Supplementary Information (SI) for Polymer Chemistry.
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Supplementary Information

Rational design and synthesis of imine linked Porous organic polymers: A bifaceted approach towards customizing the acid-base properties for heterogeneous catalysis

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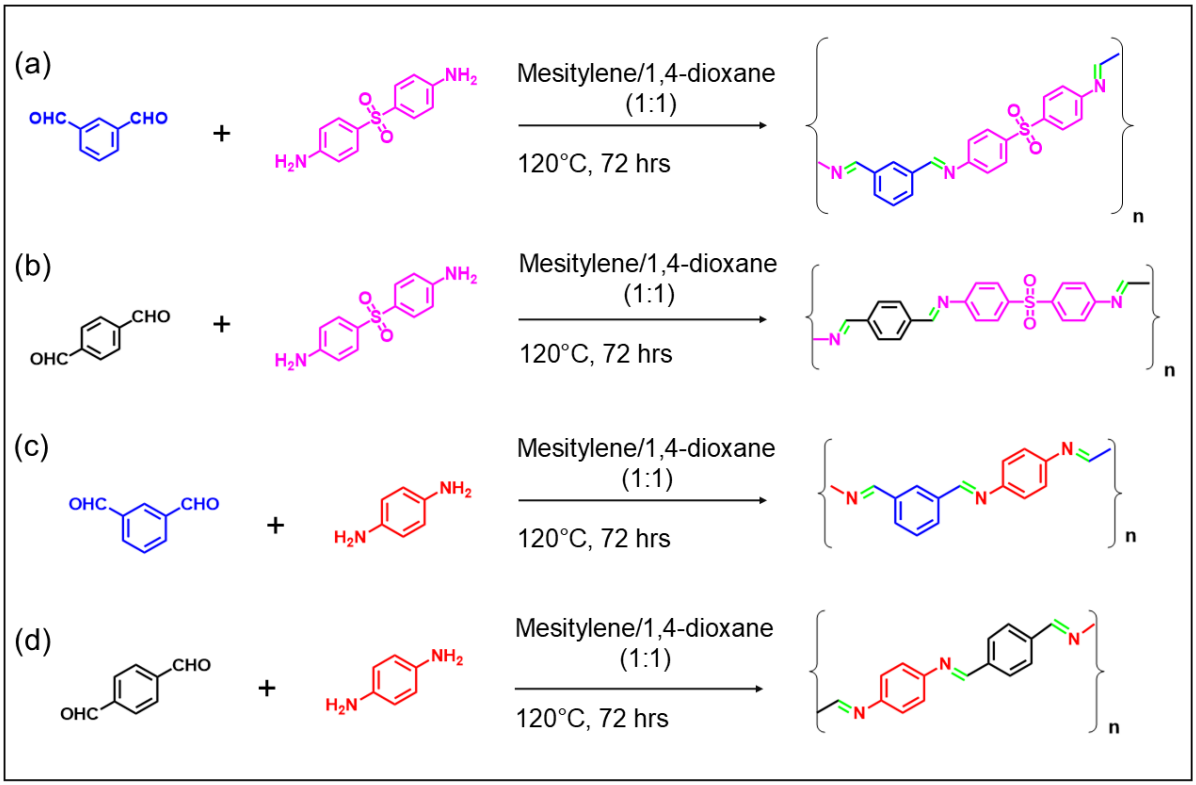
Contents

Materials and methods

All the chemicals were purchased from Sigma Aldrich, Alfa Aesar, Spectrochem, Merck and TCI and used without further purification. FT-IR spectra were recorded using Shimadzu IR Tracer 100 with DLATGS and MCT detectors. Thermogravimetric analysis were performed using Perkin Elmer Thermal Analyzer STA 8000. Powder X-ray diffraction were recorded using Rigaku XRD Smart Lab. Field Emission Scanning Electron Microscopy were obtained using Carl Zeiss model Gemini SEM 300. BET analysis was performed using Autosorb iQ-MP-MP-(2STAT)VITON. The solid state ^{13}CNMR spectra were recorded using 400 MHz Jeol solid state spectrometer ^{1}H NMR spectra were recorded on Bruker AV III 400 MHz. Temperature Programmed Desorption measurements were performed using Chemisorption catalyst analyser model: BELCAT II from MicrotracBEL Corp. XPS measurements were performed using Thermofisher K-Alpha Xray Photoelectron Spectroscopy

Synthesis of Porous organic polymers



Scheme S1. Schematic representation of the synthesis of Porous organic polymers (a) IASD, (b) TASD, (c) IAPD and (d) TAPD

Characterizations of POPs

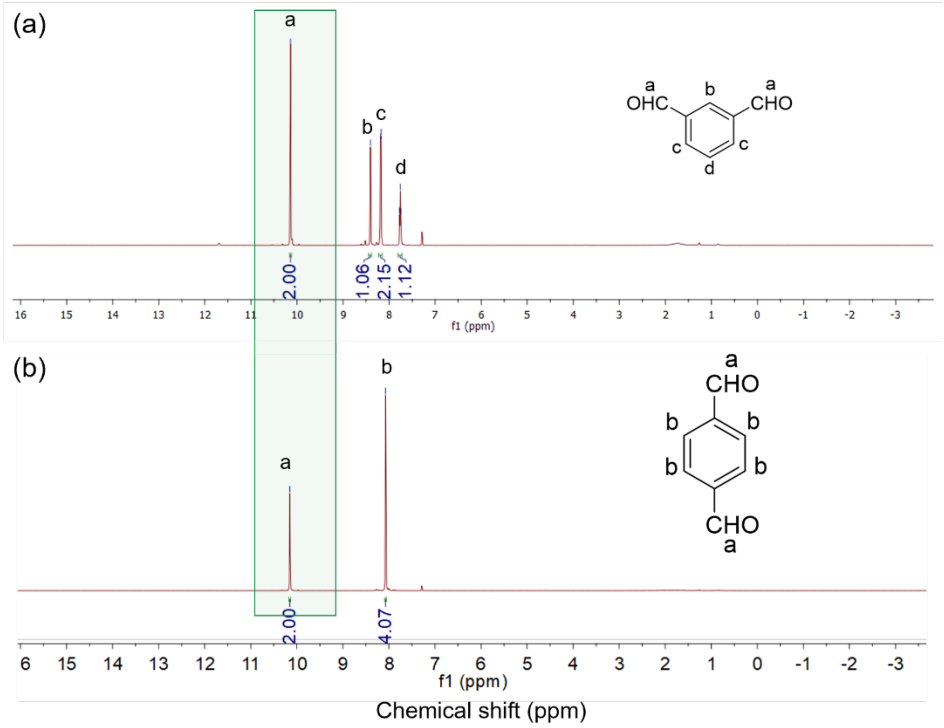


Figure S1. ^{1}H NMR spectra of (a) isophthalaldehyde (b) terephthalaldehyde ($CDCl_3$)

