Large Optical-Limiting Response in Some Solution-Processable Polyplatinaynes

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Experimental investigations of the nonlinear optical transmittance characteristics of a series of solution-processable platinum polyyne polymers at 532 nm show that they are excellent optical limiters with performance comparable or superior to those of the state-of-the-art reverse saturable absorption dyes such as fullerene C_{60} and metal phthalocyanine complexes. On the basis of results from photophysical studies, both the inclusion of a platinum chromophore for increasing the intersystem crossing rate and the formation of an intramolecular charge-transfer state between the electron-withdrawing and electron-donating moieties along the polymer chain are very effective approaches for the enhancement of the optical-limiting properties of these metal polyynes. The structural influence of the aryl linker units on the optical-limiting action has been evaluated in detail. The optical-limiting thresholds for these polymetallaynes range from 0.06 to 0.15 J/cm^2 at 82% linear transmittance, and these polymeric materials are very promising candidates for use in practical optical-limiting devices.

Introduction

Within the realm of the photonic era in the new century, conjugated polymers have attracted the research interests of many scientists for their potential application in field-effect transistors,[1] electroluminescent devices,[2] lasers,[3] and photoelectronic devices.[4] Recent research work showed that various conjugated polymers can also be exploited in nonlinear optics (NLO) for optical communication, data processing, optical switching, and so forth.[5−8] However, with the rapid development of laser technology, the damage of human eyes, optical sensors, and sensitive optical components caused by exposure to sudden intense laser pulses has driven much effort for the search for good optical limiters that possess fast response speeds and relatively high linear transmissions.[9,10] Optical limiters are devices that strongly attenuate optical beams at high intensities while exhibiting higher transmittance at low intensities. Such devices are useful for the protection of the human eye and optical sensors from intense laser beams. At present, materials practically employed for optical limiting are largely small molecules, such as fullerenes (C_{60}),[11,12] phthalocyanines,[13−15] porphyrins,[16,17] diacetylenes,[18] nanotubes,[19] and organometallic compounds.[20−23] Among these, the optical-limiting effects of organic phthalocyanines and porphyrins can be enhanced greatly upon the incorporation of heavy metal ions (such as Cu, Pb, In, Zn, etc.),[24−29] which can increase the efficiency of intersystem crossing to the triplet manifold via spin−orbit coupling. However, their poor solubility and the technical difficulties in fabricating devices have hindered their practical application so far. To hurdle these obstacles, it is important to develop other new materials for commercial exploitation.

Recent investigations indicated that some conjugated organic polyynes with good processability can act as good

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optical-limiting materials with performance comparable to that of C_{60}.[5] In comparison, much less work has been done on the optical-limiting properties of metal-containing polymers, and to our knowledge, related studies on metal−aryleneethynylene copolymers of the type *trans*-$[-Pt(PBu_3)_2-C{\equiv}CArC{\equiv}C-]_\infty$ remain relatively unexplored. So far, only some small-molecule platinum(II) arylacetylide complexes with terpyridyl[30] and phosphine ligands[31] have been studied in this area where the triplet manifold is able to play an active role in the photophysics of platinum−ethynyl compounds. They were demonstrated to exhibit strong reverse saturable absorption (RSA) for nanosecond laser pulses, suggesting that this class of complexes represents promising broadband optical-limiting materials. Indeed, these platinum polyynes can offer a large architectural flexibility in a structure, which facilitates the tailoring of their physical, optoelectronic, and chemical parameters in a very broad range by chemical modification of the Ar groups.[32a−c] In this paper, we describe the first report on a series of conjugated platinum polyynes with large optical-limiting capabilities, and the mechanisms pertaining to their nonlinear optical behavior are discussed with reference to the structure−property relationship of these metallopolymers.

Experimental Section

General. All the reagents and chemicals were purchased from Aldrich or Acros. Unless otherwise stated, they were used directly without further purification. All the solvents were carefully dried and distilled prior to use. The compounds *trans*-$[PtCl(Ph)(PEt_3)_2]$[33] and *trans*-$[PtCl_2(PBu_3)_2]$[34] were prepared by literature methods. NMR spectra were measured in $CDCl_3$ on a JEOL EX270 or a Varian Inova 400 MHz FT-NMR spectrometer, with the ^1H and ^{13}C NMR chemical shifts quoted relative to TMS and the ^{31}P chemical shifts relative to the 85% H_3PO_4 external standard. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. UV−vis spectra were obtained on the HP-8453 spectrophotometer. The photoluminescent properties and lifetimes of the compounds were probed on the Photon Technology International (PTI) Fluorescence Master Series QM1 system. Infrared spectra were recorded on a Nicolet Magna 550 series II FTIR spectrometer in CH_2Cl_2 solution or KBr pellets. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a HP 1050 system using polystyrene standards.

Optical-Limiting Measurements. To study the optical-limiting properties, the intensity-dependent transmittance and Z-scan measurements were performed with a Q-switched Nd:YAG laser at a repetition rate of 10 Hz. The laser was frequency doubled with an output wavelength of 532 nm with a 10 ns pulse width for the Gaussian mode by a frequency double crystal. The laser beam was then split into two beams by a beam splitter. One was used as the reference beam, which was received by a detector (D_1), the other was used for the sample measurement, and it was focused with a lens (f = 20 cm). After transmitting through the sample, the light beam entered another detector (D_2). The sample to be measured was moved along a rail to change the incident irradiance on it. The incident and transmitted energies were detected simultaneously by the two detectors D_1 and D_2 (LPE−1A) individually. The performance of each sample was measured as an 82% transmitting solution at 532 nm in CH_2Cl_2 in a 1 mm quartz cell.

