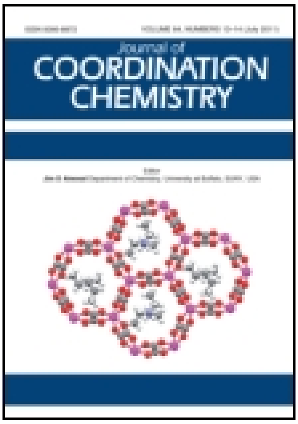

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Syntheses, crystal structures, and catalytic activities of three new Cu(II) coordination polymers based on 2-(1H-1,2,4-triazole)-1-acetic acid

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Syntheses, crystal structures, and catalytic activities of three new Cu(II) coordination polymers based on 2-(1H-1,2,4-triazole)-1-acetic acid

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Three new coordination polymers, $\{[Cu(trza)(2,2'\text{-bipy})(H_2O)]\cdot(ClO_4)\}_n$ (**1**), $\{[Cu(trza)(2,2'\text{-bipy})(H_2O)]\cdot(BF_4)\}_n$ (**2**), and $\{[Cu(trza)(4,4'\text{-bipy})]\cdot(H_2O)\cdot(ClO_4)\}_n$ (**3**) (Htrza = 2-(*1H*-1,2,4-triazole)-1-acetic acid), have been synthesized and characterized by single-crystal X-ray diffraction analysis. Both **1** and **2** exhibit 1-D chain structure while **3** displays 2-D layer structure. The catalytic activities of **1** and **3** in the green oxidative coupling of 2,6-dimethylphenol have been investigated.

Keywords: 2-(*1H*-1,2,4-Triazole)-1-acetic acid; Crystal structure; Catalytic properties

1. Introduction

Copper complexes have a variety of interesting structures and potential applications as functional materials in catalysis, molecular magnetism, metalloproteins, and enzymes [1, 2]. As a typical catalytic application of copper complexes, oxidative coupling of 2,6-dimethylphenol (DMP) has received attention, because the product of this reaction, poly(1,4-phenylene ether) (PPE), is a valuable engineering plastic [3–6]. Traditionally, the coupling reaction is carried out homogeneously in organic solvents resulting in growing environmental pollution [7–10]. The green oxidative coupling of DMP in environmentally friendly solvents with clean oxidants is extremely rare, a remaining challenge of "green chemistry and technology." The development of copper-containing catalysts suited for mild "green" conditions, and the investigation of catalytic–structural correlations have great importance of exploiting new catalysts. We prepared three Cu^{II} complexes: $\{[Cu(trza)(2,2'\text{-bipy})(H_2O)]\cdot(ClO_4)\}_n$ (**1**), $\{[Cu(trza)(2,2'\text{-bipy})(H_2O)]\cdot(BF_4)\}_n$ (**2**), and $\{[Cu(trza)(4,4'\text{-bipy})]\cdot(H_2O)\cdot(ClO_4)\}_n$ (**3**). To replace

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traditional organic media, we explored an aqueous catalytic process for the oxidative coupling of DMP by using hydrogen peroxide as oxidant and complexes **1–3** as catalysts.

2. Experimental

2.1. *Materials and measurements*

All chemicals were obtained from commercial sources and used without purification. The ligand 2-(*1H*-1,2,4-triazole)-1-acetic acid was prepared by the method described in the literature [11]. Elemental analyses (C, H, and N) were determined on a Flash EA 1112 analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} on a BRUKER TENSOR 27-FTIR spectrophotometer with pressed KBr pellets.

