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White Metallopolyynes for Optical Limiting/Transparency Trade-off Optimization**

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With the rapid development of laser technology in the photonic era, the damage of human eyes, optical sensors, and sensitive optical components caused by exposure to sudden intense laser pulses has driven many researchers to become involved in the search for effective optical limiters that possess high solubility, fast response speeds, good linear transparency, and high linear transmission.[1] Optical limiters are materials that protect sensitive electro-optical sensors against intrusive, possibly damaging, frequency-agile pulsed laser irradiation.[2] Currently, the materials employed for optical-power limiting (OPL) are largely small molecules such as fullerenes (C_{60}),[3] phthalocyanines,[2b,4] porphyrins,[5] diacetylenes,[6] nanotubes,[7] and organometallic compounds.[8] Among these, metallophthalocyanines and metalloporphyrins are the most effective optical limiters as the heavy metal effect magnifies the OPL response by enhancement of the intersystem crossing (ISC) from S_1 to T_1 states.[9] However, their poor solubility and the technical difficulties associated with fabricating OPL devices have hindered their practical applications so far. The deep colors of fullerenes, phthalocyanines, and porphyrins also hamper their use in practical devices for the protection of human eyes because there are unavoidable absorption bands in the visible wavelength region.[2a,10] While it is known that a bathochromic shift of the ground-state absorption maximum (λ_{max}) generally leads to an increase in the third-order optical nonlinearity,[11] previously reported excellent optical limiters have not yet achieved nonlinearity/transparency trade-off optimization. Recent work has shown that some conjugated organic

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polyynes are good OPL materials with a performance close to that of C_{60}; however, their λ_{max} values still go beyond 400 nm.[12] Although small-molecule platinum acetylides[13] and their dendritic structures[13e,14] have been shown to be good chromophores for OPL, less attention has been paid to the corresponding metallopolyynes,[13g] and related studies in mercury-derived arylene–ethynylene copolymers remain unexplored. Here, we report the unprecedented examples of some solution-processable white homo- and heterometallic polyynes that reveal superior OPL/transparency trade-offs.

The synthesis of the metal polyynes and their well-defined model compounds is shown in Scheme 1 (the use of long octyl chains can increase the solubility of metallopolymers). Interestingly, **Pt-Hg-P** is the first rigid-rod heteronuclear Pt^{II}/Hg^{II} σ-alkynyl polymer and is soluble in organic solvents. All compounds were isolated as stable white/off-white solids in high purity. The model compounds were investigated by comparing their electronic and structural properties with the parent polymers and studying the effect of chain length in the OPL phenomenon. The high decomposition temperatures of the samples (366–406 °C) indicate their good thermal stability. The rigid-rod nature of the polymer is best illustrated by the X-ray structure of **Pt-Hg-T** (see Supporting Information),[15] which also provides valuable structural information for the computational studies. While there is a transparency window at 532 nm for all the materials, the OPL response was measured as a 92 % transmitting solution at this wavelength using the Z-scan method. From Figure 1 a and 1 b, it is clear that all of them show excellent OPLs at a high linear transmittance of 92 %; these values are superior to current state-of-the-art materials such as C_{60}, Zn^{II}-tetrakis(4-phenyl)porphyrin (Zn-TPP), and Cu^{II}-tetrakis(*tert*-butyl)phthalocyanine (CuPc-*t*Bu_4). We also found that the mercury atom plays a key role in this enhanced OPL performance.

Based on the five-level reverse saturable absorption (RSA) mechanism,[16] the system can be reduced to a three-level one by assuming that there is no saturation, diffusion, or recombination during the laser pulse. Thus, we can neglect all the excitations higher than the first singlet excitation (S_1) provided that the ISC rate is fast (compared with the laser pulse duration) and all of the initial excitations are populated in the first triplet state (T_1). Excitation of the T_1 state leads to the nonlinear absorption, and the strong energy absorption that is accompanied by a $T_1 \rightarrow T_n$ transition serves as a major contributor to the nanosecond OPL behavior.

