SUPPLEMENTARY INFORMATION

for

Flexibility in MOFs: do scalar and group-theoretical counting rules work?

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Introduction

The following is a step-by-step derivation of the character of $\Gamma(m) - \Gamma(s)$ for the **pcb** assembly. The interested reader is also advised to try the examples in the original papers[1-3] by Guest and Fowler.

Stage 1: Build Contact polyhedra

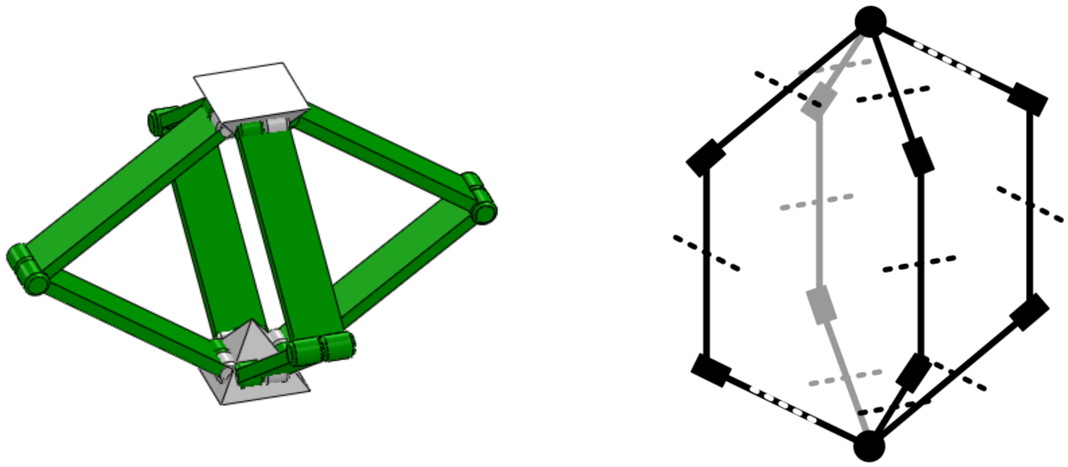

Figure S1: Contact polyhedra for the **pcb** motif. The vertices represent the two types of bodies, discs for SBU, rectangle for ligands (still simply treated as points for symmetry operations). The solid lines are the edges of the polyhedron and represent the hinges. They are decorated by segment in dashed line indicating the axis of the hinges.

The first step consists in generating what Fowler and Guest call the contact polyhedron (*C*). This 3D graph has vertices (*v*) that correspond to the bodies of the system, and edges (*e*) that correspond to the joints (hinges for carboxylate MOFs). *C* is not always an actual polyhedron and is certainly not unique but it is generally straightforward to produce one. Figures S1 displays the contact polyhedra for a **pcb** assembly (non-periodic).

Stage 2: Identify space group

At the second step, the point group *G(C)* of the contact polyhedra that also respects the axes of the hinges is determined. This is why it is actually useful to decorate *C* with segment representing such axes at the first stage. The space group of the **pcb** contact polyhedra is D_{4h}, and its character table is given in table S1.

Table S1: Character table for Group D_{4h}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Stage 3: $\Gamma_T + \Gamma_R$

The third step is very simple: the representation $\Gamma_T + \Gamma_R$ is read from the character table of G(C). For several symmetries (at least all improper ones), its character is zero, which is important to note in order to avoid unnecessary labour for some other representations.

Here,

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_T + \Gamma_R$	6	2	-2	-2	-2	0	0	0	0	0

Stage 4: $\Gamma(v, C)$ and $\Gamma_{\parallel}(e, C)$

For the fourth step, the characters for the remaining representations in the first term of equation (9) are determined by inspection on C. For a given symmetry operation, the character of $\Gamma(v, C)$ is the number of nodes (points) of C that are unshifted.

