



# Biomass Building Blocks

# Iridium Tetra(4-carboxyphenyl) Porphyrin, Calix[4]pyrrole and Tetraphenyl Porphyrin Complexes as Potential Hydrogenation Catalysts

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**Abstract:** Here we report the preparation of first examples of iridium-based organometallic macromolecules, viz., iridium-tetra (4-carboxyphenyl)porphyrin (IrTCPP), iridium-calix[4]pyrrole (IrCP) iridium-tetraphenylporphyrin (IrTPP), which are effective catalysts for hydrogenation of levulinic acid (LA) to  $\gamma$ -valerolactone (GVL) and 1,4-pentanediol under base free condi-

tions. The turnover number in the range of 1220–2850 is evident for the chosen reaction using iridium macromolecule based catalysts. The heterogenization of homogeneous IrTCPP, IrCP, and IrTPP result in stable reactivity of the catalysts for several runs.

### Introduction

Iridium-based organometallic complexes have a similar chemistry as rhodium; they possesses unique properties and are ideal catalysts for oxidative addition, hydrogenation, bond breaking, and bond making reactions in various chemical processes.<sup>[1-5,6-9]</sup> Several iridium based organometallic complexes (iridium-olefin, arene, allyl, alkyl, and carbene complexes) have been extensively studied for hydrogenation, C-H activation, and oxidative addition.<sup>[10,11]</sup> Vaska's catalyst<sup>[12]</sup> and Crabtree's catalyst<sup>[13-15]</sup> are the well-known examples of important iridium-based homogeneous catalysts used for oxidative addition and hydrogenation reactions. Recently, Bayram et al. reported the complete hydrogenation of benzene at room temperature using zero-valent iridium nanoparticles.<sup>[8]</sup> Similarly, iridium hydride based complexes possessing various coordinating ligands have been shown to be potential catalysts for hydrogenation of ketones and alcohols.<sup>[10]</sup> Also, iridium-containing pincer complex<sup>[16,17]</sup> was shown as to be a promising catalyst for the conversion of biomass derivatives. Cyclo-metallated iridium complexes have also attracted great interest owing to their unique photophysical properties.<sup>[18,19]</sup> At this juncture, to the best of our knowledge there are no reports on iridium-based macromolecules (Scheme 1). The development of such iridium complexes may broaden the scope as catalysts and may act as model molecules

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for biological, photophysical and chemical activities.<sup>[20,21]</sup> In other words, in recent years, great attention has been focused on the conversion of biomass into valuable chemicals, in which group VIII metal complexes play a vital role.<sup>[16,17,22-24]</sup> In particular, hydrogenation of levulinic acid to  $\gamma$ -valerolactone and 1,4pentanediol has a significant role as a green solvent, as well as an important intermediate in several fine chemical syntheses.<sup>[25,26]</sup> Herein, we report the preparation of novel iridiumbased macromolecules [iridium-tetra(4-carboxyphenyl)porphyrin (IrTCPP), iridium-calix[4]pyrrole (IrCP), iridium terta-phenyl porphyrin (IrTPP) and subsequently, heterogenized on a functionalized molecular sieves support. The homogeneous (IrTCPP, IrTPP, IrCP) and heterogenized iridium complexes (SBA-AM-IrTCPP/IrTPP/IrCP) are explored as catalysts for the conversion of levulinic acid under phosphane, and base-free conditions with moderate temperature and hydrogen pressure.



Scheme 1. Representative examples of iridium based macromolecules.

#### **Results and Discussion**

All of the macromolecules were prepared using the Schlenk technique by treating nucleophile (pyrrole) and electrophile

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(benzaldehyde, 4-carboxy benzaldehyde, and acetone).<sup>[27–33]</sup> The incorporation of iridium into the center of the macromolecules was carried out by using iridium trichloride (IrCl<sub>3</sub>) as the iridium source.<sup>[27–31]</sup> The structure of the ligands (TCPP, TPP, and CP), as well as iridium complexes (IrTCPP, IrTPP, and IrCP), was thoroughly investigated by various spectroscopic techniques, including FT-IR, UV/Vis, NMR, CHNS and mass analysis. Thoroughly characterized homogeneous iridium complexes were heterogenized on the surface of amino-silane modified SBA-15 materials and subsequently, both homogeneous and heterogeneous catalysts were explored for hydrogenation of levulinic acid.

