Supplementary Information

Coordination Environments and π-Conjugation in Dense Lithium Coordination Polymers

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Contents

1. Experimental details

Single crystal diffraction measurements

The crystal structure was determined by single crystal diffractometry using an Oxford Diffraction Gemini A Ultra X-ray diffractometer with Cu Kα radiation (λ = 1.54184 Å) operated at 40 kV and 40 mA for **1**–**4**, and Mo Kα radiation (λ = 0.71069 Å) operated at 50 kV and 40 mA for **5** and **6**. Data were collected under atmospheric conditions and 120K under nitrogen flow. Data collection, unit cell determination and refinement, absorption correction and data reduction were performed using the CrysAlisPro software from Agilent Technologies, except for the room temperature data of compounds **5** and **6**, which were collected by the National Crystallography Service and corrected using the CrystalClear program from Rigaku. An analytical absorption correction was performed by applying a face-based absorption correction as well as a spherical absorption correction.

Other analyses

Thermogravimetric analysis and differential scanning calorimetry were performed simultaneously using a TA Instruments Q600 SDT instrument with an air flow of 100 mL min^{-1} at a heating rate of 5 °C min^{-1}, from room temperature to 600°C. It was found that anthraquinone derivatives themselves decomposed exothermically around 400°C (Fig. S1-S4†). The lithium anthraquinone derivative hybrids show similar decomposition temperatures.

Powder X-ray diffraction (PXRD) was carried out using a Bruker-AXS D8 diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a LynxEye position sensitive detector in the Bragg-Brentano geometry. The samples were prepared by gently grinding the crystals gently using a mortar and pestle for 30 sec. Data were collected in the 2θ range of 5–60° at room temperature. The patterns were analyzed by the Pawley method using the GSAS-II software (Fig. S5 and Table S1†),[1] and plotted with zero-shift correction and background subtraction. Except for compound **2**, all of the compounds are confirmed to be phase pure.

The diffuse reflectance spectra were obtained using a PerkinElmer Lambda 750 spectrometer with an integrating sphere detector in the wavelength range of 2500 to 220 nm. The powder samples for this measurement were diluted to 5–20 wt% with dry $BaSO_4$ powder. The raw diffuse reflectance spectra were converted into the Kubelka−Munk (K-M) function, and then they were normalized by the concentrations, which were calculated from volume fractions, densities and formula weights. Regarding the pure linker molecules, the densities of 1.53 (14dhaq), 1.59 (15dhaq) and 1.86 g cm^{-3} (anthraquinone) are used from the Cambridge database (CCDC no. 106210, CSD no. DHANTQ02 and CSD no. ANTQUO08), and 1.60 g cm^{-3} is assumed for aqdc.

The structure of 2,3-dicarboxyanthraquinone could not be solved by single crystal diffraction and so with no available crystallographic information, we optimized the structure by density functional theory (DFT) using the CASTEP code[2] with the Perdew, Burke and Ernzerhof (PBE) functional[3] of a generalized gradient approximation (GGA). An initial structure of a molecule located in a cubic unit cell (a = 15 Å) was built using the Materials Studio program and simulated using the CASTEP code.

2. Thermogravimetric analysis

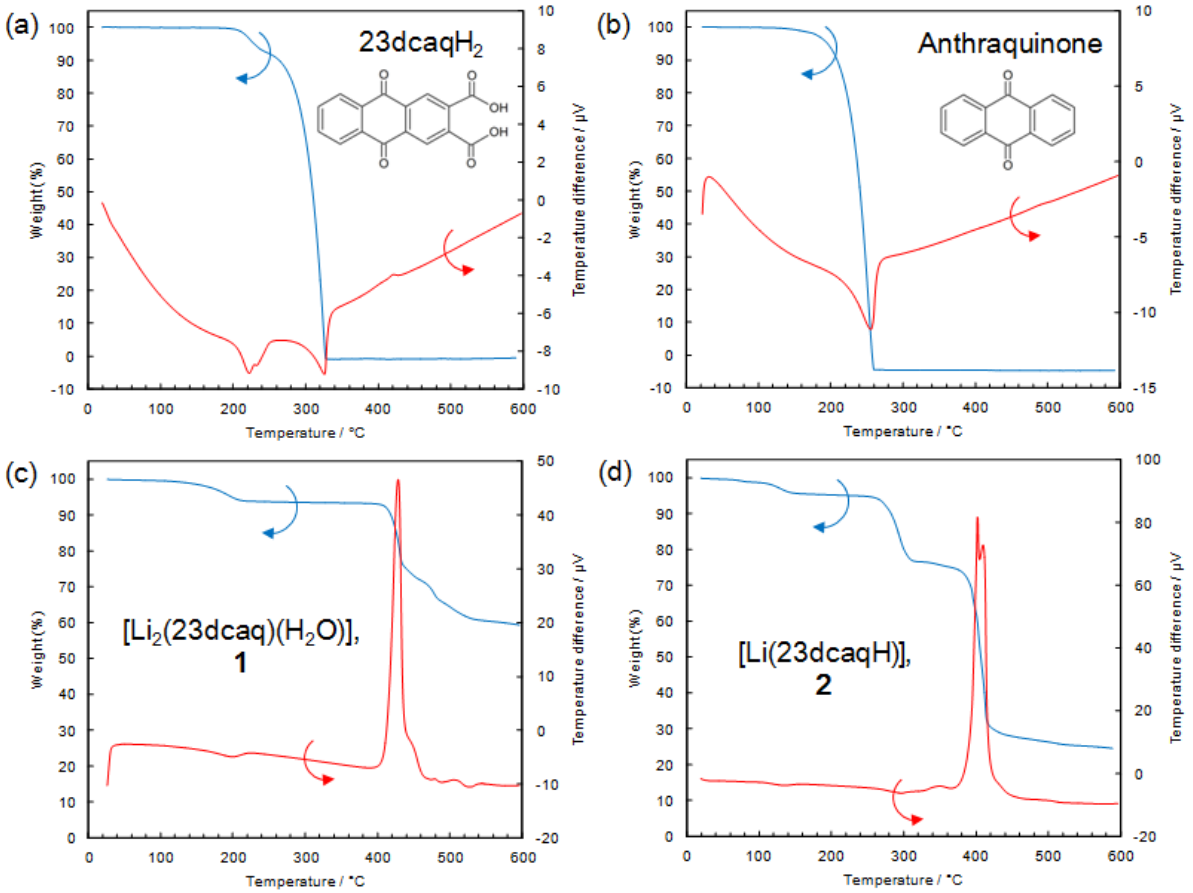

Fig. S1 Simultaneous differential scanning calorimetry (DSC)-thermogravimetric analysis (TGA) in air. (a) 23dcaqH_2. (b) Anthraquinone. (c) Compound **1**. (b) Compound **2**.

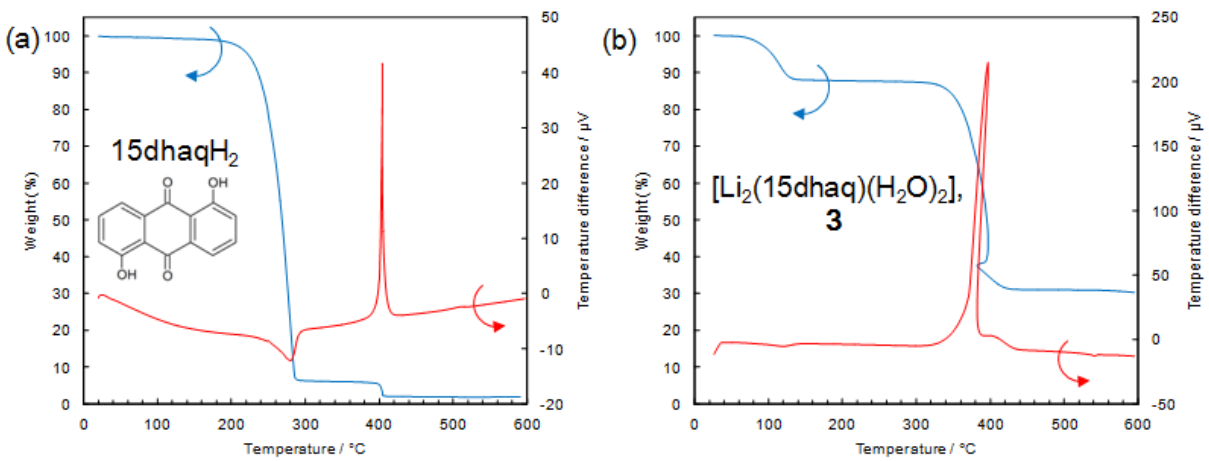

Fig. S2 DSC-TGA in air. (a) 15dhaqH_2. (b) Compound **3**.

