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Introduction

Accompanied by the wide application of lasers, the damage of both human eyes and optical sensors caused by sudden exposure to intense laser beams has pushed the development of optical power limiting materials.^{1–3} Unfortunately, the most effective traditional OPL materials, such as fullerenes (*e.g.*, C_{60}),^{4,5} phthalocyanines (Pc)^{6,7} and porphyrins^{8,9} cannot meet the requirements of their applications in practical devices for the protection of human eyes due to the intense absorption bands in the visible-light region (*ca.* 400–700 nm) induced by their large π -conjugated structures.³ This also indicates the conflict between OPL activity and transparency in traditional OPL materials, representing the key issue to be dealt with in the field of nonlinear optics. Recently, it has been reported that transition metal acetylides can show nonlinear optical properties, which should demonstrate their

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Optimized trade-offs between triplet emission and transparency in Pt(II) acetylides through phenylsulfonyl units for achieving good optical power limiting performance;

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Three Pt(II) acetylides have been prepared by coupling *trans*-[PtCl₂(PBu₃)₂] to ethynyl aromatic ligands with electron-withdrawing phenylsulfonyl units in high yields (>85%). The investigation of their photophysical behavior has shown that the unique conjugation-breaking configuration of the $-SO_2$ - linker in the phenyl-sulfonyl units can afford a very short cut-off wavelength ($\lambda_{cut-off}$) of <390 nm to the Pt(II) acetylides, furnishing excellent transparency of these compounds. Critically, the triplet quantum yields (Φ_P) of the prepared Pt(II) acetylides can be effectively enhanced from 0.52% to 15.92% through increasing the number of fluorine substituents on the phenylsulfonyl units in the organic ligands. Benefiting from their enhanced Φ_P , the phenylsulfonyl-based Pt(II) acetylides can exhibit comparable or even better optical power limiting (OPL) performance against 532 nm lasers than the state-of-the-art OPL material C_{60} , indicating their great potential in the field of laser protection. All of these results have provided a new strategy to achieve consistency between high OPL ability and good transparency for OPL materials, representing a valuable attempt for coping with key problems in the field of nonlinear optics.

potential in the field of OPL.¹⁰ More importantly, Pt(n) acetylides bearing organic phosphine ligands can exhibit outstanding transparency with very weak or even no absorption in the visible-light region while maintaining greatly enhanced OPL ability even better than C_{60} , Cu(n)-phthalocyanine and Zn(n)-porphyrin at the same time.^{11–14} Furthermore, the transparency of these Pt(n) acetylides can be optimized by tuning the configuration of the Pt(n) centers as well as copolymerization with Hg(n) ions, indicating their great advantages in achieving optimization between OPL activity and transparency.^{11,12} The success of these Pt(n) acetylides lies in their optimized consistency between transparency and triplet emission quantum yield, which can improve the OPL ability according to the reverse saturable absorption (RSA) mechanism.³ In addition, some phenylethynyl-type Pt(n) acetylides have also been employed to make prototype OPL devices.¹⁵

From the discussion aforementioned, a feasible strategy to deal with the key issues in the field of OPL materials should be fulfilling short absorption wavelengths as well as high triplet quantum yields in Pt(II) acetylides. According to the reported results, the electronic features of the organic acetylene ligands can play a very crucial role in determining both the triplet quantum yield and the transparency of transition metal acetylides.^{16–18} Hence, employing new acetylene ligands should represent a feasible way to meet the purposes aforementioned. Owing to their electron-withdrawing character, the phenylsulfonyl units

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have been employed to develop high-performance materials in organic lighting-emitting diodes (OLEDs).^{19,20} However, these phenylsulfonyl units have been rarely introduced into $Pt(\pi)$ acetylides for OPL purposes. On this basis, three $Pt(\pi)$ acetylides bearing organic acetylides with phenylsulfonyl groups have been prepared to characterize their OPL properties. The phenylsulfonyl groups can furnish the concerned $Pt(\pi)$ acetylides with a good OPL ability afforded by the enhanced triplet quantum yield and also maintain excellent transparency with no absorption beyond 400 nm at the same time. Therefore, the concerned results will present a new strategy for achieving optimized trade-offs between high OPL activity and good transparency.

