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Optically Multiresponsive Heteroleptic Platinum Dithiolene Complex with Proton-Switchable Properties

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Supporting Information

ABSTRACT: Both linear- and nonlinear-optical properties of $Bu_4N[Pt(L1)(L2)]$ (**1**; L1 = [4′,5′:5,6][1,4]-dithiino[2,3-*b*]quinoxaline-1′,3′dithiolato; L2 = (*R*)-*α*-MBAdto dithiooxamidate, where (*R*)-*α*-MBA = (*R*)-(+)-*α*-methylbenzyl) upon HCl addition at room temperature change dramatically: the color turns from deep blue to green; the luminescence switches from deep red to green; the nonlinear-optical response (first hyperpolarizability) increases by a factor of 12. Thus, **1** behaves as a unique multiresponsive optical switch whose properties can be followed by the naked eye.

Changes of the linear-optical (LO; absorption and emission of light)[1] as well nonlinear-optical (NLO)[2] properties in response to external stimuli are of current scientific interest and for several applications in devices.[3−5] Molecules suitable for second-order NLO mostly consist of an electron-donor moiety connected to an electron-acceptor moiety by a conjugated *π* bridge.[6] These chromophores show a typical donor−acceptor (D−A) charge-transfer (CT) transition falling in the low-energy region. The two moieties may be conveniently functionalized to enable the on/off switching of a property.[7] Both forms are required to be stable and easily switchable with a fast response time. Among the possible molecular switching in D−A-type chromophores, we have applied our efforts to a molecule where the acceptor moiety [(*R*)-*α*-MBAdto dithiooxamidate (L2), where (*R*)-*α*-MBA = (*R*)-(+)-*α*-methylbenzyl] can easily undergo proton exchange. The donor employed is [4′,5′:5,6]-[1,4]dithiino[2,3-*b*]quinoxaline-1′,3′dithiolato (L1). This ligand may provide the heteroleptic complex with an additional functionality. In fact, the homoleptic platinum(II) complex based on this ligand[8] exhibits in solution at room-temperature a proton-dependent emission at 572 nm well above the energy of the lowest-energy absorption.[9] The desired product was prepared as summarized in Scheme S1 in the Supporting Information (SI), where the characterization of **1** (Figures S1−S3), as well as X-ray crystallographic measurements and refinements (Tables S1 and S2 and Figures S4−S6) are described.

The molecular structure of **1** comprises the complex anion $[Pt(L1)(L2)]^-$ and the Bu_4N^+ cation (Figure 1).

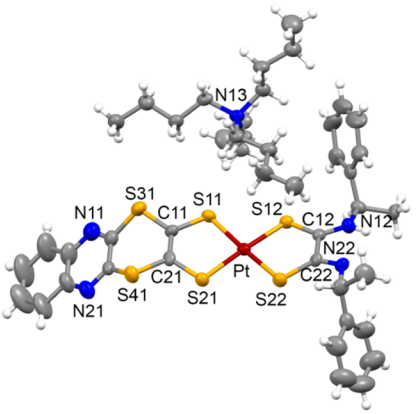

Figure 1. Molecular structure of **1** with thermal ellipsoids depicted at the 30% probability level.

The metal exhibits a square-planar geometry, with the Pt−S bond distances derived from the quinoxaline ligand slightly shorter than those derived from the dithiooxamidate ligand. This is in agreement with the different charges of the two ligand systems, 2− for the quinoxalinedithiolato system and 1− for the dithiooxamidate system. Interestingly, the two SCN moieties of the dithiooxamidate system present bond distances that reflect monoprotonation of the N(12) atom. Accordingly, the C(22)−S(22) fragment exhibits a more pronounced thiolate feature, whereas the C(12)−S(12) fragment is characterized by a more pronounced thione nature. As far as the LO properties are concerned, **1** is characterized by a broad absorption in the visible region with medium molar absorption coefficients ($\varepsilon = 5.5 \times 10^3$ M^{-1} cm^{-1}) centered at 595 nm in a CH_3CN solution with a

