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N^N Pt(II) Bisacetylide Complex with Naphthalimide and Pyrene Ligands: Synthesis, Photophysical Properties and Application in Triplet-Triplet Annihilation Upconversion

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Abstract: Two different chromophores of pyrene and naphthalimide were introduced as acetylide ligands into diimine N^N heteroleptic Pt(II) bisacetylide complex (Pt-NI-Py) to broaden the absorption bands and study the intramolecular energy transfer process. Steady state and transient spectroscopies were used for study of the photophysical properties of the complexes. The results show that the lowest triplet state of $\mbox{Pt-NI-Py}$ $(\tau_{\mbox{T}}$ = 34 $\mu s)$ is localized on the pyrene part, although the singlet state energy level of naphthalimide unit is lower. Intramolecular energy transfer processes were observed. Moreover, Pt-NI-Py shows enhanced visible light harvesting property compared with bis(pyrenylacetylide) complex (Pt-Py) and relatively triplet lower state energy level compared to bis(ethynylnaphthalimide) complex (Pt-NI). The results demonstrated that the relative singlet excited state energy levels of the different chromophores do not agree with the relative triplet state energy levels of the same chromophores. The efficient triplet state generation property (Φ_{Δ} = 0.8) gives **Pt-NI-Py** high TTA upconversion efficiency (34%).

Introduction

The transition metal complexes, such as those contain Pt(II) atoms, usually show efficient intersystem crossing (ISC) properties,^[1] and these complexes attract increasing attention in applications of photocatalysis,^[2] photovoltaics,^[3] photodynamic therapy,^[4] oxygen sensing,^[5] and triplet-triplet annihilation (TTA) upconversion.^[6-10] However, the conventional platinum (II) complexes show weak absorption of visible light.^[11,12] In order to address this problem, visible light harvesting Pt(II) complexes have been widely investigated by coupling with organic chromophores, such as pyrene,^[13] naphthalimide,^[14,15] perylene,^[16,17] and boron-dipyrromethene (Bodipy) ligands.^[18]

N^N Pt(II) bisacetylide complexes have rich excited states, good photostability and feasible derivatization,^[12,19] which make them good triplet photosensitizers.^[20,21] However, those complexes contain only one kind of ligand, as a result there is only one absorption band in the visible region. To make better use of the broad-band light source, broadening the absorption

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band of the photosensitizer is extremely important.^[22] Introducing an extra chromophore is an easy method to enhance the absorption and form new molecules that display a wealth of fundamentally interesting and potentially useful properties.^[23]

Previously, we reported a broad-band N^N Pt(II) bisacetylides complex which contains two different Bodipy ligands.^[24] The two ligands have different singlet and triplet energy levels, thus the photoexcitation energy collected by the two ligands can be funneled onto one Bodipy ligand. Although heteroleptic Pt(II) complex was obtained, the energy donor and acceptor were derivatives from one kind of chromophore, i.e. Bodipy.

Room temperature phosphorescence from Pt(II) diamine bis(pyrenylacetylide) complex (**Pt-Py**) was observed.^[13] Subsequently, the strong room temperature phosphorescence of Pt(II) diamine complex contains 1,8-naphthalimide ligands (**Pt-NI**) was also reported.^[14] The efficiencies of their applications in oxygen sensing or TTA upconversion show that both **Pt-NI** and **Pt-Py** have good triplet state generation properties.^[7,14,25] The absorption and phosphorescence emission spectra of **Pt-NI** and **Pt-Py** demonstrate the small energy gap between the lowest singlet and triplet states of this two complexes.

Herein, two different chromophores (1,8-naphthalimide and pyrene) are introduced into the Pt(dbbpy) (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) coordination center by triple bonds to form the heteroleptic complex **Pt-NI-Py** (Scheme 1). We proposed that the pyrene ligand in its singlet excited state can transfer its photoexcitation energy to the naphthalimide ligand, while the naphthalimide ligand in its triplet excited state could transfer energy backward to the triplet state of pyrene. By this 'pingpong' energy transfer process, complex **Pt-NI-Py** can make better use of the photoexcitation energy of broad-band photo source.

Results and Discussion

2.1. Design and Synthesis of the Compounds. Our hypothesis is that the coordinate pyrene part (referred as Py in the following text) with higher singlet and lower triplet energy levels than coordinate naphthalimide part (referred as NI in the following text) can be selected as the singlet energy donor and triplet energy acceptor, while NI could use as the singlet energy acceptor and triplet energy donor in heteroleptic complex Pt-NI-Py. By these two opposite energy transfer processes, Pt-NI-Py have two absorption antennae under the excitation of broadband photo source.

