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Ligand Localized Triplet Excited States in Platinum(II) Bipyridyl and Terpyridyl Peryleneacetylides

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An investigation of the photophysics of two complexes, [Pt(^{t}Bu$_3$tpy)(C≡C-perylene)]BF$_4$ (**1**) and Pt(^{t}Bu$_2$bpy)(C≡C-perylene)$_2$ (**2**), where ^{t}Bu$_3$tpy is 4,4′,4′′-tri(*tert*-butyl)-2,2′:6′,2′′-terpyridine, ^{t}Bu$_2$bpy is 4,4′-di(*tert*-butyl)-2,2′-bipyridine, and C≡C-perylene is 3-ethynylperylene, reveals that they both exhibit perylene-centered ligand localized excited triplet states (^{3}IL) upon excitation with visible light. These complexes do not display any significant photoluminescence at room temperature but readily sensitize $^1O_2$ in aerated CH_2Cl_2 solutions, as evidenced by its characteristic emission near 1270 nm. The transient absorption difference spectra were compared to bi- and tridentate phosphine peryleneacetylides intended to model the ^{3}IL peryleneacetylide excited states in addition to the related phenylacetylide-bearing polyimine analogues, with the latter model being the respective triplet charge-transfer (^{3}CT) excited states. The transient difference spectra of the two title compounds display excited-state absorptions largely attributable to perylene localized ^{3}IL states yet exhibit somewhat attenuated excited-state lifetimes relative to those of the phosphine model chromophores. The abbreviated lifetimes in **1** and **2** may suggest the involvement of the energetically proximate ^{3}CT triplet state exerting an influence on excited-state decay, and the effect appears to be stronger in **1** relative to **2**, consistent with the energies of their respective ^{3}CT states.

Introduction

The photochemistry and photophysics of platinum(II) bipyridyl and terpyridyl acetylide complexes continue to inspire fundamental and applied research interest.[1–11] Triplet states are commonly accessed in *trans*-disposed $(PBu_3)_2$Pt(II) acetylide oligomers and polymers, where excitation of the lowest singlet state produces the lower lying triplet via intersystem crossing.[12–14] In Pt(II) bipyridyl and terpyridyl structures, the opportunity presents itself to utilize charge-transfer (CT) transitions in the visible to sensitize acetylide-based ligand-localized triplet states.[9,13,15,16] While this strategy is conspicuous, there are only a handful of examples

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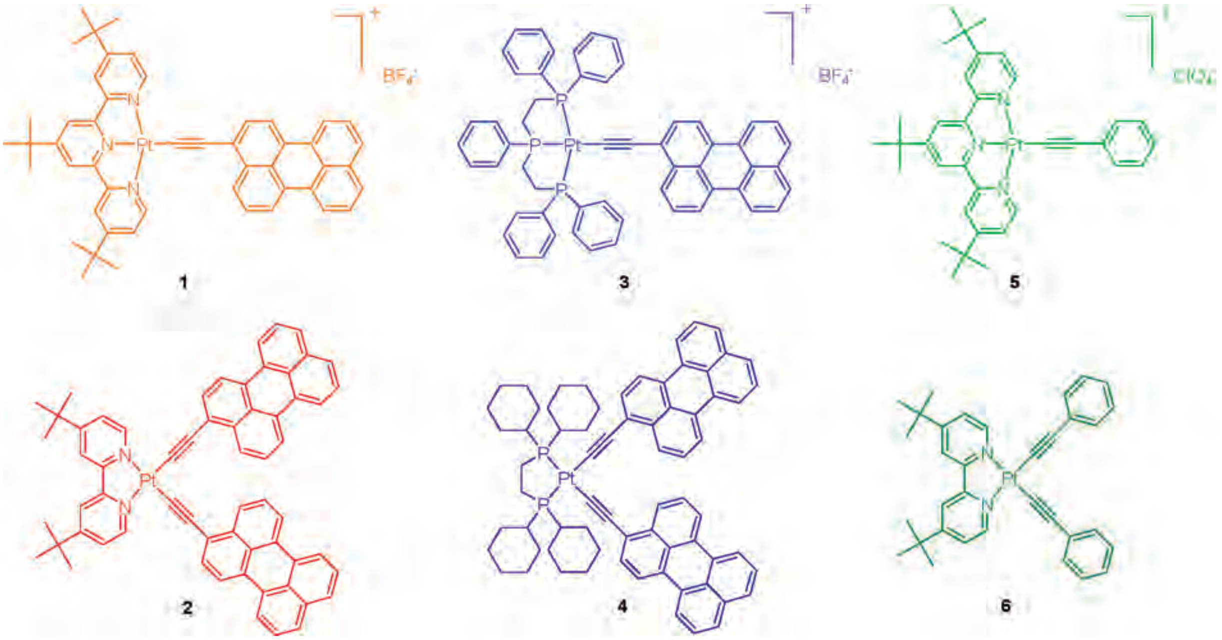
(1) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87–97.
(2) Rachford, A. A.; Goeb, S.; Castellano, F. N. *J. Am. Chem. Soc.* **2008**, *130*, 2766–2767.
(3) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447–457.
(4) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053–4062.
(5) Chan, S.-C.; Chan, M. C. W.; Wang, Y.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *Chem.—Eur. J.* **2001**, *7*, 4180–4190.
(6) Yam, V. W.-W.; Tang, R. P.-L.; Wong, K. M.-C.; Cheung, K.-K. *Organometallics* **2001**, *20*, 4476–4482.
(7) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-m.; He, Z.; Wong, K.-y. *Chem.—Eur. J.* **2003**, *9*, 6155–6166.
(8) Wong, K. M.-C.; Tang, W.-S.; Chu, B. W.-K.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2004**, *23*, 3459–3465.
(9) Castellano, F. N.; Pomestchenko, I. E.; Shikhova, E.; Hua, F.; Muro, M. L; Rajapakse, N. *Coord. Chem. Rev.* **2006**, *250*, 1819–1828.
(10) Hua, F.; Kinayyigit, S.; Cable, J. R.; Castellano, F. N. *Inorg. Chem.* **2006**, *45*, 4304–4306.
(11) Ziessel, R.; Diring, S.; Retailleau, P. *J. Chem. Soc., Dalton Trans.* **2006**, 3285–3290.
(12) Hissler, M.; Harriman, A.; Khatyr, A.; Ziessel, R. *Chem.—Eur. J.* **1999**, *5*, 3366–3381.
(13) Danilov, E. O.; Pomestchenko, I. E.; Kinayyigit, S.; Gentili, P. L.; Hissler, M.; Ziessel, R.; Castellano, F. N. *J. Phys. Chem. A* **2005**, *109*, 2465–2471.
(14) Kim, K.-Y.; Liu, S.; Kose, M. E.; Schanze, K. S. *Inorg. Chem.* **2006**, *45*, 2509–2519.
(15) Haskins-Glusak, K.; Ghiviriga, I.; Abboud, K. A.; Schanze, K. S. *J. Phys. Chem. B* **2004**, *108*, 4969–4978.
(16) Pomestchenko, I. E.; Castellano, F. N. *J. Phys. Chem. A* **2004**, *108*, 3485–3492.
(17) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389–394.

