Catalytic Poly(ethylene terephthalate) Aromatic C-H Hydroxylation for Upcycling to Specialty Chemicals and Multivariate Metal-Organic Frameworks

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ABSTRACT

Poly(ethylene terephthalate) (PET), the most-produced and recovered aromatic polyester worldwide, offers numerous opportunities for upcycling into functional materials and chemicals. Although the aromatic terephthalate segment makes up 70% of the total PET mass, and offers opportunities to access valuable highly-substituted oxygenated aromatics that are important precursors to a host of specialty chemicals and functional materials, chemical modification of the terephthalate segment has thus far achieved limited success due to the aromatic ring's electron-deficiency which deactivates it towards electrophilic attack. Herein, we demonstrate the usage of transition metal-catalysed C-H activation as a viable strategy for direct functionalisation of PET's aromatic C-H bonds in this proof-of-concept study. Ruthenium-catalysed C-H hydroxylation afforded the useful, yet synthetically-challenging highly-substituted oxygenated aromatic compound, 2-hydroxyterephthalic acid, in high selectivity and synthetically-useful conversions directly from PET. Notably, this procedure was tolerant to a range of PET plastic waste, including dye-containing textiles, other plastic contaminants, and is also amenable to gram-scale aromatic functionalisation of used real-life PET beverage bottles. The resulting 2-hydroxyterephthalic acid product can be further upcycled into multivariate hydroxylated MOFs with high porosity and crystallinity, which have proven use for many known applications. Our aromatic C-H activation strategy expands the diversity and possibilities of value-added materials and chemicals accessible from PET.

INTRODUCTION

Plastics are ubiquitous materials in modern society due to their low cost, desirable material properties, lightweight and ease of processing. However, their existing linear life cycles are suboptimal. Other than being environmentally-detrimental, landfilling and incineration results in loss of the plastics' inherent material value; while repeated recycling can cause inevitable material degradation that relegates them into lower quality products, and eventually as non-recyclable waste for disposal.[1] With the production and demand of plastics expected to remain unabated for the foreseeable future, *upcycling* is emerging as a promising alternative to *recycling*. By transforming them into more valuable products such as specialty chemicals and functional materials[2-5] through processes such as oxidations,[6-9] plastics upcycling maximises resource productivity, reduces the reliance on petrochemical feedstock for these products, and contributes towards an economically-viable post-use plastics economy.

Poly(ethylene terephthalate) (PET) is the most abundant aromatic-containing plastic produced,[10] with relatively uncomplicated waste streams and well-established collection infrastructure. Thus far, PET upcycling into industrially-viable small molecule chemicals has been largely limited to producing low-molecular weight oxygenated aliphatics from the ethylene glycol segment, with the terephthalic acid (TA) unit being structurally unchanged (Figure 1, left panel).[11-15] This is unsurprising, considering that terephthalates are inherently challenging substrates for electrophilic substitution due to their electron-deficient nature, necessitating extremely forcing conditions or highly-reactive and hazardous reagents for electrophilic sulfonation[16] or bromination.[17] As such, chemical upcycling of the TA segment has been restricted to reactions at the carboxylate units, such as via alcoholysis/

aminolysis for the production of TA esters and amides respectively that can be building blocks for functional polymers (Figure 1).[18-20] To overcome these limitations, transition metal-catalysed C-H activation offers highly-efficient avenues to functionalise unreactive C-H bonds.[21] Indeed, with the TA segment accounting for nearly 70% of the total PET mass, aromatic C-H activation can allow convenient access to functionalised terephthalates traditionally inaccessible via conventional electrophilic reactivity, under comparatively mild reaction conditions with high selectivity, yields and step-economy.

PET potentially offers convenient access to highly-functionalised oxygenated aromatic compound (OAC) containing three or more oxygenated substituents.[22] Other than being useful precursors for high-value chemicals, these compounds are of considerable interest as building blocks for functional materials owing to their structural rigidity, hydrophobicity of the aromatic unit and ease of further chemical functionalisation. In particular, 2-hydroxyterephthalic acid (2OH-TA) is especially important as an essential precursor for the synthesis of drugs,[23-25] optoelectronic materials,[26, 27] coordination polymers for applications such as gas sorption and photodegradation,[28-32] biomimetic foldamers[33] and high-strength poly(hydroxy-*p*-phenylenebenzobisoxazole) fibres (Figure 1).[34] Notably, the hydroxyl groups and its alkoxy derivatives are essential for achieving unique performance in many applications: its presence can regulate flexibility of MIL-53(Al) MOFs for high-capacity methane storage[31]; improve solubility and tuning of emission properties of conjugated oxadiazole-containing optoelectronic materials;[26] as well as being primarily responsible for increased thermal stability, tensile properties and UV-resistance of poly(hydroxy-*p*-phenylenebenzobisoxazole) fibres,[34] to name a few. However, given the low reactivity of TA towards electrophilic substitution, the

conventional production of substituted terephthalates unavoidably starts from xylenes, thus necessitating further consumption of non-renewable petrochemicals, and adds to the already substantial carbon footprint of xylene production.[35] In one route, bromination of xylene, followed by oxidation of the methyl substituents under harsh conditions first afford bromo-terephthalic acid,[36] which can then be converted to 2OH-TA.[32, 37] On the other hand, aromatic C-H functionalization of PET would allow for the use of waste plastics as a feedstock instead of xylene, thus keeping the synthetically-useful aromatic unit within circular material streams.

Herein, we demonstrate a proof-of-concept for direct aromatic hydroxylation of PET, allowing straightforward access to 2OH-TA in high selectivity and synthetically-useful conversions via C-H activation (Figure 1). While terephthalate can be hydroxylated by OH radicals, generated chemically[38] or photochemically,[39] these methods can suffer from poor preparative yields and limited selectivity. Having established that PET can be a feedstock for 2OH-TA, we also demonstrate the hydroxylation of real-life PET waste on gram-scales, and in the presence of other plastic contaminants. Furthermore, the functionalized TA units derived from plastic were further incorporated into functional multivariate metal-organic frameoworks (MOFs), yielding valuable materials of high porosity and crystallinity (Figure 1), which would otherwise be made from xylene derivatives. MOFs are materials with applications in gas storage, separation and catalysis, making them an attractive target for upcycling strategies. Our work herein sets the scene for opportunities to adapt other C-H functionalization systems from the existing literature, diversifying the materials and compounds accessible from PET, with potential for further optimization of reaction greenness, scalability, and cost-effectiveness.

