

Polymer Monoliths Containing Two-Photon Absorbing Phenylenevinylene Platinum(II) Acetylide Chromophores for Optical Power Limiting

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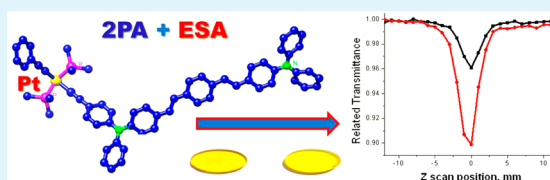
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S Supporting Information

ABSTRACT: A series of platinum(II) acetylide complexes containing *p*-phenylenevinylene and moieties end-capped with triphenylamine groups have been incorporated into poly(methyl methacrylate) (PMMA) monoliths for optical power limiting applications. The one- and two-photon photophysical properties were investigated and compared to the photophysical properties in THF. The absolute two-photon absorption cross-section values for the monolith samples were measured and are comparable to the values obtained in solution. In the PMMA monoliths, the complexes retained the important two-photon absorption and reverse saturable absorption properties necessary for optical power limiting via dual mode mechanism, and their strong nonlinear absorption property was demonstrated by the open-aperture Z-scan method. Photostability studies of the *p*-phenylenevinylene platinum(II) acetylide complexes showed two photodegradation processes: a *trans*-to-*cis* isomerization and a singlet-oxygen sensitized self-oxidative cleavage. The photostability of the least photostable complex TPV0 was increased upon incorporation into a PMMA matrix.

KEYWORDS: platinum(II) acetylide, optical power limiting, nonlinear absorption, two-photon absorption, reverse-saturable absorption



INTRODUCTION

Platinum(II) acetylide complexes containing two-photon absorption chromophores and possessing strong triplet excited state absorption (ESA) have been studied for their nonlinear absorption properties for many years with a focus on optical power limiting materials.^{1–12} When the two-photon absorption (2PA) and triplet–triplet absorption spectra have significant overlap, these complexes can exhibit particularly efficient nonlinear absorption due to a 2PA/ESA dual-mode mechanism as shown in Figure 1.^{5–15} At the outset, instantaneous two-photon absorption occurs, populating the singlet excited state

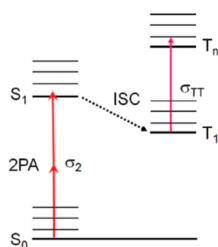


Figure 1. Four-level energy level diagram illustrating the dual-mode mechanism for nonlinear absorption involving simultaneous two-photon absorption and triplet–triplet excited state absorption. Reprinted with permission from ref 13, copyright 2010 American Chemical Society.

S_1 .¹⁶ Spin–orbit coupling due to the heavy metal Pt center(s) promotes high-efficiency intersystem crossing from the first singlet excited state to the lowest energy triplet state T_1 . A subsequent transient absorption transition to a higher triplet state, T_n , which in these types of complexes is a strongly allowed process as reflected by large molar extinction coefficients, readily gives rise to absorption of additional photons once a significant triplet population is achieved.^{1,3,17} Dual-mode nonlinear absorption utilizing both 2PA and ESA has broad temporal response, offering protection from both short pulses (fs–ps) and longer pulses (ns– μ s).^{3,14,17,18}

Optical power limiting (OPL) materials allow the transmission of low intensity light while strongly attenuating high intensity light (over a certain threshold) and are used in applications involving the protection of sensitive optical detectors, such as the human eye, from being damaged by exposure to laser light.^{14,19,20} The key property in OPL materials is strong nonlinear absorption, which makes platinum acetylide complexes good candidates for OPL applications. A significant amount of the research on platinum acetylides for OPL properties has been reported in solution experiments, but recently, attention has shifted to the incorporation of these complexes into solid-state materials in order to facilitate their

Received: February 13, 2015

Accepted: April 29, 2015

Published: April 29, 2015

use in OPL applications. Inorganic sol–gel glasses offer good stability and excellent optical quality,²¹ and platinum(II) acetylides incorporated into sol–gel materials have demonstrated good optical power limiting properties;^{22,23} however, this method of sample preparation is time-consuming, requires careful adjustment of pH and temperature, and typically requires additional functionalization of the active chromophores to reach sufficiently high concentrations for substantial optical power limiting. Polymer glasses, such as those made with poly(methyl methacrylate) (PMMA), make good solid-state hosts due to their easy processability, high optical transparency, and ability to be cut and polished to achieve good optical quality. Westlund and co-workers incorporated platinum(II) acetylides containing phenylene ethynylene units into PMMA polymer glasses as both blended and covalently bonded materials and found that the materials showed a strong attenuation of transmitted laser energy, with the highest optical power limiting properties shown by the noncovalently blended glasses.²⁴ We recently reported covalent attachment of Pt-acetylide 2PA chromophores into a PMMA host matrix and demonstrated that the resulting materials exhibit dual-mode nonlinear absorption.²⁵

The series of *p*-phenylenevinylene platinum(II) acetylide complexes in Figure 2 were recently shown to exhibit extraordinarily large two-photon absorption (2PA) cross-section values (up to 10 000 GM).^{26,27} In this work, we explored two series of chromophores to elucidate their structure–property relationships for optical power limiting. In particular, the “linear” series TPVn has two oligo *p*-phenyl-

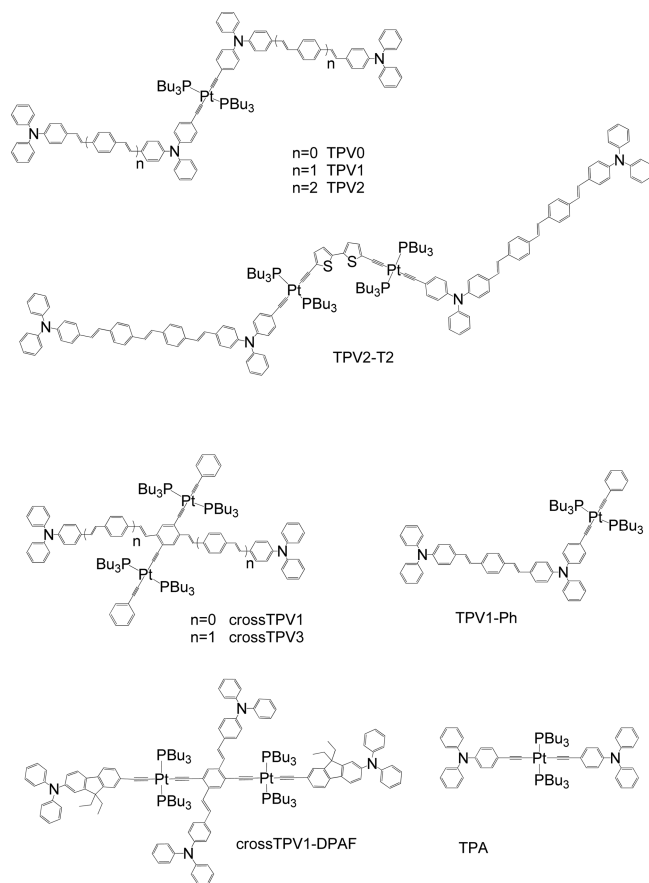


Figure 2. Structures and acronyms for the *p*-phenylenevinylene platinum(II) acetylides.

