Supporting Information

MOFs with Hydrazide and 3-Amino-1,2,4-oxadiazole-Substituted Hydroxytetrazole as Novel Nitrogen-Rich Ligands: A New Type of Energetic Materials for Ammonium Perchlorate Decomposition Catalysis

Feng Yang,[a] Zhiwei He,[*a] Rongzheng Zhang,[a] Quan Wang [a]

[a] *School of Chemical and Blasting Engineering, Anhui University of Science and Technology, Huainan 232001, China.*

Email: zhwhe@aust.edu.cn.

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1. Synthesis of AZTO-Ag, AZTO-Cu-4H_2O, AOTO-Ag and AOTO-Cu-4H_2O

Cautions! Strong acids, bases and other hazardous chemicals are used in the chemical reaction process involved in this article. Wearing protective equipment during the entire experiment is strongly recommended.

General methods: Single-crystal X-ray diffraction measurements were conducted on a Bruker Smart Apex II diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with a

graphite monochromator at 296 K. NMR spectra were recorded on Bruker AVANCE III 500MHz at 25 ºC. The onset decomposition temperature (DSC) was measured using NETZSCH DSC204 F1 Phoenix differential scanning calorimeter at a heating rate of 5 °C min^{-1} under a dry nitrogen atmosphere. Infrared spectra (IR) were obtained on a ThermoFisher NICOLETIS10 instrument at 25 °C. Impact and friction sensitivities were tested by a BAM fallhammer and friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer.

1.1 Synthesis of 5-(5-amino-1,3,4-oxadiazol-2-yl)-1H-tetrazol-1-ol (AOTO)

AZTO (2.88 g, 20 mmol) was dispersed in a 40 mL ethanol solution, and 20 ml of water dissolved in sodium bicarbonate (4.20 g, 50 mmol) was added to the aforementioned solution in batches under stirring at room temperature. When the above mixture is stirred at room temperature for 30 min, cyanogen bromide (2.54 g, 24 mmol) is added to it. After the mixture is stirred for 24 h, 20% hydrochloric acid is added to it until the PH is 3. Then continue stirring the mixture for 1 hour, filter, and rinse the filter cake with ice water to obtain a white solid product.

Yield 2.41 g (71.3%). ^{13}C NMR (125 MHz, DMSO-d_6): 165.04, 146.40, 136.43, ^{1}H NMR (500 MHz, DMSO-d_6): 7.74; IR (KBr): 3470.21, 3409.06, 3137.82, 2697.32, 1732.83, 1659.79, 1633.65, 1506.99, 1313.01, 1245.59, 1181.80, 1155.28, 1093.72, 1020.46, 999.85, 831.88, 783.67, 746.55, 674.21, 652.79 cm^{-1}; Element analysis ($C_3N_7O_2H_3$), calculated (%): C 21.31, H 1.79, N 57.98; measured (%): C 20.46, H 2.20, N 58.87.

1.2 Synthesis of the MOFs of AZTO and AOTO

Add **AZTO** (0.144 g, 1 mmol) or **AOTO** (0.169 g, 1 mmol) to 100ml of deionized water containing copper nitrate (0.093 g, 1 mmol) or silver nitrate (0.170 g, 1 mmol), stir at 70℃ for 1 hour, and then gradually add 30% nitric acid dropwise to the mixture until the solid dissolves. Continue stirring at 70℃ for another hour, filter the reaction solution while it is still hot, let the filtrate stand, and slowly cool it to room temperature. Subsequently, the product precipitates out in the form of crystals.

AZTO-Ag, yield 0.229 g (91.6 %). IR (KBr): 3269.50, 3166.16, 2358.83,

2159.76, 2032.12, 1672.79, 1603.99, 1563.75, 1556.89, 1442.58, 1393.04, 1338.46, 1308.85, 1216.60, 1168.64, 1131.12, 1092.76, 1035.85, 1011.53, 863.71, 762.28, 697.07, 604.28 cm^{-1}.

AZTO-Cu-4H_2O, yield 0.185 g (87.8 %). IR (KBr): 3187.68, 2987.17, 2358.47, 2160.50, 1978.10, 1643.20, 1590.38, 1434.35, 1326.97, 1219.91, 1199.68, 1183.95, 1075.46, 907.61, 818.12, 785.00, 702.26, 629.75 cm^{-1}.

AOTO-Ag, yield 0.254 g (92.2 %). IR (KBr): 3524.17, 3271.25, 3127.41, 2358.87, 2160.10, 2009.60, 1667.80, 1594.12, 1488.43, 1416.10, 1303.43, 1240.64, 1158.94, 1084.43, 1046.70, 1011.60, 975.51, 831.42, 774.74, 746.30, 697.88 cm^{-1}.

AOTO-Cu-4H_2O, yield 0.211 g (89.4 %). IR (KBr): 3366.06, 3237.46, 3206.44, 2160.39, 2023.68, 1665.57, 1633.54, 1514.13, 1430.31, 1316.03, 1253.25, 1179.00, 1111.48, 1098.36, 1024.36, 1002.18, 739.94, 704.54, 674.87, 645.91, 621.32 cm^{-1}.

