# **Inorganic Chemistry**

# Anthryl-Appended Platinum(II) Schiff Base Complexes: Exceptionally Small Stokes Shift, Triplet Excited States Equilibrium, and Application in Triplet–Triplet-Annihilation Upconversion

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11.0%) is quenched in the anthryl-containing complexes ( $\Phi_{\rm p} = 4.0\%$ ) and shows a biexponential decay ( $\tau_{\rm P} = 3.4 \,\mu s/87\%$  and  $18.2 \,\mu s/13\%$ ) compared to the single-exponential decay of the native Pt(II) Schiff base complex ( $\tau_{\rm P}$  = 3.7 µs). Femtosecond/nanosecond transient



absorption spectroscopy suggests an equilibrium between triplet anthracene (<sup>3</sup>An) and triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) states, with the dark <sup>3</sup>An state slightly lower in energy (1.96 eV for Pt-9An and 1.90 eV for Pt-2An) than the emissive <sup>3</sup>MLCT state (1.97 eV for Pt-9An and 1.91 eV for Pt-2An). Intramolecular triplet-triplet energy transfer (TTET) and reverse TTET take 4.8 ps/444 ps for Pt-9An and 55 ps/1.7 ns for Pt-2An, respectively. The triplet-state equilibrium extends the triplet-state lifetime of the complexes to 103  $\mu$ s (Pt-2An) or 163  $\mu$ s (Pt-9An), in comparison to the native Pt(II) complex, which shows a lifetime of 4.0 µs. The complexes were used for triplet–triplet-annihilation upconversion with perylene as the triplet acceptor. The upconversion quantum yield is up to 15%, and a large anti-Stokes shift (0.75 eV) is achieved by excitation into the singlet metal-toligand charge-transfer absorption band (589 nm) of the complexes (anti-Stokes shift is 0.92 eV with 9,10-diphenylanthracene as the acceptor).

### INTRODUCTION

Transition-metal complexes have attracted much attention in fundamental photochemistry for their applications in photocatalysis,<sup>1–4</sup> photodynamic therapy,<sup>5–8</sup> photovoltaics,<sup>9,10</sup> phos-phorescent molecular sensing,<sup>11–13</sup> photocatalytic hydrogen production,<sup>14,15</sup> nonlinear optics,<sup>16–19</sup> and triplet–tripletannihilation upconversion (TTA-UC).<sup>20-22</sup> These applications are dependent on the visible-light-harvesting ability and tripletstate lifetime of the transition-metal complexes.<sup>23-25</sup> In order to fully exploit the potentials of these compounds, it is crucial to unravel their excited-state dynamics, especially in the case of complexes containing multiple chromophores. Several such complexes have been studied, for instance, the boron dipyrromethene (Bodipy)-palladium(II) benzoporphyrin complexes, which showed forward singlet energy transfer and backward triplet energy transfer.<sup>26</sup> Bodipy-(diimine)-(dithiolate)platinum(II) complexes also showed similar properties.

We have prepared a heteroleptic N^N platinum(II) bis(acetylide) complex containing different Bodipy ligands. Fast Förster resonance energy transfer (FRET, 3.9 ps) and intersystem crossing (ISC) of the energy acceptor (ISC takes 52 ps) were observed.<sup>28</sup> In a broadband near-IR-absorbing trans-bis(trialkylphosphine)platinum(II) bis(acetylide) binuclear complex, containing different Bodipy acetylide ligands, we observed a FRET process occurring within 45 ps.<sup>29</sup> In a heteroleptic N^N (diamine)platinum(II) bis(acetylide) complex with Bodipy and naphthalenediimide ligands, a FRET process (8.2 ps) was observed.<sup>30</sup> Ruthenium(II) diimine or C^N cyclometalated iridium(III) complexes with anthryl or pyrenyl appendants have been intensively studied, and tripletstate equilibrium has been observed.<sup>31-35</sup>

Special Issue: Light-Controlled Reactivity of Metal Complexes

Received: June 30, 2020



Scheme 1. Synthesis of the Platinum Anthracene (Pt-9An and Pt-2An) and Reference (Pt-Ph) Complexes<sup>a</sup>



<sup>*a*</sup>Reaction conditions: (i) ethanol, acetic acid, reflux, 8 h, 86%; (ii) K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>PtCl<sub>4</sub>, dimethyl sulfoxide, 75 °C, 12 h, 62%; (iii) 9-anthraceneboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene/ethanol/water, 10 h, 21%; (iv) 2-anthraceneboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene/ethanol/water, 8 h, 20%; (v) phenylboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene/ethanol/water, 10 h, 27%.

One critical issue for the typical transition-metal complexes is the large difference between the absorption and emission maxima (large Stokes shifts). We define here the energy difference between the singlet (<sup>1</sup>MLCT) and triplet (<sup>3</sup>MLCT) metal-to-ligand charge-transfer states as Stokes shifts, although "Stokes shift" refers to the shift between absorption and emission for the electronic transition between states with the same electron-spin multiplicity, which translates to a large loss of excitation energy. This is detrimental for applying these triplet photosensitizers (PSs) to initiate energy or electron transfer. The typical ruthenium(II) tris(diamine) complexes present Stokes shifts of ca. 0.7 eV,36 while cyclometalated iridium(III) complexes show Stokes shifts of ca. 1.0 eV.<sup>37–39</sup> In the case of cyclometalated platinum(II) [Pt(II)] complexes such as (ppy)Pt<sup>II</sup>(acac) (ppy = 2-phenylpyridine; acac = acetylacetonate), Stokes shifts of ca. 0.6 eV are usually observed.40 Osmium(II) polyimine complexes were used in TTA-UC, owing to the direct  $S_0 \rightarrow T_1$  photoexcitation;<sup>41-43</sup> thus, a small Stokes shift is observed (0.16 eV); however, the electron spin-forbidden transition is weakly allowed (molar absorption coefficient  $\varepsilon = 3200 \text{ M}^{-1} \text{ cm}^{-1}$ ) and the triplet-state lifetime is short (12 ns).<sup>41,42</sup> The short triplet-state lifetime is detrimental to the applications. It is thus highly desired to develop transition-metal complexes showing intrinsic small Stokes shifts and long-lived triplet state.

Concerning these aspects, transition-metal Schiff base complexes, especially those containing the Salen-type Schiff base derived from N,N'-bis(salicylidene)-1,2-benzenediamine,<sup>44-46</sup> are of particular interest because the complex may contain only one ligand, and the appendant chromophore can be introduced in a feasible controllable manner. Moreover, the Pt(II) Schiff base complexes, especially those derived from 1,2-benzenediamine, show an unusual *small* Stokes shift (0.24 eV).<sup>44</sup> Previously, we observed a long-lived triplet-state lifetime by attaching a Bodipy chromophore to the coordination

framework,47 and the native coordination structure was reported by Che et al. for study of organic-light-emittingdiode materials.<sup>44,48</sup> The moderate absorption of the Pt(II) Schiff base complex in the visible range (9900  $M^{-1}$  cm<sup>-1</sup> at 554 nm) is sufficient for applications in photocatalysis or photon upconversion.<sup>49</sup> Previously, we attached a pyrenyl moiety to the Pt(II) Schiff base,<sup>50</sup> and an extended triplet-state lifetime of 13.4  $\mu$ s was observed because of the establishment of tripletstate equilibrium between the pyrenyl and Pt(II) coordination framework. When a Bodipy moiety was attached to the coordination framework of the Pt(II) complexes, a ping-pong energy transfer was observed, based on singlet FRET from Bodipy to the Pt(II) coordination framework (in 6.7 ps), followed by backward triplet energy transfer from the metal to Bodipy (in 148 ps).<sup>47</sup> Because of the large energy gap between the Bodipy (1.52 eV) and Pt(II) Schiff base (1.83 eV) triplet states, the T<sub>1</sub> state of the Bodipy-containing Pt(II) Schiff base complex is exclusively localized on Bodipy (lifetime: 103  $\mu$ s).<sup>47</sup> Pt(II) complexes containing multichromophores are rarely reported, and it is clear that diverse derivatives should be explored to fully study the photochemistry of Pt(II) Schiff base complexes.

