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Design and Synthesis of Functionalized Coordination Polymers as Recyclable Heterogeneous Photocatalysts

Cai-Ping Ye, ^a Gan Xu, ^a Zheng Wang, ^a Jie Han, ^b Lian Xue, ^a Fu-Yu Cao, ^a Qi Zhang, ^a Lin-Feng Yang, ^a Li-Zhou Lin, ^a Xu-Dong Chen^{a,}*

^a Jiangsu Collaborative Innovation Center of Biomedical Functional Materials and Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, China

^b School of Science & Technology, The Open University of Hong Kong, Kowloon, Hong Kong SAR, PR China

*Correspondence e-mail: xdchen@ninu.edu.cn

Abstract: The functionalized ligand 9.10-anthraguinone-1,4-dicarboxylate acid (H₂AQDC), has been designed and synthesized in order to develop metal-organic coordination polymers as heterogeneous catalyst with photosensitizing feature. Two major considerations of ligand design are anthraquinone moieties for photosensitizing to harvest light and carboxylate groups for polymeric coordination toward less solubility. A series of transition metal complexes based on this ligand have been synthesized subsequently, namely {Co(AQDC)(H₂O)₃·2H₂O}₀ (Co-AQDC), ${Ni(AQDC)(H_2O)_3 \cdot 2H_2O}_n$ (Ni-AQDC) { $[Cu(AQDC)(H_2O)_3][Cu(AQDC)(H_2O)_2(DMF)] \cdot (H_2O)_4$ }_n (Cu-AQDC) $\{Zn_{1.5}(AQDC)(OH)(H_2O)_2 \cdot H_2O\}_{n}$ (Zn-AQDC), {Ag₂(AQDC)(CH₃OH)}_n (Ag-AQDC). Both the ligand itself and its transition metal complexes are able to catalyze the visible-light driven oxidation reactions of alkynes into 1,2-di-ketones in air under mild conditions, in which compound Ni-AQDC demonstrates the best activity. This catalyst can be easily isolated from the reaction mixture by filtration with trace amount of loss in solution and is ready for recycled use after simple washing and drying without any need for regeneration. Remarkably, the catalyst shows no loss of activity after five catalytic cycles and X-ray powder diffraction proves no change of structure after five runs. This designed metal-organic coordination polymer represents an environmentally friendly economic and recyclable photocatalyst, constituting a good candidate for photocatalytic organic syntheses in terms of green chemistry.

Introduction

Coordination polymers constructed by organic linkers and inorganic nodes has seen rapid development in the field of supramolecular catalysis, attributed to their features such as easy isolation and potentially high atom economy.^{1.4} The intrinsic characteristics of coordination polymers, for example low solubility in common solvents, highly ordered structures and easy functionalization through design and modification, make them perfect candidates for heterogeneous catalysis. However, their applications in photocatalytic organic transformations have been scarce.^{5.9}

Visible-light driven organic transformations has in recent years attracted intense research interests owing to the natural abundance of light which is renewable and sustainable.¹⁰⁻¹⁴ Metal (Ru^{II}, Ir^{III}, Re^I and Os^{II}) polypyridine complexes¹⁵⁻¹⁷ and organic dyes¹⁸⁻¹⁹ represent two typical categories of photocatalysts for visible-light driven photoredox processes, and have been extensively studied in homogenous synthetic organic systems. Heterogeneous photocatalysts sensitizing visible light, including MOFs^{20,21} and semiconductive metal oxide,²² have also been investigated for their unique feature of easy isolation as well as the potential of recycled usage. However, most of these photocatalysts suffer from disadvantages in such aspects as difficulties in efficient recovering and significant

loss of activity during recycling. It is still highly desirable to develop efficient heterogeneous photocatalysts with good recyclability in terms of green chemistry.

In seeking photocatalysts that is recyclable, our attention has been focused in the development of coordination polymers with functionalized ligands, which might provide the possibility of heterogeneous photocatalysis. Carboxylate groups represent a very important category of binding sites in organic ligands for coordination polymers with desired structures and thus becomes an inevitable choice of our ligand design.²³ The idea of ligand functionalization was inspired by the important role of quinones in biological systems as photosensitizer²⁴⁻²⁵ and their rich redox properties involving processes such as single electron transfer and proton-coupled electron transfer.²⁶⁻²⁷ Therefore, ligand 9,10-anthraquinone-1,4-dicarboxylic acid (H₂AQDC) has been designed and synthesized. The expectation is that anthraquinone portion behaves as photosensitizer to harvest light and carboxylate groups bind metal ions to form coordination polymers. Subsequently, a series of transition metal complexes based on this ligand have been synthesized as potential photocatalysts.

