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High Efficiency Platinum Acetylide Nonlinear Absorption Chromophores Covalently Linked to Poly(methyl methacrylate)

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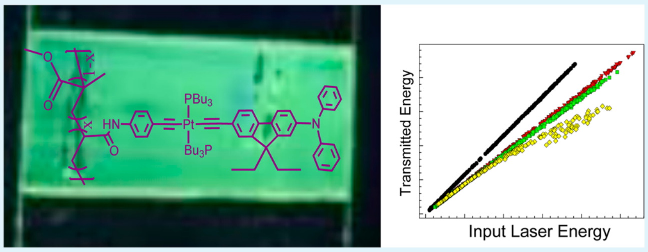
Supporting Information



ABSTRACT: We report three platinum acetylide acrylate monomers containing known two-photon absorption (TPA) chromophores and their covalent incorporation into polymers via free radical polymerization with methyl methacrylate. The photophysical properties of the platinum acetylide monomers and resulting poly(methyl methacrylate) (PMMA) copolymers were investigated to determine if the one- and two-photon photophysical properties of the chromophores were maintained in the copolymers. The photophysical properties of the series of copolymers were studied in solution and solid state with minimum shifts exhibited in the ground state absorption, photoluminescence, and triplet−triplet transient absorption spectra. The polymer films displayed markedly stronger phosphorescence and longer triplet excited state lifetimes than the polymers in solution or the monomers. The incorporation of the platinum acetylide chromophores into the PMMA copolymers allows the materials to be cast as thin films or into free-standing monoliths. Films with ~3.6 μm in thickness and monoliths with 1 mm path length were fabricated and examined. The nonlinear absorption responses of the polymers in solution were measured via the nanosecond *z*-scan method, and the solid state polymer monoliths were measured via nonlinear transmittance. Both measurements indicate that the polymers exhibited strong transmittance attenuation at input pulse energies exceeding 100 μJ.

KEYWORDS: *platinum acetylide, PMMA, polymer, nonlinear absorption, z-scan*

INTRODUCTION

Platinum acetylide chromophores are of wide interest for a number of applications including nonlinear absorption (NLA), polymer light emitting diodes, and polymer solar cells.[1−6] A feature of particular interest with respect to platinum acetylides is the fact that their intrinsic optical properties (including the NLA response) are maintained when the chromophores are incorporated into a polymeric matrix.[1,7−9] The resulting polymeric optical materials can be subjected to molecular engineering to optimize the properties for optical applications that would be difficult for platinum acetylide monomers or oligomers—the polymers can be processed to form coatings or thin films and can be characterized in solution and solid-state. In previous work the nonlinear properties of indium and zinc phthalocyanine thin films have been characterized;[10−12] however, there have been only a limited number studies of platinum acetylide polymers for NLA applications, and the polymer characterization is often conducted in solution.[9,13−17]

Experimental and theoretical investigations on a variety of Pt-acetylide oligomers and polymers have explored the relationships between structure and resulting photophysical properties.[18−21] The incorporation of Pt(II) into organic conjugated chromophores provides efficient intersystem crossing to the triplet manifold and high triplet excited state yield. Moreover, incorporation of two-photon absorption (TPA) chromophores into a Pt(II) acetylide motif facilitates population of the singlet excited state with near-infrared wavelength excitation via TPA, at which time the metal center can induce singlet-triplet intersystem crossing (ISC) quickly, leading to efficient population of the triplet excited state.[22] If the chromophore also has a large triplet−triplet absorption cross section, additional NLA via excited state absorption (ESA) within the triplet manifold is possible.[21,23−25] The ground state absorption and fluorescence spectra of Pt acetylide oligomers and polymer series often indicate a broadly delocalized singlet excited state.[26−28] The phosphorescence spectra are less affected by conjugation length, signifying a more localized triplet excited state, confined to one or two repeat units.[19,29]

Wong and co-workers have examined a series of platinum acetylide polymers based on diethynyl fluorene and carbazole-based complexes that have demonstrated strong optical power limiting capabilities in solution.[14] An investigation by Malmström and co-workers examined polymers in the solid state based on *trans*-Pt(PBu$_3$)$_2$(PE2), where PE = 4-(phenylethynyl)ethynylbenzene; the platinum acetylides were designed such that incorporation into the polymer was achieved

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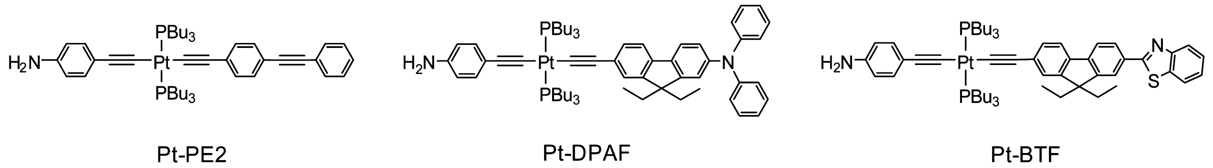

Figure 1. Chemical structures of the platinum acetylide monomers.

