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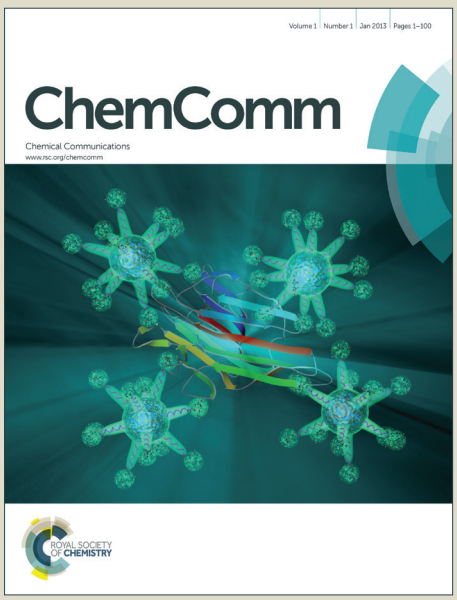

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Facile Construction of Functionalized Periodic Mesoporous Organosilica for Ir-Catalyzed Enantioselective Reduction of α-cyanoacetophenones and α-cyanoacetophenones

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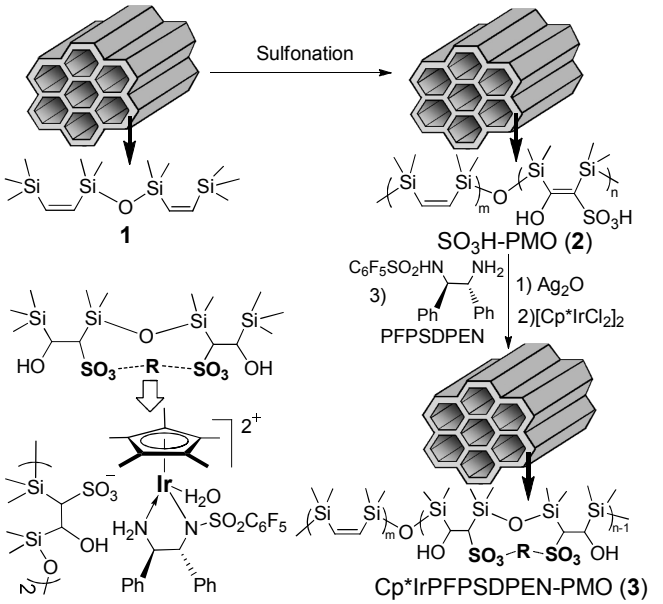
A facile method to construct chiral organoiridium-functionalized periodic mesoporous organosilica is developed. The heterogeneous catalyst displays excellent catalytic efficiency in the enantioselective reduction of α-cyanoacetophenones and α-nitroacetophenones in aqueous medium because of the hydrophobic nature and uniformly distributed active iridium species. The catalyst could be conveniently recovered and reused for eight times without loss of its catalytic activity.

Great achievement has been made on immobilization of chiral organometallic complexes using periodic mesoporous organosilicas (PMOs) as supports for constructing heterogeneous chiral catalysts.[1] Such achievement is due to the similarity of physical properties of PMOs to those of inorganosilica mesoporous materials, such as large specific surface area and pore volume, tunable pore dimension, well-defined pore arrangement, as well as high thermal and mechanical stabilities.[2] Furthermore, the potential hydrophobicity of PMO due to the intrinsic organosilicate inner surface significantly promotes organic transformation in biphasic reaction media.[3] In general, immobilization of chiral organometallic complexes within the PMO network can be achieved either by a post-grafting strategy or by a co-condensation strategy,[1a-b] which have led to many highly efficient heterogeneous chiral catalysts in various asymmetric reactions. From the synthetic methods, assembly of a PMO-based heterogeneous chiral catalyst often requires chiral ligand-derived siloxane, regardless of the strategy employed.[4] However, preparation of a pure chiral siloxane derived from a chiral ligand is very difficult because of the tedium for its purification by silica gel column chromatography. Thus, exploration of an alternative means to directly anchor a chiral ligand for for constructing heterogeneous chiral catalysts is high desirable.