2.2. *Synthesis of* $\{[Cu(trza)(2,2'\text{-}bipy)(H_2O)]\cdot(ClO_4)\}_n$ *(1)*

An aqueous solution of 0.1 mol L^{-1} NaOH (1 mL) was added to an ethanol solution (4 mL) of Htrza (0.0081 g, 0.05 mmol) and 2,2′-bipy (0.0078 g, 0.05 mmol), and then a 1 mL aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0185 g, 0.05 mmol) was added dropwise. The solution was filtered and the filtrate was allowed to stand at room temperature. Blue block-shaped single crystals were obtained after 1 week. Yield: 73% (based on Cu). Anal. Calcd for $C_{14}H_{14}ClCuN_5O_7$ (%): C, 36.42; H, 2.60; N, 15.18. Found (%): C, 36.40; H, 2.59; N, 15.19. IR data (KBr, cm^{-1}): 3565.15(w), 3362.52(w), 3144.73(w), 2952.96(m), 1637.11(s), 1603.13(m), 1539.07(m), 1495.25(m), 1473.51(m), 1447.74(m), 1387.92(s), 1316.46(m), 1287.20(s), 1222.81(w), 1140.93(m), 1078.06(s), 906.44(w), 879.08 (w), 799.65(m), 773.93(s), 733.27(m), 710.67(s), 675.44(m), 590.96(w), 522.86 (w), 420.78(w).

2.3. *Synthesis of* $\{[Cu(trza)(2,2'\text{-}bipy)(H_2O)]\cdot(BF_4)\}_n$ *(2)*

The procedure was the same as that for **1** except that $Cu(ClO_4)_2 \cdot 6H_2O$ was replaced by $Cu(BF_4)_2 \cdot 6H_2O$. Yield: 68% (based on Cu). Anal. Calcd for $C_{14}H_{14}BCuF_4N_5O_7$ (%): C, 37.28; H, 3.1; N, 15.53. Found (%): C, 37.27; H, 3.2; N, 15.55; IR data (KBr, cm^{-1}): 3567.20(w), 3354.91(w), 3136.87(w), 1635.81(s), 1603.10(m), 1537.73(m), 1472.31(m), 1446.92(m), 1386.07(s), 1287.03(s), 1110.26(s), 906.42(w), 879.06 (w), 799.65(m), 773.95(s), 709.99(s), 674.63(m), 623.85(m), 420.78(w).

2.4. *Synthesis of* $\{[Cu(trza)(4,4'\text{-}bipy)]\cdot(H_2O)\cdot(ClO_4)\}_n$ *(3)*

The procedure was the same as that for **1** except that 2,2′-bipy was replaced by 4,4′-bipy. Yield: 15% (based on Cu). Anal. Calcd for $C_{28}H_{28}Cl_2Cu_2N_{10}O_{14}$ (%): C, 36.26; H, 3.02; N, 15.11. Found (%): C, 36.27; H, 3.01; N, 15.13; IR data (KBr, cm^{-1}): 3445.93(w), 3130.94(w), 1647.31(s), 1613.77(s), 1534.51(m), 1492.36(m), 1396.13(s), 1323.55(m), 1222.29(m), 1088.64(s), 1028.70(w), 815.95(m), 672.47(m), 625.47(m), 593.04(m), 473.37(w).

Table 1. Crystallographic data and structure refinement parameters for **1**–**3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_{14}H_{14}ClCuN_5O_7$	$C_{14}H_{14}BCuF_4N_5O_3$	$C_{28}H_{28}Cl_2Cu_2N_{10}O_{14}$
Formula weight	461.28	450.65	926.58
Temperature (K)	293(2)	293(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
Unit cell dimensions (Å, °)			
a	13.040(3)	12.856(3)	9.211(4)
b	14.570(3)	14.594(3)	17.746(8)
c	9.771(2)	9.7441(19)	11.124(5)
α	90	90	90
β	107.17(3)	107.27(3)	103.6895
γ	90	90	90
Volume (Å^3), Z	1733.56, 4	1745.8(6), 4	1766.8(14), 2
Reflections collected	19,076	18,605	11,530
Reflections unique	3472	3398	6461
Refinement parameters	253	253	505
Parameter restraints	0	0	61
R(int)	0.0426	0.0385	0.0413
Absorption coefficient, μ (mm^{-1})	1.433	1.319	1.438
Calculated density (g cm^{-3})	1.728	1.715	1.742
F(000)	932	908	940
Goodness-of-fit on F^2	1.132	1.048	1.561
R_1, wR_2 ($I > 2\sigma(I)$)	0.0506, 0.1135	0.0490, 0.1432	0.0610, 0.0776
R_1, wR_2 (all data)	0.0586, 0.1188	0.0576, 0.1602	0.1123, 0.0841
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.457, −0.327	0.659, −0.573	0.719, −0.784

