Fine-Tuning of β-Substitution to Modulate the Lowest Triplet Excited States: A Bioinspired Approach to Design Phosphorescent Metalloporphyrinoids

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Supporting Information

ABSTRACT: Learning nature’s approach to modulate photophysical properties of NIR porphyrinoids by fine-tuning β-substituents including the number and position, in a manner similar to naturally occurring chlorophylls, has the potential to circumvent the disadvantages of traditional “extended π-conjugation” strategy such as stability, molecular size, solubility, and undesirable π−π stacking. Here we show that such subtle structural changes in Pt(II) or Pd(II) cis/trans-porphodilactones (termed by cis/trans-Pt/Pd) influence photophysical properties of the lowest triplet excited states including phosphorescence, Stokes shifts, and even photosensitization ability in triplet–triplet annihilation reactions with rubrene. Prominently, the overall upconversion capability (η, η = e−ΦU/τ) of Pd or Pt trans-complex is 104 times higher than that of cis-analogue. Nanosecond time-resolved infrared (TR-IR) spectroscopy experiments showed larger frequency shift of ν(C=O) bands (ca. 10 cm−1) of cis-complexes than those of trans-complexes in the triplet excited states. These spectral features, combining with TD-DFT calculations, suggest the strong electronic coupling between the lactone moieties and the main porphyrin chromophores and thus the importance of precisely positioning β-substituents by mimicking chlorophylls, as an alternative to “extended π-conjugation”, in designing NIR active porphyrinoids.

INTRODUCTION

Design of porphyrinoids active in the near-infrared (NIR) region is an ever expanding field with potential impacts in areas from fundamental understanding of natural tetrapyrrole cofactors to diverse applications in materials, biological studies, and related fields.1 Owing to electronic structures conferred by π-conjugation system, β-peripheral substituents of porphyrinoids are particularly attractive design targets and such modification is an emerging approach because of the tantalizing prospect of introducing new functionality and control of photophysical properties. The well-established “extended π-conjugation” strategies in synthetic porphyrin chemistry,2 exemplified by tetrabenzo[7]porphyrins and linearly π-expanded derivatives such as naphtho- and anthro-fused porphyrins, has been extensively demonstrated the efficiency to accumulatively extend NIR absorption and emission. However, the increasingly elevated HOMO levels along with π-conjugation extension and molecular sizes render these porphyrinoids unstable, poor solubility and π−π stacking between molecules.3

Naturally occurring tetrapyrrole pigments, such as Chl a, b, d, and f, have set a golden standard, which is capable of modulating NIR absorption (ca. 650–700 nm) by fine-tuning β-substitution with the broad structural similarity.4 Such subtle structural changes inducing distinctive spectra related to ground states have been explicitly described in de novo synthetic chlorophyll analogues, in combination with density functional theory (DFT) calculations based Gouterman’s four-orbital model.5 Another notable bonus to nature’s approach is minimizing the structural changes, avoiding the problems such as solubility, structural distortion, and undesirable π−π stacking. Despite the widespread recognition of the importance of β-substitution on the photophysics of chlorophylls,6 few systematic studies on the effects of such β-substitution on the triplet excited states. Learning how to modulate the low-lying triplet states of porphyrinoids like chlorophylls, which prevents
transferring energy to oxygen instead of carotenoids and protect chlorophylls in NIR region, is equally important. This would open new means to design NIR active porphyrinoids as optoelectronic materials, solar fuel and photosensitizers with large Stokes shift to reduce self-absorption and thus enhance energy transfer efficiency.