The molecular structures and synthesis procedures of the ligands (NI-H and Py-H) and complexes (Pt-NI-Py, Pt-NI and Pt-Py) were displayed in Scheme 1. Heteroleptic complex Pt-NI-Py

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	$\lambda_{ m abs}{}^{[a]}$	$\epsilon^{[b]}$	$\lambda_{\rm em}^{~[a]}$	$\tau^{[c]}$	$arPhi^{[d]}$	$\tau_{\rm T}^{\rm [e]}$	$arPsi_{\Delta}^{[f]}$
NI-H	350	2.70	400	0.7 ns	_[g]	_[g]	_[9]
Ру-Н	360	4.33	384	14.3 ns	_[9]	_[a]	_[9]
Pt-NI-Py	385, 420	4.63, 2.58	661, 731	42 μs, 179 μs ^[h]	4.4% ^[i] 4.0% ^[j]	34 µs	0.76 ^[i] 0.84 ^[j]
Pt-NI	414	5.06	624, 679	95 μs, 365 μs ^[h]	14%	78 μs	0.74 ^[]]
Pt-Py	386	5.95	662, 731	39 μs, 176 μs ^[h]	2.1%	32 µs	0.75 ^[i]

Table 1. Photophysical Parameters of the Acetylide Ligands and Pt(II) Complexes

[a] In toluene (1.0×10^{-5} M), in nm. [b] Molar extinction coefficient at the absorption maxima. $\varepsilon : 10^4$ M⁻¹ cm⁻¹. [c] Luminescence lifetime at room temperature. [d] Luminescence quantum yield, [Ru(dmb)₃]²⁺ ($\Phi_P = 0.073$ in deaerated acetonitrile) as the reference. [e] Triplet state lifetime. [f] Singlet oxygen generation quantum yield, [Ru(bpy)₃]²⁺ ($\Phi_{\Delta} = 0.57$ in dichloromethane) as standard. [g] Not measured. [h] Luminescence lifetime at 77 K. [i] Excited at 350 nm. [j] Excited at 470 nm.

was synthesized with a mixture of the two ligands and Pt(dbdbpy)Cl₂ under the catalysis of Cul under N₂ atmosphere.^[26,27] The ligands and reference complexes **Pt-NI** and **Pt-Py** were synthesized according to the reported methods.^[13,14,28]



Scheme 1. Synthesis of NI-H, Py-H and Pt-NI-Py, the molecular structures of Pt-NI and Pt-Py are also shown.

2.2. UV-vis Absorption and Emission Spectroscopies. The UV-vis absorption spectra of Pt-NI-Py, Pt-NI and Pt-Py were compared (Figure 1a). For **Pt-NI-Py**, broad absorption band from 320 nm to 500 nm was observed, which is due to the two different coordinated ligands. There is no shift of the absorption bands of **Pt-NI-Py** as compared to **Pt-NI** and **Pt-Py**,^[13,14] indicating that there is no electronic interaction between the two ligands at ground state.

The absorption spectra of the two ligands and three Pt(II) complexes in different solvents were also studied. With the polarity of the solvents increases, the absorption bands do not change obviously, which proved no significant electron interaction at the ground states (Figure S1). The absorption peaks and corresponding molar extinction coefficients at the absorption maxima in toluene were summarized in Table 1.

No obvious fluorescence was detected while room temperature phosphorescence was observed for **Pt-NI-Py**. The strongly quenched singlet state emission of **Pt-NI-Py** is result from the efficient ISC by the heavy atom effect of platinum, since no fluorescence emission was observed in both **Pt-NI** and **Pt-Py**. To investigate the triplet state emission properties of **Pt-NI-Py**, the normalized phosphorescence emission spectra of the three complexes were compared as well (Figure 1b).



Figure 1. The UV–vis absorption (a) and normalized phosphorescence emission spectra (b) of **Pt-NI-Py**, **Pt-NI** and **Pt-Py**, $c = 1.0 \times 10^{-5}$ M in deaerated toluene at 20 °C.

As reported by the literatures, **Pt-NI** and **Pt-Py** have strong room temperature phosphorescence emission at 624 nm and 662 nm, respectively.^[13,14] Interestingly, the phosphorescence emission bands of **Pt-NI-Py** (661 nm and 731 nm in toluene) are

almost the same as that of **Pt-Py** (Figure 1b). The phosphorescence emission (624 nm in toluene) quenching of the **NI** part suggests the possible intramolecular energy transfer process from the **NI** part to the **Py** part.

The emission properties of the ligands and complexes in different solvents were studied (Figure S2 and Figure S3). For **NI-H** and **Py-H**, the emission intensities do not change significantly with the solvent. On the contrary, phosphorescence of the complexes is quenched in polar solvents at different extent. This indicates the photoinduced electron transfer process in polar solvents, such as acetonitrile and methanol. The following electrochemistry study also supported this conclusion.



Figure 2. The emission spectra of (a) Pt-NI-Py (λ_{ex} = 400 nm), (b) Pt-Py (λ_{ex} = 380 nm) in deaerated toluene at room temperature (RT) and 77 K, *c* = 1.0 × 10⁻⁵ M.

