Ultrafast Realization of Ionic Liquids with Excellent CO_2 Absorption: A trinity study of machine learning, synthesis, and precision measurement

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ABSTRACT

Efficient CO_2 capture is indispensable for achieving a carbon-neutral society while maintaining a high quality of life. Since the discovery that ionic liquids (ILs) can absorb CO_2, various solvents composed of molecular ions have been developed and their CO_2 solubility has been studied. However, it is challenging to optimize these materials to realize targeted properties as the number of candidate ion combinations for designing novel ILs is of the order of 10^{18}. In this study, electronic-structure informatics was applied as an interdisciplinary approach to quantum chemistry calculations, and combined with machine learning to search 402,114 IL candidates to identify those with better CO_2 solubility than known materials. Guided by the machine-learning results, trihexyl(tetradecyl)phosphonium perfluorooctanesulfonate was synthesized and it was experimentally confirmed that this IL has higher CO_2 solubility than trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide, which is the previous best IL for CO_2 absorption. The method developed in this study could be transferable to gas-absorbing liquids in general, such as deep eutectic solvents (hydrogen-bonded mixed organic solvents in a broad sense), which also have numerous practical applications. Therefore, we believe that our method for developing functional liquids will significantly contribute to the development of a carbon-neutral society.

INTRODUCTION

Developing CO_2-absorbing materials with better performance is a critical step toward achieving efficient CCUS (carbon dioxide capture, utilization, and storage), which has been proposed as one strategy to address global warming.[1] While there are several types of CO_2 absorbers, the intensive study of ionic liquids (ILs: room temperature molten salts) would give basic science contributing to environmental engineering toward the development of a safe and sustainable society. ILs are highly stable (low volatility and highly heat resistant) and can be chemically designed with a wide variety of ion combinations.[2-5] ILs have been applied to various gas-fixing technologies, such as temperature/pressure swing, chemical/physical absorption, and cryogenics/membrane-based separation.[6,7]

A major limitation of the development of ILs for applications is the combinatorial explosion of the ion species, *i.e.*, there are 10^{18} ILs in theory.[2] Even when ILs are limited to physical absorbents (those not leading the CO_2 chemisorption), the optimization of the CO_2 absorption capacity is experimentally challenging. The synthesis of ILs and characterization of their physical properties are more labor intensive than for electrically neutral molecular liquids due to their high viscosities. Despite the vast number of candidates, the record for the maximum amount of CO_2 physically absorbed by an IL has not been broken for over a decade.[8] To date, performing a series of targeted syntheses followed by high-precision experimental measurements have been necessary to obtain practical CO_2 absorbers.

Machine learning has proven to be an excellent approach for such combinatorial problems.[9-13] However, to date, machine learning has not been applied to identify better ILs for CO_2 absorption in a comprehensive manner including molecular design, synthesis, and CO_2 solubility observations. One of the simple reasons is that the chemical structure of ionic species cannot be uniquely defined due to charge delocalization. In addition, slight differences in the electronic states of ionic species, which can have critical effects on the properties of ILs, are challenging to describe using fingerprints.

Considering this background, this study focused on a materials informatics approach based on quantum chemistry calculations to construct a sizeable electronic structure database for ILs (**Figure 1**). This study aimed to develop a method to search for better CO_2-absorbing ILs with high accuracy and a much shorter development time by using quantum-chemical features and machine-learning techniques (electronic structure informatics). The prediction model is proposed for quick identification of ILs with better CO_2 absorption properties which is applicable for large group of materials. To prove the effectiveness of the method, the synthesis of two promising candidates and the measuring of their CO_2 solubilities are performed.

