Extreme Complementarity in a Macrocycle-Tweezer complex

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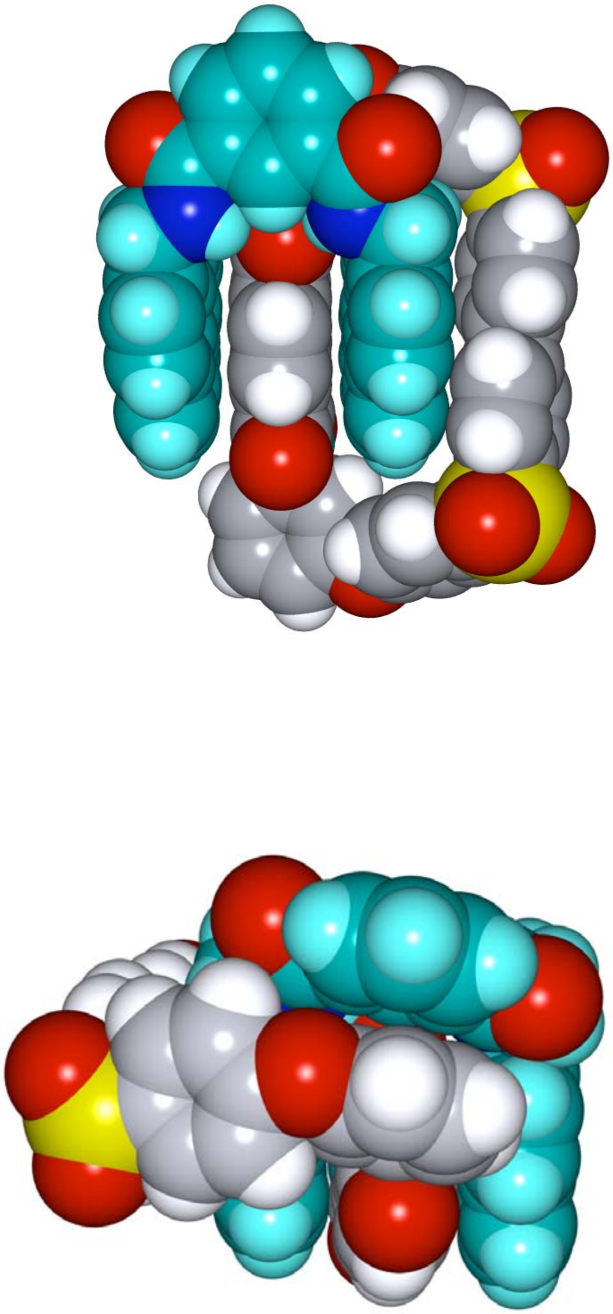
Received Date

SUPPORTING INFORMATION

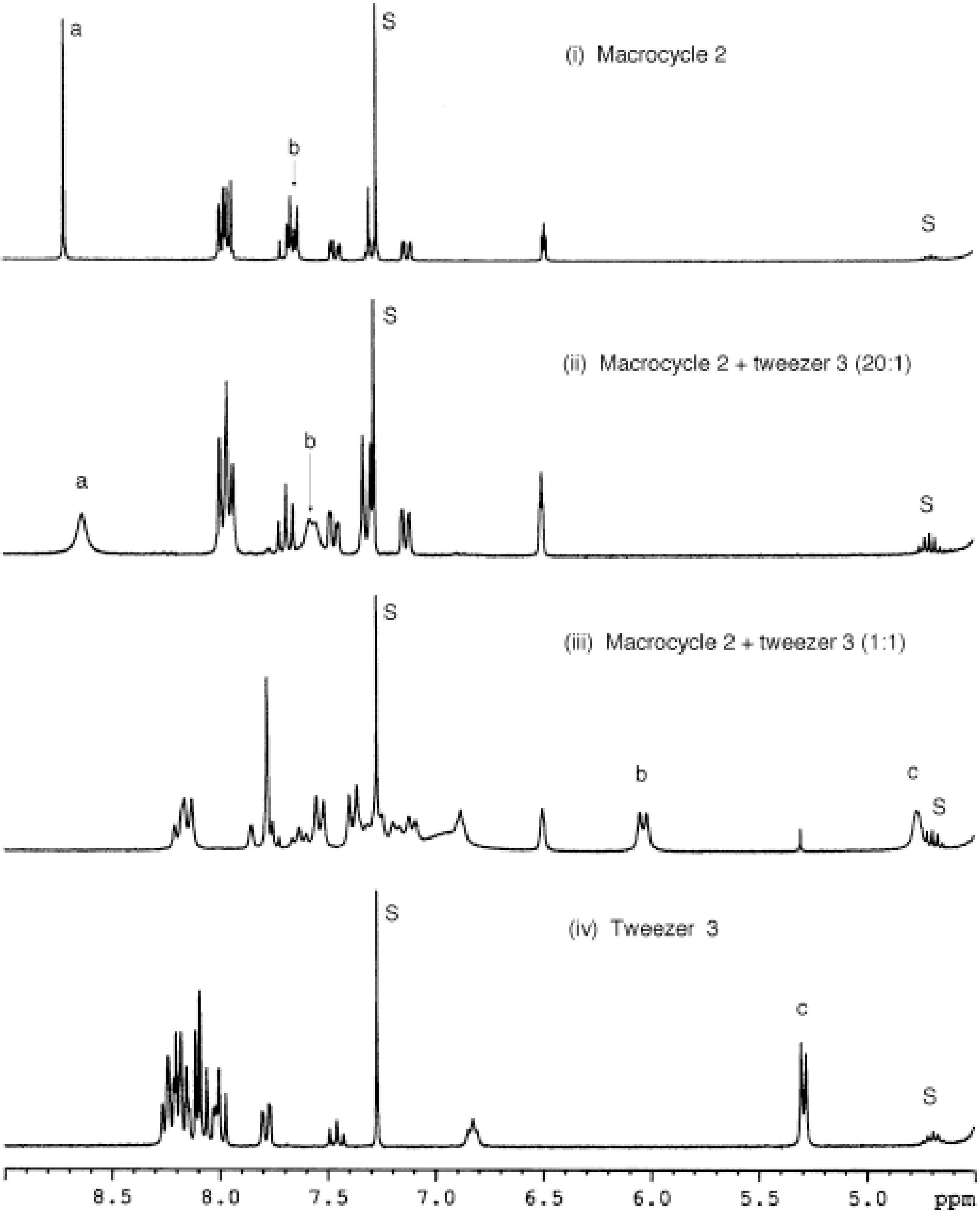
Methods and Instrumentation: Starting compounds were standard reagent grade and, unless otherwise indicated, were used without further purification. Proton and ^{13}C NMR spectra were recorded on Bruker 250 and 400 MHz spectrometers. Mass spectra (EI/CI/FAB) were run on a VG Autospec spectrometer, and MALDI-TOF spectra were measured on a SAI Lasertof instrument, using dithranol as matrix and sodium trifluoroacetate as cationizing agent. Elemental analyses were provided by Medac UK Ltd. Melting points were determined by DSC under nitrogen using a Mettler DSC20 system.

