

Supporting Information for

**Structural factors determining thermal stability limits of ionic liquid/MOF composites:
Imidazolium ionic liquids combined with CuBTC and ZIF-8**

Muhammad Zeeshan,^{†,‡} Vahid Nozari,^{†,‡} Seda Keskin,^{*,†,‡} and Alper Uzun^{*,†,‡,ξ}

[†]*Department of Chemical and Biological Engineering, Koç University, Rumelifeneri Yolu, 34450*

Sarıyer, İstanbul, Turkey

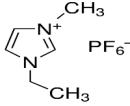
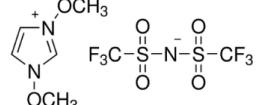
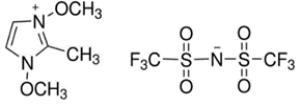
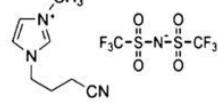
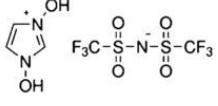
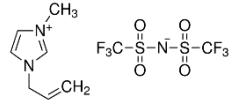
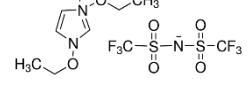
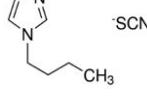
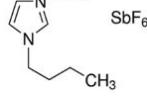
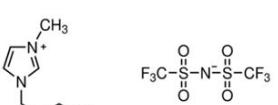
[‡]*Koç University TÜPRAŞ Energy Center (KUTEM), Koç University, Rumelifeneri Yolu, 34450*

Sarıyer, İstanbul, Turkey

^ξ*Koç University Surface Science and Technology Center (KUYTAM), Koç University,*

Rumelifeneri Yolu, Sarıyer, 34450 İstanbul, Turkey;

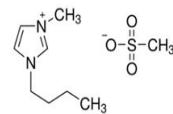
Table S1. Names and molecular structures of the imidazolium based ILs considered in this work.

Name of IL	Cation	Anion	Molecular structure
1-Ethyl-3-methylimidazolium hexafluorophosphate	[EMIM]	[PF ₆] ⁻	
1,3-Dimethoxyimidazolium bis(trifluoromethyl-sulfonyl)imide	[(MeO) ₂ IM]	[NTf ₂] ⁻	
1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide	[(MeO) ₂ MIM]	[NTf ₂] ⁻	
1-(3-Cyanopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[CPMIM]	[NTf ₂] ⁻	
1,3-Dihydroxyimidazolium bis(trifluoromethylsulfonyl)imide	[(OH) ₂ IM]	[NTf ₂] ⁻	
1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[AllylMIM]	[NTf ₂] ⁻	
1,3-Diethoxyimidazolium bis(trifluoromethylsulfonyl)imide	[(EtO) ₂ IM]	[NTf ₂] ⁻	
1-Butyl-3-methylimidazolium thiocyanate	[BMIM]	[SCN] ⁻	
1-Butyl-3-methylimidazolium hexafluoroantimonate	[BMIM]	[SbF ₆] ⁻	
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BMIM]	[NTf ₂] ⁻	

1-Butyl-3-methylimidazolium
methanesulfonate

[BMIM]

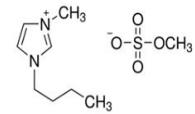
[MeSO₃]



1-Butyl-3-methylimidazolium
methyl sulfate

[BMIM]

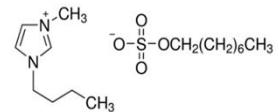
[MeSO₄]



1-Butyl-3-methylimidazolium
Octyl sulfate

[BMIM]

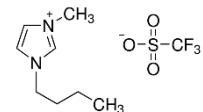
[OcSO₄]



1-Butyl-3-methylimidazolium
trifluoromethanesulfonate

[BMIM]

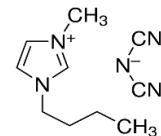
[CF₃SO₃]



1-Butyl-3methylimidazolium
dicyanamide

[BMIM]

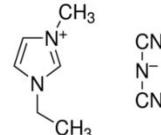
[DCA]



1-Ethyl-3-Methylimidazolium
dicyanamide

[EMIM]

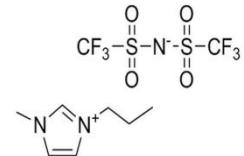
[DCA]



1-Methyl-3-propylimidazolium
bis(trifluoromethylsulfonyl)imide

[MPMIM]

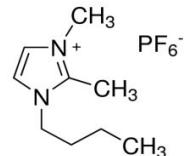
[NTf₂]



1-Butyl-2,3-dimethylimidazolium
hexafluorophosphate

[BMMIM]

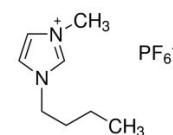
[PF₆]



1-Butyl-3-methylimidazolium
hexafluorophosphate

[BMIM]

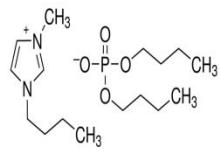
[PF₆]



1-Butyl-3-methylimidazolium
dibutylphosphate

[BMIM]

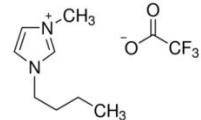
[DBP]



1-Butyl-3-methylimidazolium
trifluoracetate

[BMIM]

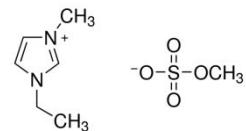
[TFA]



1-Ethyl-3-methylimidazolium
methylsulfate

[EMIM]

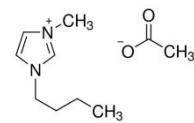
[MESO₄]



1-Butyl-3-methylimidazolium
acetate

[BMIM]

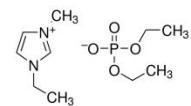
[AC]



1-Ethyl-3-methylimidazolium
diethyl phosphate

[EMIM]

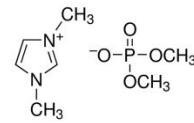
[DEP]



1,3-Dimethylimidazolium
dimethyl phosphate

[DMIM]

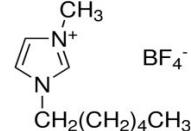
[DMP]



1-Hexyl-3-methylimidazolium
tetrafluoroborate

[HMIM]

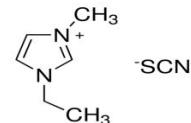
[BF₄]



1-Ethyl-3-methylimidazolium
thiocyanate

[EMIM]

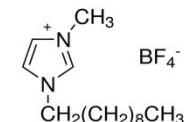
[SCN]



1-Decyl-3-methylimidazolium
tetrafluoroborate

[C₁₀MIM]

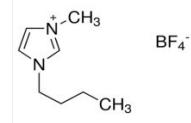
[BF₄]



1-Butyl-3-methylimidazolium
tetrafluoroborate

[BMIM]

[BF₄]



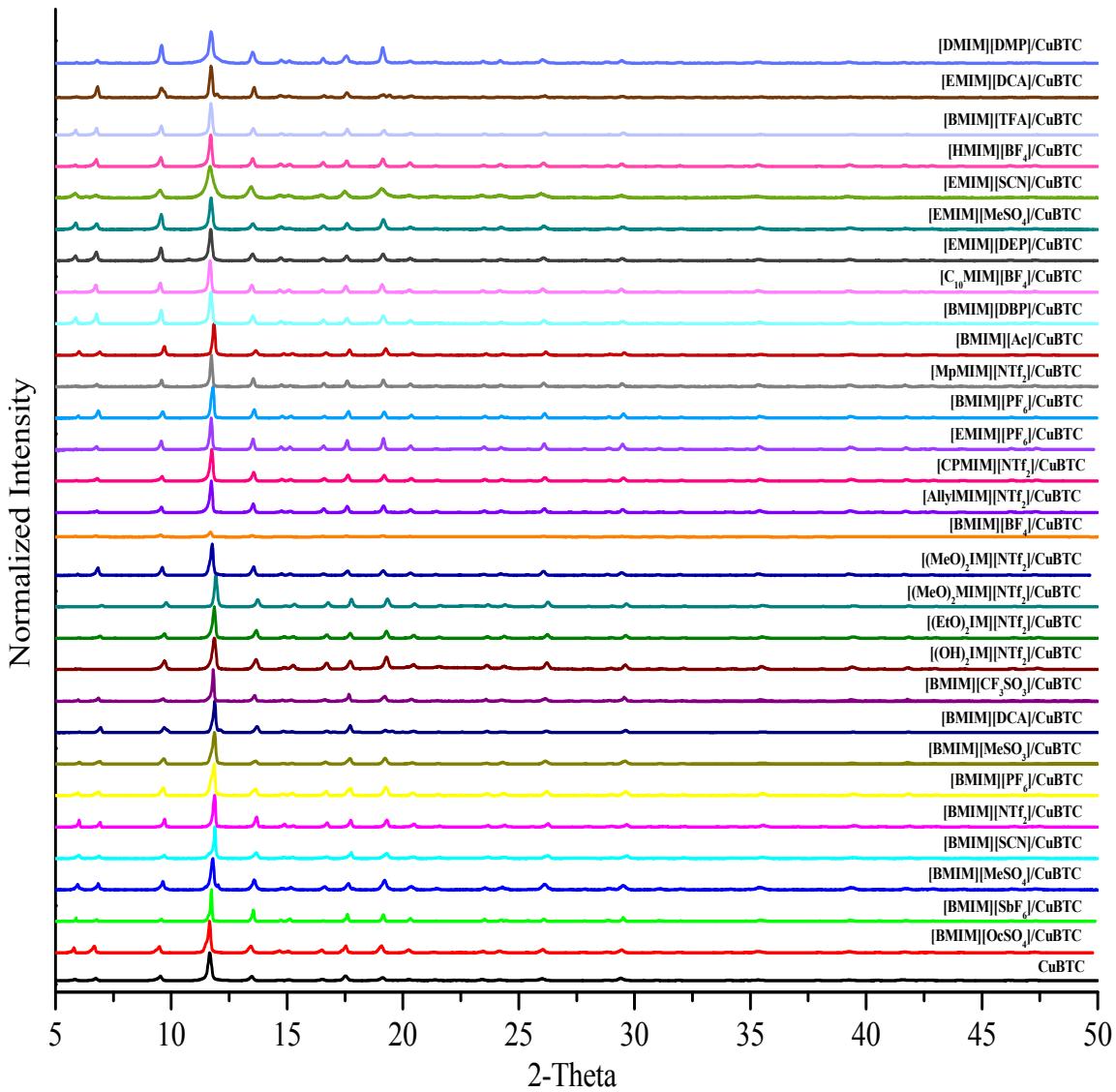


Figure S1. XRD patterns of pristine CuBTC and IL/CuBTC composites.

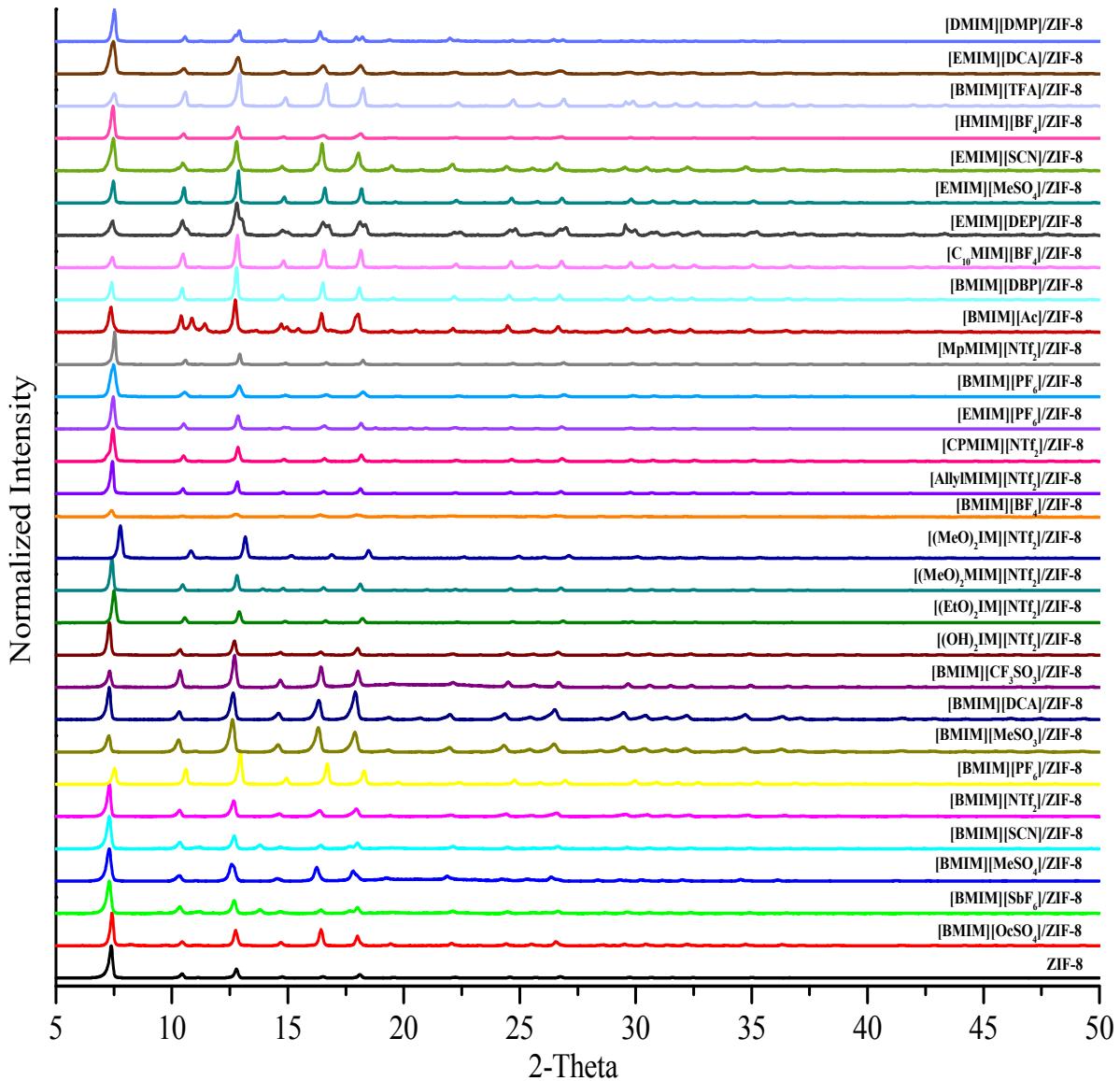


Figure S2. XRD patterns of pristine ZIF-8 and IL/ZIF-8 composites.

Table S2. BET surface area and pore volume of pristine MOFs.

Pristine MOFs	S_{BET} (m^2/g)	Pore volume (cm^3/g)
CuBTC	1324	0.52
ZIF-8	1208	0.63

Table S3. BET Surface area and pore volume of IL/MOF composites.

Cation	Anion	IL/CuBTC Composites		IL/ZIF-8 Composites	
		S _{BET} (m ² /g)	Pore volume (cm ³ /g)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
[EMIM]	[PF ₆]	238.10	0.03	308	0.19
[(MeO) ₂ IM]	[NTf ₂]	53	0.10	631	0.34
[(MeO) ₂ MIM]	[NTf ₂]	344	0.16	568	0.32
[CPMIM]	[NTf ₂]	601	0.28	726	0.39
[(OH) ₂ IM]	[NTf ₂]	6	0.02	83	0.06
[AllylMIM]	[NTf ₂]	487	0.22	0.86	0.03
[BMIM]	[BF ₄]	247 ^{*,1}	0.002 ^{*1}	177 ^{*,2}	0.11 ^{*,2}
[(EtO) ₂ IM]	[NTf ₂]	399	0.18	509	0.29
[BMIM]	[SCN]	88 ^{*,3}	0.07 ^{*,3}	48 ^{*,4}	0.02 ^{*,4}
[BMIM]	[SbF ₆]	601 ^{*,3}	0.32 ^{*,3}	221	0.01
[BMIM]	[NTf ₂]	319 ^{*,3}	0.14 ^{*,3}	2.6	0.01
[BMIM]	[MeSO ₃]	128 ^{*,3}	0.06 ^{*,3}	195	0.03
[BMIM]	[MeSO ₄]	339 ^{*,3}	0.15 ^{*,3}	233	0.02
[BMIM]	[OcSO ₄]	142 ^{*,3}	0.06 ^{*,3}	195	0.03
[BMIM]	[CF ₃ SO ₃]	357 ^{*,3}	0.16 ^{*,3}	362	0.04
[BMIM]	[DCA]	54	0.03	55	0.03
[EMIM]	[DCA]	16	0.01	51	0.01
[MPMIM]	[NTf ₂]	390	0.18	4.99	0.002
[BMMIM]	[PF ₆]	306	0.14	766	0.42
[BMIM]	[PF ₆]	364 ^{*,5}	0.06 ^{*,5}	415 ^{*,6}	0.22 ^{*,6}
[BMIM]	[DBP]	374	0.17	167	0.07
[BMIM]	[TFA]	131	0.06	491	0.30
[EMIM]	[MESO ₄]	114	0.05	329	0.21
[BMIM]	[AC]	0.77	0.01	15	0.02
[EMIM]	[DEP]	131	0.06	238	0.15
[DMIM]	[DMP]	0.94	0.003	276	0.16
[HMIM]	[BF ₄]	404	0.18	107	0.14
[EMIM]	[SCN]	3.4	0.02	129	0.12
[C ₁₀ MIM]	[BF ₄]	225	0.09	261	0.26

*BET surface area and pore volume values were obtained from the previous published works of our group.

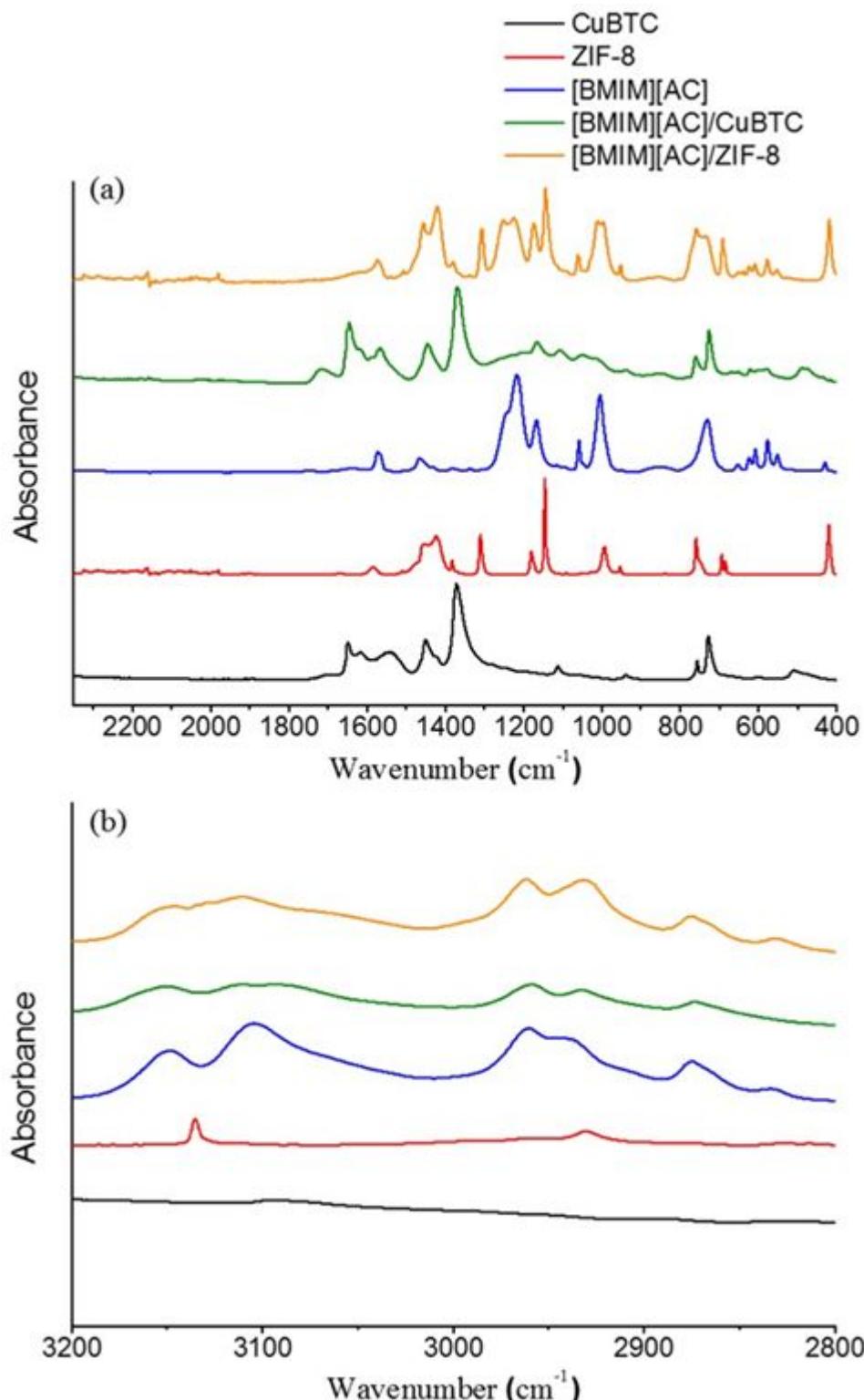


Figure S3. FTIR spectra of CuBTC, ZIF-8, [BMIM][AC], [BMIM][AC]/CuBTC, and [BMIM][AC]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

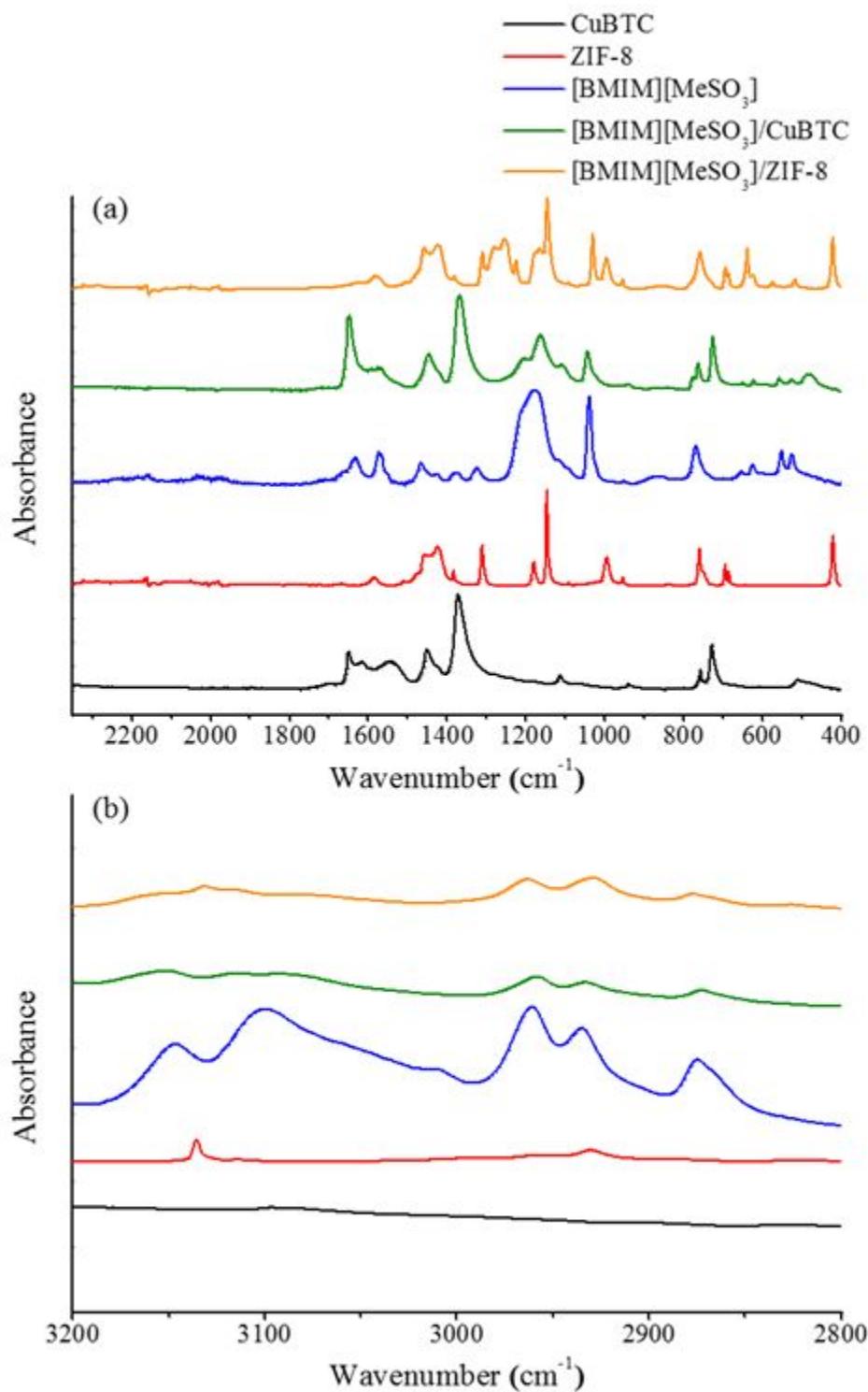


Figure S4. FTIR spectra of CuBTC, ZIF-8, [BMIM][MeSO₃], [BMIM][MeSO₃]/CuBTC, and [BMIM][MeSO₃]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

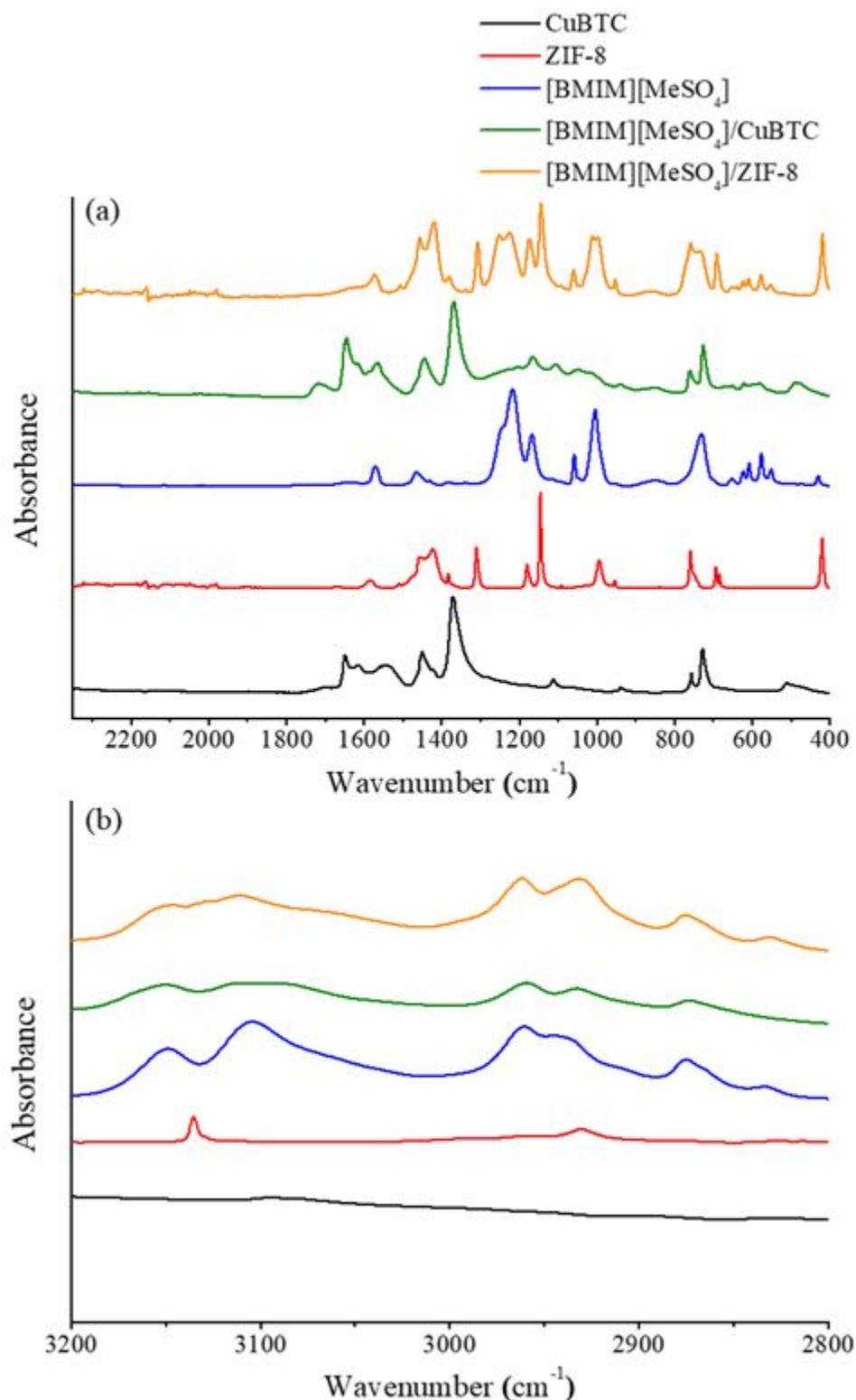


Figure S5. FTIR spectra of CuBTC, ZIF-8, [BMIM][MeSO₄], [BMIM][MeSO₄]/CuBTC, and [BMIM][MeSO₄]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

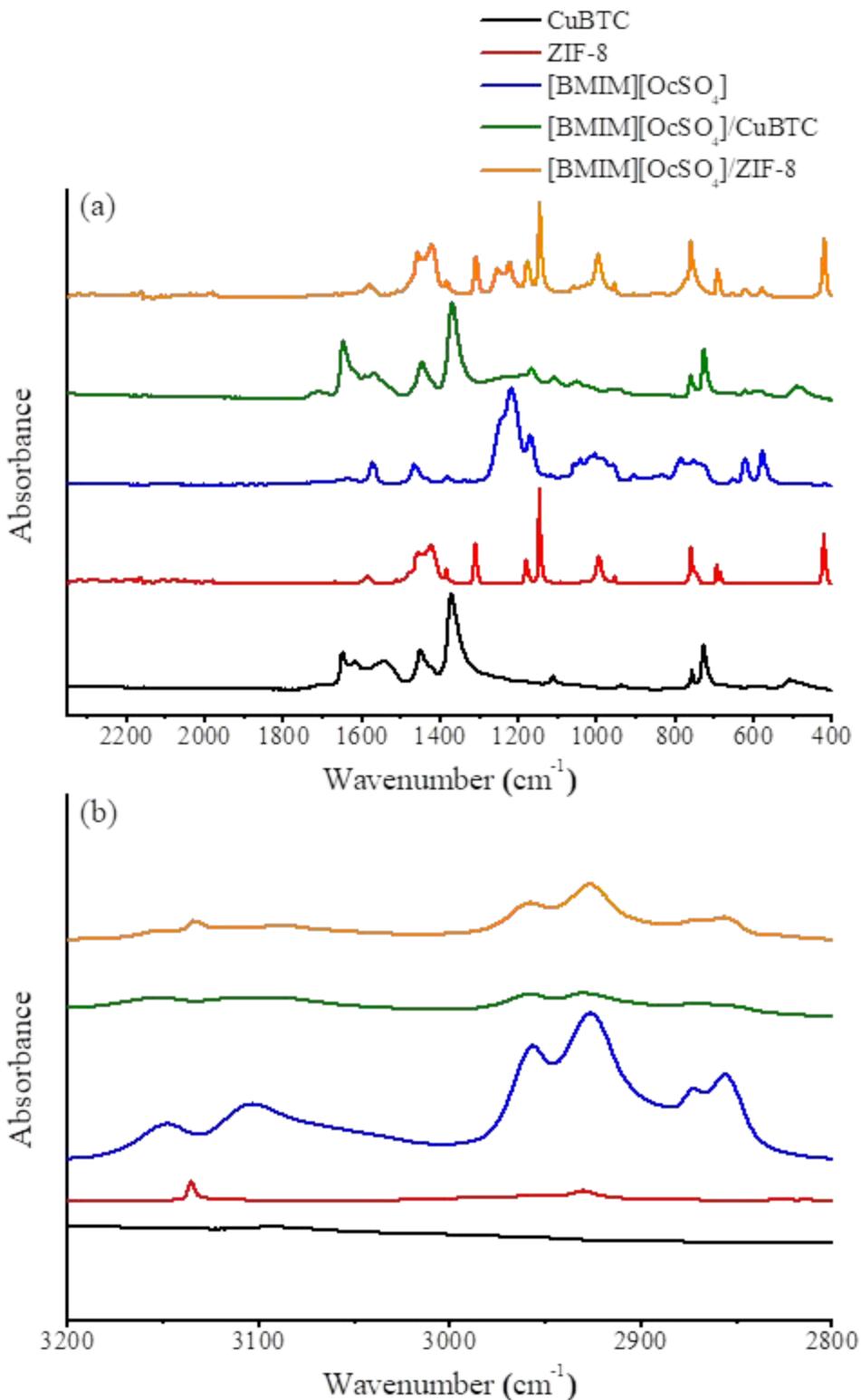


Figure S6. FTIR spectra of CuBTC, ZIF-8, [BMIM][OcSO₄], [BMIM][OcSO₄]/CuBTC, and [BMIM][OcSO₄]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

