Supporting information

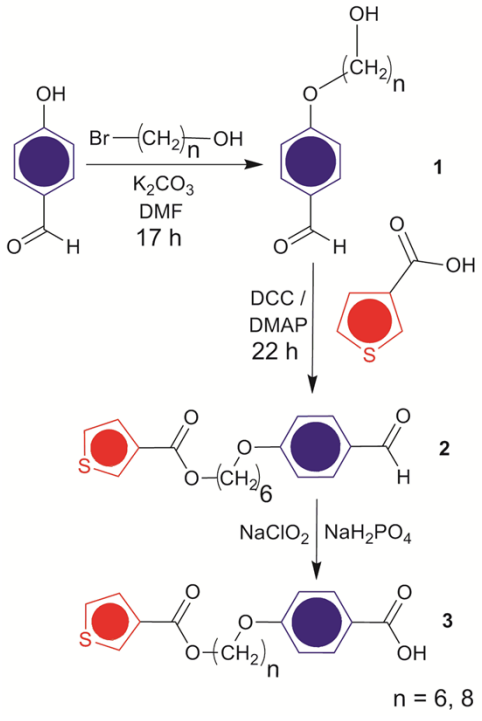
Tailoring 'specific recognition' clefts from non-specific recognition matrices in mixed molecular arrays

Synthesis of 4-(6-(thiophene-3-carbonyloxy)hexyloxy)benzoic acid (T6BA)

Materials:

4-hydroxybenzaldehyde, 6-bromohexan-1-ol, 8-bromooctan-1-ol, thiophene-3-carboxylic acid, 4-dimethylaminopyridine(DMAP), *N,N'*-dicyclohexylcarbodiimide (DCC) and dimethylformamide(DMF)were purchased from Sigma Aldrich. K_2CO_3, $NaClO_2$ and NaH_2PO_4were purchased from SRL fine chemicals Ltd.

The following synthetic scheme was adopted for the preparation of 4-(6-(thiophene-3-



Scheme 1:*Synthetic scheme for the synthesis of 4-(6-(thiophene-3-carbonyloxy)hexyloxy)benzoic acid (T6BA).*

carbonyloxy)hexyloxy)benzoic acid (T6BA).

Step 1: Synthesis of 4-(6-hydroxyhexyloxy)benzaldehyde

To a mixture solution of 4-hydroxybenzaldehyde (678.4 mg, 5.55 mmol) and 6-bromohexan-1-ol (1 g, 5.55mmol) in DMF(300 mL), K_2CO_3(3.5 g, 25mmol) was added and then refluxed for 17 hrs. The reaction mixture was poured in water (600 mL) and then extracted with ethyl acetate (600 mL). The combined extract was evaporated to dryness. The residue was column chromatographed (silica gel, dichloromethane) to obtain**1**, a colorless liquid in 87% yield.

Step 2: Synthesis of 6-(4-formylphenoxy)hexyl thiophene-3-carboxylate

Thiophene-3-carboxylic acid (5 mmol), DCC (5.5 mmol), and **1** (5 mmol) in dichloromethane (25 mL) with catalytic amount of 4-dimethylaminopyridine (DMAP) were stirred mechanically at room temperature until esterification was complete. N,N-dicyclohexylurea formed was filtered off. The filtrate was washed with water (3 × 25 mL), 5% acetic acid (3 × 25 mL) and again with water (3 × 25 mL) and dried over anhydrous sodium sulphate. Solvent was removed under the reduced pressure to give the ester **2** (Scheme 1) which was chromatographed over a column of silica gel using n-hexane–ethyl acetate (96:4, v/v) as an eluent. The synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.

