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Microporous polymers as macroligands for Cp*Rh transfer hydrogenation catalysts

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Abstract: Here we report the synthesis of two bipyridine-based porous polymers and their use as platform for the heterogenization of Cp*Rh catalytic species. These highly stable heterogeneous catalysts demonstrate their efficiency in the transfer hydrogenation of α -aryl ketones. Moreover, we show that their catalytic activity is similar to that of homogeneous analogues, highlighting the absence of diffusion limitation in the solids. We rationalize the differences in the measured activities using the Hammett parameter as descriptor of the electronic environment of the catalytic site in both homogeneous and heterogeneous systems.

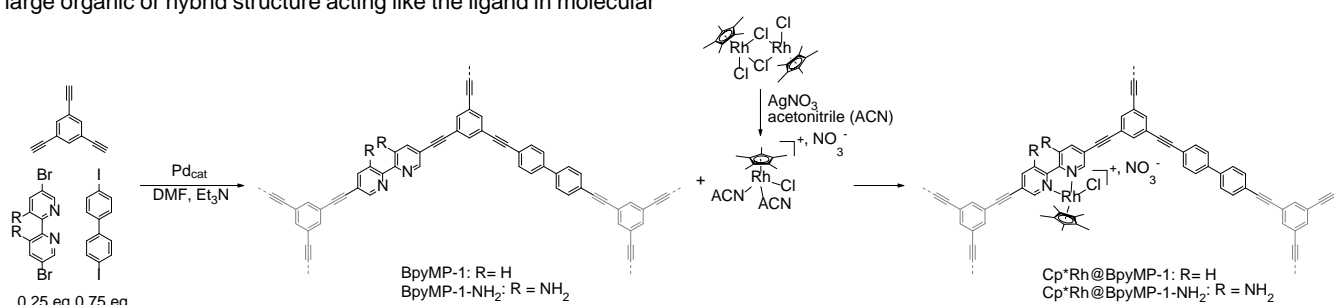
Heterogeneous catalysis allows to circumvent the problem of separation from the products and to simplify the recyclability of the catalyst. One strategy for the heterogeneous catalyst design consists in the integration or grafting of a well-defined molecular catalyst onto a solid support (heterogenization).^[1] Grafting active metal catalysts onto a surface allows also for site isolation, thus minimizing interaction and preventing possible multi-metallic deactivation.^[2] However, restrictions appear when the integration of the catalytically active centers into a solid support leads to lower performances compared to the homogeneous analogues.^[1a, 2-3]

Molecularly defined support designed as a macroligand, *i.e.* a large organic or hybrid structure acting like the ligand in molecular

complex, appears as an appealing opportunity to benefit from advantages of both homogeneous and heterogeneous catalysis. In this perspective, porous frameworks made by the repetition of a coordinating motif, like bipyridine (Bpy) based Metal-Organic Frameworks (MOF) hybrids and purely organic conjugated microporous polymers (CMP), are promising candidate platforms for molecular catalysts heterogenization.

Conjugated microporous polymers are 3D amorphous materials, first introduced by Cooper and co-workers.^[4] Their synthesis by classical carbon-carbon coupling reactions allow for the integration of metal binding sites such as bipyridines. They have been applied as host material for the fixation of Re and Ru for photocatalysis,^[5] Pd for C-C coupling reactions^[6] and recently Ir for formate decomposition.^[7]

Here we present new CMP derivatives made by using Bpy-based monomers to synthesise copolymers, named hereafter Bipyridine Microporous Polymers (BpyMP) materials. They were used as platforms for the site isolation of organometallic Cp*Rh complexes (Scheme 1). These catalysts were found to be active in the transfer hydrogenation of α -aryl ketones. Comparing the catalytic activity of our solids to that obtained using their molecular analogues, we found that no diffusion limitation occurs under the reported conditions.



Scheme 1. Synthesis of Cp*Rh@BpyMP microporous catalysts.

