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1. Introduction

Singlet oxygen (\(^{1}\)O\(_2\)) is the lowest excited state of dioxygen, representing an important reactive oxygen species and has attracted great interest in biomedical, material, and environmental sciences due to its extensive applications in photodynamic therapy (PDT), fine chemical synthesis, wastewater treatment, etc. [1–4]. Up until now, a number of chemical and photochemical methods have been developed for the in situ generation of \(^{1}\)O\(_2\). Among them, photosensitized production of \(^{1}\)O\(_2\) using various dyes (also called photosensitizers) is more prevalent [5–7]. As briefly illustrated in Figure 1a, upon photostimulation, the photosensitizer (PS) is first converted to its lowest singlet excited state \((S_1)\) followed by rapid transition to the lowest triplet excited state \((T_1)\) via fast intersystem crossing (ISC). If effective collision of PS with surrounding \(O_2\) takes place at this moment, the ground triplet-state \(O_2\) \((3\Sigma_g^-)\) is subsequently excited to generate \(^{1}\)O\(_2\) \((1\Delta_g)\) through energy transfer (EnT) from the \(T_1\) of PS to the \(3\Sigma_g^-\) state of \(O_2\) [8–10]. For an ideal PS, several characteristics should be met, including strong absorption, high ISC efficiency and long triplet excited-state lifetime (\(\tau_T\)), good photostability, etc. [11,12].
In the past few decades, several kinds of classical PSs have been explored and adequately investigated, such as aromatic hydrocarbons, quinones, porphyrins, phthalocyanines, borondipyrromethenes, and transition metal complexes [13–20]. Among them, transition metal complexes, especially Ru(II), Ir(III), Pt(II), and Au(I) complexes, exhibit advantages including large ISC rates benefiting from the strong spin-orbit coupling (SOC), rich coordination modes, and excellent structural modification abilities, endowing them with potential photosensitizing function [21–24]. In view of the larger SOC constant \( \zeta \) of the Pt atom relative to other transition metals \( \zeta \) and second \( \zeta \) excited states of O\(_2\) (right), ISC: intersystem crossing; EnT: energy transfer; FL: fluorescence; PL: phosphorescence. Nonetheless, some drawbacks, e.g., short absorption wavelengths \( \leq 450 \) nm), low molar absorptivities \( \leq 10^4 \) M\(^{-1}\) cm\(^{-1}\), and short triplet excited-state lifetimes, are found in these complexes. Therefore, continuous studies on these complexes to further improve their photosensitizing performances are necessary [28–33].

In order to address the issues mentioned above, one straightforward approach is attaching a suitable light-harvesting chromophore with strong absorptivity to the metal component though a \( \pi \)-conjugated bond [11,33–36]. For instance, Zhao and coworkers prepared bidentate \( (N^N)\)-Pt(II) complex 3 with two ethynyl napthalimide ligands, displaying a prolonged \( \tau_T \) of up to 64 \( \mu s \) (in \( N_2 \)-saturated solution) and higher \( \Phi_\Delta \) of 89% in

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**Figure 1.** (a) Simplified \( ^1\)O\(_2\) generation mechanism via energy transfer process from PS to \( ^3\)O\(_2\) (left) and electronic configurations of the ground state \( ^3\Sigma_g^\text{A} \) and first \( ^1\Lambda_g \) and second \( ^1\Sigma_g \) excited states of O\(_2\) (right). ISC: intersystem crossing; EnT: energy transfer; FL: fluorescence; PL: phosphorescence. (b) Previously reported naphthalimide-Pt(II) PSs 3–5 (upper) and two analogues, 1(PF\(_6\)) and 2, studied in this work (lower). The quantum yield for \( ^1\)O\(_2\) generation in CH\(_3\)CN is indicated for each PS.

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CH$_3$CN relative to those ($\tau_T = 0.98 \mu$s; $\Phi_\Delta = 38\%$) of a Pt(II)-ethynylbenzene analogue [35]. Similarly, they reported two tridentate (N’N’C)- and (N’N’C)-Pt(II) complexes, 4 and 5, modified with an ethynylnaphthalimide ligand to present a moderate $\Phi_\Delta$ of 57% and 65% in CH$_3$CN, respectively [36]. Herein, two tridentate Pt(II) complexes, cationic 1(PF$_6$) and neutral 2 distinguished by an N’N’N and cyclometalated N’N’C coordination mode, respectively, are presented. Both of them contain an appended ethynylnaphthalimide moiety as an additional chromophore to modulate their photophysical properties. Spectroscopic measurements demonstrate that 1(PF$_6$) and 2 show strong visible absorptions extending to ca. 550 nm and improved phosphorescence lifetimes. Meanwhile, their distinct responses to triplet oxygen ($^3$O$_2$) accompanied by the dramatic decrease in the phosphorescence intensities and highly efficient in situ generation ($\Phi_\Delta = 84–89\%$) of $^1$O$_2$ via EnT are clearly detected and fully discussed.

