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A Copper(I) [2]-Catenate Incorporating a Tetrathiafulvalene Unit

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Abstract. A copper(I) [2]-catenate incorporating an electron-donor tetrathiafulvalene unit has been synthesized and characterized.

Copper(I) [2]-catenates are coordination compounds made up with two interlocking coordinating rings.[1] Both macrocycles are entwined around the Cu^+ ion via 2,9-diphenyl-1,10-phenanthroline (dpp) subunits. The $Cu(dpp)_2^+$ complex has been shown to be both a light emitter, even in polar solvents like MeOH, and a strong reductant in the excited state.[2-5] These properties make $Cu(dpp)_2^+$ a good candidate as photoactive component (P) for charge separation in D-P-A systems, where (D) is an electron donor and (A) an electron acceptor. The D and A components could be incorporated at the periphery of a catenate,[6] as shown in figure 1.

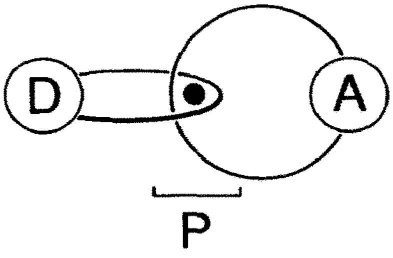
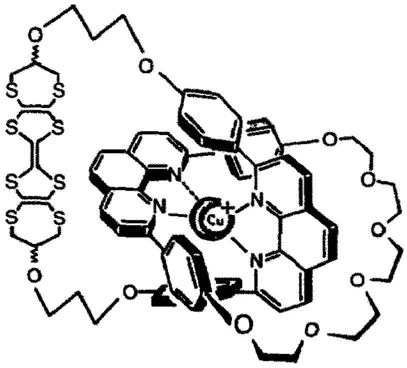


Figure 1 : A schematic donor/acceptor Cu^+ (●) [2]-catenate.



1^+

Figure 2

Tetrathiafulvalene (TTF) is known to be a good electron donor molecule : it is reversibly oxidized at 0.30 V *vs* SCE, and the resulting $TTF^{\cdot+}$ cation radical is chemically very stable. It has been extensively used in donor-acceptor organic conductors[7] and recently it has been incorporated covalently into multicomponent molecular systems such as crown ethers[8] and multistage redox assemblies.[9, 10] In this letter we wish to report the incorporation of a TTF unit in the Cu(I) [2]-catenate (1^+) represented in figure 2.

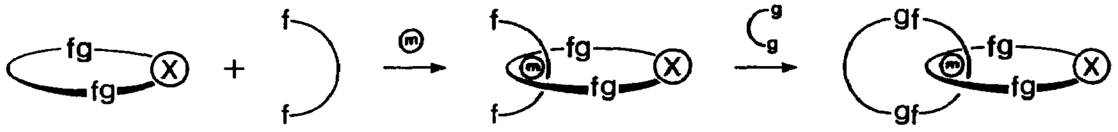
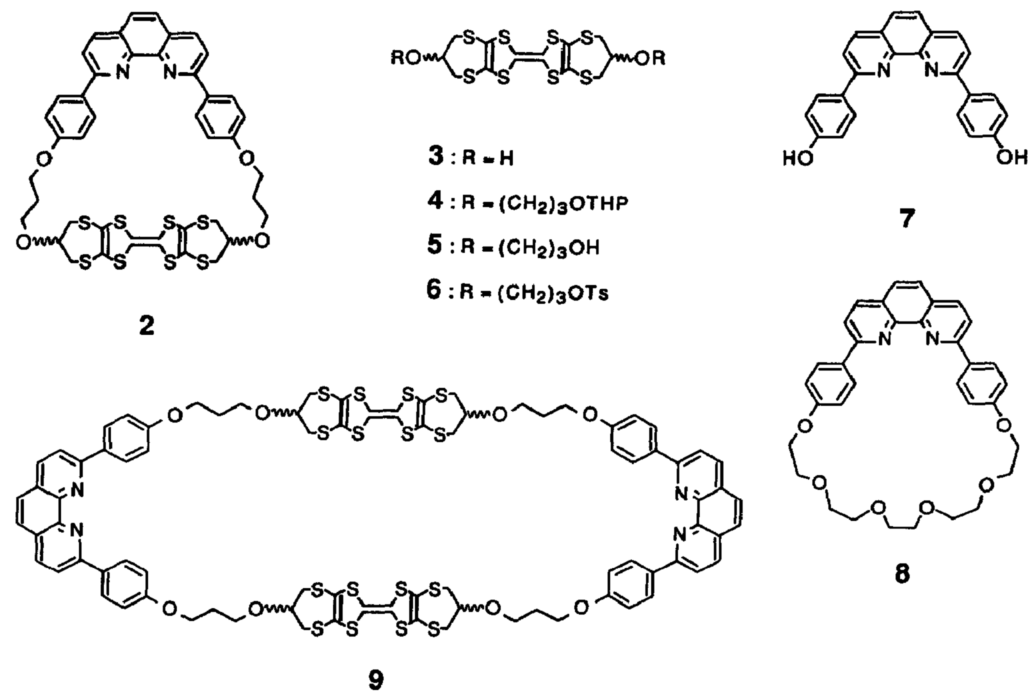


Figure 3 : Preparation of a non-symmetrical metallocatenate. Synthetic strategy based on a three-dimensional template effect induced by a transition metal. Functions f and g react to form the links. X is any function (here, the electrophore TTF), which can be incorporated in the presynthesized macrocycle.

