# J-aggregate formation in bis-(4-carboxyphenyl)porphyrins in water:pH and counterion dependence

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## SUPPORTING INFORMATION

***Synthesis of meso-carboxyphenylporphyrins MCPP, DiCPP-opp*** *and **DiCPP-adj.*** Porphyrins **MCPP**, **DiCPP-opp** and **DiCPP-adj** were obtained according to literature crossed Rothemund procedures (Rocha Gonsalves et al, *J. Heterocycles Chem.*, **1991**, *28,* 635-640) by adding adequate amounts of the appropriate benzaldehydes (benzaldehyde and 4-carboxybenzaldehyde for MCPP, benzaldehyde and 4-carboxymethylbenzaldehyde for **DiCPP-opp** and **DiCPP-adj)** and pyrrole to a refluxing mixture of glacial acetic acid and nitrobenzene. After refluxing the reaction mixture for 1 hour and removal of solvents under reduced pressure, the porphyrinic rich crude material was taken into chloroform and directly chromatographed on a silica column. This procedure provided **MCPP** directly. The synthesis of **DiCPP-opp** and **DiCPP-adj**, require preparative TLC to separate the isomeric porphyrins 5,10-bis(4-carboxymethylphenyl)porphyrin and 5,15-bis(4-carboxyphenylmethyl)porphyrin. Further alkaline hydrolysis provided the **DiCPP-opp** and **DiCPP-adj** in essentially quantitative yields. All the porphyrins studied were fully characterized by NMR and mass spectrometry (MALDI) techniques.

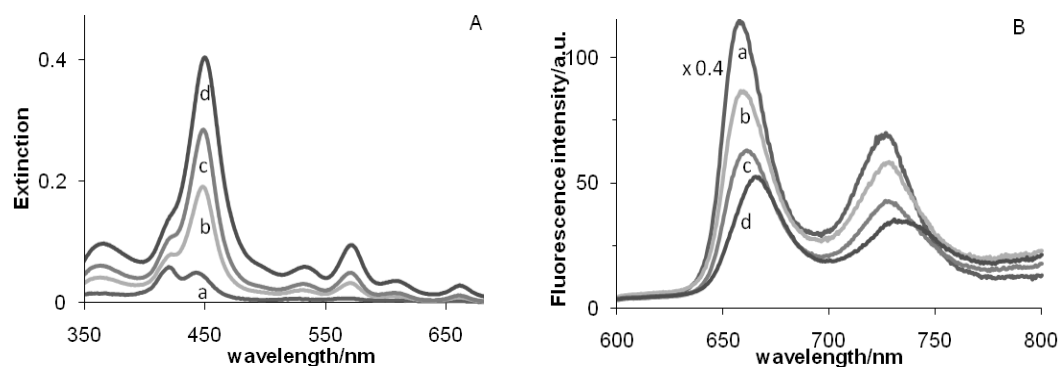*Additional optical and kinetic data of DiCPP-opp and DiCPP-adj.*



**Figure S1** – **A)** UV-Vis spectra and **B)** fluorescence emission spectra of different concentrations of **DiCPP-opp** in aqueous solution at pH=12: a) 1μM; b) 2 μM; c) 3 μM; d) 5 μM; $\lambda_{ex}$=446nm.
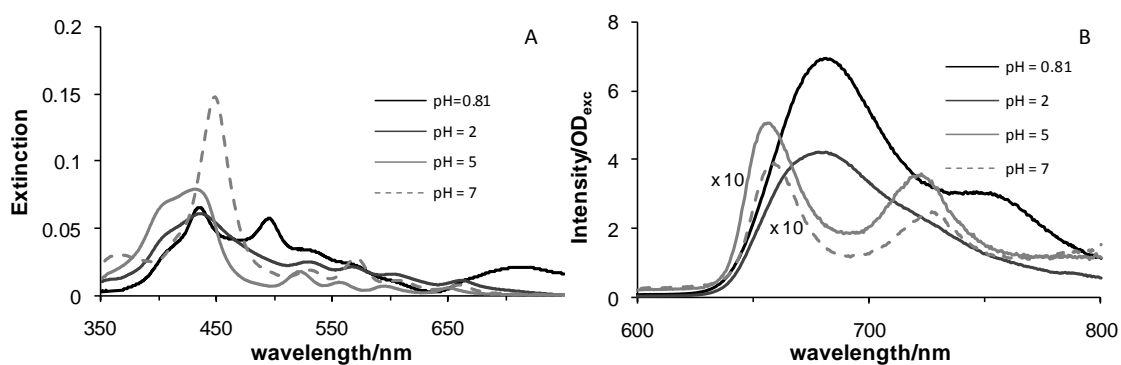