Herein we attached an anthryl moiety to the Pt(II) Schiff base complex to study the excited-state dynamics with steadystate and time-resolved transient absorption spectroscopies. We found that, although there is no electronic coupling between the coordination framework and the anthryl appendant at the ground state, phosphorescence of the native Pt(II) Schiff base unit is significantly quenched. Intramolecular triplet-triplet energy transfer (TTET) from the Pt(II) coordination framework to the anthryl unit and reverse TTET (rTTET) were studied with femtosecond transient absorption (fs TA) spectroscopy, and triplet-state equilibrium was observed with fs TA and nanosecond transient absorption (ns TA) spectroscopy. The observed triplet-state lifetime of

the studied systems is much longer compared to the previously reported pyrenylplatinum(II) Schiff base complexes.

## RESULTS AND DISCUSSION

Molecular Design and Synthesis. Several Pt(II)- and Pd(II)-Salen complexes were previously studied and used for phosphorescence oxygen sensing and TTA-UC.<sup>49,50</sup> Previously, we reported a Pt(II) Schiff base complex connected with a Bodipy unit in order to increase its visible-light-harvesting ability.<sup>47</sup> The complex shows a Bodipy-localized triplet state, with a triplet lifetime (103  $\mu$ s) much longer compared to that of the native Pt(II) Schiff base  $(3.5 \ \mu s)$ . Efficient TTA-UC was observed (quantum yield: 10.0%) using this complex as a triplet PS.

Herein we designed anthrylplatinum(II) Schiff base complexes (Pt-2An and Pt-9An) in which the anthryl unit is directly connected to the Pt(II) Schiff base coordination framework at two different positions [the 2 and 9 positions of anthracene (An)].

An is selected because its triplet energy (ca. 1.85 eV) is close to the <sup>3</sup>MLCT state of the native Pt(II) Schiff base complex (1.90 eV). The native Pt(II) Schiff base complex shows an emissive <sup>3</sup>MLCT, and phosphorescence is at ca. 650 nm<sup>44,47,50</sup> with a lifetime of 3.5  $\mu$ s.<sup>47</sup> Interestingly, the native complexes show a small Stokes shift for the absorption/phosphorescence processes, of ca. 0.23 eV, which is guite rare in the case of phosphorescent transition-metal complexes.

In Pt-2An and Pt-9An (Scheme 1), the anthryl moiety is attached to the Pt(II) Schiff base coordination framework at two different substitution positions, with the aim of investigating the effect on the photophysical and photochemical properties. The synthesis of Pt-2An, Pt-9An, and the reference (Pt-Ph) transition-metal complexes is presented in Scheme 1. The Suzuki-Miyaura coupling reaction was employed to prepare the final products with good yield. The molecular structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR and high-resolution mass spectrometry (HRMS) spectral characterizations.

Steady-State UV-Vis Absorption and Luminescence Studies. The UV-vis absorption spectra of the Pt(II) Schiff base complexes (Pt-2An and Pt-9An) are presented in Figure 1 and compared with that of the reference compound Pt-Ph. For the reference Pt-Ph, a broad and weakly structured absorption band in the 420-600 nm region is observed, centered at 575 nm. This band is attributed to the S $_0$   $\rightarrow$ <sup>1</sup>MLCT/<sup>1</sup>IL (intraligand) transition.<sup>50</sup> This can be clearly recognized from time-dependent density functional theory



Figure 1. (a) UV-vis absorption spectra of Pt-9An, Pt-2An, Pt-Ph, DPA, and An ( $c = 1.0 \times 10^{-5}$  M). (b) Fluorescence emission spectra of the compounds (optically matched solutions were used;  $\lambda_{ex} = 350$ nm; in aerated toluene at 20 °C).

(TDDFT) studies (Figure 10), in which the  $S_0 \rightarrow S_1$  transition can be essentially described as a highest occupied molecular orbital (HOMO)  $\rightarrow$  lowest unoccupied molecular orbital (LUMO) transition. HOMO is distributed on the Pt(II) metal and the  $\pi$ -conjugation framework of the complex, and LUMO is localized on the ligand but not on the Pt(II) center.<sup>50</sup> This red-shifted absorption, compared to that of the ruthenium(II) poly(diimine) or the trans-bisphosphineplatinum(II) bis-

(acetylide) complexes, is beneficial for applications. Moreover, a stronger structured absorption band is observed in the 300-430 nm range, which is attributed to the  $\pi - \pi^*$  transition of the ligands.<sup>50</sup>

The absorption spectrum of **Pt-9An** in the visible range is similar to that of **Pt-Ph**, suggesting that there are no significant electronic interactions between the Pt(II) Schiff base coordination framework and anthryl moiety at the ground state. Pt-2An shows a slightly larger molar absorption coefficient ( $\varepsilon$  = 16000 M<sup>-1</sup> cm<sup>-1</sup> at 575 nm) than Pt-Ph ( $\varepsilon$ = 11000  $M^{-1}$  cm<sup>-1</sup> at 575 nm). Also, in this case the absorption bands centered at 488 and 575 nm are assigned as a  $S_0 \rightarrow MLCT/IL$  transition, whereas the absorption band at 396 nm is due to the Schiff base ligand, similar to Pt-Ph. In the case of Pt-9An and Pt-2An, this band has some contribution from An as well.<sup>51</sup> The compounds were analyzed for absorbance in solvents with increasing polarity (Figure S14). The absorption spectra are solvent-polarity-independent, suggesting that the difference of the dipole moments of the ground and Franck-Condon singlet states is small.

The fluorescence spectra of the compounds in aerated toluene are presented in Figure 1b. The reference compound 9,10-diphenylanthracene (DPA) is highly fluorescent with an emission maximum centered at 408 nm, while almost no fluorescence was observed for all of the Pt(II) complexes.

Phosphorescence of the complexes was studied upon excitation at 530 nm ( $S_0 \rightarrow {}^1MLCT$  transition) under different atmospheres (Figure 2). In general, phosphorescence of the



Figure 2. Photoluminescence spectra of (a) Pt-9An, (b) Pt-2An, and (c) Pt-Ph under  $N_2$  and air atmospheres. (d) Phosphorescence spectra of Pt-Ph, Pt-9An, and Pt-2An. Optically matched solutions were used in each panel (A = 0.07 at 530 nm;  $\lambda_{ex}$  = 530 nm; in toluene at 20 °C).

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complexes in an aerated solution is substantially quenched, especially for **Pt-9An** and **Pt-2An** (Figure 2a,b), whereas for **Pt-Ph**, residual phosphorescence in aerated solution is still noticeable. This result indicates that the phosphorescence lifetimes of **Pt-9An** and **Pt-2An** are much longer than that of the native Pt(II) complex **Pt-Ph**.<sup>50,52</sup> It is interesting to note that the phosphorescence profiles of the three complexes are virtually the same, concerning the emission wavelength and vibrational progression, suggesting that the emissive triplet state is the same <sup>3</sup>MLCT state for all three complexes, which is further demonstrated by analysis of the spin-density surfaces of the lowest triplet excited states (Figure 11).

