nature portfolio

Peer Review File

Upcycling waste commodity polymers into high-performance polyarylate materials with direct utilization of capping agent impurities

Corresponding Author: Professor Fan Zhang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper reported a new strategy for methanolysis of PC and PET using IL catalysts and adopted a variable temperature-controlled two-stage interfacial polymerization technique to successfully prepare polyarylate with properties comparable to those of commercial grades, with kilogram-scale experiments and life cycle assessment.
However, there are some points which be considered before publication in your journal. and I so suggest the following minor revisions and state in the following:
1. For the yield calculation of the degradation process of laptop shell and optical disk, it is difficult to know the original content of PC in the product, and the paper does not mention how to calculate, so the final conversion and yield are not reliable enough. The yield of PC-catalyzed alcoholysis in Fig. 3a is 98%, which is inconsistent with the results in Fig. 2a and 112 lines in the supporting, and the products and by-products are not clearly labeled.
2. Four raw materials were selected for methanolysis in the laboratory scale test, but for the pilot scale test, laptop shells and polyester fibers, which did not appear in the small test, were selected, and the paper did not elaborate on that selection.
3. Since it was found that r-BPA methanolysis from laptop shells contained phenol capping agent instead of PTBP in the laboratory scale test, but you still chose laptop shells in the pilot scale test, did you switch to a different raw material or did you add PTBP additionally in the medium test?
4. There are some spelling mistakes, please correct them carefully.

Reviewer #2

(Remarks to the Author)
C. Li et al. report chemical recycling of polyterephthalate and polycarbonate simultaneously to generate polyarylate polymers which have additional benefits, by using metal-free ionic liquid catalyst for methanolysis. The obtained materials (polyarylated film for example) exhibit unique performance distinct from the feeding polymers – thus justify the concept of catalytic chemical upcyling. The authors demonstrated kilogram scale reaction. Before publication the authors should address the following major criticism:
1. the use of high pressure system: there is no description regarding the pressure of the reaction in the optimization and the large scale reaction. Thus it is unclear how the temperatures and pressures impact the depolymerization. This is important for reproducibility of the experiments (there is only a piece of information of working pressure 1-25 atm). Therefore the scalability of the reaction is not clearly understood although the authors showed kilogram scale reaction.
2. 1H NMR study of catalytic activity via titration: without much detailed evaluation of developed in supramolecular chemistry, medium effect, and NMR titration methods, the authors employed 1H NMR spectroscopy to “gauge” catalytic activities of different IL catalysts of different cations and anions. Since the chemical shift changes are not sole indicator for direct interactions of molecules, either authors can remove this part or should add in-depth study on the determination of binding affinity, binding modes (Job’s plot), and perhaps hydrodynamic volume of complexes by DOSY.
3. Activation barrier: Since the pressure of the reaction is not defined, the comparison with other systems is not meaningful.
4. LCA: many values are not supported. What is the recovery yield of ethylene glycol from the large scale reaction? Is this LCA reliable? It seems quite superfluous with the current conditions and multistep process. For CO_2 emission, it is highly sensitive what kind of electricity is being used – is it coal-powered or natural gas or HWS? For environmental impact, DCM is out of option to be used in polymerization. It is understandable that this is prove-of-concept work. However, careful

consideration and selection of reaction conditions should be taken when one illustrates the feasibility of the process with LCA.
5. catalyst stability: TBD and alike other guanidine and amidine bases are unstable under high pH conditions to form urea and amides. The authors may need to show the stability of the catalyst under basic conditions (also acidic) since the process requires acid/base work up conditions.
Minor comments:
SI, page 15, line 377: Recovered IL yield should be determined.
DMSO-d6 with d in talic, 6 with subscript.

Reviewer #3

(Remarks to the Author)
Review Summary:

Cheng Li and coworkers present an innovative upcycling approach to depolymerize polycarbonate (PC) and polyethylene terephthalate (PET) waste, generating high-performance polyarylate (PAR) materials with properties comparable to commercially available polyarylates. The authors provide a thorough investigation into the depolymerization process, optimizing the depolymerization rate using a non-metallic catalyst and employing the resulting depolymerized residues to produce upcycled materials directly utilizing capping agents by a two-step process based on temperature change. They further demonstrate the scalability of their process with kilogram-scale experiments and present a life cycle assessment (LCA) to support the environmental benefits of their proposed approach.

The manuscript is well-structured, clearly written, and methodologically sound, with a logical flow that makes it easy to follow. In my opinion, this work represents a valuable contribution to the literature. However, I have a few minor comments that the authors may wish to address to enhance the manuscript further.

1.- I would suggest including a discussion on the current market demand for polyarylate materials. Since the authors are utilizing commodity polymer waste streams that are widely available, it would be valuable to understand whether the proposed process could potentially produce an excess of PAR materials. A brief discussion of the authors' perspective on this matter would enhance the manuscript.

2.- In Figure 3, the assignment of bisphenol A (BPA) signals in the 1H NMR spectra would improve clarity.

3.- For the preparation of r-PAR, the presence of PTBP as a capping agent is inevitable, and the authors developed a two-stage interfacial polymerization to mitigate issues related to this agent. Could the authors comment on the effect of varying PTBP amounts during polymerization?

4.- Could the authors provide additional insights into the complex viscosity data, specifically addressing the factors that could make r-PAR less viscous at lower temperatures?

5.- Please specify the percentage of recycled content in the final r-PAR material.

Typographical and Formatting Corrections:

Figure Reference: In line 95, “Figure 1a” should be corrected to “Figure 2a.”
Inconsistent Numbering: The numbering for cumulative GWP data is inconsistent (see lines 264, 266, and 267).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I am satisfied of the answers. The revised manuscript has been improved and is good
enough to publish in Nature Communications.

Reviewer #2

(Remarks to the Author)
The authors provide additional experiments to address reviewers comments and description for high pressure reaction conditions is sufficiently address for example. However, the description and additional experiments to explain the catalytic activities with NMR chemical shift changes of MeOH is not agreeable since there are too many factors that can affect the chemical environments of MeOH in solution states. Diffusion co-efficient is also highly sensitive viscosity of the media

therefore, it does not necessarily explain the role of hydrogen bonding from the catalyst. Overall, this reviewer would agree with the observed catalytic activities for depolymerization of PET and PC and the progress to obtain new recycled flame-retarding polymer without the Figure 2 b, c and d. Bronsted acid/base catalysis reaction mechanism can be also explained by using acetic acid/TBD where TBD acts as a base and acetic acid act as a H-bond donor at the transition state. Therefore, the illustrate NMR titration and also the diffusion co-efficient do not serve as experimental data to support the proposed reaction mechanism. Such a sentence - "the Ac anions are more beneficial in activating the hydroxyl group of MeOH" - should be carefully written since the activation can happen in the activated complex (TS) not in the equilibrium conditions (as in NMR conditions). Also Figure S5 contains tetrahedral intermediate and the authors assigned that they observed tetrahedral intermediate in the solution state. Tetrahedral intermediates are considered as almost transition states (J. Org. Chem. 2004, 69, 21, 7317–7328). Therefore, the authors should add more information how this mechanism is being proposed specially (4* and 5*) or add more experimental data to support it. Overall, the revision provides sufficient data however the authors do not provide important knowledge for catalytic reaction mechanism, which is mostly based on preliminary NMR studies without kinetic and in-depth mechanistic studies.

Reviewer #3

(Remarks to the Author)
Cheng Li and coworkers have provided a comprehensive response to the reviewers' recommendations. Therefore I agree on the publication of the revised version of the manuscript.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
I would recommend to check Jencks' libido rule to discuss general acid/base catalysis for the proposed reaction mechanism, how to investigate it, and how to determine the reaction mechanism. To explain in the context of this manusscript, acetate is not a strong base to deprotonate methanol, therefore the reaction should be general catalysis (as in general vs specific acid catalysis). In this scenario, acetate is better to deprotonate guanidinium ion rather than methanol since pKa of protonated TBD should be lower (assuming that pKa of DBU is around 12, pKa Methanol >15). Since the authors may have suggested in the general acid/base catalyzed reaction mechanism, the proton transfer should be involved in the rate-determining step. Therefore, the proposed reaction mechanism (also in Angew. Chem. Int. Ed. 2021, 60, 6710) is not being supported based on what the authors undertaken. The refered ACIE 2021 paper solely relying on DFT calculation for the reaction mechanism (and the required scission energy was calculated to be 37.3 kcal/mol while the activation barrier was quite close, 32.5 kcal/mol).
Neverthelss these comments will not affect the conclusion of the manuscript if there is more focus on the chemical recycling and production of a new PAR from waste materials.

Minor commnets:
A previous ref, ChemSusChem 2021, 14, 1–31., is not identifiable.

Reviewer(s)' Comments to Author:

Reviewer #1:

This paper reported a new strategy for methanolysis of PC and PET using IL catalysts and adopted a variable temperature-controlled two-stage interfacial polymerization technique to successfully prepare polyarylate with properties comparable to those of commercial grades, with kilogram-scale experiments and life cycle assessment. However, there are some points which be considered before publication in your journal. and I so suggest the following minor revisions and state in the following:

Response: Thank you very much for your recognition of our work and your valuable suggestions.

1. For the yield calculation of the degradation process of laptop shell and optical disk, it is difficult to know the original content of PC in the product, and the paper does not mention how to calculate, so the final conversion and yield are not reliable enough. The yield of PC-catalyzed alcoholysis in Fig. 3a is 98%, which is inconsistent with the results in Fig. 2a and 112 lines in the supporting, and the products and by-products are not clearly labeled.

Response: We appreciate your feedback and have made revisions to clarify our methodology. CDs and computers, which are common sources of polycarbonate (PC), typically contain a significant percentage of PC content. For instance, CDs generally have a PC content exceeding 80%, while in the PC/ABS materials such as laptop shells, the PC content is generally around 55% or 70%. In our work, we determined the PC content of actual plastic waste, usually allowing for extended reaction times of 24 h. We also ensured complete quantification of all BPA in the waste plastics, adhering to the principle of conservation of mass. Our findings indicate that the PC content in the CDs and laptop shells utilized in our experiments is approximately 97% and 55%, respectively. Moreover, we have enhanced specific aspects of our experimental design by introducing a method for quantifying the product in actual plastics (***Modified-1***) and

a strategy for detecting by-products (***Modified-2***).

In addition, we have carefully modified the manuscript according to your suggestions. The results presented in Fig. 2a, Fig. 3a, and line 112 in the supporting information were obtained under different reaction conditions. To clarify any misunderstandings, we re-experimented and corrected the reaction conditions and results for Fig. 3a and line 112 in the supporting materials. We have also clearly quantified the products and by-products. Furthermore, the quantitative methods for DMC and EG have been added to enhance the experimental process.

