FULL PAPER

WILEY Applied Organometallic Chemistry

Highly stable polyoxometalate-resorcin[4]arene-based inorganic-organic complexes for catalytic oxidation desulfurization

Ming-Yue Yu¹ | Jin Yang¹ | Xianxiu Xu³ | Jian-Fang Ma¹ | Zhenxing Wang²

¹Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, China

²Wuhan National High Magnetic Field Center & School of Physics, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

³College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, China

Correspondence

Jin Yang and Jian-Fang Ma, Key Lab for Polyoxometalate Science, Department of Chem:

Email: yangj808@nenu.edu.cn; majf247@nenu.edu.cn Zhenxing Wang, Wuhan National High Magnetic Field Center & School of Physics, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China. Email: zxwang@hust.edu.cn

Funding information

National Natural Science Foundation of China, Grant/Award Numbers: 21471029 and 21771034 Self-assembly of a resorcin[4]arene-based ligand (TMR4A) with metal salts and $H_3PMo_{12}O_{40}\cdot xH_2O$ offers two isostructural complexes, namely, $[Ni_2Cl$ (TMR4A)₂(CH₃CN)₂]· $[PMo_{12}O_{40}]\cdot 4CH_3CN$ (1) and $[Co_2Cl(TMR4A)_2$ (CH₃CN)₂]· $[PMo_{12}O_{40}]\cdot 4CH_3CN$ (2). In both 1 and 2, one Cl⁻ anion bridges two metal cations, and each metal cation is further chelated by four 2mercaptopyridine N-oxide groups of one TMR4A, producing a $[M_2Cl$ (TMR4A)₂]³⁺ dimer (M = Ni or Co). The negative $[PMo_{12}O_{40}]^{3-}$ as a counter-anion balances the positive charge. Markedly, 1 and 2 exhibit high stability in aqueous solutions with different pH values and in organic solvents. Remarkably, the efficient heterogeneous catalytic capability for oxidative desulfurization was studied by suing 1 and 2 as recycled catalysts. Moreover, the electrochemical behaviors of the two compounds were discussed as well.

KEYWORDS

crystal structure, oxidation desulfurization, polyoxometalate, resorcin[4]arene

1 | INTRODUCTION

Polyoxometalates (POMs), a family of early transition metal oxides,^[1,2] have attracted increasing interest of chemists owing to their unique molecular structures^[3] and wide applications in various fields including catalysis,^[4] electrochemistry,^[5–8] magnetism,^[9–12] and photocatalysis.^[13–15] Particularly, POMs feature excellent catalytic performances in oxidation catalysis reactions

such as oxidative desulfurization (ODS) and alcohol oxidation.^[9,16–20] Among them, one of the most attractive catalytic reactions involving POMs is the oxidation catalysis from sulfides to sulfoxides and sulfones by virtue of low cost, high efficiency and mild reaction conditions, which are potentially applied in the chemical industry, biology and medical chemistry.^[21–23]

In this facet, POMs-based inorganic-organic hybrid materials, as recycled solid state catalysts of oxidative

desulfurization, have received considerable attention due to their intriguing structures and excellent catalytic performances.^[1,24–31] As a result, the rational design of stable POMs-based inorganic–organic hybrid complexes are of particular importance. It is well-established that organic ligands act as a key role in the rational assembly of inorganic–organic hybrid complexes.^[32–37] For example, the chelating ligands potentially support the stability of the resulting complexes.^[38,39] In this regard, functionalized resorcin[4]arenes, showing bowl-shaped aromatic cavities,^[40–45] are well-known macrocyclic ligands and excellent candidates for assembly of stable POMs-based inorganic–organic hybrid complexes.^[16]

Recently, we have conducted a study about resorcin[4] arene-based metal-organic assemblies that feature fascinating structures and functions.^[16,46-52] Based on above consideration, we designed here a resorcin[4]arene-based ligand with four bridging 2-mercaptopyridine N-oxide groups (TMR4A, Scheme 1). By self-assembly of TMR4A with metals and POMs under solvothermal conditions, we successfully obtained two new POMs-resorcin[4] arene-based complexes, [Ni₂Cl(TMR4A)₂ namely, $(CH_3CN)_2$]·[PM0₁₂O₄₀]·4CH₃CN **(1)** and $[Co_2Cl]$ $(TMR4A)_2(CH_3CN)_2] \cdot [PMo_{12}O_{40}] \cdot 4CH_3CN$ (2). Remarkably, 1 and 2 are highly stable and exhibit excellent catalytic oxidation performances as heterogeneous recycled catalysts. Besides, they also feature electrocatalytic properties for the reduction of NaNO2 and oxidation of ascorbic acid (AA).

