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Recyclable, Immobilized Transition-Metal Photocatalysts

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Dedicated to Professor Oliver Reiser on the occasion of his 60th birthday

Abstract. The use of transition-metal complexes as photocatalysts have allowed the performance of diverse organic transformations in an outstanding manner, characterized not only by high yields, TOF, and selectivity values, but also by modulating and providing access to novel molecular structures that, without them, would be difficult if not impossible. However, one of the biggest concerns regarding the use of these photocatalysts relies on the difficulties associated with their isolation from reaction media and reutilization once the chemical process ends. The above, besides contaminating reaction products and requiring out tedious purification processes, prompts the inevitable loss of the catalyst, directly affecting its recyclability. In addition, this situation results in negative outcomes from an economic and environmental perspective, since transition-metal complexes are usually expensive materials, and their unsuccessful recovery could result in leakage into the environment.

These drawbacks served as inspiration for the elaboration of the present review focused on the development of novel strategies developed during the last decade for the successful recovery of these species. The strategies summarized herein, whether for homogeneous or heterogeneous systems, are based on the use of thermotropic solvents, changes in the hydrophilic balance of the catalyst, the employment of polymers, copolymers, porous macromolecular structures, and inorganic nanostructures as support of these entities. Moreover, the use of organized and confining media, such as micelles and gels in this context, is also discussed. We hope that this review will motivate the search for new strategies to develop novel catalytic systems, understanding that high performance is based not only on yields but also on recyclability, sustainability, and responsibility to the environment.

Keywords: Transition-metal photocatalyst; Polymer support; Immobilization; Recycling; Photocatalysis

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1 Introduction

A key challenge of tackling climate change is to develop energy and materials that are renewable and sustainable. The population's unsustainable energy needs have created a global crisis of climate change. The violent global pollution problems and continuously increasing levels of CO_2 emissions due to fossil energy dependence must be overcome soon. In organic synthesis, conventional synthetic approaches for organic transformations often call for harsh reaction conditions or unsustainable high energy reagents that are simply impossible to achieve. Visible light photo redox catalysis, a powerful synthetic tool that has flourished within the last decade, has provided solutions for some of these challenges.[1–11] Aiming at robust and sustainable processes, new catalysts have been explored such as inorganic semiconductors like TiO_2[12,13] or carbene nitride[14] offering higher stabilities have been explored. Heterocyclic organic dyes[15–18] have relatively low costs, and transition-metal complexes[19,20] have been found to be the most versatile including inexpensive copper.[21–25] Unfortunately, the most eclectic photoactive transition-metal complexes (based on ruthenium and iridium) with loadings typically around 1 mol% fail to fulfill large-scale application demands, and the development of new effective recyclable materials is increasingly desirable.[26]

Photocatalysts based on Ru and Ir complexes have been commonly used as efficient catalysts for organic transformations driven by visible light.[19,20] However, despite their emergence as efficient catalysts for a wide application, the relative high cost still limits their practical uses in large scale.[27] In addition, organo-metallic photocatalysts have a notable impact on the environment because of slow degradation and tendency to act as fluorescent pollutants. Recycling and reuse of them are receiving new attention as critical components of emerging chemical technologies due to both environmental concerns and economic benefits.[28]

One of the main challenges in materials research is the conversion of solar irradiation into convenient and sustainable forms of energy useable for photocatalysis. Photosynthetic systems containing photoactive transition-metal complexes like metal-photosensitizer bonded, crosslinked and surface immobilized polymer-supported photocatalysts are suitable for such challenges and are covered in this review by representative examples. This review is divided into two parts consisting of homogeneous and heterogeneous photocatalyst using different strategies for the recovery of the expensive transition-metal complexes. The recovery of organic dyes and inorganic semiconductors are out of the scope of this review.

Alex Abramov obtained his MSc degree in Chemistry (2017) under the supervision of Prof. David Díaz Díaz at the University of Regensburg (Germany). Currently, he is pursuing his PhD at the same place, advised by Profs. David Díaz Díaz and Oliver Reiser. His research is focused on the development of functional polymeric materials and the study of photoinduced processes in confined environments.

Sebastián Bonardd earned his PhD in Chemistry and PhD in Renewable Materials Engineering (2019) from the Pontifical Catholic University of Chile and the Basque Country University, respectively. He was a postdoctoral researcher at the Center of Applied Nanotechnology at Universidad Mayor (2019-2021), after which he was awarded with a "Juan de la Cierva – Formación" postdoctoral contract funded by the Spanish Ministry of Science & Innovation (2021). Since then, he is working at the Universidad de la Laguna under the supervision of Prof. David Díaz Díaz. His main research is framed within polymer science, focusing on novel materials for energy storage and environmental remediation.

Raúl Pérez-Ruiz obtained his PhD in Chemistry (2006) at Universitat Politècnica de València (UPV). He was post-doctoral fellow at the Universities of Athens, Cologne and UPV (2007-2014). Then, he moved first to the University of Regensburg (2014-2016) and afterwards to IMDEA-Energy Institute, Madrid (2017-2018). Since 2019, he is Distinguished Researcher (Plan GenT) at UPV. His research spans photoinduced chemical transformations and molecular spectroscopy.

David Díaz Díaz received his PhD in Chemistry from the University of La Laguna, Spain (2002). Then, he joined Prof. Finn's group as postdoc at TSRI (USA). Since 2006, he has held various positions in academia and industry (Ramón y Cajal researcher, UAM, Spain, 2006; Sr. Chemist, Dow Chemical, Switzerland, 2007; Tenured Scientist, CSIC, Spain, 2009; Alexander von Humboldt Experienced Researcher, Univ. Regensburg, Germany, 2010; DFG Heisenberg Professor, Univ. Regensburg, Germany, 2013. Since 2018, he is Priv.-Doz. at the University of Regensburg, and in 2020 he was appointed as Distinguished Researcher (Beatriz Galindo, Senior) at the University of La Laguna. His main research interest focuses on soft functional materials.

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2 Homogeneous Photocatalysts

In 2018, Lipshutz and co-workers published a newly designed photocatalyst-containing surfactant, which self-aggregated to provide nanoreactors enabling photo redox catalysis in water at room temperature.[29] This platform (refereed as PQS) is based on ubiquinol, the reduced form of the dietary supplement CoQ$_{10}$. It contains a hydrophilic (mPEG) component, a lipophilic (50 carbon) side chain, and a remaining –OH group available to which a catalyst can be covalently attached and that will reside within the hydrophobic inner core where catalysis takes place. They endeavored to attach a classic photocatalyst *fac*-Ir(ppy)$_3$, which itself is insoluble in water, to PQS (Figure 1). The resulting surfactant, bearing a covalently bound iridium complex, serves not only as the source of a photo redox catalyst, but also in the form of its derived nano-micelles, as the reaction medium. Upon completion of a photo-induced process, the aqueous micellar medium containing the Ir catalyst could be readily extracted "in-flask" with a minimum amount of an organic solvent for product isolation, leaving behind the reaction medium poised for reuse.
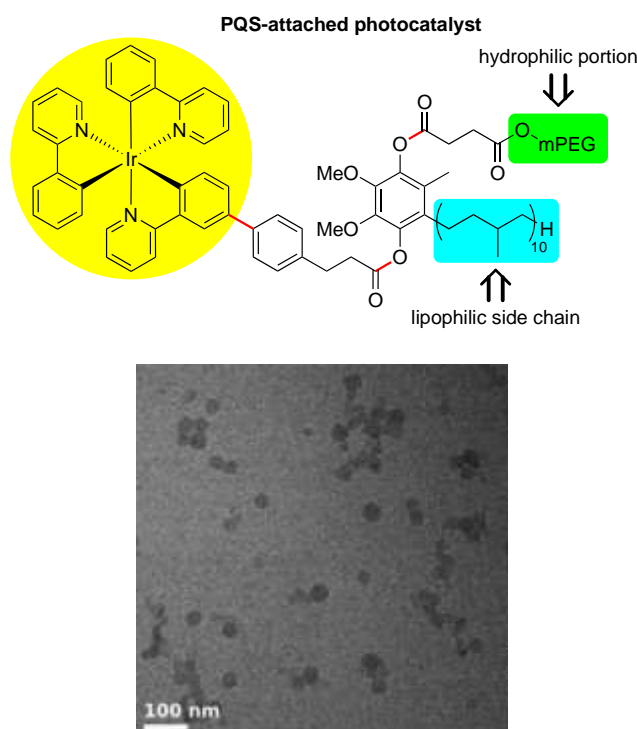
PQS-attached photocatalyst

Figure 1. Polyethyleneglycol ubiquinol succinate (PQS)-attached photocatalyst (*top*) and cryo-TEM analysis of the photocatalyst (*bottom*). Adapted with permission from reference [15]. Copyright Royal Society of Chemistry, 2018.

This concept was used for sulfonylation of a selected group of both alkenes and enol acetates given the desired products in moderate-to-excellent yields upon exposure to an Ir-containing PQS-attached photocatalyst (Figure 2), in the absence of any organic solvents or additives, and under mild conditions. In this chemistry, water serves as a "green" reaction medium, and visible light is harnessed as a safe and renewable source of chemical potential.

20 examples with 91 to 51% yield
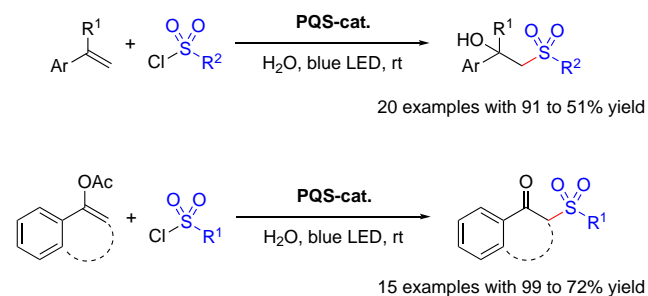
15 examples with 99 to 72% yield

Figure 2. Difunctionalisation of alkenes (*top*) and sulfonylation of enol acetates (*bottom*) catalyzed by the PQS photocatalyst.

