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Structure engineering of covalent organic frameworks as metal-free sorbents for urea recovery

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The ubiquitous presence of urea, a nitrogenous compound with diverse biological and industrial applications, poses significant environmental challenges alongside its utility. Efforts to mitigate urea's impact on ecosystems while harnessing its usefulness have motivated research into developing efficient sorbents for urea recovery from wastewater. In this study, we explore the potential of covalent organic frameworks (COFs) as promising urea adsorbents. Molecular dynamics (MD) simulations revealed strong multidentate binding between the COF and urea through hydrogen bonding, with a binding energy of $-89.90 \text{ kJ mol}^{-1}$. Moreover, through experimental investigation, we systematically examine the influence of COF surface area, functional groups, and pore size on urea adsorption efficiency. Leveraging the robust stability of the β -ketoenamine linkage, we demonstrate the recycling capability of COFs over four cycles without any loss in performance. Moreover, multivariate COFs exhibited an enhanced urea adsorption capacity of 16.58 mg g^{-1} . These findings not only advance urea-containing wastewater treatment but also hold promise for applications in diverse fields requiring urea removal.

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Introduction

Urea, an abundant nitrogenous compound ubiquitous in both biological systems and industrial processes, presents a dual nature: it serves as a valuable resource but also poses significant environmental challenges.¹ Arising as a metabolic by-product in mammals and a cornerstone in agricultural fertilizers and manufacturing, urea's versatility underscores its indispensability. However, its widespread presence in the environment raises concerns regarding pollution and ecosystem health.¹ Notably, urea contributes to eutrophication through fertilizer leaching, exacerbating surface water contamination and compromising aquatic ecosystems. As such, the need to address urea's environmental impact must be balanced with the need to harness its utility, necessitating a delicate approach. The development of efficient sorbents for urea recovery from wastewater represents a "one stone, two birds" strategy,

symbolizing a holistic endeavor toward sustainable resource management and environmental preservation.² Central to this endeavor is the intricate interplay between the surface functional groups of sorbent materials and urea molecules, facilitating their interaction. These interactions encompass a spectrum of mechanisms, including dipole-dipole interactions, hydrogen bonding, and short-range repulsive forces.¹ Numerous research efforts have been directed towards the advancement of materials tailored for urea adsorption,² spanning a diverse array of candidates such as MXene,^{3–5} activated carbon,^{6,7} metal-organic frameworks (MOFs),⁸ macromolecular,⁹ and transition-metal dichalcogenides (TMDs).¹⁰ Despite notable achievements, existing sorbents typically exhibit single functional groups, limiting their selectivity and confining them to non-specific adsorption within complex wastewater matrices.¹ This deficiency underscores the necessity for further refinement, entailing extensive synthetic modifications and purification processes. Moreover, the presence of metal elements in sorbent materials, such as TMDs, MOFs and MXene,^{4,8,10} introduces additional considerations regarding potential metal contamination in water treatment processes. Therefore, the development of efficient, metal-free urea adsorbents with easily tunable structures and properties holds significant importance.

Covalent organic frameworks (COFs) represent a novel class of two-dimensional crystalline porous polymers^{11–14} that have demonstrated numerous applications, including energy storage,^{15,16} catalysis,^{17–26} environmental remediation^{27–33} and

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others.^{34–37} Their porous structure and abundant nanochannels provide a large surface area for molecules to access, facilitating efficient adsorption processes.^{29,38} Furthermore, the extensive library of organic building blocks offers a high degree of chemical tunability for COFs,³⁹ simplifying the typically complex surface functionalization encountered in traditional carbon or inorganic sorbents.² In addition, COFs are built with strong covalent bonds⁴⁰ *via* metal-free building blocks,^{41,42} providing enhanced structural stability and circumventing concerns of heavy metal contamination from sorbents during water treatment processes.²⁹ Therefore, considering these advantages, it is hypothesized that with appropriate structure and functional group design, COFs could emerge as a promising class of urea adsorbents.

Despite theoretical simulations predicting that COFs exhibit superior urea-adsorption performance^{43,44}—principally attributable to nitrogen sites or $-OH$ functional groups capable of forming hydrogen bonds with urea,⁴⁴ no experimental validation has yet been reported. In this study, we address this gap by presenting the first experimental evidence of a series of structurally engineered β -ketoenamine-based COFs for efficient urea adsorption. The influence of crystallinity and surface area on urea adsorption was systematically investigated by constructing COFs with the same chemical structure but varying surface areas and crystallinity. Additionally, various binding groups, including cyanide (CN), carboxylic acid (COOH), hydroxyl (OH), and sulfonic acid (SO_3H) groups, were integrated into the COF skeleton to assess the effect of functional groups on urea adsorption efficiency. Furthermore, the impact of pore size on urea uptake was explored using COFs with pore sizes ranging from 1.83 nm to 2.6 nm. Moreover, harnessing the robust

stability of the β -ketoenamine linkage, the recycling capability of COFs was also assessed over four cycles without any deterioration in performances. The adsorbed urea could also be effortlessly desorbed. Finally, multivariate COFs were successfully synthesized *via* a mixed-linker strategy to increase the available adsorption sites while maintaining a relatively high surface area, resulting in an enhanced urea adsorption capacity of 16.58 mg g^{-1} . We believe that our findings not only contribute to advancements in urea-containing wastewater treatment but also hold promise in other areas requiring urea removal, such as the development of wearable artificial kidneys.³