In our effort to assemble heterogeneous catalysts through various chiral siloxanes,[5] herein we utilize a post-coordination method in the present contribution. That is, a chiral ligand was directly anchored onto a metal-functionalized PMO. No chiral ligand-derived siloxane is necessary in this process. Taking advantage of the post-coordination method and the hydrophobic feature of the PMO network, we conveniently construct a hydrophobic, chiral organoiridium-functionalized heterogeneous catalyst through the direct post-coordination of commercial (*R,R*)-pentafluorophenylsulfonyl-1,2-diphenylethylenediamine (PFPSDPEN) onto an organoiridium-functionalized PMO. As expected, the high hydrophobicity and uniformly distributed active iridium species greatly promote the enantioselective reduction of α-cyanocetophenones and α-nitroacetophenones in aqueous medium. In addition, the heterogeneous catalyst could be recovered and reused for at least eight times without loss of its catalytic activity.



Scheme 1. Preparation of catalyst **3**.

Ethenylene-bridged PMO functionalized with chiral Cp*IrPFPSDPEN, abbreviated as Cp*IrPFPSDPEN-PMO (**3**), (Cp*IrPFPSDPEN:[6] Cp* = pentamethyl cyclopentadiene, PFPSDPEN = (*R,R*)-pentafluorophenylsulfonyl-1,2-diphenylethylenediamine), was prepared as outlined in Scheme 1. First, ethenylene-bridged PMO (**1**) was obtained through the co-

condensation of 1,2-bis(triethoxysilyl)ethylene according to a reported method.[5b] Epoxidation of double bonds (–C=C–) followed by conversion of the resulting epoxide with bisulfite ions did then afford **2** in the form of a white powder.[7] Finally, continuous ion exchanges with Ag_2O[8] and then with $(Cp^*IrCl_2)_2$[9] followed by direct complexation of PFPSDPEN led to the crude heterogeneous catalyst **3**. This was subjected to Soxhlet extraction to clear its nanochannels and to obtain its pure form as a light-gray powder (see SI in the experimental and in Figures S1-5).

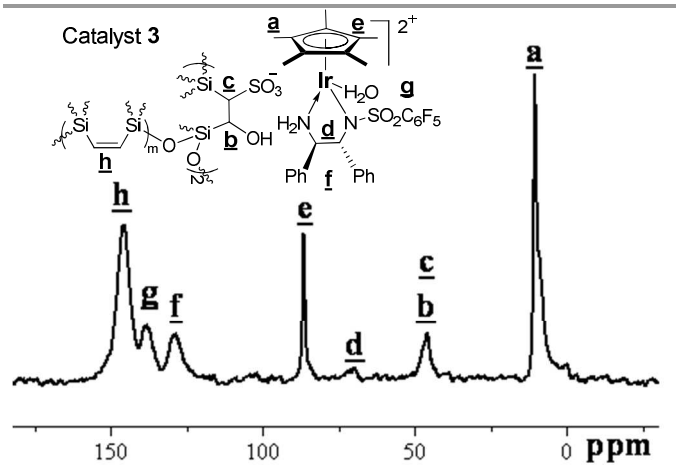


Fig.1 ^{13}C CP/MAS NMR spectrum of catalyst **3**.

Incorporation of well-defined, single-site, active iridium centers within the PMO network could be proven by solid-state ^{13}C cross-polarization (CP)/magic angle spinning (MAS) NMR spectroscopy. As shown in Figure 1, catalyst **3** produced strong, characteristic carbon signals of Si*C*H=*C*HSi groups at ~145 ppm, corresponding to the main ethenylene-bridged organosilica embedded within the PMO network. Additional weak carbon signals observed between ~43 and ~51 ppm are attributed to the Si*C*HOH and Si*C*HSO_3H groups, indicating that sulfonation occurred.[7] Both observations reveal that only a fraction of –C=C– double bonds underwent sulfonation during synthesis (corresponding to weak carbon signals), while those embedded within the pore walls were inaccessible for sulfonation (corresponding to strong carbon signals). Signals for carbon atoms of N*C*HPh groups (between ~69 and ~73 ppm) and for carbon atoms of the aromatic ring (at ~129 and ~138 ppm) of the chiral PFPSDPEN moiety could be observed clearly (marked in the spectra). Peaks at ~87 and ~11 ppm are ascribed to the carbon atoms of the Cp ring and to the carbon atoms of the *C*H_3 groups attached to Cp ring, respectively. These peaks are absent in the spectrum of **2**,[7] suggesting the formation of the Cp*IrPFPSDPEN complex. Chemical shifts of **3** are similar to those of its homogeneous counterpart, Cp*IrPFPSDPEN,[6a] demonstrating that **3** had the same well-defined single-site active species of Cp*IrPFPSDPEN. Its solid-state ^{29}Si MAS NMR spectrum further demonstrates its organosilicate network and the composition of active Cp*IrPFPSDPEN (see SI in Figure S2). Here, two strong T signals, corresponding to T^2(R–Si$(OSi)_2$(OH)) and T^3(R–Si$(OSi)_3$) (R = Cp*IrPFPSDPEN-functionalized alkyl-linked groups or ethenylene-bridged groups), reveal that R–Si$(OSi)_2$(OH) and R–Si$(OSi)_3$ comprise the main organosilicate network.[10] Similar to those of the parent counterpart, weak T^1($R(HO)_2SiOSi$), Q^3($(HO)Si(OSi)_3$), and Q^4($Si(OSi)_4$]) signals could be observed in this case.[7]

