Supplementary information

From *operando* Raman mechanochemistry to “NMR crystallography”: understanding the structures and interconversion of Zn-terephthalate networks using selective $^{17}$O-labelling.

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**FIGURE S1:** Reaction profiles corresponding to signals enlightened in Figure 1 between 1380 and 1480 cm$^{-1}$, from 1000 to 5400 s of milling reaction. Only ZTA2a and ZTA2b are present from 1000 s onwards.

**FIGURE S2:** pXRD pattern of synthesized Zn-BDC compounds (dark colours) along with simulated corresponding patterns of optimized structures (light colours). Simulated patterns of starting materials ZnO (ICSD- 67848) and H$_2$BDC (CCDC BONHUK) are indicated in order to show the purity of synthesized compounds.

**FIGURE S3:** a) FTIR spectra of ZTA1 (green), ZTA2a (red), ZTA2b (blue) and ZTA3 (purple). b): zoom on the ν(OH) region of FTIR spectra of ZTA2a-*$^{17}$OH (dark red), ZTA2b-*$^{17}$OH (dark blue) and ZTA3-*$^{17}$OH (dark purple). c) zoom on the ν$_{as}$ (COO$^{-}$) region of FTIR spectra of ZTA1-*$^{13}$BDC (dark green), ZTA2a-*$^{13}$BDC (dark red) and ZTA3-*$^{13}$BDC (dark purple).

**FIGURE S4:** a) $^{13}$C CPMAS NMR spectra of H$_2$BDC recorded with a spinning speed of 8.0, 4.2 and 15 kHz (Top) at $B_0$ = 14.1 T. b) $^{17}$O NMR spectra of H$_2$BDC* recorded at 9.4, 14.1 and 20.0 T. NMR parameters used for each multi-spinning speeds and multi-fields fits can be found in the respective tables of a) and b).

**FIGURE S5:** FTIR spectrum (2000 – 1000 cm$^{-1}$ region), in black H$_2$BDC*, both red spectra correspond to two syntheses of ZTA2a-*$^{13}$BDC.

**FIGURE S6:** ¹H NMR spectra recorded at $B_0$ = 14.1 T and $v_{rot}$ = 16 kHz. For ZTA3, the dashed blue spectrum corresponds to the ¹H NMR spectrum recorded at $B_0$ = 20.0 T and $v_{rot}$ = 60 kHz. No acid proton (~ 14 ppm) is observed in the Zn-BDC compounds.

**FIGURE S7:** Graphical plot of $\delta_{iso}(^{13}C)_{calc}$ vs. the corresponding $\delta_{iso}(^{13}C)_{exp}$.

**FIGURE S8:** a) Graphical plot of the longest C-O distance ($d_{C-O}$) of the BDC ligand vs. the corresponding $\delta_{iso}(^{13}COO)$. b) Graphical plot of the shortest C-O distance ($d_{C-O}$), of the BDC ligand vs. the corresponding $\delta_{iso}(^{13}COO)$. c) Graphical plot of difference $\Delta$ between the longest and the shortest C-O distances of the BDC ligand vs. the corresponding $\delta_{iso}(^{13}COO)$ d) Graphical plot of the carboxylate angle $\theta_{O-C-O}$ of the BDC ligand vs. the corresponding $\delta_{iso}(^{13}COO)$. Orange dots correspond to values for the final optimized structures of
Zn-BDC phases discussed in this article. Blue dots correspond to values for different other structure optimization models of ZTA3. The linear trendline corresponds to the blue set of dots. ........................................S7

FIGURE S9: $^{13}$C CPMAS NMR spectra of Zn-BDC compounds: bottom $\nu_{rot} = 8$ kHz, middle $\nu_{rot} = 4.0$ or 4.2 kHz and top simulated from calculated NMR parameters (Table 4). Dotted red lines correspond to final fits see Table S1.................................................................S7

TABLE S1: $^{13}$C CSA parameters obtained by fitting simultaneously spectra recorded at $B_0 = 14$. 1 T with two spinning speeds $\nu_{rot} = 8.0$ and 4.2/4.0 kHz..............................................................................................................S8

FIGURE S10: a) Graphical plot of the $\Omega$ vs. the corresponding $\delta_{iso}(^{13}C)_{calc}$. b) Graphical plot of the $\Omega$ vs. the corresponding longest C-O distance ($d_{C-O}$). Orange dots correspond to values for the final optimized structures of Zn-BDC phases discussed in this article. Blue dots correspond to values for different other structure optimization models of ZTA3......................................S8

FIGURE S11: $^{17}$O MQMAS spectrum of ZTA3-0H recorded at $B_0 = 18.8$ T under $\nu_{rot} = 16$ kHz. Extracted slices are fitted with parameters presented in Table 5. .................................................................S9

FIGURE S12: $^{17}$O MQMAS spectrum of ZTA3-0BDC recorded at $B_0 = 18.8$ T under $\nu_{rot} = 16$ kHz. Extracted slices are fitted with parameters presented in Table 5. .................................................................S9

FIGURE S13: a) $^{17}$O MAS NMR spectra of ZTA3-0H and b) $^{17}$O MAS NMR ZTA3-0BDC recorded at $B_0 = 9.4$, 14.1 and 20.0 T and $\nu_{rot} = 18$, 18 and 14.286 kHz respectively. Red dotted lines correspond to final fits. .................................................................S10