Results and discussion

We first designed and synthesized a β -ketoenamine type COF, 1,3,5-triformylphloroglucinol (Tp)-*p*-phenylenediamine (Pa), named Tp–Pa COF, and evaluated its efficacy in urea removal (Fig. 1a). The Tp–Pa COF was chosen due to its abundance of $C=O$ and $N-H$ groups, facilitating hydrogen bonding with NH_2 groups from urea molecules (Fig. 1a). Moreover, COFs with the β -ketoenamine linkage were selected for their enhanced stability⁴⁵ compared to imine and boron ester-based COFs. We further investigated the urea binding configuration, binding energy, and hydrogen bonding energy on Tp–Pa COFs using ReaxFF molecular dynamics (MD) simulations.⁴⁶ It should be noted that ReaxFF simulations are not limited to modeling chemical reactions; they also explicitly include non-bonded interactions such as van der Waals forces and hydrogen bonding.⁴⁷ Fig. 1b shows the initial loading of one urea molecule into a Tp–Pa COF unit cell. The simulations revealed that

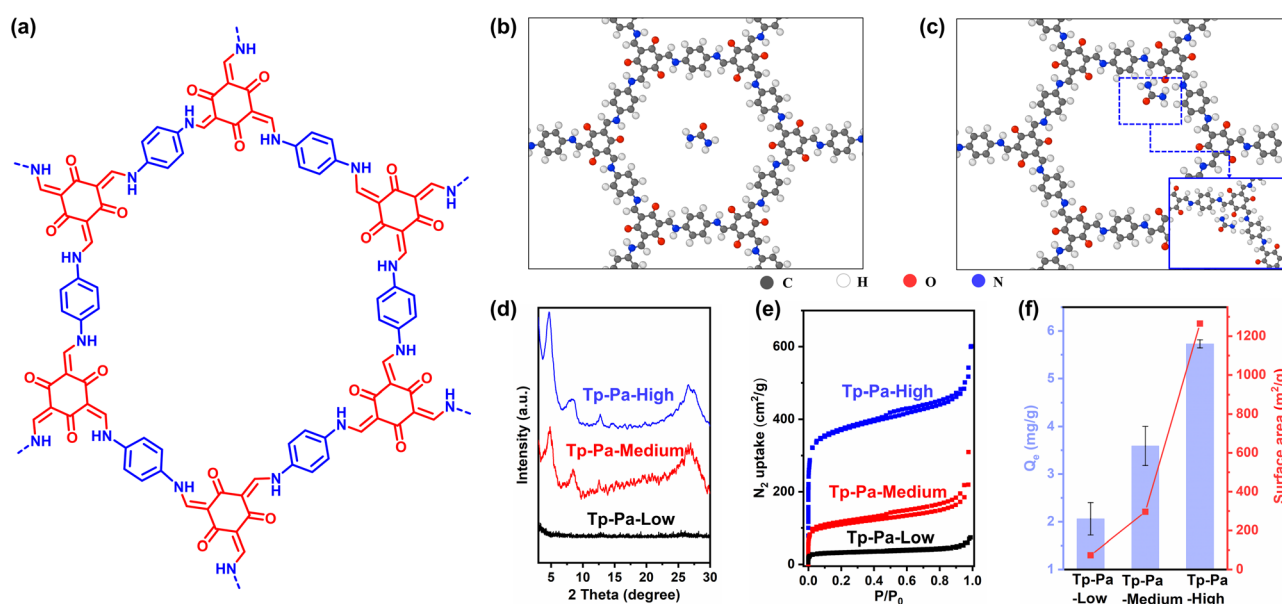


Fig. 1 (a) Chemical structure of the Tp–Pa COF. (b) Initial configuration of one urea molecule in a COF unit cell. (c) Final optimized configuration of the urea molecule in a COF unit cell. The red, black, grey, and blue balls represent oxygen, carbon, hydrogen, and nitrogen atoms, respectively. The inset box displays a zoomed-in image highlighting the urea binding on the COF. The pink circles indicate the binding sites between the COF and urea. (d) PXRD of Tp–Pa-high, -medium and -low. (e) Nitrogen adsorption isotherms of Tp–Pa-high, -medium and -low. (f) Q_e (blue axis) and surface area (red axis) of Tp–Pa-high, -medium and -low.

