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Electrical and electrochemical properties of lithium solvated electron solutions derived from 1,3,5-triphenylbenzenes

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A series of 1,3,5-triphenylbenzenes (TPBs) bearing various substituents have been made and their ability to form lithium solvated electron solutions (Li SESs) in tetrahydrofuran (THF) solution studied. It was found that the TPBs bearing electron withdrawing substituents were of too low solubility in THF to allow formation of LiSESs, whereas the unsubstituted TPB and TPBs bearing solubilizing alkyl and alkoxy substituents were able to form LiSESs in THF upon addition of lithium. The highest conductivity values for LiSESs in THF were obtained from the parent TPB, despite its lower solubility in THF compared to the alkyl- and alkoxy-substituted TPBs. The LiSES from the methoxy-substituted TPB showed a much lower conductivity, which was attributed to the electron donating effect of the alkoxy substituent making the TPB less willing to accept an electron from the lithium and thus reducing significantly the number of charge carriers generated. The alkyl-substituted TPB LiSES showed slightly lower conductivity than the parent TPB which is attributed to the insulating effects of the alkyl substituents. The conductivities of the LiSES were found to be highest for a Li:TPB ratio of 2:1 suggesting that the materials act like substituted biphenyls. All the SES showed a metal-like decrease in conductivity with rising temperature. Studies of open circuit voltage versus temperature for the LiSES made from unsubstituted TPB indicated the entropy change (ΔS) of these solutions during discharge were higher than for SESs made using biphenyl or naphthalene and much higher than for solid lithium ion battery anode materials.

Introduction

We have previously reported physical chemical, electrical and electrochemical properties of lithium solvated electron solutions (LiSESs) prepared by addition of lithium to solutions of the simplest 2-ring polycyclic aromatic hydrocarbons (PAHs) biphenyl and naphthalene [1-2], whose physical chemical, electrical and electrochemical properties have been characterized for various ratios of Li:PAH:THF (THF is tetrahydrofuran used as a solvent). A characteristic of these SESs is that they show a metal-like decrease in conductivity with increase in temperature, due to the conduction being due to delocalized electrons in the solvated PAH anions. Such solutions have potential applications as liquid based anodes in novel lithium batteries that utilize liquid based electrodes (anolytes and catholytes). [3] A significant advantage of these batteries is that they can be refilled with a new portion of lithium containing liquids after discharge, which eliminates an issue of slow rate of charge in conventional lithium ion batteries. Also,

the use of liquids would allow to achieve a higher rate of discharge due to faster kinetics in liquids comparing to solids.

Although PAH based SESs have been widely investigated and used in organic chemistry as reducing agents, using them as anolytes in such batteries is a new concept with no detailed systematic studies having been performed. In optimising Li SES performance in such batteries it is desirable to obtain a high Li:PAH ratio so as to increase the energy storage capacity of the battery. The conductivity of the SESs from biphenyl and naphthalene was found to be maximal for a ratio of Li:PAH of 2:1 corresponding to one electron being donated to each ring. To further explore the properties and potential for application of such solutions we are investigating the formation of LiSESs using other PAHs and have shown that LiSES can be made using PAHs with greater numbers of rings e.g. corannulene [4], or containing heteroatoms e.g. tetraphenylcyclopentadien-ones [5]. One group of PAHs we have been investigating are 1,3,5-triphenylbenzenes (TPBs) (Figure 1) which contain 4 benzene rings and so should be able to accept up to 4 electrons from 4 atoms of lithium, and thus have a theoretically higher energy storage capacity than biphenyl or naphthalene. We have already published an account of some preliminary investigations, in which we showed that LiSESs could be formed from unsubstituted TPB and reported their conductivity versus temperature profiles.[4] We now report more detailed investigations into LiSESs based on TPBs, including the effects of substituents upon their ability to form SESs, and the properties

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of the SES, including determination of crucial thermodynamic parameters for the SESs made from 1.

