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The Curious Case of a Parasitic Twin of the Corroles

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Abstract: An expanded porphyrinoid has been synthesized by a simple π-expansion from a contracted porphyrinoid, namely corrole. Spectroscopic, structural, and computational investigations proves peculiar π-conjugation and geometry. The perturbed redox behavior and photophysical properties account for the effect of extended π-conjugation. Owing to the strong diatropic ring current of the corrole and cross-conjugation, the molecule exhibits a non-aromatic nature for the expanded π-circuit, as evident from NICS and AICD studies

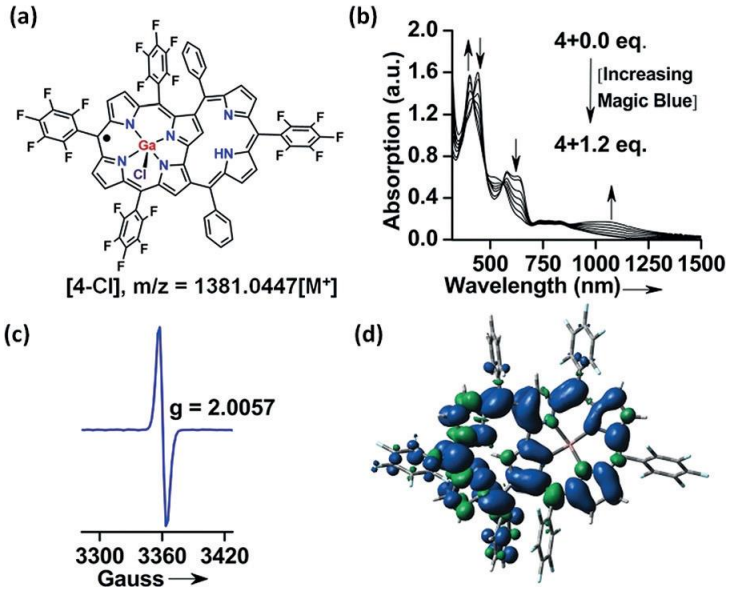
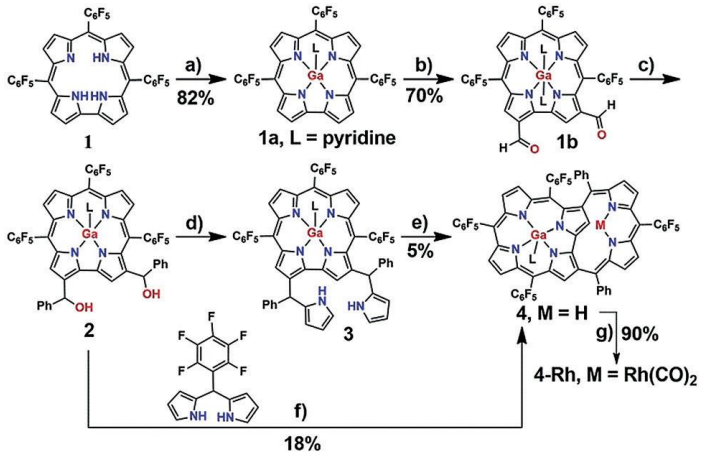


Figure 1: a) Molecular structure of chlorinated species [4-Cl] after oxidation of 4 with Magic Blue. b) UV/Vis-NIR spectral change of 4 with gradual addition of tris(4 bromophenyl)ammoniumyl hexachloroantimonatein acetonitrile. c) X-band ESR spectra of radical [4-Cl] generated in situ in toluene/DCM (1:1, v/v) at 110 K. d) Spin density of [4-Cl] calculated at RB3LYP/6-31G*(C,H,N,F,Cl)+LANL2DZ (Ga).



Scheme 1: Synthesis of 4 and 4-Rh: a) $GaCl_3$ (50 equiv), pyridine, 100°C, Ar, 2 h, 82%; b) $POCl_3$/DMF (100 equiv), 0°C, Ar, 2 h, K_2CO_3 (aq), 12 h, 70%; c) PhMgBr (10 equiv), THF, RT, Ar, 2 h, quantitative yield; d)

pyrrole (100 equiv), TFA (0.3 equiv), CH_2Cl_2, RT, Ar, 2 h; e) 2,3,4,5,6-pentafluorobenzaldehyde (1 equiv), TFA (0.3 equiv), CH_2Cl_2, 0.05 mm, RT, Ar, 3 h, pyridine, DDQ (1.5 equiv), 1 h, 5%; f) TFA (0.3 equiv), CH_2Cl_2, 0.05 mm, RT, Ar, 3 h, pyridine, DDQ (1.5 equiv), 1 h, 18%; g) $[Rh(CO)_2Cl]_2$ (5 equiv), CH_3COONa (10 equiv), CH_2Cl_2, Ar, 1 h, 50°C, 90%.

References and Notes:

1. B. Basumatary, R. V. R. Reddy, Rahul, J. Sankar; *Angew. Chem. Int. Ed.* **2018**,*57*,5052