

## **A New Tetraphenylethene-Based Schiff Base: Two Crystalline Polymorphs Exhibiting Totally Different Photochromic and Fluorescence Properties**

Hao Sun<sup>1</sup>, Shan-Shan Sun<sup>2</sup>, Fang-Fang Han<sup>1</sup>, Zhong-Hai Ni<sup>1\*</sup>, Ran Zhang<sup>1</sup>, Ming-De Li<sup>2\*</sup>

<sup>1</sup> School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, People's Republic of China

<sup>2</sup> Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Shantou 515063, People's Republic of China

## EXPERIMENTAL SECTION

**Chemicals.** All the reagents and solvents were purchased commercially (AR grade) and used without further purification.

**Characterization.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were collected on a Bruker-400 MHz spectrometer in DMSO solution with TMS as an internal standard. Mass spectra were obtained on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer. The IR spectra (reflection mode) has been recorded with FT-IR Spectrophotometer Model NICOLET iS5 (Thermo fisher, America). UV-vis spectra were recorded on Shimadzu UV-3600 with a UV-VIS-NIR spectrophotometer. The thermal bleaching rate experiment was carried out with a variable temperature UV-VIS spectrophotometer system constructed by using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer and a commercially available temperature control system. Emission spectra were performed by a HITACHI fluorescence spectrometer (F-4600). Emission spectra in low temperature were performed by a FS5 spectrofluorometer. The fs-TA measurements were carried out using a femtosecond Ti: Sapphire regenerative amplified Ti: Sapphire laser system (Coherent, Astrella-Tunable-F-1k) and femtosecond transient absorption spectrometer system (Ultrafast Systems, Helios Fire). The HYPERLINK "javascript:;" repetition frequency of amplifier, pulse width of 800 nm and output power of 800 nm from amplifier are 1 kHz, 84 fs and 7.4 W, respectively. Approximately 4% of the amplified 800 nm output from the Astrella was used to obtain the probe pulse to generate a white-light continuum (320-700 nm) based on a CaF<sub>2</sub> plate. Before passing through the sample, the probe beam is divided into two beams, one of which passes through the sample and the other one is delivered to the reference spectrometer to monitor the fluctuation of the intensity of the probe beam. Fiber optics was coupled to a multichannel spectrometer with a 1.5 nm intrinsic resolution CMOS sensor. The maximum extent of the temporal delay and instrument response function was 8000 ps and ca. 120 fs, respectively. At each temporal delay, the collected data by the acquisition system were averaged for 2 s. In the present paper,

all samples were excited by a 310 nm pump beam (from TOPAS). Crystal data of **TPENOMe** were collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo-K radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K using the  $\omega$ -scan technique. The structure was solved by direct methods with the SHELXS-97 computer program, and refined by full matrix least-squares methods (SHELXL-97) on  $F^2$ . Images were created by using Mercury program. CCDC number for **TPENOMe-a** and **TPENOMe-b** is 1828118 and 1846931, respectively, and the data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) or at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html). The photos and videos were obtained with a phone of Apple 8 plus. The laser of 450 nm and 532 nm used in Video S1 and Video S2 were commercially purchase (power output 20 mW). White light used in Video S1 was produced by a SHENYU 1005s flashlight (power output 5W).

### **Writing and erasing process**

Firstly, microcrystalline powder of **TPENOMe-a** was laid on glass sheet and appropriate patterns were printed in a non-transparent plastic film separately. Then the patterns printed on the film will be recorded when the UV light penetrates through the film and irradiates **TPENOMe-a**. Finally, the recorded patterns will be erased after white light irradiation.

### **The static encryption-decryption process**

Firstly, sticking **TPENOMe-a**, **TPENOMe-b** and a glass sheet together in particular location using double-faced adhesive tape. Secondly, a mask with specific pattern was laid on the above glass sheet. Finally, conducting the static encryption-decryption process.

