Supporting Information

For

Syntheses, Structures, and Crystal Packing of N-Confused 5,20-Diphenylporphyrin and Ag(III) Complex

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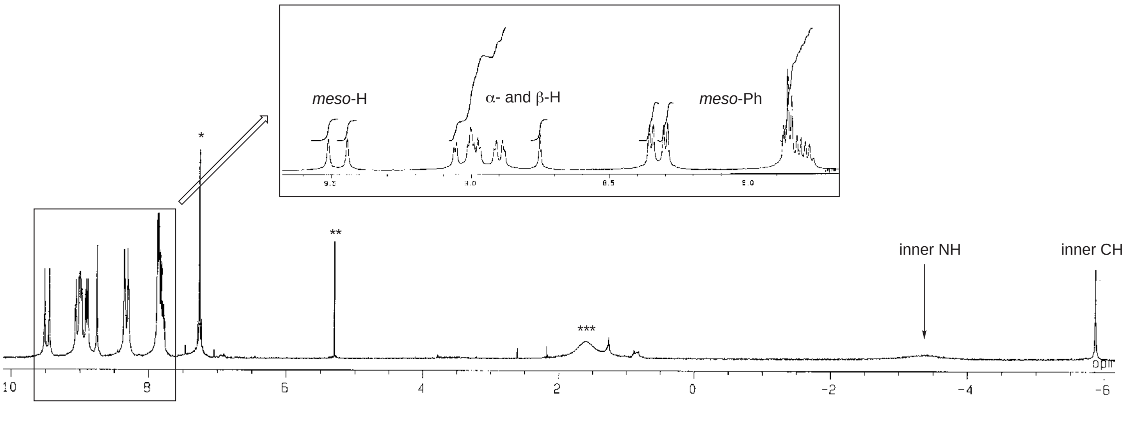
Experimental Procedures and Spectral Data for **3**, **3-Ag(III)**, and **4-Ag(II)**

(1) N-Confused 5,20-Diphenylporphyrin (**3**)

2,4-Dibenzoylpyrrole and *meso*-unsubstituted tripyrrane were prepared according to the literature, which were purified by column chromatography on silicagel (eluent: CH_2Cl_2, in both cases). 2,4-Dibenzoylpyrrole was reduced by lithium aluminum hydride (10 equiv.) and the reaction mixture was quenched with water and ice. The organic phase was separated and combined with the CH_2Cl_2 extracts from the aqueous phase. After washing with water and brine, the organic phases was dried on Na_2SO_4 and evaporated under reduced pressure. The crude residue was used in the next condensation reaction without further purification. To a stirred mixture of the reduced compound and tripyrrane (10 mM) in chloroform containing a trace of ethanol, BF_3•MeOH (1 mM) was added at room temperature. After 1 h, 3 equiv. of *o*-chloranil was added to the reaction mixture, followed by column chromatography on alumina. The fraction of porphyrins was eluted with CH_2Cl_2, and that of 5,20-NCDPP with CH_2Cl_2/methanol (5%). The NCP fraction was purified by subsequent chromatography on silicagel with CH_2Cl_2/methanol (2%) and the obtained solids was recrystallized from CH_2Cl_2/hexane to afford the product (7% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (1H, s, *meso*-H), 9.44 (1H, s, *meso*-H), 9.06–8.88 (6H, m, outer β-H), 8.75 (1H, s, outer α-H), 8.35 - 8.29 (4H, m, Ph), 7.87–7.78 (6H, m, Ph), -3.37 (2H, br, inner NH), -5.87 (1H, s, inner CH); UV/vis (CH_2Cl_2) λ_{max} (ε): 430 nm (150000), 527 (11000), 566 (6400), 705 (8000) and (DMF) λ_{max} (ε): 434 nm (100000), 579 (5800), 626 (7300), 676 (8800); FABMS: m/z 463.3 (M^++1).



