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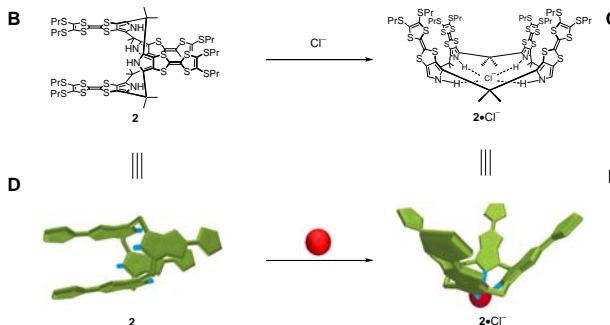
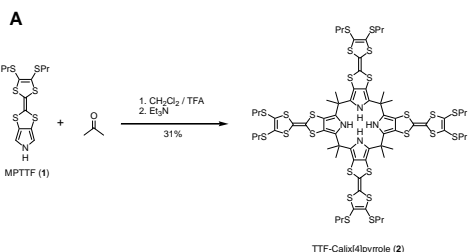
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Synthesis of the TTF-calix[4]pyrrole Receptor (2)

Anion Recognition Leading to a Conformational Change

Anion Binding Constants



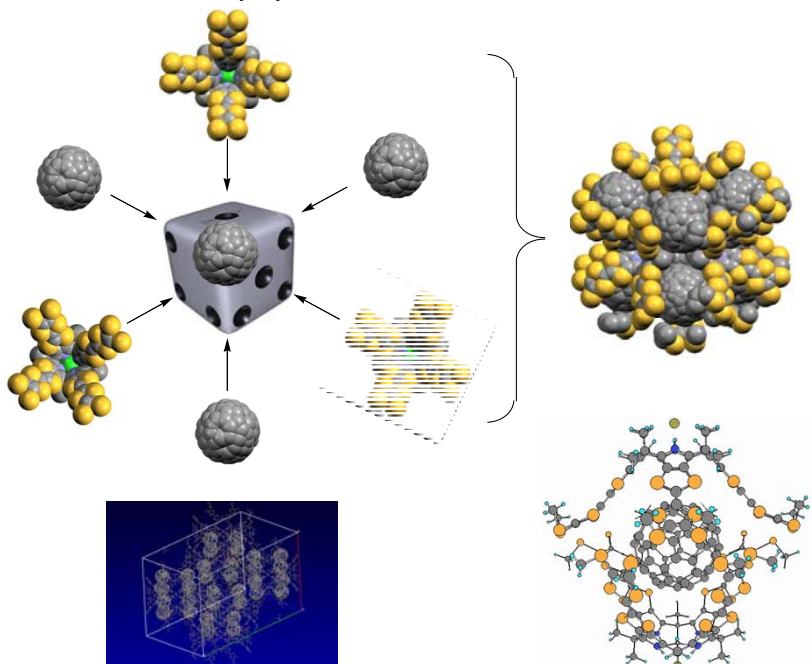
X ⁻	K _b [M ⁻¹]	ΔE [mV]
Br ⁻	58 000	-18
Cl ⁻	2 500 000	-20
CN ⁻	1 200 000	-
NO ₂ ⁻	1 200 000	-
CH ₃ CO ₂ ⁻	1 200 000	-

(A) Synthesis of the TTF-calix[4]pyrrole receptor 2. (B) A three-dimensional representation of the TTF-calix[4]pyrrole receptor 2 in its 1,3-alternate conformation. (C) A three-dimensional representation of the chloride bound TTF-calix[4]pyrrole receptor 2·Cl⁻ in its cone conformation. (D) A cartoon representation of the TTF-calix[4]pyrrole receptor 2 in its 1,3-alternate conformation. (E) A cartoon representation of the chloride bound TTF-calix[4]pyrrole receptor 2·Cl⁻ in its cone conformation.

