Exploration of glassy state in Prussian blue analogues

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ABSTRACT: Prussian blue analogues (PBAs), a class of microporous crystalline coordination frameworks, are long known for their diverse properties in porosity, magnetic, charge transport, catalysis, optics, and more. Versatile structural composition and the ability to control defect ordering through synthetic conditions offer opportunities to manipulate the functionality in the crystalline state. However, developments in Prussian blue analogues (PBAs) have primarily revolved around the ordered crystalline state, and the glassy state of PBAs has not yet been explored. Here we report the discovery of a disordered glassy state of the PBA via mechanically induced crystal–glass transformation. We found the preservation of metal–ligand–metal connectivity, confirming the short-range order and semiconductor behaviour, exhibiting an electronic conductivity value of 0.31 mS cm^{−1} at 50 °C. Mechanical-induced glass transformation also triggers changes in electronic states, where electroneutrality is compensated by introducing unconventional CN[−] vacancies. Partial disorders and ligand vacancies in recrystallized PBA give rise to an enhanced porosity, inaccessible in the crystalline parent. The present work also established a correlation between the mechanical stress required to initiate crystal–glass transformation and intrinsic mechanical properties, which are controlled by the vacancy/defect content, the presence of interstitial water, and the overall composition of PBAs.

INTRODUCTION

Prussian blue analogues (PBAs) are the family of coordination polymers assembled from octahedrally coordinated cyanide bridging metal nodes (M and M') with a parent structure of $M[M'(CN)_6]$ ¹. Variation of metal choices and their oxidation state allows alteration of the vacancies content via the hexacyanometallates withdrawal to compensate for the electroneutrality². Prussian blue (PB, $Fe^{III}[Fe^{II}(CN)_6]_{3/4} \cdot nH_2O$) itself contains a quarter of the isolated vacancy site³. A higher vacancy fraction of one-third fraction can be found in $M^{II}[M^{III}(CN)_6]_{2/3} \cdot nH_2O$, where neighbouring pairs are connected, creating a microporous network structure². With a diverse selection of metal nodes, microporous nature, and unique vacancy/defect arrangement², their contributions cover a wide range of fields from gas^{4, 5} to energy storage⁶, electronic⁷ and ion⁸ transport, magnetic^{9, 10} and optical properties^{11, 12}. Since the first synthesis of Prussian blue in 1710¹³, development progress has only been revolved around the crystalline phase, either surface modifications¹⁴ or superstructure formations¹⁵. PBAs have been long known for their structural diversity, but the amorphous/glassy state has been unexplored. Though attempts have been made, neither stable amorphous state^{16, 17} nor pure phase was achieved¹⁸. For example, pressure-induced amorphization (PIA) of $Fe[Co(CN)_6]$ to 17.4 GPa does not provide a stable amorphous PBA but decomposes into amorphous carbon nitride, nitrile oxide, metallic iron, and copper instead¹⁶.

The recent emergence of a new direction toward glass and liquid metal-organic framework/coordination polymers (MOF/CPs) has opened up a new opportunity for discovering unique properties that deviate from the crystalline norm and as a pathway to developing new materials¹⁹⁻²³. Thus far, only a few CPs and MOFs have shown the capability to undergo the glass transformation process. Most examples are melt-quenched glass, where the crystal-liquid-glass transition is mainly governed by the counterbalance between entropic/enthalpic driving forces and the kinetics of crystallization^{24, 25}. In contrast, a direct crystal-glass transformation of the mechanical-induced glass has been recognized as another path to prepare the glass and is initiated by plastic deformation under mechanical stress^{26, 27}. However, factors that dictate the mechanical-induced phase transition have yet been established. Limited 3D MOF/CP glasses libraries also restrict a rich discussion on the correlation between glassy behaviour and intrinsic defect/vacancy or structural variation. Tuneable vacancy content, pore structure, and compositional versatility make classical PBAs a suitable representative compound to enable a systematic study and precise control of functionality in MOF/CP glasses.

In this study, we report the discovery of the glassy state in PBAs through mechanical-induced crystal-glass transformation. The glassy nature was confirmed by X-ray diffuse scattering pattern, preservation of short-range order through pair distribution function (PDF) analysis, and the presence of glass transition behaviour. Unlike other coordination polymer glasses, alteration of the oxidation state while generating CN^- vacancies was observed via ⁵⁷Fe Mössbauer spectroscopy and elemental analysis. We observed an anomalous gas adsorption enhancement in recrystallized PBA with semiconductivity retention in PBA glass. Finally, we identify the origin of crystal-glass transformation by DFT under mechanical stress and generalize the correlation between the mechanical properties and glass transition difficulties by comparing the contribution of the presence of hexacyanometallate vacancies and the effect of the guest molecules.

