

Magnetocaloric behavior of REE porphyrin-based paramagnets at room temperature

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Received 25 June 2019 Accepted 20 August 2019

ABSTRACT: REE complexes with cyclic aromatic ligands are ranked as the molecular materials with both electronic functionality and a single-molecule magnet behavior at temperatures lower 80 K. At the temperature close to room, they display a positive magnetocaloric effect (MCE) often comparable with one in ferromagnetics. We were determined MCE during the magnetization of both (5,10,15,20-tetra(4-*tert*-butylphenylporphinato))ytterbium(III)chloride, (Cl)YbT'BuPP and (5,10,15,20-tetraphenylporphinato) ytterbium(III)chloride, (Cl)YbT'PP in their aqueous suspensions over the temperature range of 278–320 K and in magnetic fields from zero to 1 T by the direct microcalorimetric method. Specific heat capacity in the solid of (Cl)YbT'BuPP/(Cl)YbTPP has been directly determined in zero magnetic fields using differential scanning calorimetry. Thermodynamic parameters of ytterbium(III) complexes magnetization namely enthalpy/entropy change was determined. To improve understanding of the correlation between (Cl)YbT'BuPP/(Cl)YbTPP magnetic properties and its electronic structure, we have compared magnetic behavior of paramagnets studied with those for (Cl)MTPP where M = Gd, Eu, Tm.

KEYWORDS: porphyrins, ytterbium(III) complexes, specific heat capacity, magnetocaloric effect, magnetization thermodynamics, molecular structure effect.

INTRODUCTION

Rare earths in both elemental and ionic states are important magnetic carriers in the construction of molecular magnetic materials. REE organic complexes cause great interest in finding new functionalities and applications. Tetrapyrrole lanthanide complexes were revealed to exhibit typical single-molecule magnets (SMMs) behavior with an effective energy barrier determined by a ligand field around a lanthanide ion and a blocking temperature not exceeding 50 K [1–4]. Different strategies are useful for enhancing the ligand field effect on a lanthanide ion. Electron and spin density redistribution within a molecule achieved by a double-decker structure creating [5], macrocycle substitution [6] or a building of the molecular structure with an additional spin center [7] is very promising. Transition from REE mononuclear 1: 1 complexes to double-, triple- or quadruple-decker structures in the case of phthalocyanine/ tetraazaporphyrin/porphyrin complexes leads to the improvement many applicable properties of these compounds, namely a photochemical activity, a charge carrier concentration/mobility *i.e.* semiconductivity, photo and chemical stability [5, 8–12].

However, we recently established MCE in the monophthalocyanine gadolinium(III) complex (Cl)GdPc to be higher by almost an order of magnitude compared with corresponding double-decker GdPc₂[•] due to the prevalence intermolecular coupling of two radical spins over the intramolecular oxidation-activated spin coupling it contains [13]. The large and giant MCE at close to room temperature were obtained in the REE complexes of porphyrins with a simple 1 : 1 composition [14, 15]. A general strategy of variations in the temperature-dependent

⁶SPP full member in good standing.

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magnetic behavior through modification of the macrocyclic ligand and spin carrier was provided [16–18]. It was shown, using examples of Eu^{III}, Gd^{III}, and Tm^{III} that the porphyrin/phthalocyanine REE complexes have magnetothermal properties useful in the field of room-temperature magnetic refrigeration and hyperthermia development. The macrocycle modification is carried out in order to change a ligand field-effect on the paramagnetic carrier in the REE tetrapyrrole complexes which determines the effective energy barrier against magnetic relaxation ($U_{\rm ef}$) [2] and therefore the magnetic behavior of the paramagnets.