**Pt-Ph** has the highest phosphorescence quantum yield ( $\Phi_p = 11\%$ ); for **Pt-2An** ( $\Phi_p = 4.0\%$ ) and **Pt-9An** ( $\Phi_p = 1.0\%$ ), the phosphorescence is weaker (Figure 2d and Table 1).

|            | $\lambda_{abs}^{a}$ | $\varepsilon^{b}$ | $\lambda_{\rm em}^{a}$ | $\Phi_p^{\ c}$ | $	au_{ m p}{}^d$         | $\Phi_{\Delta}^{\ e}$ | $\tau_{\rm T}^{f}$ |
|------------|---------------------|-------------------|------------------------|----------------|--------------------------|-----------------------|--------------------|
| Pt-<br>9An | 392,<br>576         | 4.7,<br>1.0       | 653                    | 1.0            | 2.8 (84%), 17.3<br>(16%) | 63                    | 63                 |
| Pt-<br>2An | 396,<br>575         | 5.9,<br>1.6       | 658                    | 4.0            | 3.4 (87%), 18.2<br>(13%) | 77                    | 103                |
| Pt-Ph      | 393,<br>575         | 4.4,<br>1.1       | 655                    | 11             | 3.7                      | 48                    | 4.0                |
| DPA        | 395                 | 2.1               | 428                    | g              | g                        | g                     | g                  |
| An         | 379                 | 1.5               | 402                    | g              | g                        | 70                    | 450                |

<sup>*a*</sup>In toluene (1.0 × 10<sup>-5</sup> M) at 20 °C in nanometers. <sup>*b*</sup>Molar absorption coefficient at the absorption maxima.  $\varepsilon = 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . <sup>(2</sup>Phosphorescence quantum yield, in percent. <sup>*d*</sup>Phosphorescence lifetime, in microseconds. <sup>*e*</sup>Quantum yield of singlet oxygen (<sup>1</sup>O<sub>2</sub>) in percent; 2,6-diiodobis(styryl)-Bodipy ( $\Phi_{\Delta} = 59\%$  in toluene;  $\lambda_{ex} = 580 \text{ nm}$ ) was used as the standard. <sup>*f*</sup>Intrinsic triplet-state lifetime, determined based on a TTA kinetics model, in microseconds. <sup>*g*</sup>Not applicable.

Phosphorescence of the Pt(II) Schiff base complex **Pt-Ph** indicates that the <sup>3</sup>MLCT state energy is ca. 1.88 eV (approximated with the phosphorescence maxima). It has been reported that the triplet energy of An is ca. 1.85 eV.  $^{53,54}$ 

Because these two triplet states are close in energy, we expect the occurrence of TTET from the <sup>3</sup>MLCT state to the <sup>3</sup>An state, causing some quenching of the <sup>3</sup>MLCT phosphorescence. This postulation is in agreement with the observation that **Pt-9An** and **Pt-2An** show weaker phosphorescence than the native **Pt-Ph** (Table 1). Because of the close energies of <sup>3</sup>MLCT and <sup>3</sup>An, there is a rTTET from <sup>3</sup>An to <sup>3</sup>MLCT, <sup>55</sup> with the establishment of triplet-state equilibrium.<sup>25,50,56,57</sup>

Interestingly, the Stokes shift of the platinum(II) N.N'bis(3,5-di-tert-butylsalicylidene)-1,2-benzenediamine Schiff base complex is exceptionally small (0.23 eV), much smaller than that observed for the most typical phosphorescent transition-metal complexes, such as ruthenium(II) poly-(diimine) complexes (0.68 eV)<sup>36</sup> or the C^N cyclometalated iridium(III) complexes such as  $Ir(ppy)_3$  (ppy = 2-phenyl-pyridine; the typical Stokes shift is 1.22 eV).<sup>37,38,58</sup> Smaller Stokes shifts mean smaller energy loss during the photoexcitation/ISC/phosphorescence cascade photophysical processes, which is beneficial for the application of triplet PSs in photocatalysis or photon upconversion, etc.<sup>41-59</sup> It should be pointed out that the platinum(II) N,N'-bis(salicylidene)-1,2alkyldiamine Schiff base complexes (i.e., alkylamine, instead of arylamine, was used for preparation of the ligands) show a much larger Stokes shift (ca. 0.7 eV),<sup>44,49</sup> which is similar to the normal phosphorescent transition-metal complexes. For instance, a Pd(II) Schiff base (derived from diaminomaleonitrile) shows a Stokes shift of 0.47 eV.<sup>49</sup>

The triplet-state equilibrium should be affected by variation of the temperature.<sup>60</sup> By lowering the temperature, rTTET should be inhibited, causing the quenching of phosphorescence for **Pt-9An** and **Pt-2An**, which also indicates that the emissive triplet state is higher in energy than the dark triplet state, i.e., the <sup>3</sup>An state. The effect of the temperature on the phosphorescence intensity and lifetime of the complexes is presented in Figure 3. For **Pt-Ph**, the phosphorescence intensity is enhanced by 210% at decreased temperature (from 298 to 178 K; Figure 3c), which is due to the inhibited nonradiative decay at lower temperature.<sup>61,62a</sup> For **Pt-9An** and



**Figure 3.** Temperature-dependent phosphorescence spectra of (a) **Pt-9An**, (b) **Pt-2An**, and (c) **Pt-Ph** and phosphorescence lifetimes of (d) **Pt-9An**, (e) **Pt-2An**, and (f) **Pt-Ph** at a given temperature, excited with a 510 nm picosecond-pulsed diode laser,  $\lambda_{det} = 650$  nm, and  $c = 1.0 \times 10^{-5}$  M in deaerated toluene.

**Pt-2An**, interestingly, the phosphorescence intensity is reduced at lower temperature, which is anomalous (Figure 3a,b).

The effect of the temperature on the phosphorescence lifetime of the complexes was also studied (Figure 3d–f). For **Pt-Ph**, the phosphorescence lifetimes did not change in the range of 298–178 K (Figure 3f), and a lifetime of ca. 3.7  $\mu$ s with a monoexponential decay was observed. Usually the phosphorescence lifetimes are prolonged at lower temperature. Unchanged phosphorescence lifetimes were previously observed for Pt(II)/Ir(III) complexes, which show a strong spin–orbit coupling effect.<sup>62b,c</sup> For both **Pt-9An** and **Pt-2An**, the phosphorescence decays are biexponential. For **Pt-9An** at 298 K, two components, 2.8  $\mu$ s (84%) and 17.3  $\mu$ s (16%), were observed.

When the temperature was decreased from 298 to 178 K, the lifetime of the long-lived component reduced from 17.3 to 11.0  $\mu$ s, and the proportion decreased (from 16% to 3%). These observations are in agreement with the occurrence of emission from an emissive excited state lying slightly above a dark state, similar to the scenario of thermally activated delayed fluorescence.<sup>63–65</sup> The results are similar for **Pt-2An** (Table 2).

Table 2. Temperature-Dependent Phosphorescence Lifetimes  $^{a}$ 

|               | $	au_{ m p}/\mu{ m s}$ |                      |  |  |  |  |
|---------------|------------------------|----------------------|--|--|--|--|
| temperature/K | Pt-9An                 | Pt-2An               |  |  |  |  |
| 298           | 2.8 (84%)/17.3 (16%)   | 3.4 (87%)/18.2 (13%) |  |  |  |  |
| 268           | 2.8 (86%)/15.3 (14%)   | 3.4 (88%)/16.0 (12%) |  |  |  |  |
| 238           | 2.8 (89%)/14.3 (11%)   | 3.5 (90%)/13.3 (10%) |  |  |  |  |
| 208           | 2.9 (92%)/12.6 (8%)    | 3.4 (93%)/12.4 (7%)  |  |  |  |  |
| 185           | 2.8 (95%)/11.6 (5%)    | 3.6 (95%)/11.2 (5%)  |  |  |  |  |
| 178           | 2.8 (97%)/11.0 (3%)    | 3.4 (96%)/10.8 (4%)  |  |  |  |  |
| ani 1         | 1.6                    | 510 · 1 1            |  |  |  |  |

<sup>a</sup>Phosphorescence lifetime, excited with a 510 nm picosecond-pulsed diode laser and  $c = 1.0 \times 10^{-5}$  M in deaerated toluene.