We previously reported porphodilactones with two β-oxazolone moieties replacing the pyroles at opposite positions, and demonstrated that relative orientation of such moieties affects electronic structures, NIR absorption and magnetic circular dichroism (MCD) spectra. In this work, we synthesized Pd(II) and Pt(II) complexes of cis- and transporphodilactones (termed by cis/trans-Pd and cis/trans-Pt), which display the gradually red-shifted absorption, NIR phosphorescence, and accumulative Stokes shifts, compared to metal complexes of tetrapentafluorophenylporphyrin (F20TPP) and porpholactone (F20TPPL). Importantly, trans-Pt/Pd showed red-shifted phosphorescence (ca. 30–57 nm) with longer life times (30–50%); this suggests the orientation of β-oxazolone moieties not only modulate the ground states but the triplet excited states. More importantly, electrochemical studies combining with DFT calculation demonstrated that β-oxazolone replacement significantly influences LUMO rather than HOMO level, different from those in previously reported “π-expanded” porphyrinoids. Noticeably, nanosecond time-resolved infrared (TR-IR) spectroscopy experiments for cis/trans-Pt/Pd showed more frequency change of ν(C=O) bands (ca. 10 cm⁻¹) of cis complexes between ground and triplet excited states than trans complexes, indicating further the fine-tuning effect of cis/trans positioning on electronic structures. Finally, in triplet–triplet annihilation (TTA) reactions with rubrene, trans-Pd showed much higher delayed fluorescence quantum yield (1.0%) than cis-Pd (0.08%), strongly demonstrating that subtle structural changes induce significant sensitization enhancement in the NIR region. Therefore, these results herein presented reveal the importance of precisely positioning β-substituents in design NIR porphyrinoid emitters, which would be complementary to traditional NIR porphyrinoid emitters, which would be complementary to those in previously reported works and cis-H2, and their Zn complexes. HR-ESI mass spectra of cis/trans-Pt and cis/trans-Pd showed the main peaks corresponding to [M + H]⁺ or [M]⁺ of 1203.9604, 1202.9560, 1113.8927, and 1113.8948, respectively, which is according to molecular weights based on the empirical formula (Figure S25–28).

Crystals suitable for X-ray diffraction for trans/cis-Pt were obtained. Crystallographic studies revealed that both complexes crystallized in monoclinic space group, with C2 axis passing through the Pt atom, perpendicular to the porphyrinoid plane of trans-Pt and that lies in the plane of cis isomer. trans-Pt (CCDC: 1060750) clearly indicates the trans location of β-oxazolone moieties, whereas the oxygen atoms of carbonyl in cis-Pt (CCDC: 1060749) were found disordered toward two directions with equal proportions. As shown in Figure 1, for cis/trans-Pt, the Pt atom was located perfectly in the slightly distorted plane defined by the N4 cavity. The mean Pt–N (oxazolone moieties) bond distance (1.992 Å) in cis/trans-Pt is slightly shorter than that in PtF20TPP (2.018 Å) and PtF20TPPL (2.003 Å, CCDC:252892). In addition, relative orientation of the lactone moieties has slight effect on the C=C=O bond distances (1.153 and 1.196 Å, for cis- and trans-Pt respectively), which are slightly shorter than that in PtF20TPPL (1.215 Å).

Photophysical Properties. The electronic absorption spectra of cis/trans-Pt and cis/trans-Pd in dichloromethane (DCM) exhibited intense Soret bands at 402–411 nm (Figure 2), with pronounced shoulders of intensity to the blue and low-energy Q bands at ca. 607–638 nm. Compared to Pd or Pt complexes of F20TPP and F20TPPL (Table S1), the lowest energetic Q(0,0) bands of cis/trans-Pt and cis/trans-Pd redshift to 607, 623, 617, and 638 nm, respectively. Notable intense Q bands were observed in trans/Pt/Pd and the extinction coefficient ratio of lowest energetic Q(0,0) band and Soret band (εQ(0,0)/εSoret) are 0.68 and 0.69, which are larger

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Scheme 1. Synthetic Procedure for Pt(II) and Pd(II) Porphodilactones