Step 3: Synthesis of 4-(6-(thiophene-3-carbonyloxy)hexyloxy)benzoic acid

The aldehyde**2** (0.250 g, 0.75 mmol) in THF: t-BuOH (1:1, 15 mL) was cooled to 0°C and $NaClO_2$ (0.28 g, 3.1 mmol) and $NaH_2PO_4.H_2O$ (0.37 g, 3.1mmol) in 10 mL H_2O were added. The reaction mixture was warmed to RT and stirred for 12 h. The solution was then concentrated, 1N HCl (8 mL) was added, and the mixture was extracted with DCM (2 x 10 mL). The combined organic phases were washed with brine (15 mL), then dried (Na_2SO_4), and concentrated. The mixture was stirred for 4h at this temperature, and then concentrated.Flash chromatography (EtOAc/hexane, 3.5:6.5) afforded 75% of **3** as a white solid.

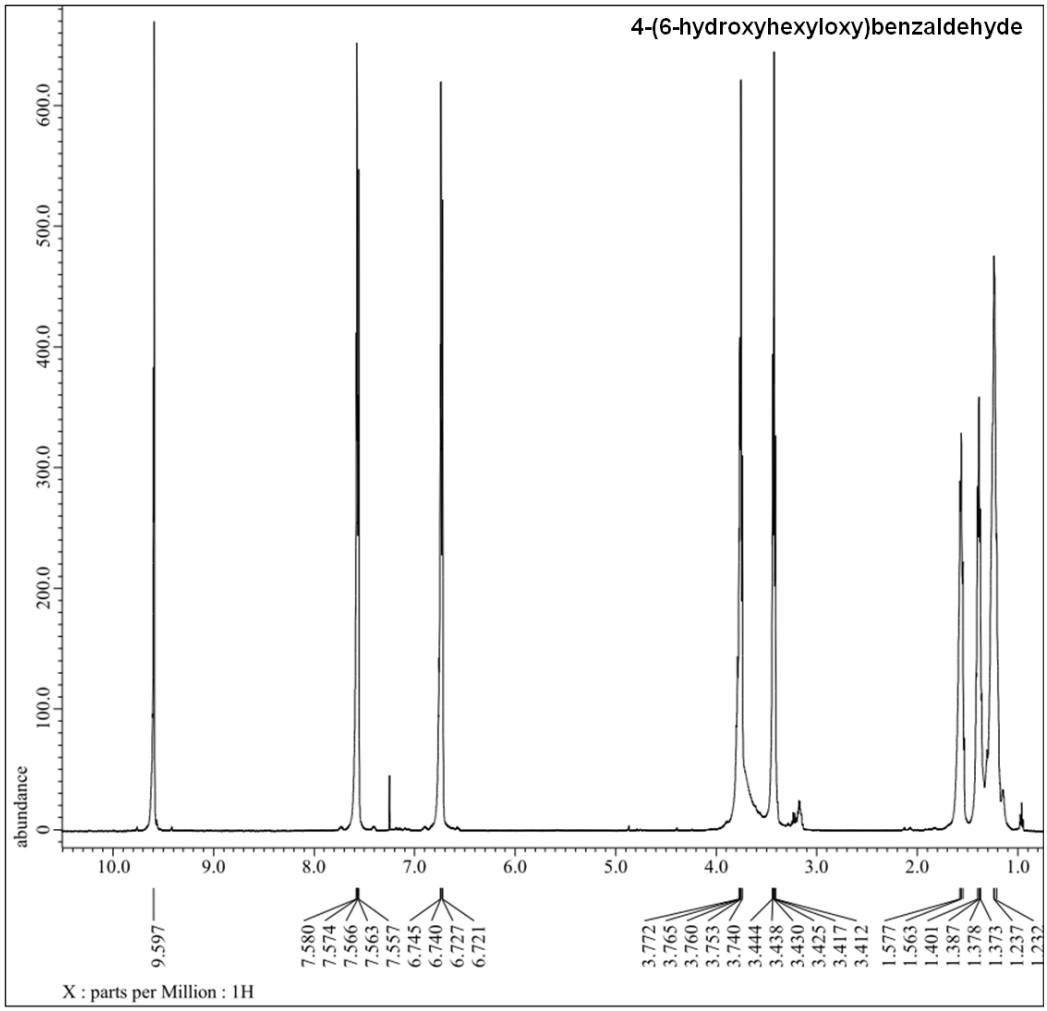


Figure S1: *H^1 NMR of 4-(6-hydroxyhexyloxy)benzaldehyde*

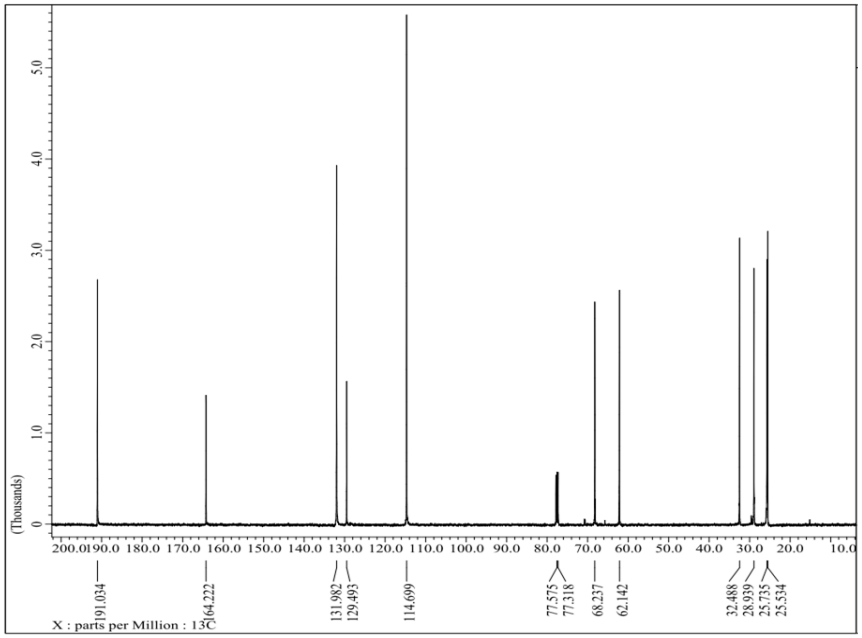


