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Broadband Optical Limiting of Novel Twisted Tetrathiafulvalene Incorporated Donor-Acceptor Material and Their Ormosil Gel Glasses

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To accomplish broadband optical limiting with high visible-light region (*ca.* 400 – 700 nm) transmittance as well as satisfy the requirement of practical application, a novel molecule **TTF-Pt(bzimb)** by connecting excellent electron donating tetrathiafulvalene and Pt(II)-incorporated electron withdrawing [Pt(bzimb)] with C-C triple bond has been rationally designed and synthesized. Chlorine substituted **Cl-Pt(bzimb)** is presented for comparison. As expected, the theoretical calculation results clearly demonstrate that **TTF-Pt(bzimb)** exhibits a twisted conformation with a dihedral angle of 50^o along C-C triple bond, and the intramolecular charge transfer existing between donor and acceptor is well evidenced by a series of experimental results such as UV-vis spectra, fluorescence spectra, and CV. Benefiting from the unique conformation, **TTF-Pt(bzimb)** and their doped Ormosil gel glasses in methyltriethoxysilane matrix exhibit broadband (532 and 1064 nm) optical limiting behaviour with high visible-light transmittance. Furthermore, **TTF-Pt(bzimb)** shows more remarkable optical limiting behaviours than the state-of-the-art optical limiting materials C_{60} under 532 nm. Thus, our results disclose one type of rational molecular design strategy for the accomplishment of remarkable optical limiting. **TTF-Pt(bzimb)** and their gel glasses would be considered as promising candidates for the application of optical limiting and nonlinear optical devices.

Introduction

Organic π-electron conjugated molecules, such as fullerene derivatives,[1-3] graphenes,[4-6] phthalocyanines,[7-10] metalloporphyrins,[11-13] organometallic compounds,[14-19] and so on,[20-22] have been devoted great efforts in optical limiting (OL) for the application of laser protection materials and devices.[23, 24] OL is a nonlinear optical process in which the transmittance of a material decreases as the input light intensity increases.[24] The general nonlinear optical response mechanisms with OL behaviour are reverse saturable absorption (RSA) at high-energy of visible-light region, and multiphoton absorption, free charge absorption, nonlinear refraction and scattering at the low-energy visible-light and/or near infrared region.[23, 24] Conventionally, an efficient approach to obtain higher nonlinear optical behaviours is using one- and two-dimensional π-conjugation extension through end-capping with electron-donating (D) and electron-withdrawing (A) moieties to effect intramolecular charge transfer (ICT) and/or accomplish multidimensional charge transfer.[19, 25, 26] Such strategies are significant to enhance OL performances. However, there are many problems to accomplish practical applications.[27-29] Because the expansion of π-conjugation may (i) compress the HOMO-LUMO gap, and create one- and/or multi-photon absorption losing at the third-order optical susceptibility $\chi^{(3)}$ application wavelengths; (ii) reduce the optical transparency characteristics in visible-light regions (*ca.* 400 – 700 nm) due to their intense absorption band originating from abound π-conjugated systems; and (iii) decrease the chemical, thermal, and/or photochemical stabilities and solubility. Marks and co-workers[30-33] discovered that a twisted π-conjugated D-A structure can efficiently avoid these problems induced by expanding π-system and prominently enhance the nonlinear optical response than planar π-conjugation systems. The twisted π-conjugated D-A molecules exhibit unprecedented hyperpolarizabilities on the order of 10-20 times larger than previously observed.[30, 33] Thus, the rational design and synthesis of twisted π-conjugated D-A structure are efficient approaches both for solving these

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† Characterization techniques, synthetic procedures, TGA, UV-vis spectra, CV, theoretical calculations, Z-scan technology, ^1H and ^{13}C NMR spectra and FTIR. For Electronic Supplementary Information (ESI) available see DOI: 10.1039/x0xx00000x

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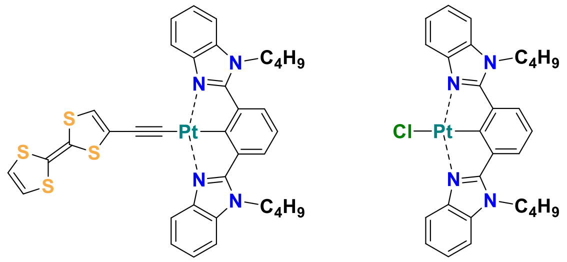

TTF-Pt(bzimb) **Cl-Pt(bzimb)**

Scheme 1 Chemical structures of **TTF-Pt(bzimb)** and model compound **Cl-Pt(bzimb)**

difficulties caused by π-conjugation extension and accomplishing high OL abilities. Unfortunately, the materials based on such strategies are not applied specifically as OL materials up to now.

