# NJC



Check for updates

Cite this: New J. Chem., 2021, **45**, 4738



**View Article Online** 

## Light-induced carboxylation of aryl derivatives with cooperative COF as an active photocatalyst and Ni(II) co-catalyst<sup>†</sup>

Pekham Chakrabortty,<sup>a</sup> Anjan Das,<sup>a</sup> Arpita Hazra Chowdhury,<sup>a</sup> Swarbhanu Ghosh,<sup>a</sup> Aslam Khan  $\mathbb{D}^{b}$  and Sk. Manirul Islam  $\mathbb{D}^{*a}$ 

The photocatalytic carboxylation of aryl derivatives was demonstrated under CO<sub>2</sub> at atmospheric pressure using a mesoporous covalent organic framework (COF) as the active photocatalyst with triethylamine (TEA) as a sacrificial electron source under visible light. A yield of greater than 91% of the isolated product was achieved with 5 mg of catalyst. The reaction cycle is dependent on the use of the Ni(dmg)<sub>2</sub> co-catalyst and the sacrificial electron donor (TEA). The reaction does not occur in the absence of light (445 nm) even at elevated reaction temperature. We have also demonstrated that a yield of 32% of the isolated product could be obtained with the use of sunlight in the catalytic cycle. Additionally, this heterogeneous catalytic system was recyclable and reusable for several cycles.

Received 1st December 2020, Accepted 1st February 2021

DOI: 10.1039/d0nj05843b

rsc.li/njc

## Introduction

Because of its benign properties, such as non-toxicity and nonflammability, carbon dioxide is an abundant, economical and renewable C1 building block. Carboxylation of carbon nucleophiles with CO<sub>2</sub> provides a straightforward approach for obtaining carboxylic acid functional groups.1-4 Indeed, carboxylic acids and their derivatives are utilized as profitable synthetic compounds and are the most important intermediates in the pharmaceutical and chemical industries.<sup>5–10</sup> The activation of  $CO_2$  is highly energy consuming due to its thermodynamic and kinetic stability.<sup>11</sup> However, in the field of photosynthesis, single-electron reduction of CO<sub>2</sub> using light is feasible and has been extensively studied.<sup>12</sup> Carboxylation of aryl derivatives with the photocatalytic use of  $CO_2$  has drawn much attention, as carboxylic acid groups can be directly accessed without the need for multi-step reactions.<sup>13</sup> To avoid the use of traditional organometallic reagents, such as organolithium or Grignard reagents, aryl halides have been extensively used as a coupling partner for aryl carboxylation. In the context of thermal catalysis, Martin and co-workers used Pd(OAc)<sub>2</sub> to carboxylate aryl bromides with CO<sub>2</sub>. It is worth noting that all of these processes need metal to reduce CO<sub>2</sub>.<sup>14</sup> Therefore, an alternative method to carboxylate aryl derivatives is needed.

In the last few years, the carboxylation of aryl derivatives with CO<sub>2</sub> using various homogeneous photocatalysts has been explored. However, the carboxylation of SP<sup>2</sup>C-H/X has not yet been widely explored using heterogeneous photocatalytic systems.<sup>15,16</sup> Jain reported the carboxylation of styrene and aryl halides using a Ru-based metal complex hybridized with Ni/NiO nanoparticles as a heterogeneous photocatalyst (Scheme 1).

#### Previous work:

(a) Visible light homogeneous catalysis with Organic dye and Ni cat

(b) Visible light heterogeneous catalysis with hybride Ru@Ni/NiO as photocatalyst

#### This work

Pł

Ph-X = Br. Cl

Scheme 1 Carboxylation of C(SP<sup>2</sup>)-H/X.

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India. E-mail: manir65@rediffmail.com; Fax: +91-33-2582-8282;

Tel: +91-33-2582-8750

<sup>&</sup>lt;sup>b</sup> King Abdullah Institute for Nanotechnology, King Saud University, Riyadh, 11451, Saudi Arabia

