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# Polyoxometalate based hybrid chiral material: Synthesis, characterizations and aerobic asymmetric oxidation reaction

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#### ABSTRACT

A new hybrid chiral material, comprising Keggin type mono ruthenium substituted phosphotungstate (PW<sub>11</sub>Ru) and chiral (R-(-)-1-cyclohexylethylamine (Cy)), was synthesized in an aqueous medium by simple ligand substitution. The bonding was confirmed by FT-IR, multinuclear NMR (<sup>31</sup>P, <sup>13</sup>C and <sup>15</sup>N), while the chirality was confirmed by CD spectroscopy and a polarimeter. The study reveals the attachment of Cy and PW<sub>11</sub>Ru through N  $\rightarrow$  Ru bond. An attempt was made to use the synthesized material as a heterogeneous catalyst for carrying out aerobic asymmetric oxidation of styrene and found that only 0.001 mg (7.9 × 10<sup>-6</sup> mmol) of Cy was sufficient to achieve very high TON.



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#### **1. Introduction**

The tailoring of inorganic-organic hybrid materials constructed from building blocks represents research in material science, crystal engineering, magnetic materials, photosensitive materials and catalysis [1–3] as they combine features of both inorganic and organic components. Polyoxometalates (POMs), an aggregate of metal-oxo species with O-donor ligands [4–7], have diverse modifiable features, depending on the elemental composition, structures as well as counteractions [8–10].

Transition metal substituted polyoxometalates (TMSPOMs), a sub class of POMs, are excellent candidates as building blocks for hybrid materials due to their electrochemical, magnetic, medicinal and catalytic properties [7–16]. They can also be rationally modified on the molecular level for shape, size, charge density, redox states as well as stability. In TMSPOMs the transition metal is coordinated with five oxygens of the POMs, while the sixth coordination site is occupied by water, which is labile and can be replaced by other ligands [9,10]. The obtained material is an inorganic-organic hybrid material based on POMs, which have potential application in material science to biology [7,8]. A number of strategies have been reported for the synthesis of hybrid materials based on POMs [8,9,14–19]. The most common two strategies [20] are (i) coordination competition where lacunary (Vacant) POMs are ligands which react with metal complexes through coordination competition to give POM coordinated metal complexes and (ii) ligand substitution where transition metal substituted POMs are starting materials, in which water ligand is replaced by an organic ligand.

Among the family of TMSPOMs, ruthenium substituted POMs attract major attention because of unique redox as well as catalytic properties. Research activities in hybrid materials were centered on ruthenium substituted POMs [21-24]. In 2000, Bonchio et al. reported the synthesis and characterization of DMSO functionalized ruthenium substituted phosphotungstate [PW<sub>11</sub>O<sub>30</sub>Rull(DMSO)]<sup>5-</sup> and evaluated its catalytic activity for oxidation of cyclooctene and adamantane to achieve 83% and 53% yields, respectively [25]. In 2005, Proust et al. [21] synthesized a series of organometallic derivatives of phosphotungstate  $[Ru(arene)Cl_2]_2$  (arene = benzene, toluene, p-cymene, hexamethylbenzene) with K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>]·14H<sub>2</sub>O and characterized spectroscopically as well as crystallographically. In 2007, the same group reported a ruthenium-nitride [22] derivative of  $[PW_{11}O_{39}\{RuN\}]$ characterized by <sup>31</sup>P, <sup>183</sup>W, and EXFES. In 2008, Kortz's group [23] reported the carbonyl-ruthenium substituted  $\alpha$ -Keggin-tungstosilicate,  $[\alpha$ -SiW<sub>11</sub>O<sub>39</sub>Ru<sup>II</sup>(CO)]<sup>6-</sup> that was characterized by spectroscopically as well as voltametrically. In the same year, Poblet [24] reported a computational study of the ruthenium nitride derivative ( $PW_{11}O_{39}\{Ru^{VI}N\}$ ). Sadakane contributed significantly towards the synthesis and characterization of different Ru substituted polyoxometalates, such as silicotungstate, germanotungstate and phosphotungstate, with ligands like DMSO, benzene, 4,4'-bipyridine and carbonyl [25–31], however catalytic activities were not reported.