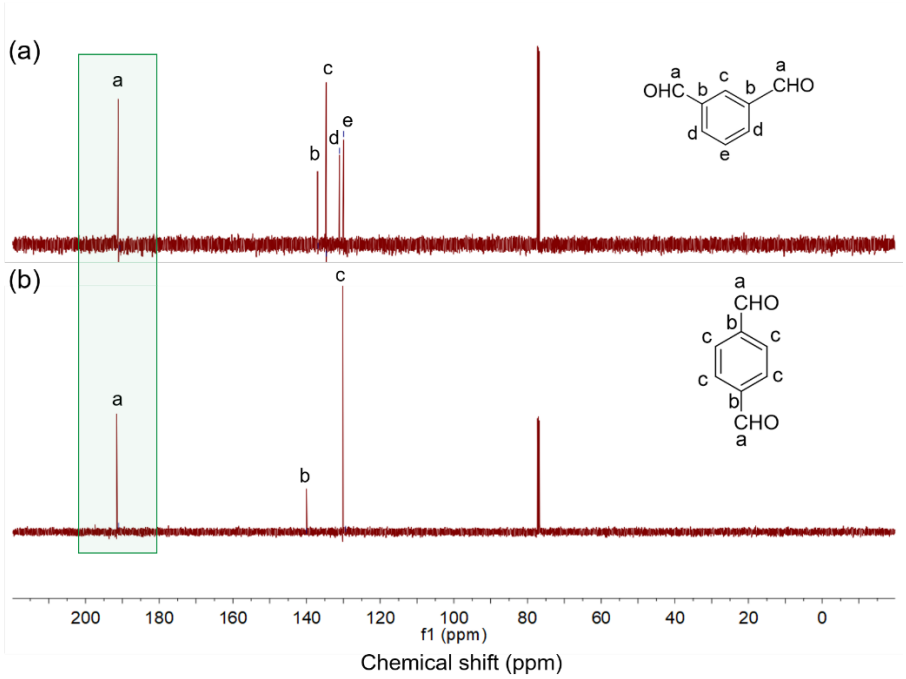


Figure S2. ^{13}C NMR spectra of (a) isophthalaldehyde (b) terephthalaldehyde ($CDCl_3$)

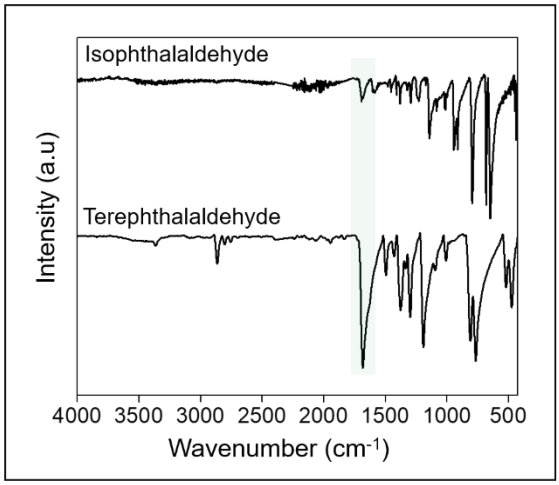


Figure S3. FT-IR spectra of monomer aldehydes

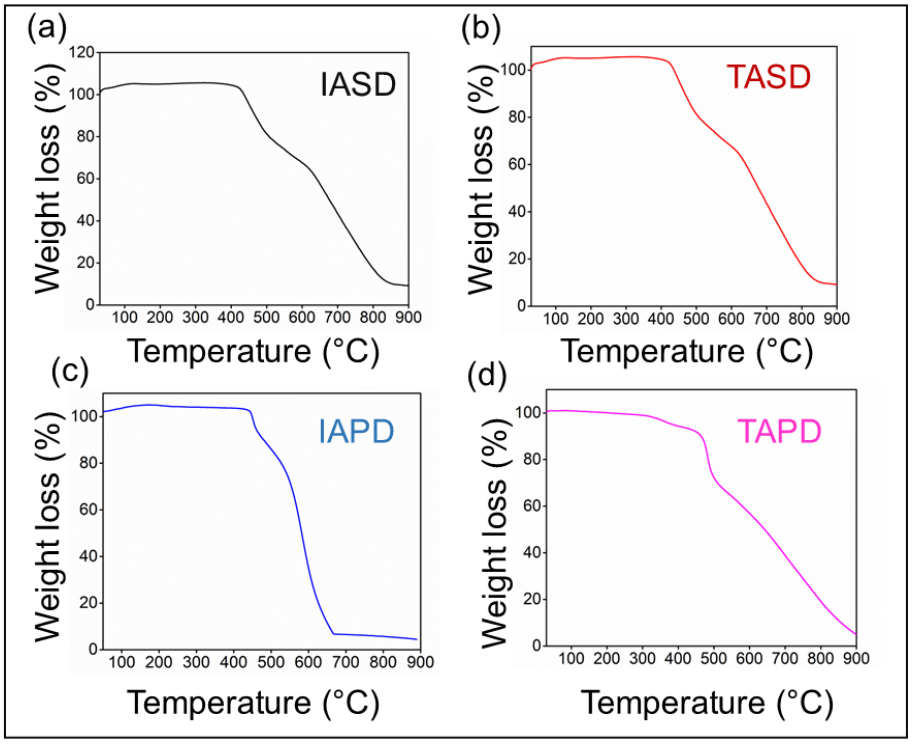


Figure S4. Thermogravimetric analysis of POPs

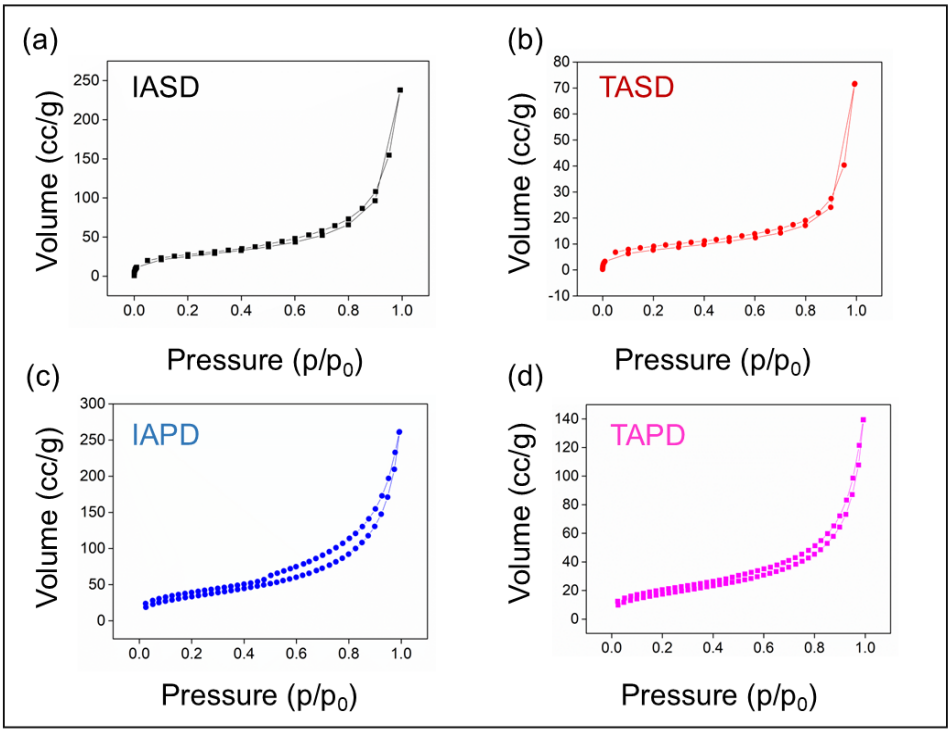


Figure S5. Brunauer-Emmett-Teller Surface area analysis of POPs

Table S1. Surface area and average pore radii for POPs

Sample	Surface area (m^2/g)	Average pore radius (nm)
IAPD	124.88	6.47
IASD	89.34	8.239
TAPD	65.01	6.64
TASD	27.118	8.17