**Electrochemical Study.** The electrochemical properties of the anthrylplatinum(II) Schiff base complexes were analyzed with cyclic voltammetry (Figure 4). An shows a reversible oxidation wave at +1.11 V [vs ferrocene/ferrocenium (Fc/Fc<sup>+</sup>)], and no reduction peak was observed in the studied potential range. **Pt-Ph** has two reversible oxidation peaks at +0.53 and +1.00 V and a reversible reduction wave at -1.96 V. For **Pt-9An**, oxidation peaks at +0.55, +0.89, and +1.14 V and



**Figure 4.** Cyclic voltammograms of (a) **Pt-9An** and (b) **Pt-2An** with the reference compounds An and **Pt-Ph**. Fc was used as an internal reference, and the value of the oxidation peak was set as 0 V. Reaction occurred in a N<sub>2</sub>-saturated dichloromethane solution containing 1.0 mM PSs and 0.10 M Bu<sub>4</sub>[NPF<sub>6</sub>] as the supporting electrolyte. Scan rate: 100 mV s<sup>-1</sup>, 20 °C.

a reduction wave at -1.98 V were observed. These first two oxidation peaks and the reduction peak are clearly assigned to the Pt(II) Schiff base coordination framework, and the third oxidation peak at +1.14 V is attributed to the anthryl moiety. Similarly for **Pt-2An**, oxidation peaks at +0.51, +0.84, and +1.10 V and a reversible reduction peak located at -1.95 V were observed. The electrochemical parameters of the compounds are presented in Table 3.

The Gibbs free-energy changes of the intramolecular photoinduced electron-transfer (PET) process of the anthrylplatinum(II) Schiff base complexes between An and <sup>3</sup>MLCT of the Pt(II) Schiff base coordination framework were calculated (Table 3),  $^{66-68}$  The Gibbs energy of PET ( $\Delta G_{CS}$ ) values for putative electron transfer are positive, indicating that the intramolecular PET process between An and <sup>3</sup>MLCT of the Pt(II) Schiff base coordination framework in Pt-9An and Pt-2An is thermodynamically unfavorable. The conclusion agrees well with the luminescence emission spectra that phosphorescence was not quenched by the charge-separated state (Figure 2d). The charge-transfer-state energy levels  $(E_{CTS})$  were also calculated and showed a decreasing trend with higher solvent polarity. The  $E_{\text{CTS}}$  value even in toluene is higher than that of <sup>3</sup>MLCT of the Pt(II) Schiff base coordination framework, which further indicated the intramolecular PET process is thermodynamically unfavorable.

**fs TA Spectroscopy.** In order to study the excited-state dynamics, fs TA measurements were performed in toluene (Figures 5 and 6). All of the complexes were excited at 575 nm, on the  $S_0 \rightarrow {}^1MLCT$  band. The data have been analyzed by global analysis, using a sequential model.

For Pt-Ph, upon photoexcitation at 575 nm (Figure S19), a broad intense excited-state absorption (ESA) band appeared in the range of 350-550 nm, and a less intense structured band in the 550-750 nm region was observed. These signals are assigned as  $S_1 \rightarrow S_n$  transitions. The 350–550 nm ESA band intensity partially decreased in 0.7 ps. Meanwhile, the features in the 550-700 nm range became more defined, assuming the typical absorption profile assigned to the <sup>3</sup>MLCT state, presenting a maximum at about 615 nm.<sup>47,69</sup> The intensity of the signal slightly decreased in about 290 ps and increased in 620 ps. The signal intensity did not decay on the time scale spanned by our spectrometer (3.3 ns). The photophysical processes of Pt-Ph can thus be interpreted in terms of a  $^{\hat{1}}$ MLCT  $\rightarrow$   $^{3}$ MLCT transition, occurring in less than 1 ps, followed by a subsequent vibrational/structural relaxation of the triplet state (Figure S19b), similar to that previously described for Pt(II) Schiff base complexes reported in the literature (<1 ps).<sup>47,69</sup> For Pt-9An, evolution-associated difference spectroscopy (EADS) spectra obtained from global analysis (Figure 5) already present some features attributable to the <sup>3</sup>MLCT state in the 550–700 nm region. We thus assign the initial spectral component to a mixed <sup>1</sup>MLCT/<sup>3</sup>MLCT state, implying that ISC partially occurs at a time scale faster than the time resolution of our measurement. The intense ESA band observed in the 400-500 nm range sharpens on the 0.8 ps time scale, and on this same time scale, the <sup>3</sup>MLCT features at longer wavelengths become more defined (evolution from black to red EADS in Figure 5b). The intense band on the blue side of the spectrum becomes even sharper on the following 4.8 ps time scale (evolution from red to green EADS in Figure 5c), while the broad structured band at 550-700 nm partially decreases in intensity on this same time scale. The signal shows only a small evolution on the following 450–490 ps time scale,

Table 3. Redox Potentials and Gibbs Free-Energy Changes of the Charge Separation ( $\Delta G_{CS}$ ) and Energy Level of the Charge-Transfer States ( $E_{CTS}$ ) of the Compounds<sup>*a*</sup>

|          |                     |                      | $\Delta G_{ m CS}/ m eV$ |      |      | $E_{ m CTS}/ m eV$ |      |      |
|----------|---------------------|----------------------|--------------------------|------|------|--------------------|------|------|
| compound | $E_{\rm OX}/{ m V}$ | $E_{\rm RED}/{ m V}$ | TOL                      | DCM  | ACN  | TOL                | DCM  | ACN  |
| An       | +1.11               | а                    | с                        | с    | С    | с                  | с    | с    |
| Pt-Ph    | +0.53, +1.00        | -1.96                | с                        | с    | С    | с                  | с    | С    |
| Pt-9An   | +0.55, +0.89, +1.14 | -1.98                | 0.59                     | 0.43 | 0.38 | 2.49               | 2.33 | 2.28 |
| Pt-2An   | +0.51, +0.84, +1.10 | -1.95                | 0.69                     | 0.42 | 0.34 | 2.57               | 2.30 | 2.22 |

<sup>*a*</sup>Cyclic voltammetry in N<sub>2</sub>-saturated dichloromethane containing 0.10 M Bu<sub>4</sub>[NPF<sub>6</sub>] as the supporting electrolyte. The counter electrode is a Pt electrode, the working electrode is a glassy carbon electrode, and the Ag/AgNO<sub>3</sub> couple is the reference electrode. Fc is used as an internal reference, and the value of the oxidation peak is set as 0 V.  $E_{00}$  is the triplet excited-state energy level approximated with the phosphorescence wavelength. TOL = toluene, DCM = dichloromethane, and ACN = acetonitrile. <sup>*b*</sup>Not observed. <sup>*c*</sup>Not applicable.



Figure 5. (a) fs TA spectra of Pt-9An in toluene. (b) Corresponding EADS spectra obtained by global analysis with a sequential model. (c) Decay kinetics at 440 nm. The short time scale is shown in the inset.  $\lambda_{ex} = 575$  nm at 20 °C.



Figure 6. (a) fs TA spectra of Pt-2An in toluene. (b) Corresponding EADS spectra obtained by global analysis with a sequential model. (c) Decay kinetics at 440 and 615 nm.  $\lambda_{ex}$  = 575 nm at 20 °C.

and the intense band peaking at 435 nm broadens on the red side (around 460 nm) in 444 ps (evolution from green to blue EADS) and sharpens in 495 ps, slightly decreasing in intensity on the following 495 ps time scale. The final spectral component has a lifetime longer than the maximum pumpprobe delay accessed by our setup (3 ns). Looking to the spectral changes occurring, in particular, in the 400-500 nm region, we propose that the <sup>3</sup>An state is formed in Pt-9An upon TTET, with the <sup>3</sup>MLCT state of the Pt(II) Schiff base coordination center as the precursor. Our conclusion is based on several observations. It is known that the <sup>3</sup>\*An state presents a sharp ESA in the range of 380-460 nm;<sup>70,71</sup> thus, a  ${}^{3}MLCT \rightarrow {}^{3}An$  process would result in the development of an ESA centered at 435 nm and the decay of the <sup>3</sup>MLCT state broad band at >600 nm, as is indeed observed.<sup>72,73a</sup> The <sup>3</sup>MLCT state energy (ca. 1.97 eV for Pt-9An, approximated with the phosphorescence maxima) is slightly higher than the triplet energy of An (ca. 1.85 eV, approximated with the phosphorescence maxima in the reported literature); therefore,

a <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>An TTET is thermodynamically feasible.<sup>32,53,54</sup> The ESA band centered at 435 nm does not totally decay on the time scale of our measurements (3.3 ns), which demonstrates the existence of a long-lived <sup>3</sup>An state.

