

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

A computational study of lithium interaction with tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) molecules

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Y. Chen^a and S. Manzhos^a

Tetracyanide molecules such as tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) have been proposed as promising candidate materials for organic battery electrodes, including lithium ion as well as sodium ion batteries. Their high theoretical capacities are in particular due to the possibility to store more than one alkali atom per molecule. Here, we present a density functional theory study of lithium attachment to TCNE and TCNQ. Trends in the Li binding strengths (which determines the electrode voltage) are presented between TCNE and TCNQ and a function of the number of attached Li atoms. We show that multiple Li attachment induces non-trivial changes in the electronic structure. Electron donation from Li/Na is possible to higher (than LUMO) unoccupied molecular orbitals as well as Li-centered orbitals. Strain effects induced by Li attachment lead to significant changes in the electronic structure and can induce changes in orbital ordering. A cyclic structure stabilized by Li attachment to TCNE is identified. We conclude that design of organic electrode materials should consider the energies of higher (than LUMO) orbitals as well as effects of structural changes on the electronic structure.

Introduction

Li ion batteries are the electrochemical battery technology providing the highest energy density, cycling rate and cycling life among commercial battery technologies.¹ However, they still require improvements.² Especially for efficient grid storage for renewable but intermittent sources of electricity (such as solar and wind) and price arbitrage, rapid charge-discharge (within minutes) is required,^{3,4} which is beyond that of present commercial Li ion batteries.² Using Li ion batteries for grid (i.e. large-scale) storage would also put a strain on materials supply, with large-scale and sustainable supply of electrode materials taking center stage. For example, about 30% of global cobalt production is consumed by Li ion batteries.⁵ Organic electrodes are a way to achieve simultaneously high rate (high power) and environment-friendly batteries. In recent years, significant progress in the development of organic electrodes has been made.⁶ Capacities on the order of 1,000 mAh/g (i.e. competitive with inorganic electrodes) and rates of up to 1000C (unprecedented for inorganic electrodes) have been reported.⁶⁻⁸ Moreover, organic electrodes are also promising for post-Li storage,^{9,10} which will have to be developed to make massive deployment of electrochemical batteries feasible.¹¹ Organic electrodes can also be fabricated from sustainable and non-toxic inputs such as biomass.^{6,12,13}

A number of experimental works on different classes of

potential organic electrode materials for Li ion batteries have been published in recent years.^{6,9,14-17} For post-Li storage, several materials have been proposed, including carboxylate and terephthalate based materials.^{9,15} Tetracyanides, such as tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), are a promising class of organic electrode materials which can be applied to Li and Na ion batteries. Cathodes made of TCNQ were reported to achieve a relatively high capacity exceeding 200 mAh/g with excellent cyclability.¹⁴ A smaller analogue, TCNE, was recently predicted to be able to store up to 5 Li or Na atoms per molecule when immobilized on a conducting graphene-based substrate,¹⁸⁻²⁰ which would result in a theoretical specific capacity of about 1,000 mAh/g_(TCNE).

Several electrode material properties determine the performance of Li (or Na etc.) ion batteries. A critical parameter is the binding/interaction energy of Li atoms with the electrode material, which determines the voltage of the battery. The interaction energy is a function of the electronic structure of the material (although other factors such as long range electrostatic interactions may have a significant effect²¹): typically, Li atoms donate their valence electron to the electrode material. The nature and energies of the resulting electronic states directly influence the energy of the combined Li-electrode material system via the band structure part of the total energy. For example, in the popular silicon anode, Li donates the electron to a state in the conduction band of Si;²² the interaction energy can be strengthened by doping Si in a way which allows the donated electron to occupy a lower-energy state at the top of the valence band.²³

^a Department of Mechanical Engineering, National University of Singapore, Block EA #07-08, 9 Engineering Drive 1, Singapore 117575, Singapore.

In organic materials, a Li atom usually donates the valence electron to the LUMO (lowest unoccupied molecular orbital) of the molecule. The analysis and design of LUMO have been used to understand and to control electrode voltage.²⁴⁻²⁶ It is, however, expected that when multiple Li atoms are attached per molecule - as is apparently the case with TCNE and TCNQ^{14,18-20} - other and higher-energy orbitals will be occupied and will influence the binding energy and ultimately the voltage. The importance of these higher-energy states is expected to change along the charge-discharge curve. Moreover, we have shown that attachment of multiple Li or Na atoms to TCNE significantly changes molecular geometry.¹⁸⁻²⁰ This strain effect can potentially significantly affect the electronic structure including the energies as well as the order of electronic states and will also change in importance along the charge-discharge curve. Further, higher-lying molecular orbitals may have competing energetics with Li-centered orbitals.

For rational design of organic electrode materials, it is therefore important to understand the changes in the electronic structure induced by Li attachment. Specifically, the role of higher-energy (than LUMO) molecular and Li-centered states and their effect on the binding energies, as well as the strain-induced changes in the electronic structure need to be understood. Here, we present a density functional theory study of Li interaction with tetracyanide molecules TCNE and TCNQ where we study these effects.

