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Luminescence

A Phosphorescent Molecular “Butterfly” that undergoes a Photoinduced Structural Change allowing Temperature Sensing and White Emission[**]

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Abstract: *A butterfly-like phosphorescent platinum(II) binuclear complex can undergo a molecular structure change in which the Pt–Pt distance shortens upon photoexcitation, which leads to the formation of two distinct excited states and dual emission in the steady state, that is, greenish-blue emission from the high-energy excited state at the long Pt–Pt distance and red emission from the low-energy excited state at the short Pt–Pt distance. This photoinduced molecular structure change has a strong dependence on the molecule's surrounding environment, allowing its application as self-referenced luminescent sensor for solid–liquid phase change, viscosity, and temperature, with greenish-blue emission in solid matrix and rising red emission in molten liquid phase. With proper control of the surrounding media to manipulate the structural change and photophysical properties, a broad white emission can be achieved from this molecular butterfly.*

Molecules capable of undergoing photoinduced structural change have attracted great interest for their potential applications as nanomachines, sensors, photoswitches, photo-energy harvesters.[1] The change of molecular structure could lead to distinct chemical and physical properties existing in a single molecule at different states. Luminescence varying upon molecular-structure change is one of the most studied phenomena, which can be triggered in various ways, such as intramolecular charge transfer or intramolecular excimer formation.[2]

Square-planar platinum(II) complexes have attracted attention for their efficient generation of triplet excited states upon photo-/electro-excitation, allowing their application as phosphorescent emitters in organic light-emitting diodes (OLEDs).[3] Mononuclear platinum complexes can form dimers and excimers through strong Pt–Pt interactions in certain circumstances.[4] By synthetically manipulating the Pt–Pt distance on a sub-nanometer level by controlling the bulkiness of the groups at the 3- and 5- positions of the bridging pyrazolate ligands, butterfly-like platinum(II) binuclear complexes with controlled photophysical properties have been obtained in a rational manner, that is, the emission changes from blue to green and red as the lowest triplet state turns from a metal-to-ligand charge transfer (MLCT) to a metal-metal-to-ligand charge transfer (MMLCT) with the decreasing of Pt–Pt distance from 3.38 Å to 2.83 Å in the ground state.[5] Further contraction of Pt–Pt distance in the excited state by 0.2–0.3 Å has been observed for one pyrazolate-bridged platinum complex and detected in many other platinum binuclear complexes with short Pt–Pt distances, such as platinum diphosphite complexes, by using X-ray spectroscopic techniques, and has also been validated by theoretical calculations.[6] Since this excited-state distortion occurs at an ultrafast speed on the time scale of femtoseconds to picoseconds, similar to that of the photoinduced “flattening” structural change for Cu^I complexes,[7] the steady-state luminescence observed in these systems with strong Pt–Pt interactions in the ground state is therefore from the sole excited state after the ultrafast structural change. To our knowledge, photoinduced structural change at a much slower pace that could allow the co-existence of two distinct excited states and dual emission in the steady state for a single molecule has not been reported.

Herein, we report our further studies on a pyrazolate bridged platinum(II) binuclear complex, BFPtPZ ([C^NPt(μ-pz′)$_2$PtC^N], C^N = 2-(2,4-difluorophenyl)pyridine, pz′ = pyrazolate, Figure 1 a), which has no Pt–Pt interaction in the ground state, but displays interesting dual emission in certain circumstances, as a result of a photoinduced molecular structure change involving a shortening of the Pt–Pt distance in the excited state. The application of this molecule as a self-referenced luminescent sensor for phase change and temperature, as well as a white emitter, is demonstrated.

