*Supplementary Information*

# Controlling macromolecular superstructures of AIE-active porphyrin by manipulating *p*H in water

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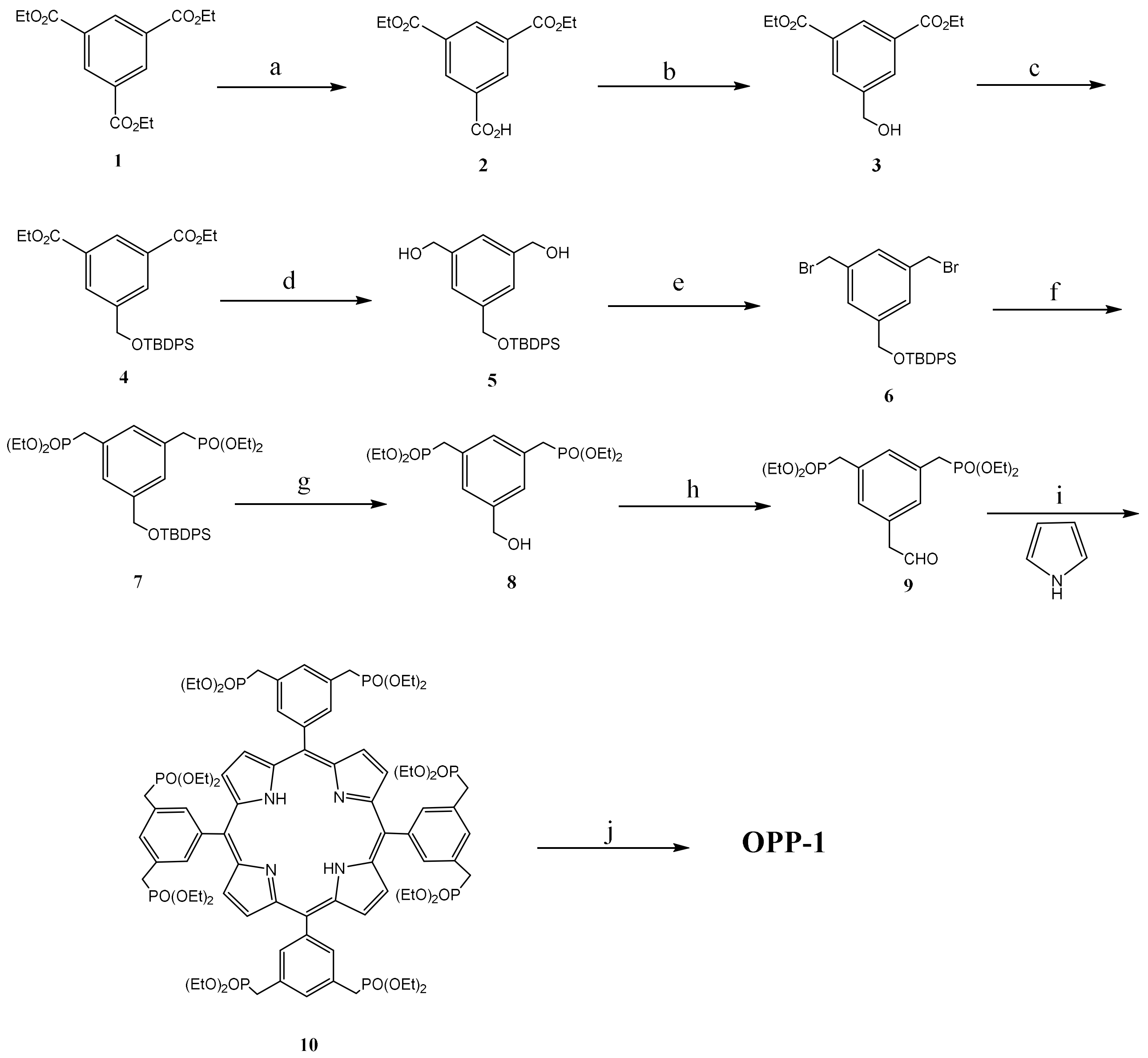
## Experimental Section

