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# Self-Assembled Polyoxometalate-Based Metal-Organic Polyhedra as an Effective Heterogeneous Catalyst for Oxidation of Sulfide

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**ABSTRACT:** Two polyoxovanadate-based metal-organic polyhedra with octahedral (oct) and rhombic dodecahedral (rdo) geometries have been constructed from a concave molecular building block and linear and triangular carboxylate ligands. VMOP-7 is constructed from { $V_5O_9Cl$ } SBU and a linear anthracene-9,10-dicarboxylic acid ligand in which all the anthracene groups are perpendicular to the edge of the octahedron. Such an arrangement mode can effectively reduce the steric hindrance between ligands. VMOP-8 is constructed from { $V_5O_9Cl$ } SBU and a triangular biphenyl 3,4,5-tricarboxylate



ligand, which exhibits an elongated rhombic dodecahedral configuration due to the geometry of the ligand. Furthermore, VMOP-8 can serve as a heterogeneous catalyst and exhibits efficient and common catalytic activity for oxidative desulfurization.

# INTRODUCTION

As a new type of inorganic-organic hybrid material, metalorganic polyhedra (MOPs) have attracted extensive interests because of their single-molecular properties, which are different from the classic crystalline MOFs with infinite structures.<sup>1-6</sup> MOPs have been applied in many fields as a new tpye of supramolecular aggregation, such as chiral separation,<sup>7,8</sup> biomedical,<sup>9,10</sup> catalysis,<sup>11,12</sup> host-guest chem- $^{13-17}$  etc. However, due to the scarcity of suitable molecular building blocks, the target synthesis of MOPs with the predictable structure is still a challenge in crystal engineering.<sup>6</sup> Unlike MOFs, the secondary building unit (SBU) used to construct MOPs required to be expanded in a controllable direction; that is to say, the SBU must have a specific curvature.<sup>18,19</sup> Encouragingly, O'Keffee and Yaghi summarized some typical geometries of MOPs from the topological perspective.<sup>1</sup> Such an excellent analysis based on reticular chemistry provides a theoretical basis for the design and synthesis of MOPs. This theory involves simplifying the SBUs into topological polygons and connecting them through linkers to form a closed polyhedron, also giving two critical angles to characterize the geometries of the polyhedra. One is the angle  $\eta$  between the expansion directions in the SBUs, and the second is the bending angle  $\theta$  of the ditopic linkers. However, since there are no advantages in the number of examples that can be referenced, it is still difficult to find suitable SBUs that meet the conditions for constructing MOPs.

Polyoxovanadates (POVs), formed by sharing edges or vertices of the VO<sub>x</sub> (x = 5 or 6) triangular bipyramid or octahedron, are a promising kind of metal–oxygen SBU to construct MOPs due to the diversity of coordination.<sup>20</sup> So far, the reported polyoxovanadate-based SBUs that can be used as

vertices to form MOPs by connecting organic linkers are composed of  $\{(VO)_3(OMe)_4\}$  (V<sub>3</sub>-SBU, 3-v);<sup>21</sup>  $\{V_4O_8Cl\}$ (V<sub>4</sub>-SBU, 4-v);<sup>22,23</sup>  $\{V_5O_9Cl\}$  (V<sub>5</sub>-SBU, 4-v);<sup>23-25</sup>  $\{V_6O_6-(OMe)_9SO_4\}$  (V<sub>6</sub>-SBU, 3-v);<sup>26-30</sup>  $\{V_7O_9(OMe)_9SO_4\}$  (V<sub>7</sub>-SBU, 3-v);<sup>31</sup> and  $\{V_6O_{11}(SO_4)(CO_2)_5\}$  (VV<sub>5</sub>-SBU, 5-v)<sup>6,32</sup> (SBU with *n* extension points is referred to as *n*-valent) (Figure 1). In 2001, Hartl et al. synthesized the first cubic VMOP with V<sub>3</sub>-SBU.<sup>21</sup> Subsequently, Zaworotko and co-worker reported several organic-inorganic hybrid nano-balls based on V4- or V5-SBU, and our group also reported a series of truncated octahedrons based on V<sub>5</sub>-SBU.<sup>23</sup> Inspiringly, rare icosahedrons based on VV5-SBU have been successfully designed and synthesized recently.<sup>6,32</sup> Combining with the theory of reticular chemistry and these elegant architectures, more novel VMOPs can be predicted and designed. Among these polyoxovanadatebased SBUs, the angle  $\eta$  of V<sub>5</sub>-SBU can be observed to change flexibly in the range of  $55-61^{\circ}$ . Therefore, V<sub>5</sub>-SBU still has greater potential to construct more VMOPs. Over the past decade, the self-assembly synthesis of VMOPs has made initial achievements, but all previous efforts have focused on the characteristics of attractive geometric cavities and unique stacking networks, where the size-matched cavities or unique pores can encapsulate fullerene guest molecules or selectively adsorb cationic dyes. Besides, a tetrahedron has permanent

