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N^N Pt(II) Bisacetylide Complexes with Oxoverdazyl Radical Ligands: Preparation, Photophysical Properties, and Magnetic Exchange Interaction between the Two Radical Ligands

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theory (DFT) computations. The transient absorption spectral studies show that the doublet excited state of the radicals are short-lived ($\tau_{\rm D} \approx 2$ ps) and nonfluorescent. Moreover, the intrinsic long-lived triplet excited state ($\tau_{\rm T} = 1.2 \ \mu$ s) of the Pt(II) coordination center was efficiently quenched by the radical ($\tau_{\rm T} = 6.9$ ps for one representative radical Pt(II) complex). The intramolecular magnetic interaction between the radical ligands through the diamagnetic Pt(II) atom was studied with temperature-dependent EPR spectroscopy; antiferromagnetic exchange interaction ($-J S_1 S_2$, $J = -5.4 \pm 0.1 \text{ cm}^{-1}$) for the complex with the shortest radical–radical distance through bridge fragments was observed. DFT computations give similar results for the sign and magnitude of the J values. For complexes with larger inter-radical distance, however, very weak coupling between the radical ligands was observed ($|J| < 0.7 \text{ cm}^{-1}$). Our results are useful for the study of the effect of a radical on the photophysical properties of the phosphorescent transition-metal complexes.

1. INTRODUCTION

Recently, stable organic diradicals and polyradicals have attracted much attention, owing to the magnetic interaction between these radicals and the observation of high-spin states, as well as for their potential application as molecular magnetic materials.^{1,2} Concerning this aspect, a transition-metal coordination framework was rarely used as a scaffold to construct stable organic radical-containing compounds for study of the magnetic coupling between the radicals, as well as the effect of radical on the photophysical properties of the coordination framework.^{3,4} A combination of the two manifolds, that is, transition-metal coordination framework and stable radicals, will be, in particular, of interest, because the rich photophysical properties of the transition-metal complexes will be tuned by the spin exchange with the radical moiety. Synergy of the optical property and the magnetic property may lead to novel materials with interesting optomagnetic properties.

paramagnetic resonance (EPR) spectroscopy, and density functional

Organic diradicals are the typical model for the study of the magnetic coupling between two spin carriers. Some empirical roles have been established, for instance, the two diradicals attached on *meta*-substituted phenyl moiety are usually *ferromagnetically* coupled, while the *para*-counterpart is usually *antiferromagnetically* coupled.^{6,7} The magnetic coupling between radical ligands mediated by Cu(I), Cu(II), Mn(II), and Au(I) coordination has been studied.^{4,8–13} Yet these studies are not correlated with the *photophysical* changes of the coordination centers with attachment of the radical ligands.^{14–16} It should be mentioned that the photochemical formation of ferromagnetic chains in two isomeric polymeric Mn(II) complexes was studied. This brings out the importance of the study of photophysical processes in the magnetic materials.¹⁷

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 $\lambda_{\rm ex} = 550 \, \rm nm, \, \tau_D = 9.0 \, \rm ps$

Scheme 1. Structures of Oxoverdazyl Radical Ligands and Pt(II) Complexes Used in This Study



However, although some topological rules for the magnetic interactions of the organic diradicals have been proposed, ^{1,2,6,18} the *sign* and the *magnitude* of the intramolecular radical-radical electron-exchange interaction in metal complexes is far from fully elucidated. Subtle variation of the radical or the metal complex coordination structure may substantially affect the electron-exchange interaction.¹⁰ For instance, the direction of the deviation from the tetrahedral geometry, either bringing the two oxoverdazyl radical moieties closer or moving the two radicals further apart, will dictate the *sign* as well as the *magnitude* of the electron exchange between the radical ligands, with the former leading to a fairly strong *ferromagnetic* interaction $(J = 47(1) \text{ cm}^{-1})^8$ and the latter leading to a weak *antiferromagnetic* interaction $(J = -2 \text{ cm}^{-1})$.¹⁰

It should be pointed out that the geometric lability of the Cu(I) coordination center upon photoexcitation is detrimental to the establishment of a persistent electron-exchange interaction between the radical ligands.^{8,19,20} In this aspect another rigid coordination framework is desired for the study of the effect of a radical ligand on the photophysical property, as well as the magnetic coupling between the radicals within the complex molecule. Previously ethynyl phenyl-nitronyl nitroxide radical ligands were used for the preparation of trans-Pt(II) bis(trialkylphosphine) bisacetylide complex.²¹ This kind of complex has a well-defined rigid coordination geometry, which is different from the Cu(I) complexes.^{22,23} Magnetic coupling of the two radical ligands through the diamagnetic Pt(II) atom was studied, and it was found that the exchange interaction between the electron spins of the two nitronyl nitroxide (NN) radical ligands is very weak (|J| < 1 cm^{-1}) for the *meta*-substituted radical. For the *para*-substituted radical complex, no exchange interaction between the two radical ligands was observed, due to the larger distance between the radical ligands; thus, the spin-exchange interaction through the diamagnetic Pt(II) atom is weak.²¹ Furthermore, the detailed photophysical property of the stable radicalcontaining complexes was rarely reported.²⁴⁻²

Our rationale is that, with the introduction of the radical ligands, the photophysical properties of the coordination center will be alternated. Although phenanthroline Pt(II)/ Pd(II) bispyridine complexes with an NN radical attached on the pyridine moiety were reported, the geometry of the radical ligands is cis, and thus the distance between the radicals is small, and stronger exchange interaction may be expected.²⁷ However, no intramolecular exchange interaction was observed with electron paramagnetic resonance (EPR) spectroscopy, and it was concluded that the 14 bonds pathway through the diamagnetic center is too long for any significant exchange interaction. The photophysical property of the complex was not studied. A N^C^N Pt(II) acetylide complex with an NN radical ligand was prepared.²⁸ Because of the monoradical feature of the molecular structure, no intramolecular magnetic interaction between radicals was studied. The photophysical property was not studied, although the N^C^N Pt(II) acetylide complex is a typical phosphorescent chromophore at room temperature.^{29,30} Recently a verdazyl radicalcontaining Ru(II) complex was reported; there is only a monoradical unit; thus, no intramolecular magnetic interaction between the radical units was studied.²⁶ The phosphorescence of the Ru(II) coordination center was not guenched by the radical ligand.

