

Supporting Information

## **Photothermal Effect of Azopyridine Compounds and Their Applications**

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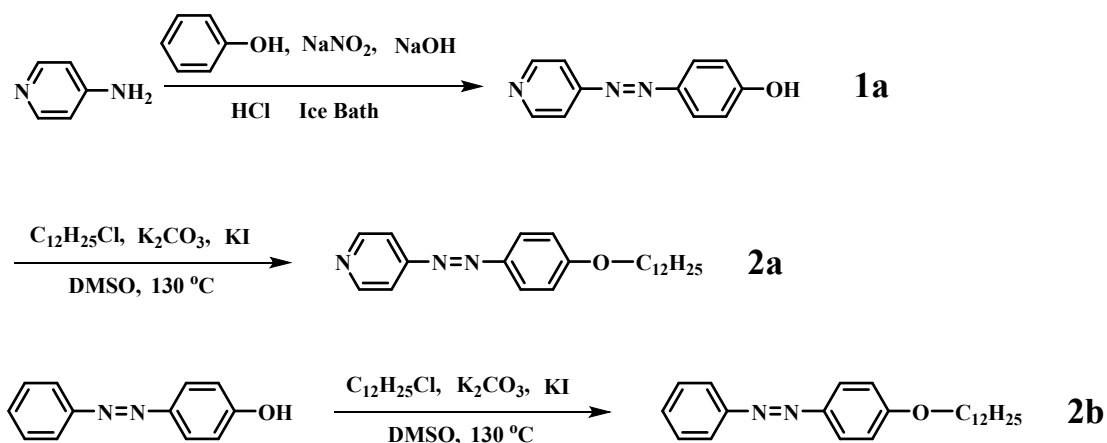
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### **1. Synthesis of compounds**

The azobenzene and azopyridine compounds were synthesized through two steps of chemical reactions, as shown in Scheme S1.



**Scheme S1.** Synthesis of the azobenzene and azopyridine compounds.

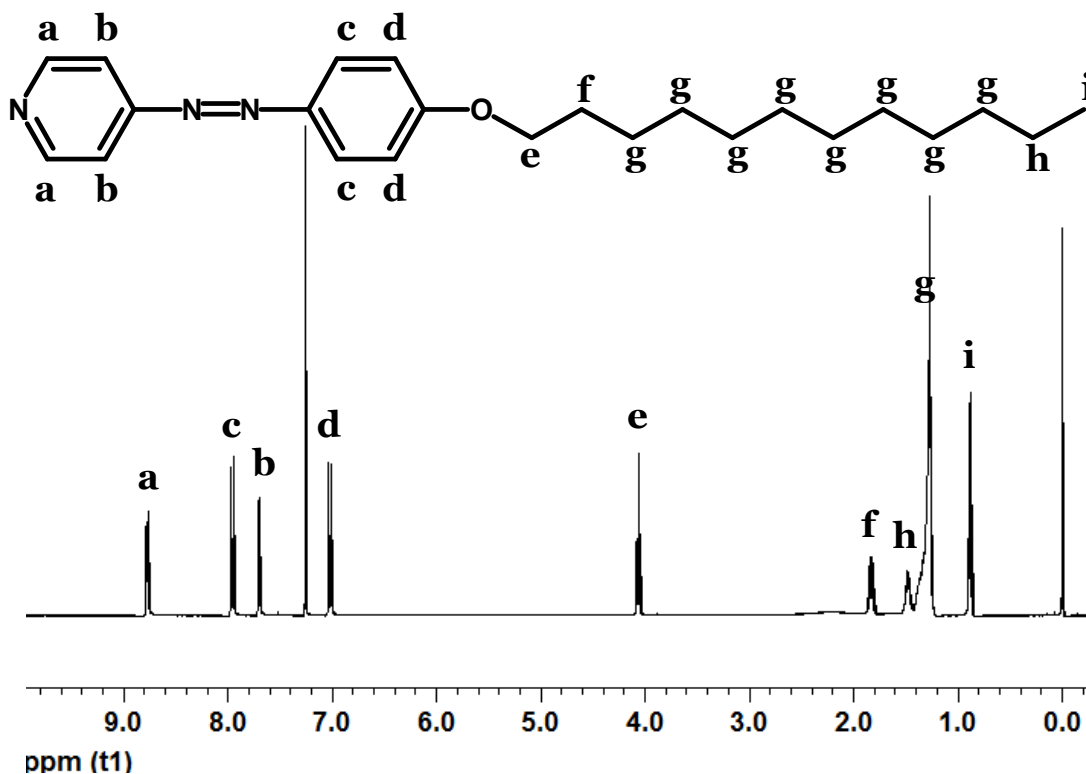
### 1.1 Synthesis of 4-(4-hydroxyphenylazo) pyridine (compound 1a)

