Structural design of porphyrin dimers using lacunary polyoxometalates and their photocatalysis

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Cofacial porphyrin dimers exhibit unique photophysical and catalytic properties derived from the arrangement of porphyrins.[1] However, conventional porphyrin dimers bridged by organic linkers or metal-ion linkers have faced challenges in achieving precise control of key structural parameters, such as lateral and rotational displacements, interfacial distance and in addressing stability issues.[2] Herein, we present a novel strategy for engineering the structures, photophysical and photocatalytic properties, and stability of cofacial porphyrin dimers by using lacunary polyoxometalates as linkers.

Hybrid **II**, formed through self-assembly of two 5,10,15,20-tetra(4-pyridyl)porphyrin molecules and four divacant $[SiW_{10}O_{36}]^{8-}$ units, exhibited a rotationally displaced but non-laterally displaced structure with an interfacial distance of 3.6 Å. In contrast, we have recently reported that a hybrid **I**,[3] which was obtained using the same polyoxometalate but with a different coordination mode, featured lateral displacement without rotation and a shorter interfacial distance (3.4 Å). Replacing $[SiW_{10}O_{36}]^{8-}$ with trivacant $[SiW_9O_{34}]^{10-}$ yielded hybrid **III**, which featured an extended interfacial distance (6.5 Å) and greater rotation. The Soret band of hybrid **II** was blue shifted compared to hybrid **I**, **III**, and free porphyrin. The Q band and fluorescence peak of hybrid **II** exhibit the most pronounced red shift. These significant changes in optical properties of hybrid **II** were likely induced by the strong π–π interactions between the porphyrins due to its tightly stacked porphyrin configuration. Furthermore, hybrid **II** exhibited enhanced resistance to $^1O_2$-induced degradation owing to the strong π–π interactions.

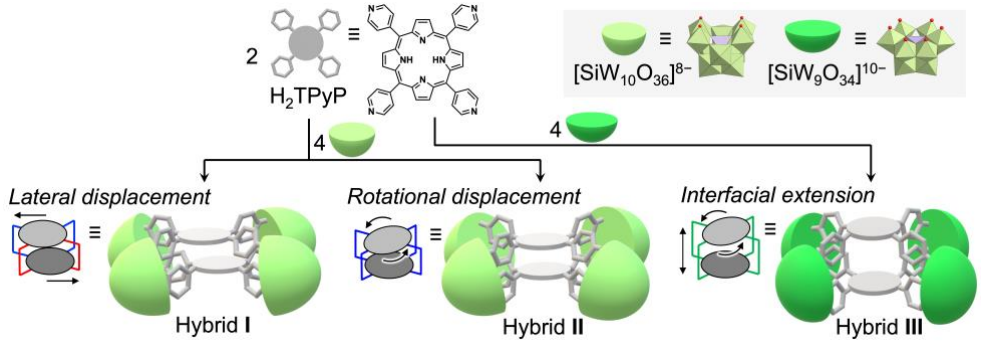

Figure 1. Schematic depiction for engineering cofacial porphyrin dimers using POM.

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