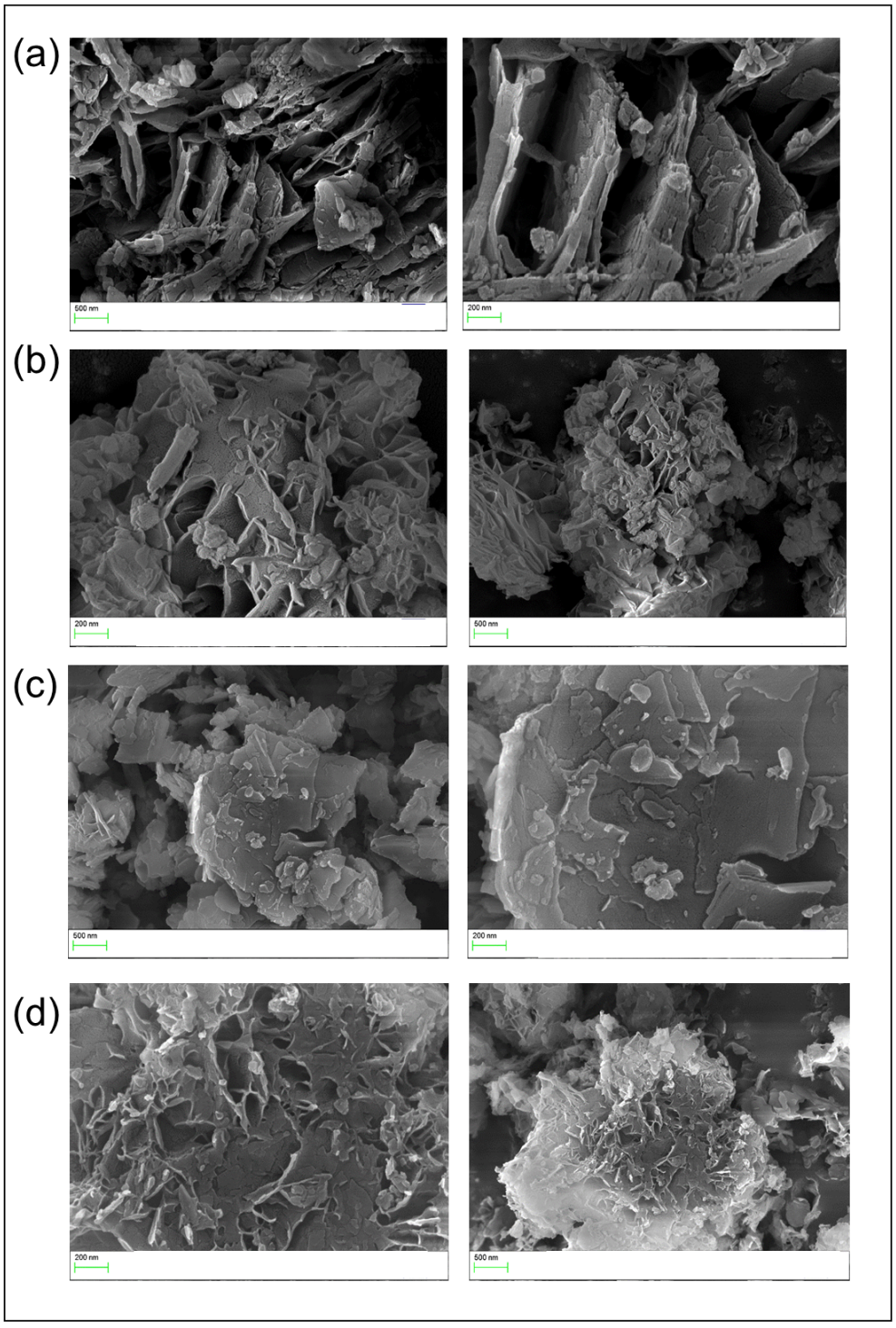


Figure S6.Field emission scanning electron microscopy images of POPs (a) IAPD, (b) IASD, (c) TAPD and (d) TASD

