ABSTRACT: Herein we discuss band gap modification of MIL-125, a TiO₂/1,4-benzenedicarboxylate (bdc) metal–organic framework (MOF). Through a combination of synthesis and computation, we elucidated the electronic structure of MIL-125 with aminated linkers. The band gap decrease observed when the monoaminated bdc-NH₂ linker was used arises from donation of the N 2p electrons to the aromatic linking unit, resulting in a red-shifted band above the valence-band edge of MIL-125. We further explored in silico MIL-125 with the diammoniated bdc-(NH₂)₂ and other functional groups (–OH, –CH₃, –Cl) as alternative substitutions to control the optical response. The bdc-(NH₂)₂ linking unit was predicted to lower the band gap of MIL-125 to 1.28 eV, and this was confirmed through the targeted synthesis of the bdc-(NH₂)₂-based MIL-125. This study illustrates the possibility of tuning the optical response of MOFs through rational functionalization of the linking unit, and the strength of combined synthetic/computational approaches for targeting functionalized hybrid materials.

Metal–organic frameworks (MOFs) are a class of structures composed of organic and inorganic building blocks. These highly ordered and porous networks are of interest for their applications in gas storage, catalysis, and photoelectronics.1–10 In particular, MOFs have the ability to behave as semiconductors when exposed to light,11,12 making them unique platforms for light harvesting and photoinduced catalysis.13 A subfield of research has thus emerged with the aim of tuning the optical response of MOFs by modifying the inorganic unit or the organic linker (length, chemical functionalization) through synthetic14,15 or computational screening.16–22 In this context, the highly porous titanium-based MOF MIL-125 (MIL = Materials of Institut Lavoisier) (Figure 1) is an interesting candidate.23 This material, which contains cyclic octamers of TiO₂ octahedra, is photochromic, which is related to the reduction of Ti(IV) to Ti(III) under UV irradiation.24

When synthesized with the 1,4-benzenedicarboxylate (bdc) linker, MIL-125 has an optical band gap in the UV region (ca. 3.6 eV/435 nm; see Figure 3a) and is an active photocatalyst for the oxidation of alcohols to aldehydes.25 MIL-125-NH₂ made with the monoaminated bdc-NH₂ linker26 was reported to be a photocatalyst with visible-light-induced activity for CO₂ reduction26 and H₂ production.27 The bdc-NH₂ linker was shown to be responsible for the extra absorption band in the visible region, indicative of a band gap reduction (to ca. 2.6 eV/475 nm).25–28 Garcia and co-workers further confirmed the ability of MIL-125-NH₂ to undergo photoinduced charge separation.29 A similar band gap reduction and red shift were reported for Zr-Uio-66 upon synthesis with bdc-NH₂, emphasizing the electronic role of the –NH₂ group in determining the optical response in MOFs.30 Coincidently, aminated linkers are becoming particularly popular in porous MOF synthesis, as polar –NH₂ groups are expected to enhance CO₂ capture, yield selective gas adsorption,31–35 and enable postsynthetic modifications.36–38

These recent findings make it necessary to develop strategies to control the band gap of MIL-125. Here we performed a combined experimental and computational study to elucidate the band structure of MIL-125 and the impact of functional groups on the bdc linker, exploring the observed red shift in MIL-125-NH₂. We then computationally predicted the beneficial impact of using the diammoniated bdc-(NH₂)₂ linker, which was confirmed by a targeted synthesis. We finally explored in silico other
potential bdc linkers (Figure 2) as candidates for optical control in MIL-125.

Amines are ring-activating substituents; as an initial study, we investigated the change in the band gap in response to increasing the concentration of monoaminated bdc-NH₂. MIL-125 (Figure 3a) and three aminated MIL-125 analogues (Figure 3b−d) were synthesized under solvothermal conditions by varying the ratio of bdc and bdc-NH₂ linkers (i.e., 10%, 50%, and 100% bdc-NH₂, equating to ~1, 6, and 12 bdc-NH₂ linkers per unit cell). Figure 3 presents scanning electron microscopy (SEM) images of these four samples and their accompanying UV spectra and powder colors. It is apparent that the absorption onset (ca. 475 nm) is similar for all of the monoaminated samples. The samples also demonstrated similar band gaps of ~2.6 eV [Table S2 in the Supporting Information (SI)], but the molar extinction coefficient notably increased in proportion with the bdc-NH₂ content. This feature was reflected in the physical crystal appearance: the yellow color increased in intensity. This characteristic absorption pattern suggests that a single −NH₂ motif is responsible for the reduced band gap of the monoaminated series of MIL-125 analogues.

