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Outer Surface Hydrophobic Shielding Strategy to Enhance the Chemical Stability of Metal-Organic Polyhedra

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Abstract: Metal-organic polyhedra (MOPs) are a promising class of crystalline porous materials with multifarious potential applications. Although MOPs and Metal-organic frameworks (MOFs) have similar potentials in terms of their intrinsic porosity and physicochemical properties, the exploitation of carboxylate MOPs is still rudimentary due to lack of systematic development addressing their chemical stability. Here we describe the fabrication of chemically robust carboxylate MOPs via outer surface functionalization as an a priori methodology which could be applied to stabilize of those MOPs system also where metal-ligand bond is not so strong. Fine-tuning of hydrophobic shielding transpire as a key facet to attain chemical inertness with retention of framework integrity under wide ranges of pH, strong acidic conditions, oxidizing and reducing media among these materials and these results are further corroborated by molecular modelling insights. Owing to the unprecedented transition from instability to chemically ultra-stable regime accompanied by ambient temperature gram-scale rapid synthesis (within seconds), a prototype strategy towards engineered construction of chemically stable MOPs is reported.

Over the last few decades, there has been an astonishing evolution of crystalline porous solid materials and have been centre of great attention to researchers across multiple disciplines.^[1,2] Among the various crystalline porous solids, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs) have emerged as a distinguished research area and on account of high surface area these materials have been explored for several applications such as selective gas storage and separation ability, sensing, catalysis, energy storage and conversion capacity etc.^[3-8] Carboxylate metal-organic polyhedra (MOPs) form a subclass of crystalline porous materials which were proposed almost at the same time as MOFs.^[9,10] Over the last few years realization of rational design strategies has yielded several hydrolytically stable MOFs and COFs [11-16] and actuated their development towards practical implementation, but lack of systematic approaches to prepare stable MOPs has severely hindered the progress of carboxylate MOPs for

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application studies relative to MOFs/COFs. Broadly, there are few strategies proposed for synthesis of porous MOPs^[17-20] but majority of carboxylate MOPs reported in the literature have been found to be hydrolytically unstable. The solid state applications of such MOPs are largely impeded owing to their instability and loss of crystallinity as an outcome of unavoidable aggregation-driven blockage of active sites on guest removal.^[21,22] Although some discrete reports have been proposed to improve stability of MOPs by enhancing the metalligand bond strength [23-25] or appending long alkyl chains [26] there has been scarcity of a broad design approach to attain chemically inert carboxylate MOPs. In principle, MOPs offer similar potential applications as MOFs including additional advantages of solution processability ^[27] for MOPs in common organic solvents which is highly sought for easy fabricating membranes, thin film devices, preparation of electrolytic solutions, various active additives in polymers, ion channel including various biochemical applications etc.^[28,29]

A generalized strategy for synthesizing chemically inert MOPs can contribute significantly to develop of structure-function relationship derived crystal engineering and boost up the growth of MOPs in view of their miscellaneous applications. Herein, we develop a prototypal synthesis strategy which allows us to prepare a series of hydrolytically stable carboxylate MOPs using grafting of hydrophobic exterior to basic building blocks and in principle this versatile approach can be applied to stabilize any MOP structures, irrespective of metal ions and nature of coordinating ligands used in the synthesis. Amino acids are chosen as building blocks as their functional groups could be smoothly modulated ^[30] where as electron-deficient anhydride decorated polar pore surfaces have often imparted excellent guest-responsive characteristic features of diimide linkers. While among transition metal ions, binuclear copper paddle wheel is well recognized for easily affording carboxylate MOPs, owing to its 4-connected secondary building units.^[31] Water stability being the key targeted criterion, deliberately enhanced steric crowding surrounding the metal coordination sites results into an ultrastable and first superhydrophobic MOP.^[32] More importantly, consequent of increased hydrophobicity, a distinct enhancement of chemical stability could be achieved by rationally tuning the alkyl functionality of the substituted diimide linkers, which was further upheld by molecular simulation studies. We hereby present the multi-gram scale quick synthesis (within seconds) of a chemically ultra-stable (wide ranges of pH, oxidizing and reducing media) MOP employing a systematic surface engineering aided hydrophobicity increment principle.