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The BpyMP-1 platform was prepared by copolymerization of 1,3,5-triethynylbenzene with 5,5'-dibromo-2,2'-bipyridine (25 mol-%) and 4,4'-diiodo-biphenyl (75 mol-%) (Scheme 1) in the presence of palladium catalyst (2 mol%).^[8] BpyMP-1-NH₂ was obtained similarly by replacing 5,5'-dibromo-2,2'-bipyridine by 3,3'-diamino-5,5'-dibromo-2,2'-bipyridine. The functionalization with the rhodium precursor was performed by infiltration with a solution of [Cp*RhCl]NO₃ (16 mol% with respect to Bpy moieties) to reach an identical Rh loading of 1.6 wt%, as determined by ICP-OES analysis, in the respective Cp*Rh@BpyMP-1 and Cp*Rh@BpyMP-1-NH₂ solids. Elemental analysis also reveals that less than 0.5 wt% of Pd remains in the final materials.

Complete copolymerization of bipyridine- and biphenyl-based monomers with triethynylbenzene was confirmed by IR spectroscopy (Figure 1, Figure S1). No band at 2100 cm⁻¹ from the terminal acetylene groups is observed. Instead a strong band at 2200 cm⁻¹ can be detected in all porous polymers corresponding to the asymmetric stretching vibration of medial triple bonds.^[9] The presence of 1,3,5-trisubstituted and para-substituted benzene moieties is confirmed by the broad vibrations around 1580 and 1490 cm⁻¹ as well as by the strong band at 820 cm⁻¹ for the para-substituted benzene (polymerized biphenyl).^[10] Bands at 1450 and 1435 cm⁻¹ are attributed to C-H deformation vibrations of the bipyridine moieties and the band at 1260 cm⁻¹ to C-N stretching vibration of aromatic amines in BpyMP-1-NH₂.^[9, 11]

In ¹³C MAS NMR spectra, signals around 140, 130 and 125 ppm can be attributed to the aromatic carbon atoms of the backbone (Figure S2 and S3). The signal at 90 ppm belongs to medial triple bonds, whereas no signal of carbon atoms from terminal triple bonds can be detected around 80 ppm. This further confirms the high degree of polymerization. The signals at 95 and 10 ppm in the spectra of the Cp^{*}Rh loaded samples belongs to the quaternary and CH₃ carbon atoms of the pentamethylcyclopentadienyl moiety respectively.

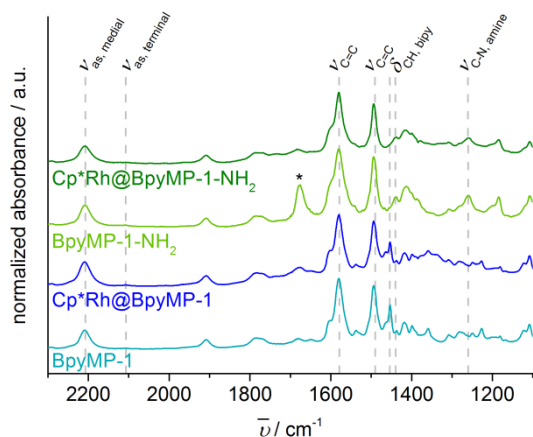
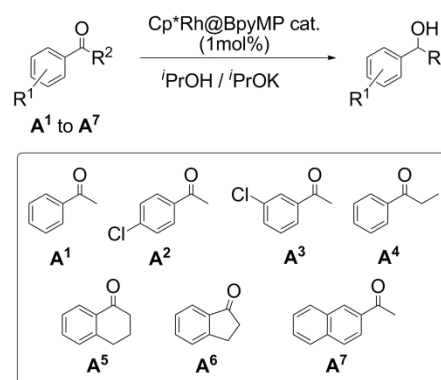


Figure 1. IR spectra of BpyMP-1 (cyan), 1.6% Cp^{*}Rh@BpyMP-1 (blue), BpyMP-1-NH₂ (pale green) and 1.6% Cp^{*}Rh@BpyMP-1-NH₂ (green). * denotes band from remaining DMF.