2 Crystallographic data

Table S1 Crystallography data sheet for AZTO-Ag and AZTO-Cu-**4H_2O**.

Comp.	**AZTO-Ag**	**AZTO-Cu-4H_2O**
Formula	C2H3AgN6O2	C4H14CuN12O8
Temperature	296(2) K	296(2) K
System Space group	Monoclinic $P2_1/n$	Monoclinic $P2_1/n$
Dimensions	a = 4.8588(3) Å b = 8.3454(4) Å c = 13.9313(7) Å a= 90° b= 93.658(2) ° g = 90°	a = 8.3514(8)Å b = 8.0290(7) Å c = 10.6850(10) Å α= 90 ° β= 102.056(3) ° γ = 90°
Volume/ $Å^3$	563.74(5)	700.66(11)
Z	4	2
Density / $g \cdot cm^{-3}$	2.957	1.999
F(000)	480	430
Theta range / °	2.847 to 30.462	2.827 to 28.344
Index ranges	-6≤h≤6, -11≤k≤11, -19≤l≤19	-8≤h≤11, -10≤k≤10, -13≤l≤14
Reflections collected	5531	7241
Independent reflections	1705 [R(int) = 0.0244]	1732 [R(int) = 0.0408]
Data/restraints/ parameters	1705 / 0 / 106	1732 / 6 / 136
Goodness-of-fit on F^2	1.080	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0570	R1 = 0.0283, wR2 = 0.0718

R indices (all data)	R1 = 0.0319, wR2 = 0.0593	R1 = 0.0388, wR2 = 0.0759
CCDC Num.	2257064	2246398

Table S2 Hydrogen bonds for AZTO-Ag.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6B)...N(3)#4	0.86(3)	2.67(3)	3.240(3)	125(3)
N(6)-H(6B)...O(2)#5	0.86(3)	2.29(3)	3.086(3)	155(3)
N(6)-H(6A)...O(1)#6	0.88(3)	2.38(3)	2.953(3)	123(3)
N(6)-H(6A)...O(2)#7	0.88(3)	2.32(3)	3.003(3)	135(3)
N(5)-H(5)...O(1)#6	0.86	2.21	2.811(3)	126.8
N(5)-H(5)...O(1)	0.86	2.05	2.735(3)	136.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+1/2 #2 -x,-y,-z+1 #3 -x+1/2,y+1/2,-z+1/2

#4 x+1/2,-y+1/2,z-1/2 #5 x+1,y,z #6 -x+2,-y+1,-z+1

#7 -x+3/2,y+1/2,-z+1/2

Table S3 Hydrogen bonds for AZTO-Cu-4H_2O.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4B)...O(3)	0.828(17)	1.935(17)	2.749(2)	167(3)
O(4)-H(4A)...O(2)#2	0.814(17)	2.12(2)	2.891(2)	158(3)
O(4)-H(4A)...N(4)#2	0.814(17)	2.51(3)	3.049(2)	125(3)
O(3)-H(3B)...N(3)#3	0.844(16)	2.112(16)	2.921(2)	160(2)
O(3)-H(3A)...O(4)#4	0.842(16)	2.187(18)	2.969(3)	154(2)
O(3)-H(3A)...O(2)#5	0.842(16)	2.60(2)	3.116(2)	120(2)
N(6)-H(6C)...O(4)#6	0.85(2)	2.40(2)	3.127(3)	145(2)
N(6)-H(6C)...N(4)#3	0.85(2)	2.50(2)	3.128(3)	131.8(18)
N(6)-H(6B)...N(2)#7	0.86(2)	2.34(2)	2.964(2)	129.3(19)
N(6)-H(6A)...O(4)#8	0.84(2)	1.96(2)	2.791(2)	168(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x+1,y,z #3 -x+1/2,y+1/2,-z+3/2

#4 -x+3/2,y-1/2,-z+3/2 #5 -x+1/2,y-1/2,-z+3/2

#6 -x+3/2,y+1/2,-z+3/2 #7 x,y+1,z #8 x-1/2,-y+3/2,z-1/2

Table S4 Crystallography data sheet for AOTO-Ag and AOTO-Cu-**4H_2O**.

Comp.	**AOTO-Ag**	**AOTO-Cu-4H_2O**
Formula	C3H2AgN7O2	C6H12CuN14O8
Temperature	296(2) K	296(2) K
System Space group	Monoclinic $P2_1/n$	Monoclinic $P2_1$
Dimensions	a = 4.8266(4) Å b = 21.9823(18) Å c = 6.3898(5) Å a= 90°	a = 8.0601(4) Å b = 9.1901(5) Å c = 10.8846(6) Å α= 90 °

	b= 106.562(2) ° g = 90°	β= 91.301(2) ° γ = 90°
Volume/ Å^3	649.83(9)	806.05(7)
Z	4	2
Density / g·cm^{-3}	2.821	1.944
F(000)	528	478
Theta range / °	3.453 to 28.288	2.901 to 27.530
Index ranges	-6≤h≤4, -295≤k≤28, -8≤l≤8	-10≤h≤9, -11≤k≤9, -14≤l≤13
Reflections collected	6435	7130
Independent reflections	1608 [R(int) = 0.0256]	1847 [R(int) = 0.0251]
Data/restraints/ parameters	1803 / 0 / 139	1847 / 0 / 145
Goodness-of-fit on F^2	1.163	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0791	R1 = 0.0281, wR2 = 0.0701
R indices (all data)	R1 = 0.0441, wR2 = 0.0806	R1 = 0.0394, wR2 = 0.0750
CCDC Num.	2259577	2252081