Constructed from naphthalene diimide (NDI) core based homologous amino acids (Scheme S1-S5, Figure S1-S8),^[33-37] the syntheses and single crystal structures of four Cu(II)-based MOPs (coined as IPMOP-n; n denotes the carboxylate amino acid variant) have been described herein (Figure 1). When amino acids are alanine (A), valine (V), isoleucine (IL) and phenyl alanine (PA), derived MOPs are IPMOP-A, IPMOP-V, IPMOP-IL and IPMOP-PA respectively.

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Figure 1. Schematic synthetic strategy for MOPs and their corresponding crystal structures following a systematic increment order of their chemical stabilities (as illustrated from bottom to top).

In the current report, we describe their gradual increment of chemical stability attributes to finally attain ultra-high stability under acidic/basic and different oxidizing and reducing conditions. Solvothermal syntheses of the MOPs (A, V, IL and PA) led to green crystals (cube and diamond shaped, depending on specific MOPs system; Scheme S6-S9). Optimization of reaction conditions guided us to obtain IPMOP at room temperature (multi-gram scale) within seconds (Figure S9 and S10), in presence of 2,6-lutidine as a base (Video S1). Crystal structure of IPMOP-A was determined by single-crystal X-ray diffraction studies while those for IPMOP-V, IPMOP-IL and IPMOP-PA were determined using synchrotron beamline radiation. Each MOP contains twelve ligand molecules and twelve water molecules to form neutral cages (Figure S11) of general formula: [Cu₁₂(L_x)₁₂(H₂O)₁₂] [L_x: corresponding ligands system L_A, L_V, L_{IL} and L_{PA}]. Each cage molecule contains twentyfour alkyl groups which exohedraly decorate the entire outer surface of the spherical cages (Figure S12-S31). All the cages have eight triangular windows with average aperture size of ~2 Å as well as average internal cavity diameter ~15 Å. Each bimetallic paddle-wheel Cu(II) unit is coordinated to two terminal water molecules: one pointed to the internal cavity of the polyhedron and another one, pointed outside the polyhedron surface.

Thermogravimetric analysis (TGA) shows loss of guest molecules until ~250 °C (Figure S32-S37) for all the four compounds. The slow loss of guest molecules can be ascribed to the presence of polar sites in the host cage having limited aperture size, which interact strongly with guest solvent molecules. Most of the guest solvent molecules could be

removed by conventional activation protocol (heating under vacuum). CO2 gas adsorption isotherms were recorded for the MOPs at 195 K,^[38] (Figure S38 and S39) which reflected similar saturation capacities for IPMOP-V (4.6 mmol), IPMOP-IL (4.3 mmol) and IPMOP-PA (4.5 mmol). This was an outcome of their isoreticular nature.^[39] Substantially lower saturation capacity for IPMOP-A (1.3 mmol) can be attributed to the solvent loss induced aggregation of individual cages, as often observed for MOPs.^[38] Ambient temperature CO₂ sorption profiles also exhibited similar CO₂ saturation capacities for IPMOP-V, IPMOP-IL and IPMOP-PA (Figure S40-S43). Although PXRD patterns of IPMOP-V indicates weak crystallinity (Figure S44), similar saturation capacity for all three compounds (IPMOP-PA, IPMOP-IL and IPMOP-V) suggests gas sorption occurs inside the intrinsic cavity of the cage molecules rather than the extrinsic intercage porosity. Due to flexible nature of the pore window, gas sorption happens inside the cage cavity even though aperture size of MOPs is smaller than the kinetic diameter of CO₂.

