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Chiral Phosphotungstate Functionalized with (S)-1-Phenylethylamine: Synthesis, Characterization, and Asymmetric Epoxidation of Styrene

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ABSTRACT: In the present work, an attempt has been made to induce chirality in coppersubstituted phosphotungstate (PW₁₁Cu) by functionalization with (S)-(+)-1-phenylethylamine (S-PEA) via a ligand substitution approach. The formation of a N \rightarrow Cu dative bond was confirmed by ¹³C NMR, while ¹H NMR, circular dichroism spectroscopy and optical rotation studies confirmed the introduction of chirality to the Keggin structure. The synthesized material was used as the heterogeneous catalyst for the asymmetric epoxidation of styrene using various green oxidants to obtain high enantiomeric excess (ee), and the reaction with molecular oxygen was found to give the best ee. Regeneration studies were carried out, and the catalyst was found to be suitable for the same. A probable mechanism is also proposed. A comparison with other copper-based polyoxometalate catalysts clearly demonstrate the superiority and novelty of the present catalyst in terms of the reaction conditions as well as the obtained ee.



■ INTRODUCTION

Chirality is a crucial issue, starting from chemistry to materials science as well as biology,¹ and has been a topic of interest for a long time, and it is still a hot topic for researchers. Chiral inorganic–organic hybrid materials based on polyoxometalates (POMs) have generated much attention because of their potential applications in the fields of synthetically specialized materials, enantioselective catalysis, and medicine.^{2,3} In light of the advantages of POMs and the importance of chirality, tremendous effort has been dedicated to the development of chiral POM-based materials. As a result, this has aroused increasing interest and become a new growing topic in recent years.

Chirality can be derived by the introduction of either chiral ligands or stereogenic side chains in POM/transition-metalsubstituted POM (TMSPOM) structures. Chiral inorganicorganic materials can be synthesized by mainly two types of approaches. The first approach is to link suitable discrete chiral polyoxoanions by simple metal cations or metal-organic segments. The drawbacks of these enantiomers are that POMs in acidic solutions are highly unstable, easily hydrolyze, and racemize rapidly to lose their optical activity. In the second approach, chiral organic ligands will be linked to achiral POMs by means of coordination bonding, covalent or electrostatic interaction.⁴ The advantages of this technique are that chirality is transferred from the organic ligand to the symmetric POM and also the new material possesses unusual characteristics. Therefore, this is the most common technique to synthesize chiral POMs.⁵ Many reviews, especially focusing on the

synthesis and design involving the second approach, are available on POM-based chiral materials. $^{6-15}$

The materials using the second approach can be designed by functionalization, and in this context, TMSPOMs can act as a set of transferable excellent building blocks for construction of the aforementioned functionally active solids. TMSPOMs can also be rationally modified on the molecular level including shape, size, charge density, redox state, and stability. The exclusive structural diversity of TMSPOMs, along with their ability to replace their aqua ligand and thereby coordinate with organic ligands, makes them excellent candidates for functionalization. They can act as excellent inorganic multidentate oxygen-donor ligands to assemble various inorganicorganic hybrid compounds with a vast range of structural properties, combining the features of both the organic and inorganic components.^{16,17} The obtained materials have potential applications in the fields of medicine, magnetism, optics, biology, catalysis, electro/photo/thermochromic systems, electrode cathodes, batteries and supercapacitors, solar energy conversion, molecular recognition, and nonlinear materials.6,18-32

 Received:
 March 3, 2021

 Published:
 July 16, 2021





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Scheme 1. Functionalization of PW11Cu with S-PEA



Despite the diversity in chiral-POM-based materials, those based specifically on transition-metal-substituted phosphotungstates are sparse. In 2005, Belai and Pope synthesized two cobalt ethylenediamine (en)-incorporated POMs, Na_{6.5}K_{5.5}[KC{Co(en)WO₄}WO(H₂O)(PW₉O₃₄)₂]·19H₂O and Na₇K₅[{Co(en)(μ -OH)₂Co(en)}{PW₁₀O₃₇Co(en)}₂]. 20H₂O, using a coordination competition approach. These complexes were the first examples of POMs that incorporate *embedded* chelated heteroatoms, which open a broad range of new steric and chiral possibilities for POMs. Of the two, the former shows mirror symmetry because of the fluxional behavior of the en ligand, despite an overall C₁ symmetry. On the other hand, in the second complex, [PW₁₀O₃₇Co-(en)]⁶⁻ is chiral in nature and functions as a bidentate ligand between two Co(en) groups.³³