the most optimized configuration involves two NH_2 groups on urea forming multidentate interactions with the $\text{C}=\text{O}$ and $\text{N}-\text{H}$ functional groups on the Tp-Pa COF (Fig. 1c). The binding energy (E_b) of $-89.90 \text{ kJ mol}^{-1}$ and the hydrogen bonding energy (E_{hb}) of $-54.51 \text{ kJ mol}^{-1}$ for urea were determined through MD simulations (Fig. S1) and calculations, using eqn (S1) and (S2). The binding energy is comparable to or exceeds previously reported urea adsorbents, such as MXene ($77.19 \text{ kJ mol}^{-1}$ to $-89.79 \text{ kJ mol}^{-1}$),³ molybdenum disulfide (around -60 kJ mol^{-1}),⁴⁸ and silicon (around -50 kJ mol^{-1}),⁴⁸ highlighting the potential of the COF for effective urea adsorption. Based on the ReaxFF MD simulation results and structural considerations, the plausible mechanism for urea adsorption on Tp-Pa COF involves a synergistic effect of multidentate hydrogen bonding and size-selective pore confinement. The Tp-Pa framework contains abundant $\text{C}=\text{O}$ and $\text{N}-\text{H}$ functional groups that strongly interact with urea's NH_2 groups through hydrogen bonding, as supported by the calculated binding energy ($-89.90 \text{ kJ mol}^{-1}$). Furthermore, the COF's pore size ($\sim 1.5 \text{ nm}$) is well suited for accommodating urea molecules ($\sim 0.3 \times 0.497 \times 0.534 \text{ nm}$), allowing efficient diffusion and maximizing contact with the internal surfaces. These features together contribute to the high affinity and effective adsorption performance of the Tp-Pa COF toward urea.

Impact of surface area and crystallinity on urea adsorption

We first examined the impact of surface area and crystallinity of COFs on the urea adsorption performance. Three Tp-Pa COFs with varying surface areas and degrees of crystallinity were synthesized by controlling the reaction time and activation solvents (see SI for details).^{49,50} These were labeled as Tp-Pa-high, Tp-Pa-medium, and Tp-Pa-low, respectively. It is noteworthy that the surface area typically exhibits a positive correlation with crystallinity in COFs, as higher crystalline COFs tend to possess a more ordered porous network and fewer structural defects.^{49,51,52}

Three Tp-Pa COFs with distinct surface areas and crystallinity were comprehensively characterized using Powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), and nitrogen sorption measurements. The PXRD spectrum of Tp-Pa-high (Fig. 1d) revealed prominent peaks at approximately 4.62° , 8.21° and 26.7° , corresponding to the (100), (210), and (001) facets, respectively, which aligns well with previous reports.⁵³ Conversely, the PXRD pattern of Tp-Pa-medium (Fig. 1d) displayed broader peaks at the same position with weaker intensity, indicative of smaller crystal domains and reduced crystallinity.⁵¹ PXRD profiles of Tp-Pa-low exhibited no discernible peaks (Fig. 1d), suggesting the presence of disordered Tp-Pa sheets in Tp-Pa-low. Moreover, FTIR spectra of all three COFs (Fig. S2) exhibited strong stretching bands at $\sim 1572 \text{ cm}^{-1}$ that correspond to the $\text{C}=\text{C}$ bonds, indicating the presence of the keto tautomer.^{53,54} Notably, no significant differences were observed among the FTIR spectra, suggesting similar chemical structures for all three Tp-Pa COFs. Nitrogen sorption measurements (Fig. 1e) revealed the Brunauer–Emmett–Teller (BET) surface areas of Tp-Pa-high, Tp-Pa-

medium, and Tp-Pa-low to be 1265.18, 296.75, and $73.50 \text{ m}^2 \text{ g}^{-1}$, respectively, aligning with the observed trend of decreasing crystallinity (Fig. 1d). Additionally, nitrogen sorption isotherms of Tp-Pa High demonstrated a sharp nitrogen adsorption increase at low relative pressures ($P/P_0 < 0.01$), indicating a well-defined microporous structure. In contrast, the other two samples did not exhibit this feature, suggesting a disorganized pore structure.⁵¹ This observation is consistent with pore size distributions derived from nitrogen sorption measurements using quenched solid density functional theory (Fig. S3). In addition, Tp-Pa-high showed a narrow and uniform pore size distribution centered at 1.5 nm . In contrast, the other two samples displayed broad pore size distributions (Fig. S3), indicating the presence of disordered structures in these samples.⁵⁰

The urea adsorption performance of Tp-Pa COFs with varying surface areas was further investigated. An initial urea concentration of 40 ppm was utilized, and after 20 hours of adsorption to reach equilibrium, the remaining urea concentration was quantitatively analyzed using the colorimetric method⁵⁵ (refer to Fig. S4 for calibration curves). As depicted in Fig. 1f, Q_e exhibits a positive correlation with surface area, increasing from 2.3 mg g^{-1} to 5.67 mg g^{-1} as the surface area of the Tp-Pa COF increases.

Impact of pore functional groups on urea adsorption

To investigate the impact of various functional groups, we designed and synthesized a series of β -ketoenamine-based COFs with additional functional groups including cyano (CN), hydroxyl (OH), carboxylic acid (COOH), and sulfonic acid (SO_3H) groups (Fig. 2a) decorated on Pa or benzidine (BD) monomers. These COFs were denoted as Tp-BD-CN, Tp-BD-OH, Tp-Pa-COOH, and Tp-Pa- SO_3H . These functional groups were selected instead of amide and amine moieties due to their straightforward synthesis, which requires no elaborate post-synthetic modifications⁵⁶ and preserves the β -ketoenamine linkage. FTIR analysis (Fig. S5–S8) of the four COFs aligned well with previous reports,^{53,57–59} confirming the successful synthesis of these β -ketoenamine-type COFs with different functional groups. However, the integration of functional groups into β -ketoenamine-based COFs resulted in decreased crystallinity, as evidenced by the broadening and weakening of peaks observed in PXRD (Fig. 2b), likely due to the presence of acidic and easily oxidized functional groups, as previously reported.⁶⁰ The BET surface areas of Tp-BD-OH, Tp-Pa-COOH, and Tp-Pa- SO_3H were measured as $87.57 \text{ m}^2 \text{ g}^{-1}$, $105.92 \text{ m}^2 \text{ g}^{-1}$, and $86.15 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. S9–S11). Meanwhile, the Tp-BD-CN COF showed a relatively high surface area of $533.6 \text{ m}^2 \text{ g}^{-1}$ (Fig. S12).

