Broad Mid-Infrared Luminescence in a Metal–Organic Framework Glass

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 Supporting Information

ABSTRACT: Metal–organic framework (MOF) glasses are a newly discovered family of melt-quenched glasses. Despite considerable progress in understanding the nature of MOF glasses, their photonic functionalities have not been found so far. Here, we report on the first breakthrough regarding the photonic functionalities of MOF glasses, that is, finding of the luminescence in melt-quenched MOF glasses. The finding was achieved on a zeolitic imidazolate framework (ZIF) series, that is, the ZIF-62 series: Zn_{1−x}Co_{x}(Im)_{1.7}(bIm)_{0.3}, x = 0, 0.1, and 0.5, where Co substitutes Zn in ZIF-62 forming single-phased solid solutions. Remarkably, we observed broadband mid-infrared (Mid-IR) luminescence (in the wavelength range of 1.5–4.8 μm) in both the crystalline and amorphous solid solutions. The intensity of the luminescence in ZIF glass is gradually enhanced by increasing the level of Co concentration. The observed Mid-IR emission originates from d–d transition of Co ions. The discovery of the luminescence in ZIF-62 glass may pave the way toward new photonic applications of bulk MOF glasses.

1. INTRODUCTION

Metal–organic frameworks (MOFs) play a significant role in numerous potential applications, from chemical engineering, energy storage to photonics and biomedicine. However, MOFs were synthesized in the form of powders with a large specific surface area. To extend the application field (i.e., ionic conductivity and porosity) of MOFs, a promising way is to produce 1D, 2D, and 3D MOF glasses by ball-milling, melt-quenching, and pressurization. Recently, such glasses were successfully made from several zeolitic imidazolate frameworks (ZIFs). ZIFs are a subset of MOFs, where metal nodes are linked by organic ligands through coordination bonds. They adopt the classical zeolite tetrahedral network structure by substituting central metal atoms (Zn or Co) for Si and Al ions and by substituting organic molecules [e.g. imidazolate (Im) (C₃H₄N₂⁻) or benzimidazolate (bIm) (C₅H₇N₂⁻)] for oxygen. Furthermore, some ZIF glasses even show permanent accessible porosity or blending structure. Despite rapid development in ZIF glass research, the photonic functionalities of these glasses have not been found so far, and hence the optical applications of ZIF glasses have not been realized. To change this situation, we have performed the present study, that is, explored whether it is possible to generate the photonic functionalities (e.g., luminescence), in ZIF glasses by tuning their compositions. If this is possible, ZIF glasses can be potentially utilized in the field of photonics. However, photonic functionalities of this new family of glasses have not been explored so far.

To reach the above-mentioned goal, here we choose the ZIF-62 system as the starting object of this study because ZIF-62 is the best glass former among the ZIF systems that we have tested until now. In addition, ZIF-62 glasses exhibit several advantages regarding physical and chemical properties, such as high transparency, feasibility of producing bulk samples, and high stability against humid air exposure. Considering these superior properties, we choose ZIF-62 as the starting materials to develop the luminescent ZIF glasses. ZIF-62 has a chemical formula of Zn(Im)_{2−x}(bIm)_{x}, where Zn ions are connected by Im and bIm in tetrahedral coordination and each Im or bIm is coordinated by two Zn ions through nitrogen atoms (Figure 1b). In the present work, our strategy is to substitute Co for Zn in ZIF-62 during the hydrothermal synthesis to form single-phased solid solutions, and then to melt-quench ZIF-62 to
Figure 1. (a–c) Schematic diagram for the preparation of the ZIF-62 single crystal containing Co ions with orthorhombic crystal structure and its laminated glass with amorphous structure. (d) TG/DTA and (e,f) XRD patterns of the C(ZIF-62:0.1Co2+) and G(ZIF-62:0.1Co2+). The insets of (e,f) are optical images of the C(ZIF-62:0.1Co2+) and G(ZIF-62:0.1Co2+). Scale bar: 200 µm.