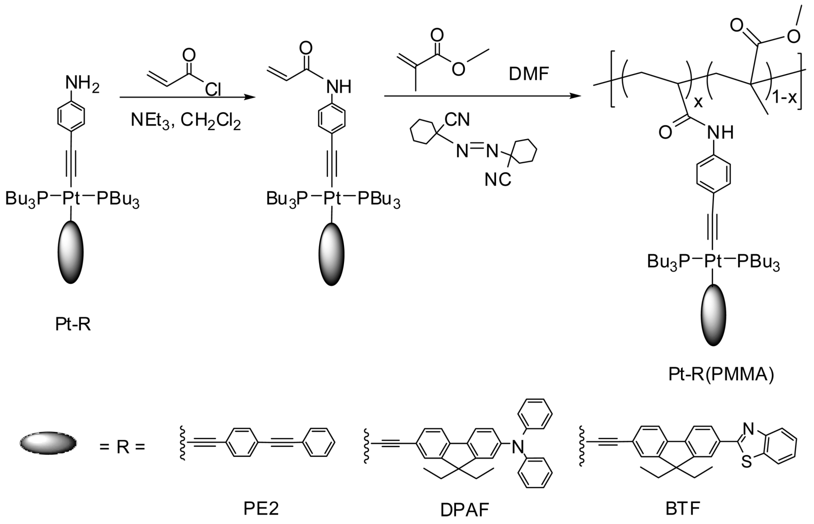

Figure 2. Synthetic route for the Pt-R(PMMA) polymers, where *R* is a PE2, DPAF, or BTF two-photon absorbing chromophore, and x = 0.017–0.12.

by dispersion into or reaction with methyl methacrylate (MMA).[13] The characterization of the resulting solid state polymethylmethacrylate (PMMA) based polymers showed that both methods resulted in platinum acetylide polymers that exhibited NLA. What is lacking in this area is the combination of Pt(II) acetylide-based high efficiency two-photon absorption NLA chromophores that can be incorporated into polymers and examined in the solid state,[30,31] with specific interest in chromophores that are covalently bound within the polymers.[13,32,33]

The aim of the present investigation was to examine how the linear and nonlinear absorption properties of platinum acetylide complexes are affected by covalent incorporation into PMMA polymers. To accomplish this goal, a set of platinum acetylide monomers were synthesized that incorporate a single 4-(phenylethynyl)ethynylbenzene (PE2), 4-(diphenylamino)-fluorene (DPAF), or 4-(benzothiazole)fluorene (BTF) chromophore and one ethynylaniline group onto the platinum acetylide core, as shown in Figure 1 (Pt-PE2, Pt-DPAF, and Pt-BTF). Previous studies have shown that the platinum acetylides that contain the DPAF and BTF units exhibit a moderately large TPA cross-section in the 600−800 nm region (100−200 GM), and efficient NLA response to nanosecond pulses via the TPA/ESA mechanism.[21,34] Thus, this study examines the effect of incorporation of these high efficiency NLA chromophores into polymer matrices on their optical and NLA response. The amine functionality on the ethynylaniline group was modified with an acrylamide unit allowing for incorporation of the chromophores into a polymer backbone via free radical polymerization with MMA, resulting in PMMA-based copolymers (Pt-PE2(PMMA), Pt-DPAF(PMMA), and Pt-BTF-(PMMA), Figure 2). Here we report the photophysical and nonlinear optical characterization of the platinum acetylide monomers and resulting polymers in solution. Additionally, the polymers are used to fabricate solid state films and monoliths; a comparison between the solution and the solid state properties of the polymeric materials is presented.

EXPERIMENTAL SECTION

Materials and Synthesis. Syntheses of the PE2, DPAF, and BTF chromophores have been described previously.[21,35] The unsymmetric chromophore containing Pt(II) acetylide monomers were synthesized and fully characterized as described in the Supporting Information. Their chemical structures, and the resulting PMMA-based polymers, are shown in Figures 1 and 2. The platinum acetylide monomers are modified at the amine with an acrylamide unit to make the complexes suitably reactive for free radical polymerization. This is achieved by reaction of the monomers with acryloyl chloride to form an acrylamide, as shown in Figure 2. The acrylate monomers are highly reactive and modification of this functionality allows the monomers to be covalently bound into the polymer backbone; the formed alkene is sensitive toward polymerization and is incorporated into the polymer backbone via copolymerization with methylmethacrylate by using methods described in the Supporting Information. A range of monomer concentrations were prepared, reaching concentrations up to 12.3 wt % of the platinum acetylide chromophores.

General Techniques. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{31}P (121 MHz) NMR spectra were recorded on a Varian Gemini or Mercury spectrometer in deuterated chloroform; chemical shifts (δ) are reported in parts per million (ppm) and referenced to tetramethylsilane or protonated solvent signals.

Unless noted, one-photon solution photophysical studies were carried out with samples contained in 1 cm × 1 cm quartz spectroscopic cuvettes. Ground state absorption spectra in solution and in film were measured on a Varian Cary 100 dual-beam spectrophotometer, with either the solution solvent or a clean blank glass slide as the instrument baseline blank. Corrected steady-state solution 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 deoxygenated for phosphorescence measurements. Low-temperature measurements were conducted in distilled HPLC grade 2-methyl tetrahydrofuran 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. Luminescence measurements of the polymer films were performed on a SPEX Fluorolog 3 spectrometer via front-face alignment.

