

Supporting Information

Experimental

Materials

All reagents and dry solvents were purchased from Sigma-Aldrich chemical company (Bangalore, India) and used as such without further purification. All solvents were purchased from SD fine chemicals, India and purified by standard methods.

Standard Porphyrin Solution. *meso*-(octaphosphonate) tetraphenyl porphyrin (OPTPP) (0.1 mM) was dissolved in mili-Q water.

Instrumentation

UV-vis Absorption Spectroscopy. UV-vis spectra were recorded on a SHIMADZU UV-vis spectrophotometer. Infrared observations were measured using PERKIN ELMER FT-IR spectrometer. Scanning electron microscopy studies were examined by S-3000N HITACHI. Stock solutions (0.1 mM) of OPTPP were made in water (pH 7.0). A 0.2 mL aliquot of the porphyrin stock solution was transferred to volumetric flask and made each of 2 mL volume. The solutions were allowed to equilibrate for several minutes upon addition of arginine prior to the spectroscopic measurements.

Fluorescence Spectroscopy. The solutions are prepared using above procedure. The solutions were excited at 418 nm wavelength.

Circular Dichroism Spectroscopy. CD spectra were measured on an AVIV 202 CD spectrometer under a nitrogen atmosphere. Experiments were performed in a quartz cell with a 1 mm path length over the range of 350-600 nm at room temperature.

Scanning Electron Microscopy. SEM images were recorded using S-3000N HITACHI to investigate the morphology of the self-assembled materials. In these examination droplets of the aqueous solution of OPTPP: L-, or D-Arg complex was placed on silicon wafer and left to dry for 30 min then coated with gold before measurements. All air dried samples were subjected to investigate morphology of self-assembled structures.

UV-vis absorption of OPTPP with D-Arg: The UV-vis absorption spectra of OPTPP in water solution at room temperature exhibit an intense band at 440 along with four typical Q-bands at 516, 558, 602 and 655 nm. The UV-vis titration of OPTPP with D-Arg resulted in significant spectral changes in the absorption bands, typically absorption of OPTPP Soret band at 440 nm decreases and at the same time an increase in peak intensity of shoulder component at 418 nm in addition along a new peak appeared at 660 nm, which may be due to upon addition of a arginine (the chiral inducer acting as a base) which making strong H-bonding between phosphonic acid of porphyrin and amino group of arginine. The 22 nm blue shift in the Soret band along with clear isosbestic point at 429 nm, clearly indicate an H-type aggregate within the assembly.