FT-IR spectra of ligands (TCPP, TPP and CP) and their corresponding iridium complexes (IrTCCP, IrTPP and IrCP), as well as surface grafted heterogenized complexes are displayed in Figure 1. All these samples show that the major bands in the region of 450–1000 cm<sup>-1</sup> are due to the in-plane bending, outof-plane bending, and the ring rotation and torsion modes of the CP, TPP, and TCPP skeleton.<sup>[27-31]</sup> The vibrational bands detected in the region of 1000–1600 cm<sup>-1</sup> are typical of symmetric and asymmetric stretching of C=C, C-N, and C-C bonds-related to skeletal pyrrole molecules. The bands appearing at 1102 and 1180 cm<sup>-1</sup> correspond to C-H asymmetric deformation modes in the pyrrole ring. CP, TPP, and TCPP showed obvious vibrational bands in the range of 3316–3446 cm<sup>-1</sup>, which correspond to N-H stretching modes derived from the pyrrole unit present in the ligands, which are absent in IrCP, IrTPP, and IrTCPP. These findings support the metalation of macromolecules (i.e., direct bonding of iridium ions to the pyrrole nitrogen in the ligands). The vibrational bands correspond to aromatic C=C (1496  $cm^{-1}$ ), C–N (1231 cm<sup>-1</sup>) stretching yielded a red shift after iridium ion incorporation. In TCPP after iridium incorporation, a new peak was observed at 609 cm<sup>-1</sup> that corresponds to the Ir-N bond. Furthermore, the vibration stretching bands characteristics of the meso-benzoic group [e.g., C=O (1700 cm<sup>-1</sup>; carboxyl functionality), C=C (1600 cm<sup>-1</sup>; aromatic), and C–O (1385 cm<sup>-1</sup>)] also shows a red shift towards 1694, 1500, and 1358 cm<sup>-1</sup> after the iridium ion incorporation (IrTCPP). Similarly, in IrTPP, an extra shoulder peak was observed at 667 cm<sup>-1</sup> and in IrCP at 672 cm<sup>-1</sup>, which corresponds to the Ir-N bond. The UV/Visible spectrum (Figure 2) of TCPP shows peaks at 426 (Soret band), 514, 550, 593, and 649 nm (Q bands). The values are in good agreement with literature reports.[31] Upon iridium ion incorporation, the pyrrole nitrogen of TCPP is coordinated to the iridium ion to form an IrTCPP complex. As a result, the intensity of Q bands is decreased, and the Soret band shows a slight blue shift (from 426 to 421 nm) that is characteristic of the formation of a metal-TCPP (Ir-TCPP) complex. This could be due to the improved structural symmetry (D4h point group). UV/Visible spectra studies once again support the formation of the iridium macromolecular complex. Similarly, TPP shows a peak at 424 nm (Soret band), 517 nm, 550 nm, 591 nm, and 649 nm (Q bands). Upon iridium ion incorporation, the pyrrole nitrogen of TPP is coordinated to the iridium ion. Consequently, the intensities of the Q bands at 517 and 550 nm decreased, and those at 591 and 649 nm disappeared. On the other hand, calix[4]pyrrole shows peaks at 230 nm with a weak shoulder at 416 nm, upon

iridium ion incorporation, the Soret band shows a slight red shift (from 230 to 271 nm) which is characteristic of the formation of IrCP complex.



Figure 1. FT-IR spectra of ligands, iridium complexes and heterogenized samples.

The <sup>1</sup>H NMR spectra of the IrTCPP complex (See ESI Figure S1) showed peaks ( $\delta$ ) at 8.86 (S, H<sub>pyrrolic</sub>), 8.40 (d, H<sub>o-phenyl ring</sub>), 8.36(d, H<sub>m-phenyl ring</sub>) respectively. These results confirm the formation of IrTCPP complex. The IrTCPP complexes display the absence of a peak in the highly shielded region at -2.74 ppm, which is characteristic of N-H protons of TCPP<sup>[25]</sup> confirmed that iridium ion is bonded to the nitrogen center of TCPP. Similarly, after the iridium ion incorporation into the calix[4]-pyrrole cavities (See ESI\* Figure S2), the absence of a broad N-H proton peak at 7.1 ppm confirms the coordination of iridium ions through the pyrrole nitrogen of the CP ligand. The other peaks characteristic of macromolecules (TCPP, TPP and CP) are identical for both ligands and iridium macromolecules (See ESI\* Figure S1, Figure S2, Figure S3). IrCP shows very weak signals appear at 7.0 and 8.3 ppm which are due to the presence of trace amount of poly-pyrrolic impurities. Similarly the peak obtained







Figure 2. UV/Visible spectra of TCPP, IrTCPP, TPP, IrTPP, CP, IrCP.

