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Redox-Switchable Chromophores Based on Metal (Ni, Pd, Pt) Mixed-Ligand Dithiolene Complexes Showing Molecular Second-Order Nonlinear-Optical Activity

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S Supporting Information

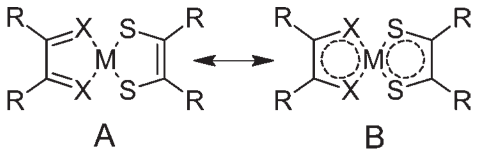
ABSTRACT: The synthesis and full characterization of the redox-active nickel triad mixed-ligand dithiolene complexes based on Bz_2pipdt = 1,4-dibenzylpiperazine-3,2-dithione and dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate ligands are reported. These complexes show a reversibly bleacheable solvatochromic peak and a remarkably high negative molecular first hyperpolarizability, whose values depend on the metal being highest for the platinum(II) compound.

The potential as second-order nonlinear-optical (NLO) chromophores of mixed-ligand metal d^8 dithiolene complexes and their analogues with the corresponding metal diiminedithiolate complexes has been recognized by Vogler and Kunkely since the early 1980s.[1] Terminal groups ($R \neq R'$) attached to the dithiolene core ($C_2S_2MC_2S_2$) in mixed-ligand complexes having different electron-withdrawing capability can induce a redistribution of the π electrons in such a way that one of the ligands can be described as a dithione and the other as a dithiolate.[2] Upon comparison to the corresponding diiminedithiolate complexes (Scheme 1, X = S and N, respectively), it can be observed that both classes of compounds bear two different unsaturated chelating ligands: one more easily reduced (dithione or diimine) and the other more easily oxidized (dithiolate).

Transition-metal diiminedithiolate complexes are the object of extensive studies because they exhibit a variety of properties that are studied for possible applications in dye-sensitized solar cells[3] and, recently, for solar-to-chemical energy conversion (photogeneration of H_2 from H_2O, platinum derivatives),[4] as well as second-order NLO chromophores.[5]

In order to exploit the potential as second-order NLO chromophores of mixed-ligand metal d^8 dithiolene complexes, experimental and theoretical studies mainly based on nickel complexes have been performed. It is found that these complexes[6] exhibit negative solvatochromism and molecular first hyperpolarizability (β_0) comparable or higher than those in the diiminedithiolate cases.[5] Theoretical studies have highlighted the factors that influence the presence or absence of second-order NLO properties for the nickel complexes upon variation of the ligand properties.[7] It is shown that, in the investigated cases, the 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligand induces major differences between the ground and excited states. Accordingly, a nickel mixed-ligand complex based on dmit shows first hyperpolarizability much higher than that of the corresponding maleonitriledithiolate (mnt) derivative.

Scheme 1



The influence of the metal has not been exploited yet. This can be related to difficulties encountered in the synthesis of palladium and platinum dithiolene mixed-ligand complexes, which are still rare,[8] because the reactions used to prepare nickel derivatives do not always work in the palladium and platinum cases.[9] This occurred in the $[M^{II}(Bz_2pipdt)(dmit)]$ case, where the nickel derivative can be easily prepared by mixing the symmetrical dicationic $[Ni(Bz_2pipdt)_2]^{2+}$ and dianionic $[Ni(dmit)_2]^{2-}$ complexes, as previously reported.[10] After several attempts to synthesize the corresponding palladium and platinum(II) complexes, we succeeded in obtaining the $[M^{II}(Bz_2pipdt)(dmit)]$ triad (M^{II} = Ni, **1**; Pd, **2**; Pt, **3**) in high yield. This method involves starting reagents $[M^{II}(Bz_2pipdt)Cl_2]$, which are obtained by reacting, in CH_3CN under reflux, equimolar amounts of Bz_2pipdt and nickel dichloride, $[Pd(CH_3CN)_2Cl_2]$ and $[Pt(DMSO)_2Cl_2]$,[11] with $(Bu_4N)_2[M^{II}(dmit)_2]$ and involves the facile displacement of two chloride ions by the chelating dmit dianion, as reported in the Supporting Information (SI).