A 10 wt% NaOH aqueous solution (20 mL) containing sodium nitrate (4.00 g, 58 mmol) and phenol (5.00 g, 53 mmol) was prepared and cooled to 0 °C. Subsequently, it was added dropwise to another aqueous solution with hydrochloric acid 45 mL (25 mL 11N hydrochloric acid and 20 mL water) and 4-aminopyridine (6.00 g, 64 mmol). The reaction mixture was stirred under an ice bath (0 °C) for 0.5 h. Then, the pH of the reaction mixture was adjusted to pH=6-7 by addition of a 10 wt% NaOH aqueous solution. A yellow precipitate was collected by filtration. The crude product was washed with water and recrystallized from acetone. After drying over a vacuum for 24 hours, the resulting bright yellow solid was obtained: yield 2.96 g (32.6 %).

### 1.2 Synthesis of 4-(4-dodecylphenylazo)pyridine (compound 2a)

1-Chlorododecane (2.05 g, 10 mmol) was dissolved in dimethyl sulfoxide (20 mL), which was added dropwise to a DMSO (20 mL) solution of K<sub>2</sub>CO<sub>3</sub> (6.90 g, 5 mmol), KI (0.01g, 0.1mmol) and 4-(4-hydroxyphenylazo)pyridine (2.00 g, 10 mmol) at 130 °C. After 5 hours, the mixture was poured into water (200 mL) and then extracted with ethyl acetate (50 mL × 3). A rotary evaporator was used to remove all of the solvent. The crude product was purified by silica gel column chromatography

with ethyl acetate as eluent; 2.24 g of the pure product was obtained as an orange powder. The NMR spectrum of compound **2a** was recorded in 5 wt% CDCl<sub>3</sub> solution, as shown in Figure 1. Yield: 61 %. Mp: 74.2 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.77 (2H, d, Ar-H), δ 7.95 (2H, d, Ar-H), δ 7.71 (2H, d, Ar-H), δ 7.03 (2H, d, Ar-H), δ 4.06 (2H, t, -O-CH<sub>2</sub>-), δ 1.85 (2H, m, -CH<sub>2</sub>-), δ 1.46 (2H, m, -CH<sub>2</sub>-), δ 1.27 (16H, m, -C<sub>8</sub>H<sub>16</sub>-), δ 0.90 (3H, t, -CH<sub>3</sub>).