Recycling of PQS-attached photocatalyst could be achieved by in-flask extraction with methyl *tert*-butyl ether (MTBE) once a reaction had reached completion. The aqueous medium containing the catalyst could then be recycled for four runs with the products isolated in yields from 70 to 88%, before an additional amount (0.5 mol%) of the PQS-catalyst was added (Figure 3). The resulting aqueous mixture could then be recycled for another five runs. Overall, the total investment of PQS-catalyst for these ten reactions was 1.5 mol% (i.e., 1500 ppm per reaction). Although, as mentioned above, the on-water reaction (i.e., in the absence of any surfactant) did not give a good result, difunctionalization of arylalkene by *fac*-Ir(ppy)$_3$ in aqueous TPGS-750-M led initially to good yield of β-hydroxysulfone. Nonetheless, in an attempt to recycle the aqueous medium, extraction under otherwise identical conditions led to loss of most of the iridium complex into the organic phase.
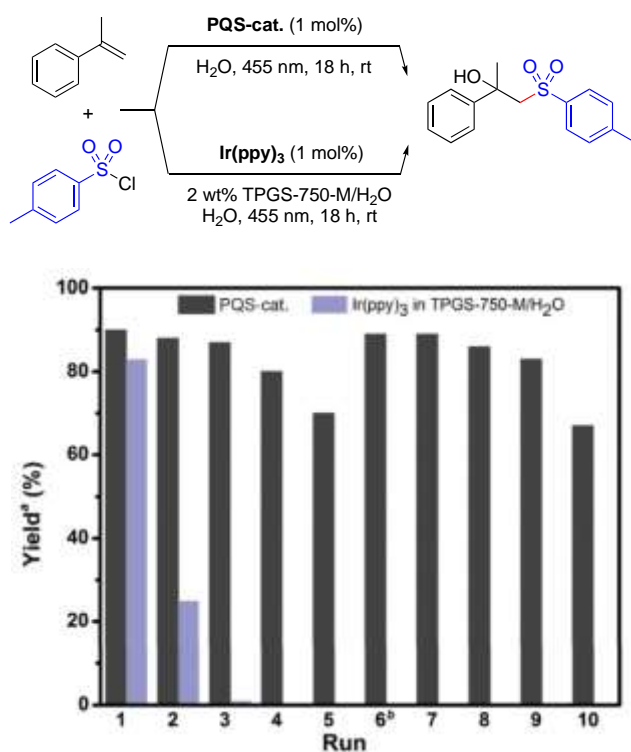
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Figure 3. Comparison between in-flask recycling of catalyst Ir(ppy)₃ in TPGS-750 M/H₂O *vs*. PQS-catalyst. [a] Isolated yields. [b] 0.5 mol% catalyst was added before the reaction. Adapted with permission from reference [15]. Copyright Royal Society of Chemistry, 2018.

As expected, therefore, the yield dropped to 25 % in the 2nd run, and only a trace of product could be detected beyond that, highlighting the importance of the covalent linkage between the photocatalyst and PQS. The entire *in-flask* recycling represents a sustainable precious metal technology.

Li, Duan and co-workers successfully developed and synthesized *fac*-Ir(hdppy)₃, a recoverable *n*-heptadecanyl-bound *fac*-Ir(ppy)₃ photocatalyst.[30]
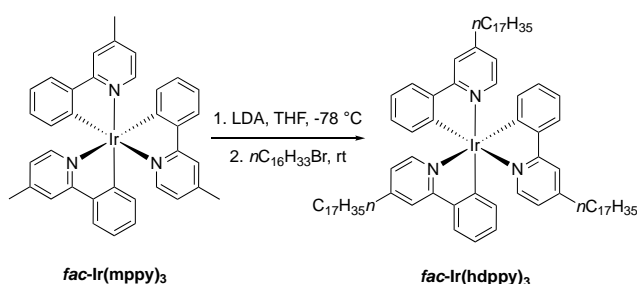

Figure 4. Synthesis of the *fac*-Ir(hdppy)₃.

Initially, *fac*-Ir(mppy)₃ was synthesized using 2-phenyl-4-methyl pyridine. Then, *fac*-Ir(mppy)₃ was treated with LDA to form the intermediate tris-lithium derivative, which further reacted with 1-bromohexadecane affording the hexadecane-bound *fac*-Ir(heptadecanyl-ppy)₃ (*fac*-Ir(hdppy)₃) (Figure 4). This photocatalyst was finally purified by silica gel

column chromatography. This catalyst shows excellent catalytic performance as well as recyclability for trifluoromethylation or difluoroacetylation of phenyl 3-phenylpropiolate to generate 3-trifluoromethylated and 3-difluoroacetylated coumarins under visible light (Figure 5) and could be easily separated from reaction products through a thermomorphic solvent (TMS) system based on the high phase-selective solubility of the long alkyl chain bound species.
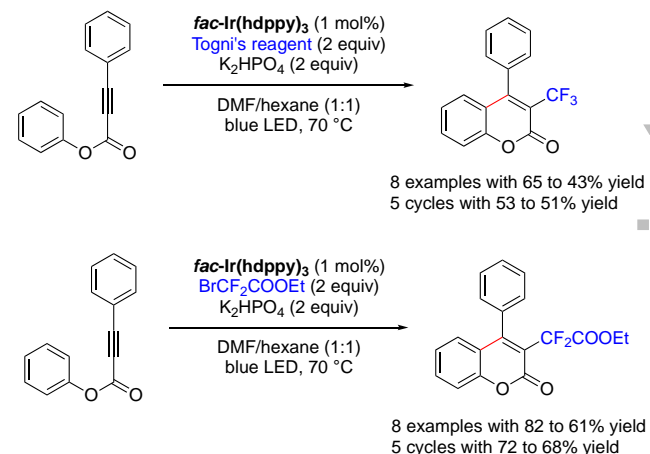

Figure 5. Cyclization to 3-trifluoromethyl-4-phenyl-coumarin (*top*) and cyclization to 3-difluoroacetyl-4-phenyl coumarin (*bottom*) catalyzed by *fac*-Ir(hdppy)₃.

In addition, the recovered upper layer of the Ir species from the initial catalyst into the reaction medium was investigated for the cyclization to 3-trifluoromethyl-4-phenyl-coumarin. After the 1st run and 5th run, the yields of the recovered *fac*-Ir(hdppy)₃ were 95% and 76%, respectively (measured by UV-vis spectroscopy). Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that the recovered yield of the Ir species was 79% after the 5th run. The photocatalyst could be reused up to five times in both reactions without significant loss of activity. These features suggest this recyclable *fac*-Ir(hdppy)₃ would be generally useful for other photo redox reactions.

Bergbreiter *et al.* reported about polyisobutylene (PIB)-bound ruthenium bipyridine [Ru(PIB-bpy)₃]²⁺ metal complexes which were prepared from PIB ligands formed by alkylation of 4,4′-dimethylbipyridine with polyisobutylene bromide (Figure 6).[31]
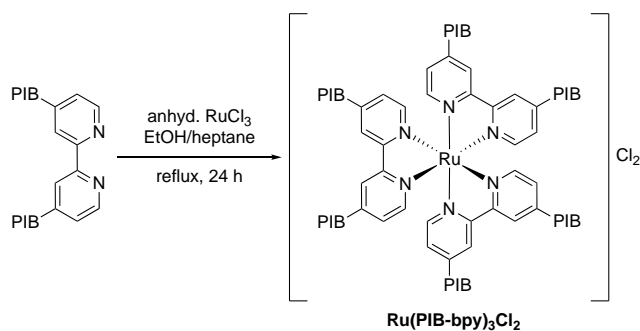
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Figure 6. Synthesis of Ru(PIB-bpy)$_3$Cl$_2$ complex.

The product Ru(PIB-bpy)$_3$Cl$_2$ complexes with at least one PIB ligand per bipyridine unit function as soluble recyclable photo redox catalysts in free radical polymerization of acrylate monomers under visible light irradiation at 25 °C with ethyl 2-bromoisobutyrate as the initiator in the presence of diisopropylethylamine (Figure 7).
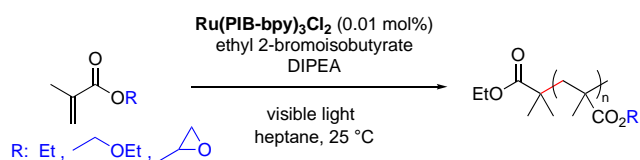

Figure 7. Free radical polymerization of acrylates using Ru(PIB-bpy)$_3$Cl$_2$.

The polyacrylate products contained only about 1 ppm Ru contamination. This PIB-bound catalyst was recyclable and showed about 50-fold less Ru leaching as compared to Ru leaching in a polymerization catalyzed by the low molecular weight Ru catalyst, Ru(bpy)$_3$(PF$_6$)$_2$. Catalyst/product separation is simple and is affected by precipitation of the polymer products, which self-separates the products from the heptane solution of the reusable catalyst. The authors described that the activity, high separability, and phase selective solubility of these PIB-bound Ru species in polymerizations of acrylates suggest that the use of these heptane-soluble supports should be generally useful for these sorts of catalysts in other photo redox processes.

Reiser and co-worker reported the facile synthesis (Figure 8) and application (Figure 9) of a polyisobutylene-polymer-tagged, iridium(III) photocatalyst.[32] The catalytic performance of this complex remains consistently high, while the installed tether allows for its convenient separation from reaction products through a thermomorphic solvent system.
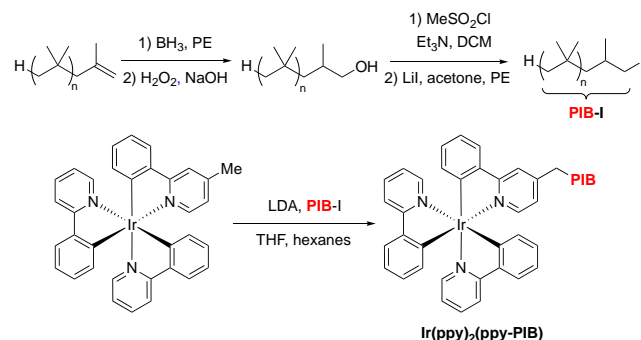

Figure 8. Upper part: synthesis of PIB-I starting from BASF Glissopal® 1000 (4, n ∼ 17). Lower part: synthesis of PIB-tagged Ir-photocatalyst.