The urea adsorption performance of different pore-functionalized COFs was further evaluated using a urea solution with an initial concentration of 40 ppm . As illustrated in Fig. 2c, Tp-BD-OH and Tp-Pa-COOH, which can form hydrogen bonds with urea, exhibited relatively high performance with Q_e values of 5.58 mg g^{-1} and 4.98 mg g^{-1} , respectively. Tp-Pa- SO_3H also demonstrated an enhanced Q_e of 4.34 mg g^{-1} compared to 3.59 mg g^{-1} for Tp-Pa-medium. Conversely, the CN group, which possesses large polarizability

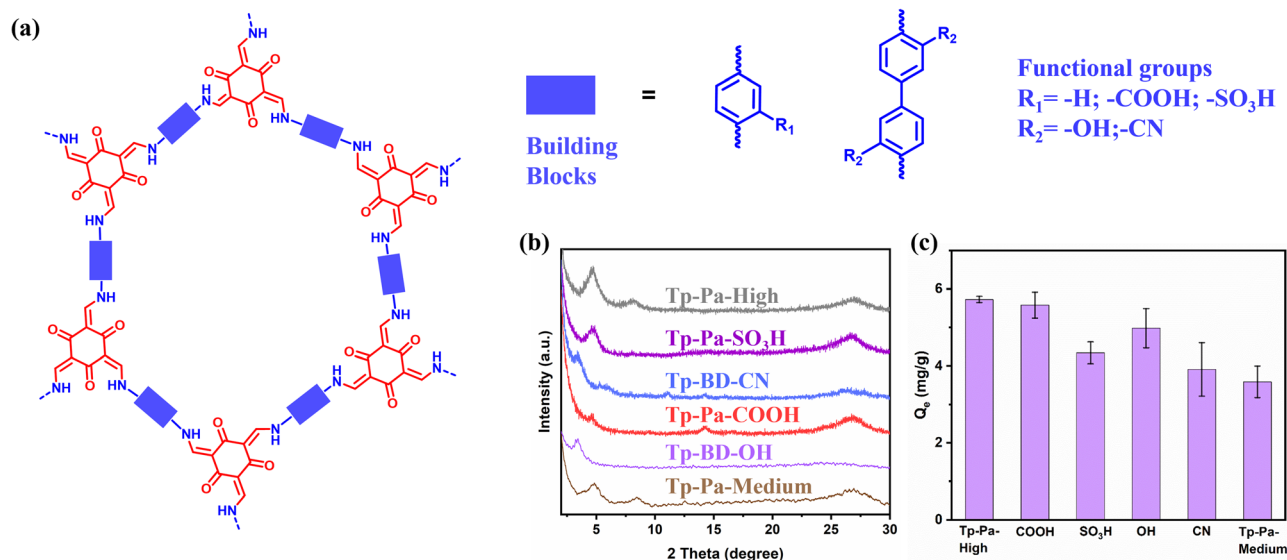


Fig. 2 (a) Structures of COFs with different functional groups used in this study. (b) PXRD of COFs with different functional groups used in this study. (c) Urea adsorption performance of COFs with different functional groups.

enabling dipole–dipole interactions,^{57,61} showed a less efficient enhancement of 3.91 mg g^{-1} compared to COOH and OH group-decorated COFs, suggesting that hydrogen bonding may play a more significant role in urea adsorption than dipole–dipole interactions. Additionally, the more hydrophilic nature of COOH and OH groups compared to CN groups aids in the diffusion of urea molecules into the COF pores.

Next, we designed and synthesized the imine counterpart of Tp–Pa by replacing the Tp monomer with benzene-1,3,5-

tricarbaldehyde (BTCA) to construct imine COF, referred to as BTCA–Pa (Fig. S13). BTCA–Pa shares a similar pore size and crystal topology with Tp–Pa but features imine linkages and lacks the abundant C=O and N–H groups in Tp–Pa.⁶² PXRD analysis of BTCA–Pa (Fig. S14) revealed sharp and prominent peaks located at 4.7° , indicative of its good crystallinity.⁶² FTIR spectra (Fig. S15) further confirmed the presence of C=N stretching bands around 1621 cm^{-2} .^{62,63} Despite its good crystallinity and chemical structure integrity, BTCA–Pa exhibited