Table S5 Hydrogen bonds for AOTO-Ag.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7A)...N(3)#5	0.86	2.11	2.951(5)	163.9
N(7)-H(7B)...N(4)#6	0.86	2.11	2.949(5)	166.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+2 #3 x-1,y,z

#4 x+1,y,z #5 x-1,y,z+1 #6 x-1/2,-y+1/2,z+1/2

Table S6 Hydrogen bonds for AOTO-Cu-**4H_2O**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7A)...N(6)#2	0.86	2.22	3.044(2)	159.3
N(7)-H(7A)...O(1)#3	0.86	2.57	3.138(2)	124.9
N(7)-H(7B)...N(2)#3	0.86	2.44	3.087(2)	132.6
N(7)-H(7B)...O(3)#4	0.86	2.50	3.172(3)	135.3
O(3)-H(3A)...O(4)#5	0.71(3)	2.15(3)	2.857(2)	176(3)
O(3)-H(3B)...O(4)#6	0.68(3)	2.31(3)	2.977(2)	170(3)
O(4)-H(4A)...N(4)	0.69(3)	2.27(3)	2.925(2)	158(3)
O(4)-H(4B)...N(3)#7	0.76(3)	2.09(3)	2.837(2)	169(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x+2,-y,-z+1 #3 x,y-1,z

#4 x,-y+1/2,z+1/2 #5 x,-y+1/2,z-1/2 #6 -x+1,y+1/2,-z+3/2

#7 -x+1,-y+1,-z+2

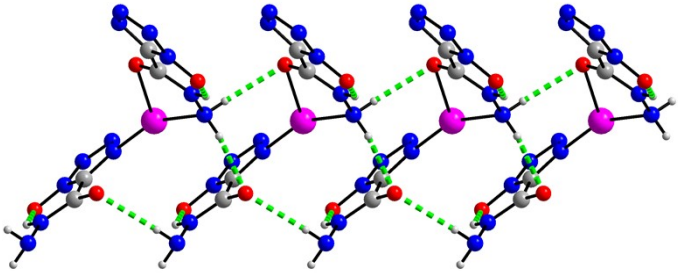

Figure S1 Ligand diagrams of AZTO-Ag in two different orientations .

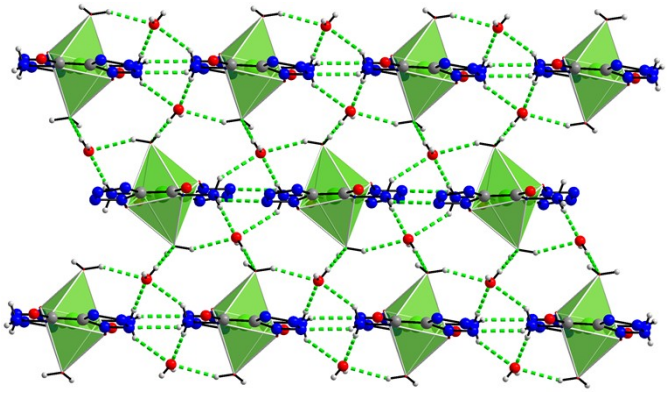

Figure S2 Hydrogen bonding connection of interlayer water molecules in AZTO-Cu-4H_2O.

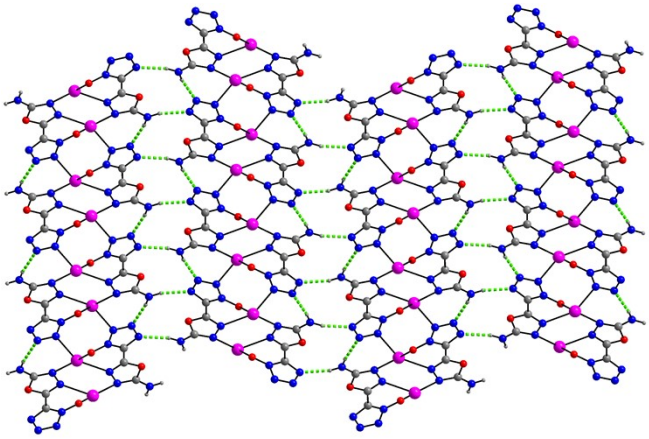

Figure S3 Hydrogen bond distribution within the two-dimensional layers of AOTO-Ag.

