

## Supporting information

### **E-Z isomerization of -C=N- bond in anthracene-based acylhydrazone derivatives under visible light**

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## **Experimental section**

### **Characterization**

<sup>1</sup>H NMR spectra were recorded with a Varian Unity 300 spectrometer (300 MHz), using dimethyl sulfoxide-*d* as solvent and tetramethylsilane (TMS) as an internal standard ( $\delta=0.00$ ). Field emission scanning electron microscopy (FE-SEM) images were taken with a JSM-6700F apparatus. Mass spectra were obtained by MALDI-TOF mass spectrometry. X-Ray diffraction was carried out with a Bruker Avance D8 X-ray diffractometer. FT-IR spectra were recorded with a Perkin-Elmer spectrometer (Spectrum One B). The xerogels were obtained by freezing and pumping the organogel of AHP-mB8 for 12 h, and then the xerogels were pressed into a tablet with KBr for FT-IR measurement. A drop of the solution was cast onto KBr to obtain the FT-IR spectrum of the solution developed from the gel under the irradiation of visible-light. Visible lights were generated by a 500 W Xe lamp with a standard band-pass filter (350-575 nm). UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer, and photoluminescence was measured on a Perkin-Elmer LS 55 spectrometer. The single crystal data were collected on a Rigaku R-Axis RAPID IP diffractometer using a graphite monochromator for Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ) at room temperature (293 K) using the  $\omega$ -scan technique. The structures were solved using direct methods and refined using full matrix least-squares techniques using the SHELXTL package. Anisotropic thermal parameters were assigned to all of the non-hydrogen atoms. The hydrogens were included in the structure factor calculation at idealized positions by using a riding model and were refined isotropically.

### **Synthesis**

4-methoxyl phenyl-9-anthracene acylhydrazone (AHP) was synthesised by having 4-methoxylbenzhydrazide reacting with 9-anthraldehyde in ethanol under reflux condition for 4 hours. The crude products were purified by repeated recrystallization from ethanol for further NMR, FT-IR and elemental analysis. FT-IR (KBr, cm<sup>-1</sup>):

3173, 3030, 2837, 1640, 1607, 1541, 1509, 1458, 1409, 1366, 1341, 1289, 1258, 1182, 1074, 837, 727. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>), ppm 11.99 (s, 1H), 9.66 (s, 1H), 8.96-8.55 (m, 3H), 8.30-8.10 (m, 2H), 8.03 (d, *J* = 8.65 Hz, 2H), 7.63 (dtd, *J* = 14.49, 6.37, 0.83 Hz, 4H), 7.13 (d, *J* = 8.66 Hz, 2H), 3.87 (s, 3H). Elemental analysis: calculated for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>, C, 77.95; H, 5.12; N, 7.90, Found: C, 78.15; H, 5.00; N, 7.89. Single-Crystal XRD data of crystal AHP after visible light irradiation: Monoclinic, space group P21, a=4.8916(10) Å, b=16.862(3) Å, c=10.630(2) Å, α=90°, β=95.71(3)°, γ=90°, d=1.349g/cm<sup>3</sup>, V=872.4(3) Å<sup>3</sup>, Z=2, T=293K, total reflections=8550, unique reflections=3959, R(int)=0.0283, GOF=1.032, Final R indices R1=0.0546, wR2=0.0945, R indices (all data) R1=0.0396, wR2=0.0898. Using the same method, compound AHP-mB8 was synthesized and characterized [25]