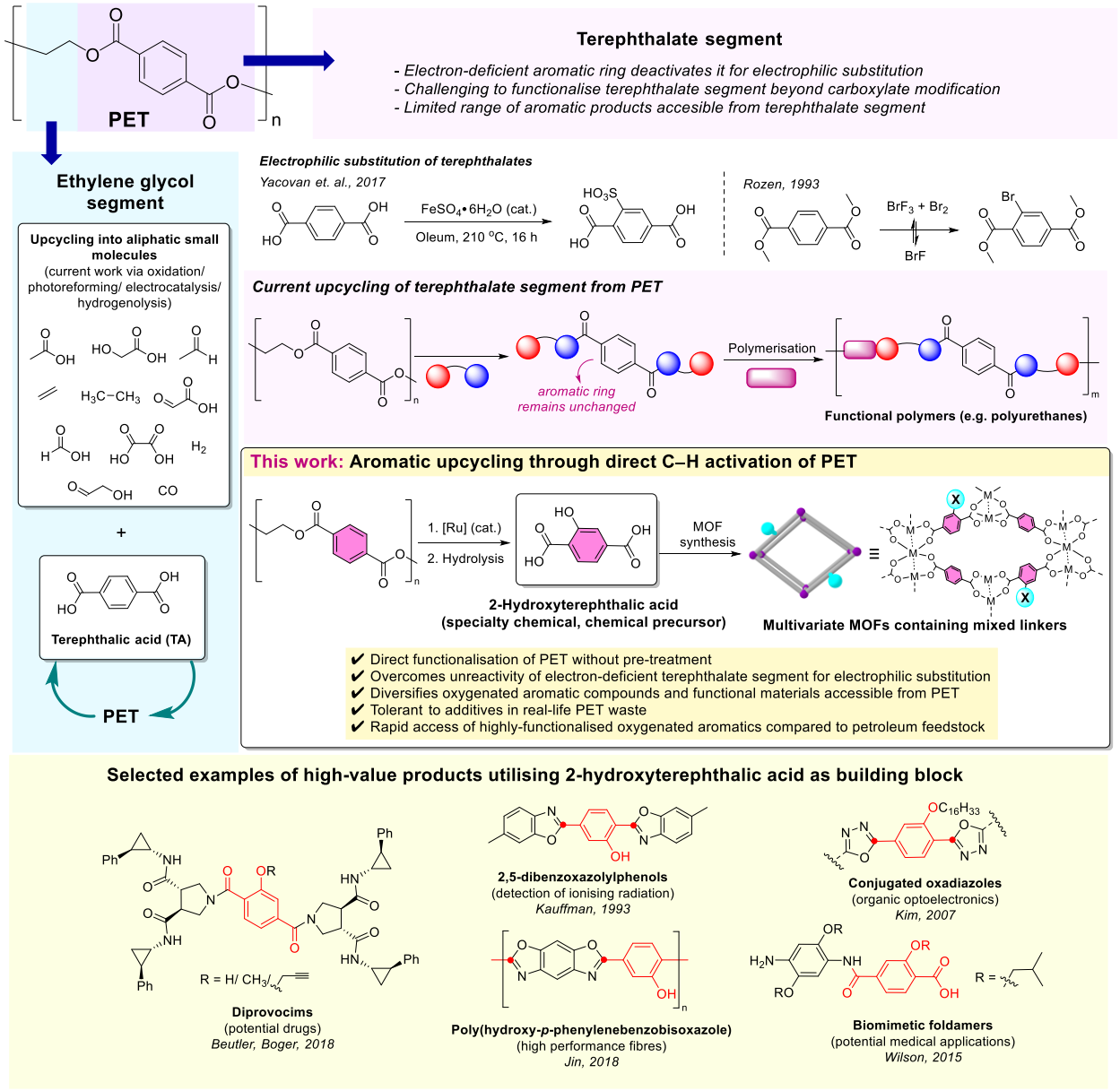


Figure 1. Existing methods for chemical upcycling of the aliphatic ethylene glycol and aromatic terephthalate segments of PET, and our strategy for aromatic PET upcycling into OACs through ruthenium-catalysed C-H hydroxylation, which serve as key building blocks of valuable chemicals and materials (selected examples provided).[25-27, 33, 34]

RESULTS AND DISCUSSION

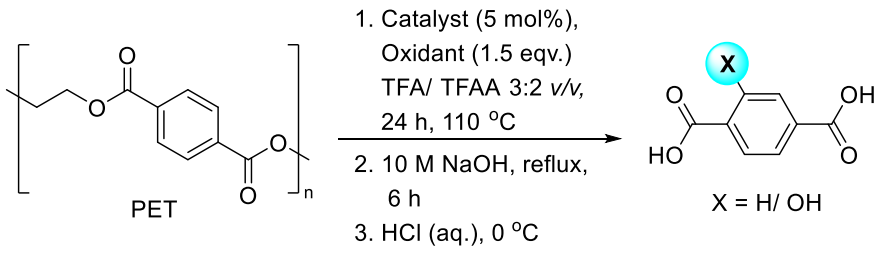
Oxidation of commercial PET resin pellets was first performed using [$RuCl_2$(*p*-cymene)]$_2$ as catalyst with Selectfluor^{TM} as the oxidant in a sealed tube (Table 1, entry 1), inspired by Rao's prior work on *ortho*-hydroxylation of small molecule arene esters.[40] This resulted in extensive polymer chain cleavage to yield a mixture of short chain oligomers (gel permeation chromatography (GPC) analysis in Figure S31A) (*vide infra*), with HR-ESI mass spectrometry (Figure 2A) suggesting successful hydroxylation. Hydrolysis of the partially-hydroxylated crude PET oligomers, followed by acidification, allowed convenient isolation of the TA derivatives by filtration, affording a mixture comprising mainly 2OH-TA and unreacted TA (Figure 2B). To confirm that no hydroxylation occurred during oligomer hydrolysis, the Ru-catalysed reaction was repeated using the same reagents except with TA under basic aqueous hydrolytic conditions (see Section S1.3 for details). No hydroxylation of TA resulted (Figure S2), confirming that aromatic hydroxylation occurred directly and exclusively on PET prior to hydrolysis.

A series of optimization and control reactions were then performed. A negative control without [$RuCl_2$(*p*-cymene)]$_2$ did not afford detectable 2OH-TA conversions (Table 1, entry 2), while doubling the Selectfluor oxidant loading did not give appreciable improvements in conversion (entry 3). Reducing the reaction temperature to 70 °C resulted in very low degrees of hydroxylation (entry 4). A shorter reaction duration (5 h), and lowering the [$RuCl_2$(*p*-cymene)]$_2$ catalyst loading from 5 mol% to 2 mol% afforded lower conversions (entries 5-6). Lower conversions were also observed when Selectfluor was replaced with the alternative oxidants Oxone®, $K_2S_2O_8$ and $NaIO_4$ (entries 7-9), whilst replacing [$RuCl_2$(*p*-cymene)]$_2$ with $Ru_2Cl_4(CO)_6$ and $Ru(CO)H_2(PPh_3)_3$ resulted in no 2OH-

TA formation under identical reaction conditions (Figures S14, S15). Although Pd catalysts have also been previously reported for *ortho*-hydroxylation of aryl esters,[41] [$RuCl_2$(*p*-cymene)]$_2$ outperformed several possible catalyst candidates using our reaction conditions (entries 10-12).

2OH-TA may also theoretically be obtained from PET by first hydrolysing the polymer to form TA, followed by TA hydroxylation. For instance, terephthalate is known to react with hydroxyl radicals to form the highly-fluorescent 2OH-TA, and hence has been used as a dosimeter for detection of these reactive oxygen species.[38] To compare this approach with the Ru-catalysed direct PET hydroxylation, we investigated TA hydroxylation under reported aqueous conditions mediated by hydroxyl radicals generated by Fenton reactions using Fe^{2+} under acidic and basic conditions, as well as between H_2O_2 and Cu^{2+} (see Section 1.3 for experimental details).[38] Of the conditions attempted, only the Fe^{2+}-mediated Fenton reaction under basic conditions (TA: H_2O_2 molar ratio of 1:20 at 2 mol% Fe^{2+} catalyst loading) afforded detectable quantities of 2OH-TA, albeit with only 4% conversion after 72 hours at room temperature (Figures S16-18). Other than providing better conversions, Ru-catalysed aromatic hydroxylation could be performed directly on PET without prior treatment or depolymerization.

Table 1. Reaction conditions for catalytic PET aromatic C-H hydroxylation.[a]



Entry	Catalyst	Oxidant	Deviation from conditions in step 1	Percentage conversion to 2OH-TA/ % [b]
1	$[RuCl_2(p\text{-cymene})]_2$	Selectfluor	-	34 ± 1
2	-	Selectfluor	No catalyst used	-
3	$[RuCl_2(p\text{-cymene})]_2$	Selectfluor	3.0 eqv. oxidant	39 ± 3
4	$[RuCl_2(p\text{-cymene})]_2$	Selectfluor	Reaction at 70 °C	4
5	$[RuCl_2(p\text{-cymene})]_2$	Selectfluor	5 h reaction	8
6	$[RuCl_2(p\text{-cymene})]_2$	Selectfluor	2 mol% catalyst loading	29 ± 1
7	$[RuCl_2(p\text{-cymene})]_2$	Oxone®	-	trace
8	$[RuCl_2(p\text{-cymene})]_2$	$K_2S_2O_8$	-	21 ± 2
9	$[RuCl_2(p\text{-cymene})]_2$	$NaIO_4$	-	4
10	$Pd(PPh_3)_2Cl_2$	Selectfluor	-	trace
11	$Pd(dppf)Cl_2$	Selectfluor	-	16
12	$Pd(OAc)_2$	Selectfluor	72 h reaction	19 ± 4

[a] All reactions were performed in a sealed tube for 24 h (300 mg PET resin, 4 mL TFA/TFAA 3:2 *v/v*) under ambient lighting, with 5 mol% catalyst loading and 1.5 eqv. oxidant (w.r.t. PET repeating unit) at 300 RPM stirring rate unless otherwise stated. TFA = trifluoroacetic acid; TFAA = trifluoroacetic anhydride. [b] Determined by ^{1}H NMR analysis of the crude hydrolysed terephthalic acid mixture (Section S2), with percentage conversion = $\frac{n_{(2OH-TA)}}{n_{(2OH-TA)} + n_{TA\ remaining}}$ x 100%; where errors are reported, values are the average of two repeats, with errors (±) given as standard deviations.

