Quantitative Mapping of Molecular Substituents to Macroscopic Properties Enables Predictive Design of Oligoethylene Glycol-Based Lithium Electrolytes
Quantitative Mapping of Molecular Substituents to Macroscopic Properties Enables Predictive Design of Oligoethylene Glycol-Based Lithium Electrolytes

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ABSTRACT: Molecular details often dictate the macroscopic properties of materials, yet due to their vastly different length scales, relationships between molecular structure and bulk properties can be difficult to predict a priori, requiring Edisonian optimizations and preventing rational design. Here, we introduce an easy-to-execute strategy based on linear free energy relationships (LFERs) that enables quantitative correlation and prediction of how molecular modifications, i.e., substituents, impact the ensemble properties of materials. First, we developed substituent parameters based on inexpensive, DFT-computed energetics of elementary pairwise interactions between a given substituent and other constant components of the material. These substituent parameters were then used as inputs to regression analyses of experimentally measured bulk properties, generating a predictive statistical model. We applied this approach to a widely studied class of electrolyte materials: oligo-ethylene glycol (OEG)−LiTFSI mixtures; the resulting model enables elucidation of fundamental physical principles that govern the properties of these electrolytes and also enables prediction of the properties of novel, improved OEG−LiTFSI-based electrolytes. The framework presented here for using context-specific substituent parameters will potentially enhance the throughput of screening new molecular designs for next-generation energy storage devices and other materials-oriented contexts where classical substituent parameters (e.g., Hammett parameters) may not be available or effective.

INTRODUCTION

Quantitative parameters for understanding molecular substituent effects have broad applications across chemistry (examples include catalysis, organic semiconductors, and molecular recognition). Through systematic examination of the impacts of substituents on the thermodynamics or kinetics of a process of interest, it becomes possible to unveil mechanistic details that can guide the design of improved processes. In materials-based systems, however, quantitatively predicting how molecular modifications will translate across length scales to yield macroscopic property changes is especially challenging. For example, in the field of organic lithium conducting electrolytes, where ion transport is controlled by a dynamic ensemble of all microscopic structures formed between the electrolyte solvent, a dissolved lithium salt, and other possible additives, novel electrolyte components are often designed using chemical intuition and Edisonian (i.e., trial and error) optimization. Although this approach has led to significant advances, it cannot provide a priori quantitative predictions of the properties of novel electrolytes.
A quantitative model for understanding the impacts of molecular substituents on bulk lithium electrolyte properties will significantly advance the development of next-generation energy storage devices that require molecularly optimized electrolytes with high ionic conductivities \(^{15}\) at room temperature, e.g., on par with current liquid carbonate electrolytes \((\sim 10 \text{ mS cm}^{-1} \text{ at } 298 \text{ K})\) or solid-state ceramics \(\text{(e.g., a sulfide-based superionic conductor with ionic conductivity of } 25 \text{ mS cm}^{-1} \text{ at } 298 \text{ K})^{16}\), yet with improved safety and processability \(^{17}\). Moreover, the approach to developing such a quantitative model could be broadly applied to other complex materials systems where molecular features drive macroscopic function.

Seeking an electrolyte system to serve as the basis for building such a model, we chose the broadly used and widely studied class of electrolytes based on the oligoethylene glycol (OEG) structural unit, e.g., glymes and poly(ethylene oxide) (PEO), and the salt LiTFSI (Figure 1a). Optimized OEG-based electrolytes display good lithium ion conductivities \(\text{(e.g., } 1.6 \text{ mS cm}^{-1} \text{ at } 303 \text{ K for tetraglyme}^{18}\text{ and up to } 0.45 \text{ mS cm}^{-1} \text{ at } 298 \text{ K})^{19}\), and promising electrochemical and mechanical stabilities \(^{17}\). Moreover, the approach to developing such a quantitative model could be broadly applied to other complex materials systems where molecular features drive macroscopic function.

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Figure 1. Experimental design principles and workflow for probing the role of substituents in oligoethylene glycol (OEG) LiTFSI-based electrolytes. (a) Substituents \((R)\) introduce new noncovalent interactions to OEG. (b) The pairwise interaction energies \((\Delta E_{i-R})\) of each substituent with \(\text{Li}^+, \text{TFSI}^-, \text{DME}, \text{and itself (self-association)}\) in the gas phase were obtained using DFT calculations. These calculated substituent parameters were then correlated to (c) experimental measurements through (d) a regression model, which then allows (e) prediction of the experimental properties of new compounds and elucidates design principles.
the same scale and are typically limited to screening the properties of isolated molecules or small clusters. Meanwhile, purely statistical approaches such as machine learning (ML) have proven helpful for learning complex correlations between bulk properties and descriptors (either based on structures or properties), but these methods typically require large data sets and have poor transferability, especially when not backed by physics-based invariants. Lastly, methods based on linear free energy relationships (LFERs) have been widely used to elucidate mechanisms of chemical reactions and catalytic transformations. For example, multidimensional regression analysis built upon LFERs has provided insights into the complex thermodynamic and kinetic effects in determining the selectivity of catalytic reactions. Nevertheless, such approaches require access to relevant descriptors (e.g., Hammett parameters or other calculated substituent parameters) that are unique to each substituent; such descriptors and methods have not, to our knowledge, been developed in the context of lithium electrolyte materials.

