Supporting Information for

In Situ Synthesis and Photocatalytic Mechanism of Cyano bridged Cu(I) polymer

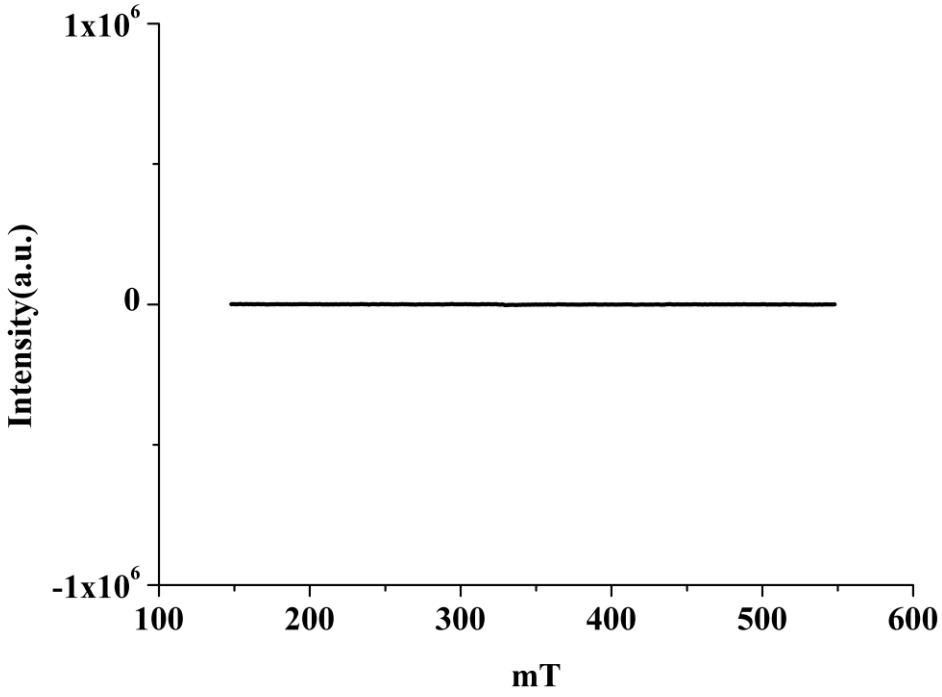
Shixiong Li[1], Chaohai Wei[1*], Yun Hu[1*], Haizhen Wu[2] & Fusheng Li[3]

[1]School of Environment and Energy, South China University of Technology, Guangzhou, 510006, P. R. China

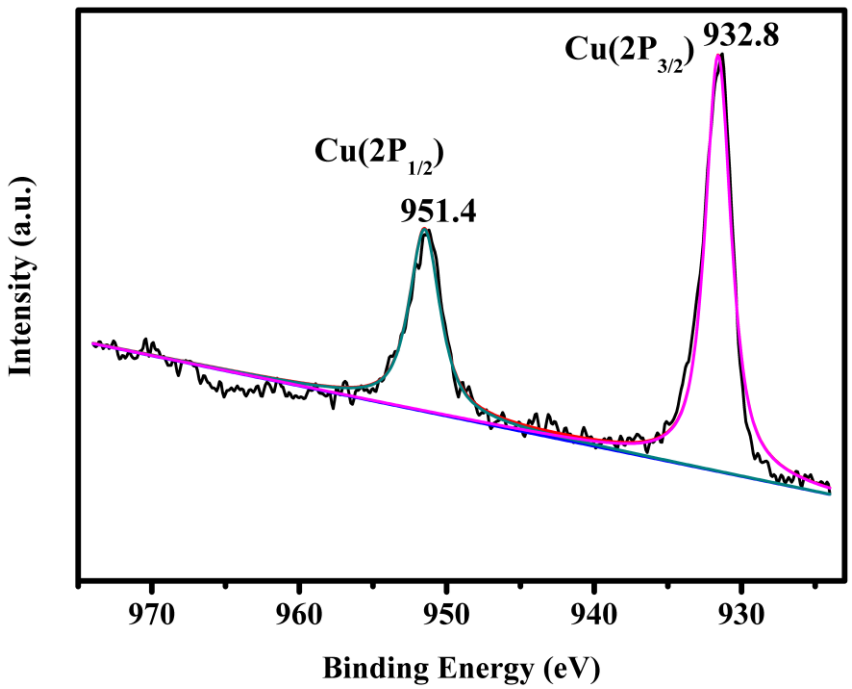
[2]School of Biology and Biological Engineering, South China University of Technology, Guangzhou, 510006, P. R. China

[3]River Basin Research Center, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

