Development and application of hybrid nanomaterial single-site catalysts by surface modification of metal oxide nanoparticles

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**NANYANG
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**DEVELOPMENT AND APPLICATION OF HYBRID NANOMATERIAL
SINGLE-SITE CATALYSTS BY SURFACE MODIFICATION OF METAL
OXIDE NANOPARTICLES**

GHOSH DWAIPAYAN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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OXIDE NANOPARTICLES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial fulfilment of the
requirement for the degree of

Master of Science

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Dr. Soo Han Sen

Authorship Attribution Statement

This thesis contains material from the paper published in the following peer-reviewed journal where I was the first author.

Chapter 2 is published as Ghosh, D.; Febriansyah, B.; Gupta, D.; Ng, L. K.-S.; Xi, S.; Du, Y.; Baikie, T.; Dong, Z.; Soo, H. S., Hybrid Nanomaterials with Single-Site Catalysts by Spatially Controllable Immobilization of Nickel Complexes via Photoclick Chemistry for Alkene Epoxidation. *ACS Nano* **2018**, *12* (6), 5903-5912.

The contributions of the co-authors are as follows:

- Asst. Prof H. S. Soo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Y. Du and Dr. T. Baikie.
- I co-designed the study with Asst. Prof H. S. Soo and performed all the laboratory work at the School of Physical and Mathematical Sciences and the Singapore Synchrotron Light Source.
- Initial complex synthesis and characterization works were performed by B. Febriansyah.
- All microscopy, including sample preparation, was conducted by L. K.-S. Ng at the Facility for Analysis, Characterization, Testing and Simulation.
- D. Gupta and Dr. Y. Du assisted in the interpretation of the X-ray absorption spectroscopy data and carried out the spectral interpretation.
- Dr S. Xi assisted in the collection of the X-ray absorption spectroscopy data.

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Abstract

Catalyst deactivation is an intriguing issue that has created immense problems not only for the industry but also for the global scientific community. Isolated single-site heterogeneous catalysts can potentially overcome these problems. In this thesis, we have explored a simple yet reproducible anchoring strategy for immobilization of molecular complexes on a wide range of metal oxide (e.g. titanium dioxide, mesoporous silica, cerium oxide, and tungsten oxide) nanoparticles to synthesize isolated single-site catalysts. Maleimide, an oxidatively stable anchoring group, forms a covalent bond with surface hydroxyl groups present on the metal oxide surface via photoclick chemistry. The hybrid nanomaterials have been extensively characterized by several techniques including UV-visible diffuse reflectance spectroscopy (UV-DRS), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FT-IR), and X-ray absorption spectroscopy (XAS). The formation of the covalent linkage was confirmed by the FT-IR spectroscopic study. The hybrid nanocomposites were found to be highly efficient for the oxidation of terminal as well as internal alkenes. The conversions of the starting materials and selectivity towards epoxide product was found to be comparable to the molecular catalyst even in environmentally benign solvents. XAS and FT-IR studies confirm the robustness of the hybrid catalyst, even after several catalytic cycles.

The photoclick anchoring technique was applied to deposit a luminescent complex precisely at the desired locations on the metal oxide nanoparticles surfaces. Overall, a facile and general approach was demonstrated to anchor molecular catalysts on a wide range of metal oxide nanomaterial surfaces. This

spatially and temporally controllable photoclick methodology can be applied to other ligands, catalysts, functional molecules, and surfaces.

Chapter 1

Introduction

1.1 Single-site catalysts

Homogeneous catalysts suffer from reusability and deactivation issues, which has prevented their large scale applications in industries. However, molecular homogeneous catalysts have several advantages over heterogeneous catalysts. For example, these molecular catalysts are easily modifiable, elucidation of reaction mechanisms are easier, there is very high selectivity of the preferred products, and the active sites of the catalysts have the same well-defined structure.¹ Heterogeneous catalysts are usually prepared by dispersing precursors on a support followed by subsequent heating under a gas stream. However, these synthetic routes result in the loss of uniformity of the coordination environment, and often only a very small fraction of these sites remain active. Hence, characterization at the molecular level becomes much more difficult and also hampers the process of rational catalyst design.

Merging the advantages of the molecular catalysts and the heterogeneous catalysts, site isolated single-site catalysts can be designed by grafting molecular coordination complexes on the solid scaffolds (Scheme 1.1). This approach provides the flexibility to rationally design and characterize the surface active sites by means of the techniques employed in the study of molecular complexes. Moreover, by isolating the active sites from one another, bimolecular deactivation pathways can be avoided.

Scheme 1.1. Isolated single site heterogeneous catalyst synthesis.

Research in the field of surface organometallic chemistry (SOMC) has gained momentum in the last two decades due to the need for better performing robust catalysts and advances in spectroscopic and computational techniques. SOMCs involving transition metal catalyst have been of immense interest as a wide variety of reactions like organic transformations, water splitting, biomass degradation, pollutant degradation, CO₂ reduction, etc., can be catalyzed by them.²

1.2 First row transition metal complexes in catalysis

First row transition metals such as vanadium (V), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu) are earth abundant and thus less expensive compared to their heavier congeners like ruthenium (Ru), iridium (Ir), rhenium (Re), and platinum (Pt). A wide range of their oxidation states can be stabilized by various ligand systems, making them interesting candidates for cost-efficient catalyst synthesis. Moreover, coordination number flexibility also adds to their advantages. Ni, Co, and Fe based coordination complex catalysts are well known to be used in various kinds of reactions, ranging from organic transformation to hydrogen evolution and

CO₂ reduction. The versatility of these first row coordination complexes enables their use as both electro- and photo-catalysts.

Earth abundant transition metal-catalyzed organic transformation is a major area of interest of the chemists for several decades. V, Fe, Co, Cu, and Ni based homogeneous catalysts have been extensively studied for various types of organic transformations including C-H activation of aromatic and aliphatic compounds, oxidation of C-H bonds, C-C bond cleavage, dehydrogenative coupling of diols and *o*-phenylenediamines, and deamidative reduction of amides to hydrocarbons.³ Many studies have been reported on catalytic oxidation of olefins to epoxides by Mn- and Ni-based catalysts. Meunier and co-workers pioneered the studies of the transition metal complex catalyzed epoxidation of olefins.⁴ Later, Burrows and co-workers reported Ni salicylaldimine complex catalyzed epoxidation of terminal and internal alkenes in the presence of sodium hypochlorite oxidant.⁵ Subsequently, reports have been published for the epoxidation of alkenes by Mn salicylaldimine complexes from Jacobsen and co-workers and by non-heme Mn complexes from Nam and co-workers.⁶

Co-ordination complexes of Co, Ni, and Cu also have been widely reported as molecular catalysts for hydrogen production, water oxidation, and CO₂ reduction reactions. Different ligand systems including porphyrin, salicylaldimine, phthalocyanine, and terpyridine⁷ have been thoroughly studied over the last decade. The ability of stabilizing different oxidation states of the metals, ease of modification, and relatively simple synthetic procedures make them ideal candidates for such studies. Moreover, these ligands can be easily modified with an anchoring group for converting them into single-site heterogeneous catalysts.⁸

1.3 Anchoring strategies

The attachment of a molecular complex on the solid surfaces can be achieved either by electrostatic interaction, known as physisorption or by the formation of a covalent bond with the solid surface, known as chemisorption. The physisorption technique depends on the π - π interaction between the solid support and the molecular catalyst. Heterogeneous catalysts synthesized by physisorption has been reported to be used in proton reduction chemistry, electron transfer mechanistic study.⁹ Though relatively simple to synthesize, the heterogeneous catalysts formed by physisorption are vulnerable to harsher reaction conditions like high temperature and pH. Moreover, the π - π interaction is known to be reversible in nature and dissociation can happen under unfavorable conditions.

Chemisorption on the other hand is known to be stable under different reaction conditions. In this case a covalent linkage is formed, usually with the surface hydroxyl groups present in the metal oxide (MO_x) surfaces. A variety of metal oxides including silica (SiO_2), titanium dioxide (TiO_2), indium tin oxide (ITO), metal chalcogenides, silicon carbide, and silicon nitride surfaces have been reported to be covalently modifiable.¹⁰

The covalent modification can either be achieved by simply mixing the two precursors in anhydrous solvents or by photo irradiation under inert conditions. Various anchoring groups have been studied over the decades for covalent modification. The silane group is one of the most commonly used anchoring groups to deposit molecular compounds on metal oxide surfaces.¹¹ Other than that,

phosphonates, carboxylates, catechols, amines, and hydroxamic acids have also been widely reported as the anchoring groups (Figure 1.1).

Figure 1.1. Different anchoring groups for covalent anchoring on metal oxide surfaces.

Phosphonates and carboxylates have been extensively studied for the anchoring of Ru dyes and metal complexes on metal oxide surfaces. Gratzel and co-workers first reported the anchoring of Ru bipyridyl complexes modified with carboxylate groups for dye sensitized solar cells (DSSC).¹² Later, Choi group reported a comparative study of anchoring efficiency of the carboxylate groups and the phosphonate groups on TiO₂ for hydrogen production under visible light.¹³ Catechols are also known to form covalent linkages with the TiO₂ and SiO₂ surfaces either in monodentate or bidentate fashion. Other known anchoring groups involve amines, hydroxamic acids, and alcohols,¹⁴ which have been studied over the last decade. However, most of these

groups are also known to coordinate to the metal centers and hence, can cause problems during the synthesis of the molecular complexes. Thus, the search for non-coordinating covalent anchoring groups brings us to the alkene based anchoring groups.

1.4 Alkene as an anchoring group

The initial reports on alkene anchoring groups were published by the Zuilhof group for the modification of surface of silicon carbide (SiC) materials.¹⁵ The surface anchoring was found to be very selective towards 254 nm irradiation and usage of 275 and 330 nm ultraviolet (UV) irradiation were ineffective. The successful anchoring of long alkyl chain increased the water droplet's static contact angle value of the surface. The surface of the silicon carbide contains hydroxyl groups (Si-OH and C-OH), which upon UV irradiation forms a covalent linkage (Si-O-C and C-O-C type) with the organic chain (Figure 1.2).

Figure 1.2. UV light (254 nm) induced covalent anchoring of alkenes on metal oxide nanoparticles.

Subsequently, they managed to functionalize the surface of SiO₂, glass, and other diamond surfaces using the same method. Hammers and co-workers extended this work to semiconductor metal oxide like TiO₂.¹⁶ As TiO₂ is widely used in

photocatalysis and DSSCs, this work paved the path for synthesizing novel catalysts and devices by photo-anchoring of molecular complexes on the metal oxide surfaces. Analogous photo-anchoring of long chain alkene anchoring group was obtained for indium tin oxide (ITO) substrate.¹⁷ The linkage occurs via formation of C-O-In(Sn) covalent bond. Zuilhof and co-workers showed that this photo-anchoring forms a highly stable monolayer on the metal oxide surface. The monolayer remains stable under a wide range of pH values as well as temperature variations. Apart from these, other materials such as, zinc oxide (ZnO), zirconium oxide (ZrO₂), tin oxide (SnO₂), gallium nitride (GaN), and gallium phosphide (GaP) have been reported to form alkyl monolayers upon reaction with long chain alkene compounds.¹⁰ Shah *et al.* reported the formation of a heterojunction by surface modification of the SnO₂ by a hydroxyl terminated alkene compound and subsequent click attachment of TiO₂ nanoparticles (Figure 1.3).¹⁸

Figure 1.3. Sequential formation of SnO₂-TiO₂ heterojunction via alkene anchoring and subsequent click chemistry.¹⁸

Recently, Moore *et al.* applied the photo-anchoring of alkene groups for the preparation of surface modified proton reduction catalysts of Co porphyrin and Co dimethylglyoxime complexes (Figure 1.4).¹⁹ The anchored complexes showed

excellent stability and high proton reduction efficiency under photoelectrocatalytic conditions.

Figure 1.4. UV light mediated anchoring of alkene modified complexes of a) Co and Fe porphyrins on GaP²⁰ and b) Co dimethylglyoxime on ITO nanoparticles for photoelectrocatalytic hydrogen production.¹⁹

Another interesting advantage of the UV light mediated photo-anchoring is spatial control and constructive photopatterning, which is impossible to achieve via a solvothermal process. This process allows local attachment of a DNA modified with alkene inside the microchannel and subsequent hybridization with a complementary fluorescent oligo-DNA (Figure 1.5a).²¹ This spatially controllable approach allows selective attachments of DNA and enzymes for construction of enzymatic cascade reaction (Figure 1.5b).²²

Figure 1.5. a) Covalent functionalization by a non-fluorescent DNA followed by hybridization with a fluorescent labelled oligo-DNA.²¹ b) Spatially selective functionalization of the microchannel by two different DNA fragments that form a part of enzymatic cascade reaction.²¹

1.5 Thesis objective

The objective of this project is to synthesize a Ni salicylaldehyde complex modified with an oxidatively stable alkene anchoring group, maleimide, and use it for covalent anchoring on metal oxide nanoparticle surfaces by photoclick chemistry. The initial phase of this project involved the synthesis and characterization of the maleimide functionalized Ni salicylaldehyde complex and UV light mediated anchoring on TiO₂ and SiO₂ nanoparticles.²³ The anchored hybrid materials were fully characterized by various spectroscopic techniques including Fourier transformed infrared spectroscopy (FTIR), ultraviolet visible diffuse reflectance spectroscopy (UV-DRS), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The synthetic technique was extended to other nanoparticle systems like cerium oxide (CeO₂) and tungsten oxide (WO₃). The single-site hybrid catalyst was then utilized in epoxidation of alkenes, as there have not been any previous report of the involvement

of alkene-anchored heterogeneous catalysts in oxidative catalysis. The hybrid catalyst was found to be very robust and active even after ten cycles of epoxidation. The XAS and FTIR spectroscopy data suggested that the Ni centre returns back to Ni²⁺ oxidation state and the ligand system remains intact, respectively, after the reaction.

Subsequently, we utilized this anchoring technique for photopatterning. The spatial and temporal control enabled us to selectively deposit a luminescent version of the Ni salicylaldimine complex at specific positions on the TiO₂ and SiO₂ nanoparticle coated surfaces. This work will be discussed in detail in the following chapter.

References

1. Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougél, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A., Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities. *Chemical Reviews* **2016**, *116* (2), 323-421.
2. Weng, Z.; Jiang, J.; Wu, Y.; Wu, Z.; Guo, X.; Materna, K. L.; Liu, W.; Batista, V. S.; Brudvig, G. W.; Wang, H., Electrochemical CO₂ Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution. *Journal of the American Chemical Society* **2016**, *138* (26), 8076-8079.
3. Dey, A.; Sasmal, S.; Seth, K.; Lahiri, G. K.; Maiti, D., Nickel-Catalyzed Deamidative Step-Down Reduction of Amides to Aromatic Hydrocarbons. *ACS Catalysis* **2017**, *7* (1), 433-437.
4. Meunier, B.; Guilmet, E.; De Carvalho, M. E.; Poilblanc, R., Sodium hypochlorite: a convenient oxygen source for olefin epoxidation catalyzed by (porphyrinato)manganese complexes. *Journal of the American Chemical Society* **1984**, *106* (22), 6668-6676.
5. Yoon, H.; Burrows, C. J., Catalysis of alkene oxidation by nickel salen complexes using sodium hypochlorite under phase-transfer conditions. *Journal of the American Chemical Society* **1988**, *110* (12), 4087-4089.
6. Miao, C.; Wang, B.; Wang, Y.; Xia, C.; Lee, Y.-M.; Nam, W.; Sun, W., Proton-Promoted and Anion-Enhanced Epoxidation of Olefins by Hydrogen Peroxide in the Presence of Nonheme Manganese Catalysts. *Journal of the American Chemical Society* **2016**, *138* (3), 936-943.
7. Zhao, W.; Huang, Y.; Liu, Y.; Cao, L.; Zhang, F.; Guo, Y.; Zhang, B., A Heterogeneous Photocatalytic Hydrogen Evolution Dyad: [(tpy. Chemistry – A European Journal **2016**, *22* (42), 15049-15057.