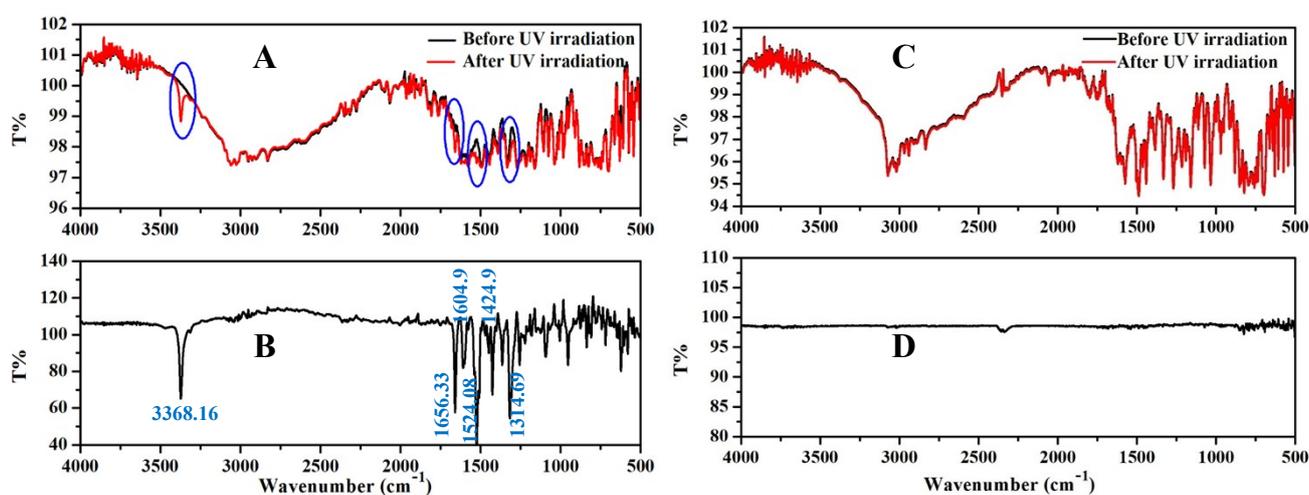
### **The dynamic encryption-decryption process**

Firstly, dividing columniform steel bars into commensurate smaller steel rods. Secondly, gluing **TPENOMe-a** and **TPENOMe-b** to the above steel rods respectively. Thirdly, in a specific numbered

square box, arranging these steel rods in particular orders. Finally, conducting the dynamic encryption-decryption process described in the manuscript.

### Synthesis of TPENOMe

Compound 4-tetraphenylethylenylamine (0.34 g, 1 mmol) and 2-hydroxy-5-methoxybenzaldehyde (0.17 g, 1 mmol) were added to EtOH (30 ml) and the mixture was refluxed for 20 min. The yellow precipitation (0.47 g) was filtered and recrystallized from EtOH. Yield: 97%.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  12.21 (s, 1H), 8.91 (s, 1H), 7.23–7.12 (m, 14H), 7.07–6.99 (m, 8H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz, DMSO)  $\delta$  163.13, 154.80, 152.31, 146.77, 143.62, 143.61, 143.54, 142.44, 140.40, 132.30, 121.34, 121.15, 120.90, 119.73, 119.66, 117.89, 115.63, 55.99, 55.39. Calculated exact mass:  $m/z$  481.204, MALDI TOF-MS:  $m/z$  481.821[M] $^+$ .



**Figure S1** (A) and (C) IR spectra of TPENOMe-a and TPENOMe-b before and after UV irradiation

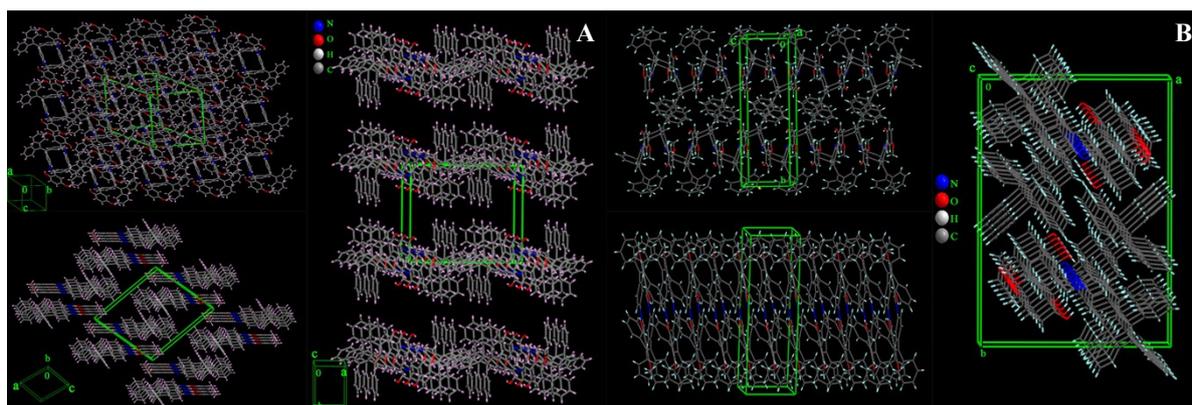
at 365 nm; (B) and (D) IR differential spectra, the data are extracted from(A) and (B).