glass state (where the ionic radius mismatch of Co²⁺ (0.58 Å) and Zn²⁺ (0.6 Å) in the tetrahedral coordination is small enough (3.33%) to easily substitute Zn by Co).47 We first synthesized ZIF-62 single crystals containing Co ions (labeled as C(ZIF-62:xCo²⁺)) with different concentrations (Zn₁₋ₓCoₓ(Im)₁₋ₓ(bIm)₀.₅, x = 0, 0.1 and 0.5) using a solvothermal method. The ZIF-62 glasses containing Co ions (labeled as G(ZIF-62:xCo²⁺)) were obtained by naturally cooling the ZIF-62 molten to room temperature (RT) in argon. We then examined the thermal and structural properties of the C(ZIF-62:xCo²⁺) and G(ZIF-62:xCo²⁺) by using various techniques such as thermogravimetry and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), scanning electron microscope with energy dispersive X-ray analysis (SEM/EDX), X-ray photoelectron spectroscopy (XPS), cross-polarization magic-angle spinning nuclear magnetic resonance (CPMAS-NMR), and Raman spectroscopy. Finally, we characterize the optical and photonic properties of both C(ZIF-62:xCo²⁺) crystal and G(ZIF-62:xCo²⁺) glass samples by means of absorption and photoluminescence (PL) spectroscopies.

2. RESULTS AND DISCUSSION

Figures 1d–f and S2 show the crystal structure and thermal properties of the C(ZIF-62:xCo²⁺) and G(ZIF-62:xCo²⁺) by XRD and TG/DTA, respectively. The XRD patterns of the C(ZIF-62:xCo²⁺) (Figures 1e and S2c) demonstrate several diffraction peaks that can be attributed to the lattice planes of orthorhombic ZIF-62 crystals (Figure 1b) (space group: Pbcn, a = 15.505 Å, b = 15.809 Å, c = 18.172 Å).16,17,18 In contrast, there is no observable peak shift with an increase of Co concentration (Figure S3c), indicating that the substitution of Zn with Co does not lead to any lattice expansion (or shrinking) of the crystal. In the DTA curve, we can see an exothermic peak around 268 °C, which is ascribed to the release of the N,N-dimethylformamide (DMF) (desolvation) from the C(ZIF-62:xCo²⁺) samples. From the TG curve, the released amount of the sample accounts for 13.5% (Figures 1d and S2a), while the Co-free ZIF-62 single crystal starts to decompose at T₆% = 580 °C, which remains unchanged up to 50% of Co doping. The melting point (Tₘ) can be clearly observed at 447 °C, which increases to 452 °C with increase in Co concentrations in the prepared solid solutions (i.e., at x = 0.5) (Figure S3a and Table S1). Upon melting of the C(ZIF-62:xCo²⁺) at 450 °C for 24 h, and subsequent cooling to RT, we obtained the glass state of the G(ZIF-62:xCo²⁺), which is confirmed by the absence of diffraction peaks in the XRD patterns (Figures 1f and S2d). Broad peaks at 2θ = 15.12° and 31.74° indicate a typical amorphous structure without a long range order. However, the intense diffraction peak at 15.12° can be ascribed to a scattering length of about 6 Å. This is the average distance between the strongest scatters in the glass (i.e., Zn–Zn and Co–Co bonds).14,17,18 These glasses with different concentration levels of Co ions demonstrate increase in the glass-transition temperature (Tₕ) from 328 to 334 °C (Figures 1d, S2b, and Table S1) as the Co concentration increases from 0 to 0.5, respectively. Consequently, the glass-forming ability (GFA) (defined as Tₖ/Tₘ) values were found to be 0.834, 0.839, and 0.837 at x = 0, 0.1, and 0.5, respectively, which almost remains unchanged with the increase in Co concentration (Figure S3b). These results suggest that the inserting of Co ions into ZIF crystals does not affect the ultrahigh GFA of the ZIF-62 glass.

