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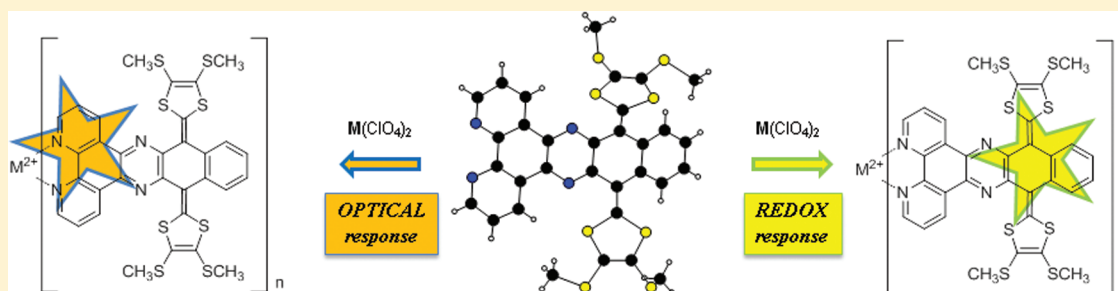
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Dual Signaling System with an Extended-Tetrathiafulvalene–Phenanthroline Dyad Acting as an Electrooptical Cation Chemosensor

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S Supporting Information



ABSTRACT: An efficient synthesis of unprecedented fused extended-tetrathiafulvalene–dipyridoquinoxaline (exTTF-dpq) dyad is described through the Horner–Wardsworth–Emmons olefination methodology from the dipyrido[3,2-*a*:2',3'-*c*]-benzo[3,4]phenazine-11,16-quinone (NqPhen) ligand starting material. This exTTF-dpq dyad is demonstrated to act as a dual redox and colorimetric sensor for cations exploiting the proximity between the redox tetrathiafulvalene and the optical phenanthroline detecting sites. Its ability for sensing cations from the d-group metal transitions (Fe^{2+} , Ni^{2+} , and Zn^{2+}) and also with varied cations such as Ca^{2+} and Pb^{2+} is presented.

INTRODUCTION

The development of chemosensors capable of recognizing cationic or anionic species has attracted much attention in recent years within the generalized area of supramolecular chemistry because of their fundamental role in biological and chemical processes.¹ In the search for applications in fields of very high impact, such as molecular recognition and sensors, the synthesis of multichromophoric architectures is of particular interest.² Moreover, the challenge for developing new ligands capable of color changes upon complexation are particularly attractive in terms of materials applications. Multisignaling sensors that utilize independent optical and electrochemical output signals are known to display special anion affinities,³ but corresponding materials for cation recognition are still rare. Ferrocene-based ligands constitute a very popular family of electroactive receptors for sensing cations through a modification of the oxidation potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple.⁴ It was recently shown that the association of ferrocene to a 1,10-phenanthroline (Phen) unit in a ferrocene–imidazophenazine dyad leads to a multichannel chemosensor for Pb^{2+} and Hg^{2+} cations.⁵

Tetrathiafulvalene (TTF) also presents a remarkable π -electron donor ability which notably results in two sequential and reversible oxidation processes, affording cation radical ($\text{TTF}^{\bullet+}$) and dication (TTF^{2+}) species.⁶ Recently, intensive work has been carried out to exploit the TTF framework as a supramolecular signaling and switching unit.⁷ On the other hand, aromatic and heterocyclic

nitrogen-based chelating units constitute well-adapted optical-responsive ligands for metal ion sensing, with a particular interest devoted to the Phen ligand.⁸ Moreover, the chelating capability of the Phen platform can be exploited to reach metal complexes exhibiting UV–vis NIR luminescent properties with investigation of energy/electron-transfer process.⁹ The association of a TTF derivative to the nitrogen-donor chelating ligand Phen is still rare.¹⁰ TTF and Phen units have been assembled through a macrocycle able to recognize different cations (Cu^+ , Ag^+ , Li^+) when part of (pre)catenate complexes.¹¹ More recently, TTF has been integrated into fused donor–acceptor dyads involving Phen¹² or dipyridoquinazoline (dppz).¹³ The latter TTF-dppz dyad provided a suitable Phen coordination site, and the addition of Fe^{2+} or Zn^{2+} cations provokes a color change from purple to blue.^{13a}