TFA/TFAA was found to play multiple roles in this reaction. Firstly, TFAA was essential for the hydroxylation to occur: when the conditions of Table 1, entry 1 were repeated in the absence of TFAA, complete absence of hydroxylation resulted (Figure S19), even in the presence of $[RuCl_2(p\text{-cymene})]_2$ and Selectfluor oxidant. Based on prior mechanistic studies,[40, 41] the reaction is likely to proceed by first coordination of Ru to the carbonyl group of PET's ester unit, followed by a directed C-H activation on the aromatic ring's adjacent ortho-position. We managed to detect the trifluoroacetate phenyl ester of 2OH-TA as an intermediate by ESI-MS after successful hydroxylation from Table 1, entry 1 (Figures 2C, S32), which was also previously detected through Pd-catalysed TFAA-mediated hydroxylation.[41] This suggested that the reaction likely proceeded through installation of a trifluoroacetate ester group that could be derived from TFAA, which then underwent hydrolysis to form the phenol during subsequent basic aqueous treatment of the oligomers. The absence of products from EG oxidation from ESI-MS analyses shows preference for sp^2 over sp^3 C-H activation, suggesting that a rebound-type mechanism catalyzed by high-valent Ru-oxo species is unlikely.

Secondly, other than enabling PET dissolution for the hydroxylation reaction to occur in the homogeneous phase, TFA/TFAA also resulted in PET chain cleavage into short oligomeric fragments: when PET was heated at 110 °C in *only* TFA/TFAA 3:2 *v/v* for 24 h, the resulting solids isolated by precipitation in water were soluble in THF, unlike PET, and were shown to be short-chain oligomers by GPC and ESI-MS analyses (Figures S31B and S36 respectively). These solids also contained numerous fluorinated species as shown by ^{19}F NMR, which were consistent with the expected chemical shifts of TFA esters (Figure S21).[41, 42] We were able to rule out the possibility of *in-situ* PET hydrolysis by residual

moisture present in the reaction, as these would have been readily reacted with and removed by TFAA present. Considering that TFA is a known solvent for PET,[43] its ability to also degrade PET by acidolysis in a similar way to acetic[44] and succinic acid[45] warrants attention when employed to facilitate PET dissolution in future studies, especially under elevated temperatures. To probe the effect of the PET polymer structure on 2OH-TA conversion, the reaction (Table 1, entry 1) was repeated using diethyl terephthalate (DETA) as a model small molecule substrate. At identical conditions and concentrations, considerably higher conversion of (66 ± 2) % (average of 2 repeats) to 2OH-TA was observed with DETA (Figure S20) compared with PET. This may be attributed to multiple factors such as greater viscosity of the PET solution which reduces mass transport of reactive intermediates, as well as non-uniform and reduced accessibility of aromatic TA segments due to specific conformations adopted by the polymer in solution. Differences in reactivity between substrates of different chain lengths has been previously observed in aliphatic C-H aminations.[46] Thus, the TFA acidolysis of PET during the reaction could have significantly facilitated polymer hydroxylation by forming shorter oligomers that are more susceptible to reactive attack.

Next, we demonstrated the feasibility of aromatic upcycling of real-life PET waste. As shown in Figure 3A, subjecting a transparent PET food container, soap bottle, a coloured PET bottle and dyed PET textiles from discarded clothing to the Ru-catalysed hydroxylation reaction at 120 °C for 72 h resulted in successful conversion to 2OH-TA in all cases (see Section 1.2 for details). This showed that the hydroxylation was tolerant to common additives found in PET plastic products, which notably included dyes, as well as antioxidants added to reduce natural polymer thermal-oxidation.[47] Additionally, the

reaction was also amenable to scale-up: 2 g of a transparent waste PET beverage bottle were subjected to the same hydroxylation conditions, affording a product mixture containing TA and 2OH-TA in ~1:1 molar ratio [conversion = (53 ± 10) % from 3 repeats] after 72 h (Figure S30). The ruthenium-containing by-products can also be easily and rapidly removed from the TA mixture with aqueous H_2O_2 (see Section S1.2 for details).[48]

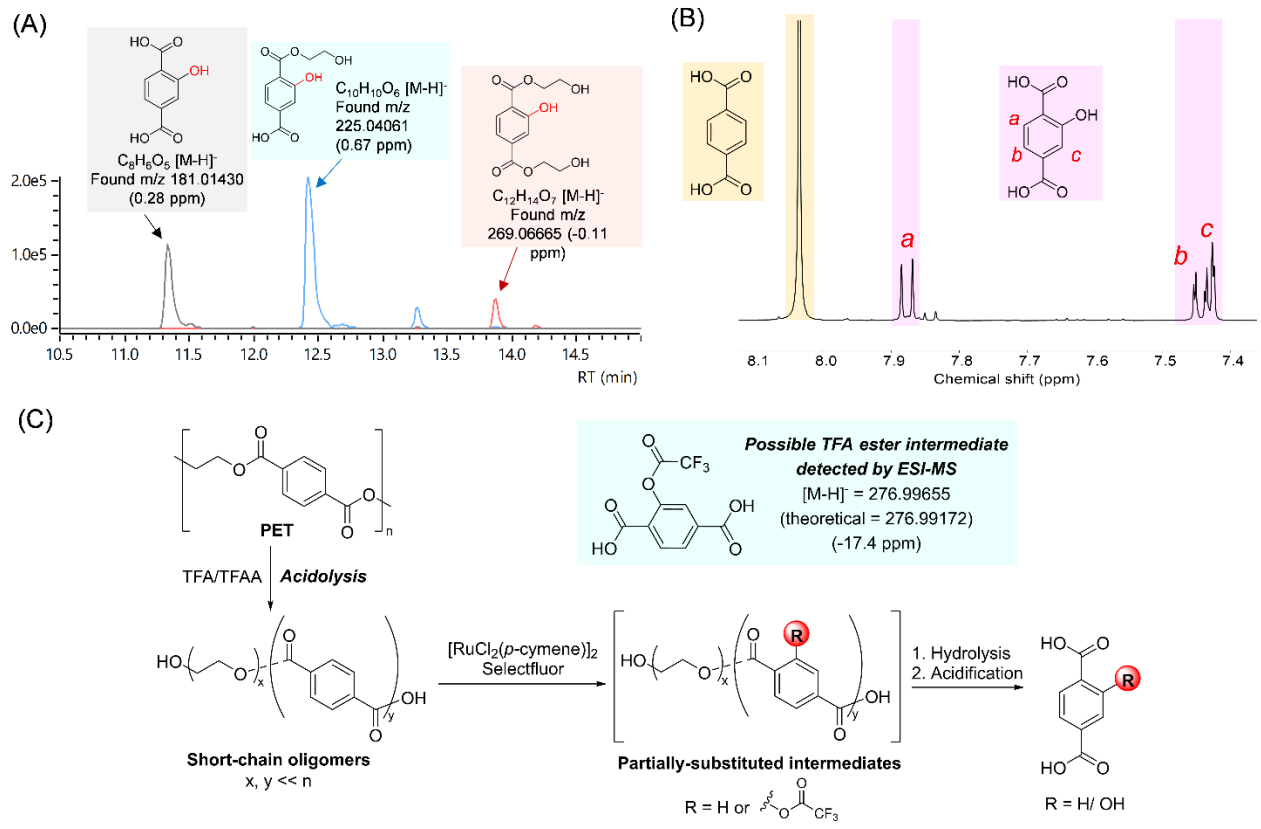


Figure 2. (A) Overlay of LC-QTOF-MS extracted ion chromatograms of hydroxylated products present in the crude product mixture from Ru-catalysed hydroxylation. Hydroxylated compounds $C_8H_6O_5$, $C_{10}H_{10}O_6$ and $C_{12}H_{14}O_7$ are putatively identified (MS and MS/MS spectra in Figure S33); (B) ^{1}H NMR spectroscopy (d_6-DMSO, 25 °C) of the aromatic products after oligomer hydrolysis, showing the dominant presence of 2OH-TA and TA; (C) Partial acidolysis of the PET polymer by

the TFA/TFAA solvent mixture, followed by Ru-catalysed hydroxylation, likely proceeding through a TFA-ester intermediate.

