Supporting Information for

Crystal structures and stimuli-responsive properties for three novel D-A type salicylhydrazide-viologen compounds with free radical property at ambient condition

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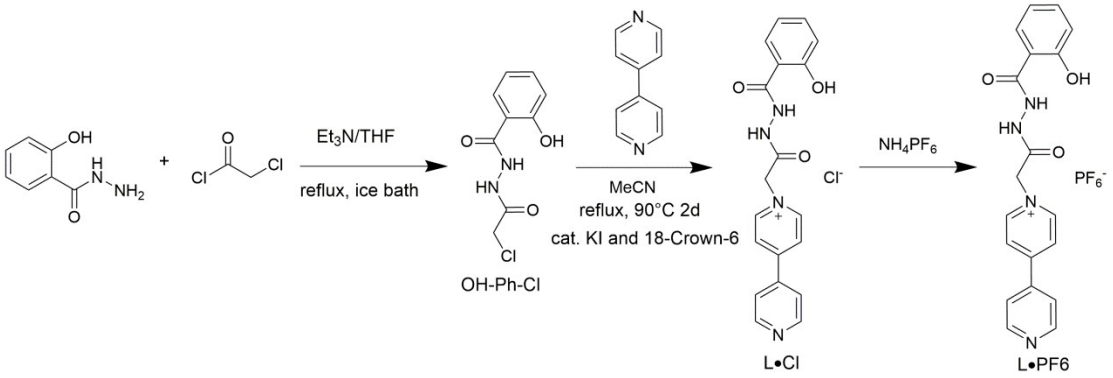
1. Synthesis and characterization of L·PF_6



Scheme S1 Synthesis of **L·PF_6**

4,4′-bipy, 2-hydroxybenzoic hydrazide, chloroacetyl chloride, Et_3N, THF, MeCN and NH_4PF_6 in AR grade were purchased commercially without further purification. Water was deionized and distilled before use.

OH-Ph-Cl: Salicylic hydrazide (0.04 mol) and triethylamine (0.04 mol) were dissolved in THF (20 mL), ice-bathed for 30 min, and a solution of chloroacetyl chloride (0.044 mol) in THF (10 mL) was added dropwise, and refluxed at 60 °C for 3 h. After cooling, the residue was washed with water, filtered with suction, and dried in vacuo to obtain 0.035 M white solid with a yield of 87.5%.

L·Cl: OH-Ph-Cl (0.039 mol) and 4,4'-bipyridine (0.083 mol) were added to MeCN (40 mL) and refluxed at 90 °C for at least 2 d. After cooling, the residue was washed with MeCN and MeOH, and suction filtered to obtain 0.030 mol purple solid with a yield of 77.0%.

L·PF_6: Take **L·Cl** and NH_4PF_6 (1:3), add H_2O (20 mL), and stir at room temperature for 2 h with a yield of 93.2%. ^{1}H NMR (600 MHz, DMSO-d6, Figure S1): 11.66 (1 H, s), 11.20 (1 H, s), 10.73 (1 H, s), 9.18 (2 H,d), 8.90 (2 H, d), 8.71 (2 H, d), 8.90 (2 H, d), 8.07 (2 H, d), 7.88 (1 H, d), 7.45 (1 H, t), 6.96 (2 H, dd), 5.68 (2 H, s). ESI-MS (Figure S2, S3): 349.1289 (Exp.), 349.1295 (Calc. for [L^+]); 144.9634 (Exp.), 144.9647 (Calc. for [PF_6^-])

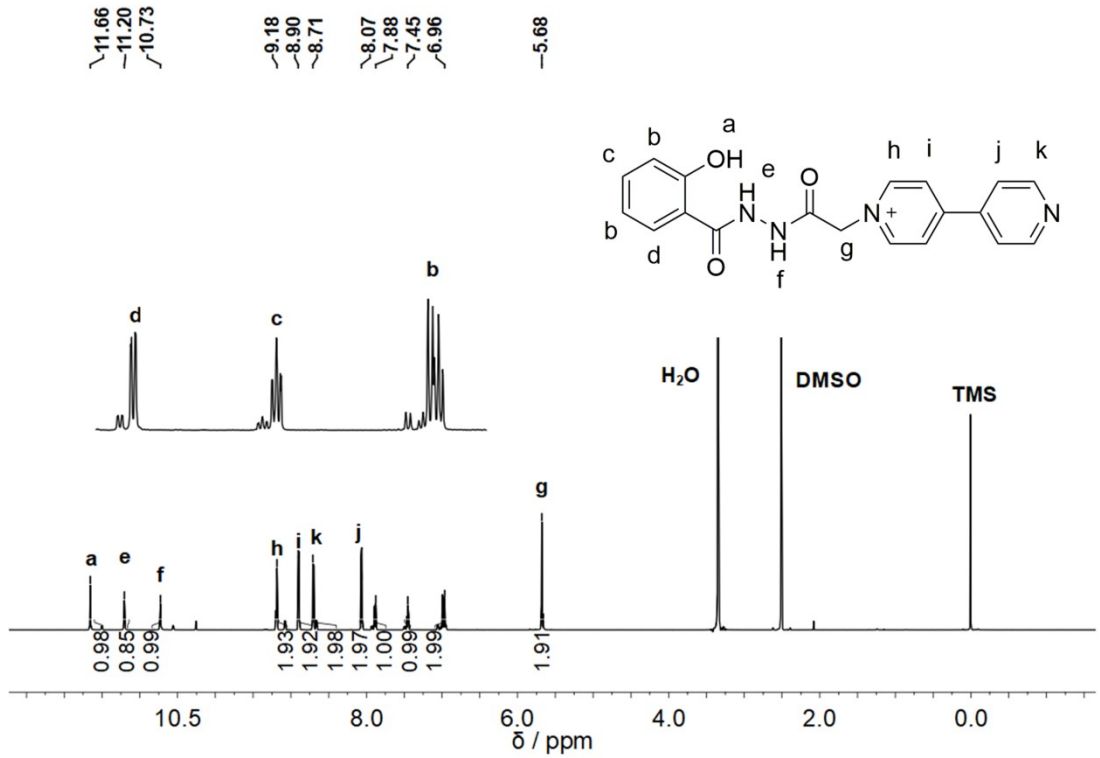


Figure S1 ^{1}H NMR spectrum for **L·PF$_6$** (DMSO-d6)

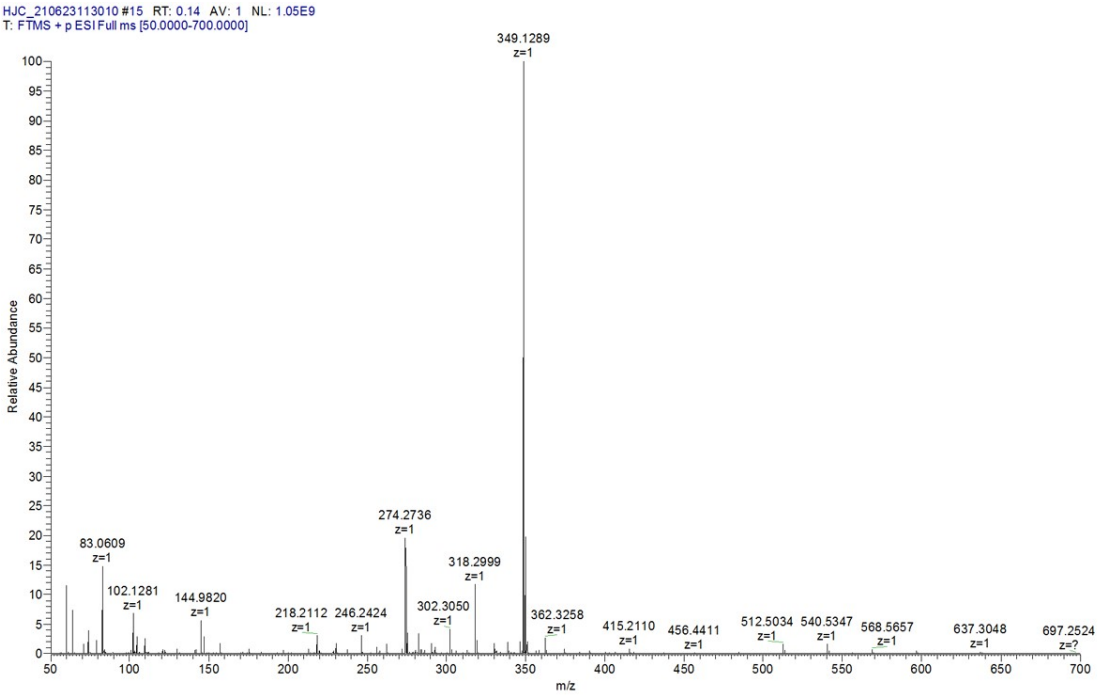


Figure S2 The Mass spectrum of **L**$^{+}$ in positive ion mode with the range of 50-700

