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Chiral Chromium Salen@rGO as Multipurpose and Recyclable Heterogeneous Catalyst

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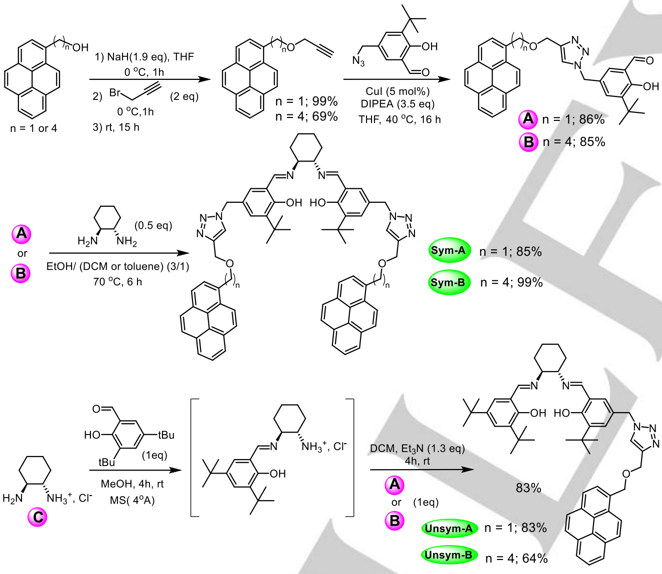
Abstract: The first immobilization of a pyrene-tagged chromium salen complex through π-π non-covalent interactions on reduced graphene oxide (rGO) is described. A very robust supported catalytic system is obtained to promote asymmetric catalysis in repeated cycles, without loss of activity or enantioselectivity. This specific behavior was demonstrated in two different catalytic reactions (up to ten reuses) promoted by chromium salen complexes, the cyclohexene oxide ring-opening reaction and the hetero-Diels-Alder cycloaddition between various aldehydes and Danishefsky's diene. Furthermore, the chiral chromium salen@rGO has been found to be compatible with a multi-substrate type use, in which the structure of the substrate involved is modified each time the catalyst is reused.

Introduction

Carbon materials have been used extensively as highly stable supports, ideally porous and mechanically resistant in catalysis, in particular for the dispersion and stabilization of metal particles or for the immobilization of organometallic complexes.[1] Their particular surface chemistry allows either covalent grafting by complementary functionalization of the support and of the ligand, or non-covalent bonding via π-π-interactions between a polyaromatic functionalized compound and the graphitic sp^2 carbon network. In the context of homogeneous supported catalysis, and precisely when valuable enantiopure chiral catalysts are engaged, their non-covalent interactions with the support are based on simple synthetic procedures avoiding its prior modification. The strength of these supramolecular interactions can be adjusted as a function of the solvent and the temperature, allowing both easy recovery of the catalyst and recycling of the support, in the event of deactivation. On the other hand, precautions must be taken to suppress metal leaching.[2] Some successes have already been reported using this immobilization strategy on different carbon supports, including the immobilization of Ru-carbene complexes to perform metathesis reactions.[3] The Au-catalyzed enyne cyclization reaction has been achieved on multi-walled CNTs[4] and Pd-based catalysts were non covalently anchored onto magnetic Co/carbon nanoparticles for Suzuki-Miyaura couplings.[5] rGO was further used for the Pd-catalyzed heterogeneous hydrogenation of alkenes and the Ru-catalyzed alcohol oxidation.[6] The diversity of application is moreover demonstrated by the Fe-catalyzed ethylene polymerization on multi-walled CNTs,[7] the Rh-promoted 1,4-addition reaction and hydrosilylation of alkynes,[8] and the Cu-catalyzed CH activation on rGO.[9] In the latter case, the carbon support not only contributes to make the catalyst insoluble but also exacerbates its activity by reducing the electron density of the copper site. Mention should be made, in each case, of the functionalization of the ligand by a pyrene group as a demonstration of its high affinity with the carbon surface by π-π-interactions. Such non-covalent anchoring on carbon surfaces proved also its utility by enhancing the cooperativity between two pyrene-tagged Pd- and Ru-complexes for hydrodefluorination.[10] In contrast, this immobilization strategy has been much less developed in the context of asymmetric catalysis, with only four examples reported, to our knowledge. In the field of Rh-promoted asymmetric hydrogenation, chiral phosphine-containing catalysts have been deposited on CNT,[11] or assembled onto rGO.[12] We have immobilized copper bis(oxazoline) complexes for the enantioselective formation of C-C bonds,[13] and more recently, the non-covalent immobilization of Rh complexes was reported for the asymmetric hydroformylation and implemented in a flow mode.[14] The use of salen-complexes is ubiquitous in asymmetric catalysis.[15] These valuable enantiopure catalysts have been immobilized on various supports or their structures modified to become insoluble species, in order to be easily recovered by filtration.[16] We describe here the first immobilization of chromium salen complexes on carbon supports[17] through π-π interactions with rGO. The high efficiency of these chromium catalysts[18] is demonstrated both in the heterogeneous asymmetric ring-opening (ARO)[19] of a *meso* epoxide and in the hetero-Diels-Alder reaction (HDA)[20] of various aldehydes. Their stability in recycling procedures is also evaluated.[21] These reactions were chosen as benchmarks for the diversity of the products to which they lead. While the ARO reaction provides precursors of cyclic 1,2-amino alcohols, the HDA reaction between aldehydes and the electron-rich Danishefsky's diene delivers enantioenriched dihydro-pyranones, important scaffolds for the preparation of various natural compounds.[22]

