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Phenylene Vinylene Platinum(II) Acetylides with Prodigious Two-Photon Absorption

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Supporting Information

ABSTRACT: The linear and nonlinear optical properties of a series of linear and cross-conjugated platinum(II) acetylide complexes that contain extended *p*-(phenylene vinylene) chromophores are reported. The complexes exhibit very high femtosecond two-photon absorption (2PA) cross section values (σ_2 up to 10 000 GM), as measured by nonlinear transmission (NLT) and two-photon excited fluorescence (2PEF) methods. The large 2PA cross sections span a broad range of wavelengths, 570−810 nm, and they overlap with the triplet excited state absorption. Spectral coincidence of high cross section 2PA and triplet absorption is a key feature giving rise to efficient dual-mode optical power limiting (OPL).

Organometallic complexes comprising a platinum(II) acetylide core linked with different *π*-conjugated chromophores are promising materials for applications requiring a strong nonlinear optical response.[1] In dual-mode optical power limiting (OPL),[2] a chromophore first undergoes ultrafast two-photon absorption (2PA) to produce the singlet state, followed by rapid intersystem crossing promoted by the heavy atom effect to afford the triplet state, which can subsequently absorb via the T_1−T_n transition. Even though a number of Pt-complexes have been demonstrated to act as efficient triplet absorbers, their maximum intrinsic 2PA cross sections are relatively low,[1e] thus impairing the practical usefulness of materials available to date. This problem is exacerbated by the fact that the currently attainable maximum peak 2PA values, $\sigma_2 \sim 10^2$−10^3 GM, typically occur only over a relatively narrow range of wavelengths.[1d]

π-Conjugated chromophores featuring triphenylamine moieties at the termini of *p*-(phenylene vinylene) repeat units are known to exhibit very high 2PA cross sections in the visible- and near-IR range of wavelengths,[3] especially if several such chromophores are linked together in a dendritic structure.[3b] However, lacking incorporated heavy atoms, the triplet−triplet (T−T) absorption in such systems is marginal. Here we combine oligomeric *p*-(phenylene vinylene) *π*-conjugated chromophores (OPV) with platinum(II) centers to achieve more than 1 order of magnitude enhancement of peak 2PA, up to $\sigma_2 \sim 10^3$−10^4 GM, while retaining the benefits of the heavy atom-assisted high intersystem crossing efficiency along with a nearly perfect match between the broad 2PA spectrum and the T−T absorption wavelength.

In order to probe the nonlinear optical response of the new organometallic chromophores, we experimentally evaluate the femtosecond 2PA cross sections across the broad wavelength range 570−1070 nm by using two alternative methods, where the first relies on two-photon excited fluorescence (2PEF) and the second directly detects the intensity-dependent nonlinear transmission (NLT). The ability to compare 2PA cross sections measured by two different approaches is critical in this study. In particular, the accuracy of the 2PEF method suffers from the fact that the fluorescence signal is weak due to the efficient intersystem crossing that is characteristic of platinum(II) acetylide chromophores.[1a] In order to overcome this shortcoming, in the present study we developed and utilized a novel NLT experimental arrangement that features automated data collection and accurate measurement of small changes in the intensity-dependent transmission ($\Delta T < 0.1\%$) as a function of the input laser wavelength (see Supporting Information (SI)).

The series of *p*-phenylene vinylene platinum(II) acetylides **TPV0**, **TPV1**, **TPV2**, **TPV1-Ph**, **crossTPV1**, **crossTPV3** (Figure 1) were prepared by CuI catalyzed reaction of *cis*-$Pt(PBu_3)_2Cl_2$ or *trans*-(chloro)(phenylacetylide)-*bis*-(tri-n-butylphosphine)platinum(II) and the corresponding terminal acetylenes in diethylamine with good yields (58−96%).[4] The terminal acetylene precursor compounds were synthesized by multistep procedures that relied on the Wittig reaction as a key step for chromophore construction (see SI for details). Complex **TPV2-T2** was synthesized by a sequential one-pot reaction using 2 equiv of the corresponding terminal alkyne, *cis*-$Pt(PBu_3)Cl_2$, and 1 equiv of 5,5′-diethynyl-2,2′-bithiophene (67%). Full synthetic details and characterization data for all of the compounds are included as SI, including the X-ray crystal structure of **crossTPV1**.

The one-photon photophysical properties of the set of chromophores are summarized in Table 1, and additional data, including full absorption and emission spectra, are provided in the SI.