2. Results and Discussion

2.1. Synthesis and X-ray Single-Crystal Diffraction Analysis

As outlined in Scheme 1, two Pt(II) complexes, 1(PF$_6$) and 2, were prepared with the one-step ancillary ligand exchange reaction of 2-dodecyl-6-ethynyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI) with the cationic precursor [(tpy)PtCl]Cl (tpy represents 2,2’-6’,2”-terpyridine) and the neutral precursor (pbpy)PtCl (pbpy denotes 6-phenyl-2,2’-bipyridine), with the assistance of KOH and a catalytic amount of CuI in a 76% and 88% yield, respectively. Their molecular structures were fully characterized with proton nuclear magnetic resonance ($^1$H NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and an elemental analysis (details are given in the Experimental Section). The introduction of the long alkyl chain ($n$-C$_{12}$H$_{25}$) into the NI ligand and the resulting complexes can significantly improve their solubilities in common organic solvents, and thus facilitate the separation and purification of these materials.

![Scheme 1](image)

Scheme 1. Synthetic routes to 1(PF$_6$) and 2. Conditions: A. (i) KOH, CH$_3$OH, 0.5 h; (ii) CuI, [(tpy)PtCl]Cl, rt, overnight; (iii) sat. KPF$_6$ (aq.). B. (i) KOH, CH$_3$OH, 0.5 h; (ii) CuI, (pbpy)PtCl, CH$_2$Cl$_2$, rt, overnight.

A single crystal of 2 suitable for the X-ray diffraction analysis was successfully obtained with slow diffusion of ethyl ether into the solution of 2 in CH$_2$Cl$_2$. The relevant crystallographic data are summarized in Table S1 and the molecular structure and stacking model are shown in Figures 2 and S1. The planar Pt component and the ethynylnaphthalimide fragment are linked together with a large dihedral angle of ca. 81° via a Pt-C σ-bond with a length of 1.97 Å (Pt1-C70). This means that these two components are almost perpendicular to each other. The Pt-C σ-bond of Pt with the cyclometalating ligand (Pt1-C10) has a slightly longer length of 2.063 Å. The two Pt-N bonds have a length of 2.000 Å (Pt1-N8; with
the middle pyridine of the tridentate ligand) and 2.062 Å (Pt1-N20; with the side pyridine), respectively (Figure 2a). These bond lengths are consistent with those of known tridentate Pt(II)-acetylene analogues [37,38]. Additionally, complex 2 crystallizes in a triclinic P2̅1 space group with two molecules being included in one unit cell. In the crystal packing, a type of chain-like supramolecular polymer is formed via the alternate π–π stackings of two intermolecular naphthalimide moieties with a distance of 3.47 Å and two cyclometalated Pt components with a distance of 3.305 Å, respectively. No effective metallophilic interaction is present in the crystal structure as the shortest detected intermolecular Pt···Pt distance is about 5.11 Å, which is much longer than the van der Waals contact distance of 3.5 Å of two Pt atoms (Figures 2b and S1).

Figure 2. Single-crystal structure of 2 with thermal ellipsoids at 50% probability level. (a) A single molecule viewed from the c axis. (b) A supramolecular polymeric structure formed with alternate π–π stackings of naphthalimide moieties (blue circle) and cyclometalated Pt components (red circle). Hydrogen atoms and counteranions (PF6−) are omitted for clarity. Selected bond lengths (Å)—Pt1-N8: 2.000, Pt1-N20: 2.062, Pt1-C10: 2.063, Pt1-C70: 1.970, C70-C69: 1.189, C69-C59: 1.437. Selected bond or torsion angles (°)—N8-Pt1-N20: 80.464, N8-Pt1-C10: 79.603, N8-Pt1-N70: 178.384, N20-Pt1-C10: 99.215, N20-Pt1-C70: 90.698, C10-Pt1-C70: 100.605, C70-Pt1-C69: 100.605, C70-C69-C59: 174.449, C70-N8-C10-Pt1: 0.656, C70-C57-N64-C60: 8.915, C57-C59-Pt-C10: 81.411.