**Table S1** Crystal data of **TPENOMe-a**.

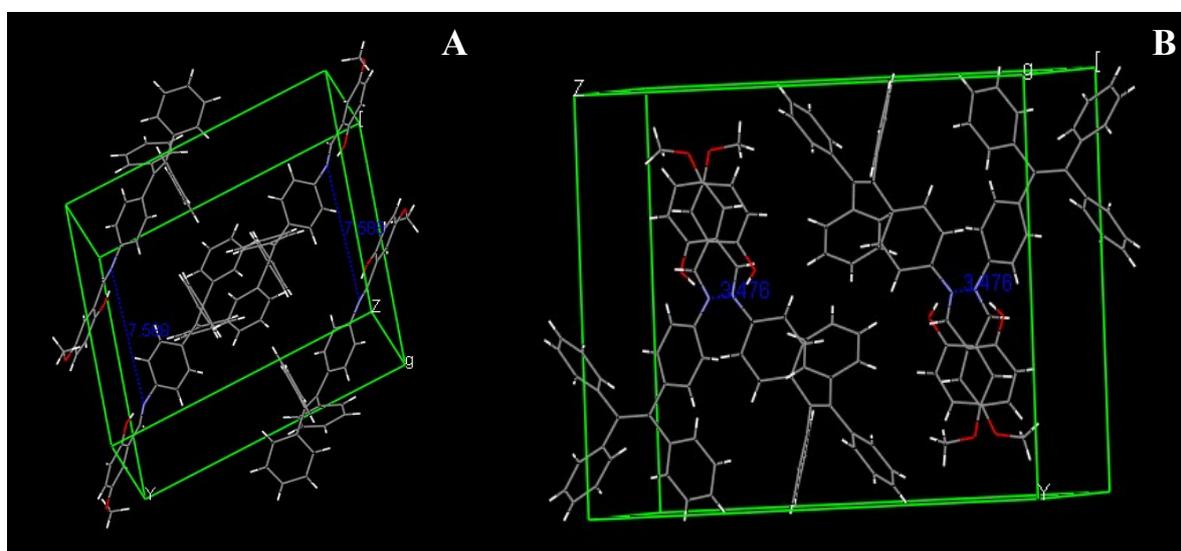
Empirical formula	C <sub>34</sub> H <sub>27</sub> N <sub>1</sub> O <sub>2</sub>	$D_c$ /(g·cm <sup>-3</sup> )	1.278
Formula weight	481.57	<i>Z</i>	4
<i>T</i> /K	293(2)	$\mu$ /mm <sup>-1</sup>	0.079
Crystal system	Monoclinic	<i>F</i> (000)	1016
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	$\theta$ range for data collection/°	2.11-26.00
<i>a</i> /(Å)	15.321(17)	Reflections with <i>I</i> > 2( <i>I</i> )	2423
<i>b</i> /(Å)	12.734(14)	GOF on <i>F</i> <sup>2</sup>	0.938
<i>c</i> /(Å)	13.342(16)	<i>R</i> <sub>1</sub> ( <i>I</i> > 2( <i>I</i> ))	0.0480
$\beta$ /(°)	106.00(2)	<i>wR</i> <sub>2</sub> (all data)	0.1180
<i>V</i> /Å <sup>3</sup>	2502(5)		

**Table S2** Crystal data of **TPENOMe-b**.

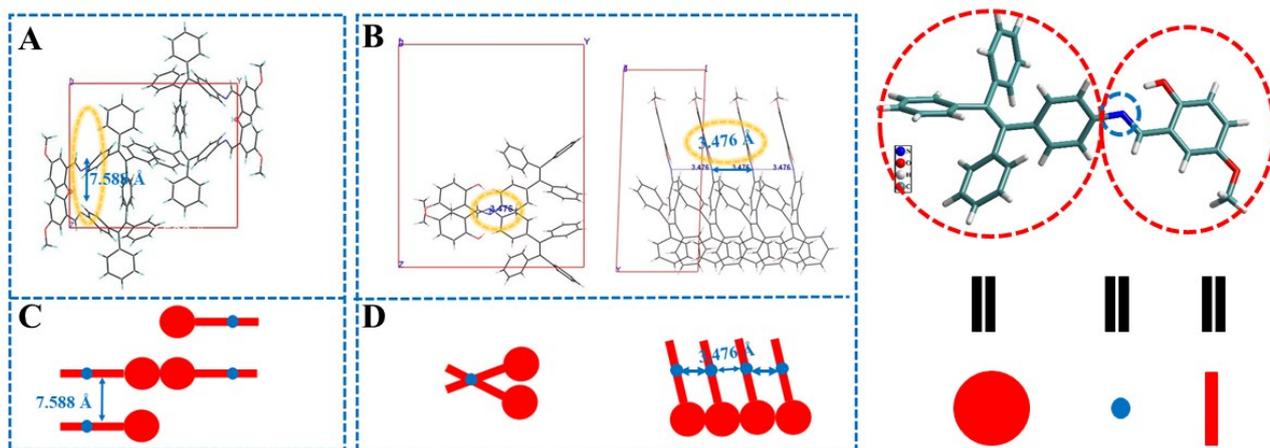
Empirical formula	C <sub>34</sub> H <sub>27</sub> N <sub>1</sub> O <sub>2</sub>	$D_c$ /(g·cm <sup>-3</sup> )	1.240
Formula weight	481.56	<i>Z</i>	4
<i>T</i> /K	293(2)	$\mu$ /mm <sup>-1</sup>	0.076
Crystal system	Monoclinic	<i>F</i> (000)	1016
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	$\theta$ range for data collection/°	3.583-29.533
<i>a</i> /(Å)	17.068(9)	Reflections with <i>I</i> > 2( <i>I</i> )	5020
<i>b</i> /(Å)	22.1154(12)	GOF on <i>F</i> <sup>2</sup>	1.008
<i>c</i> /(Å)	6.8408(4)	<i>R</i> <sub>1</sub> ( <i>I</i> > 2( <i>I</i> ))	0.0500
$\beta$ /(°)	92.044(5)	<i>wR</i> <sub>2</sub> (all data)	0.1231
<i>V</i> /Å <sup>3</sup>	2580.5(2)		