Experimental

General information

The commercially available reagents were used directly as received unless otherwise stated. All reactions were conducted under an inert 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 precoated 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 characterization

¹H-, ¹³C-, ¹⁹F- and ³¹P-NMR spectra were measured in CDCl₃ with a Bruker AXS 400 MHz NMR spectrometer with the ¹H and ¹³C NMR chemical shifts quoted relative to SiMe₄ and the ³¹P chemical shifts relative to an 85% H₃PO₄ external standard. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. UV-vis spectra were recorded with a Shimadzu UV-2250 spectrophotometer. The photoluminescent (PL) properties of the Pt(II) acetylides were measured with an Edinburgh Instruments FLS920 fluorescence spectrophotometer. The lifetimes of 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 quartz tube into a liquid nitrogen Dewar and recording the data after standing for 3 minutes. The fluorescence quantum yields ($\Phi_{\rm F}$) were determined in CH₂Cl₂ solutions at 298 K against quinine sulfate in 1.0 M H₂SO₄ $(\Phi_{\rm F} \ ca. \ 0.55)$ ²¹ Phosphorescence quantum yields $(\Phi_{\rm P})$ were measured at room temperature with deoxygenated samples. Oxygen was removed using three successive freeze-pumpthaw cycles. The $\Phi_{\rm P}$ values were determined by an integrating sphere from Edinburgh Instruments FLS920 with the excitation wavelength at 340 nm. The laser-irradiation stability of the Pt(II) acetylides was characterized by comparing the ¹H-NMR spectra of the fresh samples and the corresponding samples after Z-scan measurement.

Optical power limiting measurements

The optical power limiting properties of the Pt(n) acetylides were characterized by *Z*-scan measurements, which were performed at 532 nm for a Gaussian mode laser beam with a repetition rate of 20 Hz using a Q-switched Quantel Q-Smart 100 Nd:YAG laser. The laser beam was split into two beams using 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 our samples was measured as a 92% transmitting solution at 532 nm in CH₂Cl₂ filled in a 1 mm quartz cell.

Computational details

Geometrical optimizations were conducted using the popular B3LYP density functional theory (DFT). The basis set used for the C, H, O, N, F, P and S atoms was 6-311G(d,p), whereas effective core potentials with a LanL2DZ basis set were employed for the Pt atoms.^{22,23} The energies of the excited states of the complexes were computed by TD-DFT based on all of the ground-state geometries. All calculations were carried out using the Gaussian 09 program.²⁴

Synthesis

The brominated phenylsulfonyl compounds **S-0F-Br**, **S-1F-Br** and **S-3F-Br** were prepared using our previous method.²⁰ The ethynyl aromatic ligands were prepared by the typical Sonogashira coupling reaction.^{25–28} All of the synthetic procedures are provided in the ESI.[†]

General synthetic procedure for the Pt(II) acetylides

Under N₂ atmosphere, *trans*-[PtCl₂(PBu₃)₂] (1.0 equiv.) was added to the solution of the corresponding diethynyl aromatic ligand (2.1 equiv.) in EtN₃. Then, a small amount of CuI was added. The reaction mixture was stirred for 10 h at room temperature. After removing the solvent, the residue was purified by preparative TLC. The title compounds were obtained in high yield.

Pt-S-0F: (yield: 88%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.92 (d, *J* = 8.0 Hz, 4H), 7.76 (d, *J* = 8.0 Hz, 4H), 7.55–7.47 (m, 6H), 7.30–7.26 (m, 4H), 2.08–2.03 (m, 12H), 1.58–1.52 (m, 12H), 1.44–1.35 (m, 12H), 0.88 (t, *J* = 8.0 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.13, 136.75, 134.22, 132.88, 131.12, 129.18, 127.50, 116.11, 115.97, 108.83, 26.31, 24.35, 23.90, 13.77; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –104.74 (s, 1F); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 3.44 (¹*J*_{P-Pt} = 2321 Hz). FAB-MS (*m*/*z*): 1081 [M]⁺. Elemental analysis calcd (%) for C₅₂H₇₂O₄P₂PtS₂: C 57.71, H 6.71; found: C 57.62, H 6.58.

