

## Supporting Information

### Photocatalytic copper-catalyzed azide–alkyne cycloaddition (CuAAC) click reaction with Cu(II) coordination polymer

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## Section 1 X-ray crystallography

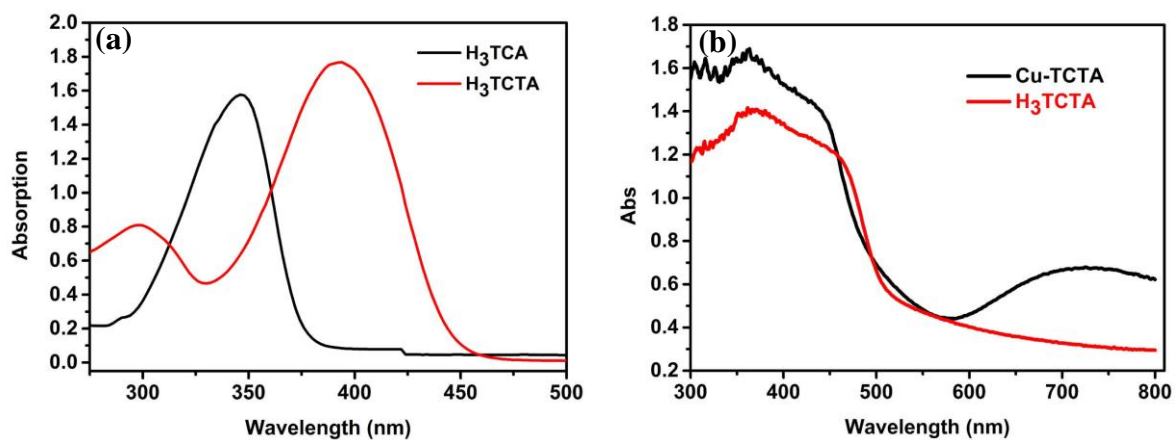
The crystallographic data of Cu-TCTA were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å) using the SMART and SAINT programs.<sup>S2,S2</sup> Routine Lorentz polarization and multi-scan absorption correction were applied to the intensity data. Their structures were determined, and the heavy atoms were identified by direct methods using the SHELXTL-97 program package.<sup>S3</sup> The remaining atoms were found from successive full-matrix least-squares refinements on  $F^2$  and Fourier syntheses. Except for the disordered carbon and oxygen atoms, the non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. In the refinement of the crystal data of Cu-TCTA, the solvent DMF molecule was disordered into two parts. Several constraints, including fixing the bond distances of these disordered atoms, were used. The crystallographic data are summarized in Table S1.

**Table S1** Crystallographic and structural refinement data.

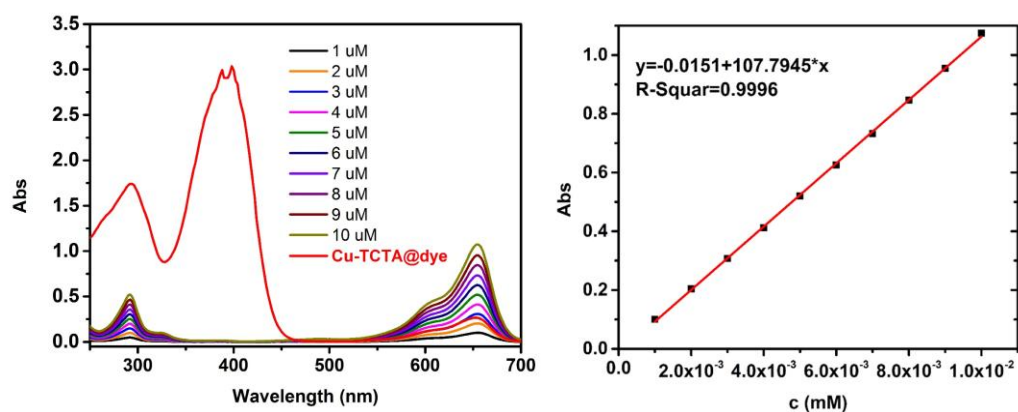
<b>Cu-TCTA</b>	
Empirical formula	C <sub>39</sub> H <sub>32</sub> CuN <sub>3</sub> O <sub>8</sub> S <sub>3</sub>
M, g mol <sup>-1</sup>	830.39
Crystal system	Monoclinic
space group	P2(1)/c
a, Å	16.213(13)
b, Å	19.359(14)
c, Å	12.323(9)
$\alpha = \gamma$ , °	90
$\beta$ , °	90.991(12)
V, Å <sup>3</sup>	3867(5)
Z	4
dcalcd, g cm <sup>-3</sup>	1.426
T, K	273(2)
Reflections collected	20944
Independent reflections	6803
$\mu$ (Mo-K $\alpha$ ), mm <sup>-1</sup>	0.782
GOOF	0.985
F(000)	1712
Fincal R Indices	$R_I^a = 0.0802$
(I > 2 $\sigma$ (I))	$wR_2^b = 0.1872$
R Indices (all data)	$R_I^a = 0.2434$
	$wR_2^b = 0.2835$
diff peak and hole, eÅ <sup>-3</sup>	0.807 and -0.262

