Organic Vapor Triggered Repeatable On−Off Crystalline-State Luminescence Switching

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Ⓢ Supporting Information

ABSTRACT: A nonporous crystalline solid consisting of an organoarsenic platinum(II) complex, i.e., a mononuclear diiodoplatinum(II) complex trans-PtI$_2$(cis-DHDAt-Bu)$_2$ (**1**) with cis-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis-(tert-butoxycarbonyl)-1,4-diarsinine (cis-DHDAtBu), shows on−off solid-state luminescence switching through reversible solvent vapor uptake and escape. The on−off switching of solid-state luminescence was achieved without changing the structure or electronic state of the organoarsenic platinum(II) complex.

On−off switching of solid-state luminescence of molecular compounds in the presence of suitable guest molecules or under specific stimuli is an attractive target for both fundamental research and practical applications, such as for sensors and optical storage molecular logic gates.[1−5] Alteration of the chemical structures or electronic intermolecular interactions of their component molecules, particularly those involving platinum(II) complexes, is the most common approach for tuning the compounds' luminescence properties (Figure 1).[6] Such chemical reactions in the solid state frequently encounter problems because of insufficient conversion, one-way reactions, or loss of their luminescence properties, leading to irreproducibility of the on−off switching. One promising approach is to efficiently control the reproducible on−off switching of the solid-state luminescence properties by altering the mode of solid-state molecular packing without using chemical reactions. However, successful examples of reproducible on−off switching of solid-state luminescence that are not based on chemical reactions or structure alteration are limited.[4] It has recently been demonstrated that seemingly nonporous solid-state structures behave as porous materials, even though these structures have no open channels or large discrete lattice voids linked by passages wide enough to allow the guest molecules to migrate between cavities.[7−9] The neighboring component molecules cooperate with one another both to relay the guest molecules through the crystal lattice and to maintain the crystalline structures. However, a limited number of examples have been reported up until now, and none of these examples of guest-selective uptake and escape in the nonporous crystals show on−off luminescence switching behavior. During the course of our studies on the synthesis of a number of different complexation structures of 1,4-dihydro-1,4-diarsinines as cyclic ditopic organoarsenic ligands to transition
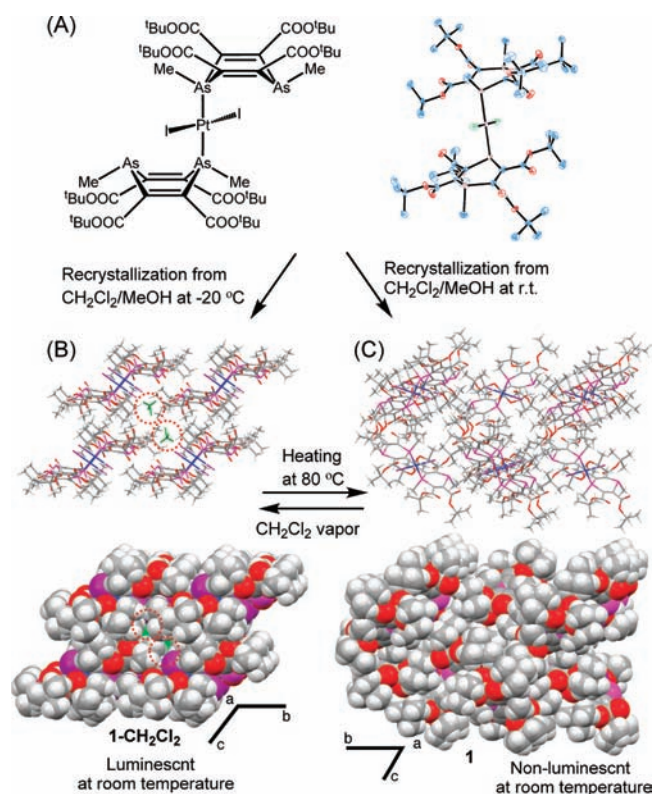

Figure 1. (A) Chemical structure and ORTEP view of **1** with thermal ellipsoids at the 50% probability level. Hydrogen is omitted. (B and C) Molecular structures (top) and space-filling projections (bottom) from the a axis showing the packing arrangement of **1**·CH$_2$Cl$_2$ (B) and **1** (C). The CH$_2$Cl$_2$ molecules (green) in **1**·CH$_2$Cl$_2$ are found to reside within voids, which are marked as dotted red circles in part B. Color code: carbon, gray; hydrogen, white; oxygen, red; iodide, purple; platinum, dark blue.