TTF with extended π -conjugation (exTTF) such as *p*-quinodimethane analogues of TTF are characterized by enhanced π -electron donor properties relative to TTF.¹⁴ The characteristic one-stage two-electron oxidation process results from reduced intramolecular Coulombic repulsion in the oxidized states thus stabilizing the cationic species.¹⁵ To our knowledge, exTTF has never been associated to a heterocyclic sp^2 nitrogen-donor chelating ligand. On this ground, this work has focused on dyad exTTF-dpq **1** based on the redox-active

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Scheme 1. Synthesis of the exTTF–dpq Dyad

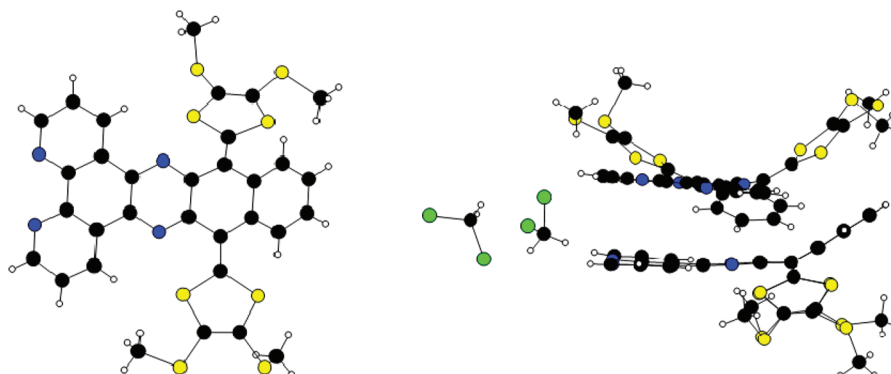
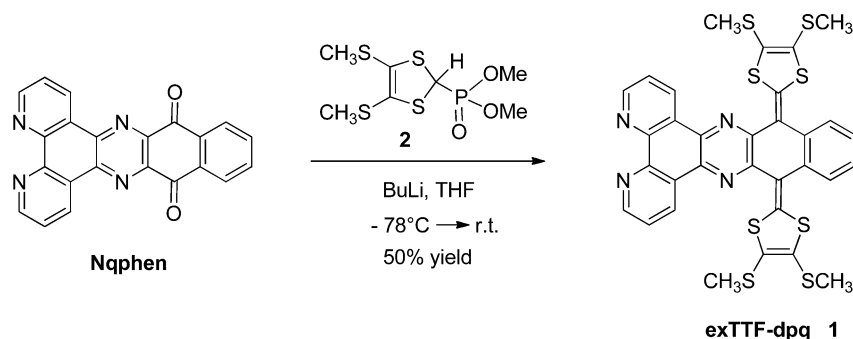


Figure 1. Left: X-ray crystallographic representation of one of the two independent molecules of exTTF–dpq dyad **1**. Right: dimerization along the *c* axis between two molecules.

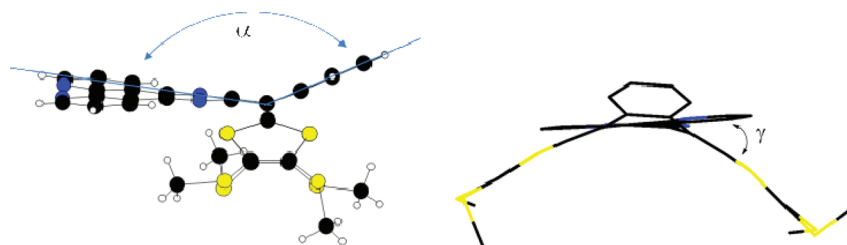


Figure 2. Distortion of the molecule defined by the angles α and γ .

electron donor exTTF and the dipyrro[3,2-*f*:2',3'-*h*]-quinoxaline (dpq) moiety containing a Phen ligand as the electron acceptor. This dyad was expected to show a particular ability for sensing cations through independent electrochemical and optical output signals strongly favored by the proximity of both optical and electrochemical sensing sites.