RESULTS AND DISCUSSION

Crystal–glass transformation. Representative PBA containing 1/3 hexacyanoferrate vacancy, $\text{K}_{2x/3}\text{Cu}^{\text{II}}[\text{Fe}^{\text{II}}_x\text{Fe}^{\text{III}}_{1-x}(\text{CN})_6]_{2/3}\square_{1/3}\cdot n\text{H}_2\text{O}$ ($\text{Cu}[\text{Fe}]_{2/3}\cdot n\text{H}_2\text{O}$), was synthesized via aqueous precipitation method^{4, 6}. Powder X-ray diffraction (PXRD) of the $\text{Cu}[\text{Fe}]_{2/3}$ resembles the face-centred cubic diffraction pattern of Prussian blue, $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_{3/4}\square_{1/4}\cdot n\text{H}_2\text{O}$ ($\text{Fe}[\text{Fe}]_{3/4}$, $a = 10.166 \text{ \AA}$), with Bragg peaks shifting toward a higher 2θ (Fig. S1)³. Unlike $\text{Fe}[\text{Fe}]_{3/4}$, Rietveld refinement of synchrotron PXRD (Fig. S2, $\lambda = 0.2020 \text{ \AA}$) reveal that $\text{Cu}[\text{Fe}]_{2/3}$ contain a slightly smaller cell parameter of $10.068 \text{ \AA}$ ($Pm\bar{3}m$, $a = 10.068 \text{ \AA}$, $R_p = 5.19\%$, $R_{wp} = 7.46\%$). Thermalgravimetric analysis (TGA, Fig. S3) of $\text{Cu}[\text{Fe}]_{2/3}$ shows two steps of weight loss associated with the release of interstitial and coordinated water with a total loss of ca. 26 wt% ($n = 4$).

To obtain the glassy state of $\text{Cu}[\text{Fe}]_{2/3}$, we conducted mechanical milling treatment of crystalline $\text{Cu}[\text{Fe}]_{2/3}$ under Ar atmosphere with a milling time of 120 min. The milling condition is identical to the formation of glassy state $\text{Cd}(1,2,4\text{-triazole})_2(\text{H}_2\text{PO}_4)_2$ reported by our group²⁷. After ball milling, the colour of $\text{Cu}[\text{Fe}]_{2/3}$ changes from olive green to indigo blue (Fig. S4). Synchrotron PXRD of the $\text{Cu}[\text{Fe}]_{2/3}$ glass ($\text{Cu}[\text{Fe}]_{2/3}\text{-g}$, Fig. 1A) demonstrates a broad diffuse scattering, proposing an amorphous nature²⁶⁻²⁸. Though the $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ retains two steps of weight loss in TGA (Fig. S3), the 2nd step is much more gradual. The thermal behaviour of $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ was further studied by a close system DSC. $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ exhibits a baseline shifting at the glass transition temperature (T_g) of 44.7 to $63.4 \text{ }^\circ\text{C}$ at a heating rate of 10 to $30 \text{ }^\circ\text{C min}^{-1}$, respectively (Fig. 1B and S5)^{26, 29}. As heating continues, an exothermic recrystallization peak is observed at crystallization temperature (T_c) of 144.8 and $154.8 \text{ }^\circ\text{C}$ at 10 and $30 \text{ }^\circ\text{C min}^{-1}$, respectively. After the DSC measurement, PXRD of the $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ sample shows partial restoration of Bragg diffraction, confirming the recrystallization process (Fig. S6). In contrast, heating under an open system (Ar flow) does not provide recrystallization, as also confirmed in variable temperature PXRD (Fig. S7). To clarify the dissimilarity between the close and open system in DSC, we prepared an activated $\text{Cu}[\text{Fe}]_{2/3}$ at $95 \text{ }^\circ\text{C}$ under vacuum ($\text{Cu}[\text{Fe}]_{2/3}'$)⁴. Although the PXRD remains unchanged (Fig. S8), total removal of interstitial water (ca. 8.2 wt%) was observed in TGA (Fig. S9). Mechanical induced crystal–glass transformation is also applicable to $\text{Cu}[\text{Fe}]_{2/3}'$ yielding $\text{Cu}[\text{Fe}]_{2/3}'\text{-g}$ with a diffuse scattering (Fig. S8), a T_g of $58.8 \text{ }^\circ\text{C}$ ($30 \text{ }^\circ\text{C min}^{-1}$, Fig. 1B), and a negligible weight loss at the T_g ($< 0.2\%$, Fig. S9). DSC of $\text{Cu}[\text{Fe}]_{2/3}'\text{-g}$ in a closed system did not provide any exothermic peak, suggesting that water vapour generated from the interstitial water in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ is required to aid the recrystallization process due to its porous nature³⁰. It is worth mentioning that thermal annealing alone is sufficient for dense CP glasses^{26, 27}.