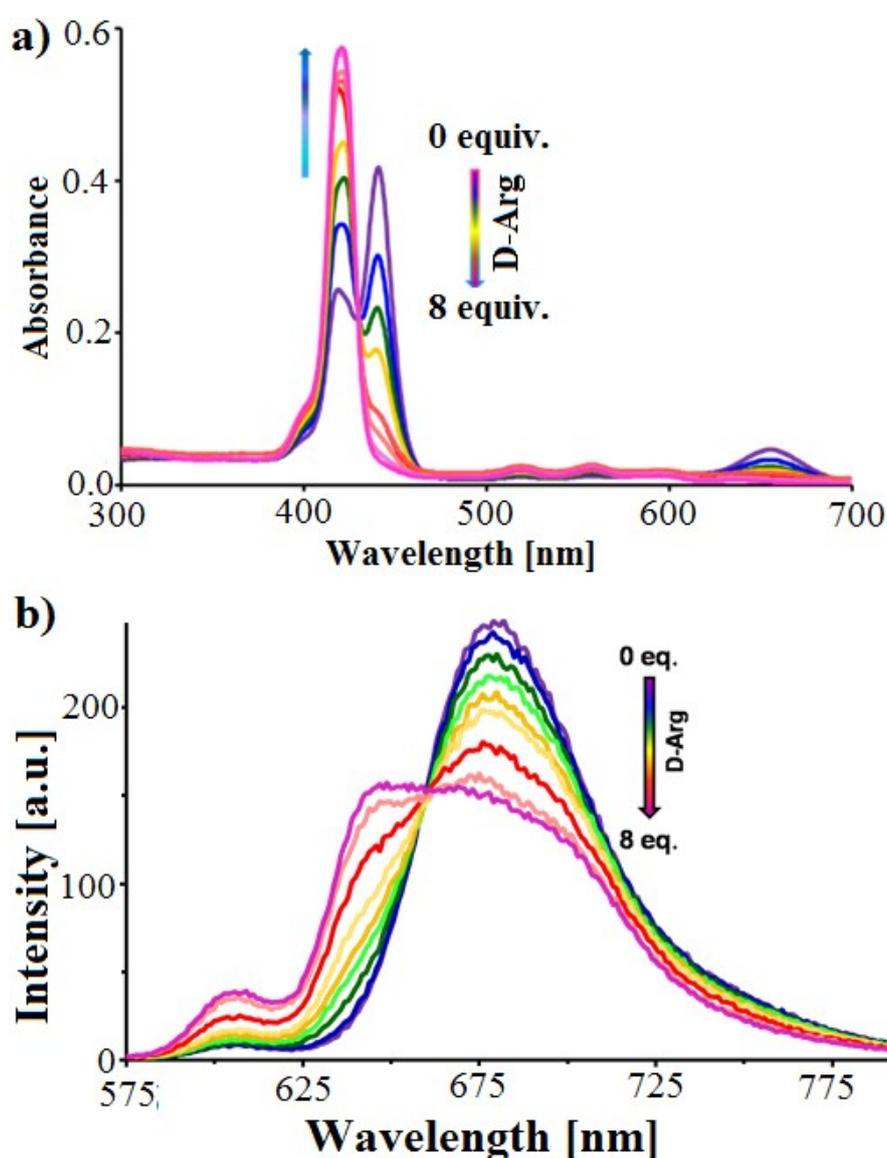


Fig. S1 (a) UV-vis and (b) fluorescence emission spectra ($\lambda_{\text{ex}} = 418 \text{ nm}$) of OPTPP ($5 \mu\text{M}$) in presence of incremental amount of D-arg (0-8 equiv.).