Excellent recycling properties were observed both in batch and in flow reactions, and especially in the latter the continuous, automatic recovery and reuse of the catalyst either from a mono- or a biphasic reaction solution is realized, making this approach attractive for large-scale applications. Reiser reported here the synthesis and application of PIB-tagged Ir(ppy)$_2$(PIB-ppy), being the first recyclable version of tris-cyclometalated *fac*-Ir(ppy)$_3$.

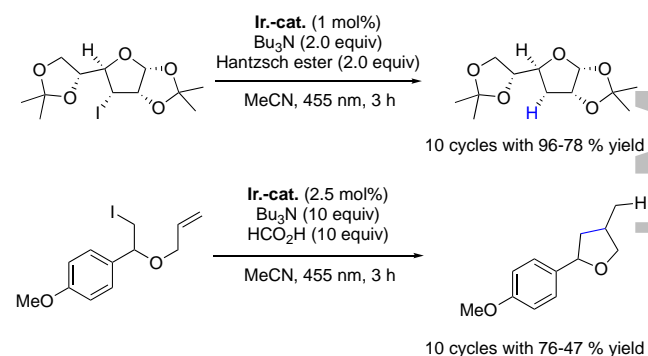**Figure 9.** Deiodation (*top*) and deiodation/cyclization (*bottom*) with recyclable Ir(ppy)$_2$(ppy-PIB).

To demonstrate the feasibility of the mentioned concept, polyisobutylene-tagged Ir(ppy)$_2$(ppy-PIB) was applied to the photochemical deiodation reaction (Figure 9, *top*). PIB-tagged Ir(ppy)$_2$(ppy-PIB) was able to catalyze the reaction essentially with the same efficiency as its non-tagged counterpart *fac*-Ir(ppy)$_3$ and the catalyst was recycled up to ten times. In addition to a simple deiodation, the catalytic performance and recycling capabilities of Ir(ppy)$_2$(ppy-PIB) in the deiodation/cyclization (Figure 9, *bottom*) were examined. Also, here the reusable catalyst variant performed well. The amount of extracted cyclization product is higher due to its less polar nature, nevertheless, the recycling behavior was not impaired.

In 2010 WenXing and co-workers presented a novel thermosensitive photocatalyst, P(NIPA-*co*-ZnMPc), which has been prepared using zinc tetra(*N*-

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carbonylacrylic)aminophthalocyanine (ZnMPc) copolymerized with *N*-isopropylacrylamide (NIPA) (Figure 10).[33] P(NIPA-*co*-ZnMPc) effectively catalyzes the oxidation of 4-chlorophenols using oxygen as oxidant under the visible light irradiation and it has higher photocatalytic activity than ZnMPc under the same condition. The UV-vis spectra of them in aqueous solution indicate that the macromolecular chains in P(NIPA-*co*-ZnMPc) restrain the aggregation of ZnMPc availability, resulting in the enhanced photocatalytic performance. The results of photocatalytic oxidation at different temperatures show that P(NIPA-*co*-ZnMPc) presents the highest photocatalytic efficiency around the lower critical solution temperature (LCST), suggesting that the macromolecular structure of P(NIPA-*co*-ZnMPc) can directly influence their photocatalytic activity. The hydrodynamic radius of this copolymer at different temperatures implies the intermolecular hydrophobic aggregation around the LCST, which is advantageous for the enrichment and the photocatalytic oxidation of 4-chlorophenol. Due to the high stability of P(NIPA-*co*-ZnMPc), it can be cyclically used in homogeneous photocatalytic oxidation and heterogeneous separation[34].
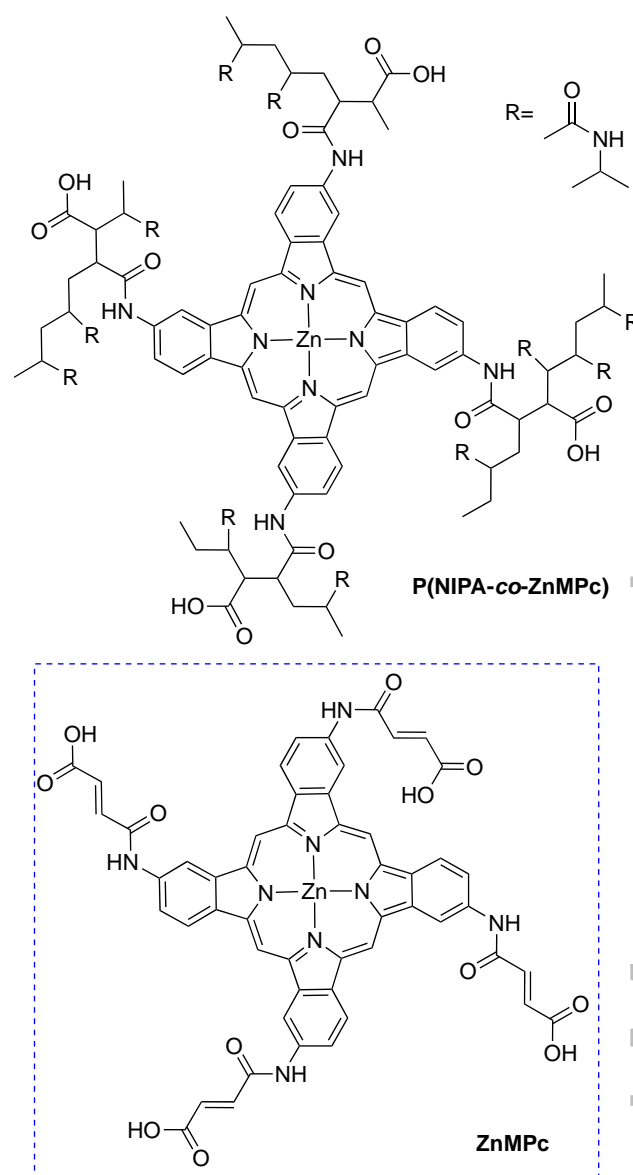

Figure 10. Chemical structures of P(NIPA-*co*-ZnPMPc) and ZnMPc.

Another zinc containing copolymer was again introduced by WangYang, WenXing *et al.*[35] This zinc tetra(methacryoyl moiety)aminophthalocyanine derivative (MeZnAPc) was synthesized by the reaction between zinc tetraaminophthalocyanine (ZnTAPc) and methacryloyl chloride (Figure 11). Atom transfer radical polymerization (ATRP) was employed as the polymerization technique to obtain a novel pH-responsive polymeric photosensitizer (PEG$_{110}$-*b*-P(DPAn-*co*-MeZnAPcm)) by copolymerizing of methoxypolyethylene glycols (mPEG) (as reducing agent), 2-(isopropylamino)ethyl methacrylate (DPA) and MeZnAPc. The results indicated that the photosensitizer presented the well pH-responsive behavior around the pH range 6.0 - 6.5 and the high photoactivity to 1,3-diphenylisobenzofuran (DPBF).
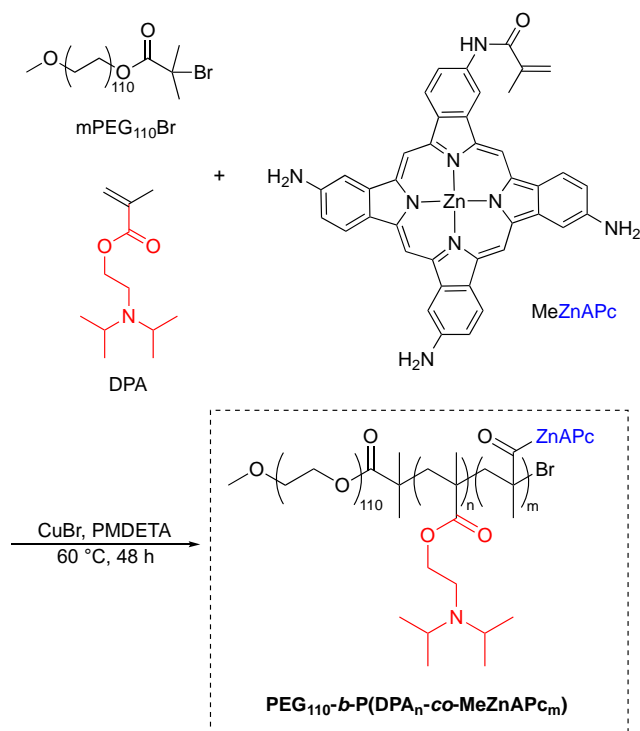
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Figure 11. Synthesis of (PEG$_{110}$-*b*-P(DPA$_n$-*co*-MeZnAPc$_m$)).

The result of photocatalysis oxidation of L-tryptophan (L-Try) suggested that zinc phthalocyanine could present high photoactivity due to its dispersity at pH 5.5 without formation of micelles, and its photoactivity decreased dramatically at pH 7.4 due to wrapping ZnTAPc into the micelles. Therefore, the novel pH-responsive polymeric photosensitizer has better application prospects in the field of photodynamic therapy.

The combined use of the photosensitizer and the cobalamin derivative as the binuclear Ru^{II}–Co^{II} complex for the photo redox catalytic system was first reported by Walder *et al.*[36] Hisaeda and co-workers presented a hybrid polymer synthesized by radical polymerization of a cobalamin derivative (vitamin B$_{12}$, VB$_{12}$) and a Ru(bpy)$_3$ complex having styrene moieties in each peripheral position (VB$_{12}$: Ru : styrene = 1 : 1 : 98), and the hybrid polymer showed photocatalytic activity for molecular transformation with visible light irradiation (Figure 12). The catalytic reaction was carried out using phenethyl bromide as a substrate. After 24 h with visible light irradiation, most of the phenethyl bromide was converted to ethylbenzene and styrene in 82% and 8% yields, respectively.
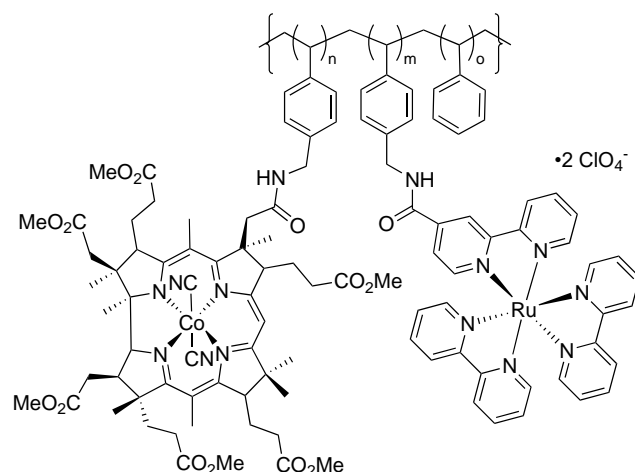

Figure 12. Photocatalytic copolymer based on cobalamin derivative (VB$_{12}$) and a Ru(bpy)$_3$ complex.