The aim of the study in this article was to establish the first MCE value in paramagnetic Yb³⁺ ions surrounded by macroheterocycles with increased aromaticity and to obtain the thermodynamic parameters of magnetization in (5,10,15,20-tetra(4-*tert*-butylphenylporphinato)) vtterbium(III)chloride, (Cl)YbT'BuPP vs. an unsubstituted analog, (5,10,15,20-tetraphenylporphinato)ytterbium(III)chloride, (Cl)YbTPP (Formulas). For this, we have performed direct determinations of MCE/the thermodynamic parameters of magnetization in aqueous suspensions and the specific heat capacity of the solid samples of the vtterbium(III) complexes. MCE and the specific heat capacity were obtained by means of the original microcalorimetric method [19] and differential scanning calorimetry (DSC), respectively. The examined compounds display positive room-temperature magnetocaloric effect when magnetic induction increases from zero to 1.0 T in adiabatic conditions. Despite the fact that magnetic characteristics of molecular magnetics are more modest than those of nonorganic magnets, the ytterbium(III) complexes MCE values are only an order of magnitude smaller than those in some nanomagnets [20, 21]. Moreover, the magnetics based on the REE porphyrin/phthalocyanine complexes are often solutionprocessable or easily sublimated; they can be conjugated with inorganic coats, quantum dots and Ag nanoparticles giving promising nonlinear optical and shift-reagent properties [22].

EXPERIMENTAL

Materials

5,10,15,20-(tetra-4-tert-butylphenyl)21H,23Hporphinato)ytterbium(III) chloride, (Cl)YbT'BuPP, was synthesized by the reaction $Yb(Cl)_2 \cdot 6H_2O$ and 5.10.15,-20-(tetra-4-tert-butylphenyl)21H,23H-porphyrin in a molar ratio of 1:5 in boiling imidazole for 30 min. The reaction mixture was dissolved in chloroform and repeatedly washed from imidazole with distilled water in a separating funnel. (Cl)YbT'BuPP was isolated by column chromatography on Al₂O₃ using chloroform, ethanol, and finally the ethanol-1% AcOH mixture. After the column, the ethanol solution was diluted with chloroform and repeatedly washed from acid with distilled water. The chloroform solution was evaporated to precipitate solid (Cl)YbT'BuPP. Then the spectral parameters of the complex were obtained. UV-vis spectrum in CHCl₃, (λ_{max} , nm (loge)): 591 (3.88), 553 (4.34), 514 (3.68), 485 (3.52) shoulder, 424 (5.64), 403 (4.63) shoulder. IR spectrum in KBr (v, cm⁻¹): 3122, 3026, 2962, 2904, 2868, 1910, 1809, 1572, 1519, 1477, 1461, 1394, 1363, 1330, 1268, 1242, 1203, 1109, 1080, 1026, 1005, 993, 908, 868, 852, 839, 810, 799, 724, 584, 561, 465, 435, 394, 383, 377, 372. (For the bands assignment see Table S1). ¹H NMR $(CDCl_3)$, δ , ppm : 8.54 (m, 4H, H_o, 3H, H_m); 7.99 (d, 4H, H_0 ; 2.63 (br. s, 6H, H_B); 2.36 (br. s, 16H, H_{CH_2}); 2.23 (d, 5H, H_m); 1.64 (s, 20H, H_{CH_3}); 0.33 (s, 2H, H_{β}). (For the spectrum see Fig. S1 in the Supporting information). MALDI-TOF MS: calc. for C₆₀H₆₀N₄YbCl — 1045.54, found — 1009.26 [M-C1]⁺, found — 474.83 $[M-4C(CH_3)_3-Cl+2K+5H]^{++}$. (For the spectrum see Fig. S2).

5,10,15,20-(*tetra-phenyl*)**21H,23H-porphinato**) *ytterbium*(*III*) *chloride*, (*Cl*)*YbTPP*, was synthesized by the reaction Yb(Cl)₃·6H₂O and 5,10,15,20-(tetra-4-*tert*-butylphenyl)21H,23H-porphyrin in a molar ratio of 1:2 in boiling imidazole for 30 min. The reaction mixture was dissolved in chloroform and repeatedly washed from