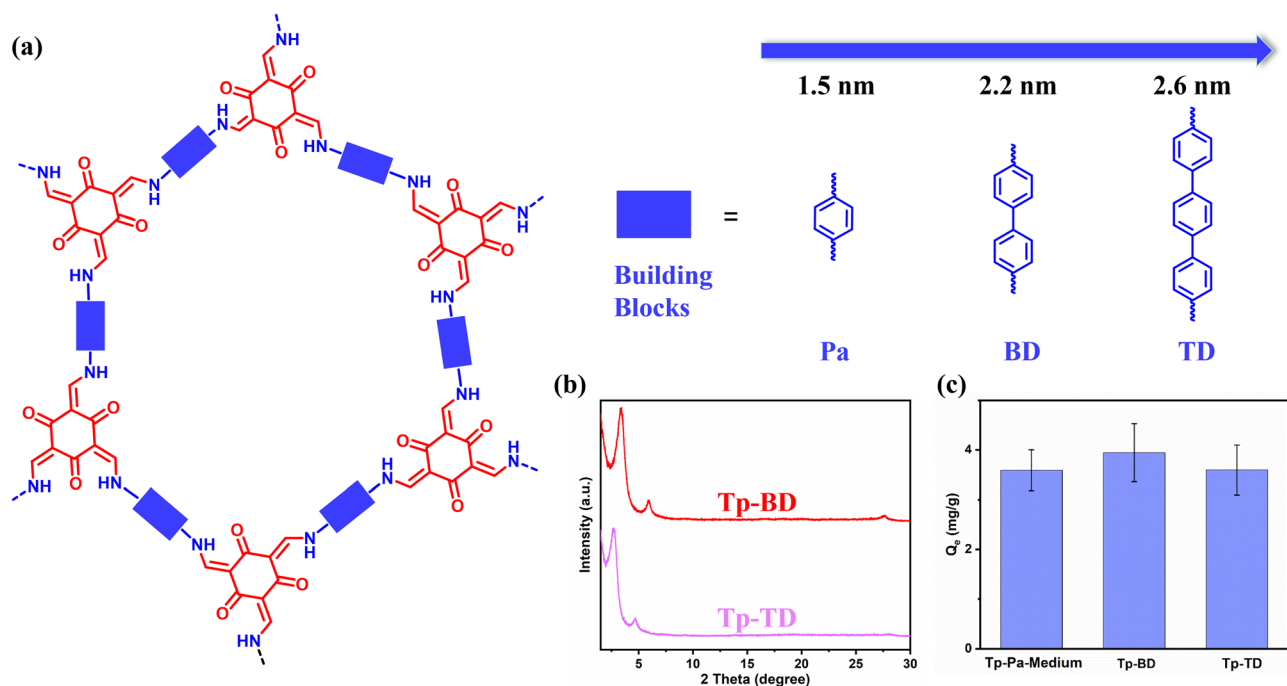


Fig. 3 (a) Structures of COFs with different pore sizes used in this study. (b) PXRD of Tp–BD and Tp–TD COFs. (c) Urea adsorption performance of COFs with different pore sizes.

relatively low urea adsorption efficiency with a Q_e value of 1.69 mg g^{-1} compared to Tp-Pa and functional group-modified Tp-Pa (Fig. S16). These results underscore the importance and necessity of abundant O- and N-containing groups in β -ketoenamine-based COFs for effective urea adsorption.

Pore size effect on urea adsorption

We conducted further investigations on the pore size effects of COFs on urea adsorption. Three distinct COFs, namely Tp-Pa-medium, Tp-BD, and Tp-TD (4,4''-diamino-*p*-terphenyl), characterized by pore sizes of 1.5 nm, 2.2 nm, and 2.6 nm, respectively, were synthesized (Fig. 3).⁶⁴ The FTIR spectra confirm the presence of the C=C bond in Tp-BD (Fig. S17) and Tp-TD COFs (Fig. S18). The PXRD patterns of the COFs exhibited sharp and prominent (100) peaks located at 2.7° , 3.4° , and 4.7° for Tp-Pa-medium, Tp-BD, and Tp-TD, respectively, with narrow half-widths at maximum of 1.7° , 1.1° , and 1.2° , indicating their high crystallinity (Fig. 1d and 3b).⁵¹ The surface area of Tp-BD

(Fig. S19) and Tp-TD (Fig. S20) was determined to be $474.9 \text{ m}^2 \text{ g}^{-1}$ and $551.6 \text{ m}^2 \text{ g}^{-1}$, respectively. Tp-Pa-medium, with a surface area ($296.75 \text{ m}^2 \text{ g}^{-1}$) comparable to that of Tp-BD and Tp-TD, was selected to ensure a fair comparison of pore size effects on urea adsorption. Subsequently, the urea adsorption performance of these COFs was assessed using a urea solution with an initial concentration of 40 ppm. The Q_e of Tp-BD and Tp-TD was determined to be 3.94 mg g^{-1} to 3.60 mg g^{-1} , respectively (Fig. 3c). These values are comparable to that of Tp-Pa-medium, which has an adsorption capacity of 3.59 mg g^{-1} . This suggests that pore size in the range we investigated may not significantly influence adsorption performance compared to other factors such as surface area, crystallinity, and functional groups. It is worth noting that this observation contrasts with previous reports on COF adsorption of larger molecules such as triphenyl phosphate and Congo red ($>1.5 \text{ nm}$), where larger pore sizes improved accessibility and uptake.^{27,65} We attribute this difference to the smaller dimensions of urea (0.3