Chemical stability aspect is examined by treating the crystals of IPMOP-PA in water, steam, solutions of widely varying pH, including harsh acidic solutions, buffer solutions, as well as subjecting to diverse oxidizing and reducing media (Figure 2, Figure S45 and S46).^[40] For assessment of water stability, IPMOP-PA was soaked in water for several months; unaltered PXRD patterns (Figure S47 and S48) point out the retention of both crystallinity and structural integrity in water. Intended for further checking water stability under more harsh conditions, the sample was placed under steam for 5 days; similar PXRD patterns afterwards indicate structural robustness of the

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Figure 2. Characterization of stability confirmation for IPMOP-PA. (a) PXRD patterns under different conditions: pH~1 (5 days), pH~11(5 days), 10N HCl (6 h), buffer solution [pH~9] (7 days), reducing media (FeSO₄ solution; 30 days), oxidizing media (fenton solution; 30 days). (b) post-treatment SC-XRD data, under different conditions.(c) Bar diagram representing the reproducibility of IPMOP-PA miscellaneous harsh treatments, navy blue: before treatment of crystal, and dark yellow: after crystal treatment. (d) CO₂ sorption isotherms recorded at 195 K after treating the adsorbent MOP under different harsh conditions: pH~1(5 days), pH~11(5 days), 10N HCl (6 h), buffer solution [pH~9] (7 days), reducing media (FeSO₄ solution; 30 days), oxidizing media (fenton solution; 30 days). (e) FE-SEM images after immersing IPMOP-PA crystals under different conditions: pH~1(5 days), pH~11(5 days), 10NHCl (6 h), buffer solution [pH~9] (7 days), reducing media (FeSO₄ solution; 30 days), 10NHCl (6 h), buffer solution [pH~9] (7 days), reducing media (FeSO₄ solution; 30 days), 0xidizing media (fenton solution; 90 days), endoxidizing media (fenton solution; 90 days), pH~11(5 days), 10NHCl (6 h), buffer solution [pH~9] (7 days), reducing media (FeSO₄ solution; 30 days), 0xidizing media (fenton solution; 90 days), reducing media (FeSO₄ solution; 30 days), 0xidizing media (feNO₄ solution; 90 days), 0

compound. Crystals of IPMOP-PA were kept immersed in a wide range of solutions with varying pH (pH~1 to pH~11) over 5 days, ensuing similar PXRD patterns (Figure S49 and S50) confirmed its exceptional stability over a wide pH-range. In addition to this, we studied TGA, gas sorption and FT-IR for different pH immersed (pH~1 and pH~11) crystals and their similar profiles demonstrate retention of the framework. Crystals of IPMOP-PA were also examined under various harsh acidic conditions, and found to exhibit super-stability (Figure S51-S53). For further introspection concerning framework stability, we dipped the crystals of IPMOP-PA in a number of oxidizing and reducing solutions over several weeks. Precise matching of all the main peaks in the experimental PXRD patterns (Figure S54-S55) implied that IPMOP-PA is exceptionally chemical stable. In addition to PXRD, we surveyed TGA, gas sorption, FT-IR, and FESEM data-sets. In all these measurements, uniform patterns reflected inertness of the framework (Figure S56-S60). Along with, inductively coupled plasma (ICP) analysis of supernatants from diversely treated chemical environments (pH=1 and 11, 10 N HCl and equivalent mixture of THF/water) were recorded. A negligible amount of copper leaching (Table S1) confirms the stability of IPMOP-PA in such chemical environments. For solution phase stability of cage molecules, we solubilized IPMOP-PA in THF media and treated with diverse chemical environment before performing UV-Vis measurement and ICP analysis. The UV-Vis spectra (Figure S61) indicates that

IPMOP-PA is also quite stable in such chemical environments under solution phase.

IPMOP-IL and IPMOP-V are also chemically stable (Figure S62-S78) but not to the extent of IPMOP-PA. IPMOP-A is neither water-stable (Figure S79 and S80), nor chemically stable. In IPMOP-A, among the twenty-four methyl groups only twelve outer methyl groups interact with oxygen centers of NDI moieties from their neighboring cages. These interactions are collectively insufficient to maintain the overall channel continuity in the guest-removed packed architecture. Besides, methyl group is sp³ hybridized, hence anticipated to assume weak interactions with NDI core. While in IPMOP-PA all benzyl groups interact with neighboring cages, sp² hybridized phenyl hydrogens strongly interact with NDI moieties from their neighboring cages leading to maintaining their long range order in bulk phase. Therefore, such electrostatic interactions seem more prominent in IPMOP-PA, relative to IPMOP-A which is further corroborated by molecular modelling results (Figure 3).