The molecular weights and polydispersity indexes of polymers were measured by gel permeation chromatography with PLgel 5 μ columns. A Spectroflow 757 ultraviolet detector calibrated against linear polystyrene standards in THF.

Nanosecond triplet−triplet transient absorption measurements of the monomers and polymers in solution were conducted using the third harmonic of a Continuum Surelite II-10 Nd:YAG laser ($\lambda = 355$ nm), with an excitation pulse of $E_p = 8$ mJ, as has been previously described.[36] Sample concentrations were adjusted to an optical density of 0.7 at the excitation wavelength. The sample solutions were prepared in THF, placed in a continuously circulating 1 cm path length borosilicate flow cell, and deoxygenated by bubbling with argon. Triplet lifetimes were calculated by fitting the transient absorption decay data with a single exponential global fitting parameter in the SpecFit analysis software.

A separate transient absorption system optimized for thin film analysis was used to study the transient absorption of thin film samples.[37] Briefly, a Surelite I-10 Nd:YAG laser with second and third harmonic generators delivered nanosecond pulses for excitation at 532 or 355 nm, respectively. A Newport 250 W quartz tungsten halogen lamp and radiometric power supply were used as the probe source. A Cornerstone 130/m motorized monochromator isolated the wavelength of detection. Two gratings were installed within the monochromator: one for ultraviolet−visible analysis (1200 l/mm blaze 500) and one for near-infrared analysis (600 l/mm blaze 1000). Output signal from the detector was collected and digitized on a Tektronics 3032B oscilloscope. Light exposure of the sample was controlled by a series of shutters. A Berkeley Nucleonics Corporation Model 575 8-channel pulse generator controlled the laser flashlamp, Q-switch delay, slow shutter, fast shutter, and oscilloscope. A Hamamatsu R928 PMT detector operated at 730 V was mounted to the monochromator in a custom base modified in-house using 5 of the 9 PMT stages for signal amplification.

Solution nonlinear absorption measurements were performed via an open-aperture z-scan apparatus.[38] Briefly, 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 Ophir 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 movement along the z-axis with greater than 100 μm positioning accuracy. The solution NLA measurements of the polymers were conducted using 1 mM solutions in THF (concentration based on the weight percentage of polymer repeat units for polymer samples).

The NLA response of the films was measured by modifying the z-scan apparatus to measure nonlinear transmittance (NLT). The sample holder on the translation stage was replaced with a film holder such that the film could be placed at the focus of the laser beam. A neutral density filter was placed directly past the OPO signal port and used to modify the energies to detector 1 and 2. The StarCom32 software program was employed to control the output of the Laserstar energy meter heads and energy meter. The films were excited at 600 nm with a Q-switch delay of 240 μs, which corresponded to a controlled energy variation of 60 μJ−1.6 mJ via adjustment of the neutral density filter.

■ RESULTS AND DISCUSSION

Polymerization and Film Fabrication. Polymers that contain the platinum acetylide chromophores were synthesized that incorporated varying concentrations of the chromophore units by weight percent of the monomer to methylmethacrylate (MMA). The platinum acetylide monomer and azo initiator, 1,1′-azobis(cyclohexanecarbonitrile), were dissolved in MMA and dimethylformamide, deoxygenated via freeze−pump−thaw vacuum degassing, and allowed to polymerize under moderate heat (65−70 °C) to form the solid platinum acetylide PMMA polymer. Covalent incorporation of the monomer into the matrix reduced the mobility of the monomer in the polymer, which limited aggregation and promoted homogeneity. PMMA is advantageous as the host polymer material due to its optical transparency and low density.[39] Concentration ranges from 1.2 to 12.3 wt % with respect to the platinum acetylide to MMA were achieved. The polymerization reactions were inhibited upon addition of higher weight percent platinum acetylide monomer, resulting in either low molecular weight or no polymer formation. This is consistent with previously examined covalently bound PMMA polymers, which could only be obtained up to 13 wt %.[13]

The number- and weight-average molecular weights and polydispersity indexes (M_n, M_w, and PDI, respectively) of the resulting polymers were determined via gel permeation chromatography relative to known molecular weights of linear polystyrene standards in THF. As shown in Table 1, the PDIs were greater than unity for the generated polymers but were relatively low for radical polymerizations, due largely to multiple, sequential precipitations of the polymers. Gel permeation chromatography showed small molecular weight distributions for the polymers. The obtained PDIs, M_n, and M_w values were dependent on the amount of monomer incorporated into the PMMA polymer: the polymers that contain less platinum acetylide monomer exhibited larger M_n and M_w values and higher PDIs, Table 1.

The PMMA-based platinum acetylide polymers were used to generate films with ~3.6 μm thickness via the doctor-blading technique onto borosilicate glass substrates (microscope slides). Free-standing solid polymer monoliths were generated using a one-half inch circular Teflon mold. The polymers were dissolved in dichloromethane, poured into the mold, and allowed to slowly dry, resulting in a free-standing monolith (did not require a glass substrate) of approximately 1 mm thickness. The monoliths exhibited the same photophysical properties as the doctor-bladed films, although the longer pathlengths of the monoliths resulted in larger linear and nonlinear absorptivity.