**Synthesis and Characterization.** cis- and trans-H2 (H2 = tetrapentafluorophenyl porphodilactone) free bases were prepared according to previously reported procedures. Pt and Pd complexes were prepared by refluxing M(acac)2 (M = Pt or Pd, S equiv, acac = acetylacetonate) with porphodilactone ligands in PhCN, yielding cis/trans-Pt and cis/trans-Pd in 10, 18, 43, and 45%, respectively (Scheme 1). The 1H NMR spectra of trans-Pt/Pd in CDC13 showed one β-H signal located in ca. δ = 8.67 ppm, whereas cis/Pt/Pd displayed more complicated β-H signals with two peaks at 8.52 and 8.62 ppm (cis-Pt), and 8.46 and 8.59 ppm (cis-Pd), respectively (Figure S9–12). 19F-NMR spectra of cis/trans-Pt/Pd showed that 20 F atoms located at 59.0–60.8, 71.5–72.6, and 82.2–83.3 ppm, using trifluoroacetic acid (TFA) as an external standard (Figure S13–16). 13C NMR spectra of cis/trans-Pt/Pd showed that carbon signals assigned for the C=O group are located at 161.9, 162.3, 162.1, and 162.3 ppm (Figure S17–20), respectively. Similar chemical shift of 13C NMR signals of C=O groups might indicate their similarity at the ground state.
than those in cis isomers (0.46 for cis-Pt and 0.34 for cis-Pd). The distinctive Q bands between trans and cis isomers suggest the orientation of β-oxazolone moieties are important to tune the energies of the frontier π-MOs, which are consistent to those observed in Zn porphodilactone complexes.\(^7\)

Upon excitation in the Soret or Q-band region, cis/trans-Pt/Pd displayed an intense luminescence in the NIR region (836–916 nm) with a red-shifted shoulder (ca. 99–142 nm) (Figure 2). The measured lifetimes (10.9, 21.0, 83.0, and 109.9 μs for cis/trans-Pt and cis/trans-Pd, respectively) in the microsecond range suggest that the emission is probably of triplet parentage, giving rise to air-sensitive phosphorescence. As shown in Table 1, the phosphorescence quantum yields were determined as 0.04, 0.06, 0.01, and 0.01 for cis/trans-Pt and cis/trans-Pd, respectively, referred to ZnTPP (Φ = 0.033 in toluene).\(^10\) Importantly, the modular and accumulative increases of Stokes shifts of either Pt or Pd complexes were observed (Table 1 and Figure S1), following the trend of porphyrin, porpholactone to cis/trans-porphodilactones. Such Stokes shifts are comparable to those obtained in Pt complexes of β-aryl fused porphyrins series of β-benzo- (161 nm), naphthalo- (202 nm) to anthra- (260 nm),\(^11\) clearly suggesting the number and orientation of β-oxazolone moieties effectively influence the phosphorescence and thus triplet excited states of metalloporphyrinoids with the broad structural similarity.

The redox properties of cis/trans-Pt/Pd, together with their porphyrin and porpholactone analogues, in DCM were examined by cyclic voltammetry using tetra-n-butylammonium hexafluorophosphate (n-Bu4NPF6) as supporting electrolyte (Figure S1–2). Electrochemical data listed in Table S2 revealed that β-lactonization in the sequence PtF20TPPL, cis- and trans-Pt results in gradual anodic shifting of the first reduction.

![Figure 1](https://example.com/f1.png)

**Figure 1.** Stick models of the single crystal X-ray structures of (a) trans-Pt and (b) cis-Pt. The C2 symmetry axis for (c) trans-Pt is perpendicular to the core porphyrin plane and (d) cis-Pt lies in the plane. The disorder of the oxygen atoms of carbonyl in cis-Pt was omitted.

![Figure 2](https://example.com/f2.png)

**Figure 2.** UV–vis (blue) and phosphorescence (red) spectra of (a) PtF20TPP, (b) PtF20TPPL, (c) cis-Pt, (d) trans-Pt, (e) PdF20TPP, (f) PdF20TPPL, (g) cis-Pd, and (h) trans-Pd in DCM at room temperature. The sample for the phosphorescence spectra measurements were through 5 freeze–pump–thaw cycles.
Table 1. Photophysical Data of Pt(II) and Pd(II) Porphodilactone

<table>
<thead>
<tr>
<th>UV–vis $\lambda_{\text{max}}$ [nm] (log $\varepsilon$ [M$^{-1}$ cm$^{-1}$])</th>
<th>phosphorescence$^a$ $\lambda_{\text{max}}$ [nm] (r)</th>
<th>Stokes shift [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Pt 366 (4.71), 391 (4.94), 408 (5.10)</td>
<td>836 (10.9), 935</td>
<td>0.04 229</td>
</tr>
<tr>
<td>trans-Pt 369 (4.87), 402 (5.18)</td>
<td>866 (21.0), 1000</td>
<td>0.06 243</td>
</tr>
<tr>
<td>cis-Pd 411 (5.22)</td>
<td>859 (83.0), 969</td>
<td>0.01 242</td>
</tr>
<tr>
<td>trans-Pd 382 (4.87), 391 (4.87), 411 (5.22)</td>
<td>916 (109.9), 1058</td>
<td>0.01 278</td>
</tr>
</tbody>
</table>

$^a$Determined in degassed DCM solutions at room temperature.

