Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information for

Reversible structural transformation of supramolecular inorganic-organic hybrid glass and zeolitic-imidazolate framework

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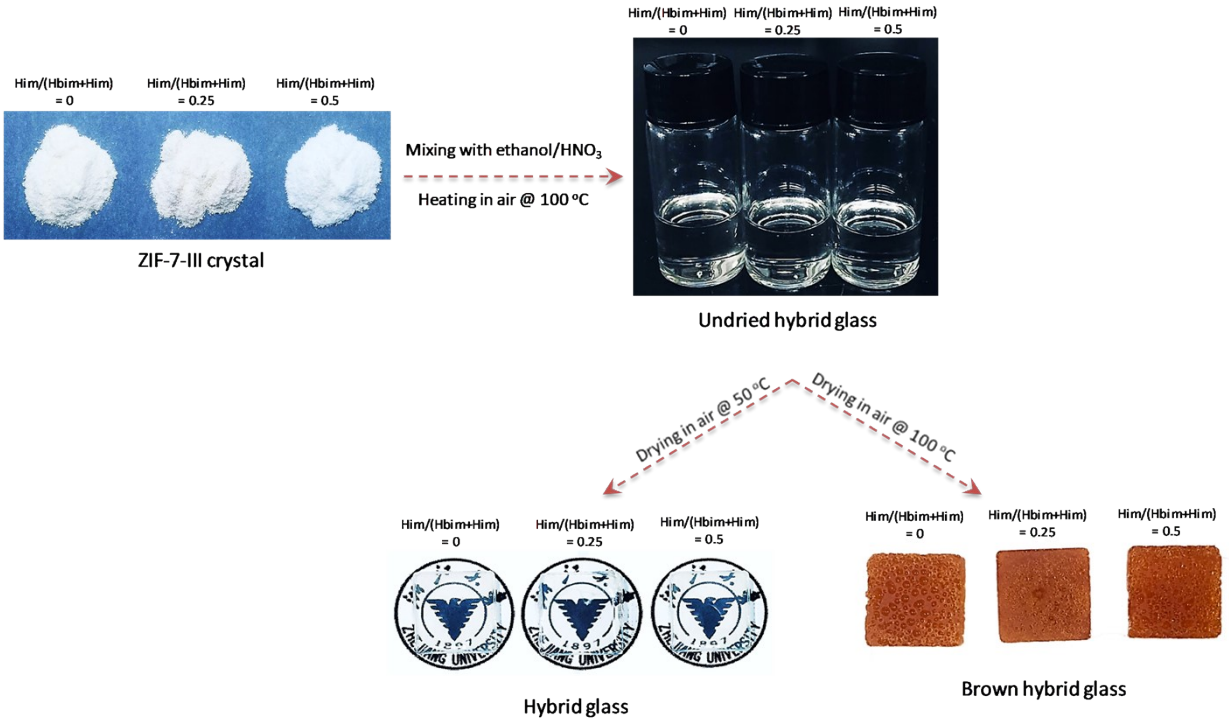

Fig. S1. Schematic illustration for the synthesis of the undried hybrid glasses, the hybrid glasses, and the brown hybrid glasses at Him/(Hbim+Him) = 0, 0.25, and 0.5.

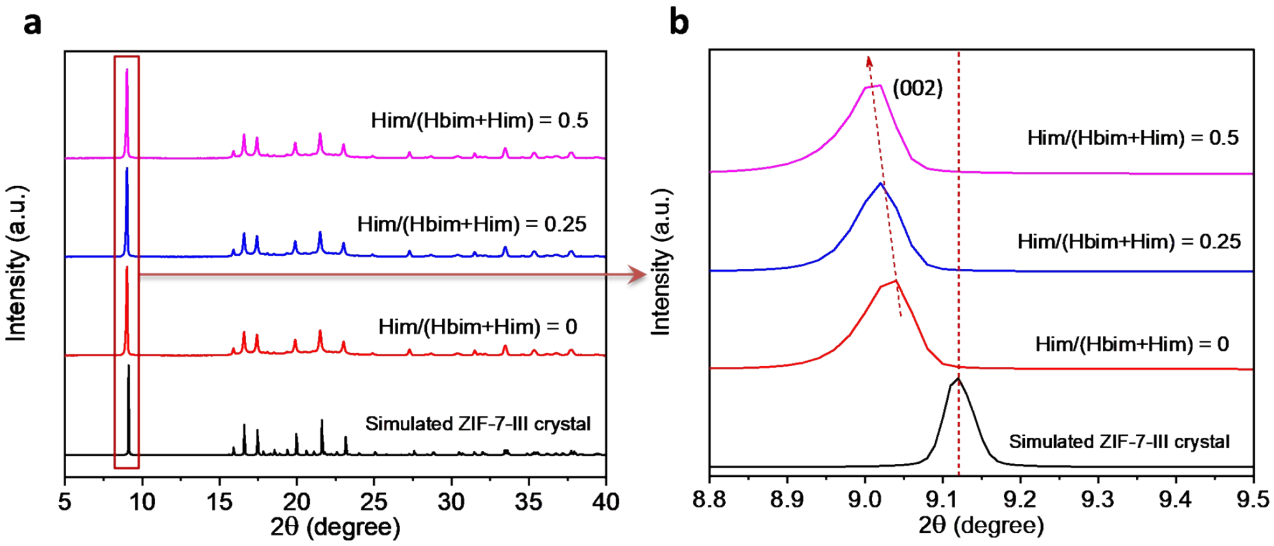

Fig. S2. a, PXRD patterns of the ZIF-7-III crystal at Him/(Hbim+Him) = 0, 0.25, and 0.5 synthesized by dissolution recrystallization method. **b,** The magnified pattern of (**a**) in the range of 8.8-9.5 degree. The observed peak shift in **b** is due to the increase of intermolecular spacing of ZIF-7-III crystal as a result of the substitution of Hbim by Him; where the molecular size of Him is smaller than that of Hbim.

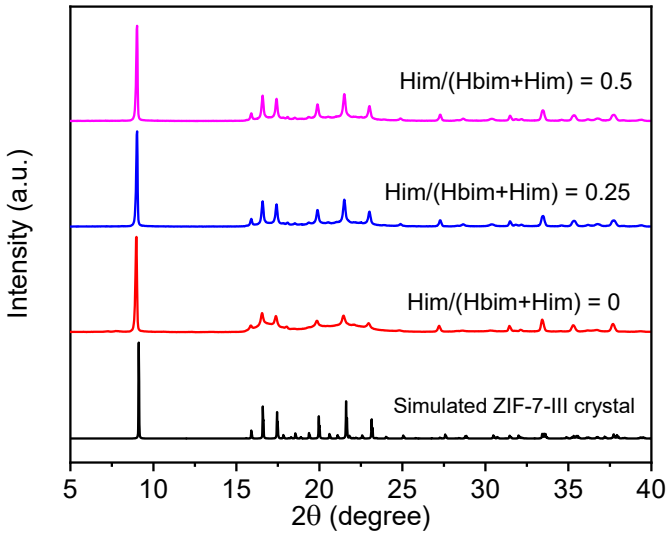

Fig. S3. PXRD patterns of the ZIF-7-III crystal at Him/(Hbim+Him) = 0, 0.25, and 0.5 synthesized by the solvothermal method.

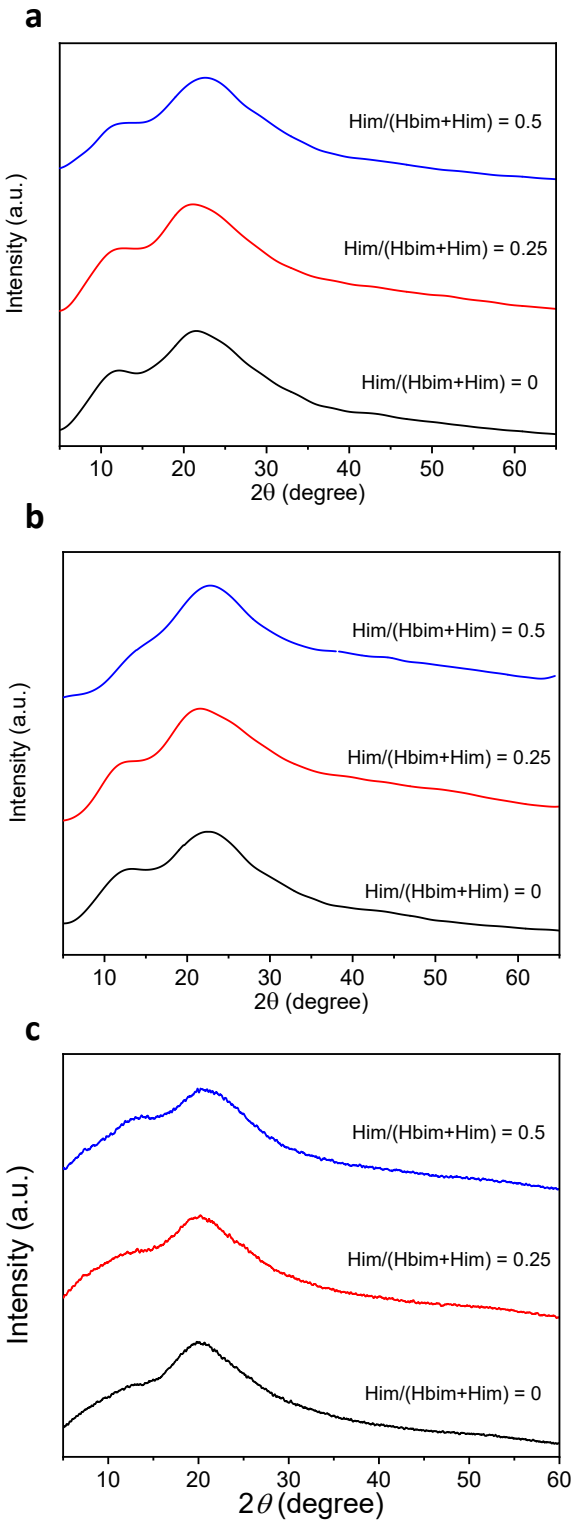

Fig. S4. PXRD patterns of the **a,** undried hybrid glasses, **b,** hybrid glasses, and **c,** brown hybrid glasses at Him/(Hbim+Him) = 0, 0.25, and 0.5.