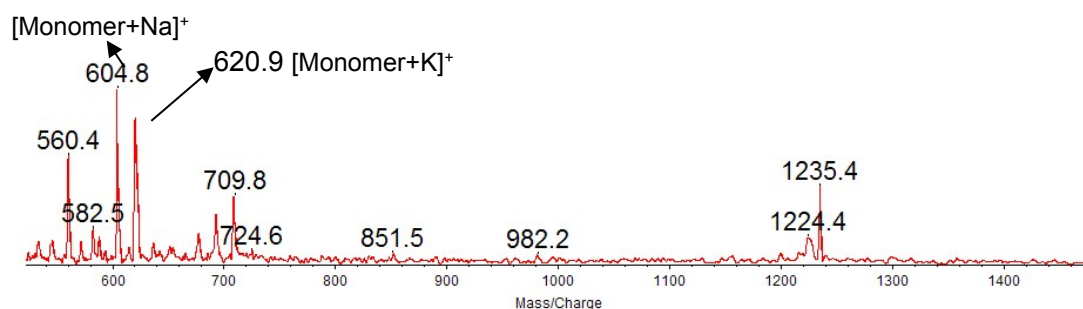
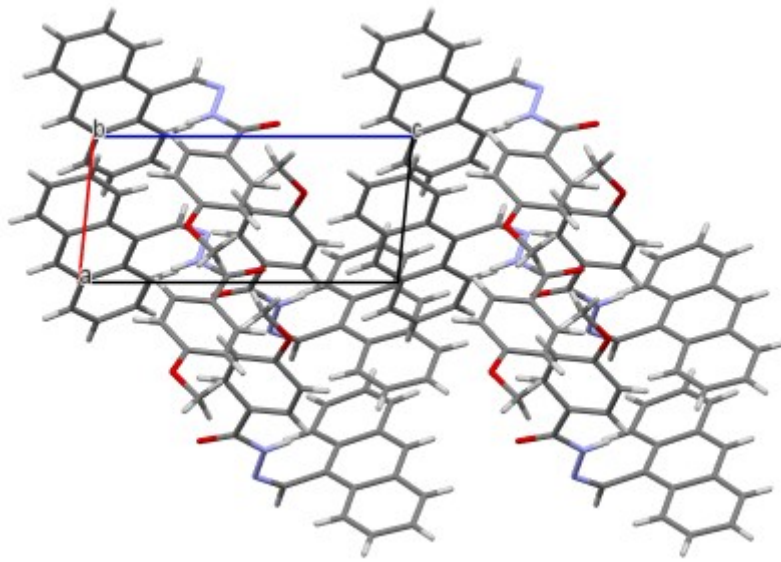
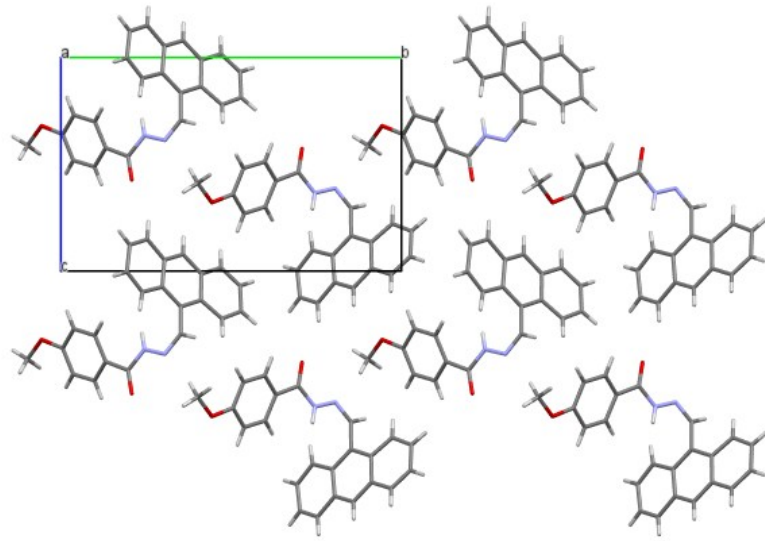


Fig. S1 MALDI-TOF mass spectrum of AHP-mB8 upon irradiation by visible light for 90 min (1mg/mL, using DMF as solvent).

Table S1. The contents of E-isomer and Z-isomer under different condition based on Fig. 2, 3 and 4.

Groups		-NH-	-HC=N-	A	B	-OCH <sub>2</sub> -
Contents of Z-isomer upon visible irradiation for different time	10 s	6.3%	6.1%	3.6%	4.1%	6.3%
	50 s	37.5%	17.4%	42.0%	26.1%	41.2%
	300 s	93.3%	95.3%	97.6%	96.0%	95.8%
Contents of E-isomer upon heated different time at boiling point after visible light irradiation for 300 s	5 min	34.6%	42.6%	36.0%	23.5%	32.9%
	10 min	49.4%	51.4%	64.9%	38.6%	49.6%
	15 min	69.2%	61.2%	70.2%	64.2%	72.0%
	25 min	100%	100%	100%	100%	100%