Tetrathiafulvalene (TTF) and its derivatives,[34-40] because of their remarkable electron donating characters, have been widely used as an efficient electron-donor unit in D-A structures with appealing nonlinear optical properties.[41-47] Most reports of TTF-based D-A conjugated molecules focus on the second-order nonlinear optical properties, whereas the OL behaviours are either investigated through the prediction of theoretical calculation,[43, 44] or experimental measurement with weak performance[41, 44-46, 48] such as single response wavelength (532 nm) and low nonlinear extinction coefficients (β_{eff} = 1.19 cm GW^{-1}). Obviously, TTF-based D-A conjugated materials still can't meet the requirement of practical application in OL device. Herein, a novel TTF-based D-A type conjugated **TTF-Pt(bzimb)** (Scheme 1) has been rationally designed and synthesized. In order to possess twisted and π-conjugated conformation simultaneously, the C-C triple bond is employed in **TTF-Pt(bzimb)** as D-A bridge to introduce the structural features of rotational freedom and π-electron conjugation. Furthermore, according to the RSA mechanism of OL behaviours, the enhancement of intersystem crossing (ISC) from the first singlet state (S$_1$) to the first triplet state (T$_1$) under heavy-metal effect can significantly improve the OL abilities.[49-51] Thus, platinum-contained 1,3-bis(N-alkylbenzimidazol-2'-yl)benzene (Pt(bzimb)) is used as electron acceptor. Meanwhile, the chlorine substituted **Cl-Pt(bzimb)** is presented as a model compound. The chemical conformations and frontier molecular orbits are predicted through theoretical calculation. As expected, the results obviously demonstrate that **TTF-Pt(bzimb)** exhibits twisted π-conjugated conformation with a dihedral angle of 50^o between TTF core and Pt(bzimb) plane. The photo-induced intramolecular charge transfer (ICT) exists between donor and acceptor, which is well consistent with the experimental results of optical spectra and CV. The OL abilities are studied through Z-scan measurements. In comparison with **Cl-Pt(bzimb)**, the solution of **TTF-Pt(bzimb)** exhibits broadband (532 and 1064 nm) optical limiting properties with high visible-light transmittance. Remarkably, the OL behaviours of **TTF-Pt(bzimb)** are higher than the state-of-the-art OL materials C$_{60}$ under 532 nm. For the convenience of practical application, the organically modified silicate (Ormosil) gel glasses of methyltriethoxysilane (MTES) matrix are employed as host materials because of their mechanical stability, facile preparation technique, and molecular level homogeneity of dopants,[52, 53] and the highly homogeneous Ormosil gel glasses of **TTF-Pt(bzimb)** are successfully prepared. The gel glasses exhibit more outstanding OL abilities than their solutions. To our best knowledge that this is the first example of TTF-incorporated materials to accomplish broadband optical limiting both in solution and gel glasses with high visible-light transmittance.

Results and Discussion

Synthesis and Characterization

TTF-Pt(bzimb) was synthesized through cross-coupling reaction between mono-ethynyl substituted TTF derivative TTF-1 and **Cl-Pt(bzimb)**. TTF-1 and **Cl-Pt(bzimb)** were synthesized according to the modified procedures of previous reports[53, 54] and the detail synthetic procedures were showed in Supporting Information (SI, ESI†). The chemical structural characterizations of **TTF-Pt(bzimb)** were processed by using ^{1}H NMR, ^{13}C NMR, element analysis (EA), and FTIR (see Experimental Section and SI). Thermogravimetric analysis (TGA) was used to characterize their thermal stability of **TTF-Pt(bzimb)** and model compound **Cl-Pt(bzimb)** (Fig. S1, ESI†). The results demonstrated that model compound **Cl-Pt(bzimb)** exhibits the first mass loss (*ca.* 4.3%) at 112 ^{o}C which belong to the loss of Cl atom (5.4%), and the greater mass loss appeared when the