To get a better understanding of the emissive triplet state, the low temperature (77 K) emission spectra were measured (Figure 2 and Figure S4). Compared to the emission at room temperature, the phosphorescence bands of the three complexes were all slightly blue-shifted at 77 K, which is attribute to the thermally induced Stokes shift (ΔEs). The small values of ΔEs (0.033 eV, 0.020 eV and 0.036 eV for **Pt-NI-Py**, **Pt-NI**, **Pt-Py**, respectively) exclude the charge transfer at emissive triplet state and reveal the ³IL excited-state assignments.^[29,30] The phosphorescence lifetime at 77 K was 3-fold longer than which measured at room temperature (Table 1).

The phosphorescence quantum yield of **Pt-NI-Py** was measured under different excitation wavelength (Table 1). The results indicate that either excite the **NI** part or excite the **Py** part, the emission quantum yields are the same (ca. 0.04), which

reflects the high intramolecular energy transfer efficiency. The emission lifetime of **Pt-NI-Py** is 34 μ s, almost the same as that of **Pt-Py** (32 μ s), while **Pt-NI** has a much longer phosphorescence lifetime of 78 μ s.

The heteroleptic complex **Pt-NI-Py** show similar emission wavelength and lifetime with **Pt-Py**, indicating that the lowest triplet state of **Pt-NI-Py** is pyrene-localized ³IL. Thus, we proposed intramolecular triplet energy transfer happened when excited at the **NI** part. To prove this photophysical process, we determined the excitation spectrum of **Pt-NI-Py** in deaerated toluene (Figure 3). Under excitation into the **NI** part, the phosphorescence of the **Py** part (with higher singlet energy level thus singlet energy transfer is excluded here) was detected. The overlapping of the absorption and excitation spectra indicates the high efficient intramolecular triplet energy transfer. This conclusion agrees with the nanosecond transient spectroscopies



Figure 3. The normalized excitation and UV–vis absorption spectra of **Pt-NI**-**Py** determined with emission wavelength at 662 nm, $c = 1.0 \times 10^{-6}$ M in deaerated toluene. 20 °C.

2.3. Electrochemical Characterization: Redox Properties of the Complexes. To illuminate the photo-induced electron transfer, the redox potentials of the complexes were studied by cyclic voltammograms (Figure 4) or differential pulse voltammetry (DPV, Figure S5).

For the reference complexes **Pt-NI** and **Pt-Py**, irreversible metal-based oxidation waves at +0.83 V and +0.35 V were observed, while a very weak oxidation wave was observed in **Pt-NI-Py** (Figure 4). To obtain the accurate redox potential value, DPV curve was determined, which shows the oxidation wave of

Table 2. Electrochemical Redox Potentials (V vs. Fc/Fc) and Driving Forces of	f Charge Recombination (Δ	GCR) and Charge Se	paration (ΔG_{CS}) and Static
Coulombic Energy ($\Delta G_S)$ for $\mbox{Pt-NI-Py}$ in Toluene, $\mbox{CH}_2\mbox{Cl}_2$ a	and CH ₃ CN.			

	oxidation / V	reduction / V	ES	$\Delta \textbf{G}_{\text{CS}}/ \textbf{eV}^{[b]}$	ΔG_{CS} / eV ^[c]	$\Delta G_{ m S}$ / eV	ΔG_{CR} / eV	$E_{\rm CS}$ / $eV^{[b]}$
Toluene	_	-	2.4	-0.39	+0.88	+0.58	-2.75	2.75
CH_2CI_2	+0.38 ^[a]	-1.79 ^[a]	8.9	-1.10	+0.17	-0.13	-2.04	2.04
CH₃CN	-	-	37.5	-1.30	-0.04	-0.33	-1.84	1.84

[a] Data from DPV measurement in CH₂Cl₂, ¹**Py**^{*} unit as the electron donor while **Pt(dbbpy)**^{*} unit as the electron acceptor. [b] E_{00} = energy level for the singlet excited state, approximated with the absorption maxima peak of pyrene ligand at 395 nm. [c] E_{00} = energy level for the triplet excited state, approximated with the phosphorescence emission wavelength at 662 nm.

