

Supporting Information

Ms. Title: The First Slipped Pseudo Quadruple-Decker of Phthalocyanines

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Synthesis and Characterizing Data of Compounds 1 and 2:

Preparation of $\text{Sm}^{\text{III}}\text{H}(\text{Pc})[\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8]$ (**1**): A mixture of $\text{Sm}^{\text{III}}(\text{Pc})(\text{acac})$ (0.05 mmol) and $\text{H}_2\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8$ (0.05 mmol) in *n*-octanol (5 mL) was refluxed for 8 h under nitrogen to give a dark-blue solution. After being cooled to room temperature, the mixture was mixed with methanol (ca. 40 mL). The precipitate formed was filtered off and washed with methanol, then it was chromatographed on a silica gel column with CHCl_3 as eluent. The first blue band containing the unsubstituted $\text{Sm}^{\text{III}}(\text{Pc})_2$ was discarded. Then the column was further eluted with 2-3% MeOH in CHCl_3 to give the desired double-decker **1**. The crude product was further purified by repeated chromatography followed by recrystallization from a mixture of CHCl_3 and MeOH to afford dark blue microcrystals (14% yield). MS (MALDI-TOF) an isotopic cluster peaking at m/z 1753.5 (calc. for MH^+ 1753.7); UV-Vis (CHCl_3) [$\lambda_{\text{max}}/\text{nm}$ (log ϵ)] 330 (4.99), 484 (4.26), 577 (4.30), 686 (5.14), 765 (4.48), 951 (sh); Anal. Calc. for $\text{C}_{96}\text{H}_{97}\text{N}_{16}\text{O}_8\text{Sm}$: C, 65.76; H, 5.58; N, 12.78. Found: C, 65.58; H, 5.85; N, 12.12.

Preparation of the slipped pseudo quadruple-decker **2**: A solution of **1** (35 mg, 0.02 mmol) and NaOH (4 mg, 0.10 mmol) in CHCl₃ / MeOH (95:5) was stirred at room temperature for 1 h. After removing the solvents under reduced pressure, the residue was repeatedly washed with MeOH and dissolved into a minimal amount of CHCl₃ / toluene (1:1). Slow diffusion of MeOH into this solution gave dark-green single crystals of **2** (34 mg, 96% yield). UV-Vis [CHCl₃ / MeOH (95:5)] [λ_{max} /nm (log ϵ)] 327 (5.38), 405 (4.93), 573 (4.88), 621 (4.98), 670 (5.43); Anal. Calc. for C₁₉₂H₁₉₂N₃₂Na₂O₁₆Sm₂: C, 64.95; H, 5.45; N, 12.62. Found: C, 64.16; H, 5.45; N, 12.25.

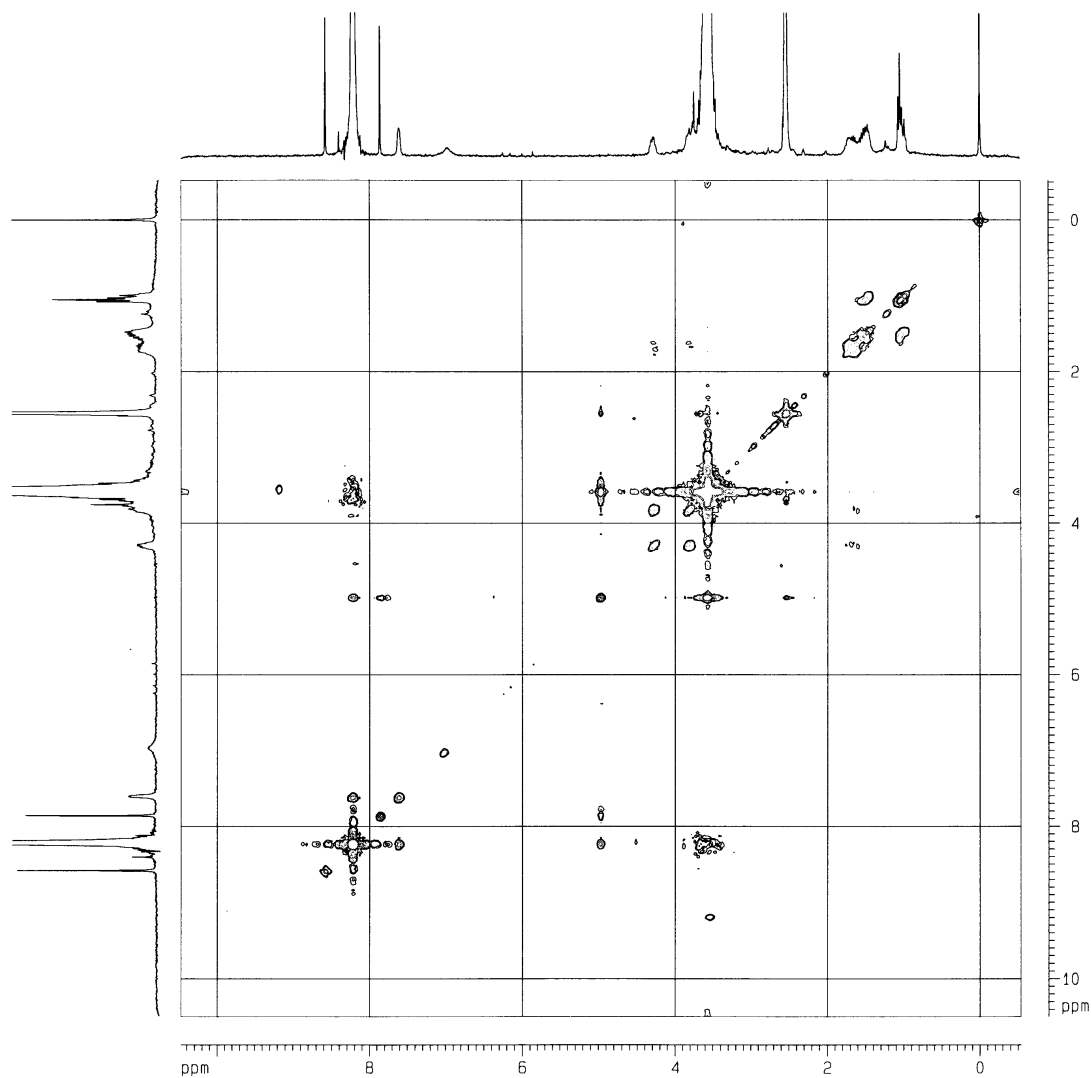


Figure S1. ^1H - ^1H COSY spectrum of $\text{Sm}^{\text{III}}\text{H}(\text{Pc})[\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8]$ (**1**) in CDCl_3 / DMSO-d_6 (1:2) in the presence of 3 equiv. of NaOD (40% in D_2O).