Figure 1 TPBs studied

Experimental

Reagents were purchased from Aldrich and used as received. Chromatographic purification was performed as flash chromatography with silica gel (40–65 μ m) or preparative thin-layer chromatography (prep-TLC) using silica gel F254 (1000 μ m) plates and solvents indicated as eluent with 0.1–0.5 bar pressure. For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 μ m F254 TLC glass plates. Visualization was accomplished with UV light. Proton (¹H NMR, 400 MHz) and carbon (¹³C NMR 100 MHz) nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz spectrometer with solvent resonances as the internal standards (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.0 ppm). MALDI TOF/MS data was obtained on a MALDI Shimadzu AXIMA spectrometer using α -cyano-4-hydroxycinnamic acid as a matrix. For the information related to the synthesis of 1–6, see the Supporting Information.

Conductivity (σ) measurements at ambient temperature of LiSES prepared from Compounds 1–3.

LiSES samples of Li_xTPB-R(THF)_{24.7} (For R = H: x = 1, 2, 3, 4; for R = nC₄H₉, x = 1; for R = OCH₃, x = 1) were prepared inside an argon-filled glovebox [1, 2, 4] and conductivity measurements were carried out using the modified method described in our previous work [4]. For simplicity, 1,3,5-triphenylbenzene where R = H will be referred to as TPB, and where R = C₄H₉ will be referred to as TPB-C₄H₉.

Conductivity (σ) vs. temperature (T) measurements

Conductivity (σ) vs. temperature (T) measurements of Li SES were carried out using modified procedure previously described for the naphthalene-based LiSES.[2] TetraCon 325 Standard conductivity cell probe that utilizes the four-electrode measuring principle with the measurement range of 1 μ S/m to 2 S/cm was used to measure the conductivity of the Li-SES. The probe was attached to a Cond 3310 meter. A sealed tube containing Li-SES with the probe dipped into the solution was assembled in a glove box. The conductivity vs. temperature measurements were performed out of the glove box using ice for cooling down the sealed tube.

Open-circuit potentials (E) vs temperature (T) measurements of Compound 1-based LiSES

From the two samples of Li_xTPB(THF)_{24.7} for x = 1, 2, 3, 4 that yield the highest and the lowest conductivities at ambient temperature, the open-circuit potentials (E) vs temperature (T) profiles were obtained using an Li/Ceramics/LiSES half-cell configuration. The method for measuring E vs T is described in our previous work. It enables the entropy and enthalpy of the cell reaction to be determined. [2]

Results and discussion

Synthesis of 1,3,5-triphenylbenzene derivatives

Compounds 1–4 were synthesized by trimerisation of the corresponding substituted acetophenones using SiCl₄ (2–3 eq.) in ethanol (Figure 2).[6] The products were obtained in good yields (60–83%). Compound 6 was synthesized in 65% yield from 4-nitroacetophenone using SOCl₂ in ethanol.[7] In order to obtain the cyano-substituted TPB 5, the strategy shown in Figure 3 was adopted. Condensation of p-iodoacetophenone with EtOH-SiCl₄ gave the iodo-TPB 7 [8] in 60% yield. Then this compound was reacted with copper (I) cyanide in refluxing anhydrous DMF [9] giving the target material 5 in 70% yield.

Conductivity (σ)

The derivatives of TPB with R = F, NO₂ and CN demonstrate low solubility in THF and metallic lithium does not react with their suspensions in THF. For the other compounds, the conductivity readings of Li_{1.0}TPB-R (THF)_{24.7} for R = H, R = nC₄H₉ and R = OCH₃ are shown in Table 1.

From Table 1, it can be seen that the LiSES prepared from TPB has the highest conductivity among the three samples. For the case of TPB where R = OCH₃, it was found that Li did not dissolve completely (about 80% of Li left remained unreacted within 24 h), which has an impact on the conductivity. The explanation of these phenomena is related to the effect of methoxy groups that enrich the aromatic core with the electron density, and, as a result, decrease the molecule's electron affinity. The insulating effect of alkyl chains when R = C₄H₉ decreases the efficiency of charge transfer between the molecules leading to a decrease in conductivity comparing to the unsubstituted TPB. Thus, only the compounds with R = H and C₄H₉ are eligible for further studies.