$R_1 = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

2.5. *Single-crystal structure determination*

The intensity data for **1** and **2** were collected at 291(2) K on a Ragiku AFC10Saturn72 CCD and **3** were collected at 293(2) K on a Bruker Smart Apex CCD; both diffractometers are equipped with graphite-monochromated Mo-Kα radiation with wavelength of 0.71073 Å using the *w*-scan technique. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were assigned with common isotropic displacement factors and included in the final refinement by using geometric constraints. The final cycle of full-matrix least-squares refinement was based on the observed reflections and variable parameters. Complex **3** is a racemic twinning and crystallizes in space group $P2_1$. All calculations were performed using SHELXS-97 and SHELXL-97 programs [12, 13]. Table 1 shows crystallographic data of **1**–**3**. Selected bond distances and angles for **1**–**3** are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of* $\{[Cu(trza)(2,2'\text{-}bipy)(H_2O)]\cdot(ClO_4)\}_n$ *(1)*

Single-crystal X-ray diffraction reveals that polymer **1** crystallizes in the monoclinic space group $P2_1/c$ and exhibits a 1-D wave-like structure. The asymmetric unit consists of one Cu(II), one trza$^-$, one 2,2′-bipy, one coordinated water molecule, and one

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

Complex **1**			
Cu(1)–N(5)#1	1.977(3)	N(1)–Cu(1)–O(1)	91.46(11)
Cu(1)–N(1)	1.986(3)	N(5)#1–Cu(1)–N(2)	97.49(12)
Cu(1)–O(1)	2.008(2)	N(1)–Cu(1)–N(2)	80.53(12)
Cu(1)–N(2)	2.038(3)	O(1)–Cu(1)–N(2)	148.21(10)
Cu(1)–O(7)	2.274(3)	O(1)–Cu(1)–O(7)	98.36(10)
N(5)#1–Cu(1)–N(1)	170.37(12)	N(2)–Cu(1)–O(7)	111.81(11)
N(5)#1–Cu(1)–O(1)	94.99(11)	N(1)–Cu(1)–O(7)	87.34(11)
N(5)#1–Cu(1)–O(7)	84.65(11)		
Complex **2**			
Cu(1)–N(3)	1.971(3)	N(3)–Cu(1)–N(4)	97.31(13)
Cu(1)–O(1)#1	2.009(2)	N(5)–Cu(1)–N(4)	80.68(14)
Cu(1)–N(5)	1.990(3)	O(1)#1–Cu(1)–N(4)	147.83(11)
Cu(1)–N(4)	2.031(3)	N(5)–Cu(1)–O(3)	87.61(12)
Cu(1)–O(3)	2.276(3)	O(1)#1–Cu(1)–O(3)	97.83(11)
N(3)–Cu(1)–N(5)	170.73(13)	N(4)–Cu(1)–O(3)	112.85(13)
N(3)–Cu(1)–O(1)#1	94.78(12)	N(3)–Cu(1)–O(3)	84.83(12)
N(5)–Cu(1)–O(1)#1	91.56(12)		
Complex **3**			
Cu(1)–O(2)#1	1.947(4)	N(8)#2–Cu(1)–N(3)	91.21(17)
Cu(1)–N(7)	2.026(4)	O(2)#1–Cu(1)–O(3)	125.63(17)
Cu(1)–N(8)#2	2.032(4)	N(7)–Cu(1)–O(3)	86.18(19)
Cu(1)–N(3)	2.058(5)	N(8)#2–Cu(1)–O(3)	92.19(19)
Cu(1)–O(3)	2.249(4)	N(3)–Cu(1)–O(3)	92.27(16)
Cu(2)–O(4)#3	1.945(4)	O(4)#3–Cu(2)–N(9)	90.29(17)
Cu(2)–N(9)	2.008(4)	N(9)–Cu(2)–N(10)#2	176.24(19)
Cu(2)–N(10)#2	2.015(4)	O(4)#3–Cu(2)–N(6)	143.68(19)
Cu(2)–N(6)	2.034(5)	O(4)#3–Cu(2)–N(10)#2	85.96(17)
Cu(2)–O(1)	2.262(4)	N(9)–Cu(2)–N(6)	90.82(17)
O(2)#1–Cu(1)–N(7)	89.14(17)	N(10)#2–Cu(2)–N(6)	92.32(17)
O(2)#1–Cu(1)–N(8)#2	88.90(17)	O(4)#3–Cu(2)–O(1)	121.38(16)
N(7)–Cu(1)–N(8)#2	176.1(2)	N(9)–Cu(2)–O(1)	91.96(19)
O(2)#1–Cu(1)–N(3)	142.08(19)	N(10)#2–Cu(2)–O(1)	89.8(2)
N(7)–Cu(1)–N(3)	92.43(18)	N(6)–Cu(2)–O(1)	94.86(17)