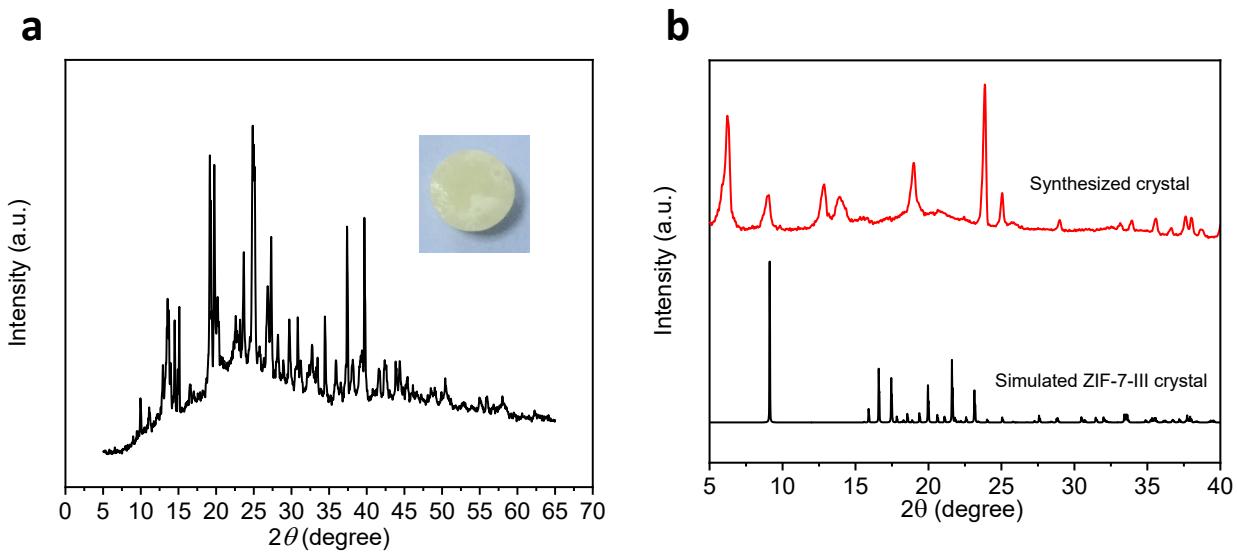

Fig. S5. PXRD patterns of the as-synthesized samples at Him/(Hbim+Him) = 0.75 using **a,** network-solvation method and **b,** solvothermal method. The inset of **a** is a photograph of the corresponding sample.

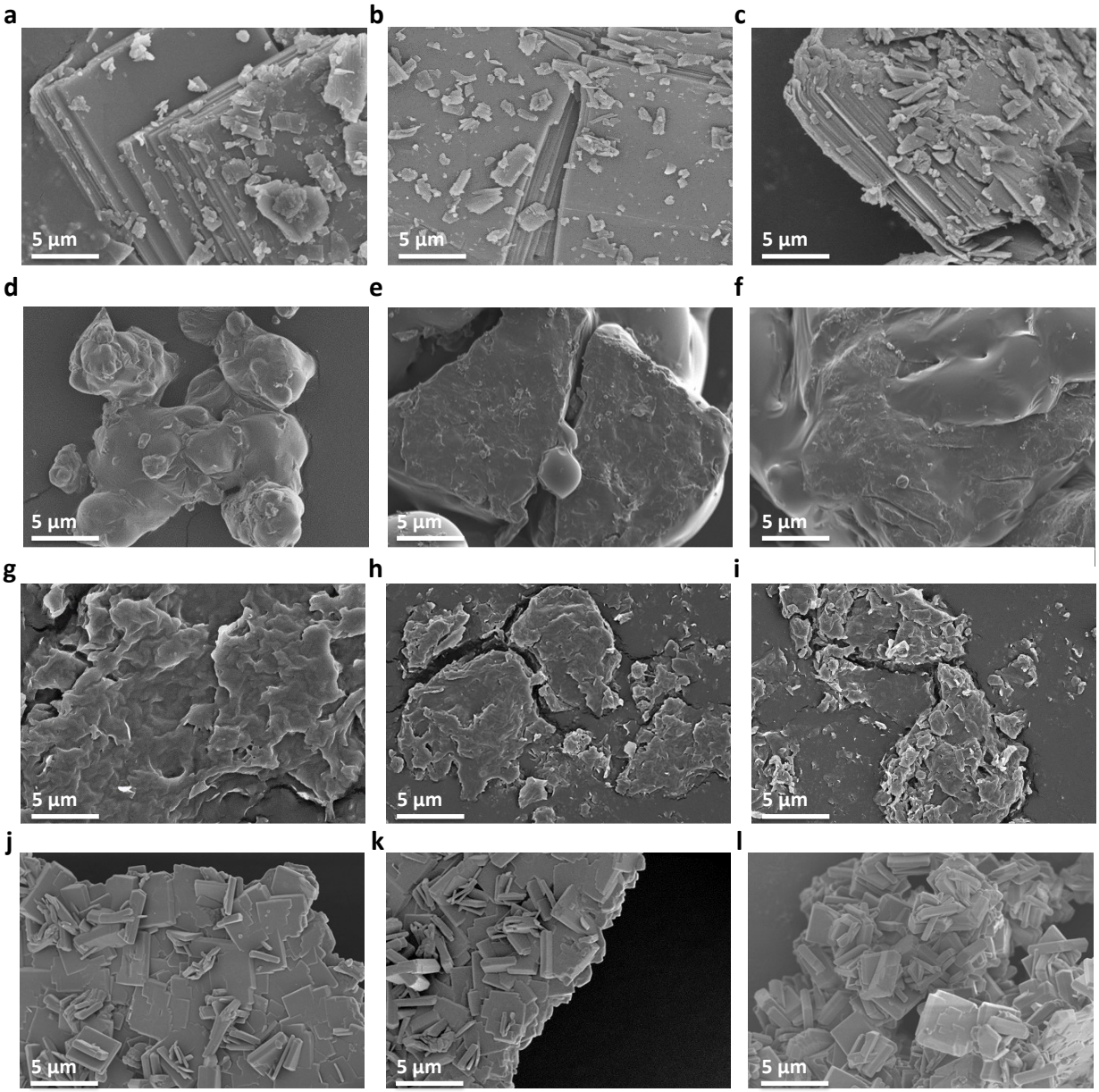

Fig. S6. SEM images of the **a-c**, ZIF-7-III crystals (solvothermal), **d-f**, hybrid glasses (solvation), **g-i**, brown hybrid glasses, and **j-l**, ZIF-7-III crystals (dissolution) at **a, d, g**, **j**, Him/(Hbim+Him) = 0, **b, e, h**, **k**, Him/(Hbim+Him) = 0.25, and **c, f, i**, **l**, Him/(Hbim+Him) = 0.5.

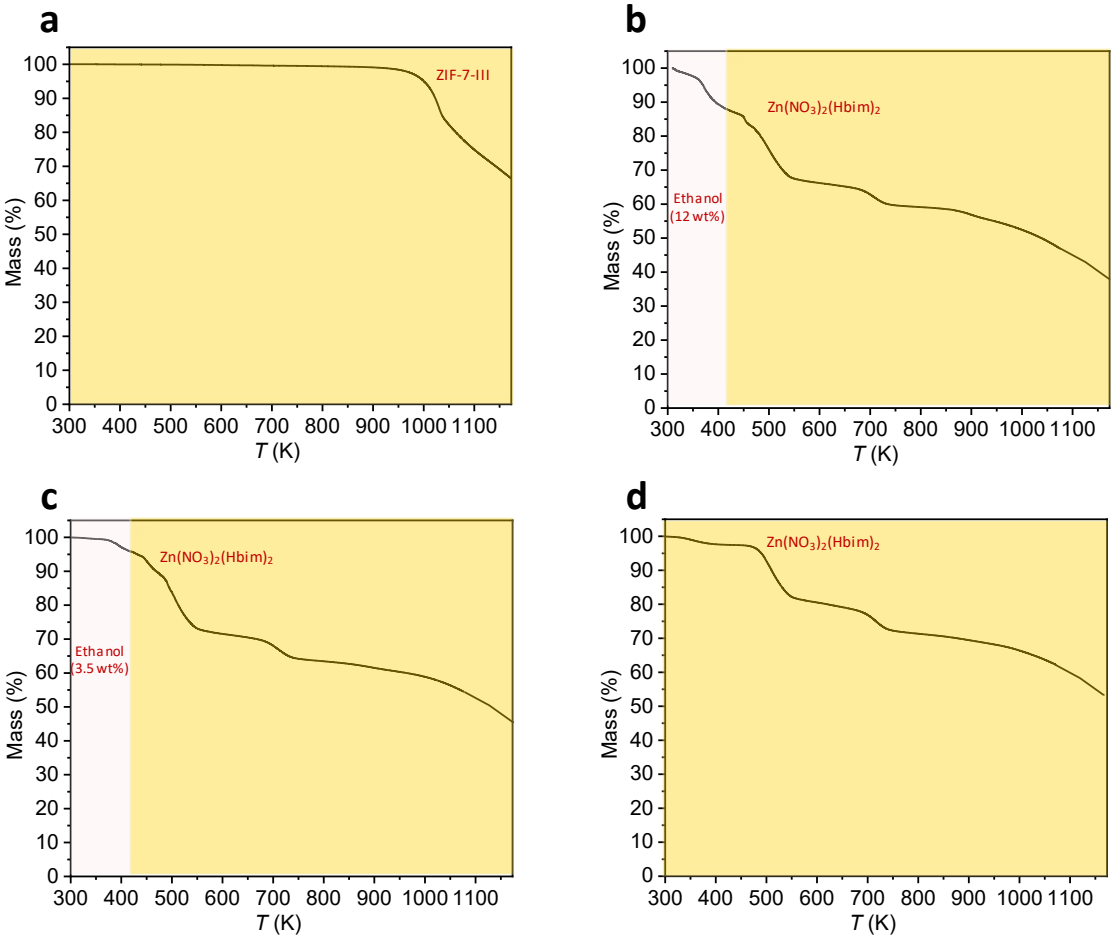

Fig. S7. TGA traces of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0.