The N^N Pt(II) bisacetylide complexes have been extensively investigated, owing to the feasible preparation, the well-defined geometry and orientation of the two acetylide ligands, the efficient intersystem crossing (ISC) and the longlived triplet excited state.^{31–34} These complexes have been widely used as photocatalysts and photosensitizers and for photoinduced charge separation and also for the study of the fundamental photochemistry and photophysics.^{35–38} However, to the best of our knowledge, no N^N Pt(II) bisacetylide complexes have been prepared with the radical ligands. Thus, neither the magnetic coupling between the radical ligands through the diamagnetic Pt(II) atom nor the effect of the coordinated radical ligands on the photophysical property of Scheme 2. Synthesis of Oxoverdazyl Radical Ligands and Pt(II) Complexes^a



^{*a*}(a) 1,10-Phenanthroline, CuI, finely ground K₃PO₄, iodobenzene, dried dimethylformamide, Ar, 90 °C, 20 h, yield: 37.2%. (b) MeOH, Ar, -30 °C, 1 h, yield: 63.4%. (c) K₂CO₃, MeOH, CH₂Cl₂, Ar, RT, 2 h, yield: 96.0%. (d) 4-Benzoquinone, toluene, Ar, 90 °C, 2 h, yield: 90.3%. Pyridinium tosylate, MeOH, Ar, RT, 30 min, yield: (e) 66.4%, (g) 85.7%, (i) 68.9%. 4-Benzoquinone, toluene, Ar, 90 °C, 1 h, yield: (f) 71.3%, (h) 78.5%, (j) 75.0%. (k) CuI, CH₂Cl₂, *i*-Pr₂NH, Ar, RT, 24 h, yield: 93.3%. CuI, CH₂Cl₂, *i*-Pr₂NH, Ar, RT, 4 h, yield: (l) 72.5%, (m) 63.0%, (n) 74.0%. (o) 64.8%.

the Pt(II) coordination center was studied. The molecular structural planarity of the Pt(II) complexes may assist in the control of the molecular packing,²⁷ which is also important for the preparation of magnetic materials.

To probe the exchange interaction between the two radical ligands in the N^N Pt(II) bistacetylide complexes, as well as the photophysical property changes of the Pt(II) center in the presence of a radical, for ISC and the triplet-state properties, we prepared a series of N^N Pt(II) bisacetylide complexes with radical ligands, in which the distance between the radical moieties, as well as the linkers between the radical center and the Pt(II) atoms, are systematically varied (Scheme 1). The photophysical properties of the complexes were studied with steady-state as well as femtosecond time-resolved optical spectroscopies. We found that the photophysical properties of the complexes were substantially changed upon attachment of the radical ligands. Moreover, intramolecular magnetic coupling between the radical ligands was studied with EPR spectroscopy as well as with theoretical computations. These studies are interesting, because the tuning of the optical property of the Pt(II) coordination center and the magnetic (exchange) interactions of the radical ligands were combined.

2. RESULTS AND DISCUSSION

2.1. Design and Synthesis of the Complexes. Previously the electron-exchange interaction between the two bidentate ligands containing an imino nitroxide radical moiety mediated by a diamagnetic Cu(I) was proven to be *ferromagnetic* with the exchange interaction of 2J = +102(2) cm^{-1.9} The rationale for this result is that the orthogonal orientation of the magnetic orbitals of the two ligands, determined by the Cu(I) coordination geometry, results in the *ferromagnetic* interaction between the two coordinated ligands. Thus, it will be interesting to investigate the exchange interaction between the two coordinated acetylide radical ligands in the N^N Pt(II) bisacetylide ligands, in which the two radical ligands are in coplanar geometry and the magnetic orbitals are not in orthogonal geometry.

However, the *sign* of the exchange interaction may be also switched by using different spin carriers, such as an oxoverdazyl radical, even with the same geometry of the coordination center. For instance, replacing the imino nitroxide radical $(2J = +102(2) \text{ cm}^{-1})^9$ with oxoverdazyl radical in the Cu(I) complex switched the exchange interaction between the two radicals to $2J = -4 \text{ cm}^{-1}$; as such, the interaction becomes *antiferromagnetic*.¹⁰ The stark difference of the intramolecular electron-exchange interaction was attributed to the different frontier molecular orbitals with the two different radical ligands (imino nitroxide vs oxoverdazyl).¹⁰ However, the effect of the coordinated radical ligands on the photophysical property of the coordination center, for instance, the ISC and the triplet-state property, was not studied.^{8,19,20}

To study the intramolecular electron-exchange interactions of the radicals within a rigid coordination framework, we prepared a series of N^N Pt(II) bisacetylide complexes, in which the inter-radical distance through bridge fragments and the substitution profile of the radicals are systematically varied (Scheme 1). We selected the oxoverdazyl radical,³⁹ a stable radical moiety, as the spin carrier. The distance between the



Figure 1. UV–Vis absorption spectra of the compounds. $c = 1.0 \times 10^{-5}$ M in toluene. 20 °C.



Figure 2. (a) Photoluminescence spectra of Pt-Ph under N₂ and air atmosphere; (b) quenching of the phosphorescence of Pt-Ph by increasing the VR-1 concentration under N₂ atmosphere; (c) Stern–Volmer plot for the quenching of the phosphorescence of Pt-Ph by VR-1 under N₂ atmosphere, monitored at 565 nm. λ_{ex} = 420 nm, c[Pt-Ph] = 1.0 × 10⁻⁵ M in toluene. 20 °C.

radical and the Pt(II) center is small in Pt-0 but larger in Pt-1, Pt-2, and Pt-3 (Scheme 1). The distance may exert a significant effect on the electron-exchange interactions. Moreover, the substitution profile of the radicals in Pt-1, Pt-2, and Pt-3 is unique in each case, which may affect the electronexchange sign and magnitude as well. All the complexes were prepared feasibly with the routine synthesis methods (Scheme 2),⁴⁰⁻⁴⁵ and the yields are moderate to satisfactory.

2.2. UV–Vis Absorption and Luminescence Properties. The absorption spectra of the parent complex Pt-Ph, Pt(II) complexes with radical ligands, and the native radicals were compared (Figure 1). Pt-Ph gives a typical metal-toligand charge transfer (MLCT) absorption band at 424 nm. For all the Pt(II) complexes studied, this band is clearly discernible. Upon coordination to the Pt(II) center, the VR-0 radical moiety in **Pt-0** shows a marked red-shift to 604 nm as compared to **VR-0** itself, which is assigned to the radical $\pi - \pi^*$ transition. This is due to the perturbation upon coordination on the π -conjugation framework. This interaction may efficiently mediate the electron-exchange interactions between the two radical ligands.⁸ No absorption was observed at a wavelength longer than 700 nm, indicating that the unpaired electron is *localized* on the verdazyl radical; thus, no intervalence absorption resulted.⁴⁶ Previously, the N^N PtCl₂ complexes (N^N is bidentate verdazyl-substituted pyridine ligands) were prepared, and a metal-to-radical ligand absorption band in the range of 550–700 nm was observed.⁴⁷

For Pt-1, Pt-2, and Pt-3, an intervening phenyl moiety was used as a linker to attach the radical moiety and the Pt(II) atoms. There is not much difference between the absorption



Figure 3. Cyclic voltammogram of the compounds. Ferrocene (Fc) was used as an internal reference. In deaerated CH_2Cl_2 solution containing 0.5 mM compound with 0.25 mM ferrocene, 0.10 M $Bu_4N[PF_6]$ as supporting electrolyte, and Ag/AgNO₃ as reference electrode; scan rates: 50 mV/s. 20 °C.

spectra of these complexes and the native radical ligands. This result indicates that there is no perturbation upon coordination on the radical moiety, which is different from **Pt-0**.