The photophysical processes occurring for **Pt-9An** can be resumed with a sequential <sup>1</sup>MLCT  $\rightarrow$  <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>An scheme, followed by some relaxation of the <sup>3</sup>An state. The EADS spectra obtained by global analysis with this sequential model, reported in Figure 5c, show that <sup>3</sup>An ESA slightly broadens on its red side (450–460 nm) on the 444 ps time scale and sharpens on the following 495 ps time scale. Moreover, the spectral components attributed to the <sup>3</sup>An state (green/blue/ magenta lines) have residual intensity in the 600–800 nm range, where the <sup>3</sup>MLCT state absorbs. These observations indicate that a mixture of <sup>3</sup>An and <sup>3</sup>MLCT states is present after about 5 ps for **Pt-9An**. Room temperature phosphorescence measured for the <sup>3</sup>MLCT state also supports the coexistence of <sup>3</sup>An and <sup>3</sup>MLCT states up to the long time delay regime (Figure 2a).

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-0.03

-0.06

400 500

#### **Inorganic Chemistry**

We also measured the fs TA spectra of Pt-2An in toluene (Figure 6a). The transient spectra of this compound are qualitatively similar to those of the previous complex, as expected, although some difference is evident in the kinetics of the observed processes. Also in this case, an intense ESA band in the 400-480 nm range is observed upon excitation at 575 nm, together with some lower-intensity bands in the 500-550 and >600 nm ranges. On the basis of the previous discussion, we assign this component to a mixed <sup>1</sup>MLCT/<sup>3</sup>MLCT state. Within 0.4 ps, the broad features at wavelengths >600 nm increase in intensity, implying further population of the <sup>3</sup>MLCT state. On the same time scale, the intense band on the blue side of the explored spectral window sharpens, suggesting the concomitant formation of some <sup>3</sup>An through a TTET process. The intensity of the overall spectral signatures increases on the following 55 ps time scale, without substantial change in the band shape. Finally, in the evolution toward the final spectral component, we observe an increase in the intensity of the broad band at >600 nm, assigned to the <sup>3</sup>MLCT, and a corresponding decrease in the intensity in the 400-480 nm spectral range, which we interpret in terms of rTTET from <sup>3</sup>An to <sup>3</sup>MLCT. Furthermore, we also observe the rise of a sharp band peaking at 737 nm in the final spectral component, which could indicate the formation of some An cation.<sup>70,71</sup> Considering that the energy of the <sup>3</sup>MLCT state (ca. 1.91 eV for Pt-2An, approximated with the phosphorescence maxima) is higher than the triplet energy of An (ca. 1.85 eV, approximated with the phosphorescence maxima in the reported literature).<sup>32,53,54</sup> and that <sup>3</sup>MLCT phosphorescence is observed at room temperature (Figure 2), we propose that also in this case an equilibrium between the <sup>3</sup>MLCT and <sup>3</sup>An states is established, similar to Pt-9An, although on a slower time scale of 1.7 ns. Looking to the relative intensities of the ESA attributed to <sup>3</sup>An and <sup>3</sup>MLCT, we infer that the equilibrium is more shifted toward <sup>3</sup>MLCT for Pt-2An compared to Pt-9An. This observation indicates that localization of the triplet state is influenced by structural factors, most probably because the different linkage between the metal framework and An modifies the overlap between the molecular orbitals localized on the two moieties, and consequently the electronic coupling among them.

ns TA Spectroscopy and Further Determination of the Triplet Excited State. ns TA spectroscopy was performed to study the triplet excited states (Figure 7). For **Pt-Ph**, pulsed-laser excitation into the  $S_0 \rightarrow {}^1MLCT$ absorption band (490 nm) induces the appearance of a broad ESA band in the range of 400–800 nm (Figure 7c), with a prominent peak centered at 440 nm and some minor bands centered at 545 and 615 nm, respectively. Note that this ESA band, due to the  $T_1 \rightarrow T_n$  transition of the <sup>3</sup>MLCT state,<sup>73b</sup> overlaps with the ground-state bleaching bands as well as the phosphorescence band. In order to confirm the transitions of the observed ESA bands, spectroelectrochemical measurements were performed (Figure S24); however, the transitions derived from the oxidized metal complex and the reduced ligand could not be differentiated clearly. Moreover, the spectra were recorded with the phosphorescence correction mode of the spectrometer; thus, attenuation of the ESA band in the range of 600-800 nm by phosphorescence is eliminated. The ESA band of the currently recorded spectra is stronger than what we previously reported.<sup>47</sup> It is important to obtain the information of the ESA band of the triplet state of the



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0.015

10 20 Time / μs

10 20 Time / μs

30

30

Figure 7. (a) Time-resolved ns TA spectra of Pt-9An and (b) the decay trace at 440 nm with a biexponential feature. The lifetime contains two components of 4.8  $\mu$ s (14%) and 18  $\mu$ s (86%). (c) Time-resolved ns TA spectra of **Pt-Ph** and (d) the experimental decay trace at 440 nm with a monoexponential feature (3.6  $\mu$ s). The lifetimes presented in parts b and d are the intrinsic lifetime ( $\tau_{\text{intrinsic}}$ ), obtained by fitting the decay traces with a kinetic model with the TTA quenching effect considered.  $c = 2.0 \times 10^{-5}$  M in deaerated toluene and  $\lambda_{ex} = 490$  nm at 20 °C.

600 700 8006

Wavelength / nm

native Pt(II) Schiff base coordination framework because we use it for analysis of the triplet-state equilibrium. The tripletstate lifetime of the complex is 4.0  $\mu$ s, similar to our previous observation  $(3.5 \ \mu s)$ .<sup>47</sup>

In the case of Pt-9An, upon excitation at 490 nm, a sharp intense ESA peak centered at 430 nm is observed (Figure 7a),<sup>73a</sup> which is the typical ESA band of the <sup>3</sup>An state.<sup>73a,74a</sup> It should be pointed out that the ESA band in the range of 600-800 nm is not a feature of the <sup>3</sup>\*An state and is instead attributed to the triplet state of the Pt(II) Schiff base coordination framework, as supported by ns TA of the reference Pt-Ph (Figure 7c).

On the basis of a comparison with the spectra measured for the reference complex, we conclude that the triplet state of Pt-9An shows spectral features of both the <sup>3</sup>MLCT and <sup>3</sup>An states; i.e., an equilibrium is established through TTET and rTTET processes, as shown by the fs TA spectra (Figure 5). The triplet-state lifetime was determined as 163  $\mu$ s by using the kinetic model with the TTA self-quenching effect considered.<sup>746</sup>

The decay traces at 440 and 626 nm were monitored separately for Pt-9An, which is related to the <sup>3</sup>An and <sup>3</sup>MLCT states, respectively, and similar lifetimes of 16 and 19  $\mu$ s were obtained  $(2 \times 10^{-5} \text{ M})$ , respectively (Figure S20a); thus, TTET and rTTET should be much faster than 7 ns (the instrument response function of the ns TA spectrometer). This is supported by fs TA spectral studies.