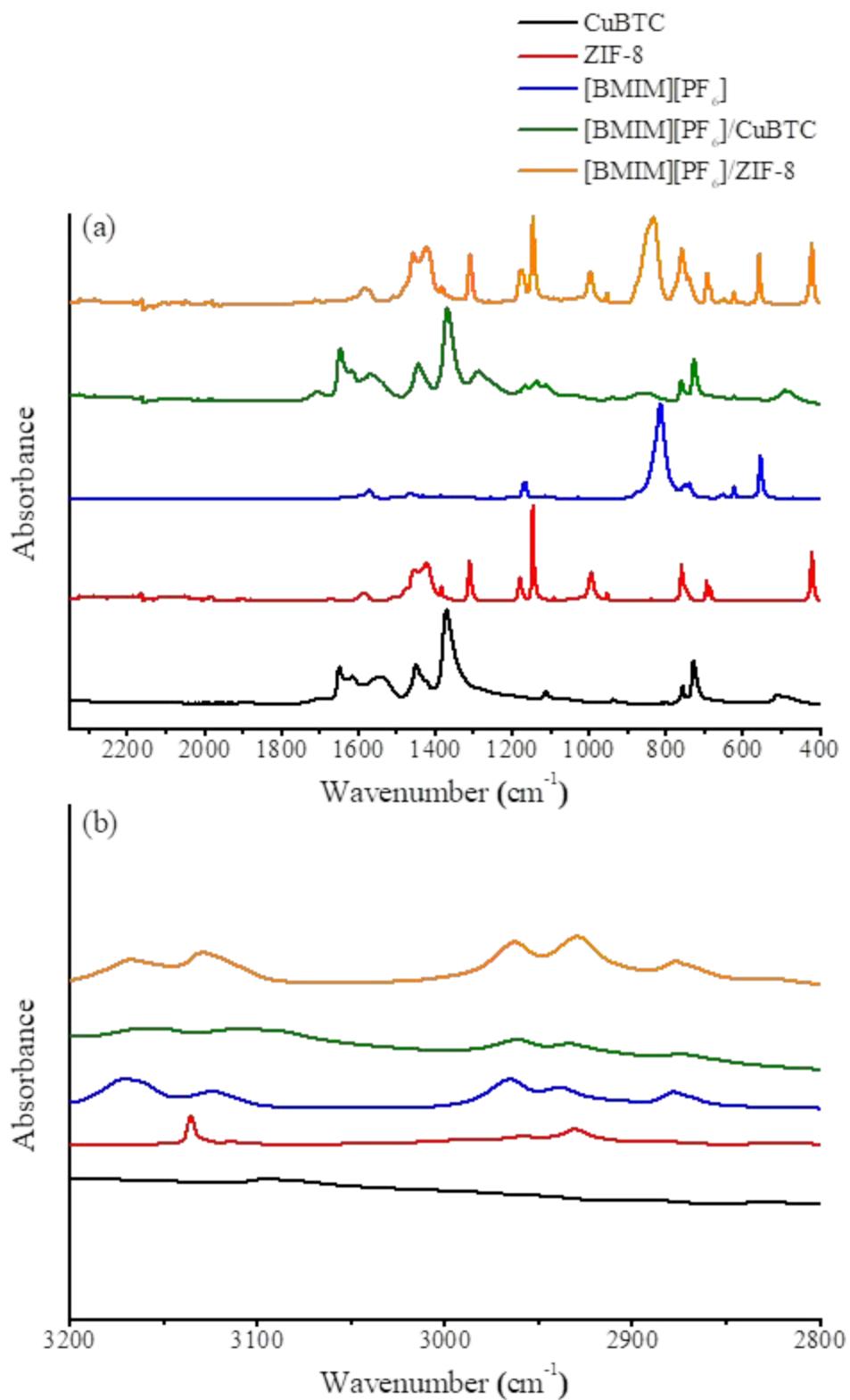


Figure S7. FTIR spectra of CuBTC, ZIF-8, [BMIM][PF₆], [BMIM][PF₆]/CuBTC, and [BMIM][PF₆]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

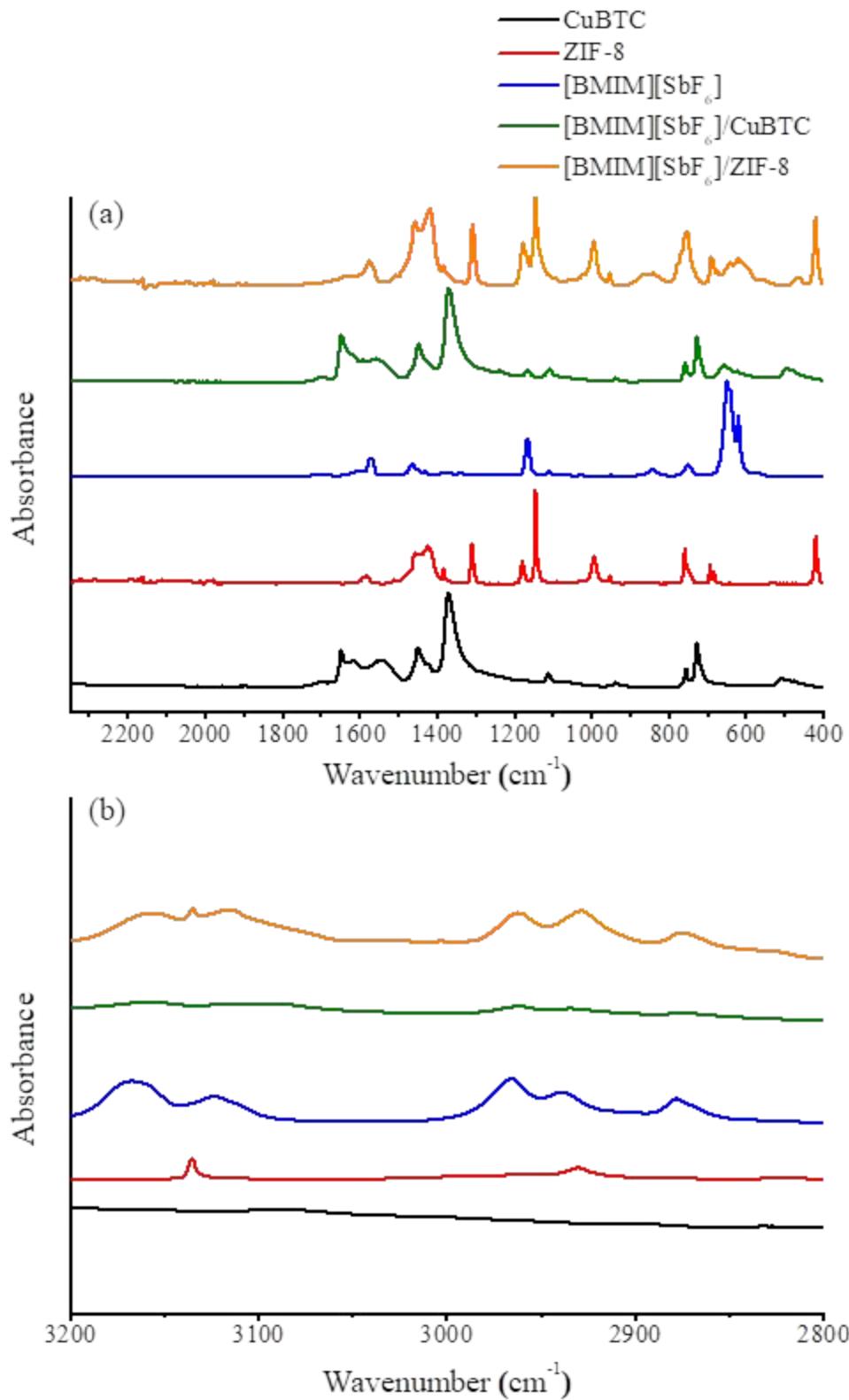


Figure S8. FTIR spectra of CuBTC, ZIF-8, [BMIM][SbF₆], [BMIM][SbF₆]/CuBTC, and [BMIM][SbF₆]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

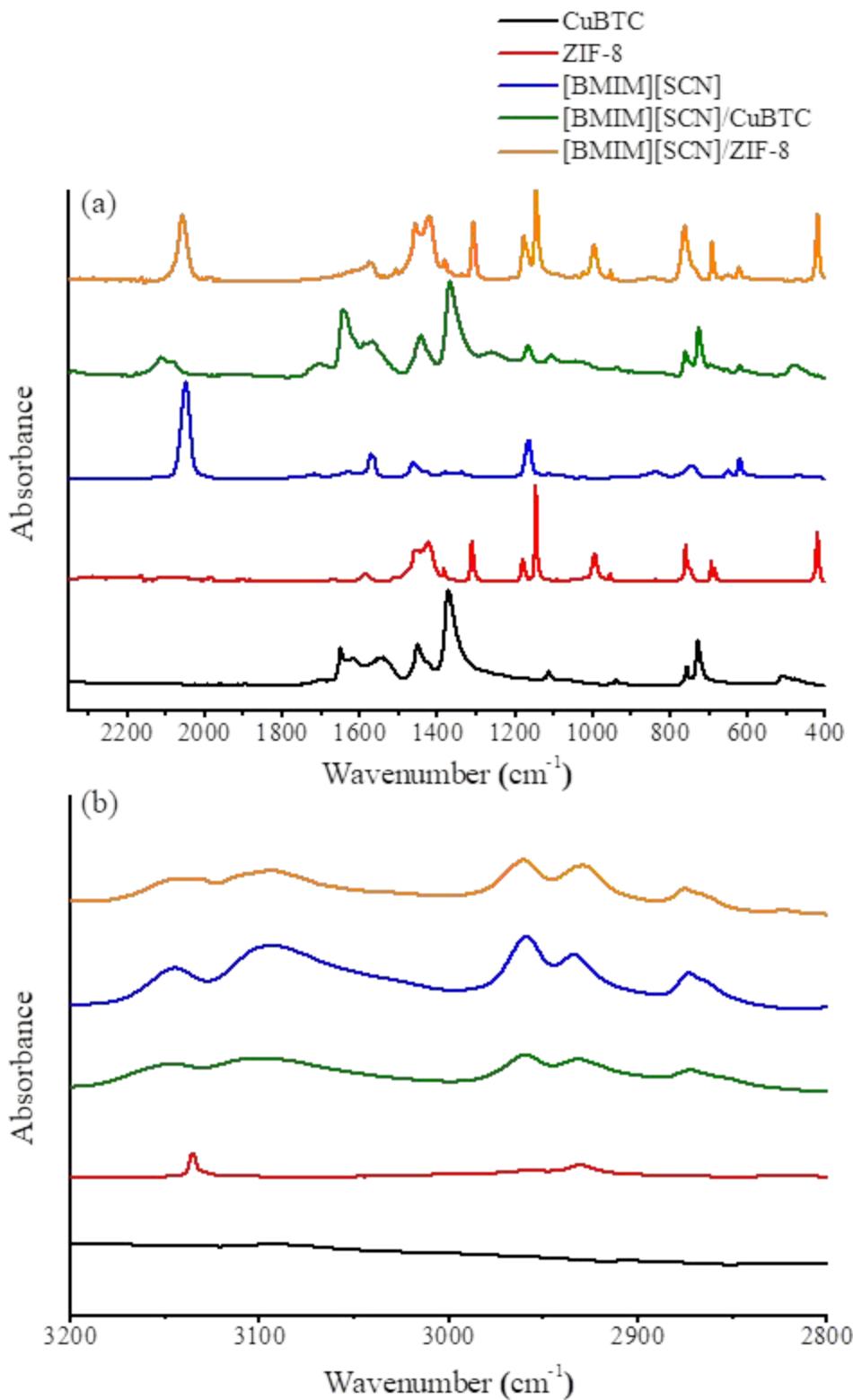


Figure S9. FTIR spectra of CuBTC, ZIF-8, [BMIM][SCN], [BMIM][SCN]/CuBTC, and [BMIM][SCN]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

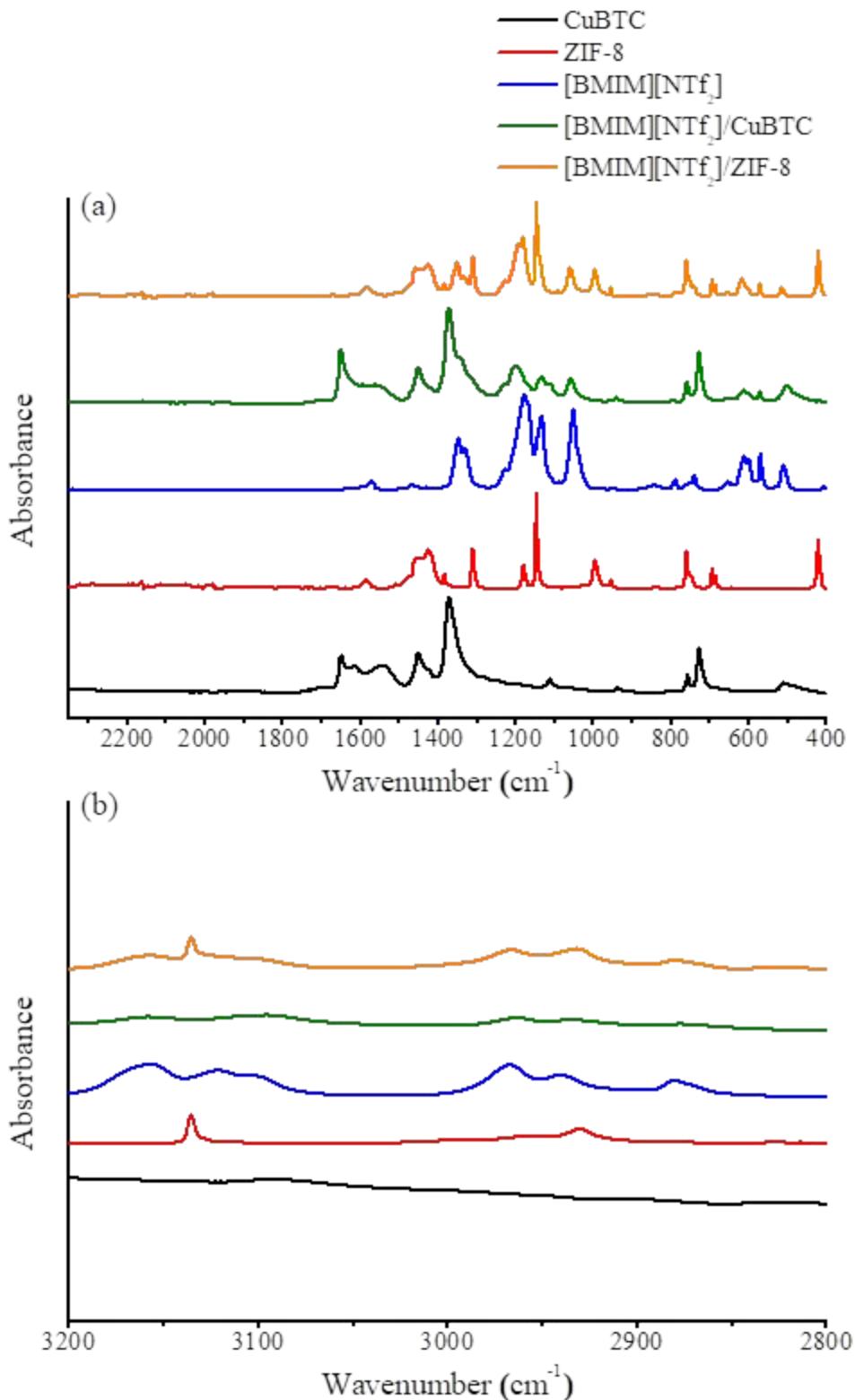


Figure S10. FTIR spectra of CuBTC, ZIF-8, [BMIM][NTf₂], [BMIM][NTf₂]/CuBTC, and [BMIM][NTf₂]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

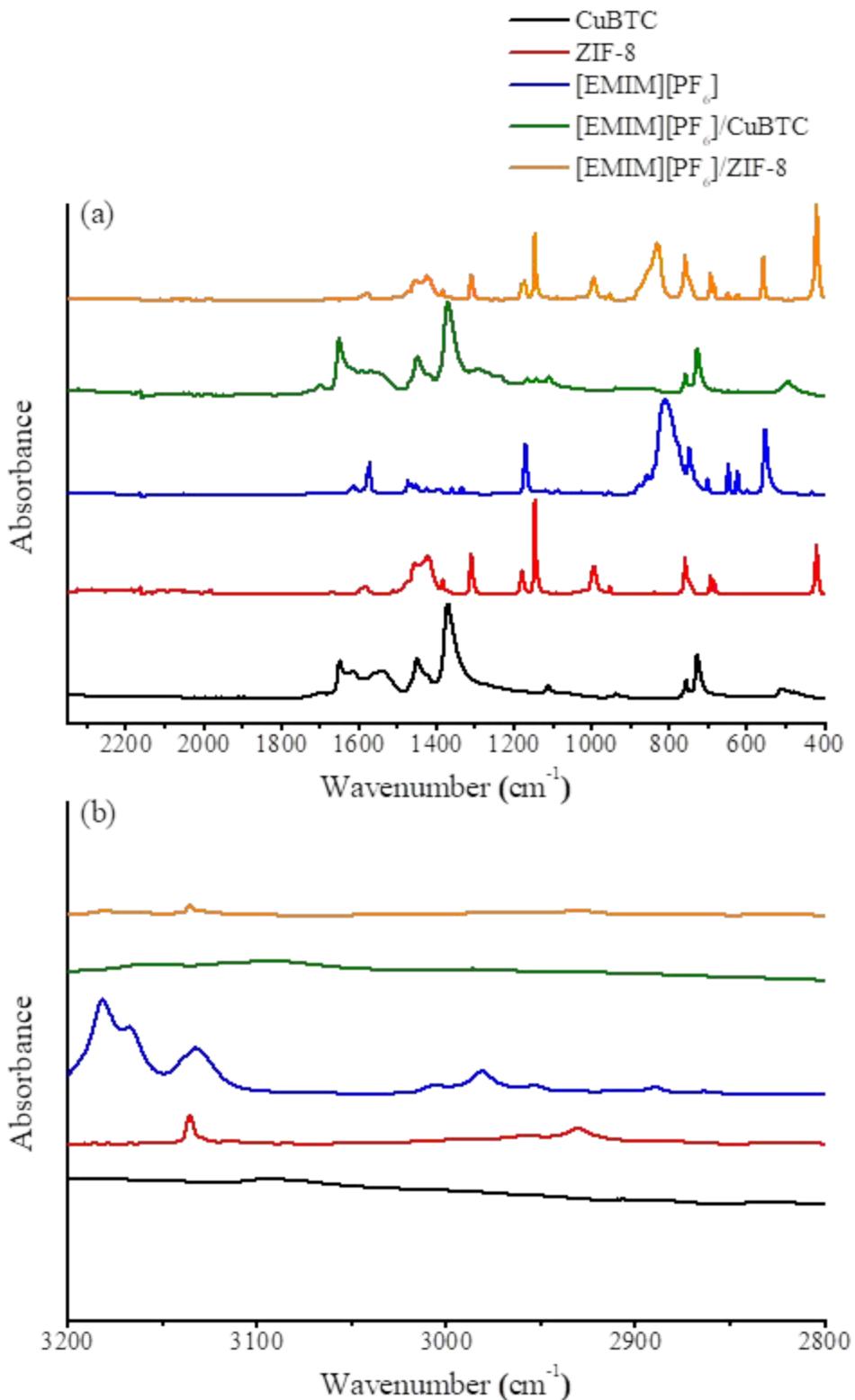


Figure S11. FTIR spectra of CuBTC, ZIF-8, [EMIM]PF₆, [EMIM]PF₆/CuBTC, and [EMIM]PF₆/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

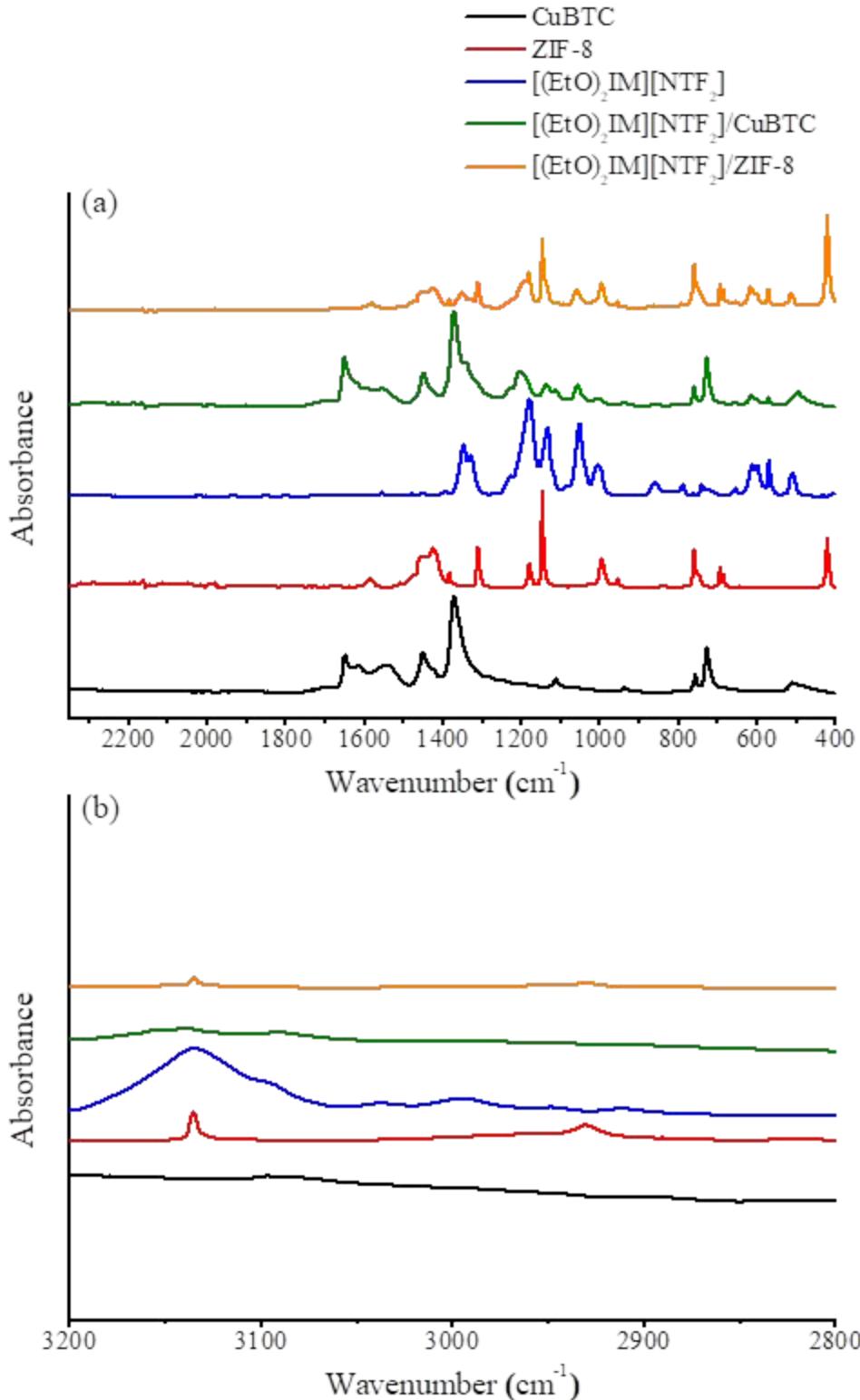


Figure S12. FTIR spectra of CuBTC, ZIF-8, $[(\text{EtO})_2\text{IM}][\text{NTF}_2]$, $[(\text{EtO})_2\text{IM}][\text{NTF}_2]/\text{CuBTC}$, and $[(\text{EtO})_2\text{IM}][\text{NTF}_2]/\text{ZIF-8}$ (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

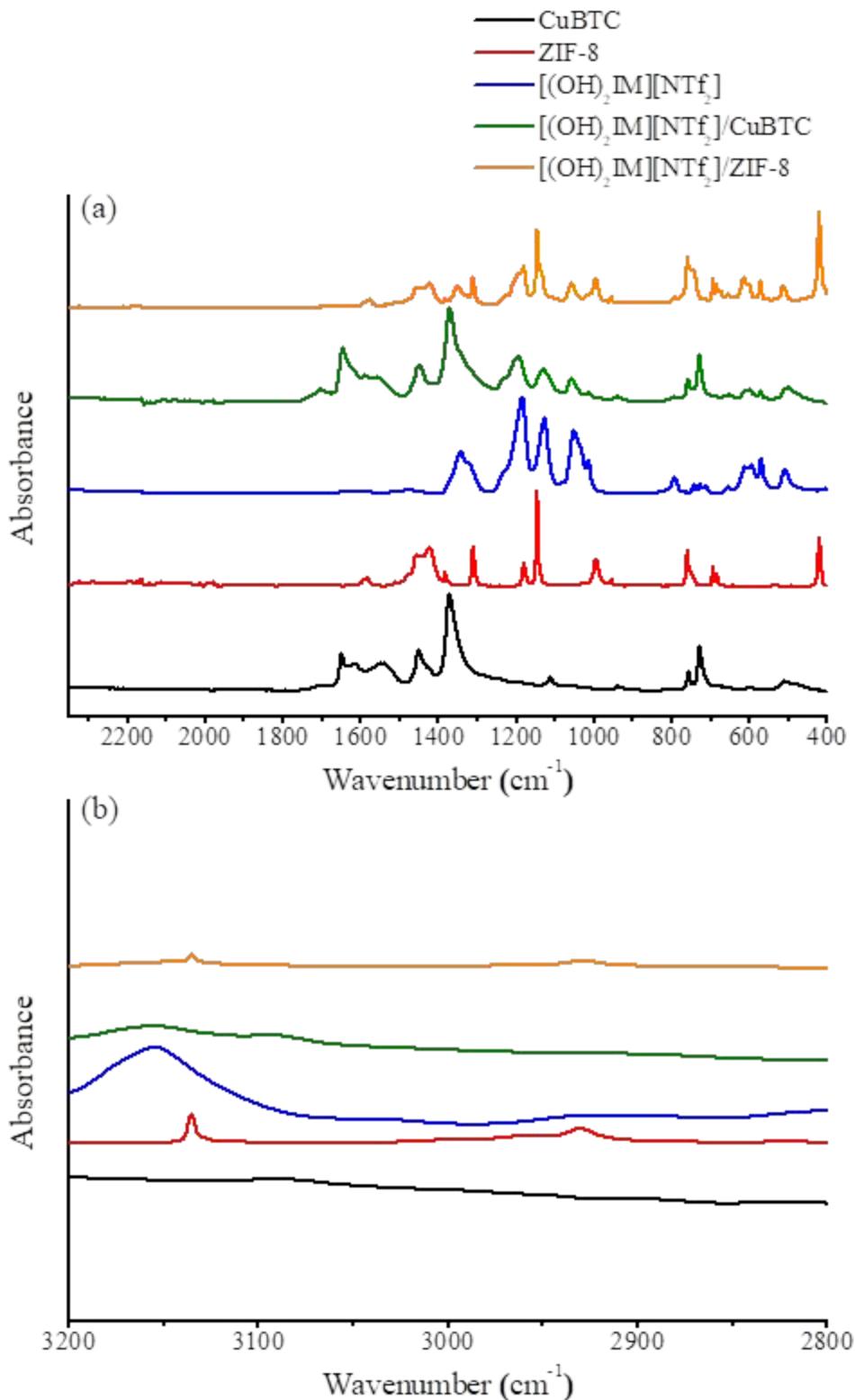


Figure S13. FTIR spectra of CuBTC, ZIF-8, $[(\text{OH})_2\text{IM}][\text{NTf}_2]$, $[(\text{OH})_2\text{IM}][\text{NTf}_2]/\text{CuBTC}$, and $[(\text{OH})_2\text{IM}][\text{NTf}_2]/\text{ZIF-8}$ (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

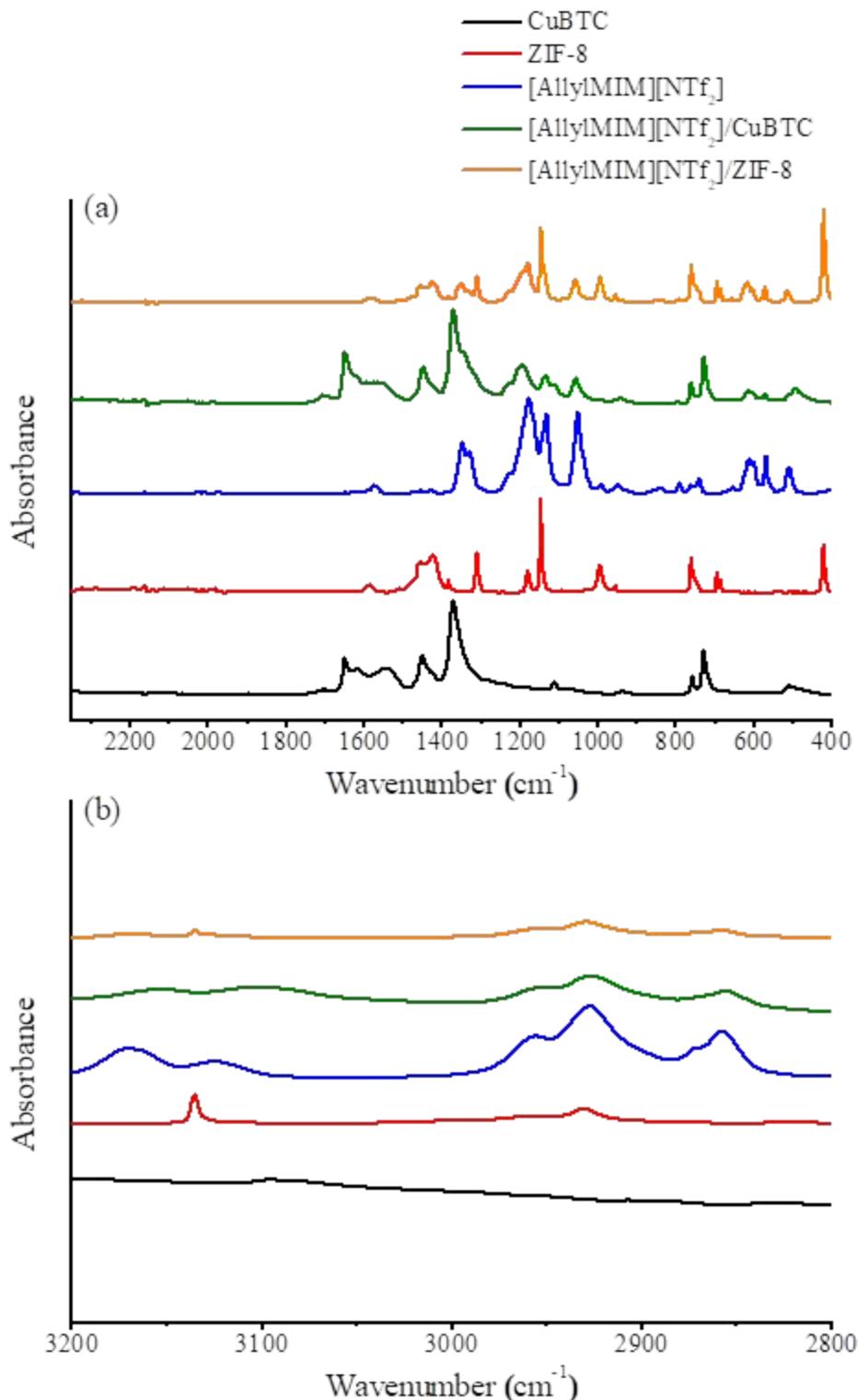


Figure S14. FTIR spectra of CuBTC, ZIF-8, [AllylMIM][NTf₂], [AllylMIM][NTf₂]/CuBTC, and [AllylMIM][NTf₂]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

