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Article

Synthesis, Structure, Characterization, and Photophysical Studies of a New Platinum Terpyridyl-Based Triad with Covalently Linked Donor and Acceptor Groups

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A new terpyridyl-containing Pt triad [Pt(pytpy)(*p*-C≡C–C_6H_4–NH–CO–$C_6H_2(OMe)_3$)]$(PF_6)_2$ (**4**), where pytpy = 4′-(4-pyridin-1-ylmethylphenyl)-[2,2′;6′,2′′]terpyridine and *p*-C≡C–C_6H_4–NH–CO–$C_6H_2(OMe)_3$ = *N*-(4-ethynylphenyl)-3,4,5-trimethoxybenzamide, has been synthesized and structurally characterized. The related donor–chromophore dyad [Pt(ttpy)(*p*-C≡C–C_6H_4–NH–CO–$C_6H_2(OMe)_3$)]PF_6 (**2**), where ttpy = 4′-*p*-tolyl-[2,2′;6′,2′′]terpyridine, and the chromophore–acceptor dyad [Pt(pytpy)(C≡CC_6H_5)]$(PF_6)_2$ (**3**), where C≡CC_6H_5 = ethynylbenzene, have also been studied. The multistep syntheses culminate with a CuI-catalyzed coupling reaction of the respective acetylene with either [Pt(ttpy)Cl]PF_6 or [Pt(pytpy)Cl]$(PF_6)_2$. X-ray and spectroscopic studies support assignment of a distorted square planar environment around the Pt(II) ion with three of its coordination sites occupied by the terpyridyl N-donors and the fourth coordination site occupied by the acetylenic carbon. Although the parent compound [Pt(ttpy)(C≡CC_6H_5)]PF_6 (**1**) is brightly luminescent in fluid solution at 298 K, dyad **2** as well as triad **4** exhibit complete quenching of the emission. The chromophore–acceptor (C–A) dyad **3** displays weak solution luminescence at room temperature with a ϕ_{rel}^{em} of 0.011 (using $Ru(bpy)_3^{2+}$ as a standard with $\phi_{rel}^{em} = 0.062$). Electrochemically, the donor–chromophore (D–C) dyad and the donor–chromophore–acceptor (D–C–A) triad exhibit both metal-based and donor ligand-based oxidations, whereas the triad and the C–A dyad show the expected pyridinium- and terpyridine-based reductions. Transient absorption studies of the dyad and triad systems indicate that although the trimethoxybenzene group acts as a reductive donor, in the present system, the pyridinium group fails to act as an acceptor.

Introduction

One of the vital steps in photosynthesis and energy conversion is photoinduced charge separation. Thus, in the design of molecularly based systems for light-to-chemical energy conversion, this is approached by the placement of suitable donor and acceptor moieties at specific positions on an absorber/chromophore to yield two- and three-component systems, i.e., dyads and triads.[1−41] In such systems, the most commonly employed chromophore is a Ru(II) tris(diimine) entity that is closely related to $Ru(bpy)_3^{2+}$ with its well-investigated ^{3}MLCT excited state.[42,43] Although charge separation may be viewed as only one of several steps

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(1) Krueger, J. S.; Mayer, J. E.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 8232−8234.

(2) Liddell, P. A.; Barrett, D.; Makings, L. R.; Pessiki, P. J.; Gust, D.; Moore, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 5350−5352.

(3) Gust, D.; Moore, T. A.; Makings, L. R.; Liddell, P. A.; Nemeth, G. A.; Moore, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 8028−8031.

(4) Gust, D.; Moore, T. A.; Liddell, P. A.; Nemeth, G. A.; Makings, L. R.; Moore, A. L.; Barrett, D.; Pessiki, P. J.; Bensassori, R. V.; Rougee, M.; Chachaty, C.; DeSchryver, F. C.; Van der Auweraer, M.; Holzwarth, A. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 846−856.

(5) Seta, P.; Bievenue, E.; Moore, A. L.; Mathis, P.; Bensasson, R. V.; Liddell, P.; Pessiki, P. J.; Joy, A.; Moore, T. A.; Gust, D. *Nature* **1985**, *316*, 653.

(6) Indelli, M. T.; Bignozzi, C. A.; Harriman, A.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3768−3779.

(7) Flamigni, L.; Armaroli, N.; Barigelletti, F.; Balzani, V.; Collin, J. P.; Dalbavie, J. O.; Heitz, V.; Sauvage, J. P. *J. Phys. Chem. B* **1997**, *101*, 5936−5943.

(8) Hossain, M. D.; Haga, M.; Monjushiro, H.; Gholamkhass, B.; Nozaki, K.; Ohno, T. *Chem. Lett.* **1997**, 573.

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that must occur in an artificial photosynthetic system (the others being photon collection and channeling, electron−hole pair creation, vectorial electron transfer, charge accumulation, and dark catalysis of the energy-storing reaction), it represents the critical initial step following photon absorption that allows productive chemistry to ensue.[1,3,4,10,34,42,44−59]

The syntheses of triads for photoinduced charge separation are often challenging because of the multistep procedures that are involved in their construction and purification.[20,27,60−62] Additionally, for Ru(II) tris(diimine)-based triads, studies of photoinduced charge separation and subsequent charge recombination are often complicated by different isomeric forms, each with its own set of rate constants for these critical electron-transfer steps.[9,42,60,61]

Recently, we reported several dyads and triads for photoinduced charge separation on the basis of the square planar Pt(II) diimine bis(acetylide) chromophore.[63−66] This chromophore is brightly emissive in fluid solution, and its excited state has been assigned as a ^{3}MLCT with an excited-state lifetime in the 10−10^3-ns range.[67−73] The specific donor−

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(9) Coe, B. J.; Friesen, D. A.; Thompson, D. W.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 4575−4584.

(10) Hung, S. C.; Macpherson, A. N.; Lin, S.; Liddell, P. A.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1995**, *117*, 1657−1658.

(11) Imahori, H.; Cardoso, S.; Tatman, D.; Lin, S.; Noss, L.; Seely, G. R.; Sereno, L.; deSilber, J. C.; Moore, T. A.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **1995**, *62*, 1009−1014.

(12) Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100*, 15926−15932.

(13) Kuciauskas, D.; Liddell, P. A.; Hung, S. C.; Lin, S.; Stone, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* **1997**, *101*, 429−440.

(14) Macpherson, A. N.; Liddell, P. A.; Lin, S.; Noss, L.; Seely, G. R.; Degraziano, J. M.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1995**, *117*, 7202−7212.

(15) McCafferty, D. G.; Friesen, D. A.; Danielson, E.; Wall, C. G.; Saderholm, M. J.; Erickson, B. W.; Meyer, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8200−8204.

(16) Moore, A. L.; Moore, T. A.; Gust, D.; Silber, J. J.; Sereno, L.; Fungo, F.; Otero, L.; SteinbergYfrach, G.; Liddell, P. A.; Hung, S. C.; Imahori, H.; Cardoso, S.; Tatman, D.; Macpherson, A. N. *Pure Appl. Chem.* **1997**, *69*, 2111−2116.

(17) Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S. C.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature* **1997**, *385*, 239−241.

(18) Sumida, J. P.; Liddell, P. A.; Lin, S.; Macpherson, A. N.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. A* **1998**, *102*, 5512−5519.

(19) Tan, Q.; Kuciauskas, D.; Lin, S.; Stone, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* **1997**, *101*, 5214−5223.

(20) Treadway, J. A.; Chen, P. Y.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A* **1997**, *101*, 6824−6826.

(21) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100−110.

(22) Flamigni, L.; Dixon, I. M.; Collin, J. P.; Sauvage, J. P. *Chem. Commun.* **2000**, 2479−2780.

(23) Dixon, I. M.; Collin, J. P.; Sauvage, J. P.; Barigelletti, F.; Flamigni, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1292.

(24) Willemse, R. J.; Piet, J. J.; Warman, J. M.; Hartl, F.; Verhoeven, J. W.; Brouwer, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 3721−3730.

(25) Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed.* **1996**, *35*, 92−95.

(26) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C. P.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607−2617.

(27) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230−4238.

(28) Kramer, C. S.; Zeitler, K.; Muller, T. J. J. *Tetrahedron Lett.* **2001**, *42*, 8619−8624.