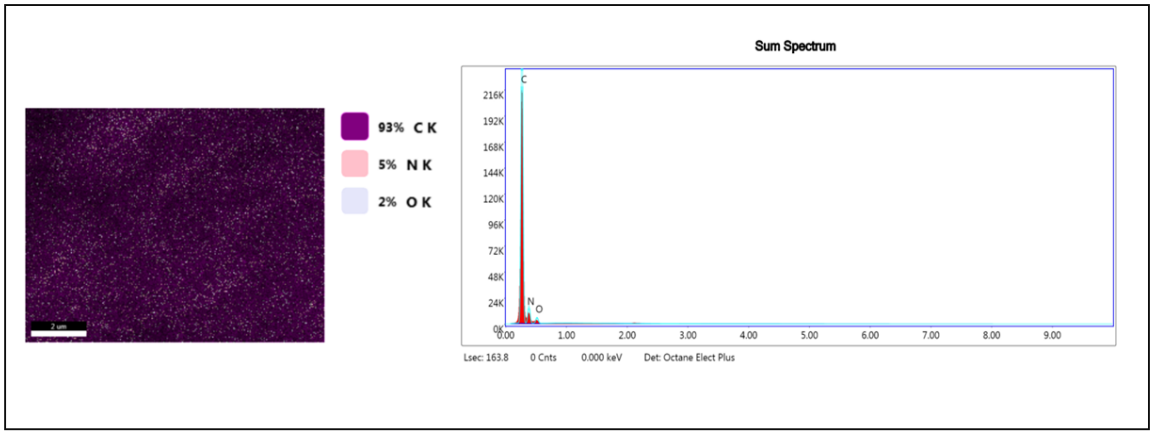


Figure S7. Elemental analysis of POP IAPD

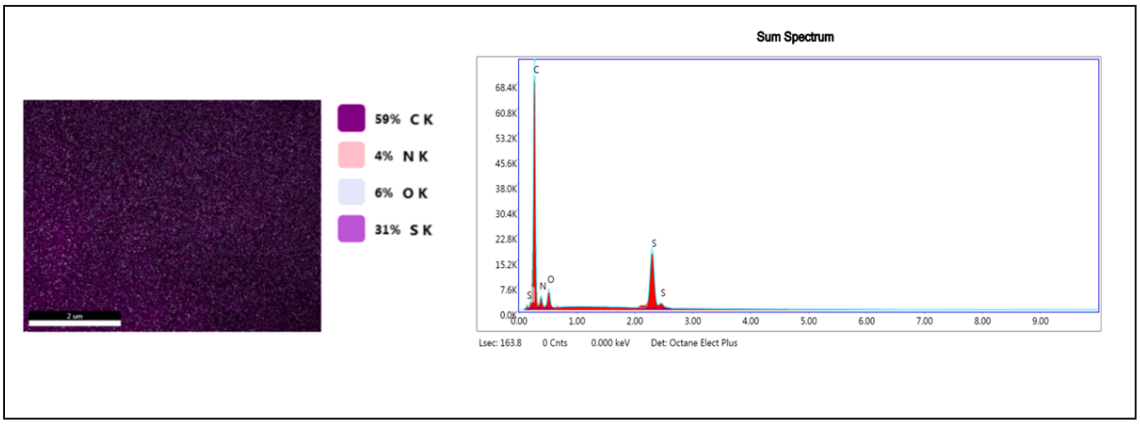


Figure S8. Elemental analysis of POP IASD

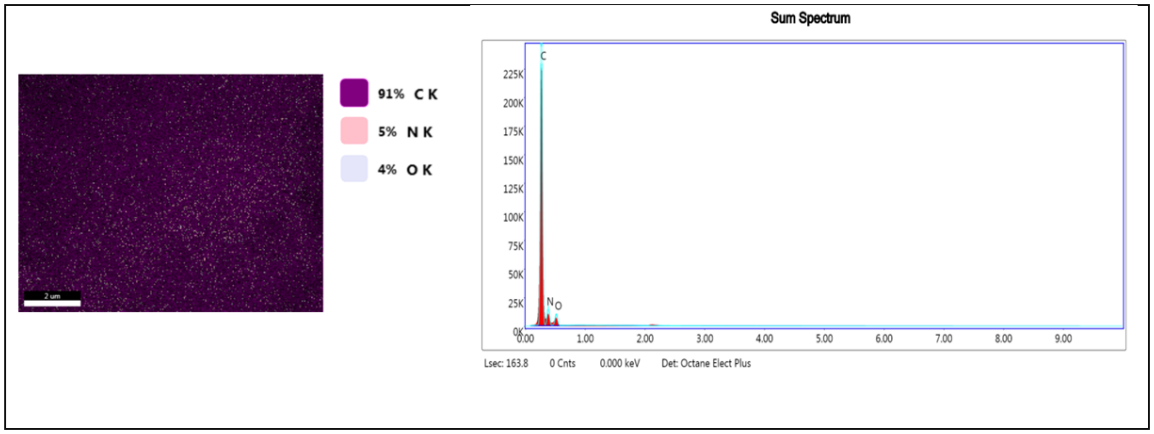


Figure S9. Elemental analysis of POP TAPD

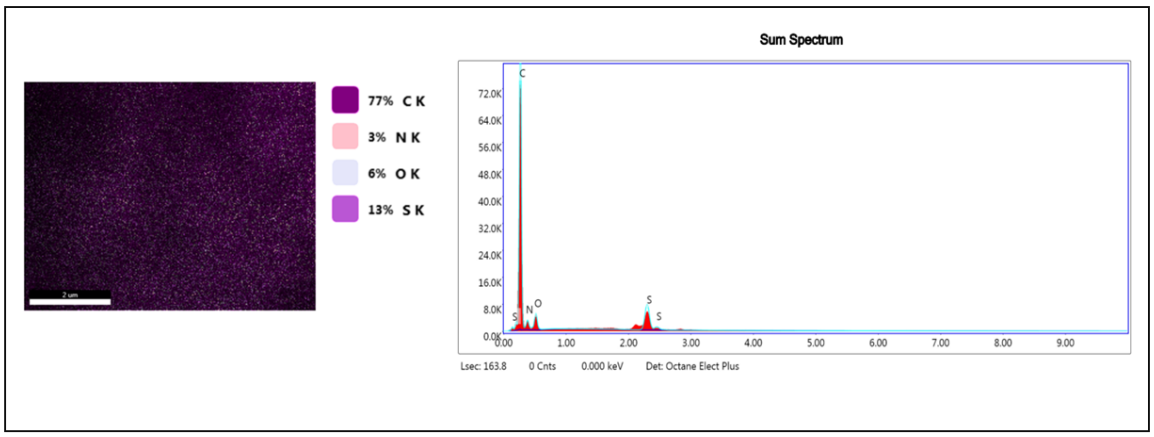


Figure S10. Elemental analysis of POP TASD

Characterization of product obtained

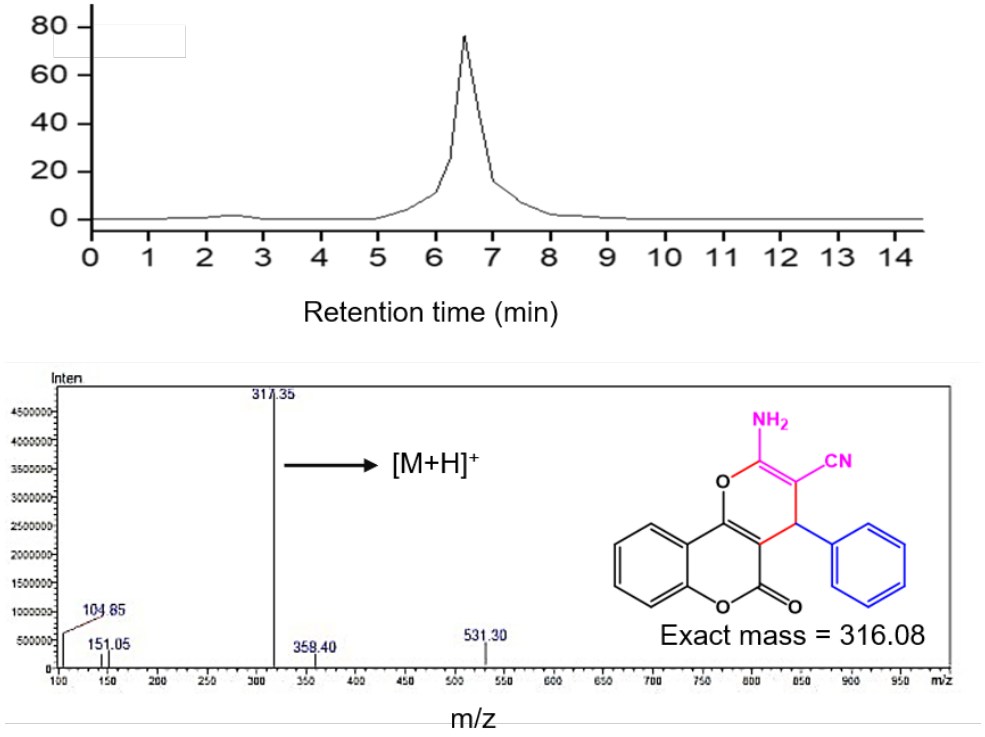


Figure S11. LC-MS analysis of pyranochromene; Calculated $[M+H]^+ = 317.08$ Observed $[M+H]^+ = 317.35$

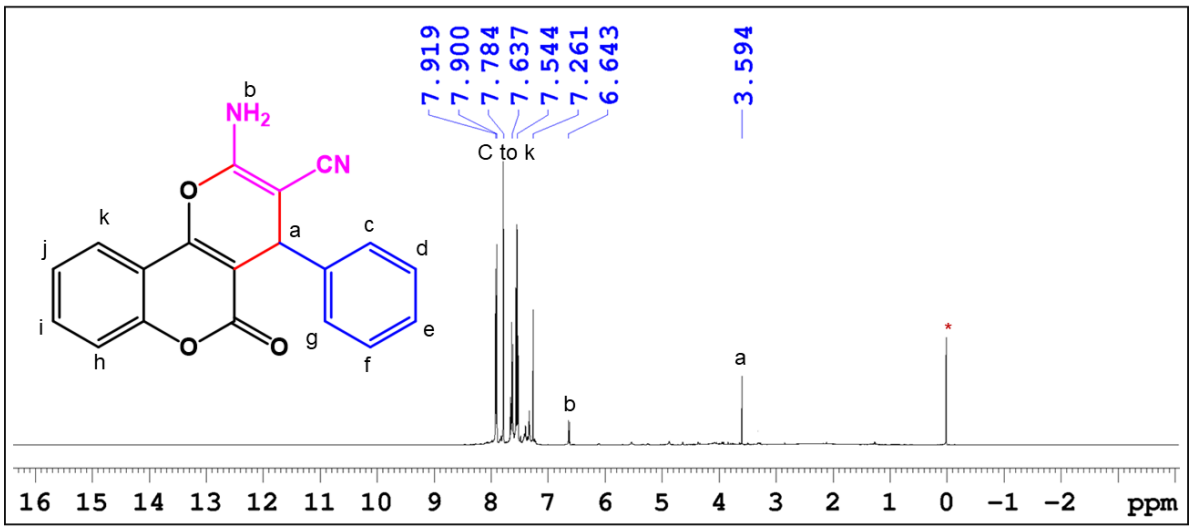


Figure S12 ^{1}H NMR spectra of pyranochromene in DMSO- d_6 at 400 MHz. (* represent Tetramethylsilane signal)