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**Figure 1.** Structures of the reported polyoxovanadate-based SBUs (SBUs with *n* extension points are referred to as *n*-valent).

porosity for selective gas adsorption.<sup>33</sup> However, the anticipative typical resistance to oxidation and flexible redox states probably caused by POVs as the important subcomponents in VMOPs are still undeveloped.

In recent years, acid rain has caused great harm to the environment and is mainly caused by sulfur oxides  $(SO_x)$  produced by the combustion of sulfur-containing fuels.<sup>34,35</sup> Therefore, reducing the sulfur content in fuels has become an urgent issue to be solved.<sup>36,37</sup> Oxidative desulfurization (ODS) has received a great deal of attention as a potential solution, which can convert oxidized sulfides into easily removable sulfones and sulfoxides.<sup>38-40</sup> As far as we know, the catalytic oxidation performance has never been studied in the reported VMOPs, so it makes sense to design and synthesize new VMOPs as the heterogeneous catalysts for sulfide oxidation. On the basis of the above, the V<sub>5</sub>-SBU is used as an extension point to successfully construct two new VMOPs (NH2Me2)12- $[(V_5O_9Cl)_6(L)_n] \cdot [MeOH]_m$ , VOMP-7 (L = H<sub>2</sub>ADC: anthracene-9,10-dicarboxylic acid, n = 12, m = 11) and VMOP-8 (L =  $H_3BPT$ : biphenyl 3,4,5-tricarboxylate, n = 8, m = 7), by connecting with the linear ligand H<sub>2</sub>ADC and a 3-connected ligand H<sub>3</sub>BPT. Remarkably, VMOP-8 also exhibits excellent catalytic activity for the oxidative desulfurization.

# EXPERIMENTAL SECTION

**Synthesis of VMOP-7.** In a solvothermal synthesis, VOSO<sub>4</sub>·*x*H<sub>2</sub>O (0.03 g, 0.18 mmol), VCl<sub>4</sub> (0.02 g, 0.10 mmol), and H<sub>2</sub>ADC (0.02 g, 0.007 mmol), were dissolved in a 3 mL mixture of DMF (*N*,*N*-dimethylformamide), MeCN (acetonitrile), and MeOH (methanol) (4:1:1, v/v/v), which was transferred to a Teflon-lined stainless steel vessel and heated to 130 °C for 48 h. After slowly cooling to room temperature, the green block crystals were obtained through filtering and washing with MeOH several times with a yield of 37% based on H<sub>2</sub>ADC. Anal. Calcd: C, 39.89; H, 1.66; N, 2.65. Found: C, 39.71; H, 1.78; N, 2.93. IR (KBr, cm<sup>-1</sup>): 3066 (br), 1701 (s), 1624 (vs), 1596 (m), 1538 (w), 1445 (s), 1329 (s), 1283 (m), 1001 (m), 901 (m), 821 (m), 789 (w), 728 (w), 675 (s), 597 (m), 522 (s).