RESULTS AND DISCUSSION

Dyad exTTF-dpq **1** was synthesized by applying the Horner–Wadsworth–Emmons (HWE) reaction using the anion phosphonate generated from compound **2**¹⁶ on the acceptor NqPhen for which we recently described an improved preparation (Scheme 1).¹⁷

The molecular structure of dyad **1** was determined by X-ray diffraction study. Compound **1** crystallizes as a 4:3 dichloromethane solvate, and the asymmetric unit contains two independent molecules. Moreover, two phenanthroline are stacked by dimerization along the *c* axis and are separated by a distance of 3.43 Å (Figure 1).

The exTTF moiety of the dyad exhibits a boat conformation of the central quinodimethane ring providing a butterfly-shaped conformation.¹⁸ This distortion from planarity can be described

in terms of the angles α and γ . The angle α formed by outer aromatic rings, i.e., the “wings of the butterfly”, presents a value close to 150° (Figure 2). This distortion is caused by the steric repulsion between the dithiole sulfur atoms and the perhydrogen atoms according to the S⋯H distances with values between 2.49 and 2.57 Å which have to be compared with the sum of the corresponding van der Waals radii (2.91 Å).¹⁹ Nevertheless, this distortion is minimized due to important S⋯N interactions with distances between 2.66 and 2.72 Å which are shorter than the sum of their van der Waals radii (3.42 Å).²⁰ The other consequence of these different S⋯H repulsions and S⋯N interactions concerns the tilting of the dithiole units, which is defined by the angle γ with values in the range from 20 to 35° (Supporting Information).

The binding and recognition abilities of dyad **1** toward various cations (Fe^{2+} , Ni^{2+} , Ca^{2+} , Pb^{2+} , Zn^{2+}) in the form of their perchlorate salts were evaluated by UV–vis spectroscopy and cyclic voltammetry using optical and electrochemical responses of phenanthroline and exTTF, respectively.

Titration experiments were carried out in CH_2Cl_2 by monitoring the changes in the UV–vis spectrum of dyad **1** upon addition of the cation species. A dramatic color change

from orange to Bordeaux was observed for each cation exposed to dyad **1** (Figure 3). Upon addition of $\text{Fe}(\text{ClO}_4)_2$, the

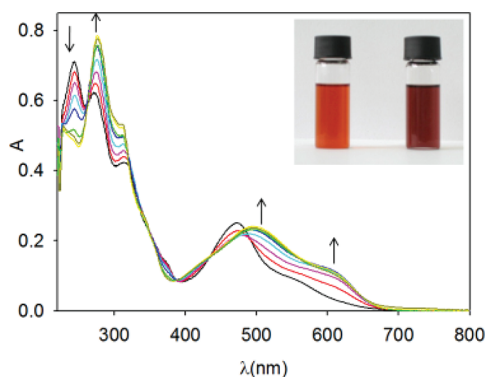


Figure 3. Absorption of dyad **1** (10^{-5} M in CH_2Cl_2) as a function of Fe^{2+} concentration. The inset shows the samples of **1** (left) and $(\mathbf{1})_3\text{Fe}$ (right) in CH_2Cl_2 .

intraligand band at the 470 nm maximum absorption decreased and well-defined isosbestic points were observable with the concomitant appearance of new bands at 492 and 600 nm. The first bathochromically shifted band could be assigned to the metal-to-ligand charge transfer (MLCT) absorption band ($d-\pi^*$).²¹ The second band could be ascribed to the intraligand charge-transfer (ILCT) transition with the exTTF acting as the donor and the dpq- Fe^{II} subunit as the acceptor.

Quantitative measurements of cation affinity were performed by monitoring the changes in the UV-vis spectra at 472 nm or at 600 nm of sensor **1** upon addition of cation. A saturation was observed after the addition of approximately 0.3 equiv in agreement with the formation of the octahedric $(\mathbf{1})_3\text{Fe}^{2+}$ complex. The dependence of the absorbance at 600 nm toward Fe^{2+} concentration (Job's plot) definitely confirms this stoichiometry with a maximum centered at a molar ratio of 0.7 (Figure 4). Similar profiles for the UV-vis spectra were

