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**COMMUNICATION**

# Metal–organic frameworks for visible light absorption *via* anion substitution

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**We report that the band gap of metal–organic frameworks (MOFs) could be tuned to absorb visible light *via* anion substitution. First of all, when an oxygen anion in the metal oxide core of IRMOF-1 is substituted with sulphur anions as $Zn_4S$ or selenium anions as $Zn_4Se$ to form IRMOF-1-S and IRMOF-1-Se, respectively, they result in density-of-states and molecular orbitals for the band gap that can utilize visible light through shifting of the Fermi level due to their electron-rich properties. This implies that the tailored band gap could provide a new route to allow the series of IRMOFs and other MOFs to be used for visible light absorption.**

Metal–organic frameworks (MOFs)[1] have been of great interest due to their excellent properties such as extremely high specific surface areas and large pore volumes, and have been studied for many promising applications such as gas storage, gas purification and separation, and heterogeneous catalysts.[2–5] Also, MOFs has been recently proven to be wonderful structures for solar energy harvesting including photocatalysts.[6–8] IRMOF-1 (also known as MOF-5)[9] is one of the most commonly studied MOFs. However, UV (ultraviolet)/Vis (visible) spectroscopy and photoluminescence spectroscopy analyses have shown that IRMOF-1 has a large band gap of 3.4 eV.[10,11] This band gap corresponds to UV light absorption with the wavelength of 364.9 nm rather than the main visible light spectrum (>400 nm) of the solar spectrum. Therefore, at present, it is highly necessary to develop a new strategy to tailor the band structure of MOFs for visible light absorption while retaining their original crystalline morphology or structure.

Our recent work demonstrated that the electronic structure of IRMOF-1 could be tuned to achieve desired band gaps ranging from semiconducting to metallic states by substitution of zinc ions in the metal oxide core by cobalt ions in IRMOF-1.[12] This strategy was also demonstrated experimentally by Botas' group.[13]

Herein, we report a facile method to allow visible light absorption on IRMOF-1 *via* anion substitution. In order to alter the electronic structure of IRMOF-1 while maintaining its structural topology, the oxygen atom of $Zn_4O$ could be substituted by a sulphur or selenium atom as shown in Fig. 1. The geometries, band structure, and density-of-states (DOS) were first determined through the generalized gradient density functional theory calculations with the periodic

boundary condition[14] using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.[15] All atoms were described by the ultrasoft-pseudopotential.[16] The electronic wave functions were expanded in a plane wave basis set with an energy cut-off of 300.0 eV and k-points sampling was carried out using the Monkhorst–Pack scheme.[17] Meanwhile, molecular orbitals[18] on the metal oxide core with organic linkers are determined using the terminal hydrogen atoms to reflect the rigid crystalline structure of the IRMOF-1 structures at the level of the hybrid B3LYP density functional theory.[19] The basis sets used to accurately describe these orbitals were based on a triple zeta polarized basis set of 6-311G*[20] for Zn, C, O, S, and Se atoms as well as a double zeta basis set of 6-31G[20] for H atoms.

Fig. 1 shows the fully optimized structures of IRMOF-1 and the anion substituted IRMOF-1 series. IRMOF-1 is composed of a metal oxide core ($Zn_4O$) and an organic linker (1,4-benzenedicarboxylate). Then, the oxygen atom in the $Zn_4O$ metal oxide core of IRMOF-1 was substituted with a sulfur atom or selenium atom, and hereafter they are referred to as IRMOF-1-S and IRMOF-1-Se, respectively. The space groups of the optimized geometries were $Fm-3m$ with $a = 26.552$ Å, $b = 26.891$ Å, and $c = 26.942$ Å for IRMOF-1, IRMOF-1-S, and IRMOF-1-Se, respectively.
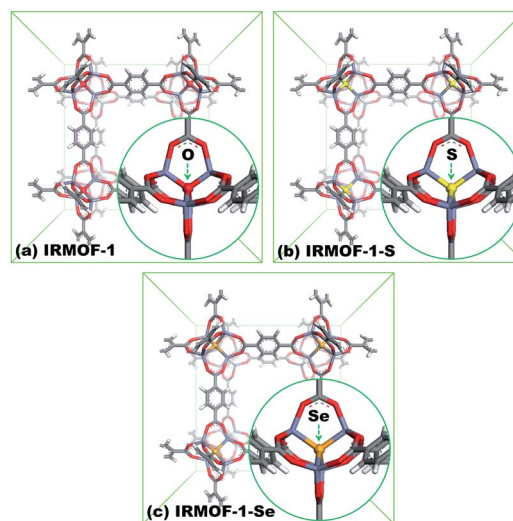