2.2. Steady-State Absorption and Emission Spectroscopies

UV-Vis absorption and steady-state emission properties of 1(PF6) and 2 were first investigated in 1,2-dichloroethane (DCE) with a concentration of 5 × 10−5 M (Figure 3 and Table 1). These two complexes display a series of intense absorption bands in the monitored spectral region of 250–600 nm with the molar extinction coefficients (εmax) of 0.6–3.1 × 104 and 2.0–4.6 × 104 M−1 cm−1, respectively (Figure 3a,c). With reference to previous reports [37–40], the high-energy vibronic-structured absorptions of 1(PF6) and 2 with the absorption maximum (λabs) below 380 nm are mainly ascribed to the ligand-centered (1LC) 1π→π* transitions of the tpy moiety, tpy and pbpy ligands, while the broad absorptions in the range of 380–550 nm can be assigned to an admixture of 1LC/charge-transfer (1CT) transitions. In comparison with precursors [(tpy)PtCl]Cl and (pbpy)PtCl, complexes 1(PF6) and 2 show red-shifted absorptions with distinctly enhanced molar absorptivities in the lower-energy region, which are also more intense than those of related Pt(II)-phenylacetylide complexes. This reflects the effective electronic interaction between the Pt component and the NI moiety, leading to the appearance of new CT absorptions. The specific assignments with more detailed information will be further discussed later with the aid of time-dependent density functional theory (TD-DFT) calculations.
Figure 3. (a,c) UV-Vis absorption and (b,d) steady-state emission of [(tpy)PtCl]Cl (non-emissive), (pbpy)PtCl, NI, 1(PF6), 2 in air-equilibrated (containing about 21% O2) or N2-saturated DCE (5 × 10⁻⁵ M). Inset: photos of 1(PF6) and 2 solutions in DCE under air-equilibrated and N2-saturated conditions upon 365 nm irradiation. Excited at 385 nm for 1(PF6) and 435 nm for 2 at rt for emission spectra.

Table 1. Photophysical parameters 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Compound</th>
<th>1(PF6)</th>
<th>2</th>
<th>NI</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>DCE</td>
<td>CH₂CN</td>
<td>DCE</td>
</tr>
<tr>
<td>(\lambda_{\text{abs}}) (nm)/(\varepsilon(10^4 \text{M}^{-1} \text{cm}^{-1}))</td>
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<td>435/1.3</td>
<td>437/3.2</td>
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<tr>
<td>(\lambda_{\text{em}}) (nm)</td>
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<td>389/2.4</td>
<td>348/2.1</td>
<td>286/3.1</td>
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<td>(\tau) (µs) air/N2</td>
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<td>0.6/4.8</td>
<td>0.27/3.2</td>
<td>0.72/7.0</td>
</tr>
<tr>
<td>(\Phi) (%) air/N2</td>
<td></td>
<td>0.3/1.9</td>
<td>0.3/1.9</td>
<td>10.6/2.0</td>
</tr>
<tr>
<td>(k_r) (10³ s⁻¹) air/N2</td>
<td></td>
<td>5.0/4.0</td>
<td>5.0/4.0</td>
<td>7.0/4.0</td>
</tr>
<tr>
<td>(k_{\text{air}}) (10⁵ s⁻¹) air/N2</td>
<td></td>
<td>16.6/2.0</td>
<td>13.8/1.4</td>
<td>41.6/6.0</td>
</tr>
<tr>
<td>(k_q) (10⁸ M⁻¹ s⁻¹)</td>
<td></td>
<td>9.1</td>
<td>18</td>
<td>7.8</td>
</tr>
<tr>
<td>(\Phi_A) (%)</td>
<td></td>
<td>--</td>
<td>89</td>
<td>--</td>
</tr>
<tr>
<td>(P_{\text{LO2}}) (%)</td>
<td></td>
<td>92</td>
<td>--</td>
<td>85</td>
</tr>
<tr>
<td>(f_{\text{TA}}) (%)</td>
<td></td>
<td>--</td>
<td>97</td>
<td>--</td>
</tr>
</tbody>
</table>

1 Monitored in specific solution with the concentration of 5 × 10⁻⁵ mol L⁻¹. The mark of "--" denotes "No determined". 2 Absolute quantum yield. 3 \(k_r = \Phi/\tau\). 4 \(k_{\text{air}} = (1 - \Phi)/\tau\). 5 Phosphorescence quenching rate constant by air (containing about 21% O2). 6 Quantum yield of \(^1\)O₂ generation with respect to that of [Ru(bpy)₃]Cl₂ in CH₂CN (\(\Phi_A = 57\%\)). 7 The proportion of triplet excited state of PS quenched with \(^3\)O₂. 8 The fraction of the triplet state of PS quenched with \(^5\)O₂, which leads to \(^1\)O₂ generation.