In 2012, Patel and Patel synthesized two chiral inorganic– organic hybrid molecules by functionalizing monomanganesesubstituted phosphotungstate with (S)-(+)-*sec*-butylamine and (R)-(-)-1-cyclohexylethylamine by a ligand substitution approach and described their detailed characterization.^{34,35} More recently, the same group reported the synthesis of a monoruthenium-substituted phosphotungstate functionalized with (R)-(-)-1-cyclohexylethylamine using the same approach and its catalytic activity for the aerobic asymmetric oxidation of styrene.³⁶

Reports are available on the synthesis and characterizations of copper-based inorganic-organic hybrid POMs having copper complexes as a countercations³⁷⁻⁵¹ consisting of phosphotungstates³⁷⁻⁴¹ and silicotungstates.^{39,42-51} However, it should be highlighted that, out of the cited references, very few reports are available where the oxidation of styrene has been carried out. In 2017, the Qiuxia group reported the use of synthesized of L- or D-pyrrolidine-2-ylimidazole-functionalized copper phosphotungstate (CuW-PYI1) for styrene oxidation using tert-butyl hydroperoxide (TBHP).⁴¹ In 2008, Mirkhani et al. reported Cu(salen)-silicotungstate for styrene oxidation using hydrogen peroxide (H_2O_2) in acetonitrile (CH_3CN) .⁴⁷ A year later (2009), Zheng et al. described the use of $\{[Cu_2(4,4'$ bpy) $(4,4'-Hbpy)_4(H_2O)_4$](SiW₁₂O₄₀)₂(H₂O)₄)_n, {[Cu₂(4,4' $bpy)(4,4'-Hbpy)_6(SiW_{12}O_{40})_3](4,4'-Hbpy)_2(H_2O)_7\}_n,$ $\{[Cu_2(\mu_2-H_2O)_2(4,4'-bpy)_3(SiW_{12}O_{40})](H_2O)_6\}_n$, and $\{[Cu_2(\mu_2-H_2O)_2(4,4'-bpy)_3(SiW_{12}O_{40})](H_2O)_6\}_n$ as catalysts for styrene oxidation using TBHP in an CH₃CN solvent.⁴⁹ After that, in 2011, He et al. reported the synthesis of (i) $[Cu_{2}^{II}(C_{5}H_{5}NCOO)_{2}(4-bpo)_{2}(H_{2}O)_{2}]$ SiW₁₂O₄₀·H₂O, (ii) $[Cu_{4}^{I}(4-bpo)_{6}]SiW_{12}O_{40}\cdot 3H_{2}O_{40}$ and (iii) $[Cu_{4}^{I}(3-bpo)_{4}]$ - $SiW_{12}O_{40}\cdot 3H_2O$ and its use for the said reaction using TBHP in CH₃CN.⁵⁰ It is worth noting that all reported catalysts do not give enantiomeric excess (ee).

A literature survey shows that monocopper-substituted phosphotungstate ($PW_{11}Cu$) has never been functionalized using a chiral organic ligand. In the present work, an attempt has been made to execute this by the functionalization of

 $PW_{11}Cu$ using a simple chiral molecule, and (S)-1-phenylethylamine (S-PEA) was chosen as the model ligand. The material was synthesized by a ligand substitution method, characterized by various techniques, and then evaluated for its catalytic activity for the asymmetric oxidation of styrene. Studies were also carried out using different green oxidants with an effort to obtain maximum ee of the chiral product, and the best oxidant was used to optimize various reaction parameters for high conversion as well as maximum ee.

EXPERIMENTAL SECTION

Material. All chemicals were of analytical reagant grade and were used as received. 12-Tungstophosphoric acid, copper chloride dihydrate, cesium chloride, sodium hydroxide, styrene, 70% *tert*-butyl hydroperoxide (TBHP), and dichloromethane were obtained from Merck. (S)-(+)-1-Phenylethylamine (*S*-PEA) was obtained from TCI Chemicals, Chennai, India, while NaHCO₃ was obtained from SRL, Mumbai, India.

Synthesis of a Chiral-Functionalized Material ($PW_{11}Cu$ -S-PEA). The synthesis of $PW_{11}Cu$ -S-PEA was carried out in two steps.

(i) Synthesis of $PW_{11}Cu$: $PW_{11}Cu$ was synthesized by the one-pot method reported previously by our group.⁵² A total of 2.88 g (1 mmol) of 12-tungstophosphoric acid was dissolved in a minimum amount of water, its pH was adjusted to 4.8 using saturated sodium hydroxide, and the solution was heated to 90 °C for 1 h. A total of 0.17 g (1 mmol) of copper chloride dissolved in water was slowly added to the hot solution, and then the mixture was refluxed for 1.5 h, followed by filtration. Solid cesium chloride (0.5 g) was immediately added, and the resulting greenish-blue precipitates were filtered, dried at room temperature, and designated as $PW_{11}Cu$.

