# Synthesis and Characterization of Biphenyl-Based Lithium Solvated Electron Solutions

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ABSTRACT: We report on the electric conductivity measurements and FTIR studies carried out on lithium solvated electron solutions (Li-SES) using biphenyl as the electron receptor and tetrahydrofuran (THF) as the solvent. Conductivity measurements carried out on samples with varying compositions of lithium, biphenyl (β), and THF reveal the highest conductivity of 12.0 mS/cm is achieved with the solution composition $Li_{1.0}\beta(THF)_{8.2}$ and a metallic behavior. Characteristic fingerprint peaks attributed to the solvated electron solution appear in the FTIR spectra. Also, from the FTIR spectra, we propose a reaction mechanism of lithium reaction with biphenyl in THF in that $Li_1\beta(THF)_{n1}$ (1 Li atom pairing with 1 biphenyl molecule) is formed first followed by $Li_2\beta(THF)_{n1}$ (2 Li atoms pairing with 1 biphenyl molecule). A better understanding of the physical properties of the Li-SES is a prerequisite in view of their optimal applications as liquid anodes in lithium batteries.
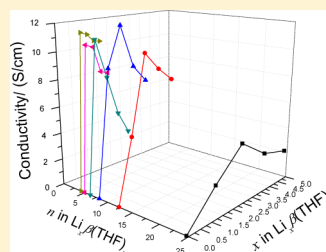
1. INTRODUCTION

The first report of solvated electron solutions goes back to 1808 when Sir Humphry Davy observed that alkali metals could dissolve in liquid ammonia to yield blue-colored solutions.[1] The solutions' color was attributed to the presence of solvated electrons formed when the alkali metal dissolved in ammonia.[2] Solvated electrons are electrons which occupy the spaces between the solvent/solute molecules and are not strongly bound to these molecules. Alkali metals such as lithium and sodium can form solvated electron solutions (Li-SES and Na-SES) with several types of molecules such as ammonia, organic radicals, and polyaromatic hydrocarbons (PAH). Till today, the most commonly known solvated electron solutions are those formed by dissolution of lithium in liquid ammonia. Solvated electron solutions are often described in a range of synthesis methods[3−6] as well for use in a range of possible applications and research fields.[7−13]

The Li-SES used in this work consist of lithium, biphenyl (β) (a simple PAH), and anhydrous tetrahydrofuran (THF) in the composition range of $Li_x\beta(THF)_n$ with $0.24 \leq x \leq 4.93$ and $4.11 \leq n \leq 24.7$. In the $Li_x\beta(THF)_n$ formulation, x and n are not stoichiometric coefficients of a defined compound; rather they account for the molar ratios of components in the solution. Equation 1 illustrates the formation of solvated electrons for the Li-SES used in this work.

$$x Li + \beta + n THF \rightarrow x Li^+ + [x e^-(\beta), (n - m)THF]$$
$$+ m THF \qquad (1)$$
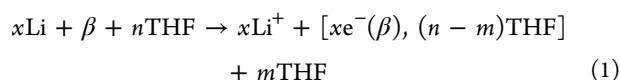
where $[x e^-(\beta), (n - m)THF]$ represents x moles of the solvated electrons and $n THF$ and $m THF$ represent n and m moles of free THF in the solution, respectively.

Biphenyl is a polyaromatic hydrocarbon consisting of two weakly coupled benzene rings that are linked together by a C−C bond. When in its solid crystalline state, biphenyl has a planar structure,[14−16] whereas, in solution state,[17−20] or in its crystalline state below 40 K,[21] biphenyl takes on a twisted structure. One of the important differences between these two structures is the degree of π-electron conjugation, which is much greater when the rings are coplanar. The amount of π-electron conjugation can be changed drastically by the addition of electrons to the biphenyl molecule such as in a SES or by the excitation of an electron in the biphenyl molecule.[22]

Here we have carried out a systematic study of lithium solvated electron solutions using FTIR spectroscopy and conductivity measurements in a broad range of x and n compositions.