Pt-S-1F: (yield: 90%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.95–7.92 (m, 4H), 7.74 (d, J = 8.0 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 7.16 (t, J = 8.0 Hz, 4H), 2.07–2.03 (m, 12H), 1.57–1.52 (m, 12H), 1.44–1.35 (m, 12H), 0.89 (t, J = 8.0 Hz, 18H); ¹³C NMR

(100 MHz, CDCl₃): δ (ppm) 141.86, 136.60, 131.17, 130.28, 130.18, 127.39, 116.56, 116.34, 108.85, 26.28, 24.33, 23.88, 13.76; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -104.74 (s, 1F); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 3.45 (¹*J*_{P-Pt} = 2321 Hz). FAB-MS (*m/z*): 1117 [M]⁺. Elemental analysis calcd (%) for C₅₂H₇₀F₂O₄P₂PtS₂: C 55.85, H 6.31; found: C 55.78, H 6.23.

Pt-S-3F: (yield: 86%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.73 (d, *J* = 8.0 Hz, 4H), 7.57 (t, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.07–2.03 (m, 12H), 1.58–1.52 (m, 12H), 1.43–1.37 (m, 12H), 0.89 (t, *J* = 8.0 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.43, 149.90, 138.33, 135.06, 131.40, 127.69, 117.63, 112.71, 112.55, 108.89, 26.30, 24.34, 23.92, 13.76; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –129.25 (d, 4F), –151.28 (t, 2F); ³¹P NMR (161.9 MHz, CDCl₃): δ (ppm) 3.50 (¹*J*_{P-Pt} = 2315 Hz). FAB-MS (*m*/*z*): 1189 [M]⁺. Elemental analysis calcd (%) for C₅₂H₆₆F₆O₄P₂PtS₂: C 52.47, H 5.59; found: C 52.37, H 5.51.

Results and discussion

Synthesis and structural characterization

The synthetic pathways of the Pt(n) acetylides bearing phenylsulfonyl units are shown in Scheme 1. With the aim of tuning the electronic features of the Pt(n) acetylides, strong

electron-withdrawing -F groups have been introduced to the phenylsulfonyl units. In order to obtain the target Pt(II) acetylides Pt-S-0F, Pt-S-1F and Pt-S-3F, the corresponding phenylsulfonylbased aromatic alkynes L-0F, L-1F and L-3F should be prepared. The starting compounds S-0F-Br, S-1F-Br and S-3F-Br for preparing the alkyne ligands L-0F, L-1F and L-3F were synthesized according to our previous methods²⁰ and the synthetic details have been provided in ESI.[†] Through highly efficient Sonogashira cross-coupling, the brominated phenylsulfonyl compounds S-OF-Br, S-1F-Br and S-3F-Br can be converted into S-OF-TMS, S-1F-TMS and S-3F-TMS, which can undergo the trimethylsilane cleaving reaction to form the aromatic alkyne ligands L-0F, L-1F and L-3F in high yields over 90% (Scheme 1). After obtaining all of the key organic ligands, the designed $Pt(\pi)$ acetylides can be easily prepared using the Sonogashira cross-coupling procedure between the ligands L-0F, L-1F and L-3F and *trans*-[PtCl₂(PBu₃)₂] in Et₃N with CuI as catalyst (Scheme 1).

The Pt(π) acetylides bearing phenylsulfonyl units have been fully characterized by ¹H, ³¹P and ¹⁹F NMR spectra. In the ¹H NMR spectra of these Pt(π) acetylides, the absence of a single peak at *ca.* 3.2 ppm, assigned to the protons in the alkyne groups, indicates successful coupling between the alkyne groups in the organic ligands and *trans*-[PtCl₂(PBu₃)₂]. The strong resonance peak with a P–Pt coupling effect at *ca.* 3.5 ppm in



Scheme 1 Synthesis of the Pt(II) acetylides bearing phenylsulfonyl units.

the ³¹P NMR spectra of these Pt(II) acetylides has clearly shown the presence of the *trans*-Pt(PBu₃)₂ units. In the ¹⁹F NMR spectrum of **Pt-S-1F**, the single resonance peak at *ca.* –104.74 ppm indicates the only –F group on the pendant phenyl ring of the sulfonyl unit. For **Pt-S-3F**, the two sets of resonance peaks at *ca.* –129.25 ppm and –151.28 ppm in its ¹⁹F NMR spectrum are consistent with its fluoro-substitution pattern.