(ii) Functionalization of PW_{11} Cu with S-PEA: A total of 0.35g (0.1 mmol) of PW_{11} Cu was dissolved in 10 mL of water by heating, and 50 μ L (0.1 mmol) of S-PEA was dissolved 10 mL of methanol. The methanolic solution of S-PEA was added dropwise to the hot, clear solution of PW_{11} Cu with stirring, and the pH was adjusted to 6.4 using dilute sodium hydroxide. The resultant mixture was refluxed for 24 h at 90 °C, cooled, filtered, and dried at 100 °C, and the light-green solid obtained was designated as PW_{11} Cu-S-PEA (Scheme 1).

Synthesis of a physical mixture of $PW_{11}Cu$ and S-PEA ($PW_{11}Cu+S$ -PEA): The physical mixture was synthesized by mixing an equimolar amount of cesium salt of $PW_{11}Cu$ (0.35g, 0.1 mmol) and S-PEA (50 μ L, 0.1 mmol). The mixture was ground properly in a mortar and pestle until it became homogeneous in nature. The light-green mixture obtained was designated as $PW_{11}Cu+S$ -PEA.

Characterization Techniques. Elemental analysis as well as thermogravimetric analysis (TGA)-differential thermal analysis was carried out using a PerkinElmer Optima-3300 RL ICP spectrometer and JSM 5610 LV EDX-SEM analyzer and a Mettler Toledo Star SW 7.01 up to 550 °C, respectively. Fourier transform infrared (FT-IR) spectra of the sample were obtained using KBr pellets on a Shimatzu IRAffinity-1S instrument. Solid-state ¹³C magic-angle-spinning (MAS) NMR was recorded in a JEOL ECX 400 MHz high-resolution multinuclear FT-NMR spectrometer for solids. ¹H NMR was carried out in deuterated water as a dispersion solvent after sonication of the sample on a Bruker AVANCE 400 MHz instrument. Electron-spin resonance (ESR) spectra were recorded on a Varian E-line Century series X-band ESR spectrometer at liquid-nitrogen temperature and

scanned from 2000 to 3000 G. Powder X-ray diffraction (XRD) patterns were obtained using a Philips PW-1830 instrument. The conditions were as follows: Cu Ka radiation (1.54 Å); scanning angle from 0° to 60°. Circular dichroism (CD) spectroscopy was carried out in a Jasco J 815 instrument.

Catalytic Activity. The oxidation of styrene was carried out with stirring using PW11Cu-S-PEA as the catalyst in a 50 mL batch reactor attached to a double-walled air condenser on a magnetic hot plate. Styrene (10 mmol), the catalyst, and 70% TBHP as an oxidant were added to the substrate. Because of the absence of any aqueous media, the catalyst remained heterogeneous. In the case of reaction with molecular oxygen (O2 as an oxidant), 100 mmol (10 mL) of styrene, the catalyst, and a small amount of TBHP as the initiator (~0.2 mL) were taken in a 50 mL two-necked round-bottom flask. O2 gas was steadily bubbled at 1 atm of pressure with continuous stirring. After the reaction was completed, the obtained mixture was extracted with dichloromethane and analyzed using a gas chromatograph (Shimatzu-2014), having a flame ionization detector with a chiral capillary column (Rt-bDEXsm) using nitrogen as the carrier gas. The products were identified by a comparison with the authentic samples of benzaldehyde and (R) and (S)-styrene epoxide, and % ee was calculated as follows:

% ee =
$$\frac{[R] - [S]}{[R] + [S]}$$
 = % R - % S

RESULTS AND DISCUSSION

Elemental analysis of $PW_{11}Cu$ and $PW_{11}Cu$ -S-PEA was carried out using inductively coupled plasma atomic emission



Figure 1. TGA of (a) PW₁₁Cu and (b) PW₁₁Cu-S-PEA.

spectrometry as well as energy-disperive X-ray spectroscopy and the obtained results were in good agreement with the theoretical ones. Theoretical for $PW_{11}Cu$: Cs, 19.95; W, 57.36; P, 0.95; Cu, 1.83; O, 19.88. Experimental: Cs, 20.01; W, 57.43; P, 0.97: Cu, 1.80; O, 19.78.