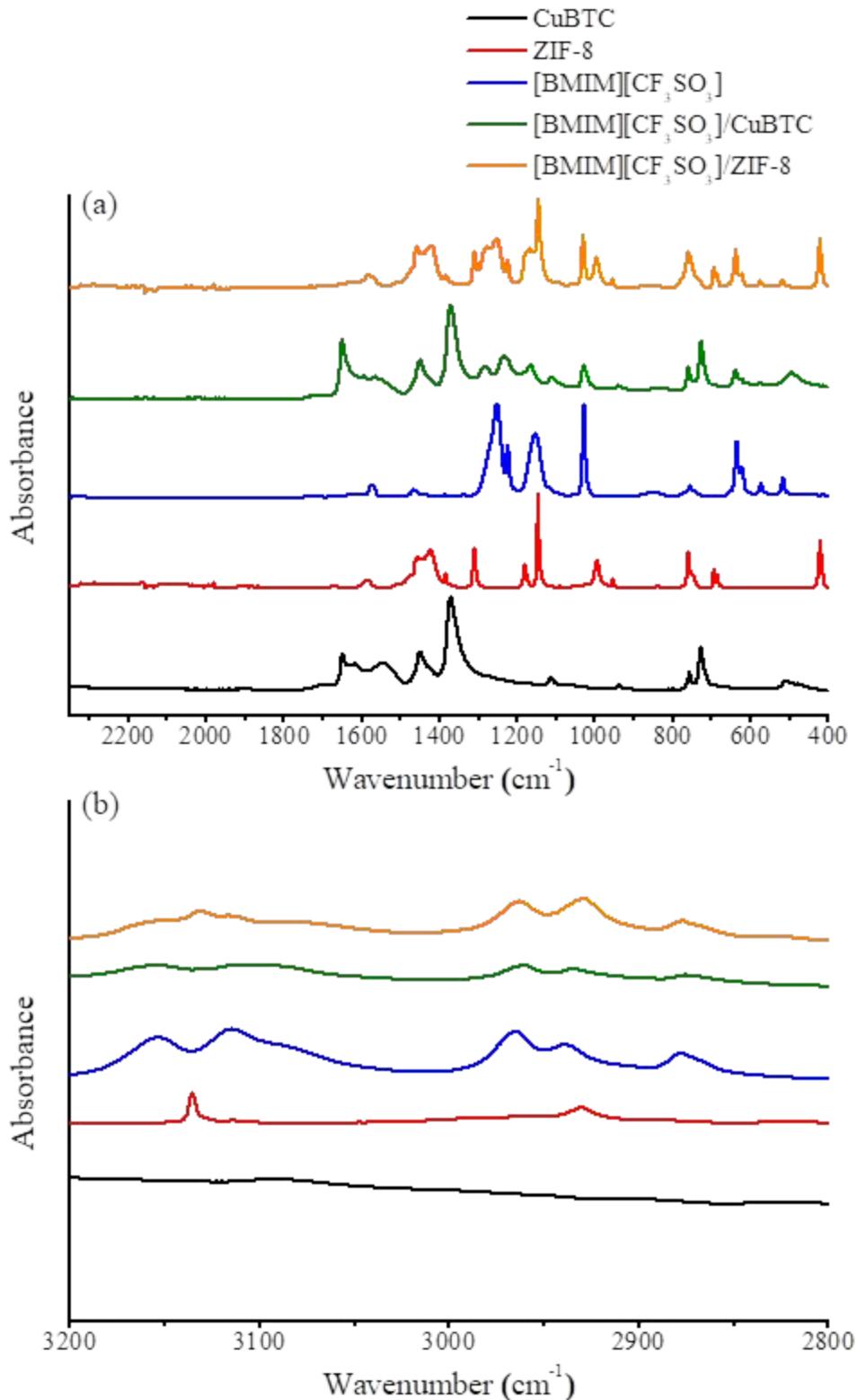


Figure S15. FTIR spectra of CuBTC, ZIF-8, [BMIM][CF₃SO₃], [BMIM][CF₃SO₃]/CuBTC, and [BMIM][CF₃SO₃]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

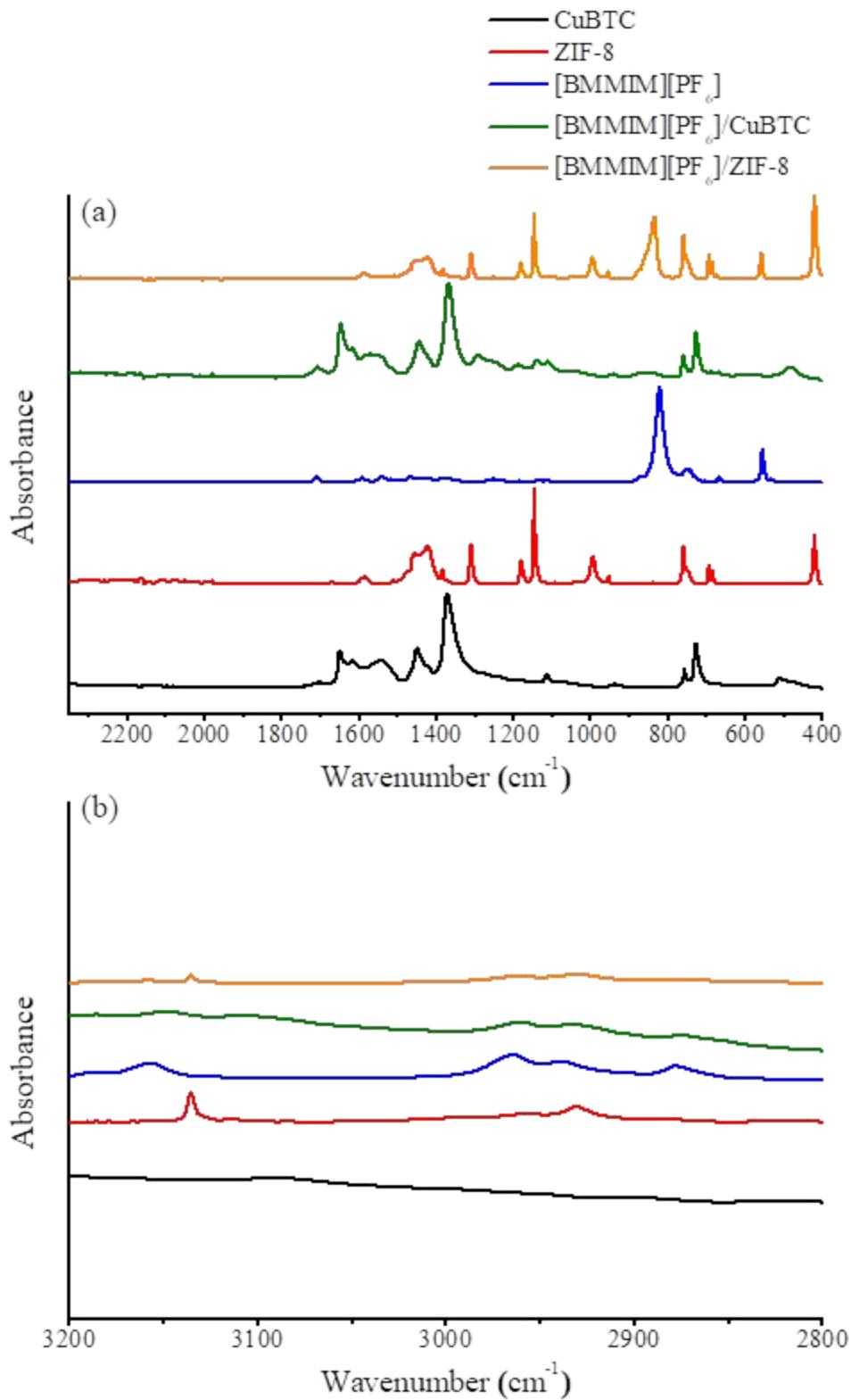


Figure S16. FTIR spectra of CuBTC, ZIF-8, [BMMIM][PF₆], [BMMIM][PF₆]/CuBTC, and [BMMIM][PF₆]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

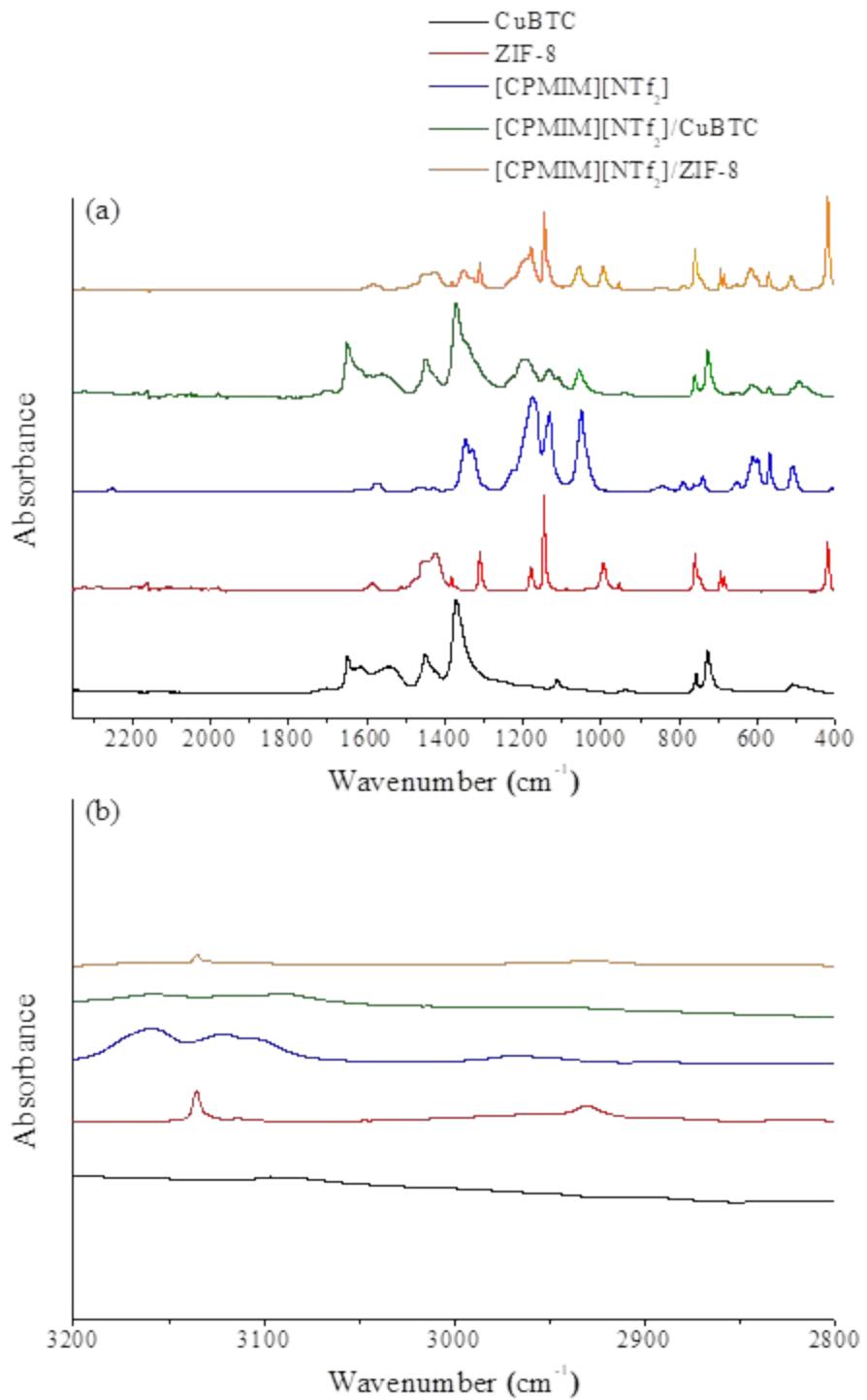


Figure S17. FTIR spectra of CuBTC, ZIF-8, [CPMIM][NTf₂], [(CPMIM)[NTf₂]/CuBTC, and [CPMIM][NTf₂]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

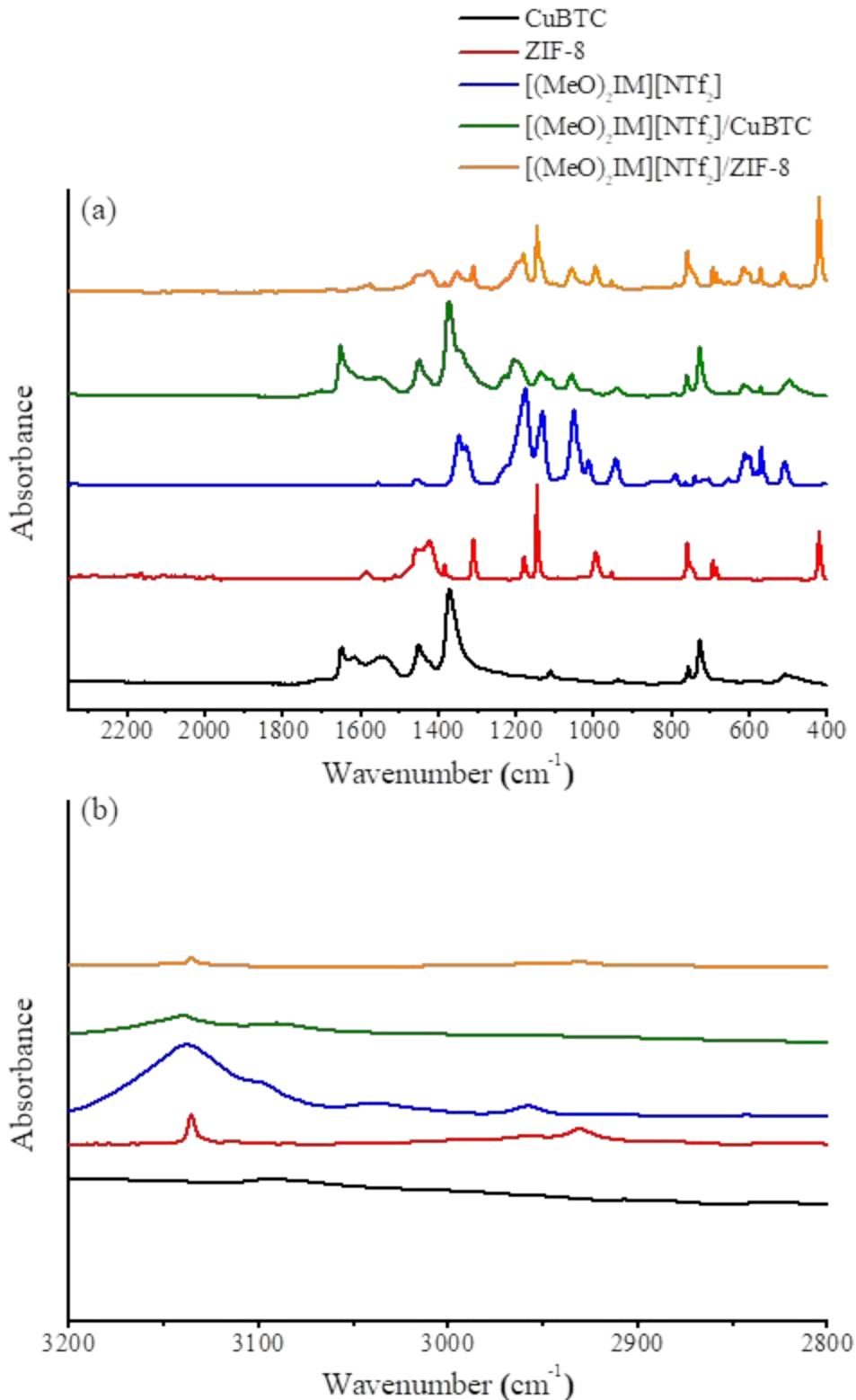


Figure S18. FTIR spectra of CuBTC, ZIF-8, $[(\text{MeO})_2\text{IM}][\text{NTf}_2]$, $[(\text{MeO})_2\text{IM}][\text{NTf}_2]/\text{CuBTC}$, and $[(\text{MeO})_2\text{IM}][\text{NTf}_2]/\text{ZIF-8}$ (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

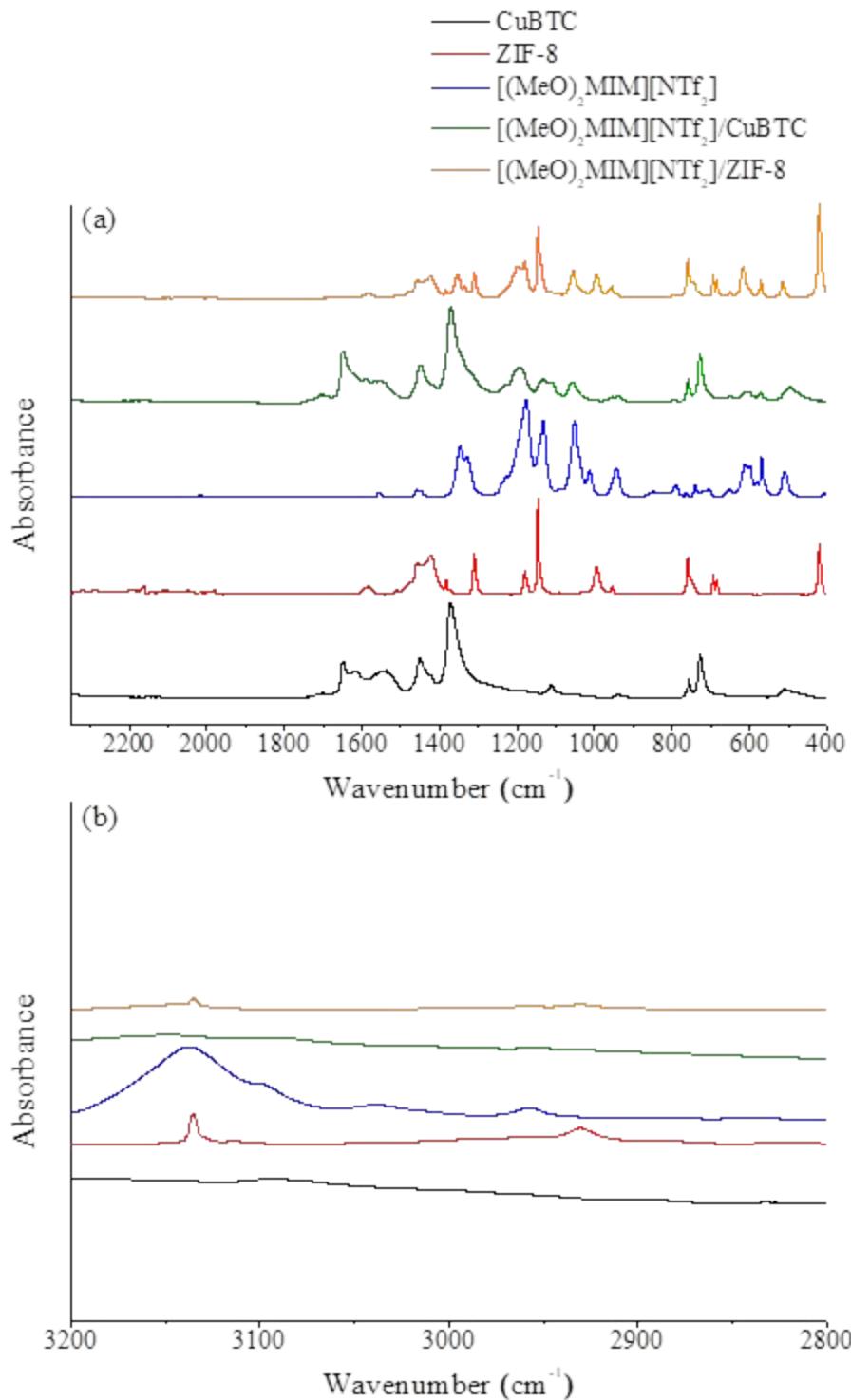


Figure S19. FTIR spectra of CuBTC, ZIF-8, $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]$, $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]/\text{CuBTC}$, and $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]/\text{ZIF-8}$ (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

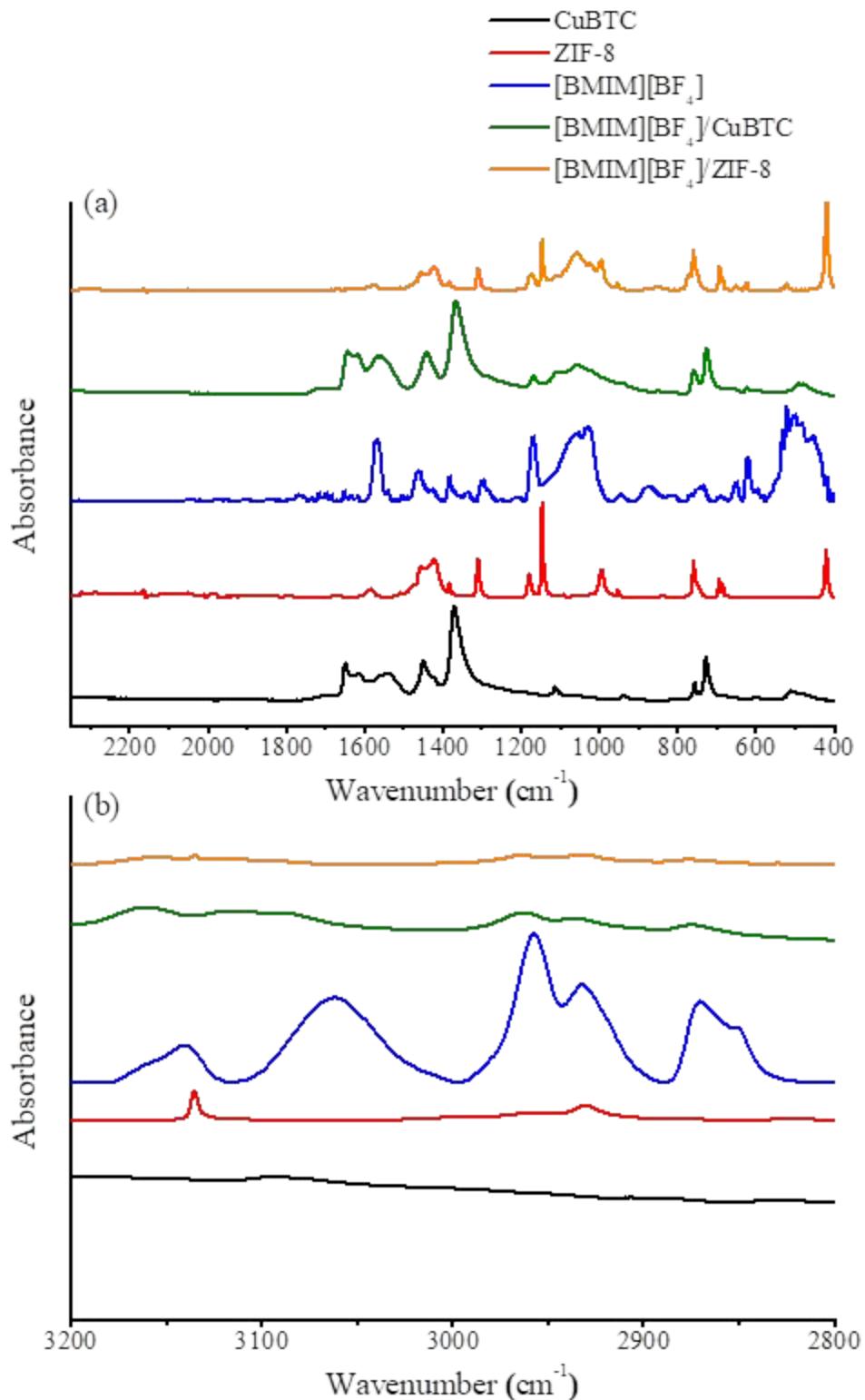


Figure S20. FTIR spectra of CuBTC, ZIF-8, [BMIM][BF₄], [BMIM][BF₄]/CuBTC, and [BMIM][BF₄]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

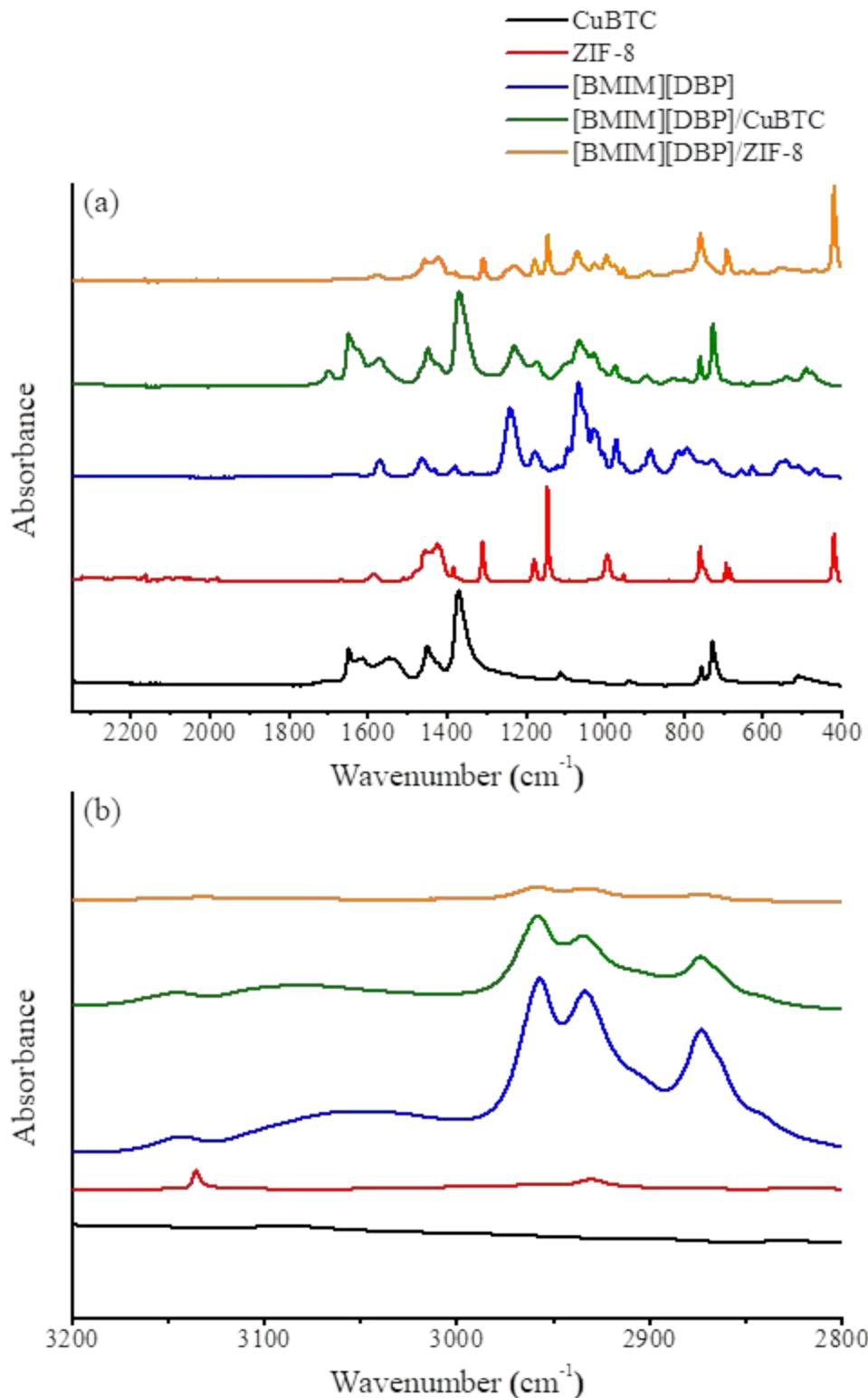


Figure S21. FTIR spectra of CuBTC, ZIF-8, [BMIM][DBP], [BMIM][DBP]/CuBTC, and [BMIM][DBP]/ZIF-8 (a) 400-2250 cm^{-1} and (b) 2800-3200 cm^{-1} .

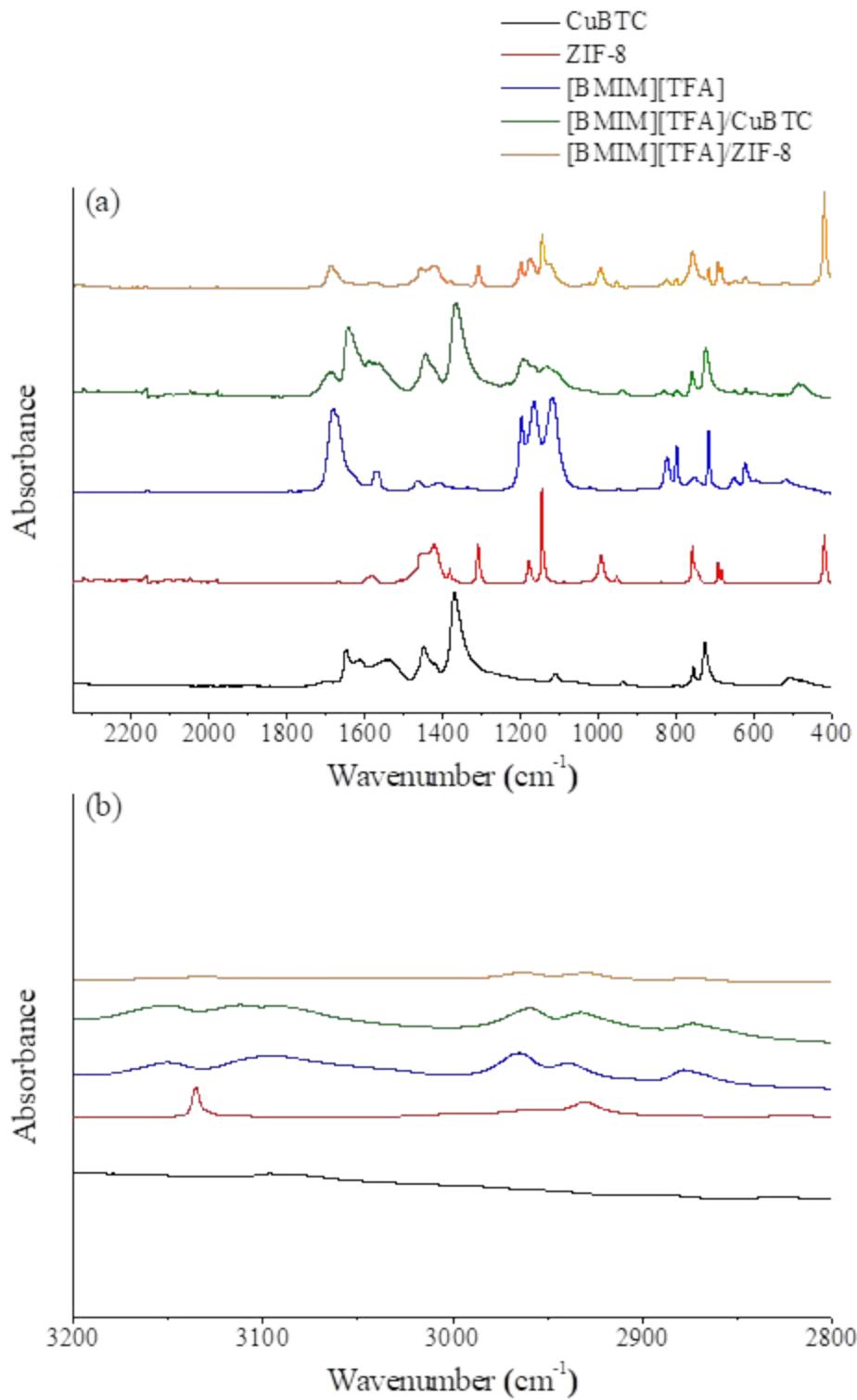


Figure S22. FTIR spectra of CuBTC, ZIF-8, [BMIM][TFA], [BMIM][TFA]/CuBTC, and [BMIM][TFA]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

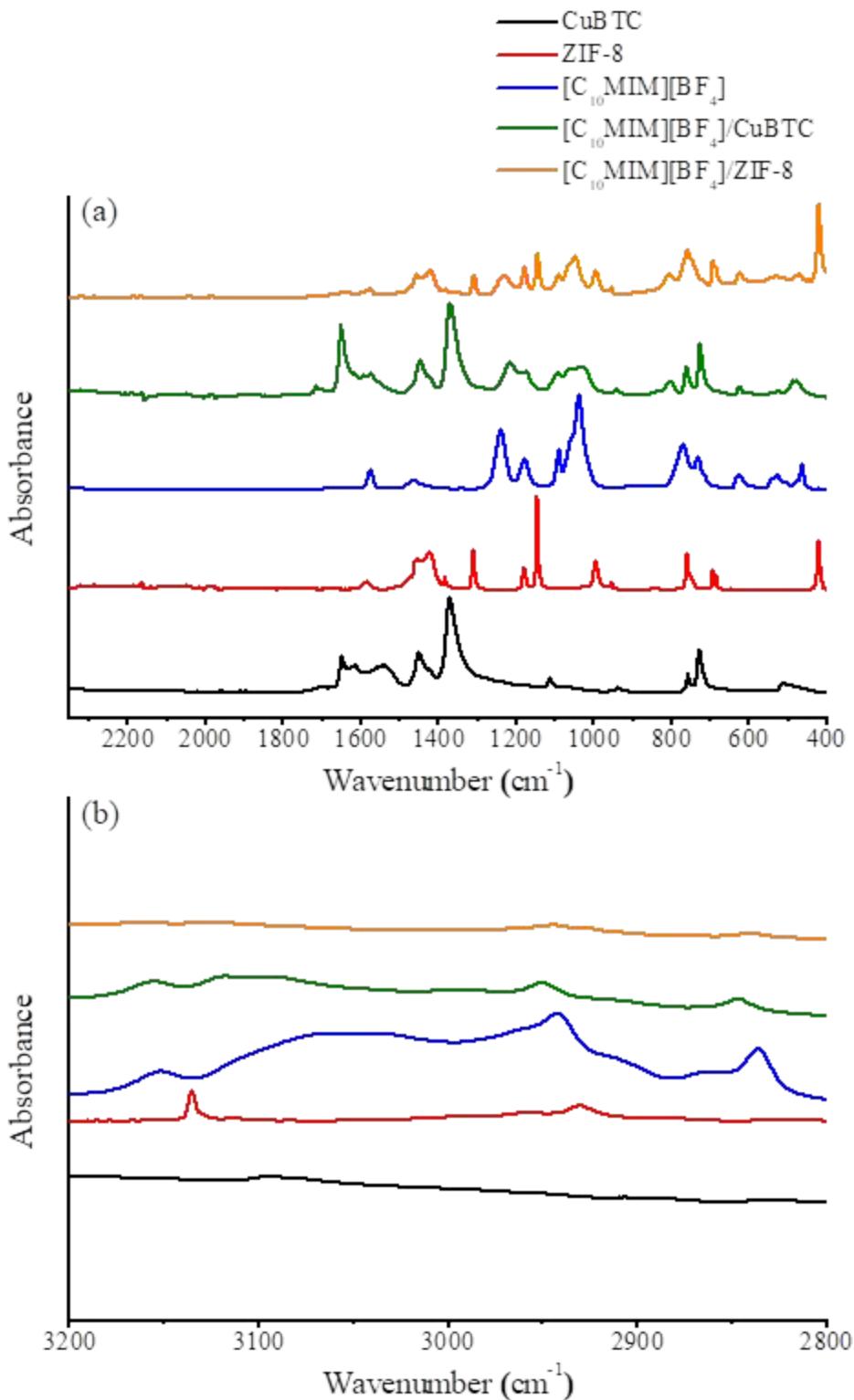


Figure S23. FTIR spectra of CuBTC, ZIF-8, $[C_{10}\text{MIM}][\text{BF}_4]$, $[C_{10}\text{MIM}][\text{BF}_4]/\text{CuBTC}$, and $[C_{10}\text{MIM}][\text{BF}_4]/\text{ZIF-8}$ (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

