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Development of Heterogeneous photocatalysts by the covalent grafting of metal complexes onto various solid supports

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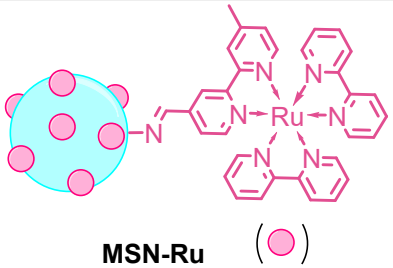
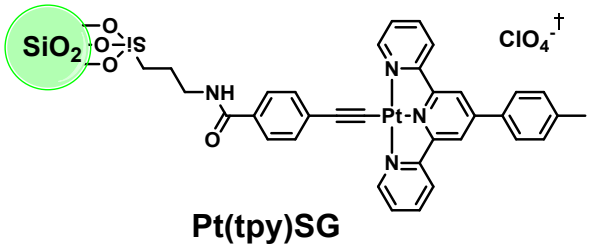
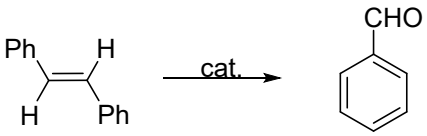
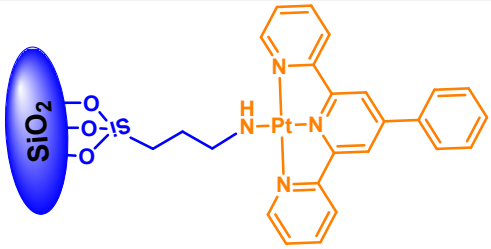
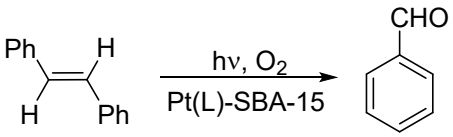
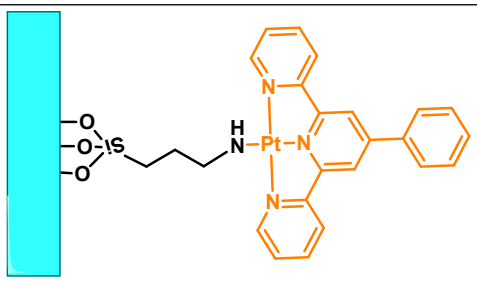
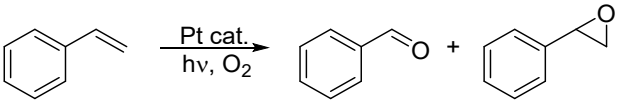
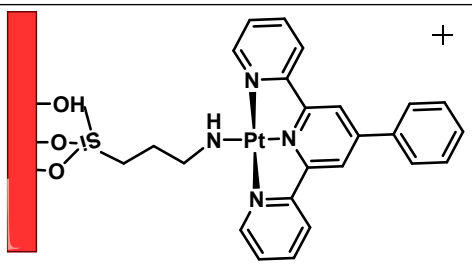
Abstract