For Pt-2An, the ESA bands of both the <sup>3</sup>MLCT and <sup>3</sup>An states were observed (Figure 8a), indicating triplet-state equilibrium. Moreover, on the basis of the amplitude ratio of the ESA bands at ca. 440 and 650 nm, the ratios for Pt-9An and Pt-2An are 4.0 and 1.7, respectively, and we suggest that the equilibrium is more shifted toward the <sup>3</sup>MLCT state for Pt-2An, compared to Pt-9An. This is a rare example where the



**Figure 8.** (a) Time-resolved ns TA spectra of **Pt-2An** and (b) the experimental decay kinetics at 440 nm with a biexponential feature. The lifetime contains two components of 19  $\mu$ s (9.5%) and 84  $\mu$ s (90.5%). The lifetime presented in the figure is the intrinsic lifetime ( $\tau_{\text{intrinsic}}$ ) obtained by fitting the decay curves with a kinetic model with the TTA quenching effect considered.  $c = 1.0 \times 10^{-5}$  M in deaerated toluene and  $\lambda_{\text{ex}} = 490$  nm at 20 °C.

geometry of analogue complexes has a significant impact on the excited-state dynamics of multichromophore transitionmetal complexes.

We observed that the equilibrium between <sup>3</sup>MLCT and <sup>3</sup>An is established on a slower time scale in the case of **Pt-2An** compared to **Pt-9An** (see the previous section). Previously, an <sup>3</sup>An/<sup>3</sup>MLCT state equilibrium was observed with the ruthenium(II) complex based on tridentate polypyridine ligands. In that case, the <sup>3</sup>An state lies below the <sup>3</sup>MLCT state by 0.05 eV (430 cm<sup>-1</sup>) and the rTTET time constant is 1.2 ns.<sup>75</sup>

The fraction of  ${}^{3}MLCT/{}^{3}An$  states and the energy gap between two states were obtained from ns TA spectroscopy and luminescence decays in the Supporting Information, demonstrating that the energies of  ${}^{3}MLCT/{}^{3}An$  states are different for **Pt-2An** and **Pt-9An**.

In a ruthenium(II) tris(bipyridine) complex appended with the anthryl unit by an amide bond, the <sup>3</sup>An state lies below the <sup>3</sup>MLCT state by 0.22 eV (1748 cm<sup>-1</sup> in ACN), and the forward TTET process is slow (67  $\mu$ s), based on phosphorescence lifetime and quantum yield analysis.<sup>76a</sup>

**Theoretical Computations.** DFT and TDDFT computations were applied to rationalize the photophysical properties. The optimized ground-state geometries of anthrylplatinum(II) Schiff base complexes are shown in Figure 9. Previously, the single-crystal molecular structure of **Pt-Ph** was reported, and the Pt(II) Schiff base unit has a planar geometry.<sup>47</sup>

For **Pt-9An** and **Pt-2An**, the respective Pt(II) Schiff base and anthryl units all have a planar configuration, but the two units are twisted against each other. The restriction of the 9anthryl-attached complex **Pt-9An** is larger, giving a larger orthogonal dihedral angle of 77° than that of 37° for **Pt-2An**.

The frontier molecular orbitals were also analyzed. On the basis of the calculated energy of the molecular orbitals (Figure 10), the attachment of an anthryl group does not change the HOMO and LUMO energies significantly. For **Pt-9An**, the HOMO is distributed on the Pt(II) coordination center and the Schiff base ligands, and the LUMO is only localized on the Schiff base ligands, without any distribution from the Pt(II) coordination center or the An moiety.

These distributions were similar to those in **Pt-Ph**. The HOMO and LUMO of **Pt-2An** exhibit similar distributions on the Pt(II) Schiff base moiety but with partial distribution on the An moiety, especially for the LUMO. These results indicate that the electronic coupling between the An and Pt(II) Schiff



**Figure 9.** Optimized ground-state  $(S_0)$  geometries of (a) **Pt-9An** and (b) **Pt-2An**. (c) Dihedral angles between the An moiety and Pt(II) Schiff base coordination framework. Calculated at the DFT//B3LYP/ GENECP level with *Gaussian 09W*.

base units at the ground state for **Pt-2An** is larger than that for **Pt-9An**.

The spin-density surfaces of the lowest triplet excited states (Figure 11) were calculated for **Pt-9An** and **Pt-2An**. The spin densities were delocalized on both the Pt(II) Schiff base and An moieties for these two complexes. These results are in accordance with the ns TA spectra (Figures 7a and 8a), for which both the ESA bands of <sup>3</sup>MLCT and <sup>3</sup>An were observed, indicating the possible triplet-state equilibrium in these two complexes.

Jablonski Diagram. The photophysical processes of the complexes upon photoexcitation are summarized in Scheme 2. Upon photoexcitation of **Pt-9An** at 575 nm, <sup>1</sup>MLCT state is populated, which has a lifetime of <1 ps, then ultrafast ISC occurs, and the <sup>3</sup>MLCT state is formed, followed by TTET with formation of the <sup>3</sup>An state within 4.8 ps. The establishment of <sup>3</sup>An/<sup>3</sup>MLCT state equilibrium was within about 440 ps. Compared with **Pt-9An**, the <sup>3</sup>An/<sup>3</sup>MLCT state equilibrium for **Pt-2An** is established on a slower time scale (the rates of TTET and rTTET are 55 ps and 1.7 ns, respectively), which was attributed to the slightly larger energy gap among the <sup>3</sup>An and <sup>3</sup>MLCT state energy gap is ca. 216 cm<sup>-1</sup>.

The phosphorescence quantum yields of the anthrylcontaining complexes are lower than those of the native Pt(II) Schiff base complex. This result implies that there is a dark triplet excited state in equilibrium with the emissive <sup>3</sup>MLCT state. The triplet-state equilibrium is further supported by temperature-dependent phosphorescence studies. The dark state was identified as the <sup>3</sup>An state by ns/fs TA spectroscopy, which also shows the existence of triplet-state equilibrium. Ultrafast spectroscopy further showed that the equilibrium is established on a faster time scale for **Pt-9An** (ca. 440 ps) compared to **Pt-2An** (1.7 ns) and that it is more shifted toward <sup>3</sup>MLCT for the latter complex. This is an interesting finding, indicating that a subtle variation in the substitution position of



Figure 10. Frontier molecular orbitals and energy of the molecular orbitals of Pt-9An, Pt-2An, and Pt-Ph, calculated at the B3LYP/GENECP level with *Gaussian 09W*.



Figure 11. Spin-density surfaces of the triplet excited state of (a) Pt-9An and (b) Pt-2An at the optimized  $T_1$  triplet-state geometry (isovalue = 0.0004 au), calculated by the TDDFT//B3LYP/ GENECP level with *Gaussian 09W*.

the anthryl appendant produces notable effects on the photophysical properties.

**TTA-UC.** The two complexes **Pt-9An** and **Pt-2An** exhibited efficient ISC (singlet oxygen quantum yield  $\Phi_{\Delta} = 63\%$  and 77% for **Pt-9An** and **Pt-2An**, respectively) and longer triplet-state lifetimes (intrinsic lifetimes  $\tau_{\rm T} = 163$  and 103  $\mu$ s **Pt-9An** and **Pt-2An**, respectively) compared to the previously reported native and aryl-appendant Pt(II) Schiff base complexes ( $\tau_{\rm T} = 2.9-21 \ \mu$ s).<sup>44,50</sup> More importantly, we observed an unusually small Stokes shift for photoexcitation/phosphorescence of the Pt(II) Schiff base coordination framework (0.23 eV). We demonstrated this advantage by using the Pt(II) Schiff base complexes as triplet PSs to increase the anti-Stokes shift of TTA-UC (Figure 12). Previously, we reported a Pt(II) Schiff base complex appended with a Bodipy unit for TTA-UC, showing an upconversion quantum yield ( $\Phi_{\rm UC}$ ) of 10%.<sup>47</sup>

For **Pt-9An** alone, a weak emission in the range of 600–800 nm was observed upon excitation with 589 nm continuous-

wave laser (Figure 12). In the presence of the triplet acceptor perylene, a strong blue emission in the range of 420-550 nm was observed, which was assigned as the upconverted perylene fluorescence emission. A similar result was observed for Pt-2An (Figure 12).

