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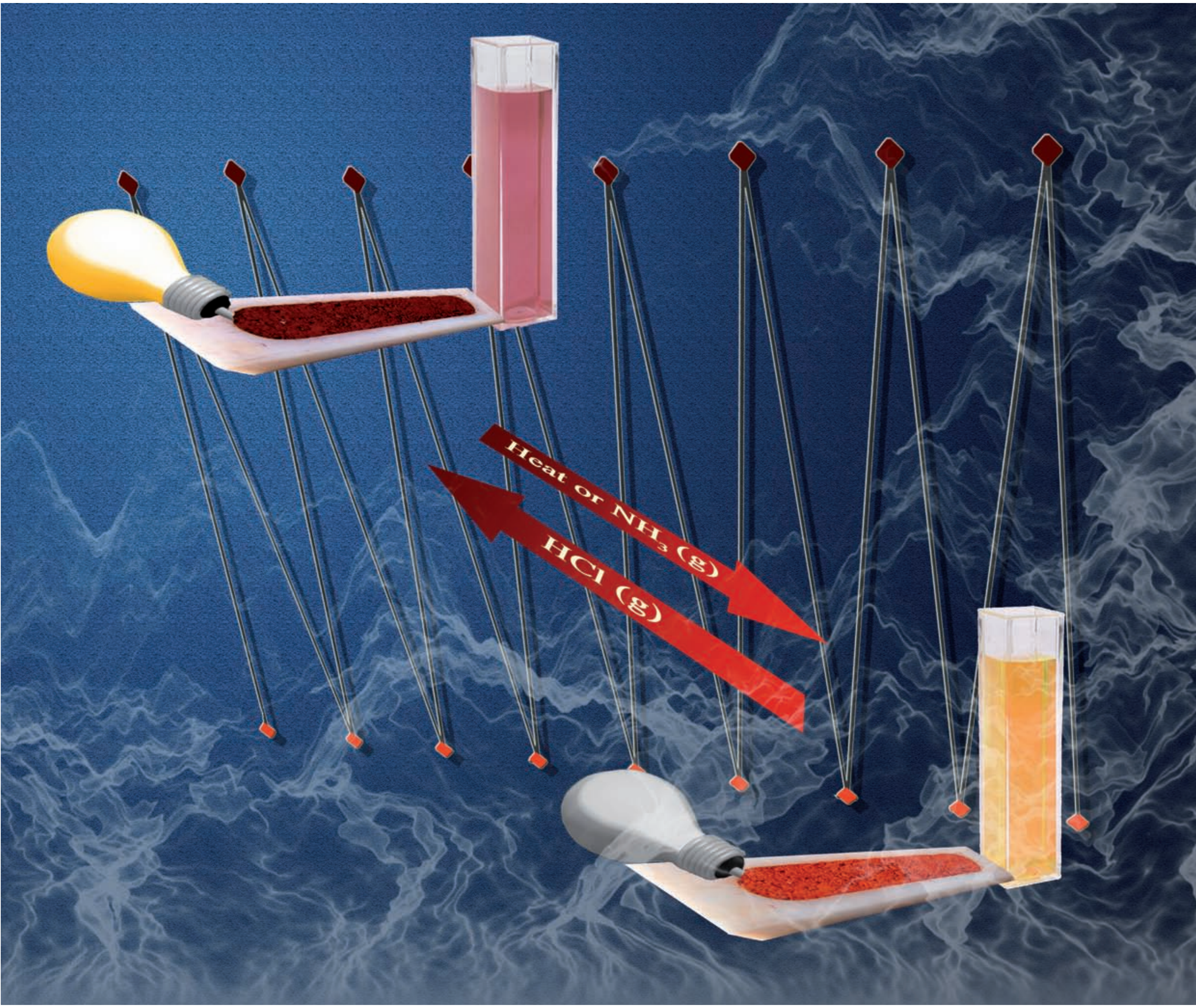

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Solid-state luminescence switching of platinum(II) dithiooxamide complexes in the presence of hydrogen halide and amine gases

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In the solid state, a non-luminescent platinum(II) dithiooxamide species adsorbs gaseous HCl, yielding a tight ion pair species which exhibits photoluminescence; the process is quantitatively reversed on heating or by exposing the sample to ammonia vapors.