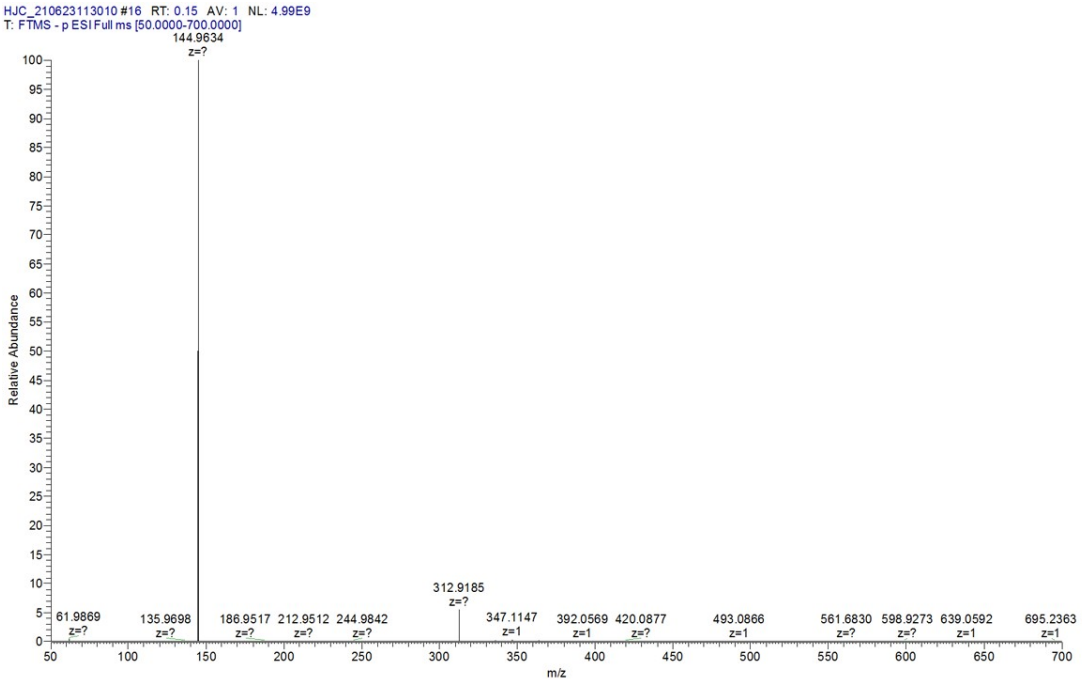


Figure S3 The Mass spectrum of PF_6^- in negative ion mode with the range of 50-700

2. Characterization

^{1}H-NMR spectra were taken with AVANCE NEO 600 MHz in DMSO-d6.

Mass spectrum was taken by Thermo Fisher Scientific Exactive Plus ultra-high resolution liquid chromatography mass spectrometry, with ESI ion source in positive and negative ion modes.

Diffuse reflection spectra were taken by SHIMADZU UV-2600 spectrometer for solid sample (step 1 nm, duration 0.1 s per step).

Thermogravimetric study (TGA) was taken by METTLED TOLEDO TGA/DSC 3+, with temperature rise or fall 400 K per hour in a nitrogen atmosphere.

Powder X-ray diffraction (PXRD) was performed on a Rigaku D/max-3c with Cu Kα radiation (λ = 1.5406 Å) in the angular range of 2θ = 5 – 50 ° at room temperature.

Electron paramagnetic resonance (EPR) measurements were obtained using a Bruker A300 instrument operating in the X-band at the room temperature.

Single crystal X-ray diffraction was taken by Bruker Apex II CCD. The measurement was made by using graphic monochromatic Mo Kα radiation (λ = 0.71073 Å) at 150 K under a cold nitrogen stream. The frame data were integrated and absorption correction using SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. All the structures were solved by the direct method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELX-97 program [1] and Olex2 [2]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms of the organic ligands were generated theoretically by the specific atoms of Olex2.

Density functional theory (DFT) calculations

The frontier molecular orbitals and Mulliken population of Compounds **1 - 3** were calculated by using b3lyp/6-31g(d,p) level in Gaussian 09 package software. The charge was set to be 1, and multiplicity was set to be 1 was set. The model for calculation is built by adopting the molecular conformation of L in the crystal structure.

Elemental analysis was taken by Vario EL Cube.