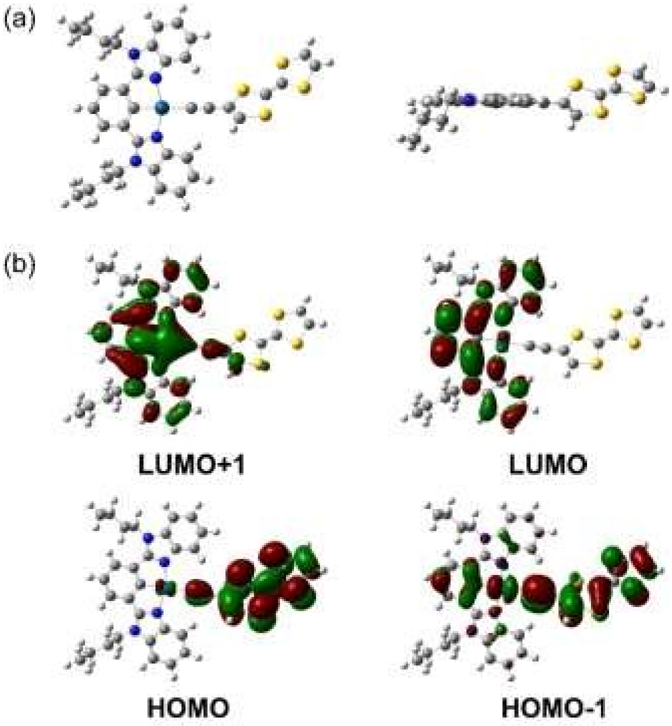

Fig. 1 (a) The TD-DFT calculated chemical structures (top and side view along bzimb ligand plane) and (b) the frontier molecular orbital distributions of **TTF-Pt(bzimb)**.

temperature reaches up to 384 °C. In comparison with **Cl-Pt(bzimb)**, compound **TTF-Pt(bzimb)** showed excellent thermal stability and didn't appear mass loss before the decomposed temperature (*ca.* 335 °C).

Theoretical calculations

To predict the relationships between the chemical conformations and photo-electronic behaviours of **TTF-Pt(bzimb)**, time-dependent density functional theory (TD-DFT) and dependent density functional theory (DFT) calculations were performed by using the Gaussian 09 program package at the B3LYP/6-31G(d,p) level. The calculated molecular conformations and the frontier molecular orbital distributions of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** were displayed in Fig. 1, Fig. S2, S3 and Table S1-S4 (ESI†). The TD-DFT calculation results demonstrate that compound **Cl-Pt(bzimb)** is structural coplanarity (Fig. S2, ESI†), the HOMO/HOMO-1 orbits delocalize on the entire molecular framework, but the LUMO+1/LUMO localized on bzimb ligand plane. Different from compound **Cl-Pt(bzimb)**, the chemical structure of **TTF-Pt(bzimb)** is not coplanar as the TTF core form dihedral angles of *ca.* 50° with Pt(bzimb) plane (Fig. 1a). The HOMO and LUMO orbits completely localize on TTF core and Pt(bzimb) ligand, respectively. However, the HOMO-1/LUMO+1 orbits partially delocalize on TTF core and Pt(bzimb) section. Furthermore, **TTF-Pt(bzimb)** exhibits more smaller band gap of 2.19 eV than **Cl-Pt(bzimb)** of 3.80 eV. These results obviously demonstrate that the twisted molecule **TTF-Pt(bzimb)** exists photo-induced ICT from TTF core to Pt(bzimb) section. Considering the global hybrid functional B3LYP may lead to the wrong structure due to the long-range charge transfer of **TTF-Pt(bzimb)**, the range-separated hybrid functional CAM-B3LYP is used to perform the calculation again with SDD basis set for Pt atom and 6-31+G(d,p) basis set for other atoms.[55] As shown in Fig. S4 (ESI†), the similar twisted structure is obtained with larger dihedral angles (*ca.* 67°) than previous calculation between TTF core and Pt(bzimb) plane.

Photo-physical properties

The UV-vis absorption spectra of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** were measured in dichloromethane (CH_2Cl_2) solution at room temperature. As depicted in Fig. 2a, both **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** exhibited double absorption bands. Wherein, the high energy absorption maximum at 302 and 306 nm for **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)**, respectively, are assigned as n-π* and π-π* transition of independently localized π-conjugation electrons of TTF and Pt(bzimb). In comparison with **Cl-Pt(bzimb)**, the slight blue-shift (4 nm) of highest absorption wavelength and more broaden absorption band (*ca.* 15 nm) of **TTF-Pt(bzimb)** at *ca.* 270-340 nm might attribute to the transition of π-electrons from bzimb ligand to TTF core. The low energy absorption maximum at 387 and 402 nm for **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)**, respectively, could be attributed to the intra-ligand (IL) π-π* transition of bzimb ligand, probably with some mixing of metal-to-ligand charge (MLCT) [dπ(Pt)→π*(N^C^N)] transition.[56, 57] However, it is interest that the absorption maximum of **TTF-Pt(bzimb)** blue-shifts about 15 nm and the relative intensity decreases compared to **Cl-Pt(bzimb)**. This phenomenon is beneficial to OL materials for the demand of high transmittance in visible-light regions (400 – 700 nm). Furthermore, as shown in Fig. S5 (ESI†), **TTF-Pt(bzimb)** appears a slight intensity broad absorption band (*ca.* 430-460 nm), which mainly originates from the photo-induced ICT from electron donating TTF to electron withdrawing Pt(bzimb). These results agree well with the TD-DFT calculations. Additionally, the fluorescence spectra of **TTF-Pt(bzimb)** and model compound **Cl-Pt(bzimb)** have also been collected and demonstrated in Fig. 2b. Compound **Cl-Pt(bzimb)** shows a strong fluorescence signal upon the excitation at 400 nm, which arises from the π-π stacking of Pt(bzimb).[56] While the fluorescence signal of **TTF-Pt(bzimb)** is almost quenched because of the photo-induced ICT from TTF core to Pt(bzimb).