Almost all reports deal with synthesis and characterization only. For the last decade, no report is available on hybrid materials based on Ru substituted polyoxometalates. Our group reported a one-step synthesis of air-stable diamagnetic undecatungstophospho(aqua)ruthenate(II) ( $PW_{11}Ru$ ) [32] and its catalytic activity for aerobic oxidation of styrene. The catalyst proved to be successful for solvent free oxidation of alkene with molecular oxygen. As an extension, we synthesize hybrid

materials using a chiral ligand, R-(-)-1-cyclohexylethyl amine (Cy). The selection was made by considering its importance as well as availability of a single nitrogen (from amine group) donor.

The synthesis of a hybrid chiral material ( $PW_{11}Ru$ -Cy) was carried out by ligand substitution, and the obtained material was systematically characterized by elemental analysis, TGA, UV-vis, FT-IR, multinuclear NMR ( $^{31}P$ ,  $^{13}C$  and  $^{15}N$  NMR), CD spectroscopy and polarimetry. The hybrid material was used as a heterogeneous catalyst for carrying out solvent free asymmetric oxidation of styrene with molecular oxygen.

#### 2. Experimental

#### 2.1. Materials

All required chemicals were of A. R. grade and used as received. 12-tungstophosphoric acid,  $H_3PW_{12}O_{40}\cdot nH_2O$  (99.99%, Loba Chemie, Mumbai), sodium acetate (assay,  $\geq$  99%), sodium bicarbonate ( $\geq$  99.7%), acetic acid and acetone were obtained from Merck and used as received. R-(-)-1-cyclohexylethyl amine (Cy) (98%) and 70% aqueous tert-butyl hydroperoxide (70 wt. % in  $H_2O$ ) were obtained from Sigma. RuCl<sub>3</sub>·3H<sub>2</sub>O (40 wt % of Ru, SRL Chemicals, Mumbai) was purified and then used.

#### 2.2. Synthesis of chiral hybrid material

The synthesis was followed in two steps.

#### 2.2.1. Synthesis of mono ruthenium substituted phosphotungstate ( $PW_{11}Ru$ )

The PW<sub>11</sub>RuO<sub>39</sub> synthesis was reproduced from the literature [32] and isolated as a sodium salt.  $H_3PW_{12}O_{40}$ ·nH<sub>2</sub>O (POMs, 1 eq 2.4 g) was dissolved in 10 mL of distilled water containing 0.6 mL acetic acid. The pH of the solution was carefully adjusted to 5.2 with sodium bicarbonate solution. The aqueous solution was heated and stirred for 15 minutes. Hot solution of 0.25 g RuCl<sub>3</sub>·3H<sub>2</sub>O was dissolved in minimum water (RuCl<sub>3</sub> was previously treated with concentrated hydrochloric acid, evaporated to dryness and then used) and added to hot tungstate solution. The final pH of the solution was heated at 80 °C with constant stirring for 30 min and filtered hot. The filtrate was refrigerated overnight for 3 days and the obtained brownish-black crystalline powder was designed as PW<sub>11</sub>Ru.

#### 2.2.2. Synthesis of hybrid material (PW11Ru-Cy)

Crystalline brownish-black PW<sub>11</sub>Ru (0.786 g) was dissolved in 10 mL of distilled water. To this aqueous solution, 0.127 g of Cy dissolved in 10 mL ethanol was added dropwise over 30 minutes with continuous stirring in order to ensure the formation of homogeneous solution and the obtained aqua-ethanolic solution was refluxed for 10 h. The resultant solution was cooled, evaporated to half of its original volume and refrigerated for 2 days. Brownish-black crystalline material was washed with alcohol and dried in a vacuum oven at 50 °C for 6 h (83% yield) and determined as PW<sub>11</sub>Ru-Cy.