8. Kuehnel, M. F.; Orchard, K. L.; Dalle, K. E.; Reisner, E., Selective Photocatalytic CO₂ Reduction in Water through Anchoring of a Molecular Ni Catalyst on CdS Nanocrystals. *Journal of the American Chemical Society* **2017**, *139* (21), 7217-7223.
9. Hanna, C. M.; Sanborn, C. D.; Ardo, S.; Yang, J. Y., Interfacial Electron Transfer of Ferrocene Immobilized onto Indium Tin Oxide through Covalent and Noncovalent Interactions. *ACS Applied Materials & Interfaces* **2018**, *10* (15), 13211-13217.
10. Pujari, S. P.; Scheres, L.; Marcelis, A. T. M.; Zuilhof, H., Covalent Surface Modification of Oxide Surfaces. *Angewandte Chemie International Edition* **2014**, *53* (25), 6322-6356.
11. Herzer, N.; Hoeppener, S.; Schubert, U. S., Fabrication of patterned silane based self-assembled monolayers by photolithography and surface reactions on silicon-oxide substrates. *Chemical Communications* **2010**, *46* (31), 5634-5652.
12. O'Regan, B.; Grätzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, *353*, 737.
13. Bae, E.; Choi, W., Effect of the Anchoring Group (Carboxylate vs Phosphonate) in Ru-Complex-Sensitized TiO₂ on Hydrogen Production under Visible Light. *The Journal of Physical Chemistry B* **2006**, *110* (30), 14792-14799.
14. Paoprasert, P.; Kandala, S.; Sweat, D. P.; Ruther, R.; Gopalan, P., Versatile grafting chemistry for creation of stable molecular layers on oxides. *Journal of Materials Chemistry* **2012**, *22* (3), 1046-1053.
15. Arafat, A.; Schroën, K.; de Smet, L. C. P. M.; Sudhölter, E. J. R.; Zuilhof, H., Tailor-Made Functionalization of Silicon Nitride Surfaces. *Journal of the American Chemical Society* **2004**, *126* (28), 8600-8601.
16. Franking, R. A.; Landis, E. C.; Hamers, R. J., Highly Stable Molecular Layers on Nanocrystalline Anatase TiO₂ through Photochemical Grafting. *Langmuir* **2009**, *25* (18), 10676-10684.
17. Li, Y.; Zuilhof, H., Photochemical Grafting and Patterning of Organic Monolayers on Indium Tin Oxide Substrates. *Langmuir* **2012**, *28* (12), 5350-5359.
18. Shah, S.; Benson, M. C.; Bishop, L. M.; Huhn, A. M.; Ruther, R. E.; Yeager, J. C.; Tan, Y.; Louis, K. M.; Hamers, R. J., Chemically assembled heterojunctions of SnO₂ nanorods with TiO₂ nanoparticles via "click" chemistry. *Journal of Materials Chemistry* **2012**, *22* (23), 11561-11567.
19. Wadsworth, B. L.; Beiler, A. M.; Khusnutdinova, D.; Jacob, S. I.; Moore, G. F., Electrocatalytic and Optical Properties of Cobaloxime Catalysts Immobilized at a Surface-Grafted Polymer Interface. *ACS Catalysis* **2016**, *6* (12), 8048-8057.
20. Khusnutdinova, D.; Beiler, A. M.; Wadsworth, B. L.; Jacob, S. I.; Moore, G. F., Metalloporphyrin-modified semiconductors for solar fuel production. *Chemical Science* **2017**, *8* (1), 253-259.
21. Vong, T.; ter Maat, J.; van Beek, T. A.; van Lagen, B.; Giesbers, M.; van Hest, J. C. M.; Zuilhof, H., Site-Specific Immobilization of DNA in Glass Microchannels via Photolithography. *Langmuir* **2009**, *25* (24), 13952-13958.
22. Vong, T.; Schoffelen, S.; van Dongen, S. F. M.; van Beek, T. A.; Zuilhof, H.; van Hest, J. C. M., A DNA-based strategy for dynamic positional enzyme immobilization inside fused silica microchannels. *Chemical Science* **2011**, *2* (7), 1278-1285.
23. Ghosh, D.; Febriansyah, B.; Gupta, D.; Ng, L. K.-S.; Xi, S.; Du, Y.; Baikie, T.; Dong, Z.; Soo, H. S., Hybrid Nanomaterials with Single-Site Catalysts by Spatially Controllable Immobilization of Nickel Complexes via Photoclick Chemistry for Alkene Epoxidation. *ACS Nano* **2018**, *12* (6), 5903-5912.

Chapter 2

Immobilization of Nickel Complexes via Photoclick Chemistry for Alkene

Epoxidation

2.1 Introduction

Catalyst deactivation is a perennial problem for homogeneous inorganic catalysts supported by organic ligands. Catalyst oligomerization, ligand oxidation, and demetallation are some of the commonly reported pathways for the degradation of catalytic activity.^{1,2} Heterogenization of molecular compounds on high surface area nanoparticulate solid supports to form isolated single-site catalysts can potentially overcome many of these inactivation pathways.³ Moreover, highly reactive intermediates such as early transition metal hydrides,⁴ iron-based water oxidation catalysts,⁵ and molecular-imprinted cavities with ruthenium catalysts,⁶ which would otherwise be unstable in solution, have been characterized and utilized through catalyst immobilization on bulk metal oxide surfaces. The anchoring of molecular compounds to produce isolated single-site hybrid heterogeneous nanocatalysts⁷ is thus still a nascent field that can address a number of catalyst deactivation problems and also offer alternative reactivity and longevity in eco-friendly solvents for highly selective, nominally homogeneous catalysts.

Several approaches have been presented for the immobilization of molecules on surfaces, especially metal oxides. Some of the most popular strategies include physisorption by electrostatic attraction or non-covalent π - π stacking in applications such as proton reduction by hydrogels⁸ or CO₂ reduction with graphitic carbon

electrodes,⁹ respectively. However, physisorption is typically reversible, especially under aqueous and/or aerobic conditions. Chemisorption can be more robust and often involves hydrolysis of silyl esters or alkynes,¹⁰⁻¹² dealkylation of metal alkyls and hydrides⁴ as well as deposition of carboxylates, phosphonates,¹³ hydroxamates, and amines on metal oxides.^{11,14,15} Nonetheless, the functional groups required are often incompatible with metallation of the ligand and there is little spatial and temporal control, since the same functional groups such as phosphonates and carboxylates are also excellent donors to Lewis acidic catalytic centers. Consequently, protection-deprotection protocols will be necessary to prevent the anchoring groups from binding and interfering with the metal catalytic activity.

Photochemical grafting of molecules by UV radiation has emerged as a strategy for the orthogonal deposition of small molecules on surfaces such as silicon, diamond, and numerous metal oxides.¹⁶⁻¹⁹ Especially notable is the work by Hamers and co-workers, where *terminal* alkenes have been grafted on hydrogen-terminated metal oxides and diamond, and employed in applications such as nanomaterial self-assembly, molecular electronics, and chemical sensing.¹⁹⁻²¹ This strategy is attractive in having a good surface substrate scope, and is often orthogonal to the catalytic and metallation reactivity since alkenes are relatively innocuous functional groups, although terminal alkenes can be vulnerable under oxidative conditions. Also, spatial and temporal control is possible with established masking approaches. To the best of our knowledge, however, even though there has been some precedence for reductive chemistry,²² there has not been any report of photochemical covalent immobilization of molecular oxidation catalysts on metal oxide nanoparticle surfaces and their applications in catalysis.

Recently, the electron-deficient maleimide group with an internal instead of a terminal alkene has been shown to be a dipolarophile that reacts rapidly with tetrazoles in a “photoclick” modification of DNA strands.²³ The maleimide group is more oxidatively robust than terminal alkenes, and can be installed at the periphery of ligands with a reasonably small number of synthetic steps. Furthermore, metal oxide semiconductor nanocrystals readily absorb UV or visible radiation, leading to effective charge extraction from the semiconductor surfaces.

Herein, we describe an exceptionally mild protocol to use UV radiation to immobilize molecular complexes on the surface of metal oxide nanoparticles through a maleimide group. The maleimide is saturated by addition of surface hydroxyl groups to the alkene to form the hydrolytically more robust succinimide group. We have further demonstrated that the functional molecular nickel (Ni) catalysts anchored on the nanoparticles can be used as heterogeneous oxidation catalysts for the epoxidation of styrene and other alkenes, with comparable reactivity *vis a vis* their homogeneous congeners. Moreover, we show that the operational stability of the catalysts increases since we are able to recycle the heterogeneous nanomaterials more effectively, and more eco-friendly non-halogenated solvents can be used. Apart from the deposition of Ni epoxidation catalysts, the photoclick methodology has been successfully applied to attach a luminescent variant of the Ni catalyst on the metal oxide nanoparticles. Our work thus illustrates a proof of concept that this orthogonal, facile, photoclick protocol can create functional nanomaterials with improved single-site catalytic activity and lifetime, using modular, independently optimized components. In addition, we can realize spatial and temporal attachment of catalysts, luminophores, and potentially other functional molecules in specifically desired amounts on nanomaterials.

2.2 Photoclick anchoring

Salicylaldehyde ligands are known for their relative ease of synthesis and ability to stabilize multiple transition metal oxidation states.²⁴ In particular, Ni salicylaldehyde complexes have been reported to homogeneously catalyze reactions such as the asymmetric aldol reaction of β -keto esters,²⁵ tetralin oxidation,²⁶ Michael addition reactions,²⁷ and epoxidation of alkenes.²⁸⁻³⁰ Some Ni alkene oxidation catalysts had been encapsulated in zeolites previously, but there was no structural characterization, the epoxide selectivity was low, and there was little evidence that the catalyst could be recycled.³¹ Here, we have prepared a Ni^{II} salicylaldehyde complex, **Ni-1** (Figure 2.1a) *via* a templated condensation of 5-chloro-2,3-diamino pyridine, a maleimide-substituted salicylaldehyde, and Ni^{II} acetate (Scheme 2.1, Experimental Section). A variant **Ni-3** was also prepared as a luminescent reporter. Another Ni^{II} congener, **Ni-2** (Figure 2.1b), without the maleimide anchoring group was synthesized in a similar fashion for comparison in control experiments.

Figure 2.1. a) Chemical structures of **Ni-1** bearing the maleimide anchoring group and b) **Ni-2**, without the maleimide group. c) Reaction scheme of the anchoring experiment. Covalent anchoring *via* the maleimide group is shown.

Titanium(IV) oxide (TiO₂), silica (SiO₂), cerium oxide (CeO₂), and tungsten oxide (WO₃) nanoparticles were chosen as the hydroxy-terminated solid supports due to their high surface area, ease of synthesis, oxidative stability, and relative abundance. Furthermore, nanomaterials offer the versatility of photocatalysis in the future since charge extraction is expected to be more expedient. Each of the photochemical

anchoring reactions was carried out using a 254 nm (125 W) UV lamp in a sealed quartz Schlenk tube under an argon atmosphere. Briefly, **Ni-1** was added into a dispersion of TiO₂ nanoparticles in anhydrous dichloromethane (DCM) under argon and the mixture was stirred vigorously for 15 minutes before the solvent was removed under reduced pressure. The flask was then filled with argon and subjected to UV irradiation for 12 hours under stirring (Figure 2.1c). Likewise, **Ni-2** was also irradiated with TiO₂ nanoparticles under the same conditions. Upon UV irradiation, the hydroxyl groups on the nanoparticle surfaces form covalent linkages by reacting with the C=C double bonds of the maleimide groups to convert into alkoxy succinimides. Both product mixtures were then washed several times with DCM and characterized by UV-visible diffuse reflectance spectroscopy (DRS).

2.3 FT-IR and UV-DRS Characterization of hybrid nanomaterials

The DRS spectrum of the reaction product between **Ni-1** and TiO₂ (**Ni-1@TiO₂**) exhibits an absorption maximum at 515 nm and a shoulder at 370 nm (black, Figure 2.2a), which corresponds to the d-d transitions and ligand-to-metal charge transfer, respectively, in **Ni-1** (red, Figure 2.2a).^{32,33} On the other hand, the sample from the reaction between **Ni-2** and TiO₂ (**Ni-2+TiO₂**) shows almost no visible light absorption (navy blue, Figure 2.2a), indicating that **Ni-1** is not merely physisorbed on the TiO₂ surface and also the critical role of the maleimide group for the covalent anchoring. Similar spectral signatures were observed in the DRS spectra when TiO₂ nanoparticles were replaced by SiO₂ nanoparticles (Figure 2.2c), commercially available CeO₂ nanoparticles (Figure 2.2e), and WO₃ nanoparticles (Figure 2.2g) under similar reaction conditions. This highlights the generality and effectiveness of our approach on insulating, semiconducting, and visible light absorbing oxide materials. The DRS spectrum of the hybrid composite between **Ni-1** and CeO₂ nanoparticles (**Ni-1@CeO₂**)

exhibits a broad absorption shoulder at 515 nm, corresponding to the same Ni centered d-d transition (sky blue, Figure 2.2e), and likewise for the molecular-nanoparticle hybrid between **Ni-1** and WO_3 (**Ni-1@WO₃**, light green, Figure 2.2g).

Figure 2.2. a) DRS spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), **Ni-2** (grey), and **Ni-2+TiO₂** (navy blue). b) The FT-IR spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), and **Ni-1+TiO₂** (royal blue) in absorbance mode. c) DRS spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), **Ni-2** (grey), and **Ni-2+SiO₂** (dark cyan). d) The FT-IR spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), and **Ni-1+SiO₂** (light cyan) in absorbance mode. e) DRS spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), **Ni-2+CeO₂** (brick red), and CeO₂ nanoparticles (violet). f) The FT-IR spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), CeO₂ nanoparticles (violet), and **Ni-1+CeO₂** (olive green) in absorbance mode. g) DRS spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), **Ni-2+WO₃** (dark yellow), and WO₃ nanoparticles (beige). h) The FT-IR spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), WO₃ nanoparticles (beige), and **Ni-1+WO₃** (light grey) in absorbance mode. For **Ni-1** and all the **Ni-1@MO_x** samples (MO_x = TiO₂, SiO₂, CeO₂, and WO₃), the absorbance band at 515 nm corresponds to the Ni centered d-d transition.

To confirm the UV stability of **Ni-1** and verify that the maleimide group was involved in covalent bond formation with the surface hydroxyl groups during the photoclick reaction, we conducted FT-IR spectroscopic measurements. The FT-IR spectra of **Ni-1** in the solid state before and after 254 nm UV irradiation remained essentially identical (Figure 2.12, Experimental Section), suggesting that the Ni^{II} complex was stable under our photochemical deposition conditions. The FT-IR spectra in the range 1400–1800 cm⁻¹ reveal that a vibrational stretching band at 1608 cm⁻¹ for **Ni-1@TiO₂** (black, Figure 2.2b) has diminished, whereas for a control reaction in which **Ni-1** and TiO₂ have been physically mixed without any UV irradiation (**Ni-1**+TiO₂), this stretching band remains intact (royal blue, Figure 2.2b). We propose that this vibrational band at 1608 cm⁻¹ corresponds to the C=C stretch of the maleimide group, which is lost upon covalent anchoring on the nanoparticle surface.³⁴ We observed similar spectral changes for **Ni-1@SiO₂** (orange, Figure 2d), **Ni-1@CeO₂** (sky blue, Figure 2.2f), and **Ni-1@WO₃** (light green, Figure 2.2h) in comparison to the controls (Figure 2.13, Experimental Section), fully consistent with our model that the **Ni-1** had become covalently attached by conversion of the maleimide group to a succinimide after reacting with the surface hydroxyls.

