Supporting Information

Ionic Liquid-functionalized amphiphilic Janus material as Pickering interfacial catalyst for asymmetric sulfoxidation in water
CONTENT:

1. Synthetic details of \( \text{HO-SiO}_2-\text{IL-Ti(salen)}_x \) (\( x = 0.05, 0.07, 0.09, 0.11 \)), \( \text{HO-SiO}_2-\text{Ti(salen)} \), and \( \text{SiO}_2-\text{IL-Ti(salen)} \).

2. Characterization of \( \text{HO-SiO}_2-\text{IL-Ti(salen)}_x \) (\( x = 0.05, 0.07, 0.09, 0.11 \)), \( \text{HO-SiO}_2-\text{Ti(salen)} \), and \( \text{SiO}_2-\text{IL-Ti(salen)} \).

3. Evaluation of catalytic activity of \( \text{HO-SiO}_2-\text{IL-Ti(salen)}_x \) in asymmetric sulfoxidation in water.
1. Synthetic details of HO-SiO$_2$-$IL$-Ti(salen)$_x$ (x= 0.05, 0.07, 0.09, 0.11), HO-SiO$_2$-Ti(salen), and SiO$_2$-$IL$-Ti(salen).

1.1 Materials and reagents

Tetraethylorthosilicate (TEOS) was obtained from Aldrich. $N$-[3-(triethoxysilyl)propyl]- 4,5-dihydroimidazole and 3-aminopropyltriethoxysilane (APTES) were obtained from Aladdin. Phenyl methyl sulfide, phenyl ethyl sulfide, 4-methoxyphenyl methyl sulfide, 2-methoxyphenyl methyl sulfide, and 4-bromophenyl methyl sulfide were obtained from J&K. 2-tert-Butyl phenol was purchased from Alfa Aesar. Other commercially available chemicals were obtained from local suppliers. All solvents were purified by standard procedures. Silica nanoparticles were synthesized according to the typical Stöber method. Ethyl phenyl sulfide, $n$-butyl phenyl sulfide, and $n$-hexyl phenyl sulfide were synthesized according to Ref.[(R,R')-$[N,N'$-(3,5-di-tert-butylsalicylidene)- 1,2-cyclohexanedicarboxamido] titanium(IV) di-isopropyl (denoted as neat complex) was synthesized according to the described procedure in Ref.

[(R,R)-$[N-(3,5-di-tert-butylsalicylidene)-N'$-(3-tert-butyl-5-chloro-methylsalicylidene)-1,2-cyclohexanedicarboxamido] titanium(IV) di-isopropyl (denoted as asymmetric chiral salen Ti$^{IV}$ complex) was synthesized as described procedure in Ref.

1.2 Methods

FT-IR spectrum were obtained using potassium bromide pellets with a resolution of 4 cm$^{-1}$ and 32 scans in the range of 400–4000 cm$^{-1}$ using an AVATAR 370 Thermo Nicolet spectrophotometer. NMR spectrum of samples was recorded on a BRUKER AVANCE-500 spectrometer with TMS as an internal standard. TEM images were obtained on a Microscope Tecnai F20 at an accelerating voltage of 200 kV. Dynamic light scattering (DLS) was performed
using a ZS90 Laser Particle Size Analyzer (Malvern UK). Samples were dispersed in ethanol (20 mg. mL\(^{-1}\)) under ultrasonication for 30 min, giving rise to a uniform solution for DLS determination. Surface wettability of the samples was investigated by the analysis of the water contact angles (WCA) on TX500TM (Kono Corp.) Samples were directly compressed without the aid of binder. A drop of deionized water was then placed on it and imaged by camera. Microscope images of sulfide-in-water emulsions were obtained on BX53M (Olympus Corp.). Titanium contents in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 300X analyzer (Perkin-Elmer Corp.). The conversion and chemoselectivity to chiral sulfoxides were analyzed by a 6890 N gas chromatograph (Agilent Co.) equipped with a capillary column (HP19091G-B213, 30 m × 0.32 mm × 0.25 lm) and a FID detector. Enantioselectivity (Ee value) of chiral sulfoxides was determined by HPLC analysis using Daicel Chiralpak AD column.

1.3 Synthesis of alkoxysilane reagents of (C\(_2\)H\(_5\)O\(_3\))\(_3\)Si-IL/Ti(salen) and (C\(_2\)H\(_5\)O\(_3\))\(_3\)Si-Ti(salen)