To investigate the photocatalytic property of the metal complexes thus synthesized, the reaction of photocatalytic oxidation of diarylethyne analogues into 1,2-diketones has been selected as the substrate reaction. 1,2-Diketones are important organic molecules for synthesizing heterocyclic compounds with biological activity, which have attracted intense synthetic interests using catalysts such as metal complexes involving Pd,²⁸⁻²⁹ Ru,³⁰⁻³¹ Au,³² and Cu,³³ and organic dye eosin Y as well.³⁴ But same issue exists that the catalysts are not recyclable, despite the large amount of efforts in this area. Our investigation has demonstrated that both the H₂AQDC ligand itself and its transition metal complexes are able to catalyze the air-oxidation reactions of alkynes to produce 1,2-diketones under the irradiation of visible light, in which the Ni(II) complex exhibits the best catalytic activity. This catalyst can be readily recovered without loss of mass and change in structure, and remarkably, it can be efficiently recycled to sustain at least five catalytic cycles without loss of activity.

Experimental Section

General materials and measurements

All reagents and solvents were purchased from commercial sources and used without further purification. The ligand H₂AQDC, was synthesized using a modified procedure as reported.³⁵ Elemental analyses were performed using a PE-240C elemental analyzer. Thermal analyses were carried out on a Mettler-Toledo TGA/DSC STARe system in the temperature range of 28 to 800 °C with a heating rate of 10 °C·min⁻¹, under nitrogen flow. Infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets in the range of 4000 to 400 cm⁻¹. Powder X-ray diffraction (PXRD) was done with a MiniFlex 600 X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 KV and 40 mA. ¹H and ¹³C NMR spectra were obtained in CDCl₃ solvent on a Bruker 400 MHz spectrometer.

Synthesis of metal complexes

{Co(AQDC)(H₂O)₃·2H₂O}_n (Co-AQDC). A mixture of Co(OAc)₂·4H₂O (12.4 mg, 0.05 mmol) and H₂AQDC (14.8 mg, 0.05 mmol) were dissolved into 5.0 mL water. After stirring, the resultant solution was allowed to evaporate at room temperature for 15 days to afford pink needle-like crystals, which were collected by filtration and washed with water and acetone (15.1 mg, yield: 68%). *Anal.* Calcd for **Co-AQDC** (C₁₆H₁₆O₁₁Co): C, 43.36; H 3.64. Found: C, 43.38; H, 3.69. IR (KBr cm⁻¹): 1672(s, C=O), 1573(vs, carboxylate C=O), 1265(s, C-O).

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 ${Ni(AQDC)(H_2O)_3 \cdot 2H_2O}_n$ (Ni-AQDC). This complex was obtained by the same procedure as that for Co-AQDC except that Ni(OAc)_2 \cdot 4H_2O was used instead of Co(OAc)_2 \cdot 4H_2O as starting material. Green crystals were obtained by filtration and washed with water and acetone (11.7 mg yield: 53%). *Anal*. Calcd for Ni-AQDC (C₁₆H₁₆O₁₁Ni): C 43.38, H 3.64; Found: C 43.37, H 3.97. IR (KBr, cm⁻¹): 1670(s, C=O), 1591(s, carboxylate C=O), 1265(s, C-O).

 $\{ [Cu(AQDC)(H_2O)_3] [Cu(AQDC)(H_2O)_2(DMF)] \cdot (H_2O)_4 \}_n \quad (Cu-AQDC). \text{ To } 3.0 \text{ mL DMF solution of } CuCl_2 \cdot 2H_2O (17.1 \text{ mg}, 0.1 \text{ mmol}) \text{ was added } H_2AQDC (29.6 \text{ mg}, 0.1 \text{ mmol}) \text{ in } 3.0 \text{ mL DMF. Filtration followed by ether diffusion afforded green crystals (34.7 mg, yield: 64%).$ *Anal.*Calcd for**Cu-AQDC**(C₃₅H₃₇O₂₂NCu₂): C 44.22, H 3.92. Found: C 44.18, H 3.89. IR (KBr, cm⁻¹): 1672(s, C=O), 1585(s, carboxylate C=O), 1265(s, C-O).

