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# Platinum(II) Terpyridyl-Acetylide Dyads and Triads with Nitrophenyl Acceptors via a Convenient Synthesis of a Boronated Phenylterpyridine

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Four new Pt(II) terpyridyl acetylide complexes which possess a covalently linked nitrophenyl moiety were prepared and studied. Specifically, the chromophore−acceptor (C−A) dyads reported here include [Pt(ptpy-ph-*p*-$\mathrm{NO_2}$)($\mathrm{C{\equiv}C-C_6H_5}$)]($\mathrm{PF_6}$)$_3$ (**1**), where ptpy-ph-*p*-$\mathrm{NO_2}$ = 4′-{4-(4-nitrophenyl)-phenyl}-[2,2′;6′,2″]terpyridine, and $\mathrm{C{\equiv}C-C_6H_5}$ = phenylacetylide and [Pt(ptpy-ph-*m*-$\mathrm{NO_2}$)($\mathrm{C{\equiv}C-C_6H_5}$)]($\mathrm{PF_6}$)$_2$ (**2**), where ptpy-ph-*m*-$\mathrm{NO_2}$ = 4′-(4-*m*-nitrophenyl-phenyl)-2,2′;6′,2″-terpyridine, as well as the related donor−chromophore−acceptor (D−C−A) triads [Pt(ptpy-ph-*p*-$\mathrm{NO_2}$)($\mathrm{C{\equiv}C-C_6H_4CH_2-PTZ}$)]$\mathrm{PF_6}$ (**3**), where $\mathrm{C{\equiv}C-C_6H_4CH_2-PTZ}$ = 4-ethynylbenzyl-N-phenothiazine, and [Pt(ptpy-ph-*m*-$\mathrm{NO_2}$)($\mathrm{C{\equiv}C-C_6H_4CH_2-PTZ}$)]$\mathrm{PF_6}$ (**4**). Transient absorption spectroscopy and electrochemical analyses were used to characterize these compounds. In contrast to previous observations for closely related multicomponent systems, it appears that, in the current systems, the nitrophenyl group is not an effective quencher of the excited state. The luminescence and transient absorption properties of the C−A dyads are virtually identical to those of the parent chromophore, [Pt(ttpy)($\mathrm{C{\equiv}C-C_6H_5}$)]$\mathrm{PF_6}$ (**5**), where ttpy = 4′-*p*-tolyl-[2,2′;6′,2″]terpyridine.

## Introduction

In the systems that achieve light-to-chemical energy conversion, photoinduced charge separation is an essential step. In efforts to better understand this process, much work has been done to construct two- and three-component systems comprised of a chromophore, an electron donor, and an electron acceptor.[1−41] Our recent work in this field focuses on square planar terpyridyl acetylide complexes of Pt(II). This chromophore has the benefit of directionality in the $^3$MLCT excitation, with the energetic electron residing primarily on the terpyridyl unit. This directionality can be exploited in the design of systems for photoinduced charge separation (PICS) and placement of electron-donating and -accepting components of such systems.[42−46] Once a viable

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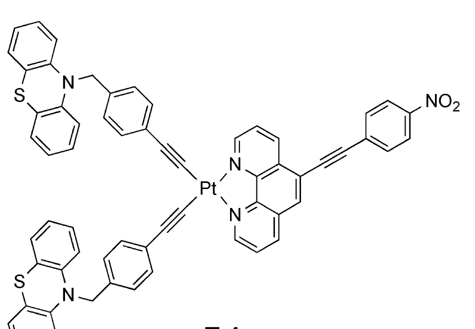
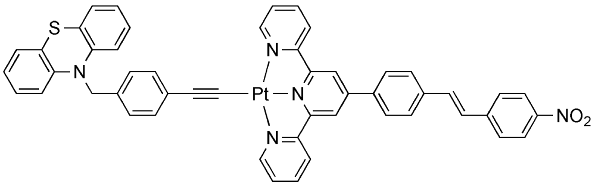
PICS system has been designed, it can then be coupled to moieties for electron or hole collection and catalysts to drive energy-storing processes.[1,3,8,24,30,32,33,35−39,47−49]

The first triad based on a platinum chromophore, **T-1**, was reported by McGarrah et al.[42,50] This complex was based on a diimine bis(acetylide) platinum coordination sphere and employed a nitrophenyl acceptor and a phenothiazine donor. This triad was observed to form a fully charge-separated state upon excitation with a lifetime of 70 ns. Inspired by this result, the syntheses and characterization of several dyads and triads based on the platinum terpyridyl acetylide chromophore were undertaken and have been described previously.[45,46] One such triad was [Pt(NO$_2$stil-tpy)(C≡C−C$_6$H$_4$CH$_2$−PTZ)](PF$_6$) (**T-2**) where NO$_2$stil-tpy = 4′-{4-[2-(4-nitrophenyl)vinyl]-phenyl}-[2,2′;6′,2″]terpyridine.

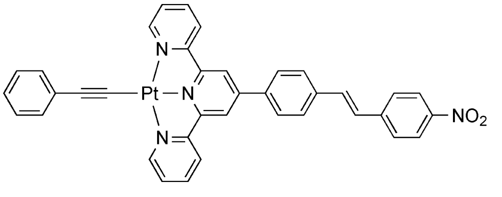


**T-1**



**T-2**

Triad **T-2** was found to exhibit complete luminescence quenching, thought to occur by a charge-transfer mechanism, similar to that observed in the study of triad **T-1**. The charge-separated state formed upon excitation of **T-2** was found to have a lifetime of 230 ns. However, the efficiency of formation of the charge-separated state was modest with only 25% of the excited molecules leading to the charge-separated state on the basis of a biexponential analysis of transient decay.[46] The related C−A dyad, [Pt(NO$_2$stil-tpy)(C≡C−C$_6$H$_5$)](PF$_6$) (**D-2**), also exhibited significant quenching of luminescence, which was attributed to a charge-transfer process in which the nitrostilbene moiety was reduced by electron transfer from the excited state of the chromophore.[46]



**D-2**

Though this result was very encouraging, the stability of the vinylene bridge remained a concern with the synthetic methodology. Steps were therefore taken to append as an electron acceptor the nitrophenyl unit through a more stable and robust aryl−aryl linkage. In this paper, we describe the syntheses of these new dyads (**1** and **2**) and triads (**3** and **4**), obtained as their PF$_6^-$ salts and based on chromophore **5**, as well as their spectroscopic and electrochemical properties.