Synthesis of Platinum Polyynes and Diynes. The preparations of five of the diethynyl ligand precursors were reported by us previously, and 2,7-diethynyl-9-(*p*-methoxybenzylidene)fluorene was prepared as described in the Supporting Information. The platinum polyynes were synthesized by the classical Sonogashira-type dehydrohalogenating polymerization between *trans*-$[PtCl_2(PBu_3)_2]$ and the appropriate ligands $HC{\equiv}CArC{\equiv}CH$.[32] In a typical run, equal moles of *trans*-$[PtCl_2(PBu_3)_2]$ and $HC{\equiv}CArC{\equiv}CH$ were added to a NEt_3/CH_2Cl_2 (1:1 v/v) mixture under a N_2 atmosphere. A small amount of CuI was then added, and the reaction mixture was stirred at room temperature (r.t.) overnight. The reaction mixture was filtered through a short silica gel pad to remove the catalyst residue. The solvent was removed, and the crude product was purified by precipitating the polymer solution in CH_2Cl_2 from MeOH. The precipitate was collected, washed with hexane, and dried under a vacuum. The yields for all the polymers are ca. 60−85%. Except for $[Pt\text{-}T(OMe\text{-}F)T]_\infty$, the spectroscopic data were known for the other five metallopolymers.[32]

$[Pt\text{-}T(OMe\text{-}F)T]_\infty$. Red powder (yield: 78%). IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2094 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.63−7.43 (m, 7H, Ar + vinyl), 7.19 (m, 2H, Ar), 6.87 (m, 2H, Ar), 3.81 (s, 3H, OMe), 2.05 (m, 12H, PCH_2), 1.53−1.18 (m, 24H, $(CH_2)_2$), 0.84 (m, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.28, 139.70, 138.31, 136.54, 136.04, 135.31, 131.26, 130.91, 130.66, 129.35, 126.45, 122.30, 118.91, 113.80 (Ar + $C{\equiv}C$), 55.16 (OMe), 26.34, 24.40, 23.84, 13.86 (Bu). ^{31}P NMR ($CDCl_3$): δ 4.06 ($^1J_{P-Pt}$ = 2352 Hz). Anal. Calcd for $C_{49}H_{68}OP_2Pt$: C, 63.28; H, 7.37. Found: C, 63.02; H, 7.11. GPC (THF): M_w = 64 810, M_n = 29 920, polydispersity = 2.17 (DP = 32). UV−vis (CH_2Cl_2): λ_{max}/nm = 388, 454 sh.

The synthetic method for the model diyne compounds of the platinum polyynes is similar to that of their corresponding polymers.

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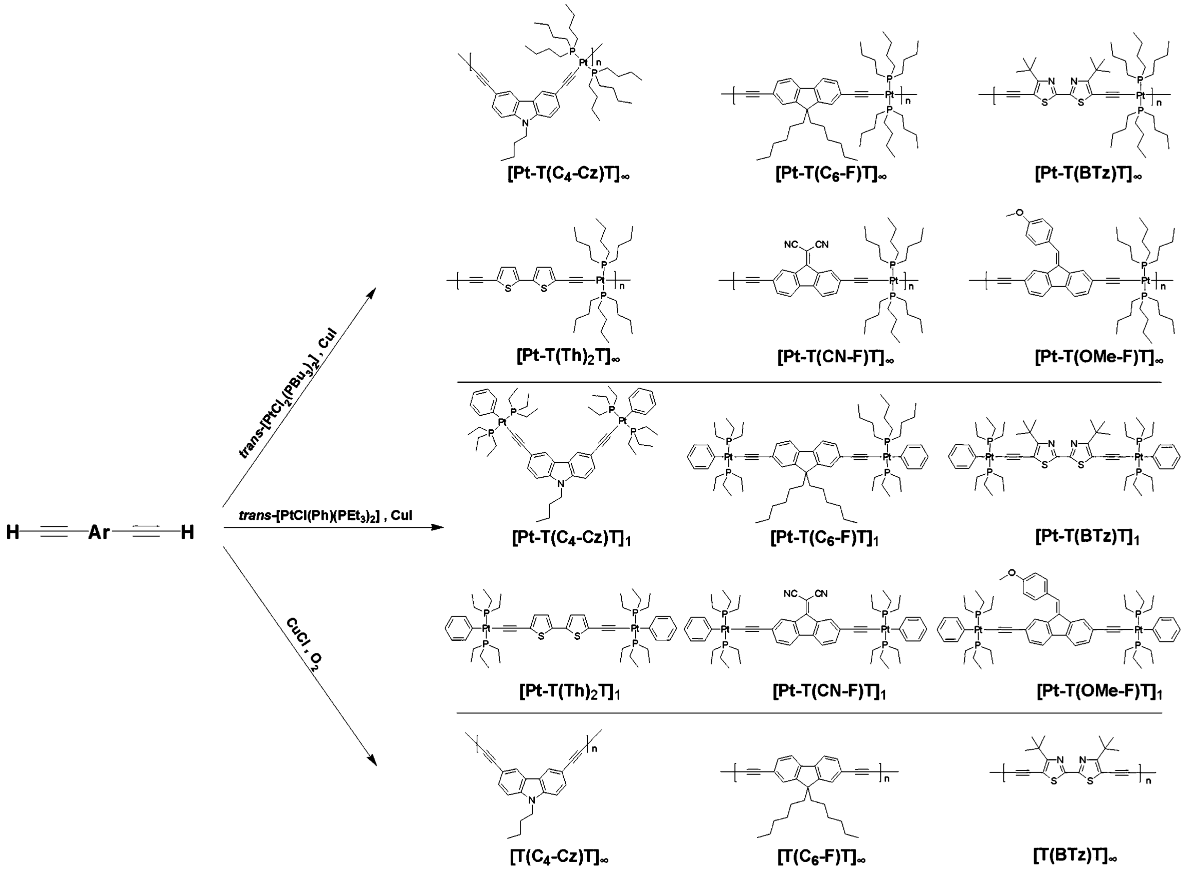
Scheme 1. Synthesis of Platinum Polyynes and Diynes and Their Organic Counterparts



Under a N_2 atmosphere, one portion of HC≡CArC≡CH and two molar equivalents of *trans*-[PtCl(Ph)(PEt$_3$)$_2$] were added to a NEt_3/CH_2Cl_2 (1:1 v/v) mixture, and CuI was then added as the catalyst. After the reaction mixture was stirred at r.t. overnight, the reaction mixture was filtered through a short pad of silica gel to remove the catalyst residue. The solvent was removed, and the residue was purified by preparative TLC using hexane/CH_2Cl_2 as the eluent. The yields range from 55 to 88%. Except for [Pt-T(OMe-F)T]$_1$, the spectral data for the other five Pt polyynes were reported previously.[32]

[Pt-T(OMe-F)T]$_1$. Orange-red solid (yield: 72%). IR (CH_2Cl_2): ν(C≡C) 2088 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.64−7.46 (m, 7H, Ar + vinyl), 7.35−7.21 (m, 8H, Ar), 6.99−6.79 (m, 4H, Ar), 6.77−6.79 (m, 2H, Ar), 3.84 (s, 3H, OMe), 1.79−1.63 (m, 24H, PCH_2), 1.15−0.87 (m, 36H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.19, 156.61, 139.59, 139.21, 138.13, 136.65, 136.00, 135.74, 131.10, 130.84, 129.53, 127.50, 127.38, 127.25, 127.22, 126.91, 126.74, 126.34, 122.17, 121.17, 121.16, 118.83, 118.73, 113.70, 113.34, 112.60, 111.08, 110.74 (Ar + C≡C), 55.13 (OMe), 15.07, 8.02 (Et). ^{31}P NMR ($CDCl_3$): δ 10.99 ($^1J_{P-Pt} = 2628$ Hz). FAB-MS (*m*/*z*): 1346 [M$^+$]. Anal. Calcd for $C_{61}H_{84}OP_4Pt_2$: C, 54.38; H, 6.28. Found: C, 54.10; H, 6.08. UV−vis (CH_2Cl_2): λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1}) = 355 sh (6.1), 371 (8.6), 452 sh (0.4).