 $\{Zn_{1.5}(AQDC)(OH)(H_2O)_2 \cdot H_2O\}_n$ (Zn-AQDC). Aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), H_2AQDC (14.8 mg, 0.05 mmol) and NaOH (4.0 mg, 0.10 mmol) were mixed together, followed by acetone diffusion to give orange crystals (17.4 mg, yield: 75%). *Anal.* Calcd for **Zn-AQDC** ($C_{16}H_{13}O_{10}Zn_{1.5}$): C 41.48, H 2.83. Found: C 41.43, H 2.83. IR (KBr, cm⁻¹): 1670(s, C=O), 1583(s, carboxylate C=O), 1265(s, C-O).

 $\{Ag_2(AQDC)(CH_3OH)\}_n$ (Ag-AQDC). The ligand H₂AQDC (14.8 mg, 0.05 mmol) was dissolved into 3.0 mL methanol and this solution was carefully layered over 2.0 mL aqueous solution of AgClO₄ (20.7 mg, 0.1 mmol), with 5.0 mL buffer layer (1:1 water and methanol). Light yellow needle-like crystals were obtained after two days (26.1 mg, yield: 55%). *Anal.* Calcd for **Ag-AQDC** (C₁₇H₁₀O₇Ag₂): C 37.67, H 1.86. Found: C 37.70, H 1.86. IR (KBr, cm⁻¹): 1664(s, C=O), 1591(s, carboxylate C=O), 1269(s, C-O).

Typical procedure for photocatalytic experiment

A mixture of photocatalyst (0.02 mmol), 1,2-diarylethyne (0.2 mmol) and 4-chlorobenzenethiol (57.8 mg, 0.4 mmol) was dissolved into 2.0 mL MeCN. The reaction mixture was stirred at room temperature under the irradiation of blue LED for 72h in ambient air. Filtration was done after the reaction is complete. The insoluble photocatalyst thus isolated is ready for recycled use after dichloromethane washing and vacuum drying. The filtrate containing final product was evaporated to dryness and subjected to column chromatography (silica gel, petroleum ether/ethyl acetate) to afford pure 1,2-diketone product. The yields reported are based on isolated pure product and characterization was done by ¹H and ¹³C NMR spectroscopy (see Supporting Information for spectra and product details).

Single crystal X-ray crystallography

Single crystal X-ray diffraction data of all five complexes were collected at 293K on Bruker APEX II CCD diffractometer operating at 50 KV and 30 mA using Mo *K*a radiation ($\lambda = 0.71073$ Å). Data was integrated by SAINT and scaled with either a numerical or multi-scan absorption correction using SADABS.³⁶ All structures were solved by direct methods or Patterson maps³⁷ and refined by full-matrix least squares on *F*² using SHELXL-2014³⁸ and OLEX2³⁹ program. All non-hydrogen atoms were refined anisotropically. Non-water hydrogen atoms were added at calculated positions and refined using a riding model. Hydrogen atoms of water molecules were located by different Fourier map and refined using riding model at restrained distance of 0.86 Å. Crystallographic data for all five complexes are summarized in Table 1 and selected bond lengths and angles are listed in Table S1. CCDC 1821544 (**Co-AQDC**), 1821545 (**Ni-AQDC**), 1821546 (**Zn-AQDC**), and 1821547 (**Ag-AQDC**) containing the supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

 Table 1
 Crystallographic data for metal complexes based on AQDC²⁻ ligand.