The normalized upconversion quantum yield<sup>76b</sup> of **Pt-9An** was determined as 10%, which is similar to the result obtained with the Pt(II) Schiff base–Bodipy complex ( $\Phi_{UC} = 10\%$ ), but in the Bodipy-appended Pt(II) Schiff base complex, the excitation was at 510 nm.<sup>47</sup> Upon 589 nm laser excitation, the upconversion quantum yield was 1.0%, which is attributed to the lower triplet-state energy of that complex.<sup>47</sup> In the case of **Pt-2An**, a higher  $\Phi_{UC}$  of 15% was observed. The upconversion is visible to the naked eye (Figure 12b). The anti-Stokes shift for these complexes is up to 0.75 eV, and the upconversion quantum yield with the current complex is 10 times higher because of the higher T<sub>1</sub> state energy (ca. 1.9 eV) of the complexes prepared in the current manuscript, compared to the Pt(II) Schiff base–Bodipy complex reported previously (triplet-state energy: 1.52 eV).<sup>47</sup>

Using a triplet acceptor showing a  $T_1$  state energy similar to that of the triplet PS will increase the anti-Stokes shift of TTA-UC further.<sup>76c</sup> Therefore, we also studied TTA-UC with DPA as the triplet acceptor/emitter (Figure S22). The upconversion quantum yield is 12% for **Pt-9An** and 19% the **Pt-2An**, and the anti-Stokes shift is 0.92 eV.

Herein we propose a novel approach to increasing the anti-Stokes shift of TTA-UC with the Pt(II) Schiff base complexes studied herein, which shows a desired small loss of excitation energy. For most of the reported PSs, the energy loss of photoexcitation/phosphorescence is large because of the large Stokes shift (this is due to the large electron exchange energy of the planar  $\pi$ -conjugation systems).<sup>61</sup> Previously, an osmium(II) tris(diimine) complex was used as the triplet PS Scheme 2. Jablonski Diagram Showing the Photophysical Processes in (a) Pt-9An and (b) Pt-2An upon Photoexcitation



<sup>*a*</sup>The energy levels of the <sup>1</sup>MLCT state originate from the UV-Vis absorption spectra. The energy level of the charge-separated state considering the intramolecular PET process of the anthrylplatinum(II) Schiff base complexes between the An and <sup>3</sup>MLCT states of the Pt(II) Schiff base coordination framework were obtained by electrochemical calculation. The energy levels of the <sup>3</sup>MLCT state were obtained from 77 K phosphorescence. The energy gap between the <sup>3</sup>MLCT and <sup>3</sup>An/<sup>3</sup>\*An states were obtained from ns TA spectroscopy and the phosphorescence decays in the Supporting Information, and T<sub>3</sub> and T<sub>4</sub> were calculated at the TDDFT//B3LYP/GENECP level with *Gaussian 09W*.



**Figure 12.** (a) Luminescence spectra of TTA-UC with **Pt-9An** and **Pt-2An** as triplet PSs and perylene (Py) as the triplet acceptor. (b) Photographs of the emissions of triplet PSs alone and the upconversion. CIE diagram of the upconversion with (c) **Pt-9An** and (d) **Pt-2An** as triplet PSs, respectively. Excitation with a 589 nm continuous-wave laser and  $c(PSs) = 1.0 \times 10^{-5}$  M and  $c(acceptor) = 4.0 \times 10^{-5}$  M in deaerated toluene at 25 °C.

for TTA-UC, which shows a small Stokes shift (0.16 eV for absorption and phosphorescence emission) because of its weakly allowed  $S_0 \rightarrow T_1$  transition.<sup>41</sup> With that Os(II) complex, an anti-Stokes shift of 0.86 eV was achieved in TTA-UC. However, the triplet-state lifetime of that Os(II) complex is short (12 ns), and the upconversion quantum yield is very low ( $\Phi_{UC} = 0.0014\%$ ).<sup>41</sup> Modifications of the Os(II) coordination motif could address this disadvantage to some extent.<sup>42,43,59,77</sup> In addition, we proposed using the red-shifted charge-transfer (CT) absorption band of electron donor/acceptor dyads for TTA-UC, but the charge-transfer absorption band is weak, and only a 0.37 eV anti-Stokes shift was achieved.<sup>78</sup> A Pd(II) Schiff base complex derived from

alkyldiamine, such as diaminomaleonitrile, was used for TTA-UC.<sup>49</sup> That complex showed a larger Stokes shift of 0.47 eV compared to the Pt(II) complexes studied herein (thus a large energy loss in the photoexcitation/phosphorescence processes), and the anti-Stokes shift for TTA-UC was 0.37 eV.<sup>49</sup> Herein we propose the platinum(II) N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-benzenediamine Schiff base complex as a novel molecular structural motif with an unusually *small* Stokes shift, to drive intermolecular energy transfer, and efficient TTA-UC was achieved with a large anti-Stokes shift (0.75 eV with perylene as the acceptor and 0.92 eV with DPA as the acceptor).

#### CONCLUSIONS

In summary, we synthesized two platinum(II) N,N'-bis(3,5-ditert-butylsalicylidene)-1,2-benzenediamine Schiff base complexes with an anthryl appendant on the phenylene unit of the Schiff base ligand, linking the anthryl moiety at either its 9 (Pt-9An) or 2 (Pt-2An) position. The intriguing property of the Pt(II) Schiff base structural motif is its small Stokes shift for the light absorption/phosphorescence processes, which is only 0.23 eV. This is in contrast to the typical C^N cyclometalated Pt(II) complexes (ca. 0.6 eV), C^N cyclometalated Ir(III) complexes (ca. 1.0 eV), or  $Ru(bpy)_3[PF_6]_2$ (ca. 0.7 eV), all showing larger Stokes shifts. A small Stokes shift indicates less energy loss for the photoexcitation/ISC processes, which is beneficial for the complexes to be used as triplet PSs to initiate electron-donor energy transfer. Phosphorescence of the Pt(II) coordination framework was quenched when the anthryl unit was attached, and temperature-dependent phosphorescence studies showed an anomalous decrease in the phosphorescence intensity at lower temperature. The phosphorescence lifetimes of the anthrylattached Pt(II) Schiff base complexes decay with biexponential kinetics ( $\tau_{\rm T}$  = 3.4  $\mu$ s/87% and 8.2  $\mu$ s/13%), in contrast to the monoexponential decay of the native Pt(II) Schiff base complex (3.7  $\mu$ s). We conclude that triplet-state equilibrium between the <sup>3</sup>An and <sup>3</sup>MLCT states is established, based on the ns TA spectroscopy studies, which indicates that the anthryl-appended complexes have a longer triplet-state lifetime  $(\tau_{\rm T} = 103 \ \mu s \text{ for } \mathbf{Pt}\textbf{-2An} \text{ and } 163 \ \mu s \text{ for } \mathbf{Pt}\textbf{-9An}) \text{ compared to}$ the native Pt(II) Schiff base complex ( $\tau_{\rm T}$  = 4.0  $\mu$ s) and the

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coexistence of the <sup>3</sup>An and <sup>3</sup>MLCT states. Interestingly, we found the triplet-excited-state dynamic is dependent on the substitution profile of the anthryl unit. For the complex with the anthryl moiety attached via the 2 position, triplet-excitedstate equilibrium is established by a fast forward intramolecular TTET (55 ps) and a slow rTTET (1.7 ns), whereas for the complex with an anthryl appendant attached via the 9 position, the forward TTET takes 4.8 ps and rTTET takes ca. 440 ps. The anthryl-containing Pt(II) Schiff base complexes were used for TTA-UC, owing to the satisfactory absorption of visible light ( $\varepsilon = 1.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 589 nm), an exceptionally small Stokes shift (0.23 eV, i.e., a small energy loss for the photoexcitation/ISC processes), and a long triplet-state lifetime ( $\tau_{\rm T}$  = 103  $\mu$ s) resulting from triplet-state equilibrium. Satisfactory TTA-UC was observed, with upconversion quantum yields of up to 15% and a large anti-Stokes shift of 0.75 eV achieved by excitation into the  $S_0 \rightarrow {}^1MLCT$ absorption band (0.92 eV with DPA as the acceptor). Our results are useful for the development of new transition-metal complex structural motifs, showing strong absorption in the visible spectral range, a small Stokes shift (which indicates less excitation energy loss for the excitation/phosphorescence processes), and a long-lived triplet state via triplet-state equilibrium (energy pooling) as well as for the application of these complexes in photocatalysis, photodynamic therapy, and photon upconversion.

