

# Near-IR Broadband-Absorbing *trans*-Bisphosphine Pt(II) Bisacetylide Complexes: Preparation and Study of the Photophysics

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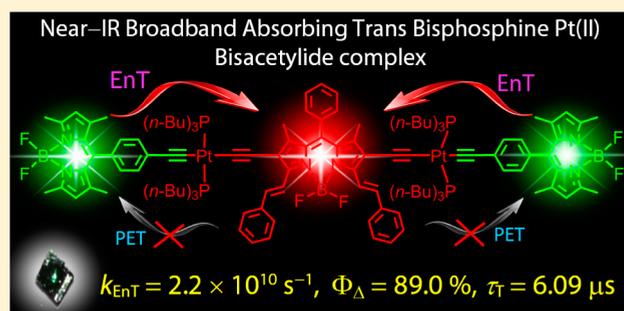
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## Supporting Information

**ABSTRACT:** Broadband near-IR absorbing *trans*-bis-(trialkylphosphine) Pt(II) bisacetylide binuclear complex (Pt-1) was prepared with boron-dipyrromethene (Bodipy) and styrylBodipy acetylide ligands. Pt-1 shows strong absorption bands at 731 and 503 nm. Singlet energy transfer (EnT) and efficient intersystem crossing of the central coordinated Bodipy ligand were proposed to be responsible for the efficient funneling of the excitation energy to the triplet-state manifold. Reference complexes containing only a single Bodipy ligand were prepared for comparison (with styrylBodipy ligand Pt-0 or Bodipy ligand Pt-2). The molecular structures were confirmed by single-crystal X-ray diffraction. The photophysical properties were studied with steady-state and time-resolved transient absorption spectroscopies, electrochemical characterization, and density functional theory/time-dependent density functional theory calculations. Dual fluorescence was observed for Pt-1. Singlet EnT in Pt-1 was proposed based on the fluorescence quenching/excitation spectra, and femtosecond transient absorption spectra (energy transfer rate constant  $k_{\text{EnT}} = 2.2 \times 10^{10} \text{ s}^{-1}$ ). With nanosecond transient absorption spectra, intramolecular triplet-state energy transfer in Pt-1 was proved. Gibbs free energy changes of charge separation indicate that the photoinduced intramolecular electron transfer in Pt-1 is thermodynamically prohibited. Intermolecular triplet transfer between Pt-2 and L-1 was studied with nanosecond transient absorption spectra; the EnT rate and energy transfer efficiency were determined as  $3.6 \times 10^4 \text{ s}^{-1}$  and 94.5%, respectively. The singlet oxygen ( $^1\text{O}_2$ ) photosensitizing of Pt-1 was improved as compared to the complexes containing only a single visible-light-absorbing chromophore.



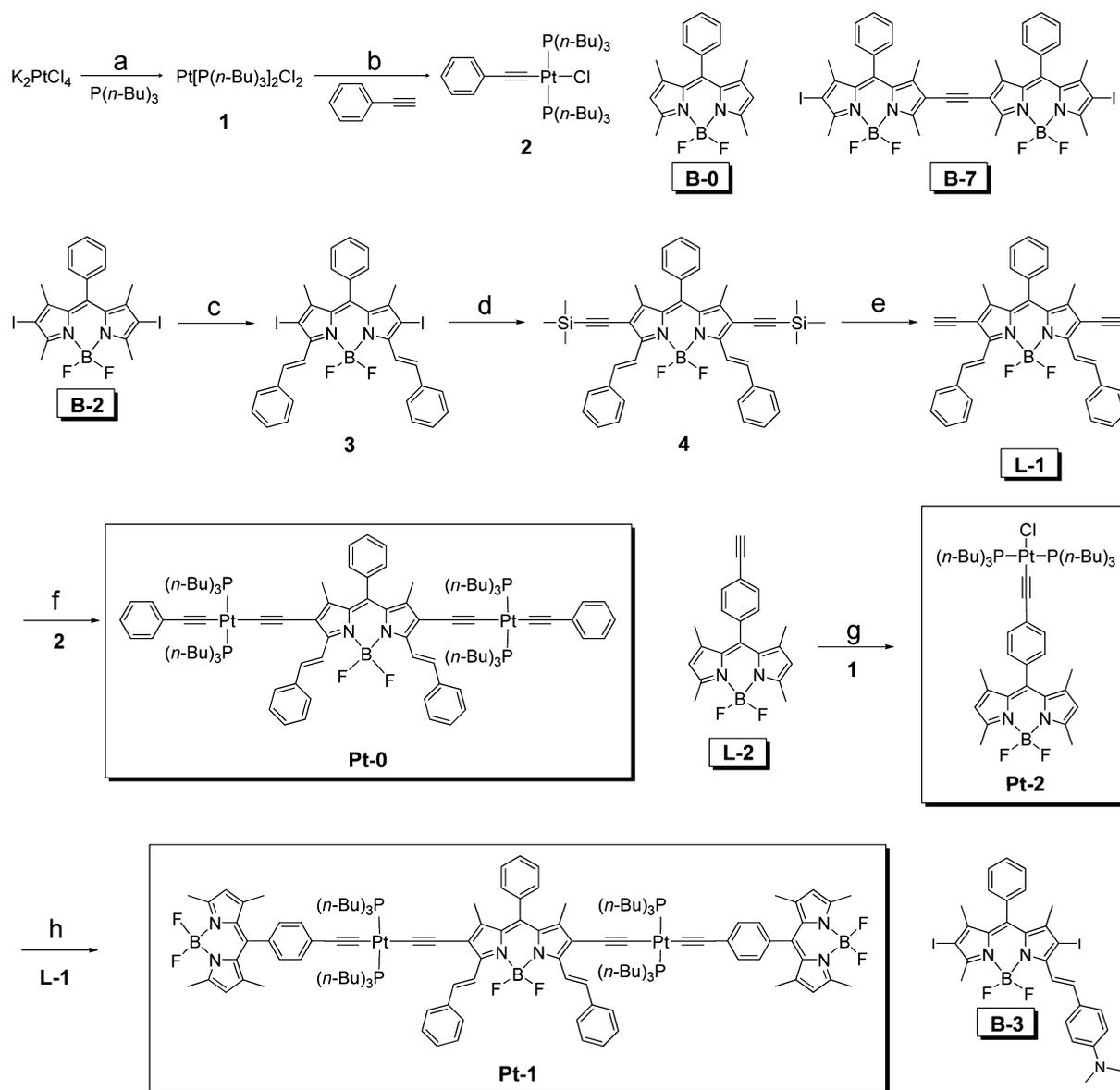
## INTRODUCTION

Transition metal complexes, such as Pt(II) complexes, have attracted much attention due to the applications in photocatalysis,<sup>1–3</sup> hydrogen ( $\text{H}_2$ ) production,<sup>4,5</sup> photoredox catalytic organic reactions,<sup>6,7</sup> electroluminescence and luminescence bioimaging,<sup>8–11</sup> molecular sensors and devices,<sup>12,13</sup> photodynamic therapy,<sup>14,15</sup> and more recently in triplet–triplet annihilation (TTA) upconversion.<sup>16–19</sup> Concerning most of these applications, the complexes play the pivotal role via photoinduced *intermolecular* energy transfer (EnT) or electron transfer (ET).<sup>19</sup> Thus, the visible-light-harvesting ability and the lifetime of the triplet excited state of the complexes are the two crucial parameters for the transition metal complexes to be used as triplet photosensitizers, because the intermolecular EnT and ET can be enhanced by the strong light absorption (a prerequisite for formation of abundant photosensitizers at excited states) and the long-lived triplet excited states.<sup>19</sup>

In this context, the conventional Pt(II) complexes are suffering from some limitations.<sup>1</sup> First, the complexes usually show very weak absorption in visible spectral region, and the absorption is usually in UV or blue range of the spectrum.<sup>20–26</sup> Very few complexes show absorption in visible spectra range.<sup>27–30</sup> Second, the lifetime of the triplet excited state is usually short, less than  $10 \mu\text{s}$ .<sup>1</sup> Third, the molecular structure profile of the complexes is based on a single visible-light-harvesting chromophore; thus, there is only one major absorption band in visible spectral range for these complexes. As a result, harvesting of the excitation energy of a broadband light source, such as solar light, is inefficient.<sup>1,19</sup>

To address the above challenges, recently we prepared a series of Pt(II),<sup>28,29,31–33</sup> Ru(II),<sup>34,35</sup> Ir(III),<sup>36–39</sup> and Re(I)

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Scheme 1. Preparation of the Complexes Pt-0 and Pt-1<sup>a</sup>

<sup>a</sup>The molecular structures of the ligands and reference complexes are also shown. (a) Deionized water, Ar, RT, 3 h, yield 57.7%. (b) Dried  $NH_4Et_2$ , Ar, 45 °C, 8 h, yield: 79.8%. (c) Benzaldehyde, acetic acid, piperidine, Ar, microwave irradiation 150 °C, 6 min, yield: 85.1%. (d) Trimethylsilylacetylene,  $Pd(PPh_3)_2Cl_2$ ,  $PPh_3$ , CuI, distilled THF,  $(Pr)_2NH$ , Ar, 68 °C, 6 h, yield: 77.0%. (e)  $Bu_4NF \cdot 3H_2O$ , distilled THF, Ar, -78 °C, 0.5 h, yield: 58.4%. (f) CuI, distilled THF, dried  $NH_4Et_2$ , Ar, RT, 0.5 h, yield: 61.9%. (g) CuI, distilled THF, dried  $NH_4Et_2$ , Ar, RT, 3 h, yield 43.0%. (h) Dried  $NH_4Et_2$ , Ar, 45 °C, 9 h, yield: 33.4%.

complexes,<sup>40,41</sup> using organic chromophores of boron dipyrromethene (Bodipy), naphthaleneimide, naphthalenediimide, perylenediimide, rhodamine, and fluorescein.<sup>19,42</sup> Strong absorption of visible light and long-lived intraligand triplet state (<sup>3</sup>IL) was observed for these complexes. These complexes have been used for photocatalysis and TTA upconversion.<sup>17,19,42</sup> We also prepared Pt(II) complexes that contain two different visible-light-absorbing chromophores; thus, broadband visible-light-absorption was observed.<sup>30,43</sup> However, there is still much room left to fully explore the molecular structural diversity of this kind of complex; for example, the absorption wavelength of these complexes are usually shorter than 600 nm. This short absorption wavelength is detrimental for luminescence bioimaging in vivo or photodynamic therapy (PDT), for which near-IR absorption/emission is desired.<sup>30,43</sup>

Second, the limited examples of the broadband absorbing complexes show only the energy acceptor's emission. Dual emission is rare for Pt(II) complexes.<sup>9,44,45</sup>

To address these limitations, herein we prepared near-IR broadband absorbing binuclear *trans*-bis(tributylphosphine) Pt(II) bisacetylide complex, which contains two types of different Bodipy ligands (Bodipy and styrylBodipy. Pt-1. Scheme 1). Bodipy was selected as the light-harvesting antenna due to its strong absorption of visible light, high fluorescence quantum yields (inhibited non-radiative decay), good photostability, and feasible derivatization.<sup>46–52</sup> The central coordinated styrylBodipy in Pt-1 is with larger  $\pi$ -conjugation framework than the peripheral coordinated Bodipy ligands (Scheme 1). The central coordinated styrylBodipy section shows absorption/emission in the near-IR region (660–800