(29) Daub, J.; Engl, R.; Kurzawa, J.; Miller, S. E.; Schneider, S.; Stockmann, A.; Wasielewski, M. R. *J. Phys. Chem. A* **2001**, *105*, 5655−5665.

(30) Hissler, M.; Harriman, A.; Khatyr, A.; Ziessel, R. *Chem.−Eur. J.* **1999**, *5*, 3366−3381.

(31) Harriman, A.; Hissler, M.; Ziessel, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4203−4211.

(32) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516−2525.

(33) DeGraziano, J. M.; Macpherson, A. N.; Liddell, P. A.; Noss, L.; Sumida, J. P.; Seely, G. R.; Lewis, J. E.; Moore, A. L.; Moore, T. A.; Gust, D. *New. J. Chem.* **1996**, *20*, 839−851.

(34) Gust, D.; Moore, A. L.; Moore, T. A. *Acc. Chem. Res.* **1993**, *26*, 198−205.

(35) Kraemer, C. S.; Mueller, T. J. J. *Eur. J. Org. Chem.* **2003**, 3534−3548.

(36) Sailer, M.; Gropeanu, R.-A.; Mueller, T. J. J. *J. Org. Chem.* **2003**, *68*, 7509−7512.

(37) Laine, P.; Bedioui, F.; Amouyal, E.; Albin, V.; Berruyer-Penaud, F. *Chem.*−Eur. *J.* **2002**, *8*, 3162−3176.

(38) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5481−5482.

(39) Ballardini, R.; Balzani, V.; Clemente-Leon, M.; Credi, A.; Gandolfi, M. T.; Ishow, E.; Perkins, J.; Stoddart, J. F.; Tseng, H.-R.; Wenger, S. *J. Am. Chem. Soc.* **2002**, *124*, 12786−12795.

(40) Lucia, L. A.; Whitten, D. G.; Schanze, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3057−3058.

(41) Fossum, R. D.; Fox, M. A.; Gelormini, A. M.; Pearson, A. J. *J. Phys. Chem. B* **1997**, *101*, 2526−2532.

(42) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519−2520.

(43) Maxwell, K. A.; Sykora, M.; DeSimone, J. M.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 71−75.

(44) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.* **1997**, *44*, 1−95.

(45) Dupray, L. M.; Devenney, M.; Striplin, D. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 10243−10244.

(46) Kaschak, D. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 4222−4223.

(47) Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 3023−3027.

(48) Kaschak, D. M.; Mallouk, T. E. *Abstr. Pap. Am. Chem. Soc.* **1997**, *214*, 358-PHYS.

(49) Kaschak, D. M.; Leau, J. T.; Waraksa, C. C.; Saupe, G. B.; Usami, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 3435−3445.

(50) Kaschak, D. M.; Johnson, S. A.; Waraksa, C. C.; Pogue, J.; Mallouk, T. E. *Coord. Chem. Rev.* **1999**, *185−186*, 403−416.

(51) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.

(52) Gust, D. *Nature* **1997**, *386*, 21−22.

(53) Gust, D.; Moore, T. A. *J. Photochem.* **1985**, *29*, 173−184.

(54) Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S.-J.; Bittersmann, E.; Luttrull, D. K.; Rehms, A. A.; DeGraziano, J. M.; Ma, X. C.; Gao, F.; Belford, R. E.; Trier, T. T. *Science* **1990**, *248*, 199−201.

(55) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.

(56) Greenfield, S. R.; Svec, W. A.; Gosztola, D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 6767−6777.

(57) Lewis, F. D.; Letsinger, R. L.; Wasielewski, M. R., Proceedings of the Twenty-Second Department of Energy Solar Photochemistry Research Conference, Chantilly, Virginia, June, 1998; pp 10−11.

(58) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519−2520.

(59) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.

(60) Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 2872−2878.

(61) Larson, S. L.; Elliot, C. M. *J. Phys. Chem.* **1995**, *99*, 6530−6539.

(62) Hu, Y.-Z.; Tsukiji, S.; Shinkai, S.; Hamachi, I. *Chem. Lett.* **1999**, *28*, 517−518.

(63) McGarrah, J. E.; Eisenberg, R. *Inorg. Chem.* **2003**, *42*, 4355−4365.

(64) McGarrah, J. E.; Kim, Y.-J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 4510−4511.

(65) Wadas, T.; Chakraborty, S.; Wang, Q. M.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2004**, 0.

(66) Chakraborty, S.; Wadas, T. J.; Hester, H.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.*, submitted for publication, 2005.

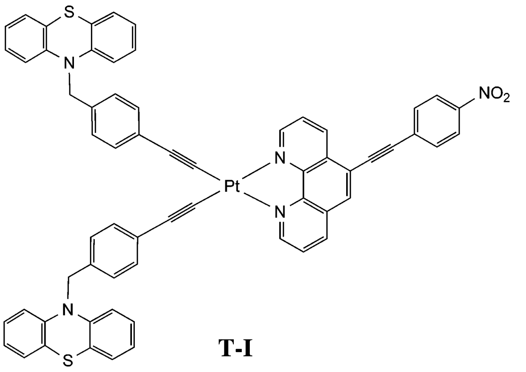
(67) Chan, S.-C.; Chan, M. C. W.; Wang, Y.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *Chem.−Eur. J.* **2001**, *7*, 4180−4190.

(68) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87−97.

(69) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1997**, *543*, 233−235.

(70) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447−457.

chromophore−acceptor (D−C−A) triad shown as **T−I** was constructed by the connection of an aromatic nitro acceptor to the diimine side of the platinum diimine bis(acetylide) chromophore through a sequence of Pd^{2+}-catalyzed coupling reactions and by the connection of a phenothiazine donor to the acetylide ligand by nucleophilic substitution. Earlier studies have revealed that the Pt diimine bis(acetylide) chromophore is stable under reductive quenching conditions but not under oxidative quenching. Spectroscopic studies of **T−I** showed that chromophore emission was completely quenched by the appended redox active moieties.[64] From transient absorption studies, it was found that excitation of the chromophore in **T−I** led to generation of the charge-separated (CS) state ($PTZ^{•+}-C-NO_2^{•-}$) within 10 ns and that it decayed to the ground state with a lifetime of 70 ns in both DMF and CH_2Cl_2. From simple electrochemical analysis, it was estimated that the charge-separated (CS) state in **T−I** transiently stored ca. 1.67 eV before back-reaction. Though the triad showed effective charge separation, it was not characterized crystallographically.



T-I

A different chromophore that has been studied recently is the cationic platinum terpyridyl acetylide system, which displays bright solution luminescence with an excited-state lifetime on the microsecond time scale.[74−76] As with the diimine bis(acetylide) chromophore, the excited state responsible for the solution luminescence is a ^{3}MLCT transition originating from a Pt(d) orbital to a π^* (terpyridine) orbital.[66,74,75,77] In addition to having the inherent properties of the platinum diimine bis(acetylide) chromophore, the cationic platinum terpyridyl acetylide system offers the potential advantages of better solubility to dyads and triads in more polar media and greater separation between donors and acceptors in the CS state.

In this paper, we report a new triad and associated dyads containing the cationic platinum terpyridyl acetylide chromophore. In addition to their syntheses and spectroscopic and electrochemical characterization, we report a crystal structure determination of the triad and transient absorption spectroscopic measurements of the D−C−A triad and the related D−C and C−A dyads. *To the best of our knowledge, this is the first structurally characterized organometallic D−C−A triad.* In the present triad system, the trimethoxybenzene acts as an efficient reductive quencher but transient absorption (TA) studies reveal that charge transfer onto the pyridinium acceptor from the photochemically generated terpyridyl radical anion does not occur.