Results and Discussion

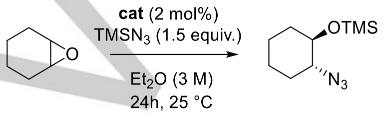
We therefore immobilized the salen complexes by π-interactions with the rGO support by placing the pyrene group far from the active chromium site (Scheme 1). This strategy aims to preserve the selectivity of the homogeneous transformation achieved in the presence of the conventional Jacobsen catalyst. We tackled the synthesis of salen catalysts tagged with one or two pyrene groups via links of different lengths, to compare both the accessibility to the active sites and their stability to recycling. Compounds **A** and **B**, as key intermediates for the synthesis of **Sym** and **Unsym** ligands were easily obtained through click reactions between 1-[(2-propyn-1-yloxy)methyl]-pyrene[23] or 1-(4-(prop-2-yn-1-yloxy)butyl)pyrene[24] and 5-(azidomethyl)-3-(tert-butyl)-2-hydroxybenzaldehyde[25] in two steps and high isolated yield (see Scheme 1 and Supporting Information). Then, classical condensation with 0.5 equivalent of (1*S*,2*S*)-cyclohexane-1,2-diamine directly afforded **Sym-A** and **Sym-B**, the latter with a metal coordinating site remote from pyrene by four methylene groups. After the preliminary preparation of the diamine monoammonium salt **C**,[26] the high yield formation of both **Unsym** ligands also occurred by successively reacting 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde then **A** (or **B**), without isolating the intermediate ammonium mono-imine. Insertion of chromium in the coordinating sites was finally performed from $CrCl_2$ in THF under argon atmosphere and then oxidation in air.[20]



Scheme 1. Synthesis of pyrene-tagged salen ligands.

The four corresponding chromium complexes **Sym-Cr** and **Unsym-Cr** (**A** and **B**) were prepared in almost quantitative yield and fully characterized by IR, UV-Vis and HRMS spectroscopy. They were first tested under homogeneous conditions, to assess the influence of their structure on their reactivity and selectivity. Cyclohexene oxide ring opening with $TMSN_3$ was chosen as the first test reaction carried out in diethyl ether. Different results in terms of activity and selectivity were obtained depending on the structure of the catalysts used (see Table 1). In our hands, the Jacobsen catalyst delivered the ring-opening product in 88 % ee, but full conversion was not achieved after 24 h of reaction. The pyrene-tagged catalysts are all more active than the reference Jacobsen catalyst. We propose that π-stacking interactions are strongly probable between the catalysts, allowing thus a favorable bimetallic interaction for highly active catalytic species. Presence of non-covalent interactions in salen-based complexes has already been investigated, to promote their association and study their influence on the catalysis, particularly for cooperativity.[27] The pyrene-tagged catalysts nevertheless differed in their selectivity. Indeed, both **Sym-Cr-A** and **Sym-Cr-B** were found to be poor enantioselective catalysts while the unsymmetric analogues were much better, with **Unsym-Cr-A** giving the target product in 81 % ee. In addition, further experiment showed that almost complete conversion (96 %) was already achieved in just 6 hours using this catalyst.