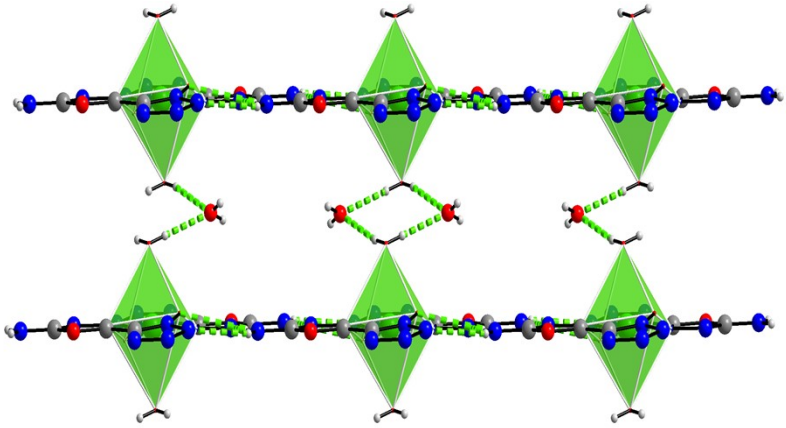

Figure S4 Hydrogen bonding connection of interlayer water molecules in AOTO-Cu-4H_2O.

3 Spectrums

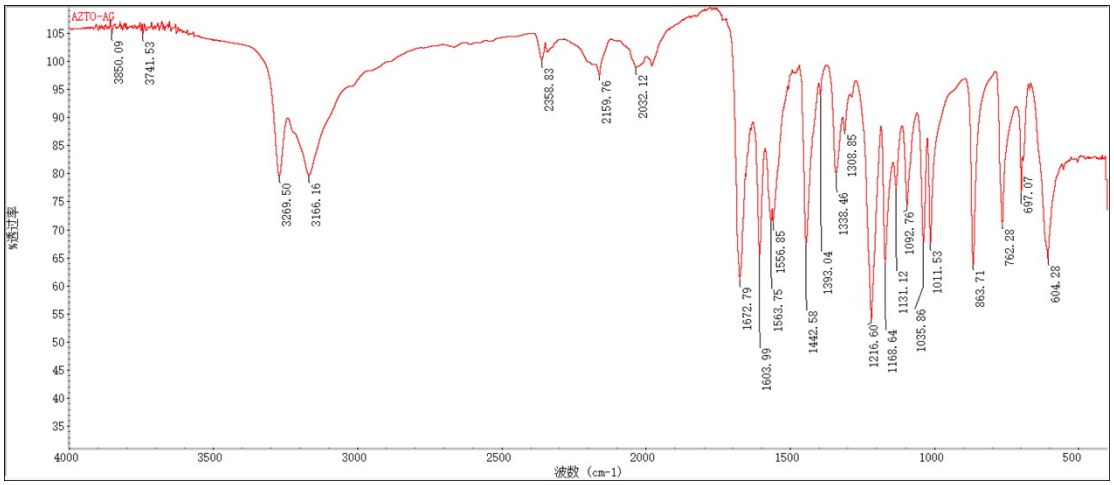

Figure S5 IR of AZTO-Ag.

Figure S6 IR of AZTO-Cu-$4H_2O$.

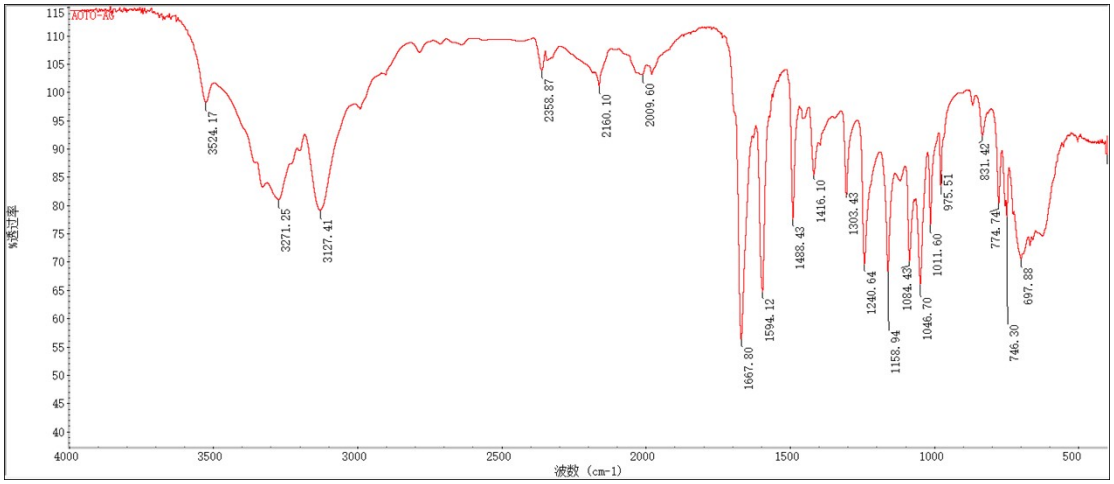

Figure S7 IR of AOTO-Ag.