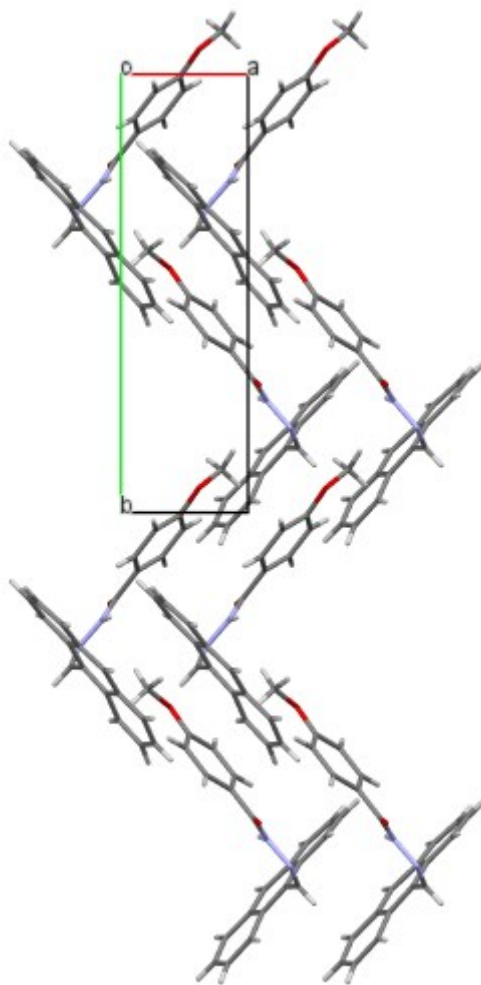


Fig. S2 The crystal packing of AHP after visible light irradiation viewed on the a, b and c axis.

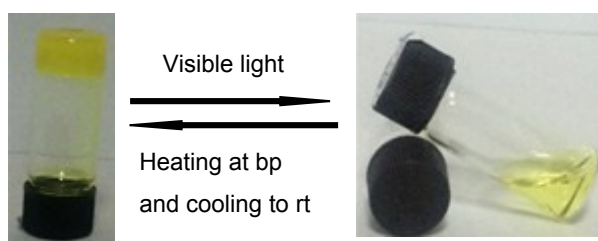


Fig. S3 Photo- and thermo-responsive phase changes of the AHP-mB8 gel from DMSO (bp, boiling point; rt, room temperature)

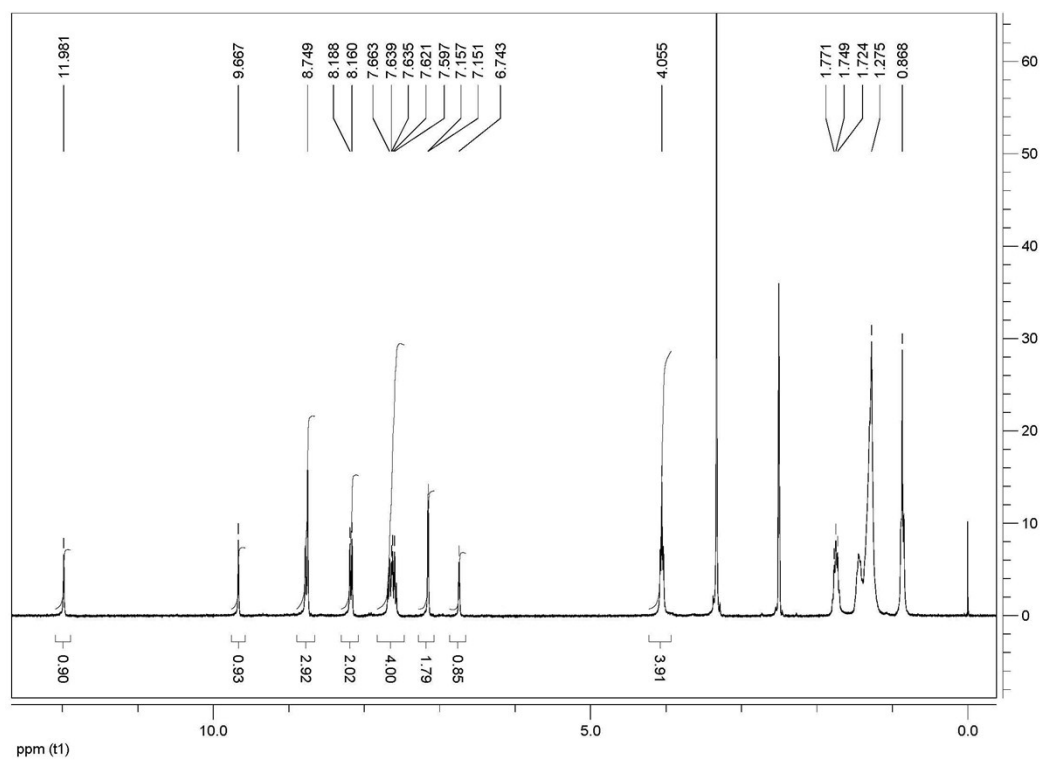


Fig. S4  $^1\text{H}$  NMR spectrum of AHP-mB8 in  $\text{DMSO}-d_6$  before photo-irradiation.

