Determining the Chemical Composition of Diamagnetic Mixed Solids via Measurements of the Magnetic Susceptibility

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Supplementary Information:

1. Experimental details
2. Tables listing the doping concentrations δ and molar magnetic susceptibilities χ_{Mol} of Examples 1-8 (**Tables S1-S8**).
3. List of experimentally obtained χ_{Mol} (**Table S9**).
4. Determination of δ of $NH_{4(1-\delta)}D_\delta Br$ (Example 1) and $NH_4I_{1-\delta}Br_\delta$ (Example 2) from lattice parameters (**Figures S1 & S2**).
5. Determination of δ of $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$ (Example 3) via measurements of the critical temperatures of the order-disorder phase transition (**Figure S3 & S4**).

1. Experimental details:

a) Magnetic susceptibility measurements:

The magnetic susceptibility was measured by the vibrating sample magnetometer (VSM) option of a Physical Properties Measurement System (PPMS) manufactured by Quantum Design, Inc. All measurements were performed at 300.00 K. The ramping speed of the applied magnetic field was set to 20 Oe/s. GE varnish was used to secure the samples onto the sample rods. The mass of the varnish was always measured so its diamagnetic contribution can be subtracted.

b) Sample preparation:

$NH_{4(1-\delta)}D_{4\delta}Br$: Ammonium bromide NH_4Br (CAS#: 12124-97-9, 99.99% in purity) was mixed in different ratios of deionized H_2O and D_2O (99.5% deuterium) to form a solution. After slow evaporation, the formed crystals were collected, grounded to powder and compressed into pellets of sizes 5 mm in diameter and 2 mm in height.

$NH_4I_{1-\delta}Br_\delta$: NH_4Br and ammonium iodide NH_4I (CAS#: 12027-06-4, 99.999%) were mixed in deionized H_2O to form a solution. The slow evaporation method was also used and the mixed crystals were grounded and compressed into pellets.

$(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$: Ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ (CAS#: 7722-76-1, $\geq$99.99%) was dissolved in different ratios of H_2O and D_2O (starting solutions are listed in Table S3). After slow evaporation, the collected crystals were grounded and pressed into pellet-form.

Pure solids of NH_4I, NH_4Br and $NH_4H_2PO_4$: powder was taken straight from the reagent bottles and compressed into disc-shaped pellets.

For the remaining five series of examples, different quantities of the ten parent compounds were dry mixed, finely grounded into powder and pressed into pellets. Their control δ were determined from the masses of the parent compounds prior to mixing. The parent compounds were: Zirconium 1,4-dicarboxybenzene MOF, $C_{48}H_{28}O_{32}Zr_6$ (UiO-66, CAS#: 1072413-89-8, $\geq$97% in purity); $C_{48}H_{22}Br_6O_{32}Zr_6$ (UiO-66-Br, CAS#: 1260119-02-5, 97%); creatine, $C_4H_9N_3O_2$ (CAS#: 57-00-1, 98%); D-glucose, $C_6H_{12}O_6$ (CAS#: 50-99-7, $\geq$99.5%), L-glutamic acid, $C_5H_9NO_4$ (CAS#: 56-86-0, $\geq$99.5%); L-leucine, $C_6H_{13}NO_2$ (CAS#: 61-90-5, 99%); terephthalic acid, $C_8H_6O_4$ (CAS#: 100-21-0, 99%); trimesic acid, $C_9H_6O_6$ (CAS#: 554-95-0, 98%); p-terphenyl, $C_{18}H_{14}$ (CAS#: 92-94-4, $\geq$99.5%); and triphenylphosphine, $C_{18}H_{15}P$ (CAS#: 603-35-0, >99%).

c) Lattice constant measurements:

The lattice constants were obtained by using a Rigaku XtaLAB CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) via the ω-φ scanning technique. Single crystals taken directly from the mother liquor were placed in paraffin oil for their analyses. The crystals were mounted on a nylon loop and placed on the goniometer for data collection. All measurements were performed at 300 K.