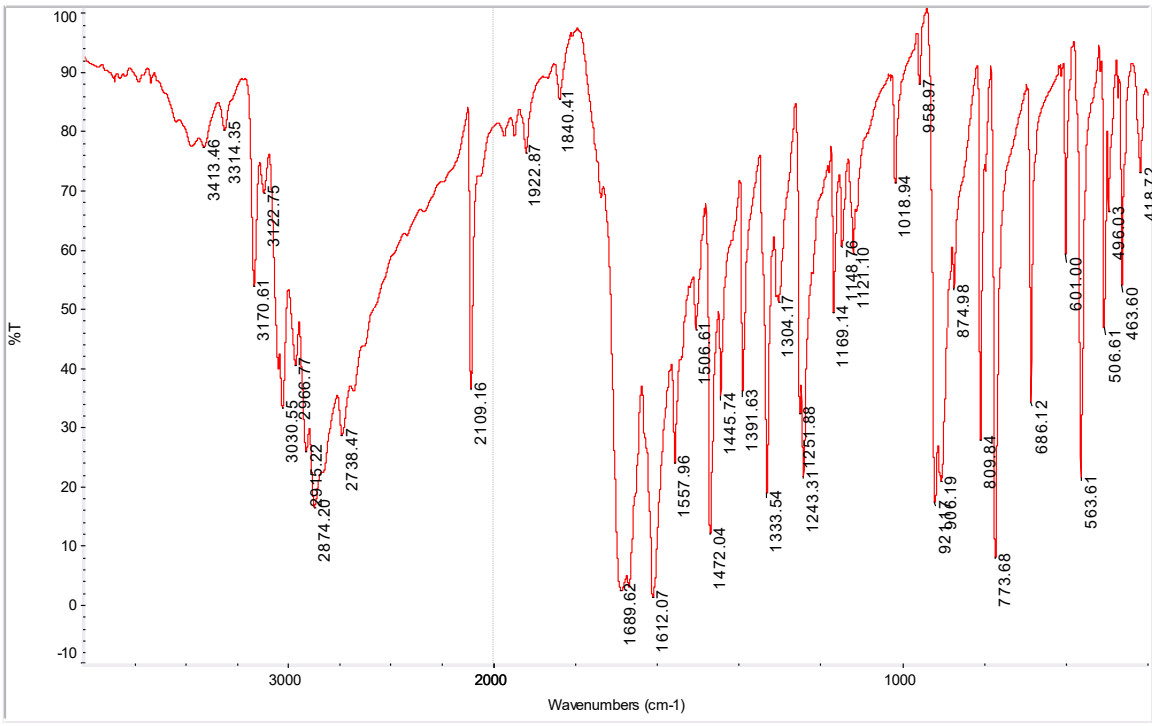
*Correspondence and requests for materials should be addressed to C. H. Wei (Email: cechwei@scut.edu.cn)



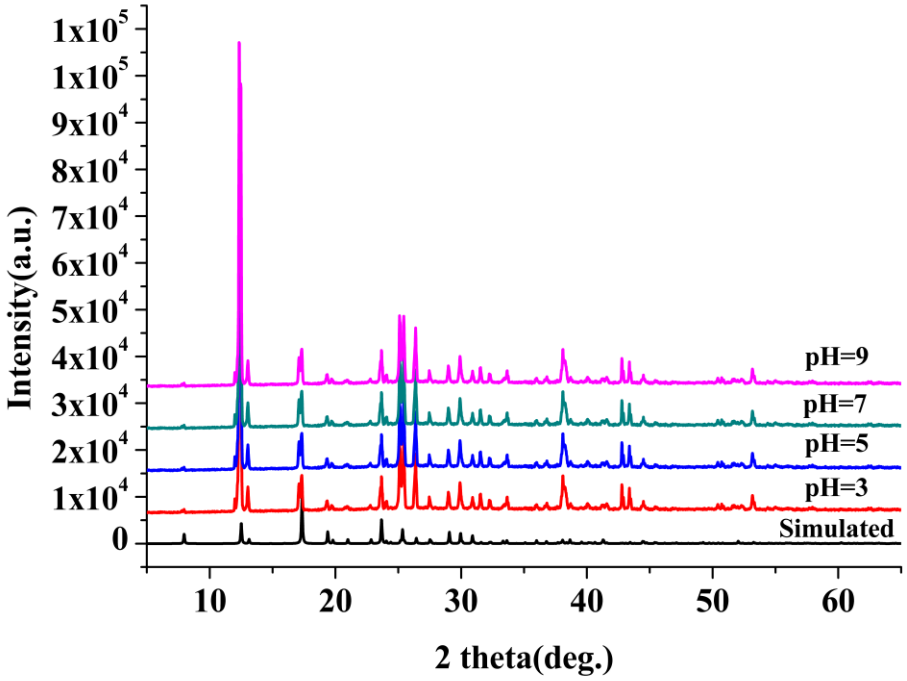
Supplementary Figure 1. EPR spectrum of powdered **1** at 173 K.