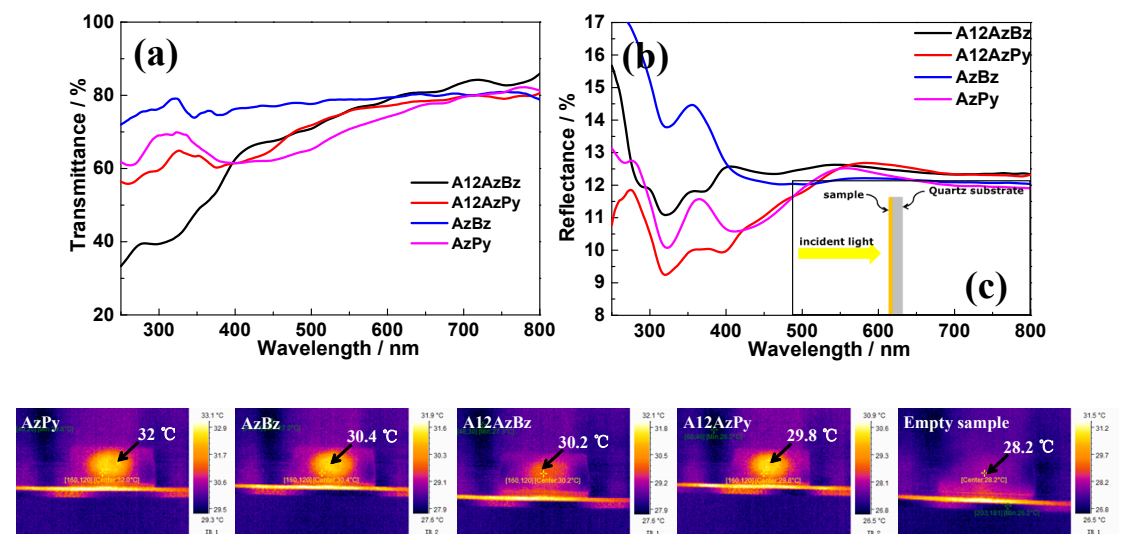


**Figure S1.** <sup>1</sup>H NMR spectrum of the A12AzPy (compound **2a**).

### 1.3 Synthesis of compound **2b**

The same procedure as described was used for compound **2b** using 4-(phenylazo)phenol replaced the 4-(4-hydroxyphenylazo)pyridine, respectively and got orange solid.

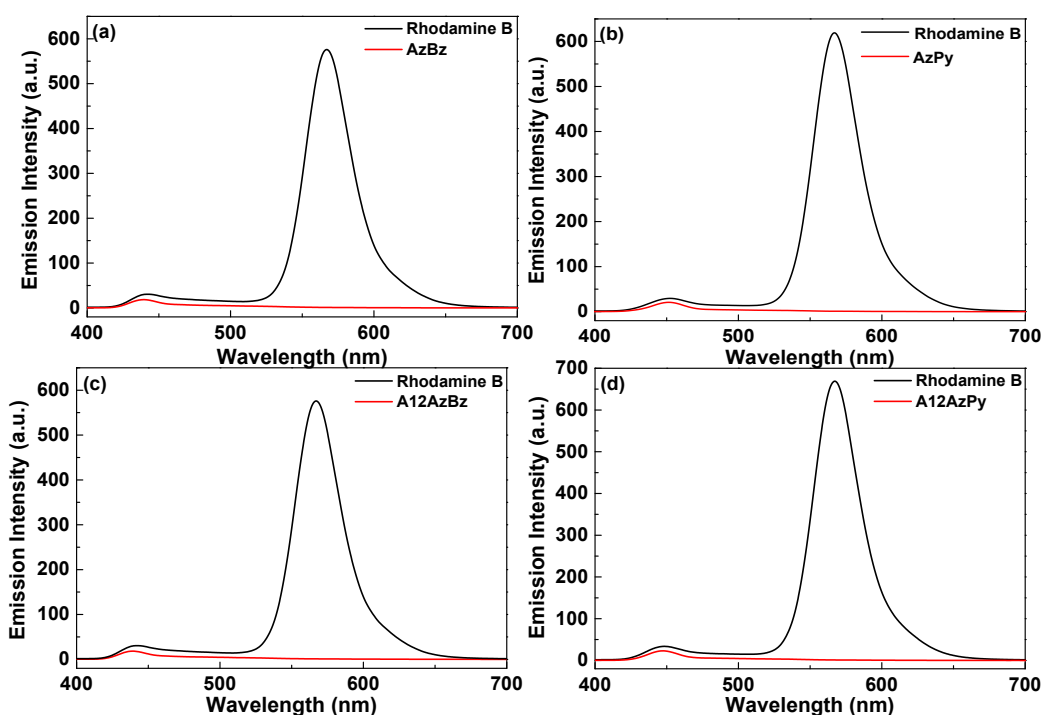
## 2. Reflectance and transmittance spectra



**Figure S2.** Transmittance (a) and reflectance (b) spectra of the azobenzene compounds (AzBz and A12AzBz) and azopyridine derivatives (AzPy and A12AzPy) in film states. The incident light came from the sample film to the quartz substrate as shown in the inset picture (c). The Infrared images at the irradiated spot were captured.