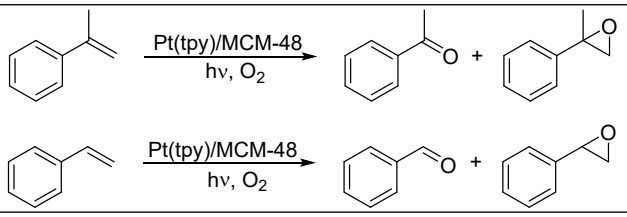
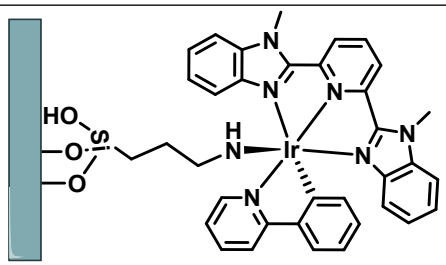
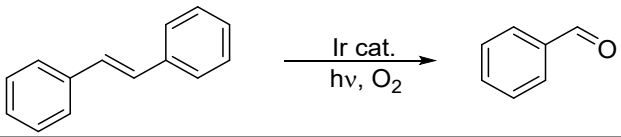
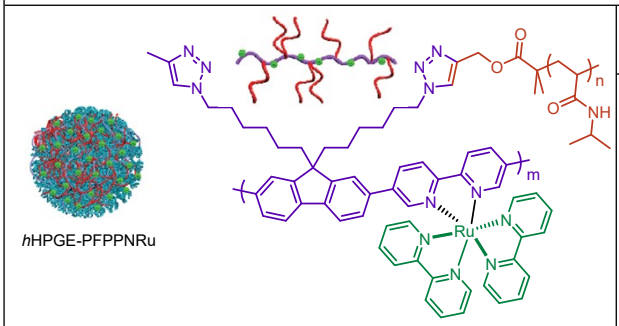
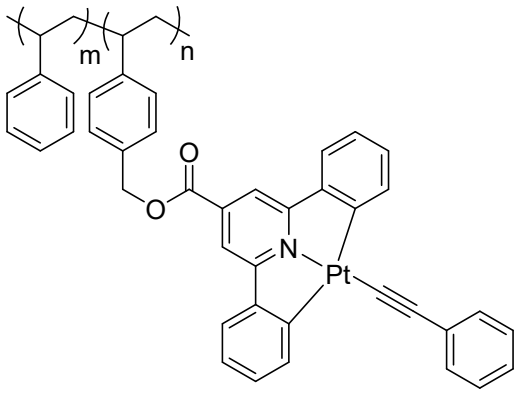
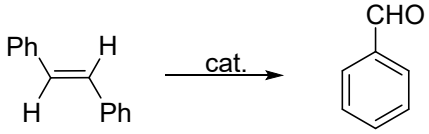
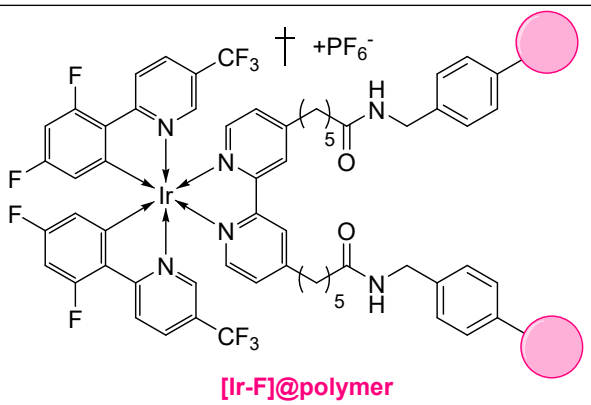
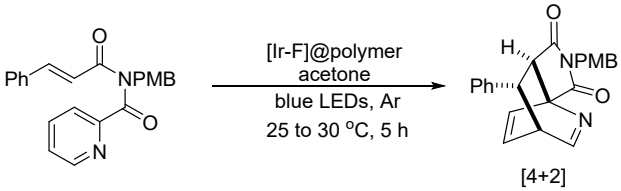
Till date, remarkable progress has been made in the development of photocatalysts owing to their high activity, selectivity and tunable light absorption in visible light range. Recently, the heterogeneous photocatalytic systems have emerged as potential candidates due to their beneficial attributes (like high surface area, ease of functionalization and facile separation etc). This article provides succinct overview of rational designing of heterogeneous photocatalysts by grafting photoactive complexes over heterogeneous support matrices via covalent grafting, their detailed characterization techniques which have been followed by landmark examples of their applications. Also, major challenges and opportunities in the forthcoming progress of these appealing areas are emphasised.

