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Novel Au¹ polyynes and their high optical power limiting performances in both solution and prototype device[†]

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Three novel Au¹ polyynes have been prepared in high yield by copolymerization between an Au¹ complex precursor and different ethynyl aromatic ligands. The investigation of their photophysical behavior has indicated that forming polyynes through polymerization not only maintains the high transparency of the concerned Au¹ polyynes similar to that of their corresponding small molecular Au¹ acetylides, but also effectively enhances their triplet (T₁) emission ability. Critically, owing to their enhanced T₁ emission ability, all the Au¹ polyynes can exhibit stronger optical power limiting (OPL) ability against 532 nm laser than the corresponding small molecular Au¹ acetylides. The Au¹ polyynes based on fluorene and triphenylamine ligands can show even better OPL performance than the state-of-the-art OPL material C₆₀, indicating their great potential in the field of laser protection. More importantly, in the prototype OPL device made by doping the fluorene-based Au¹ polyyne into polystyrene (PS) solid matrix, substantially improved OPL activity has been observed compared with that in the solution, demonstrating its great potential for practical application. All these results have provided a new strategy to achieve the consistence between the high OPL activity and good transparency for OPL materials, representing valuable attempt for developing new OPL materials with high performance to cope with the key problems in the field of nonlinear optics.

Introduction

Transition metal polyynes can be easily prepared by the crosscoupling reaction between aromatic diacetylenes and divalent transition metal ions, such as Pt", Pd" and Hg" ect.¹⁻⁴ Owing to the interaction between metal centers and organic acetylene ligands, the unique properties have been afforded to the transition metal polyynes. Hence, they can play critical roles in many fields, including organic solar cells,⁵ organic light-emitting diodes (OLEDs),⁶⁻¹⁰ ion sensors¹¹ and nanomaterials¹²⁻¹⁵ and so on. Besides, the new Pt acetylenes developed by Yang's group can form novel molecular skeletons and self-assembly structures, showing interesting properties.¹⁶⁻¹⁹ More importantly, transition metal polyynes, especially the ones with Pt^{II} centers, can show strong nonlinear optical behaviors, such as optical power limiting (OPL) effect which can be employed to protect human eyes or optical sensors from the damages in the occasion of sudden exposure to intense laser beams.²⁰ Due to their high transparency in visible light region (ca.

400-700 nm), transition metal polyynes can possess inherent advantages as high performance OPL materials over the traditional counterparts, such as fullerenes (*e.g.*, C_{60}),^{21,22} phthalocyanines (Pc),^{23,24} and porphyrins,^{25,26} since these traditional OPL materials display poor transparency in visible-light region induced by their large π -conjugated structures. It means that there is a conflict between high OPL activity and good transparency for OPL materials, representing a critical problem in the field of nonlinear optics to restrain the practical application of traditional OPL materials.²⁷ Hence, developing novel transition metal polyynes which can cope with this problem should be of great importance in view of their important applications.

Typically, only divalent transition metal ions can be possibly employed to prepare polyynes through coupling with diacetylene ligands. For example, Pt^{II} polyynes can represent the most important transition metal polyynes ever reported. On the contrary, Au¹ ions have been frequently employed to prepare small molecular Au¹ acetylides.²⁸⁻³² The Au¹ acetylides with aromatic diacetylene ligands showing different electronic features have been successfully prepared as advanced OPL materials possessing high transparency.²⁸ Furthermore, some of them can even outperform C₆₀ as novel OPL materials.^{28,29} Different from small molecules, polymers can show unique properties. For instance, both Pt^{II} and Hg^{II} polyynes can show different photophysical and OPL ability compared with their corresponding small molecular Pt^{II} and Hg^I acetylides.²⁹ However, to the best of our knowledge, Au^l polyynes have been rarely reported in the literatures. Only Puddephatt's group had prepared three Au¹ polyynes in 1993.³³ Unfortunately,

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⁺ Electronic supplementary information (ESI) available: Synthetic details for the organic ligands, Au¹ acetylides and some photophysical data. See DOI: 10.1039/x0xx00000x

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some of the Au^l polyynes are insoluble in common organic solvents and the research just concerns on synthesis without reported properties. Hence, the development of Au^l polyynes is quite desirable considering both basic photophysical investigations and applications.