2 | EXPERIMENTAL

2.1 | Materials and instruments

Chemical reagents were achieved commercially. PXRD patterns were recorded with a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized CuK α radiation ($\lambda = 0.154$ nm). C, H and N data were determined on a PerkinElmer 2400 CHN elemental analyzer. The Mattson Alpha Centauri spectrometer was used to measure IR spectra. The catalytic oxidation products of substrates were monitored by gas chromatography (GC) equipment and high performance liquid chromatography (HPLC). The CHI660b electrochemical workstation was applied to determine the electrochemical data. ¹H NMR data was determined on a Bruker 600 MHz. ICP data was measured with a Leeman Labs Prodigy inductively coupled plasma-optical atomic emission spectrometer (ICP-AES).

2.2 | Synthesis of TMR4A

The products of (**a**)-(**c**) were prepared by following the literature route.^[53] A mixture of (**c**) (5.79 g, 6 mmol), 2mercaptopyridine N-oxide sodium salt (4.48 g, 30 mmol), anhydrous K_2CO_3 (4.14 g, 30 mmol) and DMF (300 mL) was stirred under N₂ atmosphere at 90 °C for 10 hr (Scheme 1). Crude product was obtained after removal of the solvent, and then the water (200 ml) was added.



SCHEME 1 Synthetic route of the newly designed TMR4A ligand

Solid product of TMR4A was filtered, washed with water, and dried in vacuum (yield: 73%). ¹H NMR (600 MHz, DMSO): $\delta = 8.25-8.28$ (d, 4H, Ar-H), 7.81–7.83 (s, 4H, Ar-H), 7.56–7.60 (d, 4H, Ar-H), 7.36–7.40 (t, 4H, Ar-H), 7.19–7.23 (t, 4H, Ar-H), 5.97–6.00 (d, 4H, CH₂S), 4.81–4.86 (q, 4H, CH), 4.44–4.47 (d, 4H, CH₂S), 3.93–3.96 (s, 8H, OCH₂), 1.83–1.88 (d, 12H, CH₃). IR (KBr, cm⁻¹): 3853 (w), 3735 (w), 3365 (m), 3118 (m), 2966 (m), 1653 (w), 1589 (m), 1557 (m), 1471 (s), 1420 (s), 1378 (w), 1339 (w), 1301 (w), 1250 (s), 1217 (s), 1146 (m), 1091 (m), 1049 (m), 1019 (m), 976 (s), 930 (s), 838 (s), 750 (s), 706 (m), 575 (m), 503 (w), 456 (w), 419 (w).

2.3 | Synthesis of [Ni₂Cl(TMR4A)₂(CH₃CN)₂]·[PM0₁₂O₄₀]· 4CH₃CN (1)

Yellow-green rod crystals of **1** (33% based on TMR4A) were collected from solvothermal reaction of TMR4A (0.011 g, 0.01 mmol), $H_3PMo_{12}O_{40}\cdot xH_2O$ (0.018 g, 0.01 mmol), and NiCl₂·6H₂O (0.010 g, 0.04 mmol) in mixed solvents of acetonitrile (7 ml) and deionized water (1 ml) at 120 °C for 3 days. Element analysis (%) for $C_{132}H_{122}N_{14}O_{64}S_8Ni_2ClPMo_{12}$ (Mr = 4520.03): calculated C, 35.08; H, 2.72; N, 4.34; found: C, 35.47; H, 2.79; N, 4.07. IR data (KBr, cm⁻¹): 3903 (w), 3853 (w), 3801 (w), 3734 (w), 3710 (w), 3649 (w), 3446 (m), 2933 (w), 1734 (w), 1635 (w), 1541 (w), 1471 (s), 1425 (m), 1338 (w), 1300 (w), 1248 (m), 1213 (m), 1149 (m), 1063 (s), 1018 (m), 978 (s), 957 (s), 931 (m), 810 (s), 750 (s), 579 (m).

2.4 | Synthesis of [Co₂Cl(TMR4A)₂(CH₃CN)₂]·[PMo₁₂O₄₀]· 4CH₃CN (2)

Yellow rod crystals of **2** (29% based on TMR4A) were achieved from solvothermal reaction of TMR4A (0.011 g, 0.01 mmol), H₃PMo₁₂O₄₀·xH₂O (0.018 g, 0.01 mmol), and CoCl₂·6H₂O (0.010 g, 0.04 mmol) in mixed solvents of acetonitrile (6 ml) and deionized water (2 ml) at 130 °C for 3 days. Element analysis (%) for C₁₃₂H₁₂₂N₁₄O₆₄S₈Co₂ClPMo₁₂ (Mr = 4520.47): calculated C, 35.07; H, 2.72; N, 4.34; found: C, 33.75; H, 2.59; N, 4.11. IR data (KBr, cm⁻¹): 3851 (w), 3733 (w), 3444 (w), 1635 (w), 1559 (w), 1472 (m), 1427 (w), 1339 (w), 1299 (w), 1249 (w), 1213 (w), 1149 (w), 1092 (w), 1062 (m), 1019 (w), 977 (s), 960 (s), 932 (w), 880 (m), 811 (s), 753 (m), 705 (m), 647 (w), 579 (m), 502 (m).