2.4 XPS and XAS Characterization

To further ascertain the coordination environment and oxidation state of the Ni center upon anchoring to the nanoparticle surface, we conducted X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) measurements on **Ni-1@TiO₂**, **Ni-1@SiO₂**, and **Ni-1**. The Ni K-edge X-ray absorption near-edge structure (XANES) spectra of **Ni-1** (red, dashed line, Figure 2.3a), **Ni-1@TiO₂** (black, dash-dotted line, Figure 2.3a), and **Ni-1@SiO₂** (orange, dotted line, Figure 2.3a) show very similar profiles. This suggested that the oxidation state and coordination environment

of Ni remained unchanged after covalent anchoring to the nanoparticle surface. In addition, no pre-edge was observed in all the XANES spectra (Figure 2.3a), which concurred with the symmetrical square planar geometry around the Ni coordination sphere, as observed in the single crystal X-ray diffraction (XRD) structure (Figure A.18, appendix). The Fourier transform of the extended X-ray absorption fine structure (EXAFS) data in *R*-space of **Ni-1** (red, dashed line), **Ni-1@TiO₂** (black, dash-dotted line), and **Ni-1@SiO₂** (orange, dotted line, Figure 2.3b and Figure 2.15, Experimental Section) show similar, almost overlapping profiles, indicating that the Ni-O and Ni-N bond parameters in the samples are likely to be very close to those in the crystal structure of **Ni-1**. The XAS data thus confirms that no significant change in the oxidation state and coordination environment around Ni occurred upon anchoring.

Figure 2.3. a) Ni *K*-edge XANES for the region 8300-8400 eV of **Ni-1** (red, dashed), **Ni-1@TiO₂** (black, dash dotted), **Ni-1@SiO₂** (orange, dotted), and **Ni-1@TiO₂** after catalysis (light brown, solid) showing almost identical spectral features and no pre-edge. b) Fourier transforms of the EXAFS in *R*-space (*k*-weight = 3 and *k* range = 2 - 10) of **Ni-1** (red, dashed), **Ni-1@TiO₂** (black, dash dotted), **Ni-1@SiO₂** (orange, dotted), and **Ni-1@TiO₂** after catalysis (brown, solid). The grey vertical dashed line is a guide for the eye and indicates that the average bond distances of the first coordination shell around Ni appear invariant in all the samples.

The XPS spectra of **Ni-1@TiO₂** (Figures 2.4a, 2.4b and 2.7) show the presence of Ni 2p, Cl 2p, and Ti 2p signals in the sample. Similarly, the XPS spectra of **Ni-1@SiO₂** (Figures 2.4d, 2.4e, and 2.8) show the presence of Ni 2p, Cl 2p, and Si 2p signals in

the sample. The Ni 2p binding energies of **Ni-1@TiO₂** (Figure 2.4b), **Ni-1@SiO₂** (Figure 2.4e), and **Ni-1** (Figure 2.9a, Experimental Section) were found to be similar (Figure 2.10, Experimental Section), confirming the presence of Ni^{II} on the nanoparticle surfaces. The Ni 2p_{3/2} signals for **Ni-1**, **Ni-1@TiO₂**, and **Ni-1@SiO₂** appear at 853.8 eV, 853.7 eV, and 853.8 eV, respectively. The slight differences in the binding energies are likely within experimental error, although there have been reports of interfacial interactions between nanoparticles and surface-attached Ni complexes.³⁵⁻³⁷ In aggregate, we are confident that the molecular Ni^{II} catalysts remain structurally intact and are covalently anchored on the different metal oxide supports.

Figure 2.4. a) XPS survey spectrum of **Ni-1@TiO₂** showing the binding energies corresponding to Ni 2p, Ti 2p, and Cl 2p. b) Ni 2p XPS data for **Ni-1@TiO₂** with the Ni 2p_{3/2} signal at 853.7 eV and Ni 2p_{1/2} signal at 870.9 eV. c) HRTEM image of **Ni-1@TiO₂**. d) XPS survey spectrum of **Ni-1@SiO₂** showing the binding energies corresponding to Ni 2p, Si 2p, and Cl 2p. e) Ni 2p XPS data for **Ni-1@SiO₂** with Ni 2p_{3/2} signal at 853.8 eV and the Ni 2p_{1/2} signal at 871.1 eV. f) HRTEM image of **Ni-1@SiO₂**.

2.5 Heterogeneous alkene epoxidation

The catalysts were then employed in catalytic alkene epoxidation reactions to evaluate their activities and stabilities. The conditions were first optimized with **Ni-1** as a homogeneous catalyst. Different oxidants including hydrogen peroxide (H₂O₂), (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO), sodium periodate, sodium hypochlorite (NaOCl), and oxygen were screened (Table 2.3). Moreover, since **Ni-1** is poorly soluble in ethyl acetate, methanol, and acetonitrile, they are unsuitable solvents

for homogeneous catalysis. The combination of **Ni-1** (5 mol%), NaOCl (8 equivalents) as the oxidant, and DCM as the solvent gave the highest (>99%) conversion of styrene (Table 2.4). This performance is comparable with or better than previously reported alkene epoxidation catalysis.^{28, 31} We also found that less than 8 equivalents of NaOCl relative to the substrate resulted in incomplete conversions of the alkenes. Using these same optimized conditions, a number of internal and terminal alkene substrates were successfully oxidized at room temperature using **Ni-1** (Table 2.4). The homogeneous reactions showed very high conversions and the selectivity for the epoxides were found to vary from moderate for cyclooctene oxide (54%) to good (78%) for 4-chlorostyrene oxide.

Ni-1@TiO₂, **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** were all then applied as heterogeneous catalysts for alkene oxidation under similar reaction conditions, although notably, we were no longer limited by the solubility constraints of **Ni-1** in the solvents mentioned above. The conversions of the substrates in the heterogeneous reactions and selectivities were found to be similar to the homogeneous version, with the highest epoxide selectivity of 68% for 4-chlorostyrene oxide (Table 2.1, Entry 3). **Ni-1@TiO₂** performed better than **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** (Table 2.1, Entries 8, 9, and 10, respectively) both in terms of substrate conversion and selectivity for the epoxide products. Notably, all of the heterogeneous catalysts displayed higher substrate conversion as well as epoxide selectivity compared to the best previously reported metal organic framework (MOF) heterogeneous catalysts embedded with Ni salicylaldehyde complexes.³⁸ This could be due to better accessibility of the Ni catalytic centers, which are on the surface of the nanoparticles (Figures 2.4c, 2.4f, 2.14, and 2.16) unlike the MOF-based catalysts that have Ni centers embedded deep inside the porous framework.

Table 2.1. Conversion, selectivity, and substrate scope of alkene epoxidation by heterogeneous catalysts.

Entry	Substrate	% conversion of substrate ^a	Time (h)	Epoxide product	% GC yields of epoxide product ^{a,h}	TOF (h ⁻¹)
1 ^b		92	4		53	2.64
2 ^b		96	2.5		63	5.04
3 ^b		95	5.5		68	2.47
4 ^b		93	8		54	1.35
5 ^b		96	3.5		62	3.54
6 ^b		84	5		42	8.40
7 ^c		85	4		45	2.25
8 ^c		88	5.5		64	2.32
9 ^d		90	5.5		61	2.21
10 ^e		94	5		66	2.64
11 ^f		<1	6		-	-
12 ^{b,g}		<1	6		-	-

^a Compound *n*-decane was used as the GC internal standard. ^b **Ni-1@TiO₂** was used as the catalyst. ^c **Ni-1@SiO₂** was used as the catalyst. ^d **Ni-1@CeO₂** was used as the catalyst. ^e **Ni-1@WO₃** was used as the catalyst. ^f Control reaction with TiO₂ P25 nanoparticles as catalyst. ^g Control reaction without NaOCl. ^h Other products obtained were aldehydes and 1,2-diols.

To use more environmentally benign solvents,³⁹ we performed the heterogeneous catalysis using NaOCl as the oxidant in ethyl acetate, 2-methyltetrahydrofuran, dimethyl carbonate, and water (Table 2.5). In ethyl acetate, **Ni-1@TiO₂** showed slightly higher conversion of alkene and almost identical selectivity towards the epoxide product compared to the reaction in DCM. The reaction in water was remarkably fast likely due to the hydrophobic effect (Figure 2.19, Experimental Section), since the substrates and **Ni-1@TiO₂** are both hydrophobic. However, high selectivity towards 1-(4-chlorophenyl) ethane-1,2-diol as the product (GC yield 79%) was observed instead with 4-chlorostyrene as the substrate in water.

2.6 Reusability and stability study

After the reaction, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. Remarkably, the reused catalyst showed essentially quantitative conversions of the substrate for the first few recycling experiments, although the conversion and the epoxide selectivity decreased over extended reuse (Figure 2.5a). Despite the fact that the heterogeneous catalyst sample could not be completely recovered after every experiment (some remained in the reaction flasks and the centrifuge tubes) and some sample was also lost for FT-IR spectroscopic analysis, **Ni-1@TiO₂** could still be used for at least 10 consecutive cycles with 4-chlorostyrene as the substrate. In contrast, the physical mixtures of **Ni-1** and TiO₂ or SiO₂ do not survive after the first catalytic cycle and neither the supernatant (containing the dissolved Ni by-products) nor the recovered nanoparticles showed any catalytic activity in the second run (Figure 2.20 and Table 2.6, Experimental Section). The decrease in the catalytic activity of **Ni-1@TiO₂** could be due to inactivation of some of the Ni catalysts as insoluble Ni oxides on the nanoparticle surface. We observed that the Ni concentrations in the reaction aliquots

were below the detection limit of our inductively coupled plasma optical emission spectroscopy (ICP-OES) experiments, indicating that little Ni leached out during the catalytic process. To demonstrate the robustness and scalability of **Ni-1@TiO₂**, we performed four cycles of 4-chlorostyrene oxidations (0.277 g, 2.00 mmol in each cycle) since the percentage conversion remained fairly high, and isolated 0.655 g of 4-chlorostyrene oxide (53%) by reusing the same catalyst.

Figure 2.5. a) Percentage conversion of 4-chlorostyrene (black) and selectivity for epoxide (red) obtained over 10 cycles by reusing the **Ni-1@TiO₂** catalyst. b) FT-IR spectra of **Ni-1@TiO₂** before (black), and after four (light brown), eight (lilac), and 10 cycles of catalysis (light green).

Based on previously presented mechanisms for alkene epoxidations by Ni^{II} complexes, we expected the catalyst to access higher valent nickel intermediates that could potentially be unstable.²⁸ Thus, we conducted XAS experiments on the used **Ni-1@TiO₂** sample to investigate the oxidation state and coordination environment of the Ni center after catalysis. The Ni K-edge XANES spectrum of **Ni-1@TiO₂** after four cycles of catalysis (light brown, solid line, Figure 2.3a) was essentially identical with that of pristine **Ni-1@TiO₂** (black, dash-dotted line, Figure 2.3a), and **Ni-1** (red, dashed line, Figure 2.3b), indicating that there was no change in the Ni coordination environment and oxidation state of **Ni-1@TiO₂** even after four catalytic cycles. Furthermore, it is evident from the Fourier transform of the EXAFS in *R*-space (light brown, solid line, Figure 2.3b and Figure 2.15b, Experimental Section) that the average Ni-O and Ni-N bond distances, and hence the overall coordination environment, remained unchanged between the **Ni-1@TiO₂** after catalysis compared to **Ni-1** and pristine **Ni-1@TiO₂**. Likewise, the FT-IR spectroscopic fingerprint region of the recycled **Ni-1@TiO₂** samples (Figure 2.5b) displayed similar, but attenuating vibrational bands as the sample before catalysis. Evidently, some of the **Ni-1@TiO₂** survived up to 10 cycles under the harsh oxidative conditions for our alkene epoxidation reaction.

2.7 Photopatterning

This selective photoclick reaction of the maleimide anchoring group could be utilized to spatially and temporally attach luminescent reporters on the metal oxide nanoparticles, which is an advantage over indiscriminate grafting functionalities like carboxylates and phosphonates. We have been able to successfully graft a different luminescent nickel salicylaldehyde complex (**Ni-3**, Figure 2.6a), bearing the maleimide anchoring group, on SiO₂ and TiO₂ coated fluorine-doped tin oxide (FTO) films (**Ni-**

3@SiO₂-FTO and **Ni-3@TiO₂-FTO**, respectively) using 254 nm UV radiation. The designs (Figures 2.6b and 2.6c) were achieved by using a simple paper mask, which allows the photoclick reaction to occur only at specifically exposed areas of the coated FTO films. The DRS spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 2.6d) shows the absorbance maxima corresponding to **Ni-3**, indicating the presence of the complex after the photoclick reaction. The successful grafting was again confirmed by the FT-IR spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 2.6e), which show the loss of the 1605 cm⁻¹ peak, corresponding to the maleimide C=C stretch present in the **Ni-3** (wine red) spectrum.

Figure 2.6. a) Chemical structure of **Ni-3** bearing the maleimide anchoring group. Photograph of the spatially controlled photoclick deposition of **Ni-3** on b) SiO₂ and c) TiO₂ coated FTO plate. In each figure, the mask is shown on the top right. The dashed lines highlight the boundaries of the deposited patterns. A ruler has been provided to facilitate size comparison. d) DRS spectra, e) FT-IR spectra from 1400 cm⁻¹ to 1800 cm⁻¹ in absorbance mode, and f) photoluminescence spectra with 395 nm excitation of **Ni-3** (wine red), **Ni-1@SiO₂-FTO** (light magenta), and **Ni-1@TiO₂-FTO** (light violet).

The solid state photoluminescence (PL) spectra of the films exhibit the luminescent behavior of the parent **Ni-3** complex (Figure 2.6f). The PL spectrum of **Ni-3** shows an emission maximum at 530 nm when excited at 395 nm. A small blue-shift of 3 nm in the emission maximum was observed in each of the **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** samples. The **Ni-3** coated regions in the **Ni-3@SiO₂-FTO** sample were found to show PL when irradiated with a TLC lamp emitting 365 nm UV light (Figure 2.22, Experimental Section). However, the PL intensity for **Ni-3@TiO₂-FTO** was found to be attenuated compared to **Ni-3** and **Ni-3@SiO₂-FTO** (Figures 2.6f and 2.22, Experimental Section). This could be due to PL quenching after charge injection

into the semiconducting TiO_2 layer, in contrast to the insulating SiO_2 , a feature that will be further investigated for catalytic applications.

2.8 Conclusion

In conclusion, we have utilized maleimide as an oxidatively stable, photoactivated anchoring group to synthesize several hybrid single-site catalysts comprising covalently grafted Ni complexes on SiO_2 , TiO_2 , CeO_2 , and WO_3 nanoparticles. Characterization by DRS, FT-IR spectroscopy, XAS, and XPS verified that the Ni salicylaldimine complexes remained intact and were anchored covalently. Remarkably, the heterogeneous catalysts displayed conversions and selectivities for alkene epoxidation similar to their corresponding homogeneous molecular congener, but were found to be more robust, recyclable, and stable up to 10 catalytic cycles under the harsh oxidative reaction conditions in a wider range of more eco-friendly solvents. We have also been able to utilize the photoclick protocol of the maleimide anchoring group to precisely deposit the Ni complexes on specific regions. Our study thus forms the basis for future discoveries on using light to deposit functional molecular catalysts on inert or semiconducting scaffolds to create hybrid (photo)catalysts that can synergize the benefits of both homogeneous and heterogeneous catalysts. Moreover, we believe that this spatially and temporally controlled photoclick reaction to deposit functional molecules can be applied in other fields, including biosensing, renewable energy, and optoelectronic devices, for example.