Photophysical properties

The absorption properties of the phenylsulfonyl-based Pt(π) acetylides have been characterized in CH₂Cl₂ at 298 K and the data are summarized in Table 1. In their UV-vis absorption spectra (Fig. 1), all the Pt(π) acetylides exhibit intense absorption bands, which can be assigned to the metal disturbed π – π * transitions from the organic ligands.^{12,16,29} All of the absorption bands for these Pt(π) acetylides are located in the UV region before 400 nm with absorption maxima at *ca.* 340 nm (Fig. 1 and Table 1), indicating their excellent transparency in the visible light region (*ca.* 400–700 nm). In addition, the cut-off absorption wavelengths ($\lambda_{cut-off}$) for these Pt(π) acetylides show a slight bathochromic effect when increasing the number of fluorine substituents on the phenylsulfonyl units (*ca.* 380 nm for **Pt-S-0F**, 382 nm for **Pt-S-1F** and 386 nm for **Pt-S-3F**).

In the photoluminescent (PL) spectra of these Pt(II) acetylides in CH₂Cl₂ solution at 289 K, all of the complexes exhibit two emission bands centered at ca. 380 nm (Pt-S-OF and Pt-S-1F: 383 nm, Pt-S-3F: 384 nm) and 480 nm (Pt-S-0F: 476 nm, Pt-S-1F: 478 nm, Pt-S-3F: 483 nm), respectively (Fig. 2a and Table 1). The high-energy emission bands should come from the singlet states (S_1) of the metal disturbed organic ligand π - π * transitions due to their short lifetime in the order of nanoseconds (ns) (Table 1). On the contrary, the much longer lifetimes in the order of microseconds (µs) together with the large Stokes shift of ca. 130 nm should indicate the triplet state (T_1) features of the long-wavelength emission signals (Fig. 2a and Table 1). Furthermore, at a low temperature of 77 K, the long-wavelength emission signals have been substantially enhanced, also indicating their T_1 features (Fig. 2b). What should be noted is that the intensity of the T₁ emission signals of these Pt(II) acetylides enhances when increasing the number of fluorine substituents on the phenylsulfonyl units (Fig. 2a). This trend is not only supported by the decrease in the quantum yield of the S1 states ($\Phi_{\rm F}$) from **Pt-S-0F** (*ca.* 0.11%) to **Pt-S-1F** (*ca.* 0.03%) then to Pt-S-3F (ca. 0.02%), but also indicated directly by the increase





in the quantum yield of T_1 states (Φ_P) (*ca.* 0.52% for **Pt-S-OF**, 6.50% for **Pt-S-1F** and 15.92% for **Pt-S-3F**) (Table 1). Hence, it seems that introducing fluorine substituents can effectively increase the quantum yield of T_1 states, which should benefit the OPL performance of these Pt(II) acetylides.

In order to interpret the photophysical properties of these Pt(II) acetylides aforementioned, their frontier molecular orbitals and transition characteristics, showing a tight relationship with their photophysical properties, have been obtained by time-dependent density functional theory (TD-DFT) calculation. The theoretical calculation results clearly show that the HOMO \rightarrow LUMO (H \rightarrow L) transition can represent the characteristics of the S_1 state of the Pt(n) acetylides, owing to its large contribution to the transition of the S_1 state (Table 2). From the molecular orbital patterns corresponding to the $H \rightarrow L$ transition (Fig. 3), the S₁ states of these phenylsulfonylbased Pt(II) acetylides exhibit obvious ligand-centered π - π * character. Based on the theoretical results (Table 2), the formation of the S1 states should correspond to the major absorption of these Pt(II) acetylides. Hence, the dominant absorption bands of these Pt(II) acetylides show metal disturbed π - π * features. Due to different contributions from the metal d_{π} orbitals to their HOMOs and LUMOs (Table 2), the S₁ states of these Pt(II) acetylides show some metal-to-ligand charge transfer (MLCT) features as well. From their noticeable contribution to the LUMOs, the pendent phenyl ring in the phenylsulfonyl units can host electrons in the MLCT process.

Table 1 Photophysical data for the Pt(II) acetylides										
Compound	Absorption λ_{abs}^{a} (nm) 298 K	Emission λ_{em}^{a} (nm) 298 K/77 K	${\Phi_{\mathrm{F}}}^{b}$ (%)	$\Phi_{\mathrm{P}}^{}^{c}}(\%)$	Lifetime of excited states ^d S_1 state (ns)/ T_1 state (μ s)	$\lambda_{\text{cut-off}}$ (nm)				
Pt-S-0F Pt-S-1F Pt-S-3F	267, 304 ^{sh} , 340 262, 303 ^{sh} , 341 262, 306 ^{sh} , 346	$\begin{array}{c} 383,400^{\rm sh},476/468,490\\ 383,402^{\rm sh},478/468,490\\ 384,402^{\rm sh},483/469,492 \end{array}$	0.11 0.03 0.02	0.52 6.50 15.92	1.05 ns (383 nm)/48.3 μs (468 nm) 1.11 ns (383 nm)/43.2 μs (468 nm) 1.15 ns (384 nm)/28.7 μs (469 nm)	380 382 386				

