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Coherence in Metal–Metal-to-Ligand-Charge-Transfer Excited States of a Dimetallic Complex Investigated by Ultrafast Transient Absorption Anisotropy

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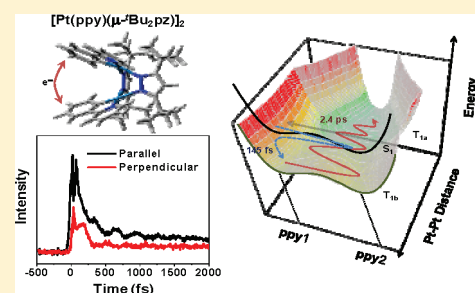
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S Supporting Information

ABSTRACT: Coherence in the metal–metal-to-ligand-charge transfer (MMLCT) excited state of diplatinum molecule $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ has been investigated through the observed oscillatory features and their corresponding frequencies as well as polarization dependence in the single-wavelength transient absorption (TA) anisotropy signals. Anticorrelated parallel and perpendicular TA signals with respect to the excitation polarization direction were captured, while minimal oscillatory features were observed in the magic angle TA signal. The combined analysis of the experimental results coupled with those previous calculated in the literature maps out a plausible excited state trajectory on the potential energy surface, suggesting that (1) the two energetically close MMLCT excited states due to the symmetry of the molecule may be electronically and coherently coupled with the charge density shifting back and forth between the two phenylpyridine (ppy) ligands, (2) the electronic coupling strength in the ¹MMLCT and ³MMLCT states may be extracted from the oscillation frequencies of the TA signals to be 160 and 55 cm^{-1} , respectively, (3) a stepwise intersystem crossing cascades follows ¹MMLCT \rightarrow ³MMLCT (T_{1b}) \rightarrow ³MMLCT (T_{1a}), and (4) a possible electronic coherence can be modulated via the Pt–Pt σ -interactions over a picosecond and survive the first step of intersystem crossing. Future experiments are in progress to further investigate the origin of the oscillatory features. These experimental observations may have general implications in design of multimetal center complexes for photoactivated reactions where coherence in the excited states may facilitate directional charge or energy transfer along a certain direction between different parts of a molecule.



I. INTRODUCTION

Quantum coherence among chromophore arrays has been observed in biological and synthetic systems, plays important roles in long-range light harvesting and electron transfer, and forms the basis for quantum computing.^{1–4} Meanwhile, many effective multielectron transfer reactions also involve structural motifs containing two or more metal centers.^{5–7} The question is therefore whether there is possible electronic coherence among charge transfer excited states in molecules/supramolecules containing multiple metal centers and whether such an electronic coherence, if it exists, will assist energy/electron flow between metal centers. Hence, investigating electronic coherence between metal centers could glean insight into how single photon events influence redox reactions at polymetallic species.

In this report, we investigate the coherence in the metal–metal-to-ligand-charge transfer (MMLCT) excited state of a photoactive diplatinum complex, where the Pt–Pt interaction is mediated by the bridging ligands.^{8,9} The complex of interest, $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ (ppy = 2-phenylpyridine; $^t\text{Bu}_2\text{pz}$ = 3,

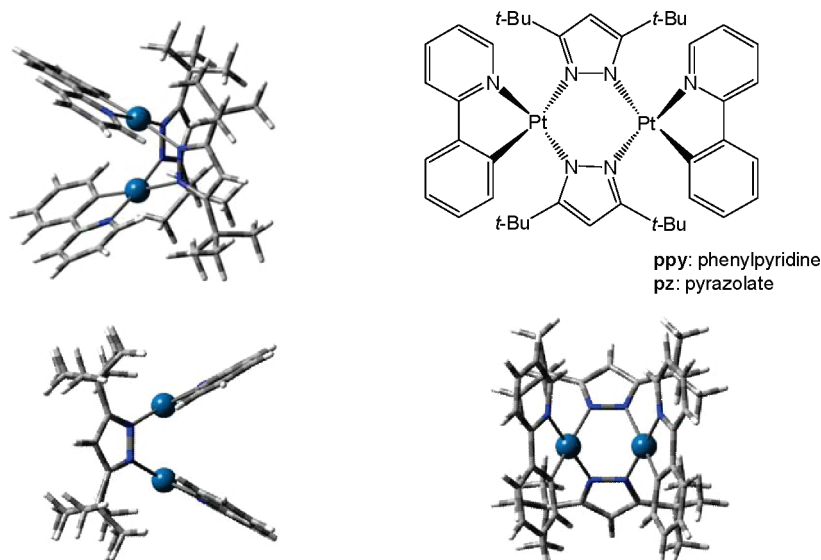
5-di-*tert*-butylpyrazolate) (Scheme 1),¹⁰ is distinct from the extensively studied $[\text{Pt}_2(\text{pop})_4]^{4-}$ (pop = pyrophosphate, $(\text{H}_2\text{P}_2\text{O}_5)^{2-}$)¹¹ in several ways: (1) the photoexcitation promotes an electron from a metal-centered antibonding $\sigma^*(5d_{z^2}-5d_{z^2})$ orbital to a ppy ligand-centered π^* orbital rather than another σ orbital; (2) it has a hinged rather than a caged conformation; (3) the π -acceptor ligands are aromatic; (4) the ground state Pt–Pt distance can be tuned by sterics exerted by the groups attached to the 3- and 5-positions of the bridging pyrazolates; (5) additionally, the two ligand centered π^* orbitals are also split in energy due to weak electronic coupling between the two halves of the molecule.¹² The most significant difference is the nature of the electronic