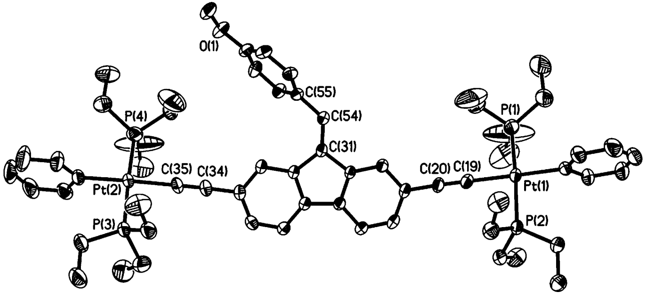


Figure 1. ORTEP drawing of the crystal structure of [Pt-T(OMe-F)T]$_1$.

X-ray Crystallography. Good quality orange crystals of [Pt-T(OMe-F)T]$_1$ were grown at r.t. by slow evaporation of its solution in CH_2Cl_2/hexane. Intensity data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) on a Bruker Axs SMART 1000 CCD area detector. The collected frames were processed with the software SAINT,[35a] and an absorption correction was applied (SADABS)[35b] to the collected reflections. The structure was solved by direct methods (SHELXTL)[36] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2. All non-hydrogen atoms were assigned with anisotropic displacement parameters. Crystal data: $C_{61}H_{85}OP_4Pt_2$; $M = 1348.35$; monoclinic; space group $P\bar{1}$; $a = 10.769(3)$, $b = 13.454(3)$, $c = 21.964(5)$ Å; $\alpha = 94.124(4)$, $\beta = 92.615(4)$, $\gamma = 101.141(4)°$; $U = 3108.6(13)$ Å^3; $Z = 2$; $T = 293$ K; μ(Mo Kα) = 4.634 mm^{-1}; 18 482 reflections measured; 13 596 unique; $R_{int} = 0.0187$; final $R_1 = 0.0372$; $wR_2 = 0.0885$ for 9096 [$I > 2\sigma(I)$] observed reflections.

Results and Discussion

Synthesis. Scheme 1 shows the chemical structures and the synthetic strategies of the platinum-containing polymers and their model complexes in the present study. The triple

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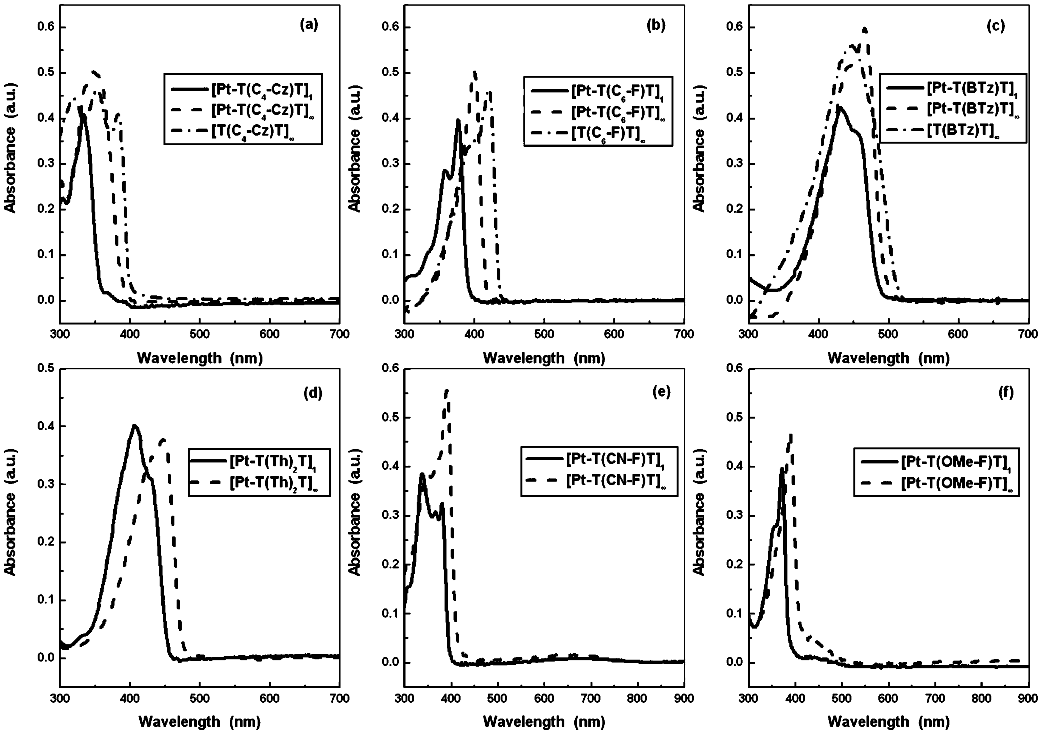

Figure 2. UV-vis linear-absorption spectra of all the optical-limiting materials in dilute CH_2Cl_2 solutions at room temperature.

