

Supporting Information

Crown ether alkali metal TCNQ complexes revisited – the impact of smaller cation complexes on their solid-state architecture and properties

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Crystal	1	2	3.H ₂ O	4.H ₂ O	5
Empirical Formula	C ₂₂ H ₂₄ LiN ₄ O ₅	C ₄₄ H ₄₈ N ₈ Na ₂ O ₁₀	C ₃₄ H ₃₀ LiN ₈ O ₆	C ₃₄ H ₃₀ N ₈ NaO ₆	C ₄₈ H ₅₆ K ₂ N ₈ O ₁₂
Formula wt/ g mol ⁻¹	431.39	894.88	653.60	669.65	1015.20
Crystal System, space group	Monoclinic, <i>P2₁/c</i>	Triclinic, <i>P-1</i>	Triclinic, <i>P-1</i>	Triclinic, <i>P-1</i>	Monoclinic, <i>C2/c</i>
a/Å	9.8106(3)	9.2736(6)	8.3032(5)	8.3408(4)	23.6351(2)
b/Å	15.2713(6)	11.0659(7)	12.4300(7)	12.4515(6)	8.17770(10)
c/Å	14.7499(6)	11.8680(6)	16.5807(12)	16.7083(9)	26.7566(3)
α/°	90	83.741(5)	97.615(5)	102.611(4)	90
β/°	102.098(4)	89.921(4)	100.354(5)	92.029(4)	98.0070(10)
γ/°	90	68.591(6)	100.015(5)	99.896(4)	90
Vol/Å ³	2160.76(14)	1126.14(12)	1633.89(18)	1663.38(15)	5121.12(10)
Wavelength / Å	0.71075	0.71075	0.71075	0.71075	0.71075
Temp / K	100(2)	100(2)	100(2)	100(2)	100(2)
Z, Calc density (Mgm ⁻³)	4, 1.326	1, 1.320	2, 1.329	2, 1.337	4, 1.317
Abs coeff (mm ⁻¹)	0.095	0.111	0.093	0.106	0.253
Crystal	Dark purple plate	Dark blue plate	Blue plate	Blue plate	Purple plate
Crystal Dimensions/ mm ³	0.05 × 0.04 × 0.01	0.08 × 0.06 × 0.01	0.08 × 0.05 × 0.02	0.16 × 0.08 × 0.02	0.26 × 0.25 × 0.04
No. of reflections collected, R _{int}	18831, 0.0505	9835, 0.0433	20928, 0.0554	11862, .	30790, 0.0160
No. of data/restraints/parameters	4942 / 0 / 289	5096 / 0 / 289	7458 / 0 / 450	11862 / 1430 / 605	5880 / 0 / 316
Final R indices [<i>F</i> ² > 2σ(<i>F</i> ²): R ₁ , wR ₂	0.0454, 0.0789	0.0576, 0.1057	0.0767, 0.1662	0.1083, 0.1871	0.0252, 0.1466
R indices (all data): R ₁ , wR ₂	0.0870, 0.0905	0.1133, 0.1242	0.1523, 0.1938	0.1466, 0.2025	0.0272, 0.0679
Largest diff. peak and hole/e Å ⁻³	0.293 , -0.213	0.597 , -0.238	0.343 , -0.268	0.596 , -0.490	0.282 , -0.214

Table S1. Crystal structure data for **1**, **2**, **3.H₂O**, **4.H₂O**, **5**

Atom	Atom	Length/Å
Li(1)	O(21)	2.251(3)
Li(1)	O(22)	2.278(3)
Li(1)	O(23)	2.307(3)
Li(1)	O(24)	2.134(3)
Li(1)	O(25)	2.081(3)
Li(1)	N(1)	2.081(3)
O(21)	C(21)	1.4256(19)
O(21)	C(30)	1.4376(19)
O(22)	C(22)	1.4332(18)
O(22)	C(23)	1.4376(19)
O(23)	C(24)	1.4373(19)
O(23)	C(25)	1.4329(19)
O(24)	C(26)	1.4329(18)
O(24)	C(27)	1.4352(19)
O(25)	C(28)	1.4307(18)
O(25)	C(29)	1.4306(18)
C(21)	C(22)	1.501(2)
C(23)	C(24)	1.509(2)
C(25)	C(26)	1.499(2)
C(27)	C(28)	1.502(2)
C(29)	C(30)	1.500(2)
N(1)	C(9)	1.154(2)
N(2)	C(10)	1.154(2)
N(3)	C(11)	1.156(2)
N(4)	C(12)	1.152(2)
C(1)	C(2)	1.431(2)
C(1)	C(6)	1.416(2)
C(1)	C(7)	1.420(2)
C(2)	C(3)	1.366(2)
C(3)	C(4)	1.425(2)
C(4)	C(5)	1.422(2)
C(4)	C(8)	1.421(2)
C(5)	C(6)	1.369(2)
C(7)	C(9)	1.421(2)
C(7)	C(10)	1.426(2)
C(8)	C(11)	1.423(2)
C(8)	C(12)	1.426(2)

Table S2. Bond Lengths for (15-crown-5)LiTCNQ (**1**)

Atom	Atom	Atom	Angle/°
O(21)	Li(1)	O(22)	74.18(9)
O(21)	Li(1)	O(23)	132.66(13)
O(22)	Li(1)	O(23)	74.20(9)
O(24)	Li(1)	O(21)	148.94(15)
O(24)	Li(1)	O(22)	106.71(12)
O(24)	Li(1)	O(23)	74.59(9)
O(25)	Li(1)	O(21)	75.94(10)
O(25)	Li(1)	O(22)	119.03(13)
O(25)	Li(1)	O(23)	151.19(14)
O(25)	Li(1)	O(24)	76.97(10)
N(1)	Li(1)	O(21)	94.05(12)
N(1)	Li(1)	O(22)	134.75(15)
N(1)	Li(1)	O(23)	84.13(11)

Atom	Atom	Atom	Angle ^o
N(1)	Li(1)	O(24)	104.95(12)
N(1)	Li(1)	O(25)	98.99(13)
C(21)	O(21)	Li(1)	112.58(11)
C(21)	O(21)	C(30)	114.33(12)
C(30)	O(21)	Li(1)	109.60(11)
C(22)	O(22)	Li(1)	105.67(12)
C(22)	O(22)	C(23)	113.09(12)
C(23)	O(22)	Li(1)	113.29(11)
C(24)	O(23)	Li(1)	110.29(11)
C(25)	O(23)	Li(1)	110.07(11)
C(25)	O(23)	C(24)	114.24(12)
C(26)	O(24)	Li(1)	111.72(12)
C(26)	O(24)	C(27)	112.88(11)
C(27)	O(24)	Li(1)	109.36(11)
C(28)	O(25)	Li(1)	115.22(12)
C(29)	O(25)	Li(1)	115.30(12)
C(29)	O(25)	C(28)	113.36(11)
O(21)	C(21)	C(22)	106.97(12)
O(22)	C(22)	C(21)	106.56(13)
O(22)	C(23)	C(24)	110.36(13)
O(23)	C(24)	C(23)	109.49(13)
O(23)	C(25)	C(26)	107.72(13)
O(24)	C(26)	C(25)	106.48(13)
O(24)	C(27)	C(28)	106.54(12)
O(25)	C(28)	C(27)	106.12(12)
O(25)	C(29)	C(30)	105.63(13)
O(21)	C(30)	C(29)	110.49(13)
C(9)	N(1)	Li(1)	157.76(15)
C(6)	C(1)	C(2)	117.23(14)
C(6)	C(1)	C(7)	120.90(15)
C(7)	C(1)	C(2)	121.87(15)
C(3)	C(2)	C(1)	121.39(15)
C(2)	C(3)	C(4)	121.26(15)
C(5)	C(4)	C(3)	117.16(14)
C(8)	C(4)	C(3)	122.24(15)
C(8)	C(4)	C(5)	120.56(14)
C(6)	C(5)	C(4)	121.62(15)
C(5)	C(6)	C(1)	121.33(15)
C(1)	C(7)	C(9)	120.98(14)
C(1)	C(7)	C(10)	122.71(14)
C(9)	C(7)	C(10)	116.21(14)
C(4)	C(8)	C(11)	120.47(15)
C(4)	C(8)	C(12)	122.09(15)
C(11)	C(8)	C(12)	116.93(14)
N(1)	C(9)	C(7)	178.23(17)
N(2)	C(10)	C(7)	178.56(17)
N(3)	C(11)	C(8)	177.00(17)
N(4)	C(12)	C(8)	177.89(18)

