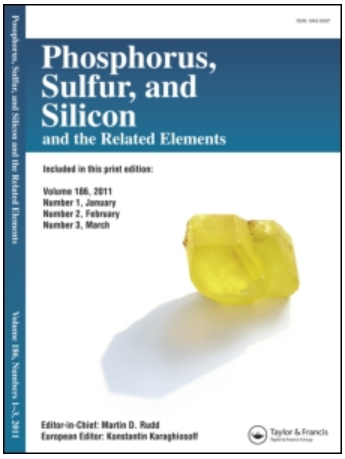

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Heterocyclic π-Donors, Macrocycles and Cage Molecules

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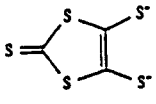
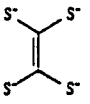
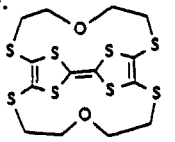
π-Donors based on TTF-units have been intensively studied due to their potential use in conducting molecular materials. It therefore appeared of interest to use the readily avaible dithiolate (**1**) for the syntheses of macrocycles, exemplified by (**3**) and (**4**) and the TTF-cage molecules (**5**) - (**7**) obtained by intramolecular coupling[1]:



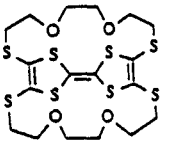
(**1**)



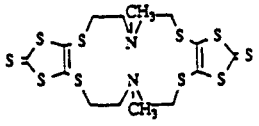
(**2**)



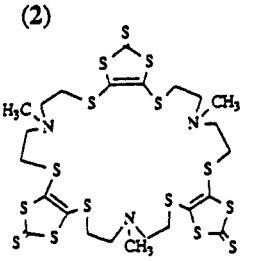
(**5**)



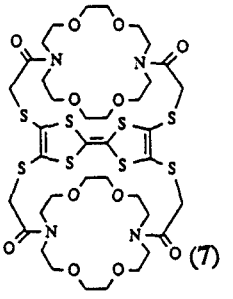
(**6**)



(**3**)

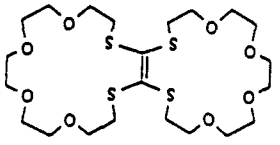


(**4**)

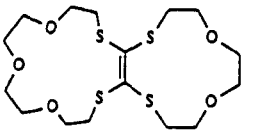


(**7**)

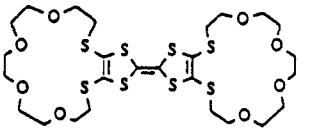
Dithiolate (**1**) is a derivative of tetrathiolate (**2**). Reaction of (**1**) either directly or stepvise gives access to annelated crowns such as (**8**) and (**9**):



(**8**)



(**9**)



(**10**)

Macrocyclic ligands of such types can complex metal-cations, for example bis-crown-TTF (**10**), which undergoes a reversible two electron reversible oxidation, show a shift of the lowest oxidation potential $E_{1/2}(1)$ to a higher potential whereas $E_{1/2}(2)$ remain unchanged upon complexation with sodium ions.

[1] (a) J. Becher, T. K. Hansen, N. Malhotra, G. Bojesen, S. Bøwadt, K. S. Varma, B. Girmay, J. D. Kilburn and A. E. Underhill, *J. Chem. Soc. Perkin 1*, **1990**, 175 and refs. cited herein, (b) T. Jørgensen, J. Becher, T. K. Hansen, K. Christiansen, P. Ropstorff and S. Larsen, *Advanced Materials*, (1991), **3**, 486.