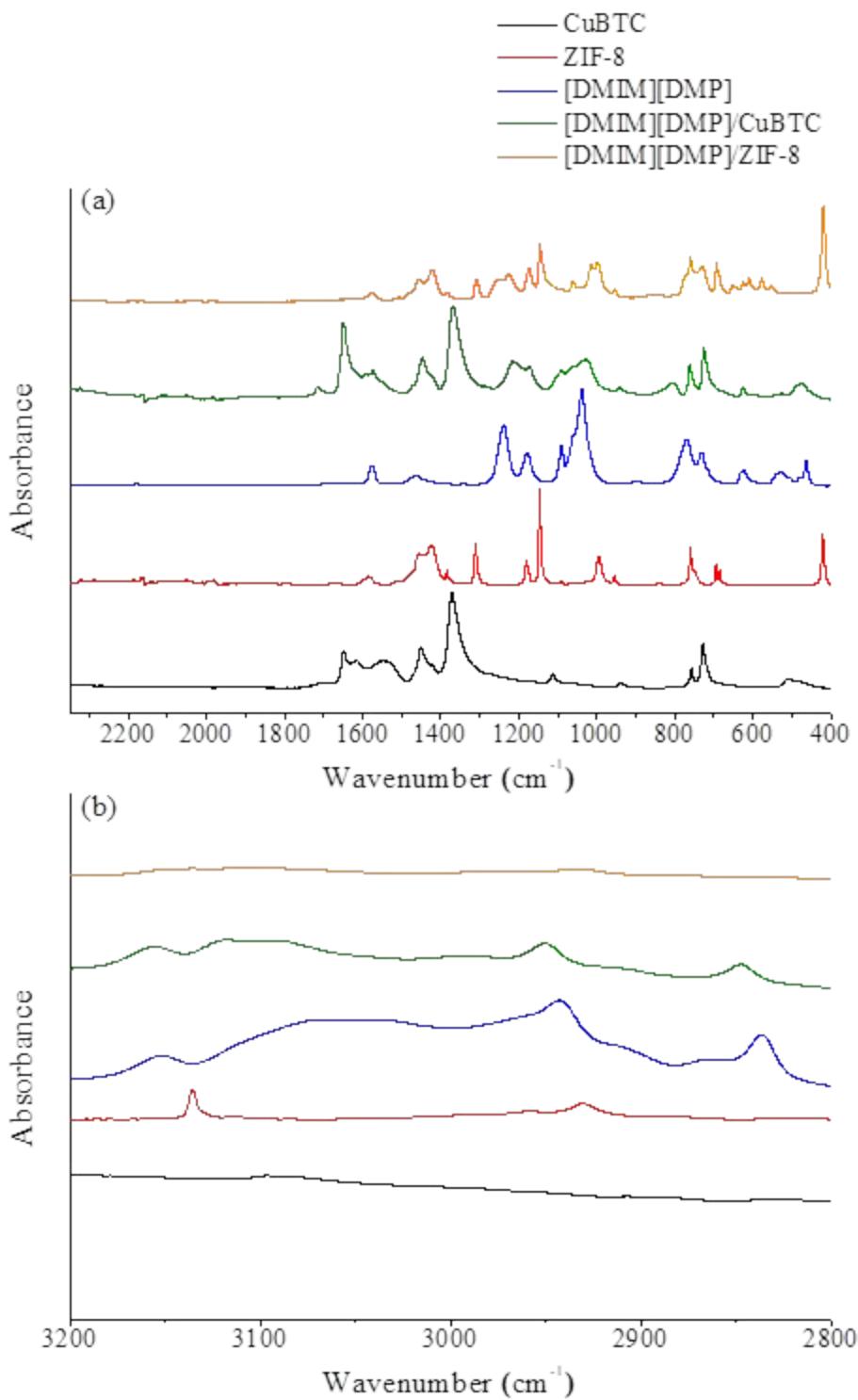


Figure S24. FTIR spectra of CuBTC, ZIF-8, [DMIM][DMP], [DMIM][DMP]/CuBTC, and [DMIM][DMP]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

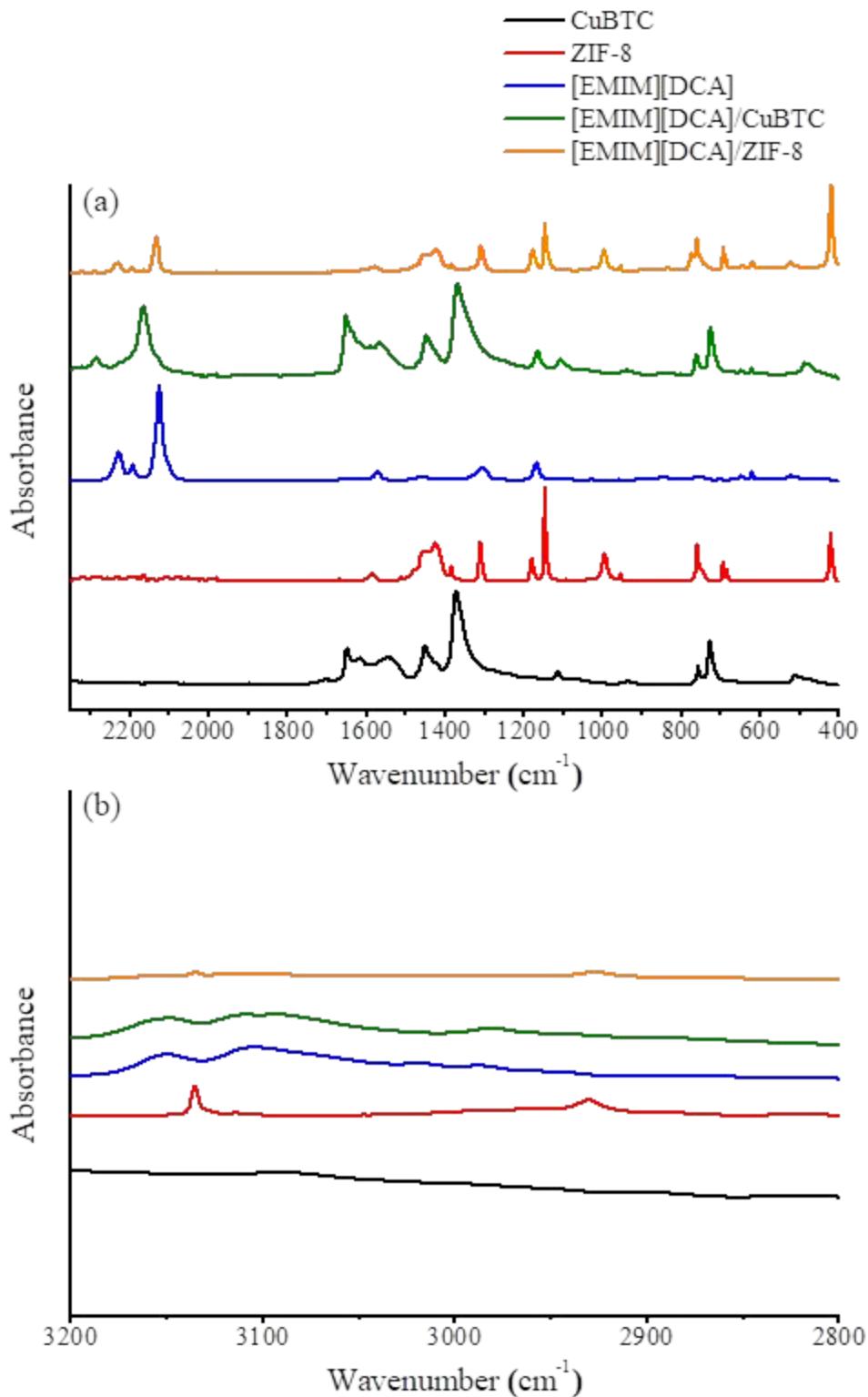


Figure S25. FTIR spectra of CuBTC, ZIF-8, [EMIM][DCA], [EMIM][DCA]/CuBTC, and [EMIM][DCA]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

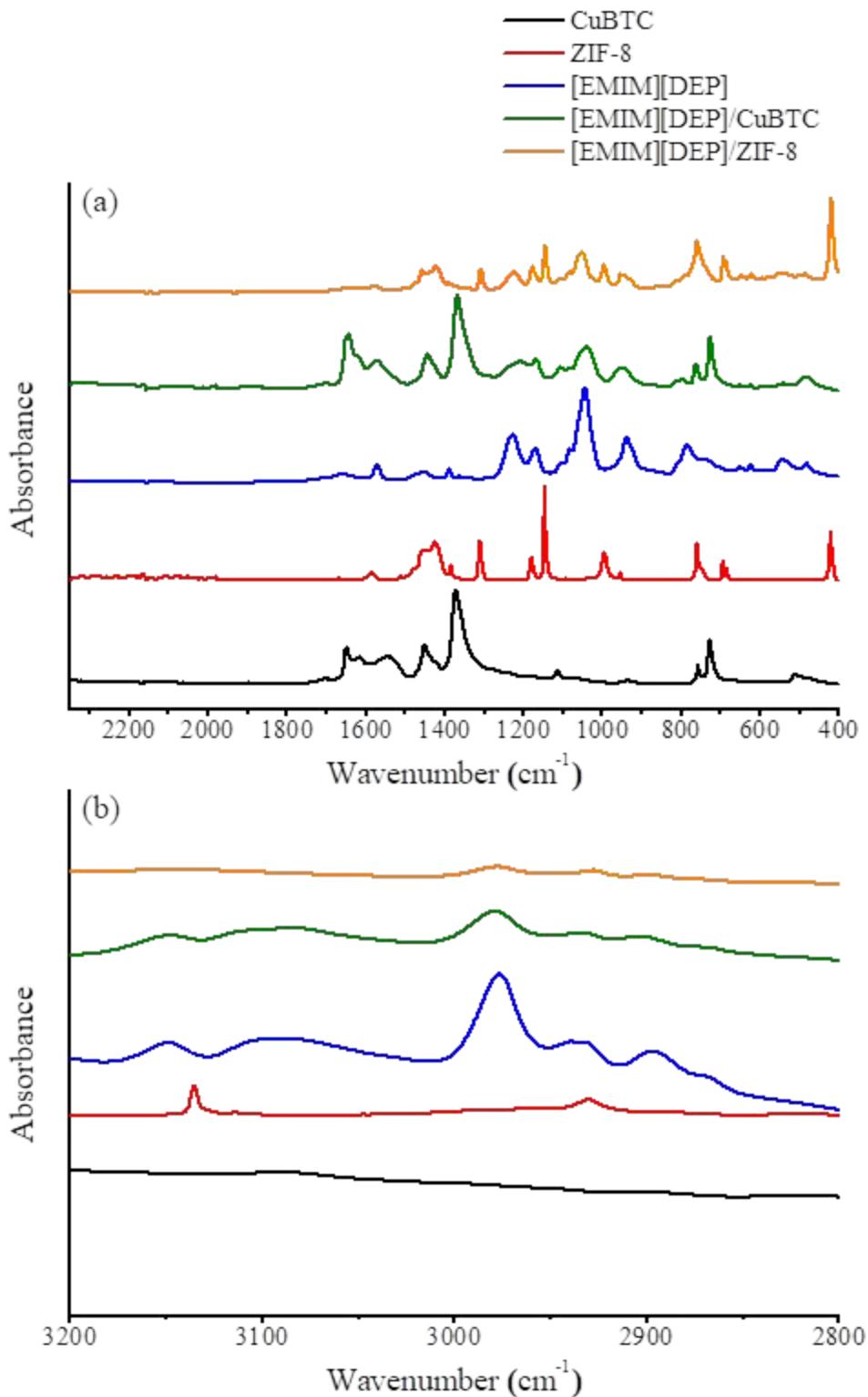


Figure S26. FTIR spectra of CuBTC, ZIF-8, [EMIM][DEP], [EMIM][DEP]/CuBTC, and [EMIM][DEP]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

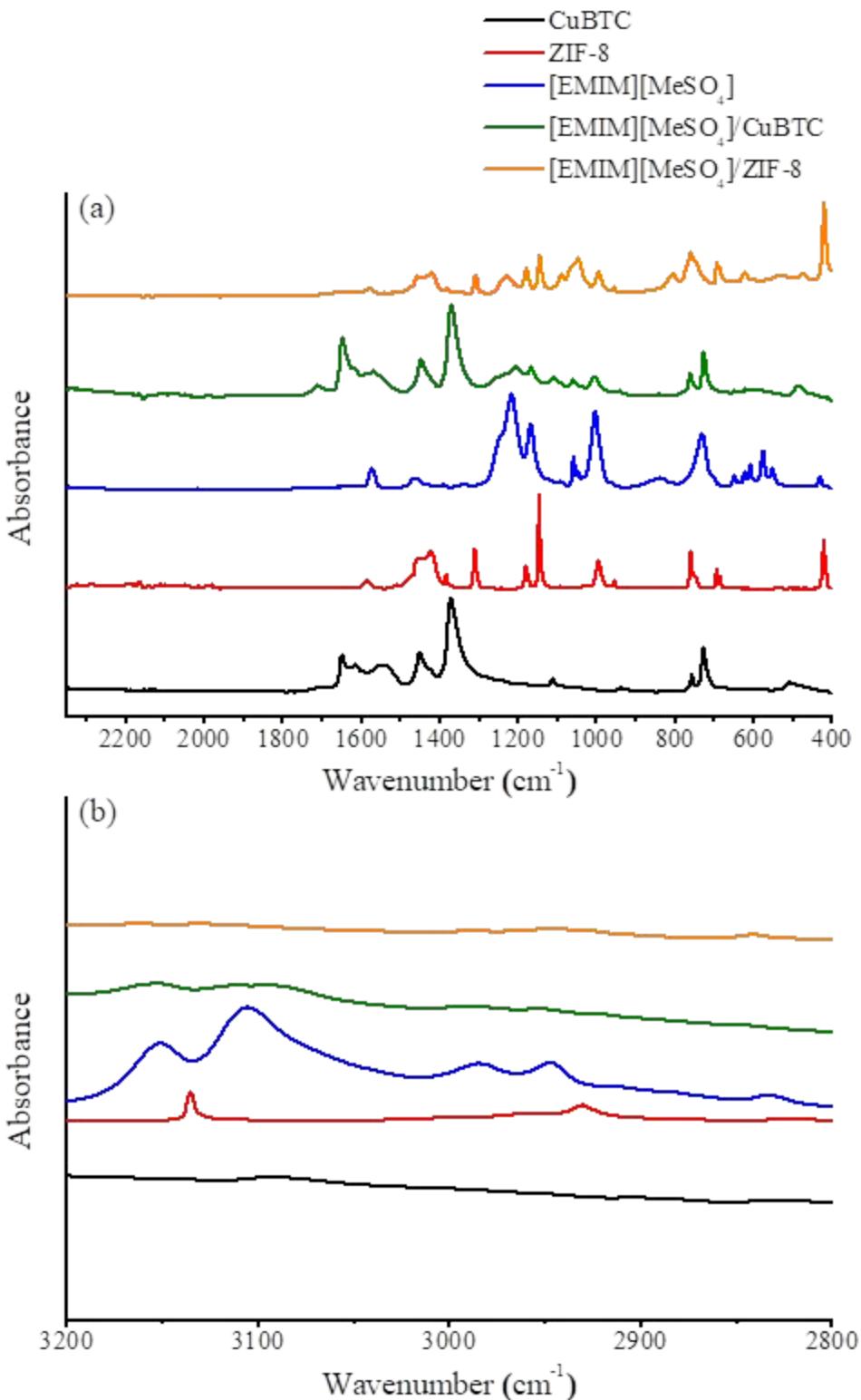


Figure S27. FTIR spectra of CuBTC, ZIF-8, [EMIM][MeSO₄], [EMIM][MeSO₄]/CuBTC, and [EMIM][MeSO₄]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

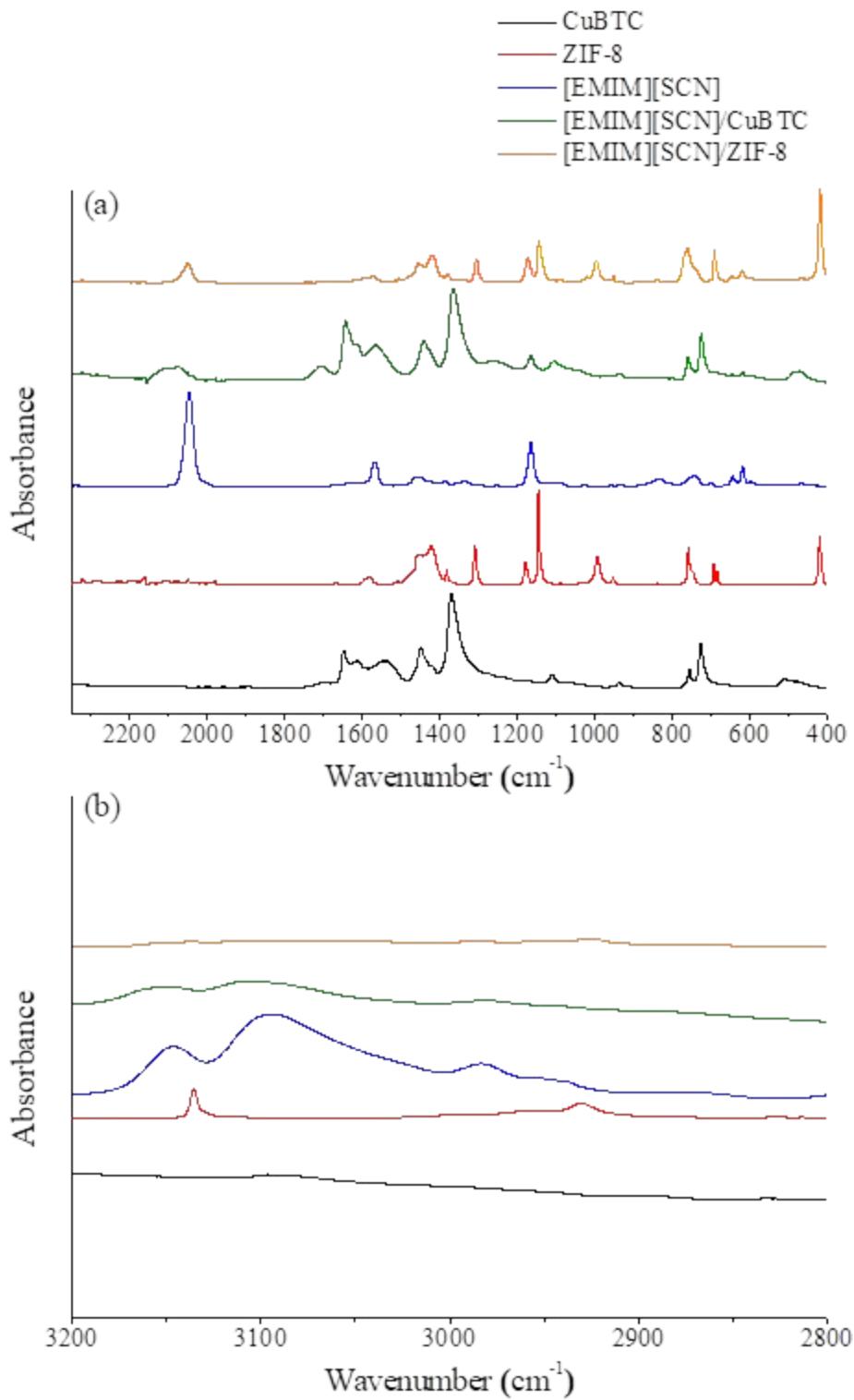


Figure S28. FTIR spectra of CuBTC, ZIF-8, [EMIM][SCN], [EMIM][SCN]/CuBTC, and [EMIM][SCN]/ZIF-8 (a) $400\text{-}2250\text{ cm}^{-1}$ and (b) $2800\text{-}3200\text{ cm}^{-1}$.

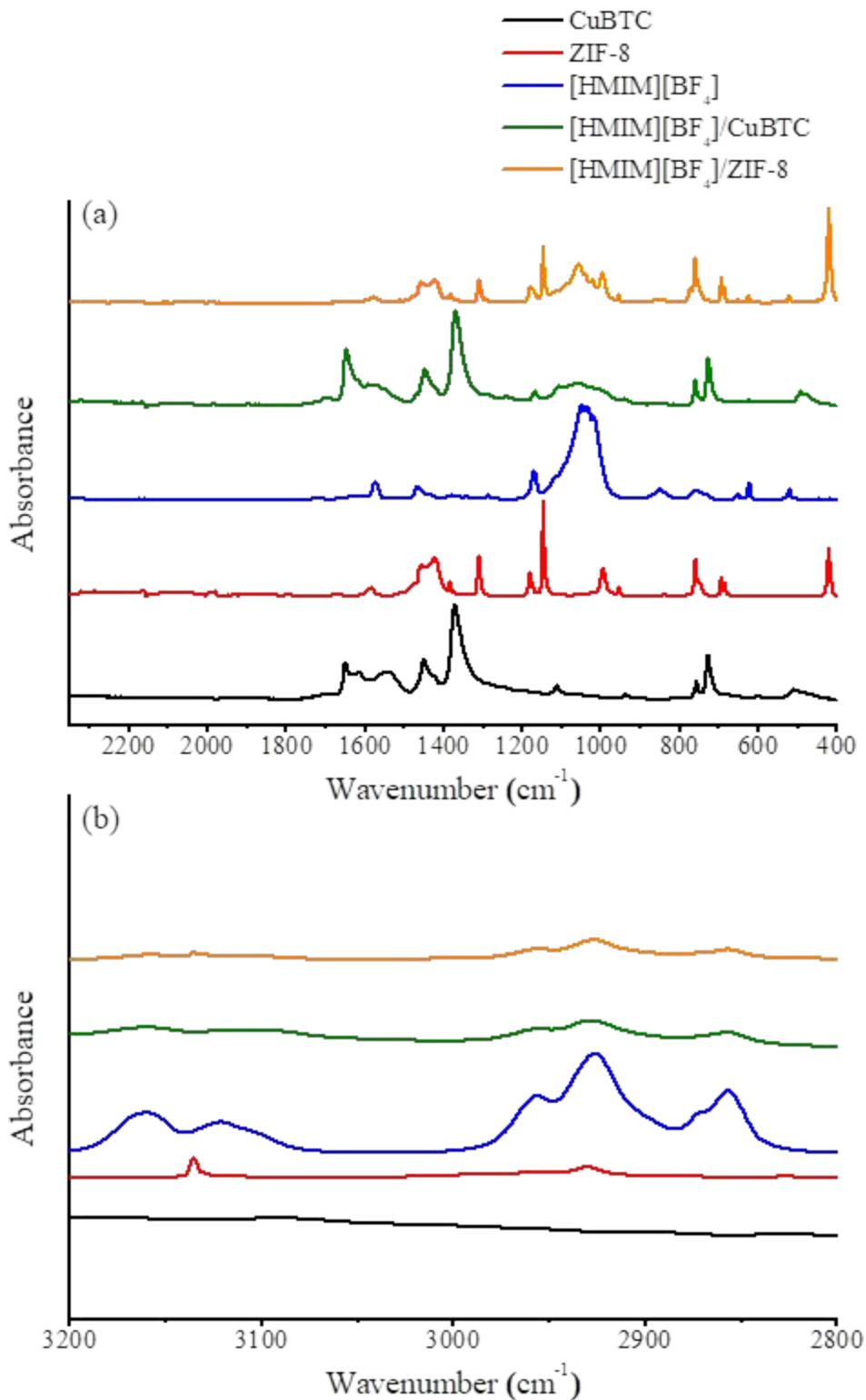


Figure S29. FTIR spectra of CuBTC, ZIF-8, [HMIM][BF₄], [HMIM][BF₄]/CuBTC, and [HMIM][BF₄]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

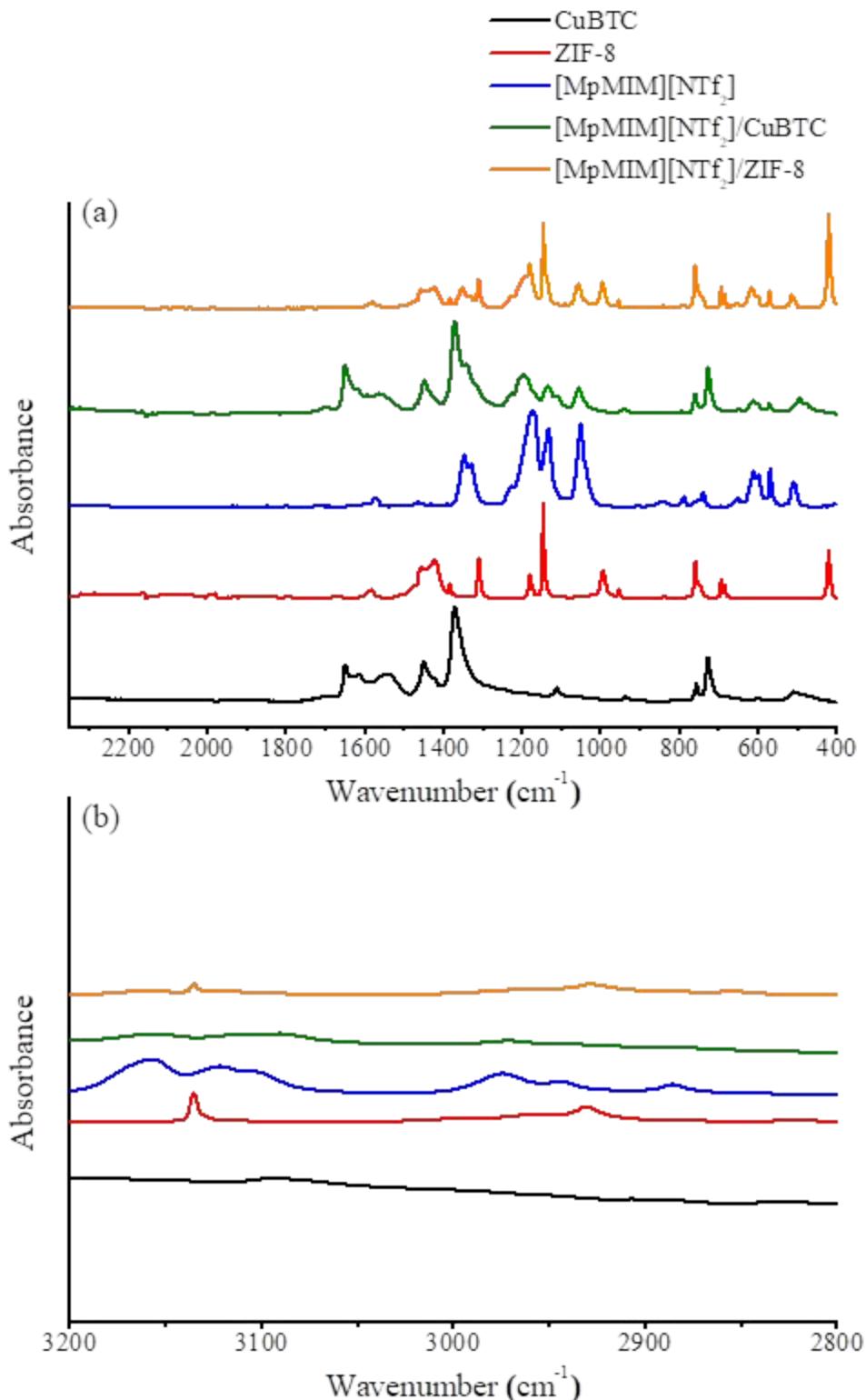


Figure S30. FTIR spectra of CuBTC, ZIF-8, [MpMIM][NTf₂], [MpMIM][NTf₂]/CuBTC, and [MpMIM][NTf₂]/ZIF-8 (a) 400-2250 cm⁻¹ and (b) 2800-3200 cm⁻¹.

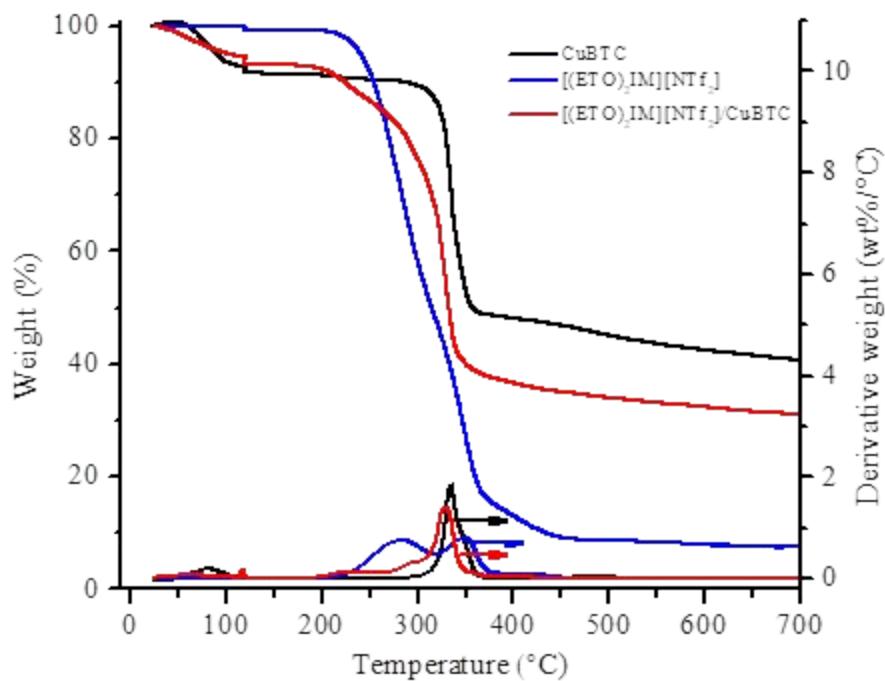


Figure S31. Thermal stability of pristine CuBTC, bulk $[(\text{ETO})_2\text{IM}][\text{NTf}_2]$, and $[(\text{ETO})_2\text{IM}][\text{NTf}_2]/\text{CuBTC}$.

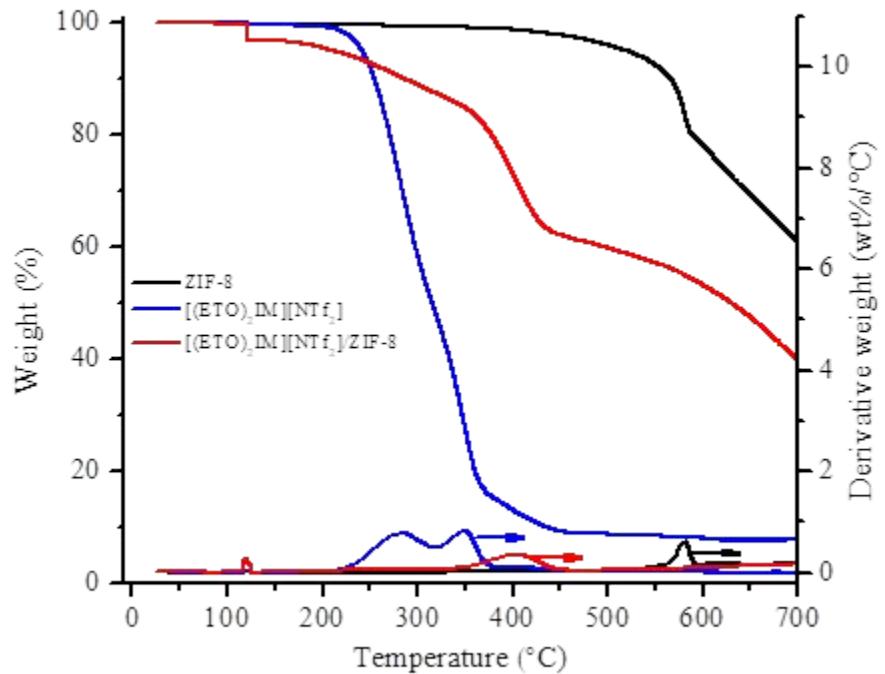


Figure S32. Thermal stability of pristine ZIF-8, bulk $[(\text{ETO})_2\text{IM}][\text{NTf}_2]$, and $[(\text{ETO})_2\text{IM}][\text{NTf}_2]/\text{ZIF-8}$.