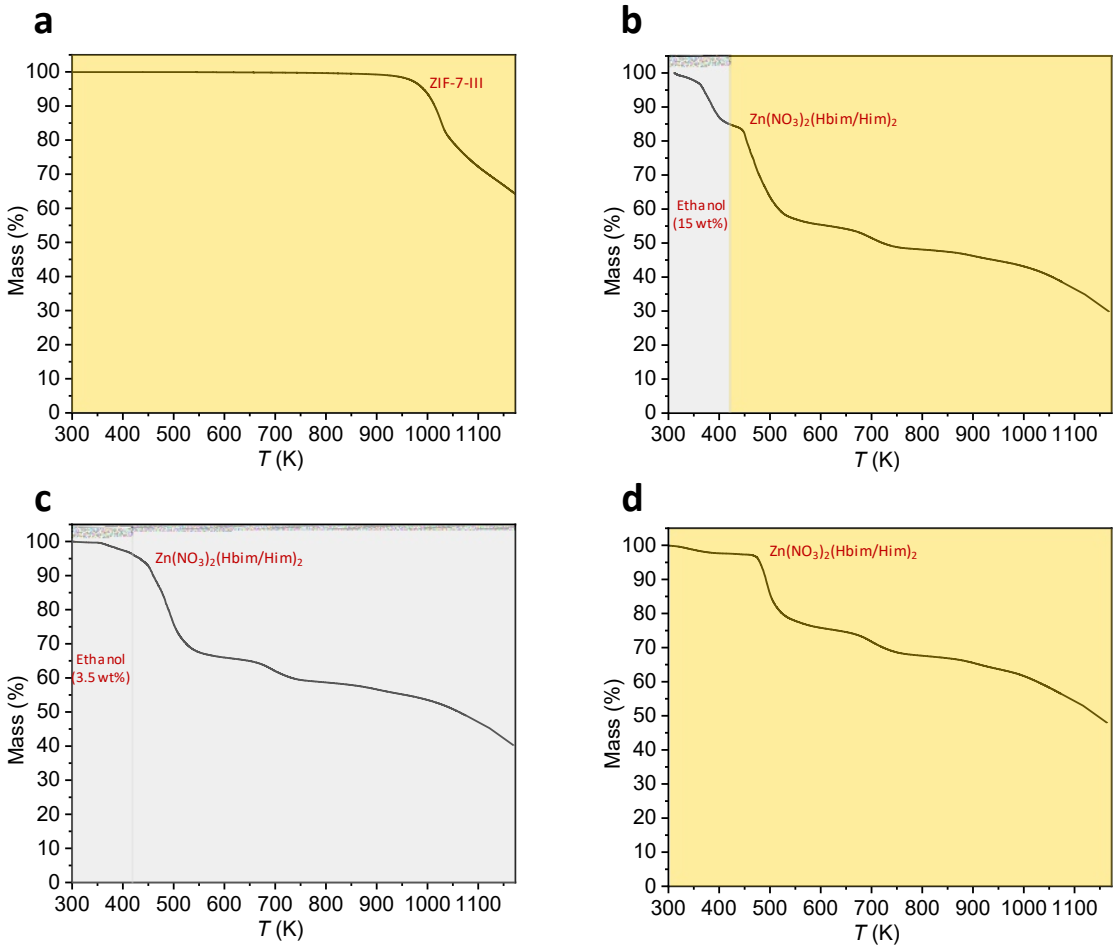

Fig. S8. TGA traces of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0.25.

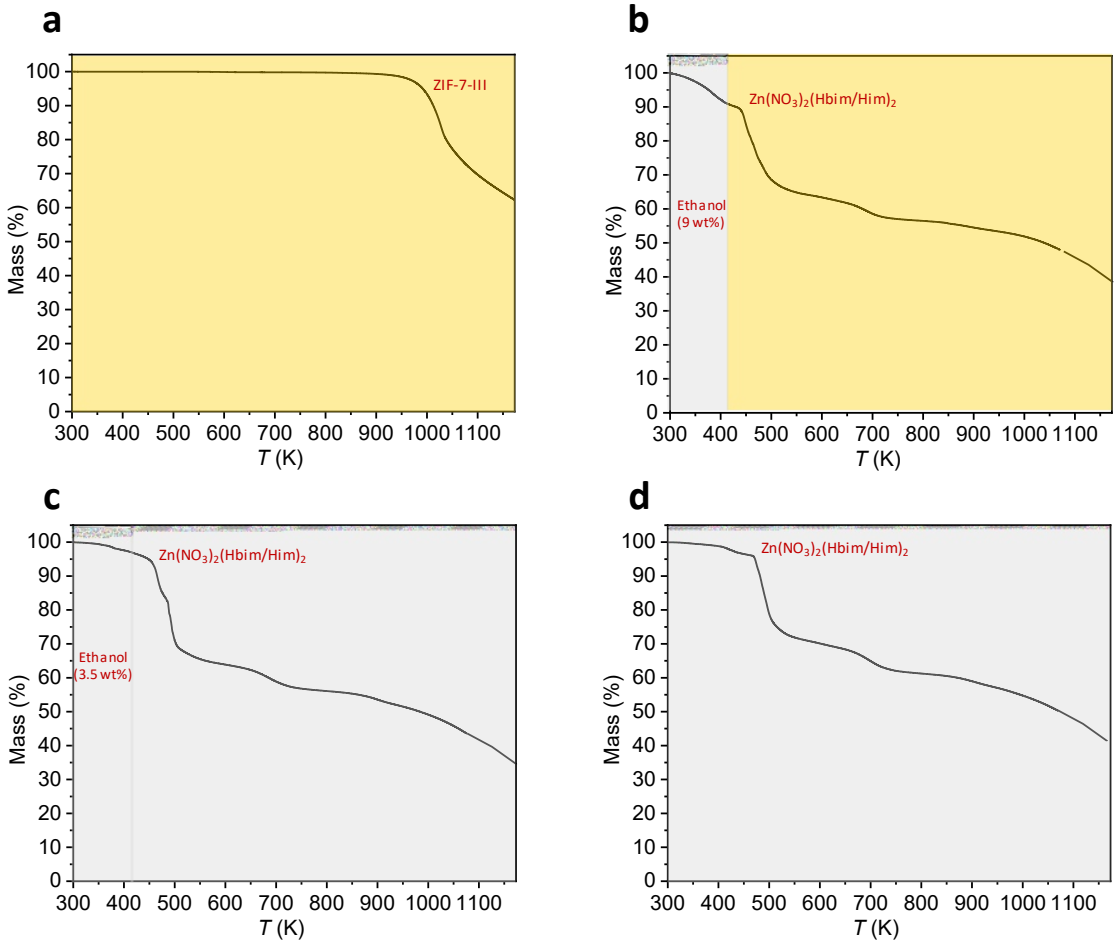

Fig. S9. TGA traces of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0.5.

Table S1. Measured glass compositions based on the TGA traces of the undried hybrid glasses, hybrid glasses, and brown hybrid glasses at different ratios of organic linkers.

Added Him/(Hbim+Him)	**Sample**	**measured by TGA (wt%)**
0	Undried hybrid glass	88 $Zn(NO_3)_2(Hbim)_2$-12 Ethanol
	Hybrid glass	96.5 $Zn(NO_3)_2(Hbim)_2$-3.5 Ethanol
	Brown hybrid glass	100 $Zn(NO_3)_2(Hbim)_2$
0.25	Undried hybrid glass	85 $Zn(NO_3)_2(Hbim/Him)_2$-15 Ethanol
	Hybrid glass	96.5 $Zn(NO_3)_2(Hbim/Him)_2$-3.5 Ethanol
	Brown hybrid glass	100 $Zn(NO_3)_2(Hbim/Him)_2$
0.5	Undried hybrid glass	91 $Zn(NO_3)_2(Hbim/Him)_2$-9 Ethanol
	Hybrid glass	96.5 $Zn(NO_3)_2(Hbim/Him)_2$-3.5 Ethanol
	Brown hybrid glass	100 $Zn(NO_3)_2(Hbim/Him)_2$

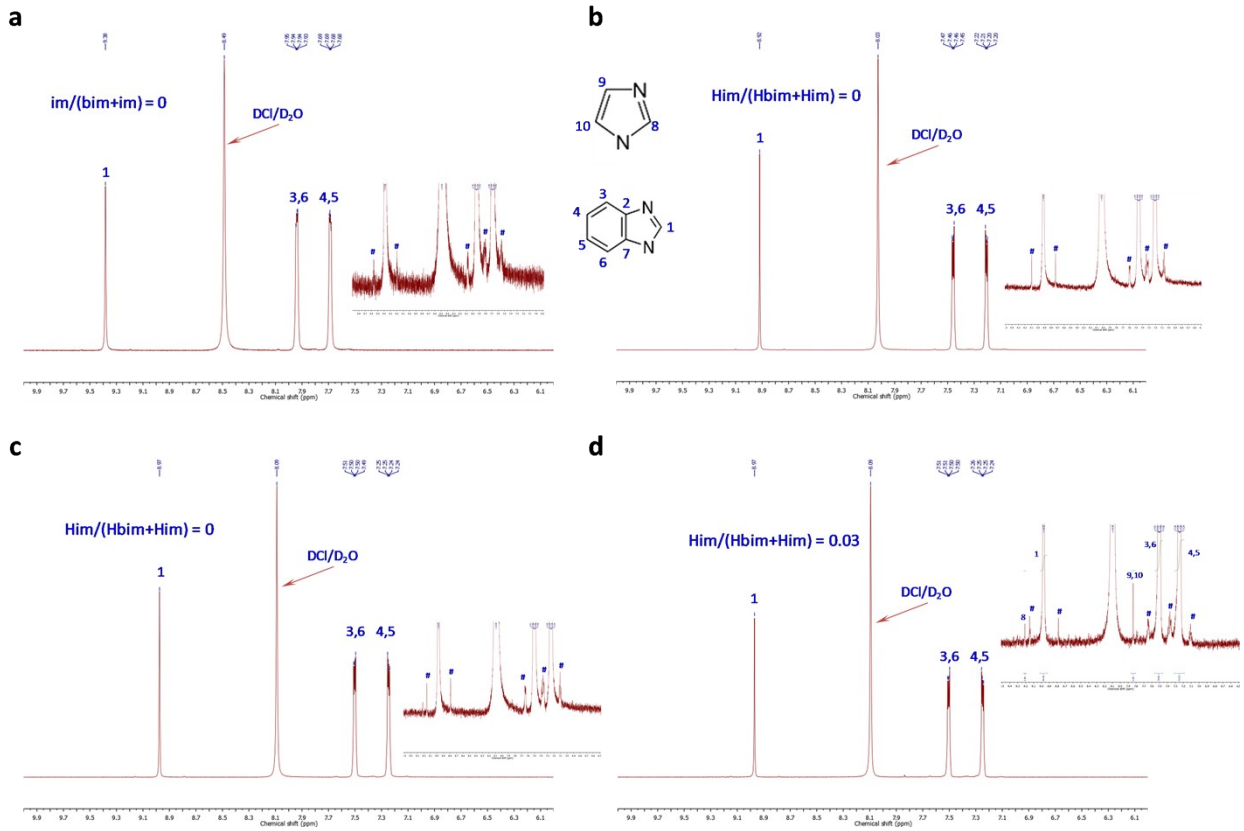

Fig. S10. Solution ^{1}H-NMR spectra of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0. The insets are the magnified ^{1}H-NMR spectra. The normalized proton integration values and the proton peak positions are in green and blue colors, respectively. The marked peaks with # are unknown. The insets are the molecular structures of Him and Hbim.