Symmetry transformations used to generate equivalent atoms in **1**: #1: $-x+1$, $y-1/2$, $-z+1/2$; in **2**: #1: $-x+2$, $y-1/2$, $-z+1/2$; #1: $x-1$, y, z; #2: x, y, $z+1$; #3: $x+1$, y, z.

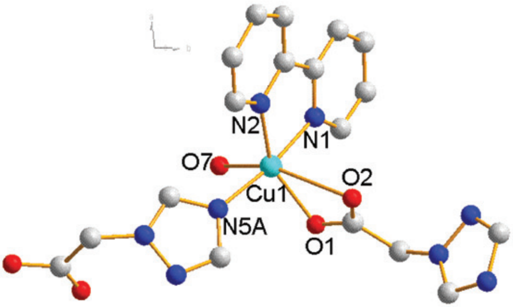


Figure 1. The coordination environment of Cu(II) in **1**. Hydrogens have been omitted for clarity.

uncoordinated ClO_4^-. As depicted in figure 1, Cu(II) lies in a distorted octahedral environment and is six-coordinate from N1 and N2 from one 2,2′-bipy, two carboxylate oxygens (O1, O2) from one trza$^-$, one nitrogen (N5A) from another equivalent trza$^-$ anionic ligand and one oxygen (O7) from water. O1, O2, N2, and O7 are in the

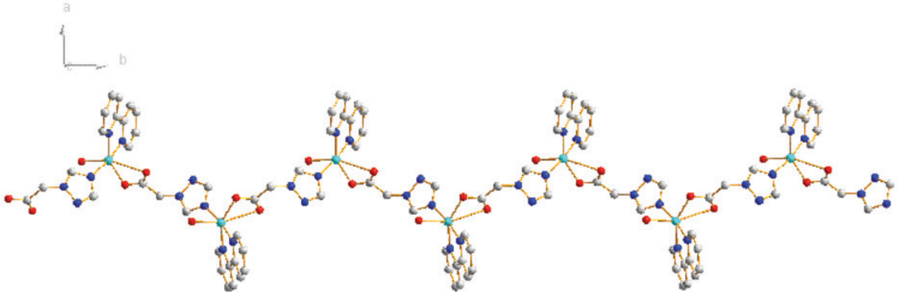


Figure 2. The 1-D chain in **1**. Hydrogens have been omitted for clarity.