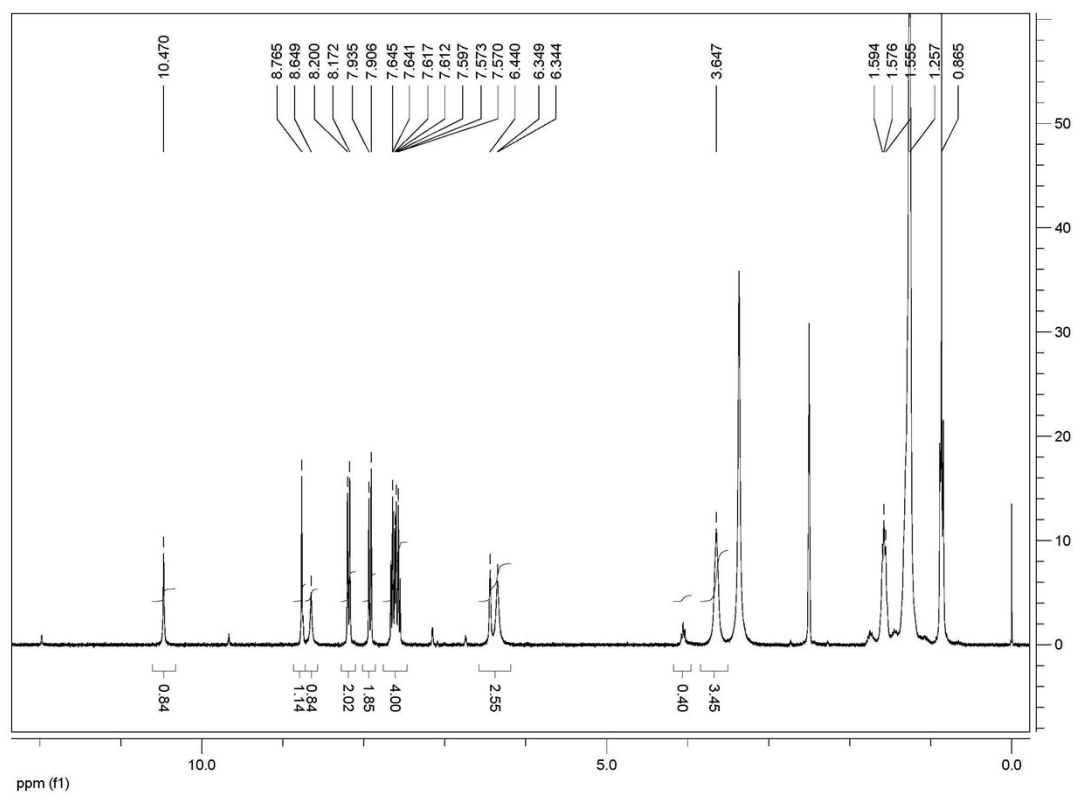


Fig. S5  $^1\text{H}$  NMR spectrum of the sol from AHP-mB8 organogel in  $\text{DMSO}-d_6$  under visible light irradiation for 30 min (5mg/mL).

