Supporting Information

A computational study of lithium interaction with tetracyanides molecules

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1. Comparison between the interaction energies of Li attached to a TCNE molecule and inserted into a TCNE crystal.

TCNE crystal in the monoclinic phase was modelled using a periodic DFT code (SIESTA),¹ a DZP basis, the PBE functional,² and the dispersion correction by Grimme.³ Core electrons were modelled with Troullier-Martins pseudopotentials.⁴ For comparison, Li-TCNE (molecule) E_{int} was also recomputed in SIESTA and is in good agreement with Gaussian results (Fig. 2 of the main text). The difference of E_{int} induced by the crystal structure could therefore be up to 2 eV.



Fig. S1 *E*_{int} of Li attached to TCNE molecule and stored in TCNE crystal (SIESTA). The no. of Li refers to attached/stored Li atoms per TCNE unit.

2. Effect of solvent on interaction energy of Li with TCNE.

Fig. S2 compares E_{int} computed in vacuum and using a PCM (polarizable continuum model) solvent model with a static relative permittivity $\epsilon = 64.9$ and a dynamic relative permittivity of $\epsilon = 2.02$ which simulates the propylene carbonate (PC) solvent.⁵ Interaction with the solvent could therefore enhance E_{int} by up to 1 eV.



Fig. S2 Solvent Effect for Li attachment to TCNE molecule (Gaussian 09).

3. Hirshfeld charges on Li atoms in Li_n-TCNE and Li_n-TCNQ complexes.

Hirshfeld charges⁶ were also calculated by Gaussian 09, which show positive charges for each Li atom in the Li_n-TCNE and Li_n-TCNQ complexes.



Fig. S3 Hirshfeld charge on Li atoms in Li_0 -TCNE (left) and Li_0 -TCNQ (right) complexes. The line shows the trend of average charge per Li atom.

4. Note on relation between E_{int} and voltages

We can estimate the *average* voltage up to a concentration x of Li from eq. 4 of Ref. 36:

$$V_{aver} = -\Delta G/(xF)$$

where F is Faraday constant and ΔG is commonly approximated with internal energy.³⁶ We note that we do not estimate here the voltage curve V(x) which requires a derivative by concentration, as the derivative is not here defined in a practically meaningful way (the "concentration" axis is very discrete).

References

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