### 1. OPP-1 synthesis

Synthesis and characterization of **OPP-1** were prepared in nine-steps with overall yield 21%, following our previous work. [S1]. The synthesis approach toward **OPP-1** starts by the commercially available **1** (triethyl benzene), which undergo a mono deprotection of easter group using KOH to afford **2** (3,5-bis(ethoxycarbonyl)benzoic acid), followed by a reduction reaction of carboxylic acid to alcohol group as seen in compound **3**. Protection of a mono alcohol group was obtained using tert-butyldiphenylsilyl chloride (TBDPSCl), following by reduction of other two easter group with lithium aluminum hydride (LAH) reagent to have **5**. Diphosphonate ethyl ester **7** was obtained in high yield (over 70 %) in two steps; bromination of two alcohol groups using carbon tetrabromide in diethyl ether to obtain **6** first, then a treatment with triethyl phosphite at 120 °C was done to afford **7**. Removing the protection group of TBDPS by react with tetrabutylammonium fluoride (TBAF) followed by oxidation of alcohol group using a reagent of pyridinium chlorochromate (PCC) to obtain a corresponding aldehyde **9**. The step of forming the porphyrin macrocycle was done by the reaction of freshly prepared **9** with an equimolar amount of pyrrole using $BF_3 \cdot OEt_2$, followed by addition of *p*-chloranil to gain octa ethyl ester porphyrin **10**. The last step is to deprotect the octa ethyl easter group using trimethylsilyl iodide (TMSI) to successfully form the targeted macrocyclic porphyrin **OPP-1** as seen in scheme 1.



**Scheme 1.** Synthesis of octaphosphonate porphyrin **OPP-1**. Reagents and conditions used in scheme are: (a) KOH, EtOH/THF, 12 h; (b) $BH3\cdot(CH_3)_2S$, 0 to 60 °C, $N_2$, overnight, THF; (c) TBDPSCl, DMAP, Py, 0 °C to rt, 24 h, DCM; (d) LAH, $N_2$, 3 h, THF; (e) $PBr_3$, diethyl ether, 0°C to rt, 4 h; (f) triethyl phosphite, 120 °C, 12 h; (g) TBAF, THF, rt, overnight; (h) PCC, DCM, at rt, 2 h, (i) $BF_3\cdot OEt_2$, DCM, at rt, 14 h, *p*-chloranil 2 h; (j) TMSI ,$CHCl_3$,–40 °C to rt, 1 h.

## 2. Standard solution of OPP-1

Stock solutions (conc. $1x10^{-3}$ M) of **OPP-1** were made in water at pH 7.0 solution. For spectral measurements, this solution was injected into each time with 2 mL of water (varying pH) in a cuvette by micropipette.

## 3. Study of UV-vis absorption and fluorescence spectroscopy

Stock solutions ($\sim 1x10^{-3}$ M) of **OPP-1** were prepared in water (pH = 7.0). A 0.2 mL aliquot of the stock solution was transferred to several different volumetric flasks in water at varying pH 3-11) and made each of 2 mL volume with addition of water (with maintaining pH values). The solutions were allowed to equilibrate for 2 h prior to the spectroscopic measurements. The most prominent features are a reduction in the peak intensity along with a significant red shift of the absorption maximum and a loss of the fine structure.

## 4. Scanning Electron Microscopy (SEM) analysis of OPP-1

The samples were characterized using a Scanning Electron Microscopy (SEM) using FEI Quanta 200 SEM (Royal Melbourne Institute of Technology (RMIT) University, Melbourne, Australia) operated at high voltage (HV) of 30 kV. Probes on silica wafer coating of **OPP-1** for enhanced reflectivity (NSC15/AIBS), with a typical resonance frequency of 325 kHz and a force constant of 40 N/m, were used for microscopy imaging. Sample on silica wafer surface of **OPP-1** were prepared by spin-coating the freshly prepared solution ($1x10^{-4}$ M in water, at varying pH = 3.0 to 11.0) by silica coating at 2000 rpm and the solvent was allowed to bloated by filter paper before introduction into the vacuum system. Upon spin-coating and after few waiting for 2h remaining aqueous solution was removed by tapping with filter paper and images were collected. The width and length were accomplished by measure in micrometre of assembled supramolecules of **OPP-1**.