Table 1. Homogeneous ARO of cyclohexane oxide, catalysts comparison[a]



Catalyst	Conv (%) [b]	ee (%) [c]
Jacobsen Cat.	78	88
Sym-Cr-A	86	26
Unsym-Cr-A	>99	81
Sym-Cr-B	98	8
Unsym-Cr-B	>99	70

[a] substrate, 0.5 mmol, [3 M] in Et_2O. [b] determined by GC with dodecane as internal standard. [c] determined by GC (see Supporting Information).

We propose that the absence of two *t*Bu groups in the *para* position of the phenol, in the **Sym-Cr** catalysts, due to the bifunctionalization by the pyrene groups is the cause for this significant decrease in enantioselectivity. On the other hand, the accessibility of the catalytic sites in these symmetrical species can be constrained by a possible π-π intramolecular stacking between the two adjacent pyrene groups. In contrast, **Unsym-Cr-A** allowed complete conversion and led to the best enantioselectivity value for the series. This catalyst was therefore chosen for the rest of the study.

Its immobilization onto the carbon surface was achieved by impregnation of the rGO suspension with a solution of **Unsym-Cr-A** in DCM with a mass ratio of 4/1. After 24 hours of stirring at room temperature, the solid was filtered off, washed with DCM and vacuum dried.

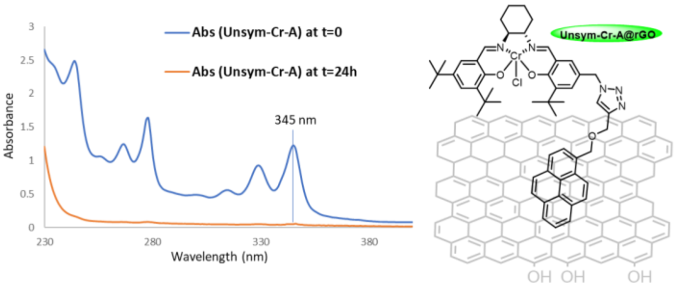


Figure 1. Immobilization of **Unsym-Cr-A** on rGO.

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The efficiency of the immobilization was monitored by UV-Vis analyses (see Figure 1 and Supporting Information for details).

A calibration line curve for **Unsym-Cr-A** was indeed obtained by measuring the absorbance (Abs) of solutions with different concentrations at the λ_{max} (345 nm, see blue trace in Figure 1). After 24 h, analysis of the supernatant (orange trace) indicated that 90% of the complex has been deposited, what was confirmed by weighing the resulting solid.

Furthermore, X-ray photoelectron spectroscopy was conducted on powders of both unmodified rGO support and **Unsym-Cr-A@rGO**. The wide-scan spectra are shown in Figure 2a. The presence of signals arising from Cr2p, N1s and Cl2p core-levels was clearly noticed on the spectrum of **Unsym-Cr-A@rGO**, proving that the catalyst had been successfully grafted. The narrow-scan spectra for Cr2p, N1s and Cl2p were then measured (Figure 2b), which allowed to determine the position in energy of the three elements, as well as their atomic ratios. The Cr2p core-level spectrum consists of two main peaks corresponding to the spin-orbit components $Cr2p_{3/2}$ and $Cr2p_{1/2}$, situated at 577.2 eV and 586.9 eV, respectively, and separated by 9.7 eV. These values allowed to assign the Cr^{3+} according to the literature.[28] The Cl2p and N1s spectra are centred at 198.7 eV and 400.5 eV respectively. Expecting information on the catalyst structure, experimental determination of the Cr/Cl content in **Unsym-Cr-A@rGO** was performed and is comparable to the theoretical value (1), as well as the N/Cl ratio (5), undoubtedly revealing the presence of intact **Unsym-Cr-A** on the surface.