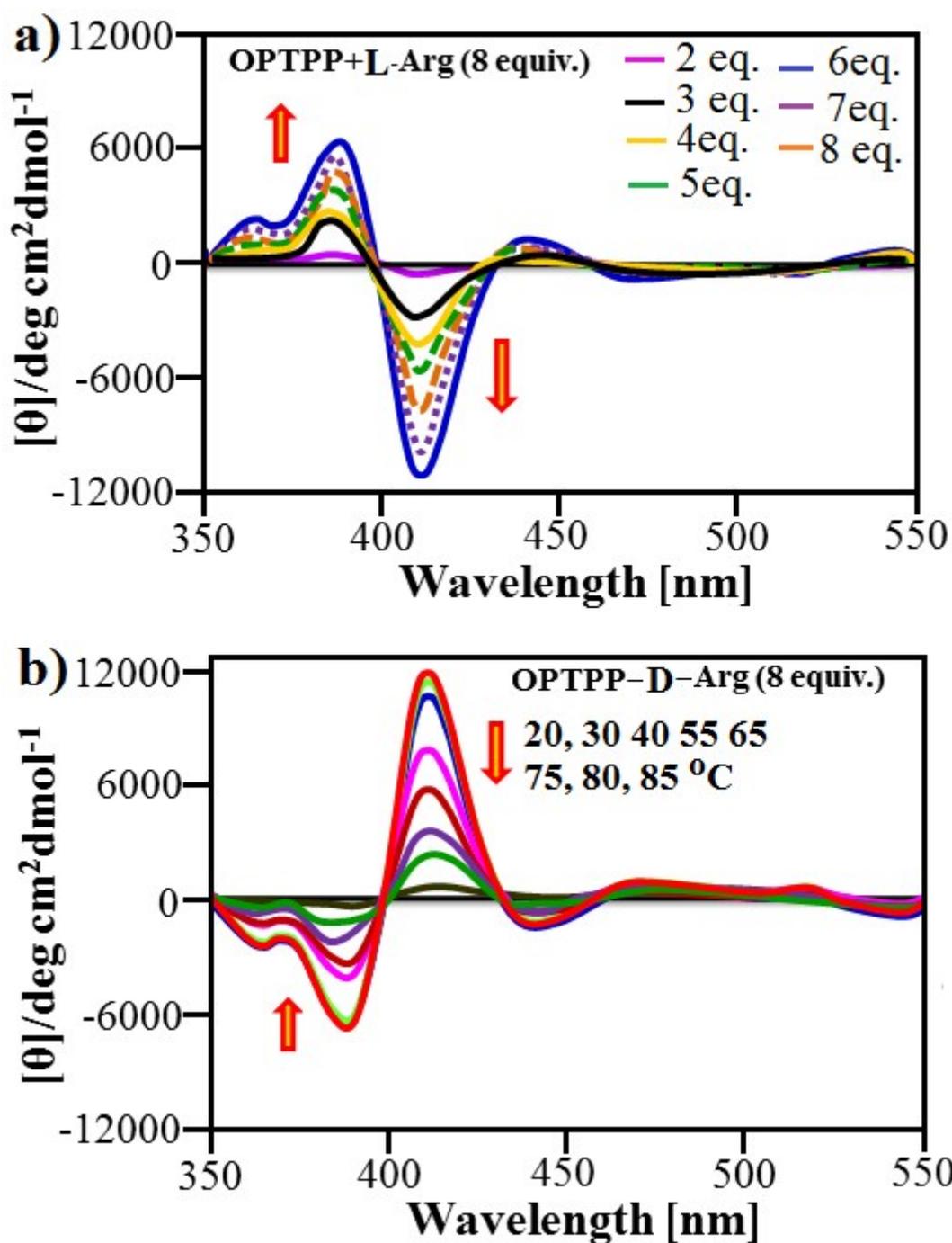


Fig. S2 Changes in CD spectra of OPTPP (5 μM): (a) upon addition of 0-8 equiv. L-Arg and (b) temperature dependent (20 and 85 $^{\circ}\text{C}$) CD spectra of OPTPP-D-Arg in 90% acetonitrile in THF in Milli-Q water.

