Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

From partial to complete neutralization of 2,5-dihydroxyterephthalic acid in the Li-Na system: crystal chemistry and electrochemical behavior of $Na_2Li_2C_8H_2O_6$ *vs*. Li

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Figure S1. Description of the expected dual redox activity in the *p*-DHT^{4-} ligand.

Figure S2. Structure of **1** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers.

Figure S3. Structure of **2** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers.

Figure S4. Structure of **3** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers.

Figure S5. Structure of **4** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers.

Figure S6. Photographs of crystals (compounds **1**, **3** and **4**) obtained after a slow evaporation process at room temperature (24°C).

Figure S7. Comparison of FTIR spectra for $Na_2(Li_2)$-*p*-DHT (up) and Li_4-*p*-DHT (down), respectively.

Table S1. Range of selected bond lengths (Å) and bond angles (°) of compounds **1** – **4**.

Table S2. Hydrogen-bond geometry (Å, º) for **1**.

Table S3. Hydrogen-bond geometry (Å, º) for **2**.

Table S4. Hydrogen-bond geometry (Å, º) for **3**.

Table S5. Hydrogen-bond geometry (Å, º) for **4**.

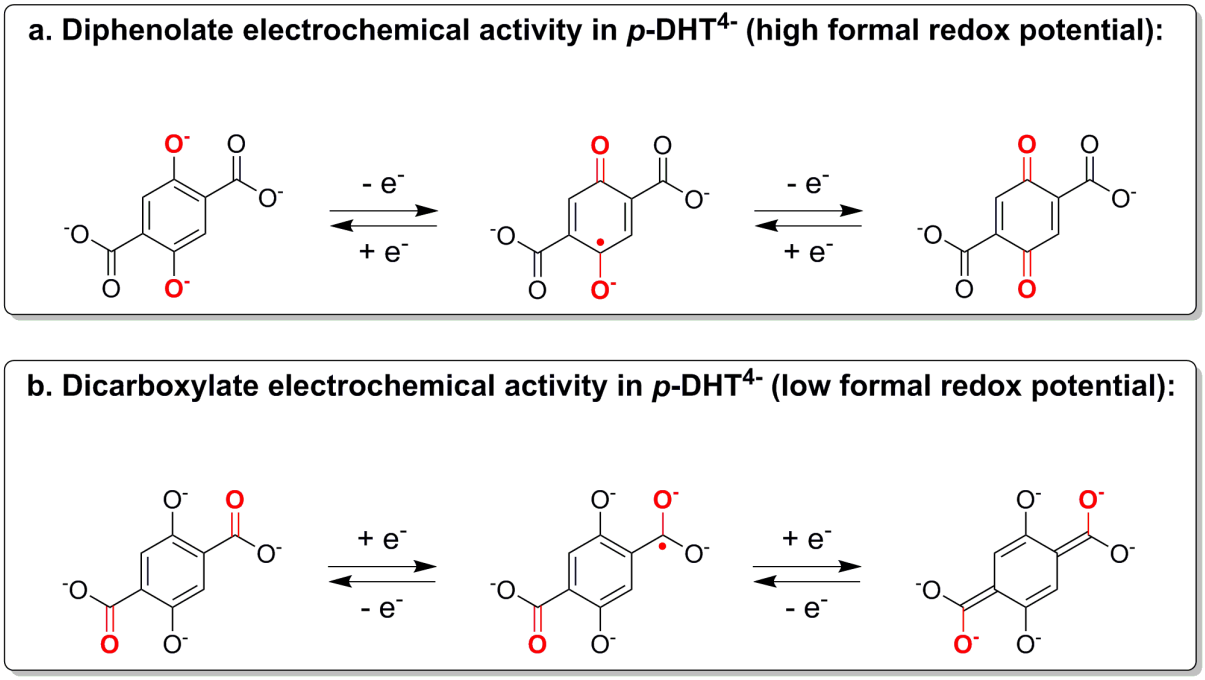


Figure S1. Description of the expected dual redox activity in the *p*-DHT^{4-} ligand.

Table S1. Range of selected bond lengths (Å) and bond angles (°) of compounds **1** – **4**.