2.5 | Catalytic oxidative desulfurization

Substrate (0.4 mmol), catalyst (2 μ mol), 70% tert-butyl hydroperoxide (TBHP) (1 mmol) were dissolved in dichloromethane (CH₂Cl₂) (5 ml). The reaction system was stirred and heated in a water bath at 50 °C. IR spectra were used to monitor the oxidation product. GC and HPLC were utilized to calculated the conversion (Figures S1-S6). The HPLC was used to calculate the conversions of 4,6-DMDBTO and 4,6-DMDBTO₂ with CH₃OH:H₂O (99:1) and others with CH₃OH:H₂O (4:1).

2.6 | X-ray crystallography

The Oxford Diffraction Gemini R CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda =$ 0.71073 Å) was used to determine crystallographic data of **1** and **2** at room temperature. Their structures were solved by direct methods using SHELXS-2013 and refined by the full-matrix least-squares method with SHELXL-2013 program within WINGX.^[54–56] Non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms of carbons were generated geometrically (hydrogen atoms of C62, C64 and C66 from acetonitrile molecules were not included in the model). The disordered atoms (O31 and O31', O32 and O32') of the [PMo₁₂O₄₀]^{3–} anion in both **1** and **2** were split over two sites with the occupation factor of 0.5, respectively. Table S1 provided the crystallographic data.

3 | **RESULTS AND DISCUSSION**

3.1 | Structural description of $[Ni_2Cl (TMR4A)_2(CH_3CN)_2] \cdot [PMo_{12}O_{40}] \cdot 4CH_3CN$ (1) and $[Co_2Cl(TMR4A)_2(CH_3CN)_2] \cdot [PMo_{12}O_{40}] \cdot 4CH_3CN$ (2)

Crystallographic analysis reveals that the structures of **1** and **2** are isostructural and belong to the same triclinic system with space group *P*-1 (Table S1). Thereby, the structure of **1** will be depicted in detail. In the asymmetric unit of **1**, there exists one TMR4A ligand, one crystallographically independent Ni (II) cation, half of a Cl^- anion, half of a $[PMo_{12}O_{40}]^{3-}$ anion, one coordinated acetonitrile molecule and two free acetonitrile molecules. Figure S7 shows that each Ni²⁺ is coordinated by four O atoms (O9-O12) of four 2-mercaptopyridine N-oxide groups of the same TMR4A ligand, one N atom (N5) of one acetonitrile molecule, and one Cl⁻ anion giving rise to an octahedral coordination geometry. The Ni-O distances vary from 1.998(6) to 2.030(5) Å, and the Ni-N bond length is 2.071(9) Å (Table S2). Interestingly, two

Ni (II) cations are bridged by one Cl⁻ anion to generate a dimer with the Ni…Ni distance of 5.524 Å (Figure 1a). Similarly, the distance of Co…Co in **2** is 5.479 Å (Figure S8). It is worth noting that each free $[PMo_{12}O_{40}]^{3-}$ anion acts as a counter-anion and balances the positive charge. Furthermore, each $[PMo_{12}O_{40}]^{3-}$ anion is interlinked with two neighboring dimeric $[Ni_2Cl(TMR4A)_2(CH_3CN)_2]^{3+}$ species *via* C-H…O hydrogen bonds to produce a chain (Figure 1b, Table S3). For **1** and **2**, the free void volumes after removal of lattice solvents are approximately 10.6% and 10.7%, respectively, calculated with PLATON.^[57]

3.2 | Chemical stability

Chemical stability of inorganic–organic hybrid compounds is quite important for exploring their underlying properties.^[58] Thus, the chemical stability of **1** and **2** was studied in organic solvents and aqueous solutions of various pH values (0–13). As illustrated in Figures 2a and 2b, PXRD patterns demonstrate the structures of **1** and **2** still remained unchanged after they were soaked in different organic solvents such as acetonitrile, acetone, methanol, ethanol, dichloromethane or water for 12 h. Further, their PXRD patterns have no obvious changes after they were immersed in aqueous solutions of different pH values (Figures 2c and 2d). The results verify that both **1** and **2** have good stability and resistance to acid or base.

3.3 | Catalytic oxidative desulfurization

Currently, sulfur-based compounds have led to serious pollution to the environment.^[59,60] In general, these sulfur-containing species could be converted into sulfones via oxidation catalysis using suitable catalysts.^[61-64] The POMs-based inorganic-organic hybrid materials are valuable catalysts for the effective catalytic oxidative desulfurization. Thus, the oxidative desulfurization performances were studied by using the stable POMs-containing complexes 1 and 2. At the beginning, the optimized reaction condition was explored by using the methyl phenyl sulfide (MBT) as a typical substrate (Scheme 2). The ODS process was performed in 5 ml CH₂Cl₂ at 50 °C with 1 as catalyst (2 µmol), TBHP as oxidant (1 mmol) and diphenyl as internal standard.^[16] The GC analyses indicate that 69% of MBT was converted into the corresponding sulfoxide and sulfone at 50 °C for 1 h (entry 3, Table 1). Accordingly, the conversions of MBT were enhanced by 54% and 44%, respectively, compared with the catalytic reactions without catalyst or in the presence of NiCl₂·6H₂O and TMR4A (entries 1 and 2, Table 1). The