Real-world PET waste streams typically contain a variety of polymer impurities, even in segregated bottle recycling bins. The need to separate PET from these contaminants therefore require additional sorting steps that would incur further cost. To investigate how polymer impurities can affect the PET aromatic hydroxylation, reactions were performed on waste PET bottle scraps in the presence of PE bottle caps, HDPE plastic bags and polystyrene packaging waste (Styrofoam), which are commonly discarded together with waste PET bottles. Additionally, in anticipation of the introduction of poly(ethylene furanoate) (PEF) as a possible future bio-based replacement for PET,[49] and is hence likely to be discarded together with PET in the same waste stream, we also attempted PET hydroxylation in the presence of commercially-available PEF resins. In all cases, these additional plastic contaminants could be easily removed by filtration after basic hydrolysis of the hydroxylated PET oligomers (Figure 3B), yielding clean mixtures of TA and 2OH-TA after subsequent hydrolysis and acidification, with these plastic contaminants chemically unmodified after the reaction (Figures S26-29). These findings underscored the tolerance of the Ru-catalysed hydroxylation to these plastic impurities, affording similar conversions of PET to 2OH-TA in all cases.

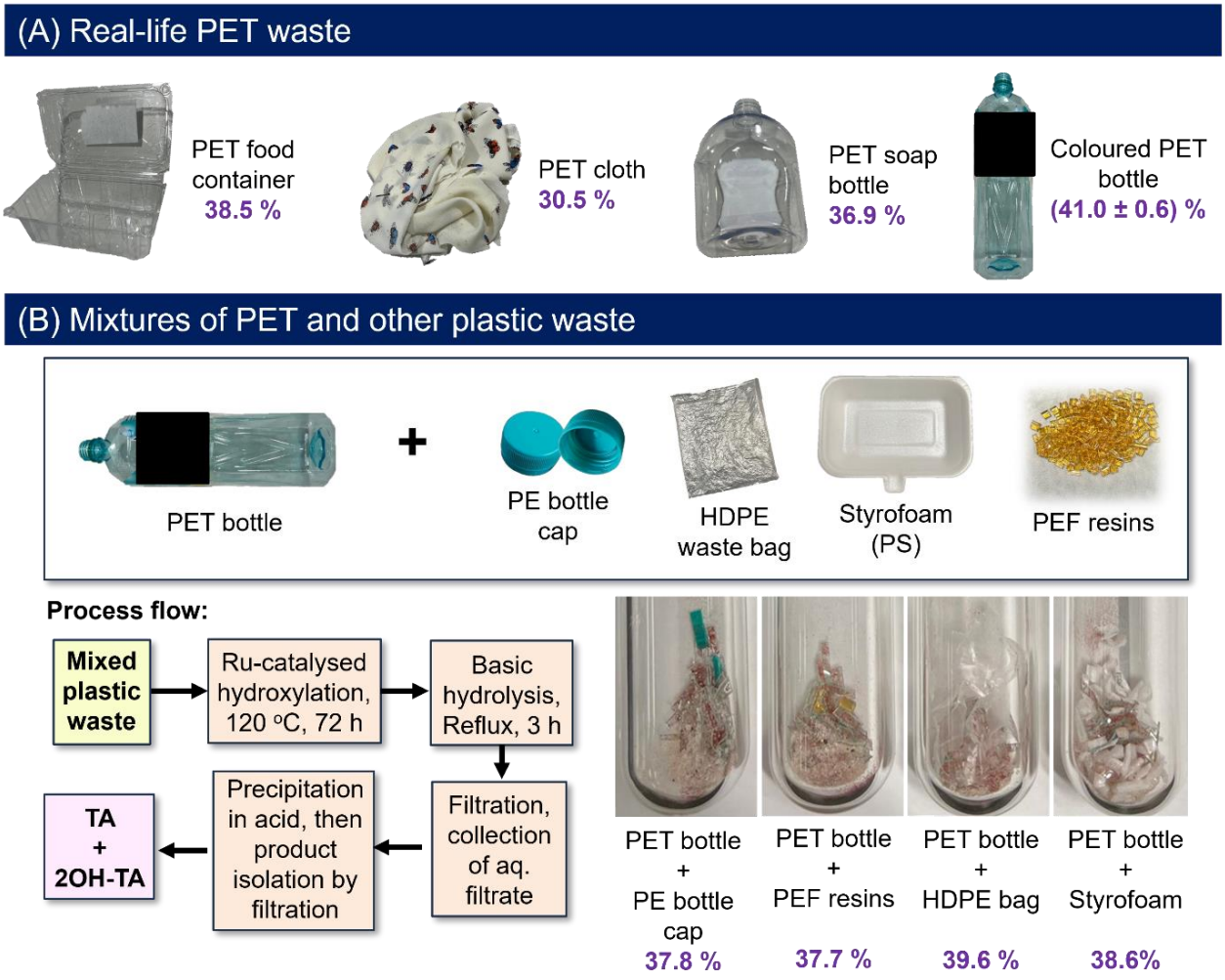


Figure 3. Conversion of (A) real-world PET plastic waste, containing dyes and additives, to 2OH-TA. Conversions to 2OH-TA for the coloured PET bottle are the average of two repeats, with errors (±) given as standard deviations; (B) a PET plastic bottle in the presence of polymer impurities such as PE, PS and PEF. Percentage values provided are percentage conversions to 2OH-TA. Reaction conditions: 300 mg PET beverage bottle waste (brand redacted), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), Selectfluor (1.5 eqv. w.r.t. PET repeating units), TFA/TFAA 3:2 *v/v*, 120 °C, 72 h. Commercially-available PEF resins were used due to the inability to source for real-life PEF waste at the time of writing.

We then sought to further enhance the value of the aromatic-functionalized PET by upcycling it into more advanced materials. We chose metal-organic frameworks (MOFs) as our target platform due to their broad industrial applications and the growing interest in their synthesis from alternative feedstock such as waste plastics.[50] Although converting PET waste into MOFs could significantly reduce reliance on petrochemicals,[50] reported upcycling processes only yield MOFs containing unfunctionalized terephthalate,[51-53] thus limiting the range of applications for PET-derived MOFs. Our work, which increases the organic functionality of the TA core, expands the variety of functional MOFs that can be produced. Furthermore, MOFs can accommodate linkers with various functional groups within the same structure, forming solid solutions or multivariate MOFs.[54] This allows for the TA and 2OH-TA mixture to be upcycled as is to multivariate MOFs without further purification. Specifically, we targeted MIL-53(Al) and UiO-66, benchmark MOFs known for their chemical stabilities and many proven applications. Hydroxylation of these MOFs' ligands is known to enhance their properties,[30, 31, 55] and the hydroxyl groups also can serve as sites for further functionalization,[29, 56] for diverse applications such as hydrogen adsorption, methane storage and augmenting proton conductivity for solid electrolytes.