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	Co-AQDC	Ni-AQDC	Cu-AQDC	Zn-AQDC	Ag-AQDC
Empirical formula	C ₁₆ H ₁₆ CoO ₁₁	C ₁₆ H ₁₆ NiO ₁₁	C35H37Cu2NO22	C ₁₆ H ₁₃ O ₁₀ Zn _{1.5}	C17H10Ag2O7
Fw	443.22	443.00	950.73	463.32	542.00
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P21/c	P21/c	P21/c	P2₁/c	Pbca
a(Å)	10.693(2)	10.6610(18)	6.6984(11)	6.8037(11)	11.383(6)
b(Å)	21.451(4)	21.487(4)	21.754(4)	14.962(2)	9.236(5)
c(Å)	7.7724(14)	7.76743(13)	26.573(4)	15.720(3)	30.142(15)
<i>α</i> (°)	90	90	90	90	90
β (°)	102.437(2)	102.258(2)	96.302(2)	98.280(2)	90
γ(°)	90	90	90	90	90
V(Å)	1740.9(6)	1717.9(5)	3846.7(11)	1555.0(4)	3169(3)
Ζ	4	4	4	4	8
D _c (g·cm ⁻³)	1.691	1.713	1.642	1.979	2.272
µ(mm⁻¹)	1.048	1.192	1.198	2.394	2.511
F(000)	908	912	1952	936	2083
$R_1^{a}, w R_2^{b} [I > 2\sigma(I)]$	0.0328, 0.0865	0.0317, 0.0764	0.0718, 0.1368	0.0271, 0.0643	0.0307, 0.0619
R_1^{a} , wR_2^{b} (all data)	0.0456, 0.0937	0.0419, 0.0825	0.1391, 0.1602	0.0361, 0.0678	0.0506, 0.0686
(Δρ)max, (Δρ)min (e Å ⁻³)	0.89, -0.54	0.67, -0.44	1.05, -1.04	0.47, -0.52	0.72, -0.84

Results and Discussion

Design and Synthesis:

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Quinones are important photosensitive compounds in biological systems.²⁴⁻²⁵ Natural benzoquinones and anthraquinones participate in Type I and Type II photosensitization to produce singlet oxygen and superoxide anion for photooxidation reactions.⁴⁰⁻⁴¹ The nature and position of substituents determine the photochemical properties of anthraquinone derivatives, by affecting the electronic states and electron transitions. For example, 2-Cl-anthraquinone has shown exceptional reactivity over its analogs as photosensitizer in catalyzing certain organic transformations under the irradiation of fluorescent lamp.⁴²⁻⁴⁵ Anthraquinone moiety has thus been chosen as the functional group of our designed ligand for developing metal-organic coordination polymer with photosensitizing activity.

On the other hand, ligand with carboxylate groups has proven to be very successful in constructing coordination polymers such as metal-organic frameworks.¹⁹ So the combination of carboxylate groups with anthraquinone moiety might constitute perfect candidate for our designed ligand. Regarding the positions of substituting carboxylate groups, a preferable arrangement is *para*-positioned for polymeric coordination. And furthermore, close arrangement of the carboxylate and carbonyl groups will lead to significant steric hindrance between them, so that carboxylate groups will hold angles to the phenyl rings. As a result, the conjugation between anthraquinone plane and carboxylate groups will be broken, and the photochemical properties of the anthraquinone portion might be better maintained.

Therefore, the functionalized ligand 9,10-anthraquinone-1,4-dicarboxylic acid has been synthesized as a white solid in three steps using a modified procedure of the literature method.³¹. And transition metal complexes involving Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) based on AQDC²⁻ ligand have been prepared as crystalline solid by common solution method for synthesizing coordination compounds. All metal complexes were characterized by means of single-crystal and powder X-ray diffractions, infrared spectra and elemental analyses and their thermo-stabilities were studied (See Supporting Information for PXRD patterns and TGA curves).

Structure Analysis:



Scheme 1. Versatile coordination modes of the AQDC²⁻ ligand in its metal complexes.

A common feature of these coordination complexes is that they are all polymeric, indicating less solubility in common organic solvents and therefore dictating the possibility of heterogeneous catalysis and potential of easy recycling. Ascribed to rich coordination chemistry of carboxylate groups, the AQDC²⁻ ligand exhibits various coordination modes in this series of transition metal complexes (Scheme 1), resulting in versatile polymeric structures.

Complexes **Co-AQDC** and **Ni-AQDC** are isostructural, crystallizing in monoclinic space group $P2_1/c$. In both complexes, each metal center adopts a distorted octahedral geometry, coordinating to two carboxylate oxygen atoms from two symmetry related AQDC²⁻ ligands and four coordinated water molecules (Fig. 1a). The AQDC²⁻ ligands take μ_2 -bridging mode with both carboxylate groups participating into coordination. 2D layers in (010) plane has been formed through the connection of AQDC²⁻ ligands and μ_2 -bridging water molecules, which further packed together through the interactions of hydrogen bonding and π - π stacking (Fig. 1b and 1c).