The NI ligand shows a \(^1\)LC emission band at 400 nm (Figure 3b). Complex (pbpy)PtCl displays a triplet LC (\(^3\)LC) emission band at 560 nm (Figure 3d) [41], while complex [(tpy)PtCl]Cl is non-emissive at rt [42,43]. In comparison, complexes 1(PF6) and 2 display a similar lower-energy emission with vibronic characteristics in DCE (5 × 10⁻⁵ M). Under the air-equilibrated condition, the emission of 1(PF6) locates at 620 nm with an absolute quantum yield (\(\Phi_{\text{air}}\)) of 0.3% and lifetime (\(\tau_{\text{air}}\)) of 0.6 µs, and the emission of complex 2 is observed at 640 nm with \(\Phi_{\text{air}}\) of 0.3% and \(\tau_{\text{air}}\) of 0.72 µs. Meanwhile, at the N₂-saturated condition, both emissions exhibit a distinct intensity enhancement (\(\Phi_{\text{N2}} = 1.9\%\)) and elongated lifetimes with \(\tau_{\text{N2}}\) of 4.8 and 7.0 µs, respectively (Tables 1 and S2). These properties are superior to those of two Pt(II) precursors and reported Pt(II)-phenylacetylide.
analagues [37–39]. The highly O₂-dependent emissions indicate their phosphorescence features. In accordance with the previous works [36,40,44] and TD-DFT calculations, the phosphorescences of 1(PF₆) and 2 are considered to stem from the Pt-perturbed π→π*(1LC) transition of the NI fragment (see further discussions in following section). Furthermore, benefiting from the long lifetimes of triplet excited states and the good photostability of 1(PF₆) and 2, their phosphorescence emissions showed a good reversibility in response to the alternate saturation with N₂ and air (containing about 21% O₂). Under repeated treatment with N₂ and air for eight cycles, the phosphorescence intensity showed no apparent attenuation, indicative of their potentials for O₂ sensing (Figure S2).

Considering that the ¹O₂ generation experiment is often measured in CH₃CN [3,9], other than DCE, the comparative study of the spectroscopic properties of 1(PF₆) and 2 in these two solvents was subsequently conducted (Figure S3). For cationic 1(PF₆), the lowest energy absorption band displays a distinct hypsochromic shift from 465 nm in DCE to 437 nm in the more polar CH₃CN. The negative solvatochromic effect suggests that the dipole moment of 1(PF₆) in the ground state is larger with respect to that in the excited state and the ground-state molecules are better stabilized with solvation than the excited-state molecules [44,45]. In contrast, the absorptions of neutral 2 in DCE and CH₃CN display an insignificant spectral change. In a sense, the obvious solvent polarity-dependent absorption spectral shift of 1(PF₆) points to its more CT-contributed character of the lowest-lying singlet electronic transition relative to that of 2. Unlike the absorption spectra, the phosphorescence profiles of 1(PF₆) and 2 almost remain unchanged in these two solvents under air/N₂-saturated conditions, indicative of their dominant ³LC transition characters as mentioned above.

2.3. Theoretical Calculations

To further elucidate the electronic structures of 1(PF₆) and 2, DFT and TD-DFT calculations were carried out. In order to save time and cost, the calculations were performed on the two corresponding model complexes, [Me-1]⁺ and Me-2, with a methyl group as the substituent on the nitrogen atom of the NI fragment. The crystallographic data of 2 were used to build the initial structures for the geometry optimization of [Me-1]⁺ and Me-2 at the ground state (S₀) and the lowest-lying triplet state (T₁). The DFT-optimized structures of Me-2 and [Me-1]⁺ at the ground state show smaller dihedral angles between NI and the Pt fragments with respect to that of 2 in the crystal state (Figure S4). The highest occupied molecular orbitals (HOMOs) are mainly related to the ethynylnaphthalimide moiety (89% for [Me-1]⁺ and 82% for Me-2) with a minor contribution of Pt (8.2% for [Me-1]⁺ and 13.6% for Me-2). The lowest unoccupied molecular orbital (LUMO) of [Me-1]⁺ is primarily localized on the tpy fragment (86%) with a minor distribution on Pt (5.6%), but that of Me-2 has almost equal contributions from pbpy (50%) and NI fragments (46%) with a little participation of Pt (4%) (Figure 4c,d). More detailed information on the frontier molecular orbitals of [Me-1]⁺ and Me-2 is displayed in Figures S5 and S6.

