Electronic Supplementary Material (ESI) for Nanoscale.

Increasing the thermopower of crown-ether-bridged anthraquinones

Supplementary Informantion

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1. Geometries of molecules and complexes

The DFT code (SIESTA) was used to obtain fully relaxed geometries of the isolated molecules **1** and **2**, and their complexes with tetrathiafulvalene (TTF), tetracyanoethylene (TCNE), alkali cations and their couterions BF_4 and PF_6**. C**omplexes were formed by adding an alkali cation and its counter ion to molecule **1** or **2 (**single cation). In the same way**,** the second cation and its counter ion added to configuration to form sandwich case. In both cases (single and double cation), TTF or TCNE has added to the complexes to form the final configuration (for instance, **AQ 15C5 + (PF_6^- + Na^+)** + **TCNE**).

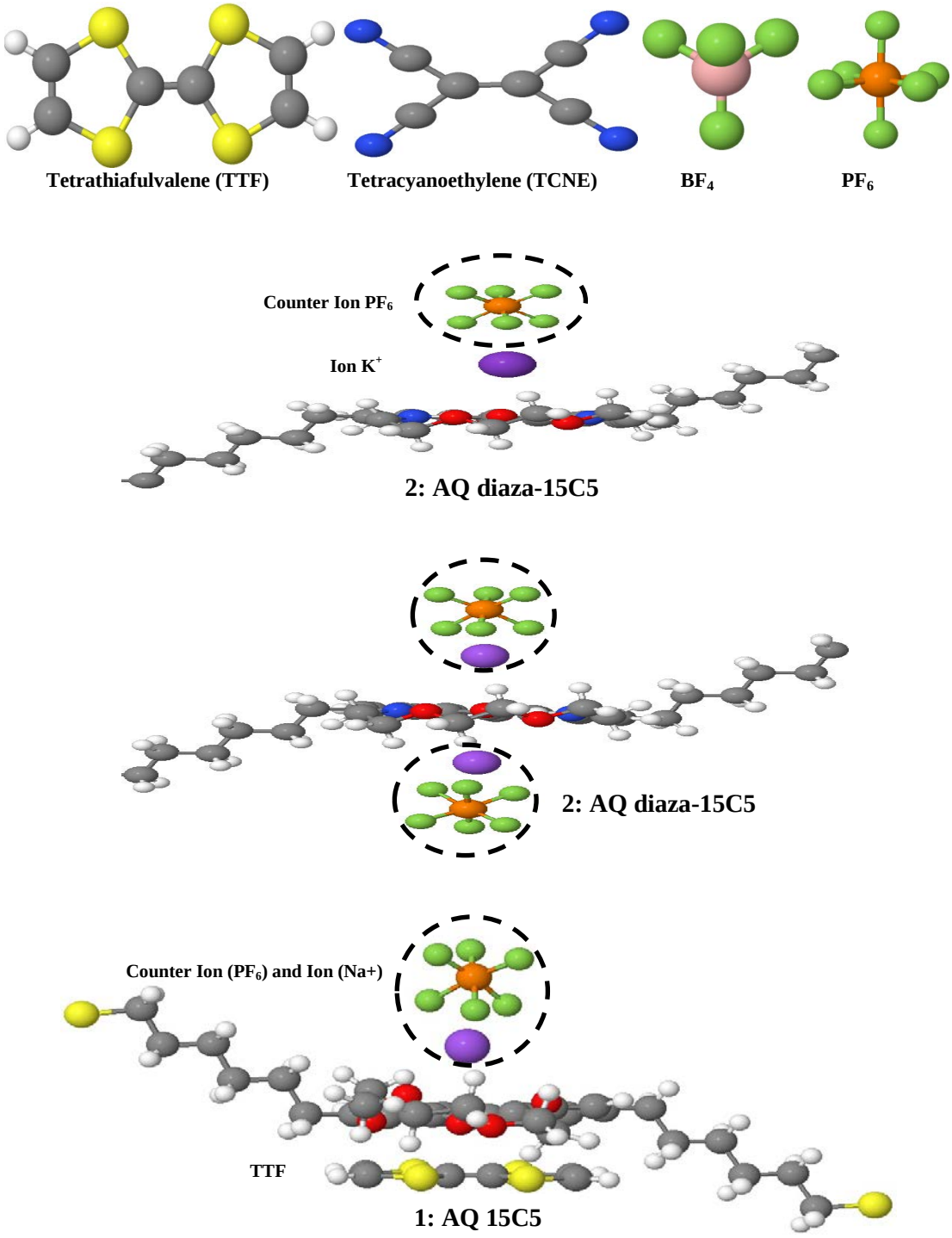
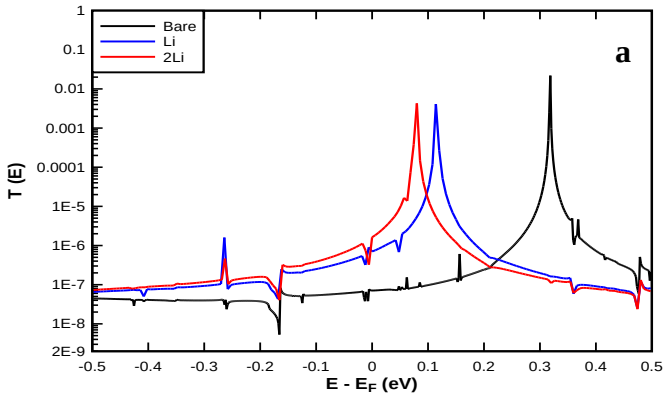
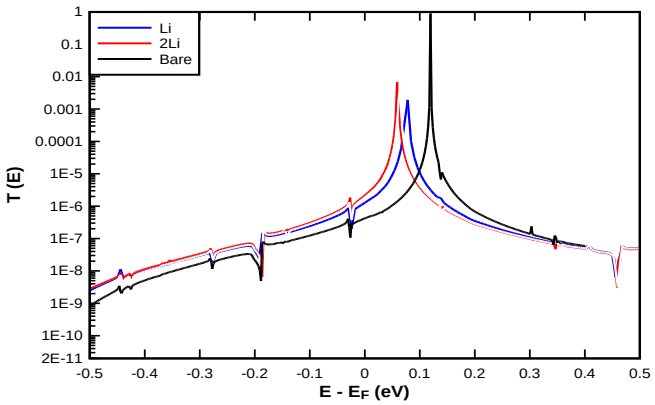