On this basis, three novel Au¹ polyynes bearing organic acetylides with different structures have been prepared through employing a precursor complex with two Au¹ centers connected by 1,4bis(diphenylphosphino)benzene ligand. The basic photophysical behaviors together with their OPL ability have been investigated. For the first time, the triplet emission enhancement has been observed in these soluble Au¹ polyynes. Importantly, the great potential as new OPL materials has been found in these Au¹ polyynes as well. The concerned results will not only provide valuable photophysical and OPL information of these novel Au¹ polyynes for developing new high-performance OPL materials, but also present a new strategy for developing rarely explored Au¹ polyynes.

Experimental

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General information

The commercially available reagents were used directly as received. All reactions were proceeded under a nitrogen atmosphere. The solvents were purified by standard methods under dry nitrogen prior to use. The reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminum plates. Flash column chromatography and preparative TLC were carried out using silica gel. All Sonogashira reactions were carried out with Schlenk techniques under a nitrogen atmosphere.

Physical measurements

¹H-, ¹³C- and ³¹P-NMR spectra were measured in CDCl₃ solvent with a Bruker AXS 400MHz NMR spectrometer with the ¹H and ¹³C NMR chemical shifts quoted relative to SiMe₄ and the ³¹P chemical shifts relative to the 85% H₃PO₄ external standard. Fast atom bombardment (FAB) mass spectra for characterizing the molecular weight of the small molecular compounds were recorded on a Finnigan MAT SSQ710 system. UV-vis spectra were recorded with a PerkinElmer Lambda 950 spectrophotometer. The photoluminescent (PL) properties of the Au¹ polyynes were measured with an Edinburgh Instruments FLS920 fluorescence spectrophotometer. The lifetimes for the excited states were measured by a single photon counting spectrometer from Edinburgh Instruments FLS920 with a 360 nm picosecond LED lamp as the excitation source, while those at 77 K were obtained with the excitation from a Xenon flash lamp. The PL spectra and lifetimes at 77 K were obtained by dipping the degassed CH₂Cl₂ solution in a thin guartz tube into liquid nitrogen Dewar and recording the data after standing 3 minutes. The fluorescent quantum yields ($\Phi_{\rm F}$) were determined in CH₂Cl₂ solutions at 298 K against guinine sulfate in 1.0 M H₂SO₄ ($\Phi_F ca. 0.56$).³⁰ Phosphorescence quantum yields (Φ_P) were measured at room temperature with an integrating sphere from Edinburgh Instruments FLS920 with excitation wavelength at 340 nm. The molecular weights of these Au^l polyynes were determined by Waters 2695 GPC in CHCl₃. The molecular weights

were estimated by using a calibration curve of polystyrene standards. The thermal gravimetric analysis (TGA) was performed on METTLER TOLEDO TGA2 star system under nitrogen with a heating rate of 20 K min⁻¹.

Optical power limiting measurements

Optical power limiting properties of the Au^l polyynes were characterized by Z-scan measurements, which were performed at 532 nm for Gaussian mode laser beam with a repetition rate of 20 Hz from a Q-switched Quantel Q-Smart 100 Nd:YAG laser. The laser beam was split into two beams by a beam splitter. One was used as the reference beam, which was received by a power detector (D1), the other was focused with a lens (f = 25 cm) for the sample measurement. After transmitting through the sample, the light beam entered another power detector (D2). The sample to be measured was moved automatically along a rail to change the incident irradiance on it. The incident and transmitted powers were detected simultaneously by the two power detectors D1 and D2 individually. The OPL performance of each of the solution samples in CH₂Cl₂ was measured in a 1 mm guartz cell. The prototype device is prepared by casting the polystyrene (PS) solution (0.2 g mL⁻¹) in CH₂Cl₂ with *ca*. 3.0-wt% doping level of **P-Au-FLU** into a PTFE mode. Then, it was left on a clean bench for 3 days at 298 K to obtain the solid plate as prototype OPL device.

Computational details

Geometrical optimizations were conducted using the popular B3LYP density functional theory (DFT). The basis set used for C, H, O, N and P atoms was 6-311G(d, p), whereas effective core potentials with a LanL2DZ basis set were employed for Au atom.^{35,36} The energies of the excited states of the complexes were computed by TD-DFT based on all the ground-state geometries. All calculations were carried out by using the Gaussian 09 program.³⁷

Synthesis

The ethynyl aromatic ligands were prepared by the typical Sonogashira coupling reaction.⁷⁻⁹ All the synthetic procedures are provided in the Electronic Supplementary Information (ESI).