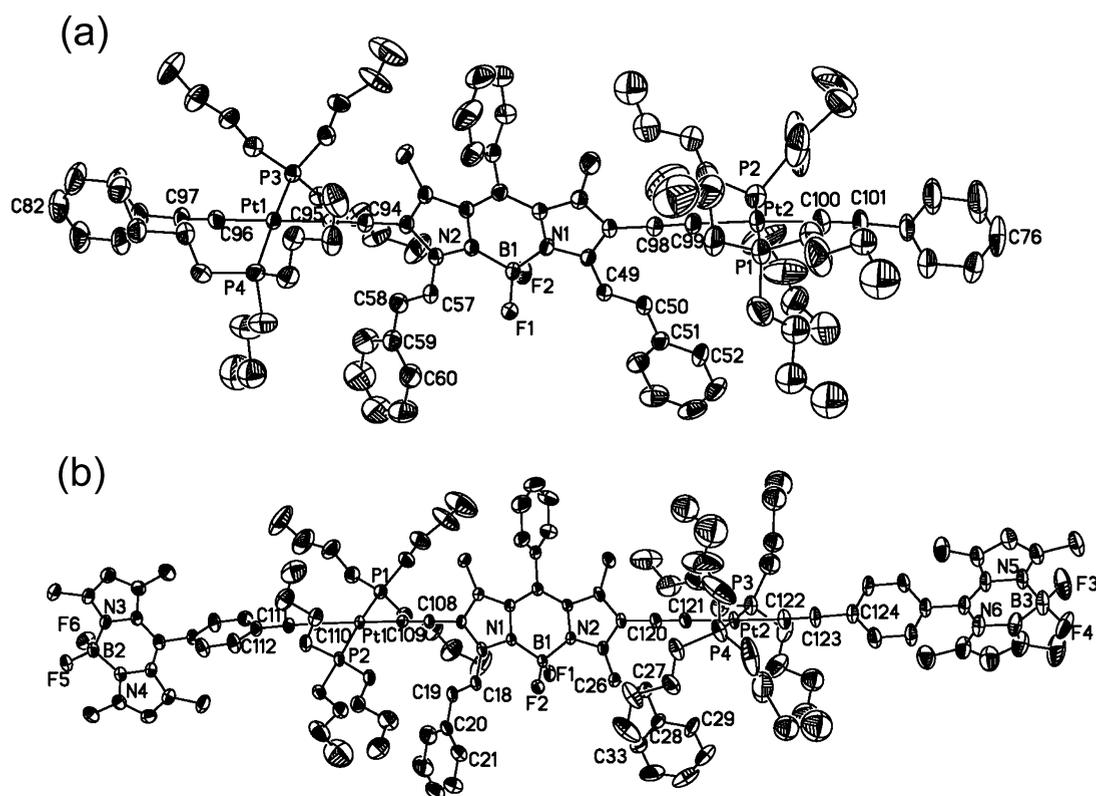


Figure 1. ORTEP view of the single-crystal structure of (a) Pt-0 and (b) Pt-1 with 30% thermal ellipsoids.

nm), and the peripheral coordinated Bodipy ligands give strong absorption at 500 nm. The photophysical properties of the complexes were studied with steady-state and time-resolved transient spectroscopy. Ultrafast singlet-energy transfer via the through-bond energy-transfer (TBET) mechanism was proposed for the broadband visible-light-absorbing complex, because the spectral overlap integral is too small to ensure a fast fluorescence-resonance energy-transfer (FRET) EnT process (Förster mechanism). Dual emission was observed, which is unprecedented for *trans*-bisphosphine Pt(II) bisacetylide complexes. The complex shows efficient singlet oxygen ( $^1\text{O}_2$ ) photosensitizing ability ( $\Phi_\Delta = 89.0\%$ ). Intramolecular and intermolecular triplet-energy transfers were studied with nanosecond time-resolved transient absorption spectroscopy.

## RESULTS AND DISCUSSION

**Design and Synthesis of the Complexes.** *trans*-Bis-(trialkylphosphine) Pt(II) bisacetylide complexes are of particular interest because it is feasible to introduce heteroleptic (different) visible-light-absorbing ligands into the molecules, simply by using different acetylide ligands.<sup>53–55</sup> Recently we prepared N<sup>^</sup>N Pt(II) bisacetylide complex with heteroleptic acetylide ligands.<sup>56</sup> But two different acetylide ligands are unable to be introduced in a stepwise way. Previously unmodified Bodipy ligands were used for preparation of the Pt(II) complexes, but the absorption wavelength is shorter than 600 nm.<sup>28,30,43</sup> Herein we used styrylBodipy as an acetylide ligand, which shows absorption at 648 nm. Upon coordination with Pt(II), the absorption is shifted to 731 nm, that is, in the near-IR region. To the best of our knowledge, no *trans*-bis(trialkylphosphine) Pt(II) bisacetylide complexes have been reported showing absorption in near-IR spectral region.<sup>53–55,57</sup>

The attachment of ethynyl moieties to Bodipy is via Sonogashira coupling reactions (Scheme 1).<sup>38,58</sup> StyrylBodipy ligand L-1 was obtained by the condensation of Bodipy with benzaldehyde.<sup>50</sup> Pt-1 was prepared with Pt-2 and L-1 as the starting materials. All the compounds were obtained in moderate-to-satisfactory yields. The molecular structures were fully verified with  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and high-resolution mass spectrometry (HRMS).

**Single-Crystal Molecular Structures.** The molecular structures of Pt-0 and Pt-1 were determined by single-crystal X-ray diffraction (Figure 1 and Table 1).<sup>59</sup> For Pt-0, the two Pt(II) coordination centers take planar square geometries. For example, the bond angle of C(96)–Pt(1)–P(3) is  $91.22(13)^\circ$ , the bond angle of C(95)–Pt(1)–C(96) is  $178.79(18)^\circ$ , and the P(3)–Pt(1)–P(4) bond angle is  $176.84(4)^\circ$ . A similar result was observed for the Pt(2) coordination center. These values are close to a previously reported *trans*-bis-(trialkylphosphine) Pt(II) bisacetylide complex.<sup>53</sup> The Pt(1)–C(95) bond length is 1.992(4) Å, which is close to the previously reported values (1.981–2.015 Å).<sup>53</sup> The C≡C bond lengths are in the range of 1.193–1.209 Å, which is close to the literature values (1.192–1.233 Å).<sup>59</sup>

For the coordinated styrylBodipy, the two styryl moiety planes twisted toward the  $\pi$ -core of the Bodipy chromophore, presumably due to the steric hindrance exerted by the two Pt(II) coordination centers and the phosphine ligands. For example, the dihedral angles of C(49)–C(50)–C(51)–C(52) and C(57)–C(58)–C(59)–C(60) were observed as  $12.611^\circ$  and  $22.140^\circ$ , respectively. Previously in an uncoordinated styrylBodipy molecule, the dihedral angles of the two styryl moieties with the  $\pi$ -core of the Bodipy chromophore are much smaller.<sup>60</sup> Pt-0 shows a rodlike long molecule axial of 30.6527 Å (the distance of C(76) to C(82)), with the C–Pt–C bond

Table 1. Crystallographic Data for Pt-0 and Pt-1

complexes	Pt-0	Pt-1
sum formula	C <sub>101</sub> H <sub>143</sub> B <sub>3</sub> F <sub>2</sub> N <sub>2</sub> P <sub>4</sub> Pt <sub>2</sub>	C <sub>127</sub> H <sub>169</sub> B <sub>3</sub> F <sub>6</sub> N <sub>6</sub> P <sub>4</sub> Pt <sub>2</sub>
<i>M</i> (g mol <sup>-1</sup> )	1948.04	2440.17
temperature/K	296(2)	296(2)
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	21.7912(18)	15.292(3)
<i>b</i> (Å)	14.8974(12)	17.398(3)
<i>c</i> (Å)	33.153(3)	25.540(4)
$\alpha$ (deg)	90.00	102.092(3)
$\beta$ (deg)	108.1610(10)	94.011(3)
$\gamma$ (deg)	90.00	103.690(3)
volume/Å <sup>3</sup>	10 226.4(14)	6403.9(19)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> /g·cm <sup>-3</sup>	1.265	1.265
crystal size (mm)	0.34 × 0.28 × 0.26	0.35 × 0.27 × 0.15
<i>F</i> (000)	4008	2516
$\mu$ (Mo <i>K</i> $\alpha$ )/mm <sup>-1</sup>	2.841	2.288
$\theta$ (deg)	1.88–28.27	1.52–28.41
reflections collected	62 775	47 943
independent reflections	24 775	31 660
parameters	1239	1526
largest diff. peak and hole (e Å <sup>-3</sup> )	0.822, -0.543	1.358, -0.721
goodness of fit	1.012	1.014
<i>R</i> <sup>a</sup>	0.0477 <sup>b</sup>	0.0496 <sup>b</sup>
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.0823 <sup>b</sup>	0.1113 <sup>b</sup>

<sup>a</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$ ; [ $F_o > 4\sigma(F_o)$ ]. <sup>b</sup>On the basis of all data.

angles of C(95)–Pt(1)–C(96) and C(99)–Pt(2)–C(100) at 178.79(18)° and 177.3(2)°, respectively.<sup>59</sup>

On the basis of the single-crystal structure of Pt-1, a rodlike geometry was found, with the B(2)–B(3) distance of 39.4989 Å. The two Pt(II) coordination centers are close to planar square geometry. For example, the P(1)–Pt(1)–P(2) bond angle is 173.44(5)°, and the C(109)–Pt(1)–C(110) bond angle is 176.80(18)°. The bond lengths of the acetylide C≡C bonds are in the range of 1.201–1.205 Å, which is close to the literature values.<sup>59</sup> Another distinct feature is the non-coplanar geometry of the styryl moiety with the Bodipy chromophore. For example, the dihedral angle of C(18)–C(19)–C(20)–C(21) is 18.998°, and the dihedral angle of C(26)–C(27)–C(28)–C(33) is 0.127°. Furthermore, we found that the coordinated moieties on the long axial of the Pt(II) coordinated rod are not in a straight line. For example, C(110)–C(111)–C(112) is 176.0(5)°, C(111)–C(110)–Pt(1) is 173.2(4)°, C(123)–C(122)–Pt(2) is 173.3(5)°, and C(122)–C(123)–C(124) is 173.3(6)°. Similar deviation was also found for other *trans*-bis(trialkylphosphine) Pt(II) bisacetylides complexes.<sup>53</sup> In less congested Pt(II) complexes, a nearly straight coordination axial was found.<sup>61</sup> Similar geometries were observed for Pt-0 (Tables S1 and S2, see Supporting Information).

**UV–vis Absorption Spectra and Fluorescence Spectra.** The UV–vis absorptions of the complexes were studied (Figure 2). The references Pt-0 and Pt-2, which contain only the styrylBodipy or the Bodipy chromophore, give only one major absorption band at 734 or 504 nm, respectively. Notably, the absorption of the ligand L-1 is red-shifted by 86 nm upon coordination with Pt(II). For Pt-2, however, the absorption wavelength is similar to the free ligand L-2. The different absorption of the two complexes is due to the derivatization

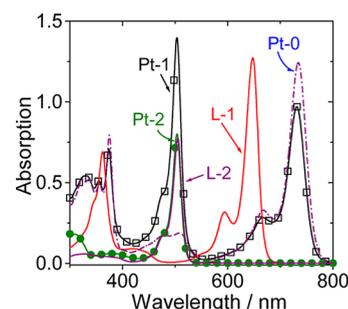


Figure 2. UV–vis absorption spectra of the compounds. *c* = 1.0 × 10<sup>-5</sup> M in toluene, 20 °C.