$$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|; \quad ^bR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$$

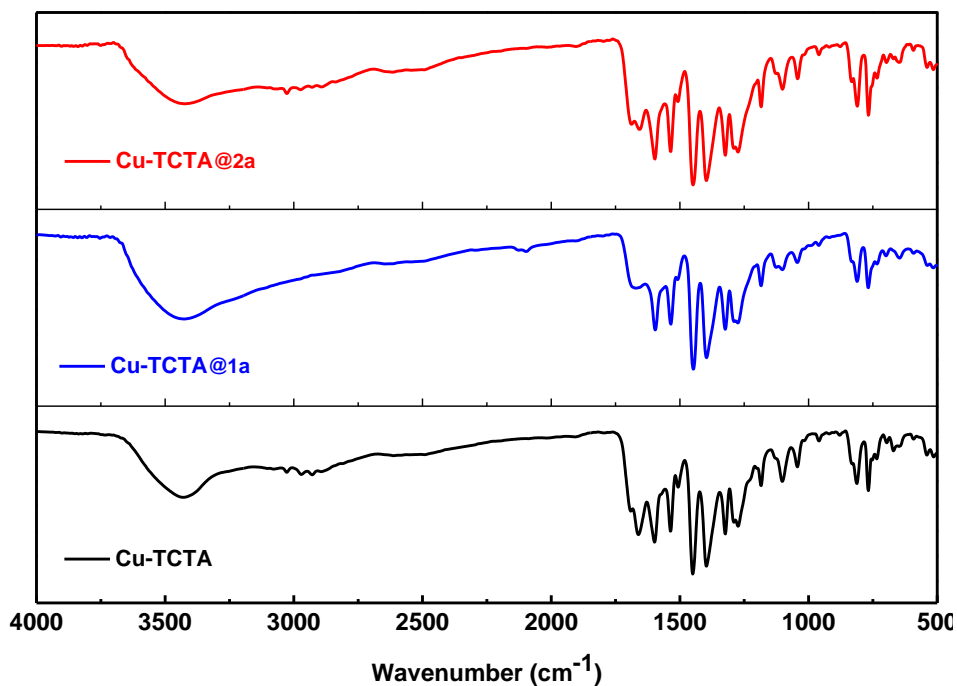
## Section 2 Characterizations of catalysts



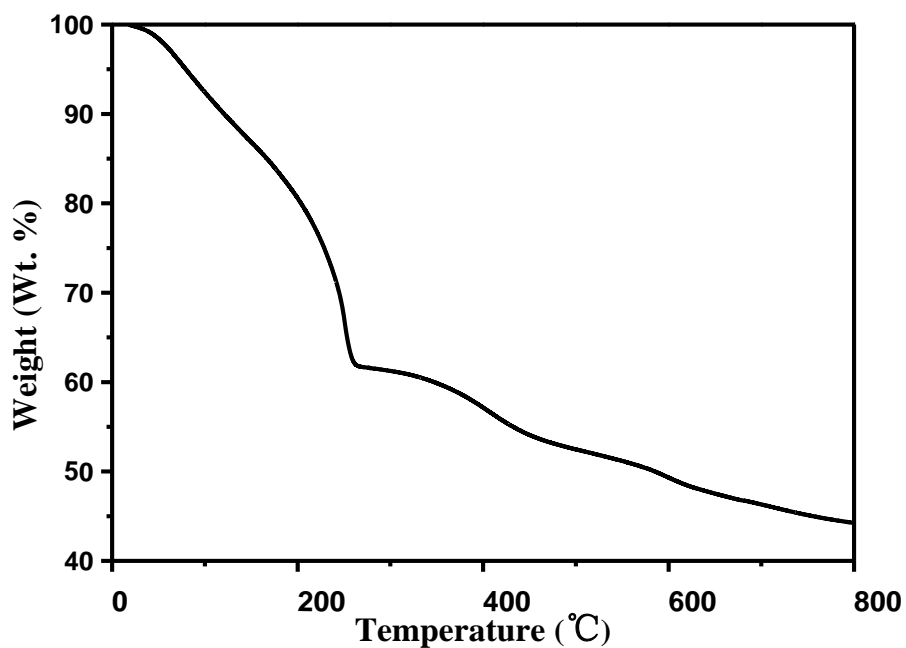
**Fig. S1** (a) The UV-vis absorption of H<sub>3</sub>TCA and H<sub>3</sub>TCTA in N,N-dimethyl formamide (DMF). (b) Solid-state UV-vis absorption spectra of H<sub>3</sub>TCTA and Cu-TCTA.