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0nj05843b

<sup>(</sup>c) Visible light heterogeneous catalysis with COF as photocatalyst

#### Paper

In this context, covalent organic frameworks (COFs) have recently been shown to be an effective alternative, as a new group of photoactive heterogeneous materials for light-induced organic transformations and CO<sub>2</sub> reduction.<sup>17</sup> Because of their versatile and tunable electronic characteristics, crystallinity, structure, and porosity, COFs have emerged as a potential heterogeneous photocatalyst. Additionally, COFs have effective light harvesting ability and charge transferability, likely because of their  $\pi$ -electron conjugation. In spite of their huge advantages, COFs have hardly been explored as active photocatalysts under visible light for catalytic organic transformations, aside from CO<sub>2</sub> reduction. So, herein, we report the carboxylation of aromatic compounds and halides via SP<sup>2</sup>C-H/X activation using a suitable COF as the active heterogeneous photocatalyst with a suitable Ni catalyst under visible light as the energy source.18-21

## **Experimental section**

#### Synthesis of TpPa-1

For the synthesis of TpPa-1, 1.35 mmol (145.8) of paraphenylenediamine (Pa-1) and 7.5 mmol (1426.5 mg) of paratoluene sulphonic acid (PTSA) were taken in a mortar and pestle and evenly grinded for few minutes. After that, 2,4,6triformyl phloroglucinol (TFP) (0.9 mmol) was added gradually over a period of 15 min, and the reaction mixture was crushed properly until it turned into a dough-like material. Then 1000-1500 µL of deionized water was mixed in to make the reaction mixture viscous. After that, the paste of COF precursors was poured into a Teflon-lined steel autoclave and then kept under static conditions in a programmable oven for 6 h at 60 °C and then 10 h at 90 °C. The resulting TpPa-1 COF was transferred into a succession chamber and washed multiple times with N,N-dimethylacetamide (DMAc) followed by excess acetone to remove the unreacted residues. The resulting crude product was kept under vacuum for 24 h at room temperature to remove moisture. Finally, the deep-orange TpPa-1 COF was obtained in 85% isolated yield (Scheme 2).



Scheme 2 Synthesis of TpPa-1.

# Benzoic acid formation process over the porous TpPa-1 COF photocatalyst

CO2 reduction was performed photocatalytically in benzoic acid by the combination of haloarene derivatives (0.1 mmol), 10 mg of Ni(dmg)<sub>2</sub>, triethylamine (TEA, 1 mmol, 0.133 mL) in 5 mL acetonitrile in the presence of 15 mg of COF TpPa-1 in a 25 mL round-bottom flask. The reaction was allowed to run under irradiation of blue LED light (445 nm) at room temperature for 24 h with nonstop magnetic stirring. After completion of the reaction, filtration was used to separate COF TpPa-1 and then the filtrate was dried under vacuum. After evaporation of the solvent, solid benzoic acid was transferred into a 50 mL two-neck round bottom flask. 1 g of potassium bicarbonate and 20 mL of dry acetonitrile were transferred into that round bottom flask; then methyl iodide was added dropwise over 2 h under continuous stirring for a further 6 h under an N2 atmosphere. After completion of the reaction, the product was purified by column chromatography using 2% ethyl acetate-hexene as the eluent. The formation of methyl benzoate was confirmed using <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopies.

## Results and discussion

#### Characterization

**Powder X-ray diffraction (PXRD) analysis.** The PXRD pattern of the 2D-COF, namely, **TpPa-1**, is displayed in Fig. 1. The as-obtained material exhibits two distinct diffraction peaks of moderate intensity, located at diffraction angles of 4.7° and 27.7°. Importantly, it can be seen from the PXRD pattern of **TpPa-1** that the crystalline aspect of the ordered hexagonal COF featuring an intense peak (intensity count of 1409.6) is caused by the (100) facet, located at a diffraction angle of 4.7°. It reveals moderate crystallinity owing to



Fig. 1 (a) Small-angle and (b) wide-angle PXRD patterns of the  $\ensuremath{\text{TpPa-1}}$  material.

the decreased rotational freedom of the building blocks. As shown in Fig. 1b, the obvious hump-shaped peak at a diffraction angle of 26.5° can be ascribed to the existence of  $\pi$ - $\pi$  stacking between the aryl groups in the structure of the 2D ordered layered sheets of COF. This poor peak is caused by the (001) facet. Employing the Bragg equation (n = 1 for the 100 facets,  $\lambda = 0.15406$  nm and  $n\lambda =$  $2d \sin \theta$ ), the measured *d* spacing value ( $d_{100}$ ) between the (100) facets was found to be about 1.87 nm, whereas the interlayer *d*-spacing ( $d_{001}$ ) of the 2D-COF, named **TpPa-1**, was calculated to be about 3.20 Å. The determined *d* spacing between the (001) facets also corresponds to the  $\pi$ - $\pi$  stacking distance between the  $\pi$ -bonded 2D-COF sheets. Intriguingly, the unit cell parameter determined from the PXRD pattern ( $a_{100} = 2.16$ ) is fairly close to the summation of the wall thickness and pore size, as described in Fig. 1a.