FIGURE 1 (a) View of the dimeric structure of **1**. (b) View of the hydrogen-bonded supramolecular chain between the $[Ni_2Cl(TMR4A)_2(CH_3CN)_2]^{3+}$ cations and $[PMo_{12}O_{40}]^{3-}$ anions. Symmetry code: ^{#1} -*x*, -*y*-1, -*z* + 2



FIGURE 2 PXRD patterns in different solvents and aqueous solutions with different pH values for 1 (a and c) and 2 (b and d)



SCHEME 2 Catalytic oxidation of MBT catalyzed by 1

result indicates that the POM units act as a key role during ODS process. Further, when catalytic reaction time was prolonged, the conversion reached 99% within 3 hr (entries 4 and 5, Table 1). When the reaction temperature was reduced to 40 °C, ca. 92% conversion of MBT was achieved within 3 hr (entry 6, Table 1). Nevertheless, when the TBHP was replaced by 3% hydrogen peroxide (H₂O₂), only 32% MBT was converted into the corresponding product at 50 °C for 3 hr (entry 7, Table 1). Further, the solvent effect on the catalytic oxidation desulfurization performance was also investigated. The conversions of MBT in methanol, ethanol and acetonitrile were 59%, 96% and 92%, respectively, after 3 hr (entries 8-10, Table 1). Hence, the optimized reaction condition was chosen in the existence of 2 µmol 1, 1 mmol TBHP, and 5 ml CH₂Cl₂ at 50 °C for 3 hr.

To further verify the catalytic performance of 1, a series of sulfur-based compounds were subsequently selected as catalytic reaction substrates (Table 2). Noticeably, the monophenyl thioethers, such as methyl phenyl sulfide, ethylthiobenzene, allyl phenyl sulfide, 4methoxythioanisole, 4-bromothioanisole and 4chlorothioanisole, can be completely oxidized to be the corresponding products within 3 h (entries 2-6, Table 2). For these substrates, the effects of the substituted groups on the catalytic performances are almost negligible. Nevertheless, for the 4-nitrothioanisole with the strong electron-withdrawing group, the total conversion 6 of 11 WILEY Organometallic-Chemistry

TABLE 1 Catalytic oxidative desulfurization results under various conditions^a

Entry	Catalyst	Oxidant	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	None	TBHP	CH_2Cl_2	50	1	15
2	NiCl ₂ ·6H ₂ O, TMR4A	TBHP	CH_2Cl_2	50	1	25
3	1	TBHP	CH_2Cl_2	50	1	69
4	1	TBHP	CH_2Cl_2	50	2	94
5	1	TBHP	CH_2Cl_2	50	3	>99
6	1	TBHP	CH_2Cl_2	40	3	92
7	1	H_2O_2	CH_2Cl_2	50	3	32
8	1	TBHP	methanol	50	3	59
9	1	TBHP	ethanol	50	3	96
10	1	TBHP	acetonitrile	50	3	92

 $^{\mathrm{a}}\text{Reaction}$ conditions: oxidant (1 mmol), 1 (2 $\mu\text{mol})$, substrate (0.4 mmol) and solvent (5 ml).

TABLE 2 Results of the catalytic oxidation of thioethers catalyzed by 1 and 2^a

Entry	Substrates	Yields (%) for 1	Yields (%) for 2
1	€ S S S S S S S S S S S S S S S S S S S	>99	>99
2		>99	>99
3	C s s s s s s s s s s s s s s s s s s s	>99	>99
4	H ₃ CO	>99	>99
5	Br	>99	>99
6	ci s	>99	>99
7	O2N S	92 99 ^b	95 99 ^e
8		87 >99 ^b	93 >99 ^b
9		65 >99 ^c	60 >99 ^c
10	L'S L	46 88 ^d	39 88 ^d
11	ſ∑_s	18 69 ^d	16 70 ^d

^aReaction conditions: **1** (2 µmol), TBHP (1 mmol), substrate (0.4 mmol), CH₂Cl₂ (5 ml), 50 °C, 3 hr. ^bReaction time: 5 hr. ^cReaction time: 10 hr. ^dReaction time: 14 hr. ^eReaction time: 4.5 hr.

is lower than others under the same condition (entry 7, Table 2). With the prolonged reaction time (5 hr), the conversion is up to 99% (entry 7, Table 2). Similarly, for diphenyl sulfide with the large steric hindrance, it also took 5 h to accomplish the complete conversion of the substrate (entry 8, Table 2). In contrast, the thiophene sulfides are more difficult to be oxidized.^[65] After 10 hr, the catalytic conversion of dibenzothiophene (DBT) reached 99%. However, the conversions of 4.6dimethyldibenzothiophene (4,6-DMDBT) and benzothiophene (BT) were only up to 88% and 69%, respectively, when the reaction time was extended to 14 hr (entries 9-11, Table 2). The result mainly arises from the electron density as well as steric hindrance around sulfur atom for thiophene sulfides.^[66] We also investigated the catalytic activity of isostructural 2 under the same condition. Like 1, 2 exhibits good catalytic performances for the oxidative desulfurization (Figures S9 and S10, Table 2).