Figure 3. Nanosecond transient IR spectra of (a) PtF$_{20}$TPPL, (b) cis-Pt, (c) trans-Pt, (d) PdF$_{20}$TPPL, (e) cis-Pd, and (f) trans-Pd in CH$_3$CN at selected time delays following 355 nm laser irradiation.

Potential differences of ca. 0.20, 0.37, and 0.46 V compared with PtF$_{20}$TPP, whereas negligible changes in the first oxidation potentials were observed. A similar trend was observed in the Pd series. As a consequence, the electrochemically determined HOMO–LUMO gaps for trans-Pt/Pd are smaller than those of their porphyrin or porpholactone or cis-isomer counterparts, consistent with the trend of DFT calculated HOMO–LUMO gaps. These results demonstrate that the replacement of pyrrole by $\beta$-oxazolone moiety is more effective to tune LUMO energy than HOMO and more resistant to oxidative condition, in contrast to those observed in “$\pi$-extension” NIR porphyrins, in which more increase of HOMO energy than LUMO.$^{1-4}$

Time Resolved Infrared Spectroscopy and Computational Studies. To gain further insights into the triplet excited state properties, we performed time-resolved infrared (TRIR) spectroscopy experiments for the characteristic C=O bond stretching vibrations of metalloporpholactones or metalloporphyrins, which allows us to distinguish the nature of electronic structures related to the triplet states.$^{1,2}$ In the TRIR spectra of PtF$_{20}$TPPL and cis/trans-Pt (Figure 3a–c) upon the irradiation of nanosecond 355 nm laser, the ground state bleaching bands of PtF$_{20}$TPPL (1789 cm$^{-1}$), cis-Pt (1783 cm$^{-1}$), and trans-Pt (1781 cm$^{-1}$) were observed, in accompany with the appearance of positive bands for PtF$_{20}$TPPL (1766 cm$^{-1}$), cis-Pt (1813 cm$^{-1}$), and trans-Pt (1797 cm$^{-1}$), which are air sensitive and microsecond scaled lifetimes. These positive bands are assigned to C=O stretching vibrations in the triplet states and match well with the theoretically predicted vibrational frequencies (Table S3). Similar TRIR results were obtained for PdF$_{20}$TPPL and cis/trans-Pd (Figure 3d–f).

Comparison of the IR bands in the triplet state relative to ground state showed a remarkable difference between MF$_{20}$TPPL and cis/trans-M (M = Pd and Pt). For example, the $\nu$(C=O) IR band of PtF$_{20}$TPPL displayed a shift of 23 cm$^{-1}$ to the lower frequency in the triplet state compared to that in its ground state, whereas those for cis-Pt and trans-Pt showed 30 and 16 cm$^{-1}$ shifts to the higher frequency, respectively. Similar changes of $\nu$(C=O) IR bands (shift of 23 cm$^{-1}$ to the lower frequency for PdF$_{20}$TPPL and shifts of 38 and 31 cm$^{-1}$ to the higher frequency for cis/trans-Pd, respectively) were observed for Pd complexes. It shows here that the C=O vibrational frequencies are sensitive to the electronic transition from the ground to the triplet excited states, suggesting the strong electronic coupling between the lactone moieties and the main porphyrin chromophores. Thus, the carbonyl group C=O introduced by $\beta$-lactonization can
serve as a vibrational signature to reflect the electronic structure change upon excitation. Moreover, the C=O vibrational frequency change from the S0 state to the T1 state is sensitive to the extent of β-lactonization and cis/trans positioning, demonstrating further fine-tuning ability of β-dioxazolone moieties on the excited state electronic structures. Generally, the hypsochromic shift in ν(C=O) can be resulted from the inductive effect of the more highly electronegative substituent, such as nitrogen, oxygen, or halogen atom, while an extension of the conjugated system can cause bathochromic shift.13 The inductive and conjugation effects can be further understood by the combined theoretical calculations as follows.