Theoretical for PW₁₁Cu-S-PEA: P, 0.87; W, 57.05; Cs, 19.29; Cu, 1.79; O, 17.89; C, 2.71; N, 0.40. Experimental: P, 0.76; W, 56.65; Cs, 19.45; Cu, 1.81; O, 17.45; C, 2.91; N, 0.51.

TGA of S-PEA shows 99.2% weight loss up to 150 °C. TGA of PW₁₁Cu-S-PEA (Figure 1) shows an initial weight loss of 1.8% up to 120 °C attributed to the loss of adsorbed water as well as partial decomposition of the organic ligand. A further weight loss of 1.7% up to 370 °C is attributed to complete decomposition of SPEA. The total number of calculated water molecules is found to be 1. From elemental analysis as well as



Figure 2. FT-IR spectra of (a) $PW_{11}Cu$ (b) S-PEA, and (c) $PW_{11}Cu$ -S-PEA.

TGA, the molecular formula of the synthesized material is proposed to be $Cs_5[PW_{11}O_{39}Cu(C_8H_{11}N)]\cdot H_2O$.

Figure 2 shows the FT-IR spectra of $PW_{11}Cu$, S-PEA, and $PW_{11}Cu$ -S-PEA. The FI-IR spectrum of $PW_{11}Cu$ shows characteristic bands at 1103 and 1068, 964, 887, and 821 and 488 cm⁻¹ corresponding to P–O, W=O, W–O–W, and Cu–O bonds, respectively. The FT-IR spectrum of pure *S*-PEA shows characteristic bands of –NH stretching vibrations at 3433 cm⁻¹, aromatic ring stretching at 3062 and 3032 cm⁻¹, methyl stretching at 2924 cm⁻¹, and C=C stretching at 1490 and 1450 cm⁻¹. The FT-IR spectrum of PW₁₁Cu-S-PEA shows bands of both PW₁₁Cu and *S*-PEA but with a slight shift in all of the bands, indicating functionalization of the POM with an organic ligand. Along with this, an additional band is observed at 516 cm⁻¹, attributed to Cu–N stretching vibrations.

To confirm the functionalization, ¹³C MAS and ¹H NMR were recorded. The chemical shift values of pure and functionalized *S*-PEA are shown in Table 1, while the spectra are presented in Figure 3. The characteristic peaks of *S*-PEA at 126.9, 128.5, and 147.9 ppm correspond to aromatic carbons, that at 25.6 ppm corresponds to methyl carbon, and that at 51.3 ppm corresponds to chiral carbon.

The ¹³C NMR spectrum of PW₁₁Cu-S-PEA (Figure 3a) shows all of the characteristic peaks with shifting, indicating the intact structure of the ligand as well as successful functionalization. The chiral carbon shows a downfield shift from 51.3 to 74.9 ppm. Similarly, the chemical shift of the methyl carbon also is highly deshielded, giving a peak at 66.4 ppm. The drastic shift of δ values toward the downfield region is attributed to the loss of electronegativity around the adjacent nitrogen, indicating that the lone pair of electrons is used up for the formation of a N \rightarrow Cu dative bond. On the other hand, the aromatic carbons displaying an upfield shift may be due to the electron-rich POM unit, which shields the aromatic carbons. Further, the inducement of S-PEA is confirmed by ¹H NMR spectra (Figure 3b,c).

The ¹H NMR spectrum of *S*-PEA (Figure 3b) shows a broad methyl group as a singlet at 1.191 ppm, a chiral proton was observed at 3.872 ppm, and a phenyl ring proton was observed at 7.236 ppm. The ¹H NMR spectrum of PW₁₁Cu-S-PEA (Figure 3c) shows a downfield shift with a broad peak at 7.37 ppm of an aromatic proton of *S*-PEA and a peak at 1.419 ppm of a methyl group proton. This confirms the formation of a N→Cu dative bond, which results in a decrease in the electron pubs.acs.org/IC

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Table 1. ¹³C MAS NMR Chemical Shifts of S-PEA and PW₁₁Cu-S-PEA



Figure 3. (a) ¹³C MAS NMR spectrum of PW₁₁Cu-S-PEA and ¹H NMR spectra of (b) S-PEA and (c) PW₁₁Cu-S-PEA

density around the protons, making them more deshielded compared to the protons of S-PEA.

The ESR spectra of $PW_{11}Cu$ and $PW_{11}Cu$ -S-PEA are shown in Figure 4. It is well-known that $PW_{11}Cu$ gives a five-line hyperfine spectrum characteristic of copper(II) in octahedral or distorted octahedral geometry. $PW_{11}Cu$ -S-PEA shows a similar spectrum, indicating that copper exists in the 2+ state even after functionalization with retention of the geometry. The decrease in the intensity of the hyperfine lines is attributed to interactions of the copper center with the ligand, as expected.