bonds are abbreviated by T, fluorene rings by F, carbazole rings by Cz, bithiazole rings by BTz, and bithiophene rings by $(Th)_2$. Model compounds and polymers are differentiated by use of the subscripts 1 and ∞, respectively. The diethynyl ligand precursors HC≡CArC≡CH can be used to furnish dinuclear and polymeric complexes of platinum by adaptation of the dehydrohalogenation procedures using the CuI/NEt_3 catalytic system. The feed mole ratio of the platinum chloride precursors and the diethynyl ligands were 2:1 and 1:1 for the dimer and polymer syntheses, respectively. The platinum polyynes [Pt-T(C_4-Cz)T]$_\infty$, [Pt-T(C_6-F)T]$_\infty$, [Pt-T(BTz)T]$_\infty$, [Pt-T$(Th)_2$T]$_\infty$, [Pt-T(CN-F)T]$_\infty$, and [Pt-T(OMe-F)T]$_\infty$ were isolated in good yields by silica column chromatography. The platinum dimers [Pt-T(C_4−Cz)T]$_1$, [Pt-T(C_6−F)T]$_1$, [Pt-T(BTz)T]$_1$, [Pt-T$(Th)_2$T]$_1$, [Pt-T(CN−F)T]$_1$, and [Pt-T(OMe-F)T]$_1$ were obtained in high purity and yields by preparative TLC on silica, and they were investigated as model complexes for the electronic and structural properties of the parent polymers. The organic polyynes [T(C_4−Cz)T]$_\infty$, [T(C_6−F)T]$_\infty$, and [T(BTz)T]$_\infty$ were prepared by the oxidative self-coupling of the appropriate diethynyl compounds under the CuCl/O_2 catalytic system.[37] The IR, NMR (^{1}H, ^{13}C, and ^{31}P), and MS spectra and elemental analysis data have characterized the chemical structures of the compounds thoroughly. The molecular weights of the organic and organometallic polyynes were estimated by GPC analyses against polystyrene. The IR spectra of these platinum polyynes and diynes give a characteristic ν(C≡C) absorption at ca. 2080−2099 cm^{-1}, which together with the singlet peak observed in the respective ^{31}P {^{1}H} NMR spectrum indicates a trans geometry of the square-planar $Pt(PR_3)_2(alkynyl)_2$ (R = Et or Bu) unit. The three-dimensional molecular structure of [Pt-T(OMe-F)T]$_1$, as confirmed by X-ray crystallography, also helped in elucidating the polymer structure in the solid state (Figure 1). The average bond angle of 175.4(5)° for the Pt−C≡C unit conforms to the linear geometry of the rodlike polymers. The exo double bond C(31)−C(54) is distorted from planarity by only 7.5°. There is a shortening of the C(54)−C(55) bond [1.477(6) Å] and a lengthening of the C(31)−C(54) bond [1.337(6) Å], suggesting possible π conjugation.

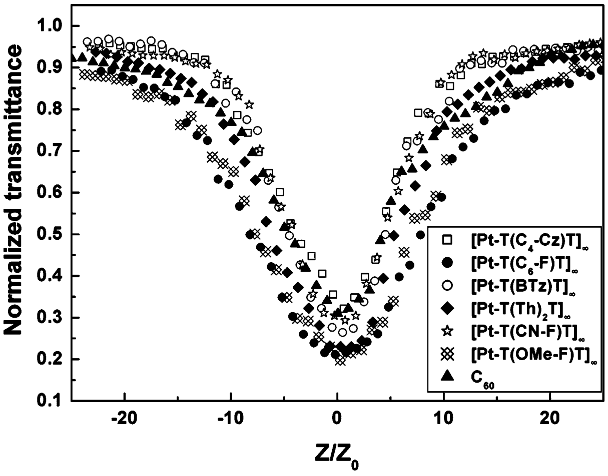

Figure 3. Open aperture Z-scan results for the six platinum polyynes and C_{60} solutions at the same linear transmittance of 82%.

Optical-Limiting Properties of Platinum Polyynes. All the samples are stable toward air and laser light under the experimental conditions. For characterizing the optical-limiting properties at 532 nm excitation, the materials should show weak ground-state absorption at this wavelength. The

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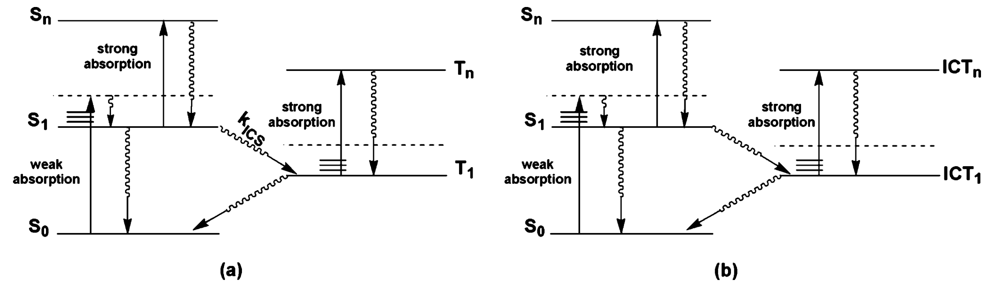

Figure 4. Two possible optical-limiting mechanisms for the platinum polyynes.

Table 1. Lifetime of the S_1 State for Platinum Polyynes

platinum polyynes	lifetime of S_1 state (ns)[a]
[Pt-T(C_4-Cz)T]$_\infty$	1.90
[Pt-T(C_6-F)T]$_\infty$	0.98
[Pt-T(BTz)T]$_\infty$	1.04
[Pt-T(Th)$_2$T]$_\infty$	0.87
[Pt-T(CN−F)T]$_\infty$	2.24
[Pt-T(OMe-F)T]$_\infty$	1.48

[a] Measured at room temperature in CH_2Cl_2 solution with the excitation wavelength at 337 nm.

UV−vis spectra for all the platinum polymers and dimers taken in CH_2Cl_2 at r.t. are gathered in Figure 2. Clearly, there is a transparent window at 532 nm for all the materials. The absorption bands in the range of 300−500 nm are assigned to the $\pi-\pi^*$ transitions of the bridging ligands. But, for polymers [Pt-T(CN−F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$ and their corresponding dimers [Pt-T(CN−F)T]$_1$ and [Pt-T(OMe-F)T]$_1$, there are absorption bands caused by the intramolecular charge-transfer (ICT) state.[38] The broad ICT weak absorption bands for [Pt-T(CN−F)T]$_\infty$ and [Pt-T(CN−F)T]$_1$ lie beyond 600 nm, and those for [Pt-T(OMe-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_1$ appear as shoulders in the 400−500 nm region.