Owing to the short lifetime of the S_1 state (< 10 ns), the triplet state plays a pivotal role in the nonlinear optical process, therefore photoluminescence (PL) spectra were

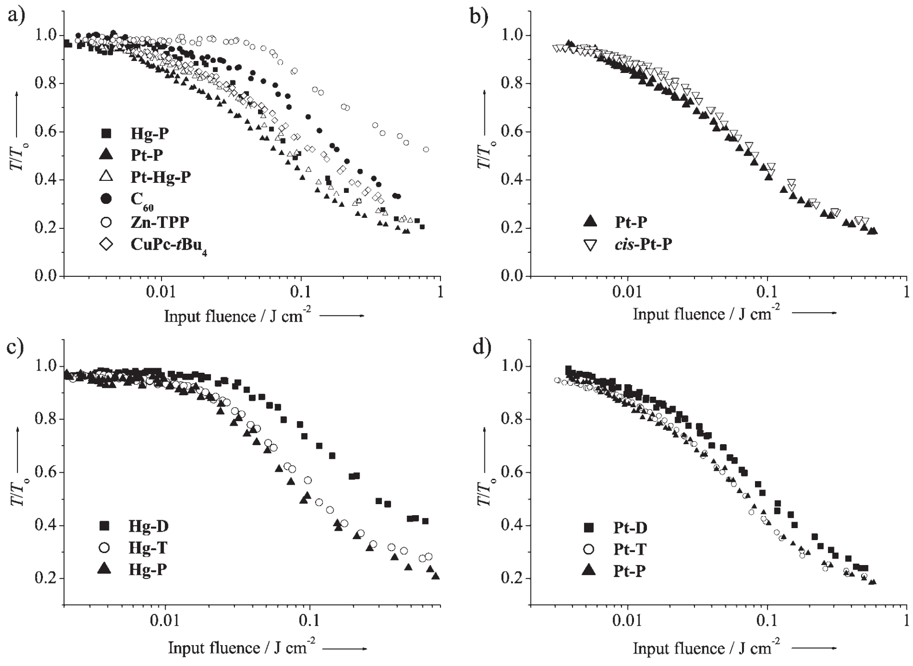
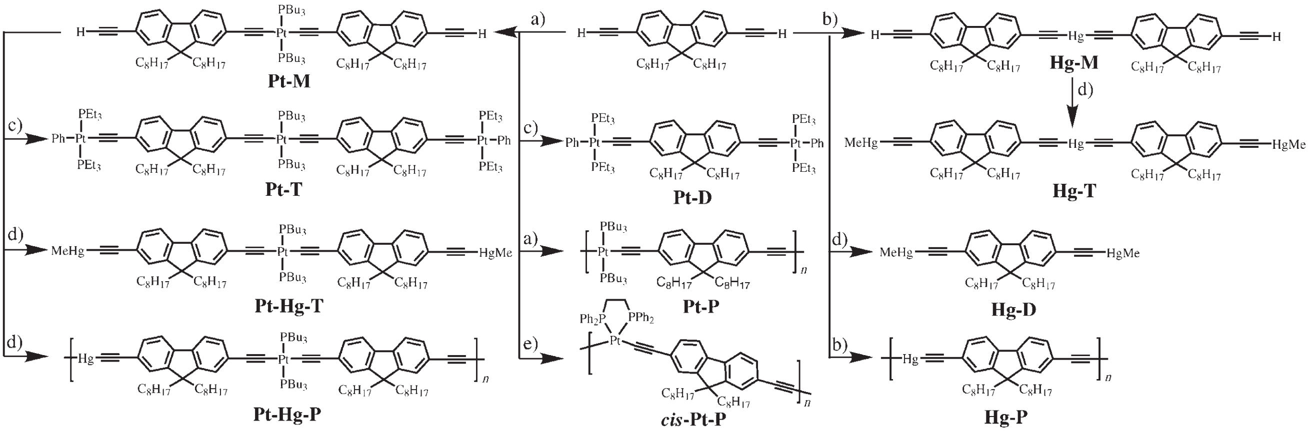


Figure 1. Normalized transmittance (T/T_o) of metal polyynes and their model complexes at the same linear transmittance ($T_o = 92\%$) versus incident fluence ($T_o = 86\%$ for C_{60}, Zn-TPP, and CuPc-*t*Bu_4).