The poor intensity of the (100) facet of the 2D-COF sheets may be caused by COF exfoliation.<sup>22,23</sup> The breadth of the (001) facet, owing to stacking between the COF layers, reduces with an increase in layer number of the obtained COF. The broader (001) plane of the as-synthesized COF may suggest that the sample is exfoliated. As described in Fig. 2,  $PD_{NLDFT}$  (average pore diameter) was found to be about 1.9 nm with the help of non-local density functional theory (NLDFT). PV (total pore volume in cm<sup>3</sup> g<sup>-1</sup>) was observed to be about 0.278.

#### WT (wall thickness) = $a_{100} - PD_{NLDFT}$

 $N_2$  adsorption/desorption isotherm. The  $N_2$  isotherm was obtained at 77 K to gather clear information about the permanent porosity and BET (Brunauer–Emmett–Teller) surface area of the synthesized sample. The  $N_2$  isotherm of **TpPa-1** is presented in Fig. 2, which represents the combined features of the type I and type IV patterns. Type I and IV isotherms were fit to this sorption profile, confirming the microporous and mesoporous features of the ordered COF. The copious quantity of  $N_2$  uptake in the relative pressure range of 0–0.1 bar indicates that several micropores exist in the structure of the 2D-COF. Observed from this sorption profile, the stable pore volume and BET surface area of the 2D-COF were 0.278 cm<sup>3</sup> g<sup>-1</sup> and 199.83 m<sup>2</sup> g<sup>-1</sup>, respectively. The pore size distribution curve of **TpPa-1** was established with the help of NLDFT to get hidden information about the pattern of pore size distribution, and the outcome confirms the existence of several



0.4

 $= 199.832 \text{ m}^2/\text{g}$ 

Relative Pressure(P/P<sub>o</sub>)

0.6

Surface Area

0.2



Fig. 3 (a) FT-IR spectrum of the COF  $(\mbox{TpPa-1})$  material and (b) the magnified FT-IR spectrum.

identical micropores with dimensions of *ca.* 1.9 nm (inset of Fig. 2). This outcome is well consistent with previously reported work. The as-prepared 2D-COF (**TpPa-1**) has permanent porosity with a superior BET surface area and moderate crystallinity.<sup>24,25</sup> The decreased surface area can be caused by the partial crystalline destruction.

**FTIR analysis.** The Fourier-transform infrared (FTIR) spectrum of the synthesized COF material is depicted in Fig. 3. The broad band at 3420.9 cm<sup>-1</sup> signifies the N–H bond stretching frequency. The stretching vibration of hydroxyl groups (O–H) is supposed to appear at 3200–3600 cm<sup>-1</sup>, which may be overlapped with the wide N–H band.<sup>26</sup> Therefore, the possibility of the presence of residual –OH groups in the COF framework cannot be ignored. The sharp peak at 2919 cm<sup>-1</sup> relates to the C–H stretching frequency. The intense bands at 1593.1 and 1257.1 cm<sup>-1</sup> originate from C=C and C–N groups, respectively, and this observation confirms the occurrence of a β-ketoenamine-linked COF structure.



Fig. 4 FE-SEM images of the COF (**TpPa-1**) material at different magnifications (a–d).

400

300

200

0.0

0.012 0.010 0.008

0.00

N<sub>2</sub> uptake [cc/g at STP]

Adsorption Desorption

1.0

0.8



Fig. 5 Ultra high resolution TEM images of the COF (**TpPa-1**) material at different scales: (a) 0.5  $\mu$ m; (b) 0.1  $\mu$ m; (c) 20 nm; (d) 0.1  $\mu$ m; (e) 20 nm; (f) 10 nm.