Direct use of the mixture of TA and 2OH-TA obtained from the hydrolysis of the functionalised PET (from transparent waste bottles) for MOF synthesis provided a straightforward route to synthesizing both MOFs (denoted herein as UiO-66$_{PET-OH}$ and MIL-53$_{PET-OH}$) containing the mixture of linkers (see Section S1.2 for details) (Figure 4A). Briefly, UiO-66$_{PET-OH}$ was synthesized following reported methods[57] using aqueous HCl as an additive. The best conditions for synthesizing MIL-53$_{PET-OH}$ was found to utilize formic acid as a modulator and DMF as a solvent,[58] since aqueous synthesis of MIL-53 results in

unreacted terephthalic acid trapped in the pores and low yields, leading to poor reproducibility of the final composition of the MOF. The crystallinity of both MOFs was confirmed by X-ray diffraction (XRD) analysis (Figure 4B), and it is noteworthy that synthesis of MIL-53 using the mixed TA and OH-TA ligand system under the modulated DMF synthesis route led to better crystallinity than when using pure TA (Figure S40), suggesting that the hydroxyl groups have some structure directing effects. ^{1}H NMR analysis of the digested MOFs confirmed the incorporation of both TA and 2OH-TA into the final products in ratios similar to those present in the functionalized PET (Figures S37, S38), showing that there were no obvious inherent preferences for either ligand in UiO-66 and MIL-53 synthesis. N_2 absorption at 77 K and CO_2 absorption at 273.15 K were also measured for both MOFs to demonstrate their porosities (Figure 4C). Gratifyingly, the porosities of our functionalized MOFs obtained from upcycling of PET were comparable to the MOFs prepared from commercial TA (Figures S47, 49).

For comparison, analogous MOFs were synthesized using pure, commercially sourced 2-hydroxyterephthalic acid, yielding UiO-66-OH and MIL-53(Al)-OH and their gas sorption behavior and thermal stabilities were measured (see Section S4.4). CO_2 adsorption at 273.15 K revealed notable differences for MIL-53(Al)-OH (Figure S54). At low pressure, MIL-53(Al)-OH exhibits lower CO_2 uptake than MIL-53(Al)$_{PET\text{-}OH}$, which may indicate that the hydroxylated framework initially adopts a "very narrow pore" (*vnp*) form. This form is likely stabilized by strong intra-framework hydrogen bonding, as reported in related systems such as MIL-53-NH_2.[59] The gradual increase in uptake and slight desorption hysteresis suggest a possible pressure-induced transition from the *vnp* to the narrow-pore (*np*) form. In contrast, MIL-53(Al)$_{PET\text{-}OH}$, which contains approximately

half the amount of hydroxylated linkers (Figure S39), shows higher uptake at low pressures, consistent with a more open pore state under the same conditions.

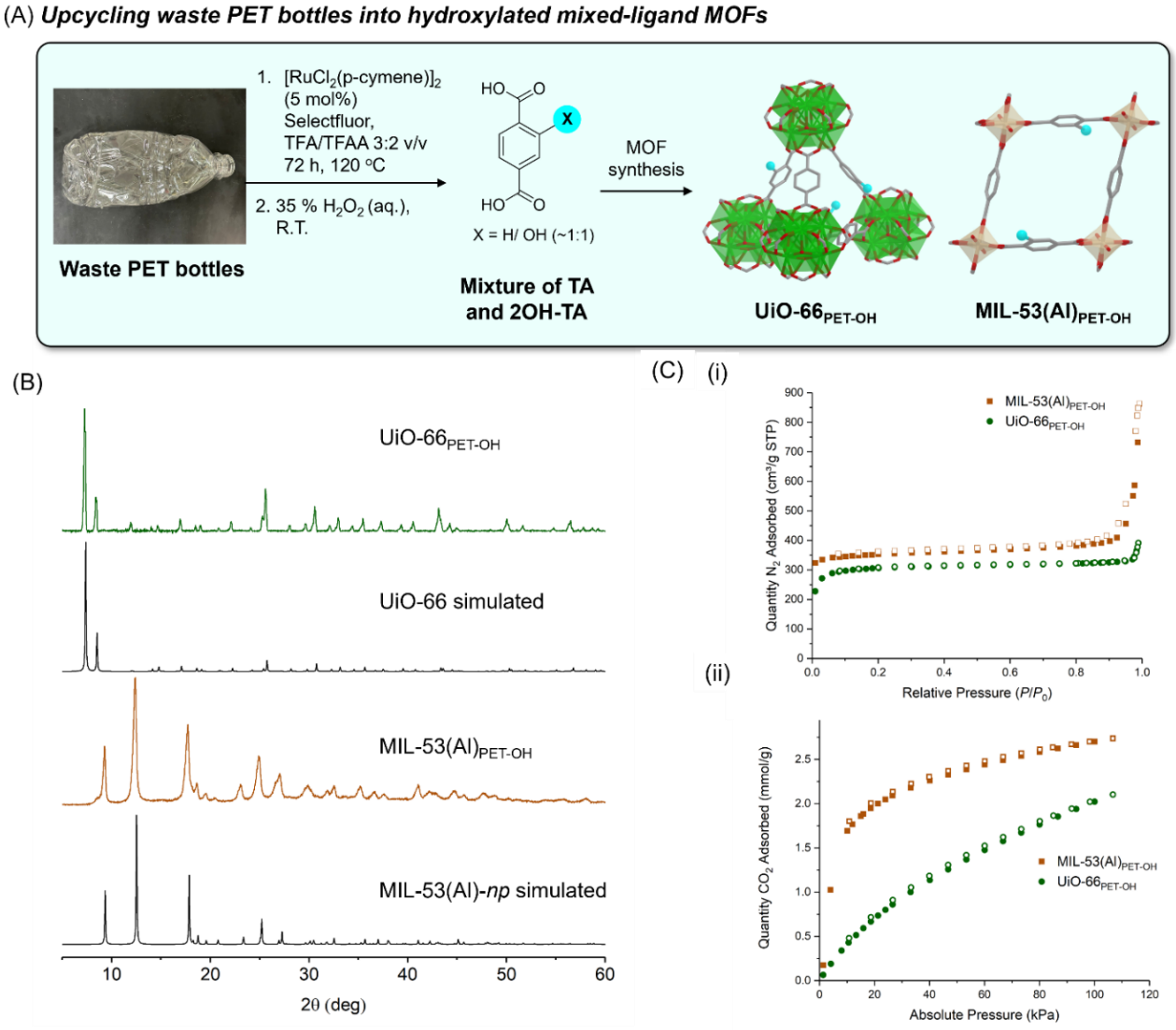


Figure 4. (A) Upcycling waste PET bottles to mixed-ligand UiO-66$_{PET-OH}$ and MIL-53(Al)$_{PET-OH}$ MOFs containing TA and 2OH-TA; (B) X-ray diffraction (XRD) pattern of UiO-66$_{PET-OH}$ and MIL-53(Al)$_{PET-OH}$ synthesized from functionalized PET and simulated MOF XRD for comparison[60, 61]; (C)(i) N_2 absorption isotherms at 77 K and (ii) CO_2 absorption isotherms at

273.15 K for UiO-66$_{PET\text{-}OH}$ and MIL-53(Al)$_{PET\text{-}OH}$. Solid marks denote absorption isotherms and hollow marks denote desorption isotherms

CONCLUSIONS

In conclusion, we have demonstrated a simple one-pot Ru-catalysed, direct aromatic hydroxylation of PET plastics, achieving high selectivity for the 2OH-TA specialty chemical in synthetically-useful conversions. Although the PET polymer structure was found to elicit lower degrees of functionalization as compared to the diethyl terephthalate model compound, TFA-mediated PET acidolysis occurred during the reaction to yield low molecular weight oligomers that likely increased the substrate's susceptibility to hydroxylation. Using these conditions, a range of real-life PET waste could be successfully hydroxylated directly, even in the presence of common plastic contaminants. Successful gram-scale hydroxylation of waste PET bottles afforded a mixture of TA and 2OH-TA, which can be further upcycled into even more valuable multivariate hydroxyl-containing MOFs with excellent crystallinity and porosity.