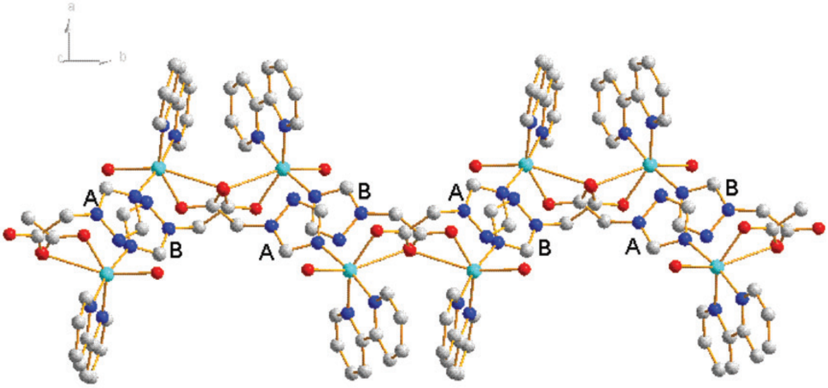


Figure 3. The π–π stacking interactions in **1**. Hydrogens have been omitted for clarity.

equatorial plane, N1 and N5A are in axial sites. The ClO_4^- only balances the charges and does not participate in coordination. The Cu–N bond lengths vary from 1.977(3) to 2.038(3) Å. The Cu–O bond lengths range between 2.008(2) and 2.274(3) Å. The Cu(II)'s are connected along the *b*-axis through trza$^-$ to form 1-D chains (figure 2).

As depicted in figure 3, **1** has π–π interactions between contiguous triazole rings (A and B). The triazole rings are parallel with an interplanar distance of 2.2265 Å.

3.2. *Crystal structure of* $\{[Cu(trza)(2,2'\text{-bipy})(H_2O)]\cdot(BF_4)\}_n$ *(2)*

The structure of **2** is analogous to that of **1** except that the BF_4^- replaces the ClO_4^-. Accordingly, no details about the structure of **2** are discussed here.

3.3. *Crystal structure of* $\{[Cu(trza)(4,4'\text{-bipy})]\cdot(H_2O)\cdot(ClO_4)\}_n$ *(3)*

Complex **3** is a 2-D coordination polymer and crystallizes in the monoclinic space group *P2₁*. The asymmetric unit contains two Cu(II)'s, two trza$^-$, two 4,4′-bipy, two uncoordinated water molecules, and two ClO_4^-. As depicted in figure 4, Cu1 (or Cu2) shows a distorted tetragonal pyramid, coordinated by N7, N8B (N9, N10B) from two

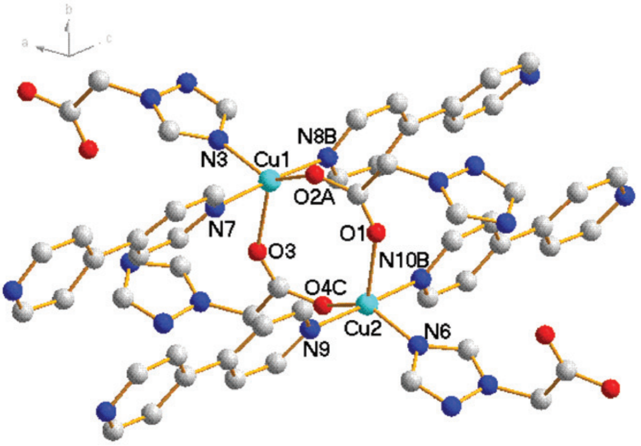


Figure 4. The coordination environment of Cu(II) in **3**. Hydrogens have been omitted for clarity.

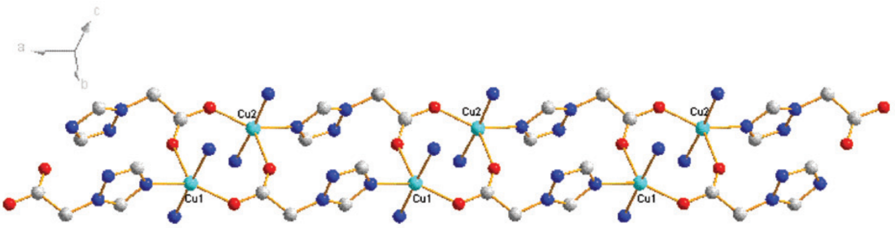


Figure 5. The 1-D double chain of $[Cu(trza)]_n$ in **3**. Hydrogens have been omitted for clarity.