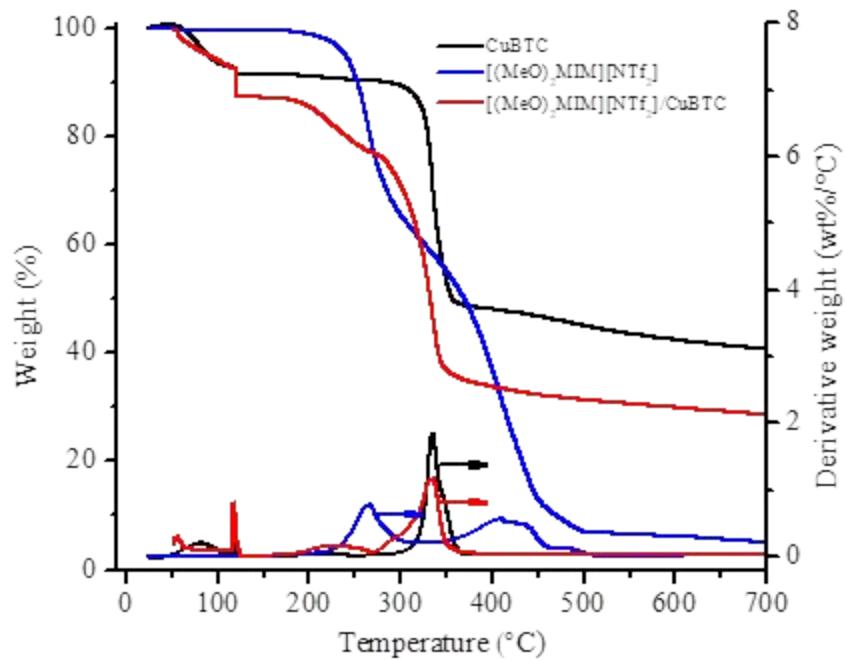


Figure S33. Thermal stability of pristine CuBTC, bulk $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]$, and $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]/\text{CuBTC}$.

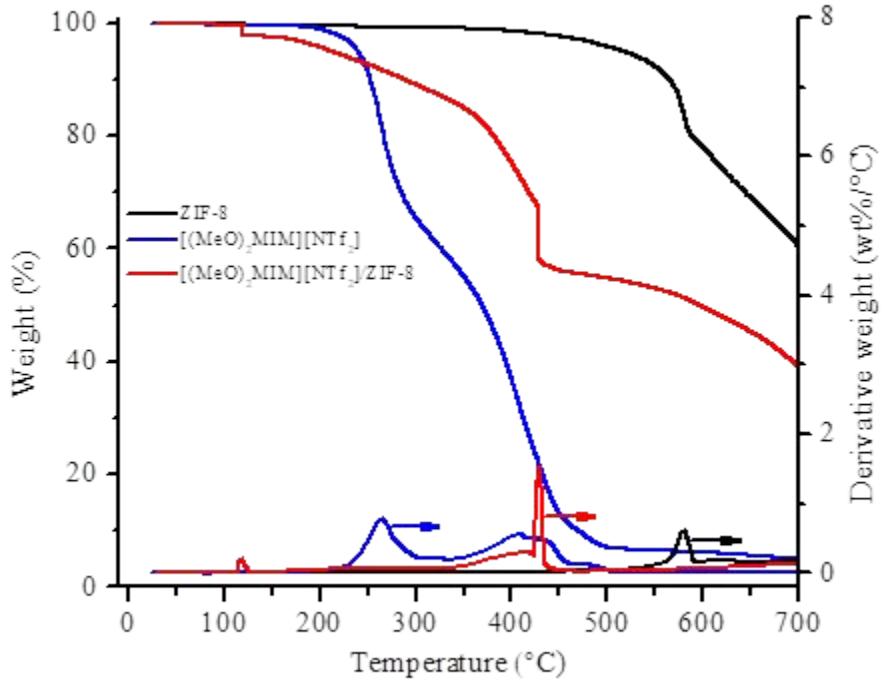


Figure S34. Thermal stability of pristine ZIF-8, bulk $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]$, and $[(\text{MeO})_2\text{MIM}][\text{NTf}_2]/\text{ZIF-8}$.

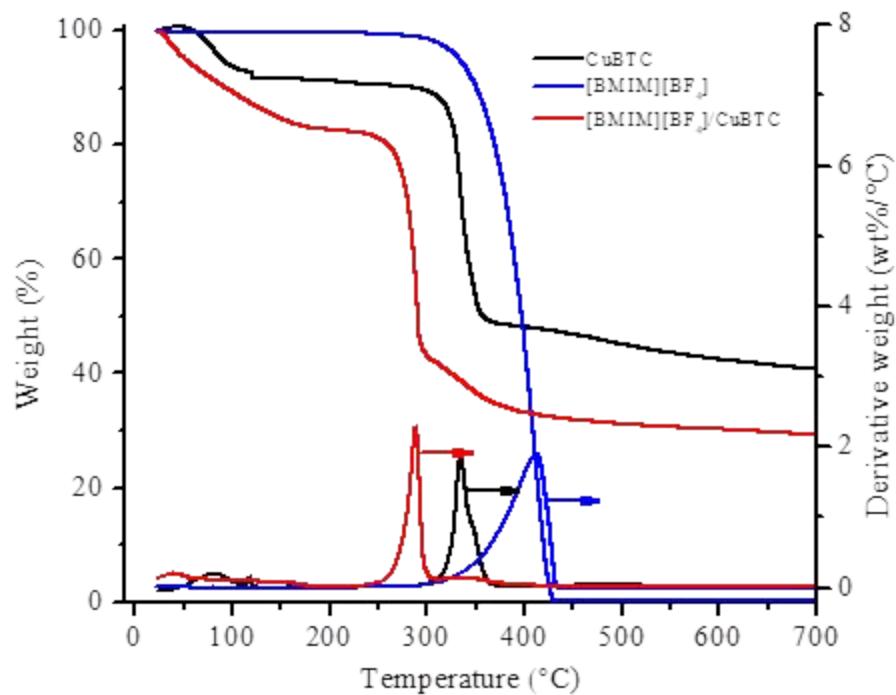


Figure S35. Thermal stability of pristine CuBTC, bulk [BMIM][BF₄], and [BMIM][BF₄]/CuBTC.

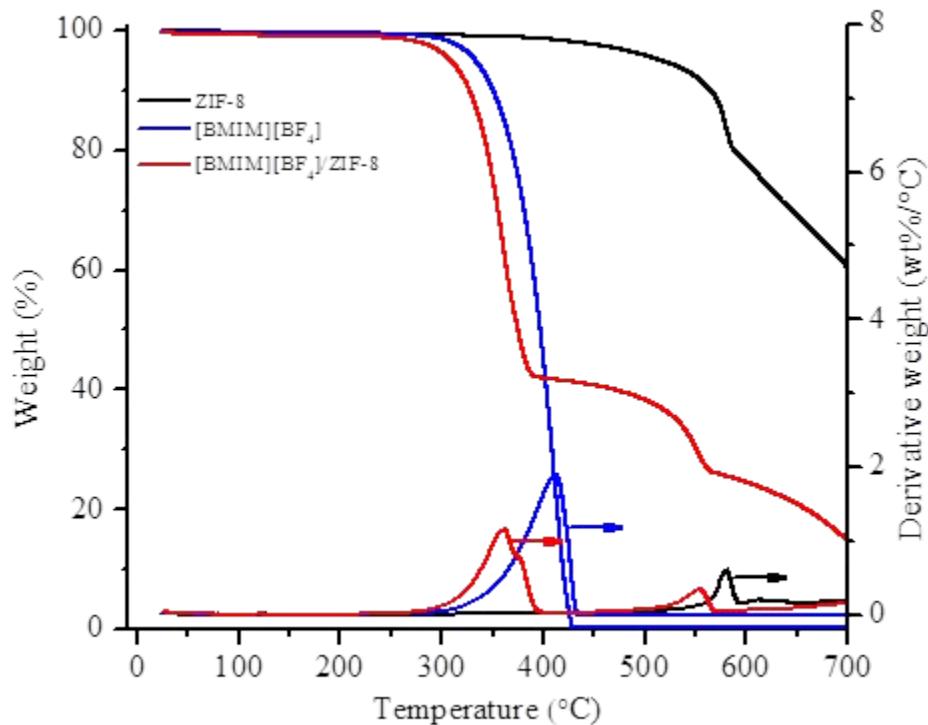


Figure S36. Thermal stability of pristine ZIF-8, bulk [BMIM][BF₄], and [BMIM][BF₄]/ZIF-8.

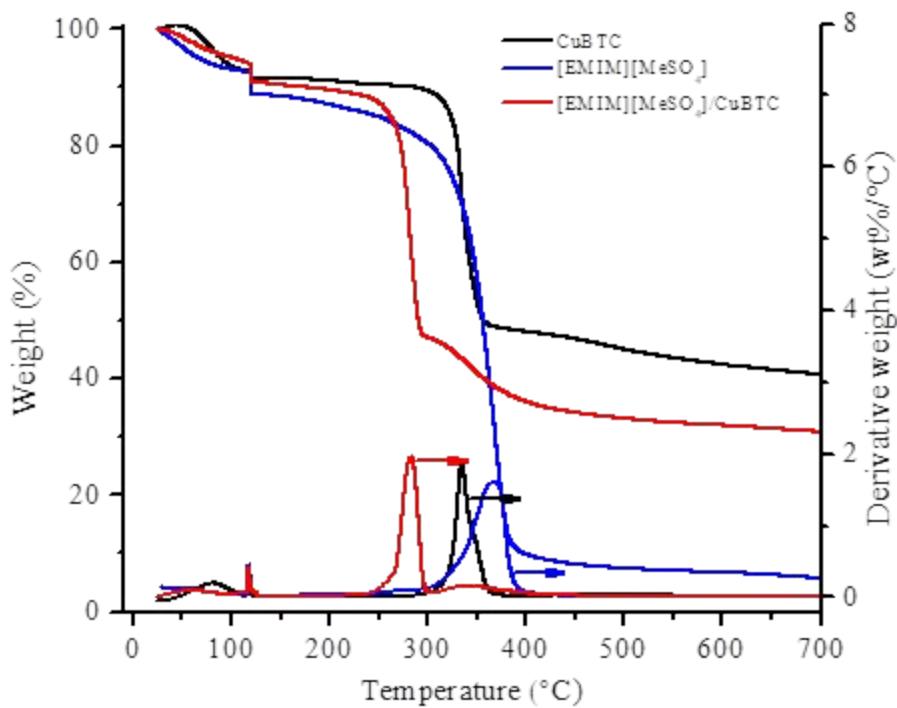


Figure S37. Thermal stability of pristine CuBTC, bulk [EMIM][MeSO₄], and [EMIM][MeSO₄]/CuBTC.

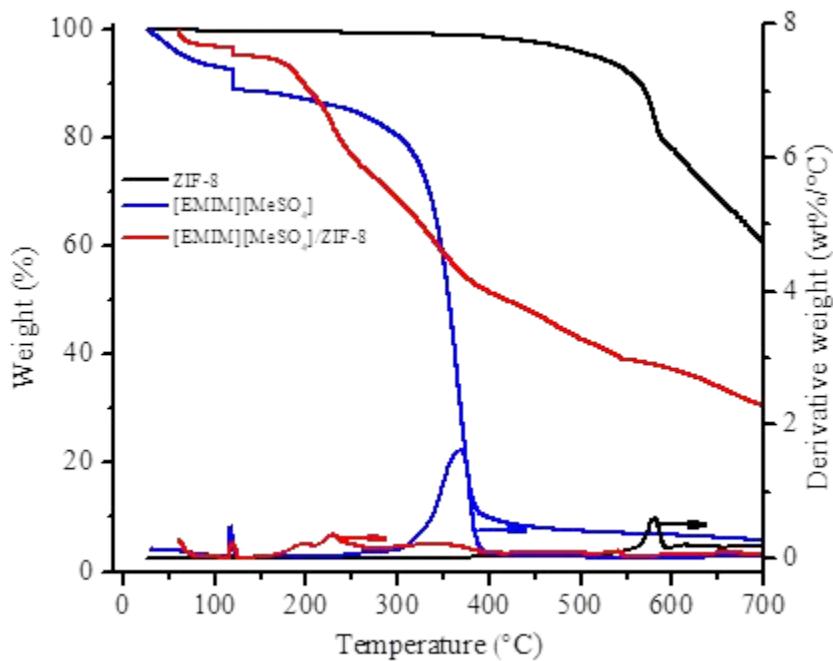


Figure S38. Thermal stability of pristine ZIF-8, bulk [EMIM][MeSO₄], and [EMIM][MeSO₄]/ZIF-8.

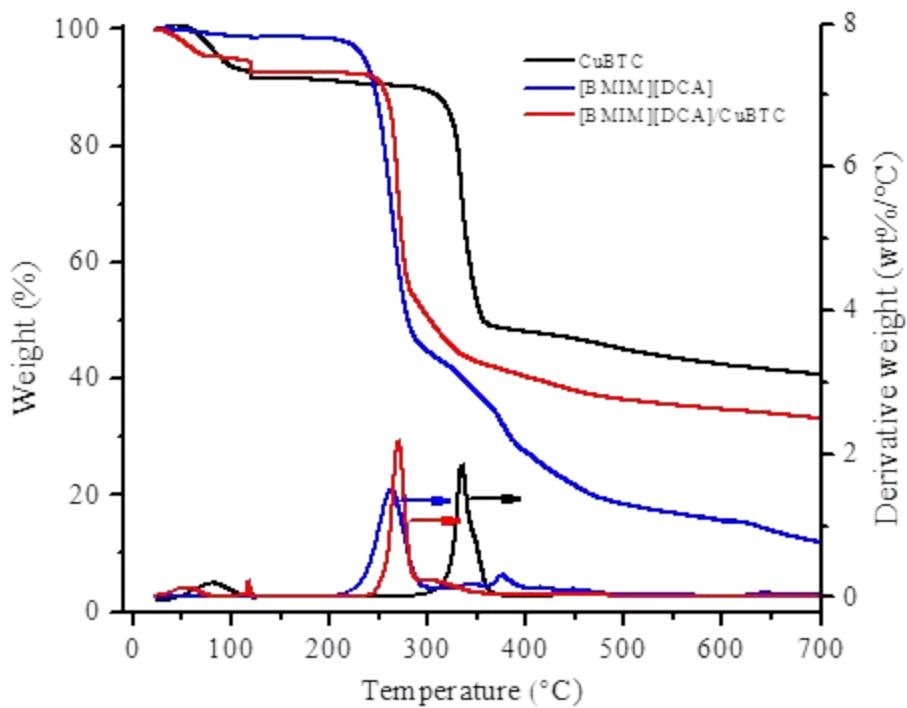


Figure S39. Thermal stability of pristine CuBTC, bulk [BMIM][DCA], and [BMIM][DCA]/CuBTC.

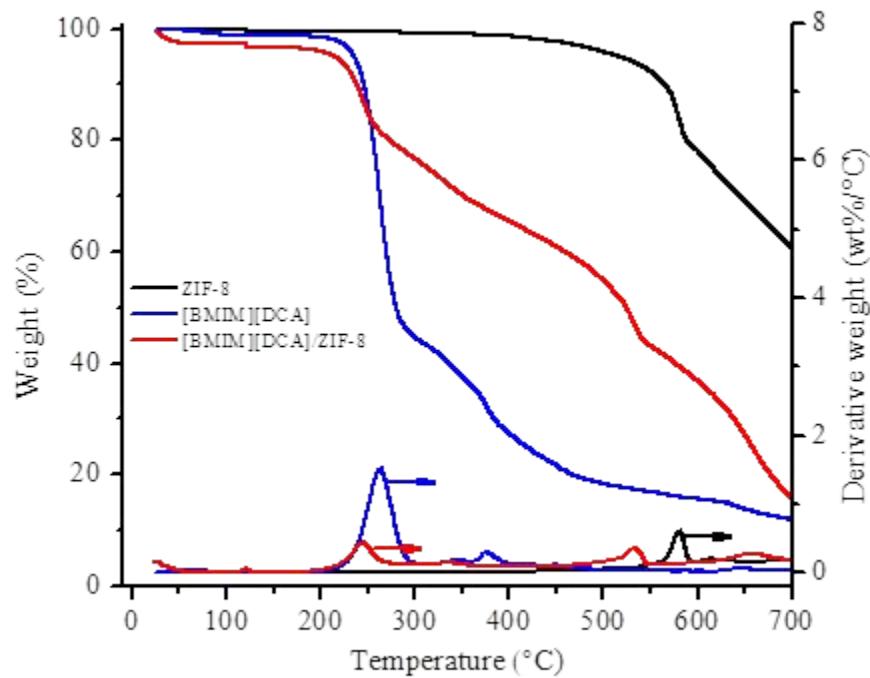


Figure S40. Thermal stability of pristine ZIF-8, bulk [BMIM][DCA], and [BMIM][DCA]/ZIF-8.

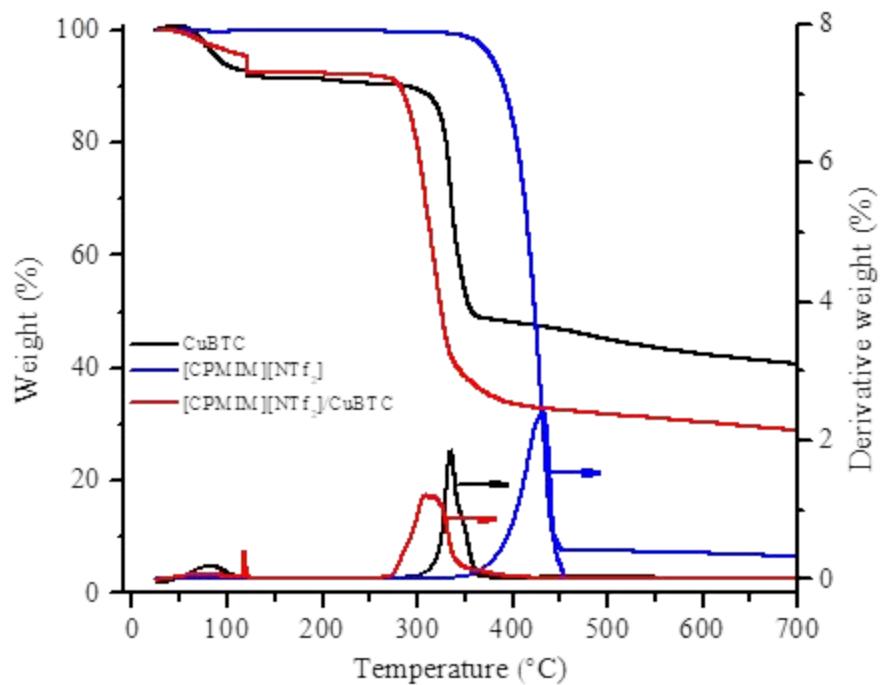


Figure S41. Thermal stability of pristine CuBTC, bulk [CPMIM][NTf₂], and [CPMIM][NTf₂]/CuBTC.

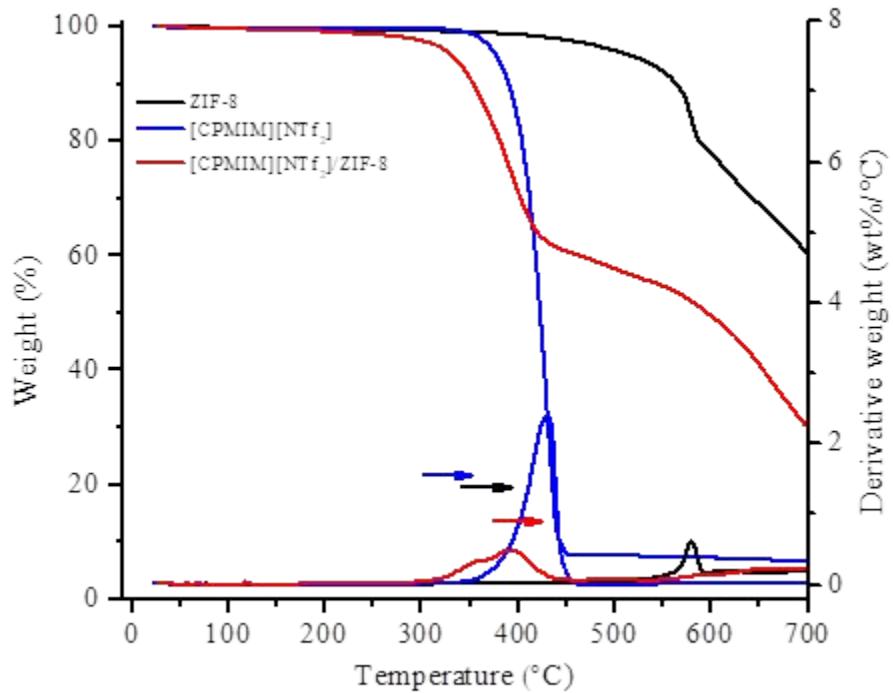


Figure S42. Thermal stability of pristine ZIF-8, bulk [CPMIM][NTf₂], and [CPMIM][NTf₂]/ZIF-8.

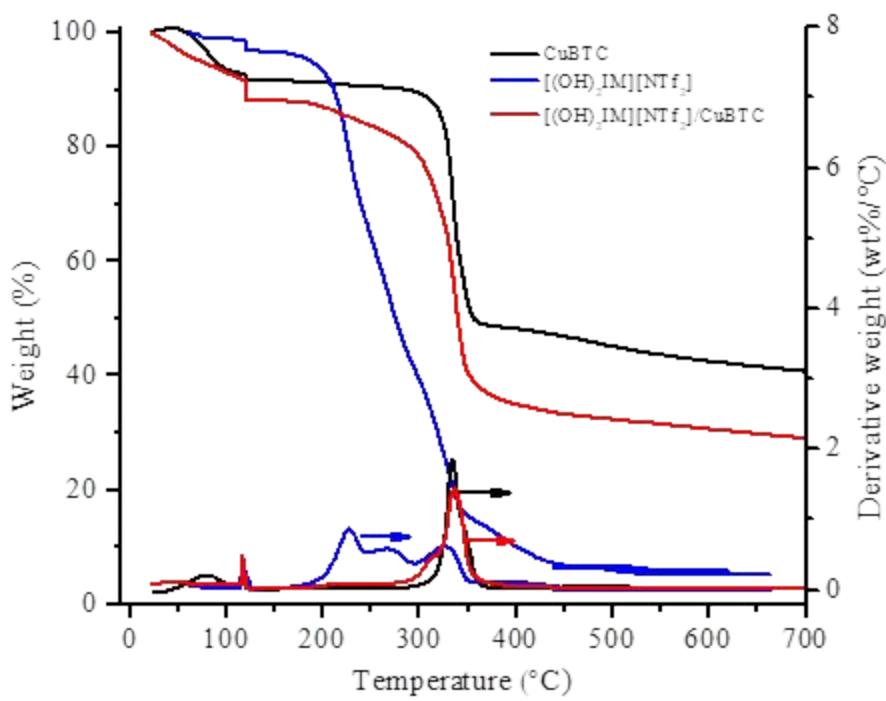


Figure S43. Thermal stability of pristine CuBTC, bulk $[(\text{OH})_2\text{IM}][\text{NTf}_2]$, and $[(\text{OH})_2\text{IM}][\text{NTf}_2]/\text{CuBTC}$.

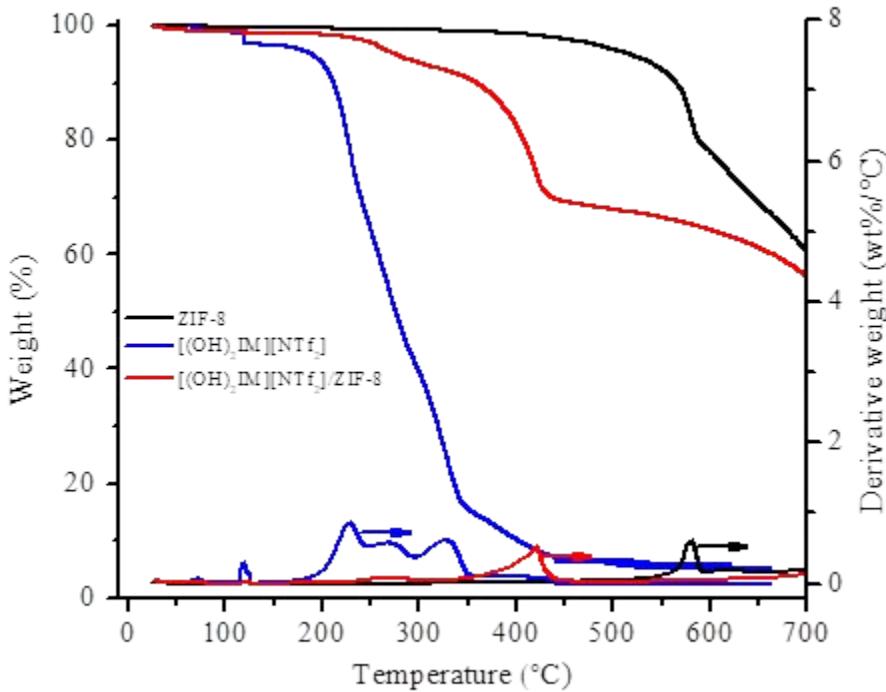


Figure S44. Thermal stability of pristine ZIF-8, bulk $[(\text{OH})_2\text{IM}][\text{NTf}_2]$, and $[(\text{OH})_2\text{IM}][\text{NTf}_2]/\text{ZIF-8}$.

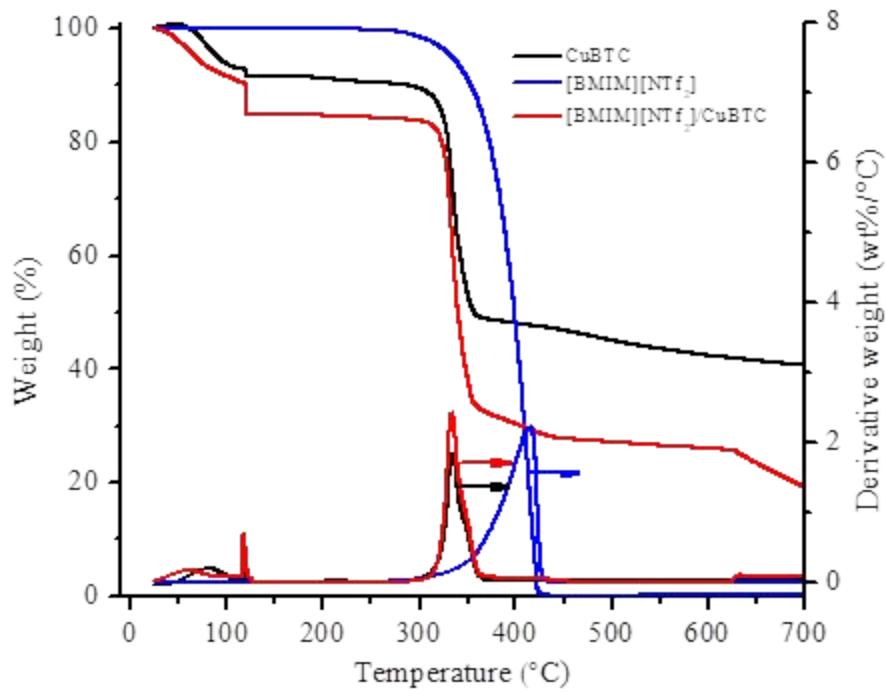


Figure S45. Thermal stability of pristine CuBTC, bulk [BMIM][NTf₂], and [BMIM][NTf₂]/CuBTC.

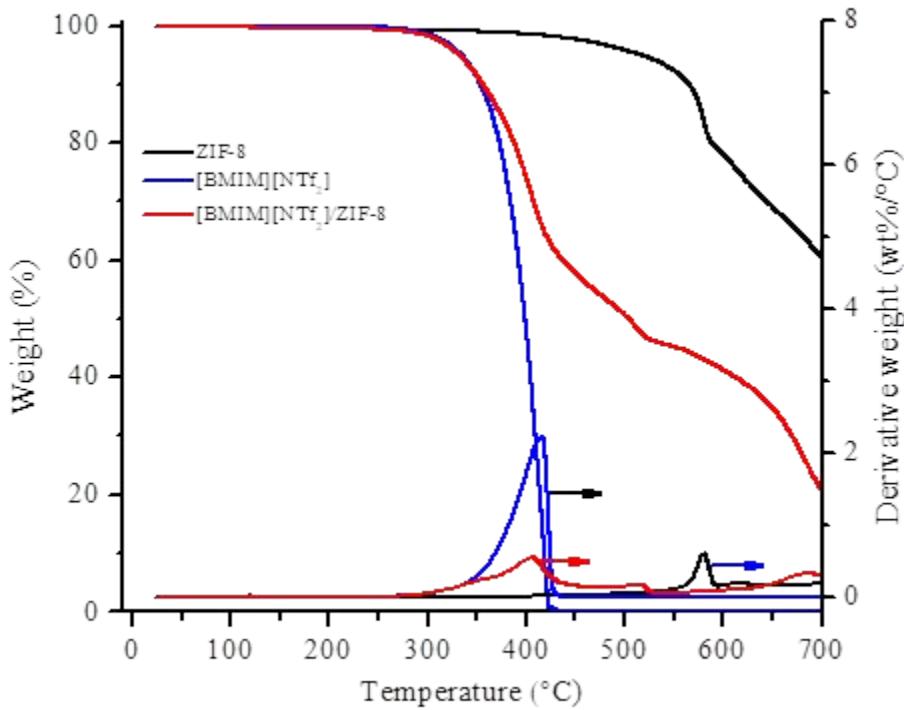


Figure S46. Thermal stability of pristine ZIF-8, bulk [BMIM][NTf₂], and [BMIM][NTf₂]/ZIF-8.

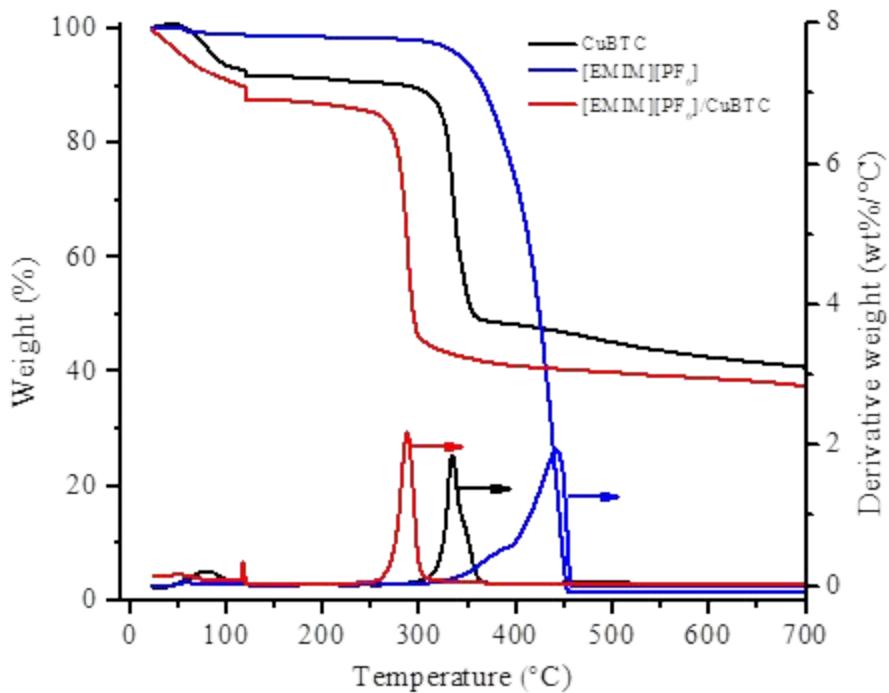


Figure S47. Thermal stability of pristine CuBTC, bulk [EMIM][PF₆], and [EMIM][PF₆]/CuBTC.

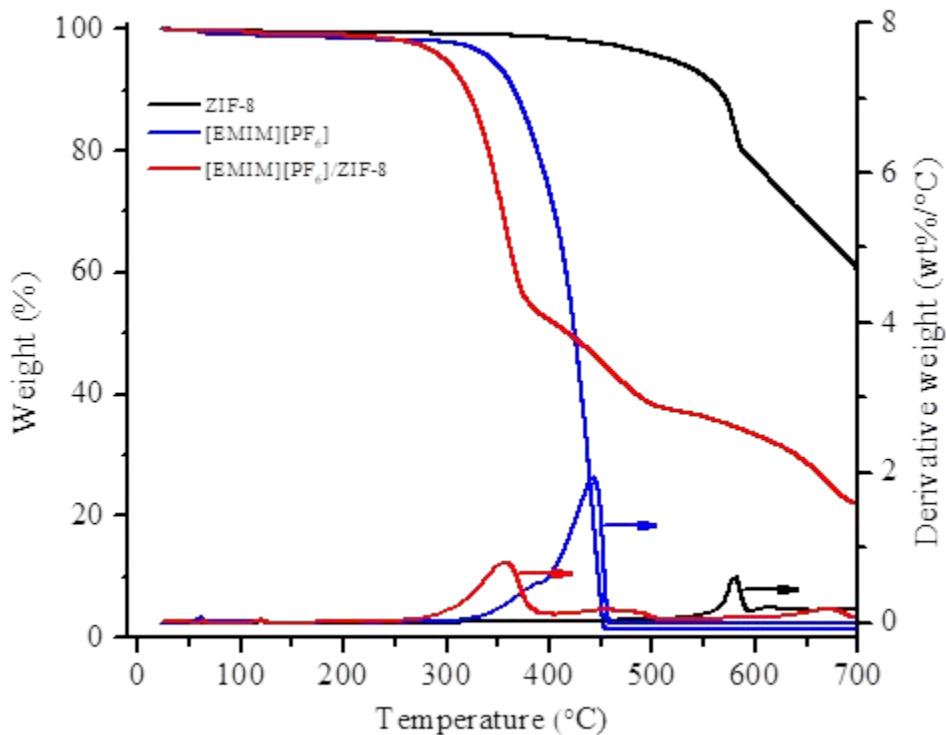


Figure S48. Thermal stability of pristine ZIF-8, bulk [EMIM][PF₆], and [EMIM][PF₆]/ZIF-8.