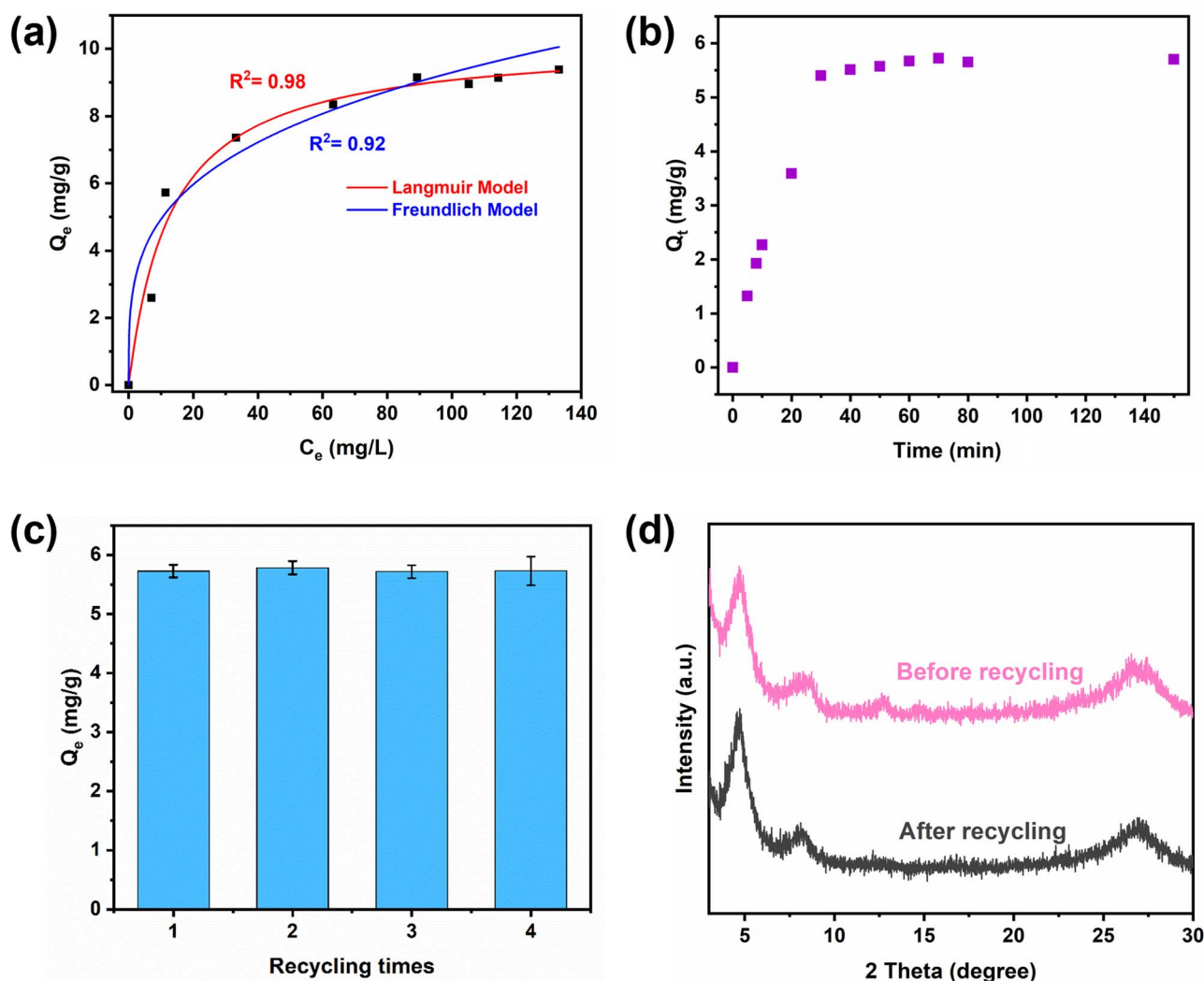


Fig. 4 (a) Urea adsorption isotherms using the Tp-Pa-high COF. The experimental adsorption data (filled black squares) were fitted to the Langmuir model (red curves) and Freundlich model (blue curves). (b) Urea adsorption kinetics using the Tp-Pa-high COF with a urea concentration of 40 ppm. Q_t stands for urea adsorption at different time intervals. (c) Urea adsorption performance after different recycling times. (d) PXRD of the Tp-Pa-high COF before and after recycling.

$\times 0.497 \times 0.534$ nm) compared to the COF pore size range explored in this study (1.5–2.6 nm), indicating that size-exclusion effects are negligible.

Adsorption isotherms and kinetics

Adsorption isotherms and kinetics were explored using the Tp–Pa–high COF as the benchmark material. For the determination of adsorption isotherms, the equilibrium urea adsorption capacity was measured across the initial urea concentration ranging from 0 to 180 ppm (Fig. 4a). The isotherm curve was then fitted to both the Langmuir and Freundlich models (Fig. 4a). The Langmuir model exhibited better fitting ($R^2 = 0.98$) compared to the Freundlich model ($R^2 = 0.92$), with a maximum adsorption capacity of 10.25 mg g^{-1} , which aligns with the experimental value of approximately 9.4 mg g^{-1} . The successful fitting to the Langmuir model suggests a homogeneous adsorption process,⁵ characterized by a urea monolayer adhering to the COFs. Furthermore, a detailed examination of the adsorption kinetics of Tp–Pa–high was conducted using an initial urea concentration of 40 ppm. The adsorption capacity at different time intervals (Q_t) displayed rapid enhancement within the initial 30 minutes, followed by attaining equilibrium with slight variations observed over extended durations (Fig. 4b). The adsorption kinetics fits better with the pseudo-second-order model (Fig. S21) over the pseudo-first-order model (Fig. S22).