Scheme 1. Paramagnets chemical structure

imidazole with distilled water in a separating funnel. (Cl) YbT'BuPP was isolated by column chromatography on Al_2O_3 with the using chloroform, chloroform–ethanol (1:2 vol%), and finally the ethanol-1% AcOH mixture. After the column, the ethanol solution was diluted with chloroform and repeatedly washed from acid with distilled water. The chloroform solution was evaporated to precipitate the solid (Cl)YbTPP. Then the spectral parameters of the complex were obtained. UV-vis spectrum in CHCl₃, (λ_{max} , nm (log ϵ)): 588 (3.73), 551 (4.35), 511 (3.66), 483 (3.46), 421 (5.64), 401 (4.64). IR spectrum in KBr (v, cm⁻¹): 371, 378, 409, 426, 442, 462, 522. 579, 622, 636, 660, 701, 723, 753, 799, 832, 848, 881, 990, 1007, 1034, 1070, 1156, 1177, 1202, 1233, 1275, 1290, 1331, 1440, 1478, 1518, 1539, 1575, 1596, 1705, 1811, 1890, 1951, 2529, 2614, 2855, 2925, 2962, 3021, 3054, 3076, 3101, 3432. (For the bands assignment see ESM, Table S2). ¹H NMR (CDCl₂), δ , ppm 11.66 (br. s, 6H, H_m); 9.67 (br. s, 2H, H_m); 8.57 (d 4H, H_o); 8.00 (d, 4H, H_o); 5.96 (br. s, 3H, H_p); 4.19 (d, H, H_p); -0.39 (br. s, 8H, H_{β}). (For the spectrum see Fig. S3). MALDI-TOF MS: calc. for C₄₄H₂₈N₄YbCl — 821.15, found — 786.93 $[M-Cl+H]^+$, found 474.81 $[M-Cl+2K+3H]^{++}$. (For the spectrum see Fig. S4).

All reagents were of analytical grade. Yb(Cl)₃·6H₂O, chloroform, imidazole, ethanol, AcOH, and 5,10,15,20-(tetra-phenyl)21H,23H-porphyrin were purchased from Sigma–Aldrich. 5,10,15,20(Tetra-4-*tert*-butylphenyl)-21H,23H-porphyrin were synthesized by Gruzdev [23].

Crystalline samples of (Cl)YbT'BuPP and (Cl)YbTPP were used for the 1.7 weight percentage water suspensions. There were no changes in the chemical composition of the solids during a microcalorimetric and DSC experiments, which was confirmed by spectrophotometry.

Equipment

Magnetocaloric effects of paramagnetics were studied in the temperature range from 278 to 340 K and at the magnetic inductions of 0.2, 0.4, 0.6, 0.8, and 1.0 T using the special calorimetric device, the isothermal-shell microcalorimeter, the shape and construction of which are detailed in the work [19]. The microcalorimetric cell full of ytterbium complex suspension together with the isothermal shell was placed in the gap of the electromagnet. Adiabatic conditions for magnetization process were achieved by rapid magnetic field changes. The temperature fluctuation of 0.0002 °C in the thermostatically controlled calorimetric cell space during the calorimetric experiment and the setup sensitivity of 2×10^{-5} K were maintained. The error in MCE measurements, which were repeated five times, did not exceed 2%.

Heat capacities with an error of about 2% were measured in zero fields by means of a 204 F1 Phoenix DSC calorimeter (NETZSCH, Germany). Heat capacities in magnetic fields were obtained by microcalorimetric experiment performed as described above. The UV-vis spectra were measured on Agilent 8453 UV-vis spectrophotometers; IR spectra were recorded on a VERTEX 80v spectrometer; mass spectra was performed on Shimadzu AXIMA Confidence mass spectrometer and ¹H NMR spectra were recorded on a Bruker AVANCE-500 spectrometer.

2.3. Calculation of thermodynamic parameters

The amount of heat Q_{MCE} (J/g), which was allocated because of the magnetocaloric effect in a magnetic material when magnetic field was switched on in the isothermal conditions, was calculated by Equation 1.

$$Q_{\rm MCE} = Q_{\rm J} \left(\Delta T / \Delta T_{\rm J} \right), \tag{1}$$

Here Q_J (J/g) is the Joule heat, injected in the calorimetric experiment, ΔT_J and ΔT are the values of the absolute temperature change of the calorimetric system resulting from injecting the Joule heat and the magnetic field change, respectively. The numerical MCE values, ΔT_{MCE} (K) were calculated by using the heat balance Equation (2) [24].

$$Q_{\rm MCE} = m_{\rm (M)} C_{p(\rm M)} \Delta T_{\rm MCE}$$
(2)

Here, ΔT_{MCE} is the temperature change that is MCE, $m_{(M)}$ (g) and $C_{p(M)}$ (J/g K) are the mass and specific heat capacity of the magnetic material. The enthalpy change, ΔH (J/mol), in the magnetic material resulting from the changes in the magnetic field was determined from the experimental values of Q_{MCE} .