The molecular structural characterization of **1**, previously described,[10] and of **2** and **3**, reported in this work,[12] indicates in all complexes that four sulfur atoms from the two different ligands define the coordination environment of the metals, which are in a slightly distorted square-planar geometry because the donor systems of the two ligands are not exactly coplanar. In fact, the

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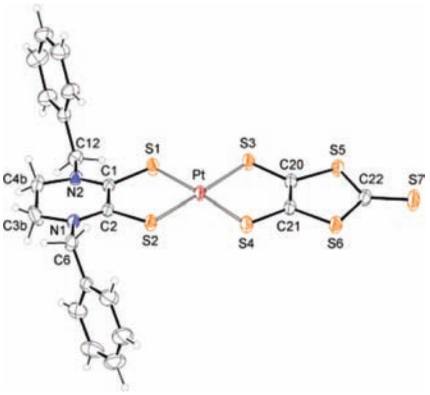

Figure 1. View of the molecule in **3**, with the atomic numbering scheme adopted also for **2**. Thermal ellipsoids are drawn at the 30% probability level. Most significant bond distances (Å) in **2**: Pd−S1 2.308(2); Pd−S2 2.271(2); Pd−S3 2.317(2); Pd−S4 2.292(2); C1−S1 1.690(5); C2−S2 1.693(5); S3−C20 1.744(6); S4−C21 1.741(5); C1−C2 1.450(7); C20−C21 1.349(7). Most significant bond distances (Å) in **3**: Pt−S1 2.2720(7); Pt−S2 2.2706(7); Pt−S3 2.2898(7); Pt−S4 2.2904(7); C1−S1 1.700(3); C2−S2 1.691(2); S3−C20 1.739(3); S4−C21 1.741(3); C1−C2 1.475(3); C20−C21 1.339(4).

Table 1. NLO Data of [M(Bz_2pipdt)(dmit)] Collected in DMF Solutions

	$\mu\boldsymbol{\beta}$ (10^{-48} esu)	$\mu\boldsymbol{\beta}_0$ (10^{-48} esu)
1	−6100	−926
2	−5360	−1146
3	−10 000	−2011

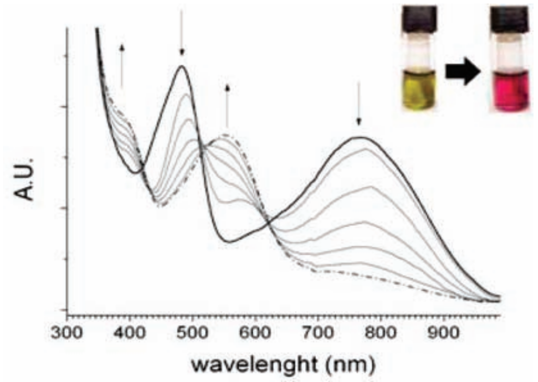

Figure 2. Visible−near-IR spectra of [Pt(Bz_2pipdt)(dmit)] (3.0×10^{-4} M) in 0.1 M [TBA][BF_4]/DMF at 233.15 K (thick line) and a monoreduced complex (dashed line). The potential was held at −0.6 V vs Ag/AgCl.

angle between the two SCCS donor systems is ∼5° in **2** and ∼8° in **3**. Tables reporting bond distances and angles are available in the SI. As reported in Figure 1, the M−S bond distances involving dmit are, on average, slightly longer than those originating from Bz_2pipdt. In addition, by inspection of the C−C and C−S bond distances of the $C_2S_2MS_2C_2$ core of **2** and **3**, a significant difference of the electronic structure of Bz_2pipdt with respect to dmit is apparent. Bz_2pipdt exhibits longer C−C and shorter C−S bond distances compared to dmit. Accordingly, the former can be described as a dithione (*push* ligand) and the latter as a dithiolate (*pull* ligand). Thus, **2** and **3** can be reasonably associated with the **A** limiting form (π-localized structure) of Scheme 1.

Complexes **1**−**3** are characterized in the visible−near-IR region by a broad absorption at low energy with medium molar absorption coefficients [λ_{max} (nm) = 858, ε (mol^{-1} dm^3 cm^{-1}) 10.6×10^3 (**1**); 819, 11.3×10^3 (**2**); and 827, 14.8×10^3 (**3**) in *N*,*N*-dimethylformamide (DMF)] and a negative solvatochromism, as shown in Figure S1 in the SI for **3** as an example. The energy of this absorption depends linearly on the solvent parameter proposed by Cummings and Eisenberg to determine the relative degree of solvatocromism for M(diimine)(dithiolate) complexes, where M = Pt, Pd, and Ni.[5b] The slope of the linear plot displayed in Figure S2 in the SI for **3** provides the relative degree of solvatochromism (1.6), which falls in the range found for M(diimine)(dithiolate) complexes. Previous theoretical studies on nickel mixed-ligand dithiolene complexes show that the highest occupied molecular orbital (HOMO) is formed by a mixture of metal and dithiolate orbitals, while the dithione orbitals make a predominant contribution to the lowest unoccupied molecular orbital (LUMO). A mixed-metal/ligand-to-ligand charge-transfer character has been tentatively assigned to the low-energy peak, which should be mainly related to the HOMO−LUMO transition.