The reaction did not proceed under dark conditions. In contrast, the conversion of phenethyl bromide was decreased to 66% when they used a 1:1 mixture of the Ru complex Ru(bpy)$_3$]Cl$_2$ and VB$_{12}$ catalyst. Intramolecular electron transfer from the Ru complex to VB$_{12}$ should be accelerated in the polymer. Of course, the reaction did not proceed when they used the Ru complex or VB$_{12}$ catalyst alone.
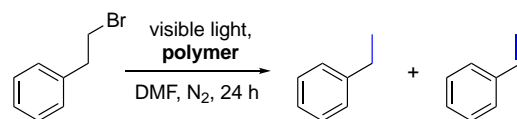

Figure 13. Photodehalogenation of phenylethyl bromide catalyzed by the polymer shown in Figure 12.

To emphasize this polymer-supported effect, a catalytic reaction was carried out at a more dilute concentration. Under this condition, the effect of the polymer was clearly observed compared to the previous condition, and the reaction efficiency of the polymer system was dramatically enhanced compared to that of the non-polymer system. The present system is economical in reducing the amount of catalyst, and, therefore, would be readily applicable to the design of an eco-friendly catalyst.[37]

The copolymer (VB$_{12}$-BVIm-Ru polymer) was synthesized from the corresponding monomers VB$_{12}$, Ru(bpy)$_3$ derivative and the ionic liquid monomer [BVIm]Cl by radical polymerization using AIBN as the initiator (Figure 14). The first two monomers have a styrene moiety with an amide linkage to the VB$_{12}$ and ruthenium trisbipyridine complexes.[38] By immobilizing a VB$_{12}$ complex and a Ru(II) trisbipyridine photosensitizer in a polymerized ionic liquid (PIL), a visible light-driven photocatalyst was developed. The Ru(II) trisbipyridine photosensitizer in the copolymer showed an enhanced emission compared to that of the monomer in the ionic liquid, 1-butyl-4-methylimidazolium

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bis(trifluoromethanesulfonyl)amide. The copolymer showed an enhanced photocatalytic activity in various ionic liquids for 1,1-bis(4-chloro- phenyl)-2,2,2-trichloroethane (DDT) dechlorination with ∼ 99 % conversion after visible light irradiation for 2 h and a relatively higher quantum yield compared to the monomer mixture in the ionic liquid due to the rigidochromic effect of the polymer. Furthermore, both the VB$_{12}$ catalyst and photosensitizer in the polymer were easily recycled for use with the ionic liquid solvent without any loss of catalytic activity, thus this catalytic system is environmentally friendly.
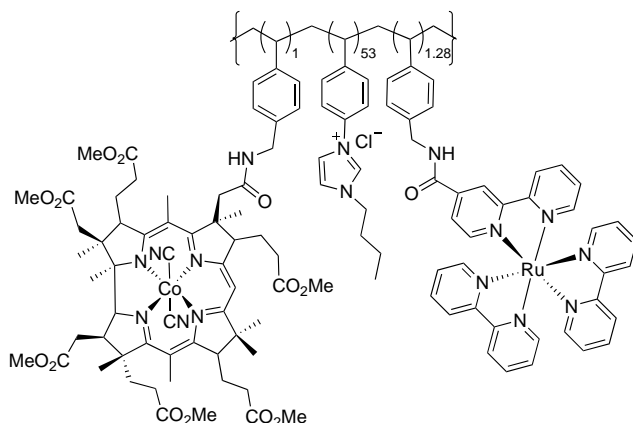

Figure 14. Photocatalytic active VB$_{12}$-BVIm-Ru copolymer.

3 Heterogeneous Photocatalysts

Kobayashi *et al.* successfully immobilized an iridium-based polypyridyl complex, through the use of the well-established suspension polymerization method (Figure 15), and demonstrated its effectiveness as a visible light photocatalyst for the aerobic cross-dehydrogenative coupling (CDC) reaction between *N*-aryl tetrahydroisoquinolines and various P–H nucleophiles under visible light irradiation (Figure 16).[27]
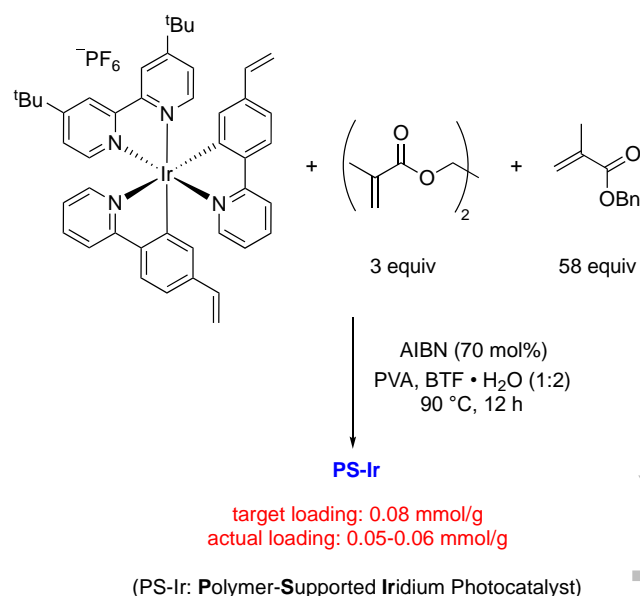

target loading: 0.08 mmol/g
actual loading: 0.05-0.06 mmol/g

(PS-Ir: **P**olymer-**S**upported **Ir**idium Photocatalyst)

Figure 15. Immobilization of monomeric iridium complex via suspension polymerization.

It was found that the catalyst could be reused at least four times without a noticeable loss of catalytic activity with minimal levels of iridium leaching (0.1-0.3% leaching).
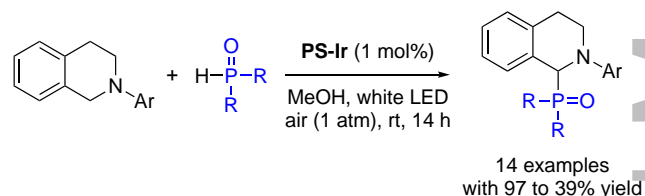

14 examples
with 97 to 39% yield

Figure 16. Cross-dehydrogenative coupling reaction catalyzed by **PS-Ir**.

Lin and co-workers reported a successful incorporation of the Ru and Ir phosphors into robust PCPs by cobalt carbonyl-mediated cyclotrimerization reaction of the end alkyne groups on the monomers (Figure 17).[39] The resultant framework materials are stable in various solvents, including concentrated hydrochloric acid, and are thermally and oxidatively stable in air up to 350 °C and are highly active in catalyzing visible light-driven aza-Henry reactions (Table 1) between nitromethane or nitroethane and tertiary aromatic amines, α-arylation of bromomalonate via intermolecular C-H functionalization, and oxyamination of an aldehyde with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO).
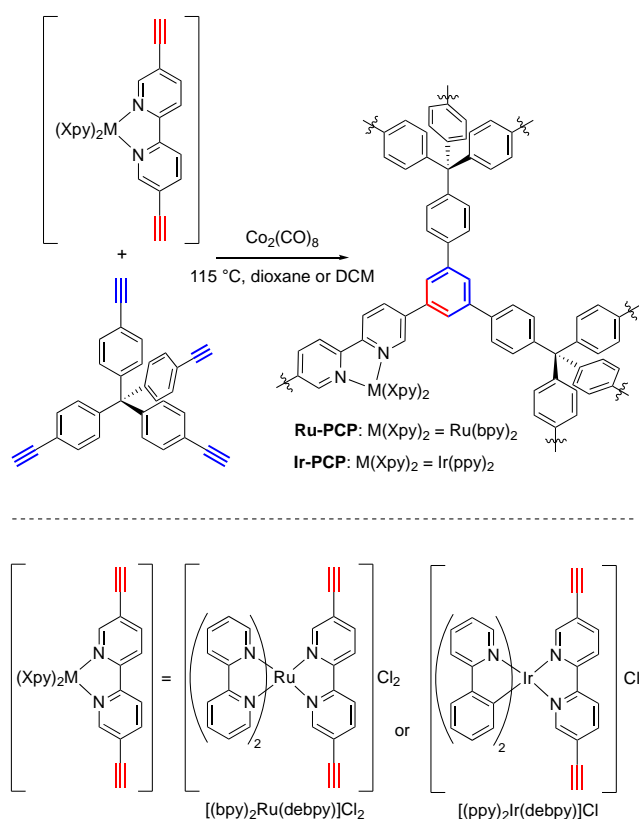
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Figure 17. Synthesis of **Ir-PCP** and **Ru-PCP** by a cobalt-catalyzed cyclotrimerization reaction.