2. EXPERIMENTAL SECTION

The preparation of $Li_x\beta(THF)_n$ was carried out at ambient temperature in a glovebox filled with argon. Lithium granules, anhydrous tetrahydrofuran (THF), and biphenyl were obtained from Sigma Aldrich and stored in a glovebox. The preparation proceeded via the following steps: First, predefined amounts of THF, biphenyl, and Li were measured out separately. The amounts of THF and Li are defined by n and x moles, respectively, where $4.11 \leq n \leq 24.7$ and $0.24 \leq x \leq 4.93$. Second, biphenyl was dissolved in THF in a glass bottle to give a transparent, colorless solution. Third, the Li granules were added to the PAH/THF solution and the bottle was sealed. Then, the mixture was subjected to overnight stirring using a glass-coated magnetic bar.

Conductivity measurements were carried out in an argon atmosphere at ambient temperature inside the glovebox to avoid contamination with moisture. Measurements were performed using a TetraCon 325 Standard conductivity cell probe attached

to a Cond3310 meter. The TetraCon 325 cell is based on the four-electrode method. The meter was precalibrated using a standard KCl solution. The reference voltage ensures that measurements indicate the actual conductivity of the solution independent of the condition of the electrodes.

FT-IR analysis was conducted on the following six $Li_x\beta$-$(THF)_n$ samples: THF only ($x = 0$, $n = \infty$); β in THF ($x = 0$, $n = 2.47$) and for $x = 1.23$, $n = 24.7$; $x = 2.46$, $n = 24.7$; $x = 3.70$, $n = 24.7$; and finally $x = 4.93$, $n = 24.7$.

The FT-IR spectra were collected using a Shimadzu IRPrestige-21 in the absorbance mode. A KBr glass cell was used for holding the Li-SES samples. Loading of a sample into the cell was carried out in a glovebox filled with argon. The sample was injected into the KBr cell using a glass syringe.

3. RESULTS AND DISCUSSION

The color of the $Li_x\beta(THF)_n$ solutions ranges from dark blue for low concentrations of Li to dark green for higher concentrations of Li. This is consistent with the observation of Melero et al.[23] that, when they dissolved an excess of lithium in biphenyl in the mole ratio of 12:1 in THF, a deeply greenish-blue colored suspension was obtained. They suggested that this color resulted from the presence of biphenyl dianions generated by lithium metal reduction of biphenyl in the solution.

3.1. Volume Change with Biphenyl Concentration in THF.
In an attempt to find out the actual concentration of biphenyl based on the final volume of biphenyl in THF, 100 mL of THF was used to dissolve biphenyl. We measured the total volume, V, of biphenyl in THF solutions $Li_0\beta(THF)_n$ as a function of the THF/biphenyl molar ratio n; $4.11 \leq n \leq 24.7$. The data are depicted in Figure 1. This shows a linear dependence following eq 2.

$$V = 160.7\left(\frac{1}{n}\right) + 102.9 \tag{2}$$

Total Volume, V_t/ ml
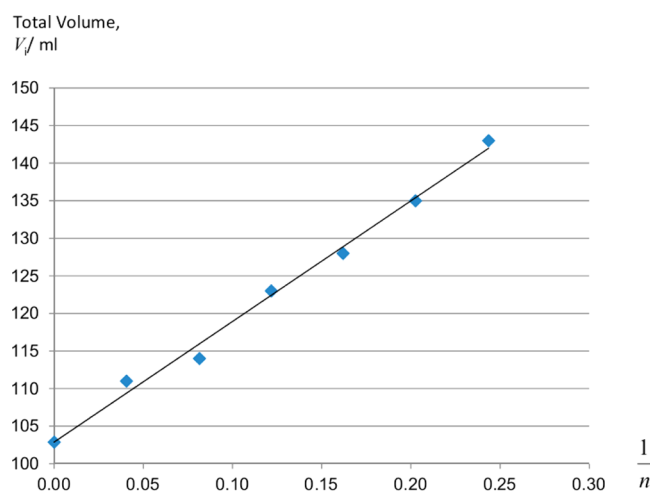
Figure 1. Change in volume of the $Li_0\beta(THF)_n$ (no Li present) solution with biphenyl/THF molar ratio $1/n$ at ambient temperature.