(C\(_2\)H\(_5\)O\(_3\))\(_3\)Si-IL/Ti(salen) was synthesized through \(N\)-alkylation of terminal imidazole groups in \(N\)-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole with methyl chloride group (–CH\(_2\)Cl) at 5-position of asymmetric chiral salen Ti\(^{IV}\) complex, as shown in Scheme 1. Asymmetric chiral salen Ti\(^{IV}\) complex (5 mmol, 3.51 g) was mixed with \(N\)-[3-(triethoxysilyl)propyl]-4,5- dihydroimidazole (5.2 mmol, 1.43 g) in dry toluene (100 mL). The corresponding mixture was stirred at 110 °C for 24 h under argon atmosphere. After removal of solvent, the residue was wash was \(n\)-hexane, and then dried under vacuum at room temperature for 12 h, giving (C\(_2\)H\(_5\)O\(_3\))\(_3\)Si-IL/Ti(salen). FT-IR (KBr): \(\gamma_{\text{max}}/\text{cm}^{-1}\) 3400, 2953, 2864, 1645, 1564, 1480, 1438, 1390, 1349, 1326, 1243, 1219, 1157, 1120, 1099, 805, 764, 742, 713, 621, 509, 470. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.63-6.96
(m, 4 H, ArH), 4.63 (m, 1 H, N-CH-N in IL), 4.36 (m, 2 H, CH=NH), 3.80-3.79 (m, 6 H, CH2-CH2-O), 3.70-3.68 (m, 2 H, CH2-CH2-CH3 of iPrO), 3.49 (m, 2 H, -N-CH2-Ph-), 3.28 (m, 2 H, N-CH-CH-N in cyclohexyl), 2.95-2.94 (m, 6 H, CH2-CH2-N-CH2-CH2-N in IL), 1.52 (m, 2 H, Si-CH2-CH2-CH2-N), 1.66 (m, 2 H, Si-CH2-CH2-CH2-N), 1.41-1.39 (m, 8 H, CH-CH2-CH2-CH2-CH2-CH in cyclohexyl), 1.31-1.29 (m, 27 H, H in Cyc, H in 2 H, Si-CH of iPrO), 0.56 (m, 2 H, Si-CH2-CH2-CH2-N).

As shown in Scheme 1, the preparation procedure of (C2H5O)3Si-Ti(salen) was similar to that of (C2H5O)3Si-IL/Ti(salen), except for the use of 3-aminopropyltriethoxysilane instead of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole during N-alkylation. FT-IR (KBr): γmax/cm⁻¹ 3432, 2960, 2930, 2864, 1747, 1645, 1552, 1516, 1472, 1387, 1266, 1100, 884, 808, 805, 672, 586, 469. ¹H NMR (500 MHz, CDCl3): δ (ppm): 7.36-6.97 (m, 4 H, ArH), 4.41-4.33 (m, 2 H, CH=NH), 3.74-3.69 (m, 6 H, CH2-CH2-O), 3.58-3.57 (m, 2 H, CH-CH2-CH of iPrO), 3.48 (m, 2 H, -N-CH2-Ph-), 3.30-3.28 (m, 2 H, N-CH-CH-N in cyclohexyl), 1.59 (m, 2 H, Si-CH2-CH2-CH2-N), 1.54 (m, 2 H, Si-CH2-CH2-CH2-N), 1.43-1.40 (m, 8 H, CH-CH2-CH2-CH2-CH2-CH in cyclohexyl), 1.38-1.34 (m, 27 H, H in t-butyl), 1.24-1.23 (m, 21 H, CH2-CH2-O-Si and CH3-CH-CH3 of iPrO), 0.67 (m, 2 H, Si-CH2-CH2-CH2-N).

![Scheme S1](image)

**Scheme S1** Synthesis of alkoxysilane reagents of (C2H5O)3Si-IL/Ti(salen) and (C2H5O)3Si-Ti(salen).
1.4 Preparation of IL-functionalized JNPs catalyst of HO-SiO$_2$-IL-Ti(salen)$_x$ (where $x$ represented the titanium content in samples, $x$= 0.05, 0.07, 0.09, and 0.11 mmol/g)

Janus-type catalysts of HO-SiO$_2$-IL-Ti(salen)$_x$ were synthesized through a classic method based on the Pickering emulsions of wax-in-water, as shown in Scheme S2.

![Scheme S2](image)

**Scheme S2** Schematic representation of HO-SiO$_2$-IL-Ti(salen)$_x$ by wax emulsion method.

*Synthesis of SiO$_2$ nanoparticles (denoted as SiO$_2$-OH).* Silica nanoparticles which were synthesized according to the modified Stöber method$^1$ were treated with piranha solution (3:1 mixture of concentrated H$_2$SO$_4$ and 30% H$_2$O$_2$) at 80 °C and 350 rpm for 0.5 h. The treated silica nanoparticles were centrifuged (5000 rpm, 10 min), washed with deionized water, and dried at 80 °C under vacuum. FT-IR: $\gamma_{max}$/cm$^{-1}$ 3437, 1630, 1080, 970, 798.

*Synthesis of solid wax droplets trapped silica nanoparticles (denoted as wax@SiO$_2$-OH).* Wax@SiO$_2$-OH were synthesized on the basis of a wax-in-water emulsion using cetyltrimethylammonium bromide (CTAB) as a surfactant.$^5$ SiO$_2$-OH (0.25 g) and paraffin wax (2.5 g) were added to the aqueous solution (20 mL) of CTAB with different concentration (0.36, 0.54, 0.72 mmol.L$^{-1}$ and 0.90 mmol.L$^{-1}$). The SiO$_2$-OH particles became more hydrophobic with the surfactant concentration increasing, penetrating more deeply into the wax phase. It thus reduced the exposed surface of SiO$_2$-OH for modification.$^6$ The resulting mixtures were incubated at 75 °C for 0.5 h, and then vigorously stirred under 12 000 rpm for 10 min. After being rapidly cooled to room temperature, wax@SiO$_2$-OH droplets with various area of exposed SiO$_2$ surface
were obtained. The wax droplets were filtered, washed with deionized water to remove the excess and weakly attached silica nanoparticles, and then dried at 25 °C under vacuum for 24 h.