4,4′-bipy ligands, N3 (N6) and O2A, O3 (O1, O4B) from three individual trza$^-$. N7, O3, O2A, and N8B (N9, O4B, O1, and N10B) are in the base of the tetragonal pyramid with N3 (N6) apical. The Cu–N bond lengths vary from 2.008(4) to 2.058(5) Å. The Cu–O bond lengths are 1.945(5)–2.262(4) Å. The O–Cu–N angles are 85.96(17)143.68(19)°, N–Cu–N angles are 90.82(17)176.24(19)°, and O–Cu–O angles are 121.38(16)–125.63(17)°.

In **3**, with its chelating-bridging carboxyl and bridging triazole, each trza$^-$ is bound to three Cu(II) centers as a tridentate ligand. In the [100] direction, adjacent Cu(II) ions are linked by carboxyl to generate a 1-D $[Cu_2(trza)_2]_n$ double chain (figure 5). In the double chain, two contiguous Cu(II) ions are fused through bidentate carboxylate to form a bimetallic unit $[Cu_2(OCO)_2]$ and a 16-number ring $[Cu_2(trza)_2]$; the Cu$\cdots$Cu distance is 4.1370(17) Å in $[Cu_2(OCO)_2]$ and 6.9443(27) Å in $[Cu_2(trza)_2]$. Adjacent chains are fused through 4,4′-bipy, generating a 2-D layer in the *ac* plane (figure 6).

As depicted in figure 7, there are π–π interactions between contiguous triazole rings or between 4,4′-bipy rings in **3**. The interplanar distance and the dihedral angle of contiguous triazole rings are 4.0065 Å and 8.2°. The interplanar distance and the dihedral angle of contiguous 4,4′-bipy rings are 3.9507 Å and 5.0°. There are also hydrogen bonds from uncoordinated water (O13 or O14) to hydrogens of O6, O8, or O9 of perchlorate or the nitrogen (N5) of triazole, forming four kinds of hydrogen bonds (table 3). The hydrogen-bond distances of O(13)$\cdots$O(6), O(14)$\cdots$O(8),

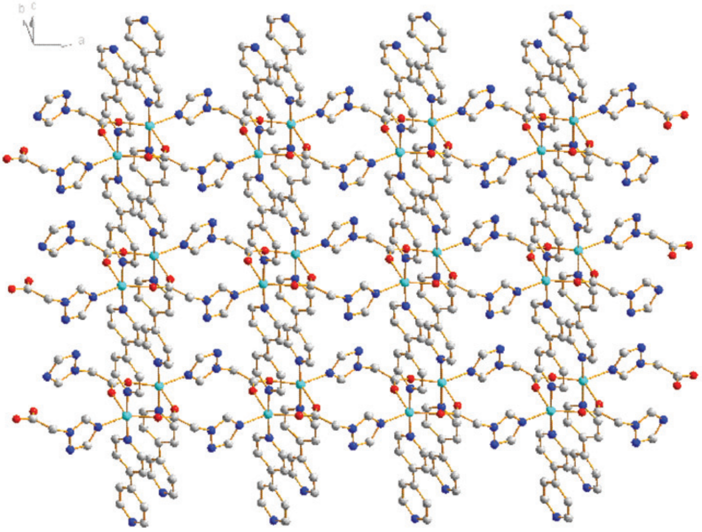


Figure 6. The 2-D layer in **3**. Hydrogens have been omitted for clarity.