2.9 EXPERIMENTAL SECTION

Synthesis of dendritic SiO₂ nanoparticles

Cetyltrimethylammonium chloride (CTAC) solution (25 wt%, 24 mL) and triethanolamine (TEOA, 0.16 mL, 0.18g, 1.21 mmol) were added in a 100 mL round bottom flask filled with de-ionized water (36 mL) and the mixture was stirred gently at 60 °C for 1 h. Subsequently, tetraethyl orthosilicate (4 mL, 18.0 mmol) in cyclohexane (16 mL) was carefully added to the surfactant solution in an oil bath at 60 °C, with a stirring at a rate of about 150 rpm. The reaction flask was then kept at 60 °C with stirring for 12 h to obtain the white powder product (0.53g, 49%). The product was collected by centrifugation and washed three times with ethanol. The product was extracted once with a 0.6 wt % ammonium nitrate in ethanol solution at 60 °C for 6 h, followed by calcination at 550 °C for 5 h at a ramping rate of 1 °C min⁻¹ to remove the surfactant completely.

Processing of TiO₂ P25 nanoparticles

Prior to use in the anchoring reaction, the commercially purchased TiO₂ P25 nanoparticles (Sigma-Aldrich) were treated with piranha solution to remove any surface organic impurities and hydroxylate the surface to facilitate anchoring. In a typical procedure, TiO₂ P25 nanoparticles (40 mg, 0.50 mmol) were soaked in freshly prepared piranha solution (conc. H₂SO₄: H₂O₂ = 3:1) for 2 h. Subsequently, it was washed thoroughly with de-ionized water and dried in a furnace at 300 °C for 3 h to remove traces of H₂SO₄. It was then dried at 120 °C for 5 h under vacuum to remove any remaining surface moisture.

Ni-1@TiO₂

A degassed, anhydrous DCM (5 mL) solution of Ni-1 (10 mg, 0.013 mmol) was added to an oven dried quartz glass Schlenk tube. Pre-processed TiO₂ P25 nanoparticles (21 mg, 0.26 mmol) was then added. The Schlenk tube was sonicated for 5 min before the solvent was removed under vacuum. The solid mixture was stirred under UV irradiation (254 nm, 125 watt) for 8 h. After the reaction, the nanoparticles were collected and washed several times by DCM to remove any excess and unbound **Ni-1** present.

Ni-1@SiO₂

Ni-1@SiO₂ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, dendritic SiO₂ nanoparticles (30 mg, 0.50 mmol) were used.

Ni-1@CeO₂

Ni-1@CeO₂ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, CeO₂ nanoparticles (43 mg, 0.25 mmol) were used.

Ni-1@WO₃

Ni-1@WO₃ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, WO₃ nanoparticles (58 mg, 0.25 mmol) were used.

General procedure for alkene epoxidation with Ni-1 homogeneous catalyst

To a solution of alkene (0.50 mmol) in 2.0 mL dichloromethane (DCM) was added **Ni-1** (18.7 mg, 0.025 mmol), *n*-decane (97.5 μ L, 0.500 mmol) and tetra-*n*-butylammonium bromide (8.0 mg, 0.025 mmol). Finally, 1.8 mL of 0.70 M sodium hypochlorite solution was added to the mixture and stirred vigorously at room temperature. After the reaction, 100 μ L of organic layer was withdrawn using a syringe,

diluted with DCM in a 10 mL volumetric flask, and subjected to gas chromatography mass spectrometry (GC-MS) measurements.

Alkene epoxidation using heterogeneous Ni-1@TiO₂ catalyst

To a solution of alkene (0.10 mmol) in 2 mL DCM, was added **Ni-1@TiO₂** (23.5 mg), *n*-decane (19.5 μ L, 0.100 mmol), tetra-*n*-butylammonium bromide (2.0 mg, 6.0 μ mol), and aqueous sodium hypochlorite (0.36 mL, 0.70 M). The mixture was stirred vigorously at room temperature. After the reaction was complete, the reaction mixture was carefully transferred to a centrifuge tube and the catalyst was recovered by centrifugation and washed with water, ethanol, and DCM. Finally, it was dried under vacuum before being re-used for subsequent cycles. To prepare the GC-MS sample, 500 μ L of the organic layer was withdrawn using a syringe and diluted with DCM in a 10 mL volumetric flask.

Alkene epoxidation using heterogeneous Ni-1@SiO₂ catalyst

The alkene epoxidation was conducted following the same procedure as for **Ni-1@TiO₂**, but **Ni-1@SiO₂** (25.5 mg) was used instead of **Ni-1@TiO₂**.

Gas chromatography (GC) analysis of alkene epoxidation

DCM was used as the solvent for GC analyses of the samples. The measurements were performed using a Thermo Fisher Scientific Trace GC Ultra DSQ-II GC-MS machine. Compound *n*-decane was used as the internal standard.

UV-visible diffuse reflectance spectroscopy (DRS) measurements

DRS was measured with a Shimadzu 3600 UV-vis-NIR spectrophotometer with BaSO₄ as an internal standard.

Fourier transform infrared (FT-IR) spectroscopy measurements

FT-IR spectroscopy measurements were carried out with a Bruker Vertex 80v FT-IR spectrometer. In a typical experiment, about 1.5 mg of the sample was mixed with about 30.0 mg of potassium bromide (KBr) to make a pellet. The pellets were made with a Specac Atlas manual hydraulic press 15T at 10 ton pressure. The FT-IR experiments were conducted in transmission mode with data collected from 400 to 4000 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) experiments

The XPS samples were prepared by coating the solid, powdered samples on SPI double-sided adhesive carbon tape. The XPS data obtained was processed using the CasaXPS software. The spectra were calibrated internally by setting the C 1s signal at 284.6 eV.

High-Resolution Transmission Electron Microscopy (HRTEM) imaging

The sample preparation involved sonication of an aliquot of the powder in analytical grade ethanol for 10 min. A single drop of the colloidal solution was deposited on a thin-film carbon coated copper TEM grid and dried in air. HRTEM images were taken using a JEOL JEM 2100 microscope operated at 200 kV.

X-ray absorption spectroscopy (XAS)

X-ray absorption fine structure (XAFS) characterization at the Ni K-edge was carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS).⁴⁰ All

XAS measurements were collected with a ring energy of 0.7 GeV and a ring current of ca. 200 mA. A Si(111) crystal monochromator was used and the data were collected in transmission mode at ambient temperatures. The X-ray energy was calibrated at the inflection point of the absorption edge of a nickel foil. Data analysis was carried out with the programs Athena and Artemis included in the Demeter package (version 0.9.25). Each of the powder samples was prepared as a pellet using a pelletizer of diameter 10 mm and mounted on the sample holder for the XAS measurement. ARTEMIS fittings were carried out with k -weight = 1,2,3; k range = 3 – 12.69, and R range = 1 – 3 Å.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements

The samples were measured using a Thermo Scientific iCAP 7000 series ICP-OES spectrometer. Standard solutions were prepared by dissolving appropriate amounts of Ni standards (Inorganic Ventures) in 3 % (v/v) nitric acid (HNO₃). All samples were prepared using 4.5 mL ICP grade HNO₃ (70 %, Inorganic Ventures) and diluted into a 100 mL volumetric flask using ultrapure water. For the catalyst loading experiment, **Ni-1@TiO₂** (23.5 mg) and **Ni-1@SiO₂** (25.5 mg) samples were treated with 4.5 mL ICP grade nitric acid in a 15 mL centrifuge tube for 1 h before adding 5 mL ultrapure water. The undissolved parts were removed by repeated centrifugation and washing with ultrapure water (5 mL X 5). All the dissolved parts were collected together in a 100 mL volumetric flask and filled up to the 100 mL mark using ultrapure water. For the catalyst leaching study, the heterogeneous reaction mixture was centrifuged to remove the solids and 0.5 mL of the aliquot was collected and treated with 4.5 mL HNO₃ for 1 h before diluting to 100 mL using ultrapure water.

The Ni content for **Ni-1@TiO₂** was found to be 0.212 mmol/g of the catalyst, whereas for **Ni-1@SiO₂** it was found to be 0.197 mmol/g of the catalyst. For the catalyst leaching experiment the Ni content of the sample was found to be below the detection limit of the equipment.

Static contact angle measurements

The samples were measured using a Theta Life tensiometer equipped with a Fireware digital camera. The measurements were done using sessile drop method with 4 μ L drop volume. The samples were prepared by spin-coating a dispersion of 10 mg of the sample in 0.5 mL of methanol at 300 rpm on glass substrates. To minimize errors, multiple samples were prepared and measurements were performed at different positions of the substrate.

Dynamic light scattering (DLS) measurements of homogeneous Ni-1 reaction mixture

To check the presence of any particles in the biphasic reaction mixture, the aqueous and DCM phases were separated and checked separately during catalysis. In the DCM phase, particles were not observed. However, in the aqueous phase, micron-sized large particles were detected, which could be aggregates of the insoluble **Ni-1** complex particles in the aqueous phase. Nonetheless, at the end of the reaction, both phases showed no particles again, suggesting that the **Ni-1** aggregates redissolve into DCM.

Spatially controlled deposition of Ni complexes on nanoparticle-coated FTO

The photoclick experiments were performed in a Schlenk flask made of quartz under an argon atmosphere using a 254 nm UV source (125 watt). The paper masks were attached to the SiO₂- and TiO₂-coated FTO plates with Teflon tape and placed in the Schlenk

flask. In each experiment, a DCM solution (10 mL) of **Ni-3** (23 mg, 0.026 mmol) was added. The solution was bubbled with argon for 10 min before being sealed and irradiated with UV for 10 h. After the irradiation, the plates were removed and rinsed with DCM to remove any unanchored complex, and then dried in air.

Compound 2-hydroxy-3-(2-methoxyethoxy)benzaldehyde (2)

Compound **2** was synthesized according to a method reported previously, with minor modifications.⁴¹ NaH (0.800 g of a 60% dispersion in oil, 20.2 mmol) was suspended in anhydrous dimethyl sulfoxide (DMSO, 12 mL) in an oven-dried Schlenk flask equipped with a dropping funnel. The suspension was placed in an ice-bath. A solution of 2,3-dihydroxybenzaldehyde (1.40 g, 10.2 mmol) in DMSO (10 mL) was added dropwise into the ice-cooled mixture under a flow of argon over the period of 1 hour. After the addition was complete, the dark orange solution was stirred at room temperature for 30 minutes before (2-methoxyethoxy)-*p*-toluenesulfonate (1.92 mL, 10.2 mmol) was added in one portion. The solution was stirred for another 5 hours. Water (100 mL) was added carefully to quench the reaction. The solution was extracted with CHCl₃ (3 × 30 mL) and the aqueous layer was acidified to pH 2 with 1 M HCl (20 mL) solution. The color of the solution changed to yellow from dark orange upon acidification. The aqueous layer was extracted with CHCl₃ (3 × 30 mL) and the organic phases were combined

together. The organic layer was rinsed with 1 M HCl (2×30 mL), dried over anhydrous Na_2SO_4 , and filtered. The solvent was removed *in vacuo* to give an orange colored oil. The residue was purified by silica gel column chromatography (hexane:ethyl acetate = 5:1) and 2-hydroxy-3-(2-methoxyethoxy)benzaldehyde (1.66 g, 83.0%) was isolated as a pale yellow solid.

^1H NMR (300 MHz, CDCl_3): δ 3.46 (s, 3 H, CH_3), 3.79 (t, $J = 6.0$ Hz, 2 H, CH_2), 4.22 (t, $J = 6.0$ Hz, 2 H, CH_2), 6.94 (t, $J = 9.0$ Hz, 1 H, ArH), 7.20 (m, 2 H, ArH), 9.94 (s, 1 H, CHO), 10.94 (s, 1 H, OH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 59.4, 69.4, 71.1, 119.7, 121.2, 121.4, 125.5, 147.6, 152.4, 196.4.

HR-MS calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4$, $[\text{M}+\text{H}]^+$ $m/z = 197.0814$, found 197.0806.

Compound 2-hydroxy-3-(2-methoxyethoxy)-5-nitrobenzaldehyde (3)

To a stirring solution of **2** (1.25 g, 5.48 mmol) in a 1:1 mixture of water and acetonitrile (20 mL) was added sodium nitrite (1.47 g, 21.4 mmol). The resulting mixture was cooled to 0 °C before 3.85 M sulfuric acid (16.6 mL) was added slowly into the reaction flask over a period of 30 minutes. Upon addition, the reaction flask was put in a chiller and the solution was stirred at 0 °C for 24 hours. After that, the mixture was diluted with CH_2Cl_2 (20 mL) to dissolve any precipitate that was formed during the course of reaction and the aqueous layer was subsequently neutralized with 1 M sodium bicarbonate (60

mL). The product was then extracted with CH₂Cl₂ (2 x 20 mL), before the combined organic layer was washed with saturated brine (2 x 30 mL), dried over sodium sulfate, and filtered. Removal of the solvent afforded **3** as a beige solid (1.2 g, 77 %).

¹H NMR (300MHz, CDCl₃): δ = 3.47 (s, 3 H, CH₃), 3.84 (t, *J* = 4.8 Hz, 2 H, CH₂), 4.30 (t, *J* = 4.8 Hz, 2 H, CH₂), 8.02 (d, *J* = 3.0 Hz, 1 H, ArH), 8.24 (d, *J* = 3.0 Hz, 1 H, ArH), 10.03 (s, 1 H, CHO), 11.54 (s, 1 H, OH).

¹³C{¹H} NMR (75 MHz, DMSO-*d*₆): δ = 58.2, 69.0, 70.0, 111.6, 116.1, 121.6, 139.4, 148.3, 156.4, 189.8.

HR-MS calcd for C₁₀H₁₂NO₆, [M+H]⁺ *m/z* = 242.0670, found 242.0665.

Elemental analyses for C₁₀H₁₁NO₆ calculated: C, 49.80; H, 4.60; N, 5.81; found C, 49.62; H, 4.87; N, 5.68.

Compound 2-(1,3-dioxolan-2-yl)-6-(2-methoxyethoxy)-4-nitrophenol (**4**)

In a 250 mL round bottom flask, **3** (1.00 g, 4.13 mmol) was dissolved in toluene (80 mL) and treated with *p*-TsOH (0.012 g, 0.053 mmol). The mixture was stirred with moderate heating until it became homogenous before ethylene glycol (0.48 mL, 8.3 mmol) was added. The resulting mixture was then brought to a vigorous reflux for 16 hours. Upon cooling

to room temperature, the mixture was subsequently washed with water (2 x 20 mL) and saturated brine (20 mL). The resulting solution was then dried over anhydrous sodium sulfate, filtered, and concentrated to dryness using rotary evaporation to give **4** as a milky yellow solid (1.04 g, 88.0 %).

^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ = ~3.32 (s, 3 H, CH_3), 3.72 (t, J = 4.8 Hz, 2 H, CH_2), 3.96

(m, 2 H, CH_2), 4.09 (m, 2 H, CH_2), 4.28 (t, J = 4.8 Hz, 2 H, CH_2), 6.02 (s, 1 H, CH), 7.82 (d, J = 3.0 Hz, 1 H, ArH), 7.88 (d, J = 3.0 Hz, 1 H, ArH), 10.5 (s, 1 H, OH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{DMSO-}d_6$): δ = 58.63, 65.33, 69.27, 70.54, 97.86, 108.76, 115.92, 125.03, 139.46, 147.26, 152.40.