From the Figure S2, the transmittance of the AzBz, A12AzBz, AzPy and A12AzPy are 75.0 %, 39.7 %, 76.5 % and 61.4 %, respectively, which is corresponding to their absorption peak. According to the formula:  $A = \log(1/T)$ , neglecting reflection at the sample surface. The absorptivity of the AzBz, AzPy, A12AzBz and A12AzPy are 12.5 %, 11.6 %, 40.1 % and 21.1 %, respectively. The temperature at the irradiated spot on AzPy, AzBz, A12AzPy, A12AzBz films and the empty sample are 32.0 °C, 30.4 °C, 30.2 °C, 29.8 °C, and 28.2 °C, respectively.

## 3. Fluorescence quantum yield measurements



**Figure S3.** Fluorescence emission spectra of AzBz (a), AzPy (b), A12AzBz (c) and A12AzPy (d). And their excitation at 387, 401, 388 and 398nm, respectively.

**Table S1.** Measured fluorescence quantum yield ( $\Phi_f$ ).

Compounds	AzBz	AzPy	A12AzBz	A12AzPy	Rhodamine B
$\Phi_f$	0.031	0.032	0.030	0.033	0.900

Fluorescence quantum yield measurements, using Rhodamine B as reference ( $\Phi_f=0.9$ ) in ethanol, were performed at room temperature for a THF solution with azobenzene and azopyridine compounds. The measured fluorescence quantum yield ( $\Phi_f$ ) are shown in Table S1.

#### 4. Mechanical testing

To determine the mechanical force produced by the photocontrollable adhesive of A12AzPy sample, tensile tests were examined. A summary of all the tensile test results is given in Table S2. Figure S4 shows the stress-strain curves of A12AzPy for

five times.

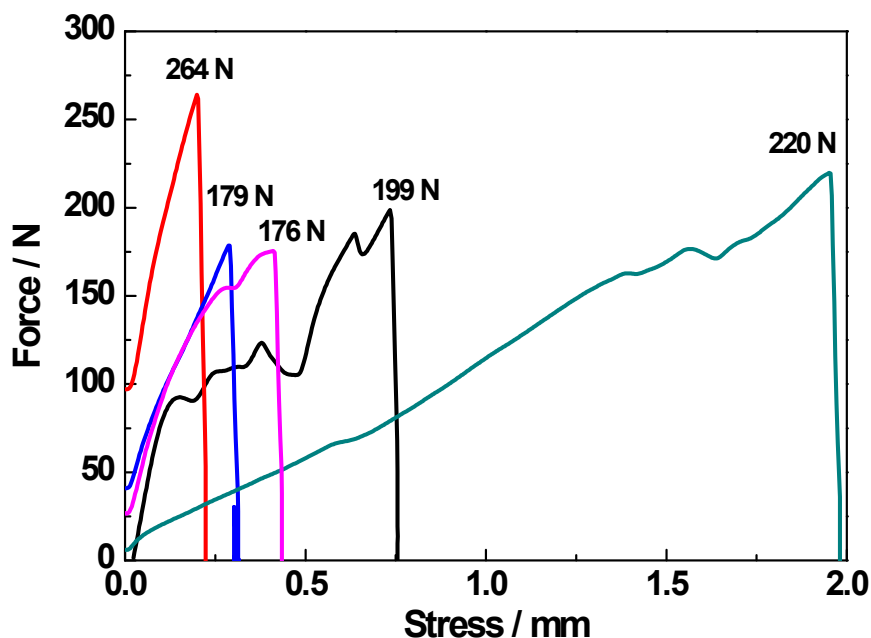


Figure S4. Mechanical properties of A12AzPy.

Table S2. Measured tensile force and stress of A12AzPy.