The heat capacity of the samples in magnetic fields was experimentally determined using the same apparatus following known methods [25]. It was established that the heat capacity values of samples in zero field and in magnetic fields up to 1 T are close to or lie within the limits of experimental error. Therefore, the heat capacity of samples was measured in zero magnetic fields by the DSC method.

The values of changes in the entropy of the studied molecular magnetics in magnetic field, ΔS (J/g K) were calculated by Equation 3

$$\Delta S = -C_{p(M)} \,\Delta T_{MCE}/T \tag{3}$$

Here, $C_{p(M)}$ is the specific heat capacity, ΔT_{MCE} is the magnetocaloric effect; *T* is the absolute temperature.

RESULTS AND DISCUSSIONS

Chemical structure of ytterbium complexes

The molecular structure of synthesized (Cl)YbT^{t-}BuPP/(Cl)YbTPP strictly corresponds to the formulas (Scheme 1), which follow from the spectral UV-vis, IR, and MALDI-TOF MS data (see Experimental section, Figs 1 and 2 and Supporting information). UV-vis spectra of complexes conforming the ytterbium +3 oxidation



Fig. 1. UV-vis spectra of (Cl)YbT'BuPP (1–4) and (Cl)YbTPP (5) in CHCl₃. $C_{(Cl)YbT'BuPP}$ (1) 5.88·10⁻⁶, (2) 5.19·10⁻⁶, (3) 2.3 10⁻⁵, and (4) 1.73·10⁻⁵ mol/L. 1, 3 — initial, 2, 4 — after microcalorimetric experiment



Fig. 2. IR spectra of (Cl)YbT'BuPP (top) and (Cl)YbTPP (down) in KBr

degree are "normal type" [26] and are consistent with data in the literature [9]. The IR spectra clearly corresponds to the manifestation of the signals of ytterbium(III) complexes bonds and fragments including Yb-Cl and Yb-N. The studied complexes display ¹H NMR spectra typical of paramagnetic metal porphyrins [27]. Finally, the chemical structure is also confirmed by two signals in each



Fig. 3. Temperature dependencies of the specific heat capacity of the samples in a zero magnetic field. Sample 1 - (Cl) YbT'BuPP, Sample 2 - (Cl)YbTPP. (DSC data, with the experimental uncertainty 1.5%)

mass spectrum assigned to a single and doubly charged molecular ion (see Experimental section). The invariability of the samples after microcalorimetric experiments is confirmed by the data in Fig. 1 and Fig. S5. The work of extracting a sample from a sealed capsule after a DSC experiment is very laborious. In this case, it was not executed. However, it has been performed for many other samples, always showing immutability [28].

Specific heat capacity in solid

The temperature dependences of the specific heat capacity of the samples of the studied paramagnetics in zero magnetic fields are represented in Fig. 3.

The gradual increase in the (Cl)YbTPP C_p-T dependence is consistent with the corresponding MCE decrease (see below). A more complex view of this dependence in the case of (Cl)YbT'BuPP is not reflected in the corresponding MCE–*T* dependence of the same type on (Cl) YbT'PP (Figs 4 and 5 below). Therefore not high (Cl) YbT'BuPP curve maximum should be interpreted as a result of structure improvement in the solid with the temperature growth [29]. This may be due to the removal of voids and the associated increase in the regularity of the crystal structure of the ytterbium(III) complex. Unsubstituted (Cl)YbTPP does not display such behavior. Notice that the C_p values of both paramagnets differ little.

