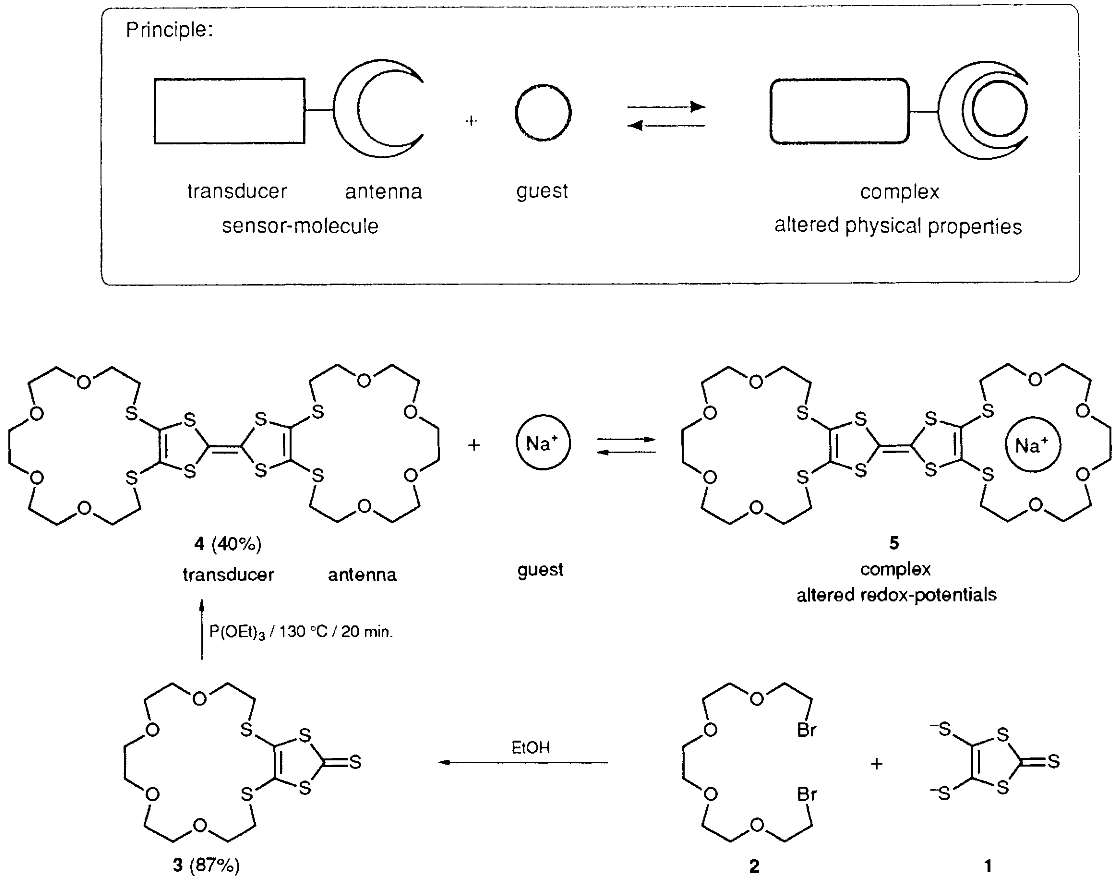
A Sodium Ion-sensitive Tetrathiafulvalene: Preparation and Redox Properties

Thomas K. Hansen,* Tine Jørgensen and Jan Becher
Department of Chemistry, University of Odense, 5230 Odense, Denmark

The new tetrathiafulvalene derivative **4** has been synthesized in good yield, two crown ether moieties being annelated to the tetrathiafulvalene skeleton in the 2,3 and 6,7-positions; the redox potential of this compound has been shown to be sensitive to the presence of sodium ions.

Tetrathiafulvalene (TTF) and its numerous derivatives have been studied intensively[1] since the spectacular discovery of high conductivity[2] and superconductivity in salts of TTF derivatives.[3] Likewise huge efforts have been invested in the area of crown ethers, cryptands and related macrocyclic ligands.[4] However only sporadic reports of combinations of these two areas have appeared in the chemical literature.[5,6] Based on our experience with the versatile synthon 2-thioxo-

To our knowledge no experiments have been reported aimed at influencing redox properties of tetrathiafulvalenes *via* complexation of alkali metal ions in an annelated crown moiety, but a low-yield synthesis related to the one presented here has been reported by Otsubo *et al.*,[5] although the crown in that case was smaller. We employed diethylene, triethylene and tetraethylene glycol dibromides and obtained oligomeric mixtures for which chromatography was needed in order to



Scheme 1 Principle of sensor molecules. Synthesis of **4** as an example.