Figure 2. Synthesis of 1,3,5-triphenylbenzene derivatives by acetophenone condensation

Figure 3. Synthesis of 5

R in $\text{Li}_x\text{TPB-R}(\text{THF})_{24.7}$	σ (mS/cm)
H (1)	1.55
nC_4H_9 (2, TPB- C_4H_9)	0.663
OCH_3 (3)	0.0047

Table 1. Conductivity readings of $\text{Li}_{1.0}\text{TPB-R}(\text{THF})_{24.7}$ for R = H, nC_4H_9 and OCH_3 at 22°C Figure 4. ^1H NMR spectra of pure TPB (bottom), the crude product derived from $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ upon quenching with iodine (middle) and the crude product derived from $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ upon quenching with iodine (top) (solvent: CDCl_3). The peak related to the TPB middle ring is at 7.79ppm.

The measured conductivity values readings of $\text{Li}_x\text{TPB}(\text{THF})_{24.7}$ and $\text{Li}_x\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ for $x = 1, 2, 3$, and 4 are shown in Table 2. From the Table 2, it can be seen that $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ has the highest conductivity and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ has the lowest conductivity for TPB. The conductivity of TPB- C_4H_9 solutions demonstrate a similar correlation versus the amount of Li per PAH vs conductivity, however, the conductivity has almost twice much lower values, which is related to the insulating effect of the alkyl chains described before. The values of conductivity for the studied Li SESs based on TBSs are lower than the maximum values for naphthalene (12.0 mS/cm for $\text{Li}_{0.5}(\text{N})(\text{THF})_{6.2}$) and biphenyl (12.4 mS/cm for $\text{Li}_{0.5}(\beta)(\text{THF})_{6.2}$) based Li SES. However, since these solutions are much more concentrated compared to the studied TPB based Li SESs. The conductivities of Li SES based on unsubstituted TPB might be much higher at higher concentrations (lower TPB:THF ratio).

The observation that in both the cases the conductivity increases from $x = 1$ to $x = 2$ and then decreases from $x = 2$ to $x = 4$ requires more detailed discussion. The explanation of this phenomenon is related to the Pearson hardness of lithium [10]. The metal tends to interact with high charge density centres,

x	σ (mS/cm) TPB	σ (mS/cm) [TPB- C_4H_9]
1	1.55	0.663
2	1.87	0.728
3	1.37	0.603
4	1.13	0.505

Table 2. Conductivity readings of $\text{Li}_x\text{TPB}(\text{THF})_{24.7}$ and $\text{Li}_x\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ for $x = 1, 2, 3$ and 4 at 22°C.

which are the σ -bonds in the TPB molecule, leading to σ -bond cleavage reactions. These reactions produce species with C-Li bonds, where the charge is localized on particular atoms, which leads to a decrease in electric conductivity compared to the situation where the charge is delocalized over the entire TPB molecule. The products from our attempts to recover the starting TPB from the solutions with 2 and 4 equivalents of lithium per TPB by means of quenching the solutions with iodine (equimolar to the amounts of lithium) give support to this argument. We found that TPB can be recovered from $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ solutions using iodine in THF. Although some products of TPB molecule decomposition are present in the resulting mixture, the amount of TPB present in the crude product was 38% by weight (defined by NMR), and, after recrystallization from ethanol, TPB was recovered in 50% comparing yield based on to the amount used for the Li SES preparation. On the other hand, the amount of TPB present in the crude product derived from $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ was only 2 wt % (defined by NMR), the rest is a complex mixture of decomposition products and oligomers, as seen in the NMR spectra of the crude product. The comparison between ^1H NMR spectra of pure TPB, the crude product derived from $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ and the one derived from $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ upon quenching with iodine are shown at in the Figure 4. Our results are in agreement with the observations reported previously, where a derivative of TPB was treated with excessive amounts of lithium metal, which led to destruction of TPB framework [11]. HPLC and GC/MS analysis of the hydrolysed reaction mixture showed various products, including terphenyls, biphenyls, styrene and oligomers formed due to polymerization of the fragments.

Figure 5 demonstrates correlation between temperature and conductivity for solutions of TPB and $\text{C}_4\text{H}_9\text{TPB}$ containing 2 and 4 equivalents of Li per PAH. All the conductivity vs temperature plots show a negative slope (conductivity decreases with temperature); the same trend as is seen for metals and Li SES based on naphthalene and biphenyl. However, this correlation is not completely linear, unlike the plots seen for metals and Li SES based on naphthalene and biphenyl.

