Supplementary Material (ESI) for Chemical Communications

6-Azahemiporphycene: a further example of corrole metamorphosis

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Electronic Supplementary Information

Reagents and solvents (Sigma-Aldrich, Fluka and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Silica gel 60 (70-230 mesh) was used for chromatography.
^{1}H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). UV-vis spectra were measured on a Cary 50 spectrophotometer. Mass spectra were recorded on a VGQuattro spectrometer in the positive-ion mode, using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix (FAB), or on a Voyager DE STR Biospectrometry workstation in the positive mode, using α-cyano-4-hydroxycinnamic acid as a matrix (MALDI).

General procedure for preparation of 6-azahemiporphycene derivatives.
A solution of corrole (0.1 mmol), 4-amino-4H-1,2,4-triazole (1.1 mmol), and NaOH (0.5 mmol) was refluxed in toluene/ethanol (10:1) and the reaction progress was monitored by TLC and UV/Vis spectroscopy. After disappearance of the starting material, the solvent was evaporated under vacuum and the crude mixture purified by chromatography on silica gel using CH_2Cl_2/hexane (70:30) as eluent.

3-(NO_2)-6-aza-5,11,16-tris-(4-tert-butylphenyl)hemiporphycene.
Yield 44%. Found: C, 78.4; H, 6.4; N, 11.0. $C_{49}H_{48}N_6O_2$ requires C, 78.2; H, 6.4; N, 11.2%. UV/Vis: $\lambda_{max}(CH_2Cl_2)$, nm 395 (log ε 4.53), 448 (4.68), 615 (3.97) and 693 (3.6); ^{1}H NMR: $\delta_H(CDCl_3$, *J* [Hz]) 8.77 (1 H, s, *β*-pyrrole), 8.23 (2 H, dd, *β*-pyrrole), 8.08 (2 H, d, *J* 8.2, Phenyl), 7.94 (2 H, d, *J*=8.2, Phenyl), 7.90 (1 H, d, *J* 4.4, *β*-pyrrole), 7.75 (6 H, m, *β*-pyrrole + Phenyl), 7.60 (5 H, m, *β*-pyrrole + Phenyl), 1.54 (18 H, s, *tert*-Butyl), 1.41 (9 H, s, *tert*-Butyl); MS (FAB): m/z 754 (M+).

6-aza-5,11,16-tris-(4-tert-butylphenyl)hemiporphycene.
Yield 56%. Found: C, 82.9; H, 7.1; N, 9.7. $C_{49}H_{49}N_5$ requires C, 83.1; H, 7.0; N, 9.9%. UV/Vis: $\lambda_{max}(CH_2Cl_2)$, nm 417 (log ε 5.22) and 573 (4.27); ^{1}H NMR $\delta_H(CDCl_3$, *J* [Hz]) 8.93 (1 H, d, *J* 4.0, *β*-pyrrole), 8.80 (1 H, d, *J* 4.4, *β*-pyrrole), 8.72 (1 H, d *J* 3.7, *β*-pyrrole), 8.63 (1 H, d, *J* 4.4, *β*-

pyrrole), 8.41 (4 H, m, *β*-pyrrole + Phenyl), 8.30 (1 H, d, *J* 4.6, *β*-pyrrole), 8.10 (3 H, m, *β*-pyrrole + Phenyl), 7.96 (2 H, d, *J* 8.2, Phenyl), 7.79 (4 H, m, *β*-pyrrole + Phenyl), 7.71 ppm (2 H, d, *J* 8.1, Phenyl), 4.25 (1 H, s, NH), 3.13 (1 H, s, NH), 1.60 (9 H, s, *tert*-Butyl), 1.58 (9 H, s, *tert*-Butyl), 1.54 (9 H, s, *tert*-Butyl); MS (MALDI): m/z 708 (M+).

