

Supplementary Information for

“Multiple weak supramolecular interactions stabilize a surprisingly twisted As₂L₃ structure”

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Synthesis of ligand H₂L:

4,4'-Dibromomethyldiphenylmethane (**1**) was prepared by modified version of literature procedures: Diphenylmethane (3.03 g, 18 mmol) and paraformaldehyde (1.08 g) were combined with 30 mL HBr (33% in HOAc) at room temperature. ZnBr₂ (6 g, 27 mmol) was slowly added and the mixture heated to 95 °C overnight. After cooling to room temperature, the off-white solid material was filtered and washed with water.

Recrystallization from benzene yielded the intended product as a white, microcrystalline solid (3.97 g, 62%). δ_{H} (300 MHz; CDCl₃) 7.22 (4 H, d, J = 8.1), 7.11 (4 H, d, J = 8.1), 3.92 (2 H, s), 3.70 (4 H, s).

4,4'-Dimercaptomethyldiphenylmethane: Dibromide **1** (0.616 g, 1.74 mmol) was slurried in 15 mL EtOH and thiourea (0.288 g, 3.78 mmol) was added. The mixture was heated to 70 °C for 16 hours, then cooled to room temperature and concentrated to half the original volume. Diethyl ether was added to precipitate a white solid, which was filtered and washed with additional ether, then air-dried to yield the dithiuronium bromide salt (**2**, 0.679 g, 75%). Under nitrogen atmosphere, **2** (0.177 g, 0.35 mmol) was treated with aqueous NaOH (2N, 10 mL) and heated to 100 °C for 2 hours. After cooling to room temperature, the reaction mixture was washed with degassed diethyl ether, then acidified with concentrated HCl. The aqueous mixture was then extracted three times with ether, then concentrated *in vacuo* to yield H₂L as white solid (88 mg, 96%) δ_{H} (300 MHz; CDCl₃) 7.22 (4 H, d, J = 8.1), 7.11 (4 H, d, J = 8.1), 3.92 (2 H, s), 3.70 (4 H, d, J = 7.5), 1.72 (2 H, t, J = 7.5).

Figure S1: gHMBC of As₂L₃ (500 MHz, CD₂Cl₂, -20 °C).

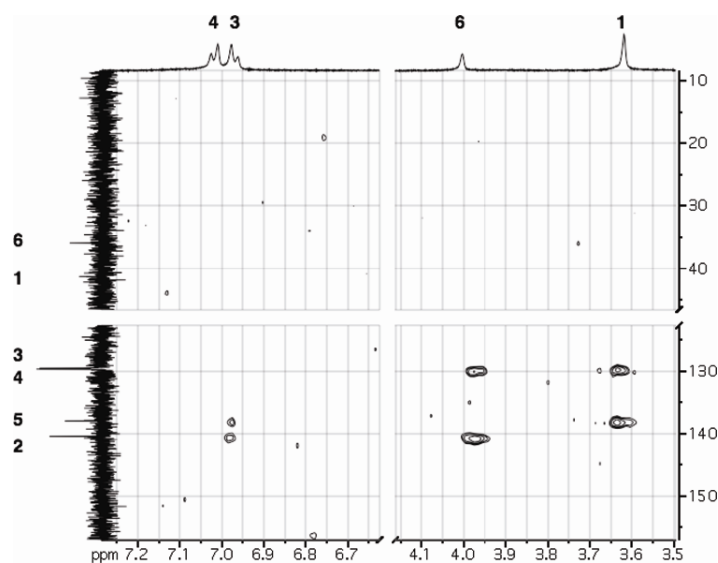


Figure S2: gHMQC of As_2L_3 (500 MHz, CD_2Cl_2 , -20°C).