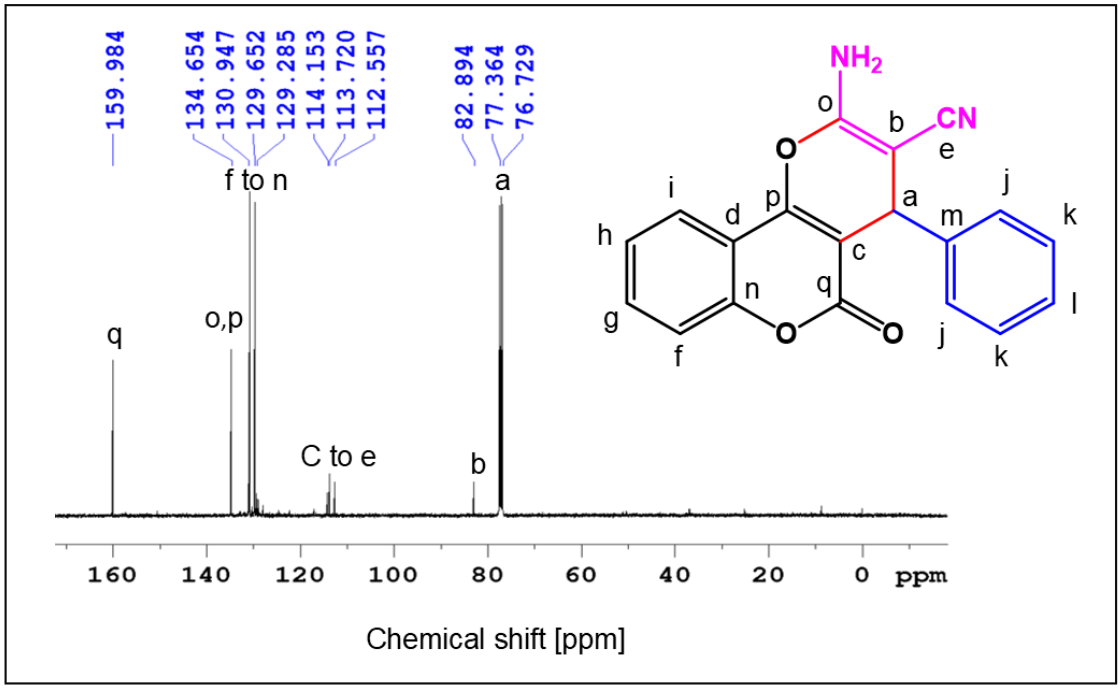
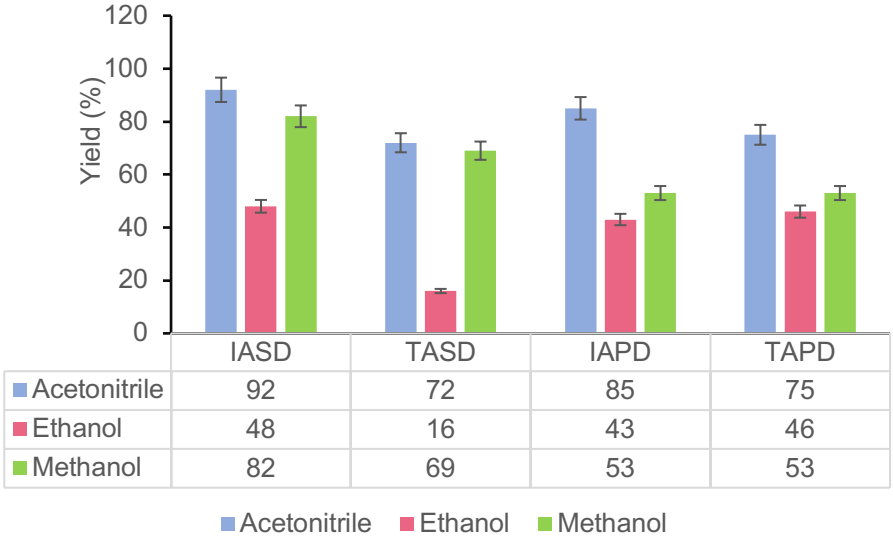


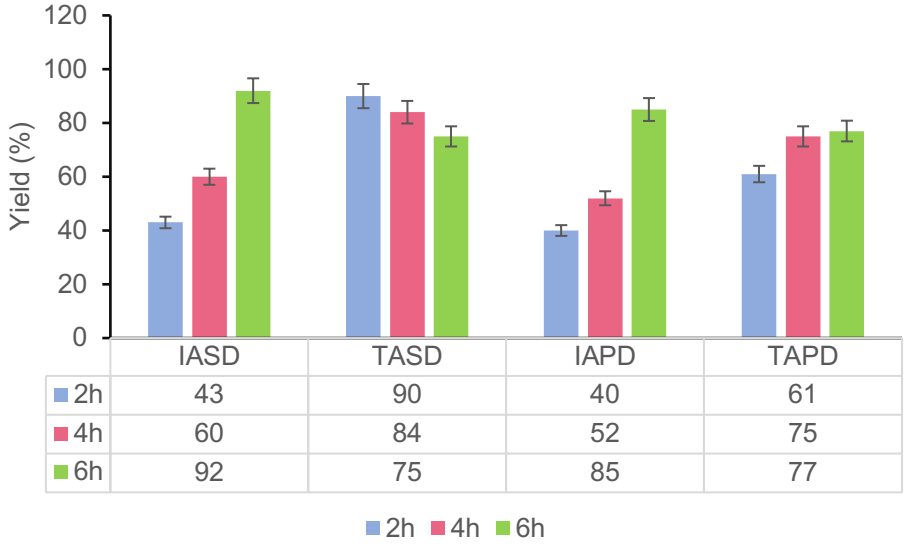
Figure S13. ^{13}C NMR spectra of pyranochromene in d_6-DMSO at 101 MHz

Catalytic synthesis of pyranochromene: optimization of reaction parameters



	IASD	TASD	IAPD	TAPD
Acetonitrile	92	72	85	75
Ethanol	48	16	43	46
Methanol	82	69	53	53

Figure S14. Effect of solvent on % yield (0.3 mmol reactants/room temperature/20 mg catalyst)



	IASD	TASD	IAPD	TAPD
2h	43	90	40	61
4h	60	84	52	75
6h	92	75	85	77

Figure S15. Effect of time on % yield of reaction (0.3 mmol reactants/room temperature/ Acetonitrile /20 mg catalyst)