Pt-NI-Py at +0.38 V (DPV, Figure S5). Comparably, the reduction waves of the three complexes are all near -1.79 V, which is attributed to reduction of the Pt(dbbpy) unit.^[19,24]

The redox potential data of **Pt-NI-Py**, together with the spectral measurements and geometry optimization data were used for evaluation of the Gibbs free energy changes ($\Delta G_{\rm CS}$) of the photoinduced intramolecular electron transfer process, as well as calculation of the energy level of the charge-transfer state ($E_{\rm CS}$, Table 2). The Weller equation (Eq. 1 and Eq. 2) for the $\Delta G_{\rm CS}$ and static Coulombic energy ($\Delta G_{\rm S}$), as given in the following:

$$\Delta G_{\rm CS} = e \left[E_{\rm OX} - E_{\rm RED} \right] - E_{00} + \Delta G_{\rm S}$$
 (Eq. 1)

$$\Delta G_{\rm S} = -\frac{e^2}{4\pi\epsilon_{\rm S}\epsilon_0 R_{\rm CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{R_{\rm D}} + \frac{1}{R_{\rm A}}\right) \left(\frac{1}{\epsilon_{\rm REF}} - \frac{1}{\epsilon_{\rm S}}\right) \quad ({\rm Eq.~2})$$

where e is the electronic charge, $E_{\rm OX}$ is half-wave potential for one-electron oxidation of the electron-donor unit (+0.38 V), $E_{\rm RED}$ is half-wave potential for one-electron reduction of the electronacceptor unit (-1.79 V); E_{00} is the energy of the 0–0 transition energy gap between the lowest excited state and the ground state, $\epsilon_{\rm S}$ is static dielectric constant of the solvents, $R_{\rm D}$ is the radius of the electron donor (pyrene, 3.51 Å), $R_{\rm A}$ is the radius of the electron acceptor (Pt(dbbpy), 4.90 Å), $R_{\rm CC}$ is the center-tocenter separation distance between the electron donor and electron acceptor (from the DFT optimized geometry, 12.3 Å), $\epsilon_{\rm REF}$ is the static dielectric constant of the solvent used for the electrochemical studies, ϵ_0 is permittivity of free space.^[31,32]

$$E_{CS} = e[E_{OX} - E_{RED}] + \Delta G_S$$
 (Eq. 3)

$$\Delta G_{\rm CR} = -(\Delta G_{\rm CS} + E_{00}) \tag{Eq. 4}$$

Energies of the charge-separated states (E_{CS}) and charge recombination energy state (ΔG_{CR}) of **Pt-NI-Py** were calculated by the reported methods (Eq. 3 and Eq. 4).^[32]



Figure 4. Cyclic voltammograms of (a) **Pt-Py**, **Pt-NI** and **Pt-NI-Py**. Ferrocene (Fc) was used as internal reference ($E_{1/2} = +0.17$ V, Fc⁺/Fc). In deaerated CH₂Cl₂ solutions containing 0.5 mM photosensitizers and ferrocene (0.2 mM), 0.10 M Bu₄NPF₆ as supporting electrolyte, Ag/AgNO₃ reference electrode. Scan rates: 100 mV/s.

In toluene, charge transfer state is exo-energetic or thermodynamically allowed from the singlet state ($\Delta G_{CS} = -0.39$ eV), but completely inhibited from triplet state ($\Delta G_{CS} = +0.88$ eV).

This reasonable in consideration of the charge transfer energy level. The charge-transfer state (CS) is the lowest singlet state, which has higher energy level than the lowest triplet state. But the situation changed when high polar solvent is used. For instance, the CS state can quench the phosphorescence in acetonitrile or methanol (Figure S3).

2.4. DFT Calculations. The ground state geometry and the electronic excited states of **Pt-NI-Py** were calculated by the Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TDDFT) methods with the Gaussian 09W software.^[33] Due to the charge transfer process and the presence of platinum heavy atom, the CAM-B3LYP/GENECP basis is selected for the calculation.^[34–36]



Figure 5. Selected frontier molecular orbitals involved in the excitation and triplet excited states of **Pt-NI-Py**, calculated by DFT at the CAM-B3LYP/GENECP level with Gaussian 09W, the butyl group was simplified as methylamine in the calculation. Key: CT = charge-transfer state, ISC = intersystem crossing.

At the ground state, the naphthalimide ligand has a coplanar geometry toward the Pt(dbbpy) coordination center, while the pyrene ligand is noncoplanar with the platinum core. Moreover, there is no π conjugation between the two ethynyl ligands. The selected frontier molecular orbitals of **Pt-NI-Py** are presented in Figure 5. The HOMO is located on the pyrene ligand while the LUMO is spread over the Pt(dbbpy) part, which is in agree with the electrochemical results.

The S₃ and S₄ states are featured as the mixed MLCT and IL transition states (Table 3). The energy level of the first singlet excited state (S₁) is 2.87 eV, in accordance with the result of the electrochemistry calculation (2.75 eV). The second triplet excited state (T₂) is a typical ³IL state, attributed by the transition localized on the **NI** part. After activated by the intersystem crossing (ISC) from S₁ state, the T₂ state transfer the triplet energy to the lowest triplet excited state (T₁) by internal conversion, which finally gives the phosphorescence emission.^[5]

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2.5. Nanosecond Transient Absorption Spectroscopy. In order to investigate the triplet excited state of the complexes, the nanosecond transient absorption spectra and decay traces were studied (Figure 6).