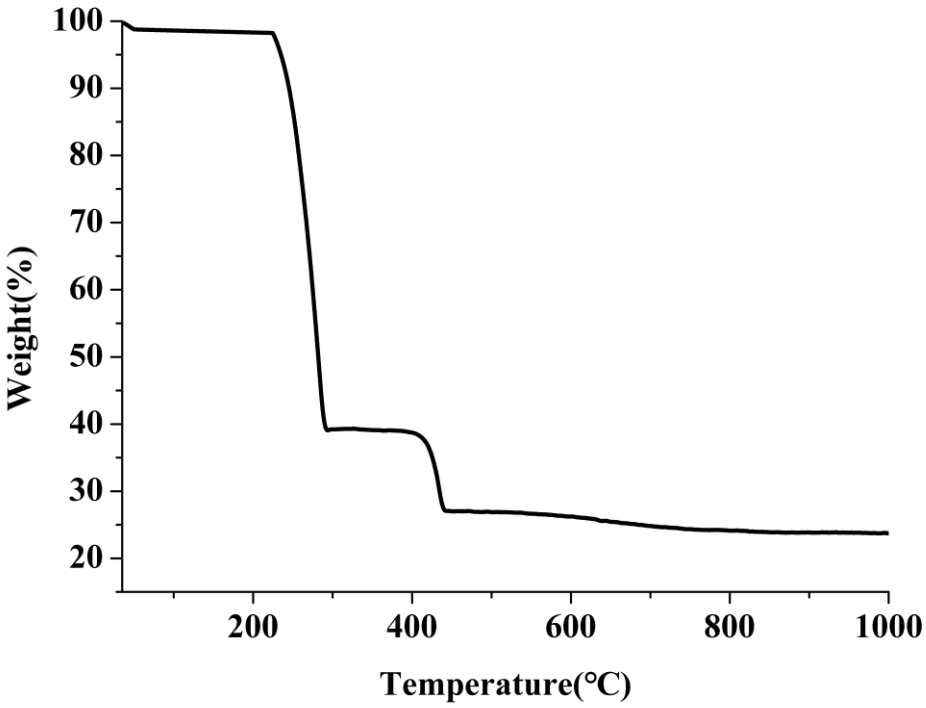
Supplementary Figure 2. XPS spectra of Cu2p region of the **1**.



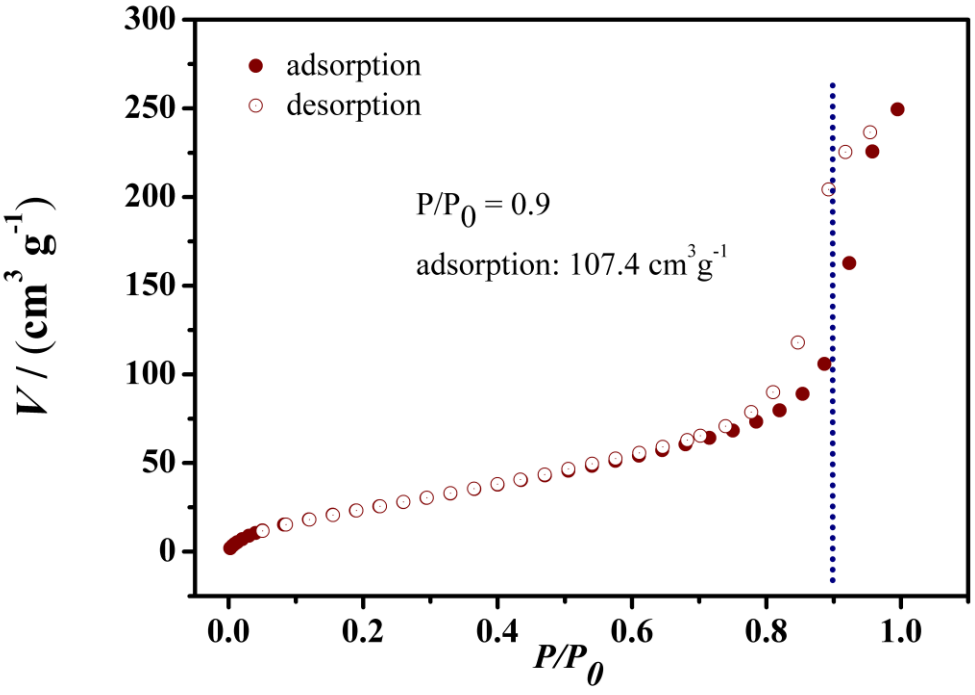
Supplementary Figure 3. IR spectrum of **1**.



