

Supplementary Information

Tunability of Electronic Band Gaps from Semiconducting to Metallic States via Tailoring Zn Ions in MOFs with Co Ions

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Representative structures for each cobalt substitution rate

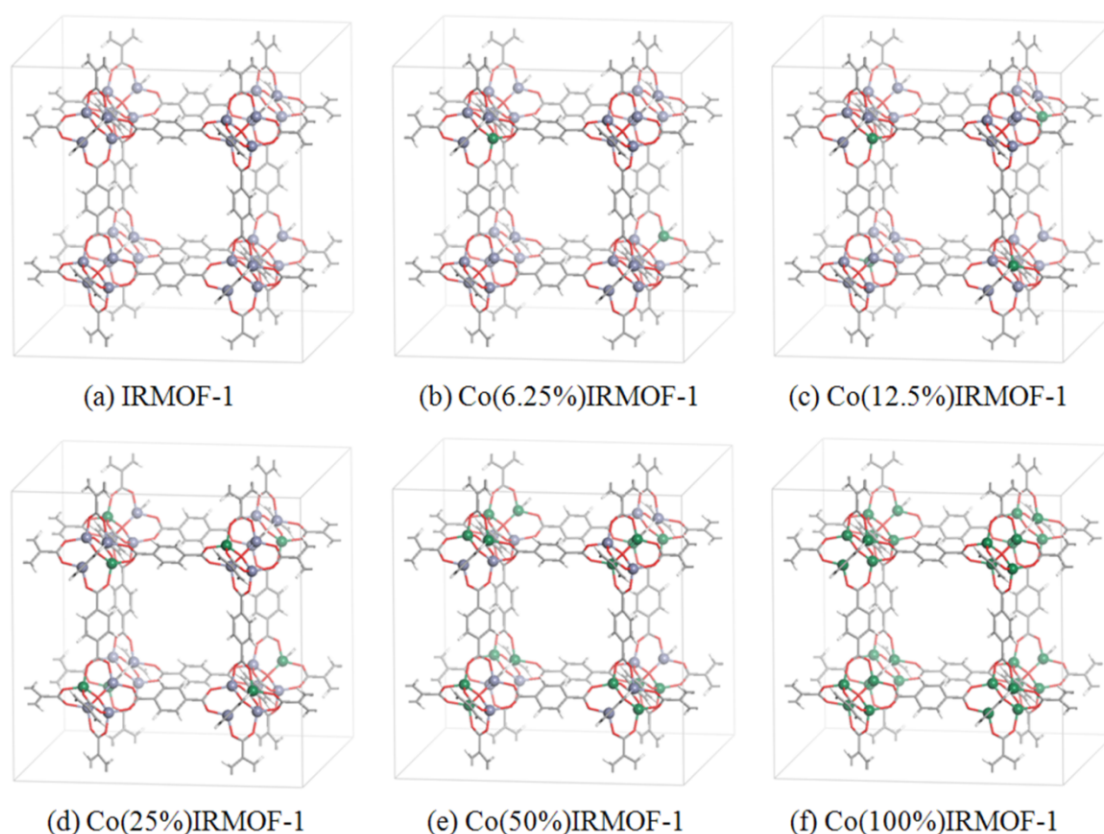


Fig. S1 Representative structures for each cobalt substitution rate, where Co, Zn, C, O, and H are shown in green, violet, grey, red, and white, respectively. All atoms are drawn by a stick model except Co and Zn, which are drawn with a ball and stick model for emphasis. (a) IRMOF-1, (b) Co(6.25%)IRMOF-1, (c) Co(12.5%)IRMOF-1, (d) Co(25%)IRMOF-1, (e) Co(50%)IRMOF-1, (f) Co(100%)IRMOF-1.

Fig. S1 shows representative structures for each cobalt substitution rate. In this study, we adopted a mixed atom model, where the substituents are not located at the same position periodically, but are randomly located with the same substitution rate. Therefore, the position of substituted cobalt atom is randomly distributed. However, the substitution rate is unchanged during the calculation. Crystallographic information files (CIF) for each material were given as supplementary files. In the CIF, the position of cobalt atom were given as zinc atom, however, that position can be a zinc atom or a cobalt atom with fixed substitution rate because we used the mixed atom model.