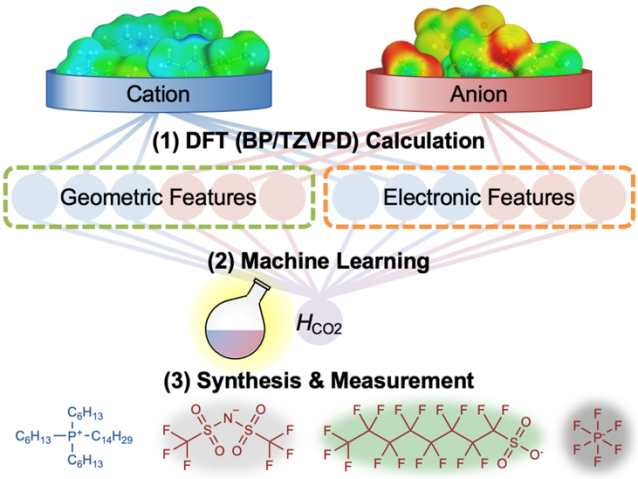


Figure 1. Concept of this study. Performing machine learning, synthesis, and precision measurement, the ILs with excellent CO_2 solubilities were realized in a short period.

METHODS

First, a theoretical screening was performed based on quantum chemistry calculations and machine learning. Following our previous studies,[14,15] 6,991 stable ion structures (6,933 cations and 58 anions in **Figure 2** and **Table 1**) were explored by density functional theory calculations at the BP/TZVP-D3 level.[16-20] Using the surface-charge-density distributions (σ-profiles)[21-24] and the optimal structures, the geometric and electronic features given in **Table 2** were calculated for all of

the ions. Then, a set of Henry's law constant (H_{CO_2}) values at 298.15 K was evaluated by COSMO-RS theory[21-23,25] for 20,000 ILs (randomly selected from the total 402,114 candidates). Half of this set were used to train a machine learning model to predict H_{CO_2} for the other IL candidates in this study. Using a cycle of feature selection, model creation, and performance evaluation, the essential molecular (ion) features for the CO_2 absorption problem were systematically selected (wrapper method).[26] For model creation, the Gaussian process regression method with the ARDMatern 5/2 kernel[27] and 5-fold cross-validation were applied to the standardized data. The performance of the created model was evaluated with 10,000 sets of test data from the value of the coefficient of determination (R^2), the root mean squared error (RMSE), and the mean absolute error (MAE). Using the well-trained model, superior ILs for CO_2 absorption were predicted within a minute. The quantum chemistry and statistical thermodynamics calculations and machine learning were performed with TURBOMOLE 7.0.[28], COSMOtherm C30_1705[29], and MATLAB[30] packages.

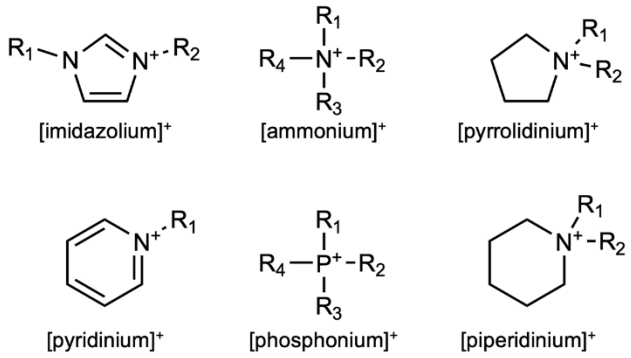


Figure 2. General structures of the cations.

Table 1. List of anions.