Modified-1:

The catalytic methanolysis of PC or PET was carried out in a 15 mL stainless-steel autoclave with magnetic stirring. In a typical procedure, 0.5 g of PC or PET (w_1), 2 mL of MeOH, and 0.25 mmol of catalyst were transferred into the autoclave together. Then it was heated to 100 °C or 150 °C and kept for 2 h. After cooling, the obtained mixture was filtered and washed with methanol to obtain the residual PC or PET. The residual PC or PET was washed, dried at 70 °C for 12 h, and then weighed (w_2) to calculate the conversion of PC or PET. The filtrate was concentrated, and the residue was extracted with ethyl acetate and deionized water. The r-BPA or r-DMT (w_3) could be obtained from the organic phase by rotary evaporation. In the case of real plastics, the non-reactive substance (w_4) remains, and the theoretical content of PC or PET is determined through repeated controlled experiment with extended reaction times of 24 h. The purity of the r-BPA and r-DMT was analyzed by ^{1}H

$$\text{PC conversion} = \frac{w_1\text{-}w_2}{w_1\text{-}w_4} \times 100\%$$

$$\text{BPA yield} = \frac{w_3 \times \text{Purity}_{BPA} \times M_{\text{PC}}}{M_{\text{BPA}} \times (w_1\text{-}w_4)}$$

where M_{PC} and M_{BPA} are the molar mass of the PC unit and BPA.

$$\text{PET conversion} = \frac{w_1\text{-}w_2}{w_1\text{-}w_4} \times 100\%$$

$$\text{DMT yield} = \frac{w_3 \times \text{Purity}_{DMT} \times M_{\text{PET}}}{M_{\text{DMT}} \times (w_1\text{-}w_4)}$$

where M_{PET} and M_{DMT} are the molar mass of the PET unit and DMT.

Modified-2:

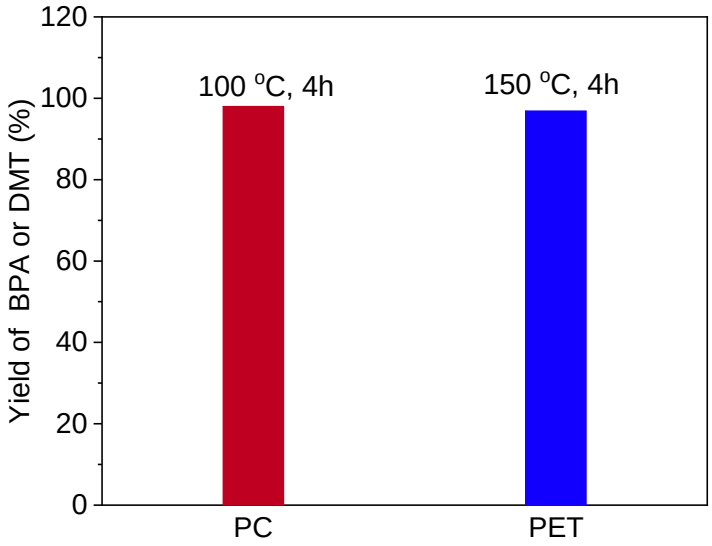

Fig. S9 Catalytic methanolysis of PC and PET. Condition: catalyst (0.25 mmol), plastics (0.5 g) and MeOH (4 mL).

Post-processing: At the end of the reaction, the obtained mixture was filtered and washed with methanol to obtain the residual plastics. Then, the residual plastics powder was washed, dried at 70 °C for 12 h, and weighed of plastics powder to calculate the conversion. To quantify DMC or EG, methanol with the products was quantitatively volumized in a 25 ml volumetric flask. The DMC and EG were quantified using external standard methods. The above solvents were concentrated, and the residue was extracted with ethyl acetate and deionized water. The monomers (r-BPA, r-DMT) could be obtained from the organic phase by rotary evaporation and the mass of the products was recorded. The purity of the monomers was analyzed by ^{1}H NMR.

Analysis of DMC and EG:

DMC: Gas chromatography (GC) analysis was recorded on a gas chromatograph (Agilent 7820) equipped with a capillary column (HP-5, 30 m × 320 μm × 0.25 μm) using a flame ionization detector with a flow rate of 1 mL min^{-1} using the following method: the oven temperature was held at 50 °C for 5 min and then increased linearly to 250 °C over 20 min with a final hold of 5 min.

EG: Ethylene glycol content was detected on Shimadzu (LC-2050) high-performance liquid chromatography (HPLC) equipped with a UV detector and a liquid chromatography column Aminex® HPX-87H. The mobile phase was 8 mM H_2SO_4 solution at 35 °C with a flow rate of 0.6 mL· min^{-1}. Operation method: equal degree operation for 20 minutes.

Experimental result:

Polymers	*T* (°C)	Time (h)	Conversion (%)	BPA yield (%)	DMC yield (%)
PC	100	4	99	97.3 ± 1.0	95.3 ± 10.0
Polymers	*T* (°C)	Time (h)	Conversion (%)	DMT yield (%)	EG yield (%)
PET	150	4	99	98.7 ± 0.5	93.0 ± 1.8

2. Four raw materials were selected for methanolysis in the laboratory scale test, but for the pilot scale test, laptop shells and polyester fibers, which did not appear in the small test, were selected, and the paper did not elaborate on that selection.

Response: Thank you for your insightful question. We appreciate your interest in the selection of raw materials for our pilot scale test. Same kind of laptop shell have been used as reactant both in laboratory tests and our pilot scale test. The black polyester containing certain dyes employed in the pilot scale test is comparable in purity to the

white polyester fabric used in the laboratory tests. Because black polyester containing dyes is more representative of waste fabrics in life, we chose it for large scale test. This choice was made to enhance the relevance of our findings to real-world applications. To clarify, we added a sentence in the revised manuscript. “The selection of black polyester, which contains dyes, is more representative of practical applications than white polyester fabric; therefore, we opted for this material for our large-scale testing.” In addition, we revised **Supplementary Fig. 16** containing the mechanical crushing step to clarify that same kind of laptop shell is used both in laboratory tests and our pilot scale test

Fig. R1 Left: Polyester fabric without coloring; Right: Polyester fabric with coloring.

Modified:

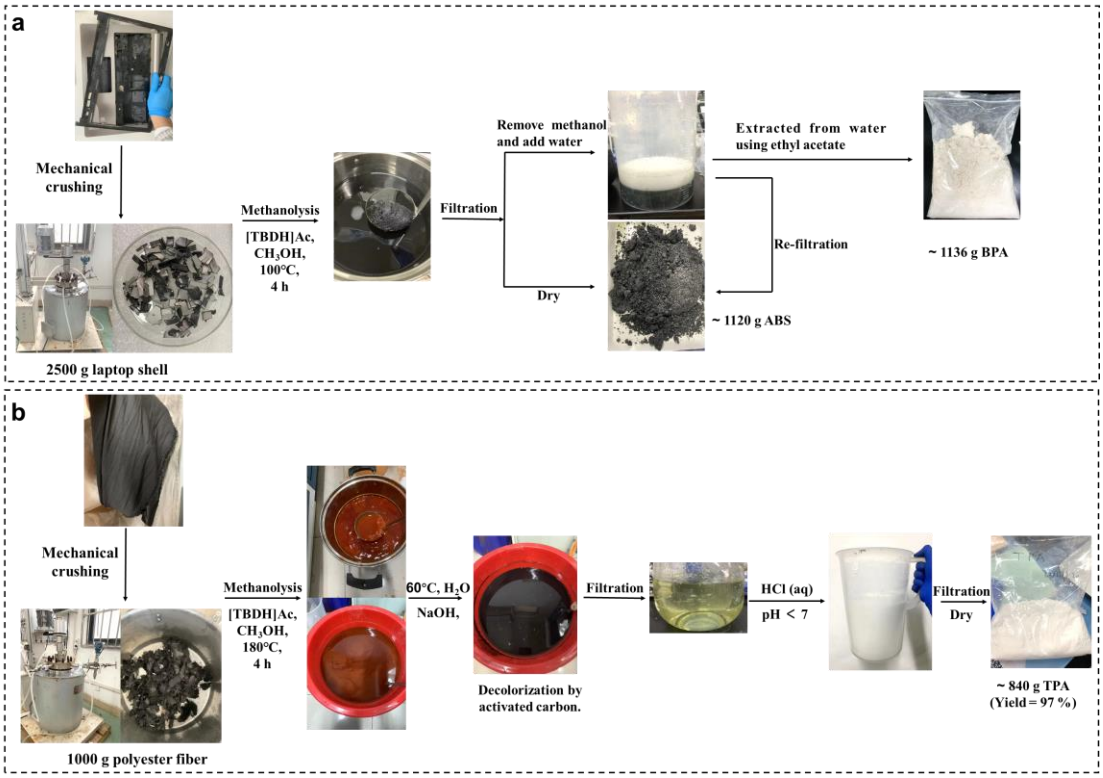

Fig. S16 The process of kilogram-gram scale experiments of waste polymers methanolysis (10 L high-pressure reactor). (a) Laptop shell. (b) Polyester fiber.

3. Since it was found that r-BPA methanolysis from laptop shells contained phenol capping agent instead of PTBP in the laboratory scale test, but you still chose laptop shells in the pilot scale test, did you switch to a different raw material or did you add PTBP additionally in the medium test?

Response: Thanks for your excellent question. In response to your inquiry about the use of laptop shells in the pilot scale test, we indeed observed that the r-BPA methanolysis from the laptop shells contained phenol as a capping agent, rather than the expected PTBP. To address this variability, we conducted further investigations by using CD material containing PTBP agent in the large-scale test. In this subsequent experiment, we performed methanolysis on 80.0 g waste CDs and achieved high-yield of recovered BPA (96%). Then, 22.8 g (0.1 mol) of r-BPA-CD was polymerized with 10.2 g (0.05 mol) of TPC and 10.2 g (0.05 mol) of IPC following the same procedure

as for the PAR, yielding r-PAR-CD. The yield polymer powder was hot-pressed into a thin film (**Fig. S17a**). The DSC was conducted to characterize the r-PAR-CD, and the glass transition temperature (T_g) was in the range of 192.3 °C (**Fig. S17b**), which is comparable to that of the r-PAR or U-100. The r-PAR-CD film material also exhibits excellent transmittance and flexibility.

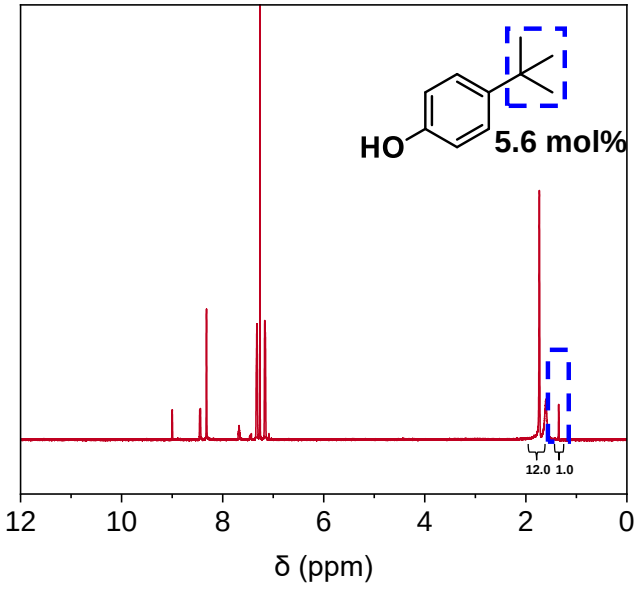

Fig. R2 The ^{1}H NMR spectrum of r-PAR-CD.