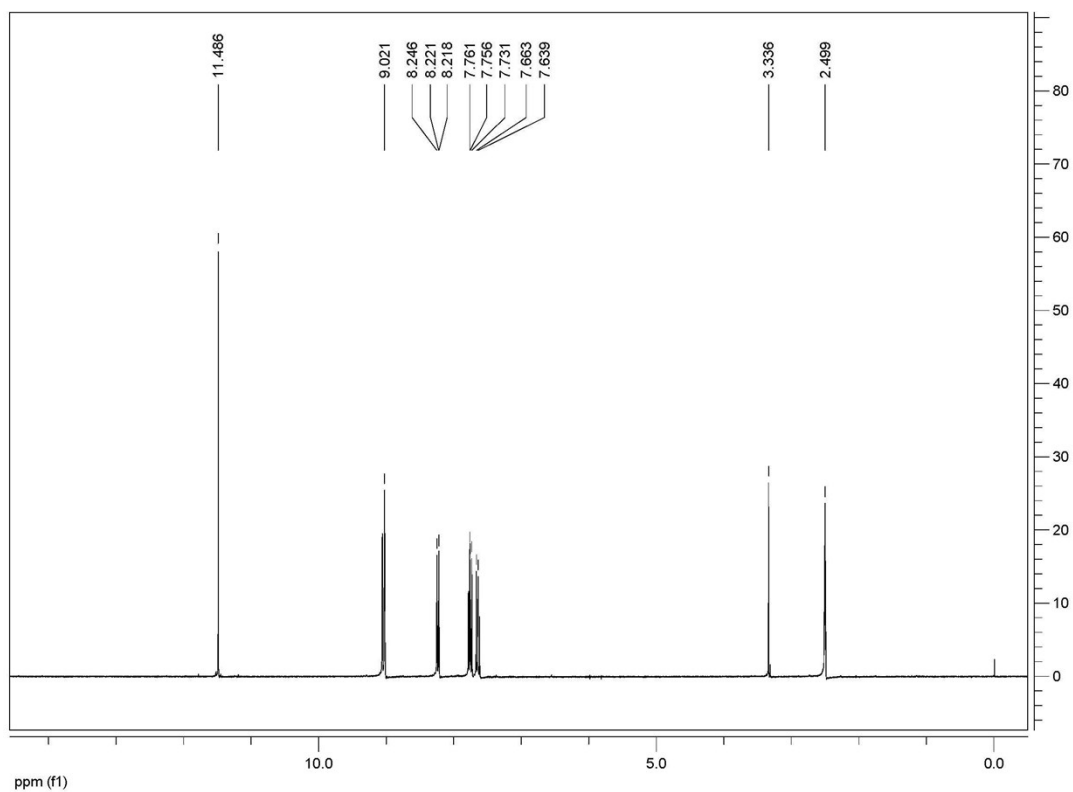


Fig. S6  $^1\text{H}$  NMR spectrum of anthraldehyde in  $\text{DMSO-}d_6$ .