Table S3. Bond Angles for (15-crown-5)LiTCNQ (**1**)

Atom	Atom	Atom	Atom	Angle/°
Li(1)	O(21)	C(21)	C(22)	-36.25(17)
Li(1)	O(21)	C(30)	C(29)	-34.12(16)
Li(1)	O(22)	C(22)	C(21)	-56.86(15)
Li(1)	O(22)	C(23)	C(24)	-34.26(17)
Li(1)	O(23)	C(24)	C(23)	-44.79(16)
Li(1)	O(23)	C(25)	C(26)	-35.28(16)
Li(1)	O(24)	C(26)	C(25)	-53.85(17)
Li(1)	O(24)	C(27)	C(28)	48.86(16)
Li(1)	O(25)	C(28)	C(27)	34.83(17)
Li(1)	O(25)	C(29)	C(30)	-46.49(17)
O(21)	C(21)	C(22)	O(22)	63.19(16)
O(22)	C(23)	C(24)	O(23)	53.05(17)
O(23)	C(25)	C(26)	O(24)	58.23(17)
O(24)	C(27)	C(28)	O(25)	-54.00(16)
O(25)	C(29)	C(30)	O(21)	51.88(17)
C(21)	O(21)	C(30)	C(29)	93.34(15)
C(22)	O(22)	C(23)	C(24)	85.95(16)
C(23)	O(22)	C(22)	C(21)	178.67(13)
C(24)	O(23)	C(25)	C(26)	-159.98(13)
C(25)	O(23)	C(24)	C(23)	79.80(16)
C(26)	O(24)	C(27)	C(28)	173.89(13)
C(27)	O(24)	C(26)	C(25)	-177.59(13)
C(28)	O(25)	C(29)	C(30)	177.67(13)
C(29)	O(25)	C(28)	C(27)	170.70(13)
C(30)	O(21)	C(21)	C(22)	-162.18(13)
C(1)	C(2)	C(3)	C(4)	-0.2(2)
C(2)	C(1)	C(6)	C(5)	-0.7(2)
C(2)	C(1)	C(7)	C(9)	1.1(2)
C(2)	C(1)	C(7)	C(10)	-175.10(15)
C(2)	C(3)	C(4)	C(5)	-0.5(2)
C(2)	C(3)	C(4)	C(8)	-178.39(15)
C(3)	C(4)	C(5)	C(6)	0.5(2)
C(3)	C(4)	C(8)	C(11)	173.27(14)
C(3)	C(4)	C(8)	C(12)	1.7(2)
C(4)	C(5)	C(6)	C(1)	0.1(2)
C(5)	C(4)	C(8)	C(11)	-4.6(2)
C(5)	C(4)	C(8)	C(12)	-176.17(15)
C(6)	C(1)	C(2)	C(3)	0.7(2)
C(6)	C(1)	C(7)	C(9)	-178.37(14)
C(6)	C(1)	C(7)	C(10)	5.4(2)
C(7)	C(1)	C(2)	C(3)	-178.75(15)
C(7)	C(1)	C(6)	C(5)	178.79(15)
C(8)	C(4)	C(5)	C(6)	178.46(14)

Table S4. Torsion Angles for (15-crown-5)LiTCNQ (1)

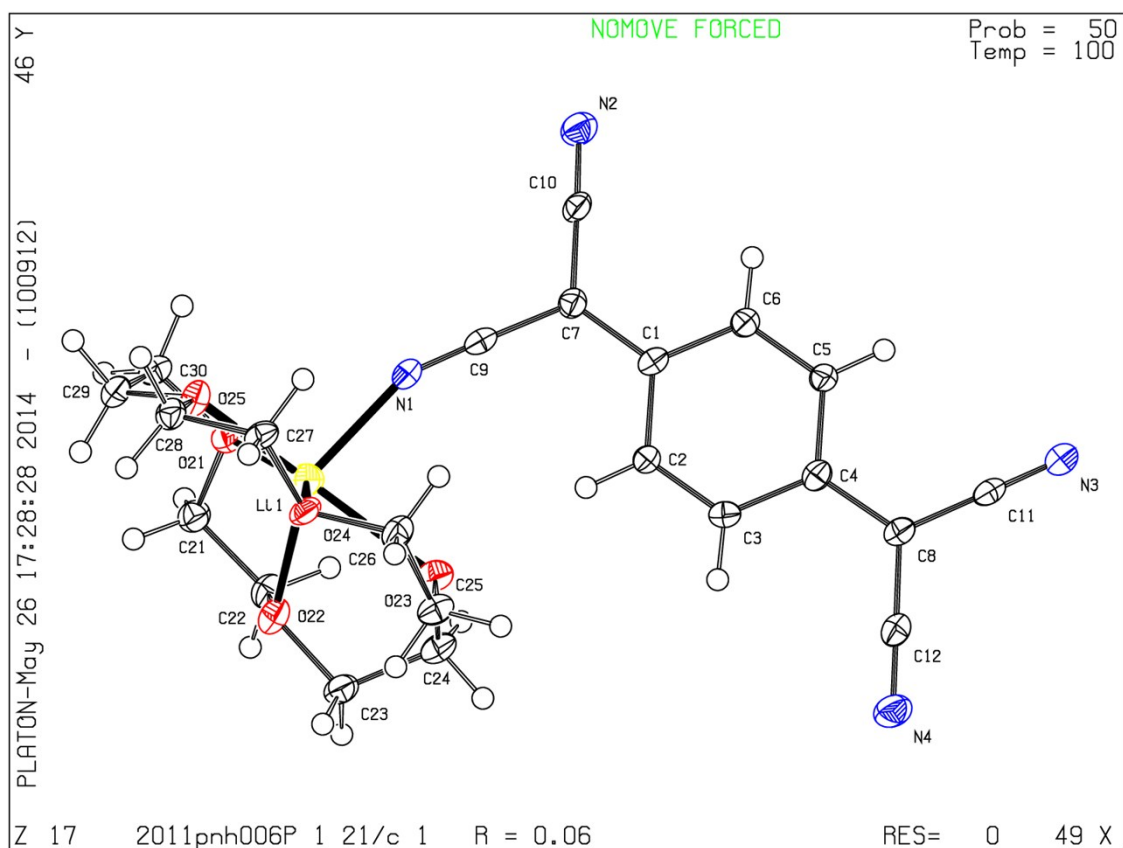


Figure S1. A fully labelled plot of the moieties within the symmetric unit of (15-crown-5)LiTCNQ (**1**)

Atom	Atom	Length/Å
Na(1)	N(1)	2.499(2)
Na(1)	N(3) ¹	2.497(2)
Na(1)	O(21)	2.4192(18)
Na(1)	O(22)	2.4012(17)
Na(1)	O(23)	2.4733(18)
Na(1)	O(24)	2.4496(18)
Na(1)	O(25)	2.4602(17)
C(1)	C(2)	1.417(3)
C(1)	C(6)	1.419(3)
C(1)	C(7)	1.412(3)
C(2)	C(3)	1.362(3)
C(3)	C(4)	1.418(3)
C(4)	C(5)	1.424(3)
C(4)	C(8)	1.413(3)
C(5)	C(6)	1.361(3)
C(7)	C(9)	1.419(3)
C(7)	C(10)	1.423(3)
C(8)	C(11)	1.413(3)
C(8)	C(12)	1.426(3)
C(9)	N(1)	1.148(3)
C(10)	N(2)	1.153(3)
C(11)	N(3)	1.151(3)
C(12)	N(4)	1.147(3)
C(21)	C(22)	1.498(3)
C(21)	O(21)	1.429(3)

Atom	Atom	Length/Å
C(22)	O(22)	1.424(3)
C(23)	C(24)	1.498(4)
C(23)	O(22)	1.427(3)
C(24)	O(23)	1.432(3)
C(25)	C(26)	1.503(3)
C(25)	O(23)	1.436(3)
C(26)	O(24)	1.423(3)
C(27)	C(28)	1.500(3)
C(27)	O(24)	1.425(3)
C(28)	O(25)	1.427(3)
C(29)	C(30)	1.501(3)
C(29)	O(25)	1.424(3)
C(30)	O(21)	1.429(3)

¹-x,2-y,2-z

Table S5. Bond Lengths for (15-crown-5)NaTCNQ (**2**).