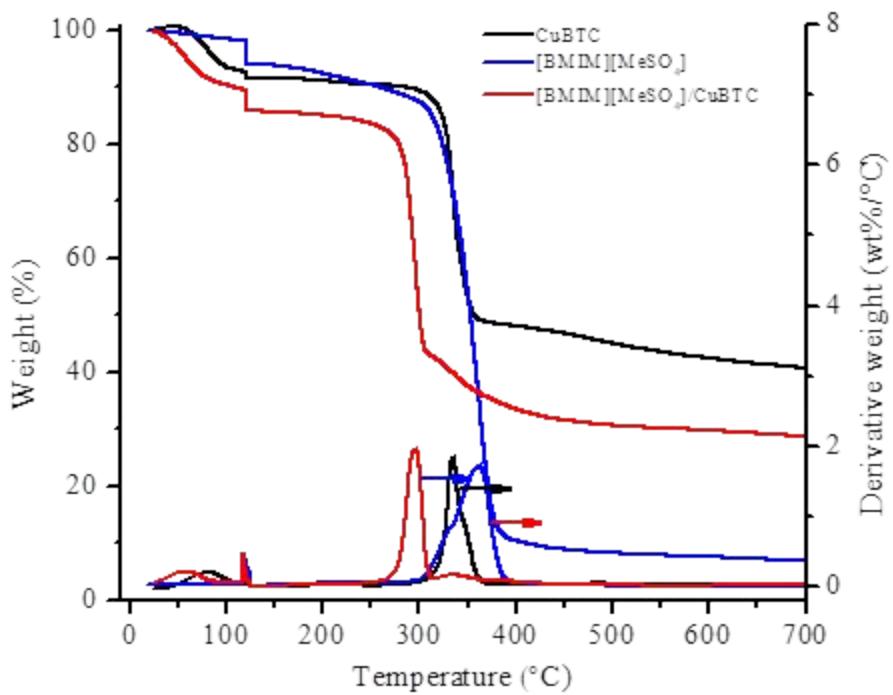


Figure S49. Thermal stability of pristine CuBTC, bulk [BMIM][MeSO₄], and [BMIM][MeSO₄]/CuBTC.

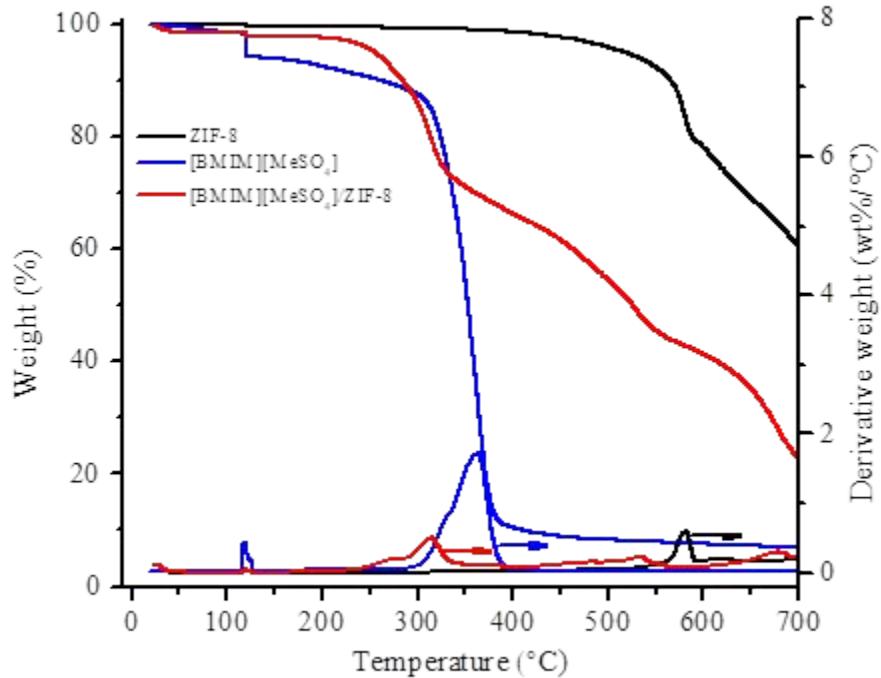


Figure S50. Thermal stability of pristine ZIF-8, bulk [BMIM][MeSO₄], and [BMIM][MeSO₄]/ZIF-8.

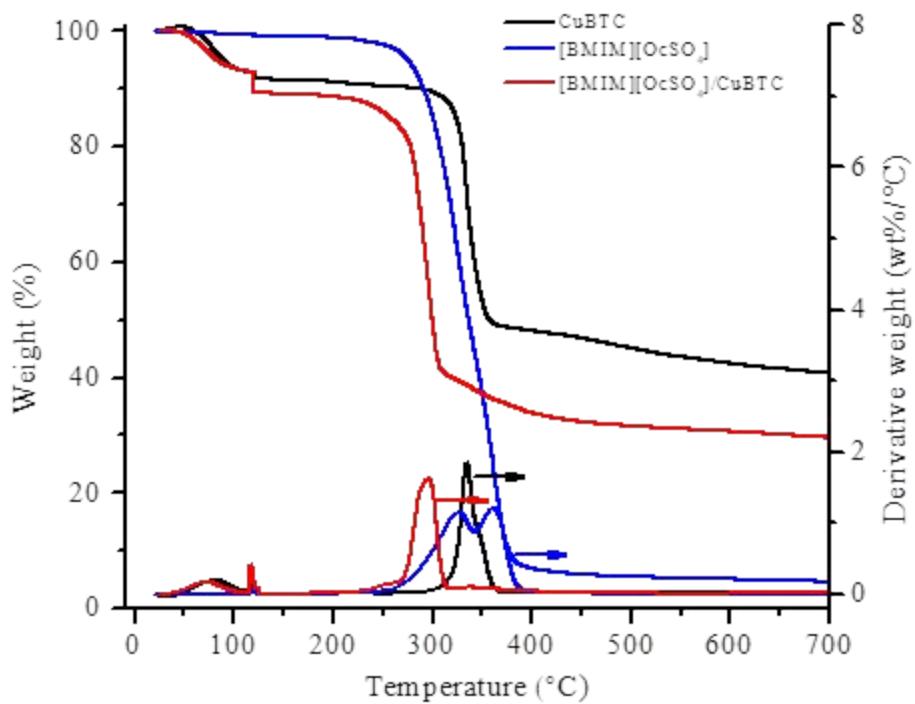


Figure S51. Thermal stability of pristine CuBTC, bulk [BMIM][OcSO₄], and [BMIM][OcSO₄]/CuBTC.

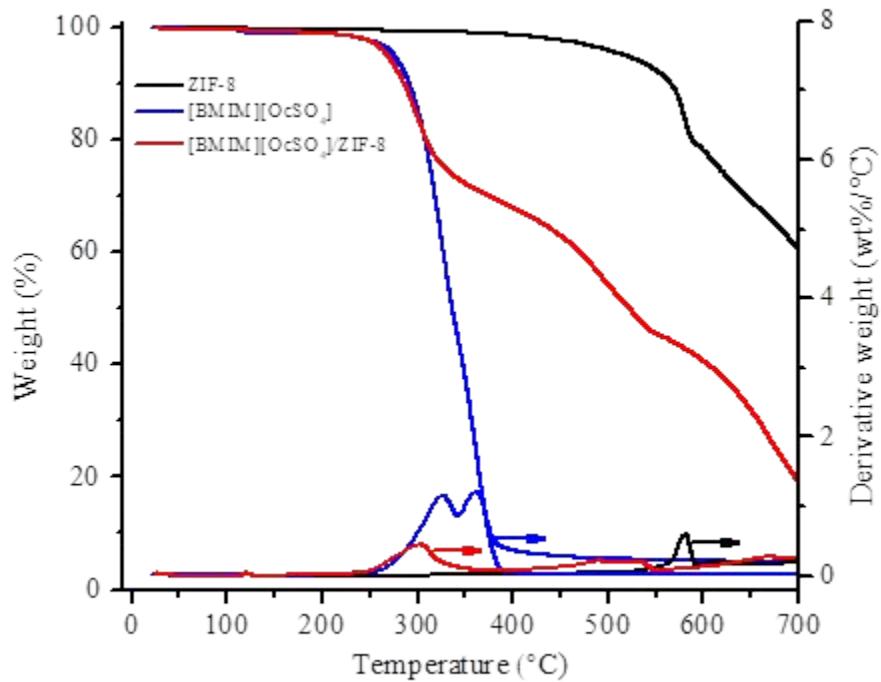


Figure S52. Thermal stability of pristine ZIF-8, bulk [BMIM][OcSO₄], and [BMIM][OcSO₄]/ZIF-8.

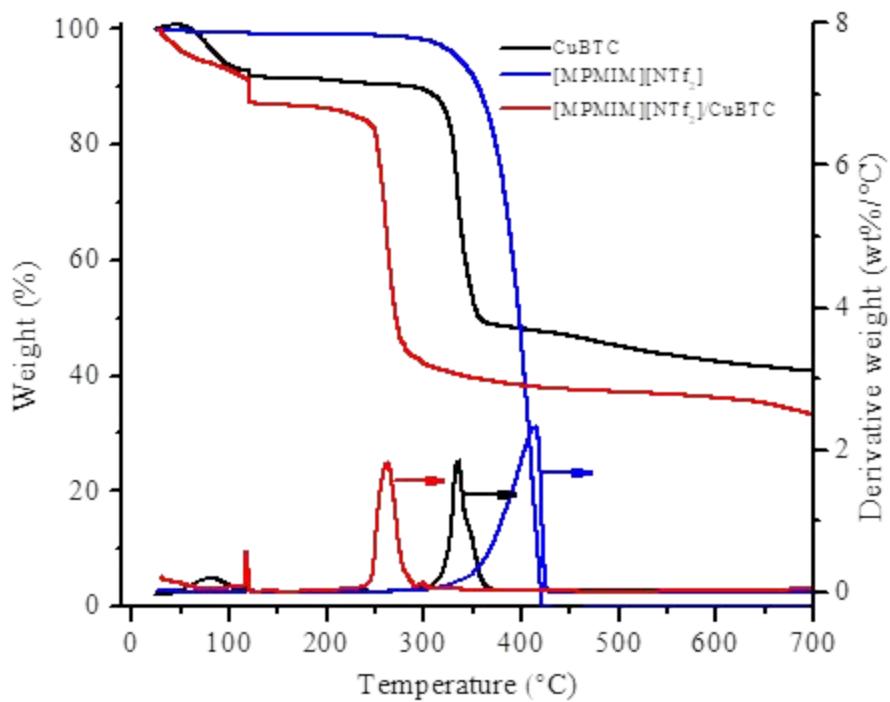


Figure S53. Thermal stability of pristine CuBTC, bulk [MPMIM][NTf₂], and [MPMIM][NTf₂]/CuBTC.

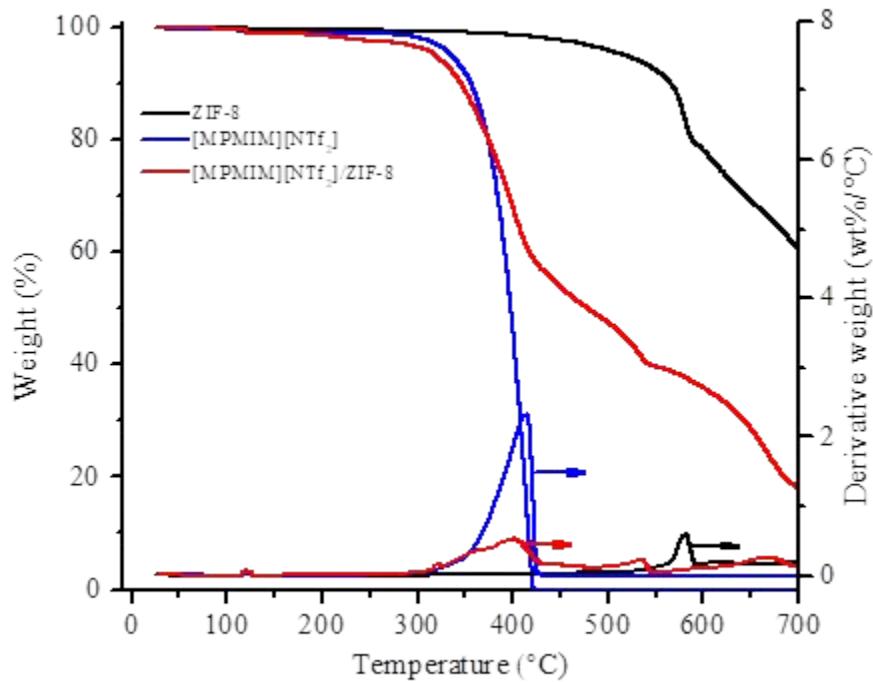


Figure S54. Thermal stability of pristine ZIF-8, Bulk [MPMIM][NTf₂], and [MPMIM][NTf₂]/ZIF-8.

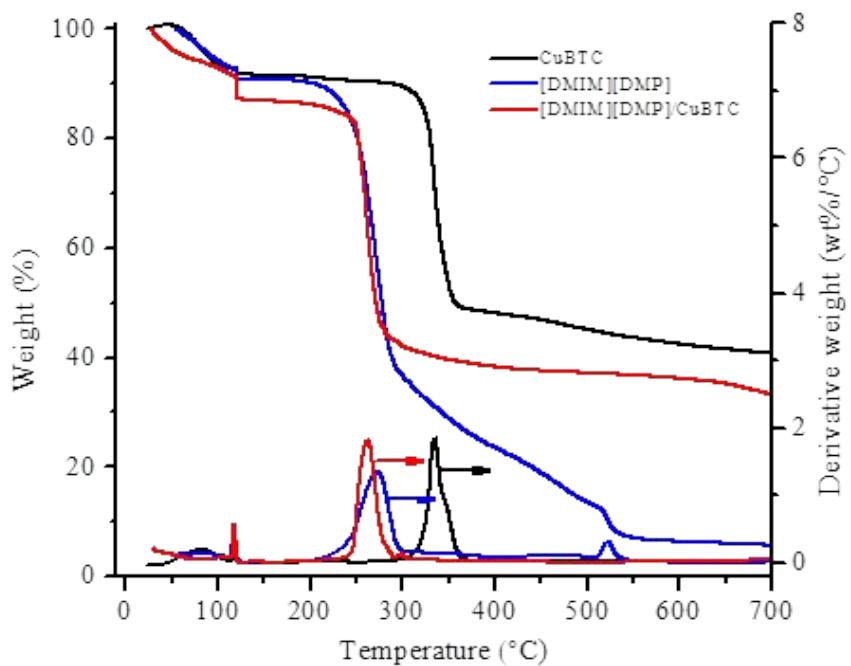


Figure S55. Thermal stability of pristine CuBTC, bulk [DMIM][DMP], and [DMIM][DMP]/CuBTC.

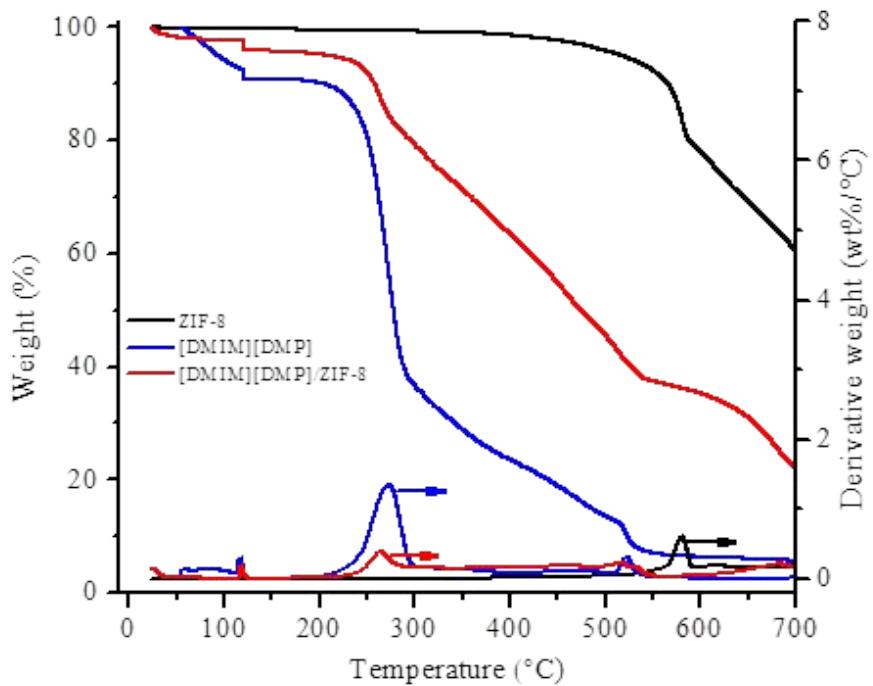


Figure S56. Thermal stability of pristine ZIF-8, bulk [DMIM][DMP], and [DMIM][DMP]/ZIF-8.

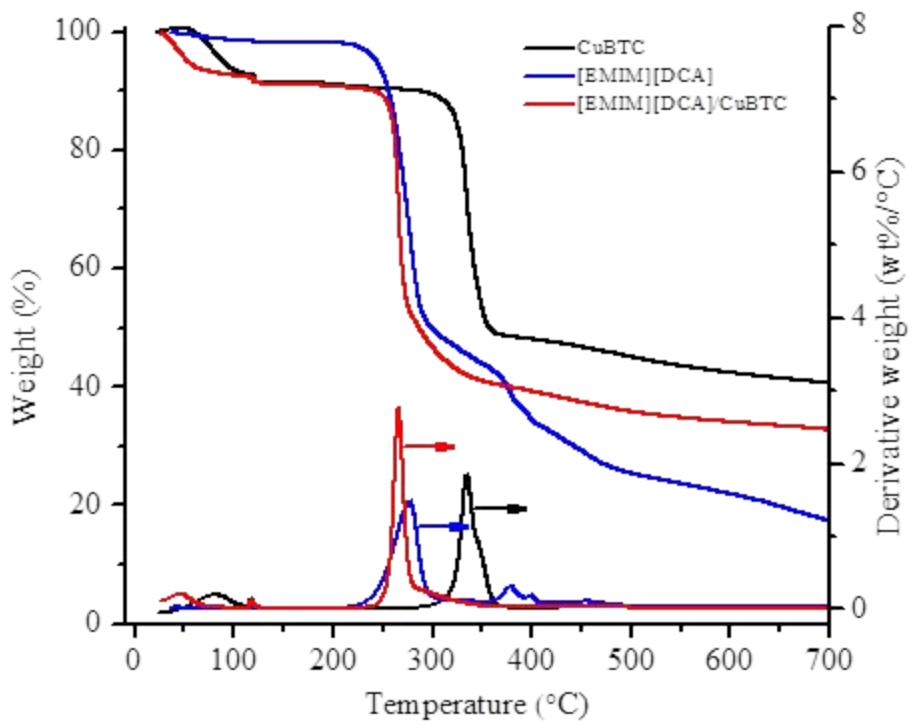


Figure S57. Thermal stability of pristine CuBTC, bulk [EMIM][DCA], and [EMIM][DCA]/CuBTC.

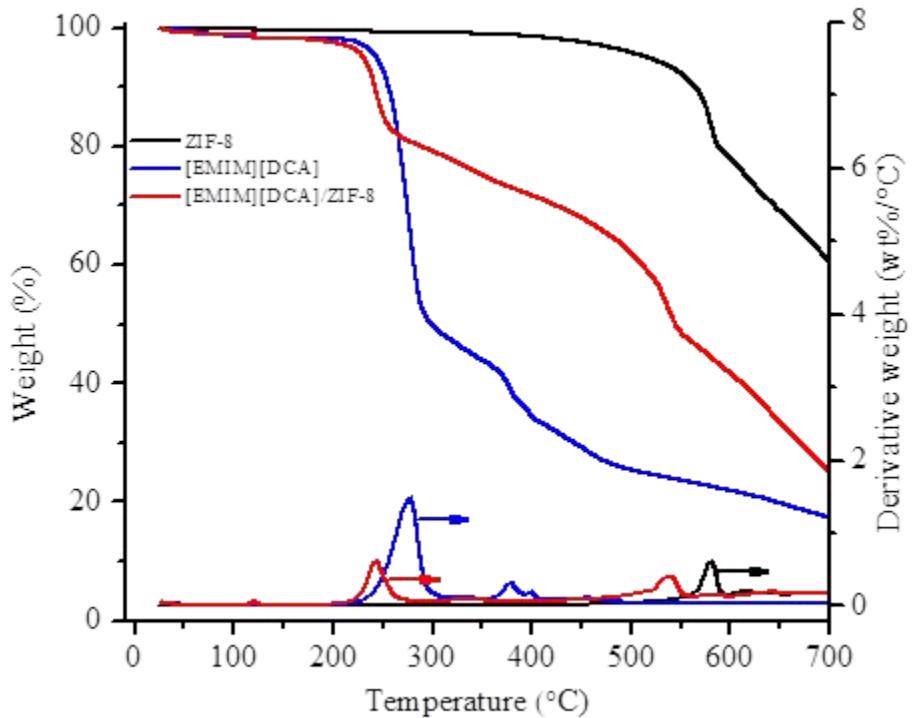


Figure S58. Thermal stability of pristine ZIF-8, bulk [EMIM][DCA], and [EMIM][DCA]/ZIF-8.

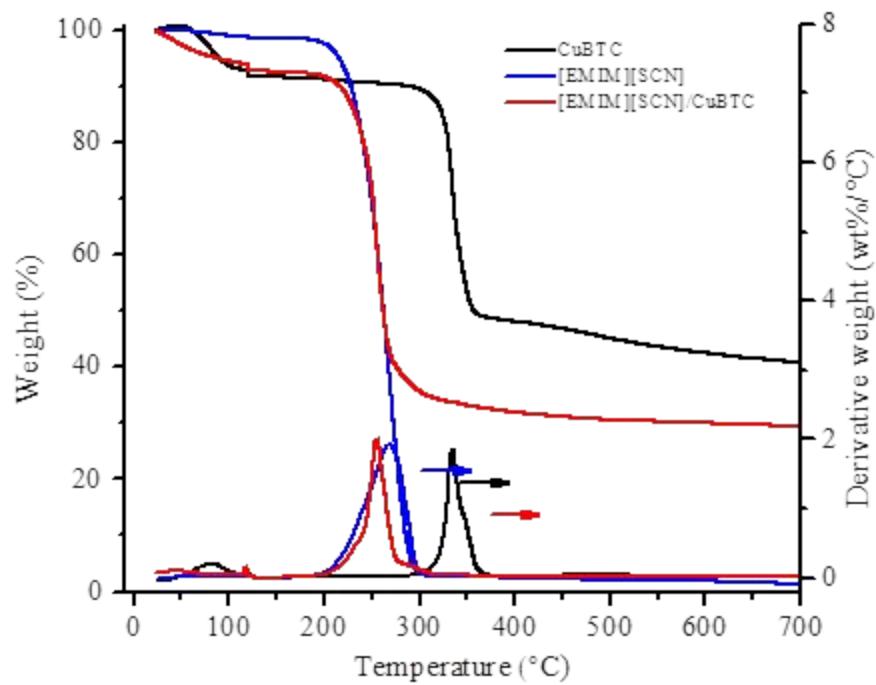


Figure S59. Thermal stability of pristine CuBTC, bulk [EMIM][SCN], and [EMIM][SCN]/CuBTC.

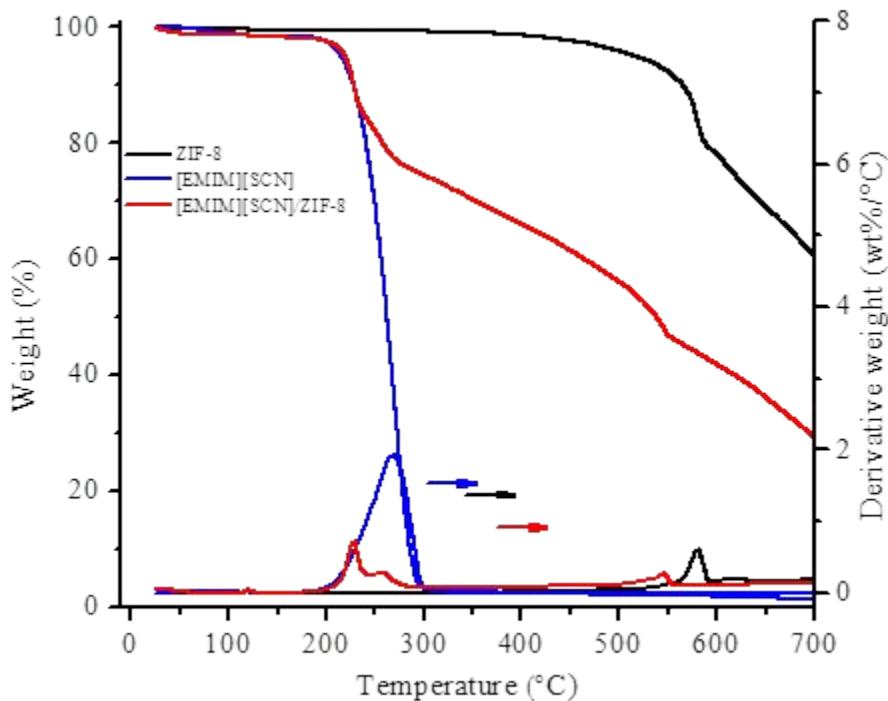


Figure S60. Thermal stability of pristine ZIF-8, bulk [EMIM][SCN], and [EMIM][SCN]/ZIF-8.

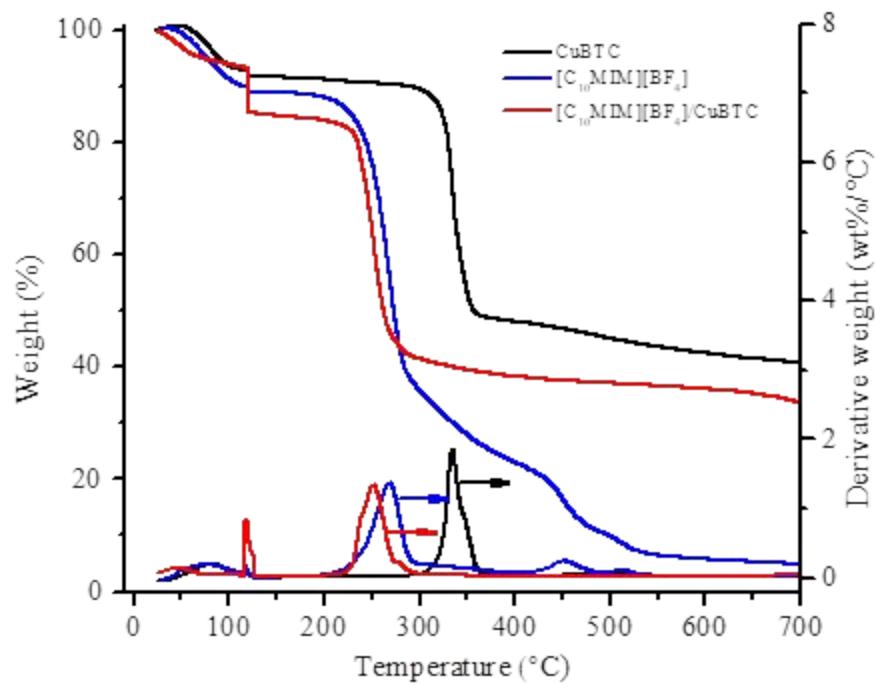


Figure S61. Thermal stability of pristine CuBTC, bulk $[C_{10}MIM][BF_4]$, and $[C_{10}MIM][BF_4]/CuBTC$.

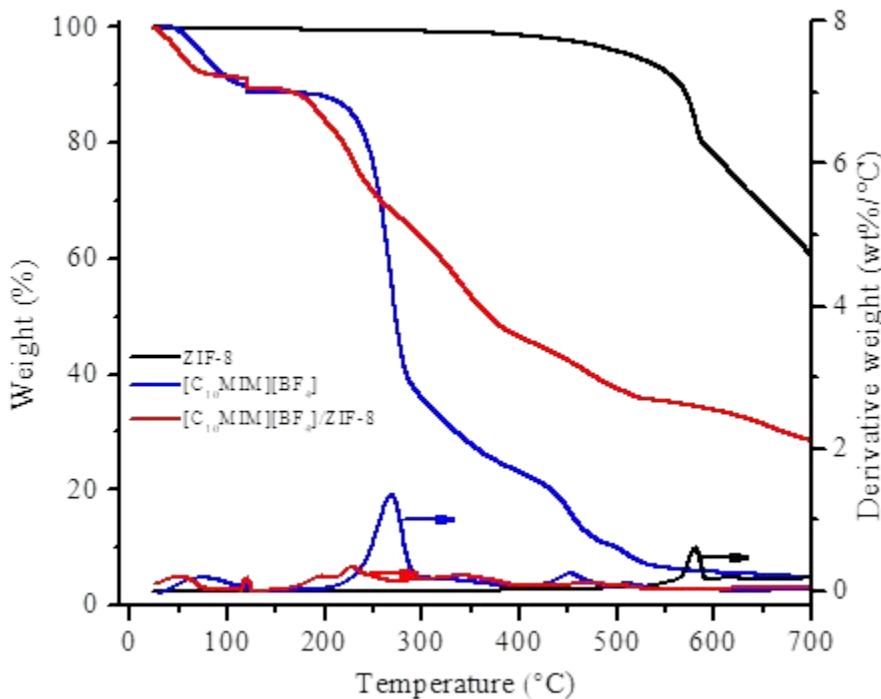


Figure S62. Thermal stability of pristine ZIF-8, bulk $[C_{10}MIM][BF_4]$, and $[C_{10}MIM][BF_4]/ZIF-8$.

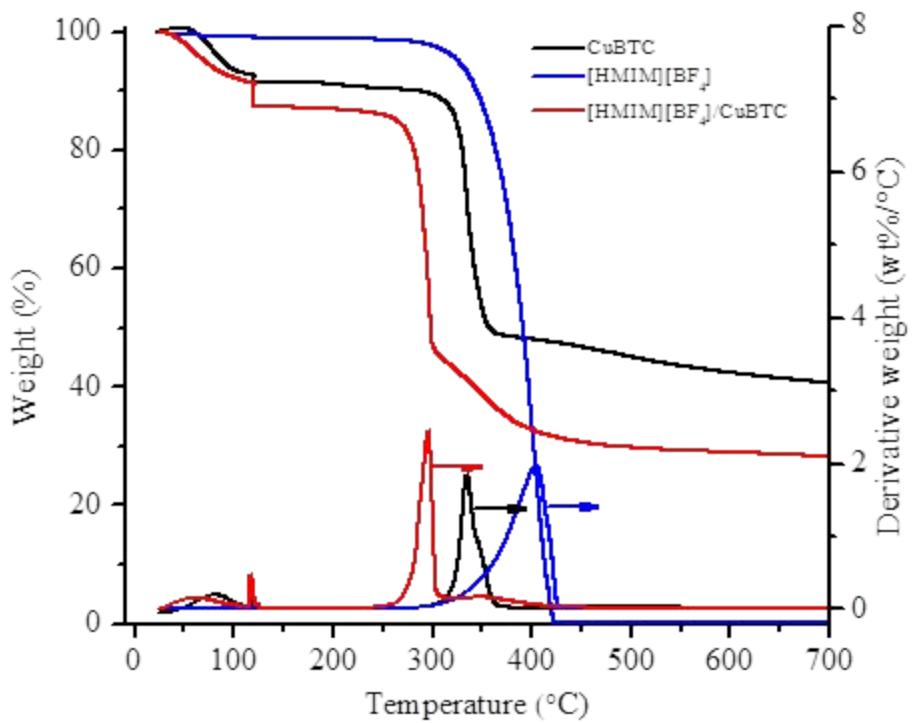


Figure S63. Thermal stability of pristine CuBTC, bulk [HMIM][BF₄], and [HMIM][BF₄]/CuBTC.