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Scheme 1. Optimized Molecular Structure of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ 

transitions in $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ which are considered as metal–metal-to-ligand-charge-transfer (MMLCT) in nature when the Pt–Pt distance is short, but changes to a metal-to-ligand-charge-transfer (MLCT) transition when the Pt–Pt distance is long.^{8,9} In both transitions, electron density is depleted from a Pt(II)–Pt(II)-centered HOMO and shifted to one of the ppy ligands (LUMO). The similarity between the two molecules is that the light-induced electronic transition will remove an electron from the antibonding σ^* orbital, resulting in a higher Pt–Pt bond order and a contraction of the Pt–Pt distance as observed in previous X-ray transient absorption spectroscopy^{13,14} solution X-ray scattering,¹⁵ and X-ray diffraction.¹⁶ In this new series of cyclometalated diplatinum complexes first reported by Ma and Thompson,^{8,9} and later modified to a non-fluorinated version of the complex by Castellano and co-workers,¹⁰ pyrazolate bridging ligands provide a scaffolding to allow ground state metal–metal interactions while the degree of the interaction is tuned by the bulkiness of the groups at the 3- and 5- positions of the pyrazolate bridges. The more steric hindrance provided by the pyrazolate substituents forces the two Pt atoms to be closer to each other in this A-frame geometry.

When bulky ^tBu groups are used, the Pt–Pt distance is 2.83 Å as revealed by the single crystal X-ray structure.¹³ This relatively short Pt–Pt distance, compared to that of the ground state $[\text{Pt}_2(\text{pop})_4]^{4-}$ at >2.9–3.0 Å¹⁶ leads to strong metal–metal interactions through $5d_{z^2}$ – $5d_{z^2}$ overlap. The lowest energy $^3\text{MMLCT}$ configuration originates from the electronic transition from the $d\sigma^*$ orbital to π^* orbitals on the ppy ligands.

Here we report an experimental observation that suggests the possibility of electronic coherence in the MMLCT states of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ after the photoexcitation as evidenced by single-wavelength transient absorption anisotropy at 510 nm. Strongly anticorrelated polarization dependent coherent oscillations in transient absorption anisotropy decays are presented along with discussions on their implications related to electronic coupling between the two halves of the molecules, coupling with the vibrational motions of Pt–Pt stretching, and intersystem crossing (ISC) pathways.

II. EXPERIMENTAL METHODS

Sample Preparation and Steady-State Measurements.

Materials and Synthesis. The details of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ (1) synthesis have been described by Rachford et al.¹⁰ and in the Supporting Information of our previous publication.¹³ Rhodamine 6G (Exciton) was used as received.

Photophysical Measurements. Most of the spectroscopic measurements have been described previously.¹³ Briefly, static UV–vis absorption spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer. The triplet-state lifetime of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene solution was measured using nanosecond flash photolysis with excitation pulses obtained from the second harmonic output of a Nd:YLF regenerative amplifier laser ($\lambda = 527$ nm, 1 kHz, 0.5 mJ/pulse and 5 ps pulse duration).¹³ A xenon flash lamp operating at 100 Hz was synchronized with one of every ten laser pulses. A mechanical shutter was controlled to block and unblock the laser excitation to obtain the optical density changes. The decay of the difference signal was measured and processed using a PMT detector and a digital oscilloscope. A continuously flowing sample of 0.7 mM solution of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene is measured in a 0.5 mm thick flow cell. The solution sample reservoir was purged with nitrogen gas for ~30 min prior to the pump–probe measurements to remove dissolved oxygen gas from the sample.

Raman Spectroscopy. The off-resonance Raman spectrum of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ was collected on a Renishaw inVia Reflex Raman microscope equipped with a 785 nm HPNIR diode laser for sample excitation. Both powder (~1 mg) and single crystal samples were excited by focusing 1% laser power of the 785 nm beam through the 50× objective on a glass microscope slide covered with aluminum foil. For single crystal measurements, a crystal face perpendicular to laser excitation was selected. Both sample types gave quantitatively similar spectra. All spectra represent 64 accumulations with cosmic ray removal. Edge filters that cut on at 90 cm^{-1} from the Rayleigh line were used during data collection. Sample integrity was examined by visually inspecting the sample before and after data collection as well as

collection of consecutive spectra on the identical sampling location. No sample degradation was observed.