**Fig. 1** Model images of (a) IRMOF-1, (b) IRMOF-1-S, (c) IRMOF-1-Se, where Zn, C, O, S, Se and H are shown in violet, grey, red, yellow, dark yellow, and white, respectively.

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Due to the relatively large atomic sizes of S and Se relative to O, the lattice parameters are found to increase with S or Se anion substitution, although the space groups were maintained as $Fm-3m$ during geometry optimization.

Fig. 2 shows the band structures and partial density-of-states (PDOS) of IRMOF-1 and substituted IRMOF-1 series. In Fig. 2a, the calculated band gap ($E_g$) of 3.5 eV for IRMOF-1 agrees well with the experimental one (3.4 eV), thus implying that density functional theory using the PBE exchange–correlation functional is effective to describe electronic structures of the IRMOF-1 system. The band gap of IRMOF-1 corresponds to the light absorption edge of 351.4 nm, which lies in the UV light range. Consequently, we expect that IRMOF-1 would not show photoactivity under visible light irradiation, corresponding with the main portion of the solar spectrum. In the case of IRMOF-1-S, Fig. 2c shows that the band gap was 3.30 eV, slightly decreased by 0.23 eV relative to IRMOF-1. With this band gap, IRMOF-1-S is photoactive under light irradiation <375.9 nm, but it still lies in the UV light range. However, in the case of IRMOF-1-Se, Fig. 2e demonstrates the band gap has been greatly reduced to 2.91 eV, thus the light absorption edge lies on 426.3 nm. Consequently, this result implies that it will show great photoactivity under visible light (>400 nm) irradiation, which could result in greatly enhanced photocatalytic properties such as water splitting. Fig. 2b, d, and f show partial density-of-states for IRMOF-1, IRMOF-1-S, and IRMOF-1-Se, respectively. The PDOS of IRMOF-1 shows a relatively large gap. Meanwhile, when the S anion is substituted to IRMOF-1, as shown in Fig. 2d, it was found that the conduction band migrated towards the Fermi level, leading to a reduced band gap. Furthermore, in the case of IRMOF-1-Se (Fig. 2f), a new valence band has been generated around the Fermi level and the conduction band has been also moved towards the Fermi level, which results in a reduced band gap capable of absorbing visible light. Also, the valence and conduction bands are found to be mainly composed of p-orbitals.

Meanwhile, the d-orbital from zinc ions in the metal oxide core does not play a crucial role in the band gaps due to the lack of empty d-orbitals of zinc ions. From these phenomena, it could be concluded that the reduced band gap by anion substitution is mainly attributed to anions in the metal oxide core or benzenes in the organic linker rather than zinc ions in the metal oxide core. Therefore, the local density of states (LDOS) of substituted anions and benzenes were investigated in order to ascertain the effects of anion substitution on the band gap change.