**Microscopic analysis.** As observed from the field emission scanning electron microscopy (FE-SEM) results (Fig. 4), the micromorphology of **TpPa-1** demonstrated that this obtained COF is made up of multiple asymmetrical rods that are partially twisted, resulting in the formation of a network structure. The FE-SEM images of the COF material demonstrate a one-dimensional micro-wire-like morphology of the system. The TEM images (Fig. 5a and b) suggest that small nano-fibers with diameters of *ca.* 0.1–0.16  $\mu$ m are aggregated together to build the micro-wire-like network structure. Furthermore, the porous structure of the material is clearly visible from the high-magnification TEM images (Fig. 5c, e and f), which supports the surface area analysis data.

X-ray photoelectron spectroscopy (XPS) analysis. In order to find out all the information garnered about the chemical composition of the obtained samples, XPS was carried out to prominently characterize the covalently bonded  $\pi$ -conjugated 2D-COF.



Fig. 6 XPS survey scan measurement on **TpPa-1** (a), C 1s narrow scan (b), N 1s narrow scan (c) and O 1s narrow scan measurement (d) on the assynthesized 2D-COF (**TpPa-1**).



Fig. 7 Cyclic voltammetry of TpPa-1

The prominent characterization of the 2D-COF (**TpPa-1**) was carried out by XPS, as presented in Fig. 6. Upon deconvolution, the C 1s spectrum obtained from XPS can be fitted into three components: the carbon atoms of C–N/C–O (286.3 eV); those of C–C/C—C (284.6 eV); and those of C—O (289.0 eV) (Fig. 6b). The N 1s spectrum measured by XPS can be deconvoluted into two contributions appearing at 403.5 and 400.1 eV, suggesting that N species exist in the form of C–N linkages (*i.e.* enamine nitrogen), as shown in Fig. 6c.<sup>27,28</sup> As displayed in Fig. 6d, the O 1s spectrum suggests that two clearly visible distinct peaks at binding energies of 531.3 and 533.4 eV can be assigned to the oxygen atoms of C—O and C–O within the as-prepared 2D-COF, revealing the existence of keto–enol tautomerism. More intriguingly, the **TpPa-1** material predominantly exists in the keto form. Additionally, it partially adopts the enol isomer (trace amount).

#### Cyclic voltammetry (CV) analysis

CV analysis of the 2D-COF (**TpPa-1**) was conducted at a scan rate of 10 mV s<sup>-1</sup> and domain of -0.3 to 0.4 V in (1 M) sulfuric acid with the help of a reference electrode (Ag/AgCl) (Fig. 7). The corresponding reduction potential of the ground state of the photocatalyst **TpPa-1** was estimated ( $E_{1/2} = 0.0112$  V vs. Ag/AgCl).

Using the ground state reduction potential of COF **TpPa-1** ( $E_{1/2} = 0.011$  V vs. Ag/AgCl), the excited state oxidation potential

Table 1	Deviations from the optimal reaction conditions <sup>a</sup>				
	Ph-I	1. <b>TpPa-1</b> , Ni(dmg) <sub>2</sub> MeCN, TEA, Blue LED ➤ Ph-COOCH <sub>3</sub> 2. Mel, K <sub>2</sub> CO <sub>3</sub>			
Entry	<b>TpPa-1</b> (mg)	Co-catalyst (5 mol%)	hv (nm)	Temp. (°C)	Yield <sup>b</sup> (%)
1	5	_	455	25	21
2	5	$Ni(dmg)_2$	_	25	0
3	_	$Ni(dmg)_2$	455	25	0
4	5	$Ni(dmg)_2$	455	60	87
5	5	$Ni(dmg)_2$	455	80	88
6	2	p-Terphenyl	455	25	56
7	5	$Ni(dmg)_2$	Sunlight	25	32

 $^a$  All reactions were performed with 0.5 mmol (0.056 mL) of the substrate under 1 atm of CO<sub>2</sub>.  $^b$  Calculated from  $^1{\rm H}$  NMR spectra using triphenylmethane as the internal standard.







<sup>*a*</sup> All reactions were carried out with 0.5 mmol of substrate, **TpPa-1** (5 mg), Ni(dmg)<sub>2</sub> (5 mol%), CO<sub>2</sub> (1 atm), TEA (1 eq.), MeCN (5 mL). <sup>*b*</sup> Calculated for the <sup>1</sup>H-NMR spectra using triphenylmethane as the internal reference.

for COF **TpPa-1** was estimated from the emission maxima of the normalized emission spectra (581 nm).  $E_{1/2}(PS^{\bullet^+}/PS^*) = -2.114 \text{ V} vs. \text{ Ag/AgCl}$  was also obtained.

