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Stereochemical Effects on Platinum Acetylide Two-Photon Chromophores

Abigail H. Shelton,[†] Silvano R. Valandro,[‡] Randi S. Price,[†] Galyna G. Dubinina,[†] Khalil A. Abboud,[†] Geoffrey Wicks,[§,∥] Aleksander Rebane,*[,∥,⊥] Muhammad Younus,*[,‡] and Kirk S. Schanze*[,‡]

[†]Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611, United States

[‡]Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249, United States

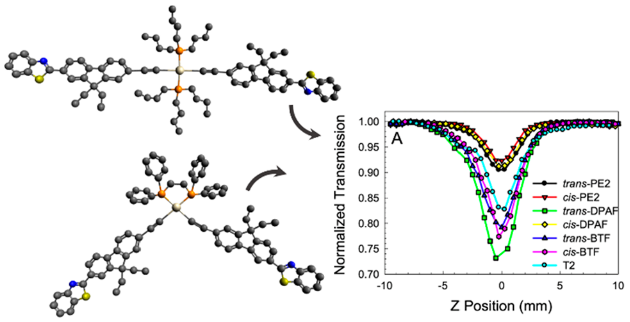
[§]ILX Lightwave, Bozeman, Montana 59717, United States

[∥]Physics Department, Montana State University, Bozeman, Montana 59715, United States

[⊥]National Institute for Chemical Physics and Biophysics, Tallinn, 12618, Estonia

Supporting Information

ABSTRACT: A series of *cis*-platinum(II) acetylide complexes containing two-photon-absorbing chromophores have been synthesized and characterized to explore the effects of stereochemistry on the nonlinear absorption properties. The molecules feature 4-(phenylethynyl)phenylethynylene (PE2), diphenylaminofluorene (DPAF), and benzothiazolylfluorene (BTF) ligands. The photophysical properties were investigated under one- and two-photon conditions and compared to the known *trans* analogues via UV−visible absorption, photoluminescence, femtosecond and nanosecond transient absorption (TA), nanosecond z-scan, and femtosecond two-photon absorption (2PA). The bent *cis* complexes exhibit blue shifts in the absorption, emission, femtosecond, and nanosecond TA spectra along with lower molar extinction coefficients and lower phosphorescence yields relative to the *trans* complexes suggesting less efficient Pt-induced spin−orbit coupling and intersystem crossing in the *cis* configuration. The *cis* chromophores are noncentrosymmetric and therefore show dipolar behavior with a pronounced 2PA in the 0−0 transition of the $S_0 \rightarrow S_1$ band, while the *trans* complexes show quadrupolar behavior with a forbidden 0−0 transition. In the $S_0 \rightarrow S_n$ region, both *cis* and *trans* complexes show intense two-photon-absorption bands (up to 3700 GM by the peak cross section for *cis*-BTF) which contain a significant contribution from the excited state absorption ($S_1 \rightarrow S_n$). All six complexes exhibit comparable nonlinear absorption response with a significant contribution from triplet−triplet absorption that slightly favors *trans* complexes but is more strongly dependent upon the structure of the π-conjugated chromophore.



■ INTRODUCTION

Platinum acetylide chromophores often display strong nonlinear absorption (NLA) over a wide spectral region and linear transmission through most of the visible region. This provides researchers with the opportunity to investigate the spin-forbidden $S_0 \rightarrow T_1$ state absorption, intersystem crossing (ISC) to the triplet manifold, and triplet−triplet excited state absorption ($T_1 \rightarrow T_n$).[1−3] The introduction of different π-conjugated ligands of varying lengths in platinum acetylide complexes has been shown to elicit advantageous effects on the one- and two-photon photophysical properties.[4−7] The platinum metal center induces efficient ISC to a long-lived triplet excited state; therefore, these platinum acetylides are well-suited for a dual-mode NLA process from a nanosecond laser pulse that combines two-photon absorption (2PA) from the singlet ground state ($S_0 \rightarrow S_n$) with excited state absorption (ESA) from the triplet state ($T_1 \rightarrow T_n$).[8−10]

The majority of the photophysical investigations reported to date have focused on linear platinum acetylide complexes in the *trans* configuration at the metal center.[1,4,8,11−17] This focus is partially due to the thermodynamic instability of the *cis* isomer with respect to the *trans* isomer in solution, specifically when the auxiliary ligands are monodentate phosphines such as PBu_3 and PEt_3.[18] However, platinum acetylides can be constrained into the *cis* configuration by the incorporation of chelating auxiliary groups such as bidentate phosphines (e.g., 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis-(diphenylphosphino)propane (dppp)),[19,20] diimine ligands such as 2,2′-bipyridine,[19,21] or more recently bidentate bis(imidazolin-2-ylidenes).[22]

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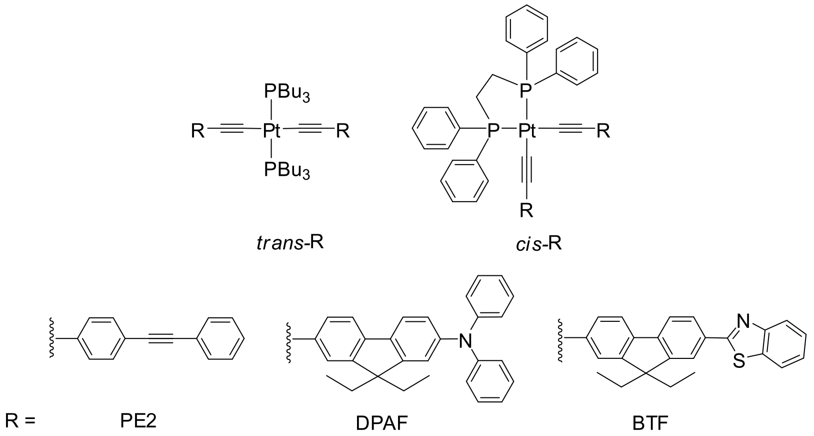

Figure 1. Chemical structures of the two-photon-absorbing platinum acetylides in the *cis* and *trans* geometries.

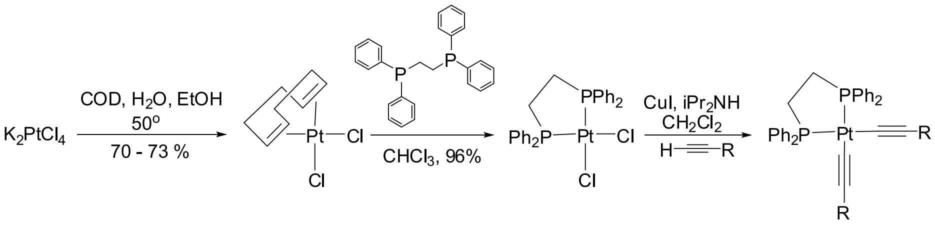

Figure 2. Synthetic scheme for *cis*-platinum acetylides.