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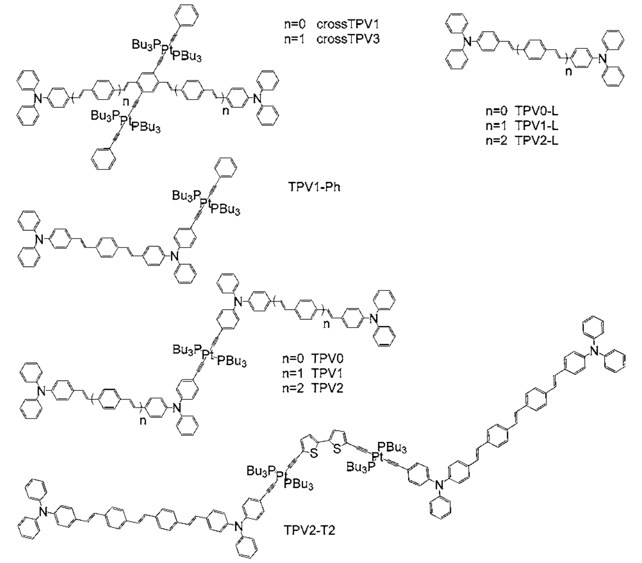

Figure 1. Structures and acronyms for *p*-(phenylene vinylene) platinum(II) acetylide chromophores.

Table 1. One-Photon Photophysical Properties in THF Solution

name	λ_{abs}[a] (log ε)	λ_{fl}[a]	Φ_{fl}[b]	τ_{fl}, ns	$\lambda_{T\text{-}T}$[a]	$\tau_{T\text{-}T}$, μs	Φ^1O_2[c]
TPV0	395 (5.13)	459	0.10	0.18	585	0.3	0.13
TPV1	415 (5.32)	502	0.30	0.78	678	1.19	0.73
TPV2	424 (5.47)	525	0.52	1.15	687	67.9	0.51
TPV1-Ph	415 (4.97)	502	0.46	1.44	671	0.59	0.35
TPV2-T2	423 (5.39)	522	0.28	0.66	683	0.79	0.79
crossTPV1	355 (5.05)	476, 507	0.01	<0.1[d]	662	0.85	0.83
crossTPV3	415 (5.03)	501, 537	0.04	<0.1[d]	719	0.43	0.98

[a] Wavelengths are in nm. [b] Measured at rt using 9,10-diphenylanthracene in cyclohexane as a standard (Φ_{fl} = 0.75).[5] Estimated error in values is ±15%. [c] Measured in $CDCl_3$ using terthiophene as a standard (Φ^1O_2 = 0.73).[6] Estimated error in values is ±15%. [d] Lifetime is less than the instrument time resolution which is ~100 ps.

For the **TPVn** series, the peak molar absorptivity values increase with the length of the π-conjugated unit, while the absorption and fluorescence maxima red-shift in the same sequence. The cross-conjugated chromophores exhibit very broad absorption for λ < 525 nm, with two band maxima. For **cross-TPV1** the absorption maximum is at 355 nm, and as the length of the OPV unit increases in **crossTPV3**, the long wavelength band ($\lambda \approx$ 415 nm) becomes more pronounced. These trends suggest that the shorter wavelength absorption arises from the Pt-CC-phenylene-CC-Pt unit,[7] while the longer wavelength transition arises from the OPV chromophore axis. Inspection of the fluorescence quantum yields and lifetimes (Φ_{fl} and τ_{fl}) in Table 1 reveals several interesting trends. First, for the **TPVn** series Φ_{fl} and τ_{fl} increase with the length of the OPV chromophore. This suggests that a competing nonradiative decay process (likely intersystem crossing, ISC, *vide infra*) becomes less efficient as the OPV length increases. This effect is consistent with decreased spin–orbit coupling as the size of the OPV ligand increases, due to less mixing of Pt-centered orbitals in the frontier orbitals. Second, **TPV2-T2** and the cross conjugated chromophores exhibit comparatively low Φ_{fl} and τ_{fl} values, suggesting that ISC is efficient in these systems.

In order to provide more insight into the triplet states of the chromophores, ns–μs transient absorption spectroscopy was carried out. Figure 2 shows representative transient absorption spectra, and the full set of spectra is in the SI. Each of the chromophores exhibits strong, broad T–T absorption throughout the visible and near-IR regions, with bleaching corresponding to the ground state absorption. The T–T bands are noticeably narrower and more intense for the cross-conjugated complexes, signaling that triplet chromophore is influenced by the Pt centers.