enevinylene (OPV) chromophores linked to a platinum center through a triphenylamine group with an increasing number OPV units ($n = 0–2$, where n is the number of phenylenes between the terminal triphenylamine groups). The complex TPV2-T2 has two OPVn chromophores each connected to a platinum atom that is linked through a bithiophene (T2) bridge. The cross-conjugated series crossTPVn feature a pair of cross-conjugated axes: one that contains an OPV unit and a second that consists of an organometallic platinum acetylide where two platinum atoms are attached to the central phenylene unit of the OPV ($n = 1–3$, where n is the number of phenylene rings between the terminal triphenylamine groups in the OPV axis). The complex crossTPV1-DPAF contains two diphenylaminofluorene (DPAF) groups linked to the platinum centers of the organometallic axis. The DPAF units are of interest, as previous work has demonstrated that this particular chromophore exhibits strong 2PA absorption.^{5,13,16,28}

In this study, we continue the investigation of *p*-phenylenevinylene platinum(II) acetylide complexes with measurements of the triplet molar extinction coefficients and photostability studies, along with elucidating the photophysical properties and optical power limiting properties of these chromophores when incorporated into PMMA glass monoliths (Figure 3). The one-photon photophysics and 2PA properties



Figure 3. PMMA monoliths containing *p*-phenylenevinylene platinum(II) acetylide complexes for optical power limiting applications: (left) crossTPV1-DPAF and (right) TPV2-T2.

in the solid-state are reported, including the absolute 2PA cross sections. The solid-state properties and optical power limiting performance for the solid monolith materials are compared to those of the same series of complexes as previously reported in solution.

RESULTS AND DISCUSSION

Photophysical Properties of Molecular Complexes and Monoliths. A preliminary report described the synthesis and photophysical characterization of some members of the series of complexes that were used in this investigation.²⁶ Here, we provide a summary of the results for all members of the complexes. Photophysical studies on the series of complexes shown in Figure 2 were performed in THF solution to explore the structure–property relationship of increasing OPV chain length. Table 1 summarizes the photophysical properties for the families of linear and cross-conjugated complexes in THF solution.²⁶

The absorption spectra of the complexes in THF solution are shown in Figure 4. All complexes are yellow in color and have no significant ground state absorption at wavelengths longer than 525 nm, a desired property for nonlinear absorption chromophores. The extended phenylenevinylene units exhibit red-shifted absorption due to their increased conjugation length. In the cross-conjugated complexes, as the length of

Table 1. Summary of One-Photon Photophysical Properties in THF

name	λ_{abs}^a	$\epsilon (\times 10^4)^a$	λ_{fl}^a	Φ_{fl}^b	$\langle \tau_f \rangle$ (ns)	$\lambda_{\text{T-T}}^a$	$\epsilon_{\text{T}} (\times 10^4)^a$	$\tau_{\text{TA}} (\mu\text{s})$	$\Phi^1\text{O}_2^c$
TPV0	395 ^e	13.5 ^e	459 ^e	0.10 ^e	0.18 ^e	585 ^e	7.4	0.3 ^e	0.13 ^e
TPV1	415 ^e	20.9 ^e	502 ^e	0.30 ^e	0.78 ^e	678 ^e	11.0	1.19 ^e	0.73 ^e
TPV2	424 ^e	29.5 ^e	525 ^e	0.52 ^e	1.15 ^e	687 ^e	10.0	67.9 ^e	0.51 ^e
TPV2-T2	423 ^e	24.5 ^e	522 ^e	0.28 ^e	0.66 ^e	683 ^e	39.3	0.79 ^e	0.79 ^e
TPV1-Ph	415 ^e	9.33 ^e	502 ^e	0.46 ^e	1.44 ^e	671 ^e	18.1	0.59 ^e	0.35 ^e
crossTPV1	355 ^e	11.2 ^e	476 ^e	0.01 ^e	<0.1 ^{d,e}	662 ^e	7.7	0.85 ^e	0.83 ^e
	405 ^e	7.6 ^e	507 ^e						
crossTPV3	343 ^e	9.5 ^e	501 ^e	0.04 ^e	<0.1 ^{d,e}	719 ^e	8.1	0.43 ^e	0.98 ^e
	415 ^e	10.7 ^e	537 ^e						
crossTPV1-DPAF	301 ^f	8.7 ^f	478 ^f	0.005 ^f	<0.1 ^{d,f}	660 ^f	11.8	0.96 ^f	NA
	381 ^f	21.4 ^f	511 ^f						

^aWavelengths of absorption and emission maxima are in nm. Extinction coefficients in units of $\text{M}^{-1}\text{cm}^{-1}$. ^bMeasured at RT using 9,10-diphenylanthracene in cyclohexane as a standard ($\Phi_{\text{fl}} = 0.75$).²⁹ ^cMeasured in CDCl_3 using terthiophene as a standard ($\Phi^1\text{O}_2 = 0.73$).³⁰ ^dLifetime is less than the instrument time resolution which is ~ 100 ps. ^ePreviously published data.²⁶ ^fPreviously published data.²⁷

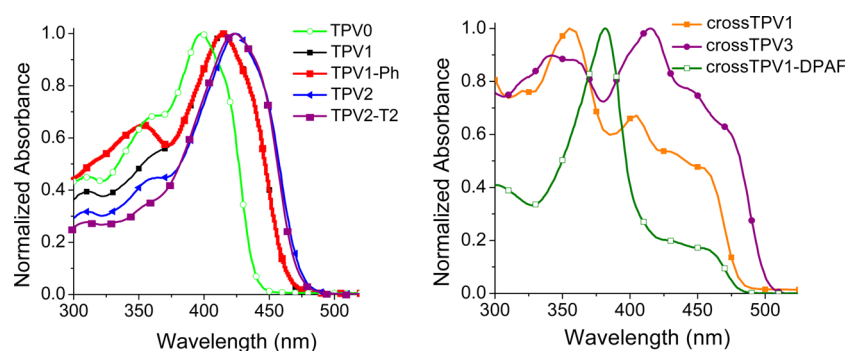


Figure 4. Normalized absorption spectra for the (left) linear and (right) cross-conjugated phenylenevinylene platinum(II) acetylide complexes in THF.

the OPV unit is increased, the long wavelength band ($\lambda \approx 415$ nm) becomes more pronounced, such as in crossTPV3. This suggests that the shorter wavelength band is due to the Pt-CC-phenylene-CC-Pt unit while the longer wavelength transition arises from the OPV chromophore axis.