HR-MS calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_7$, $[\text{M}+\text{H}]^+ m/z$ = 286.0927, found 286.0916. Elemental analyses for $\text{C}_{12}\text{H}_{15}\text{NO}_7$ calculated: C, 56.46; H, 6.71; N, 5.49; found C, 56.59; H, 6.54; N, 5.62.

Compound 4-amino-2-(1,3-dioxolan-2-yl)-6-(2-methoxyethoxy)phenol (5)

Palladium on carbon (Pd/C, 0.15 g, 10% by mass) was added to a solution of **4** (0.75 g, 2.6 mmol) in THF (15 mL). The mixture was stirred under an atmosphere of H_2 (15 bar) in a large Parr pressure reactor at room temperature for 16 hours. The catalyst

was then filtered off through a fine frit layered with a pad of Celite, before the resulting green solution, which gradually turned red, was directly used in the next step to avoid any polymerization complications.

^1H NMR (300 MHz, $\text{DMSO-}d_6$): $\delta = \sim 3.31$ (s, 3 H, CH_3), 3.66 (t, $J = 4.8$ Hz, 2 H, CH_2), 3.87 (m, 2 H, CH_2), 3.97-4.01 (m, 4 H), 4.53 (s, 2 H, NH_2), 5.89 (s, 1 H, CH), 6.24 (d, $J = 3.0$ Hz, 1 H, ArH), 6.26 (d, $J = 3.0$ Hz, 1 H, ArH), 7.51 (s, 1 H, OH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{DMSO-}d_6$): $\delta = 58.94, 65.17$ (2 C), 67.70, 68.75, 71.05, 102.33, 104.66, 125.16, 136.19, 141.10, 147.40.

HR-MS calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_5$, $[\text{M}+\text{H}]^+ m/z = 256.1185$, found 256.1187.

Compound **(Z)-4-((3-(1,3-dioxolan-2-yl)-4-hydroxy-5-(2-methoxyethoxy)phenyl)amino)-4-oxobut-2-enoic acid (6)**

To a stirring solution of **5** in THF from the previous step was added maleic anhydride (0.60 g, 6.2 mmol). The product precipitated within 10 minutes of stirring and the mixture was then stirred for an additional 30 to 50 minutes to ensure that **5** completely reacted. The resulting precipitate was finally collected by filtration and washed with THF to remove any impurities, which resulted in an intense yellow colored solid of **6** (0.68 g, 73% overall from two steps).

^1H NMR (300 MHz, DMSO- d_6): $\sim$ 3.32 (s, 3 H, CH_3), 3.70 (t, $J = 4.8$ Hz, 2 H, CH_2), 3.91-4.03 (m, 6 H), 5.97 (s, 1 H, CH), 6.30 (d, $J = 12$ Hz, 1 H, CHCH), 6.41 (d, $J = 12$ Hz, 1 H, CHCH), 7.22 (d, $J = 3.0$ Hz, 1 H, ArH), 7.38 (d, $J = 3$ Hz, 1 H, ArH), 8.60 (s, 1 H, C(O)NH), 10.3 (s, 1 H, OH), 13.4 (s, 1 H, C(O)OH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6): $\delta = 58.2, 64.6$ (2 C), 68.4, 70.2, 98.1, 106.6, 110.6, 124.4, 129.9, 131.2, 131.3, 142.0, 146.5, 162.7, 166.8. HR-MS calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_8$, $[\text{M}+\text{H}]^+ m/z = 354.1189$, found 354.1187.

Elemental analyses for $\text{C}_{16}\text{H}_{19}\text{NO}_8$ calculated: C, 54.39; H, 5.42; N, 3.96; found C, 54.68; H, 5.23; N, 3.88.

Compound **5-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-2-hydroxy-3-(2-methoxyethoxy)-benzaldehyde (7)**

In a 50 mL round bottom flask, **6** (1.00 g, 2.84 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC.HCl) (0.71 g, 3.7 mmol) were dissolved in DMF (10 mL), after which the reaction mixture was stirred at 80 °C for 18 hours. Subsequently, the solvent was removed under reduced pressure using Schlenk line techniques and the resulting oil was then diluted with CH_2Cl_2 (20 mL). The mixture was subsequently washed with water (2 x 15 mL) and brine (15 mL), before it was dried

over sodium sulfate, filtered, and concentrated *in vacuo* to obtain a bright yellow solid. This was dissolved in acetone (20 mL) before conc. HCl was added (4.0 μ L). The mixture was subsequently stirred at room temperature for 2 hours to ensure that all starting material had reacted, before it was neutralized with 1 M sodium bicarbonate (70 μ L). Following that, the solvent was removed under vacuum and the resulting solid was diluted with CH₂Cl₂ (20 mL). The solution was then rinsed with water (2 x 10 mL) and saturated brine (10 mL), after which it was dried over sodium sulfate and filtered. Solvent removal using rotary evaporation gave **7** as yellow solid (0.70 g, 85 %).

¹H NMR (300 MHz, DMSO-*d*₆): δ = ~3.31 (s, 3 H, CH₃), 3.70 (t, *J* = 4.8 Hz, 2 H, CH₂), 4.15 (t, *J* = 4.8 Hz, 2 H, CH₂), 7.17 (s, 2 H, CHCH), 7.20 (d, *J* = 3.0 Hz, 1 H, ArH), 7.28 (d, *J* = 3.0 Hz, 1 H, ArH), 10.3 (s, 1 H, CHO), 10.4 (s, 1 H, OH).

¹³C{¹H} NMR (75 MHz, DMSO-*d*₆): δ = 58.2, 68.7, 70.0, 118.0, 118.6, 122.3, 122.9, 134.6, 147.8, 150.6, 170.0 (2 C), 190.9 (2 C).

HR-MS calcd for C₁₄H₁₄NO₆, [M+H]⁺ *m/z* = 292.0821, found 292.0809. Elemental analyses for C₁₄H₁₃NO₆ calculated: C, 57.73; H, 4.50; N, 4.81; found C, 57.37; H, 4.29; N, 4.52.

Scheme 2.1. Synthetic route to **Ni-1**. **Ni-1**

To a solution of **7** (0.300 g, 1.03 mmol) and 2,3-diamino-5-chloropyridine (0.0750 g, 0.515 mmol) in CH_2Cl_2 (10 mL) was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.141 g, 0.567 mmol). The mixture was then brought to reflux while stirring for 16 hours under a N_2 atmosphere. Upon cooling to room temperature, the solvent was removed under reduced pressure, after which toluene was added into the reaction flask. The resulting suspension was then subjected to thorough sonication and agitation before filtration to collect the precipitate. The crude solid obtained was finally washed with toluene followed by ether and dried under vacuum to afford **Ni-1** as a dark red powder (0.33 g, 85%).

^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ = ~3.38 (s, 6 H), 3.69 (m, 4 H), 3.97 (m, 4 H), 6.80 (d, J = 7.0 Hz, 2 H), 7.05 (s, 1 H), 7.13(m, 7 H), 8.39 (s, 2 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6): δ = 58.14 (2 C), 67.61, 67.75, 70.02 (2 C), 116.08, 116.43, 119.37, 119.85, 123.56 (2 C), 124.65 (2 C), 125.87, 130.92, 134.77 (4 C), 145.88 (2 C), 149.86, 156.25, 157.05 (2 C), 157.76 (4 C), 158.92 (2 C), 170.36.

$\nu_{\text{max}}/\text{cm}^{-1}$ = 448, 695, 825, 948, 1022, 1151, 1247, 1368, 1444, 1541, 1609, 1708, 2821, 2880, 2931, 2989.

HR-MS calcd for $\text{C}_{33}\text{H}_{27}\text{ClN}_5\text{NiO}_{10}$, $[\text{M}+\text{H}]^+ m/z$ = 746.0800, found 746.0798

Elemental analyses for $\text{C}_{33}\text{H}_{26}\text{ClN}_5\text{NiO}_{10}$ calculated: C, 53.08; H, 3.51; N, 9.38; found C, 53.11; H, 3.69; N, 9.47.

Ni-2

To a solution of **2** (0.300 g, 1.53 mmol) and 2,3-diamino-5-chloropyridine (0.110 g, 0.765 mmol) in methanol (12 mL) was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.210 g, 0.842 mmol). The mixture was then brought to reflux while stirring for 16 hours under a N_2 atmosphere. Subsequently, the mixture was cooled to ambient temperature and the resulting precipitate was filtered through a fine frit, after which the residue was rinsed with methanol, toluene, and diethyl ether. The solid was dried under vacuum to yield **Ni-2** as a maroon powder (0.38 g, 88%).

^1H NMR (300 MHz, DMSO- d_6): $\delta = \sim 3.35$ (s, 6 H), 3.67 (t, $J = 5.0$ Hz, 4 H), 4.14 (t, $J = 5.0$ Hz, 4 H), 6.59 (m, 2 H), 7.01 (d, $J = 7.0$ Hz, 2 H), 7.17 (d, $J = 2.0$ Hz, 1 H), 7.24 (d, $J = 8.0$ Hz, 1 H), 8.39 (d, $J = 2.0$ Hz, 1 H), 8.75 (d, $J = 2.0$ Hz, 1 H), 9.83 (s, 1 H), 10.00 (s, 1 H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): $\delta = 59.07$ (2 C), 67.98, 68.06, 70.98 (2 C), 115.41, 115.55, 117.16, 117.51, 119.83 (2 C), 122.86 (2 C), 125.62, 129.57, 136.40, 144.02, 149.80, 151.88, 155.13 (2 C), 159.07 (2 C), 159.27.

$\nu_{\text{max}}/\text{cm}^{-1}$ 449, 544, 739, 928, 1099, 1198, 1245, 1407, 1430, 1533, 1587, 2815, 2873, 2924, 2978.

HR-MS calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_3\text{NiO}_6$, $[\text{M}+\text{H}]^+ m/z = 556.0785$, found 556.0783.

Elemental analyses for $\text{C}_{25}\text{H}_{24}\text{ClN}_3\text{NiO}_6 \cdot \text{H}_2\text{O}$ calculated: C, 52.35; H, 4.56; N, 7.31; found C, 52.75; H, 4.39; N, 7.47.

Ni-3

To a solution of **7** (0.300 g, 1.03 mmol) in ethanol (15 mL) was added 1-naphthylamine (0.147 g, 1.03 mmol) and a few drops of glacial acetic acid (0.10 mL). The reaction mixture was stirred for 14 hours, after which the solvent was removed under reduced

pressure. Subsequently, Ni(OAc)₂·4H₂O (0.125 g, 0.500 mmol), triethylamine (0.0505 g, 0.500 mmol), and ethanol (15 mL) were added and the mixture was heated to reflux for 10 hours. The product that precipitated was collected by filtration and washed with ethanol, toluene, and diethyl ether, and then dried under vacuum to provide **Ni-3** as a green powder (0.36 g, 82%).

¹H NMR (500 MHz, DMSO-d₆): δ = 3.40 (s, 6 H), 3.78 (t, *J* = 4.0 Hz, 4 H), 4.31 (t, *J* = 4.0 Hz, 4 H), 7.04 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.61 (m, 6 H), 7.91 (s, 4 H), 8.05 (m, 4 H), 8.17 (d, *J* = 7.3 Hz, 2 H), 8.34 (d, *J* = 7.3 Hz, 2 H), 8.45 (s, 2 H).

HR-MS calcd for C₄₈H₃₉N₄NiO₁₀, [M+H]⁺ *m/z* = 889.2020, found 889.2014.

Elemental analyses for C₄₈H₃₈N₄NiO₁₀ calculated: C, 64.81; H, 4.31; N, 6.30; found C, 65.05; H, 4.17; N, 6.34.

Figure 2.7. (a) Ti 2p XPS data for **Ni-1@TiO₂** with the Ti 2p_{3/2} signal at 458.3 eV and Ti 2p_{1/2} signal at 463.9 eV. (b) Cl 2p XPS data for **Ni-1@TiO₂** with the Cl 2p_{3/2} signal at 200.2 eV and Cl 2p_{1/2} signal at 201.9 eV. (c) C 1s XPS data for **Ni-1@TiO₂** with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample. Black lines represent the experimental spectra, while the red and blue lines represent fittings.

Figure 2.8. (a) Si 2p XPS data for **Ni-1@SiO₂** with the Si 2p signal at 104.8 eV. (b) Cl 2p XPS data for **Ni-1@SiO₂** with the Cl 2p_{3/2} signal at 200.3 eV and Cl 2p_{1/2} signal at 202.1 eV. (c) C 1s XPS data for **Ni-1@SiO₂** with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample. Black lines represent the experimental spectra, while the red and blue lines represent fittings.

Figure 2.9. (a) Ni 2p XPS data for **Ni-1** with the Ni 2p_{3/2} signal at 853.8 eV and Ni 2p_{1/2} signal at 870.8 eV. (b) Cl 2p XPS data for **Ni-1** with the Cl 2p_{3/2} signal at 200.4 eV and Cl 2p_{1/2} signal at 202.1 eV (c) C 1s XPS data for **Ni-1** with the peak at 284.6 eV from the carbon tape substrate being used for calibration of the sample.

Comparison of Ni XPS spectra

Figure 2.10. Comparison of the Ni 2p XPS spectra for **Ni-1** (red), **Ni-1@TiO₂** (black), and **Ni-1@SiO₂** (orange), also demonstrating that the oxidation states of Ni in these samples are almost identical.

Fourier transform infrared (FT-IR) spectroscopy measurements

Figure 2.11. (a) Comparison of FT-IR spectra of **Ni-1** (red), TiO₂ (green), and **Ni-1@TiO₂** (black) from 400 cm⁻¹ to 4000 cm⁻¹. (c) Comparison of FT-IR spectra of **Ni-1** (red), SiO₂ (magenta), and **Ni-1@SiO₂** (orange) from 400 cm⁻¹ to 4000 cm⁻¹.

Figure 2.12. (a) Comparison of FT-IR spectra of **Ni-1** before (red) and after (purple) 254 nm UV irradiation from 400 cm⁻¹ to 4000 cm⁻¹. b) Expanded spectra of **Ni-1** before (red) and after (purple) 254 nm UV irradiation from 500 cm⁻¹ to 2000 cm⁻¹.

Figure 2.13. Comparison of the FT-IR spectra from 1000 cm^{-1} to 2000 cm^{-1} of (a) **Ni-2+TiO₂** before (light pink) and after washing (blue); (b) **Ni-2+SiO₂** before (pink) and after washing (dark cyan); (c) **Ni-2+CeO₂** before (light sky blue) and after washing (brick red); and (d) **Ni-2+WO₃** before (light yellow) and after washing (dark yellow). After washing with DCM, the peaks corresponding to **Ni-2** are no longer present, confirming that little to no anchoring or physisorption occurred. Moreover, the peaks at 1608 cm^{-1} and 1709 cm^{-1} , corresponding to the maleimide C=C and C=O stretches respectively, are not detectable in the spectra of the rinsed samples.

Figure 2.14. HRTEM images of a) **Ni-1@WO₃** and b) **Ni-1@CeO₂** nanoparticles.