FIGURE S14: a) $^{17}$O MAS NMR spectra of ZTA2a-0H and b) $^{17}$O MAS NMR ZTA2a-0BDC recorded at $B_0 = 9.4$, 14.1, 18.8 and 20.0 T and $\nu_{rot} = 18$, 18, 16 and 14.286 kHz respectively. Red dotted lines correspond to final fits. .................................................................S10

FIGURE S15: $^{17}$O MAS NMR spectra of ZTA2b-0H at $B_0 = 9.4$, 14.1 and 20.0 T and $\nu_{rot} = 18$, 18, 16 and 14.286 kHz respectively. Red dotted lines correspond to final fits. .................................................................S11

FIGURE S16: $^{17}$O MAS NMR spectra of ZTA1-0BDC recorded at $B_0 = 14.1$ and 20.0 T and $\nu_{rot} = 18$ and 14.286 kHz respectively. Red dotted lines correspond to final fits. .................................................................S11

FIGURE S17: Graphical plot of a) the shortest distance ($d_{Zn-O}$) vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$, b) the $d_{C-O}$ distance vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$ and c) the $\theta_{Zn-O-C}$ angle vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$...........S12

FIGURE S18: Graphical plot of the $^{17}$O QI parameters $C_Q$ and $\eta_Q$: a) the shortest distance ($d_{Zn-O}$) vs. the corresponding $C_Q$ (left) and $\eta_Q$ (right), b) the $d_{C-O}$ distance vs. the corresponding $C_Q$ (left) and $\eta_Q$ (right), and c) the $\theta_{Zn-O-C}$ angle vs. the corresponding $C_Q$ (left) and $\eta_Q$ (right)............................................S13

FIGURE S19: a) In black the Raman spectra of $d_4$-H$_2$BDC and H$_3$BDC, in grey the Raman spectrum of the Perspex jar used for operando experiments. b) $\nu$(CD) region of Raman spectra of $d_4$-H$_2$BDC, ZTA1-d$_4$BDC and ZTA2a-d$_4$BDC.............S14
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Figure S7: Graphical plot of $\delta_{\text{iso}}^{(13)}\text{C}_{\text{calc}}$ vs. $\delta_{\text{iso}}^{(13)}\text{C}_{\text{exp}} / \text{ppm}$

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$R^2 = 0.945$

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Table S2: $^{13}$C CSA parameters obtained by fitting simultaneously spectra recorded at $B_0 = 14.1$ T with two spinning speeds $\nu_{rot} = 8.0$ and 4.2/4.0 kHz.

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 172.1 ± 0.3                 | 136.9 ± 0.4     | 0.05 ± 0.01 |
| 174.0 ± 0.1                 | 140.0 ± 2.4     | 0.13 ± 0.03 |

**ZTA3**

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 137.0 ± 0.1                 | 206.6 ± 4.5     | 0.26 ± 0.09 |
| 129.8 ± 0.1                 | 210.5 ± 0.8     | 0.40 ± 0.05 |
| 128.4 ± 0.1                 | 221.1 ± 0.8     | 0.19 ± 0.01 |

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 172.1 ± 0.1                 | 137.3 ± 0.2     | 0.23 ± 0.01 |

**ZTA2b**

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 135.6 ± 0.2                 | 215.1 ± 6.7     | 0.29 ± 0.02 |
| 130.3 ± 0.1                 | 193.2 ± 10.4    | 0.68 ± 0.33 |
| 129.4 ± 0.1                 | 241.2 ± 6.4     | 0.32 ± 0.06 |

**ZTA2a**

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 172.5 ± 0.2                 | 139.9 ± 8.2     | 0.34 ± 0.15 |
| 175.7 ± 0.1                 | 137.5 ± 0.4     | 0.19 ± 0.01 |
| 136.7 ± 0.1                 | 210.3 ± 2.6     | 0.29 ± 0.03 |
| 132.2 ± 0.2                 | 231.3 ± 2.8     | 0.36 ± 0.02 |

**ZTA1**

| $\delta_{iso}(^{13}C)$ / ppm | $\Omega$ / ppm | $\kappa$ |
|-----------------------------|----------------|---------|
| 176.6 ± 0.1                 | 154.7 ± 6.3     | 0.03 ± 0.20 |
| 135.0 ± 0.1                 | 210.4 ± 5.9     | 0.23 ± 0.03 |
| 131.2 ± 0.2                 | 221.1 ± 3.3     | 0.35 ± 0.01 |

Figure S10: a) Graphical plot of the $\Omega$ vs. the corresponding $\delta_{iso}(^{13}C)_{calc}$. b) Graphical plot of the $\Omega$ vs. the corresponding longest C-O distance ($d_{C-O}$). Orange dots correspond to values for the final optimized structures of Zn-BDC phases discussed in this article. Blue dots correspond to values for different other structure optimization models of ZTA3.
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Figure S17: Graphical plot of a) the shortest distance ($d_{Zn-O}$) vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$, b) the distance $d_{C-O}$ vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$ and c) the $\theta_{Zn-O-C}$ angle vs. the corresponding $\delta_{iso}(^{17}O)_{calc}$. 
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