Scheme 1. Synthesis of the metal polyynes and model complexes. a) *trans*-$[PtCl_2(PBu_3)_2]$, CuI, *i*Pr_2NH; b) $HgCl_2$, NaOMe; c) *trans*-$[PtPh(Cl)(PBu_3)_2]$, CuI, *i*Pr_2NH; d) MeHgCl, NaOMe; e) $[PtCl_2(dppe)]$, CuI, *i*Pr_2NH. dppe = 1,2-bis(diphenylphosphanyl)ethane.

measured for the singlet and triplet states (Figure 2). These PL spectra show an intense triplet emission at 77 K, which is attributed to the strong spin–orbit coupling between the ligand π and the metal d orbitals in the polyynes.[13c,d] To confirm this, molecular orbital calculations on **Pt-M**, **Hg-M**, and **Pt-Hg-T** as models for **Pt-P**, **Hg-P**, and **Pt-Hg-P**, respectively, were carried out at the B3LYP level of density functional theory based on their experimental geometries. In general, the HOMO and LUMO are mainly confined to the π and π* orbitals of the conjugated organic ligands, although mixing of the metal d_π orbitals with the ligand π orbitals in the HOMOs can also be seen. The contribution of the d_π orbitals of Pt^{II} in both **Pt-M** and **Pt-Hg-T** and Hg^{II} in **Hg-M** to the HOMOs of their corresponding complexes is 13.2 %, 10.2 %, and 0.5 %, respectively, according to the Mulliken population analysis (see Supporting Information). It is known that spin–orbit coupling increases with the extent of metal–ligand orbital mixing, therefore **Pt-P** and **Pt-Hg-T**, which show a stronger spin–orbit coupling effect, have a more effective ISC that gives rise to a larger OPL response according to the RSA mechanism. These theoretical results were confirmed experimentally by the observation of weak triplet emission at room temperature in **Pt-P** and **Pt-Hg-P**, which is almost absent in **Hg-P**, and their slightly stronger OPL compared with that of **Hg-P**. In spite of this, the OPL performance of **Hg-P** is still attractive, and indicates that the OPL effect is not only induced by the triplet absorption. To look for a possible mechanism, we can see from the DFT results that the contribution from the d_π orbitals of Hg^{II} to the HOMO of **Hg-M** is only 0.5 %, while the metal p_π orbitals contribute 19.6 % to its LUMO. This reveals that the $S_0 \rightarrow S_1$ electronic transition of **Hg-P** due to $\pi(C{\equiv}CR) \rightarrow \pi^*(C{\equiv}CR)$ orbitals also possesses charge-transfer (CT) character.[9b] Its OPL effects may be enhanced by the strong absorption of CT states, which is known to be beneficial to OPL in other organometallic systems.[13b]

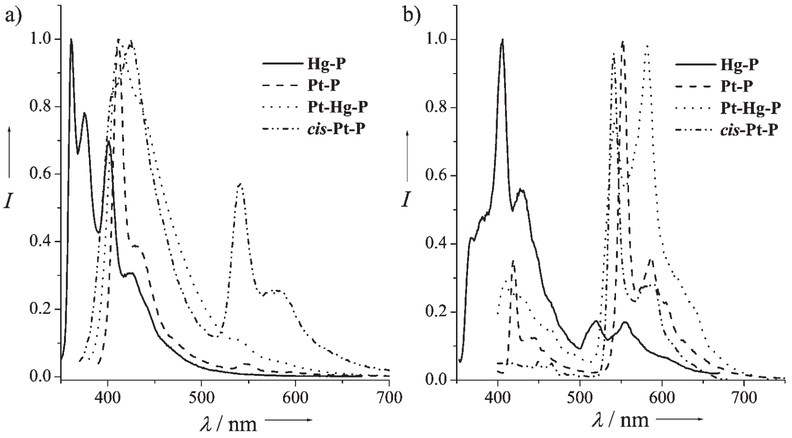


Figure 2. PL spectra for the metal polyynes in CH_2Cl_2 at a) 298 K and b) 77 K.