10.1021/ic702454k CCC: $40.75

Chart 1. Structures of Complexes **1**−**6**



where ligand-localized triplet states have been sensitized to visible light in these structures.[9,17–19]

In the present work, we report two new Pt(II) CT complexes, [Pt(^{t}Bu$_3$tpy)(C≡C-perylene)]BF$_4$ (**1**) and Pt(^{t}Bu$_2$bpy)(C≡C-perylene)$_2$(**2**), where ^{t}Bu$_3$tpy is 4,4′,4″-tri(*tert*-butyl)-2,2′:6′,2″-terpyridine, ^{t}Bu$_2$bpy is 4,4′-di(*tert*-butyl)-2,2′-bipyridine, and C≡C-perylene is 3-ethynylperylene. The phosphine analogues, [Pt(P3)(C≡C-perylene)]BF$_4$ (**3**) and [Pt(P2)(C≡C-perylene)$_2$] (**4**), where P3 is bis[(2-diphenylphosphino)ethyl]phenylphosphine and P2 is 1,2-bis(dicyclohexylphosphino)ethane, have been prepared and studied in order to examine the nature of localized peryleneacetylide intraligand excited states (^{3}IL). In conjunction with these complexes, the respective charge-transfer model complexes, [Pt(^{t}Bu$_3$tpy)-(C≡C-Ph)]ClO$_4$ (**5**) and Pt(^{t}Bu$_2$bpy)(C≡C-Ph)$_2$ (**6**), are also examined to compare the characteristics of molecules exhibiting low lying triplet charge-transfer excited states (^{3}CT). The structures of complexes **1**−**6** are shown in Chart 1. Complexes **1**−**4** readily sensitize ^{1}O$_2$ emission in aerated solutions upon visible excitation, implying that the lowest energy excited state in these complexes is triplet in nature. Time-resolved spectroscopic studies of all six complexes indicate that the excited states of the title compounds are most consistent with a ^{3}IL excited state localized on the peryleneacetylide(s) rather than the ^{3}CT photophysics more commonly observed in Pt(II) terpyridyl and bipyridyl acetylide chromophores.

Experimental Section

General Methods. All reactions were carried out under an inert and dry argon atmosphere by using standard techniques. Anhydrous CH$_2$Cl$_2$, diisopropylamine, and triethylamine suitable for synthesis were freshly distilled over CaH$_2$. All other reagents from commercial sources were used as received. ^{1}H NMR and ^{13}C-{^{1}H} NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. All chemical shifts are referenced to the residual solvent signals previously referenced to TMS, and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). ^{31}P NMR spectra were run on a Varian VXR-400 spectrometer, and chemical shifts were related to external 85% H$_3$PO$_4$. EI mass spectra (70 eV) were measured in-house by using a direct insertion probe in a Shimadzu QP5050A spectrometer. FT-IR spectra were measured with a ThermoNicolet IR 200 spectrometer.

Preparations. [Pt(^{t}Bu$_3$tpy)Cl]BF$_4$,[20] Pt(^{t}Bu$_2$bpy)Cl$_2$,[21] [bis[2-(diphenylphosphino)ethyl]phenylphosphine platinum triflate]triflate,[22] [1,2-bis(dicyclohexylphosphino)ethane platinum dichloride],[23] 3-ethynylperylene,[24] complex **5**,[25] and complex **6**[3,26] were synthesized according to the literature procedures and yielded satisfactory masses and ^{1}H NMR spectra.

General Synthetic Procedure. A Schlenk flask was charged with the appropriate platinum(II) chloride precursor, 3-ethynylperylene, and CH$_2$Cl$_2$/*i*-Pr$_2$NH for **1** and **3** or DMF/Et$_3$N for **2**. The solution was degassed for 30 min. CuI (10% mol) was added, the solution was stirred at room temperature for 12 h, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography, followed by recrystallization in a mixture of CH$_2$Cl$_2$/cyclohexane.

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(18) Pomestchenko, I. E.; Luman, C. R.; Hissler, M.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2003**, *42*, 1394–1396.

(19) Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S.-T. *J. Am. Chem. Soc.* **2004**, *126*, 4958–4971.

(20) Lai, S.; Chan, M. C. W.; Cheung, K.; Che, C. *Inorg. Chem.* **1990**, *29*, 4262–4267.

(21) Hodges, K. D.; Rund, J. V. *Inorg. Chem.* **1975**, *14*, 525–528.

(22) Annibale, G.; Bergamini, P.; Cattabriga, M. *Inorg. Chim. Acta* **2001**, *316*, 25–32.

(23) ALQaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. G.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149–12150.

(24) Inouye, M.; Hyodo, Y.; Nakazumi, H. *J. Org. Chem.* **1999**, *64*, 2704–2710.