Encouraged by the DSC results and vapour assisted recrystallization in some MOF/CP glasses, we attempted to reconstruct the crystalline framework from the glassy state^{20, 26, 30, 31}. The $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ was exposed to humid air (85 RH%) at $80 \text{ }^\circ\text{C}$ for 72 h. Again, the colour alters to garnet red (Fig. S4). The synchrotron PXRD pattern confirms recrystallization with a shorter cell length of $10.001 \text{ \AA}$ ($Pm\bar{3}m$, $R_p = 6.74\%$, $R_{wp} = 9.09\%$, Fig. 1A, S10, and S11). The recrystallized state is henceforth denoted as $\text{Cu}[\text{Fe}]_{2/3}\text{-c}$. Though $\text{Cu}[\text{Fe}]_{2/3}\text{-c}$ exhibits smaller unit cells, TGA reveals that the interstitial water content is boosted to ca. 27.5 wt% (Fig. S12). Activation of $\text{Cu}[\text{Fe}]_{2/3}\text{-c}$ provides a highly porous $\text{Cu}[\text{Fe}]_{2/3}\text{-c}'$. Recrystallization was also tracked by scanning electron microscopy (SEM). After the recrystallization process, recovery of discrete crystal nature was observed with an indistinguishable domain size as the $\text{Cu}[\text{Fe}]_{2/3}$ (Fig. S13).

Fig. 1 Crystal–glass transformation and recrystallization of $\text{Cu}[\text{Fe}]_{2/3}$. **(A)** Synchrotron PXRD of $\text{Cu}[\text{Fe}]_{2/3}$, $\text{Cu}[\text{Fe}]_{2/3\text{-g}}$, and $\text{Cu}[\text{Fe}]_{2/3\text{-c}}$ ($\lambda = 0.2020 \text{ \AA}$). **(B)** Enthalpic response comparison between $\text{Cu}[\text{Fe}]_{2/3\text{-g}}$ and $\text{Cu}[\text{Fe}]_{2/3'\text{-g}}$ at $30 \text{ }^\circ\text{C min}^{-1}$. **(C)** Pair distribution function (PDF) and PDF peak assignment of $\text{Cu}[\text{Fe}]_{2/3}$, $\text{Cu}[\text{Fe}]_{2/3\text{-g}}$, and $\text{Cu}[\text{Fe}]_{2/3\text{-c}}$. Cu, Fe, C, N, and O atoms are represented as green, brown, grey, blue, and red spheres, respectively. H atoms are omitted for clarity. **(D)** Comparison of cross-sectional SEM images of hot-pressed $\text{Cu}[\text{Fe}]_{2/3}$ (left) and $\text{Cu}[\text{Fe}]_{2/3\text{-g}}$ (right). Scale bar = $2 \text{ }\mu\text{m}$ and $100 \text{ }\mu\text{m}$ for enlarging and inset, respectively.

Chemical structures in glass and recrystallize phases. With an absence of Bragg diffraction observed in the glassy state, we further probed the short-to-intermediate-range order in the local structure of the $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ via Synchrotron X-ray total scattering. Fourier transformation and Lorch modification of the Faber–Ziman total structure factor, $S(Q)$, to pair distribution functions (PDFs), $G(r)$, provide information on atom pair distance histograms (Fig. 1C)³²⁻³⁴. Peak features of the glass phase remain mostly identical to the crystalline $\text{Cu}[\text{Fe}]_{2/3}$ up to ca. 5.3 Å with slightly reduced amplitude. This corresponds to the retention of the $\text{C}\equiv\text{N}$, $\text{Fe}-\text{C}$, and $\text{Cu}-\text{N}$ bonds of the coordination network, besides the $\text{Cu}-\text{O}$ bond of the coordinated water adjacent to the hexacyanoferrate vacancy site. The preserved range includes the nearby $\text{Cu}-\text{Fe}$ correlation pair (4.94 Å, label VII in Fig. 1C) and the preservation of $\nu(\text{C}\equiv\text{N})$ band between 2177 and 2104 cm^{-1} under infrared spectroscopy (Fig. S14), suggesting that metal–ligand–metal ($\text{Cu}-\text{N}\equiv\text{C}-\text{Fe}$) connectivity remains intact after the mechanical-induced crystal–glass transformation process. PDF of $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ suggests a slightly smaller pair distance as compared to the $\text{Cu}[\text{Fe}]_{2/3}$ ^{19-21, 25, 27}. Note, the $\text{Cu}-\text{Fe}$ correlation of $\text{Cu}[\text{Fe}]_{2/3}$ is ca. 5.03 Å, corresponding to the cell parameter of 10.063 Å suggested by Rietveld refinement. Above 5.3 Å, the PDF of the $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ exhibits lower peak intensity and peaks broadening as the periodicity diminishes. Partial retention of correlations between the diagonal $\text{Cu}-\text{Cu}/\text{Fe}-\text{Fe}$ (X), diagonal $\text{Cu}-\text{Fe}$ (XI), and in-plane $\text{Cu}-\text{Cu}/\text{Fe}-\text{Fe}$ (XIII) nearest neighbours in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ is observed at ca. 6.86, 7.94 and 9.76 Å, respectively. These values are smaller than the pair distances of ca. 7.13, 8.66, and 10.06 observed in $\text{Cu}[\text{Fe}]_{2/3}$ (Fig. 1C and S15). Apart from slight deviation of octahedral geometry around Cu and Fe with bonds angles is expected to alter from 90° in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$, shortened pair distance occurs due to partial reduction of Fe^{III} to Fe^{II} , which will be discussed in the next section^{35, 36}.