3. Supplementary data

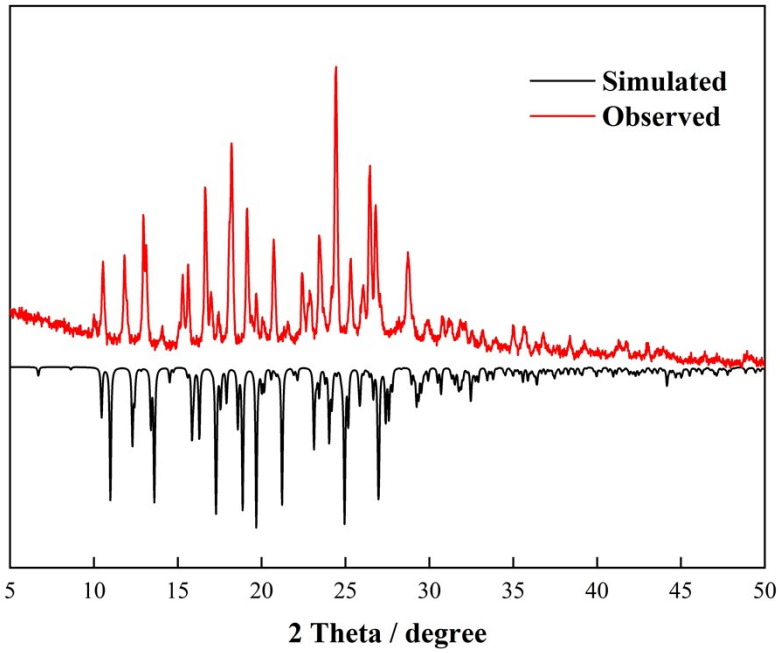


Figure S4 PXRD pattern of compound **1**

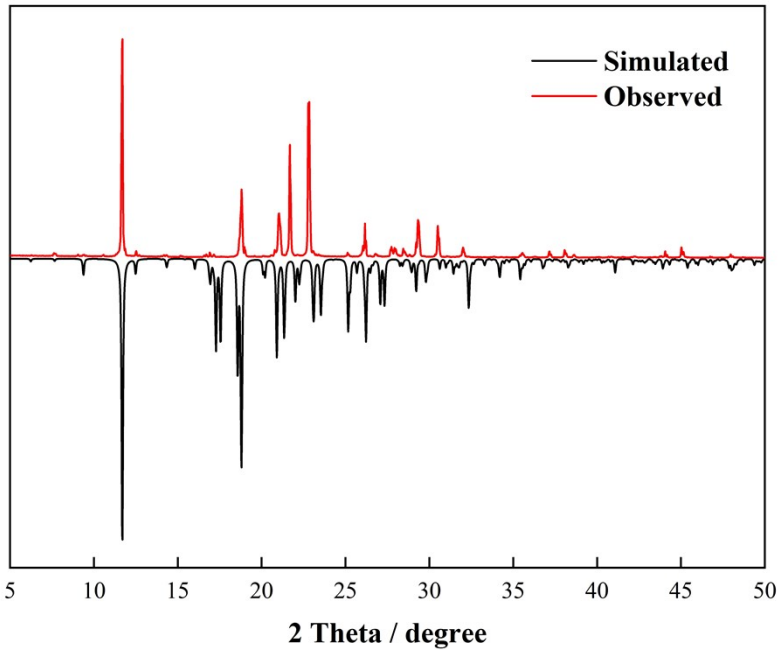


Figure S5 PXRD pattern of compound **2**

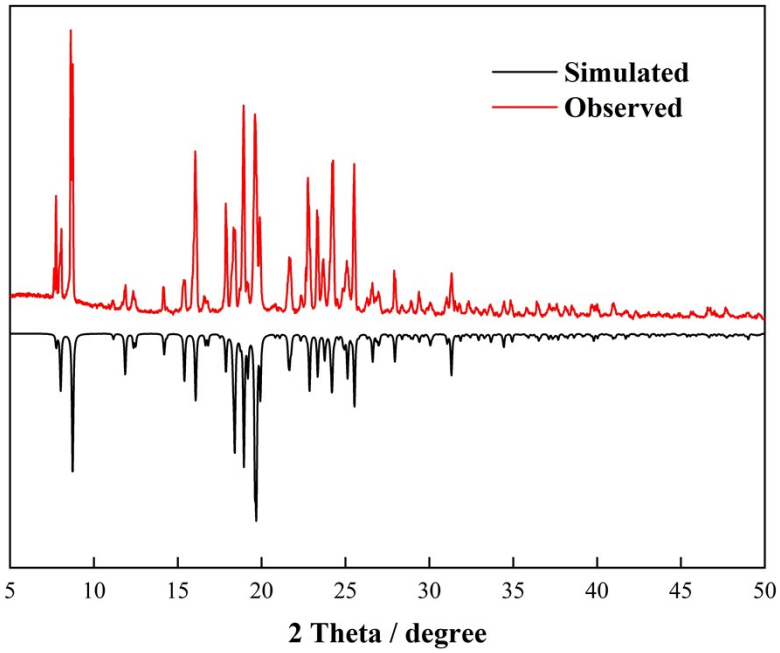


Figure S6 PXRD pattern of compound **3**

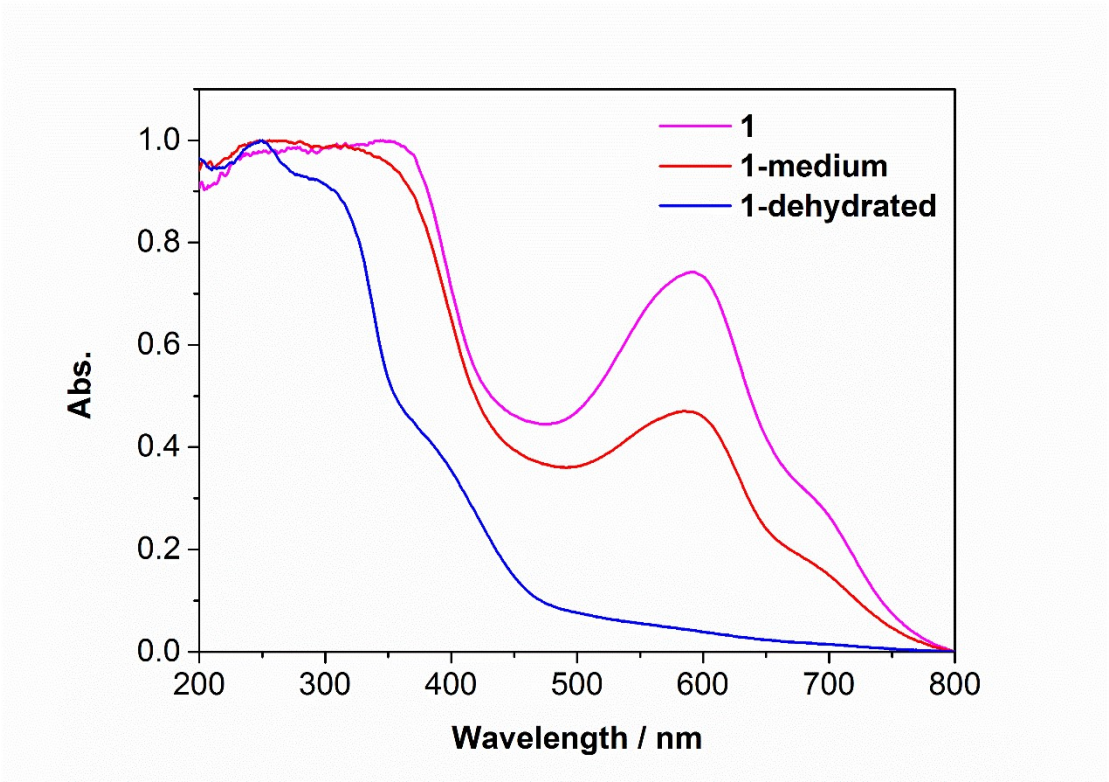


Figure S7 the DRS spectra of compound **1**, **1-medium** and **1-dehydrated**

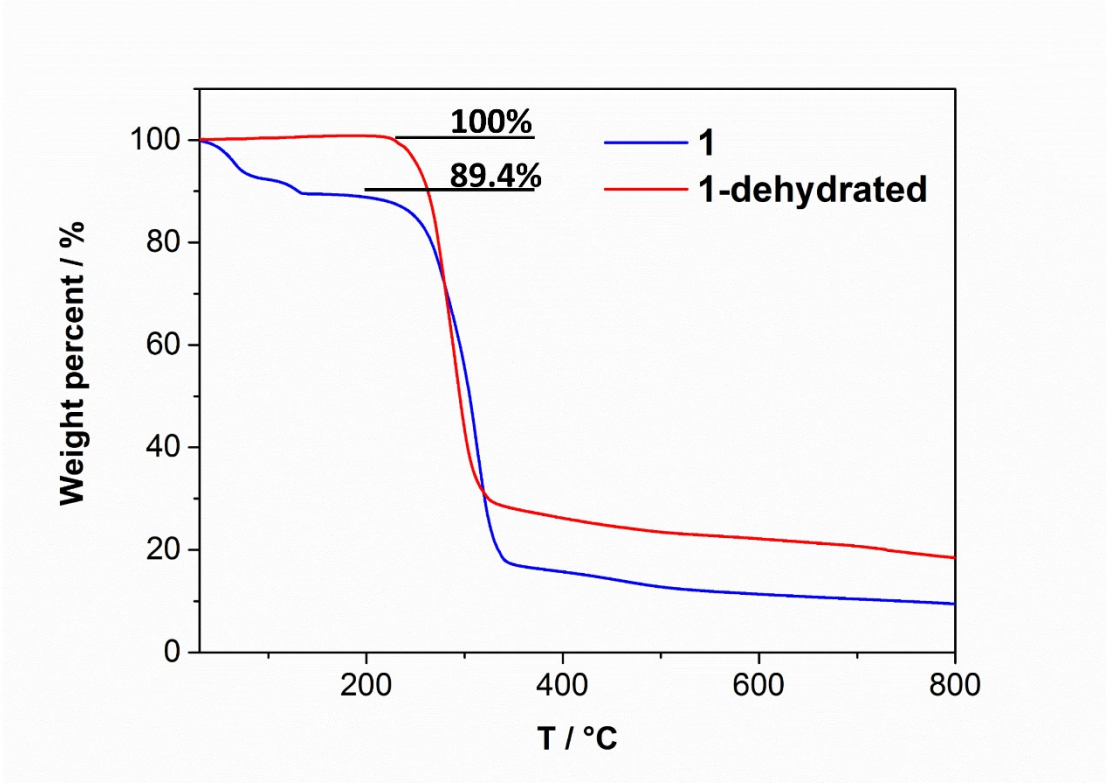


Figure S8 TG curve of compound **1** and **1-dehydrated.**

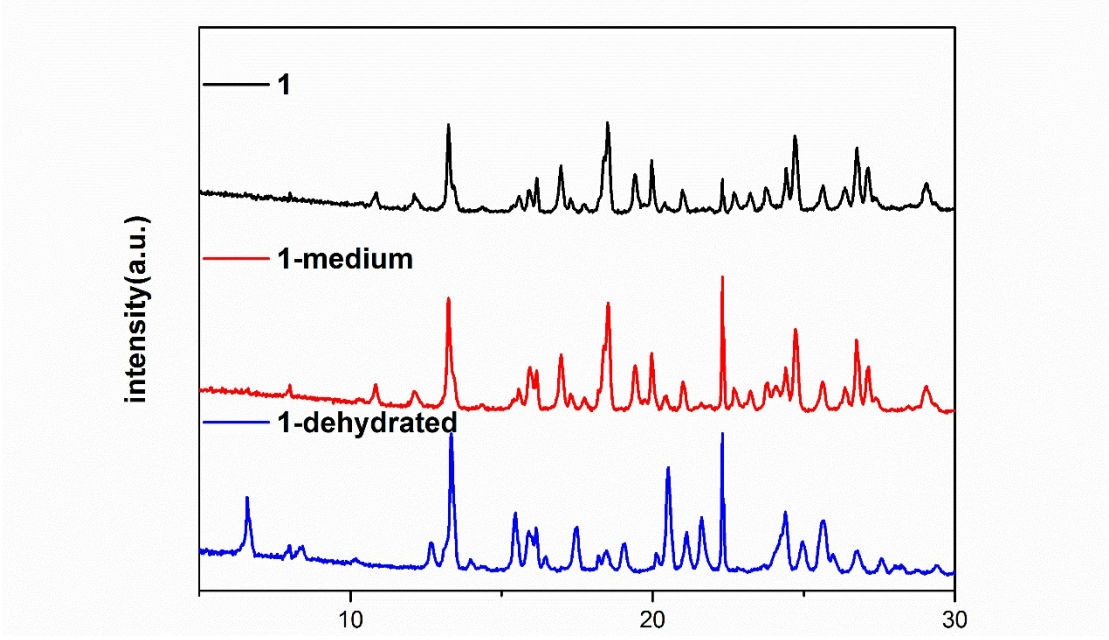


Figure S9 PXRD patterns of the powders with compound **1**, **1-medium** and **1-dehydrated**

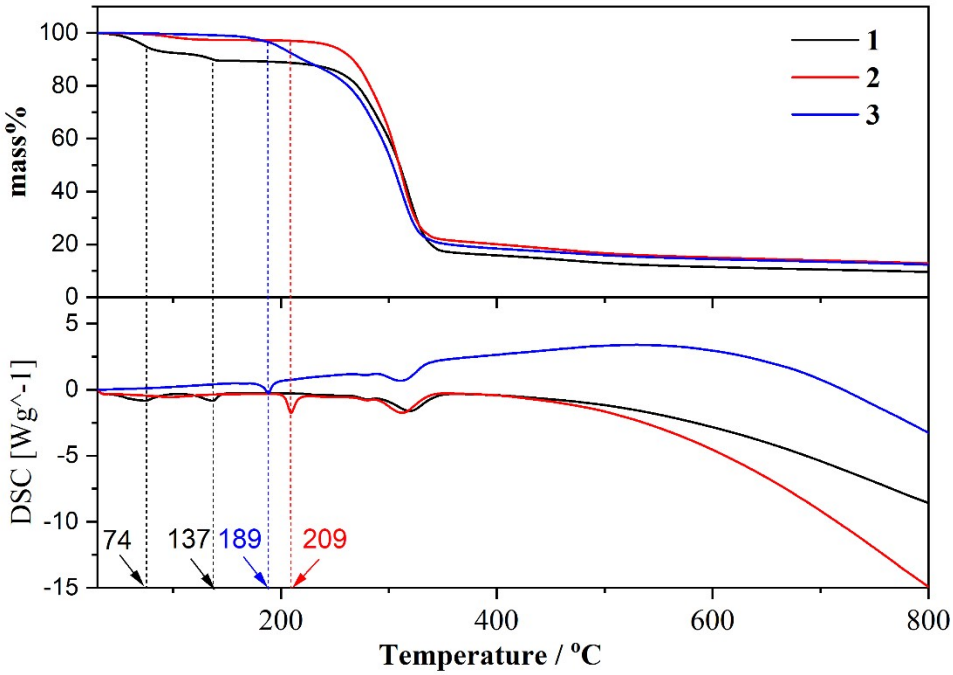


Figure S10 TG and DSC curves of compounds **1** – **3**.

Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5988.8(19)	578.3(6)	5102.6(13)	31.6(4)
O2	3265.5(14)	1884.7(5)	4628.9(12)	32.6(4)
O3	6645.3(14)	2145.4(5)	6500.0(12)	31.1(4)
N1	4641.2(16)	1345.6(4)	5986.1(13)	24.6(4)
N2	4613(2)	1680.9(6)	6916.0(16)	24.3(4)
N3	6645(2)	2796.2(6)	8339.7(15)	22.8(4)
N4	11902(2)	4830.8(6)	9750.0(16)	24.7(4)
C1	5107(3)	690.2(8)	4007.2(19)	24.5(5)
C2	4148(2)	1124.4(8)	3872.1(19)	22.5(5)