The equation is valid up to the saturation of biphenyl in THF at ambient temperature in argon, which is around $1/n = 0.25$.

For example, in a molar solution of biphenyl in THF, $n = 11.11$ mol. The corresponding volume is 117.3 mL according to eq 2.

We observed the viscosity of the $Li_x\beta(THF)_n$ solution increased not only when there is an increase in the molar ratio of β/THF but also when lithium was dissolved to form a SES.

3.2. Conductivity Studies of Li-SES.
The conductivity data of $Li_x\beta(THF)_n$ solutions is shown in Figure 2. The following observations can be made:
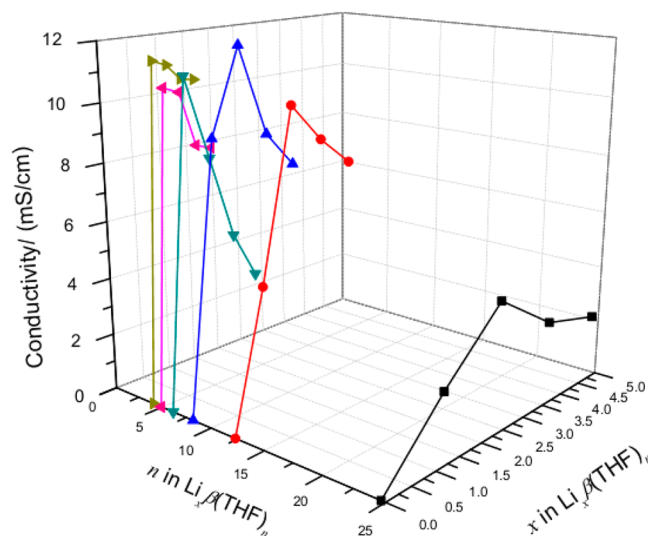
Figure 2. Li-SES electrical conductivity versus biphenyl THF composition, "n", and Li/biphenyl mole ratio "x" in $Li_x\beta(THF)_n$ compositional formulas.

(1) When no lithium is present in the β/THF solution, the conductivity is below the measuring range of the conductivity meter. This indicates that, when only biphenyl is dissolved in THF, there is too small an amount of, if any, charge carriers in the solution, and so conductivity is close to zero.

(2) Conductivity can only be measured when Li is added, which indicates sufficient charge carriers were formed in the process of Li dissolution.

(3) For the three samples with biphenyl concentration in THF, such that $n < 8.22$, the maximum conductivity is achieved when the Li:β ratio is in the range between 0.5:1 and 1:1. By contrast, for the other three samples, where the concentration of biphenyl in THF is such that $n > 8.22$, the maximum conductivity is achieved when the Li:β molar ratio is around 1:1.

(4) The highest conductivity measured is around 12.0 mS/cm and was achieved with the composition $Li_{1.0}\beta(THF)_{8.2}$.

Initially, as the lithium concentration increases, the conductivity increases as well. Then, the conductivity goes through a maximum before decreasing or leveling off. At low concentrations, the conductivity should be controlled by the concentration of charge carriers, whereas, at higher concentrations, the viscosity should be the controlling factor. In the Li-SES, charge carriers consist of both Li^+ and solvated electrons. Our conductivity measurements account for both cationic and "anionic" contributions.

A preliminary study on the temperature dependence of conductivity σ carried out on $Li_{1.0}\beta(THF)_{12.3}$ solution in the temperature range 14.6 °C < T < 22.5 °C showed a metallic behavior, i.e., decrease in conductivity with temperature with quasi-linear behavior, $\sigma = -0.0971T + 13.244$ (T in °C).