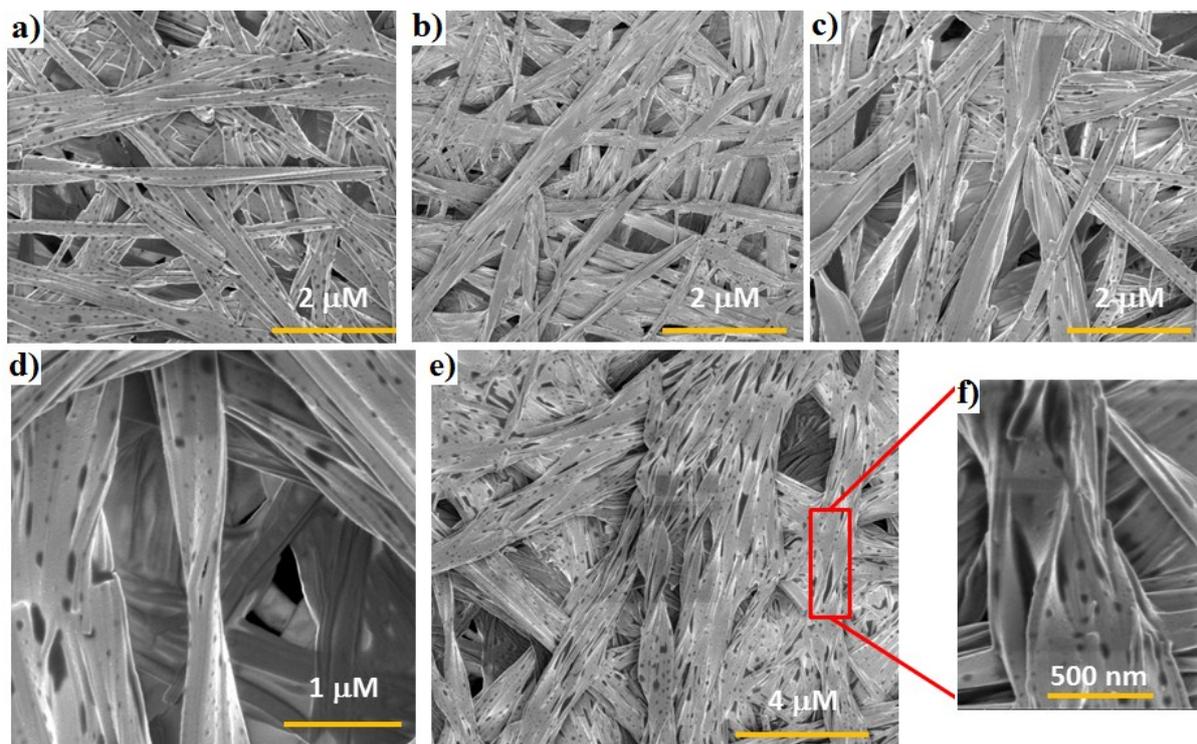


Fig. S3 SEM micrographs of OPTPP (10 μM) with varying ratio of D-Arg: (a) 1:2, (b) 1:4, (c) 1:6, (d & e) 1:8 and (f) is high magnification of 'e'. It can be clearly seen that 1:2 and 1:4 v/v ratio of OPTPP–D-Arg produces tubules and belt like morphology, with ratio 1:6 v/v belts begin to form twisted ribbons, and 1:8 v/v of OPTPP–D-Arg clearly shows right handed helical structures.

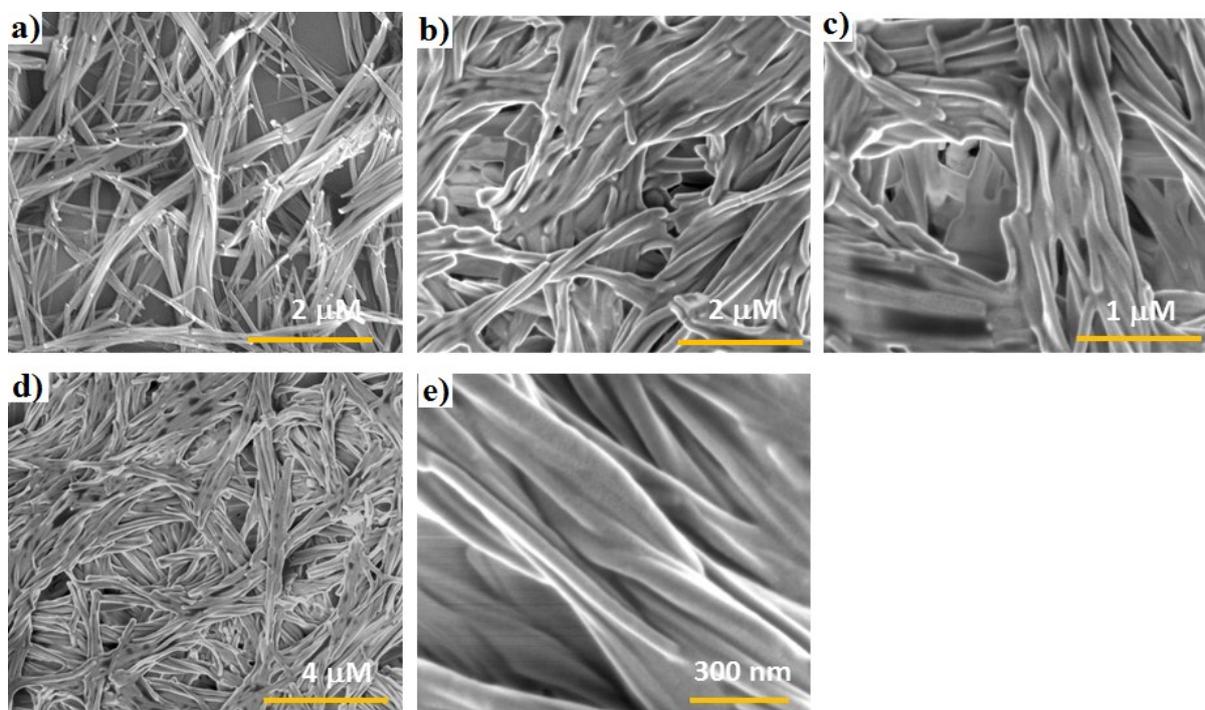


Fig. S4 SEM micrographs of OPTPP (10 μM) with varying ratio of L-Arg: (a) 1:2, (b) 1:4, (c) 1:6 and (d & e) 1:8. It can be clearly seen that 1:2 ratio of OPTPP–L-Arg produces short tubules and 1:2 and 1:4 v/v ratio of OPTPP–L-Arg produces tubules, 1:4 & 1:6 v/v produces

left-handed twisted tubules, and 1:8 v/v of OPTPP–L-Arg clearly shows left handed helical structures.