After recrystallization, our result shows the restoration of pair correlation beyond 5.3 Å in the $\text{Cu}[\text{Fe}]_{2/3}\text{-c}$ (Fig. 1C). Uniform peaks shifting toward a lower pair distance confirm the lattice parameter shrinkage due to the partial reduction of Fe centre with a $\text{Cu}-\text{Fe}$ correlation of 5.00 Å. The PDF features of $\text{Cu}[\text{Fe}]_{2/3}\text{-c}$ are identical to $\text{Cu}[\text{Fe}]_{2/3}$ peaks without any additional phase (Fig. S15 and S16). Though most of the features are restored, PDF contains slightly diminished peak amplitude, suggesting the existence of partial disorders³⁷. The amplification of pair correlation at ca. 3.7 Å (V) and 4.0 Å (VI) correspond with the inclusion of additional interstitial water, which is also observed in TGA (Fig. S12).

Another important preferable character of glass is the ability to form a grain-boundary free monolith^{23, 26}. We first prepared a thin monolith disk of $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ with a thickness of ca. 250 μm and 16 mm in diameter (Fig. S17) via hot pressing technique at 80°C under vacuum³⁸. In contrast to $\text{Cu}[\text{Fe}]_{2/3}$, neither grain-boundary nor major crack was observed in the $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ under cross-section SEM (Fig. 1D).

Alteration of oxidation states. Oxidation states of the $\text{M}'\text{-CN}$ terminal are distinguishable through the $\nu(\text{C}\equiv\text{N})$ shifts between 2000 and 2200 cm^{-1} via infrared spectroscopy³⁹. The CN^- linker binds the metal nodes via a σ -donation of a weak antibonding 5σ orbital together with a metal π -back-donation to antibonding π -orbital. A decrease in $\nu(\text{C}\equiv\text{N})$ mode is expected when a transition metal node with lower oxidation presents in the structure due to the addition of electrons in the $2p\pi^*$ antibonding orbital. In $\text{Cu}[\text{Fe}]_{2/3}$ (Fig. S14), we found coexistence of $\nu(\text{C}\equiv\text{N})$ band at 2177 and 2104 cm^{-1} corresponding to $\text{Fe}^{\text{III}}\text{-C}\equiv\text{N}-\text{Cu}^{\text{II}}$ and $\text{Fe}^{\text{II}}\text{-C}\equiv\text{N}-\text{Cu}^{\text{II}}$, respectively. The presence of mixed valency

corresponds to the incorporation of A-site K^+ cation^{39,40}. $Cu[Fe]_{2/3}$ -g, $Cu[Fe]_{2/3}$ -c, and $Cu[Fe]_{2/3}$ -c', on the other hand, exhibit domination of single $\nu(C\equiv N)$ mode at $2087\text{--}2100\text{ cm}^{-1}$ from $Fe^{II}\text{--}C\equiv N\text{--}Cu^{II}$, suggesting that partial reduction of Fe^{3+} node occurs during ball milling process⁴¹.

We performed ^{57}Fe Mössbauer spectroscopy at room temperature to support these oxidation state assignments (Fig. S18). The fitting parameters are summarized in Table S1. Best-fitting for the $Cu[Fe]_{2/3}$ requires two doublets with isomer shift (IS) and quadrupole splitting (QS) of -0.088 mm s^{-1} , 0.179 mm s^{-1} and -0.159 mm s^{-1} , 0.556 mm s^{-1} , confirming the coexistence of hexacyanoferrate with 51.1% Fe^{II} ($S = 0$) and 48.9% Fe^{III} ($S = 1/2$), respectively^{42–44}. After transformation to $Cu[Fe]_{2/3}$ -g, we observed a significant shifting in the Fe^{II} ($S = 0$) and Fe^{III} ($S = 1/2$) ratio to 67.0% and 33.0%, respectively. This Fe^{II} ($S = 0$) dominance remains unchanged for recrystallized $Cu[Fe]_{2/3}$ -c and $Cu[Fe]_{2/3}$ -c'. Indeed, these assignments are also close parallel to the FT-IR, confirming that the Fe^{III} site is partially reduced to Fe^{II} via the mechanical milling process⁴¹.