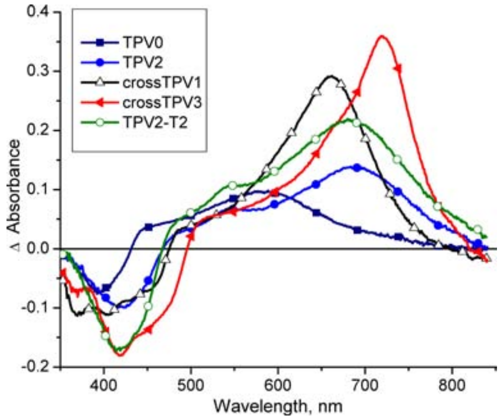

Figure 2. Transient absorption difference spectra of selected Pt-complexes, following nanosecond-pulsed 355 nm excitation, ca. 10 mJ/pulse in argon-purged THF.

The triplet lifetimes are listed in Table 1 ($\tau_{T\text{-}T}$), and it can be seen that $\tau_{T\text{-}T}$ increases substantially with OPV length. This trend parallels that seen in the fluorescence lifetimes, and it is consistent with decreased Pt-induced spin–orbit coupling with increased length of the OPV.[8] In addition, the triplet lifetimes of **TPV2-T2** and the cross-conjugated chromophores are comparatively low, suggesting significant spin–orbit coupling in these systems. Finally, the last column of Table 1 lists the singlet oxygen yields observed using the chromophores as sensitizers. These values in general reflect lower limits for the ISC yields (Φ_{ISC}), and the data indicate in general that the yields are high and they are largest for **TPV1**, **TPV2-T2**, and the cross-conjugated chromophores. In most cases $\Phi_{fl} + \Phi^1O_2 \approx 1$, which supports the notion that $\Phi_{ISC} \approx \Phi^1O_2$ and further that the dominant paths for relaxation of the singlet state are via fluorescence and intersystem crossing.

The 2PA absorption spectra and absolute cross section values were measured with the wavelength tunable output of an amplified Ti-sapphire source (80–120 fs) by using the NLT and 2PEF methods (pulse repetition rates 100 Hz and 1 kHz, correspondingly) as described in the SI. Figure 3 shows plots of 2PA cross section vs wavelength over the 570–1070 nm range (lower horizontal scale) for all seven Pt-acetylide chromophores, along with three representative free ligands in THF solution.

In general, data measured using the NLT method (blue filled symbols) correlate very well with those measured by the 2PEF method (red open symbols). The 2PEF-based values of **TPV0-L** and **TPV1-L** correspond well with those reported earlier.[3] A