C3	3266(3)	1236.2(8)	2732.1(19)	26.2(5)
C4	3317(3)	935.1(9)	1749(2)	30.5(5)
C5	4255(3)	506.4(8)	1898(2)	30.0(5)
C6	5131(3)	384.4(8)	3012(2)	28.9(5)
C7	3993(2)	1483.8(8)	4851(2)	24.1(5)
C8	5647(2)	2062.0(8)	7099.3(19)	22.9(5)
C9	5429(3)	2399.1(8)	8146(2)	27.4(5)
C10	7870(3)	2762.0(8)	9261.3(19)	27.3(5)
C11	8961(3)	3143.9(8)	9490(2)	27.7(5)
C12	8792(2)	3575.6(8)	8772.1(18)	21.5(5)
C13	7566(2)	3579.8(8)	7767.8(19)	23.1(5)
C14	6513(3)	3188.3(8)	7562(2)	24.5(5)
C15	9853(2)	4016.0(8)	9098.2(19)	21.9(5)
C16	10573(3)	4100.0(8)	10289.4(19)	25.1(5)
C17	11576(3)	4506.7(8)	10573(2)	25.7(5)
C18	11187(3)	4754.2(8)	8609(2)	25.5(5)
C19	10159(2)	4359.1(8)	8242.4(19)	24.0(5)
O1W	3218(2)	2846.3(6)	5584.1(15)	34.9(4)
O2W	274(2)	2939.2(7)	6211.9(18)	45.1(5)
O3W	14(2)	2078.9(8)	7547(2)	54.9(5)
O4W	2549(2)	1521.0(7)	8516.7(16)	36.3(4)
O5W	1817(3)	474.9(7)	8695.1(18)	48.2(5)
P1	7613.4(9)	901.2(2)	9306.5(6)	38.01(19)
F1	6045(2)	746.9(6)	8405.9(16)	67.2(5)
F2	8149(3)	1221.9(8)	8297.5(18)	95.0(7)
F3	8488.3(19)	409.9(6)	8938.4(14)	55.9(4)
F4	7086(2)	576.2(6)	10340.2(14)	57.2(4)
F5	6772(2)	1387.3(6)	9714.4(17)	76.9(6)
F6	9197(2)	1051.2(6)	10239.1(15)	61.5(5)