## Catalysis

The COF **TpPa-1** photocatalyst (5 mg), along with the Ni(dmg)<sub>2</sub> co-catalyst (5 mol%), was initially investigated for the carboxylation of iodobenzene (0.5 mmol) with CO<sub>2</sub> (1 atm) under visible light irradiation, by employing 20 W blue light under continuous stirring for 5 h using acetonitrile as a solvent and triethylamine (TEA) as a sacrificial electron source. The formation of the carboxylated product was initially confirmed with <sup>13</sup>C NMR by monitoring the peak at 172 ppm. To determine the yield and to isolate the product, methyl esterification using K<sub>2</sub>CO<sub>3</sub> and MeI in the same solution was applied after the catalytic run. The yield of the products was determined from <sup>1</sup>H NMR using triphenylmethane as the internal reference. Under this reaction condition, iodobenzene was converted to benzoic acid with 86% yield calculated from <sup>1</sup>H NMR spectra.

To further improve the yield of the carboxylation product and determine the role of other reaction parameters, it was necessary to screen more co-catalysts and reaction conditions. It was observed that without the use of any co-catalyst, only 21% of the methyl esters of the carboxylated products could be obtained from iodobenzene (Table 1, entry 1). Without the use of light, there was no formation of the products, indicating the exclusive dependency on light for the progress of the reaction (Table 1, entry 2). Again, the role of the photocatalyst COF, **TpPa-1**, was confirmed by carrying out one reaction without it, in which there was no formation of product (Table 1, entry 3).

#### Paper

To improve the reaction yield and to determine the role of temperature, two reactions were carried out at the elevated temperatures of 60 °C and 80 °C (Table 1, entries 4 and 5). Surprisingly, upon elevation of temperature, a slight improvement in the product yield was observed, eliminating the role of temperature. Since *p*-terphenyl is a commonly used co-catalyst in homogeneous photocatalysis for carboxylation, it was used in our reaction too. However, a drop in the yield of the product was observed (Table 1, entry 6). This could be due to the mismatch in the redox potential values of *p*-terphenyl and COF TpPa-1. When the reaction was exposed to sunlight for 24 h, 32% yield was noticed (Table 1, entry 7). This may be due to the low intensity of the light. So, from these control experiments, we observed that 5 mg of TpPa-1, along with 5 mol% Ni(dmg)<sub>2</sub> at 25 °C using TEA as a sacrificial electron source in acetonitrile under a 20 W blue LED, are the optimum reaction conditions.

With the optimized reaction conditions in hand, the substrate generality of the reaction was examined using various functionalized aryl iodides, bromides and chlorides (Table 2). Aryl iodides bearing electron-withdrawing ( $-NO_2$ ) and electron-donating groups ( $-CH_3$ ,  $-OCH_3$ ) were examined. Substrates containing the electron-withdrawing group  $-NO_2$  produced the corresponding esters with slightly improved yields (Table 2, entries 2–4). However, substrates containing the electron-donating groups  $-CH_3$ 



<sup>*a*</sup> All reactions were performed with 0.5 mmol of the substrates, **TpPa-1** (5 mg), Ni(dmg)<sub>2</sub> (5 mol%), CO<sub>2</sub> (1 atm), TEA (1 eq.), MeCN (5 mL). <sup>*b*</sup> Calculated for the <sup>1</sup>H NMR spectra using triphenylmethane as the internal reference.

and  $-OCH_3$  substrates produced the products with slightly reduced yields (Table 2, entries 5 and 6). This catalytic protocol works well with other halides such as Cl and Br. Aryl bromides with both electron-withdrawing and donating groups as substituents produced the corresponding products in good to moderate yields (Table 2, entries 7 and 8). Likewise, aryl chlorides were also very effective in producing the products in good to moderate yields (Table 2, entries 10–12).

Next, we applied our catalytic system to the carboxylation of benzene derivatives by  $C(SP^2)$ –H activation. Although carboxylation of the  $C(SP^2)$ –H bond is difficult compared to the  $C(SP^2)$ –X bond, with this catalytic system the benzene derivatives were able to produce the corresponding products in good yields. Benzene and nitrobenzene produced the corresponding products in 68% and 70% yield, respectively (Table 3, entries 1 and 2).