#### 2.3. Characterization

Elemental analysis was carried out using a JSM 5610 LV combined with INCA instrument for EDX-SEM analyzer for the quantitative identification of metal ions. Thermogravimetric analysis was carried out on a Mettler Toledo Star SW 7.01 up to 600 °C in air with heating rate of 5 °C/min. The UV-visible spectrum was recorded at ambient temperature on a Perkin Elmer 35 LAMBDA instrument using a 1 cm quartz cell. FT-IR spectra of the samples were recorded as KBr pellets on a Perkin Elmer instrument. Solution NMR spectra (<sup>31</sup>P, <sup>13</sup>C and <sup>15</sup>N) were recorded in D<sub>2</sub>O and in CDCl<sub>3</sub> on Bruker ACF 300 MHz instruments. Cyclic voltammetry was performed on a CH 600 °C system at room temperature in aqueous solution using platinum as the working electrode, Ag/AgCl reference electrode and platinum rod as a counter ion electrode. Optical activity was measured using a JASCO (J-815 CD Spectrometer, model no: J-815-150L) and a JASCO (P-2000 Digital Polarimeter).

#### 2.4. Catalytic activity

The catalytic activity was evaluated for the solvent free oxidation of styrene using molecular oxygen as an oxidant and an activator (70% solution of tert-butyl hydroper-oxide (TBHP)) as a co-oxidant. Oxidation was performed in a batch type reactor oper-ated under atmospheric pressure. In a standard reaction, 25 mg of PW<sub>11</sub>Ru-Cy was added to a three-necked round bottom flask containing terminal olefins and initiator TBHP (0.014 g) at 80 °C. The reaction initiated at 1 atm pressure of O<sub>2</sub> with continuously stirring on a magnetic hot plate.

After completion of the reaction, the reaction mixture was cooled and then 10% aqueous Na<sub>2</sub>CO<sub>3</sub> solution was added with constant stirring. The resultant mixture (organic and aqueous) was allowed to stand for 15–20 min to separate the two distinct layers. The aqueous layer was collected and concentrated HCl was added with slow stirring. No formation of white precipitates of benzoic acid ruled out the over oxidation reaction. The organic layer was extracted with dichloromethane and analyzed by an Agilent Technologies 6890 N gas chromatograph (FID, 19091 G-B213 chiral capillary column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ mm}$ )) using nitrogen as a carrier gas with a flow rate of 30 ml/min. The injector temperature, detector temperature, and oven temperature were 250°C, 250°C and 100°C, respectively. Authentic samples of benzaldehyde, R-and S-configuration styrene epoxides were used as the standards to determine the yields by comparison of peak height and area.

#### 3. Results and discussion

#### 3.1. Characterization

In spite of many crystallization attempts, we could not produce suitable crystals for Xray diffraction. Crystallization issues associated with hybrid materials are quite common [15, 33–39] and therefore other analytical tools were exploited to explore the compound. For  $PW_{11}Ru$ , the observed values for the elemental analysis are in agreement with the theoretical values. Anal. Calc.: Na, 3.6; W, 64.3; P, 0.98; Ru, 3.2; O, 26.9.



Figure 1. UV-vis spectra of (a) PW<sub>11</sub>Ru and (b) PW<sub>11</sub>Ru-Cy.

Found: Na, 3.9; W, 63.9; P, 0.96; Ru, 3.1; O, 29.6. The number of water molecules was calculated from TGA curve for PW<sub>11</sub>Ru-Cy which shows 8% weight loss corresponding to loss of 14 water molecules. From the elemental analysis and thermal techniques the chemical formula of the complex is proposed as  $Na_5[PW_{11}O_{39}Ru(H_2O)]\cdot 13H_2O$  (PW<sub>11</sub>O<sub>39</sub>Ru) [32].

For PW<sub>11</sub>Ru-Cy, the observed values for the elemental analysis are also in agreement with the theoretical values. Anal. Calc.: Na, 3.65; W, 64.25; P, 0.98; Ru, 3.24; O, 23.38; C, 3.05; H, 0.99; N, 0.46. Found: Na, 3.55; W, 64.10; P, 0.96; Ru, 3.20; O, 23.26; C, 3.0; H, 0.96; N, 0.45. The calculated number of water molecules from TGA is 7. From the elemental and thermal analyses, the chemical formula of the isolated complex is proposed as Na<sub>5</sub>[PW<sub>11</sub>O<sub>39</sub>Ru(C<sub>8</sub>H<sub>17</sub>N)]·7H<sub>2</sub>O (PW<sub>11</sub>O<sub>39</sub>Ru-Cy).