Atom	Atom	Atom	Angle/°
N(3) ¹	Na(1)	N(1)	79.30(7)
O(21)	Na(1)	N(1)	104.10(7)
O(21)	Na(1)	N(3) ¹	90.59(6)
O(21)	Na(1)	O(23)	139.42(6)
O(21)	Na(1)	O(24)	134.08(6)
O(21)	Na(1)	O(25)	67.07(6)
O(22)	Na(1)	N(1)	160.82(7)
O(22)	Na(1)	N(3) ¹	82.74(6)
O(22)	Na(1)	O(21)	69.25(6)
O(22)	Na(1)	O(23)	70.51(6)
O(22)	Na(1)	O(24)	113.76(6)
O(22)	Na(1)	O(25)	106.00(6)
O(23)	Na(1)	N(1)	112.28(7)
O(23)	Na(1)	N(3) ¹	79.41(6)
O(24)	Na(1)	N(1)	84.04(6)
O(24)	Na(1)	N(3) ¹	135.06(7)
O(24)	Na(1)	O(23)	68.92(6)
O(24)	Na(1)	O(25)	68.45(6)
O(25)	Na(1)	N(1)	86.71(6)
O(25)	Na(1)	N(3) ¹	149.94(7)
O(25)	Na(1)	O(23)	130.64(6)
C(2)	C(1)	C(6)	116.8(2)
C(7)	C(1)	C(2)	121.4(2)
C(7)	C(1)	C(6)	121.80(19)
C(3)	C(2)	C(1)	121.9(2)
C(2)	C(3)	C(4)	121.2(2)
C(3)	C(4)	C(5)	117.1(2)
C(8)	C(4)	C(3)	121.2(2)
C(8)	C(4)	C(5)	121.7(2)
C(6)	C(5)	C(4)	121.4(2)
C(5)	C(6)	C(1)	121.5(2)
C(1)	C(7)	C(9)	121.5(2)
C(1)	C(7)	C(10)	121.43(19)
C(9)	C(7)	C(10)	116.8(2)
C(4)	C(8)	C(12)	122.3(2)
C(11)	C(8)	C(4)	121.6(2)
C(11)	C(8)	C(12)	116.0(2)

Atom	Atom	Atom	Angle/°
N(1)	C(9)	C(7)	177.8(2)
N(2)	C(10)	C(7)	177.7(2)
N(3)	C(11)	C(8)	179.3(2)
N(4)	C(12)	C(8)	178.9(3)
C(9)	N(1)	Na(1)	130.77(17)
C(11)	N(3)	Na(1) ¹	140.49(17)
O(21)	C(21)	C(22)	108.06(18)
O(22)	C(22)	C(21)	108.35(19)
O(22)	C(23)	C(24)	108.11(19)
O(23)	C(24)	C(23)	107.73(19)
O(23)	C(25)	C(26)	111.84(19)
O(24)	C(26)	C(25)	107.36(19)
O(24)	C(27)	C(28)	107.52(19)
O(25)	C(28)	C(27)	107.58(18)
O(25)	C(29)	C(30)	107.13(18)
O(21)	C(30)	C(29)	108.39(19)
C(21)	O(21)	Na(1)	114.94(13)
C(30)	O(21)	Na(1)	116.12(13)
C(30)	O(21)	C(21)	113.34(17)
C(22)	O(22)	Na(1)	107.11(13)
C(22)	O(22)	C(23)	112.86(18)
C(23)	O(22)	Na(1)	110.00(13)
C(24)	O(23)	Na(1)	108.95(13)
C(24)	O(23)	C(25)	113.64(18)
C(25)	O(23)	Na(1)	111.26(13)
C(26)	O(24)	Na(1)	114.82(14)
C(26)	O(24)	C(27)	113.07(17)
C(27)	O(24)	Na(1)	114.58(13)
C(28)	O(25)	Na(1)	107.69(12)
C(29)	O(25)	Na(1)	102.12(13)
C(29)	O(25)	C(28)	114.12(17)

¹-x,2-y,2-z

Table S6. Bond Angles for (15-crown-5)NaTCNQ (**2**)

Atom	Atom	Atom	Atom	Angle/°
C(1)	C(2)	C(3)	C(4)	0.8(3)
C(2)	C(1)	C(6)	C(5)	-2.3(3)
C(2)	C(1)	C(7)	C(9)	179.2(2)
C(2)	C(1)	C(7)	C(10)	-7.1(3)
C(2)	C(3)	C(4)	C(5)	-2.5(3)
C(2)	C(3)	C(4)	C(8)	177.0(2)
C(3)	C(4)	C(5)	C(6)	1.8(3)
C(3)	C(4)	C(8)	C(11)	3.3(3)
C(3)	C(4)	C(8)	C(12)	179.3(2)
C(4)	C(5)	C(6)	C(1)	0.6(3)
C(5)	C(4)	C(8)	C(11)	-177.2(2)
C(5)	C(4)	C(8)	C(12)	-1.1(3)
C(6)	C(1)	C(2)	C(3)	1.7(3)
C(6)	C(1)	C(7)	C(9)	-1.6(3)
C(6)	C(1)	C(7)	C(10)	172.1(2)
C(7)	C(1)	C(2)	C(3)	-179.2(2)
C(7)	C(1)	C(6)	C(5)	178.5(2)
C(8)	C(4)	C(5)	C(6)	-177.7(2)
C(21)	C(22)	O(22)	Na(1)	-60.13(19)
C(21)	C(22)	O(22)	C(23)	178.66(18)
C(22)	C(21)	O(21)	Na(1)	-27.9(2)

Atom	Atom	Atom	Atom	Angle/°
C(22)	C(21)	O(21)	C(30)	-164.71(19)
C(23)	C(24)	O(23)	Na(1)	46.4(2)
C(23)	C(24)	O(23)	C(25)	171.05(18)
C(24)	C(23)	O(22)	Na(1)	51.3(2)
C(24)	C(23)	O(22)	C(22)	170.88(18)
C(25)	C(26)	O(24)	Na(1)	43.1(2)
C(25)	C(26)	O(24)	C(27)	177.11(19)
C(26)	C(25)	O(23)	Na(1)	43.5(2)
C(26)	C(25)	O(23)	C(24)	-80.0(2)
C(27)	C(28)	O(25)	Na(1)	-58.44(19)
C(27)	C(28)	O(25)	C(29)	-171.03(18)
C(28)	C(27)	O(24)	Na(1)	-35.8(2)
C(28)	C(27)	O(24)	C(26)	-169.96(19)
C(29)	C(30)	O(21)	Na(1)	14.0(2)
C(29)	C(30)	O(21)	C(21)	150.29(19)
C(30)	C(29)	O(25)	Na(1)	68.04(17)
C(30)	C(29)	O(25)	C(28)	-176.07(18)
O(21)	C(21)	C(22)	O(22)	59.2(2)
O(22)	C(23)	C(24)	O(23)	-67.3(2)
O(23)	C(25)	C(26)	O(24)	-57.9(2)
O(24)	C(27)	C(28)	O(25)	63.7(2)
O(25)	C(29)	C(30)	O(21)	-56.3(2)

Table S7. Torsion Angles for (15-crown-5)NaTCNQ (**2**)