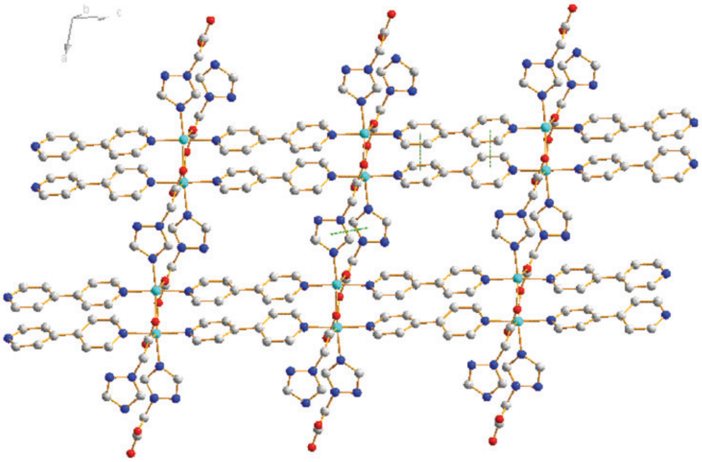


Figure 7. The π–π stacking interactions in **3**. Hydrogens have been omitted for clarity.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **3**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(14)–H(4W)···O(9)	0.80	2.64	3.213(9)	129.8
O(14)–H(3W)···O(8)	0.84	2.25	3.031(9)	154.4
O(13)–H(1W)···N(5)	0.84	2.28	3.083(7)	160.0
O(13)–H(2W)···O(6)	0.84	2.47	3.250(8)	155.4

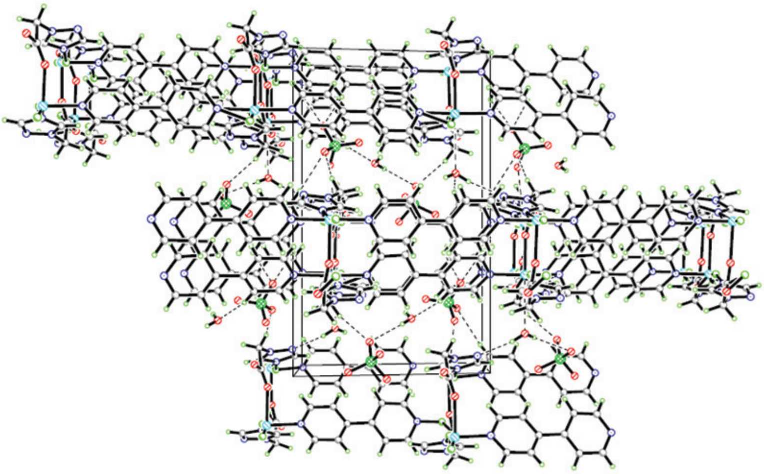


Figure 8. The 3-D supramolecular structure of **3**.

O(14) $\cdots$ O(9), and O(13) $\cdots$ N(5) are 3.250(8) Å, 3.031(9), 3.213(9), and 3.083(7) Å. As shown in figure 8, π–π interactions and hydrogen bonds further link the 2-D layers to form a stable 3-D supramolecular framework.

The structure of **3** is clearly distinguished from those of $\{[Cu(tza)(phen)](ClO_4)\}_n$ and $[Cu(Himc)_2]$ in which similar ligands tetrazole-1-acetate and 1*H*-imidazole-2-carboxylic acid are employed, respectively [14, 15]. $[Cu(Himc)_2]$ is a mononuclear structure. Polymer $\{[Cu(tza)(phen)](ClO_4)\}_n$ has a 1-D zigzag double-chain structure in which Cu(II) is coordinated by three nitrogens from one phen, one tza, and two oxygens from two tza ligands. Each tza is μ_3-bridging, linking Cu(II) ions into a 1-D zigzag double-chain structure. The 3-D supramolecular structure is formed by π–π stacking and C–H non-classical hydrogen bonds. By contrast with $\{[Cu(tza)(phen)](ClO_4)\}_n$, in **3**, Cu(II) ions are linked by trza$^-$ generating a $[Cu_2(trza)_2]_n$ double chain. In this regard, there is comparability in them. Differently, the latter form a 2-D layer structure by adjacent chains fused through 4,4′-bipy.

