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Tetrathiafulvalene-Based Podands for Pb^{2+} Recognition

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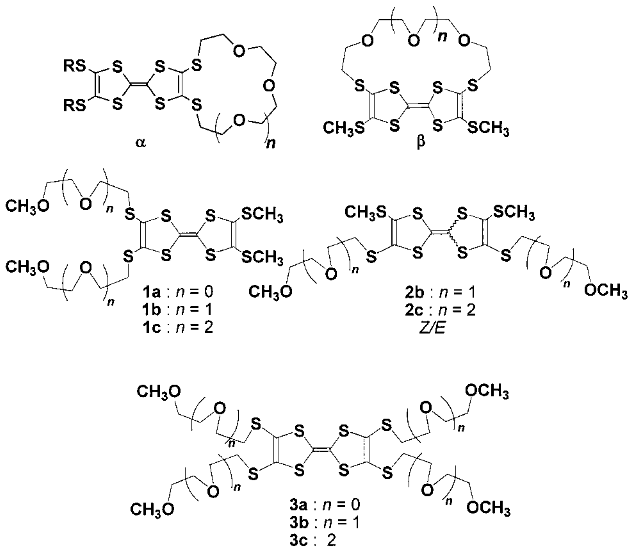
The synthesis and design optimization of a series of new redox-reponsive ligands built around the tetrathiafulvalene electroactive core and incorporating two to four pendant polyether binding sites are described. A comparative study of the recognition properties of these podand-TTFs for lead(II) has been carried out by cyclic voltammetry. The design optimization produced a ligand (**1c**) that exhibits a remarkably high affinity for lead(II), as shown by electronic absorption spectroscopy, ^{1}H NMR titration studies and cyclic voltammetry.

Introduction

Molecular recognition phenomena occupy a central place in supramolecular chemistry. Of particular importance are the host–guest interactions that lead to a physicochemical signal, as for instance in the case of redox-responsive ligands for which the binding of a given guest induces an electrochemical signature.[1] These systems are built from the covalent association of a binding unit to an electroactive moiety such as a quinone derivative or a metallocene. In this context, and thanks to the great variety of synthetic strategies developed for its functionalization,[2] the tetrathiafulvalene (TTF) moiety has become in the last decade a possible redox subunit of such receptors. The main feature of this alternative electroactive probe lies in its easy oxidation to two stable oxidation states ($\text{TTF}^{\cdot+}$ and TTF^{2+}). Therefore, pioneering work on this topic, developed in particular by Becher et al., has focused on the fusion of a crown-ether ring to the 2,3-positions of the redox framework to produce receptors of the type **α** designed for metal-cation recognition.[3] For some years we have contributed to this area of research, in particular, through the synthesis of TTF-based receptors in which a crown-ether subunit is covalently linked to the 2,7-positions of the TTF skeleton[4] (model **β**). Such systems present better recognition properties than derivatives **α** providing that the binding chain is long enough.[5] It appears therefore that the relative location of the binding unit and the electroactive counterpart is decisive for the sensing properties of the receptor.



Acyclic receptors (podands) for cation binding proliferate in the literature. Synthetic routes to these systems are indeed straightforward and do not require high-dilution conditions as is often the case with macrocyclic receptors (for example, **α** or **β**). Therefore they can be produced on larger scales which can be crucial for the application of such receptors to environmental problems. Podands are also more flexible than their crown-ether analogues, which may allow suitable conformational organization for the binding of a given guest. Conversely, though they can exhibit high-binding constants, they are known to be less specific binders than crown ethers.[6]

Surprisingly, although several examples of crown-TTFs are already known,[3–5] very few cases of podand-TTFs have been described so far.[7]

Podand-TTFs are also of interest because of their ability to retain the integrity of the electrochemical properties of the TTF probe, whatever the length of the podand arm.

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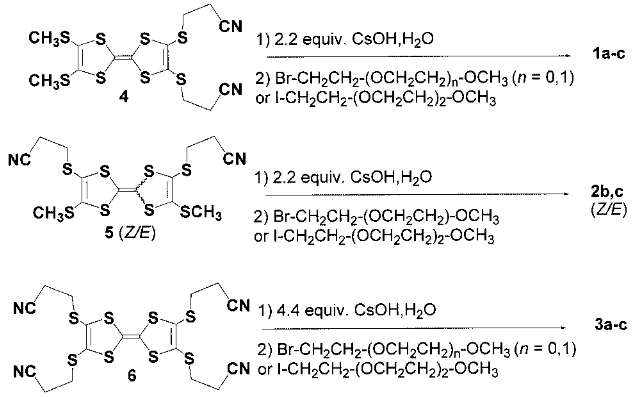
This is not the case with crown-TTFs such as **β**; the TTF part of such crown-TTFs with short binding chains is not planar and therefore lose their electrochemical reversibility.