2. Tables listing the doping concentrations δ and molar magnetic susceptibilities χ_{Mol} of examples 1-8.

The obtained molar magnetic susceptibility χ_{Mol} and doping concentration δ of the series of samples in Examples 1 to 8 (Figures 4 to 11) are listed in Tables S1 to S8, respectively. χ_{Mass} is the measured mass magnetic susceptibility for every sample. A comparison of δ obtained with the magnetic susceptibility method and control is also provided in the last columns. The difference in δ obtained from the current method and from a second control method was on average 1.86%, which is nearly twice as the theoretical expected value. This discrepancy may be attributed to uncertainties of the control method and errors introduced during the weighing process of the samples.

δ in starting solution	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10⁻⁶)	χ_{Mol} (cm³/mol ×10⁻⁶)	δ from χ_{Mol}	δ from lattice constant	δ-χ_{Mol} / δ-control %
0.00	35.4	− 0.50066(6)	− 49.036(6)	0	0	--
0.25	17.2	− 0.50200(12)	− 49.555(10)	0.192(5)	0.187	2.67
0.67	16.4	− 0.50495(12)	− 50.744(61)	0.634(25)	0.626	1.28
0.83	39.8	− 0.50564(5)	− 50.972(55)	0.719(22)	0.747	− 3.75
0.999×3	14.7	− 0.50718(14)	− 51.674(14)	0.980	0.980	--

Table S1. Measured values of the $NH_{4(1-\delta)}D_{4\delta}Br$ series: mass magnetic susceptibility χ_{Mass}, molar magnetic susceptibility χ_{Mol} and doping concentration δ from two methods. "δ in starting solution" takes into account the molar quantities of the reagent: H_2O plus D_2O. The last column contrasts the obtained values of δ via the χ_{Mol} and XRD methods by taking their ratio minus one and multiplying by 100.

δ in starting solution	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10⁻⁶)	χ_{Mol} (cm³/mol ×10⁻⁶)	δ from χ_{Mol}	a from XRD (Å)
0.00	41.6	− 0.44133(5)	− 63.968(7)	0	7.2758
0.06	12.8	− 0.44381(16)	− 63.065(87)	0.060(6)	7.2530
0.09	18.3	− 0.44435(11)	− 62.870(67)	0.073(4)	7.2481
0.25	16.4	− 0.45087(12)	− 60.671(73)	0.221(4)	7.1859
0.98	25.6	− 0.49588(8)	− 49.871(68)	0.944(3)	4.0590
1.00	35.4	− 0.50066(6)	− 49.036(6)	1	4.0659*

Table S2. Measured values of the $NH_4I_{1-\delta}Br_\delta$ series; *value from Ref. 28.

δ in starting solution	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm^3/mol ×10^{-6})	δ from χ_{Mol}	δ from T_C	δ-χ_{Mol} / δ-control %
0.00	13.1	− 0.50177(15)	− 57.717(18)	0	0	--
0.20	21.4	− 0.50695(9)	− 58.692(34)	0.124(7)	0.120	3.33
0.40	6.5	− 0.51296(31)	− 59.853(60)	0.274(10)	0.261	4.98
0.60	8.9	− 0.51578(22)	− 60.448(73)	0.351(8)	0.336	4.46
0.80	7.8	− 0.52678(26)	− 62.640(99)	0.644(11)	0.644	0.00

Table S3. Measured values of the $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$ series.

δ in starting mixture	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm^3/mol ×10^{-6})	δ from χ_{Mol}	δ-χ_{Mol} / δ-control %
0.000	6.5	− 0.35796(31)	− 765.11(66)	0	--
0.497	9.9	− 0.40877(20)	− 776.83(107)	0.501(7)	0.80
0.720	11.3	− 0.43495(18)	− 781.90(125)	0.718(7)	− 0.28
0.852	10.4	− 0.45481(19)	− 788.70(141)	0.867(8)	1.76
1.000	10	− 0.47386(20)	− 788.52(33)	1.000	--

Table S4. Measured values of the $[UiO\text{-}66\text{-}Br]_{(1-\delta)}[UiO\text{-}66]_\delta$ series.