Nitrogen physisorption isotherms recorded for both the pristine polymers and the Rh-functionalized ones show a hysteresis, characteristic for the swelling behaviour of porous polymers (Figure S5). The apparent surface area^[12] determined by the BET method for BpyMP-1 and BpyMP-1-NH₂ was 680 ± 30 m²/g and 700 ± 20 m²/g, respectively. As expected the porosity slightly decreases upon Cp^{*}Rh insertion to 570 ± 30 m²/g for Cp^{*}Rh@BpyMP-1 and 680 ± 10 m²/g for Cp^{*}Rh@BpyMP-1-NH₂.

Having these novel Cp^{*}Rh(bpy)-based porous polymers in hand, we investigated their catalytic potential in the α-aryl ketones transfer hydrogenation to give the corresponding alcohols using isopropanol as hydrogen donor (Scheme 2). We note that under conditions reported in literature, e.g. at 82°C in ⁱPrOH/ⁱPrOK,^[13] the transfer hydrogenation of acetophenone occurs even without any catalyst (40 % conversion after 18 hours). We thus investigated this reaction under smoother conditions and we

accordingly reduced the temperature to 60°C, consequently lowering the catalytic activity.



Scheme 2. Transfer hydrogenation α-aryl ketones **A**¹ to **A**⁷ catalyzed by Cp^{*}Rh@BpyMP catalysts.

The BpyMP-based heterogeneous catalysts were compared to homogeneous counterparts based on 2,2'-bipyridine (bpy) and 5,5'-bis(phenylethynylene)-2,2'-bipyridine (bpebpy) ligand, the latter being the closest molecular analogue to BpyMP-1.

We note that the palladium, remaining from the synthesis, in the BpyMP structures is not active, as the same conversion (<1% after 3h) can be observed over the pristine BpyMP-1 network and in a reaction performed without any catalyst (Table 1, entries 1 and 2).

Table 1. Transfer hydrogenation of α-aryl ketones into alcohols catalyzed by Cp^{*}Rh@BpyMP-1, Cp^{*}Rh@BpyMP-1-NH₂ and molecular analogues.^[a]

Entry	Catalyst	Ketone	TOF (h ⁻¹) ^[b]
1	none	A ¹	(X = 0.8 %) ^[c]
2	BpyMP-1 (without Rh)	A ¹	(X = 0.5 %) ^[c]
3	Cp [*] Rh(bpy)Cl ₂	A ¹	2.66 ± 0.13
4	Cp [*] Rh(bpebpy)Cl ₂	A ¹	1.55 ± 0.08
5	Cp [*] Rh@BpyMP-1	A ¹	1.76 ± 0.09
6	Cp [*] Rh@BpyMP-1-NH ₂	A ¹	2.96 ± 0.15
7	Cp [*] Rh@BpyMP-1-NH ₂	A ²	2.48 ± 0.12
8	Cp [*] Rh@BpyMP-1-NH ₂	A ³	3.32 ± 0.16
9	Cp [*] Rh@BpyMP-1-NH ₂	A ⁴	0.90 ± 0.05
10	Cp [*] Rh@BpyMP-1-NH ₂	A ⁵	0.67 ± 0.03
11	Cp [*] Rh@BpyMP-1-NH ₂	A ⁶	0.44 ± 0.10
12	Cp [*] Rh@BpyMP-1-NH ₂	A ⁷	2.03 ± 0.19

[a] Reaction conditions: 60°C, molar ratio of Ketone / KOH / catalyst: 100 / 10 / 1 in ⁱPrOH. [b] Initial TOF determined after 3 hours and expressed as mol of product/(mol of Rh · time). [c] Conversion X after 3 hours are given in parentheses in the absence of Cp^{*}Rh.

Both homogeneous and heterogeneous catalytic systems were found to efficiently catalyze the reduction of acetophenone (**A**¹) into 1-phenyl-ethanol (Table 1, entries 3 - 6). The highest TOF (~3 h⁻¹) for the conversion of acetophenone into 1-phenyl-ethanol was achieved using Cp*Rh@BpyMP-1-NH₂ as catalyst.