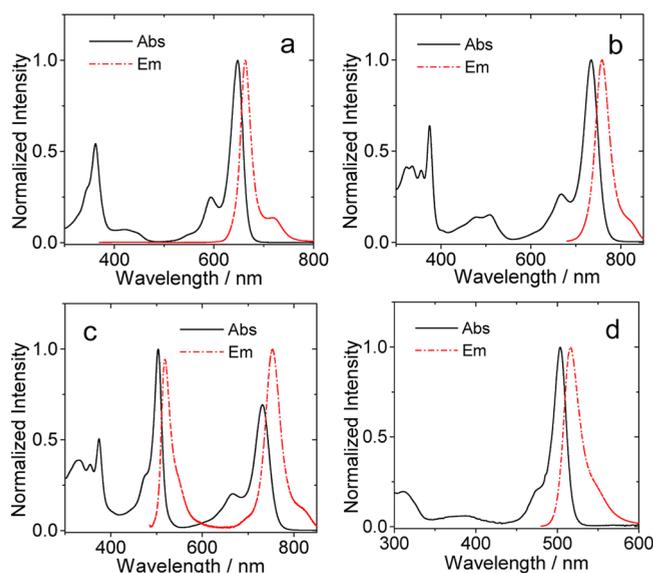
position of the ethynyl on Bodipy moiety and thus the different perturbation on the  $\pi$ -conjugation framework of the chromophore.

For Pt-1, which contains two different types of Bodipy ligands as visible-light-harvesting antenna, two major absorption bands were observed at 503 and 731 nm (Figure 2). The absorption maxima of Pt-1 is the sum of Pt-0 and Pt-2; thus, there is no significant electronic interaction between the two kinds of Bodipy ligands in Pt-1 at the ground state. Moreover, there is no  $\pi$ -conjugation across the Pt(II) atoms, otherwise the absorption wavelength of Pt-1 will be drastically different from that of Pt-0 and Pt-2. This finding is different from a previous result that delocalized Franck–Condon singlet-excited state was proposed.<sup>25</sup> To the best of our knowledge, *trans*-bisphosphine Pt(II) bisacetylides complexes showing near-IR absorption, like Pt-1, were not reported.<sup>55,62,63</sup> Recently we prepared N^N Pt(II) bisacetylides complex with heteroleptic acetylides ligands.<sup>56</sup> But the complex does not show any absorption in near-IR range.

Notably the complexes Pt-0, Pt-1, and Pt-2 show very strong absorption in visible region, which was rarely reported for *trans*-bisphosphine Pt(II) bisacetylides complexes.<sup>53,55,62–64</sup> For example, the molar absorption coefficients ( $\epsilon$ ) of Pt-1 at 503 and 731 nm are 1.4 × 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup> and 9.7 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively.

The UV–vis absorption spectra and the luminescence spectra of the compounds were studied (Figure 3). For ligand L-1, emission band at 663 nm was observed (Figure 3a), which is a mirror to the absorption band on lower-energy side. The lifetime of the emission was determined as 5.55 ns. Note the small Stokes shift of the emission is typical for Bodipy fluorophores.<sup>50,65–67</sup> For Pt-0, the emission band is at 758 nm (Figure 3b). The small Stokes shift and the short luminescence lifetime of Pt-0 (1.84 ns) indicated that the emission of Pt-0 is fluorescence of the coordinated styrylBodipy ligand, not phosphorescence.<sup>46</sup> This result reveals the interesting photophysics of Pt(II) complexes; that is, no phosphorescence was observed even with two Pt(II) atoms coordinated to the  $\pi$ -conjugation framework of the same styrylBodipy ligand, which is in stark contrast to a previous observation that strong room-temperature (RT) phosphorescence of Bodipy ligand was observed with a N^C^N auxiliary coordination ligand ( $\Phi_p$  = 3.5%).<sup>29</sup>

For Pt-1, two emission bands were observed (Figure 3c). The small Stokes shifts and the short luminescence lifetimes of the two emission bands (2.22 and 1.95 ns) suggest that the emission bands are fluorescence. Previously we prepared a Pt(II) complex that contains two different coordinated Bodipy



**Figure 3.** Comparison of the normalized UV-vis absorption spectra and emission spectra of (a) L-1 ( $\lambda_{\text{ex}} = 362$  nm), (b) Pt-0 ( $\lambda_{\text{ex}} = 670$  nm), (c) Pt-1 ( $\lambda_{\text{ex}} = 480$  nm), (d) Pt-2 ( $\lambda_{\text{ex}} = 470$  nm).  $c = 1.0 \times 10^{-5}$  M in toluene, 20 °C.

ligands; only the fluorescence of the energy acceptor was observed.<sup>43</sup>

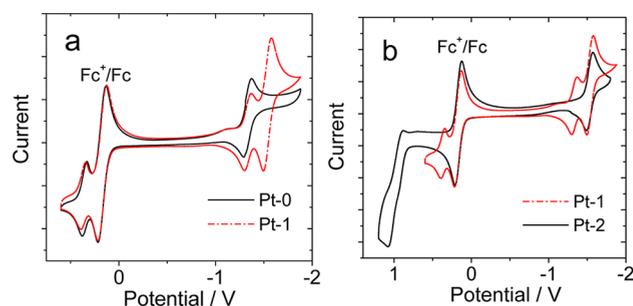
We propose a through-bond singlet-energy-transfer for Pt-1,<sup>48</sup> instead of the resonance energy transfer, since the emission of the peripheral Bodipy ligand overlap *poorly* with the absorption band of the central coordinated styrylBodipy ligand. The poor spectral overlap between the singlet-energy donor and the energy acceptor may result in inefficient FRET. Similar emission band with small Stokes shift was observed for Pt-2 (Figure 3d). The emission band can be attributed to the fluorescence emission of the Bodipy ligand.

The solvent polarity-dependency of the UV-vis absorptions of the compounds were studied (Figure S21, see Supporting Information). No substantial changes were observed for the UV-vis absorption of the compounds with variation of the solvent polarity. Thus, we conclude that there is no substantial interaction or charge transfer for the compounds at ground states. The Franck-Condon states of the compounds were not affected by the solvent polarity. The solvent dependency of the luminescence of the compounds was studied (Figure S22, see Supporting Information). For ligand L-1, the emission intensity and wavelength do not change significantly with

variation of the solvent polarity. For the coordinated L-1, that is, complex Pt-0, however, the emission intensity is dependent on the solvent polarity; the emission intensity was reduced in polar solvents as compared with that in nonpolar solvents such as toluene.

It should be pointed out that the quenched luminescence intensity of Pt-1 in polar solvents is unlikely due to intramolecular charge transfer (ICT); otherwise, the emission wavelength of the emission bands will change substantially with variation of the solvent polarity.<sup>68</sup> The photophysical properties of the compounds were summarized in Table 2.

**Electrochemical Studies: Cyclic Voltammetry.** The electrochemical properties of the complexes were studied by cyclic voltammetry versus Fc(+0) (Figure 4). For the



**Figure 4.** Cyclic voltammogram of Pt-1, Pt-0, and Pt-2. Ferrocene (Fc) was used as internal reference ( $E_{1/2} = +0.17$  V, Fc<sup>+</sup>/Fc). In deaerated DCM solution containing 0.5 mM photosensitizers with the ferrocene, 0.10 M Bu<sub>4</sub>N[PF<sub>6</sub>] as supporting electrolyte, Ag/AgNO<sub>3</sub> reference electrode, scan rates: 100 mV/s. 20 °C.

reference complex Pt-0, a reversible oxidation wave was observed for which the half-wave potential  $E_{1/2}$  is +0.18 V, whereas in the cathodic scan, a reversible reduction was observed in which the half-wave potential  $E_{1/2}$  is -1.51 V (Figure 4a). For Pt-2, a reversible reduction wave was observed for which the half-wave potential  $E_{1/2}$  is -1.70 V, whereas in the oxidation region, an irreversible oxidation wave was observed in which the potential is +0.91 V (Figure 4b).

For Pt-1 in the cathodic scanning, two reversible waves at -1.50 and -1.70 V were observed, which is the sum of the reduction waves of the reference complexes Pt-0 and Pt-2. In the anode region, a reversible oxidation wave at +0.20 V was observed for Pt-1. This result indicates that there is no electronic interaction between the chromophores in Pt-1; otherwise, the reduction potentials of Pt-1 should be

**Table 2. Photophysical Properties of the Ligands and the Pt(II) Complexes<sup>a</sup>**

	$\lambda_{\text{abs}},^a$ nm	$\epsilon^b$	$\lambda_{\text{em}},^a$ nm	$\Phi_{\text{F}},\%$	$\Phi_{\Delta},\%$	$\tau_{\text{F}},^c$ ns	$\tau_{\text{T}},^d$ $\mu\text{s}$
L-1	362/648	6.9/12.7	663	23.6 <sup>e</sup>	<i>f</i>	5.55	<i>f</i>
Pt-0	734	12.4	758	2.26 <sup>g</sup>	37.0 ± 0.6 <sup>h</sup>	1.84	5.82
Pt-1	503/731	14.0/9.7	518/754	1.46 <sup>i</sup> /1.77 <sup>i</sup> /2.65 <sup>g</sup>	89.0 ± 1.3 <sup>j</sup> /27.8 ± 0.4 <sup>h</sup>	2.22/1.95	6.09
Pt-2	504	7.7	516	36.7 <sup>i</sup>	12.1 ± 0.2 <sup>j</sup>	2.67	708.55

<sup>a</sup>In toluene ( $c = 1.0 \times 10^{-5}$  M). <sup>b</sup>Molar absorption coefficient.  $\epsilon: 1 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>. <sup>c</sup>Luminescence lifetimes.  $c = 1.0 \times 10^{-5}$  M. <sup>d</sup>Triplet state lifetimes.  $c = 1.0 \times 10^{-5}$  M, in deaerated toluene. <sup>e</sup>Fluorescence quantum yields. B-7 ( $\Phi_{\text{F}} = 9.3\%$ ) was used as standard for L-1 ( $\lambda_{\text{ex}} = 584$  nm). <sup>f</sup>Not applicable. <sup>g</sup>Fluorescence quantum yields. B-3 ( $\Phi_{\text{F}} = 9.5\%$ ) was used as standard for Pt-0 and Pt-1 ( $\lambda_{\text{ex}} = 640$  nm). For Pt-1 the fluorescence quantum yield belongs to the emission band at 754 nm. <sup>h</sup>Singlet oxygen quantum yields. Methylene blue (MB  $\Phi_{\Delta} = 57\%$  in DCM) was used as standard for Pt-0 and Pt-1 ( $\lambda_{\text{ex}} = 670$  nm). <sup>i</sup>Fluorescence quantum yields. B-0 ( $\Phi_{\text{F}} = 72\%$  in THF) was used as standard for Pt-1 ( $\lambda_{\text{ex}} = 483$  nm) and Pt-2 ( $\lambda_{\text{ex}} = 470$  nm). For Pt-1, the first quantum yield is for the emission at 518 nm, and the second quantum yield is for the emission at 754 nm. <sup>j</sup>Singlet oxygen quantum yields, in toluene. Rose Bengal (RB  $\Phi_{\Delta} = 80\%$  in MeOH) was used as standard for Pt-1 and Pt-2 ( $\lambda_{\text{ex}} = 516$  nm).

substantially different from that of the reference compounds. The redox potentials of the complexes were summarized in Table 3.

**Table 3. Electrochemical Potentials Versus Fc(+0)<sup>a</sup>**

compound	oxidation, V	reduction, V
Pt-0	+0.18	-1.51
Pt-1	+0.20	-1.50, -1.70
Pt-2	+0.91	-1.70

<sup>a</sup>Cyclic voltammetry in deaerated DCM containing a 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte; counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO<sub>3</sub> couple as the reference electrode. [Ag<sup>+</sup>] = 0.1 M, 0.5 mM photosensitizers in deaerated DCM. 20 °C.

