### Accepted Manuscript

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S0010-8545(15)30101-6
http://dx.doi.org/doi:10.1016/j.ccr.2015.12.011
CCR 112180
Coordination Chemistry Reviews
1-12-2015
20-12-2015

Please cite this article as: O. Horváth, Z. Valicsek, M.A. Fodor, M.M. Major, M. Imran, G. Grampp, A. Wankmüller, Visible light-driven photophysics and photochemistry of water-soluble metalloporphyrins, *Coordination Chemistry Reviews* (2016), http://dx.doi.org/10.1016/j.ccr.2015.12.011

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## ACCEPTED MANUSCRIPT

Visible light-driven photophysics and photochemistry of water-soluble metalloporphyrins

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#### **Highlights:**

- Cationic Mn(III), Co(III) and Ni(II) porphyrins show characteristic fluorescence
- Their long-lived triplet excited states play key roles in photocatalytic systems
- Anionic Ln(III) mono- and bisporphyrins exhibit similar photoinduced properties
- Their photolysis at the Soret-band produces a radical type intermediate
- However, during their irradiation at the Q-bands, a stable photoproduct appears

#### Abstract

Metal ions can form normal (in-plane) metalloporphyrins, fitting into the central hole of the porphyrin ring, or several of them are located out of the ligand plane, resulting in sitting-atop (SAT) complexes. Kinetically inert water-soluble complexes of Mn(III), Co(III), and Ni(II) with 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin display a weak, short-lived fluorescence. This can be affected by elongation of the alkyl substituent and using micellar environment in the case of Mn(III) porphyrins. In the presence of a suitable electron donor (triethanolamine, TEOA) and acceptor (methylviologen,  $MV^{2+}$ ), these metalloporphyrins proved to be efficient photocatalysts transferring electrons between the ground-state donor and acceptor via outer-sphere mechanism. In these systems triplet excited-state Mn(III) and Co(II) porphyrins are dynamically quenched with TEOA. The Mn(II) and Co(II) complexes formed in this way need also photoexcitation for the transfer of electron to the ground-state

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