Table S2 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	37.3(10)	27.6(9)	27.3(9)	-3.0(7)	-0.3(7)	14.2(7)
O2	38.8(10)	20.8(8)	36.4(9)	-0.5(7)	3.3(8)	8.9(7)
O3	29.6(9)	31.4(9)	35.6(9)	-7.3(7)	14.7(8)	-6.3(7)
N1	29.5(10)	16.7(9)	26.7(10)	-2.7(8)	3.3(8)	1.3(8)
N2	25.5(10)	21.5(9)	27.5(10)	-5.8(8)	9.5(8)	-3.5(8)
N3	23.7(10)	20.3(9)	25.4(10)	-3.3(8)	7.3(8)	-1.5(7)
N4	24.0(10)	20.8(9)	29.4(11)	-1.3(8)	5.8(8)	0.1(8)
C1	25.6(12)	21.5(11)	25.7(12)	2.6(9)	3.5(10)	-1.5(9)
C2	23.0(11)	17.8(11)	26.9(12)	1.8(9)	5.2(9)	-4.1(9)
C3	25.7(12)	22.6(11)	29.5(13)	4.8(10)	3.4(10)	-0.2(9)
C4	33.0(13)	32.1(13)	24.7(12)	3.0(10)	1.7(10)	-3.2(10)
C5	34.6(13)	29.6(12)	26.5(12)	-5.3(10)	7.2(10)	-4.8(10)
C6	31.7(13)	23.7(12)	31.4(13)	-2.6(10)	6.8(10)	3.6(10)
C7	20.9(11)	20.7(11)	30.7(13)	1.1(9)	4.8(10)	-3.4(9)
C8	20.2(11)	22.1(11)	26.5(12)	0.5(9)	5.0(10)	2.4(9)
C9	28.0(12)	25.3(12)	30.7(12)	-4.7(10)	10.6(10)	-5.8(10)
C10	34.2(13)	23.8(12)	24.0(12)	2.1(9)	5.8(10)	-1.2(10)
C11	29.3(13)	25.0(12)	25.9(12)	2.1(10)	-1.7(10)	-3.0(10)
C12	21.4(11)	21.9(11)	22.7(11)	-2.4(9)	7.6(9)	0.6(9)
C13	23.3(11)	21.9(11)	24.7(12)	1.9(9)	6.2(9)	2.3(9)
C14	21.5(11)	26.3(12)	24.7(12)	-2.5(9)	2.1(9)	2.9(9)
C15	19.0(11)	20.0(11)	27.2(12)	-0.5(9)	5.9(9)	2.6(9)
C16	26.7(12)	23.6(11)	25.2(12)	2.5(9)	5.3(10)	-1.3(9)
C17	25.0(12)	26.4(12)	24.6(12)	-1.7(10)	2.2(9)	0.3(9)
C18	26.5(12)	23.2(11)	27.4(12)	5.0(9)	6.5(10)	0.5(9)
C19	23.7(11)	25.1(11)	22.6(11)	-0.4(9)	2.7(9)	1.0(9)
O1W	42.2(10)	25.3(9)	36.0(10)	-2.9(8)	4.6(8)	5.1(8)
O2W	39.1(12)	41.9(11)	54.0(12)	0.7(9)	8.3(10)	0.7(9)
O3W	33.5(11)	62.6(14)	66.0(14)	20.7(11)	3.4(10)	-6.4(10)
O4W	36.5(10)	34.1(10)	40.6(10)	0.5(8)	13.1(8)	-3.0(8)
O5W	58.5(14)	40.7(11)	44.1(12)	0.9(9)	7.1(10)	0.3(10)
P1	52.1(4)	28.0(3)	30.2(4)	0.8(3)	-0.7(3)	-3.4(3)
F1	71.6(12)	44.3(9)	68.7(12)	-2.3(8)	-27.3(10)	-4.0(8)
F2	135(2)	83.8(14)	65.8(13)	30.8(11)	18.2(13)	-42.1(13)
F3	57.9(10)	55.5(10)	57.3(10)	-19.4(8)	19.2(8)	0.4(8)
F4	70.5(11)	54.6(10)	52.5(10)	11.4(8)	26.6(9)	8.2(9)
F5	92.9(14)	39.7(9)	82.3(13)	-14.5(9)	-21.1(11)	26.1(9)
F6	60.3(11)	46.2(9)	66.2(11)	-8.4(8)	-16.3(9)	-6.1(8)

Table S3 List of bond lengths (Å) for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.355(3)	C5	C6	1.375(3)
O2	C7	1.231(2)	C8	C9	1.524(3)
O3	C8	1.218(2)	C10	C11	1.369(3)
N1	N2	1.381(2)	C11	C12	1.392(3)
N1	C7	1.348(2)	C12	C13	1.392(3)
N2	C8	1.333(3)	C12	C15	1.481(3)
N3	C9	1.468(3)	C13	C14	1.366(3)
N3	C10	1.334(3)	C15	C16	1.388(3)
N3	C14	1.350(3)	C15	C19	1.390(3)
N4	C17	1.336(3)	C16	C17	1.376(3)
N4	C18	1.334(3)	C18	C19	1.379(3)
C1	C2	1.405(3)	P1	F1	1.5786(17)
C1	C6	1.392(3)	P1	F2	1.5647(19)
C2	C3	1.396(3)	P1	F3	1.5975(17)
C2	C7	1.486(3)	P1	F4	1.5899(17)
C3	C4	1.377(3)	P1	F5	1.5882(18)
C4	C5	1.383(3)	P1	F6	1.6029(16)

Table S4 Bond angles for compound **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	N2	119.24(14)	C11	C12	C15	120.61(19)
C8	N2	N1	119.43(17)	C13	C12	C15	121.98(19)
C10	N3	C9	120.03(18)	C14	C13	C12	120.4(2)
C10	N3	C14	120.99(18)	N3	C14	C13	120.1(2)
C14	N3	C9	118.97(18)	C16	C15	C12	120.25(19)
C18	N4	C17	117.30(18)	C16	C15	C19	117.68(19)
O1	C1	C2	119.34(19)	C19	C15	C12	122.06(19)
O1	C1	C6	121.42(19)	C17	C16	C15	119.4(2)
C6	C1	C2	119.2(2)	N4	C17	C16	123.1(2)
C1	C2	C7	125.31(19)	N4	C18	C19	123.6(2)
C3	C2	C1	118.4(2)	C18	C19	C15	118.8(2)
C3	C2	C7	116.33(19)	F1	P1	F3	90.55(9)
C4	C3	C2	121.9(2)	F1	P1	F4	90.24(10)
C3	C4	C5	119.1(2)	F1	P1	F5	90.85(10)
C6	C5	C4	120.4(2)	F1	P1	F6	178.96(11)
C5	C6	C1	121.0(2)	F2	P1	F1	90.33(11)
O2	C7	N1	121.78(19)	F2	P1	F3	91.50(12)
O2	C7	C2	120.92(19)	F2	P1	F4	179.43(12)
N1	C7	C2	117.28(18)	F2	P1	F5	89.59(13)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	C8	N2	125.04(19)	F2	P1	F6	90.71(11)
O3	C8	C9	122.53(18)	F3	P1	F6	89.34(9)
N2	C8	C9	112.42(18)	F4	P1	F3	88.41(9)
N3	C9	C8	109.89(17)	F4	P1	F6	88.72(10)
N3	C10	C11	120.4(2)	F5	P1	F3	178.22(10)
C10	C11	C12	120.3(2)	F5	P1	F4	90.48(10)
C11	C12	C13	117.38(19)	F5	P1	F6	89.24(9)

Table S5 Hydrogen bonding data sheet for compound **1**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	N4[1]	0.82	1.86	2.667(2)	167.5
N1	H1A	O1	0.86	1.98	2.631(2)	131.7
N2	H2	O4W	0.86	1.96	2.813(3)	174.3
O1W	H1WA	O2	0.856(17)	1.918(18)	2.765(2)	170(3)
O1W	H1WB	O4W[2]	0.878(17)	1.968(18)	2.844(2)	175(3)
O2W	H2WA	O1W	0.876(18)	1.905(19)	2.779(3)	175(3)
O2W	H2WB	F6[3]	0.881(18)	2.090(19)	2.965(2)	172(3)
O3W	H3WA	O2W	0.883(17)	1.901(19)	2.764(3)	165(3)
O3W	H3WB	O3[4]	0.874(19)	2.13(3)	2.918(3)	150(4)
O3W	H3WB	F2[4]	0.874(19)	2.47(4)	2.996(3)	119(3)
O4W	H4WA	O5W	0.869(17)	1.984(18)	2.851(3)	176(3)
O4W	H4WB	O3W	0.868(17)	1.819(18)	2.685(3)	175(3)
O5W	H5WA	F4[5]	0.863(18)	2.25(2)	3.065(3)	157(4)
O5W	H5WB	F3[4]	0.872(19)	2.10(3)	2.941(3)	162(6)

Symmetry codes: 2-X,-1/2+Y,3/2-Z; [2]+X,1/2-Y,-1/2+Z; [3]-1+X,1/2-Y,-1/2+Z; [4]-1+X,+Y,+Z; [5]1-X,-Y,2-Z.