It is known that the complex **Pt-Ph** gives phosphorescence at room temperature (567 nm, $\Phi_p = 42.4\%$).⁴⁸ For the complexes containing radical ligands, however, the phosphorescence was completely quenched. This strong quenching effect may be due to the strong spin-exchange interaction between the radical and the Pt(II) coordination framework of the complexes and the formation of "trap states" to enhance the internal conversion (EIC).^{18b}

Previously the N^N PtCl₂ and N^N PdCl₂ complexes were prepared (N^N is pyridine ligand attached with imino nitroxide radical), and the intermolecular magnetic interaction was studied. It was stated that the luminescence of the N^N PtCl₂ coordination center was quenched.⁴⁹ However, the N^N PtCl₂ shows weak intrinsic phosphorescence at 77 K, which is different from the N^N Pt(II) bis(acetylide) complexes used in this study; the N^N Pt(II) bis(acetylide) coordination center is strongly phosphorescent at room temperature.^{40-42,44,50-53}

To confirm that the quenching of the phosphorescence by the radical is not due to an intermolecular interaction, we studied the quenching of the phosphorescence of the parent complex **Pt-Ph** by the radical compound **VR-1** (Figure 2). With the increasing concentration of **VR-1**, the intensity of the phosphorescence band at 565 nm was reduced.

To study the kinetics of the intermolecular quenching efficiency, the intensity of the phosphorescence band at 565 nm of **Pt-Ph** was monitored. The Stern–Volmer quenching constant was calculated as $K_{SV} = 1.20 \times 10^4 \text{ M}^{-1}$ (Figure 2c). The bimolecular quenching constant was calculated as $1.00 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ according to eq S2 in the Supporting Information. The diffusion-controlled bimolecular quenching

rate constant was calculated as 1.12×10^{10} M⁻¹ s⁻¹, and the quenching efficiency was calculated as 89.5%, which indicates that there is an efficient quenching process between VR-1 and **Pt-Ph**. However, the phosphorescence of **Pt-Ph** has not been totally quenched, even if **VR-1** is 5 equiv compared with **Pt-Ph**. Thus, the *intermolecular* quenching process is less efficient than the *intramolecular* quenching process. The calculation procedure is given in the Supporting Information.

2.3. Electrochemical Studies: Intramolecular Photoinduced Electron Transfer. The cyclic voltammetry of the native radicals and complexes was studied (Figure 3). For VR-0, the reduction potential and the oxidation potential are both more positive than the other radical ligands. This is due to the influence of the phenyl part. All the oxidation waves and reduction waves of the four radicals are reversible, and the potentials are shown in Table 1.

For Pt-1, Pt-2, and Pt-3 in the cathodic scanning range, two reversible reduction waves were observed (Figure 3f-h). They are the sum of the reduction waves of Pt-Ph and the native radical ligands (Supporting Information, Figure S38b-d). In the anode region, a quasi-reversible wave was observed. For Pt-0, there are two reversible reduction waves, which have the half-wave potential $E_{1/2}$ of -1.07 and -1.98 V. Comparing the two waves with the reference complex Pt-Ph and the native ligand VR-0, it gives a shift of ~0.15 V (Supporting Information, Figure S38a). In the anode region, a pseudoreversible wave with half-wave potential $E_{1/2}$ of +0.62 V and an irreversible wave at +0.42 V were observed. This is also different from the other Pt(II) complexes. These results indicate that there is an electronic interaction between the radical parts and the Pt(II) center in Pt-0. However, in Pt-1, Pt-2, and Pt-3, there is no such electronic interaction; this is based on the fact that the reduction potentials of these Pt(II) complexes are the same as that of the reference compounds.

Table 1. Electrochemical Potentials of the Compounds (vs Fc/Fc^+)^{*a*}

compound	oxidation, V	reduction, V
VR-0	+0.59	-0.91
VR-1	+0.47	-1.04
p-VR	+0.49	-1.01
m-VR	+0.49	-1.01
Pt-0	+0.42, +0.62	-1.07, -1.98
Pt-1	+0.47	-1.04, -1.87
Pt-2	+0.44	-1.04, -1.91
Pt-3	+0.45	-1.04, -1.89
Pt-Ph	+0.49	-1.87

^{*a*}Cyclic voltammetry in deaerated CH₂Cl₂ containing 0.10 M Bu₄NPF₆ as supporting electrolyte; counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode. $c[Ag^+] = 0.1$ M, 0.5 mM compound with 0.25 mM ferrocene in deaerated CH₂Cl₂. 25 °C.

This is in agreement with the magnetic property (discussed in Sections 2.5 and 2.6), which indicates that **Pt-0** is a stronger antiferromagnetic system compared with the other complexes. For all the complexes, the current for the first reduction is almost double compared to the second reduction process (Figure 3e-h). According to the Randles-Sevcik equation (Supporting Information, eq S6), the magnitude of the current is directly proportional to the concentration of the electroactive species. In this work, one molecule contains two verdazyl ligand moieties and one Pt-bpy moiety (bpy = 4,4'-di*tert*-butyl-2,2'-bipyridine), and thus the reaction concentration of first reduction process (Verdazyl ligand moiety) is double that of the second reduction process (Pt-bpy moiety). The redox potentials of the Pt(II) complexes and the native radical ligands are summarized in Table 1.

The Gibbs free energy changes (ΔG_{CS}) of the photoinduced electron transfer shown in Table 2 were calculated with the

Table 2. Free Energy Changes of Charge Separation (ΔG_{CS}) and Charge-Separated States Energy Level (E_{CS}) of the Compounds in Different Solvents^{*a*}

	$\Delta G_{ m CS}$, eV		$E_{\rm CS}$, eV			
	TOL	DCM	ACN	TOL	DCM	ACN
Pt-0 ^b	-0.71	-0.99	-1.07	+1.48	+1.20	+1.13
Pt-1 ^b	-0.24	-0.86	-1.03	+1.96	+1.34	+1.17
Pt-2 ^b	-0.35	-0.89	-1.03	+1.85	+1.31	+1.16
Pt-3 ^b	-0.26	-0.86	-1.03	+1.93	+1.33	+1.17
³ Pt-Ph*→VR-1	-0.03	-0.71	-0.90	+2.17	+1.48	+1.30

^{*a*}The emissive T_1 state of **Pt-Ph** was used as the E_{00} value for the calculation of the ΔG_{CS} values. ^{*b*}Direction of intramolecular electron transfer is ³Pt* \rightarrow radical. TOL stands for toluene, DCM stands for dichloromethane, and ACN stands for acetonitrile.