To present microscopic insights into the stability aspect of IPMOPs, binding energies among the cages (most stable and least stable compounds) were estimated. For each IPMOP, energies for a single unit cell (E_{uc}) and a single cage (E_{cage}) was separately calculated, followed by estimation of binding energy (ΔE) i.e. $\Delta E = (E_{uc} - nE_{cage})/n$, where *n* is the number of cages in a unit cell. For IPMOP-A and IPMOP-PA, the binding energies are -94.06, and -150.74 kcal mol⁻¹, respectively. This energy

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Figure 3. Structural insight and solution processability study of IPMOPs. (a) Contact areas between cages: (I) IPMOP-A; (II) IPMOP-PA. (b) 195 K CO₂ sorption isotherms for phase-I (as-synthesized), and phase-III (reprecipitation after dissolving in THF) of IPMOP-PA. Phase-II represents THF-dissolved solution phase for IPMOP-PA. (c) Water droplet cast on the surface of the pelletized IPMOPs: WCA values for (I) IPMOP-A: ~74°; (II) IPMOP-V: ~118°; (III) IPMOP-IL: ~130°; (IV) IPMOP-PA: ~155°.

increases in the order of IPMOP-A <IPMOP-PA, as attributed to the increasing size of alkyl functional group of the substituted diimide linkers. Figure 3a shows structures of the two IPMOPs, green circles highlight the contact areas between neighbouring cages. It is obvious that the contact area increases with increasing size of alkyl functional groups involved. In Figure 3a, the -CH₃ groups of IPMOP-A offer only a small contact area while in IPMOP-PA, the aromatic groups are interpenetrate between the neighbouring cages i.e. leading to maximal contact area. With increasing contact area, increasing binding energy leads to stronger interactions, corresponding to the maintenance of long range order in solid state, which is consistent with our experimental observations.

Unlike extended frameworks, solution-processability of MOPs offer multifarious advantages over other porous materials.^[41] Encouraged by our obtained results, solution-processability for IPMOP-PA was assessed and found to be solution-processable in tetrahydrofuran (THF); as confirmed by gas sorption measurement of Phase-I (as-synthesized) and Phase-III (reprecipitation after dissolving in THF) (Figure 3b and Figure S81-S86, Table S2). Among this IPMOP series, we observed that the solubility increases with increasing size of the alkyl functional groups upto a certain limit, beyond which the MOP solubility decreases with higher alkyl groups. Among IPMOPs, IPMOP-A is insoluble in common solvents, while rest are soluble in THF (Figure S87-S92 and Table S3), and thus solubility was found to increase from IPMOP-V to IPMOP-PA to IPMOP-IL. For hydrophobicity, the surface hydrophobicity was confirmed from water contact angle (WCA) measurements of all IPMOPs (Figure 3c) and found that WCA also tuned from hydrophilic (WCA~74°) to superhydrophobic region (WCA~154°) (Table S4) for the first time for MOPs system.

A potentially extensive class of ultra-stable material is afforded by employing hydrophobic shielding as a cornerstone design principle. This basic outline principle can be used to attain chemical stability of MOP compounds, where metal-ligand bond is weak in nature. The strategic decoration of diverse alkyl groups on the outer surface of the cages (stemming from the ligands) not only increased the hydrophobicity around the metal center, but also assisted in retaining the robust nature of the overall framework, affirmed from molecular simulations. We believe, the present findings for realization of chemically addressable MOPs will offer simple, straight forward strategic approaches for the development of diverse stable cage based frameworks for future applications.

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Schematic diagram for correlation between hydrophobicity and chemical stability of MOPs. Enhancement of chemical stability consequent of their increment in hydrophobicity although the internal core of each cage is similar. Outer green surface indicate the hydrophobicity shielding while inner core represent the same internal cage molecule.

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