From the Z-scan curves for all six platinum polyynes measured in CH_2Cl_2 (Figure 3), all of them show excellent optical-limiting behavior. Experiments with CH_2Cl_2 alone afforded no detectable optical-limiting effect, indicating that the solvent contribution is negligible. When the sample is far from the focus ($Z/Z_0 = 0$) and the incident irradiance upon it is weak, the transmittance of the sample remains almost constant and shows a linear optical property (i.e., obeying Beer's law). But when the sample is close to the focus and the incident irradiance is strong, the transmittance of the sample decreases and the optical-limiting effect appears. It is apparent that [Pt-T(C_6-F)T]$_\infty$, [Pt-T(Th)$_2$T]$_\infty$, and [Pt-T(OMe-F)T]$_\infty$ yield the strongest optical limiting, and these properties are superior to that of C_{60}, which was recognized as an excellent optical-limiting material.[11] Polymetallaynes [Pt-T(C_4-Cz)T]$_\infty$, [Pt-T(BTz)T]$_\infty$, and [Pt-T(CN−F)T]$_\infty$ also exhibit very good optical-limiting properties, which are comparable to that of C_{60}.

To interpret the Z-scan data obtained, we have to deal with the optical-limiting mechanism. According to the five-level model for the RSA mechanism (see Figure 4a),[39] the molecules in the ground state (S_0) initially absorb optical energy and are excited to the first singlet state (S_1). After the S_1 state gains a certain population, it can absorb optical energy strongly and leaps to the higher singlet state (S_n) to induce the optical-limiting effect or undergo the intersystem crossing (ISC) to the first triplet state (T_1). When the molecules in the T_1 state gain a certain population, they can absorb optical energy to reach the higher triplet state (T_n). The strong energy absorption accompanied with the $T_1 \rightarrow T_n$ transition leads to the optical-limiting action. Owing to the short lifetime (<10 ns) of the singlet state (see Table 1), it is the triplet excited-state absorption that contributes to the nanosecond optical-limiting process.[6,39] To support this, the photoluminescence (PL) spectra (Figure 5) for the singlet and triplet states were measured. For [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(C_6-F)T]$_\infty$, their PL spectra show obvious triplet emissions at 77 K, which peak at 450 and 545 nm, with the measured triplet lifetimes being 5.88 and 13.87 μs, respectively. This observation is attributable to the significant spin−orbit coupling between the ligand and platinum ion in metal polyynes, but triplet emission was not observed for the free ligand at the same temperature. The singlet state lifetimes for [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(C_6-F)T]$_\infty$ are 1.90 and 0.98 ns, respectively. For pulse lengths less than the lifetime of the triplet state, the triplet state will act as an accumulation site. It can be confirmed that the optical-limiting effect of [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(C_6-F)T]$_\infty$ was induced mainly by the triplet absorption. From Figure 5a and b, the triplet emission of [Pt-T(C_6-F)T]$_\infty$ can be observed even at r.t., while there is no triplet emission for [Pt-T(C_4-Cz)T]$_\infty$ at 298 K. On the basis of these data, it can be concluded that the ISC process for [Pt-T(C_6-F)T]$_\infty$ is more efficient than that for [Pt-T(C_4-Cz)T]$_\infty$. Accordingly, the strength of the optical-limiting response follows the order [Pt-T(C_6-F)T]$_\infty$ > [Pt-T(C_4-Cz)T]$_\infty$. The stronger optical limiting of the former can be attributed to its higher triplet excited-state quantum yield, consistent with the experimental results shown in Figure 3.

As for [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$, there is no obvious triplet emission in their PL spectra (Figure 5c and d) even at 77 K, so their optical-limiting effect might not be induced by the triplet absorption. It can be anticipated that both [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$ show a different optical-limiting mechanism compared to that for [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(C_6-F)T]$_\infty$. It is well-known that thiophene and thiazole are electron-rich, five-membered aromatic systems with six π electrons.[6,32e,32f] These moieties can act as donors (D) in the backbone of [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$, and the platinum ions can act as strong acceptors (A), leading to donor−acceptor (D−A) structures along the polymeric chain. Because of the presence of strong D−A

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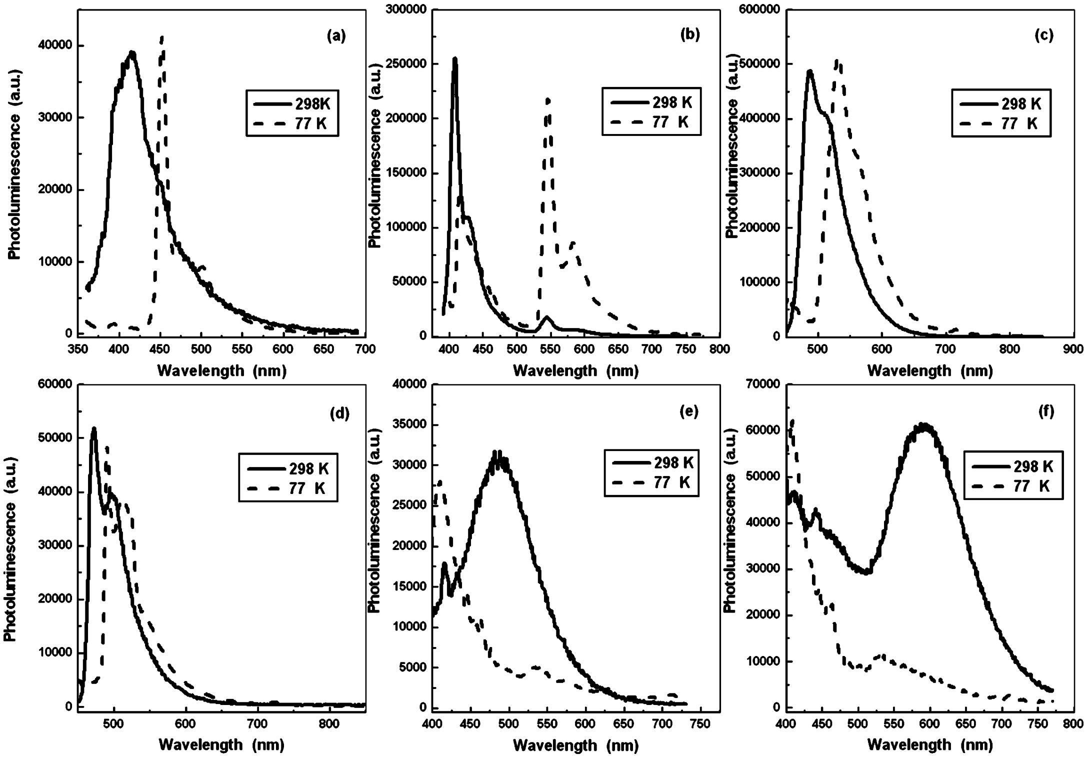

