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Highly Emitting Concomitant Polymorphic Crystals of a Dinuclear Rhenium Complex

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Abstract: The dinuclear complex $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}4,5\text{-}(Me_3Si)_2\text{-pyridazine})]$ gives in the solid state two polymorphs (yellow, **1Y**, and orange, **1O**), which can be either concomitantly or separately obtained on varying the crystallization rate. Both crystal phases exhibit intense photoluminescence from the lowest lying triplet metal-to-ligand charge transfer state, much stronger than in solution (quantum yields 0.56 and 0.52, for **1O** and **1Y** respectively, vs 0.06 in toluene), likely due to the restricted rotation of the Me_3Si groups in the solid state. A clean, irreversible **1O** → **1Y** single-crystal-to-single-crystal phase transition occurs at 443 K, as revealed by variable temperature X-ray diffraction analysis. In spite of the absence of any strong intermolecular interactions in both forms, **1O** and **1Y** show very different absorption and emission maxima (λ_{abs} 370 and 393 nm, λ_{em} 534 and 570 nm, for **1Y** and **1O**, respectively). This behavior highlights the importance of the local organization of molecular dipoles in perturbing the photophysical properties of the molecule in the crystal.

We report on a dinuclear rhenium complex which exhibits a unique combination of unusual properties: a higher emission quantum yield in the solid state than in solution, concomitant formation of two highly luminescent polymorphs, and clean single-crystal-to-single-crystal conversion of one form into the other.

Interest in luminescent materials able to efficiently emit in the solid state is continuously growing, because in most applications the dyes are used as solid films. Although rigid environments are expected to freeze rotovibrational relaxation pathways,[1] luminescence efficiency often decreases in the solid state with respect to fluid solution, due to concentration quenching, affecting both organic[2] and organometallic emitters.[3] However, an increasing number of systems exhibiting enhanced solid state emission have been reported.[4−9] In most cases restriction of the intramolecular rotation has been identified as the main cause for this effect,[4] for which the term Aggregation Induced Emission Enhancement has been coined.[5] The importance of bulky substituents in reducing concentration quenching effects has also been highlighted.[6] Other intra- or intermolecular phenomena have been invoked as well, such as conformational changes, $\pi-\pi$ stacking,[7] hydrogen bonds,[8] or J-aggregates,[9] which cause rearrangements of the energy levels and population, in some cases, of more emissive excited states.

Noteworthy, crystalline aggregates sometimes proved to be more efficient emitters than their amorphous counterpart, showing the influence of molecular packing on the solid-state emission.[10] The availability of different crystalline phases (polymorphs) of a luminescent molecule provides the best opportunity to study the relationship between crystal packing and optical properties.[8a,11,12] We report here on two stable concomitant polymorphs of the dinuclear complex $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}4,5\text{-}(Me_3Si)_2\text{pyridazine})]$ (**1**, Figure 1), both showing photoluminescence quantum yields (PLQYs, 0.52 and 0.56 respectively) almost 1 order of magnitude higher than those when in solution.

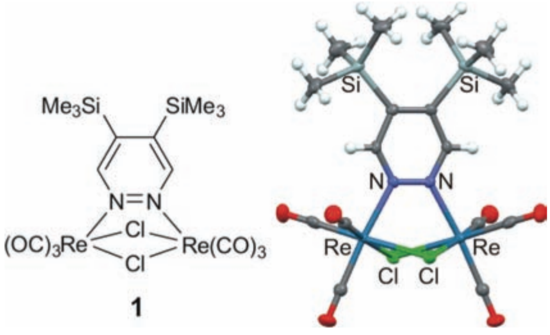

Figure 1. Schematic drawing and ORTEP view of $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}4,5\text{-}(Me_3Si)_2\text{pyridazine})]$ (**1**). The ORTEP view refers to the molecule as found in the **1Y** phase.

The new compound belongs to the recently reported class of dinuclear, luminescent Re(I) complexes of general formula $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}1,2\text{-diazine})]$,[13,14] which exhibit intense emission in solution from triplet metal-to-ligand charge transfer (^{3}MLCT) excited states. The derivatives with alkyl groups in both of the β positions of pyridazine (hereafter referred to as R_2pydz) show the highest PLQYs (0.44−0.53 in deaerated toluene, λ_{em} 550 nm).[15]

Complex **1**, obtained by reacting $Re(CO)_5Cl$ with a stoichiometric amount of $4,5\text{-}(Me_3Si)_2$pyridazine, has a much smaller electrochemical HOMO−LUMO gap (2.54 eV) than complexes containing R_2pydz's (2.90 eV), as a result of an easier reduction (one-electron, reversible, diazine-centered process, occurring at a potential 0.32 V higher than that of complexes with R_2pydz's; Figure S1 in the Supporting Information). The easy reduction agrees with LUMO stabilization arising from its partial delocalization on the silicon atoms as also supported by DFT calculations (see Figure S2 in the Supporting Information).