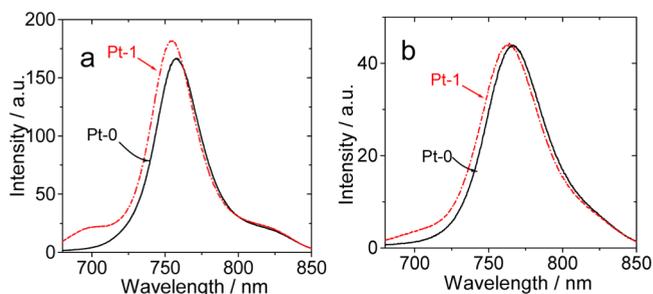
Intramolecular photoinduced electron transfer may exert significant effect on the photophysical properties of multichromophore transition metal complexes, such as the luminescence property or the triplet-state property.<sup>69–72</sup> The Gibbs free energy changes ( $\Delta G_{CS}$ ) of the photoinduced electron transfer were calculated with the Rehm–Weller equation.<sup>72,73</sup> The results show that the electron transfer in Pt-1 is thermodynamically prohibited (Table 4). This conclusion is in agreement with the spectroscopy studies.

**Table 4. Free Energy Changes of Charge Recombination ( $\Delta G_{CR}$ ), Charge Separation ( $\Delta G_{CS}$ ), and Charge Separated States Energy Level ( $E_{CST}$ ) of Pt-1 with the Coordinated StyrylBodipy as the Electron Donor and the Peripheral Bodipy as the Electron Acceptor<sup>a</sup>**

electron transfer	$\Delta G_{CR}$ , eV	$\Delta G_{CS}$ , eV	$E_{CST}$ , eV
<sup>1</sup> StyrylBodipy* → Bodipy <sup>b</sup>	-2.32 <sup>c</sup>	+0.67 <sup>c</sup>	+2.32 <sup>c</sup>
	-1.81 <sup>d</sup>	+0.16 <sup>d</sup>	+1.81 <sup>d</sup>
	-1.67 <sup>e</sup>	+0.02 <sup>e</sup>	+1.67 <sup>e</sup>
<sup>3</sup> StyrylBodipy* → Bodipy <sup>b</sup>	-2.32 <sup>c</sup>	+1.37 <sup>c</sup>	+2.32 <sup>c</sup>
	-1.81 <sup>d</sup>	+0.86 <sup>d</sup>	+1.81 <sup>d</sup>
	-1.67 <sup>e</sup>	+0.72 <sup>e</sup>	+1.67 <sup>e</sup>

<sup>a</sup>The arrow means the direction of charge transfer. <sup>b</sup>Electron transfer process in Pt-1. <sup>c</sup>In toluene. <sup>d</sup>In dichloromethane. <sup>e</sup>In MeCN.

**Intramolecular Energy and Electron Transfer.** To study the photoinduced electron transfer in Pt-1, the emission intensity of Pt-0 and Pt-1 was compared (Figure 5). Given an electron transfer occurred after photoexcitation, the fluorescence emission intensity of Pt-1 should be weaker than that of

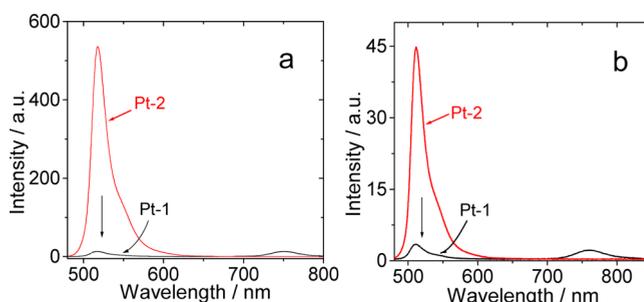


**Figure 5.** Fluorescence emission spectra of Pt-0 and Pt-1 ( $\lambda_{ex} = 670$  nm, optically matched solutions were used) in different solvents of (a) toluene and (b) MeCN. 20 °C.

Pt-0; note that Pt-0 is an analogue of the energy acceptor in Pt-1.

However, the experiments demonstrated that the fluorescence emission intensity of Pt-1 is similar to that of Pt-0 (Figure 5a; optically matched solutions were used). Similar results in solvents with different polarity were observed (Figure S23, see Supporting Information). Same result was observed even in polar solvent such as acetonitrile (Figure 5b). It is known that electron transfer is more favored in polar solvents. Therefore, we conclude that there is no significant photoinduced electron-transfer process in Pt-1,<sup>70,74,75</sup> which is in agreement with the electrochemical studies and the Gibbs free energy changes ( $\Delta G_{CS}$ ) of the electron transfer.

To study the energy-transfer process in Pt-1, the fluorescence intensities of Pt-2 and Pt-1 were compared (Figure 6). Pt-2 is the analogue of the energy donor unit in

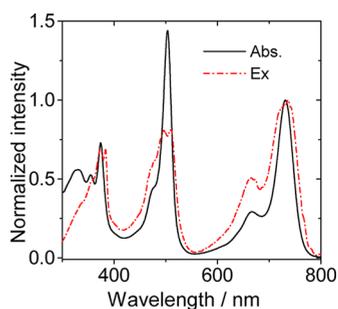


**Figure 6.** Fluorescence emission spectra of Pt-1 and Pt-2 ( $\lambda_{ex} = 473$  nm; optically matched solutions were used) in (a) toluene and (b) MeCN. 20 °C.

Pt-1. It was found that the fluorescence emission intensity of Pt-2 was significantly quenched in Pt-1. This quenching effect of the fluorescence of the peripheral Bodipy ligand is attributed to energy transfer, since we proved with the Gibbs free energy changes ( $\Delta G_{CS}$ ) that intramolecular electron transfer is prohibited in Pt-1.<sup>74</sup>

Same quenching effect was observed in toluene, as well as in dichloromethane (DCM), MeCN, and MeOH; thus, this quenching effect is unlikely due to polarity-enhanced ICT effect (Figure S24, see Supporting Information). The EnT rate constants were estimated at  $k_{EnT} = 9.0 \times 10^9$  s<sup>-1</sup> using eq 5.<sup>74</sup> This predicted value agrees with the femtosecond transient absorption spectroscopy ( $k_{EnT} = 2.2 \times 10^{10}$  s<sup>-1</sup>, see later section). This value is smaller as compared with the previously reported  $7.8 \times 10^{11}$  s<sup>-1</sup> for a Bodipy–Pt(II) porphyrin complex.<sup>76</sup> For a Bodipy–AzaBodipy triad, for which the spectral overlap between the emission of the energy donor and the absorption of the energy acceptor is not significant, the rate constant of the EnT is  $1.2 \times 10^{11}$  s<sup>-1</sup>.<sup>70</sup> These large FRET rate constants, despite the poor spectral overlap, may be attributed to through-bond-energy-transfer (TBET).<sup>77–80</sup>

Recently Akkaya et al. proposed to use the fluorescence excitation spectra to evaluate the singlet EnT efficiency.<sup>75</sup> Thus, the fluorescence excitation spectra of the compounds were studied. The excitation spectra of the compounds were recorded (Figure 7). For Pt-1, the excitation at 503 nm is half of the UV–vis absorption; therefore, we propose the FRET efficiency is ca. 50%. We noted the discrepancy for the EnT efficiency evaluated by the luminescence quenching and the excitation spectra.<sup>81</sup> However, the comparison of the excitation spectra with the UV–vis absorption spectrum in Figure 7



**Figure 7.** Comparison of the normalized UV-vis absorption and the luminescence excitation spectra of **Pt-1** ( $\lambda_{\text{em}} = 770$  nm).  $c = 1.0 \times 10^{-5}$  M in toluene at 20 °C.

unambiguously confirmed that there is singlet energy transfer from the peripheral Bodipy ligands to the central coordinated styrylBodipy ligand.<sup>70,74,75</sup>

**Nanosecond Transient-Absorption Spectroscopy.** To study the triplet-excited state of the complexes, the nanosecond transient-absorption spectroscopy of the complexes was studied (Figure 8).<sup>58,82,83</sup> For **Pt-0**, significant bleaching band at 741 nm was observed upon nanosecond pulsed laser excitation. Minor bleaching band at 369 nm was also observed; thus, the  $T_1$  triplet state of **Pt-0** is localized on the Bodipy unit. The transient was significantly quenched in aerated solution (Figure S25a, see Supporting Information). Thus, the signal can be attributed to the triplet state of the complex.

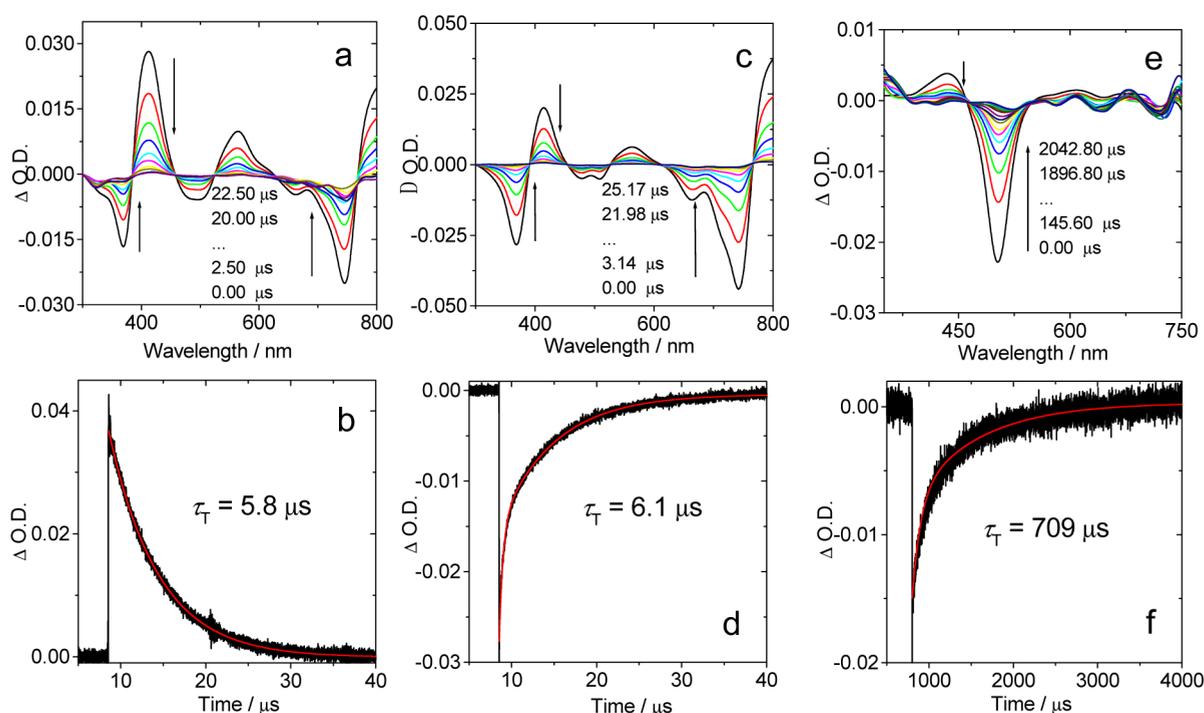
The triplet-state lifetime was determined as 5.8  $\mu\text{s}$ , which is much shorter than a similar *trans*-bis(trialkylphosphine) bisacetylide complex with Bodipy ligand (not styrylBodipy ligand.  $\tau_T = 128$   $\mu\text{s}$ ).<sup>29</sup> However, this lifetime is close to that observed with heavy atom effect ( $\tau_T = 1.8$   $\mu\text{s}$ ).<sup>84</sup> Previously we prepared a  $C_{60}$ -styrylBodipy dyad, for which a much longer triplet-state lifetime was observed (71–123  $\mu\text{s}$ ).<sup>85</sup> The different

triplet-state lifetime may be due to the different steric hindrance of the styryl moiety; with bulky substitution on the 2,6-position, the coplanarity of the  $\pi$ -conjugation framework is compromised (which is confirmed by the molecular structures determined with the single-crystal X-ray diffraction). As a result, the lifetime of the triplet state of styrylBodipy was reduced.

