. G.; Gorbunova, Y. G.; Tsvadze, A. Yu.; Selektor, S. L. Octopus-Type Crown-Bisphthalocyaninate Anchor for Bottom-Up Assembly of Supramolecular Bilayers with Expanded Redox-Switching Capability. *Small* **2022**, *18* (2), 2104306. <https://doi.org/10.1002/smll.202104306>.
- Nagel, S.; Lener, M.; Keil, C.; Gerdes, R.; Łapok, Ł.; Gorun, S. M.; Schlettwein, D. Electrochromic Switching of Evaporated Thin Films of Bulky, Electronic Deficient Metallo-Phthalocyanines. *J. Phys. Chem. C* **2011**, *115* (17), 8759–8767. <https://doi.org/10.1021/jp2010748>.
- Sekhosana, K. E.; Shumba, M.; Nyokong, T. Electrochemical and Non-Linear Optical Behavior of a New Neodymium Double-Decker Phthalocyanine. *Polyhedron* **2017**, *138*, 154–160. <https://doi.org/10.1016/j.poly.2017.09.033>.
- Turek, P.; Petit, P.; Andre, J. J.; Simon, J.; Even, R.; Boudjema, B.; Guillaud, G.; Maitrot, M. A New Series of Molecular Semiconductors: Phthalocyanine Radicals. *J. Am. Chem. Soc.* **1987**, *109* (17), 5119–5122. <https://doi.org/10.1021/ja00251a012>.
- Pushkarev, V. E.; Tomilova, L. G.; Nemykin, V. N. Historic Overview and New Developments in Synthetic Methods for Preparation of the Rare-Earth Tetrapyrrolic Complexes. *Coordination Chemistry Reviews* **2016**, *319*, 110–179. <https://doi.org/10.1016/j.ccr.2016.04.005>.
- Selektor, S. L.; Shokurov, A. V.; Arslanov, V. V.; Gorbunova, Y. G.; Birin, K. P.; Raitman, O. A.; Morote, F.; Cohen-Bouhacina, T.; Grauby-Heywang, C.; Tsvadze, A. Yu. Orientation-Induced Redox Isomerism in Planar Supramolecular Systems. *J. Phys. Chem. C* **2014**, *118* (8), 4250–4258. <https://doi.org/10.1021/jp411936k>.
- Liu, C.; Yang, W.; Zhang, Y.; Jiang, J. Quintuple-Decker Heteroleptic Phthalocyanine Heterometallic Samarium–Cadmium Complexes. Synthesis, Crystal Structure, Electrochemical Behavior, and Spectroscopic Investigation. *Inorg. Chem.* **2020**, *59* (23), 17591–17599. <https://doi.org/10.1021/acs.inorgchem.0c02816>.

ARTICLE

- (16) Korostei, Y. S.; Pushkarev, V. E.; Tolbin, A. Yu.; Dzuban, A. V.; Chernyak, A. V.; Konev, D. V.; Medvedeva, T. O.; Talantsev, A. D.; Sanina, N. A.; Tomilova, L. G. Sandwich Quadruple-Decker Binuclear Lanthanide(III) Complexes Based on Clamshell-Type Phthalocyanine Ligand: Synthesis and Physicochemical Studies. *Dyes and Pigments* **2019**, *170*, 107648. <https://doi.org/10.1016/j.dyepig.2019.107648>.
- (17) Pushkarev, V. E.; Tomilova, L. G.; Tomilov, Y. V. Synthetic Approaches to Lanthanide Complexes with Tetrapyrrole Type Ligands. *Russ. Chem. Rev.* **2008**, *77* (10), 875–907. <https://doi.org/10.1070/RC2008v077n10ABEH003879>.
- (18) Huang, C.; Wang, K.; Sun, J.; Jiang, J. Planar Binuclear Phthalocyanine-Containing Sandwich-Type Rare-Earth Complexes: Synthesis, Spectroscopy, Electrochemistry, and NLO Properties. *Eur J Inorg Chem* **2014**, No. 9, 1546–1551. <https://doi.org/10.1002/ejic.201301485>.
- (19) Corker, G. A.; Grant, B.; Clecak, N. J. An Explanation of the Electrochromism of Lutetium Diphthalocyanine. *J. Electrochem. Soc.* **1979**, *126* (8), 1339–1343. <https://doi.org/10.1149/1.2129273>.