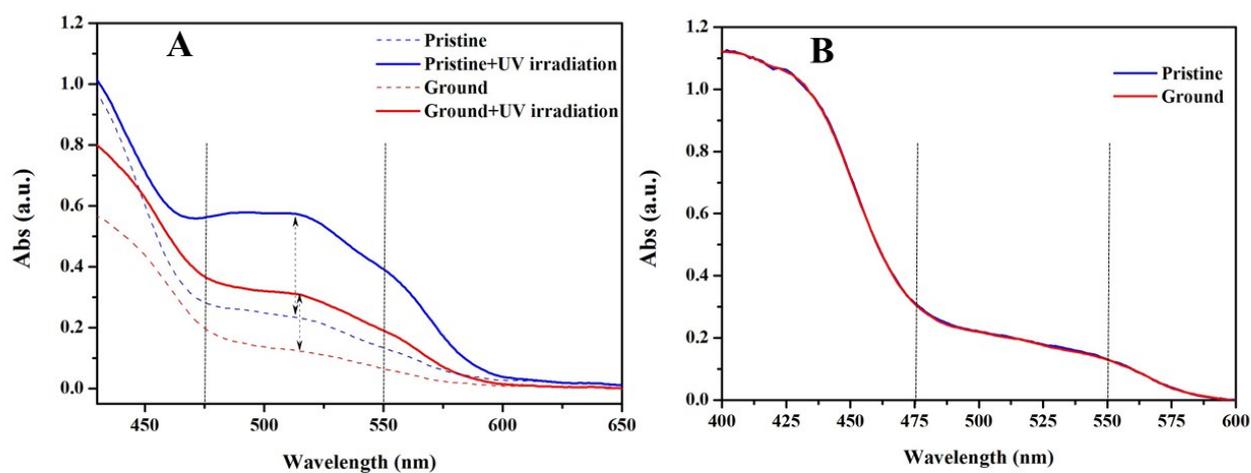
**Figure S2** The 3D packing models of **TPENOMe-a** (A) and **TPENOMe-b** (B).



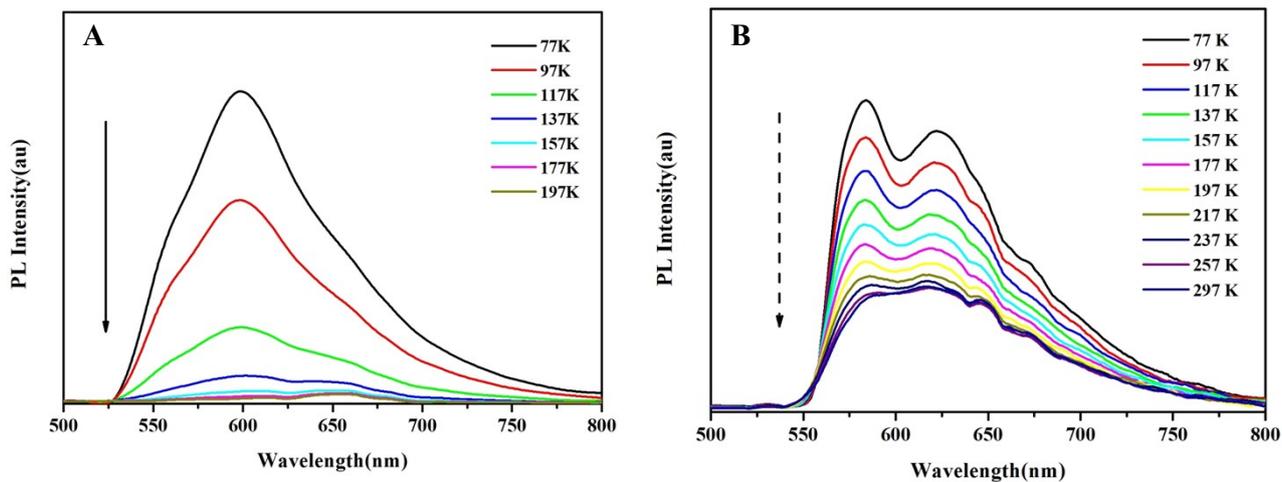
**Figure S3** The distance between adjacent N in **TPENOMe-a** (A) and **TPENOMe-b** (B).



