Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Monitoring the formation of TTF dimers by Na^+ complexation

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1- Materials and methods

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1- Materials and methods

Unless otherwise noted, solvents and starting products were commercially available and used without further purification. ^{1}H-NMR titration studies were carried out by adding small volumes of concentrated solutions of the metal cation (as the perchlorate salt) dissolved in acetonitrile-d$_3$ to a solution of the calixarene receptor (1-3 mM) in CD_2Cl_2:CD_3CN (1:1).

2- Synthetic procedure

Compound 6. To a suspension of *tert*-butyl calix[4]arene **4** (0.120 mg, 0.121 mmol) in anhydrous CH_2Cl_2 (20 mL) were added successively under nitrogen, DCC (50 mg, 0.242 mmol), DMAP (29 mg, 0.242 mmol), HOBT (33 mg, 0.242 mmol) and finally hydroxymethyl-TTF **5** dissolved in 20 ml of dry CH_2Cl_2. The reaction mixture was stirred at room temperature during two days. The resulting suspension was filtered and after addition of CH_2Cl_2 (100 ml), the organic layer was washed with water and dried over $MgSO_4$. After concentration under reduced pressure, the product was purified by recrystallisation (CH_2Cl_2/CH_3OH/C_5H_{12}), and an orange solid was isolated (70 mg, 41% yield). m.p. = 197-199°C; ^{1}H NMR (500 MHz): 7.10 (s, 4H, ArH), 6.76 (s, 2H, H$_a$), 6.60 (s, 8H, ArH + H$_{b+c}$), 5.25 (s, 4H, OC$\underline{H}_2$COOCH_2TTF), 4.93 (s, 4H, OCH_2TTF), 4.90 (4H, 12.8 Hz, ArCH_2Ar), 4.60 (s, 4 H, OCH_2CONEt$_2$), 3.44 (m, 8H, OC$\underline{H}_2$$CH_3$), 3.19 (d, 4H, 12.8, Ar$CH_2$Ar), 1.27 (s, 18 H, *t*Bu), 1.25 to 1.09 (m, 6H, NCH_2CH_3), 0.92 (s, 18 H, *t*Bu); ^{13}C NMR (125 MHz, acetone D$_6$): 171.28 (OCO), 168.19 (NCO), 154.72 and 154.29 (Ar ipso), 145.67 and 145.14 (Ar para), 135.74 and 133.20 (Ar ortho), 126.55 and 125.71 (Ar meta), 132.15, 120.34, 120.31, 119.89 (lateral C=C TTF), 111.83, 109.65 (central C=C TTF), 73.61 (O*C*H$_2$CONEt$_2$), 71.19 (O*C*H$_2$COOTTF), 61.12 (OCH_2TTF), 41.81 and 40.57 (N*C*H$_2$CH$_3$), 34.54, 34.25 ($\underline{C}(CH_3)_3$), 32.74 (ArCH_2Ar), 31.95 and 31.61 (tBu), 14.85 and 13.65 (N$CH_2\underline{C}H_3$); FT-IR (KBr, cm^{-1}): 1760 (OC=O), 1653 (NC=O); HRMS-ESI$^+$ (M+ Na): Calcd 1445.426, found 1445.429.

3- Na^+ titration study (^{1}H-NMR)