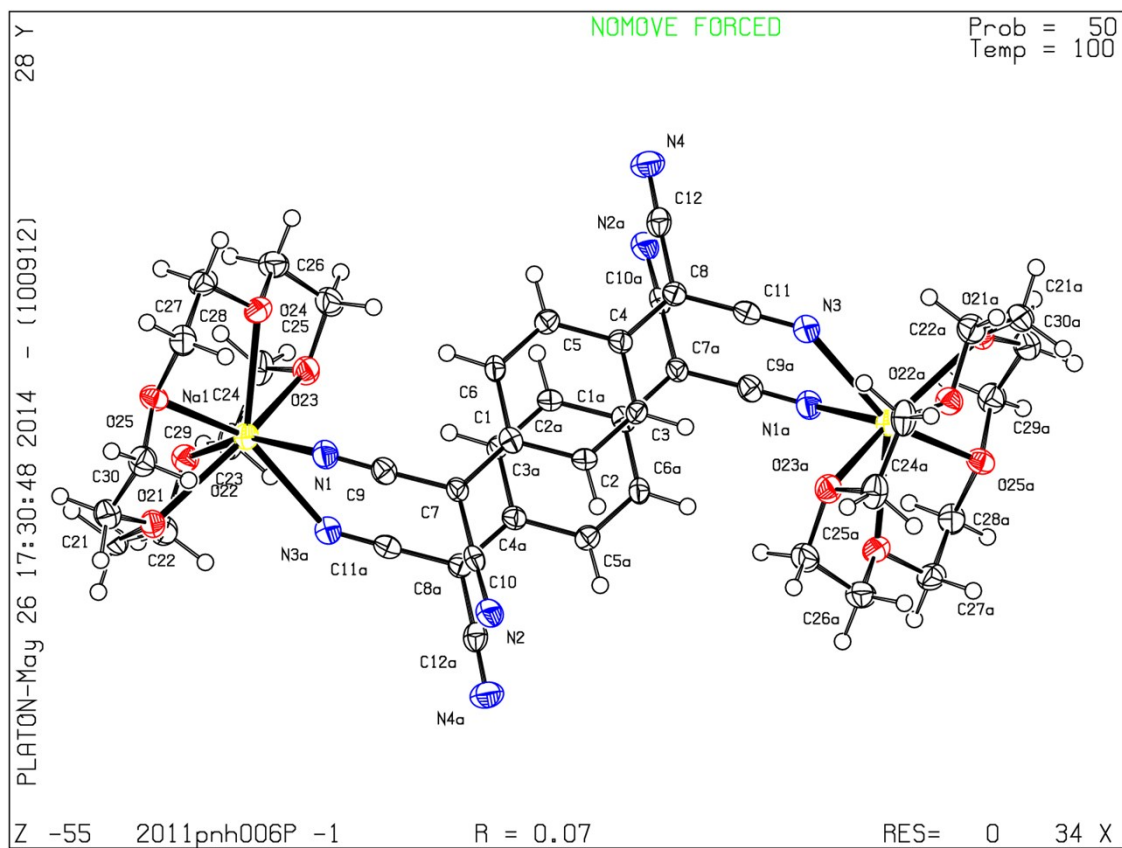


Figure S2. A fully labelled plot of the moieties within the symmetric unit of (15-crown-5)NaTCNQ (**2**)

Atom	Atom	Length/Å
O(301)	C(301)	1.431(4)
O(301)	C(310)	1.420(4)
O(301)	Li(1)	2.217(7)
O(302)	C(302)	1.429(4)
O(302)	C(303)	1.410(4)
O(302)	Li(1)	2.308(7)
O(303)	C(304)	1.425(4)
O(303)	C(305)	1.429(4)
O(303)	Li(1)	2.163(6)
O(304)	C(306)	1.421(4)
O(304)	C(307)	1.427(4)
O(304)	Li(1)	2.420(7)
O(305)	C(308)	1.423(4)
O(305)	C(309)	1.416(4)
O(305)	Li(1)	2.150(6)
O(401)	Li(1)	1.938(6)
C(301)	C(302)	1.507(5)
C(303)	C(304)	1.499(5)
C(305)	C(306)	1.509(4)
C(307)	C(308)	1.501(5)
C(309)	C(310)	1.505(5)
N(101)	C(109)	1.152(4)
N(102)	C(110)	1.150(4)
N(103)	C(111)	1.155(4)
N(104)	C(112)	1.155(4)
C(101)	C(102)	1.434(4)
C(101)	C(106)	1.437(4)
C(101)	C(107)	1.392(4)
C(102)	C(103)	1.356(4)
C(103)	C(104)	1.434(4)
C(104)	C(105)	1.434(4)
C(104)	C(108)	1.392(4)
C(105)	C(106)	1.348(4)
C(107)	C(109)	1.428(4)
C(107)	C(112)	1.421(4)
C(108)	C(110)	1.432(4)
C(108)	C(111)	1.422(4)
N(201)	C(209)	1.149(4)
N(202)	C(210)	1.156(4)
N(203)	C(211)	1.154(4)
N(204)	C(212)	1.152(4)
C(201)	C(202)	1.437(4)
C(201)	C(206)	1.433(4)
C(201)	C(207)	1.392(4)
C(202)	C(203)	1.356(4)
C(203)	C(204)	1.434(4)
C(204)	C(205)	1.431(4)
C(204)	C(208)	1.394(4)
C(205)	C(206)	1.351(4)
C(207)	C(209)	1.429(4)
C(207)	C(210)	1.419(4)
C(208)	C(211)	1.423(4)
C(208)	C(212)	1.434(4)

Table S8. Bond Lengths for (15-crown-5)Li(TCNQ)₂H₂O (**3.H₂O**)

Atom	Atom	Atom	Angle/°
C(301)	O(301)	Li(1)	109.9(2)
C(310)	O(301)	C(301)	113.2(2)
C(310)	O(301)	Li(1)	109.4(3)
C(302)	O(302)	Li(1)	114.3(2)
C(303)	O(302)	C(302)	114.1(3)
C(303)	O(302)	Li(1)	113.7(2)
C(304)	O(303)	C(305)	111.5(2)
C(304)	O(303)	Li(1)	112.1(2)
C(305)	O(303)	Li(1)	117.1(3)
C(306)	O(304)	C(307)	113.9(2)
C(306)	O(304)	Li(1)	104.3(2)
C(307)	O(304)	Li(1)	109.1(2)
C(308)	O(305)	Li(1)	117.7(2)
C(309)	O(305)	C(308)	114.4(2)
C(309)	O(305)	Li(1)	116.3(3)
O(301)	C(301)	C(302)	105.0(3)
O(302)	C(302)	C(301)	105.7(3)
O(302)	C(303)	C(304)	107.0(3)
O(303)	C(304)	C(303)	107.6(3)
O(303)	C(305)	C(306)	107.9(3)
O(304)	C(306)	C(305)	105.6(2)
O(304)	C(307)	C(308)	111.0(3)
O(305)	C(308)	C(307)	106.4(2)
O(305)	C(309)	C(310)	106.1(3)
O(301)	C(310)	C(309)	106.2(3)
O(301)	Li(1)	O(302)	71.4(2)
O(301)	Li(1)	O(304)	145.0(3)
O(302)	Li(1)	O(304)	141.4(3)
O(303)	Li(1)	O(301)	125.6(3)
O(303)	Li(1)	O(302)	72.6(2)
O(303)	Li(1)	O(304)	72.53(19)
O(305)	Li(1)	O(301)	74.0(2)
O(305)	Li(1)	O(302)	145.4(3)
O(305)	Li(1)	O(303)	129.0(3)
O(305)	Li(1)	O(304)	72.1(2)
O(401)	Li(1)	O(301)	107.7(3)
O(401)	Li(1)	O(302)	93.3(2)
O(401)	Li(1)	O(303)	113.8(3)
O(401)	Li(1)	O(304)	86.0(3)
O(401)	Li(1)	O(305)	99.0(3)
C(102)	C(101)	C(106)	117.6(3)
C(107)	C(101)	C(102)	121.7(3)
C(107)	C(101)	C(106)	120.7(3)
C(103)	C(102)	C(101)	121.2(3)
C(102)	C(103)	C(104)	121.1(3)
C(103)	C(104)	C(105)	117.6(3)
C(108)	C(104)	C(103)	121.0(3)
C(108)	C(104)	C(105)	121.4(3)
C(106)	C(105)	C(104)	121.4(3)
C(105)	C(106)	C(101)	121.2(3)
C(101)	C(107)	C(109)	121.8(3)
C(101)	C(107)	C(112)	122.6(3)
C(112)	C(107)	C(109)	115.4(3)
C(104)	C(108)	C(110)	122.6(3)
C(104)	C(108)	C(111)	121.8(3)
C(111)	C(108)	C(110)	115.6(3)
N(101)	C(109)	C(107)	178.8(3)
N(102)	C(110)	C(108)	177.7(3)
N(103)	C(111)	C(108)	178.7(3)
N(104)	C(112)	C(107)	178.6(4)