Wide-angle powder XRD spectra of $PW_{11}Cu$ and $PW_{11}Cu$ -S-PEA are shown in Figure 5. $PW_{11}Cu$ shows characteristic peaks of PW_{11} from 25 to 35° 2 θ values,⁵² indicating the presence of PW_{11} in the synthesized complex. In addition, it also shows peaks at 48 and 50° 2 θ , conforming the presence of copper(II).⁵³ The powder XRD pattern of $PW_{11}Cu$ -S-PEA is similar to that of unfunctionalized $PW_{11}Cu$, indicating an intact

structure of the Keggin unit. Further, a slight shift in the 2θ value of copper in the case of PW₁₁Cu-S-PEA may be due to chemical interaction between nitrogen and copper.

Optical rotation studies were carried out using a pulse polarimeter to get an idea about the presence of chirality in the synthesized catalyst. A stock solution containing 5 mg of PW₁₁Cu-S-PEA in 10 mL of double-distilled water was prepared. After a blank run using distilled water, the stock solution was placed in a sample holder and the relative optical rotation was recorded. While the pure ligand showed an optical rotation ranging from $[\alpha]_D^{20}$ -37 to -410, the synthesized material gave a relative optical rotation value of -0.74710. This confirmed that the synthesized material showed chirality; however, the very small value compared to that of pure ligand was attributed to two reasons: (a) the sparingly soluble nature of the material and (b) a much lower concentration of the chiral ligand in the synthesized material (5.64 × 10⁻⁶ mmol).



Figure 4. ESR spectra of (a) PW₁₁Cu and (b) PW₁₁Cu-S-PEA.



Figure 5. Powder XRD spectra of (a) $\mathsf{PW}_{11}\mathsf{Cu}$ and (b) $\mathsf{PW}_{11}\mathsf{Cu}\text{-}S\text{-}\mathsf{PEA}.$

The presence of chirality is further confirmed by CD spectroscopy.

The CD spectra of PW₁₁Cu-S-PEA (Figure 6) shows only a single strong Cotton effect at around 250 nm, which is the fingerprint region for $O \rightarrow W$ charge transfer in Keggin structures.⁵⁴ Figure 6 also indicates that optical rotation activity has been induced in the POM moiety because of chemical interaction with the chiral ligand, confirming the observations of the polarimetry experiment. The intensity of the induced chirality seems to be much less, which may be because of the much lower concentration of the chiral ligand (5.64 × 10⁻⁶ mmol) as well as the poor solubility of the synthesized complex, as explained previously.

Asymmetric Oxidation of Styrene. The oxidation of styrene was carried out using TBHP as the oxidant, and various parameters were optimized with the aim of obtaining



Figure 6. CD spectra of PW₁₁Cu-S-PEA.



Figure 7. Effect of the catalyst amount (styrene, 10 mmol; TBHP, 2 mL; time, 16 h; temperature, 60 $^{\circ}$ C).



Figure 8. Effect of time (catalyst amount, 20 mg; styrene, 10 mmol; TBHP, 2 mL; temperature, 60 $^{\circ}$ C).

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Table 2. Effect of the Oxidants

		% selectivity						
oxidant	% conversion	benzaldehyde	(R)-styrene oxide	(S)-styrene oxide	ee			
TBHP ^a	36	63	2	1				
TBHP ^b	35	40	25	28	6			
$H_2O_2^c$	N.A.							
O_2^d	43	63	13	18	16			

^aWithout catalyst; styrene, 10 mmol; TBHP, 2 mL; time, 12 h; temperature, 60 °C. ^bCatalyst amount, 20 mg; styrene, 10 mmol; TBHP, 2 mL; time, 12 h; temperature, 60 °C. ^cCatalyst amount, 20 mg, styrene, 10 mmol; H_2O_2 , 30 mmol; time, 12 h; temperature, 80 °C. ^dCatalyst amount, 20 mg, styrene, 100 mmol; O_2 , 1 atm; TBHP, 0.2 mL; time, 12 h; temperature, 80 °C.

maximum ee. The reaction was carried out at different catalyst amounts from 10 to 20 mg (Figure 7), and a steady increase in the conversion and selectivity of styrene oxide were observed. As expected, a higher selectivity of the S isomer was obtained, but a maximum ee of only 4 was attained. From the results obtained, 20 mg of catalyst was considered to be optimum.