Figure 2.15. a) Expanded view of the Ni *K*-edge XANES for the region 8340-8380 eV of **Ni-1** (red, dashed line), **Ni-1@TiO₂** (black, dash-dotted line), **Ni-1@SiO₂** (orange, dotted line), and **Ni-1@TiO₂** after four catalytic cycles (light brown, solid line), showing almost identical spectral features. b) Expanded view of the first coordination shell in the Fourier transforms of the EXAFS data in *R*-space (*k*-weight = 3 and *k* range = 2 - 10) of **Ni-1** (red, dashed line), **Ni-1@TiO₂** (black, dash-dotted line), **Ni-1@SiO₂** (orange, dotted line), and **Ni-1@TiO₂** after four catalytic cycles (light brown, solid line). The grey vertical dashed line is a guide for the eye and indicates that the average bond distances of the first coordination shell around Ni appear invariant in all the samples.

Figure 2.16. a) STEM image of Ni-1@TiO_2 . b) EDX overlay of Ti (cyan) and Ni (red) for Ni-1@TiO_2 . c) EDX overlay of Ti (cyan) and Cl (magenta) for Ni-1@TiO_2 . d) EDX spectrum of Ni-1@TiO_2 .

Table 2.2. STEM-EDX elemental composition table for Ni-1@TiO_2

Element	Weight %	Atom %
O(K)	44.8	70.9
Cl(K)	1.10	0.79
Ti(K)	51.5	27.2
Ni(K)	2.64	1.14

Figure 2.17. GC calibration curves for compound (a) 4-chlorostyrene (b) 4-chlorostyrene oxide (c) styrene (d) styrene oxide (e) 4-methoxystyrene (f) 4-methoxystyrene oxide (g) cyclooctene (h) cyclooctene oxide (i) 1-octene (j) 1,2-epoxycyclooctane. The response factor represents the peak area ratio of analyte and *n*-decane (peak area of analyte/peak area of *n*-decane) and the molar ratio represents the ratio of the concentration of analyte and *n*-decane (conc. of analyte in mM/conc. of *n*-decane in mM).

Calculations for the Ni content in Ni-1@CeO₂ and Ni-1@WO₃

Figure 2.18. (a) DRS of different amounts of **Ni-1**. (b) Calibration curve based on the absorbance of **Ni-1** at 515 nm *versus* the amount used. The gradient was found to be $0.0423 \mu\text{mol}^{-1}$ (c) DRS spectrum of **Ni-1@CeO₂** (24 mg). The absorbance at 515 nm was found to be 0.12, which corresponds to a Ni content of 0.118 mmol/g (d) DRS spectrum of **Ni-1@WO₃** (25 mg). The absorbance at 515 nm was found to be 0.11, which corresponds to a Ni content of 0.104 mmol/g.

The Ni contents of **Ni-1@CeO₂** and **Ni-1@WO₃** were calculated based on their respective DRS absorbance values at 515 nm. The peak at 515 nm corresponds to the Ni centered d-d transition of **Ni-1**. The Ni contents for **Ni-1@CeO₂** and **Ni-1@WO₃** were found to be 0.118 mmol/g and 0.104 mmol/g of CeO₂ and WO₃, respectively.

Table 2.3. Homogeneous alkene epoxidation by **Ni-1** with different oxidants.

Entry	Oxidant	% Conversion of substrate ^{a,b}	Time (h)	% GC yields of epoxide product ^b
1	Hydrogen peroxide	<5	6	<1
2	TEMPO	<1	6	-
3	Aerial oxygen	-	12	-
4	Sodium periodate	28	6	<10
5	NaOCl	98	3.5	63

^a The compound styrene was used as the substrate. ^b The compound *n*-decane was used as the internal standard.

Method for turnover frequency (TOF) calculation

For the homogeneous catalysis, the TOF was calculated using the formula

$$\text{TOF} = \frac{(\text{number of mmol of product formed})}{(\text{number of mmol of Ni-1 used}) \times (\text{time of the reaction in hour})}$$

For example, in Table S3, entry 1, the reaction was performed with 0.50 mmol of styrene and 0.025 mmol of **Ni-1**. The reaction took 3.5 hours to complete and the styrene oxide yield by GC was found to be 63%. Hence, the TOF for this reaction was calculated using the aforementioned formula and found to be 3.60 h⁻¹.

For the heterogeneous catalysis experiments, 5.0 μmol of **Ni-1** content was used in each run. The weight of catalyst added was calculated based on their respective Ni contents. The reactions were performed with 0.10 mmol of alkenes and the TOFs were calculated using the same formula above.

Table 2.4. Conversion, selectivity, and substrate scope of alkene epoxidation by **Ni-1**^a.

Entry	Substrate	% Conversion of substrate ^b	Time (h)	Epoxide product	% GC yields of epoxide products ^b	TOF (h ⁻¹)
1		>99	3.5		63	3.60
2		>99	2		75	7.50
3		>99	5		78	3.12
4		>99	2.5		74	5.92
5		95	5		54	2.16

^a The reactions were performed in DCM and the compound *n*-decane was used as the internal standard. ^b NaOCl was used as the oxidant.

Table 2.5. Heterogeneous alkene epoxidation by **Ni-1@TiO₂** in different solvents.

Entry	Solvent	% Conversion of substrate ^{a,b}	Time (h)	Phase transfer catalyst	% GC yields of epoxide product ^b	TOF (h ⁻¹)
1	Dichloromethane	92	4	TBAB ^e	53	2.65
2	Ethyl acetate	95	2	TBAB ^e	51	5.10
3	Ethyl acetate	90	5	TBAP ^f	47	1.90
4	Dimethyl carbonate	87	2.5	TBAB ^e	32	2.56
5 ^c	Water	98	1	-	27	5.40
6 ^d	Water	97	1	-	5	-
7	2-Methyl-tetrahydrofuran	-	6	TBAB ^e	-	-

^a Compound 4-chlorostyrene was used as the substrate. ^b Compound *n*-decane was used as the internal standard. ^c Borate buffer (pH 9.3) was used. ^d Phosphate buffer (pH 7) was used. ^e TBAB represents tetrabutylammonium bromide. ^f TBAP represents tetrabutylammonium hexfluorophosphate.

Figure 2.19. Contact angle images of a) unmodified glass substrate, b) glass coated with TiO_2 , and c) glass substrate coated with **Ni-1@TiO₂**. Here θ represents the static contact angle value. Coating with TiO_2 increases the hydrophilicity, probably due to the presence of the surface hydroxyl groups. On the other hand, coating with **Ni-1@TiO₂** increases the hydrophobicity due to the presence of the hydrophobic Ni complexes on the surface of the nanoparticles.

Catalytic activity and stability studies of Ni-1 physically mixed with metal oxide nanoparticles

Figure 2.20. DRS spectra of (a) **Ni-1**+TiO₂ (blue) and after one cycle of epoxidation catalysis (brick red), and (b) **Ni-1**+SiO₂ (light cyan) and after one cycle of epoxidation catalysis (dark magenta). Comparison of the FT-IR spectra of (c) **Ni-1**+TiO₂ (blue) and after one cycle of epoxidation catalysis (brick red), and (d) **Ni-1**+SiO₂ (light cyan) and after one cycle of epoxidation catalysis (dark magenta) from 1000 to 2000 cm⁻¹.

Table 2.6. Heterogeneous alkene epoxidation by the physically mixed **Ni-1**+TiO₂ and **Ni-1**+SiO₂.

Entry	Catalyst	% Conversion of substrate ^a	Time (h)	% GC yields of epoxide products ^b	TOF (h ⁻¹)
1	Ni-1 +TiO ₂ in 1 st cycle	>99	4.5	73	3.24
2	Ni-1 +TiO ₂ residue after centrifugation in 2 nd cycle	<2	6	-	-
3 ^c	Ni-1 +TiO ₂ supernatant from 1 st cycle	<2	6	-	-
4	Ni-1 +SiO ₂ 1 st cycle	>99	4.5	70	3.11
5	Ni-1 +SiO ₂ residue after centrifugation in 2 nd cycle	<1	6	-	-
6 ^c	Ni-1 +SiO ₂ supernatant from 1 st cycle	<2	6	-	-

^a The substrate 4-chlorostyrene was used for this study. ^b The epoxide product is 4-chlorostyrene oxide. ^c After the nanoparticles were separated by centrifugation, another 0.10 mmol of 4-chlorostyrene was added.

Figure 2.21. DLS spectrum of the aqueous layer of the biphasic alkene epoxidation reaction involving **Ni-1**.

Figure 2.22. a) Photograph of spatially controlled deposition of **Ni-3** on SiO_2 and TiO_2 coated FTO under visible light. The dashed lines highlight the edges. b) The coated plates under 365 nm UV from a TLC lamp. The **Ni-3@SiO₂-FTO** (left) plate shows better brighter photoluminescence compared to **Ni-3@TiO₂-FTO** (right).

Figure 2.23. a) SEM image of **Ni-3@SiO₂-FTO**. b) EDX overlay of Si (green) and Ni (red) for **Ni-3@SiO₂-FTO**. EDX mapping of c) Si (green) and d) Ni (red) for **Ni-3@SiO₂-FTO**. e) EDX spectrum of **Ni-3@SiO₂-FTO**.

REFERENCES

1. van Leeuwen, P. W. N. M., Decomposition Pathways of Homogeneous Catalysts. *Appl. Catal., A* **2001**, *212*, 61-81.
2. Crabtree, R. H., Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure. *Chem. Rev.* **2015**, *115*, 127-150.
3. Pelletier, J. D. A.; Basset, J. M., Catalysis by Design: Well-Defined Single-Site Heterogeneous Catalysts. *Acc. Chem. Res.* **2016**, *49*, 664-677.
4. Basset, J. M.; Coperet, C.; Soulivong, D.; Taoufik, M.; Cazat, J. T., Metathesis of Alkanes and Related Reactions. *Acc. Chem. Res.* **2010**, *43*, 323-334.
5. Klepser, B. M.; Bartlett, B. M., Anchoring a Molecular Iron Catalyst to Solar-Responsive WO₃ Improves the Rate and Selectivity of Photoelectrochemical Water Oxidation. *J. Am. Chem. Soc.* **2014**, *136*, 1694-1697.
6. Muratsugu, S.; Tada, M., Molecularly Imprinted Ru Complex Catalysts Integrated on Oxide Surfaces. *Acc. Chem. Res.* **2013**, *46*, 300-311.
7. Sheet, D.; Halder, P.; Paine, T. K., Enhanced Reactivity of a Biomimetic Iron(II) α -Keto Acid Complex through Immobilization on Functionalized Gold Nanoparticles. *Angew. Chem. Int. Ed.* **2013**, *52*, 13314-13318.
8. Weingarten, A. S.; Kazantsev, R. V.; Palmer, L. C.; McClendon, M.; Koltonow, A. R.; Samuel, A. P. S.; Kiebal, D. J.; Wasielewski, M. R.; Stupp, S. I., Self-Assembling Hydrogel Scaffolds for Photocatalytic Hydrogen Production. *Nat. Chem.* **2014**, *6*, 964-970.
9. Blakemore, J. D.; Gupta, A.; Warren, J. J.; Brunschwig, B. S.; Gray, H. B., Noncovalent Immobilization of Electrocatalysts on Carbon Electrodes for Fuel Production. *J. Am. Chem. Soc.* **2013**, *135*, 18288-18291.

10. Borah, P.; Ma, X.; Nguyen, K. T.; Zhao, Y. L., A Vanadyl Complex Grafted to Periodic Mesoporous Organosilica: A Green Catalyst for Selective Hydroxylation of Benzene to Phenol. *Angew. Chem. Int. Ed.* **2012**, *51*, 7756-7761.
11. Pujari, S. P.; Scheres, L.; Marcelis, A. T. M.; Zuilhof, H., Covalent Surface Modification of Oxide Surfaces. *Angew. Chem. Int. Ed.* **2014**, *53*, 6322-6356.
12. Wei, P. J.; Yu, G. Q.; Naruta, Y.; Liu, J. G., Covalent Grafting of Carbon Nanotubes with a Biomimetic Heme Model Compound To Enhance Oxygen Reduction Reactions. *Angew. Chem. Int. Ed.* **2014**, *53*, 6659-6663.
13. Muresan, N. M.; Willkomm, J.; Mersch, D.; Vaynzof, Y.; Reisner, E., Immobilization of a Molecular Cobaloxime Catalyst for Hydrogen Evolution on a Mesoporous Metal Oxide Electrode. *Angew. Chem. Int. Ed.* **2012**, *51*, 12749-12753.
14. Soo, H. S.; Agiral, A.; Bachmeier, A.; Frei, H., Visible Light-Induced Hole Injection into Rectifying Molecular Wires Anchored on Co₃O₄ and SiO₂ Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 17104-17116.
15. Alphazan, T.; Mathey, L.; Schwarzwald, M.; Lin, T. H.; Rossini, A. J.; Wischert, R.; Enyedi, V.; Fontaine, H.; Veillerot, M.; Lesage, A.; Emsley, L.; Veyre, L.; Martin, F.; Thieuleux, C.; Coperet, C., Monolayer Doping of Silicon through Grafting a Tailored Molecular Phosphorus Precursor onto Oxide-Passivated Silicon Surfaces. *Chem. Mater.* **2016**, *28*, 3634-3640.
16. Nichols, B. M.; Butler, J. E.; Russell, J. N.; Hamers, R. J., Photochemical Functionalization of Hydrogen-Terminated Diamond Surfaces: A Structural and Mechanistic Study. *J. Phys. Chem. B* **2005**, *109*, 20938-20947.
17. Wang, X. Y.; Ruther, R. E.; Streifer, J. A.; Hamers, R. J., UV-Induced Grafting of Alkenes to Silicon Surfaces: Photoemission *versus* Excitons. *J. Am. Chem. Soc.* **2010**, *132*, 4048-4049.
18. Franking, R.; Kim, H.; Chambers, S. A.; Mangham, A. N.; Hamers, R. J., Photochemical Grafting of Organic Alkenes to Single-Crystal TiO₂ Surfaces: A Mechanistic Study. *Langmuir* **2012**, *28*, 12085-12093.
19. Wang, X. Y.; Landis, E. C.; Franking, R.; Hamers, R. J., Surface Chemistry for Stable and Smart Molecular and Biomolecular Interfaces *via* Photochemical Grafting of Alkenes. *Acc. Chem. Res.* **2010**, *43*, 1205-1215.
20. Zhang, L. H.; Zhu, D.; Nathanson, G. M.; Hamers, R. J., Selective Photoelectrochemical Reduction of Aqueous CO₂ to CO by Solvated Electrons. *Angew. Chem. Int. Ed.* **2014**, *53*, 9746-9750.
21. Shah, S.; Benson, M. C.; Bishop, L. M.; Huhn, A. M.; Ruther, R. E.; Yeager, J. C.; Tan, Y. Z.; Louis, K. M.; Hamers, R. J., Chemically Assembled Heterojunctions of SnO₂ Nanorods with TiO₂ Nanoparticles *via* "Click" Chemistry. *J. Mater. Chem.* **2012**, *22*, 11561-11567.
22. Khusnutdinova, D.; Beiler, A. M.; Wadsworth, B. L.; Jacob, S. I.; Moore, G. F., Metalloporphyrin-Modified Semiconductors for Solar Fuel Production. *Chem. Sci.* **2017**, *8*, 253-259.
23. Arndt, S.; Wagenknecht, H. A., "Photoclick" Postsynthetic Modification of DNA. *Angew. Chem. Int. Ed.* **2014**, *53*, 14580-14582.
24. Cozzi, P. G., Metal-Salen Schiff base Complexes in Catalysis: Practical Aspects. *Chem. Soc. Rev.* **2004**, *33*, 410-421.
25. Mouri, S.; Chen, Z. H.; Matsunaga, S.; Shibasaki, M., Direct Catalytic Asymmetric Aldol Reaction of β -keto Esters with Formaldehyde Promoted by a Dinuclear Ni₂-Schiff Base Complex. *Chem. Commun.* **2009**, 5138-5140.
26. Bhattacharjee, S.; Jeong, K. E.; Jeong, S. Y.; Ahn, W. S., Synthesis of a Sulfonato-Salen-Nickel(II) Complex Immobilized in LDH for Tetralin Oxidation. *New J. Chem.* **2010**, *34*, 156-162.
27. Shepherd, N. E.; Tanabe, H.; Xu, Y. J.; Matsunaga, S.; Shibasaki, M., Direct Catalytic Asymmetric Vinylogous Mannich-Type and Michael Reactions of an α,β -Unsaturated γ -Butyrolactam under Dinuclear Nickel Catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 3666-3667.