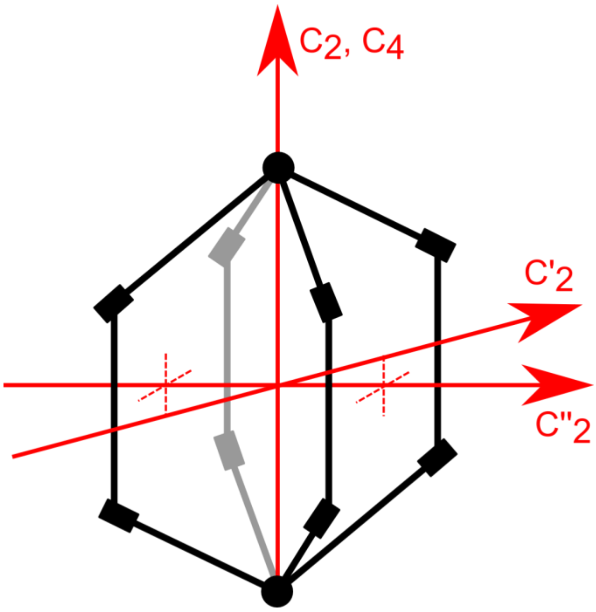

Fig S2: Nodes of C and symmetry operations for $\Gamma(v, C)$

As seen in fig. S2 for **pcb**, C contains 10 nodes, of two types. The C_2 and C_4 rotations shift all but two nodes, hence a character of 2. The two other types of rotations shift all nodes, and have a character of 0, and the remaining symmetries are not required due to the zeroes of $\Gamma_T + \Gamma_R$. Therefore,

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma(v, C)$	10	2	2	0	0	-	-	-	-	-

The character of $\Gamma_{\parallel}(e, C)$ is the number of vectors along the edges of C that are unshifted minus the number of vectors that are inverted on their edge.

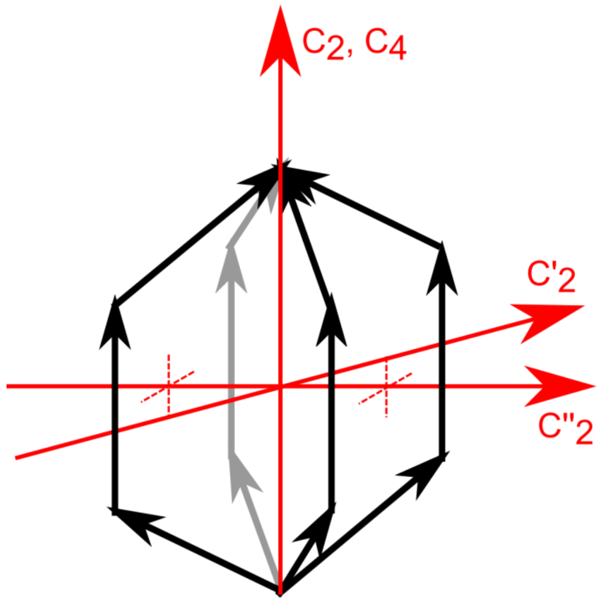

Fig S3: Edges of C and Symmetry operations for $\Gamma_{\parallel}(e, C)$

As seen in fig. S3 for **pcb**, C contains 12 edges, of two types. The C_2 and C_4 rotations shift all edges, hence a character of 0. The C'_2 rotation inverts two edges for a character of -2. The C''_2 rotation shift all edges, and has a character of 0, and the remaining symmetries are not required due to the zeroes of $\Gamma_T + \Gamma_R$. Therefore,

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\parallel}(e, C)$	12	0	0	-2	0	-	-	-	-	-

Γ_0 is the trivial representation with a character of 1 for all symmetries.

Stage 5: Γ_f

The fifth step is the most difficult, conceptually, and because it does not benefit from the zeroes of $\Gamma_T + \Gamma_R$. For MOFs with hinges perpendicular to the ligand, the characters of the representation of the freedoms Γ_f can be obtained from the fact that for each symmetry operation, the character of the hinge χ_{hinge} is the product of the character χ_R of a rotation (axial vector, pseudovector) on the hinge axis by the character $\chi_{\parallel e}$ of a (radial) vector on the edge e.

Most rotations and improper rotations actually shift the edges and have a character of 0, with the exception of C'$_2$ which inverts two edges, as seen in fig. S4 ($\chi_{\parallel e} = -1$). But C'$_2$ also inverts the rotation vectors ($\chi_R = -1$), so the resulting character is actually positive, at 2.