**Fig. S2** (a) Left: UV-vis measurements of methylene blue dye released from Cu-TCTA (red curve) and UV-vis spectra of different concentrations of methylene dye. Right: The standard linear relationship between the absorption and concentration.



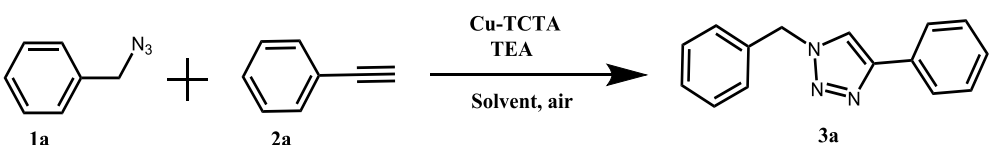
**Fig. S3** Comparison of the IR spectra of Cu-TCTA, Cu-TCTA@1a and Cu-TCTA@2a.



**Fig. S4** TGA plot of as-synthesized Cu-TCTA, exhibiting two steps of weight loss processes and indicating that the framework was stable up to ~200 °C. The initial weight loss can be attributed to the weight loss of solvents (ethanol and DMF) in the pore of framework. The second weight loss is assigned to the decomposition of ligand H<sub>3</sub>TCTA.

### Section 3 Catalysis details

**Table S2** Effect of the Solvent on the Photocatalytic CuAAC Using Cu-TCTA as the Catalyst. <sup>a</sup>



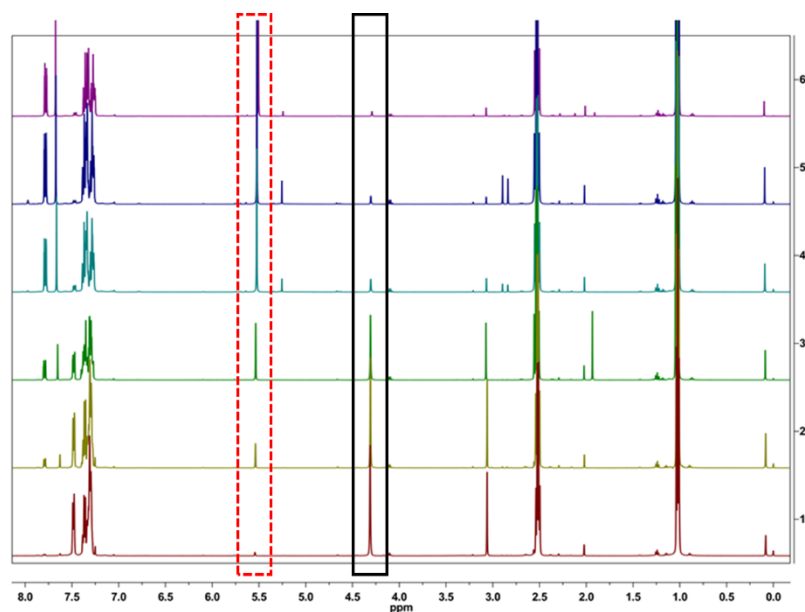
Entry	Solvent	Electron Donor (ED)	% Yield of <b>3a</b>	
			Light <sup>b</sup>	Dark
1	CH <sub>3</sub> CN	TEA	20.8	trace
2	EtOH	TEA	30.7	4.5
3	THF	TEA	68.5	4.0
4	CH <sub>2</sub> Cl <sub>2</sub>	TEA	84.0	4.3
5	CDCl <sub>3</sub>	TEA	94.3	8.4
6	CDCl <sub>3</sub>	none	trace	ND
7 <sup>c</sup>	CDCl <sub>3</sub>	TEA	2.9	ND

<sup>a</sup> Reaction conditions: Cu-TCTA (0.5 mol %), azide/alkyne/ED (1:1:1), room temperature, 6 h. Yields were calculated by <sup>1</sup>H NMR analysis in CDCl<sub>3</sub>. <sup>b</sup> Household light irradiation at 7 mW/cm<sup>2</sup>. <sup>c</sup> Catalyst was H<sub>3</sub>TCTA.