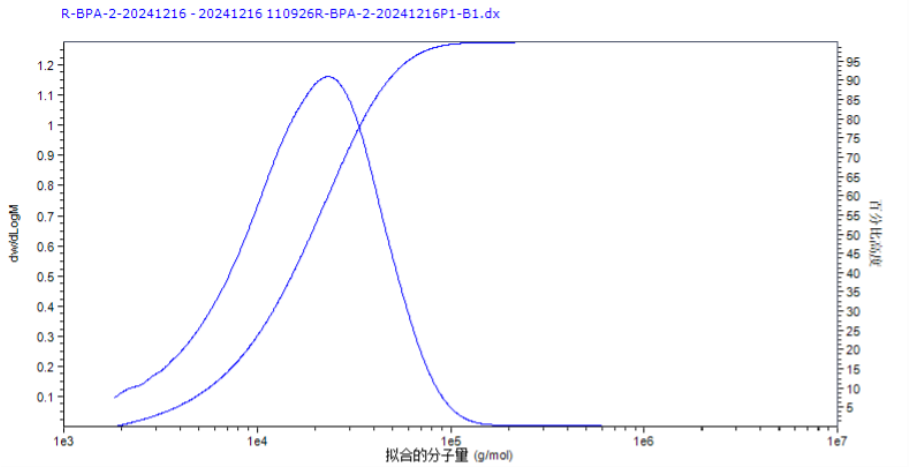

Fig. R3 GPC data of r-PAR-CD.

Modified:

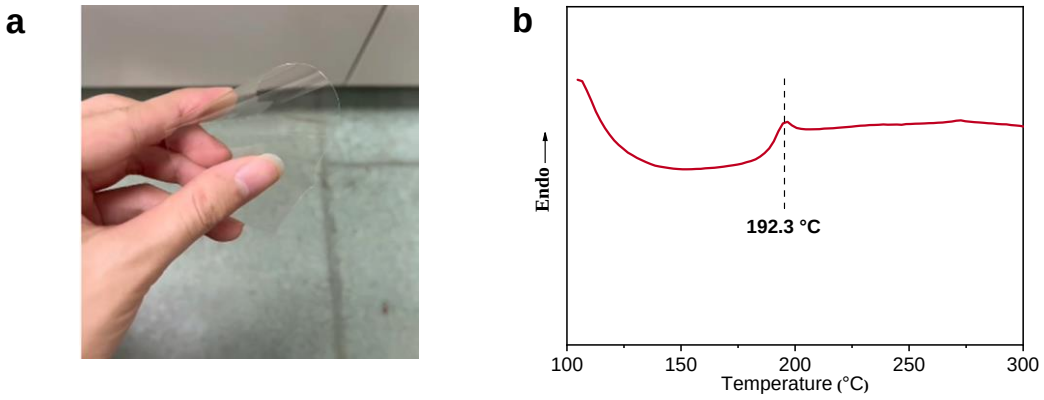

Fig. S17 (a) The photograph of r-PAR-CD film (thickness: ~200 μm) hot-pressed at 280 °C. (b) DSC curve of r-PAR-CD.

Note: The r-PAR-CD film was produced as following procedure: 80.0 g of CDs was degraded and 69.5 g of r-BPA-CD was recovered (yield: 96%); Subsequently, the r-BPA-CD (22.8 g, 0.1 mol) was polymerized with TPC (10.2 g, 0.05 mol)/IPC (10.2 g, 0.05 mol) to yield r-PAR-CD film materials using the same method for r-PAR from laptop shells.

4. There are some spelling mistakes, please correct them carefully.

Response: Thanks for your suggestion. We revised the whole manuscript carefully to avoid grammatical and spelling errors.

Reviewer #2:

C. Li et al. report chemical recycling of polyterephthalate and polycarbonate simultaneously to generate polyarylate polymers which have additional benefits, by using metal-free ionic liquid catalyst for methanolysis. The obtained materials (polyarylated film for example) exhibit unique performance distinct from the feeding polymers – thus justify the concept of catalytic chemical upcyling. The authors demonstrated kilogram scale reaction. Before publication the authors should address the following major criticism:

Response: Thank you for your positive comments on our work, and we appreciate your valuable suggestions.

1. The use of high pressure system: there is no description regarding the pressure of the reaction in the optimization and the large scale reaction. Thus it is unclear how the temperatures and pressures impact the depolymerization. This is important for reproducibility of the experiments (there is only a piece of information of working pressure 1-25 atm). Therefore, the scalability of the reaction is not clearly understood although the authors showed kilogram scale reaction.

Response: Revealing the pressure of the reaction system is particularly important, and we appreciate your valuable suggestion. The advantage of this catalytic system is that no co-solvent is required. As a result, the pressure of the reaction is close to the saturated vapor pressure of methanol at the work-up conditions. Here, we have modified the **Note of Supplementary Fig. 9** and added **Supplementary Fig. 1** and **Supplementary Table 4.** to clearly state the effect of temperatures and the pressures for kilogram-scale experiments.

Modified-1:

Reaction equipment: A 20 mL 316L stainless-steel autoclave with magnetic stirring. The working pressure is 3.2 atm at 100 °C and the working pressure is 13.5 atm at 150 °C.

Modified-2:

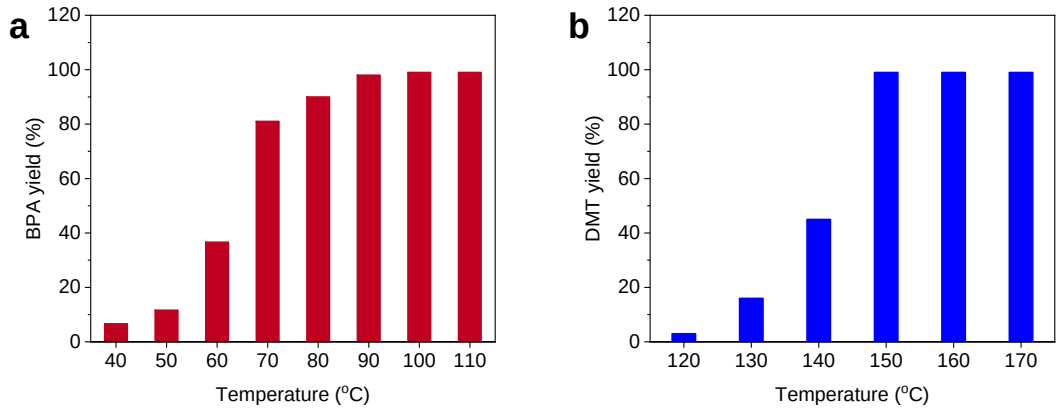

Fig. S1 The effect of temperature on methanolysis. Catalytic methanolysis of (a) PC, (b) PET. Condition: [TBDH]Ac (0.25 mmol), plastics (0.5 g), MeOH (2 mL), 4 h.

Modified-3:

Table S4. The operational parameters of kilogram scale reaction.

Polymers	Reaction time (h)	Reaction temperature (°C)	Heating time (min)	Real-time temperature(°C)	System pressure (MPa)	Stirring rate (rpm)	Stirring form
PC	4	100	0	28.5	0.0	265	Mechanical mixing
			20	30.0	0.0		
			40	40.8	0.0		
			60	76.5	0.1		
			70	100.1	0.3		
			310	102.2	0.3		
PET	4	150	0	28.5	0.0	265	Mechanical mixing
			20	32.2	0.0		

40	45.5	0.0
60	83.1	0.2
80	105.2	0.4
100	128.8	0.9
115	149.2	1.41
355	150.8	1.40

2. ^{1}H NMR study of catalytic activity via titration: without much detailed evaluation of developed in supramolecular chemistry, medium effect, and NMR titration methods, the authors employed ^{1}H NMR spectroscopy to "gauge" catalytic activities of different IL catalysts of different cations and anions. Since the chemical shift changes are not sole indicator for direct interactions of molecules, either authors can remove this part or should add in-depth study on the determination of binding affinity, binding modes (Job's plot), and perhaps hydrodynamic volume of complexes by DOSY.

Response: Thanks for raising the questions. As you suggested, the binding modes (Job's plot) and the DOSY analysis of the complexes were further studied to reveal the binding affinity of ILs with MeOH (**Fig. 2d**, **Supplementary Figs.5 and 6** and **Supplementary Table 1**). We have added the discussion in the revised manuscript.

Modified:

We next used Job's plot analysis[42,43] by NMR to estimate the binding affinity of MeOH with the anions (**Supplementary Figs. 5**). The results revealed the polarization of methanol by ILs was stronger with increasing amounts of ionic liquid. When the amount of ionic liquids is less than 40%, the Ac anions are more beneficial in activating the hydroxyl group of MeOH, especially at reaction condition (0.5% amount of ionic liquids within MeOH). Furthermore, diffusion-ordered spectroscopy (DOSY) provided

further evidence for the ability of different ILs to activate methanol (**Fig. 2d**, **Supplementary Fig. 6** and **Supplementary Table 1.**). In the DOSY analyses, we observed that a 0.54-mM solution of free MeOH exhibits a diffusion coefficient (D) of 8.49×10^{-10} m^2 s^{-1}. Upon adding 0.1 equiv of [TBDH]Ac, there was a largest decrease of D_{MeOH} (8.05×10^{-10} m^2 s^{-1} vs 8.49×10^{-10} m^2 s^{-1}) compared with other ILs with different anions, highlighting a strong interaction of the MeOH with the Ac anion. Collectively, these results further support the conclusion that [TBDH][Ac] is more effective in activating the hydroxyl group of MeOH.