Next, when the reaction time was varied from 8 to 12 h, there was an increase in the conversion and selectivity of epoxide along with its ee (Figure 8). With a further increase in the reaction time, no increase in the conversion was observed, but the selectivity and ee of the S isomer of epoxide were

reduced. Hence, 12 h was considered to be the optimum time for the reaction.

With a view to obtain better ee, the reaction was carried out using different green oxidants, and the results are presented in Table 2. The reactions using H_2O_2 and molecular O_2 were carried out at 80 °C; however, a few drops of TBHP (~0.2 mL) was added as the initiator in the case of molecular O_2 . It is interesting to note that, despite the lower selectivity of the epoxide, the reaction with molecular O_2 gave a higher ee of 16. This can be explained as follows.

It is known that in olefinic solvents, such as styrene, TBHP undergoes decomposition to give styrene oxide.55 The obtained result, a racemic mixture (Table 2, entry 1) with TBHP in the absence of catalyst, is as expected. On the other hand, TBHP in the presence of chiral catalyst gives almost a similar conversion, but the epoxide is no longer racemic (ee = 6). This may be due to the introduction of chirality. Further, it can be assumed that the majority of the TBHP molecules undergo self-disproportionation, while a small number of molecules interact with the catalyst, thereby giving a small ee. In the case of molecular O_{2i} self-disproportionation does not occur, and hence the entire oxidant has to interact with the catalyst to form an intermediate, which leads to the formation of epoxide with a high value of ee. The addition of a few drops of TBHP is expected to initiate the reaction, i.e., to convert molecular O_2 to a superoxo radical (a detailed explanation is given in the Probable Reaction Mechanism section). Further



Figure 9. Various reaction parameters: (a) time (catalyst amount, 20 mg; styrene, 100 mmol; O_2 , 1 atm; TBHP, 0.2 mL; temperature, 80 °C); (b) catalyst amount (styrene, 100 mmol; O_2 , 1 atm; TBHP, 0.2 mL; time, 12 h; temperature, 80 °C); (c) temperature (catalyst amount, 20 mg; styrene, 100 mmol; oxidant O_2 , 1 atm; TBHP, 0.2 mL; time, 12 h).

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Table 3. Effect of S-PEA

entry	catalyst	% conversion	benzaldehyde	(R)-styrene oxide	(S)-styrene oxide	ee
1	PW ₁₁ Cu ^a	13	99			
2	S-PEA ^b	0.3	100			
3	PW ₁₁ Cu-S-PEA ^c	43	63	13.2	18.3	16
4	$PW_{11}Cu$ -S-PEA ^d	22	80	8	9	6
5	$PW_{11}Cu+S-PEA^d$	15.2	72.6	13.5	13.4	0.25

^{*a*}Catalyst amount: 19.2 mg. ^{*b*}Catalyst amount: 0.8 mg. ^{*c*}Catalyst amount, 20 mg, styrene, 100 mmol; O₂, 1 atm; TBHP, 0.2 mL; time, 12 h; temperature, -80 °C. ^{*d*}Catalyst amount, 20 mg, styrene, 100 mmol; O₂, 1 atm; TBHP, 0.2 mL; time, 4 h; temperature, -80 °C.

Table 4. Effect of the Oxidant and Scavenger

		%			
catalyst	% conversion	benzaldehyde	(R)- styrene oxide	(S)- styrene oxide	ee
02 ^{<i>a</i>}	1	100			
ТВНР ^Ь	1.7	62.5	18.1	18.7	1.6
TBHP + O_2^c	22	80	8	9	6
$TBHP + O_2 + scavenger^d$	23	80	8	9	6

^{*a*}Catalyst amount, 20 mg; styrene, 100 mmol; O₂, 1 atm; time, 4 h; temperature, 80 °C. ^{*b*}Catalyst amount, 20 mg; styrene, 100 mmol; TBHP, 0.2 mL; time, 4 h; temperature, 80 °C. ^{*c*}Catalyst amount, 20 mg; styrene, 100 mmol; O₂, 1 atm; TBHP, 0.2 mL; time, 4 h; temperature, 80 °C. ^{*d*}Catalyst amount, 20 mg; styrene, 100 mmol; O₂, 1 atm; TBHP, 0.2 mL; time, 5 h (4 h + 1 h); temperature, 80 °C.



Figure 10. Heterogeneity test.