These efforts have also led to the development of a facile synthesis of 4′-(4-boronato-phenyl)-2,2′;6′,2″ terpyridine, ptpy-B(OH)$_2$, that had been reported synthesized by a more arduous route.[51,52] Suzuki couplings with ptpy-B(OH)$_2$ for the preparation of the desired ligand-acceptor derivatives proved to be facile under standard conditions.[52,53]

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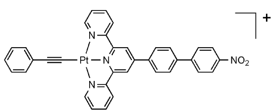
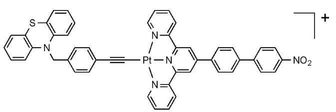


**1**



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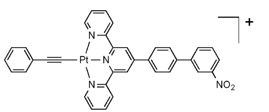

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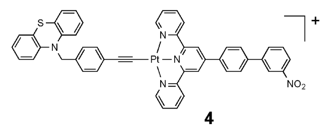

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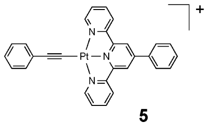
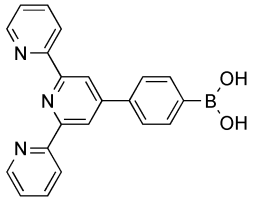


**5**



**ptpy-B(OH)$_2$**

## Experimental Section

**Materials.** The chemicals N,N-dimethylformamide, acetonitrile, tetrahydrofuran, dimethylsulfoxide, copper(I) iodide, ammonium acetate, ammonium hexafluorophosphate ($NH_4PF_6$), 2-acetylpyridine, pinnacol, triethylamine, triphenylphosphine, cesium carbonate, 4-bromonitrobenzene, and 3-iodonitrobenzene (Aldrich); electrochemical-grade tetrabutylammonium hexafluorophosphate and potassium *tert*-butoxide (Fluka); 4-formylphenylboronic acid (Boron Molecular), potassium tetrachloroplatinate; and palladium(II) acetate (Strem Chemical) were used without further purification.

The syntheses of N-(4-ethynylbenzyl)-phenothiazine and $Pt(DMSO)_2Cl_2$ were carried out according to literature procedures.[42,46] The chromophore $[Pt(ttpy)(C{\equiv}C-C_6H_5)]PF_6$ (**5**) and the donor−chromophore dyad $[Pt(ttpy)(C{\equiv}C-C_6H_4CH_2-PTZ)]PF_6$ (**D-2′**) were used as previously prepared.[46] Syntheses were performed under nitrogen with solvents purified by passing the degassed solvent through columns containing activated molecular sieves and activated alumina.[54] All other reagents were of spectroscopic grade and used without further purification.

**Characterization.** $^1$H NMR spectra were recorded on a Bruker Avance-500 spectrometer (500 MHz). Mass determinations were accomplished by electrospray ionization mass spectrometry and atmospheric pressure chemical ionization (APCI) 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 glassy carbon working electrode, Pt wire auxiliary electrode, and Ag wire reference electrode were used. For all measurements, samples were degassed with nitrogen. Also, 0.10 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, while ferrocene was employed as an internal redox reference. All redox potentials are reported relative to the ferrocenium/ferrocene ($Fc^+/Fc$) couple (0.4 V vs SCE for MeCN, 0.45 V vs SCE for DMF),[55] and all scans were done at 100 mV/s. Absorption spectra were recorded using a Hitachi U2000 scanning spectrophotometer (200−1100 nm).

Emission and excitation spectra were obtained using a Spex Fluoromax-P fluorimeter 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 were prepared in butyronitrile using NMR tubes in a circular quartz-tipped immersion Dewar filled with liquid nitrogen.

Transient absorption spectra were carried out using an Applied Photophysics LKS60 flash photolysis system with a Quantel Brilliant B Nd:YAG laser pumped OPOTEK OPO at various delays following excitation at various wavelengths between 420 and 500 nm. The spectra were assembled from decays measured at every 10 nm. Individual decays were analyzed as single or double exponentials using a Marquardt−Levenberg algorithm included with the LKS60 software. Kinetic analysis, where appropriate, was made by global analysis using the PRO-K software package (Applied Photophysics).

**4′-(4-Boronato-phenyl)-2,2′;6′,2″-terpyridine, ptpy-B(OH)$_2$ (L1).** A solution of 4-formylphenylboronic acid (4.00 g, 26.7 mmol) and pinnacol (4.70 g, 39.8 mmol) was prepared in THF (60 mL) and stirred for 1 h. A 500 mL, two-necked flask was charged with potassium *tert*-butoxide (8.00 g, 71.4 mmol) and THF (60 mL). The flask was then equipped with a reflux condenser and a 100 mL pressure-equalizing addition funnel. This addition funnel was charged with THF (60 mL) and 2-acetylpyridine (6.2 mL, 55.3 mmol). The reaction flask was then placed under a $N_2$ atmosphere, and the THF solution of 2-acetylpyridine was added dropwise to the solution of potassium *tert*-butoxide over 1 h, with vigorous stirring. This produced a pale pink suspension. The addition funnel was then charged with the solution of 4-formylphenylboronic acid and pinnacol. This solution was added dropwise to the white suspension over the course of 1 h, with vigorous stirring, producing a yellow-orange suspension, which gradually became an opaque, cherry red solution with an additional 1.5 h of stirring. A solution of ammonium acetate (10 g, excess) was prepared in ethanol (60 mL) and glacial acetic acid (50 mL). This solution was added directly to the red solution in the reaction flask to give a translucent, yellow solution. The addition funnel was removed and replaced with a glass stopper. This solution was then heated at reflux for 16 h. After cooling, the yellow solution was decanted into a flask, and the persisting crystals of ammonium acetate were washed with THF, which was likewise decanted into the same flask. The volatiles were removed by rotary evaporation to give a brown sludge. This was treated with water and a 10% HCl solution and heated until the sludge had completely dissolved. After cooling, the solution was neutralized with aqueous ammonium hydroxide. To drive hydrolysis of the

