Supporting Information

Novel TCNQ-stacking motifs in (12-crown-4)-complexes of Alkali Metal TCNQ Salts

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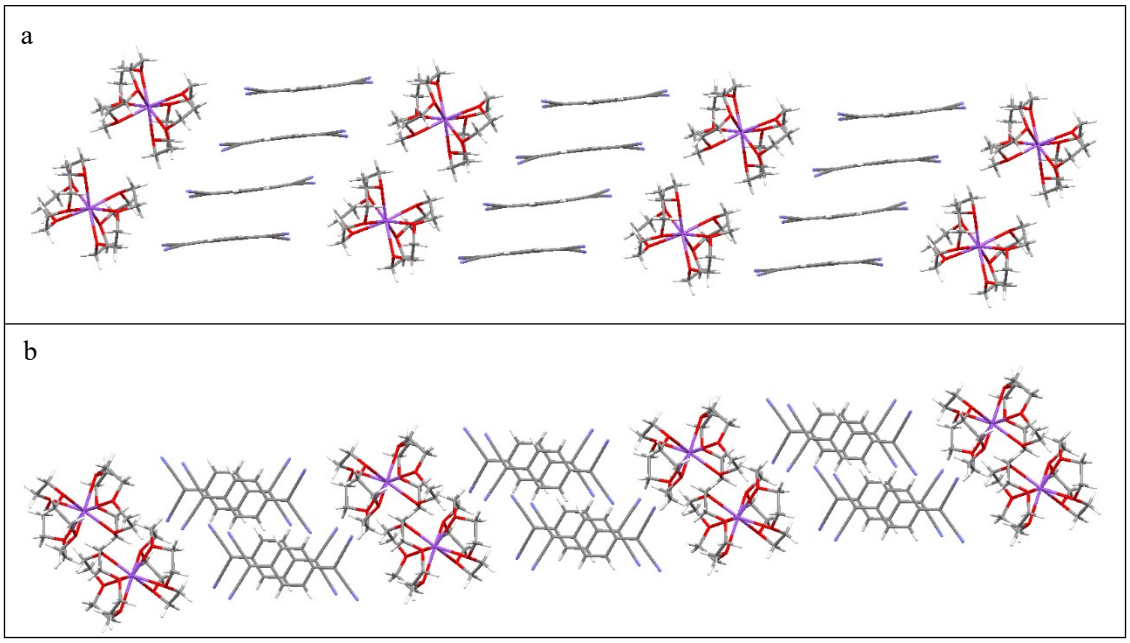

Fig. S1 Side (a) and top (b) views of the sheets of face-to-face π-stacked columns of TCNQ dimers formed by $(12\text{-crown-4})_2Na(TCNQ)_2$ (**4**), revealing the long-axis slipped of the TCNQ dimer. This packing motif is consistent with what Akutagawa and co-workers reported[1]