The Ru-catalysed upcycling of PET's unreactive aromatic segment reported herein is advantageous for the possibility of directly using PET waste and mixtures without pretreatment or prior depolymerization, preparative-scale TA conversions, and relatively mild reaction conditions compared to forcing reactivity typically required to achieve electrophilic substitution on TA (Figure 1). However, there are several important considerations that need to be taken into account for future development of PET hydroxylation, such as in potential industrial translation. Firstly, the usage of TFA and TFAA is indispensable for the current reaction conditions, which provided superior

conversions to Fenton oxidation of TA monomers in more benign aqueous media under ambient conditions. TFA is hence a major by-product of the process, from its usage as reaction solvent, as well as production from basic hydrolysis and acidification of TFAA and the trifluoromethyl ester intermediates formed during the reaction. It is thus imperative that waste streams are properly treated to avoid releasing TFA into the environment due to its persistence and potential health hazards.[62, 63] To this end, the bulk of the TFA could be potentially recovered from aqueous waste through reactive distillation,[64] with any residual TFA remaining eliminated using activated carbon materials[65] or converted to benign non-fluorinated products through photoreductive fluorination.[66] The recovered TFA can be used for subsequent reactions and dehydrated to regenerate TFAA through established processes.[67] Additionally, there is further potential for improving the sustainability of the process for industrial translation, which results in not only reduced toll on the environment, but also reduced operating expenditure through avoidance of large-scale specialised waste disposal. For instance, although our findings showed that Selectfluor elicited better conversions than potassium persulfate, the latter could be more suited for industrial deployment due to its lower cost and more environmentally-benign side-products formed after the reaction. Strategies such as immobilization of the Ru complexes onto solid supports[68] could improve cost effectiveness by allowing catalyst recovery and reusability for multiple reaction runs compared to homogeneous-phase catalysts. Indeed, life cycle assessments and techno-economic analyses will undoubtedly prove instructive in guiding the environmental impact and economic viability of scale-up process development. Our proof-of-concept study significantly enhances the value of PET as feedstock for upcycling by expanding the range of high-value products accessible from the traditionally-overlooked

aromatic segment, setting the scene for future development of new processes with enhanced sustainability and scalability.

EXPERIMENTAL SECTION

Details on materials and instrumentation, methods for hydroxylation of different PET plastics and mixtures, as well as synthesis of MOFs (UiO-66, UiO-66-OH, MIL-53(Al) and MIL-53(Al)-OH) are provided in the Supporting Information.

General procedure for PET aromatic hydroxylation to 2OH-TA (Table 1, entry 1)

PET pellets (300 mg, 1.56 mmol repeating units), Selectfluor^{TM} (829 mg, 2.34 mmol) and [RuCl2(p-cymene)]2 (48 mg, 0.078 mmol, 5 mol% w.r.t. PET repeating units) were weighed into a Schlenk tube. TFA (2.4 mL) was then added, followed by TFAA (1.6 mL) portionwise, before the flask was sealed and heated at 110 °C for 24 hours under stirring at 300 RPM. Upon cooling the reaction tube to room temperature, the tube was carefully and slowly opened (CAUTION: degassing and bubbling of the reaction solution can be expected), and its contents were added dropwise to a 10 M NaOH solution (25 mL) chilled in an ice bath. The basified solution was warmed to room temperature, before heating under reflux for 6 hours. The dark-coloured suspension was then filtered over celite, and the filtrate was added dropwise to vigorously-stirred 5 M HCl (75 mL) chilled in an ice bath over 30 minutes, whereupon a suspension was obtained. The suspension was chilled for a further hour at 0 °C, before being filtered and dried in vacuo to obtain the mixture of terephthalic acid and 2OH-TA. **[1]Synthesis of UiO-66$_{PET-OH}$**

A 50-mL screw capped glass bottle was charged with a mixture of terephthalic acid and 2OH-TA consisting of 52 mol% terephthalic acid and 48% 2OH-TA (174 mg, ~0.52 mmol terephthalic acid and ~0.48 mmol 2OH-TA) in 20 mL of DMF. $ZrCl_4$ (233 mg, 1 mmol) was added, followed by

100 μL of 36% hydrochloric acid. The mixture was agitated under ultrasonication till a homogenous solution formed, then placed in a preheated oven at 130 °C for 24 hours. After cooling to room temperature, the colourless powder was collected by suction filtration, rinsed with a small amount of DMF and then with ethanol. The collected solids were then redispersed in water (20 mL) and heated to 80 °C for 2 hours to remove DMF from within the MOF pores. The MOF was then collected again by filtration and dried in an oven at 80 °C for 1 hour.

Synthesis of MIL-53(Al)$_{PET\text{-}OH}$

A 50-mL screw capped glass bottle was charged with $AlCl_3 \cdot 6H_2O$ (510 mg, 2.1 mmol), the mixture of terephthalic acid and 2OH-TA (368 mg, 1.1 mmol terephthalic acid, 1.0 mmol 2OH-TA), 30 mL DMF and 8 mL formic acid. The mixture was agitated under ultrasonication till a homogenous solution formed, then placed in a preheated oven at 120 °C for 24 hours. After cooling to room temperature, the off-white powder was collected by suction filtration, rinsed with a small amount of DMF and then with ethanol. The samples were then activated at 160 °C for 24 hours to remove all DMF within the pores. Before activation, the MIL-53(Al)$_{PET\text{-}OH}$ was in a large pore form, and contracted to a narrow pore form after activation.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, materials and methods; ^{1}H NMR spectra and ESI mass spectrometry analyses of products, and characterization of MOF samples

through ^{1}H NMR, XRD, TGA and BET analyses.

AUTHOR INFORMATION

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

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REFERENCES

1. *The New Plastics Economy: Rethinking the future of plastics* Ellen MacArthur Foundation: 2016.
2. Jehanno, C.; Alty, J. W.; Roosen, M.; De Meester, S.; Dove, A. P.; Chen, E. Y. X.; Leibfarth, F. A.; Sardon, H., Critical advances and future opportunities in upcycling commodity polymers. *Nature* **2022,** *603* (7903), 803-814.
3. Zhao, X.; Boruah, B.; Chin, K. F.; Đokić, M.; Modak, J. M.; Soo, H. S., Upcycling to Sustainably Reuse Plastics. *Adv. Mater.* **2021,** *n/a* (n/a), 2100843.

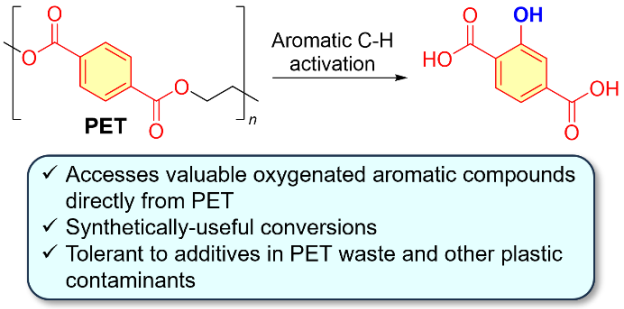
4. Nguyen, B.-N. T.; Lim, J. Y. C., Emerging green approaches for valorization of plastics with saturated carbon backbones. *Trends in Chemistry* **2024,** *6* (3), 100-114.
5. Guselnikova, O.; Semyonov, O.; Sviridova, E.; Gulyaev, R.; Gorbunova, A.; Kogolev, D.; Trelin, A.; Yamauchi, Y.; Boukherroub, R.; Postnikov, P., "Functional upcycling" of polymer waste towards the design of new materials. *Chem. Soc. Rev.* **2023,** *52* (14), 4755-4832.
6. Ong, A.; Wong, Z. C.; Chin, K. L. O.; Loh, W. W.; Chua, M. H.; Ang, S. J.; Lim, J. Y. C., Enhancing the photocatalytic upcycling of polystyrene to benzoic acid: a combined computational-experimental approach for acridinium catalyst design. *Chem. Sci.* **2024,** *15* (3), 1061-1067.
7. Ong, A.; Teo, J. Y. Q.; Feng, Z.; Tan, T. T. Y.; Lim, J. Y. C., Organocatalytic Aerobic Oxidative Degradation of Polystyrene to Aromatic Acids. *ACS Sustainable Chem. Eng.* **2023,** *11* (34), 12514-12522.
8. Pifer, A.; Sen, A., Chemical Recycling of Plastics to Useful Organic Compounds by Oxidative Degradation. *Angew. Chem. Int. Ed.* **1998,** *37* (23), 3306-3308.
9. Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Vega Herrera, D. E.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J., Chemical Recycling of Polystyrene to Valuable Chemicals via Selective Acid-Catalyzed Aerobic Oxidation under Visible Light. *J. Am. Chem. Soc.* **2022,** *144* (14), 6532-6542.
10. Global primary plastic waste generation by polymer, 2019. https://ourworldindata.org/grapher/plastic-waste-polymer (accessed 26 Dec 2023).
11. Zhou, H.; Ren, Y.; Li, Z.; Xu, M.; Wang, Y.; Ge, R.; Kong, X.; Zheng, L.; Duan, H., Electrocatalytic upcycling of polyethylene terephthalate to commodity chemicals and H2 fuel. *Nat Commun* **2021,** *12* (1), 4679.
12. Han, M.; Zhu, S.; Xia, C.; Yang, B., Photocatalytic upcycling of poly(ethylene terephthalate) plastic to high-value chemicals. *Appl. Catal. B: Environ.* **2022,** *316*, 121662.
13. Bhattacharjee, S.; Guo, C.; Lam, E.; Holstein, J. M.; Rangel Pereira, M.; Pichler, C. M.; Pornrungroj, C.; Rahaman, M.; Uekert, T.; Hollfelder, F.; Reisner, E., Chemoenzymatic Photoreforming: A Sustainable Approach for Solar Fuel Generation from Plastic Feedstocks. *J. Am. Chem. Soc.* **2023,** *145* (37), 20355-20364.
14. Wu, P.; Lu, G.; Cai, C., Cobalt–molybdenum synergistic catalysis for the hydrogenolysis of terephthalate-based polyesters. *Green Chem* **2021,** *23* (21), 8666-8672.
15. Wu, Y.; Wang, X.; Kirlikovali, K. O.; Gong, X.; Atilgan, A.; Ma, K.; Schweitzer, N. M.; Gianneschi, N. C.; Li, Z.; Zhang, X.; Farha, O. K., Catalytic Degradation of Polyethylene Terephthalate Using a Phase-Transitional Zirconium-Based Metal–Organic Framework. *Angew. Chem. Int. Ed.* **2022,** *61* (24), e202117528.
16. Yacovan, A.; Barda, Y.; Mirilashvili, S.; Baron, S. A. Process for preparing 1.1.3-trioxo-1.2-benzothiazole-6-carboxamide. 2017.
17. Rozen, S.; Lerman, O., Bromination of deactivated aromatics using bromine trifluoride without a catalyst. *J. Org. Chem.* **1993,** *58* (1), 239-240.
18. Tan, M. Y.; Goh, L.; Safanama, D.; Loh, W. W.; Ding, N.; Chien, S. W.; Goh, S. S.; Thitsartarn, W.; Lim, J. Y. C.; Fam, D. W. H., Upcycling waste poly(ethylene terephthalate) into polymer electrolytes. *J Mat Chem A* **2022,** *10* (46), 24468-24474.
19. Liu, Z.; Zhang, H.; Liu, S.; Wang, X., Bio-based upcycling of poly(ethylene terephthalate) waste to UV-curable polyurethane acrylate. *Polym. Chem.* **2023,** *14* (10), 1110-1116.