Figure 5. PL spectra at 298 and 77 K in CH$_2$Cl$_2$ for (a) [Pt-T(C$_4$-Cz)T]$_\infty$, (b) [Pt-T(C$_6$-F)T]$_\infty$, (c) [Pt-T(BTz)T]$_\infty$, (d) [Pt-T(Th)$_2$T]$_\infty$, (e) [Pt-T(CN-F)T]$_\infty$, and (f) [Pt-T(OMe-F)T]$_\infty$.

components, when [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$ are exposed to the strong incident irradiance of the laser beam, there will be ICT states between the metal ion and the ligand. In such cases, the possible optical-limiting mechanism for [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$ is portrayed in Figure 4b. The molecules leap to the first singlet state (S$_1$) from the ground state (S$_0$) upon the absorption of optical energy. Following this, they can absorb optical energy strongly to get excited to the higher singlet state (S$_n$) to induce the optical-limiting effect or undergo the nonradiative decay process to form the ICT$_1$ state. When the molecules in the ICT$_1$ state gain a certain population, absorption of optical energy takes place, and they will be excited to the higher ICT$_n$ state. The strong energy absorption together with the ICT$_1$ → ICT$_n$ process gives rise to the optical-limiting behavior of [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$. From Figure 3, [Pt-T(BTz)T]$_\infty$ shows an inferior optical-limiting response as compared to that of [Pt-T(Th)$_2$T]$_\infty$. As we know, the thiazole unit is a hybrid of the electron-rich thienyl and electron-deficient pyridyl groups. So the electron-withdrawing imine structure in the thiazole unit in [Pt-T(BTz)$_2$T]$_\infty$ will probably disturb the charge-transfer event between the bithiazole unit and the platinum ion, hindering the formation of the ICT state. This suggests that the optical-limiting action of [Pt-T(BTz)T]$_\infty$ and [Pt-T(Th)$_2$T]$_\infty$ is likely induced by the ICT state.

In a related context, two other polymers, [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$, were designed and synthesized. As mentioned earlier, the occurrence of the ICT process in [Pt-T(CN-F)T]$_\infty$ by the introduction of two strongly electron-withdrawing cyano substituents at the fluorene periphery results in the deep blue color in solution and a weak ICT band peaking at about 660 nm in its UV−vis spectrum (Figure 2e). To our surprise, its optical-limiting response is just similar to that of [Pt-T(BTz)T]$_\infty$ (Figure 3). This observation can be explained in the following way. The second hyperpolarizability, γ, which characterizes the third-order nonlinear optical activity of molecules, shows the relationship in expression 1 for the D−A substitution pattern in one-dimensional conjugated molecules:[40]

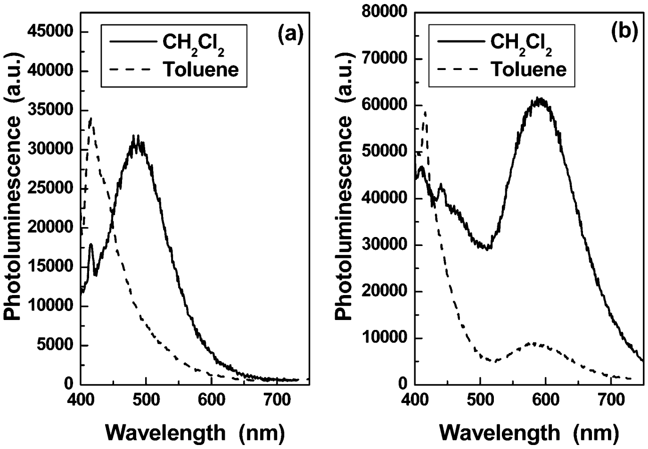

Figure 6. PL spectra for (a) [Pt-T(CN-F)T]$_\infty$ and (b) [Pt-T(OMe-F)T]$_\infty$ in CH$_2$Cl$_2$ and toluene at 298 K.

$$\gamma(\mathrm{A-A}) < \gamma(\mathrm{D-D}) < \gamma(\mathrm{D-A}) \qquad (1)$$

There are excessive strong acceptors (A) in the backbone of [Pt-T(CN-F)T]$_\infty$, making the electron donors (D) less sufficient. Instead, conjugation of the fluorene nucleus in [Pt-T(OMe-F)T]$_\infty$ is increased by incorporating the methoxy

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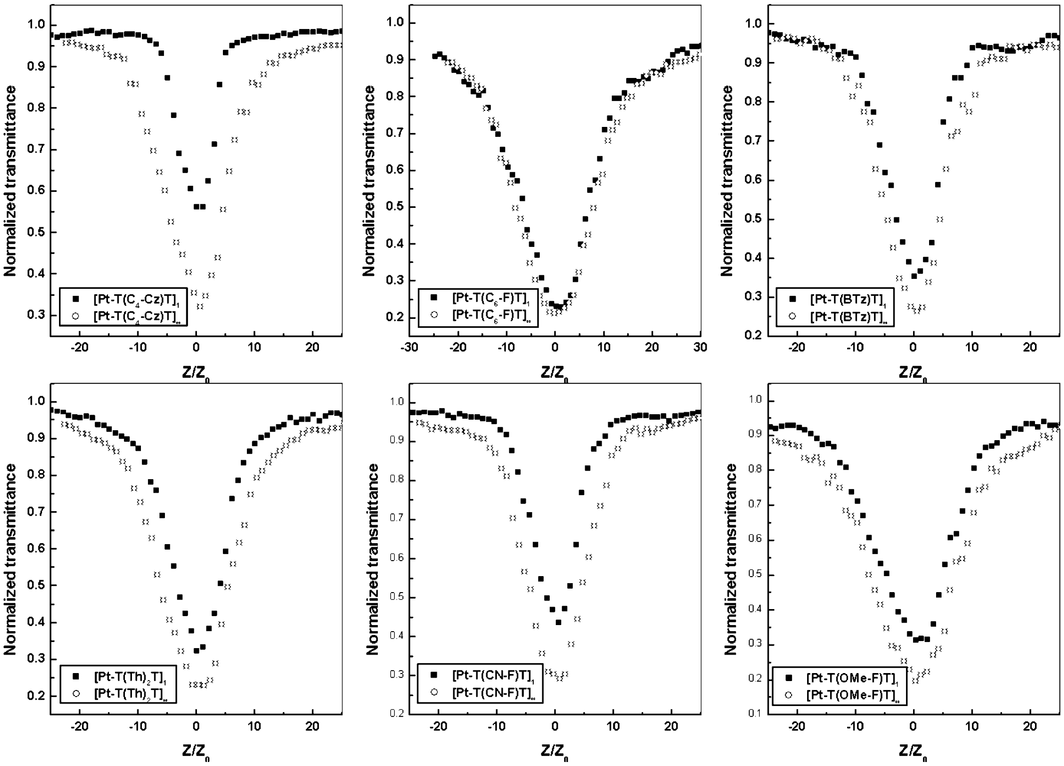