We have therefore engaged in the systematic study of a series of podand-TTFs with, as a single recognition target, the lead(II) cation. Indeed, investigations on a single cation will allow the direct impact of geometric changes in the receptor during the design optimization process to be evaluated. Moreover, owing to its toxicity, research directed at controlling the amount of this cation in the environment is of prime importance.

In order to gain a better understanding of the cation-complexation process in TTF-based redox-responsive ligands, design optimization for the recognition of Pb^{2+} was achieved through systematic variation of the chains lengths and of their relative location around the TTF framework. Herein we report on the synthesis of a new family of electroactive receptors built around the TTF core and incorporating two or four polyether chains (Scheme 1). The binding properties of these receptors towards Pb^{2+} have been studied by cyclic voltammetry. The remarkable affinity of **1c** towards Pb^{2+} was investigated by ^1H NMR spectroscopy and UV/Vis titration studies and, as previously shown in a preliminary communication,[8] the redox-switchable behaviour of this system is demonstrated by cyclic voltammetry.



Scheme 1. Synthesis of the di- and tetrasubstituted podand-TTFs.

Result and Discussion

Synthesis

The synthetic strategy for podand-TTFs **1**–**3** was inspired by the thiolato protection–deprotection method developed by Becher et al.[9] in which the cyanoethylsulfanyl group is used as a protecting agent. Two or four polyether chains of various lengths were introduced onto the TTF framework through, in the former case, either vicinal 2,3-disubstitution on the periphery of the TTF unit or by 2,6-disubstitution.

The key intermediates were the previously reported[9b] dicyano- (**4**, **5**) and tetracyano-TTF (**6**) derivatives (Scheme 1). An appropriate amount of cesium hydroxide was used as the base to afford in each case the corresponding di- or tetrathiolate TTF intermediates which were then converted into the target compounds **1**–**3** by reaction with the corresponding α-halogenated poly(ethylene glycol) chain. In the case of compounds **2b** and **2c**, inseparable (*E*)/(*Z*) isomeric mixtures were obtained.

Binding Properties – a) Design Optimization

In our complexation studies we focused on the binding affinity between these podand-TTF derivatives and Pb^{2+}. Interestingly, the presence of a redox probe in the structure allows cyclic voltammetry (CV) to be easily used to analyze these systems.

Generally speaking, recognition of a given metal cation by TTF-based redox-responsive ligands is manifested by a positive shift of the first redox potential (E^1_{ox}), which corresponds to a decrease in its π-donating ability as a result of the binding of a positively charged guest ion in close proximity to the TTF unit.[3,4] For high host–guest affinity, this E^1_{ox} shift is expected to reach a maximum value for one equivalent of added cation, in accordance with the formation of a 1:1 stoichiometric complex. Conversely, the second redox potential remains constant however much metal cat-