In addition, the catalytic reaction kinetics of DBT and 4,6-DMDBT were also explored using 1 as catalyst (Figure 3). The catalytic process was monitored every 2 h. At the beginning of 4 hr, the conversions of DBT and 4,6-DMDBT are significantly enhanced, and become relatively slow afterward. After 14 hr, 99% and 88% of DBT and 4,6-DMDBT were converted into the corresponding oxide products, respectively. Moreover, DBT was used as the model substrate to study the heterogeneity of ODS process. Catalyst 1 was filtered after the conversion reached 65% (3 hr). As illustrated in Figure 4, almost no additional oxide product was produced after removing the catalyst. Nevertheless, in the presence of catalyst 1, the conversion of DBT increased slowly with the prolonged reaction time. The ICP data shows that no Ni (II) ions were found in the filtrate. The result



FIGURE 4 The conversions of DBT catalyzed by **1** with the increasing reaction time (**A**) and filtrate by taking catalyst **1** from the reaction system after 3 h (B)

demonstrates the heterogeneity of the catalytic oxidation process.

Furthermore, the reusability and structural stability of catalyst **1** were also explored. As shown in Figure 5, catalyst **1** still remains the good catalytic performance after five cycles by using MBT as substrate. Moreover, the PXRD patterns and FT-IR spectra demonstrate the structural stability of catalyst **1** (Figures S11 and S12a).

As illustrated in Scheme S1, a possible catalytic reaction mechanism was proposed.^[67,68] The DBT and $[PMo_{12}O_{40}]^{3-}$ were taken as examples of the substrate and POM, respectively. At the beginning, the $[PMo_{12}O_{40}]^{3-}$ (a) was converted to be peroxometal intermediate (b) by TBHP with the release of tert-butanol (TBA). Afterward, the DBT was oxidized to be dibenzothiophene 5-oxide (DBTO) by the peroxometal



FIGURE 3 The catalytic reaction kinetic curves of DBT and 4,6-DMDBT catalyzed by **1**



FIGURE 5 Recycled experiments of 1 for oxidation of MBT

8 of 11 WILEY Organometallic

intermediate. Then, the peroxometal intermediate was recovered to be the $[PMo_{12}O_{40}]^{3-}$ after catalytic oxidation reaction. A similar catalytic process occurred when DBTO was converted to be dibenzothiophene-5,5-dioxide (DBTO₂).

3.4 | Electrochemical properties

Usually, POMs are employed as electrocatalysts owing to their structural stability after undergoing electron transfer processes.^[8,69–73] Considering the stability of **1** and **2** in a wide pH values, electrochemical experiments were conducted in 0.5 M H₂SO₄ using modified carbon paste electrodes (**1**-CPE and **2**-CPE). They feature similar electrocatalytic activities in the same potential range (-0.3 to +1.0 V). The cyclic voltammetry curves of **1**-CPE and **2**-CPE in 0.5 M H₂SO₄ were determined at a scan rate of 50 mM/s. As shown in Figure 6a, three pairs of reversible redox peaks (I-I', II-II' and III-III') were observed with the average peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at -0.052, +0.219 and + 0.379 V for **1** and - 0.051, +0.218

and + 0.374 V for **2**, respectively, which are probably related to three consecutive two-electron transfer of the Mo center in $[PMo_{12}O_{40}]^{3-}$ anion.^[74,75] Moreover, one irreversible oxidation peak appeared at +0.566 and + 0.553 V for **1** and **2**, respectively, probably arising from the oxidation of Ni (II) or Co (II). In addition, the cyclic voltammetry curves at different scan rates have also been studied in 0.5 M H₂SO₄. As depicted in Figures 6b and S13, the peak currents are proportional to the scan rates, demonstrating the surface-controlled redox processes for **1**-CPE and **2**-CPE.^[74,76,77]

Furthermore, the bifunctional electrocatalytic activities for **1**-CPE and **2**-CPE were also explored in 0.5 M H_2SO_4 . As illustrated in Figure 7a, the reduction peak currents continue to increase with adding NaNO₂, whereas the oxidation peak currents go down, demonstrating the occurrence of the reduction of NO_2^- . It is noteworthy that the oxidation peak current is enhanced sharply with the increased concentrations of ascorbic acid (AA) (Figure 7b). The result proves that **1**-CPE and **2**-CPE also have electrocatalytic properties for the oxidation of AA.