For all homogeneous and heterogeneous catalysts a slow deactivation occurs over time resulting in a decrease in activity after three hours (see Figure S9). We note that the most active heterogenized catalyst Cp*Rh@BpyMP-1-NH₂ could be reused for 3 times without a significant decrease in activity after 3 h of reaction.

For the most active catalyst, namely Cp*Rh@BpyMP-1-NH₂, we evaluated different α -aryl ketones as substrates. As shown in the Table 1, similar activities can be observed for substituted acetophenones, with the highest activity reaching 3.3 h⁻¹ in the case of 2-chloro-acetophenone (**A**³, entry 6). The catalytic activity is significantly decreased below 1 h⁻¹ when cyclic ketones or longer alkyl chain ketones were used as substrates (**A**⁴ to **A**⁶ in entries 7 - 9). However we can exclude major diffusion limitation within the porous macroligand as for the bulkier 2-acetonaphthone (**A**⁷, entry 10) a TOF of 2.0 h⁻¹ was achieved. A relative rigidity of the substrate at the reactive C=O bond, like in cyclic ketones **A**⁵ and **A**⁶, might hinder the formation of Rh transition species, lowering the corresponding activity. Similarly, having a quite symmetrical bulkiness around the C=O bond, like in the ethyl phenyl ketone **A**⁴, could limit the approach of the substrate to the Rh active center. This hindering effect might further be enhanced by the steric constraints at the molecular level imposed by the cavity walls.

The Cp*Rh@BpyMP-1-NH₂ is found to be stable after recycling for 3 runs using **A**¹ as substrate, a slight decrease in activity is observed during the fourth run (Figure S10). This reduced activity might arise from pore blocking due to base accumulation during recycling process (Figures S14 to S17 and associated discussion).

To evaluate the influence of the different bpy-substituents on the activity of heterogeneous systems, we extended the scope of host frameworks also to bpy-based MOFs, namely UiO-67-bpy and MOF-253 (see Supporting Information for detailed characterizations). Both MOFs has been already applied in different catalytic reaction as macroligands, including Cp*Rh-functionalized ones.^[14] The Cp*Rh@UiO-67-bpy and Cp*Rh@MOF-253, containing similar Rh loadings (ca. 2 wt%) both show lower TOF values (0.698 ± 0.035 h⁻¹ and 0.455 ± 0.023 h⁻¹ respectively) than BpyMP-based catalysts for the transfer hydrogenation of the acetophenone.

The comparison of the different heterogeneous macroligands was realized by applying the Hammett-correlation. Such a correlation is well established for homogeneous catalysts but has not yet been reported for heterogeneous organometallic- or organocatalysts.

Therefore, in the case of acetophenone substrate, we plotted the logarithm of the ratio between the TOF of a selected (macro)ligand with a substituent R with respect to the TOF obtained with bipyridine used as reference ligand (R = H, $\sigma_H = 0$) against its Hammett constant (σ):

$$\lg\left(\frac{TOF_R}{TOF_{R=H}}\right) = \rho \cdot \sigma_R,$$

with σ_R being the Hammett constant of the substituent R and ρ the reaction constant which depends on the reaction conditions, e.g. solvent or temperature. Hammett constant values were attributed to the corresponding R substituents according to literature.^[15]

Here we found a unique linear correlation followed by both homogeneous and heterogeneous catalysts, covering Hammett constants from -0.02 (for *meta*-amino in BpyMP1-NH₂) to 0.66 (for *meta*-aluminum carboxylate in MOF-253) (Figure 2). The fact that heterogeneous BpyMP and MOF-based catalysts follow the same linear correlation than homogeneous molecular species proves that the performance of the catalysts depends only on the substituents electronic properties for both homogeneous and heterogeneous systems, further excluding any diffusion limitation inside these porous materials. The low Hammett constant of the BpyMP-1-NH₂ based catalyst give rise to the highest electron density on the rhodium,^[16] which causes the highest activity of this catalyst in the transfer hydrogenation reaction.