Methods

The calculations were performed using density functional theory (DFT) with the hybrid B3LYP²⁷ functional and the 6-31+g(d,p) basis set. We have confirmed that using larger basis sets (including 6-311g with different numbers of polarization functions - with options d and 2d, p and 2p, and diffusion functions - with options + and ++) did not perceptibly affect the results. However, the inclusion of diffuse basis functions was found to be necessary. Spin polarized calculations were used for open shell complexes. All calculations were done using Gaussian 09.²⁸

The interaction energy (E_{int}) of Li atoms with the molecule was computed as

$$E_{int} = (E_{nLi/mol} - E_{mol} - nE_{Li})/n, \quad (1)$$

where $E_{nLi/sys}$ is the total energy of a complex with n Li atoms attached to mol , where mol is a TCNE or TCNQ molecule; E_{mol} is the total energy of mol , and E_{Li} is the total energy of a Li atom. The interaction energy in eq. 1 is thus per Li atom, and a negative value for E_{int} corresponds to thermodynamically preferred attachment.

Results and discussion

Li attachment to TCNE

Many attachment configurations were tried for the attachment of multiple Li atoms to the TCNE molecule, and stable configurations were found with up to four attached atoms.^{18-20,29} Fig. 1 shows the structures of Li_n -TCNE complexes with the lowest energy for each n ($n=1...4$).

The interaction energy E_{int} for each complex is summarized in Fig. 2. With the increase of the number of attached Li atoms, the interaction energy increases i.e. binding of Li atoms to the TCNE molecule weakens. For all $n=1...4$, E_{int} are lower than the cohesive energy of Li metal ($E_{coh}^{Li} = -1.67$ eV),^{30,31} which implies that Li atoms prefer to attach to the TCNE molecule rather than to form bulk Li metal. That is, TCNE can act as an anode material with up to 4 Li atoms attached per molecule, which corresponds to a specific capacity of 837 mAh/g.

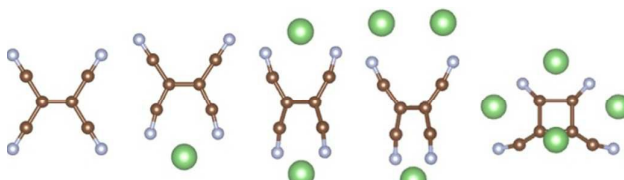


Fig. 1 Left to right: the TCNE molecule and lowest-energy Li_n -TCNE complexes, $n=1...4$. Atom colour scheme here and elsewhere: C – brown, N – blue, Li – green, H – pink. Visualization here and elsewhere is by VESTA.³²

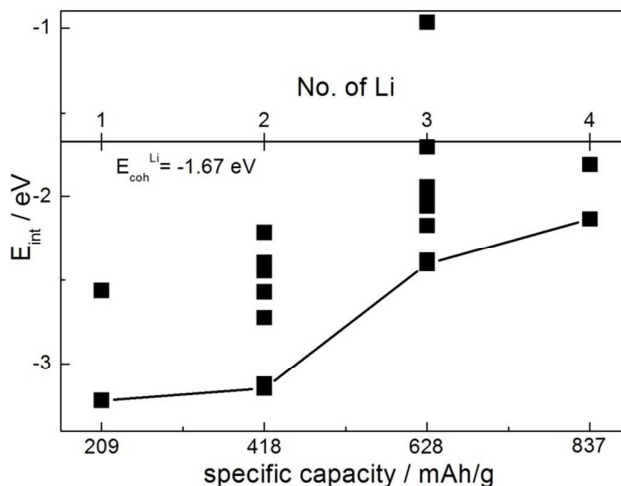


Fig. 2 The interaction energies of Li with TCNE, per Li atom, in Li_n -TCNE complexes. The line connects the lowest energy structures while symbols correspond to all identified stable structures. The axis showing No. of Li atoms crosses the energy axis at the cohesive energy of Li, -1.67 eV.

We now consider the electronic structure of the Li_n -TCNE complexes and specifically which states (orbitals) are contributing to E_{int} and ultimately will determine the voltage. A TCNE molecule and a Li atom form a donor-acceptor complex.^{33,34} When one Li atom is attached to TCNE, it donates one (valence) electron to the LUMO of the molecule (shown on the left in the bottom row of Fig. 3), which forms the (single occupied molecular orbital) SOMO of the Li_1 -TCNE complex (the second one in the bottom row of Fig. 3). When a second Li atom is attached, it also donates one electron to the LUMO of the TCNE molecule, which now forms the (doubly occupied)

HOMO of Li_2 -TCNE complex (the third one in the bottom row of Fig. 3). After another (third) Li atom is attached, the electron it donates will *not* occupy the higher unoccupied molecular orbitals which has the nodal structure similar to LUMO+2 (we did not find a LUMO+1-like orbital in these complexes) of the TCNE molecule (the first one in the top row of Fig. 3); it would instead occupy the bonding orbital formed by the 2 close Li

atoms, which becomes the SOMO of the Li_3 -TCNE complex (the third one in the middle row of Fig. 3). It is because the energy of this orbital (~ -3.79 eV) is much lower than that of the LUMO+2-like orbital (~ -1.83 eV) and higher than the LUMO-like orbital (~ -5.25 eV). The attachment of the fourth Li atom results in double occupancy of this orbital, which becomes the HOMO of the Li_4 -TCNE complex.