Here, we introduce a strategy based on multidimensional LFERs that provides quantitative correlations between molecular substituents and bulk properties in OEG-based electrolytes (Figure 1). This approach does not require an existing set of substituent parameters or modeling the exact dynamic ensemble of all microscopic species in such systems. Instead, it leverages simple DFT calculations to obtain pairwise interaction energies that serve as unique descriptors for substituents in OEG-based electrolytes (Figure 1b). Simple statistical models (Figure 1d, regression analysis) based on the Arrhenius (main text) and Vogel–Tammann–Fulcher (VTF, Section S4 in the SI) equations are then used to correlate these descriptors (substituent parameters) with experimentally observed variables obtained for a small library of synthesized OEG-based electrolytes. The regression generated a quantitative model that provides mechanistic insights into the role of substituents in these electrolytes as well as the ability to predict the properties of new OEG-based electrolytes (Figure 1e). The latter was verified by the synthesis and characterization of three OEG-based electrolytes that were predicted and observed to have comparably high, medium, and low conductivity. To the best of our knowledge, this work comprises the first example of using elementary energy-to-ensemble property mapping in the context of organic materials, providing unique insights into a broadly important class of electrolytes for next-generation energy storage applications.

## MODEL SYSTEM DESIGN

### General Approach and Model System Design.

To begin, we designed and obtained 11 OEGs with different substituents introduced to 6–7 ethylene glycol (EG) units (Figure 2a, see Sections S2 and S6 in the SI for synthetic procedures and molecular characterization data). The parent octaglyme was included to provide a library of 12 experimental compounds with substituents that span a range of chemical characteristics including hydrogen bond donors (e.g., triazole, urea, thiourea, thiourea-hydroxyl group) and acceptors (e.g., triazole, carbonate, urea, thiourea, thiourea-hydroxyl group), Lewis acids (e.g., glycolate)diboron, benzenedicarboxylic ester) and bases (e.g., carbonate, triazole, thioether, hydroxyl), and nonpolar aromatics (e.g., xylenes). The structures of substituents used for DFT calculations are defined as the smallest fragment separated by ether oxygen atoms from the OEG chain and terminated by methyl groups (Figure 2b). A general, unambiguous procedure for selecting the substituent structure, which can be applied to newly designed OEG derivatives, can be found in the SI (Section S1). Four substituent (R)−derived binary complexes and their pairwise interaction energies in the gas phase (R−Li+), (R−TFSI, R−EG, and R−R) are used to represent the additional intermolecular interactions induced by the substituents in the bulk phase (Figure 1a,b); these interactions will ultimately perturb the electrolyte properties relative to the parent electrolyte based on octaglyme (we used a first-order approximation assuming that these 4 interaction energies can capture the underpinning physical factors affecting ion diffusion; other potential substituent effects, such as inductive effects introduced to the OEG chain by substituents, are expected to be comparatively small and thus are not explicitly included in our regression model). The key goal of this work is to build a model that allows us to explain and predict these perturbations, which, due to competing outcomes associated with each interaction, would be very difficult using chemical intuition alone. For example, one could reasonably hypothesize that increasing R−Li+ and R−TFSI interaction strengths could promote salt dissociation and therefore increase ionic conductivity; one could also reasonably hypothesize, however, that increasing these interactions would increase viscosity and therefore decrease ionic conductivity.

In order to quantify the strengths of these four pairwise interactions, DFT calculations of the substituent fragments (Figure 2b) and an isolated dimethoxyethane (DME), the latter representing octaglyme, are used (Figure 1b), providing a set of substituent parameters that can be mapped onto the experimentally measured properties of these electrolytes. Then, the experimentally measured conductivity and viscosity of each electrolyte (Figure 1c) were correlated to these DFT-obtained parameters through regression analysis to generate a predictive model (Figure 1d).

## RESULTS AND DISCUSSION

### Temperature-Dependent Ionic Conductivity and Viscosity Measurements.

The temperature-dependent molal ionic conductivity (normalized by molal concentration in mol kg−1) and viscosity of each of the 12 OEG-based oligomers blended with LiTFSI at a Li/O ratio of 1/12 are provided in Figure 2c,d, respectively (see Figure S1 for examples of raw electrochemical impedance spectroscopy and Figure S2 for absolute ion conductivity data). We selected a constant Li/O ratio (1/12, commonly used for OEG-based electrolytes) to better isolate the differences between these substituents. Only ether oxygen atoms were counted for the Li/O ratio, and the resulting molality of the 12 electrolyte mixtures ranges from 1.1–2.1 mol kg−1. The results clearly show that the changes of molecular substituents significantly impact these ensemble properties, with variations in conductivity and viscosity that span ~3 orders of magnitude. The range of the molar conductivities of the 12 OEG−LiTFSI-based electrolytes at 353 K (0.0005−0.004 S cm−1/mol kg−1) is consistent with the reported molar conductivity of glyme−LiTFSI mixtures (0.5–3 S cm2 mol−1 = 0.0005–0.003 S cm−1/ mol L−1). At 353 K, the density of OEG−salt mixtures is usually ~1 kg L−1. In addition, molal conductivity and viscosity are inversely correlated (see Figure S3 for the correlations between conductivity and molar viscosity, also known as Walden analysis), in agreement with data collected for glyme-based electrolytes as well. Finally, introducing sub-
stituents was generally observed to lower molal ionic conductivity and increase viscosity compared to the parent octaglyme-based electrolyte.