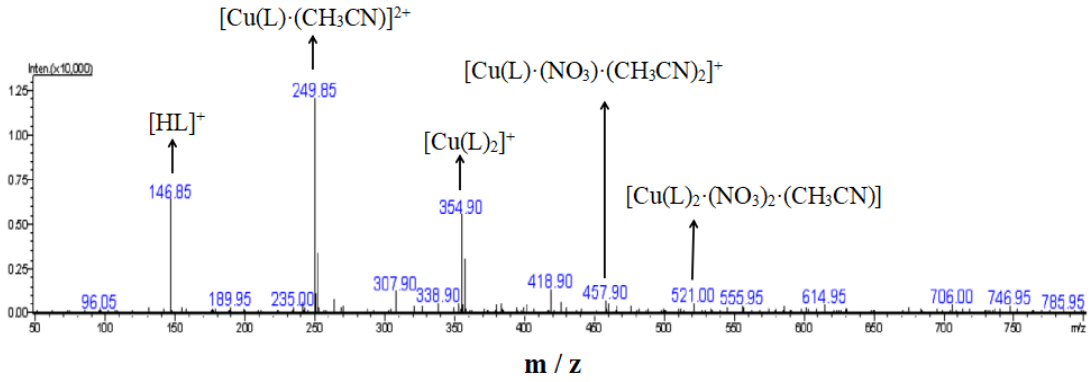
Supplementary Figure 4. Simulated and measured XRPD patterns of **1**.



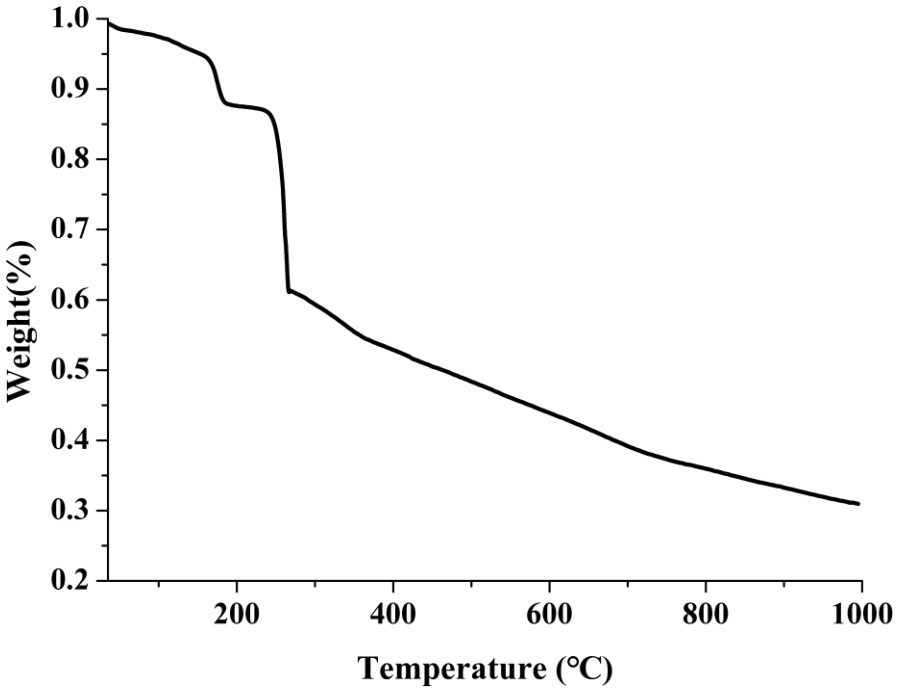
Supplementary Figure 5. TGA of **1**.



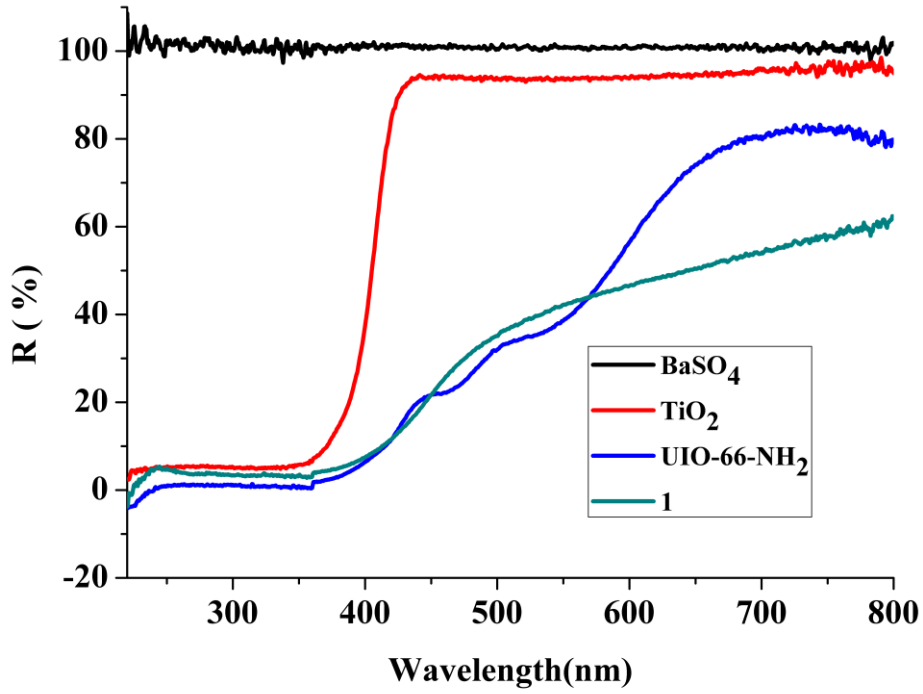
Supplementary Figure 6. The N_2 adsorption/desorption experiment of **1**.