Figure S2: *C^{13} NMR of 4-(6-hydroxyhexyloxy)benzaldehyde*

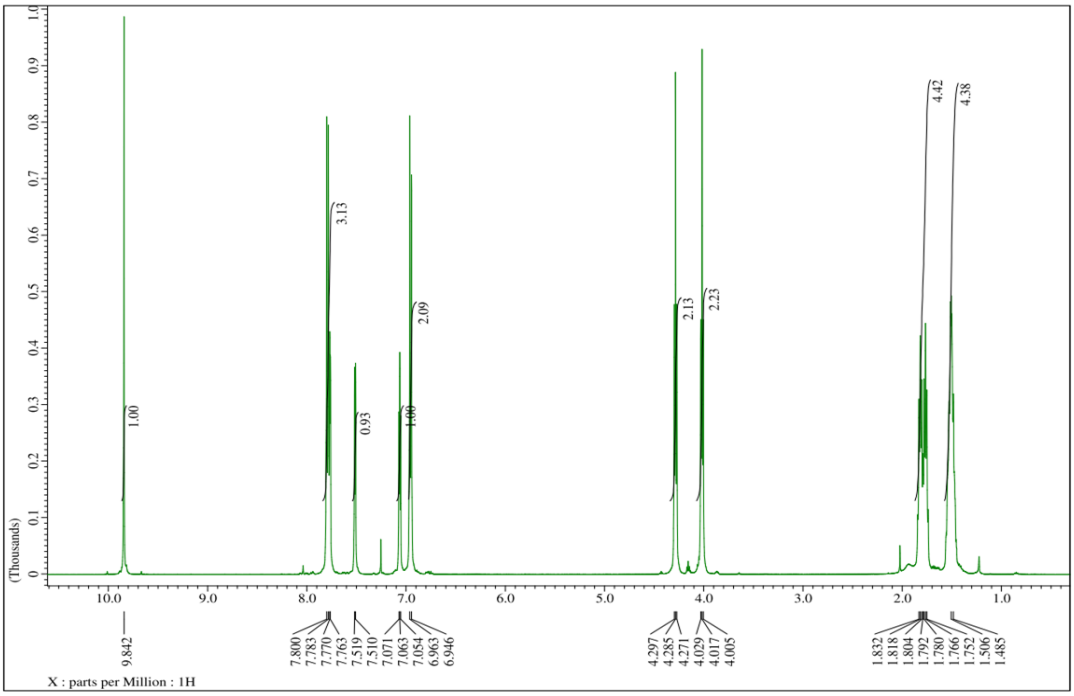


Figure S3: *H^{1} NMR of 6-(4-formylphenoxy)hexyl thiophene-3-carboxylate*

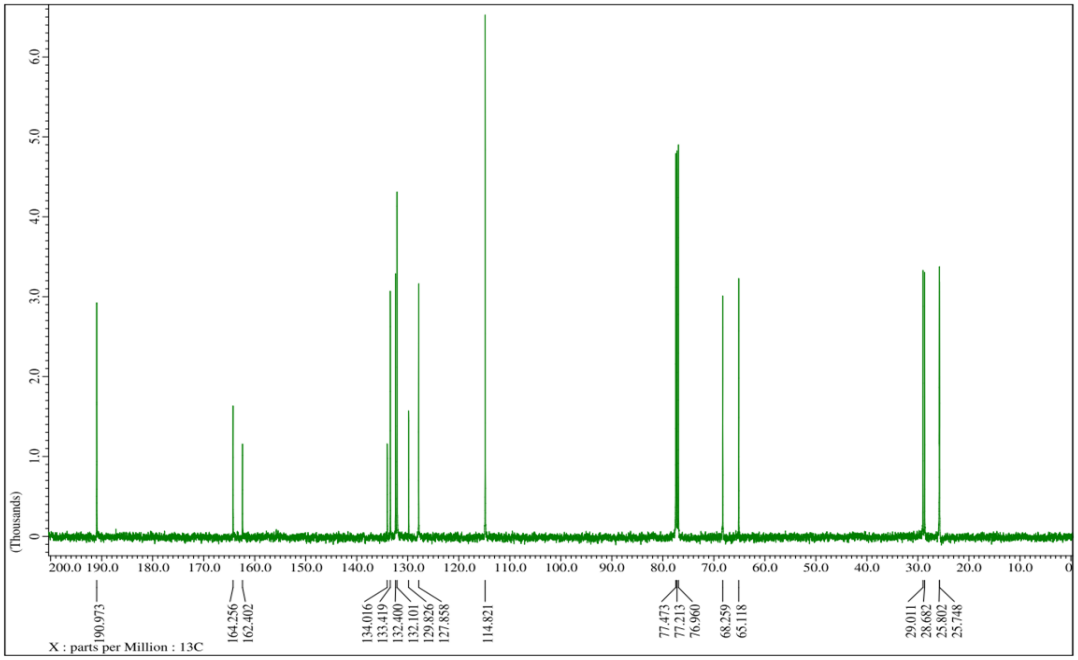


Figure S4: *C^{13} NMR of 6-(4-formylphenoxy)hexyl thiophene-3-carboxylate*

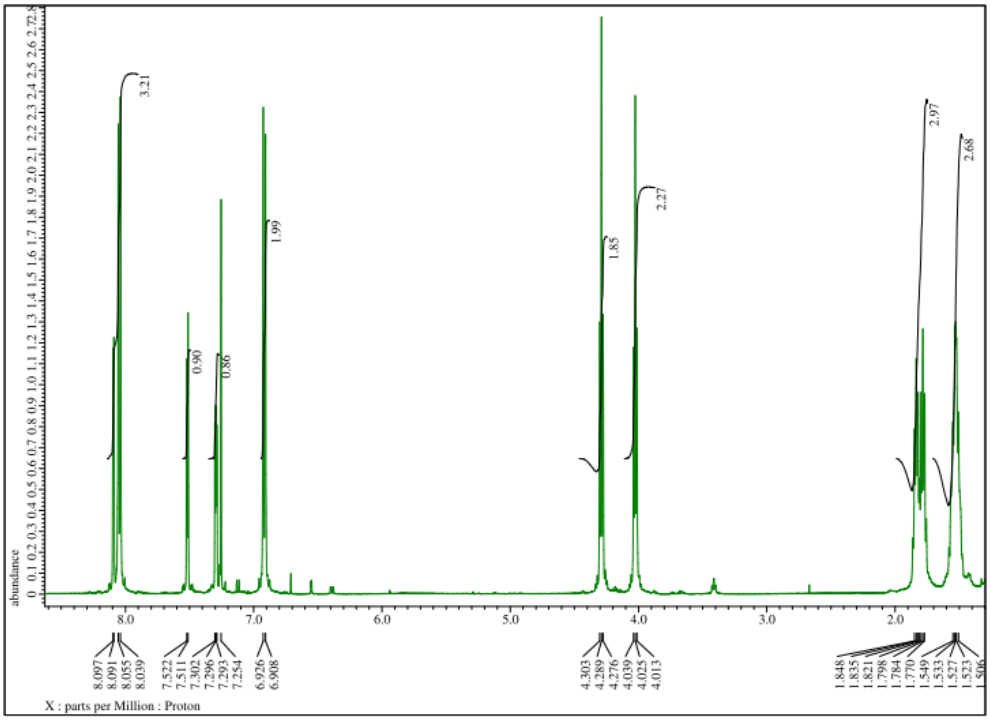


Figure S5: *H^{1} NMR of 4-(6-(thiophene-3-carbonyloxy)hexyloxy)benzoic acid*