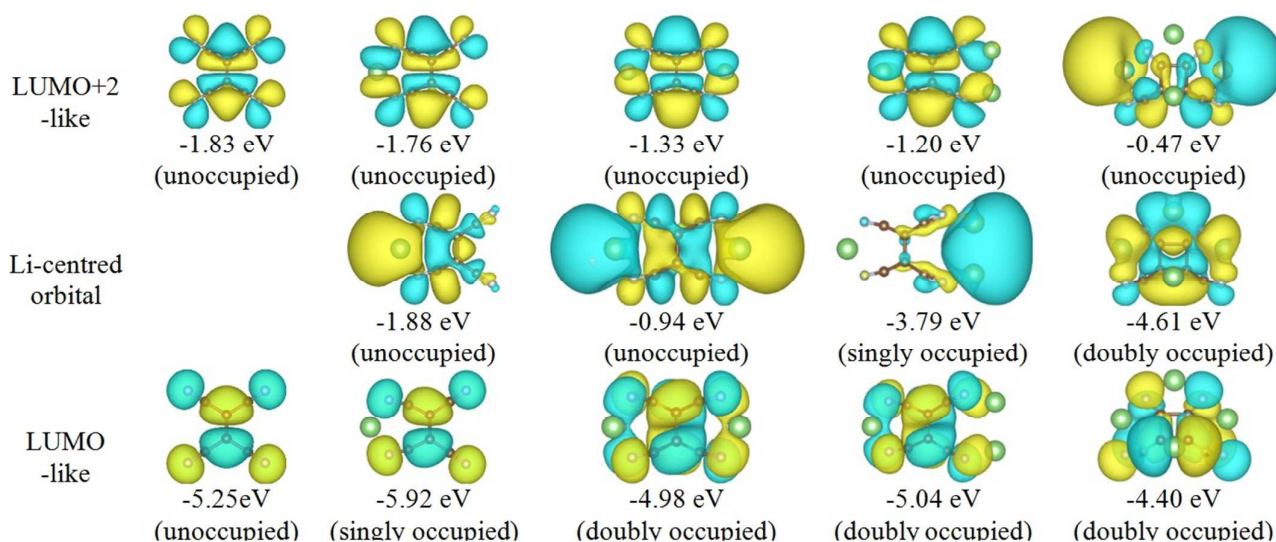


Fig. 3 Orbitals relevant for Li attachment to TCNE in Li_n -TCNE complexes with $n=0..4$ (left to right, the leftmost column for $n=0$ corresponds to the free molecule) corresponding to molecular LUMO+2-like (top row) and LUMO-like (bottom row) orbitals, as well as the lowest-energy Li-centred orbital (middle row). Here and elsewhere, the isosurfaces are at $0.012 e^{1/2} \text{Å}^{-3}$.

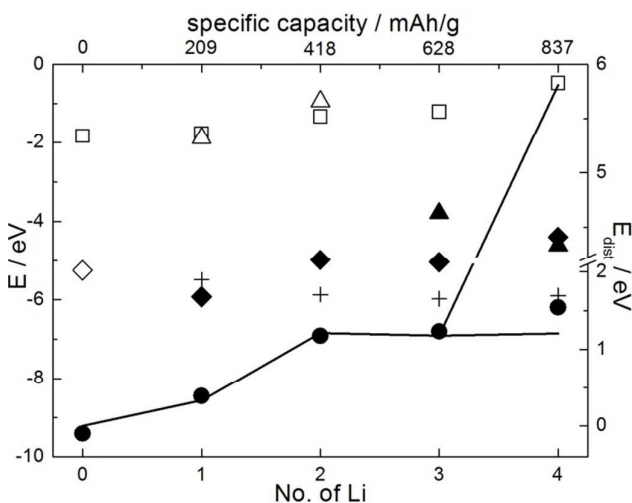


Fig. 4 Symbols: Orbital energies (left scale) relevant for Li attachment to TCNE in Li_n -TCNE complexes. Empty symbols: unoccupied orbitals, filled symbols: occupied orbitals. The symbols correspond to molecular LUMO+2-like (□), LUMO-like (○) and HOMO-like (●) orbitals, as well as lowest-energy Li-centred orbital (△) and LUMO of free and distorted TCNE (+). In complexes with an odd number of electrons, the lowest energy of the near-degenerate orbital pair is shown. The line shows the distortion energies of the TCNE molecule (right scale) at its geometry in Li_n -TCNE complexes. At $n=4$, this line forks into a TCNE-like molecule (that follows the general trend) and the squaraine-like molecule that does not (see main text). Data are shown for the lowest-energy complexes for each n .

The occupancies and energies of the key orbitals for Li_n -TCNE complexes are shown in Fig. 4. The orbital energies are trending up with the number of attached Li atoms, which correlates with the weakening of E_{int} with n shown in Fig. 2. The trend also holds for molecular HOMO-like orbitals. It is clear from Fig. 1 that significant distortions of molecular structure are induced by Li attachment. In Fig. 4, we also plot the strain energy (E_{dist}), which is the energy cost to distort the molecule to the geometry it assumes in the Li_n -TCNE complexes. The strain energy tracks well the dependence of HOMO-like orbitals on the no. of Li and reflects HOMO-like orbital's destabilization by the distortion. Fig. 4 also shows (as "+") the LUMO energies of the distorted molecule without Li attachment; the distortion stabilizes LUMO. Comparing this trend with the trend of the energy of the LUMO-like orbital in the Li_n -TCNE complexes, it is clear that there is competition between stabilization due to strain and destabilization due to Li attachment.