Yet, to satisfy the electroneutrality principle⁴⁵, partial elimination of CN^- is required. To confirm, we further tracked the change in weight fraction of C and N via elemental analysis (Table S2). After 2 h of mechanical milling, C and N weight fraction reduced from 23.7% and 27.7% to 22.7% and 27.0%, respectively, confirming the formation of CN vacancies to accommodate the reduction from Fe^{III} to Fe^{II} ⁴⁶. Raman spectroscopy also shows a higher degree of deformation around $N\text{--}Cu\text{--}N$ and $Fe\text{--}CN$ in $Cu[Fe]_{2/3}$ -g, which is also retained in $Cu[Fe]_{2/3}$ -c and $Cu[Fe]_{2/3}$ -c' (Fig. S19)^{47, 48}. Moreover, Fe K-edge extended X-ray absorption fine structure (EXAFS) fittings reveal the change in coordination environment around Fe centre ($Fe\text{--}CN$) after the mechanical milling process, where the coordination number decreases from 6.0 in $Cu[Fe]_{2/3}$ to 4.4 in $Cu[Fe]_{2/3}$ -g (Fig. S20, S21, and table S3)⁴⁶. Though partial restoration of $Fe\text{--}CN$ is observed in $Cu[Fe]_{2/3}$ -c after recrystallization, the coordination number of 5.4 supports the formation of the unsaturated metal site due to partial elimination of CN^- .

Fig. 2 (A) N_2 adsorption isotherms at 77 K of $Cu[Fe]_{2/3}$, $Cu[Fe]_{2/3}$ -g, and $Cu[Fe]_{2/3}$ -c'. Adsorption and desorption processes are represented by Filled and hollow symbols, respectively. **(B)** Electronic conductivity of $Cu[Fe]_{2/3}$, $Cu[Fe]_{2/3}$ -g, and $Cu[Fe]_{2/3}$ -c' measured under an Ar atmosphere.

Enhance porosity via crystal–glass–crystal transformation. The existence and nature of the extended micropore networks in PBAs relies on the long-range arrangement of correlated hexacyanometallate vacancies^{2, 4, 5}, implying the presence of inaccessible cavities where the gas molecules cannot diffuse in during the experimental timescale⁴⁹. Partial amorphization of some crystalline MOFs through a lightly shear/uniaxial deformation has been demonstrated to open up these closed pockets through the formation of dangling linkers in computational studies. Up to 48.5% and 20.8% increases in the accessible surface area have been demonstrated, theoretically, under shear and compression strain in $\text{Cu}_3(1,3,5\text{-tris}(1H\text{-pyrazol-4-yl)benzene})_2$ ⁵⁰. Moreover, the presence of ligand vacancy also leads to the accessibility of hidden pore cavities⁴⁹. Inspired by these findings, we explored the enhancement of the accessible surface area through the restoration of PBA crystals. Identical to most porous 3D MOFs, glass transformation reduces the pore accessibility in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ as demonstrated by N_2 adsorption at 77 K (Fig. 2A)^{51, 52}. Negligible gas uptake with the Brunauer–Emmett–Teller (BET) surface area of $6.2 \text{ m}^2 \text{ g}^{-1}$ was observed, a significant decrease from the $\text{Cu}[\text{Fe}]_{2/3}$ ($293 \text{ m}^2 \text{ g}^{-1}$). Unlike other CPs/MOFs, where recrystallization induced less than 100% recovery of the gas uptake compared with their pristine states would be expected³⁰, we find an increase in the N_2 uptake of $\text{Cu}[\text{Fe}]_{2/3}\text{-c'}$ with a BET surface area of $585 \text{ m}^2 \text{ g}^{-1}$. The partial retention of the amorphous phase and the elimination of CN^- linkers during the mechanical milling process, described in the previous section, would generate local bypassing routes, resulting in a more accessible/connective porous network^{46, 49, 50}.

Semiconductivity of glass. The electron transport mechanism in PBA is composition-dependent. It can be classified as ranging from semiconductive in PBAs with a relatively narrow bandgap⁵³ to nearest-neighbour hopping due to the localized $3d$ electron in $\text{Fe}[\text{Fe}]_{3/4}$ and Berlin green with band insulator characteristics (10^{-7} to $10^{-11} \text{ S cm}^{-1}$)^{54, 55}. A relatively low ligand-field splitting predicted for Cu-hexacyanoferrate among the metal hexacyanoferrates makes it a suitable candidate to elucidate the electronic conductivity in a glassy state⁵⁶. The transport mechanism can be classified as class II mixed-valence compounds according to Robin–Day, where charges transfer between localized charge carriers through thermally activated electron hopping^{53, 57-59}. We evaluated the conductivity of $\text{Cu}[\text{Fe}]_{2/3}$ in each state by AC impedance spectroscopy under the Ar atmosphere to exclude the possible contribution from proton conductivity (Fig. S22 to S24). No sign of polarization from migrated ions is observed in all I–V curves. In the experimental range, we found the domination of semiconductive behaviour in $\text{Cu}[\text{Fe}]_{2/3}$, $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$, and $\text{Cu}[\text{Fe}]_{2/3}\text{-c'}$ (Fig. 2B). With the presence of $\text{Fe}^{\text{II/III}}$ mixed valency, $\text{Cu}[\text{Fe}]_{2/3}$ exhibits the highest conductivity of 0.18 and 0.99 mS cm^{-1} at 30 and 50°C , respectively. Slightly smaller conductivity values are observed in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ and $\text{Cu}[\text{Fe}]_{2/3}\text{-c'}$ as Fe^{III} content diminished. Still, we find conductivity retention in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ of 0.31 mS cm^{-1} at 50°C , even in a glassy state. Comparing $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ and $\text{Cu}[\text{Fe}]_{2/3}\text{-c'}$, which share a comparable $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ fraction, amorphous $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ shows a higher conductivity than crystalline $\text{Cu}[\text{Fe}]_{2/3}\text{-c'}$ throughout the experimental temperature regime. It is worth mentioning that the absence of long-range order usually suppresses the electronic conductivity in most semiconductive glass due to the formation of trapped states in defect sites⁵⁸. However, short-range metal–ligand–metal connectivity is preserved in $\text{Cu}[\text{Fe}]_{2/3}\text{-g}$ with a shorter pair distance between metal nodes, plausibly compensate for the lack of long-range order^{60, 61}.