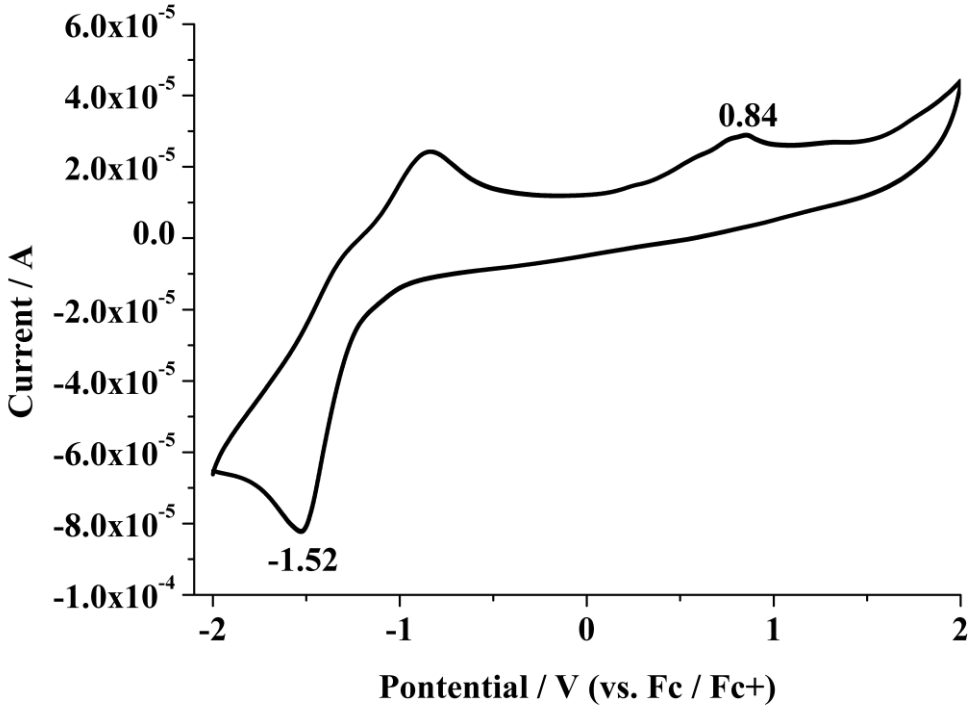
Supplementary Figure 7. ESI mass spectra of $[Cu(L)_2·(H_2O)_2·(NO_3)_2]$ in acetonitrile after heating at 130℃.



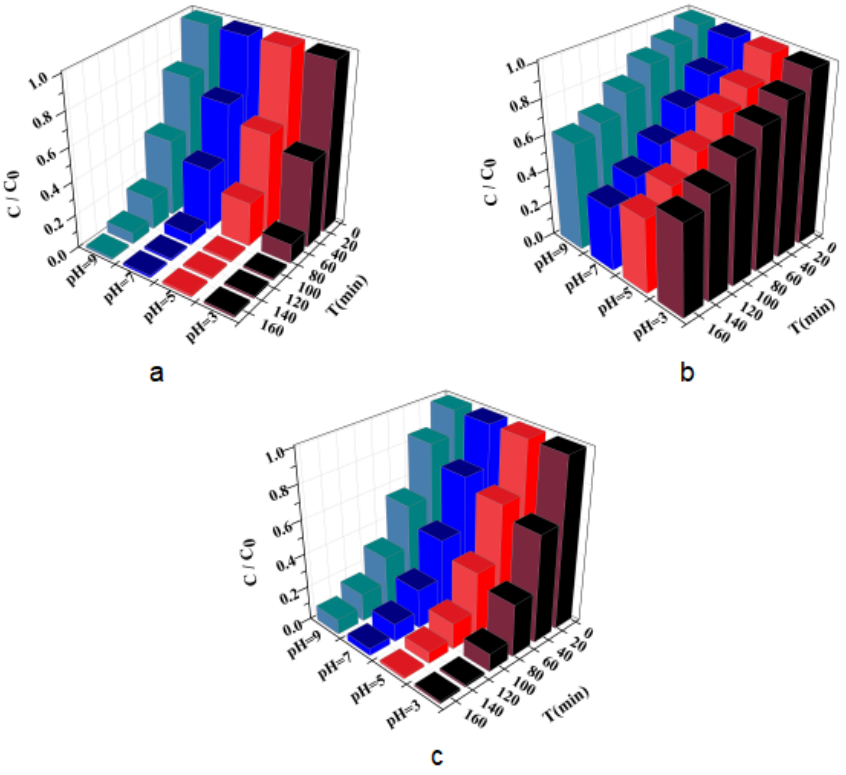
Supplementary Figure 8. TGA of $[Cu(L)_2·(H_2O)_2·(NO_3)_2]$.