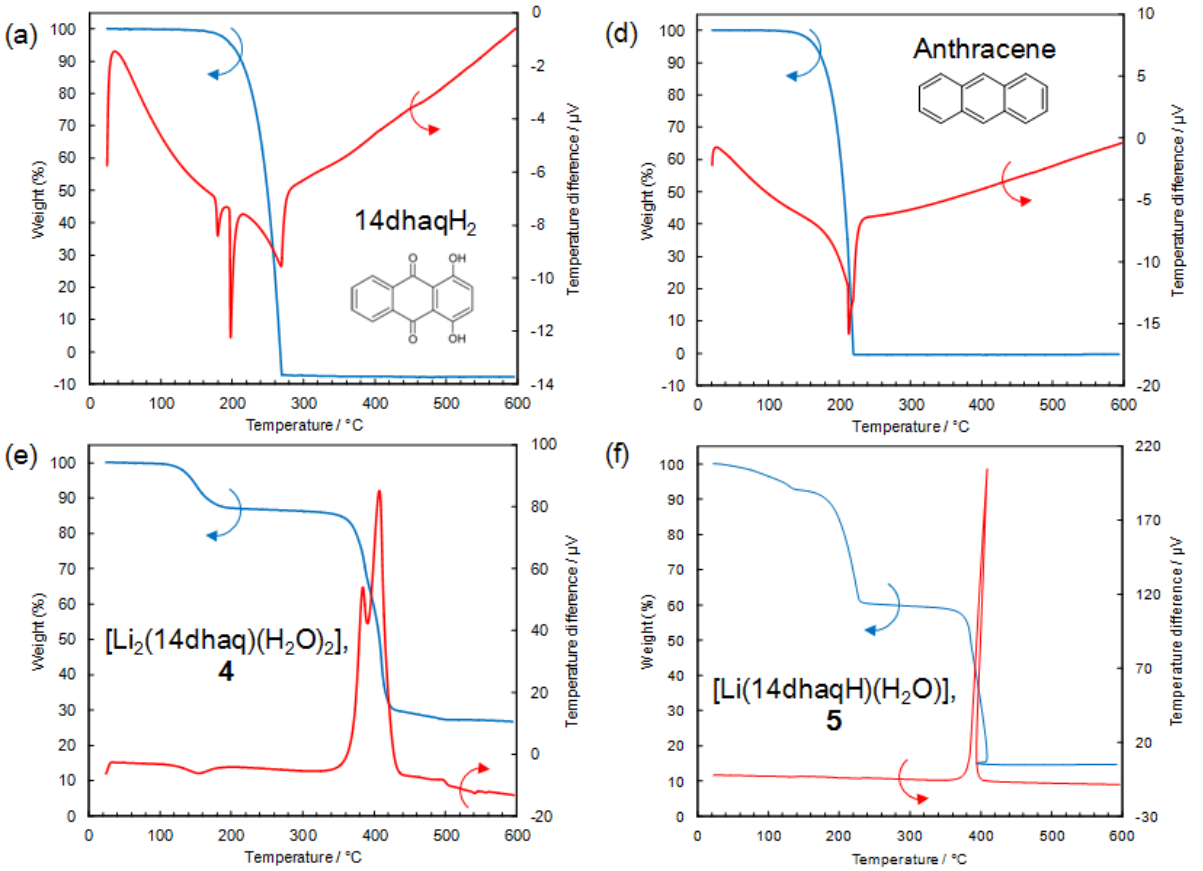

Fig. S3 DSC-TGA in air. (a) 14dhaqH_2. (b) Anthracene. (c) Compound **4**. (d) Compound **5**.

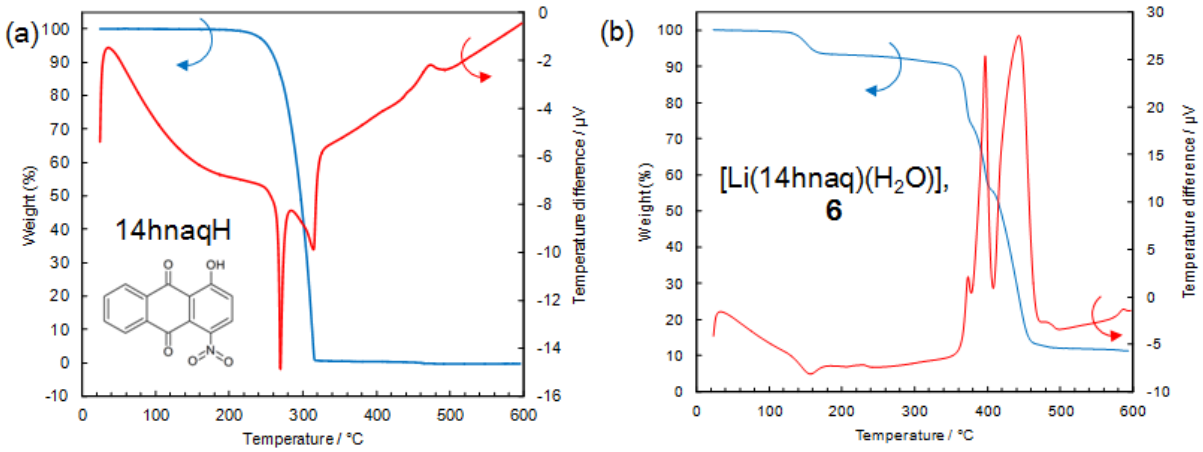

Fig. S4 DSC-TGA in air. (a) 14hnaqH. (b) Compound **6**.

3. Powder X-ray diffraction data

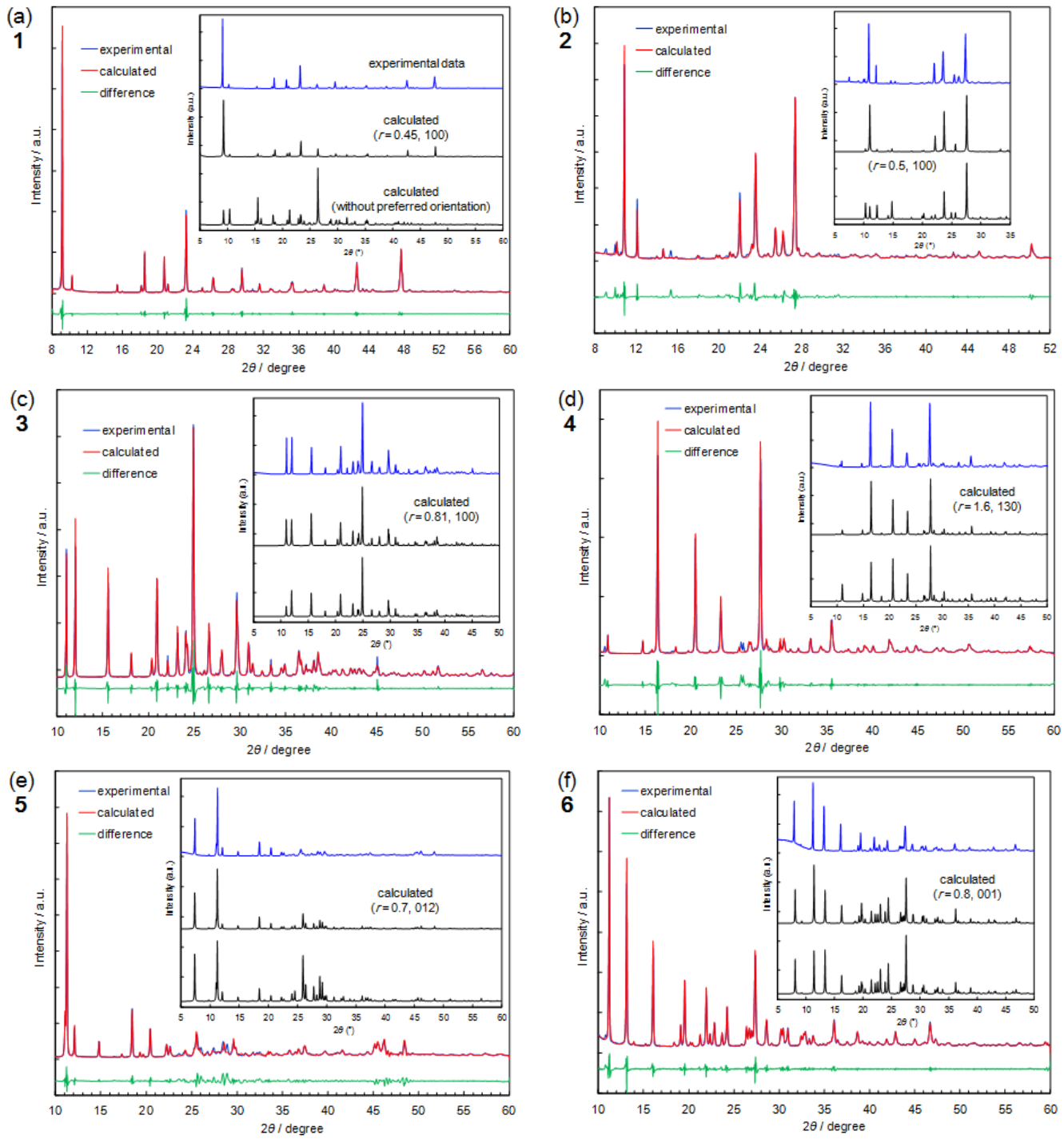

Fig. S5 Powder X-ray patterns of (a) Compound **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**. The experimental data (blue curves) are fitted with the data simulated by the Pawley method (red curves) using the GSASII program[1]. Inset: the presence of preferred orientation was simulated using the March-Dollase formula with the Mercury program[4].

