Cluster Compounds

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Temperature-Dependent Fluorescence of Cu_5 Metal Clusters: A Molecular Thermometer[**]

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The accurate measurement of temperature is of increasing importance as it is required for widespread applications (electronic devices, biology, medical diagnostics).[1] In this context, fluorescence thermometry has already shown great potential, and a variety of molecules have been proposed as luminescent molecular thermometers.[2–12] Herein, we describe Cu_5 metal cluster **1** (Figure 1) that presents remarkable photophysical properties, both in solution and as the solid, characterized by temperature-dependent emission intensity and lifetime that change significantly in the range between −45 and +80 °C. These properties allow for an unprecedented accuracy in temperature determination by fluorescence measurements, with the high sensitivity and the high temporal (sub-millisecond) and spatial (sub-micrometer) resolution typical of photoluminescence spectroscopy.

Complex **1** can be seen as a metal nanoparticle composed of five copper atoms bound to three highly conjugated dianionic cationic ligands $(EtNC(S)PPh_2NPPh_2C(S)NEt)^-$; Figure 1 A).[13,14] Its absorption spectrum presents a broad and unstructured band below 450 nm (Figure 2 A). The system is luminescent in all phases, both at room temperature and at 77 K (Figure 2 B) and no dependence on the solvent was observed. A summary of the photophysical properties is shown in Table 1.

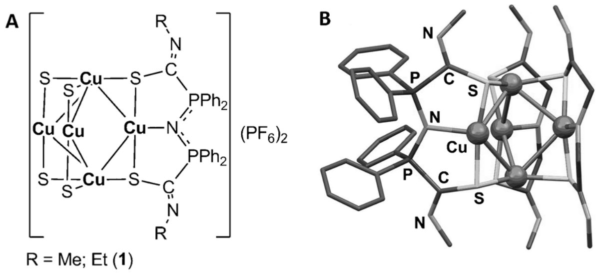

Figure 1. A) The trizwitterionic dicationic Cu_5 clusters. B) $[Cu_5(MeNC(S)PPh_2NPPh_2C(S)NMe)_3](PF_6)_2$. For clarity, only one ligand is fully shown. In (B) the phenyl groups of the other two ligands and the PF_6 counteranions are omitted.

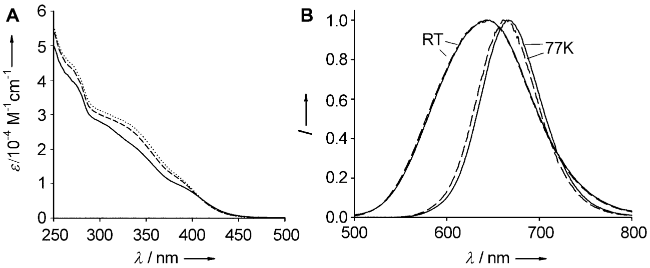

Figure 2. A) Electronic absorption spectra of **1** in water (——), dichloromethane at RT (•••••), and EtOH/MeOH (1:1 v/v) at RT (-----). B) Emission spectra upon excitation at 405 nm of **1** at RT in 1 % (w/v) SDS in water (——) and dichloromethane (-----). Emission spectra upon excitation at 405 nm of **1** at 77 K in dichloromethane (——) and EtOH/MeOH (1:1 v/v; -----).

Importantly, the emission quantum yields and the excited-state lifetimes of **1** are the same in deoxygenated solutions, thus suggesting that these properties are independent on the

Table 1: Photophysical properties of **1** at room temperature and in a rigid matrix at 77 K.

T	Phase	λ_{max}[a] [nm]	lifetime [ns]
RT	solid	660	540
RT	1 % (w/v) SDS in water	636	510
RT	CH_2Cl_2	642	440
77 K	CH_2Cl_2	665	Opaque matrix
RT	EtOH/MeOH (1:1 v/v)	645	490
77 K	EtOH/MeOH (1:1 v/v)	661	38.9 μs

[a] λ_{exc} 405 nm.

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presence of O_2. In contrast, with regards to temperature, the emission quantum yields and excited-state lifetimes decrease by about two orders of magnitude between −45 and +45 °C (Figure 3). The decay of the emission is monoexponential in all cases.

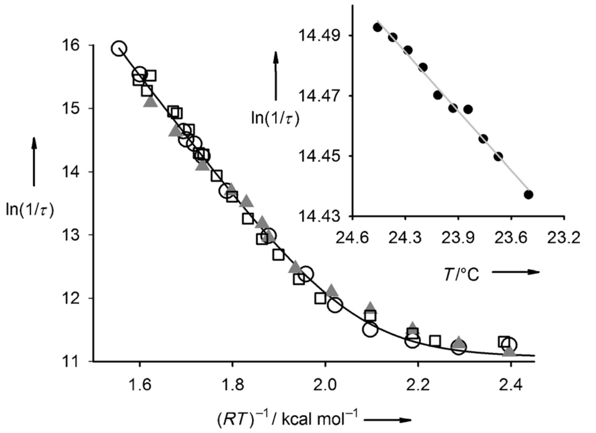

Figure 3. Arrhenius plots of **1** in dichloromethane (○ for the lifetime and □ for the luminescence intensity) and at the solid state (▲ for the lifetime). Inset: Arrhenius plots of the lifetime of **1** in 1% (w/v) SDS in distilled water.