The temperature-dependent conductivity and viscosity data were analyzed using the Arrhenius equation (\( \ln Y_m = \ln A - \frac{E_a}{kT} \)), from which activation energy, \( E_a \), and pre-exponential factor, \( A \), were extracted (Tables S1 and S2) for each electrolyte, with excellent fit (Figures S4 and S5). The fitted \( E_a \) of the octaglyme-based electrolyte (conductivity, 0.29 ± 0.02 eV; and viscosity, 0.29 ± 0.02 eV) is close to the reported values for related OEG-based electrolytes (e.g., \( E_a \) of the conductivity of 2 M LiTFSI in tetraglyme was reported to be 0.34 eV).55 Interestingly, \( E_a \) for the octaglyme electrolyte is the lowest among the 12 oligomers, and the introduction of substituents leads to considerable increases in \( E_a \) (the highest \( E_a \) is 0.65 eV for conductivity and 0.66 eV for viscosity, both for benzenediboronic ester). The increase in \( E_a \) across different oligomers is mirrored by the growth in \( A \) (Figure S6), an effect known as the enthalpy–entropy compensation.56,57

As the molal conductivity and viscosity (Figure 2c,d) exhibit some temperature-dependent deviation from the Arrhenius model, we also analyzed the data using the VTF equation (\( \ln A - \frac{E_a}{k(T - T_0)} \)), where \( T_0 = T_g - 50 \) K and \( T_g \) is glass transition temperature),58 yielding a similar goodness-of-fit (Figures S4 and S5 and Tables S3 and S4) as the Arrhenius equation-based analysis. Unlike the Arrhenius model which yields \( E_a \) values spanning a wide range (0.30–0.65 eV), the values of \( E_a \) and \( A \) obtained from the VTF model are quite close to each other (e.g., \( E_a \) for conductivity ranges from 0.10 to 0.13 eV, Figure S7 and Tables S1–S4), presumably due to the inclusion of experimentally determined \( T_g \) (\( T_0 = T_g - 50 \) K) values in the VTF fitting equation. The \( T_g \) values for these oligomers span a wide range of temperatures (40 K, Section S7

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**Figure 2.** (a) Library of OEG derivatives that contain varied substituents (R) studied in this work. (b) R groups used for pairwise DFT calculations (see Section S1 for general rules for selecting the structure of the R group for a given oligomer). (c) Temperature-dependent molal ionic conductivities and (d) inverse viscosities of OEG–LiTFSI electrolytes (LiTFSI, Li/O = 1/12). The molality of LiTFSI in each sample (1.1–2.1 mol kg\(^{-1}\)) was determined by the number of moles of LiTFSI divided by the mass of the oligomer. The parent octaglyme electrolyte is shown in red; all other substituents are color-coded as shown in part b.
and Table S5) and were found to correlate well to molal conductivity, viscosity, and the Arrhenius $E_a$ (Figures S8 and S9). As a result, the fitted $E_a$ based on the VTF equation is less informative in reflecting the difference between the modified oligomers, which to a large degree is due to $T_g$. Thus, in the following sections, where we try to connect substituent parameters to characteristic physical properties of these OEG electrolytes, we selected the Arrhenius equation to build our regression model upon and to obtain the free energy relationship. In addition, the Arrhenius model has other advantages including simplicity (fewer fitting parameters), not requiring an experimentally measured $T_g$ (or predicted $T_g$ in the cases of new compounds), and ease of comparison with previous reports on glyme-based electrolytes. To understand the underpinning cause of the vastly different conductivities of these OEG−LiTFSI electrolytes, we used Raman spectroscopy to confirm a similarly high degree of LiTFSI dissociation for each electrolyte. The vibration band in the range 720−760 cm$^{-1}$ (corresponding to the S−N symmetric stretching vibration coupled with the CF$_3$ bending of TFSI$^-$) has been shown to enable quantification of the relative population of free and coordinated TFSI$^-$,\textsuperscript{59,60} and we first verified our capability of conducting the same analysis by obtaining the trend for salt dissociation in various glyme−LiTFSI-based electrolytes (monoglyme < triglyme < tetraglyme, Figure S10), in agreement with the literature\textsuperscript{52,54}.

Subsequently, Raman spectra in the same range (720−760 cm$^{-1}$) were collected on 6 selected OEG−LiTFSI electrolytes (Figure S11), revealing high degrees of salt dissociation comparable with octaglyme−LiTFSI for all cases (<20% monodentate LiTFSI contact ion pair). These results suggest that the difference observed in ionic conductivity of these electrolytes (Figure 2c) cannot be reasonably explained by changes in free ion concentrations.

Based on the fact that the molal conductivities of these electrolytes inversely correlate to viscosities (Figure 2c,d and Figure S3), and previous works show that the reciprocal of viscosity is approximately equated to ionic mobility,\textsuperscript{61,62} the primary reason for the conductivity of these OEG−LiTFSI electrolytes to vary is the change of ionic mobility. Increasing intermolecular interactions between polymer chains have been shown to decrease ion mobility,\textsuperscript{63} motivating our approach of connecting pairwise interaction energies to the conduction properties of OEG−LiTFSI electrolytes.