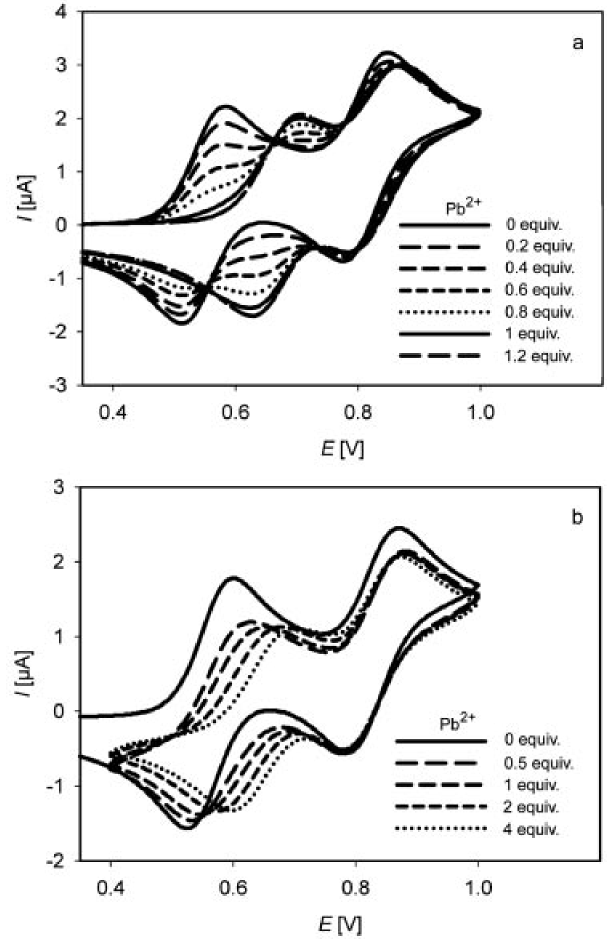


Figure 1. Experimental cyclic voltammograms of (a) **1c** and (b) **3b** in the presence of increasing amounts of Pb^{2+} [$Pb(ClO_4)_2$]; [podand-TTF] = 10^{-3} mol L^{-1}, CH_2Cl_2/CH_3CN (1:1), [Bu_4NPF_6] = 10^{-1} mol L^{-1}, v = 100 mV s^{-1}, AgCl/Ag.

Table 1. Oxidation peak potentials (E^1_{ox}, E^2_{ox}) for podand-TTFs **1**–**3** and shifts of potentials (ΔE^1_{ox}, ΔE^2_{ox}) in the presence of [Pb(ClO_4)$_2$] (vs. Ag/AgCl).

	1a	**1b**	**1c**	**2b**	**2c**	**3a**	**3b**	**3c**
E^1_{ox} [mV]	0.57	0.58	0.58	0.59	0.60	0.60	0.60	0.59
ΔE^1_{ox} [mV]	0	+60	+120	0	+75	0	+120	[c]
$n(Pb^{2+})$[a] [equiv.]		>4	1		>8		>8	
E^2_{ox}[b] [mV]	0.85	0.86	0.85	0.86	0.87	0.86	0.87	0.86[c]

[a] Pb^{2+} equivalents needed to reach a constant ΔE^1_{ox} value. [b] ΔE^2_{ox} = 0 mV in all cases. [c] Irreversible redox systems upon addition of Pb^{2+}.

ion is added to the solution, which is attributed to the expulsion of the cation to outside the cavity because of electrostatic interactions between the cation and the doubly charged oxidized TTF^{2+} unit. We should also bear in mind the fact that a high binding ability of a given redox receptor for a given guest does not necessarily mean good electrochemical recognition since good communication between the redox probe and the ligating unit is crucial, for which they need to be in close proximity.[1d]

With these electrochemical properties in mind, we can evaluate the effects of the following geometric parameters on the electrochemical recognition ability of the podand-TTFs **1**–**3** just by observing the E^1_{ox} behaviour. Selected CVs from this study are presented in Figure 1 and peak potentials values (E^i_{ox}) as well as their evolution upon addition of Pb^{2+} are collected in Table 1.

Podand Arm Length

By gradually introducing Pb^{2+} to the system, better electrochemical recognition of Pb^{2+} is observed for the three series (**1**, **2** and **3**) as the length of the podand arm increases. The derivative with the shortest chain in each series (**1a**, **2b** and **3a**) does not exhibit any variation in E^1_{ox}. The positive shift of E^1_{ox} gradually increases (see the Supplementary information) in each series by incorporating an additional oxyethylene fragment into the podand arm. Values as high as ΔE^1_{ox} = +120 mV are observed for **1c** and **3b** (Figure 1). Compound **1c** is also the only case of all the series for which there is no need to add an excess of Pb^{2+} to reach the maximum E^1_{ox} shift, which indicates good electrochemical recognition properties. Interestingly, oxidation of **1c** to the cation-radical state gives rise to a two-wave behaviour (the signature of the free ligand **1c** gradually disappears to the benefit of the complex) which is quite uncommon for TTF-based ligands and which confirms that a high binding constant can be anticipated for the **1c**·Pb^{2+} complex.

Podand Arm Location

By comparing the electrochemical responses of receptors with identical podand arms, that is, **1b** and **2b** on the one hand and **1c** and **2c** on the other, it appears that the location of the binding units is quite significant with series **1** being far superior for a given poly(oxyethylene) chain length. This may be ascribed to two factors: a) Ligand **2** exists as a (*Z*)/(*E*) isomeric mixture and the two geometries do not present the same cationic binding capabilities and b) the geometry of the binding cavity, which, owing to the shape of the TTF skeleton, is larger in the case of series **2** and therefore needs longer chains to attain a favourable bowl-shape symmetry to receive a metallic cation guest.