General synthetic procedure for the Au¹ polyynes

Under N₂ atmosphere, **L-2Au** (1.0 equiv) was added to the solution of the corresponding diethynyl aromatic ligand (1.0 equiv) in CH₂Cl₂/MeOH (v:v = 2:1). Then, NaOH (1.1 equiv) in MeOH solution (0.1 M) was added. The reaction mixture was stirred for 10 h at room temperature. After removing the solvent, the residue was dissolved in small amount of CH₂Cl₂ and filtered by a syringe filter (PTFE, 0.45 μ m) to remove the insoluble part. Then, it was precipitated in MeOH and the precipitation was repeated for two times. The Au¹ polyynes were obtained in high yield as off-white solid.

P-Au-FLU: (Yield: 86%). ¹H NMR (400 MHz, CDCl₃): δ(ppm) 7.63-7.44 (m, 30H, Ar), 1.88 (br, 4H, $-CH_2-$), 1.22-0.86 (m, br, 36H, $-CH_2-$), 0.86 (t, 6H, $-CH_3$), 0.54 (br, 4H, $-CH_2-$); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 42.44; GPC: $M_n = 2.0 \times 10^4$ g mol⁻¹, PDI = 1.9 (against polystyrene standards); Anal. Found: C 60.96, H 5.68.

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P-Au-TPA: (Yield: 85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.58-7.49 (m, 24H, Ar), 7.33 (d, 4H, Ar), 7.03 (d, 2H, Ar), 6.89 (d, 4H, Ar), 6.82 (d, 2H, Ar), 3.92 (br, 2H, $-\text{OCH}_2-$), 1.76 (br, 2H, $-\text{CH}_2-$), 1.51-1.26 (m, br, 18H, $-\text{CH}_2-$), 0.87 (s, br, 3H, $-\text{CH}_3$); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 42.42; GPC: $M_n = 1.8 \times 10^4$ g mol⁻¹, PDI = 2.1 (against polystyrene standards); Anal. Found: C 57.93, H 4.56, N, 1.21.

P-Au-CAZ: (Yield: 89%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21 (br, 2H, Ar), 7.62-7.50 (m, 26H, Ar), 7.24 (d, 2H, Ar), 4.20 (t, 2H, -NCH₂-

), 1.84-1.80 (m, 2H, -CH₂-), 1.52-1.23 (m, 18H, -CH₂-), 0.88 (t, 3H, -CH₃); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 42.46; GPC: M_n = 1.6 × 10⁴ g mol⁻¹, PDI = 1.9 (against polystyrene standards); Anal. Found: C 56.73, H 4.33, N, 1.01.

Results and discussion

Synthesis and structural characterization

SMe₂AuCl L-2Au L-1 P-Au-FLU NaOH L-2 MeOH/CH2Cl2 P-Au-TPA L-3 P-Au-CAZ

Scheme 1 Synthesis of the Au¹ polyynes.

The limitation of monovalent ion Au¹ for synthesis of polyynes comes from the fact that it can only couple with one acetylene group. Obviously, obtaining complex precursor with two Au¹ centers should afford the opportunity to prepare Au¹-based polyynes just like the well explored Pt^{II} -based polyynes. Inspired by the complex precursor Ph_3PAuCI employed to prepare small molecular Au^I acetylides, dinuclear **L-2Au** have been designed and prepared (Scheme 1). In **L-2Au**, two Au–CI

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bonds have made $\mbox{L-2Au}$ possible to couple with diethynyl aromatic ligand to obtain $\mbox{Au}^{\rm I}$ polyynes.

In order to obtain **L-2Au**, the key organic phosphine ligand 1,4-bis(diphenylphosphino)benzene (**L-2P**) was prepared in advance (Scheme 1). The **L-2P** can be prepared in a high yield of *ca*. 80% by the lithiation of 1,4-diiodobenzene at low temperature and then adding chlorodiphenylphosphine (Scheme 1). After obtaining **L-2P**, the precursor complex **L-2Au** can be easily obtained as white solid by adding **L-2P** to the solution of Me₂SAuCl with a molar ratio of 1 : 2. In the ³¹P NMR spectrum of **L-2Au**, the single resonance peak at *ca*. 33.04 ppm has clearly shown the presence of the AuPPh₂-Ph-Ph₂PAu unit, since the ³¹P signal for **L-2P** appears at *ca*. -5.07 ppm.

