# Dioxole Functionalized Metal-Organic Frameworks

Phuong V. Dau, Luis R. Polanco and Seth M. Cohen*

*Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, United States, 92093*

# SUPPORTING INFORMATION

* To whom correspondence should be addressed. E-mail: scohen@ucsd.edu. Telephone: (858) 822-5596.

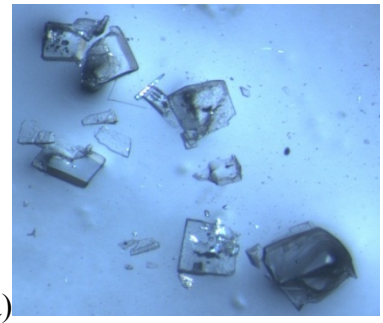
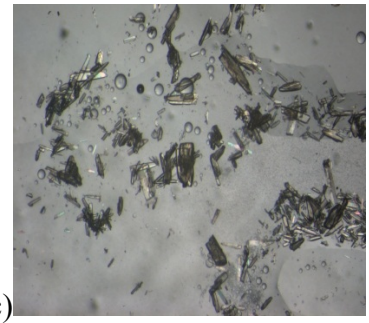
a)  b)  c) 

**Figure S1.** Pictures of IRMOF-1-dioxole (a), MOF-1-dioxole (b), and BMOF-2-dioxole (c).

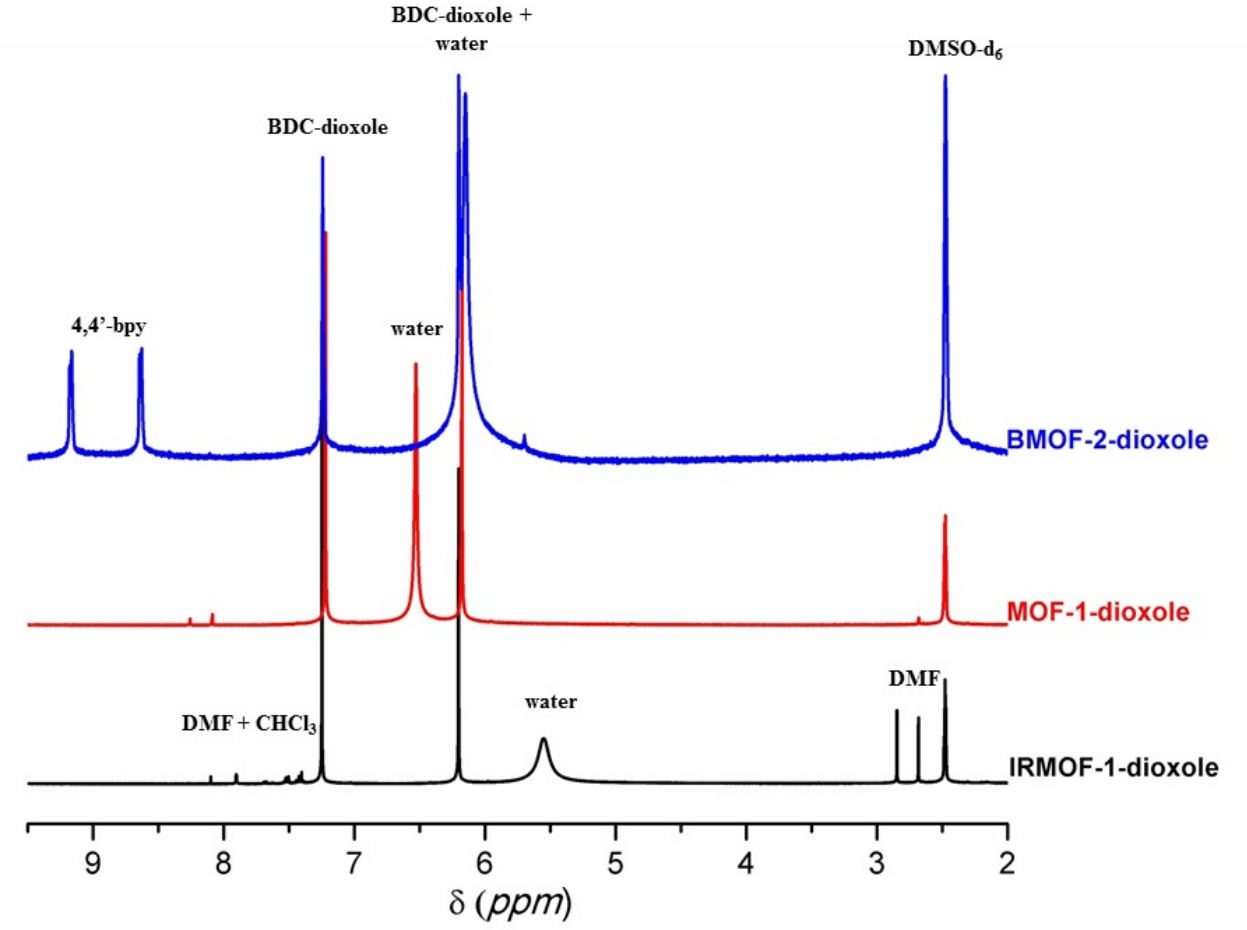



**Figure S2.** $^{1}$H NMR after digestion of IRMOF-1-dioxole, MOF-1-dioxole, and BMOF-2-dioxole.

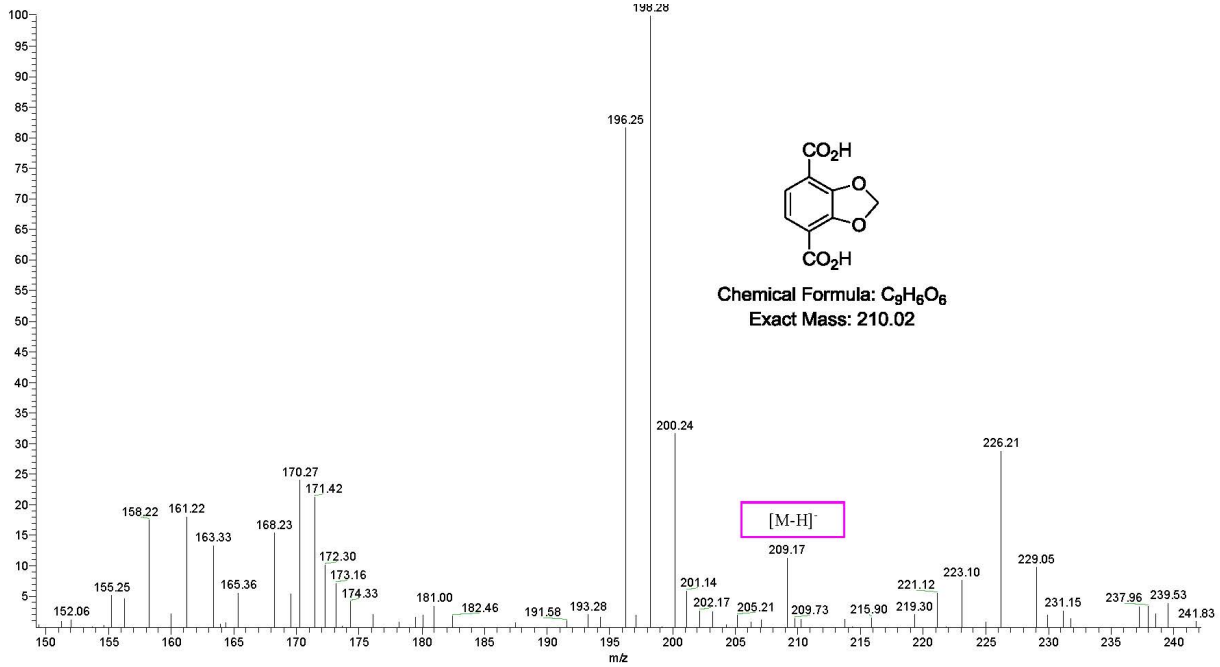



**Figure S3.** ESI-MS of digested IRMOF-1-dioxole.

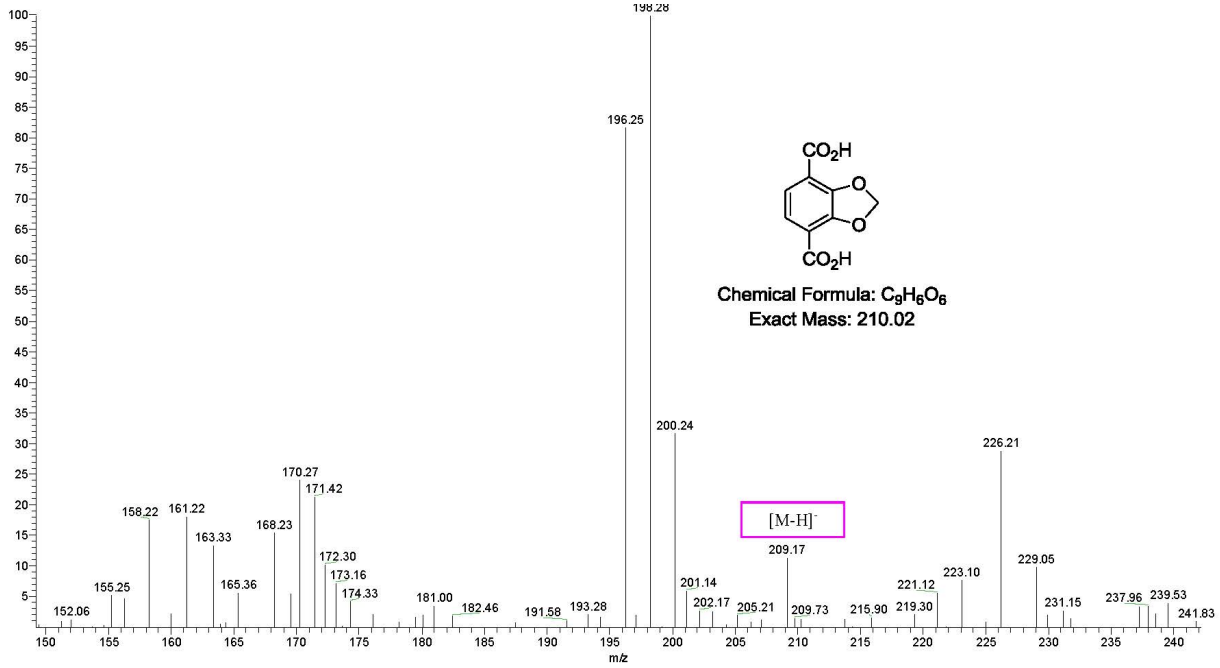