For **Pt-2**, significant bleaching band at 504 nm was observed upon nanosecond pulsed laser excitation at 503 nm (Figure 8e). The lifetime was determined as 709  $\mu\text{s}$ . Thus, we conclude that the triplet-excited state is localized on the Bodipy moiety.

For **Pt-1**, as previously confirmed, singlet-energy transfer from the peripheral Bodipy ligands to the central coordinated styrylBodipy ligand occurs. Thus, **Pt-1** was selectively excited into the peripheral coordinated Bodipy parts ( $\lambda_{\text{ex}} = 500$  nm). Interestingly, no bleaching band at 504 nm was observed, which is different from **Pt-2**. Instead, intensive bleaching band at 741 nm was observed, which is similar to **Pt-0**. Thus, we conclude that triplet state is confined on the central coordinated Bodipy ligand upon selective excitation into the peripheral Bodipy part.<sup>86</sup> Since we confirmed the triplet-state formation in **Pt-2**, and the fact that no triplet state is localized on the peripheral Bodipy in **Pt-1**, we propose that intramolecular triplet-triplet-energy transfer (TTET) exists for **Pt-1**. Since no increasing stage was observed for the transient signal at 741 nm, we propose the triplet state  $E_nT$  in **Pt-1** is fast ( $k \gg 1 \times 10^8$   $\text{s}^{-1}$ . The time-resolution of the nanosecond transient absorption spectrometer is 10 ns). Previously it was reported that the intramolecular triplet-state energy-transfer rate constant is  $1.0 \times 10^{10}$   $\text{s}^{-1}$  for a Bodipy-Pt(porphyrin) complex.<sup>76</sup>

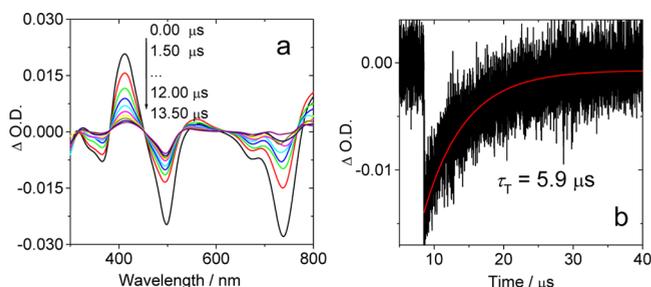
The above result confirms that the excitation energy harvested by the energy donor, that is, the peripheral coordinated Bodipy part, can be funneled efficiently into the energy acceptor, either through intramolecular singlet energy transfer or TTET. **Pt-1** was also excited with pulsed laser at



**Figure 8.** Nanosecond transient absorption spectra. (a) **Pt-0** and (b) decay curve at 420 nm ( $\lambda_{\text{ex}} = 510$  nm); (c) **Pt-1** and (d) decay curve at 490 nm ( $\lambda_{\text{ex}} = 500$  nm); (e) **Pt-2** and (f) decay curve at 490 nm ( $\lambda_{\text{ex}} = 503$  nm).  $c = 1.0 \times 10^{-5}$  M in deaerated toluene at 20 °C.

725 nm, that is, selectively into the energy-acceptor part. Exactly the same transient spectra was observed, and the triplet-state lifetime was determined as 6.5  $\mu\text{s}$  (Figure S26, see Supporting Information).

The triplet-state property of Pt-1 in polar solvent such as acetonitrile was studied (Figure 9). Triplet-excited state was



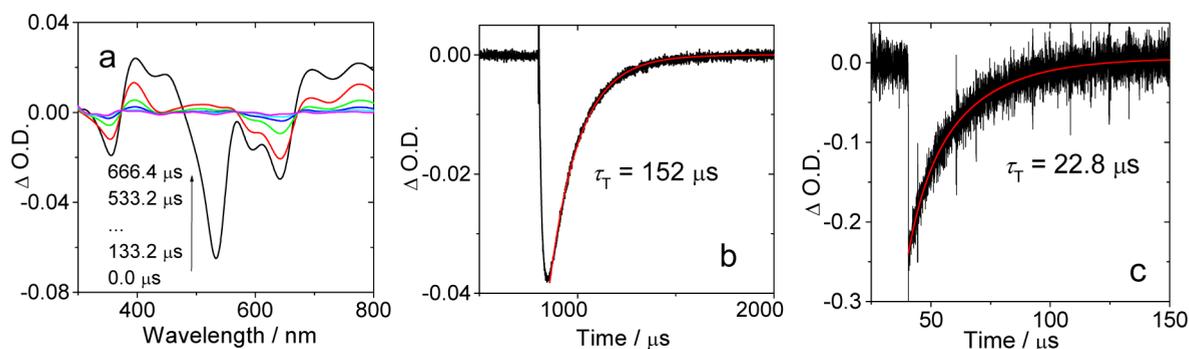
**Figure 9.** (a) Nanosecond transient absorption spectra of Pt-1; (b) decay curve of Pt-1 at 490 nm ( $\lambda_{\text{ex}} = 500$  nm).  $c = 1.0 \times 10^{-5}$  M in deaerated MeCN at 20 °C.

observed with lifetime of 5.9  $\mu\text{s}$ , which is close to the triplet-state lifetime in nonpolar solvent such as toluene (6.1  $\mu\text{s}$ , Figure 8d). Thus, the photoinduced electron-transfer effect in Pt-1 is not significant, which is in agreement with the study of the Gibbs free energy changes (Table 4) and the fluorescence spectra (Figure 5). A recently reported broadband visible-light-absorbing N<sup>^N</sup> Pt(II) bisacetylde complex with heteroleptic acetylde ligands shows longer triplet-state lifetime of 68.21  $\mu\text{s}$ .<sup>56</sup>

The triplet state of the ligand L-1 was produced with the sensitization method; that is, 2,6-diiodoBodipy (B-2, Scheme 1) was used as the triplet-state energy donor (photosensitizer) and L-1 as the triplet-state energy acceptor (Figure 10).<sup>87</sup>

The triplet-state lifetime of B-2 was reduced to 22.8  $\mu\text{s}$  in the presence of L-1. Note the intrinsic triplet-state lifetime of B-2 is 179.8  $\mu\text{s}$  (Figure S27, see Supporting Information). The bleaching band at 647 nm was determined with a lifetime of 152  $\mu\text{s}$ , which is much longer than that of Pt-1. This value is close to a previously reported triplet-state lifetime of styrylBodipy compounds observed with C<sub>60</sub>-StyrylBodipy dyads, that is, intramolecular sensitization method (71.5–123.2  $\mu\text{s}$ ).<sup>91</sup>

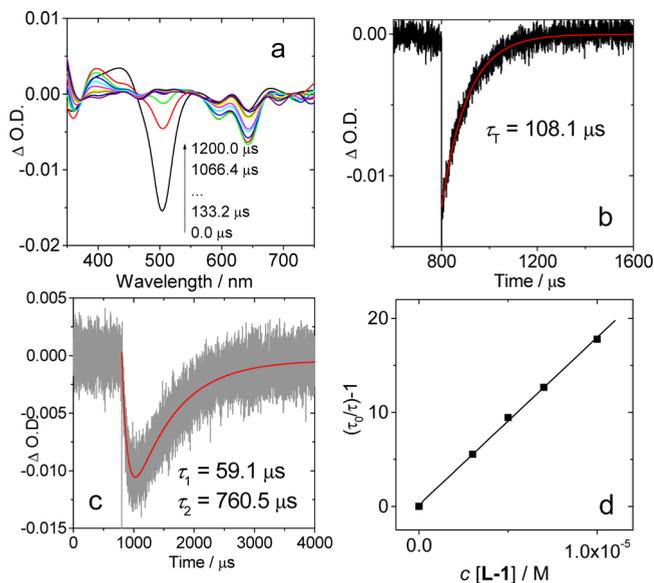
Long-range energy transfer is important in photosynthesis.<sup>87,88</sup> Normally long-range intermolecular energy transfer is inefficient. For example, FRET will not occur for the mixture of the energy donor and energy acceptor in solution.<sup>89</sup>



**Figure 10.** (a) Nanosecond time-resolved transient absorption spectra of the mixture of B-2 (sensitizer) and L-1 (triplet-energy acceptor). (b) Decay curve at 647 nm ( $\lambda_{\text{ex}} = 528$  nm) and (c) decay curve at 532 nm ( $\lambda_{\text{ex}} = 528$  nm).  $c = 1.0 \times 10^{-5}$  M in deaerated toluene at 20 °C.

Intermolecular triplet-state energy transfer is rarely studied.<sup>87</sup> Intermolecular triplet-state energy transfer is normally inefficient due to the short lifetime of the excited state of the energy donor. For Pt-2, however, the triplet-state lifetime is very long (709  $\mu\text{s}$ ); thus, long-range intermolecular triplet-energy transfer with Pt-2 is possible. To study the triplet-energy transfer in Pt-1, complex Pt-2 was also used as triplet-state energy donor, and the ligand L-1 was used as triplet-state energy acceptor. This mixture can be used as a model for studying of the triplet-state energy transfer in Pt-1.

With increasing concentration of L-1, the lifetime of the bleaching band at 504 nm was reduced, and a new bleaching band at 642 nm was observed (Figure 11, and Supporting



**Figure 11.** Nanosecond transient absorption spectra and the decay curves of the mixture of complex Pt-2 and ligand L-1. (a) Molar ratio is 1:0.3 (Pt-2/L-1); decay curves at (b) 490 nm and (c) 640 nm ( $\lambda_{\text{ex}} = 503$  nm), molar ratio is 1:0.3 (Pt-2/L-1); (d) Stern-Volmer plots for lifetime quenching of Pt-2 with increasing concentration of L-1.  $\lambda_{\text{ex}} = 503$  nm.  $[\text{Pt-2}] = 1.0 \times 10^{-5}$  M. In deaerated toluene at 20 °C.

Information Figure S28). The change of the transient absorption spectra upon increasing the triplet-energy acceptor L-1 was attributed to the intermolecular triplet-energy transfer and the produce of the triplet state of L-1.