In accord with the smaller HOMO−LUMO gap, both the ^{1}MLCT absorption and the ^{3}MLCT emission of **1** in solution (Table 1, Figures S3−S4 in the Supporting Information) are red-shifted with respect to the complexes with R_2pydz's.[16] More interesting is the reduction of the PLQY (0.06 vs 0.50) and the shortening of the

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10.1021/ja106772v

excited state lifetime (0.7 vs 5 μs), with a k_{nr} value which is 1 order of magnitude higher than those observed for complexes with R_2pydz's (ca. 10^6 vs 10^5 s^{-1}). The value nicely fits into the energy-gap-law plot concerning the family of $[Re_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-}1,2\text{-}diazine)]$ complexes with different substituents in the 4,5-positions (Figure S5), indicating that the vibrational states involved in the radiationless deactivation remain the same throughout the whole series.[17] In a butyrronitrile rigid matrix at 77 K (Figure S6 in the Supporting Information) the emission is strongly blue-shifted (Table 1), in agreement with the rigidochromic effect, usually observed for emission from charge transfer excited states.[18] The relatively short value of the radiative lifetime and the structureless nature of the emission band suggest that the lowest emitting level maintains a ^{3}MLCT character also at low temperature.[19]

Table 1. Absorption and Emission Data for **1**, in Solution (Room Temperature and 77 K) and in the Two Crystal Phases, upon Excitation at $\lambda = 400$ nm

Sample	λ_{abs} [nm]	λ_{em} [nm]	τ_{em} [μs]	Φ	ηk_r ($\times$ 10^{-4} s^{-1})	k_{nr} ($\times$ 10^{-6} s^{-1})
1[a]	394[b]	612	0.7	0.06	8.6	1.35
1[c]	—	547	21.2	—	—	—
phase **1Y**	370[d]	534[e]	5.8[e]	0.56[e]	9.6[e]	0.07[e]
phase **1O**	393[d]	570[e]	4.1[e]	0.52[e]	12.2[e]	0.12[e]

[a] Measured in deaerated toluene solution, at room temperature (1×10^{-5} M). [b] ε 1.0×10^4 M^{-1} cm^{-1}. [c] Butyrronitrile rigid matrix at 77 K. [d] Dispersion in KBr. [e] Crystalline samples.

During the crystallization process the concomitant formation of two crystalline phases of compound **1** was observed (yellow, **1Y**, and orange, **1O**). The concurrent existence of polymorphs has long been recognized, but rarely studied,[20] although it provides a unique chance for investigating the factors governing molecular packing. Because concomitant polymorphs are nearly energetically equivalent structures, kinetic rather than thermodynamic contributions offer the best tool for obtaining each phase alone. By modifying the crystallization rate it was thus possible to separately isolate the two forms (see Supporting Information).

The structure of the two crystal phases has been established by means of single-crystal X-ray diffractometric analysis. The molecule has an idealized C_2 symmetry, due to the conrotatory movement of the two Me_3Si substituents around the $C_{diazine}{-}Si$ bond, in both phases (Figure 1).

In the yellow (monoclinic) **1Y** polymorph the asymmetric unit contains only half a molecule (the C_2 symmetry being crystallographically imposed), while in the orange (orthorhombic) **1O** phase the asymmetric unit contains two molecules. However, no major perturbation of the molecular geometry induced by packing interactions seems to be detectable.

With molecular polarity assumed as an ordering parameter, both species can be described as layered structures. As shown in Figure 2, in the **1Y** phase layers are made by equally oriented molecules, with the pyridazine rings lying in the layer's plane, while in the **1O** phase layers consist of a zigzag organization of the molecules, with the pyridazine rings making an angle of ca. 70° with the layer's plane. In the **1Y** phase layers of opposite macroscopic polarity are alternated along the [1 0 −1] direction, while in the **1O** phase the polarity alternates every two layers stacked along the [0 0 1] direction (see Figure 3).

As judged from the respective volume-per-molecule values (*V*/*Z*, both at RT and 100 K; see Supporting Information) **1O** is more densely packed than **1Y**. Accordingly, enthalpy should favor the formation of **1O** while entropy that of **1Y**. At relatively 'low' temperatures, entropy has a limited role, so that the formation of **1Y** should be driven by kinetic factors, as experimentally confirmed (see Supporting Information).

On raising the temperature, **1Y** could become more stable than **1O**. Indeed, Differential Scanning Calorimetry (DSC) on microcrystalline powders of **1O** (Figure S9) shows at 443 K an endothermic (ΔH ca. 1.4 kJ/mol) peak related to the **1O** → **1Y** phase transition[21] and, eventually, at 603 K the melting of **1Y**. Variable temperature single crystal X-ray diffraction of **1O** showed that the transition at 443 K is an irreversible[21] **1O** → **1Y** single-crystal-to-single-crystal phase transition that only slightly affects the crystallinity.[22]

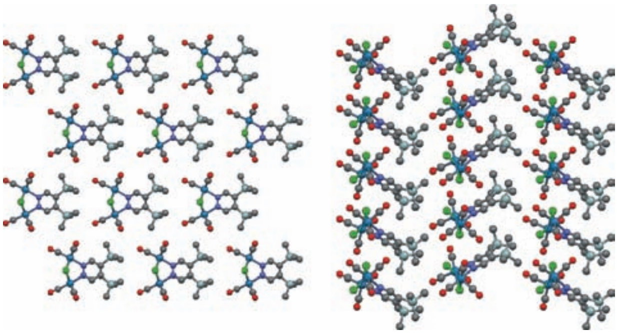

Figure 2. A view of the layers of "equally oriented" molecules in **1Y** (left) vs **1O** (right).