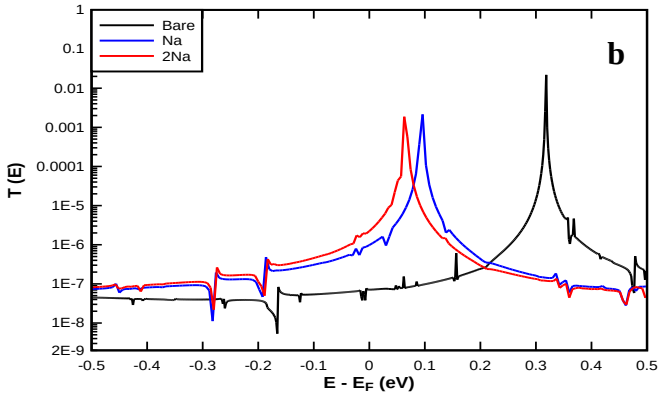
Figure S1 Examples of fully relaxed geometries. The first row shows isolated molecules of TTF, TCNE, BF_4 and PF_6. The second row shows a complex of **2** (ie AQ diaza-15C5) with (PF_6^- + K^+) The third row shows a complex **2** with two (PF_6^- + K^+)s. The fourth row shows a complex of **1 (**AQ 15C5) with TTF and (PF_6^- + Na^+)

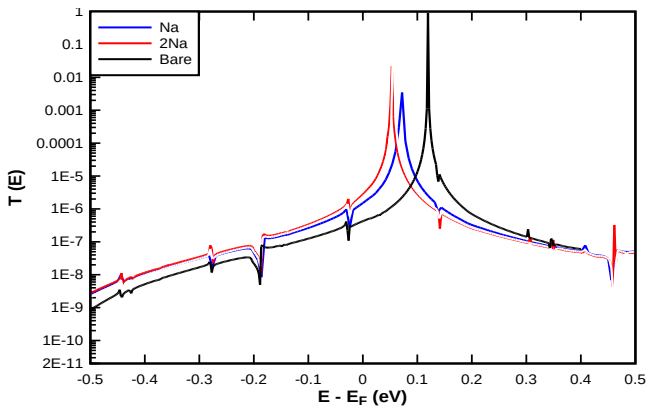
2. Transmission coefficients as a function of energy