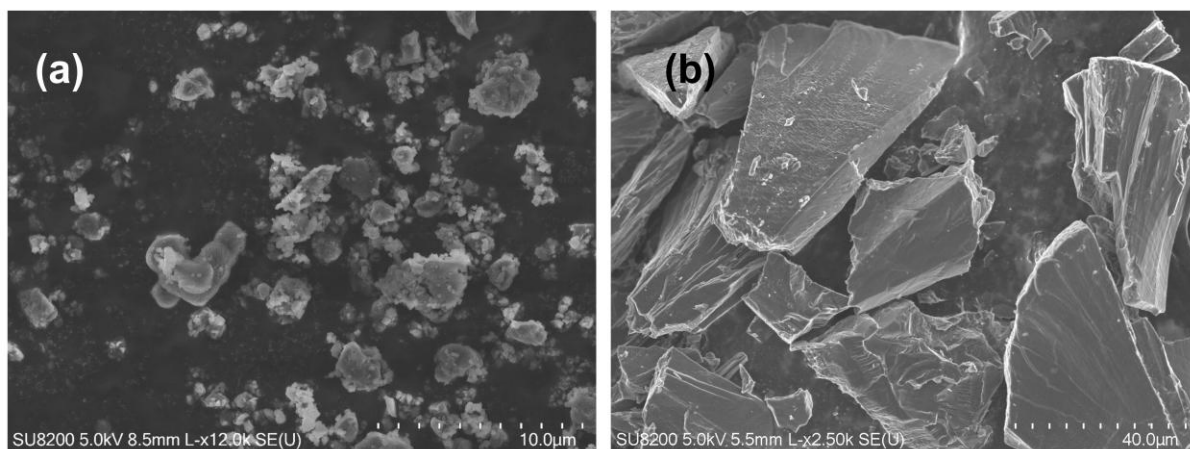
**Table S3** Kinetic study of the photocatalytic reaction of **1a** and **2a** in CDCl<sub>3</sub> upon irradiation.

Entry	Time(h)	% Yield of <b>3a</b>	
		A	B <sup>a</sup>
1	1	2.4	
2	2	13.1	
3	3	36.6	36.6
4	4	87.7	
5	5	93.4	
6	6	94.3	43.3

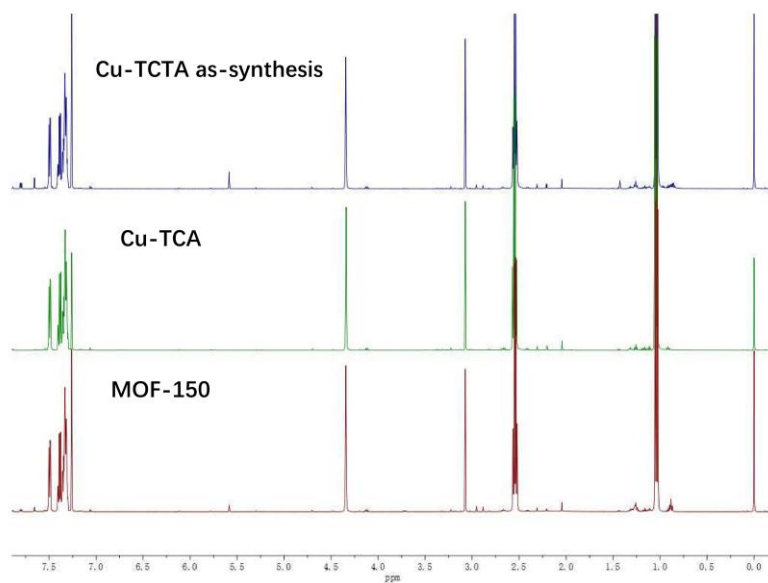
<sup>a</sup>The catalyst was removed after 3h.



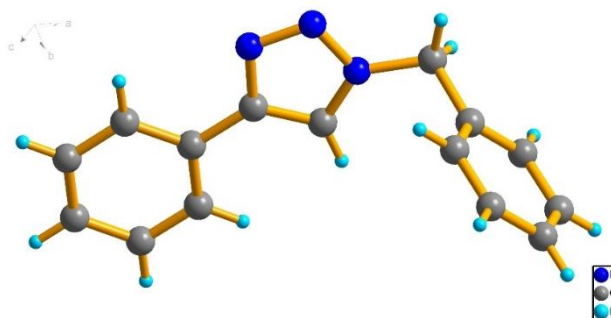
**Fig. S5**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) monitoring of the click reaction progress using catalyst Cu-TCTA, showing the increasing tendency of the peaks at around 5.54, 7.65, 7.78 and 7.80 ppm, while the gradual vanish of the peaks at around 3.07, 4.31, 7.47 and 7.49 ppm, respectively, with the proceeding of the reaction.