Atom	Atom	Atom	Angle/°
C(206)	C(201)	C(202)	117.6(3)
C(207)	C(201)	C(202)	120.7(3)
C(207)	C(201)	C(206)	121.6(3)
C(203)	C(202)	C(201)	121.2(3)
C(202)	C(203)	C(204)	120.8(3)
C(205)	C(204)	C(203)	118.0(3)
C(208)	C(204)	C(203)	120.6(3)
C(208)	C(204)	C(205)	121.4(3)
C(206)	C(205)	C(204)	121.1(3)
C(205)	C(206)	C(201)	121.2(3)
C(201)	C(207)	C(209)	121.4(3)
C(201)	C(207)	C(210)	121.8(3)
C(210)	C(207)	C(209)	116.7(3)
C(204)	C(208)	C(211)	122.9(3)
C(204)	C(208)	C(212)	121.2(3)
C(211)	C(208)	C(212)	116.0(3)
N(201)	C(209)	C(207)	178.7(4)
N(202)	C(210)	C(207)	178.8(4)
N(203)	C(211)	C(208)	179.0(3)
N(204)	C(212)	C(208)	178.7(3)

Table S9. Bond Angles for (15-crown-5)Li(TCNQ)₂H₂O (**3.H₂O**)

Atom	Atom	Atom	Atom	Angle/°
O(301)	C(301)	C(302)	O(302)	-59.3(3)
O(302)	C(303)	C(304)	O(303)	54.5(4)
O(303)	C(305)	C(306)	O(304)	-61.9(3)
O(304)	C(307)	C(308)	O(305)	-53.1(3)
O(305)	C(309)	C(310)	O(301)	56.3(4)
C(301)	O(301)	C(310)	C(309)	-174.2(3)
C(302)	O(302)	C(303)	C(304)	-164.6(3)
C(303)	O(302)	C(302)	C(301)	165.4(3)
C(304)	O(303)	C(305)	C(306)	167.1(3)
C(305)	O(303)	C(304)	C(303)	172.6(3)
C(306)	O(304)	C(307)	C(308)	-81.6(3)
C(307)	O(304)	C(306)	C(305)	173.3(3)
C(308)	O(305)	C(309)	C(310)	-178.0(3)
C(309)	O(305)	C(308)	C(307)	-169.8(3)
C(310)	O(301)	C(301)	C(302)	-177.2(3)
Li(1)	O(301)	C(301)	C(302)	60.2(3)
Li(1)	O(301)	C(310)	C(309)	-51.4(3)
Li(1)	O(302)	C(302)	C(301)	32.1(3)
Li(1)	O(302)	C(303)	C(304)	-31.0(4)
Li(1)	O(303)	C(304)	C(303)	-53.9(4)
Li(1)	O(303)	C(305)	C(306)	36.1(4)
Li(1)	O(304)	C(306)	C(305)	54.6(3)
Li(1)	O(304)	C(307)	C(308)	34.4(3)
Li(1)	O(305)	C(308)	C(307)	48.2(4)
Li(1)	O(305)	C(309)	C(310)	-35.4(4)
C(101)	C(102)	C(103)	C(104)	-0.8(4)
C(102)	C(101)	C(106)	C(105)	0.6(4)
C(102)	C(101)	C(107)	C(109)	-1.8(5)
C(102)	C(101)	C(107)	C(112)	-176.8(3)
C(102)	C(103)	C(104)	C(105)	1.3(4)
C(102)	C(103)	C(104)	C(108)	-179.0(3)
C(103)	C(104)	C(105)	C(106)	-0.9(4)
C(103)	C(104)	C(108)	C(110)	-0.3(5)

Atom	Atom	Atom	Atom	Angle/°
C(103)	C(104)	C(108)	C(111)	178.3(3)
C(104)	C(105)	C(106)	C(101)	-0.1(5)
C(105)	C(104)	C(108)	C(110)	179.3(3)
C(105)	C(104)	C(108)	C(111)	-2.1(5)
C(106)	C(101)	C(102)	C(103)	-0.2(4)
C(106)	C(101)	C(107)	C(109)	175.1(3)
C(106)	C(101)	C(107)	C(112)	0.2(5)
C(107)	C(101)	C(102)	C(103)	176.9(3)
C(107)	C(101)	C(106)	C(105)	-176.4(3)
C(108)	C(104)	C(105)	C(106)	179.5(3)
C(201)	C(202)	C(203)	C(204)	0.3(4)
C(202)	C(201)	C(206)	C(205)	-1.0(4)
C(202)	C(201)	C(207)	C(209)	-176.6(3)
C(202)	C(201)	C(207)	C(210)	-1.3(5)
C(202)	C(203)	C(204)	C(205)	-0.8(4)
C(202)	C(203)	C(204)	C(208)	178.9(3)
C(203)	C(204)	C(205)	C(206)	0.4(4)
C(203)	C(204)	C(208)	C(211)	0.3(5)
C(203)	C(204)	C(208)	C(212)	-179.5(3)
C(204)	C(205)	C(206)	C(201)	0.5(4)
C(205)	C(204)	C(208)	C(211)	180.0(3)
C(205)	C(204)	C(208)	C(212)	0.2(4)
C(206)	C(201)	C(202)	C(203)	0.6(4)
C(206)	C(201)	C(207)	C(209)	1.0(5)
C(206)	C(201)	C(207)	C(210)	176.3(3)
C(207)	C(201)	C(202)	C(203)	178.3(3)
C(207)	C(201)	C(206)	C(205)	-178.7(3)
C(208)	C(204)	C(205)	C(206)	-179.2(3)

Table S10. Torsion Angles for (15-crown-5)Li(TCNQ)₂H₂O (**3.H₂O**)

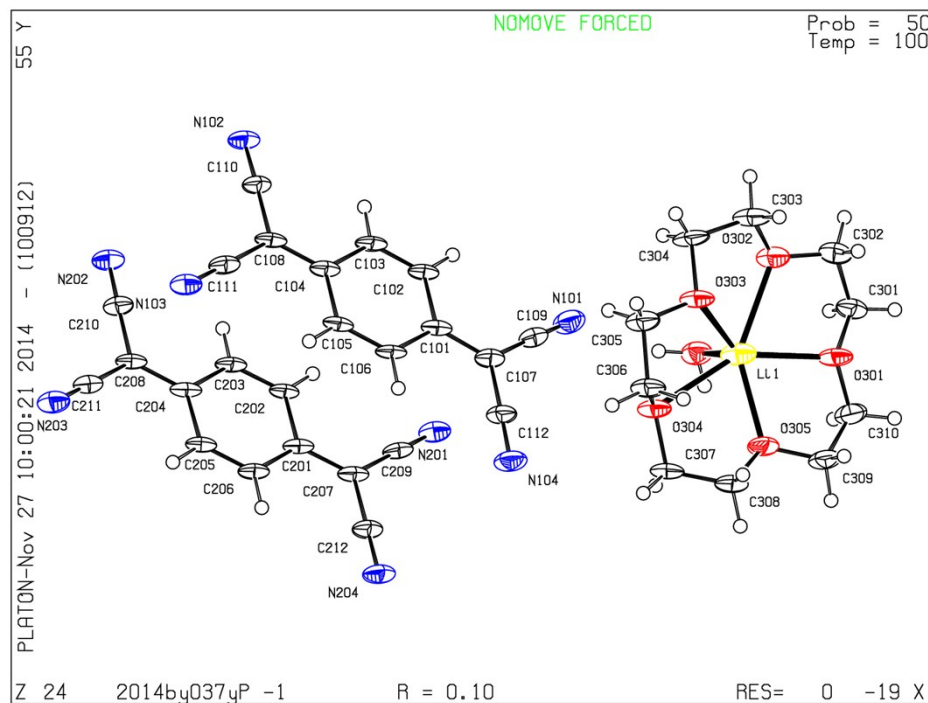


Figure S3. A fully labelled plot of the moieties within the symmetric unit of
(15-crown-5)Li(TCNQ)₂H₂O (**3.H₂O**)