Table S1 Lattice constants obtained by the Pawley fitting of PXRD data obtained at room temperature.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula [a]	$[Li_2(23dcaq)(H_2O)]$	[Li(23dcaqH)]	$[Li_2(15dhaq)(H_2O)_2]$	$[Li_2(14dhaq)(H_2O)_2]$	[Li(14dhaqH)(H_2O)]	[Li(14hnaq)(H_2O)]
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	*Pnma*	$P2_12_12_1$	$P2_12_12_1$
a / Å	19.0773(2)	8.164896(82)	8.055738(183)	7.147473(31)	3.689834(126)	4.891781(142)
b / Å	9.48840(25)	10.663485(220)	5.180540(121)	16.046487(421)	16.218389(398)	13.265583(252)
c / Å	7.46618(25)	14.685145(290)	14.802469(299)	10.717791(45)	18.271770(395)	19.087416(404)
α (°)	90	90	90	90	90	90
β (°)	94.7112(48)	101.5625(42)	94.9587(50)	90	90	90
γ (°)	90	90	90	90	90	90
V / Å^3	1346.91(6)	1252.63(4)	615.44(2)	1229.24(3)	1093.44(5)	1238.63(5)
wR (%) [b]	10.95	13.77	12.53	15.13	13.12	6.48

[a] "23dcaq^{2-}" is 2,3-dicarboxyanthraquinone anion ($C_{16}H_6O_6^{2-}$), "15dhaq^{2-}" is 1,5-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), "14dhaq^{2-}" is 1,4-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), and "14hnaq^{1-}" is 1-hydroxy-4-nitroanthraquinone anion ($C_{16}H_6O_5N^-$). [b] *wR* is weighted reliability factors with background.

4. FTIR data

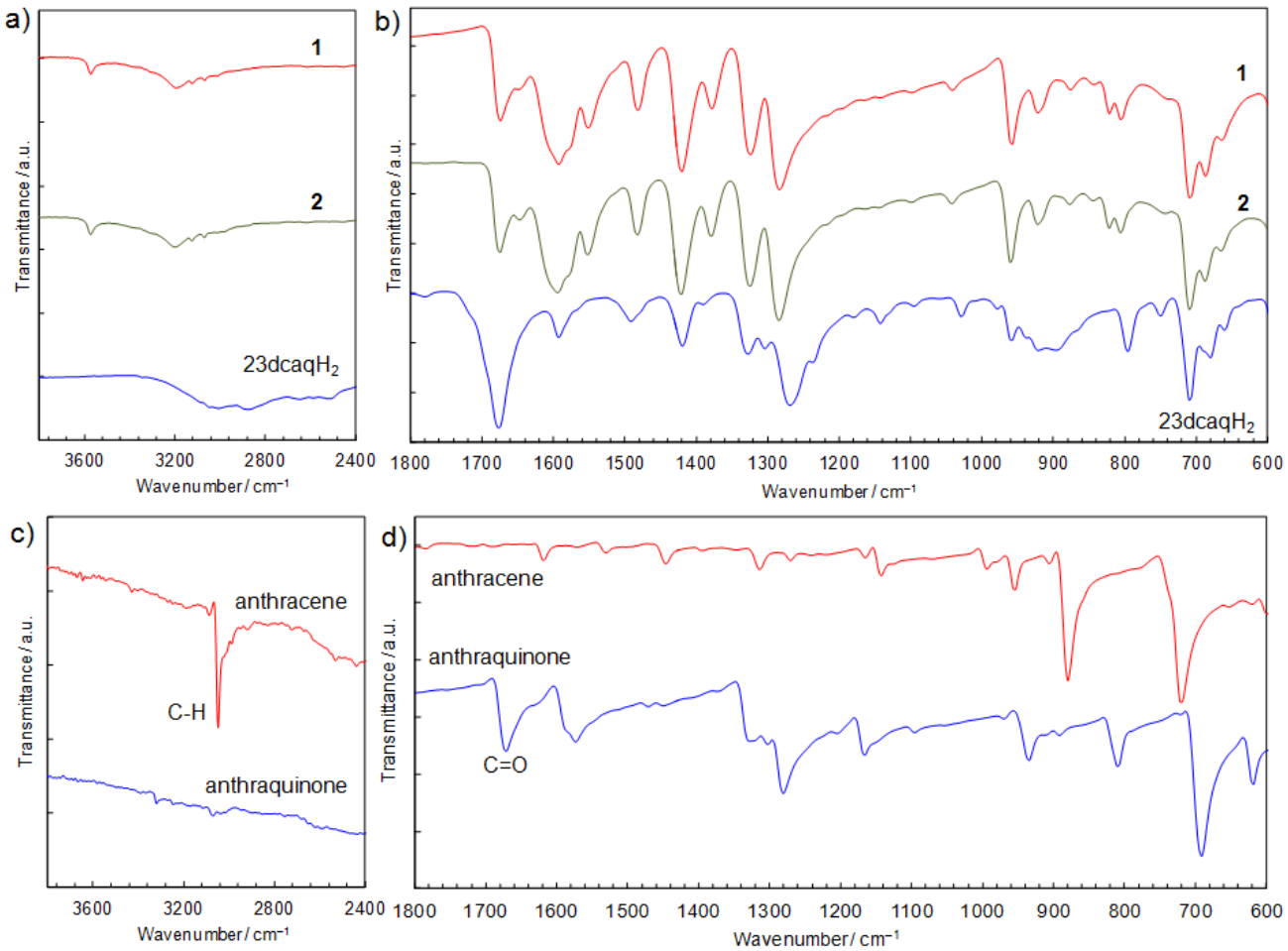

Fig. S6 FTIR spectra. (a, b) **1**, **2** and protonated linker, 23dcaqH_2. (c, d) Anthraquinone and anthracene. The spectra of **1** and **2** are identical, suggesting hydration of **2** to form **1**, especially at the surface in the range where the ATR method can detect the signals from molecules.