Table 1. CHNS analysis result of TCPP, IrTCPP, CP, IrCP, TPP, IrTPP.

Material	% of carbon Theoretical	Experimental	% of nitrogen Theoretical	Experimental	% of hydrogen Theoretical	Experimental
	value	value	value	value	value	value
ТСРР	72.90	71.25	7.09	6.21	3.82	4.60
Ir TCPP	57.39	58.38	5.51	5.79	2.78	3.23
CP	78.46	78.02	8.74	8.39	13.07	13.32
IrCP	51.56	50.16	8.59	8.90	4.95	4.44
TPP	85.97	85.40	9.11	9.80	4.92	4.10
IrTPP	62.88	61.09	6.67	6.59	3.36	3.17

at 2.089 ppm on IrTCPP is derived from acetone proton (which is used for washing).

Similarly, the CHNS analysis of macromolecular ligands (CP, TPP, and TCPP) and the corresponding metallo-macromolecules are summarized in Table 1. The percentage of C, H, and N in both the ligands and iridium complexes, show that the calculated values are well-match with the theoretical values (Table 1). The formation of iridium complexes were further confirmed by mass spectral analysis, where parent ion peak appeared at 1034.37 [ $C_{44}H_{28}$ IrN<sub>4</sub>Cl(H<sub>2</sub>O), Calculated *m*/*z* = 1033.43], 669.49 [ $C_{28}H_{32}N_4$ IrCl(H<sub>2</sub>O), Calculated *m*/*z* = 670.20] and 840.05 [ $C_{44}H_{28}N_4$ IrCl calculated *m*/*z* = 840] respectively for IrTCPP, IrCP and IrTPP.

Thoroughly characterized, homogeneous catalysts (IrTCPP, IrCP, IrTPP) were grafted on the aminosilane functionalized SBA-15 (SBA-AM) materials. The presence of organo amine and metallo-macromolecules are evident from FT-IR spectra (Figure 1), which show that, vibrational bands appear around at 2920, 1557, and 1492 cm<sup>-1</sup>, which are characteristics of C-H stretching, N-H bending, and NH<sub>2</sub> wagging modes of vibration of the organic and amine functionality present on the SBA-15 surface. A broad vibrational band appeared at 1660 cm<sup>-1</sup> in SBA-AM-IrTCPP, which confirms the formation of amide linkage between the meso-carboxybenzyl group of the porphyrin group and NH<sub>2</sub> of the functionalized SBA-15. The presence of all vibrational bands characteristic of IrTCPP, IrCP, and IrTPP (Figure 1) support the notion that the iridium molecular structure remains intact after the grafting on the functionalized SBA-15 surface. The low angle powder X-ray diffraction patterns of SBA-15 and SBA-AM-IrTCPP, SBA-AM-IrTPP, and SBA-AM-IrTPP were shown in Figure 3. It can be seen from the figure that the intense peak

observed at 20 around 0.80 corresponds to (100) diffraction planes, accompanying the small peaks assigned to (110) and (200) diffraction planes characteristic of hexagonal SBA-15 structure. For the macromolecule encapsulated SBA-15 material, the intensity of the diffraction peak decreased drastically, which is due to the presence of bulk IrTCPP/IrTPP/IrCP inside the channel of SBA-15. However, the diffraction peaks correspond to (100) plane remain intact with broadening supports that the material did not collapse after the grafting of bulk metal complex on the amino-functionalized SBA-15 (Figure 3).



Figure 3. Low angle powder XRD patterns of SBA-15, SBA-AM-IrTCPP, SBA-AM-IrCP and SBA-AM-IrTPP.

Adsorption isotherm of SBA-15 materials exhibit (Figure 4) a sharp uptake in the relative pressure  $(p/p_0)$  range between 0.6 and 0.8. due to multilayer capillary adsorption with capillary condensation of nitrogen and is characteristic of type IV iso-





therm. A well-defined hysteresis loop of type H1 was evident according to the IUPAC classification, which is associated with the capillary condensation in open-ended cylindrical mesopores.<sup>[34]</sup>



Figure 4.  $N_2$  sorption isotherm of (A) SBA-15 (B) SBA-AM-IrTPP, (C) SBA-AM-IrCP and (D) SBA-AM-IrTCPP.