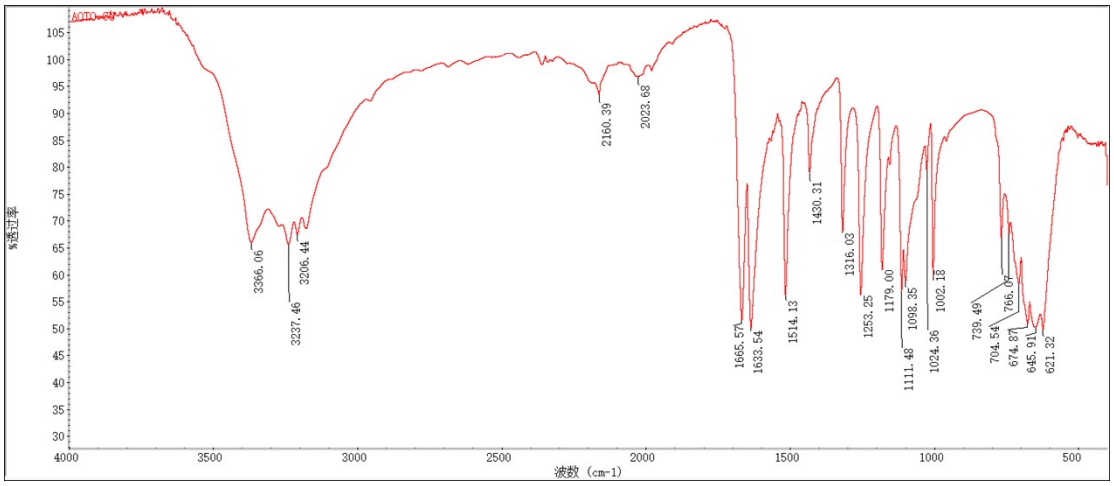

Figure S8 IR of AOTO-Cu-**4H_2O**.

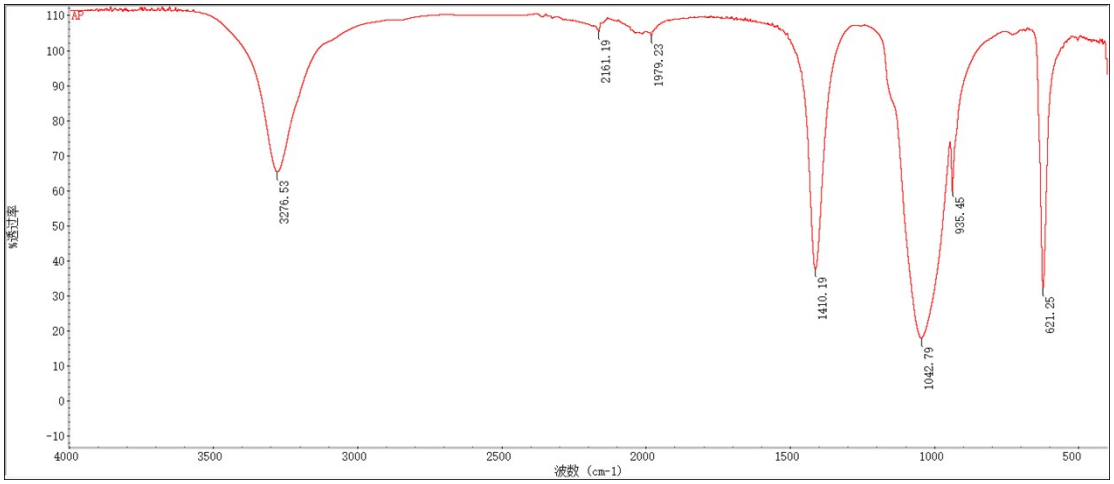

Figure S9 IR of AP.

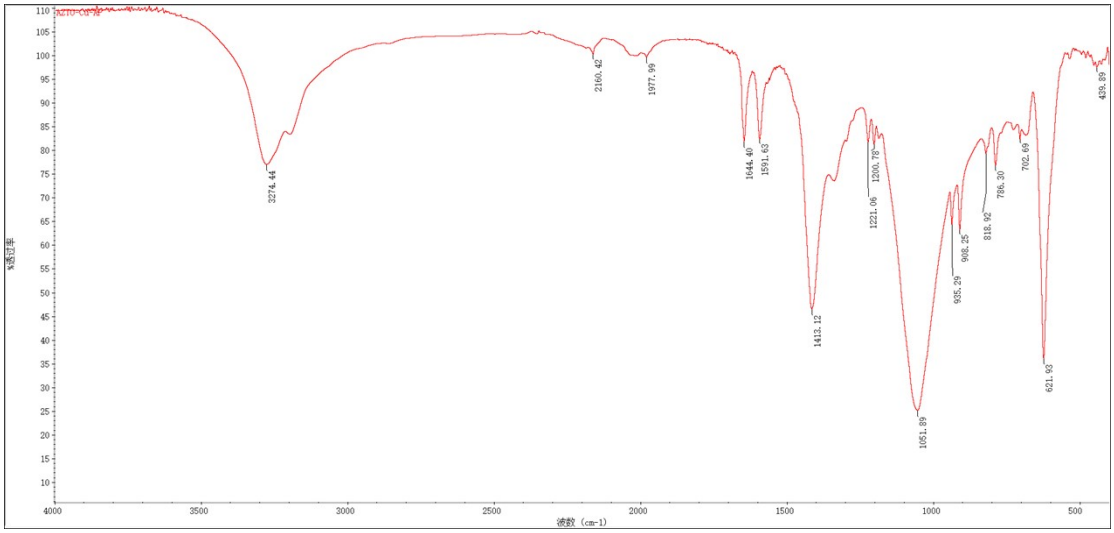

Figure S10 IR of mixture (AZTO-Cu-**4H_2O**-AP).