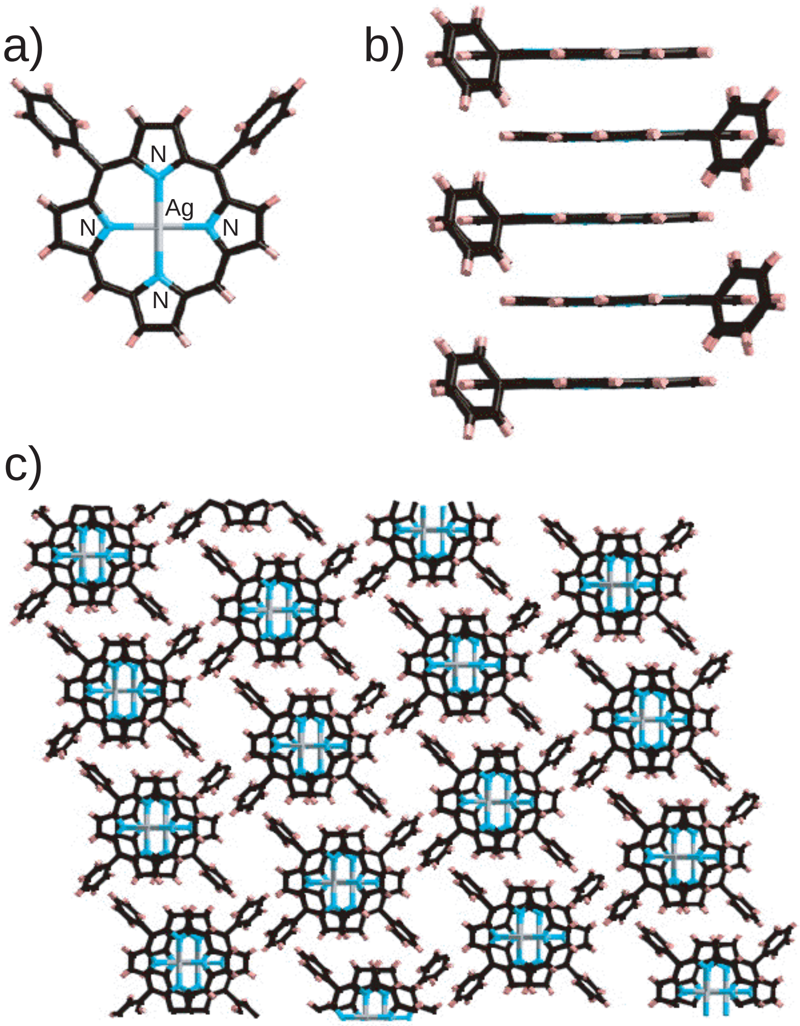
Supporting Figure 1. ^{1}H NMR of **3** (500 MHz, $CDCl_3$), *: $CHCl_3$, **: CH_2Cl_2, ***: H_2O.

(2) N-Confused 5,20-Diphenylporphyrin Ag(III) complex (**3-Ag(III)**)

Free base NCDPP **3** (40 mg, 86 μmol) was treated with silver(I) trifluoroacetate (59 mg, 0.27 mmol) in dichloromethane (30 ml) and methanol (5 ml) at room temperature. After 2 h, the solvent was removed in vacuo. After the column chromatography on silicagel (eluent: CH_2Cl_2/methanol (2%)), the residue were recrystallized from CH_2Cl_2/hexane to afford the product (20 mg, 35 μmol, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (1H, s, *meso*-H), 9.84 (1H, s, *meso*-H), 9.56 (1H, s, outer α-H), 9.08–9.03 (6H, m, outer β-H), 8.24-8.17 (4H, m, Ph), 7.79–7.75 (6H, m, Ph); UV/vis (CH_2Cl_2) λ_{max} (ε): 440 nm (110000), 510 (12000), 623 (5000), FABMS: m/z 567.2 (M^+).

(3) 5,10-Diphenylporphyrin Ag(II) complex (**4-Ag(II)**)

Free base 5,10-diphenylporphyrin (20 mg, 43 μmol) was treated with silver(I) acetate (16 mg, 94 μmol) in DMF (4 ml). After refluxing for 30 minutes, addition of water to the reaction mixture allowed the crude mixture to be precipitated. Subsequent chromatography on alumina (eluent: CH_2Cl_2) and recrystallization from CH_2Cl_2/methanol gave the complex (22 mg, 39 μmol, 91%): UV/vis (CH_2Cl_2) λ_{max} (ε) : 413 nm (280000), 529 (16000), FABMS: m/z 569.2 (M^++1).



Supporting Figure 2. Molecular structure of **4-Ag(II)**; (a) top view, (b) side view, and (c) packing diagram from *b*-axis. The solvent molecules are omitted for clarity.