3.4. *Catalytic activities of 1 and 3*

Poly(1,4-phenylene ether) (PPE) is a valuable industrial thermoplastic with excellent mechanical properties and chemical resistance, so the oxidative coupling polymerization of 2,6-dimethylphenol (DMP) using copper complexes as catalysts to produce PPE has received considerable attention [16, 17]. However, green oxidative coupling of DMP in environmentally friendly solvents with clean oxidants and development of efficient copper-containing catalysts suited for milder "green" conditions are desired.

In 2008, Zhang *et al.* [18] reported an aqueous catalysis process of oxidative coupling of DMP using hydrogen peroxide as oxidant and several copper complexes as catalysts and optimized reaction conditions of this reaction system. Herein, we study the catalytic activities of **1** and **3** in the same optimized reaction conditions to exploit new

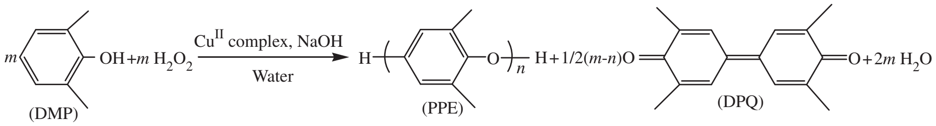
Table 4. Oxidative coupling of DMP catalyzed by **1** and **3**.[a]

Catalysts	Conversion (%)[b]	Yield (%)[b]		Selectivity (%)[c]
		PPE	DPQ	
1	72	39.5	18.8	67.8
3	88	32.7	9.8	76.9

[a] Optimized conditions: DMP (1 mmol), NaOH (1 mmol), H_2O_2 (20 μL), and catalyst (0.02 mmol) in 5 mL of water for 8 h at 50°C.

[b] Conversions and isolated yields based on the DMP, average of two runs.

[c] Selectivity = ([PPE] × 100)/([PPE] + [DPQ]).



Scheme 1. The oxidative coupling of 2,6-dimethylphenol in water.

catalysts (table 4). The oxidative coupling polymerization of 2,6-dimethylphenol in water is shown in scheme 1.

In the general procedure for catalytic oxidative coupling of 2,6-dimethylphenol (122 mg, 1 mmol), sodium hydroxide (40 mg, 1 mmol), and sodium *n*-dodecyl sulfate (SDS) (29 mg, 0.1 mmol) were dissolved in water (5 mL) in a 10 mL flask. The 2 mol% complex that was ground well into appropriate sizes prior to use was added to the above solution, and the mixture was vigorously stirred under air at 50°C. Then, hydrogen peroxide (30% aqueous solution) was slowly added into the mixture using a microinjector every 15 min for two times. After 8 h, the reaction was stopped and sodium chloride (1.17 g, 0.02 mol) was added into the mixture. Then the mixture was transferred into a separatory funnel, a few milliliters of CH_2Cl_2 as the extractant was added and the organic materials were extracted, which was repeated three times. The organic extracts were combined and dried with anhydrous $MgSO_4$. The solvent, after being filtered, was evaporated *in vacuo*. The products were separated by preparative TLC performed on dry silica gel plates with ethyl ether–petroleum ether (1 : 3 v/v) as the developing solvents.

4. Conclusions

Three inorganic–organic supramolecular networks based on 2-(*1H*-1,2,4-triazole)-1-acetic acid and Cu(II) salts have been prepared and structurally characterized by single-crystal X-ray diffraction. Using **1** and **3** as catalysts, an aqueous catalytic process for oxidative coupling of 2,6-dimethylphenol show that **1** and **3** have significant advantages compared with those employed in organic systems from the standpoint of "green chemistry."

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center (CCDC 777491, 777492, and 777493). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; E-mail: teched@chemcrys.cam.ac.uk).

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