Figure 6. The nanosecond transient absorption spectra and decay trace of **Pt-NI-Py** (a and b), **Pt-NI** (c and d), **Pt-Py** (e and f), $\lambda_{ex} = 355$ nm, $c = 1.0 \times 10^{-5}$ M, in deaerated toluene, 20 °C.

For **Pt-NI**, upon 355 nm pulsed laser photoexcitation, a bleaching band at 420 nm was observed, which is in agreement with the steady UV absorption band (Figure 6c).^[6] The broad absorption band in the range of 470 nm – 720 nm is the excited state absorption (ESA) of $T_1 \rightarrow T_n$ transitions, which is the similar as the reported results (broad transient absorption band at 650 nm).^[14] The triplet lifetime of **Pt-NI** is detected as 78 µs (Figure 6d). For **Pt-Py**, much more structured ESA bands were determined, while the ground state bleaching signal was observed at 380 nm (Figure 6e) and the corresponding decay time is 32 µs (Figure 6f). Note that the triplet lifetime is concentration dependent.



Scheme 2. Simplified Jablonski diagram illustrating the photophysical processes involved in **Pt-NI-Py**. The energy levels of the excited state are derived from the spectroscopic data. [**NI**] stands for the ethynyl-1,8-naphthalimide moiety while [**Py**] stands for the ethynylpyrene moiety in **Pt-NI-Py**. TN, DCM and ACN stand for toluene, dichloromethane and acetonitrile, respectively.

Table 3. Electronic Excitation Energies (eV) and Oscillator Strengths (f), Main Configurations and CI Coefficients of the Low-Iying Electronic Excited States of Complex Pt-NI-Py, Calculated by TDDFT // CAM-B3LYP / GENECP, Based on the DFT // CAM-B3LYP / GENECP Optimized Ground State Geometries.

	Electronic transition	Energy ^[a]	f ^{b]}	Composition ^[c]	CI ^[d]	Character
Singlet	$S_0 \to S_1$	2.87 eV / 432 nm	0.085	$H \to L$	0.632	MLCT
	$S_0 \to S_3$	3.48 eV / 356 nm	0.217	$H-3 \rightarrow L$	0.617	MLCT
				$H-1 \rightarrow L+1$	0.196	ILCT
	$S_0 \to S_4$	3.54 eV / 351 nm	0.587	$H-1 \rightarrow L+1$	0.442	ILCT
				$H \rightarrow L + 4$	0.342	ILCT, MLCT
	$S_0 \to S_6$	3.70 eV / 335 nm	0.452	$H \rightarrow L + 4$	0.483	ILCT
Triplet	$S_0 \to T_1$	1.78 eV / 695 nm	0.000 ^[e]	$H \rightarrow L + 4$	0.602	ILCT
	$S_0 \to T_2$	1.95 eV / 635 nm	0.000 ^[e]	$H-1 \rightarrow L+1$	0.528	ILCT
	$S_0 \to T_3$	2.75 eV / 451 nm	0.000 ^[e]	$H \to L$	0.509	MLCT

[a] Only the selected low-lying excited states are presented, the butyl group was simplified as methylamine in the calculation. [b] Oscillator strengths. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the *f* values are zero.

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Interestingly, the transient absorption spectrum of **Pt-NI-Py** is approximately the same as **Pt-Py**, with single bleaching band at 370 nm (Figure 6a) with a decay time of 34 μ s (Figure 6b). The absence of **NI** bleaching signal in **Pt-NI-Py** and similar triplet lifetime of **Pt-NI-Py** and **Pt-Py** may owe to the efficient triplettriplet energy transfer (TTET) from the **NI** part to the **Py** part, which is in consistent of the excitation spectroscopy (Figure 3).

Furthermore, we studied the intermolecular triplet energy transfer process. With the adding of **Pt-Py** into the solution of **Pt**. **NI**, the bleaching signal at 420 nm decreased while the bleaching signal at 370 nm generated simultaneously (Supporting Information, Figure S6). The increasing phase of the decay curve at 370 nm indicated the formation and accumulation of the triplet state of **Pt-Py** via intermolecular TTET, whereas the decreasing phase at 420 nm demonstrated the enhanced decay of the triplet excited state of **Pt-NI**. Notably, the decay time decreased fast with the raise of the **Pt-Py** / **Pt-NI** molar ratio (Supporting Information, Figure S7). The intramolecular TTET rate constants are ca. $8.0 \times 10^3 \text{ s}^{-1} - 8.7 \times 10^4 \text{ s}^{-1}$, depending on the molar ratio of the triplet acceptor. The intermolecular energy transfer efficiency is up to ca. 0.87.^[37,38]

The photophysical processes in **Pt-NI-Py** were illustrated in a simplified Jablonski diagram (Scheme 2). The two acetylide ligands were excited at different wavelength. Then ISC occurred, the **NI** part is with triplet state energy level of 1.99 eV, higher than the **Py** unit. Thus, the T₁ excited state of **Pt-NI-Py** will be localized on the **Py** part. This conclusion is supported by the phosphorescence emission spectrum (Figure 1b) and nanosecond transient absorption spectroscopy (Figure 6a). In acetonitrile, the charge separated state has a lower energy level than the **Py** localized triplet state. As a result, the phosphorescence is quenched by the charge separation in acetonitrile, which was revealed by the emission spectrum (Supporting Information, Figure S3a).