These three LiSES samples, with the highest and the lowest conductivities for TPB, and the highest conductivity for $\text{C}_4\text{H}_9\text{TPB}$ were then selected for open-circuit potentials (E) vs temperature (T) study.

Figure 5. The conductivity vs. temperature correlation for $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ (black), $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ (red), $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ (blue), $\text{Li}_{4.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ (pink).

Open-circuit potentials (E) vs temperature (T) profiles of Compound 1-based LiSES

The E vs T profiles of $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$, $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$, and $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ in Li/Ceramics/LiSES half-cell configurations are shown in Figure 6.

As seen from Figure 6, the OCV for $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ is much lower than for the two other solutions, which is also a result of TPB aromatic core decomposition. The OCV value obtained for $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ vs. Li is the lowest among all LiSES reported so far. The obtained values of OCV at 22 °C (295K) for the studied molecules and compositions are shown in Table 3. The table also demonstrates the theoretical energy density (D_{th}) of these materials comparing to graphite electrode (C_6) versus LiCoO_2 (E vs $\text{Li}^+/\text{Li} = 4.2$ V). The values were calculated considering the following discharge reaction:

Using the equation [12]:

$$D_{th} = E_c \frac{nF}{3.6M_r}$$

Where E_c is a potential of Li SES vs LiCoO_2 , C_{th} is the theoretical gravimetric capacity, n is a number of electrons transferred from Li SES to LiCoO_2 , F is Faraday constant, M_r is a molecular weight of PAH, and 3.6 is a coefficient to convert the units.

As seen from the Table 3, the obtained values of theoretical energy density for the studied PAH are lower than the value for graphite. The value for $\text{C}_4\text{H}_9\text{TPB}$ is the lowest showing that the incorporation of alkyl chains leads to decrease of theoretical energy density value while increasing solubility. All the tabulated D_{th} values are calculated for PAH themselves, not their solutions, meaning that the energy density of Li SES, depending on the concentration, should be lower. However, the Li SES of certain concentration should demonstrate higher energy density comparing to vanadium redox batteries having specific energy density of 5 – 20 Wh/kg [13].

From Figure 6, the slopes of $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$, $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ are -4.32 mV K^{-1} , -2.64 mV K^{-1} and -1.00 mV K^{-1} respectively. From the thermodynamics equations,

$$\Delta S = nF \frac{\partial E}{\partial T} \quad (1)$$

and,

$$\Delta H = -nF \left(E - T \frac{\partial E}{\partial T} \right) \quad (2)$$

the enthalpy changes and the entropy changes of the half-cell reactions are computed and presented in Table 4. These state functions are important for understanding of electrodes behaviour in a cell and comparison between electrodes. In particular, entropy represents the influence of temperature on parameters of a battery.

Figure 6. Open-circuit potentials (E) vs temperature (T) profiles of $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ (red), $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ (blue) and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ (black) in Li/Ceramics/LiSES half-cell configurations

PAH	Li:PAH ratio	E vs Li^+/Li (V) at the ratio	E vs LiCoO_2 (V)	D_{th} (Wh/kg)
C_6	1	0.1	4.1	1526
TPB	4	0.5	3.7	1296
TPB	2	0.7	3.5	613
$\text{C}_4\text{H}_9\text{TPB}$	2	0.7	3.5	396
N	1	0.8	3.4	712
β	1	0.7	3.5	609

Table 3. E vs Li^+/Li , E vs LiCoO_2 , and calculated theoretical energy density (D_{th}) for the studied Li SES. C_6 denotes graphite electrode.

Sample	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
$\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$	-190	-417
$\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$	-74	-96
$\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$	-142	-255

Table 4. ΔH and ΔS of the $\text{Li}_x\text{TPB}(\text{THF})_{24.7}/\text{Li}$ half-cells for $x = 1$ and 2 and $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}/\text{Li}$ half-cell

Table 4 compares the entropy changes of half-cell reactions of TPB-based LiSES and those LiSES prepared using naphthalene and biphenyl, against the solid oxide-based LIB cathode (LiCoO_2) and anode (graphite) materials. As can be seen the changes in entropy (ΔS) are greater for the LiSES than for the standard anodes used in LIBs, which can be attributed to their being in a liquid as opposed to a solid state, which allows for more degrees of freedom. The ΔS for the TPB systems are of the same order as the values for biphenyl or naphthalene, however, the value for $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ is much lower, which could be related to the side reaction happening upon the Li SES formation.