In addition, catalyst **3** produced a IV–type nitrogen adsorption-desorption isotherm with H_2 hysteresis loop (see SI in Figure S3) while its small-angle X-ray diffraction (XRD) pattern (see SI in Figure S4) exhibited a well-resolved peak at 2θ = 0.8°–1.0°, indicating its ordered dimensional-hexagonal (*P6mm*) mesporous channels.[5b,7] Transmission electron microscopy (TEM) images further confirmed the ordered dimensional-hexagonal pore arrangements (Figure 2a, 2b). It is worth mentioning that the TEM image with a chemical mapping revealed that the iridium active centers were uniformly distributed within the PMO network (Figure 2c), demonstrating the formation of site-isolated active species proved by its ^{13}C CP/MAS NMR spectrum.

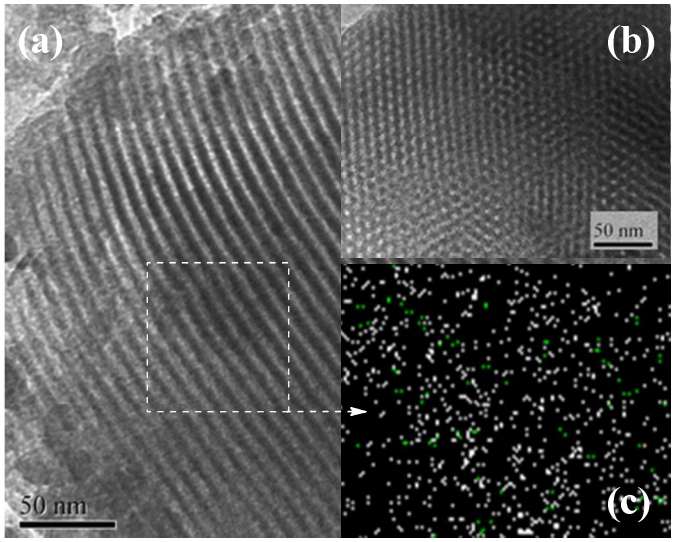


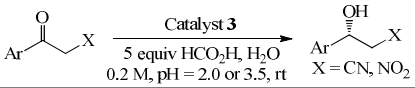
Fig.2 TEM images of catalyst **3** viewed along the [100] (a) and [001] (b) directions. (c) TEM image with a chemical mapping of **3**, showing the distribution of Si (white) and Ir (green).

Table 1 summarized the general applicability of catalyst **3** in the enantioselective reduction of α-cyanoacetophenones and α-nitroacetophenones in aqueous medium, in which the asymmetric reaction with the hydrogen source HCO_2H and 0.25 % mol PMO as a catalyst was carried out according to a reported method.[6a] In general, high conversions, no side products, and high enantioselectivities were obtained for all tested substrates. Taking enantioselective reduction of benzoylacetonitrile as a example, it was found that catalyst **3** produced (*R*)-3-hydroxy-3-phenylpropanenitrile with >99% conversion and 96% ee value. Such an ee value is slightly higher than that of Cp*IrPFPSDPEN (entry 1 vs entry 1 in brackets, Table 1), even higher than that obtained with the mixed SO_3H-PMO (**2**) and its homogeneous Cp*IrPFPSDPEN as a catalyst (entry 2), indicating that the coordination environment of catalyst **3** remained its original homogeneous situation that could be confirmed by X-ray photoelectron spectroscopy (XPS) investigation (see SI in Figure S5). In addition, the asymmetric reaction could be run at much higher substrate-to-catalyst mole ratio without apparently affecting its ee value, as exemplified by the enantioselective reduction of benzoylacetonitrile at substrate-to-catalyst mole ratio of 600 (entry 3, Table 1).