Hybrid density functional theory (B3LYP14) calculations were performed using cc-pvdz basis sets for C, N, H, F, and O atom and the LANL2DZ basis set15 for Pt and Pd atom, taking into account the relativistic effects implicitly. Based on the optimized structures, the atomic polar tensors (APT) charge difference for T1 and S0 is first characterized, which can properly characterize the inductive effect.16 Figure 4 shows the APT charge difference between triplet and singlet state calculated with the B3LYP functional.

APT charge difference on the carbonyl group and the adjacent oxygen between T1 and S0 for PtF20TPPL, cis- and trans-Pt. (For Pd porpholactones, similar results are provided in Figure S3). From S0 to T1, more negative charges are shown on the electron withdrawing oxygen, in accompany with the depletion of electron density on the carbonyl group. For cis- and trans-Pt, obvious APT charge difference is shown on the substituent oxygen (−0.238 and −0.228), indicating strong inductive effect that may lead to the hypsochromic shift of ν(C=O) for the triplet cis-Pt and trans-Pt. For PtF20TPPL, the inductive effect is quite weak as shown by the small APT charge difference on the substituent oxygen (−0.04).

Additionally, molecular frontier orbital calculations were performed to characterize the conjugation effect, which also governs the C=O vibrational frequency. The promotion of an electron from HOMO to LUMO results in an electronic transition for singlet state, while the corresponding orbitals in the triplet manifold are the singly occupied molecular orbitals SOMO-1 and SOMO-2. The molecular orbital feature of SOMO-2 resembles LUMO (Figures S5 and S6), while SOMO-1 differs HOMO profoundly. Comparison of SOMO-1 (T1) with HOMO (S0) of PtF20TPPL, cis-Pt and trans-Pt is shown in Figure 5. (Similar results for Pd porpholactones are provided in Figure S4). For PtF20TPPL, the conjugation along O–C–C in HOMO is extended to O–C–C–N in SOMO-1. This makes the carbonyl group to be of larger single bond character in the triplet state and thus the ν(C=O) is shifted to lower frequency. Considering the weak inductive effect in PtF20TPPL, the conjugation effect should become predominant and result in lowering of the triplet IR frequency in total, and a red-shift of 23 cm⁻¹ was indeed observed in the experiment. For cis-Pt, the O–C–C conjugation in HOMO and SOMO-1 are almost the same. Therefore, the triplet ν(C=O) IR band is mainly blue-shifted due to the predominant inductive effect. For trans-Pt, the extension of conjugation from O–C–C in HOMO to O–C–C–N in SOMO-1 is again displayed. This conjugation effect should then decrease the blue-shifts of the triplet ν(C=O) IR band caused by the inductive effect and result in less total blue-shifts compared with cis-Pt, which is consistent with the TRIR spectral results that the triplet ν(C=O) IR bands display blue-shifts of 30 cm⁻¹ for cis-Pt and 16 cm⁻¹ for trans-Pt (Figure 3).

Interestingly, the above analysis suggests that β-lactonization and cis/trans positioning play subtle roles in modulating the frontier molecular orbitals, through which the triplet electronic structures and energies are effectively tuned, as manifested by vibrational frequency shifts in TRIR spectra and phosphorescence wavelength shifts, respectively. As shown in Figure 5, the introduced O–C–C conjugation favors decreasing the T1−S0 energy gap, and this energy gap is further reduced from cis to trans positioning because of the further conjugation extension from O–C–C in HOMO to O–C–C–N in SOMO-1 for trans-Pt. The trend of conjugation extension in frontier molecular orbitals coincides with the phosphorescence red-shifts of 90, 188, and 218 nm for PtF20TPPL, cis-Pt and trans-Pt compared with PtF20TPP, respectively. Furthermore, the calculated phosphorescence emission wavelength were consistent to experimental results (Table S4).