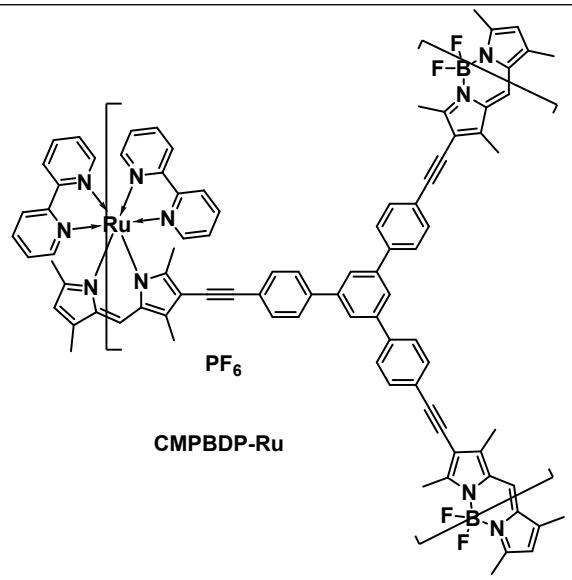
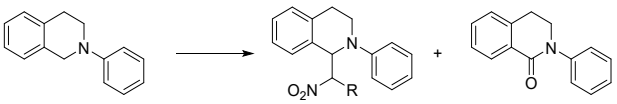
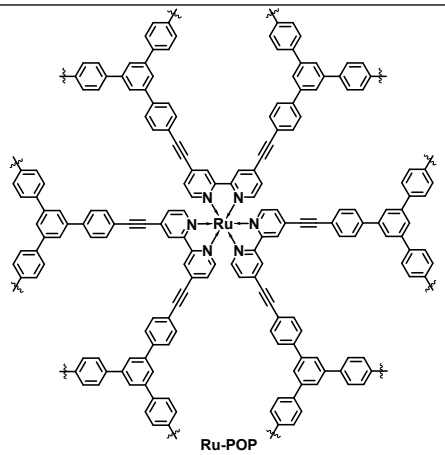
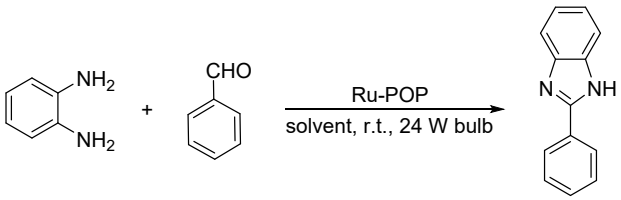
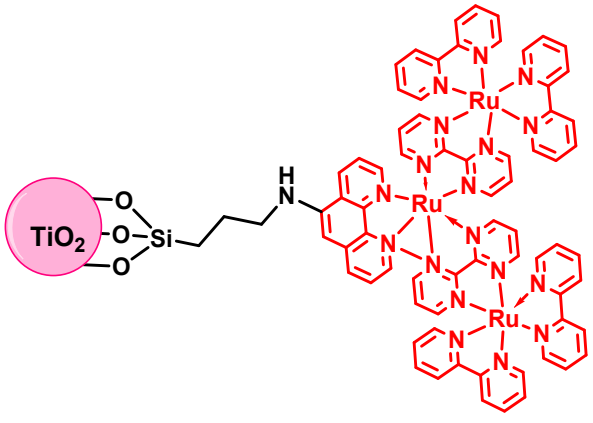
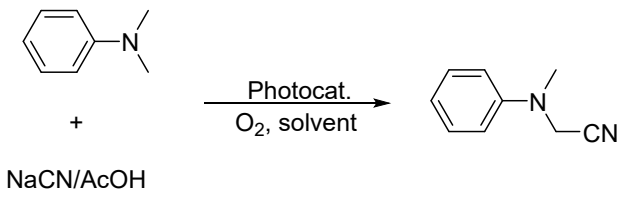
Table of Content