The transparency of the C(ZIF-62:xCo²⁺) and G(ZIF-62:xCo²⁺) under parallel and crossed-polarized light was checked using optical microscopy as shown in Figure S4. The recorded optical images under parallel and crossed-polarized light modes both indicate high transparency and optical isotropy for crystals and glasses. Cooling of ZIF-62 molten in argon results in morphological changes to layer-like G(ZIF-62:xCo²⁺) glass.
To examine the morphology of the synthesized single crystals and glasses, SEM images were measured for the C(ZIF-62:xCo²⁺) and G(ZIF-62:xCo²⁺) (Figures 2a, S5, and S6). The SEM images of the C(ZIF-62:xCo²⁺) reveals that the single crystals containing Co ions with different x-values were precipitated in the form of shapeless continuous frameworks. However, a mixture of spherical nanocrystals (<100 nm) and microcrystals (>1 μm) (Figure S5) was observed, suggesting the possibility of ZIF-62 single crystals to crystallize in the shape of nano-/microspheres. The size of these nano-/microcrystals increases with the x-value, indicating that the increase of Co concentration facilities the formation of microcrystals rather than nanocrystals. On the other hand, the microstructure of the glass G(ZIF-62:xCo²⁺) differs greatly from that of the crystal C(ZIF-62:xCo²⁺). Lamellated morphology (Figures 2a and S6) was observed in G(ZIF-62:xCo²⁺) with highly ordered layer configuration. However, the natural cooling of the ZIF-62 liquid containing Co ions to RT induces the survived molecular units to accumulate on each other forming laminated glass. From elemental analysis, these shapeless continuous frameworks, nano-/microcrystals (Figure S7), and lamellated glass morphology (Figures 2b–d and S9) are enriched in Zn, C, N, and Co ions with homogeneous distribution of the constituent elements, suggesting that the synthesized single crystals and glasses are indeed single phased solid solutions and it is not a physical mixture of pure ZIF-62-Zn and ZIF-62-Co. The molar ratios of Co/(Zn + Co) ions (Figure S8) in C(ZIF-62:xCo²⁺) are 0.107 and 0.42 for x = 0.1 and 0.5, respectively. On the other hand, from XPS spectra (Figure S10 and Table S1), the molar ratio of Co/(Zn + Co) was calculated, recording 0.097 and 0.48 for C(ZIF-62:0.1Co²⁺) and C(ZIF-62:0.5Co²⁺), which are more accurate values in comparison with EDX values and match with the nominal Co concentration added during synthesis. The XPS spectra of G(ZIF-62:0.5Co²⁺) and C(ZIF-62:0.5Co²⁺) for Zn, N, C, and Co orbitals are identical, implying no obvious change in their chemical environments.

A molar Im/(Im + bIm) ratio of 0.1 was used during the synthesis process, targeting ZIF-62 crystals with the composition of Zn₁₋ₓCoₓ(Im)₁.₇₅(bIm)₀.₂₅. However, from solution ¹H NMR measurements (Figure S14), the bIm/(Im + bIm) ratios were found to be 0.15 and 0.16 for Co free ZIF-

**Figure 2.** (a) SEM of Co-free ZIF-62 glass and its EDX maps for (b) Zn, (c) C, and (d) N.

**Figure 3.** Raman spectra of the C(ZIF-62:0.5Co²⁺) and G(ZIF-62:0.5Co²⁺) in the range of (a) 400–1800 and (b) 65–400 cm⁻¹. (c) ¹⁵N and (d) ¹³C CPMAS-NMR spectra of the C(ZIF-62:0.1Co²⁺) and G(ZIF-62:0.1Co²⁺). Spinning sidebands are marked with asterisks (*). The insets of (c,d) show the molecular structure of ZIF-62.
62 crystals and glass, demonstrating the chemical compositions of $\text{Zn(Im)}_{1.70} \cdot \text{(bIm)}_{0.30}$ and $\text{Zn(Im)}_{1.68} \cdot \text{(bIm)}_{0.32}$, respectively. In addition, solution $^1\text{H}$ NMR spectra of ZIF-62 crystals and glass containing Co ions (at $x = 0.5$) (Table S1 and Figure S15) record molar bIm/(Im + bIm) ratio of 0.16 (i.e., $\text{Zn}^{0.5} \cdot \text{Co}^{0.5} \cdot \text{(Im)}_{1.68} \cdot \text{(bIm)}_{0.32}$) and 0.17 (i.e., $\text{Zn}^{0.5} \cdot \text{Co}^{0.5} \cdot \text{(Im)}_{1.66} \cdot \text{(bIm)}_{0.34}$), respectively. $^1\text{H}$ NMR data indicate that the bIm is incorporated preferentially over Im in the framework as a result of the higher acidity of bIm compared to Im.14,18 On the other hand, the molar bIm/(Im + bIm) ratios of the melt-quenched glasses are slightly higher than those of the parent crystals, implying that some Im linker decomposes during melting. The linker ratio slightly increased from 0.15 to 0.16 upon the addition of Co to the synthesis mixture (i.e., $x = 0.5$), suggesting the preference of bIm to coordinate with Co rather than Zn.