Figure 7. Comparison of the optical-limiting behavior for the platinum polyynes and diynes at the same linear transmittance of 82%.

electron donor in order to strengthen the electron-donating ability of the ligand chromophore. From the UV−vis spectrum of [Pt-T(OMe-F)T]$_\infty$ (Figure 2f), there is a broad ICT absorption shoulder that tails off to 500 nm. In the presence of such a ligand structure that could promote the formation of the ICT state, [Pt-T(OMe-F)T]$_\infty$ shows a much stronger optical-limiting response than those of [Pt-T(CN-F)T]$_\infty$ as well as C_{60} at the same linear transmittance (Figure 3). To confirm that the optical-limiting actions of [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$ are induced by the absorption of the ICT state, their PL spectra were also obtained at 298 and 77 K (Figure 5e and f). From the spectral data, it can be revealed that the emission bands around 425 nm are assigned to the $S_1 \rightarrow S_0$ transition of the corresponding ligand in [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$. The emission bands at ∼500 nm for [Pt-T(CN-F)T]$_\infty$ and 600 nm for [Pt-T(OMe-F)T]$_\infty$ at 298 K could be assigned to the $ICT_1 \rightarrow S_0$ transition rather than the $T_1 \rightarrow S_0$ transition, because they are almost absent at 77 K and, at the same time, the higher-lying emission bands at around 425 nm are enhanced in intensity. If the emission bands at the longer wavelength for [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$ would be caused by the $T_1 \rightarrow S_0$ transition, they should increase in intensity at 77 K, reminiscent of those for [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(C_6−F)T]$_\infty$. Moreover, additional good evidence for the ICT state in these polymers is shown by the dual fluorescence in their PL spectra, which is found to be solvent-dependent (see Figure 6).[41] The PL spectra for [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$ in CH_2Cl_2 and toluene were recorded at 298 K. Clearly, when a more polar solvent such as CH_2Cl_2 is used, the emission band in the long wavelength region is enhanced while the one in the shorter wavelength region is weakened. The PL spectra measured in the less-polar toluene solvent show the opposite trend, suggesting the presence of ICT states in these metal polyynes. In addition to this, the lifetimes for the lower-lying emission bands for [Pt-T(CN-F)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$ are very short at 3.29 and 3.50 ns, respectively, which preclude emissions from the long-lived triplet excited state. If we compare [Pt-T(C_4-Cz)T]$_\infty$ and [Pt-T(OMe-F)T]$_\infty$, where both the carbazolyl and methoxy moieties can be regarded as electron-donating groups, the nonradiative process to form the ICT state will occur more easily in [Pt-T(OMe-F)T]$_\infty$ than in [Pt-T(C_4-Cz)T]$_\infty$ by virtue of the longer conjugation length and more delocalized π system in the former. Hence, the intersystem crossing process will be unlikely to occur and no triplet emission can be observed in [Pt-T(OMe-F)T]$_\infty$.

Effect of Chain Length and Metal Chromophore. Figure 7 gives the optical-limiting results for all the platinum dimers compared to their corresponding polymers. We note that nearly all the platinum polyynes show better optical-limiting responses than those of their corresponding dimers. Hence, the optical-limiting effect of the polyynes is contributed not only by the single repeating segment but the entity that is delocalized over more than one repeated unit. Apparently, the platinum ion can make a contribution to the π-electron conjugation along the polyyne backbone via interaction of its d orbitals with the conjugated π orbitals of the ligands, which agrees with the bathochromic shift of the absorption maximum of the platinum polyynes relative to that of their diynes (Figure 2), and such an interaction was known to enhance optical nonlinearities.[42] Among all the

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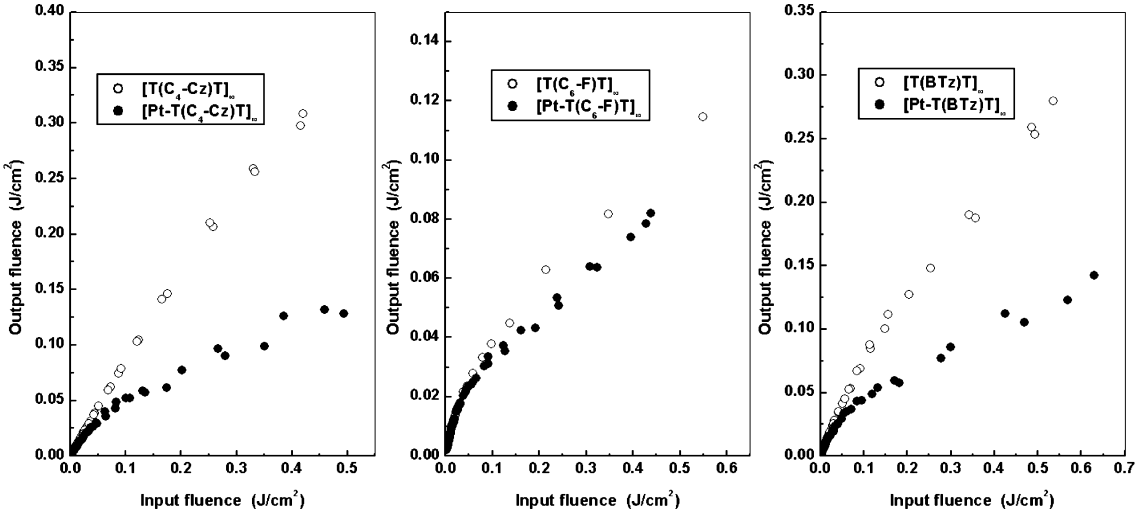

Figure 8. Comparison of the optical-limiting properties for the platinum polyynes and organic polyynes at the same linear transmittance of 82%.