3.3. FTIR Studies of Li-SES.
The FTIR spectra of $Li_x\beta(THF)_n$ solutions are shown in Figure 3 together with the
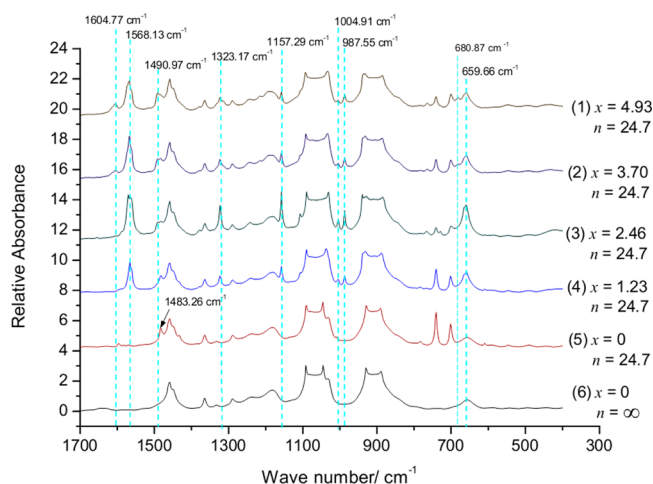
Figure 3. Comparison between the Li-SES FT-IR spectra of decreasing Li:biphenyl mole ratios against the spectra of THF and biphenyl in THF.
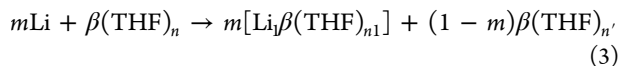

Figure 4. (a) FT-IR spectrum in the 1700–1100 cm^{-1} range, with biphenyl in THF background subtracted. (b) FT-IR spectra in the 1040–980 cm^{-1} range and in the 800–600 cm^{-1} range with biphenyl in THF background subtracted.

spectra of THF only ($x = 0$, $n = \infty$) and of biphenyl in THF ($x = 0$, $n = 24.7$).

Spectra 1–4 in Figure 3 are from the $\text{Li}_x\beta(\text{THF})_n$ samples where $n = 24.7$ and $x > 0$. Comparing with spectrum 5, where $x = 0$, $n = 24.7$, additional modes are found which can be attributed to the formation of the Li-SES: 1604.77, 1568.13, 1323.17, 1157.29, 1107.14, 1004.91, and 987.55 cm^{-1}. Besides these new modes, there are also two existing modes from spectrum 5 that undergo changes in intensity as the amount of Li increases in the Li-SES: They are (1) a peak shift from 1483.26 to 1490.77 cm^{-1}, including changes in intensity to the peak, and (2) changes in peak intensity at 659.66 cm^{-1}.
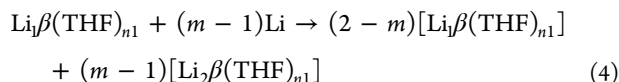
Figure 4 shows the Li-SES spectra after the subtraction of the background spectrum, $x = 0$, $n = 24.7$. To account for the additional peaks appearing in the Li-SES, the following two possible models are proposed.

