

Molecular Brake Based on the Zn(II) Porphyrin Dimer: Dynamic Behavior in Solution and Ultrathin Films

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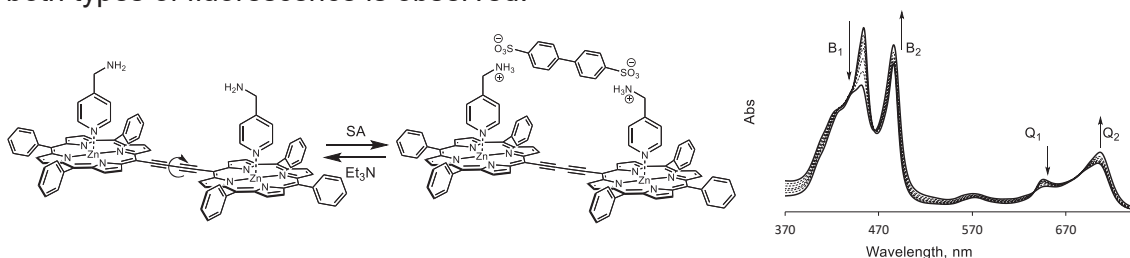
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Various types of covalently bonded dimers, trimers and oligomers based on porphyrin backbone are of interest due to their ability to form extremely large π -conjugated systems and, therefore, to display charge, energy and electron transfer properties. Optical properties of such systems usually are different from the corresponding monomers. Interestingly, UV-Vis spectra of the some mentioned systems are sensible to their geometry.¹

Herein we describe a porphyrin dimer molecule containing two macrocycles interconnected by a butadiyne bridge, that allows them flipping around the axis of the linker. Dimer solution in dichloromethane is a mixture of conformers with different dihedral angles between porphyrin rings and, consequently, different degree of π -conjugation. It has a great influence on a UV-Vis spectrum of the dimer. Adding of a bidentate “handle” molecule or matched sulfonic acid/triethylamine combination hinder flipping process, that can be monitored by UV-Vis spectroscopy (Scheme 1). Surprisingly, it does not influence on luminescence spectra, since only orthogonal and planar conformers emit after excitation.² Excited planar form has lower energy, therefore, ‘orthogonal emission’ was observed at low temperatures or if dimer is chemically locked in this position.³ However, we found that close packing of Langmuir-Blodgett films, composed of dimer molecules, also hinder the flipping process so, that both types of fluorescence is observed.



Scheme 1. Switching of the dimer with sulfonic acid/triethylamine system (left) monitored by UV-Vis spectra (right) in dichloromethane solution.

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References

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