Conjugated twistacene as high-performance optical limiting material for ultrafast broadband laser protection

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Abstract: High-performance optical limiting (OL) is of great importance in laser protection application. Although the research of OL lasts for decades, most existing material can not possess all the desired merits such as low threshold, high linear transmittance, especially broadband and ultrafast respondence. Here, the multi-functional OL in conjugated twistacene was reported through experiments and theory. Results show that broadband OL with fast switching speed can be achieved from 480 nm-700 nm based on effective three-photon absorption. Moreover, low OL thresholds (0.15 J/cm^2) and extremely high linear transmittance (92% at 532 nm) are simultaneously observed. All these combined advantages in one material shows tremendous potential in ultrafast laser protection for human eye and photonic devices.

Key words: twistacene; nonlinear absorption; two-photon induced excited-state; optical limiting
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用于超快宽带激光防护的共轭扭曲并苯高性能光限幅材料

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摘 要:高性能的光限幅对激光防护应用来说非常重要。虽然光限幅相关的研究持续了几十年,但是绝大多数的已知光限幅材料无法兼顾低限幅阈值、高线性透过率和宽带、超快响应。从实验和理论上报道一种基于共轭扭曲并苯分子的多功能光限幅材料。研究结果显示,借助等效三光子吸收,该材料

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能够在 480~700 nm 的光谱范围内实现光限幅并具备快速的响应能力。此外,样品还同时具备低限幅阈值(0.15 J/cm^2)和极高的线性透过率(532 nm 时 92%)。该光限幅材料集以上所有优点于一身,在用于人眼和光子器件的超快激光防护领域具有巨大的前景。

关键词: 扭曲并苯; 非线性吸收; 双光子诱导激发态; 光限幅

0 Introduction

Optical limiting (OL) is one of the most important applications of nonlinear optics. Via absorbing the excess energy of the incident laser, OL materials help to protect light sensitive detectors from critical laser damage. For decades, great efforts have been made to develop novel OL materials[1] and technology[2-3]. To evaluate whether a material is suitable for OL application, several properties are usually considered: (1) OL threshold, which directly reflects the capability of OL; (2) High linear transmittance, to minimize the attenuation of light signals before they enter the protected detector; (3) OL window in spectrum, which guarantees the flexible employing towards tunable lasers. With the development and application of ultrafast laser sources in science and industry, (4) Responding speed is also desired for OL materials. However, to the best of our knowledge, OL material that combines all these properties was reported rarely.

For most existing OL materials, OL is achieved via excited state absorption (ESA)[4-5], two-photon absorption (2PA)[6-7] and nonlinear scattering (NLS)[8-9]. 2PA is ideal for its broadband response with high linear transmittance[10]. Yet thresholds are usually hard to be reached for pure 2PA materials since high input intensity are required to activate 2PA [6, 11-12]. To overcome this disadvantage, two-photon induced excited-state absorption (2P-ESA)[13-14] is employed to enhance the OL performance in a wide window. In most OL materials, ESA from a triplet state (T1) is employed [1]. However, the populating of a triplet state through inter-system crossing (ISC, ~10^{-12} s typically) limits the initiating time of OL. To realize ultrafast broadband OL, two-photon induced singlet state absorption could be the most feasible mechanism.

In our previous research [15], compounds containing twist acene units were designed and synthesized to realize ultrafast broadband reverse saturable absorption based on a long-lived singlet state with a wide absorptive band (470-1 100 nm). Experiments displayed that this broadband reverse saturable absorption could be activated via laser pulses from femtoseconds to nanoseconds. Here we further explore the OL properties of compound DPDA. The ultrafast broadband OL along with high transmittance and low threshold are validated via experiments and theoretical analysis. All the results indicate DPDA as a high-performance OL material, which has great potential in laser protection application.

1 Results and discussion

The molecular structure of DPDA is described in Fig.1, while the details of synthesis and characterization could be found elsewhere[15].