- (20) Shokurov, A. V.; Kutsyala, D. S.; Martynov, A. G.; Raitman, O. A.; Arslanov, V. V.; Gorbunova, Yu. G.; Tsvadze, A. Y.; Selektor, S. L. Modulation of Transversal Conductivity of Europium(III) Bisphthalocyaninate Ultrathin Films by Peripheral Substitution. *Thin Solid Films* **2019**, *692*, 137591. <https://doi.org/10.1016/j.tsf.2019.137591>.
- (21) Takamatsu, S.; Ishikawa, N. A Theoretical Study of a Drastic Structural Change of Bis(Phthalocyaninato)Lanthanide by Ligand Oxidation: Towards Control of Ligand Field Strength and Magnetism of Single-Lanthanide-Ionic Single Molecule Magnet. *Polyhedron* **2007**, *26* (9–11), 1859–1862. <https://doi.org/10.1016/j.poly.2006.09.020>.
- (22) Takamatsu, S.; Ishikawa, T.; Koshihara, S.; Ishikawa, N. Significant Increase of the Barrier Energy for Magnetization Reversal of a Single-4f-Ionic Single-Molecule Magnet by a Longitudinal Contraction of the Coordination Space. *Inorg. Chem.* **2007**, *46* (18), 7250–7252. <https://doi.org/10.1021/ic700954t>.
- (23) Konarev, D. V.; Khasanov, S. S.; Batov, M. S.; Martynov, A. G.; Nefedova, I. V.; Gorbunova, Y. G.; Otsuka, A.; Yamochi, H.; Kitagawa, H.; Lyubovskaya, R. N. Effect of One- and Two-Electron Reduction of Terbium(III) Double-Decker Phthalocyanine on Single-Ion Magnet Behavior and NIR Absorption. *Inorg. Chem.* **2019**, *58* (8), 5058–5068. <https://doi.org/10.1021/acs.inorgchem.9b00131>.
- (24) Ren, B.; Sheng, N.; Gu, B.; Wan, Y.; Rui, G.; Lv, C.; Cui, Y. Changing Optical Nonlinearities of Homoleptic Bis(Phthalocyaninato) Rare Earth Praseodymium Double-Decker Complexes by the Redox Reaction. *Dyes and Pigments* **2017**, *139*, 788–794. <https://doi.org/10.1016/j.dyepig.2017.01.007>.
- (25) Ouedraogo, S.; Meunier-Prest, R.; Kumar, A.; Bayo-Bangoura, M.; Bouvet, M. Modulating the Electrical Properties of Organic Heterojunction Devices Based On Phthalocyanines for Ambipolar Sensors. *ACS Sens.* **2020**, *5* (6), 1849–1857. <https://doi.org/10.1021/acssensors.0c00877>.
- (26) Chen, Y.; Li, D.; Yuan, N.; Gao, J.; Gu, R.; Lu, G.; Bouvet, M. Tuning the Semiconducting Nature of Bis(Phthalocyaninato) Holmium Complexes via Peripheral Substituents. *J. Mater. Chem.* **2012**, *22* (41), 22142. <https://doi.org/10.1039/c2jm35219b>.
- (27) De Saja, J. A.; Rodríguez-Méndez, M. L. Sensors Based on Double-Decker Rare Earth Phthalocyanines. *Advances in Colloid and Interface Science* **2005**, *116* (1–3), 1–11. <https://doi.org/10.1016/j.cis.2005.03.004>.
- (28) Freddi, S.; Marzuoli, C.; Pagliara, S.; Drera, G.; Sangaletti, L. Targeting Biomarkers in the Gas Phase through a Chemoresistive Electronic Nose Based on Graphene Functionalized with Metal Phthalocyanines. *RSC Adv.* **2023**, *13* (1), 251–263. <https://doi.org/10.1039/D2RA07607A>.
- (29) Rodríguez-Méndez, M. L.; Medina-Plaza, C.; García-Hernández, C.; Rodríguez, S.; García-Cabezón, C.; Paniagua, D.; Rodríguez-Pérez, M. A.; De Saja, J. A. Improvement of Electrocatalytic Effect in Voltammetric Sensors Based on Phthalocyanines. *J. Porphyrins Phthalocyanines* **2016**, *20* (01n04), 413–420. <https://doi.org/10.1142/S1088424616500218>.
