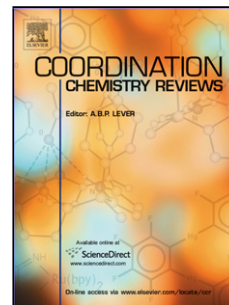


Accepted Manuscript

Title: Metallocenes Meet Porphyrinoids: Consequences of a “Fusion”

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PII: S0010-8545(15)00055-7
DOI: <http://dx.doi.org/doi:10.1016/j.ccr.2015.02.005>
Reference: CCR 112015

To appear in: *Coordination Chemistry Reviews*

Received date: 14-11-2014
Revised date: 5-2-2015
Accepted date: 8-2-2015

Please cite this article as: A. Vecchi, P. Galloni, B. Floris, S.V. Dudkin, V.N. Nemykin, Metallocenes Meet Porphyrinoids: Consequences of a “Fusion”, *Coordination Chemistry Reviews* (2015), <http://dx.doi.org/10.1016/j.ccr.2015.02.005>

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In this review, we discussed historic as well as recent developments in the chemistry and potential applications of metallocenyl-containing porphyrins, their analogues, BODIPYs, and azaBODIPYs reported between 1977 and mid 2014. Synthetic pathways for preparation of metallocenyl-containing porphyrinoids with σ -bonded in η^1 -fashion and π -bonded in η^5 -, and η^6 -fashion organometallic substituents are highlighted in details. Compounds with metallocenyl substituents directly connected to the aromatic core as well as systems in which organometallic substituents connected to the core ligand via spacer are discussed. Redox-, and photophysical properties of these systems were highlighted in conjunction with their potential application in molecular electronics, light-harvesting, sensor devices, and photocatalysis. Although the first report on ferrocenyl-containing porphyrins is dated back to 1977, the general field of metallocenyl porphyrins and their analogues is still under development. Recent emerging of the ferrocene-containing BODIPY and azaBODIPY systems also opens a large number of exciting opportunities in fundamental and applied research. Electron-transfer processes in metallocenyl-containing donor-antennae or donor-antennae-acceptor dyads and triads could easily result in formation of the charge-separated states useful in light-harvesting. Long-range metal-metal coupling between metallocenyl substituents allows to generate and to study the mixed-valence states and electron-migration in porphyrinoids could result in potential use of these systems in molecular information storage and photocatalysis. Redox-switchable fluorescent quenching opens a new area of oxidation-controlled imaging with potential applications in industry, environmental monitoring, and medicine. Although at this moment, it is not clear whether or not metallocenyl-containing porphyrins and their analogues could be able to emerge to our everyday life and solve some fundamental problems, it is clear that these systems have potential to do so.

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