Furthermore, compared to the parent sample (SBA-AM), SBA-AM-Ir TCPP, SBA-AM-IrTPP, and SBA-AM-IrCP samples showed a drastic decrease in surface area and pore volume. The decrease in pore volume and pore size confirms that the iridium-based macromolecules are well encapsulated on the surface of SBA-15-AM (Table 2).

Table 2. Textural properties of SBA-15, SBA-AM, SBA-AM-IrTCPP, SBA-AMIrCP, and SBA-AM-IrTPP.

Sample code	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	BJH Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	BJH Pore size [nm]
SBA-15	757.6	0.57	7.2
SBA-15 AM	243	0.44	6.7
SBA-15-AM-IrTCPP	66.7	0.13	5.7
SBA-AM-IrCP	69.2	0.15	5.0
SBA-AM-IrTPP	164.0	0.30	5.1

The iridium content present in the heterogeneous catalysts were calculated using the ICP-AES technique, and it shows about 1.62, 4.67 and 0.85 wt.-% of Ir in SBA-AM-IrCP, SBA-AM-IrTPP, respectively (Table S1 ESI\*).

Further to understand the thermal stability of the heterogenized catalysts (SBA-AM-IrCP/TCPP/TPP) thermo-gravimetric analysis was carried out and the results are displayed in Figure 5. TGA profile of all the heterogeneous catalyst did not show any appreciable weight loss in the temperature range of 25 – 200 °C, which suggest that the heterogenized samples are stable up to 200 °C. The observed weight loss in the temperature range of 200–600 °C corresponds to the decomposition of macromolecules (porphyrin and calix[4]pyrrole) and the linker organo-amine present in the heterogenized catalysts. Based on TGA studies, the catalytic studies on heterogeneous catalysts, the reaction temperature set below its decomposition temperature.

To understand the nature of the active species, present on the surface, XPS has been carried out, and the Ir 4f core level spectra of SBA-AM-IrTCPP, SBA-AM-IrCP and SBA-AM-IrTPP samples are shown in Figure 6. The XPS spectrum of both the IrTCPP and IrCP grafted samples show two prominent peaks due to spin-orbital splitting of Ir 4f<sub>7/2</sub> and Ir 4f<sub>5/2</sub> with binding energies at 61.33 eV and 64.30 eV indicating that iridium is exclusively present with Ir (III) oxidation state on the surface and might act as the centre of hydrogenation reaction.<sup>[23]</sup> Similarly SBA-AM-IrTPP shows peaks at 60.09 eV and 64.24 eV characteristic of iridium in trivalent oxidation state. The signal observed at 399 eV in the N 1S XPS spectra is characteristic of N-ligand present in the complexes coordinated with Ir<sup>3+</sup>, confirming the existence of Ir (III) centred TCPP, CP, TPP units in SBA-AM-IrTCPP, SBA-AM-IrCP, SBA-AM-IrTPP respectively<sup>[23]</sup> (Figure 7). Further the XPS spectra of C 1s, Cl 2p also supports the existence of IrTCPP, IrCP, IrTPP in the heterogeneous grafted samples (See ESI\* Figure S4, S5).



Figure 6. XPS of Ir 4f in SBA-AM-IrTCPP, SBA-AM-IrCP, SBA-AM-IrTPP.



Figure 5. TGA profile of fresh and used iridium complexes grafted heterogeneous catalysts.







Figure 7. N 1s XPS spectra of SBA-AM-IrCP, SBA-AM-IrTCPP and SBA-AM-IrTPP.

HR-TEM micrograph (Figure 8) of a representative heterogenized catalyst viz., SBA-AM-Ir-CP is shown in Figure 8. The TEM images of SBA-AM-Ir-CP is providing evidence that the hexagonal honeycomb type mesoporous structure of SBA-15 retains long range ordering even after grafting of bulk macrocyclic iridium complex.



Figure 8. High resolution transmission electron microscopy (HRTEM) micrographs of SBA-AM-Ir-CP.

The developed iridium-based homogeneous macromolecular catalysts (IrCP, IrTCPP, IrTPP) and their heterogenized SBA-AM-IrTCPP, SBA-AM-IrTPP, SBA-AM-IrCP samples were investigated for catalytic hydrogenation of levulinic acid to  $\gamma$ -valerolactone and 1, 4 pentane-diol (Scheme 2).