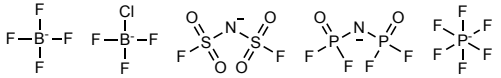
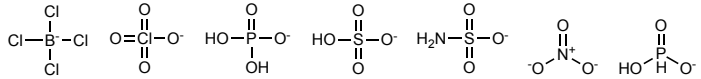
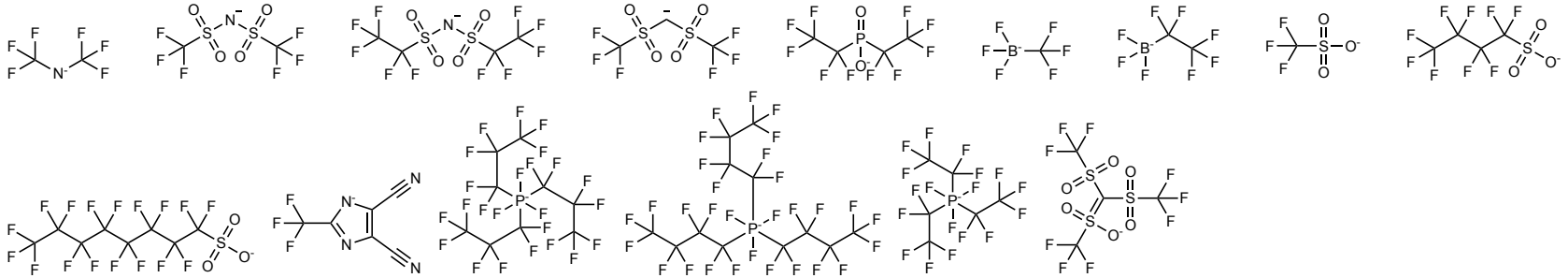
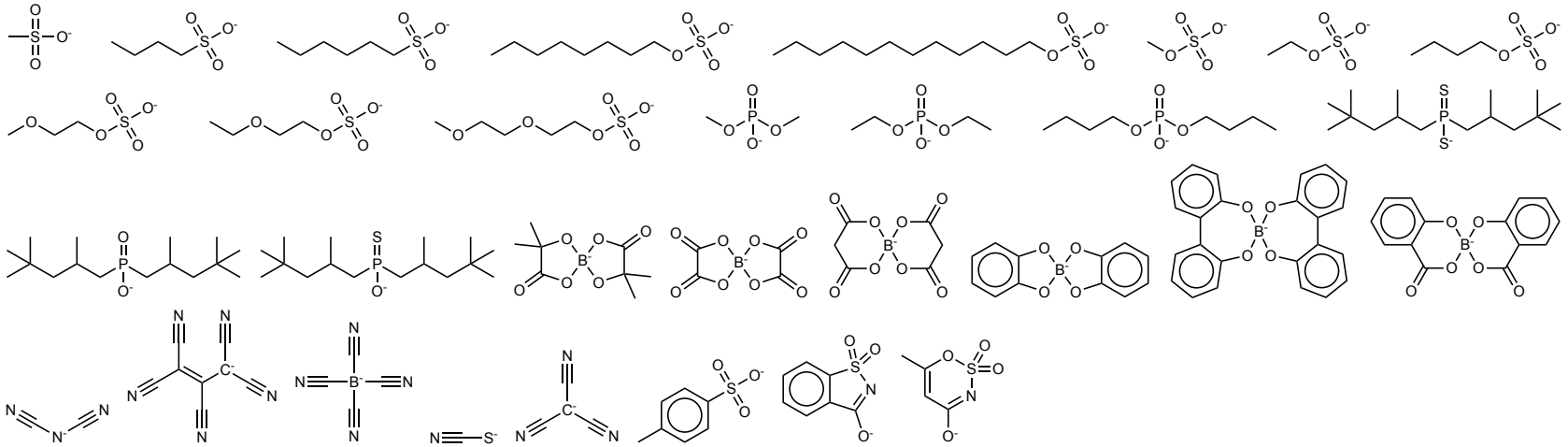
Class	Structures
Fluorine-inorganic	
Nonfluorine-inorganic	
Fluorine-organic	
Nonfluorine-organic	

Table 2. Features used.