To study the kinetics of the intermolecular energy transfer, the decay trace at 640 nm was monitored. Interestingly, the decay is featured with biphasic character; that is, there is first a sharp increase of the bleaching at 640 nm, and then a slow decay process was observed (Figure 11c). Similar results were observed in Figure 10b. The fast increase of the transient is attributed to the production of the triplet state of **L-1** via the intermolecular triplet-energy transfer, and thereafter the relatively slow decay of the transient is attributed to the decay of the triplet state of **L-1**. The exceptionally long lifetime of the triplet state is probably due to the low concentration of **L-1** molecule at triplet state. The triplet-state intermolecular energy-transfer rate constant was calculated as on  $1 \times 10^4 \text{ s}^{-1}$  scale (which is concentration-dependent) according to eq 6 (Table 5). The triplet-state energy-transfer

**Table 5. Rate Constant ( $k_{\text{ET}}$ ) and Efficiency ( $\Phi_{\text{ET}}$ ) for the Triplet–Triplet Energy Transfer in the Mixture of Pt–1 and Pt–2<sup>a</sup>**

Pt–2/L–1	$k_{\text{ET}}$ ( $\text{s}^{-1}$ )	$\Phi_{\text{ET}}$ (%)
1.0:0.3	$1.6 \times 10^4$	92.2
1.0:0.5	$2.0 \times 10^4$	92.3
1.0:0.7	$2.4 \times 10^4$	91.4
1.0:1.0	$3.6 \times 10^4$	94.5

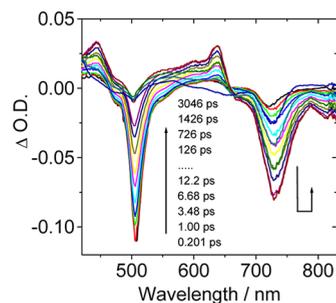
<sup>a</sup>In deaerated toluene. 20 °C.

efficiency was calculated as ca. 92% according to eq 7. These values are similar to that observed with intra-assembly (hydrogen-bonded molecular assembly) triplet-state energy transfer in a  $\text{C}_{60}$ -ferrocene hydrogen-bonding molecular assembly ( $9.2 \times 10^5 \text{ s}^{-1}$ ), which indicates that the intermolecular triplet-energy transfer is efficient.<sup>88</sup> Previously a sub-phthalocyanine/zinc tetra-*tert*-butylphthalocyanine triplet-state energy transfer was observed to show similar triplet-state energy transfer  $k = 4.2 \times 10^5 \text{ s}^{-1}$ .<sup>87</sup>

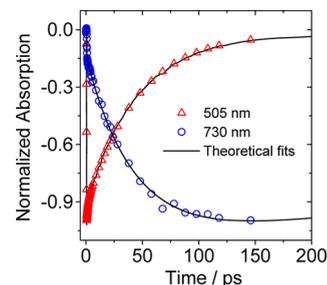
The Stern–Volmer quenching constant of Pt–2/L–1 was calculated as  $K_{\text{SV}} = 1.78 \times 10^6 \text{ M}^{-1}$  (Figure 11d). The bimolecular quenching constant was calculated as  $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  according to eq 8. Quenching efficiency was given by eq 9, where  $k_0$  is the diffusion-controlled bimolecular quenching rate constants, which can be calculated with the Smoluchowski eq 10.<sup>89</sup>

The molecular radius of the energy donor (Pt–2) is 8.7 Å, and that of quencher (L–1) is 8.6 Å. According to eq 11 the diffusion coefficient of the energy donor (Pt–2) is  $4.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , and that of the quencher (L–1) is  $4.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (in deaerated toluene at 20 °C). Thus,  $k_0$  was calculated as  $1.11 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The quenching efficiency was calculated as 22.7% according to eq 9, which indicates that there is an efficient triplet-state energy transfer between Pt–2 and L–1 in the mixture.

**Femtosecond Transient Absorption Spectroscopy.** Ultrafast pump–probe experiments were performed for study of the singlet EnT (Figure 12). Ultrafast pump–probe experiments were performed for Pt–0, Pt–1, and Pt–2 at appropriate pump wavelengths (Figures 12 and 13 and Supporting Information, Figures S29–S33). It is expected that singlet EnT may occur only for Pt–1, which contains two different kinds of Bodipy unit. Upon excitation of Pt–1 at 505 nm, bleaching bands were observed around 505 and 730 nm, where the Bodipy and styrylBodipy give steady-state absorption, respectively (Figure 12). Transient absorption



**Figure 12.** Femtosecond transient absorption spectra of Pt–1 ( $\lambda_{\text{ex}} = 505 \text{ nm}$ ).  $c = 1.0 \times 10^{-5} \text{ M}$  in deaerated toluene at 20 °C.



**Figure 13.** Decay curves of Pt–1 at 505 and 730 nm ( $\lambda_{\text{ex}} = 505 \text{ nm}$ ).  $c = 1.0 \times 10^{-5} \text{ M}$  in deaerated toluene at 20 °C.

spectra of Pt–1 show that the bleaching signal around 505 nm decreases, while the bleaching signal around 730 nm increases, simultaneously.

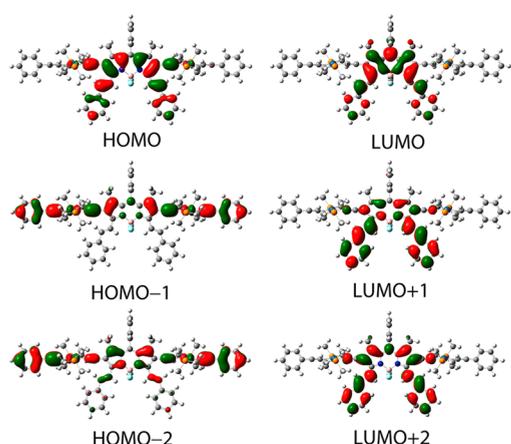
The decay time of the bleaching signal for Bodipy (505 nm) is  $\sim 45 \text{ ps}$  ( $k_{\text{EnT}} = 2.2 \times 10^{10} \text{ s}^{-1}$ ), which is approximately equal to the rise time of the bleaching signal for styrylBodipy (730 nm) in Pt–1 (Figure 13). These results give strong evidence of singlet EnT from Bodipy to styrylBodipy. Previously a Bodipy–AzaBodipy triad was studied, for which the spectral overlap between the emission of the energy donor and the absorption of the energy acceptor is not significant; the rate constant of the EnT is  $1.2 \times 10^{11} \text{ s}^{-1}$ .<sup>70</sup> Recently we prepared N<sup>^N</sup> Pt(II) bisacetylide complex with heteroleptic acetylide ligands.<sup>56</sup> The singlet-energy transfer rate constant is 10-fold faster,  $2.6 \times 10^{11} \text{ s}^{-1}$ .

The positive signal (excited-state absorption, ESA) represents  $S_1 \rightarrow S_n$  transition of Bodipy and styrylBodipy and  $T_1 \rightarrow T_n$  transition of styrylBodipy. The ESA signals around 430 and 620 nm can be attributed to  $S_1 \rightarrow S_n$  transition of Bodipy due to appearance of these signals at zero time delay upon excitation of Bodipy. The other ESA signals around 445 and 635 nm increased after singlet EnT process; therefore, these signals can be attributed to  $S_1 \rightarrow S_n$  transition of styrylBodipy. In addition to that, evidence of  $T_1 \rightarrow T_n$  transition is obtained from positive signals that were placed around 420 and 560 nm probe wavelengths. These signals appear after  $\sim 1 \text{ ns}$ .

We also checked whether any energy transfer from styrylBodipy to Bodipy with an extra pump–probe experiment upon excitation styrylBodipy (730 nm) for Pt–1. There are bleach signals of ground state (730 nm) and photoinduced charge-transfer state (810 nm) of styrylBodipy, and no energy transfer is seen as expected (Figures S29a and S31, see Supporting Information).

**Density Functional Theory Computations.** The ground-state geometry and the excited states of the near-IR absorbing complex Pt–0 were studied with density functional theory

(DFT) and time-dependent density functional theory (TDDFT) computations (Figure 14). The optimized P–Pt–

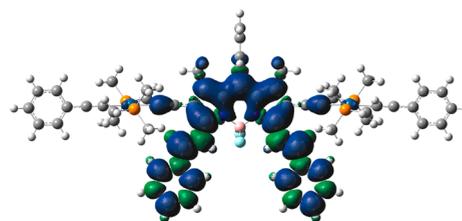


**Figure 14.** Electron density maps of the frontier molecular orbitals of Pt–0 based on the optimized ground-state geometry. Calculated at the B3LYP/GENECP/LANL2DZ level with Gaussian 09W.

P bond angles are  $179.779^\circ$  and  $179.782^\circ$ , which is similar to the structure determined with the single-crystal molecular structure. The C≡C bond lengths are in the range of 1.2277–1.2290 Å, also in agreement with the experimental values.

The singlet and triplet excited states of Pt–0 were studied with TDDFT computations. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the low-lying excited states ( $S_1$  state and  $T_1$  state, Table 6). Thus,  $S_1$  state, as well as the  $T_1$  state, is localized on the coordinated styrylBodipy moiety, which is in agreement with the steady-state and the time-resolved transient absorption spectra of the complex. The spin density surface of Pt–0 was also studied; the results show the spin density is localized on the coordinated Bodipy (Figure 15).

**Singlet Oxygen Photosensitizing.** The singlet oxygen ( $^1O_2$ ) photosensitizing ability of the complexes was compared (Figure 16). 1,3-Diphenylisobenzofuran (DPBF) was used as  $^1O_2$  scavenger for monitoring the  $^1O_2$  production. First the  $^1O_2$  photosensitizing ability of Pt–0 and Pt–1 was compared upon selective photoexcitation into the energy donor in Pt–1. At 503 nm, Pt–1 shows stronger absorption than Pt–0. However, no enhanced  $^1O_2$  photosensitizing should be observed given no energy transfer exists in Pt–1. The results show that Pt–1 is



**Figure 15.** Isosurfaces of spin density of Pt–0. Calculated at the optimized triplet-state geometries at B3LYP/GENECP/LANL2DZ level with Gaussian 09W.

more efficient than Pt–0 to produce  $^1O_2$  (Figure 16a). Thus, singlet EnT in Pt–1 is confirmed.

Similar results were obtained with white light excitation (Figure 16b). Pt–1 is more efficient than Pt–0 and Pt–2 for production of  $^1O_2$ . These results confirm the singlet EnT in Pt–1 and that the broadband absorption of Pt–1 is advantageous for Pt–1 to be used for photocatalysis.

The  $^1O_2$  photosensitizing ability of Pt–1 and Pt–2 was also compared, upon excitation at the same wavelength (Figure 16c). The result shows that Pt–1 is more efficient than Pt–2 as  $^1O_2$  photosensitizer upon excitation at 503 nm. Thus, intramolecular singlet EnT was confirmed for Pt–1, and the intersystem crossing is weak in Pt–2.

