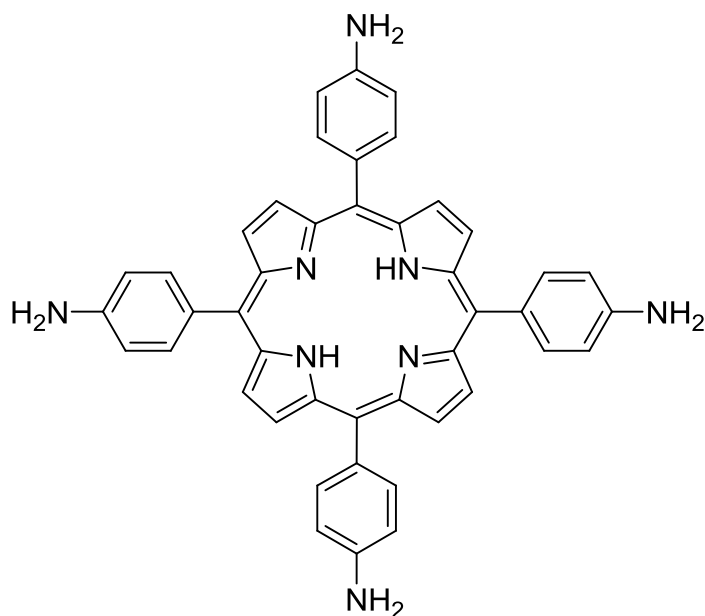


Platinum-nanogaps for single-molecule electronics: roomtemperature stability (electronic supporting information)

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Synthetic procedure 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (H_2TAPP)



A literature procedure¹ was used to synthesize **1**. 4-nitrobenzaldehyde (5.5 g, 36.4 mmol) and acetic anhydride (6 mL, 63.6 mmol) were dissolved in propionic acid (150 mL). The solution was refluxed, to which pyrrole (2.5 mL, 36.0 mmol) was slowly added. After refluxing for 30 minutes, the resulting mixture was filtered to obtain a black solid which was washed with water and methanol, and dried under vacuum. The dried powder was dissolved in pyridine

(40 mL), and subsequently refluxed for 1 hour. After cooling, the resulting precipitate was collected by filtration and washed with acetone to give 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin as purple crystals (1.0 g, 1.26 mmol, 14% yield). The product was dissolved in hot HCl (aq, 500 mL) at 70°C, to which was added $SnCl_2 \cdot 2H_2O$ in large excess (~ 25 equivalents). The resulting mixture was stirred at 70°C for 2 hours and the reaction was monitored by TLC. After neutralization with aqueous NH_3 , the resulting greyish product was collected by filtration and gradient flash chromatography (CH_2Cl_2 /acetone) was performed to obtain the pure product **1** (770 mg, 1.14 mmol, 90 %). Spectral data were in accordance with reported values.¹: 1H NMR (400 MHz, $CDCl_3$): δ -2.71 (s, 2H, pyrrole NH), 4.03 (bs, 8H, Ar- NH_2), 7.07 (d, $J = 7.2$ Hz, 8H, 5,10,15,20-Ar 3,5-H), 7.99 (d, $J = 7.2$ Hz, 8H, 5,10,15,20-Ar 2,6-H), 8.90 (s, 8H, β -pyrrole).

1. Yuasa, M.; Oyaizu, K.; Yamaguchi, A.; Kuwakado, M., Micellar cobaltporphyrin nanorods in alcohols. *Journal of the American Chemical Society* **2004**, *126* (36), 11128-11129.