Compound		Distance (Å) and angle (°) ranges
1		
Li1 tetrahedra	Li1–O x4	1.989(4) – 2.003(4)
	O–Li1–O x6	102.23(16) – 113.61(17)
Li2 tetrahedra	Li2–O x4	1.881(3) – 1.965(4)
	O–Li2–O x6	103.48(16) – 113.67(17)
2		
Li1 tetrahedra	Li1–O x4	1.898(3) – 2.038(3)
	O–Li1–O x6	91.48(11) – 118.08(15)
Li2 tetrahedra	Li2–O x4	1.904(3) – 1.990(3)
	O–Li2–O x6	103.87(13) – 117.51(15)
3		
Na1A octahedra	Na1A–O x6	2.3519(19) – 2.5325(18)
	O–Na1A–O *cis* x12	75.51(7) – 112.26(7)
	O–Na1A–O *trans* x3	154.00(7) – 175.57(7)
Na2A octahedra	Na2A–O x6	2.3466(19) – 2.5121(18)
	O–Na2A–O *cis* x12	75.91(7) – 108.63(7)
	O–Na2A–O *trans* x3	153.07(7) – 177.38(7)
Na1B octahedra	Na1B–O x6	2.3272(19) – 2.4836(18)
	O–Na1B–O *cis* x12	75.85(7) – 106.40(7)
	O–Na1B–O *trans* x3	151.34(7) – 177.56(7)
Na2B octahedra	Na2B–O x6	2.3669(19) – 2.5647(18)
	O–Na2B–O *cis* x12	75.97(7) – 110.19(7)
	O–Na2B–O *trans* x3	156.14(7) – 173.83(7)
4		
Li1 tetrahedra	Li1–O x4	1.8995(18) – 1.989(2)
	O–Li1–O x6	95.48(8) – 118.75(10)
Na1 octahedra	Na1-O x6	2.3115(10) – 2.6521(10)
	O–Na1–O *cis* x12	74.67(3) – 114.05(3)
	O–Na1–O *trans* x3	154.24(3) – 167.14(4)

Table S2. Hydrogen-bond geometry (Å, º) for **1**.

O—H···*O*	*O*—H	H···*O*	*O*···*O*	*O*—H···*O*
O3—H3···O41	0.91 (3)	1.70 (3)	2.5468 (19)	153 (3)
O6—H6···O12	0.95 (3)	1.58 (3)	2.4853 (18)	157 (3)
O1—H11···O42^{v}	0.87 (3)	1.93 (3)	2.797 (2)	172 (3)
O1—H12···O5^{iii}	0.80 (3)	2.09 (3)	2.864 (2)	161 (3)
O2—H21···O4^{vi}	0.87 (2)	1.98 (2)	2.829 (2)	165 (4)
O2—H22···O11^{vii}	0.83 (4)	2.00 (4)	2.808 (2)	164 (3)
O4—H41···O2^{i}	0.86 (2)	1.99 (2)	2.833 (2)	168 (5)
O4—H42···O3^{vi}	0.85 (3)	1.99 (3)	2.836 (2)	172 (3)
O5—H51···O1^{viii}	0.83 (3)	2.13 (3)	2.935 (2)	162 (2)
O5—H52···O12^{v}	0.95 (3)	1.78 (4)	2.711 (2)	165 (3)

Symmetry codes: (i) *x*, *y*, *z*-1; (iii) *x*, *y*, *z*+1; (v) -*x*+1, -*y*+1, -*z*+1; (vi) -*x*+2, -*y*+2, -*z*+1; (vii) -*x*+2, -*y*+1, -*z*+2; (viii) -*x*+1, -*y*+2, -*z*+1.