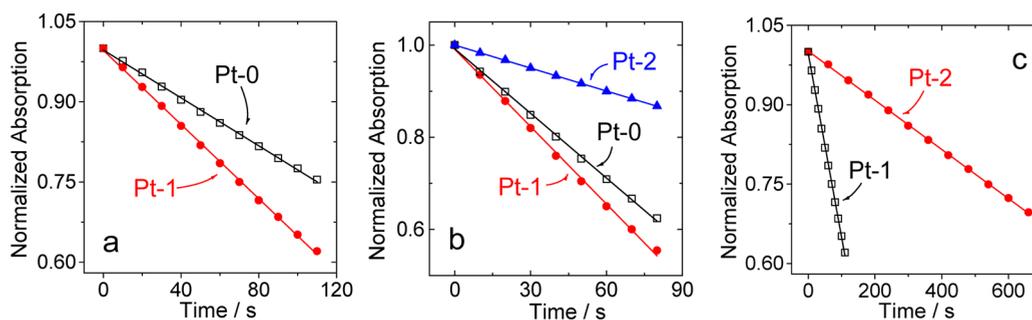
## CONCLUSIONS

*trans*-Bis(tributylphosphine) Pt(II) bisacetylide complex (Pt–1) was prepared, which shows strong broadband visible-light/near-IR absorption at both 503 nm ( $\epsilon = 1.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 731 nm ( $\epsilon = 9.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). The complex contains two peripheral coordinated Bodipy ligands and a centrally coordinated styrylBodipy ligand, which show absorption at 503 and 731 nm, respectively. Reference complexes (Pt–0 and Pt–2), which contain a *single* visible-light-harvesting Bodipy ligand, were prepared for comparison. The photophysical properties of the complexes were studied with steady-state and femtosecond/nanosecond time-resolved transient-absorption spectroscopies. Dual fluorescence at 518 and 754 nm was observed for Pt–1, which is rare for Bodipy-containing Pt(II) complexes. No phosphorescence was observed for Pt–1. With fluorescence emission spectra and excitation spectra, singlet EnT in Pt–1 was confirmed ( $\Phi_{\text{EnT}} = 50\%$ ). TBET mechanism was proposed to be responsible for the ultrafast singlet EnT in Pt–1, due to the poor spectral overlap, yet fast energy transfer. Femtosecond transient absorption indicated the intramolecular singlet EnT is

**Table 6.** Excitation Energies (eV) and Corresponding Oscillator Strengths ( $f$ ), Main Configurations, and CI Coefficients of the Low-Lying Electronically Excited States of Pt–0, Calculated by TDDFT//B3LYP/LANL2DZ, Based on the DFT//B3LYP/LANL2DZ Optimized Ground-State Geometries

TDDFT/B3LYP/LANL2DZ						
	electronic transition	energy [eV/nm] <sup>a</sup>	$f^b$	composition <sup>c</sup>	CI <sup>d</sup>	character
singlet	$S_0 \rightarrow S_1$	1.91/648	0.8572	H→L	0.6852	MLCT
	$S_0 \rightarrow S_3$	2.46/503	0.4345	H–2→L	0.6297	MLCT/ILCT
	$S_0 \rightarrow S_9$	3.28/378	0.8707	H→L+1	0.4953	MLCT
	$S_0 \rightarrow S_{19}$	3.73/333	0.6393	H–1→L+1	0.5331	MLCT/ILCT
triplet <sup>e</sup>	$S_0 \rightarrow T_1$	0.95/1311	0.0000	H→L	0.6989	MLCT
	$S_0 \rightarrow T_2$	1.92/645	0.0000	H–1→L	0.5501	MLCT/ILCT
	$S_0 \rightarrow T_3$	1.945/637	0.0000	H–2→L	0.4799	MLCT/ILCT

<sup>a</sup>Only the selected low-lying excited states are presented. <sup>b</sup>Oscillator strengths. <sup>c</sup>Only the main configurations are presented. <sup>d</sup>The CI coefficients are in absolute values. <sup>e</sup>No spin–orbital coupling effect was considered; thus, the  $f$  values are zero.



**Figure 16.** Comparison of the singlet oxygen ( $^1\text{O}_2$ ) photosensitizing of (a) Pt-0 and Pt-1 ( $\lambda_{\text{ex}} = 503$  nm,  $c = 1.0 \times 10^{-5}$  M, respectively). (b) Pt-0, Pt-1, and Pt-2 (xenon lamp was used as light source). [Pt-0] and [Pt-1] =  $1.0 \times 10^{-5}$  M; [Pt-2] =  $2.0 \times 10^{-5}$  M. (c) Pt-1 and Pt-2 ( $\lambda_{\text{ex}} = 503$  nm, optically matched solutions were used), [Pt-1] =  $1.0 \times 10^{-5}$  M. In toluene, 20 °C.

fast:  $k_{\text{EnT}} = 2.2 \times 10^{10} \text{ s}^{-1}$ . Gibbs free energy changes ( $\Delta G_{\text{CS}}$ ) and steady-state luminescence studies show that the photo-induced intramolecular electron transfer in Pt-1 is prohibited. With nanosecond time-resolved transient-absorption spectra, intramolecular triplet-state energy transfer was proved, and the  $T_1$  state of Pt-1 is only confined on the central coordinated Bodipy ligand. Intermolecular triplet-state energy transfer was studied with nanosecond time-resolved transient absorption spectra ( $k_{\text{EnT}} = 3.6 \times 10^4 \text{ s}^{-1}$  and  $\Phi_{\text{EnT}} = 94.5\%$ ). With singlet oxygen ( $^1\text{O}_2$ ) photosensitizing experiments, we proved that the broadband visible-light-absorbing of Pt-1 is beneficial for the complex to be used as triplet photosensitizers. These studies will be useful for designing near-IR absorbing Pt(II) complexes and for the application of these complexes in luminescent bioimaging and photodynamic therapy studies.

## EXPERIMENTAL SECTION

**Materials.** Solvents were dried or distilled for synthesis.  $\text{K}_2\text{PtCl}_4$  was purchased from Aladdin Chemical Co., Ltd. (P. R. China). B-2 was synthesized according to literature methods.<sup>58</sup>

**Analytical Measurements.** All chemicals are analytically pure and used as received. NMR spectra were recorded by Bruker 500 MHz spectrometer and OXFPRD NMR 400 MHz spectrometer with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as standard at 0.00 ppm. HRMS was accomplished with GCT time-of-flight (TOF) mass spectrometer (Waters, U.K.) and matrix-assisted laser desorption/ionization (MALDI) micro MALDI TOF mass spectrometer (Waters, U.K.). Fluorescence spectra were measured on an RF5301 PC spectrofluorometer (Shimadzu, Japan). Absorption spectra were recorded on UV2550 UV-vis spectrophotometer (Shimadzu, Japan).

**Synthesis of 1.**<sup>90</sup>  $\text{K}_2\text{PtCl}_4$  (1.04 g, 2.5 mmol) was dissolved in 20 mL of deionized water under argon atmosphere (Ar).  $\text{P}(\text{tBu})_3$  (1.07 g, 5.3 mmol) was injected. Then the mixture was stirred under Ar at room temperature (RT) for 3 h. After the reaction was finished, the solid was filtrated out and purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ ). 1 was collected as a white solid (0.97 g, yield: 57.7%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.02–1.96 (m, 12H), 1.55–1.50 (m, 12H), 1.49–1.40 (m, 12H), 0.95 (t, 18H,  $J = 7.2$  Hz). TOF-HRMS ( $[\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{P}_2\text{Pt}]^+$ ): calcd  $m/z = 669.2726$ , found  $m/z = 669.2731$ .

**Synthesis of 2.**<sup>30</sup> 1 (435 mg, 0.65 mmol) was dissolved in 30 mL of dried  $\text{NH}_2\text{Et}$  under Ar. Phenylacetylene (61 mg, 0.60 mmol) was injected. Then the mixture was stirred under Ar at 45 °C for 8 h. After the reaction was finished, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /petroleum ether (PE) = 1:5, v/v). 2 was collected as a light yellow solid (382 mg, yield: 79.8%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.25–7.18 (m, 4H), 7.16–7.11 (m, 1H), 2.04–1.98 (m, 12H), 1.62–1.52 (m, 12H), 1.49–1.40 (m, 12H), 0.92 (t, 18H,  $J = 7.3$  Hz). MALDI-TOF-HRMS ( $[\text{C}_{32}\text{H}_{59}\text{ClP}_2\text{Pt} - \text{Cl}]^+$ ): calcd  $m/z = 700.3740$ , found  $m/z = 700.3727$ .

**Synthesis of 3.**<sup>84</sup> B-2 (28 mg, 0.05 mmol) was dissolved in 3 mL of dried dimethylformamide. Benzaldehyde (21 mg, 0.2 mmol) was added, followed by three drops of acetic acid and three drops of piperidine before the mixture was saturated by Ar. Then the mixture was subjected to microwave irradiation for 6 min at 150 °C under Ar. After the reaction was finished, 25 mL of water was added. The solid was filtrated out and purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /PE = 1:4, v/v). 3 was collected as a dark green solid (32 mg, yield: 85.1%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.16 (d, 2H,  $J = 16.7$  Hz), 7.74–7.66 (m, 6H), 7.56–7.54 (m, 3H), 7.45–7.41 (m, 4H), 7.38–7.34 (m, 2H), 7.31–7.29 (m, 2H), 1.46 (s, 6H). MALDI-TOF-HRMS ( $[\text{C}_{33}\text{H}_{25}\text{BF}_2\text{I}_2\text{N}_2]^+$ ): calcd  $m/z = 752.0168$ , found  $m/z = 752.0184$ .

**Synthesis of 4.**<sup>29</sup> 3 (70 mg, 0.09 mmol) was dissolved in 5 mL of distilled tetrahydrofuran (THF) before 2.5 mL of ( $^i\text{Pr}$ ) $_2\text{NH}$  was added under Ar.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (17 mg, 0.02 mmol) and  $\text{PPh}_3$  (13 mg, 0.05 mmol) were added, followed by  $\text{CuI}$  (9.4 mg, 0.05 mmol). Trimethylsilylacetylene (35 mg, 0.36 mmol) was injected before the mixture was stirred under Ar for 6 h at 68 °C. After the reaction was finished, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /PE = 1:4, v/v). 4 was collected as a dark green solid (48 mg, yield: 77.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.44 (d, 2H,  $J = 16.3$  Hz), 7.79 (d, 2H,  $J = 16.5$  Hz), 7.65 (d, 4H,  $J = 7.5$  Hz), 7.53–7.52 (m, 3H), 7.45–7.41 (m, 4H), 7.37–7.34 (m, 2H), 7.30–7.28 (m, 2H), 1.51 (s, 6H), 0.27 (s, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 146.9, 140.4, 139.4, 136.8, 134.6, 132.5, 129.5, 129.4, 129.3, 128.8, 128.1, 127.8, 118.6, 112.9, 86.4, 29.7, 1.0. MALDI-TOF-HRMS ( $[\text{C}_{43}\text{H}_{43}\text{BN}_2\text{F}_2\text{Si}_2]^+$ ): calcd  $m/z = 692.3026$ , found  $m/z = 692.3005$ .

**Synthesis of L-1.**<sup>29</sup> 4 (34.6 mg, 0.05 mmol) was dissolved in 3 mL of distilled THF.  $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$  (0.2 M in THF, 1 mL) was added dropwise at  $-78$  °C under Ar, and the solution was kept at  $-78$  °C for  $\sim 0.5$  h (monitored by thin-layer chromatography until the starting material had been completely consumed). After the reaction was finished, 20 mL of water and 30 mL of  $\text{CH}_2\text{Cl}_2$  were added. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /PE = 1:4, v/v). L-1 was collected as a dark green solid (16 mg, yield: 58.4%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.37 (d, 2H,  $J = 16.6$  Hz), 7.78 (d, 2H,  $J = 16.2$  Hz), 7.67 (d, 4H,  $J = 7.6$  Hz), 7.55–7.54 (m, 3H), 7.45–7.41 (m, 4H), 7.37–7.36 (m, 2H), 7.31–7.30 (m, 2H), 3.57 (s, 2H), 1.52 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.5, 146.2, 140.0, 139.2, 137.0, 134.7, 132.6, 129.4, 129.3, 129.2, 128.8, 127.7, 118.8, 114.0, 104.1, 98.9, 77.2, 29.7. MALDI-TOF-HRMS ( $[\text{C}_{37}\text{H}_{27}\text{BF}_2\text{N}_2]^+$ ): calcd  $m/z = 548.2235$ , found  $m/z = 548.2269$ .