#### EXPERIMENTAL SECTION

**General Methods and Materials.** All of the chemicals and solvents used were of analytical-grade purity and were used as received. Solvents were dried and distilled before being used for synthesis. A UV-2550 spectrophotometer (Shimadzu Ltd., Japan) was used to measure UV–vis absorption spectra. Luminescence spectra were recorded on a FS5 spectrofluorometer (photon-counting detection mode; Edinburgh Instruments Ltd., U.K.). To record the luminescence lifetime of the samples, an OB920 luminescence lifetime spectrometer was used (Edinburgh Instruments Ltd., U.K.), using a 510 nm picosecond pulse laser (pulse width, 200 ps; maximum average power, 5 mW; Edinburgh Instruments Ltd., U.K.) for excitation.

Synthesis of Pt-9An. Under a N2 atmosphere, compound 2 (162.0 mg, 0.20 mmol), 9-antharaceneboronic acid (44.0 mg, 0.20 mmol), and Na<sub>2</sub>CO<sub>3</sub> (65.0 mg, 0.45 mmol) were added in a mixed solvent of ethanol/toluene/water (20 mL, 2:4:1, v/v). Then Pd(PPh<sub>3</sub>)<sub>4</sub> (9.0 mg, 0.007 mmol, 5 mol %) was added, and the reaction mixture was refluxed for 10 h. After completion of the reaction, the reaction mixture was cooled to room temperature. Dichloromethane was added to the reaction mixture, and then the mixture was washed with water  $(2 \times 100 \text{ mL})$ . The organic layer was collected and dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure to give a crude solid. The crude product was purified with column chromatography (silica gel, dichloromethane) to give a red solid (38 mg, yield: 21%). Mp: >250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  13.40 (s, 2H), 8.64 (s, 2H), 7.46 (d, J = 2.4 Hz, 2H), 7.24 (d, J = 2.4 Hz, 2H), 7.11–7.03 (m, 5H), 6.81–6.77 (m, 5H), 1.47 (s, 18H), 1.33 (s, 18H). <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  164.5, 148.8, 148.6, 137.7, 137.6, 134.9, 131.3, 131.1, 130.2, 129.5, 128.6, 127.9, 127.4, 126.3, 126.0, 125.3, 121.0, 117.7, 114.8, 36.3, 34.1, 31.2, 29.7. TOF-MALDI-HRMS  $([C_{50}H_{54}N_2O_2Pt + H]^+)$ . Calcd: m/z 910.3911. Found: m/z910.3915.

Synthesis of Pt-2An. The synthesis was similar to the above method described for Pt-9An by using 2-antharaceneboronic acid (44.0 mg, 0.20 mmol). The crude product was purified with column chromatography (silica gel, dichloromethane) to give a red solid (36 mg, yield: 20%). Mp: >250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.97 (s, 1H), 8.89 (s, 1H), 8.54 (s, 1H), 8.47 (s, 1H), 8.29 (s, 1H), 8.25

Synthesis of Pt-Ph. Under a N<sub>2</sub> atmosphere, compound 2 (80.0 mg, 0.10 mmol), phenylboronic acid (18.0 mg, 0.15 mmol), and K<sub>2</sub>CO<sub>3</sub>(42.0 mg, 0.30 mmol) were added in a mixed solvent of ethanol/toluene/water (20 mL, 2:6:2, v/v). Then Pd(PPh<sub>3</sub>)<sub>4</sub> (9.0 mg, 0.007 mmol, 5 mol %) was added. The reaction mixture was refluxed for 10 h. After completion of the reaction, the reaction was cooled to room temperature. The mixture was dissolved with dichloromethane and then washed with water (2  $\times$  100 mL). The organic layer was collected and dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (silica gel, dichloromethane) to give a dark-red solid (32 mg, yield: 27%). Mp: >250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.92 (s, 1H), 8.87 (s, 1H), 8.10 (d, J = 1.3 Hz, 1H), 8.02 (d, I = 8.6 Hz, 1H), 7.69–7.67 (m, 4H), 7.52–7.49 (m, 3H), 7.44–7.41 (m, 1H), 7.34 (d, I = 2.4 Hz, 1H), 7.32 (d, I = 2.4Hz, 1H), 1.59 (s, 18H), 1.36 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  164.4, 164.3, 148.5, 148.3, 140.1, 139.7, 137.6, 131.1, 129.0, 128.0, 127.9, 127.8, 127.2, 125.6, 120.8, 115.0, 113.2, 36.2, 33.9, 31.3, 29.7. TOF-MALDI-HRMS ( $[C_{42}H_{50}N_2O_2Pt + H]^-$ ). Calcd: *m*/*z* 810.3598. Found: m/z 810.3570.

**ns TA Spectroscopy.** ns TA spectral measurements were carried out with a LP980 laser flash photolysis spectrometer (Edinburgh Instruments, U.K.). The samples were excited with a nanosecond pulsed laser (Opolette, OPOTEK, USA; the wavelength is tunable in the range of 210–2400 nm). The typical laser energy is 5 mJ pulse<sup>-1</sup>. The sample solution was purged for 15 min in order to saturate the solution with N<sub>2</sub>. The L900 software was used to analyze the data. The triplet-state lifetimes were obtained by fitting of the decay traces with a kinetic model with the TTA quenching effect considered.<sup>74b,79,80</sup>

**fs TA Spectroscopy.** A Ti:sapphire laser amplifier, an optical parametric amplifier system with 50 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS), and a commercial pump probe experimental setup (Spectra Physics, Helios) with a white-light-continuum probe was used for the experiments, the white-light-continuum probe pulses were generated in a 200  $\mu$ m CaF<sub>2</sub> nonlinear crystal, and spectrally tunable pump femtosecond pulses (370–550 nm; a few microjoules pulse energy) were generated in an optical parametric amplifier (TOPAS, light conversion). A 2-mmthick cuvette containing the sample was used. Changes in the absorbance were monitored by focusing the transmitted probe light through the solution onto a broadband UV–vis detector.

**Theoretical Computations.** DFT and TDDFT were used for geometry optimization and energy calculation of all of the compounds in a vacuum. Geometry optimization of the ground and excited states was conducted at the B3LYP/GENECP level. The *Gaussian 09W* program package was used for the calculations.<sup>81</sup>

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01932.

<sup>1</sup>H and <sup>13</sup>C NMR and HRMS data, photophysical spectra, triplet-equilibrium calculations of the complexes, synthesis of compounds, and coordinates of the optimized geometries (PDF)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

J.Z. thanks the National Science Foundation of China (Grants 21673031, 21761142005, and 21911530095), the State Key Laboratory of Fine Chemicals (Grant ZYTS201901), and the Fundamental Research Funds for the Central Universities (Grant DUT19TD28) for financial support.

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