^a Binding constants obtained from ITC experiments carried out in 1,2-dichloroethane at 298 K between TTF-calix[4]pyrrole receptor 2 and Br⁻, Cl⁻, CN⁻, NO₂⁻ or CH₃CO₂⁻ ions.

^b Maximum ΔE displacement in the first oxidation potential of TTF-calix[4]pyrrole receptor 2 upon addition of 1.2 equiv. of n-Bu₄NX to a 1,2-dichloroethane solutions at 298 K of 2.

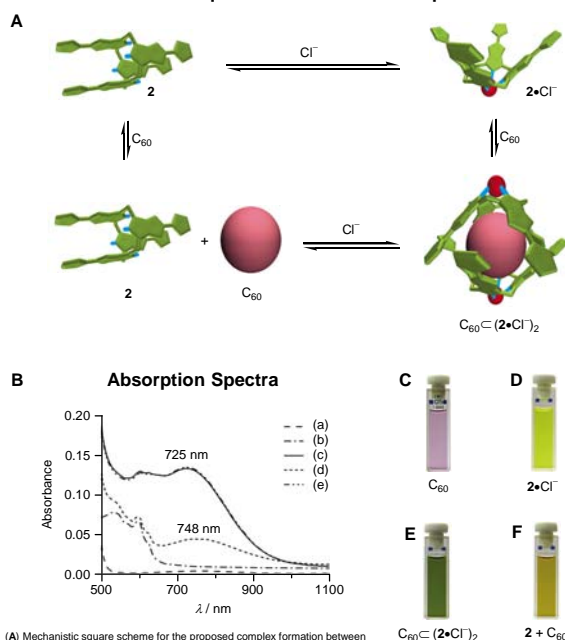
X-Ray Crystal Structure and Force Field Model



Unit cell of the solid state co-complex between C₆₀ and 2·Cl⁻ containing approximately 38 C₆₀ and 24 2·Cl⁻ units.

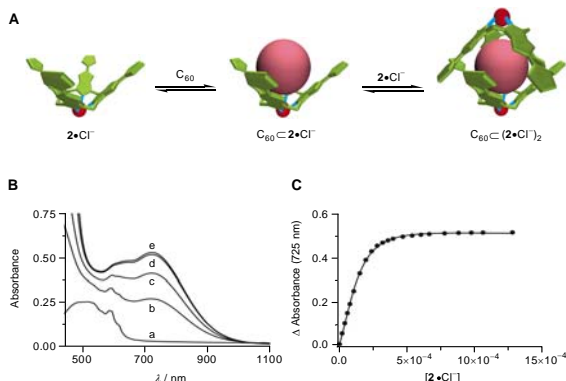
Force field-generated model of the proposed 2:1 complex (i.e., C₆₀-(2·Cl⁻)₂), as reoptimized at the B3LYP/3-21G level.

Mechanistic Square Scheme of the Complexation



(A) Mechanistic square scheme for the proposed complex formation between the receptor 2 and C₆₀ in the presence of chloride ions. (B) Absorption spectra recorded in dichloroethane at 298 K of (a) TTF-calix[4]pyrrole 2 (0.135 mM), (b) C₆₀ (0.0687 mM), (c) 2·Cl⁻ + C₆₀ (0.5 equiv), (d) 2 + C₆₀ (0.5 equiv), (e) 2 + C₆₀ (0.5 equiv) and then n-Bu₄NCl (excess). (C) A solution of C₆₀ in dichloroethane. (D) A solution of 2·Cl⁻ in dichloroethane. (E) A solution of 2·Cl⁻ + C₆₀ (0.5 equiv) in dichloroethane. (F) A solution of 2 + C₆₀ (0.5 equiv) in dichloroethane.