Scheme 2. Mechanistic Evaluation of Styrene Epoxidation



Table 5. Recycle Study^a

		% selectivity					
catalyst	% conversion	benzaldehyde	(R)- styrene oxide	(S)-styrene oxide	ee		
PW ₁₁ Cu-S- PEA	43	63	13.2	18.3	16		
R ₁ -PW ₁₁ Cu- S-PEA	42	64	13	18	16		
R ₂ -PW ₁₁ Cu- S-PEA	42	63	13	18	16		

 $^aCatalyst amount, 20 mg; styrene, 100 mmol; O_2, 1 atm; TBHP, 0.2 mL; time, 12 h; temperature, 80 <math display="inline">^\circ C.$



Figure 11. FT-IR spectra of (a) PW₁₁Cu-S-PEA and (b) R-PW₁₁Cu-S-PEA.

The reaction was monitored at different time intervals, and the results are presented in Figure 9a. The highest ee was obtained at 12 h, while beyond 12 h, polymerization of styrene was observed. Hence, 12 h was considered to be the optimum time for the reaction. Next, the reaction was carried out over different catalyst amounts (Figure 9b). It was observed that, although the change in conversion was negligible, there was a significant change in the ee. An amount of 20 mg gave the best ee and hence was considered to be the optimum amount of catalyst. Finally, the reaction was carried out at different

Table 6

temperatures, and the results are shown in Figure 9c. As expected, the conversion and ee toward the *S* isomer increase with an increase in the temperature from 60 to 80 °C. Beyond 80 °C, polymerization of styrene was observed, and, hence, the temperature for the reaction was optimized at 80 °C.

The optimized conditions for 43% conversion and 16 ee are as follows: catalyst amount, 20 mg (the active amount of *S*-PEA is 0.68 mg, 5.64×10^{-6} mmol); styrene, 100 mmol; O₂, 1 atm; TBHP, 0.2 mL; time, 12 h; temperature, 80 °C.

Control Experiments: Effect of \hat{S} **-PEA.** In order to study the role of the organic ligand as well as to confirm chemical interaction, experiments were carried out with PW₁₁Cu, *S*-PEA, and PW₁₁Cu+*S*-PEA (physical mixture) under optimized conditions, and the results are shown in Table 3. The reaction does not proceed (negligible conversion) in the presence of an organic ligand alone, while the single product, benzaldehyde without any epoxide in the case of PW₁₁Cu, can be attributed to the absence of chirality in the reaction system. However, it can be clearly seen that the functionalized material shows a substantial increase in conversion with significant ee. This may be attributed to the synergic effect between PW₁₁Cu and *S*-PEA, where PW₁₁Cu stabilized the chirality of *S*-PEA.

The catalytic activity of both the functionalized material (entry 4) and physical mixture (entry 5) was carried out under optimized conditions but for 4 h (Table 3). If any chemical interaction in the physical mixture exists, an almost similar result should be obtained for entries 4 and 5, but the negligible ee clearly confirms that either the S-PEA moiety is almost free or it is attached with $PW_{11}Cu$ via electrostatic interaction only.

Probable Reaction Mechanism. In order to understand the mechanism, the reactions were carried out only in the presence of a small amount of oxygen and TBHP separately (entries 1 and 2 in Table 4), and no significant conversion was obtained with either one. The obtained results indicate that TBHP is required to initiate the reaction in terms of the activation of molecular O_2 in a superoxo anion radical. The formed superoxo anion radical will bind to copper, in place of one of the surface oxygen atoms, in the form of an end-on superoxo (it should be noted that, in PW₁₁Cu, copper is coordinated to three bridging and two surface oxygen atoms). Here we assume (i) unlike W=O bonds, which are covalent, Cu–O are coordinated bonds and (ii) in general, copper forms a stronger coordinate bond with amine nitrogen than oxygen. Hence, superoxide can temporarily substitute for one of the