Atom	Atom	Length/Å
C(301)	C(302)	1.505(10)
C(301)	O(301)	1.425(8)
C(302)	O(302)	1.430(8)
C(303)	C(304)	1.507(11)
C(303)	O(302)	1.429(8)
C(304)	O(303)	1.429(9)
C(305)	C(306)	1.503(12)
C(305)	O(303)	1.417(9)
C(306)	O(304)	1.438(8)
C(307)	C(308)	1.516(13)
C(307)	O(304)	1.417(10)
C(308)	O(305)	1.415(9)
C(309)	C(310)	1.507(11)
C(309)	O(305)	1.416(9)
C(310)	O(301)	1.430(9)
O(301)	Na(1)	2.387(4)
O(302)	Na(1)	2.396(5)
O(303)	Na(1)	2.380(5)
O(304)	Na(1)	2.374(5)
O(305)	Na(1)	2.286(5)
C(601)	C(602)	1.504(15)
C(601)	O(601)	1.418(14)
C(602)	O(602)	1.434(13)
C(603)	C(604)	1.505(16)
C(603)	O(602)	1.432(14)
C(604)	O(603)	1.425(14)
C(605)	C(606)	1.503(18)
C(605)	O(603)	1.402(14)
C(605)	C(706)	1.50(4)
C(606)	O(604)	1.432(15)
C(607)	C(608)	1.513(17)
C(607)	O(604)	1.419(15)
C(607)	O(704)	1.37(3)
C(608)	O(605)	1.415(14)
C(609)	C(610)	1.510(16)
C(609)	O(605)	1.419(14)
C(610)	O(601)	1.430(13)
O(601)	Na(1)	2.628(16)
O(602)	Na(1)	2.237(12)
O(603)	Na(1)	2.284(13)
O(604)	Na(1)	2.571(18)
O(605)	Na(1)	2.537(14)
Na(1)	O(401)	2.230(5)
Na(1)	O(704)	2.47(3)
C(101)	C(102)	1.440(6)
C(101)	C(106)	1.435(5)
C(101)	C(107)	1.393(6)
C(102)	C(103)	1.347(6)
C(103)	C(104)	1.436(5)
C(104)	C(105)	1.435(6)
C(104)	C(108)	1.390(6)
C(105)	C(106)	1.351(6)
C(107)	C(109)	1.433(6)
C(107)	C(110)	1.426(6)
C(108)	C(111)	1.437(6)
C(108)	C(112)	1.431(6)
C(109)	N(101)	1.146(5)
C(110)	N(102)	1.143(6)
C(111)	N(103)	1.152(5)
C(112)	N(104)	1.146(5)

Atom	Atom	Length/Å
C(201)	C(202)	1.434(6)
C(201)	C(206)	1.432(5)
C(201)	C(207)	1.390(6)
C(202)	C(203)	1.348(6)
C(203)	C(204)	1.435(5)
C(204)	C(205)	1.432(6)
C(204)	C(208)	1.398(6)
C(205)	C(206)	1.350(6)
C(207)	C(209)	1.423(6)
C(207)	C(210)	1.432(6)
C(208)	C(211)	1.434(6)
C(208)	C(212)	1.427(6)
C(209)	N(201)	1.148(5)
C(210)	N(202)	1.144(6)
C(211)	N(203)	1.148(5)
C(212)	N(204)	1.142(6)
O(704)	C(706)	1.43(4)

Table S11. Bond Lengths for (15-crown-5)Na(TCNQ)₂H₂O (**4.H₂O**)

Atom	Atom	Atom	Angle/°
O(301)	C(301)	C(302)	107.6(6)
O(302)	C(302)	C(301)	107.5(6)
O(302)	C(303)	C(304)	107.3(7)
O(303)	C(304)	C(303)	107.6(7)
O(303)	C(305)	C(306)	107.9(7)
O(304)	C(306)	C(305)	104.7(7)
O(304)	C(307)	C(308)	106.7(8)
O(305)	C(308)	C(307)	106.7(7)
O(305)	C(309)	C(310)	108.0(7)
O(301)	C(310)	C(309)	111.9(6)
C(301)	O(301)	C(310)	114.2(5)
C(301)	O(301)	Na(1)	109.9(4)
C(310)	O(301)	Na(1)	109.5(4)
C(302)	O(302)	Na(1)	111.1(4)
C(303)	O(302)	C(302)	113.1(6)

Atom	Atom	Atom	Angle ^o
C(303)	O(302)	Na(1)	107.2(5)
C(304)	O(303)	Na(1)	115.4(4)
C(305)	O(303)	C(304)	113.3(6)
C(305)	O(303)	Na(1)	112.8(4)
C(306)	O(304)	Na(1)	104.1(4)
C(307)	O(304)	C(306)	114.0(6)
C(307)	O(304)	Na(1)	105.3(5)
C(308)	O(305)	C(309)	114.3(7)
C(308)	O(305)	Na(1)	114.9(4)
C(309)	O(305)	Na(1)	111.2(4)
O(601)	C(601)	C(602)	107.2(17)
O(602)	C(602)	C(601)	108.5(17)
O(602)	C(603)	C(604)	107.0(18)
O(603)	C(604)	C(603)	106.8(18)
O(603)	C(605)	C(606)	112(2)
O(603)	C(605)	C(706)	128(5)
O(604)	C(606)	C(605)	110(2)
O(604)	C(607)	C(608)	102(2)
O(704)	C(607)	C(608)	133(2)
O(605)	C(608)	C(607)	108.7(18)
O(605)	C(609)	C(610)	106.8(16)
O(601)	C(610)	C(609)	109.8(16)
C(601)	O(601)	C(610)	114.0(14)
C(601)	O(601)	Na(1)	100.4(14)
C(610)	O(601)	Na(1)	106.2(11)
C(602)	O(602)	Na(1)	120.6(11)
C(603)	O(602)	C(602)	112.9(15)
C(603)	O(602)	Na(1)	112.2(11)
C(604)	O(603)	Na(1)	100.0(15)
C(605)	O(603)	C(604)	115.1(15)
C(605)	O(603)	Na(1)	101.7(13)
C(606)	O(604)	Na(1)	107.3(14)
C(607)	O(604)	C(606)	116(2)
C(607)	O(604)	Na(1)	100.9(14)
C(608)	O(605)	C(609)	111.5(16)
C(608)	O(605)	Na(1)	114.6(12)
C(609)	O(605)	Na(1)	118.0(12)
O(301)	Na(1)	O(302)	71.00(15)
O(303)	Na(1)	O(301)	139.38(18)
O(303)	Na(1)	O(302)	69.70(17)
O(304)	Na(1)	O(301)	140.37(17)
O(304)	Na(1)	O(302)	118.25(18)
O(304)	Na(1)	O(303)	70.42(18)
O(305)	Na(1)	O(301)	73.24(15)
O(305)	Na(1)	O(302)	127.26(18)
O(305)	Na(1)	O(303)	141.97(19)
O(305)	Na(1)	O(304)	71.79(16)
O(602)	Na(1)	O(601)	68.7(4)
O(602)	Na(1)	O(603)	74.7(4)
O(602)	Na(1)	O(604)	134.6(5)
O(602)	Na(1)	O(605)	134.3(4)
O(602)	Na(1)	O(704)	147.7(8)
O(603)	Na(1)	O(601)	118.7(5)
O(603)	Na(1)	O(604)	67.3(5)
O(603)	Na(1)	O(605)	129.1(5)
O(603)	Na(1)	O(704)	73.2(8)
O(604)	Na(1)	O(601)	108.9(6)
O(605)	Na(1)	O(601)	65.5(4)
O(605)	Na(1)	O(604)	64.4(5)
O(401)	Na(1)	O(301)	96.36(17)
O(401)	Na(1)	O(302)	119.63(19)