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **2**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2628(3)	6675.5(15)	5538.3(6)	30.2(5)
O2	8338(3)	6090.1(15)	4795.5(6)	30.0(5)
O3	5991(4)	4625.5(18)	6196.7(7)	46.2(6)
N1	6414(4)	5668.6(17)	5419.0(7)	23.2(5)
N2	7915(4)	4851.2(17)	5560.6(7)	23.3(5)
N3	8827(4)	3125.8(17)	6585.8(7)	26.1(5)
N4	5451(4)	2082.3(18)	8853.6(8)	27.1(5)
C1	3164(4)	7375(2)	5203.2(9)	22.6(6)
C2	5142(4)	7193(2)	4961.3(8)	21.0(6)
C3	5680(4)	7930(2)	4624.6(9)	24.2(6)

Atom	*x*	*y*	*z*	U(eq)
C4	4323(5)	8811(2)	4520.4(9)	28.6(7)
C5	2358(5)	8971(2)	4756.6(9)	29.5(7)
C6	1793(5)	8262(2)	5096.4(9)	27.4(6)
C7	6754(4)	6273(2)	5047.0(9)	21.0(6)
C8	7571(5)	4374(2)	5961.6(9)	28.5(6)
C9	9249(5)	3475(2)	6106.6(9)	29.9(7)
C10	10195(5)	3465(2)	6962.1(9)	29.9(7)
C11	9700(5)	3221(2)	7411.9(9)	29.4(7)
C12	7734(4)	2620(2)	7484.3(9)	21.5(6)
C13	6382(5)	2282(2)	7083.5(9)	27.7(6)
C14	6960(5)	2529(2)	6642.4(10)	30.3(7)
C15	7062(4)	2376(2)	7963.8(9)	21.4(6)
C16	8144(4)	2856(2)	8364.5(9)	25.3(6)
C17	7279(5)	2692(2)	8795.7(9)	27.7(6)
C18	4462(5)	1591(2)	8469.8(10)	32.7(7)
C19	5199(5)	1704(2)	8025.7(10)	29.2(7)
P1	3477.6(12)	5254.9(6)	8435.3(3)	29.9(2)
F1	3053(3)	6337.9(14)	8705.7(6)	52.5(5)
F2	3844(3)	5948.8(14)	7973.7(6)	42.7(4)
F3	775(3)	5200.2(14)	8268.0(9)	64.1(6)
F4	3079(4)	4588.9(16)	8890.1(7)	67.2(6)
F5	6156(3)	5323.8(15)	8590.4(7)	51.7(5)
F6	3847(3)	4193.0(14)	8151.6(6)	47.0(5)
O1W	4393(4)	4987(2)	7081.8(9)	65.9(7)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	32.9(11)	33.6(11)	26.5(11)	7.5(9)	14.7(8)	8.6(9)
O2	27.5(10)	32.8(11)	31.4(11)	9.6(9)	12.4(8)	7.4(8)
O3	63.8(15)	51.7(15)	26.4(12)	14.4(10)	21.0(11)	29.8(11)
N1	27.1(12)	23.5(12)	19.5(12)	3.2(10)	5.1(9)	8.2(10)
N2	28.7(12)	23.6(12)	18.4(12)	2.8(10)	6.2(9)	6.8(10)
N3	34.3(13)	24.5(13)	19.8(12)	3.3(10)	4.1(10)	6.2(10)
N4	30.4(13)	26.5(13)	24.9(13)	0.5(10)	6.5(10)	1.3(10)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	26.2(14)	25.9(15)	16.0(14)	-1.0(12)	3.2(11)	0.2(11)
C2	23.5(13)	23.0(14)	16.1(13)	-1.9(11)	-0.7(11)	0.6(11)
C3	25.6(14)	28.0(16)	19.4(14)	0.7(12)	4.8(11)	-0.8(12)
C4	33.8(16)	25.8(16)	26.4(16)	7.1(13)	3.5(12)	1.8(12)
C5	34.0(16)	24.5(15)	30.1(16)	1.7(13)	2.9(12)	8.6(12)
C6	29.0(15)	31.2(16)	23.1(15)	-0.5(13)	7.5(12)	6.9(12)
C7	23.6(14)	21.4(14)	17.3(14)	1.3(11)	-1.1(11)	-1.6(11)
C8	38.2(16)	29.3(16)	18.7(15)	0.9(13)	6.3(12)	8.8(13)
C9	39.8(17)	31.2(16)	19.5(15)	5.5(12)	7.6(12)	11.1(13)
C10	32.0(16)	29.5(17)	28.3(16)	3.6(13)	3.2(13)	-4.9(13)
C11	34.8(16)	33.1(17)	20.0(15)	-0.7(13)	0.8(12)	-6.4(13)
C12	26.3(14)	16.8(13)	21.4(14)	1.4(11)	2.0(11)	4.4(11)
C13	29.3(15)	27.6(16)	26.0(16)	-1.2(12)	1.4(12)	-4.6(12)
C14	32.9(16)	30.8(16)	26.3(16)	-1.0(13)	-1.6(12)	-0.9(13)
C15	25.1(14)	16.8(14)	22.2(14)	2.6(11)	1.2(11)	5.1(11)
C16	26.2(14)	26.1(15)	23.3(15)	3.2(12)	1.0(12)	-1.5(11)
C17	31.3(15)	30.6(16)	20.4(15)	0.7(12)	-0.6(12)	1.5(13)
C18	37.1(16)	29.1(17)	33.2(17)	1.6(14)	9.5(14)	-6.1(13)
C19	32.9(16)	29.5(16)	25.7(16)	-4.2(13)	5.6(12)	-7.1(13)
P1	26.1(4)	25.7(4)	38.6(5)	-4.1(3)	6.2(3)	0.5(3)
F1	72.9(13)	34.1(10)	55.1(12)	-13.6(9)	29.9(10)	-0.8(9)
F2	50.2(11)	42.0(11)	36.7(10)	-1.8(8)	8.3(8)	-0.9(8)
F3	24.6(9)	30.0(10)	137(2)	6.6(12)	0.9(10)	0.9(8)
F4	95.3(16)	48.3(13)	62.8(14)	18.3(10)	32.5(12)	2.6(11)
F5	33.3(10)	55.5(12)	63.0(13)	-10.3(10)	-13.4(9)	-1.6(9)
F6	46.9(10)	33.7(10)	57.3(12)	-17.2(9)	-12.3(9)	12.1(8)
O1W	59.6(16)	79.8(19)	60.2(17)	-4.0(15)	14.8(13)	-5.2(14)

Table S8 List of bond lengths for compound **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.356(3)	C5	C6	1.379(4)
O2	C7	1.234(3)	C8	C9	1.525(4)
O3	C8	1.223(3)	C10	C11	1.372(4)
N1	N2	1.383(3)	C11	C12	1.397(4)
N1	C7	1.334(3)	C12	C13	1.387(4)
N2	C8	1.321(3)	C12	C15	1.485(3)
N3	C9	1.474(3)	C13	C14	1.364(4)
N3	C10	1.340(3)	C15	C16	1.386(4)
N3	C14	1.338(3)	C15	C19	1.394(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N4	C17	1.329(3)	C16	C17	1.383(4)
N4	C18	1.336(3)	C18	C19	1.378(4)
C1	C2	1.406(3)	P1	F1	1.5992(18)
C1	C6	1.389(4)	P1	F2	1.6088(18)
C2	C3	1.392(3)	P1	F3	1.5899(19)
C2	C7	1.494(3)	P1	F4	1.578(2)
C3	C4	1.377(4)	P1	F5	1.5705(18)
C4	C5	1.386(4)	P1	F6	1.5897(18)

