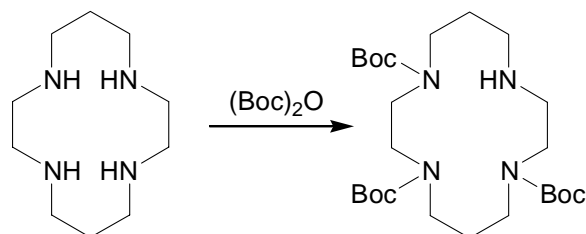


ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Synthesis of 1-(4-nitrophenyl)-1,4,8,11-tetraaza-cyclotetradecane

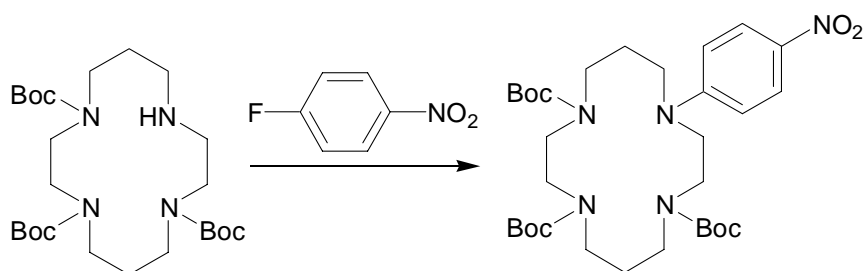
Step 1



Cyclam (1.0 g, 5 mmol) was dissolved in dried dichloromethane (200 mL) and triethylamine was added (25 mmol) under dinitrogen atmosphere. The reaction mixture was stirred and a solution of di-*tert*-butyl-dicarbonate (1.96 g, 9 mmol) in dried dried dichloromethane (60 mL) was added dropwise. After cooling the reaction mixture to -15°C , another portion of *tert*-butoxy-dicarbonate (6 mmol) was added, and the mixture was stirred at room temperature overnight. The solution was treated with 0.5 N Na_2CO_3 and the organic solution dried over Na_2SO_4 . The solvent and the excess of triethylamine were removed in vacuo and the residue was purified by liquid chromatography (silica gel, ethyl acetate/methanol 9:1, $R_f=0.5$).

MS (CH_3CN , ESI): m/z 501.2 ($\text{M}+\text{H}^+$, 100%).

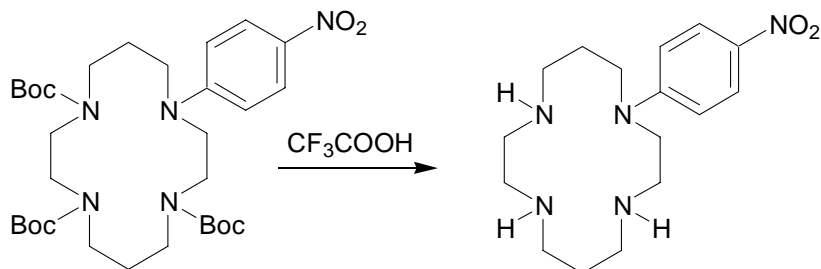
Step 2



A solution of 1-fluoro-4-nitrobenzene (0.212 mL, 2 mmol) in toluene (25 mL) was added dropwise to a boiling solution of 1,4,8-Tris(*tert*-butoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane (0.5g, 1 mmol) and triethylamine (0.278 mL, 2 mmol) in toluene (75 mL). The solution was maintained under reflux for 24 hrs. The solvent and the excess of triethylamine were removed in vacuo and the residue was purified by liquid chromatography (silica gel, ethyl acetate/hexane 2:3, $R_f=0.5$).

MS (CH₃CN, ESI): *m/z* 623,4 (M+H⁺, 100%).

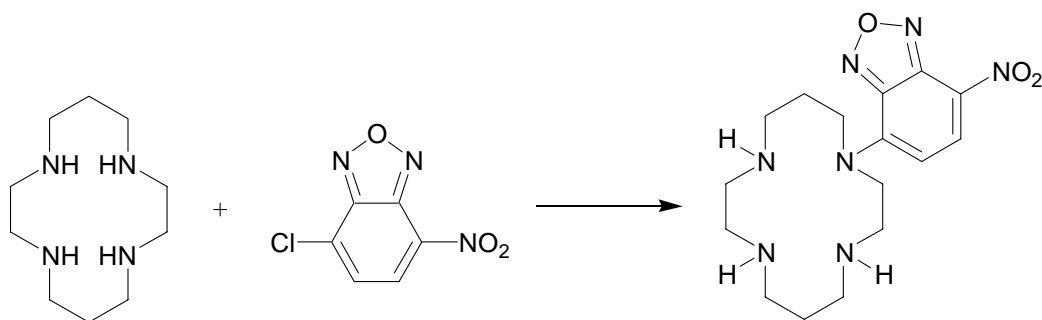
Step 3



1,4,8-Tris(*tert*-butoxycarbonyl)-11-(4-nitrophenyl)-1,4,8,11-tetraazacyclotetradecane (0.59 g, 0.95 mmol) was dissolved in dichloromethane (10 mL) and trifluoroacetic acid was added (1 mL). The solution was stirred at room temperature under a dinitrogen atmosphere for 1 hour. The solution was then concentrated at rotavapor at 25°C to give a dark yellow precipitate, which was dissolved in 5 mL of ethyl acetate and then precipitated with diethyl ether. The solid was separated through filtration and dried under vacuum overnight.

MS (CH₃CN, ESI): *m/z* 322,2 (M+H⁺, 100%).

Synthesis of 1-(4-nitrobenzofurazyl)-1,4,8,11-tetraaza-cyclotetradecane



A solution of 4-chloro-7-nitro-benzofurazan in toluene (2 mmol in 40 mL) was added dropwise to a boiling solution of cyclam in toluene (10 mmol in 150 mL). The solution was maintained under reflux for 3 hrs. On cooling, unreacted cyclam precipitated and was separated through filtration. The solution was then concentrated at the rotavapor to give a ruby red precipitate, which was separated through filtration under vacuum and dried under vacuum.

MS (CH₃CN, ESI): *m/z* 364,2 (M+H⁺, 100%).

$^1\text{H NMR}$ (400 MHz, CD_3CN): δ 1.4-3.0 ppm, (m, 16H); 4.0 ppm, (s, 1H); 4.1 ppm, (s, 1H); 6.2 ppm, (d, 1H); 8.4 ppm, (s, 1H).

Elemental analysis: calculated for $\text{C}_{16}\text{H}_{25}\text{N}_7\text{O}_3$: C 52.89%, H 6.89%, N 27.00%; found: C 52.64%, H 6.93%, N 26.88%.

Figure S1

Titration of an aqueous solution 2×10^{-5} M in **2**, buffered at pH = 4.75, with a standard solution of Cu^{2+} . On metal addition, the band at 474 nm, due to **2**, decreases, while the bands at 337 nm and at 268 nm strengthen. On titration, the orange solution turns yellow. Inset: absorbance at 474 nm vs. equivalents of Cu^{II} (n)