Fig. 3 shows the LDOS of the center anion atom in the metal oxide core and the benzene ring in the organic linker, where the total LDOSs were mainly composed of p orbitals in all cases. As compared with the PDOS in Fig. 2, it is revealed that the main electron density of the conduction band is attributed to the electron density from the benzene ring in the organic linker. In the case of IRMOF-1, shown in Fig. 3a, the valence band and conduction band are mainly composed from the DOS of benzene, where the peak-to-peak distance of the
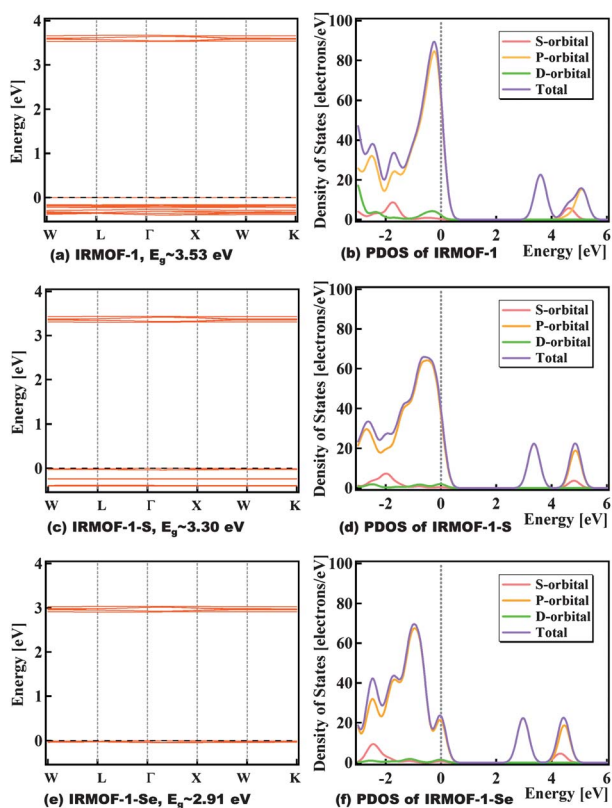


**Fig. 2** Band structures of (a) IRMOF-1, (c) IRMOF-1-S, (e) IRMOF-1-Se, and partial density of states of (b) IRMOF-1, (d) IRMOF-1-S, (f) IRMOF-1-Se. The Fermi levels are located on 0 eV (dashed lines).
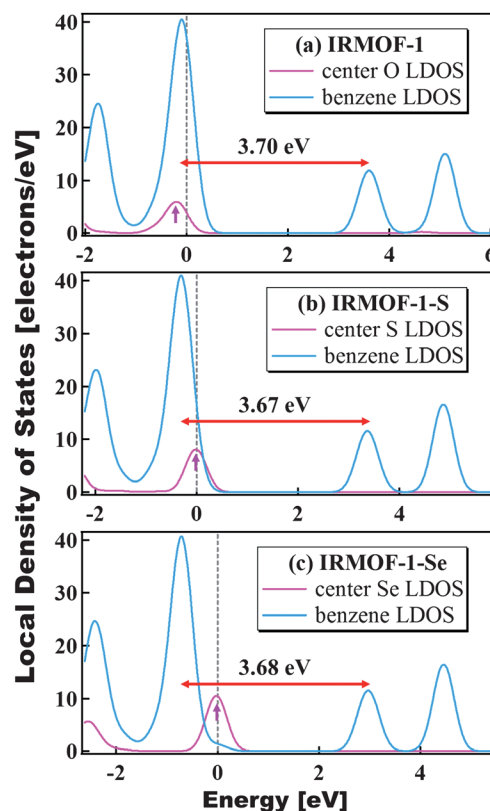


**Fig. 3** Local density of states of (a) IRMOF-1, (b) IRMOF-1-S, (c) IRMOF-1-Se, where the distances between bands around the valence band and conduction band of benzene LDOS are denoted as red arrows with eV. Pink arrows indicate the band position near the valence band of the center anion atoms. The Fermi levels are located on 0 eV (dashed lines).

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valence and conduction bands is 3.70 eV (indicated by a red arrow). Also, the electron density of the center oxygen anion in IRMOF-1 lies below the Fermi level. Meanwhile, it was observed that the shape of benzene LDOS for IRMOF-1-S (Fig. 3b) and IRMOF-1-Se (Fig. 3c) showed no significant change relative to IRMOF-1 with a peak-to-peak distance of 3.67 eV for IRMOF-1-S and 3.68 eV for IRMOF-1-Se. However, from the center anion LDOSs (Fig. 3b and c), it is found that the substituted center anions generate a new valence band between the peak-to-peak of benzene LDOS, and thus form a new Fermi level, which results in the decreased band gap for the cases of IRMOF-1-S and IRMOF-1-Se. It is believed that anion substitution does not affect LDOS for benzene due to the geometrical distance between the center anion in the metal oxide core and benzene in the organic linker, such that the LDOS of benzene could be maintained in all the cases. However, the Fermi level has been regenerated by the substituted S or Se anions, such that the band gaps are reduced in particular, because S or Se atoms are electron-rich atoms relative to the O atom of IRMOF-1; this is considered to be the main reason for the reduced band gap of IRMOF-1-S and IRMOF-1-Se.

