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Tetrathiafulvalene–phenanthroline macrocycles as redox responsive sensors for metal ions

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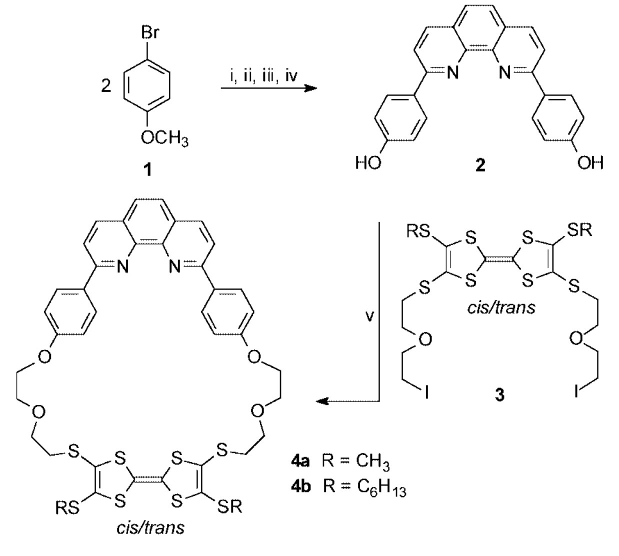
Macrocycles containing a redox-active tetrathiafulvalene unit together with a phenanthroline ligand are able to recognise different metal ions (Cu^+, Ag^+ and Li^+) when part of a precatenate complex.

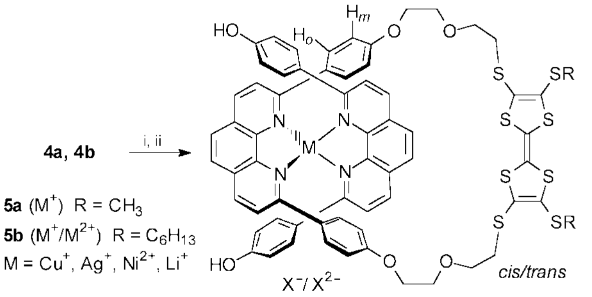
The redox responsive unit tetrathiafulvalene (TTF) has been incorporated into a number of oxygen, nitrogen and sulfur based crown ethers, resulting in sensors that are able to recognise alkali metal ions as well as silver and barium ions.[1] The strategy of using the templating abilities of Cu^+ to coordinate two phenanthroline ligands in a tetrahedral complex, originally developed by Sauvage and coworkers,[2] has been employed to prepare a TTF-containing Cu(I)-catenate.[3] Using this same strategy, we now report the use of TTF as a sensor unit for the metal ions Cu^+, Ag^+ and Li^+ in precatenate complexes (**5a**,**b**, **7**).

Synthesis of TTF–phenanthroline macrocycles **4a**,**b** were accomplished, using a modified procedure,[2] according to the route outlined in Scheme 1. First, *p*-anisyllithium was prepared by lithiation of *p*-bromoanisole using Bu^{t}Li and it was subsequently treated with 1,10-phenanthroline, affording a disubstituted tetrahydrophenanthroline derivative. Re-aromatisation upon treatment with MnO_2 afforded 2,9-di(*p*-methoxyphenol)-1,10-phenanthroline. Cleavage of the methylphenyl ether proceeded almost quantitatively in a reaction with anhydrous pyridinium hydrochloride, and after neutralisation with NaOH the diphenol **2** was isolated. *O*-alkylation of **2** with the TTF–diiodide **3**[4] under high-dilution conditions in the presence of Cs_2CO_3 gave the TTF–phenanthroline macrocycles **4a**,**b** in yields of 50–60%.

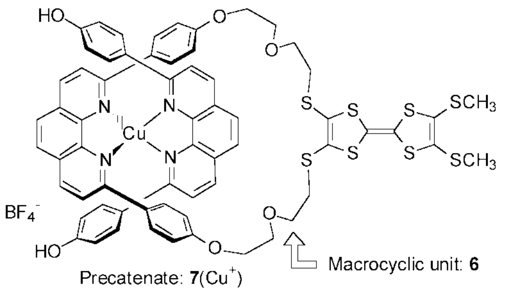
To a 1:1 mixture of the macrocycle and a metal salt, either $Cu(CH_3CN)_4BF_4$, $AgBF_4$, $NiSO_4{\cdot}7H_2O$ or $LiPF_6$, in CH_2Cl_2–CH_3CN (1:1) was added one equivalent of the molecular thread **2** dissolved in a very small amount of DMF (Scheme 2). In order to ensure the highest possible degree of complexation, the mixture was stirred overnight and then concentrated *in vacuo* to the solid complexes **5a**,**b**. The macrocycle **6** and its Cu^+ precatenate **7** were prepared in a similar manner.