(25) Shikhova, E.; Danilov, E. O.; Kinayyigit, S.; Pomestchenko, I. E.; Tregubov, A. D.; Camerel, F.; Retailleau, P.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2007**, *46*, 3038–3048.

(26) Chan, S.; Chan, W.; Wang, Y.; Che, C.; Cheung, K.; Zhu, N. *Chem.—Eur. J.* **2001**, *7*, 4180–4190.

Complex 1 was prepared using the general synthetic procedure from [Pt(^{t}Bu$_3$tpy)Cl]BF$_4$ (100 mg, 0.15 mmol), 3-ethynylperylene (41 mg, 0.15 mmol), CuI (1.9 mg, 0.01 mmol), DMF (3 mL), and *i*-Pr$_2$NH (1 mL); chromatography was performed on alumina, eluting with 99/1 CH$_2$Cl$_2$/methanol (v/v) to 98/2 CH$_2$Cl$_2$/methanol (v/v) to give 104 mg (73%) of **1** as a red solid after recrystallization. ^{1}H NMR (400.1 MHz, *d*$_3$-acetonitrile/*d*$_6$-dimethylsulfoxide (v/v 1/1)): δ 8.56 (d, $^3J = 6$ Hz, 1H), 8.27 (m, 1H), 8.44 (s, 2H), 8.12 (d, $^3J = 8$ Hz, 1H), 7.99 (s, 2H), 7.84 (s, 2H), 7.75 (m, 1H), 7.62 (m, 2H), 7.48 (d, $^3J = 7$ Hz, 1H), 7.43 (t, $^3J = 8$ Hz, 1H), 7.36 (m, 1H), 7.25 (d, $^3J = 7$ Hz, 1H), 7.15 (m, 1H), 7.09 (t, $^3J = 7$ Hz, 1H), 6.91 (t, $^3J = 8$ Hz, 1H), 1.60 (s, 18H), 1.47 (s, 9H). ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_3$-acetonitrile/*d*$_6$-dimethylsulfoxide (v/v 1/1)): δ 168.6, 167.4, 159.7, 154.7, 151.7, 151.2, 151.0, 137.2, 131.9, 127.5, 125.9, 125.3, 123.8, 122.9, 122.3, 122.0, 119.9, 102.9, 94.8, 37.9, 36.6, 30.1, 29.6. FT-IR (KBr, cm^{-1}): 3053, 2960, 2901, 2866, 2103 ($\nu_{C\equiv C}$), 1617, 568, 1481, 1419, 1402, 1387, 1370, 1257, 1052 (ν_{B-F}), 917, 808, 767. ES-MS *m*/*z* (nature of the peak, relative intensity): 871.2 ([M − BF$_4$]$^+$, 100). Anal. Calcd for C$_{49}$H$_{46}$N$_3$PtBF$_4$: C, 61.38; H, 4.84; N, 4.38. Found: C, 61.22; H, 4.19; N, 4.18.

Complex 2 was prepared using the general synthetic procedure from Pt(^{t}Bu$_2$bpy)Cl$_2$ (96 mg, 0.18 mmol), 3-ethynylperylene (124 mg, 0.45 mmol), CuI (3 mg, 0.016 mmol), CH$_2$Cl$_2$ (10 mL), and *i*-Pr$_2$NH (5 mL); chromatography was performed on alumina, eluting with 80/20 CH$_2$Cl$_2$/cycloxehane (v/v) to 99/1 CH$_2$Cl$_2$/cyclohexane (v/v) to give 113 mg (62%) of **2** as a deep-carmin solid after recrystallization. ^{1}H NMR (400.1 MHz, *d*$_6$-dimethylsulfoxide/*d*$_4$-methanol (v/v, 9/1)): δ 9.86 (d, $^3J = 6$ Hz, 2H), 8.84 (d, $^3J = 8$ Hz, 2H), 8.16 (m, 10H), 8.01 (s, 2H), 7.77 (d, $^3J = 8$ Hz, 2H), 7.64 (m, 6H), 7.46 (td, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H), 7.40 (t, $^3J = 8$ Hz, 2H), 1.49 (s, 18H). ^{13}C{^{1}H} NMR (100.6 MHz, *d*$_6$-dimethylsulfoxide/*d*$_4$-methanol (v/v 9/1)): δ 162.5, 157.8, 149.9, 124.2, 123.6, 122.4, 121.9−121.7 (multiple peaks), 121.2, 119.2−118.8 (multiple peaks), 118.3, 118.0, 117.6, 117.4, 117.0, 113.9, 112.7, 112.6, 111.7, 103.9, 96.8, 39.1, 31.8. FT-IR (KBr, cm^{-1}): 3040, 2963, 2094 ($\nu_{C\equiv C}$), 1617, 1576, 1495, 1416, 1386, 1240, 807, 766. ES-MS *m*/*z* (nature of the peak, relative intensity): 1014.2 ([M + H]$^+$, 100). Anal. Calcd for C$_{62}$H$_{46}$N$_2$Pt: C, 73.43; H, 4.57; N, 2.76. Found: C, 73.04; H, 4.22; N, 2.55.