^{*a*} Measured in CH_2Cl_2 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 313 nm while the Φ_F of the standard is 55%. ^{*c*} Measured using an integrating sphere at 298 K, the excitation wavelength was set at 340 nm. ^{*d*} 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 CH_2Cl_2 with the excitation at 360 nm and that of the T₁ states was measured at 77 K in the same solvent with the same excitation wavelength.



Fig. 2 Photoluminescence (PL) spectra for the Pt(II) acetylides in CH_2Cl_2 solution at both 298 K (a) and 77 K (b).

Clearly, increasing the number of fluorine substituents on the pendant phenyl moieties will enhance their electron-accepting ability, which will facilitate the $H \rightarrow L$ transitions and lower the energy level of the S_1 states in these Pt(II) acetylides. As a result, the absorption maxima and $\lambda_{cut-off}$ for these Pt(II) acetylides should show a bathochromic effect from **Pt-S-0F** to **Pt-S-3F**, which coincides well with the experimental results (Table 1).

According to the heavy atom effect, emission signals from the decay of T_1 states can typically be detected due to

the spin-orbit coupling (SOC) effect, which can facilitate the formation of the T_1 states through the intersystem crossing (ISC) process. It has been shown that the SOC effect in the transition metal acetylides can be enhanced effectively by mixing the d orbitals of the heavy metal centers and the π orbitals of the organic ligands. By this way, the transition processes in the concerned systems will exhibit more obvious metal-involved characters rather than just the ligand-centered $\pi - \pi^*$ features. Hence, the effective mixing of the orbitals between both heavy metal centers and organic ligands will enhance the SOC effect to facilitate the formation of the T₁ states. From the MO distributions of these Pt(II) acetylides (Fig. 3), it can be seen clearly that the d_{π} orbitals of the Pt(π) centers give noticeable contribution (>20%) to the HOMOs, while the LUMOs are mainly located on the π orbitals of the organic ligands. Based on the calculation results in Table 2, the H \rightarrow L transitions can represent the features of the transitions to the T1 states to a large extent. These results indicate the effective mixing of the orbitals from the Pt(II)centers and the corresponding organic ligands and hence there is a strong SOC effect in these Pt(II) acetylides. As a result, all of them can show T_1 emission bands even at 298 K (Fig. 2a).

Besides the H \rightarrow L transition, the HOMO-2 (H-2) \rightarrow LUMO+1 (L+1) transition also contributes to the character of the T₁ states associated with these Pt(II) acetylides (Table 2). The π orbitals of the pendent phenyl ring in the phenylsulfonyl units can substantially contribute to the LUMO+1 orbital of these Pt(II) acetylides (Fig. 3). When increasing the number of fluorine substituents on the pendant phenyl moieties, the contribution from their π orbitals to the LUMO+1 increases (*ca.* 35.2% for **Pt-S-0F**, 39.4% for **Pt-S-1F** and 45.3% for **Pt-S-3F**). Hence, increasing the number of fluorine substituents can improve the degree of orbital mixing between the Pt(II) centers and the organic ligands. So, the SOC effect for these Pt(II) acetylides should fall in the order of **Pt-S-3F** > **Pt-S-1F** > **Pt-S-0F**. As a result, **Pt-S-3F** can show the highest T₁ emission intensity, while **Pt-S-0F** gives the lowest T₁ emission intensity (Fig. 2a).

Optical power limiting properties

Owing to their T_1 states being induced by the heavy metal centers through the SOC effect, these Pt(n) acetylides can exhibit OPL behavior induced by the strong absorption ability

