Engineering conjugation in *para*-phenylene-bridged porphyrin tapes.

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Streszczenie

We report the synthesis of 7 new para-phenylene-bridged zinc porphyrin dimers, five of which were characterized by single-crystal X-ray analysis. A variety of links were tested for holding the paraphenylene bridges in p-conjugation with the porphyrins, and the natures of these restraining links strongly influence the properties of the porphyrin dimers. The keto-linked dimer exhibits a long-lived singlet excited state and strong fluorescence at 960 nm (1.7% quantum yield) in contrast to most previously reported conjugated porphyrin tapes, which are essentially non-emissive. Replacement of the cross-conjugated keto links by directly conjugated C–C bonds eradicates the fluorescence and shifts the absorption maximum to 1077 nm. On the other hand, replacement of the keto links with nonconjugated CPh2 links confers fluorescence at 736 nm (10% quantum yield) and results in remarkably similar one- and two-photon absorption behavior to that of meso–meso ethynylene-bridged porphyrin dimers (peak two-photon cross section: 7,300 GM at 878 nm). Cross-conjugated keto links do more than just hold the para-phenylene bridge coplanar with the porphyrins; they reduce the HOMO– LUMO gap, although to a lesser extent than direct p-conjugated links. Planarized para-phenylenebridged porphyrin dimers provide insights into the relationship between previously investigated classes of conjugated porphyrin oligomers, and they open up possibilities for the synthesis of new types of near-IR two-photon absorbing dyes.