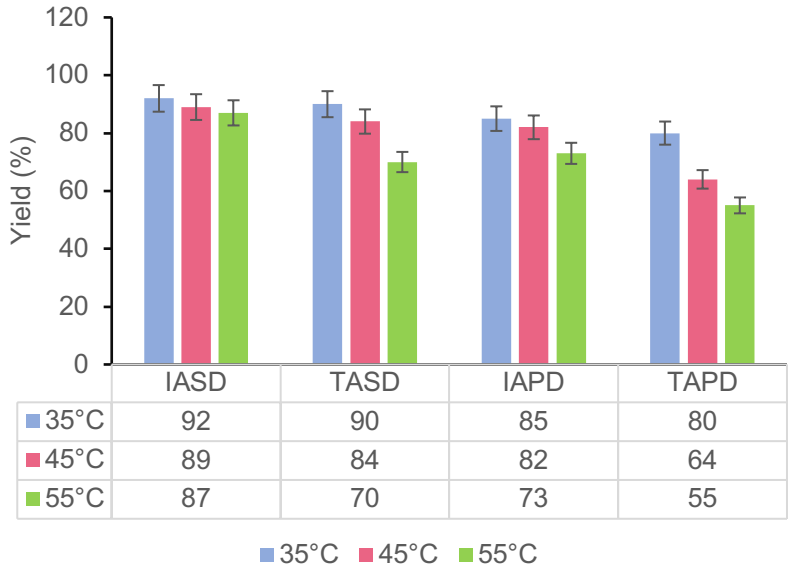


Figure S16. Effect of temperature on % yield of reaction (0.3 mmol reactants/Acetonitrile/20 mg catalyst)

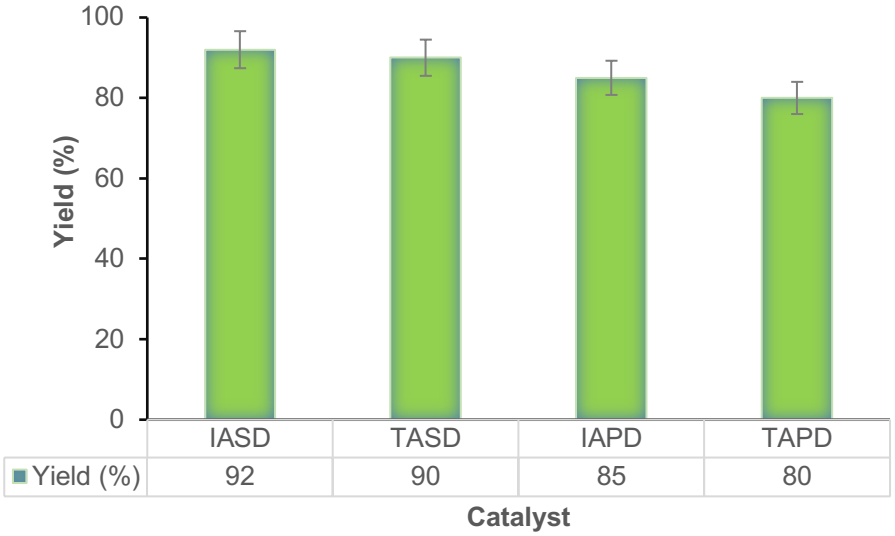
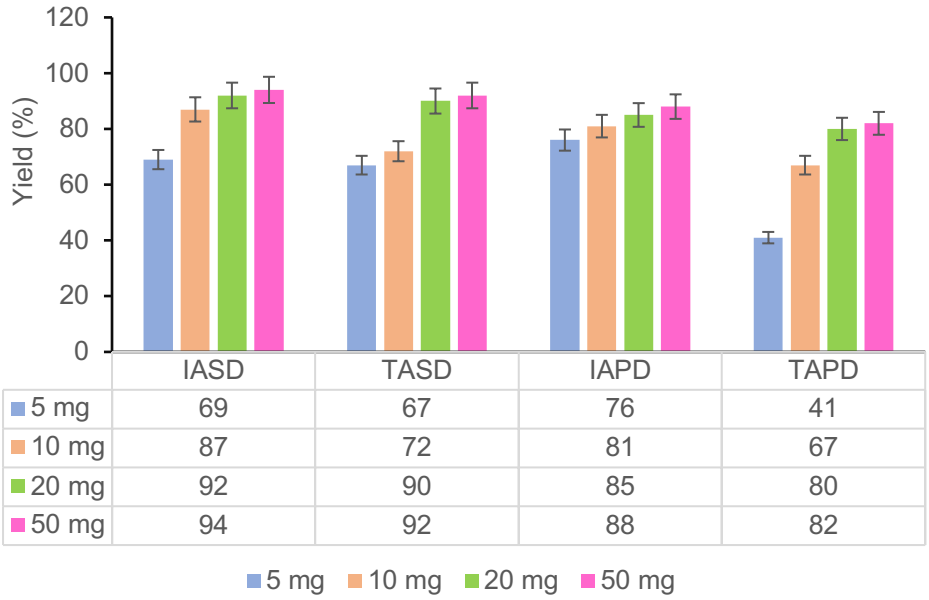
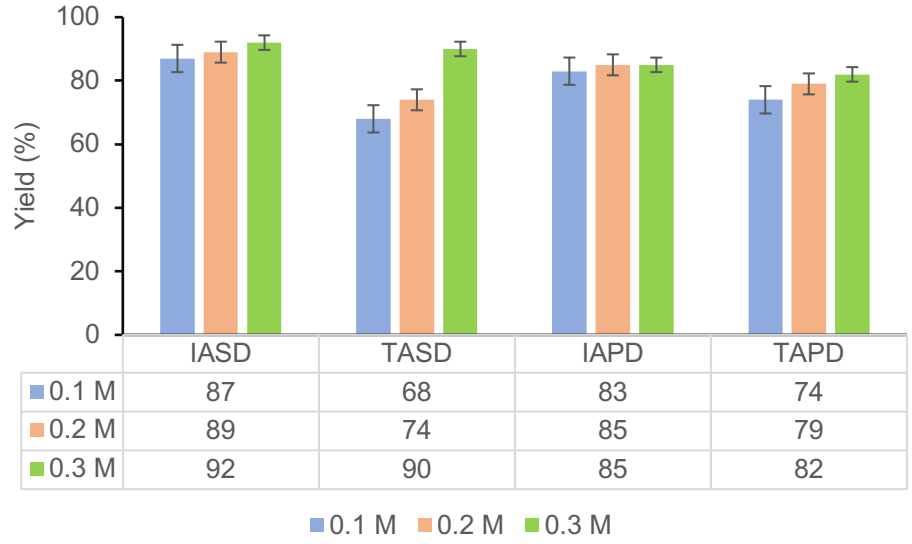


Figure S17. Effect of catalyst on % yield of reaction (0.3 mmol reactants/ Acetonitrile /room temperature/20 mg catalyst)



	IASD	TASD	IAPD	TAPD
5 mg	69	67	76	41
10 mg	87	72	81	67
20 mg	92	90	85	80
50 mg	94	92	88	82

Figure S18. Effect of amount of catalyst loaded on % yield of reaction (0.3 mmol reactants/Acetonitrile/room temperature)



	IASD	TASD	IAPD	TAPD
0.1 M	87	68	83	74
0.2 M	89	74	85	79
0.3 M	92	90	85	82

Figure S19. Effect of concentration of substrate on % yield of reaction (Acetonitrile/room temperature/20 mg catalyst)