To investigate the local structure of the prepared crystals and glasses, we recorded Raman spectra of both C(ZIF-62:Co) and G(ZIF-62:Co) (Figures 3 and S12). The Raman spectra of the C(ZIF-62:Co) (Figures 3a and S12a) reveal vibration frequencies typical for the tetrahedral ZIF-62 structure.10,14 The peak at 1278 cm$^{-1}$ (Figure S12c) is attributed to the symmetric stretching of C–N bond in the organic linker, which is slightly blue-shifted as the $x$-value increases. In the low wavenumber range (65–400 cm$^{-1}$) (Figures 3b and S12b), the rocking $\delta$(Zn–N), symmetric $\nu_s$(Zn–N), and asymmetric $\nu_a$(Zn–N) stretching vibrations of the Zn–N bond, as well as the symmetric $\nu_s$(Co–N) stretching of the Co–N bond, can be observed at 149, 179, 253, and 320 cm$^{-1}$, respectively.15-24 These results suggest that the Co and Zn ions are coordinated with the same organic linkers (Im and bIm). In addition, the peaks at 78 and 120 cm$^{-1}$ indicate that the coordinated organic ligands to Co and Zn ions have some vibration modes with low phonon energy, which possibly arise from the rotation of these species.5,24 After formation the ZIF glasses, Raman spectra of the G(ZIF-62:Co) (Figures 3a,b and S12a) illustrate the same vibration frequencies as those of C(ZIF-62:Co), which become broadened as a result of the transformation from crystalline into glass state. While, low wavenumber peaks gradually disappear with increasing Co content. This confirms that no decomposition or evaporation took place during the melting-cooling process, and Zn–N and Co–N bonds and organic linker structure remain retained after quenching.17

To unravel the molecular structure of the prepared crystals and glasses, we measured the $^{15}$N and $^{13}$C spectra of C(ZIF-62:Co) and G(ZIF-62:Co) by CPMAS-NMR (Figures 3 and S13). The $^{15}$N spectra of C(ZIF-62:Co) and G(ZIF-62:Co) (Figures 3c and S13a,b) show two sharp peaks at 172 and 156 ppm, which are attributed to the N atoms in Im (N1 and N2) and bIm (N3 and N4), respectively (see the inset in Figure 3c).16,25 The $^{13}$C spectra of C(ZIF-62:Co) and G(ZIF-62:Co) (Figures 3d and S13c,d) display all the carbon resonances of both Im and bIm, which overlap with each other, producing three broad peaks at 142, 126, and 117 ppm. In addition, there is a single peak located at 149.6 ppm, which is attributed to C1 of bIm (see the inset in Figure 3d). These results are in good agreement with previous reports of the ZIF-62 single crystal.10,14

Figure 4. (a) Energy level diagrams of CoO$_4$ and CoN$_4$ units and the possible PL mechanisms. (b) PL intensities of the C(ZIF-62:Co$^{2+}$) and G(ZIF-62:Co$^{2+}$) at different values of $x$. (c) Absorption spectra of the C(ZIF-62:Co$^{2+}$) and G(ZIF-62:Co$^{2+}$). (d) PL spectra of the C(ZIF-62:Co$^{2+}$) and G(ZIF-62:Co$^{2+}$) under excitation by 980 nm LDs.
C(ZIF-62:xCo^{2+}) and G(ZIF-62:xCo^{2+}) are broadened with increasing Co content because of the paramagnetic effect of Co ions. Compared with the spectra of C(ZIF-62:xCo^{2+}), all the peaks of the ^15N and ^13C NMR of G(ZIF-62:xCo^{2+}) become wider because of the transformation from crystalline into amorphous phase, but without peak shift. Importantly, the ^15N and ^13C spectra of both C(ZIF-62:xCo^{2+}) and G(ZIF-62:xCo^{2+}) are almost identical, implying that the organic linkers are survived in the quenched glasses.