Time-Resolved TA Anisotropy Measurement. The femto-second time-resolved single-wavelength transient absorption (TA) anisotropy apparatus consisted of a visible collinear optical parametric amplifier (OPA, Coherent Lasers) pumped by Ti:sapphire regenerative amplifier laser (RegA9000, Coherent Lasers) at a 150 kHz repetition rate, and an optical detection system.¹⁷ The output beam from the RegA had a power of about 1.5 W, which was used to produce a wavelength tunable OPA output for the pump and probe beams in the spectral range of 490–700 nm. The resulting laser pulses at 510 nm were selected for the TA experiments which had a 50 fs pulse duration measured through the autocorrelation at sample position by optical Kerr effect signal of MeOH (Figure S1 in the Supporting Information). The spectral width of the pulses was $\sim 400\text{ cm}^{-1}$. The pump and probe beams were focused and overlapped at the sample position. The time delay between the pump and probe beams was controlled by varying the optical path of the pump beam through a translation stage. The polarizations of pump and probe beams were defined by combinations of half-wave plates ($\lambda/2$) and linear polarizers. The polarization directions of the pump and probe beams were at vertical and 45° relative to the vertical directions, respectively. The transmission signals after the sample, the parallel (I_{\parallel}) and perpendicular (I_{\perp}) to the polarization direction of the pump beam, were separated by a cube polarizer and then recorded simultaneously by using two identical silicon photodiodes and two identical lock-in amplifiers. The magic angle (I_M) and anisotropy (r) traces were obtained using the following equations at each delay time

$$I_M = \frac{I_{\parallel} + 2I_{\perp}}{3}, \quad r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (1)$$

The phase of TA signals obtained from the lock-in amplifiers provides a clue of the origin of TA signals. Because the TA signals of rhodamine 6G at 510 nm are mainly originated from the ground-state bleaching,¹⁸ the reverse phase of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ TA signals compared with that of rhodamine 6G indicates that the TA signals of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ are mainly originated from the induced absorption from the MMLCT state.

Density Functional Theory (DFT) Calculations. Density functional theory (DFT) calculations were performed and described previously.¹³ Briefly, the calculations were performed with the Gaussian 03 program. The B3LYP functional^{19,20} was employed with the chosen basis set of the 6-31G(d,p) for the nonmetal atoms (hydrogen, carbon, nitrogen) and the LANL2DZ effective core potential (ECP) and corresponding basis set functions²¹ for the platinum atoms. The geometry of the singlet ground state was calculated using restricted formalisms, and the geometry of lowest triplet excited states was optimized using unrestricted formalisms. The frequency calculation was performed with the same B3LYP and basis sets using the optimized geometry.

III. RESULTS

The $d^8\text{--}d^8$ Interaction of Platinum(II) Centers. The Pt(II) atoms in the ground state $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ are respectively ligated by three nitrogen atoms and one carbon atom. Additionally, the *tert*-butyl (^tBu) groups on each of the two pyrazole (pz) ligands exert steric forces that cause the two Pt atoms to approach each other. Consequently, the $5d_{z^2}$ orbitals of the two Pt(II)

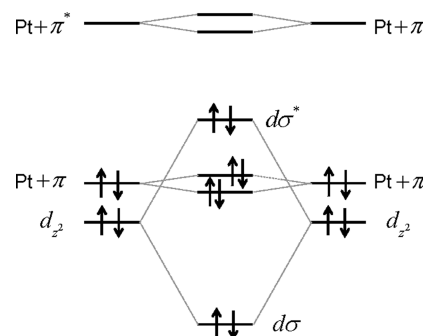


Figure 1. MO interactions between platinum(II) atoms and between ppy ligands.

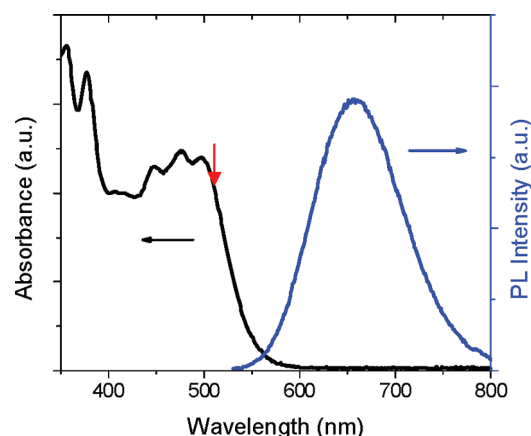


Figure 2. Steady-state absorption and emission spectra of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene. The excitation wavelength of 510 nm used for the TA measurements is marked by the red arrow.