- (30) Steybe, F.; Simon, J. Ionoelectronics: Synthesis and Surface Grafting of an Unsymmetrical Lutetium Bisphthalocyanine Bearing Four Crown-Ether Moieties and Four Hexanoic Acid Side Chains. *New J. Chem.* **1998**, *22* (12), 1305–1306. <https://doi.org/10.1039/a807376g>.
- (31) El-Khouly, M. E.; Ito, O.; Smith, P. M.; D'Souza, F. Intermolecular and Supramolecular Photoinduced Electron Transfer Processes of Fullerene–Porphyrin/Phthalocyanine Systems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2004**, *5* (1), 79–104. <https://doi.org/10.1016/j.jphotochemrev.2004.01.003>.
- (32) Nolte, R. J. M. Supramolecular Phthalocyanine Assemblies — a Linstead Career Award Paper. *J. Porphyrins Phthalocyanines* **2020**, *24* (11n12), 1243–1257. <https://doi.org/10.1142/S1088424620300062>.
- (33) Antipin, I. S.; Alfimov, M. V.; Arslanov, V. V.; Burilov, V. A.; Vatsadze, S. Z.; Voloshin, Y. Z.; Volcho, K. P.; Gorbachuk, V. V.; Gorbunova, Y. G.; Gromov, S. P.; Dudkin, S. V.; Zaitsev, S. Yu.; Zakharova, L. Ya.; Ziganshin, M. A.; Zolotukhina, A. V.; Kalinina, M. A.; Karakhanov, E. A.; Kashapov, R. R.; Koifman, O. I.; Konovalov, A. I.; Korenev, V. S.; Maksimov, A. L.; Mamardashvili, N. Zh.; Mamardashvili, G. M.; Martynov, A. G.; Mustafina, A. R.; Nugmanov, R. I.; Ovsyannikov, A. S.; Padnya, P. L.; Potapov, A. S.; Selektor, S. L.; Sokolov, M. N.; Solovieva, S. E.; Stoikov, I. I.; Stuzhin, P. A.; Suslov, E. V.; Ushakov, E. N.; Fedin, V. P.; Fedorenko, S. V.; Fedorova, O. A.; Fedorov, Y. V.; Chvalun, S. N.; Tsvadze, A. Yu.; Shtykov, S. N.; Shurpik, D. N.; Shcherbina, M. A.; Yakimova, L. S. Functional Supramolecular Systems: Design and Applications. *Russ. Chem. Rev.* **2021**, *90* (8), 895–1107. <https://doi.org/10.1070/RCR5011>.
- (34) Victoria Martínez-Díaz, M.; Bottari, G. Supramolecular Organization of Phthalocyanines: From Solution to Surface. *J. Porphyrins Phthalocyanines* **2009**, *13* (04n05), 471–480. <https://doi.org/10.1142/S1088424609000747>.
- (35) Zheng, B.-D.; Ye, J.; Zhang, X.-Q.; Zhang, N.; Xiao, M.-T. Recent Advances in Supramolecular Activatable Phthalocyanine-Based Photosensitizers for Anti-Cancer Therapy. *Coordination Chemistry Reviews* **2021**, *447*, 214155. <https://doi.org/10.1016/j.ccr.2021.214155>.
- (36) Li, X.; Park, E.; Kang, Y.; Kwon, N.; Yang, M.; Lee, S.; Kim, W. J.; Kim, C.; Yoon, J. Supramolecular Phthalocyanine Assemblies for Improved Photoacoustic Imaging and Photothermal Therapy. *Angew Chem Int Ed* **2020**, *59* (22), 8630–8634. <https://doi.org/10.1002/anie.201916147>.

- (37) Pierre Bassoul; Thierry Toupance; Jacques Simon. Semiconductivity and Gas-Sensing Properties of Crown-Ether-Substituted Lutetium Bisphthalocyanines. *Sensors and Actuators B* **1995**, *26*, 150–152. [https://doi.org/10.1016/0925-4005\(94\)01576-4](https://doi.org/10.1016/0925-4005(94)01576-4).
- (38) Ma, P.; Chen, Y.; Sheng, N.; Bian, Y.; Jiang, J. Synthesis, Characterization and OFET Properties of Amphiphilic Mixed (Phthalocyaninato)(Porphyrinato)Europium(III) Complexes. *Eur J Inorg Chem* **2009**, No. 7, 954–960. <https://doi.org/10.1002/ejic.200801134>.