Molecular systems capable of exhibiting on/off switching of luminescence in the presence of suitable substrates or under specific conditions are being extensively investigated since they are of interest in various applicative and fundamental research fields, such as sensors and molecular logic gates and machines.[1] However, whereas luminescence switching in solution is very well documented, luminescence switching in the solid state, related to coordination of gases to switchable molecular species, *i.e.* as a consequence of site-specific interactions at the molecular level, is far less common.[2,3] A recent interesting example is the luminescence switching exhibited by crystals of a dinuclear (bipyridine)platinum(II) complex bridged by pyridine-2-thiolate ions, in the presence of organic vapors of acetonitrile or ethanol.[4]

Herein we report the solid-state switching of the luminescence of a Pt(II) complex based on dithiooxamide ligands, $[Pt(R_2\text{-dto})_2]$ (**2**; dto = dithiooxamide; R = butyl. See Fig. 1), in the presence of gaseous HCl. The solid-state luminescence switching can be reversed by heating the complex powder or in the presence of ammonia vapors.†

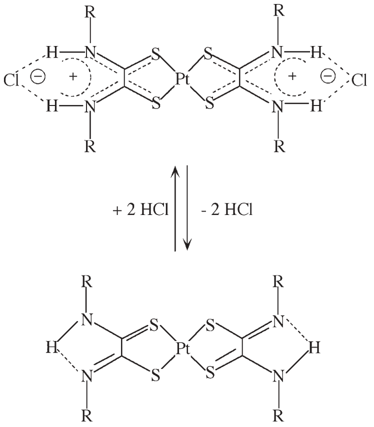

Fig. 1 Structural formulas of **1** and **2** and their conversion scheme. R is butyl.

The reaction between *N*,*N*′-dialkyl-dithiooxamides and *cis*-$[PtL_2Cl_2]$ complexes (L = Me_2SO, Me_2S), carried out in low polarity non-coordinating solvents, gives rise to tight ion pairs of general formula $\{[Pt(R_2\text{-dto-H})_2]^{2+}\ (Cl^-)_2\}$ in high yields (for R = butyl, **1**);[5,6] HCl can be easily removed from these ion pairs by means of nitrogen bases, Broensted basic solvents, hydrogen carbonate salts, or by column chromatography (alumina or silica gel),[6] yielding $[Pt(R_2\text{-dto})_2]$ complexes.

The $\{[Pt(R_2\text{-dto-H})_2]^{2+}\ (X^-)_2\}$ ion pairs (X = Cl, Br, I) emit from a charge transfer excited state (namely, a Pt/S → dto CT triplet state), whereas the $[Pt(R_2\text{-dto})_2]$ species (hereafter called "unprotonated", for simplicity) are not luminescent.[5] The absorption spectra of the tight ion pairs and their "unprotonated" homologous species are also notably different from one another, with the ion pairs absorbing at significantly lower energy than the corresponding "unprotonated" ones. This process was investigated in detail in solution a decade ago,[5] when it was also shown that it is common to a series of Pt(II) species carrying various amide substituents (including the compounds **1** and **2** reported here); it is not limited to HCl, but can also involve HBr and HI and therefore, in principle, any HX species (X = pseudohalogen group). The situation is shown in Fig. 1.