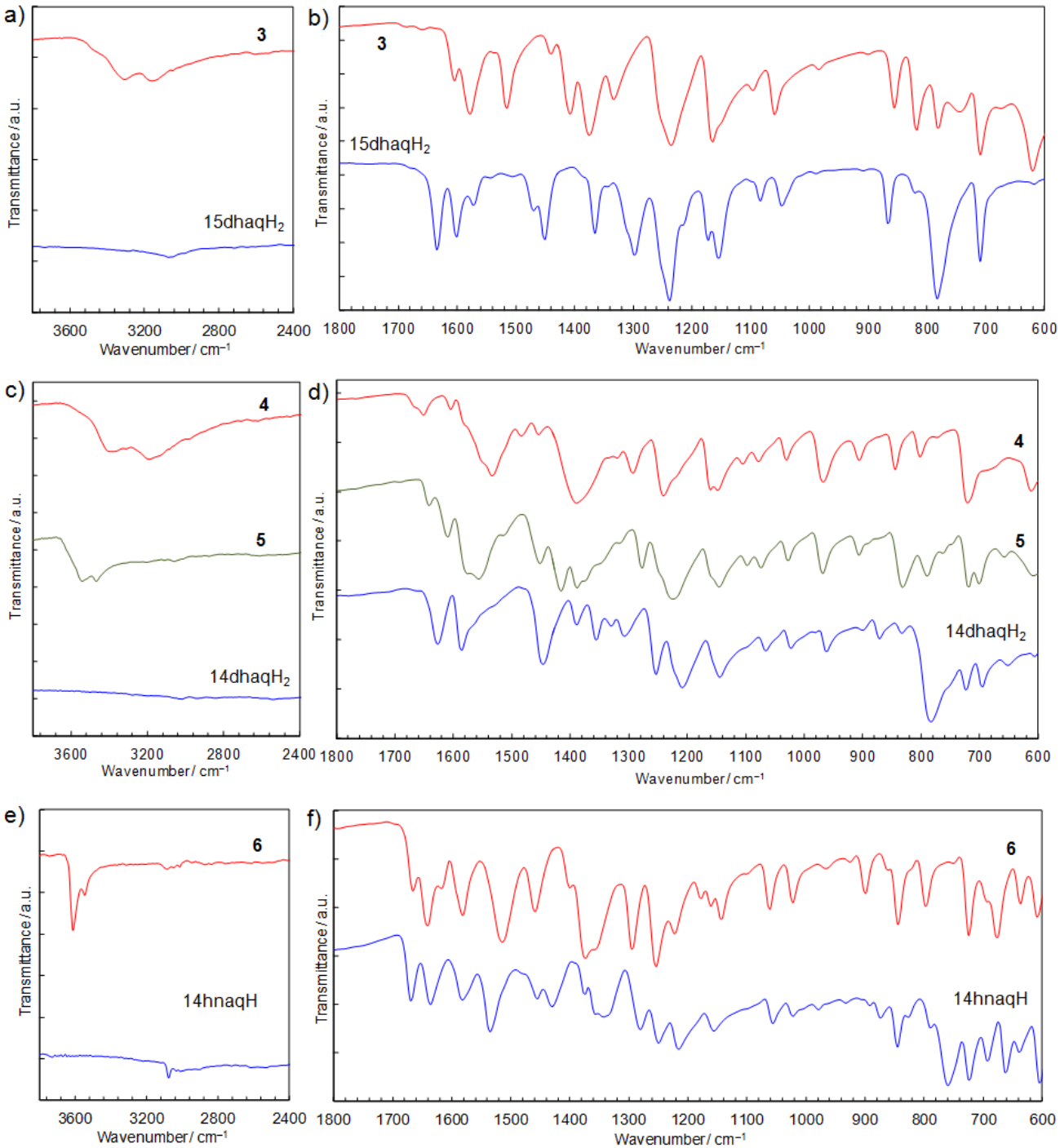

Fig. S7 FTIR spectra. (a, b) **3** and protonated linker, 15dhaqH_2. (c, d) **4**, **5** and protonated linker, 14dhaqH_2. (e, f) **6** and protonated linker, 14hnaqH.

5. Structure data obtained by single crystal diffraction at 120 K and room temperature

Table S2 Summary of crystal data for lithium anthraquinone-derivative hybrids at 120 K.

Compound	1	2	3	4	5	6
Formula [a]	$[Li_2(23dcaq)(H_2O)]$	[Li(23dcaqH)]	$[Li_2(15dhaq)(H_2O)_2]$	$[Li_2(14dhaq)(H_2O)_2]$	$[Li(14dhaqH)(H_2O)]$	$[Li(14hnaq)(H_2O)]$
Formula weight / g	326.10	302.16	288.10	288.10	264.15	293.15
Asymmetric unit	$Li_2C_{16}H_8O_7$	$LiC_{16}H_7O_6$	$LiC_7H_5O_3$	$LiC_7H_5O_3$	$LiC_{14}H_9O_5$	$LiC_{14}H_8O_6N$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pnma$	$P2_12_12_1$	$P2_12_12_1$
a / Å	18.9997(7)	8.07990(18)	8.0703(3)	7.1641(3)	3.8011(2)	4.8535(3)
b / Å	9.4546(3)	10.64630(18)	5.14969(18)	16.1044(9)	15.9753(11)	13.0952(10)
c / Å	7.4275(3)	14.6639(3)	14.7759(5)	10.7351(7)	18.0272(9)	18.9644(12)
α (°)	90	90	90	90	90	90
β (°)	95.743(4)	102.507(2)	95.073(3)	90	90	90
γ (°)	90	90	90	90	90	90
V / Å^3	1327.55(9)	1231.47(4)	611.67(4)	1238.53(11)	1094.68(11)	1205.33(14)
Density / g cm^{-3}	1.632	1.630	1.564	1.545	1.603	1.615
Z	4	4	4	8	4	4
R_1 (%), wR_2 (%)	4.41, 11.93	3.27, 9.38	2.94, 8.12	5.51, 13.75	5.72, 14.88	4.66, 12.85
GOF	1.038	1.093	1.040	1.035	1.049	1.071
Temperature / K	120	120	121	122	120	120

[a] "23dcaq^{2-}" is 2,3-dicarboxyanthraquinone anion ($C_{16}H_6O_6^{2-}$), "15dhaq^{2-}" is 1,5-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), "14dhaq^{2-}" is 1,4-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), and "14hnaq^{1-}" is 1-hydroxy-4-nitroanthraquinone anion ($C_{16}H_6O_5N^-$).

Table S3 Summary of crystal data and structural information for lithium anthraquinone-derivative hybrids at room temperature.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula [a]	$[Li_2(23dcaq)(H_2O)]$	$[Li(23dcaqH)]$	$[Li_2(15dhaq)(H_2O)_2]$	$[Li_2(14dhaq)(H_2O)_2]$	$[Li(14dhaqH)(H_2O)]$[g]	$[Li(14hnaq)(H_2O)]$
Formula weight / g	326.10	302.16	288.10	288.10	264.15	293.15
Asymmetric unit	$Li_2C_{16}H_8O_7$	$LiC_{16}H_7O_6$	$LiC_7H_5O_3$	$LiC_7H_5O_3$	$LiC_{14}H_9O_5$	$LiC_{14}H_8O_6N$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pnma$	$P2_12_12_1$	$P2_12_12_1$
a / Å	19.0868(8)	8.1681(4)	8.0719(3)	7.1681(3)	3.6746(2)	4.8953(4)
b / Å	9.4849(4)	10.6558(5)	5.18214(18)	16.0902(6)	16.1112(11)	13.2668(10)
c / Å	7.4588(3)	14.7002(7)	14.8188(5)	10.7456(6)	18.1111(14)	19.1081(14)
α (°)	90	90	90	90	90	90
β (°)	94.757(4)	101.680(5)	94.926(3)	90	90	90
γ (°)	90	90	90	90	90	90
V / Å^3	1345.66(10)	1252.97(10)	617.57(4)	1239.37(9)	1072.22(13)	1240.97(17)
Density / g cm^{-3}	1.610	1.591	1.549	1.544	1.545	1.569
Z	4	4	4	8	4	4
R_1 (%), wR_2 (%)	3.40, 9.74	3.49, 9.93	3.40, 10.17	5.28, 13.05	8.29, 21.68	7.00, 17.45
GOF	1.040	1.036	1.097	1.046	1.065	1.080
Dimensionality [b]	I^0O^2	I^0O^2	I^0O^1	I^0O^1	I^1O^0	I^1O^0
Polyhedra connectivity [c]	Li1: $C^0E^1F^0$ Li2: $C^0E^2F^0$	Li1: $C^0E^0F^0$	Li1: $C^0E^1F^0$	Li1: $C^0E^1F^0$	Li1: $C^2E^0F^0$	Li1: $C^2E^0F^0$
ECoN [d]	Li1: 3.92 Li2: 4.38	Li1: 3.90	Li1: 3.94	Li1: 3.98	Li1: 4.19	Li1: 3.98
δ_{tet} [e]	Li1: 10.9(7) Li2: 16.5(4)	Li1: 9.0(9)	Li1: 13.4(5)	Li1: 13.9(1)	Li1: 13(2)	Li1: 13(2)
Coordination environment [f]	Li1: $C^2K^1W^1$ Li2: C^4W^1	Li: C^3K^1	Li: $K^2P^1W^1$	Li: $K^2P^1W^1$	Li: $K^1P^3W^1$	Li: $K^1P^2W^1$
Selected π–π distance / Å (centroid to centroid of rings)	A–A: 3.729 A–B: 3.810	A–A: 3.686 A–B: 3.857	A–B: 3.734 A–C: 3.648	A–C: 3.566	A–B: 3.420 B–C: 3.551	A–B: 3.592 B–C: 3.643

[a] "23dcaq^{2-}" is 2,3-dicarboxyanthraquinone anion ($C_{16}H_6O_6^{2-}$), "15dhaq^{2-}" is 1,5-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), "14dhaq^{2-}" is 1,4-dihydroxyanthraquinone anion ($C_{16}H_6O_4^{2-}$), and "14hnaq^{1-}" is 1-hydroxy-4-nitroanthraquinone anion ($C_{16}H_6O_5N^-$).
[b] Inorganic connectivity, I^n, where M–X–M bonds extend the structure, and organic connectivity, O^m, where M–ligand–M extend the structure.
[c] Numbers of corner sharing (C^x), edge sharing (E^y) and face sharing (F^z) polyhedra.
[d] Effective coordination number (ECoN) defined as summation of the bond weight.[5]
[e] Tetrahedral distortion defined as root mean squared deviation from the ideal tetrahedral angle.[6] Where a Li atom is more than 4-coordinate, only the O atoms from the shortest four Li-O bonds have been included.
[f] Numbers of oxygen atoms coming from carboxylate (C^w), keto- (K^x), water (W^y) and phenoxide (P^z) groups.
[g] The structure determined at room temperature has disorder on the H_2O site, and we used occupancy of 0.21. This is probably due to the dehydration temperature (Fig. S3). Since the structure determined at 120 K does not have this, we call this structure as $[Li(14dhaqH)(H_2O)]$.