Photosensitizing Property of Metalloporphodilactones in the NIR Region. To demonstrate the potential application of metalloporphodilactones in the NIR region, in this work, we chose rubrene as a triplet acceptor with a low-lying triplet state (Eg = 1.14 eV) and performed triplet–triplet annihilation (TTA) reaction with cis/trans-Pd for the longer lifetime than Pt complexes.17 Dynamic Stern–Volmer (S–V) analysis of triplet energy transfer rate constants of rubrene (acceptor) with cis/trans-Pd showed similar S–V constants of 1.80 and 1.81 × 10⁵ M⁻¹ s⁻¹ for cis/trans-Pd (Figures S7–8), indicating rubrene has comparable quenching efficiency to the triplet states of cis/trans-Pd. As shown in Figure 6a, the preliminary results showed trans-Pd is most effective among cis/trans-Pt/Pd and emitted the strongest upconverted fluorescence from rubrene (λem = 561 nm) upon excitation at 635 ± 5 nm. Plotting emission intensity vs laser power density (635 ± 5 nm) reveals the nonlinear nature of the TTA process using

![Figure 4. APT charge difference between triplet and singlet state calculated with the B3LYP functional.](Image)

![Figure 5. HOMO of singlet state and SOMO-1 of triplet state calculated with the B3LYP functional. Isovalue: 0.02.](Image)
Interestingly, if extinction coefficient was taken in account to evaluate the overall upconversion capability ($\eta$, $\eta = \varepsilon \Phi_{\text{UC}}$), proposed by Zhao and co-workers, the trans-Pd showed significantly larger $\eta$ value ($7.80 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$) than the other 3 complexes (Table 2). More importantly, trans-Pd or Pt trans complex displays $\eta$ value $10^4$ times higher than the cis analogue. These results strongly suggested the importance of the orientation of $\beta$-oxazolone moieties on the triplet energy transfer process, as evidenced by the larger $\Phi_{\text{UCs}}$ or $\eta$s in trans-Pt/Pd than cis analogues for the longer triplet lifetimes and Q-band absorptions.

## CONCLUSION

Taken together, we synthesized Pd and Pt complexes of cis- and trans-porphodilactones and investigated their photophysical properties related to the lowest triplet excited states. As expected, the gradually red-shifted absorption and NIR emission from metalloporphyrin, porpholactone, and cis/ trans-porphodilactones were observed, demonstrating the number and orientation of $\beta$-oxazolone moieties influence their photophysical properties. cis/trans-Pt/Pd display remarkable Stokes shifts, which are comparable to tetraenporphyrins and linearly $\pi$-expanded derivatives, demonstrating that $\beta$-lactonization efficiently lowers the lowest triplet states. The orientation of $\beta$-oxazolone moieties also affects the lowest triplet excited states of metalloporphyrinoids, which is evidenced by different C=O stretching vibration in excited states. Computational studies have been performed to provide insights into the electronic structures and spectroscopic properties of cis/trans-Pt/Pd, which offers a better understanding on the nature of the orientation of $\beta$-oxazolone moieties on the excited state energy. In addition, trans-Pt/Pd showed more efficient energy transfer to rubrene to generate delayed fluorescence than cis analogues in TTA reactions, suggesting the importance of subtle changes in porphyrin periphery on the photosensitizing ability. This work provides a benchmarked example of modulating NIR phosphorescence with the structural similarity, in contrast to the traditional “extended $\pi$-conjugation” strategies and would be important to design NIR porphyrinoids as optoelectronic materials, solar fuel, and photosensitizers.

## EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were performed under an inert nitrogen atmosphere. UV–visible spectra were recorded on an Agilent 8453 UV–vis spectrometer equipped with an Agilent 89090A thermostat (±0.1 °C) at 25.0 °C. The emission spectra and lifetimes were recorded on an Edinburgh Analytical Instruments FL920 lifetime and steady state spectrometer (450 W Xe lamp, PMT R928 and Hamamatsu R5509). Mass spectra were measured on a Bruker APEX IV FT-ICR Mass Spectrometer (ESI-MS). IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer as KBr pellets. $^1$H NMR spectra were measured on a Bruker ARX400 (400 MHz) or AVANCE III (500 MHz) spectrophotometer; $^{13}$CNMR (CF$_3$COOH as external standard) and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III spectrophotometer (471 MHz for $^{13}$F, 126 MHz for $^{13}$C). For the optical measurements in liquid solution, spectrograde DCM, CH$_3$CN and toluene were used as purchased from Alfa-Aesar.