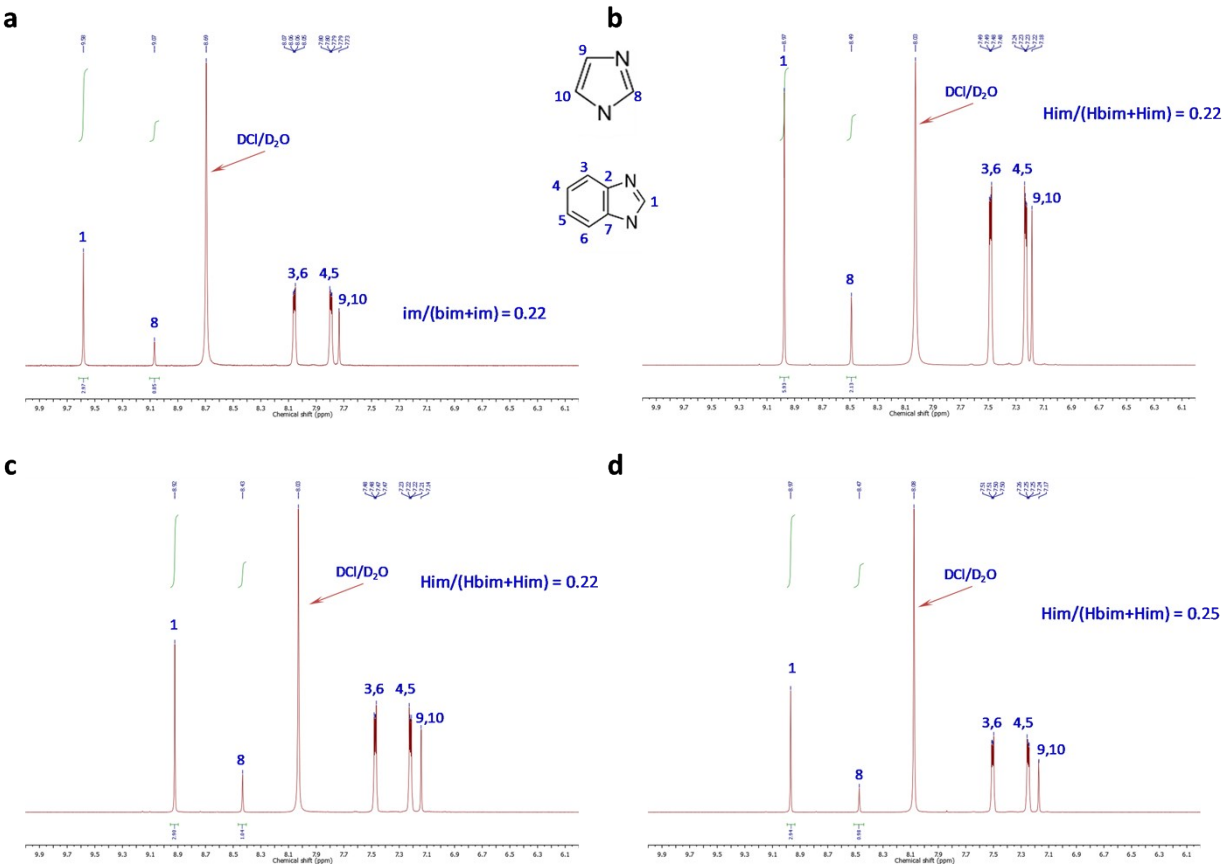

Fig. S11. Solution ^{1}H-NMR spectra of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0.25. The normalized proton integration values and the proton peak positions are in green and blue colors, respectively. The insets are the molecular structures of Him and Hbim.

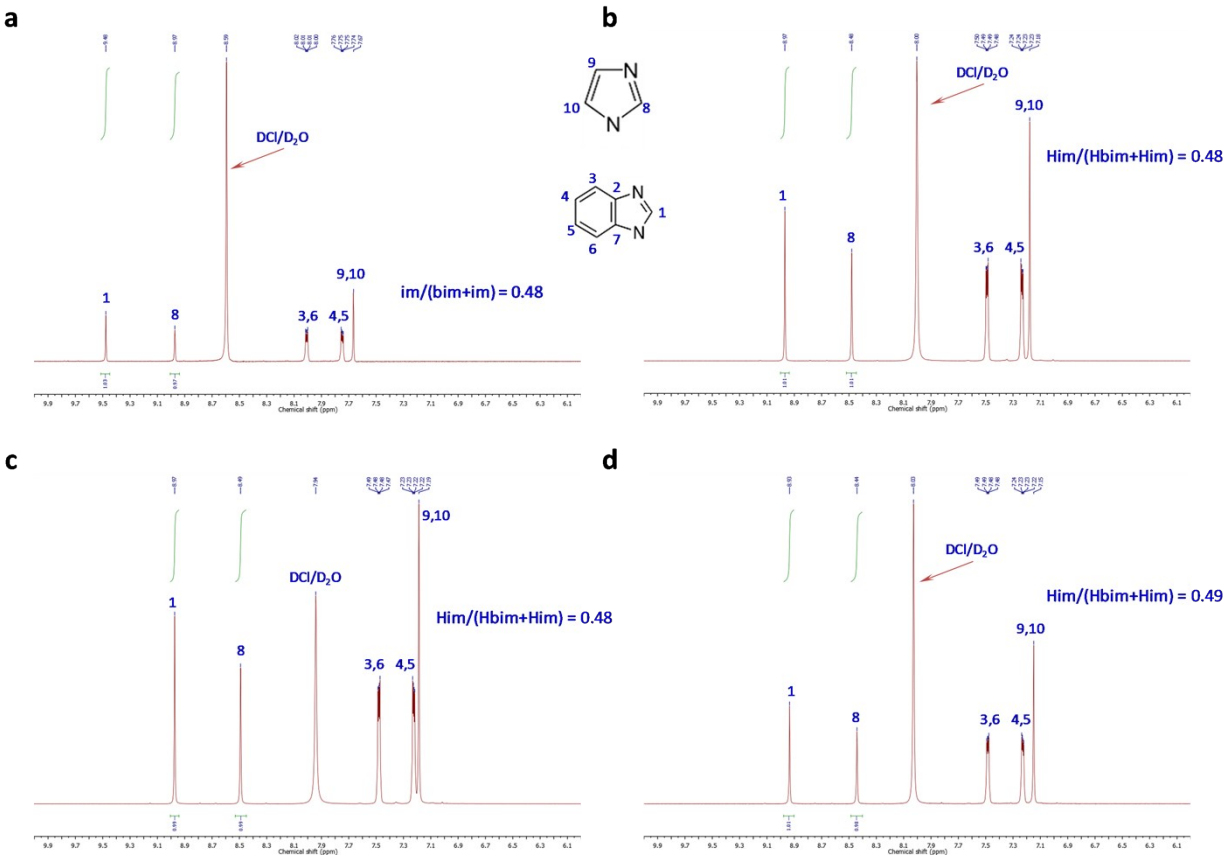

Fig. S12. Solution ^{1}H-NMR spectra of the **a,** ZIF-7-III crystal, **b,** undried hybrid glass, **c,** hybrid glass, and **d,** brown hybrid glass at Him/(Hbim+Him) = 0.5. The normalized proton integration values and the proton peak positions are in green and blue colors, respectively. The insets are the molecular structures of Him and Hbim.

Table S2. Measured Him/(Hbim+Him) ratio and the detailed compositions for the prepared ZIF-7-III crystals, undried hybrid glasses, hybrid glasses, and brown hybrid glasses, based on the TGA, ICP-MS, CHNO, and NMR measurements.

Sample	Added Him/(Hbim+Him)	Measured Him/(Hbim+Him)	Composition (wt%)
ZIF-7-III crystal	0	0	$Zn_2(bim)_4$
Undried hybrid glass	-	0	88 $Zn(NO_3)_2(Hbim)_2$-12 Ethanol
Hybrid glass	-	0	96.5 $Zn(NO_3)_2(Hbim)_2$-3.5 Ethanol
Brown hybrid glass	-	0.03	100 $Zn(NO_3)_2(Hbim)_{1.94}(Him)_{0.06}$
ZIF-7-III crystal	0.25	0.22	$Zn_2(bim)_{3.22}(im)_{0.88}$
Undried hybrid glass	-	0.22	85 $Zn(NO_3)_2(Hbim)_{1.61}(Him)_{0.44}$-15 Ethanol
Hybrid glass	-	0.22	96.5 $Zn(NO_3)_2(Hbim)_{1.61}(Him)_{0.44}$-3.5 Ethanol
Brown hybrid glass	-	0.25	100 $Zn(NO_3)_2(Hbim)_{1.5}(Him)_{0.5}$
ZIF-7-III crystal	0.5	0.48	$Zn_2(bim)_{2.08}(im)_{1.92}$
Undried hybrid glass	-	0.48	91 $Zn(NO_3)_2(Hbim)_{1.04}(Him)_{0.96}$-9 Ethanol
Hybrid glass	-	0.48	96.5 $Zn(NO_3)_2(Hbim)_{1.04}(Him)_{0.96}$-3.5 Ethanol
Brown hybrid glass	-	0.49	100 $Zn(NO_3)_2(Hbim)_{1.02}(Him)_{0.98}$

Table S3. Results of elemental analysis for the as-synthesized ZIF-7-III crystals, undried hybrid glasses, hybrid glasses, and brown hybrid glasses at different ratios of organic linkers.

Measured Him/(Hbim+Him)	Sample	measured (CHNO+ICP-MS) (wt%)					Calculated (wt%)					Composition (wt%)
		Zn	C	H	N	O	Zn	C	H	N	O	
0	ZIF-7-III crystal	22.65	55.35	3.33	18.89	<0.01	21.84	56.11	3.34	18.71	-	$Zn_2(bim)_4$
0	Undried hybrid glass	14.05	40.44	3.99	17.19	24.39	13.52	41.02	4.05	17.38	24.03	88 $Zn(NO_3)_2(Hbim)_2$-12 Ethanol
0	Hybrid glass	15.49	39.16	3.12	18.93	23.31	14.83	39.94	3.18	19.06	22.99	96.5 $Zn(NO_3)_2(Hbim)_2$-3.5 Ethanol
0.03	Brown hybrid glass	15.89	39.65	3.01	19.09	23.12	15.37	39.49	2.82	19.75	22.57	100 $Zn(NO_3)_2(Hbim)_{1.94}(Him)_{0.06}$
0.22	ZIF-7-III crystal	24.12	52.02	3.27	20.55	<0.01	23.83	52.48	3.28	20.41	-	$Zn_2(bim)_{3.22}(im)_{0.88}$
0.22	Undried hybrid glass	14.05	37.8	4.21	17.88	26.11	13.88	38.4	4.29	17.83	25.6	85 $Zn(NO_3)_2(Hbim)_{1.61}(Him)_{0.44}$-15 Ethanol
0.22	Hybrid glass	16.02	35.82	3.05	20.27	24.93	15.75	36.53	3.11	20.25	24.36	96.5 $Zn(NO_3)_2(Hbim)_{1.61}(Him)_{0.44}$-3.5 Ethanol
0.25	Brown hybrid glass	16.15	35.51	2.95	20.51	24.88	16.33	35.97	2.75	20.98	23.98	100 $Zn(NO_3)_2(Hbim)_{1.5}(Him)_{0.5}$
0.48	ZIF-7-III crystal	26.95	47.72	3.19	22.63	<0.01	26.22	48.12	3.21	22.45	-	$Zn_2(bim)_{2.08}(im)_{1.92}$
0.48	Undried hybrid glass	16.22	33.15	3.55	20.59	27.03	15.85	33.79	3.6	20.36	26.4	91 $Zn(NO_3)_2(Hbim)_{1.04}(Him)_{0.96}$-9 Ethanol
0.48	Hybrid glass	17.16	31.99	2.99	21.94	26.52	16.81	32.67	3.03	21.6	25.89	96.5 $Zn(NO_3)_2(Hbim)_{1.04}(Him)_{0.96}$-3.5 Ethanol
0.49	Brown hybrid glass	17.34	31.85	2.85	22.12	26.42	17.41	31.97	2.66	22.37	25.57	100 $Zn(NO_3)_2(Hbim)_{1.02}(Him)_{0.98}$