**DFT Calculations of Substituent-Based Pairwise Interaction Energies.** The interaction energies of binary complexes between each substituent and Li$^+$, TFSI$^-$, DME, and itself (Figure 1b), which represent supramolecular interactions (e.g., electrostatic, hydrogen bond, van der Waals) in the electrolyte, were computed using DFT (Figure 3). The pairwise noncovalent interaction energies induced by the substituents (BP86-D3/def2-SVP) normalized to the maximum values within the series (e.g., $\Delta E_{Li-R}$ is normalized by dividing each energy value by the maximum $\Delta E_{Li-R}$ value within the series). Top, Li$^+$ interaction, $\Delta E_{Li-R}$; bottom, DME interaction, $\Delta E_{DME-R}$; left, TFSI$^-$ interaction, $\Delta E_{TFSI-R}$; right, substituent−substituent interaction, $\Delta E_{R-R}$. Each panel a−l corresponds to 1 of the 12 substituents, with the chemical structure noted on the plot.
3 and Table S6). We chose the DFT functional (BP86-D3/ def2-SVP) to minimize computational cost while maintaining good accuracy for noncovalent interactions, particularly through empirical dispersion corrections.64,65 We additionally computed the interaction energies at a more expensive ω-B97/ xD/def2-TZVP level of theory. The higher level of theory with long-range correlated DFT functional is well benchmarked and highly accurate for noncovalent interactions.66 For comparison, the results obtained from the higher level of theory (Tables S8 and S9) showed similar trends and slightly different values compared to the lower level of theory selected for this work (Tables S6 and S7).

These interaction energies (Figure 3 and Table S6) were used subsequently in the regression fitting of temperature-dependent conductivity and viscosity data. For each calculation, randomly generated initial geometries for a binary complex between the substituent model and its counterparts (Li+, TFSI−, DME, or itself) were optimized in the gas phase (see Section S1 in the SI for the general methods and Section S8 for the optimized geometries). Interaction energies ($\Delta E_{Li-R}$, $\Delta E_{TFSI-R}$, $\Delta E_{DME-R}$, and $\Delta E_{R-R}$) in the gas phase were then obtained based on the single point energies of the optimized geometry relative to the individual unimolecular species; the values for each electrolyte are provided as 4-dimensional representations in Figure 3.

Our calculations show that, among the 4 interactions, $R-Li^+$ is the strongest for all substituents. Its value ranges from −4.3 to $\sim2.5$ eV ($\sim420$ to $\sim250$ kJ mol$^{-1}$), with the ratio between maximum and minimum $\sim2$. (Glycolato)diboron, carbonate, urea, and thioether display the strongest $Li^+$ binding (greater than $\sim3.5$ eV = $\sim350$ kJ mol$^{-1}$) among the 12 substituents.

Thiourethane, triazole, thiourea, o-xylene, and benzenedicarboxylic ester substituents have intermediate $Li^+$ binding (−3 to $\sim3.5$ eV or $\sim300$ to $\sim350$ kJ mol$^{-1}$), and DME, p-xylene, and hydroxyl groups have the weakest $Li^+$ binding (−2.5 to $\sim3$ eV or $\sim250$ to $\sim300$ kJ mol$^{-1}$), as shown in Figure 3 and Figure S12. The other three interactions are weaker than $R-Li^+$, following the order of $R-TFSI^− > R-R > R-DME$. The strength of the $R-TFSI^−$ interaction ranges from $\sim130$ to $\sim70$ kJ mol$^{-1}$, with the max/min ratio also $\sim2$. Stronger $R-TFSI^−$ interactions were seen among the substituents with hydrogen bond donors such as triazole, urea, thiourea, and thiourethane (−1 to $\sim1.3$ eV or $\sim100$ to $\sim130$ kJ mol$^{-1}$ Figure S12), while groups such as DME display weaker $R-TFSI^−$ interactions (Figure S12). On the contrary, the strengths of the $R-R$ and $R-DME$ interactions for the 12 electrolytes both vary in a relatively greater range with max/min $\sim4$ ($\Delta E_{R-R}$ ranges from $\sim1$ to $\sim0.27$ eV or $\sim100$ to $\sim26$ kJ mol$^{-1}$, and $\Delta E_{R-DME}$ ranges from $\sim0.7$ to $\sim0.2$ eV or $\sim70$ to $\sim20$ kJ mol$^{-1}$, Figure S12). It is notable that substituents with hydrogen bond donors/acceptors (urea, thiourea, thiourethane), $\pi$-systems (benzenedicarboxylic ester), and strong dipoles (urea, thiourea, thiourethane, and triazole) display strong self-association ($R-R$ and $R-DME$ interactions).

As these 4 interaction energies are expected to establish a multidimensional description of chemical modifications of the OEG electrolytes, we checked for correlations between them (Figure S12) as well as for potential correlations with other commonly used substituent parameters (i.e., meta and para Hammett constants and dipole moments, Table S10 and Figures S13–S15). The strengths of the $R-Li^+$ interaction do not appear to correlate to other interactions. The $R-R$
interaction shows a linear correlation with $R-DME$ ($r^2 = 0.82$), presumably on account of similar underpinning binding motifs (e.g., hydrogen bond, dipole–dipole). The $R-R$ interaction also displays a weaker linear correlation ($r^2 = 0.49$) with $R-TFSI^-$. Lastly, plots of these calculated binding energies against meta and para Hammett constants and dipole moments revealed no trends (Figures S13a, S14a, and S15a), suggesting that our calculations captured features of these substituents that are not represented by these existing substituent parameters.