2.6. TTA Upconversion. Owing to the absorption of the complexes in visible range and the long triplet state lifetime, the three complexes **Pt-NI-Py**, **Pt-NI** and **Pt-Py** were used as triplet photosensitizers in application of triplet-triplet annihilation (TTA) upconversion. 9,10-diphenylanthracene (DPA) with a lower triplet state energy of 1.77 eV was chosen as the triplet energy acceptor.^[8,39] As discussed in the steady emission part, the phosphorescence of the three complexes were quenched at different levels in acetonitrile or methanol (Figure S3). This means the triplet states of the complexes can be quenched in polar solvents, thus toluene was selected as the solvent to avoid the CS state (1.84 eV in acetonitrile) quenching process.

Strong upconverted DPA fluorescence emission was observed under the sensitizing of **Pt-NI** and **Pt-Py**, as well as **Pt-NI-Py** (Figure 7). The TTA quenching parameters and upconversion quantum yields (Φ_{UC}) were calculated and presented in Table 4. The quantum yields of **Pt-NI** and **Pt-Py** are 28% and 15%, respectively. The much higher quantum yields than the reported values (18% for **Pt-NI** and 14% for **Pt-Py** in acetonitrile)^[7] is reasonable, since the quenching of triplet states is prohibitive in toluene.

The higher Φ_{UC} value of **Pt-NI** than **Pt-Py** can be attributed to longer triplet lifetime. Interestingly, the Φ_{UC} of **Pt-NI-Py** is larger

than Pt-NI, although the triplet lifetime of Pt-NI-Py (34 µs) is much shorter than Pt-NI (78 µs). We propose this is due to the higher triplet state generation ability of Pt-NI-Py (approximated as the singlet oxygen quantum yields. Table 1) as well as the better matched energy levels of photosensitizer and acceptor (0.11 eV for Pt-NI-Py/DPA and 0.22 eV for Pt-NI/DPA). According to our previous study, larger triplet sates energy gap do increase the bimolecular quenching process between the sensitizer and acceptor, but this is not sufficient for a high upconversion quantum yield, since the triplet state generation ability of the photosensitizer is also important for upconversion.^[40]



Figure 7. (a) Upconverted DPA fluorescence and the residual phosphorescence emission of the Pt(II) sensitizers ($c = 1.0 \times 10^{-5}$ M in deaerated toluene), excited by blue laser ($\lambda_{ex} = 443 \pm 3$ nm, 83 mW / cm²) at room temperature, the asterisks indicate the scattered excitation laser. For **Pt-NI-Py**, *c* [DPA] = 3.8 × 10⁻⁵ M; for **Pt-NI**, *c* [DPA] = 3.7 × 10⁻⁵ M; for **Pt-Py**, *c* [DPA] = 5.7 × 10⁻⁵ M. (b) CIE diagram of the upconversion emission.



Figure 8. Upconverted DPA emission intensity at 410 nm as a function of the 443 \pm 3 nm incident laser power in a mixture of **Pt-NI-Py** (1.0 μ M) and DPA (3.8 μ M) in deaerated toluene. The solid blue and red lines are fitting results with slopes of 2.0 and 1.0 in the low- and high-density regions, respectively.

To assess the triplet state generation abilities of **Pt-NI-Py**, **Pt-NI** and **Pt-Py**, the singlet oxygen generation quantum yields (Φ_{Δ}) of the three photosensitizers were measured with DPBF as the ¹O₂ scavenger (Table 1). Upon excitation of the complexes at 350 nm, similar singlet oxygen quantum yields (Φ_{Δ}) were observed for **Pt-NI-Py** (0.76), **Pt-NI** (0.74) and **Pt-Py** (0.75).

With higher triplet state generation ability, the more efficient upconversion of **Pt-NI-Py** than **Pt-NI** is rationalized. It should be

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noted that the major absorption band of **Pt-NI-Py** is under 500 nm, and small anti-Stokes shift was obtained in TTA upconversion. Thus, much room is left for designing of new

photosensitizers giving larger anti-Stokes shift.