From the optical image (Figure S1), the introduction of optically active Co ions with a particle-filled 3d orbital (3d^2) into the ZIF-62 host results in strong purple coloration. Generally, the spectroscopic properties of Co ions depend on how and to whom they are coordinated according to the crystal field theory. Normally, Co ions in an oxygen-coordinated tetrahedral site show three absorption peaks at 390 nm (^4A_2(4F) → ^4T_1(4F)), 1.5 μm (^4A_2(4F) → ^4T_1(4F)), and 2.3 μm (^4A_1(4F) → ^4T_1(4F)) (Figure 4a), while in the case of nitrogen-coordinated tetrahedral site (Figure 4a), in which the crystal field strength is stronger, these absorption peaks significantly shifted to around 570, 1100, and 3500 nm, respectively. The absorption spectra of both C(ZIF-62:xCo^{2+}) and G(ZIF-62:xCo^{2+}) (Figure S1c,d) display peaks at 570 nm and 1.1 μm, confirming that the Co ions are in the nitrogen tetrahedral site. Moreover, the full width at half-maximum of the broad absorption peak (Figure 4c) at 1.1 μm slightly increases by Δλ = 35 nm as a result of the transformation of the prepared crystal into glass, while the absorption peak of Co doped glasses is usually much wider than those in crystalline materials. This observation suggests that the crystal field and/or site-symmetry around Co ions may be slightly decreased after quenching, indicating the highly ordered local structure around Co in ZIF glass (i.e., the structural ordering around cobalt in ZIF-62 glass is high like those in ZIF-62 single crystals but it slightly decreased compared to that of the parent ZIF-62 crystal).

The PL spectra of both C(ZIF-62:xCo^{2+}) and G(ZIF-62:xCo^{2+}) in the mid-infrared (Mid-IR) region were recorded under excitation by 980 nm laser diodes (LDs) (Figure S11a,b). The Co-free ZIF-62 crystal and glass do not show any luminescence. In contrast, remarkably the crystalline and glassy solid solutions containing Co ions exhibit broadband Mid-IR emission in the wavelength range of 1.5−4.8 μm, which gradually increases the intensity with increasing x-value (Co content). On the other hand, the Mid-IR luminescence intensity of the G(ZIF-62:xCo^{2+}) is stronger than that of C(ZIF-62:xCo^{2+}) (Figure 4b,d), which is probably linked with the surface/morphology/scattering effect, and it is not an intrinsic property of the glass. This is the first observation of luminescence in a ZIF-62 glass, which could potentially be important for photonic applications of MOF glasses, for example, Mid-IR lasers. The broadband emission spectrum consists of two overlapped peaks, which can be assigned to the ^4T_1(4F) → ^4T_1(4F) transition (2.45 μm) and the ^4T_2(4F) → ^4A_1(4F) transition (3.5 μm) (Figure 4a). From the emission spectra, the PL bands for both groups of samples show fine energy band structures, which can be attributed to the microstructural distortion in ZIF-62 because of the larger tetrahedral units, for example, compared to those in oxide materials.

The organic linkers may strongly suppress the rate of nonradiative relaxation process, allowing ZIF-62 glass containing Co ions to emit Mid-IR luminescence. This may explain the detection of Mid-IR emission of ZIF-62 glass containing Co ions compared to any other glasses. In comparison with other Mid-IR luminescent Co-doped materials, there are many crystals doped with Co that demonstrate Mid-IR emission such as mixed halides (AgClBr₃, Co (3.5−5.2 μm)), fluorides (MgF₂,Co (1.6−2.1 μm)), and sulfides (ZnS:Co (2.5−4 μm)). These Mid-IR luminescent crystals illustrate broad emission bands especially in case of Co-doped mixed halides and sulfides, which cover only about 1.7 μm or less of the Mid-IR range. However, the melt-quenched ZIF-62 glass containing Co ions is characterized by broad Mid-IR luminescence, which covers about 3.3 μm (i.e. from 1.5 to 4.8 μm) of the Mid-IR range. The Mid-IR emission that observed in ZIF-62 glass is much wider than those in mixed halides and sulfides doped with Co ions. The observation of broad Mid-IR luminescence in ZIF-62 glass containing Co ions may enable potential photonic applications such as broadband tunable Mid-IR lasers.

