Supporting Information

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Experimental

Experimental Conditions

All NMR samples were prepared using deuterated solvents supplied by Sigma Aldrich. ^{1}H NMR was performed at 250MHz and ^{13}C NMR at 60MHz using a Bruker AC-250 with 5mm CH probe. UV analysis was carried out using a Hitachi U-2010 spectrophotometer. IR samples were recorded neat (without using Nujol or KBr) on a Perkin Elmer Spectrum RX I FT-IR spectophotometer with integral DuraSampl IR-II. Analytical GPC was conducted at room temperature using a low molecular weight setup consisting of 2x600mm PL gel 5um (500Å). All samples were run using Fisher GPC grade supplied to the columns by a Waters 515 HPLC Pump at 1.00 mlmin^{-1}. Samples were prepared in THF and spiked with toluene as a flow marker, before being injected through a 200ul sample loop with a Gilson 234 Auto Injector. Sample concentration was monitored using an Erma ERC-7512 refractive index detector. Data was analysed using Polymer Labs proprietary software.

General Titration Procedure

A stock solution of ZnTPP was made up in dichloromethane (1x10^{-6}M). This was then used to prepare a solution of the pyridine-cored hyperbranched polymer (1x10^{-2}M). The porphyrin stock was used to make up the pyridyl/polymer solution to maintain the concentration of porphyrin throughout the titration. 2ml of the porphyrin stock solution (ligand free) was accurately measured into a dried quartz glass cuvette and aliquots of ligand/polymer solution between 10µl and 100µl were added increasing as the titration progressed. UV wavelength scans were taken after each aliquot, monitoring the Soret band at 418nm. Solutions were made fresh and used within 3hr of preparation. Titrations were repeated at least twice to verify subsequently calculated binding constants. The UV peak for tetraphenylporphyrin comes around 418nm and when complexed (to either the HBP or 3-acetoxy-pyridine) shifted to 425nm (±1-2nm).

Copolymerisation of 3,5-Diacetoxbenzoic Acid and Acetoxypyridine (PEH-AcPy)

3,5-Diacetoxybenzoic acid (25.00g, 105mmol) and 3-acetoxypyridine (7.20g, 0.5eq, 52.50mmol) were heated under nitrogen to 200^{o}C with diphenyl ether solvent (25.00g). After 45min the temperature was lowered to 180^{o}C and acetic acid removed under vacuum for 1hr. The reaction mixture was dissolved in THF and precipitated into methanol. This step was repeated until the removal of all starting materials was confirmed by ^{1}H NMR. The white product was then dried under vacuum to give purified polymer. Yield 19.3g; ^{1}HNMR ($CDCl_3$) 8.56 (br m, 2H, [AcPy] Ar *o*-CH), 8.08-7.63 (br m, 26H, [Polymer] Ar *o*-CH), 7.58-7.09 (br m, 15H, [Polymer] Ar *p*-CH + [AcPy] Ar *o*-CH), 2.32 (s, 42H, [Polymer] -CH_3); IR ν 3090, 2940, 1741 (COOR), 1525, 1347 (NO_2), 1593 cm^{-1}; NMR-Mn 3450; GPC-Mn 3000, PD 1.42

Additional Figures

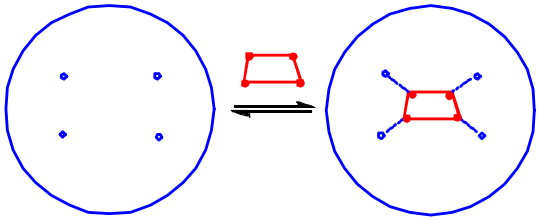

Figure 1: *Schematic representation showing the methodology for non-covalent core/focal point incorporation*

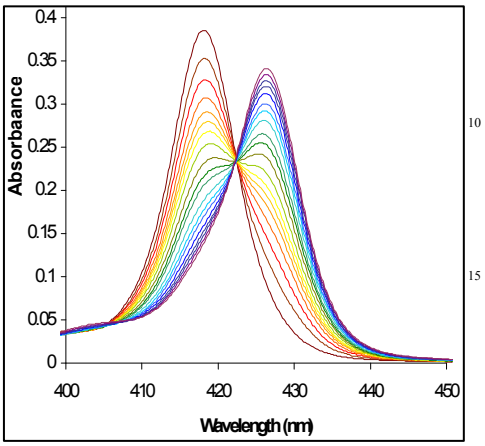

Figure 2: *UV/Vis titration overlays for PEHAcPy.*

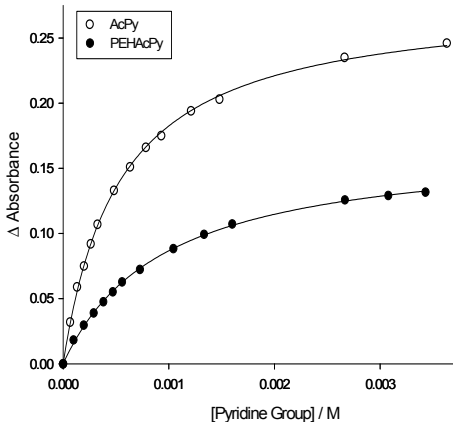

Figure 3: *Binding curves of PEHAcPy and AcPy. The points represent experimental data and the lines the best fit to a 1:1 binding equation (sigma plot)*