Experimental Section

Materials. The chemicals 4′-*p*-tolyl-[2,2′;6′,2″]terpyridine (ttpy), *N*,*N*-dimethylformamide, dimethyl sulfoxide, copper(I) iodide, ammonium hexafluorophosphate (NH_4PF_6), 3,4,5-trimethoxybenzoyl chloride (**L1**), 4-ethynylaniline (**L2**) (Aldrich), electrochemical-grade tetrabutylammonium hexafluorophosphate (Fluka), biotech-grade *N*,*N*-dimethylformamide and MeCN (Aldrich), potassium tetrachloroplatinate, and $[Ru(bpy)_3](PF_6)_2$ (Strem Chemical) were used without further purification. Triethylamine was purified by distillation from KOH pellets. The syntheses of 4′-(*p*-bromomethylphenyl)-2,2′:6′2″-terpyridine (Br-ttpy) and $[Pt(ttpy)Cl]PF_6$ were carried out according to literature procedures.[63,66] Syntheses were performed under Ar with degassed solvents that were purified by passing the degassed solvent through columns containing activated molecular sieves and activated alumina.[78] All other reagents were of spectroscopic grade and were used without further purification.

Characterization. Infrared spectra were obtained from KBr pellets using a Shimadzu 8400 S FT-IR spectrometer, and ^{1}H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz). Mass determinations were accomplished by atmospheric pressure ionization electrospray (API-ES) and atmospheric pressure chemical ionization (APCI) mass spectrometries using a Hewlett-Packard Series 1100 mass spectrometer (model A) equipped with a quadrupole mass filter. Cyclic voltammetry experiments were conducted on an EG&G PAR 263A potentiostat/galvanostat using a three-electrode single-compartment cell. A Pt wire (for anodic processes)/glassy carbon (for cathodic processes) working electrode, a Pt wire auxiliary electrode, and a $Ag/AgNO_3$ (0.01 M in MeCN) reference electrode were used. For all measurements, samples were degassed with argon. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and ferrocene was employed as an internal redox reference. All redox potentials were reported relative to the ferrocenium/ferrocene (Fc^+/Fc) couple (0.4 V vs SCE),[79] and all scans were done at 50 millivolts per second. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200−1100 nm).

Emission and excitation spectra were obtained using a Spex Fluoromax-P fluorometer corrected for instrument response. Monochromators were positioned with a 2-nm band-pass, and solution samples were degassed by at least four freeze−pump−thaw cycles. Frozen glass samples (1:4 MeOH/EtOH) were prepared in NMR tubes using a circular quartz-tipped immersion dewar filled with liquid nitrogen.

Transient absorption spectra were measured using laser excitation (N_2-pumped coumarin 460 at 460 nm or Quantel Brilliant Nd/YAG at 532 nm) by filtering the emitted light through a Heath-McPherson

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(71) Whittle, C. E.; Weinstein, J. A.; Geore, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053−4062.

(72) Wadas, T. J.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2003**, *42*, 3772−3778.

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

(74) Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 4476−4482.

(75) Yam, V. W.-W.; Tang, R. P.-L.; Wong, K. M.-C.; Ko, C.-C.; Cheung, K.-K. *Inorg. Chem.* **2001**, *40*, 571−574.

(76) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 6506−6507.

(77) Yang, Q.-Z.; Wu, L.-Z.; Wu, Z.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2002**, *41*, 5653−5655.

(78) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(79) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

model EU-700 monochromator and detecting the emitted light with a Hamamatsu R928 PMT with a Lecroy 9370 digital oscilloscope. The excitation source was a 470-nm output of a Coherent Infinity 40-100 Nd/YAG laser or the output of a Quantel Brilliant Nd/YAG at 532 nm. A 150-W Xe arc lamp (Osram) was used as the light source for the analytical beam.

N-(4-Ethynylphenyl)-3,4,5-trimethoxybenzamide, (p-C≡C−C_6H_4−NH−CO−$C_6H_2(OMe)_3$) (L3). A 100-mL round-bottom flask was charged with 3,4,5-trimethoxybenzoyl chloride (**L1**) (0.20 g, 0.83 mmol) and 15 mL of dichloromethane followed by 0.4 mL of freshly distilled NEt_3. The solution was then stirred for 5 min followed by the cannular transfer of a solution of 4-ethynylaniline (**L2**) (0.10 g, 0.83 mmol) in 10 mL of dichloromethane. The reaction was stirred at room temperature for 96 h. The resulting solution was dried in vacuo to give a yellow oil. The liquid was then triturated with cold ether, resulting in solid yellowish product. Yield: 232 mg (90%). ^{1}H NMR ($CDCl_3$): δ 8.39 (1H, br s), 7.76 (2H, d, $J = 7$ Hz), 7.52 (2H, d, $J = 7$ Hz), 7.20 (2H, s), 5.57 (1H, s), 3.98 (6H, s), 3.93 (3H, s). FT-IR (KBr) ν/cm^{-1}: 3400 (ν_{NH}), 2150 (vw) ($\nu_{C\equiv C}$), 1648 (ν_{CO}), 1412 (ν_{CN}), 706 (vw) (ν_{NH}). MS (APCI): m/z 312.1 [(M + 1)].

4′-(4-Pyridin-1-ylmethylphenyl)-[2,2′;6′,2″]-terpyridine hexafluorophosphate, [pytpy]PF_6 (L4). A 100-mL round-bottom flask was charged with Br-ttpy (0.50 g, 1.2 mmol) and 80 mL of pyridine. The system was heated at reflux for 48 h. The reaction was concentrated to dryness, and the residue was redissolved in 50 mL of distilled water. A saturated aqueous solution of NH_4PF_6 was added, and the resulting solution was stirred at room temperature for 3 h. The white solids were collected on a medium-porosity glass frit and washed with distilled water, cold ethanol, and diethyl ether. Yield: 465 mg (71%). ^{1}H NMR (CD_3CN): δ 8.78 (2H, d, $J = 6$ Hz), 8.75 (2H, s), 8.71−8.69 (4H, m), 8.54 (1H, t, $J = 8$ Hz), 8.05 (2H, t, $J = 7$ Hz), 8.01−7.96 (4H, m), 7.62 (2H, d, $J = 8$ Hz), 7.45 (2H, t, $J = 6$ Hz), 5.81 (2H, s). MS (positive API-ES): m/z 401.0 [(M − PF_6)]$^+$.

[Pt(pytpy)Cl]$(PF_6)_2$. A 100-mL round-bottom flask was charged with pytpy(PF_6) (0.15 g, 0.28 mmol), $Pt(DMSO)_2Cl_2$ (0.30 g, 0.71 mmol), and 50 mL of $CHCl_3$. The resulting solution was heated at 50 °C for 24 h. The heterogeneous mixture was filtered through a medium-porosity glass frit, and the precipitate was washed with cold ethanol and diethyl ether. Yield: 181 mg (70%). ^{1}H NMR (DMSO-d_6): δ 9.29 (2H, d, $J = 5$ Hz), 9.04 (2H, s), 9.03 (2H, d, $J = 8$ Hz), 8.87 (2H, d, $J = 8$ Hz), 8.69 (1H, t, $J = 8$ Hz), 8.60 (2H, t, $J = 8$ Hz), 8.30 (2H, d, $J = 8$ Hz), 8.25 (2H, t, $J = 7$ Hz), 8.02 (2H, t, $J = 7$ Hz), 7.86 (2H, d, $J = 8$ Hz), 6.00 (2H, s). MS (positive API-ES): m/z 315.8 [(M − 2PF_6)/2]$^+$, 776.8 [(M − PF_6)]$^+$.

[Pt(ttpy)(p-C≡C−C_6H_4−NH−CO−$C_6H_2(OMe)_3$)]PF_6 (2). A Schlenk tube was charged with [Pt(ttpy)Cl]PF_6 (0.100 g, 0.14 mmol), N-(4-ethynylphenyl)-3,4,5-trimethoxybenzamide (0.100 g, 0.34 mmol), CuI (0.003 g, 0.017 mmol), NEt_3 (0.2 mL), and 10 mL of DMF. The reaction mixture was stirred at room temperature for 96 h. To the resulting red solution was added a saturated solution of NH_4PF_6 in water to precipitate the product. The brown product was collected by filtration and washed with water, ethanol, and diethyl ether. The material was recrystallized by vapor diffusion of diethyl ether into a mixed MeCN and $CHCl_3$ solution of **2**. Yield: 55 mg (40%). ^{1}H NMR (DMSO-d_6): δ 10.19 (1H, s), 9.25 (2H, d, $J = 5$ Hz), 9.06 (2H, s), 8.91 (2H, d, $J = 8$ Hz), 8.58 (2H, t, $J = 8$ Hz), 8.15 (2H, d, $J = 7$ Hz), 7.98 (2H, t, $J = 7$ Hz), 7.77 (2H, d, $J = 8$ Hz), 7.54−7.51 (4H, m), 7.30 (2H, s), 3.89 (6H, s), 3.75 (3H, s), 2.46 (3H, s). MS (positive API-ES): m/z 829.0 [(M − PF_6)]$^+$. FT-IR (KBr) ν/cm^{-1}: 2117 (vw) ($\nu_{C\equiv C}$). Anal. Calcd for $PtC_{40}H_{33}N_4O_4PF_6\cdot 4H_2O$: C, 45.92; H, 3.92; N, 5.35. Found: C, 45.16; H, 3.12; N, 5.08.