The absorption of BFPtPZ in dichloromethane (DCM) at room temperature is shown in Figure 1 c. The lowest structured absorption at 462 nm ($\varepsilon \approx 50\,\text{M}^{-1}\,\text{cm}^{-1}$) can be assigned to the spin-forbidden metal-to-ligand charge transfer (MLCT) transition,[3,8] suggesting no Pt–Pt metal–metal-to-ligand charge transfer (MMLCT). In other words, if we consider the two 2-(2,4-difluorophenyl)pyridyl ligands as butterfly wings, the molecular butterfly stays in the wing-spreading ground state with a long Pt–Pt distance in both the

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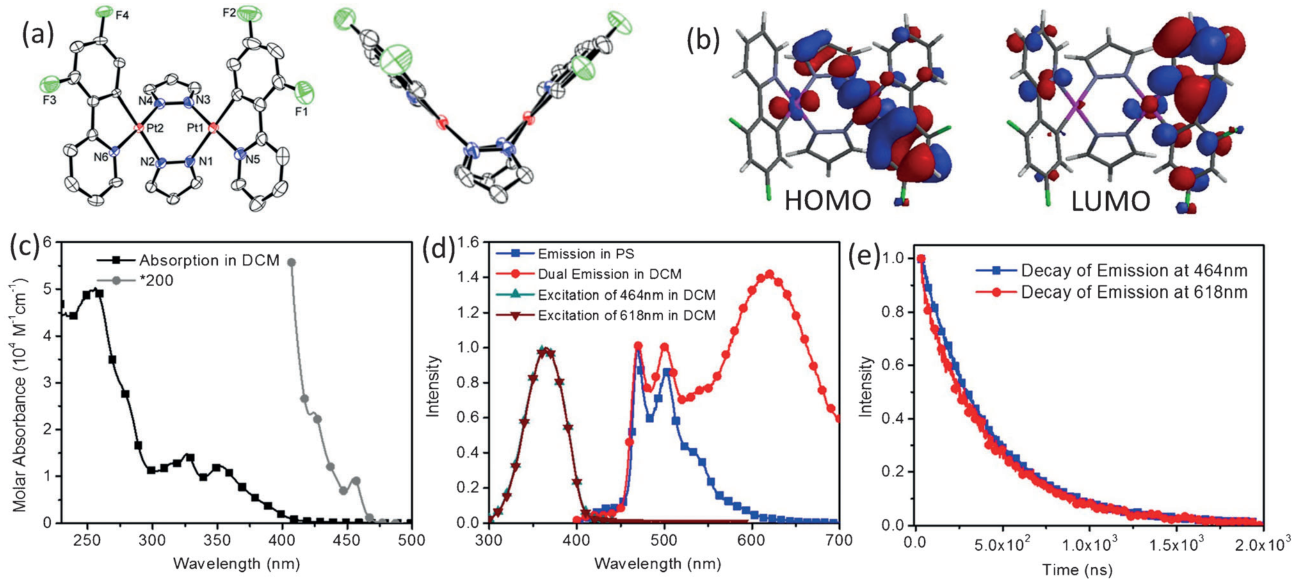

Figure 1. a) The molecular structure of BFPtPZ. b) HOMO and LUMO surface plots for BFPtPZ by DFT calculations. c) Absorption spectrum of BFPtPZ in CH_2Cl_2 at room temperature; the gray line with circles represents a 200-fold magnification of the black line with filled squares. d) Emission spectra of BFPtPZ in polystyrene (PS) and in CH_2Cl_2 at room temperature, and excitation spectra for peak emissions at 464 nm and 618 nm. e) Decay curves for two peak emissions of BFPtPZ in CH_2Cl_2 at room temperature, with lifetimes calculated to be approximately 0.37 μs for both.

solid state and solution phases. Density functional theory (DFT) calculations confirm there is no Pt–Pt interaction in the ground state of BFPtPZ, with the highest occupied molecular orbital (HOMO) localized mainly on the phenyl ring and the lowest unoccupied molecular orbital (LUMO) on the pyridine ring (Figure 1 b), almost identical to those of its mononuclear counterpart, but significantly different to those of a platinum binuclear complex with a short Pt–Pt distance.[5] (See Supporting Information Figure S2).