**Establishing a Quantitative Model from Experimental Data and Calculated Energetics.** With our experimental results (Figure 2c,d) and calculated substituent parameters (Figure 3) in hand, we set out to build a quantitative model relating these two data sets through regression analysis. We note that the experimental conductivity and viscosity data do
such as catalysis, the experimental conductivity and (Figure S15b). Thus, as has been observed in other contexts Hammett constants, or the dipole moments of each substituent respectively, and the pre-exponential factor and the activation energy, components of the oligomers, establishing a baseline value of compensation. The term simulations. Both MD and DFT values are normalized using the maximum values within the series.

Given that the Arrhenius expression can model our experimental conductivity and viscosity data well (see above), we correlated the substituent-dependent DFT interaction energies (Figure 3) to the activation energy and the pre-exponential factor in the Arrhenius equation:

\[
\ln Y = \ln A_0 + b(a_1 \Delta E_{Li-R} + a_2 \Delta E_{TFSI-R} + a_3 \Delta E_{DME-R} + a_4 \Delta E_{R-R}) - E_{a0} + a_1 \Delta E_{Li-R} + a_2 \Delta E_{TFSI-R} + a_3 \Delta E_{DME-R} + a_4 \Delta E_{R-R} - kT
\]

where the intercept parameters \(A_0\) and \(E_{a0}\) represent the OEG components of the oligomers, establishing a baseline value of the pre-exponential factor and the activation energy, respectively, and \(b\) is a constant reflecting enthalpy–entropy compensation.\(^{57}\) The term \(a_1 \Delta E_{Li-R} + a_2 \Delta E_{TFSI-R} + a_3 \Delta E_{DME-R} + a_4 \Delta E_{R-R}\) comprises a linear combination of substituent-dependent DFT interaction energies (Figure 3), which accounts for substituent-induced perturbations to the oligomers. The values of \(a_i\) reflect the importance of the corresponding substituent parameters. We note that higher-order polynomial terms, including cross-terms between these interaction energies, may add capacity to the model but, given the size of the data set, would result in overfitting. The regression analysis of the experimental conductivities (Figure 4a) and viscosities (Figure 4b) yielded good fitting results (\(R^2 \geq 0.98\)) and provided two unique sets of fitted constants \((A_0, E_{a0}, b, a_i\) where \(i = 1, 2, 3,\) and \(4\)) for conductivity and viscosity. To verify the regression model, we examined the values of the fitted parameters. The value of \(b\) (conductivity, 27.3; viscosity, 25.8) is close to the actual enthalpy–entropy compensation factors of these electrolyte–salt mixtures determined by individual fitting of the temperature-dependent data (conductivity, 27.6; viscosity, 27.6; Figure 5b). The values of \(E_{a0}\) (conductivity, 0.24 eV; viscosity, 0.24 eV) are close to unmodified glymes (e.g., \(E_1\) of octaglyme conductivity, 0.29 ± 0.02 eV; viscosity, 0.29 ± 0.02 eV; Tables S2 and S3) with 0.05 eV difference. The "predicted" activation energy of each oligomer as determined by the regression \((E_{a0} + \sum a_i \Delta E_i)\) also matches well with the actual activation energy obtained from fitting individual temperature-dependent data (Figure S18).

We note that the activation energy in the Arrhenius equation does not correspond to a single molecular process, but rather a combination of thermal activation and changes in free volume,\(^{66,67}\) suggesting that there is no simple correlation between the fitted \(E_i\) and any of the DFT-calculated pairwise interaction energies individually.

Testing of the Model by Predicting the Properties of New OEG–LiTFSI-Based Electrolytes. To test the ability of our model to predict the properties of new OEG–LiTFSI electrolytes, we manually generated a library of 32 new substituents, calculated their substituent parameters, and predicted the conductivity and viscosity of the corresponding electrolytes using the regression model with the fitted parameters (Table S7). Guided by perceived ease-of-synthesis, we selected and synthesized three new OEG derivatives (Figure 5a) from the 32 predictions. The 3 new compounds are based on propylene (Figure 5b), disopropylsilyl (Figure 5c), and sulfone (Figure 5d) substituents, which were predicted to yield electrolytes with high, medium, and low molar conductivity, respectively. Notably, the propylene-substituted electrolyte (Figure 5b), in addition to 4 of the other manually generated electrolytes, was predicted to have
greater conductivity ($0.86 \text{ mS cm}^{-1}/\text{mol kg}^{-1}$ at 298 K, predicted value) than the parent octaglyme electrolyte ($0.54 \text{ mS cm}^{-1}/\text{mol kg}^{-1}$ at 298 K, experimental value), suggesting that subtle, difficult-to-predict substituent modifications (e.g., the addition of a single methylene group) can be exploited to improve upon the properties of classical OEG-based electrolytes.