**Synthesis of VMOP-8.** The mixture of  $VOSO_4$ ,  $xH_2O$  (0.03 g, 0.18 mmol),  $VCl_4$  (0.02 g, 0.10 mmol), and ( $H_3BPT$ ) (0.02 g, 0.007 mmol) was dissolved in 2 mL of DMF (*N*,*N*-dimethylformamide), 0.3 mL of MeOH, and 0.2 mL of MeCN and transferred to a Teflon-lined stainless steel vessel heated to 130 °C for 48 h. After slowly cooling to

room temperature, green crystals were obtained (washed with MeOH) with a yield of 58% based on  $H_3BPT$ . Anal. Calcd: C, 29.56; H, 1.15; N, 3.09. Found: C, 29.97; H, 1.26; N, 3.87. IR (KBr, cm<sup>-1</sup>): 3029 (br), 1714 (w), 1657 (w), 1609 (m), 1542 (w), 1484 (s), 1448 (m), 1413 (s), 1288 (w), 1114 (w), 986 (vs), 859 (w), 759 (w), 722 (s), 632 (m).

Single-Crystal X-ray Structure Determination of the VMOPs. The crystallographic data and structural refinements are given in Table S1. Intensity data were collected at 298 K on a Bruker D8 VENTURE with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) for the VMOP-8 crystal sample and Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) for the crystallographic VMOP-7. The data were collected using the program APEX 3 and processed using the program SAINT routine in APEX 3. The structures were solved by direct methods with OLEX-2 and refined by full-matrix least-squares techniques with the SHELXL-2014 program. The countercations or disordered solvents cannot be accurately assigned from the weak reflections. Thus, the SQUEEZE routine in PLATON was applied in order to model the diffuse electron density caused by disordered dimethylamine molecules and solvents. The restrained DFIX, SIMU, and ISOR instructions were used to make the structures more reasonable.

**Catalytic Oxidative Desulfurization.** 70% *tert*-butyl hydroperoxide (TBHP) (128.7 mg, 1 mmol) and substrate (0.4 mmol) were added into a 15 mL round-bottom flask with 5 mL of methanol, and **VMOP-8** (10 mg, 0.002 mmol) was added as the catalyst. The reaction system was kept at room temperature or 50 °C for 1-12 h with stirring. The conversion rate of methyl phenyl sulfide (MBT) was detected by gas chromatography (GC), and the remaining substrates were detected by high performance liquid chromatography (HPLC). The corresponding sulfoxide and sulfone products were identified by Fourier transform infrared (IR) spectra.

# RESULTS AND DISCUSSION

**Structures of VMOP-7 and VMOP-8.** Single-crystal X-ray diffraction analysis revealed that **VMOP-7** crystallized in tetragonal space group  $P4_2/n$ , while **VMOP-8** crystallized in the tetragonal system with space group I4/mmm. The phase purities of **VMOP-7** and **8** were confirmed by comparison of the observed and calculated powder X-ray diffraction (PXRD) patterns (Figure S1). The molecular size of **VMOP-7** is about  $25 \times 25 \times 25$  Å<sup>3</sup> and  $22 \times 22 \times 31$  Å<sup>3</sup> for **VMOP-8** (Figure S2). In these two cage structures, the {V<sub>5</sub>O<sub>9</sub>Cl} cluster, as the primary secondary building block, is formed by five vanadium atoms with two coordination modes by sharing the edges of the polyhedra centered on the V atom (Figure 2). One



Figure 2. Structure of  $\{V_5O_9Cl\}$   $(V_5-SBU)$  and the coordination mode of vanadium atoms. Four  $\{VO_5Cl\}$  octahedra share the quadrangled edge with the  $\{VO_5\}$  apex to form the  $V_5$ -SBU.

vanadium V1 atom is coordinated with five oxygen atoms to form a tetragonal pyramidal  $\{VO_5\}$  cluster in which the V–O bond distances range from 1.577 to 1.886 Å. The other four vanadium atoms form six-coordinate octahedral  $\{VO_5Cl\}$ clusters, and their bond distances between vanadium atoms and oxygen atoms are between 1.573 and 2.027 Å (Table S2).