Model 1 - $\text{Li}_1\beta(\text{THF})_{n1}$ is formed first following eq 3:
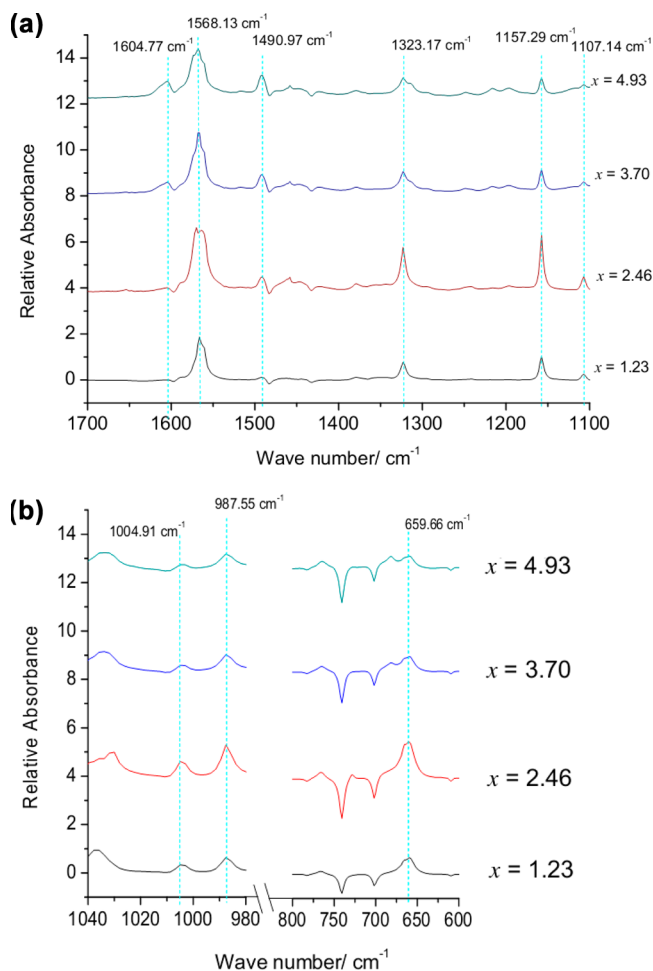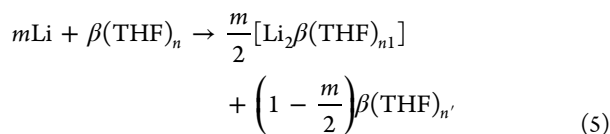For $0 \leq m \leq 1$,

$$m\text{Li} + \beta(\text{THF})_n \rightarrow m[\text{Li}_1\beta(\text{THF})_{n1}] + (1-m)\beta(\text{THF})_{n'} \tag{3}$$

then followed by the formation of $\text{Li}_2\beta$ for $m > 1$:

$$\text{Li}_1\beta(\text{THF})_{n1} + (m-1)\text{Li} \rightarrow (2-m)[\text{Li}_1\beta(\text{THF})_{n1}]$$
$$+ (m-1)[\text{Li}_2\beta(\text{THF})_{n1}] \tag{4}$$

As biphenyl has two benzene rings, the postulate here is that one biphenyl molecule should be able to coordinate with at least two Li atoms. Hence, from eqs 3 and 4, when $m = 2$, there is only $\text{Li}_2\beta(\text{THF})_{n1}$. Model 1 is based on the assumption that 1 Li atom will react with 1 biphenyl molecule first in an excess of biphenyl in THF, as shown in eq 3. When every biphenyl molecule in THF has reacted with one Li atom to form $\text{Li}_1\beta(\text{THF})_{n1}$, subsequent Li atoms will react with $\text{Li}_1\beta(\text{THF})_{n1}$ to form $\text{Li}_2\beta(\text{THF})_{n1}$.

Model 2 - $\text{Li}_2\beta(\text{THF})_{n1}$ is formed first following eq 5:
For $0 < m < 2$,

$$m\text{Li} + \beta(\text{THF})_n \rightarrow \frac{m}{2}[\text{Li}_2\beta(\text{THF})_{n1}]$$
$$+ \left(1 - \frac{m}{2}\right)\beta(\text{THF})_{n'} \tag{5}$$

In a preliminary DFT study, it was found that, in the Li–naphthalene–THF system, the $\text{Li}_2(\text{naphthalene})$ form is thermodynamically more favorable than the $\text{Li}_1(\text{naphthalene})$ form.[24] The difference between naphthalene and biphenyl is that naphthalene consists of two benzene rings that are fused and sharing two carbon atoms between them, whereas biphenyl consists of two benzene rings that are joined together by a single —C—C— bond between one carbon atom on each benzene ring.