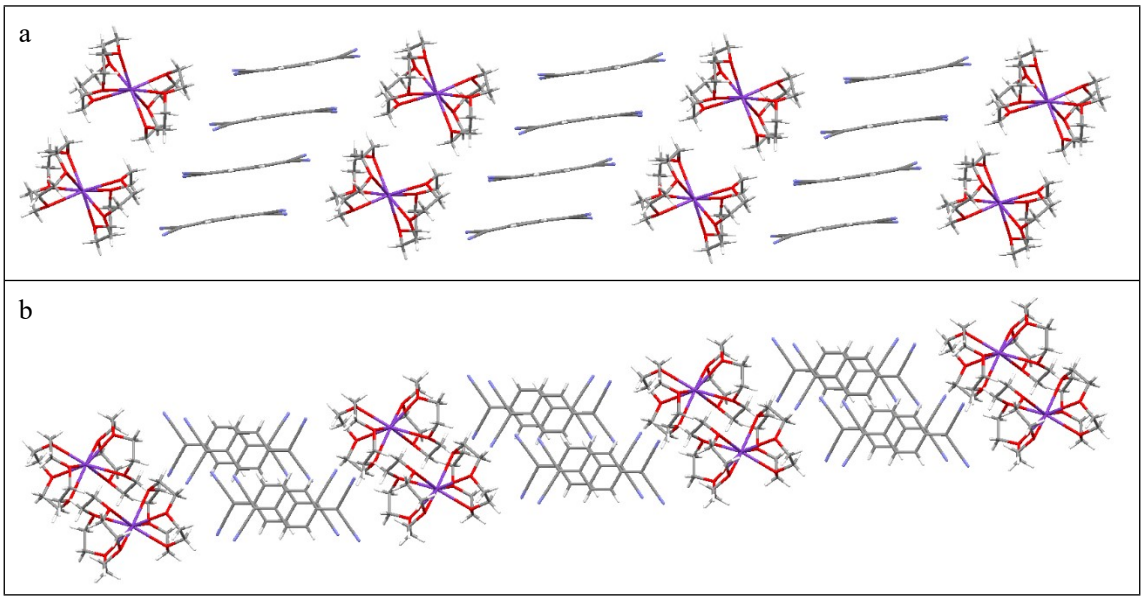

Fig. S2 Side (a) and top (b) views of the sheets of face-to-face π-stacked columns of TCNQ dimers formed by $(12\text{-crown-4})_2K(TCNQ)_2$ (**5**), revealing the long-axis slipped of the TCNQ dimer

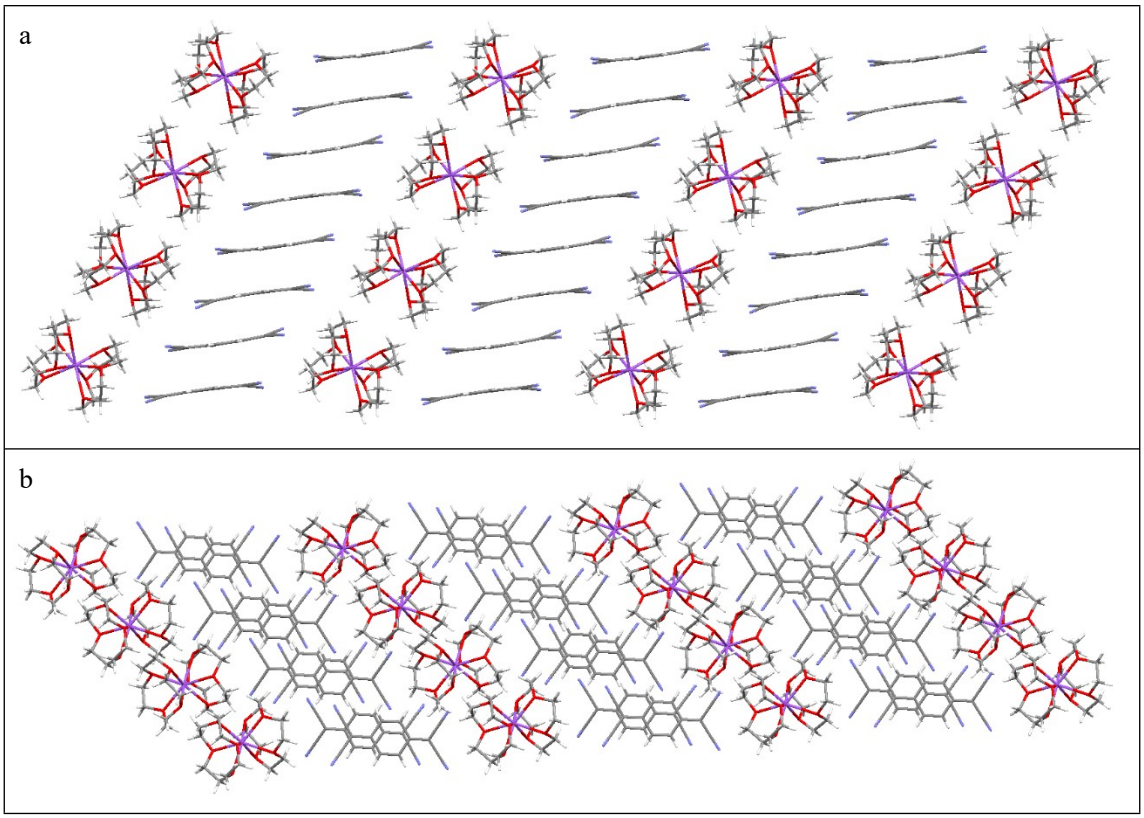

Fig. S3 Side (a) and top (b) views of the packing motif of the alternating infinite columns of TCNQ units and the corresponding cation barrels in $(12\text{-crown-4})_2Na(TCNQ)_2$ (**4**)