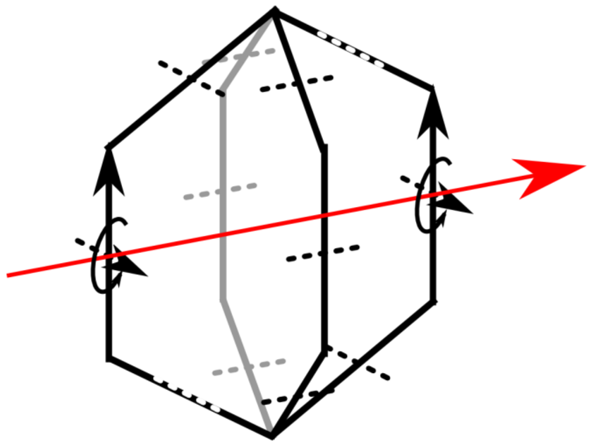

Fig S4: Effects of C'$_2$ for Γ_f

The inversion and dihedral mirror also shifts all edges, and have a character of 0. This is not the case for the σ_v and σ_h mirrors.

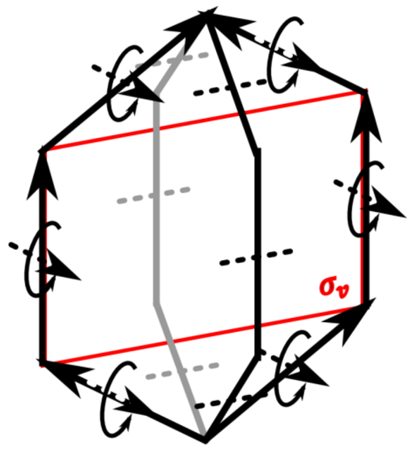

Fig S5: Effects of σ_v for Γ_f

Fig. S5 shows that σ_v keeps six edges unchanged ($\chi_{\parallel e} = 1$), and that the rotations having their axes perpendicular to the mirror plane are also unchanged ($\chi_R = 1$), for a character of 6.

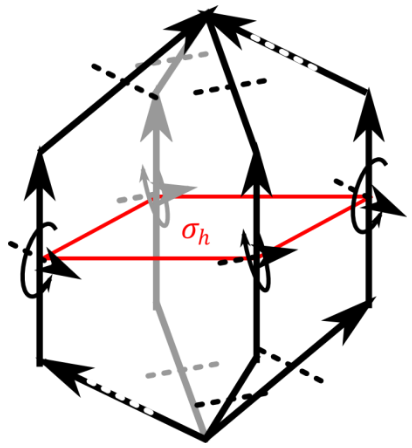

Fig S6: Effects of σ_h for Γ_f

Fig. S6 shows that σ_h inverts four edges ($\chi_{\parallel e} = -1$), and that the rotations having their axes in the mirror plane are also inverted ($\chi_R = -1$), for a character of 4. Then

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_f	12	0	0	2	0	0	0	4	6	0

Stage 5: projecting the irrep

Finally, the various additions, subtractions and multiplications can be applied to the representations to obtain $\Gamma(m) - \Gamma(s)$, which can then be projected onto the irreps. We used spreadsheets developed by Niece[4] to speed up these routine tasks.

Table S2: Character table for the calculations

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma(v, C)$	10	2	2	0	0	-	-	-	-	-
$-$ $\Gamma_{\parallel}(e, C)$	12	0	0	-2	0	-	-	-	-	-
$-$ Γ_0	1	1	1	1	1	-	-	-	-	-
$=$	-3	1	1	1	-1	-	-	-	-	-
$\times$ $\Gamma_T + \Gamma_R$	6	2	-2	-2	-2	0	0	0	0	0
$=$	-18	2	-2	-2	2	0	0	0	0	0
$+$ Γ_f	12	0	0	2	0	0	0	4	6	0
$= \Gamma(m) - \Gamma(s)$	-6	2	-2	0	2	0	0	4	6	0
$\Gamma(m) - \Gamma(s) = [A_{1g}] - A_{2g} - B_{2g} - E_g - A_{1u} - 2B_{1u}$										

References

1. P. W. Fowler and S. D. Guest, *International Journal of Solids and Structures*, 2000, **37**, 1793-1804.
2. S. D. Guest and P. W. Fowler, *Mechanism and Machine Theory*, 2005, **40**, 1002-1014.
3. S. D. Guest and P. W. Fowler, *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, 2014, **372**, 20120029.
4. B. K. Niece, *J. Chem. Educ.*, 2012, **89**, 1604-1605.