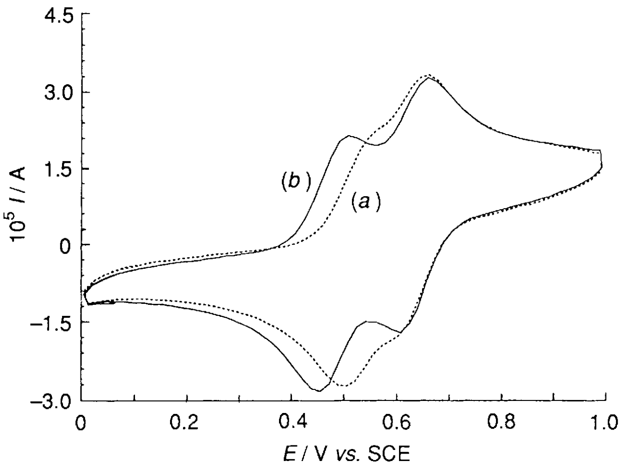
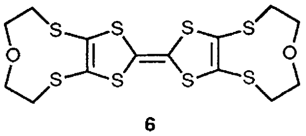


Fig. 1 CV of **4** (*a*) with and (*b*) without sodium ions present



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at 130 °C it was possible to couple **3** to give the TTF derivative **4** in 40% yield.‡

This compound did not form crystalline complexes with Na^+ although a 2 : 1 complex was reported in the triethylene experiment of Otsubo *et al.*[5] The redox properties of **4** were investigated using cyclic voltammetry (CV). Fig. 1(*b*) shows the trace recorded§ for compound **4**, alone and Fig. 1(*a*) that for compound **4** in the presence of 100 equiv. of sodium hexafluorophosphate. It is evident that a relatively large change in redox potential is induced in the TTF unit and that the E_{pa1} and E_{pc1} are shifted to more positive (anodic) potential, whereas E_{pa2} and E_{pc2} seem unchanged. The reason for this behaviour is assumed to be associated with the electrostatic repulsion between the positively charged sodium ion and the radical cation generated upon oxidation of the TTF unit, which will lower the stability constant of the complex. Owing to the overlapping peaks it is impossible to read a precise value of the new peak position without simulation, but the shift is estimated to be 80–90 mV. In order to ascertain that the observed shift is really due to complexation and not ion pairing effects additional experiments were carried out. In the presence of lithium hexafluorophosphate (100 equiv.), no shift was observed, whereas a shift of *ca.* 10 mV was observed in the presence of potassium hexafluorophosphate (100 equiv.). Based on published data[8] the affinity sequence of this crown size can be predicted to be: $Na^+ > K^+ > Li^+$, which is in full accord with the magnitudes of the shifts that we observed. Furthermore another crowned derivative

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‡ Preparation of **4**. The thione **3** (0.40 g) was placed in a dry 10 ml two-necked flask under nitrogen. Freshly distilled triethyl phosphite (5 ml) was added and the mixture heated to 130 °C for 20 min. Then the flask was placed in a refrigerator until crystallization was complete. The crude product was filtered off and recrystallized from ethyl acetate to yield orange crystals (0.15 g, 40%); m.p. 98–99 °C; δ_H (250 MHz, $CDCl_3$, Me_4Si) 3.04 (8H, t) 3.67 (34H, s) and 3.75 (8H, t); *m/z* (EI) 736 (M^+, 100%); ν_{max} (KBr) 1118 cm^{-1}; satisfactory elemental analyses.

§ CV experiments were carried out using dry acetonitrile as solvent, containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. The electrodes were made of platinum, the reference was the standard calomel electrode, and the scan rate was 100 mV s^{-1}. The concentration of **4** was 1 mg cm^{-3}.

was synthesized using diethylene glycol dibromide as electrophile. After coupling, the TTF derivative **6** with a very small crown was obtained. Based on the small size of the cavity and the fact that only one oxygen donor atom is present, it can safely be assumed that **6** will not complex alkali ions. Indeed when identical CV experiments as has been described for **4** were carried out with **6** no detectable shift was observed with any of the three alkali ions employed.

Based on the results above and additional evidence [from NMR and PDMS (Plasma Desorption Mass Spectrometry)] which will be presented in the full paper we conclude that the TTF unit can function as a redox-active unit which is sufficiently polarizable to be influenced by alkali metal ions complexed in a crown ether moiety annelated to the TTF-unit.

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