					% conversion	% selectivity			
series no.	catalyst	oxidant	solvent	time (h)/ temp (°C)		BzOH	styrene oxide	ee	ref
1	CuW-PYI1	TBHP		120/40	71.9		36.7		41
2	Cu(salen)-POM		CH ₃ CN	4/80	84	95.2	4.8		47
3	${[Cu_2(4,4'-bpy)(4,4'-Hbpy)_4(H_2O)_4](SiW_{12}O_{40})_2(H_2O)_4}_n$	TBHP	CH ₃ CN	10/70	48.5	87	12.2		
		TBHP	CH ₃ CN	10/70	44.9	90.2	8.5		
	{ $[Cu_2(\mu_2H_2O)_2(4,4'-bpy)_3(SiW_{12}O_{40})](H_2O)_6$ }	TBHP	CH ₃ CN	10/70	79.5	43.1	55.9		
	$ \{ [Cu_2(\mu_2-OH)(4,4'-bpy)_3(SiW_{12}O_{40})(H_2O)] [Cu_2(\mu_2-O)(4,4'-bpy)_4(H_2O)_2]_{0.5}(H_2O)_3 \}_n $	ТВНР	CH ₃ CN	10/70	74.4	55.7	44		
4	$[Cu^{II}_{2}(C_{5}H_{5}NCOO)_{2}(4-bpo)_{2}(H_{2}O)_{2}]$ SiW ₁₂ O ₄₀ ·H ₂ O	TBHP	CH ₃ CN	10/70	90.6	33.7	44.7		50
	$[Cu_{4}^{I}(4-bpo)_{6}]SiW_{12}O_{40}\cdot 3H_{2}O$	TBHP	CH ₃ CN	7/70	93.8	35.4	35.6		
	$[Cu_{4}^{I}(3-bpo)_{4}]SiW_{12}O_{40}\cdot 3H_{2}O$	TBHP	CH ₃ CN	5/70	56	43.1	49.5		
5	PW ₁₁ Cu-S-PEA (present work)	O ₂		12/80	43	63	(R)/18	16	

surface oxygen atoms, and thus the formed end-on superoxo species is responsible for the epoxidation of the substrate held in the vicinity of copper and chiral ligands (Scheme 2). In other words, S-PEA acta as a directing group, orienting the surface in such a way that it results in the formation of a specific stereoisomer. The catalyst is recovered after completion of the reaction, and FT-IR was taken in order to confirm no degradation/loss of the organic ligand. The participation of a superoxo radical is further supported by carrying out the experiment in the presence of a radical scavenger (entry 4 in Table 4), and almost the same results indicate that the reaction proceeds via the formation of a superoxo radical. The slight increase in the conversion may be due to the reaction of styrene with the reactive species that is already present in the reaction mixture.

Finally, on the basis of two well-known factors, (a) TBHP is a well-known radical initiator and (b) styrene oxide is formed as an intermediate during styrene oxidation only when the radical mechanism is followed, we are quite confident that the reaction follows a radical mechanism. However, more work is required to confirm the said results.

Heterogeneity Test. In order to prove the heterogeneous nature of the catalyst, the reaction was run for 8 h, after which the catalyst was filtered out and the reaction was continued for a further of 2 h. The reaction mixtures after 8 h as well as after completion were analyzed, and the results are presented in Figure 10. No changes in % conversion and selectivity indicate that the catalyst is truly heterogeneous in nature.

Regeneration Study. Because of its heterogeneous nature, the catalyst was easily regenerated by a simple centrifugation, followed by washing with methanol and air drying. This was used for the same reaction under optimized conditions. As seen in Table 5, the catalyst gave almost the same activity up to two cycles, indicating that it can be reused multiple times. A slight decrease in conversion may be attributed to the loss incurred during the process of regeneration.

In FT-IR, all of the bands of the fresh catalyst were replicated in the recycled one, indicating that the catalyst remains stable during the course of the reaction and also after recycling (Figure 11).

Comparison Study. From Table 6, it is seen that, for all of the reported copper-based inorganic–organic hybrid catalysts, styrene epoxidation has been carried out in the presence of TBHP (except one case) as the oxidant in CH₃CN as the solvent. It is also seen that all reported systems are inactive toward enantiomer selectivity. The superiority of the present catalyst lies in terms of ee using molecular O_2 as a greener oxidant under solvent-free conditions.

CONCLUSION

PW₁₁Cu was successfully functionalized with a chiral organic ligand, S-PEA, by a ligand substitution approach and thorough characterization confirmed the formation of a N→Cu dative bond with retention of the POM structure as well as the chirality. Further, the material was evaluated as a heterogeneous catalyst for the asymmetric oxidation of styrene, and with a view to obtain high ee, different oxidants were used. Even though TBHP gave high selectivity for epoxide, the best ee was obtained when molecular O₂ was used as the oxidant and TBHP as the initiator. The novelty of the present catalyst lies in the solvent-free aerobic asymmetric epoxidation of styrene as well as in obtaining good ee with a very low concentration of 5.64×10^{-6} mmol for S-PEA.

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A.P.: conceptualization, writing (review and editing), and supervision. R.S.: methodology, software, and writing (original draft). J.P.: graphical abstract, reproduction of the results, and writing (review and editing).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.P. and J.P. thank the Science and Engineering Research Board (New Delhi, India; Project EMR/2016/005718) for financial support. The authors also thank the Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, India, for ¹H NMR analysis.

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