The UV-Vis spectrum of PW<sub>11</sub>Ru in water shows a W $\rightarrow$ O charge-transfer peak at 291 nm accompanied by a  $\lambda_{max}$  at 428 nm (Figure 1a) assigned to d-d transitions because of Ru(II). The ability of the ruthenium center substituted in polyoxometalate to coordinate with ligand is well documented in the literature [21–24]. In general, changes in the position or shape or increase in the intensity of ligand field band was observed when water was replaced by any other ligand. The change of the ligand field band was observed for a number of ligands for the Co(II) complex undecatungstocobalto(II) by Weakly *et al.* [34]. In the present case, the UV-vis spectrum of PW<sub>11</sub>Ru-Cy in water shows two peaks, one at 291 and another  $\lambda_{max}$  at 436 nm (Figure 1b). The shift in  $\lambda_{max}$  from 428 to 436 nm may be due to the replacement of labile water by an amine, consistent with the substitution reaction. Thus, the UV-vis spectrum indicates bonding between Ru (of PW<sub>11</sub>Ru) and N (of Cy). This is further supported by FT-IR spectra.

The FT-IR bands for  $PW_{11}O_{39}Ru$ ,  $PW_{11}O_{39}Ru$ -Cy and Cy are presented in Table 1.  $PW_{11}Ru$  shows bands at 1075 cm<sup>-1</sup>, 1035 cm<sup>-1</sup>, 940 cm<sup>-1</sup>, 812 cm<sup>-1</sup> and 754 cm<sup>-1</sup> corresponding to P-O, W = O and W-O-W, respectively. Cy shows bands at 1296 cm<sup>-1</sup>, 1264 cm<sup>-1</sup> and 1154 cm<sup>-1</sup> attributed to C-N stretching vibration, 1599 cm<sup>-1</sup> corresponds to N-H stretching, 2922 cm<sup>-1</sup> and 1449 cm<sup>-1</sup> for C-H stretch and band, respectively.

FT-IR spectrum of PW<sub>11</sub>Ru-Cy shows bands of both, PW<sub>11</sub>Ru and Cy. Weak bands at 2926 cm<sup>-1</sup> and 1448 cm<sup>-1</sup> were observed for PW<sub>11</sub>Ru-Cy which is attributed to the symmetric and asymmetric stretching vibrations of aliphatic C-H bonds, respectively. These results confirm coordination of PW<sub>11</sub>Ru with Cy. After formation of PW<sub>11</sub>Ru-Cy,

#### 6 🕢 A. PATEL AND K. PATEL

Table 1. FT-IR Frequency data.

POMs	P-0	W = O	W-O-W	Ru–O	Ru-N	C-N	N-H	C-H
PW <sub>11</sub> Ru	1078 1038	937	812 759	644	-	-	-	-
Су					-	1296 1264 1154	1599	2922 1449
PW <sub>11</sub> Ru-Cy	1075 1035	940	812 754		588	1200	1627	2926 1448



Figure 2. <sup>31</sup>P NMR of (a) PW<sub>11</sub>Ru and (b) PW<sub>11</sub>Ru-Cy.

the vibration bands that originated from the C-N bond are merged and only a broad shoulder at  $1200 \text{ cm}^{-1}$  is observed. Further, a significant shift from  $1599 \text{ cm}^{-1}$  to  $1627 \text{ cm}^{-1}$  for N-H stretch is observed. This indicates formation of N $\rightarrow$ Ru bond. As a result of decrease in electron density on N, N-H bond length increases which leads to the shift. Formation of a new band at  $588 \text{ cm}^{-1}$  also supports the formation of N $\rightarrow$ Ru bond.

Multinuclear NMR (<sup>31</sup>P, <sup>13</sup>C and <sup>15</sup>N) spectra are a critical means to examine binding. <sup>31</sup>P NMR spectra for  $PW_{11}Ru$  and  $PW_{11}Ru$ -Cy are shown in Figure 2a and b. No significant change in the chemical shift confirms that the Keggin unit remains intact after introduction of Cy to  $PW_{11}Ru$ . Thus, from <sup>31</sup>P NMR, the functionalization could not be supported as the central P is quite far from N of Cy. However, to confirm, <sup>13</sup>C NMR and <sup>15</sup>N NMR were recorded.