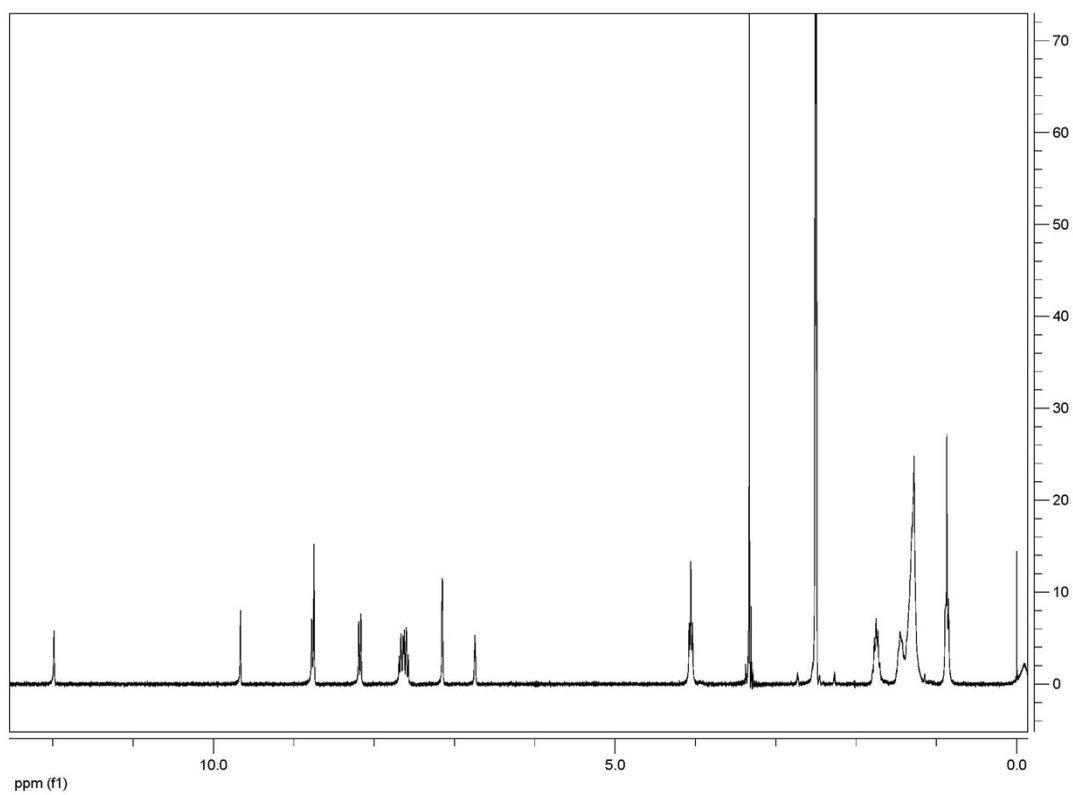


Fig. S7 The  $^1\text{H}$  NMR spectrum of AHP-mB8 in  $\text{DMSO-}d_6$  heated at  $40^\circ\text{C}$  in the dark for 120 min.

The  $^1\text{H}$  NMR chemical shift value of -NH proton of AHP-mB8 before photo-irradiation was at 11.98 ppm [*Org. Biomol. Chem.*, 2012, 10, 6973–6979; *Tetrahedron* 2016, **72**, 3073-3076] (Fig. S4). If it is the hydrolysis of the imine in DMSO induced by photo-irradiation, the -CHO proton of anthraldehyde at 11.49 ppm should be observed (Fig. S6), whereas there only one proton signal at 10.47 ppm (ascribed to -NH proton signal) is observed after photo-irradiation (Fig. S5), which demonstrates that the changes of the  $^1\text{H}$  NMR spectrum after photo-irradiation is not the hydrolysis of the imine in DMSO. In addition, the sample got hot during the irradiation and the temperature was lower than 35°C even after irradiation for 3 hours, while far below the gel-sol transition temperature. And the  $^1\text{H}$  NMR spectrum of AHP-mB8 in DMSO-*d*<sub>6</sub> heated at 40°C in the dark remained unchanged. So it can be confirmed that the changes of the  $^1\text{H}$  NMR spectrum after photo-irradiation was not due to heating by the light source.

So it can be confirmed that the responsive behaviour of AHP-mB8 upon irradiation by visible light was due to the E-Z isomerizations of -C=N- group induced by light, rather than the hydrolysis of the imine or thermal effect.