20. Foster, J. C.; Zheng, J.; Arifuzzaman, M.; Rahman, M. A.; Damron, J. T.; Guan, C.; Popovs, I.; Galan, N.; Demchuk, Z.; Saito, T., Closed-loop recycling of semi-aromatic polyesters upcycled from poly(ethylene terephthalate). *Cell Rep Phys Sci* **2023,** *4* (12), 101734.
21. Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J., Mild metal-catalyzed C–H activation: examples and concepts. *Chem. Soc. Rev.* **2016,** *45* (10), 2900-2936.
22. Lim, J. Y. C., Low-Temperature Catalytic Approaches for Upcycling Plastics into Oxygenated Aromatic Compounds. *ChemCatChem* **2025,** *17* (4), e202401626.
23. Weinert, E. E.; Dondi, R.; Colloredo-Melz, S.; Frankenfield, K. N.; Mitchell, C. H.; Freccero, M.; Rokita, S. E., Substituents on Quinone Methides Strongly Modulate Formation and Stability of Their Nucleophilic Adducts. *J. Am. Chem. Soc.* **2006,** *128* (36), 11940-11947.
24. Prescher, H.; Schweizer, A.; Frank, M.; Kuhfeldt, E.; Ring, J.; Nitschke, L., Targeting Human CD22/Siglec-2 with Dimeric Sialosides as Novel Oligosaccharide Mimetics. *J. Med. Chem.* **2022,** *65* (15), 10588-10610.
25. Morin, M. D.; Wang, Y.; Jones, B. T.; Mifune, Y.; Su, L.; Shi, H.; Moresco, E. M. Y.; Zhang, H.; Beutler, B.; Boger, D. L., Diprovocims: A New and Exceptionally Potent Class of Toll-like Receptor Agonists. *J. Am. Chem. Soc.* **2018,** *140* (43), 14440-14454.
26. Bolton, O.; Kim, J., Design principles to tune the optical properties of 1,3,4-oxadiazole-containing molecules. *J. Mater. Chem.* **2007,** *17* (19), 1981-1988.
27. Kauffman, J. M.; Bajwa, G. S., Synthesis and photophysical properties of fluorescent 2,5-dibenzoxazolylphenols and related compounds with excited state proton-transfer. *J. Heterocycl. Chem.* **1993,** *30* (6), 1613-1622.
28. Li, Z.-M.; Qiao, Y.; Liu, C.-B.; Zhou, Y.-F.; Wang, X.-Y.; Charpentier, P. A.; Che, G.-B.; Xu, W. Z.; Liu, L.-H.; Zhu, E.-W., Syntheses, crystal structures, adsorption properties and visible photocatalytic activities of highly stable Pb-based coordination polymers constructed by 2-(2-carboxyphenyl)imidazo(4,5-f)-(1,10)phenanthroline and bridging linkers. *Dalton Trans* **2018,** *47* (23), 7761-7775.
29. Himsl, D.; Wallacher, D.; Hartmann, M., Improving the Hydrogen-Adsorption Properties of a Hydroxy-Modified MIL-53(Al) Structural Analogue by Lithium Doping. *Angew Chem Int Ed.* **2009,** *48* (25), 4639-4642.
30. Yamada, T.; Shirai, Y.; Kitagawa, H., Synthesis, Water Adsorption, and Proton Conductivity of Solid-Solution-Type Metal–Organic Frameworks Al(OH)(bdc-OH)x(bdc-NH2)1−x. *Chem. Asian J.* **2014,** *9* (5), 1316-1320.
31. Kundu, T.; Shah, B. B.; Bolinois, L.; Zhao, D., Functionalization-Induced Breathing Control in Metal–Organic Frameworks for Methane Storage with High Deliverable Capacity. *Chem. Mater.* **2019,** *31* (8), 2842-2847.
32. Zhao, Y.; Wu, H.; Emge, T. J.; Gong, Q.; Nijem, N.; Chabal, Y. J.; Kong, L.; Langreth, D. C.; Liu, H.; Zeng, H.; Li, J., Enhancing Gas Adsorption and Separation Capacity through Ligand Functionalization of Microporous Metal–Organic Framework Structures. *Chem. Eur. J.* **2011,** *17* (18), 5101-5109.
33. Rodriguez-Marin, S.; Murphy, N. S.; Shepherd, H. J.; Wilson, A. J., Design, synthesis and conformational analyses of bifacial benzamide based foldamers. *RSC Adv.* **2015,** *5* (126), 104187-104192.
34. Zhang, J.; Jin, N.; Gao, J., Superior comprehensive performance of a rigid-rod poly(hydroxy-p-phenylenebenzobisoxazole) fiber. *Polymer* **2018,** *149*, 325-333.
35. *The Future of Petrochemicals: Towards more sustainable plastics and fertilisers*; International Energy Agency (IEA): Paris, 2018.