Scheme 2. Hydrogenation of levulinic acid on iridium based macromolecular catalysts.

The reaction was carried out in an autoclave reactor with the required amount of catalyst (0.01 g Homogeneous catalyst, 0.100 g Heterogeneous catalyst), substrate (5 mmol), and solvent (5 mL) under 10 bar hydrogen pressure for 12 h. The product was confirmed by GC and FT-IR spectroscopic methods. All homogeneous catalysts were studied for several cycles by the introduction of 5 mmol of levulinic acid after each run (Table 3).  $\gamma$ -valerolactone and 1, 4 pentanediol were obtained as the major products. The formation of  $\gamma$ -valerolactone was further confirmed by FT-IR spectral studies (Figure S6 ESI\*), which showed a shoulder peak at 1721 cm<sup>-1</sup>, which is characteristic of C-O present in the lactone group. The homogeneous catalysts (IrTCPP, IrTPP, and IrCP) showed conversion levels of 90–100 % even after several cycles.

In case of IrTCPP and IrTPP, during the initial run,  $\gamma$ -valerolactone was obtained, and in subsequent runs, the formation of diol was predominant, which is due to the presence of water molecule obtained as the by-product. The presence of the carboxylate group on IrTCPP makes the system relatively hydrophilic, and thus the by-product formed might facilitate more diols in the fourth and fifth cycles. In other words, the case of IrTPP and IrCP complexes, although the water was formed as a by-product, the more hydrophobic environment might facilitate better selectivity of  $\gamma$ -valerolactone. To improve the catalytic stability, the homogeneous IrTCPP, IrTPP, and IrCP catalysts were heterogenized on the surface of amino-functionalized SBA-15, and the heterogeneous SBA-AM-IrTCPP, SBA-AM-IrCP, and SBA-AM-IrTPP catalysts were studied for the chosen reaction. Table 4 summarizes the catalytic activity of heterogenized catalysts, for

Table 3. Hydrogenation of leuvlinic aci	over various iridium macro-molecules. <sup>[a</sup>
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Catalyst	No. of cycles	Conv. [%]	Selectivity		TON
			γ-valero-lactone	1,4-pentane-diol	
IrTCPP	1	88.5	91.5	8.5	434
	2	100	30	70	924
	3	98.8	28.5	71.5	1408
	4	98.1	23.7	76.3	1889
	5	98.5	19	81	2850
IrTPP	1	100	100	0	403
	2	95.1	77.4	22.6	787
	3	99.3	75.2	28.8	1187
	4	95.9	65.9	34.1	1574
IrCP	1	100	72.5	27.5	312
	2	98.8	76.6	23.4	621
	3	97.6	74.6	25.4	926
	4	96.4	92.1	7.9	1227

[a] Reaction conditions: Levulinic acid 5 mmol, IrTCPP= 0.0102 mmol (10 mg), IrTPP= 0.0124 mmol (10 mg), IrCP=0.016 mmol (10 mg), temperature 100 °C, DMF 5 mL, H<sub>2</sub> pressure 10 bar.





Table 4. Hydrogenation of levulinic acid using heterogenous catalyst and their Recyclability.<sup>[a]</sup>

Catalyst	No. of cycles	Conv. [%]	Selectivity γ-valerolactone	1,4-pentanediol
SBA-AM-IrTCPP	1	100	6	94
	2	99	3	97
	3	98	3	97
	4	62	29	71
SBA-AM-IrTPP	1	100	7.9	92.1
	2	89	29.5	70.4
	3	82.8	18.7	81.3
	4	79.2	15.4	84.9
SBA-AM-IrCP	1	100	3.8	96.2
	2	100	0.9	99.1
	3	100	3.9	96.1
	4	100	1.8	98.2

[a] Reaction conditions: Levulinic acid 5 mmol, Catalyst=100 mg, temperature 120 °C, DMF 5 mL, H<sub>2</sub> pressure 10 bar.

which we found complete conversion of levulinic acid with exclusive formation of 1,4-pentane diol in all cases. For the heterogeneous catalysts SBA-AM-IrTCPP and SBA-AM-IrTPP, the conversion was decreased considerably after the third cycle. This loss in activity might be due to the chemisorption of reactant molecules on the surface of mesoporous materials, which block the active sites. The SBA-AM-IrCP catalyst showed the complete conversion of levulinic acid even after several cycles and retain its activity.