**Synthesis of HO-SiO₂-IL-Ti(salen).** The obtained dried wax@SiO₂-OH (2.0 g) were mixed with (C₂H₅O)₃Si-IL/Ti(salen) (0.2 mmol, 0.2 g) in anhydrous methanol solution (20 mL). The mixtures were stirred at 25 °C under 100 rpm for 12 h. Exposed surface of SiO₂-OH in wax@SiO₂-OH was thus decorated with the IL/Ti(salen)-containing alkoxysilane reagent through silylation reaction, giving solid wax trapped wax@SiO₂-IL/Ti(salen). Then, chloroform was used to dissolve the paraffin wax at 40 °C, thereby releasing the IL/Ti(salen)-modified silica nanoparticles. After centrifugation, the residue was washed with chloroform and anhydrous ethanol for several times, and dried under vacuum at 40 °C for 24 h. The obtained samples were denoted as HO-SiO₂-IL-Ti(salen)ₓ (x= 0.05, 0.07, 0.09, 0.11). Their representative structure was shown in Chart S1. HO-SiO₂-IL-Ti(salen)₀.₀₅: FT-IR: γₘₐₓ/cm⁻¹: 3441, 2972, 2926, 2871, 1648, 1547, 1520, 1462, 1109, 807, 620, 472. Titanium content: 0.05 mmol/g. HO-SiO₂-IL-Ti(salen)₀.₀₇: FT-IR: γₘₐₓ/cm⁻¹: 3420, 3292, 3973, 3923, 2871, 1643, 1550, 1459, 1382, 1321, 1100, 941, 805, 690, 621, 468. Titanium content: 0.07 mmol/g. HO-SiO₂-IL-Ti(salen)₀.₀₉: FT-IR: γₘₐₓ/cm⁻¹: 3420, 3128, 2954, 2853, 2360, 1643, 1541, 1455, 1097, 939, 867, 805, 691, 621, 466. Titanium content: 0.09 mmol/g. HO-SiO₂-IL-Ti(salen)₀.₁₁: FT-IR: γₘₐₓ/cm⁻¹: 3420, 2970, 2920, 1643, 1542, 1458, 1385, 1100, 956, 805, 621, 467. Titanium content: 0.11 mmol/g.

**Selectively labeling HO-SiO₂-IL-Ti(salen)₀.₀₇ with Pd NPs.** To confirm the Janus characteristic of obtained HO-SiO₂-IL-Ti(salen)ₓ, Pd NPs was used to selectively label one side of typical HO-SiO₂-IL-Ti(salen)₀.₀₇ surface. Amino groups were introduced to the hydroxyl side of the silica JNPs in advance to absorb the Pd NPs via electrostatic interaction, based on affiliation between
the Pd NPs and amine groups. **HO-SiO$_2$-IL-Ti(salen)$_{0.07}$** was dispersed in a methanol solution (5.0 mL) containing (3-aminopropyl) triethoxysilane (0.2 mmol, 0.04 g), and incubated at 75 °C and 150 rpm for 12 h, leading to the formation of amino-modified JNPs of **NH$_2$-SiO$_2$-IL-Ti(salen)$_{0.07}$**. A methanol solution (20 mL) containing the resulting amino-modified silica JNPs (0.2 g) was mixed with an aqueous solution containing PdCl$_2$ (28.3 mL, 0.01 M) under vigorous stirring. Lysine (20 mL of aqueous solution, 0.53 M) was then added dropwise within 30 min, and followed by the addition of NaBH$_4$ (10 mL of aqueous solution, 0.35 M). After stirring for 30 min at room temperature, Pd-labeled JNPs were collected by centrifugation (5000 rpm, 20 min), washed with ethanol three times, and then dried under vacuum for subsequent experiments.

1.5 Preparation of **IL**-free counterpart of **HO-SiO$_2$-Ti(salen)$_{0.07}$** (where 0.07 represented the titanium content in samples)

For comparison, a **IL**-free counterpart of **HO-SiO$_2$-Ti(salen)$_{0.07}$** (Chart S1), in which Ti(salen) units were directly located on the hemispheres of SiO$_2$ nanoparticles through an alkyl linker, was prepared as the control catalyst. The preparation procedure was similar to that of **HO-SiO$_2$-IL-Ti(salen)$_{0.07}$**, except for the use of (C$_2$H$_5$O)$_3$Si-Ti(salen) instead of (C$_2$H$_5$O)$_3$Si-IL-Ti(salen) during silylation. FT-IR: $\gamma_{\text{max}}$/cm$^{-1}$ 3420, 2924, 2856, 1643, 1547, 1517, 1462, 1388, 1100, 955, 805, 669, 469. Titanium content: 0.07 mmol/g.

1.6 Preparation of uniform counterpart of **SiO$_2$-IL-Ti(salen)**

To investigate the “Janus effect” of **SiO$_2$-IL-Ti(salen)**, the uniform counterpart of **SiO$_2$-IL-Ti(salen)** (Chart S1), in which Ti(salen) was are uniform distributed on the surface of SiO$_2$ nanoparticles through IL linker, was prepared as the other control catalyst. Bare SiO$_2$-OH nanoparticulars (0.2 g) was incubated with (C$_2$H$_3$O)$_3$Si-IL-Ti(salen) (0.2 mmol, 0.2 g) in methanol
(20 mL) at 25 °C under 100 rpm for 12 h. During the procedure, the abundant surface hydroxyl groups (–OH) of SiO₂-OH were silylated with (C₂H₃O)₃Si-IL/Ti(salen). Removal of the unreacted (C₂H₃O)₃Si-IL-Ti(salen) afforded the **SiO₂-IL-Ti(salen)**. FT-IR (KBr): \( \gamma_{\text{max}}/\text{cm}^{-1} \): 2954, 1643, 1455, 1442, 1109, 940, 805, 692, 621, 466. Titanium content: 0.12 mmol/g.

