Controlling the reactivity of hydride-based ions in the solid state is important for hydrogen-related functions such as hydrogen (H\textsubscript{2}) storage, heterogeneous hydrogenation catalysis and ion conduction\textsuperscript{1,2}. Hydride-based ions include hydride (H\textsuperscript{−}) and molecular ions such as borohydride (BH\textsubscript{4}−) and alanate (AlH\textsubscript{4}−), and they exhibit a strong electron-donating ability\textsuperscript{3}. The reactive character causes high sensitivity to moisture in the air, and it has been a challenge to design the dual properties of high reactivity of hydrides and air stability in the solid state. For example, the dehydrogenation reactivity and air stability are in a trade-off, and control of the reactivity of BH\textsubscript{4}− has been demanded. For this purpose, we synthesize a series of BH\textsubscript{4}−-based coordination polymers/metal–organic frameworks. The reactivity of BH\textsubscript{4}− in the structures is regulated by coordination geometry and neighboring ligands, and one of the compounds [Zn(BH\textsubscript{4})\textsubscript{2}(dipyridylpropane)] exhibits both high dehydrogenation reactivity (1.4 wt% at 179 °C) and high air stability (50 RH% at 25 °C, 7 days). Single crystal X-raydiffraction analysis reveals that H\textsuperscript{+⋯H\textsuperscript{−}} dihydrogen interactions and close packing of hydrophobic ligands are the key for the reactivity and stability. The dehydrogenation mechanism is investigated by temperature-programmed desorption, in situ synchrotron PXRD and solid-state NMR.

The attempts to incorporate reactive BH\textsubscript{4}− into CP structures readily lead to the reduction of metal ions or decomposition of organic ligands. There are many reports on polymeric crystal structures consisting of metal ions and bridging BH\textsubscript{4}−.\textsuperscript{20} On the other hand, the extended BH\textsubscript{4}−-based crystal structures constructed from metal ions and organic bridging ligands are limited: ([Mg(BH\textsubscript{4})\textsubscript{2}(pyrazine)\textsubscript{2}] and [Th(OTr\textsubscript{2}Mes\textsubscript{2})(BH\textsubscript{4})\textsubscript{2}(4,4′-bipyridyl)]) were the only examples reported in the Cambridge Crystallographic Data Centre (CCDC) database.\textsuperscript{21,22} As shown in previous studies, neutral N-donor ligands are suitable to incorporate BH\textsubscript{4}− as a counter anion in CP structures. We then used commercially available Mg(BH\textsubscript{4})\textsubscript{2} and Ca(BH\textsubscript{4})\textsubscript{2} for CP synthesis using neutral N-donor ligands under Ar. The solution reaction using Mg(BH\textsubscript{4})\textsubscript{2} and 4,4′-bipyridyl in acetonitrile (MeCN) afforded a polymeric structure. Ca(BH\textsubscript{4})\textsubscript{2} with poor solubility in organic solvents is not suitable for solution reactions. A solvent-free mechanochemical reaction of Ca(BH\textsubscript{4})\textsubscript{2} and...
pyrazine produced crystalline powder of CP. On the other hand, the synthetic attempts using other pyridyl-based ligands afforded amorphous powder or no solid product. This is because of a weak coordination interaction between hard Mg$^{2+}$ or Ca$^{2+}$ and soft N-donor ligands according to Hard and Soft Acids and Bases (HSAB) theory. The theory says that so...
after air exposure for 7 days (Fig. S30†). Humidified conditions are harsh enough to hydrolyze BH4− in most of the MBHs.