Encapsulation of C₆₀ and Binding Constants

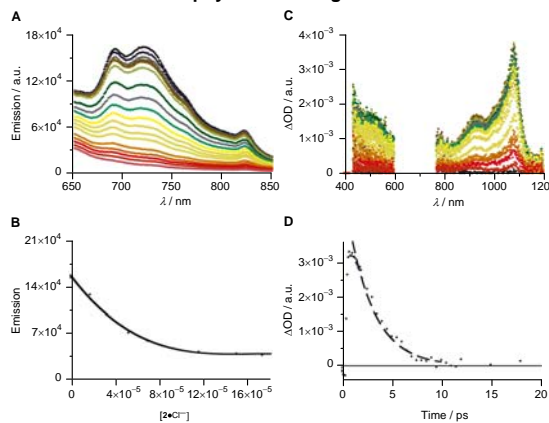


(A) Equilibria leading to the formation of C₆₀·2·Cl⁻ and C₆₀·(2·Cl⁻)₂. (B) Absorption spectra recorded in dichloroethane at 298 K of (a) C₆₀ (0.2 mM), (b) C₆₀ + 2·Cl⁻ (0.5 equiv), (c) C₆₀ + 2·Cl⁻ (1.0 equiv), (d) C₆₀ + 2·Cl⁻ (2.0 equiv), (e) C₆₀ + 2·Cl⁻ (6.0 equiv). (C) Changes in the CT band at 725 nm on titration of 2·Cl⁻ with C₆₀ (0.2 mM) in a dichloroethane solution at 298 K.

X ⁻	K _b (M ⁻¹)	K _c (M ⁻¹)
Br ⁻	4 800	4 400
Cl ⁻	1 900	16 400

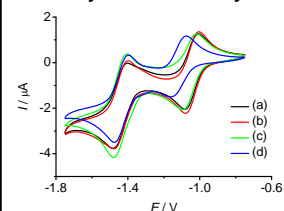
Binding constants between TTF-calix[4]pyrrole 2 and C₆₀ in dichloroethane solution containing 1.2 equiv. of the Br⁻ or Cl⁻ ions, as determined by UV-Vis spectroscopy at 298 K.

Photophysical Investigations



(A) Steady state fluorescence of 5.38 × 10⁻⁶ M solution C₆₀ in dichloroethane upon adding variable concentrations of 2·Cl⁻ (1.72 × 10⁻⁵ M – 2.87 × 10⁻⁴ M) (B) Fluorescence intensity at 690 nm of C₆₀·2·Cl⁻ / C₆₀·(2·Cl⁻)₂ in dichloroethane. The 2·Cl⁻ concentrations vary from 1.72 × 10⁻⁵ M to 2.87 × 10⁻⁴ M, while the C₆₀ concentration is constant with 5.38 × 10⁻⁶ M. (C) differential absorption spectra (visible) obtained upon femtosecond flash photolysis (740 nm) of C₆₀·(2·Cl⁻)₂ in nitrogen saturated dichloroethane with several time delays between 0 and 10 ps at room temperature – arrows indicate the evolution of differential changes (D) Time-absorption profiles of the spectra shown above at 1080 nm.

Cyclic Voltammetry



Cyclic voltammograms recorded in dichloroethane at 298 K of (a) C₆₀ (0.2 mM), (b) C₆₀ + n-Bu₄NCl (4 equiv), (c) C₆₀ + 2 (2 equiv), (d) C₆₀ + 2 (2 equiv) + n-Bu₄NCl (4 equiv).

C ₆₀	E _{1/2} (V)	ΔE _{1/2} (V)
C ₆₀ + Cl ⁻	0	0
C ₆₀ + 2	+0.004	+0.003
C ₆₀ + 2	+0.001	-0.011
C ₆₀ ·(2·Cl ⁻) ₂	+0.007	-0.074

First redox potential of C₆₀ and its displacement observed upon the addition of n-Bu₄NCl, 2, and 2 + n-Bu₄NCl to a dichloroethane solution at 298 K of C₆₀.

References:

K. A. Nielsen et al. JACS, 126, 2004, 16296
K. A. Nielsen et al. JACS, 128, 2006, 2444