To explain the thermosensitive behaviour of this complex, quantum chemistry calculations were necessary to quantitatively describe its electronic states. Time-dependent density functional theory (TD-DFT) calculations were performed[15] at the B3LYP level with the SV(P) basis set as implemented in the TURBOMOLE V5.10 program.[16–18]

The seven lowest electronically calculated excited singlet states lay at 438, 435, 407, 404, 382, 378, and 365 nm (S_1 to S_7, respectively), in the range covered by the spectra shown in Figure 2. All these excited singlet states share low to medium oscillator strengths (f_0) for the transition from the ground state, with S_1 to S_7 having values of 0.0106, 0.0031, 0.0919, 0.0818, 0.0446, 0.0491, and 0.0052, respectively. Consistently, the initial molecular orbitals of all the transitions are located in the core of the cluster, therefore they interact weakly with the environment and are less prone to radiationless decay than to an excitation involving the ligands. For the first six excited singlet states, the final orbital is the metal centered LUMO, (Figure 4A), while for S_7 it is the ligand centered LUMO+1 (Figure 4B).

This model is supported by the analysis of $\tau(T)$, which were fitted as a function of temperature according to an Arrhenius-like behaviour:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_0} + A\exp\left(-\frac{\Delta E}{k_B T}\right) \quad (1)$$

where τ_0 is the excited state lifetime at 0 K, A is the pre-exponential factor and ΔE is the activation energy to reach the fast decaying state S_7. An analogous equation was applied to the emission intensity values. Arrhenius plots of lifetimes and emission spectra areas are shown in Figure 3.

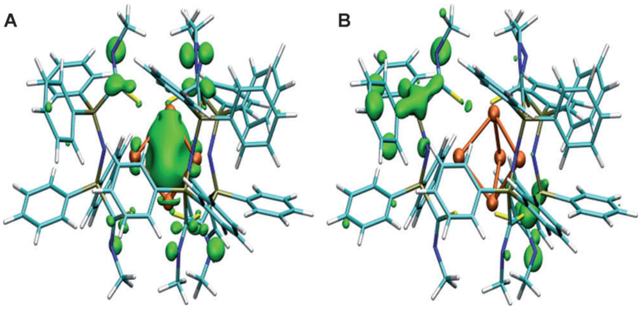

Figure 4. Molecular orbitals of **1**. A) Lowest unoccupied molecular orbital (LUMO). B) Second lowest unoccupied molecular orbital (LUMO+1).

Thus, two photophysical parameters of **1** can be used to measure temperature: the fluorescent quantum yield and the excited-state lifetime. This last one is of particular interest being an intensive physical variable.

The activation energies, obtained from the plotting of the lifetimes, are 9.8 kcal mol⁻¹ in 1% (w/v) SDS distilled water, 9.7 kcal mol⁻¹ in dichloromethane, and 8.8 kcal mol⁻¹ in the solid state. The analogous values obtained from the areas of the emission spectra are 9.4 and 9.5 kcal mol⁻¹ in water and dichloromethane, respectively.

In principle, the occurrence of nonradiative processes could lead to local heating upon irradiation. This is a problem intrinsic to all fluorescent molecular thermometers because in these systems temperature influences the equilibrium between competing radiative and nonradiative transitions. This effect must be significant especially if large intensity changes have to be observed (a crucial feature for measuring small temperature gradients). However, in the present case, the high sensitivity offered by luminescence spectroscopy allows the use of very low irradiation intensities. The excess heat is dispersed into the environment in a much shorter time than the excited-state lifetime (around several microseconds or even milliseconds) that is used to measure the temperature, thus making the problem of local heating negligible.

The experimental and computational findings can be summarized as:

1) It is extremely rare that the electronically excited states of a molecule have entirely different features from one another. The electronic excitations centered at the core of the metal cluster interact weakly with the environment and are less prone to radiationless decay than an excitation that involve the ligands themselves.
2) Upon population of the singlet excited state S_1, all other excited states are accessed according to the Boltzmann equilibration. S_1–S_6 have a long natural lifetime; their decay to the ground state is slow because of the low oscillator strength (radiative decay is nearly forbidden), and of the sheltered environment (slow radiationless decay).[19,20] The different spatial distribution of the S_7 state opens a new channel that makes it decay very rapidly.
3) The equilibration is faster than the decay of S_1.
4) The lifetime of the lower excited states is only weakly affected by the media, in particular the lifetime of S_1 should be almost unaffected by it.