Rehm–Weller equation (Supporting Information, eq S7). The calculation procedure is given in the Supporting Information. The free energy changes are negative values, even in a low-polar solvent such as toluene. With the increase of solvent polarity, the free energy changes become more negative. This indicates in these complexes that it may have photoinduced intramolecular electron transfer and that it should be more significant in a highly polar solvent. Intermolecular photo-induced electron transfer was also studied, and the $\Delta G_{\rm CS}$ values were also shown in Table 2. The negative value indicates

the photoinduced intermolecular electron transfer between Pt-Ph and VR-1.

2.4. Femtosecond Transient Absorption Spectroscopy. To study the decay kinetics of the excited states of the radicals and the corresponding Pt(II) complexes, ultrafast pump-probe experiments were performed for VR-0, VR-1, p-VR, and m-VR at the appropriate pump wavelength of 550 nm (Figure 4), and a white light continuum was used as a probe beam. According to the steady-state absorption spectra (Figure 1), VR-0 should show a ground-state bleaching (GSB) band around 550 nm, but it overlaps with the positive signal and with strong scattered light from the excitation beam (Figure 4a). The positive signal across the probe window is attributed to the excited-state absorption (ESA). We assign this ESA to absorption from D_1 , which decays fast (1.5 ps). No fluorescence was observed. The decay times of the ESA signal at 430 nm are compiled in Table 3. The femtosecond transient absorption spectra of VR-0, p-VR, and m-VR gave similar results (Figure 4b-d). The doublet excited-state lifetimes of these verdazyl radicals are ca. 2 ps. To the best of our knowledge, the excited-state lifetimes of verdazyl radical were not reported yet. All these stable radicals share a common feature, that is, the doublet excited state (D_1) is short-lived (<3) ps), and they are all nonfluorescent. An aromatic diimide radical anion has been reported; the doublet excited-state lifetime is 6 ps.⁵⁴

Ultrafast pump-probe experiments were also performed for **Pt-Ph** at the pump wavelength of 400 nm (Supporting Information, Figure S39). The positive signal seen from 350 to 750 nm is due to ESA. The bleaching band at 380-450 nm overlaps with the positive signal, where **Pt-Ph** gives steady-state absorption bands. The absorption spectra did not change in the probe window. By analyzing the decay curves we determined the ISC process occurs faster than 20 fs (beyond the resolution of our setup); otherwise, we should detect a growth of the ESA band at 650 nm. The long-lived transient, which does not decay in the pump-probe experiment, is due to ESA from the triplet state, in agreement with the nanosecond transient absorption spectra (Supporting Information, Figure S40).

The ultrafast transient absorption spectra of Pt-0 in CH₂Cl₂ were recorded with 400 and 550 nm pumps, which selectively excite the MLCT band (Figure 5a) and the radical moiety (D_0) \rightarrow D_n transition, Figure 5b), respectively. With the pump at 400 nm (Figure 5a), the bleaching band at ca. 600 nm overlaps with the ESA signal, which covers the visible range. In consideration of the bleaching signals being overlapped with the ESA signals in both Pt-Ph and Pt-0, the ESA signals are similar in both cases. Thus, the ESA signal of Pt-0 is assigned to triplet excited-state absorption. However, the triplet state of **Pt-0** has a dramatically short lifetime, $\tau_{\rm T}$ = 6.9 ps (Figure 5c), which is much shorter than the intrinsic T_1 state lifetime (³MLCT, 1.2 μ s, **Pt-Ph**. Supporting Information, Figure S40). Considering the electron spin-exchange interaction, the short triplet-state lifetime of the coordination framework can be explained by the spin-allowed decay of the radical moiety (D₁ $\rightarrow D_0$).^{18b,55} The ISC processes of both $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ can be enhanced by the radical unit.⁵⁶ This significant quenching of the excited state in the Pt(II) complex is attributed to the direct link of the π -conjugated radical moiety to the Pt(II) center, which is different from those of nitroxide radical labeled chromophores, which may show long-lived excited states.⁵⁶⁻⁵⁸ With the pump wavelength at 550 nm, the



Figure 4. Femtosecond transient absorption spectra at different delay times of compounds. (a) VR-0, (b) VR-1, (c) p-VR, and (d) m-VR. Decay curves of (e) VR-0, (f) VR-1, and (h) m-VR at 430 nm. Decay curve of (g) p-VR at 420 nm. λ_{ex} = 550 nm, in toluene at 20 °C.

Table 3. Lifetimes of ESA of Different Compounds in Ultrafast Pump-Probe Experiments

compound	τ , ps ($\lambda_{\rm ex}$ = 400 nm)	τ , ps ($\lambda_{\rm ex}$ = 550 nm)
VR-0 ^a	Ь	1.5
VR-1 ^a	Ь	2.1
p-VR ^c	Ь	2.7
m-VR ^a	Ь	2.2
Pt-Ph ^d	е	Ь
$Pt-0^d$	6.9 ^f	9.0 ^{<i>f</i>}
Pt-1 ^d	9.9 (86%)/1300 (14%) ^g	7.5 ^h

^{*a*}Decay traces at 430 nm, in toluene. ^{*b*}Not measured. ^{*c*}Decay traces at 420 nm, in toluene. ^{*d*}In CH₂Cl₂. ^{*e*}Not observed. ^{*f*}Decay traces at 500 nm. ^{*g*}Decay traces at 460 nm. ^{*h*}Decay traces at 440 nm.

radical moiety was excited (Figure 5b). By analyzing the decay trace at 500 nm we obtained the excited-state lifetime: $\tau = 9.0$ ps. This signal can be attributed to the D₁ state of a radical moiety in complex.

The ultrafast transient absorption spectra of **Pt-1** in CH₂Cl₂ were also recorded upon two different excitation wavelengths (Figure 6). With the pump wavelength at 400 nm (Figure 6a), the MLCT band was selectively excited. The decay trace of the ESA band of **Pt-1** obtained at 460 nm contains two time components (Figure 6c). The long component is 1300 ps (14%), which is assigned to the quenched triplet state. The short component is 9.9 ps (86%), which is assigned to the lifetime of the D₁ state of the radical. The absorption spectrum at 21.4 ps delay time is the ESA from the T₁ state, similar to the ESA of **Pt-0** ($\tau_{\rm T} = 6.9 \,\mu$ s), considering the bleaching band is overlapped with ESA band. With the pump wavelength at 550 nm (Figure 6b), the radical moiety is selectively excited. The lifetime obtained by monitoring the decay at 440 nm is 7.5 ps, which is attributed to the D₁ state of the radical. This

lifetime is longer than that of the native radical ligands ($\tau_{\rm D} = 2$ ps). The difference between the lifetimes can be due to the coordination of the radical ligands to the Pt(II) center.