FTIR spectroscopy

FTIR is a powerful technique to demonstrate the nature of OPTPP self-assembly. Figure show the FTIR spectra of monomeric OPTPP molecule, L-Arg-assisted OPTPP and D-Arg-assisted OPTPP assembly. In the FTIR spectrum of OPTPP monomer, the presences of peaks at 2766, 2683 and 2483 cm^{-1} are ascribed to the O=P-OH stretch. However, there is no peak is observed in the FTIR spectra of assembled OPTPP with both L-Arg and D-Arg, suggesting that there occurred a reaction between O=P-OH group with amino acid in L-Arg or D-Arg. Furthermore, a shift of about 50 cm^{-1} from 1720 in O-H stretch of OPTPP monomer to 1670 cm^{-1} in O-H stretch of assembled OPTPP is also observed which indicates the presence of H bonding in assembly.

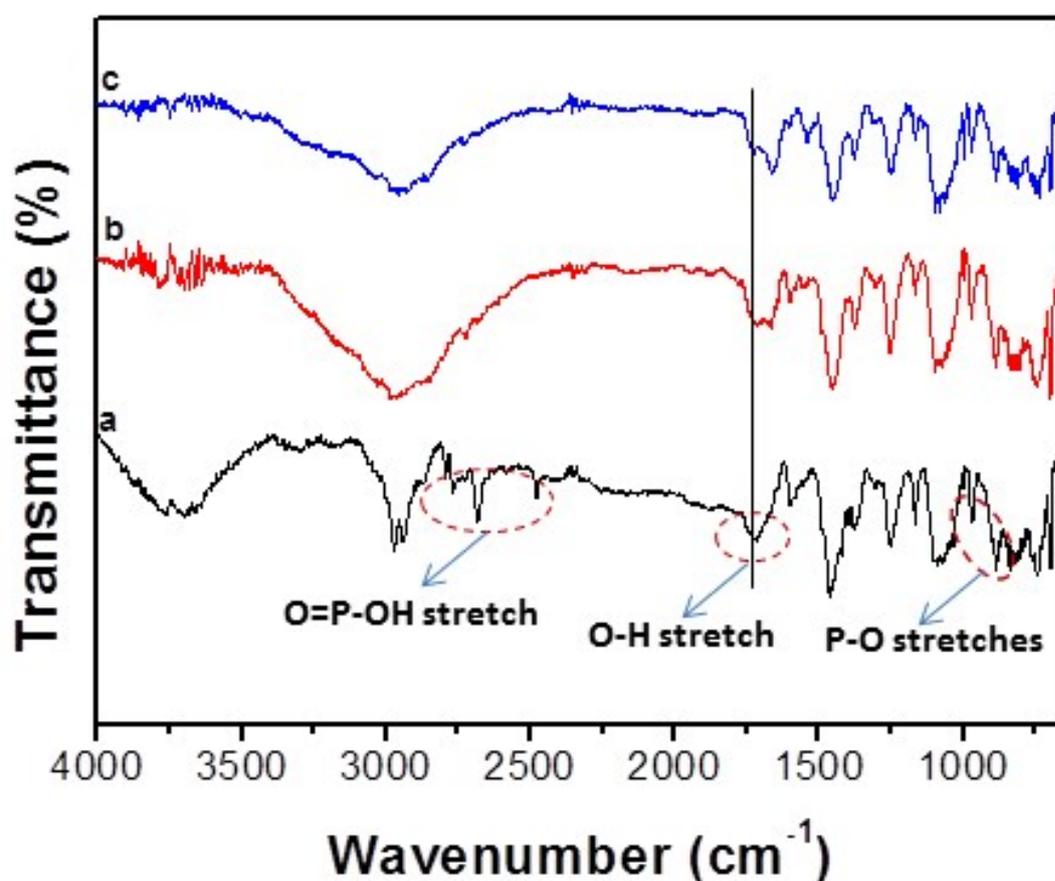
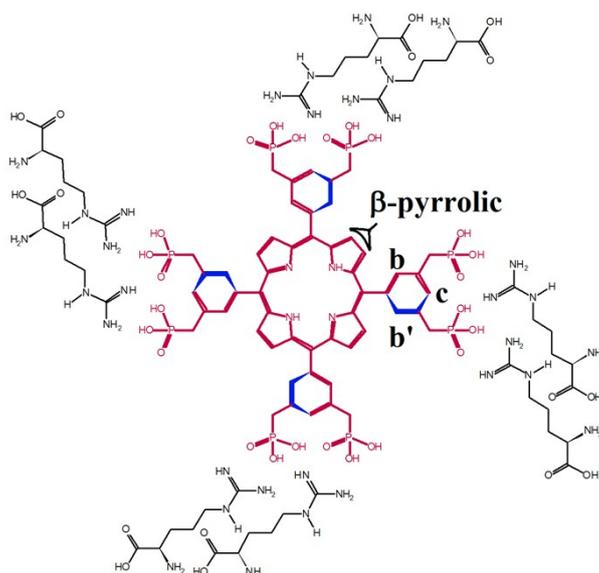


Fig. S5 FTIR spectrum of OPTPP (a), and self-assembled left-handed helical structure of OPTPP-L-arg (b), and OPTPP-D-arg on Silicon surface.