Table 1. Polymer Molecular Weights and PDIs

chromophore	theoretical[a] monomer (% wt)	actual[b] monomer (% wt)	M_n	M_w	PDI
PE2	2.5	1.7	190 500	309 400	1.62
PE2	10	9.1	189 100	290 000	1.53
DPAF	5.6	3.5	207 100	351 400	1.70
DPAF	10	6.6	57 300	88 500	1.55
BTF	1.0	1.2	252 100	501 500	1.99
BTF	5.0	4.7	145 100	272 300	1.88
BTF	10	12.3	83 800	140 800	1.67

[a] Weight percent of monomer to MMA in polymerization reaction. [b] Calculated from ground-state absorption of polymer and molar absorptivity of monomer.

Ground State Absorption. Figure 3 presents the ground state absorption of the platinum acetylide monomers in solution and the polymers in solution and solid state. Represented is the ground state absorption of the doctor-bladed polymer films. The monomers are characterized prior to modification of the aniline functionality due to the relative instability of the acrylamide monomers. PMMA does not exhibit ground state absorption above 300 nm. The monomers and polymers display a strong absorption band in the near-UV region that is very similar to the absorption of the free chromophores.[14,15,38,40] The ground state absorption spectra of the polymers in solution, doctor-bladed film, and monoliths are nearly identical to the spectra of the monomers. The observed absorption spectra are similar to those seen for other complexes that contain PE2, BTF, or DPAF chromophores.[21,35,40] Note that the absorption maxima red-shift in the order Pt-PE2 < Pt-DPAF < Pt-BTF (see Table 2); the former two chromophores absorb primarily in the near-UV region, with the films exhibiting a faint yellow color. The Pt-BTF absorption peaks at ~400 nm, and consequently, this film exhibits a more pronounced yellow color due to the visible absorption of the BTF chromophore.

Steady State Photoluminescence. The photoluminescence emission of the monomers and polymers were examined with excitation at the ground state absorption maxima. The room temperature solution measurements were conducted in deoxygenated THF and the polymer film emissions were measured in air. The photoluminescence emission spectra are shown in Figure 4, and the triplet excited state lifetimes and other photophysical parameters are summarized in Table 2. With some variations depending on structure and conditions, each of the polymers and monomer complexes features two emission bands (Figure 4): one at relatively short wavelength (λ < 500 nm) that is fluorescence from the singlet state, and a structured emission band at longer wavelength (λ > 500 nm) that is phosphorescence from the triplet state. In argon-purged solution, Pt-PE2(PMMA) and Pt-BTF(PMMA) exhibit nearly identical emission as the Pt-PE2 and Pt-BTF monomers, respectively (see Figure 4a and c). In particular, both materials exhibit fluorescence and phosphorescence with approximately the same relative intensity. The Pt-PE2(PMMA) and Pt-BTF(PMMA) polymers as solid films exhibit fluorescence emission similar to the solution measurements but also exhibit strong, structured phosphorescence emission. The magnitude of the phosphorescence is such that the fluorescence appears weak, despite being of a similar absolute intensity as observed in the solution measurements (this is because the phosphorescence intensity is enhanced in the film samples). Interestingly, the films' emission was measured in air, but apparently oxygen is unable to quench the phosphorescent state due to its low diffusivity in the PMMA matrix.[41] Pt-DPAF and Pt-DPAF(PMMA) in solution do not exhibit phosphorescence in argon-purged THF under ambient conditions (see blue spectrum in Figure 4b); as such, phosphorescence emission was obtained by measuring the photoluminescence of the samples in 2-methyl-THF at 77 K, as shown in the black and red spectra. By contrast, the Pt-DPAF(PMMA) polymer film exhibited strong phosphorescence at 530 nm in when studied in air at room temperature.

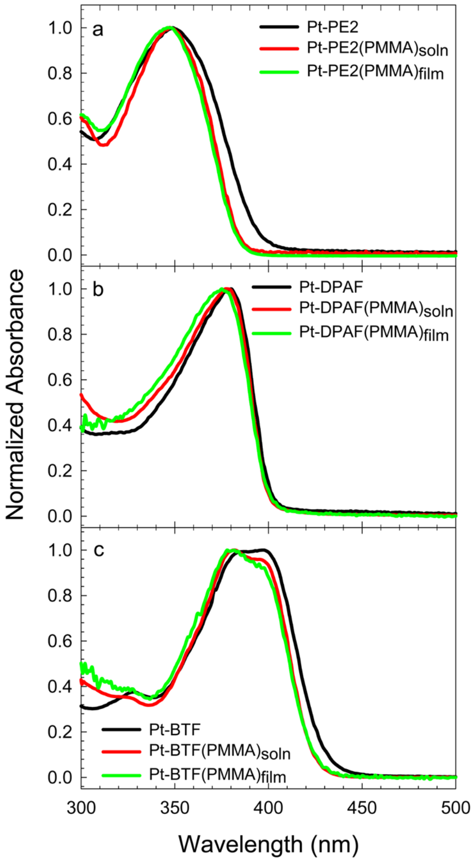

Figure 3. Ground state absorption spectra of the monomers and polymers by chromophore type: (a) PE2 series, (b) DPAF series, and (c) BTF series. The Pt-R monomers in THF are shown in black, the Pt-R(PMMA) polymers in THF are shown in red, and the Pt-R(PMMA) polymer doctor-bladed films are shown in green (9.1% Pt-PE2(PMMA), 3.5% Pt-DPAF(PMMA), and 12.3% Pt-BTF(PMMA).