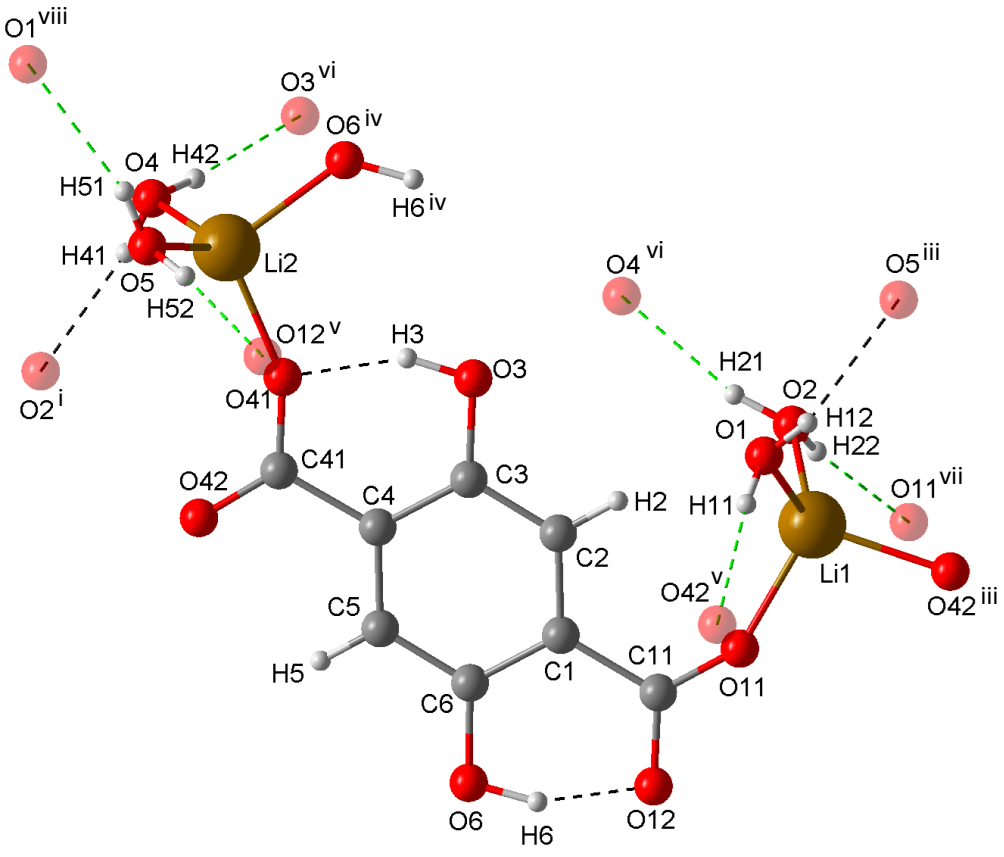


Figure S2. Structure of **1** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers. Symmetry codes: (i) *x*, *y*, *z*-1; (iii) *x*, *y*, *z*+1; (iv) *x*, *y*+1, *z*; (v) -*x*+1, -*y*+1, -*z*+1; (vi) -*x*+2, -*y*+2, -*z*+1; (vii) -*x*+2, -*y*+1, -*z*+2; (viii) -*x*+1, -*y*+2, -*z*+1.

Table S3. Hydrogen-bond geometry (Å, º) for **2**.

O—H···*O*	*O*—H	H···*O*	*O*···*O*	*O*—H···*O*
O3—H3···O41	0.95 (3)	1.66 (3)	2.5466 (15)	155 (3)
O6—H6···O12	0.88 (3)	1.77 (3)	2.5609 (16)	148 (3)
O1—H11···O9^{iii}	0.79 (3)	2.10 (3)	2.870 (2)	165 (3)
O1—H12···O8^{iv}	0.85 (3)	1.97 (3)	2.8031 (18)	168 (2)
O7—H71···O11^{v}	0.85 (2)	2.02 (2)	2.8548 (17)	169 (2)
O7—H72···O42^{vi}	0.85 (3)	1.94 (3)	2.7868 (17)	173 (3)
O8—H81···O12^{vii}	0.80 (3)	2.01 (3)	2.7895 (17)	165 (3)
O8—H82···O3^{iv}	0.86 (3)	1.89 (3)	2.7473 (18)	175 (2)
O9—H91···O6^{viii}	0.85 (3)	2.00 (3)	2.8432 (18)	173 (3)
O9—H92···O7^{ix}	0.80 (3)	2.08 (3)	2.8531 (17)	162 (2)

Symmetry codes: (iii) *x*, *y*, *z*+1; (iv) -*x*+1, -*y*+2, -*z*+1; (v) *x*, *y*, *z*-1; (vi) -*x*, -*y*+1, -*z*; (vii) -*x*, -*y*+1, -*z*+1; (viii) *x*+1, *y*+1, *z*; (ix) -*x*+1, -*y*+2, -*z*.