δ in starting mixture	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm^3/mol ×10^{-6})	δ from χ_{Mol}	δ-χ_{Mol} / δ-control %
0.000	14.3	− 0.57157(14)	− 74.950(18)	0	--
0.223	11.0	− 0.57770(18)	− 82.892(426)	0.217(14)	− 2.69
0.410	17.2	− 0.58260(12)	− 88.311(466)	0.417(16)	1.71
0.880	20.0	− 0.59230(10)	− 104.032(375)	0.908(15)	3.19
1.000	14.0	− 0.59383(14)	− 106.98(3)	1.000	--

Table S5. Measured values of the $[creatine]_{(1-\delta)}[D\text{-}glucose]_\delta$ series.

δ in starting mixture	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm^3/mol ×10^{-6})	δ from χ_{Mol}	δ-χ_{Mol} / δ-control %
0.000	14.0	− 0.55413(14)	− 81.529(21)	0	--
0.146	13.6	− 0.57626(15)	− 83.430(24)	0.147(2)	0.68
0.590	9.6	− 0.64620(21)	− 89.057(36)	0.581(3)	− 1.52
0.651	13.3	− 0.65777(15)	− 89.936(33)	0.649(3)	− 0.31
1.000	13.3	− 0.72033(15)	− 94.486(20)	1.000	--

Table S6. Measured values of the $[L\text{-}glutamic\ acid]_{(1-\delta)}[L\text{-}leucine]_\delta$ series.

δ in starting mixture	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm^3/mol ×10^{-6})	δ from χ_{Mol}	δ-χ_{Mol} / δ-control %
0.000	23.0	− 0.52028(9)	− 86.434(14)	0	--
0.170	17.0	− 0.50826(12)	− 88.276(62)	0.172(4)	1.18
0.632	19.4	− 0.48052(10)	− 93.243(109)	0.634(6)	0.32
0.685	13.9	− 0.47819(14)	− 93.866(122)	0.678(7)	− 1.02
1.000	12.5	− 0.46240(16)	− 97.168(33)	1.000	--

Table S7. Measured values of the [terephthalic acid]$_{(1-\delta)}$[trimesic acid]$_\delta$ series.

δ in starting mixture	Sample mass (mg)	χ_{Mass} (emu/g-Oe ×10^{-6})	χ_{Mol} (cm³/mol ×10^{-6})	δ from χ_{Mol}	δ-χ_{Mol} / δ-control %
0.000	13.7	− 0.68065(15)	− 178.54(4)	0	--
0.209	17.4	− 0.68291(11)	− 174.34(98)	0.219(48)	4.78
0.281	14.8	− 0.68359(14)	− 173.16(75)	0.282(29)	− 0.36
0.589	17.1	− 0.68676(12)	− 167.68(85)	0.567(40)	− 3.74
1.000	11.8	− 0.69208(17)	− 159.39(4)	1.000	--

Table S8. Measured values of the [triphenylphosphine]$_{(1-\delta)}$[p-terphenyl]$_\delta$ series.

3. List of experimentally obtained χ_{Mol}.

Compound name	χ_{Mol} (cm³/mol ×10^{-6}) (Experimental)	χ_{Mol} (cm³/mol ×10^{-6}) (Expected)	Sample purity (%)
NH$_4$Br	− 49.036(6)	− 47.9	99.99
ND$_4$Br	− 51.674(14)*	N/A†	100 -d
NH$_4$I	− 63.968(7)	− 63.9	99.999
NH$_4$H$_2$PO$_4$	− 57.717(18)	− 63.86	99.99
ND$_4$D$_2$PO$_4$	− 65.402(30)*	N/A†	100 -d
C$_{48}$H$_{28}$O$_{32}$Zr$_6$	− 788.52(33)	N/A‡	≥97
C$_{48}$H$_{22}$Br$_6$O$_{32}$Zr$_6$	− 765.11(66)	N/A‡	>97
Creatine	− 74.950(18)	− 77.39	98
D-glucose	− 106.98(3)	− 101.5	≥99.5
L-glutamic acid	− 81.529(21)	− 78.5	≥99.5
L-leucine	− 94.486(20)	− 84.9	99
terephthalic acid	− 86.434(14)	− 84.22	99
Trimesic acid	− 97.168(33)	− 97.68	98
Triphenylphosphine	− 178.54(4)	− 187.0	>99
p-terphenyl	− 159.39(4)	− 157.8	≥99.5

Table S9. List of χ_{Mol} values of the parent compounds obtained experimentally at 300 K. The expected values of χ_{Mol} were calculated from addition of Pascal's constants taken from Ref. 26.
*98% deuteration.
†Pascal's constants of ND$_4$ not available in existing literature.
‡Pascal's constant of the –Zr covalent bond also not available.