In summary, all materials exhibit the fluorescence and phosphorescence in solution and in solid films. The phosphorescence is relatively more efficient for the polymer samples when they are measured in the solid state, and the absence of phosphorescence quenching when the films are measured in air suggests that the PMMA matrices have a low oxygen permeability.

Triplet–Triplet Transient Absorption. The triplet excited state for the model complexes and polymers was further studied via transient absorption spectroscopy. First, as shown in Figure 5, near-UV excitation at 355 nm of the complexes and polymers in degassed THF solution generates strongly absorbing transients with lifetimes in the microsecond time domain. The negative bands ranging from 350 to 400 nm correspond to ground state absorption bleaching, while the positive and moderately intense bands are due to the triplet–triplet (T_1–T_n) excited state absorption, consistent with the triplet absorption properties of other platinum acetylide complexes and polymers.[42−46] The triplet excited state lifetimes of the polymers in solution are modestly longer than the lifetimes of the monomers. In general, the transient absorption spectra for the monomers and polymers are similar, exhibiting strong and broad absorption across most of the visible region, with maxima in the 600–700 nm region, suggesting that platinum acetylide polymers can undergo enhanced NLA due to the T_1–T_n excited state absorption (ESA).

Note that a red-shift occurs in the transient absorption maxima for the polymers relative to the monomers of the same chromophore, as summarized in Table 2. The observed red shift in the transient absorption spectra from the monomer to

Table 2. Summary of Photophysical Properties of the Polymer Series in THF

complex	Abs (nm)[a]	ε (M^{-1} cm^{-1})	Fl$_{max}$ (nm)[b]	Ph$_{max}$ (nm)[c]	$\lambda_{T1\text{-}Tn}$ (nm)[d]	τ_{TA} (μs)[e]
PE2	298	50 040	412, 335			
Pt-PE2	349	65 500	408	526, 561	572	1.2
Pt-PE2(PMMA)$_{soln}$	347		432	526, 561	596	2.3
Pt-PE2(PMMA)$_{film}$	347		378	523, 558	560	31.3
DPAF	369	144 789	395, 412			
Pt-DPAF	380	152 000	397	531, 578	617	0.73
Pt-DPAF(PMMA)$_{soln}$	378		398, 454	530, 578	638	6.8
Pt-DPAF(PMMA)$_{film}$	374		422	530, 569	590	39.2
BTF	350	75 660	395			
Pt-BTF	397	73 800	440	568	659	2.3
Pt-BTF(PMMA)$_{soln}$	382		432	567	668	3.7
Pt-BTF(PMMA)$_{film}$	378		431	565	590	36.5

[a] Ground state absorption maxima. [b] Fluorescence spectra, obtained by excitation at ground state absorption maxima. [c] Phosphorescence spectra, obtained by excitation at ground state absorption maxima. [d] Triplet–triplet transient absorption maxima. [e] Triplet excited state lifetimes, calculated from the transient absorption spectra.