Excellent yields, mostly >90%, similar to the metal-catalyst monomer counterparts, were reported. Interestingly, most of the PCP-catalyzed aza-Henry reactions had higher conversions than those catalyzed by their homogeneous counterparts. They also examined in their work the recyclability and reusability of the PCP catalysts. **Ir-PCP** and **Ru-PCP** were readily recovered from the reaction mixtures via simple filtration.
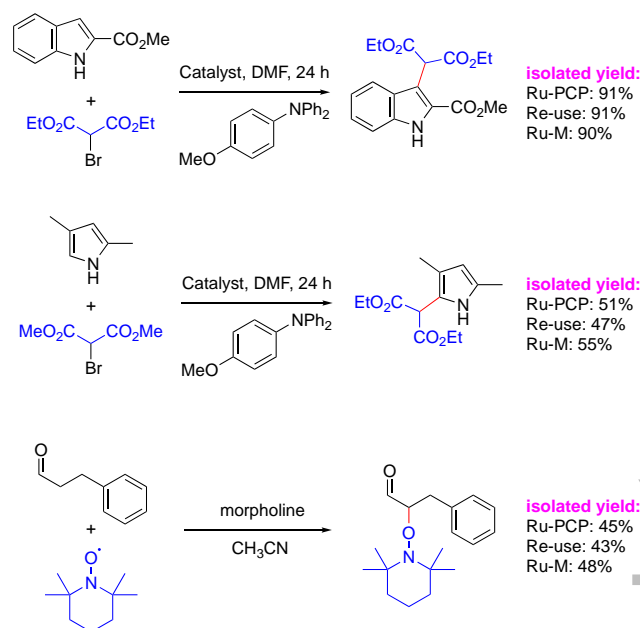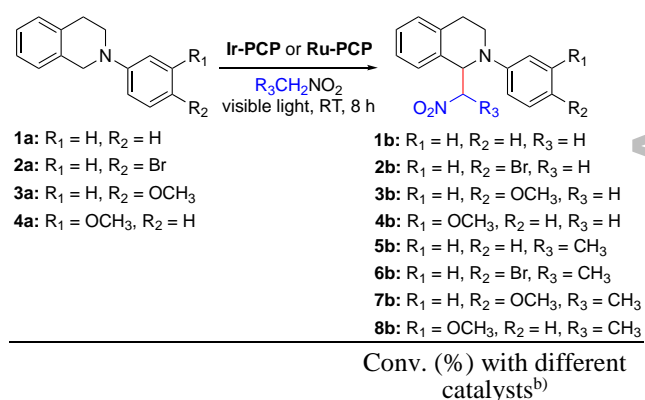

Figure 18. **Ru-PCP**-catalyzed α-arylation of bromomalonate and oxyamination of 3-phenylpropanal. The **Ru-PCP** catalyst was readily recovered and reused for these reactions.

The recovered catalyst showed no deterioration of conversion for aza-Henry reactions after recycling four times. Furthermore, UV-vis analysis of the supernatant showed no sign of Ir/Ru complex leaching into the solution. This is further supported by the absence of Ir or Ru in the supernatants of the PCP-catalyzed reaction mixtures by ICP-MS. They also demonstrated the applicability of the PCP photocatalysts in other visible light driven reactions. **Ru-PCP** efficiently catalyzed the α-arylation of bromomalonate via direct intermolecular C-H functionalization as well as oxyamination of 3-phenylpropanal, with isolated product yields comparable to those of the homogeneous control catalyst.

Table 1. Photocatalytic aza-Henry reactions.[a]

1a: R_1 = H, R_2 = H
2a: R_1 = H, R_2 = Br
3a: R_1 = H, R_2 = OCH$_3$
4a: R_1 = OCH$_3$, R_2 = H

1b: R_1 = H, R_2 = H, R_3 = H
2b: R_1 = H, R_2 = Br, R_3 = H
3b: R_1 = H, R_2 = OCH$_3$, R_3 = H
4b: R_1 = OCH$_3$, R_2 = H, R_3 = H
5b: R_1 = H, R_2 = H, R_3 = CH$_3$
6b: R_1 = H, R_2 = Br, R_3 = CH$_3$
7b: R_1 = H, R_2 = OCH$_3$, R_3 = CH$_3$
8b: R_1 = OCH$_3$, R_2 = H, R_3 = CH$_3$

| Entry | Amine substrate | Product | Conv. (%) with different catalysts[b] | | | |
			Ir-M	Ir-PCP	Ru-M	Ru-PCP
1	**1a**	**1b**	99	94	85	90

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2	**2a**	**2b**	99	97	84	87
3	**3a**	**3b**	81	91	90	>99
4	**4a**	**4b**	79	98	65	85
5	**1a**	**1b**	94	94	81	84
6	**2a**	**2b**	73	75	57	78
7	**3a**	**3b**	86	97	62	95
8	**4a**	**4b**	66	86	76	91

[a] All the reactions were run at room temperature for 8 h with 1 mol% Ir-based catalyst or 0.2 mol% Ru-based catalyst. [b] Conversions were determined by integrating the ^{1}H NMR spectra. Ir-M and Ru-M are Ir monomer [(ppy)$_2$Ir(debpy)]Cl and Ru monomer [(bpy)$_2$Ru(debpy)]Cl$_2$, respectively. [c] With nitromethane as solvent. [d] With nitroethane as solvent.

The **Ru-PCP** catalyst could be readily recovered and reused for all of these reactions with no or little drop in the isolated yields of the products (Figure 18). These results illustrate the generality of the phosphorescent PCP materials in catalyzing photo-driven organic transformations. The ability to recover and reuse such heterogeneous PCs can not only eliminate the contamination of organic products by trace amounts of heavy metals but also reduce processing and waste disposal costs in large-scale reactions.

Lin and co-workers also reported two different cross-linked polymers based on Ru(bpy)$_3^{2+}$ chromophores with tetra-alkynyl substituents at 4,4'- or 5,5'-position of two bipyridine moieties. These were synthesized through Eglinton alkyne homocoupling (Figure 19) with high yields and extremely high chromophore loadings (ca. 90%).[40] TEM images of both **Ru-CP1** and **Ru-CP2** showed that they are aggregates of spherical nanoparticles of ca. 100 nm in diameter and act as insoluble but dispersible photosensitizers by taking advantage of redox-active ^{3}MLCT excited states of the chromophores. Steady-state UV-vis absorption and emission spectra and time-resolved phosphorescence spectra were recorded, and they showed a broad absorption between 300 and 800 nm with two or three additional discernible absorption bands. Compared with Ru-1 and Ru-2, the ^{1}MLCT peaks in **Ru-CPs** 1 and 2 became broadened and showed a slight redshift, which is beneficial for absorbing the solar radiation. In the steady-state phosphorescence spectra, the emission maximum λ_{max} centered at 705 nm for **Ru-CP1** and at 696 nm for **Ru-CP2**.
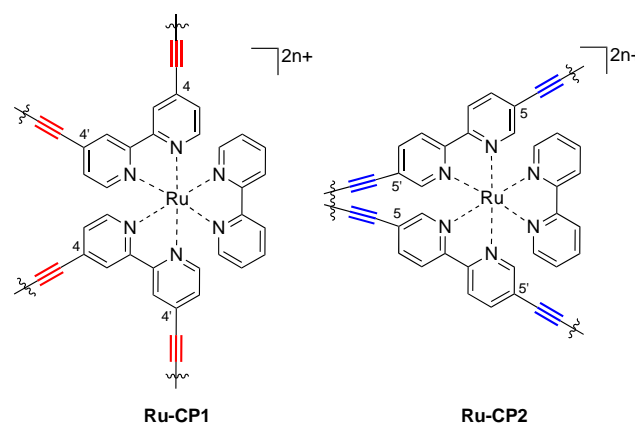

Figure 19. Schematic representation of **Ru-CP1**- and **Ru-CP2**-containing polymers.

Interestingly, the phosphorescence maximum λ_{max} of **Ru-CP1** exhibited obvious redshift in comparison with that of monomer Ru-1 owing to the increased effective conjugation length of ligands in **Ru-CP1** and aggregation of **Ru-CP1** in the particle. The PCPs are almost nonporous with small surface areas based on the nitrogen adsorption experiments at 77 K but efficiently catalyze a range of organic transformations (aza-Henry reaction, aerobic oxidative coupling of amine, and reductive dehalogenation reaction) in the presence of visible light. The yields for the CPs were again higher than that of the monomers and also higher than those reported for the cyclotrimerization-obtained PCPs. The excellent photocatalytic activities are attributed to high content of light-absorbing Ru(bpy)$_3^{2+}$ chromophores as well as excited-state energy migration from the chromophores in the interior of the polymer particle to the reactive sites on the surface of the polymer particle.

Nonporous, phosphorescent cross-linked polymers (**Ru-CP3** and **Ir-CP**) were synthesized via Pd-catalyzed Sonogashira cross-coupling reactions between tetrakis(4-ethynylphenyl)methane and dibrominated Ru(bpy)$_3^{2+}$ or Ir(ppy)$_2$(bpy)$^+$, respectively (Figure 20).[41] The resultant particulate cross-linked polymer materials have very high catalyst loadings (76.3 wt.% for **Ru-CP3** and 71.6 wt.% for **Ir-CP**) and are nonporous with negligibly small surface areas. Transmission electron microscopy (TEM) images showed that **Ru-CP3** and **Ir-CP** are composed of interconnected nanoparticles with dimensions of 100-200 nm and the particles were stable up to 300 °C in air. The cross-linked polymers were insoluble in water and all the organic solvents evaluated. Despite their nonporous nature, the insoluble CP materials served as highly active and recyclable heterogeneous PCs for a range of organic transformations such as aza-Henry reaction, aerobic amine coupling, and dehalogenation of benzyl bromoacetate. The **Ru-CP3** is a highly effective PC for all the six aza-Henry reactions with 88% to >99% conversions at 0.2 mol% **Ru-CP3** loadings. It was also easily recovered from the reaction mixture by centrifugation and reused four times without any loss of activity. At 1 mol% loading,

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Ru-CP3 efficiently catalyzed aerobic oxidative coupling of a series of primary amines with 84-99% conversions in 1 h, again comparable with that of the homogeneous catalyst. These conversions are higher than those of the homogeneous counterparts.
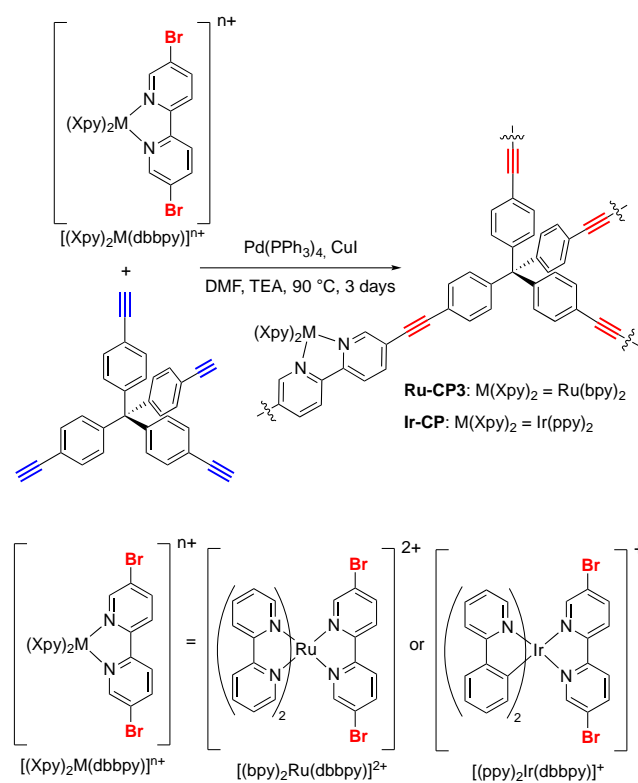

Figure 20. Synthesis of **Ru-CP3** and **Ir-CP** by Pd-catalysed Sonogashira cross-coupling reaction.