**Figure S4.** ESI-MS of digested MOF-1-dioxole.

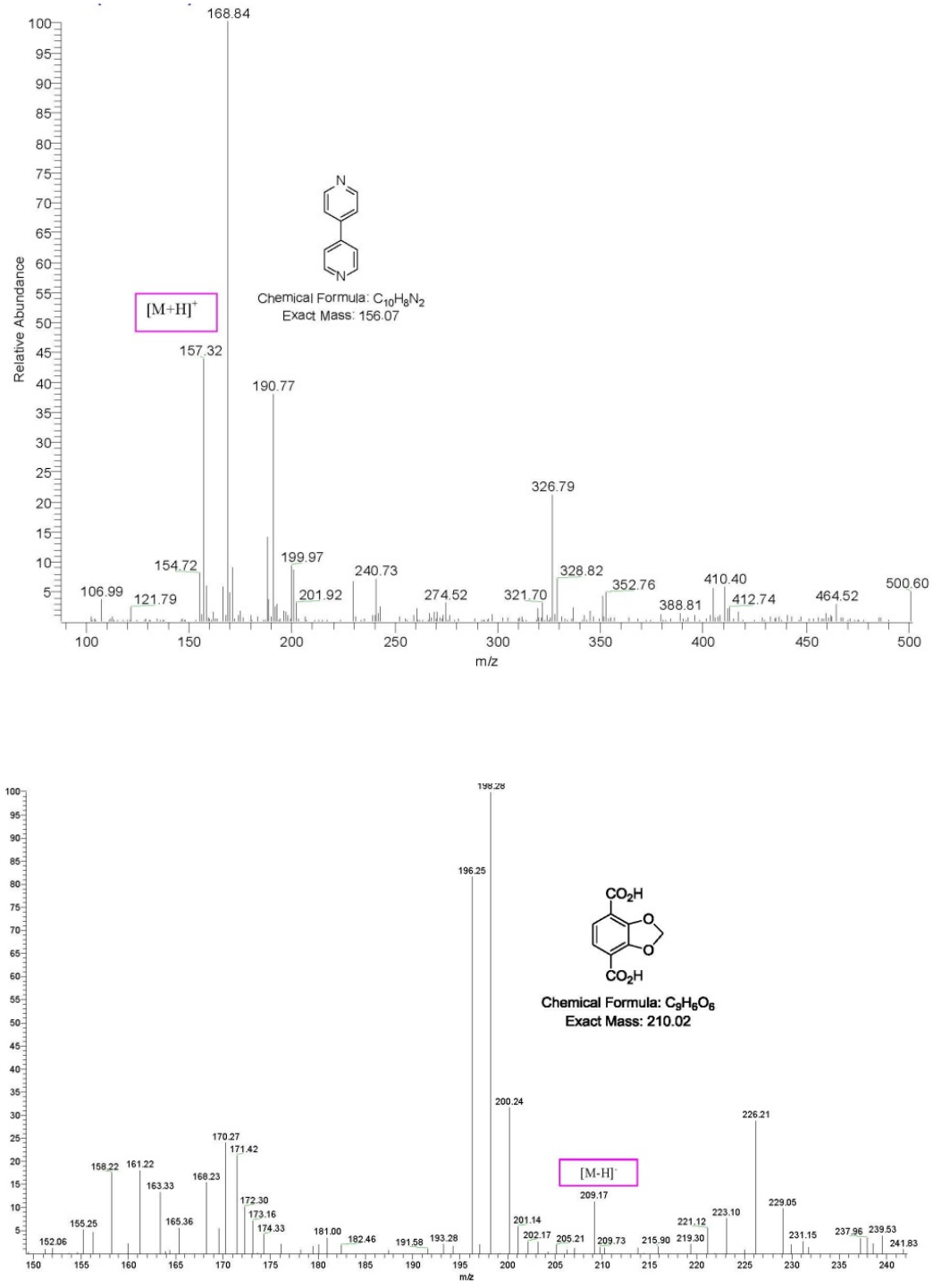



**Figure S5.** ESI-MS of digested BMOF-2-dioxole.

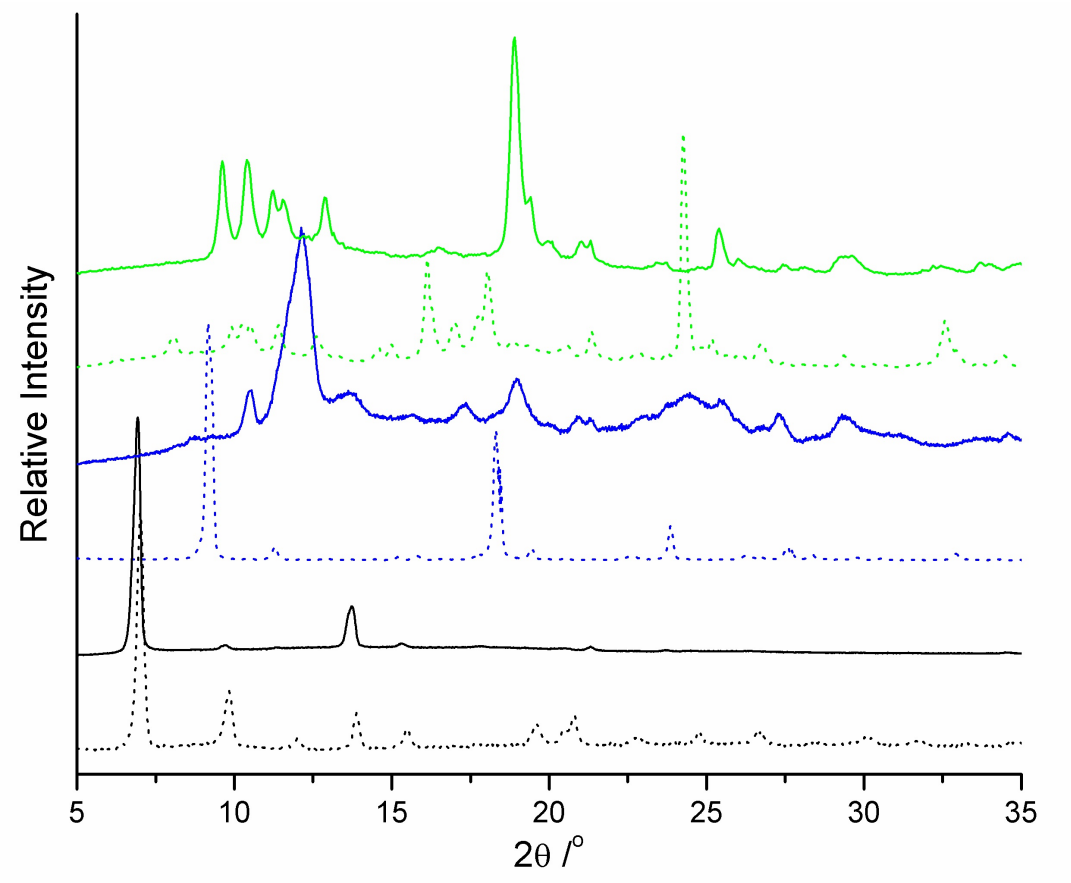



**Figure S6.** PXRD of the dioxole-functionalized MOFs prior to (dotted lines) and after (solid lines) activation. IRMOF-1-dioxole (black), MOF-1-dioxole (blue), and BMOF-2-dioxole (green).

**Table S1.** Summary of BET surface areas measurements of MOFs.

| MOFs | BET 1 ($m^2/g$) | BET 1 ($m^2/g$) | BET 1 ($m^2/g$) | Average ± Std ($m^2/g$) |
|---|---|---|---|---|
| **IRMOF-1-dioxole** | 2564 | 2565 | 2420 | 2516 ± 83 |
| **MOF-1-dioxole** | 437 | 393 | 454 | 428 ± 31 |
| **BMOF-2-dioxole** | 3 | 5 | 7 | 5 ± 2 |

**Table S2.** Summary of calculated void volume per unit cell, and the percentage of void volume per unit cell of each framework.

| MOF | Void Volume per unit cell ($Å^3$)[1] | Percentage of void volume per unit cell (%) |
|---|---|---|
| IRMOF-1-dioxole | 11938 | ~69 |
| MOF-1-dioxole | 2228 | ~42 |
| BMOF-2-dioxole | 465[2] | ~28 |

[1] The void volume was calculated by using PLATON.[1]

[2] The *N,N*-dimethylformamide molecule was removed before the estimation of void volume.