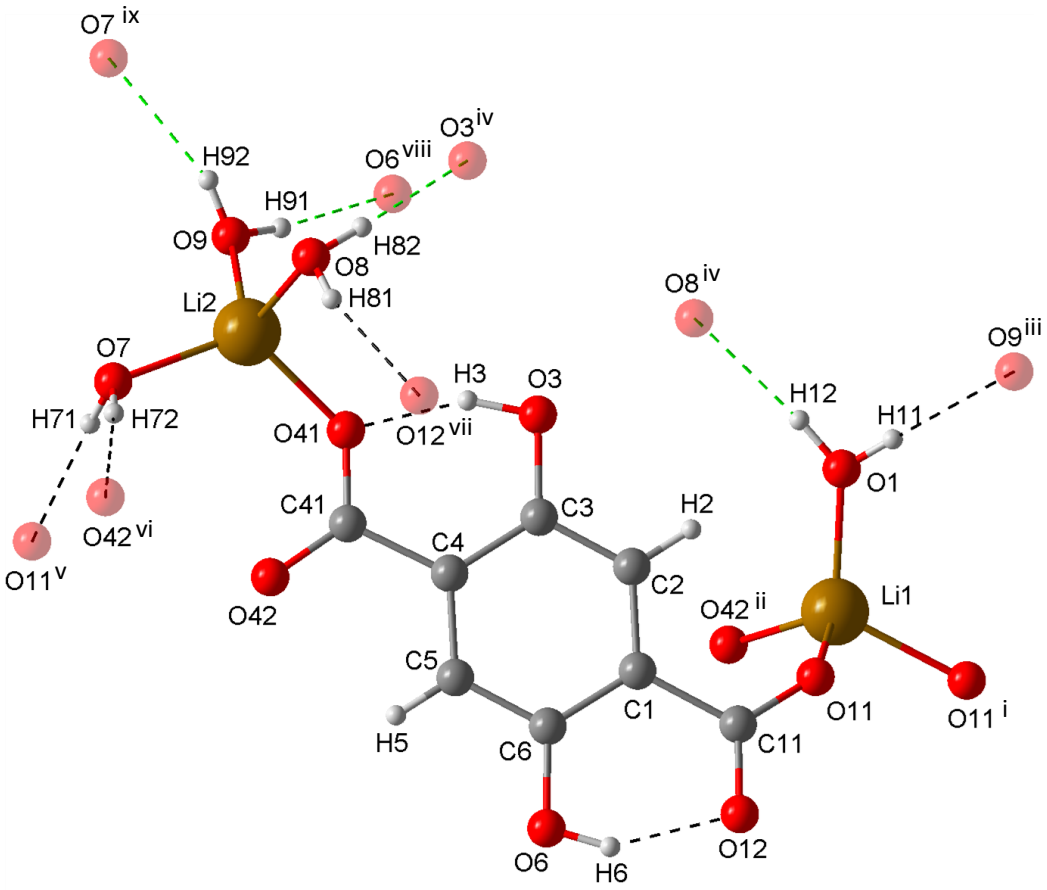


Figure S3. Structure of **2** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers. Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*, *y*, *z*+1; (iv) -*x*+1, -*y*+2, -*z*+1; (v) *x*, *y*, *z*-1; (vi) -*x*, -*y*+1, -*z*; (vii) -*x*, -*y*+1, -*z*+1; (viii) *x*+1, *y*+1, *z*; (ix) -*x*+1, -*y*+2, -*z*.

Table S4. Hydrogen-bond geometry (Å, º) for **3**.