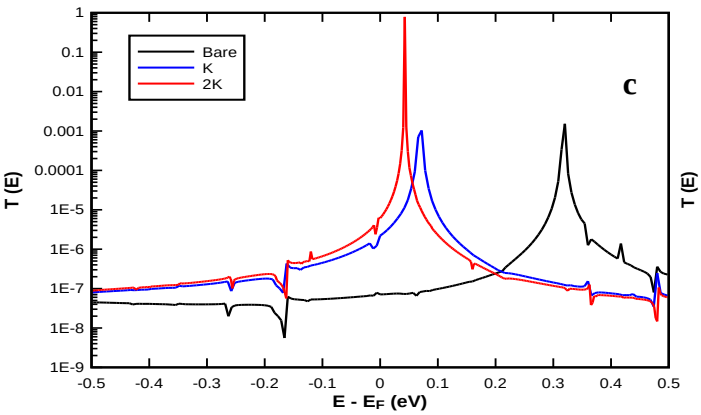
The figures below show the transmission coefficient T(E) calculated for the bare molecule, bare molecule + single alkali cation and bare molecule + two alkali cations, for three different cations: Li^+, Na^+ and K^+ , for both molecules **1** and **2**.

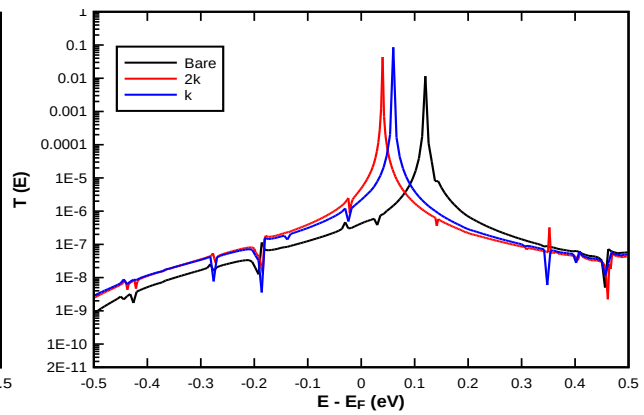

Bare
Li
2Li
a
T (E)
E - E_F (eV)


Li
2Li
Bare
T (E)
E - E_F (eV)


Bare
Na
2Na
b
T (E)
E - E_F (eV)


Na
2Na
Bare
T (E)
E - E_F (eV)


Bare
K
2K
c
T (E)
E - E_F (eV)


Bare
2k
k
T (E)
E - E_F (eV)

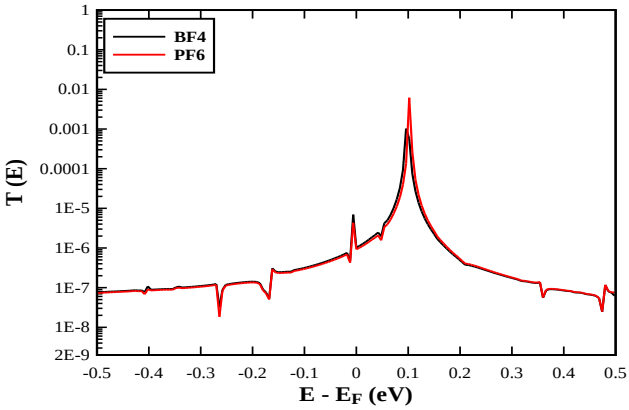

BF4
PF6
T (E)
E - E_F (eV)

Figure S2 | Zero bias transmission coefficient, $T(E)$ of 2 (left column) and 1 (right column) with a single cation and double cations, (a) Li^+, (b) Na^+ and (c) K^+, The bottom panel shows T(E) obtained using different counter ions BF_4 and PF_6 with (NC + Li^+)

3. Calculated thermopower as a function of temperature

Thermopower calculated from figure S2 using eq.2, for single and double cations of Li^+, Na^+ and K^+.