Complex 3. A Schlenk flask was charged with [bis[2-(diphenylphosphino)ethyl]phenylphosphine platinum triflate]triflate (50 mg, 4.86×10^{-2} mmol), 3-ethynylperylene (14 mg, 5.10×10^{-2} mmol), and CH$_2$Cl$_2$. The solution was stirred for 30 min, poured into 10 mL of a saturated solution of NaBF$_4$, and stirred again for 10 min. The organic extracts were washed with water and dried over cotton absorbent. The solvent was removed by rotary evaporation. The residue was purified by column chromatography on alumina, eluting with CH$_2$Cl$_2$/petroleum ether (15/85 v/v) to CH$_2$Cl$_2$/MeOH (99/1 v/v) to give 43 mg (80%) of **3** as an orange solid after recrystallization. ^{1}H NMR (300.0 MHz, CDCl$_3$): δ 8.16−7.86 (m, 14H), 7.35 (d, $^3J = 8$ Hz, 1H), 7.65 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H), 7.56−7.41 (m, 17H), 7.27 (d, $^3J = 8$ Hz, 1H), 7.10 (t, $^3J = 8$ Hz, 1H), 3.52−3.33 (m, 4H), 2.38−2.27 (m, 4H). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 134.8, 134.7, 134.1, 133.9, 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 132.2, 131.3, 131.2, 131.1, 130.0, 129.9, 129.8, 129.6, 129.3, 128.6, 128.5, 128.2, 127.9, 127.8, 127.5, 126.8, 126.6, 126.4, 125.7, 124.1, 122.1, 120.3, 120.2, 119.8, 112.8, 85.6, 27.0, 26.5. ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$): δ 92.2 (s), 92.2 (d, $^1J = 1988$ Hz), 39.2 (s), 39.2 (d, $^1J = 2508$ Hz). FT-IR (solid, cm^{-1}): 3052, 2922, 2095 ($\nu_{C\equiv C}$), 1570, 1483, 1435, 1386, 1237, 1100, 1050, 812. ES-MS *m*/*z* (nature of the peak, relative intensity): 1004.4 ([M − BF$_4$]$^+$, 100). Anal. Calcd for C$_{60}$H$_{53}$BF$_4$P$_3$Pt: C, 62.73; H, 4.65. Found: C, 62.51; H, 4.42.

Complex 4 was prepared using the same procedure as that for complex **1** from [1,2-bis(dicyclohexylphosphino)ethane platinum dichloride] (50 mg, 0.07 mmol), 3-ethynylperylene (42 mg, 0.15 mmol), CuI (1 mg, 7.26×10^{-3} mmol), CH$_2$Cl$_2$ (10 mL), and *i*-Pr$_2$NH (2 mL); chromatography was performed on alumina, eluting with 15/85 CH$_2$Cl$_2$/petroleum ether (v/v) to 70/30 CH$_2$Cl$_2$/petroleum ether (v/v) to give 75 mg (88%) of **4** as an orange solid after recrystallization. ^{1}H NMR (300.0 MHz, CDCl$_3$): δ 8.75 (d, $^3J = 8$ Hz, 2H), 8.17−8.09 (m, 8H), 7.67−7.60 (m, 6H), 7.48−7.38 (m, 6H), 2.50−2.31 (m, 8H), 1.96−1.26 (m, 40H). ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$): δ 62.5 (s), 62.5 (d, $^1J = 1988$ Hz). FT-IR (solid, cm^{-1}): 3046, 2923, 2849, 2088 ($\nu_{C\equiv C}$), 1567, 1496, 1443, 1384, 1265, 808, 764. ES-MS *m*/*z* (nature of the peak, relative intensity): 1167.5 ([M + H]$^+$, 100). Anal. Calcd for C$_{70}$H$_{70}$P$_2$Pt: C, 71.96; H, 6.04. Found: C, 71.72; H, 5.82.

Photophysical Measurements. Static UV−vis absorption spectra were measured with a Varian 50 Bio spectrophotometer. Corrected steady-state luminescence spectra were obtained with a PTI Instruments spectrofluorimeter equipped with a Peltier cooled InGaAs detector using lock-in detection. This fluorimeter operates under the control of FeliX32 software from PTI. A Coherent Innova 300 argon-ion laser was used as the excitation source where the 488 nm output (38.2 mW) was isolated using a diffraction grating in concert with several optics including a 488.0 nm band-pass filter. The laser power was measured with a Molectron Power Max 5200 power meter. All photophysical measurements were conducted at ambient temperature, 22 ± 2 °C. All luminescence samples were prepared with spectroscopic grade CH$_2$Cl$_2$ in 1 cm^2 anaerobic quartz cells (Starna Cells), degassed by solvent-saturated high purity argon for at least 35 min prior to the measurements, and maintained under argon atmosphere throughout the experiments. Fluorescence lifetime measurements were obtained by time-correlated single-photon counting on an Edinburgh Analytical Instruments (FLSP 920) spectrofluorimeter equipped with a pulsed H$_2$ flash lamp (nF900). The instrument response function was collected using a dilute solution of Ludox at the detection wavelength. Reconvolution of the fluorescence decay and instrument response function was performed within the Edinburgh software in conjunction with least-squares lifetime fitting. Finally, the data was exported and plotted using Origin 7.5. The fluorescence quantum yields of **3** and **4** in dichloromethane were determined relative to perylene in ethanol ($\Phi_{fl} = 0.92$),[27] and values reported herein represent an average of at least three independent measurements. In some instances, single photon counting experiments in the near-IR were performed at the University of Victoria, Victoria, BC, using a NIR-PMT detector (R5509, Hamamatsu) cooled to −80 °C.

Transient absorption spectra were collected on a Proteus spectrometer (Ultrafast Systems) equipped with a 150 W Xe-arc lamp (Newport), a Bruker Optics monochromator equipped with two diffraction gratings blazed for visible and near-IR dispersion, respectively, and Si or InGaAs photodiode detectors (DET 10A and DET 10C, Thorlabs) optically coupled to the exit slit of the monochromator. Excitation at 475 nm (2 mJ/pulse) from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an optical absorbance of 0.4 at the excitation wavelength. The data consisting of a 128-shot average were analyzed by Origin 7.5

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(27) Montalti, M.; Credi, A.; Prodi, L.; Gandolfini, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press LLC: Boca Raton, FL, 2005.