atoms can strongly interact with each other to form the bonding and antibonding orbitals ($d\sigma_{\text{Pt-Pt}}$ and $d\sigma^*_{\text{Pt-Pt}}$), respectively (Figure 1). In contrast, interactions between MOs dominated by the π -orbitals of the two phenyl pyridine (ppy) ligands are relatively weak because their long spatial separation distance of 5.39 \AA is far beyond distances for any direct covalent bond between them (Figure S3, Supporting Information). As a result, the lowest energy HOMO \rightarrow LUMO transition in $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ can be assigned to the MMLCT transition where one electron resides at the Pt–Pt centered antibonding $d\sigma^*_{\text{Pt-Pt}}$ is promoted to one of the ppy ligand centered π^* MOs (Figure 1).⁹

Steady-State Spectroscopic Measurements. Figure 2 shows the steady-state absorption and emission spectra of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene. Three low-energy absorption bands at 444, 475, and 507 nm are attributed to the MMLCT absorption originated from electronic transitions from the antibonding $d\sigma^*_{\text{Pt-Pt}}$ to ppy-based in-phase π^* orbital.¹⁰ The higher energy bands in the steady-state absorption spectrum are denoted as the Pt centered MLCT states or/and the $\pi\text{--}\pi^*$ transitions of the ppy ligands.²² The broad and featureless emission peak with a large Stokes shift of 4480 cm^{-1} is assigned as the phosphorescence from the $^3\text{MMLCT}$ state.¹⁰ The emission quantum yield was measured to be 0.032 in argon saturated toluene solution.

Magic Angle and Anisotropic Transient Absorption Measurements. Figure 3 shows single-wavelength TA signals as a function of the delay time between the pump and probe at

510 nm for $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene at room temperature. The “magic angle” TA signal fits deconvoluted exponential functions with three time constants; the first and second time constants are 145 fs and 2.4 ps, respectively, while the third one is too long to measure within the time window of the experiment (i.e., ~ 10 ps). Since the triplet state lifetime of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene at room temperature is $0.85 \mu\text{s}$ (Figure S4, Supporting Information), a plateau signal remains in the induced absorption from the $^3\text{MMLCT}$ state. The fast component with a time constant of 145 fs contributes to $>85\%$ of the total TA signal amplitude at this wavelength (Table 1). Because there is no detectable rise component in the magic angle TA trace and $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ is directly excited to its $^1\text{MMLCT}$ state at 510 nm, we expect that the fast decay dynamics are caused by the deactivation process from this $^1\text{MMLCT}$ state. Due the strong spin–orbital coupling of high Z Pt atoms, the 145 fs time constant can be plausibly assigned to the $^1\text{MMLCT}$ lifetime, implying that the ISC between the $^1\text{MMLCT}$ and $^3\text{MMLCT}$ states is indeed very rapid.

While the magic angle TA kinetics trace decay smoothly, both the parallel and perpendicular TA kinetics traces show strong oscillatory features superpositioned with the respective intensity decays. Three striking characteristics in this set of kinetics curves are observed: (1) a coherence in the oscillation launched from the $^1\text{MMLCT}$ state is maintained up to ~ 2 ps, (2) two oscillation components with different oscillatory frequencies occur in consecutive order, and (3) the oscillatory features in the parallel and perpendicular spectra are anticorrelated in terms of phasing, which will be elaborated further in the Discussion section below.

In order to rule out any artifact from the single wavelength transient anisotropy measurements, we carried out the identical measurements on a dye molecule, Rhodamine 6G, under the

same experimental conditions. The TA anisotropy trace of Rhodamine 6G in MeOH is clearly flat on the time scale of ~ 2 ps, completely lacking any evidence of oscillatory features. In comparison, the oscillatory features in the TA anisotropy trace of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ are clearly observed (Figure 4) after the raw data of the anticorrelated parallel I_{\parallel} and perpendicular I_{\perp} signals are processed according to eq 1. More interestingly, the initial anisotropy value of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ is larger than 0.4, which we cautiously suggest the possibility that at least two electronic states are coherently coupled.^{23,24} In order to separate the anisotropy component due to the coherent movement of the exciton from the pure rotational correlation function of the molecule, the anisotropy trace was fit to a superposition of exponential decay functions and a residual of oscillatory anisotropy. The residual of anisotropy exhibits two oscillation frequencies taking place sequentially, 320 cm^{-1} during 0–200 fs after photoexcitation, and then 110 cm^{-1} during 200–2000 fs, respectively (Table 1). These sequential oscillatory frequencies are well-matched with the fast Fourier transform (FFT) result (Figure S5, Supporting Information).