Recycling and recovery ability

The recycling and urea recovery capability of COFs was further investigated, with Tp–Pa–high serving as the model COF.

Leveraging the robust stability of the β -ketoenamine linkage, minimal change in adsorption capacity was observed even after four cycles (Fig. 4c), consistently achieving Q_e values around $5.6\text{--}5.7 \text{ mg g}^{-1}$. Additionally, the PXRD pattern (Fig. 4d) and FTIR spectra (Fig. S23) of the recycled COFs closely resembled those of the pristine COFs. Next, tetrahydrofuran/ethanol (volume ratio = 1 : 1) was utilized to extract the urea from Tp–Pa–high, resulting in an impressive urea recovery amount of $5.16 \pm 1.03 \text{ mg g}^{-1}$ and a recovery ratio of approximately $91.1 \pm 18.2\%$. These findings underscore the promising potential of COFs as emerging adsorbents for efficient urea removal and recovery for fertilizer applications.

Mixed-linker COFs for urea adsorption

Although integrating active adsorption sites can enhance the availability of active sites, the reduction in surface area and crystallinity may compromise urea diffusion and the exposure of active sites.⁵⁸ To tackle this challenge, we implemented a mixed-linker strategy to synthesize multivariate COFs, aiming to maintain a high surface area while enhancing the grafting density of adsorption sites.^{58,66} This involved the synthesis of multivariate COFs using a three-component system comprising Tp, Pa, and Pa–COOH (Fig. 5a), with a chosen ratio of Pa : Pa–COOH of 4 : 1. This ratio was shown to preserve the COFs' surface area⁵⁸ while incorporating a reasonable amount of functional groups. The resulting COFs, denoted as Tp–Pa : Pa–COOH, were thoroughly characterized to assess their structural and functional properties. PXRD analysis of Tp–Pa : Pa–COOH (Fig. 5b) revealed distinct peaks at 4.66° , 8.15° , and 26.5° , indicative of well-defined crystallinity. Moreover, BET surface area measurements (Fig. 5c) demonstrated the retention of

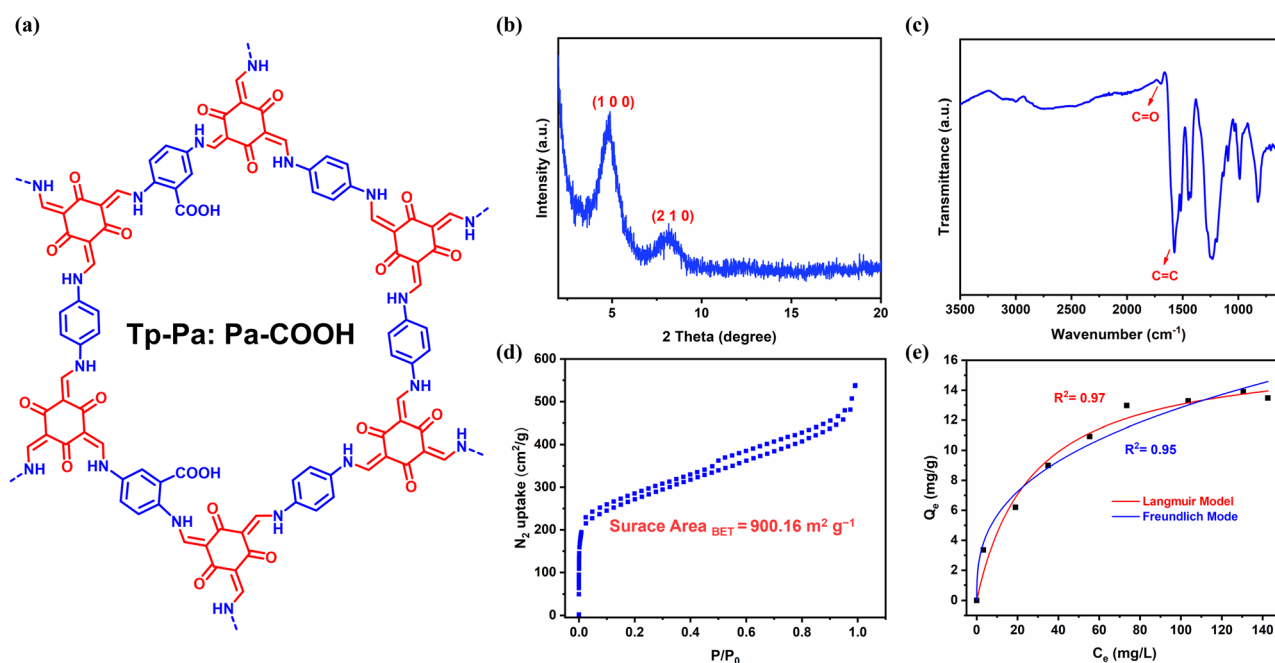


Fig. 5 (a) Scheme of Tp–Pa : Pa–COOH. Pa : Pa–COOH = 8 : 2. (b) PXRD of Tp–Pa : Pa–COOH. (c) FTIR of Tp–Pa : Pa–COOH. (d) Nitrogen adsorption isotherms of Tp–Pa : Pa–COOH. (e) Urea adsorption isotherms using the Tp–Pa : Pa–COOH COF. The experimental adsorption data (filled black squares) were fitted to the Langmuir model (red curves) and Freundlich model (blue curves).