Electronic structure calculations on the same series of monoaminated MIL-125-NH₂ solids were performed using density functional theory (DFT) as described in the SI. Figure 4a,b depicts the valence band (VB) and conduction band (CB) orbitals, respectively, for standard MIL-125. The upper VB is composed of bdc aromatic 2p orbitals. Introducing a single bdc-NH₂ linker per unit cell (i.e., to give 10%-MIL-125-NH₂) breaks the original I4/mmm symmetry and splits the VB into a high-energy occupied state (depicted in blue in Figure 4c). The other aromatic bands are also split within 0.3 eV of each other and contribute to the VB-1,2...12. Because of the strong electron-donating characteristics of aromatic amines, the modified VB is 1.2 eV above that of MIL-125 (depicted with the blue arrow in Figure 4c), resulting in the lower band gap. This localized electronic modification results in a flat band in k space, which emphasizes the absence of long-range chemical interactions.

Further calculations were carried out by systematically increasing the amine content from 1 to 12 bdc-NH₂ linkers per unit cell (Figure 4d). It is apparent that the VB is modified upon amination of the linker while the lower CB is unchanged. Thus, a single −NH₂ group electronically saturates MIL-125. The band structure of 10%-MIL-125-NH₂ (blue in Figure 4c) depicts a localized noninteracting state, which was observed for all of the monoaminated systems independent of the bdc-NH₂ content.

The amine functional motif plays a crucial role in the band structure of MIL-125. We therefore considered the plausible extension of further increasing the electron density of the aromatic motifs through polyamination of the bdc linker. Selecting diaminated bdc-(NH₂)₂ (Figure 2 right) as a potentially interesting linker, we constructed a 10%-MIL-125-(NH₂)₂ model as a mixture of 10% bdc-(NH₂)₂ and 90% bdc and computed its band structure (shown in green in Figure 4c). This model may be compared to its monoaminated analogue (shown in blue in Figure 4c). Our calculations predicted that 10%-MIL-125-(NH₂)₂ would exhibit a larger red shift due to the increase in aromatic electronic density, with a resultant band gap of 1.28 eV.

Figure 2. Neutral linking molecules explored in this study: (left) monosubstituted linkers bdc-R; (right) diaminated linker bdc-(NH₂)₂.

Figure 3. SEM images of (a) MIL-125, (b) 10%-MIL-125-NH₂, (c) 50%-MIL-125-NH₂, (d) 100%-MIL-125-NH₂, and (e) 10%-MIL-125-(NH₂)₂/90%-MIL-125-NH₂, with their respective UV spectra and powder colors. All of the monoaminated systems show the same absorption onset.
This presents a further band gap decrease of 1.1 eV relative to the 10%-monoaminated analogue.

We subsequently targeted the synthesis of a diaminated MIL-125 derivative, which was successfully achieved with a mixture of 10% bdc-(NH$_2$)$_2$ and 90% bdc-NH$_2$ (Figure 3e). This compound differs from the 10%-MIL-125-(NH$_2$)$_2$ model described in the previous paragraph by the presence of bdc-NH$_2$ instead of bdc. We did not isolate the 10%-MIL-125-(NH$_2$)$_2$, but our compound should act electronically in a similar fashion, since the amine motifs are indeed noninteracting and produce highly localized electronic bands. Optical measurements (Figure 3e) revealed a further band gap decrease of 1.1 eV for this solid relative to the monoaminated samples to give an optical band gap of 1.3 eV, shifting the absorption onset to the red/IR region. This is in striking agreement with the above computational prediction.