Fig. 3 (A) Schematic diagram of the correlation between milling duration for mechanical crystal–glass transformation and vacancy fractions in PBAs. Green, brown, grey, blue, and red spheres represent M, M', C, N, and O, respectively. H atoms are omitted for clarity. (B) PXRD of $Fe[Fe]_{3/4-g}$ after mechanical milling for 0, 2, 8, 24, 48, and 144 h. ($\lambda = 1.5406 \text{ \AA}$). (C) PDFs of $Fe[Fe]_{3/4-g}$ (144 h milling), $Cu[Fe]_{2/3-g}$ (2 h milling), and $Cu[Fe]_{2/3'-g}$ (2 h milling).

Correlation between vacancies fraction and hydration on glass formation. Mechanical milling introduces shear and compression stress beyond the elastic stability limits of the crystals, resulting in a crystal-to-glass phase transition⁶². While the quantity of structural defects is difficult to control in other MOF/CP glasses⁶³, the tuneable vacancy/defect and compositional versatility in PBAs inspire us to generalize the correlation between vacancy fraction and hydration on glass-forming difficulty. Hereafter, PBAs with the nominal composition of $M^{II}[M^{III}(CN)_6] \cdot nH_2O$, $M^{II}[M^{III}(CN)_6]_{3/4} \cdot nH_2O$, $M^{II}[M^{III}(CN)_6]_{2/3} \cdot nH_2O$ are denoted as $M[M']$, $M[M']_{3/4}$, and $M[M']_{2/3}$, respectively.

The presence of $M'(CN)_6$ defect sites reduces connectivity and mechanical compression resistance, affecting the bulk modulus under pressure¹⁷. According to previous report¹⁷, the bulk moduli of $Mn[Co]_{2/3}$, $Cd[Co]_{2/3}$, and $Mn[Pt]$ by second-order Birch-Murnaghan fitting^{64, 65} are 6.5(7), 6.5(4), and 33(2) GPa, respectively. While the substitution of the metal between $Mn[Co]_{2/3}$ and $Cd[Co]_{2/3}$ negligibly contributed to the mechanical properties, bulk modulus of $Mn[Pt]$ increased by a factor of 5 with the inclusion of additional $M'(CN)_6$. Moreover, another work⁶⁶ demonstrated that isostructural

Mn[Pt] and Fe[Pt] also exhibit identical compressibility upon compression. Likewise, we expected that the intrinsic $M(CN)_6$ defects in PBA generally reduce the resistance to mechanical stress and should therefore shorten the milling time to achieve a fully amorphized state (Fig. 3A). We extended the library toward the conventional Prussian blue with a quarter vacancy, $Fe[Fe]_{3/4}$. Unlike $Cu[Fe]_{2/3}$, which undergoes crystal–glass transformation under 2 h of ball milling, results show that a lower defect fraction $Fe[Fe]_{3/4}$ remains highly crystalline under the same milling condition. The amorphous characters were then observed after 144 h of mechanical milling (Fig. 3B). We also found a glass transition temperature at T_g of 64.9 and 76.4 °C at a heating rate of 10 and 30 °C min⁻¹, confirming the glassy nature of $Fe[Fe]_{3/4}$ -g (Fig. S25). We acquired X-ray total scattering of the $Fe[Fe]_{3/4}$ -g at room temperature to evaluate the local structure. PDF, $G(r)$ in Fig. 3C shows sharp features at a short scattering distance ($r < 5.4$ Å) confirm the preservation of Fe–C≡N–Fe connectivity in $Fe[Fe]_{3/4}$ -g with a nearby Fe–Fe pair distance of ca. 5.03 Å. In comparison, the Fe–Fe correlation in crystalline $Fe[Fe]_{3/4}$ is 5.08 Å³. In higher r -space (Fig. S26), detailed examination reveals quasiperiodic oscillations²⁵ that continue to at least 35 Å even after 144 h of mechanical milling, much larger than that observed in $Cu[Fe]_{2/3}$ -g with 2 h of identical treatment (Fig. S27). The presence of extended-range structural correlations mimics density fluctuation caused by topological and chemical ordering, which is also found in structurally disordered glassy AX_2 inorganic systems, such as $ZnCl_2$ and $GeSe_2$ ⁶⁷⁻⁶⁹, and network-forming liquid/glassy MOFs/CPs^{20, 25}. Lack of sufficient void space and lower degree of freedom in $Fe[Fe]_{3/4}$ -g also affects the recrystallization process. Only minor restoration of the Bragg diffraction is observed through the vapour-assisted recrystallization at 80 °C (85 RH%) for 72 h ($Fe[Fe]_{3/4}$ -c, Fig. S28).