### Synthesis of cis-Pt and trans-Pt. trans- or cis-H$_2$ (80 mg, 0.079 mmol) and Pt(acac)$_2$ (155 mg, 5 equiv) were dissolved in 10 mL of PhCN and was refluxed for 48 h under N$_2$. The solvent was removed under reduced pressure. Then the mixture was dissolved in 5 mL of CHCl$_3$/CH$_3$OH ($v/v = 1:1$) mixing solvent, and excess Zn(AcO)$_2$·2H$_2$O was added. The reaction mixture was refluxed for 3 h, and the remaining free base ligands were reacted. trans- and cis-Pt were obtained after silica column chromatography in the yield of 18 and 10%, respectively.

### Synthesis of cis-Pt and trans-Pt. trans- or cis-H$_2$ (80 mg, 0.079 mmol) and Pd(acac)$_2$ (120 mg, 5 equiv) were dissolved in 10 mL of PhCN and was refluxed for 12 h under N$_2$. The solvent was

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### Table 2. Upconversion Quantum Yield ($\Phi_{\text{UC}}$) and Overall Upconversion Capability ($\eta$) of cis-Pt, trans-Pt, cis-Pd and trans-Pd with Rubrene

<table>
<thead>
<tr>
<th>sensitizer</th>
<th>$\Phi_{\text{UC}}$ (%)</th>
<th>$\eta$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Pt</td>
<td>0.04</td>
<td>0.23</td>
</tr>
<tr>
<td>trans-Pt</td>
<td>0.18</td>
<td>2.30</td>
</tr>
<tr>
<td>cis-Pd</td>
<td>0.08</td>
<td>3.6</td>
</tr>
<tr>
<td>trans-Pd</td>
<td>1.02</td>
<td>78000</td>
</tr>
</tbody>
</table>

$^{a}$Upconversion quantum yield $\Phi_{\text{UC}}$. Excited with 635 ± 5 nm laser diode (central wavelength located at 639 nm, 55 mW). With the prompt fluorescence of methylene blue as the standard ($\Phi = 0.03$ in methanol), $c$ (sensitizers) = 3.0 μM, $c$ (rubrene) = 180 μM. In degassed toluene, 20 °C. $^b$The overall upconversion capability $\eta = \varepsilon \Phi_{\text{UC}}$ $\varepsilon$ means the extinction coefficient at 639 nm in toluene.

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Figure 6. (a) Images of the upconverted fluorescence of rubrene with cis-Pt, trans-Pt, cis-Pd, and trans-Pd as sensitizers inside the 1 cm quartz cell (3.0 μM sensitizers and 180 μM acceptor, $\lambda_{ex} = 635 \pm 5$ nm, 55 mW, central wavelength located at 639 nm, no optical filters were used); (b) upconverted emission intensity profile of rubrene following selective excitation (635 ± 5 nm laser) of trans-Pd measured as a function of incident power density in degassed toluene; (c) emission intensity at 561 nm from panel b, plotted as a function of the incident light power. The asterisks in panel b indicate the scattered light of the excitation laser. The red line in panel c represents the best quadratic fit to the data.
removed under reduced pressure. trans- and cis-Pd were obtained after silica column chromatography in the yield of 45 and 43%, respectively. trans-Pd: 1H NMR (400 MHz, CDCl3) δ 8.66 (s, 4H). HRMS (ESI+) m/z [M]+: calcd for C17H14F2N2O2Pd 1115.8948, found: 1115.8972. cis-Pd: 1H NMR (400 MHz, CDCl3) δ 8.59 (s, 2H), 8.46 (s, 2H). HRMS (ESI+) m/z [M]+: calcd for C17H14F2N2O2Pd 1115.8948, found: 1115.8948.