**Chart S1** The representative structures of neat complex, **HO-SiO₂-IL-Ti(salen)**, **HO-SiO₂-Ti(salen)**, and **SiO₂-IL-Ti(salen)**.

2. Characterization of **HO-SiO₂-IL-Ti(salen)**, \( x = 0.05, 0.07, 0.09, 0.11 \), **HO-SiO₂-Ti(salen)\(_{0.07}\)**, and **SiO₂-IL-Ti(salen)**

2.1 FT-IR

Partially coating chiral salen Ti\( ^{IV} \) complex on SiO₂ surface through an IL linker was confirmed by FT-IR spectroscopy. Fig. S1 shows the FT-IR spectra of **HO-SiO₂-IL-Ti(salen)\(_{0.07}\)** and **HO-SiO₂-Ti(salen)\(_{0.07}\)**, as well as the **HO-SiO₂-Ti(salen)\(_{0.07}\)**, pristine SiO₂-OH nanoparticles and **SiO₂-IL-Ti(salen)** for comparison. Pristine SiO₂-OH nanoparticles showed distinct characteristic bands at 807, 1616 and 3420 cm\(^{-1}\), which was assigned to the skeletal vibrations of Si-C, Si-O and O-H groups, respectively (Fig. S1a).\(^7\) Upon modification with (C₂H₃O)₃Si-IL-Ti(salen), the O-H stretching vibration (at 3420 cm\(^{-1}\)) disappeared (Fig. S1b).\(^8\) This could be interpreted as evidence that the hydroxyl groups participated in silylation with the IL/Ti(salen)-containing organosiloxane.
As a result, chiral salen Ti$^{IV}$ complex was grafted on SiO$_2$ surface through a flexible IL linker. Indeed, the FT-IR spectrum of SiO$_2$-IL-Ti(salen) exhibited the stretching vibrations of C=N in Ti(salen) (at 1648 cm$^{-1}$) and imidazole ring in IL moiety (at 622 cm$^{-1}$). While, the O-H stretching vibration (at 3420 cm$^{-1}$) was present in the FT-IR spectrum of HO-SiO$_2$-IL-Ti(salen)$_{0.07}$, although its intensity was significantly decreased (Fig. S1c). It was evidence for the partial modification of SiO$_2$ surface with (C$_2$H$_5$O)$_3$Si-IL-Ti(salen). Logically, the hydroxyl group buried in wax was intact during the silylation process. The region-selective modification endowed HO-SiO$_2$-IL-Ti(salen)$_x$ with not only catalytic reactivity, but also interfacial activity, which were crucial in Pickering interfacial catalysis. IL-free counterpart of HO-SiO$_2$-Ti(salen)$_{0.07}$ exhibited similar FT-IR spectrum to HO-SiO$_2$-IL-Ti(salen)$_{0.07}$, except for the absence of the characteristic stretching vibrations of the imidazole ring at 621 cm$^{-1}$ (Fig. S1d vs. S1c). The results correlate with the Janus geometry of HO-SiO$_2$-Ti(salen)$_{0.07}$ and the inexistence of imidazolium-based IL linker. Notably, the active species of Ti(salen) was intact during the grafting as its characteristic bands in SiO$_2$-supported samples are identical to those in neat complex (Fig. S1b-d vs. S1e).
Fig. S1 FT-IR spectra of bare SiO$_2$-OH (a), SiO$_2$-IL-Ti(salen) (b), HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (c), the recovered HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ after the 7th reuse (c‘), HO-SiO$_2$-Ti(salen)$_{0.07}$ (d), and neat complex (e).

2.2 TEM

TEM images were used to obtain information on the particle size and morphology of as-prepared samples of SiO$_2$-OH, HO-SiO$_2$-IL-Ti(salen)$_x$ ($x$=0.05, 0.07, 0.09, 0.11), SiO$_2$-IL-Ti(salen) and HO-SiO$_2$-Ti(salen)$_{0.07}$, as shown in Fig. S2. Particles with an approximately spherical shape and average diameter of ca. 40 nm were observed on the image of SiO$_2$-OH (Fig. S2A). The size and morphology did not significantly change after anchoring the Ti(salen) moiety onto the partial silica surface using an imidazolium-based IL linker (Fig. S2B-E). This finding suggested that the silica core was intact during immobilization and that the functional reaction occurred only on the particle surface. To confirm the Janus characteristic of HO-SiO$_2$-IL-Ti(salen)$_x$, we further modified the hydroxyl side of typical HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ with 3-aminopropyltriethoxysilane through silylation, and labelled the amino with Pd nanoparticles (NPs). Indeed, the Pd NPs mainly adsorbed on one side of the silica JNPs in the TEM image of Pd-labelled sample (Fig. S2H). The nanometer size, together with asymmetric dispersion of catalytically active centers on the surface, made HO-SiO$_2$-IL-Ti(salen)$_x$ efficient in aqueous asymmetric sulfoxidation. Additionally, uniform SiO$_2$-IL-Ti(salen) (Fig. S2F) and IL-free HO-SiO$_2$-Ti(salen)$_{0.07}$ (Fig. S2G) also showed the approximately spherical particles with an average particle diameter of ca. 40 nm in the corresponding TEM image.
2.3 Particle size distribution analysis