Employing the similar synthetic strategy of Au¹ acetylides, the Au^I polyynes **P-Au-FLU**, **P-Au-TPA** and **P-Au-CAZ** have been prepared by the cross-coupling between L-2Au and the diethynyl aromatic ligand L-1, L-2 and L-3 (Scheme S1), respectively. In the ¹H NMR spectra of these Au¹ polyynes (Figure S1, S2 and S3), the absence of the single peak at ca. 3.1 ppm assigned to the proton in the acetylene groups indicates their successful coupling with L-2Au. The obvious resonance peak at ca. 42.4 ppm in the ³¹P NMR spectra of these Au¹based polyynes has clearly shown the presence of the AuPPh₂-Ph-Ph₂PAu units. The broad multi peaks in the range of *ca.* 1.5-1.3 ppm in the ¹H NMR spectra can be assigned to the ndodecyl groups in all the Au^l-based polyynes. For P-Au-TPA, the broad signal at ca. 3.9 ppm can be ascribed to the protons from -OCH₂- unit. The -NCH₂- group has induced the peak at 4.2 ppm in the ¹H NMR spectrum of **P-Au-CAZ**. All these NMR data have clearly indicated the successful synthesis of these novel Au¹-based polyynes. With polystyrene (PS) as standards, the number-average molecular weights (M_n) of these Au¹based polyynes range from 1.8×10^4 to 2.0×10^4 with polydispersity indices (PDIs) about 2.0 (Figure S4).

Photophysical and thermal properties

Absorption behaviors of the Au^l polyynes have been characterized in CH₂Cl₂ at 298 K (Figure 1) and the corresponding data are presented in Table1. In their UV-vis absorption spectra (Figure 1), the intense absorption bands for all the Au['] polyynes can be assigned to the metal disturbed $\pi - \pi^*$ transitions from the organic ligands. All the absorption bands located in the UV region indicate the excellent transparency of these Au¹ polyynes in the visible light region (ca. 400-700 nm) (Figure 1 and Table 1). Owing to the strong electron-donating feature of the triphenylamine moiety to facilitate π - π * transition of L2, P-Au-TPA exhibits a maximum absorption band in much longer wavelength region compared with P-Au-FLU and P-Au-CAZ (Figure 1). In addition, the absorption spectra for these Au¹ polyynes exhibit great resemblance to their corresponding Au¹ acetylides M-Au-FLU, M-Au-TPA and M-Au-CAZ (Scheme S1), respectively (Figure 1). These absorption spectra are quite similar to those of the corresponding ligands as well (Figure S1 in ESI). This result also indicates that the strong absorption bands of these Au polyynes have been induced by the π - π * transitions associated with the organic ligands. Owing to the fact that transition properties of the transition metal polyynes can show similarity to their repeating units,¹⁰ the molecular orbital (MO) patterns (Figure

2) together with time-dependent density functional theory (TD-DFT) results (Table 2) have been obtained to understand the absorption behavior of these Au¹ polyynes. From the TD-DFT results in Table 2, the HOMO→LUMO transition can show the characters of the transition process from the ground state (S_0) to the first singlet state (S1) due to its large contribution over 90%. Furthermore, the $S_0 \rightarrow S_1$ transition typically response the key absorption processes. On this basis, from the MO patterns of both HOMO and LUMO for the repeating units of these Au[']polyynes (Figure 2), it can be seen clearly that their HOMO→LUMO transitions show obvious interligand charge transfer (ILCT) features from the π orbitals of the organic diethynyl aromatic ligands to the π^* orbitals of 1,4bis(diphenylphosphino)benzene (L-2P) coordinated with the Au centers. Hence, the UV absorption of these Au' polyynes should exhibit π - π ^{*} characters with ILCT feature. These MOs display alike patterns to those of our reported Au¹ acetylides with similar diacetylene ligand.²⁸ In addition, these Au¹ polyynes also show nearly identical absorption spectra to their corresponding Au acetylides (Figure 1). These results clearly demonstrate indicate the validity of employing the MOs of the repeating units to explain the absorption characters of the corresponding Au['] polyynes.

The cut-off absorption wavelength ($\lambda_{cut-off}$) for the Au¹ polyynes is 374 nm for P-Au-FLU, 402 nm for P-Au-TPA and 383 nm for P-Au-CAZ, respectively. Clearly, according to the data in Table 1, these values are identical to their corresponding Au¹ acetylides (374 nm for M-Au-FLU, 402 nm for M-Au-TPA and 383 nm for M-Au-CAZ). It seems that the polymerization does not induce obvious bathochromic effect in the $\lambda_{\text{cut-off}}$ of the Au^{I} polyynes. These results indicate that high transparency can be successfully maintained after forming Au¹ polyynes. Based on the tetrahedron configuration of P centers, the conjugation of the backbones of these Au^l polyynes can be effectively broken to furnish them with short absorption wavelengths which are similar to those of the corresponding small molecular Au^l acetylides M-Au-FLU, M-Au-TPA and M-Au-CAZ (Figure 1 and Table 1). In addition, the thermal stability of these Au polyynes had been characterized by thermogravimetric analysis (TGA) under a nitrogen flow. The initial decomposition temperatures (307 °C for P-Au-FLU, 295 °C for P-Au-TPA and 303 °C for P-Au-CAZ, Figure S6) can indicate the high thermal stability of these Au¹ polyynes.