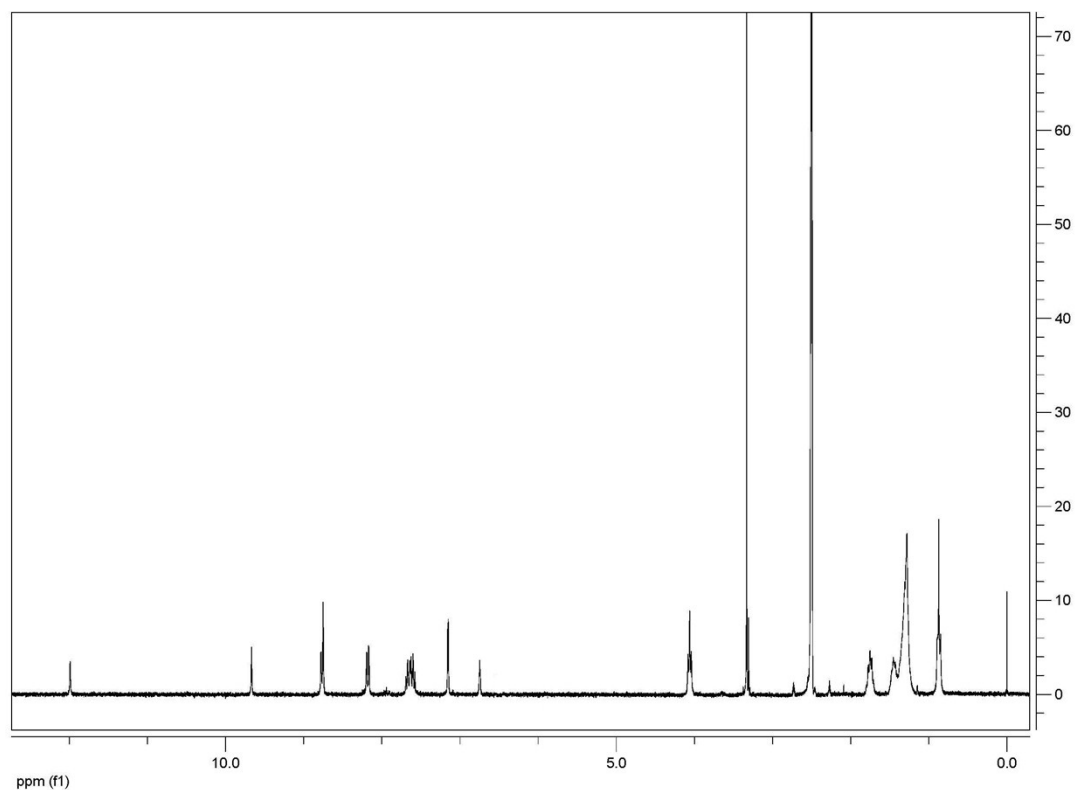


Fig. S8 The  $^1\text{H}$  NMR spectrum of AHP-mB8 in  $\text{DMSO-}d_6$  heated for 40 min at  $150^\circ\text{C}$  after visible light irradiation for 10 min.

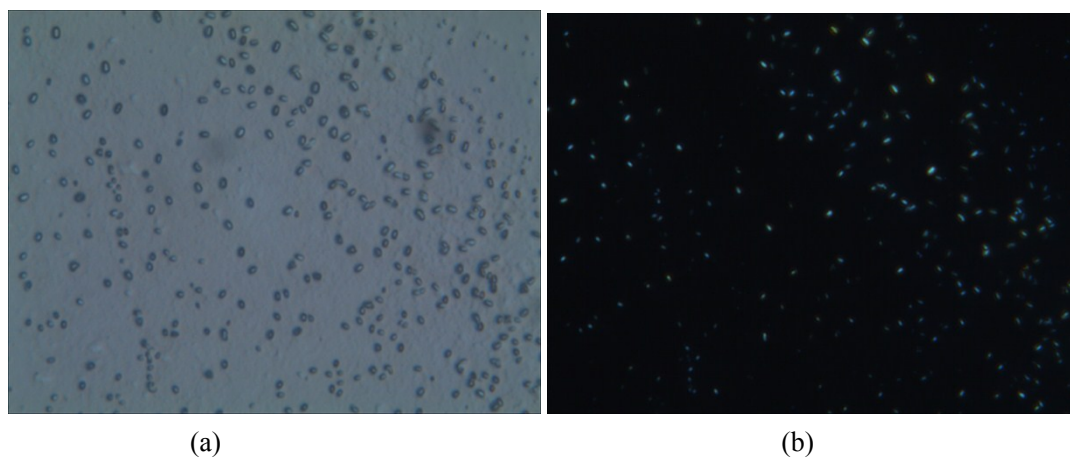


Fig. S9 (a) Optical micrographs of the AHP-mB8 gel from cyclohexane upon irradiation by visible light at 60 min ( $\times 400$ ), (b) polarized optical micrographs of (a).

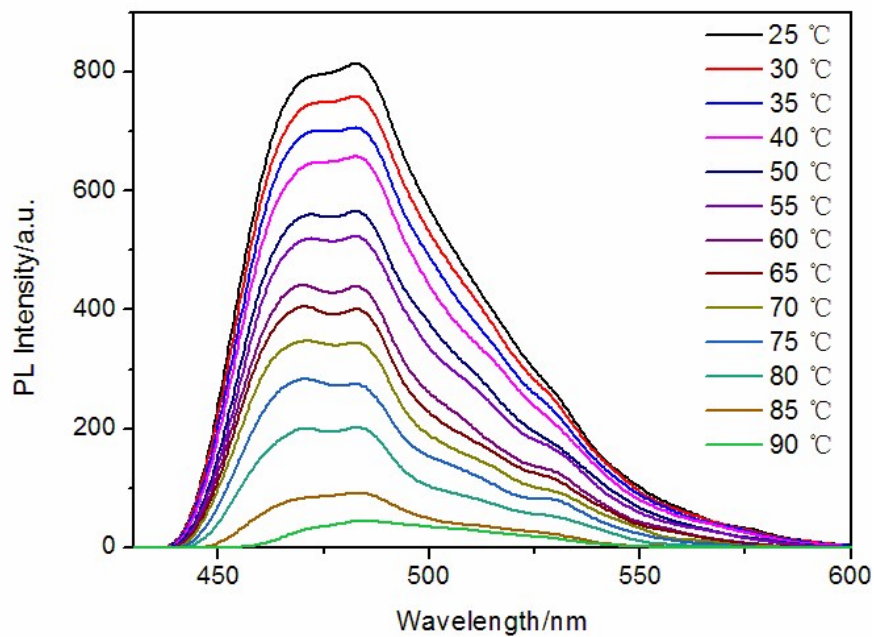


Fig. S10 The temperature-dependence of the fluorescence emission of AHP-mB8 gel (1.5 mg/mL) from cyclohexane.