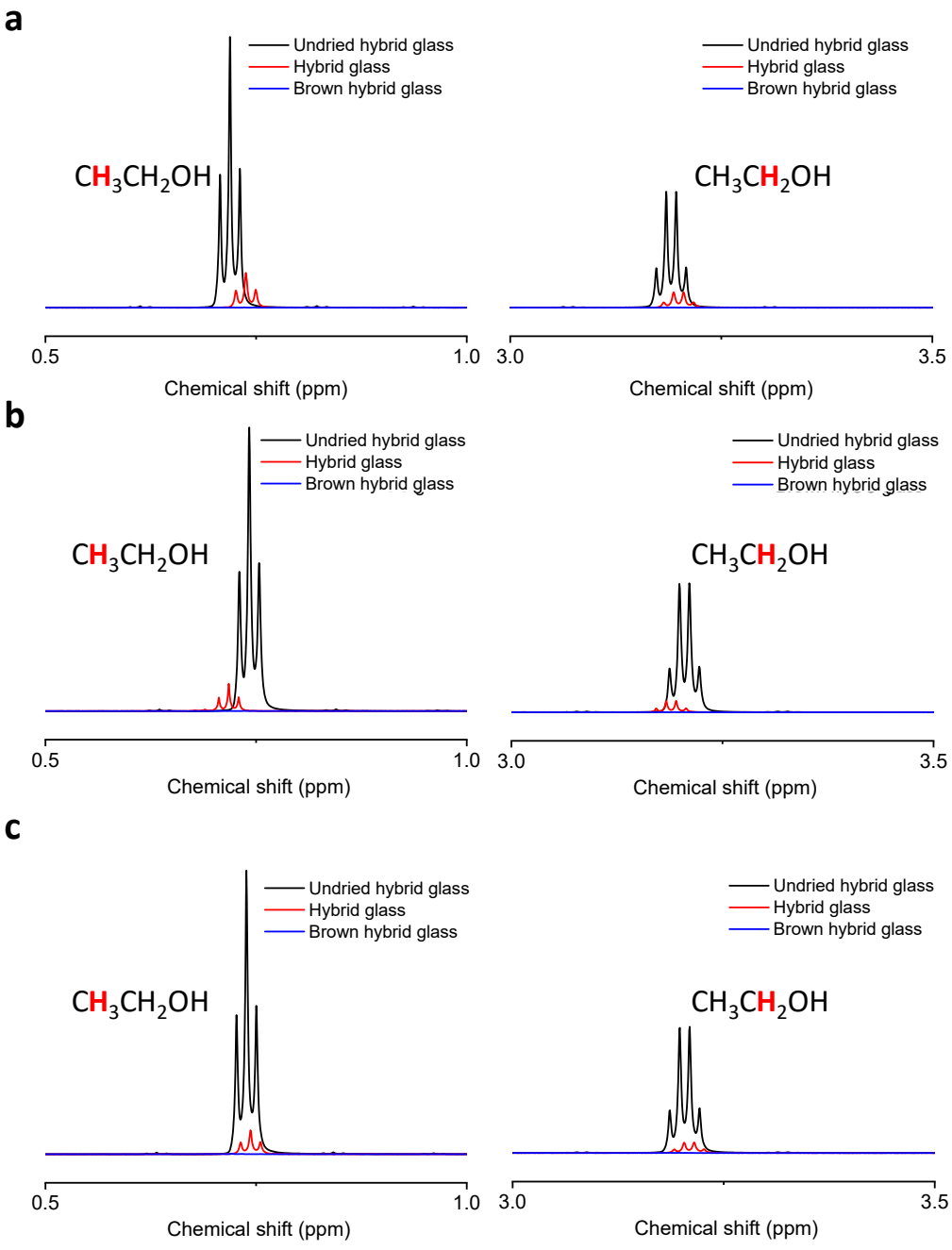

Fig. S13. Solution ^{1}H-NMR spectra of the undried hybrid glasses, hybrid glasses, and brown hybrid glasses at **a,** Him/(Hbim+Him) = 0, **b,** Him/(Hbim+Him) = 0.25, and **c,** Him/(Hbim+Him) = 0.5.

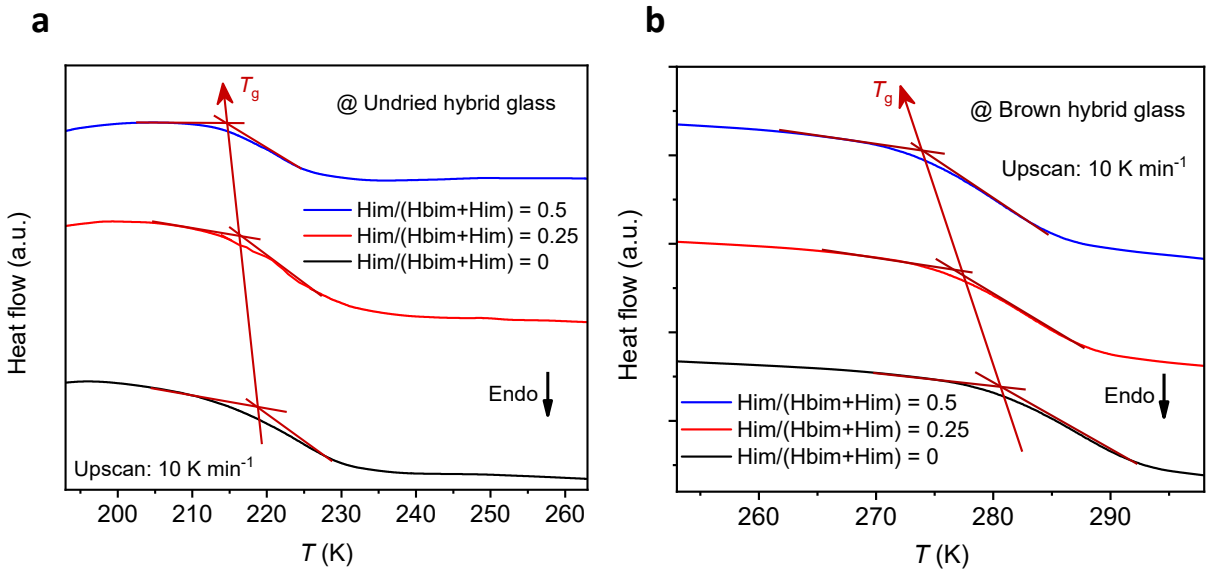

Fig. S14. DSC traces of the **a,** undried hybrid glasses and **b,** brown hybrid glasses at Him/(Hbim+Him) = 0, 0.25, and 0.5.

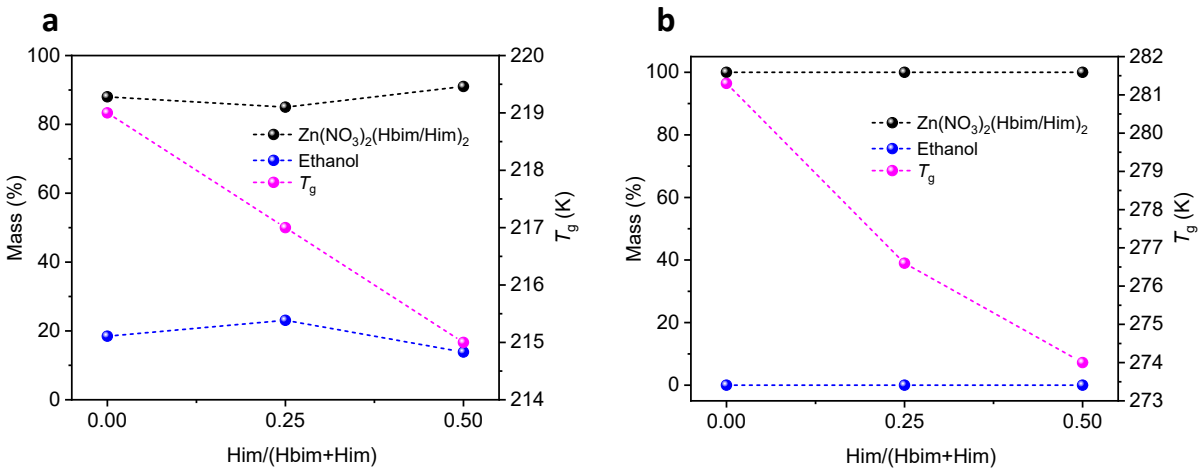

Fig. S15. The composition of the as-synthesized glasses and the T_g value as a function of the organic linkers ratio for **a,** undried hybrid glasses and **b,** brown hybrid glasses.

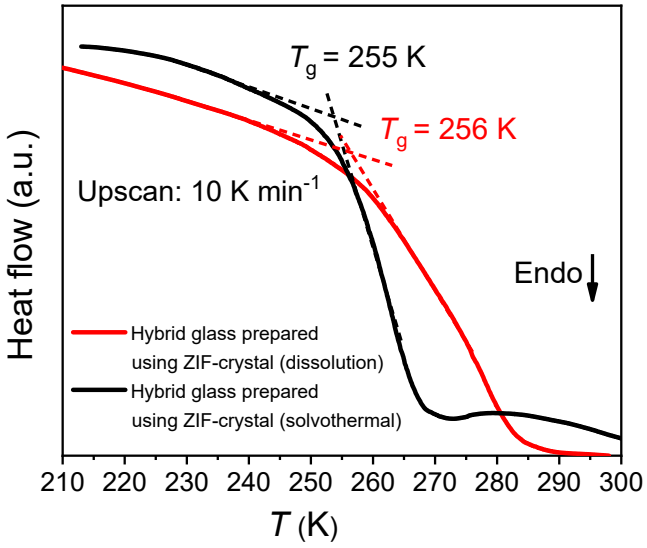

Fig. S16. DSC traces of the prepared hybrid glasses using ZIF-7-III crystals that prepared by solvothermal and dissolution-recrystallization methods at Him/(Hbim+Him) = 0.