Time-Resolved Infrared Spectroscopy. The triplet excited state formation upon UV excitation was monitored by step-scan, time-resolved Fourier transform infrared (TR-FTIR) absorption spectroscopy. The TR-FTIR instrument comprises a Nicolet Nexus 870 step-scan FTIR spectrometer, a Spectra Physics Lab170 Nd YAG laser, a pulse generator (Stanford Research DG535) to initiate the laser pulse and achieve synchronization of the laser with data collection, two digitizers (internal 100 kHz 16-bit digitizer and external 100 MHz 14-bit GAGE CS14100 digitizer) which offer fast time resolution and a wide dynamic range as needed, and a personal computer to control the whole experiment. The detector used in this work is the photovoltaic MCT (0.5 mm) equipped with a fast internal preamplifier (50 MHz).

There are two outputs from the detector: output DC, corresponding to the value of the static interferogram, and output AC, corresponding to the time-resolved change of the interferogram. The AC signal was then amplified by an external preamplifier (Stanford Research, SR560). The differential absorbance spectra is calculated based on equation:

$$\Delta A = A_{\text{AC}} - A_{\text{DC}} = \log_{10}(1 - I_{\text{AC}}/I_{\text{DC}})$$

where $I_{\text{DC}}$ and $I_{\text{AC}}$ are the single-beam intensity spectra corresponding to static (DC) and dynamic (AC) channels. $\Delta A_{\text{AC}}$ is calibrated before being used in the equation because different gain is applied to the AC channel.

The third harmonic of Nd:YAG laser (335 nm) operating at 10 Hz repetition rate was used in the experiments. The laser excitation beam was directed through an iris aperture (3 mm in diameter) and then overlapped with the infrared beam in the sample cell within the sample compartment of the FTIR spectrometer. The laser beam energy after the aperture was 3 mJ per pulse. A Harrick flow cell with 2 mm-thick CaF2 windows (path-length: 500 μm) was used for the measurements. The closed flow system is driven by a peristaltic pump (ColeParmer Masterflex) to refresh the sample before every laser pulse.

Theoretical Calculations. We carried out density functional theory calculations as implemented in the program package Gaussian 09 using the hybrid density functional theory, i.e., Becke’s three-parameter nonlocal exchange functional with the nonlocal correlation parameter nonlocal exchange functional of Lee, Yang, and Parr (B3LYP). The cc-pvdz basis set was used for Pt and Pd atoms taking into account the relativistic effects. The theoretical calculations were performed as local minima using vibrational frequency calculations, which confirmed that all of the computed vibrational frequencies were real. The molecular orbitals and atomic polar tensors (APT) charges of Pt and Pd porphyrinoids in the singlet and triplet states were calculated at the same level. In general, DFT calculations with the B3LYP hybrid functional tend to overestimate the vibrational frequencies, so all calculated vibrational frequencies were scaled by a factor 0.9614, according to Koch and Holthausen.

Upconversion Quantum Yields Measurement. The upconversion quantum yield ($\Phi_{\text{UC}}$) of cis-Pt, trans-Pt, cis-Pd, and trans-Pd with rubrene were determined in degassed toluene with the prompt fluorescence of the methylene blue (Φm = 0.03 in methanol) as standard and calculated with the following equation:

$$\Phi_{\text{UC}} = 2\Phi_{\text{m}}(A_{\text{std}}/A_{\text{unk}})(I_{\text{unk}}/I_{\text{std}})^{2}$$

where $\Phi_{\text{UC}}$, $A_{\text{unk}}$, and $I_{\text{unk}}$ represents the quantum yield, absorbance, and integrated photoluminescence intensity; $I_{\text{unk}}$ represents the refractive indices of the solvent used for the samples; and symbols with “std” stand for the corresponding parameter for the standard.

**ASSOCIATED CONTENT**

■ Supporting Information

These materials are available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06332.

Transient absorption spectra; cyclic voltammetry data; Stern–Volmer analysis; and 1H NMR, 13C NMR, 19F NMR, IR and ESI-MS spectra (PDF)

Photophysical data of metalloporphyrins (CIF) Photophysical data of porpholactones (CIF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