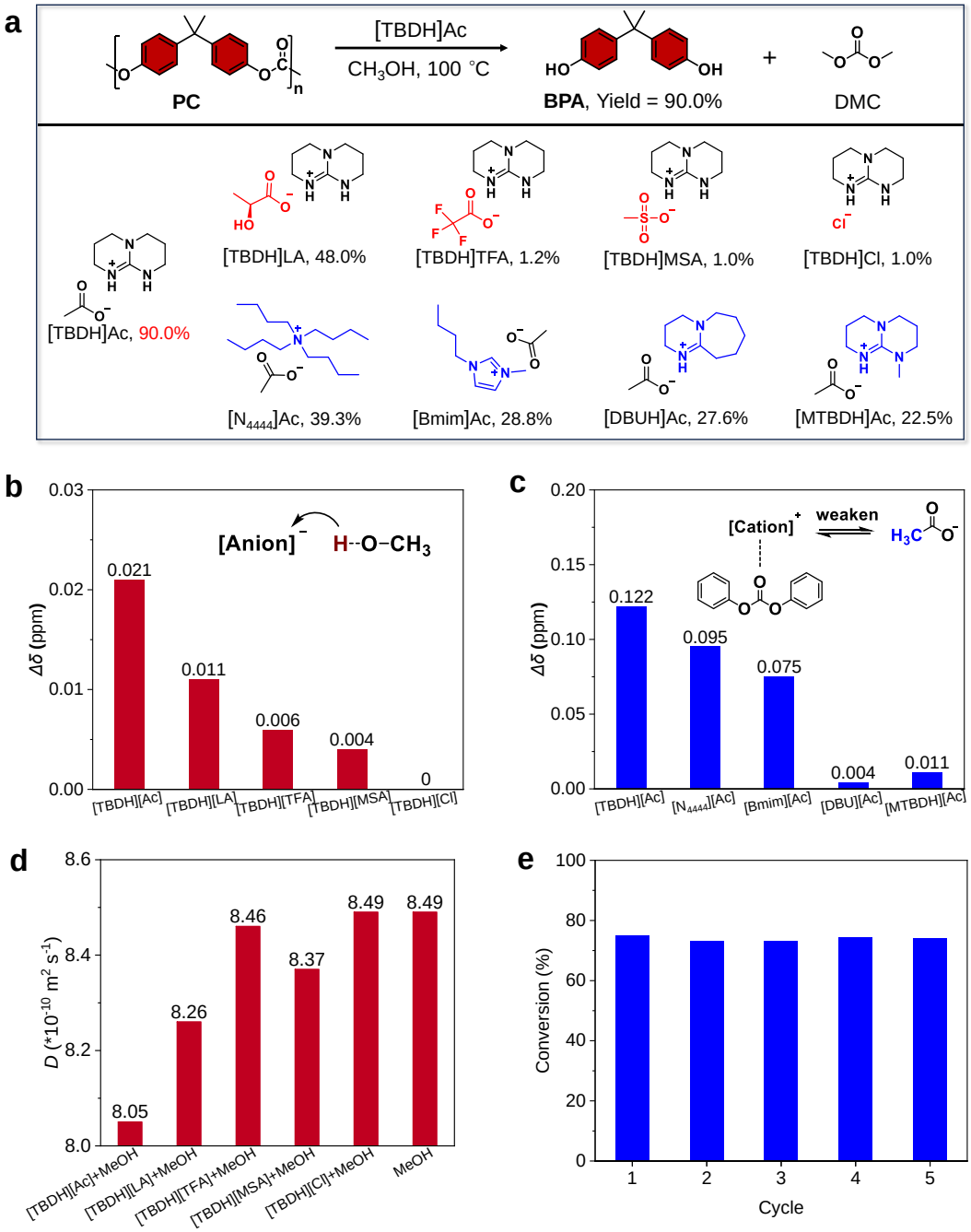

Fig. 2 Catalytic methanolysis of PC under mild conditions. (a) Effect of the anions and cations of ionic liquids on PC methanolysis. Condition: catalyst (0.25 mmol), PC (0.5 g), MeOH (2 mL), 100 °C, 2 h. (b) Chemical shift changes of the hydroxyl group of MeOH with the addition of ILs with different anions. (c) Chemical shift changes of the methyl group in acetate anion of ILs with different cations interacted with DPC. (d) The diffusion coefficient (*D*) of MeOH with the addition of ILs with different anions. (e) Evaluation of the stability of [TBDH]Ac in PC methanolysis. Condition: catalyst (0.25 mmol), PC (0.5 g), MeOH (2 mL), 100 °C, 1.5 h.

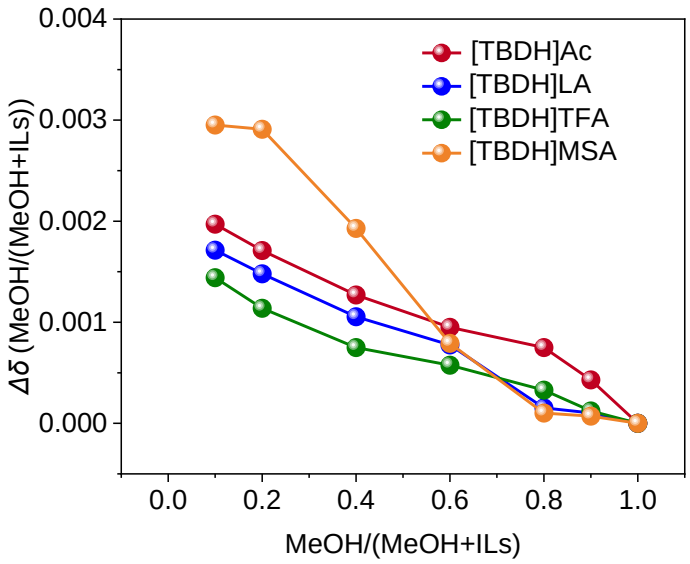

Fig. S5 Job's plot analysis of the mixture of MeOH and ILs with different anions in DMSO-d_6 at 25 °C. Various amounts of the ILs were added to the MeOH. The chemical shifts of the methyl group of MeOH were monitored to obtain the plots.

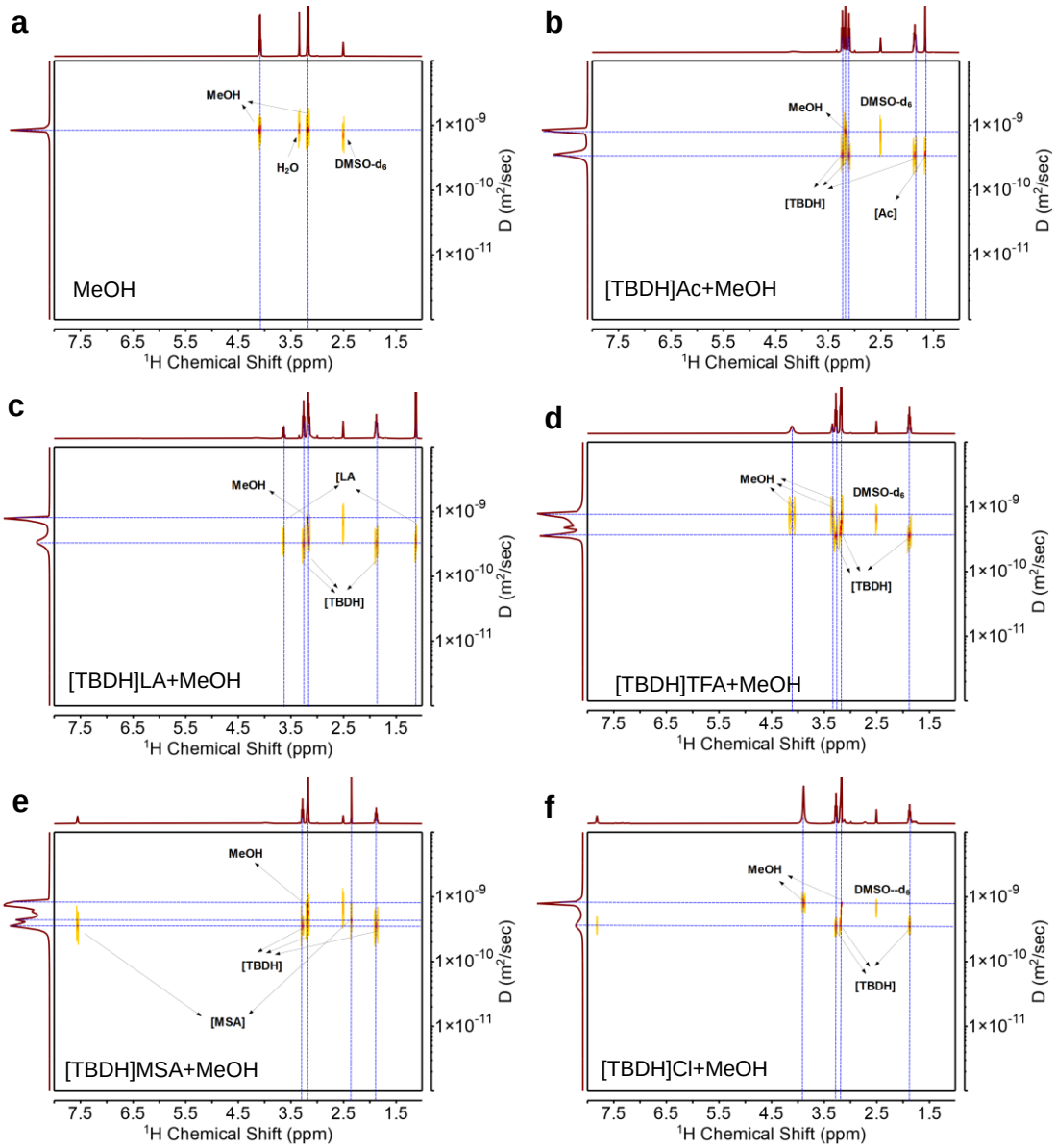

Fig. S6 Two-dimensional DOSY NMR spectra of (a) MeOH, (b) the mixture of MeOH and [TBDH]Ac (9:1), (c) the mixture of MeOH and [TBDH]LA (9:1), (d) the mixture of MeOH and [TBDH]TFA (9:1), (e) the mixture of MeOH and [TBDH]MSA (9:1), and (f) the mixture of MeOH and [TBDH]Cl (9:1) in DMSO-d_6 at 25 °C.

Table S1. Summary of the diffusion coefficients for the different complexes.

Entry	Sample	D_{MeOH} (m^2 s^{-1})
1	MeOH	$8.49 \cdot 10^{-10}$
2	[TBDH]Ac + MeOH	$8.05 \cdot 10^{-10}$

3	[TBDH]LA + MeOH	$8.26 \cdot 10^{-10}$
4	[TBDH]TFA + MeOH	$8.46 \cdot 10^{-10}$
5	[TBDH]MSA + MeOH	$8.37 \cdot 10^{-10}$
6	[TBDH]Cl + MeOH	$8.49 \cdot 10^{-10}$

3. Activation barrier: Since the pressure of the reaction is not defined, the comparison with other systems is not meaningful.

Response: Thank you for your valuable comments. As you mentioned, the comparison with other systems is not meaningful when the pressure of the reaction is different. Usually, the pressure of PC methanolysis is close to the saturated vapor pressure of methanol in the absence of co-solvents. However, the reaction temperatures and solvents of the literature mentioned in the manuscript are different. Thus, we have deleted the Figure of Ea comparison and carefully modified the manuscript to correct the description of the comparison of the activation barrier.

4. LCA: many values are not supported. What is the recovery yield of ethylene glycol from the large-scale reaction? Is this LCA reliable? It seems quite superfluous with the current conditions and multistep process. For CO_2 emission, it is highly sensitive what kind of electricity is being used – is it coal-powered or natural gas or HWS? For environmental impact, DCM is out of option to be used in polymerization. It is understandable that this is prove-of-concept work. However, careful consideration and selection of reaction conditions should be taken when one illustrates the feasibility of the process with LCA.