On the basis of the known solution behavior, we tested the solid-state luminescence properties of the Pt(II) dithiooxamide complexes, and found that the different photophysical properties for the tight ion pairs and the "unprotonated" species are also retained in these conditions. Indeed, in the solid state **1** exhibits photoluminescence quite similar to that reported in solution (see Fig. 2), so a Pt/S → dto CT attribution still holds, whereas the excited state of compound **2** only decays by radiationless processes. The transition from **2** to **1** is easily obtained in the solid state: when **2** is exposed to HCl vapors for a few seconds, the color of the solid changes, passing from an initial orange-red to purple-brown (see Fig. 3), indicating formation of **1**.[7] At the same time, photoluminescence takes place. The so-formed **1** is identical to that independently prepared in solution, and is very stable at room temperature, as demonstrated by the constancy of its optical properties after several days. However, **1** can be quantitatively converted into **2** by heating the powder in an oven at 80 °C for 10 min. Several cycles have been performed, and no substantial degradation of the starting material has been noted, at least for 8 cycles. Fig. 4 shows some of these cycles, followed by luminescence. The procedure can obviously be started from **1**. In

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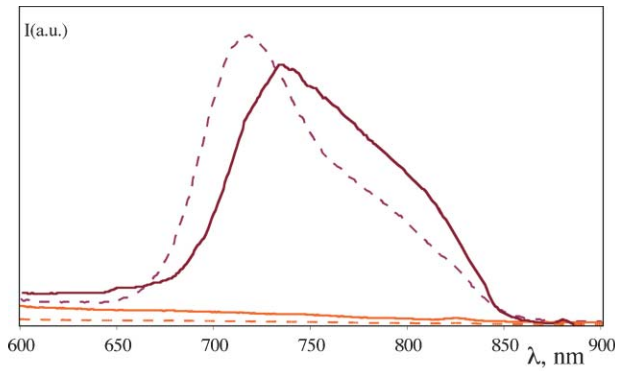

Fig. 2 Luminescence spectra of **1** in the solid state (solid purple) and in dichloromethane solution (dashed purple). Orange curves are the emission responses of **2** under the same conditions. Excitation wavelength is 464 nm. Lifetime of **1** emission in the solid state is 28 ns, comparable with the solution lifetime (25 ns).[5] Excitation wavelength for emission lifetimes, 408 nm.

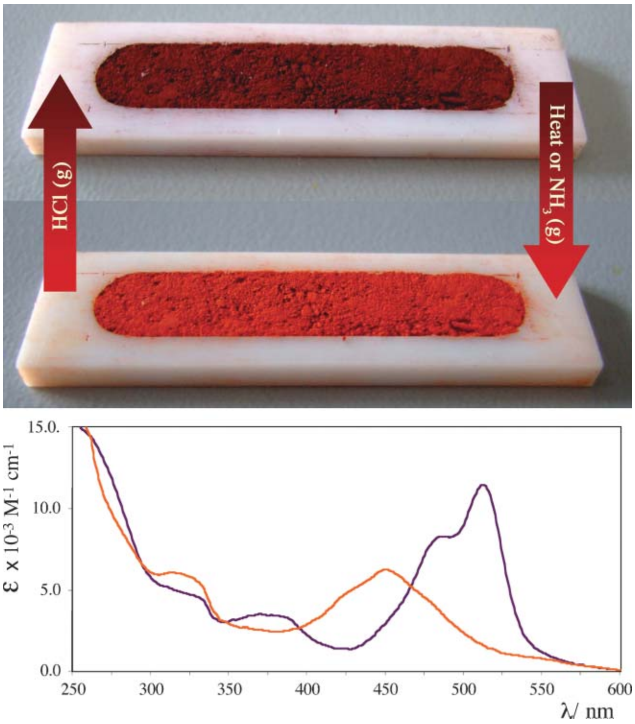

Fig. 3 Color changes obtained by converting solid **1** (the purple-brown species) to **2** (the orange-red species). For comparison, in the bottom panel the absorption spectra of **1** (purple) and **2** (orange) in dichloromethane are shown.