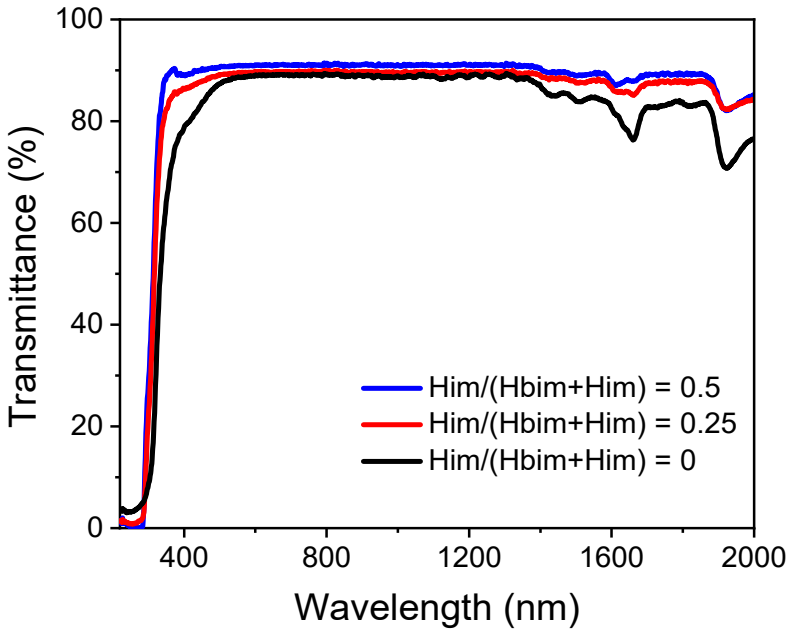

Fig. S17. UV-Vis-NIR transmission spectra of the hybrid glasses with a 1 mm in thickness at Him/(Hbim+Him) = 0, 0.25, and 0.5.

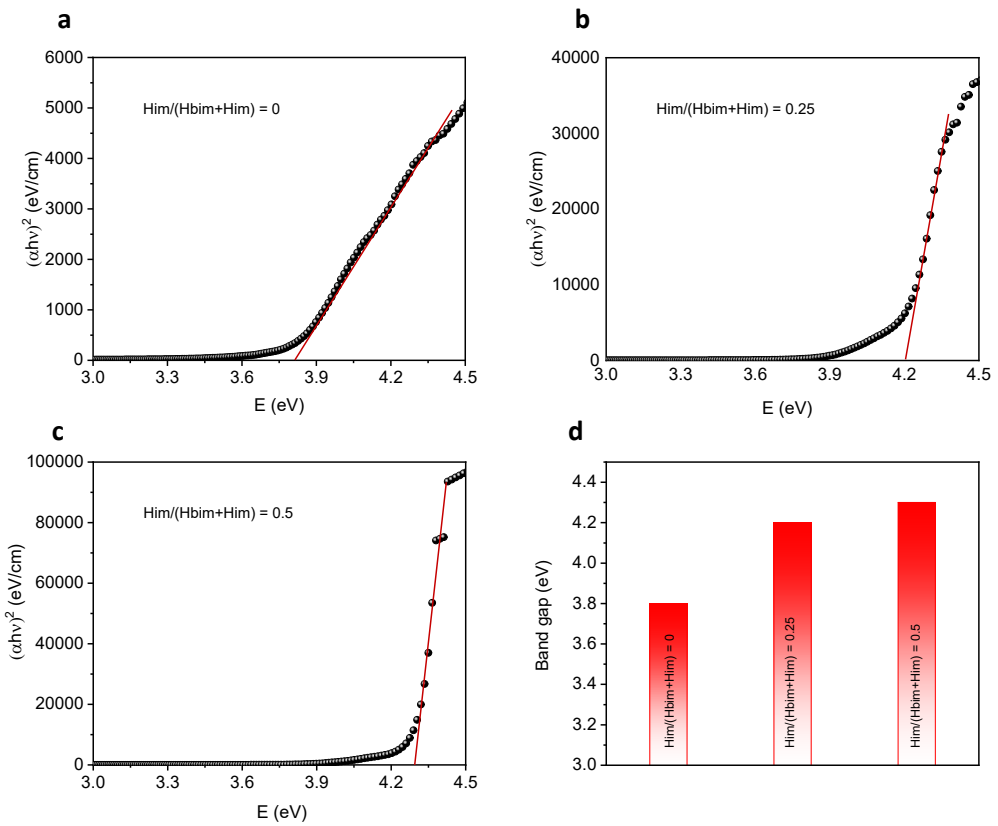

Fig. S18. Tauc's plot of the hybrid glasses at **a,** Him/(Hbim+Him) = 0, **b,** Him/(Hbim+Him) = 0.25, and **c,** Him/(Hbim+Him) = 0.5. **d,** Dependence of the band gap of glass on the organic linkers ratio.

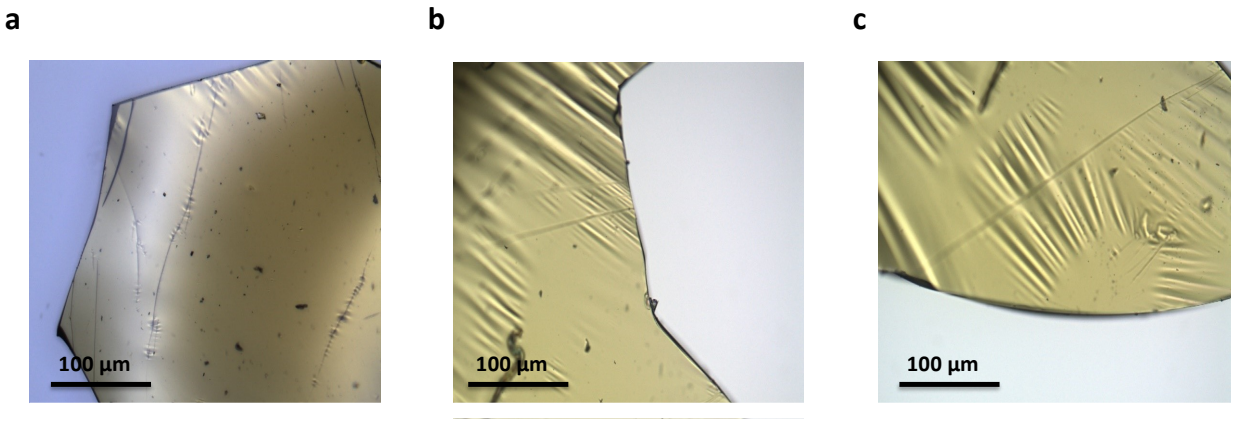

Fig. S19. Optical images of the brown hybrid glasses at **a,** Him/(Hbim+Him) = 0, **b,** Him/(Hbim+Him) = 0.25, and **c,** Him/(Hbim+Him) = 0.5.

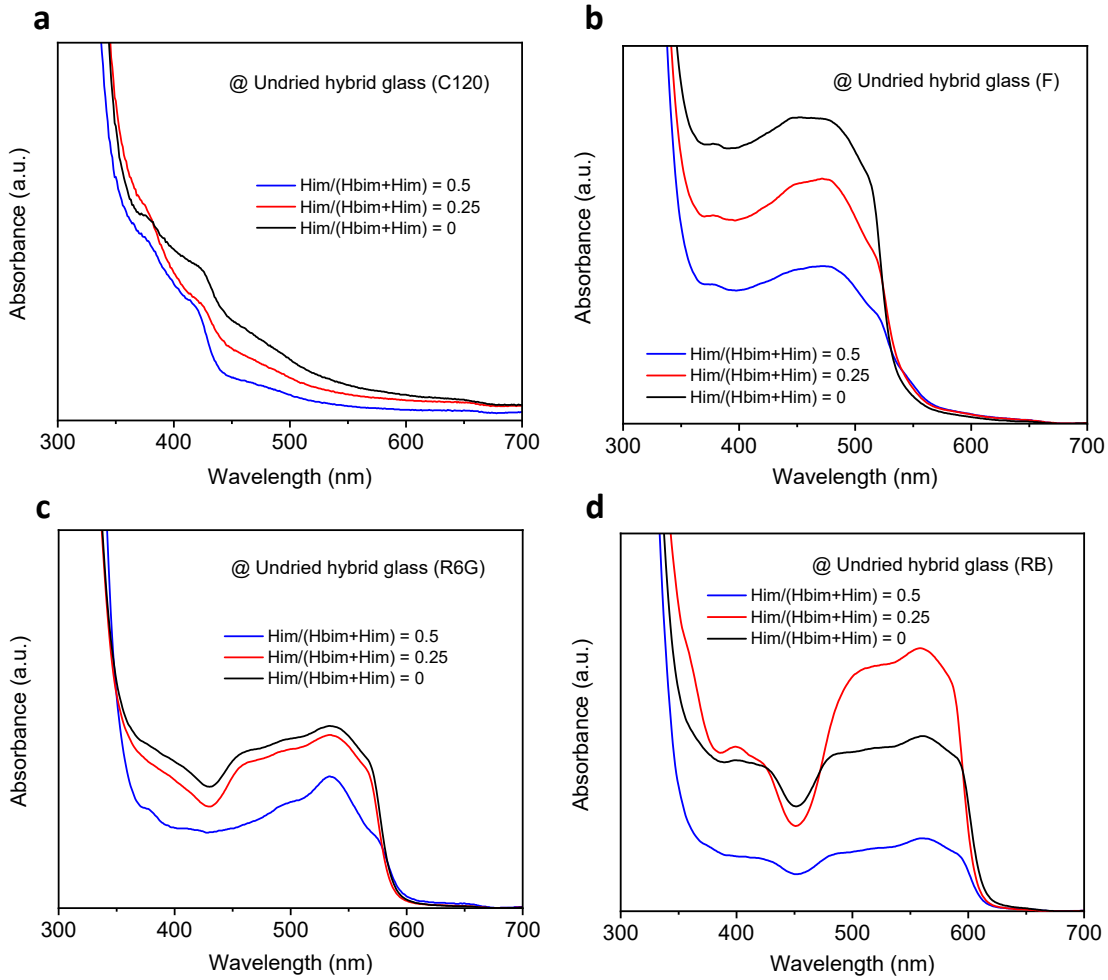

Fig. S20. UV-Vis absorption spectra of the undried hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