Stable *cis*-platinum acetylide complexes have been studied for their intraligand and charge transfer properties and for use in white[23,24] and red[25] organic light emitting diodes, neutral molecular squares,[26−29] coordination spheres,[30,31] and as molecular tweezers,[32,33] applications which are aided by the locked geometry and the near 90° angles formed between the ligand arms. Most investigations within this research area have focused on 1,4-diethynylbenzene or 4,4-diethynylbiphenyl ancillary ligands, and variations, within monomeric or multiplatinum species. Despite the growing amount of literature on *cis*-platinum complexes, very few studies have reported the photophysical response (photoluminescence, transient absorption, or nonlinear absorption), and most are not designed to exhibit 2-photon absorption (2PA) and excited state absorption (ESA).[34,35]

Herein we report the synthesis of three novel *cis*-platinum acetylide complexes and make comparisons between their one- and two-photon photophysical properties relative to the previously reported *trans* analogues. The diphenylaminofluorene (DPAF) and benzothiazolefluorene (BTF) chromophores utilized are both large cross section 2PA chromophores; these donor and acceptor chromophores were incorporated onto platinum metal cores by acetylide linkages in both *cis* and *trans* geometries. *trans*-PE2 (bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II)) has become a common benchmark for platinum acetylide chemistry which shows moderate NLA.[11,15,36,37] As such, the *cis* and *trans* geometries of PE2 were also investigated. This series of Pt complexes, with structures shown in Figure 1, has allowed for the elucidation of stereochemical effects on their photophysical properties. The photophysical properties were evaluated by ground state absorption, steady state emission spectroscopy, triplet−triplet transient absorption, and nonlinear absorption.

EXPERIMENTAL SECTION

Materials and Synthesis. PE2,[1] DPAF, and BTF chromophores,[8] *trans*-PE2, *trans*-DPAF, *trans*-BTF,[8] 1,5-cyclooctadiene platinum(II) dichloride,[38] and *cis*-diphenylphosphineethaneplatinum(II) dichloride[39] were synthesized according to literature procedures. The synthesis route for obtaining the *cis* complexes is shown in Figure 2 and further described in the Supporting Information. The first intermediate was synthesized by reaction of K_2PtCl_4 with 1,5-cyclooctadiene (COD) in ethanol, according to the method described by Baker.[38] The obtained COD product was then reacted with 1,2-bis(diphenylphosphino)ethane (dppe) to synthesize the Pt(dppe)Cl_2 precursor.[39] As has previously been examined with similar dppe-bound platinum complexes, the Pt(dppe)Cl_2 precursor was utilized to generate the target *cis* complexes by reaction with the corresponding chromophores.[19,40] The dppe chelating auxiliary group is incorporated into the *cis* complexes to increase the thermodynamic stability of the generated complexes in addition to locking the geometry into the *cis* configuration.

General Techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer in deuterated chloroform; chemical shifts (δ) are reported in parts per million and referenced to tetramethylsilane or protonated solvent signals. Elemental analyses were performed by the University of Florida Spectroscopic Services.

X-ray intensity data was collected at 100 K on a Bruker SMART diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT and integrated using three-dimensional profiling algorithms.[41] The resulting data were reduced to produce *hkl* reflections, their intensities, and estimated standard deviations. The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied based on indexed and measured faces.

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The molecular structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement.[42] The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms.

Unless noted, one-photon photophysical studies were carried out with samples contained in 1 × 1 cm quartz or glass spectroscopic cuvettes. Ground state absorption spectra were measured on a Varian Cary 100 dual-beam spectrophotometer. Corrected steady-state emission measurements were performed on a Photon Technology International (PTI) photon counting fluorescence spectrometer; sample concentrations were adjusted to produce optically dilute solutions, $OD_{max} < 0.20$. Samples were argon purged for 20 min for phosphorescent measurements. Low-temperature measurements were conducted in distilled HPLC grade 2-methyltetrahydrofuran and placed in a standard NMR tube. The tube was then inserted into a liquid nitrogen filled silvered finger Dewar and placed into the PTI spectrometer sample holder. Quantum yields were calculated against $Ru(bpy)_3Cl_2$ in air-saturated deionized water ($\Phi = 0.0379$).[43]

Fluorescence lifetimes for the PE2 complexes were obtained by a PicoQuant FluoTime 100 Compact Fluorescence Lifetime Spectrophotometer which has a minimum time resolution of 100 ps. A UV-pulsed diode laser provided the excitation at 375 nm ($P < 10$ mW). The laser was pulsed using an external BK Precision 4011A 5 MHz function generator. Decays were obtained using the biexponential fitting parameters within the PicoQuant PicoHarp software. Fluorescence lifetimes for the DPAF and BTF complexes were obtained using a PicoQuant FluoTime 300 spectrometer equipped with a frequency doubled, Coherent Chameleon Ti:sapphire femtosecond laser as the source. The temporal resolution of the FT-300 system is ~5 ps.

Nanosecond triplet−triplet transient absorption measurements were conducted using the third harmonic of a Continuum Surelite II-10 Nd:YAG laser ($\lambda = 355$ nm), with an excitation pulse energy of 8 mJ; this instrumentation has been described previously.[44] Sample concentrations were adjusted to an optical density of 0.7 at the excitation wavelength. The sample solutions were placed in a continuously circulating 1 cm path length flow cell holding a volume of 10 mL. The sample solutions were prepared in THF and deoxygenated by bubbling with argon.

Triplet excited state lifetimes were calculated from the transient absorption spectra with software developed in-house using samples prepared identically to those used for nanosecond triplet−triplet transient absorption measurements. The software and instrumentation have been described previously, though the system has been modified to incorporate a Surelite Continuum I Nd:YAG laser for excitation at 355 nm.[45] The lifetimes were such that the arc lamp pulser was not necessary.

Nanosecond NLA measurements were performed via an open-aperture z-scan apparatus developed in-house.[46] The excitation wavelength was generated by a Continuum Surelite OPO Plus pumped with the third harmonic (355 nm) of a Continuum Surelite II-10 Nd:YAG laser. The laser beam was split with a 50:50 beam splitter to two OPH PE10-SH V2 pyroelectric detectors, which measured the transmitted pulse energy as a function of the input pulse energy using an Ophir Laserstar dual-channel optical laser energy meter. The beam was focused with a 25.4 mm diameter, 50.8 mm focal length concave lens. A ThorLabs motorized translation stage (Z825B and TDC001) allowed millimeter movement along the z-axis.

To acquire femtosecond transient absorption, a double-beam subpicosecond pump−probe technique was used. Pump and probe pulses were generated by an amplified Ti:sapphire laser (Astrella, Coherent, Inc.) displaying at 800 nm with pulse width 100 fs and 1 kHz repetition rate coupled with an optical paramagnetic amplifier (Coherent) used for pulse pump generation. The probe pulse was a continuum generated by the fundamental focused onto a sapphire plate. Transient absorption spectra were obtained using a Helios Fire transient absorption spectrometer (Ultrafast Systems). The sample solutions were excited at 380 nm and constantly stirred to avoid photodegradation. Transient absorption data were analyzed using global analysis and singular value decomposition (SVD) by the Surface Xplorer PRO program from Ultrafast System.

The femtosecond 2PA measurements were performed in benzene solutions by the nonlinear transmission method, and 2PA cross section values were calculated as described in a previous article and using Rhodamine B in H_2O and PPV in DCM as a reference standard.[47] Briefly, the optical parametric amplifier (OPA; wavelength 550−810 nm SHS and 800−1140 nm SHI, pulse duration 80−100 fs) output beam at a 100 Hz pulse repetition rate was directed through the sample prepared at concentrations $c \sim 10^{-3}$ M in a standard spectroscopic cuvette. Two identical 10 mm diameter silicon photodetectors (Thorlabs, DET100A) were used to measure the laser pulse reflected from two glass beam pick-off plates positioned, accordingly, before and after the sample. The analog signals from the photodetectors were digitized using a DAQ board (National Instruments, Model PCI-6011). The dependence of the sample transmission (defined as the ratio of the signal from the second detector divided by the signal from the first detector) on the incident intensity was evaluated by varying the energy of the incident pulse in the range, $P_{in} = 1.0–100\ \mu J$ using a neutral density filter attenuator wheel (Thorlabs) mounted on a stepper motor. The estimated accuracy of the measured transmission value is about 0.1%. A laser energy meter (Nova II, Ophir) was used to measure the pulse energy at the input to the sample. The beam diameter at the sample was 0.4−2.0 mm and varied depending on the OPA wavelength. A digital CCD camera (Stingray, Allied) was used to measure the spatial beam intensity profile at the sample. The DAQ board, the attenuator wheel, the energy meter, and the CCD camera were controlled with a PC/LabView routine. A second harmonic generation autocorrelator (Clark MXR) was used to measure the temporal autocorrelation width of the laser pulses.