3. CONCLUSIONS

Through the present work, we discovered broadband Mid-IR luminescence in ZIF-62 single crystals and glasses containing Co ions arising from d→d transition of Co ions. The strength of the luminescence can be enhanced by increasing the concentration level of Co ions. The results imply that the ZIF-62 crystal and glass containing Co ions are new Mid-IR luminescent materials for photonic applications. We have also investigated the structural properties of both crystalline and amorphous ZIF-62 solid solutions containing Co ions. Our results suggest that the prepared ZIF-62 single crystals are shapeless continuous frameworks that can be transformed to laminated glasses upon melt-quenching. In addition, the laminated glasses exhibit ultrahigh GFA and a similar local structure to that of the parent crystalline MOF.

4. EXPERIMENTAL SECTION

Zn(NO₃)₂·6H₂O (99.9%), Co(NO₃)₂·6H₂O (99.9%), Im (99.5%), blm (99%), and DMF (99%) were used as raw materials. As shown in Figure 1a,b, to synthesize Zn₁₋ₐCoₐ(Im)₁₋ₓ(bIm)ₓ·6H₂O (a = 0) crystals with x = 0, 0.1, and 0.5, the Zn(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Im, and blm with the molar ratio 1− x:0:13.5:1.5, x = 0, 0.1, and 0.5, were dissolved into 50 mL of DMF and then transferred into a 100 mL Teflon bottle. The bottle was tightly sealed and placed in an electric oven at 130 °C for 5 days. After cooling to RT, both colorless and transparent purple single crystal pieces were obtained from pure Zn-ZIF-62 and ZIF-62 containing Co ions, respectively, and they were purified by filtration and washing three times with DMF and drying at 100 °C for 6 h (Figure S1). The corresponding ZIF-62 glasses (Figure 1c) were prepared by heating the transparent ZIF-62 crystals in a tube furnace at 5 K/min to 450 °C in argon for 24 h and then by cooling the ZIF-62 liquids naturally to RT.

In order to characterize the thermal properties of the prepared ZIF-62 crystals and glasses containing Co ions, the TG/DTA curves were acquired using a CRY-Z differential thermal analyzer at the upscan rate of 10 °C/min in argon. The optical images were recorded using an OLYMPUS BX53M optical microscope equipped with a SC180-CCD camera.
absorption spectra were measured using a Lambda 900 spectrophotometer (PerkinElmer, USA). The PL spectra were recorded with a spectrofluorometer (JHR 320, Jobin-Yvon, France) equipped with a 980 nm LDs. The XRD patterns were collected to identify the crystal structure using an XPERT-PRO-PANAlytical-Netherlands instrument with Cu Kα radiation (λ = 1.5418 Å). The EDX maps and SEM images were measured to characterize the morphology by the ULTRA-55 SEM system. To evaluate the network structure of ZIF-62 crystals and glasses containing Co ions, the Raman spectra were obtained by a Raman spectrometer (HR 800, Jobin-Yvon, France) equipped with a 514.5 nm argon laser as the excitation source. The XPS measurements were performed to characterize the binding energies of the Zn, Co, N, and C using a Thermo Scientific ESCALAB 250Xi spectrometer, using a monochromatic Al Kα source. Solid-state NMR experiments were carried out on a Bruker Avance III HD 500 MHz NMR system equipped with a 4 mm MAS-NMR probe. The typically recycle delay is 1 s, and the signals were accumulated over 8192 scans. The 13C and 15N spectra were second calibrated to adamantane using a monochromatic Al Kα source. Solid-state NMR experiments were carried out on a Bruker Avance III HD 500 MHz NMR system equipped with a 4 mm MAS-NMR probe. The typically recycle delay is 1 s, and the signals were accumulated over 8192 scans. The 13C and 15N spectra were second calibrated to adamantane using a monochromatic Al Kα source.

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**REFERENCES**

1. Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; et al. Methane Storage in Flexible Metal-Organic Frameworks with Intrinsic Thermal Management. *Nature* 2015, 527, 357–361.

2. Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Llàtés i Xamena, F. X.; Gascon, J. Metal-Organic Framework Nanosheets in Polymer Composite Materials for Gas Separation. *Nat. Mater.* 2014, 14, 48–52.

3. Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The chemistry and Applications of Metal-Organic Frameworks. *Science* 2013, 341, 1230444.

4. Yang, H.; Wang, X. Secondary-Component Incorporated Hollow MOFs and Derivatives for Catalytic and Energy-Related Applications. *Adv. Mater.* 2018, 1800743.

5. Hao, J.; Xu, X.; Fei, H.; Li, L.; Yan, B. Functionalization of Metal-Organic Frameworks for Photoactive Materials. *Adv. Mater.* 2018, 30, 1705634.

6. Quah, H. S.; Chen, W.; Schreyer, M. K.; Yang, H.; Wong, M. W.; Ji, W.; Vittal, J. J. Multiphoton Harvesting Metal–Organic Frameworks. *Nat. Commun.* 2015, 6, 7954.

7. Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. Metal–Organic Frameworks as Efficient Materials for Drug Delivery. *Angew. Chem., Int. Ed.* 2006, 45, 5974–5978.

8. Jiang, X.; Zhang, L.; Liu, S.; Zhang, Y.; He, Z.; Li, W.; Zhang, F.; Shi, Y.; Lü, W.; Li, Y.; et al. Ultrathin Metal-Organic Framework: An Emerging Broadband Nonlinear Optical Material for Ultrafast Photonics. *Adv. Opt. Mater.* 2018, 6, 1800561.

9. Bennett, T. D.; Tan, J. C.; Yue, Y.; Baxter, E.; Ducati, C.; Terrill, N. J.; Yeung, H. H. M.; Zhou, Z.; Chen, W.; Henke, S.; et al. Hybrid Glasses from Strong and Fragile Metal-Organic Framework Liquids. *Nat. Commun.* 2015, 6, 8079.

10. Bennett, T. D.; Yue, Y.; Li, P.; Qiao, A.; Tao, H.; Greaves, N. G.; Richards, T.; Lampronti, G. I.; Redfern, S. A. T.; Blanc, F.; et al. Melt-Quenched Glasses of Metal-Organic Frameworks. *J. Am. Chem. Soc.* 2016, 138, 3484–3492.

11. Longley, L.; Collins, S. M.; Zhou, C.; Smales, G. J.; Norman, S. E.; Brownhill, N. J.; Ashling, C. W.; Chater, P. A.; Tovey, R.; Schönlieb, C. B.; et al. Liquid Phase Blending of Metal-Organic Frameworks. *Nat. Commun.* 2018, 9, 2135.

12. Zhou, C.; Longley, L.; Krajnc, A.; Smales, G. J.; Qiao, A.; Ercar, I.; Doherty, C. M.; Thornton, A. W.; Hill, A. J.; Ashling, C. W.; et al. Metal-Organic Framework Glasses with Permanent Accessible Porosity. *Nat. Commun.* 2018, 9, 5042.

13. Umeyama, D.; Horike, S.; Inukai, M.; Itakura, T.; Kitagawa, S. Reversible Solid-to-Liquid Phase Transition of Coordination Polymer Crystals. *J. Am. Chem. Soc.* 2015, 137, 864–870.

14. Qiao, A.; Bennett, T. D.; Tao, H.; Krajnc, A.; Mali, G.; Doherty, C. M.; Thornton, A. W.; Mauro, J. C.; Greaves, G. N.; Yue, Y. A Metal-Organic Framework with Ultrahigh Glass-Forming Ability. *Sci. Adv.* 2018, 4, No. eaao6827.

15. Qiao, A.; Tao, H.; Carson, M. P.; Aldrich, S. W.; Thirion, L. M.; Bennett, T. D.; Mauro, J. C.; Yue, Y. Optical Properties of a Melt-Quenched Metal-Organic Framework Glass. *Opt. Lett.* 2019, 44, 1623–1625.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01559.

Optical photograph; DTA curves, XRD patterns, and GFA values; optical images; SEM images; XPS spectra; PL and absorption spectra; Raman spectra; NMR spectra; SEM/EDX images of the prepared crystals and glasses; and tabulated molar ratios and parameter values of both the synthesis-added and measured samples (PDF)

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**Notes**

The authors declare no competing financial interest.