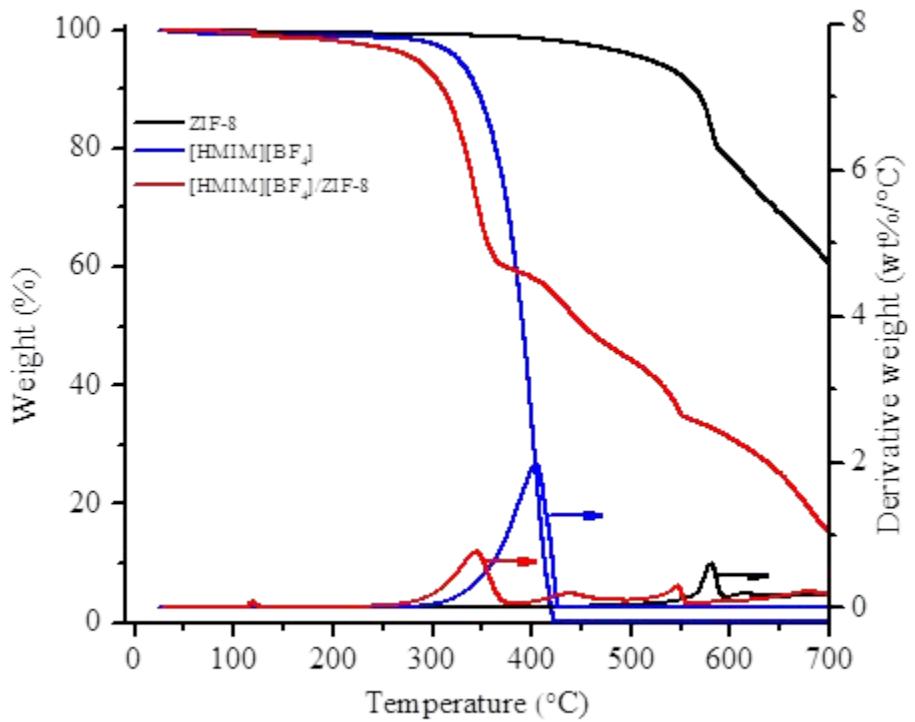


Figure S64. Thermal stability of pristine ZIF-8, bulk [HMIM][BF₄], and [HMIM][BF₄]/ZIF-8.

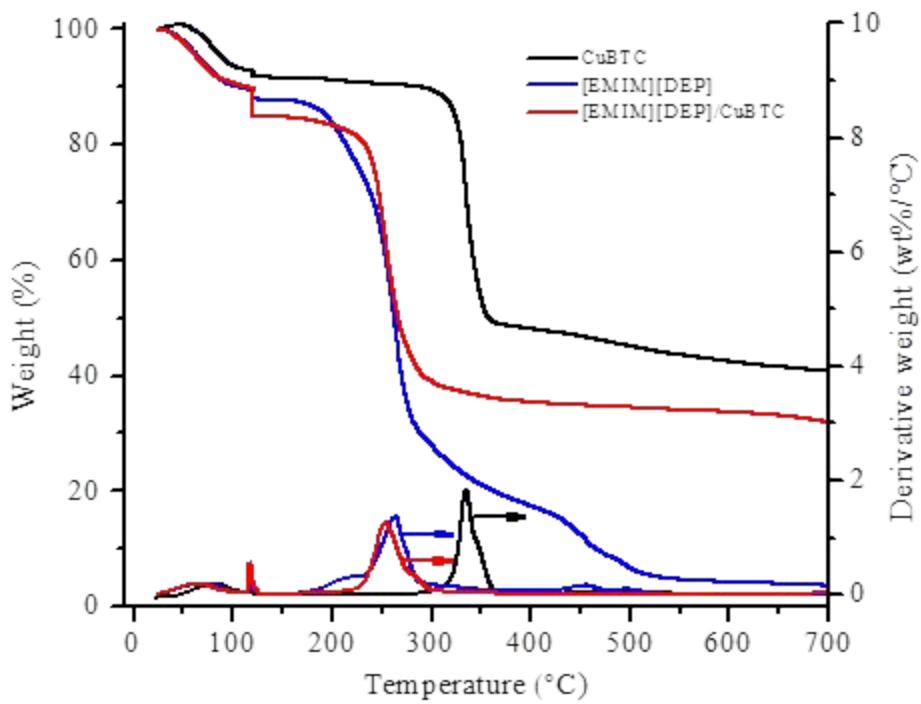


Figure S65. Thermal stability of pristine CuBTC, bulk [EMIM][DEP], and [EMIM][DEP]/CuBTC.

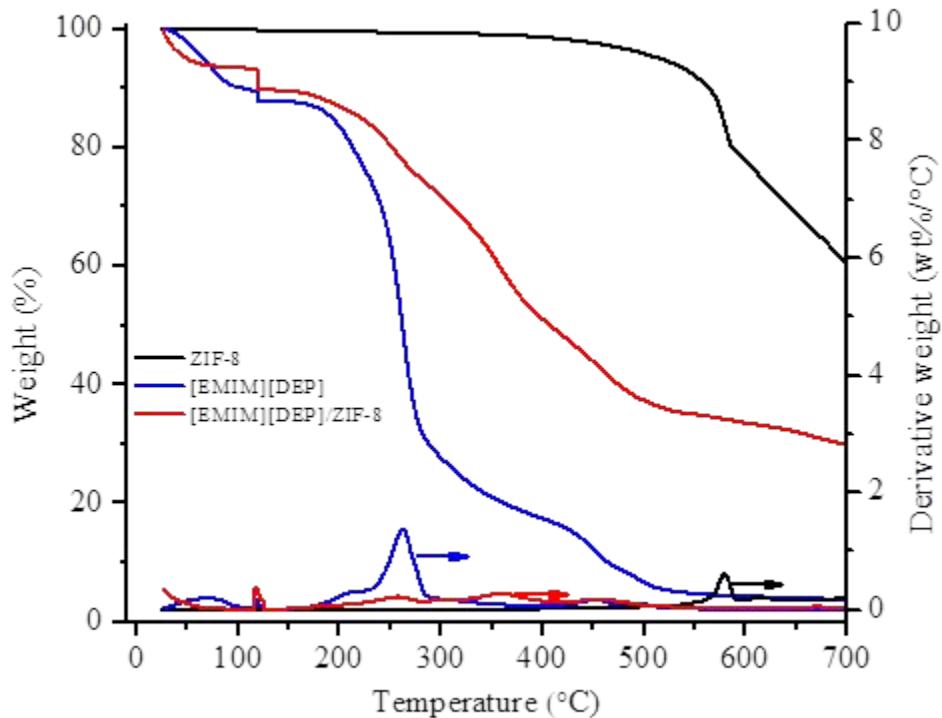


Figure S66. Thermal stability of pristine ZIF-8, bulk [EMIM][DEP], and [EMIM][DEP]/ZIF-8.

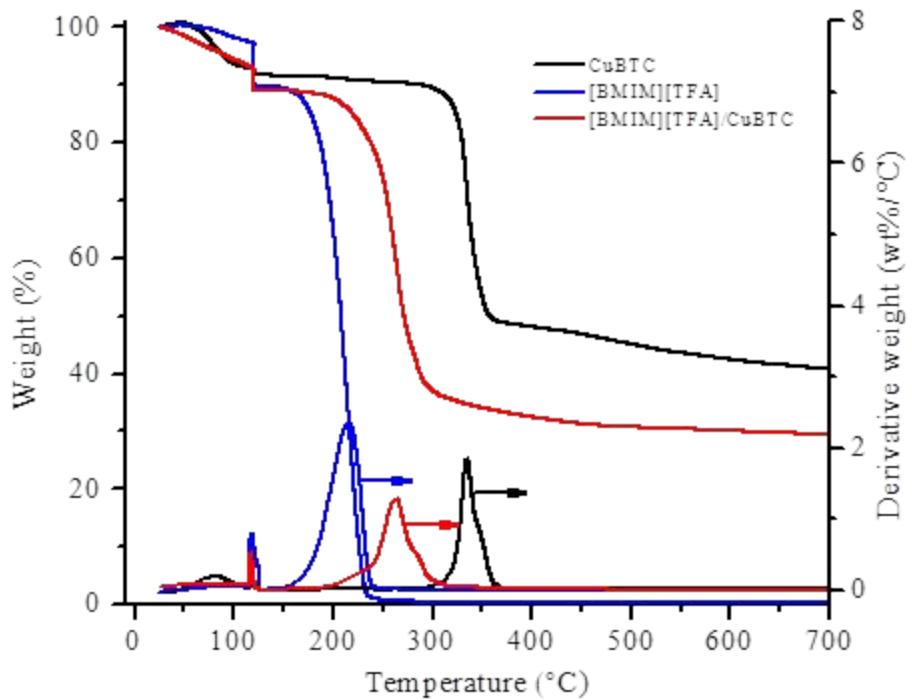


Figure S67. Thermal stability of pristine CuBTC, bulk [BMIM][TFA], and [BMIM][TFA]/CuBTC.

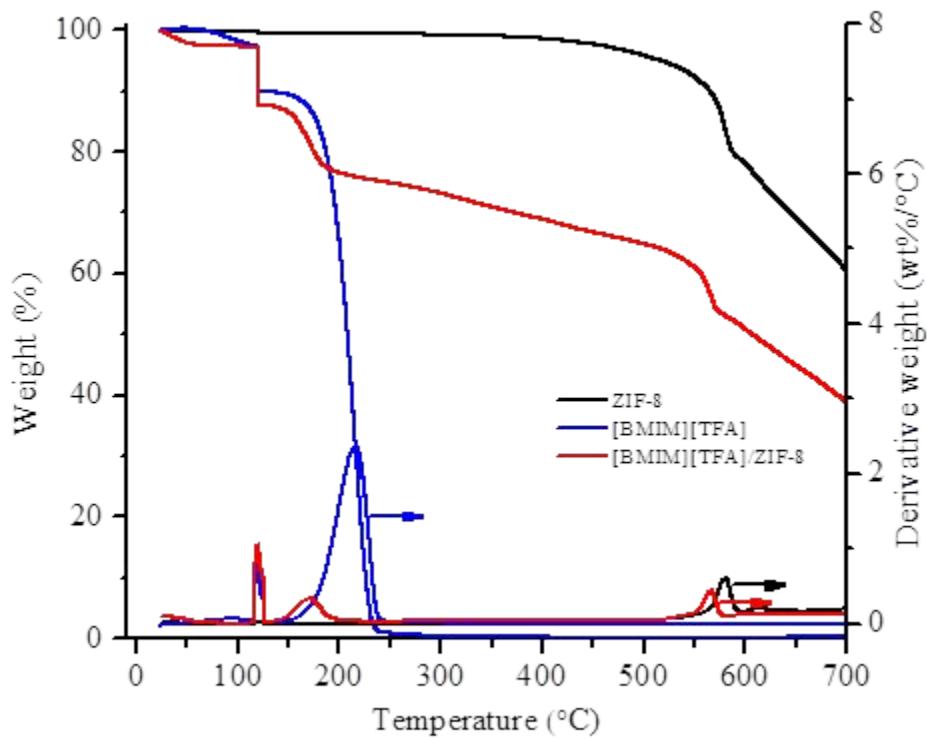


Figure S68. Thermal stability of pristine ZIF-8, bulk [BMIM][TFA], and [BMIM][TFA]/ZIF-8.

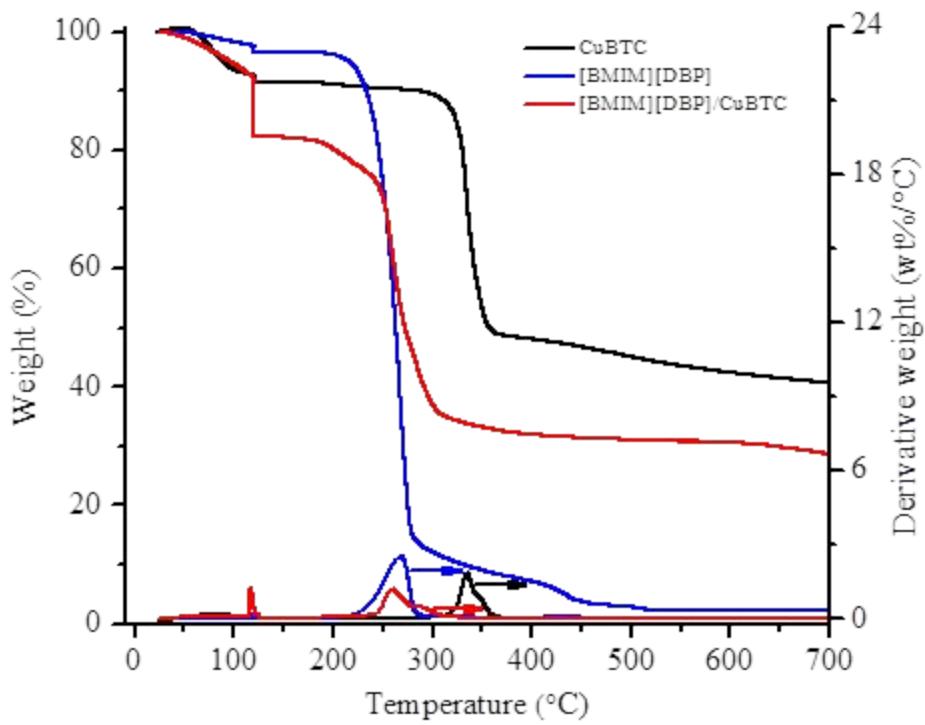


Figure S69. Thermal stability of pristine CuBTC, bulk [BMIM][DBP], and [BMIM][DBP]/CuBTC.

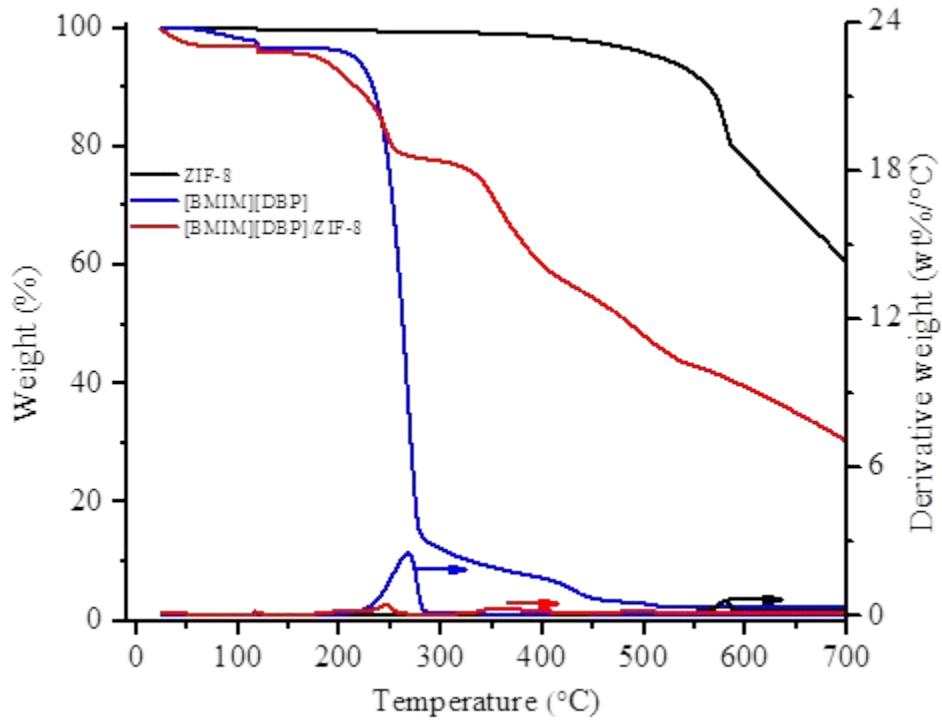


Figure S70. Thermal stability of pristine ZIF-8, bulk [BMIM][DBP], and [BMIM][DBP]/ZIF-8.

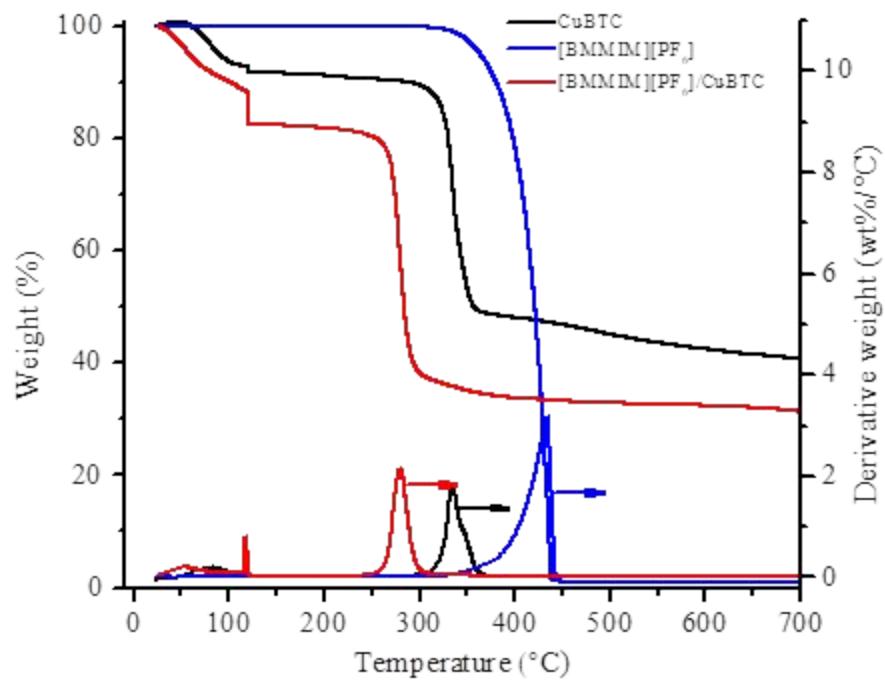


Figure S71. Thermal stability of pristine CuBTC, bulk [BMMIM][PF₆], and [BMMIM][PF₆]/CuBTC.

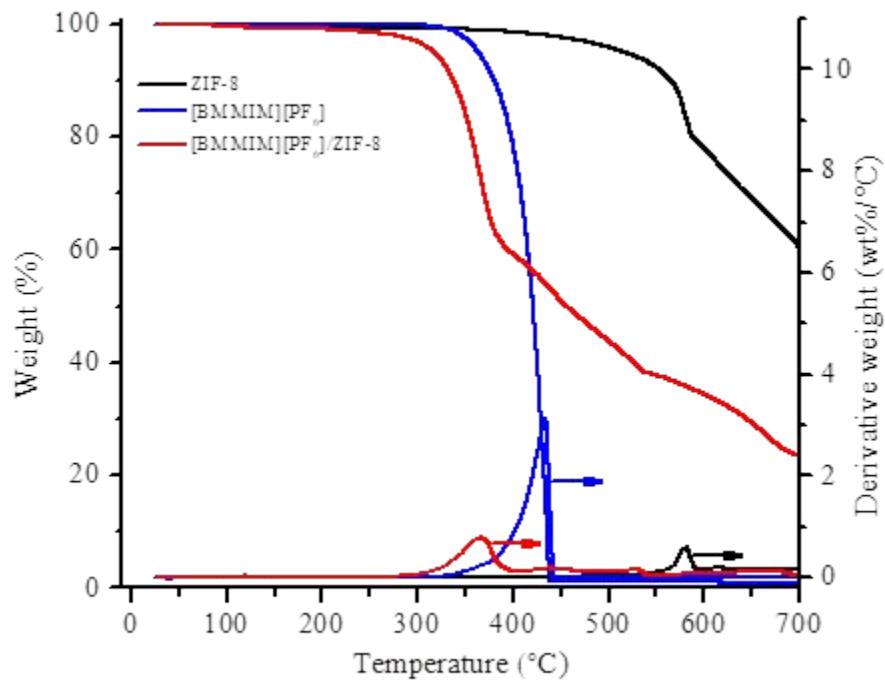


Figure S72. Thermal stability of pristine ZIF-8, bulk [BMMIM][PF₆], and [BMMIM][PF₆]/ZIF-8.

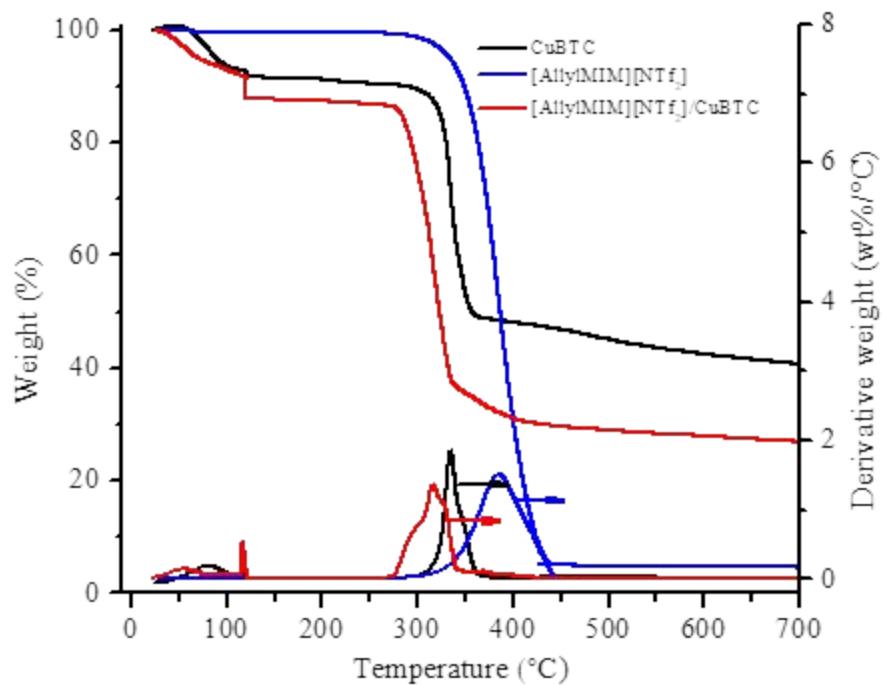


Figure S73. Thermal stability of pristine CuBTC, bulk [AllylMIM][NTf₂], and [AllylMIM][NTf₂]/CuBTC.

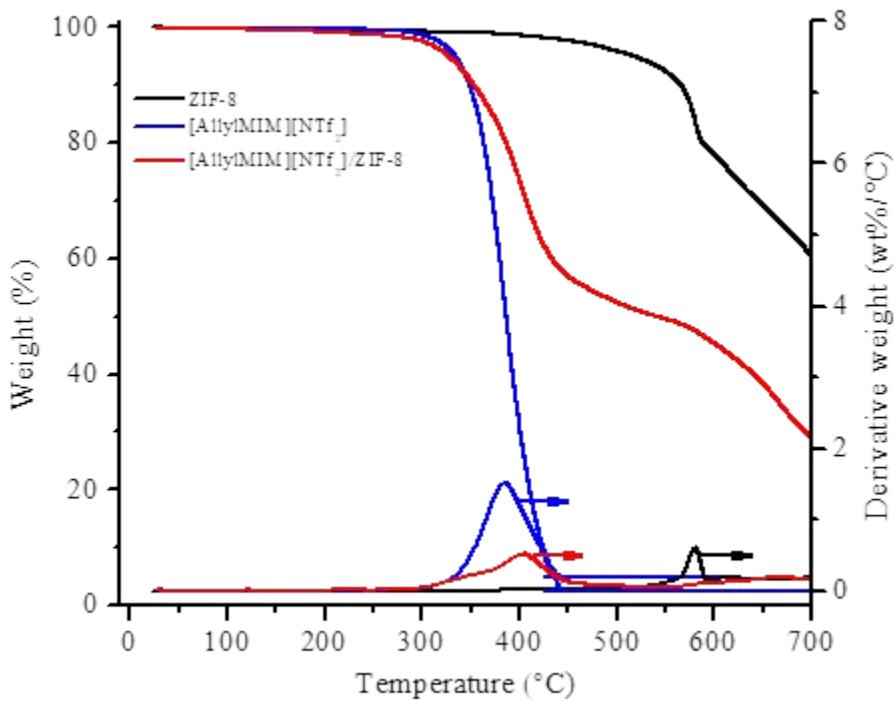


Figure S74. Thermal stability of pristine ZIF-8, bulk [AllylMIM][NTf₂], and [AllylMIM][NTf₂]/ZIF-8.

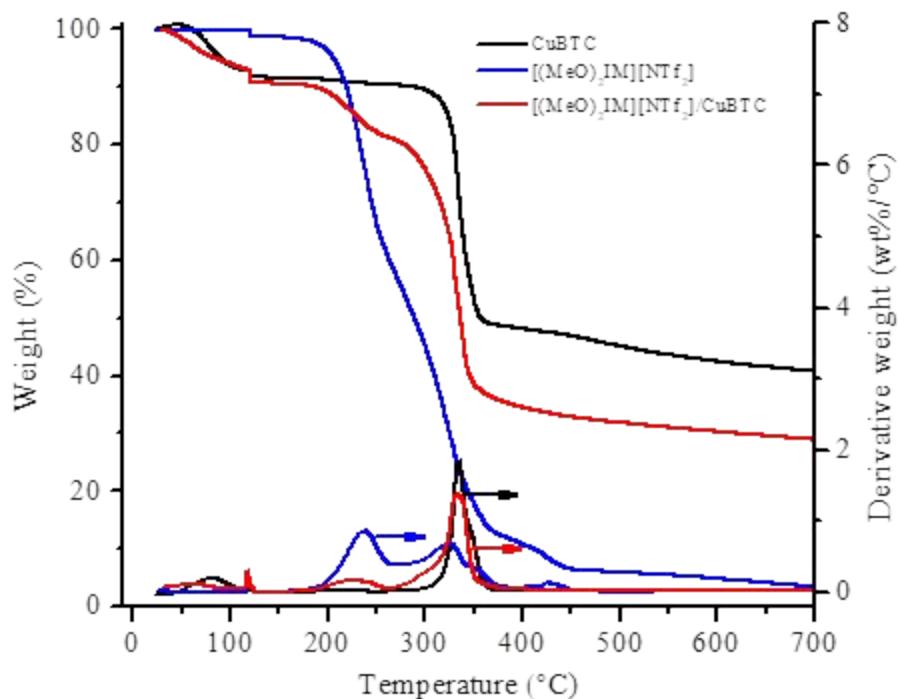


Figure S75. Thermal stability of pristine CuBTC, bulk $[(\text{MeO})_2\text{IM}][\text{NTf}_2]$, and $[(\text{MeO})_2\text{IM}][\text{NTf}_2]/\text{CuBTC}$.

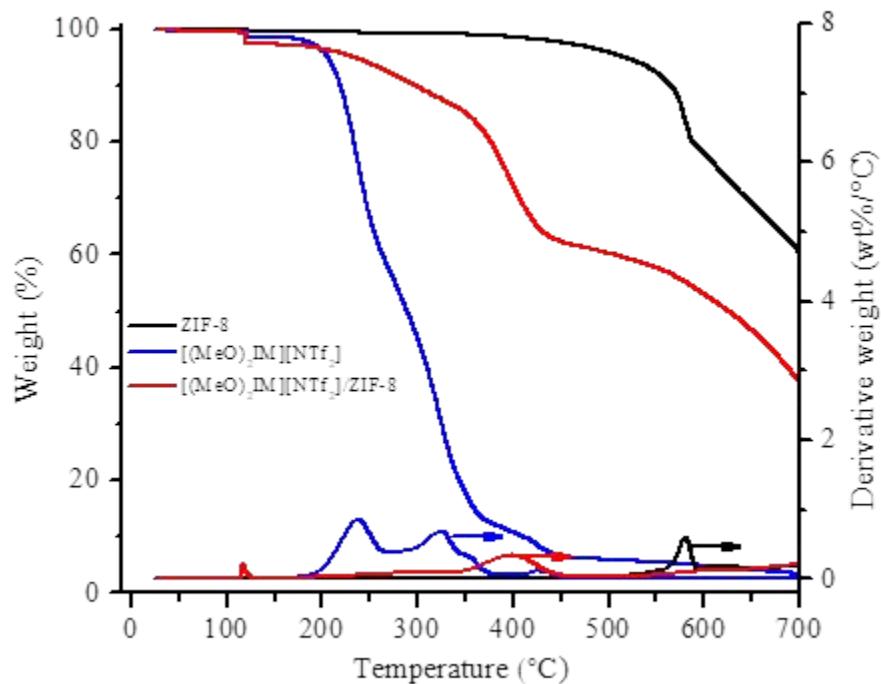


Figure S76. Thermal stability of pristine ZIF-8, bulk $[(\text{MeO})_2\text{IM}][\text{NTf}_2]$, and $[(\text{MeO})_2\text{IM}][\text{NTf}_2]/\text{ZIF-8}$.

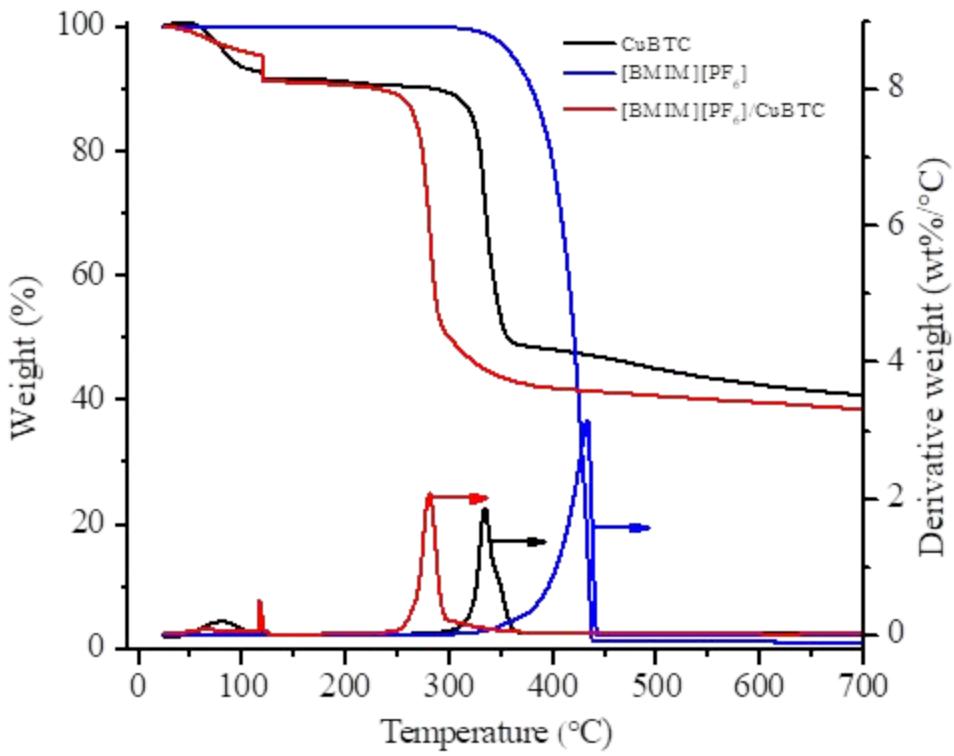


Figure S77. Thermal stability of pristine CuBTC, bulk [BMIM][PF₆], and [BMIM][PF₆]/CuBTC.

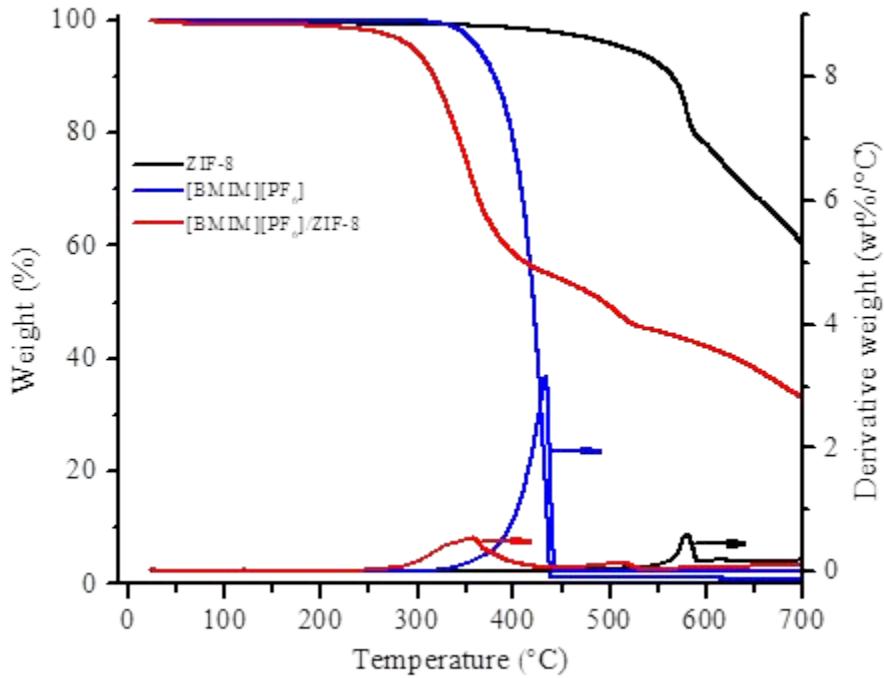


Figure S78. Thermal stability of pristine ZIF-8, bulk [BMIM][PF₆], and [BMIM][PF₆]/ZIF-8.

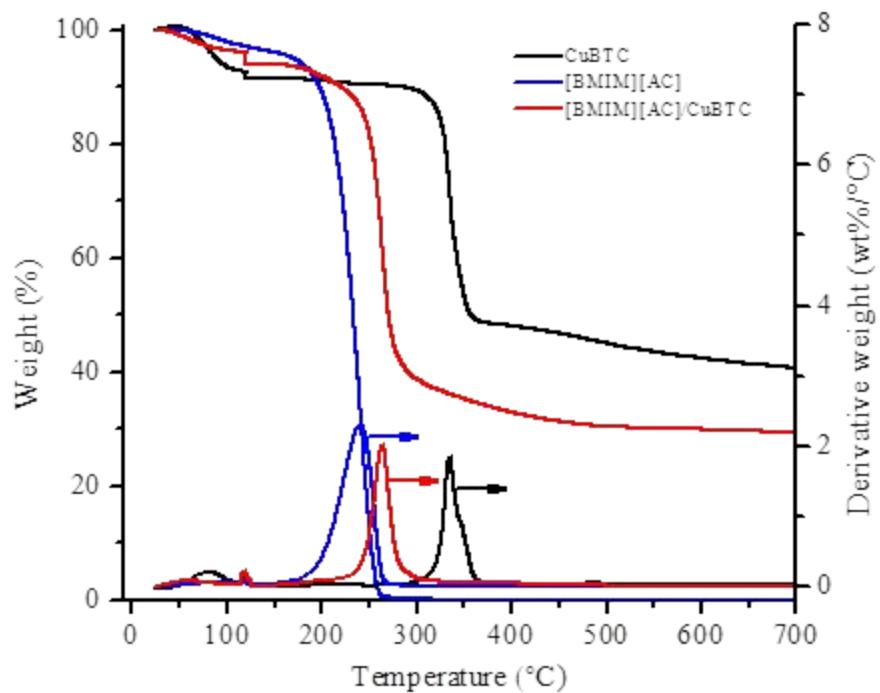


Figure S79. Thermal stability of pristine CuBTC, bulk [BMIM][AC], and [BMIM][AC]/CuBTC.