Scheme 1 *Reagents and conditions:* i, Bu^{t}Li (2.5 equiv.), Et_2O, −30 °C; ii, 1,10-phenanthroline (0.27 equiv.), toluene, room temp.; iii, MnO_2, CH_2Cl_2, room temp.; iv, C_5H_5N, conc. HCl, 210 °C; 39% (4 steps); v, Cs_2CO_3 (3 equiv.), DMF, 60 °C, 50–60%.



Scheme 2 *Reagents and conditions:* i, MX (1 equiv.) [$Cu(CH_3CN)_4BF_4$, $AgBF_4$, $NiSO_4{\cdot}7H_2O$ or $LiPF_6$], CH_2Cl_2–CH_3CN (1:1), room temp.; ii, 2,9-(*p*-hydroxyphenyl)-1,10-phenanthroline (1 equiv.)/DMF, room temp.



The isolated complexes were first studied by ^1H NMR spectroscopy.† Significant chemical shift changes relative to the free macrocycle were observed for the aromatic protons of **5a**,**b** when $M^+ = Cu^+$, Ag^+ or Li^+ and for **7**(Cu^+) (Table 1). In particular, a *ca.* 1 ppm upfield shift of the eight *ortho* and *meta* phenolic protons on the macrocyclic unit confirmed that the complexations had occurred nearly quantitatively for these three metal ions, however, integration of signals were compli-

Table 1 Selected ^1H NMR chemical shifts[a] in $CDCl_3$–CD_3CN (1:1)

Compound	δH_m	$-\Delta(\delta H_m)$/ppm	δH_o	$-\Delta(\delta H_o)$/ppm
4a	7.17	—	8.44	—
5a(Cu^+)	6.00	1.17	7.38	1.06
5b(Ag^+)	6.20 (br)	~0.97	7.50 (br)	~0.94
5b(Li^+)	6.13 (br)	~1.04	7.35 (br)	~1.09
5b(Ni^{2+})	7.16	0.01	8.47	−0.03
6	7.22	—	8.46	—
7(Cu^+)	5.97	1.25	7.26	1.20

[a] For **7**: values from the macrocyclic unit; for **5a**,**b**: average values from the macrocyclic and thread units.

cated by rather broad signals for both the Ag^+ and Li^+ precatenates. A purity of *ca*. 95% is estimated for the isolated complex **7**(Cu^+) from its relatively simple ^1H NMR spectrum (devoid of *cis/trans* isomerism). No significant changes in the proton resonances of the macrocyclic unit were observed for the isolated product containing Ni^{2+}, indicating that the Ni^{2+}-precatenate had not been formed at all. This zero-yield is probably a result of the reluctance of a Ni^{2+} complex to adopt the tetrahedral geometry enforced by the precatenate structure.

Both MALDI and ESI mass spectrometry are useful techniques for characterising precatenates of this type. Studies on the Cu^+ based precatenates show that an applicable amount of the complex is transferred to the gas phase without dethreading. Thus, the mass spectra of **5a**(Cu^+) and **7**(Cu^+) reveal a peak at *m/z* 1291 ($z = 1$) which can be assigned to the singly charged Cu^+ containing precatenate (without the BF_4^- counter ion). However, fragmentation peaks corresponding to the dethreaded macrocycle with and without Cu^+ are also seen.

The redox behaviour of the complexes was studied by cyclic voltammetry and differential pulse voltammetry.[5] The voltammograms of the precatenate **5a**(Cu^+) (Fig. 1(a),(b)) show large anodic shifts relative to the free macrocycle of both the first and second TTF redox potentials as a result of the electrostatic influence exerted by the metal ion (Table 2). In between the two TTF oxidations, Cu^+ is oxidised to Cu^{2+}. The generated Cu^{2+} is not expelled but maintained in the complex since the second TTF oxidation is also affected by the presence of a positively charged metal center. It is noteworthy that the cyclic voltammogram of **5a**(Cu^+) shows the three redox processes to be reversible.

For **5b**(Ag^+) the two TTF oxidations are also shifted to higher potentials, which indicates that the Ag^+ ion is also complexed after the first TTF oxidation. However, even though the ^1H NMR spectrum in $CDCl_3$–CD_3CN (1 : 1) showed clear evidence for the formation of the **5b**(Li^+) precatenate, the TTF redox potentials were almost unaltered according to differential pulse voltammetry. Thus, it seems that the precatenate is disrupted in the relatively polar solvent (0.1 M NBu_4PF_6 in CH_2Cl_2) used for the electrochemical studies. In agreement with this observation, Sauvage and coworkers found that the Li^+ complex was unstable in the polar solvent DMF.[6] For **7**(Cu^+) the first TTF oxidation is significantly shifted, whereas the second is less influenced.