The ultrafast transient absorption spectra of **Pt-2** and **Pt-3** in CH_2Cl_2 were recorded upon excitation with a 400 and 550 nm pump (Supporting Information, Figures S41 and S42). The photophysical processes are similar to those of **Pt-1**. The kinetics in each case is given in the Supporting Information, Table S1. The photophysical processes of the complexes and the radical ligands are summarized in Scheme 3. Although the spin–spin exchange interaction of the Pt complexes is antiferromagnetic, the exchange is not strong (see below). Thus, the singlet and triplet states due to the spin exchange of the two radical ligands are energetically close to each other. The states with almost equal energies are shown in the light blue background (Scheme 3).

2.5. EPR Spectroscopy and the Magnetic Susceptibility: Intramolecular Magnetic Interactions between the Radical Ligands. The continuous-wave (CW) EPR spectra of the radical ligands in fluid solution at room temperature were first recorded (Figure 7). The radical ligands show the typical hyperfine coupling (hfc) pattern, due to the four ¹⁴N nuclei that are not equivalent in pairs. The spin-Hamiltonian system is

$$H = g\mu_{\rm B}S + \sum_{i=1}^{2} a_{\rm NI}SI_i + \sum_{i=3}^{4} a_{\rm N2}SI_i$$
(1)

where $S = \frac{1}{2}$, and I = 1. The *g* factor and the hfc constants were summarized in Table 4. These results are similar to those observed for the oxoverdazyl radicals.⁵⁹

The CW-EPR of the complexes in solution was also studied (Figure 8). The EPR spectra of the complexes are shown



Figure 5. (a, b) Femtosecond transient absorption spectra at different delay times; (c, d) decay curves at 500 nm of Pt-0. (a, c) $\lambda_{ex} = 400$ nm (S₀ \rightarrow ¹MLCT), (b, d) $\lambda_{ex} = 550$ nm (D₀ \rightarrow D₁). In CH₂Cl₂ at 20 °C.



Figure 6. (a, b) Femtosecond transient absorption spectra at different delay times; decay curves at (c) 460 and (d) 440 nm of Pt-1. (a, c) $\lambda_{ex} = 400$ nm (S₀ \rightarrow ¹MLCT). (b, d) $\lambda_{ex} = 550$ nm (D₀ \rightarrow D₁). In CH₂Cl₂. 20 °C.

Scheme 3. Simplified Jablonski Diagram to Illustrate the Photophysical Processes of the Native Radicals and the Pt ${\rm Complexes}^a$



"Key: S, D, T, and Q represent the singlet, doublet, triplet, and quintet states, respectively. Pt-bpy represents Pt with the 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand moiety. R represents the oxoverdazyl radical ligand moiety. The star (*) represents which moiety was excited. ¹Pt-bpy and ³Pt-bpy represent ¹MLCT and ³MLCT, respectively.

together with the spectra of the radicals, and they practically do not differ from them apart from the width of the signals. An exception is **Pt-0**, but the difference of the **Pt-0** spectrum from the radical for the liquid solution is small. As will be shown below for the frozen solution, both the shape of the spectrum and the temperature dependence of the signal intensity demonstrate the manifestation of exchange interactions between radicals. The presence of the impurities of monoverdazyl radical masks it in the spectra of the liquid solution.

We selected **Pt-0** for a detailed study of the intramolecualr electron spin-exchange interactions between the radicals (Figure 9). The **Pt-0** sample was dissolved in toluene and liquid crystal 5CB with a concentration of 1 mM (Supporting Information, Figure S43). In both cases there is the impurity of monoverdazyl radical (monoVR). The shape of the EPR spectra of **Pt-0** in toluene is broad due to there being different configurations of the molecule. Therefore, we used liquid crystal 5CB as the matrix, which is oriented in a magnetic field. The temperature dependence of the EPR integral intensity was fitted by eq 2 (Figure 9b)

EPR intensity
$$\approx \frac{1}{kT(3 + \exp(-J/kT))}$$
 (2)

where J is the parameter of the isotropic exchange interaction, and T is temperature. From a fitting of experiment data with an

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Figure 7. EPR spectra (black) and simulation (red) of (a) VR-0, (b) VR-1, (c) p-VR, and (d) m-VR. $c = 1.0 \times 10^{-4}$ M in 2-methyltetrahydrofuran. 20 °C.

Table 4. Spin-Hamiltonian Parameters of Radicals in FluidSolution of Toluene

parameters	VR-0	VR-1	p-VR	m-VR
$g \pm 0.0005$	2.0037	2.0038	2.0037	2.0038
$a_{\rm N1}~({\rm MHz}) \pm 0.005$	17.78	17.59	17.55	17.63
$a_{\rm N2}~({\rm MHz}) \pm 0.005$	13.53	13.14	13.15	13.07

isolated two-spin model ($H = -J S_1 S_2$), $J = -5.4 \pm 0.1 \text{ cm}^{-1}$ was obtained, that is, antiferromagnetic interaction. Previously the intramolecular magnetic coupling of benzene-bridged verdazyl diradicals were studied, and the results show that the meta-diradical shows a ferromagnetic coupling of $J = 19.3 \pm 1.7 \text{ cm}^{-1}$, whereas the para-diradical shows antiferromag-

netic coupling $J = -29.73 \pm 0.03$ cm^{-1.6} Recently a N^C^N Pt(II) acetylide complex containing an NN radical acetylide ligand was prepared,²⁸ but the complex molecule contains only a single radical; thus, the intramolecular magnetic interactions between radical ligands is not applicable to the complex.

Previously N^N Pt(II)/Pd(II) bispyrdine complexes were prepared with the nitronyl nitroxide radical attached on the pyridine ligand. Despite the small intramolecular distance between the radicals, no magnetic interaction between the radicals was observed.²⁷ Intramolecular magnetic coupling between the two coordinated NN radicals in a *trans*-Pt(II) bis(phosphine) bisacetylide complexes was studied, and it was found that the exchange interaction through the diamagnetic Pt(II) atom is weak ($|J| < 1 \text{ cm}^{-1}$).²¹ The intramolecular



Figure 8. EPR spectra of (a) Pt-0, (b) Pt-1, and (c) Pt-2. $c = 1.0 \times 10^{-4}$ M in toluene. 20 °C.

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Figure 9. (a) Temperature dependence of the CW-EPR spectra of **Pt-0**. The impurity of the mono-**VR-0** is not shown; (b) temperature dependence of the EPR integral intensity. (inset) Temperature dependence of the product of the EPR integral intensity and of temperature. In liquid crystal SCB, $c = 1.0 \times 10^{-3}$ M.