**Table S3.** Crystallographic data for IRMOF-1-dioxole.

| | |
|---|---|
| Identification code | IRMOF-1-dioxole |
| Empirical formula | $C_{27}H_{12}O_{19}Zn_4$ |
| Formula weight | 949.72 |
| Temperature | 250(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Cubic |
| Space group | *Fm-3m* |
| Unit cell dimensions | $a = b = c = 25.896(3)$ Å<br>$\alpha = \beta = \gamma = 90$ ° |
| Volume | 17367(3) $Å^3$ |
| Z | 8 |
| Density (calculated) | 0.726 $mg/m^3$ |
| Absorption coefficient | 1.608 $mm^{-1}$ |
| F(000) | 3712 |
| Crystal size | 0.15 x 0.10 x 0.10 $mm^3$ |
| Theta range for data collection | 2.96 to 42.55°. |
| Index ranges | -19<=h<=15, -12<=k<=21, -17<=l<=19 |
| Reflections collected | 4602 |
| Independent reflections | 312 [$R_{(int)} = 0.0421$] |
| Completeness to theta = 42.55° | 85.7 % |
| Data / restraints / parameters | 312 / 0 / 29 |
| Goodness-of-fit on $F^2$ | 1.218 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0481$, $wR_2 = 0.1577$ |
| R indices (all data) | $R_1 = 0.0537$, $wR_2 = 0.1543$ |
| Largest diff. peak and hole | 0.290 and -0.194 $e.Å^{-3}$ |

**Table S4.** Crystallographic data for MOF-1-dioxole.

| | |
|---|---|
| Identification code | MOF-1-dioxole |
| Empirical formula | $C_{18}H_8O_{12}Zn_2$ |
| Formula weight | 546.98 |
| Temperature | 200(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Tetragonal |
| Space group | *P* $4_1$ $2_1$ 2 |
| Unit cell dimensions | $a = b = 19.5078(11)$ Å<br>$c = 13.8150(8)$ Å<br>$\alpha = \beta = \gamma = 90°$. |
| Volume | 5257.4(5) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.382 $mg/m^3$ |
| Absorption coefficient | 1.875 $mm^{-1}$ |
| F(000) | 2176 |
| Crystal size | 0.50 x 0.30 x 0.25 $mm^3$ |
| Theta range for data collection | 1.48 to 28.27°. |
| Index ranges | -17<=h<=18, 0<=k<=25, 0<=l<=18 |
| Reflections collected | 6219 |
| Independent reflections | 6219 [$R_{(int)} = 0.0000$] |
| Completeness to theta = 28.27° | 97.1 % |
| Max. and min. transmission | 0.6514 and 0.4541 |
| Data / restraints / parameters | 6219 / 0 / 271 |
| Goodness-of-fit on $F^2$ | 1.065 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0466$, $wR_2 = 0.1198$ |
| R indices (all data) | $R_1 = 0.0533$, $wR_2 = 0.1169$ |
| Absolute structure parameter | 0.020(2) |
| Largest diff. peak and hole | 1.307 and -0.832 $e.Å^{-3}$ |

**Table S5.** Crystallographic data for BMOF-2-dioxole.

| | |
|---|---|
| Identification code | BMOF-2-dioxole |
| Empirical formula | $C_{31}H_{23}N_3O_{13}Zn_2$ |
| Formula weight | 776.26 |
| Temperature | 250(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | *P-1* |
| Unit cell dimensions | $a$ = 10.8947(6) Å $\alpha$ = 81.540(2)°<br>$b$ = 10.9708(6) Å $\beta$ = 89.016(2)°<br>$c$ = 13.9891(7) Å $\gamma$ = 87.658(2)° |
| Volume | 1652.35(15) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.560 $mg/m^3$ |
| Absorption coefficient | 1.522 $mm^{-1}$ |
| F(000) | 788 |
| Crystal size | 0.25 x 0.15 x 0.10 $mm^3$ |
| Theta range for data collection | 2.37 to 25.34°. |
| Index ranges | -13<=h<=13, -12<=k<=13, -16<=l<=16 |
| Reflections collected | 14015 |
| Independent reflections | 5482 [$R_{(int)}$ = 0.0735] |
| Completeness to theta = 25.34° | 90.7 % |
| Max. and min. transmission | 0.9872 and 0.8742 |
| Data / restraints / parameters | 5482 / 0 / 442 |
| Goodness-of-fit on $F^2$ | 1.076 |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0632, $wR_2$ = 0.1635 |
| R indices (all data) | $R_1$ = 0.1103, $wR_2$ = 0.1498 |
| Largest diff. peak and hole | 1.125 and -0.768 $e.Å^{-3}$ |

**Reference.**

1. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.