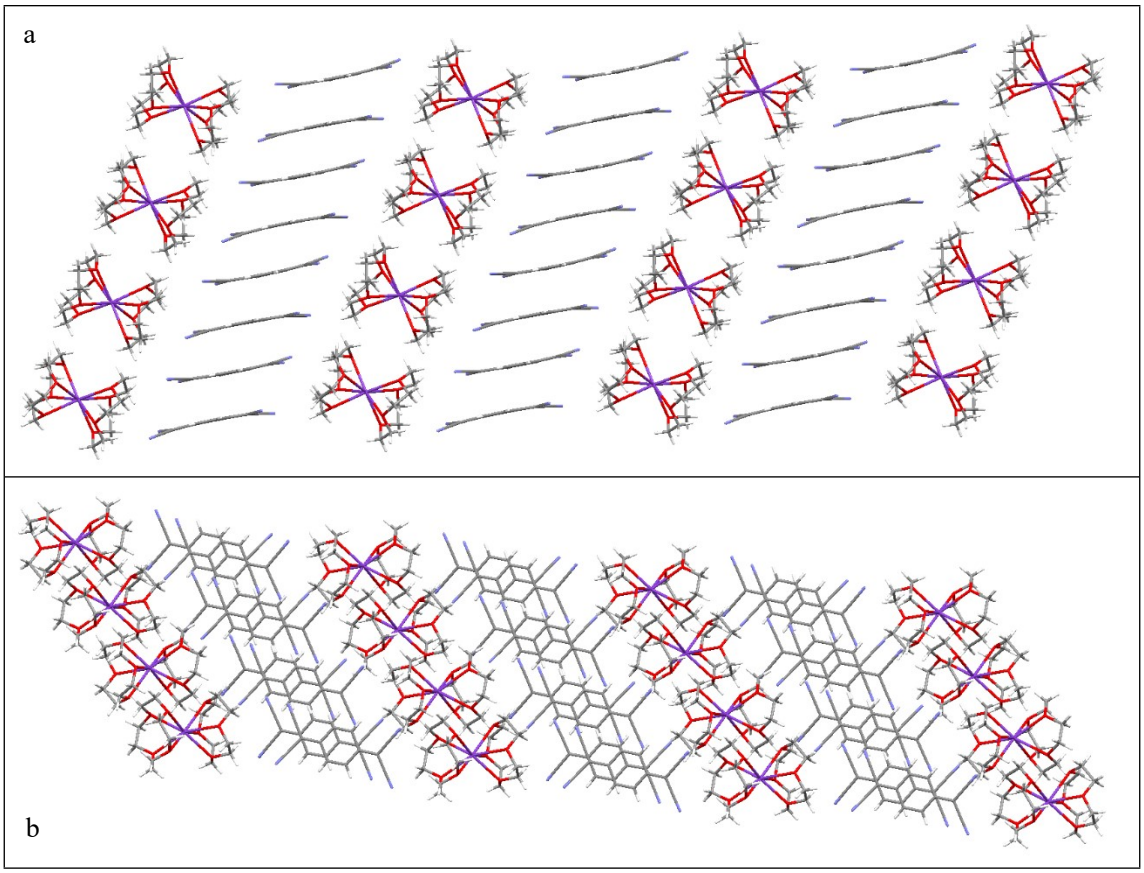

Fig. S4 Side (a) and top (b) views of the packing motif of the alternating infinite columns of TCNQ units and the corresponding cation barrels in (12-crown-4)$_2$K(TCNQ)$_2$ (**5**)