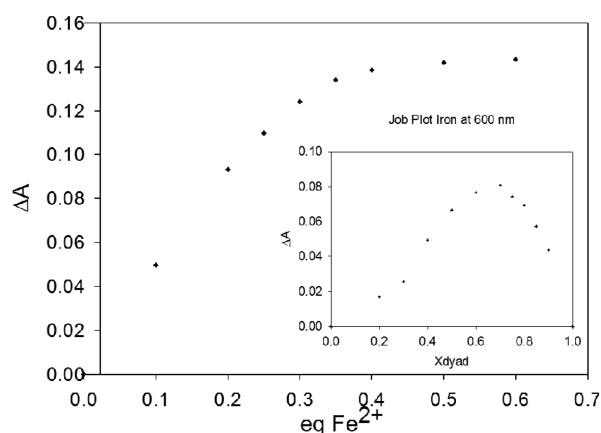


Figure 4. Plots of absorbance at 600 nm for **1** upon addition of iron(II) perchlorate. Inset: Job's plot analyses at 600 nm confirming the 3:1 stoichiometry.

observed upon titration of dyad **1** with a saturation around 0.3 equivalent for Ni^{2+} , Ca^{2+} , Zn^{2+} , and Pb^{2+} cations. From Job's plot analyses, these spectral changes were also ascribed to the formation of 1:3 complexes (Supporting Information).

The second signal output was validated by using cyclic voltammetry in order to follow the cation binding by sensor **1** (Figure 5). Cyclic voltammetry in CH_2Cl_2 showed that dyad **1**

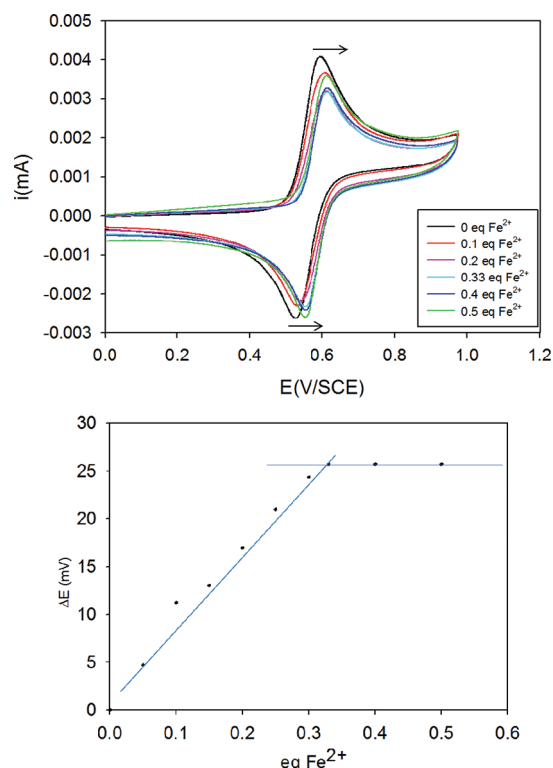


Figure 5. Voltammograms of dyad **1** in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9:1) solution (5×10^{-4} M) using Bu_4NPF_6 (0.1 M) as the supporting electrolyte as a function of Fe^{2+} concentration (top). Plot of the shift of the potential E_1^{ox} with added equivalents of $\text{Fe}(\text{ClO}_4)_2$ (bottom).

exhibited a quasi-reversible two-electron oxidation wave at $E_1^{\text{ox}} = +0.56$ V (vs SCE). The progressive addition of aliquots of metal salts resulted in a positive shift of the two-electron oxidation wave of ex-TTF with ΔE in the range from 20 to 35 mV for a 0.3 equivalent of Fe^{2+} , Ni^{2+} , Ca^{2+} , Pb^{2+} , and Zn^{2+} cations. The cation coordination leads to a significant change in redox potential with an anodic shift due to the fact that the sensor-cation complex is more difficult to oxidize. Such a voltammetric response on the two-electron oxidation wave was previously exploited only in the case of crown ether derivatives of 9,10-bis(1,3-dithiol-2-ylidene)anthracene for sensing metal cations.²²

In conclusion, the results presented herein demonstrate that an original donor-acceptor dyad with extended-TTF and phenanthroline-based ligand can display efficient sensing ability toward metal cations. The detection process can be performed through both optical and electrochemical measurements, thus exploiting the proximity of the donor and acceptor parts. This dual optical-electrochemical chemosensor could be used as well as for d-group metal transitions (Fe^{2+} , Ni^{2+} , and Zn^{2+} cations) but also with varied cations such as Ca^{2+} and Pb^{2+} . These results pave the way for developing efficient multifunctional molecular materials which could allow the complexation of cations in aqueous solution thanks to the versatility of the synthesis which allows the introduction of hydrophilic groups on the 1,3-dithiole moieties.