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shoulder at higher energy (~500 nm) and a quite intense (ε = 10.3 × 10^3 M^{-1} cm^{-1}) absorption band at 375 nm. Upon the addition of HCl, the color of the solution changes from deep blue to green. A related substantial change in the absorption profile is observed (Figure 2). In particular, the lowest absorption band

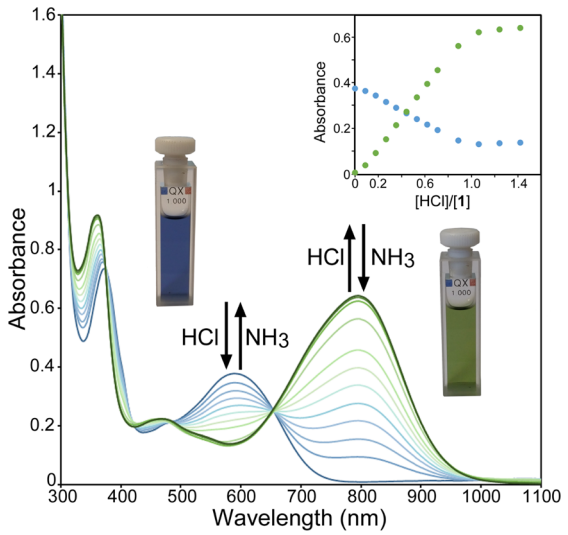

Figure 2. Variation of the absorption upon successive additions of HCl (10 μL, 10^{-3} M) and NH_3 (10 μL, 10^{-3} M) to a solution of **1** in CH_3CN (1 mL, 1 × 10^{-4} M). In the inset, plots of the absorbance values at 588 nm (blue) and 795 nm (green) against [HCl]/[**1**] are reported.

disappears, whereas a new one is formed at higher wavelengths (800 nm). The presence of well-defined isosbestic points (at 486 and 652 nm) suggests that two absorbing species are involved in the transformation process, which is complete for a 1:1 molar ratio between HCl and **1**. The absorption intensity of the formed species (**2**) does not increase upon further HCl addition (see the inset in Figure 2).

Previous studies by Campagna, Lanza, and co-workers.[10] showed that platinum homoleptic complexes coordinated to *N,N′*-dialkyldithiooxamidate ligands formed tight-contact ion pairs with HX (X = Cl, Br, I), where the N··H··X interactions play a role in stabilizing the ion-pair species. Also in the present case, HCl addition to **1** solutions results in protonation of the N atom on L2, and the N−H··Cl interactions significantly affect the properties of the formed complex anion, **2** (X = Cl), as supported by DFT calculations (vide infra and Figures S7−S10). The trend observed in the spectra of **1** upon the addition of different halo acids is reported in Figure S11. Density functional theory (DFT) and time-dependent DFT (TD-DFT)[11−17] calculations in CH_3CN allow one to relate the low-frequency peaks mainly to a highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) transition (Figures 3 and S9 and S10). A predominant contribution to the HOMO is provided by a mixture of π-dithiolate and metal orbitals, while a π^*-dithiooxamidate orbital gives a predominant contribution to the LUMO (LL′CT = ligand-to-ligand charge transfer with some metal contribution). When **1** interacts with HCl, the HOMO energy is not affected while the LUMO is stabilized in agreement with the observed shift to longer wavelength of the CT band. It is worth noting that the LUMO+1, a π orbital of the quinoxaline moiety, is raised in energy.

Upon irradiation in the visible region at 450 nm, the complex shows switchable proton-dependent photoluminescence in