6. Structure data of selected LCPs

Table S4 Summary of crystallographic and structural information for typical lithium organic frameworks at room temperature.

Compound	Lithium formate anhydrous	Lithium formate monohydrate	Lithium acetate dihydrate	Dilithium oxalate	Dilithium malonate	Dilithium terephthalate	Dilithium squarate	Dilithium carbonate
Formula	$[Li(HCO_2)]$	$[Li(HCO_2)(H_2O)]$	$[Li(CH_3CO_2)(H_2O)_2]$	$[Li_2(C_2O_4)]$	$[Li_2(C_3H_2O_4)]$	$[Li_2(C_8O_4)]$	$[Li_2(C_4O_4)]$	$[Li_2(CO_3)]$
Space group	*C*2/*c*	*Cmmm*	*Cmmm*	$P2_1/n$	$P2_1/c$	$P2_1/c$	*C*2/*m*	*C*2/*c*
a / Å	12.0519(3)	6.483(4)	6.820(7)	3.400	7.232(2)	8.36	7.10733(28)	8.35884(12)
b / Å	12.0497(3)	9.973(7)	10.88(1)	5.156	7.041(1)	5.13	9.5627(4)	4.97375(6)
c / Å	13.5108(3)	4.847(5)	6.620(7)	9.055	9.085(2)	8.48	3.29733(11)	6.19377(8)
α (°)	90	90	90	90	90	90	90	90
β (°)	101.003(3)	90	90	95.6	114.53(2)	93.15	101.1050(26)	114.789(1)
γ (°)	90	90	90	90	90	90	90	90
V / Å^3	1925.98(9)	313.4(4)	491.2(9)	157.980	420.86(17)	363.131	219.908	233.78
Density / g cm^{-3}	1.434	1.483	1.339	2.142	1.830	1.628	1.902	2.099
ECoN [a]	4.00	3.99	3.75	3.89	3.85, 3.89	3.96	4.00	3.91
Coordination environment [b]	C^4	C^3W^1	C^2W^2	C^4	C^4	C^4	C^4	C^4
Li-O length / Å	1.92–1.96	C^3: 1.92, 1.94, 1.95 W^1 : 1.97	C^2: 1.90 W^2 : 2.05	1.94, 2.00, 2.03, 2.08	2.09, 1.96, 1.94, 1.93 1.95, 1.91, 1.91, 2.04	1.91, 1.98, 1.98, 1.98	1.95, 1.95, 1.96, 1.96	1.90, 1.94, 1.97, 2.03
Dimensionality [c]	I^3O^0	I^1O^0	I^0O^1	I^2O^1	I^3O^0	I^2O^1	I^1O^2	I^3O^0
Polyhedra connectivity [d]	$C^2E^1F^0$	$C^2E^0F^0$	$C^0E^1F^0$	$C^4E^2F^0$	$C^2E^1F^0$	$C^2E^1F^0$	$C^2E^1F^0$	$C^4E^1F^0$
δ_{tet} [e]	9.5(8), 10.1(7), 10.3(7), 11.3(6)	3.(2)	12.3(1)	20.06(2)	15.801(15), 11.45(3)	10.5(8)	10.860(8)	8(2)
Reference	This work	7	8	9	10	11	12	13

[a] Effective coordination number (ECoN) defined as summation of the bond weight.[5]
[b] Coordination numbers with carboxylate (C^α), squarate (C^α), carbonate (C^α) and water (W^δ).
[c] Inorganic connectivity, I^n, where M–X–M bonds extend the structure, and organic connectivity, O^m, where M–ligand–M extend the structure.
[d] Numbers of corner sharing (C^x), edge sharing (E^y) and face sharing (F^z) polyhedra.
[e] Tetrahedral distortion defined as root mean squared deviation from the ideal tetrahedral angle.[6]

Table S5 Summary of structural information for anhydrous lithium tartrate frameworks determined at 120 K.

Compound	Lithium hydrogen L-tartrate, **1**	Dilithium L-tartrate, **2**	Dilithium L-tartrate, **3**	Dilithium *meso*-tartrate, **4**	Dilithium D,L-tartrate, **5** [f]	Dilithium *meso*-tartrate, **6**	Dilithium *meso*-tartrate, **7**	Dilithium D,L-tartrate, **8**	Dilithium L-tartrate, **9**
Formula	[LiH(L-$C_4H_4O_6$)]	[Li_2(L-$C_4H_4O_6$)]	[Li_2(L-$C_4H_4O_6$)]	[Li_2(*meso*-$C_4H_4O_6$)]	[Li_2(D,L-$C_4H_4O_6$)]	[Li_2(*meso*-$C_4H_4O_6$)]	[Li_2(*meso*-$C_4H_4O_6$)]	[Li_2(D,L-$C_4H_4O_6$)]	[Li_2(L-$C_4H_4O_6$)]
Space group	$P2_1$	$P2_12_12_1$	$C222_1$	$P2_1/c$	$C2/c$	$P2_1/c$	Cc	$P2_1/c$	$C2$
ECoN [a]	4.0573	3.9604, 3.9909, 3.9408, 3.9945	3.9927	3.9383	3.9981, 3.9812/3.9695	3.9851	3.9935, 3.9416	3.9772, 3.9321	3.9567, 3.9684
Coordination environment [b]	C^3H^2	C^3H^1	C^3H^1	C^3H^1	C^3H^1	C^3H^1	C^3H^1	C^3H^1	C^3H^1
Li-O length / Å	C^3: 1.935-2.030 H^2: 1.940, 2.469	C^3: 1.890-1.970 H^1: 1.939-1.996	C^3: 1.918-1.957 H^1:1.929	C^3: 1.882-1.966 H^1:1.966	C^3: 1.897-1.956 H^1:1.953, 1.959	C^3: 1.908-1.958 H^1: 1.946	C^3: 1.932-2.013 H^1: 1.910, 1.941	C^3: 1.908-2.000 H^1: 1.933, 1.989	C^3: 1.886-1.986 H^1: 1.933, 1.947
Dimensionality [c]	I^0O^3	I^1O^2	I^1O^2	I^1O^2	I^1O^2	I^1O^2	I^1O^2	I^1O^2	I^1O^2
Polyhedra connectivity [d]	$C^0E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$	$C^2E^0F^0$
δ_{tet} [e]	9.5(11)	4(4), 7(3), 9(2), 6(3)	12.6(14)	13.3(14)	4(5), 5(4)/12(3)	5(2)	15.7(8), 14.0(9)	5(3), 8,5(15)	6.2(14), 5.6(15)
Reference	17	17	17	17	17	16	16	16	16

[a] Effective coordination number (ECoN) defined as summation of the bond weight.[5]
[b] Coordination numbers with carboxylate (C^x) and hydroxyl (H^y).
[c] Inorganic connectivity, I^n, where M–X–M bonds extend the structure, and organic connectivity, O^m, where M–ligand–M extend the structure.
[d] Numbers of corner sharing (C^x), edge sharing (E^y) and face sharing (F^z) polyhedra.
[e] Tetrahedral distortion defined as root mean squared deviation from the ideal tetrahedral angle.[6] Where a Li atom is more than 4-coordinate, only the O atoms from the shortest four Li-O bonds have been included.
[f] Disordered structure: where appropriate, values including the O atom of major and minor occupancy are separated by "/".

Table S6 Summary of structural information for hydrated lithium tartrate frameworks determined at 120 K. [f]

Compound	Dilithium D,L-tartrate dihydrate **10**	Dilithium *meso*-tartrate hemihydrate, **11**	Lithium hydrogen *meso*-tartrate monohydrate, **12**	Lithium hydrogen L-tartrate monohydrate, **13**	Dilithium D,L-tartrate trihydrate, **14**
Formula	$[Li(D,L\text{-}C_4H_4O_6)(H_2O)_2]$	$[Li_2(meso\text{-}C_4H_4O_6)(H_2)_{0.5}]$	$[LiH(meso\text{-}C_4H_4O_6)(H_2O)]$	$[LiH(L\text{-}C_4H_4O_6)(H_2O)]$	$[Li_2(D,L\text{-}C_4H_4O_6)(H_2O)]$
Space group	*P*-1	$C222_1$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
ECoN [a]	4.7905, 3.9064	3.9772, 3.9687	4.8534	4.9677, 4.6617	3.7940-4.8961
Coordination environment [b]	$C^2H^1W^2$, $C^2H^1W^1$	C^3H^1, $C^2H^1W^1$	$C^2H^1W^2$	$C^2H^2W^2$, $C^2H^2W^1$	$C^1H^0W^3$, $C^2H^2W^1$
Li-O length / Å	C^2: 1.855-2.017 H^1: 1.919, 2.193 W^1: 1.971 W^2: 1.999-2.052	C^3: 1.953-1.984 C^2: 1.918, 1.958 H^1: 1.920-1.949 W^1: 1.998	C^2: 2.102, 2.104 H^1:1.9677 W^2: 2.006, 2.054	C^2: 2.023-2.300 H^2:1.984-2.596 W^1: 2.053 W^2: 1.999-2.049	C^1: 1.918-1.937 C^2:1.984-2.146 H^2:2.032-2.101 W^1: 2.123-2.227 W^3: 1.913-2.099
Dimensionality [c]	I^0O^2	I^1O^2 Plus isolated Li dimers	I^1O^0	I^0O^1	I^0O^2
Polyhedra connectivity [d]	$C^1E^0F^0$	$C^1E^0F^0$, $C^2E^0F^0$	$C^0E^2F^0$	$C^0E^1F^0$	$C^1E^0F^0$
δ_{tet} [e]	17.3(4), 11.1(7)	15.0(8), 16.2(8)	18.8(3)	49.0(4), 34.9(7)	$C^1H^0W^3$: 5.6(13)-7.7(11), $C^2H^2W^1$: 22.5(3)-32.3(2)
Reference	17	17	17	17	17