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Overall bond valence sum (BVS) calculations indicate that the V1 ion in the center apex is +5, while the remaining four V2 ions at the bottom are +4, and this result is consistent with previous reports (Tables S2 and S3).<sup>25</sup> Each {V<sub>5</sub>O<sub>9</sub>Cl} cluster is coordinated with four carboxylate ligands, generating a fourconnected vertex. Six  $\{V_5O_9Cl\}$  vertexes are further bridged by eight organic ligands, thereby affording an octahedron (VMOP-7) and a rhombic dodecahedron (VMOP-8). The 12 negative charges are balanced by dimethylamine cations  $(H_2NMe_2)^+$  (the byproduct of *in situ* decomposition of DMF molecules), which can be confirmed by the swell peaks near  $3500 \text{ cm}^{-1}$  in the IR spectra and TGA curves (Figures S3, S4). For VMOP-7, each cage is composed of 250 atoms, including 6 V<sub>5</sub>-SBUs and 12 H<sub>2</sub>ADC ditopic linkers. When the V<sub>5</sub>-SBUs are regarded as quadrilateral faces, both of the polyhedra display similar truncated octahedral geometries (Figure 3).



Figure 3. Self-assembly of VMOPs from tetragonal V<sub>5</sub>-SBUs and linear or triangular ligands. Simplified polyhedral diagrams clearly show two different windows. Triangular recessed windows for VMOP-7 (left); rectangular windows for VMOP-8 (right).

However, in order to reduce the steric hindrance during the self-assembly, the plane of each anthracene points to the center of the octahedron to form a carambola-like non-convex truncated octahedron with a triangle recessed window on each face. Additionally, this arrangement results in only a small remaining inner cavity, which is found to be 364 Å<sup>3</sup> after an estimate of the VOIDOO program based on the 1.4 Å probe (Figure 4a). For VMOP-8, if eight H<sub>3</sub>BPT ligands are approximated as isosceles triangles, as shown in Figure 3, eventually an elongated truncated octahedron is generated, which is an ordinary convex polyhedron, and the internal cavity volume is calculated to be 1133 Å<sup>3</sup> (Figure 4b). Meanwhile, the rectangular window can be observed with a size of 3.3 Å × 11.5 Å. The packing structure of VMOP-8 is



Figure 4. VOIDOO-calculated void space as shown (yellow mesh) within the crystal structure of VMOP-7 (a) and VMOP-8 (b).

shown in Figure S5a, therein each molecule is arranged in the closest stacking mode along crystallographic axes, and the distance between the two adjacent molecules is 21 Å (Figure S5b). However, the packing structure of VMOP-7 is different from that of VMOP-8. Three crystal axes are not perpendicular to each other, and the distance between two adjacent molecules is 23 Å (Figure S6).

In order to understand the configuration of the two VMOPs in-depth, the topological analysis is applied to the analysis of the two structures. As shown in Figure 5, if each  $V_5$ -SBU is



**Figure 5.** Topological analysis based on VMOP-7, **8.** (a) 4-connected {V<sub>5</sub>O<sub>9</sub>Cl}, 2-connected ligand H<sub>2</sub>ADC, and 3-connected ligand H<sub>3</sub>BPT. (b) The size of VMOP-7 is 25 Å. (c) VMOP-8, 31.4 Å. (d) {V<sub>5</sub>O<sub>9</sub>Cl} is regarded as 4-valent SBU,  $\eta = 60^{\circ}$  (in VMOP-7),  $\eta = 43.6^{\circ}$  (in VMOP-8). The bending angle  $\theta$  of the ditopic linker H<sub>2</sub>ADC is 180°; H<sub>3</sub>BPT serves as 3-valent SBU with  $\eta_2 = 43.6^{\circ}$ . (e, f) H<sub>2</sub>ADC act as ditopic linkers; H<sub>3</sub>BPT serves as 3-valent SBU. VMOP-7 can be simplified into an octahedron (otc), while VMOP-8 can be simplified into a more sophisticated rhombic dodecahedron (rdo). (g–i) Replacing the original topological vertices by a quadrilateral, two derived topological polyhedrons otc-a and rdo-a were obtained.