5) The absence of fatigue implies that structural reorganization plays a small role in the working of the molecular thermometer (by the calculations we were unable to locate a structurally different arrangement of the Cu_5 core both in S_0 and in S_1).

On the basis of these five points, a tentative mechanism is outlined in Figure 5.

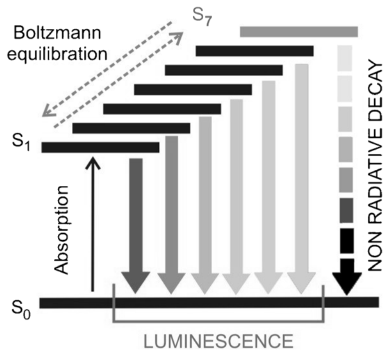

Figure 5. Schematic representation of the mechanism of the molecular thermometer.

Because of the large variation of the photophysical properties with temperature, the system can be used to measure temperature changes of less than 0.1 degrees (showing a relative variation greater than 0.5% K^{-1}, as required)[7,12] in a very large temperature range, including room temperature (inset in Figure 3) and the physiological temperature (37°C), with an error of ±0.01°C. These characteristics, together with the almost total independence of the measured values on other experimental conditions, including oxygen concentration, make this system one of the most versatile molecular thermometers reported to date.[21–23]

To demonstrate the potential of **1** to measure temperature changes in real systems, we investigated its emission changes when spotted on different surfaces. We used a very simple (and inexpensive) apparatus made up of a plastic container filled with water, a UV lamp for excitation (365 nm), and a standard webcam for image collection (see the Supporting Information for the details on the experimental setup). The use of webcams complemented by optimized light sources allows for a dramatic simplification of the system design in many applications.[24] Initially, **1** was spotted on aluminium foil, cotton fabric, and a plastic plaster, which were then put in contact with the plastic container filled with water at a temperature of 60°C. The water temperature was constantly monitored while cooling to room temperature, and images were synchronously acquired.

Figure 6A shows the webcam image of the different fabrics at 30°C and Figure 6B the intensity of only the camera red channel. This picture reveals that most of the emission is captured by this channel, thus allowing the observation of the distribution of **1** on the different surfaces. The adhesion of **1** was not optimized in this experiment, nevertheless it was very good and only limited inhomogeneity was observed for all substrates. Moreover, the intensity of the camera red channel, averaged over the whole spot, can be conveniently measured to monitor the temperature-induced fluorescence changes (Figure 6C). The plots of this parameter versus the temperature show the same emission change (same slope) for the three spots (aluminium, cotton, and plastic), except for the different offset values, which are most likely due to the different thicknesses of the samples. This remarkable result indicates that even in the solid state, within a physiological temperature range and on different substrates, the temperature–emission relationship of **1** is maintained. Based on these findings we envisage future applications of **1** in real devices.

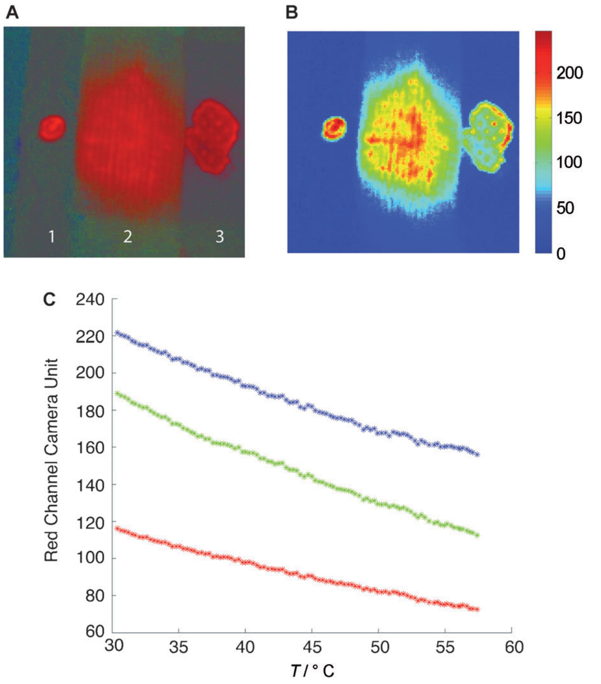

Figure 6. A) Spots of **1** on aluminium foil (1), cotton fabric (2), and a plastic plaster (3) at 30°C under a UV lamp and imaged by a webcam. B) Camera red channel image of Figure 6A. C) Intensity of the red channel, averaged over pixels of the spots, versus the water temperature. Aluminum (blue), Cotton (green), Plastic plaster (red). The intensity is distributed in the interval 0–255 related to the 8 bit image resolution of the webcam.

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