Fig. 1 UV-vis absorption spectra for the Au^{l} polyynes and their corresponding Au^{l} acetylides in CH_2CI_2 at 298 K.

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Table 1 Photophysical data for the Au¹ polyynes and their corresponding Au¹ acetylides.

compound	Absorption λ_{abs} (nm) ^{<i>a</i>}	Emission λ_{em} (nm) ^a	${\it \Phi}_{\tt F}{}^{b}$	Lifetime of excited states ^c	$\lambda_{ ext{cut-off}}$
	298K	298 К / 77 К	(%)	S1 state (ns) / T1 state (μs)	(nm)
P-Au-FLU	276, 306, 319, 344, 362	392, 411 ^{sh} , 530, 576 / 532, 570, 582	0.51	10.0 ns (392 nm) / 478.2 μs (532 nm)	374
P-Au-TPA	276, 309, 335 ^{sh} , 366	433 / 498, 527, 540, 555	0.69	1.8 ns (433 nm) / 527.7 μs (498 nm)	402
P-Au-CAZ	276, 304 ^{sh} , 315, 336, 357 ^{sh} , 375	383 ^{sh} , 402, 438, 473 / 440, 470, 485	0.12	120.0 ns (402 nm) / 398.6 μs (440 nm)	383
M-Au-FLU	275, 306, 320, 342, 360	388, 411 / 533, 570, 582	2.71	1.5 ns (388 nm) / 358.8 μs (533 nm)	374
M-Au-TPA	275, 308, 338 ^{sh} , 368	420 / 499, 528, 541, 556	1.80	2.9 ns (420 nm) / 516.4 μs (499 nm)	402
M-Au-CAZ	281, 305 ^{sh} , 316, 335, 356 ^{sh} , 375	381, 400, 432, 466 / 439, 465, 483	0.22	110.0 ns (400 nm) / 447.2 μs (439 nm)	383

^{*a*} Measured in CH₂Cl₂ at a concentration of *ca*. 10⁻⁵ M. sh: Shoulder. ^{*b*} Measured using quinine sulfate in 1.0 M H₂SO₄ as the standard. According to the UV–vis absorption of the compounds, the excitation wavelength was set at 334 nm while the Φ_F of the standard is 56%. ^{*c*} The numbers in parentheses are the emission wavelengths of the S₁ and T₁ states. The lifetime of the S₁ state was measured at 298 K in degassed CH₂Cl₂ with the excitation at 360 nm and that for the T₁ states was measured at 77 K in the same solvent with the same excitation wavelength.



Fig. 2 Molecular orbital (MO) patterns for the repeating units of the Au^{\dagger} polyynes based on their optimized S₀ geometries. (a) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-FLU**, (c) repeating unit for **P-Au-FLU**.

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Compound	Contribution of d_{π} orbitals to HOMO ^a (Au1/Au2)	Contribution of d_{π} orbitals to LUMO ^{<i>a</i>} (Au1/Au2)	Largest coefficient in the Cl expansion of the T ₁ state ^b	Percentage contribution of the transition to the T ₁ state ^b	Largest coefficient in the CI expansion of the S ₁ state ^b	Percentage contribution of the transition to the S ₁ state ^b	Oscillator strength (f) of the $S_0 \rightarrow S_1$
P-Au-FLU	3.6% / 0%	1.2% / 1.4%	H-1→L+3 (0.51172)	52.40% 22.3%	H→L	96.60%	0.0287
			H-1→L+5		(0.69505)		
			(-0.33379)				
P-Au-TPA	1.6% / 0%	1.2% / 1.2%	$H \! \rightarrow \! L$	83.80%	H→L	90.80%	0.0381
			(0.64746)		(0.67383)		
P-Au-CAZ	0.1% / 3.4%	1.1% / 1.1%	H→L	81.50%	H→L	94.70%	0.0016
			(0.63845)		(0.68822)		

Table 2 TD-DFT results for the Au^I polyynes based on their optimized S₀ geometries.

^a The data were obtained by exporting DFT results with the software AOMix. ^b H \rightarrow L represents the HOMO to LUMO transition. Cl stands for configuration interaction.