Compound reference	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{28}H_{36}LiN_4O_8$	$C_{28}H_{36}N_4NaO_8$	$C_{40}H_{40}LiN_8O_8$	$C_{40}H_{40}N_8NaO_8$	$C_{40}H_{40}KN_8O_8$
Formula weight	563.55	579.60	767.74	783.79	799.90
Temperature/K	100	120	100	100	100
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	C2/c	P-1	P-1	P-1
a/Å	16.8468(3)	17.191(2)	8.2066(4)	8.1103(2)	8.0221(2)
b/Å	20.5523(4)	20.518(2)	13.7299(6)	13.6858(4)	13.6455(3)
c/Å	8.3102(2)	8.3079(9)	17.8792(8)	17.7029(5)	18.3816(5)
α/°	90	90	72.441(4)	78.737(2)	80.507(2)
β/°	90.541(2)	90.131(6)	83.006(4)	86.244(2)	85.505(2)
γ/°	90	90	86.623(4)	85.714(2)	85.457(2)
Volume/Å^3	2877.20(10)	2930.4(5)	1905.87(16)	1919.11(9)	1973.99(9)
Z	4	4	2	2	2
Reflections collected	24070	8484	23161	24017	25643
Independent reflections	2545	3351	8699	8743	9014
	R_{int}=0.0600	R_{int}=0.1059	R_{int}=0.0517	R_{int}=0.0224	R_{int}=0.0241
	R_{sigma}=0.0304	R_{sigma}=0.1351	R_{sigma}=00872	R_{sigma}=0.0302	R_{sigma}=0.0299
Data/restraints/parameters	2545/474/296	3351/544/295	8699/0/514	8743/0/514	9014/0/538
Final R indexes [I>=2σ (I)]	R_1=0.0388	R_1=0.0839	R_1=0.0529	R_1=0.0375	R_1=0.0405
	wR_2=0.0929	wR_2=0.1982	wR_2=0.0987	wR_2=0.0879	wR_2=0.0976
Final R indexes [all data]	R_1=0.0554	R_1=0.1905	R_1=0.1237	R_1=0.0583	R_1=0.0597
	wR_2=0.1014	wR_2=0.2922	wR_2=0.1151	wR_2=0.0946	wR_2=0.1042
Deposition number	2101940	2101941	2101942	2101943	2101944

Table S1. Crystallographic information of TCNQ complexes **1-5** in this study

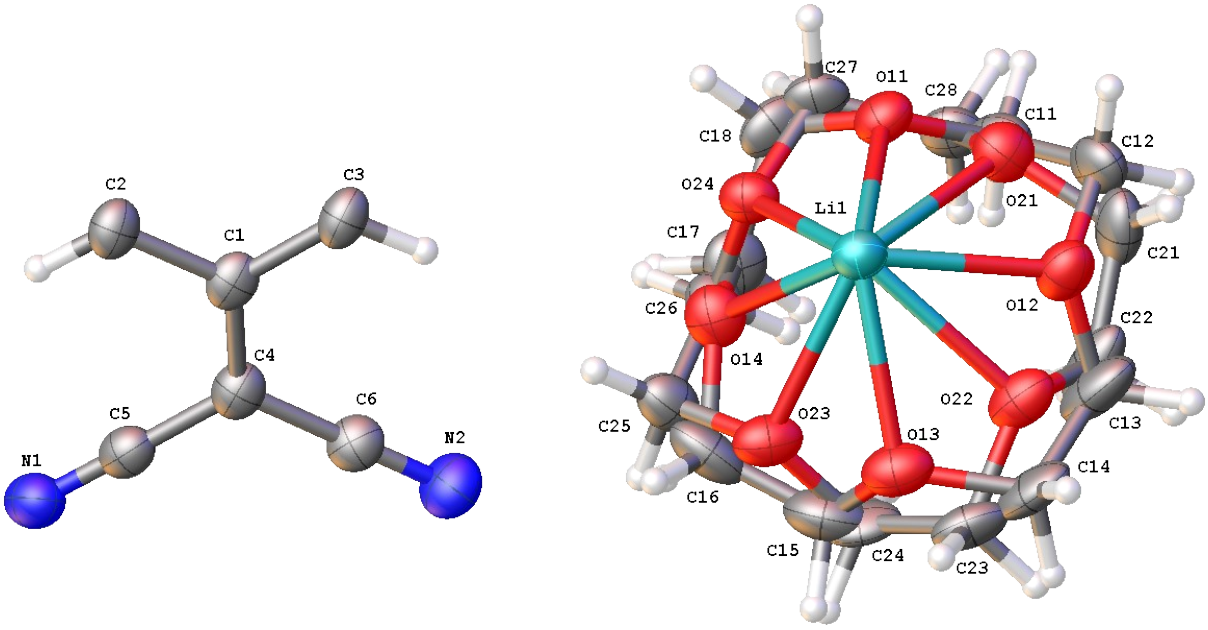

Fig. S5 A fully labelled plot of the moieties within (12-crown-4)$_2$Li(TCNQ) (**1**) in this study.