reduced to a 4-valent vertex, the H<sub>2</sub>ADC ligand acts as a ditopic linker, while the H<sub>3</sub>BPT ligand serves as a 3-valent SBU. **VMOP-7** can be simplified into an octahedron (**otc**), while a more sophisticated rhombic dodecahedron (**rdo**) is achieved with the same simplification for **VMOP-8**. Both polyhedra belong to edge-transitive polyhedra, although they have different configurations. As summarized in the reticular chemistry of MOPs proposed by O'Keffee and Yaghi, for an octahedron, it is composed of one kind of SBU as vertex linked by a ditopic linker, and including two extreme cases,  $\eta = 60^\circ$ ,  $\theta = 180^\circ$  and  $\eta = 90^\circ$ ,  $\theta = 90^\circ$ , corresponding to the limit conditions, respectively.<sup>1</sup> The geometry of **VMOP-7** almost meets the conditions of the first extreme case (Figure 5d,e). While, for a rhombic dodecahedron, three extreme cases include  $\eta_1 = 48.2^\circ$ ,  $\eta_2 = 120^\circ$ ;  $\eta_1 = 70.5^\circ$ ,  $\eta_2 = 109.5^\circ$ ; and  $\eta_1 =$ 

90°,  $\eta_2 = 60^\circ$ , representing three different geometries. The topology of **VMOP-8** ( $\eta_1 = 43.6^\circ$ ,  $\eta_2 = 120^\circ$ ) conforms to the first extreme case, and a small deviation in  $\eta_1$  (48.2–43.6 = 4.6°) was observed to coordinate the effect caused by the shape of H<sub>3</sub>BPT on topology (Figure 5d,f). In addition, the angle of V<sub>5</sub>-SBU in **VMOP-8** is also the minimum value found so far. Further inspired by reticular chemistry, the vertices in the simplest topology can be as extension points, replacing the original topological vertices by a polygon with the number of sides equal to the valence of those vertices; two new derived networks are obtained and denoted as **otc-a** and **rdo-a**, respectively, as shown in Figure 5g–i.

**Catalyst Properties.** Researchers have paid attention to the catalytic oxidation of sulfides because sulfone and sulfoxide often play an essential role in the synthesis of many industrial products. POMs are given priority as well-known and environmentally friendly redox catalysts.<sup>41–44</sup> VMOP-8 was chosen as a catalyst to study its catalytic performance for sulfoxidation reaction. First, a preliminary study of VMOP-8 for the oxidation of methyl phenyl sulfide (MBT) was carried out. In methanol solvent, VMOP-8 (0.002 mmol) is used as the catalyst, *tert*-butyl hydroperoxide (TBHP 1 mmol) as the oxidant for the reaction (Scheme 1), and the conversion rate is

Scheme 1. Schematic Representation of Sulfoxidation Reaction with MBT as an Example under VMOP-8 and TBHP



monitored by gas chromatography (GC). At room temperature, the conversion of MBT quickly reached 90% within 10 min (Figure S7). After 1 h of reaction, the conversion rate is close to 100% (Figure 6a). As a control experiment, the conversion rate of MBT is only 22% in the blank control test after 1 h without catalysts (Figure S8). Thus, we can conclude that VMOP-8 can efficiently catalyze the sulfur oxidation reaction.

A series of substrates were then selected for sulfur oxidation under the same conditions to evaluate the generality of VMOP-8 as a catalyst. As shown in Table 1, the conversion rate of diphenyl sulfide can reach more than 99% within 4 h

Table 1.	Results	of Sulfoxida	tion Reactions	Catalyzed	by
VMOP-8	at Diffe	erent Condit	ions <sup>a</sup>		

Entry	Substrate	Temperature (°C)	Time (h)	Conv. (%) <sup>b</sup>
1	Ċ, s∖	25	1	100
2	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	25	1	>99
3	O <sub>2</sub> N S	25	1	81.3
4		25	1	76.7
			4	>99
5	(	25	12	69.1
		50	6	97.2
6		25	12	54.4
		50	6	83.7
7		25	12	30.3
		50	12	96.7

<sup>*a*</sup>Reaction conditions: substrate (0.4 mmol), **VMOP-8** (0.002 mmol), TBHP (1 mmol), and MeOH (5 mL). <sup>*b*</sup>Isolated conversions were calculated by GC or HPLC.