IV. DISCUSSION

Quantum Beat between Two Electronic States. To understand the coherent oscillatory feature, we first considered a scenario of a vibrational wavepacket motion in the ground or excited state. One should notice that the second oscillation frequency of 110 cm^{-1} in the anisotropy decay is very close to the Pt–Pt stretching mode (ν_{20}) of 108.5 cm^{-1} (Figure S8, Supporting Information). Additionally, because $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ shows a strong Pt–Pt contraction in the excited state,¹³ the enhanced Pt–Pt stretching mode in the MMLCT state seemed to match with our result. However, some aspects from our experimental observation cannot be explained by a wavepacket motion model. First, a wavepacket motion generally does not have anticorrelation between parallel and perpendicular signals. Instead, a wavepacket motion on one potential energy surface only displays a unidirectional variation in the transition dipole moment. To generate anticorrelated parallel and perpendicular signals, at least two coupled transition dipole moments with different directions are needed. Second, two sequential oscillatory components are also unusual. Although the second oscillatory component seems to be related to a wavepacket motion in the ground state, the first and second oscillatory frequencies occur sequentially, not impulsively as it would due to the stimulated Raman process. Finally, $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ exhibits a huge amplitude of the residual anisotropy. Although the absolute value of the initial TA anisotropy alone is insufficient for directly quantifying the transition dipole moment change due to contributions from multiple sources (i.e., ground-state bleaching, induced absorption, and stimulated emission) to the TA signals,^{25,26} the unusually large amplitude of the residual anisotropy cannot be

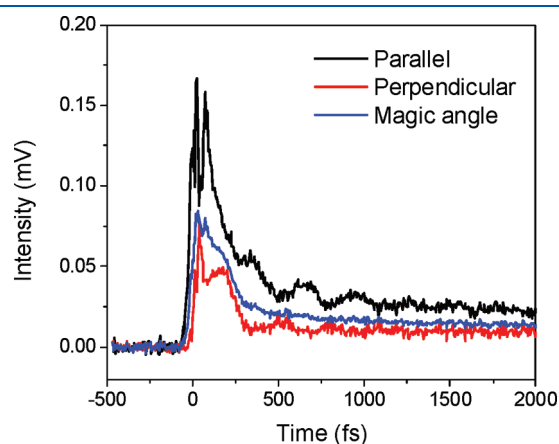


Figure 3. Parallel, perpendicular, and magic angle TA signals for $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ in toluene as a function of the probe delay time in toluene at room temperature after photoexcitation at 510 nm.

Table 1. Photophysical Parameters of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$. (Excitation Wavelength for TA, 510 nm)

	absorption/nm	emission/nm	Stokes shift/ cm^{-1}	TA	
				magic angle (amp.)	oscillation frequency in the anisotropy (dephasing time)
$[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$	444, 475, 507	657	4480	$145 \pm 4 \text{ fs}$ (85.5%)	$320 \pm 19 \text{ cm}^{-1}$ ($60 \pm 12 \text{ fs}$)
				$2.39 \pm 0.61 \text{ ps}$ (5.9%)	$110 \pm 1.5 \text{ cm}^{-1}$ ($670 \pm 94 \text{ fs}$)
				long (8.6%)	

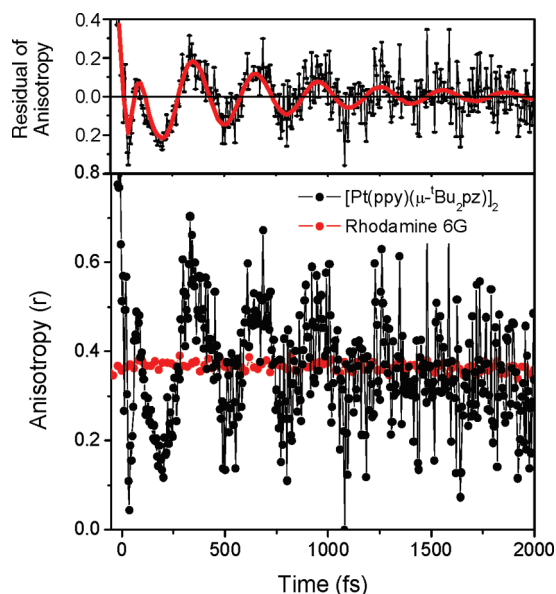
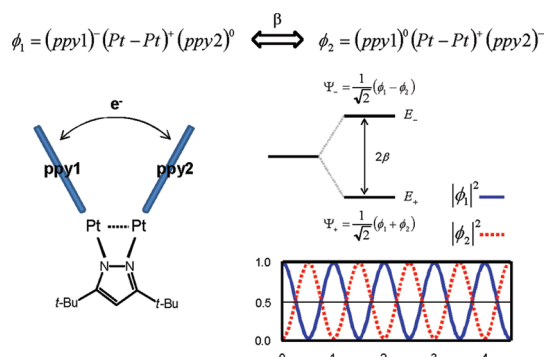


Figure 4. TA anisotropy spectrum at 510 nm and its residual with an oscillation fitting line superimposed. The red dots are the anisotropy values of Rhodamine 6G in MeOH after photoexcitation at 510 nm.