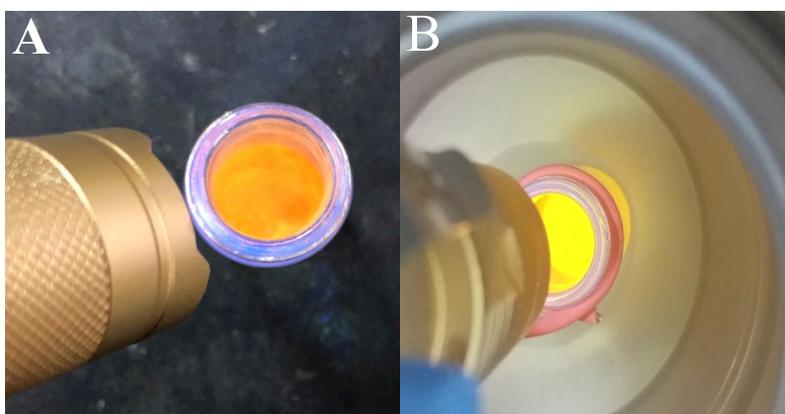
**Figure S4** The packing model around salicylaldimine group in **TPENOMe-a** (A) and **TPENOMe-b** (B), and their schematic diagrams (C) and (D).



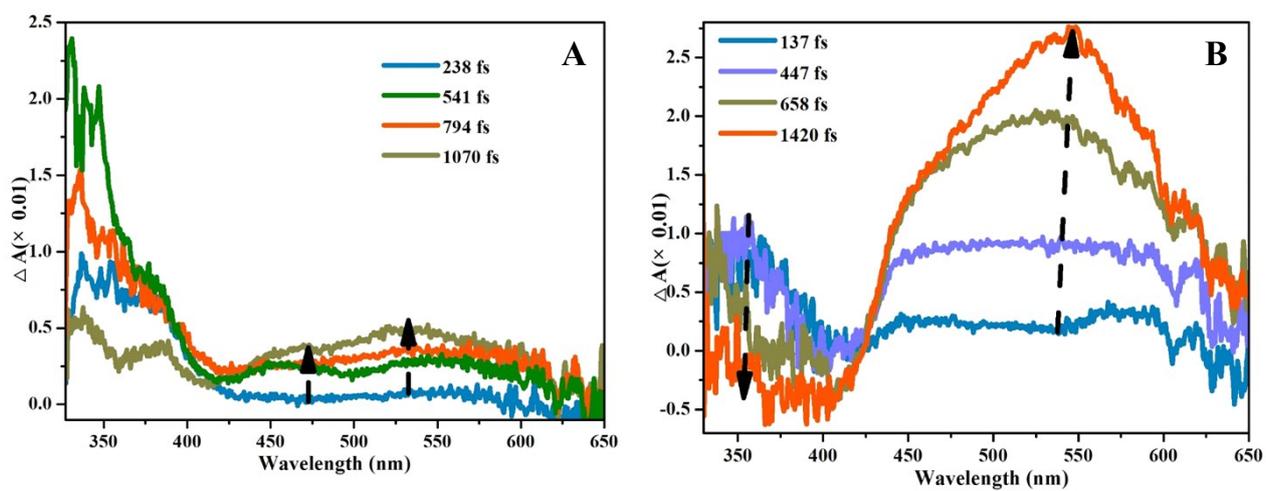
**Figure S5** UV-DRS of **TPENOMe-a** and **TPENOMe-b** before and after grinding, respectively.