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pinnacol ester to give the free boronic acid, the suspension was twice more acidified with HCl and heated, then neutralized with ammonium hydroxide. After the final neutralization, the suspension was filtered to give a gummy solid. This material was sonicated in a mixture of THF/Et$_2$O (50:50 v/v) to give an off-white, powdery solid which was collected by filtration and washed with an addition of Et$_2$O, then dried in vacuo. Yield: 3.000 g (32%). $^1$H NMR (DMSO-d$_6$): $\delta$ 8.79 (2H, d, *J* = 5 Hz), 8.76 (2H, s), 8.71 (2H, d, *J* = 8 Hz), 8.24 (2H, s), 8.07 (2H, td, *J* = 8, 2 Hz), 8.03 (2H, d, *J* = 8 Hz), 7.93 (2H, d, *J* = 8 Hz), 7.56 (2H, dd, *J* = 5, 1 Hz). MS (positive APCI, methanol solvent): *m*/*z* 382 [ptpy-B(OMe)$_2$]$^+$

**4′-(4-*p*-Nitrophenyl-phenyl)-2,2′;6′,2″-terpyridine, ptpy-ph-*p*-NO$_2$ (L2).** A 100 mL, two-necked flask was charged with Cs$_2$CO$_3$ (0.550 g, 1.70 mmol), Pd(OAc)$_2$ (0.017 g, 0.076 mmol), and PPh$_3$ (0.080 g, 0.30 mmol). This was fitted with a reflux condenser and a septum, then placed under N$_2$. THF (50 mL) was added via syringe, and the resulting suspension was stirred for 30 min. To this was added a solution of **L1** (0.600 g, 1.70 mmol) in THF (10 mL) via syringe. The reaction mixture rapidly became emerald green and was allowed to stir for 10 min before the addition of a solution of 4-bromonitrobenzene (0.310 g, 1.54 mmol) in THF (10 mL) via syringe. The resulting mixture was stirred at 80 °C for 48 h. A total of 150 mL of water was added to the resulting tan suspension, and the solids were separated by filtration. The solid was washed by vigorous sonication in MeOH/H$_2$0 (10:1, v:v) and filtered again, whereupon it was washed with cold methanol followed by diethyl ether/hexane (1:1, v:v) and dried in vacuo. Yield: 0.391 g (59%). $^1$H NMR (CDCl$_3$): $\delta$ 8.84 (2H, s), 8.79 (2H, d, 5 *J* = Hz), 8.74 (2H, dt, *J* = 8, 1 Hz), 8.38 (2H, dt, *J* = 9, 2 Hz), 8.09 (2H, dt, *J* = 8, 2 Hz), 7.94 (2H, td, *J* = 8, 2 Hz), 7.86 (2H, dt, *J* = 9, 2 Hz), 7.82 (2H, dt, *J* = 7, 2 Hz), 7.42 (2H, ddd, *J* = 8, 5, 1 Hz). MS (positive APCI): *m*/*z* 431 [M]$^+$.

**4′-(4-*m*-Nitrophenyl-phenyl)-2,2′;6′,2″-terpyridine, ptpy-ph-*m*-NO$_2$ (L3).** This was prepared in the same way as **L2**, substituting 3-bromonitrobenzene for 4-bromonitrobenzene (0.384 g, 1.54 mmol). Yield: 0.410 g (62%). $^1$H NMR (CDCl$_3$): $\delta$ 8.84 (2H, s), 8.79 (2H, d, *J* = 5 Hz), 8.74 (2H, d, *J* = 8 Hz), 8.58 (1H, t, *J* = 2 Hz), 8.28 (1H, dd, *J* = 8, 2 Hz), 8.10 (1H, dt, *J* = 8, 2 Hz), 8.04 (1H, d, *J* = 8 Hz), 7.94 (2H, td, *J* = 8, 2 Hz), 7.83 (2H, dt, *J* = 9, 1 Hz), 7.70 (1H, t, *J* = 8 Hz), 7.58 (1H, m), 7.42 (2H, ddd, *J* = 8, 5, 1 Hz). MS (APCI): *m*/*z* 431 [M]$^+$.

**[Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$.** A 25 mL round-bottom flask was charged **L2** (0.281 g, 0.652 mmol), Pt(DMSO)$_2$Cl$_2$ (0.250 g, 0.607 mmol), and MeCN (10 mL). The flask was equipped with a reflux condenser, and the suspension was stirred at 80 °C for 48 h. At this time, excess NH$_4$PF$_6$ was added, followed by water (20 mL), and the mixture was stirred for 15 min. The ochre solid was collected by filtration and washed with chloroform and ether to remove any free ligand. Yield: 0.355 g (72%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 9.10 (2H, s), 8.97 (2H, d, *J* = 6 Hz), 8.91 (2H, d, *J* = 8 Hz), 8.60 (1H, t, *J* = 2 Hz), 8.58 (2H, t, *J* = 8 Hz), 8.40 (2H, d, *J* = 6 Hz), 8.38 (2H, d, *J* = 7 Hz), 8.17 (2H, d, *J* = 9 Hz), 8.14 (2H, d, *J* = 9 Hz), 8.00 (2H, t, *J* = 6 Hz), 7.86 (1H, t, *J* = 8 Hz).

**[Pt(ptpy-ph-*m*-NO$_2$)Cl]PF$_6$.** This was prepared in the same way as **[Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$**, excepting the substitution of **L2** with **L3**. Yield: 0.427 g (87%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 9.06 (2H, s), 8.93 (2H, d, *J* = 6 Hz), 8.89 (2H, d, *J* = 7 Hz), 8.61 (1H, t, *J* = 2 Hz), 8.58 (2H, td, *J* = 8, 2 Hz), 8.37 (2H, d, *J* = 8 Hz), 8.33 (2H, m), 8.13 (2H, d, *J* = 9 Hz), 7.97 (2H, t, *J* = 7 Hz), 7.85 (1H, t, *J* = 8 Hz).