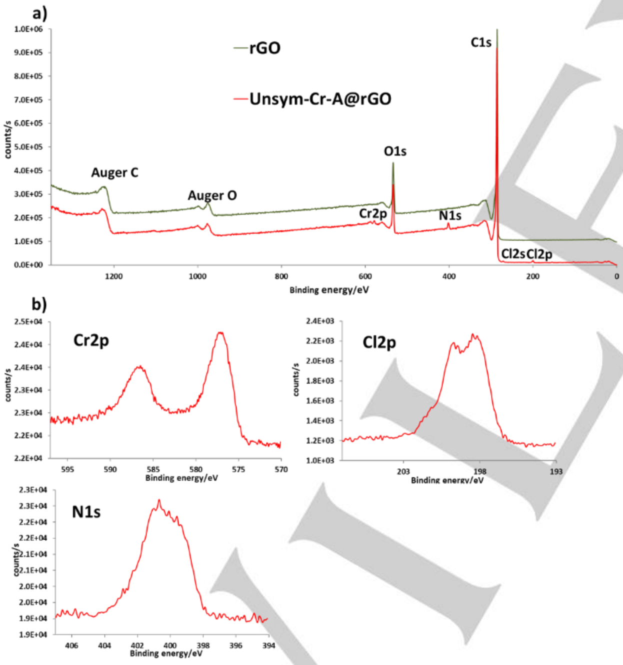
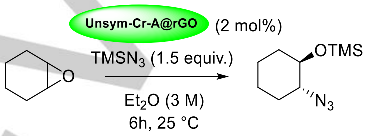


Figure 2. a) XPS spectra for rGO and **Unsym-Cr-A**@rGO. b) narrow-scan spectra for Cr2p, N1s and Cl2p.

The heterogeneous catalysis was then performed under conditions exactly matching the one used for the tests with the non-supported catalysts. A black suspension (3M in substrate) was obtained, corresponding to the introduction of a 2 mol % catalytic ratio. Pleasingly, the first **Unsym-Cr-A@rGO** catalysis in the ARO of cyclohexene oxide afforded the ring-opened product with complete conversion after 6 h, indicating no detrimental effect of the support on the catalytic activity, which is often the case in heterogeneous reactions. However, the target product was isolated with a decreased enantioselectivity value than that observed under homogeneous conditions (see Table 2, entry 1). After completion, the supernatant from the first run of heterogeneous catalysis was filtered off and the supported complex was washed with diethyl ether, the reaction solvent. It was then dried under vacuum, before its reuse by further addition of substrate. The second use of the supported catalyst was also successful, as were subsequent ones, allowing 10 uses of the same batch of catalyst. The enantiomeric excess reached 79 %, fortunately almost equal to the high values obtained under homogeneous conditions (Table 2).

Table 2. Heterogeneous ARO of cyclohexane oxide with **Unsym-Cr-A@rGO**, recycling experiments [a]



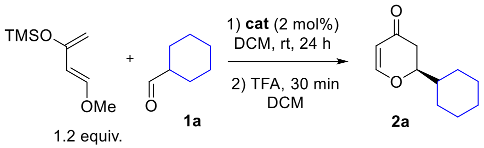
Catalyst	Conv (%) [b]	ee (%) [c]
Run 1	>99	63
Run 2	>99	75
Run 3	>99	75
Run 4	>99	76
Run 5	>99	79
Run 6	>99	76
Run 7	98	76
Run8	98	75
Run 9	96	72
Run 10	96	68

[a] substrate, 0.5 mmol, [3 M] in Et_2O. [b] determined by GC with dodecane as internal standard. [c] determined by GC (see Supporting Information)

The immobilization of **Unsym-Cr-A** on rGO thus did not alter its activity and the enantioselectivity values remained also very high in this procedure. Altogether, an important increase in the calculated TON of the catalyst is thus obtained by its simple reuse after filtration.

A second reaction, namely the HDA reaction between aldehydes and *trans*-1-methoxy-3-trimethylsilyloxy-buta-1,3-diene, was tested to evaluate the extent of application of **Unsym-Cr-A@rGO** in asymmetric catalysis. To ensure the efficiency of the modified complexes, the performances of **Sym-Cr-A** and **Unsym-Cr-A** were again compared with the Jacobsen complex in the HDA reaction involving cyclohexane carboxaldehyde in DCM (Table 3). In this case again, the unsymmetrical pyrene-derived complex **Unsym-Cr-A** provided activity and enantioselectivity values very close to those obtained by the Jacobsen catalyst, with **Sym-Cr-A** far less active. The study therefore continued using **Unsym-Cr-A** with rapid screening for solvents, but neither Me-THF nor diethyl ether outperformed DCM in terms of activity (61 and 67 % yield, respectively), nor of selectivity (78% ee). A new batch of **Unsym-Cr-A@rGO** was prepared and the catalysis was first carried out in DCM as was the homogeneous reaction. The first **Unsym-Cr-A@rGO** catalysis afforded the dihydropyranone with conversion and enantioselectivity values close to those obtained in homogeneous conditions.