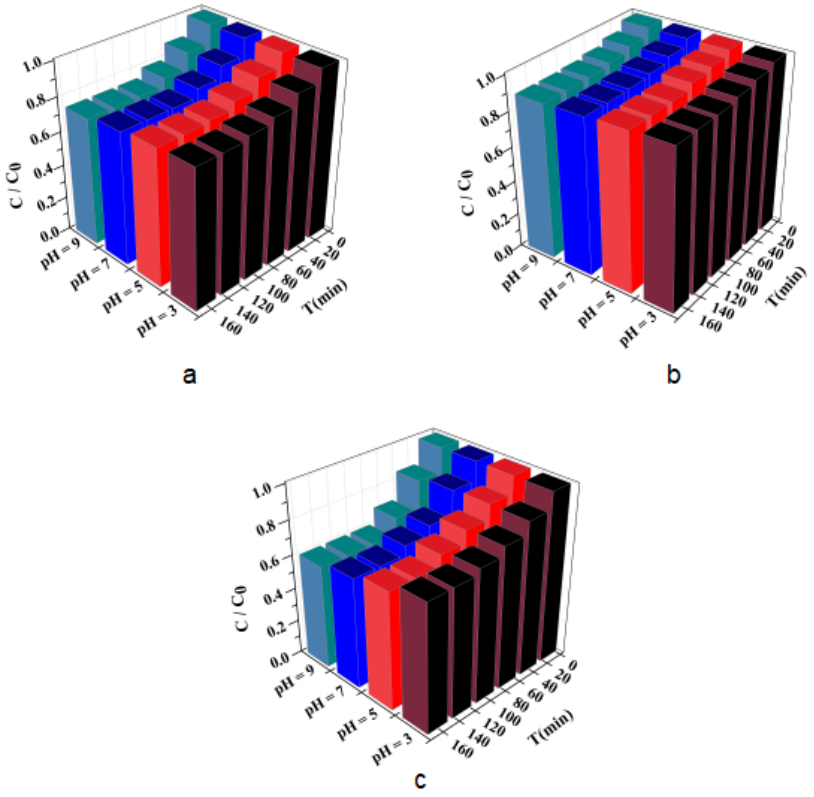
Supplementary Figure 9. UV-Vis DRS of **1**, UIO-66-NH_2 and TiO_2.



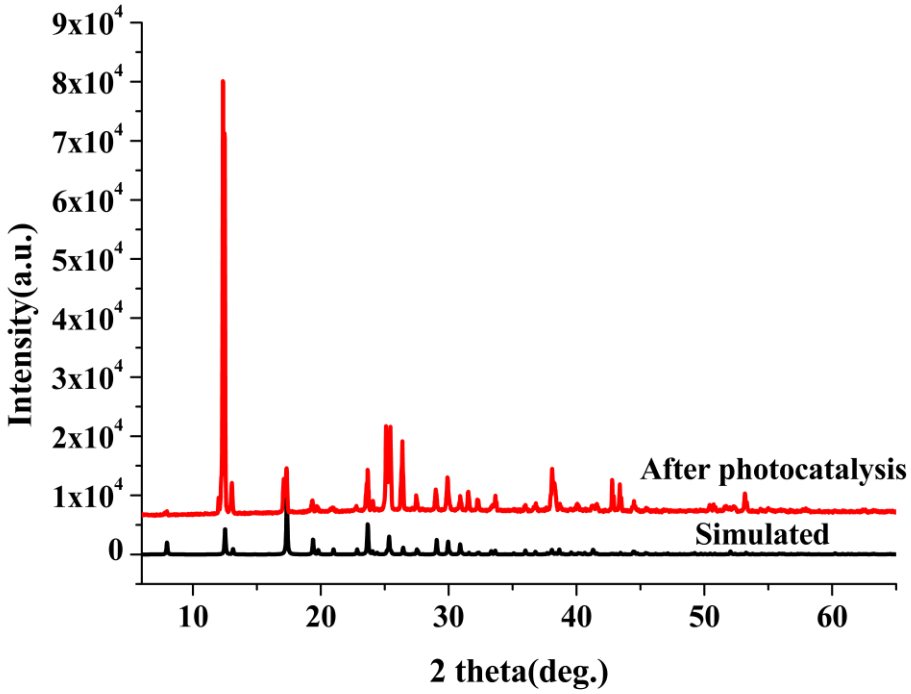
Supplementary Figure 10. Cyclic voltammograms of **1** on platinum plates in an acetonitrile solution of 0.1 mol/L Bu_4NPF_6 at a sweep rate of 0.1 V/s.