The fluorescence quantum yields and lifetimes for the complexes in solution are listed in Table 1 and demonstrate several interesting trends. For the linear TPVn series, the fluorescence quantum yields and lifetimes increase with the length of the OPV segments. This suggests that intersystem crossing (ISC) becomes less efficient with increased conjugation along the OPV chromophore due to decreased spin-orbit coupling. The decrease in spin-orbit coupling arises because the contribution of the Pt centered orbitals to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) wave functions decreases as the π -conjugated system becomes larger.⁵ Singlet oxygen quantum yields provide an indirect measure of the triplet yield, $\Phi_{\text{ISC}} \approx \Phi^1\text{O}_2$. In agreement, with the increasing fluorescence quantum yields, the singlet oxygen yields decrease with increasing OPV length, except for TPV0 which exhibits considerable singlet oxygen-sensitized photodegradation as discussed later. (This suggests that the reduced singlet oxygen yield for TPV0 is because the complex quenches singlet oxygen.) TPV2-T2 has a significantly lower fluorescence lifetime and lower fluorescence quantum yield than TPV2 demonstrating that ISC is particularly efficient in the presence of the two platinum atoms bridged by bithiophene in the linker between the two OPV chromophores. The crossTPVn complexes have very low fluorescence quantum yields (<5%)

and short fluorescence lifetimes (<100 ps) indicative of especially efficient ISC promoted by the two platinum centers attached to the center phenyl ring.

PMMA monoliths that contain the organometallic chromophores were prepared by in situ polymerization of methyl methacrylate (MMA) with azoisobutyronitrile (AIBN) initiator under nitrogen atmosphere, as described in the Experimental Section, with final chromophore concentration between 1.2–2.8 mM. The absorption spectra of the PMMA monoliths could not be measured because the absorbance was too large. The photoluminescence spectra of the monoliths for selected Pt-complexes compared to the spectra obtained in argon-purged THF solution are shown in Figure 5. Photoluminescence spectra for all of the PMMA monolith samples can be found in the Supporting Information. Phosphorescence is not observed from the complexes in either solution or monoliths. For the linear series, the emission maxima of the monolith samples are increasingly blue-shifted compared to measurements in solution as the OPV segment is lengthened (the relative shifts increasing from ~ 1 nm for TPV0 to ~ 24 nm in TPV2-T2) probably due to interaction of the chromophores with the polar PMMA host. In the cross-conjugated complexes, the blue-shift in the emission spectra is much smaller (2–5 nm) between solution and solid-state measurements. In addition, the fluorescence of crossTPVn complexes display pronounced vibrational structure, which may be due to the steric constraints imposed by the cross-conjugated structures. CrossTPV1-DPAF shows a much broader emission, which may be due to emission from multiple chromophore segments, and the altered shape in the PMMA matrix may be due to internal filter effect (overlap of ground

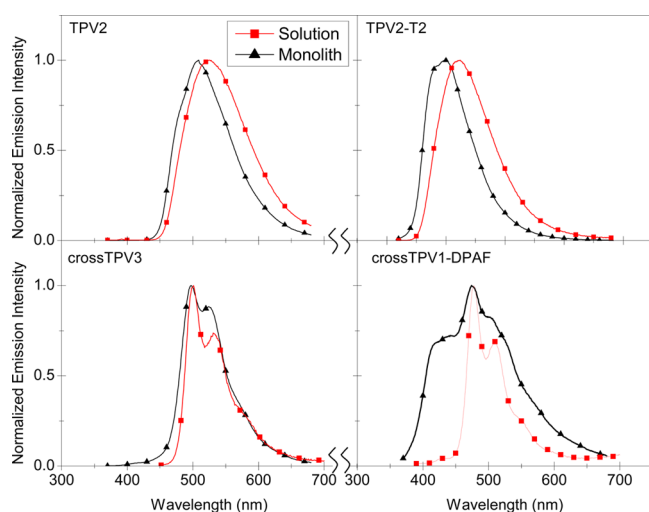


Figure 5. Representative photoluminescence spectra of selected complexes TPV2, TPV2-T2, crossTPV3, and crossTPV1-DPAF (red) in argon-purged THF solution and (black) in the PMMA monoliths.

state absorption with the fluorescence) on the blue side of the emission band.

Nanosecond transient absorption (TA) spectroscopy was used to measure the triplet–triplet absorption spectra and triplet decay lifetimes of the complexes in solution and monoliths. Spectra of selected complexes are shown in Figure 6, and the spectra of the rest of the complexes are provided in

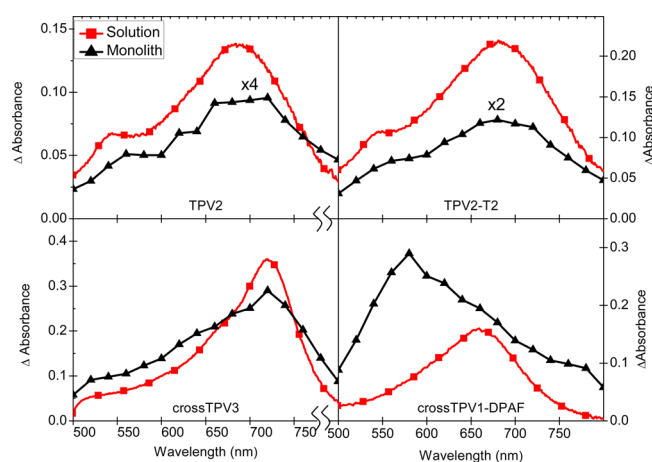


Figure 6. Representative transient triplet–triplet absorption spectra obtained for selected complexes TPV2, TPV2-T2, crossTPV3, and crossTPV1-DPAF (red) in THF solution and (black) in the PMMA monoliths following nanosecond pulsed excitation ($\lambda_{\text{exc}} = 355$ nm). Pulse energies were approximately 5 mJ/pulse for solution measurements and 600 μ J/pulse for monolith measurements.

the Supporting Information. The nanosecond TA difference spectra in solution show strong, broad triplet–triplet absorption throughout the visible and near-IR, and the strongest absorption is observed for complexes with the longer conjugated ligands TPV2, TPV2-T2, and crossTPV3 (Figure 6). In general, the TA amplitude is stronger for the crossTPVn complexes compared to the corresponding linear chromophores (e.g., crossTPV3 vs TPV2). Given that the molar absorptivity for the triplet is similar in the two series (see

below), this difference in signal amplitude likely reflects that intersystem crossing is more efficient in the crossTPVn series.