The relationship between the peak intensity of $\text{Li}_x\beta(\text{THF})_{24.7}$ and x for the seven new peaks from Figure 4 is presented in Figure 5. With the exception of the 1604.77 cm^{-1} peak in Figure 5a which shows the intensity of the peak increasing with the Li concentration in the Li-SES, the other six peaks show an increase and then a maximum of about $x = 2.46$ and a subsequent decrease in intensity. The origin of the 1604.77 cm^{-1} peak appearing after Li is added to the biphenyl in THF is likely due to the localization effect of the π electrons in the biphenyl aromatic rings. When a Li atom donates one electron to one of the two benzene rings of biphenyl, the biphenyl becomes an anion and the localized —C=C— in the anion ring shows up as the 1604.77 cm^{-1} peak. Also, the existing peak from the biphenyl in THF (spectrum 5 in Figure 3) is shifted from 1483.26 to 1490.77 cm^{-1}. The original peak at 1483.26 cm^{-1} is due to the aromatic —C=C— stretching vibration.[25] The peak shift from 1483.26 cm^{-1} to a higher wavenumber position of 1490.77 cm^{-1}
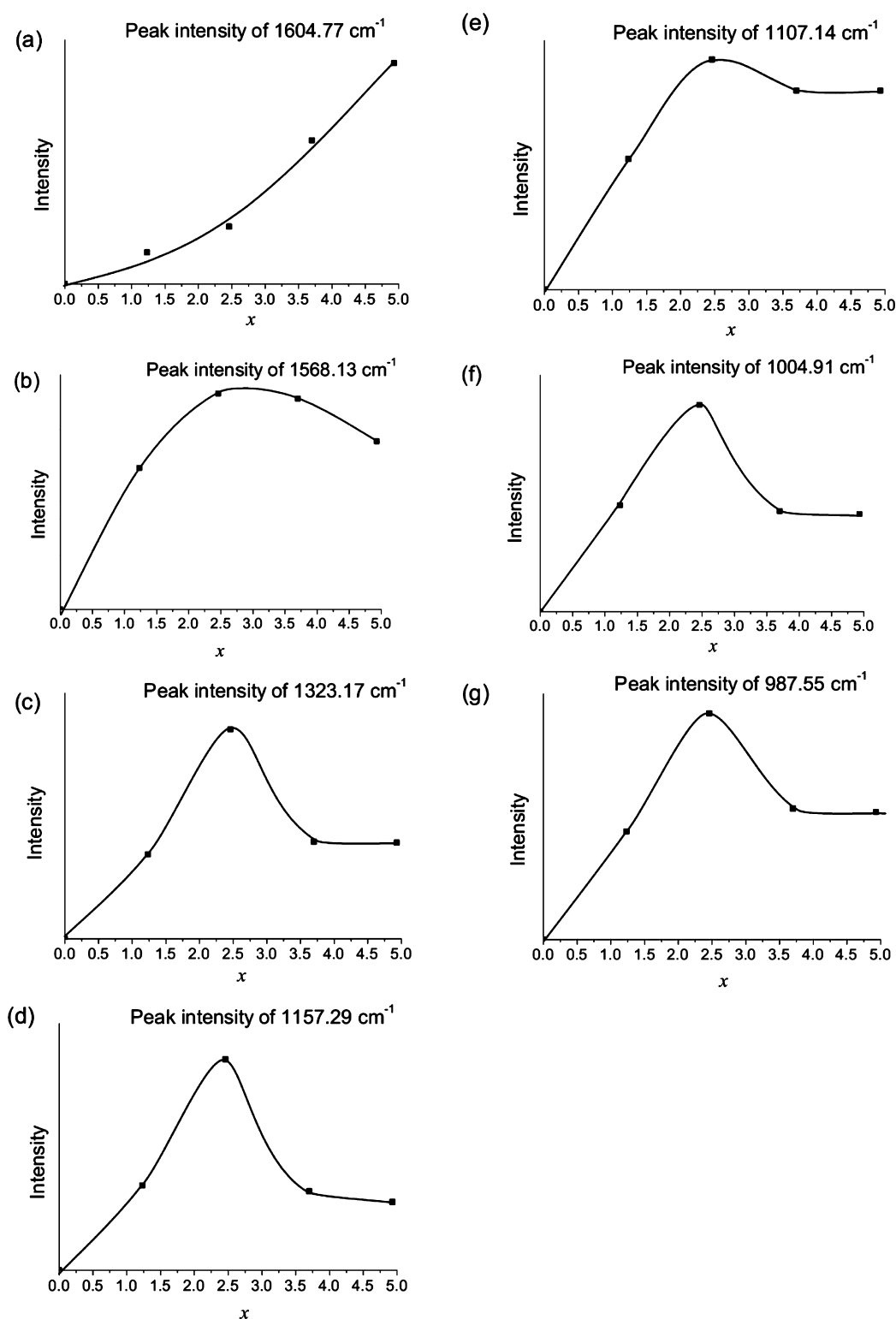
Figure 5. Relationship between IR peak intensity and lithium composition x.