**[Pt(ptpy-ph-*p*-NO$_2$)(C≡C−C$_6$H$_5$)]PF$_6$ (1).** A 10 mL round-bottom flask was charged with [Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$ (0.080 g, 0.10 mmol), CuI (0.006 g, 0.03 mmol), and DMF (4 mL). The flask was sealed with a septum and placed under N$_2$. Phenylacetylene (0.02 mL, 0.2 mmol) was added via syringe, followed by triethylamine (0.03 mL, 0.3 mmol). The reaction mixture was stirred in the dark for 48 h. The brown solution was treated with Et$_2$O (50 mL) to effect precipitation of an ochre solid, which was collected by filtration, washed with Et$_2$O, and dried in vacuo. Yield: 0.052 g (60%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 9.25 (2H, d, *J* = 6 Hz), 9.18 (2H, s), 8.94 (2H, d, *J* = 8 Hz), 8.60 (2H, t, *J* = 8 Hz), 8.40 (4H, m), 8.17 (4H, t, *J* = 9 Hz), 8.00 (2H, t, *J* = 7 Hz), 7.54 (2H, d, *J* = 8 Hz), 7.38 (2H, t, *J* = 7 Hz), 7.30 (1H, t, *J* = 7 Hz). HRMS calcd for PtC$_{35}$H$_{23}$N$_4$O$_2$: 726.1463. Found: 726.14911. Anal. calcd for PtC$_{35}$H$_{23}$N$_4$O$_2$PF$_6$: C, 48.16; H, 2.64; N, 6.42. Found: C, 45.50; H, 2.52; N, 6.11.

**[Pt(ptpy-ph-*m*-NO$_2$)(C≡C−C$_6$H$_5$)]PF$_6$ (2).** This compound was prepared in a way directly analogous to that of **1**, excepting the use of [Pt(ptpy-ph-*m*-NO$_2$)Cl]PF$_6$ in place of [Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$. Yield: 0.054 g (62%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 9.23 (2H, d, *J* = 6 Hz), 9.17 (2H, s), 8.94 (2H, d, *J* = 8 Hz), 8.64 (1H, s), 8.59 (2H, t, *J* = 8 Hz), 8.40 (2H, d, *J* = 8 Hz), 8.34 (2H, m), 8.16 (2H, d, *J* = 8 Hz), 7.99 (2H, t, *J* = 7 Hz), 7.87 (1H, t, *J* = 8 Hz), 7.54 (2H, d, *J* = 8 Hz), 7.38 (2H, t, *J* = 7 Hz), 7.30 (1H, t, *J* = 7 Hz). HRMS calcd for PtC$_{35}$H$_{23}$N$_4$O$_2$: 726.1463. Found: 726.14563. Anal. calcd for PtC$_{35}$H$_{23}$N$_4$O$_2$PF$_6$: C, 48.16; H, 2.64; N, 6.42. Found: C, 49.86; H, 2.68; N, 6.33.

**[Pt(ptpy-ph-*p*-NO$_2$)(C≡C−C$_6$H$_4$CH$_2$−PTZ)]PF$_6$ (3).** A 10 mL round-bottom flask was charged with [Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$ (0.080 g, 0.10 mmol), CuI (0.006 g, 0.03 mmol), N-(4-ethynyl-benzyl)-phenothiazine (0.047 g, 0.15 mmol), and DMF (4 mL). The flask was sealed with a septum and placed under N$_2$. Triethylamine (0.04 mL, 0.4 mmol) was added via syringe, and the reaction mixture was stirred in the dark for 48 h. The resultant red solution was treated with Et$_2$O (100 mL) to effect precipitation of a red solid, which was collected by filtration, washed with Et$_2$O, and dried in vacuo. Yield: 0.082 g (76%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 9.00 (2H, s), 8.95 (2H, s), 8.77 (2H, d, *J* = 7 Hz), 8.42 (2H, t, *J* = 8 Hz), 8.35 (2H, d, *J* = 9 Hz), 8.28 (2H, d, *J* = 8 Hz), 8.09 (2H, d, *J* = 8 Hz), 8.02 (2H, d, *J* = 8 Hz), 7.80 (2H, t, *J* = 6 Hz), 7.34 (2H, d, *J* = 8 Hz), 7.26 (2H, d, *J* = 8 Hz), 7.18 (2H, d, *J* = 8 Hz), 7.10 (2H, t, *J* = 7 Hz), 6.95 (2H, t, *J* = 8 Hz), 6.81 (2H, d, *J* = 8 Hz), 5.11 (2H, s). HRMS calcd for PtC$_{48}$H$_{32}$N$_5$O$_2$S: 937.1919. Found: 937.18848. Anal. calcd for PtC$_{48}$H$_{32}$N$_5$O$_2$SPF$_6$: C, 53.23; H, 2.96; N, 6.47. Found: C, 52.46; H, 2.71; N, 6.40.

**[Pt(ptpy-ph-*m*-NO$_2$)(C≡C−C$_6$H$_4$CH$_2$−PTZ)]PF$_6$ (4).** This compound was prepared in a way directly analogous to that of **3**, starting with [Pt(ptpy-ph-*m*-NO$_2$)Cl]PF$_6$ in place of [Pt(ptpy-ph-*p*-NO$_2$)Cl]PF$_6$. Yield: 0.087 g (80%). $^1$H NMR (DMSO-*d$_6$*): $\delta$ 8.98 (2H, s), 8.94 (2H, s), 8.76 (2H, d, *J* = 8 Hz), 8.55 (1H, s), 8.41 (2H, t, *J* = 7 Hz), 8.28 (4H, m), 8.07 (2H, d, *J* = 8 Hz), 7.80 (3H, m), 7.34 (2H, d, *J* = 8 Hz), 7.26 (2H, d, *J* = 8 Hz), 7.18 (2H, d, *J* = 8 Hz), 7.10 (2H, t, *J* = 7 Hz), 6.95 (2H, t, *J* = 8 Hz), 6.81 (2H, d, *J* = 8 Hz), 5.11 (2H, s). HRMS calcd for PtC$_{48}$H$_{32}$N$_5$O$_2$S: 937.1919. Found: 937.19073. Anal. calcd for PtC$_{48}$H$_{32}$N$_5$O$_2$SPF$_6$: C, 53.23; H, 2.96; N, 6.47. Found: C, 53.44; H, 2.73; N, 6.20.