Response: Thanks for your comments. The LCA of this work was supported by Integrated Knowledge Company for our Environment (IKE) Company (http://www.ike-global.com/), which has also published research work on the LCA of waste plastic (*Environ. Sci. Technol.* **58**, 16386-16398 (2024)). An important realization is that LCA is less related to reaction conditions, but more closely related to material input/output and energy consumption. To obtain data on power, steam, etc.

closer to industrial production, this LCA not only refers to the parameters of the kilogram scale reaction but also refers to the data available in the real existing process cases of IKE company. Therefore, we consider that these analyses are reliable in theory. For CO_2 emission, the distribution of electricity used by LCA is 52% thermo-electricity, 45% hydroelectricity, 1.8% wind electricity, and 1.2% other electricity. This data comes from the China Electric Power Statistical Yearbook 2020. The upstream input of thermal electricity is shown in the following:

Item	Quantity	Unit
Input:		
Raw coal	4.17×10^{-4}	t
Cleaned coal	0	t
Limestone	0.02	Kg
Natural gas	2.68×10^{-3}	m^3
Diesel oil	6.67×10^{-5}	kg
Heat-engine plant	1.84×10^{-14}	Item(s)
Coal gangue	10.48	g
Coke	0	t
Coke gas	4.84×10^{-3}	m^3
Other gas	6.24×10^{-5}	m^3
Crude oil	5.35×10^{-7}	kg
Gasoline	1.79×10^{-7}	kg
Fuel oil	5.86×10^{-5}	kg
Petroleum coke	1.20×10^{-4}	kg
Output:		
Thermo- electricity	1.0	kWh

In this prove-of-concept work, the reaction conditions are mild in the present process design compared to most of the known research. For environmental impact, it is undeniable that DCM is not a green solvent. However, DMC is the most commonly used solvent for PAR synthesis (*Macromolecules* **26**, 5287-5294 (1993); *Polym. Degrad. Stabil.* 94 1261-1266 (2009); *Polymer.* **186**, 122047 (2020); *New. J. Chem.* **48**,

10497-10506 (2024)). Importantly, the DMC is easily recycled during interfacial polymerization, because the water and oil phases are layered.

Finally, we have modified the manuscript and supplementary information. The process of r-PAR synthesis was demonstrated as shown in **Supplementary Fig. 22**. The LCA calculations used 93% as the yield of ethylene glycol based on the results in **Supplementary Fig. 9**. Additionally, the details of the electricity of the LCA calculation are described in the supplementary information.

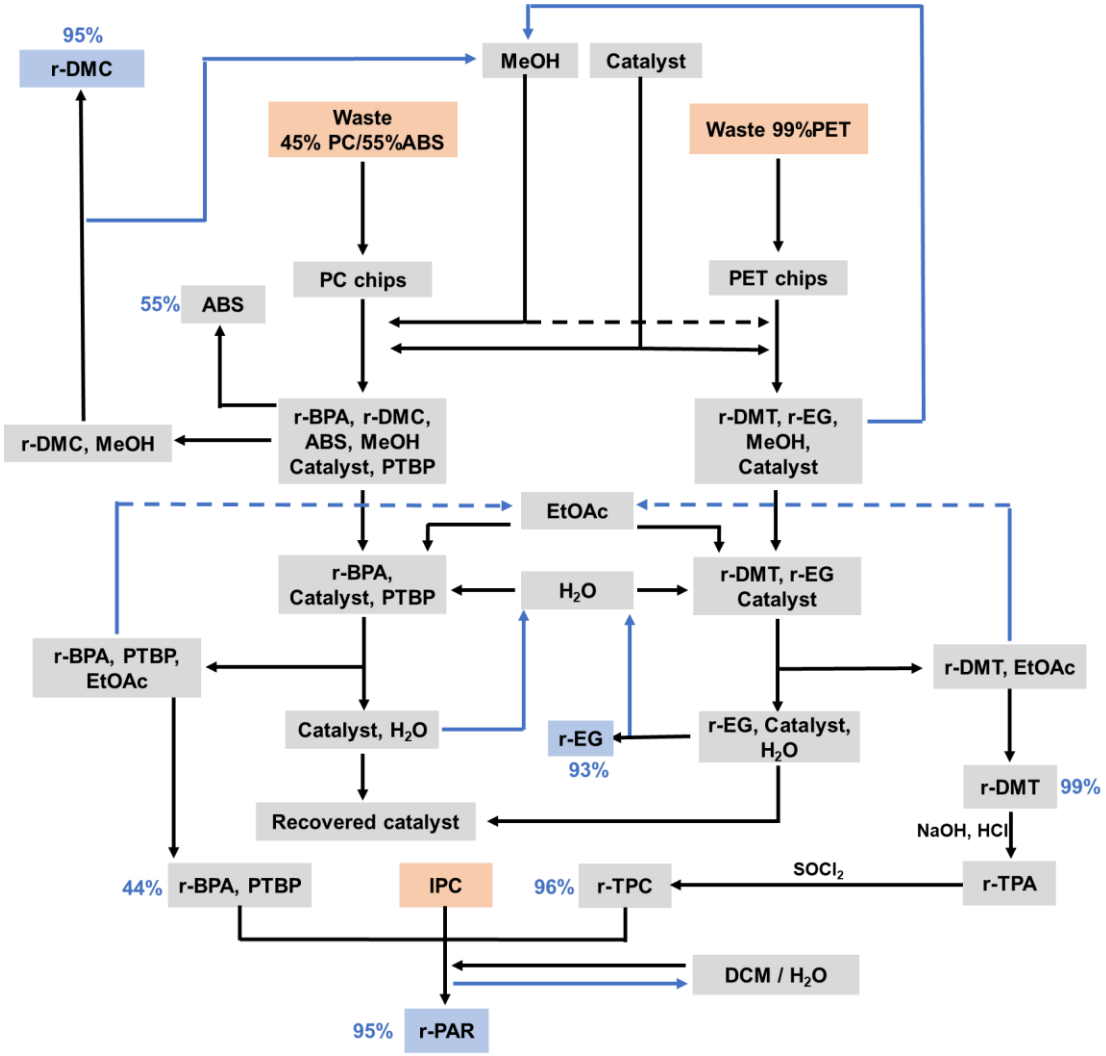

Fig. S22 Detailed process of co-upcycling of waste PC and PET to high-performance special engineering plastics- polyarylates. The blue lines indicate the solvent recovery. The blue numbers indicate the product yield of the current step used by the LCA.

5. catalyst stability: TBD and alike other guanidine and amidine bases are unstable under high pH conditions to form urea and amides. The authors may need to show the stability of the catalyst under basic conditions (also acidic) since the process requires acid/base work up conditions.

Response: Thank you for your question. Ionic liquids (ILs), consisting of organic cations and inorganic/organic anions, can be designed with unique properties and thus have been widely used in many areas. Particularly, in chemical reactions, ILs can be used as solvents or catalysts and have shown promising application potential. ILs have been reported to be capable of catalyzing the decomposition of PC and PET without adding any acid or base. (*Sci. Adv.* **9**, eade7971 (2023); *Green Chem.* **22**, 3122-3131 (2020); *Green Chem.* **20**, 1205-1212 (2018); *ACS Sustainable Chem. Eng.* **6**, 13114-13121 (2018); *Chem. Eng. J.* **388**, 124324 (2020); *Angew. Chem. Int. Ed.* **60**, 6710-6717 (2021)). In this work, the methanolysis of PC and PET have been catalyzed by ILs is also achieved without the addition of any additives. However, methanolysis under acid/base work-up conditions is also possible in practical applications. The results of catalyst stability under acid/base conditions were tested by NMR as shown as follows:

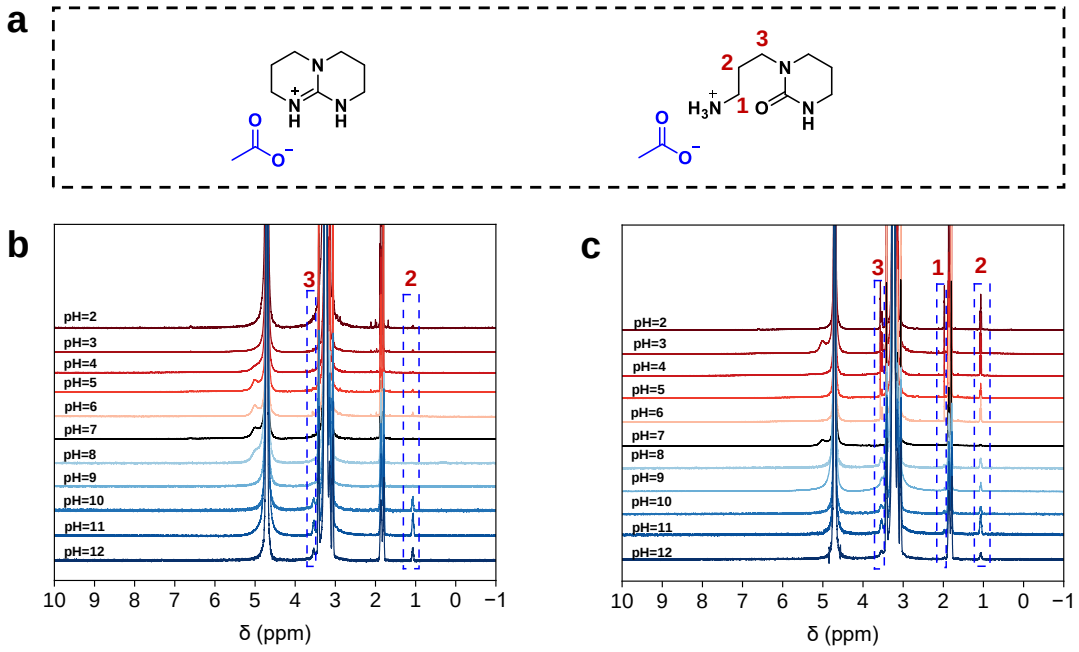

Fig. R4 The stability test of [TBDH]Ac under acid/base conditions. (a) The

structure of TBDH and its possible decomposers. (b) Condition: [TBDH]Ac (0.25 mmol), plastics (0.5 g), MeOH with Ac or NaOH (2 mL), 100 °C, 4 h. (c) Conditions: Condition: [TBDH]Ac (0.25 mmol), plastics (0.5 g), MeOH with Ac or NaOH (2 mL), 150 °C, 4 h.

The reaction temperature of PC (100 °C) and PET (150 °C) methanolysis was simulated to test the catalyst stability. The pH of the methanol was adjusted by using acetic acid and NaOH. The results showed that the TBDH structure was not broken at 100 °C and pH 7-9 and at 150 °C and pH 7. The catalyst structure is unstable under more acid or base conditions to form urea and amides, which is consistent with the results reported in the literature (*Org. Process Res. Dev.* **23**, 1860-1871 (2019)). Overall, as shown in our studies, ILs can stably catalyze the methanolysis of PC and PET without the addition of any acid or base.

Minor comments:

SI, page 15, line 377: Recovered IL yield should be determined.

DMSO-d6 with d in talic, 6 with subscript.

Response: We apologize for the misleading results. We have added the recovered IL yield in the revised manuscript. The recovered IL yield is about 90%. For example, an initial amount of 0.0500 g of IL was input, and about 0.0452 g of IL was recovered after the reaction.