The recovered catalyst after simple filtration was reused three times, showing no deterioration in conversion percentage. Similarly, a visible light-driven dehalogenation of benzyl bromoacetate catalysed by 1 mol% **Ru-CP3** catalyst also gave complete substrate transformation in 8 h. The efficiency of this system is described as a light-harvesting mechanism, which involves collection of photons by exciting the ^{3}MLCT states of the phosphors and migration of the excited states to the particle surface. This is proposed to account for the very high catalytic activities of these nonporous CPs.

Li *et al.* developed a convenient strategy for the preparation of iridium(III)-complex-connected porous organic polymers.[42] The synthesis of two highly stable [Ir(ppy)$_2$(d^{t}bbpy)]$^+$ (ppy: phenylpyridine, d^{t}bbpy: 4,4′-di(*tert*-butyl)-2,2′-bipyridine)-linked porous organic polymers, **Ir-POP-1** and **Ir-POP-2**, from Pd-catalyzed coupling reactions of a tetrakisphenyl-methane borate and two [Ir(ppy)$_2$(d^{t}bbpy)]$^+$- derived bromides (Figure 21).
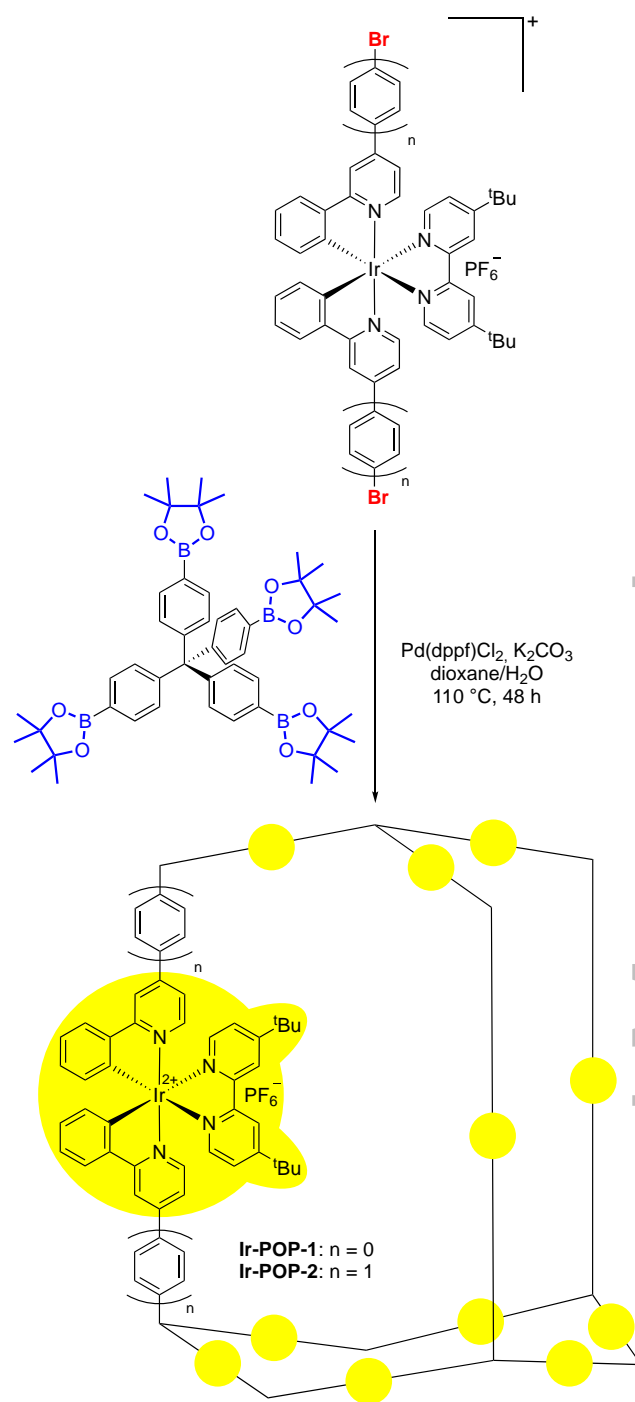

Figure 21. The synthesis of polymers **Ir-POP-1** and **Ir-POP-2**.

Both polymers were insoluble in common solvents including water, DMF, DMSO, acetonitrile and acetone, whereas the controls of the non-polymerized equivalents were soluble in the above organic solvents. Thermogravimetric analyses revealed that the two polymers were stable up to 350 °C (10% weight loss).
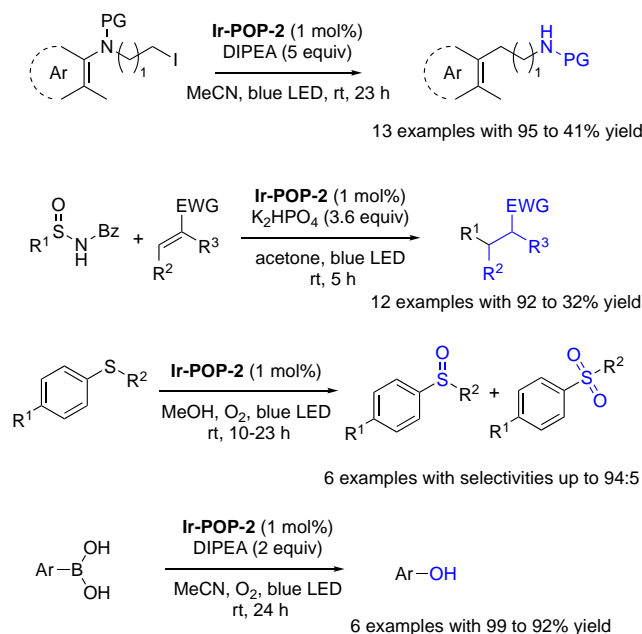
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Figure 22. Rearrangement of alkyl iodides to form the related alkylamines (first), conjugate addition between *N*-benzoyl alkylsulfinamides and Michael acceptors (second), photocatalytic oxidation of sulfides (third) and photocatalytic hydroxylation of arylboronic acids catalyzed by **Ir-POP-2**.

The permanent porosities of **Ir-POP-1** and **Ir-POP-2** were investigated by nitrogen sorption measurement at 77 K. Their Brunauer–Emmett–Teller (BET) surface areas were determined to be 29 and 124 m^2 g^{-1}, respectively. The value of **Ir-POP-2** was significantly larger than that of **Ir-POP-1**, which was consistent with the elongated linkers of its backbone and suggested that **Ir-POP-2** might exhibit higher photocatalytic activity.

Indeed, **Ir-POP-2**, exhibited highly efficient heterogeneous photocatalytic activity for a broad-scope of organic transformations including intramolecular Smiles-Truce rearrangement of alkyl iodides, desulfurative conjugate addition for the C–C bond formation and aerobic oxidations of sulfides and arylboronic acids to form sulphones and phenols (Figure 22). For all the transformations, the new porous photocatalyst exhibits very high or previously unattainable recyclability. It is worth noting that, for all the organic transformations, **Ir-POP-2** containing an identical amount of the iridium complex exhibits heterogeneous photocatalytic activities that are comparable with those of the homogeneous prototype complexes. Thus, they propose that the new catalytic polymer possesses pores that are large enough to allow electron transfer between the embedded, excited iridium complexes and discrete organic substrates. The work demonstrated that transition-metal complex-

embedded in porous organic polymers can achieve extremely high stability of the backbones and high recyclability, a key feature for sustainable heterogeneous catalysis.

A novel and versatile advance toward recycling was developed by Díaz, Reiser *et al*.[28] A pumping setup was developed based on the use of a swellable/shrinkable cross-linked polymer material. The organo-/hydrogel was made of poly(ethylene glycol) methyl ether methacrylate (PEGMA) with 3-azidopropyl methacrylate (AzpMA) as monomers and di(ethylene glycol) dimethacrylate (DEGDMA) as the cross-linking moiety. This platform enabled the grafting of an Ir catalyst (Ir(ppy)$_2$(h5yppy)) containing an alkyne group via an alkyne-azide [3 + 2] click reaction (Figure 23). It is worth mentioning that this represented a novel recycling pumping mechanism in the field (**Fehler! Verweisquelle konnte nicht gefunden werden.**).
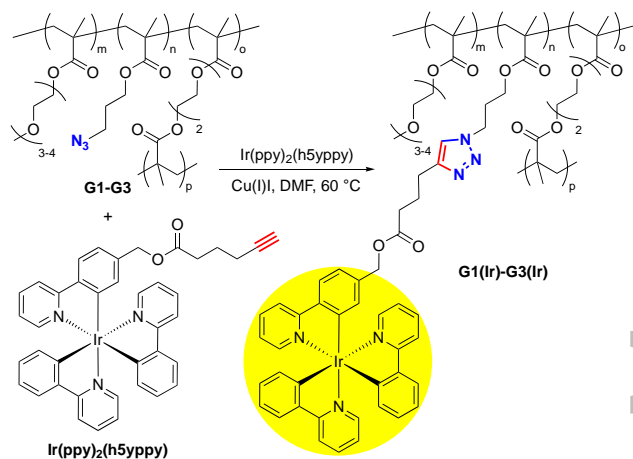

Figure 23. Synthetic approach towards the crosslinked polymers **G1-G3(Ir)**.