Scheme 2. Illustration of Proposed Alternative Coherent Electronic Interaction Model with Electronic Couplings of the Two States from Each Half of the Molecule, the Resulting Energy Level Splitting, and Coherent Oscillatory of the Electron Density of the Two Local MMLCT States



produced by a wavepacket motion on one potential energy surface (Figure 4).

As a result of the above analysis, we now consider an alternative model of electronic coherence between two nearly isoenergetic states to explain the anticorrelated TA anisotropy. Because the ppy ligands in $[\text{Pt}(\text{ppy})(\mu\text{-Bu}_2\text{pz})_2]$ are widely separated as the two branches of the “A” frame, the electronic couplings between the ppy ligands are weak and nonbonding. Such a weak coupling could result in two nearly degenerate in-phase and out-of-phase electronic states, Ψ_+ and Ψ_- which can be respectively expressed by a linear combination between the two local MMLCT states,^{27,28} ϕ_1 and ϕ_2 , shown in Scheme 2. The energetic splitting between Ψ_+ and Ψ_- depends on the coupling strength β between ϕ_1 and ϕ_2 . From the first-order perturbation theory, when Ψ_+ and Ψ_- are coherently excited,

the total electronic state undergoes a time evolution expressed as

$$\Psi(t) = \frac{1}{\sqrt{2}}\Psi_+e^{-iE_+t/\hbar} + \frac{1}{\sqrt{2}}\Psi_-e^{-iE_-t/\hbar} \quad (2)$$

where E_+ and E_- are the energies of Ψ_+ and Ψ_- states, respectively. As a result, the probability density can be expressed as^{27,28}

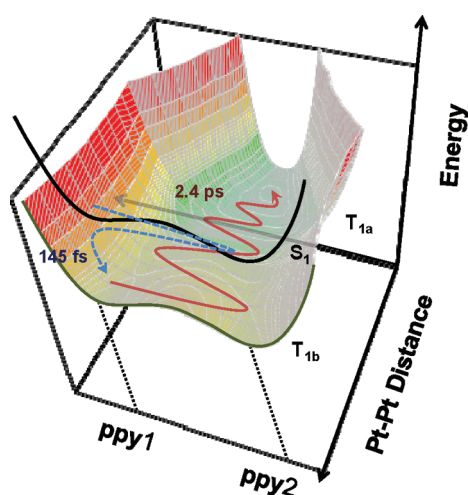
$$|\Psi(t)|^2 = \cos^2(\beta t/\hbar)\phi_1^2 + \sin^2(\beta t/\hbar)\phi_2^2 \quad (3)$$

The electron density localized on either half of the diplatinum chromophore moves back and forth between the two ppy ligands with a time period of $\hbar/2\beta$. Such coherent exciton motions could be observed if (a) the two eigenstates, separated in energy by 2β , can be simultaneously excited, (b) the coherent exciton oscillation period is shorter than the dephasing time, and (c) the transition dipoles have different orientations for the two coupling states of the two halves of the molecule. When the exciton oscillates back and forth between the two states, the induced absorption signal will be modulated accordingly.

On the basis of this alternative electronic coherence model, the two sequentially occurring oscillatory components with frequencies of 320 and 110 cm^{-1} could be attributed to interactions between the $^1\text{MMLCT}$ states and between the $^3\text{MMLCT}$ states, respectively. If this model is valid, the coupling strengths (β) between the two $^1\text{MMLCT}$ states and between the two $^3\text{MMLCT}$ states can be assigned as 160 and 55 cm^{-1} , respectively, using the oscillation frequencies in the anisotropy and eq 3. Consequently, the coherent oscillation can be understood as interaction between two local MMLCT states and it can be assigned as an electron recurrent motion. To further confirm this electronic coherence model, future measurements will be conducted at other excitation wavelengths, using transient emission and on other diplatinum complexes.¹⁰