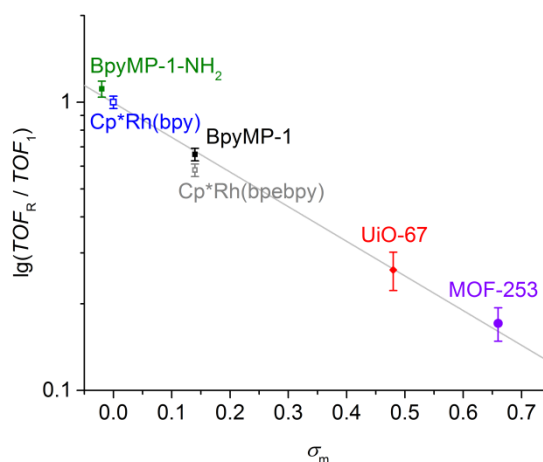


Figure 2. Hammett plot of TOF of transfer hydrogenation reaction of acetophenone into 1-phenyl-ethanol over different homogeneous and heterogeneous catalysts.

In conclusion we introduced bipyridine containing Microporous Polymers as novel macroligand platforms for efficient heterogenization of organometallic catalysts. The activity of heterogeneous Cp*Rh catalytic centers can be tuned by rationally choosing adequate functional pending groups onto such macroligands, as demonstrated here for the transfer hydrogenation of α -aryl ketones. The absence of diffusion limitation inside the porous system and a catalytic behavior identical to that of molecular analogues make BpyMP very appealing heterogeneous macroligand for organometallic catalysts. The good correlation between homogeneous and heterogeneous catalyst highlights also the preservation of the electronic environment around the active site upon heterogenization. The obtained catalysts are long range solids but can be considered as molecularly analogous to homogeneous complexes when it comes to catalysis. Such species further bring closer homogeneous and heterogeneous catalysis.

Experimental Section

Synthesis of BpyMP catalysts. The synthesis of BpyMP materials was done according to a modified literature procedure.^[9]

For a typical synthesis of BpyMP-1, 100.0 mg (0.66 mmol) 1,3,5-triethynylbenzene, 310.1 mg (0.75 mmol) 4,4'-diiodobiphenyl, 86.0 mg (0.25 mmol) 5,5'-dibromo-2,2'-bipyridine and 15.7 mg (13.4 μ mol) Pd(PPh₃)₄ were added to a flame dried glass flask inside a glove box. The glass vial was sealed with a teflon septum. Outside the glove box, 12 ml of anhydrous DMF and 6 ml of anhydrous NEt₃ were added and the glass vial was placed in an oil bath. The reaction mixture was heated to 100 °C for 24 h. After cooling down to room temperature the yellow solid was purified by soxhlet extraction using CHCl₃ for 6 h and using MeOH overnight.

For a typical infiltration, (6 mol-% Rh) 100 mg BpyMP-1 were dispersed in 3.7 ml dry MeOH, then 1.05 ml of 15 μ mol/ml [Cp*RhCl]NO₃ in acetonitrile were added, and the suspension was stirred for 24 h at room temperature to yield 1.6% Cp*Rh@BpyMP-1. The supernatant was removed by centrifugation and the yellow solid washed with MeOH for 2 days.

Catalysis. Transfer hydrogenation was carried out under Ar atmosphere in glass vials containing approximately 2.2 μ mol catalyst in 2 ml of 0.011 mM deaerated KOH solution in 2-PrOH. After activating the catalyst for 1 h at 60 °C 0.21 mmol ketone were added and the reaction mixture heated to 60 °C for 24 h. After certain time intervals 50 μ l of the reaction mixture were sampled, diluted in 1 ml Et₂O and extracted with brine. The organic phase was analyzed by HPLC using a Shimadzu LC 2010 liquid chromatograph equipped with a AS-H column (isocratic mode: *n*-hexane : 2-PrOH, 97 : 3, V : V, detection @ 215 nm). To estimate an error the largest relative error determined from two consecutive measurements of the same sample was applied to all data given.

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Keywords: Microporous Polymers • Heterogenization • Transfer Hydrogenation • Hammett parameter

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