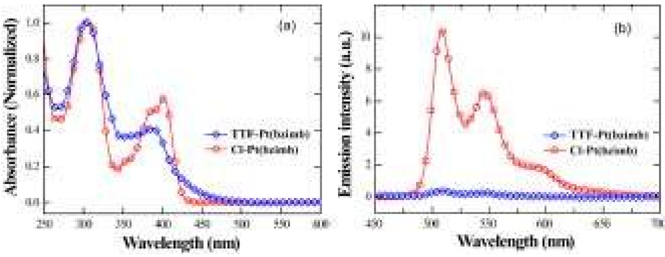

Fig. 2 (a) Normalized UV-vis and (b) Fluorescence spectra of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** in CH_2Cl_2 solution ($c = 2.0 \times 10^{-5}$ M, RT).

Electrochemical properties

The electrochemical behaviours of **TTF-Pt(bzimb)** and model compound **Cl-Pt(bzimb)** were investigated by cyclic voltammetry (CV) *vs* Fc/Fc⁺. As shown in Fig. S6 (ESI†), **TTF-Pt(bzimb)** exhibited three reversible redox potentials, therein, the redox potentials ($E_{1/2}^1$ = 0.36 V and $E_{1/2}^2$ = 0.59 V) correspond to the typical reversible redox behaviours of intrinsic TTF framework. Moreover, a new reversible redox potential ($E_{1/2}^3$ = 0.94 V) could be attributed to Pt(bzimb), and

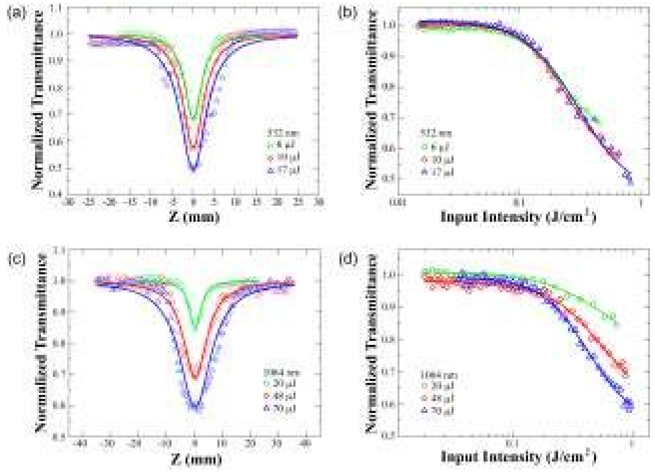

Fig. 3 (a, c) Open aperture Z-scan data and theoretically fitted curves (solid curves) and (b, d) corresponding plots of normalized transmittance *vs* incident intensity of **TTF-Pt(bzimb)** under (a, b) 532 nm with different energies of 6 μJ, 10 μJ, and 17 μJ, and (c, d) 1064 nm with different energies of 20 μJ, 48 μJ, and 70 μJ. The open symbols and solid lines represent the experiment results and theoretical fits, respectively.

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Table 1 NLO coefficients of **TTF-Pt(bzimb)**, model compound **Cl-Pt(bzimb)** and C_{60} in 1,1,2,2-tetrachloroethane solution with identical linear transmittance of 85% at 532 nm.