Comparison of the TA difference spectra of crossTPV1, crossTPV3, and crossTPV1-DPAF in solution reveals that there is a red-shift in the transient absorption spectrum with increasing conjugation length of the OPV axis. Furthermore, the spectra of crossTPV1-DPAF (λ_{max} of $T_1-T_n = 660$ nm) and crossTPV1 are very similar (λ_{max} of $T_1-T_n = 660$ and 662 nm, respectively). Taken together, these results point to the fact that the triplet exciton in the cross conjugated complexes is mainly localized along the OPV axis and there is little influence from the phenylene-ethynylene conjugated axis.

The triplet molar absorptivity (ϵ_T) for all of the Pt(II)-acetylide complexes was determined by relative actinometry using benzophenone (see the Experimental Section for details), and the values are listed in Table 1. The triplet molar absorptivity generally increases with the length of the OPV segment, but all of the complexes have particularly large triplet molar extinction coefficients, especially TPV2-T2. Interestingly, comparison of the absorptivity of TPV2-T2 ($\epsilon_T = 393,000 \text{ M}^{-1} \text{ cm}^{-1}$) to that of a structurally related complex that contains the same bithiophene triplet chromophore ($\epsilon_T = 101,000 \text{ M}^{-1} \text{ cm}^{-1}$)¹³ makes it quite clear that the conjugated OPV units substantially enhance the triplet molar absorptivity.

Turning to the properties of the triplet state in the PMMA glasses, Figure 6 compares the TA difference spectra for selected Pt complexes in the PMMA monoliths with those in THF solution. The transient absorption difference spectra for the monoliths retains the strong, broad absorption seen in THF; however, the triplet decay lifetimes are substantially longer (greater than the capability of our instrument to measure, $\tau > 2$ ms). In most cases, there is not a significant shift in the triplet–triplet absorption spectra upon incorporation of the chromophores into the PMMA host for all of the linear and cross-conjugated Pt(II) complexes, indicating that the structure of the triplet state is similar in the liquid and rigid media. One interesting exception is crossTPV1-DPAF, which exhibits a significantly blue-shifted triplet–triplet absorption in the PMMA compared to that of complex in THF solution. A blue-shift in the TA difference spectra was also observed for films that contain the Pt-DPAF chromophore covalently linked to poly(methyl methacrylate).²⁵ The origin of the blue shift is unclear, but one possibility is that it arises from partial photoionization of the DPAF unit in the PMMA matrix. This notion is supported by the fact that the DPAF radical cation has a strong absorption in the 500–550 nm region.³¹

Two-Photon Photophysical Properties. Two photon absorption (2PA) spectra and cross sections (σ_2) of the monoliths were obtained with good accuracy using the collimated-beam femtosecond nonlinear transmission method.²⁶ The 2PA spectra and cross-section values for the TPV1, crossTPV1, and crossTPV3 doped monoliths were measured and compared to those previously reported for THF solutions of the complexes (Figure 7). The 2PA cross sections for the monoliths were calculated based on the estimated chromophore concentrations listed in Table 2. The complexes exhibit strong 2PA over a wide spectral range of wavelengths, 560–800 nm, with σ_2 increasing toward shorter wavelengths. At shorter wavelengths, 700–800 nm, TPV1 showed the largest peak 2PA cross section, $\sigma_2 \sim 3000 \text{ GM}$. Note the remarkably good correspondence between the 2PA spectra measured in monoliths and the values obtained in THF solution for the same complexes.²⁶ In the shorter wavelength region, < 600 nm,

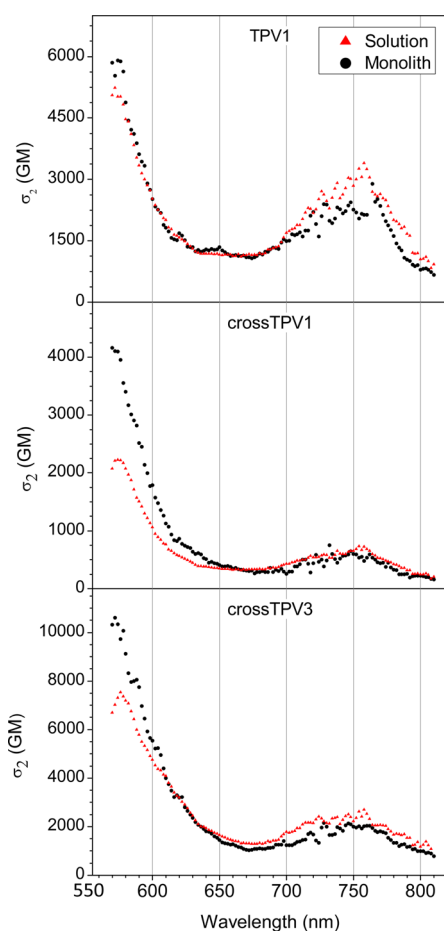


Figure 7. (Black) Two-photon absorption (2PA) spectra and absolute cross-section values measured by NLT method for the TPV1, crossTPV1, and crossTPV3 monoliths compared to (red) the 2PA spectra obtained in THF.

Table 2. Nonlinear Absorption Properties of PMMA Monoliths

monolith	thickness (mm)	calculated chromophore concentration (mM)	% transmission at $z = 0$ from z-scan	2PA cross section at 680 nm (GM)
TPV1-Ph	1.0	2.0	76	NA
TPV0	2.6	2.8	47	NA
TPV1	1.0	2.0	60	1200 ^a 1190 ^b
TPV2	1.0	2.8	54	NA
TPV2-T2	2.4	1.2	56	NA
crossTPV1	1.0	1.8	61	340 ^a 280 ^b
crossTPV3	1.0	1.9	61	1330 ^a 1110 ^b
crossTPV1-DPAF	2.0	1.7	72	NA

^a2PA Cross-Section measured in THF by NLT method. ^b2PA cross-section measured in PMMA monolith by NLT method.

the 2PA cross section values of the monoliths are slightly higher than that in the solutions suggesting that in the solid environment S_1-S_n singlet excited state absorption may have a larger contribution than in solution, likely due to slower vibrational relaxation in the solid state. Most importantly for

the OPL application, the exceptional spectral overlap between the 2PA and the triplet–triplet excited state absorption is retained in the PMMA host.

The dual-mode nonlinear absorption property for the complexes in solution and in PMMA monoliths was probed by open-aperture z-scan with 10 ns pulses at 680 nm, as shown in Figure 8. (Note that at this wavelength there is no ground state absorption, and thus excitation occurs via 2PA.) Monoliths containing TPV0, TPV2-T2, and crossTPV1-DPAF were approximately 2 mm thick, but all other monoliths were cut and polished to 1 mm thickness (Table 2). The platinum acetylide complex Pt-DPAF, whose one- and two-photon properties have been well studied,⁵ was included in all solution runs (Figure 8a) as a point of reference for comparison. A blank PMMA monolith was included in the monolith z-scans (Figure 8b) as a baseline reference.