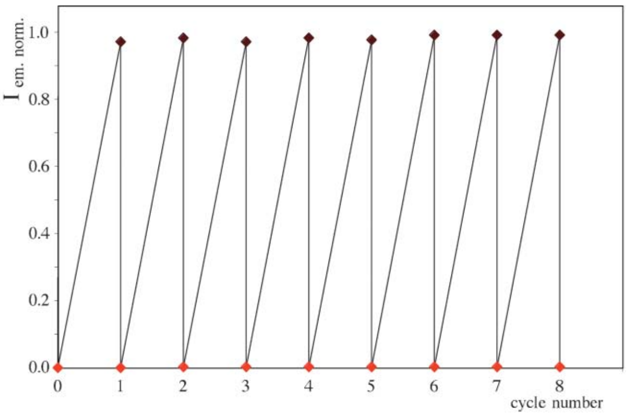

Fig. 4 Values of I_{em} (λ_{exc} = 464 nm, isosbestic point) for solid sample of **2** (orange) exposed to HCl vapors to yield **1** (purple) and heated to restore **2** *vs.* cycle number.

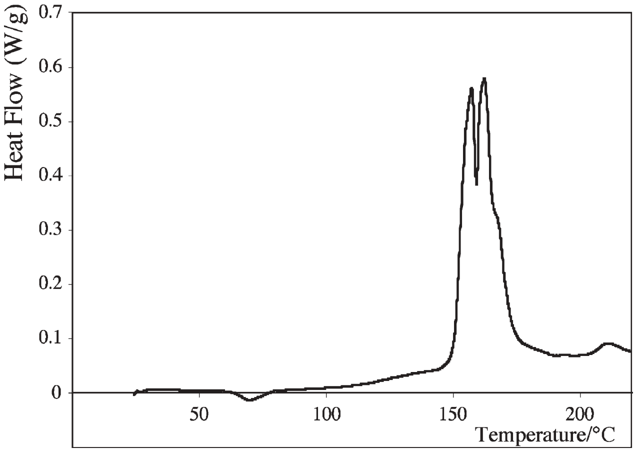

Fig. 5 Differential scanning calorimetry of **1**. Temperature increase rate, 2.5 °C min^{-1}.

this case, the first step is heating to prepare the non-luminescent compound **2**.

The solid-state **1** → **2** transition has also been evaluated by temperature programmed techniques.‡ A sample of 2.4 mg of **1** was placed in a sealed sample pan (120 μL) to be studied in a differential scanning calorimeter apparatus. On increasing the temperature by 2.5 °C min^{-1} in the range 30–250 °C, two thermal transitions of similar extent take place in the very small temperature range of 155–165 °C (see Fig. 5). This phenomenon is attributed to the sequential loss of the two HCl molecules linked to **1**. The overall thermal exchange measured in these conditions is 186.8 J g^{-1}.[8] Moreover, an analogous experiment carried out in a thermogravimetric analysis apparatus with an open pan made it possible to estimate the related weight loss to be close to 10%. This percentage is in fair agreement with the loss of two HCl molecules from **1**.

An interesting variation is that the solid-state **1** → **2** transition is obtained at room temperature by exposing **1** to NH_3 vapors.[9] In these conditions, after several cycles NH_4Cl is clearly formed and can be analyzed by standard methods. Even in this case, no damage or degradation of the starting material is observed after at least 10 cycles.

In conclusion, we report the potential of Pt(II) dithiooxamide complexes to exhibit luminescence switching in the presence of HCl vapors. The luminescence switching can be reversed by heating or by NH_3 vapors. These results are appealing in view of the interest in searching for hydrogen halide and hydrogen pseudohalide gas sensors.[10] The sensitivity of the luminescence of the title species to amines may also open up interesting potential applications, since molecules that exhibit useful optoelectronic responses when exposed to amines could be used to detect compounds used in the manufacture of drugs, pesticides, dyes, preservatives and disinfectants, as well as in the food industry.[11] Moreover, we would like to stress that the luminescence of the studied compounds can be switched on/off by two *different gas inputs*, HCl and NH_3, a non common behavior for luminophores, yielding gas-activated luminescent molecular logic gates.