Podand Arm Number

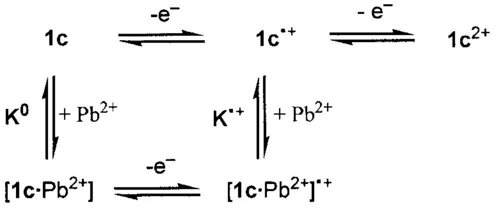
In the case of the four-podand-arm derivatives **3**, we find again the same tendency as observed for compounds **1** and **2**, that is, an increase in electrochemical Pb^{2+} recognition with increasing chain length. Nevertheless, the shape of the CV becomes more difficult to rationalize particularly in the case of **3c** for which electrochemical irreversibility gradually appears upon addition of Pb^{2+}. Since compounds **3** can be regarded as a geometric combination of **1** and **2**, this electrochemical behaviour is attributed to the competition that is likely to occur between the four binding sites on the periphery of the TTF molecule.

Note that derivatives with pendant arms at the 2,3-positions (series **1**) appear more efficient in Pb^{2+} recognition than those of series **2**. Interestingly, this observation contradicts the results of the investigation with crown-TTF derivatives, for which we demonstrated that electrochemical recognition of metal cations is better when the crown moiety is fused along the long axis of TTF (2,7-positions)[4b,4c] than to the vicinal 2,3-positions.[3] This apparent contradiction can be explained by the higher rigidity of a crown-ether unit relative to a binding cavity generated by two podand arms. Indeed, whereas the association constants can be larger with crown-ether units, the rigidity of the macrocyclic binding part prevents/moderates the through-space interaction between the guest cation and the redox probe. Therefore, to be efficient in TTF-based redox-responsive ligands, crown subunits must be directly connected in proximity to the central $S_2C{=}CS_2$ part of the TTF framework, where the electron density is higher. Indeed, no or moderate electrochemical responses are observed for crown-ethers fused to the vicinal 2,3-positions,[3] that is, located too far away from the central sulfur atoms. On the contrary, both poly(oxyethylene) arms of a podand-TTF are intrinsically flexible and are able to adopt the right conformation to bind a guest and to place it in close proximity over the plane of the TTF core providing that the arms are long enough, which is the case with compound **1c**.

Binding Properties – b) the 1c·Pb^{2+} Complex

From these data, compound **1c** appears to be an excellent candidate for promoting electrochemical Pb^{2+} recognition. Interestingly, E^2_{ox} remains unchanged for **1c** (as for all compounds **1**–**3**). Therefore, at this potential, expulsion of the cation to outside the cavity must take place.

From these electrochemical data and by using the DIGISIM 3.0 simulation program (BAS)[4b,4c,10] we could evaluate the binding constants for the equilibria shown in the square scheme presented in Scheme 2 and in Figure 2 ($K^0 = 10^{5.5}$, $K^{\cdot+} = 10^{3.3}$ $L\,mol^{-1}$). These values correspond to a high binding ability for the neutral TTF-based receptor **1c**, a lower one for the cation-radical state and expulsion of the metallic cation for the dicationic TTF^{2+} state, as expected from the gradually increasing electrostatic repulsive interactions that occur within the Pb^{2+} complex upon the sequential oxidation of **1c**.



Scheme 2. Square scheme for the electrochemical titration of **1c** with Pb^{2+}.

