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Synthesis and spectral properties of aromatically π-extended coumarin-fused *meso*-tetraphenylpyridoporphyrins

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An annulative π-extension of porphyrins has been accomplished by a reaction of copper(II) 2-amino-5,10,15,20-tetraphenylporphyrin with aromatic aldehydes and 4-hydroxycoumarin in the presence of a stoichiometric amount of trichloroacetic acid in *o*-dichlorobenzene at reflux temperature under one-pot operation. The resulting π-conjugated copper(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins are obtained in 56–66% isolated yields after chromatographic purification and characterized on the basis of spectral data analysis. These newly constructed copper(II) coumarin-fused pyridoporphyrins undergo demetallation in the presence of sulfuric acid in chloroform to produce free-base porphyrin analogues which on zinc insertion using $Zn(OAc)_2$ in $CHCl_3$-MeOH afford zinc(II) coumarin-fused *meso*-tetraphenylpyridoporphyrins in good yields. After structural identification, the photophysical characteristics of pyridoporphyrin macrocycles have been analysed by using UV-Vis spectroscopy. The preliminary results reveal a remarkable bathochromic shift in the electronic absorption spectra of coumarin-fused *meso*-tetraphenylpyridoporphyrins in contrast to the non-π-extended *meso*-tetraphenylporphyrin macrocycles.

Keywords: Absorption spectra, Bathochromic shift, π-Extension, One-pot synthesis, Pyridoporphyrins