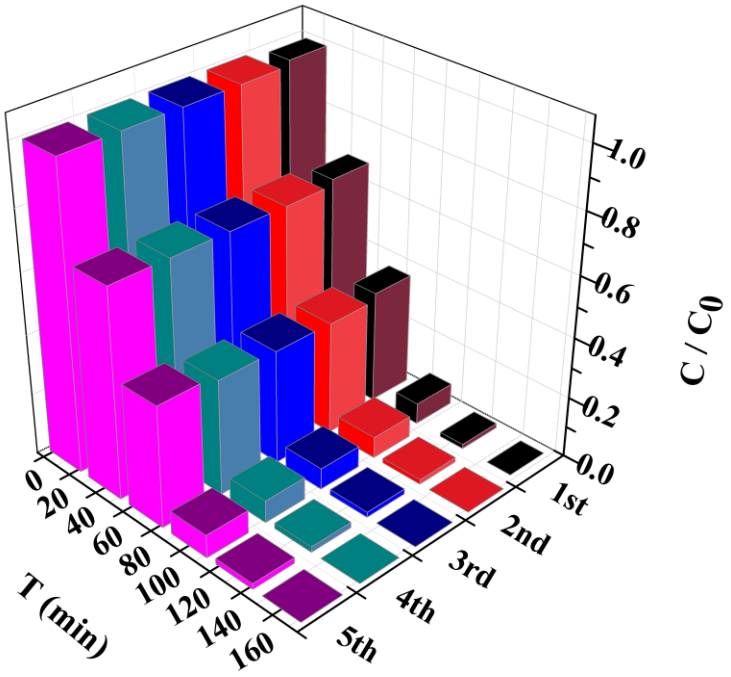
Supplementary Figure 11. Photocatalytic degradation of MB at pH 3-9 of **1** (a); TiO_2 (b) and UIO-66-NH_2 (c).



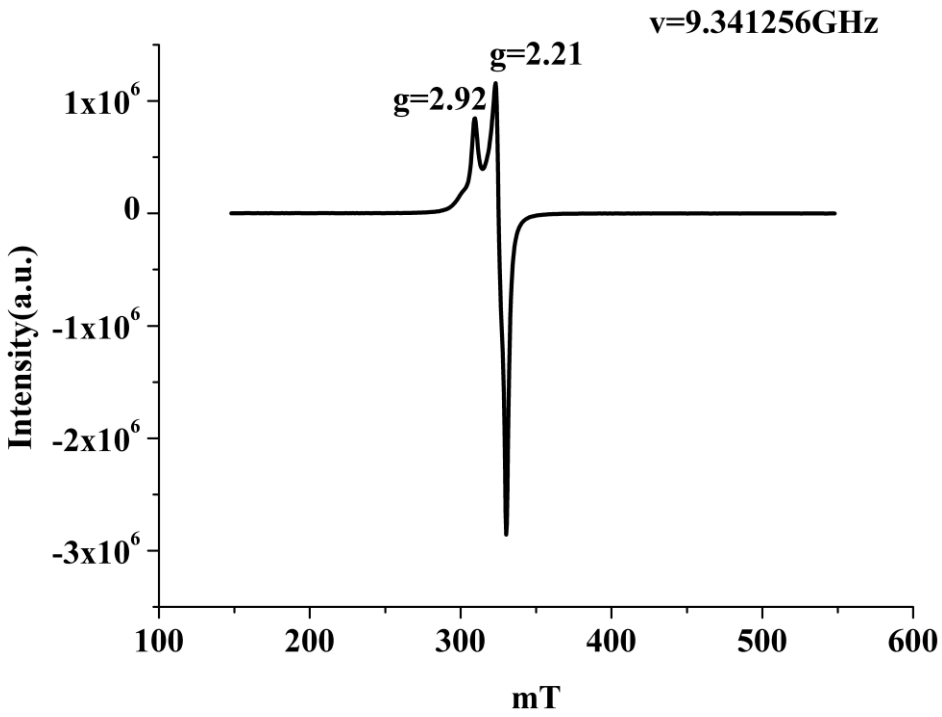
Supplementary Figure 12. The adsorbed amount of MB at pH 3-9 of **1** (a), TiO_2 (b) and UIO-66-NH_2.



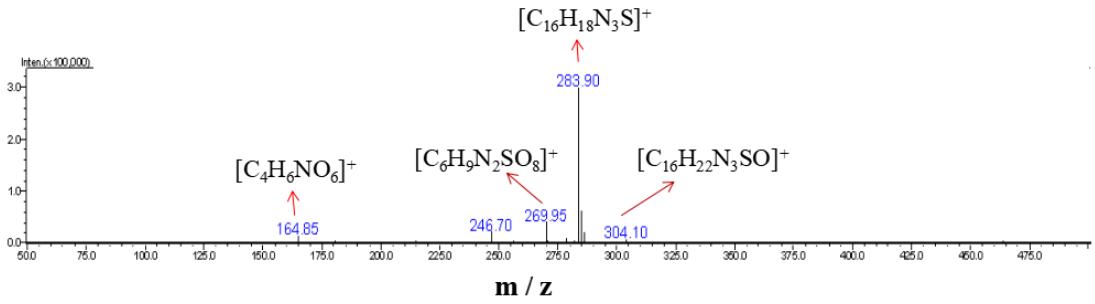
Supplementary Figure 13. Simulated and after photocatalysis XRPD patterns of **1**.