These results show that across the charge-discharge curve of an organic material, a number of states will in general determine the voltage and not just the molecular LUMO. Further, when multiple Li atoms are attached, Li-centered orbitals will compete in energy with molecular states and may be occupied. Moreover, we find that this competition is affected by the distortion of geometry induced by Li attachment: the ordering of unoccupied molecular states will

change as well as the corresponding energies. For example, the LUMO+1 and LUMO+2 of free and distorted TCNE in the $\text{Li}_1\text{-TCNE}$ complex (the second one in Fig. 1) swap due to the distortion and both their energies increase and become similar in energy with a Li-centered orbital. After Li atoms are attached, there are no identifiable LUMO+1-like orbitals in these complexes. In $\text{Li}_{3,4}\text{-TCNE}$ complexes, Li-centered orbitals are significantly lower in energy than LUMO+2-like orbitals and are occupied, while LUMO+2-like orbitals remain unoccupied.

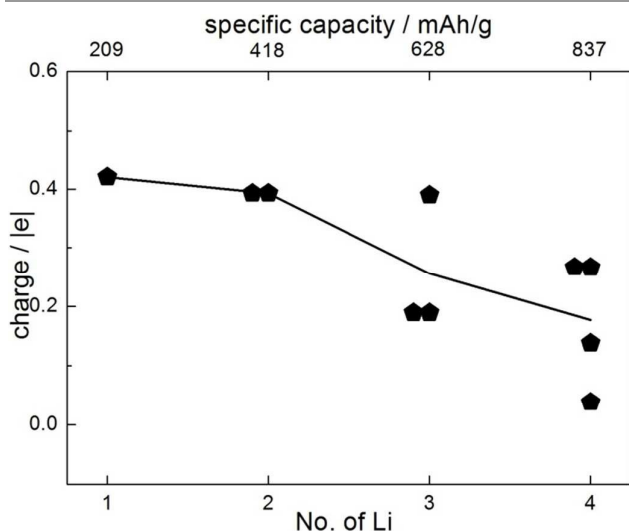


Fig. 5 Mulliken charge on Li atoms in $\text{Li}_n\text{-TCNE}$ complexes. The line shows the trend of average charge per Li atom.

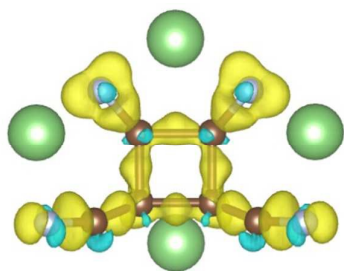


Fig. 6 Charge density difference between the total electron density of the lowest energy $\text{Li}_4\text{-TCNE}$ complex and the sum of atomic densities, evidencing the C-C bond formation by density accumulation along the bond.

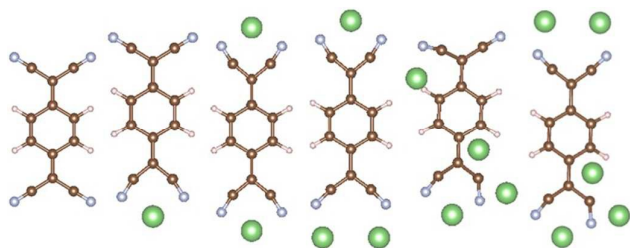


Fig. 7 Left to right: the TCNQ molecule and lowest-energy $\text{Li}_n\text{-TCNQ}$ complexes, $n=1\dots 5$.

The decrease in the magnitude of E_{int} with the number of attached Li atoms also correlates with the average (per Li)

charge donation from Li to the molecule, as shown in Fig. 5, which shows Mulliken charges on all Li atoms as well as the average (Hirshfeld charges³⁵ were also computed and are shown in SI). There is significant difference in charges on different Li atoms which is explained by the fact that some electrons occupy molecule-centred orbitals (resulting in a significant positive charge on Li) and some Li-centred orbitals (resulting in electron charge remaining on Li).

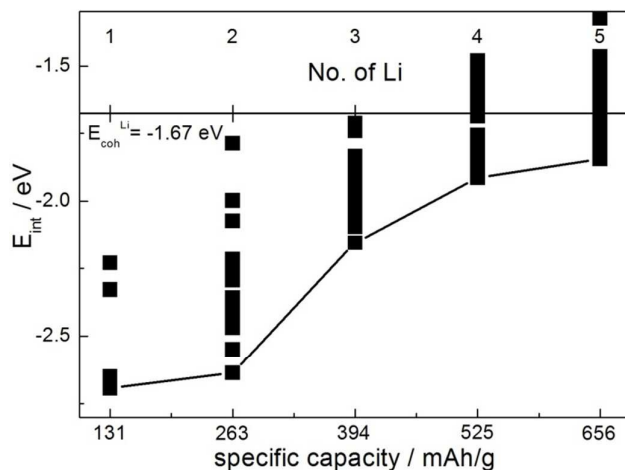


Fig. 8 The interaction energies of Li with TCNQ, per Li atom, in $\text{Li}_n\text{-TCNQ}$ complexes. The line connects the lowest energy structures while symbols correspond to all identified stable structures. The axis showing No. of Li crosses the energy axis at the cohesive energy of Li, -1.67 eV.