We further evaluate the relationship between interstitial water and a degree of disorder in PBA. In contrast to melt-quenched glass, where no nuclei of starting phase remain in the undercooled liquid, the glass produced by mechanical milling can exist in numerous thermodynamically unstable transient states⁷⁰. Fig. 3C and S29 show PDF of glasses prepared from full hydrate ($Cu[Fe]_{2/3}$ -g) and dehydrate ($Cu[Fe]_{2/3}$ -g) $Cu[Fe]_{2/3}$. Weaker $Cu[Fe]_{2/3}$ -g peaks amplitudes in short-range pairs distance ($r < 5.3$ Å) as well as peaks broadening at intermediate r region, as compared to $Cu[Fe]_{2/3}$ -g, is observed with a minor contraction of Cu–Fe pair distance (ca. 4.89 Å). Since the PDF provides the probability of finding an atom at a specific pair distance and displaying it as a weighted histogram, these are particularly evident for a higher degree of disorder in $Cu[Fe]_{2/3}$ -g^{37, 71, 72}. The exclusion of interstitial water directly influences the framework integrity toward mechanical stress under milling conditions. It is worth mentioning that the inclusion of solvent drastically changes the mechanical properties of porous materials^{17, 73}. Under compression, the bulk modulus of defective Mn[Co]_{2/3} doubles from 6.5(7) to 15.18(6) GPa with the inclusion of D₂O¹⁷. Similar behaviour was also observed in Cu-based HKUST-1 and MOF-5, where the bulk modulus increases substantially in penetrating pressure-transmitting medium compared to the nonpenetrating one^{74, 75}. Though our analysis has been intentionally simplified by neither acknowledging the inclusion of alkali cation nor the role of the Jahn-Teller effect², the results show a direct correlation between the intrinsic defect fractions and the presence of interstitial water on the resistance upon glass-forming via mechanical stimuli.

Fig. 4 (A) Spatial dependence of Young's modulus (E), linear compressibility (β), and shear modulus (G) of $\text{Fe}[\text{Fe}(\text{CN})_6]$, $\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, and $\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4}\square_{1/4} \cdot 3.5\text{H}_2\text{O}$. Since the G cannot be directly represented in 3D space, plots represent values range by enclosing the translucent maxima surface on an opaque minima surface. **(B)** Evolution of the stability criteria for compression ($\lambda = C_{11} + 2C_{12} + P$), ($\lambda = C_{11} - C_{12} - 2P$), and shear ($\lambda = C_{44} - P$) of $\text{Fe}[\text{Fe}(\text{CN})_6]$, $\text{Fe}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, and $\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4}\square_{1/4} \cdot n\text{H}_2\text{O}$ as a function of hydrostatic pressure. C_{11} , C_{12} , and C_{44} are the moduli for axial compression, dilation on compression, and shear, respectively. The dashed line indicates the stability limit for each mode (unstable when $\lambda < 0$). $\text{Fe}[\text{Fe}(\text{CN})_6]$ represents the effect of the absence of interstitial water, while $\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4}\square_{1/4} \cdot n\text{H}_2\text{O}$ describes the contribution of the hexacyanometallate vacancies.

Elastic tensor analysis. To further understand the relationship between the composition of PBAs and the mechanical stability under applied stress, elastic components (C_{ij}) were calculated based on energy-minimised structures of $\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, $\text{Fe}[\text{Fe}(\text{CN})_6]$, and $\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4} \cdot 3.5\text{H}_2\text{O}$ (Fig. 4A). These simplified series represent the defect-free PBAs, the influence of the absence of interstitial water, and the effect of quarter hexacyanometallate vacancy, respectively. The defect-free $\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ demonstrates the highest ability to resist compression, linear stress, and shear deformation among the three, with an average Voigt-Reuss-Hill Bulk (K), Young's (E), and shear (G)