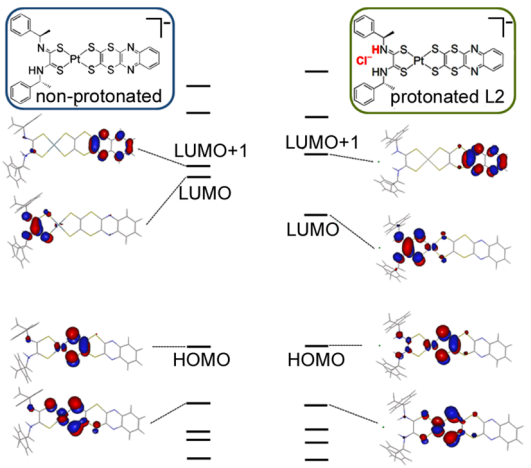

Figure 3. Frontier molecular orbitals of **1** (left) and **2** (right). Calculations were performed with the PCM method in acetonitrile, B3LYP/6-31+G(d)-SDD.[11]

solution at room temperature (Figure 4). The emission color can be tuned from deep red (715 nm) to bright green (570 nm)

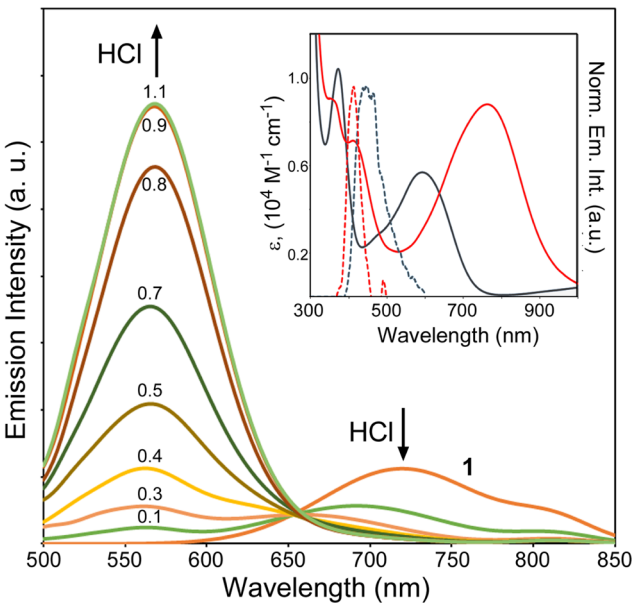

Figure 4. Emission change upon successive additions of HCl (10 μL, 10^{-2} M) to a solution of **1** in CH_3CN (1.5 mL, 5 × 10^{-4} M). Molar ratios [HCl]/[**1**] are indicated. The excitation wavelength was 450 nm. In the inset, the excitation spectra (dashed lines) are compared to the absorption spectra (solid lines) in a CH_3CN solution of **1** (black) and **2** (red).

upon the addition of 1 equiv of HCl, while the subsequent addition of NH_3 totally quenches the green band and restores the initial conditions (see Figure S12). Interestingly, both of these emissions are dependent on the excitation wavelength (see the inset in Figure 4), and no photoluminescence is detected upon excitation of the lowest absorption band corresponding to the HOMO−LUMO transition as well as in the UV part of the absorption spectrum. These results may suggest an unusual anti-Kasha−Vavilov behavior[18−20] for **1** in the both unprotonated and protonated forms[21] (see also Figure S13).

A similar behavior was recently found for the homoleptic platinum complex with ligand L1, $[Pt(L1)_2]^-$.[8] In this last case,

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irradiation at 420 nm under neutral conditions in a solution at room temperature yields an emission peak at 572 nm, which is well above the energy to the lowest absorption peak at 1085 nm associated with the HOMO−1 → SOMO transition. Emission was attributed to the HOMO−1 ← LUMO transition, involving orbitals localized on the quinoxaline moiety. On the other hand, the homoleptic $[Pt(HL2)_2]$ complex is nonluminescent in the neutral form. This complex becomes emissive at 700 nm upon HCl addition as a contact ion pair formulated as $[Pt(H_2\text{-}R_2\text{-}dto)_2^{2+}(Cl)_2]$.[22,23] Reversibility of this property is also observed upon NH_3 addition. Therefore, a comparison of the emissive properties of **1** with respect to the corresponding homoleptic complexes as well as the sequence of molecular orbitals (Figures 3 and S10) suggests that the process originates mainly from intraligand charge-transfer (ILCT) transitions involving L1 orbitals of the dithiolate moiety, with some metal contribution, and the ligand periphery localized on the quinoxaline moiety (LUMO+1) in both **1** and **2**, similarly to $[Pt(L1)_2]^-$. In the present case, L2 acts as a reversible proton acceptor, and the synergistic combination of the two ligands L1 and L2 allows tuning of the emission color of L1 through the proton-switchable properties of L2. The rather low quantum yields evaluated through the relative method (6.4×10^{-5} for **1** and 1.4×10^{-4} for **2**) and the room temperature decay times estimated from spectral data falling in the picosecond range (14 ps for **1** and 4 ps for **2**; see the SI and Table S3) point out that the radiative decay channel in both **1** and **2** is strongly quenched by other deactivation pathways. Therefore, it must be underlined that the term "anti-Kasha" emission is herein used with caution to describe an apparent phenomenon related to the observed spectral features. Transient absorption experiments currently underway will help to clarify the peculiar photocycle leading to the apparent anti-Kasha emission in this complex.