Compound	Contribution of d_{π} orbitals to HOMO ^{<i>a</i>}	Contribution of d_{π} orbitals to LUMO ^{<i>a</i>}	Largest coefficient in the CI expansion of the T_1 state ^b	Percentage contribu- tion of the transition to the T_1 state ^b	Largest coefficient in the CI expansion of the S_1 state ^b	Percentage contribu- tion of the transition to the S_1 state ^b	Oscillator strength (f) of the S ₁ \leftarrow S ₀ transition
Pt-S-0F	20.5%	9.0%	$H \rightarrow L (0.59511)$ $H-2 \rightarrow L+1 (0.24365)$	70.8% 11.9%	$H \rightarrow L (0.68936)$ 358.61 nm	95.0%	1.5324
			479.32 nm				
Pt-S-1F	20.7%	9.0%	$H \rightarrow L (0.59784)$	71.5%	$H \rightarrow L (0.68998)$	95.2%	1.5360
			$H-2 \rightarrow L+1 (0.24972)$ 480.13 nm	12.5%	358.61 nm		
Pt-S-3F	21.0%	6.6%	$H \rightarrow L (0.58101)$	67.5%	$H \rightarrow L (0.68649)$	94.3%	1.4718
			$H-2 \rightarrow L+1 (0.23510)$ 480.70 nm	11.1%	362.00 nm		

Table 2 Contribution of the metal d_{π} orbitals to the HOMO and LUMO together with the TD-DFT calculation results

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



Fig. 3 Critical molecular orbitals involved in the S1 and T1 transitions of the Pt(II) acetylides. (a) Pt-S-0F, (b) Pt-S-1F, (c) Pt-S-3F

of the T_1 states. From the PL spectra of the Pt(II) acetylides, the emission signals from the decay of the T_1 states can even be observed at 298 K (Table 2). Hence, the phenylsulfonyl-based Pt(II) acetylides should show promising OPL ability. In addition, the OPL behavior of the Pt(II) acetylides bearing phenylsulfonyl units has been rarely investigated. So, it should be of great importance to study the OPL performance of these Pt(II) acetylides in view of both evaluating their potential as new OPL materials and providing valuable structure–property information for guiding the design of high-performance Pt(II) acetylides for OPL applications. Bearing this in mind, the OPL properties of these Pt(II) acetylides have been investigated.

From their UV-vis spectra, all three of the Pt(n) acetylides are highly transparent at 532 nm, indicating their low ground-state absorption at this wavelength. This result makes them suitable for the characterization of their OPL properties against a 532 nm laser beam. Hence, the OPL behaviors of these Pt(n)acetylides have been characterized in CH_2Cl_2 with a linear transmittance T_0 of *ca.* 92% (Fig. 4) through the *Z*-scan method under an open-aperture mode. From the *Z*-scan curves, where



Fig. 4 Open-aperture Z-scan results for the Pt(\parallel) acetylides (T_{o} ca. 92%) together with that for C₆₀ (T_{o} ca. 86%).

the transmittance (*T*) of the sample is a function of the *Z*-position (against focal point Z = 0) of the sample along the *Z* direction (Fig. 4), it can be seen clearly that the *T* of the Pt(π) acetylide solution remains almost constant far from the focal point, showing linear optical properties (*i.e.* obeying Beer's law). It means that the Pt(π) acetylide solution exhibits linear optical behavior under weak incident irradiance. However, when the sample is moved towards the focus to increase incident irradiance upon it, the *T* of the sample decreases and the OPL effect appears (Fig. 4) to show a nonlinear optical effect.

Based on the photophysical properties of these $Pt(\pi)$ acetylides presented in the previous section, their OPL mechanism can be explained as follows. According to the previous results and the obvious T1 emission bands (Fig. 2a and b), the OPL effect associated with these Pt(II) acetylides can be assigned to reverse saturable absorption (RSA) from the T_1 states (Fig. 5a).^{12,16} The molecules of the $Pt(\pi)$ acetylides in the ground state (S₀) can be excited initially to the first singlet state (S_1) by laser irradiance. Due to the strong SOC effect induced by the Pt(n) centers, the S_1 states can be swiftly converted into the T₁ states through the ISC process. Owing to the relatively long laser pulse duration in the order of nanoseconds, the fast ISC process and the long-lived T₁ state, the molecules in the T_1 state can reach a certain population easily and then absorb laser energy strongly to reach a higher triplet state (T_n) in the laser pulse duration to induce the OPL effect (Fig. 5a). Therefore, it is the strong absorption from the T_1 states that furnishes these Pt(II) acetylides with OPL ability (Fig. 5a). Owing to the very short lifetime ($\sim 1 \text{ ns}$) of the S₁ state (Table 1), the energy absorption from the $S_1 \rightarrow S_n$ transition can be neglected in the contribution to the nanosecond OPL response in these Pt(II) acetylides. Clearly, if the proposed mechanism is valid, the compound with a higher T_1 quantum yield should show better OPL performance. From the Z-scan curves, it is obvious that the OPL ability of these Pt(II) acetylides falls in the order of Pt-S-3F > Pt-S-1F > Pt-S-0F, which is in good agreement with the order of their T_1 quantum yields (Fig. 2a and Table 1). This result should indicate that the proposed OPL mechanism associated with these $Pt(\pi)$ acetylides is reasonable.