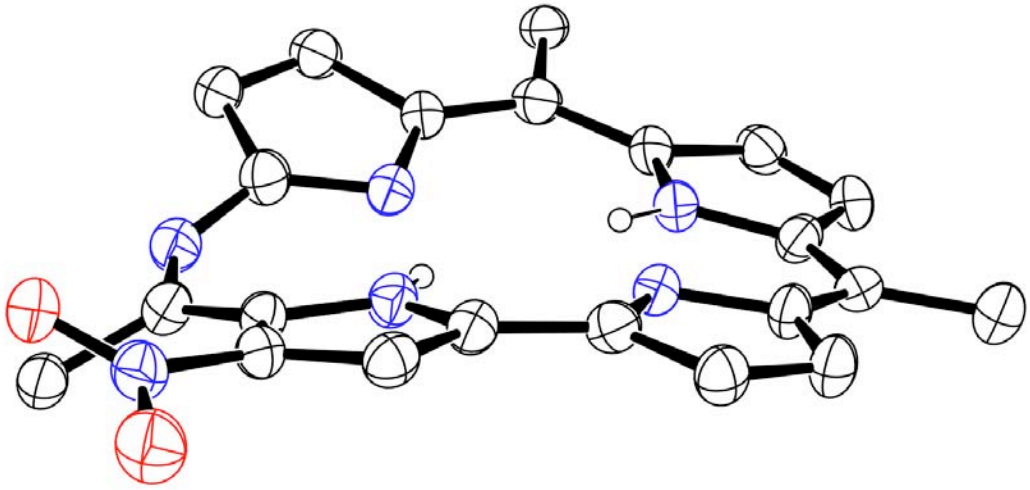

Figure S1. Side view of 3-(NO_2)-ttbuazahempH_2 crystal structure

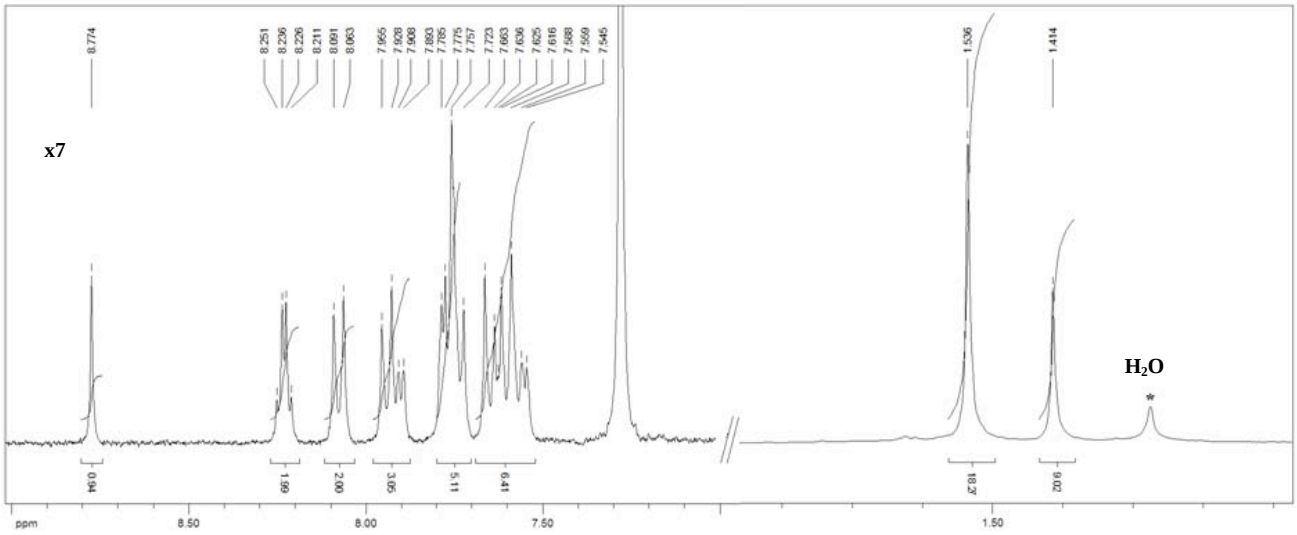

Figure S2. ^{1}H NMR spectrum of 3-(NO_2)-ttbuazahempH_2

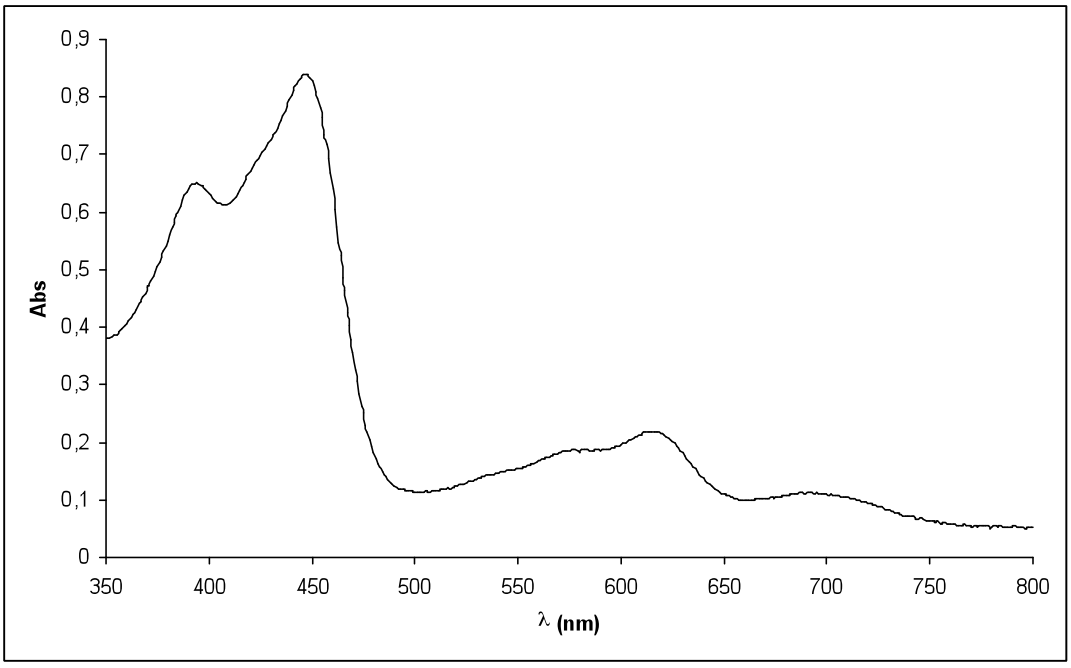