DLS was used to further determine the change in nanoparticles size after modification, as shown in Fig. S3. Bare SiO$_2$-OH showed the mean hydrodynamic diameter of 141 nm (Fig. S3A). Modification of IL-Ti(salen) moiety on the surface resulted in an increase in the hydrodynamic diameter. Logically, the more IL-Ti(salen) moiety on SiO$_2$-OH surface, the larger the nanoparticles size became. Indeed, JNPs with x = 0.05, 0.07, 0.09, and 0.11 mmol/g gave hydrodynamic diameter of ca. 190, 225, 295, and 325 nm, respectively (Fig. S3B). When the silica surface was uniformed covered by IL-Ti(salen), the hydrodynamic diameter was up to 342 nm (Fig. S3C). IL-free counterpart of HO-SiO$_2$-Ti(salen)$_{0.07}$ showed a smaller average hydrodynamic diameter (ca. 209 nm) than HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (225 nm) (Fig. S3D vs. S3B). Furthermore, we noticed that the sizes for nanoparticles determined by DLS were larger than from TEM,
probably due to the presence of a solvation layer on the particles.

![Size distribution graphs](image)

**Fig. S3** Size distribution of SiO$_2$-OH (A), HO-SiO$_2$-IL-Ti(salen)$_x$ (x= 0.05, 0.07, 0.09, 0.11) (B), SiO$_2$-IL-Ti(salen) (C) and HO-SiO$_2$-Ti(salen)$_{0.07}$ (D) in methanol at a concentration of 1.0 mg mL$^{-1}$ at room temperature.

2.4 Pickering emulsions stabilized by HO-SiO$_2$-IL-Ti(salen)$_x$

Successful creation of emulsion can be confirmed by optical micrographs, as shown in Fig. S4. Spherical emulsions droplets with a controlled size at the micrometer scale were observed in the Pickering emulsion stabilized by HO-SiO$_2$-IL-Ti(salen)$_x$. The average size of these droplets was varied with their degree of hydrophobization. HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ gave the smallest emulsion droplets with diameter of ca. 12 μm (Fig. S4B). Further enhancing or reducing the Ti(salen) content on JNPs led to the increased emulsion droplets size accordingly (Fig. S4A, S4C, and S4D vs. S4B). A possible explanation might be that the JNPs became more hydrophobic with the Ti(salen) increasing, penetrating more deeply into the oil phase.$^6$ It thus reduced the surface
exposed to continuous water phase. For HO-SiO$_2$-IL-Ti(salen)$_x$ (x= 0.05 and 0.07), the available particles with larger hydrophilic surface might be sufficient to fully cover the droplet interfaces. In this case, the droplet size reduced with increasing Ti(salen) content as a consequence of enhanced interparticle hydrophobic effect (Fig. S4B vs. S4A). When the hydrophilic area decreased beyond a critical value, the particles available were initially insufficient to fully cover the oil-water interfaces, as the case of HO-SiO$_2$-IL-Ti(salen)$_x$ (x= 0.09 and 0.11). As a result, the emulsion droplets underwent a “limited coalescence” process to minimize the free energy until the particle layer at interface was dense enough to prevent further coalescence. The extent of coalescence was increased with the degree of hydrophobization of JNPs, which increased the droplets size accordingly (Fig. S4D vs. S4C vs. S4B). The preferred sizes of emulsion droplets determined the interfacial area of corresponding Pickering emulsion, which hence affected the interfacial mass transfer in Pickering interfacial catalysis. Benefiting from the Janus characteristic, HO-SiO$_2$-Ti(salen)$_{0.07}$ as an emulsifier also gave the stable emulsions with droplets diameter of ca. 65 μm (Fig. S4F). Different from JNPs-stabilized emulsions which are thermodynamically stable, the Pickering emulsions stabilized with uniform SiO$_2$-IL-Ti(salen) particles are only kinetically stable and thus can undergo destabilization (Fig. S4E). Stable Pickering emulsions together with controllable interfacial area made HO-SiO$_2$-IL-Ti(salen)$_x$ the desirable Pickering interfacial catalysts for asymmetric sulfoxidation in water.
Fig. S4 Optical microscopy image of the sulfide-in-H$_2$O emulsions stabilized HO-SiO$_2$-IL-
Ti(salen)$_{0.05}$ (A), HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (B), HO-SiO$_2$-IL-Ti(salen)$_{0.09}$ (C), HO-SiO$_2$-IL-Ti(salen)$_{0.011}$ (D), SiO$_2$-IL-Ti(salen) (E), and HO-SiO$_2$-Ti(salen)$_{0.07}$ (F). Chiral salen Ti$^{IV}$ catalyst (0.1 g) and methyl phenyl sulfide (0.2 mL) were suspended in water (1 mL) and stirred (10 000 rpm) for 10 min, before the images were taken.