In contrast to the greenish-blue emission observed for BFPtPZ in a solid-state polystyrene (PS) matrix, dual emission across a broad visible region (excited at 360 nm) was recorded in CH_2Cl_2 solution as shown in Figure 1 d and Figure S1. The excitation spectra for the greenish-blue emission at 464 nm and red emission at 618 nm are identical, suggesting same ground state for the dual emission and no direct photoexcitation pathway to the red-emitting excited state. The same shape of emission spectra recorded under different excitations as shown in Figure S1b also supports our argument. Interestingly, similar emission lifetimes for those emissions were recorded to be approximately 0.37 μs with the decay curves shown at Figure 1 e. The decay rate was then calculated to be approximately 3×10^6 s^{-1}. The low-energy red emission of BFPtPZ in solution is almost identical to the emission of the pyrazolate bridged platinum complex with short Pt–Pt distance of 2.83 Å in the solid state,[5] suggesting a structural change of BFPtPZ with the Pt–Pt distance decreasing upon photoexcitation that leads to the formation of a new low-energy excited state. Indeed, this dual emission behavior has not been observed for pyrazole bridged platinum complexes containing other cyclometallating ligands, for example, 2-phenylpyridine, 2-(2′-thienyl)pyridine), 7,8-benzoquinoline, and 1-phenylisoquinoline, where there is no Pt–Pt interaction in either the ground state or the excited state and there is monochromatic emission from the sole excited state at long Pt–Pt distances.[9] No such dual emission has been observed either for other platinum binuclear complexes with short Pt–Pt distances, where there is Pt–Pt interaction in both the ground state and excited states that results in ultrafast Pt–Pt contraction and monochromatic emission from the sole excited state at short Pt–Pt distances.[9] These results suggest that the cyclometallating ligands, in particular the fluorine substituents, play a significant role in controlling the excited-state properties.

Figure 2 shows the proposed mechanism of structural change associated with the shortening of the Pt–Pt distance in the excited state. Upon light absorption, BFPtPZ is excited to a singlet ligand-center/metal-to-ligand charge transfer (LC/MLCT) excited state (S_1), which undergoes ultrafast intersystem crossing (ISC)[10] to form the first triplet state with

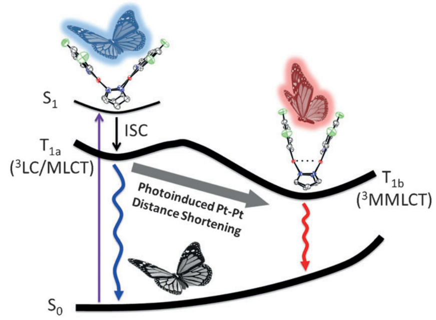

Figure 2. Potential-energy curves and transitions for the molecular butterfly BFPtPZ involving a photoinduced structural change as a result of photoinduced Pt–Pt distance shortening, and generation of dual emission.

a long Pt–Pt distance without Pt–Pt interaction (T_{1a}, ^{3}LC/MLCT). This high-energy triplet excited state can undergo either radiative decay with greenish-blue phosphorescence, or fast Pt–Pt distance shortening to form the second low-energy excited state with strong Pt–Pt interaction and red emission (T_{1b}, ^{3}MMLCT). In other words, this molecular butterfly can generate both greenish-blue and red emission when it "flaps" its "wings" under light excitation. Similar shortening of the Pt–Pt distance in the excited state has been observed for platinum dinuclear complexes with short Pt–Pt distances and strong Pt–Pt interactions in the ground state.[6] Considered as one of the competitive non-radiative decay processes (K_{nr}) to the radiative decay of greenish-blue emission (K_r), this structural change of BFPtPZ in its excited state with Pt–Pt distance shortening takes place at a rate higher than that of the radiative decay of greenish-blue emission in CH_2Cl_2 solution, provided the low quantum efficiency (QE) of the greenish-blue emission ($QE = K_r/(K_r+K_{nr})$). The slightly higher intensity of the red emission than that of the greenish-blue emission as shown in Figure 1d also supports the structural change at a higher rate than that of the greenish-blue emission, because the red emission occurs after the non-radiative structural change. Quantitative analysis of the rates for all the transitions in Figure 2 is under way. A theoretical study using the DFT(B3PW91) method by Sakaki and co-workers has also suggested this co-existence of two triplet excited states with different molecular geometries for BFPtPZ, that is, T_{1a}-local minimum with greenish-blue emission and T_{1b}-global minimum with red emission.[11] And a moderate Gibbs free-energy difference between the two excited states is considered as the driving force for the structural change, which also allows for the co-existence of two distinct excited states.[11] Note that the dual emission of BFPtPZ in solution is concentration independent, while the dual emission achieved by intermolecular excimer formation for a typical mononuclear platinum complex is highly concentration dependent.[4b] This is not surprising if we consider the steric bulk of the molecular structure of BFPtPZ which prevents intermolecular interactions and intermolecular excimer formation.