Figure 3a and b show <sup>13</sup>C NMR spectra for Cy as well as  $PW_{11}Ru$ -Cy. The values for the chemical shift are presented in Table 2. No significant shift in the cyclic ring carbon <sup>(a-e)</sup>CH<sub>2</sub> indicates that the amine remains intact in the synthesized material. The significant upfield shift for <sup>h</sup>CH<sub>3</sub> and <sup>f</sup>C-C-NH<sub>2</sub> may be due to the bond formation between N of Cy and Ru of  $PW_{11}Ru$ . Once the Ru-N bond forms, the electron density on N atom decreases, which leads to the downfield shift. The N attached to the stereogenic center shows downfield shift of 0.9 ppm. The result is as expected.



Figure 3. <sup>13</sup>C NMR of (a) Cy and (b) PW<sub>11</sub>Ru-Cy.

Table 2.	NMR	chemical	shift.
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	Chemical	shift (ppm)
Functional group	Су	PW <sub>11</sub> Ru-Cy
<sup>h</sup> CH₃	20.797	14.986
<sup>(a-e)</sup> CH <sub>2</sub> (ring carbon)	26.384-29.069	25.318-28.297
<sup>g</sup> C-NH <sub>2</sub>	51.573	52.436
<sup>f</sup> C-C-NH <sub>2</sub>	45.443	40.789

In order to confirm the formation of the N $\rightarrow$ Ru bond, <sup>15</sup>N NMR spectra of Cy and PW<sub>11</sub>Ru-Cy were recorded (Figure 4a and b). A comparison of the <sup>15</sup>N NMR spectrum of Cy with that of PW<sub>11</sub>Ru-Cy showed a significant chemical shift from 199.98 to 194.36 ppm, because the electron density at N (*i.e.* a lone pair on N in Cy) shifted towards POMs and results in the considerable downfield shift in the PW<sub>11</sub>Ru-Cy. Thus, <sup>15</sup>N NMR study confirms the formation of N $\rightarrow$ Ru bond.

The cyclic voltammograms of  $PW_{11}Ru$  and  $PW_{11}Ru$ -Cy were recorded in aqueous solution (Figure 5a and b). The cyclic voltammogram of  $PW_{11}Ru$  shows one redox couple at -0.60 V corresponding to the Ru(II/III) couple, while  $PW_{11}Ru$ -Cy shows one redox



Figure 4. <sup>15</sup>N NMR of Cy (left) and PW<sub>11</sub>Ru-Cy (right).



**Figure 5.** Cyclic voltammetry in water of (a) PW<sub>11</sub>Ru and (b) PW<sub>11</sub>Ru-Cy.

couple at -0.74 V corresponding to the Ru(II/III) couple. The obtained potential for PW<sub>11</sub>Ru-Cy is more negative than that of PW<sub>11</sub>Ru. This may be due to the fact that the N donates its lone pair of electrons to Ru and the Ru center becomes more electron rich and more easily oxidized at a lower potential. Thus, the shift for PW<sub>11</sub>Ru-Cy as compared to PW<sub>11</sub>Ru is as expected and confirms the presence of N $\rightarrow$ Ru bond formation.

To examine the chiroptical and stability of synthesized material in the CD spectra were carried out in water (Figure 6). The spectrum exhibits only a single negative Cotton effect at 250 nm. This is a region characteristic of the oxygen-to-tungsten charge-transfer bands of Keggin polyoxoanions [40]. The induced circular dichroism (ICD) in the POM clusters can be seen in the CD spectra [41]. Optical rotation of Cy and PW<sub>11</sub>Ru-Cy was found to be  $[\alpha]$ 20/D-3.8 and  $[\alpha]$ 20/D-3.2, respectively, confirming that the functionalized material is chiral.

#### 3.2. Catalytic activity

A neat reaction (without catalyst) was performed and showed no conversion, indicating that there is no autooxidation taking place. In order to study the role of TBHP the same reactions were carried under two different conditions: (i) alkene + oxidant + TBHP and (ii) alkene + oxidant + PW<sub>11</sub>Ru-Cy. In both cases, the



Figure 6. CD Spectroscopy of PW<sub>11</sub>Ru-Cy.