Atom	Atom	Atom	Angle ^o
O(401)	Na(1)	O(303)	94.1(2)
O(401)	Na(1)	O(304)	108.35(17)
O(401)	Na(1)	O(305)	101.60(19)
O(401)	Na(1)	O(601)	119.0(4)
O(401)	Na(1)	O(602)	107.6(3)
O(401)	Na(1)	O(603)	118.1(4)
O(401)	Na(1)	O(604)	111.7(5)
O(401)	Na(1)	O(605)	94.1(4)
O(401)	Na(1)	O(704)	84.6(9)
O(704)	Na(1)	O(601)	131.9(8)
O(704)	Na(1)	O(605)	72.0(8)
C(106)	C(101)	C(102)	117.6(4)
C(107)	C(101)	C(102)	120.8(4)
C(107)	C(101)	C(106)	121.5(4)
C(103)	C(102)	C(101)	121.3(4)
C(102)	C(103)	C(104)	121.0(4)
C(105)	C(104)	C(103)	117.9(4)
C(108)	C(104)	C(103)	121.4(4)
C(108)	C(104)	C(105)	120.7(4)
C(106)	C(105)	C(104)	121.0(4)
C(105)	C(106)	C(101)	121.2(4)
C(101)	C(107)	C(109)	122.5(4)
C(101)	C(107)	C(110)	121.6(4)
C(110)	C(107)	C(109)	115.8(4)
C(104)	C(108)	C(111)	122.2(4)
C(104)	C(108)	C(112)	122.4(4)
C(112)	C(108)	C(111)	115.4(4)
N(101)	C(109)	C(107)	178.8(5)
N(102)	C(110)	C(107)	179.0(6)
N(103)	C(111)	C(108)	178.6(5)
N(104)	C(112)	C(108)	179.0(5)
C(206)	C(201)	C(202)	117.5(4)
C(207)	C(201)	C(202)	120.7(4)
C(207)	C(201)	C(206)	121.8(4)
C(203)	C(202)	C(201)	121.3(4)
C(202)	C(203)	C(204)	121.0(4)
C(205)	C(204)	C(203)	117.8(4)
C(208)	C(204)	C(203)	121.2(4)
C(208)	C(204)	C(205)	121.0(4)
C(206)	C(205)	C(204)	121.1(4)
C(205)	C(206)	C(201)	121.3(4)
C(201)	C(207)	C(209)	122.2(4)
C(201)	C(207)	C(210)	121.6(4)
C(209)	C(207)	C(210)	116.1(4)
C(204)	C(208)	C(211)	122.6(4)
C(204)	C(208)	C(212)	121.8(4)
C(212)	C(208)	C(211)	115.6(4)
N(201)	C(209)	C(207)	178.6(5)
N(202)	C(210)	C(207)	179.4(6)
N(203)	C(211)	C(208)	178.0(5)
N(204)	C(212)	C(208)	179.3(5)
C(607)	O(704)	Na(1)	107.4(18)
C(607)	O(704)	C(706)	115(4)
C(706)	O(704)	Na(1)	116(3)
O(704)	C(706)	C(605)	97(3)

Table S12. Bond Angles for (15-crown-5)Na(TCNQ)₂·H₂O (**4.H₂O**)

Atom	Atom	Atom	Atom	Angle [°]
C(301)	C(302)	O(302)	C(303)	-165.6(7)
C(301)	C(302)	O(302)	Na(1)	-44.9(7)
C(302)	C(301)	O(301)	C(310)	-174.1(6)
C(302)	C(301)	O(301)	Na(1)	-50.6(7)
C(303)	C(304)	O(303)	C(305)	162.9(7)
C(303)	C(304)	O(303)	Na(1)	30.7(8)
C(304)	C(303)	O(302)	C(302)	-178.0(7)
C(304)	C(303)	O(302)	Na(1)	59.2(9)
C(305)	C(306)	O(304)	C(307)	-178.7(7)
C(305)	C(306)	O(304)	Na(1)	-64.5(6)
C(306)	C(305)	O(303)	C(304)	-165.3(7)
C(306)	C(305)	O(303)	Na(1)	-31.9(9)
C(307)	C(308)	O(305)	C(309)	165.9(8)
C(307)	C(308)	O(305)	Na(1)	35.6(10)
C(308)	C(307)	O(304)	C(306)	171.3(7)
C(308)	C(307)	O(304)	Na(1)	57.8(8)
C(309)	C(310)	O(301)	C(301)	89.9(8)
C(309)	C(310)	O(301)	Na(1)	-33.8(7)
C(310)	C(309)	O(305)	C(308)	177.7(7)
C(310)	C(309)	O(305)	Na(1)	-50.2(7)
O(301)	C(301)	C(302)	O(302)	64.8(8)
O(302)	C(303)	C(304)	O(303)	-60.2(10)
O(303)	C(305)	C(306)	O(304)	65.8(9)
O(304)	C(307)	C(308)	O(305)	-63.7(11)
O(305)	C(309)	C(310)	O(301)	57.0(9)
C(601)	C(602)	O(602)	C(603)	166(2)
C(601)	C(602)	O(602)	Na(1)	29(3)
C(602)	C(601)	O(601)	C(610)	171.5(18)
C(602)	C(601)	O(601)	Na(1)	58.4(19)
C(603)	C(604)	O(603)	C(605)	-173(2)
C(603)	C(604)	O(603)	Na(1)	-65(2)
C(604)	C(603)	O(602)	C(602)	-166(2)
C(604)	C(603)	O(602)	Na(1)	-26(3)
C(605)	C(606)	O(604)	C(607)	-116(3)
C(605)	C(606)	O(604)	Na(1)	-4(3)
C(606)	C(605)	O(603)	C(604)	179(3)
C(606)	C(605)	O(603)	Na(1)	72(2)
C(607)	C(608)	O(605)	C(609)	160(3)
C(607)	C(608)	O(605)	Na(1)	23(3)
C(607)	O(704)	C(706)	C(605)	151(4)
C(608)	C(607)	O(604)	C(606)	-171(2)
C(608)	C(607)	O(604)	Na(1)	73.6(19)
C(608)	C(607)	O(704)	Na(1)	2(4)
C(608)	C(607)	O(704)	C(706)	-129(6)
C(609)	C(610)	O(601)	C(601)	-168(2)
C(609)	C(610)	O(601)	Na(1)	-58.9(17)
C(610)	C(609)	O(605)	C(608)	-170(2)
C(610)	C(609)	O(605)	Na(1)	-35(3)
O(601)	C(601)	C(602)	O(602)	-63(3)
O(602)	C(603)	C(604)	O(603)	64(3)
O(603)	C(605)	C(606)	O(604)	-44(4)
O(603)	C(605)	C(706)	O(704)	-59(9)
O(604)	C(607)	C(608)	O(605)	-67(3)
O(605)	C(609)	C(610)	O(601)	64(3)
Na(1)	O(704)	C(706)	C(605)	25(8)
C(101)	C(102)	C(103)	C(104)	0.3(6)
C(102)	C(101)	C(106)	C(105)	0.8(6)
C(102)	C(101)	C(107)	C(109)	-1.3(6)
C(102)	C(101)	C(107)	C(110)	-176.2(4)

Atom	Atom	Atom	Atom	Angle/°
C(102)	C(103)	C(104)	C(105)	0.6(5)
C(102)	C(103)	C(104)	C(108)	-179.8(4)
C(103)	C(104)	C(105)	C(106)	-0.8(6)
C(103)	C(104)	C(108)	C(111)	-179.7(4)
C(103)	C(104)	C(108)	C(112)	0.7(6)
C(104)	C(105)	C(106)	C(101)	0.1(6)
C(105)	C(104)	C(108)	C(111)	-0.1(6)
C(105)	C(104)	C(108)	C(112)	-179.7(4)
C(106)	C(101)	C(102)	C(103)	-0.9(6)
C(106)	C(101)	C(107)	C(109)	176.9(4)
C(106)	C(101)	C(107)	C(110)	2.0(6)
C(107)	C(101)	C(102)	C(103)	177.3(4)
C(107)	C(101)	C(106)	C(105)	-177.4(4)
C(108)	C(104)	C(105)	C(106)	179.6(4)
C(201)	C(202)	C(203)	C(204)	0.5(6)
C(202)	C(201)	C(206)	C(205)	1.2(6)
C(202)	C(201)	C(207)	C(209)	1.1(6)
C(202)	C(201)	C(207)	C(210)	177.7(4)
C(202)	C(203)	C(204)	C(205)	-0.3(6)
C(202)	C(203)	C(204)	C(208)	-179.7(4)
C(203)	C(204)	C(205)	C(206)	0.6(6)
C(203)	C(204)	C(208)	C(211)	179.0(4)
C(203)	C(204)	C(208)	C(212)	-1.9(6)
C(204)	C(205)	C(206)	C(201)	-1.0(6)
C(205)	C(204)	C(208)	C(211)	-0.4(6)
C(205)	C(204)	C(208)	C(212)	178.8(4)
C(206)	C(201)	C(202)	C(203)	-0.9(6)
C(206)	C(201)	C(207)	C(209)	-176.2(4)
C(206)	C(201)	C(207)	C(210)	0.3(6)
C(207)	C(201)	C(202)	C(203)	-178.3(4)
C(207)	C(201)	C(206)	C(205)	178.5(4)
C(208)	C(204)	C(205)	C(206)	180.0(4)
O(704)	C(607)	C(608)	O(605)	-18(5)
C(706)	C(605)	O(603)	C(604)	164(5)
C(706)	C(605)	O(603)	Na(1)	57(5)