Figure S3. UV-visible spectrum of 3-(NO_2)-ttbuazahempH_2

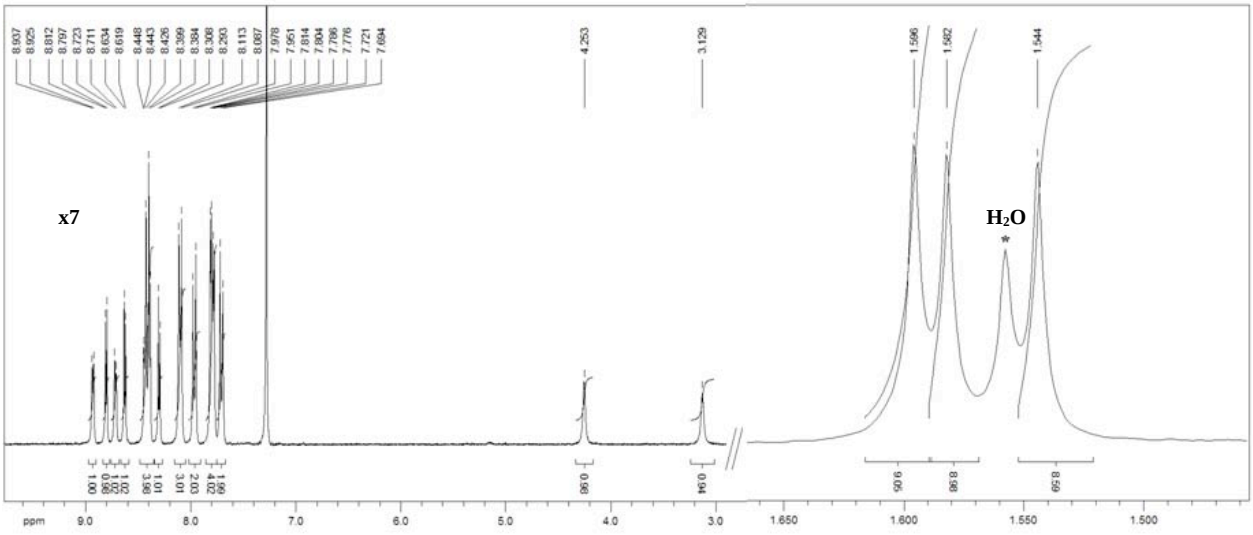

Figure S4. ^{1}H NMR spectrum of ttbuazahempH_2

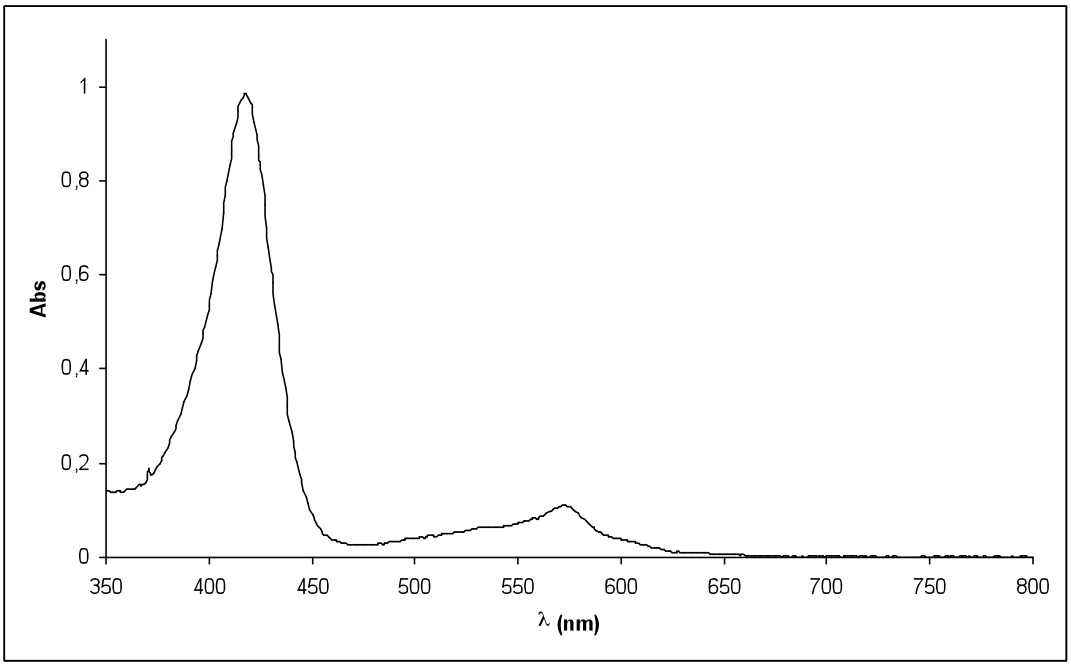

Figure S5. UV-visible spectrum of ttbuazahempH_2