Magnetocaloric effect in paramagnetics studied

The field and temperature dependences of MCE in the studied molecular paramagnetics are shown in Figs 4 and 5 (for the MCE magnitude in (Cl)YbTPP as a function of both the magnetic field induction and the temperature see Fig. S6). Generally, the temperature dependence of MCE in (Cl)YbT'BuPP does not repeat straight-line temperature dependence of specific heat Q_{MCE} shown in Figs 6 and 7 below. These data show the presence of lattice contribution that was mentioned in the previous section in MCE (see Fig. 5 and Eq. 2).



Fig. 4. Magnitudes of the magnetocaloric effects in (Cl)Yb'BuTPP as functions of magnetic induction (a) and temperature (b). The experimental uncertainty of the MCE measurements was 2%



Fig. 5. Temperature dependencies of ΔT_{MCE} in the samples at changed magnetic field for B = 0.2; 1.0 T. Sample 1 — (Cl) YbT'BuPP, Sample 2 — (Cl)YbTPP. The experimental uncertainty of the MCE measurements was 2%

The experimental fact of positive room-temperature MCE in the samples of ytterbium(III) complexes shows that the paramagnetic nature of the Yb³⁺ ion is preserved in its tetrapyrrole complexes. They are also manifested in the typical NMR spectrum. The (Cl)YbT'BuPP MCE value is not high enough to be very promising in magnetic cooling practice but the paramagnetics we deal with have a set of other useful properties, namely, effective UV-vis absorption (see Experimental section) and nuclear magnetic resonance shift reagent properties [30, 31] reflected also in the (Cl)YbT'BuPP ¹H NMR spectrum in the downfield shift of tert-butyl group signals (see Experimental section). These are located at 1.62 ppm in the spectrum of uncoordinated H₂T'BuPP [31] but at 2.86 and 2.17 ppm in the spectra of paramagnetic Co^{II}T'BuPP and (AcO)Mn^{III}TAP(4-'BuPh)₈ (TAP is tetraazaporphin dianion), respectively [23, 32]. Simple 1 : 1 REE porphyrin complexes can be selected as half-sandwich precursors for countless homoleptic/heteroleptic bis/tris-complexes with both a single-molecule magnetism [33-38] and an optical activity [39]. Finally, REE porphyrins being solution-processed can be coated like the porphyrin *d*-metal complexes [40, 41]

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on metallic surfaces and magnetic nanoparticles (MNPs) comprising magnetite.

The highest room-temperature MCE values, 0.0046 and 0.028 K for (Cl)YbT'BuPP and (Cl)YbTPP, respectively, are obtained at the magnetic induction of 1.0 T and at the lowest temperature taken. The corresponding MCE values of 0.623, 0.449, and 0.281 K were earlier obtained respectively for Eu³⁺, Gd³⁺, and Tm³⁺ complexes of similar composition, (Cl)LnTPP (Ln is lanthanide ion) [15]. As it is known [42], elemental gadolinium and thulium are ferromagnetic, unlike paramagnetic europium and ytterbium. The picture changes in the case of their tetrapyrrolic complexes. The decrease of MCE in (Cl)YbTPP by an order of magnitude is logical but the higher MCE in (Cl)EuTPP within (Cl)LnTPP studied should be explained by regularities of its valence electron shell, $4f^65s^25p^6$ forcing conditions of Ln³⁺ — macrocycle dianion π interactions. Eu³⁺ and Yb³⁺ in the (Cl)LnTPP structure are similar to each other in the desire to complement their *f*-shell to stable $4f^7$ and $4f^{44}$, respectively due to a dative π bonding with the aromatic system of the macrocycle. This property was confirmed in many experimental facts united as "gadolinium fractures" on the dependence "composition-property" graphs. We have obtained [10, 43, 44] similar fractures examining the dependence of the kinetic stability constants for tetrapyrrole complexes on the serial number of the *f* element in the periodic table (for graphic representation of k - Zdependence see Fig. S7). However, a different situation of Eu and Yb in the lanthanide series leads to the opposite consequences of the mentioned π bonding in the magnetic behavior of their porphyrin complexes. The contribution to the (Cl)YbTPP spin state from the dative Yb-N π bonds is negative, unlike in the case of (Cl)EuTPP in which the spin improviement is achieved. Notice that such interaction does not appear in lanthanide non-cyclic ligand complexes whose magnetic behavior is determined by magnetic properties of one isolated Ln(III) ion and antiferromagnetic exchange couplings between the neighboring Ln(III) ions in the crystalline samples [45]. Thus, the use of the REE tetrapyrrole complexes is one of



Fig. 6. The (Cl)YbT'BuPP specific heat temperature dependencies at different magnetic fields showed in Fig.