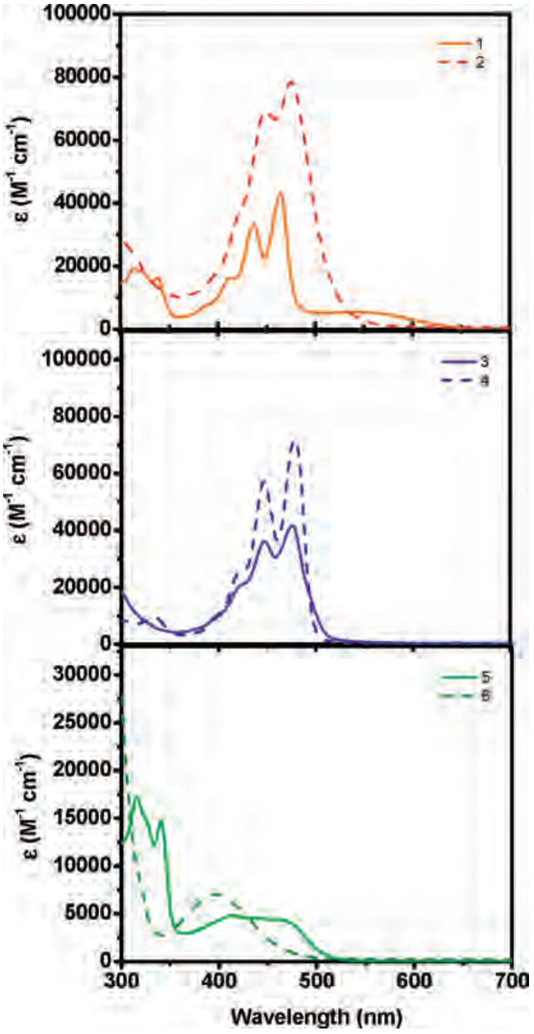

Figure 1. Absorption spectra of complexes **1**−**6** in CH_2Cl_2 at room temperature.

software. Solution concentrations were OD ∼ 0.15 and OD ∼ 0.4 for photoluminescence and transient absorption measurements, respectively.

Results and Discussion

Absorption and $^1O_2$ Emission Sensitization. The absorption spectra of compounds **1**−**4** in CH_2Cl_2 are displayed in Figure 1, plotted as extinction coefficient versus wavelength. The peryleneacetylide chromophore(s) in complexes **1**−**4** are largely responsible for the structured low energy $\pi-\pi^*$ transitions between 400−500 nm. The lowest energy bands are substantially red shifted relative to the free perylene-C≡C−H species (456 nm in CH_2Cl_2, $\varepsilon = 41000$ M^{-1} cm^{-1}). In **1**, the lowest energy transitions with small relative extinction coefficients are assigned as charge-transfer (CT) in nature, and the strong, structured perylene-localized $\pi-\pi^*$ transitions are positioned at slightly higher energy. The CT assignment is supported by the fact that, in the analogous triphos model chromophore (**3**), there are no corresponding long wavelength absorption bands. However, in the bipyridyl peryleneacetylide system (**2**), the anticipated CT absorption bands in the visible are obscured by the strong perylene-localized $\pi-\pi^*$ transitions, which appear broadened relative to the sharp and more distinct vibronic features exhibited by **1**, **3**, and **4**. At first glance, the spectral broadening in **2** might potentially indicate ground-state intramolecular interactions between the neighboring, *cis*-disposed acetylides or even perhaps intermolecular π-stacking between perylene moieties. Since the structurally similar diphos model system (**4**) does not exhibit similar broadening, we conclude that intramolecular interactions are not responsible for the shape of the ground-state absorption spectrum in **2**. Intermolecular π-stacking events potentially contributing to the breadth and distortion of the bands are ruled out by the fact that the entire electronic spectrum of **2** strictly obeys the Beer−Lambert law over all concentration ranges used in the present optical experiments, which have an upper limit of 6.4×10^{-4} M (see Figure S1 of the Supporting Information), and the normalized spectra can be completely superimposed in the spectral region of interest. Since the highest occupied molecular orbital (HOMO) in metal-acetylide chromophores exhibiting CT character significantly combines metal and acetylide ligand electron density,[28,29] most absorption features characteristic of the model structures (free acetylene ligand and appropriate Pt(II) phenylacetylide complex) do not simply add together.[9,13,16,18,25,30,31] In our experience, the bands associated with both ligand-localized and CT transitions red shift relative to the corresponding model chromophores in all instances. Additionally, the use of the diphos (**4**) and triphos (**3**) models yields reasonable estimates of how linkage to Pt(II) affects the ligand-localized transitions in the acetylide relative to the free acetylene. As stated above, significant red shifts and slight spectral broadening in the $\pi-\pi^*$ transitions are observed in peryleneacetylene upon bonding with Pt(II). In the CT phenylacetylide model complexes **5** and **6**, broad low energy CT absorptions are readily observed and are not obscured by low energy ligand-localized $\pi-\pi^*$ transitions. Comparison of the absorption spectra of **1** and **5** shows how the attachment of the peryleneacetylide chromophore substantially affects the position of the CT transitions relative to the corresponding phenylacetylide structure. Although there are a combination of responsible electronic perturbations on both the metal and the ligand, which induce such a significant red shift in **1**, the important result is that the CT transitions are red shifted on the order of several thousand wavenumbers.[32] Assuming that an identical shift occurs in the CT bands of **2**, this would superimpose a broad low energy absorption band similar to that observed in **6**, at approximately 440 nm in the spectrum of **4**, qualitatively accounting for the spectral broadening seen in **2**.

The emission profile typical of platinum complexes with a ^{3}CT excited state is quantitatively quenched in complexes

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(28) Zhou, X.; Zhang, H.-X.; Pan, Q.-J.; Xia, B.-H.; Tang, A.-C. *J. Phys. Chem. A* **2005**, *109*, 8809–8818.

(29) Liu, X.-J.; Feng, J.-K.; Meng, J.; Pan, Q.-J.; Ren, A.-M.; Zhou, X.; Zhang, H.-X. *Eur. J. Inorg. Chem.* **2005**, 1856–1866.

(30) Goeb, S.; Rachford, A. A.; Castellano, F. N. *Chem. Commun.* **2008**, 814–816.

(31) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1400–1403.

(32) This assumes that an identical energy shift is observed in the CT bands in the bipyridyl complex in relation to the terpyridyl complex.