NMR spectroscopy

NMR demonstrates the interaction of phosphonic acid group of OPTPP and amino functional group of arginine during self-assembly as shown in Figure S6. The ^1H NMR (D_2O) spectra of monomeric OPTPP molecule, the presence of peaks at 9.08, 8.49 and 7.89 ppm are ascribed to β -pyrrolic (8H), aromatic (b&b', 8H) and aromatic (C, 4H). Upon addition of 2 equiv. of D-arginine, β -pyrrolic peak broaden with slight shift to 9.21 ppm, expectedly aromatic peaks shifted to 8.01 and 7.76 ppm with shift of about 0.48 and 0.13 ppm, respectively. These shift in aromatic peaks of OPTPP is clearly demonstrated the presence of H-bonding in assembly. Furthermore, ^{31}P NMR spectra of OPTPP gives two peaks 22.34 and 20.21 ppm, upon addition of D-arginine (16 equiv.) peaks shifted to 22.37 and 17.94 ppm. The aromatic ^1H NMR shifts of OPTPP and ^{31}P NMR of phosphonate acid shift clearly demonstrated the presence of H-bonding in assembly (Fig. S6 and S7).



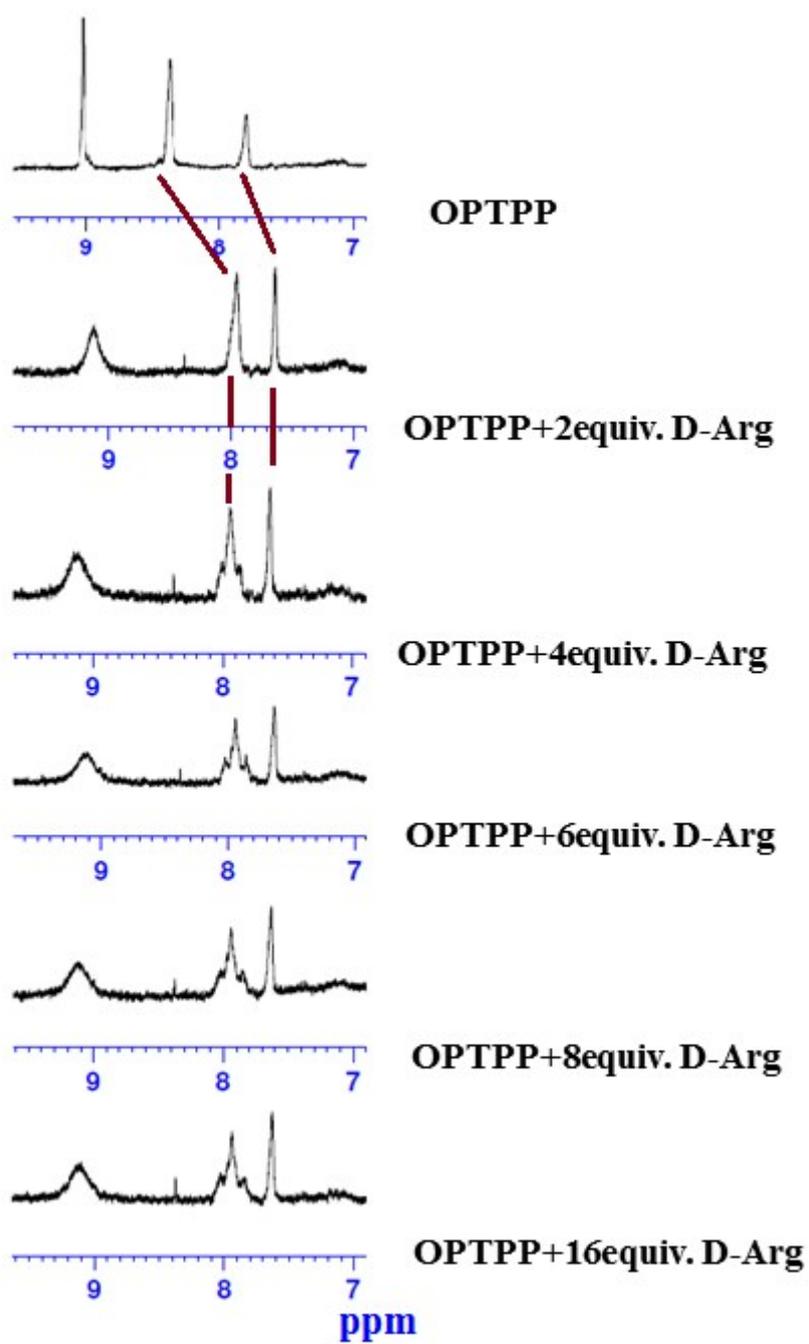


Fig. S6 ¹H NMR spectrum of OPTPP and OPTPP with addition of 2-16 equiv. D-arginine in D₂O.

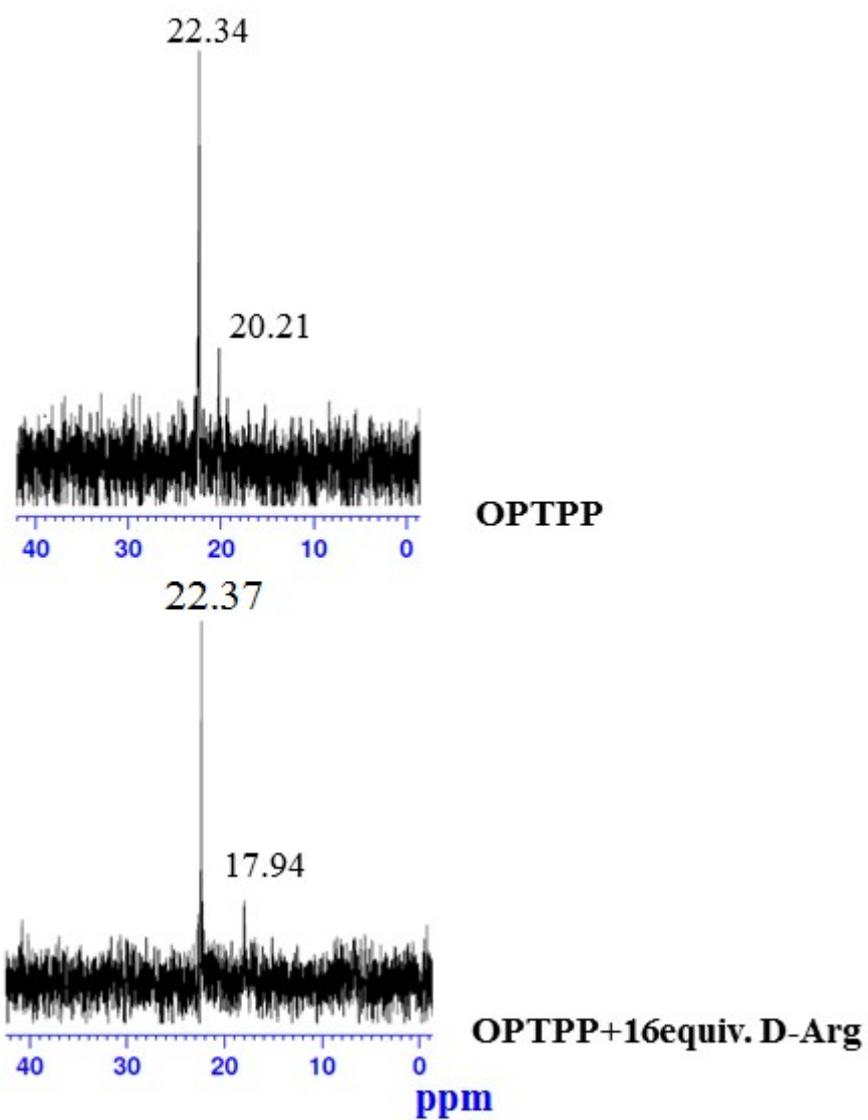


Fig. S7 ^{31}P NMR spectrum of OPTPP and OPTPP with 16 equiv. D-arginine in D_2O .