Table 4. Upconversion-Related Parameters of the Photosensitizers ^[a]						
	$K_{\rm SV}$ / 10 ⁴ M ^{-1[b]}	$k_{\rm q}$ / 10 ⁹ M ⁻¹ ·s ^{-1[c]}	$f_Q^{[d]}$	${{{{\varPhi}_{{\sf{UC}}}}^{[e]}}}$		
Pt-NI-Py	8.5	2.5	0.22	0.34		
Pt-NI	23	2.9	0.26	0.28		
Pt-Pv	7.0	2.2	0.19	0.15		

[a] In deaerated toluene, **DPA** as the triplet acceptor, excited at 460 nm, 20 °C. [b] Stern-Volmer quenching constants. [c] Bimolecular quenching constants. $K_{SV} = k_q \times \tau_0$, τ_0 is the triplet state lifetime of the sensitizer without acceptors. [d] The quenching efficiency. [e] The TTA upconversion quantum yields, Ru(dmb)₃ (Φ = 7.3%) was used as the standard, excited with 445 nm laser.

Figure 8 shows the double-logarithm plots generated by the intensity of the upconverted emission from DPA at 410 nm as a function of incident power density at 445 nm. A slope change from 1.92 to 1.06 was observed, indicative of quadratic dependence for low power density and linear dependence for high power density, respectively.^[41,42] The laser power chosen in the TTA upconversion quantum yield measurement is within the liner part to guarantee the max value is obtained.^[43]



Figure 9. The quenching phosphorescence intensities of the complexes (a) **Pt-NI-Py**, (b) **Pt-NI** and (c) **Pt-Py** as a function of the increasing DPA concentration. (d) The Stern–Volmer quenching curves in deaerated toluene. The concentration of triplet photosensitize is 1.0×10^{-5} M, λ_{ex} = 460 nm.

The intermolecular TTET processes between the triplet photosensitizes and DPA energy acceptor were quantitatively studied by the quenching phosphorescence intensities of the

platinum complexes Pt-NI-Py, Pt-NI and Pt-Py (Figure 9). With increasing molar ratio of DPA acceptor, the the phosphorescence intensities of photosensitizes are all quenching at different rate. This trend is well linear fitted as the Stern-Volmer quenching curves (Figure 9d).[44,45] The Stern-Volmer quenching constant of Pt-NI is much larger than Pt-NI-Py and Pt-Py (Table 4). This is main caused by the big lifetime differences of Pt-NI-Py (34 µs), Pt-NI (78 µs) and Pt-Py (32 µs). On the other hand, Pt-NI-Py, Pt-NI and Pt-Py have similar bimolecular quenching constants and quenching efficiencies, which reflect the similar triplet generation abilities of the three complexes.

Conclusions

In summary, we have prepared new N^N platinum bisacetylide complex (Pt-NI-Py) with two different acetylide ligands, which has broad absorption band and high triplet state generation ability (Φ_{Λ} = 0.8). The intramolecular charge-transfer and triplet energy transfer processes were studied in detail with steady state and time-resolved spectroscopies, as well as theoretical computation. The intramolecular energy transfer process results in the pyrene localized ³IL as the emissive triplet state in Pt-NI-Py. Thus, the introducing of naphthalimide ligand broaden the absorption band to the visible range without changing the lowest triplet state. High TTA upconversion quantum yield ($\Phi_{UC} = 0.34$) shows the potential application of Pt-NI-Py as a good triplet photosensitizer. Moreover, we found that chromophore (e.g. ethynyl naphthalimide) with lower singlet state energy level may have higher triplet state energy levels. Thus, it is not reliable to predict the relative triplet state energy level based on the relative singlet state energy levels of different chromophores, and vice versa. Our results are useful for the design of platinum photosensitizers with broad-band absorption properties and high triplet state quantum yields.

Experimental Section

Materials. The solvents used for synthesis were analytically pure and were dried before use, while chromatographically pure solvents were used for measurements. K₂PtCl₄ was purchased from Aladdin Chemical Co., Ltd (P. R. China). Ligands **NI-H**^[14] and **Py-H**^[46], as well as complexes **Pt-NI**^[14] and **Pt-Py**^[13] were prepared according to the reported procedures.

Analytical Measurements. All the ¹H NMR spectra were recorded in CDCl₃ solutions with TMS as standard at 0.00 ppm by a Bruker 400 MHz spectrometer. The high-resolution mass spectrum (HRMS) for the platinum complex was detected in a TOF MALDI-HR MS system (UK). Fluorescence and phosphorescence emission spectra were determined on a RF5301 PC spectrofluorometer (Shimadzu, Japan) while the absorption spectra were measured on a UV2550 UV-vis spectrophotometer (Shimadzu, Japan). The excitation spectrum was collected by FS5 fluorescence spectrophotometer (Edinburgh Instruments Ltd). The nanosecond transient absorption spectra and decay curves were recorded on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, Livingston, UK).