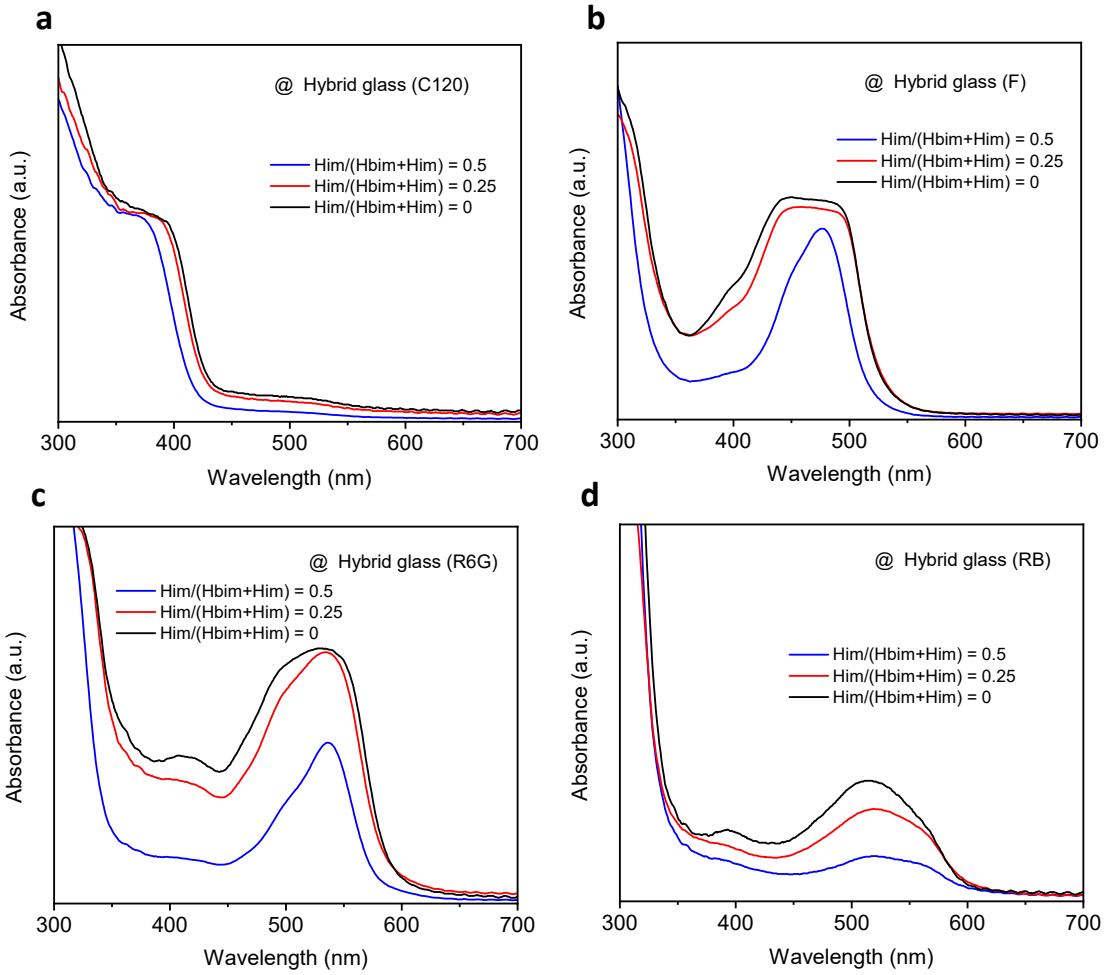

Fig. S21. UV-Vis absorption spectra of the hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

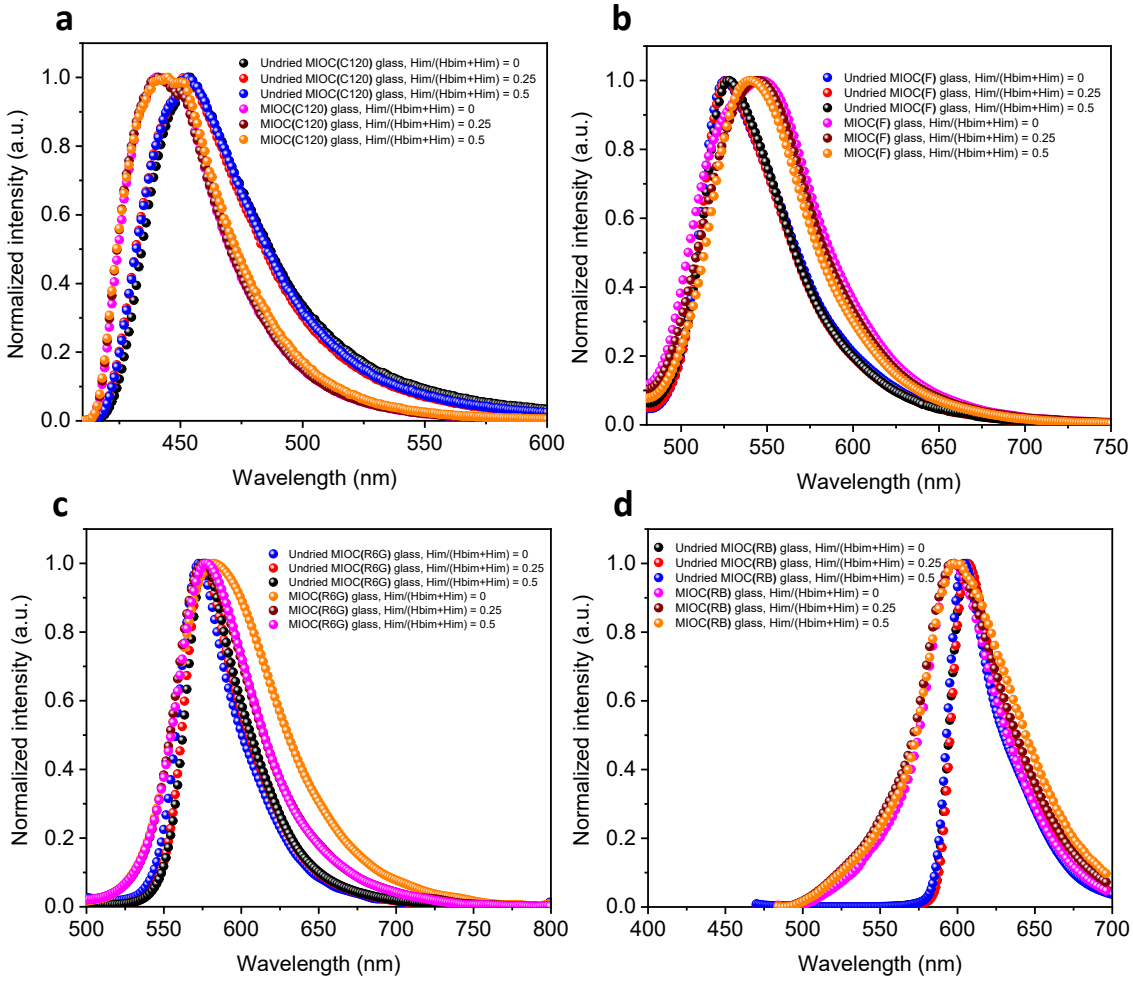

Fig. S22. PL spectra the undried hybrid glasses and hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

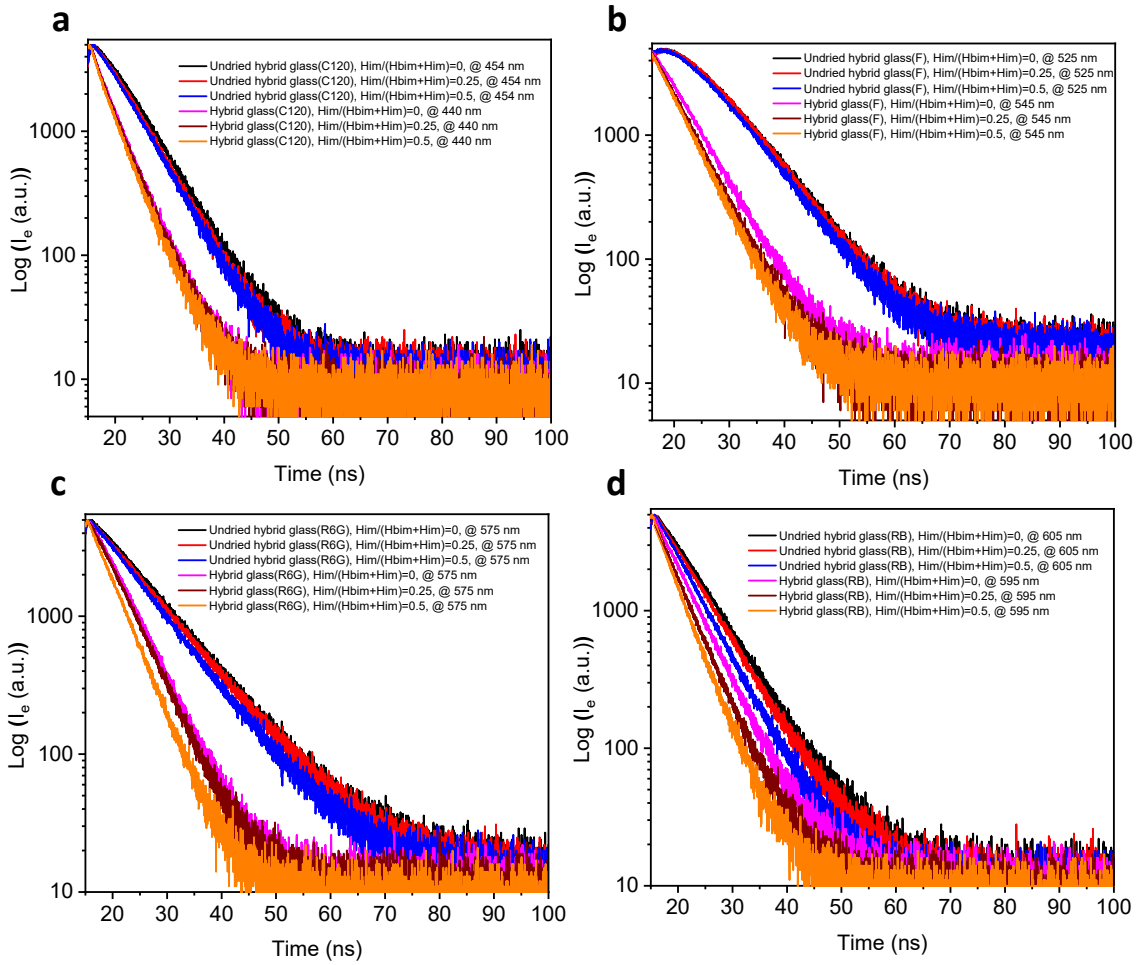

Fig. S23. PL decay curves of the undried hybrid glasses and hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