- (39) Martínez-Díaz, M. V.; Rodríguez-Morgade, M. S.; Feiters, M. C.; Van Kan, P. J. M.; Nolte, R. J. M.; Stoddart, J. F.; Torres, T. Supramolecular Phthalocyanine Dimers Based on the Secondary Dialkylammonium Cation/Dibenzo-24-Crown-8 Recognition Motif. *Org. Lett.* **2000**, *2* (8), 1057–1060. <https://doi.org/10.1021/ol0055972>.
- (40) Yoshimoto, S.; Suto, K.; Tada, A.; Kobayashi, N.; Itaya, K. Effect of Adlayer Structure on the Host–Guest Recognition between Calcium and Crown-Ether-Substituted Phthalocyanine Arrays on Au Single-Crystal Surfaces. *J. Am. Chem. Soc.* **2004**, *126* (25), 8020–8027. <https://doi.org/10.1021/ja048760n>.
- (41) D'Souza, F.; Maligaspe, E.; Ohkubo, K.; Zandler, M. E.; Subbaiyan, N. K.; Fukuzumi, S. Photosynthetic Reaction Center Mimicry: Low Reorganization Energy Driven Charge Stabilization in Self-Assembled Cofacial Zinc Phthalocyanine Dimer–Fullerene Conjugate. *J. Am. Chem. Soc.* **2009**, *131* (25), 8787–8797. <https://doi.org/10.1021/ja903467w>.
- (42) D'Souza, F.; Maligaspe, E.; Sandanayaka, A. S. D.; Subbaiyan, N. K.; Karr, P. A.; Hasobe, T.; Ito, O. Photochemical Charge Separation in Supramolecular Phthalocyanine–Multifullerene Conjugates Assembled by Crown Ether-Alkyl Ammonium Cation Interactions. *J. Phys. Chem. A* **2010**, *114* (41), 10951–10959. <https://doi.org/10.1021/jp1028195>.
- (43) Kellner, I. D.; Hahn, U.; Torres, T.; Drewello, T. Salt Cluster Attachment to Crown Ether Decorated Phthalocyanines in the Gas Phase. *J. Phys. Chem. A* **2018**, *122* (6), 1623–1633. <https://doi.org/10.1021/acs.jpca.7b10156>.
- (44) Lu, H.; Kwak, I.; Park, J. H.; O'Neill, K.; Furuyama, T.; Kobayashi, N.; Seabaugh, A.; Kummel, A.; Fullerton-Shirey, S. K. Solution-Cast Monolayers of Cobalt Crown Ether Phthalocyanine on Highly Ordered Pyrolytic Graphite. *J. Phys. Chem. C* **2015**, *119* (38), 21992–22000. <https://doi.org/10.1021/acs.jpcc.5b05233>.
- (45) Ishikawa, N.; Kaizu, Y. Biradical State in Phthalocyanine (2 + 2) Tetramer Composed of Two Bis (Phthalocyaninato) Lutetium Radicals. *Chemical Physics Letters* **1993**, *203* (5–6), 472–476. [https://doi.org/10.1016/0009-2614\(93\)85294-X](https://doi.org/10.1016/0009-2614(93)85294-X).
- (46) Robertson, A.; Ikeda, M.; Takeuchi, M.; Shinkai, S. Allosteric Binding of K⁺ to Crown Ether Macrocycles Appended to a Lanthanum Double Decker System. *BCSJ* **2001**, *74* (5), 883–888. <https://doi.org/10.1246/bcsj.74.883>.
- (47) Gorbunova, Yu. G.; Lapkina, L. A.; Martynov, A. G.; Biryukova, I. V.; Tsvadze, A. Yu. Lanthanide Crownphthalocyaninates: Synthesis, Structure, and Peculiarities of Formation. *Russian Journal of Coordination Chemistry* **2004**, *30* (4), 245–251. <https://doi.org/10.1023/B:RUCO.0000022799.63314.fc>.
- (48) Ishikawa, N.; Kaizu, Y. Cation- and Solvent-Induced Formation of Supramolecular Structures Composed of Crown-Ether Substituted Double-Decker Phthalocyanine Radicals. *J. Phys. Chem. A* **2000**, *104* (44), 10009–10016. <https://doi.org/10.1021/jp002109z>.