In CH₂Cl₂ solution at 298 K, both P-Au-FLU and P-Au-CAZ exhibit two emission bands in their photoluminescent (PL) spectra (Figure 3 and Table 1). Due to their short lifetime in the order of nanosecond (ns) (Figure S8 and Table 1), the high-energy emission bands should be fluorescent signal coming from radiative decay of the singlet states (S₁) associated with the metal disturbed organic ligand π - π^* transitions. On the contrary, the long-wavelength emission bands should be induced by the decay of the triplet states (T_1) , since they possess much longer lifetimes in the order of microsecond (us) and large Stokes shift of ca. 170 nm for P-Au-FLU and 104 nm P-Au-CAZ (Figure 3 and Table 1). Furthermore, the long-wavelength emission signals have been substantially enhanced at low temperature of 77 K, indicating their T₁ characters as well (Figure S7). It seems that P-Au-TPA might not possess obvious triplet emission band at 298 K, since only the singlet emission can be observed at ca. 433 nm (Figure 3b). However, the emission profile for P-Au-TPA becomes much wider after ca. 460 nm than that of M-Au-TPA (Figure 3b).







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Fig. 3 Photoluminescent (PL) spectra for the Auⁱ polyynes and their corresponding Auⁱ acetylides in CH₂Cl₂ solution at 298 K. (a) P-Au-FLU and M-Au-FLU (b) P-Au-TPA and M-Au-TPA (c) P-Au-CAZ and M-Au-CAZ

This can be ascribed to the overlapping between singlet and triplet emission bands in **P-Au-TPA**. Clearly, all the Au¹ polyynes can show stronger triplet emission compared with their corresponding Au¹ acetylides (Figure 3), indicating their higher triplet quantum yield.

This conclusion is also supported by their lower fluorescence quantum yields ($\Phi_{\rm F}$) (0.51% for **P-Au-FLU**, 0.69% for **P-Au-TPA** and 0.12% for **P-Au-CAZ**) with respect to that of their corresponding Au¹ acetylides (2.71% for **M-Au-FLU**, 1.80% for **M-Au-TPA** and 0.22% for **M-Au-CAZ**) (Table 1). The enhancing of triplet emission in these Au¹ acetylides might be ascribed to the fact that polymerization can restrain the movement of different blocks in the polymer backbone to reduce the nonradiative decay of the T₁ states.



Fig. 4 Natural transition orbital (NTO) patterns for $S_0 \rightarrow T_1$ excitation of the repeating units from the Au¹ polyynes based on their on their optimized T_1 geometries. (a) repeating unit for **P-Au-FLU**, (b) repeating unit for **P-Au-TPA**, (c) repeating unit for **P-Au-CAZ**

Compound	NTO ^a	Contribution percentages of metal $d\pi$ orbitals and π orbitals of ligands to NTOs b (%)				
		Au1	Au2	L1	L2	
P-Au-FLU	н	2.34	0.00	97.35	0.00	
	Р	3.37	0.00	95.00	0.00	
P-Au-TPA	н	3.34	0.00	96.20	0.08	
	Р	7.80	0.15	66.71	13.94	
P-Au-CAZ	н	4.69	0.00	94.67	0.15	
	Р	9.30	0.24	52.80	21.72	

Table 3 NTO Results for the repeating units from the Au^{I} polyynes based on their optimized T_{1} geometries.

^a H and P represent NTO hole and particle orbital, respectively. ^a Au1 and Au2 represent the two Au¹ centers,

while L1 indicates the two aromatic diacetylene ligands and L2 represents the organic phosphine ligand L-

2P.

In order to clearly elucidate the PL behaviors of these Au^I polyynes, the natural transition orbital (NTO) results for their repeating units have been obtained based on the optimized T_1 geometries for the $S_0 \rightarrow T_1$ excitation. Figure 4 displays the NTO pattern and Table 3 provides the concerned NTO results. The NTO patterns for the repeating unit of **P-Au-FLU** have shown that both

hole (H) and particle (P) orbitals are mainly located on one fluorenebased diethynyl ligand (97.35% and 95.00%, respectively) (Figure 4 and Table 3). Hence, the large percentage of $H \rightarrow P$ transition (97.5%) should indicate ligand-centered ${}^{3}\pi$ - π^{*} feature for the T₁ emission in **P-Au-FLU**. From the NTO patterns for the repeating units in both **P-Au-TPA** and **P-Au-CAZ**, the T₁ emission in **P-Au-TPA**