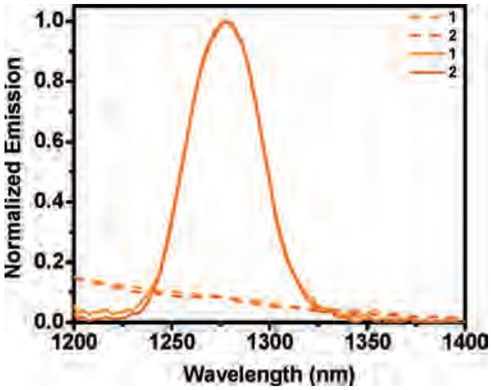

Figure 2. Steady-state $^1O_2$ luminescence spectra of complexes **1** and **2** measured in aerated (solid lines) and degassed (dashed lines) CH_2Cl_2 solutions and measured using 488 nm laser excitation at 32.8 mW incident power.

1 and **2**. This suggests that the lowest energy excited state is likely perylene-based in nature. These complexes do not exhibit the singlet fluorescence characteristic of the free perylene-CCH species. However, their model phosphine analogues (**3** and **4**) exhibit weak fluorescence at 505 and 493 nm with fluorescence quantum yields (Φ_{fl}) of 0.013 and 0.034, respectively (see Figure S2 of the Supporting Information). Time-correlated single-photon counting measurements performed on these chromophores at short wavelengths yield fluorescence lifetimes of 4.17 and 2.5 ns for **3** and **4**, respectively (see Figures S3−S5 of the Supporting Information). The triplet nature of these excited states can be indirectly identified by their ability to sensitize $^1O_2$ photoluminescence, which has a characteristic narrow spectrum near 1270 nm.[33] The data presented in Figure 2 clearly demonstrates that, upon air equilibration of the CH_2Cl_2 solutions, excitation of **1** and **2** with visible light results in the sensitization of $^1O_2$ emission. This sensitization does not occur under the same conditions when the same solutions are thoroughly degassed (Figure 2). Complexes **3** and **4** display the analogous behavior; these combined static photophysical observations strongly suggest that the lowest energy excited state in **1**−**4** is most likely triplet perylene-acetylide in nature. Hence, nanosecond transient absorption spectroscopy was employed to definitively characterize the low lying triplet state present in these chromophores.

Transient Absorption Spectroscopy. The transient absorption difference spectra of complexes **1**−**6** measured at select delay times following nanosecond laser pulses are presented in Figures 3 and 4. The current data provides emission-corrected spectral difference profiles for compounds **5** and **6** between 400 and 1400 nm. To our knowledge, the near-IR difference spectra of these two chromophores have not been reported to date. The difference spectra acquired for the remaining chromophores (**1**−**4**) are not emission corrected, as these samples do not render any long-lived photoluminescence in degassed solutions. Single wavelength kinetic traces and their respective fits with residuals, in addition to the lifetimes determined from these fits, are collected in each panel. The spectrum observed in each case appears promptly within the ∼10 ns instrument response, so no information could be obtained on the spectral evolution of the transients. All of the transients are long-lived, consistent with a triplet excited-state parentage, and in every case, the excited-state absorptions and bleaching features self-consistently recover to the baseline exhibiting single exponential kinetics.

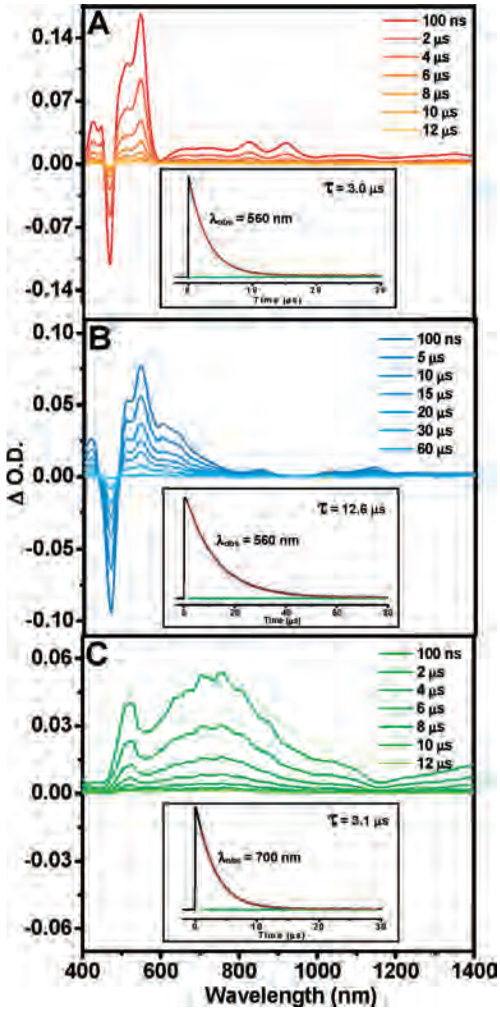

Figure 3. Selected transient absorption difference spectra of **1** (A), **3** (B), and **5** (C) measured in deaerated CH_2Cl_2 following a 475 nm, a 5−7 ns fwhm, and a 2 mJ laser pulse. Single wavelength kinetic traces (black), single exponential fits (red), and residuals (green) are inset in each panel.

The transient absorption difference spectrum of **1** (Figure 3A) does not resemble what is typically observed for the charge-transfer excited state in structurally related molecules (Figure 3C).[4,9,13,18,25,34] The difference spectrum in **1** exhibits two intense positive OD bands at 430 and 545 nm with a high energy shoulder at 510 nm and a single intense ground-state bleach centered at 470 nm. The bleach coincides with the strong ground-state absorption associated with singlet $\pi-\pi^*$ transitions of the peryleneacetylide chromophore. The fact that this absorption is bleached on a long time scale and kinetically recovers with the positive OD transients indicates that the peryleneacetylide chromophore has likely crossed to the

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[33] Zhang, X.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 12797–12803.

[34] Guo, F.; Sun, W.; Liu, Y.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 4055–4065.