O—H···*O*	*O*—H	H···*O*	*O*···*O*	*O*—H···*O*
O2*A*—H2*A*···O11*A*	0.84 (4)	1.71 (3)	2.487 (2)	155 (3)
O5*A*—H5*A*···O42*A*	0.89 (4)	1.64 (4)	2.476 (2)	156 (3)
O1*A*—H11*A*···O12*B*^{xi}	0.79 (3)	2.12 (3)	2.852 (2)	156 (3)
O3*A*—H31*A*···O12*B*^{xi}	0.93 (4)	1.92 (4)	2.826 (3)	166 (3)
O3*A*—H32*A*···O4*A*^{ix}	0.88 (4)	1.98 (4)	2.856 (3)	177 (4)
O4*A*—H41*A*···O4*B*^{xii}	0.90 (4)	1.79 (4)	2.692 (2)	177 (4)
O4*A*—H42*A*···O41*B*^{iii}	0.87 (4)	1.93 (4)	2.722 (2)	151 (3)
O6*A*—H61*A*···O41*B*^{v}	0.77 (3)	2.21 (3)	2.933 (2)	155 (3)
O6*A*—H62*A*···O41*A*	0.79 (3)	1.95 (4)	2.730 (2)	169 (3)
O2*B*—H2*B*···O11*B*	0.84 (3)	1.70 (3)	2.492 (2)	156 (3)
O5*B*—H5*B*···O42*B*	0.84 (4)	1.68 (3)	2.469 (2)	156 (3)
O1*B*—H11*B*···O12*A*^{iv}	0.77 (3)	2.09 (3)	2.840 (2)	165 (3)
O3*B*—H31*B*···O3*A*^{xiii}	0.93 (4)	1.76 (4)	2.687 (3)	174 (4)
O3*B*—H32*B*···O41*A*^{v}	0.87 (4)	1.93 (4)	2.710 (2)	149 (3)
O4*B*—H41*B*···O3*B*^{i}	0.91 (5)	1.95 (5)	2.852 (3)	174 (4)
O4*B*—H42*B*···O12*A*^{iv}	0.88 (4)	1.98 (4)	2.841 (3)	166 (4)
O6*B*—H61*B*···O41*A*^{v}	0.78 (3)	2.25 (3)	2.956 (2)	152 (3)
O6*B*—H62*B*···O12*B*^{xiv}	0.83 (4)	1.94 (4)	2.756 (2)	168 (3)

Symmetry codes: (i) *x*+1, *y*, *z*; (iii) -*x*+1, -*y*, -*z*+1; (iv) *x*, *y*-1, *z*; (v) -*x*, -*y*, -*z*+1; (ix) *x*-1, *y*, *z*; (xi) *x*, *y*-1, *z*-1; (xii) -*x*+1, -*y*-1, -*z*+1; (xiii) -*x*, -*y*-1, -*z*+1; (xiv) -*x*, -*y*+1, -*z*+2.