Fig. 7. The specific heat temperature dependencies of samples for B = 0.2; 1.0 T. Sample 1 — (Cl)YbT'BuPP, Sample 2 — (Cl) YbTPP

the ways of the deriving molecular paramagnets with the controlled magnetic properties.

Thermodynamic parameters of ytterbium(III) complexes magnetization

Figures 6 and 7 represent the experimental temperature dependences of specific heat, Q_{MCE} , released by ytterbium(III) complexes due to MCE (for the temperature dependences of specific heat released by (Cl)YbTPP at different magnetic fields see Fig. S8).

The Q_{MCE} values grow with an increase in magnetic induction and decrease with a temperature rise. Higher Q_{MCE} values in (Cl)YbTPP compared with these in the *tert*-butyl-substituted analog correspond to the peculiarities in the MCE values (see Eq. 2).

The temperature dependences of the calculated enthalpy changes, ΔH (J/mol), under magnetization are shown in Figs 8 and 9. These values are the direct parameters for estimating the cooling capacity of magnets.

Comparative examination of temperature dependences of the specific heat, specific heat capacity and MCE in two ytterbium(III) complexes have shown the lattice and electronic contributions in MCE value due to the



Fig. 8. Temperature dependences of enthalpy change in (Cl) YbT'BuPP due to MCE in different magnetic fields



Fig. 9. Temperature dependences of ΔH in the samples at the magnetic field of 1.0 T. Sample 1 — (Cl)YbT'BuPP, Sample 2 — (Cl)YbTPP



Fig. 10. Temperature dependences of ΔS in the samples at the magnetic field of 1.0 T. Sample 1 — (Cl)YbT'BuPP, Sample 2 — (Cl)YbTPP

improvement of the crystalline structure when temperature grows and ytterbium–macrocycle spin density redistribution, respectively. To confirm these conclusions, we have explored the values of changes in the entropy of the studied molecular paramagnetics in the magnetic field, ΔS at different magnetic inductions and temperatures (Fig. 10). The straight lines represent temperature dependences of ΔS , as one would expect. These confirm the compensation effect from the lattice negative contributions decreasing with the temperature growth on a negative electronic contribution in MCE. The uncompensated electronic contribution in (Cl)YbTPP MCE being less than the one in (Cl)YbT'BuPP due to the *tert*-butyl groups absence is reflected in the ΔT_{MCE} - T/Q_{MCE} -T dependences which are a concave curve (Figs 5 and 7).

CONCLUSIONS

(5,10,15,20-tetra(4-*tert*-butylphenylporphinato)) and (5,10,15,20-tetraphenylporphinato)ytterbium(III) chlorides have been synthesized using porphyrin base coordination with ytterbium(III) chloride to investigate the presence of a room-temperature magnetocaloric effect and to observe practically useful thermodynamic parameters of their magnetization. Direct determination of MCE/magnetization thermodynamic parameters in aqueous suspensions and specific heat capacity in a solid for the ytterbium(III) complexes in comparison with the Eu^{III}, Gd^{III} and Tm^{III} analogs was performed by the microcalorimetric and DSC methods, respectively. tert-Butyl-substituted and unsubstituted tetraphenylporphyrin complexes display positive MCE of 0.0046 and 0.028 K at 278 K and magnetic induction of 1.0 T associated with the Yb^{III} spin state and redistribution of spin density between the spin carrier and the macrocycle π electron system. Lanthanide ion/macrocyclic peripheral substitution in the lanthanide porphyrins is useful as a way of improving magnetocaloric properties of molecular paramagnets of this class.