and **P-Au-CAZ** should show ligand-centered ${}^{3}\pi$ - π^{*} feature as well. However, noticeable contribution from the phosphine ligand L-2P to the particles of the repeating units of **P-Au-TPA** and **P-Au-CAZ** (13.94% and 21.72%, respectively) can be clearly seen (Table 3). So, besides the dominated ligand-centered ${}^{3}\pi$ - π^{*} feature, the T₁ emission in **P-Au-TPA** and **P-Au-CAZ** should also exhibit slight ILCT character as well. From the data in Table 3, the Au¹ centers give negligible contribution to the transition process responsible for the T₁ emission of these Au¹ polyynes. Accordingly, the T₁ emission of these Au¹ polyynes should dominantly exhibit ligand-centered ${}^{3}\pi$ - π^{*} feature, which has been indicated by the structured line-shape of their PL spectra at 77 K (Figure S7). This outcome indicates the good consistency between experimental and theoretical results. It also reflects the rationality of the employed strategy for the theoretical calculations.

Optical power limiting behaviors

Compared with their small molecular Au¹ acetylides, these novel Au¹ polyynes can exhibit much stronger T_1 emission ability at 298 K, indicating their much higher quantum efficiencies of the T_1 states. Hence, they should show great potential in OPL application. To the best of our knowledge, only several small molecular Au¹ acetylides have been reported with high OPL activity.^{28,29} The OPL behavior of neutral Au¹ polyynes has been rarely explored. Based on the reverse saturable absorption (RSA) mechanism of T_1 states for nano-second laser,³ the much higher T_1 quantum yield associated with these Au¹ polyynes should enhance their OPL ability effectively. Therefore, it should be of great importance to investigate their OPL performances in view of both evaluating their potential as new OPL materials and providing valuable structure-property information for guiding the design of highly efficient OPL materials. Hence, the OPL properties of these Au¹ polyynes have been investigated.

The high transparency at 532 nm associated with these Au polyynes (Figure 1) makes it suitable to characterize their OPL properties against 532 nm laser beam due to their low ground-state absorption at this wavelength. Accordingly, the OPL performances of these Au¹ polyynes have been characterized in CH₂Cl₂ with the high linear transmittance T_o of ca. 95% (Figure 5) through Z-scan method with an open-aperture mode. Based on the Z-scan curves where the transmittance (T) of the sample is a function of Zposition (against focal point Z=0) of the sample along the Z direction (Figure 5), it can be detected clearly that the T of the Au¹ polyyne solution can remain constant when the sample stays far from the focal point with weak incident laser irradiance, showing linear optical property (i.e. obeying Beer's law). However, when the sample is moved towards the focus to increase the incident laser irradiance upon it, the T of the sample decreases and the OPL response appears (Figure 5), showing nonlinear optical effect. The OPL behaviors of these Au^l polyynes can be explained as the RSA process of their T₁ states (Figure S9). Owing to the relatively long duration of the laser pulse in nano-second order, the T₁ states with long lifetime in micro-second range can easily accumulate a certain population through fast inter-system crossing (ISC) process induced by the Au^{1} centers via the first singlet states (S₁) formed by the weak absorption of laser irradiance. Finally, the strong absorption of the laser irradiance accompanied with the $T_1 \rightarrow T_n$ (T_n : higher

triplet states) transition will account for the OPL effect of these Au polyynes (Figure S9).



Fig. 5 Open-aperture *Z*-scan results for the Au¹ polyynes (T_o ca. 95%) together with that for C₆₀ (T_o ca. 86%).

As shown in Figure 5, all the Au¹ polyynes can show improved OPL ability compared with the corresponding small molecular Au acetylides. This result clearly indicates the advantage of preparing Au' polyvnes as OPL materials over small molecular Au' acetylides. Based on the RSA mechanism of the T₁ states (Figure S9), their enhanced OPL performances can be ascribed to the much higher quantum yield of the T1 states at 298 K compared with that of the corresponding Au¹ acetylides (Figure 2). With carbazole-based ligand, P-Au-CAZ shows inferior OPL performance compared with both P-Au-FLU and P-Au-TPA (Figure 5). The OPL results for the corresponding small molecular Au¹ acetylides can show the same trend (Figure 5). Similar results have been obtained in the Pt^{II} analogs as well.³⁴ Based on the line-shape of the T₁ emission bands together with the theoretical results, the T_1 states of these Au^l polyynes exhibit the feature of ligand-centered ${}^{3}\pi$ - π^{*} . The T₁ states from the carbazole-based ligands might possess much weaker absorption ability than those derived from triphenylamine and flourene units. Hence, the OPL results aforementioned can be obtained (Figure 5). Except P-Au-CAZ, both P-Au-FLU and P-Au-TPA can even show stronger OPL effect than C₆₀, one of the state-of-theart OPL materials. Taking their both high OPL activity and excellent transparency in visible light region into consideration (Figure 5 and 1), these Au^l polyynes can successfully fulfill the excellent consistence between the high OPL activity and good transparency, showing great potential in the OPL field.