3. The evaluation of catalytic activity of HO-SiO$_2$-IL-Ti(salen)$_x$ in asymmetric sulfoxidation in water.

3.1 General procedure for asymmetric sulfoxidation in water

Ti$^{IV}$-based catalyst (1.25 mol% of substrate) was stirred with sulfides (0.5 mmol) in deionized water (1 mL) at 25 °C. H$_2$O$_2$ (30 wt.%, 0.6 mmol) was then added dropwise over 15 min. The resulting mixture was stirred at 25 °C. Reaction progress was monitored on GC. After the reaction, the catalyst was recovered by centrifugation, washed with ethyl acetate, dried in a vacuum, and finally recharged with fresh substrate and oxidant for the next catalytic cycle. The reaction solution was extracted with ethyl acetate (3 × 4 mL). Combined organic layer was dried over anhydrous sodium sulfate and was concentrated in vacuo. Notably, although ethyl acetate was used to extract a small amount of sulfide in the present work, this approach should be redundant in large-scale industrial processes, in which the oily product phase can be directly separated from water after catalyst removal. Further purification of the residue by chromatography on silica gel (petroleum ether/ethyl acetate, 1.5: 1) afforded chiral sulfoxides. The depurated sulfoxides have been identified by $^1$H NMR spectra. Ee values of the products were determined by HPLC analysis using the Daicel chiralpak AD columns.

Phenyl methyl sulfoxide: The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig.
S5 and S6). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) (ppm): 7.65-7.64 (m, 2 H, ArH), 7.52-7.49 (m, 3 H, ArH), 2.71 (s, 3 H, S-CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) (ppm): 43.90 (CH\(_3\)), 123.53, 129.38, 131.09, 145.57 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, injector temperature and detector temperature were 250 °C, column temperature was 180 °C, \(t_{\text{phenyl methyl sulfoxide}}\) = 2.1 min; ee value was determined by HPLC (\(i\)-PrOH/n-hexane = 2.5: 7.5 (v/v); flow rate = 1.0 mL/min; 25 °C; \(\lambda = 254\) nm; major enantiomer \(t_R\) = 7.7 min, minor enantiomer \(t_S\) = 9.7 min (see Fig. S7-S10)

**Fig. S5** \(^1\)H NMR of phenyl methyl sulfoxide.
Fig. S6 $^{13}$C NMR of phenyl methyl sulfoxide

Fig. S7 HPLC of phenyl methyl sulfoxide obtained over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (ee value = 98%).
Fig. S8 HPLC of phenyl methyl sulfoxide obtained over SiO$_2$-IL-Ti(salen) (ee value = 82%).

Fig. S9 HPLC of phenyl methyl sulfoxide obtained over HO-SiO$_2$-Ti(salen)$_{0.07}$ (ee value = 94%)
**Fig. S10** HLPC of phenyl methyl sulfoxide obtained over neat complex (ee value = 70%).

**Phenyl ethyl sulfoxide**: The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S11 and S12). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.51-7.50 (m, 2 H, ArH), 7.41-7.40 (m, 3 H, ArH), 2.84-2.64 (m, 2 H, S-CH$_2$-CH$_3$), 1.10-1.07 (m, 3 H, S-CH$_2$-C). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 5.94 (CH$_3$), 50.27 (CH$_2$), 124.16, 129.13, 130.92, 143.29 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, the injector temperature and the detector temperature were 250 °C, the column temperature was 180 °C, $t_{phenyl ethyl sulfoxide} = 2.2$ min; ee value was determined by HPLC ($i$-PrOH/n-hexane = 2.5: 7.5 (v/v)); flow rate = 1.0 mL/min; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R = 7.0$ min, minor enantiomer $t_S = 8.8$ min (see Fig. S13-S16).
Fig. S11 $^1$H NMR of phenyl ethyl sulfoxide.

Fig. S12 $^{13}$C NMR of phenyl ethyl sulfoxide.
Fig. S13 HLPC of phenyl ethyl sulfoxide obtained over HO-SiO$_2$-$\text{IL}$-Ti(salen)$_{0.07}$ (ee value = 97%).

Fig. S14 HLPC of phenyl ethyl sulfoxide obtained over SiO$_2$-$\text{IL}$-Ti(salen) (ee value = 84%).
Fig. S15 HPLC of phenyl ethyl sulfoxide obtained over HO-SiO₂-Ti(salen)₀.₀₇ (ee value = 88%).

Fig. S16 HPLC of phenyl ethyl sulfoxide obtained over neat complex (ee value = 75%).

Phenyl n-butyl sulfoxide: The product has been identified by ¹H and ¹³C NMR spectra (see Fig.
S17 and S18. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.65-7.63 (m, 2 H, Ar$H$), 7.54-7.52 (m, 3 H, Ar$H$), 2.82-2.79 (m, 2 H, S-CH$_2$-), 1.76-1.60 (m, 2 H, S-CH$_2$-CH$_2$-), 1.48-1.43 (m, 2 H, S-CH$_2$-CH$_2$-CH$_2$-), 0.95-0.92 (m, 3 H, S-CH$_2$-CH$_2$-CH$_2$-CH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 13.66 (CH$_3$), 21.90 (CH$_2$), 24.16 (CH$_2$), 57.09 (CH$_2$), 124.05, 129.20, 130.93, 144.02 (ArC).

Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, the injector temperature and the detector temperature were 250 °C, the column temperature was 180 °C, $t_{\text{phenyl n-butyl sulfoxide}}$ = 2.6 min; ee value was determined by HPLC (i-PrOH/n-hexane = 2.5: 7.5 (v/v)); flow rate = 1.0 mL/min; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R$ = 5.6 min, minor enantiomer $t_S$ = 7.1 min (see Fig. S19-S22).

Fig. S17 $^1$H NMR of phenyl $n$-butyl sulfoxide.
Fig. S18 $^{13}$C NMR of phenyl $n$-butyl sulfoxide.

Fig. S19 HLPC of phenyl $n$-butyl sulfoxide obtained over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (ee value = 98%).
Fig. S20 HLPC of phenyl \( n \)-butyl sulfoxide obtained over \( \text{SiO}_2-\text{IL-} \text{Ti(salen)} \) (ee value = 87%).