a relatively high surface area of $900.16 \text{ m}^2 \text{ g}^{-1}$, affirming the efficacy of our mixed-linker approach. FTIR spectra (Fig. 5d) corroborated the presence of key functional groups, including C=C stretching at around 1570 cm^{-1} and C=O stretching at around 1692 cm^{-1} originating from the COOH groups, further confirming the successful synthesis. The adsorption isotherm of Tp-Pa:Pa-COOH closely adhered to the Langmuir model (Fig. 5e), suggesting that the incorporation of extra COOH sites did not significantly alter the adsorption mechanism. Notably, the calculated Q_{max} value of 16.58 mg g^{-1} represented a more than 30% enhancement compared to Tp-Pa-high, indicating a substantial improvement in urea adsorption capacity. Furthermore, our approach offers an additional advantage over traditional carbon-based materials by enabling the incorporation of various functional groups into a single material. This versatility enhances the potential of COF adsorbents for selective targeting of specific molecules.

Justification of using COFs as adsorbents for urea recovery

Finally, it is crucial to justify the significance and broad interest of COFs as adsorbents for urea recovery. First, the metal-free nature of COFs presents a notable advantage. In contrast to porous materials incorporating metal components, such as MXenes and MOFs, the use of COFs mitigates potential concerns regarding metal ion leaching into aqueous systems, which could lead to contamination. Moreover, active metal centers present in MOFs and MXenes might catalyze the decomposition of urea, thereby diminishing its recovery efficiency. For example, the Brønsted or Lewis acid sites in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can catalyze the hydrolysis of urea, leading to the formation of ammonium and carbon dioxide.⁶⁷

COFs also exhibit unique advantages over other metal-free materials, such as activated carbon, including their diverse, designable, and tunable functional groups.⁶⁸ These characteristics provide significant potential for the design of COFs that can selectively adsorb urea from complex aqueous environments with varying pH levels and a broad spectrum of competing organic molecules.⁶⁸ Furthermore, it is worthwhile to mention that the adsorption capacities of existing carbon-based materials show considerable variation, even among similar types.^{6,7,69–72} For instance, the reported maximum adsorption capacity (Q_{m}) for activated carbon ranges from 1.2 mg g^{-1} to 877.9 mg g^{-1} , with equilibrium urea concentrations (C_{e}) spanning from 200 ppm to 60 000 ppm (Table S1).^{69–72} This wide range likely results from differences in experimental conditions, fitting models, and other methodological factors, making direct comparisons of adsorbent efficiencies across different studies challenging.⁶⁹ To address this, we conducted urea adsorption experiments under standardized conditions using several commercially available adsorbents, including activated charcoal (AC), hydroxyl-modified carbon nanotubes (CNT-OH), chitosan, and cellulose. These materials demonstrated Q_{e} values of 0.312 mg g^{-1} for AC, 0.129 mg g^{-1} for CNT-OH, 0.05 mg g^{-1} for chitosan, and 0.22 mg g^{-1} for cellulose, which were significantly lower than that of Tp-Pa-high (5.67 mg g^{-1}) under comparable conditions (Table S2). This comparative

analysis underscores the potential of COFs as adsorbents for urea, particularly for effective extraction of urea at relatively low concentrations.

Conclusion

In summary, we successfully demonstrated β -ketamine-based COFs as efficient sorbents for urea removal and recovery. Through systematic studies, we elucidated the significant influence of surface area/crystallinity, functional groups, and pore size on urea adsorption efficiency. Notably, COFs with higher surface area and crystallinity exhibited enhanced adsorption, while functional groups capable of hydrogen bonding with urea demonstrated higher adsorption capacity compared to the functional groups with dipolar interaction. Moreover, β -ketamine-based COFs exhibited excellent recycling capability, maintaining efficiency over four consecutive cycles. Finally, employing a mixed-linker strategy, we synthesized multivariate COFs with an enhanced urea adsorption capacity of 16.58 mg g^{-1} . These findings not only advance urea-containing wastewater treatment but also hold promise for various applications requiring urea removal. Moving forward, we will evaluate COF urea adsorption in real wastewater matrices—such as urine, which contains high concentrations of competing ions (*e.g.*, PO_4^{3-} , SO_4^{2-}) and organic metabolites (*e.g.*, creatinine, uric acid).

Author contributions

Y. Z. and Y. L. contributed equally to this work. Y. Z., Y. L., and J. L. designed and conceptualized the research; Y. Z., Y. L., X. W., W. T., and T. X. performed the materials synthesis and characterization; J. H. L. performed MD simulation; Y. Z., X. W., Y. M. L. and Y. F. performed the urea adsorption experiments. All authors analyzed the data and discussed the results; Y. Z. and J. L. wrote and revised the paper. J. L. supervised the whole project.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data supporting the findings of this study are provided in the SI or are available from the corresponding author upon reasonable request.

Materials and methods, experimental details, and additional characterization data including PXRD, FTIR, nitrogen sorption tests. See DOI: <https://doi.org/10.1039/d5ta04077a>.

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