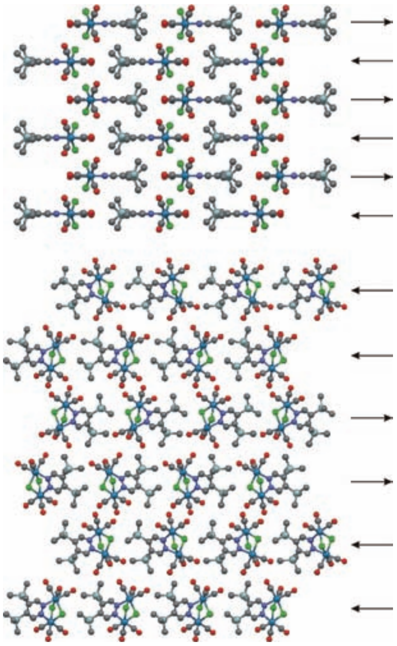

Figure 3. Stacking of the layers in **1Y** (above) vs **1O** (below). Small arrows next to the layers highlight the orientation of their macroscopic dipole moment. Additional views can be found in the Supporting Information (Figures S7 and S8).

The photophysical data for the two polymorphs are summarized in Table 1. The solid state emission spectra of crystals of the two phases are shown in Figure 4. Two features have to be remarked upon.

First, both absorption and emission bands of **1O** are red-shifted with respect to **1Y**. Since the structural data rule out any specific strong intermolecular interactions (such as $\pi{-}\pi$ stacking or H/J-aggregates) in both forms, the different energies may be ascribed to the different local packing (enclosure spheres) of the independent molecules in the two polymorphs and, in particular, to the different local organizations of molecular dipoles. This highlights how packing can perturb the photophysical properties of the molecules, even in the absence of particularly short interactions.

Second, both of the crystalline phases exhibit intense photoluminescence (PLQY > 0.50), much stronger than the moderate luminescence observed in solution. The lifetime decays are for both crystals monoexponential, in the microsecond region, suggesting that the emission occurs from only one excited state, with strong ^{3}MLCT character.

The restricted rotation of the Me$_3$Si groups in the crystals is most likely responsible for the enhancement of the emission with respect to the solution. Actually, all the alternative mechanisms proposed to explain the aggregation induced emission appear not at work here, as the structural data rule out any close intermolecular interactions. As pointed out by a reviewer, this is the first time that intramolecular motions of nonconjugated rotors quench the emission of a fluorophore in solution (the k_{nr} values in solution are more than 10 times larger than those in the solid state, while the k_r values are closely comparable, Table 1). We think that this is attributable to the involvement of the Me$_3$Si groups in the LUMO, even in the absence of true conjugation (the analogous complex containing the 4-*t*-Bupydz ligand exhibits intense emission in solution[14]).

A PMMA thin film of **1** emits at ca. 560 nm (see Supporting Information), with a PLQY intermediate between those of solution and crystals, in agreement with the intermediate intramolecular mobility expected for a molecule dispersed in a film with respect to the solution and the crystal phase, respectively.

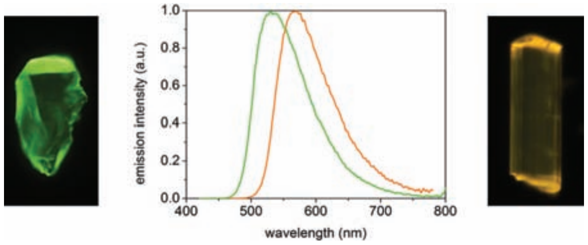

Figure 4. Emission spectra of **1Y** (green trace) and **1O** (orange) as single crystals, upon excitation at $\lambda = 400$ nm. Sideview images of crystals of **1Y** (left) and **1O** (right) under UV light.

In conclusion, the behavior of **1** can be described in terms of quenching the emission in solution and restoring the emitting properties in the solid state, following restriction of the intramolecular rotation.[5] An increase of PLQY on going from diluted solutions to aggregates has been previously observed for a few other tricarbonyl Re(I) complexes,[23] though this is the first time that the effect is discussed for clean crystalline phases. A feature common to all these rhenium complexes is the presence of bulky substituents on the chromophoric ligands, which prevent a close intermolecular approach. Is this a necessary condition for observing enhanced emission upon aggregation? Further investigation will be required to answer this question and shed more light upon the interplay between enhancing and quenching effects arising from aggregation, and then upon the requirements for designing efficient solid state phosphorescent rhenium emitters.

Acknowledgment. The work was funded by Italy's MIUR (FIRB 2003, RBNE033KMA).

Supporting Information Available: Details on the preparation and characterization of **1** in solution and in solid (including 11 figures and 5 tables). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA106772V