■ RESULTS AND DISCUSSION

Structures and Synthesis. The new series of *cis*-[Pt(dppe)(L_2)] complexes (L = 4-(phenylethynyl)-phenylethynylene (PE2), diphenylaminofluorene (DPAF), and benzothiazolylfluorene (BTF)) were prepared by the reaction of *cis*-[Pt(dppe)Cl_2] with the appropriate acetylene ligand in the presence of CuI catalyst (Figure 2). The complexes were characterized by spectroscopic and elemental analysis. The molecular structures of *cis*-PE2 and *cis*-BTF were determined by single crystal X-ray crystallography (see the Supporting Information for the X-ray analysis data).

In all complexes, the ^1H NMR spectrum gave expected peaks around $\delta = 2.32–2.46$ for the characteristic methylenic

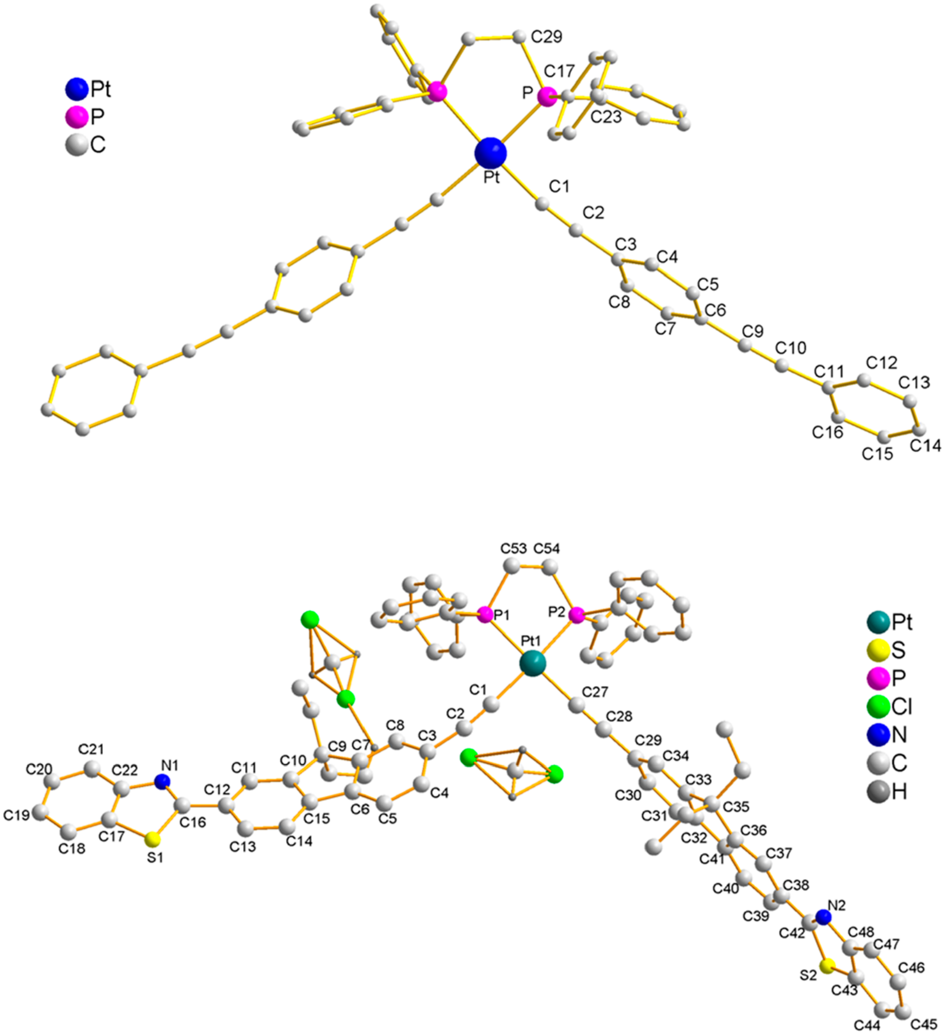

Figure 3. Molecular structures for *cis*-PE2 (top) and *cis*-BTF (bottom) with atomic numbers. The hydrogen atoms are omitted for clarity.

Table 1. Select Bond Distances (Å) and Angles (deg) Observed in *cis*-PE2 and *cis*-BTF

distance	*cis*-PE2	*cis*-BTF	angle	*cis*-PE2	*cis*-BTF
Pt−P1	2.271(2)	2.2649(7)	P1−Pt−P′	85.77(11)	86.33(2)
Pt−P2	–	2.2709(7)	C1−Pt−C1′	94.0(5)	91.38(10)
P1−C29	1.846(5)	–	P1−Pt−C1	90.1(2)	90.82(7)
Pt−C1	2.011(8)	2.013(3)	P′−Pt−C1′	175.8(3)	91.42(7)
C1−C2	1.195(9)	1.203(3)	Pt−C1−C2	172.4(6)	170.8(2)
C2−C3	1.435(7)	1.439(4)	Pt−C27−C28	–	178.1(2)
C6−C9	1.434(7)	–	C1−C2−C3	176.4(6)	170.0(3)
C9−C10	1.184(8)	–	C27−C28−C29	–	176.9(3)
C10−C11	1.449(8)	–	C2−C3−C4	121.2(5)	–
C6−C15	–	1.471(4)	C6−C9−C10	177.2(6)	–
C32−C41	–	1.461(3)	C9−C10−C11	175.8(8)	–
C12−C16	–	1.471(4)			
C38−C42	–	1.468(4)			

protons. The complexes with DAPF and BTF chromophores displayed signals as quartets at $\delta \sim 1.08{-}2.06$ for the diastereotopic CH_2 protons and $\delta \sim 0.30$ as triplets for the CH_3 protons in the fluorene moiety. All complexes displayed complex multiplets and doublets at $\delta \sim 6.97{-}8.02$ for the aromatic protons. The ^{31}P NMR spectrum of all complexes gave singlets at $\delta \sim 42$ with satellites ($^{1}J_{(Pt-P)} = 2278{-}2280$ Hz). These spectroscopic data are consistent with the previously published *cis*-Pt(dppe) acetylide complexes.[39,48]