It is noteworthy that the electronic properties of substituents at the Ar moiety of acetophenones did not affect enantioselectivities, that is, various electron-withdrawing and electron-donating substituents of the Ar moiety led to the same efficiency (entries 4–10). The asymmetric reaction was also suitable for the enantioselective

reduction of α-nitroacetophenones. Similarly, high conversions, no side products, and high enantioselectivities could also be obtained with several α-nitroacetophenones (entries 11–15).

Table 1. Enantioselective reduction of α-cyano and α-nitroacetophenones.[a]



Entry	Ar	X	Time	Conv. (%)[b]	Ee (%)[b]
1	Ph	CN	12	99	96(94)[c]
2	Ph	CN	14	99	92 [d]
3	Ph	CN	24	92	95 [e]
4	*p*-FPh	CN	12	99	93
5	*m*-ClPh	CN	12	99	93
6	*p*-BrPh	CN	12	99	93
7	*p*-MePh	CN	12	99	97
8	*m*-MeOPh	CN	12	99	94
9	*2*-furyl	CN	12	99	96
10	2-thiophenyl	CN	15	99	98
11	Ph	NO_2	10	99	97
12	*p*-FPh	NO_2	10	99	96
13	*p*-ClPh	NO_2	10	99	93
14	*p*-MePh	NO_2	10	99	96
15	*p*-MeOPh	NO_2	15	99	96

[a] Reaction conditions: catalyst **3** (20.0 mg, 2.0 μmol of Ir, based on the ICP analysis), α-cyanoacetophenones (α-nitroacetophenones) (0.80 mmol) and the aqueous solution of formic acid (5.0 equiv. 1.0 M formate solution, 0.2 M overall concentration, for X = CN, pH = 3.5; for X = NO_2, pH = 2.0), at room temperature (25 °C) for 10-24 h. [b] Determined by chiral HPLC analysis (see SI in Figures S11, S13). [c] Data in the bracket were obtained using the homogenoous Cp*IrPFPSDPEN as a catalyst. [d] Data were obtained using the mixed SO_3H-PMO (**2**) and its homogeneous Cp*IrPFPSDPEN as a catalyst. [e] Data were obtained using the catalyst **3** with substrate-to-catalyst mole ratio of 600.

It is worth mentioning that the asymmetric reaction catalyzed by **3** had reaction rate higher than that attained with its homogeneous counterpart, Cp*IrPFPSDPEN.[6a] For example, we found that the enantioselective reduction of benzoylacetonitrile catalyzed by **3** could reach completion within 12 h, whereas the reaction catalyzed by Cp*IrPFPSDPEN required 24 h. Notably, the greatly enhanced reaction rate attained with **3** is due to the uniformly distributed single-site iridium active species and the highly hydrophobic PMO network (see SI in Figures S6-S9). To confirm this conclusion, the kinetic profile of the enantioselective reduction of benzoylacetonitrile catalyzed by **3** and by Cp*IrPFPSDPEN were investigated. The results show that the initial activity of **3** was higher than that of Cp*IrPFPSDPEN; the initial TOF values were 94.2 and 39.0 mol/(mol.h), respectively (see SI in Figure S10).

Important considerations in the design of any heterogeneous catalyst are ease of separation by simple filtration and retention of catalytic activity and enantioselectivity of the recovered catalyst after multiple cycles. We found that **3** could be recovered easily and reused in eight consecutive reactions for enantioselective reduction of benzoylacetonitrile. In eighth recycle, catalyst **3** still afforded the desired products with 98.2% conversion and 95.2% *ee* value (see SI in Table S1 and Figure S12). Apparently, the high recyclability should be due to the low leaching of Ir, in which the amount of Ir in eighth is 30.09 mg per gram of catalyst and only 6.7% of Ir was lost.

In conclusions, by taking advantage of a direct post-coordination method, we conveniently construct one ethenylene-bridged, hydrophobic, chiral organoiridium-functionalized heterogeneous catalyst. This catalyst displays excellent catalytic activity and high enantioselectivity in the enantioselective reduction of α-cyanoacetophenones and α-cyanoacetophenones in aqueous medium. As presented in this study, the excellent catalytic activity and high enantioselectivity are attributed to the high hydrophobicity and uniformly distributed single-site iridium active species within the PMO material, which significantly promote organic transformation in aqueous medium. In addition, the heterogeneous catalyst could be recovered and reused for at least eight times without loss of its catalytic activity. This strategy here offers a facile means to construct a hydrophobic chiral oganometal-functionalized PMO with high catalytic performance.

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Notes and references

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