We have corrected the error in **Fig. 3b** and the part of **Characterization** about the DMSO-d_6.

Reviewer #3:

Review Summary:

Cheng Li and coworkers present an innovative upcycling approach to depolymerize polycarbonate (PC) and polyethylene terephthalate (PET) waste, generating high-performance polyarylate (PAR) materials with properties comparable to commercially available polyarylates. The authors provide a thorough investigation into the depolymerization process, optimizing the depolymerization rate using a non-metallic catalyst and employing the resulting depolymerized residues to produce upcycled materials directly utilizing capping agents by a two-step process based on temperature change. They further demonstrate the scalability of their process with kilogram-scale experiments and present a life cycle assessment (LCA) to support the environmental benefits of their proposed approach.

The manuscript is well-structured, clearly written, and methodologically sound, with a logical flow that makes it easy to follow. In my opinion, this work represents a valuable contribution to the literature. However, I have a few minor comments that the authors may wish to address to enhance the manuscript further.

Response: Thank you for your support of our work, and we appreciate your valuable suggestions.

1. I would suggest including a discussion on the current market demand for polyarylate materials. Since the authors are utilizing commodity polymer waste streams that are widely available, it would be valuable to understand whether the proposed process could potentially produce an excess of PAR materials. A brief discussion of the authors' perspective on this matter would enhance the manuscript.

Response: Thanks for your suggestion. According to your suggestion, we have added a brief discussion to highlight the potential and market value of PAR, on page 3 Line 71.

PAR is one kind of high-performance special engineering plastics derived from bisphenol A, terephthaloyl chloride and isopjthaloyl chloride, and it has been widely applied to aerospace, electronics, automobiles, functional membrane, etc for its excellent thermal stability, mechanical properties and outstanding optical transparency [38-40].

[38] Bhowmik, P.K. & Han, H. Fully aromatic liquid-crystalline polyesters of phenyl-substituted 4,4'-biphenols and 1,1'-binaphthyl-4,4'-diol with either 2-bromoterephthalic acid, *Macromolecules*, **26**, 5287-5294 (1993).

[39] Zhang, Y., Yan, G.-m., Zhang, G., Liu, S.-L. & Yang, J. Synthesis of high transparency polyarylates containing cyclohexane group, *Polymer.* **186**, 122047 (2020).

[40] Wang, Z. F., Liu, Y. Y., Wang, B. L., Long, X. B. & Yao, W. L. Synthesis and properties of novel block-structured polyarylates containing fluorene: a two-step interface polymerization, *New. J. Chem.* **48**, 10497-10506 (2024).

2. In Figure 3, the assignment of bisphenol A (BPA) signals in the ^{1}H NMR spectra would improve clarity.

Response: Thank you for your careful review. According to your suggestion, we have improved the assignment of bisphenol A (BPA) signals in the ^{1}H NMR spectra.

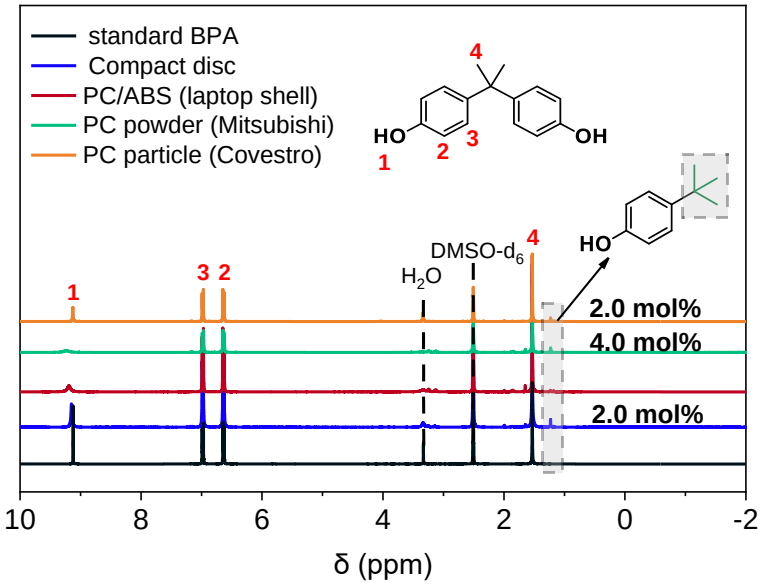

Fig. 3 (b) ^{1}H NMR spectra of standard BPA and r-BPA recycled from various waste PC. (DMSO-d_6, 400 MHz).

3. For the preparation of r-PAR, the presence of PTBP as a capping agent is inevitable, and the authors developed a two-stage interfacial polymerization to mitigate issues related to this agent. Could the authors comment on the effect of varying PTBP amounts during polymerization?

Response: We thank the reviewer for your valuable suggestion. According to your suggestion, we further studied the effect of varying PTBP amounts for PAR polymerization using our two-stage polymerization method. We have modified the manuscript and supplementary information, as shown in **Supplementary Figs. 13** and **Supplementary Table 2**.

Modified:

Considering the content of the capping agent may significantly influence the two-stage polymerization method, we further investigated the effect of PTBP in the range of 2-5% (**Supplementary Fig. 13**). As shown in **Supplementary Table 2**, the M_n of the produced PAR ranged from 1.38 to 1.77×10^4, while the Mw was approximately 4.91 to 6.38×10^4. These results indicate that the two-stage interface polymerization technique

is effective across a relatively wide range of capping agents remaining within r-BPA.

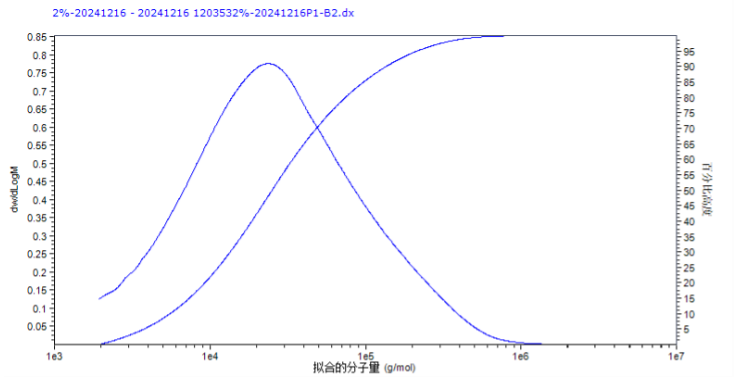

Fig.R5 The GPC data of 2%-PTBP.

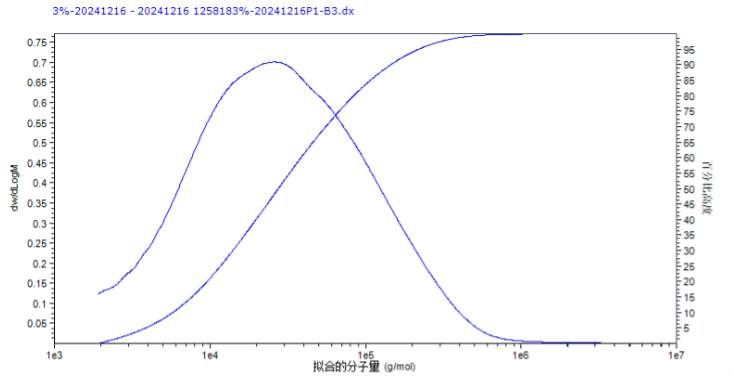

Fig. R6 The GPC data of 3%-PTBP.

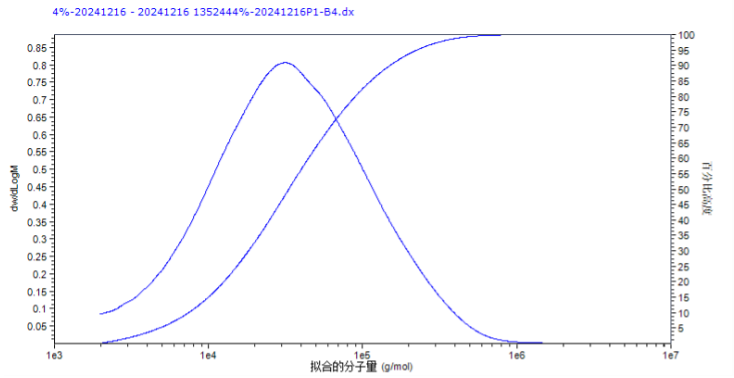

Fig. R7 The GPC data of 4%-PTBP.

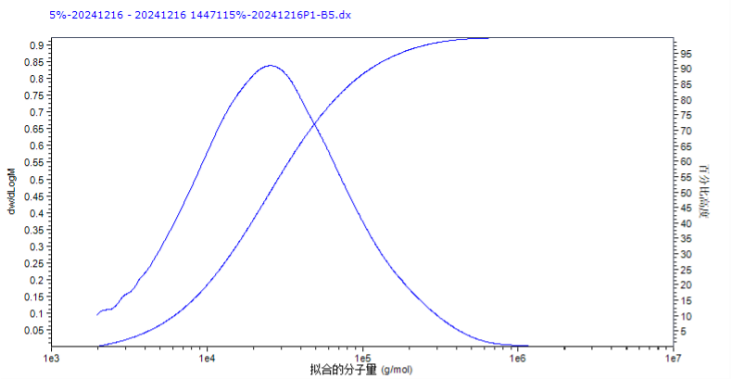

Fig. R8 The GPC data of 5%-PTBP.

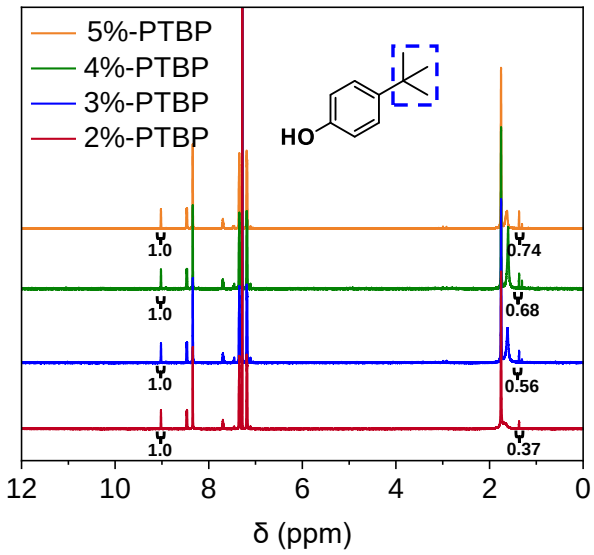

Fig. S13. The ^{1}H NMR spectra of PAR with different end-capping agents of PTBP (2-5%). (TPC+IPC): BPA= 1:0.975; the content of PTBP is in the range of 2-5%.

Table S2. The molecular weight of PAR with different contents of end-capping agent PTBP.