Figure 10. (a) Temperature dependence of the $\chi_M T$ products for Pt-0, Pt-1, and Pt-3; the solid lines represent the fitting curves with the spin-Hamiltonian $H = -J S_1 S_2$. (b) Isothermal magnetization curves for Pt-1 at 3, 4, and 5 K.

magnetic interaction between the two NN radicals in a N^N Pd(II) bis(nitronyl nitroxide) complex was reported to be antiferromagnetic, $J/k_{\rm B} = -36 \text{ K.}^{46} \text{ A trans Ru(II)}$ bisacetylide complex [Ru(dppe)($-C \equiv C-R)_2$] (dppe = 1,2-bis-(diphenylphosphino)ethane, R = *p*-phenyl oxoverdazyl radicals or *p*-phenyl NN radicals) was prepared, and it was found that the magnetic coupling between the two NN radicals through the dimagnetic Ru(II) unit is antiferromagnetic ($J = -2 \text{ cm}^{-1}$ for the NN radical and $J = -4 \text{ cm}^{-1}$ for the verdazyl radical).⁶⁰ To the best of our knowledge, for the first time the photophysical property and the electron-spin exchange interaction of the radical ligands in a N^N Pt(II) bisacetylide complex were studied.

The variable-temperature magnetic susceptibility measurement for **Pt-0**, **Pt-1**, and**Pt-3** were investigated in the temperature range of 2–300 K under 1 kOe dc field (Figure 10). The experimental $\chi_{\rm M}T$ values for the three complexes at room temperature are 0.74, 0.75, and 0.74 cm³ mol⁻¹ K, respectively, which are consistent with the expected value of 0.75 cm³ mol⁻¹ K for two S = 1/2 spins with g = 2. As shown in Figure 10a, when cooled, the $\chi_{\rm M}T$ values gradually go down in a wide temperature range from 300 to 25 K for **Pt-0** and from 300 to 50 K for **Pt-1** and **Pt-3**. Below 25 or 50 K, the $\chi_{\rm M}T$ values show a sharper decrease, reaching 0.52, 0.40, and 0.46 cm³ mol⁻¹ K at 2 K for the three complexes, respectively. The temperature dependence of $\chi_{\rm M}T$ products was fitted with spin-Hamiltonian $H = -J S_1S_2$ (Figure 10). The exchange coupling

constant J was obtained as -0.57×10^{-3} cm⁻¹ (g = 1.97), $-0.28 \times 10^{-3} \text{ cm}^{-1}$ (g = 2.00), and $-0.60 \times 10^{-3} \text{ cm}^{-1}$ (g = 1.99) for Pt-0, Pt-1, and Pt-3, respectively, indicating the antiferromagnetic interaction in all three complexes. Variabletemperature variable-field (VTVH) measurements were performed on Pt-1 (Figure 10b). The isothermal curves show negligible nonsuperposition, suggesting the absence of zero-field splitting. The plots of $1/\chi_{\rm M}$ versus T can be wellfitted by the Curie–Weiss law (Supporting Information, Figure S44), yielding $C = 0.67 \,^{\circ}$ C, $\theta = -2.02 \,^{\circ}$ K for **Pt-0**, $C = 0.77 \,^{\circ}$ C, $\theta = -5.02$ K for Pt-1, C = 0.68 °C, $\theta = -4.16$ K for Pt-3. It should be mentioned that these data were obtained with powder samples, which are different from that for the EPR measurement (in frozen solutions) and density functional theory (DFT) computations (see below, for individual molecules, in vacuum); the intermolecular interaction may also play a part and influence the fitting coupling constants.

2.6. DFT Computations: The Electron Exchange Interactions between the Radical Ligands. To study the intramolecular magnetic (spin) exchange interaction of the diradicals, we performed unrestricted DFT calculations for different spin states of the diradicals investigated. For the oxoverdazyl radical ligands (Figure 11), the spin density surfaces are similar to those of the previous report,⁶ and significant spin leakage to the phenyl linker or the ethynyl moiety was observed, which is important for the intramolecular magnetic coupling either through Pt(II) or through space.



Figure 11. Geometric structure and isosurfaces of the spin density of (a) VR-0, (b) VR-1, (c) p-VR, and (d) m-VR. Calculated with the Gaussian 09 program at the UB3LYP/6-31G(d) level.

The optimized geometries of **Pt-0** and **Pt-3** are shown in Figure 12. The optimized geometries and spin density surfaces of **Pt-1** and **Pt-2** are similar to those of **Pt-3** depending on the variance of the radicals (Supporting Information, Figure S45). As shown in Figure 12, the optimized geometries of the N^AN Pt(II) bisacetylide complexes varied for different radicals. **VR-0** and **m-VR** are coplanar with the Pt(II) coordination center, while **p-VR** is tilted. The coplanar complexes show the delocalization of π -electrons and account for the result of the electrochemical potentials in Table 1. On the one hand, the **Pt-0** and the Pt(II) moiety; on the other hand, both radical ligands are tilted in **Pt-1**. In **Pt-3**, only one radical ligand (**p-VR**) is tilted. The calculated highest occupied molecular orbital (HOMO) energy levels (-3.72, -3.83, -3.78, and -3.78 eV for **Pt-0**, **Pt-1**, **Pt-2**, and **Pt-3**, respectively) are consistent with the order of oxidation potential (**Pt-0** < **Pt-2** \approx **Pt-3** < **Pt-1**).

The spin density surfaces of the singlet open shell, triplet, and quintet states of **Pt-0** and **Pt-3** were also calculated (Figure 12). As expected, the spin density surfaces of the singlet and triplet diradical open-shell states are localized on the ligands, with no leakage to the N^N ligand moiety.

Pt-3 has both p-VR and m-VR radicals, which show similar geometries and spin densities with Pt-1 and Pt-2 (Supporting Information, Figure S45). Interestingly, in the case of the triplet state of antiferromagnetic systems (Pt-0, Pt-1, Pt-2, and Pt-3) we observed a spin density value at Pt(II). The spin densities at Pt(II) are -9.7×10^{-3} , -1.0×10^{-3} , 1.4×10^{-3} , and 8.1×10^{-5} bohr⁻³ for the triplet states of Pt-0, Pt-1, Pt-2, and Pt-3, respectively. The contribution of Pt(II) to the spin density surface in Pt-0 is ~10 times more than that of other complexes. This result implies that the intramolecular magnetic coupling interaction in Pt-0 would be stronger than those in other complexes. Furthermore, the larger separation of the radicals in Pt-1, Pt-2, and Pt-3 also makes the magnetic coupling interaction in those systems much weaker than that in Pt-0. The amount of separation can be analyzed by considering the sum of linked bond lengths between radicals. For example, the linked bonds between the radicals in Pt-0 are composed of two C–N, two C–C, two C \equiv C, and two C–Pt. In this way, the sum of the bond lengths in Pt-1, Pt-2, and Pt-3 is longer (23.2, 20.5, and 21.8 Å for Pt-1, Pt-2, and Pt-3, respectively) than that in Pt-0 (11.9 Å). This result is in good agreement with the tendency of the calculated *I* values of the complexes (*I* = -4.552, -0.018, -0.097, and -0.680 cm⁻¹ for Pt-0, Pt-1, Pt-2, and Pt-3, respectively, although the J values depend not only on bond lengths), in that Pt-0 is a strong antiferromagnetic system and the other complexes are a weakly coupled system. The calculated J value of Pt-0 is close to the experimental results, $J = -5.4 \pm 0.1 \text{ cm}^{-1}$.