Fig. S21 HLPC of phenyl \( n \)-butyl sulfoxide obtained over \( \text{HO-SiO}_2-\text{Ti(salen)}_{0.07} \) (ee value = 90%).
**Phenyl t-hexyl sulfide**: The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S23 and S24). $^1$H NMR (CDCl$_3$, 500 MHz): δ (ppm): 7.32-7.31 (m, 2 H, ArH), 7.28-7.25 (m, 2 H, ArH), 7.16-7.15 (m, 1 H, ArH), 7.16-7.15 (m, 1 H, ArH), 2.76-2.73 (m, 2 H, S-CH$_2$), 1.70-1.57 (m, 2 H, S-CH$_2$-CH$_2$), 1.38-1.34 (m, 2 H, S-CH$_2$-CH$_2$-CH$_2$), 1.24-1.22 (m, 4 H, S-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 0.83-0.80 (s, 3 H, S-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$). $^{13}$C NMR (CDCl$_3$, 125 MHz): δ (ppm): 13.93 (CH$_3$), 22.10 (CH$_2$), 22.34 (CH$_2$), 28.30 (CH$_2$), 31.30 (CH$_2$), 57.32 (CH$_2$), 123.99, 129.17, 130.89, 143.97 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, the injector temperature and the detector temperature were 250 °C, the column temperature was 180 °C, $t_{phenyl \ t\text{-butyl sulfoxide}}$ = 3.5 min; ee value was determined by HPLC ($i$-PrOH/ $n$-hexane = 2.5: 7.5 (v/v)); flow rate = 1.0 mL/min; 25 °C; λ = 254 nm; major enantiomer $t_R = 5.2$ min , minor enantiomer $t_S = 6.4$ min (see Fig. S25-S28).
Fig. S23 $^1$H NMR of phenyl $n$-hexyl sulfide.

Fig. S24 $^{13}$C NMR of phenyl $n$-hexyl sulfide.
Fig. S25 HLPC of phenyl n-hexyl sulfide obtained over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (ee value = 97%).

Fig. S26 HLPC of phenyl n-hexyl sulfide obtained over SiO$_2$-IL-Ti(salen) (ee value = 89%).
Fig. S27 HLPC of phenyl \( n \)-hexyl sulfide obtained over HO-SiO\(_2\)-Ti(salen)\(_{0.07}\) (ee value = 94%).

Fig. S28 HLPC of phenyl \( n \)-hexyl sulfide obtained over neat complex (ee value = 65%).

\textbf{p-Methoxyphenyl methyl sulfoxide}: The product has been identified by \(^1\)H and \(^{13}\)C NMR spectra (see Fig. S29 and S30). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) (ppm): 7.54-7.52 (d, 2 H, ArH),
6.98-6.96 (d, 2 H, ArH), 3.78 (s, 3 H, -OCH₃), 2.63 (s, 3 H, S-CH₂). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm): 43.99 (SCH₃), 55.53 (OCH₃), 114.86, 125.47, 136.59, 161.98 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, injector temperature and detector temperature were 250 °C, column temperature was 180 °C, tₚ-methoxyphenyl methyl sulfoxide = 11.7 min; ee value was determined by HPLC ([PrOH/n-hexane = 2.5: 7.5 (v/v)); flow rate = 1.0 mL/min; 25 °C; λ = 254 nm; major enantiomer tᵣ = 9.4 min and minor enantiomer tₛ = 11.4 min (see Fig. S31 - S34).

Fig. S29 ¹H NMR of p-methoxyphenyl methyl sulfoxide.
Fig. S30 $^{13}$C NMR of $p$-methoxyphenyl methyl sulfoxide.

Fig. S31 HPLC of $p$-methoxyphenyl methyl sulfoxide obtained over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (ee value = 88%).
Fig. S32 HPLC of \( p \)-methoxyphenyl methyl sulfoxide obtained over SiO\(_2\)-IL-Ti(salen) (ee value \( = 69\% \)).

Fig. S33 HPLC of \( p \)-methoxyphenyl methyl sulfoxide obtained over HO-SiO\(_2\)-Ti(salen)\(_{0.07}\) (ee value \( = 81\% \)).
Fig. S34 HLPC of \( p \)-methoxyphenyl methyl sulfoxide obtained over neat complex (ee value = 49%).

**o-Methoxyphenyl methyl sulfoxide:** The product has been identified by \(^1\)H and \(^{13}\)C NMR spectra (see Fig. S35 and S36). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) (ppm): 7.80-7.15 (m, 4 H, Ar\( H \)), 3.86 (s, 3 H, -OCH\(_3\)), 2.74 (s, 3 H, S-CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta \) (ppm): 41.22 (SCH\(_3\)), 55.71 (OCH\(_3\)), 110.59, 121.71, 124.64, 131.96, 133.12, 154.82 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, injector temperature and detector temperature were 250 °C, the column temperature was 180 °C, \( t_o \).\( p \)-methoxyphenyl methyl sulfoxide = 9.8 min; ee value was determined by HPLC (\( i \)-PrOH/\( n \)-hexane = 2: 8 (v/v)); flow rate = 1.0 mL/min; 25 °C; \( \lambda = 254 \) nm; major enantiomer \( t_R \) = 10 min and minor enantiomer \( t_S \) = 12.2 min (see Fig. S37-S40).
Fig. S35 $^1$H NMR of o-methoxyphenyl methyl sulfoxide.