Fig. 1 (a) Coordination geometry of Ni(II) center and binding mode of ligand in **Ni-AQDC**. (b) 2D network in **Ni-AQDC**. (c) Packing diagram of **Ni-AQDC**. Symmetry codes: ⁱ x-1, -y+1/2, z-1/2; ⁱⁱ x, -y+1/2, z-1/2; ⁱⁱⁱ x, -y+1/2; ⁱⁱⁱⁱ x, -y+1



Fig. 2 (a) Coordination geometries of Cu(II) centers and binding mode of ligand in **Cu-AQDC**. (b) 1-D chain structure in **Cu-AQDC** with *pseudo*-isostructural units. (c) Packing diagram of **Cu-AQDC**. Symmetry code: ⁱ x, y+1, z; ⁱⁱ x, y-1, z.

As shown in Fig. 2, the Cu(II) centers in **Cu-AQDC** adopt pyramidal coordination mode, with water ligands sitting on the apex of the pyramid at elongated coordination distances (Fig. 2a). Two carboxylate O atoms from oppositely positioned AQDC^{2–} ligands and one water molecule occupy three of the four corners of the pyramid base. The other corner is occupied by water and dimethylformamide alternatively to form *pseudo*-isostructural motifs, which are connected alternatively to form 1D chain structure along [010] direction (Fig. 2b). Hydrogen bonding and π - π stacking further assemble the chains into higher dimension (Fig. 2c).

There are two symmetry independent Zn(II) cations in **Zn-AQDC**, both taking slightly distorted octahedral geometry. Four symmetry related AQDC^{2–} ligands and two hydroxyl ions constitute the coordination sphere of one Zn(II) ion. And the other Zn(II) ion binds with two symmetry related AQDC^{2–} ligands, two water molecules and two hydroxyl ions (Fig. 3a). The hydroxyl ion exhibits a μ_3 -bridging mode, connecting three adjacent Zn(II) atoms to form a Zn₃ motif, which are further linked together by AQDC^{2–} ligand to generate a 3D non-porous supramolecular architecture (Fig. 3b). The AQDC^{2–} ligand links four Zn(II) cations through its carboxylate groups (Scheme 1).



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Fig. 3 (a) Coordination geometries of Zn(II) centers and binding mode of ligand in **Zn-AQDC**. (b) Packing diagram of **Zn-AQDC**. Symmetry codes: ⁱ x, -y+1/2, z-1/2; ⁱⁱ -x+1, y+1/2, -z+1/2; ⁱⁱⁱ -x+1, -y+1, -z; ^{iv} -x, -y+1, -z; ^v -x, y-1/2, -z+1/2.



Fig. 4 (a) Coordination geometries of Ag(I) centers and binding mode of ligand in **Ag-AQDC**. (b) 2-D bilayered structure in **Ag-AQDC**. (c) The 3D network structure of **Ag-AQDC**. Symmetry code: ⁱ -x+1/2, y+1/2, z; ⁱⁱ x+1, y, z; ⁱⁱⁱ -x+1, -y+1, -z+1; ^{iv} -x+1/2, y-1/2, z; ^v x-1, y, z.

Complex **Ag-AQDC** crystallizes in orthorhombic space group *Pbca*, in which short argentophilic interaction at 2.869 Å has been observed (Fig. 4a). The dimeric Ag-Ag moiety containing two crystallographically independent Ag(I) cations is surrounded by five symmetry related AQDC^{2–} ligands and one coordinated methanol molecule, which link

the dimeric moieties into 2D bilayer sheet (Fig. 4b). The layered structures further stack by Van der Waals interactions into 3D structure (Fig. 4c).

In accord with our ligand design, the two carboxylate groups of AQDC²⁻ ligand are not in the plane of the conjugated system due to steric hindrance with neighboring carbonyl groups, bearing dihedral angles ranging from 55.4° to 89.2° for this family of coordination polymers (Table 2). The ligand is slightly bent in it coordination polymers, as indicated by the dihedral angles of the two carbonyl groups and the central six-member ring and the deviation of atoms of the anthraquinone plane (Table 2).