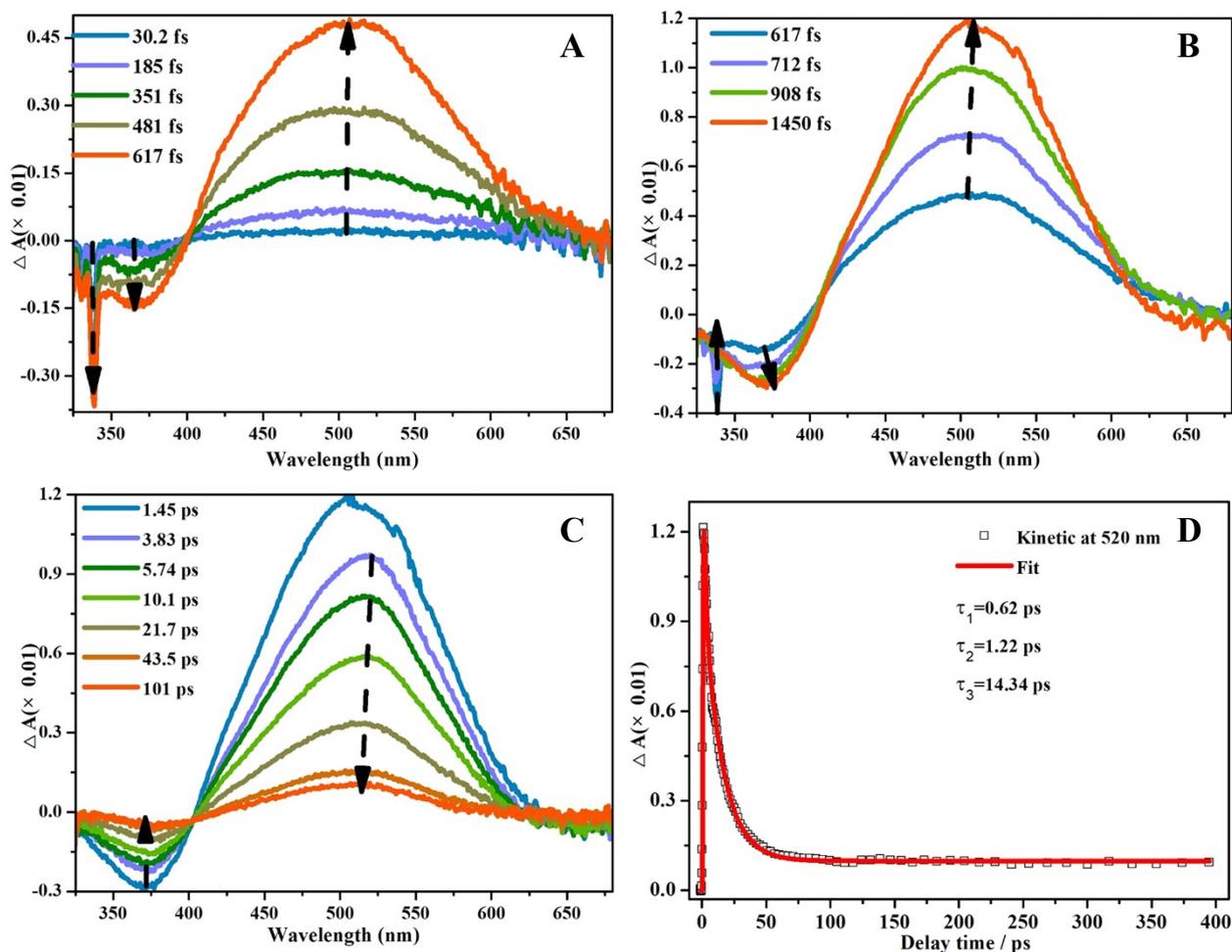
**Figure S6** The fluorescence property of **TPENOMe-a** (A) and **TPENOMe-b** (B) at various temperature.



**Figure S7** The photos of **TPENOMe-a** at 300 K (A) and 77 K (B) under 365 nm UV light.



**Figure S8** Femtosecond transient absorption spectra of **TPENOMe-a** (A) and **TPENOMe-b** (B) at earlier time excited by 310 nm.