In addition to these LO properties, **1** exhibits also proton-switchable NLO properties. Protonation−deprotonation NLO switches in solution are commonly studied by the hyper-Rayleigh-scattering (HRS) technique working at 1064 nm incident wavelength, which, however, suffers the limitation of possible overestimation of the value of the quadratic hyperpolarizability due to resonance.[24−26] To achieve more reliable data, the electric-field-induced second-harmonic-generation (EFISH) technique was employed to determine the second-order NLO response of the molecular chromophore **1** in $CHCl_3$ solutions, working at a nonresonant 1907 nm incident wavelength, from which $\mu\beta_\lambda$ can be obtained,[27] (see the SI for experimental details).[28] More recently, a second-order NLO response by the EFISH technique has been reported for protonation−deprotonation NLO switches applied to organic[29] and organometallic[30] compounds. A remarkable $\mu\beta_{1907}$ value increase for **1** by a factor of 4 (from -735×10^{-48} esu for **1** to -2980×10^{-48} esu for **2**) is obtained. By taking into consideration the calculated μ value for **1** and **2** (12.6 and 3.9 D, respectively), the obtained β values show an increase by a factor of 12 (60 and 735×10^{-30} esu for **1** and **2**, respectively). It is worth noting that the $\mu\beta_\lambda$ value determined on the **1**·HCl solution after NH_3 addition suggests that the NLO-phore **1** is restored. The negative sign of $\mu\beta_\lambda$ values is in agreement with a decrease of the dipolar moments in the excited states, as reflected by the negative solvatochromism observed for the involved CT peaks (Figure S14). Similar behavior was observed for M(diimine)(dithiolate) complexes,[31] that have been largely investigated by Eisenberg's group and others for their NLO[32−34] and luminescent properties[32] and as sensitizers or photocatalysts for light-to-chemical energy conversion.[35−37] Several organic[24−26,38−41] and organometallic[30,42−47] molecules based on D−π-A moieties have been shown to undergo a variation of hyperpolarizability upon variation of the D−A strength or of the π bridge induced by external stimuli, including protonation. Similarly, proton-switchable emission has been found.[18,48,49] Remarkably, in the case under discussion, color, second-order NLO response, and emission all undergo switching upon protonation.

In conclusion, **1** behaves as a versatile multiresponsive optical switch. Coordination to the metal ion of L1 and L2, each of them a carrier of functionality, in a square-planar geometry allows one to reach a favorable arrangement for second-order NLO and for reversible interactions with HCl through L2. These interactions affect both the LO and NLO properties. This peculiarity is accompanied by an uncommon behavior of the emission properties of **1**. Thus, **1** represents a unique candidate that should stimulate interest in deepening its remarkable properties both for pure scientific reasons and for potential applications as a multiresponsive optical switch whose changes, accompanied by color tuning, can be followed by the naked eye.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00238.

Preparation and characterization of **1**, details on X-ray crystallography, DFT and TD-DFT computational studies, additional absorption and emission spectra including those of L1, photophysical parameter evaluation, details on NLO measurements, and solvatochromism (PDF)

Accession Codes

CCDC 1497428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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