Ascribed to the existence of coordinated and lattice water molecules, rich intra- and inter- molecular hydrogen bonds exist in the crystal packing of these compounds except that of the Ag(I) complex, leading to more stabilized stacking as solid materials (Table 3). Some of the hydrogen bonds are pretty strong with donor to acceptor distances between 2.5 to 2.6 Å.

Table 2 Metrics of ligand conformation in metal complexes.

	Dihedral angels (°)				Atomic deviation of the	
	carboxylate	groups VS	carbonyl groups VS attached six-member ring		anthraquinone plane (Å)	
	attached b	enzyl ring			Mean	Maximum
Co-AQDC	55.4(2)	86.1(2)	2.3(2)	12.1(1)	0.134(3)	-0.350(2)
Ni-AQDC	55.5(2)	86.1(2)	2.1(2)	11.7(1)	0.130(3)	0.340(2)
	88.1(2)	86.3(2)	2.9(1)	2.7(1)	0.048(7)	0.098(5)
Cu-AQDC	89.2(2)	87.4(2)	1.8(1)	1.8(1)	0.028(6)	0.066(5)
Zn-AQDC	80.1(1)	76.6(1)	3.6(1)	2.0(1)	0.054(2)	-0.112(2)
Ag-AQDC	64.2(2)	74.9(1)	3.2(3)	9.3(3)	0.132(6)	-0.301(4)

Table 3 Hydrogen bonding parameters in metal complexes of AQDC²⁻ ligand (Å and deg).

D-H A	d(H…A)	d(D…A)	∠DHA
Co-AQDC			
O10W-H10WA…O1	2.154	2.933	150.300
O10W-H10WB…O11W	2.142	2.979	164.470
O9W-H9WB…O10W	2.063	2.905	166.062
O7W-H7WB⋯O3 ⁱ	1.780	2.585	154.794
OW7-HW7A⋯O5 ⁱⁱ	1.751	2.576	159.894
D8W-H8WB…O6 [™]	1.863	2.705	165.982
O8W-H8WA…O11W ^{iv}	2.001	2.848	168.359
D9W-H9WB…O4 ^v	1.869	2.701	162.360
Symmetry codes: ⁱ x+1, -y+3/2, z+1/2; ⁱⁱ x, -y+3/2, z-1/2; ⁱⁱⁱ x, -y+3/2, z+1/2; ^{iv} -x+2, y+1/2, -z+3/2; ^v x+1, y, z.			
	Ni-AQ	DC	
D8W-H8WB…O11W	1.992	2.835	166.484
O9W-H9WB…O10W	2.061	2.896	163.418
D10W-H10WA…O1	2.072	2.921	168.737
D11W-H11WB…O2 ⁱ	2.089	2.933	166.727
O7W-H7WB⋯O3 ⁱ	1.752	2.573	158.801
O7W-H7WA⋯O5 ⁱⁱ	1.750	2.563	156.915
O8W-H8WA…O6 ^ⅲ	1.851	2.702	170.113
J9W-H9WA…O4 [™]	1.858	2.697	164.820
Symmetry codes: ⁱ x-1, -y+1/2, z-1/2; ⁱⁱ x, -y+1/2, z+1/2; ⁱⁱⁱ x, -y+1/2, z-1/2; ^{iv} x-1, y, z.			

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Cu-AQDC					
O13W-H13WB…O7	1.955	2.810	170.958		
O14W-H14WB…O20W	1.876	2.597	140.334		
O14W-H14WA…O21W	1.818	2.669	170.098		
O17W-H17WB…O18W	1.878	2.673	152.855		
O18W-H18WA…O5 ⁱ	1.966	2.809	166.373		
O19W-H19WB…O4 ⁱ	1.988	2.775	151.954		
O20W-H18WB…O12 ⁱ	1.949	2.732	146.128		
O21W-H21WA…O9 ⁱ	1.962	2.804	165.840		
Symmetry codes: ⁱ -x+2, -y+1, -z+1.					
Zn-AQDC					
O9W-H9WB…O10W	1.775	2.635	176.233		
O8W-H8WB…O6 ⁱ	1.906	2.734	161.009		
O9W-H9WA…O6 ⁱ	2.137	2.931	153.444		
08W-H8WA…O3 ⁱⁱ	1.970	2.815	166.963		
O10W-H10WB…O8 ^ⅲ	2.038	2.856	158.443		
O10W-H10WA…O2 ⁱ ∕	1.968	2.819	170.130		
Symmetry codes: ⁱ -x+1, y, z; ⁱⁱ x-1, -y+1/2, z-1/2 ⁱⁱⁱ -x, y+1/2, -z+1/2; ^{iv} -x+1, -y+1, -z+1.					

