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## Heterocyclic $\pi$ -Donors, Macrocycles and Cage Molecules

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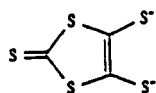
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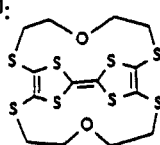
$\pi$ -Donors based on TTF-units have been intensively studied due to their potential use in conducting molecular materials. It therefore appeared of interest to use the readily available dithiolate (1) for the syntheses of macrocycles, exemplified by (3) and (4) and the TTF-cage molecules (5) - (7)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



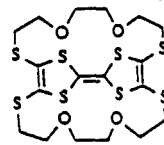
(1)



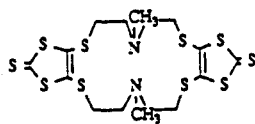
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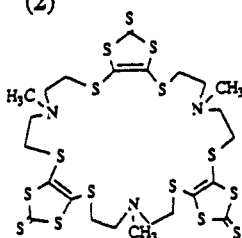
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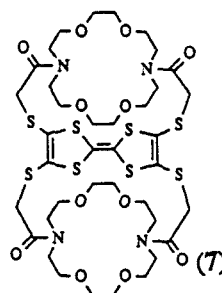
(6)



(3)

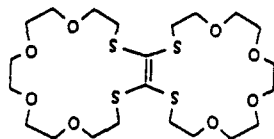


(4)

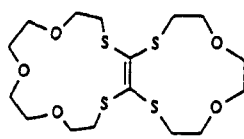


(7)

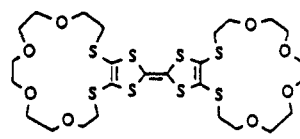
Dithiolate (1) is a derivative of tetrathiolate (2). Reaction of (1) either directly or stepwise gives access to annelated crowns such as (8) and (9):



(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.