Catalyst			Selecti		
	Amount (mg)	Conversion (%)	Styrene oxide	Benzaldehyde	ee (R)
PW <sub>11</sub> Ru-Cy	5	12	67	33	9
	10	26	72	28	12
	15	41	65	35	11
	20	58	68	22	10
	25	78	70	30	14
	30	81	65	25	12

Table 3. Effect of catalyst amount.

Substrate; styrene (100 mmol); O2 (4 ml/min); TBHP, 0.15 mmol; reaction time, 4 h; temperature, 80 °C.

reaction did not progress significantly, indicating that both TBHP and catalyst are required for the reaction, where TBHP act as an initiator for PW<sub>11</sub>Ru-Cy.

#### 3.2.1. Effect of catalyst amount

The effects of catalyst amount on the conversion and selectivity are shown in Table 3. In the present study epoxidation of styrene gives styrene oxide as well as benzaldehyde. With an increase in the amount of catalyst, % conversion also increases as expected. However, selectivity for the product is not significantly affected, maybe because of the presence of Cy which stabilized the formation of styrene oxide. For the present case, 25 mg of the catalyst was optimized and further optimization was performed using the same amount.

#### 3.2.2. Effect of reaction time

The distribution of the product changes with an increase in reaction time (Table 4). After 2 h, 82% of styrene oxide was observed. As reaction time increased the product selectivity towards styrene oxide shifted from 82% to 70%, and after 6 h styrene oxide product selectivity was 58%. Due to the known industrial importance of styrene oxide, the reaction time was optimized at 4 h.

The optimized conditions are: styrene (100 mmol);  $O_2$  (4 ml/min); TBHP, 0.15 mmol; catalyst, 25 mg; temperature, 80 °C with high TON (9,819).

#### 10 👄 A. PATEL AND K. PATEL

#### Table 4. Effect of reaction time.

			Selecti		
Catalyst	Reaction time (h)	Conversion (%)	Styrene oxide	Benzaldehyde	ee (R)
PW <sub>11</sub> Ru-Cy	2	57	82	18	9
	4	78	70	30	14
	6	84	58	42	11

Substrate; styrene (100 mmol); O2 (4 ml/min); TBHP, 0.15 mmol; catalyst, 25 mg; temperature, 80 °C.

#### Table 5. Effect of Cy.

Catalyst		Selecti		
	Conversion (%)	Styrene oxide	Benzaldehyde	ee (R)
PW <sub>11</sub> Ru	94	54	46	-
PW <sub>11</sub> Ru-Cy	78	70	30	14

Conversion based on substrate; styrene, 100 mmol;  $O_2$  (4 ml/min); TBHP, catalyst, 25 mg (The active amount of Cy is 0.001 mg,  $7.9 \times 10^{-6}$  mmol); reaction time, 4 h.

Table 6. % conversion and % selectivity for oxidation of styrene (with and without catalyst).

Catalyst			Selecti		
	Reaction time (h)	Conversion (%)	Styrene oxide	Benzaldehyde	ee (R)
PW <sub>11</sub> Ru-Cy	2	57	82	18	9
PW <sub>11</sub> Ru-Cy	4	58	81	19	8

Substrate; styrene (100 mmol);  $O_2$  (4 ml/min); TBHP, 25 mg catalyst; temperature, 80 °C.

#### 3.2.3. Effect of Cy

To evaluate the effect of ligand, the oxidation of styrene was carried out using PW<sub>11</sub>Ru as well as PW<sub>11</sub>Ru-Cy in optimized conditions and the distribution of products are reported in Table 5. PW<sub>11</sub>Ru showed 94% conversion for styrene with 54% selectivity towards styrene oxide whereas PW<sub>11</sub>Ru-Cy showed 89% conversion with 70% selectivity towards styrene oxide. The difference in the catalytic activity can be explained on the basis of the structural difference between PW<sub>11</sub>Ru and PW<sub>11</sub>Ru-Cy. The difference in the % conversion may be due to the bulkiness of the ligand, while the increase in % selectivity of styrene oxide for PW<sub>11</sub>Ru-Cy is mainly due to the electron-donating ability of the organic ligand, which facilitates formation of the formed styrene oxide. However, the observed low ee selectivity may be due to the very low concentration of Cy,  $7.9 \times 10^{-6}$  mmol, in the optimized amount.