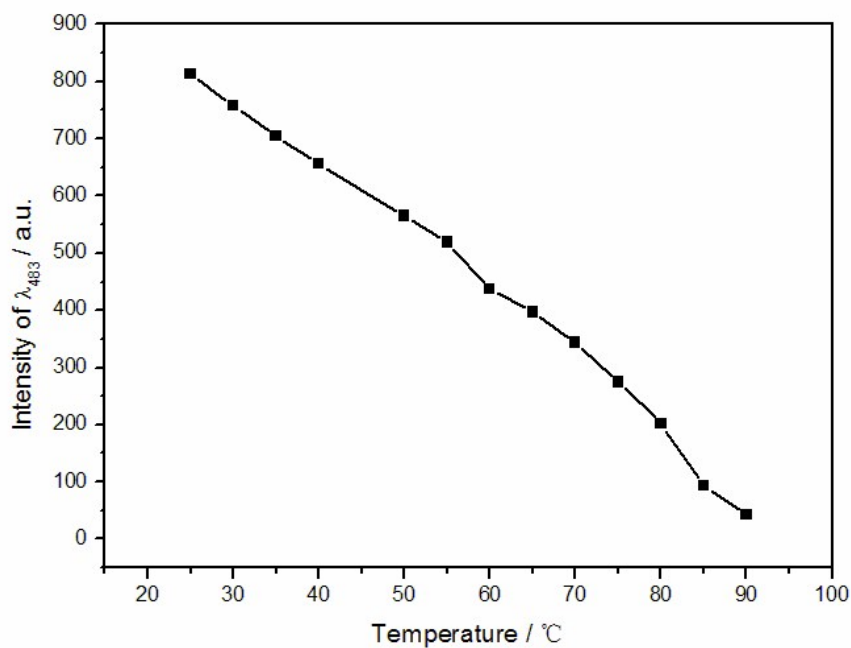


Fig. S11 The variation of the fluorescence intensity ( $\lambda=483$  nm) with temperature based on Fig. S10.

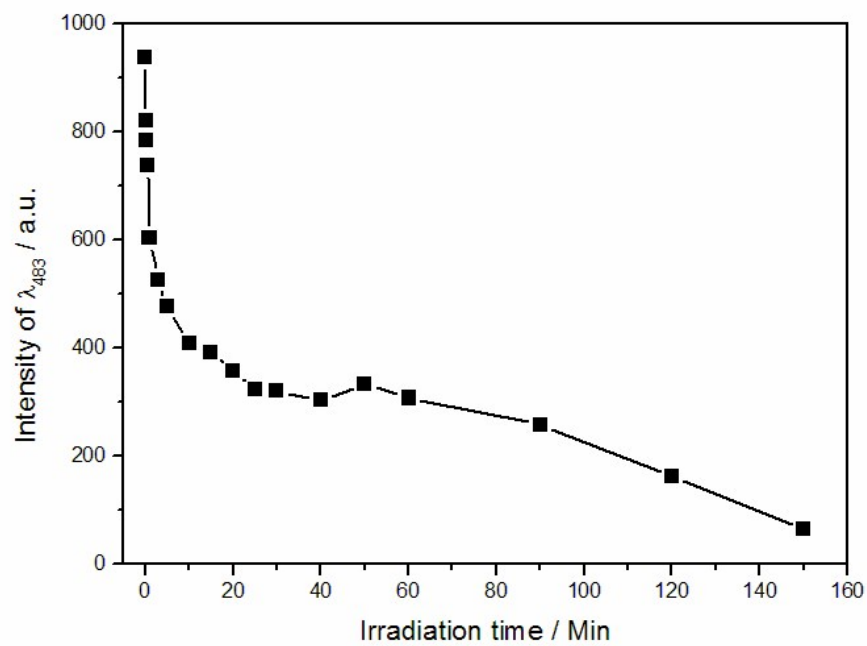


Fig. S12 The variation of the fluorescence intensity ( $\lambda=483$  nm) with visible light irradiation time based on Fig. 8.