Table 3. Homogeneous HDA of cyclohexane carboxaldehyde, catalysts comparison [a]

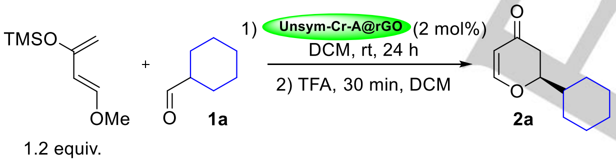


Catalyst	Conv 1a (%) [b]	Yield 2a (%) [c]	ee 2a (%) [d]
Jacobsen Cat.	84	69	78
Sym-Cr-A	23	-	80
Unsym-Cr-A	73	61	78

[a] substrate, 0.5 mmol, [5 M] in DCM. [b] determined by GC with dodecane as internal standard. [c] isolated yield. [d] determined by GC (see Supporting Information).

In this case also and ideally, the presence of the support did not impact the chiral catalyst efficiency. This was verified by using unmodified rGO in the reaction conditions, which resulted in no conversion after 24 h of stirring. After complete conversion, the heterogeneous catalyst was recovered by filtration and several solvents were tested to wash the supported complex between each reuse (see Table 4). The reaction solvent, cold DCM, was initially used during the first three cycles which led to the conservation of the enantioselectivity but to a constant decrease in the conversion with each recycling (entries 1-4).

Table 4. Heterogeneous HDA of cyclohexane-carboxaldehyde with **Unsym-Cr-A@rGO** in DCM [a]

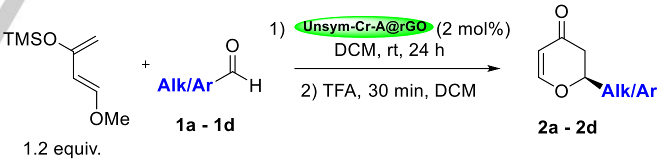


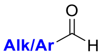
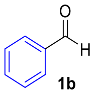
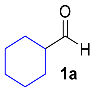
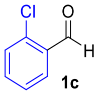
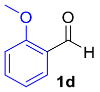
Entry	Run	Conv 1a (%) [b]	ee 2a (%) [c]	Washing Solvent
1	1	55	81	DCM
2	2	61	81	DCM
3	3	49	81	DCM
4	4	14	71	Acetone
5	5	85	79	Acetone
6	6	82	81	Acetone
7	7	79	79	Acetone
8	8	79	79	Et_2O
9	9	79	80	-
10	1	82	80	Et_2O
11	2	85	81	Et_2O
12	3	86	80	Et_2O
13	4	78	80	Et_2O
14	5	74	81	Et_2O
15	6	76	81	Et_2O
16	7	68	81	-

[a] substrate, 0.5 mmol, [5 M] in DCM, rt, 24 h. [b] determined by GC with dodecane as internal standard (see Supporting Information). [c] determined by GC (see Supporting Information).

The even more important decrease (14 % conversion) during the 4th use of the supported catalyst led to carrying out the following washes with cold acetone. Interestingly, this resulted in the complete recovery of the catalyst activity and enantioselectivity for its 5th use (entry 5), values which were maintained for the next four runs. We propose that acetone is both a polar solvent which promotes π-stacking type interactions, and a favourable medium for the dispersion of the rGO carbon sheets, which allows a better accessibility to the catalytic sites.[3a] The recovery procedure was however not facilitated by the use of acetone as washing solvent because of settling difficulties. Thus, after the 8th run, this same catalytic batch was washed with cold diethyl ether, and gratifyingly, the next run afforded the same results in terms of activity and enantioselectivity (entries 8-9).The validity of this optimized washing procedure in diethyl ether was verified by the preparation of a new batch of **Unsym-Cr-A@rGO**, which was involved in a new recycling experiment (entries 10-16); efficient catalysis occurred for seven reuses of the supported catalyst, with excellent stability of the enantioselectivity values of the transformation.
The scope of this recovery procedure via non-covalent interactions was tested for the HDA of various aldehydes. Consequently, three aromatic aldehydes reacted with Danishefsky's diene under homogeneous conditions with **Unsym-Cr-A** and the corresponding dihydropyranones were isolated with good enantioselectivity values (see Supporting Information). Then, another batch of **Unsym-Cr-A@rGO** was prepared and used to catalyse the heterogeneous HDA reaction of these aldehydes successively, by changing the structure of the substrate at each reuse of the supported complex (Table 5).