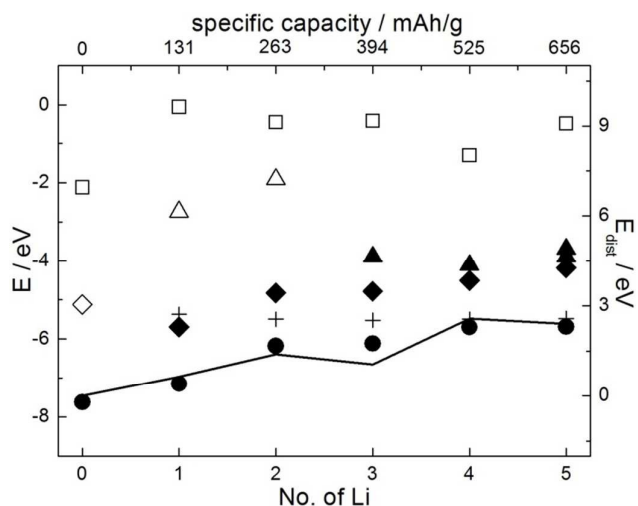


Fig. 9 Symbols: Orbital energies (left scale) relevant for Li attachment to TCNQ in $\text{Li}_n\text{-TCNQ}$ complexes. Empty symbols: unoccupied orbitals, filled symbols: occupied orbitals. The symbols correspond to molecular LUMO+1-like (\square), LUMO-like (\diamond) and HOMO-like (\circ) orbitals, as well as lowest-energy Li-centred orbital (Δ) and LUMO of free and distorted TCNQ ($+$). In complexes with an odd number of electrons, the lowest energy of the near-degenerate orbital pair is shown. The line shows the distortion energies of the TCNQ molecule (right scale) for the lowest energy $\text{Li}_n\text{-TCNQ}$ complexes.

In the $\text{Li}_4\text{-TCNE}$ complex, we also observed formation of a squaraine-like cyclic structure shown in Fig. 1 on the right. This is the lowest-energy structure. There is a C-C bond formation between two CN moieties, as evidenced by the accumulation

of the electron density between the corresponding C atoms (Fig. 6). Upon removal of Li, the structure does relax to the TCNE equilibrium geometry. The other stable Li_4 -TCNE structure whose energy is marked on Fig. 2 is TCNE-like, as are all Li_{1-3} -TCNE structures. This TCNE-like structure follows the trend in E_{dist} in Fig. 4 which holds for all TCNE-like structures (lower prong of the E_{dist} curve). The E_{dist} of the cyclic structure lies outside the trend (upper prong). This is therefore a different species which is stabilized by the attachment of and charge donation from Li.

Li attachment to TCNQ

Similarly to TCNE molecule, the attachment of multiple Li atoms to the TCNQ molecule was studied, and we found that

up to five Li atoms can be attached and form stable configurations in which E_{int} is stronger than the cohesive energy of Li metal ($E_{coh}^{Li} = -1.67$ eV). Fig. 7 shows Li_n -TCNQ complexes with the lowest energy for each n ($n=1\dots5$). Fig. 8 shows the interaction energy E_{int} for each complex. Similarly to TCNE, the binding strength of Li atoms to the TCNQ molecule weakens with the number of attached Li atoms. Therefore, TCNQ is also a promising candidate as an anode material; attachment of up to 5 Li atoms per molecule would correspond to a specific capacity of 656 mAh/g. The theoretical capacity of TCNQ therefore exceeds 600 mAh/g and is much larger than was achieved experimentally to date.¹⁴