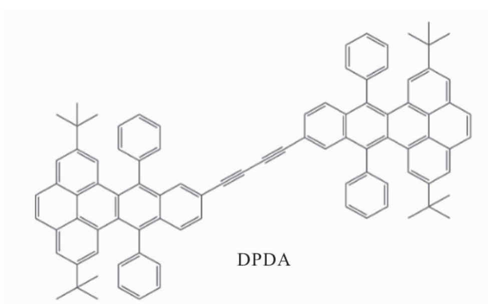

Fig.1 Molecular structure of compound DPDA

Broadband OL of DPDA was examined via femtoseconds pulses at different wavelengths.

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Toluene solution of DPDA (~6×10^{-4} M) containing in a 1 cm path cuvette was prepared for testing. Optical parametric amplifier (Orpheus, Light Conversion) was employed as femtoseconds laser source. The output wavelengths were tuned from 480 nm to 700 nm in this work with 190 fs (FWHM) pulse width, results plotted in Fig.2. Noted that the absorption spectra of DPDA peaks at 361/402/425 nm and the absorptive edge is around 465 nm, which means the linear absorption of DPDA sample will monotonically decrease with the increasing of incident wavelength in the selected test region.

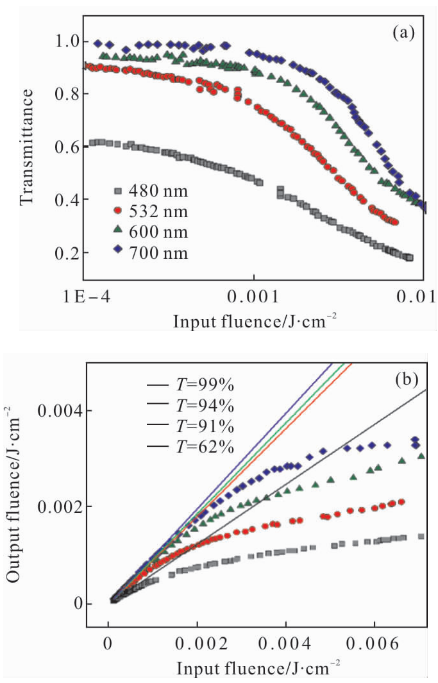

Fig.2 Femtoseconds OL of DPDA under 480 nm, 532 nm, 600 nm and 700 nm, respectively

Results shows that extremely high transmittance of DPDA toluene solution was measured in 10 mm path cuvette. OL is achieved through the total tested spectral region with thresholds (F_{th}) listed in Tab.1. One may find from Fig.2 that the shape of OL curves change with the increasing of incident wavelengths. For shorter wavelength like 480 nm, the transmittance curve decays gently versus input fluence (logarithmic scale). While for longer wavelengths (600 nm & 700 nm), transmittance is relatively high at the beginning and it decreases much faster afterward than 480 nm. This could be interpreted by the competition between effective two-photon absorption (2PA) and effective three-photon absorption (3PA). Effective 2PA and 3PA both contribute to the total absorption of the material. The contribution of 2PA is proportionate to the incident laser intensity I, which belongs to third-order optical nonlinearity, while the contribution from 3PA is proportionate to I^2, which is fifth-order nonlinearity. With a higher order, 3PA may be relatively weak at low energy levels, but it will play a key role with the increase of incident laser energy. As for DPDA, 2PA and ESA (which could be considered as effective 2PA), dominate the nonlinear absorption in short wavelengths against 2P-ESA (could be considered as effective 3PA). When the wavelength increases, the decrease of linear absorption (ground-state absorption) limited the generation of one-photon induced excited-state. In this case, ESA is weakened, and 2P-ESA takes control. With the increase of incident laser energy, 2P-ESA dominates the nonlinear absorption of DPDA, results in the quickly descend transmittance curve in OL experiment.

Tab.1 Parameters of femtoseconds broadband OL of DPDA

	480 nm	532 nm	600 nm	700 nm
T^*	0.62	0.92	0.94	0.99
F_{th}^{**}/J·cm^{-2}	3.1×10^{-3}	3.6×10^{-3}	6.1×10^{-3}	7.0×10^{-3}

* The effect of pure solvent and reflection of the cuvette has been removed

**Defined as the value of incident fluence when the actual transmittance is half of the linear transmittance

As a result, OL thresholds under 480 nm, 532 nm, 600 nm and 700 nm femtoseconds pulses are recorded as 3.1 mJ/cm^2, 3.6 mJ/cm^2 6.1 mJ/cm^2

