

Optical Spectroscopy Revealing Unusual *Cis*-diprotonated Metallophthalocyanines

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Photophysical studies of protonation of a series of zinc and magnesium metallophthalocyanines non-peripherally substituted with various alkoxy groups (Fig. 1) revealed unusual behaviour of molecules containing magnesium ions, strongly contrasting with properties of their zinc analogues. Whereas protonation of the studied zinc metallophthalocyanines lead to a bathochromic shift of their absorption and fluorescence spectra and shortening of their fluorescence lifetimes to a degree reflecting the number of attached protons, shifts of the spectra of the magnesium derivatives and changes of their fluorescence lifetimes are a non-monotonic function of the protonation degree: the bathochromic shift of the doubly protonated form is smaller than that of the monoprotected one (Fig 2). Similarly, the fluorescence lifetime of the doubly protonated magnesium derivative is longer than that of its monoprotected form. This observation can be explained in terms of the four-orbital Gouterman model by formation of the *cis*-diprotonated form of the doubly protonated molecule (with protons attached to adjacent bridging nitrogen atoms) [1]. Such a protonation pattern is untypical for metallophthalocyanines and observation of a *cis*-diprotonated form has not been reported in the past.

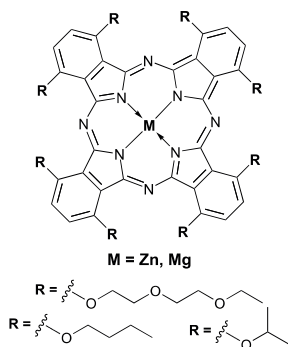


Fig. 1. Structures of studied metallophthalocyanines.

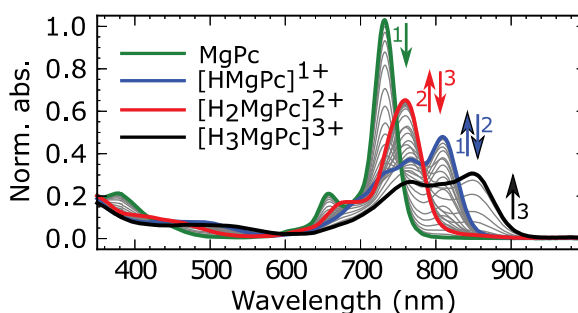


Fig. 2. Changes of absorption spectra of a magnesium metallophthalocyanine nonperipherally substituted with trioxanonyl groups observed during titration with acid.

REFERENCES

1. P. Kasprzycki, L. Sobotta, S. Lijewski, M. Wierzchowski, T. Goslinski, J. Mielcarek, C. Radzewicz, P. Fita, *Phys. Chem. Chem. Phys.* 2017, **19**, 21390-21400.