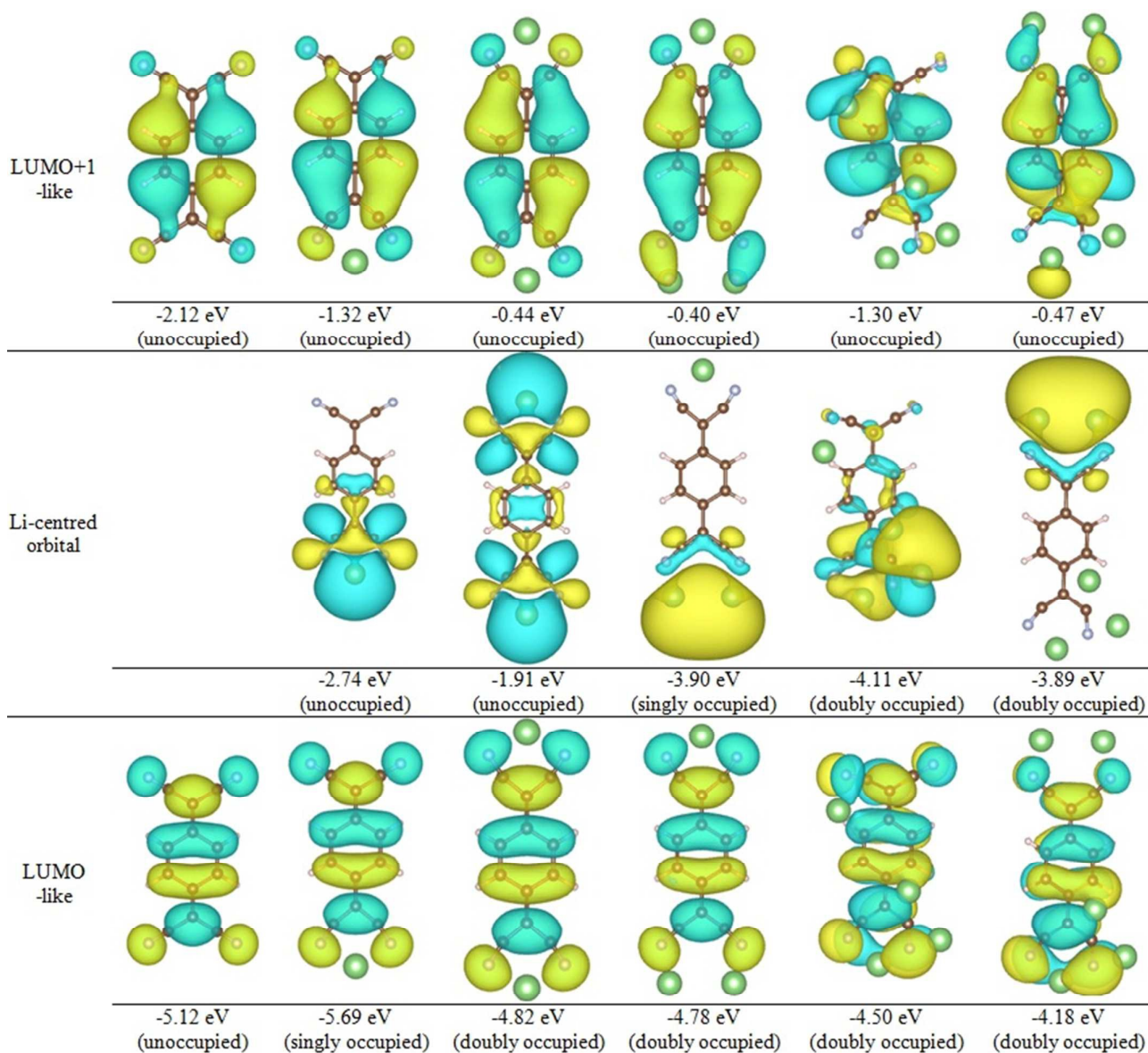


Fig. 10 Orbitals relevant for Li attachment to TCNQ in Li_n -TCNQ complexes with $n=0\dots5$ corresponding to molecular LUMO+1-like (top row) and LUMO-like (bottom row) orbitals, as well as the lowest-energy Li-centred orbital (middle row). For $n=5$, one more Li-centred orbital (not shown) is occupied.

Journal Name

ARTICLE

The experimental capacity of up to 263 mAh/g corresponds to the attachment of only 2 Li atoms per molecule.¹⁴ The average voltage for the attachment of 1 or 2 Li atoms following from Fig. 8, $V = E_{coh}^{Li} - E_{int}$,³⁶ is about 1 V, which is lower than the voltages reported with crystalline TCNQ, of about 3 V.¹⁴ We have confirmed that the difference of this magnitude can be induced by considering the crystal structure of these materials (Fig. S1) and may be due to the long-range electrostatic interactions missing in the present model that focuses on the electronic structure. The interaction with the solvent can also strengthen E_{int} by up to 1 V (Fig. S2). Comparing Fig. 8 to Fig. 2 suggests that with TCNE it must be possible to achieve higher voltages than with TCNQ, by up to 0.5 V at low Li concentrations, i.e. TCNE may be more suitable as a cathode material than TCNQ.

We now consider the electronic structure of the Li_n -TCNQ complexes. A TCNQ molecule and a Li atom can form a donor-acceptor complex.^{33,34} The pattern electron donations when several Li atoms are attached to TCNQ to form Li_n -TCNQ complexes is similar with that of Li_n -TCNE complexes as shown in Fig. 9. When the first Li atom is attached to TCNQ, it donates one (valence) electron to the LUMO of the molecule (shown on the left in the bottom row of Fig. 10), which forms the SOMO of the Li_1 -TCNQ complex (the second one in the bottom row of Fig. 10). When a second Li atom is attached, it also donates one electron to the LUMO of the TCNQ molecule, which now forms the HOMO of Li_2 -TCNQ complex (the third one in the bottom row of Fig. 10). After another (third) Li atom is attached, the electron it donates will *not* occupy the higher unoccupied molecular orbitals (LUMO+1) of the TCNQ molecule (the first one in the top row of Fig. 10); it would instead occupy the bonding orbital formed by the 2 close Li atoms, which becomes the SOMO of the Li_3 -TCNQ complex (the third one in the middle row of Fig. 10). The attachment of the fourth Li atom results in double occupancy of this orbital, which becomes the HOMO of the Li_4 -TCNQ complex. When the fifth Li atom is attached, the electron it donates will occupy the bonding orbital formed by another pair of 2 close Li atoms, which becomes the SOMO of the Li_5 -TCNQ complex (the fifth one in the middle row of Fig. 10). The multiple Li atoms attachment leads to more bonding orbitals created by close Li atoms, which are lower than LUMO+1 of the TCNQ molecule and will be occupied preferentially.