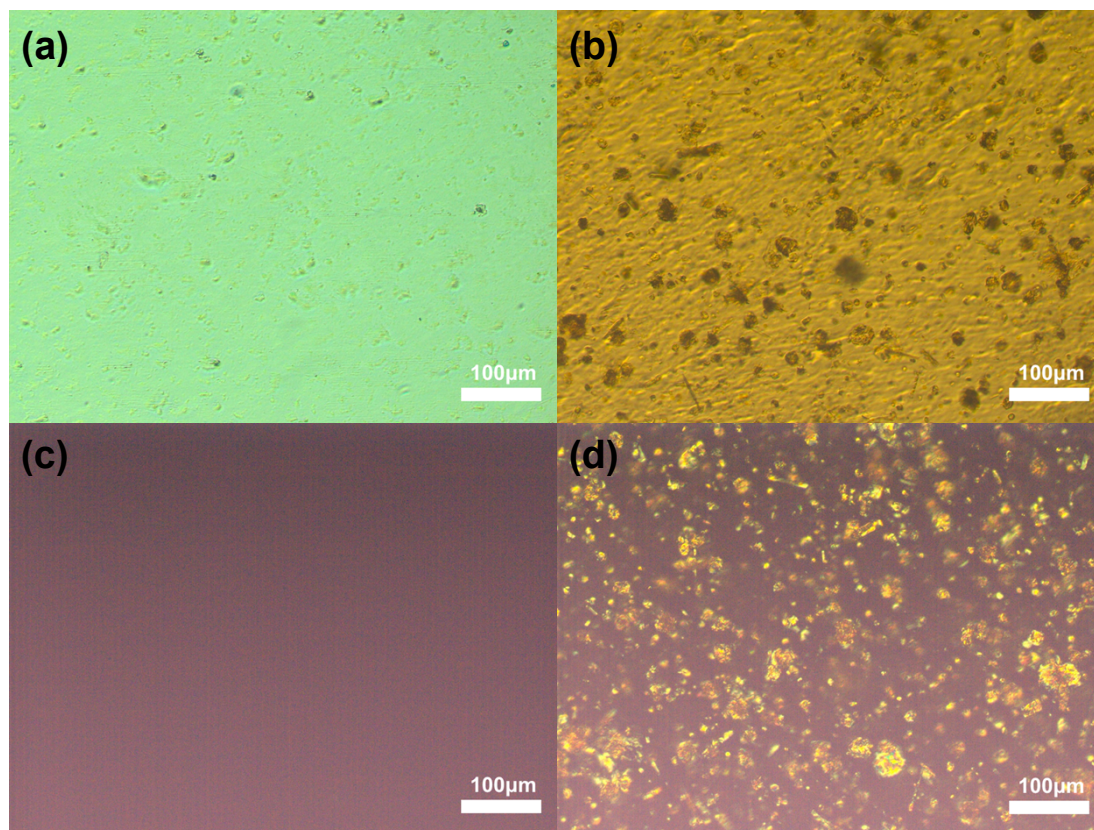
Force / N	264	179	176	199	220
Stress / mm	0.22	0.31	0.44	0.75	1.98

## 5. Fabrication of the A12AzPy/PVA bilayer

The PVA substrate layer was obtained by dissolving 10 g PVA in 90 g water. The A12AzPy/PVA solution was obtained by dissolving 0.3 wt% A12AzPy in the PVA solution. First the PVA solution was cast onto a glass substrate. After evaporation the water, casting the A12AzPy/PVA solution on the first layer. So far the A12AzPy/PVA bilayer was obtained by peeling off from the substrate. Film thick was measured using a micrometer. Typical thickness of the A12AzPy/PVA bilayer was approximately 150  $\mu\text{m}$ .

The distribution of A12AzPy in PVA is shown in Figure S5. Figure S5a & 5b are the top view optical photograph images of PVA film and A12AzPy/PVA bilayer,

respectively. The pure PVA film was transparent, but yellow can be observed in the A12AzPy/PVA bilayer because of the existence of chromophores. In the POM pictures (Figure S5c & 5d), the dispersion of crystallized A12AzPy can be clearly obtained because PVA is isotropy.



**Figure S5.** The distribution of A12AzPy in PVA. The top view optical photograph images of PVA film (a) and A12AzPy/PVA bilayer (b). The polarizing optical micrograph (POM) picture of PVA film (c) and A12AzPy/PVA bilayer (d).

Supporting **Video S1.** Multiple cycles of A12AzPy as intelligent stickup adhesive.

Supporting **Video S2.** Bending movement of A12AzPy/PVA bilayer film upon UV irradiation.