#### 3.2.4. Heterogeneity test

For rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 °C after 2 h and the filtrate was allowed to react to completion of reaction (4 h). The reaction mixture after 2 h and filtrate were analyzed by gas chromatography. The results are presented in Table 6. No change in % conversion, as well as % selectivity, was found. On the basis of the results, it can be said that the present catalyst is truly heterogeneous.

#### 3.2.5. Recycling and regeneration of the catalyst

In order to investigate the stability of the catalyst during oxidation, the catalyst was recovered by simple filtration after completion of the reaction. The recovered catalyst

Catalyst			Selecti		
	Reaction time (h)	Conversion (%)	Styrene oxide	Benzaldehyde	ee (R)
PW <sub>11</sub> Ru-Cy	4	78	70	30	14
R1-PW <sub>11</sub> Ru-Cy	4	77	69	31	13
R2-PW <sub>11</sub> Ru-Cy	4	75	70	30	13

#### Table 7. Recycling of the catalyst.

Substrate; styrene (100 mmol); O2 (4 ml/min); TBHP, 25 mg catalyst; temperature, 80 °C.

Tuble 6. TT in specific of fresh and regenerated catalyst.								
POMs	P-O	W = O	W-O-W	Ru-N	C-N	N-H	C-H	
PW <sub>11</sub> Ru-Cy	1075 1035	940	812 754	581	1200	1627	2926 1448	
Rec. PW <sub>11</sub> Ru-Cy	1075 1035	941	810 763	586	1200	1635	2926 1350	

Table 8. FT-IR spectra of fresh and regenerated catalyst.

was washed with dichloromethane and dried at 100 °C for regeneration (designated as R1-PW<sub>11</sub>Ru-Cy). Oxidation of styrene was then carried out with the regenerated catalyst, under the optimized conditions (R1-PW<sub>11</sub>Ru-Cy). The obtained results are presented in Table 7. The regenerated catalyst did not show appreciable change in the activity, indicating that the catalyst is stable and can be regenerated for repeated use. However, the minor change in the conversion may be due to loss of the catalyst during the regeneration process.

The structural stability of the regenerated catalyst was confirmed by FT-IR (Table 8). All the bands of the catalyst were retained even after recycling, which indicates that the material remains stable and intact during the course of the reaction and also after regeneration. Slight shifts observed for the vibrational frequencies of recycled catalyst are attributed to attachment of the reaction substrate to the material.

The mechanism for oxidation of styrene follows either of two pathways: (a) acetal intermediate via peroxo species formation, where epoxide is not generated and (b) epoxide intermediate via radical generation in which a radical initiator is used. In the present case, since TBHP is used as an initiator for the activation, the reaction is expected to follow the radical mechanism [42].

#### 3.2.6. Comparison with reported catalysts

Reports are available in which functionalized ruthenium-based catalyst had been synthesized and characterized [25–31]. However, only one group has reported catalytic activity for oxidation of cyclooctene and adamantine; no study is available on the asymmetric oxidation of styrene [25]. This is the first instance of a chiral material based on Ru substituted phosphotungstate and Cy as a catalyst for asymmetric oxidation of styrene.

#### 4. Conclusion

We report the functionalization of Keggin type  $PW_{11}Ru$  with chiral Cy moiety via ligand substitution. FT-IR and multinuclear NMR (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR) studies indicate the formation of N $\rightarrow$ Ru bond. Chirality was demonstrated using CD spectroscopy and polarimetry. Cyclic voltammetry study indicates the presence of Ru(II). Our studies reveal the attachment of Cy to the PW<sub>11</sub>Ru without distortion of the structure as well 12 👄 A. PATEL AND K. PATEL

as with retainment of chirality. The synthesized hybrid material has potential of being used as a stable recyclable catalyst, with very high TON of 9,819. Future studies will focus on increasing the % selectivity and % ee for styrene oxide.

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#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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