

Spectral manifestation of substitution of out-of-plane ligands in metallophthalocyanines

A. Starukhin^{1,*}, V. Knyukshto¹, A. Gorski², V. Chernii³, I. Tretyakova³, M. Kijak², and P. Kowalska²

¹B.I. Stepanov Institute of Physics, NAS of Belarus, Minsk, Belarus

²Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

³V.I.Vernadskii Institute of General and Inorganic Chemistry, NAS of Ukraine, Kyiv, Ukraine

Abstract. In our study, we demonstrate the splitting effect of long-wavelength bands in absorption spectra (excitation of fluorescence) of the series of Zn(II), Ti(IV), Zr(IV) and Hf(IV) phthalocyanines at low temperatures. The effect has been explained by the shift of metal ion out of the plane of phthalocyanine macrocycle, the transformation of macrocycle to nonplanar “dome” conformation and additional loss the high symmetry of macrocycle.

The molecules of metalloporphyrins and metallophthalocyanines belong to the high symmetry group D_{4h} and exhibit only two wide absorption bands in the visible spectrum range at ambient temperature. The long-wavelength band corresponds to the two doubly degenerate purely electronic transitions whilst shorter - to the transitions to the vibrational sublevels of these states [1]. In the case of metalloporphyrins, the double degeneracy of electronic transitions can be removed at low temperatures due to Jahn-Teller instability or a few others factors and the energy gap between the electronic states becomes higher than 100 cm^{-1} [2-4]. In this context, it seems quite interesting to investigate the splitting effects of long-wavelength bands in the absorption spectra of metallophthalocyanines containing ligands coordinated to the central metal atom and thus located out of the macrocyclic plane and compare the data with results gained for symmetrical metallophthalocyanines and metalloporphyrins. As a reference in our studies, symmetrical metallocomplex - Zn(II) phthalocyanine was selected. The phthalocyanines containing Zn(II), Ti(IV), Zr(IV) and Hf(IV) ions were studied in the current work. The structures of Zn tetra-tert-butylphthalocyanine ($t\text{-BuPcZn}$) and complex of Zr or Hf phthalocyanine with two out-of-plane dibenzoylmethanate ligands (PcMDbm_2) are presented on Fig. 1. The set of absorption and fluorescence excitation experiments of phthalocyanine metallocomplexes have been carried out at low temperatures (ranging from 9 to 77 K) in 2-methyltetrahydrofuran forming an optical transparent rigid glassy matrix at these conditions.

Upon the above-mentioned In the case of $t\text{-BuPcZn}$ the splitting of the long-wavelength band at 77 K was not so obvious. While, for compounds with out-of-plane ligands the

* Corresponding author: a_starukhin@mail.ru

splitting in the case of PcZrCl_2 has the value about 120 cm^{-1} , and reaches the maximum value (260 cm^{-1}) for PcZrDbm_2 metallocomplex (Fig. 2).



Fig. 1. Structure of 1-BuPcZn (1) and PcMDbm_2 ($M = \text{Zr}, \text{Hf}$) (2).

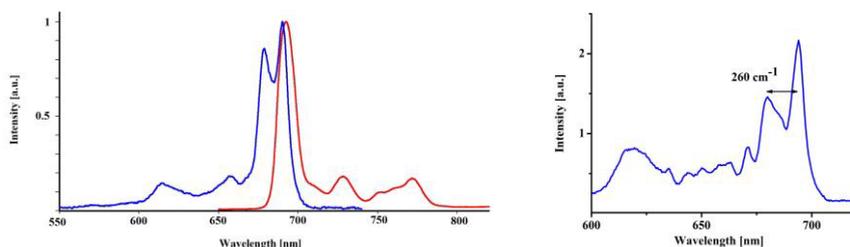


Fig. 2. Fluorescence excitation (blue) and emission (red) spectra of PcZrDbm_2 in 2-methyltetrahydrofuran at 77 K, left, and fluorescence excitation spectrum of PcZrDbm_2 at 9 K, right.

Quantum-chemical calculations, DFT methods implemented in Gaussian09 software package, were carried out for all metallocomplexes. The optimization of the molecular ground state geometry was performed using the B3LYP functional with SVP basis set. On the basis of the experimental data and molecular modeling results, we assume that the main reason for the splitting of the long-wavelength bands in the absorption spectra is the shifting of the metal ion out of the plane of the phthalocyanine macrocycle. According to calculations there is no out-of-plane shift in the case of PcZn , whereas for PcZrCl_2 and PcZrDbm_2 the shift value equals $1,03\text{ \AA}$ and $1,24\text{ \AA}$, respectively. For PcHfDbm_2 the values of calculated shift ($1,24\text{ \AA}$) and shift obtained from the analysis of X-ray structure ($1,194\text{ \AA}$) [5] are well correlated and support the accuracy of performed simulations.

The splitting of long-wavelength bands in the absorption spectra of metallophthalocyanines containing out-of-plane ligands is considered to be caused by the transition of macrocyclic core to the nonplanar “dome” conformation [4,6] and additional loss by macrocycle a fourfold symmetry.

This work was supported by the European Union’s Horizon 2020 research and innovation programme under grant agreement No 645628.

References

1. K.N. Solovyov, L.L. Gladkov, A.S. Starukhin, S.F. Shkirman, *The Spectroscopy of Porphyrins: Vibrational States* (Nauka i Technika, Moscow, 1985) (in Russian)
2. G. Jansen, M. Noort, *Spectrochim. Acta* **32**, 747 (1976)
3. A.S. Starukhin, A.M. Shulga, *Opt. Spectrosc.* **98**, 780 (2005)
4. V.N. Knyukshto, A.M. Shulga, E.I. Sagun, E.I. Zenkevich, *J. Appl. Spectr.* **65**, 900 (1998)
5. V. Chernii, I. Tretyakova, V. Bon, O. Severinovskaya, S. Volkov, *Dyes Pigm.* **94**, 187 (2012)
6. D.L.E. Cullen, F. Meyer, *Acta Crystallographica B* **32**, 2259 (1976)