[a] Effective coordination number (ECoN) defined as summation of the bond weight.[5]
[b] Coordination numbers with carboxylate (C^x) and hydroxyl (H^y).
[c] Inorganic connectivity, I^n, where M–X–M bonds extend the structure, and organic connectivity, O^m, where M–ligand–M extend the structure.
[d] Numbers of corner sharing (C^x), edge sharing (E^y) and face sharing (F^z) polyhedra.
[e] Tetrahedral distortion defined as root mean squared deviation from the ideal tetrahedral angle.[6] Where a Li atom is more than 4-coordinate, only the O atoms from the shortest four Li-O bonds have been included.
[f] Numbering scheme as used in Reference 15.

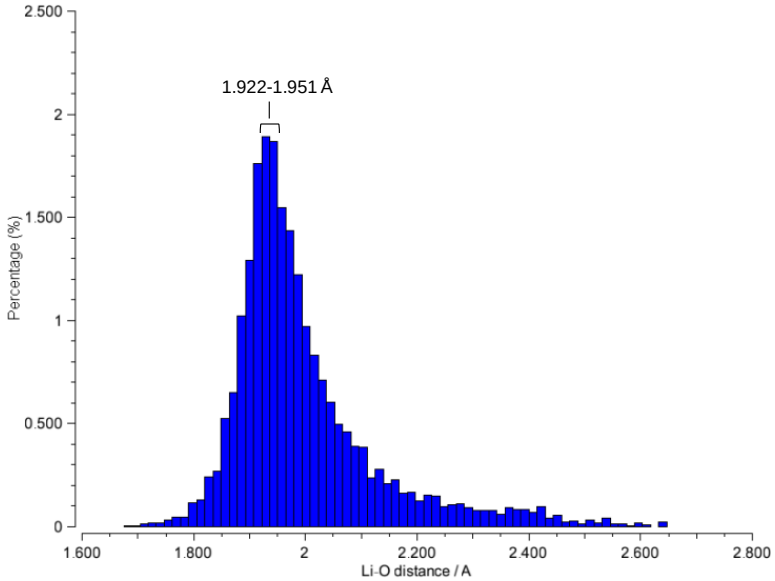

Fig. S8 Li-O bond lengths in structures determined at 270−300K (CCDC database).

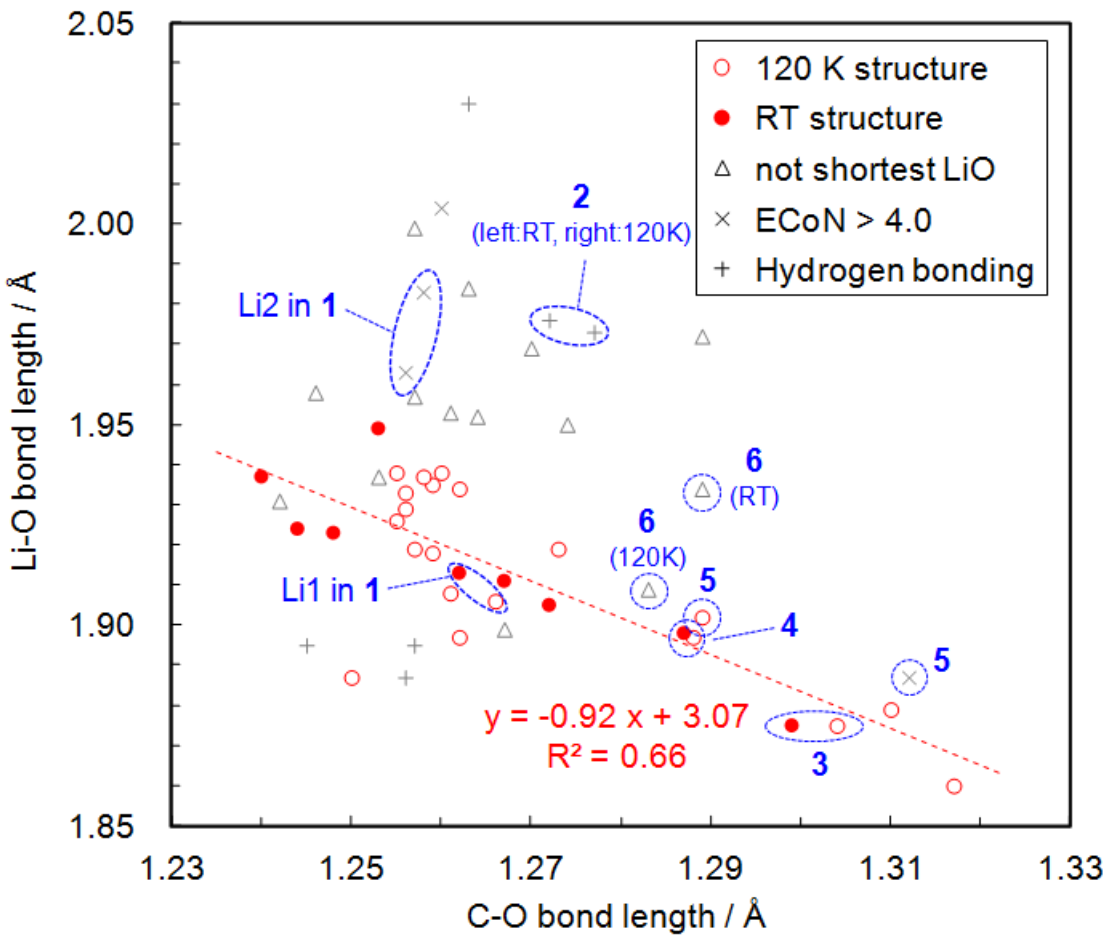

Fig. S9 The same plot shown in Figure 1 with the notation for the data of compounds **1**−**6**.

7. Coordination environments in reported MOFs containing the 23dcaq linker

There are five hybrid structures containing the 23dcaq linker.[14] Ca, Cd and Mn ions have similar coordination environments (Fig. S8a-f) and are coordinated by two oxygen atoms of a carboxylate group, and three oxygen atoms of three carboxylate groups and two water molecules ($C^5A^0W^2$). The oxygen atoms of the both carboxylate groups are not in the same plane as the anthraquinone molecule. Ni ions (Fig. S8g, h) are coordinated with an oxygen atom of a carboxylate group and five water molecules ($C^1A^0W^5$). The oxygen atoms of the both carboxylate groups are not in the same plane as the anthraquinone molecule. Zn ions are coordinated with two oxygen atoms of a carboxylate group, two oxygen atoms of two carboxylate groups and two water molecules ($C^4A^0W^2$). The oxygen atoms of one carboxylate group (C1, Fig S8i, j) are in the same plane as the anthraquinone molecule, while the oxygen atoms of the other carboxylate groups are not in the same plane. The C-C bond length between the former one and the anthraquinone part is shorter than for the other carboxylate, indicating partial double bonding between the two sp^2 carbon atoms.