Class	Feature			Symbol
Geometric	Volume			V
	Surface area			A
	Molecular weight			MW
	Number of conformers			N_{conf}
Electronic	$M_i = \int p(\sigma) f_i(\sigma) d\sigma$ [a]		$f_i(\sigma)$	
	σ-moments			
		2nd	σ^2	M_2
		3rd	σ^3	M_3
		4th	σ^4	M_4
		5th	σ^5	M_5
		6th	σ^6	M_6
	Hydrogen bonding (HB) moments[b]			
		acceptor	$\begin{cases} 0 & (+\sigma \le \sigma_{\mathrm{HB}}) \\ \sigma + \sigma_{\mathrm{HB}} & (+\sigma > \sigma_{\mathrm{HB}}) \end{cases}$	$M_{\mathrm{HB}acc}$
		donor	$\begin{cases} 0 & (-\sigma \le \sigma_{\mathrm{HB}}) \\ \sigma - \sigma_{\mathrm{HB}} & (-\sigma > \sigma_{\mathrm{HB}}) \end{cases}$	$M_{\mathrm{HB}don}$

a) $p(\sigma)$: σ-profile, which represents surface charge density distribution σ.
b) Threshold $\sigma_{\mathrm{HB}} = 0.1$ was used.

Then, a set of experimental confirmations was also performed. As reported in the next section, we focused on the following three representative IL candidates $[P_{66614}][A]$ (A = PFOS, PF_6, TFSA), where $[P_{66614}]^+$, $[PFOS]^-$, $[PF_6]^-$, and $[TFSA]^-$ are the trihexyl(tetradecyl)phosphonium cation, and perfluorooctanesulfonate, hexafluorophosphate, and bis(trifluoromethanesulfonyl)amide anions, respectively. These ILs were synthesized according to methods in the literature.[31,32] The density (ρ), viscosity (η), and CO_2 solubility (x_{CO_2}) under atmospheric to high pressure conditions were measured for the ILs using a vibrating tube densimeter (Anton Paar, DMA 5000M), a rotating-cylinder viscometer (Anton Paar, Stabinger SVM 3000), and a magnetic suspension balance (Rubotherm GmbH) (see Supporting Information and references[33-39]). H_{CO_2} was evaluated for the ILs as the

solubility gradients ($\frac{\partial p}{\partial x_{\mathrm{CO_2}}}$) in the region of $x_{\mathrm{CO_2}} < 0.1$. Finally, the Gibbs energy ($\Delta_{abs}G^{\infty}$), enthalpy ($\Delta_{abs}H^{\infty}$), and entropy ($\Delta_{abs}S^{\infty}$) of CO_2 absorption for the ILs were experimentally obtained using the following thermodynamic relations (1)-(3) as a function of $\ln H_{\mathrm{CO_2}}$,[40]

$$\Delta_{abs}G^{\infty} = RT \ln H_{\mathrm{CO_2}} \quad (1)$$

$$\Delta_{abs}H^{\infty} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{\Delta_{abs}G^{\infty}}{T}\right)\right] = -RT^2\left[\frac{\partial\left(\ln H_{\mathrm{CO_2}}\right)}{\partial T}\right] \quad (2)$$

$$\Delta_{abs}S^{\infty} = \frac{\Delta_{abs}H^{\infty} - \Delta_{abs}G^{\infty}}{T} = -RT\left[\frac{\partial\left(\ln H_{\mathrm{CO_2}}\right)}{\partial T}\right] - R\left(\ln H_{\mathrm{CO_2}}\right) \quad (3)$$

where $\Delta_{abs}H^{\infty}$ and $\Delta_{abs}S^{\infty}$ are closely related to the solute–solvent interaction strength and the free volume size of the solvent.

RESULTS AND DISCUSSION

The accuracy of the machine-learning was confirmed by the learning curves (**Figure 3**). It was shown that highly accurate H_{CO2} predictions (R^2> 0.90, RMSE< 1.5 MPa, MAE< 0.13 MPa) were achieved when 12 features were applied (**Figure 3(a)**). The wrapper method clarified that the first- and second-most important features were geometric *V* and electronic M_2. This is considered reasonable because CO_2 molecules are physically absorbed in the polar voids that consist of ions in the ILs. It was also confirmed that the 10,000 sets of training data (2% of the candidates) were sufficient for obtaining an accurate model (**Figure 3(b)**).