[Pt(pytpy)(C≡C−C_6H_5)]$(PF_6)_2$ (3). The procedure for the synthesis of **2** was followed except that [Pt(pytpy)Cl]$(PF_6)_2$ (0.157 g, 0.17 mmol) was used instead of [Pt(ttpy)Cl]PF_6 and ethynyl−benzene (0.04 g, 0.34 mmol) was used instead of N-(4-ethynylphenyl)-3,4,5-trimethoxybenzamide. The material was recrystallized by vapor diffusion of diethyl ether into a mixed MeCN/$CHCl_3$ (5:2) solution of **3**. Yield: 84 mg (50%). ^{1}H NMR (DMSO-d_6): δ 9.29 (2H, d, $J = 6$ Hz), 9.19 (2H, d, $J = 5$ Hz), 9.05 (2H, s), 8.84 (2H, d, $J = 8$ Hz), 8.69 (1H, t, $J = 8$ Hz), 8.56 (2H, t, $J = 8$ Hz), 8.27−8.23 (4H, m), 7.96 (2H, t, $J = 6$ Hz), 7.84 (2H, d, $J = 8$ Hz), 7.49 (2H, d, $J = 7$ Hz), 7.34 (2H, t, $J = 7$ Hz), 7.26 (1H, t, $J = 7$ Hz), 5.99 (2H, s). MS (positive API-ES): m/z 348.6 [(M − 2PF_6)/2]$^+$, 841.8 [(M − PF_6)]$^+$. FT-IR (KBr) ν/cm^{-1}: 2117 (vw) ($\nu_{C\equiv C}$). Anal. Calcd for $PtC_{35}H_{26}N_4P_2F_{12}\cdot CHCl_3$: C, 39.04; H, 2.44; N, 5.06. Found: C, 38.83; H, 2.14; N, 4.50.

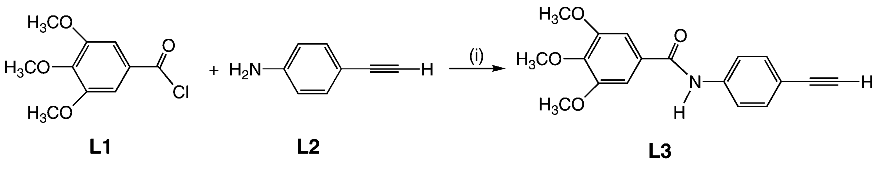
[Pt(pytpy)(p-C≡C−C_6H_4−NH−CO−$C_6H_2(OMe)_3$)]$(PF_6)_2$ (4). The procedure for the synthesis of **3** was followed except that N-(4-ethynylphenyl)-3,4,5-trimethoxybenzamide (0.100 g, 0.34 mmol) was used instead of ethynyl−benzene. The material was recrystallized by vapor diffusion of diethyl ether into a mixed MeCN/$CHCl_3$ (5:2) solution of **4**. Yield: 132 mg (65%). ^{1}H NMR (DMSO-d_6): δ 10.20 (1H, s), 9.29 (4H, d, $J = 6$ Hz), 9.08 (2H, s), 8.88 (2H, d, $J = 8$ Hz), 8.69 (1H, t, $J = 8$ Hz), 8.60 (2H, t, $J = 8$ Hz), 8.29−8.24 (4H, m), 8.02 (2H, t, $J = 6$ Hz), 7.86 (2H, d, $J = 8$ Hz), 7.77 (2H, d, $J = 8$ Hz), 7.54 (2H, d, $J = 8$ Hz), 7.30 (2H, s), 5.60 (2H, s), 3.90 (6H, s), 3.76 (3H, s). MS (positive API-ES): m/z 453.1 [(M − 2PF_6)/2]$^+$, 1051.1 [(M − PF_6)]$^+$. FT-IR (KBr) ν/cm^{-1}: 3400 (vw) (ν_{NH}), 2150 (vw) ($\nu_{C\equiv C}$), 1657 (ν_{CO}), 1412 (ν_{CN}), 680 (vw) (ν_{NH}). Anal. Calcd for $PtC_{45}H_{37}N_5O_4P_2F_{12}\cdot 1/2CHCl_3$: C, 43.48; H, 2.98; N, 5.57. Found: C, 43.25; H, 2.30; N, 5.77.

X-ray Structural Determination of Complex 4. Deep red crystals were grown by vapor diffusion of ether into an acetonitrile solution of **4** at ambient temperature. A single crystal was mounted under Paratone-8277 oil onto a glass fiber and immediately placed in a cold nitrogen stream at −173 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Bruker-AXS APEX-II CCD area detector system equipped with a fine focus molybdenum-target X-ray tube operated at 1.5 kW (50 kV, 30 mA). A total of 2424 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 10 s/frame using a detector-to-crystal distance of 5.00 cm (maximum 2θ angle of 56.6°), with the total data collection time being 12 h. Frames were integrated to a maximum 2θ angle of 56.6° with the Bruker-AXS SAINT program, and Laue symmetry revealed a monoclinic crystal system. The final unit cell parameters (at −173 °C) were determined from the least-squares refinement of three-dimensional centroids of >11 897 reflections. The space group was assigned as $P2(1)/n$. Intensity data were corrected for absorption with the SADABS program. The structure was solved by direct methods and refined by employing full-matrix least-squares on F^2. All non-hydrogen atoms of the cation were refined anisotropically, and hydrogen atoms were included in idealized positions. The structure refined to the final residuals found in Table 1.

Results and Discussion

Syntheses and Characterizations. The donor-based acetylide ligand (**L3**) was synthesized as shown in Scheme 1 by the reaction of acyl chloride, **L1**, with 4-ethynylaniline, **L2**. The acceptor-functionalized terpyridyl ligand (pytpy)PF_6 (**L4**)

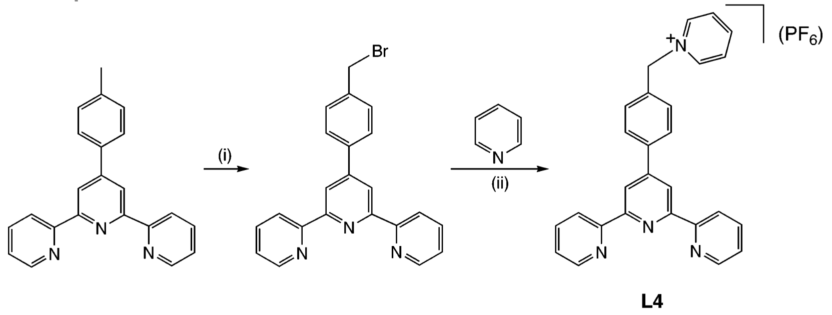
Scheme 1



(i) Dichloromethane, NEt_3, RT, 4 d

90%

Scheme 2



71%

(i) *N*-bromosuccinamide, dibenzoylperoxide, CCl_4, 100 °C
(ii) neat, 48 h, reflux; NH_4PF_6 (aq), 3 h, RT

Table 1. Crystallographic Data for Complex **4**

empirical formula	$C_{47}H_{40}F_{12}N_6O_4P_2Pt$
fw	1237.88
T (K)	100
μ (Å)	0.71073
cryst syst	monoclinic
space group	$P2(1)/n$
Z	4
a (Å)[a]	7.0192(5)
b (Å)[a]	16.7279(11)
c (Å)[a]	40.818(3)
α (deg)[a]	90
β (deg)[a]	92.1870(10)
γ (deg)[a]	90
V (Å^3)	4789.3(6)
ρ_{calcd} (g cm^{-3})	1.717
μ (mm^{-1})	3.095
abs correction	SADABS[b]
transm range	0.734−0.671
θ range (deg)	1.32−28.29
no. of data	11897
no. of params	578
GOF[c]	1.109
R1, wR2 ($I > 2\sigma$)[d]	0.0487, 0.1137
R1, wR2 (all data)[d]	0.0548, 0.1165

[a] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small because systematic error is not included. More reasonable errors might be estimated at 10× the reported value. [b] The SADABS program is based on the method of Blessing: Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, *51*, 33. [c] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters. [d] R1 = $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (a\cdot P)^2 + b\cdot P]$ and $P = [(\mathrm{Max};0,F_o^2) + 2\cdot F_c^2]/3$.

was synthesized by bromination of ttpy, followed by heating the bromo derivative to reflux in neat pyridine as shown in Scheme 2.