36. Ritter, J. C. Process for the Synthesis of Halogenated Aromatic Diacids. 2008.
37. Ritter, J. C. Process for the synthesis of hydroxy aromatic acids. 2008.
38. Barreto, J. C.; Smith, G. S.; Strobel, N. H. P.; McQuillin, P. A.; Miller, T. A., Terephthalic acid: A dosimeter for the detection of hydroxyl radicals in vitro. *Life Sci.* **1994,** *56* (4), PL89-PL96.
39. Day, M.; Wiles, D. M., Photochemical degradation of poly(ethylene terephthalate). III. Determination of decomposition products and reaction mechanism. *J. Appl. Polym. Sci.* **1972,** *16* (1), 203-215.
40. Yang, Y.; Lin, Y.; Rao, Y., Ruthenium(II)-Catalyzed Synthesis of Hydroxylated Arenes with Ester as an Effective Directing Group. *Org. Lett.* **2012,** *14* (11), 2874-2877.
41. Shan, G.; Yang, X.; Ma, L.; Rao, Y., Pd-Catalyzed C□H Oxygenation with TFA/TFAA: Expedient Access to Oxygen-Containing Heterocycles and Late-Stage Drug Modification. *Angew Chem Int Ed.* **2012,** *51* (52), 13070-13074.
42. Hugenberg, V.; Haufe, G., Facile synthesis of α,α-difluoroalkyl aryl thioethers and their oxidative desulfurization–fluorination to trifluorides. *J. Fluorine Chem* **2010,** *131* (9), 942-950.
43. Pulido, B. A.; Habboub, O. S.; Aristizabal, S. L.; Szekely, G.; Nunes, S. P., Recycled Poly(ethylene terephthalate) for High Temperature Solvent Resistant Membranes. *ACS Appl. Polym. Mater.* **2019,** *1* (9), 2379-2387.
44. Peng, Y.; Yang, J.; Deng, C.; Deng, J.; Shen, L.; Fu, Y., Acetolysis of waste polyethylene terephthalate for upcycling and life-cycle assessment study. *Nat Commun* **2023,** *14* (1), 3249.
45. Hoang, C. N.; Nguyen, N. T.; Ta, S. T.; Nguyen, N. N.; Hoang, D., Acidolysis of Poly(ethylene terephthalate) Waste Using Succinic Acid under Microwave Irradiation as a New Chemical Upcycling Method. *ACS Omega* **2022,** *7* (50), 47285-47295.
46. Ciccia, N. R.; Shi, J. X.; Pal, S.; Hua, M.; Malollari, K. G.; Lizandara-Pueyo, C.; Risto, E.; Ernst, M.; Helms, B. A.; Messersmith, P. B.; Hartwig, J. F., Diverse functional polyethylenes by catalytic amination. *Science* **2023,** *381* (6665), 1433-1440.
47. Karayannidis, G. P.; Sideridou, I. D.; Zamboulis, D. X., Antioxidants for poly(ethylene terephthalate). In *Plastics Additives: An A-Z reference*, Pritchard, G., Ed. Springer Netherlands: Dordrecht, 1998; pp 95-107.
48. Knight, D. W.; Morgan, I. R.; Proctor, A. J., A simple oxidative procedure for the removal of ruthenium residues from metathesis reaction products. *Tetrahedron Lett.* **2010,** *51* (4), 638-640.
49. Eerhart, A. J. J. E.; Faaij, A. P. C.; Patel, M. K., Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ. Sci.* **2012,** *5* (4), 6407-6422.
50. El-Sayed, E.-S. M.; Yuan, D., Waste to MOFs: sustainable linker, metal, and solvent sources for value-added MOF synthesis and applications. *Green Chem.* **2020,** *22* (13), 4082-4104.
51. Lo, S.-H.; Senthil Raja, D.; Chen, C.-W.; Kang, Y.-H.; Chen, J.-J.; Lin, C.-H., Waste polyethylene terephthalate (PET) materials as sustainable precursors for the synthesis of nanoporous MOFs, MIL-47, MIL-53(Cr, Al, Ga) and MIL-101(Cr). *Dalton Trans.* **2016,** *45* (23), 9565-9573.
52. Deleu, W. P. R.; Stassen, I.; Jonckheere, D.; Ameloot, R.; De Vos, D. E., Waste PET (bottles) as a resource or substrate for MOF synthesis. *J. Mater. Chem. A* **2016,** *4* (24), 9519-9525.

53. Dyosiba, X.; Ren, J.; Musyoka, N. M.; Langmi, H. W.; Mathe, M.; Onyango, M. S., Feasibility of Varied Polyethylene Terephthalate Wastes as a Linker Source in Metal–Organic Framework UiO-66(Zr) Synthesis. *Ind. Eng. Chem. Res.* **2019,** *58* (36), 17010-17016.
54. Helal, A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M., Multivariate metal-organic frameworks. *Nat Sci Rev* **2017,** *4* (3), 296-298.
55. Shigematsu, A.; Yamada, T.; Kitagawa, H., Wide Control of Proton Conductivity in Porous Coordination Polymers. *J. Am. Chem. Soc.* **2011,** *133* (7), 2034-2036.
56. Yang, Z.; Ying, Y.; Pu, Y.; Wang, D.; Yang, H.; Zhao, D., Poly(ionic liquid)-Functionalized UiO-66-(OH)2: Improved Interfacial Compatibility and Separation Ability in Mixed Matrix Membranes for CO2 Separation. *Ind. Eng. Chem. Res.* **2022,** *61* (22), 7626-7633.
57. Katz, M. J.; Brown, Z. J.; Colón, Y. J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K., A facile synthesis of UiO-66, UiO-67 and their derivatives. *Chem. Commun.* **2013,** *49* (82), 9449-9451.
58. Wang, Z.; Babucci, M.; Zhang, Y.; Wen, Y.; Peng, L.; Yang, B.; Gates, B. C.; Yang, D., Dialing in Catalytic Sites on Metal Organic Framework Nodes: MIL-53(Al) and MIL-68(Al) Probed with Methanol Dehydration Catalysis. *ACS Appl. Mater. Interfaces* **2020,** *12* (47), 53537-53546.
59. Serra-Crespo, P.; Gobechiya, E.; Ramos-Fernandez, E. V.; Juan-Alcañiz, J.; Martinez-Joaristi, A.; Stavitski, E.; Kirschhock, C. E. A.; Martens, J. A.; Kapteijn, F.; Gascon, J., Interplay of Metal Node and Amine Functionality in NH2-MIL-53: Modulating Breathing Behavior through Intra-framework Interactions. *Langmuir* **2012,** *28* (35), 12916-12922.
60. Øien, S.; Wragg, D.; Reinsch, H.; Svelle, S.; Bordiga, S.; Lamberti, C.; Lillerud, K. P., Detailed Structure Analysis of Atomic Positions and Defects in Zirconium Metal–Organic Frameworks. *Cryst. Growth Des.* **2014,** *14* (11), 5370-5372.
61. Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G., A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. *Chemistry – A European Journal* **2004,** *10* (6), 1373-1382.
62. Arp, H. P. H.; Gredelj, A.; Glüge, J.; Scheringer, M.; Cousins, I. T., The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA). *Environ. Sci. Technol.* **2024,** *58* (45), 19925-19935.
63. Dekant, W.; Dekant, R., Mammalian toxicity of trifluoroacetate and assessment of human health risks due to environmental exposures. *Arch Toxicol* **2023,** *97* (4), 1069-1077.
64. Mahajan, Y. S.; Shah, A. K.; Kamath, R. S.; Salve, N. B.; Mahajani, S. M., Recovery of trifluoroacetic acid from dilute aqueous solutions by reactive distillation. *Sep. Purif. Technol.* **2008,** *59* (1), 58-66.
65. Zhou, J.; Saeidi, N.; Wick, L. Y.; Xie, Y.; Kopinke, F.-D.; Georgi, A., Efficient removal of trifluoroacetic acid from water using surface-modified activated carbon and electro-assisted desorption. *J. Hazard Mater* **2022,** *436*, 129051.
66. Jiao, H.; Zhang, C.; Yang, M.; Wu, Y.; Zhou, Q.; Hoffmann, M. R., Photoreductive defluorination of trifluoroacetic acid (TFA) in the aqueous phase by hydrated electrons. *Chem Eng J* **2022,** *430*, 132724.
67. Amiet, L.; Disdier, C. Process for the preparation of trifluoroacetic anhydride. 1986.
68. Balcar, H.; Bek, D.; Sedláček, J.; Dědeček, J.; Bastl, Z.; Lamač, M., RuCl2(p-cymene)(PCy3) immobilized on mesoporous molecular sieves as catalyst for ROMP of norbornene and its derivatives. *J. Mol. Catal. A Chem.* **2010,** *332* (1), 19-24.

ToC Graphic


PET
Aromatic C-H activation
HO
OH
OH
✓ Accesses valuable oxygenated aromatic compounds directly from PET
✓ Synthetically-useful conversions
✓ Tolerant to additives in PET waste and other plastic contaminants