metals, we have found that flexibility of the bond angles around the arsenic center is an inherent property of the organoarsenic compounds.[10] The flexibility of the arsenic ligands might be a main reason for the nonluminescent properties of most of these organoarsenic complexes at room temperature, in contrast to their phosphorus analogues. We found, as described herein, that a nonporous crystalline solid of an organoarsenic

platinum(II) complex shows on−off solid-state luminescence switching through reversible and guest-selective uptake and escape. The crystal trapped atmospheric organic vapor molecules despite the absence of large pores in the static solid-state structure. On−off switching of solid-state luminescence was achieved without changing the structure or electronic state of the organoarsenic platinum(II) complex.

The mononuclear diiodoplatinum(II) complex trans-PtI$_2$(cis-DHDAtBu)$_2$ (**1**) with cis-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis($tert$-butoxycarbonyl)-1,4-diarsinine (cis-DHDAtBu)[10] was recrystallized from CH$_2$Cl$_2$ and methanol at −20 °C to produce a red-orange crystal of trans-PtI$_2$(cis-DHDAt-Bu)$_2$·2CH$_2$Cl$_2$ (**1**·CH$_2$Cl$_2$) suitable for X-ray crystallographic analysis. Solvent molecules were found to reside within voids between the stacked molecules, but no large cavities were observed in the crystal structure, i.e., the void volume is 1.1% of the total crystal volume (see Figure S1 in the Supporting Information, SI). In the crystal packing of **1**·CH$_2$Cl$_2$, CH$_2$Cl$_2$ molecules are connected to $tert$-butoxycarbonyl groups through the formation of C−H···Cl and C−H···O hydrogen bonds and exhibit no interactions with the metal center (see Figure S2 in the SI). The ^{1}H NMR spectrum of **1**·CH$_2$Cl$_2$ also suggested the existence of 2 mol equiv of CH$_2$Cl$_2$ (see Figure S3 in the SI). The crystals of **1**·CH$_2$Cl$_2$ exhibited very intense red luminescence (λ_{max} = 658 nm), even at room temperature (Figure 2A). The luminescence decay time and quantum yield
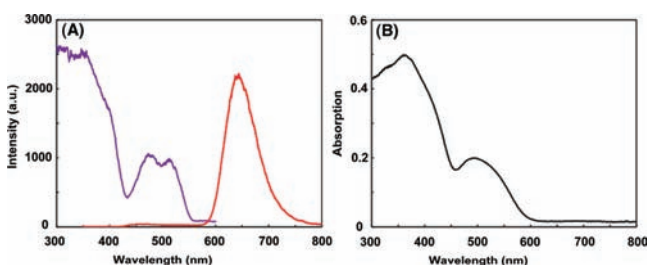

Figure 2. Room-temperature luminescent and optical absorption spectra of the crystals of **1**·CH$_2$Cl$_2$, which was obtained by recrystallization of trans-PtI$_2$(cis-DHDAtBu)$_2$ from CH$_2$Cl$_2$/MeOH at −20 °C. (A) Room-temperature excitation (purple; λ_{em}= 658 nm) and emission (red; λ_{ex}= 390 nm) spectra in the solid state and (B) optical absorption spectrum in the solid state at room temperature.

of the crystals of **1**·CH$_2$Cl$_2$ were 5.2 μs and 54.2%, respectively. The emission is attributed to phosphorescence because of its long emission lifetime in the microsecond regime. The excitation spectrum measured at room temperature (Figure 2A) matches the solid-state absorption spectra of the crystals of **1**·CH$_2$Cl$_2$ at 298 K (Figure 2B). Recrystallization of trans-PtI$_2$(cis-DHDAtBu)$_2$ from acetone and toluene at room temperature produced crystals of trans-PtI$_2$(cis-DHDAt-Bu)$_2$·2acetone (**1**·acetone) and trans-PtI$_2$(cis-DHDAt-Bu)$_2$·2toluene (**1**·toluene), respectively, which also showed strong room-temperature solid-state luminescence. Crystallographic data and ^{1}H NMR spectra for **1**·acetone and **1**·toluene suggested the existence of 2 mol equiv of acetone and toluene, respectively (see Figures S4−S6 in the SI). In the crystal packing of **1**·acetone, acetone molecules are also connected to $tert$-butoxycarbonyl groups through the formation of C−H···O hydrogen bonds (see Figure S7 in the SI).