In order to obtain insight into the excited state characters of 1(PF₆) and 2, TD-DFT calculations were performed for the optimized S₀ structures of Me-2 and [Me-1]⁺, and the predicted vertical excitations from S₀ to various singlet (Sₙ) excited states are summarized in Table 2. The simulated singlet absorption spectra are shown in Figure 4a,b. The S₀→S₁ excitations were predicted to locate at 470 nm for [Me-1]⁺ with an oscillator strength (f) of 0.2487 and at 440 nm with f of 0.3582 for Me-2, respectively. These excitations are in good agreement with the observed lowest-energy absorption maximum of 465 nm for 1(PF₆) and 437 nm for 2, respectively. The S₀→S₁ excitations of [Me-1]⁺ and Me-2 are both dominated by the HOMO→LUMO electronic transitions and they can be interpreted as the major ligand-to-ligand charge-transfer (¹LNIL₄py,CT) and mixed ¹LCNI/¹LNIL₄bpyCT (bpy stands for the bipyridine segment of the pbpy ligand) transitions, respectively, which are in accordance with the observation of their solvent-dependent absorptions.
Figure 4. (a,b) TD-DFT-computed singlet vertical excitations (black) and simulated absorption spectra (blue) of (a) [Me-1]$^+$ and (b) Me-2. (c,d) Isodensity plots of the major frontier molecular orbitals associated with the S$_0$→S$_1$ vertical excitations based on optimized S$_0$ geometries (isovalue = 0.03) and the energy level diagrams of (c) [Me-1]$^+$ and (d) Me-2.

Table 2. Selected TD-DFT-computed singlet vertical excitations from S$_0$ to S$_n$ states based on optimized S$_0$ structure $^a$.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Electronic Transitions</th>
<th>E (eV)</th>
<th>$\lambda$ (nm)</th>
<th>$f$</th>
<th>Major Transitions (Percentage)</th>
<th>Characters</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me-1]$^+$</td>
<td>S$_0$→S$_1$</td>
<td>2.64</td>
<td>470</td>
<td>0.2487</td>
<td>HOMO→LUMO (97%)</td>
<td>L$<em>{NI}$/L$</em>{tpy}$CT/ML$_{tpy}$CT</td>
</tr>
<tr>
<td></td>
<td>S$_0$→S$_2$</td>
<td>3.17</td>
<td>390</td>
<td>0.0114</td>
<td>HOMO→LUMO+1 (97%)</td>
<td>L$<em>{NI}$/L$</em>{tpy}$CT/ML$_{tpy}$CT</td>
</tr>
<tr>
<td></td>
<td>S$_0$→S$_3$</td>
<td>3.20</td>
<td>388</td>
<td>0.4426</td>
<td>HOMO→LUMO+2 (57%)</td>
<td>L$<em>{NI}$/L$</em>{tpy}$CT/ML$_{tpy}$CT</td>
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<tr>
<td></td>
<td>S$_0$→S$_4$</td>
<td>3.28</td>
<td>378</td>
<td>0.1013</td>
<td>HOMO→LUMO−1→LUMO (40%)</td>
<td>ML$<em>{tpy}$CT/L$</em>{NI}$/L$_{tpy}$CT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO→LUMO−1→LUMO+1 (55%)</td>
<td>ML$<em>{tpy}$CT/L$</em>{NI}$/L$_{tpy}$CT</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HOMO→LUMO+2 (41%)</td>
<td>L$<em>{NI}$/L$</em>{tpy}$CT/ML$_{tpy}$CT</td>
</tr>
<tr>
<td>Me-2</td>
<td>S$_0$→S$_1$</td>
<td>2.81</td>
<td>440</td>
<td>0.3582</td>
<td>HOMO→LUMO (93%)</td>
<td>L$<em>{CI}$/L$</em>{NI}$/L$<em>{tpy}$CT/ML$</em>{tpy}$CT</td>
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<td>S$_0$→S$_2$</td>
<td>2.92</td>
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<td>0.0019</td>
<td>HOMO→LUMO−1→LUMO (71%)</td>
<td>IL$<em>{tpy}$/L$</em>{tpy}$/L$<em>{NI}$/L$</em>{tpy}$CT</td>
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<td></td>
<td>S$_0$→S$_3$</td>
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<td>408</td>
<td>0.4450</td>
<td>HOMO→LUMO−1→LUMO+1 (24%)</td>
<td>IL$<em>{tpy}$/L$</em>{tpy}$/L$<em>{tpy}$/L$</em>{NI}$/L$_{tpy}$CT</td>
</tr>
</tbody>
</table>

$^a$ Calculation method: PBE1PBE/6-311G$^*$/SDD.