Our model does indeed enable prediction of viscosity and conductivity for these novel OEG\textendash;LiTFSI-based electrolytes, as shown in Figure 5e\textendash;h. The propylene-, diisopropylsilyl-, and sulfone-substituted electrolytes displayed the predicted high to medium to low conductivity and inverse viscosity trend, respectively. In addition, the experimentally measured molal conductivities and viscosities of the 3 new electrolytes at 298 K, for example (propylene, 0.62 mS/mol kg$^{-1}$ and 0.59 P; diisopropylsilyl, 0.24 mS/mol kg$^{-1}$ and 2.0 P; sulfone, 0.086 mS/mol kg$^{-1}$ and 10.9 P), closely match the predicted values at the same temperature (propylene, 0.86 mS/mol kg$^{-1}$ and 0.62 P; diisopropylsilyl, 0.37 mS/mol kg$^{-1}$ and 1.60 P; sulfone, 0.052 mS/mol kg$^{-1}$ and 16.8 P), indicating excellent accuracy of the prediction. These results show that our model, which is based on mapping pairwise interaction energies as substituent parameters to ensemble properties, can identify new materials with enhanced properties compared to the training set.

We note that our model also predicted that fluorinated OEG-derivatives would display improved properties (Figure S19). During the course of preparing this manuscript, Bao and co-workers reported similar fluorinated OEGs.\textsuperscript{70} Although their system is slightly different from ours (e.g., salt used and the length of the OEGs), their data generally agree with our prediction that fluorinated substituents can result in highly conductive OEG electrolytes (Figure S19).

Supporting the Physical Basis for Our DFT-Calculated Substituent Parameters Using Molecular Dynamics (MD) Simulations. As discussed above, our model allows for the prediction of novel OEG\textendash;LiTFSI electrolyte properties from simple DFT-calculated pairwise interaction energies. While successful, we sought to determine if these energies realistically reflect bulk solvation energies and solvation structures. Thus, we conducted MD simulations for three of the OEG-based (thiourea, propylene, and sulfone) LiTFSI electrolytes in the bulk phase (see Section S5 in the SI for more details). In general, the solvation structures and time-averaged interaction energies of the 3 electrolytes extracted from classical MD matched well with the elementary DFT calculations (Figures 6 and 7).

First, the geometry optimizations of the four complexes ($R$\textendash;Li, $R$\textendash;TFSI$^-$, $R$\textendash;DME, and $R$\textendash;R) were repeated using classical interatomic potentials instead of DFT. The resulting pairwise interaction energies ($\Delta E_{\text{MD}}^{\text{min}}$) are the MD calculated versions of the substituent parameters discussed above, allowing us to validate the classical interatomic potentials

| (a) | DFT | MD | (b) | DFT | MD | (c) | DFT | MD |
|-----|-----|----|-----|-----|----|-----|-----|----|
| $R$\textendash;Li$^+$ | ![DFT] | ![MD] | ![DFT] | ![MD] | ![DFT] | ![MD] |
| $R$\textendash;TFSI$^-$ | ![DFT] | ![MD] | ![DFT] | ![MD] | ![DFT] | ![MD] |
| $R$\textendash;R | ![DFT] | ![MD] | ![DFT] | ![MD] | ![DFT] | ![MD] |
| $R$\textendash;EO | ![DFT] | ![MD] | ![DFT] | ![MD] | ![DFT] | ![MD] |

Figure 7. Examples of solvation structures involving $R$\textendash;Li$^+$, $R$\textendash;TFSI$^-$, $R$\textendash;R, and $R$\textendash;EO interactions extracted from MD simulations and DFT optimized geometries of the same interactions using (a) thiourea-, (b) sulfone-, and (c) propylene-based electrolytes. MD simulations were conducted using the entire OEG molecule in the condensed phase. DFT calculations were based on substituents (vide supra) in the gas phase.
and to provide a solid basis of comparison between gas phase (DFT) and condensed phase calculations (MD). Next, condensed phase simulations of electrolytes were conducted and provided time-averaged interaction energies, \( E_{\text{MD}}(t) \), for \( R-\text{Li}, R-\text{TFSI}, R-\text{DME}, \) and \( R-R \). Comparing these three interaction energies reveals that while their absolute values differ, they show very similar trends across the 3 electrolytes studied (Figure 6). For example, the \( E_{\text{MD}}(t) \) values (Figure 6, yellow bars) are close to the \( \Delta E_{\text{R-R}} \) (DFT-calculated energies) values, suggesting that the DFT-calculated substituent parameters reflect the strength of the actual intermolecular interactions in the condensed phase to some degree.

In addition, the condensed phase simulations allowed us to manually extract solvation structures involving the substituents. We note that, for structures involving \( R-\text{TFSI}, R-\text{DME}, \) and \( R-R \) interactions, on account of their shallower potential energy surfaces (all of these interactions are much weaker than EO-Li+ interactions), the configurational degrees of freedom are high. As a result, the structures shown in Figure 7 are representatives of many other possible configurations. However, common features shared by the structures obtained from condensed phase simulations and DFT calculations can still be observed. First, we note that, for the solvation structures extracted from MD for all three OEG derivatives, Li+ is solvated by the entire OEG derivative, with the formation of 3–4 pairs of close contacts between the ether oxygen atoms (Figure 7, all \( R-\text{Li} \) structures). This finding agrees with previously reported Li+ coordination in a synergistic fashion (Figure 7). While the DFT structures do not have 4 ether oxygens available due to the fragmented substituents, such Li–ether oxygen close contact and substituent participation are still present in all the DFT optimized complexes as well. We also observed the presence of hydrogen bonds between the CH2 groups adjacent to oxygen atoms and TFSI- in both the MD and DFT structure, consistent with previous work. For thiourea, strong NH hydrogen bonding with TFSI- in both the MD and DFT structures (Figure 7a) was observed in both MD and DFT structures. Thus, while the MD and DFT structures are not exactly the same, their common features suggest that the gas phase calculations on molecular fragments are able to match some of the characteristic solvation structures observed in the simulated condensed phase.