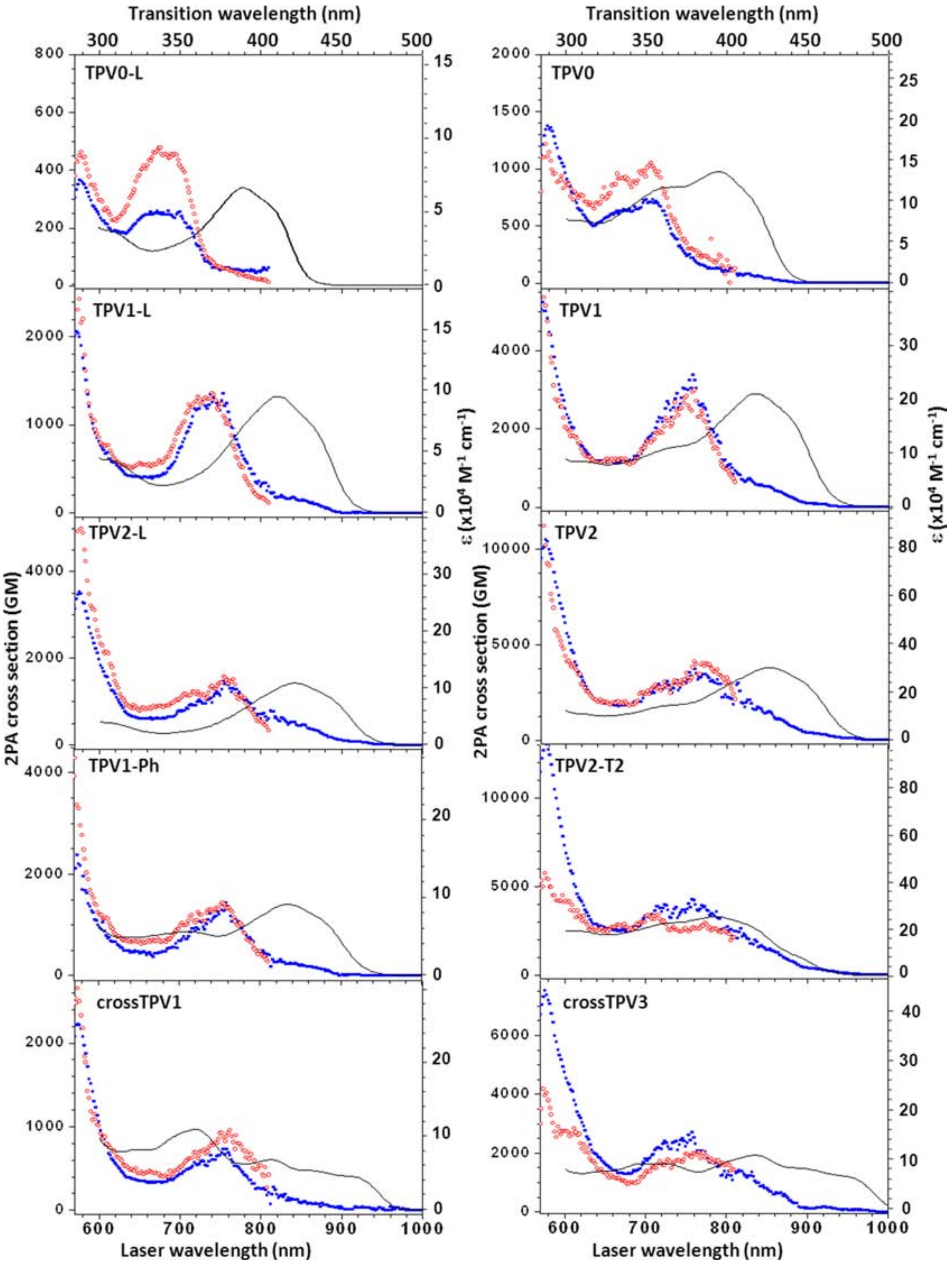

Figure 3. 2PA spectra of Pt-complexes and their chromophore ligands in THF solution measured by NLT method (blue filled symbols) and by fluorescence excitation method (red open symbols). Linear absorption spectrum (black line) calibrated in transition wavelength (upper horizontal scale) is shown for comparison.

certain discrepancy in the NLT peak values in **TPV0-L** and **TPV0** may be caused by partial bleaching of high concentration samples used in the NLT experiment. The linear absorption spectrum of each chromophore is shown in Figure 3 for comparison (black line).

Several features are significant with respect to the 2PA spectra of the chromophores. Specifically, each system exhibits pronounced 2PA with σ_2 greater than 500 GM over a broad spectral window, in some cases ranging from 600 to 900 nm. In addition, the peak 2PA cross sections for the complexes that contain the longest OPV segment exhibit $\sigma_2 > 10\,000$ GM. Finally, the cross-conjugated chromophores exhibit particularly broad and intense 2PA spectra, with $\sigma_2 > 1000$ GM between 600 and 800 nm. In each case, there is an outstanding overlap between the 2PA absorptions and the T-T absorptions (Figure 2), which is optimal when considering application of the chromophores in dual-mode OPL. Preliminary z-scan experiments using nanosecond pulses support the idea that these chromophores are very effective pulse limiters (see SI, Figure S61b)

The 2PA spectra of the complexes show a distinct peak at transition wavelengths shorter than the S_0−S_1 transition in the one-photon absorption (1PA) spectra, which can be explained by alternative parity selection rules for 1PA and 2PA transitions.[3c] By analogy to the 1PA spectra, the 2PA bands red-shift with increasing π-conjugation length. Note that the peak 2PA values increase approximately 2-fold going from single ligand chromophores **TPV0-L** and **TPV1-L** to the corresponding Pt-complexes **TPV0** and **TPV1**, and more than 2-fold going from **TPV2-L** to **TPV2**. The observation that in **TPV-T2** and **crossTPV3** the NLT shows larger 2PA cross sections at the shorter wavelengths than 2PEF may be due to the excited state absorption occurring from excited singlet state during the duration of the laser pulse, thus further augmenting the strong nonlinear-optical response.

In conclusion, a series of *p*-(phenylene vinylene) substituted platinum acetylide chromophores have been synthesized and investigated under one- and two-photon excitation. Nanosecond transient absorption shows that all of the chromophores feature strong, broad T−T absorption in the visible and near-infrared. The 2PA spectra for the chromophores were measured by using the traditional 2PEF approach, and with a newly developed NLT approach, and two approaches afford consistent spectral profiles and absolute maximum σ_2 values. The chromophores feature considerable σ_2 in a spectral region that overlaps nicely with the region of large T−T absorption. The results suggest that the OPV-based platinum acetylide systems are promising candidates for practical application as the active chromophores in broad temporal and frequency responsive optical power limiting materials. Investigations in progress seek to characterize the efficacy of these chromophores to exhibit a broad-band nonlinear absorption response in solution and in solid matrices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray structure of **crossTPV1**, experimental details, characterization and photophysical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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