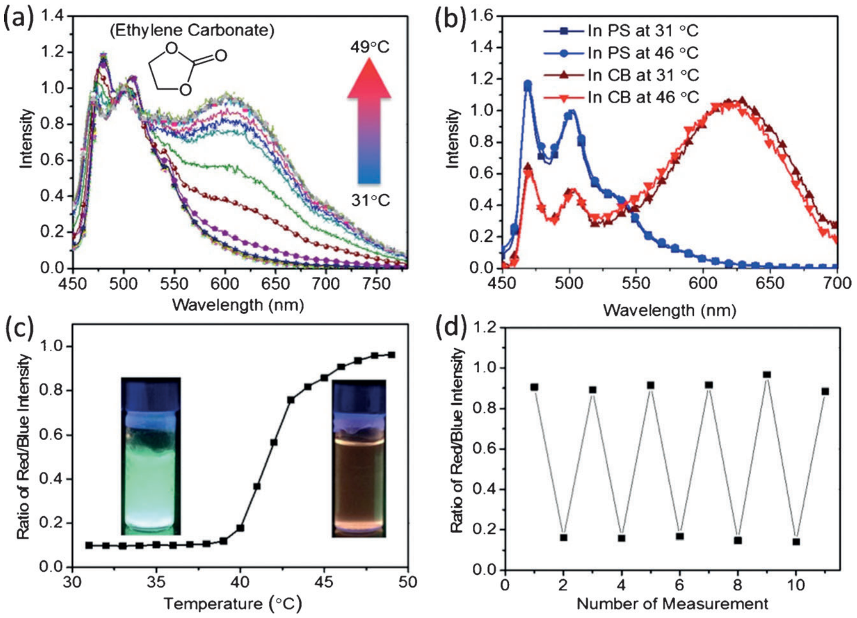

Figure 3. a) The normalized emission spectra of BFPtPZ in ethylene carbonate at various temperatures from 31 °C to 49 °C. b) Emission spectra of BFPtPZ in polystyrene (PS) chlorobenzene (CB) at the temperatures of 31 °C and 46 °C. c) A correlation between the temperature and the ratio of luminescent intensities of peak red emission and greenish-blue emission of BFPtPZ in ethylene carbonate. Inset: Photographs showing the luminescence in solid ethylene carbonate (left) and in molten ethylene carbonate (right). d) Multiple-run reversibility experiments of the luminescence responses of BFPtPZ to temperature variation in ethylene carbonate.

This shortening of the Pt–Pt distance, or molecular butterfly wing folding, is environment dependent, as it involves mechanical motion. In a solid-state matrix, the molecule is frozen preventing the molecular structure change. Whereas in solution or the gas phase, the molecule can undergo structural change, allowing for dual emission upon photoexciation. This environment-dependent luminescence affords the application of BFPtPZ as a sensor for solid–liquid phase change or viscosity mapping.[12] We have used ethylene carbonate (EC), a solvent with melting point of 35–38 °C, as the phase-change system to demonstrate this sensing capability. Figure 3a shows the emission spectra of BFPtPZ in ethylene carbonate at different temperatures. We find an increase in the emission intensity between 550–750 nm after the ethylene carbonate melts at around 39 °C with the emission maximum reached at around 43 °C. The emission returns to the initial level after cooling, suggesting a reversible molecular structural change. We have also characterized two control samples, BFPtPZ in polystyrene (PS) and BFPtPZ in chlorobenzene (CB), to confirm that the change of luminescence is a result of phase and viscosity changes, rather than pure temperature variation. As shown in Figure 3b, almost no spectral changes were observed upon the change of temperature, which is not surprising if we consider that within the temperature window PS and CB remain in the solid and liquid phases, respectively.