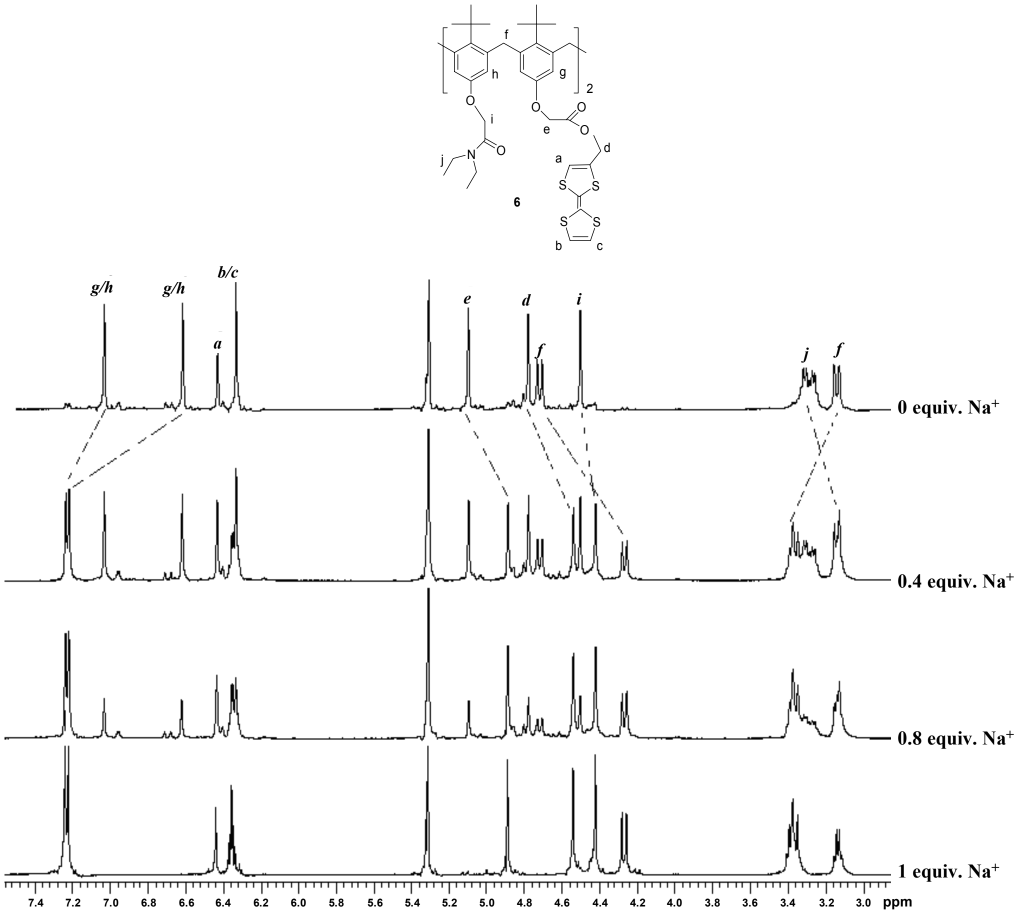

Figure S1. ^{1}H-NMR titration of compound **6** (CD_3CN / CD_2Cl_2), in the presence of $NaClO_4$.

4- Spectroelectrochemical study

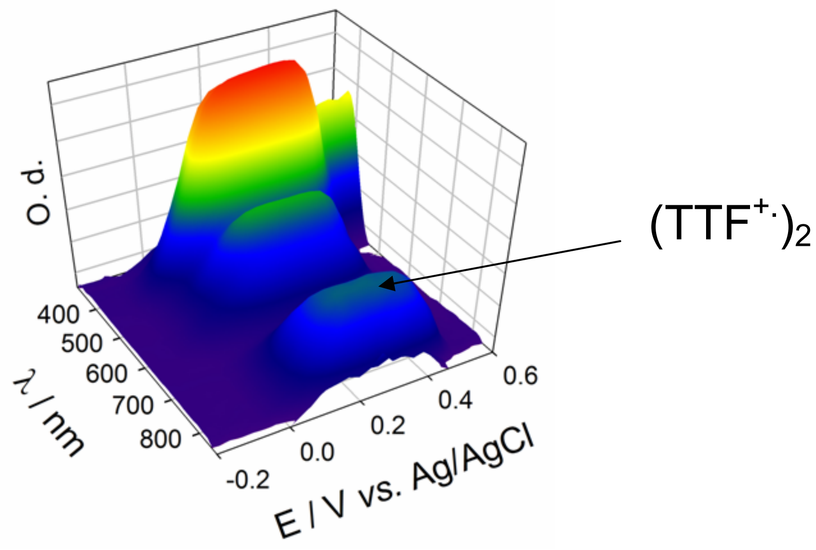

Figure S2 : Spectroelectrochemistry in thin layer (d≈50µm); conditions (Pt, ∅=2mm); [**6**] = 0.75 mM in CH_2Cl_2/CH_3CN (1/1), Bu_4NPF_6 (0.2 mol.L^{-1}), scan rate 0.125 mV s^{-1}.