- (49) Grishina, A. D.; Gorbunova, Y. G.; Zolotarevsky, V. I.; Pereshivko, L. Ya.; Enakieva, Y. Yu.; Krivenko, T. V.; Savelyev, V.; Vannikov, A. V.; Tsvadze, A. Yu. Solvent-Induced Supramolecular Assemblies of Crown-Substituted Ruthenium Phthalocyaninate: Morphology of Assemblies and Non-Linear Optical Properties. *J. Porphyrins Phthalocyanines* **2009**, *13* (01), 92–98. <https://doi.org/10.1142/S1088424609000231>.
- (50) Gao, Y.; Ma, P.; Chen, Y.; Zhang, Y.; Bian, Y.; Li, X.; Jiang, J.; Ma, C. Design, Synthesis, Characterization, and OFET Properties of Amphiphilic Heteroleptic Tris(Phthalocyaninato) Europium(III) Complexes. The Effect of Crown Ether Hydrophilic Substituents. *Inorg. Chem.* **2009**, *48* (1), 45–54. <https://doi.org/10.1021/ic801040z>.
- (51) Gorbunova, Y. G.; Martynov, A. G.; Tsvadze, A. Yu. Crown-Substituted Phthalocyanines: From Synthesis Towards Materials. In *Handbook of Porphyrin Science (Volume 24); Handbook of Porphyrin Science*; World Scientific Publishing Company, 2012; Vol. 25, pp 271–388. https://doi.org/10.1142/9789814397605_0015.
- (52) Martynov, A. G.; Gorbunova, Yu. G.; Tsvadze, A. Yu. Crown-Substituted Phthalocyanines—Components of Molecular Ionoelectronic Materials and Devices. *Russ. J. Inorg. Chem.* **2014**, *59* (14), 1635–1664. <https://doi.org/10.1134/S0036023614140046>.
- (53) Safonova, E. A.; Martynov, A. G.; Nefedov, S. E.; Kirakosyan, G. A.; Gorbunova, Y. G.; Tsvadze, A. Yu. A Molecular Chameleon: Reversible pH- and Cation-Induced Control of the Optical Properties of Phthalocyanine-Based Complexes in the Visible and Near-Infrared Spectral Ranges. *Inorg. Chem.* **2016**, *55* (5), 2450–2459. <https://doi.org/10.1021/acs.inorgchem.5b02831>.
- (54) Gorbunova, Y. G.; Grishina, A. D.; Martynov, A. G.; Krivenko, T. V.; Isakova, A. A.; Savel'ev, V. V.; Nefedov, S. E.; Abkhalimov, E. V.; Vannikov, A. V.; Tsvadze, A. Yu. The Crucial Role of Self-Assembly in Nonlinear Optical Properties of Polymeric Composites Based on Crown-Substituted Ruthenium Phthalocyaninate. *J. Mater. Chem. C* **2015**, *3* (26), 6692–6700. <https://doi.org/10.1039/C5TC00965K>.
- (55) Horii, Y.; Kishiue, S.; Damjanović, M.; Katoh, K.; Breedlove, B. K.; Enders, M.; Yamashita, M. Supramolecular Approach for Enhancing Single-Molecule Magnet Properties of Terbium(III)-Phthalocyaninato Double-Decker Complexes with Crown Moieties. *Chemistry A European J* **2018**, *24* (17), 4320–4327. <https://doi.org/10.1002/chem.201705378>.
- (56) Martynov, A. G.; Polovkova, M. A.; Berezhnoy, G. S.; Sinelshchikova, A. A.; Dolgushin, F. M.; Birin, K. P.; Kirakosyan, G. A.; Gorbunova, Y. G.; Tsvadze, A. Yu. Cation-Induced Dimerization of Heteroleptic Crown-Substituted Trisphthalocyaninates as Revealed by X-Ray Diffraction and NMR Spectroscopy. *Inorg. Chem.* **2020**, *59* (13), 9424–9433. <https://doi.org/10.1021/acs.inorgchem.0c01346>.
- (57) Lapkina, L. A.; Larchenko, V. E.; Kirakosyan, G. A.; Tsvadze, A. Yu.; Troyanov, S. I.; Gorbunova, Y. G. Cation-Induced Dimerization of Crown-Substituted Phthalocyanines by Complexation with Rubidium Nicotinate As Revealed by X-Ray Structural Data. *Inorg. Chem.* **2018**, *57* (1), 82–85. <https://doi.org/10.1021/acs.inorgchem.7b01983>.