Catalytic Studies:

Diphenylethyne is used as the substrate to optimize the reaction conditions (Table 4). An initial investigation revealed that the ligand itself is capable of catalyzing the reaction at 63% yield (Entry 1). Screening of different solvents as reaction medium revealed that acetonitrile (MeCN) performs much better than tetrahydrofuran (THF), dichloromethane (DCM), and methanol (MeOH) in mediating the reaction (Entries 2-5). Water contents of the solvent was found to affect the yield of the reaction significantly. Neither anhydrous acetonitrile (Entry 6) nor those doped with excess amount of water (Entries 7 and 8) as the reaction solvent performs better than commercially available acetonitrile with 0.13% water content (determined by Carl-Fischer titration). Minimum amount of photocatalyst required for satisfactory yield is 0.1 equivalent (entries 2, 9-11). Further studies indicate that almost no reactions occurs in absence of any one of the elements including photocatalyst, 4-chlorobenzenethiol, blue LED and air (entries 12-15).

Table 4 Optimization of Reaction Conditions

	=	photocatalyst 4-chlorobenzenethiol blue LED, air, 72h slovent	2a	
Entry	Photocatalyst (mol%)	Solvent	yield(%)	
1	H ₂ AQDC (10)	MeCN	63	
2	Ni-AQDC (10)	MeCN	81	
3	Ni-AQDC (10)	THF	0	
4	Ni-AQDC (10)	DCM	trace	
5	Ni-AQDC (10)	MeOH	trace	
6	Ni-AQDC (10)	MeCN ^a	37	
7	Ni-AQDC (10)	MeCN ^b	74	
8	Ni-AQDC (10)	MeCN ^c	51	
9	Ni-AQDC (3)	MeCN	trace	
10	Ni-AQDC (5)	MeCN	52	
11	Ni-AQDC (7)	MeCN	71	
12 ^d	Ni-AQDC (10)	MeCN	0	
13 ^e	Ni-AQDC (10)	MeCN	trace	
14	_	MeCN	0	
15 ^f	Ni-AQDC (10)	MeCN	0	
Reaction conditions (unless otherwise specified): diphenylethyne (0.2 mmol), 4-chlorobenzenethiol (0.4 mmol), photocatalyst, solvent (2 mL), irradiated by 20 W blue LED (450nm-470nm) in air at room temperature for 72 h. Commercially available solvents containing trace amount of H ₂ O were used				

temperature for 72 h. Commercially available solvents containing trace amount of H₂O were used unless otherwise specified. ^a Anhydrous. ^b Doped with 50 µL water (3% water content). ^c Doped with 500 µL water (24% water content). ^d In the dark. ^e Without 4-chlorobenzenethiol. ¹ Under N₂ atmosphere (1 atm).

As shown in Table 5, screening of transition metal complexes of AQDC²⁻ ligand shows that **Zn-AQDC** and **Ag-AQDC** exhibit comparable catalytic activities (57-68%, Entry 18 and 19) as that for the ligand, while **Co-AQDC** and **Cu-AQDC** complexes catalyze the reaction at only 35-37% yield (Entry 16 and 17). It is notable that isostructural pair **Co-AQDC** and **Ni-AQDC** behaves very different in promoting the photooxidation reaction, therefore we can conclude that structures of these complexes and coordination modes of metal centers/ligand are not decisive factors for the catalytic activity of the complexes. There might be some synergistic effect of AQDC²⁻ ligand and Ni(II) center in **Ni-AQDC** that enhances the catalytic activity of the complex.

	end to blue LED, air, 72h CH ₃ CN	2a	
Entry	Photocatalyst (mol%)	yield(%)	
1	H ₂ AQDC (10)	63	
2	Ni-AQDC (10)	81	
16	Co-AQDC (10)	37	
17	Cu-AQDC (10)	35	
18	Zn-AQDC (10)	68	
19	Ag-AQDC (10)	65	
Reaction conditions same as that for Entry 2 in Table 4.			

Table 5
 Screening of photocatalysts.