The z-scan results of the complexes in THF solution in Figure 8a clearly demonstrate the enhanced nonlinear absorption of nanosecond pulses that arises from the ESA of the triplet state. All complexes in solution and PMMA monoliths exhibit strong nonlinear response to nanosecond laser pulses at 680 nm. By contrast, the free ligands (studied only in solution) exhibit relatively little nonlinear absorption. This is due to the fact that the free ligands have low triplet yields and, consequently, lack triplet–triplet absorption. (The 2PA cross sections of the free ligands and corresponding metal complexes are similar.)²⁶ By comparison, the Pt-acetylide complexes show considerably enhanced nonlinear absorption of the nanosecond pulses presumably due to a combination of 2PA and ESA. Consistent with the trends in 2PA cross-sectional values and triplet–triplet absorption molar extinction coefficients, the longer conjugated OPVs, such as TPV2, TPV2-T2, and crossTPV3, display stronger attenuation of the transmittance in the z-scan experiments. In general, the linear complexes, TPVn, which contain two OPV ligands, have larger 2PA cross section values and triplet molar extinction coefficients, and tended to exhibit stronger nonlinearity in the z-scan experiments compared to the complexes containing the cross-conjugated complexes.

Unfortunately, due to varying thickness and chromophore concentration in the monoliths, the open-aperture z-scan results cannot be directly compared between samples; however, as summarized in Table 2 along with the measured thicknesses and calculated concentrations of the monoliths, the NLA of the monoliths exhibits the same general trend as that in solution. Comparing the crossTPV1 and crossTPV3 monoliths, which have equal thickness and approximately the same calculated chromophore concentration, larger NLA response is observed in the latter sample, which features the longer OPV segment length. Similarly, when the open-aperture z-scan results for TPV1-Ph, TPV1, and TPV2 are compared, the NLA increases with increasing length of the OPV unit. The TPV0 monolith had a particularly strong z-scan response, which may be due to the more than 2-fold greater thickness for this sample; however, it is unclear from these results whether the NLA of PMMA monoliths benefit more from increased thickness or concentration. The TPV2-T2 monolith, which has less than half the thickness of the TPV2 monolith but double the concentration, exhibits less NLA than that of TPV2. On the basis of the solution z-scan results, the TPV2-T2 monolith would be expected to be the most effective nonlinear absorber. Surprisingly, the crossTPV1-DPAF monolith, with similar concentration but double the path length of crossTPV1 and

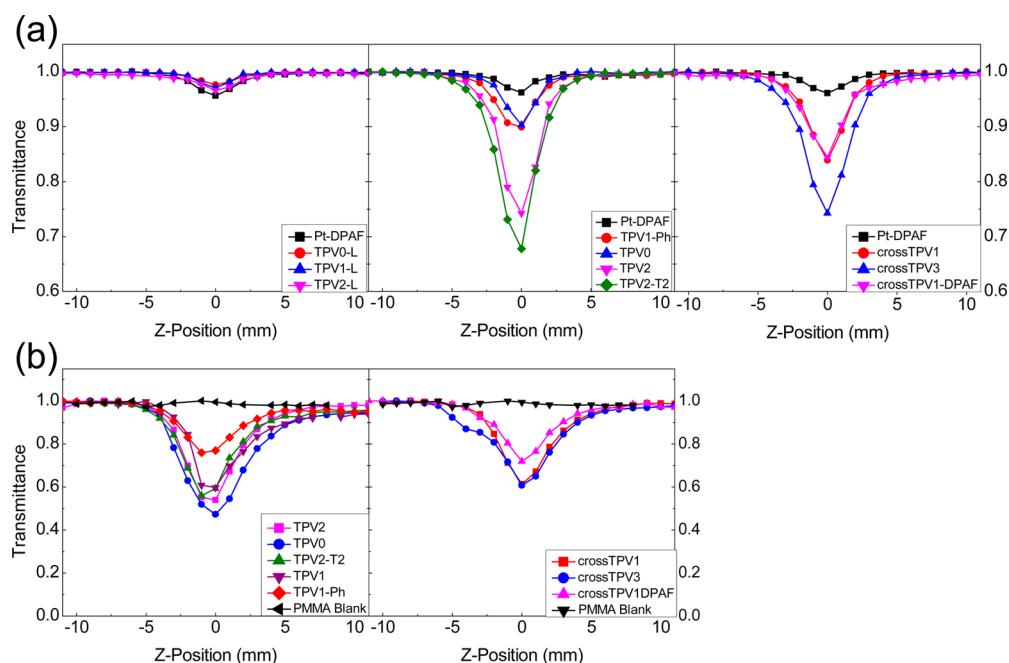


Figure 8. Open-aperture z-scan plots for the (a) solutions (1 mM concentration in THF, 1 mm path length cuvette) and (b) PMMA monoliths (see Table 2 for concentration and thickness) containing the linear and cross-conjugated platinum(II) acetylide complexes. Excitation was at 680 nm (approximately 700 $\mu\text{J}/\text{pulse}$).

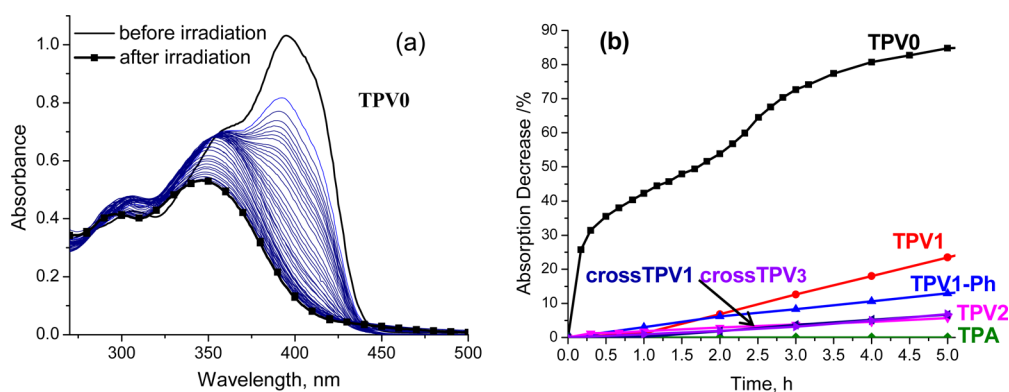


Figure 9. (a) UV-visible absorption spectra of TPV0 in THF under continuous irradiation at 400 nm (15 mW). The changes in UV-vis absorption spectra were measured with an initial 10 min interval and then every 1 h. (b) Photodegradation (%) vs time (hr) in THF at 400 nm, 15 mW. The photodegradation vs time data for TPA coincides with the x-axis. For TPA, in the absence of the absorption at 400 nm, the sample was irradiated, and change in absorption was detected at the band maximum.

crossTPV3, had the weakest response of all the monoliths except for TPV1-Ph. Further studies are in progress to elucidate the effects of increased concentration and path length on the NLA response of polymer monoliths.