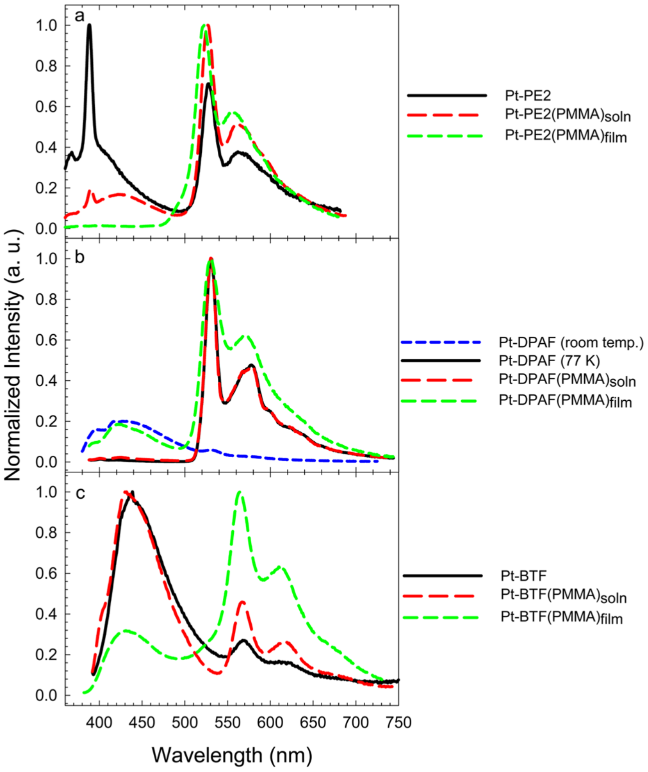

Figure 4. Photoluminescence spectra of monomer and polymer series. (a) Pt-PE2 (black) and Pt-PE2(PMMA) (red) solutions in argon-purged THF and 9.1% doctor-bladed Pt-PE2(PMMA) film (green) in air. (b) Pt-DPAF (black) and Pt-DPAF(PMMA) (red) solutions in argon-sparged methyl-THF at 77 K, Pt-DPAF (blue) in argon-purged THF at room temperature, and 3.5% doctor-bladed Pt-DPAF-(PMMA) film (green) in air. (c) Pt-BTF (black) and Pt-BTF(PMMA) (red) solutions in argon-purged THF and 12.3% doctor-bladed Pt-BTF(PMMA) film (green) in air. Samples were excited at the ground state absorption maxima.

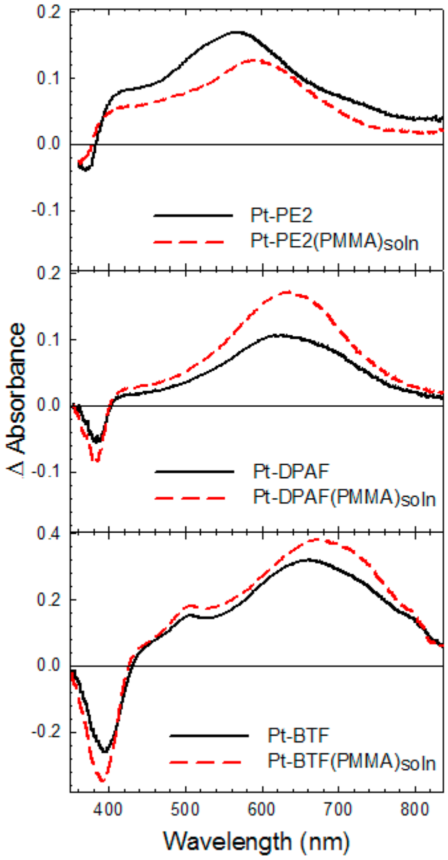

Figure 5. Transient absorption spectra of the monomers (black solid) and polymers (red dashed) in deoxygenated THF after nanosecond-pulsed 355 nm excitation, 8 mJ input energy. Samples have matched absorbances of 0.7 at the wavelength of excitation. Spectra shown for the following samples: 9.1% Pt-PE2(PMMA), 3.5% Pt-DPAF-(PMMA), and 12.3% Pt-BTF(PMMA).

the polymer is the result of the change in the functionality (amine to amide) within the ancillary phenyl substituent rather than from incorporation into the PMMA backbone. This was demonstrated by comparing the transient absorption band maxima for the acrylamide-functionalized monomers with those of the polymers (data not shown).

Transient absorption spectra of the polymer films were also measured, and the spectra are shown in Figure 6 while the decay lifetimes and T_1–T_n band maxima are listed in Table 2. There are some notable differences between the transient absorption properties of the polymers in solution and in film. First, the triplet–triplet absorption band maxima for the films are strongly blue-shifted compared to those of the solution samples. This shift is quite reproducible and is believed to be a

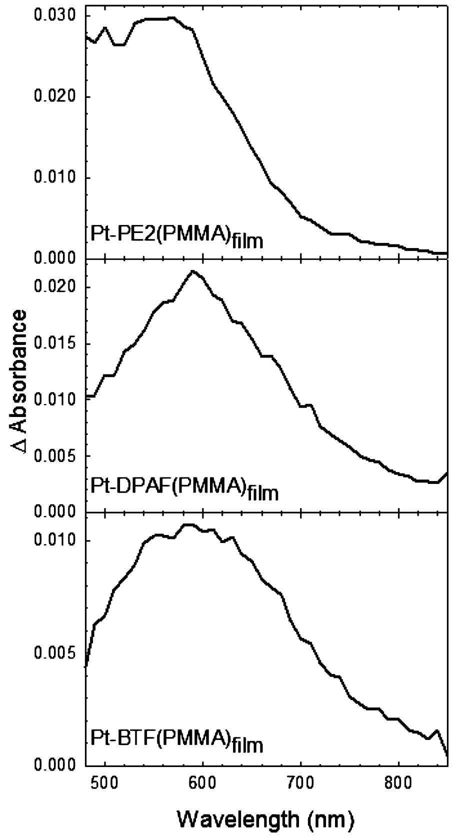

Figure 6. Transient absorption spectra of doctor-bladed polymer films following 355 nm excitation, 5 ns pulsewidth, 250 μJ. Spectra acquired at ~2 μs delay following excitation. The polymers shown are: 9.1% Pt-PE2(PMMA), 3.5% Pt-DPAF(PMMA), and 12.3% Pt-BTF(PMMA).

matrix effect resulting from the incorporation of the platinum acetylide chromophores into the solid state. In addition to the blue shift, the triplet excited state lifetimes exhibited by the polymer films are substantially longer than the polymers in solution. This change is likely due to several effects, including the low permeability of oxygen in the PMMA matrix (reducing the quenching dynamics) and also possibly a reduction in the triplet nonradiative decay rate due to the rigid environment provided by the polymer matrix. Note that the increase in the triplet lifetimes for the polymer films is consistent with the significant enhancement seen in the phosphorescence of the films.