**R–R Self-Association Governs Conductivity and Viscosity.** With the MD simulations supporting the physical basis for our DFT-calculated substituent parameters, we now analyze the fitted regression model to obtain design principles for the OEG–LiTFSI-based electrolytes. The absolute value of \( a_i \) indicates the magnitude of the impact of the corresponding interaction energy on conductivity and viscosity with greater absolute value meaning more significant impact. The sign of \( a_i \) indicates the direction of the impact with positive \( a_i \) indicating that increasing the corresponding pairwise interaction energy will lead to higher conductivity and lower viscosity while negative \( a_i \) indicates the opposite. As shown in Table 1, \( a_i \) for both conductivity and viscosity have negative signs, and their absolute values (\( a_{\text{Li+}} = -0.63 \) and \( a_{\text{TFSI-}} = -0.67 \)) for conductivity and viscosity, respectively) are much larger than those of \( a_i \) and

| Table 1. Summary of Fitting Results |
|------------------------------------|
| \( r^2 \) | RMSE | \( A_0 \) | \( E_{\text{fi}} \) (eV) | \( b \) | \( a_{\text{Li+}} \) | \( a_{\text{TFSI-}} \) | \( a_{\text{DME}} \) | \( a_{\text{dimer}} \) |
|---------------------|-----|----------|------------|-----|----------|----------|----------|----------|
| conductivity       | 0.98 | 0.31     | 11.9       | 0.24| 27.3     | 0.013    | 0.079    | 0.20      | -0.63    |
| viscosity          | 0.99 | 0.31     | 2.37 \times 10^4 | 0.24| 25.8     | 0.015    | 0.092    | 0.22      | -0.67    |

*In \( Y = \ln A_0 + b(a_1 \Delta E_{\text{Li+-R}} + a_2 \Delta E_{\text{TFSI- R}} + a_3 \Delta E_{\text{DME-R}} + a_4 \Delta E_{\text{TFSI-DME}} + a_5 \Delta E_{\text{Li+-dimer}})/kT \), where \( Y \) is either conductivity or viscosity determined by experiments, \( \Delta E_i \) is substituent parameter, and \( A_0 \), \( b \), and \( a_i \) are fitted parameters.*
is weaker than conductivity (at 298 K, correlation (Figures S16d and S17d) with experimental indicating that the and 0.22 for conductivity and viscosity, respectively),

viscosity than the other interactions.

polar substituents (dipole moment >1.5 D) correlate well with explain the observed change in properties, dipole moments of to demonstrate the significance of each substituent parameter.

The predicted properties were color-coded onto the lines where a single line represents a unique set of substituent parameters (Figure 8a, more saturated color corresponds to higher conductivity and lower viscosity). The results showed that electrolytes with high conductivity and low viscosity (more saturated lines) mostly cluster at the region of low self-association energy, suggesting that the self-association (ΔER−R) has the most significant impact on the properties. Consistently, the single interaction energy ΔER−R showed the highest correlation (Figures S16d and S17d) with experimental conductivity (at 298 K, r² = 0.86; at 363 K, r² = 0.81) and viscosity (at 298 K, r² = 0.85; at 363 K, r² = 0.88) data. The coordinates were also separated (Figure 8b and Figure S20b) to demonstrate the significance of each substituent parameter. It is interesting to note that the strength of the R−R interaction is weaker than R−Li+ and R−TFSI− in general; however, it can still have a more significant impact on conductivity and viscosity than the other interactions.

Finally, we note that, while dipole moment alone does not explain the observed change in properties, dipole moments of polar substituents (dipole moment >1.5 D) correlate well with ΔER−R and experimental conductivity (Figure S21). Thus, as a first approximation, nonpolar substituents are more promising than highly polar substituents when optimizing the conductivity of OEG electrolytes.

Proposed Mechanism for the Role of Substituents in OEG−LiTFSI Electrolytes. Combining all experimental and theoretical results, here we formulate a mechanism showing how substituents impact the properties of OEG−LiTFSI electrolytes. First, our results show the following: LiTFSI is highly dissociated in all of the studied electrolytes (Raman spectroscopy, Figure S11). The main origin of the vastly different conductivity is the change of ion mobility (Raman spectroscopy and Walden analysis, Figures S11 and S3). Li+ is primarily solvated by EO segments with R groups participating in a cooperative manner (MD, Figure 7). DFT-calculated substituent parameters can reflect condensed phase solvation (Figure 6). The R−R self-interaction (ΔER−R substituent parameter) dominates the ionic conductivities and viscosities in the regression model (Figure 8). Thus, the major impact of substituents on the resulting conductivity of OEG−LiTFSI electrolytes is the additional intermolecular interactions (as probed by ΔER−R) between the electrolyte molecules reducing the mobility of the solvated Li+ ions (OEG-Li+ complexes as the charge carriers, Figure 9). For example, stronger self-association interactions between the substituents can induce higher energetic barriers for the Li+ cation to diffuse with the oligomer molecule solvating it and/or to hop between molecules (Figure 9), manifested as higher viscosity as well as higher fitted activation energy, Ea (viscosity vs ΔER−R, Figure S17; Ea vs ΔER−R, Figure S22).