In order to understand the decrease in catalytic activity after third cycle, thermo-gravimetric analysis of the used heterogeneous catalysts was studied and the results are displayed in Figure 5. The used SBA-AM-Ir-TCPP and SBA-AM-Ir-TPP showed an increase in weight loss compared to fresh catalysts in the temperature range of 200-600 °C, which supports the chemisorption of reactant molecules on the surface of mesoporous catalysts (Figure 5). The chemisorption of organic molecules on the surface of mesoporous molecule may leads to block the accessibility of reactant molecule on active sites of the heterogeneous catalysts and hence results decrease in catalytic activity after third cycles. Further, the nature of the used heterogeneous catalysts were followed by HRTEM, FT-IR and ICP AES analysis. The HR TEM of a representative used catalyst viz., SBA-AM-Ir-CP catalysts is shown in Figure S7, which showed the uniform mesoporous with long range ordering retained even after the catalytic reaction. Further the ICP AES analysis shows that the iridium content in the used catalysts showed iridium content of 3.41, 1.43 and 0.6 respectively for U-SBA-AM-IrTCPP, U-SBA-AM-IrCP, and U-SBA-AM-IrTPP respectively (Table S1 ESI\*). The decrease in iridium content in SBA-AM-IrTCPP, and the presence of relatively less iridium content on SBA-AM-IrTPP results decrease in activity after 4<sup>th</sup> cycle. The intactness of iridium content on the surface of SBA-AM-IrCP facilitates the retention of activity even after several cycles. Further, the filtrate obtained from reaction mixture after 1 h of reaction using SBA-AM-IrCP did not show any appreciable conversion of levulinic acid further confirm that there is no leaching of iridium complex on SAB-AM-IrCP. In addition, the FT-IR spectra of the used catalysts (Figure S8 ESI\*) also supports that even after the catalytic reaction, the nature of heterogeneous catalysts are retaining its structure without any significant changes.

#### Conclusions

In summary, this is the first report on preparation of iridium containing calix-[4]-pyrrole and porphyrin based complexes. The formation of IrTCCP, IrTPP and IrCP evident from proton NMR, Mass spectra and CHNS studies. The presence of iridium in the +3 oxidation state was confirmed from XPS studies. The studies revealed that both the homogeneous organometallic complexes as well as heterogeneous catalysts show promising activity for the levulinic acid hydrogenation with the formation of  $\gamma$ -valerolactone and 1,4-pentane-diol as the major product. Both homogeneous and heterogeneous catalysts retain their activity even after several runs.

## **Experimental Section**

Preparation of the Catalyst: All experiments were conducted using the Schlenk technique. Before the experiments, all the solvents and starting materials were dried by standard procedure.<sup>[27]</sup>

Synthesis of Ir-Meso-Tetra-(4-carboxyphenyl)phenylporphyrin Complex (IrTCPP): Meso-tetra-(carboxyphenyl) porphyrin (TCPP) was prepared by dissolving freshly dried pyrrole (2.3 mmol) and 4-formyl benzoic acid (2.33 mmol) in 100 mL propionic acid and the mixture was refluxed for 4 hours.<sup>[27-32]</sup> The initial mixture was yellow in colour, which turn to green and subsequently it became brownish black in colour. The product solution was cooled to room temperature and introduced methanol (50 mL) in an ice bath with stirring. The deep purple crystals were precipitated, which was filtered and washed using methanol. The resulting solid was re-crystallised and purified (yield 18 %). The iridium incorporated meso-tetra-(4-carboxyphenyl) porphyrin (IrTCPP) was prepared by dissolving the 1 mmol Iridium chloride (IrCl<sub>3</sub>·6H<sub>2</sub>O) in acetone followed by the addition of 1 mmol TCPP under inert atmosphere and refluxed for 24 hours. The precipitate was collected and thoroughly washed with acetone. Deep green coloured shiny crystals are formed. Yield: 82 %. HR-MS m/z= 1034.37 [C<sub>44</sub>H<sub>28</sub>IrN<sub>4</sub>Cl(H<sub>2</sub>O), Calculated m/z= 1033.43],  $^1\text{H}$  NMR (400 MHz, [D\_6]DMSO): 8.86 (S, H\_{pyrrolic}), 8.40 (d, H<sub>O-phenyl ring</sub>), 8.36 (d, H<sub>m-phenyl ring</sub>) respectively.