## Results and Discussion

**Syntheses and Characterization.** The phenyl terpyridine bearing a boronic acid substituent, ptpy-B(OH)$_2$, was prepared via a synthetic methodology developed by Constable et al. for the preparation of phenyl terpyridines.[56,57] By

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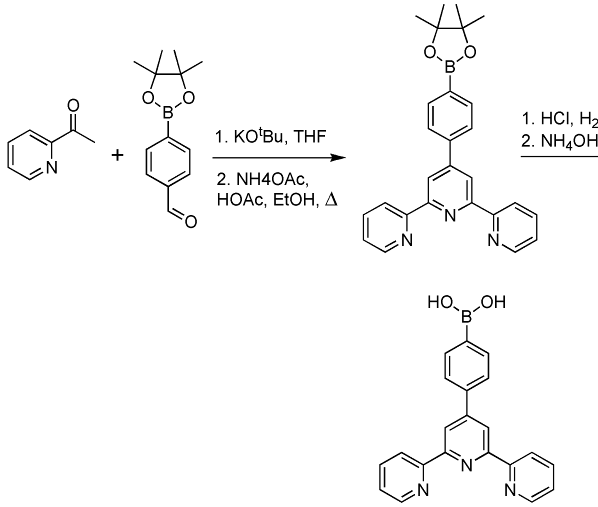
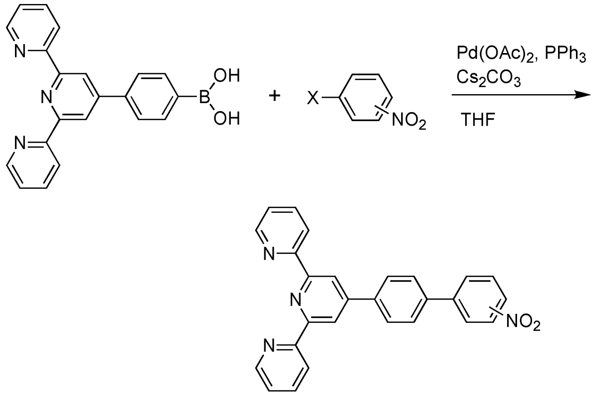
(56) Constable, E. C.; Kariuki, B.; Mahmood, A. *Polyhedron* **2003**, *22*, 687–698.

protecting the boronic acid moiety as a pinnacolate ester, this method proved both facile and amenable to multigram scale synthesis of the desired ligand. Deprotection in aqueous acid furnished the free acid form in reasonable yield (eq 1). Suzuki couplings between ptpy-B(OH)$_2$ and various aryl halides proved successful under standard conditions and gave acceptable yields of pure products without the need for chromatography (eq 2).[52,53]

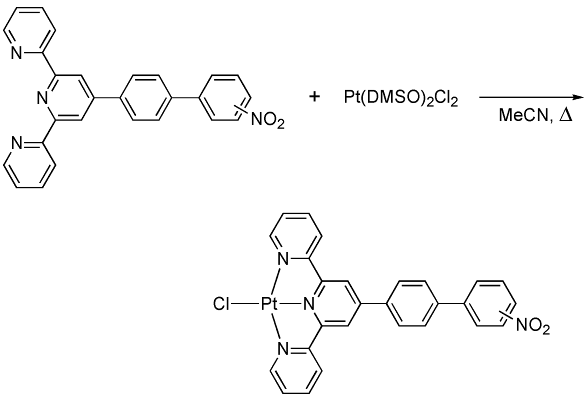


(1)

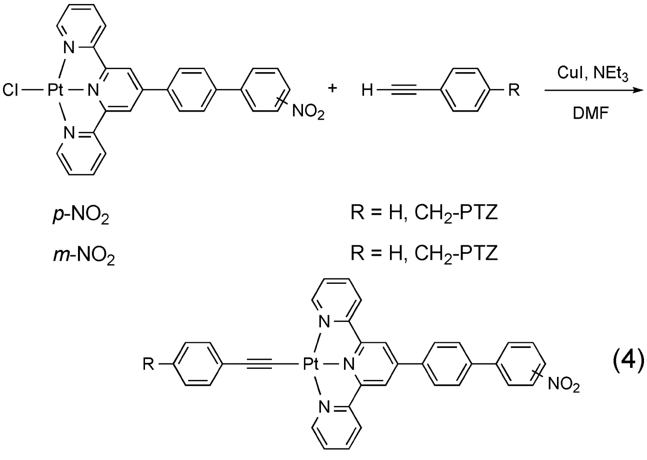


(2)

Coordination of Pt(II) proceeded smoothly under standard conditions to give the platinum(II) terpyridyl chlorides (eq 3).[45,46,58−63] Subsequent CuI-catalyzed exchange of chloride for acetylide ligands was somewhat slow compared to previously studied compounds, requiring slightly higher CuI loadings for timely reaction (eq 4).[45,63−68]



(3)



(4)

**1**, **3**
**2**, **4**

The new complexes were characterized by $^1$H NMR spectroscopy and HRMS, with each giving data consistent with the assigned structure. All of the ligands and complexes have distinct, well-resolved patterns in the their aromatic proton resonances, which are attributable to the protons on the pyridine and substituted phenyl rings. The pyridine resonances ($\delta$ 7.8−9.4) are particularly informative, as they shift substantially upon the coordination of Pt(II) and upon the exchange of chloride for acetylide, particularly the protons nearest the acetylene moiety. Mass spectroscopy is also particularly convenient in analyzing these platinum-containing compounds, as platinum gives a characteristic isotopic pattern. Elemental analyses of platinum terpyridyl acetylide complexes are frequently found to be low in carbon, as is the case here, because of difficulties with incomplete combustion; despite this problem, a high purity of the compounds is indicated by other characterization methods, particularly NMR spectroscopy.