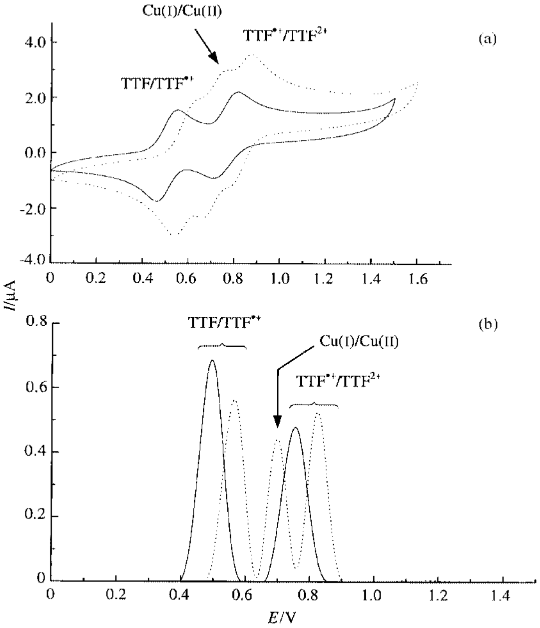


Fig. 1 (a) Cyclic voltammogram (scan rate 100 mV s^{-1}) and (b) differential pulse voltammogram of **4a** (—) and **5a**(Cu^+)BF_4^- (···) in CH_2Cl_2 containing 0.1 M NBu_4PF_6.

Table 2 Differential pulse data (*vs*. Ag/AgCl) in CH_2Cl_2 containing 0.1 M NBu_4PF_6

Compound	E_{ox}^1/V (TTF$^{\cdot+}$/TTF^{+})	ΔE_{ox}^1/V	E_{ox}^2/V (TTF$^{\cdot+}$/TTF^{2+})	ΔE_{ox}^2/V
4a	0.49	—	0.75	—
4b	0.53	—	0.78	—
5a(Cu^+)[a]	0.56	0.07	0.82	0.07
5b(Ag^+)	0.58	0.05	0.85	0.07
5b(Li^+)	0.54	0.01	0.79	0.01
6	0.44	—	0.80	—
7(Cu^+)[b]	0.54	0.10	0.83	0.03

[a] $E_{ox}(Cu^+/Cu^{2+}) = 0.70$ V. [b] $E_{ox}(Cu^+/Cu^{2+}) = 0.69$ V.

In conclusion, we have investigated the ability of TTF–phenanthroline macrocycles to form precatenate complexes with different metal ions. The appearance of large shifts in the two TTF redox potentials for the Cu^+ and Ag^+ complexes demonstrates the advantage of employing such macrocycles as possible redox responsive sensors for transition metal ions.

Notes and references

† *Selected data* for **6**: δ_H(250 MHz, $CDCl_3$–CD_3CN 1 : 1): 8.46 (d, *J* 8.9 Hz, 4H, H_o), 8.35 (d, *J* 8.5 Hz, 2H, $H_{4/7}$), 8.14 (d, *J* 8.5 Hz, 2H, $H_{3/8}$), 7.82 (s, 2H, $H_{5/6}$), 7.22 (d, *J* 8.9 Hz, 4H, H_m), 4.34 (t, *J* 4.9 Hz, 4H, OCH_2), 3.85 (t, *J* 4.9 Hz, 4H, OCH_2), 3.79 (t, *J* 6.4 Hz, 4H, SCH_2), 3.08 (t, *J* 6.4 Hz, 4H, SCH_2), 2.24 (s, 6H, SCH_3); MS(PD): *m/z* 865 (M^+). Calc. for $C_{40}H_{36}N_2O_4S_8$: C, 55.53; H, 4.19; N, 3.24. Found: C, 55.33; H, 4.11; N, 3.16%. For **7**(Cu^+)BF_4^-: δ_H (250 MHz, $CDCl_3$–CD_3CN 1 : 1): δ 8.63 (d, 2H, *J* 8.4 Hz, $H_{4'}/H_{7'}$), 8.53 (d, 2H, *J* 8.4 Hz, H_4/H_7), 8.24 (s, 2H, $H_{5'}/H_{6'}$), 8.05 (s, 2H, H_5/H_6), 7.88 (d, 2H, *J* 8.6 Hz, $H_{3'}/H_{8'}$), 7.85 (d, 2H, *J* 8.6 Hz, H_3/H_8), 7.41 (d, 4H, *J* 8.6 Hz, $H_{o'}$), 7.26 (d, 4H, *J* 8.6 Hz, H_o), 6.86 (s, 2H, OH), 5.98 (d, 4H, *J* 8.6 Hz, $H_{m'}$), 5.97 (d, 4H, *J* 8.6 Hz, H_m), 3.74 (t, 4H, *J* 6.2 Hz, OCH_2), 3.53 (2 × t, 8H, *J* 5.0 Hz, OCH_2), 3.26 (t, 4H, *J* 6.2 Hz, SCH_2), 2.41 (s, 6H, SCH_3); MS(ES): *m/z* 1291 $(M-BF_4)^+$.

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