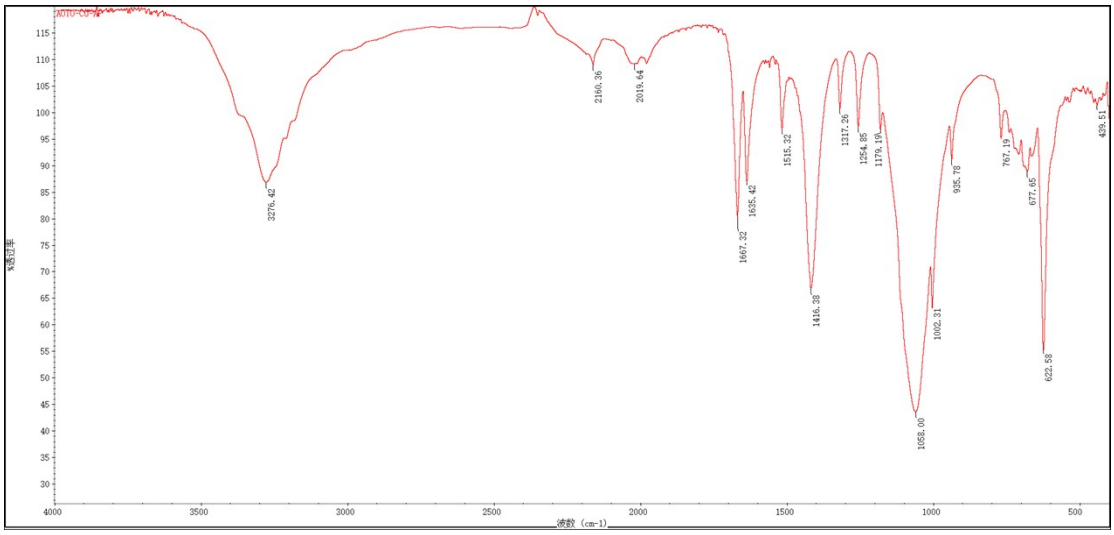

Figure S11 IR of mixture (AOTO-Cu-**$4H_2O$**-AP).

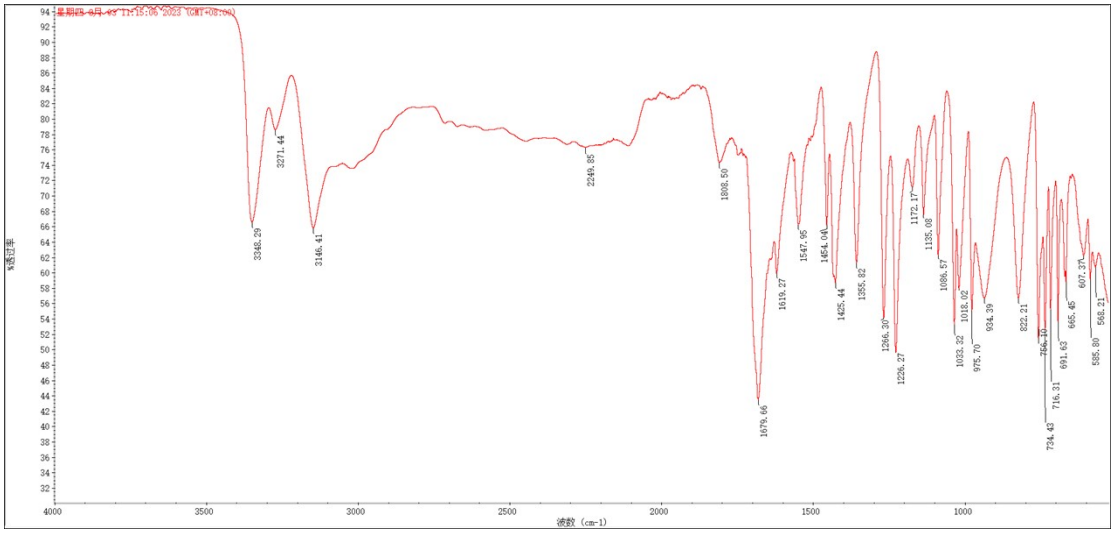

Figure S12 IR of AOTO.