28. Yoon, H.; Burrows, C. J., Catalysis of Alkene Oxidation by Nickel Salen Complexes Using Sodium Hypochlorite Under Phase-Transfer Conditions. *J. Am. Chem. Soc.* **1988**, *110*, 4087-4089.
29. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Shams, E.; Rasouli, N., Catalytic Epoxidation of Olefins with Hydrogen Peroxide by Hybrid Complex Containing Nickel(III) Schiff Base Complex Covalently Linked to Polyoxometalate. *Appl. Catal., A* **2008**, *334*, 106-111.
30. Chatterjee, D.; Mukherjee, S.; Mitra, A., Epoxidation of Olefins with Sodium Hypochlorite Catalyzed by New Nickel(II)-Schiff Base Complexes. *J. Mol. Catal. A: Chem.* **2000**, *154*, 5-8.
31. Ferreira, R.; Garcia, H.; de Castro, B.; Freire, C., (Salen)Nickel-Catalyzed Epoxidations in the Homogeneous and Heterogeneous Phase: The Implications of Oxygen on the Efficiency and Product Selectivity. *Eur. J. Inorg. Chem.* **2005**, 4272-4279.
32. Garg, B. S.; Kumar, D. N., Spectral Studies of Complexes of Nickel(II) with Tetradentate Schiff bases Having N₂O₂ Donor Groups. *Spectrochim. Acta, Part A* **2003**, *59*, 229-234.
33. Anthonysamy, A.; Balasubramanian, S., Synthesis, Spectral, Thermal and Electrochemical Studies of Nickel (II) Complexes with N₂O₂ Donor Ligands. *Inorg. Chem. Commun.* **2005**, *8*, 908-911.
34. Liu, Y. L.; Wang, Y. H., Preparation and Characterization of Multifunctional Maleimide Macromonomers and their Cured Resins. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3178-3188.
35. Dillard, J. G.; Taylor, L. T., X-Ray Photoelectron Spectroscopic Study of Schiff Base Metal Complexes. *J. Electron. Spectrosc. Relat. Phenom.* **1974**, *3*, 455-460.
36. Salavati-Niasari, M.; Bazarganipour, M., Covalent Functionalization of Multi-Wall Carbon Nanotubes (MWNTs) by Nickel(II) Schiff-Base Complex: Synthesis, Characterization and Liquid Phase Oxidation of Phenol with Hydrogen Peroxide. *Appl. Surf. Sci.* **2008**, *255*, 2963-2970.
37. Shao, H.; Muduli, S. K.; Tran, P. D.; Soo, H. S., Enhancing Electrocatalytic Hydrogen Evolution by Nickel Salicylaldimine Complexes with Alkali Metal Cations in Aqueous Media. *Chem. Commun.* **2016**, *52*, 2948-2951.
38. Huang, Y. B.; Liu, T. F.; Lin, J. X.; Lu, J. A.; Lin, Z. J.; Cao, R., Homochiral Nickel Coordination Polymers Based on Salen(Ni) Metalloligands: Synthesis, Structure, and Catalytic Alkene Epoxidation. *Inorg. Chem.* **2011**, *50*, 2191-2198.
39. Alder, C. M.; Hayler, J. D.; Henderson, R. K.; Redman, A. M.; Shukla, L.; Shuster, L. E.; Sneddon, H. F., Updating and Further Expanding GSK's Solvent Sustainability Guide. *Green Chem.* **2016**, *18*, 3879-3890.
40. Du, Y.; Zhu, Y.; Xi, S.; Yang, P.; Moser, H. O.; Breese, M. B. H.; Borgna, A., XAFCA: A New XAFS Beamline for Catalysis Research. *J. Synchrotron Radiat.* **2015**, *22*, 839-843.
41. Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. Self-Assembling Nickel Clusters Form Binding Sites for Alkali Metal Cations: Novel Analogs of Enolate Aggregates *J. Am. Chem. Soc.* **1993**, *115*, 5962-5969.

Chapter 3

Summary and outlook

3.1 Summary

To summarize, this work has addressed the synthesis of a novel Ni salicylaldimine complex bearing oxidatively stable maleimide anchoring groups and its covalent anchoring to a range of metal oxide nanoparticles. The covalent anchoring via photoclick chemistry showed particular preference for UV light of 254 nm and the covalent linkage formation was confirmed by the change in the FT-IR spectrum. The possibility of surface adsorption was rejected after control reactions involving physical mixing of **Ni-1** and metal oxide nanoparticles without light irradiation did not show any change in the FT-IR stretching frequency of C=C bond present in the maleimide group. Moreover, no anchoring was found to happen for the complex **Ni-2**, which did not contain the maleimide anchoring group. These control experiments clearly showed the importance of maleimide, as the anchoring group.

The XPS and XAS measurements were carried out on the hybrid systems, which clearly showed no change in the oxidation state of Ni centre upon anchoring. The nanomaterials were also characterized by TEM and SEM techniques. After complete characterization, the single-site hybrid nanocatalysts were used in epoxidation of linear, cyclic, and aromatic alkenes. In dichloromethane (DCM), excellent conversion of the alkenes and moderate to high selectivity for the epoxide products were observed. However, DCM being a halogenated compound, is not environmentally

benign. Thus, several environment friendly solvents were screened including water, ethyl acetate, dimethyl carbonate, and 2-methyl tetrahydrofuran. Though the reaction in water was found to proceed extremely fast, the selectivity towards the epoxide product was below 20%. However, in ethyl acetate, conversion and selectivity nearly similar to the DCM was observed.

The heterogeneous catalyst was found to be very robust and can be reused up to ten catalytic cycles. Though the conversion and epoxide selectivity dropped after four cycles, the ligand environment was found to be intact even after ten catalytic cycles. The XAS also suggested that the oxidation state of the Ni centre changes back to +2 after the consumption of the starting material.

The photoclick chemistry was successfully utilized for photopatterning of the SiO₂ and TiO₂ coated fluorine doped tin oxide (FTO) plates. The photoclick method provides unprecedented spatial and temporal control over the deposition of luminescent molecules, which can never be achieved in normal solution phase and solvothermal anchoring methods. The patterning was done using a simple paper mask, which allowed interaction between the metal oxide nanoparticles and the UV light only at specific places, where eventually anchoring occurred. The pattern prepared on TiO₂ film was found to be poorly luminescent compared to the one over SiO₂ film, due to efficient charge transfer to the TiO₂ layer.

Thus, maleimide was found to be a versatile anchoring group for covalent modification of various metal oxide surfaces for different applications.

3.2 Future outlook

The versatility and spatial and temporal controllability of the maleimide group can potentially be used for different biological applications. The oxidative stability of the maleimide group can be an added advantage for biological applications.

Other than biological applications, alkene modified photocatalysts can be covalently attached to the surfaces of different metal oxides. The unique interaction between the molecular photocatalyst and the metal oxide nanoparticle might result in unusual product formation or distribution.

Gazi and co-workers from our group previously reported V Schiff base photocatalysts for selective and efficient C-C bond cleavage.¹ Work is currently undergoing for development of covalently attached heterogeneous V catalysts for their potential application in photocatalytic C-C bond cleavage.

References

1. Gazi, S.; Đokić, M.; Moeljadi, A. M. P.; Ganguly, R.; Hirao, H.; Soo, H. S., Kinetics and DFT Studies of Photoredox Carbon–Carbon Bond Cleavage Reactions by Molecular Vanadium Catalysts under Ambient Conditions. *ACS Catalysis* **2017**, 7 (7), 4682–4691.

Appendix

Figure A.1. The ^1H NMR spectrum of **2** in CDCl_3 .

Figure A.2. The ^{13}C NMR spectrum of **2** in CDCl_3 .

Figure A.3. The ¹H NMR spectrum of **3** in CDCl₃.

Figure A.4. The ^{13}C NMR spectrum of **3** in CDCl_3 .

Figure A.5. The ^1H NMR spectrum of **4** in DMSO-d_6 .

Figure A.6. The ¹³C NMR spectrum of **4** in DMSO-d₆.

Figure A.7. The ^1H NMR spectrum of **5** in DMSO-d_6 .

Figure A.8. The ^{13}C NMR spectrum of **5** in DMSO-d_6 .

Figure A.9. The ^1H NMR spectrum of **6** in DMSO-d_6 .

Figure A.10. The ^{13}C NMR spectrum of **6** in DMSO-d₆.

Figure A.11. The ¹H NMR spectrum of **7** in DMSO-d₆.

Figure A.12. The ^{13}C NMR spectrum of **7** in DMSO-d_6 .

Figure A.13. The ^1H NMR spectrum of **Ni-1** in DMSO-d_6 .

Figure A.14. The ^{13}C NMR spectrum of **Ni-1** in DMF- d_7 . The expanded region from δ 140 to 160 ppm is shown in the inset.

Figure A.15. The ¹H NMR spectrum of Ni-2 in DMSO-d₆.

Figure A.16. The ^{13}C NMR spectrum of Ni-2 in CDCl_3 .

Figure A.17. The ^1H NMR spectrum of **Ni-3** in DMSO-d₆.

Figure A.18. Oak-Ridge thermal ellipsoid plot (ORTEP) of **Ni-1** with KPF₆. The thermal ellipsoids are drawn at the 50% probability level.

A red plate-like specimen of C₃₆H₃₃ClF₆KN₆NiO₁₁P, with approximate dimensions 0.040 × 0.240 × 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 1.28 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 46706 reflections to a maximum θ angle of 28.71° (0.74 Å resolution), of which 10451 were independent (average redundancy = 4.469, completeness = 99.4%, $R_{\text{int}} = 15.15\%$, $R_{\text{sig}} = 17.54\%$) and 4823 (46.15%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 9.9868(11)$ Å, $\underline{b} = 14.5340(16)$ Å, $\underline{c} = 15.0145(16)$ Å, $\alpha = 84.521(3)^\circ$, $\beta = 80.681(3)^\circ$, $\gamma = 70.752(3)^\circ$, volume = 2028.3(4) Å³, are based upon the refinement of the XYZ-centroids of 2777 reflections above 20 $\sigma(I)$ with $6.137^\circ < 2\theta$

$< 39.91^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.897. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7450 and 0.9690. The final anisotropic full-matrix least-squares refinement on F^2 with 682 variables converged at $R1 = 6.97\%$ for the observed data, and $wR2 = 17.30\%$ for all data. The goodness-of-fit was 1.003. The largest peak in the final difference electron density synthesis was $0.792 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.840 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.105 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.644 g/cm^3 and $F(000)$ was 1024 e^- .

Table A.1. Crystal data for **Ni-1** with KPF₆.

Chemical formula	C ₃₆ H ₃₃ ClF ₆ KN ₆ NiO ₁₁ P	
Formula weight	1003.91 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.240 x 0.400 mm	
Crystal habit	red plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9868(11) Å	α = 84.521(3)°
	b = 14.5340(16) Å	β = 80.681(3)°
	c = 15.0145(16) Å	γ = 70.752(3)°
Volume	2028.3(4) Å ³	
Z	2	
Density (calculated)	1.644 g/cm ³	
Absorption coefficient	0.782 mm ⁻¹	
F(000)	1024	

Table A.2. Structure refinement parameters for **Ni-1** with KPF₆.

Theta range for data collection	3.01 to 28.71°
Index ranges	-13≤h≤13, -19≤k≤19, -20≤l≤20
Reflections collected	46706
Independent reflections	10451 [R(int) = 0.1515]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Max. and min. transmission	0.9690 and 0.7450
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10451 / 437 / 682
Goodness-of-fit on F ²	1.003
Final R indices	4823 data; I>2σ(I) R1 = 0.0697, wR2 = 0.1300
	all data R1 = 0.1848, wR2 = 0.1730
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0624P)^2+0.3623P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.792 and -0.840 eÅ ⁻³
R.M.S. deviation from mean	0.105 eÅ ⁻³

Table A.3. Selected bond lengths (Å) for **Ni-1** with KPF₆.

C1-N3A	1.36(2)	C1-C5	1.382(8)
C1-C2	1.394(6)	C1-N1	1.415(5)
C2-N3	1.342(7)	C2-C5A	1.39(2)
C2-N2	1.409(5)	C3-N3	1.340(7)
C3-C4	1.396(7)	C4-C5	1.396(8)
C4-Cl1	1.713(6)	C3A-N3A	1.33(2)
C3A-C4A	1.381(18)	C4A-C5A	1.409(19)
C4A-Cl1A	1.726(17)	C6-N1	1.309(5)
C6-C7	1.401(6)	C7-C12	1.416(6)
C7-C8	1.417(6)	C8-O1	1.323(5)
C8-C9	1.422(6)	C9-O2	1.375(5)
C9-C10	1.383(6)	C10-C11	1.410(6)
C11-C12	1.357(6)	C11-N4	1.442(6)
C13-O7	1.196(5)	C13-N4	1.403(6)
C13-C14	1.498(7)	C14-C15	1.306(7)
C15-C16	1.495(7)	C16-O8	1.206(6)
C16-N4	1.390(6)	C17-O2	1.436(5)
C17-C18	1.487(7)	C18-O3	1.415(6)
C18-K1	3.438(6)	C19-O3	1.389(7)
C20-N2	1.308(5)	C20-C21	1.412(6)
C21-C26	1.414(6)	C21-C22	1.415(6)
C22-O4	1.314(5)	C22-C23	1.430(6)
C23-O5	1.370(5)	C23-C24	1.384(6)
C24-C25	1.397(6)	C25-C26	1.364(6)

C25-N5	1.432(6)	C27-O9	1.207(6)
C27-N5	1.402(6)	C27-C28	1.482(7)
C28-C29	1.312(7)	C29-C30	1.504(7)
C30-O10	1.204(6)	C30-N5	1.394(6)
C31-O5	1.439(5)	C31-C32	1.483(7)
C32-O6	1.428(6)	C33-O6	1.447(7)
K1-O3	2.903(4)	N1-Ni1	1.858(3)
N2-Ni1	1.861(4)	Ni1-O1	1.841(3)
Ni1-O4	1.852(3)		

Table A.4. Anisotropic atomic displacement parameters ($\text{\AA}^2$) for **Ni-1** with KPF_6 .