FIGURE 6 Cyclic voltammograms for 1-CPE and 2-CPE in 0.5 M H_2SO_4 : (a) scan rate: 50 mV/s and (b) scan rates: 50–400 mV/s. Inset: linear curves of the anode and the cathode peak currents of I-I' versus scan rates



FIGURE 7 Cyclic voltammograms for 1-CPE and 2-CPE in 0.5 M H_2SO_4 : (a) different concentrations of NaNO₂ at 50 mV/s, inset: the relationship between cathode peak currents of II' and concentrations of NaNO₂. (b) different concentrations of AA at 50 mV/s, inset: the relationship between anode peak currents of IV and the concentrations of AA

4 | CONCLUSIONS

isostructural Two POMs-resorcin[4]arene-based hybrid inorganic-organic materials have been solvothermally synthesized using a resorcin[4]arene functionalized ligand. The hybrid materials represent a rare example of metal-coordinated POMs-resorcin[4]arenebased hybrid dimers. Remarkably, 1 and 2 are highly stable in organic solvents and aqueous solutions of various pH values. Significantly, they can be employed as excellent recycled heterogeneous catalysts for oxidative desulfurization. Strikingly, they are also potentially utilized as electrocatalysts for the reduction of NaNO2 and the oxidation of AA.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 21771034 and 21471029).

ORCID

Jian-Fang Ma D https://orcid.org/0000-0002-4059-8348

REFERENCES

- [1] Y.-F. Song, R. Tsunashima, Chem. Soc. Rev. 2012, 41, 7384.
- [2] H. N. Miras, J. Yan, D.-L. Long, L. Cronin, Chem. Soc. Rev. 2012, 41, 7403.
- [3] H. Wu, J. Yang, Z.-M. Su, S. R. Batten, J.-F. Ma, J. Am. Chem. Soc. 2011, 133, 11406.
- [4] I. V. Kozhevnikov, Chem. Rev. 1998, 98, 171.
- [5] W. Luo, J. Hu, H. Diao, B. Schwarz, C. Streb, Y.-F. Song, Angew. Chem. Int. Ed. 2017, 56, 4941.
- [6] M.-T. Li, X.-Y. Yang, J.-S. Li, N. Sheng, G.-D. Liu, J.-Q. Sha, Y.-Q. Lan, *Inorg. Chem.* 2018, 57, 3865.
- [7] F. Dhifallah, M. S. Belkhiria, L. Parent, N. Leclerc, E. Cadot, *Inorg. Chem.* 2018, 57, 11909.
- [8] J.-Q. Sha, X.-Y. Yang, Y. Chen, P.-P. Zhu, Y.-F. Song, J. Jiang, ACS Appl. Mater. Interfaces 2018, 10, 16660.
- [9] S. She, C. Gao, K. Chen, A. Bayaguud, Y. Huang, B.-W. Wang, S. Gao, Y. Wei, *Inorg. Chem.* **2018**, *57*, 963.