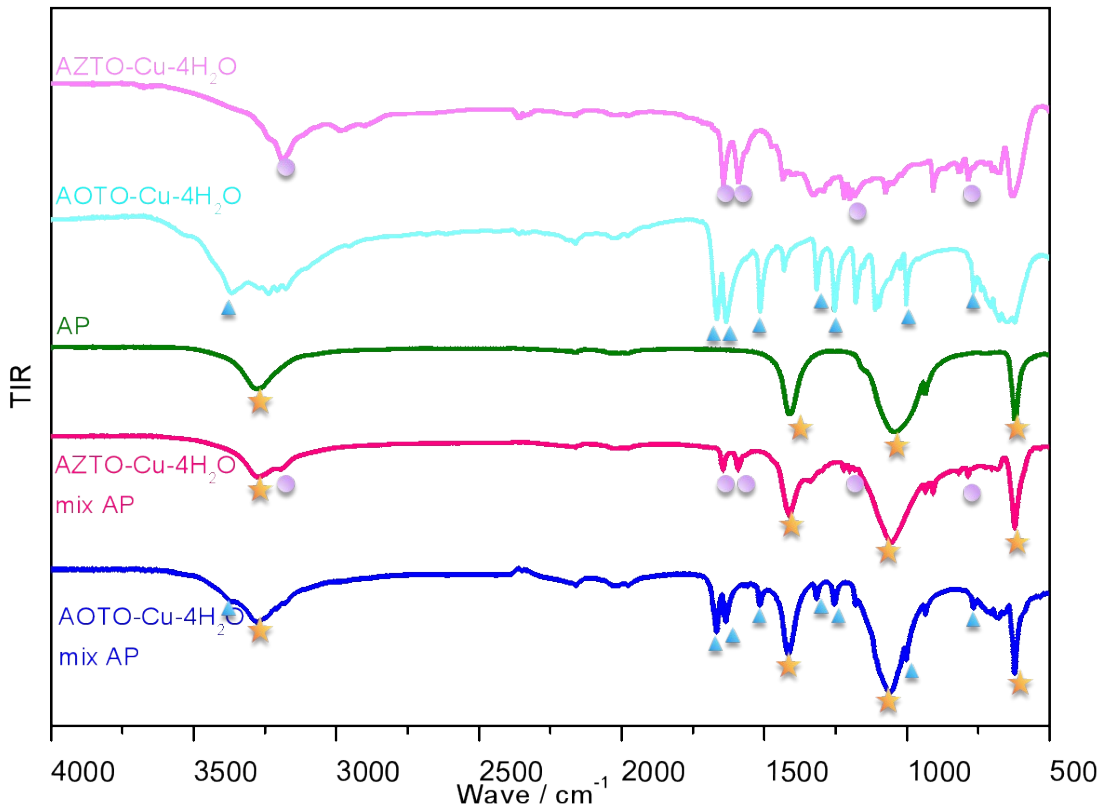

Figure S13 Infrared spectra of AZTO-Cu, AOTO-Cu, AP, and the mixture obtained by mixing AZTO-Cu and AOTO-Cu with AP respectively.

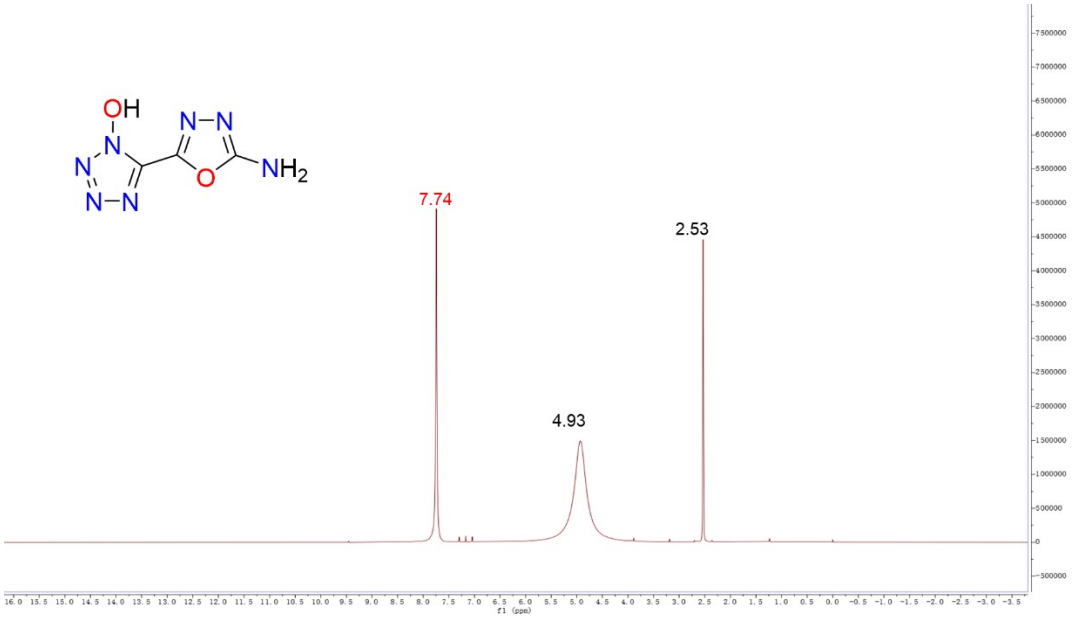

Figure S14 ^{1}H NMR spectrum of AOTO (DMSO-d_6).