■ EXPERIMENTAL SECTION

The following chemicals were obtained commercially and were used without any purification. Thin-layer chromatography (TLC) was performed on aluminum sheets coated with neutral aluminum oxide 60 F₂₅₄. Column chromatography of dyad **1** was carried out on deactivated neutral alumina [deactivation by addition of H₂O (7 g) in neutral aluminum oxide 50–200 μ m (100 g)]. Chemical shifts in ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra are reported as δ values in ppm using the residual peak of the solvent as an internal reference.

ExTTF-dpq **1.** To a solution of phosphonate **2** (910 mg, 3 mmol) (freshly prepared and crystallized using CH₂Cl₂/petroleum ether as a mixture of solvents) in anhydrous THF (40 mL) under nitrogen atmosphere was added dropwise at –78 °C *n*-BuLi 2.5 M in hexane (1.32 mL, 3.3 mmol). After the solution was stirred for 15 min at –78 °C, compound **NqPhen** was added as a solid and by small fractions (108.6 mg, 0.3 mmol). The reaction mixture was allowed to stand at room temperature under stirring for 24 h. After addition of methanol (20 mL), the solvent was concentrated under vacuum. The residue was purified by a first chromatography on deactivated neutral alumina using CH₂Cl₂ then CH₂Cl₂/CH₃OH (4/1 V/V) as eluents. A second chromatography on deactivated neutral alumina using CH₂Cl₂/CH₃OH (9/1 V/V) as eluent afforded compound **1**, which was isolated in a 50% yield (104 mg) as a Bordeaux powder after precipitation using CH₂Cl₂ and petroleum ether as a mixture of solvents. ¹H NMR (CD₂Cl₂, 500 MHz) δ : 9.15 (m, 2H); 7.80 (dd, 1H, ³J = 5.5 and 9.5 Hz); 7.71 (dd, 1H, ³J = 5.5 and 13.5 Hz); 7.38 (dd, 1H, ³J = 5.5 and 9.5 Hz); 2.44 (s, 3H); 2.41 (s, 3H). ¹³C NMR (CD₂Cl₂, 125 MHz) δ : 151.0, 146.2, 145.1, 143.2, 134.4, 133.7, 131.9, 131.7, 127.4, 127.3, 126.2, 124.7, 124.2, 119.1, 19.7, 19.2. MS MALDI/TOF (dithranol, CH₂Cl₂) *m/z*: 718 (M⁺). HR-MS (ESI): calcd for C₃₂H₂₂N₄S₈ = (M⁺) 717.96046, found 717.96097; calcd for C₃₂H₂₃N₄S₈ = (M + H)⁺ 718.96829, found 718.96667. Anal. Calcd for C₃₂H₂₂N₄S₈ (719.06): C, 53.45; H, 3.08; N, 7.79. Found: C, 53.22; H, 3.17; N, 7.92.

X-ray single-crystal diffraction data were collected at 293 K on a diffractometer equipped with a graphite monochromator utilizing Mo K α radiation (λ = 0.71073 Å).

Crystallographic data for **1**: C₃₂H₂₂N₄S₈, *M* = 718.04, Bordeaux prism, 0.25 × 0.22 × 0.07 mm³, triclinic, space group *P*-1, *a* = 12.564(2) Å, *b* = 15.406(4) Å, *c* = 19.363(3) Å, α = 89.76(2)°, β = 80.24(1)°, γ = 79.32(2)°, *V* = 3628.3(12) Å³, *Z* = 1, ρ_{calc} = 1.433 g/cm³, μ (Mo K α) = 0.633 mm^{–1}, *F*(000) = 1606, θ_{min} = 2.13°, θ_{max} = 26.04°, 52931 reflections collected, 13877 unique (*R*_{int} = 0.063), parameters/restraints = 857/0, *R*1 = 0.1342 and *wR*2 = 0.3237 using 9114 reflections with *I* > 2 σ (*I*), *R*1 = 0.1799 and *wR*2 = 0.3510 using all data, GOF = 1.107, –0.648 < $\Delta\rho$ < 0.880 e Å^{–3}. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 835842.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, characterization data, and electrochemical and UV–visible titration results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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