Table 5. Heterogeneous HDA of various aldehydes with **Unsym-Cr-A@rGO** [a]



	Run	Conv (%) [b]	ee (%) [c]	Yield (%) [d]	Run	Conv (%) [b]	ee (%) [c]
 1b	**1**	68	64	60	**5**	83	64
 1a	**2**	63	81	30	**6**	70	81
 1c	**3**	76	63	65	**7**	85	60
 1d	**4**	75	64	71	**8**	84	63

[a] substrate, 0.8 mmol, [5 M] in DCM, rt, 24 h, washing with Et_2O. [b] determined by GC with dodecane as internal standard (see Supporting Information). [c] determined by GC (see Supporting Information). [d] isolated yield

A first run was thus devoted to the transformation of benzaldehyde **1b**, resulting in the isolation of the corresponding dihydropyranone **2b** with a good yield and an enantioselectivity value of 64 % ee, even slightly better than that obtained under homogeneous conditions (Table 5, run 1 and Supporting Information for comparison). After washing with diethyl ether, the recovered catalyst was then engaged in the transformation of cyclohexane-carboxaldehyde **1a** (Table 5, run 2).

The subsequent recycling procedure involved consecutively two other aromatic aldehydes (**1c-d**, runs 3-4). If the heterogeneous catalysis turned out to be slightly less effective in terms of activity compared to the results obtained under homogeneous conditions (Table 5 and Supporting Information), similar enantioselectivity values could nevertheless be obtained. The products were easily recovered without being contaminated by traces of dihydropyranones prepared in the previous runs.

Finally, recovered **Unsym-Cr-A@rGO** after the 4th run was reassigned to the HDA of benzaldehyde (run 5), interestingly offering improved activity and the same enantioselectivity for the target product **2b**. Recycling was continued again with the other three substrates (**1a**, **1c** and **1d**) while maintaining its efficiency (runs 6-8), as clear evidence of the stability of the procedure.

Spent **Unsym-Cr-A@rGO** was also subjected to XPS-analyses and the Cr to C ratio was compared to that determined for the fresh supported catalyst (see Supporting Information). Within the limits of precision of the analysis, no leaching of active species could be determined; with regard to the stability of the catalytic values, no degradation of the chromium complex has occurred, obviously. In addition, **Unsym-Cr-A@rGO** was stirred for 18 h in DCM and the resulting solution was collected after filtration without decreasing the temperature. No catalytic activity was detected after adding substrates to this solution, proving that there is no release of the active species during the heterogeneous catalysis reaction.

Conclusion

To conclude, non-covalent attachment of a Cr-salen complex on rGO was proved to afford an efficient supported catalyst to produce highly enantioenriched compounds when engaged in recycling procedures. Using two different asymmetric catalytic transformations as a test, the ARO and the HDA reactions, various valuable scalemic compounds were easily isolated in their pure form. This also applies when the supported catalyst is engaged in a multi-substrate procedure. For both types of reactivity, we demonstrated that a single pyrene group covalently linked to the enantiopure salen unit was sufficient to retain the activity values of the parent Cr-salen complex and allow its grafting to the support surface by non-covalent π-π interactions. As expected however, the nature of the solvent used for the reaction and for the products recovery after completion was of major importance. In this context, the use of ether as a polar solvent allowed the dispersion of the rGO sheets, therefore maintaining accessibility to the catalytic sites. Numerous stable recycling operations have been carried out, highlighting the possibility of using chiral organometallic catalysts heterogenized by weak interactions. Such non-covalent bindings result from easy synthesis of the catalyst and from the absence of support modification. As far as we know, this is the first immobilization of salen derivatives on carbon surfaces by π-π interactions, and its success opens the way for many extensions, given the wide applicability of these complexes in asymmetric catalysis. Work is in progress to further extend this procedure to different asymmetric catalytic transformations with other pyrene-tagged salen complexes, both in batch and in flow conditions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Asymmetric catalysis • Cr-salen complexes • Supported catalysts • reduced Graphene Oxide • Recycling

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A pyrene-tagged Cr-salen complex immobilized by π-π interactions at rGO surface delivers a robust, reusable, heterogeneous catalyst efficient in several asymmetric catalytic reactions