The removal of CH$_2$Cl$_2$, acetone, and toluene from the crystals of **1**·CH$_2$Cl$_2$, **1**·acetone, and **1**·toluene was accomplished by heating them at 80, 90, and 130 °C, respectively, for

a few minutes at atmospheric pressure and produced room-temperature nonluminescent crystals of **1**. No removal of the solvent molecules was observed when the crystals of **1**-CH$_2$Cl$_2$, **1**-acetone, and **1**-toluene were placed under reduced pressure at room temperature. Crystallographic data suggested that no solvent molecules were included in the crystals of **1** and that the void volume is 6.0% of the total crystal volume (see Figure S8 in the SI). This value is smaller than the void volume of 14.7% estimated after excluding the solvent molecules in the crystals of **1**·CH$_2$Cl$_2$. No significant differences in the bond lengths and angles for trans-PtI$_2$(cis-DHDAtBu)$_2$ with and without the solvent molecules were recognized, which suggests that there was no alteration of the chemical structures of the component molecules (see Table S2 in the SI).

When the crystals of **1** were exposed to CH$_2$Cl$_2$, acetone, or toluene vapors at room temperature, the crystalline solid exhibited very intense red luminescence within a few seconds. The ^{1}H NMR spectra of the crystals that had been exposed to CH$_2$Cl$_2$, acetone, or toluene vapors onto the crystals of **1** suggest the existence of 2 mol equiv of the solvent molecules. Reproducible on−off switching of solid-state luminescence was achieved through the heating and subsequent exposure of the crystals to the vapor molecules. Several cycles were performed, and no substantial degradation of the starting material was noted, at least for four cycles (Figure 3A,B).

The crystallinity and identity of the heating and solvent uptake products were confirmed by powder X-ray diffraction (XRD). The crystals of **1**·CH$_2$Cl$_2$ were heated at 80 °C, and the diffraction pattern was matched with that of the simulated powder XRD patterns of the crystals of **1** calculated from the crystallographic data (Figure 3C). The diffraction pattern of the crystal after the subsequent uptake of acetone vapor in the crystals of **1** was in agreement with the crystallographic data for the crystals of **1**·acetone (Figure 3D). This is in accordance with a complete crystal phase transition caused by the heating and uptake of the solvent vapors.

The solid-state absorption spectra of the crystals of **1**·CH$_2$Cl$_2$ and **1** at room temperature had peaks in the same region with similar shape, suggesting a similar photoexcitation process in both of the crystals (see Figure S9 in the SI). This suggests that the on−off switching of solid-state luminescence in the present complex is not derived from modification or alteration of the chemical structures of their component molecules. The absorption maximum at 358 nm is derived from mixed metal (d$_M$)-to-ligand (s/p$^*_{As}$)/ligand (p$_{Cl}$)-to-ligand (s/p$^*_{As}$) charge-transfer (MLCT/LLCT) transitions, according to a time-dependent density functional theory calculation.[10] Because no metal−metal interaction existed in either crystal according to the crystallographic data, the long-wavelength absorption maxima at 500 nm were tentatively assigned to spin-forbidden ^{3}MLCT transitions.