Acknowledgments

This work was carried out under partial financial support from the Russian Foundation for Basic Research (Project No. 16-03-00578-a and 18-43-370022-r-a) and from the Program of the State Academies of Sciences (Subject No. 0092-2014-0002 and 0092-2014-0003). This work was carried out with the help from the Centre for Joint Use of Scientific Equipment, The Upper Volga Region Center of Physicochemical Research, and from the PhD I. A. Khodov.

Supporting information

Figures S1–S8 and Tables S1 and S2 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

 Pushkarev VE, Tomilova LG and Nemykin VN. Coord. Chem. Rev. 2016; 319: 110–179.

- 2. Magnani N. Int. J. Quantum Chem. 2014; 114: 755–759.
- Ishikawa N, Sugita M, Ishikawa T, Koshihara S-Y and Kaizu Y. J. Am. Chem. Soc. 2003; 125: 8694–8695.
- 4. Wang H, Cao W, Liu T, Duan C and Jiang J. *Chem.* — *Eur. J.* (2013); **19**: 2266–2270.
- Kratochvílová I, Šebera J, Paruzel B, Pfleger J, Toman P, Marešová, Havlová Š, Hubík P, Buryi M, Vrňata M, Słota R, Zakrzyk M, Lančok J and Novotný M. Synth. Metals 2018; 236: 68–78.
- Biswas S, Bejoymohandas KS, Das S, Kalita P, Reddy MLP, Oyarzabal I, Colacio E and Chandrasekhar V. *Inorg. Chem.* 2017; 56: 7985–7997.
- Korolev VV, Lomova TN, Maslennikova AN, Korolev DV, Shpakovsky DB, Zhang J and Milaeva ER. J. Magn. Magn. Mater. 2016; 401: 86–90.
- 8. J. Jiang (Ed.) Functional Phthalocyanine Molecular Materials. Springer: Berlin Heidelberg, 2018.
- 9. Lomova TN, Axially coordinated metal porphyrins in Science and Application. URSS, 2018.
- Lomova TN, Andrianova LG and Berezin BD. *Zh. Fiz. Khim* [in Russian] 1987; 61: 2921–2928.
- 11. Lomova TN and Andrianova LG, *Russ. J. Coord. Chem.* 2004; **30**: 660–664.
- Lomova TN, Sokolova TN, Morozov VV and Berezin BD. *Koord. Khim.* 1994; 20: 637–640.
- Korolev VV, Lomova TN, Ramazanova AG, Korolev DV and Mozhzhukhina EG. J. Organomet. Chem. 2016; 819: 209–215.
- Korolev VV, Korolev DV, Lomova TN, Mozhzhukhina EG and Zakharov AG. *Rus. J. Phys. Chem.* (Russian) 2012; **86**: 504–508; (Engl. Transl.) 2012; **86**: 578–582.
- Lomova TN, Korolev VV and Zakharov AG. *Mater. Sci. Eng. B* 2014; **186**: 54–63.
- Korolev VV, Lomova TN, Ramazanova AG and Mozhzhukhina EG. Synth. Metals 2016; 220: 502–507.
- Korolev VV, Lomova TN, Ramazanova AG and Mozhzhukhina EG. *Mendeleev Commun.* 2016; 26: 301–303.
- Korolev VV, Lomova TN, Korolev DV, Ramazanova AG, Mozhzhukhina EG and Ovchenkova EN. In Advanced Environmental Analysis: Applications of Nanomaterials, Vol. 2. RSC Detection Science Series, Hussain CM and Kharisov CM. (Eds.) 2017, RSC Publishing: Cambridge, pp. 14–47.
- 19. Korolev VV, Korolev DV and Ramazanova AG. *J. Therm. Anal. Calorim.* 2018; **136**: 937–941.
- Anikin MS, Tarasov EN, Kudrevatykh NV, Osadchenko VH and Zinin AV. *Acta Phys. Pol.*, A 2015; 127: 635–637.
- Piskorsky P, Korolev DV, Valeev RA, Morgunov RB, Kunitsyna EI. Physics and Engineering of Permanent Magnets. Td. E.N. Kablov. Moskow: VIAM. (2018) [in Russian].