The molecular quadratic optical nonlinearities were determined by the electric-field-induced second-harmonic generation (EFISH) technique. The setup used allows the determination of the scalar product $\mu\boldsymbol{\beta}$ (μ = dipole moment; $\boldsymbol{\beta}$ = vector part of the quadratic hyperpolarizability tensor). The measurements performed at 1907 nm and using DMF solutions provide $\mu\boldsymbol{\beta}$ values with an uncertainty of about 10%. These and the extrapolated values to zero frequency (calculated as reported in the SI) are summarized in Table 1.

The obtained $\mu\boldsymbol{\beta}_0$ values for these complexes are much larger than those exhibited by d^8 metal diimidedithiolate complexes, cited above,[5,13] and notably the largest value is found for the platinum complex. To the best of our knowledge, the $\mu\boldsymbol{\beta}_0$ values of these mixed-ligand dithiolene complexes are among the highest values so far reported for metal complexes[14] and are also high compared to those of organic second-order NLO chromophores, for example, the Disperse Red One, proposed for electrooptic polymers.[15] NLO activity is expected for **1**−**3** also as poled polymers but not in the solid state because the crystals crystallize in a centrosymmetric space group.

Cyclic voltammetric experiments performed on DMF solutions (the supporting electrolyte was 0.1 M Bu_4NBF_4) of the complexes show that **1**−**3** are redox-active and exhibit two reversible (or quasi-reversible) reduction waves centered at −0.41 (**1**) and −0.36 (**2**), −0.39 V (**3**) and −0.91 (**1**), and −0.81 (**2**) and −0.84 V (**3**) (see Figure S3 in the SI, where cyclic voltammograms of **3** recorded at 293 K with different scan rates in a DMF solution are displayed) and one irreversible anodic peak near +0.69 (**1**), +0.84 (**2**), and +0.86 V (**3**). The reduction processes should predominantly involve Bz_2pipdt, which is expected to give a predominant contribution to the LUMO, and the oxidation wave should be mostly relatable to dmit, which is expected to give a predominant contribution to the HOMO. Spectroelectrochemical experiments on DMF solutions of **2** and **3** have shown bleaching of the solvatochromic peak on monoreduction, as shown in Figure 2 (the monoreduction of **1** did not give sufficiently stable species for monitoring of their spectral features). These results suggest that a redox switching of the molecular first hyperpolarizabilities can be achieved with these palladium and platinum mixed-ligand complexes. It has recently been shown that robust switchable dithiolene complex films can be prepared for electrochromism,[16] and the current work demonstrates that this approach can also be exploited for switchable NLO materials. Methods for the tuning of molecular NLO responses are attracting interest,[17] following the first report on a reversible redox switching of the first hyperpolarizability dated in the late 1990s.[18]

In conclusion, the synthesis and structural, electrochemical, and spectroscopic characterization of the novel [M(Bz_2pipdt)(dmit)] (M^{II} = Pd, **2**; Pt, **3**) are reported. Moreover, the molecular quadratic optical nonlinearities of **1**−**3** have been determined. It is found that **1**−**3** exhibit large negative second-order polarizabilities, whose values depend on the metal being highest for the platinum compound. These findings, combined with the spectroelectrochemical behavior of **2** and **3**, make these complexes promising novel candidates to be investigated for applications based on redox switching of molecular first hyperpolarizabilities.[19]

ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Data collection was performed with a Bruker Smart ApexII diffractometer. **2**: $C_{21}H_{18}N_2PdS_7$, M = 629.19, triclinic, space group $P\bar{1}$, a = 7.828(3) Å, b = 12.132(4) Å, c =13.872(5) Å, α = 95.191(6)°, β = 106.113(5)°, γ = 104.301(6)°, V = 1208.4(8) $Å^3$, T = 293(2) K, Z = 2, 12 926 measured reflections, 4163 unique (R_{int} = 0.0601). R1 = 0.0433 [$I > 2\sigma(I)$], wR2 = 0.1079 (all data), CCDC 786344. **3**: $C_{21}H_{18}N_2PtS_7$, M = 717.88, triclinic, space group $P\bar{1}$, a = 7.969(1) Å, b = 12.082(1) Å, c = 13.983(1) Å, α = 75.645(1)°, β = 75.462(2)°, γ = 72.984(1)°, V = 1223.8(2) $Å^3$, T = 293(2) K, Z = 2, 19 442 measured reflections, 7106 unique (R_{int} = 0.0290). R1 = 0.0246 [$I > 2\sigma(I)$], wR2 = 0.0503 (all data), CCDC 786345.

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