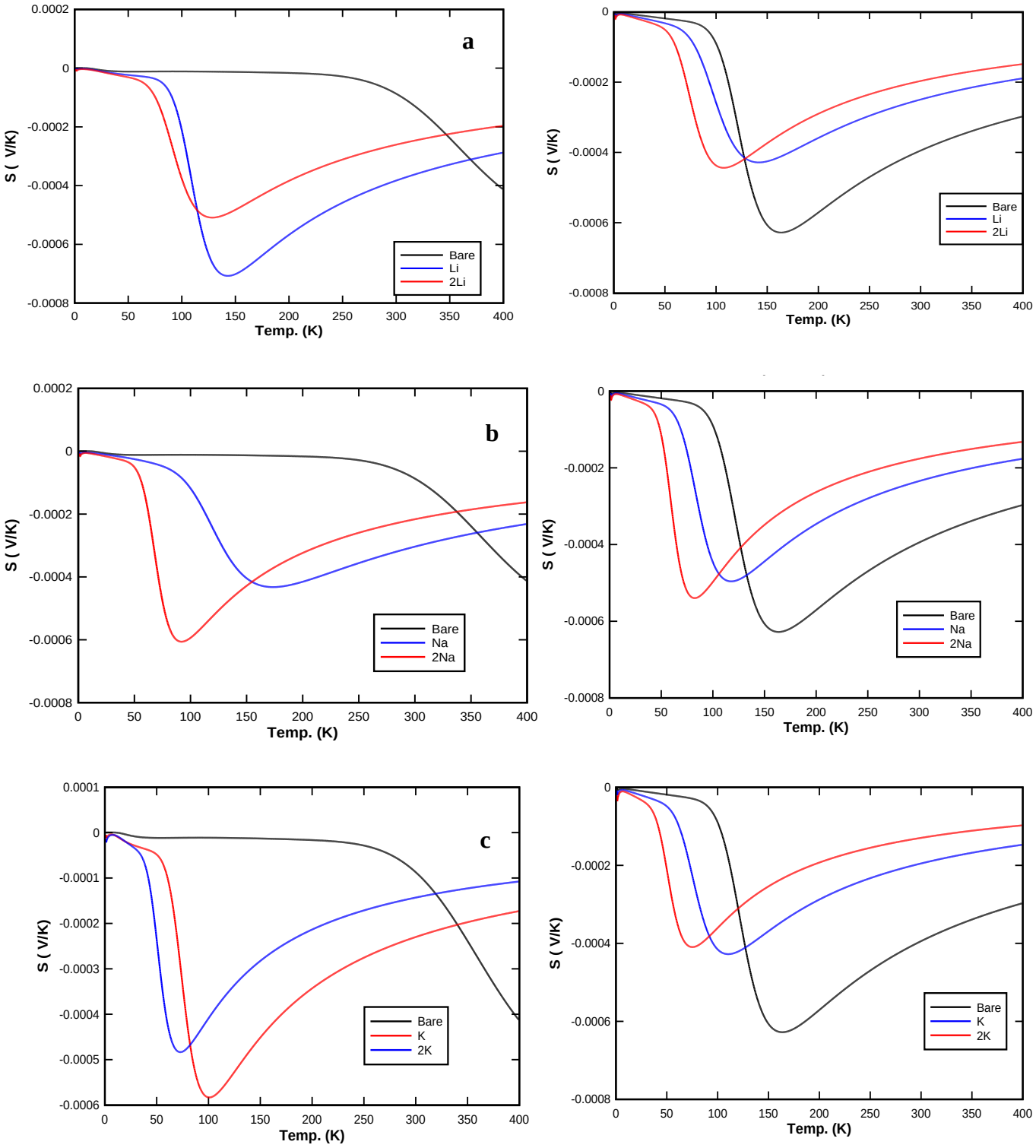


Figure S3 | Thermopowers from Figure S2. left (**2**), right (**1**)

4. Calculated thermopower for complexes with various dopants and cations

Thermopower calculated using eq.2 for two dopants TTF and TCNE with single and double alkali Li^+, Na^+ and K^+. Left figures, NC + TTF yield the highest S and the bare is the lowest, complexes varying between them. Similar behaviour at high T, but at low T some complexes are as good as OC + TTF.