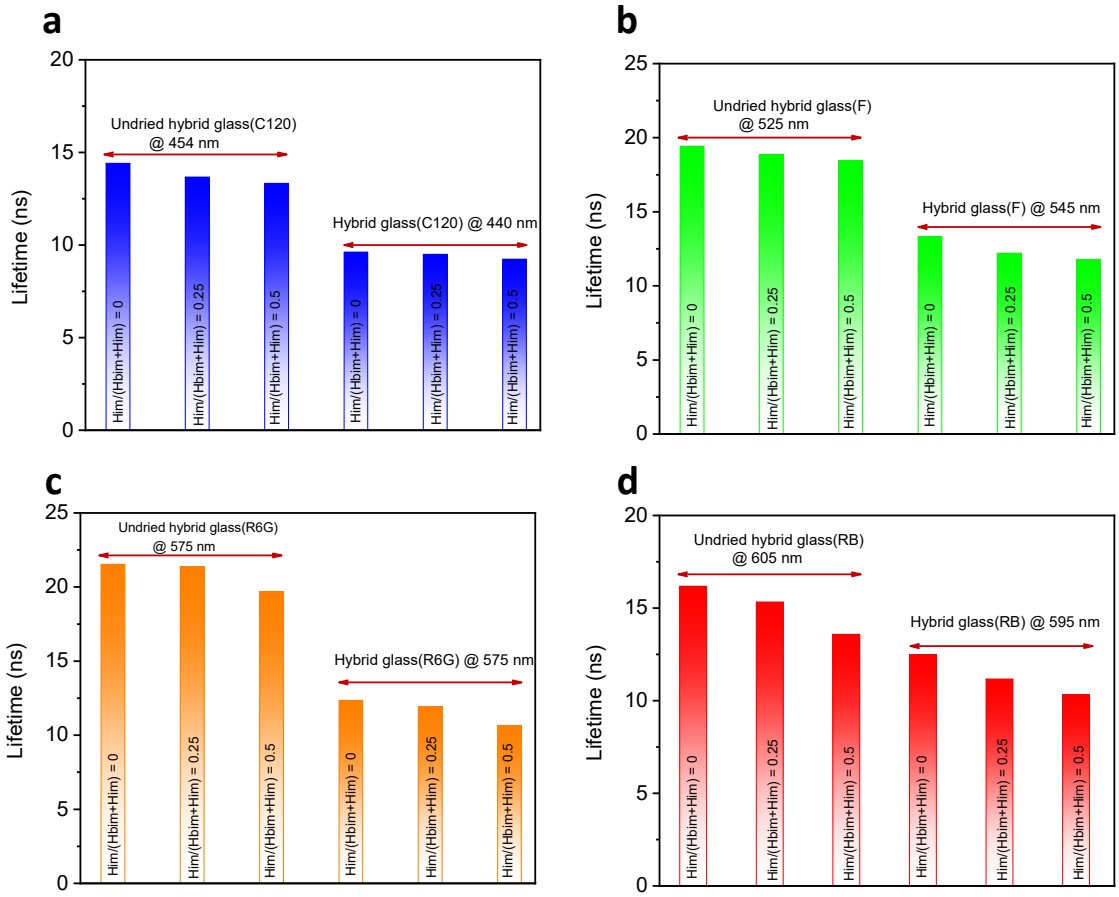

Fig. S24. Lifetime values of the undried hybrid glasses and hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

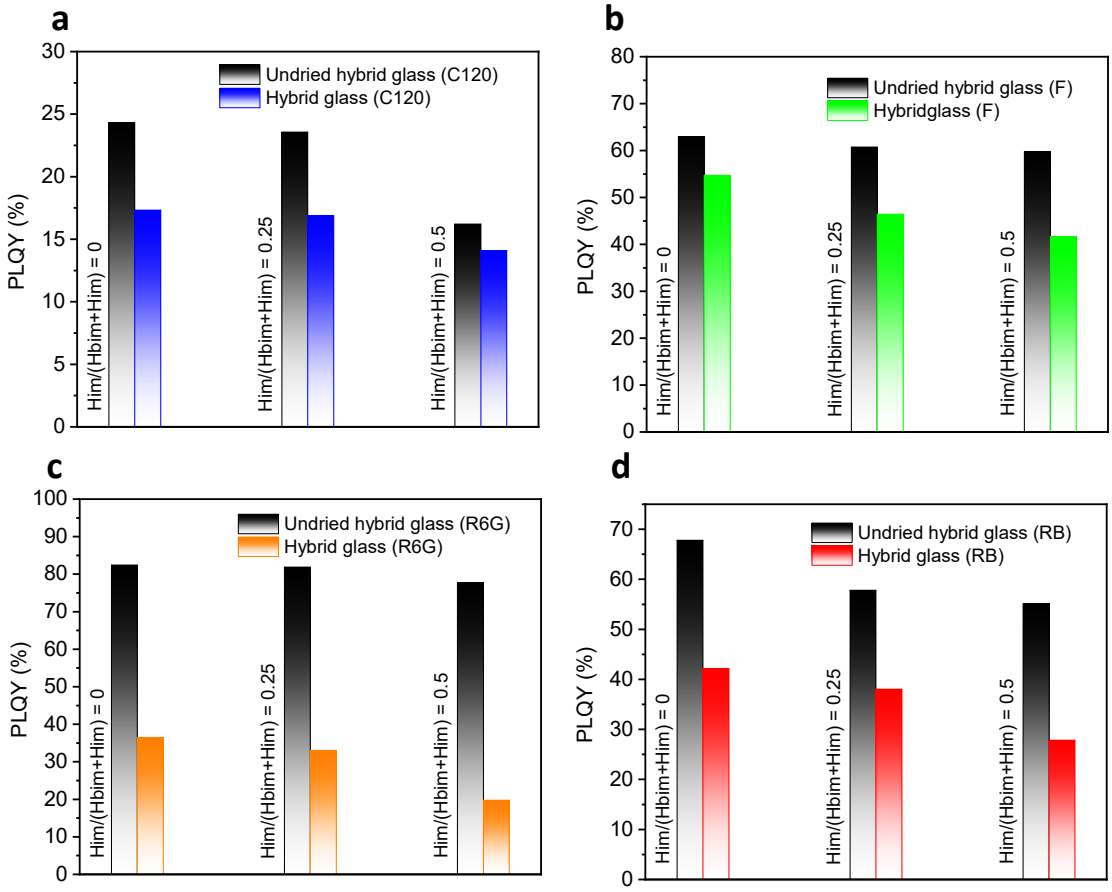

Fig. S25. PLQY of the undried hybrid glasses and hybrid glasses doped with **a,** C120, **b.** F, **c,** R6G, and **d,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5.

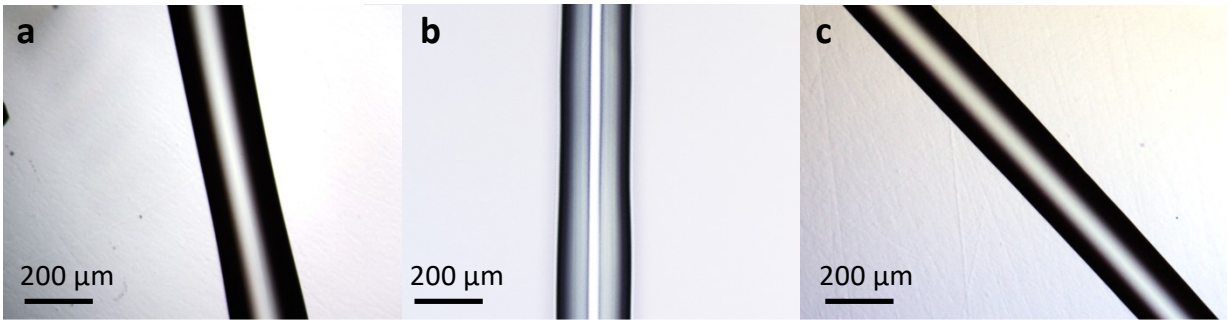

Fig. S26. Optical microscope images of the undoped hybrid glass fiber at **a,** Him/(Hbim+Him) = 0, **b,** Him/(Hbim+Him) = 0.25, and **c)** Him/(Hbim+Him) = 0.5.

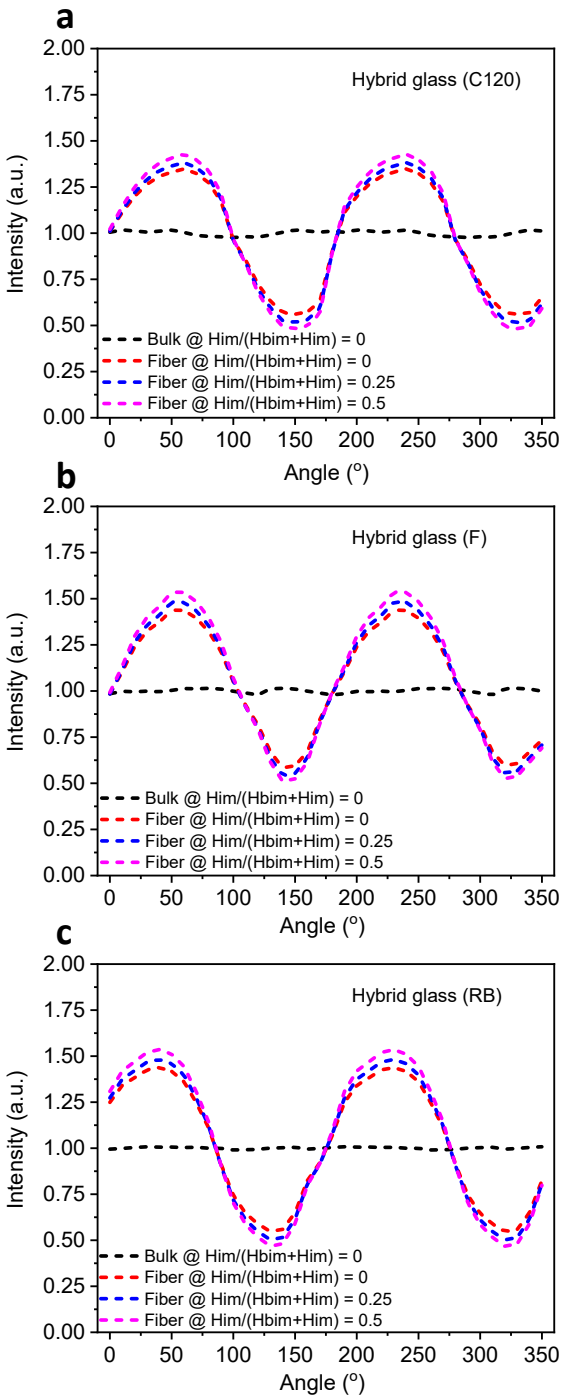

Fig. S27. The variation of integrated PL intensity with different polarization angles for the dried hybrid fiber and bulk glass doped with **a,** C120, **b,** F, and **c,** RB at Him/(Hbim+Him) = 0, 0.25, and 0.5, under the excitation of polarized laser parallel to the fiber axis. The glass fibers doped with C120, F, and RB (a diameter of 200 μm) and bulk glasses were excited by 405 nm and 460 nm polarized lasers, respectively.