- (58) Lapkina, L. A.; Sinelshchikova, A. A.; Birin, K. P.; Larchenko, V. E.; Grigoriev, M. S.; Tsvadze, A. Yu.; Gorbunova, Y. G. Cation-Induced Dimerization of Crown-Substituted Gallium Phthalocyanine by Complexing with Alkali Metals: The Crucial Role of a Central Metal. *Inorg. Chem.* **2021**, *60* (3),

ARTICLE

- 1948–1956.
<https://doi.org/10.1021/acs.inorgchem.0c03408>.
- (59) Safonova, E. A.; Martynov, A. G.; Zolotarevskii, V. I.; Nefedov, S. E.; Gorbunova, Y. G.; Tsvadze, A. Yu. Design of UV-Vis-NIR Panchromatic Crown-Phthalocyanines with Controllable Aggregation. *Dalton Trans.* **2015**, *44* (3), 1366–1378. <https://doi.org/10.1039/C4DT02759K>.
- (60) Lapkina, L. A.; Gorbunova, Y. G.; Gil, D. O.; Ivanov, V. K.; Konstantinov, N. Yu.; Tsvadze, A. Yu. Synthesis, Spectral Properties, Cation-Induced Dimerization and Photochemical Stability of Tetra-(15-Crown-5)-Phthalocyaninato Indium(III). *J. Porphyrins Phthalocyanines* **2013**, *17* (06n07), 564–572. <https://doi.org/10.1142/S1088424613500648>.
- (61) Nikolaitchik, A. V.; Korth, O.; Rodgers, M. A. J. Crown Ether Substituted Monomeric and Cofacial Dimeric Metallophthalocyanines. 1. Photophysical Studies of the Free Base, Zinc(II), and Copper(II) Variants. *J. Phys. Chem. A* **1999**, *103* (38), 7587–7596. <https://doi.org/10.1021/jp9911651>.
- (62) Toupance, T.; Ahsen, V.; Simon, J. Ionoelectronics. Cation-Induced Nonlinear Complexation: Crown Ether- and Poly(Ethylene Oxide)-Substituted Lutetium Bisphthalocyanines. *J. Am. Chem. Soc.* **1994**, *116* (12), 5352–5361. <https://doi.org/10.1021/ja00091a046>.
- (63) Toupance, T.; Benoit, H.; Sarazin, D.; Simon, J. Ionoelectronics. Pillarlike Aggregates Formed via Highly Nonlinear Complexation Processes. A Light-Scattering Study. *J. Am. Chem. Soc.* **1997**, *119* (39), 9191–9197. <https://doi.org/10.1021/ja9644438>.
- (64) Thami, T.; Chassenieux, C.; Fretigny, C.; Roger, J.-P.; Steybe, F. Columnar Aggregates of Crown Ether Substituted Phthalocyanines Perpendicularly Anchored on a Surface via a Selective Binding Site. *J. Porphyrins Phthalocyanines* **2002**, *06* (09), 563–570. <https://doi.org/10.1142/S1088424602000701>.
- (65) Zvyagina, A. I.; Aleksandrov, A. E.; Martynov, A. G.; Tameev, A. R.; Baranchikov, A. E.; Ezhov, A. A.; Gorbunova, Y. G.; Kalinina, M. A. Ion-Driven Self-Assembly of Lanthanide Bis-Phthalocyaninates into Conductive Quasi-MOF Nanowires: An Approach toward Easily Recyclable Organic Electronics. *Inorg. Chem.* **2021**, *60* (20), 15509–15518. <https://doi.org/10.1021/acs.inorgchem.1c02147>.
- (66) Martynov, A. G.; Polovkova, M. A.; Berezhnoy, G. S.; Sinelshchikova, A. A.; Khrustalev, V. N.; Birin, K. P.; Kirakosyan, G. A.; Gorbunova, Y. G.; Tsvadze, A. Yu. Heteroleptic Crown-Substituted Tris(Phthalocyaninates) as Dynamic Supramolecular Scaffolds with Switchable Rotational States and Tunable Magnetic Properties. *Inorg. Chem.* **2021**, *60* (12), 9110–9121. <https://doi.org/10.1021/acs.inorgchem.1c01100>.