Table S13. Torsion Angles for (15-crown-5)Na(TCNQ)₂H₂O (**4.H₂O**)

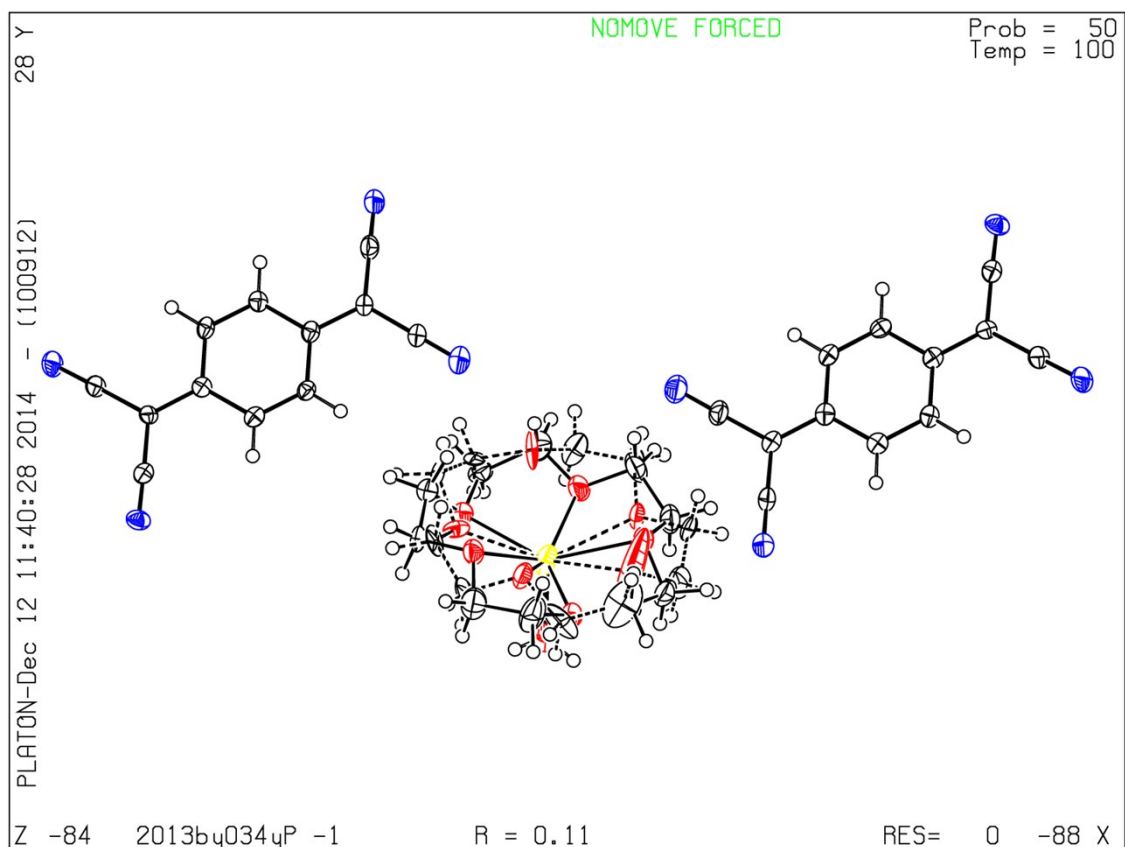


Figure S4. A fully labelled plot of the moieties within the symmetric unit of (15-crown-5)Na(TCNQ)₂·H₂O (**4.H₂O**)

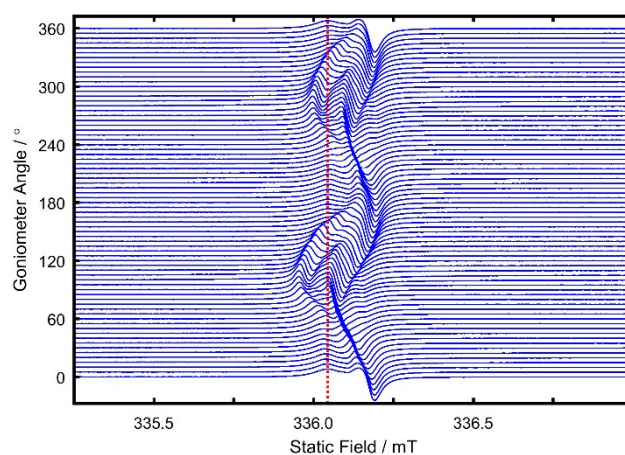


Figure S5. High-resolution EPR roadmap of TCNQ salt **1** at 300 K. At this low temperature the triplet exciton signal is very broad (see Figure 11) hence the spectrum is dominated by a narrow central feature. Using a small modulation amplitude of only 25 μ T it is possible to discern two overlapping signals i) an orientation independent species as indicated by the red line and ii) a signal with slight g -anisotropy which further splits at some orientations indicating association with the two crystallographically distinct stacks of TCNQ dimers. The same single crystal was used as in Figure S6, however note the difference in sweep width.

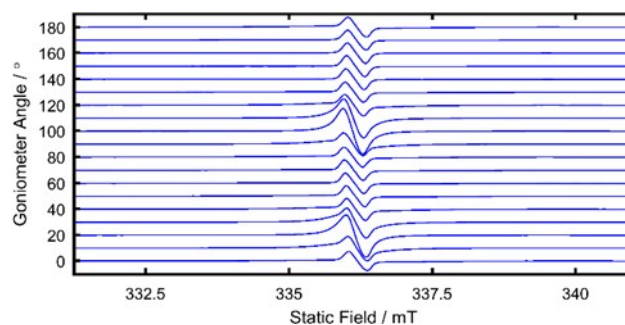


Figure S6. Orientation dependence of the EPR spectra of TCNQ salt **1** at 340K. A high modulation depth of 400 μ T is used to aid observation of the triplet exciton signal whose linewidth is strongly orientation dependent.

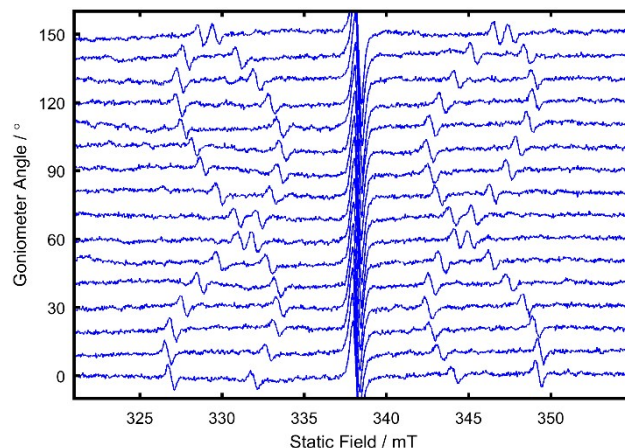


Figure S7. EPR roadmap of TCNQ salt **5** at 380 K for comparison with Figure **12**. Note that the thermally populated localised triplet exciton in this salt gives rise to four outer lines with a strong orientation dependence, one doublet arising from each of the two crystallographically distinct columns of TCNQ dimers. Although the rotation axis is such that the characteristic ‘crossing over’ of the triplet signals is not observed in this case, this has been reported previously hence we can be confident of the assignment.¹

References

- 1 R.C. Hynes *et al.*, *J Chem Soc Faraday Trans*, 1991, **87**(4), 2229–2233