X-ray Crystallography. Suitable single crystals of *cis*-PE2 and *cis*-BTF were grown via vapor diffusion of diethyl ether into THF and diethyl ether into DCM, respectively, for X-ray crystallography. The molecular structures of *cis*-PE2 and *cis*-BTF are shown in Figure 3 and compared to the structures of *trans*-PE2[28,49] and *trans*-BTF,[8] and select interatomic bond distances and angles are shown in Table 1. The hydrogen atoms have been removed from both structures for clarity. The geometry around the platinum metal center in *cis*-PE2 is approximately square planar, with a sum of the angles around the metal center being 359.97°. The *cis*-PE2 P−Pt−C1 and P−Pt−C1′angles of 90.1(2) and 175.3(3)°, respectively, are similar to those of other known *cis*-platinum acetylides.[27] The smallest angle around the platinum metal is that subtended by the dppe ligand, as anticipated due to the expected bite angle of the dppe ligand onto a platinum center.[27,50] The platinum acetylide units deviate more strongly from the expected linear angle of 180° within the *cis* complex; the *cis* complex has a Pt−C1−C2 angle of 172.4(6)° while the *trans* analogue exhibits an angle of 176.7(5)°. However, the angle observed in *cis*-PE2 is consistent with those of other similar *cis*-platinum acetylides such as 174.3(5)° in $Pt(C{\equiv}CH)_2(dppe)$,[27] 168.0(3)° in $Pt(C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)_2(dppe)$,[20] and 171.9(4)° in $Pt(C{\equiv}CC_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}C{\equiv}CH)_2(dppe)$.[20] The −C≡C− bond proximal to the platinum metal center in *cis*-PE2 is longer than the distal −C≡C− bond, 1.195(9) Å versus 1.184(8) Å. This bond is longer than those observed in Cl−C≡C−Cl systems of 1.183 Å, but notably shorter than the −C≡C− bond length observed in *trans*-PE2 of 1.229(8) Å.[49] Davy and co-workers suggest that the lengthening of the acetylide bond observed in *trans*-PE2 is the result of $d\pi-\pi^*$ back-bonding in the phenylethynyl chromophore, as is especially evident for the −C≡C− adjacent to the metal center.[49] The shorter distal −C≡C− bond in *trans*-PE2 (1.191(9) Å), in addition to the average dihedral angle of 14.9° between the two phenyl groups, indicates that the conjugation does not extend throughout the PE2 chromophore. The observed bond lengths in *cis*-PE2 suggest that $d\pi-\pi^*$ back-bonding could occur in the chromophore, particularly near the platinum center, but to a smaller extent than observed in *trans*-PE2. Interestingly, the average dihedral angle in *cis*-PE2 of 11.0° is smaller than the 14.9° angle observed in *trans*-PE2, which would promote conjugation throughout the chromophore in the *cis* geometry.

Similar to *cis*-PE2, the geometry around the platinum center of *cis*-BTF is approximately square planar and the angle subtended by the dppe ligand is 86.33(2)°, the smallest of the four angles around the metal center. The P1−Pt−C1 and P1−Pt−C27 angles of 90.82(7) and 177.53(7)°, respectively, are consistent with previously reported *cis*-platinum acetylides.[27] The Pt−C1 and Pt−C27 bond lengths of 2.013(3) and 2.010(3) Å within the *cis*-BTF complex are slightly longer than the comparative Pt−C1 bonds of the *trans*-BTF of 2.000(3) Å. Similarly, the Pt−P1 and Pt−P2 bond lengths of 2.2649(7) and 2.2709(7) Å within the *cis*-BTF complex are slightly shorter than the comparative Pt−C1 bonds of the *trans*-BTF of 2.2941(7) Å. Common within platinum acetylides is the observation that the Pt−P bond lengths are 0.2−0.4 Å longer than the Pt−C bond lengths, regardless of the geometry around the platinum center.[19,20,27,49,51] Taken together, the observed *cis*-BTF and *trans*-BTF platinum bond lengths further indicate that the dppe ligand and geometry around the platinum center affect the length deviation more so than the choice of chromophore.

The crystal structure of *cis*-BTF displayed a small degree of disorder within one benzothiazole portion of one chromophore. The effect of this disorder is most apparent when examining the bond angles of the chromophores. The Pt−C27−C28 bond angle of 178.1(2)° is more linear than the Pt−C1−C2 angle of 170.8(2)°. However, both angles are within the expected region for *cis*-platinum acetylides.[20,27] The Pt−C≡C bond angle of 176.6(3)° observed in *trans*-BTF also shows a slight deviation from linearity. The acetylide bond lengths are nearly identical in both complexes: 1.203(3) Å for C1−C2 and 1.201(4) Å for C27−C28 within *cis*-BTF, and 1.208(4) Å for *trans*-BTF, suggesting similar conjugation across the acetylide portions of the complexes.

Absorption and Emission Spectroscopies. The photophysical characterization (photoluminescence and two-photon absorption and nonlinear absorption) of *trans*-PE2, *trans*-DPAF, and *trans*-BTF has previously been reported.[1,4,8,11] As such, the *trans* complexes were examined here to provide benchmarks for comparison to the novel *cis* complexes to elucidate the impact of the stereochemical effects on one- and two-photon photophysical properties. Ground state absorption spectra for the *cis*- and *trans*-platinum acetylide series in THF solution are shown in Figure 4a−c, and the wavelength maxima and molar absorption coefficients are listed in Table 2. The $S_0 \rightarrow S_1$ absorption maxima for the complexes in the *cis* geometry are blue-shifted relative to the absorption maxima observed for the corresponding *trans* complexes. In addition to the observed blue shift, the *cis*-platinum acetylides exhibit a more pronounced vibrational structure relative to the *trans* complexes. This observation has also been noted in similar 4-ethynylstilbene *cis*- and *trans*-platinum acetylide complexes.[19] The pronounced structure implies that electron−vibrational coupling is stronger in the *cis* complexes. The blue shift suggests a weaker interaction between the chromophores in the *cis* complexes, suggesting that the singlet excited state is more localized on a single ligand. In contrast, the red shift in *trans*-platinum acetylides, and the absence of vibronic structure, suggests weaker electron−vibrational coupling, which implies a larger degree of delocalization in the S_1 excited state due to the proximity and mixing of the Pt $d\pi$ and acetylide π^* orbitals.

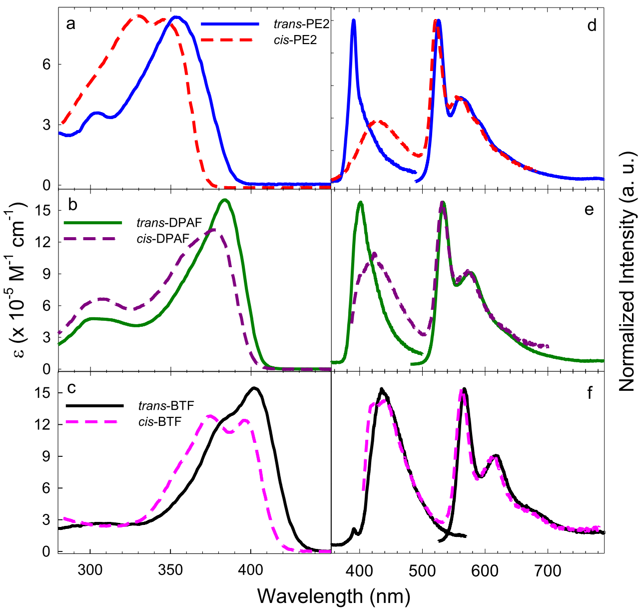

Figure 4. Ground state absorption (left panels, in THF) and emission spectra (right panels, in deoxygenated THF at room temperature) of *cis* complexes.

The *trans* complexes exhibit larger extinction coefficients than do the *cis* complexes for both the DPAF and BTF series.