1. *N,N'*-bis(1-pyrenylmethyl)isophthalamide (3): To a mixture of 9-aminomethylpyrene hydrochloride (268 mg, 1 mmol) and triethylamine (0.5 mL) in dichloromethane (10 mL) was added isophthaloyl chloride (95 mg, 0.47 mmol) solution in dichloromethane (10 mL). The mixture was stirred at ambient temperature overnight. The white precipitate so formed was filtered off and washed with water and methanol to afford the title compound (152 mg, 54%), m.p. 378 °C; ^{1}H NMR (DMSO-d$_6$, 250 MHz) 9.37 (t, J = 5.6 Hz), 8.51 (d, J = 9.4 Hz, 2H), 8.49 (s, 1H), 8.28 (m, 8H), 8.16 (s, 4H), 8.07 (m, 6H), 7.59 (t, J = 7.8 Hz), 5.24 ppm (d, J = 5.5 Hz, 4H); ^{13}C NMR (DMSO-d$_6$, 63 MHz) 166.2, 134.9, 133.2, 131.1, 130.6, 130.4, 128.8, 128.5, 127.9, 127.7, 127.4, 127.1, 126.6, 125.6, 125.5, 125.1, 124.4, 124.3, 123.6, 41.5 ppm; MS (CI): m/z = 593 (30%) [M]$^+$; Elemental analysis: Calcd. for $C_{42}H_{28}N_2O_2$: C 85.11, H 4.76, N 4.72; Found C 84.30, H 4.69, N 4.58%.

2. *N,N'*-bis(1-pyrenylmethyl)pyridine-2,6-dicarboxamide (4): To a mixture of 9-aminomethylpyrene hydrochloride (268 mg, 1 mmol) and triethylamine (0.5 mL) in dichloromethane (10 mL) was added 2,6-pyridinedicarbonyl dichloride (96 mg, 0.47 mmol) solution in dichloromethane (10 mL). The mixture was stirred at ambient temperature overnight. The mixture was extracted with water. the organic extracts were then dried ($MgSO_4$) and then the solvent was evaporated. The residue was purified by column chromatography (SiO_2: dichloromethane-methanol, 99/1) to yield **4** as a pale yellow solid (230 mg, 83%), m.p. 418 °C; ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol, 250 MHz) 8.19 (d, J = 7.5 Hz, 4H), 8.02 (m, 11H), 7.90 (m, 4H), 7.79 (d, J = 7.9 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 5.15 ppm (d, J = 5.6 Hz, 4H); 13C NMR ($CDCl_3$/hexafluoropropan-2-ol, 63 MHz) 164.2, 147.6, 139.2, 131.5, 130.7, 129.7, 128.9, 128.6, 128.0, 127.5, 126.8, 126.6, 126.1, 125.8, 125.2, 124.9, 124.1, 124.0, 122.2, 119.6, 119.5, 115.0, 42.1 ppm; MS (MALDI-TOF): m/z = 616 [M+Na]$^+$; Elemental analysis: Calcd. for $C_{41}H_{27}N_3O_2$: C 82.95, H 4.58, N 7.07; Found C 82.77, H 4.53, N 6.99%.



Supplementary figure A: Space-filling diagrams of complex **5**, showing the range of electronically complementary π-stacking interactions



Supplementary Figure B: Complexation shifts in the ^{1}H NMR spectrum of macrocycle **2** in the presence of tweezer molecule **3** at 20:1 and 1:1 mole ratios in $CDCl_3/(CF_3)_2CHOH$ (6:1 v/v) solution. Note particularly the broadening and eventual disappearance of the naphthalene-dimide singlet resonance *a*, the extreme upfield shift (1.60 ppm) of the doublet resonance *b* arising from the protons adjacent to the biphenyl linkage in **2**, and the marked upfield shift of the methylene resonance *c* associated with the tweezer molecule **3** (S = solvent resonance).