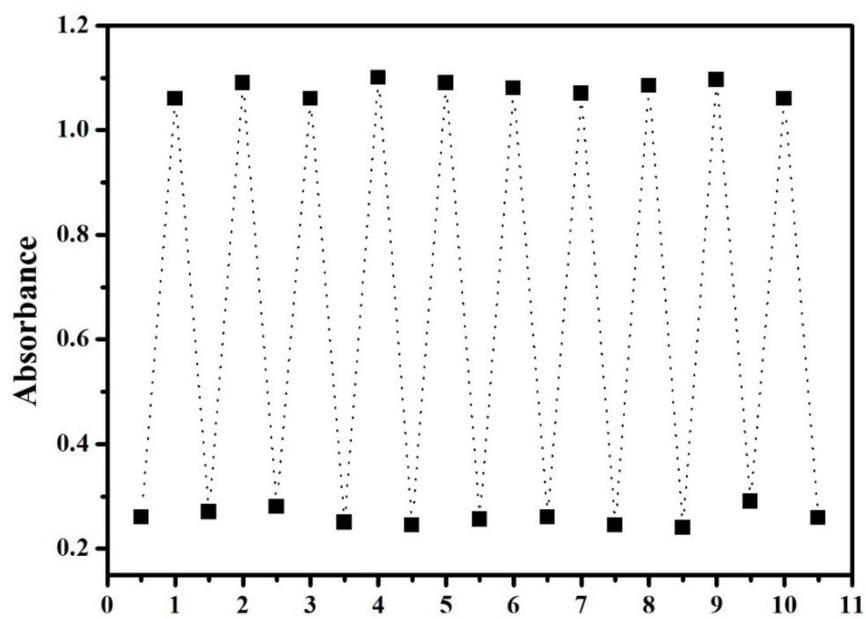


**Figure S9** Femtosecond transient absorption spectra (A, B and C) and the kinetics at 520 nm (D) of TPENOMe in acetonitrile excited by 310 nm.

**Table S3** The influence of different wavelength light on the color change of TPENOMe.

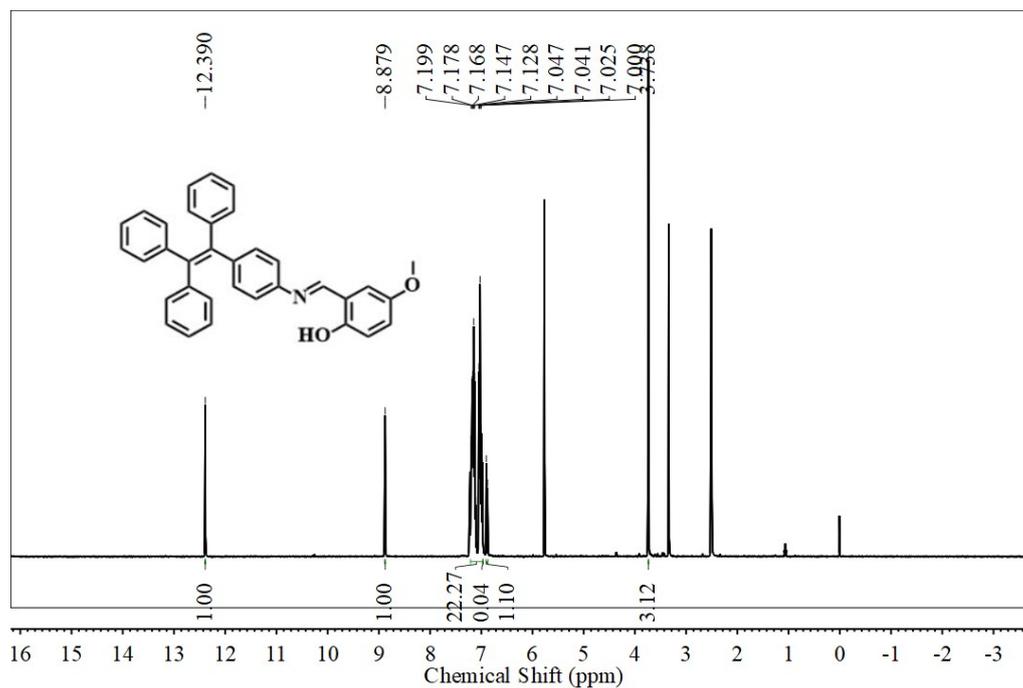
Wavelength/nm	300	330	360	390	420	450	460	490	520	550	570
Color change	Y <sup>a</sup>	Y	Y	Y	Y	Y	N	N	N	N	N
Color recovery	N <sup>b</sup>	N	N	N	N	N	Y	Y	Y	Y	Y

