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Crystalline adducts of the Lawsone molecule (2-hydroxy-1,4-naphthaquinone): optical properties and computational modelling

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Supporting Information



Figure S1 Simulated powder X-ray diffraction (PXRD) pattern of the crystalline adduct **1a** (main), calculated from the crystal structure, together with the pattern recorded from powder filtered from solution (inset). The similarity between the patterns suggests that the filtrate does not contain significant impurities e.g. from Lawsone or the coformer.



Figure S2 Simulated powder X-ray diffraction (PXRD) pattern of the crystalline adduct **1b** (main), calculated from the crystal structure, together with the pattern recorded from powder filtered from solution (inset). The similarity between the patterns suggests that the filtrate does not contain significant impurities e.g. from Lawsone or the coformer.



Figure S3 Simulated powder X-ray diffraction (PXRD) pattern of the crystalline adduct **1c** (main), calculated from the crystal structure, together with the pattern recorded from powder filtered from solution (inset). The similarity between the patterns suggests that the filtrate does not contain significant impurities e.g. from Lawsone or the coformer. Note that some peaks are absent in the pattern from the filtrate due to reflections from preferred orientations.



Figure S4 Simulated powder X-ray diffraction (PXRD) pattern of the crystalline adduct **1d** (main), calculated from the crystal structure, together with the pattern recorded from powder filtered from solution (inset). The similarity between the patterns suggests that the filtrate does not contain significant impurities e.g. from Lawsone or the coformer. Note that some peaks are absent in the pattern from the filtrate due to reflections from preferred orientations.

	Cocrystal 1a	Cocrystal 1b Cocrystal 1c		Cocrystal 1d	
a/Å	10.6360(3)	3.8157(1)	22.5402(9)	13.6937(12)	
b/Å	4.7798(1)	28.0772(7)	50.511(2)	5.1534(3)	
c/Å	23.0987(9)	11.2326(3)	4.6451(2)	17.5288(12)	
α/°	90	90	90	90	
β / °	96.131(2)	96.542(2)°	90	92.329(7).	
γ / °	90	90	90	90	
Density / g cm ⁻³	1.435	1.474	1.373	1.447	
Volume / Å ³	1167.57(6)	1195.56(5)	5288.6(4)	1235.97(16)	
Ζ	2	2	8	4	
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	
Space group	$P2_1/n$	$P2_1/n$	Fdd2	$P2_1/n$	
Temperature / K	180	180	180	300K	
F(000)	524	552	2288	560	
Goodness-of-fit on F^2	0.905	1.040	1.083	1.014	
R	0.0390	0.0578	0.0261	0.0445	
wR2	0.0920	0.1227	0.0630	0.1047	
Reflections collected	6685	10270	3385	5890	
Independent reflections	2626	4108	972	2880	
R(int)	0.0337	0.0505	0.0292	0.0201	

 Table S1 Crystallographic data for the single-crystal X-ray structures of the crystalline adducts 1a-1d.



Figure S5 ATR FT-Near IR spectra of the crystalline adducts **1a-1d**. Arrows on the inset plot mark the positions of the OH combination bands, which confirm that **1a**, **1c** and **1d** are cocrystals, while **1b** is a salt.



Figure S6 ATR spectra (stretching frequencies) of 1a-1d.



Figure S7 DSC and TGA traces of the crystalline adducts **1a-1d**. The melting points are in agreement with the fact that **1a**, **1c** and **1d** are cocrystals, while **1b** is a salt, as the latter has the higest melting point.



Figure S8 First derivatives of the reflectance spectra in Fig. 4 (a), obtained by numerical differentiation of the experimental data using a seven-point finite-difference stencil.

Table S2 Comparison of the DFT-optimised lattice parameters of the crystalline adducts **1a-1d** to the experimentally-measured values. Note that the calculations on **1d** did not predict any relaxation of the cell shape or volume, and hence the lattice parameters remained identical to those of the experimental structure used as input.

	<i>a</i> / Å	<i>a</i> / Å	<i>a</i> / Å	α / °	β / °	γ / °	$V/\text{\AA}^3$
1a Expt.	10.636	4.780	23.099	90.000	96.131	90.000	1167.57
1a Calc.	10.566	4.942	23.194	90.000	96.706	90.000	1202.79
Δ / %	-0.65	3.39	0.41	0.00	0.60	0.00	3.02
1b Expt.	3.816	28.077	11.233	90.000	96.542	90.000	1195.56
1b Calc.	4.068	27.758	11.081	90.000	96.642	90.000	1242.72
Δ / %	6.60	-1.14	-1.35	0.00	0.10	0.00	3.94
1c Expt.	22.540	50.511	4.645	90.000	90.000	90.000	5288.58
1c Calc.	22.255	50.930	4.799	90.000	90.000	90.000	5439.36
Δ / %	-1.27	0.83	3.31	0.00	0.00	0.00	2.85
1d Expt.	13.694	5.153	17.529	90.000	92.329	90.000	1235.97
1d Calc.	13.694	5.153	17.529	90.000	92.329	90.000	1235.97
Δ / %	0.00	0.00	0.00	0.00	0.00	0.00	0.00



Figure S9 Comparison of the structure of **1b** in the gas phase and in the solid state, illustrating the difference in the position of the H atom.



Figure S10 Comparison of the frontier orbitals of Lawsone (1), coformer b, and the gasphase 1b.



Figure S11 Comparison of the frontier orbitals of Lawsone (1), coformer c, and the gasphase 1c.



Figure S12 Comparison of the frontier orbitals of coformer d and the d_2 dimer.



Figure S13 Comparison of the frontier orbitals of Lawsone (1), the dimer of coformer d, and the gas-phase 1d.



Figure S14 Comparison of the frontier orbitals of the gas-phase and corresponding crystalline form of 1b.



Figure S15 Comparison of the frontier orbitals of the gas-phase and corresponding crystalline of 1c.



Figure S16 Comparison of the frontier orbitals of the gas-phase and corresponding crystalline form of 1d.