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

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Supramolecular superstructures are controlled by *p*H dependent self-assembly of octaphosphonatetetraphenyl-porphyrin-**1** (**OPP-1**) in aqueous solution. UV-Vis absorption spectroscopy shows decreasing in the intensity of **OPP-1** in the *p*H range 3.0 to 6.0, which is correlated to *H*-type aggregates. However, absorption shifts to bathochromic (red-shift) under the influence of *p*H 8.0-11.0 range, which is typical for a *J*-type aggregate in absorbance spectrum as a result of supramolecular self-organisation constructed as compared to free **OPP-1** (molecules transitioned to a monomeric positions). In these, the **OPP-1** aggregated outside the surface *p*H 8.0-11.0 range is similar to growth of worm-like micelles. However, at *p*H range 3.0-6.0, **OPP-1** is aggregated inside the surface. Self-assembled **OPP-1** have been visualised on silicon wafer by Scanning Electron Microscopy (SEM), and it clearly shows that petite rod-like aggregates are formed at *p*H 5.0 and 6.0. Interestingly, **OPP-1** assemble into directional growth to produce worm-like micelle aggregates at *p*H 8.0 and 9.0, respectively. The main driving force of assembled supramolecules are basically based on *H*-bonding and stacking between central core of porphyrin. Finally, Dynamic Light Scattering (DLS) study supports mode of aggregation of short rods and growth of worm-like micelles in basic *p*H and X-ray diffraction (XRD) study clearly demonstrates that self-assembled structures are crystalline in nature. This interesting *p*H-dependent self-assembly phenomenon is based on **OPP-1** (synthetic analogue to natural occurring porphyrins) and can provide basis for development of novel conducting materials as well as biomaterials in the future.

Keywords: Supramolecular structures, Worm-like micelles, AIE-active aggregates, Scanning Electron Microscopy, Dynamic Light Scattering, X-Ray diffraction