As can be seen in Fig. 9, the trend of orbital energies with the number of attached Li atoms is also consistent with the weakening of E_{int} , Fig. 8. Similarly to Li_n -TCNE complexes, the strain energy for Li_n -TCNQ complexes tracks well the dependence of HOMO-like orbitals on the no. of Li. What's more, the geometry distortion induced by Li attachment

affects the ordering of unoccupied molecular states and the corresponding energies, which makes the Li-centered orbitals competitive in energy with molecular states and be occupied. Differently from TCNE, LUMO+1-like orbitals of Li_n -TCNQ complexes can easily be identified after Li atoms attachment.

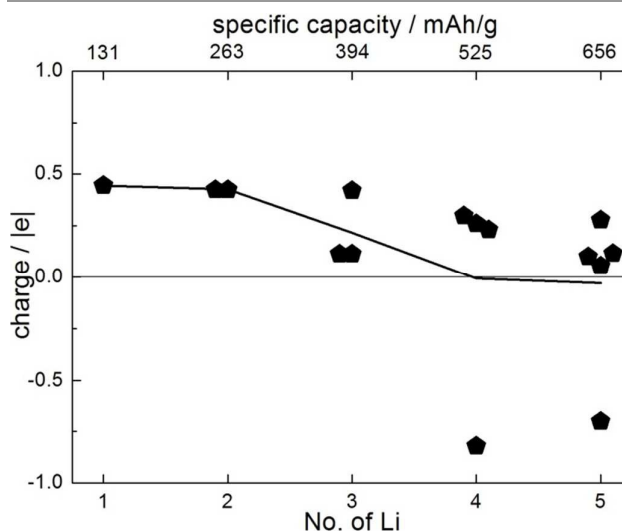


Fig. 11 Mulliken charge on Li atoms in Li_n -TCNE complexes. The black line shows the trend of average charge per Li atom. The horizontal line shows neutral charge, that is 0 |e|.

The decrease in the magnitude of E_{int} with the number of attached Li atoms also correlates with the average (per Li) charge donation from Li, as shown in Fig. 11. There is significant difference in charges on different Li atoms which is explained by the fact that some electrons occupy molecule-centred orbitals and some Li-centred orbitals. The occupation of Li-centred orbitals significantly lowers the average charge donation, so much so that in Li_4 -TCNQ and Li_5 -TCNQ, the Mulliken charge on TCNQ is near-0 or even slightly positive in the case of Li_5 -TCNQ. (Hirshfeld charges are shown in SI. Although Mulliken charge for one of Li atoms in Li_4 -TCNQ or Li_5 -TCNQ is negative, it shows positive Hirshfeld charge, Fig. S3).

The results of Li attachment to TCNQ therefore also show, as do Li_n -TCNE results, that a number of states will determine the voltage across the charge-discharge curve of an organic material, including Li-centered orbitals.

Conclusions

We performed a comparative density functional theory study of lithium attachment to TCNE and TCNQ molecules as

prospective electrode materials for organic Li ion batteries. TCNE and TCNQ can attach up to 4 and 5 Li atoms respectively, with the binding energy stronger than the cohesive energy of Li, which would correspond to a specific capacity of 837 and 656 mAh/g, respectively. TCNE is predicted to result in higher voltages than TCNQ by up to 0.5 V i.e. TCNE is more apt to be used as a cathode material than TCNQ.

The binding energy of Li (which determines the electrode voltage) follows from the electronic structure of Li_n -TCNE/TCNQ complexes. The attachment of Li forms donor-acceptor complexes, in which Li atoms donate their valence electron into higher-lying states which could be unoccupied molecular orbitals or Li-centered orbitals. There is a competition between them. This competition is compounded by changes in the energies, and sometimes in the order, of electronic states induced by geometry changes which the molecule undergoes upon Li attachment.

Specifically, when attaching up to two Li atom, donated electrons occupy molecular LUMO-like orbitals. When more than 2 Li atoms are attached, donated electrons would populate Li-centered orbitals. With multiple Li atoms attachment, the distortion of tetracyanide molecules leads to swaps between unoccupied molecular orbitals (MOs) and energy increase of unoccupied MOs which leads to preferred occupation of Li-centered orbitals. The energies of the orbitals which become occupied due to Li attachment are trending up with the number of attached Li atoms which correlates with the weakening of E_{int} . The strain energy for Li_n -TCNE/TCNQ complexes tracks well the dependence of HOMO-like orbitals on the no. of Li atoms and reflects HOMO destabilization by the distortion. Therefore, a number of states determine E_{int} and not just the molecular LUMO, and the identity of these states will change across the charge-discharge curve of an organic material and will include Li-centered orbitals.

We conclude that design of organic electrode materials should consider the energies of higher (than LUMO) orbitals as well as effects of structural changes on the electronic structure.