**Absorption and Emission Spectra.** The room-temperature absorption spectra of the complexes were measured in MeCN and are shown in Figure 1. All of the complexes exhibit features in the range of 300−800 nm which are

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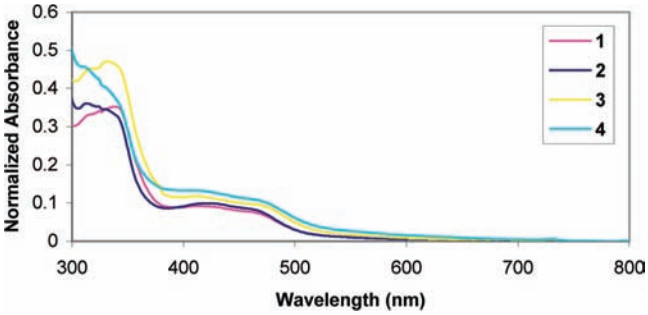


**Figure 1.** Room-temperature absorption spectra of the complexes **1**−**4** in $1 \times 10^{-5}$ M MeCN.

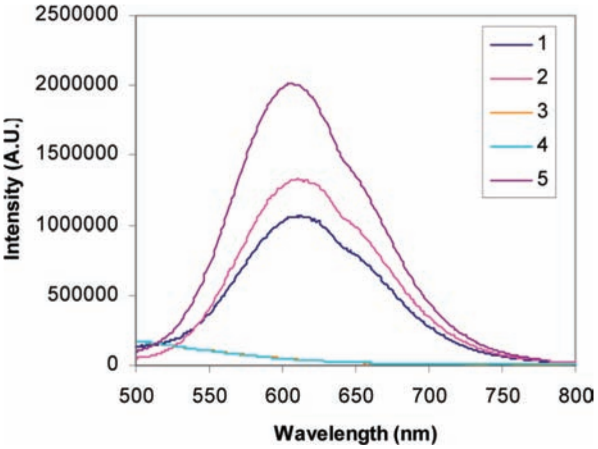


**Figure 2.** Room-temperature emission spectra of complexes **1**−**5** in $1 \times 10^{-5}$ M MeCN. Overlap exists in the spectra of **3** and **4**.

consistent with previously studied platinum terpyridyl acetylide complexes.[45,46] The higher-energy absorptions (300−370 nm) are assigned as intraligand transitions, while the broad, weaker absorptions ($\varepsilon \sim 9000-11000$ $M^{-1}cm^{-1}$) at lower energies (410−500) nm are assigned as $^1$MLCT, (d$\pi$(Pt) → $\pi$*(tpy)), absorptions.[45,46,64,69−74]

Room-temperature emission studies of the dyads and triads were conducted in degassed MeCN (Figure 2). The C−A dyads **1** and **2** were found to be emissive in solution, with luminescence profiles virtually identical to that of the parent chromophore **5**, and at slightly lower intensities. The quantum yields for emission for dyads **1** and **2** were found to be 0.011 and 0.012, respectively, using $Ru(bpy)_3^{2+}$ as a standard with $\phi_{rel}^{em} = 0.062$. These values can be compared to the quantum yield of 0.025 measured for **5**.[75] The triads **3** and **4** were nonemissive at room temperature in an acetonitrile solution. However, when studied in a frozen butyronitrile glass at 77 K, both triads were found to have emission features similar to that previously reported for the related D−C dyad **D-2′** (Figure 3).[46] A faint vibronic progression is also observable in the frozen glass emission spectrum of **3**, consistent with previous observations for platinum terpyridyl acetylides.[45,46,64,76] That the triads are emissive in a frozen glass but are nonemissive in a room-temperature solution is consistent with a charge-transfer quenching process having a substantial solvent reorganizational barrier.

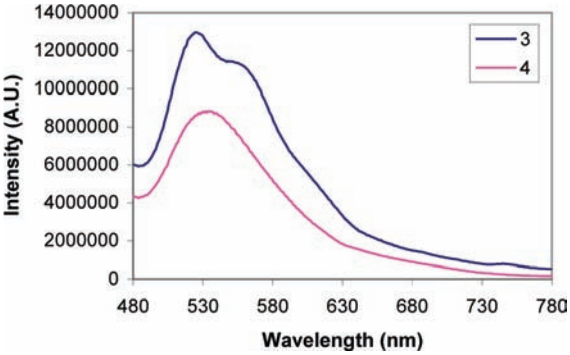


**Figure 3.** Emission spectra of complexes **3** and **4** in butyronitrile at 77 K.

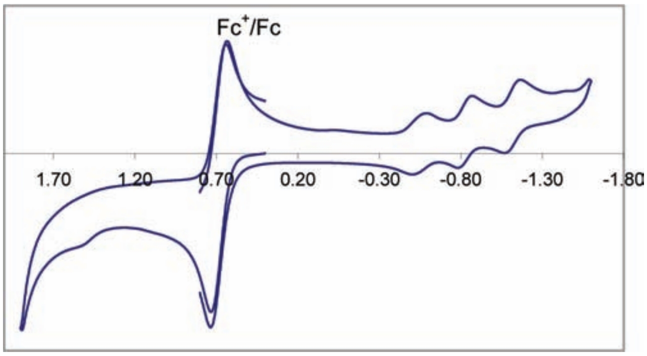
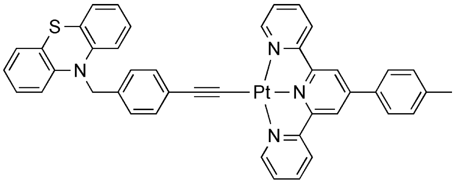


**Figure 4.** Cyclic voltamogram of complex **1** in DMF with 0.1 M $NBu_4PF_6$ and ferrocene added as a reference, recorded at 100 mV/s. Values have been adjusted to NHE, $1.8 - {}^{-}1.6$ V.