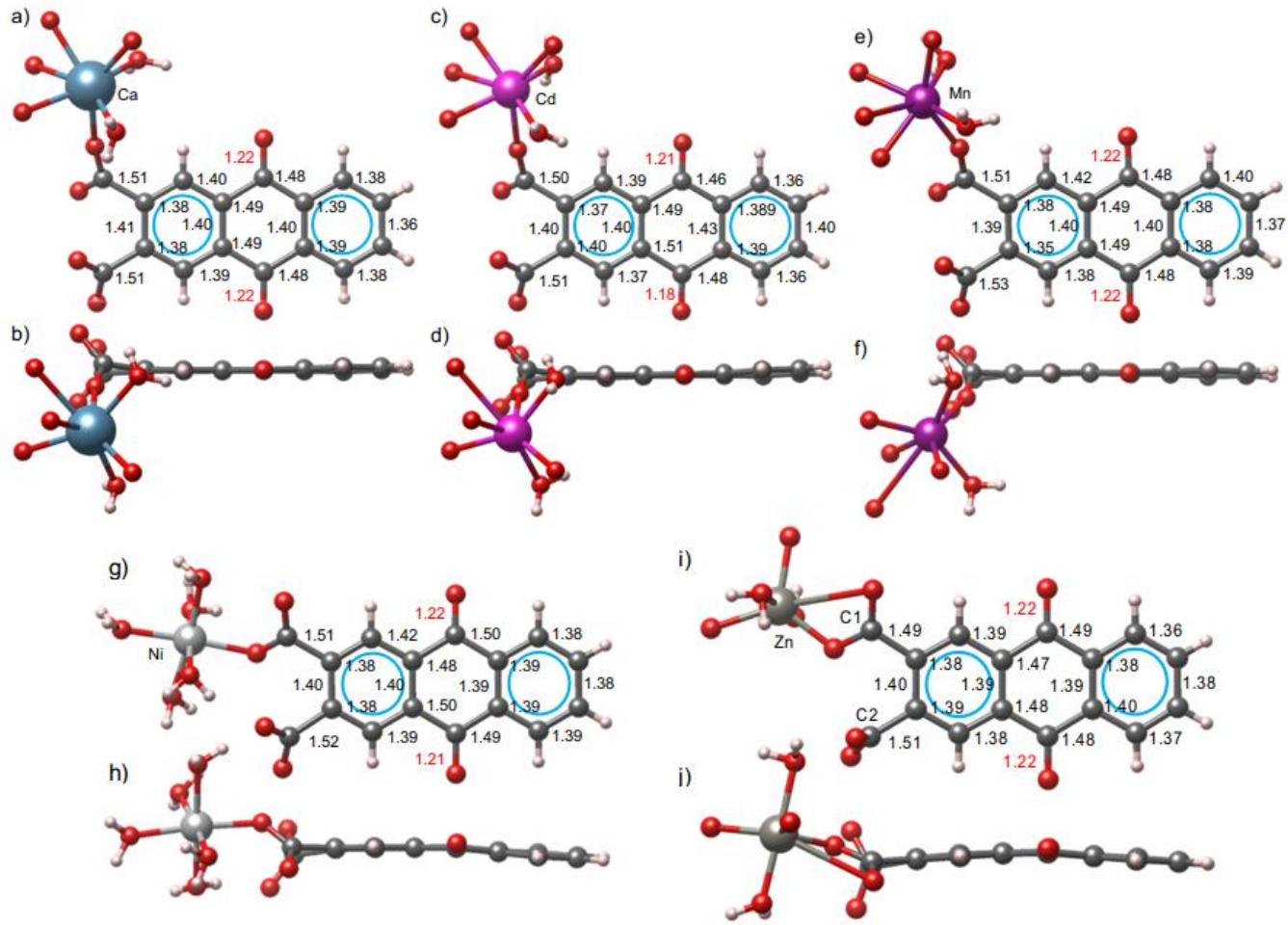

Fig. S10 Coordination environments and bond length of Ca(23dcaq) hydrate (a, b), Cd(23dcaq) hydrate (c, d), Mn(23dcaq) hydrate (e, f), Ni(23dcaq) hydrate (g, h) and Zn(23dcaq) hydrate (I, j) measured at 293K, reported in Journal of Materials Chemistry, 21, 6595-6601 (2011). The blue circles illustrate strong π-conjugation in C-C bonds close to the typical aromatic C-C bond of 1.39 Å.

8. Optical absorption measurements

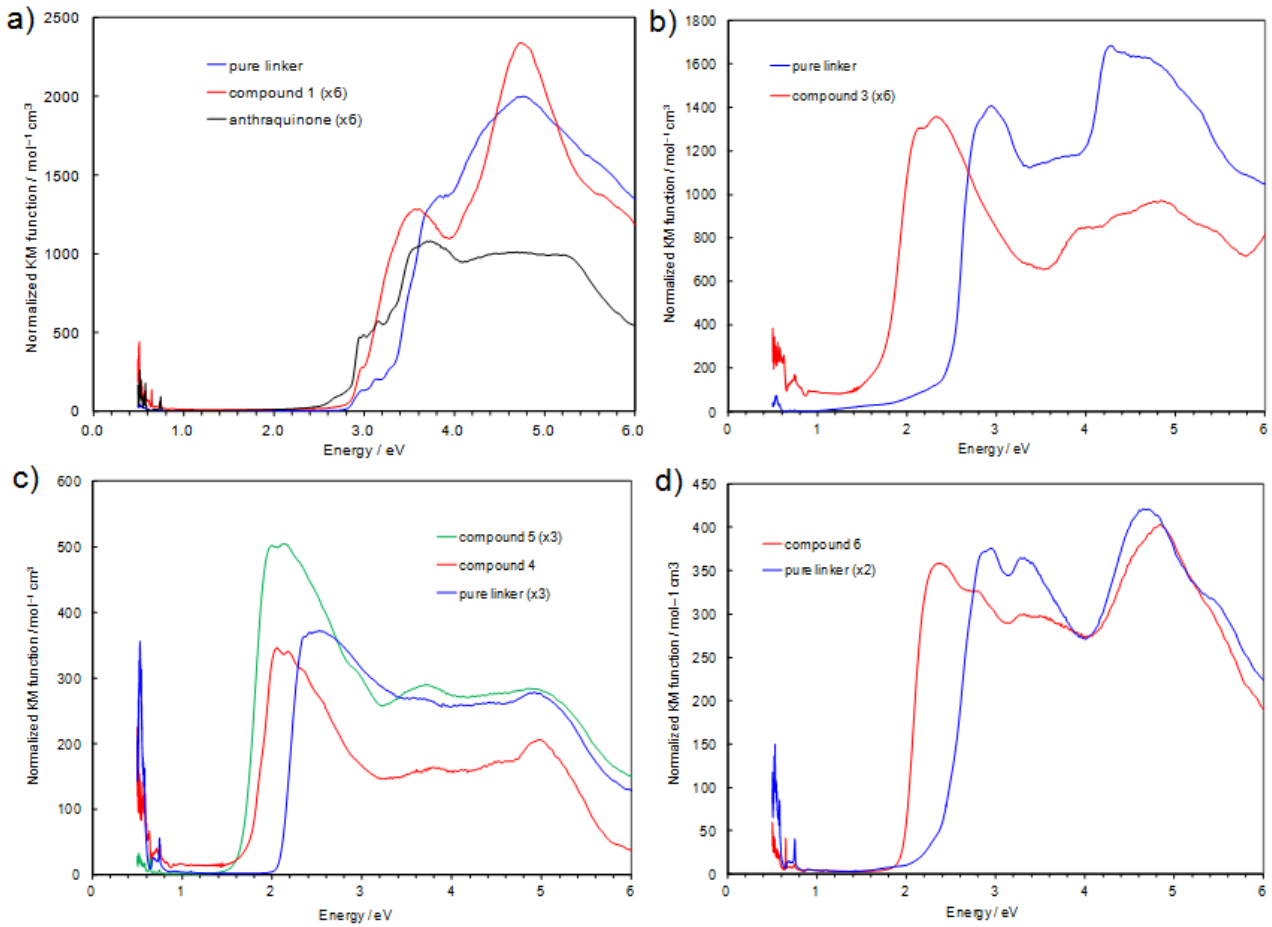

Fig. S11 Kubelka-Munk functions obtained by UV-vis absorption measurements. (a) Compound **1** compared with pure linker molecules (23dcaqH_2) and anthraquinone. (b) Compound **3** compared with pure linker molecules (15dhaqH_2). (c) Compounds **4** and **5** compared with pure linker molecules (14dhaqH_2). (d) Compound **6** compared with pure linker molecules (14hnaqH).

9. Additional compound, 7, [Li_2(15dhaq)(H_2O)$_5$]

Regarding the 15dhaq linker, we obtained red plate-like crystals of [Li_2(15dhaq)(H_2O)$_5$], **7**, which crystallized in the $P\bar{1}$ space group (a = 5.0112(2), b = 7.5031(4), c = 21.0358(8), α = 97.619(4), β = 91.892(4), and γ = 108.338(5)). 15dhaqH_2 aqueous solution (0.1 mmol/3mL) was mixed with LiOH (1.44 mmol) and pyrazine (0.12 mmol) in a well-sealed borosilicate glass vial, heated at 90°C for 6 d and 100°C for 3 h, and then gradually (~7 h) cooled down to room temperature. The crystals were recovered by filtration under reduced pressure, rinsed with ethanol, and then dried in air.