Samples	λ [nm]	I_0 [a] [μJ]	$T_{\min}$ [b] [%]	F_{on} [c] [J cm^{-2}]	β_{eff} [d] [cm GW^{-1}]
TTF-Pt(bzimb)	532	6	68	0.11	156
		10	57	0.11	136
		17	49	0.13	138
Cl-Pt(bzimb)		10	89	0.32	32
		17	83	0.33	48
C_{60}		6	73	0.07	153
		10	65	0.10	127
		17	60	0.11	109
TTF-Pt(bzimb)	1064	20	84	0.26	60
		48	69	0.19	80
		70	59	0.19	95

[a] incident intensity; [b] the minimum transmittance at the position Z = 0; [c] optical energy-limiting onset fluence (F_{on}) at normalized T = 95%; [d] nonlinear extinction coefficient.

the oxidation potential (0.98 V) slightly decreases *ca.* 20 mV compared to the irreversible redox potential of **Cl-Pt(bzimb)** (1.00 V). These results disclose that the electrons independently localize on TTF Framework and Pt(bzimb) at ground state is beneficial to the production of photo-induced ICT.

Open aperture Z-scan

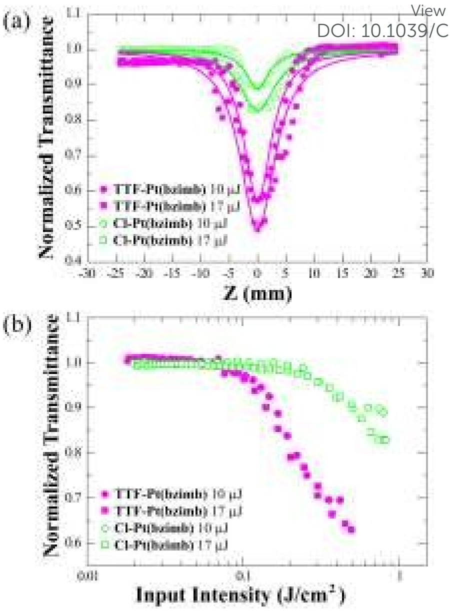

Fig. 4 The comparison of OL properties of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** at 532 nm with different energies of 10 μJ and 17 μJ; (a) Open-aperture Z-scan curves with normalized transmittance, (b) corresponding plots of normalized transmittance *vs* incident intensity.

In order to investigate the OL abilities of this novel twisted π-electron D-A molecule, the open-aperture Z-scan measurements were carried out both in solution and gel glasses by Nd: YAG laser (532 and 1064 nm, 8 ns, 10 Hz) with different levels of laser intensities (I). The 1,1,2,2-tetrachloroethane solutions with the identical linear transmittance (T_0) of 85% and gel glasses with different molar ratios between **TTF-Pt(bzimb)** and MTES were applied. The measurement setups and detail experimental procedures are depicted in Supporting Information, and all data are collected in Table 1 and 2. The optical nonlinearities of samples through detecting the transmittance of a Gaussian beam as a function of the test sample's position (Z) relative to laser focus (Fig. S7, ESI†). As depicted in Fig. 3a and 3c, the Z-scan curves of **TTF-Pt(bzimb)** at different intensities under wavelengths 532 and 1064 nm exhibit nonlinear optical responses. Thus, **TTF-Pt(bzimb)** is a typical OL material. The OL abilities increase along with the enhancement of laser intensities, the corresponding minimum normalized transmittances ($T_{\min}$) at the position of Z = 0 are 68% (6 μJ), 57% (10 μJ), and 49% (17 μJ) under 532 nm, and 84% (20 μJ),

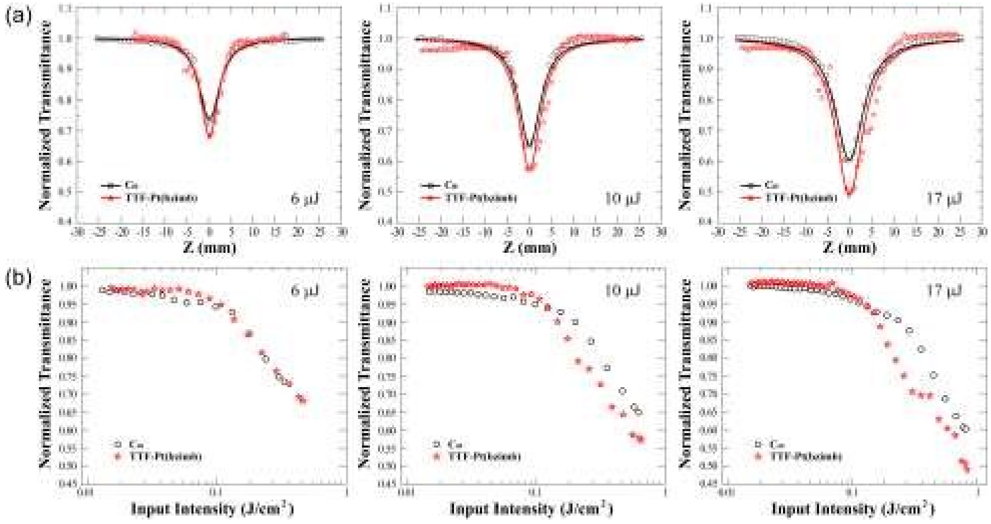

Fig. 5 (a) Open aperture Z-scan data and theoretically fitted curves (solid curves) and (b) corresponding plots of normalized transmittance *vs* incident intensity of **TTF-Pt(bzimb)** and C_{60} at different energies under 532 nm.