**D-2'**

**Electrochemistry.** Cyclic voltammetry studies were performed on all of the complexes in DMF with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Figure 4 gives a cyclic voltamogram for **1**). *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 versus SCE taken for the Fc/Fc$^+$ couple in MeCN and 0.45 V versus SCE for the Fc/Fc$^+$ couple in DMF.*

The electrochemical behavior of the parent chromophore **5** and D−C dyad **D-2′** have been reported previously.[46] The

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

| compound | oxidation $E_{1/2}$/V | reduction $E_{1/2}$/V |
|---|---|---|
| **1** | 1.56[a] | −0.54, −0.82, −1.11 |
| **2** | 1.50[a] | −0.54, −0.83, −1.08 |
| **3** | 1.5,[a,b]1.02[c] | −0.55, −0.82, −1.12 |
| **4** | 1.51,[a]1.03[c] | −0.53, −0.85, −1.10 |
| **5** | 1.54[a] | −0.58, −1.10 |
| **D-2′** | 1.49,[a]1.09[c] | −0.60, −1.10 |

[a] Irreversible under experimental conditions. [b] Weak couple, difficult to determine potential. Potential in volts vs NHE (see the Experimental Section). [c] Reversible when anodic scan limited to 1.4 V.

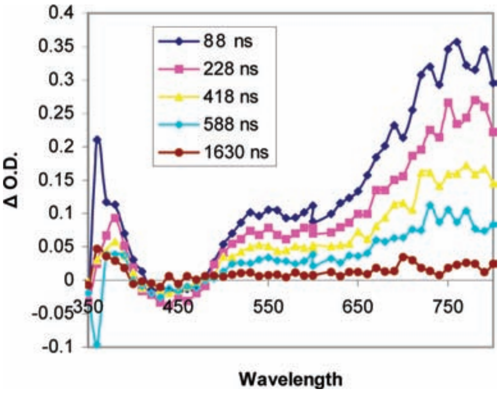

**Figure 5.** Transient absorption spectrum of C−A dyad **1** (0.08 mM in MeCN) at room temperature in MeCN ($\lambda_{exc}$ = 440 nm).

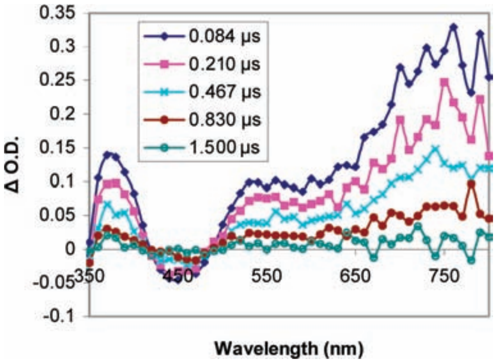

**Figure 6.** Transient absorption spectrum of C−A dyad **2** (0.08 mM in MeCN) at room temperature in MeCN ($\lambda_{exc}$ = 440 nm).

dyads in the present study show the expected number of oxidation and reduction waves, and the results are listed in Table 1. The first oxidation for the phenothiazine moiety proved to be reversible when the anodic limit of the scan was kept lower than 1.4 V, but it exhibited a loss in the current intensity of the cathodic wave when the scan was extended to higher potentials. The Pt-based oxidations were irreversible and had greater intensity when using a Au disk working electrode.

**Transient Absorption Studies.** To probe the dynamics of charge transfer in these systems, nanosecond transient absorption studies were performed on **1**−**4** at 298 K in MeCN. The results for **1**−**3** are shown in Figures 5−7; the results for **4** are virtually identical with the results for **3** in Figure 7. The spectra were collected immediately after excitation at 470 nm (pulse < 10 ns). The spectra were assembled from decays measured at every 10 nm.

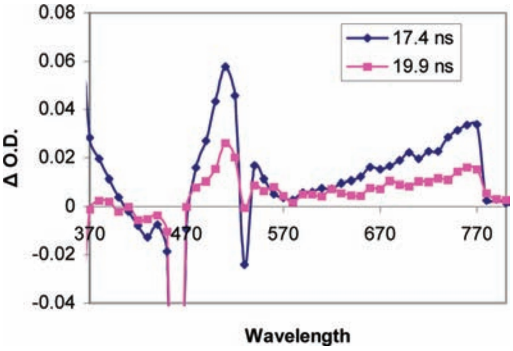

**Figure 7.** Transient absorption spectrum of D−C−A triad **3** (0.08 mM in MeCN) at room temperature in MeCN ($\lambda_{exc}$ = 440 nm).

The transient absorption spectra of the C−A dyads **1** and **2** (Figures 5 and 6) are virtually indistinguishable from that previously observed for the parent chromophore **5**.[45,46] All three complexes display positive absorptions at 360 nm and broad unresolved absorptions between 520 and 800 nm with maxima at ca. 740 nm and a bleach at 420−460 nm, which is still observed when the excitation wavelength is varied. All of these features decay with a rate constant of $1.6 \times 10^6$ s$^{-1}$.

The transient absorption features of the D−C−A triads **3** and **4** are also virtually identical to those previously reported for the related D−C dyad **D-2′**, which correspond to a ($PTZ^+$−Pt−$tpy^-$) charge-separated state.[46] Both **3** and **4** exhibit absorptions with maxima at 510 nm and broad envelopes between 550 and 770 nm, which decay in less than 30 ns (Figure 7). These features are consistent with the phenothiazine radical cation. Most importantly, in none of the transient absorption spectra of triads **3** and **4** is there ever observed an absorption which can be attributed to the nitrophenyl radical anion. If formed by charge transfer, this radical would be expected to give absorptions with a $\lambda_{max}$ near 350 and 460 nm.[77]

The absence of transient absorptions resulting from the nitrophenyl radical anion for complexes **1**−**4** is somewhat surprising, as the nitrophenyl moiety has previously functioned as an electron acceptor in the closely related triad systems **T-1** and **T-2**.[43,46] That the nitrophenyl unit does not accept an electron from the excited state of the chromophore is consistent with the absence of luminescence quenching in dyads **1** and **2** and the similarity of the transient absorption spectra of **1** and **2** with that of the central chromophore **5**.

From the transient absorption data of triads **3** and **4**, it appears that reductive quenching is rapid (<10 ns) and produces a charge-separated species in which the phenothiazine moiety is oxidized and the chromophore reduced, as was observed previously in the study of dyad **D-2′**. Subsequent charge transfer from the reduced chromophore to the nitrophenyl unit would not be predicted to be a thermodynamically favorable process on the basis of electrochemical data (Table 1). The chromophore moiety undergoes reduction at −0.55 V and would not be expected to transfer an electron to the nitrophenyl unit ($E_{red}$ = −0.82 V). Therefore, a pathway in which the chromophore first undergoes reductive quenching by the donor cannot lead to full charge separation.