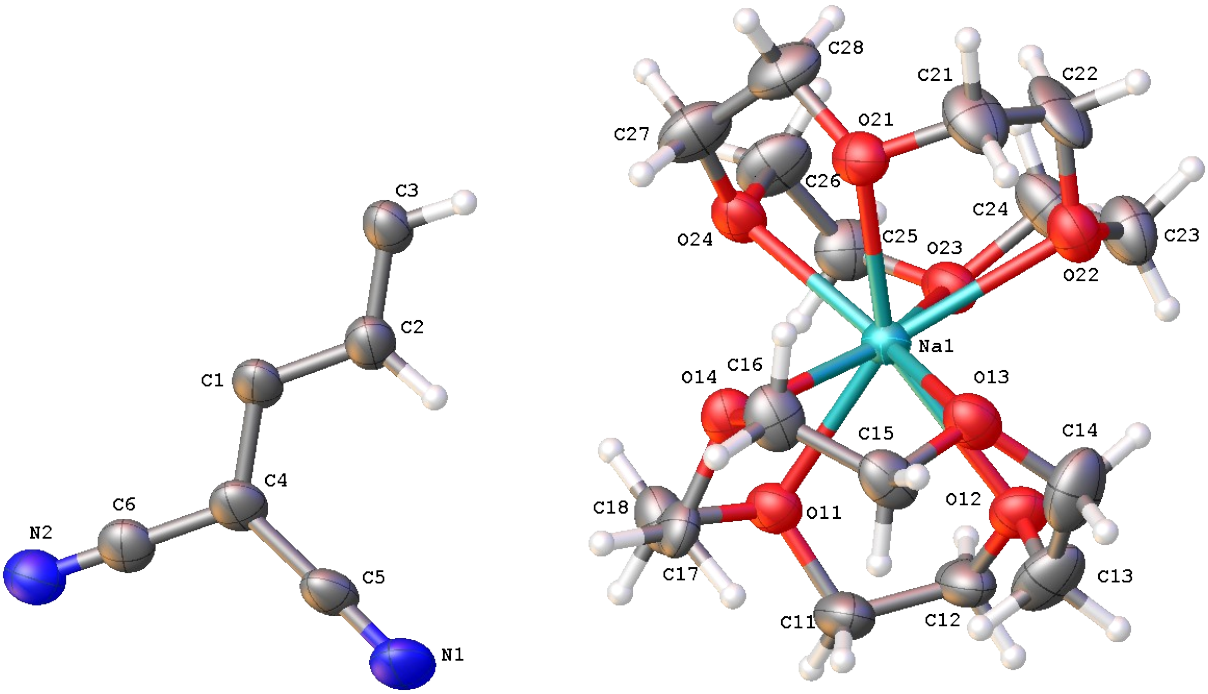

Fig. S6 A fully labelled plot of the moieties within (12-crown-4)$_2$Na(TCNQ) (**2**) in this study.