Table 2. Comparison of the Optical-Limiting Performance of Platinum Polyynes with Some Reported Materials

materials	optical limiting threshold (J/cm^2)[a]	linear transmittance (%)	sample thickness (mm)	reference
PbPc(β-CP)$_4$	0.070	62	*b*	24
CuPcR$_8$ [c]	0.30	68	10	44
(*R*)-TMBO-CuPc[d]	0.30	76	1	45
MPc; M = Si, Ge, etc.	0.10	84	10	13
C_{60}	0.18	55	2	46
C_{60}	0.14	78	1	this work
$[Pt\text{-}T(C_4\text{-}Cz)T]_\infty$	0.15	82	1	this work
$[Pt\text{-}T(C_6\text{-}F)T]_\infty$	0.056	82	1	this work
$[Pt\text{-}T(BTz)T]_\infty$	0.12	82	1	this work
$[Pt\text{-}T(Th)_2T]_\infty$	0.085	82	1	this work
$[Pt\text{-}T(CN\text{-}F)T]_\infty$	0.13	82	1	this work
$[Pt\text{-}T(OMe\text{-}F)T]_\infty$	0.063	82	1	this work

[a] The optical-limiting threshold is defined as the input light fluence at which the output light fluence is 50% of that predicted by linear transmittance. [b] Not reported. [c] R = pentyloxy. [d] (*R*)-tetrakis(2-methoxy-1,1′-binaphthalen-2′-oxy)copper phthalocyanine.

metal diynes, only $[Pt\text{-}T(C_6\text{-}F)T]_1$ shows an optical-limiting property closest to that of its platinum polyynes $[Pt\text{-}T(C_6\text{-}F)T]_\infty$. This result reflects that its optical-limiting effect is dominated by the triplet excited-state absorption of the ligand since its triplet emission can also be observed at r.t.,[32d] and all other effects will just play a minor role in its NLO behavior.

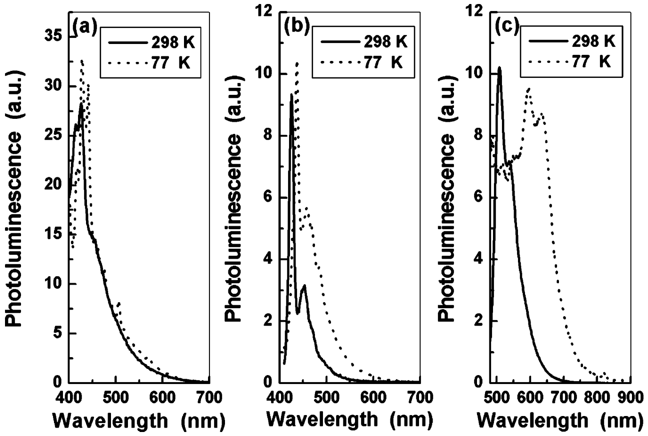

Figure 9. PL spectra of the organic polyynes at 298 and 77 K in CH_2Cl_2 for (a) $[T(C_4\text{-}Cz)T]_\infty$, (b) $[T(C_6\text{-}F)T]_\infty$, and (c) $[T(BTz)T]_\infty$.

To investigate the effect of heavy metals on the optical limiting of poly(aryleneethynylene)s, three purely organic polyynes, namely, $[T(C_4\text{-}Cz)T]_\infty$, $[T(C_6\text{-}F)T]_\infty$, and $[T(BTz)T]_\infty$, were prepared and their optical-limiting behavior was also studied. Figure 8 compares the input−output curves for the organic and organometallic polyynes. Polyynes $[T(C_4\text{-}Cz)T]_\infty$, $[T(C_6\text{-}F)T]_\infty$, and $[T(BTz)T]_\infty$ each have an optical-limiting response weaker than that of $[Pt\text{-}T(C_4\text{-}Cz)T]_\infty$, $[Pt\text{-}T(C_6\text{-}F)T]_\infty$, and $[Pt\text{-}T(BTz)T]_\infty$, respectively. The light energy transmitted started to deviate from Beer's law with an increasing input of light fluence, and the sample solution became increasingly less transparent as the fluence rose. Thus, the transmittances of the samples were found to decrease as the laser fluence increased, characteristic of optical limiting. The PL spectra of $[T(C_4\text{-}Cz)T]_\infty$ and $[T(C_6\text{-}F)T]_\infty$ (Figure 9a and b) indicate that there is no triplet emission at 77 K. Thus, the optical-limiting abilities of the organic polyynes can be markedly improved through the insertion of heavy metal ions into the main chain of the polyynes, just like the strategy employed by small-molecule optical-limiting materials in such compounds as phthalocyanine and porphyrin.[13,16,43] Although there is evidence of detecting a triplet emission in its PL spectrum, $[T(BTz)T]_\infty$

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still shows inferior optical-limiting properties compared to that of its metal-containing counterpart [Pt-T(BTz)T]$_\infty$. This observation reveals that it is the ICT state that would play the major role in controlling the optical limiting of the polyynes with an electron-rich ligand segment.

Table 2 lists the optical-limiting thresholds of our platinum polyynes, which is an important parameter to characterize the merit of these optical limiters. Here, all the platinum polyynes possess very low optical-limiting thresholds at 82% linear transmittance. Nearly all the platinum polyynes show lower optical-limiting thresholds than that of the benchmark fullerene C_{60}, and some of them even show optical-limiting thresholds comparable to those of some state-of-the-art phthalocyanine dyes. The optical limiters with the lowest thresholds for induced absorption are [Pt-T(C_6-F)T]$_\infty$ followed by [Pt-T(OMe-F)T]$_\infty$, whose characteristics could approach those necessary for a practical device. We noticed no photodegradation at the pulse repetition rate of 10 Hz. These results certainly indicate that these platinum polyynes are very valuable optical-limiting materials that should have great potential to excel in the advancement of practical devices.

Concluding Remarks

In this work, we report the first study on a series of soluble platinum polyynes that can show substantial optical limiting for a nanosecond laser pulse at 532 nm and display optical-limiting thresholds equal to or lower than those reported for other optical-limiting materials currently in use. An examination of their photophysics suggests that these polyplatinaynes follow two different optical-limiting mechanisms, which may be attributed to their structural variations. To sum up here, two important strategies can be adopted to enhance the optical-limiting properties of poly(aryleneethynylene)s. One is to make use of the heavy metal atom effect to increase the yield of the triplet states through spin−orbit coupling, while the second is to create suitable D−π−A components in the conjugation path of the metal polyynes to facilitate the formation of ICT states. For many optical power-limiting applications, solid films are desirable. Further work is underway to elucidate the response of polymer films to optical pulses for the realization of practical devices.

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Supporting Information Available: Preparations of ligand precursors and organic polyynes, experimental procedures for the Z-scan technique, the emission spectra, and tables of X-ray crystal data for [Pt-T(OMe-F)T]$_1$ (PDF). An X-ray crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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