Type of half-cell	ΔS ($\text{J K}^{-1}\text{mol}^{-1}$)
$\text{Li}_{0.5}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-420
$\text{Li}_{1.0}\beta(\text{THF})_{24.7}$ (Biphenyl-based)	-467
$\text{Li}_{1.0}N(\text{THF})_{24.7}$ (Naphthalene-based)	-290
$\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$	-417
$\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$	-96
$\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$	-255
$\text{Li}_x\text{CoO}_2/\text{Li}$	$-70 < \Delta S < 20$
$\text{Li}_x\text{C}_6/\text{Li}$	$-20 < \Delta S < 65$

Table 5. Entropy changes ΔS for LiSES/Li ΔS for comparison against $\text{Li}_x\text{CoO}_2/\text{Li}$ half cell where $0 < x < 1$. Data for $\text{Li}_x\text{CoO}_2/\text{Li}$ is obtained from ref [14] and for $\text{Li}_x\text{C}_6/\text{Li}$ from ref [15].

Configurational entropy is the main component of the total entropy measured in all materials and displayed in Table 4. It relates to the degree of freedom lithium ions have in each chemical environment. It is interesting to note the highest entropy value of $-417 \text{ J K}^{-1}\text{mol}^{-1}$ is achieved in $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ suggesting a high mobility of lithium ions and associated solvated electrons in this Li-SES material. Entropy dropped to $-96 \text{ J K}^{-1}\text{mol}^{-1}$ when the lithium content increased from 2 to 4 in $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ due to concentration effect on ion and electron mobility. It also dropped to $-255 \text{ J K}^{-1}\text{mol}^{-1}$ for $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ perhaps due to steric effects arising from the larger size of the PAH. As expected the lowest entropy values are found in solid state LiCoO_2 cathode and graphite anode materials owing to a highly confined structure. The higher configurational entropy value in $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$ as compared to $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ and $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$, and of the LiSESs in general compared to the solid electrode materials has conflicting effects, since it readily decreases the operating voltage with increasing temperature, while concomitantly enhancing lithium mobility, which is favourable for battery application. The overall balance between these factors would decide if LiSESs show better or worse overall performance than solid electrodes in batteries.

Conclusions

The suspensions of TPB with $R = \text{CN}$, F and NO_2 in THF do not react with metallic lithium due to the very low solubility of these compounds in THF. The reaction rate of TPB with $R = \text{OMe}$ and Li is low due to its higher electron density at the aromatic core compared to the unsubstituted TPB.

The conductivity of $\text{Li}_x\text{TPB}(\text{THF})_{24.7}$ and $\text{Li}_x\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ increases with increased number of added Li atoms until $x = 2$ and then decreases after $x = 2$, which is related to the decomposition of the TPB molecules when $x > 2$.

Conductivity vs. temperature correlation for $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$, $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ has a negative trend, which is similar to that's seen for metals and for the SESs based on naphthalene and biphenyl. However, unlike for metals and naphthalene or biphenyl based LiSES, this relation is not completely linear.

Concerning the $\text{Li}_x\text{TPB}(\text{THF})_{24.7}/\text{Li}$ (for $x = 1$ and 2) half cell thermodynamics data, we conclude that:

1. Calculated ΔS for $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$, $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ are mostly configurational (mixing) entropy for each of their respective solution systems.
  2. Calculated ΔS for $\text{Li}_{2.0}\text{TPB}(\text{THF})_{24.7}$, $\text{Li}_{2.0}\text{TPB-C}_4\text{H}_9(\text{THF})_{24.7}$ and $\text{Li}_{4.0}\text{TPB}(\text{THF})_{24.7}$ are high, probably because the LiSES is in a liquid phase which gives its molecules more degrees of freedom than are found in solid electrode materials.
- These results suggest that LiSESs based on TPB with 2 lithium atoms per TPB may be suitable for use as anolytes in liquid-based refuelable batteries.

Conflicts of interest

There are no conflicts to declare

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