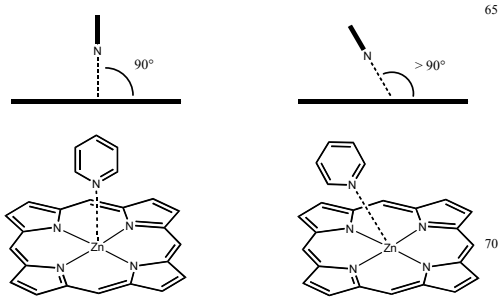

Figure 4: *A schematic representation of the angular dependence of binding and shift for pyridine bound to a metallated porphyrin. On the left hand side the pyridine is perfectly bound/orientated within the shielded region of the porphyrin. This leads to a maximum effect regarding chemical shift (of the pyridine protons). However, if sterics or geometry prevent optimal binding (as portrayed on the right hand side of the figure), then the pyridine is less perfectly orientated and any shifts will be reduced*

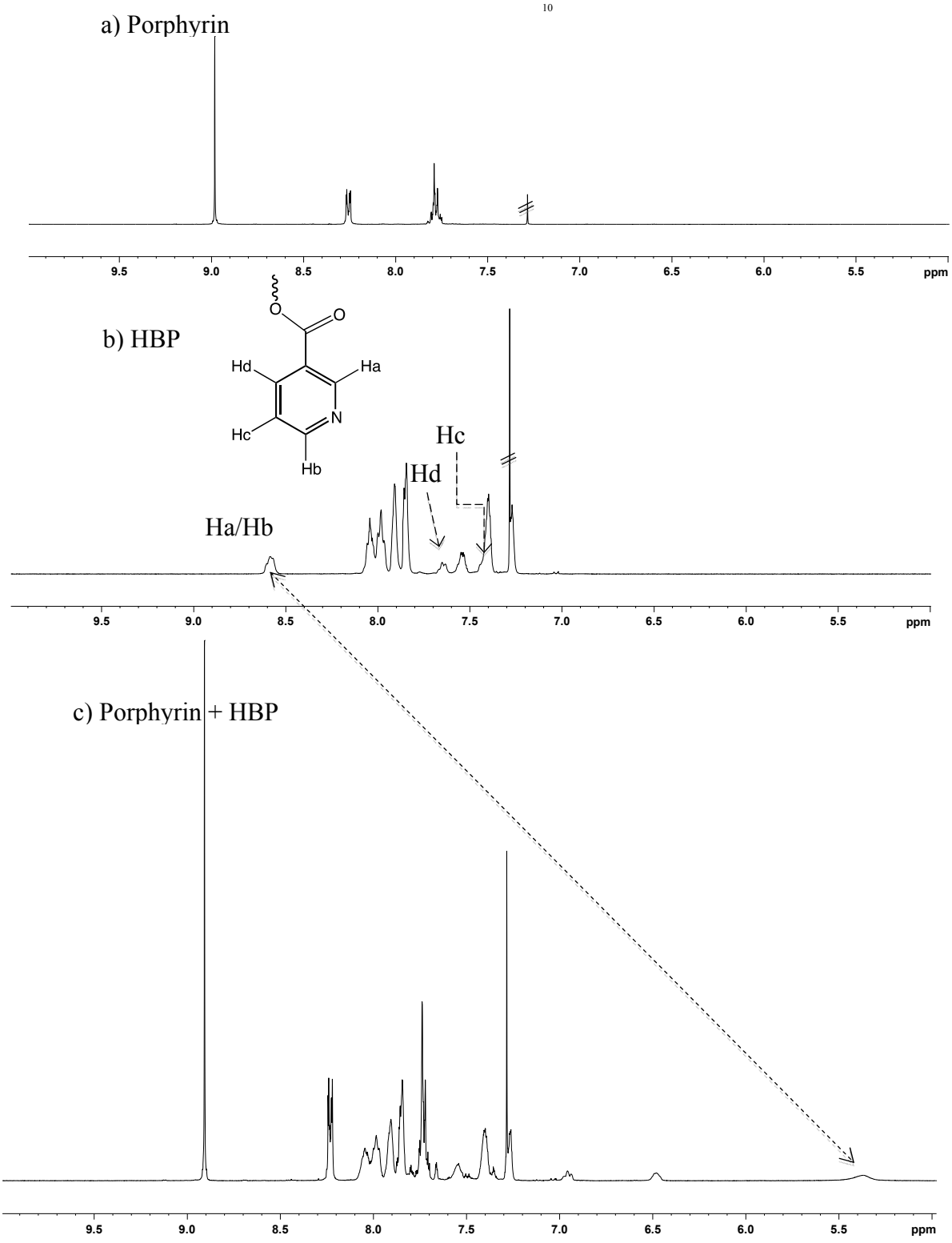

Figure 5: *NMR spectra of tetraphenyl porphyrin, HBP **3** and the resulting complex **4***