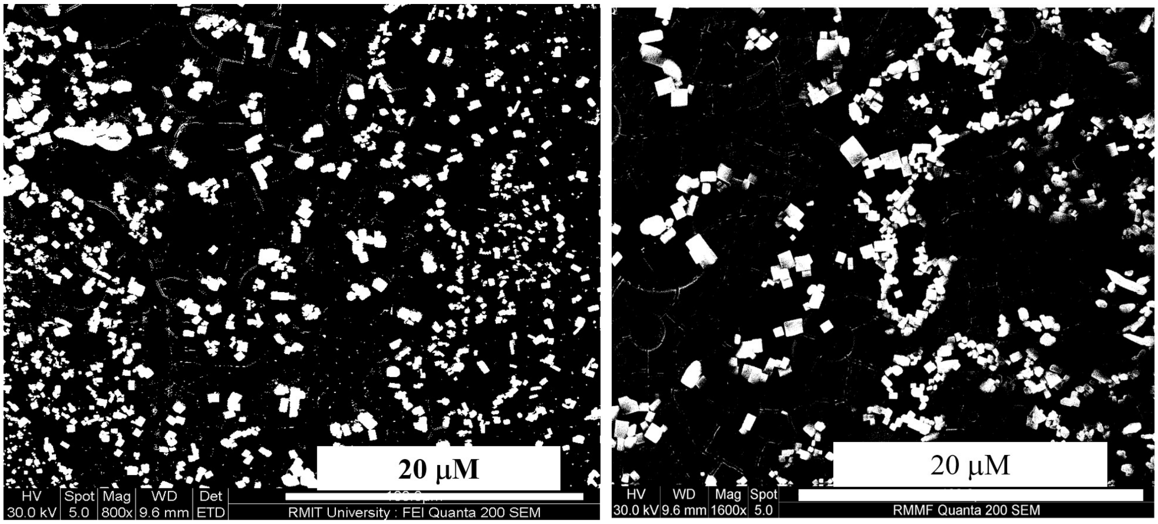


**Figure S1.** SEM micrograph of **OPP-1** in aqueous medium: (a) at pH = 4.0 and pH = 3.0, respectively, in these aqueous medium, one can clearly see micellar rod-like structures tend to combine together to produce dense rod-like morphology.

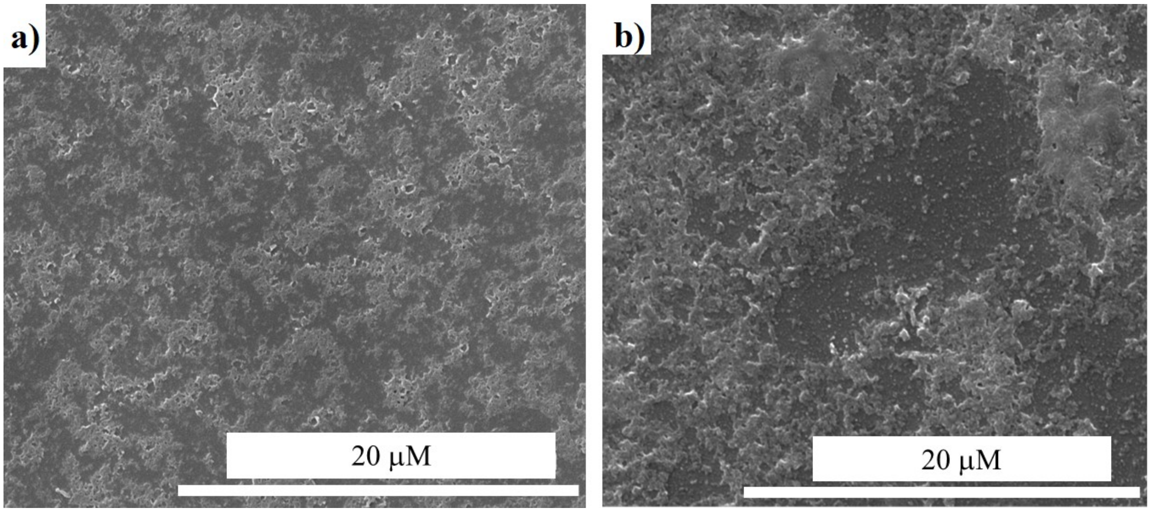


**Figure S2.** SEM images of **OPP-1** ($10^{-4}$ M) from aqueous medium by spin-cast on silicon wafer plate after removing excess water by filter paper. In both the basic pH's = 11 and 10, micellar worm-like structures tend to united together to produce dense morphology.

## Reference

S1. S. V. Bhosale, M.B. Kalyankar, S. V. Bhosale, S.J. Langford and R. Oliver, *Eur. J. Org. Chem.* **2009**, 4128-4134.