4. Determination of δ of the NH$_{4(1-\delta)}$D$_\delta$Br series (Example 1) and NH$_4$I$_{1-\delta}$Br$_\delta$ series (Example 2) from lattice parameters.

The doping concentration δ was also extracted from measured lattice parameters of NH$_{4(1-\delta)}$D$_\delta$Br (Figure S1) and NH$_4$I$_{1-\delta}$Br$_\delta$ (Figure S2) as a means to check the accuracy of the obtained δ from our magnetic measurements.

The lattice constants were obtained by using a Rigaku XtaLAB CCD

diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) via the ω-φ scanning technique. Single crystals taken directly from the mother liquor were placed in paraffin oil for their analyses. The crystals were mounted on a nylon loop and placed on the goniometer for data collection. All measurements were performed at 300 K.
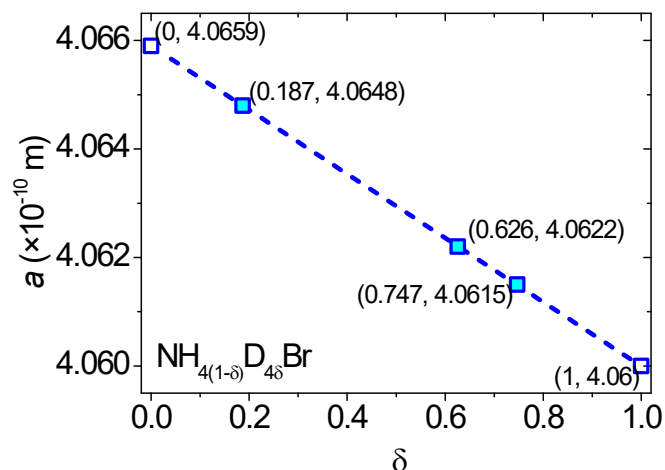
Fig. S1. Lattice constant a vs. isotope concentration. Open squares represent the lattice constants of NH_4Br and ND_4Br according to Levy *et al.*[28] and Havighurst *et al.*[9] The three solid squares are the obtained lattice constants of the three mixed solids and their corresponding δ.
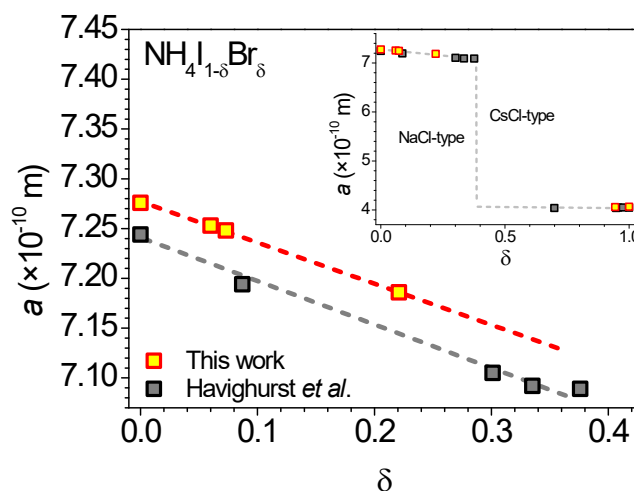

Fig. S2. Lattice constant a vs. halide concentration. Yellow squares are data from the last two columns of Table 2. Grey squares are data from Havighurst *et al.*[9] Dashed lines are linear fits. Inset shows how a is no longer additive when $\delta > 0.37$.

5. Determination of δ of the $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$ series (Example 3) via measurements of the critical temperatures of the order-disorder phase transition.