Also, molecular orbital calculations for the metal oxide core of IRMOF-1, IRMOF-1-S, and IRMOF-1-Se were also determined. Fig. 4 denotes model images, highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for IRMOF-1 and anion substituted IRMOF-1 series, where geometry optimizations were carried out only on the metal oxide core (the metal ions connected with the organic linkers terminated with hydrogen atoms), because the organic linkers are not involved in band gap changes, as revealed by the LDOS analysis. The calculated

HOMO orbitals demonstrate that the orbital population has been greatly increased on the center atoms according to anion substitution. Furthermore, even conjugation (indicated by an arrow) occurs with neighbouring zinc ions. This is in good agreement with the conclusions that substituted anions form new Fermi levels and thus lead to reduced band gaps as revealed by LDOSs. Meanwhile, the LUMO orbitals of IRMOF-1 are significantly delocalized, which accounts for the large band gap of IRMOF-1. Meanwhile, in the case of IRMOF-1-S and IRMOF-1-Se, it was found that the orbital overlapping occurred around carboxylate (indicated by an arrow), which also appears to be attributable to the reduced band gap energies of anion substituted IRMOF-1 series.

## Conclusions

We found a facile method to allow visible light absorption on IRMOF-1 *via* anion substitution. In order to alter the electronic structure of IRMOF-1 while maintaining its structural topology, the oxygen atom of $Zn_4O$ have been substituted by sulphur anions as $Zn_4S$ or selenium anions as $Zn_4Se$ to form IRMOF-1-S or IRMOF-1-Se, respectively. These substitutions were proven to result in density-of-states and molecular orbitals matching with the band gap that can utilize visible light through shift of the Fermi level due to their electron-rich properties. Consequently, these results imply that our anion substitution method might be a novel approach for the design of many advanced MOF photocatalysts capable of providing high efficiency for solar-energy conversion.

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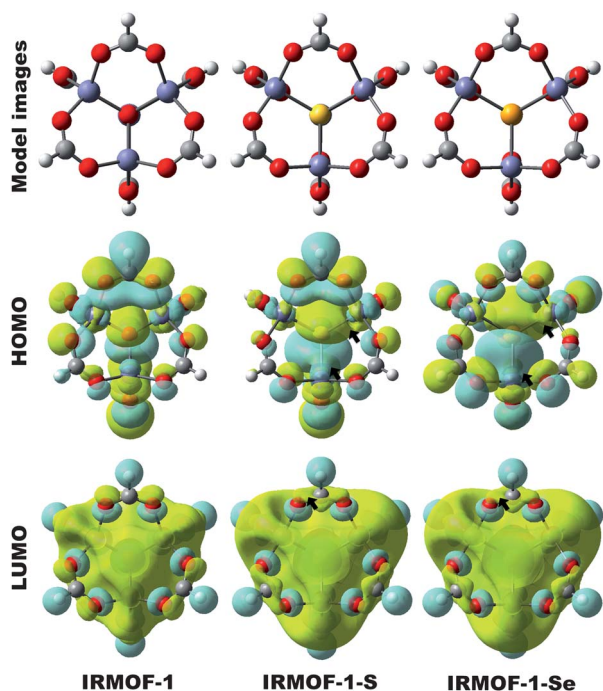


**Fig. 4** Model images, HOMO and LUMO orbitals of IRMOF-1, IRMOF-1-S, and IRMOF-1-Se, where blue and yellow surfaces indicate α- and β-orbitals, respectively. Zn, C, O, S, Se, and H are shown in violet, grey, red, yellow, dark yellow, and white, respectively. Black arrows denote the position of enhanced conjugation in the anion substituted IRMOF-1 series.

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