Extensive investigations are planned in our laboratories to extend this study to clarify several points such as: (i) effect of substituents on amide nitrogens on the ion pair equilibria; (ii) possible extension to other hydrogen halide or pseudo-halide groups, as well as to other amines; (iii) complete thermal and kinetic analysis of the processes; (iv) limit of sensitivity.

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Notes and references

† Luminescence experiments were performed with a Horiba Jobin-Yvon Fluoromax P fluorimeter, equipped with a red-sensitive phototube, and with an Edinburgh OB 900 single-photon-counting spectrometer, by using a Hamamatsu PLP-2 laser diode as source (408 nm). Electronic absorption spectra were recorded with a Jasco V-560 spectrophotometer.

‡ For temperature programmed techniques, TA Instruments Q-100 and DSC-2950 were used.

1 See for example: (*a*) A. P. De Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (*b*) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; (*c*) V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003; (*d*) L. Prodi, *New J. Chem.*, 2005, **29**, 20.

2 A noticeable exception is the extensively studied field of luminescent oxygen sensors,[3] where anyway the interaction is not site-specific.

3 See for example: (*a*) W. Su, R. Schmidt, M. Whaley, J. N. Demas, B. A. DeGraff, E. K. Karikari and B. L. Farmer, *Anal. Chem.*, 1995, **67**, 3172; (*b*) F. N. Castellano and J. R. Lakowicz, *Photochem. Photobiol.*, 1998, **67**, 179; (*c*) G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo and S. Campagna, *Anal. Chem.*, 1998, **23**, 5019; (*d*) B. A. DeGraff and J. N. Demas, in *Reviews in Fluorescence*, ed. C. Geddes and J. R. Lakowitz, Springer, Netherlands, 2005, vol. 2, p. 125.

4 M. Kato, A. Omura, A. Toshikawa, S. Kishi and Y. Sigimoto, *Angew. Chem., Int. Ed.*, 2002, **41**, 3183. For other examples of Pt(II) complexes exhibiting vapochromism and vapoluminescence in the solid state, see also: T. J. Wadas, Q. M. Wang, K. J. Kim, C. Flaschenreim, T. N. Blanton and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 16841; W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, Z. He and K.-Y. Wong, *Chem.–Eur. J.*, 2003, **9**, 6155 and refs. therein.

5 G. Rosace, G. Giuffrida, G. Guglielmo, S. Campagna and S. Lanza, *Inorg. Chem.*, 1996, **35**, 6816. Formation of the tight ion pair moves the inherently emitting Pt/S → dto CT level to lower energy compared to the "unprotonated" species. This makes the radiative transition an effective decay process by decreasing the CT mixing with upper, non-luminescent excited states.

6 (*a*) G. Rosace, G. Bruno, L. Monsù Scolaro, F. Nicolò, S. Sergi and S. Lanza, *Inorg. Chim. Acta*, 1993, **208**, 59; (*b*) S. Lanza, G. Bruno, F. Nicolò, G. Callipari and G. Tresoldi, *Inorg. Chem.*, 2003, **42**, 4545; (*c*) S. Lanza, G. Callipari, F. Loiseau, S. Serroni and G. Tresoldi, *Inorg. Chem.*, 2005, **44**, 6717.

7 Experimental work-up: 36 mg of **2** were anchored on a Teflon substrate and the plate was exposed to HCl vapors for 5 seconds. Then a representative sample (8 mg) was dissolved in $CDCl_3$ (0.5 mL). NMR spectra were identical to those of **1** prepared according to reported methods[5].

8 In thermal experiments, peak temperatures and relative ratio, as well as the overall thermal exchange, depend on various factors, including the temperature increase rate. For example, the overall thermal exchange increases to 198.7 $J\ g^{-1}$ for a 10 °C min^{-1} temperature increase rate, and in these conditions the two processes coalesce. Thermal inertness is responsible for such an effect. A detailed investigation will be reported in due course.

9 Experimental work-up is similar to that reported in note 7, with the exception that the sample containing the Teflon substrate is exposed to NH_3 vapors.

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