We have recognized the salient problem of how to increase the optical transparency range while maintaining the OPL response of the polymers constant. In order to improve the transparency window of **Pt-P** further, it is highly desirable to reduce its dragged absorption tail behind 400 nm by reducing the π-conjugation. Normally, if the π-conjugation is reduced the optical nonlinearity, and hence the OPL effect, will be lessened.[17] However, from Figure 1 c and 1 d it is evident that the conjugation factor will become less important as the chain length is increased up to the trimer, and **Hg-T** (or **Pt-T**) shows almost the same OPL as that of **Hg-P** (or **Pt-P**). As the order of π-delocalization through the metal chromophore is Pt^{II} > Hg^{II}, we expect that coupling of Hg^{II} to the backbone of **Pt-P** breaks the π-conjugation to some extent but favorably optimizes the transparency/nonlinearity trade-off. As mentioned earlier, intramolecular CT states exist between the Hg ion and the conjugated ligand that would also contribute to the OPL action of **Pt-Hg-P**. So, copolymerization of **Pt-M** with Hg^{II} ion in the polyyne backbone will shorten the conjugation length of the ligands and result in a higher energy triplet state accompanied by an increase in the triplet quantum yield (Φ_P), in accordance with the energy-gap law for the triplet states in metal polyynes.[18] This is also reflected by the lower singlet quantum yield (Φ_F) of **Pt-Hg-P** compared with that of **Pt-P** (see Supporting Information). Pertaining to the RSA mechanism, we note that the contribution of an increased Φ_P of **Pt-Hg-P** to OPL can compensate for the loss in OPL due to interruption of the conjugation by Hg, hence **Pt-Hg-P** still shows a similar OPL to that of **Pt-P** (Figure 1 a). In addition, **Pt-Hg-P** has an improved transparency window for optimizing the properties of OPL materials of this kind ($\lambda_{max} = 386$ nm for **Pt-Hg-P** vs. 399 nm for **Pt-P**, with the former being whiter than the latter). By following the same approach to increase Φ_P through such a conjugation-breaking strategy, *cis*-**Pt-P** was designed and synthesized.[19] By changing from a *trans*- to a *cis*-configured Pt^{II} unit, the conjugation chain in *cis*-**Pt-P** remains disturbed ($\lambda_{max} = 364$ nm). What is remarkable here is that *cis*-**Pt-P** shows almost the same OPL as **Pt-P** (Figure 1 b), thus indicating that the negative effect on OPL caused by conjugation-interruption can be overcome effectively by the positive contribution of increased Φ_P. This is supported by the much stronger triplet emission at 298 K (Figure 2 a) and much lower Φ_F for *cis*-**Pt-P** compared with that of **Pt-P**.

Comparing the UV/Vis spectra of the polyynes and common optical-limiting materials currently in use (Figure 3), the merits of our polyynes as RSA optical limiters for protecting eyes and optical sensors are obvious. They are all white powders with very good transparencies in the visible region, and *cis*-**Pt-P** in particular has a high triplet yield, all of which makes these metallopolyynes excellent for OPL applications. Some of the best ever materials, including CuPc-*t*Bu$_4$, Zn-TPP, and C_{60}, are all deeply colored with strong visible absorption bands, therefore their poor optical transparencies will make them less competitive with our metallopolyynes as optical limiters for the protection of human eyes.

The performance of excited-state absorbers can be quantitatively characterized by the Figure of Merit factor

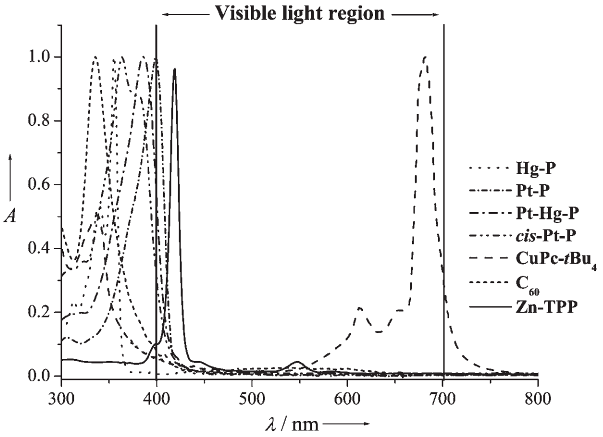


Figure 3. Comparison of the optical transparency of our metal polyynes with some good optical limiters.

σ_{eff}/σ_o, where σ_{eff} and σ_o are the effective excited-state and ground-state absorption cross-sections, respectively. From Table 1, it is clear that our metallopolymers are efficient OPLs with very impressive σ_{eff}/σ_o values (18.3–20.8), which exceed by a factor of about five that of C_{60}, a benchmark optical limiter. These figures are also remarkably higher than those of various popular metal phthalocyanines. Moreover, *cis*-**Pt-P**, **Pt-P**, and **Pt-Hg-P** manifest very low optical-limiting thresholds in the narrow range of 0.07–0.11 $\mathrm{J\,cm^{-2}}$ at 92 % linear transmittance; these characteristics approach those necessary for a practical device. These thresholds are comparable to those of the best InPc and PbPc dyes (T_o = 84 %) currently in use (Table 1).