(Figure S9). In addition, two kinds of substrates with different electron effect substituents were also used, under the same reaction conditions for 1 h. The conversion rate of 4-nitromethyl phenyl sulfide with an electron-withdrawing group was 81.33%, while 4-methoxy-methyl phenyl sulfide with an electron-donating group was almost completely converted (Figures S10 and S11). From the experimental results, we can draw a conclusion that the electron-withdrawing group in the substrate is not conducive to the catalytic oxidation process of



**Figure 6.** (a) Conversion curve of methyl phenyl sulfide with different reaction times. (b) Dynamic conversion curve of diphenyl sulfide catalyzed by **VMOP-8** (blue) and filter out the catalyst during the reaction (orange). Reaction conditions: substrate (0.4 mmol), **VMOP-8** (0.002 mmol), TBHP (1 mmol), and MeOH (5 mL), 25 °C.

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thioether, whereas, for sulfur-containing aromatic substrates, such as dibenzothiophene, 4,6-dimethyl dibenzothiophene, and benzothiophene, the conversion rates, respectively, reach to 69.1%, 54.4%, and 30.3% after 12 h (Figures S12-S14). These results show that the sulfur oxidation of thiophene substrates is more difficult than that of thioether, and the catalytic effect of the catalyst on the oxidation process of such substrates is not ideal at room temperature. Therefore, in order to improve the conversion rate, the reaction temperature was increased to 50 °C. The conversion rate of the two dibenzothiophene substrates reached 97.2% and 83.7% after 6 h, and the corresponding sulfoxide and sulfone products were identified by IR spectra (Figure S15). Besides, benzothiophene can also be effectively oxidized, and its conversion rate can reach 96.7% after 12 h. Next, diphenyl sulfide was also selected to study the dynamics of catalytic oxidation at 1 h intervals. As shown in Figure 6b, the catalyst was hot filtered in a set of parallel reactions and the solution continued to react, but the conversion rate hardly improved. This further indicates that VMOP-8 plays a vital role in the oxidation of thioethers as a heterogeneous catalyst.

The results of sulfur oxidation experiments show that **VMOP-8** is a good and general heterogeneous oxidation catalyst. The possible catalytic mechanism of **VMOP-8** can be inferred from the work of the typical polyoxovanadates windmill-shaped V<sub>8</sub> cluster applied to oxidative desulfurization (Scheme 2).<sup>19</sup> First, in the presence of the oxidant TBHP, the

# Scheme 2. Proposed Catalytic Mechanism for the Oxidation of Sulfides with VMOP-8



exposed POV-based  $V_5$  clusters are converted into metal peroxide intermediates. Next, the sulfur-containing aromatic substrate is oxidized by the peroxovanadate intermediate and gets oxygen atoms to form sulfoxide; the regeneration of the catalysts also accompanies this process. Finally, sulfoxide can be further nucleophilically attacked by metal peroxide intermediates and oxidized to sulfone. Most likely, the catalytic oxidation process is too fast and results in poor product selectivity. Therefore, follow-up work will focus on improving the selectivity of sulfoxide or sulfone as single products and exploring better reaction conditions for replacing TBHP with environmentally friendly oxidants.

# CONCLUSION

In summary, two new VMOPs based on the  $\{V_sO_oCl\}$  SBU and organic ligands with different configurations were successfully synthesized under solvothermal conditions. Through topology analysis, the geometry of VMOP-7 is an octahedron (otc) and the configuration of VMOP-8 is a rhombic dodecahedron (rdo). The angle  $\eta = 43.6^{\circ}$  of V<sub>5</sub>-SBU in VMOP-8 is also the smallest in the reported VMOPs. In addition, the catalytic oxidation performance of VMOP-8 was explored for oxidative desulfurization. According to the results, VMOP-8 can effectively catalyze the conversion of sulfurcontaining substrates to sulfone and sulfoxide. This research provides a new perspective for developing more excellent properties of VMOPs. Besides, the selectivity of the catalyst will be improved in the follow-up work and the environmentally friendly catalyst will be tried to explore better conditions.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01375.

The figures of the powder X-ray diffractions, IR spectra, TGA curves, and additional structural figures. All GC and HPLC spectra used to calculate the conversion rate of the oxidation of sulfide reactions (PDF)

# **Accession Codes**

CCDC 2024517 and 2024518 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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