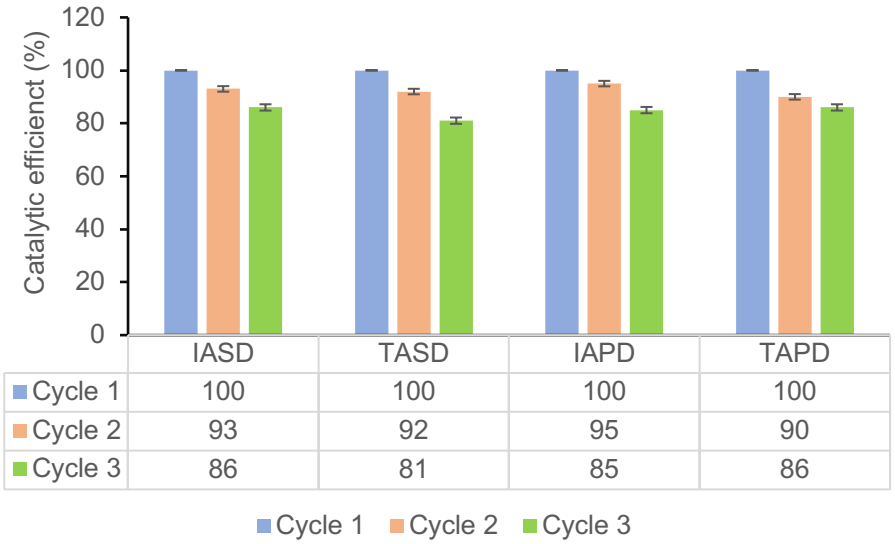


Figure S20. Recyclability test performed for each polymer catalyst (0.3 mmol reactants/Acetonitrile/room temperature/20 mg catalyst)

The structural integrity of the catalyst after reaction has been confirmed by FT-IR, PXRD, XPS and BET analysis using IASD as the model catalyst.

The FT-IR spectra of the used catalyst retained the characteristic imine vibrational band around 1600 cm^{-1}. Moreover there was no significant shifts in the observed peaks which confirms the stability of the sample after reaction.

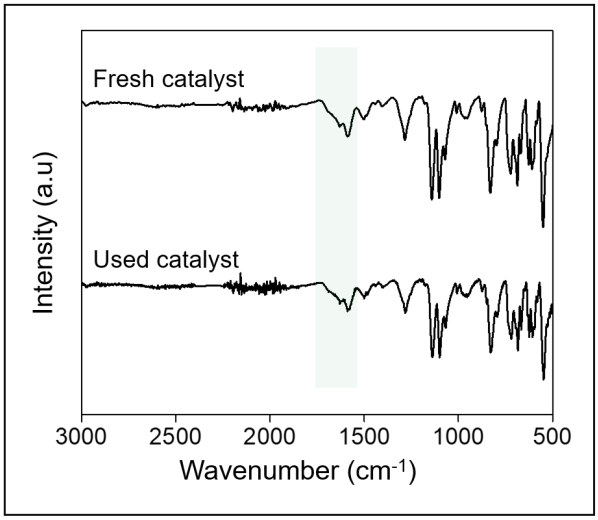


Figure S21. FT-IR spectra of fresh and used polymer IASD

The PXRD pattern of fresh and used polymers showed all the characteristic peaks in the spectra. There was no shift in the peak positions. The slight broadening of the base region might be attributed to decrease in crystallite size, micro strain, lattice defects or amorphization.

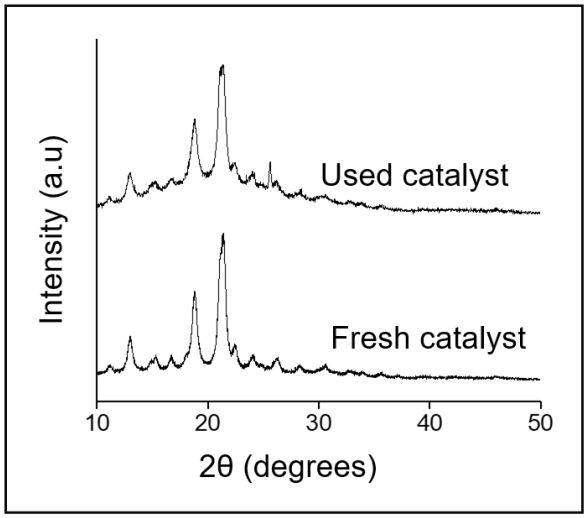


Figure S22. PXRD of fresh and used polymer IASD

The XPS survey scan of fresh and used polymers was also compared. The characteristic peaks corresponding to C1S, O1S, N1S and S 2P were obtained. There was no shift in the peak positions confirming the structural integrity after reaction.

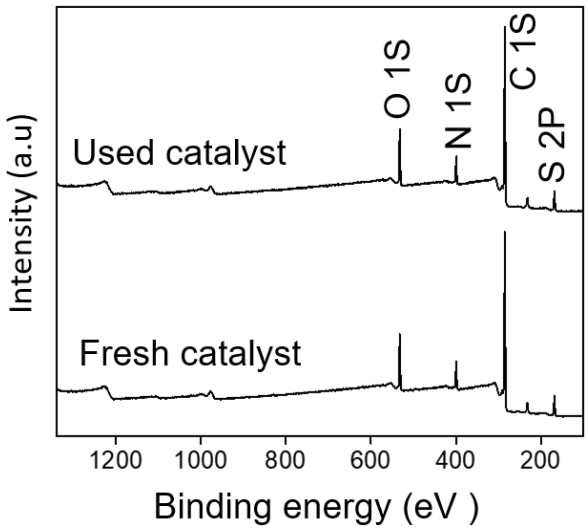


Figure S23. XPS survey scan of fresh and used polymer IASD

The surface area of fresh and used catalysts were compared using the polymer TASD (polymer with lowest surface area obtained) as a model candidate. It was observed that a very slight decrease in the surface area was observed. The average pore radii have reduced considerably might be because of the pore collapse.

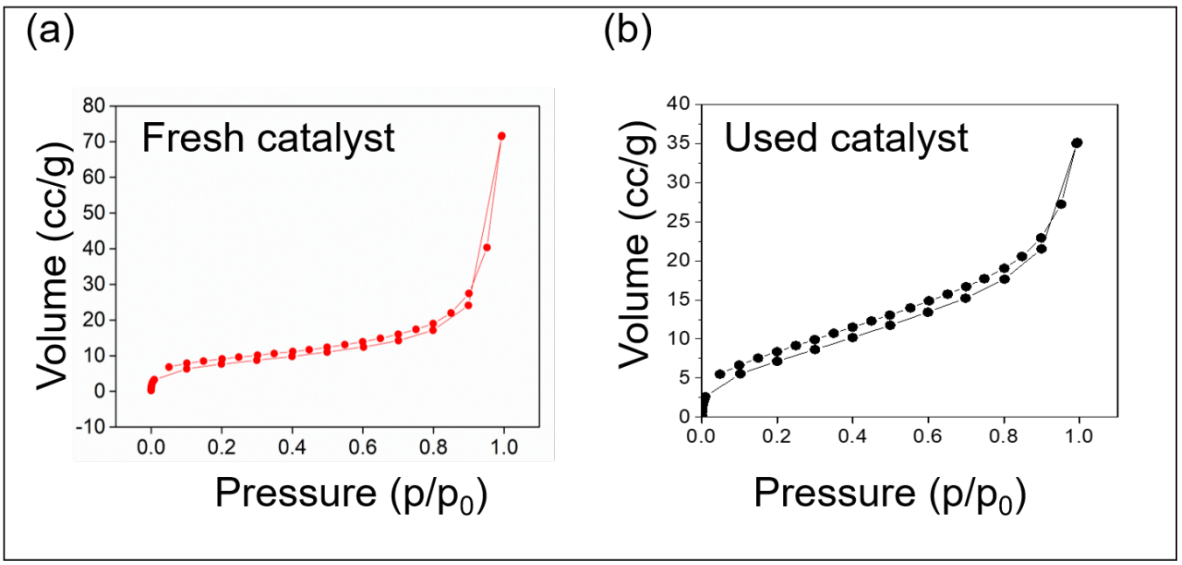


Figure S24. BET surface area analysis of fresh and used polymer TASD

Table S2. Surface area of fresh and used catalysts

Sample	Surface area (m^2/g)	Average pore radius (nm)
Fresh catalyst	27.118	8.17
Used catalyst	26.618	4.08