Table 2. One-Photon Photophysical Properties of the *cis*- and *trans*-Platinum Acetylide Series in THF

complex	$\mathrm{Abs}_{\mathrm{max}}$[a] (nm)	ε ($\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$)	$\mathrm{Fl}_{\mathrm{max}}$[b] (nm)	Φ_F[c]	τ_F[d] (ps)	$\mathrm{Ph}_{\mathrm{max}}$[e] (nm)	Φ_P[c]
trans-PE2	353	83 381	391	0.0005	<100[f]	527	0.011
cis-PE2	330 (345)	84 015	425	0.0003	<100[f]	522	0.0011
trans-DPAF	382	159 892	401	0.0073	9.6[g]	534	0.33
cis-DPAF	376	131 628	424	0.0052	4.8[g]	536	0.0353
trans-BTF	402	154 574	437	0.0087	11[g]	566	0.11
cis-BTF	375 (396)	128 024	415	0.041	36[g]	563	0.042

[a] Ground state absorption maximum. [b] Fluorescence maximum, obtained by excitation at ground state absorption maximum. [c] Quantum yield relative to $\mathrm{Ru(bpy)_3}^{2+}$ in air-saturated deionized water, $\Phi = 0.0379$. [d] Fluorescence lifetime measured at maximum of fluorescence emission. [e] Phosphorescence maximum, obtained by excitation at ground state absorption maximum. [f] Measured with FT-100 instrument; lifetime is shorter than instrument response of ~100 ps. [g] Measured with FT-300 instrument; minimum response is ~5 ps. Lifetime listed is dominant decay component of two- or three-component decay function. See Table S-1 for full listing of decay parameters.

Additionally, the DPAF complexes both exhibit similar, but larger, absorptivities than do the BTF congeners. In comparison to the DPAF and BTF complexes, the *cis*- and *trans*-PE2 complexes display similar, but lower molar absorptivity values. The red shifts of the absorption maxima and increases in extinction coefficients in the *trans* complexes relative to the *cis* complexes indicate increased π-conjugation that may extend through the platinum acetylide to a greater extent.

Emission spectra of the *cis*- and *trans*-platinum acetylide series are shown in Figure 4d−f. The fluorescence and phosphorescence of the complexes can be distinguished by comparing the emission in air-saturated and deoxygenated solutions—the phosphorescence is largely quenched in the presence of oxygen. As such, the bands at shorter wavelength (400−500 nm) in Figure 4d−f are the fluorescence, whereas the longer wavelength bands (500−700 nm) arise from phosphorescence. All six complexes except *cis*-BTF feature relatively weak fluorescence with low quantum yields (Table 2). The most efficient fluorescence was observed in *cis*-BTF ($\Phi_F \sim 0.04$), and the weakest emission was observed in PE2 complexes ($\Phi_F \sim 0.0005$). The generally low fluorescence yields precluded us from reliably measuring the 2PA spectra by femtosecond two-photon excitation (2PEF), and therefore the nonlinear transmission (NLT) technique was used (see below).[47] The fluorescence lifetimes (τ_F's) for the complexes were found to be very short, consistent with the low emission yields, suggesting that a rapid nonradiative process (ISC) dominates decay of the singlet state.

The fluorescence maxima of the *cis* complexes (PE2 and DPAF) are red-shifted relative to the *trans* complexes (Table 2) showing that the *cis* complexes' emissive states are slightly lower in energy than their *trans* analogues. However, no significant red shift is observed for *cis*/*trans*-BTF. The phosphorescence spectra of each *cis* and *trans* pair are almost identical, exhibiting only a small red shift from the *cis* to the *trans* congeners. This finding suggests that the luminescent $^3\pi,\pi^*$ state is the same within each set, which implies that the ligand-based chromophore, not the coordination geometry, is influencing the transition. The phosphorescence emission appears to originate from a $^3\pi,\pi^*$ state which is efficiently populated via spin−orbit coupling between the excited chromophore and the heavy metal platinum atom. Moreover, it is likely that the triplet exciton is localized on a single π-conjugated ligand and not delocalized across the metal center. This observation is consistent with similar π-conjugated platinum acetylide systems that also show a localized triplet excited state.[8,52−56] The photoluminescence spectra of the *cis* complexes also show no evidence for metal-to-ligand charge transfer (MLCT) emission involving the ancillary ligand, which would appear as broad, structureless emission bands.[19] Note that the *trans* complexes show generally higher phosphorescence quantum yields compared to their *cis* cogeners (Table 2).

The phosphorescence lifetimes and triplet decay rates are summarized in Table 3. Assuming that the triplet excited state is populated only through excitation of the ground state to form the singlet excited state, followed by ISC, then the rate of radiative decay of the triplet, k_p, can be determined by eq 1:

$$k_p = \Phi_p/(\Phi_{\mathrm{ISC}}\tau_p) \tag{1}$$

where Φ_p and Φ_{ISC} are the quantum yields of phosphorescence and intersystem crossing, respectively, and τ_p, the phosphorescence decay lifetime, is defined by $\tau_p = 1/(k_p + k_{nr})$, where k_{nr} is the rate of all nonradiative processes from the triplet excited state. Assuming that $\Phi_{\mathrm{ISC}} \sim 1$ [while it is clear that this is an assumption, given the short singlet lifetimes and low fluorescence yields, the assumption likely only introduces at most a 10% error in the estimated k_p and k_{nr} values], we compute the k_p and k_{nr} values in Table 3. The most notable aspect of these values is the difference in the radiative decay rate (k_p) for the corresponding *cis* and *trans* isomers. In particular, the radiative rates of the *trans* isomers are 3−5 times higher in each pair. This difference is most likely due to a slightly more effective spin−orbit coupling in the *trans* configuration compared to the *cis* which consequently leads to enhanced radiative decay for the former.

Table 3. Triplet Excited State Properties of *cis*- and *trans*-Platinum Acetylide Series in THF

complex	λ_{max} (nm)	τ_T[a] (μs)	τ_p[b] (μs)	k_p[c] ($10^2\ \mathrm{s}^{-1}$)	k_{nr}[d] ($10^4\ \mathrm{s}^{-1}$)
trans-PE2	577	15.4	48.9	2.2	2.0
cis-PE2	556	17.8	35.9	0.31	2.8
trans-DPAF	612	8.9	61.3	54	1.6
cis-DPAF	597	3.3	36.7	9.6	2.7
trans-BTF	507, 660	13.3	75.6	14	1.3
cis-BTF	633	6.5	80.5	5.2	1.2

[a] Triplet lifetime from transient absorption decay. Triplet lifetimes by transient absorption are shorter due to triplet−triplet annihilation. [b] Phosphorescence lifetime. [c] Radiative decay rate. [d] Nonradiative decay rate. Rates calculated by using the corresponding phosphorescence lifetime (τ_p).

Transient Absorption Spectroscopy. Nanosecond transient absorption spectra of the six platinum acetylides (Figure

5) were measured in deoxygenated THF to provide additional information about the triplet excited states. Pulsed photoexcitation of the platinum acetylide complexes with the third harmonic output (355 nm) of a Q-switched Nd:YAG laser affords transient absorption due to the triplet excited state that is strong and broad throughout most of the visible region. An additional observation in the triplet−triplet (TT) spectra is a blue shift of the *cis* complexes relative to their *trans* analogues. This is in contrast to the previously investigated stilbene-containing platinum acetylides, in which virtually identical transient absorption spectra were observed for *trans*-Pt-$(PBu_3)_2(4\text{-}ES)_2$, *cis*-Pt(dppe)$(4\text{-}ES)_2$, and *cis*-Pt(*t*-Bu-bpy)$(4\text{-}ES)_2$ (where 4-ethynylstilbene is abbreviated 4-ES and 4,4′-di-*tert*-butyl-2,2′-bipryidine is abbreviated *t*-Bu-bpy).[19] However, the stilbene complexes also exhibited short-lived triplet excited state lifetimes (~100 ns) and triplet−triplet (TT) absorption that extended from 400 to 600 nm and bore strong resemblance to that of *trans*-stilbene. In contrast, the *cis* and *trans* complexes reported herein are unable to undergo such nonradiative decay as a result of twisting; as such, the triplet excited state lifetimes of the examined complexes are much longer than the stilbene derivatives. Sun et al. reported the photophysical characterization of a *cis*-diimine platinum acetylide that contains two BTF chromophores.[34,35] Similar to the observed *cis* and *trans* complexes of this study, the *cis*-diimine platinum complex also exhibited a TT absorption spectrum that was blue-shifted approximately 50 nm from the TT absorption maximum of the *trans*-BTF analogue and a triplet lifetime of 10.8 μs.[34,35]