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Table 2 NLO coefficients of **TTF-Pt(bzimb)** in MTES gel glasses (**G1**, **G2**, and **G3**) with different concentration under the wavelengths of 532 and 1064 nm.

Samples	T_0 [a] [%]	λ [nm]	I_0 [b] [μJ]	T_{min} [c] [%]	F_{on} [d] [J cm^{-2}]	β_{eff} [e] [cm GW^{-1}]
G1	86	532	10	18	0.05	227
		1064	110	29	0.25	45
G2	77	532	10	20	0.04	279
		1064	110	23	0.21	52
G3	41	532	10	14	0.03	393
		1064	110	12	0.10	112

[a] the linear transmittance at 532 nm; [b] incident intensity; [c] the minimum transmittance at the position $Z = 0$; [d] optical energy-limiting onset fluence (F_{on}) at normalized T = 95%; [e] nonlinear extinction coefficient. The thickness of all glasses is 1 mm.

69% (48 μJ), and 59% (59 μJ) under 1064 nm, respectively.

The OL plots of normalized transmittance *vs* incident intensity are extracted by theoretically fitting from Z-scan data. As depicted in Fig. 3b and Fig. 3d, the transmittance shows no appreciable decrease before the optical energy-limiting onset fluence (F_{on}, which defined as the fluence where transmittance starts to fall to 95% of its original value[58]) of *ca.* 0.11 J cm^{-2} under 532 nm, which obeys the Beer's Law. However, when the intensities increase as the sample moves toward the laser focus, the normalized transmittance decreases and deviates from linearity, suggesting a typical OL behaviour. Furthermore, **TTF-Pt(bzimb)** exhibits OL properties when the F_{on} reach up to *ca.* 0.21 J cm^{-2} under 1064 nm. The nonlinear extinction coefficients (β_{eff}) are high up to 136 - 156 cm GW^{-1} and 60 - 95 cm GW^{-1} corresponding to 532 and 1064 nm wavelengths, respectively. The increase of β_{eff} at 1064 nm implies that the observed OL behaviour of TTF-Pt(bzimb) is influenced by multiple nonlinear optical responses.[19, 59-61] These results show that the novel **TTF-Pt(bzimb)** is an excellent OL material exhibiting broadband spectra OL ability and low F_{on}. In contrast, **Cl-Pt(bzimb)** only exhibits weaker OL behaviours under 532 nm (Fig. 4), higher F_{on} of *ca.* 0.33 J cm^{-2}, and lower nonlinear coefficient β_{eff} of 32 – 48 cm GW^{-1} at laser intensity above 6 μJ.

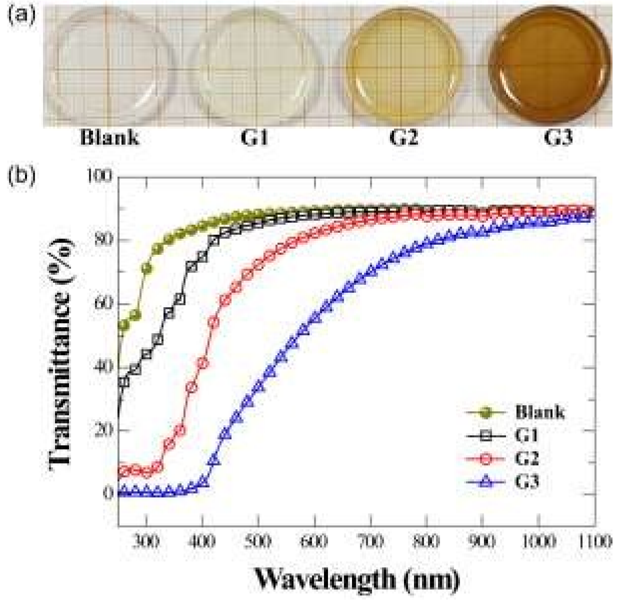

Fig. 6 (a) The gel glasses photos of **TTF-Pt(bzimb)** with different concentrations; (b) transmittance spectra of gel glasses.