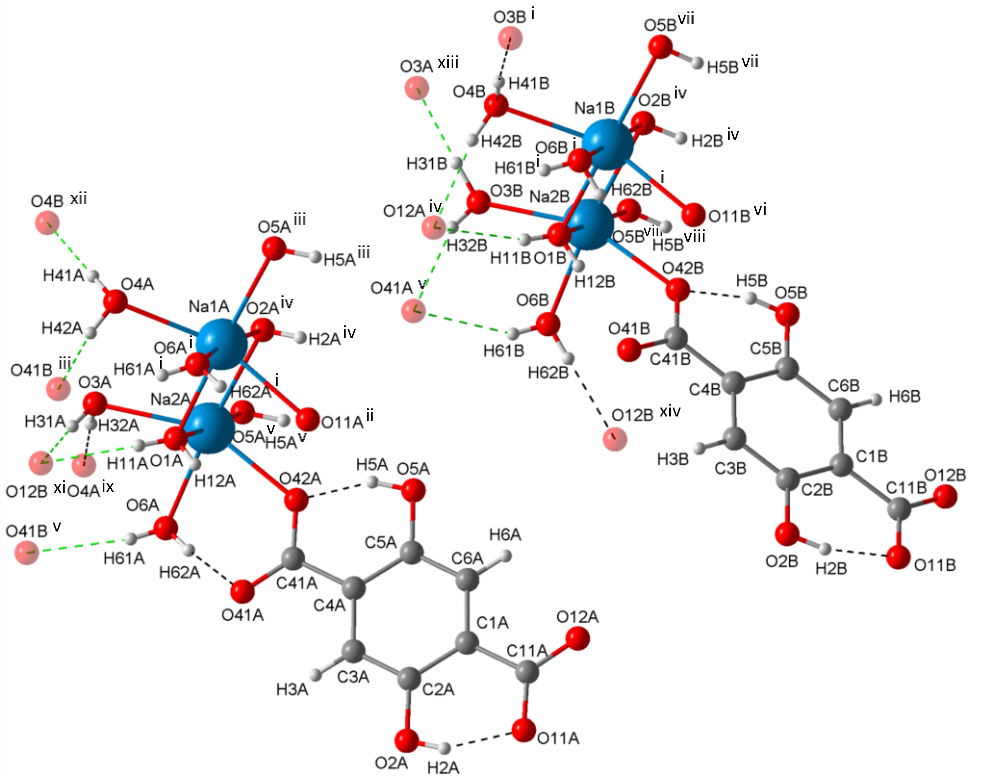


Figure S4. Structure of **3** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers. Symmetry codes: (i) *x*+1, *y*, *z*; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*, -*z*+1; (iv) *x*, *y*-1, *z*; (v) -*x*, -*y*, -*z*+1; (vi) -*x*+1, -*y*+1, -*z*+2; (vii) -*x*+1, -*y*, -*z*+2; (viii) -*x*, -*y*, -*z*+2; (ix) *x*-1, *y*, *z*; (xi) *x*, *y*-1, *z*-1; (xii) -*x*+1, -*y*-1, -*z*+1; (xiii) -*x*, -*y*-1, -*z*+1; (xiv) -*x*, -*y*+1, -*z*+2.

Table S5. Hydrogen-bond geometry (Å, º) for **4**.

O—H···*O*	*O*—H	H···*O*	*O*···*O*	*O*—H···*O*
O1—H11···O5^{v}	0.811 (19)	2.068 (19)	2.8583 (13)	164.7 (17)
O1—H12···O3^{vi}	0.869 (18)	1.855 (18)	2.7214 (11)	174.8 (17)
O4—H41···O3^{vii}	0.84 (2)	2.03 (2)	2.8625 (13)	171.1 (19)
O4—H42···O2^{vii}	0.82 (2)	1.96 (2)	2.7800 (13)	176.5 (18)
O5—H51···O3^{viii}	0.84 (2)	1.86 (2)	2.7042 (12)	177.8 (19)
O5—H52···O11^{ix}	0.843 (19)	2.11 (2)	2.9432 (13)	169.8 (17)

Symmetry codes: (v) *x*, *y*, *z*+1; (vi) *x*-1, *y*, *z*+1; (vii) -*x*+2, -*y*+1, -*z*+1; (viii) -*x*+2, -*y*, -*z*; (ix) -*x*+1, -*y*, -*z*+1.