Nonlinear Absorption Properties. The PMMA-based polymers were designed to enable incorporation of platinum acetylides that contain two photon absorbing chromophores into a solid glassy matrix under conditions where the chromophores are well dispersed and not subject to aggregation effects. The one-photon photophysical results described above indicate that the chromophores are indeed well dispersed in the polymeric matrix, and they exhibit well-behaved photophysics characteristic of the monomeric chromophores in dilute solution. In order to investigate whether the outstanding optical properties exhibited by the polymeric chromophores extend to multiphoton absorption, their nonlinear absorption (NLA) response was investigated in solution and in film when subjected to 5 ns laser pulses. The response of the polymers in 1 mM solutions (matched chromophore concentration) in benzene is shown in Figure 7 and compared against the known DPAF-capped diplatinum acetylide complex, T2 (see the Supporting Information for structure), which has been previously reported and gives among the highest response previously observed at 600 nm.[34] The excitation wavelength of 600 nm was selected due to the lack of any ground state absorption at this wavelength, the known TPA spectra of the chromophores,[21] and their strong triplet triplet absorption in this spectral region. The results show that at this wavelength, the response of the polymeric chromophores varied in the series Pt-PE2(PMMA) ~ Pt-BTF(PMMA) < Pt-DPAF-(PMMA) ~ T2. This trend is in accord with the findings of a more detailed study which compares the near-infrared two photon absorption and NLA response of a series of monomeric platinum acetylides that contain the PE2, DPAF, and BTF chromophores.[1,21] Given that the Pt-PE2, -DPAF, and -BTF complexes feature no ground state absorption at 600 nm but strong T_1–T_n absorption, the NLA response to nanosecond pulses is clearly due to a dual mode mechanism involving initial excitation via TPA, combined with excited state absorption via the T_1–T_n transition. The comparatively weaker NLA response of the Pt-PE2(PMMA) and Pt-BTF(PMMA) materials is due to the fact that these the Pt-PE2 and Pt-BTF chromophores have lower two photon absorption cross sections at 600 nm compared to Pt-DPAF.[1,21]

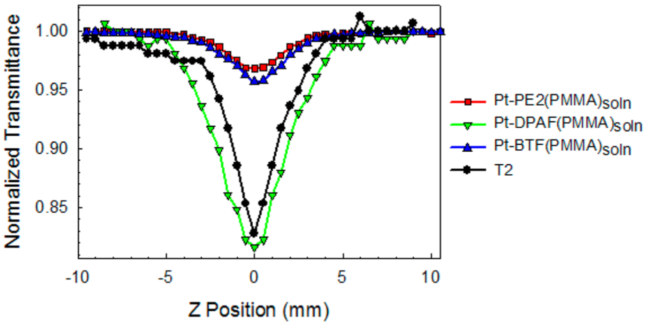

Figure 7. Open aperture nanosecond *z*-scan NLA response of 1 mM polymer solutions: (9.1% Pt-PE2(PMMA)$_{\text{soln}}$) red squares, (12.3% Pt-BTF(PMMA)$_{\text{soln}}$) blue up triangles, (3.5% Pt-DPAF(PMMA)$_{\text{soln}}$) green down triangles against T2 (black circles) in THF with excitation at 600 nm, 850 μJ, 5 ns pulsewidth.

Preliminary experiments showed that it was difficult to conduct the nanosecond *z*-scan studies on film or monolith samples of the polymeric chromophores. As such the monolith samples were probed by using nonlinear transmittance (NLT). The NLT measurements were accomplished by modification of the *z*-scan apparatus—the monolith samples were placed at the focus of the laser beam and the laser input energy was varied. The resulting NLT response for two monolith series at an excitation wavelength of 600 nm is shown in Figure 8. The first series, as shown in Figure 8a, consisted of three monoliths containing the three different polymeric chromophores, Pt-PE2(PMMA-1.7), Pt-DPAF(PMMA-3.5), and Pt-BTF(PMMA-1.2) (where the numbers represent the weight percent loading of the chromophore in the polymer sample used; see Table 1). The second NLT series shown in Figure 8b, examined the effect of the weight percent of Pt-BTF chromophore incorporated into the Pt-BTF(PMMA) sample on the nonlinear response of the monolith (loadings used were 1.2%, 4.7%, and 12.3%; see Table 1).