The syntheses of the complexes [Pt(ttpy)Cl](PF_6) and [Pt(pytpy)Cl](PF_6)$_2$ were carried out by a modification of a previously reported method with the conditions shown in Scheme 3.[80−82] The reaction was observed to be heterogeneous in $CHCl_3$ at reflux. Complexes **2**−**4**, corresponding respectively to D−C and C−A dyads and a D−C−A triad, were synthesized following the previously reported route in Scheme 4, and the chromophore, complex **1**, has been previously reported.[66,77] Formation of the Pt−acetylide bond is based on a CuI-catalyzed chloride-to-alkyne exchange[77,83−86] that has been used and described previously.[33,36,64,69,87] The complexes were isolated by filtration and purified by recrystallization after dissolution in a minimum volume of MeCN, addition of chloroform, and vapor diffusion of diethyl ether into the solution at ambient temperature. The complexes were characterized by ^{1}H NMR, FT-IR, and mass spectrometry. Though satisfactory elemental data were obtained for most of the compounds, repeated attempts on dried, spectroscopically pure samples of compound **2** led to analytical results that were always low in C and H. The D−C−A triad **4** was structurally characterized by X-ray crystallography as described below.

The ^{1}H NMR spectra of the ligands and the complexes show characteristic resonances. The acetylenic proton resonance (5.57 ppm) in the free ligand **L3** disappears on complexation of the ligand, whereas the N−H signal in the free ligand undergoes a downfield shift in **2** and **4**. The broad signal corresponding to this N−H resonance in **L3**, **2**, and **4** at 8.39, 10.19, and 10.20 ppm, respectively, disappears upon

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(80) Howe-Grant, M.; Lippard, S. J. Compounds of Biological Interest: 28. Metallointercalation Reagents: Thiolato Complexes of (2,2′:6′,2″″-Terpyridine)platinum(II). In *Inorganic Syntheses*; Busch, D. H., Ed.; John Wiley and Sons: New York, 1980.
(81) Romeo, R.; Scolaro, L. M. *Inorg. Synth.* **1998**, *32*, 153−158.
(82) Arena, G.; Calogero, G.; Campagna, S.; Scolaro, L. M.; Ricevuto, V.; Romeo, R. *Inorg. Chem.* **1998**, *37*, 2763−2769.
(83) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *145*, 101−108.
(84) Sonogashira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291.
(85) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromol. Chem.* **1997**, *10*, 879.
(86) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.
(87) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115−137.

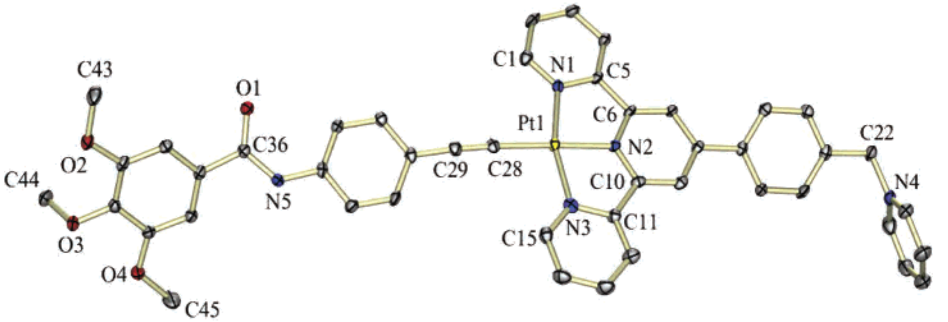
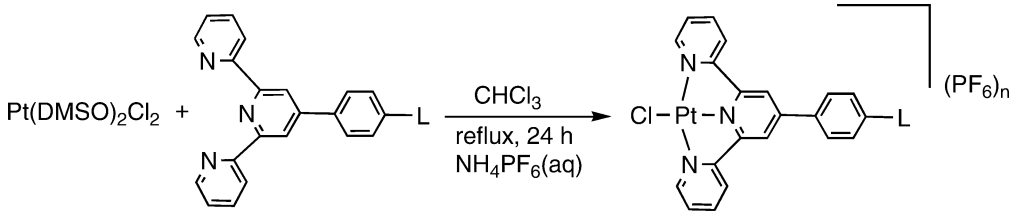
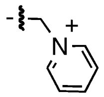


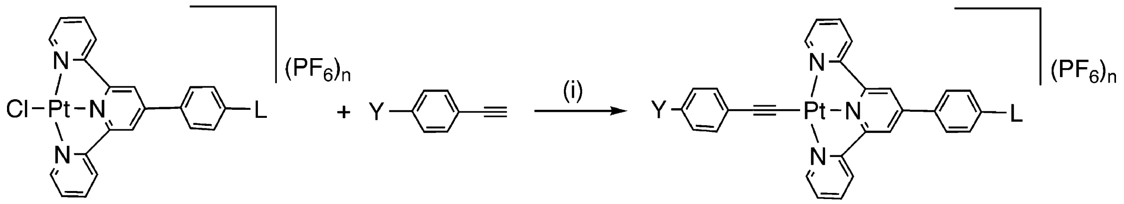
Figure 1. Ortep diagram of the dicationic triad **4** at 50% probability ellipsoids. Hydrogen atoms and solvent molecules of crystallization have been omitted for clarity.

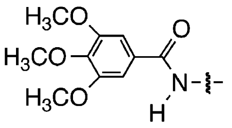
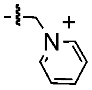
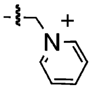
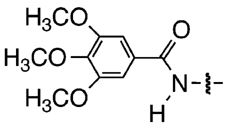
Scheme 3



L	Product complex	n	Yield
$-CH_3$	$[Pt(ttpy)Cl]PF_6$	1	64%
	$[Pt(pytpy)Cl](PF_6)_2$	2	70%

Scheme 4



L	Y	n	Product complex	Yield
$-CH_3$	H	1	**1**	
$-CH_3$		1	**2**	40%
	H	2	**3**	50%
		2	**4**	65%

(i) CuI (10 mol%), DMF, NEt_3, NH_4PF_6 (aq).

exchange with D_2O. The two aromatic singlets of protons adjacent to $-OCH_3$ in **L3**, **2**, and **4** appear at the most upfield positions in the aromatic region. The methoxy protons in these compounds are seen as two resonances in 2:1 ratios

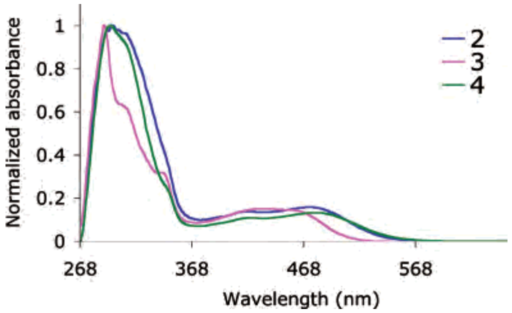


Figure 2. Normalized room-temperature absorption spectra of the D−C dyad (**2**), C−A dyad (**3**), and D−C−A triad (**4**) in MeCN.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**

bond lengths		bond angles	
Pt(1)−N(1)	2.025(4)	N(1)−Pt(1)−N(2)	80.30(16)
Pt(1)−N(2)	1.963(4)	N(2)−Pt(1)−N(3)	80.95(17)
Pt(1)−N(3)	2.023(4)	N(3)−Pt(1)−C(28)	98.3(2)
Pt(1)−C(28)	1.978(5)	N(1)−Pt(1)−C(28)	100.45(19)
C(28)−C(29)	1.208(7)	Pt(1)−C(28)−C(29)	176.6(5)
N(5)−C(36)	1.352(6)	C(28)−C(29)−C(30)	176.4(5)
N(5)−C(33)	1.417(6)	C(32)−C(33)−N(5)	123.6(4)
C(36)−O(1)	1.229(6)	C(33)−N(5)−C(36)	128.8(4)
C(36)−C(37)	1.498(7)	N(5)−C(36)−O(1)	124.1(5)
		N(5)−C(36)−C(37)	116.2(4)
		C(19)−C(22)−N(4)	111.9(4)

between 3.93 and 3.98 ppm in **L3** and 3.75 and 3.90 ppm in **2** and **4**, and the tolyl methyl resonance in **2** appears as expected at 2.46 ppm.