Some crystalline powder samples changed to amorphous in a few minutes (5, Mg2+ and 10, Ca2+) or 1 day (3–4, 6–9, Mn2+). Notably, among the BH4−-CPs, Zn2+-based CPs (1 and 2) exhibited high air stability. In particular, 2 exhibits IR spectra identical before and after air exposure for 7 days in Fig. 2B. In addition, 2 retains highly crystalline peaks in PXRD (Fig. 2B, inset). The results demonstrate improved air stability of 2, and the mechanisms are discussed based on the crystal structure of 2. Although many structural parameters affect the air stability, we classify the main contributions to the high air stability of 2 as the (i) metal–ligand coordination bond (ii) dihydrogen bonding and (iii) packing structure. 2 shows higher air stability than the isostructural Mn2+-based 3. In general, a metal–ligand bond is an essential parameter to determine the air stability of CPs.27 The Zn–N bond in tetrahedral geometry is known to construct highly stable CPs.28 Meanwhile, limited examples of CPs with Mn–N in tetrahedral geometry have been reported, and most of them are sensitive to air.29,30 The tendency of air stability depending on metal ions is also suggested by a survey of the CCDC database.31 Fig. 3C displays the dihydrogen bond between BH4− and the neighboring dipiridylpropane (dpp) in the structure of 2. In addition to the X-ray diffraction analysis, the geometry optimization on 2 utilizing DFT calculation suggests that dihydrogen bonds form as well (Fig. S46†). In general, dihydrogen bonding stabilizes a crystal structure by the electrostatic interaction between oppositely charged hydrogen atoms,32,33 and the interaction lowers the electron donating ability of BH4−. The intermolecular interaction and packing structure are also essential for air stability, because they affect the diffusion of H2O molecules in the structure. BH4− is surrounded by the hydrophobic propyl group (2.545–3.010 Å) as shown in Fig. 2D, which avoids the attack of H2O. In addition, the concentration of hydrophobic species around BH4− of 2 was compared with that of other CPs showing different air stability. The number of carbon atoms away from the boron atoms of BH4− within 5 Å was counted for 2, 9 and 10 (Fig. S47†). 2 shows a higher concentration of carbon atoms than 9 and 10 (the total number of carbon atoms within 5 Å, 2: 47, 9: 39, 10: 16), which also contributes to the high air stability of 2.34

As 2 exhibited exceptionally high air stability, the dehydrogenation properties of 2 were characterized. The TGA profile under Ar exhibits a characteristic weight loss of 1.4 wt% at 170 °C with a second weight loss at 260 °C (Fig. S26†). The released chemical species at 170 °C were analyzed using temperature-programmed desorption (TPD) as shown in Fig. 3A. The release of H2 (m/z = 2) starts from 108 °C and peaks are observed at 179 and 203 °C in the TPD profile, corresponding to the weight loss (1.4 wt%) at 170 °C in TGA. The observed dehydrogenation temperature for 2 is higher than that of [NaZn(BH4)3] (103 °C), which is due to the stabilization effect of BH4− in 2. In spite of
the higher air stability of 2 than NaBH₄. 2 exhibits a lower dehydrogenation temperature than NaBH₄ (170 vs. 505 °C). Note that dpp ligands decrease the amount of H₂ release per weight, and the 1.4 wt% of H₂ is smaller than that of the MBHs. The close contact of each BH₄⁻ enables dehydrogenation at a lower temperature. The inset of Fig. 3A displays the closest distance between B–H···H–B (2.645 Å), which is comparable to that of Zn²⁺-based MBHs [[LiZn₂(BH₄)₅]: 2.482 Å; [NaZn(BH₄)₃]: 2.291 Å]. Tetrahedral geometry in 2 is suitable to arrange BH₄⁻ in close proximity. The variable temperature synchrotron PXRD experiments indicate the structural expansion of 2 upon heating (25–226 °C, Fig. S38 and S39†). 2 does not exhibit an amorphous phase before dehydrogenation at 179 °C, and metallic Zn peaks are observed above 180 °C. The dehydrogenation of two BH₄⁻ produces one molecule of H₂ and subsequently reduces Zn²⁺ to metallic Zn.