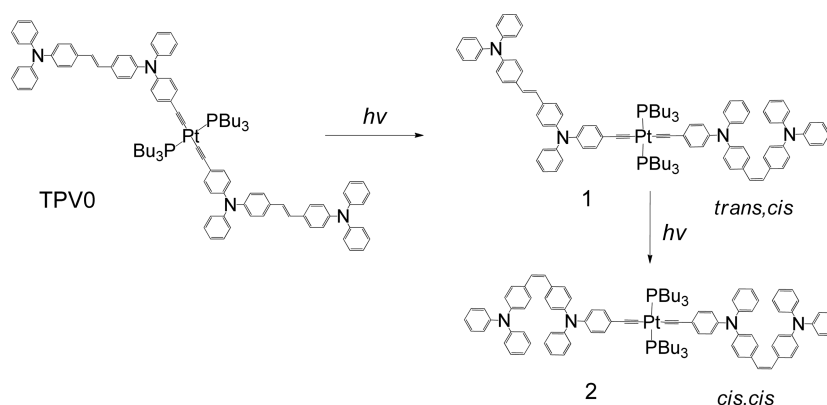
Photostability Studies. Long-term photostability is an important property of any material that is to be used in a nonlinear absorption application. In the course of this investigation, we found that some of the complexes undergo photochemical reaction upon light exposure. To understand the photochemistry and its implications on the application of the chromophores, we carried out experiments using UV-visible absorption spectroscopy to follow the time course of the reactions, combined with photoproduct analysis by using ^1H NMR and mass spectroscopy. The relative photostability of the complexes was investigated, and the photochemical products were identified. The photochemical studies were performed by continuous irradiation of air saturated THF solutions at 400 nm (power = 15 mW), and the absorption spectra were measured

with an initial interval of 10 min and then every 1 h. Selected results are provided here, and more details including the ^1H NMR characterization of the photoproducts is in the Supporting Information.

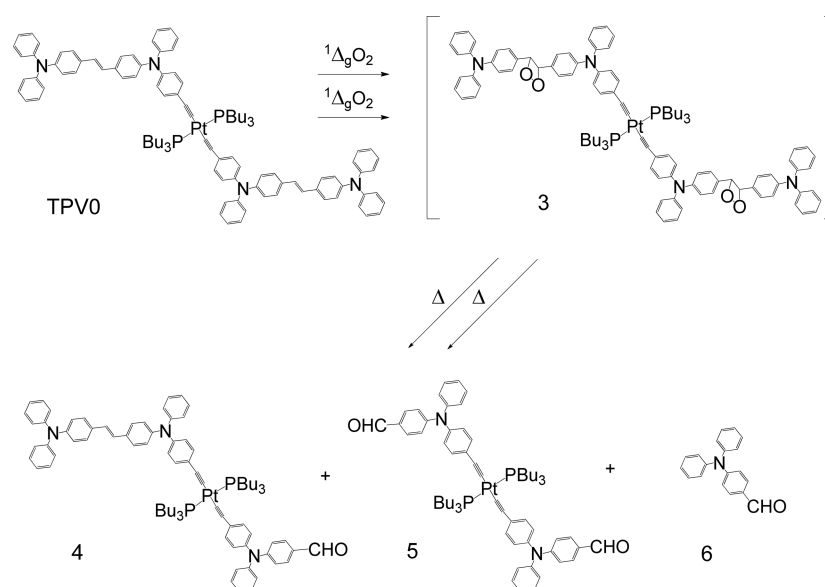
Figure 9 summarizes the results of time-dependent changes in the UV-visible absorption of the complexes; Figure 9a shows the spectral changes for TPV0, and Figure 9b illustrates the change in the absorption at the band maximum for all of the complexes. The least photostable complex was TPV0 (Figure 9a), while all the other complexes were considerably more photostable, exhibiting a <20% change in the visible absorption after 5 h of continuous irradiation. Except for TPV0, which showed more complicated photochemistry comprising two phases in the temporal profile, all of the complexes showed the same trend: the intensity of long-wave absorption band decreased linearly with increasing irradiation time (Figure 9b).

Interestingly, across the series of complexes the photostability increased with the length of the OPV: TPV0 \ll TPV1

Scheme 1



Scheme 2



$< \text{TPV1-Ph} < \text{TPV2} \sim \text{crossTPV1} \sim \text{crossTPV3}$. As supported by the photoproduct studies outlined below, it was hypothesized that the photoreactivity is associated with the double bond in the OPV segments, and the reaction is accelerated by the presence of electron donor triphenylamino groups at the end of the OPV segments. In the complexes with the longer OPV segments, the reactivity is suppressed for reasons outlined below. To demonstrate the fact that the reaction is associated with the OPV double bonds, we subjected model complex TPA (structure in Figure 2) which lacks the double bonds to irradiation. As shown in Figure 9b, this complex does not display any observable change in the UV-visible absorption spectrum even after prolonged irradiation in air-saturated THF solution.

Inspection of Figure 9a clearly indicates that the photochemistry of TPV0 occurs in two kinetic phases: an initial rapid phase ($t < 20$ min) which is associated with rapid photobleaching of the long wavelength absorption (~ 390 nm) accompanied by the appearance of a shorter wavelength band at (~ 350 nm). The slower phase ($t > 30$ min) is characterized by uniform decrease of the 350 nm band. In order to identify the chemical nature of the two photodegradation processes for TPV0 the ^1H NMR spectrum was monitored during irradiation and the photoreaction products were isolated and identified by

using mass spectrometry and ^1H NMR (see Supporting Information for details). The initial photoreaction for TPV0 can be assigned to sequential *trans* \rightarrow *cis* photoisomerization of the two double bonds (Scheme 1) which is evident by the disappearance of the *trans*-ethylene peak at 6.97 ppm and the appearance of a new *cis*-ethylene peak at 6.45 ppm in the ^1H NMR spectrum that is characteristic of *cis,cis* complex 1 (see Figures S4 and S5). The photoisomerization of TPV0 is similar to that observed in *trans*-stilbene and related platinum(II) complexes, and it likely involves the lowest triplet excited state of the TPV0 complex.^{32,33} Interestingly, *trans* \rightarrow *cis* photoisomerization is not observed for the longer OPV complexes. This is consistent with the observation of increased photostability in *trans,trans*-1,4-distyrylbenzene compared to *trans*-stilbene, and may be associated with a change in the electronic nature of the lowest π,π^* excited state in the longer OPV segments (from 1^1B_u to 2^1A_g).³⁴

The second photodegradation process was assigned to oxidative cleavage of the double bond by efficient sensitization of singlet oxygen with the sequential formation of dioxetane 3 as an adduct and a mixture of symmetrical and unsymmetrical aldehydes 4–6 as the final products. This process was observed for all Pt-complexes upon irradiation and detected as a superposition of peaks at ~ 9.8 – 10.0 ppm in ^1H NMR spectra

(see Supporting Information for details). For TPV0, one of the photodegradation products, 4-(diphenylamino)benzaldehyde (6 in Scheme 2) was isolated and identified. The two electron-donor triphenylamine groups attached to both sides of the double bond in TPV0 significantly increased its electron-rich character and reactivity toward singlet oxygen. This explains the accelerated photobleaching of TPV0 upon irradiation in comparison to the other Pt-complexes.