10 of 11 WILEY-Organometallic Chemistry

- [10] X. Wang, S. Liu, Y. Liu, D. He, N. Li, J. Miao, Y. Ji, G. Yang, *Inorg. Chem.* **2014**, *53*, 13130.
- [11] J. Jia, Y. Niu, P. Zhang, D. Zhang, P. Ma, C. Zhang, J. Niu, J. Wang, *Inorg. Chem.* 2017, 56, 10131.
- [12] Y. Wang, X. Kong, W. Xu, F. Jiang, B. Li, L. Wu, *Inorg. Chem.* 2018, 57, 3731.
- [13] S.-T. Zheng, G.-Y. Yang, Chem. Soc. Rev. 2012, 41, 7623.
- [14] A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, *Chem. Rev.* 2010, 110, 6009.
- [15] B. Liu, J. Yang, G.-C. Yang, J.-F. Ma, Inorg. Chem. 2013, 52, 84.
- [16] B.-B. Lu, J. Yang, Y.-Y. Liu, J.-F. Ma, Inorg. Chem. 2017, 56, 11710.
- [17] L.-X. Cai, S.-C. Li, D.-N. Yan, L.-P. Zhou, F. Guo, Q.-F. Sun, J. Am. Chem. Soc. 2018, 140, 4869.
- [18] X.-L. Hao, Y.-Y. Ma, H.-Y. Zang, Y.-H. Wang, Y.-G. Li, E.-B. Wang, Chem. – Eur. J. 2015, 21, 3778.
- [19] H. An, Y. Hou, L. Wang, Y. Zhang, W. Yang, S. Z. Chang, *Inorg. Chem.* 2017, 56, 11619.
- [20] L. Ni, J. Patscheider, K. K. Baldridge, G. R. Patzke, Chem. Eur. J. 2012, 18, 13293.
- [21] W. Zhao, C. Yang, Z. Cheng, Z. Zhang, Green Chem. 2016, 18, 995.
- [22] J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang, C. L. Hill, C. Hu, Angew. Chem. Int. Ed. 2017, 56, 4473.
- [23] A. Bijelic, M. Aureliano, A. Rompel, Angew. Chem. Int. Ed. 2018, 57, 2.
- [24] Y. Hou, H. An, Y. Zhang, T. Hu, W. Yang, S. Chang, ACS Catal. 2018, 8, 6062.
- [25] H. Yu, J. Wang, Y. Zhai, M. Zhang, S. Ru, S. Han, Y. Wei, *ChemCatChem* 2018, 10, 4274.
- [26] B. Gole, U. Sanyal, R. Banerjee, P. S. Mukherjee, *Inorg. Chem.* 2016, 55, 2345.
- [27] B. Mondal, K. Acharyya, P. Howlader, P. S. Mukherjee, J. Am. Chem. Soc. 2016, 138, 1709.
- [28] G. Cai, H.-L. Jiang, Angew. Chem. Int. Ed. 2017, 56, 563.
- [29] D.-M. Chen, C.-X. Sun, C.-S. Liu, M. Du, Inorg. Chem. 2018, 57, 7975.
- [30] Y. Pan, D. Li, H.-L. Jiang, Chem. Eur. J. 2018, 24, 18403.
- [31] M. S. Deshmukh, A. Chaudhary, P. N. Zolotarev, R. Boomishankar, *Inorg. Chem.* 2017, 56, 11762.
- [32] S. Yuan, J.-S. Qin, J. Su, B. Li, J. Li, W. Chen, H. F. Drake, P. Zhang, D. Yuan, J. Zuo, H.-C. Zhou, *Angew. Chem. Int. Ed.* 2018, *57*, 12578.
- [33] D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, Angew. Chem. Int. Ed. 2012, 51, 10307.
- [34] A. Schoedel, M. Li, D. Li, M. O'Keeffe, O. M. Yaghi, *Chem. Rev.* 2016, 116, 12466.
- [35] A. Santiago-Portillo, J. F. Blandez, S. Navalón, M. Álvaro, H. García, Catal. Sci. Technol. 2017, 7, 1351.
- [36] D. Yuan, D. Zhao, D. Sun, H.-C. Zhou, Angew. Chem. Int. Ed. 2010, 49, 5357.
- [37] B. Roy, R. Saha, A. K. Ghosh, Y. Patil, P. S. Mukherjee, *Inorg. Chem.* 2017, 56, 3579.
- [38] T. Imamura, T. Maehara, R. Sekiya, T. Haino, *Chem. Eur. J.* 2016, 22, 3250.

- [39] P. La Manna, C. Talotta, G. Floresta, M. De Rosa, A. Soriente, A. Rescifina, C. Gaeta, P. Neri, *Angew. Chem. Int. Ed.* 2018, 57, 5423.
- [40] R. S. Patil, C. Zhang, J. L. Atwood, Chem. Eur. J. 2016, 22, 15202.
- [41] S. E. Matthews, S. Cecioni, J. E. O'Brien, C. J. MacDonald, D. L. Hughes, G. A. Jones, S. H. Ashworth, S. Vidal, *Chem. – Eur. J.* 2018, 24, 4436.
- [42] Q. Zhang, L. Catti, J. Pleiss, K. Tiefenbacher, J. Am. Chem. Soc. 2017, 139, 11482.
- [43] K. Su, F. Jiang, J. Qian, L. Chen, J. Pang, S. M. Bawaked, M. Mokhtar, S. A. Al- Thabaiti, M. Hong, *Inorg. Chem.* 2015, 54, 3183.
- [44] A. Mohammadia, M. Barikanib, A. H. Doctorsafaeia, A. P. Isfahanic, E. Shamsa, B. Ghalei, *Chem. Eng. J.* 2018, 349, 466.
- [45] T. Skorjanc, D. Shetty, S. K. Sharma, J. Raya, H. Traboulsi, D. S. Han, J. Lalla, R. Newlon, R. Jagannathan, S. Kirmizialtin, J.-C. Olsen, A. Trabolsi, *Chem. – Eur. J.* 2018, 24, 8648.
- [46] B.-B. Lu, J. Yang, G.-B. Che, W.-Y. Pei, J.-F. Ma, ACS Appl. Mater. Interfaces 2018, 10, 2628.
- [47] B.-B. Lu, W. Jiang, J. Yang, Y.-Y. Liu, J.-F. Ma, ACS Appl. Mater. Interfaces 2017, 9, 39441.
- [48] W.-Y. Pei, G. H. Xu, J. Yang, H. Wu, B. L. Chen, W. Zhou, J.-F. Ma, J. Am. Chem. Soc. 2017, 139, 7648.
- [49] S.-T. Zhang, J. Yang, H. Wu, Y.-Y. Liu, J.-F. Ma, Chem. Eur. J. 2015, 21, 15806.
- [50] S.-S. Zhao, J. Yang, Y.-Y. Liu, J.-F. Ma, Inorg. Chem. 2016, 55, 2261.
- [51] Q.-Y. Zhai, J. Su, T.-T. Guo, J. Yang, J.-F. Ma, J.-S. Chen, *Cryst. Growth des.* 2018, 18, 6046.
- [52] Y.-J. Hu, J. Yang, Y.-Y. Liu, S. Y. Song, J.-F. Ma, Cryst. Growth des. 2015, 15, 3822.
- [53] H. Boerrigter, W. Verboom, D. N. Reinhoudt, J. Org. Chem. 1997, 62, 7148.
- [54] G. M. Sheldrick, SHELXL-97, Programs for X-ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany 1997.
- [55] G. M. Sheldrick, SHELXL-97, Programs for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany 1997.
- [56] L. J. Farrugia, WINGX: A Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, U.K. 1988.
- [57] A. L. Spek, Acta Crystallogr. Sect. C: Struct. Chem. 2015, 71, 9.
- [58] W. Jiang, J. Yang, Y.-Y. Liu, S. Y. Song, J.-F. Ma, *Inorg. Chem.* 2017, 56, 3036.
- [59] J. F. Palomeque-Santiago, R. López-Medina, R. Oviedo-Roa, J. Navarrete-Bolaños, R. Mora-Vallejo, J. A. Montoya-de la Fuente, J. M. Martínez-Magadán, *Appl. Catal., B* 2018, 236, 326.
- [60] B. Zhang, Z. Jiang, J. Li, Y. Zhang, F. Lin, Y. Liu, C. Li, J. Catal. 2012, 287, 5.
- [61] B. N. Bhadra, J. Y. Song, N. A. Khan, S. H. Jhung, ACS Appl. Mater. Interfaces 2017, 9, 31192.
- [62] X. Zeng, X. Xiao, J. Chen, H. Wang, Appl. Catal., B 2019, 248, 573.