Preparation of Iridium calix[4]pyrrole (IrCP): The synthesis of metal incorporated calix[4]pyrrole was carried out in an inert nitrogen atmosphere. Meso-octamethylcalix[4]pyrrole (CP) was prepared as per the described procedure earlier.<sup>[29–32]</sup> About 3 mL of pyrrole and 15 mL of acetone was added to round-bottomed flask and





allowed to stir for few minutes in an ice bath. Then 2.5 mL 37 % HCl was added to the above mixture and the solution became colorless. subsequently change into milky yellow. After completion of the reaction the brownish precipitate was formed which was separated and dried. The precipitate was further washed using acetone results white fine powder. The Iridium (Ir) incorporated meso-octamethylcalix[4]pyrrole (IrCP) was prepared by the following method. About 0.5 g (1 mmol) of CP was dissolved in 15 mL acetone and kept for stirring. Then 1 mmol of iridium salt (0.298 g, IrCl<sub>3</sub>. XH<sub>2</sub>O) was dissolved in 5 mL acetone and added into the RB flask containing calix[4]pyrrole. The reaction mixture was allowed to reflux for 12 hours. After completion of the reaction the solvent was removed, the product was washed with acetone, dried and collected which is brown in colour (yield: 86 %). HR-MS m/z= 669.49  $[C_{28}H_{32}N_4]rCl(H_2O)$ , Calculated m/z = 670.20], <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  5.65(d, H<sub>pyrrolic</sub>), 1.51(s, H<sub>meso</sub> CH<sub>3</sub>).

Synthesis of Ir-Tetraphenylporphyrin Complex (IrTPP): Meso-tetraphenylporphyrin (TPP) was prepared by refluxing freshly dried pyrrole (0.027 mol) and benzaldehvde (0.028 mol) in 100 mL of propionic acid, for 2 h.<sup>[27-33]</sup> After the stipulated period, the reaction mixture was cooled to 25 °C, filtered, and washed thoroughly with methanol. The resulting purple crystals were air-dried and washed with dichloromethane (yield 12 %).<sup>[25,29]</sup> The liridium-incorporated meso-tetraphenylporphyrin (IrTPP) complex was prepared by dissolving metal salt (IrCl<sub>3</sub>·XH<sub>2</sub>O; 1 mmol) in 5 mL of dry acetone, followed by introducing the solution containing 1 mmol of TPP in 45 mL of dry acetone. The final mixture was refluxed under N<sub>2</sub> atmosphere for 24 h. After completion of the reaction, the solvent was removed, and washed several time with pentane to remove impurities, after which the deep purple coloured product was isolated (yield: 73 %). HR-MS m/z=840.05 [C44H28N4IrCl calculated m/z = 840]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.91(s, H<sub>pyrrolic</sub>), 8.28 (m, H<sub>o</sub>), 7.8(m, H<sub>m,p</sub>).

Synthesis of SBA-15: In a typical procedure, about 4.0 g of the  $EO_nPO_{70}EO_n$  copolymer was dissolved in 180 g of 1.6 M HCl solution. To this solution 8.50 g of TEOS (tetraethyl orthosilicate) was added and the resulting mixture was allowed to stir continuously at 35–40 °C for 24 hours and then additionally for 24 hours at 100 °C under static conditions. The products were filtered, dried, and calcined at 550 °C. The calcined SBA 15 was used as a solid support material.

Synthesis of Functionalised SBA 15 (SBA-AM): The calcined SBA-15 support (6.5 g) was pre-activated at 200 °C in an air oven, followed by drying in a vacuum, in a round-bottomed flask to remove the physisorbed molecules. Subsequently, a pre-determined amount (3 mmol/g of solid support) of (3-aminopropyl) trimethoxy silane was introduced to the activated SBA-15 support material.<sup>[34]</sup> The mixture was refluxed in dry toluene (30 mL/g of support) for 24 h under N<sub>2</sub> atmosphere. This procedure was repeated thrice to completely convert the surface silanol groups into organofunctional silanes. The resultant mixture was cooled to room temperature, washed with dichloromethane, and then dried in vacuo to get the final product, which was denoted as SBA-AM.