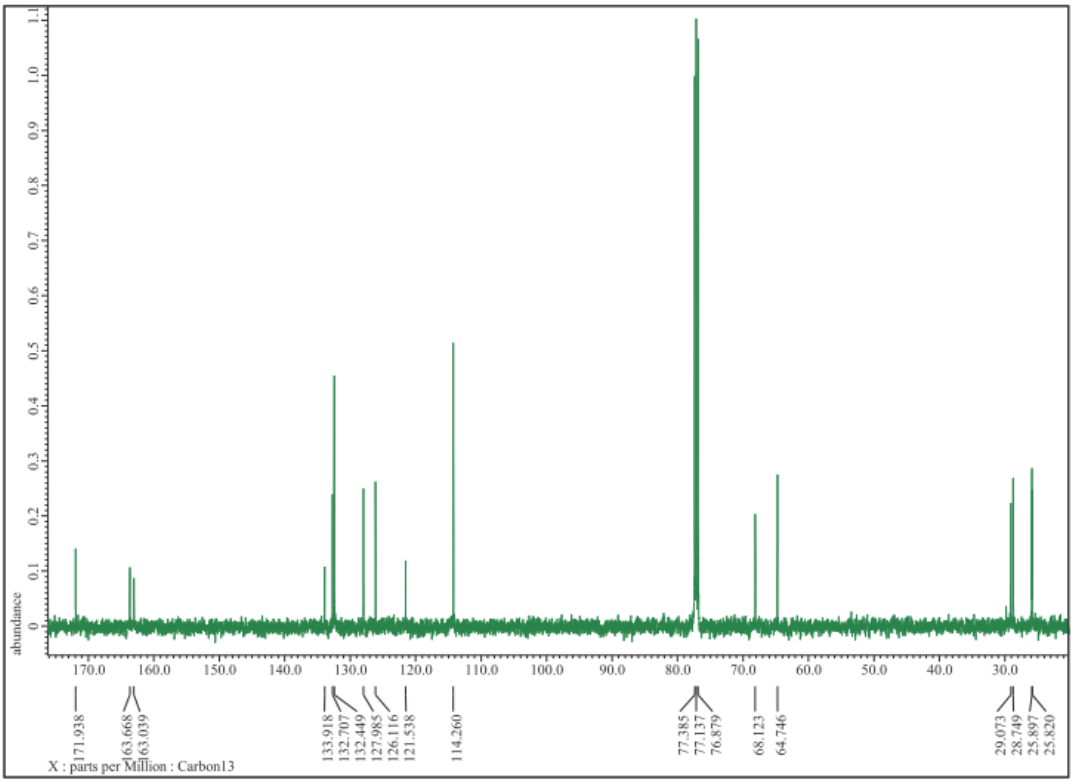


Figure S6: *C^{13} NMR of 4-(6-(thiophene-3-carbonyloxy)hexyloxy)benzoic acid.*

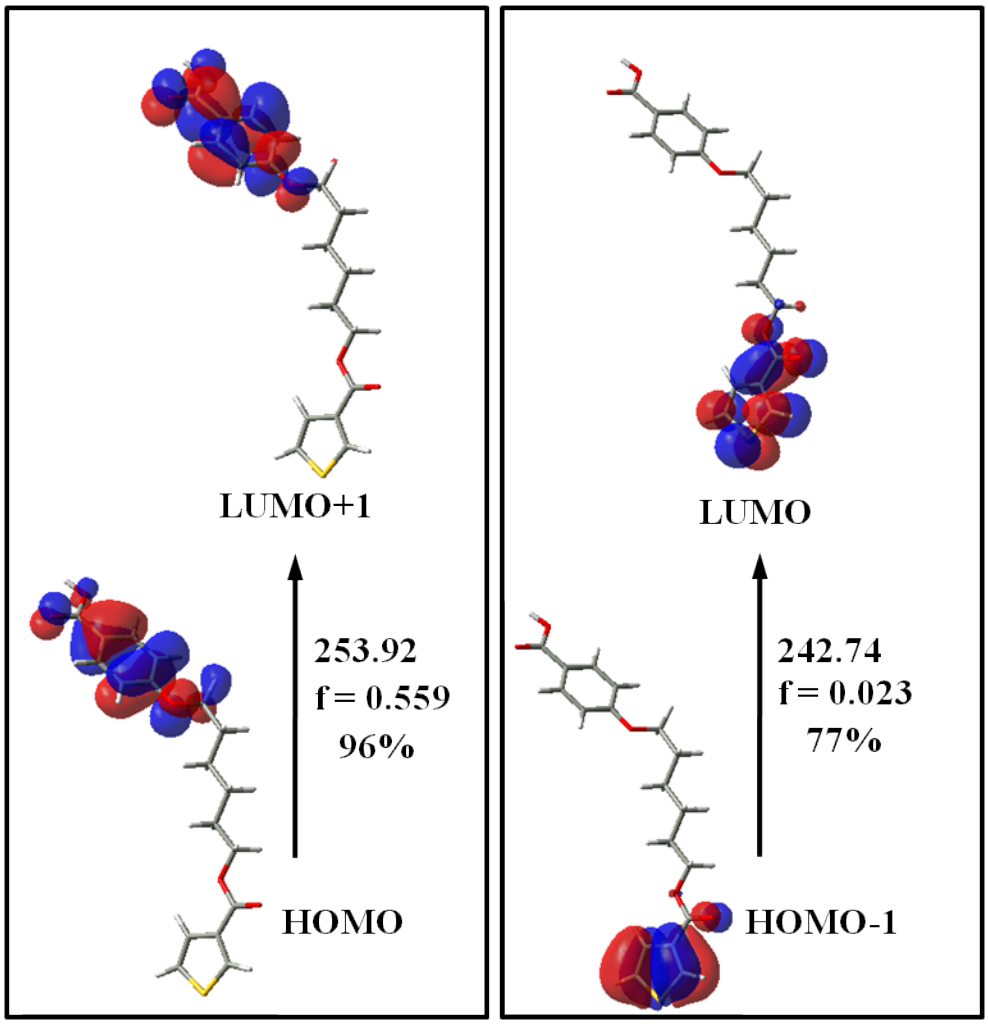


Figure S7. Isodensity plots of HOMO-1, HOMO, LUMO and LUMO+1 of monomeric T6BA in methanol derived from TD-DFT calculations. Two main allowed electronic transitions in T6BA involving either benzoic acids or thiophene moiety are presented. The orbitals involving electronic transition LUMO+1←HOMO with oscillator strength, f = 0.559 happen to be on benzoic acid and the next electronic transition (LUMO←HOMO-1) which is weak in terms of oscillator strength, f = 0.023 involves orbitals located on thiophene. Frontier molecular orbitals

were determined using TD-DFT (Time dependent density functional theory) at B3LYP/6-31G(d) level of theory with implicit solvation using IEFPCM model.