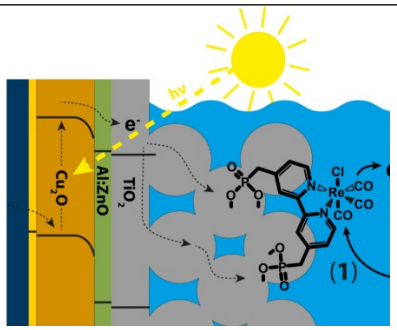
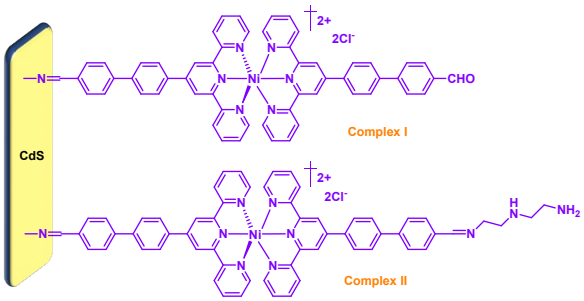
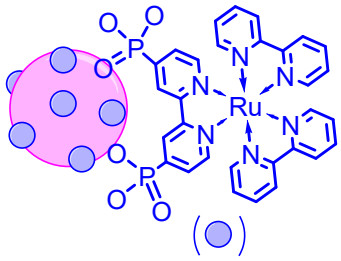
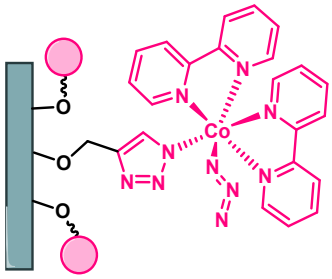
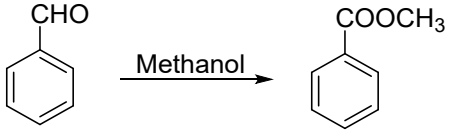
1. Characterization of the covalent grafting approach to transform homogeneous photocatalysts to heterogeneous composites

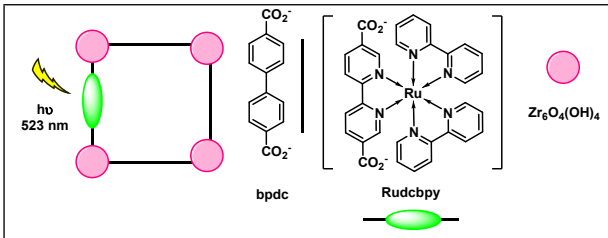
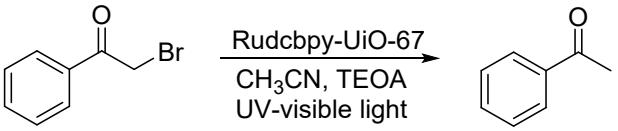
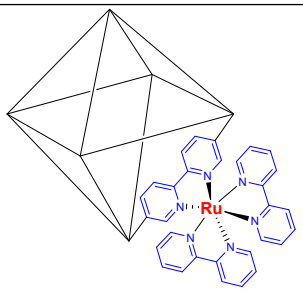
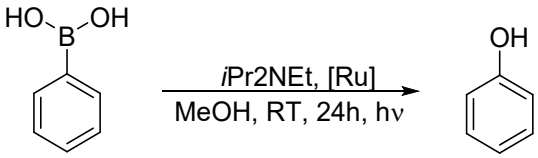
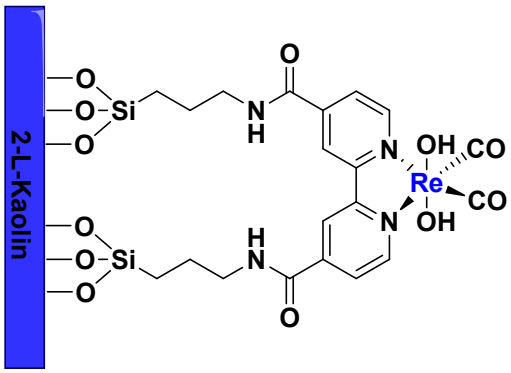
Table S1. Various examples of photoactive motif grafted over heterostructures, their characterization and application.