Finally, we note that the molecular weights of the oligomers studied here fall between common solvents such as glymes and entangled polymer electrolytes (Figure S23). Thus, for electrolytes based on polymers with molecular weights in the entanglement regime, the conduction mechanism (i.e., chain segmental motion) is different from the oligomers used in this study. There has been a report, however, showing that interchain interactions in such polymer electrolytes can negatively impact Li+ conductivity, which mirrors our findings in the oligomer regime and suggests that there are intrinsic similarities between the liquid-like OEG−LiTFSI electrolytes and entangled polymer electrolytes above their Тg. We envision that, for polymer electrolytes with high molecular weights, although their entanglement prevents Li+ from diffusing with individual macromolecules, interchain self-association interactions can still create energy barriers that

Figure 9. Proposed mechanistic view (a) weak and (b) strong self-association interactions between substituents can result in high and low ionic conductivity, respectively.

Δa1 (a1 = 0.013 and 0.015, a2 = 0.079 and 0.092, and a3 = 0.20 and 0.22 for conductivity and viscosity, respectively), indicating that the R−R self-association might be the dominant factor impacting the large changes in the conductivity and viscosity of these electrolytes (Figures S16d and S17d).

To examine the role of R−R self-association in further detail and to determine if it applies to a broader set of electrolytes beyond those studied above, a parallel coordinate analysis (conductivity, Figure 8; viscosity, Figure S20) was conducted using the prediction model. 1000 virtual substituents were generated using a Monte Carlo approach. Each virtual substituent has 4 randomly generated substituent parameters (interaction energies) within the range established by the previous DFT-calculated substituent parameters. While these virtual substituents do not necessarily have corresponding chemical structures, they sample the whole space of all possible combinations of the substituent parameters. Thus, predicting the molal conductivity and viscosity of these virtual substituents allows us to understand general features of the regression model.

The predicted properties were color-coded onto the lines where a single line represents a unique set of substituent parameters (Figure 8a, more saturated color corresponds to higher conductivity and lower viscosity). The results showed that electrolytes with high conductivity and low viscosity (more saturated lines) mostly cluster at the region of low self-association energy, suggesting that the self-association (ΔER−R) has the most significant impact on the properties. Consistently, the single interaction energy ΔER−R showed the highest correlation (Figures S16d and S17d) with experimental conductivity (at 298 K, r² = 0.86; at 363 K, r² = 0.81) and viscosity (at 298 K, r² = 0.85; at 363 K, r² = 0.88) data. The coordinates were also separated (Figure 8b and Figure S20b) to demonstrate the significance of each substituent parameter. It is interesting to note that the strength of the R−R interaction is weaker than R−Li+ and R−TFSI− in general; however, it can still have a more significant impact on conductivity and viscosity than the other interactions.

Finally, we note that, while dipole moment alone does not explain the observed change in properties, dipole moments of polar substituents (dipole moment >1.5 D) correlate well with ΔER−R and experimental conductivity (Figure S21). Thus, as a first approximation, nonpolar substituents are more promising than highly polar substituents when optimizing the conductivity of OEG electrolytes.

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increase $T_g$ enhance crystallinity, and decrease segmental motion dynamics that support Li$^+$ conduction when above $T_g$. Thus, it may be possible to utilize our method to study the impact of substituents on polymer electrolytes beyond entanglement. In addition, we also envision that the approach demonstrated here can be replicated (with some modifications) to quantitatively study and predict the properties of OEG electrolytes at various salt concentrations and with multiple substituents.

Safety Statement. No unexpected or unusually high safety hazards were encountered.

■ CONCLUSIONS

We reported a new method of quantitatively evaluating the impact of substituents on the properties of OEG–LiTFSI-based electrolytes. The method is complementary to the commonly used MD, DFT, and purely statistical approaches to understanding the impacts of molecular modifications to electrolytes and is less limited by the difficulties of obtaining a complete dynamic ensemble of the complex electrolyte–salt mixtures. Our framework is based on mapping the complex ensemble properties (e.g., conductivity and viscosity) to a set of custom-built substituent parameters easily obtained from DFT-calculated pairwise interaction energies. Using this method, we predicted the properties of newly designed OEG-electrolytes and experimentally verified 3 of these predictions with one of them having slightly enhanced conductivity compared to the parent octaglyme. In addition, our model revealed physical insights and design principles for OEG–LiTFSI-based electrolytes. We found that the self-association interaction is the most significant factor to consider when introducing substituents to OEG–LiTFSI-based electrolytes as this interaction can greatly impact the mobility of charge carriers within the electrolytes. While the method demonstrated here uses OEG–LiTFSI-based electrolytes as the model system, we envision that it can be applied in a wide range of similar systems where substituent modifications are introduced to a primary structure, and where pairwise noncovalent interaction energies can be used as substituent parameters to describe these modifications.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acscentsci.0c00475.

General methods, compound synthesis and characterization, supporting figures and tables, regression analysis based on VTF model, molecular dynamic simulations, NMR spectra, differential scanning calorimetry (DSC) data, and geometry of DFT optimized structures (PDF)

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Notes
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