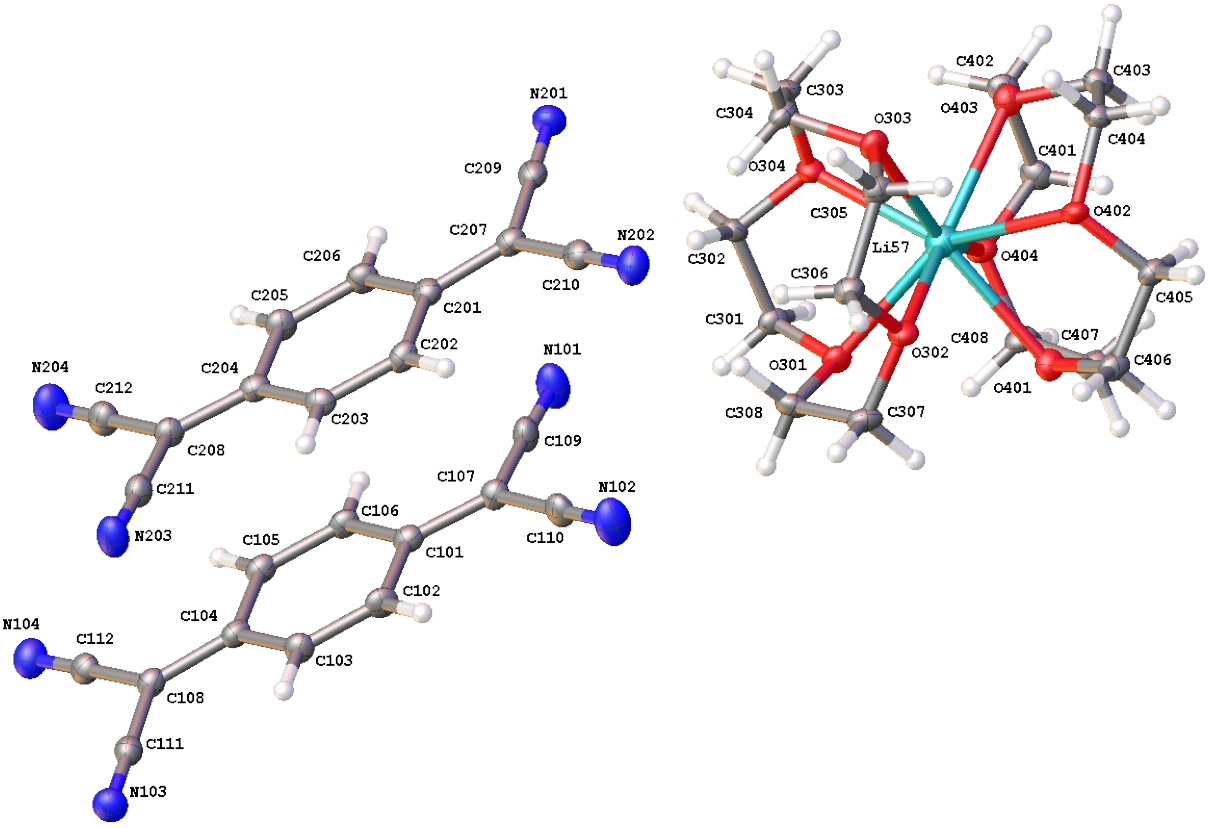

Fig. S7 A fully labelled plot of the moieties within (12-crown-4)$_2$Li(TCNQ)$_2$ (**3**) in this study.