Sample	M_n (g/mol)	M_w (g/mol)	PDI
PAR-2%PTBP	13879	55594	4.00
PAR-3%PTBP	14471	60580	4.19
PAR-4%PTBP	17752	63813	3.59
PAR-5%PTBP	14770	49153	3.33

4. Could the authors provide additional insights into the complex viscosity data, specifically addressing the factors that could make r-PAR less viscous at lower temperatures?

Response: Thanks for your constructive comments. From the complex viscosities experiment (**Fig. 4f**), it can be found that the polymer melts complex viscosities show a decreasing trend as the temperature rises from 280 °C to 320 °C. Also, it can be observed that r-PAR shows a relatively lower viscosity at 280-310 °C and a similar viscosity at high temperature (310-320 °C) as that of commercial product U-100. The main reason is that the inherent viscosity of r-PAR (0.53 dL/g) is relatively lower than U-100 (0.55 dL/g). Lower molecular weight means less entanglement in the molecular chain (it is consistent with the T_g results). Additionally, the polydispersity index (PDI) of r-PAR (2.94) is much larger than U-100 (2.10), the smaller molecular weight polymer chain in the resin of r-PAR plays a plasticizer role, especially during the lower testing temperature, so r-PAR shows much smaller complex viscosity during lower testing temperature (280-310 °C). However, when the temperature continues to rise, the melt complex viscosity of polymers is mainly contributed by the high molecular weight component, and the high molecular weight portion of r-PAR and U-100 is similar, then the viscosities of these two samples are almost the same.

5. Please specify the percentage of recycled content in the final r-PAR material.

Response: Thanks for your comments. We couldn't agree more that the percentage of recycled content is a significant indicator used to measure the value of recycled plastics. Therefore, we have added the percentage of recycled content in **Fig. 4a** and given the calculation equation.

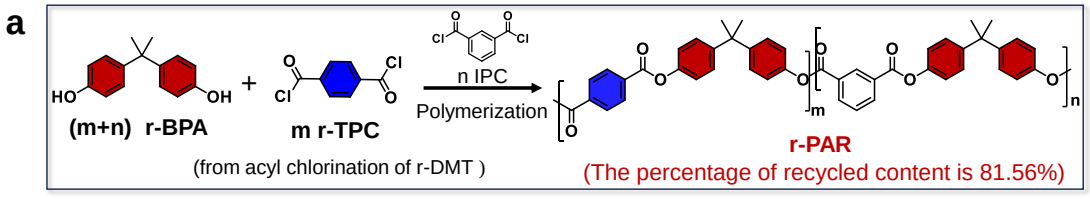

Fig. 4 (a) Schematic reaction pathway for co-upcycling of waste PC and PET into r-PAR. The percentage of recycled content (RC) is calculated as follows: RC = Σ m (C, H, O)/ M (r-PAR), where Σ m (C, O, H) is the sum of the masses of the elements recovered from the waste plastic in the structural unit and M (r-PAR) is the relative molecular mass of a structural unit of r-PAR.

Typographical and Formatting Corrections:

Figure Reference: In line 95, "Figure 1a" should be corrected to "Figure 2a." Inconsistent Numbering: The numbering for cumulative GWP data is inconsistent (see lines 264, 266, and 267).

Response: We apologize for the misleading results. We have carefully modified the manuscript according to your suggestion.

Modified:

1. Initially, a variety of ILs with different anions and cations were synthesized to systematically investigate their potential as catalysts in PC methanolysis, as illustrated in **Fig. 2a**.

2. The cumulative GWP of commercial plastics is as high as 9,190 kg CO_2 t^{-1} under current waste management models (Path 1+2).

Reviewer(s)' Comments to Author:

Reviewer #1:

I am satisfied of the answers. The revised manuscript has been improved and is good enough to publish in Nature Communications.

Response: Thank you for your constructive feedback. We are pleased that you are satisfied with all the revisions. Your valuable comments have greatly improved the quality of the paper. We appreciate your support.

Reviewer #2:

The authors provide additional experiments to address reviewers comments and description for high pressure reaction conditions is sufficiently address for example. However, the description and additional experiments to explain the catalytic activities with NMR chemical shift changes of MeOH is not agreeable since there are too many factors that can affect the chemical environments of MeOH in solution states. Diffusion co-efficient is also highly sensitive viscosity of the media therefore, it does not necessarily explain the role of hydrogen bonding from the catalyst. Overall, this reviewer would agree with the observed catalytic activities for depolymerization of PET and PC and the progress to obtain new recycled flame-retarding polymer without the Figure 2 b, c and d. Bronsted acid/base catalysis reaction mechanism can be also explained by using acetic acid/TBD where TBD acts as a base and acetic acid act as a H-bond donor at the transition state. Therefore, the illustrate NMR titration and also the diffusion co-efficient do not serve as experimental data to support the proposed reaction mechanism. Such a sentence - "the Ac anions are more beneficial in activating the hydroxyl group of MeOH" - should be carefully written since the activation can happen in the activated complex (TS) not in the equilibrium conditions (as in NMR conditions). Also Figure S5 contains tetrahedral intermediate and the authors assigned that they observed tetrahedral intermediate in the solution state. Tetrahedral intermediates are

considered as almost transition states (J. Org. Chem. 2004, 69, 21, 7317–7328). Therefore, the authors should add more information how this mechanism is being proposed specially (4* and 5*) or add more experimental data to support it. Overall, the revision provides sufficient data however the authors do not provide important knowledge for catalytic reaction mechanism, which is mostly based on preliminary NMR studies without kinetic and in-depth mechanistic studies.

Response: Thank you for your valuable feedback and thoughtful comments. We appreciate your agreement with the observed superior catalytic activities for PET and PC depolymerization. As you previously suggested, we have added experiments on Job's plot and DOSY in the last revision. However, regarding your concerns about the NMR chemical shift changes of MeOH, we acknowledge that multiple factors can influence its chemical environment in solution, which complicates interpretation. We also recognized that diffusion co-efficient is highly sensitive viscosity of the media, therefore, the DOSY experiment may not necessarily explain the role of hydrogen bonding from the catalyst. As the reviewer proposed, the new added Job's plot and the diffusion co-efficient experiment may not serve as experimental data to support the proposed reaction mechanism. Thus, we have removed the data related to the Job's plot and DOSY analysis. As reported in the literature (*ACS Sustainable Chem. Eng.* 2022, 10, 17261−17273; *Green Chem.* 2020, 22, 3122 – 3131; *ACS Sustainable Chem. Eng.* 2018, 6, 15127−15134), titration experiments were usually used to study how a catalyst activates the substrate. We have preserved this data (**Figure S2**), but this manuscript will not perform more in-depth mechanistic studies.

In addition, the reviewer proposed that "Bronsted acid/base catalysis reaction mechanism can be also explained by using acetic acid/TBD where TBD acts as a base and acetic acid act as a H-bond donor at the transition state." However, there may be a misunderstanding here. The ionic liquid catalyst is not a combination of organic bases (TBD) and organic acids (Ac). Instead, the protons of acetic acid are transferred into the TBD to form an ion-pair structure. Typically, the anion acts as a nucleophilic reagent to activate the methanol, and the cation acts as an H-bond donor to activate the carbonyl

group. This is also reported within previous refs, such as *Angew. Chem. Int. Ed.* 2021, 60, 6710–6717 and *ChemSusChem* 2021, 14, 1–31.

We fully agree with your comment that proposing a detailed mechanism, as seen in Ref., would require further in-situ characterization and DFT theoretical support (*Nat. Comm.* 2024, 15, 6266; A*CS Sustainable Chem. Eng.* 2023, 11, 43, 15544–15555). We considered deeper investigation using in-situ NMR or FT-IR, but the reaction conditions for methanolysis limited our ability to conduct these experiments. While we acknowledge this limitation on the mechanism, we believe our findings still provide some insight into the role of ionic liquids in activating methanol and DPC. In addition, the key findings of the manuscript are metal-free efficient methanolysis and upcycling of PC and PET into PAR directly utilizing the capping agent by a two-stage interface polymerization technique. A deep understanding of the mechanism of methanolysis would not be the most important advance here. Therefore, we removed the possible mechanistic process in SI and modified it to a schematic of MeOH and DPC to be activated by [TBDH]Ac (**Figure S2a**).

Once again, thank you for your thoughtful and helpful comments, which have greatly improved the clarity of our manuscript. In response to your suggestions, we have revised the manuscript accordingly, as shown in the modified version.

Modified:

As shown in **Fig. 2b and Supplementary Fig. 1**, the catalytic activity of [TBDH]Ac for polyester methanolysis exhibits a gradual increase as the reaction temperature rises. At 100 °C, the conversion of PC during methanolysis nearly reaches 100% after 4 hours. Inspired by previous work[28,42,43], we examined the activation of MeOH and PC using iILs through NMR spectroscopy, employing diphenyl carbonate (DPC) as a model compound for PC. The activation of the carbonyl group in DPC by [TBDH] was indirectly supported by the observed weakening of the electrostatic interaction between [TBDH] and the acetate ion ([Ac]), as indicated by chemical shifts

1 and 4 in **Supplementary Fig. 2b.** Additionally, when [TBDH]Ac was mixed with methanol, the acetate anion induced a downfield chemical shift in the methanol hydroxyl group (see **Supplementary Fig. 2c**), indicating the methanol reactant was activated. These experiments indicate that [TBDH]Ac operates via Brønsted acid/base catalysis, in which the acetate anion acts as a nucleophilic reagent to activate methanol, while the TBD cation functions as a hydrogen bond donor to activate the carbonyl group. It is essential to recognize that various factors can influence the chemical environment in solution, complicating the interpretation of results. A more comprehensive understanding of the mechanism necessitates additional *in situ* characterization and calculations.