Fig. S36 $^{13}$C NMR of o-methoxyphenyl methyl sulfoxide.
**Fig. S37** HLPC of $o$-methoxyphenyl methyl sulfoxide obtained over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (ee value = 97%).

**Fig. S38** HLPC of $o$-methoxyphenyl methyl sulfoxide obtained over SiO$_2$-IL-Ti(salen) (ee value = 90%).
Fig. S39 HLPC of o-methoxyphenyl methyl sulfoxide obtained over \( \text{HO-SiO}_2\text{-Ti(salen)}_{0.07} \) (ee value = 92%).

Fig. S40 HLPC of o-methoxyphenyl methyl sulfoxide obtained over neat complex (ee value = 71%).
**p-Bromophenyl methyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S41 and S42). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 7.66-7.65 (d, 2 H, ArH), 7.52-7.50 (d, 2 H, ArH), 2.70 (s, 3 H, S-CH$_3$). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm): 43.96 (SCH$_3$), 125.17, 125.49, 132.59, 144.82 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 40 mL/min, injector temperature and detector temperature were 250 °C, the column temperature was 180 °C, $t_{p\text{-bromophenyl methyl sulfoxide}} = 11.2$ min; ee value was determined by HPLC ($i$-PrOH/n-hexane = 2.5: 7.5 (v/v)); flow rate = 1.0 mL min$^{-1}$; 25 °C; $\lambda = 254$ nm; major enantiomer $t_R = 8.0$ min and minor enantiomer $t_S = 9.8$ min (see Fig. S43-S46).

![Fig. S41 $^1$H NMR of p-bromophenyl methyl sulfoxide.](image)
Fig. S42 $^{13}$C NMR of $p$-bromophenyl methyl sulfoxide.

Fig. S43 HPLC of $p$-bromophenyl methyl sulfoxide obtained over $\text{HO-SiO}_2$/IL-Ti(salen)$_{0.07}$ (ee value = 95%).
**Fig. S44** HLPC of $p$-bromophenyl methyl sulfoxide obtained over SiO$_2$-IL-Ti(salen) (ee value = 68%).

**Fig. S45** HLPC of methyl $p$-bromophenyl sulfoxide obtained over HO-SiO$_2$-Ti(salen)$_{0.87}$ (ee value = 85%).
3.2 Asymmetric sulfoxidation for kinetic measurement

Kinetics was employed to further evaluate the advantage of Pickering interfacial catalysis as well as the positive effects of IL moiety on the catalytic efficiency. The selected catalyst (1.25 mol% of substrate) was stirred with methyl pheny sulfide (0.5 mmol) in deionized water (1.0 mL) at 25 °C. H₂O₂ (30 wt.%, 0.6 mmol) was then added into the mixture within 5 min. To determine the rate of sulfoxidation, aliquots at an interval of 15 min were drawn from the reaction mixture, filtered through organic membrane with ethyl acetate as an extracting agent, and analyzed by GC.

Corresponding kinetic curves and rate curves are shown in Fig. S47. Clearly, HO-SiO₂-IL-Ti(salen)₉.₀₇ benefitted from the amphiphilic Janus characteristic, affording higher efficiency than the uniform particle of SiO₂-IL-Ti(salen) (Fig. S47a vs. S47c). This observation demonstrated that Pickering interfacial catalysis indeed promoted aqueous sulfoxidation through the formation of stable Pickering emulsion. Actually, apart from maximizing the interfacial contact area to
promote mass transfer, the emulsion droplet created a confined hydrophobic environment for the aqueous catalysis. It was evident from the gradient increase in the conversion of sulfide over HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ (Fig. S47A-a). The corresponding observed rate constant ($k_{obs}$) initially rose rapidly due to the dramatically increasing concentration of reactants in hydrophobic compartments during emulsification, went through a maximum, and then drastically decreased due to a dilution effect (Fig. S47B-a). The confined catalysis together with interfacial catalytic effects synergistically resulted in high efficiency of HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ in the aqueous asymmetric sulfoxidation. While, despite also Pickering interfacial catalysis, the $k_{obs}$ over HO-SiO$_2$-Ti(salen)$_{0.07}$ was always lower than that over HO-SiO$_2$-Ti(salen)$_{0.07}$ (Fig. S47b vs. S47a). The observations agreed with active role of the imidazolium-based IL linker in the overall reaction mechanism, which ensured conformational freedom of the active sites, enhanced mass transfer of regents and stabilized the reactive intermediates. The high efficiency of HO-SiO$_2$-IL-Ti(salen)$_{0.07}$ was consistent with our hypothesis that enhanced interphase mass transfer, as well as synergistic action of dense active species, was crucial for efficient aqueous sulfoxidation, and this could be achieved by endowing chiral salen Ti$^{IV}$ catalyst with interfacial activity. For this reason, it was not surprising that the traditional neat complex was inactive and provided the lowest $k_{obs}$ in water due to the poor water-solubility of catalyst and sulfide (Fig. S47d).
Fig. S47 Fitted kinetic curves (A) and rate curves (B) of asymmetric sulfoxidation of methyl phenyl sulfide by $\text{HO-SiO}_2\text{-IL-Ti(salen)}_{0.07}$ (a), $\text{HO-SiO}_2\text{-Ti(salen)}_{0.07}$ (b), $\text{SiO}_2\text{-IL-Ti(salen)}$ (c), and neat complex (d) in water.

References


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