For practical application of OPL materials, solid state is definitely much more preferable than solution state, considering the convenience of device fabrication and utilization. Therefore, several types of Pt^{II} acetylides have been either physically doped or chemically attached to a solid matrix to make prototype OPL devices.³⁹⁻⁴¹ Unfortunately, Au^I acetylides have never been employed to construct such devices. Hence, for its best OPL performances among these Au^I polyynes, **P-Au-FLU** has been doped in polystyrene (PS) with ca. 3.0-wt% doping level to make prototype device to characterize its OPL ability for 532 nm laser.

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Fig. 6 Normalized transmittance of **P-Au-FLU** doped PS plate and its solution at the same linear transmittance (*To ca.* 90%) versus incident fluence.



Fig. 7 Photoluminescent (PL) spectra for P-Au-FLU in both solution and doped PS film with doping level of *ca*. 3-wt% at 298 K.

The prepared doped PS thin plate with a thickness of ca. 0.8 mm can show very high transparency, possessing T_0 of ca. 90% at 532 nm (inset Figure 6). With increasing input laser fluence upon the prototype OPL device based on P-Au-FLU, decreasing of transmittance has been detected at much lower input laser fluence level compared with the solution sample (Figure 6), revealing that the prototype OPL device can show greatly improved OPL performance compared with the solution. For the prototype OPL device, its optical limiting threshold (F_{th}) which is defined as the input light fluence at which the output light fluence is 50% of that predicted by linear transmittance is ca. 0.14 J cm⁻², while that for the solution sample is higher than 0.4 J cm⁻². This result should indicate that these Au¹ polyynes can possess very desirable features for fabricating practical OPL devices. Meanwhile, the films of these Au' polyynes had been made by spin-coating and their atomic force microscopy (AFM) images were obtained (Figure S10). Obviously, the films of these Au^l polyynes can show high quality with low rootmean-square (RMS) roughness less than 2.6 nm, favouring devices fabrication.

In order to explain the enhancement of OPL ability of P-Au-FLU in PS solid matrix, its PL spectrum in doped PS film has been obtained (Figure 7). Compared with that in solution, the PL pattern for P-Au-FLU in PS solid matrix shows T₁ dominated emission feature rather than the S₁ dominated character in solution (Figure 7), indicating the much higher T_1 quantum yield (ca. 0.28) than that in the solution (ca. 0.02). The T₁ dominated emission pattern is also observed in P-Au-CAZ and P-Au-TPA doped PS films (Figure S11). The increased T₁ quantum yield can be ascribed to the fact that the solid PS matrix has effectively restrained the momentum of the polymer skeleton of P-Au-FLU to promote the radiative decay of the T₁ states. Based on RSA mechanism of the T₁ states (Figure S9), the improved T₁ quantum yield of **P-Au-FLU** in PS matrix should benefit its OPL performances. Hence, the results in Figure 6 can be reasonably obtained. It also indicates the validity of the RSA mechanism of the T₁ states for explaining the OPL behavior of these Au' polyynes. The prototype device based on **P-Au-FLU** should represent the best OPL performance ever achieved by the Aubased materials.

Conclusions

Based on a dinuclear Au¹ complex monomer, three new Au¹ polyynes have been successfully developed. Photophysical investigation has found that polymerization can effectively promote T_1 emission to benefit their OPL performance against 532 nm laser based on the RSA mechanism of the T_1 states. Hence, two of the three Au¹ polyynes can show even better OPL performance than the state-of-the-art OPL material C₆₀, indicating their potential in the field of OPL. Importantly, the Au¹ polyyne based on the fluorene ligand doped in PS solid matrix can show greatly improved OPL activity compared with its solution under linear transmittance as high as 90%, indicating its great potential for fabricating OPL device. These results provide not only a new way to synthesize Au¹ polyynes, but also an outlet to develop new OPL materials with high performances and practical application potential.

Conflicts of interest

There are no conflicts to declare.

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TOC

Novel Au^I polyynes and their high optical power limiting performances in both solution and prototype device[†]

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Soluble Au^I polyynes bearing different organic ligands have been prepared to show enhanced triplet emission and high optical power limiting performances.