Thus, the overall study concludes that the slight decrease in activity of the catalyst after every cycle might be attributed to the tendency of deactivation of catalyst due to amorphization and pore collapse in a minor extent

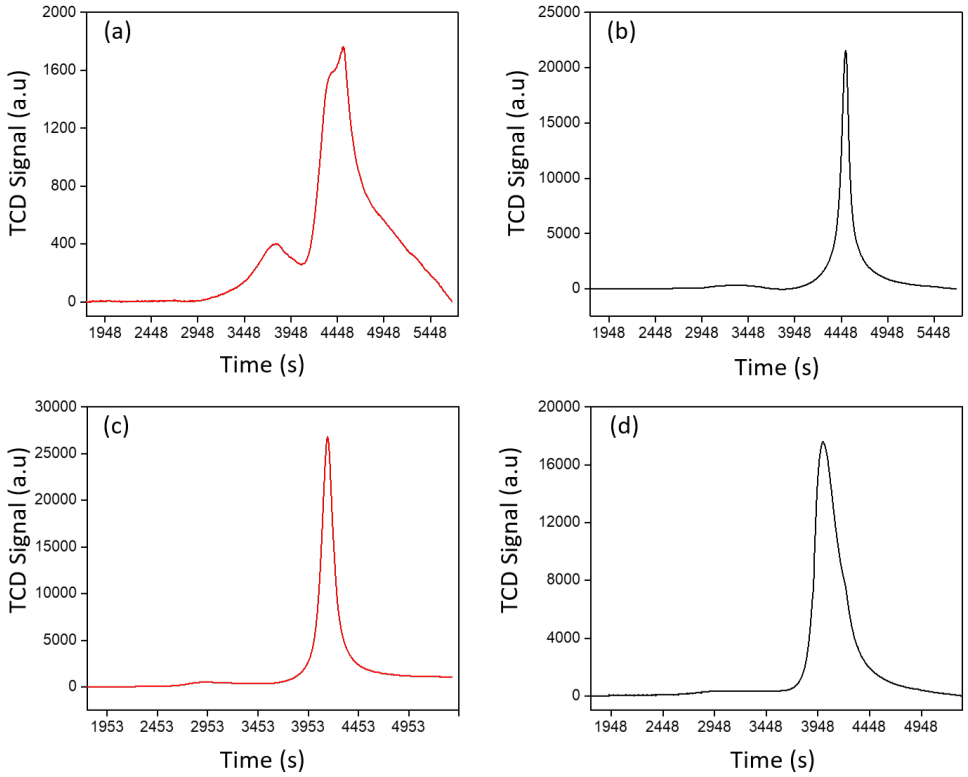


Figure S26. CO_2 TPD analysis for (a) TASD (b) IASD, NH_3 TPD analysis for (c) TASD (d) IASD.

Table S3. Comparison with other literature reports

Sl no.	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%)	Reference
1	DBU	H_2O	Reflux	7	92	1
2	TBAB	H_2O	120	45	91	2
3	$(NH_4)_2PO_4$/S-Proline	H_2O/EtOH	RT	120	81	3
4	[Sipim][HSO_4]	no	100	30	94	4
5	Nano ZnO	H_20	70	180	87	5
6	Fe_3O_4–proline MNPs	EtOH	RT	1440	92	6
7	Hexamethylenetetramine	EtOH	Reflux	15	92	7
8	[DMAP-PEG1_{000}-DIL][BF_4]	H_2O	100	30	92	8
9	TAP-POP	EtOH	RT	60	95	9

10	IASD	Acetonitrile	RT	360	92	This work (structure-activity study of 4 analogous POPs by tuning the surface acid-base properties)

References

1. Khurana, J.M., Nand, B. and Saluja, P., 2010. DBU: a highly efficient catalyst for one-pot synthesis of substituted 3, 4-dihydropyrano [3, 2-c] chromenes, dihydropyrano [4, 3-b] pyranes, 2-amino-4H-benzo [h] chromenes and 2-amino-4H benzo [g] chromenes in aqueous medium. *Tetrahedron*, *66*(30), 5637-5641.
2. Khurana, J.M. and Kumar, S., 2009. Tetrabutylammonium bromide (TBAB): a neutral and efficient catalyst for the synthesis of biscoumarin and 3, 4-dihydropyrano [c] chromene derivatives in water and solvent-free conditions. *Tetrahedron Letters*, *50*(28), 4125-4127.
3. Abdolmohammadi, S. and Balalaie, S., 2007. Novel and efficient catalysts for the one-pot synthesis of 3, 4-dihydropyrano [c] chromene derivatives in aqueous media. *Tetrahedron Letters*, *48*(18), 3299-3303.
4. Niknam, K. and Piran, A., 2013. Silica-Grafted Ionic Liquids as Recyclable Catalysts for the Synthesis of 3, 4-Dihydropyrano [c] chromenes and Pyra-no [2, 3-c] pyrazoles. *Green Sustain. Chem*, *3*(1.10), 4236.
5. Paul, S., Bhattacharyya, P. and Das, A.R., 2011. One-pot synthesis of dihydropyrano [2, 3-c] chromenes via a three component coupling of aromatic aldehydes, malononitrile, and 3-hydroxycoumarin catalyzed by nano-structured ZnO in water: a green protocol. *Tetrahedron Letters*, *52*(36), 4636-4641.
6. Azizi, K. and Heydari, A., 2014. A simple, green, one-pot synthesis of magnetic-nanoparticle-supported proline without any source of supplemental linkers and application as a highly efficient base catalyst. *RSC Advances*, *4*(13), 6508-6512.

7. Wang, H.J., Lu, J. and Zhang, Z.H., 2010. Highly efficient three-component, one-pot synthesis of dihydropyrano [3, 2-c] chromene derivatives. *Monatshefte für Chemie-Chemical Monthly*, *141*(10), 1107-1112.
8. Hosseinian, A., Soleimani, O. and Yarahmadi, H., 2024. Tris (2-hydroxyethyl) ammonium lactate an effective and biodegradable catalyst for the preparation of 3, 4-dihydropyrano [c] chromene derivatives. *Journal of the Iranian Chemical Society*, *21*(4), 1069-1077.
9. Shunmughanathan, M., Madankumar, N. and Pitchumani, K., 2018. Triaminopyrimidine Based Porous Organic Polymers: Synthesis, Characterization and Catalytic Applications in One-pot Room Temperature Synthesis of Dihydropyranopyranes. *ChemistrySelect*, *3*(48), 13743-13750.