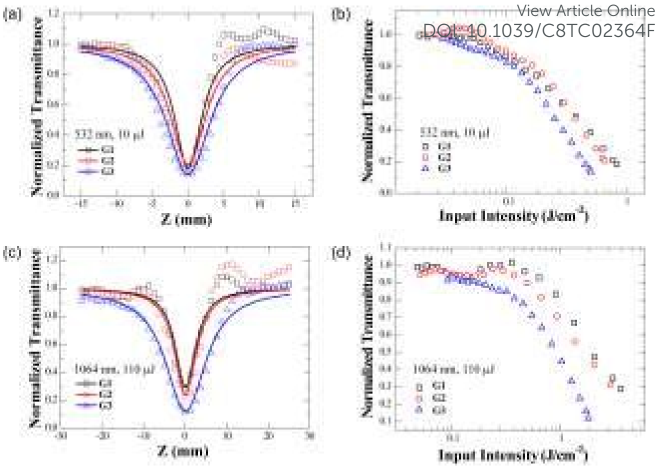

Fig. 7 (a, c) Open aperture Z-scan data and theoretically fitted curves (solid curves) and (b, d) corresponding plots of normalized transmittance *vs* incident intensity of **TTF-Pt(bzimb)** in gel glasses with different concentrations at (a, b) 532 nm, 10 μJ (c, d) 1064 nm, 110 μJ. The open symbols and solid lines represent the experiment results and theoretical fits, respectively.

For evaluating the advantages of **TTF-Pt(bzimb)** as OL materials, the state-of-the-art OL materials C_{60}[24] is used for comparison. Unlike **TTF-Pt(bzimb)**, C_{60} only shows OL properties under 532 nm at the same T_0 of *ca.* 85% in CH_2Cl_2 solution, and **TTF-Pt(bzimb)** exhibits more outstanding OL properties at the different energies under 532 nm. As shown in Table 1 and Fig. 5, the T_{min} of C_{60} are 73%, 65%, and 60% at energies of 6 μJ, 10 μJ, and 17 μJ, respectively, which are higher than corresponding **TTF-Pt(bzimb)**. Furthermore, the β_{eff} of C_{60} 109 – 153 cm GW^{-1} are lower than corresponding **TTF-Pt(bzimb)** solution.

Based on the excellent OL properties of **TTF-Pt(bzimb)**, their highly homogenous gel glasses doped in MTES with different concentrations were prepared successfully for the convenient application of optical limiting (Fig. 6). The molar ratios of **TTF-Pt(bzimb)** and MTES in glasses **G1**, **G2**, and **G3** were 1 : 300, 1 : 100, and 1 : 30, respectively. The blank glass was used for comparison. The linear transmittances (532 nm) of blank glass, **G1**, **G2**, and **G3** are of 88%, 86%, 77%, and 41%, respectively. As demonstrated in Fig. 7 and Table 2, the gel glasses of **TTF-Pt(bzimb)** exhibit more outstanding OL properties than their solution under broadband wavelengths (532 and 1064 nm), which would be attributed to the molecular aggregation of **TTF-Pt(bzimb)** in MTES matrix. The nonlinear transmittance T_{min} of glass **G1** can reduce to 18% at input intensity 10 μJ under 532 nm. Compared with **G1**, the T_{min} of **G2** and **G3** does not show more significant decline along with the increase of **TTF-Pt(bzimb)** concentration, the T_{min} of **G2** and **G3** is of 20% and 14%, respectively. The corresponding β_{eff}

of **G1**, **G2**, and **G3** increased along with the concentration of **TTF-Pt(bzimb)** is high up to 227, 279 and 393 cm GW^{-1}, respectively. Likewise, these gel glasses exhibit excellent OL abilities under 1064 nm at 110 μJ intensity. The corresponding T_{min} of **G1**, **G2**, and **G3** is of 29%, 23%, and 12%, respectively. The β_{eff} of **G1**, **G2** and **G3** is of 45, 52, and 112 cm GW^{-1}, respectively. These results disclose that **TTF-Pt(bzimb)** and their gel glasses exhibit broadband OL properties with high visible-light transmittance and would be considered as remarkable candidates in the application of OL and nonlinear optical devices.

Experimental sections

Unless otherwise indicated, all materials and reagents were commercially available and used without further purification. Compounds TTF-1 and **Cl-Pt(bzimb)** were synthesized according to previous reports.[54, 56, 57] Because of the unstable properties of compound TTF-1 and its precursor compounds to an acidic condition, the synthesis and characterization procedures should proceed under neutral or alkaline conditions.