In general the NLT experiments reveal that all of the polymer samples exhibit some degree of nonlinear absorption response. The series which compares the response of the three Pt-acetylide chromophores (at relatively low weight percent

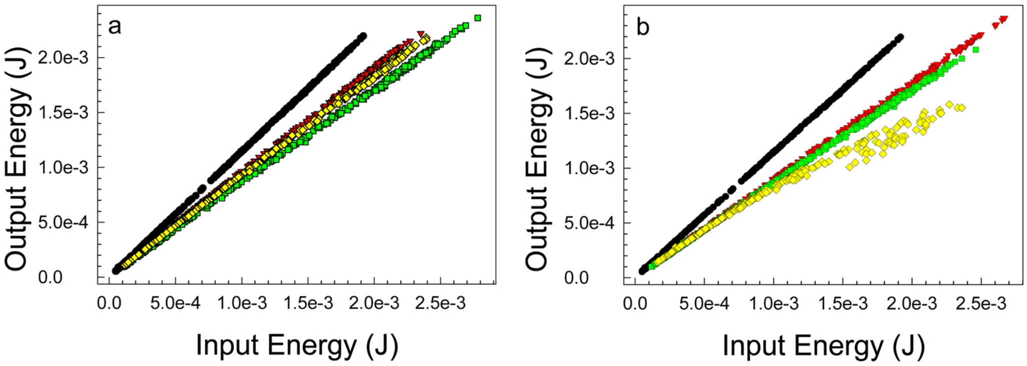

Figure 8. Nonlinear transmittance response of polymer monoliths via nanosecond excitation at 600 nm, 5 ns pulsewidth, beam waist diameter ~100 μm: (a) 1.7% Pt-PE2(PMMA) = red triangles, 3.5% Pt-DPAF(PMMA) = green squares, 1.2% Pt-BTF(PMMA) = yellow diamonds, blank = black circles. (b) Varying percent incorporation of Pt-BTF(PMMA) monoliths: 1.2% Pt-BTF(PMMA) = red triangles, 4.7% Pt-BTF(PMMA) = green squares, 12.3% Pt-BTF(PMMA) = yellow diamonds, blank = black circles.

loading, Figure 8a) shows that the NLT response varies in the series Pt-PE2(PMMA) ~ Pt-BTF(PMMA) < Pt-DPAF-(PMMA). Note that this ordering is the same as observed in the solution *z*-scan experiments and is also consistent with other work which suggests that the NLA response of the Pt-DPAF chromophore is stronger than that of the Pt-BTF or -PE2 systems.[21] The comparatively weak NLA response for this set is mainly due to the fact that the chromophore concentration is the polymers is comparatively low in this data series. The effect of increasing the chromophore loading in the monolith is clearly evident in the series of data shown in Figure 8b. Here it can be seen that the NLA response of the Pt-BTF(PMMA) monoliths increases systematically with chromophore loading. The sample with 12.3% by weight chromophore displays a relatively pronounced nonlinear absorption response for input energy >1 mJ.

SUMMARY AND CONCLUSION

In the present investigation we sought to develop an approach that allows covalent linking of platinum acetylide nonlinear absorption chromophores into PMMA as a glassy host matrix, allowing fabrication of NLA materials that can be used as coatings or free-standing optical monoliths. In order to accomplish the goal, we designed a series of platinum acetylide based monomers that contain π-conjugated donor- or acceptor-ligands that have been previously shown to exhibit moderately large TPA in the near-infrared region. Each monomer was functionalized with a reactive acrylamide unit that allows incorporation of the monomers into a PMMA host polymer via copolymerization with methylmethacrylate under free radical polymerization conditions. The organometallic chromophores were incorporated into PMMA at loadings up to 12% by weight; however, further increase in loading was not possible because the polymerization was inhibited, apparently by the platinum acetylide monomer. Three different π-conjugated units were incorporated into the polymer system (PE2, DPAF, and BTF), a result which displays the generality of the approach that was developed.

Central to the goals of this effort was the characterization of photophysical properties of the polymeric chromophores in solution and the solid state. Minimal shifts in the ground state absorption and photoluminescence were observed for the polymeric chromophores, both in solution and solid state relative to the monomeric chromophores. However, the polymer films displayed markedly stronger phosphorescence than the polymers in solution or the monomers, even when the films were measured in air-saturated conditions. The intersystem crossing rates from the singlet to the triplet excited state is near unity for similar platinum acetylide monomers and oligomers.[21,34] As such, it is suggested that the polymer films exhibit stronger phosphorescence and longer triplet excited state lifetimes because the nonradiative relaxation decay pathways are less accessible in the solid state polymer than in the polymer solution, and also because oxygen quenching is precluded in the polymer film matrix. The polymeric chromophores also exhibit strong triplet−triplet transient absorption in the visible region, both in solution and in solid films. The triplet−triplet absorption band for the chromophores in the polymer films was slightly blue-shifted relative that that for the same chromophores in solution. The blue shift is believed to result from a matrix effect, possibly precluding a specific geometric relaxation of the chromophore in the restricted medium provided by the PMMA matrix.

Finally, nonlinear absorption experiments carried out on the polymeric chromophores in solution and in films show that the chromophores remain active in optical pulse limiting. The NLA response is relatively weak for the samples that contain ~1% weight chromophore loading; however, at increased loading, the NLA response is improved substantially. One obstacle for the widespread application of the approach developed here is the fact that the upper limit for loading of the chromophores in the PMMA host matrix was ~10 − 12%, due to inhibition of the free radical polymerization by the platinum acetylide chromophore.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete synthesis procedures, analytical data, NMR data, film and monolith formation, film triplet−triplet transient absorption instrumentation and structure of T2 NLA reference chromophore. 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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