Catalyst	Characterization Catalytic Application	Ref.
SiO_2 support		
 **MSN-Ru**	The successful immobilization of the photoactive moiety was confirmed by UV-Vis. Recycle: 5 Oxidation of thioanisole	1
 **Pt(tpy)SG**	By UV spectroscopy Photosensitized oxidation of alkenes 	2
	Measuring the absorbance by diffusion reflectance UV-visible spectroscopy Recycle: 10 Photooxidation of olefins under oxygen 	3
	By analysing the Pt content grafting of the moiety confirmed. Additionally, X-ray absorption measurements to evaluate the chemical nature of Pt. FTIR confirm a strong peak at around 1.5 Å confirm formation of Pt-N bond. Selective photooxidation of styrene derivatives by molecular oxygen 	4
	By determining the amount of Pt loading. Further confirmed by FTIR extended XAFS (EXAFS) displayed a strong peak accredit to an Pt-N bond. Selective oxidation of styrene derivatives in the presence of molecular oxygen	5

		
	Normalized X-ray absorption near-edge structure (XANES) spectra was recorded to confirm the grafting of moiety. In the FTs of the Ir LIII-edge X-ray absorption finestructure (EXAFS) spectra, strong peak at ~1.5 Å accredited to IrN and IrC bond. Photoinduced Aerobic Oxidation 	6
Polymer support		
	XPS was utilized to characterize the catalyst. RAFT polymerization	7
 **PolyPt(pbp)L**	By UV spectroscopy Photosensitized oxidation of alkenes 	2
 **[Ir-F]@polymer**	Recycled: 10 Pyridine Dearomatization Reaction  [4+2]	8

	Characterized by FTIR, NMR, SEM, ICP, TEM, UV, PXRD, BET etc. Recycle: 7 Oxidative C-H functionalization by Ru(II) photocatalytically and nitroalkanes as nucleophiles to give Aza Henry reaction. 	9
	XRD, NMR, SAXS, TEM, Elemental mapping and UV-Vis spectroscopy were utilized to confirm the formation of photocatalyst. Visible light-induced reduction of aromatic azides to amines 	10
	The formation of the framework was confirmed by BET, NMR, EDX, UV Vis Spectra, FTIR etc Recycle: 12 Synthesis of 2-substituded benzimidazole 	11
Semiconductor supports		
	The formation of TiO_2 immobilized ruthenium polyazine complex was determined by numerous methods including XRD, SEM, TEM, ICP-AES, CHNS, UV-Vis, NMR, 13C NMR and FTIR spectroscopy. Recycle: 8 Oxidative cyanation of tertiary amines. 	12

	The presence of grafted catalyst was confirmed by FTIR, UV-Vis transmission spectra, X-ray photoelectron spectroscopy	13
	CO_2 photoreduction to CO	
	The presence of the Ni-based complex grafting was confirmed by EDX analysis. Additionally, the successful covalent link between CdS–DETA and Ni Complex have been determined by Raman and FTIR spectra.	14
	The photocatalytic activity of the catalyst was examined for H_2 production is evaluated in the presence triethylamine. The system displays excellent TONs and TOF of up to 43 815 and 0.47 s^{-1} for 26 h, respectively	
 PS-Co_3O_4 NPs	ATR-IR spectra were recorded to confirm the grafting of the PS moiety over Co_3O_4.	15
	photo-oxidize water into O_2	
Carbon nitride support		
 Co@npg-C_3N_4	STEM elemental mapping of Co@npg-C_3N_4 catalyst confirm the successful grafting of cobalt complex over the modified carbon nitride sheets. Further, various vibration bands of FT-IR approve the formation of catalyst. High resolution XPS spectrum also confirm heterogenization of cobalt complex Recycle:6	16
	Conversion of aldehydes to ester 	
MOF		
	XRD patterns, BET surface area, thermogravimetric analysis, ICP-OES, diffuse reflectance absorption and emission spectra were recorded to confirm the formation of the catalyst.	17

	Debromination of α-bromoketones 	
 **UiO-67-Ru(bpy)$_3$**	The successful grafting of the ruthenium moiety was confirmed by NMR and XRD. Recycle :5. Aerobic oxidative hydroxylation of arylboronic acids 	18
	Kaolin	
	The existence of diimine-tricarbonyl Re(I) units in Re-L-Kaolin is confirmed by ATR-FTIR spectra. Re-L-Kaolin presence was further confirmed by strong absorption band at 395 nm attributed to metal-to-ligand charge transfer (MLCT) excitation. CO_2 reduction to CO	19

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