Figure 12. Geometric structure and isosurfaces of the spin density of singlet open shell, lowest triplet, and quintet states (Q_1) of (a) Pt-0 and (b) Pt-3. Calculated with the Gaussian 09 program at the (U)B3LYP/6-31G(d) level for C, N, H, and O and at the (U)B3LYP/LanL2DZ level for Pt.

electronic state	Pt-0	Pt-1	Pt-2	Pt-3
S ₀	11.35/11.34	-79.09/-79.09	-15.12/-15.11	-14.58/-48.46
T_0	11.37/11.37	-79.09/-79.09	-15.12/-15.12	-15.29/-76.25
T_1	33.25/-41.87	-31.27/-11.36	-10.18/-14.81	-16.73/-45.21
Q	3.72/3.72	-5.45/-5.45	-13.10/-13.09	-13.71/-9.36

Table 5. Dihedral Angles (deg) between the Pt(II) Coordination Center and Radical Ligands

The quenched triplet state of the complexes by the presence of the radical ligands can be understood by the coplanar geometry in the quintet state (Figure 12). We inferred that the planarity of complexes contributes the π -conjugation system and induces strong electron-exchange interaction. To check the effect of planarity on the magnitude of exchange coupling, we calculated |J| values of complexes according to the rotation along the C(sp)- $C(sp^2)$ bond, which connects the tetrazine (in Pt-0) or phenyl (in Pt-1, Pt-2, and Pt-3) to the acetylide ligand with dihedral angle of 0, 30, 60, 90, 120, 150, and 180°. According to this calculation, the |J| value was found to increase with the molecular tendency to adopt coplanar geometry (Supporting Information, Figure S46). This is beneficial for enhancing the ISC and may be responsible for the fast decay of the triplet state of the Pt(II) coordination center (no triplet state was observed for the complexes with nanosecond transient absorption spectra).^{56,61} The dihedral angles between the Pt(II) coordination center and the radical ligands may also be related to the kinetics of the ISC. As seen in Table 5, the arrangement of radical ligands showing more planarity in lowest singlet (S_0) , lowest triplet (T_0) , and the quintet (Q_1) states of **Pt-0** may cause the relatively faster ISC in comparison with Pt-1, Pt-2, and Pt-3. The dihedral angles in the T₁ state of Pt-1, Pt-2, and Pt-3 are significantly reduced compared with the T₀ states. Thus, Pt-1, Pt-2, and Pt-3 may also have a fast ISC through the T_1 .

3. CONCLUSION

We prepared a series of N^N Pt(II) bis(acetylide) complexes with oxoverdazyl radical acetylide ligands; the aim of this work is to study the intramolecular electron spin-spin exchange interaction between the radical ligands of the Pt(II) complexes and the effect of the electron spin of the stable radical on the photophysical properties of phosphorescent Pt(II) coordination framework. Steady-state and time-resolved transient optical spectroscopies, EPR spectroscopy, as well as DFT computations were used to characterize the complexes. We found that the length of the linker between the Pt(II) center and the spin carrier exerts a significant effect on the photophysical property and the magnetic property of the complexes. The intrinsic long-lived triplet excited state ($\tau_{\rm T}$ = 1.2 μ s) of the Pt(II) coordination center was efficiently quenched by the presence of the radical ($\tau_{\rm T}$ = 6.9 ps for **Pt-0**), and the doublet excited state of the radicals was found to be short-lived ($\tau_{\rm D} \approx 2 \text{ ps}$) and nonfluorescent. The intramolecular electron-exchange interaction between the radical ligands through the diamagnetic Pt(II) was studied with EPR. With a shorter linker between the Pt(II) center and the oxoverdazyl radical ligands, antiferromagnetic interaction between the two radical ligands was observed $(J = -5.4 \pm 0.1 \text{ cm}^{-1})$; thus, the ground state is a singlet state (S_0 state), and a triplet state (T_0 state) lies slightly above it. For the complexes with larger interradical distance, however, very weak intramolecular spin exchange between the radical ligands was observed (|J| < 0.7cm⁻¹). The sign and the magnitude of the electronic spin–spin

exchange was successfully reproduced with DFT computations. Our results show that, when radicals directly connect to a Pt(II) center or with a phenyl linker, the radicals give a weak antiferromagnetic interaction and also a short excited-state lifetime in the N^N Pt(II) bisacetylide complexes. These observations are useful for the further design of radical-containing transition complexes with longer linkers for optomagnetic applications.

4. EXPERIMENTAL SECTION

4.1. General Methods. Solvents were dried before used for synthesis. Carbohydrazide and pyridinium tosylate were purchased from Beijing Ouhe Technology Co., Ltd. 3-Trimethylsilylpropynal was purchased from J&K Scientific Ltd. K₂PtCl₄ was purchased from Aladdin Chemical Co., Ltd. 4-Ethynyl-benzaldehyde, 3-ethynyl-benzaldehyde, and 2-ethynyl-benzaldehyde were synthesized according to literature methods.^{62,63} Dichloro(4,4'-di-*tert*-butyl-2,2'-bipyridine)platinum(II) (7) was synthesized according to a literature method.⁶⁴

All chemicals were analytically pure and used as received. NMR spectra were recorded by a Bruker Avance II 400 spectrometer with deuterated dimethyl sulfoxide (DMSO- d_6) and CDCl₃ as solvent and tetramethylsilane (TMS) as standard at 0.00 ppm. High-resolution mass spectrometery (HRMS) was accomplished with a time-of-flight (TOF) mass spectrometer (Agilent), Q-TOF mass spectrometer (Waters), a and matrix-assisted laser desorption/ionization (MALDI) micro MALDI TOF mass spectrometer (Waters). Elemental analyses (C, H, and N) were performed on a PerkinElmer model 240C elemental analyzer. The Fourier transform infrared (FT-IR) spectroscopy was recorded on a Thermo Fisher Infrared Spectrometer (6700) with a KBr disk. Absorption spectra were recorded on a UV2550 UV–vis spectrophotometer (Shimadzu Ltd.). Luminescence spectra were measured on an RF5301 PC spectrofluorometer (Shimadzu Ltd.).