Table S9 lists of bond angles for compound **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	N2	121.5(2)	C13	C12	C11	116.6(2)
C8	N2	N1	116.8(2)	C13	C12	C15	121.1(2)
C10	N3	C9	120.4(2)	C14	C13	C12	121.3(3)
C14	N3	C9	119.0(2)	N3	C14	C13	120.6(3)
C14	N3	C10	120.4(2)	C16	C15	C12	121.9(2)
C17	N4	C18	116.8(2)	C16	C15	C19	117.1(2)
O1	C1	C2	119.1(2)	C19	C15	C12	120.9(2)
O1	C1	C6	121.0(2)	C17	C16	C15	119.4(3)
C6	C1	C2	119.8(2)	N4	C17	C16	123.7(3)
C1	C2	C7	124.7(2)	N4	C18	C19	123.7(3)
C3	C2	C1	118.1(2)	C18	C19	C15	119.2(3)
C3	C2	C7	117.1(2)	F1	P1	F2	87.97(10)
C4	C3	C2	122.0(2)	F3	P1	F1	89.45(11)
C3	C4	C5	119.2(2)	F3	P1	F2	88.86(11)
C6	C5	C4	120.2(3)	F4	P1	F1	91.18(11)
C5	C6	C1	120.6(2)	F4	P1	F2	178.90(11)
O2	C7	N1	121.7(2)	F4	P1	F3	90.43(12)
O2	C7	C2	122.3(2)	F4	P1	F6	90.20(11)
N1	C7	C2	116.0(2)	F5	P1	F1	90.52(11)
O3	C8	N2	122.3(2)	F5	P1	F2	89.85(10)
O3	C8	C9	122.2(2)	F5	P1	F3	178.72(13)
N2	C8	C9	115.4(2)	F5	P1	F4	90.86(12)
N3	C9	C8	108.4(2)	F5	P1	F6	90.78(10)
N3	C10	C11	120.9(3)	F6	P1	F1	178.09(11)
C10	C11	C12	120.2(3)	F6	P1	F2	90.63(10)
C11	C12	C15	122.3(2)	F6	P1	F3	89.22(10)

Table S10 Hydrogen Bonding Data Sheet for compound **2**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	N4[1]	0.82	1.87	2.645(3)	158.3
N1	H1A	O1	0.86	1.87	2.579(3)	138.7
N2	H2	O2[2]	0.86	1.92	2.745(3)	160.3
O1w	H1wa	F2	\	\	2.857(2)	\
O1w	H1wb	O3	\	\	2.799(2)	\

Symmetry codes: [1]1/2-X,1/2+Y,3/2-Z; [2]2-X,1-Y,1-Z

Note: H1wa and H1wb are highly disordered between the two sets of (D, A) pairs, which are (O1w, F2) and (O1w, O3) respectively.

Table S11 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4398.1(13)	1794(4)	7022.4(11)	85.9(10)
O2	3297.4(14)	3151(3)	8349.7(12)	85.6(10)
O3	2538.8(12)	2615(3)	6896.2(11)	64.4(7)
N1	3570.5(13)	3429(3)	7418.4(13)	61.5(9)
N2	3079.6(14)	4247(3)	7317.9(12)	55.3(8)
N3	1712.8(12)	4529(3)	6520.3(12)	46.1(7)
N4	146.3(14)	3821(4)	3853.9(14)	65.0(9)
C1	4158.2(16)	1948(4)	8027.5(15)	49.0(9)
C2	4534.9(18)	1483(4)	7586.6(17)	62.7(11)
C3	5033(2)	717(5)	7725(2)	91.5(16)
C4	5152(2)	383(5)	8294(2)	88.9(15)
C5	4778(2)	787(4)	8736.4(19)	74.1(13)
C6	4286.3(18)	1565(4)	8599.5(17)	59.6(10)
C7	3637.3(17)	2857(4)	7947.6(17)	54.2(10)
C8	2581.0(17)	3735(4)	7080.7(14)	47.0(9)
C9	2043.2(16)	4673(4)	7072.0(14)	50.1(9)
C10	1775.2(17)	5444(3)	6101.8(16)	52.0(9)
C11	1480.7(17)	5304(4)	5578.7(16)	54.7(10)
C12	1114.4(15)	4223(3)	5472.1(15)	47.0(9)
C13	1071.5(19)	3288(4)	5911.7(18)	69.1(12)
C14	1370.5(19)	3459(4)	6428.2(18)	68.6(12)
C15	784.1(15)	4075(3)	4907.1(16)	48.2(9)
C16	833(2)	4970(5)	4468.2(18)	83.9(15)
C17	513(2)	4799(5)	3955.0(19)	90.1(16)
C18	94(2)	2966(5)	4283(2)	86.1(15)
C19	395(2)	3046(4)	4804.6(19)	81.9(14)
P1	3449.0(5)	4286.6(11)	5489.3(5)	63.8(4)
F1	4048.2(14)	5109(3)	5397.9(13)	122.1(11)

Atom	*x*	*y*	*z*	U(eq)
F2	3665.1(15)	3247(3)	5020.7(11)	109.7(10)
F3	3118.1(17)	5096(3)	5007.2(14)	140.8(13)
F4	3227.6(16)	5295(3)	5972.7(13)	122.3(11)
F5	3767.0(11)	3447(3)	5990.8(10)	87.5(8)
F6	2856.5(12)	3427(3)	5587.5(12)	104.5(9)
O1S	3373.5(17)	6655(3)	7852.9(15)	95.3(11)
N1S	3111.3(16)	7414(4)	8757.8(16)	69.0(10)
C1S	3101(3)	6559(5)	8337(3)	93.6(16)
C2S	3429(3)	8641(5)	8689(2)	118(2)
C3S	2755(2)	7271(6)	9291(2)	105.3(18)

Table S12 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	86(2)	124(3)	47.0(17)	6.3(17)	12.8(15)	48.7(19)
O2	84(2)	112(3)	60.7(18)	13.7(17)	25.4(17)	30.5(19)
O3	80.8(19)	41.0(16)	71.2(18)	-9.7(14)	-5.5(15)	7.1(14)
N1	54.5(19)	81(2)	48.9(19)	2.4(18)	2.9(16)	21.9(19)
N2	60(2)	52.1(19)	54.3(19)	-6.5(16)	-7.1(16)	12.3(18)
N3	52.1(18)	37.2(17)	49.1(18)	-0.7(15)	-8.8(14)	1.3(15)
N4	61(2)	75(2)	59(2)	-5.4(19)	-12.1(17)	-12(2)
C1	52(2)	52(2)	43(2)	1.8(18)	1.7(18)	0.5(19)
C2	62(3)	77(3)	49(2)	2(2)	2(2)	16(2)
C3	93(3)	118(4)	64(3)	6(3)	8(3)	46(3)
C4	85(3)	98(4)	83(3)	2(3)	-12(3)	38(3)
C5	89(3)	74(3)	59(3)	4(2)	-14(3)	12(3)
C6	64(3)	61(3)	54(2)	1(2)	5(2)	0(2)
C7	50(2)	61(3)	51(2)	0(2)	3(2)	-2(2)
C8	62(3)	44(2)	34.8(19)	0.2(17)	-2.3(18)	1(2)
C9	61(2)	44(2)	45(2)	-3.0(17)	-4.2(18)	6.9(19)
C10	64(2)	37(2)	56(2)	1.0(19)	-10(2)	-6.0(19)
C11	67(2)	42(2)	55(2)	8.7(18)	-12(2)	-5(2)
C12	48(2)	39(2)	55(2)	-4.5(19)	-5.2(18)	1.3(18)
C13	84(3)	50(3)	73(3)	11(2)	-25(2)	-24(2)
C14	83(3)	54(3)	69(3)	20(2)	-20(2)	-16(2)
C15	46(2)	43(2)	55(2)	-1.3(19)	-7.0(18)	0.0(18)
C16	97(3)	80(3)	75(3)	14(3)	-30(3)	-43(3)
C17	109(4)	94(4)	67(3)	21(3)	-27(3)	-43(3)
C18	98(4)	74(3)	85(3)	4(3)	-35(3)	-36(3)
C19	104(3)	69(3)	73(3)	15(2)	-31(3)	-34(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	80.7(8)	53.2(7)	57.5(7)	5.1(5)	-4.7(6)	-2.4(6)
F1	126(2)	104(2)	136(3)	-0.3(19)	18(2)	-56.9(19)
F2	172(3)	84(2)	73.1(17)	-21.2(15)	25.6(17)	-9.2(19)
F3	193(3)	111(2)	119(2)	57(2)	-45(2)	12(2)
F4	164(3)	85(2)	118(2)	-23.4(18)	25(2)	25(2)
F5	90.9(17)	94.8(19)	76.7(16)	11.2(14)	-20.1(14)	11.9(15)
F6	82.9(18)	114(2)	117(2)	28.0(18)	-12.6(16)	-26.6(17)
O1S	124(3)	93(3)	68(2)	-14(2)	0(2)	0(2)
N1S	73(2)	63(2)	71(2)	-5(2)	-6.8(19)	-6.8(19)
C1S	109(4)	75(4)	96(4)	-13(3)	-25(4)	3(3)
C2S	171(6)	85(4)	98(4)	-13(3)	-4(4)	-23(4)
C3S	105(4)	137(5)	73(3)	-7(3)	12(3)	-5(4)