The gel-immobilized catalysts allowed a convenient setup to carry out catalytic reactions making use of the swelling/ deswelling properties of the material. In the loading step, the substrates, which were pre-dissolved in a polar solvent like DMF, DMSO, CH$_3$CN or H$_2$O were added to a septum closed vial containing the cross-linked polymer gel (**G1–3(Ir)**) with a syringe, upon which the gel soaked and swelled to its maximum capacity. In the reaction step, the gel system was subjected to irradiation, initiating the reaction inside the pores of the swollen material. Subsequently, the gel was washed several times with a 1:1 mixture of acetone/hexanes to collect the products by simple diffusion and deswelling of the material. In the last step, the gel material was subjected to vacuum for drying and shrinking to its original form, closing one pumping cycle routine.
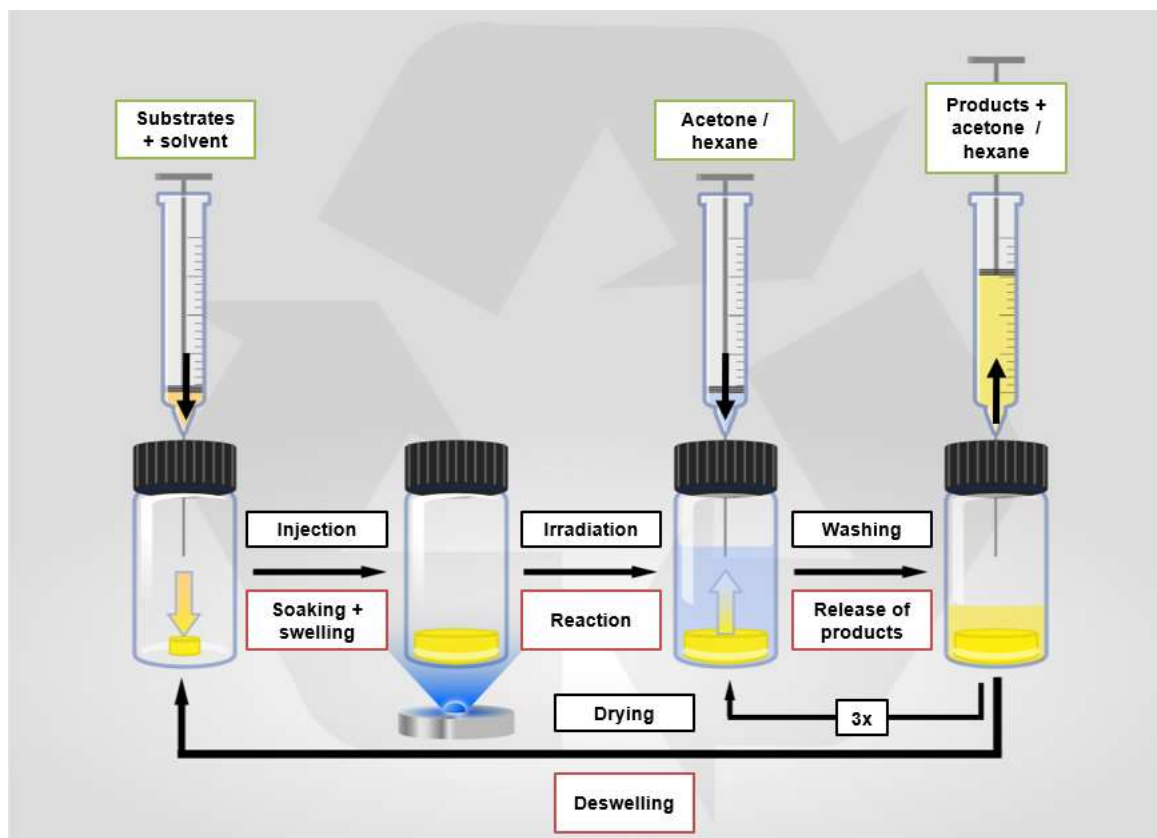
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Figure 24. Pumping recycling setup for the iridium catalysts immobilized on cross-linked polymer gel support.

To benchmark the gel catalysts, the photocatalytic *E* to *Z* isomerization (Figure 25, *top*) reaction and a [2 + 3] cycloaddition (Figure 25, *bottom*) with a benzyl azide and an unstrained alkene was evaluated, which takes place inside of the pores of the solid material. The reactions were comparable to those performed in solution with homogeneous Ir(ppy)$_3$ with respect to yields and reaction times but did not require an inert atmosphere. Recycling and reuse of the catalytically active cross-linked organogel were possible for up to 5 cycles, being determined by catalyst leaching (5-16% per cycle), which represents the major limitation of the approach.
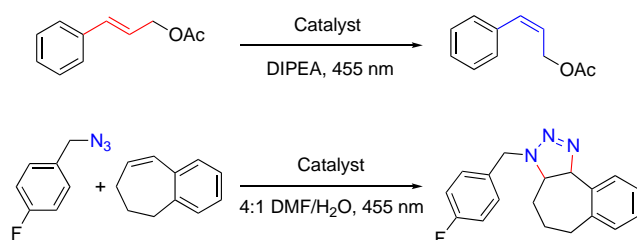
ambient temperature by employing visible light photocatalysis by Choi *et al*.[43] By simply coating a layer of Nafion onto SiO$_2$ particles, the cationic Ru(bpy)$_3^{2+}$ dye can be bound onto SiO$_2$/Nf through electrostatic attraction as shown in Figure 26. Successful polymerization of methacrylates (methyl-MA, butyl-MA, cyclohexyl-MA, benzyl-MA and glycidyl-MA) using α-bromoisobutyrate as an initiator and using household fluorescent lamp as a light source was realized. The Nafion coated silica immobilized ruthenium catalyst could be easily prepared, recycled and reused many times without loss of catalytic activity.
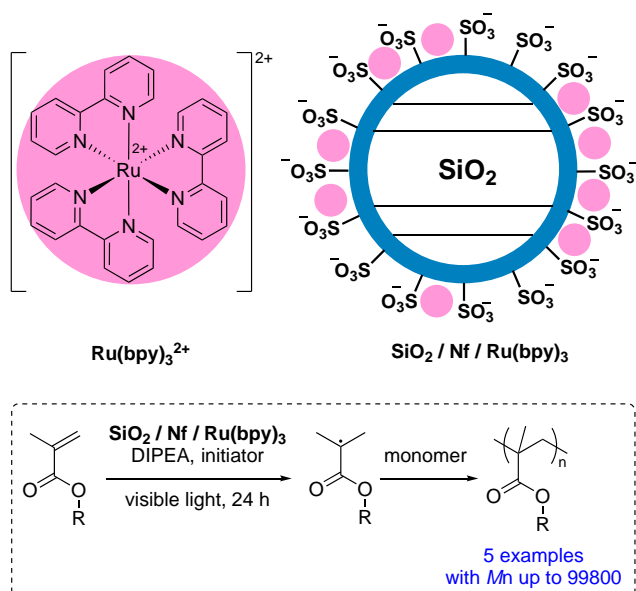

Figure 25. Isomerization (*top*) and [2+3] cycloaddition (*bottom*) reactions using **G(Ir)**.

A recyclable and stable ruthenium catalyst immobilized onto silica was developed (Figure 26) for photo-initiated free radical polymerization under

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Figure 26. Illustration of immobilized ruthenium complex catalyst on Nafion polymer coated silica support (*top*). Free radical polymerization of methyl methacrylates via visible light photocatalysis using Nafion coated silica immobilized ruthenium catalyst (*bottom*).

The proposed mechanism for these transformations starts with $Ru(bpy)_3^{2+}$ confined in the Nafion layer being excited to $Ru(bpy)_3^*$ upon absorbing a visible light photon, which is reductively quenched by a sacrificial electron donor DIPEA to generate a powerful single electron reductant $Ru(bpy)_3^+$ ($E_0 \approx -1.09$ V_{NHE} in CH_3CN). The strong reductant $Ru(bpy)_3^+$ removes the bromide from the initiator, to generate a carbon-centered radical species. The $Ru(bpy)_3^+$ reductant is then oxidized to $Ru(bpy)_3^{2+}$ again in the photo redox cycle. This explains why the $Ru(bpy)_3^+$ shows higher TONs on the photocatalytic initiation radicals. The photo-generated carbon-centered radicals can further react with methacrylate monomer to initiate the polymerization process. The immobilized to $Ru(bpy)_3^{2+}$ catalyst could be easily separated from polymer solution by centrifugation for reuses. Importantly, this process also can be performed using almost any source of visible light, including both fluorescent light bulbs and ambient sunlight. The present heterogeneous photocatalytic transformation of organics can be used as an easy, convenient, and economic process as an alternative to the traditional thermal or photo-based free radical initiation methods in a series of radical-mediated organic reactions.