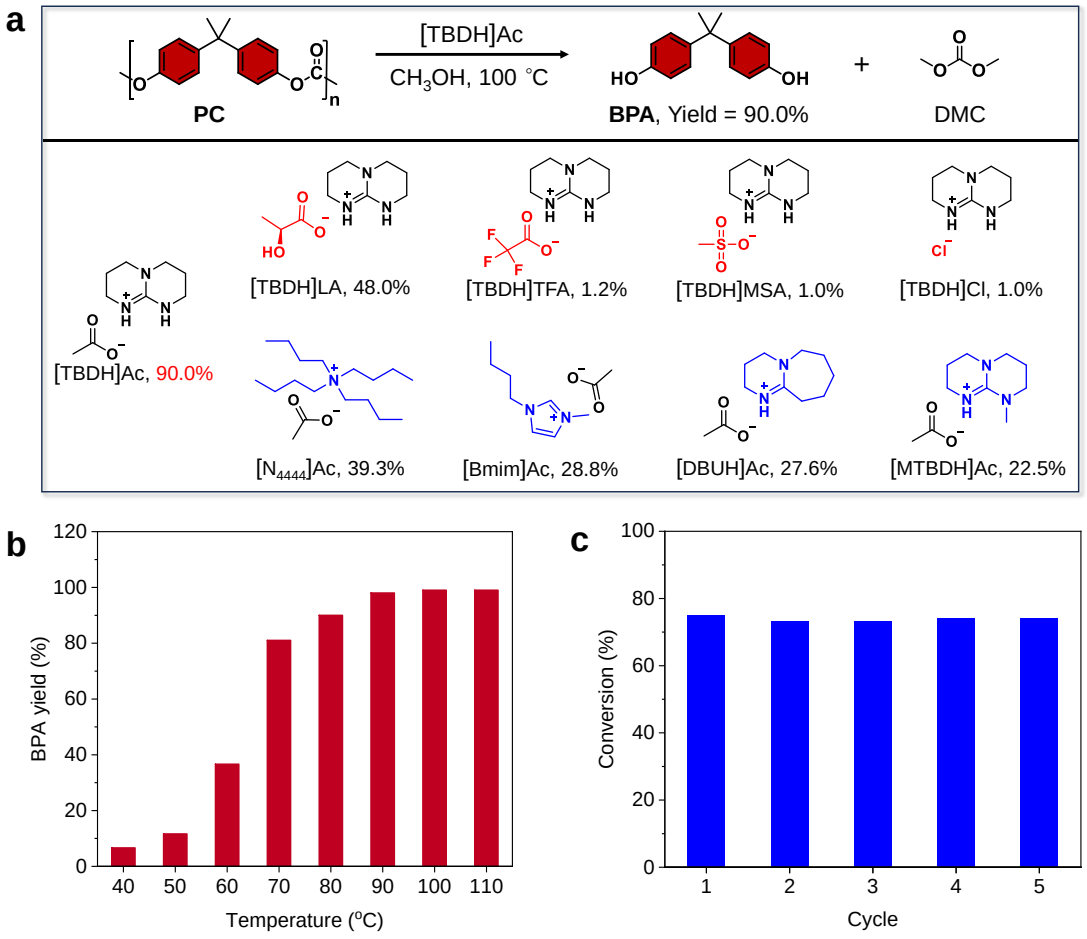

Fig. 2 Catalytic methanolysis of PC under mild conditions. (a) Effect of the anions and cations of ionic liquids on PC methanolysis. Condition: catalyst (0.25 mmol), PC (0.5 g), MeOH (2 mL), 100 °C, 2 h. (b) The effect of temperature on PC methanolysis. Condition: [TBDH]Ac (0.25 mmol), PC (0.5 g), MeOH (2 mL), 4 h. (c) Evaluation of the stability of [TBDH]Ac in PC methanolysis. Condition: catalyst (0.25 mmol), PC

(0.5 g), MeOH (2 mL), 100 °C, 1.5 h.

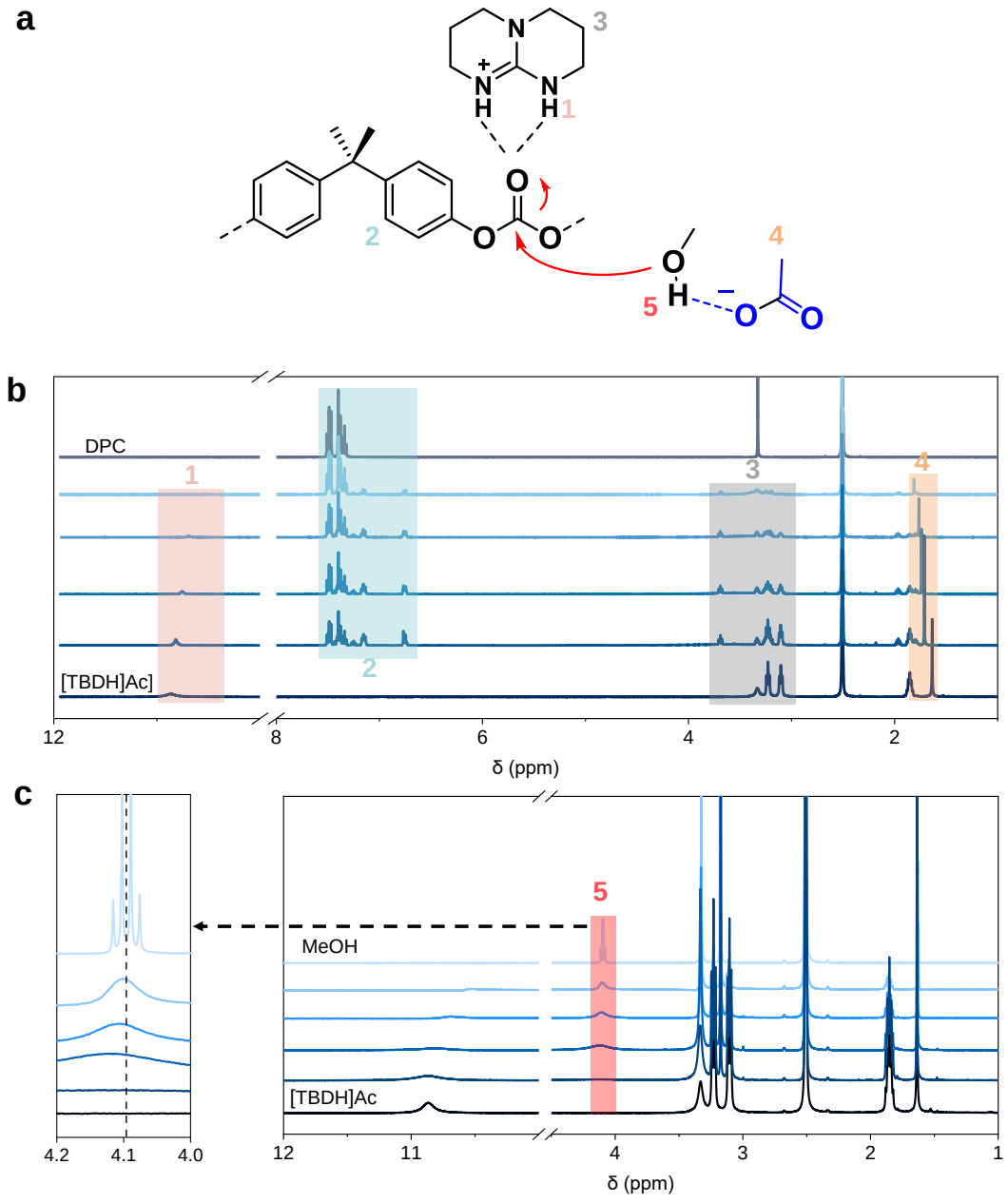

Fig. S2 (a) Modelled dual activation mechanism for PC and methanol by [TBDH]Ac. (b) ^{1}H NMR spectra of the interaction between [TBDH]Ac and MeOH, according to the order of spectrum from top to bottom, mole ratio of [TBDH]Ac/MeOH was 0/1, 1/20, 1/10, 1/5, 1/3.33, and 1/0. (c) ^{1}H NMR spectra of the interaction between [TBDH]Ac and DPC, the mole ratio of [TBDH]Ac/DPC was 0/1, 1/5.6, 1/2.8, 1/1.4, 1/0, and 1/0.

Reviewer 3#

Cheng Li and coworkers have provided a comprehensive response to the reviewers' recommendations. Therefore I agree on the publication of the revised version of the manuscript.

Response: Thank you for your positive feedback. We appreciate your acknowledgment of our comprehensive revisions and are grateful for your support in agreeing to the publication of the revised manuscript.

Reviewer(s)' Comments to Author:

Reviewer #2:

I would recommend to check Jencks' libido rule to discuss general acid/base catalysis for the proposed reaction mechanism, how to investigate it, and how to determine the reaction mechanism. To explain in the context of this manusscript, acetate is not a strong base to deprotonate methanol, therefore the reaction should be general catalysis (as in general vs specific acid catalysis). In this scenario, acetate is better to deprotonate guanidinium ion rather than methanol since pKa of protonated TBD should be lower (assuming that pKa of DBU is around 12, pKa Methanol >15). Since the authors may have suggested in the general acid/base catalyzed reaction mechanism, the proton transfer should be involved in the rate-determining step. Therefore, the proposed reaction mechanism (also in Angew. Chem. Int. Ed. 2021, 60, 6710) is not being supported based on what the authors undertaken. The refered ACIE 2021 paper solely relying on DFT calculation for the reaction mechanism (and the required scission energy was calculated to be 37.3 kcal/mol while the activation barrier was quite close, 32.5 kcal/mol).

Neverthelss these comments will not affect the conclusion of the manuscript if there is more focus on the chemical recycling and production of a new PAR from waste materials.

Response:

We appreciate your insightful comments. We check with the Jencks' libido rule and suppose both $TBDH^+$ and MeOH are nearly incapable of donating protons, as indicated by their pKa values (both at ca. 15 in water). Additionally, the conjugate base of MeOH, the alkoxide anion (MeO^-), is significantly more basic than the acetate anion (Ac^-), which makes direct proton transfer quite challenging. Thus, we propose that the acetate anion mainly activates the hydrogen atom of MeOH through intermolecular hydrogen bonding, thereby aiding the transesterification process. In the revised text, we have described that the catalyst primarily serves to activate methanol through mechanisms

like hydrogen bonding or electrostatic interactions, without enforcing full proton transfer. We suppose this partial activation is essential for reducing the energy barrier in the following reaction steps, like transesterification, while keeping the catalytic system stable. This view reinforces that the catalyst's role is to enhance reactivity without necessitating full proton transfer without the presence of reactive substrates. Our mechanism aligns with the findings in the literature (Angew. Chem. Int. Ed. 2021, 60, 6710), which highlights methanol activation as a key step. This perspective is broadly supported in the field of ionic liquid-catalyzed transesterification reactions (Sci. Adv. 2018, 4, eaas9319; Green Chem. 2021, 23, 1871-1882; Green Chem., 2020, 22, 3122-3131).

Once again, thank you for your thoughtful and helpful comments. We have made the corresponding revisions to ensure the accuracy and relevance of the cited literature according to your suggestions.

Modified:

As shown in **Fig. 2b and Supplementary Fig. 1**, the catalytic activity of [TBDH]Ac for polyester methanolysis exhibits a gradual increase as the reaction temperature rises. At 100 °C, the conversion of PC during methanolysis nearly reaches 100% after 4 hours. Previous studies have demonstrated that the hydrogen bonds formed between ionic liquids and reactants facilitate the cleavage of C-O bond[28,42-44]. We examined the activation of MeOH and PC using ILs through NMR spectroscopy, employing diphenyl carbonate (DPC) as a model compound for PC. The hydrogen bonding of the carbonyl group in DPC with [TBDH] was indirectly supported by the observed weakening of the electrostatic interaction between [TBDH] and the acetate ion ([Ac]), as indicated by chemical shifts 1 and 4 in **Supplementary Fig. 2b.** Additionally, when [TBDH]Ac was mixed with methanol, ^{1}H NMR spectroscopy further demonstrated significant hydrogen bonding between the hydroxyl group of MeOH and the acetate anion (see **Supplementary Fig. 2c**), indicating the methanol reactant was activated. These experiments indicate that [TBDH]Ac operates via a synergetic way, in which the acetate anion acts as a nucleophilic reagent to activate methanol, while the TBD cation functions as a hydrogen bond donor to activate the carbonyl group.