Finally, we extended the computational exploration to three potential MIL-125 analogues. Amines are one of the stronger electron-donating substituents; weaker electron-donating substituents should reduce the band gap to a lesser extent. The introduction of 10% bdc-R (R = −OH, −CH$_3$, −Cl; Figure 2 left) per unit cell resulted in flexible band gap control between 3.5 and 2.4 eV (Figure 5). The weakest electron-donating group, −CH$_3$, moderately decreases the band gap to 3.5 eV. Aromatic halides are more chemically complex and may be either weakly electron-donating or -withdrawing. In MIL-125, −Cl acts as a weak electron donor with a predicted band gap similar to that for the −CH$_3$ group. The −OH group is more electron-donating than −CH$_3$ and −Cl, which is reflected by the predicted band gap of 2.8 eV for the 10%-MIL-125-OH model. The −Br and −CF$_3$ substituents were also computed. Our results suggest that −Br motifs produce band gap control similar to −Cl, but the crystal could not be stabilized above eight substitutions per unit cell. The −CF$_3$ group is strongly electron-withdrawing, potentially

Figure 4. (a, b) Frontier electron density of unsubstituted MIL-125: (a) the valence band is composed of the bdc C 2p orbitals (shown on the right), making these favorable for linker-based band gap modifications; (b) the conduction band is composed of O 2p orbitals and Ti 3d orbitals (shown on the right), suggesting that modifications of the aromatic bdc units are unlikely to affect the CB. Isovalue = 0.001 e Å$^{-3}$. (c) PBEsol band structures for synthetic MIL-125 (black), 10%-MIL-125-NH$_2$ (blue), 10%-MIL-125-(NH$_2$)$_2$/90%-MIL-125-NH$_2$ (orange) and the theoretical 10%-MIL-125-(NH$_2$)$_2$ (green). The orange bands, which have been truncated to improve the clarity of the band structures, maintain flat characteristics. The enlarged section emphasizes the VB-1...12 of the 11 nondegenerate monoamine bands. The energies are adjusted such that the highest occupied non-amine band is at 0 eV. The changes in the occupied VBs are depicted by the arrows. PBEsol is a qualitative approach; band structures could not be computed at the HSE06 level of theory because of the system size. (d) HSE06-calculated VB and CB energies of MIL-125-NH$_2$ models containing increasing numbers of bdc-NH$_2$ linkers (i.e. 0 (MIL-125) to 12 (100%-MIL-125-NH$_2$)) per unit cell. The degree of amination does not affect the band gap.

Figure 5. HSE06-predicted band gaps of MIL-125 (black) and its analogues containing functionalized bdc linkers. Substitutions of ca. 10% (i.e., one functionalized linker per unit cell) were made, unless otherwise stated. Control of the band gap was achieved by varying the substituent.
lowering a CB+\pi band into the band gap. It was found that the inclusion of −CF3 resulted in destabilization of the Ti−O bond, and a single substitution produced an unstable crystal. Thus, −NH2, −OH, −CH3, and −Cl are the most promising and favorable substitutions.

In conclusion, we have elucidated the specific role of the −NH3 group of the monoaminated bdc-NH2 linker in lowering the optical band gap of the titanium-containing MIL-125-NH2 (ca. 2.6 eV). We confirmed that electronic modifications of the aromatic motifs are localized and directly control the optical properties through modification of the valence band. DFT calculations showed that the optical response of MIL-125 may be tailored toward absorption in the visible region through rational selection of substituents of the aromatic bdc linker. The diaminated bdc-(NH2)2 linker was expected to demonstrate the most significant red shift. This prediction was confirmed by the synthesis of 10%-MIL-125-(NH2)2/90%-MIL-125-NH2 (1.3 eV/950 nm). From the experimental perspective, we have described the synthesis of a MIL-125 derivative with mixed monoaminated linkers. This methodology can be further extended to the most significant red shift.

ASSOCIATED CONTENT

Supporting Information
Synthetic procedures; PXRD, N2 sorption, and optical band gap data; and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

A.W. was supported a Royal Society University Research Fellowship, while C.H.H. and D.T. were funded under an ERC Starting Grant. The work benefited from the University of Bath’s High Performance Computing Facility and access to the HECToR supercomputer through membership of the U.K.’s HPC Materials Chemistry Consortium, which is funded by the EPSRC (Grant EP/F0067496).

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NOTE ADDED AFTER ASAP PUBLICATION

Reference 26 was replaced on July 16, 2013.