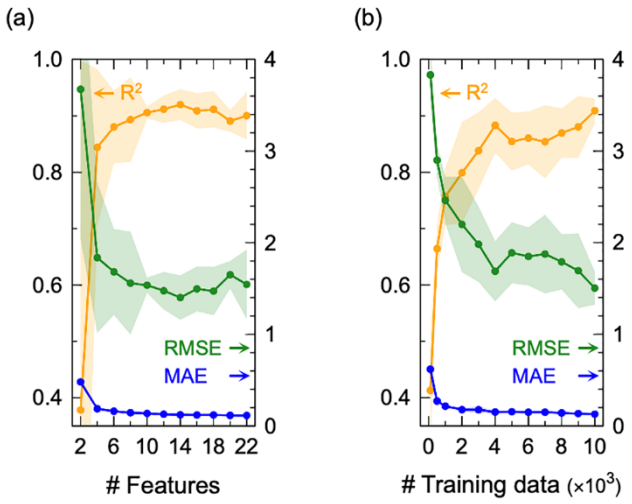


Figure 3. Learning curves with respect to the number of (a) features and (b) training data. For (a), the order of the features to add was determined by the wrapper method to maximize the accuracy.

Then, the verified machine-learning model was applied to predict H_{CO2} for all 402,114 IL candidates. To the best of our knowledge, $[P_{66614}][TFSA]$ has the highest CO_2 solubility per molar fraction.[8] Even though many previous experimental and theoretical studies have designed CO_2-absorbing ILs, there has been no report of a material superior to $[P_{66614}][TFSA]$ in the last decade. It should be noted that our machine-learning model reveals that there should be over 75,000 candidate ILs with comparable or larger CO_2 solubilities than the state-of-the-art material ($[P_{66614}][TFSA]$). Of course, this does not mean that all of them will show the predicted performance if they can be synthesized. However, this large number indicates that there is indeed huge potential for further development of CO_2-absorbing ILs.

Considering the anion effect governing IL properties[41,42] and the best IL example $[P_{66614}][TFSA]$ mentioned above,[8] we decided to investigate two phosphonium-based ILs ($[P_{66614}][PFOS]$ and $[P_{66614}][PF_6]$) which had better predicted H_{CO2} values (2.78 and 2.91 MPa, respectively) than $[P_{66614}][TFSA]$ (3.06 MPa). For the three ILs, the densities and the viscosities were determined to evaluate the specific volumes of the ILs (**Figures S2-S4**, **Tables S2** and **S4**). Both the mole fraction and molarity-scaled CO_2 solubilities were also measured (**Figure 4** and **Table S6**). The solubilities proportional to pressure means that the ILs absorb CO_2 by a physisorption mechanism.

The CO_2 solubility increased in the anion order of PF_6^- < $TFSA^-$ < $PFOS^-$. The large numbers of fluorine atoms and S=O bonds in $PFOS^-$ can develop strong interactions between the anion and CO_2, which leads to the largest anion–CO_2 contact probability for $PFOS^-$ ($PFOS^-$: 0.318, $TFSA^-$: 0.232, PF_6^-: 0.151) in the COSMO-RS results. The absorption Gibbs energy of $[P_{66614}][PFOS]$ was the most stable among the three ILs due to the large negative enthalpy (**Table 3**).

In this study, we focused on the predictivity of the CO_2 solubility only by assuming that all cation/anion pairs would produce liquids instead of solids. Nevertheless, the fact that we have succeeded in identifying a better IL ($[P_{66614}][PFOS]$) for CO_2 physisorption means that the electronic structure informatics technique could be further optimized to quicky identify better IL-based CO_2 absorbents in the future.