### Mechanism

A possible mechanism of this light-dependent carboxylation of aryl-X/H to form the corresponding carboxylic acids is depicted in Fig. 8. Upon photo-excitation, **TpPa-1** goes into a photo-excited state ( $E_{\text{PS}^{+/PS^{*}}} = -2.114 \text{ V}$  vs. Ag/AgCl). Upon reducing Ni(II) to Ni(0), it comes back to the ground state by oxidative quenching. After relaxation, upon accepting an electron from TEA ( $E_{1/2} = -2.5 \text{ V}$  vs. Ag/AgCl) **TpPa-1** becomes regenerated. Then, upon excitation, it undergoes additional reaction cycles. During the Ni



Fig. 8 Proposed mechanism of photocatalytic carboxylation.



catalytic cycle, the oxidative addition of Ar–X takes place, converting Ni(0) to Ni( $\pi$ ). Eliminating X<sup>-</sup>, Ni( $\pi$ ) is restored to Ni(1). Upon further insertion of CO<sub>2</sub> into Ni(1) and elimination of ArCOO<sup>-</sup>, the Ni(0) catalyst gets regenerated for further cycles. When the reaction was carried out in presence of TEMPO (radical inhibitor), there was no formation of the product, confirming the radical pathway of the reaction. This could indicate the formation of a complex with **TpPa-1**<sup>•+</sup> and TEMPO, deactivating the catalyst.

# Recyclability of the TpPa-1 COF catalyst

To carry out the recycling experiment, iodobenzene was selected as the model substrate under the optimized reaction conditions. On completion of the reaction, the COF, **TpPa-1**, was isolated and purified by washing it multiple times with acetonitrile. Surprisingly, we noticed no important alteration in its activity in terms of isolated yield. Therefore, this recycling experiment was repeated up to five times without any considerable reduction in the activity (Fig. 9). This study demonstrates the industrial importance of **TpPa-1** as a photocatalyst for carboxylation reactions.

## Conclusions

In summary, the photocatalytic carboxylation of  $C(SP^2)$ -X/H with  $CO_2$  was demonstrated utilizing the **TpPa-1** COF as the active photocatalyst together with Ni(dmg)<sub>2</sub> as a co-catalyst. The reaction proceeds with excellent yield under 1 atm pressure of  $CO_2$  along with visible light irradiation. Control experiments demonstrate that the reaction does not progress in the absence of the co-catalyst. Furthermore, even elevated temperatures cannot start the reaction under dark conditions. Therefore, the reaction can be readily controlled by light alteration. A detailed study for the mechanism of photocatalytic  $CO_2$  fixation has been established with spectroscopic analysis. Furthermore, the photocatalyst is also easily recoverable and reusable for up to five cycles without being deactivated.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

S. M. I. acknowledges the Department of Science and Technology, DST-SERB (project reference no. CRG/2020/000244), New Delhi, Board of Research in Nuclear Sciences (BRNS), Project reference no. 37(2)/14/03/2018-BRNS/37003, Govt. of India, for providing financial support. A. Das is grateful to the University Grants Commission for D. S. Kothari's postdoctoral fellowship (Award letter no. F.4-2/2006(BSR)/CH/18-19/0010). A. K. thanks the Researchers Supporting Project (Grant no. RSP-2021/127), King Saud University, Riyadh, Saudi Arabia for financial support. We acknowledge the Department of Science and Technology (DST) and the University

Grant Commission (UGC) New Delhi, India for providing support to the Department of Chemistry, the University of Kalyani under the FIST and SAP programs. P. Chakrabortty is thankful to SVMCM, WB GOVT for her fellowship. S. M. I. is thankful to the University of Kalyani for his personal research grant. A. H. Chowdhury is thankful to the University of Kalyani for her URS fellowship. We are grateful to the Department of Science and Technology (DST) New Delhi, India for providing support to the University of Kalyani under the PURSE program.