- (67) Martynov, A. G.; Gorbunova, Y. G.; Tsvadze, A. Yu. Potassium-Promoted Anionic Selectivity of Lanthanide Bis(Tetra-15-Crown-Phthalocyaninate) Complexes. *Prot Met Phys Chem Surf* **2011**, *47* (4), 465–470. <https://doi.org/10.1134/S2070205111040125>.
- (68) Hückstädt, H.; Tutaß, A.; Göldner, M.; Cornelissen, U.; Homborg, H. Conformational Heterogeneity in Diphtalocyaninato(2-)Metalates(III) of Sc, Y, In, Sb, Bi, La, Ce, Pr, and Sm. *Z. anorg. allg. Chem.* **2001**, *627* (3), 485–497. [https://doi.org/10.1002/1521-3749\(200103\)627:3<485::AID-ZAAC485>3.0.CO;2-N](https://doi.org/10.1002/1521-3749(200103)627:3<485::AID-ZAAC485>3.0.CO;2-N).
- (69) Lindle, J. R.; Bartoli, F. J.; Boyle, M. E. Third-Order Optical Nonlinearities of Bis(Phthalocyanines). *J. Phys. Chem.* **1992**, *96*, 5847–5852.
- (70) Markovitsi, D.; Tran-Thi, T.-H.; Even, R.; Simon, J. NEAR INFRARED ABSORPTION SPECTRA OF LANTI-IANIDE BIS-PHTHALOCYANINES. *Chemical Physics Letters* **1987**, *137* (2).
- (71) Konami, H.; Hatano, M.; Kobayashi, N.; Osa, T. Redox Potentials of a Series of Lanthanide-Bisphthalocyanine Sandwich Complexes. *Chemical Physics Letters* **1990**, *165* (5), 397–400. [https://doi.org/10.1016/0009-2614\(90\)85448-L](https://doi.org/10.1016/0009-2614(90)85448-L).
- (72) Kobayashi, N. Dimers, Trimers and Oligomers of Phthalocyanines and Related Compounds. *Coordination Chemistry Reviews* **2002**, *227* (2), 129–152. [https://doi.org/10.1016/S0010-8545\(02\)00010-3](https://doi.org/10.1016/S0010-8545(02)00010-3).
- (73) Isago, H. Spectral Study on One-Electron-Oxidized Di(Phthalocyaninato)Rare-Earths(III). *J. Porphyrins Phthalocyanines* **2012**, *16* (07n08), 861–869. <https://doi.org/10.1142/S1088424612500861>.
- (74) Koike, N.; Uekusa, H.; Ohashi, Y.; Harnood, C.; Kitamura, F.; Ohsaka, T.; Tokuda, K. Relationship between the Skew Angle and Interplanar Distance in Four Bis(Phthalocyaninato)Lanthanide(III) Tetrabutylammonium Salts ([NBuⁿ₄][Ln^{III}Pc₂]; Ln = Nd, Gd, Ho, Lu). *Inorg. Chem.* **1996**, *35* (20), 5798–5804. <https://doi.org/10.1021/ic960158d>.
- (75) Chabach, D.; De Cian, A.; Fischer, J.; Weiss, R.; Bibout, M. E. M. Mixed-Metal Triple-Decker Sandwich Complexes with the Porphyrin/Phthalocyanine/Porphyrin Ligand System. *Angew. Chem. Int. Ed. Engl.* **1996**, *35* (8), 898–899. <https://doi.org/10.1002/anie.199608981>.
- (76) Rittenberg, D. K.; Sugiura, K.; Sakata, Y.; Arif, A. M.; Miller, J. S. Bis(Phthalocyaninato)Gadolinium(III) Hexacyanobutadienide(1-), [GdPc₂]⁺[C₄(CN)₆]⁻. An Electron Transfer Salt with Four Paramagnetic Sites. *Inorg. Chem.* **2001**, *40* (15), 3654–3655. <https://doi.org/10.1021/ic010187a>.
- (77) Bian, Y.; Li, L.; Wang, D.; Choi, C.; Cheng, D. Y. Y.; Zhu, P.; Li, R.; Dou, J.; Wang, R.; Pan, N.; Ng, D. K. P.; Kobayashi, N.; Jiang, J. Synthetic, Structural, Spectroscopic, and Electrochemical Studies of Heteroleptic Tris(Phthalocyaninato) Rare Earth Complexes. *Eur J Inorg Chem* **2005**, No. 13, 2612–2618. <https://doi.org/10.1002/ejic.200400920>.