Molecular Structure of the Triad. The molecular structure of the triad **4** is shown in Figure 1 with important bond lengths and angles given in Table 2. The complex consists of a distorted square planar geometry around the Pt(II) center with three coordination sites occupied by the terpyridyl ligand and the fourth taken up by the acetylide donor. The average Pt−N distance cis to the acetylide carbon is 2.024(4) Å, and the distance trans to the acetylide carbon is 1.963(4) Å. These agree well with the respective Pt−N distances of 2.02(7) and 2.005(6) Å in $[Pt(tpy)(pip_2NCNH_2)^{3+}]$[88] and 2.026(7) and 1.945(6) Å in $[PtCl(btpyxa)](PF_6)$,[89] where btpyxa = 4,5-bis(terpyridyl)-2,7-di-*tert*-butyl-9,9-dimethylxanthene. The Pt−C (acetylide) distance is 1.978(5) Å, which is in good agreement with previously reported Pt−C (acetylide) distances of 1.98(1) and 2.00(2) Å for $Pt(trpy)(C{\equiv}CC_6H_5)PF_6$[74] and $Pt(tpy)(C{\equiv}C-C{\equiv}CH)OTf$,[76] respectively. Deviations from a square planar geometry for Pt(II) is seen with a N(1)−Pt−C(28) cis angle of 100.45(19)° and an average N−Pt−N bite angle of 80.63(17)°, resulting from the constraints of the chelating terpyridine ligand. The C−O bond lengths for the amide group and the methoxy substituents agree well with literature reports.[90−92] In the D−C−A triad **4**, the edge-to-edge separation between the donor and the acceptor moieties is 27.95 Å.

Absorption and Emission Spectra. The room-temperature absorption spectra of the dyad and triad complexes were measured in MeCN and can be seen in Figure 2. All of the complexes exhibit intense multiple absorptions between 600 and 200 nm. The higher energy absorptions (λ < 350 nm) have extinction coefficients (ϵ) on the order of 10^4 dm^3 mol^{-1} cm^{-1} and are assigned as intraligand transitions originating primarily within the acetylide and terpyridyl ligands, as well as charge-transfer transitions involving the $Pt-C{\equiv}CR$ moieties.[77,93] The transitions with $\lambda > 400$ nm are less intense (ϵ is on the order of 10^3 dm^3 mol^{-1} cm^{-1}) and are tentatively assigned as ^{3}MLCT transitions corresponding to $d_\pi(Pt) \rightarrow \pi^*(tpy)$.[75,77,94−98] However, interpretation of the MLCT bands is complicated by the fact that these bands clearly are composed of two distinct transitions. A similar observation has been made previously for the related Pt(II) diimine bis(acetylide) complexes.[71] Also to be noted is the fact that in going from **3** to the amide-containing dyad **2** and triad **4**, the MLCT absorption band shifts from 462 to 478 and 482 nm, respectively. This red shift is consistent with the notion that the HOMO is predominantly metal based. As the donor ability of the acetylide increases in going from **3** to **2** and **4** by virtue of the trimethoxybenzamide group, the Pt center becomes more electron rich, moving the d_π HOMO higher in energy and leading to red-shifted MLCT absorption.

The room-temperature emission spectra of all of the complexes were measured in degassed MeCN. Previous reports have shown that chromophore **1** is strongly emissive and has a lifetime on the microsecond time scale.[66,74,77] The complexes that have the trimethoxybenzene donor group attached to the chromophore, namely, D−C dyad **2** and D−C−A triad **4**, are observed to be nonemissive in fluid solution (Table 3) suggesting that reductive quenching of the chromophore excited state (^{3}MLCT) in these systems is occurring by electron transfer from the trimethoxybenzamide fragment. In contrast, the C−A dyad **3** is weakly emissive at room temperature in MeCN (Figure 3) with a quantum yield of 0.011 (using $Ru(bpy)_3^{2+}$ as a standard with $\phi_{rel}^{em} = 0.062$) and a 650-ns excited-state lifetime. The parent complex, **1**, has a quantum yield of 0.022 and an excited-state lifetime of 700 ns. If it is assumed that the radiative and nonradiative decay pathways of the chromophore of the C−A dyad **3** are the same as those of the parent complex **1** except for the electron-transfer quenching of the attached acceptor, then the rate constant for the excited-state electron transfer is found to be 1.1×10^5 s^{-1} ($\tau_{\mathbf{3}}^{-1} - \tau_{\mathbf{1}}^{-1}$). Thus, oxidative quenching of the excited state by the pyridinium

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(88) Jude, H.; Bauer, J. A. K.; Connick, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 3446−3447.

(89) Okamura, R.; Wada, T.; Aikawa, K.; Nagata, T.; Tanaka, K. *Inorg. Chem.* **2004**, *43*, 7210−7217.

(90) Vicente, J.; Abad, J.-A.; Herenandez-Mata, F. C.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848−3849.

(91) Vorogushin, A. V.; Wulff, W. D.; Hansen, H.-J. *J. Am. Chem. Soc.* **2002**, *124*, 6512−6513.

(92) Kavallieratos, K.; de Gala, S. R.; Austin, D. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2325−2326.

(93) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2226−2230.

(94) Yam, V. W.-W.; Tang, R. P.-L.; Wong, K. M.-C.; Lu, X.-X.; Cheung, K.-K.; Zhu, N. *Chem.−Eur. J.* **2002**, *8*, 4066−4076.

(95) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 6506−6507.

(96) Yam, V. W.-W.; Lee, V. W.-M. *J. Chem. Soc., Dalton Trans.* **1997**, 3005−3010.

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

(98) Hui, C.-K.; Chu, B. W.-K.; Zhu, N.; Yam, V. W.-W. *Inorg. Chem.* **2002**, *41*, 6178−6180.

Table 3. Photophysical Properties of Pt Complexes

compound	λ_{ab}/nm (ϵ/dm^3 mol^{-1} cm^{-1})^a	λ_{em}/nm^a	λ_{em}/nm^b	$\phi_{em}{}^c$
1	268 (40700), 290 (34100), 314 (22500), 341 (19900), 430 (7400), 469 (5600)	630	550	0.022
2	298 (38600), 423 (5300), 478 (6000)		574	0.032×10^{-2}
3	292 (32300), 310 (20800), 344 (10500), 462 (4800)	615	552	0.0113
4	298 (54600), 417 (6000), 482 (7300)		580	0.012×10^{-2}

[a] Recorded at room temperature in MeCN. [b] Recorded at 77 K in 1:4 MeOH/EtOH. [c] Determined using $Ru(bpy)_3{}^{2+}$ (with $\phi_{rel}{}^{em} = 0.062$) as a standard in MeCN at room temperature.

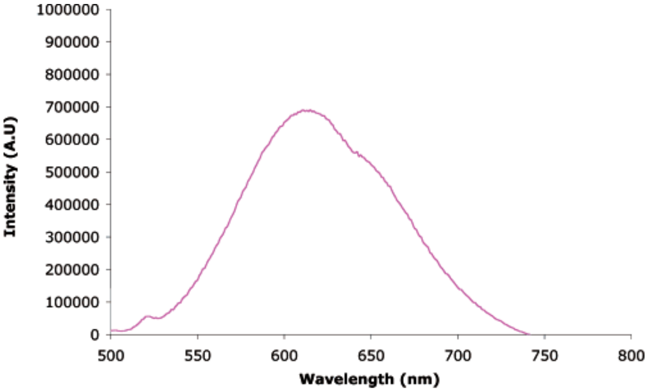

Figure 3. Room-temperature emission spectrum of the C−A dyad (**3**) in degassed MeCN.