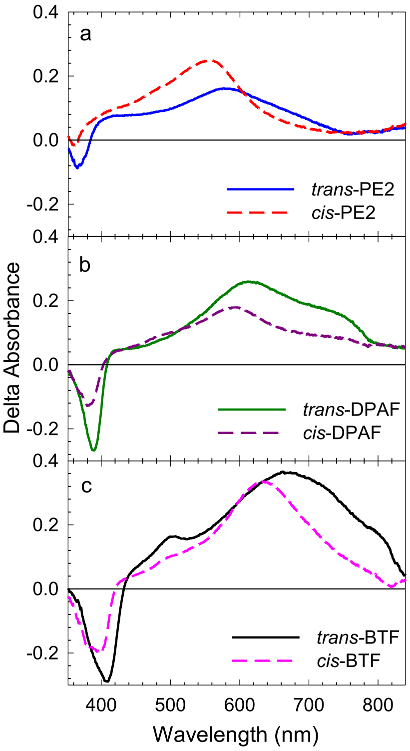

Figure 5. T_1−T_n absorption spectra in deoxygenated THF after nanosecond-pulsed 355 nm excitation of *cis*- and *trans*-Pt acetylides with PE2 (a), DPAF (b), and BTF (c) chromophores.

The superimposable nature of the phosphorescence bands within each *cis* and *trans* pair suggests that the emissive triplet excited state is the same within each set. This trend has been observed in similar platinum acetylide systems and is proposed to be the result of the triplet emissive state being localized on a single chromophore.[8,52−56] However, the observed shifts in the TT absorption between the *cis* and *trans* pairs suggest that the

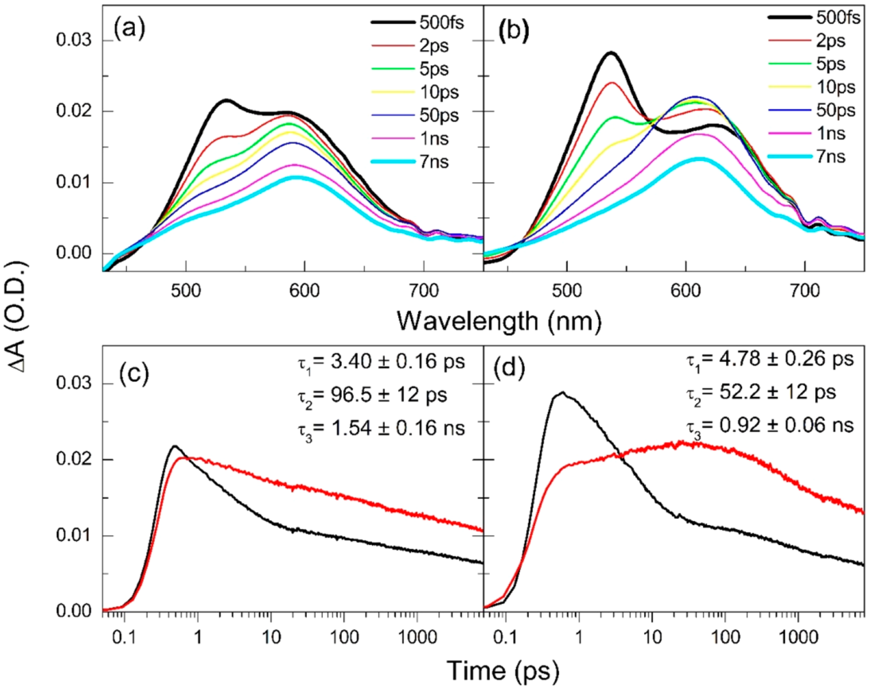

Figure 6. Femtosecond transient absorption spectra and decays of *cis*-DPAF (a) and *trans*-DPAF (b) in THF after a 380 nm excitation pulse. Kinetics traces for *cis*-DPAF (c) and *trans*-DPAF (d) at 530 (black) and 600 nm (red). The lifetimes shown in the insets were obtained by global analysis of the time-resolved transient absorption spectral data.