Furthermore, the spin density distributions of [Me-1]$^+$ and Me-2 were calculated on the optimized T$_1$ geometries to probe the natures of the phosphorescence of 1(PF$_6$) and 2 (Figure 5). The results show that the spin densities are mainly distributed on the $\pi$-orbitals of the ethynylnaphthalimide moiety with a minor involvement of the d-orbital of Pt metal. On the basis of these results, we tentatively assign the low-energy phosphorescence of 1(PF$_6$) and 2 to the Pt-perturbed $^3$LC transition of the ethynylnaphthalimide segment. This assignment is consistent with the fact that the phosphorescence of complexes 1(PF$_6$) and 2 involves similar solvent polarity-independent vibronic structures and emission wavelength range.
2.4. Singlet Oxygen Generation

The small triplet radiative transition rate constants \( (k_r) \), even at the \( N_2 \)-saturated condition, which is \( 4 \times 10^5 \text{ s}^{-1} \) for 1(PF\(_6\)) and \( 2.7 \times 10^3 \text{ s}^{-1} \) for 2, respectively, result in their low \( \Phi_{\text{N}2} \) of ca. 1.9% (Table 1). Moreover, \( \Phi_{\text{N}2} \) as well as the average \( \tau \) are further diminished under the air-equilibrated condition along with the relatively large nonradiative transition rate constants \( (k_{\text{nr}}) \) in the order of \( 10^6 \text{ s}^{-1} \). The phosphorescence diminishment under the air-equilibrated condition can be rationalized with Equation (1) as a result of the emission quenching with \( ^3\text{O}_2 \) [46].

\[
\frac{\tau_{\text{N}2}}{\tau_{\text{air}}} = \frac{\Phi_{\text{N}2}}{\Phi_{\text{air}}} = 1 + k_q \tau_{\text{N}2}[^3\text{O}_2] \\
\]

wherein \( [^3\text{O}_2] \) represents the concentration of \( ^3\text{O}_2 \) and is taken as \( 1.6 \times 10^{-3} \text{ M} \) in air-equilibrated DCE at rt [47] and \( \tau_{\text{N}2} \) and \( \tau_{\text{air}} \) are phosphorescence lifetimes under \( N_2 \)-saturated and air-equilibrated conditions, respectively. On the basis of Equation (1), the phosphorescence quenching rate constants \( (k_q) \) were calculated to be ca. 9.1 and \( 7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) for 1(PF\(_6\)) and 2, respectively, which are comparable with those of other known Pt analogues [28,48]. These \( k_q \) values are around 1/9 of the diffusion-controlled rate constant \( (k_{\text{diff}}) \), given that \( k_{\text{diff}} \) is taken to be \( 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) in DCE at rt. This suggests that the phosphorescences of 1(PF\(_6\)) and 2 are quenched with \( ^3\text{O}_2 \) exclusively through an EnT process [49].

The generation of \(^1\text{O}_2 \) was further quantified by integrating the NIR emission of \(^1\text{O}_2 \) at 1270 nm in air-equilibrated CH\(_3\)CN of 1(PF\(_6\)) and 2 in comparison with that of [Ru(bpy)_3]Cl\(_2\) as the reference compound (Figures 6 and S7). By plotting the emission integrals of \(^1\text{O}_2 \) \((I_{\text{O}2})\) as a function of the absorbances \((A)\) at the excitation wavelength of 435 nm in a series of solutions of these compounds with variable concentrations, three linearly fitted curves with different slopes, \( S(I_{\text{O}2}/A) \), are obtained (Figure 6b). The quantum yields of the \(^1\text{O}_2 \) generation of 1(PF\(_6\)) and 2 were thus estimated to be 89% and 84%, respectively, according to Equation (2), in which \( \Phi_{\Delta,\text{ref}}, I_{\text{O}2,\text{ref}}, A_{\text{ref}}, \) and \( S(I_{\text{O}2,\text{ref}}/A_{\text{ref}}) \) are the various parameters of the reference standard [Ru(bpy)_3]Cl\(_2\) (\( \Phi_\Delta = 57\% \) in CH\(_3\)CN) [49,50]. The determined \( \Phi_\Delta \) of these complexes are comparable with or even higher than those of known tridentate Pt(II)-arylacetylide analogues [36,53–55].