Discussion about the role of organic linkers

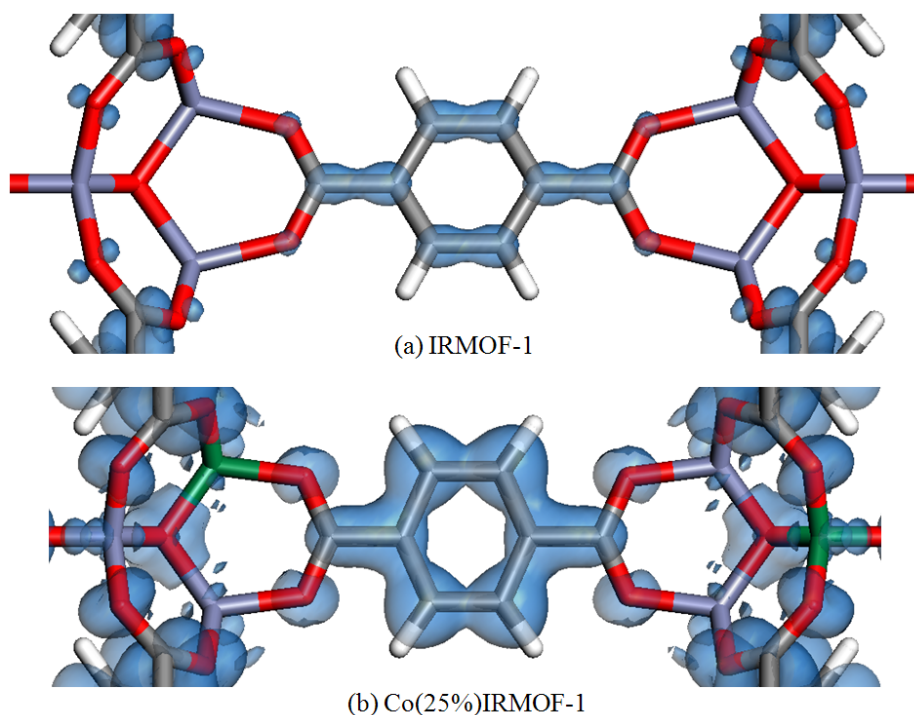


Fig. S2 (a) Accumulation images of alpha orbitals of (a) IRMOF-1 between 0 eV and 3.540 eV and (b) Co(25%)IRMOF-1 between 0 eV and 3.545, where Co, Zn, C, O, and H are shown in green, violet, grey, red, and white, respectively. This magnified image is a top view of a benzene ring (organic linker).

In order to further elucidate the cause of the band gap change when cobalt ions are substituted into the metal cluster, we have performed molecular orbital calculations on metal cluster in case of IRMOF-1 and Co(25%)IRMOF-1. We also explored the role of organic linkers in band gap change when cobalt atoms are substituted to IRMOF-1 structure. The orbital calculation was carried out by Castep code with same level of band structure calculation. Fig. S2 shows accumulation images of alpha orbitals of IRMOF-1 between 0 eV and 3.540 eV and Co(25%)IRMOF-1 between 0 eV and 3.545. In the organic linker part, benzene ring, IRMOF-1 shows little p-orbital conjugation, however, p-orbital conjugation is enhanced in case of Co(25%)IRMOF-1, that leads to the decrease of band gap. The enhanced orbital overlapping in the metal cluster part and the enhanced p-orbital conjugation in the organic linker part could be the answer to why band gap changes when cobalt atoms are substituted.

Discussion about lattice parameter change

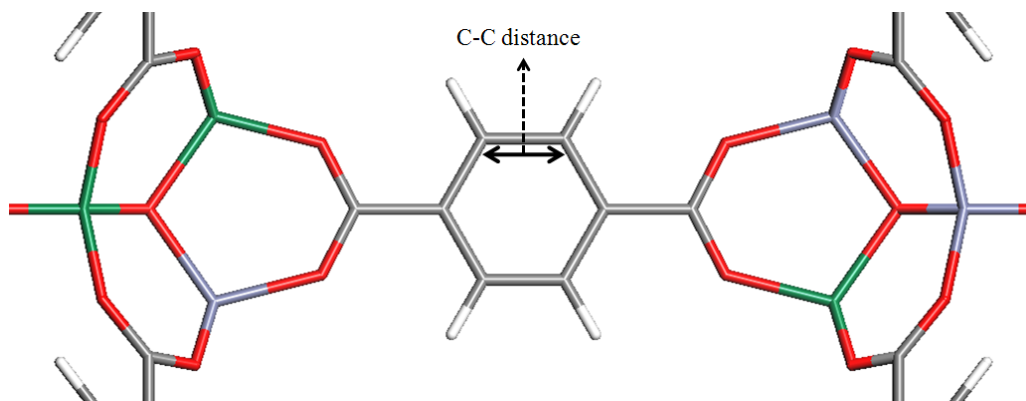


Fig. S3 Magnified top view of a benzene ring (organic linker) in the CoIRMOF-1 structure, where Co, Zn, C, O, and H are shown in green, violet, grey, red, and white, respectively. Distance between carbon-carbon in the organic linker is indicated.

Structure	Lattice parameter (Å)	C-C distance (Å)	Band gap (eV)
IRMOF-1	26.552	1.398	3.53
Co(6.25%)IRMOF-1	26.099	1.390	3.08
Co(12.5%)IRMOF-1	25.027	1.371	2.42
Co(25%)IRMOF-1	23.430	1.344	0
Co(50%)IRMOF-1	24.578	1.364	0
Co(100%)IRMOF-1	26.194	1.396	0.14

Table. S1 Lattice parameter, C-C distance and band gap for each cobalt substitution rate.

In addition, we find that the lattice parameter depends on the cobalt substitution rate due to small ion radius of cobalt atom relative to zinc atom. Therefore, as cobalt substitution rate increases to the value less than 50%, we find that the lattice parameter is reduced, while when the substitution is larger than 50%, it is determined that the lattice parameter starts to increase again. This is implying that the lattice parameter depends not only on the cobalt ion radius but also on the p-orbital conjugation in the organic linker. Table. S1 shows the lattice parameter, the C-C distance, and the band gap for each cobalt substitution rate, where the C-C distance in a benzene ring is indicated in Figure S3. The C-C distance is found to result in the decrease of the band gap, from IRMOF-1 to Co(25%)IRMOF-1 as shown in Table S1. However, when the band gap increases, from Co(50%)IRMOF-1 to Co(100%)IRMOF-1, the C-C distance increase again. From these phenomena, we can explain that the band gap change affects the size of organic linker because the smaller band gap means enhanced p-orbital conjugation that leads to the shrinkage of C-C distance of benzene ring. Lattice parameter change shows same tendency with C-C distance. Hence, change of the size of organic linker also affects lattice parameter through p-orbital conjugation change. Therefore, we can know that lattice parameter depends not only on the cobalt ion radius in the metal cluster but also on the p-orbital conjugation in the organic linker.

Notes

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