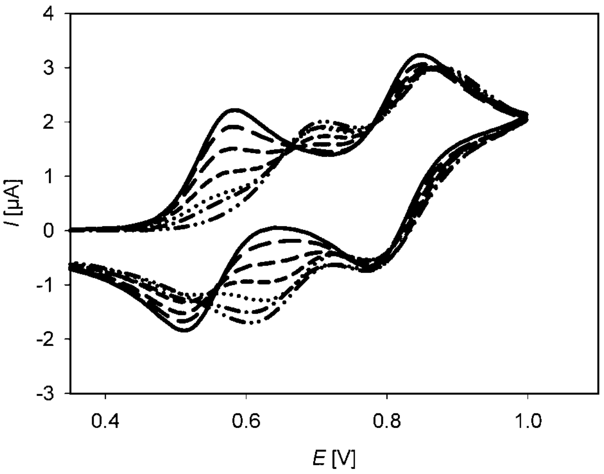


Figure 2. Simulated cyclic voltammograms of **1c** in the presence of increasing amounts of $Pb(ClO_4)_2$. The simulated data were fitted to experimental results for **1c** [10^{-3} $mol\,L^{-1}$ in CH_2Cl_2/CH_3CN (1:1)] at 293 K and 100 $mV\,s^{-1}$. All simulations were carried out with the same set of parameters except for the Pb^{2+} equivalent concentration which was changed in accord with the experimental voltammograms. Charge transfer parameters: $ks = 0.01$ $cm\,s^{-1}$, $\alpha = 0.5$. Chemical reaction parameters: $K^0 = 3.5\times10^5$ $L\,mol^{-1}$, $k_f{}^0 = 1\times10^9$ $L\,mol^{-1}\,s^{-1}$ and $K^{\cdot+} = 1.8\times10^3$ $L\,mol^{-1}$, $k_f{}^{\cdot+} = 1\times10^9$ $L\,mol^{-1}\,s^{-1}$. Diffusion coefficient: $D = 1.15\times10^{-5}$ $cm^2\,s^{-1}$.

The remarkable binding affinity of **1c** towards Pb^{2+} could also be checked by electronic absorption and ^1H NMR spectroscopy. When controlled amounts of lead perchlorate were introduced into a solution containing podand-TTF **1c**, modifications to the UV/Vis spectrum could be observed (Figure 3). The occurrence of inflection points at $\lambda = 335$ and 418 nm reveals the coexistence in solution of the two species in equilibrium: free **1c** and the corresponding 1:1 Pb^{2+}complex. From these data, the binding constant K^0 could be determined using the Benesi–Hildebrand method,[11] giving a K^0 value of $10^{5.0}$ $L\,mol^{-1}$ [CH_3CN/CH_2Cl_2 (1:1); 20 °C].

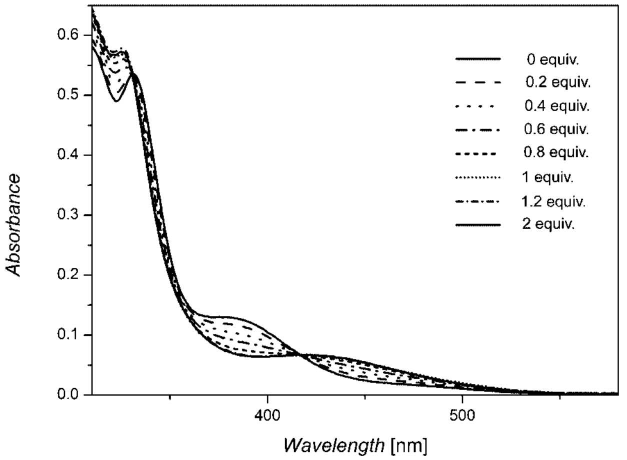


Figure 3. UV/Vis titration curves for **1c** [4×10^{-5} $mol\,L^{-1}$ in CH_3CN/CH_2Cl_2 (1:1)] in the presence of increasing amounts of Pb^{2+} [$Pb(ClO_4)_2$].

Finally, the strong affinity of **1c** towards Pb^{2+} was confirmed by a ^1H NMR titration. The free ligand **1c** exhibits a well-resolved ^1H NMR spectrum (Figure 4, a). The gradual addition of Pb^{2+} led to significant changes in the ^1H NMR spectrum. The signals affected are those of the binding chains, where the complexation takes place. The resolution is affected, in agreement with a fast equilibrium process (Figure 4, b), until one equivalent of the lead cation has been added (Figure 4, c), which confirms the 1:1 stoichiometry of the complex. This is also illustrated by plotting the variation of the chemical shifts against the amount of Pb^{2+} introduced, which produces a plateau at one equivalent of the metal cation (Figure 5). From these data and by using the EQNMR program,[12] an average K^0 value of $10^{4.9}$ $L\,mol^{-1}$ was determined from the different ^1H NMR signals and on the basis of a 1:1 **1**·Pb^{2+} complex (CD_3CN, 20 °C).

Conclusion

We have proposed a synthetic access to a family of new TTF-based redox-switchable ligands that incorporate binding polyether chains. The best candidate (**1c**) for Pb^{2+} complexation was developed by design optimization and presents unprecedented electrochemical recognition properties among the TTF family. The high binding affinity was confirmed by ^1H NMR and UV/Vis titration studies. As a continuation of this work new modified surfaces incorporating the structure of receptor **1c** are currently being developed that address the electrochemical binding and release of a guest (cation sponge model), similar to that recently described by our group.[8]