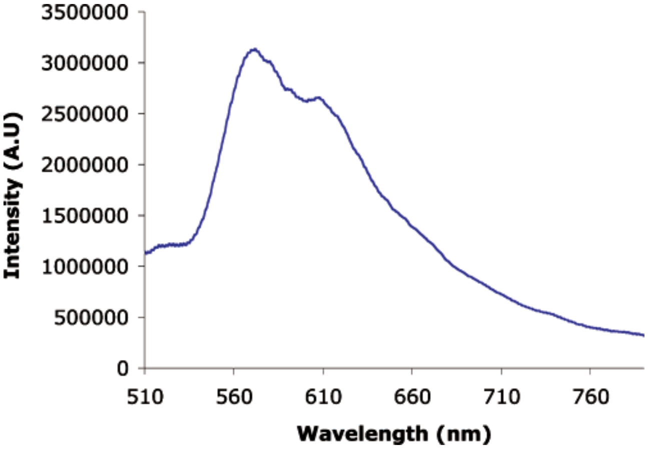

Figure 4. Emission spectrum of complex **2** in MeOH/EtOH (1:4) glass at 77 K.

acceptor is orders of magnitude slower than reductive quenching by the trimethoxybenzamide donor of **2**.

Despite the emission quenching of the D−C dyad and triad in fluid solution, all of the complexes are luminescent in a rigid matrix (4:1 EtOH/MeOH glass) at 77 K. Figure 4 displays the glass emission spectrum of complex **2**. The spectrum shows the vibronic progression that is common with other Pt terpyridine acetylide systems.[74,77] Although emission lifetime data were not obtained, the strong emission of all the complexes in the matrix suggests that neither reductive nor oxidative electron-transfer quenching occurs in the frozen matrix. This is the case for light-induced electron-transfer processes that have significant solvent and inner-shell reorganizational barriers to electron transfer; quenching is shut down because of the large barrier for medium reorganization in the rigid matrix.

Table 4. Electrochemical Data^a ($E_{1/2}{}^b$) for Pt Complexes and Free Ligands**.**

compound	oxidation $E_{1/2}$/V(ΔE/mV)	reduction $E_{1/2}$/V(ΔE/mV)
1	1.68^c	−0.55, −1.06
2	1.57,^{c} 1.82^c	−0.63 (80), −1.09 (40)
3	1.87^c	−0.46,^{c} −0.63 (90), −1.09 (140)
4	1.51,^{c} 1.80^c	−0.45,^{c} −0.64 (110), −1.12 (140)
L3	1.48,^{c} 1.78 (160)	
L4		−0.65,^{c} −0.93 (60)

[a] Measured using 0.1 M tetrabutylammonium hexafluorophosphate in MeCN at 50 mV/s at 293 K. Potential in volts is vs NHE as calibrated using the ferrocene/ferrocenium couple at 0.40 V vs SCE (see the Experimental Section). [b] $E_{1/2}$ = (1/2)(E_{max}(cathodic) + E_{max}(anodic)). [c] Irreversible under experimental conditions.

Electrochemistry. Cyclic voltammetry studies were performed on all of the complexes in MeCN with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. *All of the redox potentials are reported relative to NHE with the Fc/Fc$^+$ couple used as an internal redox standard and a value of 0.4 V vs SCE taken for the Fc/Fc$^+$ couple.* The electrochemistry of the parent chromophore **1** has been reported previously.[66] The dyads and triad in the present study show the expected number of oxidation and reduction waves, and the results are listed in Table 4. Donor−chromophore dyad **2** exhibits two quasireversible reductions at −0.63 and −1.09 V, whereas the chromophore−acceptor dyad **3** and triad **4** undergo an additional irreversible reduction at ca. −0.45 V (Table 4). All of the complexes show an irreversible oxidation at 1.82−1.80 V, and the complexes having the trimethoxybenzene donor (**2** and **4**) exhibit another, less-anodic, oxidation at 1.57−1.51 V. For comparison, free ligand **L3** shows a first-oxidation wave at 1.48 V.

From the electrochemical behavior of free ligand **L4** and complexes **2**−**4**, the two quasireversible couples, which appear to be independent of the substituents on the terpyridine, are assigned as the two successive reductions of the terpyridine ligand. Similar observations have been reported previously, and the assignments made here are consistent with those described for other platinum terpyridine systems.[74,77,99−101] The one-electron irreversible reduction at ca. −0.45 V for the C−A dyad and the D−C−A triad is assigned as the pyridinium reduction, which has been reported to result in dimerization of the pyridinyl radicals.[9,102] The acceptor-functionalized terpyridine ligand **L4** shows the same behavior, except the potentials are cathodically shifted relative to those of the metal complexes. The second

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(99) Wong, K. M.-C.; Tang, W.-S.; Chu, B. W.-K.; Zhu, N.; Yam, V. W. W. *Organometallics* **2004**, *23*, 3459−3465.

(100) Brodsky, A. E.; Gordienko, L. L.; Degtiarev *Electrochim. Acta* **1968**, *13*, 1095−1100.

(101) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2902−2911.

(102) Bard, A. J. *Encyclopedia of Electrochemistry of the Elements. Organic Section*; Marcel Dekker: New York, 1986.

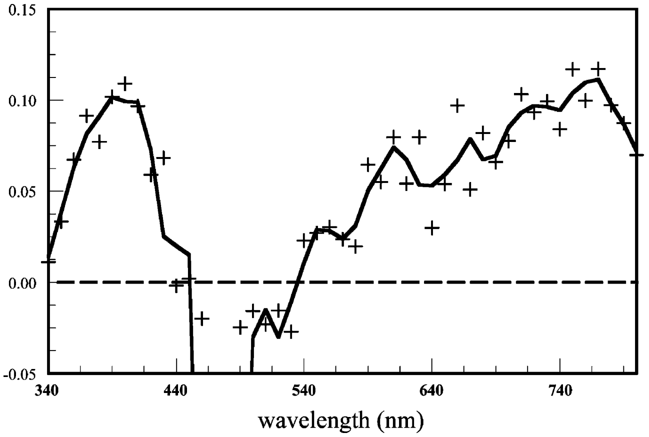

Figure 5. Transient absorption spectrum of the donor−chromophore dyad **2** (0.08 mM in MeCN) at room temperature 19 ns after pulsed excitation (λ_{exc} = 470 nm). The spectrum is developed from decays obtained each 10 or 20 nm.

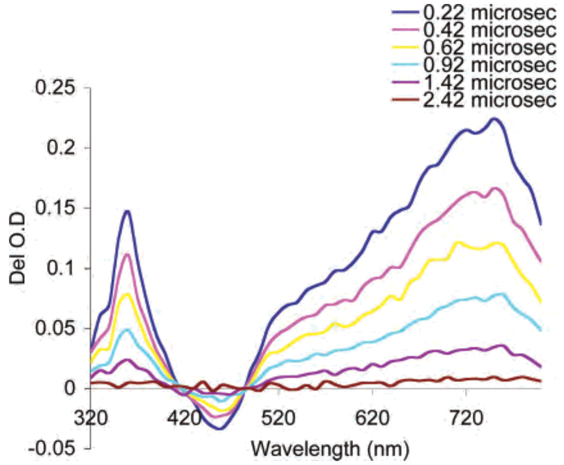

Figure 6. Transient absorption spectra of the chromophore−acceptor dyad **3** (0.08 mM in MeCN) at room temperature (λ_{exc} = 470 nm). The spectra are developed by measurement of the decays each 10 or 20 nm.

terpyridine reduction for **L4**, which is possibly more negative than the experimental potential window, is not observed.