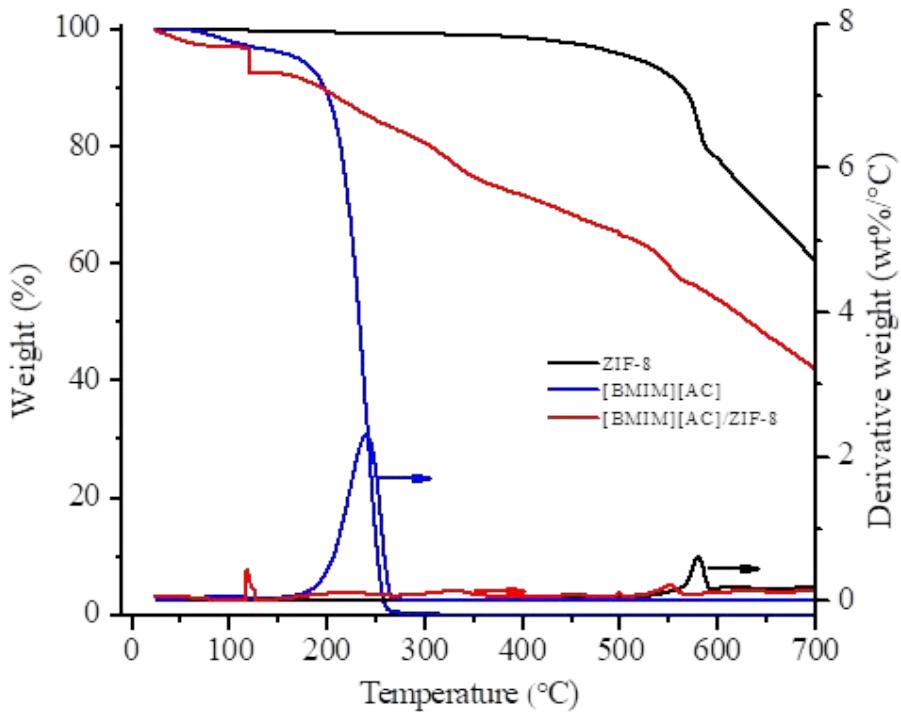


Figure S80. Thermal stability of pristine ZIF-8, bulk [BMIM][AC], and [BMIM][AC]/ZIF-8.

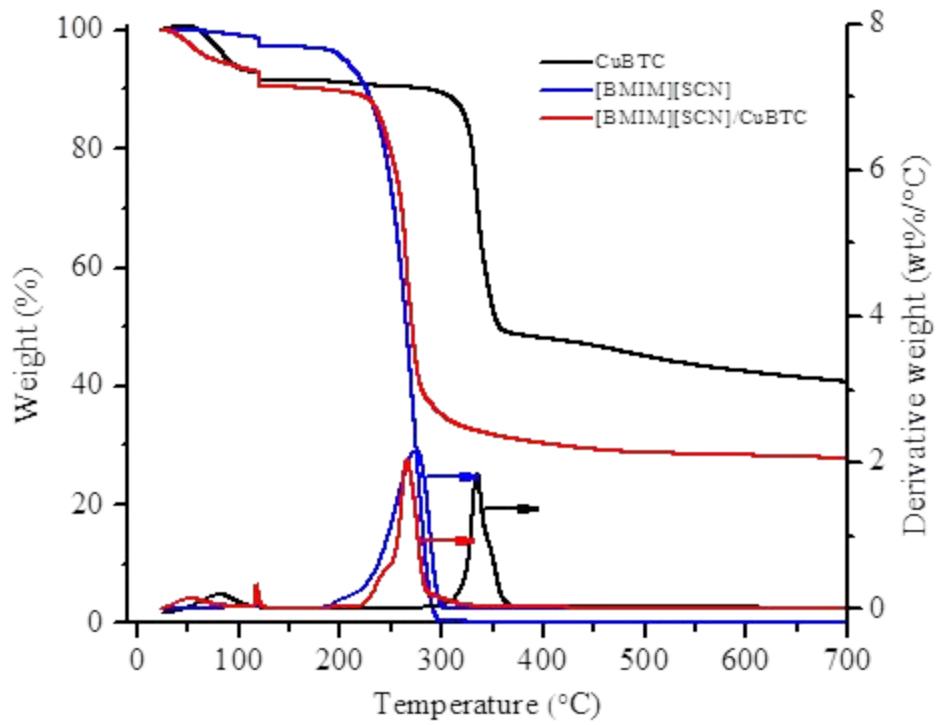


Figure S81. Thermal stability of pristine CuBTC, bulk [BMIM][SCN], and [BMIM][SCN]/CuBTC.

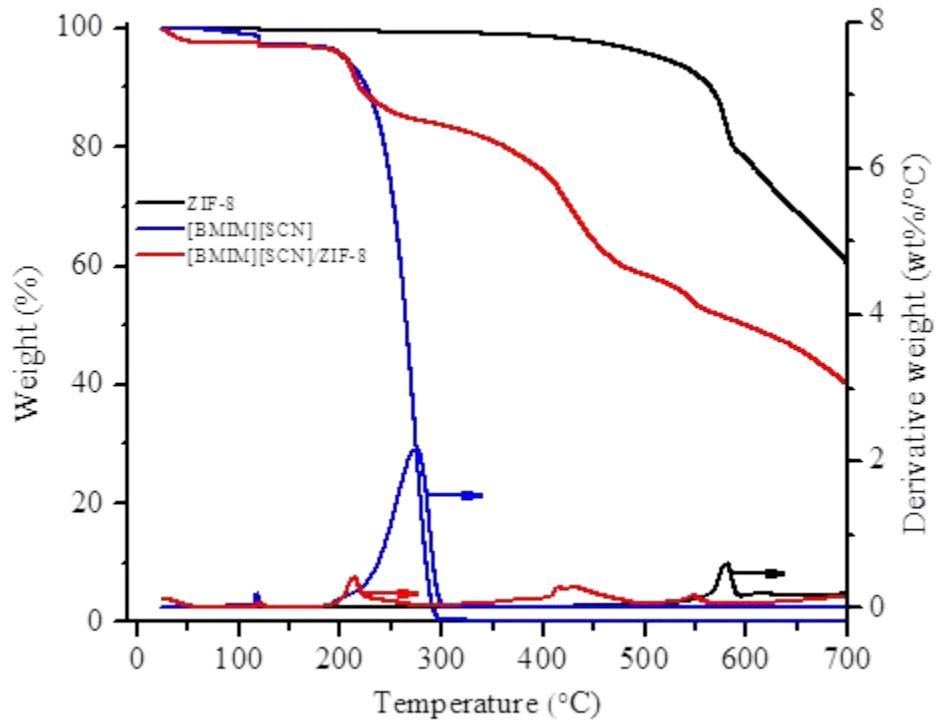


Figure S82. Thermal stability of pristine ZIF-8, bulk [BMIM][SCN], and [BMIM][SCN]/ZIF-8.

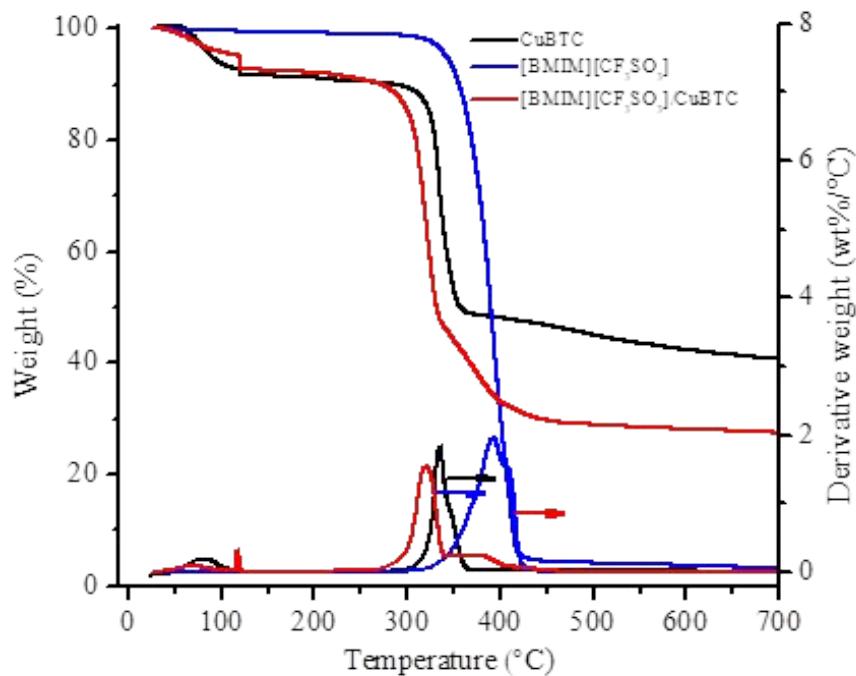


Figure S83. Thermal stability of pristine CuBTC, bulk [BMIM][CF₃SO₃], and [BMIM][CF₃SO₃]/CuBTC.

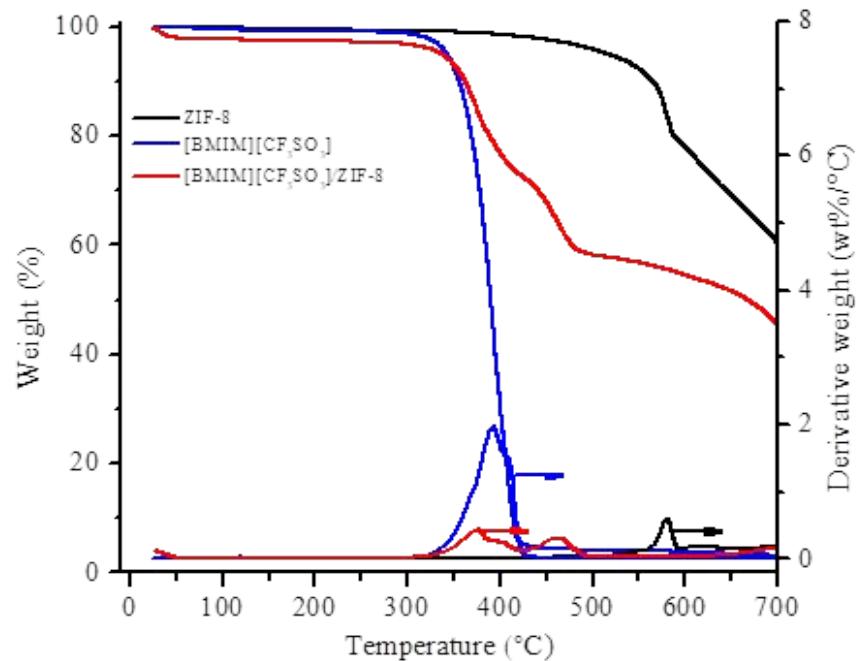


Figure S84. Thermal stability of pristine ZIF-8, bulk [BMIM][CF₃SO₃], and [BMIM][CF₃SO₃]/ZIF-8.

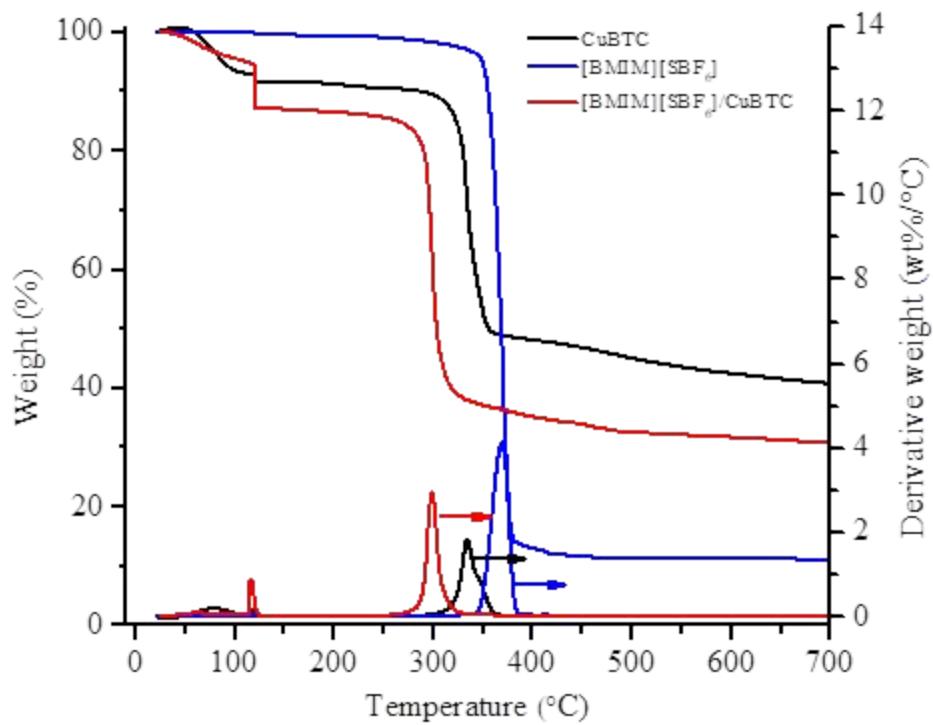


Figure S85. Thermal stability of pristine CuBTC, bulk [BMIM][SbF₆], and [BMIM][SbF₆]/CuBTC.

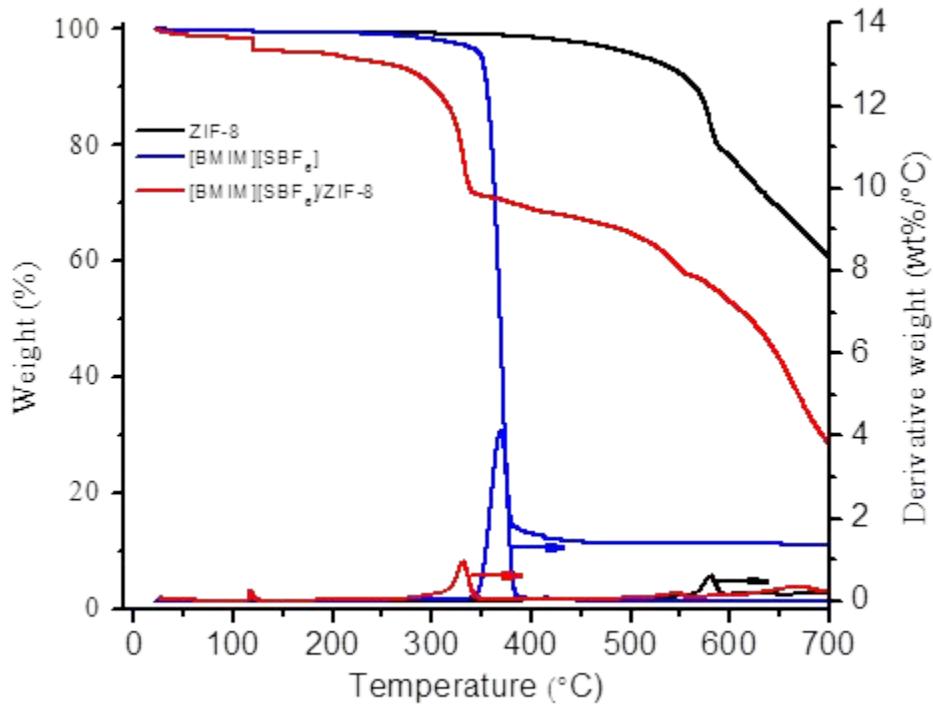


Figure S86. Thermal stability of pristine ZIF-8, bulk [BMIM][SbF₆], and [BMIM][SbF₆]/ZIF-8.

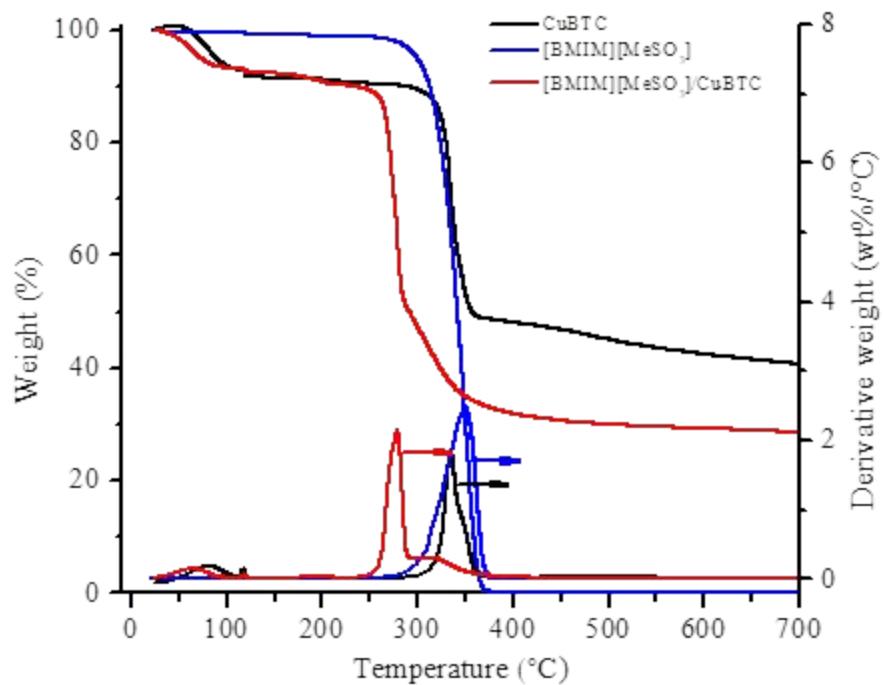


Figure S87. Thermal stability of pristine CuBTC, bulk [BMIM][MeSO₃], and [BMIM][MeSO₃]/CuBTC.

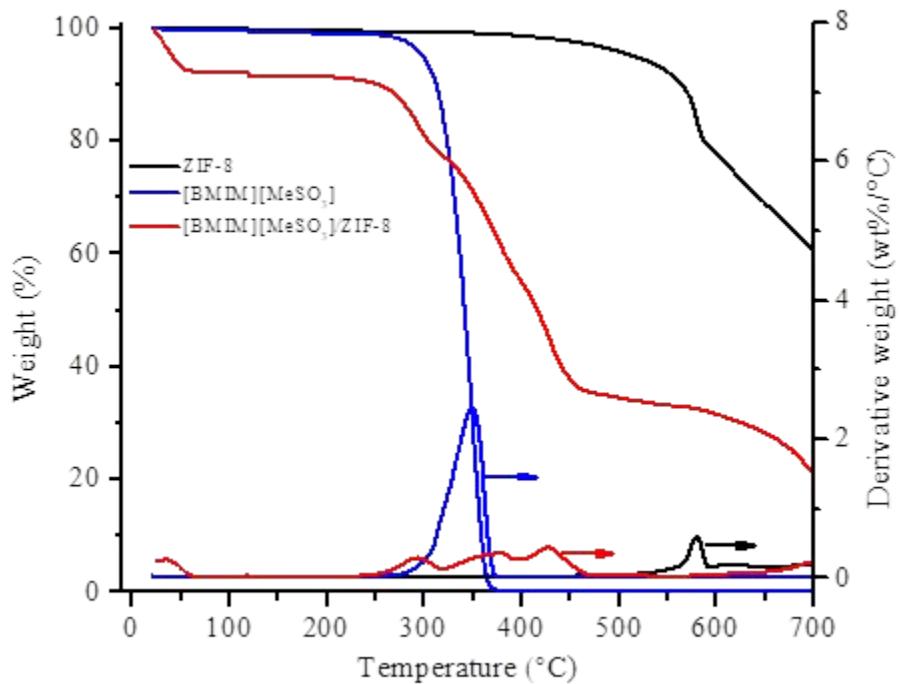


Figure S88. Thermal stability of pristine ZIF-8, bulk [BMIM][MeSO₃], and [BMIM][MeSO₃]/ZIF-8.

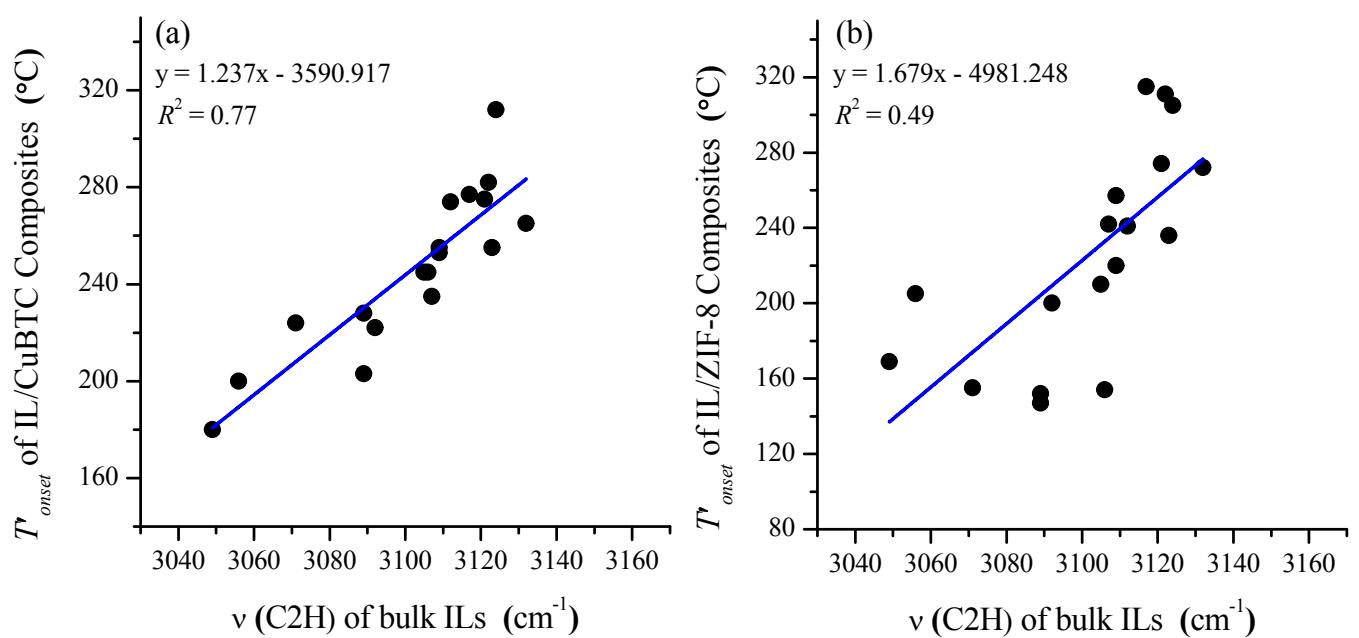


Figure 89. Relation between T'_{onset} of IL/MOF composites and $\nu(\text{C2H})$ of bulk ILs: (a) IL/CuBTC composites; (b) IL/ZIF-8 composites.

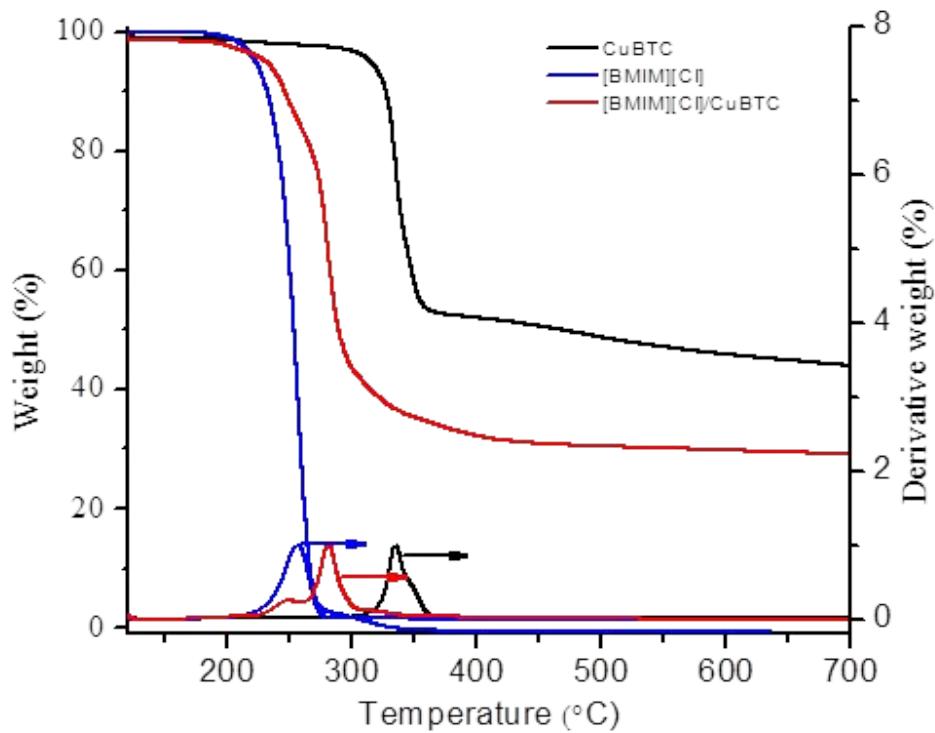


Figure 90. Thermal stability of pristine CuBTC, bulk [BMIM][Cl], and [BMIM][Cl]/CuBTC.

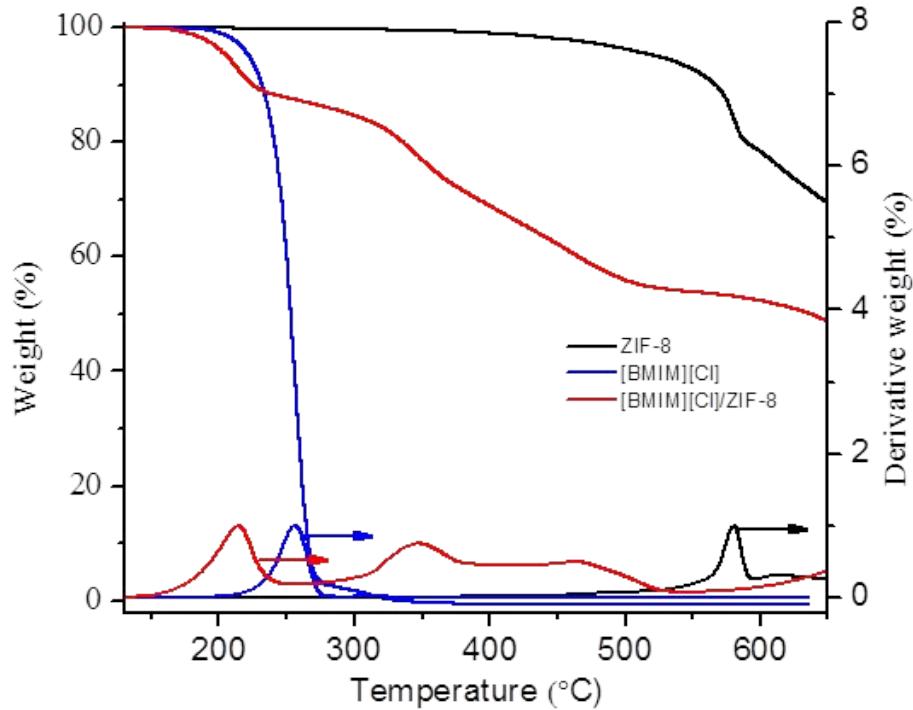


Figure 91. Thermal stability of pristine ZIF-8, bulk [BMIM][Cl], and [BMIM][Cl]/ZIF-8.

Table S4. Structural descriptor of cations considered for QSPR analysis.

Cations	E _{HOMO} (eV)	E _{LUMO} (eV)	Dipole (debye)	CPK Area (Å ²)	CPK Ovality	CPK Volume (Å ³)	Polarizability (m ³)	ZPE (kJ/mol)
EMIM	-11.91	-5.23	1.67	160.59	1.26	135.44	50.78	442.07
BMIM	-11.8	-5.14	5.67	201.11	1.34	172.26	53.77	591.36

Table S5. Structural descriptor of anions considered for QSPR analysis.

Anions	E _{HOMO} (eV)	E _{LUMO} (eV)	Dipole (debye)	CPK Area (Å ²)	CPK Ovality	CPK Volume (Å ³)	Polarizability (m ³)	ZPE (kJ/mol)
PF ₆	-5.54	4.06	0	103.96	1.21	75.2	45.21	47.57
MeSO ₃	-1.97	3.4	4.12	97.76	1.18	71.05	45.87	130.54
CF ₃ SO ₃	-2.93	3.78	4.11	115.64	1.23	85.53	46.73	69.45
Ac	-0.97	3.78	3.85	81.54	1.11	59.49	45.07	125.67
TFA	-2.26	4.12	4.7	99.24	1.16	73.96	45.86	66.24
OcSO ₄	-2.52	1.57	20.43	250.73	1.47	208.61	57.33	660.84
SbF ₆	9.68	-11.56	0	115.97	1.26	83.4	43.21	42.39
MeSO ₄	-2.45	3.28	4.06	108.48	1.21	79.61	46.48	142.68
DCA	-1.79	3.76	1.02	86.61	1.12	64.27	45.28	55.33
SCN	-1.09	3.98	1.66	69.54	1.07	49.4	44.18	22.6
BF ₄	-4.55	4.45	0	77.27	1.1	55.06	43.72	36.26
NTf ₂	-4.37	3.04	0.24	203.57	1.44	157.62	52.41	137.09
DEP	-2.51	2.83	6.88	177.75	1.35	141.69	51.6	390.72
Cl	-0.74	6.2	0	39.9	1	23.7	41.65	0

Table S6. Coefficients of the multiple linear regression models.

Composite	b_0	<i>CPK ovality (cation)</i>	<i>Dipole (cation)</i>	<i>E_{HOMO} (anion)</i>	<i>E_{LUMO} (anion)</i>	<i>CPK area (anion)</i>
	-61.305779	141.584973	-	-1.078196	-	8.233680
IL/CuBTC	<i>CPK volume (anion)</i>	<i>Polarizability (anion)</i>	<i>ZPE (anion)</i>	<i>R²</i>	Multiple R	Adjusted <i>R²</i>
	-9.535733	-	-	0.99	0.99	0.99
	b_0	<i>CPK ovality (cation)</i>	<i>Dipole (cation)</i>	<i>E_{HOMO} (anion)</i>	<i>E_{LUMO} (anion)</i>	<i>CPK area (anion)</i>
IL/ZIF-8	-123.204190	-	6.495490	-17.891239	-20.423683	-
	<i>CPK volume (anion)</i>	<i>Polarizability (anion)</i>	<i>ZPE (anion)</i>	<i>R²</i>	Multiple R	Adjusted <i>R²</i>
	-	8.071835	-0.280061	0.99	0.99	0.96

Units= *Dipole (debye)*; *E_{HOMO} (eV)*; *E_{LUMO} (eV)*; *CPK volume (Å³)*; *CPK Area (Å²)*; *Polarizability (m³)*; *ZPE (kJ/mol)*.

Multiple R is the correlation coefficient and shows how strong the linear relationship between dependent and independent variables. *R²* values generally increased when a new parameter is added to the model, while adjusted *R²* values only increase when the newly added parameter improves the quality of the fit.

References:

- (1) Sezginel, K. B.; Keskin, S.; Uzun, A. Tuning the Gas Separation Performance of CuBTC by Ionic Liquid Incorporation. *Langmuir* **2016**, *32* (4), 1139–1147.
- (2) Koyuturk, B.; Altintas, C.; Kinik, F. P.; Keskin, S.; Uzun, A. Improving Gas Separation Performance of ZIF-8 by [BMIM][BF₄] Incorporation: Interactions and Their Consequences on Performance. *J. Phys. Chem. C* **2017**, *121* (19), 10370–10381.
- (3) Nozari, V.; Keskin, S.; Uzun, A. Toward Rational Design of Ionic Liquid/Metal-Organic Framework Composites: Effects of Interionic Interaction Energy. *ACS Omega* **2017**, *2* (10), 6613–6618.
- (4) Zeeshan, M.; Keskin, S.; Uzun, A. Enhancing CO₂/CH₄ and CO₂/N₂ Separation Performances of ZIF-8 by Post-Synthesis Modification with [BMIM][SCN]. *Polyhedron* **2018**, *155*, 485–492.
- (5) Nozari, V.; Zeeshan, M.; Keskin, S.; Uzun, A. Effect of Methylation of Ionic Liquids on the Gas Separation Performance of Ionic Liquid/Metal-Organic Framework Composites. *CrystEngComm* **2018**, *20* (44), 7137–7143.
- (6) Kinik, F. P.; Altintas, C.; Balci, V.; Koyuturk, B.; Uzun, A.; Keskin, S. [BMIM][PF₆] Incorporation Doubles CO₂ Selectivity of ZIF-8: Elucidation of Interactions and Their Consequences on Performance. *ACS Appl. Mater. Interfaces* **2016**, *8* (45), 30992–31005.