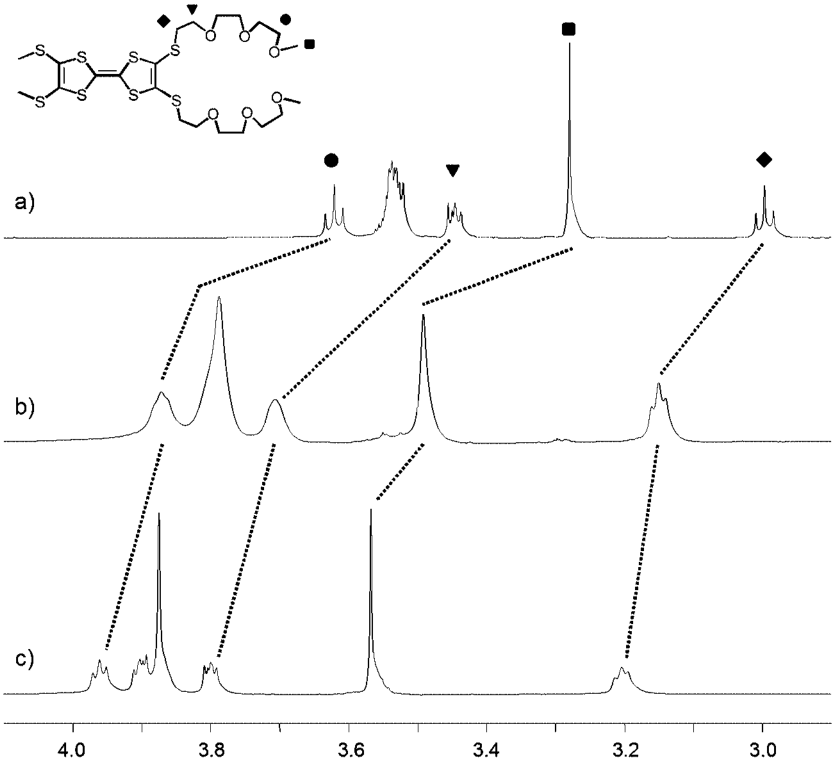


Figure 4. Evolution of the ^1H NMR spectrum of **1c** in CD_3CN upon gradual addition of $Pb(ClO_4)_2$; (a) 0 equiv., (b) 0.2 equiv., (c) 1 equiv.

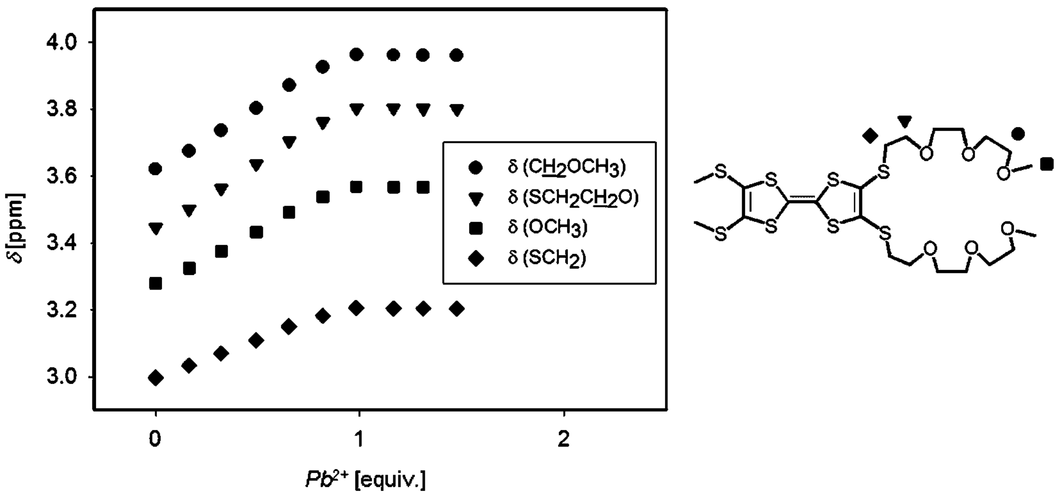


Figure 5. ^1H NMR titration curves for **1c** (1 mM in CD_3CN) with Pb^{2+} [$Pb(ClO_4)_2$].