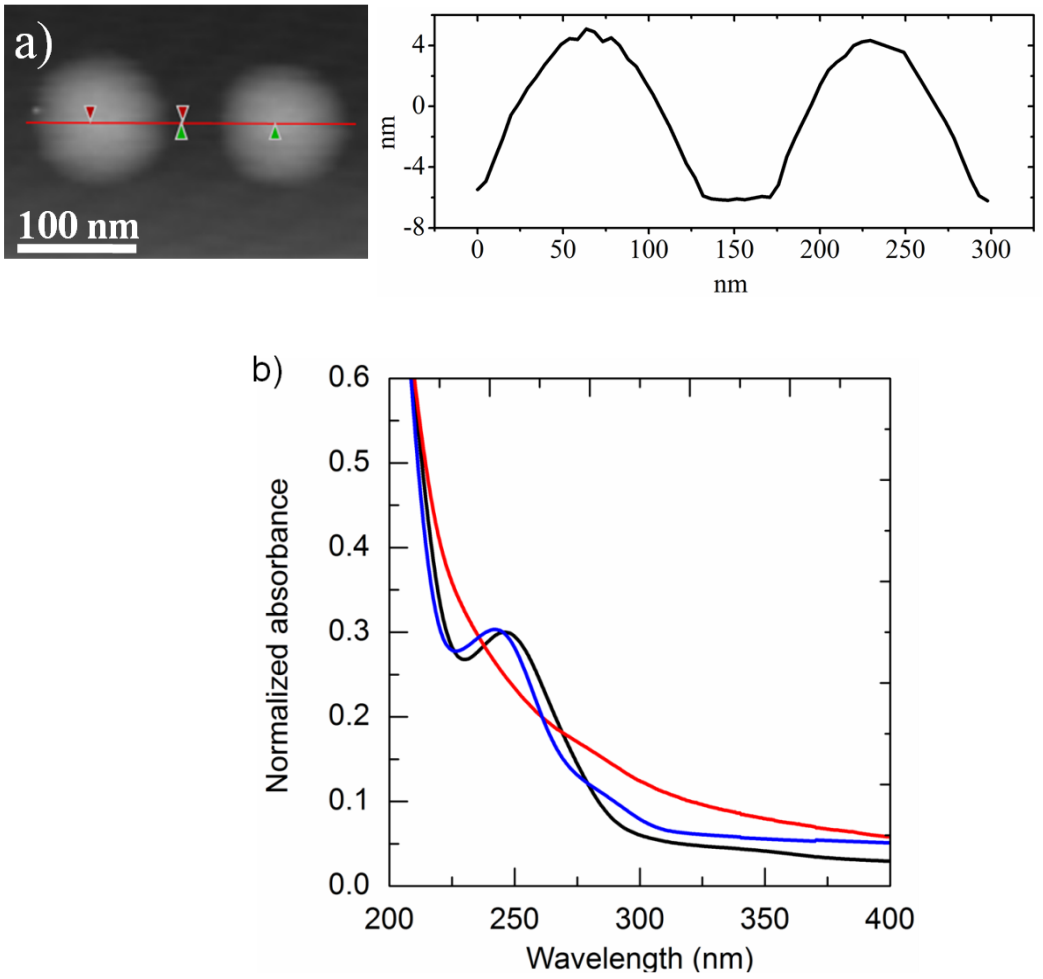


Figure S8. a) Topographic non-contact mode AFM image of stripe-like domains treated with β-CD. Image is acquired on a Si (100) substrate. The line profile across the twin domains suggest binding of β-CD onto thiophene part of the T6BA while benzoic acid end is anchored onto to Silicon (100). The excess height suggests aggregation of β-CD