Dalton Transactions

Under the optimized reaction conditions, the generality and scope of this photocatalytic system using **Ni-AQDC** as catalyst were then examined with a series of diarylethynes as substrates (Table 6). Moderate to good yields have been obtained for the reaction series with products listed in Table 6. It is notable that easily oxidized formyl group remains intact during the oxidation process (**2I** in Table 6), indicating good oxidizing selectivity in functional groups. Diarylethyne comprising thienyl group could also be oxidized into corresponding 1,2-diketones at 72% yield.



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The **Ni-AQDC** catalyst therefore represents an efficient heterogeneous catalyst for this reaction system and can be easily recovered by filtration after the reaction, attributed to very poor solubility in reaction medium. To determine the amount of catalyst loss during the catalytic process, we determined the concentration of Ni element remaining in the solution after the reaction, through inductive coupled plasma emission spectrum (ICP). The result shows that only 0.04 µg/mL of Ni element presents in the filtrate, accounting for 0.0068% loss of the catalyst, which means that the photocatalyst can be efficiently recovered. Powder X-ray diffraction patterns of the **Ni-AQDC** catalyst before and after the catalytic reaction reveal no change in the material structure, indicating the fact that the catalyst stays intact during the catalytic process. The high recovery yield and good stability of the catalyst dictate the possibility of recycled use.



Fig. 5 (a) Recyclability of Ni-AQDC catalyst. (b) Powder X-ray diffraction patterns of the Ni-AQDC catalyst before and after recycling.

Consequently, the recyclability and reusability of **Ni-AQDC** catalyst is evaluated by such oxidation reactions using diphenylethyne as the substrate. The catalyst is recovered from the reaction system by filtration, washed with dichloromethane, dried under vacuum, and subjected to catalytic use again without any operation of regeneration. Upon four times of recycled use, the **Ni-AQDC** complex is still able to efficiently catalyze the reaction without significant loss of activity, demonstrating good recyclability as a photocatalyst (Fig. 5a). The yields with recycled catalyst are comparable to that with as-synthesized catalyst, all at ~80% level. Powder X-ray diffraction (PXRD) pattern of the photocatalyst after five catalytic cycles is in good agreement with that of the as-synthesized **Ni-AQDC** complex (Fig. 5b).



Scheme 2. Proposed reaction mechanism.

In presence of 2.0 equivalent 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), no product was detected from the reaction system under standard conditions, being a sign of possible radical pathway for the transformation. Based on this and above mentioned observations, a plausible reaction mechanism has been proposed (Scheme 2). Upon irradiation by visible light, the **Ni-AQDC** catalyst converts to excited state, which undergoes reductive quenching by thiophenol to generate its semiquinone form accompanied by the formation of thiophenyl radical (**A**). Radical addition involving thiophenyl radical, water and diphenylethyne affords intermediate **B**, which reacts with O₂ to generate intermediate **C**. Redox reaction between semiquinone **Ni-AQDC(H)**^{*} and intermediate **C** gives rise to the formation of 1,2-diketone and ground state **Ni-AQDC**.

Conclusions

To develop novel heterogeneous photocatalysts, the quinone functionalized dicarboxylate ligand 9,10-anthraquinone-1,4-dicarboxylate acid has been designed and synthesized, followed by the syntheses of a family of transition metal complexes. The ligand shows versatile coordination modes in these metal complexes to result in various polymeric structures. These coordination polymers are able to catalyze the reaction of visible-light driven aerobic oxidation of alkynes into 1,2-di-ketones under ambient conditions. The **Ni-AQDC** complex exhibits enhanced catalytic activity as compared to the ligand itself, representing the best one among the family of metal complexes over a broad scope of substrates with moderate to good yield. Recovery of the catalyst is as simple as filtration, washing and drying, with only 0.0068% loss in solution determined by ICP. Remarkably, the recovered catalyst can be used again to catalyze the reaction without any need of regeneration for at least five times with persistently good activity. X-ray powder diffractions before and after five catalytic runs reveal no structure change of the **Ni-AQDC** catalyst, demonstrating good stability. This catalyst represents an environmentally friendly economic and recyclable photocatalyst with good performance, which might be used conveniently in light-irradiated flow reactors as fixed bed catalyst. This ligand design strategy is potentially useful in the development of functional metal-organic hybrid materials with versatile applications.

Conflicts of interest

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There are no conflicts of interest to declare.

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