Sequential and Long-Lived Coherent Oscillation. Figure 4 shows that the oscillation features in the TA anisotropy with two sequentially occurring frequencies persist for almost 2 ps. Since $[\text{Pt}(\text{ppy})(\mu\text{-Bu}_2\text{pz})_2]$ was first excited to the $^1\text{MMLCT}$ state that underwent an ultrafast ISC from $^1\text{MMLCT}$ to $^3\text{MMLCT}$ within 145 fs, the long-lasting coherent oscillations imply that the initial coherence was maintained even after the ISC process. This phenomenon is similar with retained vibrational coherence during the ISC studied by Schrauben and co-worker.²⁹ This long-lasting coherence suggests that the $^1\text{MMLCT}$ and $^3\text{MMLCT}$ states are strongly coupled and the time constant for the electronic dephasing between the $^1\text{MMLCT}$ states ϕ_1 and ϕ_2 is longer than that of the ISC. However, the apparent Stokes shift of 4480 cm^{-1} in the emission spectrum (Figure 2) reveals a large energy gap between the $^1\text{MMLCT}$ and $^3\text{MMLCT}$ states. Therefore, it is puzzling why the coherence is retained after the ISC. In order to search an answer to the puzzling question, we turn to theoretical work performed on similar molecules. Saito et al. reported potential energy curves (PECs) of an almost identical dinuclear Pt(II) complex, the fluorinated-ppy version originally studied by Thompson and co-workers,⁹ and revealed that there are two triplet states, T_{1a} and T_{1b} , with different geometries at their respective PEC minima (Scheme 3).³⁰ The T_{1a} state is generated from the electronic transition of HOMO (mainly $\sigma_{\text{Pt-Pt}}^*$ MO) \rightarrow LUMO, depleting the antibonding electron density and enhancing the bond order which is responsible for the Pt–Pt distance contraction. In comparison, the T_{1b} state is mainly generated via ligand centered transitions

Scheme 3. Energy Relaxation Diagram with Potential Energy Curves of $[\text{Pt}(\text{ppy})(\mu\text{-}^i\text{Bu}_2\text{pz})_2]$



(HOMO-1 \rightarrow LUMO) with no electron density change from the antibonding σ^* MO. Therefore, the T_{1b} state has a similar geometry at the local PEC minimum with that of the ground-state S_0 in terms of the Pt–Pt distance. Saito's calculations³⁰ revealed some critical trends in the excited state PECs as the Pt–Pt distance in the S_0 state decreases: (1) the energies of PEC minima for the T_{1a} and T_{1b} states are both lowered relative to that of the ground state S_0 ; (2) the energy gap between the PEC minima of the T_{1a} and T_{1b} states increases because of the stabilization of the T_{1a} state; and (3) the difference in the Pt–Pt distances corresponding to the PEC minima for the T_{1a} and T_{1b} states contracts. Consequently, Saito et al. concluded that as the Pt–Pt distance in the S_0 state becomes shorter due to sterics, the two triplet state PECs become nested, losing the local minimum for the T_{1b} state while stabilizing the T_{1a} state.³⁰ If this hypothesis is correct, we expect that the ISC takes place along a cascade pathway originating from the $^1\text{MMLCT}$ state to the $^3\text{MMLCT}$ state at the same equilibrium geometry ($S_1 \rightarrow T_{1b}$) and thereafter the excited population in the $^3\text{MMLCT}$ state relaxes to the global minimum ($T_{1b} \rightarrow T_{1a}$), which is shown as a contraction in the Pt–Pt distance (Scheme 3). Therefore, the first step in the ISC is mediated via the transition from the PECs of the S_1 and T_{1b} states in ~ 145 fs, supported by the observed time constant for the stimulated emission, and then the second step is the structural relaxation/PECs crossing from the T_{1b} to T_{1a} state, characterized most likely by the medium decay component with a 2.4 ps time constant. The second step may be also accompanied by a relaxation process from the hot vibrational to the zero-vibrational level in the $^3\text{MMLCT}$ state. We suggest that this time constant for the molecular transformation from the Franck–Condon geometry to the thermally equilibrated geometry is accompanied by the contraction of the Pt–Pt distance.

Anticorrelated Oscillations in TA Anisotropy. If the initial electronic transition involves one transition dipole, the initial anisotropy value at delay time $t = 0$ is a function of the angle (θ) between the absorbing and probing transition dipole moments³¹ expressed as

$$r_0 = \frac{3 \cos^2 \theta - 1}{5} \quad (4)$$

When the pump and probe transition dipoles are collinear, $r_0 = 0.4$. Wynne and Hochstrasser described in general the transient anisotropy from the optical pump–probe measurements in the presence of two degenerate states with electronic coherence, which included excitation, emission, and stimulated Raman contributions to r_0 .^{24,32} Because $[\text{Pt}(\text{ppy})(\mu\text{-}^i\text{Bu}_2\text{pz})_2]$ has possible contributions at 510 nm from the ground state bleaching, excited state absorption, and stimulated emission, their individual contributions to r_0 are difficult to quantify under the current experimental condition. The discussion here will focus only on the anticorrelated oscillations in the parallel and perpendicular TA signals that can be possibly produced by two coupled transition dipoles with different orientations.^{32,33} We can extract the relative orientation between the two transition dipoles from the values of the anisotropy at different time delays. The amplitude of the residual anisotropy is very large and its upper limit value of 0.4 at $t = 0$ oscillates to its lower limit value of -0.2 at $t \sim 200$ fs, which suggests that the relative angle between the two coupled transition dipole moments is near orthogonal (Figure S6, Supporting Information). On the basis of the optimized molecular structure, we found that the MMLCT transition induces the electron density shift from the central Pt atoms and pz groups to the pyridine side of the ppy ligands. If we assume that a transition dipole moment is aligned with the direction of charge density variation, the transition dipole moments of the MMLCT states individually point to the pyridine groups in ppy ligands from the centroid of the Pt–Pt bond. We calculated the angle between the pyridine groups in ppy ligands centered by the centroid of Pt–Pt bond by using the optimized molecular structure for the ground state and found that the angle of 81.4° matched well with the result of the anisotropy results.