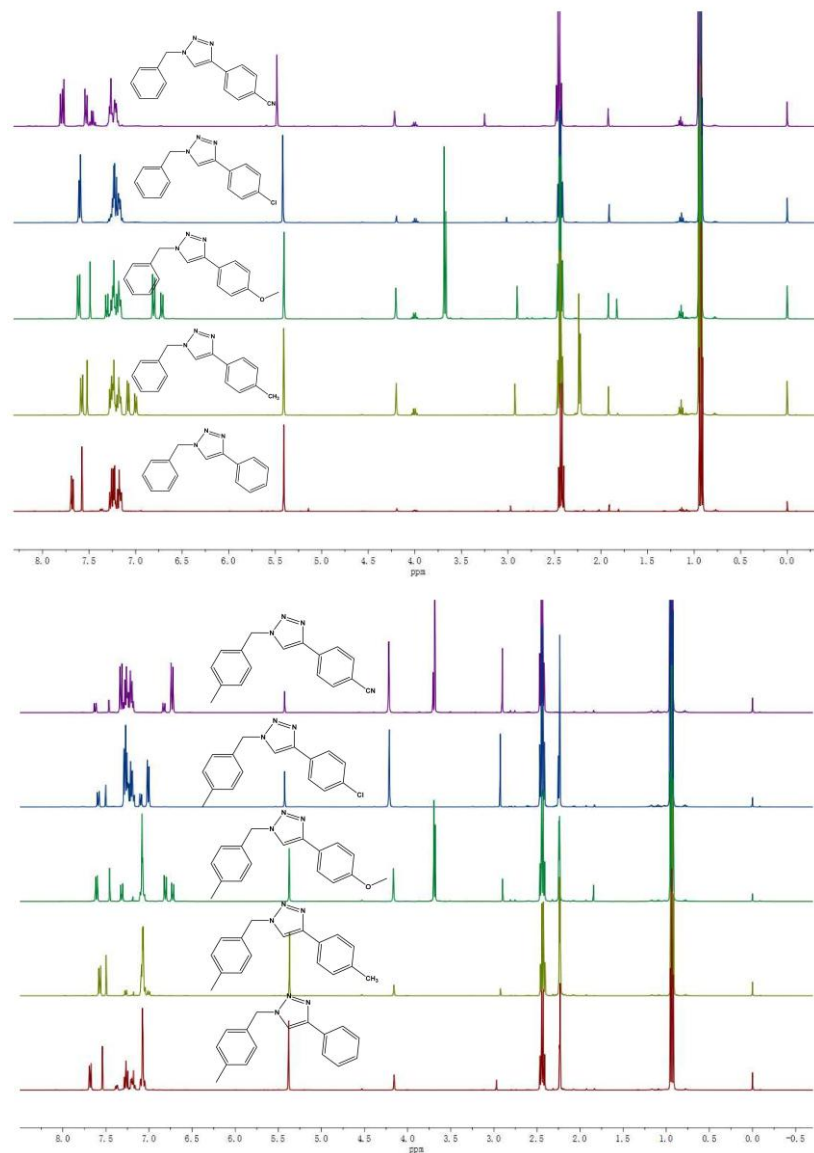
**Fig. S6** The scanning electron microscopy (SEM) image of Cu-TCTA (a) by grinding and as-synthesized (b).



**Fig. S7** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of the click reaction after 6 h using catalyst Cu-TCTA as-synthesized, Cu-TCA and MOF-150. Yields of them are 7%, Trace and 2%, respectively.



**Fig. S8** The single-crystal X-ray diffraction structure of product 3a.



**Fig. S9** The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra of the mixture after 6h reaction.



## Section 4 References

- S1. SMART, *Data collection software (version 5.629)*; Bruker AXS Inc., Madison, WI, **2003**.
- S2. SAINT, *Data reduction software (version 6.45)*; Bruker AXS Inc., Madison, WI, **2003**.
- S3. Sheldrick, G. M. *SHELX-97, Program for crystal structure solution*; University of Göttingen:  
Göttingen, Germany, **1997**.