Due to the high absorption of the PMMA monoliths, direct observation of photodegradation in the monoliths could not be measured. To compare the photostability of TPV0 in solid PMMA host material vs solution, a PMMA spin-coated film (5% wt. TPV0, $\sim 1 \mu\text{m}$ thick) was fabricated, and the same photodegradation conditions for TPV0 in THF solution were applied to the PMMA film. A much slower change in absorbance proved marked increase of photostability for TPV0 in PMMA film (Figure 10). The first process *trans*-to-

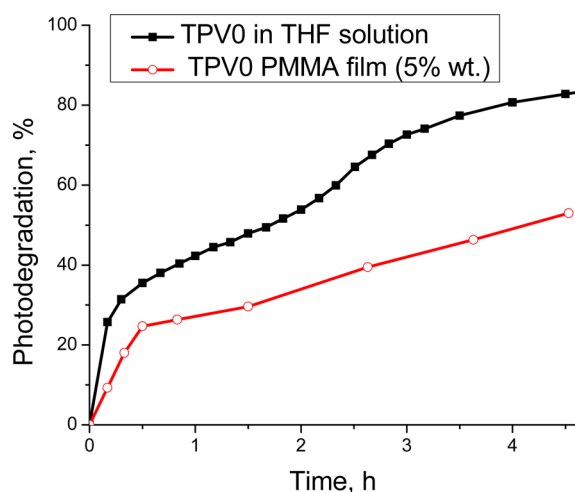


Figure 10. Photodegradation vs time for TPV0 in THF solution and in 5% wt. PMMA film.

cis isomerization still occurs; however, the pathway associated with oxidation by singlet oxygen was attenuated in the PMMA matrix, likely due to the low permeability of oxygen in PMMA.

SUMMARY AND CONCLUSION

A series of linear and cross-conjugated phenylenevinylene platinum acetylide complexes with terminal triphenylamine groups were synthesized and incorporated into PMMA glass monoliths for solid-state study of their one- and two-photon photophysical properties with a focus on their application to optical power limiting materials by dual-mechanism nonlinear absorption. Most important for OPL application, all the properties important to nonlinear absorption are retained in the solid state with increased photostability by the polymer host. The shape of the fluorescence spectra of the monoliths are similar to those for THF solutions, with increasing blue-shift in the emission maxima with longer OPV chains, particularly for the linear TPV n complexes, where the blue-shift ranges from 1 nm for TPV0 to 24 nm for TPV2-T2. The triplet molar extinction coefficients for the platinum complexes in THF are particularly large and increase with OPV unit length up to $393\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for TPV2-T2. Triplet–triplet absorption measured in solution and in PMMA monolith are strong over a wide spectral window in the visible to near-IR region with little shift in the transient absorption band maxima upon

incorporation into the PMMA monolith for all complexes except crossTPV1-DPAF, which shows a dramatic blue-shift. Absolute two-photon absorption cross-sectional values of the complexes in the monoliths were measured by collimated beam femtosecond nonlinear transmission method and are consistent with the solution measurements. Remarkable good spectral overlap between the triplet–triplet excited state absorption and 2PA necessary is retained in solid phase, suggesting efficient dual-mode nonlinear absorption in a broad range of wavelengths. Open-aperture z-scan measurement demonstrates the strong nonlinear absorption of the Pt(II)-acetylide complexes in THF solution and PMMA monoliths to nanosecond laser pulses at 680 nm. Upon attachment of the ligands to platinum atoms the nonlinear absorption measured by z-scan is enhanced many-fold, illustrating the contribution of the triplet excited-state to the nonlinear absorption. Following the trends in 2PA and triplet molar extinction coefficients, the strongest nonlinear absorption is found with the longer OPV chains, with TPV2, TPV2-T2, and crossTPV3 having the greatest nonlinear absorption with the best OPL performance from both the linear and cross-conjugated series.

Through photostability studies in THF, it was found that all complexes undergo self-sensitized oxidative cleavage by singlet oxygen upon exposure to short wavelength visible light (400 nm, 15 mW). In addition, TPV0 showed a second relatively rapid photoprocess: a significant *trans*-to-*cis* photoisomerization and a “self”-oxidative cleavage as well. Incorporation of TPV0 into a PMMA film increased stability toward the oxidative cleavage photodegradation process due to low permeability of oxygen into the polymer film. Future endeavors, alongside the design of increasingly efficient NLA chromophores, are focused on improved methods of achieving solid state OPL materials with a focus on greater stability, higher concentrations of incorporated chromophores, and more effective optical power limiting.

EXPERIMENTAL SECTION

Materials. The synthesis of the linear and cross-conjugated complexes in Scheme 1 have been reported previously.^{26,27} PMMA monoliths were prepared by a procedure adapted from Westlund and co-workers.²⁴ The platinum(II) acetylide chromophores (initial concentration 1 mM) and 6 mg of azoisobutyronitrile (AIBN) were dissolved in 1.1 mL of inhibitor-free methyl methacrylate (MMA). The solution was poured into a 0.5 in. circular Teflon mold and placed in an oven to polymerize at 50 °C for 3 days, then at 80 °C for 3 days. Some of the initial PMMA monoliths showed a darkening of the top surface of the monolith indicative of decomposition of the chromophore, so the procedure was modified with a gentle nitrogen flow into the oven to reduce oxygen-sensitized degradation. All monoliths prepared under N_2 appeared homogeneous with no evidence of degradation and were highly transparent (Figure 1). Some gas bubbles were trapped near the edges of the monoliths; however, they did not obstruct the photophysical measurements. Trapped bubbles did not occur when monoliths were prepared without N_2 flow.