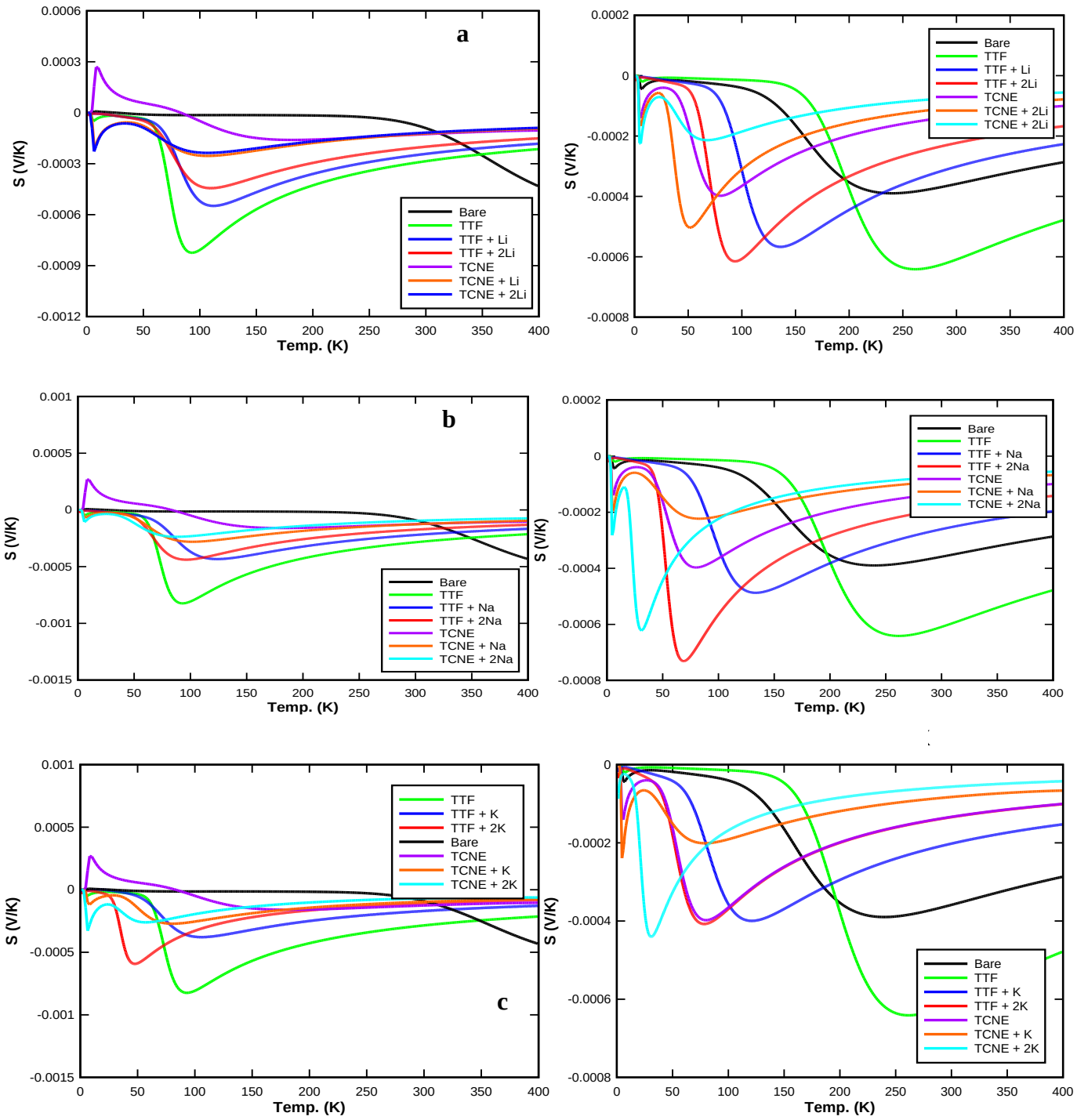


Figure S4 | Thermopower for bare molecule and with TTF and TCNE + three different alkalis for **2** left and **1** right.