**Synthesis of Pt-0.**<sup>28</sup> 2 (30 mg, 0.04 mmol) and L-1 (10 mg, 0.02 mmol) were dissolved in the mixture of distilled THF (2 mL) and dried  $\text{NH}_2\text{Et}$  (2 mL) under Ar.  $\text{CuI}$  (2 mg, 0.01 mmol) was added before the mixture was stirred for 0.5 h at RT. After the reaction was finished, 20 mL of water and 30 mL of  $\text{CH}_2\text{Cl}_2$  were added. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  mL). The combined

organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/PE = 1:3, v/v). **Pt-0** was collected as a dark green solid (22 mg, yield: 61.9%). Crystals were obtained by slow liquid diffusion of *n*-hexane into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.93 (d, 2H, *J* = 16.5 Hz), 7.82 (d, 2H, *J* = 16.5 Hz), 7.62 (d, 4H, *J* = 7.8 Hz), 7.48 (t, 3H, *J* = 5.5 Hz), 7.37–7.27 (m, 12H), 7.20 (t, 4H, *J* = 15.3 Hz), 7.11 (t, 2H, *J* = 15.0 Hz), 2.09–2.03 (m, 24H), 1.55–1.50 (m, 24H), 1.43 (s, 6H), 1.37–1.27 (m, 24H), 0.82 (t, 36H, *J* = 14.5 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.8, 140.8, 138.0, 137.6, 137.1, 136.3, 133.2, 131.0, 129.2, 129.0, 128.9, 128.7, 128.5, 128.0, 127.7, 125.0, 120.1, 120.0, 119.8, 119.6, 109.7, 108.2, 108.0, 107.9, 102.5, 29.9, 26.5, 24.6, 24.5, 24.4, 24.3, 24.1, 24.0, 13.9. MALDI-TOF-HRMS ([C<sub>101</sub>H<sub>143</sub>BF<sub>2</sub>N<sub>2</sub>P<sub>4</sub>Pt<sub>2</sub>]<sup>+</sup>): calcd *m/z* = 1946.9559, found *m/z* = 1946.9431.

**Synthesis of Pt-1.**<sup>28</sup> **Pt-2** (30 mg, 0.03 mmol) and **L-1** (8 mg, 0.015 mmol) were dissolved in the mixture of distilled THF (3 mL) and dried NHET<sub>2</sub> (3 mL) under Ar. CuI (3 mg, 0.015 mmol) was added before the mixture was stirred for 3 h at RT. After the reaction was finished, 20 mL of water and 30 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/PE = 1:1, v/v). **Pt-1** was collected as a dark green solid (16 mg, yield: 43.0%). Crystals were obtained by slow liquid diffusion of *n*-hexane into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 8.91 (d, 2H, *J* = 16.3 Hz), 7.83 (d, 2H, *J* = 16.2 Hz), 7.62 (d, 4H, *J* = 7.6 Hz), 7.49 (t, 3H, *J* = 6.2 Hz), 7.38–7.34 (m, 8H), 7.32–7.31 (m, 2H), 7.28 (d, 2H, *J* = 7.4 Hz), 7.09 (d, 4H, *J* = 8.0 Hz), 5.97 (s, 4H), 2.55 (s, 12H), 2.11–2.06 (m, 24H), 1.60–1.53 (m, 24H), 1.45 (d, 18H, *J* = 3.8 Hz), 1.36–1.29 (m, 24H), 0.82 (t, 36H, *J* = 14.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.2, 150.7, 143.2, 142.3, 140.7, 137.8, 137.5, 137.0, 136.0, 133.0, 131.5, 131.2, 130.9, 129.7, 128.9, 128.8, 128.7, 128.5, 128.4, 127.5, 121.1, 119.8, 118.9, 118.8, 118.7, 110.7, 110.6, 110.5, 109.4, 102.6, 29.7, 26.4, 24.4, 24.3, 24.2, 24.1, 23.9, 14.6, 13.7, 12.7. MALDI-TOF-HRMS ([C<sub>127</sub>H<sub>169</sub>B<sub>3</sub>F<sub>6</sub>N<sub>6</sub>P<sub>4</sub>Pt<sub>2</sub>]<sup>+</sup>): calcd *m/z* = 2439.1838, found *m/z* = 2439.1865.

**Synthesis of Pt-2.**<sup>43</sup> **L-2** (35 mg, 0.10 mmol) and **1** (80 mg, 0.12 mmol) were dissolved in 8 mL of dried NHET<sub>2</sub> under Ar. The mixture was stirred for 9 h at 45 °C. After the reaction was finished, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/PE = 1:1, v/v). **Pt-2** was collected as a yellow solid (33 mg, 33.4%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 7.33 (d, 2H, *J* = 8.2 Hz), 7.09 (d, 2H, *J* = 8.2 Hz), 5.97 (s, 2H), 2.55 (s, 6H), 2.06–2.01 (m, 12H), 1.63–1.55 (m, 12H), 1.48–1.41 (m, 18H), 0.92 (t, 18H, *J* = 7.3 Hz). MALDI-TOF-HRMS ([C<sub>45</sub>H<sub>72</sub>BF<sub>2</sub>N<sub>2</sub>ClP<sub>2</sub>Pt]<sup>+</sup>): calcd *m/z* = 981.4568, found *m/z* = 981.4573.

**Nanosecond Transient Absorption Spectroscopy.** Nanosecond transient absorption spectroscopy was studied with a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, Livingston, U.K.). The samples were purged with N<sub>2</sub> for 15 min before measurements, and the N<sub>2</sub> gas flow was kept constant during the measurement. The signal was digitized with a Tektronix TDS 3012B oscilloscope.

**Femtosecond Transient Absorption Spectroscopy.** The ultrafast pump–probe transient absorption spectroscopy measurements were performed using a Ti:sapphire laser amplifier–optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) and a commercial setup of ultrafast transient absorption spectrometer (Spectra Physics, Helios). Pulse duration was measured as 100 fs. Wavelengths of the pump beam were chosen according to the steady-state absorption spectra of the studied compounds. White light continuum generated with a sapphire crystal was used as a probe beam.

**Cyclic Voltammetry.** Cyclic voltammetry was performed under a 100 mV/s scan rate, in CHI610D Electrochemical workstation (Shanghai, China). The measurements were performed at room temperature with tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N-

[PF<sub>6</sub>], 0.1 M) as the supporting electrolyte, glassy carbon electrode as the working electrode, and platinum electrode as the counter electrode. Dichloromethane was used as the solvent, and ferrocene (Fc) was added as the internal reference. The solution was purged with N<sub>2</sub> before measurement, and the N<sub>2</sub> gas flow was kept constant during the measurement.

**The Gibbs Free Energy Changes (ΔG<sub>CS</sub>) of the Photoinduced Electron Transfer.** ΔG<sub>CS</sub> was calculated with the Rehm–Weller equation.<sup>72,73</sup>

$$\Delta G_{CS} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_S \quad (\text{eq } 1)$$

$$\Delta G_S = -\frac{e^2}{4\pi\epsilon_s\epsilon_0 R_{CC}} - \frac{e^2}{8\pi\epsilon_0} \left( \frac{1}{R_D} + \frac{1}{R_A} \right) \left( \frac{1}{\epsilon_{REF}} - \frac{1}{\epsilon_s} \right) \quad (\text{eq } 2)$$

where ΔG<sub>S</sub> is the static Coulombic energy, *e* is electronic charge, E<sub>OX</sub> is half-wave potential for one-electron oxidation of the electron-donor unit, E<sub>RED</sub> is half-wave potential for one-electron reduction of the electron-acceptor unit, and E<sub>00</sub> is energy level for the singlet-excited state approximated with the fluorescence emission wavelength or for the T<sub>1</sub> state energy of styrylBodipy. ε<sub>s</sub> is static dielectric constant of the solvent, R<sub>CC</sub> is center-to-center separation distance determined by DFT optimization of the geometry, R<sub>D</sub> is the radius of the electron donor determined by DFT optimization of the geometry, R<sub>A</sub> is the radius of the electron acceptor determined by DFT optimization of the geometry, ε<sub>REF</sub> is the static dielectric constant of the solvent used for the electrochemical studies, and ε<sub>0</sub> is the permittivity of free space. The solvents used in the calculation were toluene (ε<sub>s</sub> = 2.4), DCM (ε<sub>s</sub> = 9.1), and MeCN (ε<sub>s</sub> = 37.5).

$$E_{CS} = e[E_{OX} - E_{RED}] + \Delta G_S \quad (\text{eq } 3)$$

$$\Delta G_{CR} = -(\Delta G_{CS} + E_{00}) \quad (\text{eq } 4)$$

The energy transfer rate constant was calculated with eq 5.

$$k_{ET} = \left[ \frac{\Phi_{PL}(\text{Bodipy})}{\Phi_{PL}} - 1 \right] / \tau(\text{Bodipy}) \quad (\text{eq } 5)$$

where [Φ<sub>PL</sub>(Bodipy)]/Φ<sub>PL</sub> is the fluorescence quantum yield ratio of the Bodipy unit in **Pt-2** and **Pt-1**, and τ(Bodipy) is the S<sub>1</sub> state lifetime of **Pt-2** (Table 2).

The triplet-state intermolecular energy-transfer rate constant was calculated with eq 6. The triplet-state energy-transfer efficiency was calculated with eq 7.

$$k_{ET} = (1/\tau_2) - (1/\tau_1) \quad (\text{eq } 6)$$

$$\Phi_{ET} = 1 - \tau_2/\tau_1 \quad (\text{eq } 7)$$

where τ<sub>1</sub> and τ<sub>2</sub> are triplet-state lifetime of the rising stage and decline stage of decay curves, respectively (Figure 11 and Supporting Information Figure S28).

The bimolecular quenching constant was calculated according to eq 8.

$$k_q = K_{SV}/\tau_0 \quad (\text{eq } 8)$$

where τ<sub>0</sub> is the triplet-state lifetime of the triplet-energy donor.

Quenching efficiency was given by eq 9, where k<sub>0</sub> is the diffusion-controlled bimolecular quenching rate constants, which can be calculated with the Smoluchowski eq 10.<sup>89</sup>

$$f_Q = k_q/k_0 \quad (\text{eq } 9)$$

$$k_0 = 4\pi RND/1000 = \frac{4\pi N}{1000} (R_f + R_q)(D_f + D_q) \quad (\text{eq } 10)$$

where *D* is the sum of the diffusion coefficients of the energy donor (D<sub>f</sub>) and quencher (D<sub>q</sub>), and *N* is Avogadro's number. *R* is the collision radius, the sum of the molecular radii of the energy donor (R<sub>f</sub>) and the quencher (R<sub>q</sub>).

Diffusion coefficients can be obtained from Stokes–Einstein equation:<sup>89</sup>

$$D = kT/6\pi\eta R \quad (\text{eq 11})$$

where  $k$  is Boltzmann's constant,  $\eta$  is the solvent viscosity, and  $R$  is the molecule radius.

**Density Functional Theory Calculations.** Geometry optimization was calculated by using the B3LYP functional, the vertical excitation energy was calculated with the TDDFT method based on the singlet ground-state geometry. All the calculations were performed with Gaussian 09W software (Gaussian, Inc.).<sup>91</sup>

**Single-Crystal X-ray Diffractions.** The crystal was mounted on glass fibers for X-ray measurement. Reflection data were collected at RT on a Bruker AXS SMART APEX II CCD diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and an  $\omega$  scan mode. All the measured independent reflections ( $I > 2\sigma(I)$ ) were used in the structural analyses, and semiempirical absorption corrections were applied using SADABS program. The structures were solved by the direct method using SHELXL-97. The hydrogen atoms of the organic frameworks were fixed at calculated positions geometrically and refined by using a riding model. In particular, the atoms on the phosphine ligand are found to be disordered and modeled over two split positions. All corresponding non-hydrogen atoms were refined by using the "Sadi" and "Simu" restraints to make the parameters of the disordered atoms more reasonable. CCDC No. (Pt–O): 1054164; CCDC No. (Pt–1): 1054152.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

<sup>1</sup>H NMR and <sup>13</sup>C NMR data, selected bond lengths and angles, HRMS and photophysical spectra, and DFT/TDDFT calculation of the complexes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01107.

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### Notes

The authors declare no competing financial interest.

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