on the SAM surface. b) Experimental UV-visible spectra of T6BA(blue line), β-cyclodextrin(red line) and inclusion complex (black line).

Additional Information

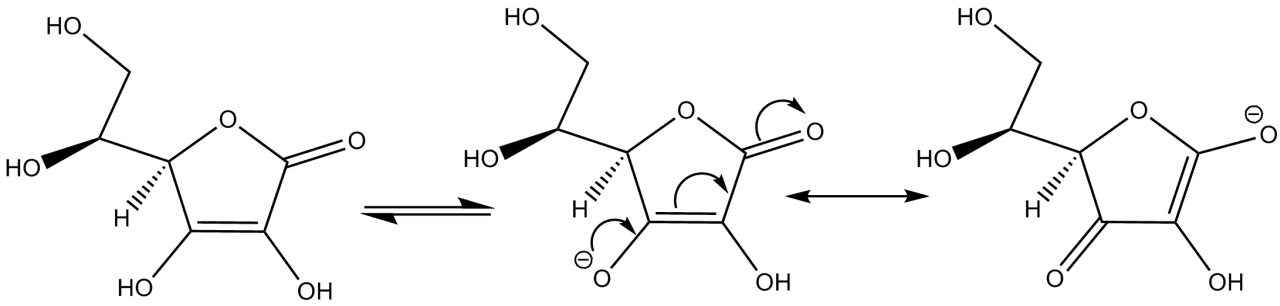


Figure A1. Resonance structures of Ascorbic Acid.

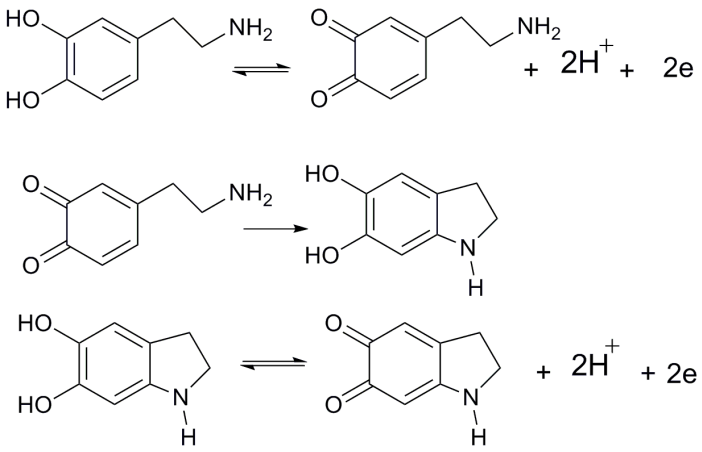


Figure A2. ECE (Electron transfer – chemical reaction – Electron transfer) mechanism.