π-Extended Porphyrins

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π-Extended porphyrin systems have been studied extensively with regard to their application to materials science. A number of optical applications necessitate that the dye absorbs far into the red region. Modifications to the porphyrin periphery to accommodate this condition can be achieved by extending the conjugation of the porphyrin π-system, which will cause a bathochromic shift in the absorption spectrum.[1,2] To further enhance the applicability of porphyrins for these processes, near-infrared absorption and large two-photon absorption (2PA) cross-section values are desirable. With photomedicine, as there is a wavelength dependency of the penetration of light through biological tissues, porphyrins with enhanced π-conjugation are necessary for deeper targeting as these will have a bathochromic shift in their absorption profiles and should display superior 2PA.

The extension of the porphyrin π-system can be achieved via the generation of conjugated and triply-linked polyporphyrins, or from the synthesis of monomeric porphyrins containing exocyclic rings, such as pyrylium salts. Triply-linked porphyrin arrays can be synthesized in excellent yields from monomeric precursors, via cationic radical coupling and exhibit a substantial red shift in absorption.[3] Their applicability, however, for use in optoelectronics is hindered due to their short lived excited states. Alternatively, cycloaddition reactions on monomeric porphyrins are widely known, generating perturbed macrocycles, also showing enhanced photophysical properties.[4] The resulting product causes a significant distortion of the porphyrin macrocycle. Tetrapyrroles with exocyclic rings have biological significance but in spite of this synthetic derivatives of such are not that common. Resulting from the perturbation of the macrocycle and the extension of π-conjugation in the case of porphyrin arrays, these species exhibit a bathochromic shift in their absorption profiles. These materials should thus exhibit utility in photomedicine and as novel optical materials which can mimic natural systems.

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