Catenate 1^+ consists of two different dpp-containing macrocycles, a TTF-functionalized one (**2**) and a pentaethyleneoxy-locked macrocycle (**8**). It was therefore synthesized using the two-step Cu(I)-templated strategy represented in figure 3.[11]



3 : R = H

4 : R = $(CH_2)_3OTHP$

5 : R = $(CH_2)_3OH$

6 : R = $(CH_2)_3OTs$

Figure 4

We chose to start with 2 as the preformed macrocycle, the last cyclisation step being a reaction well known to us.[11,12] The structures of the compounds involved are represented in figure 4. The synthesis of 2 relied on the recent development of symmetrically functionalized TTF derivatives.[13] Thus diol 3[14] was deprotonated with NaH in THF and reacted with 2 eq. of THP-protected bromopropanol, affording 4 in 80% yield. Deprotection with TsOH in refluxing ethanol afforded 5 in 95% yield, which was further tosylated with TsCl/pyridine in 70% yield. 6 was then reacted with 2,9-diphenol-1,10-phenanthroline in high dilution conditions using Cs_2CO_3 as a base in DMF (argon atmosphere, 65°C).[11] The desired macrocycle 2 was obtained in 13% yield after chromatography (Al_2O_3, CH_2Cl_2/hexane, 80:20) as an orange crystalline solid[15]. In addition, the dimeric species 9, containing two dpp subunits bridged by two TTF linkers, was isolated (0.2% MeOH in CH_2Cl_2) in 29% yield. It is noteworthy that the proportion of dimer 9 is surprisingly high (total yield : 42%; monomer/dimer, 30:70) as compared to what is observed in the synthesis of 8 (monomer : 45%).[11] This might reflect the effect of a long and rigid linker such as 5 containing a rod-like unit (extended TTF) which thus makes it more adapted to dimer formation than to the 1+1 cyclisation leading to a relatively small cycle (36-membered ring).

Macrocycle 2 has then been incorporated into a precatenate Cu(I) complex (see figure 3) by mixing stoichiometric amounts of 2 (in CH_2Cl_2), $Cu(CH_3CN)_4BF_4$ (in CH_3CN), and 7 (in DMF). The crude product was combined with the diiodo derivative of pentaethyleneglycol[11] in DMF. The reaction mixture was heated to 65°C under Ar and a suspension of Cs_2CO_3 in DMF was added within 1h *via canula*. After work-up, anion exchange with KPF_6 and chromatography (silica, 0.5-0.8% MeOH in CH_2Cl_2) the desired catenate was obtained in 14% isolated yield as a dark red solid. The reaction also produced free 8 and the symmetrical catenate made up with two macrocycles 8.[11]

Catenate 1^+ was characterized by an intense peak at 1517.8 Da/e (M^+) in the ES-MS spectrum. The ^{1}H NMR spectrum[15] shows that this compound consists of two diastereomeric species, a major one (77%) and a minor one (23%).[16] They result from the fact that the stereogenic carbon atoms, linking the seven-membered dithiolene rings to the remaining of the molecule, have two relative configurations : one in which the methine protons are in *syn* and the other in which they are in *anti* positions.[17] To the former correspond two different conformations of the macrocycle 2 : endo-endo and exo-exo, and to the latter, two equivalent conformations : endo-exo and exo-endo. Since 2 (exo-exo) has the largest cavity, it is likely to lead to the less sterically crowded precatenate, and thus to the major [2]-catenate diastereomer.

The next step towards the synthesis of a Cu(I) catenate donor/acceptor triad will be the incorporation of an electron acceptor unit in the other macrocycle.

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15. ^{1}H NMR data (200 MHz, CD_2Cl_2). **2** : 2.11 (4H, qn), 2.50 (4H, q), 2.94 (4H, dd), 3.78 (4H, t), 3.92 (2H, m), 4.19 (4H, t), 7.10 (2H, d), 7.79 (2H, s), 8.11 (2H, d), 8.33 (2H, d), 8.42 (4H, d). **9** : 2.11 (8H, m), 2.50 (8H, m), 2.94 (8H, d), 3.78 (8H, m), 3.92 (4H, m), 4.19 (8H, m), 7.10 (4H, dd), 7.79 (4H, s), 8.11 (4H, d), 8.33 (4H, d), 8.42 (8H, dd). **1** : 1.97 (4H, qn), 2.87 (4H, m), 2.95 (4H, dd), 3.50-3.89 (24H, m), 3.87 (4H, s), 4.10 (2H, m), 6.02 (4H, d), 6.18 (4H, d), 7.27 (4H, d), 7.38 (4H, d), 7.84 (2H, d), 7.88 (2H, d), 8.00 (2H, s), 8.17 (2H, s), 8.41 (2H, d), 8.63 (2H, d).
16. This is an average ratio. One fraction of the chromatography contained the pure major isomer, of which the ^{1}H NMR data are given above.
17. In fact, the free macrocycle **2** is a mixture of two diastereomers too, as are its TTF precursors.

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