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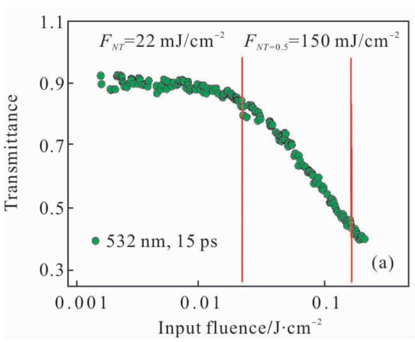
and 7.0 mJ/cm^2, respectively. Strong OL can be accessed across a spectral region wider than 200 nm (480 –700 nm). Thus, the broadband absorptive response of DPDA is validated by experiment.

Experiments under multi –wavelengths femtoseconds pulses clearly showed that DPDA solution could achieve OL in a wide spectral region with relatively low thresholds. According to the existing 2P–ESA theory[16], the effect of 2P–ESA is proportional to the pure 2PA of the material and the pulse width when the lifetime of excited state is much longer than the pulse duration (The ESA lifetime of DPDA was measured to be 10 ns)[15]. The large 2PA and long singlet state lifetime in DPDA bring benefits to the generation and accumulation of excitons in first singlet state, which enhance 2P –ESA. Moreover, high linear transmittance is displayed for wavelengths longer than 480 nm. Inspired by these results, further test was conducted under 15 ps, 532 nm laser source (GKPPL–1064–1–20), and displayed in Fig.3.



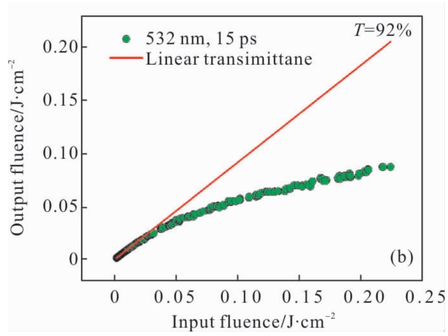


Fig.3 OL of DPDA under the excitation of 532 nm, 15 ps laser pulses

Strong OL was observed in the same DPDA sample under the excitation. The actual transmittance decreases to 90% of the linear transmittance at 22 mJ/cm^2, and the 150 mJ/cm^2 threshold is reached for further increasing incident fluence. The fast descend of transmittance from 22 mJ/cm^2 to 150 mJ/cm^2 indicates the strong impact of 2P–ESA. Compared to femtosecond OL experiment, the longer pulse width in picosecond OL would further boost the ESA in 2P –ESA according to the theory.

The threshold (150 mJ/cm^2) measured in DPDA solution is among the lowest values that have been reported (Tab.2). Although some of listed OL materials show lower thresholds, DPDA in this work simultaneously possess low thresholds, high linear transmittance and broadband response. This unique superiority makes DPDA a remarkable material for OL applications.

Tab.2 Comparison with the reported novel OL materials

Sample	Wavelength/pulse width	T	F_{th}/J·cm^{-2}	Mechanism	Ref.
DPDA/toluene	532 nm/190 fs	0.92	0.003 6	TP–ESA	This work
DPDA/toluene	532 nm/5 ps	0.92	0.15	TP–ESA	This work
C_{60}/toluene	532 nm/7 ns	0.63	~0.1	ESA	[17]
$Si(OR)_2Pcl_4$	532 nm/8 ns	0.95	~0.3	ESA	[18]
$[WS_4Cu_4I_2(py)_6]$/DMF	532 nm/40 ps	0.73	0.07	ESA	[19]
2/THF	770 nm/100 fs	–	0.000 54	TPA	[20]
GO dispersions/H_2O	532 nm/32 ps	0.50	~0.1	TPA, ESA	[21]

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2 Conclusion

In summary, the OL properties of DPDA/toluene solution are investigated via different pulsed lasers. Results indicates that the OL of DPDA based on 2P-ESA has three advantages as low threshold, high linear transmittance and broadband responses under femtoseconds and picoseconds regimes. Each of the three properties in DPDA is comparable to the best OL materials that have been reported, suggesting that DPDA is a superior OL material with great potential for application.

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