For the series $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$, δ was extracted from the critical temperature T_C of its order-disorder phase transition according to $\delta = (T_C - 148\ K) / 94\ K$.[33] Figure S3 shows the cooling and warming runs at 2 K/min of the mixed samples

with their respective T_C's. Figure S4 is a graphical representation of the linear relationship between the measured T_C's with δ. In each case, δ was obtained from the average T_C value of the cooling and warming curves.

The dielectric constants of the mixed crystals of the series $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$ were obtained from their measured capacitances with an E4980A LCR meter from Agilent Technologies. The electrodes were in to form of silver paint applied onto the surfaces perpendicular to the *b*-axis direction of the crystals. The applied electric field and frequency were ~5 V/cm and 1 kHz, respectively.
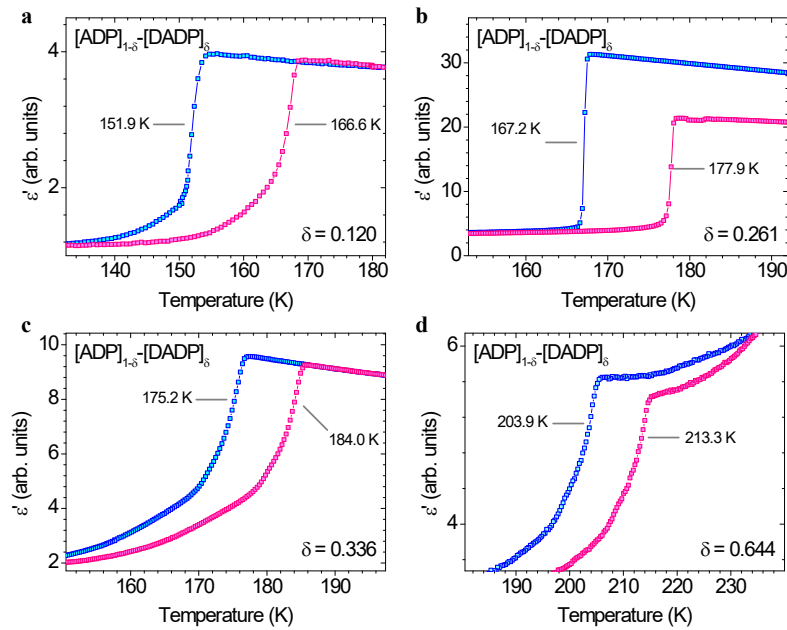
Fig. S3. Dielectric constant of the series $(NH_4H_2)_{1-\delta}(ND_4D_2)_\delta PO_4$, [ADP]$_{1-\delta}$-[DADP]$_\delta$, with respect to temperature. The obtained δ for the cases when a) $\delta = 0.120$; b) $\delta = 0.261$; c) $\delta = 0.336$; and d) $\delta = 0.644$ were obtained from the average of the critical temperatures T_C during cooling and warming for each sample.
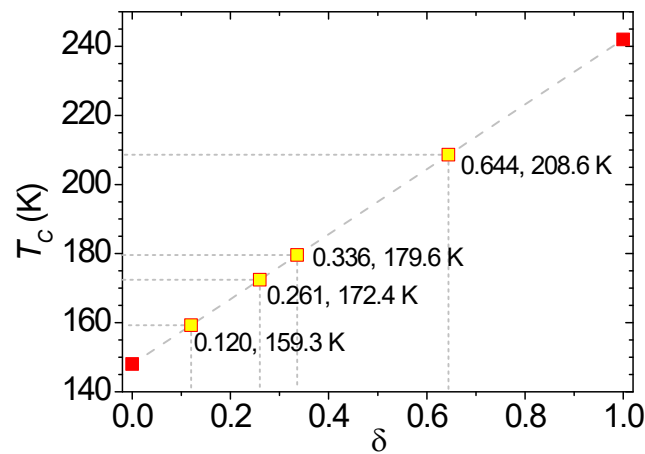
Fig. S4. The equation $\delta = (T_C - 148\ K) / 94\ K$ was employed to obtain δ from T_C. Red squares represent the parent compounds $NH_4H_2PO_4$ and $ND_4D_2PO_4$; yellow squares the four mixed samples.