\[
\frac{\Phi_\Delta}{\Phi_{\Delta,\text{ref}}} = \frac{I_{\text{O}2} \times A_{\text{ref}}}{I_{\text{O}2,\text{ref}} \times A} = \frac{S(I_{\text{O}2}/A)}{S(I_{\text{O}2,\text{ref}}/A_{\text{ref}})} \\
\]

Figure 5. Spin density distributions of [Me-1]° and Me-2 calculated based on optimized T\(_1\) geometries (isovalue = 0.0004).
were prepared according to the previous reports [56,57].

wherein $3\text{O}_2$, which leads to the generation of $1\text{O}_2$, are calculated to be ca. 97% and 99% for $[\text{Ru(bpy)}_3\text{Cl}_2$ as the reference compound (Figures 6 and S7). By plotting exothermic, leading to the excited-state energies of the T 1 state ($E_{T1,00}$) of $1(\text{PF}_6$ and $2$, respectively, with Equation (4).

$$P_{T,\text{O}2} = 1 - \left(\frac{\tau_{\text{Air}}}{\tau_{\text{N}2}}\right)$$

The values of $f_{\text{T}A\text{A}}$ in Equation (3), standing for the fraction of the triplet state quenched with $3\text{O}_2$, which leads to the generation of $1\text{O}_2$, are calculated to be ca. 97% and 99% for $1(\text{PF}_6$ and $2$, respectively.

3. Experimental Section

3.1. General Information for Synthesis and Characterization

A Bruker Advance 400 MHz spectrometer was employed to measure the $^1\text{H}$ NMR spectra in the designated solvents. The $^1\text{H}$ NMR data are reported in ppm with respect to the residual protons of deuterated solvents. An Autosflex III matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer was used to measure the high-resolution mass spectra. The elemental analysis was obtained on a Flash EA 1112 or Carlo Erba 1106 analyzer. Ligand NI and the precursor complexes [(tpy)PtCl][Cl and (pdpy)PtCl were prepared according to the previous reports [56,57].

Synthesis of $1(\text{PF}_6$). Into a round-bottom flask containing the NI ligand (214 mg, 0.55 mmol, 1.1 equiv) and KOH (56 mg, 1.0 mmol, 2.0 equiv), 20 mL of CH₃OH was injected under a $N_2$ atmosphere. The obtained mixture was stirred at rt for 0.5 h. After that, [(tpy)PtCl][Cl (250 mg, 0.50 mmol, 1.0 equiv) and Cul (57 mg, 0.30 mmol, 0.60 equiv) were added and the mixture was bubbled with $N_2$ for 10 min. After stirring at rt overnight, the mixture was concentrated, followed by the addition of the proper amount of ethyl ether. The appeared precipitate was collected using filtration. The obtained solid was then dispersed in 20 mL of CH₃OH, followed by the addition of 20 mL of a saturated aq. KPF₆ solution. After stirring for an additional 3 h at rt, the precipitate was collected using filtration, and washed with $H_2O$, ethyl ether, and CH₃Cl₂ successively to give 210 mg of $1(\text{PF}_6$ as a red solid in a 76% yield. $^1\text{H}$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.15 (t, $J = 4.8$ Hz, 2H), 8.80 (t, $J = 8.4$ Hz, 1H), 8.50–8.70 (m, 5H), 8.47–8.53 (m, 3H), 8.38 (t, $J = 7.6$ Hz, 1H), 7.88–7.97 (m, 4H), 4.03 (t, $J = 7.6$ Hz, 2H), 1.64 (t, $J = 7.6$ Hz, 2H), 1.23–1.33 (m, 18H), 0.85 (t,
1.2 Hz, 1H), 7.20 (td, 1.1 equiv) and KOH (28 mg, 0.5 mmol, 2.0 equiv), 20 mL of CH$_3$Cl while their low-energy phosphorescences are both associated with the SCRF and solvent model based on density (SMD) [59].

Tau Fluorescence lifetime spectrometer C11367 of Hamamatsu Photonics. The absolute generation (84–89%) of $^{1}$O$_2$ via an EnT process. Thus, these complexes have potential for $^{1}$O$_2$ sensing and PDT in the future.