## References

- 1 P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1988, **88**, 747–764.
- 2 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 3 T. Sakakura and K. Kohno, Chem. Commun., 2009, 1312-1330.
- 4 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933–5947.
- 5 A. Correa and R. Martín, Angew. Chem., Int. Ed., 2009, 48, 6201-6204.
- 6 K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, 40, 2435–5224.
- 7 R. Martín and A. W. Kleij, *ChemSusChem*, 2011, 4, 1259–1263.
- 8 Y. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, 48, 9956-9964.
- 9 M. Börjesson, T. Moragas, D. Gallego and R. Martin, ACS Catal., 2016, 6, 6739–6749.
- 10 Y.-Y. Gui, W.-J. Zhou, J.-H. Ye and D.-G. Yu, *ChemSusChem*, 2017, **10**, 1337–1340.
- 11 S. P. Bew, in *Comprehensive Organic Functional Groups Transformation II*, ed. A. R. Katritzky and R. J. K. Taylor, Elsevier, Oxford, UK, 2005, p. 19.
- 12 L. J. Goosen, N. Rodriguez and K. Goosen, *Angew. Chem., Int. Ed.*, 2008, **47**, 3100–3120.
- 13 A. Correa and R. Martin, Angew. Chem., Int. Ed., 2009, 48, 6201–6204.
- 14 H. Maag, *Prodrugs of Carboxylic Acids*, Springer, New York, NY, USA, 2007, pp. 703–729.
- 15 Q.-Y. Meng, S. Wang and B. Konig, *Angew. Chem.*, 2017, 56, 13426–13430.
- 16 K. Shimomaki, K. Murata, R. Martin and N. Iwasawa, J. Am. Chem. Soc., 2017, 139, 9467–9470.
- 17 (a) S. Saini, H. Singh, P. K. Prajapati, A. K. Sinhaand and S. L. Jain, *ACS Sustainable Chem. Eng.*, 2019, 7, 13; (b) A. Das, R. K. Mondal, P. Chakrabortty, S. Riyajuddin, A. H. Chowdhury, S. Ghosh, A. Khan, K. Ghosh and S. M. Islam, *Mol. Catal.*, 2021, 499, 111253.
- 18 J. Schneider, H. Jia, J. T. Muckerman and E. Fujita, *Chem. Soc. Rev.*, 2012, **41**, 2036–2051.
- 19 E. B. Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev and A. B. Bocarsly, *J. Am. Chem. Soc.*, 2010, 132, 11539–11551.

- 20 J. Low, L. Zhang, B. Zhu, Z. Liu and J. Yu, ACS Sustainable Chem. Eng., 2018, 6, 15653–15661.
- 21 P. Sarkar, S. Riyajuddin, A. Das, A. H. Chowdhury, K. Ghosh and S. M. Islam, *Mol. Catal.*, 2020, **484**, 110730.
- 22 H. Wei, S. Chai, N. Hu, Z. Yang, L. Wei and L. Wang, *Chem. Commun.*, 2015, **51**, 12178–12181.
- 23 X. Mu, J. Zhan, J. Wang, W. Cai, B. Yuan, L. Song and Y. Hu, *J. Colloid Interface Sci.*, 2019, **539**, 609–618.
- 24 (a) S. Ghosh, R. A. Molla, U. Kayal, A. Bhaumik and S. M. Islam, *Dalton Trans.*, 2019, 48, 4657–4666; (b) S. Sarkar, S. Ghosh, J. Mondal and S. M. Islam, *Chem. Commun.*, 2020, 56, 12202–12205; (c) R. Khatun, S. Biswas, I. H. Biswas, S. Riyajuddin, N. Haque, K. Ghosh and S. M. Islam, *J. CO*<sub>2</sub> Util., 2020, 40, 101180.
- 25 S. Karak, S. Kandambeth, B. P. Biswal, H. S. Sasmal, S. Kumar, P. Pachfule and R. Banerjee, *J. Am. Chem. Soc.*, 2017, 139, 1856–1862.
- 26 (a) S. Ghosh, T. S. Khan, A. Ghosh, A. H. Chowdhury, M. A. Haider, A. Khan and S. M. Islam, *ACS Sustainable Chem. Eng.*, 2020, 8, 5495–5513; (b) M. Sengupta, A. Bag, S. Ghosh, P. Mondal, A. Bordoloi and S. M. Islam, *J. CO<sub>2</sub> Util.*, 2019, 34, 533–542; (c) P. Sarkar, A. H. Chowdhury, S. Riyajuddin, S. Biswas, K. Ghosh and S. M. Islam, *New J. Chem.*, 2020, 44, 744–752.
- 27 T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin and N. M. D. Brown, *Carbon*, 2005, 43, 153–161.
- 28 A. P. Dementjev, A. De Graaf, M. C. M. Van de Sanden, K. I. Maslakov, A. V. Naumkin and A. A. Serov, *Diamond Relat. Mater.*, 2000, 9, 1904–1907.