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Quadruple hydrogen bonded self-assemblies of 5,5'-bisdiazo-dipyrromethane

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S1. Synthesis of compounds 1 and 2.

(i) A 0.5 M solution of the aromatic amine (5 mmol) and aqueous HCl (4 mL) in water (4 mL) was treated with a 0.5 M solution of NaNO₂ (0.35 g, 5 mmol) in water (10 mL), and the mixture was stirred at room temperature for 0.5 h.

(ii) The diazonium salt solution previously prepared (5.0 mmol) was added drop wise to the solution of dipyrromethane (0.5 g, 2.5 mmol) in acetonitrile (25 ml) and three drops of acetic acid. The combined solution was maintained at room temperature for 2 h with stirring. After this time, EtOAc (25 ml) and water (25 ml) were added. The organic layer was separated and washed with water (20 ml) and dried with anhydrous MgSO₄. The dried solution was evaporated and the residue was purified by column chromatography on silica.

Compound 1: orange powder, 0.58 g, yield 57%, m.p.=177 °C, ¹H NMR (400MHz, CDCl₃); δ 9.28 (s, 2H, pyrrole NH), 7.69 (d, J=4 Hz, 4H, CH), 7.39 (t, J=8 Hz, 4H, CH), 7.30 (t, J=7.2 Hz, 2H, CH), 6.92 (d, J=4 Hz, 2H, Py CH), 6.19 (d, J=4 Hz, 2H, Py CH), 1.79 (q, J=7.2 Hz, 4H, -CH₂-), 0.59 (t, J=7.2 Hz, 6H, -CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 8.5, 27.2, 44.0, 111.3, 117.4, 122.0, 122.2, 129.3, 141.9, 146.0, 152.7; FAB-MS: 411 (M+1); Elemental analysis: C₂₅H₂₆N₆: Calcd: C, 73.14; H, 6.38; N, 20.47. Found: C, 73.05; H, 6.40; N, 20.55.

Compound 2: orange powder, 0.59 g, yield 54%, m.p.=235 °C, ¹H NMR (400MHz, CDCl₃); δ 9.11 (s, 2H, pyrrole NH), 7.61 (d, J=8 Hz, 4H, CH), 7.15 (t, J=8 Hz, 4H,

CH), 6.89 (d, $J=4$ Hz, 2H, Py CH), 6.22 (d, $J=4$ Hz, 2H, Py CH), 2.37 (s, 6H, -CH₃), 1.89 (q, $J=7.2$ Hz, 4H, -CH₂-), 0.66 (t, $J=7.2$ Hz, 6H, -CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 7.94, 21.4, 27.7, 43.9, 110.6, 115.9, 121.8, 129.6, 139.4, 140.8, 145.7, 150.6; FAB-MS: 439 (M+1); Elemental analysis: C₂₇H₃₀N₆: Calcd: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.85; H, 6.62; N, 19.39.

S2. ¹H NMR spectrum of **2** in CDCl₃ solution showing the dimerization induced shift changes (concentrations from bottom to top: 2, 5, 10, 15, 20, 25 mM).