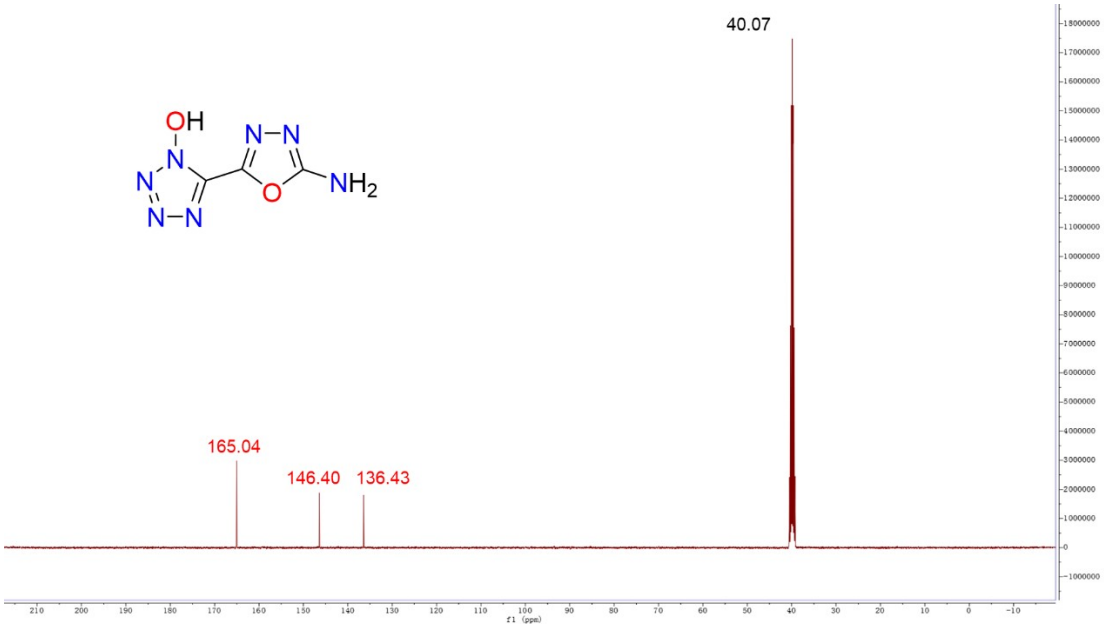

Figure S15 ^{13}C NMR spectrum of AOTO (DMSO-d_6).

4 Parameters of nonisothermal kinetics

Table S7 The activation energy and critical temperatures T_{p0} and T_{pb} of the mixture calculated using the Kissinger's and Ozawa's methods.

	E_k (kJ mol^{-1})	R_k	E_o (kJ mol^{-1})	R_0	T_{p0} (°C)	T_{pb} (°C)
AZTO-Cu-**4H$_2$O**-AP	144.3	0.998	146.7	0.998	297.1	302.4
AOTO-Cu-**4H$_2$O**-AP	91.4	0.991	96.4	0.993	269.4	276.3

5 DSC curves of AZTO and AOTO

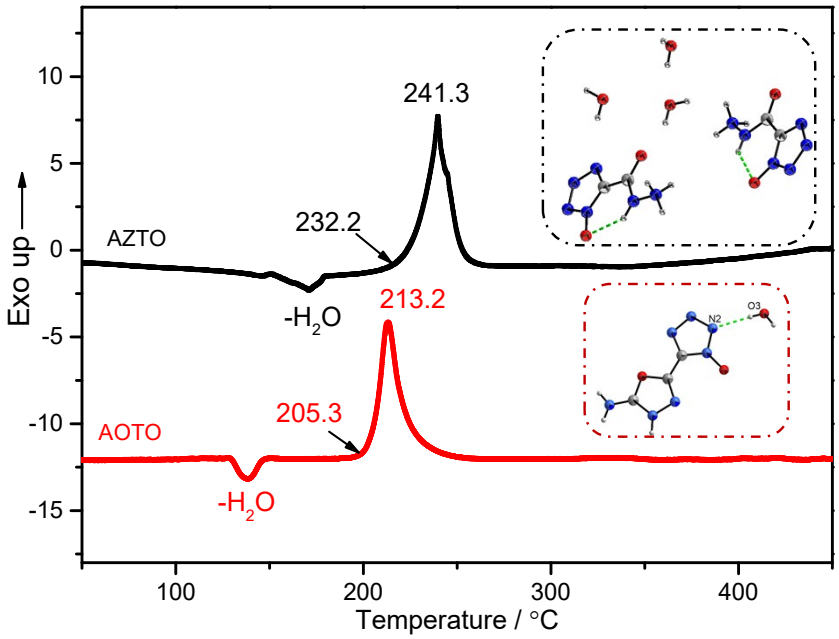

Figure S16 The differential scanning calorimetry (DSC) curves of compounds **AZTO** and

AOTO at a heating rate of 5 K min^{-1}.