- 22. Oluwole D, Yagodin AV, Britton J, Martynov AG, Gorbunova YG, Tsivadze AYu and Nyokong T. *Dalton Trans.* 2017; **46**: 16190–16198.
- 23. Bichan NG, Ovchenkova EN, Gruzdev MS and Lomova TN. J. Struct. Chem. 2018; **59**: 711–719.
- 24. M. M. Popov. *Termometriya i Kalorimetriya*. Izdatel'stvo Moskovskogo Universiteta: Moscow, Russia, 1954 [in Russian].
- Ramazanova AG, Balmasova OV, Korolev DV and Korolev VV. In *Magnetite: Structure, Properties* and Applications. 2011, Nova Science Publishers Inc: New York, pp. 143–178.
- 26. Mack J and Stillman MJ. J. Porphyrins Phthalocyanines 2001; 5: 67–76.
- Walker FA. In Handbook of Porphyrin Science (Vol. 6). 2010, World Scientific Publishing Company, Singapore, pp. 1–337.
- Lomova TN, Korolev VV, Bichan NG, Ovchenkova EN, Ramazanova AG, Balmasova OV and Gruzdev MS. *Synth. Met.* 2019; 253: 116–121.
- 29. Gurek AG, Basova T, Luneau D, Lebrun C, Kol'tsov E, Hassan AK and Ahsen V. *Inorg. Chem.* 2006; **45**: 1667–1676.
- Horrocks WV and Wong C-P. J. Am. Chem. Soc. 1976; 98: 7157–7162.
- Mao J, Zhang Y and Oldfield E. J. Am. Chem. Soc 2002; 124: 13911–13920.
- Ovchenkova EN, Bichan NG, Kudryakova NO, Ksenofontov AA and Lomova TN. *Dyes Pigm*. 2018; 153: 225–232.
- Dey A, Kalita P, and Chandrasekhar V. ACS Omega 2018; 3: 9462–9475.
- 34. Gao F, Li Y-Y, Liu C-M, Li Y-Z and Zuo J-L. *Dalton Trans.* 2013; **42**: 11043–11046.

- Branzoli F, Carretta P, Filibian M, Zoppellaro G, Graf MJ, Galan-Mascaros JR, Fuhr O, Brink S and Ruben M. J. Am. Chem. Soc 2009; 131: 4387–4396.
- Chen Y, Liu C, Ma F, Qi D, Liu Q, Sun H-L and Jiang J. Chem. — Eur. J. 2018; 24: 8066–8070.
- Ishikawa N, Mizuno Y, Takamatsu S, Ishikawa T and Koshihara S. *Inorg. Chem.* 2008, 47: 10217–10219.
- Woodruff DN, Winpenny REP and Layfield RA. *Chem. Rev.* 2013; **113**: 5110–5148.
- Zhang X, Muranaka A, Lv W, Zhang Y, Bian Y, Jiang J and Kobayashi N. *Chem. — Eur. J.* 2008; 14: 4667–4674.
- Herper HC, Bernien M, Bhandary S, Hermanns CF, Krüger A, Miguel J, Weis C, Schmitz-Antoniak C, Krumme B, Bovenschen D, Tieg C, Sanyal B, Weschke E. Czekelius C, Kuch W, Wende H and Eriksson O. *Phys. Rev. B* 2013; 87: 174425 (15 pages).
- 41. Modisha P, Antunes E, Mack J and Nyokong T. *Int. J. Nanosci.*12 (2013) 1350010 (10 pages).
- Jensen J and Mackintosh AR. Rare Earth Magnetism Structures and Excitations. The International Series of Monographs on Physics, Berman J, Edwards SF, Llewellyn Smith CH and Rees M (Series Eds.) Clarendon Press: Oxford, 1991.
- Lomova TN and Klyueva ME. In *Encyclopedia* of Nanoscience and Nanotechnology, Vol. 2., Russian Academy of Sciences: Ivanovo, Russia, 2004, pp. 565–585.
- 44. Berezin BD and Lomova TN. *Dissociation Reactions of Complex Compounds*. Moscow: Nauka, 2007.
- 45. Yang F, Yang G-P, Wu Y, Yan Y, Liu J, Gao R, Zhang W-Y and Wang Y-Y. *J. Coord. Chem.* 2018; **71**: 2702–2713.