Ishida *et al.* synthesized periodic mesoporous organosilica (PMOs) containing the visible-light photosensitizer (Ru(PS)) and the catalyst (Ru(Cat)) for CO_2 reduction as the heterogeneous photocatalysts (**Fehler! Verweisquelle konnte nicht gefunden werden.**).[44] The Ru(PS) and Ru(Cat) units were embedded in PMO by coordination with the bipyridyl ligands consisting of the pore wall of the PMO. The molar fractions (x and y) of the Ru(PS) and Ru(Cat) units were estimated with EDX measurements and CO quantification in the photo-decarbonylation, respectively.
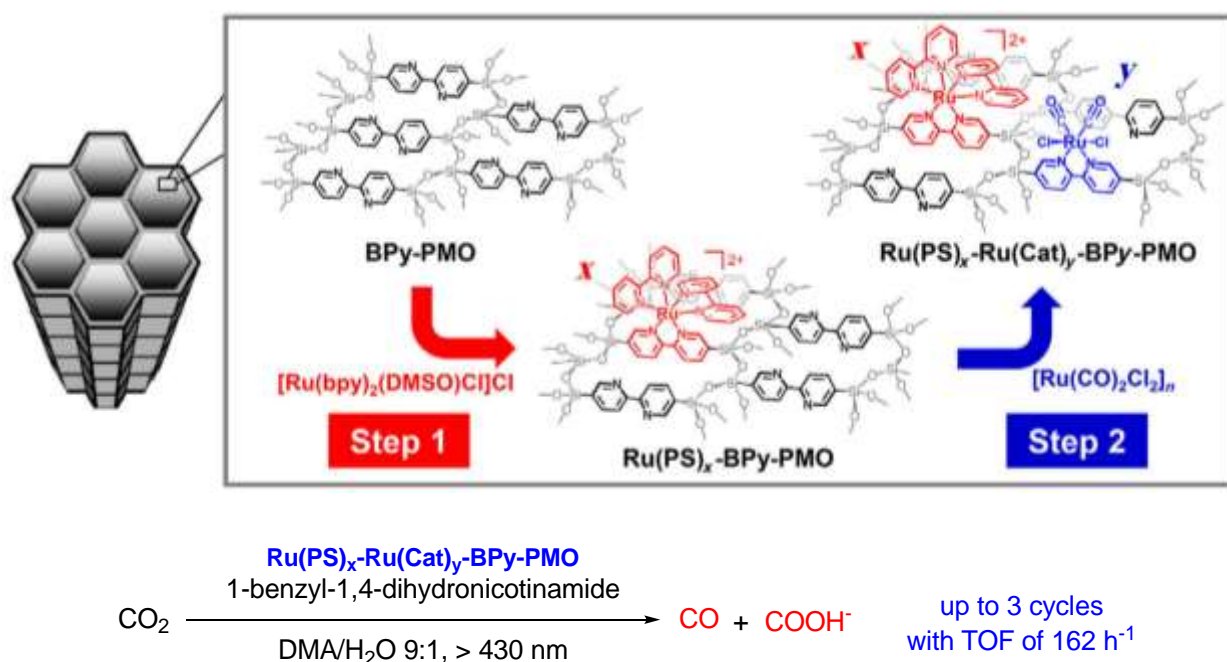

Figure 27. Schematic representation of two-step synthesis for **Ru(PS)$_x$-Ru(Cat)$_y$-BPy-PMO**, in which x and y represent the molar fractions of the Ru(PS) and Ru(Cat) to the whole bipyridyl units of BPy-PMO, respectively (*top*). Photochemical CO_2 reduction by Ru(PS)$_x$-Ru(Cat)$_y$-BPy-PMO (*bottom*). Reprinted with permission from reference [30]. Copyright John Wiley and Sons, 2017.

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The novel ruthenium modified PMOs were further characterized by TEM and XRD measurements, which showed that they maintained the periodic mesoporous structures. The photochemical reduction catalyzed by **Ru(PS)$_x$-Ru(Cat)$_y$-BPy-PMO** was evaluated in the presence of 1-benzyl-1,4-dihydronicotinamide (BNAH) as the electron donor in CO_2-saturated DMA/water (9:1 v/v). The catalysts efficiently reduced CO_2 to yield CO and formate. We found that the ratios (x/y) of the molecular fractions of the Ru(PS) and Ru(Cat) units affected the product selectivity (CO/HCOO$^-$). In addition, the recycling experiments showed that **Ru(PS)$_x$-Ru(Cat)$_y$-BPy-PMO** has high durability in repeated photocatalytic CO_2 reduction.

Duan and co-workers published a consecutive photo-induced electron-transfer (conPET) process found with perylene diimide (PDI) which overcomes the limitation of visible-light photocatalysis. By the incorporation of PDI into a metal-organic polymer **Zn-PDI**, a heterogeneous approach was achieved to tackle the poor solubility and strong tendency to aggregate of the PDIs that restricted the exploitation of this outstanding homogeneous process.[45] The interaction between metal-PDI coordination and $\pi\cdots\pi$ stacking of the organized PDI arrays in Zn-PDI facilitates the conPET (**Fehler! Verweisquelle konnte nicht gefunden werden.**) process for the visible light-driven reduction of aryl halides (-I, -Cl, -Br) by stabilizing the radical-anion intermediate and catalyst-substrate interacted moiety and C-H aromatic substitution (-I, -Cl, -Br) with *N*-methyl pyrrole (Figure 29).
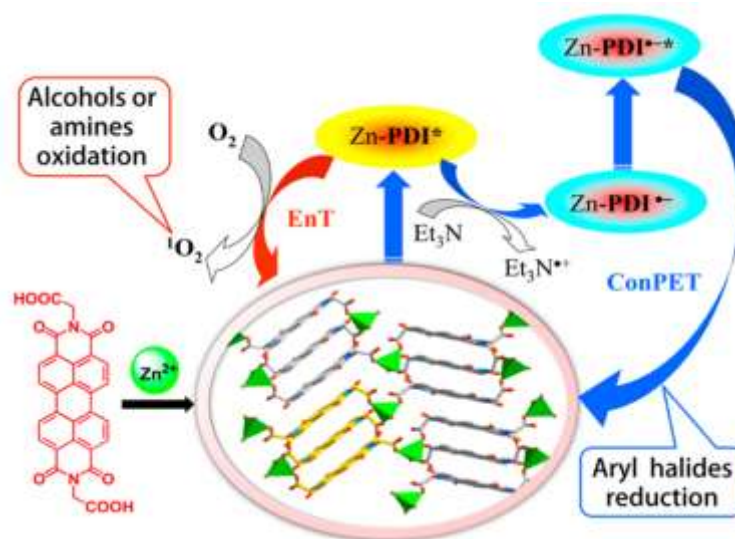

Figure 28. Diagram illustrating the strategy of assembling insoluble PDI into organized arrays in porous solid **Zn-PDI** to obtain an efficient photocatalyst for the visible-light-driven reduction of aryl halides and oxidation of alcohols and amines. Reprinted with permission from [31]. Copyright American Chemical Society, 2016.

The organized arrangement of PDI J-aggregates provides sufficient active sites, leaving enough space for substrate-catalyst interaction, and decreased self-quenching, making **Zn-PDI** a better catalyst than its homogeneous counterpart for the significant visible-light-driven reduction of aryl halides. These synergistic effects between the PDI arrays and Zn sites further render **Zn-PDI** photoactivity for fundamental oxidation of benzyl alcohols and amines.
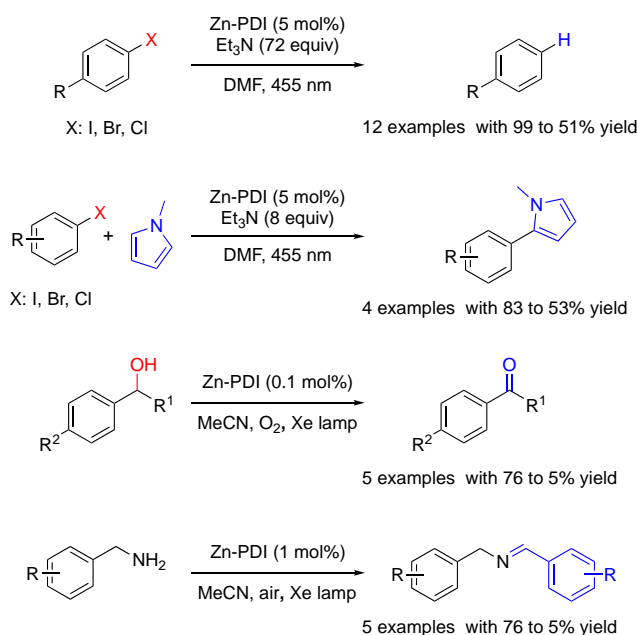
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Figure 29. Photoreduction of various aryl halides by **Zn-PDI** and C-H aromatic substitution with *N*-methyl pyrrole. Photooxidation of benzyl alcohols and amines by **Zn-PDI** due to the synergistic interaction between PDI stacks and Zn Nods.

4 Conclusions

During the last decade we have witnessed the immense growing that visible light photo redox catalysis has experienced. The organic chemistry community has dedicated most of the efforts towards the development of the design of new photocatalysts with adequate redox properties in their excited states, permitting to expand the reactivity window. Synthetic approaches that are difficult or inaccessible by conventional nonphotochemical transformations can be successfully achieved by employing appropriate photocatalysts and therefore to foster new synthetic routes. In this context, inorganic semiconductors, organic dyes or transition-metal based complexes have been found to act as efficiently photocatalysts under visible light irradiation. In particular, organometallic complexes based on iridium or ruthenium meet perfectly with the requisites to photocatalyze a widespread chemical transformation. Despite the fact that they have a notable impact on the environment due to almost negligible degradation, the high cost limits their utility for large scale procedures. To circumvent this drawback, research focusing on their recycling and reuse has attracted considerable attention from an environmental and an economical viewpoint. As a matter of fact, immobilization of these expensive transition-metal complexes with special attention of photoactive iridium or ruthenium derivatives in polymers to be further recovered in different photoreactions appears to be a potential approach. Therefore, this review has covered the endeavours towards the development on the preparation of new homogeneous/heterogeneous metal-containing

polymer-attached photocatalyst systems as well as the strategies for their successfully recovery and reuse. This has allowed to span some photoreactions that was otherwise impossible to achieve with the transition-metal complex photocatalyst alone. These chemical and technological advances have complemented past and existing activities in photo redox catalysis. Thus, enormous chances as well as challenges are still present for fabricating novel catalytic systems with superior efficiency in the photochemical transformations. Consequently, synthesis of novel recyclable photocatalysts and their application in photo redox catalysis will be always welcomed.

Acknowledgements

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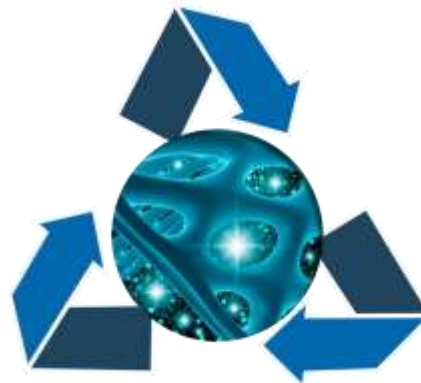[12] L. E. Oi, M. Y. Choo, H. V. Lee, H. C. Ong, S. B. A. Hamid, J. C. Juan, *RSC Adv.* **2016**, *6*, 108741–108754.

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REVIEW

Recyclable, Immobilized Transition-Metal
Photocatalysts

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