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C1	0.019(2)	0.024(2)	0.020(2)	-0.0021(18)	-0.0013(18)	-0.0085(19)
C2	0.017(2)	0.029(2)	0.017(2)	-0.0061(18)	0.0028(18)	-0.0083(19)
C3	0.025(3)	0.024(3)	0.018(3)	0.003(2)	-0.001(2)	-0.010(3)
C4	0.021(3)	0.025(3)	0.013(3)	-0.001(2)	-0.002(2)	-0.010(3)
C5	0.024(3)	0.016(4)	0.021(3)	-0.002(3)	-0.002(2)	-0.006(3)
N3	0.021(4)	0.028(3)	0.025(3)	-0.002(2)	-0.004(2)	-0.009(2)
Cl1	0.0340(9)	0.0328(9)	0.0241(8)	-0.0033(6)	-0.0079(6)	-0.0154(7)
C3A	0.023(7)	0.025(6)	0.022(7)	0.000(5)	-0.005(6)	-0.012(6)
C4A	0.023(7)	0.026(6)	0.019(7)	-0.003(5)	-0.004(6)	-0.011(5)
C5A	0.023(9)	0.026(6)	0.019(8)	-0.003(5)	-0.004(7)	-0.008(6)
N3A	0.025(8)	0.026(7)	0.021(7)	-0.002(6)	-0.002(6)	-0.014(6)
Cl1A	0.060(6)	0.038(4)	0.043(5)	-0.008(3)	-0.010(4)	-0.029(4)
C6	0.016(2)	0.032(3)	0.016(2)	-0.006(2)	-0.0002(19)	-0.011(2)
C7	0.021(3)	0.022(3)	0.012(2)	-0.0026(19)	0.0063(19)	-0.008(2)
C8	0.026(3)	0.022(3)	0.019(2)	-0.003(2)	0.004(2)	-0.008(2)
C9	0.026(3)	0.030(3)	0.022(3)	-0.005(2)	0.000(2)	-0.011(2)
C10	0.032(3)	0.021(3)	0.032(3)	-0.004(2)	0.003(2)	-0.011(2)
C11	0.028(3)	0.022(3)	0.026(3)	0.000(2)	0.000(2)	-0.007(2)
C12	0.021(3)	0.033(3)	0.025(3)	0.000(2)	-0.001(2)	-0.014(2)
C13	0.030(3)	0.026(3)	0.048(3)	0.003(3)	-0.001(3)	-0.009(2)
C14	0.037(3)	0.027(3)	0.045(3)	0.008(2)	-0.002(3)	-0.008(3)
C15	0.053(4)	0.023(3)	0.036(3)	0.004(2)	-0.007(3)	-0.011(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	0.046(4)	0.027(3)	0.038(3)	-0.002(2)	-0.005(3)	-0.019(3)
C17	0.035(3)	0.032(3)	0.044(3)	-0.005(3)	-0.008(3)	-0.017(2)
C18	0.044(4)	0.045(4)	0.053(4)	-0.009(3)	-0.009(3)	-0.028(3)
C19	0.157(9)	0.150(9)	0.070(6)	-0.056(6)	0.023(6)	-0.103(7)
C20	0.023(3)	0.027(3)	0.022(2)	-0.001(2)	0.001(2)	-0.014(2)
C21	0.022(3)	0.031(3)	0.019(2)	0.004(2)	-0.003(2)	-0.011(2)
C22	0.020(3)	0.030(3)	0.020(2)	0.000(2)	0.002(2)	-0.010(2)
C23	0.023(3)	0.033(3)	0.020(2)	-0.001(2)	-0.001(2)	-0.010(2)
C24	0.031(3)	0.036(3)	0.020(3)	0.003(2)	-0.007(2)	-0.011(2)
C25	0.028(3)	0.033(3)	0.020(3)	0.003(2)	-0.004(2)	-0.010(2)
C26	0.025(3)	0.029(3)	0.028(3)	0.001(2)	0.000(2)	-0.011(2)
C27	0.040(4)	0.046(4)	0.027(3)	0.004(3)	-0.002(3)	-0.011(3)
C28	0.054(4)	0.031(3)	0.032(3)	0.016(2)	-0.015(3)	-0.010(3)
C29	0.050(4)	0.035(3)	0.036(3)	-0.004(3)	-0.019(3)	-0.008(3)
C30	0.045(4)	0.030(3)	0.034(3)	-0.001(2)	-0.018(3)	-0.008(3)
C31	0.031(3)	0.048(3)	0.025(3)	-0.004(2)	-0.008(2)	-0.018(3)
C32	0.036(3)	0.052(4)	0.035(3)	-0.006(3)	-0.013(3)	-0.022(3)
C33	0.079(6)	0.117(7)	0.076(6)	-0.059(5)	-0.009(4)	-0.011(5)
C34	0.052(4)	0.079(5)	0.076(5)	-0.026(4)	0.018(4)	-0.029(4)
C35	0.050(4)	0.066(5)	0.070(5)	0.020(4)	-0.011(4)	-0.016(3)
C36	0.038(4)	0.069(5)	0.055(4)	-0.004(4)	-0.003(3)	-0.022(3)
P1	0.030(2)	0.040(3)	0.022(2)	0.0023(19)	-0.0016(18)	-0.015(2)
F1	0.027(4)	0.072(4)	0.036(4)	0.013(3)	-0.001(3)	0.001(3)
F2	0.073(4)	0.071(4)	0.036(3)	-0.018(3)	0.006(3)	-0.029(3)

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
F3	0.046(3)	0.038(3)	0.059(4)	0.016(3)	-0.005(3)	-0.019(2)
F4	0.059(4)	0.078(5)	0.044(4)	-0.026(4)	-0.014(3)	-0.015(4)
F5	0.058(3)	0.048(3)	0.055(4)	0.021(3)	0.006(3)	-0.021(3)
F6	0.033(4)	0.064(5)	0.040(4)	0.014(3)	-0.014(3)	-0.016(3)
P1A	0.056(7)	0.037(6)	0.037(7)	0.012(5)	-0.018(6)	0.000(6)
F1A	0.053(12)	0.106(16)	0.046(13)	0.053(10)	0.007(8)	0.012(10)
F2A	0.065(9)	0.105(14)	0.026(7)	0.020(8)	-0.008(6)	-0.012(9)
F3A	0.159(19)	0.093(14)	0.16(2)	-0.008(14)	-0.065(17)	-0.075(13)
F4A	0.065(11)	0.114(18)	0.028(8)	0.021(11)	-0.013(7)	0.014(12)
F5A	0.113(16)	0.063(12)	0.20(3)	-0.036(15)	-0.032(18)	-0.049(11)
F6A	0.051(13)	0.052(12)	0.060(14)	0.018(10)	0.011(10)	0.007(9)
K1	0.0362(7)	0.0325(6)	0.0241(6)	-0.0047(5)	-0.0051(5)	-0.0117(5)
N1	0.016(2)	0.021(2)	0.0162(19)	-0.0021(16)	0.0005(16)	-0.0073(17)
N2	0.020(2)	0.023(2)	0.021(2)	-0.0004(17)	-0.0009(17)	-0.0085(17)
N4	0.030(2)	0.020(2)	0.034(2)	0.0077(18)	-0.0051(19)	-0.0111(19)
N5	0.038(3)	0.032(2)	0.025(2)	0.0086(19)	-0.010(2)	-0.014(2)
N6	0.031(3)	0.052(3)	0.032(3)	0.007(2)	-0.013(2)	-0.009(2)
Ni1	0.0225(3)	0.0242(3)	0.0184(3)	-0.0010(2)	-0.0025(3)	-0.0093(3)
O1	0.0246(18)	0.0256(18)	0.0193(16)	-0.0020(14)	-0.0042(14)	-0.0087(14)
O2	0.035(2)	0.0281(19)	0.0316(19)	-0.0041(15)	-0.0035(16)	-0.0146(16)
O3	0.045(2)	0.050(2)	0.037(2)	-0.0167(18)	-0.0022(19)	-0.0211(19)
O4	0.0261(18)	0.0229(18)	0.0200(17)	-0.0004(14)	-0.0046(14)	-0.0083(14)
O5	0.034(2)	0.0311(19)	0.0229(18)	-0.0006(15)	-0.0089(15)	-0.0151(16)
O6	0.046(3)	0.048(2)	0.057(3)	-0.017(2)	-0.017(2)	-0.007(2)

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
O7	0.032(2)	0.038(2)	0.085(3)	0.024(2)	0.001(2)	-0.0111(19)
O8	0.042(2)	0.042(2)	0.076(3)	0.020(2)	-0.017(2)	-0.027(2)
O9	0.044(3)	0.050(3)	0.050(3)	0.020(2)	0.000(2)	-0.015(2)
O10	0.035(2)	0.039(2)	0.058(3)	-0.0030(19)	-0.009(2)	-0.0118(19)
O11	0.048(2)	0.058(3)	0.032(2)	0.0088(19)	-0.0162(19)	-0.006(2)

Table A.5. Selected bond angles (°) for **Ni-1** with KPF₆.

C6-N1-Ni1	126.3(3)	C1-N1-Ni1	113.7(3)
C20-N2-Ni1	126.9(3)	C2-N2-Ni1	113.4(3)
O1-Ni1-N1	94.99(14)	O4-Ni1-N1	179.71(15)
O1-Ni1-O4	84.90(13)	N1-Ni1-N2	85.62(16)
O1-Ni1-N2	179.23(15)	O4-Ni1-N2	94.49(15)
C8-O1-Ni1	127.1(3)		

Table A.6. Atomic coordinates and equivalent isotropic atomic displacement parameters ($\text{\AA}^2$) for **Ni-1** with KPF_6 .

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.7851(5)	0.5653(3)	0.5216(3)	0.0206(10)
C2	0.7259(5)	0.6468(3)	0.4667(3)	0.0211(10)
C3	0.8262(7)	0.7422(4)	0.5260(4)	0.0224(14)
C4	0.8892(8)	0.6655(5)	0.5848(4)	0.0189(13)
C5	0.8675(13)	0.5756(5)	0.5832(7)	0.0202(15)
N3	0.7434(8)	0.7344(4)	0.4671(5)	0.0243(14)
Cl1	0.99077(16)	0.67962(10)	0.66093(9)	0.0285(5)
C3A	0.898(4)	0.6335(19)	0.601(2)	0.022(4)
C4A	0.855(4)	0.7197(17)	0.550(2)	0.022(4)
C5A	0.775(5)	0.723(2)	0.480(3)	0.022(4)
N3A	0.872(6)	0.553(2)	0.586(3)	0.022(4)
Cl1A	0.8891(9)	0.8242(6)	0.5706(5)	0.043(3)
C6	0.8005(4)	0.3999(3)	0.5506(3)	0.0203(10)
C7	0.7768(5)	0.3122(3)	0.5391(3)	0.0191(10)
C8	0.6895(5)	0.3055(3)	0.4760(3)	0.0229(11)
C9	0.6691(5)	0.2139(3)	0.4711(3)	0.0255(11)
C10	0.7349(5)	0.1332(3)	0.5237(3)	0.0285(12)
C11	0.8243(5)	0.1422(3)	0.5837(3)	0.0259(11)
C12	0.8432(5)	0.2291(3)	0.5926(3)	0.0253(11)
C13	0.0442(6)	0.0264(4)	0.6424(4)	0.0354(13)

C14	0.0720(6)	0.9351(4)	0.7018(4)	0.0378(13)
C15	0.9525(6)	0.9151(4)	0.7256(3)	0.0378(14)
C16	0.8352(6)	0.9917(4)	0.6845(3)	0.0351(13)
C17	0.5488(5)	0.1253(4)	0.4026(3)	0.0347(13)
C18	0.4830(6)	0.1356(4)	0.3186(4)	0.0433(15)
C19	0.5706(10)	0.1077(7)	0.1648(5)	0.113(3)
C20	0.5805(5)	0.7020(3)	0.3516(3)	0.0228(11)
C21	0.4928(5)	0.6953(3)	0.2892(3)	0.0234(11)
C22	0.4651(5)	0.6076(3)	0.2794(3)	0.0234(11)
C23	0.3726(5)	0.6093(4)	0.2155(3)	0.0254(11)
C24	0.3136(5)	0.6939(4)	0.1654(3)	0.0291(12)
C25	0.3428(5)	0.7795(4)	0.1765(3)	0.0275(12)
C26	0.4306(5)	0.7804(3)	0.2369(3)	0.0276(12)
C27	0.3603(6)	0.9233(4)	0.0748(3)	0.0393(14)
C28	0.2541(6)	0.0118(4)	0.0405(3)	0.0400(14)
C29	0.1249(6)	0.0068(4)	0.0676(3)	0.0398(14)
C30	0.1355(6)	0.9137(4)	0.1234(4)	0.0361(13)
C31	0.2623(5)	0.5184(4)	0.1438(3)	0.0329(12)
C32	0.2473(5)	0.4197(4)	0.1511(3)	0.0377(13)
C33	0.4279(8)	0.3355(6)	0.0353(5)	0.092(3)
C34	0.1520(7)	0.4047(5)	0.8327(5)	0.069(2)
C35	0.2033(6)	0.2308(5)	0.8658(4)	0.0637(19)
C36	0.0761(6)	0.3078(5)	0.7417(4)	0.0534(17)
P1	0.8702(8)	0.3140(6)	0.0901(5)	0.0300(13)
F1	0.7061(7)	0.3699(6)	0.0758(6)	0.051(2)
F2	0.8411(6)	0.3693(4)	0.1819(3)	0.059(2)

F3	0.8208(5)	0.2300(3)	0.1481(4)	0.0479(18)
F4	0.8917(7)	0.2587(5)	0.0011(4)	0.060(2)
F5	0.9167(5)	0.3996(4)	0.0346(4)	0.056(2)
F6	0.0312(7)	0.2597(7)	0.1047(6)	0.046(2)
P1A	0.870(3)	0.3060(19)	0.0932(17)	0.047(4)
F1A	0.708(2)	0.3784(18)	0.0998(17)	0.083(10)
F2A	0.8335(15)	0.2781(14)	0.1960(8)	0.071(6)
F3A	0.823(2)	0.2146(12)	0.0717(19)	0.124(9)
F4A	0.8991(19)	0.3228(17)	0.9882(9)	0.081(8)
F5A	0.917(2)	0.3905(12)	0.1117(19)	0.118(10)
F6A	0.032(2)	0.2336(18)	0.0913(18)	0.064(9)
K1	0.56274(12)	0.34746(8)	0.25615(7)	0.0304(3)
N1	0.7497(4)	0.4824(3)	0.5052(2)	0.0179(8)
N2	0.6435(4)	0.6305(3)	0.4057(2)	0.0212(9)
N4	0.8978(4)	0.0562(3)	0.6347(3)	0.0276(10)
N5	0.2816(4)	0.8664(3)	0.1238(3)	0.0308(10)
N6	0.1452(4)	0.3162(3)	0.8111(3)	0.0391(11)
Ni1	0.63447(6)	0.50403(4)	0.41486(4)	0.02124(17)
O1	0.6257(3)	0.3789(2)	0.42225(19)	0.0228(7)
O2	0.5817(3)	0.2133(2)	0.4094(2)	0.0304(8)
O3	0.5841(4)	0.1449(3)	0.2435(2)	0.0417(9)
O4	0.5188(3)	0.5255(2)	0.32521(19)	0.0228(7)
O5	0.3490(3)	0.5225(2)	0.2102(2)	0.0276(8)
O6	0.3823(4)	0.3456(3)	0.1314(3)	0.0499(11)
O7	0.1269(4)	0.0670(3)	0.6069(3)	0.0548(12)
O8	0.7100(4)	0.9989(3)	0.6933(3)	0.0507(11)

Appendix

O9	0.4891(4)	0.9018(3)	0.0647(3)	0.0507(11)
O10	0.0407(4)	0.8851(3)	0.1629(3)	0.0438(10)
O11	0.0160(4)	0.3765(3)	0.6941(2)	0.0484(11)

Publication

1. Ghosh, D.; Febriansyah, B.; Gupta, D.; Ng, L. K.-S.; Xi, S.; Du, Y.; Baikie, T.; Dong, Z.; Soo, H. S., Hybrid Nanomaterials with Single-Site Catalysts by Spatially Controllable Immobilization of Nickel Complexes via Photoclick Chemistry for Alkene Epoxidation. *ACS Nano* **2018**, *12* (6), 5903-5912.