Experimental Section

NMR spectra were recorded with a Bruker Advance DRX500 spectrometer operating at 500 and 125.7 MHz for ^1H and ^{13}C NMR spectroscopy, respectively; δ values are given in ppm (relative to TMS). ^1H NMR titration experiments were carried out as follows (constant temperature: 22 °C): several NMR tubes were each filled with 15.0 mg of the ligand and an appropriate amount of $Pb(ClO_4)_2$ (i.e., 0, 0.2, 0.4, 0.6, ... equiv., respectively) and the total volume was then adjusted to 1 mL with CD_3CN. Electrochemical experiments were carried out with a PAR273 Potentiostat-Galvanostat in a three-electrode single-compartment cell equipped with platinum microelectrodes (area 7.85×10^{-3} cm^2), a platinum-wire counter electrode and a AgCl/Ag reference electrode. Cyclic voltammetry was performed in dichloromethane/acetonitrile (1:1 v/v) solutions (SDS, HPLC grade) containing tetrabutylammonium hexafluorophosphate (0.10 M, Fluka). Solutions were degassed by argon bubbling prior to each experiment, which were performed under an inert atmosphere. The two shortest (n = 0, 1) α-brominated poly(ethylene glycol) chains are commercially available. The longest one [n = 2, 1-(2-iodoethoxy)2-(2-methoxyethoxy)-ethane] was synthesized by tosylation and subsequent iodination of the corresponding alcohol (75% overall yield) by adapting a previously described procedure.[13]

General Procedure for the Synthesis of Podand-TTFs 1–3: The dicyano- or the tetracyano-TTF derivative **4**, **5** or **6** was dissolved in dried DMF. The solution obtained was degassed by nitrogen bubbling for 10 min. Then the appropriate amount (2.2 equiv. or 4.4 equiv., respectively) of cesium hydroxide monohydrate (CsOH, H_2O) dissolved in a minimum of dried methanol was added dropwise. The mixture was stirred for 10 min and an excess (2.4 equiv. or 4.8 equiv., respectively) of the appropriate halogenated polyether chain was then added. The solution was stirred under nitrogen for an additional 2 h. The solvent was then evaporated under vacuum and the residue dissolved in dichloromethane. The organic phase was washed three times with water and dried with magnesium sulfate. Finally, the product was purified by silica gel chromatography.

2,3-Bis(2-methoxyethylsulfanyl)-6,7-bis(methylsulfanyl)tetrathiafulvalene (1a): $C_{14}H_{20}O_2S_8$, orange solid, yield 68%, m.p. 74 °C. ^1H NMR ($CDCl_3$): δ = 3.57 (t, 4 H, CH_2O), 3.37 (s, 6 H, CH_3O), 3.00 (t, 4 H, CH_2S), 2.42 (s, 6 H, SCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 127.98 127.52 (lateral C=C), 110.82, 110.51 (central C=C), 71.13 (CH_2O), 58.78 (OCH_3), 35.46 (SCH_2), 19.14 (SCH_3) ppm. HRMS (EI): calcd. 475.9691; found 475.9229 $[M]^{+\cdot}$.

2,3-Bis[2-(2-methoxyethoxy)ethylsulfanyl]-6,7-bis(methylsulfanyl)tetrathiafulvalene (1b): $C_{18}H_{28}O_4S_8$, red solid, yield 64%, m.p. 62 °C. ^1H NMR ($CDCl_3$): δ = 3.72–3.59 (m, 8 H, CH_2O), 3.59–3.51 (t, 4 H, SCH_2CH_2O), 3.35 (s, 6 H, CH_3O), 3.00 (t, 4 H, CH_2S), 2.40 (s, 6 H, SCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 127.81, 127.40 (lateral C=C), 111.107, 110.63 (central C=C), 71.81, 70.38, 70.05 (CH_2O), 59.09 (OCH_3), 35.28 (SCH_2CH_2O), 19.21 (SCH_3) ppm. MS (EI): *m/z* = 563 $[M]^{+\cdot}$.

2,3-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl}-6,7-bis(methylsulfanyl)tetrathiafulvalene (1c): $C_{22}H_{36}O_6S_8$, red oil, yield 90%. ^1H NMR ($CDCl_3$): δ = 3.71 (t, 4 H, CH_2OMe), 3.65–3.52 (m, 12 H, CH_2O), 3.47 (m, 4 H, SCH_2CH_2O), 3.27 (s, 6 H, OCH_3), 3.07 (t, 4 H, SCH_2), 2.45 (s, 6 H, SCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 128.86, 128.24 (lateral C=C), 111.02, 110.75 (central C=C), 72.75, 71.31, 71.25, 71.12, 70.76 (CH_2O), 58.85 (OCH_3), 36.45 (SCH_2CH_2O), 19.04 (SCH_3) ppm. HRMS (EI): calcd. 652.0266; found 652.0277 $[M]^{+\cdot}$. $C_{22}H_{36}O_6S_8$ (653.03): calcd. C 40.46, H 5.56; found C 40.87, H 5.51.