Synthesis of SBA-AM-IrTCPP/IrCP/IrTPP: The grafting of the iridium complexes on the functionalised material (SBA-AM) was achieved by introducing 0.5 mmol iridium complex (IrTCPP/IrCP/IrTPP) dissolved in 3 mL DMF, in to 1 g of support material suspended in 50 mL dry methanol, followed by refluxing for 24 h under N<sub>2</sub> atmosphere. Subsequently, the metalloporphyrin (IrTCPP/IrCP/IrCP)-grafted materials were collected by separating the solvent and washing with methanol and dichloromethane; afterward, the prod-

uct was vacuum-dried. Grafted on materials were represented as SBA-AMIrTCPP, SBA-AM-IrCP, SBA-AM-IrTPP.

Catalytic Studies: In a typical reaction, 5 mmol Levulinic acid (0.5 mL) and 5 mL DMF (Solvent) was introduced into a 50 mL autoclave: 0.01 g of homogeneous catalysts [IrTCPP (0.0102 mmol), IrCP (0.0160 mmol), IrTPP (0.0124 mmol)] was added in to the autoclave. Subsequently, the autoclave was flushed with H<sub>2</sub> several times. The reaction was charged with the required  $H_2$  pressure of 10 bar. The reaction was performed at 100 °C, for 12 h. In the case of heterogeneous catalyst, the catalyst was activated for 2 hours at 80 °C and vacuum dried. About 0.1 g of the catalyst (SBA-AM-IrTCPP, SBA-AM-IrCP, and SBA-AM-IrTPP) was added to the autoclave containing 5 mmol Levulinic acid and 5 mL DMF and flushed with H<sub>2</sub>. The reaction was charged with the required  $H_2$  pressure of 10 bar. The reaction was performed at 120 °C, for 12 h. After completion of reaction, the reactor was cooled to room temperature, and the excess H<sub>2</sub> was vented out. The results were analysed quantitatively by gas chromatography using an FID detector equipped with an HP 88 column (Mayora Analytical Model 2100). The products were further confirmed by GC, GC- MS and FT-IR data.

Characterization: FT-IR spectra of all the materials were recorded on Perkin-Elmer spectrum-2 FTIR in the range of 400–4000 cm<sup>-1</sup> using KBr method and were collected with 4 cm<sup>-1</sup> resolutions and 120 scans. UV/Vis spectra were recorded on Perkin Elmer Lambda 35 spectrometer. Elemental analyses were performed on an Elementar-Vario Micro Cube by grinding the sample in to fine powder and packed in aluminum foil. The <sup>1</sup>H NMR spectra of the complex were recorded using CDCl<sub>3</sub>/DMSO as solvent and TMS as the standard on a Bruker AVANCEIII 400 instrument. ESI-TOF mass spectra were recorded on a BrückermaXis mass spectrometer using methanol as the solvent. Powder X-ray diffraction patterns of all the heterogenized materials were collected on a Bruker-D8 high resolution X-ray diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda$ =1.5418), between 2 $\theta$  range of 0.5-10 ° with a scan speed and step size of 0.5 °/min and 0.02 ° respectively. The textural properties (BET surface area, BJH average pore volume) of the heterogenized samples were followed by  $N_2$ sorption measurements at -196 °C using an automatic micropore physisorption analyser (Micrometrics ASAP 2020, USA). The samples were degassed at 110 °C for 10 h. under 10-3 Torr pressure prior to each run. Thermo gravimetric analyses (TGA) performed using a TGA instrument (Perkin Elmer STA 6000), under a nitrogen atmosphere with a heating rate of 10 °C/min, ranging from 40 to 850 °C. X-ray photoelectron spectra (XPS) of the catalysts were recorded by using a custom-built ambient pressure photoelectron spectrometer (Prevac, Poland) that was equipped with a VG Scienta's R3000HP analyser and a MX650 monochromator.<sup>[27]</sup> A monochromatic Al- $K_a$ X-ray was generated at 450 W and used for measuring the XPS data of the above samples. Base pressure in the analysis chamber was maintained in the range of  $2 \times 10^{-10}$  Torr. The energy resolution of the spectrometer was set at 0.7 eV at a pass energy of 50 eV. The binding energy (BE) was calibrated with respect to the Au <sup>4</sup>f<sub>7/2</sub> core level at 84.0 eV. The error in the reported BE values is within 0.1 eV. Elemental composition present in the final materials was determined using ICP-AES. The morphology of the materials were analysed using a High Resolution Transmission Electron Microscope (HR-TEM) Model of FEI -TECNAI G2-20 TWIN with LaB6 filament operated at 200 kV.

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