We also observed the formation of a squaraine-like species which is stabilized by the attachment of four Li atoms to TCNE.

Acknowledgements

This was supported by the Ministry of Education of Singapore (grant MOE2014-T2-2-006).

References

- 1 M. M. Thackeray, C. Wolverton and E. D. Isaacs, *Energy Environ. Sci.*, 2012, **5**, 7854-7863.
- 2 J. B. Goodenough, *Energy Environ. Sci.*, 2014, **7**, 14-18.
- 3 E. Barbour, I. A. G. Wilson, I. G. Bryden, P. G. McGregor, P. A. Mulheran and P. J. Hall, *Energy Environ. Sci.*, 2012, **5**, 5425-5436.
- 4 C. J. Barnhart, M. Dale, A. R. Brandt and S. M. Benson, *Energy Environ. Sci.*, 2013, **6**, 2804-2810.
- 5 C. Lupi and M. Pasquali, *Miner. Eng.*, 2003, **16**, 537-542.

- 6 Y. L. Liang, Z. L. Tao and J. Chen, *Adv. Energy Mater.*, 2012, **2**, 742-769.
- 7 K. Koshika, N. Sano, K. Oyaizu and H. Nishide, *Macromol. Chem. Phys.*, 2009, **210**, 1989-1995.
- 8 X. Han, G. Qing, J. Sun and T. Sun, *Angewandte Chemie International Edition*, 2012, **51**, 5147-5151.
- 9 A. Abouimrane, W. Weng, H. Eltayeb, Y. Cui, J. Niklas, O. Poluektov and K. Amine, *Energy Environ. Sci.*, 2012, **5**, 9632-9638.
- 10 Y. NuLi, Z. Guo, H. Liu and J. Yang, *Electrochem. Commun.*, 2007, **9**, 1913-1917.
- 11 A. K. Shukla and T. P. Kumar, *J. Phys. Chem. Lett.*, 2013, **4**, 551-555.
- 12 H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, *ChemSusChem*, 2008, **1**, 348-355.
- 13 Z. Song and H. Zhou, *Energy Environ. Sci.*, 2013, **6**, 2280-2301.
- 14 Y. Hanyu and I. Honma, *Scientific Reports*, 2012, **2**.
- 15 Y. Park, D. S. Shin, S. H. Woo, N. S. Choi, K. H. Shin, S. M. Oh, K. T. Lee and S. Y. Hong, *Adv. Mater. (Weinheim, Ger.)*, 2012, **24**, 3562-3567.
- 16 T. Yasuda and N. Ogihara, *Chem. Commun. (Cambridge, U. K.)*, 2014, **50**, 11565-11567.
- 17 N. Ogihara, T. Yasuda, Y. Kishida, T. Ohsuna, K. Miyamoto and N. Ohba, *Angewandte Chemie - International Edition*, 2014, **53**, 11467-11472.
- 18 Y. Chen and S. Manzhos, *MRS Online Proceedings Library*, 2014, **1679**, DOI: 10.1557/opl.2014.1849.
- 19 Y. Chen and S. Manzhos, *Mater. Chem. Phys.*, 2015, **156**, 180-187.
- 20 Y. Chen and S. Manzhos, in *Proceedings of the 14th Asian Conference on Solid State Ionics (ACSSI-2014)*, Research Publishing Services, Singapore, pp. 374-380.
- 21 M. Saubanière, M. B. Yahia, S. Lebègue and M. L. Doublet, *Nat Commun*, 2014, **5**.
- 22 I. M. Oleksandr, L. T. Teck and M. Sergei, *Appl. Phys. Express*, 2013, **6**, 027301.
- 23 F. Legrain and S. Manzhos, *J. Power Sources*, 2015, **274**, 65-70.
- 24 Z. Song, Y. Qian, X. Liu, T. Zhang, Y. Zhu, H. Yu, M. Otani and H. Zhou, *Energy Environ. Sci.*, 2014, **7**, 4077-4086.
- 25 Z. Song, Y. Qian, T. Zhang, M. Otani and H. Zhou, *Advanced Science*, 2015, DOI: 10.1002/advs.201500124.
- 26 R. Precht, R. Hausbrand and W. Jaegermann, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6588-6596.
- 27 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377.
- 28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2009.
- 29 J. H. Her, P. W. Stephens, R. A. Davidson, K. S. Min, J. D. Bagnato, K. van Schooten, C. Boehme and J. S. Miller, *J. Am. Chem. Soc.*, 2013, **135**, 18060-18063.
- 30 C. Kittel, *Introduction to Solid State Physics*, Wiley, Hoboken, NJ, 2005.

ARTICLE

Journal Name

- 31 E. Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press, Cambridge, 2003.
- 32 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272-1276.
- 33 W. R. Hertler, W. Mahler, L. R. Melby, J. S. Miller, R. E. Putscher and O. W. Webster, *Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics*, 1989, **171**, 205-216.
- 34 J. S. Miller, *Angewandte Chemie International Edition*, 2006, **45**, 2508-2525.
- 35 F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, **44**, 129-138.
- 36 M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho and J. Joannopoulos, *Phys. Rev. B*, 1997, **56**, 1354-1365.