(*Z*)- and (*E*)-2,7(6)-Bis[2-(2-methoxyethoxy)ethylsulfanyl]-3,6(7)-bis(methylsulfanyl)tetrathiafulvalene (2b): $C_{18}H_{28}O_4S_8$, red oil, yield 80%. ^1H NMR ($CDCl_3$): δ = 3.62–3.76 (m, 8 H, CH_2O), 3.50–3.60 (m, 4 H, SCH_2CH_2O), 3.38 (s, 6 H, CH_3O), 3.01 (t, 4 H, CH_2S), 2.44 (s, 6 H, SCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 130.9, 124.2 (lateral C=C), 110.8 (central C=C), 71.8 à 70.0 (CH_2O), 59.1 (OCH_3), 35.3 (SCH_2CH_2O), 19.1 (SCH_3) ppm. HRMS (EI): calcd. 563.9753; found 563.9752 $[M]^{+\cdot}$.

(*Z*)- and (*E*)-2,7(6)-Bis{2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl}-3,6(7)-bis(methylsulfanyl)tetrathiafulvalene (2c): $C_{22}H_{36}O_6S_8$, red oil, yield 70%. ^1H NMR ($CDCl_3$): δ = 3.64–3.68 (m, 16 H, CH_2O), 3.54–3.56 (m, 4 H, SCH_2CH_2O), 3.37 (s, 6 H, CH_3O), 2.99 (t, 4 H, CH_2S), 2.42 (s, 6 H, SCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 130.9, 124.3 (lateral C=C), 110.7 (central C=C), 71.9, 70.0 (CH_2O), 59.1 (OCH_3), 35.4 (SCH_2CH_2O), 19.1 (SCH_3) ppm. HRMS (EI): calcd. 652.0278; found 652.0272 $[M]^{+\cdot}$.

2,3,6,7-Tetrakis(2-methoxyethylsulfanyl)tetrathiafulvalene (3a): $C_{18}H_{28}O_4S_8$, yellow solid, yield 68%, m.p. 76 °C. ^1H NMR ($CDCl_3$): δ = 3.58 (t, 8 H, CH_2O), 3.38 (s, 12 H, CH_3O), 3.01 (t, 8 H, CH_2S) ppm. ^{13}C NMR ($CDCl_3$): δ = 127.94 (lateral C=C), 110.40 (central C=C), 71.03 (CH_2O), 58.81 (OCH_3), 35.42 (SCH_2) ppm. HRMS (EI): calcd. 563.9716; found 563.9753 $[M]^{+\cdot}$.

2,3,6,7-Tetrakis[2-(2-methoxyethoxy)ethylsulfanyl]tetrathiafulvalene (3b): $C_{26}H_{44}O_8S_8$, red oil, yield 64%. ^1H NMR ($CDCl_3$): δ = 3.74–3.59 (m, 16 H, CH_2O), 3.59–3.50 (m, 8 H, SCH_2CH_2O), 3.38 (s, 12 H, CH_3O), 3.02 (t, 8 H, CH_2S) ppm. ^{13}C NMR ($CDCl_3$): δ = 127.87 (lateral C=C), 110.51 (central C=C), 71.85, 70.44, 70.06 (CH_2O), 59.14 (OCH_3), 35.39 (SCH_2CH_2O) ppm. MS (EI): *m/z* = 740.02 $[M]^{+\cdot}$.

2,3,6,7-Tetrakis{2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl}-tetrathiafulvalene (3c): $C_{34}H_{60}O_{12}S_8$, red oil, yield 70%. ^1H NMR ($CDCl_3$): δ = 3.75 (t, 8 H, CH_2OMe), 3.67–3.63 (m, 24 H, CH_2O), 3.55 (m, 8 H, SCH_2CH_2O), 3.38 (s, 12 H, CH_3O), 3.26 (t, 8 H, CH_2S) ppm. ^{13}C NMR ($CDCl_3$): δ = 127.9 (lateral C=C), 110.5 (central C=C), 71.9, 71.8, 71.6, 70.3, 70.1 (CH_2O), 59.0 (OCH_3), 35.4 (SCH_2CH_2O) ppm. MS (MALDI-TOF): *m/z* = 916.2 $[M]^{+\cdot}$.

Supporting Information (for details see the footnote on the first page of this article): Electrochemical titrations (CV) of podand-TTFs **1b**, **2c** and **3b** in the presence of Pb^{2+}.

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