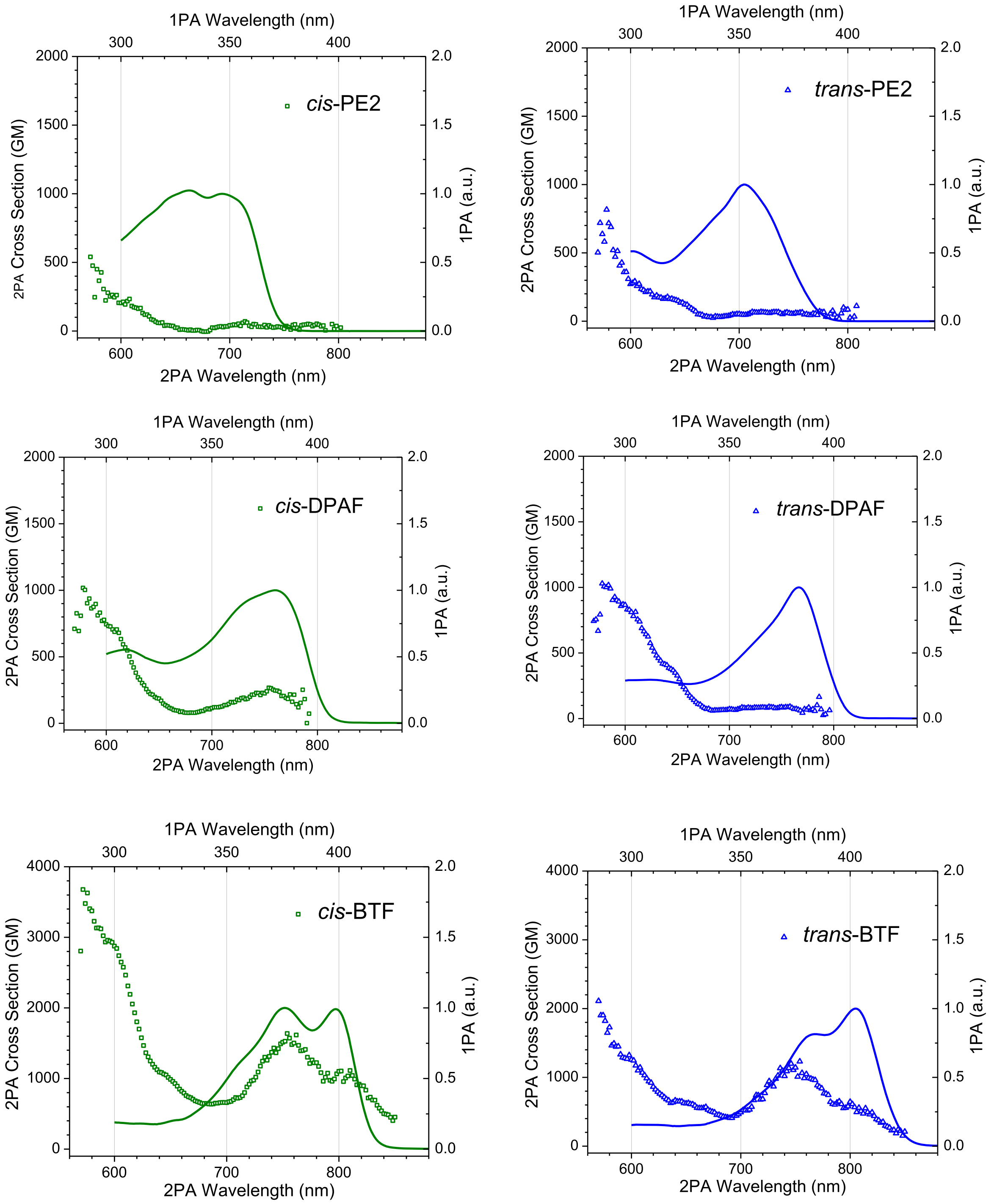

Figure 7. 2PA spectra and 2PA cross sections (left vertical axis) of *cis* (left column) and *trans* (right column) complexes in THF. Lower horizontal axes, 2PA laser wavelength; upper horizontal, 1PA transition wavelength. 1PA normalized absorption spectra in THF (solid line) are shown for comparison.

T_n state is more delocalized in the *trans* isomers, or that there is a difference in conformation for the two isomers in the triplet state that is influencing the TT absorption.

Femtosecond transient absorption spectra were measured for the DPAF and BTF complexes (Figure 6 and Figure S-1) to examine the effect of stereochemistry on the early time excited state dynamics. The spectra of both complexes exhibit complex changes in band shape and amplitude occurring over the time scale of 100 fs−7 ns. As a starting point, it is quite evident that the spectra for both complexes at the longest delay time are the same as the spectra observed on the nanoseconds to microseconds time scale (Figure 5b) and is attributed to the triplet state. However, at earlier times, there are substantial changes that are difficult to assign to specific processes. First, for both complexes, at 500 fs after excitation there is a strong and relatively narrow band with a peak at ∼525 nm which decays within 20 ps. Global analysis of the transient absorption dynamics reveals that for both complexes this relaxation has a lifetime of ∼4 ps, with a slightly faster decay in *cis*-DPAF compared to *trans*-DPAF. This lifetime of this process

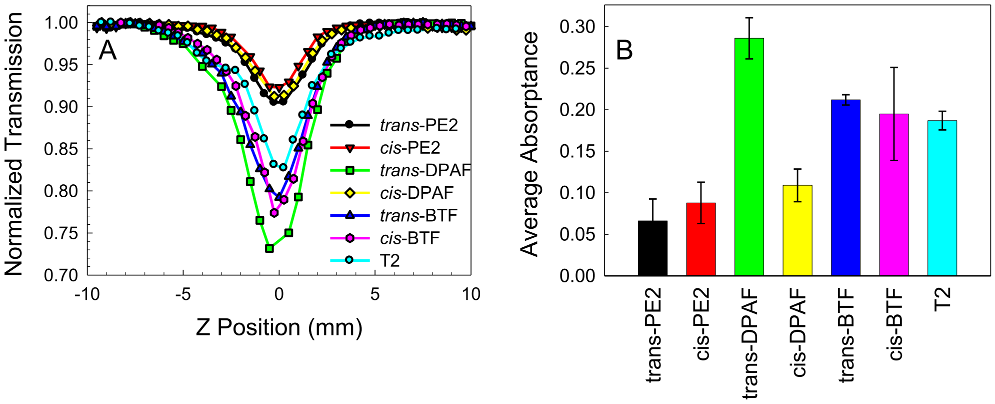

Figure 8. (A) NLA nanosecond open-aperture z-scan response (1 mM in THF; for *cis*-DPAF in 1:24 DCM/THF mixture). Samples were excited with nanosecond pulses at 600 nm and 750 μJ input energy. (B) Average nonlinear absorptance (1 − transmittance) relative to DPAF-based diplatinum acetylide, T2.

corresponds approximately to the fluorescence lifetime (Table 2), which suggests that the relaxation process corresponds to ISC, suggesting that k_{ISC} in the DPAF complexes is ~10^{11} s^{-1}. After the initial rapid spectral dynamics attributed to ISC, the changes in the spectra are more subtle, being characterized by a blue shift and decrease in amplitude of the remaining excited state absorption band centered at ~600 nm. These slower dynamics take place on the 50−500 ps time scale and are likely due to structural relaxation in the triplet excited state. Similar dynamics are observed for the *cis*- and *trans*-BTF complexes (Figure S-1); however, in these complexes the large amplitude dynamics associated with ISC occur in the 10−30 ps time scale. Note that this is consistent with the observation that the fluorescence lifetimes of the BTF complexes are longer for these complexes.

Nonlinear Absorption Spectroscopy. Femtosecond two-photon absorption measurements were performed for all six complexes with the goal of determining their two-photon absorption spectra and cross sections (σ_2 values). In this study the nonlinear transmittance (NLT) method was used,[47] as it is more accurate than the two-photon excited fluorescence (2PEF) method due to the relatively weak fluorescence for the complexes. However, at the shorter wavelength ($S_0 \rightarrow S_n$ region) it was recently reported[57] that NLT measurement gave the peak 2PA cross section 5 times as large as those obtained from the 2PEF measurements as a result of overlapping with the singlet excited state absorption which occurs on the same ultrafast time scale.

Chromophores that are centrosymmetric (quadrupolar) typically exhibit 2PA at higher energy (shorter wavelength) compared to the one-photon absorption. This is because the "dipolar" term in the 2PA cross section is zero for centrosymmetric chromophores, and therefore the $S_0 \rightarrow S_1$ transition is forbidden for 2PA (see ref 58 for a cogent discussion of the theory). As a consequence, the intensity in 2PA for centrosymmetric chromophores is in $S_0 \rightarrow S_2$ and higher transitions. By contrast, in chromophores that lack centrosymmetry (dipolar) the 2PA is dominated by the dipolar term,[58] and the 2PA spectrum is degenerate with the one-photon absorption. In this case both the 2PA and one-photon $S_0 \rightarrow S_1$ transitions are allowed. Previous studies have shown that *trans*-platinum complexes in 2PA spectra show typical quadrupolar behavior[59,60] with a forbidden 0−0 transition, more pronounced vibronic components at higher energy than the $S_0 \rightarrow S_1$ band, and allowed transitions to higher-energy states ($S_0 \rightarrow S_n$) at shorter wavelengths (λ < 650 nm). By contrast, we anticipated in this work that the corresponding *cis*-platinum complexes would exhibit typical dipolar behavior, with the 2PA spectra occurring at the same energy as the one-photon absorption spectra.

As expected, *trans*-PE2 and *trans*-DPAF do not exhibit significant two-photon absorption in the region corresponding to the 0−0 transition but instead show peaks that are not completely resolved at ~640−650 nm which overlap with the strong singlet excited state absorption at ~580−600 nm with σ_2 as large as 1000 GM (Goeppert-Mayer unit; Figure 7). However, due to the stronger electron withdrawing effect of the benzothiazole ring, *trans*-BTF shows dipolar behavior in the two-photon spectrum with significant absorption in the 0−0 transition (up to ~1000 GM) and at ~2000 GM at shorter wavelengths with contribution from the singlet ESA. For the *cis* complexes, the lack of symmetry (C_i) results in a permanent dipole moment which increases with the introduction of electron withdrawing or electron donating functionality. This typical dipolar behavior of the ligand rings decreases according to BTF > DPAF ≫ PE2. As a result, pronounced peaks in the 0−0 transition coincide with the one-photon-absorption (1PA) peaks observed for *cis*-BTF and *cis*-DPAF complexes with lower intensities for *cis*-PE2 while the corresponding *trans* isomers do not exhibit any significant peaks in this region. Large σ_2 values in the 0−0 and $S_0 \rightarrow S_n$ region were obtained for *cis*-BTF (1640 GM at 755 nm and 3680 GM at 575 nm); lower values were obtained for *cis*-DPAF (270 GM at 755 nm and 1020 GM at 580 nm) and less for *cis*-PE2 (70 GM at 715 nm and 540 GM at 570 nm).