Synthesis of Pt(dbbpy)Cl₂. The complex was synthesized by a modified literature procedure.^[47] To a mixture of 4,4'-di-*tert*-butyl-2,2'-bipyridine (135 mg, 0.5 mmol) and K₂PtCl₄ (208 mg, 0.5 mmol) in 15 mL distilled water, HCl aqueous solution (1.0 mL, 4 M) was added under stirring. Then the reaction mixture was refluxed for 2 h. After the mixture was cool to room temperature, light yellow product precipitated. Pure product was obtained after filtration, washing with hot water, methanol and ether (240 mg, yield: 90%). ¹H NMR (400 MHz, CDCl₃) δ 9.46 (d, *J* = 4.0 Hz, 2H), 7.89 (s, 2H), 7.49 (d, *J* = 4.0 Hz, 2H), 1.47 (s, 18H).

Synthesis of Pt-NI-Py. Under Ar atmosphere, Pt(dbbpy)Cl₂ (106 mg, 0.20 mmol), **NI-H** (55 mg, 0.20 mmol) and **Py-H** (43 mg, 0.20 mmol) were dissolved dichloromethane (12 mL). Diisopropylamine (0.6 mL) was added to the mixture via syringe, followed by the catalyst Cul (4 mg, 0.020 mmol). Then the mixture was stirred at room temperature for 12 h. The solvents were removed under reduced pressure, and the solid was purified by column chromatography (silica gel, CH₂Cl₂ as the eluent). **Pt-NI-Py** was collected as a dark orange solid (81 mg, yield 42%). **Pt-Py** (29 mg, yield: 16%) and **Pt-NI** (63 mg, yield: 31%) were isolated as the side products. For **Pt-NI-Py**, ¹H NMR (400 MHz, CDCl₃) δ 9.87 (d, *J* = 5.8 Hz, 1H), 9.69 (d, *J* = 5.8 Hz, 1H), 9.30 (d, *J* = 8.0 Hz, 1H), 9.06 (d, *J* = 8.0 Hz, 1H), 8.50 (t, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 8.12–7.91 (m, 10H), 7.60 (d, *J* = 5.3 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 4.18 (t, *J* = 7.5 Hz, 2H), 1.71 (m, 2H), 1.43–1.40 (m, 20H), 0.98 (t, *J* = 8.0 Hz, 3H). HRMS: calcd ([C₅₄H₄₇N₃O₂Pt]⁺) *m/z* = 964.3316, found *m/z* = 964.3317.

Cyclic Voltammetry. CV and DPV curves were performed on a threeelectrodes (working electrode: glassy carbon electrode; counter electrode: platinum electrode; reference electrode: Ag/AgNO₃ electrode) CHI610D electrochemical workstation (Shanghai, China). The measurements were performed in deaerated dichloromethane at a 100 mV/s scan rate at room temperature. Ferrocene (Fc) was used as the internal reference and tetrabutylammonium hexafluorophosphate (Bu₄N[PF₆], 0.1 M) as the supporting electrolyte.

DFT Calculations. All the calculations were performed with Gaussian 09W software (Gaussian Inc.).^[33] CAM-B3LYP/GENECP hybrid and basis were used for the ground state geometry optimization, as well as the vertical excitation energy calculation. The energy of the singlet and triplet excited states were calculated by the time-dependent DFT (TD-DFT) method based on the ground-state geometry optimized by DFT methodology.

TTA Upconversion. A diode-pumped solid-state (DPSS) continuous lasers with a 2 × 3 mm diameter (443 ± 3 nm) was used as the excitation photo source for the TTA upconversion experiments. The laser power was measured by a VLP-2000 pyroelectric meter. The solutions were degassed by bubbling with N₂ and the upconverted emission was detected by the RF 5301PC spectrofluorometer (Shimadzu, Japan). The upconversion quantum yields (Φ_{UC}) were calculated by the reported method, and the equation is listed below (Eq. 5).^[48]

$$\Phi_{\rm UC} = 2\Phi_{\rm std} \left(\frac{A_{\rm std}}{A_{\rm sam}}\right) \left(\frac{I_{\rm sam}}{I_{\rm std}}\right) \left(\frac{\eta_{\rm sam}}{\eta_{\rm std}}\right)^2$$
(Eq. 5)

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Entry for the Table of Contents

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Heteroleptic Pt(II) complex with naphthalimide and pyrene acetylide ligands (**Pt-NI-Py**) was prepared. Broad absorption band and pyrene localized room temperature phosphorescence was observed (Φ_P = 4%). Efficient singlet oxygen generation (Φ_{Δ} = 80%) and high TTA upconversion quantum yield (Φ_{UC} = 34%) verified **Pt-NI-Py** a good triplet photosensitizer.



Luminescent Materials

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N^N Pt(II) Bisacetylide Complex with Naphthalimide and Pyrene Ligands: Synthesis, Photophysical Properties and Application in Triplet-Triplet Annihilation Upconversion