The monoliths were cut to about 1 mm thickness using a thin rotary blade (Dremel Tools) and polished by hand using fine grit sandpaper on a flat surface for photophysical measurement. Different concentrations of chromophore were attempted, but monoliths containing higher initial concentrations ($>2 \text{ mM}$) of chromophore were partially opaque due to phase separation, which causes light scattering. Monolith solutions were prepared to 1 mM initial concentration before polymerization. Final calculated concentrations of the polymerized monoliths were approximated by using the density of PMMA (1.2 g/mL) and the final weights after polymerization. Weight loss due to the evaporation of MMA in the monoliths was

inconsistent due to uncontrolled flow of N_2 into the oven. It is assumed that the monoliths are homogeneous and that cutting and polishing the monoliths do not change their concentration. Table 2 lists the final thickness and calculated concentration of each monolith.

Photophysical Measurements. One-photon photophysical properties for solutions were measured using a 1 cm path length quartz or borosilicate cuvette in spectroscopic grade, dry THF. Solutions were deoxygenated by purging with argon for phosphorescence and transient absorption measurements. Ground state absorption spectra were collected on a Varian Cary 100 dual-beam spectrophotometer with THF as the instrument baseline blank. Corrected steady-state emission measurements were collected by a Photon Technology International (PTI) photon counting fluorescence spectrophotometer with optically dilute solutions, $OD_{max} < 0.10$. Fluorescence quantum yields were measured at room temperature in air-saturated THF using 9,10-diphenylanthracene in cyclohexane as a standard ($\Phi_f = 0.75$).²⁹ Nanosecond triplet–triplet transient absorption was measured in a continuously circulating 1 cm path length borosilicate cuvette in argon-purged THF solutions. The third harmonic of a Continuum Surelite II-10 Nd:YAG laser at 355 nm (10 mJ/pulse) was used as the pump, and a PerkinElmer LS1130–3 pulsed xenon lamp was used as the probe source. The transient absorption signal was detected with a gated-intensified CCD mounted on a 0.18 M spectrograph (Princeton PI-Max/Acton Pro 180) after an initial camera delay of 50 ns. Samples were prepared to an optical density of 0.4 at the excitation wavelength. Triplet lifetimes were calculated with a single-exponential global fitting of the transient absorption decay data using SpecFit analysis software. Triplet molar extinction coefficients were determined by relative actinometry using benzophenone ($\Phi_T = 1.00$, $\epsilon_T = 7870 \text{ L mol}^{-1} \text{ cm}^{-1}$)^{35,36} as the actinometer in benzene.

Monolith experiments were performed with freestanding samples, open to atmosphere without a cuvette. Absorption spectra were not obtained due to saturated OD. Emission spectra were obtained by a front-face excitation/emission geometry on a Spex Fluorolog 3 spectrophotometer. Transient absorption measurements on monoliths cut to a thickness of approximately 1 mm were made using an in-house designed TA instrument dedicated to solid-state measurements. The third harmonic of a Continuum Surelite I-10 Nd:YAG laser at 355 nm (600 μJ /pulse) was used as the pump beam in an antiparallel alignment to the probe beam provided by a 250 W QTH lamp (Newport). Single-wavelength transient absorption decays were acquired as an average of 128 shots every 20 nm using a Hamamatsu R928 PMT and an in-house modified base using 5 of the 9 stages for amplification. The transient absorption spectrum was obtained with a custom Matlab program to convert the transient absorption decays at each wavelength to a transient absorption spectrum at $t = 0$. The transient absorption of the monoliths did not fully decay to baseline in the time scale of the instrument (2 ms) so transient absorption lifetimes could not be determined.

Fluorescence lifetimes for both THF solutions and monoliths were obtained by time-correlated single photon counting technique (TCSPC) with a PicoQuant FluoTime 100 compact fluorescence lifetime spectrophotometer. A UV-pulsed diode laser provided excitation at 375 nm (power <10 mW). The laser was pulsed by a PDL800-B pulsed diode laser driver. Fluorescence decays were obtained for at least five wavelengths across the emission spectrum using 10 nm bandpass interference filters for solution measurements in air-saturated THF and analyzed by a global fit as average amplitude-weighted from the fluorescence decays using biexponential fitting parameters (FluoFit software). Fluorescence lifetimes were acquired and fit at one wavelength for comparison to solution measurements.

Nanosecond nonlinear transmission measurements were performed via an open-aperture z-scan apparatus. The excitation wavelength, 680 nm, 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 pyroelectric detectors, which measured the transmitted pulse energy through the sample 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-accuracy computer controlled movement along the z-axis. Solution samples were prepared with dry-THF to a concentration of 1 mM and put into a 1 mm path length quartz cuvette for analysis. A sample of Pt-DPAF was used as a reference standard for comparison between different runs. Monolith samples cut to approximately 1 mm thickness were placed between two glass slides with a few drops of refractive index matching fluid (Newport F-IMF-105, 1.52 at 589 nm).

The 2PA measurements were performed using collimated beam femtosecond nonlinear transmission technique. A detailed description of the laser system and experimental procedure was given previously.^{26,37} Briefly, the laser system comprised a Ti:sapphire femtosecond oscillator (Lighthouse Inc.), femtosecond regenerative amplifier (Legend H, Coherent Inc.), and an optical parametric amplifier, OPA (TOPAS-C, Light Conversion). The second harmonic of the signal output of the OPA was continuously tunable from 540 to 810 nm with the maximum pulse energy, 10–200 μJ . The maximum average pulse duration was 80–120 fs (fwhm). The OPA output beam was slightly expanded and then collimated with long focal length lenses ($f = 500\text{--}1000 \text{ mm}$) to give an average beam diameter on the sample, $d = 0.3\text{--}1.0 \text{ mm}$. The beam diameter was optimized to minimize spurious nonlinear effects such as self-focusing, which may occur in the sample and in the optical elements at high photon flux values. The pulse energy incident at the sample was changed by means of a continuously variable reflective circular attenuator (Thorlabs, maximum OD = 2.0). Nonlinear transmittance of the sample as a function of the incident pulse energy was determined by measuring the relative pulse energy before and after the sample with two silicon photodiodes (Thorlabs, PDA10A). The measured nonlinear transmittance as a function of incident pulse energy was fitted with a linear function. The 2PA cross sections at each wavelength were determined by comparing the intensity-dependent transmittance slope values of the sample with those obtained in 1 cm path length solution of 2PA reference standards under same experimental conditions. Rhodamine B solution in methanol, fluorescein solution in H_2O (pH 11), and bis-diphenylanimostilbene solution in dichloromethane were used as reference standards.³⁷

■ ASSOCIATED CONTENT

📄 Supporting Information

Photoluminescence spectra and transient absorption spectra of all complexes in solution and in PMMA monolith, photo-degradation experimental procedure and NMR spectra of photodegradation products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01456.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Air Force Office of Scientific Research (Grant Nos. FA-9550-06-1-1084 and FA9550-09-1-0219) and the U.S. National Science Foundation (Grant No. CHE-1151624).

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