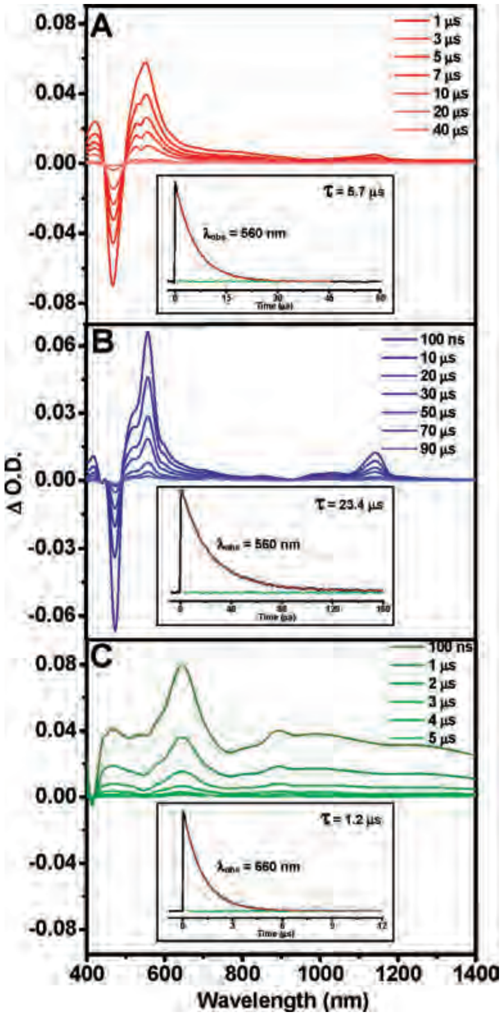

Figure 4. Selected transient absorption difference spectra of **2** (A), **4** (B), and **6** (C) measured in deaerated CH_2Cl_2 following a 475 nm, a 5−7 ns fwhm, and a 2 mJ laser pulse. Single wavelength kinetic traces (black), single exponential fits (red), and residuals (green) are inset in each panel.

triplet excited state, in essence depleting the ground-state singlet transitions. The remaining transient features do not agree with the one electron reduction of the terpyridine moiety, as we previously determined in the case of **5**, nor do they agree with the visible to near-IR difference spectrum of **5** (Figure 3C).[25] A broad transient featuring multiple distinguishable bands is also observed between 600 and 1000 nm in **1**; beyond this is a continuous region of low excited-state absorption that extends across the near-IR throughout our remaining detection range. The weak low-energy features do indeed correspond with some of the strong features observed in the analogous experiment performed on CT model **5** (Figure 3C). However, given the significant differences between the data obtained in Figure 3A (**1**) and C (**5**) and the strong spectral coincidences between Figure 3A (**1**) and B (**3**), we conclude that the triplet excited-state compositions in **1** and **3** are identical, assigned as ^{3}IL in nature, and localized on the peryleneacetylide subunit. The triphos model **3** notably lacks a low lying CT state, so the long-lived spectroscopic features in this complex must be associated exclusively with the ^{3}IL excited state of peryleneacetylide. While the spectral features in **1** and **3** are quite similar, their excited-state dynamics are quite disparate. In the case of **3**, all transients possess a lifetime of 12.6 μs in degassed CH_2Cl_2, which is more than 4 times that of **1** ($\tau = 3.0$ μs) measured under the same conditions. If exactly the same excited state is sensitized in both molecules, one would anticipate a closer match in lifetime. Interestingly, **5**, which was selected as a model chromophore whose transient absorption features would best describe that of a ^{3}CT excited state, possesses a lifetime of 3.0 μs, in agreement with our previous measurements.[25] It appears that, while the spectral features of **1** seem to be associated with a ^{3}IL peryleneacetylide localized excited state as observed in **3**, its lifetime corresponds precisely to that of the analogous CT chromophore **5**. Since we cannot make comparisons using photoluminescence spectroscopy, we cannot precisely affirm with confidence that the lifetime data results from configuration mixing of energetically proximate ^{3}CT and ^{3}IL states present in **1**, which would indeed yield excited-state properties in **1** that are essentially a superposition of those exhibited by **3** and **5**.[16,30,35] Since the ground-state CT absorption bands are present at low energy in **1**, it seems reasonable to speculate that the ^{3}IL(peryleneacetylide) state may lie close in energy to the ^{3}CT state, while, in the bipyridine complex (**2**), the ^{3}CT states should lie much higher in energy relative to the ^{3}IL state. This assumes similar singlet−triplet energy gaps present in both chromophores. If this is indeed the case, one would expect stronger configuration mixing in **1** relative to **2**, which would be most evident in the observed excited-state lifetime. As shown below, compound **2** is much longer lived than **1**, which implies weaker configuration mixing in the excited-state manifold in the former. Without question, the ^{3}IL excited state in peryleneacetylide is indeed accessed in both **1** and **3**, and this state dominates the excited-state absorption spectroscopy in these chromophores.

The transient absorption difference spectrum of **2** (Figure 4A) exhibits intense transient absorptions and ground-state bleaching features attributable to the peryleneacetylide moieties analogous to those observed above in **1** and **3** (Figure 3). In **2**, excited-state absorptions are revealed at 420 and 550 nm; the latter is substantially stronger in intensity and closely matches the features observed in **1** and **3**. Beyond the excited-state absorption at 550 nm, the spectrum tails off into a broad featureless absorption past 1000 nm until the observation of a third low-energy absorption feature at 1140 nm. This peak was not readily observable in complex **1**. However, it was observed in **3** and is again present in **4** (see below). The characteristic ground-state bleach of the ^{1}perylene $\pi-\pi^*$ transition occurs at 470 nm. Again, the remaining transient absorption features in **2** do not resemble the spectrum obtained from one electron reductive spectroelectrochemistry of the bipyridine complex and are not accounted for in the CT model complex (Figure 4C).[36] The

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(35) Liu, S.; Schanze, K. S. *Chem. Commun.* **2004**, 1510–1511.