Synthesis of TTF-Pt(bzimb)

A mixtures of TTF-1 (27 mg, 0.12 mmol) in 15 mL degassed CH_2Cl_2 and NaOH (12 mg, 0.30 mmol) in 5 mL degassed CH_3OH were stirred at room temperature for 0.5 h under N_2 protection. Then a solution of **Cl-Pt(bzimb)** (66 mg, 0.10 mmol) in 10 mL degassed CH_2Cl_2 was added, and the mixture refluxed overnight under N_2 protection. Cooled down to RT and filtered, the precipitate was washed successively with water, methanol and diethyl ether. Subsequent recrystallization through diffusing diethyl ether into a concentrated CH_2Cl_2 solution, and a yellow powder was obtained (53 mg, yield: 63%). ^{1}H NMR (400 MHz, dichloromethane-d_2, 298 K): δ 8.59 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.27 (m, 5H), 6.40 (s, 2H), 6.28 (s, 1H), 4.83 (t, J = 7.5 Hz, 4H), 1.91 (m, 4H), 1.48 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, dichloromethane-d_2, 298 K): δ 164.19, 141.77, 135.51, 134.45, 133.86, 124.40, 124.13, 123.95, 123.58, 119.60, 119.36, 119.28, 115.72, 109.90, 45.19, 32.38, 20.64, 13.92. Anal. calcd for $C_{36}H_{32}N_4PtS_4$: C, 51.23; H, 3.82; N, 6.64; S, 15.12. Found: C, 50.93; H, 3.91; N, 6.36; S, 15.03. IR spectrum (KBr, cm^{-1}): 3064, 2955, 2927, 2868, 2362, 2341, 2063, 1515, 1501, 1482, 1443, 1358, 1311, 1294, 1175, 1101, 1010, 795, 777, 742, 651.

Preparation of gel glasses

The **TTF-Pt(bzimb)**/MTES gel glass were prepared with the modified method of the previous report.[52] By using hydrolysis and polycondensation of MTES in acidic medium (H_2O/HCl, pH = 2.5). The mixture of MTES, ethanol and distilled water (v/v, 5 : 5 : 1) was stirred overnight at room temperature and evaporated out the solvent to initial volume. Then the solution of **TTF-Pt(bzimb)** in $CHCl_3$ was added into the sol with a certain molar concentration. Finally, the mixed sols were dried for several days to obtain the **TTF-Pt(bzimb)**/MTES gel glasses with a uniform thickness.

Conclusion

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In summary, we rationally design and synthesis a novel twisted π-conjugated D-A type molecule **TTF-Pt(bzimb)**, based on the electron donating TTF moiety and electron withdrawing Pt(bzimb), and C-C triple bond is used for D-A bridge. The chemical conformation and frontier molecular orbits are predicted firstly by using theoretical calculations. The results clearly demonstrate that **TTF-Pt(bzimb)** exists dihedral angle of *ca*. 50º between TTF core and Pt(bzimb) along with C-C triple bond, but there is no significant influence on conjugated properties, and photo-induced ICT is existing between donor and acceptor. Furthermore, these results are well verified by photo/electronic measurements. The experimental results disclose that the twisted D-A type **TTF-Pt(bzimb)** exhibits high visible-light transmittance and displays broader photo-induced ICT absorption band at 430 – 500 nm than model compound **Cl-Pt(bzimb)**. The CV results demonstrate that **TTF-Pt(bzimb)** owns three reversible redox potentials indicating the independent localization of electrons on donor TTF core and acceptor Pt(bzimb). The highly homogenous Ormosil gel glasses of MTES matrix doped with **TTF-Pt(bzimb)** are prepared to satisfy the practical application in OL. Open aperture Z-scan obviously discloses that the solutions and gel glasses of **TTF-Pt(bzimb)** exhibit excellent OL properties with high visible-light transmittance under broadband limiting wavelength (532 nm and 1064 nm). **TTF-Pt(bzimb)** shows better OL properties than the state-of-the-art OL materials C_{60}. In brief, the concerned results should represent a rational molecular design strategy and a valuable candidate material for accomplishing broadband OL as well as constructing nonlinear optical devices.

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Table of Contents use only

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Authors: Jibin Sun, Biao Yuan, Xueqing Hou, Chaoxian Yan, Xingming Sun, Zheng Xie,* Xiangfeng Shao,* Shuyun Zhou

A novel tetrathiafulvalene incorporated D-A molecule TTF-Pt(bzimb) is rationally designed and synthesized for broadband optical limiting.