moduli of 114.7, 113.4, and 42.5 GPa, respectively (Fig. S32)⁷⁶. Elimination of interstitial water results in a minor to moderate decrease in stiffness of Fe[Fe(CN)₆], where $K = 111.6$ GPa (−2.7 %), $E = 98.7$ GPa (−13.0 %), and $G = 36.5$ GPa (−14.1 %). Interstitial voids allow a certain degree of flexibility, thus lowering the framework stiffness. More details can be obtained by analysing the spatial dependence of mechanical properties calculated from the elastic component (Fig. 4A, S34 to S41, and Table S4)^{77, 78}. The theoretical Young's modulus (E) of Fe[Fe(CN)₆]·2H₂O shows an E_{max} of 274.4 GPa along the primary axis where the acting stress is parallel to the metal–ligand connectivity. The E_{min} of 51.4 GPa can be found at diagonal positions, resulting in an anisotropy value ($E_{\text{max}}/E_{\text{min}}$) of 4.8. E_{max} and E_{min} were reduced to 217.3 and 48.2 GPa in Fe[Fe(CN)₆] with a smaller degree of anisotropy of 4.5 since the alignment of interstitial water lightly disturbed the symmetry of Fe[Fe(CN)₆]·2H₂O. The exclusion of 25% occupancy of hexacyanometallate in Fe[Fe(CN)₆]_{3/4}·3.5H₂O, results in a dramatic decrease in the average K and E values to 37.3 (−67.5 %) and 84.4 (−25.6 %) GPa, respectively (Fig. 4A, S32 and S42 to 45). The presence of vacancy sites reduces framework connectivity, which significantly lowers the resistance toward applied stress. Identical behaviour was also observed in other MOFs/CPs, where linkers or metal vacancies result in higher compressibility and lower mechanical stability under applied stress^{79, 80}. A higher degree of anisotropy was also observed in spatial dependence of E , β (linear compressibility), and G (shear modulus). Despite a low G_{max} value of 78.6 GPa, Fe[Fe(CN)₆]_{3/4}·3.5H₂O exhibits a relatively high G_{min} (18.8 GPa) and low G anisotropy of 4.2, which results in a moderate average G of 37.6 (−11.5 %). The hydrogen-bonded network constructed from coordinated waters binds to the coordinatively unsaturated metal sites, and interstitial water contributes to resisting the shear deformation¹⁷. These variations highlight the opportunity to understand the mechanical crystal–glass transformation process through controls over the PBA composition.

The fundamental cause of the crystal-to-glass transition under mechanical stress was further elucidated by monitoring the evolution of elastic constants of PBAs under hydrostatic compression (Fig. 4B)^{62, 73}. Under applied compression, the stability criteria of Fe[Fe(CN)₆]_{3/4}·3.5H₂O diminishes drastically in all modes due to the framework softening. However, the origin of elastic instability of the framework is appeared to be initiated by the shear-mode deformation ($C_{44} < 0$), which is estimated to begin at $P = 0.06$ GPa. In contrast, the result indicates that the deformation of Fe[Fe(CN)₆]·2H₂O and Fe[Fe(CN)₆] can only be triggered by the shear mode softening at a pressure much higher than that of Fe[Fe(CN)₆]_{3/4}·3.5H₂O. These results highlight the impact of hexacyanometallate vacancy on the mechanical-induced crystal–glass transformation process. Moreover, compared between Fe[Fe(CN)₆]·2H₂O and Fe[Fe(CN)₆], the presence of interstitial water delays the phase transition onset pressure by altering the shear modulus of the unstressed material.

CONCLUSIONS

In summary, the foregoing results demonstrate the first confirmation of glassy states in Prussian blue analogues. Mechanical induced crystal–glass transformation successfully converts crystalline PBAs to amorphous solids, exhibiting glass transition behaviour. Synchrotron X-ray total scattering results with PDF analysis confirm the preservation of short-range order with the retention of metal–ligand–metal connectivity. Apart from the physical structure, partial alteration of the oxidation state from Fe^{III} to Fe^{II} was recognized with CN[−] elimination to satisfy electroneutrality. Furthermore, the

observation of an enhancement in N₂ gas uptake in recrystallized Cu[Fe]_{2/3}-c (585 m² g⁻¹) and the demonstration of electronic conductivity in glassy Cu[Fe]_{2/3}-g (0.31 mS cm⁻¹ at 50 °C) also initiated a foundation toward the functionality of PBA glasses. Finally, we correlate the contribution of intrinsic vacancy and interstitial water to mechanical properties. Intrinsic stoichiometry plays a dominant role in structural rigidity and thus increases the requirement for mechanical stress to initiate the crystal–glass transformation. The presence of interstitial water also contributes to the stiffness of the framework. This work thus introduces PBA as a new family of CP/MOF glasses and establishes the foundation for the fundamental understanding of mechanical-induced glass.

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Author contributions

S.H. designed the project with N.M. N.M. synthesised PBAs and prepared the glassy compounds. N.M. collected and analysed powder X-ray diffraction, thermalgravimetric analysis, scanning electron microscopy, differential scanning calorimetry, infrared spectroscopy, N₂ adsorption, and conductivity measurement. S.K. collected and analysed Raman. R.I., S. K., and R.O. collected and analysed ⁵⁷Fe Mössbauer. Computational calculations were done by H.M.L., S.B., and Y.K. K.O. and N.M. collected and analysed X-ray total scattering. S.H. and N.M. wrote the paper, and all the authors contributed to revising the paper.

Competing interests

The authors declare no competing interests.

Materials & Correspondence.

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