This compound is a molecular complex having a I^0O^0 dimensionality. The Li ions are coordinated by four oxygen atoms, from one keto group (Li-O bond length, 1.92 Å), a phenoxide group (1.86 Å) and two water molecules (1.94 Å and 1.96 Å). In addition, non-coordinated water molecules exist in the crystal structure. The anthraquinone molecules are stacked along the a axis.

Interestingly, contrary to the framework structure **3**, [Li_2(15dhaq)(H_2O)$_2$], the C-C bond lengths between the keto group and the close phenoxide group become longer (1.46 Å to 1.49 Å), while those between the keto group and the far phenoxide group become shorter (1.49 Å to 1.45 Å). This is consistent with the fact that the Li-O bond with the phenoxide oxygen atoms in **7** is longer than that in **3**. These indicate that the charge states in the organic molecules are determined not only by the direct coordination with Li^+ but also by other coordination bonds in the crystal structure.

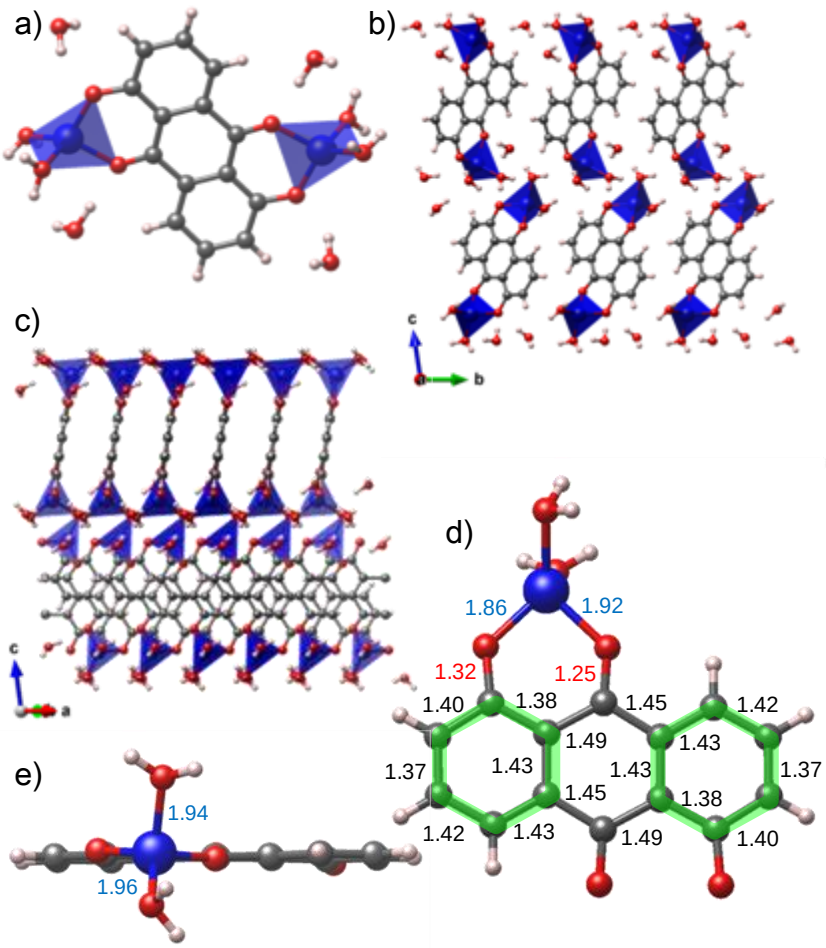

Fig. S12 Crystal structure of **7**. The green highlights in panel d illustrate strong π-conjugation in C-C bonds close to the typical aromatic C-C bond of 1.39 Å.

10. Bond order analysis of aq-based LCPs

The typical bond lengths of C-O bonds and C-C bonds are known to be 1.35 Å and 1.54 Å for bond order 1 (single bond), 1.27 Å and 1.39 Å for bond order 1.5 (aromatic bond, carboxylate, etc), and 1.20 Å and 1.34 Å for bond order 2 (double bond), respectively. We illustrate the bond orders in 1,4-dhaq and 1,5-dhaq as follows.

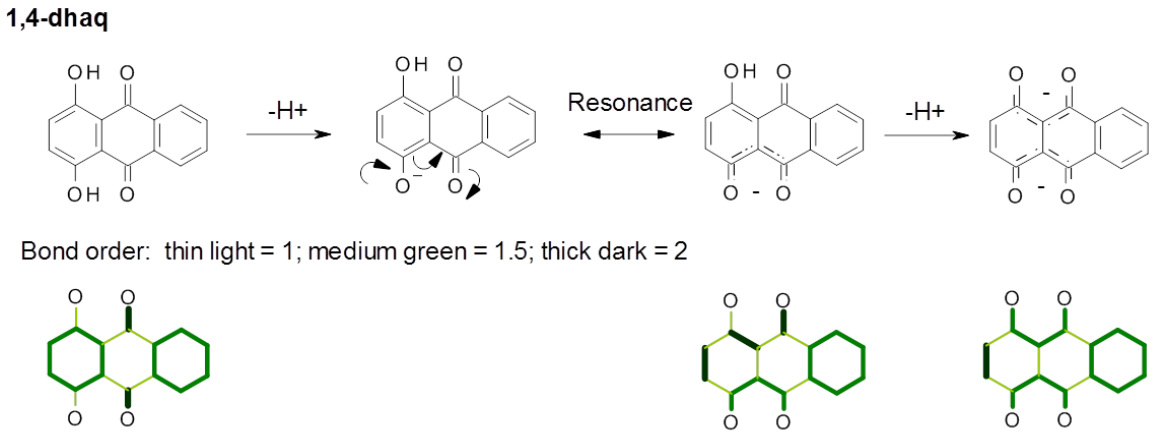

Fig. S13 π-electron resonance and bond orders in 1,4-dhaq and its anions.

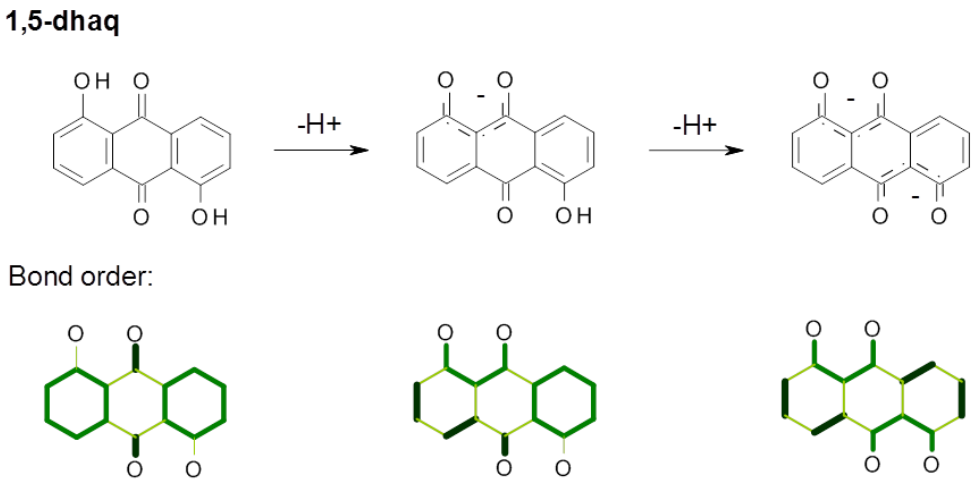

Fig. S14 π-electron resonance and bond orders in 1,5-dhaq and its anions.

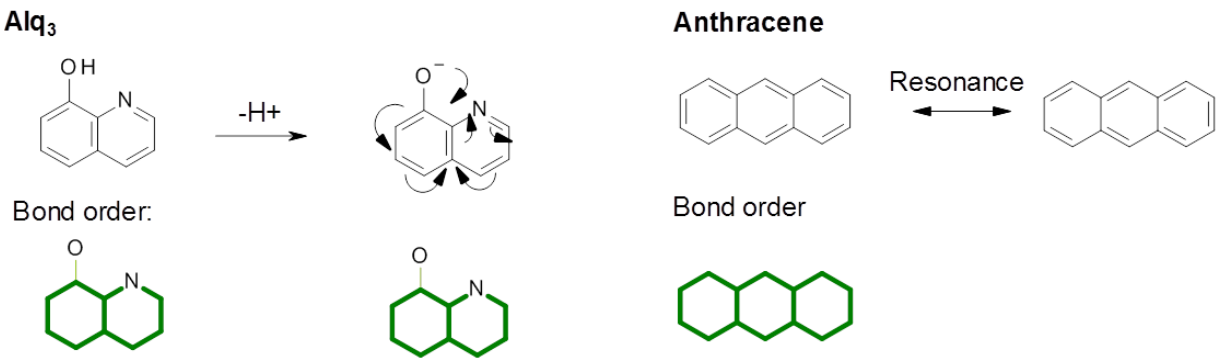

Fig. S15 π-electron resonance and bond orders in 8-tris-hydroxyquinoline and anthracene

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