In conclusion, two tridentate Pt(II) complexes, i.e., cationic $^{1}$PF$_6$ and neutral 2, modified with an ethynylnaphthalimide chromophore, were successfully synthesized and characterized. These complexes possess strong UV-Vis absorptions and vibronically structured phosphorescence emissions at 620–640 nm in nonpolar DCE and polar CH$_3$CN. Theoretical calculations suggest that the lowest-energy absorption bands of $^{1}$PF$_6$ and 2 are mainly associated with the $^{1}$L$_{NL}$L$_{ppy}$CT and mixed $^{1}$L$_{NL}$/$^{1}$L$_{NL}$L$_{ppy}$CT transitions, respectively, while their low-energy phosphorescences are both associated with the $^{3}$LC transition of the ethynylnaphthalimide moiety. Benefitting from the long lifetimes of phosphorescence, these two complexes exhibit highly sensitive and reversible responses to $^{1}$O$_2$ with the high-yield generation (84–89%) of $^{1}$O$_2$ via an EnT process. Thus, these complexes have potential for $^{1}$O$_2$ sensing and PDT in the future.

3.2. Information on Other Physical Measurements

A TU-1810DSPEC spectrometer of Beijing Purkinje General Instrument Co., Ltd., Beijing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt. An F-380 spectrofluorimeter of Tianjin Gang-dong Sci. & Tech. Development Co., Ltd., Tianjing, China., was used to measure the absorption spectra at rt.

X-ray single-crystal crystallography. A Rigaku Saturn 724 diffractometer was employed to obtain the X-ray diffraction data on a rotating anode (Mo Kα radiation, 0.71073 Å) at 173 K. The structure was analyzed using the direct method with SHELXS-9758 and refined on Olex 2.59. Crystallographic data are summarized in Table S1.

DFT and TD-DFT calculations. The Gaussian 09 package was employed for the DFT and TD-DFT calculations with the PBE1PBE exchange correlation functional [58]. The SDD basis set was used for Pt and 6-311G* for other atoms [26]. For all calculations, the solvent effect of 1,2-dichloroethane was taken into account using the self-consistent reaction field (SCRF) and solvent model based on density (SMD) [59].

4. Conclusions

In conclusion, two tridentate Pt(II) complexes, i.e., cationic $^{1}$PF$_6$ and neutral 2, modified with an ethynylnaphthalimide chromophore, were successfully synthesized and characterized. These complexes possess strong UV-Vis absorptions and vibronically structured phosphorescence emissions at 620–640 nm in nonpolar DCE and polar CH$_3$CN. Theoretical calculations suggest that the lowest-energy absorption bands of $^{1}$PF$_6$ and 2 are mainly associated with the $^{1}$L$_{NL}$L$_{ppy}$CT and mixed $^{1}$L$_{NL}$/$^{1}$L$_{NL}$L$_{ppy}$CT transitions, respectively, while their low-energy phosphorescences are both associated with the $^{3}$LC transition of the ethynylnaphthalimide moiety. Benefitting from the long lifetimes of phosphorescence, these two complexes exhibit highly sensitive and reversible responses to $^{1}$O$_2$ with the high-yield generation (84–89%) of $^{1}$O$_2$ via an EnT process. Thus, these complexes have potential for $^{1}$O$_2$ sensing and PDT in the future.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11110438/s1, Table S1: Crystallographic data of 2; Table S2: Detailed lifetime data; Figure S1: Molecular dimer in one unit cell and the stacking model of 2; Figure S2: Responsibility of phosphorescence intensity of 1(PF$_6$) and 2 upon repeated exposure of N$_2$ and air; Figure S3: Solvent effect of absorption and emission for 1(PF$_6$) and 2; Figure S4: Single-crystal structure of 2 and optimized structures of [Me-1] and Me-2 at ground state; Figures S5 and S6: Isodensity plots of frontier molecular orbitals (MOs) of [Me-1] and Me-2, respectively; Figure S7: Absorption and NIR emission of O$_2$ generated with photosensitization of 1(PF$_6$) and 2 and reference [Ru(bpy)$_3$]$_2^{2+}$ in CH$_3$CN with different diluted concentrations; Figures S8–S11: $^1$H NMR and MS spectra of 1(PF$_6$) and 2; Data S1: cartesian coordinates of DFT-optimized S$_0$ and T$_1$ structure of [Me-1]$^+$ and Me-2.

Author Contributions: Conceptualization, Y.-W.Z. and Z.-L.G.; methodology, Z.-L.G.; software, Z.-L.G.; validation, Y.-W.Z.; formal analysis, Z.-L.G. and Y.-W.Z.; investigation, Z.-L.G., Q.-J.P., and D.-X.M.; resources, Z.-L.G.; data curation, Z.-L.G.; writing—original draft preparation, Z.-L.G.; writing—review and editing, Y.-W.Z.; visualization, Z.-L.G. and Y.-W.Z.; supervision, Y.-W.Z.; project administration, Y.-W.Z.; funding acquisition, Y.-W.Z. All authors have read and agreed to the published version of the manuscript.

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