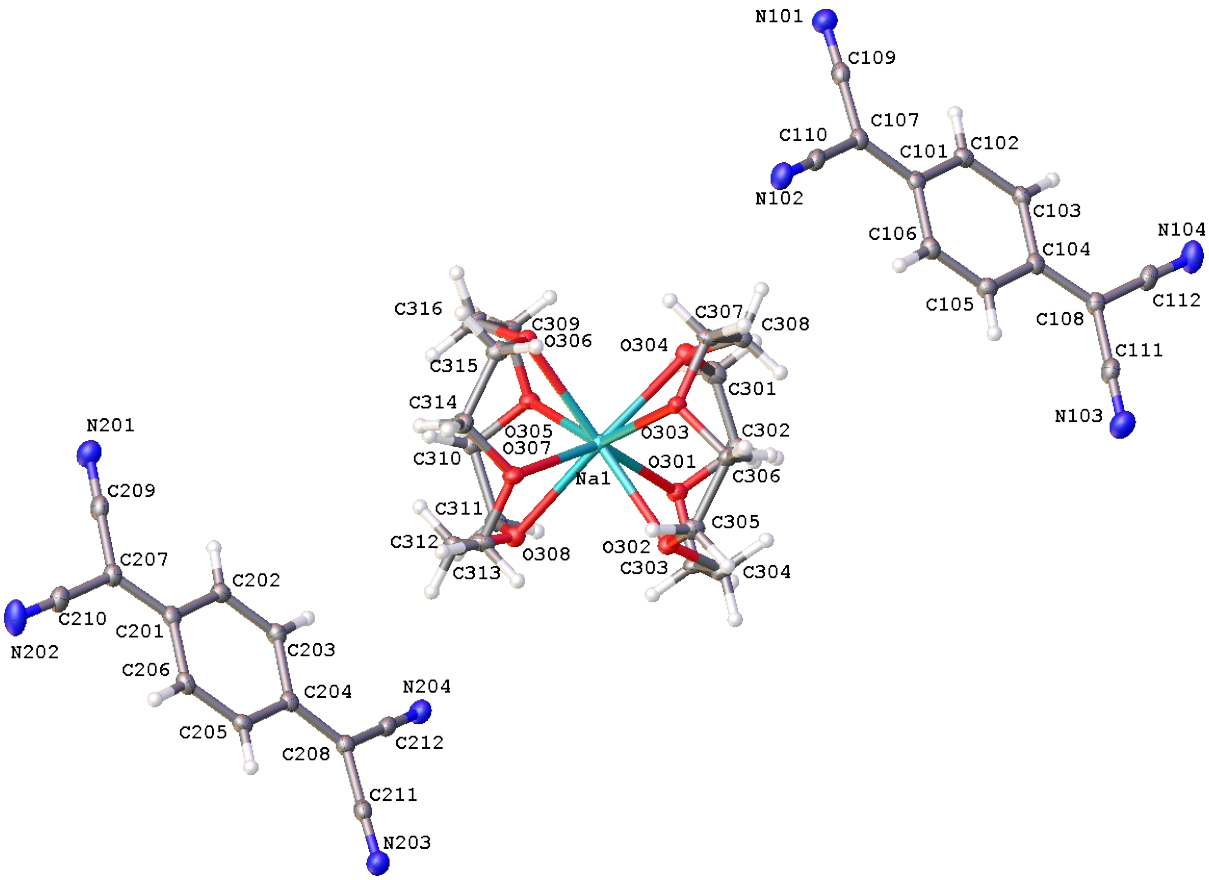

Fig. S8 A fully labelled plot of the moieties within (12-crown-4)$_2$Na(TCNQ)$_2$ (**4**) in this study.

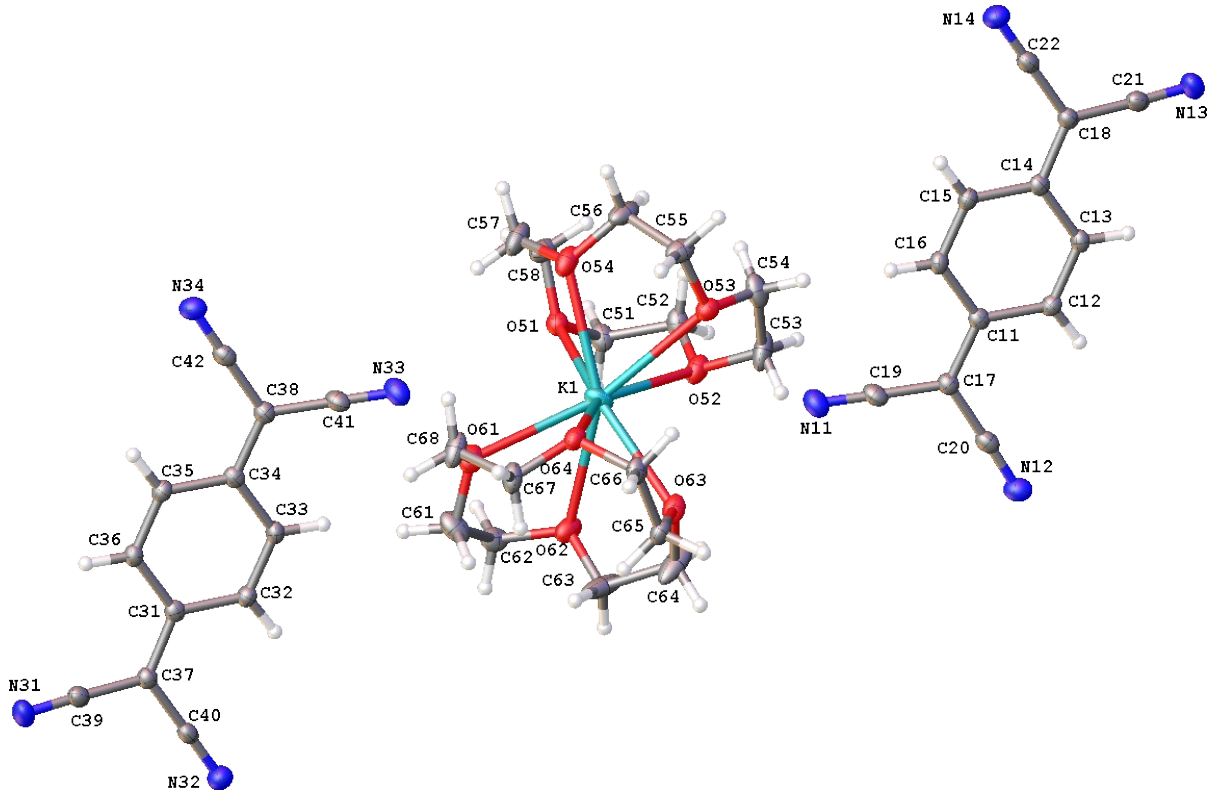

Fig. S9 A fully labelled plot of the moieties within (12-crown-4)$_2$K(TCNQ)$_2$ (**5**) in this study.

Reference

(1) K. Sambe, N. Hoshino, T. Takeda, T. Nakamura, T. Akutagawa, *Cryst. Growth Des.,* 2020, **20,** 3625-3634.