a: Y = Yes; b: N = No

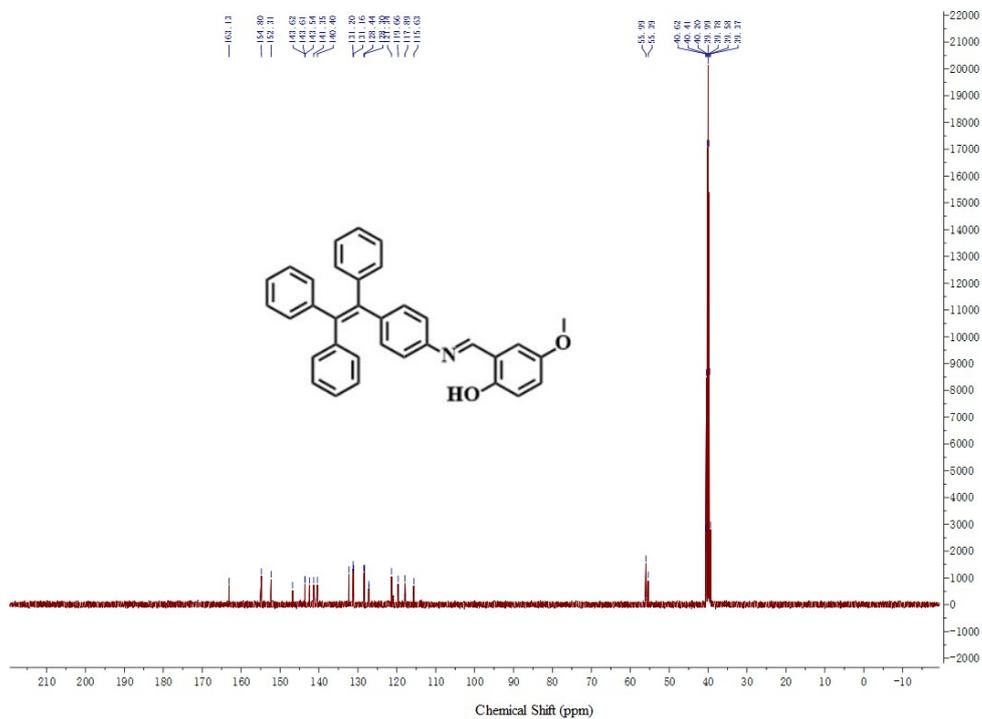


**Figure S10** The fatigue resistance of TPENOMe-a.

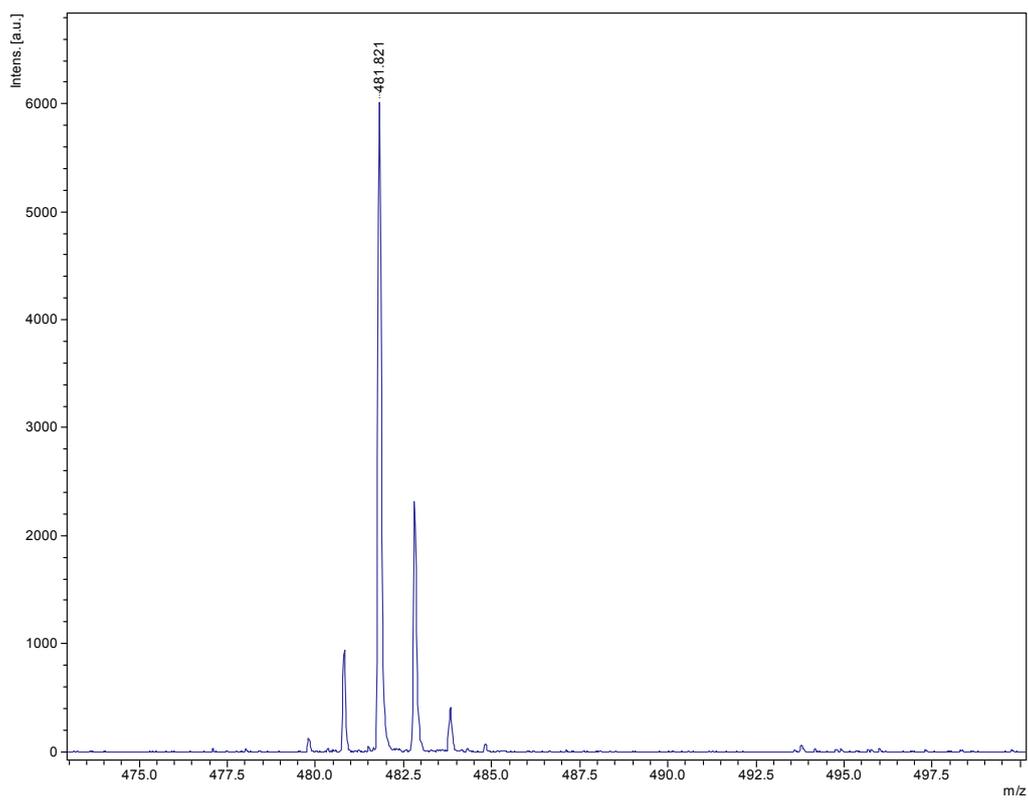
**$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MALDI TOF-MS spectrum of TPENOMe-a.**



**Figure S11**  $^1\text{H}$  NMR spectrum of TPENOMe-a.



**Figure S12**  $^{13}\text{C}$  NMR spectrum of TPENOMe-a.



**Figure S13** MALDI TOF-MS spectrum of **TPENOMe-a**.