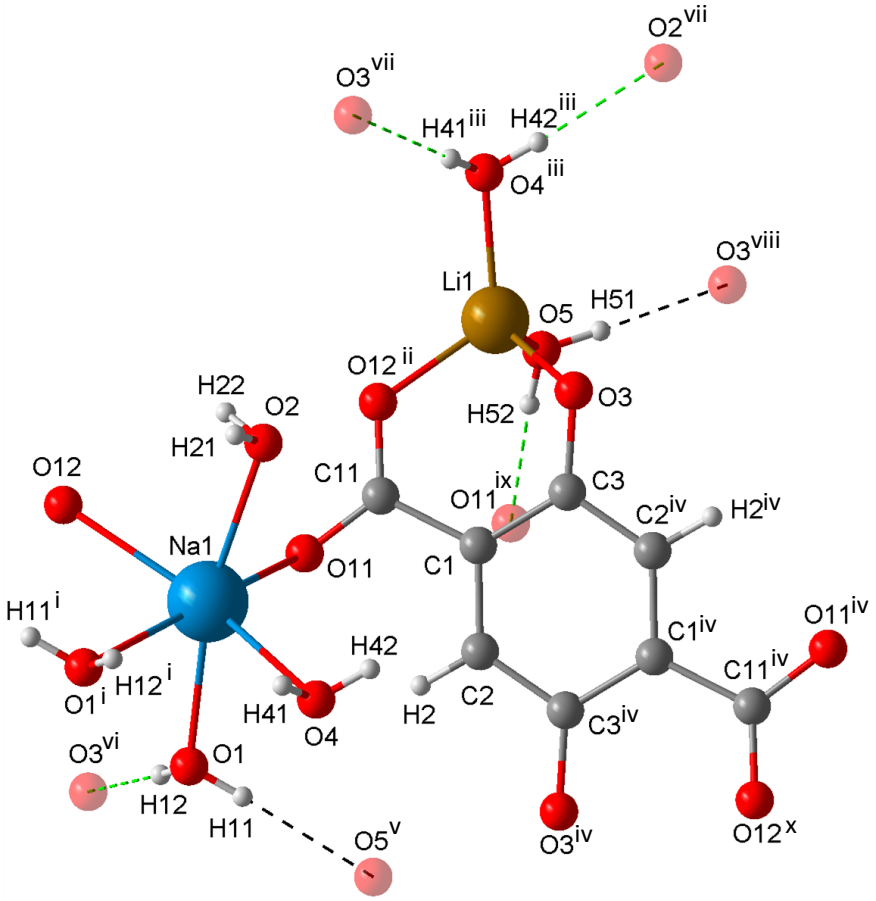
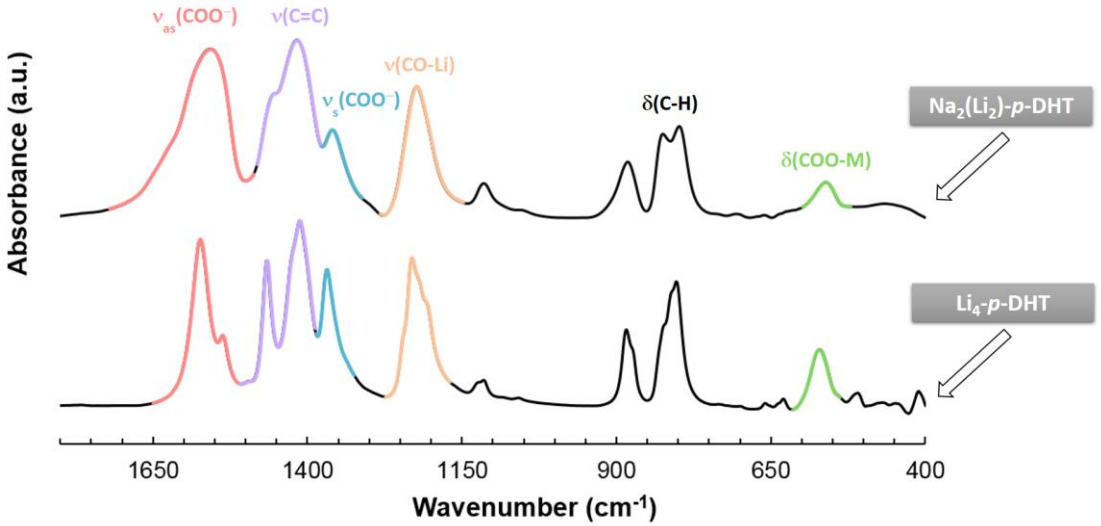


Figure S5. Structure of **4** with hydrogen bonds in dashed lines, in green, H-bonds between 2-D layers. Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*, *y*, *z*-1; (iv) -*x*+2, -*y*, -*z*+1; (v) *x*, *y*, *z*+1; (vi) *x*-1, *y*, *z*+1; (vii) -*x*+2, -*y*+1, -*z*+1; (viii) -*x*+2, -*y*, -*z*; (ix) -*x*+1, -*y*, -*z*+1; (x) *x*+1, *y*-1, *z*.

Figure S6. Photographs of crystals (compounds **1**, **3** and **4**) obtained after a slow evaporation process at room temperature (24°C).



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