Electron Recurrence Motion. If the origin of those oscillation features in Figures 3 and 4 was electronic coherence, the coupling strength of the $^3\text{MMLCT}$ state would be about three times smaller than that of the $^1\text{MMLCT}$ state, according to the 2β values extracted from the two sequentially occurring oscillation frequencies in the TA anisotropy decay. The strong absorption band of the $^1\text{MMLCT}$ state shown in Figure 2 indicates that the magnitude of the transition dipole moment is large;³⁴ thus the coherent oscillation in the $^1\text{MMLCT}$ state can be understood as the interaction between the two above-mentioned transition dipole moments if the electronic coherence model is valid. The questions are then (a) whether this model would stand when the amplitude of the transition dipole moment changes in the $^3\text{MMLCT}$ state and (b) why would the oscillation last so long.

According to our DFT calculation results, the π^* orbitals of ppy ligands are mixed with the 5d orbitals of Pt atoms connected through the $\sigma_{\text{Pt-Pt}}$ and $\sigma^*_{\text{Pt-Pt}}$ bonding (Figure S7, Supporting Information). If the calculation only include the two ppy ligands with the same positions as in the whole molecule while removing the Pt atoms and the bridging pz groups, the MO energy splitting between the ligand π^* MO dominating LUMO and LUMO+1 was significantly reduced, indicating that interactions between the two ppy ligands are mediated by the Pt–Pt bond.^{35,36} Therefore, it is likely that the interaction between ppy ligands in the $^3\text{MMLCT}$ state seems to mainly depend on the through-bond interaction coupled by the Pt–Pt bond. Subsequently, the electron recurrent motion in the $^3\text{MMLCT}$ state could be modulated by the Pt–Pt stretching mode at the T_{1b} state, the first $^3\text{MMLCT}$ state that retains the Pt–Pt distance as that of the ground state. As the Pt–Pt bond finally contracts at the PEC minimum of the T_{1a} state, the oscillatory features are lost perhaps

due to the drastic increase of the energy splitting of LUMO and LUMO+1 which exceeds the 400 cm^{-1} bandwidth of the pump pulse. Hence the transformation in the geometry eventually destroys the possible electronic coherence. Further investigations are planned in the future to verify this mechanism in the excited state dephasing.

V. CONCLUSION

We have investigated the origin of the observed distinct oscillatory features in the single wavelength TA anisotropy of a diplatinum molecule $[\text{Pt}(\text{ppy})(\mu\text{-Bu}_2\text{pz})]_2$ with a pseudo-2-fold symmetry as possible electronic coherence between two halves of the molecule. An excited state pathway on the potential energy surface is proposed, which suggests that (1) the MMLCT transitions originated from the symmetry related two halves of the molecule are electronically and coherently coupled with electron density oscillating back and forth between the two π -acceptor ligands, (2) the electronic coupling strength in the $^1\text{MMLCT}$ and $^3\text{MMLCT}$ states can be clearly distinguished to be 160 and 55 cm^{-1} , respectively, (3) a possible intersystem crossing pathway can be described as a cascade with the progression $^1\text{MMLCT} \rightarrow ^3\text{MMLCT} (\text{T}_{1b}) \rightarrow ^3\text{MMLCT} (\text{T}_{1a})$, and (4) the electronic coupling coherence via the Pt–Pt through-bond interactions was sustained over 1 ps and survived the first intersystem crossing while the structural factor mediating the coupling remains unchanged. Although confirmation of the proposed electronic coherence must be obtained through future experiments, the current findings here may have general implications in design of multimetal center complexes for photoactivated reactions where electronic coherence facilitates directional charge or energy transfer along a certain direction between different parts of a molecule.

■ ASSOCIATED CONTENT

S Supporting Information. Instrumental response function (IRF), energetic MO diagram, nanosecond TA data, theoretical oscillation feature of the anisotropy, solid powder Raman spectrum and calculated Raman activity, and time-resolved TA magic angle and anisotropy spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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