Since the solid–liquid phase change process is temperature dependent, BFPtPZ could actually act as an indirect luminescent thermometer. The dual emission from BFPtPZ enables self-referenced ratiometric temperature measurement.[13] Figure 3c shows the correlation between the temperature and the ratio of luminescent intensity of peak red emission and greenish-blue emission for BFPtPZ in ethylene carbonate. Notably, the luminescence displays a drastic ratiometric transition, a more than 8-fold leap, when the temperature rises from 39 °C to 43 °C. The reversibility of this sensing was also examined. Figure 3d shows the multiple-run reversibility experiments of the luminescence responses to temperature variation. The results indicate that no hysteresis exists during a cycle of heating and cooling and no declining signal occurs during multiple-run tests, monitoring the ratios of emission intensities at 39 °C and 43 °C. Different from typical luminescent molecular probes for temperature, whose emission shows direct dependence on the temperature, this self-referenced luminescent molecular thermometer probes the change of temperature by monitoring the temperature-dependent phase transfer between solid and liquid, and the change of viscosity. In other words, the range of temperature that this molecule can sense varies upon the matrix materials. Figure 4a shows the correlations between the temperature and luminescence responses of BFPtPZ in other matrixes with different melting points, dibenzyl carbonate (29–33 °C) and ethyl methyl sulfone (32–37 °C). Investigation of BFPtPZ as a viscosity sensor and detailed photophysical characterization as a function of temperature and viscosity are under way.

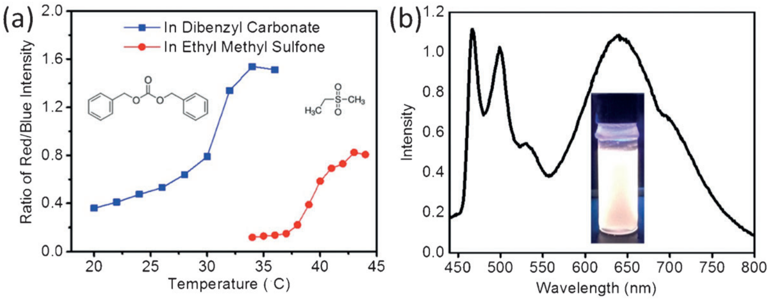

Figure 4. a) Correlations between the temperature and the ratio of luminescent intensities of peak red emission and greenish-blue emission of BFPtPZ in dibenzyl carbonate and ethyl methyl sulfone. b) The normalized emission spectrum of BFPtPZ in CH_2Cl_2 at −77 °C. Inset: photograph of the sample.

The controllable dual emission across a broad visible region could afford the generation of white emission from a single molecule.[14] Figure 4b shows the emission spectrum and image of BFPtPZ in CH_2Cl_2 at −77 °C, which has a CIE coordinate of (0.39, 0.37). The white emission has much higher brightness and quantum yield at low temperature (−77 °C) than that at room temperature, because thermally activated nonradiative decays could be suspended and the emission blue shifts slightly at low temperature.[15] No concentration-dependent energy-transfer complication was observed in this single-molecule system, as the unpopulated ground state of the red emitting excited state blocks the energy transfer between the high-energy greenish-blue emitting species with a long Pt–Pt distance to the low-energy red emitting species with a short Pt–Pt distance. To our knowledge, this is the first example of a white phosphorescent molecule based on the formation of two distinct excited states by a photoinduced structural change.

In summary, we have demonstrated a simple phosphorescent “molecular butterfly” complex that can generate dual emission when it “flaps its wings” upon photoexcitation. The distinct luminescent properties of this binuclear platinum complex in different environments can be utilized for the sensing of solid–liquid phase change, viscosity, and temperature. With control of the photoinduced structural change of the Pt–Pt distance in this compound, the co-existence of two distinct excited states, one with high energy at a long Pt–Pt distance and the other with low energy at a short Pt–Pt distance, and then dual emission with extensive coverage of the visible light region can be achieved, leading to white emission from a single molecule. Our current research efforts involve detailed studies of the excited-state dynamics of this molecule and related materials in a variety of media using ultrafast time-resolved spectroscopies and theoretical calculations. Studies of the substituent effect on the photoinduced structural change, and characterization of the nano-motion and photomechanical energy conversion of platinum complexes based molecular butterflies on surfaces are underway.

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