Table S13 List of Bond lengths for **3.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.357(4)	C10	C11	1.365(5)
O2	C7	1.220(4)	C11	C12	1.380(5)
O3	C8	1.213(4)	C12	C13	1.381(5)
N1	N2	1.381(4)	C12	C15	1.487(5)
N1	C7	1.346(5)	C13	C14	1.360(5)
N2	C8	1.330(4)	C15	C16	1.354(5)
N3	C9	1.460(4)	C15	C19	1.369(5)
N3	C10	1.337(4)	C16	C17	1.377(5)
N3	C14	1.336(5)	C18	C19	1.364(6)
N4	C17	1.298(5)	P1	F1	1.574(3)
N4	C18	1.310(5)	P1	F2	1.573(3)
C1	C2	1.385(5)	P1	F3	1.552(3)
C1	C6	1.389(5)	P1	F4	1.579(3)
C1	C7	1.482(5)	P1	F5	1.587(2)
C2	C3	1.381(5)	P1	F6	1.584(3)
C3	C4	1.364(6)	O1S	C1S	1.259(6)
C4	C5	1.367(6)	N1S	C1S	1.292(6)
C5	C6	1.375(5)	N1S	C2S	1.434(6)
C8	C9	1.518(5)	N1S	C3S	1.454(5)

Table S14 lists of bond angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	N2	119.5(3)	C14	C13	C12	120.5(4)
C8	N2	N1	118.8(3)	N3	C14	C13	120.8(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	N3	C9	119.6(3)	C16	C15	C12	122.2(3)
C14	N3	C9	119.8(3)	C16	C15	C19	115.6(4)
C14	N3	C10	120.5(3)	C19	C15	C12	122.1(4)
C17	N4	C18	115.2(4)	C15	C16	C17	120.2(4)
C2	C1	C6	117.7(3)	N4	C17	C16	124.4(4)
C2	C1	C7	125.8(3)	N4	C18	C19	124.6(4)
C6	C1	C7	116.5(3)	C18	C19	C15	119.9(4)
O1	C2	C1	118.4(3)	F1	P1	F4	90.58(18)
O1	C2	C3	121.5(4)	F1	P1	F5	90.44(17)
C3	C2	C1	120.1(4)	F1	P1	F6	178.47(18)
C4	C3	C2	120.6(4)	F2	P1	F1	90.54(17)
C3	C4	C5	120.7(4)	F2	P1	F4	178.29(17)
C4	C5	C6	118.7(4)	F2	P1	F5	89.85(16)
C5	C6	C1	122.2(4)	F2	P1	F6	88.76(17)
O2	C7	N1	120.1(4)	F3	P1	F1	91.25(19)
O2	C7	C1	122.3(4)	F3	P1	F2	90.82(19)
N1	C7	C1	117.5(3)	F3	P1	F4	90.4(2)
O3	C8	N2	124.6(3)	F3	P1	F5	178.18(19)
O3	C8	C9	121.3(3)	F3	P1	F6	90.13(18)
N2	C8	C9	114.0(3)	F4	P1	F5	88.85(16)
N3	C9	C8	109.8(3)	F4	P1	F6	90.08(18)
N3	C10	C11	120.1(3)	F6	P1	F5	88.19(15)
C10	C11	C12	121.0(3)	C1S	N1S	C2S	120.5(5)
C11	C12	C13	117.1(3)	C1S	N1S	C3S	123.0(5)
C11	C12	C15	121.2(3)	C2S	N1S	C3S	116.2(4)
C13	C12	C15	121.7(3)	O1S	C1S	N1S	126.2(5)

Table S15 Hydrogen Bonding Data Sheet for **3**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	N4[1]	0.82	1.87	2.663(4)	163.1
N1	H1A	O1	0.86	1.98	2.623(4)	130.7
N2	H2	O1S	0.86	1.99	2.800(5)	156.0

Symmetry codes: [1]1/2+X,1/2-Y,1-Z.

Table S16 Calculated spin population at the b3lyp/6-31g** level for **1**

1	O	-0.4667	23	C	-0.08049
2	O	-0.52905	24	H	0.064091
3	O	-0.51058	25	C	0.155257
4	H	0.282644	26	H	0.108284
5	N	-0.36345	27	C	-0.0565
6	H	0.252962	28	H	0.082899
7	N	-0.434	29	C	0.230688
8	N	-0.32676	30	H	0.150643
9	H	0.25098	31	C	-0.04563
10	N	-0.41787	32	H	0.070946
11	C	0.596353	33	C	-0.0676
12	C	-0.1005	34	H	0.060914
13	H	0.112339	35	C	0.155749
14	C	0.121246	36	H	0.109522
15	C	0.588805	37	C	-0.10504
16	C	0.235554	38	H	0.112266
17	C	-0.07859	39	C	-0.15341
18	H	0.070974	40	H	0.19507
19	C	0.025442	41	H	0.168669
20	C	0.08244	42	C	-0.033
21	C	0.244647	43	H	0.076226
22	H	0.163579			

Table S17 Calculated spin population at the b3lyp/6-31g** level for **2**

1	O	-0.5381	23	H	0.105835
2	O	-0.50683	24	C	-0.08215
3	H	0.280678	25	H	0.066475
4	O	-0.50423	26	C	0.566115
5	N	-0.34638	27	C	-0.08436
6	H	0.267888	28	H	0.068992
7	N	-0.27868	29	C	0.229898
8	H	0.244878	30	H	0.15168
9	N	-0.43271	31	C	-0.06693
10	N	-0.41347	32	H	0.06077
11	C	0.236245	33	C	-0.10228
12	C	0.580124	34	H	0.108228
13	C	0.138885	35	C	-0.0342
14	C	0.091401	36	H	0.076911
15	C	0.022959	37	C	-0.14724
16	C	-0.06035	38	H	0.190646
17	H	0.085992	39	H	0.174175
18	C	0.158077	40	C	0.154148
19	H	0.109084	41	H	0.108745
20	C	-0.04656	42	C	0.249801
21	H	0.0734	43	H	0.151341
22	C	-0.10891			

Table S18 Calculated spin population at the b3lyp/6-31g** level for **3**

1	O	-0.46824	23	C	0.223511
2	N	-0.43745	24	C	-0.11122
3	N	-0.32431	25	H	0.110791
4	H	0.250905	26	C	0.253403
5	O	-0.51123	27	H	0.159382
6	H	0.281985	28	C	-0.06602
7	N	-0.35765	29	H	0.08422
8	H	0.248851	30	C	-0.03889
9	O	-0.51857	31	H	0.071969
10	N	-0.40531	32	C	-0.10517
11	C	0.603808	33	H	0.060692
12	C	0.224197	34	C	-0.03564
13	H	0.148935	35	H	0.076261
14	C	0.141548	36	C	0.16063
15	C	0.125227	37	H	0.101265
16	C	-0.1472	38	C	-0.09288
17	H	0.206683	39	H	0.062894
18	H	0.143094	40	C	0.153158
19	C	0.041268	41	H	0.102886
20	C	0.582546	42	C	-0.05942
21	C	-0.10632	43	H	0.059655
22	H	0.105743			

[1] Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst. C*. **2015**, *71*, 3-8.
[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.