Table 1: Comparison of the optical limiting parameters of metal polyynes with some state-of-the-art materials.

Compound	F_{th} [J cm^{-2}][a]	T_o [%][b]	L [mm][c]	σ_{eff}/σ_o[d]
[{tri(*n*-hexyl)siloxy}InPc][4a]	0.070	84	10	16[4a]
[{tri(*n*-hexyl)siloxy}AlPc][4a]	0.26	84	10	10[4a]
[{tri(*n*-hexyl)siloxy}GaPc][4a]	0.12	84	10	14[4a]
PbPc(β-CP)$_4$[20a]	0.070	62	[e]	[e]
CuPc-*t*Bu$_4$[20b]	0.10	[e]	[e]	[e]
CuPc-*t*Bu$_4$	0.13	86	1	6.20
C_{60}[20c]	0.18	55	2	[e]
C_{60}	0.19	84	1	3.89
Hg-P	0.11	92	1	20.81
Pt-P	0.070	92	1	19.07
Pt-Hg-P	0.083	92	1	18.32
cis-**Pt-P**	0.080	92	1	18.62

[a] Optical-limiting threshold, F_{th}, defined as the input light fluence at which the output light fluence is 50% of that predicted by linear transmittance. [b] T_o is the linear transmittance. [c] Sample thickness. [d] $\sigma_{eff}/\sigma_o = \ln T_{sat}/\ln T_o$, where σ_{eff} is the effective excited-state absorption cross-section, σ_o is the ground-state absorption cross-section, and T_{sat} is the transmittance at the saturation fluence. [d] Not reported.

In conclusion, we have reported the first study of a series of soluble and tractable metallopolyynes with substantial OPL responses that perform better than some state-of-the-art optical limiters. Importantly, we can greatly improve the transparency window of the polyynes in the visible regime, whilst maintaining their OPL performance, by interrupting π-conjugation by copolymerizing with Hg and tuning the Pt geometry. These results are an encouraging milestone in the progress towards commercially viable optical-limiting polymers with optimized transparency/OPL trade-offs.

Experimental Section

Pt-Hg-T: **Pt-M** (0.100 g, 0.068 mmol) and MeHgCl (0.043 g, 0.169 mmol) were mixed in MeOH/CH_2Cl_2 (40 mL, 1:40, v/v) to form a clear solution. A basic NaOMe solution (1.0 mL, 0.2 mmol$\,L^{-1}$ in MeOH) was added to the mixture at room temperature. After stirring the mixture overnight at room temperature, it was filtered and the filtrate was allowed to evaporate slowly to form pale-yellow crystals of **Pt-Hg-T**. These were collected and recrystallized from a CH_2Cl_2/MeOH (3:1, v/v) solution (yield: 0.085 g, 66 %).

cis-**Pt-P**: 2,7-Diethynyl-9,9-dioctylfluorene (0.055 g, 0.126 mmol), [$PtCl_2$(dppe)] (0.083 g, 0.126 mmol), and CuI (3 mg) were mixed in NEt_3/CH_2Cl_2 (40 mL, 1:10, v/v) at room temperature. After stirring overnight at room temperature, the reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated and the solution was poured into MeOH (50 mL). The polymer powder was collected, washed with hexane, and dried under vacuum (yield: 0.097 g, 75 %).

Pt-Hg-P: **Pt-M** (0.150 g, 0.102 mmol) and $HgCl_2$ (0.028 g, 0.102 mmol) were dissolved in MeOH/CH_2Cl_2 (40 mL, 1:50, v/v) at room temperature. A basic NaOMe solution (1.2 mL, 0.2 mmol$\,L^{-1}$ in MeOH) was added. After stirring the reaction mixture overnight at room temperature, it was filtered through a short pad of silica gel to remove the insoluble solid. The solvent was removed under reduced pressure. The residue was dissolved in a minimum volume of CH_2Cl_2 (6 mL) and the solution poured into MeOH (50 mL). The white precipitate was collected by filtration and washed with hexane to afford the copolymer (yield: 0.125 g, 73 %). All the spectroscopic data can be found in the Supporting Information.

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