The electrochemical behavior of the free ligand **L3** shows two oxidation waves, one of which may be amide-centered and the other centered on the aromatic ring of the trimethoxybenzamide ligand fragment. For the dyad and triad systems, the irreversible oxidation at 1.87 V for C−A dyad **3** is the Pt(II) → Pt(III) oxidation whereas the first irreversible oxidations for D−C dyad **2** and triad **4** at 1.51 and 1.57 V, respectively, correspond to the first trimethoxybenzamide oxidation. Although it is probable that the second irreversible oxidation for **2** and **4** is the metal-centered Pt(II) → Pt(III) oxidation, we cannot at this juncture rule out that the second oxidation is also on the donor ligand as suggested by the electrochemistry of **L3**. However, the former assignment is favored, especially in light of the Pt-centered oxidation seen for the chromophore (**1**)[66] as well as that seen for C−A dyad **3** in the same region.

Transient Absorption Studies. To study charge transfer and the nature of charge separation in the complexes, nanosecond transient absorption studies were performed on all of the samples at 298 K in MeCN and are shown in Figures 5 and 6. The transient absorption spectra of the D−C dyad (Figure 5) and the D−C−A triad are virtually identical, with a positive absorption at 400 nm and a broad absorption pattern between 550 and 800 nm. The spectra were collected immediately after excitation at 470 nm (pulse < 5 ns); the large negative absorption between 450 and 490 nm (Figure 5) is due to scattered light from the laser. The C−A dyad (Figure 6) shows positive absorption at 360 nm, a broad absorption between 520 and 800 nm with a maximum at 740 nm, and a bleach at 420−460 nm, with all of the features decaying with a lifetime of 650 ns.

The broad envelope between 550 and 800 nm in the TA spectrum of the dyads and the triad corresponds at least in part to the absorption expected for the ttpy$^{\bullet -}$ radical anion generated in the ^{3}MLCT excited state.[27,37] The increased conjugation of the terpyridine ligand with the tolyl group serves to shift the ttpy$^{\bullet -}$ absorption to lower energy.[66] Both the transient absorption lifetime and features of C−A dyad **3** (Figure 6) are identical to those of chromophore **1** with a positive absorption at 360 nm, a broad absorption between 520 and 800 nm with a maximum at 740 nm, and a bleach at 420−460 nm, all of which decay with a rate constant of 1.59×10^6 s^{-1}.[66] This clearly indicates that the TA spectrum of **3** is actually that of the parent chromophore and that charge transfer to the pyridinium acceptor is not occurring in this system. In contrast, the donor−chromophore dyad **2** (Figure 5) exhibits trimethoxybenzamide$^{\bullet +}$ transient absorption at 400 nm,[103,104] indicating that electron transfer from the donor group onto the chromophore has taken place. The TA spectrum of triad **4** is experimentally identical to that of D−C dyad **2**, with the transients of both **2** and **4** exhibiting lifetimes of less than 20 ns.

On the basis of these results as well as literature reports,[105−109] it is evident that although the trimethoxybenzamide moiety acts effectively as a reductive quencher for the Pt chromophore, subsequent electron transfer to the pyridinium acceptor does not happen in the present system, making triad **4** only partially successful in achieving photoinduced charge separation. The failure of the pyridinium group to function as an electron acceptor in **4** does not appear to be one of insufficient electrochemical driving force, as the results of Table 4 suggest that the terpyridyl radical anion should be sufficiently reducing to drive electron transfer to the acceptor. Instead, we think the failure lies in the *relative* rates of electron transfer: on one hand, forward to the pyridinium and charge separation and on the other, back to

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(103) O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2733−2779.

(104) Ichinose, N.; Tanaka, T.; Kawanishi, S.; Suzuki, T.; Endo, K. *J. Phys. Chem. A* **1999**, *103*, 7923−7926.

(105) Liu, T.; Callis, P. R.; Hesp, B. H.; Groot, M.; Buma, W. J.; Broos, J. *J. Am. Chem. Soc.* **2005**, *127*, 4104−4113.

(106) Noronha, M.; Lima, J. C.; Lamosa, P.; Santos, H.; Maycock, C.; Ventura, R.; Macanita, A. L. *J. Phys. Chem. A* **2004**, *108*, 2155−2166.

(107) Sandanayaka, A. S. D.; Sasabe, H.; Araki, Y.; Furusho, Y.; Ito, O.; Takata, T. *J. Phys. Chem. A* **2004**, *108*, 5145−5155.

(108) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733−1740.

(109) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219−7223.

the donor and charge recombination. Experimental evidence indicates that the latter is favored. Although the back electron transfer very likely lies in the Marcus inverted region, on the basis of previous reports, with an estimated ΔE for the reaction of ca. 2.25 V, it is still much faster than the rate for forward electron transfer from the reduced Pt(ttpy) center to the pyridinium (approximately 0.7 V, exergonic). This may relate to the coupling between the redox components in the two competing electron transfers, noting that the pyridinium group connects to the terpyridyl ligand through a saturated methylene linkage and an intervening, noncoplanar phenyl ring, whereas for the back electron transfer, the reduced ttpy and oxidized trimethoxybenzamide may be coplanar with better coupling through the Pt d_π orbitals. Although a large solvent-reorganization energy may be anticipated for Pt(II)/Pt(III) oxidation, it is thought that this would affect the initial charge-separation step rather than the charge-recombination step involving $D^+-Pt-ttpy^-$.

Failure to achieve full charge separation in D−C−A molecular triads has been noted previously in a $Ru(tpy)_2^{2+}$-based system.[27,110] The quenching in that system is oxidative in nature to an attached methylviologen acceptor, but subsequent electron transfer from a linked phenothiazine donor does not occur. The inability to achieve D^+-C-A^- charge separation in this Ru(II) system was attributed to an “unfavorable electronic factor” and the presence of a $-CH_2-$ bridge between the donor and the oxidized chromophore.[27,110] The observation is entirely analogous to the present situation in which electron transfer between a reduced chromophore and an acceptor does not happen. The parallel in behavior between these triad systems extends to observations of component dyads. For the C−A dyad **3** reported here, efficient quenching is *not* seen, and for the $Ru(tpy)_2^{2+}$ D−C dyad with PTZ, quenching does not occur. We note, however, that although the $-CH_2-$ bridge is a factor in inhibiting full charge separation in the triad reported here (**4**) as well as in the $Ru(tpy)_2^{2+}$-based system described earlier, the methylene bridge by itself is insufficient to block electron transfer, as examples have been reported in which successful charge separation between components linked by $-CH_2-$ has been achieved for both Ru and Pt triad systems.[20,42,64,66,111−113]

The electronic coupling between redox components as a function of the linkage connecting them, as well as the driving force dependence for the electron transfers between these components, are factors firmly in mind as work on Pt-based systems for photoinduced charge separation continues. The design of future systems will hinge also on evaluating the potentially very large reorganizational energies (both nuclear and solvent) associated with thermal and light-induced electron transfer involving square planar Pt(II) complexes.

Conclusions

The D−C−A triad $[Pt(pytpy)(p\text{-}C{\equiv}C-C_6H_4-NH-CO-C_6H_2(OMe)_3)](PF_6)_2$ **(4)** has been prepared along with the relevant model D−C (**2**) and C−A (**3**) dyads. All of the complexes exhibit characterization data consistent with distorted square planar coordination for the Pt(II) ion. Although the parent chomophore (**1**) is brightly luminescent in fluid solution, the D−C dyad and triad exhibit complete quenching of emission in fluid solution. For C−A dyad **3**, weak solution luminescence with $\phi_{em} = 0.011$ (relative to $Ru(bpy)_3^{2+}$) indicates that the quenching is not as efficient as that seen for donor-containing systems for reductive quenching. Cyclic voltammetry studies confirm the one-electron oxidation of the trimethoxybenzamide donor linked to the aryl acetylide ligand in the D−C dyad and triad. All of the complexes show the quasireversible reductions corresponding to the coordinated terpyridyl ligand, and the C−A dyad **3** and triad **4** undergo an additional facile irreversible pyridinium-based reduction. Transient absorption studies confirm the presence of a trimethoxybenzamide$^{\bullet+}$ radical cation, though the pyridinium group fails to act as an effective acceptor.

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Supporting Information Available: X-ray data for **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(110) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P. *Chem. Soc. Rev.* **2004**, *33*, 147−155.

(111) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081−8087.

(112) Cooley, L. F.; Headford, C. E. L.; Elliott, C. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6673−6682.

(113) Jones, J. W. E.; Bignozzi, C. A.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167−1178.