**Figure S2 -** UV-Vis (A) and fluorescence emission (B) spectra of **DiCPP-opp** (5 μM) in aqueous solution at different pH ($\lambda_{exc}$=446 nm).
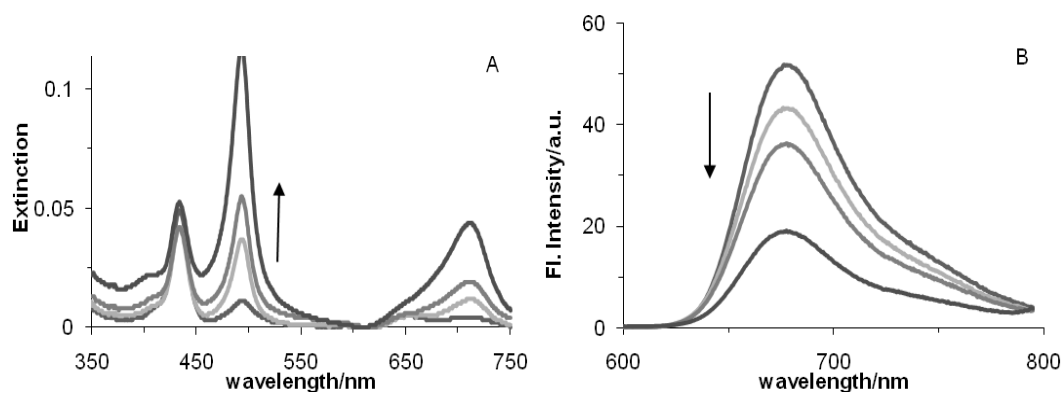
**Figure S3** – **A**) UV-Vis spectra and **B**) fluorescence emission spectra of **DiCPP-adj** in aqueous $HNO_3$ (pH=0.8) obtained at different porphyrin concentrations (1 – 5 μM); $\lambda_{ex}$=436 nm.
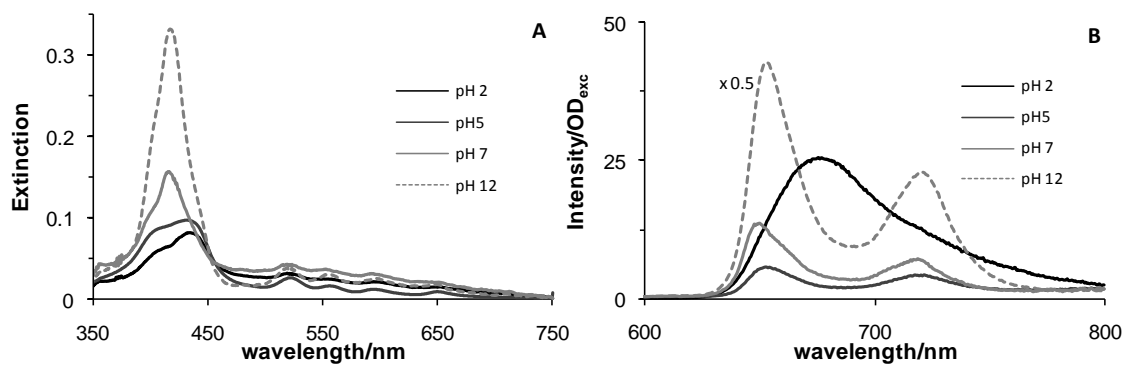


**Figure S4 -** UV-Vis (A) and fluorescence emission (B) spectra of **DiCPP-adj** (5 μM) in aqueous solution at different pH ($\lambda_{exc}$=436 nm).
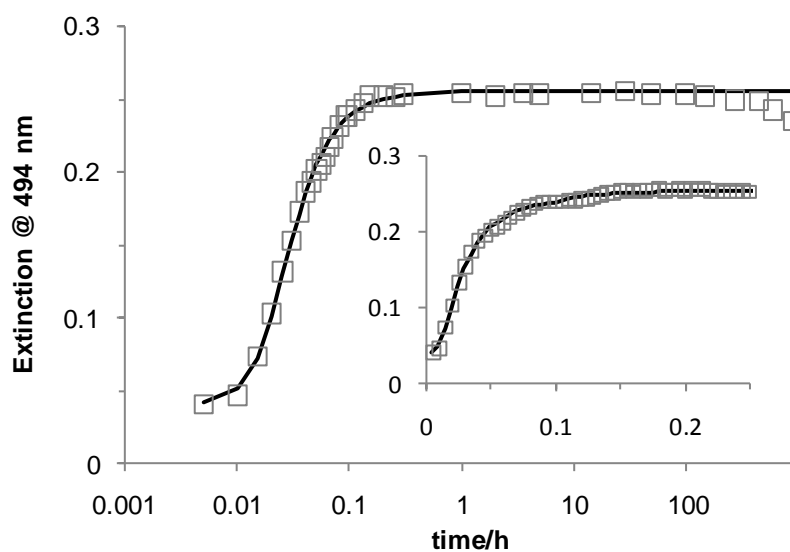
**Figure S5**– Kinetic profile for the aggregation of **DiCPP-adj** (5 μM) in aqueous solution at pH=0.8 (HNO$_3$): data (squares) and fit (line) obtained using eq. 6 of REF: R. F. Pasternack, C. Fleming, S. Herring, P. J. Collings, J. de Paula,G. De Castro and E. J. Gibbs, *Biophys. J.,* 2000, **79**, 550-560. Inset: Magnification of early times at linear scale.