Supplementary Figure 14. Cycle runs of **1** for the degradation of MB at pH=7.



Supplementary Figure 15. In situ EPR spectrum of **1** sample under 175 W high-pressure mercury lamp radiation catalyzed the MB at 173 K.



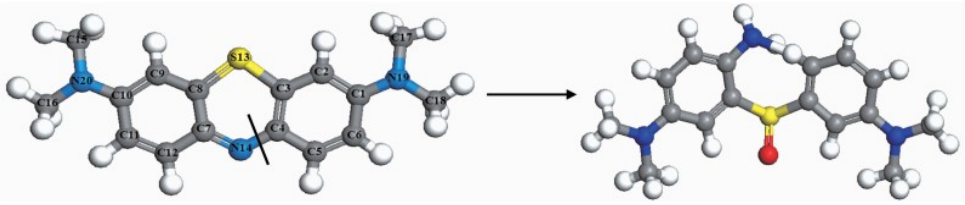
Supplementary Figure 16. ESI mass spectra of **1** photocatalytic degradation of MB.

Supplementary Table 1. The zeta potential vs. pH curves of **1**, UIO-66-NH_2 and TiO_2.

pH	Zeta potential (mV)		
	1	UIO-66-NH_2	TiO_2
3	38.52	27.5	18.84
5	23.5	16.59	5.81
7	11.12	5.74	-9.84
9	-5.68	-9.56	-22.35

Supplementary Table 2. Frontier electron densities on atoms of MB calculated by DFT analysis.

Atom (number)	$2FED^2_{HOMO}$	$FED^2_{HOMO} + FED^2_{LUMO}$
C(1)	0.0025	0.0937
C(2)	0.0076	0.0780
C(3)	0.0844	0.0525
C(4)	0.0981	0.2257
C(5)	0.0260	0.0167
C(6)	0.0009	0.0799
C(7)	0.0981	0.2258
C(8)	0.0844	0.0525
C(9)	0.0076	0.0780
C(10)	0.0025	0.0934
C(11)	0.0009	0.0799
C(12)	0.0259	0.0167
S(13)	0.0019	0.0009
N(14)	1.4971	0.7485
C(15)	0.0000	0.0171
C(16)	0.0000	0.0171
C(17)	0.0000	0.0171
C(18)	0.0000	0.0171
N(19)	0.0002	0.0217
N(20)	0.0002	0.0216



Supplementary Table 3. Crystallographic Data of **1**.

Polymer **1**			
Empirical formula	$C_{17}H_{12}CuN_5O_2$	Z	4
Formula weight	381.86	Dcaled, (g/cm^3)	1.676
Temperature (K)	293(2)	S	1.05
Wavelength (Å)	0.71073	Limiting indices	$-6 \le h \le 5$; $-17 \le k \le 18$; $-18 \le l \le 28$
Crystal system	Orthorhombic	F(000)	776
Space group	*Pbcn*	θ(°)	3.0 to 28.3
a (Å)	4.8345(1)	Refs collected total / unique	4432 / 1746
b (Å)	14.1398(5)	$(\Delta/\sigma)_{max}$	0.001
c (Å)	22.1826(8)	Data/restraints/paramets	1746 / 0 / 114
α (°)	90	μ(mm^{-1})	1.46
β (°)	90	Final R indices; [I>2σ(I)]	$R_1 = 0.042$; $wR_2 = 0.106$
γ (°)	90	$\Delta\rho_{max}/\Delta\rho_{min}$	0.57 / -0.86

Volume (Å^3)	1516.38(8)	$R_{(int)}$	0.022

Supplementary Table 4. Selected Bond Lengths (nm) and Bond Angles (°) for **1**.

Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)
N(1)-Cu(1)	2.343(2)	C(9)-Cu(1)	1.918(2)	N(3)-Cu(1)	1.918(2)
Angle	(°)	Angle	(°)	Angle	(°)
N(1)^A-Cu(1)-N(1)	113.89(11)	N(3)-Cu(1)-N(1)	90.68(9)	N(3)^A-Cu(1)-N(1)	106.63(9)
N(3)^A-Cu(1)-N(3)	148.29 (14)	C(9)-Cu(1)-N(1)	90.68(9)	O(1)-C(2)-N(2)	120.8 (2)

Symmetry codes: (A) −x+1, y, −z+3/2.

Supplementary Table 5. Hydrogen bonds of **1**.

D-H···A	D-H/ Å	H···A/ Å	D···A/ Å	D-H···A
N(2)-H(2)···O(1)^B	0.86	1.94(1)	2.802(3)	177(1)

Symmetry codes: (B) −x+1, −y+2, −z+1.