indicates that the π electrons in the aromatic ring have become more localized.[26]

For the other peaks in Figure 5b−g including the peak at 659.66 cm^{-1} from the biphenyl in the THF spectrum in Figure 3, it can be seen that the peaks have a maximum intensity at a Li:β mole ratio of ~1:1 before decreasing for higher mole ratios. These peaks are characteristic for Li-SES using biphenyl in THF. Accordingly, model 1 seems more likely than model 2; that is, the

intermediate species formed when Li metal is dissolved in biphenyl in THF is initially $Li_1\beta(THF)_{n1}$ followed by $Li_2\beta$-$(THF)_{n1}$. After every free biphenyl molecule has bonded with one Li, there will only be $Li_1\beta(THF)_{n1}$ in THF. The subsequent product when Li is added to $Li_1\beta(THF)_{n1}$ is $Li_2\beta(THF)_{n1}$. From Figure 3, there are two additional peaks formed at 1604.77 and 680.87 cm^{-1} when the Li/β ratio is greater than 1 (spectra 1 and 2). The appearance of these two additional peaks can be

attributed to the formation of $Li_2\beta(THF)_{n1}$. Also, the intensity of these two peaks increases with increasing Li: β mole ratio indicating an increase in the population of $Li_2\beta(THF)_{n1}$.

Since $Li_1\beta(THF)_{n1}$ is an asymmetric molecule, as more $Li_1\beta(THF)_{n1}$ is formed, the intensity of its characteristic peaks becomes higher. A symmetric molecule is IR-inactive, and hence, we will not expect any IR peaks for symmetric molecules. When only $Li_2\beta(THF)_{n1}$ molecules are left in the solution after all the $Li_1\beta(THF)_{n1}$ have become $Li_2\beta(THF)_{n1}$, the peak intensities decrease. The peaks do not disappear totally because $Li_2\beta(THF)_{n1}$ is not necessarily symmetric and planar. While it might be possible for some molecules of $Li_2\beta(THF)_{n1}$ to exist in a symmetric form in the SES, there might be other instances where the two benzene rings of the $Li_2\beta(THF)_{n1}$ may not be planar. This is because of the structure of the biphenyl molecule, where the two benzene rings can rotate around their internal C−C bond which links the rings together. More studies are necessary for better understanding of the structure of the $Li_x\beta(THF)_n$ system, including modeling by *ab initio* computational methods.

4. CONCLUSIONS

Li-SES were prepared with biphenyl as the electron receptors and THF as the solvent. We found the highest electric conductivity to be ∼12 mS/cm, which is achieved in the $Li_{1.0}\beta(THF)_{8.2}$ solution. We also found Li-SES to show a metallic behavior. FTIR studies suggest $Li_1\beta(THF)_{n1}$ is formed first followed by $Li_2\beta(THF)_{n1}$ when Li is dissolved in $\beta(THF)$ in the $Li_x\beta(THF)_n$ system for increasing x. Preliminary OCV measurements in a Li half-cell of the following configuration:

$$(-)Pt/Li/ceramics\ membrane/Li_{1.0}\beta(THF)_{12.3}/Pt(+)$$
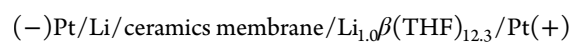
give OCV ∼ 0.68 V. Therefore, Li-SES can potentially be used as a liquid anode for lithium battery application as disclosed in a US Patent.[8] More studies are ongoing to further understand the electrical transport properties of Li-SES and to further describe their phase diagram.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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9060

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