The crystals of **1** showed intense emission at −196 °C without any spectral shift (see Figure S10 in the SI). These crystals exhibited the same red luminescence (λ_{max} = 652 nm) as the crystals of **1**·CH$_2$Cl$_2$ at room temperature. The excitation spectrum of the crystals of **1** measured at −196 °C matches the solid-state absorption spectrum at room temperature, which is the same as that of the crystals of **1**·CH$_2$Cl$_2$. In general, decreasing temperatures prevent nonradiative relaxation processes. In the recently studied aggregation-induced emission and crystallization-induced emission (CIE) processes, luminogens are emissive in their aggregation and crystal states but nonluminescent in their solution and amorphous states.[11]
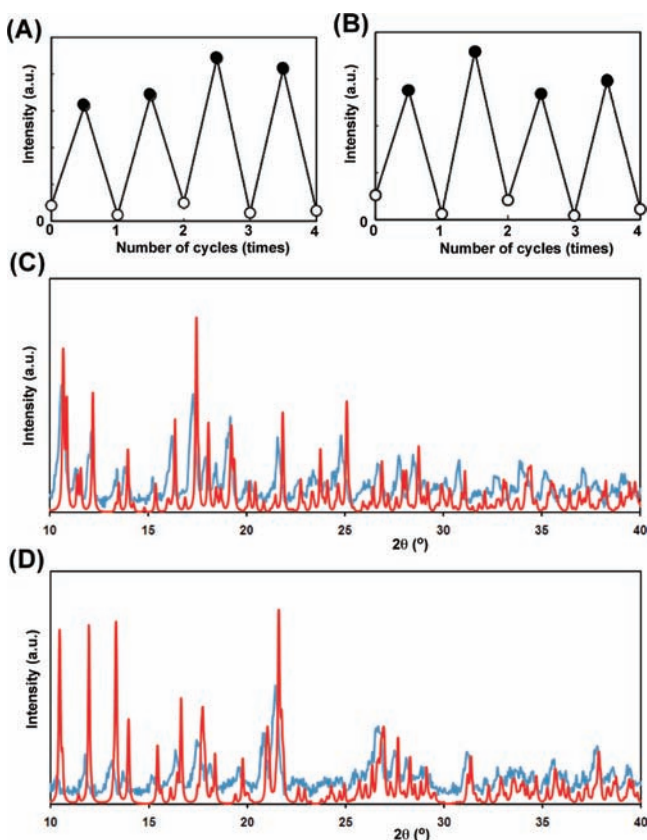
Figure 3. Reproducible on−off switching of the solid-state luminescence and diffraction patterns. A plot of the relative intensity of solid-state luminescence of the crystals of **1** against the amount of heating and exposure with CH_2Cl_2 (A) and toluene (B) vapors starting from the crystals of **1**, which was prepared by heating the crystals of **1**·CH_2Cl_2 at 80 °C. (C) (blue) Diffraction pattern of the crystals at 296 K after heating the crystals of **1**·CH_2Cl_2 at 80 °C and (red) simulated powder XRD patterns of the crystals of **1** calculated from the crystallographic data, which were collected at 109 K. (D) (blue) Diffraction pattern of the crystal at 296 K after the uptake of acetone vapor in the crystals of **1**, which was prepared by heating the crystals of **1**·CH_2Cl_2 and (red) simulated powder XRD patterns from crystallographic data for the crystals of **1**·acetone, which was collected at 296 K.

These feature shifts are triggered by the restriction of the molecular motions, which blocks the nonradiative path. In our present discovery, the room-temperature nonluminescent crystals of **1** became emissive at room temperature through selective guest uptake into the crystal. We propose that the conformational fixation due to crystal packing with suitably shaped solvent molecules is a possible reason for the observed luminescence induction even at room temperature. Despite a lack of porosity for accommodating the solvent vapor molecules in the material, transport of solvent molecules through the solid occurs readily until a thermodynamically stable crystal structure is achieved. The cavities holding the guest molecules in the crystals of **1**·CH_2Cl_2 are made up of the *tert*-butoxycarbonyl groups of *trans*-PtI$_2$(*cis*-DHDA*t*Bu)$_2$. The weak hydrogen bonds between the cavities and solvent molecules forming thermodynamically stable packing arrangements might trigger solvent uptake into the crystal.

In summary, the organic solvent molecules freeze the fluctuations in the crystals at room temperature by stabilizing the crystal packing. The removal of vapor molecules was achieved within a few minutes by heating the crystals under atmospheric pressure, and the vapor molecules were taken up into the nonporous crystal within a few seconds. Our findings in the field of nonporous materials may provide additional tools for the development of functional crystalline materials with specific properties. Detailed studies and applications of other guest molecules are underway to gain an understanding of the essential guest selectivity and other properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Details of experimental procedures, X-ray crystallographic data, ^{1}H NMR spectra, additional packing arrangements and optical data, DSC traces, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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