4.2. General Methods to Synthesize Pt-0, Pt-1, and Pt-2. Complex 7 (80 mg, 0.15 mmol), verdazyl radical (132 mg, 0.375 mmol), and CuI (6 mg, 0.03 mmol) were dissolved in the mixture of CH₂Cl₂ (15 mL) and *i*-Pr₂NH (3 mL) under Ar. Then the mixture was stirred for 4 h at RT. After the reaction was finished, water (20 mL) was added. The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na2SO4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: CH₂Cl₂/ MeOH = 100:1, v/v, for Pt-0; CH₂Cl₂ for Pt-1 and Pt-2). Pt-0 was collected as a green solid (110 mg, 0.11 mmol), yield: 72.5%. MALDI-TOF-HRMS ($[C_{50}H_{44}N_{10}O_2P]^-$): calcd m/z 1011.3297, found m/z 1011.3274. FT-IR (KBr, cm⁻¹): 3434, 3066, 2961, 2925, 2119, 1696, 1618, 1487, 1417, 1316, 1217, 1175, 1121, 1029, 849. mp > 250 °C. Elem. Anal. $[C_{50}H_{44}N_{10}O_2Pt + 0.1 CH_2Cl_2 + C_6H_{14}]$ calcd: C, 60.88; H, 5.30; N, 12.66; found: C, 60.89; H, 5.09; N, 12.34%. Pt-1 was obtained as a green solid (110 mg, 0.09 mmol), yield: 63.0%. MALDI-TOF-HRMS ($[C_{62}H_{52}N_{10}O_2Pt]^-$): calcd m/z1163.3923, found m/z 1163.3898. FT-IR (KBr, cm⁻¹): 3435, 3069, 2963, 2925, 2110, 1699, 1601, 1486, 1410, 1300, 1246, 1173, 1122, 1028, 845. mp > 250 °C. Elem. Anal. $[C_{62}H_{52}N_{10}O_2Pt + 0.1 CH_2Cl_2]$ + 0.9 C₆H₁₄], calcd: C, 64.84; H, 5.22; N, 11.20; found: C, 65.16; H, 4.85; N, 11.08%. Pt-2 was obtained as a green solid (129 mg, 0.11 mmol), yield: 74.0%. MALDI-TOF-HRMS ($[C_{62}H_{52}N_{10}O_2Pt]^-$): calcd m/z 1163.3923, found m/z 1163.3937. FT-IR (KBr, cm⁻¹): 3438, 3064, 2961, 2926, 2106, 1700, 1617, 1485, 1416, 1298, 1250,

1162, 1119, 1028, 848. mp 221.3–222.2 °C. Elem. Anal. $[C_{62}H_{52}N_{10}O_2Pt + 0.9 C_6H_{14}]$, calcd: C, 65.19; H, 5.24; N, 11.28; found: C, 65.53; H, 4.82; N, 10.89%.

4.3. Synthesis of Pt-3. Complex 7 (80 mg, 0.15 mmol), p-VR (53 mg, 0.15 mmol), m-VR (53 mg, 0.15 mmol), and CuI (6 mg, 0.03 mmol) were dissolved in the mixture of CH2Cl2 (15 mL), and i-Pr₂NH (3 mL) was added under Ar atmosphere. Then the mixture was stirred for 4 h at RT. After the reaction was finished, water (20 mL) was added. The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over anhydrous Na2SO4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, eluent: CH₂Cl₂). Pt-3 was obtained as a brown solid (113 mg, 0.10 mmol), yield: 64.8%. MALDI-TOF-HRMS ($[C_{62}H_{52}N_{10}O_2Pt]^-$): calcd m/z 1163.3923, found m/z 1163.3906. FT-IR (KBr, cm⁻¹): 3435, 3066, 2964, 2927, 2109, 1699, 1618, 1485, 1409, 1299, 1248, 1172, 1121, 1030, 845. mp 195.9-197.2 °C. Elem. Anal. [C₆₂H₅₂N₁₀O₂Pt + 0.1 CH₂Cl₂ + 0.8 C₆H₁₄], calcd: C, 64.71; H, 5.15; N, 11.28; found: C, 64.73; H, 4.88; N, 11.46%.

4.4. Cyclic Voltammetry. Cylic voltammetry was performed under a 50 mV/s scan rate, in a CHI610D electrochemical workstation. The measurements were performed at room temperature with tetrabutylammonium haxafluorophosphate ($Bu_4N[PF_6]$, 0.1 M) as the supporting electrolyte, glassy carbon electrode as the working electrode, and platinum electrode as the counter electrode. Dichloromethane was used as the solvent, and ferrocene (Fc) was added as the internal reference. The solution was purged with N_2 before measurement, and the N_2 gas flow was kept constant during the measurement.

4.5. Femtosecond Transient Absorption Spectroscopy. The transient absorption (TA) spectra were measured by optical femtosecond pump-probe spectroscopy. The output of a mode-locked Ti-sapphire amplified laser system (Spitfire Ace, Spectra-Physics) with a wavelength of 800 nm, pulse width of 35 fs, repetition rate of 1 kHz, and average power of 4 W was split into two beams (10:1). The strong beam was converted into UV-vis-IR in the range of 240–2400 nm by use of an Optical Parametric Amplifier (TOPAS, Light Conversion) and used as a pump beam. The weaker beam after passing a variable delay line (up to 6 ns) was focused in a 3 mm thickness rotated CaF₂ plate to produce a white light continuum (WLC), which was used as a probe beam. A home-built pump-probe setup was used for obtaining the transient absorption spectra and kinetics.

The relative polarization direction between the pump and probe beams was set to the magic angle (54.7°) to avoid the effect of the molecular rotational diffusion on kinetics. The entire setup was controlled by a personal computer (PC) with the help of LabView software (National Instruments). All measurements were performed at room temperature under aerated conditions. The experimental data were fitted to a multiexponential decay function deconvoluted with the instrument response function. The overall time resolution was $\sim 20-30$ fs.

4.6. Electron Paramagnetic Resonance Spectroscopy. The CW-EPR spectra were recorded at room temperature using an Elexsys E-580 spectrometer (Bruker) at the X-band, with a 100 kHz field modulation. The temperature dependence of the EPR spectra in the temperature range of 4-100 K was studied with a helium-flow cryostat (Oxford Instruments).

4.7. Theoretical Computations. The DFT calculations were performed using the Becke's three parametrized Lee–Yang–Parr (B3LYP) exchange correlation functional with the LanL2DZ effective core potential for Pt and 6-31G* basis sets for the other atoms. Singlet, triplet, and quintet spin states were considered for the diradicals investigated. All the calculations were done by a suite of Gaussian 09 programs.⁶⁵

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01575.

Experimental procedures, nanosecond and femtosecond transient absorption experimental details, molecular structure characterization, additional spectra (PDF)

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Notes

The authors declare no competing financial interest.

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