Applied Organometallic 11 of 11 Chemistry

- [63] L. Liu, F. Guo, J. Xu, J. Hu, H. Wang, H. Liu, M. Wang, Fuel 2019, 244, 439.
- [64] L. Sun, T. Su, J. Xu, D. Hao, W. Liao, Y. Zhao, W. Ren, C. Deng, H. Lü, *Green Chem.* 2019, 21, 2629.
- [65] J. Yin, J. Wang, Z. Li, D. Li, G. Yang, Y. Cui, A. Wang, C. Li, Green Chem. 2015, 17, 4552.
- [66] S. Otsuki, T. Nonaka, N. Takashima, W. H. Qian, A. Ishihara, T. Imai, T. Kabe, *Energy Fuels* **2000**, *14*, 1232.
- [67] S. Meninno, A. Parrella, G. Brancatelli, S. Geremia, C. Gaeta, C. Talotta, P. Neri, A. Lattanzi, Org. Lett. 2015, 17, 5100.
- [68] M. Craven, D. Xiao, C. Kunstmann-Olsen, E. F. Kozhevnikova, F. Blanc, A. Steiner, I. V. Kozhevnikov, *Appl. Catal.*, B 2018, 231.
- [69] Y.-J. Wang, Y.-Y. Zhou, H.-G. Hao, M. Song, N. Zhang, S. Yao, J.-H. Yan, Z.-M. Zhang, T.-B. Lu, *Inorg. Chem.* 2018, 57, 1342.
- [70] C. Singh, S. Mukhopadhyay, S. K. Das, Inorg. Chem. 2018, 57, 6479.
- [71] A. Boulmier, A. Vacher, D. Zang, S. Yang, A. Saad, J. Marrot,
 O. Oms, P. Mialane, I. Ledoux, L. Ruhlmann, D. Lorcy, A. Dolbecq, *Inorg. Chem.* 2018, *57*, 3742.
- [72] X.-L. Wang, R. Zhang, X. Wang, H.-Y. Lin, G.-C. Liu, H.-X. Zhang, Dalton Trans. 2017, 46, 1965.
- [73] H. Guo, C. Gong, X. Zeng, H. Xu, Q. Zeng, J. Zhang, Z. Zhong, J. Xie, *Dalton Trans.* 2019, 48, 5541.

- [74] J.-S. Qin, D.-Y. Du, W. Guan, X.-J. Bo, Y.-F. Li, L.-P. Guo, Z.-M. Su, Y.-Y. Wang, Y.-Q. Lan, H.-C. Zhou, J. Am. Chem. Soc. 2015, 137, 7169.
- [75] L. Qian, X. Yang, Electrochem. Commun. 2005, 7, 547.
- [76] L. Cheng, X. Zhang, X. Xi, B. Liu, S. Dong, J. Electroanal. Chem. 1996, 407, 97.
- [77] X. Wang, J. Li, A. Tian, D. Zhao, G. Liu, H. Lin, Cryst. Growth des. 2011, 11, 3456.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Yu M-Y, Yang J, Xu X, Ma J-F, Wang Z. Highly stable polyoxometalateresorcin[4]arene-based inorganic-organic complexes for catalytic oxidation desulfurization. *Appl Organometal Chem.* 2019;e5169. <u>https://doi.org/10.1002/aoc.5169</u>