Nonlinear absorption (NLA) of the *cis* and *trans* complexes were conducted via an open-aperture nanosecond z-scan apparatus in 1 mM solutions in THF using the 5 ns/600 nm pulses from an OPO pumped by the third harmonic output of a Q-switched Nd:YAG laser, Figure 8. (*cis*-DPAF was not readily soluble in THF at the concentrations needed for the nanosecond z-scan experiments; as such, the measurements of this sample were conducted in a 1:24 DCM/THF solution mixture.) The 600 nm excitation wavelength was selected due to the lack of appreciable ground state absorption at this wavelength for all complexes. Therefore, the excitation mechanism is presumed to occur via 2PA. The NLA response of the platinum acetylide complexes were compared to T2, a previously studied diplatinum acetylide complex with a dithiophene core and end-capped with DPAF chromophores that exhibits strong NLA response at 600 nm excitation (structure in Figure S-2).[61] Figure 8A shows representative nanosecond z-scan results for the seven complexes. Figure 8B shows the average percent absorptance (absorptance = 1 − transmittance) at the laser focus, $z = 0$ mm, for the seven complexes as the average of multiple z-scan trials. *trans*-DPAF exhibits the strongest overall NLA response, with an average absorptance of 0.29, whereas *cis*-DPAF exhibits a weaker absorptance of 0.11. The *cis*- and *trans*-BTF pair exhibit similar responses of 0.20 and 0.21, respectively. Both PE2 complexes exhibit NLA response, but markedly less than the other complexes. These results suggest that chromophore selection (e.g, DPAF vs BTF) is more critical to the NLA response strength than is the geometry (e.g., *cis* vs *trans*) at the platinum center. However, it is clear *trans*-DPAF exhibits noticeably stronger attenuation than its *cis* counterpart.

General Discussion. As noted in the Introduction, many previous studies have explored the photophysics and nonlinear absorption of platinum acetylide complexes.[2−4,8,47,60,62,63] It is reasonably well-established that complexes that feature acetylide ligands with π-donor or π-acceptor structures display pronounced NLA for nanosecond laser pulses via a mechanism that combines 2PA from the singlet ground state ($S_0 \rightarrow S_n$) with excited state absorption (ESA) due to the long-lived triplet state.[4,8,47] The objective of the current investigation was to explore whether the stereochemistry at the Pt(II) center elicits any effects on the photophysics of the complexes, and on their two-photon absorption and long pulse NLA response. Taken together, the results presented herein reveal that the stereochemistry has relatively minor effects on the complexes' photophysics. This is not be surprising, given that the triplet excited states, which dominate the photophysics, are mainly localized on a single acetylide ligand.[14,52,56] Nevertheless, careful consideration of the data presented here suggests that there are subtle, yet potentially significant, differences in the photophysics of the *trans* and *cis* complexes. First, as noted above (Table 2), the phosphorescence yields for the *trans* isomers are moderately enhanced relative to the corresponding *cis* forms. This effect is due to enhanced radiative decay rates (Table 3), which points to the possibility that the spin−orbit coupling induced by the Pt(II) metal center is enhanced in the *trans* isomers. Some insight into the origin of enhanced comes from the comparison of the acetylide −C≡C− bond lengths in corresponding *cis* and *trans* isomers. The crystal structure comparison of *cis*- and *trans*-PE2 shows longer platinum −C≡C− bond lengths in the *trans* complexes, suggesting a higher degree of dπ−π* back-bonding. However, this trend does not extend to the BTF complexes, so a definitive correlation between the length of the acetylide CC bond, back-bonding, and spin−orbital coupling remains elusive.

Second, the femtosecond two-photon-absorption spectra revealed that *trans* complexes show a typical quadrupolar behavior with no significant peaks in the 0−0 transition of the $S_0 \rightarrow S_1$ band whereas the *cis* complexes in the lack of C_i symmetry exhibit more likely dipolar behavior with a significant 2PA peak cross section in the 0−0 transition region (up to 1670 GM by the peak cross section for *cis*-BTF). At the shorter wavelengths (<650 nm) both *cis* and *trans* isomers show large two-photon absorption (up to 3700 GM for *cis*-BTF) to the higher energy state ($S_0 \rightarrow S_n$) with presumably significant contribution of ESA from the singlet manifold ($S_1 \rightarrow S_n$).

The triplet excited states were further probed via triplet−triplet transient absorption. The six complexes exhibit relatively strong and broad transient absorption across most of the visible region. The transient absorption maxima appear to be dependent on chromophore selection, whereas the delta absorption strength observed is more dependent on the stereochemistry of the platinum center.

The nanosecond NLA responses of the complexes were measured via a open-aperture z-scan using 600 nm/5 ns pulses benchmarked relative to the previously studied complex T2. The only clear correlation to emerge from the z-scan is that the DPAF and BTF complexes give rise to much greater attenuation compared to the PE2 complexes. This is due to the fact that the former have significantly greater σ_2 values in the 600 nm region. However, disappointingly there is not a clear correlation with respect to complex stereochemistry in the long pulse attenuation results. While *trans*-DPAF is clearly much more effective compared to *cis*-DPAF, a analogous difference is not seen for the *cis/trans*-BTF pair.

SUMMARY AND CONCLUSIONS

An investigation was carried out to compare the photophysics and nonlinear absorption behavior of a series of Pt acetylide complexes that consist of *cis* and *trans* isomer pairs. The results find that, in general, the photophysical properties are not strongly influenced by stereochemistry. This may not be surprising given that the long-lived excited states are mainly localized on a single π-conjugated ligand. However, there are substantial differences in the two-photon-absorption spectra that are related to the effect of complex stereochemistry on the local symmetry of the π-conjugated chromophores. The net effect is that the *trans* isomers, which are centrosymmetric, display weak 2PA in the spectral region degenerate with the 1PA absorption. By contrast, the *cis* isomers, which lack centrosymmetry, feature relatively strong 2PA in the degenerate spectral region.

Despite the lack of significant differences in photophysics, overall this family of Pt acetylide chromophores exhibits pronounced nonlinear absorption in the red and near-infrared spectral regions arising from instantaneous 2PA combined with excited state absorption due to the long-lived triplet excited state. The properties of these complexes are favorable for application of the chromophores in high performance frequency and temporally agile nonlinear absorption materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b07823.

Complete synthesis procedures, analytical data, NMR data, and X-ray crystallographic files of *cis*-PE2 and *cis*-BTF (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kirk.schanze@utsa.edu.
*E-mail: muhammad.younus@utsa.edu.
*E-mail: rebane@physics.montana.edu.

ORCID

Silvano R. Valandro: 0000-0002-4652-768X
Aleksander Rebane: 0000-0003-4330-5544

Kirk S. Schanze: 0000-0003-3342-4080

Notes

The authors declare no competing financial interest.

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