The environment of BH₄⁻ after the dehydrogenation was characterized by solid-state ¹¹B magic angle spinning (MAS) nuclear magnetic resonance (NMR). The ¹¹B NMR spectrum of pristine 2 shows two peaks at −45 and −47 ppm, and both peaks correspond to crystallographically independent BH₄⁻ (Fig. 3B, inset). The dehydrogenized 2 displays ¹¹B peaks at −8, 0, 15, and 30 ppm in Fig. 3B, and was further characterized by using the 2D multi-quantum (MQ) MAS NMR spectrum (Fig. S42†). To identify the resultant boron species, a 2D ¹H/¹¹B through-bond heteronuclear multiple quantum coherence (HMQC) experiment was performed (Fig. S43†). The ¹¹B peaks observed at −8 and 0 ppm correlate with the proton at 2 ppm, indicative of a B–H bond. These boron species are assigned to the [(BH₃)₂dpp] complexes. Meanwhile, the remaining two ¹¹B peaks (15, 30 ppm) do not exhibit a clear correlation, indicating no direct bond between these boron species and hydrogen atoms. The ¹¹B peak at 15 ppm corresponds to elemental boron and matches well with the simulated one (Fig. S44†), while the ¹¹B peak at 30 ppm corresponds to B-3N species (e.g., [B(dpp)ᵢ]ᵢ). The 2D ¹H/¹³C heteronuclear correlation spectrum clearly exhibits the ¹H and ¹³C peaks corresponding to the aromatic ring and aliphatic chain of dpp, indicating that dpp does not decompose during dehydrogenation (Fig. S45†).

The first peak of H₂ release at 179 °C in TPD corresponds to the dehydrogenation of BH₄⁻ (eqn (1)). The release of toxic B₂H₆ is suppressed by the complexation with the N-donor dpp ligand to form [(BH₃)₂dpp] as revealed by solid-state NMR and IR spectra (Fig. S40†). The second peak of H₂ release at 203 °C in TPD corresponds to the further dehydrogenation of [(BH₃)₂dpp]. Solid-state NMR suggests that [(BH₃)₂dpp] partly forms elemental boron and B-3N species such as [B(dpp)ᵢ] through the dehydrogenation (eqn (2)). 2 arranged BH₄⁻ and nitrogen atoms of dpp close to each other in a 1 : 1 ratio (B···N distance: 3.450 and 3.462 Å, Fig. S35†). 2 maintains the crystal structure before dehydrogenation at 179 °C as observed by in situ PXRD. The results indicate that the pre-organized environment of BH₄⁻ in 2 is preserved before the dehydrogenation, leading to the release of pure H₂ without B₂H₆.

Conclusions

By considering suitable combinations of metal ions and N-donor ligands, we have constructed 10 coordination polymer crystals involving reactive BH₄⁻ with various coordination
geometries. In particular, \([\text{Zn}(\text{BH}_4)_2(\text{dipyridylpropane})]\) demonstrated both high dehydrogenation reactivity and high air stability. The crystal structure of 2 was intact under humidified conditions (50 RH% at 25 °C, 7 days) which indicates exceptionally high air stability as compared with conventional MBHs. This is due to the strong metal–ligand bond, the electrostatic stabilization by dihydrogen bonding, and close packing of the hydrophobic group with BH$_4^–$. In spite of the stabilization of BH$_4^–$, the dehydrogenation reactivity was maintained (pure H$_2$, 1.4 wt%, 179 °C). Tetrahedral geometry in 2 arranged two BH$_4^–$ closely, which accelerated the dehydrogenation. We demonstrated that crystal engineering of coordination polymers and metal–organic frameworks expands the library of hydride-based crystal structures and their properties.

**Conflicts of interest**

There are no conflicts to declare.

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**References**

31 In CCDC database, the reported examples of \([\text{Zn}(\text{X})_2(\text{pyridyl})_2]\) are greater than twice of the hydrated geometry, \([\text{Zn}(\text{X})_2(\text{pyridyl})_2(\text{H}_2\text{O})_2]\) (1306 vs. 814 hits). By contrast, Mn$^{2+}$ prefers the hydrated structure (unhydrated: 28 hits, hydrated: 375 hits).