(36) Hua, F.; Kinayyigit, S.; Rachford, A. A.; Shikhova, E. A.; Goeb, S.; Cable, J. R.; Adams, C. J.; Kirschbaum, K.; Pinkerton, A. A.; Castellano, F. N. *Inorg. Chem.* **2007**, *46*, 8771–8783.

intense transient absorption features of **2** are in good agreement with those of the respective diphos analogue **4** (Figure 4B), which serves as a model chromophore containing only perylene-centered excited states and effectively reproduces the cis geometry in **2**. Excited-state absorptions are observed at 420, 560, and 1140 nm in **4**; the 1140 nm feature is clearly discernible in this molecule and must be characteristic of one of the peryleneacetylide triplet-to-triplet absorptions. Ground-state bleaching is again observed at 470 nm, consistent with the production of the ^{3}IL peryleneacetylide triplet state, which effectively nulls the corresponding singlet ground-state absorptions on the microseconds time scale. The most disparate differences between **2** and **4** are the excited-state lifetimes and the relative intensities of the low-energy feature at 1140 nm. The measured lifetime of 23.4 μs in complex **4** is significantly longer than that of complex **2** (5.7 μs). Given that the excited-state lifetimes of both **2** and **4** greatly exceed that of **6** ($\tau = 1.2$ μs) and the transient difference spectra of **2** and **4** are essentially superimposed, the lowest excited state in **2** is assigned as ^{3}IL in nature, localized on one of the peryleneacetylide chromophores. The lifetime differences are again significant between **2** and **4**, which may imply that some excited-state configuration mixing takes place in **2** but is not likely as strong an interaction as that seen in **1** (see above). This trend would be anticipated based on the relative energetic differences between the ^{3}CT and ^{3}IL states implied by the differences in the ground-state electronic spectra in **1** and **2**.

Another hypothesis regarding the excited states present in **1** and **2** is a thermal equilibrium between the ^{3}CT and the ^{3}IL states.[37–42] Although convenient for the explanation of the observed excited-state lifetimes, it becomes difficult to assign such an interaction due to the complete lack of emission in these chromophores. In addition, one would expect to observe transient absorption features attributable to both types of excited states in the difference spectra. The sheer intensity of the ^{3}IL absorptions and the apparent lack of significant contributions from the ^{3}CT state, as ascertained by comparison to model chromophores **5** and **6**, argues against an excited-state equilibrium model governing excited-state decay in **1** and **2**.

In the absence of detectable phosphorescence emanating from all of the Pt−acetylide complexes in this study, an alternative method for estimating the triplet-state energies within these complexes becomes necessary. Therefore, a series of triplet-state quenchers ranging from high (*p*-terphenyl, 20 160 cm^{-1}) to low (O$_2$, 7690 cm^{-1}) triplet energy were used to dynamically quench the excited-state absorption feature present at 560 nm in **4** (see Table S1 of the Supporting Information). All of the quencher triplet-state energies are conveniently collected in a single reference.[27] On the basis of all of the data presented above, we believe that the ^{3}IL energy in **4** will be representative of the lowest triplet state in molecules **1**−**4**. The most efficient diffusion controlled dynamic quenching only occurs when the lower triplet-energy quenchers such as tetracene (10 240 cm^{-1}) and O$_2$ are utilized; therefore, the ^{3}IL state lies above 10 240 cm^{-1} yet is likely close in energy to perylene (12 260 cm^{-1}), as log k_q in the latter instance is 7.59. No dynamic quenching was observed whatsoever using 9,10-diphenylanthracene (DPA, 13 710 cm^{-1}) or *p*-terphenyl. Therefore, we conclude that the ^{3}IL state in molecules **1**−**4** lies somewhere near ~12 000 cm^{-1}. Unfortunately, not enough energetically appropriate quenchers could be identified for the construction of a proper Sandros plot.[43,44]

Conclusions

Compounds **1** and **2** represent simple molecular designs that impart long lifetime excited states into synthetically facile metal−organic systems, important for applications in photonics and excited-state chemistry schemes. Excited-state absorption data measured for **1** and **2** were collected throughout the visible and near-IR and were directly compared to the transient absorption difference spectra obtained for the analogous CT (**5** and **6**) and ^{3}IL (**3** and **4**) model chromophores, leaving little room for ambiguity in the spectroscopic assignments. The transients produced in **1** and **2** are quite consistent with the transient spectra obtained in the analogous phosphine structures, strongly supporting a ^{3}IL peryleneacetylide localized lowest triplet excited-state in both instances. Specifically, the ground-state bleaches observed are consistent with several peak wavelengths associated with ground-state absorptions in the peryleneacetylide systems, and the absorption transients largely match the intensity and positions of the analogous peaks in **3** and **4**. The peryleneacetylide localized triplet state assignment is also consistent with the singlet O$_2$ sensitization studies and the long-lived absorption transients measured for these structures. Transient absorption-based Stern−Volmer quenching studies reveal that the ^{3}IL state in compounds **1**−**4** lies at approximately 12 000 cm^{-1} in CH$_2$Cl$_2$. The complexes in this study are unique in that long-lived excited states are produced without generating any corresponding photoluminescence, which may be desirable under certain circumstances.

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(37) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1992**, *96*, 2917–2920.

(38) Simon, J. A.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X.; Thummel, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 11012–11022.

(39) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.

(40) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154–8161.

(41) Tyson, D. S.; Luman, C. R.; Zhou, X.; Castellano, F. N. *Inorg. Chem.* **2001**, *40*, 4063–4071.

(42) McClenaghan, N. D.; Barigelletti, F.; Maubert, B.; Campagna, S. *Chem. Commun.* **2002**, 602–603.

(43) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355–2374.

(44) Walters, K. A.; Ley, K. D.; Schanze, K. S. *Chem. Commun.* **1998**, 1115–1116.

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Supporting Information Available: Concentration-dependent electronic spectra of **2**, fluorescence spectra of **3** and **4**, TCSPC intensity decays, and TA-based Stern−Volmer quenching data. This material is available free of charge via the Internet at http://pubs.acs.org.

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