Fig. 5 (a) Optical power limiting mechanisms involved in the $Pt({\scriptstyle II})$ acetylides. (b) Comparison of the color of the $Pt({\scriptstyle II})$ acetylides and $C_{60}.$

Based on the RSA mechanism for the nanosecond laser aforementioned, developing materials with high triplet quantum vields as well as short absorption wavelengths should represent a feasible outlet to fulfill good trade-offs between high OPL activity and good transparency. From the results aforementioned, employing organic ligands with strong electron withdrawing fluorinated phenylsulfonyl units can effectively promote the formation of T₁ states (Fig. 2a and Table 1) which can enhance the OPL ability of the concerned compounds. Facilitating the formation of T₁ states has also been observed in the Pt(II) acetylides with electron withdrawing ligands bearing oxadiazole and triarylborane units.¹⁶ However, the reported Pt(II) acetylides show the absorption maxima located in much longer wavelength regions (ca. 364 nm for the oxadiazole-based Pt(II) acetylides and 381 nm for the triarylborane-based Pt(II) acetylides) due to the conjugation of the oxadiazole and triarylborane units.¹⁶ However, the electron withdrawing ligands of these phenylsulfonylbased Pt(II) acetylides exhibit different features. The configuration of the -SO₂- linker can effectively break the conjugation between the two phenyl rings in the phenylsulfonyl units. The theoretical results have clearly proved this conclusion (Fig. 3). Hence, the shortconjugated ligands bearing electron withdrawing -SO2- units and -F groups will exhibit both much shorter absorption maxima (ca. 340 nm for Pt-S-0F, 341 nm for Pt-S-1F and 346 nm for Pt-S-3F) and high T_1 quantum yields (Table 1). So, in view of the reported $Pt(\pi)$ acetylides with electron withdrawing ligands, these Pt(II) acetylides can show greater advantages in achieving excellent trade-offs between high OPL activity and good transparency.

In order to evaluate the advantages of these Pt(n) acetylides as OPL materials, their OPL performances and the transparency features have been compared to that of C_{60} , one of the state-of-the-art RSA OPL materials. Even at higher T_0 of ca. 92%, Pt-S-OF can show nearly identical OPL ability to that of C₆₀. More importantly, bearing organic ligands with stronger electron withdrawing ability, both Pt-S-1F and Pt-S-3F can even outperform C₆₀ (Fig. 4). Besides the attractive OPL ability of these $Pt(\pi)$ acetylides, their exceptional transparency also indicates their importance in the field of OPL. All of the $Pt(\pi)$ acetvlide samples are off-white with nearly no absorption in the visible light region (ca. 400-700 nm). However, traditional C_{60} displays a very dark color, indicating very poor transparency in the visible light region (Fig. 5b). Furthermore, these $Pt(\pi)$ acetylides can show good laser-irradiation stability, since their ¹H-NMR spectra can be maintained nearly unchanged before and after Z-scan measurement (Fig. S1 in ESI⁺). All of these results will definitely provide valuable clues for dealing with the key issues associated with achieving trade-offs between high OPL activity and good transparency.

Conclusions

Employing different phenylsulfonyl-based ligands bearing -F groups, three Pt(II) acetylides have been successfully prepared. It has been found that the fluorinated phenylsulfonyl ligands can effectively enhance the quantum yield of the T1 states to benefit OPL performance of these Pt(II) acetylides against a 532 nm laser. Hence, the Pt(II) acetylides can show comparable or even better OPL performance than the state-of-the-art OPL material C₆₀, indicating their potential in the field of OPL. Besides their encouraging OPL ability, these Pt(II) acetylides can exhibit exceptional transparency with nearly no absorption bands in the visible light region. Compared with traditional analogs, the advantages associated with these $Pt(\pi)$ acetylides lie in the unique configuration and electron withdrawing features of the phenylsulfonyl-based ligands to fulfill excellent trade-offs between high OPL activity and good transparency. The concerned results should represent a valuable strategy to solve the key problems associated with RSA OPL materials.

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