Two explanations can be offered to explain the difference in behavior of the nitrophenyl moiety in triads **3** and **T-1**. One relates to the difference in chromophore oxidation potential between a neutral Pt(phenanthroline)($C{\equiv}C-C_6H_4R)_2$ entity as in **T-1** and a cationic Pt(terpyridyl)($C{\equiv}C-C_6H_4R)^+$ complex as in **3**. On the basis of the charge, the relative donating capacity of the ligand set for each, and the excited-state oxidation potentials for the chromophores, **T-1** will possess a greater tendency for oxidative quenching and electron transfer to nitrobenzene upon excitation than **3**. A second factor to consider is the charge-transfer pathway in the two systems. More specifically, there is likely to be greater electronic communication between the phenanthroline moiety and the nitrophenyl acceptor in triad **T-1** than between the terpyridine moiety and the nitrophenyl acceptor in triad **3**. Aside from the increased distance between these species in the latter, the *p*-phenylene unit in **3** is expected to be orthogonal or twisted relative to a coplanar orientation of the chromophore and the nitrophenyl acceptor, which would retard electron transfer. This orientation would not be expected in triad **T-1**, where steric factors will not be significant, owing to the intervening acetylene bridge.

**Intermolecular Quenching Studies.** The difference in acceptor behavior between triads **3** and **T-2** has a different rationalization. In **T-2**, the acceptor moiety can be viewed as nitrostilbene rather than nitrobenzene. The former will undergo reduction more easily than the latter and will also have better conjugation for connecting chromophore with acceptor and transferring charge than is likely for the latter in **3** (and **4**). To further probe the energetics of charge transfer, nitrostilbene and nitrobenzene were compared in their ability to quench the luminescence of the parent chromophore, **5**, in fluid solution. Nitrostilbene was found to quench with a rate approaching the diffusion limit, $k = 4.6 \times 10^9\ s^{-1}$. Nitrobenzene, however, was not observed to reduce the emission intensity of the chromophore at concentrations up to 1000 times that of the chromophore. This result was unexpected, given the minor difference in reduction potentials of nitrobenzene and nitrostilbene, with the latter undergoing reduction at less than 0.1 V more positive than nitrobenzene. As possible oxidative quenchers of the central chromophore, nitrobenzene and nitrostilbene may lie near the threshold for thermodynamically favorable charge transfer, as discussed further below.

An energy-transfer quenching mechanism involving nitrostilbene is also possible with the platinum terpyridyl acetylide chromophore. The triplet energy of nitrostilbene has been reported as ~2.0 eV.[78] The triplet energy of the chromophore may be taken as the $\lambda_{max}$ of the 77 K frozen glass emission, or 550 nm (2.2 eV). Thus, a triplet−triplet energy transfer from the chromophore to the nitrostilbene would be expected to be energetically favorable and may account for the quenching behavior observed here and in the previously reported chromophore−acceptor dyad **D-2** and triad **T-2**.[46] Also, for the previously studied dyad **D-2**, transient absorption data are consistent with the triplet state of nitrostilbene.[46,79] In contrast, energy transfer to the nitrophenyl moiety would not be expected, as the lowest triplet energy for nitrobenzene has been reported at >2.6 eV.[80]

Additional insight is gained by a thermodynamic analysis of the charge-transfer process using the Rehm−Weller equation (eq 5). With this equation, it is found that oxidative quenching of the excited state of the chromophore with the nitrophenyl acceptor would be unfavorable. For this calculation, the oxidation potential of the chromophore, $E_D°$, is estimated as 1.5 V versus NHE from the onset of the anodic wave. However, this value introduces a significant source of uncertainty in the calculations to follow, as the process is irreversible. The excited triplet energy, $\Delta E^*$, is 2.2 eV, as described above, and the work term is set to 0 for an intramolecular process.

$$\Delta G = |E_D° - E_A°| - \Delta E^* + w \qquad (5)$$

From the electrochemical behavior of complexes **1** and **2**, as well as ligands **L1** and **L2**, the nitrophenyl reduction can be taken as −0.82 V versus NHE. Thus, oxidative quenching of the central chromophore by this species would be predicted to be unfavorable by ~0.1 eV for the process. While the result may be viewed as unexpected in light of earlier observations, it is consistent with all of the current data for complexes **1**−**4**.[46]

## Conclusions

The D−C−A triads [Pt(ptpy-ph-*p*-$NO_2$)($C{\equiv}C-C_6H_4CH_2-$PTZ)]$PF_6$ (**3**) and [Pt(ptpy-ph-*m*-$NO_2$)($C{\equiv}C-C_6H_4CH_2-$PTZ)]$PF_6$ (**4**) have been prepared along with the corresponding C−A dyads **1** and **2**. The characterization data of each of these compounds support the assigned structures and are similar to previously reported analogous multicomponent systems. The syntheses of these complexes were greatly facilitated by the improved preparation of the previously reported terpyridyl derivative, 4′-(4-boronatophenyl)-2,2′;6′,2″-terpyridine, ptpy-B(OH)$_2$.[51,52] These compounds were prepared for comparison with earlier studies of the closely related triad **T-2** and dyad **D-2** bearing a nitrostilbene acceptor.[46] On the basis of the previous findings, it was expected that the nitrophenyl acceptor would function to oxidatively quench the excited state of the central chromophore. However, the current data indicate that, in contrast to the behavior of triad **T-2** and dyad **D-2**, the complexes described here do not exhibit any charge-transfer quenching to the nitrophenyl moiety or electron transfer to nitrophenyl from the reduced chromophore. This may be due to the slight difference in electrochemical potential for the reduction of the accep-

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tors, or differences in the pathway for charge transfer. Additional analysis also suggests that the nitrostilbene moiety may quench the chromophore through an energy-transfer process rather than the charge-transfer process initially proposed. With the synthetic methodology described here, it will be possible to systematically vary the acceptor, with the ultimate aim of generating multicomponent systems that can achieve long-lived charge-separated states.

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