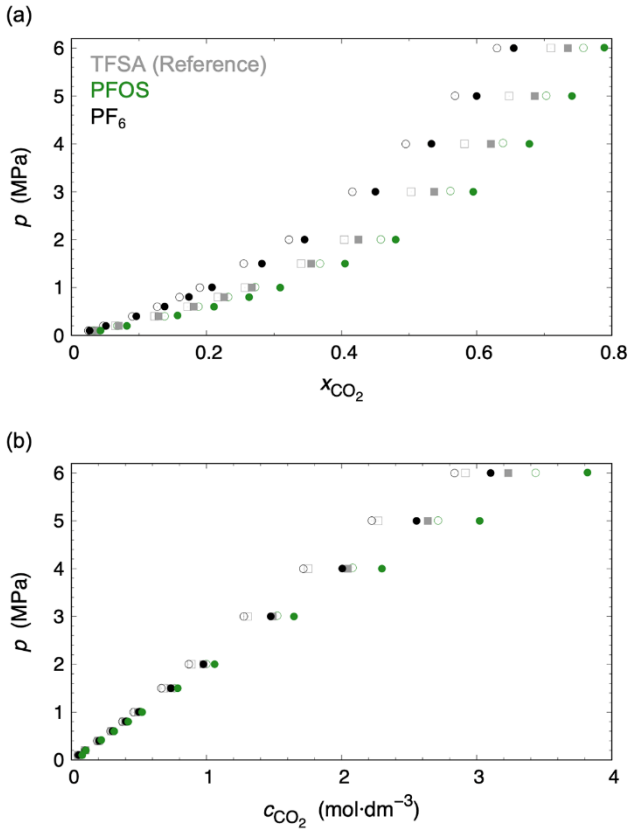


Figure 4. CO_2 solubility scaled by (a) mole fraction x_{CO_2} and (b) molarity c_{CO2} (mol·dm^{-3}) in $[P_{66614}][A]$ (A = TFSA, PFOS, and PF_6). Using the molar mass M_{CO2} and the mass fraction X_{CO2} of CO_2, c_{CO2} was calculated by $c_{CO2} = \rho_L \times X_{CO2}/M_{CO2}$. Closed and opened points are data at 313.15 K and 333.15 K, respectively.

Table 3. Henry's law constants H_{CO2} (MPa), Gibbs energy $\Delta_{abs}G^{\infty}$ (kJ·mol^{-1}), enthalpy $\Delta_{abs}H^{\infty}$ (kJ·mol^{-1}), and entropy $\Delta_{abs}S^{\infty}$ (J·mol^{-1}·K^{-1}) of CO_2 absorption evaluated experimentally for [P_{66614}][A] (A = TFSA, PFOS, and PF_6).

	H_{CO2}		$\Delta_{abs}G^{\infty}$	$\Delta_{abs}H^{\infty}$	$\Delta_{abs}S^{\infty}$
	@313.15 K	@333.15 K			
TFSA	2.85	3.04	2.72	−2.62	−17.1
PFOS	2.41	2.71	2.29	−8.11	−33.2
PF_6	4.09	4.39	3.67	−2.88	−20.9

CONCLUSIONS

In this study, we succeeded in predicting and synthesizing novel ILs with high CO_2 solubility based only on the geometric and electronic structures of the constituent cations and anions. The IL [P_{66614}][PFOS] predicted by our machine-learning model had a higher CO_2 solubility than the state-of-the-art [P_{66614}][TFSA]. Both of the geometric and electronic feature values of the ions used in machine learning were uniquely determined from the results of quantum chemical calculations. Thus, new ionic species with functional group introductions, elemental substitutions, and other modifications could also be systematically considered to accelerate research without being hindered by the enormous chemical space of ILs. Expansion of the database and studies of other ILs (and deep eutectic solvents), including their CO_2 separation selectivity and absorption kinetics, are currently underway.

Author Contributions

N.K. and H.M. conceived the project. N.K. generated the molecular library and performed machine learning supervised by H.M. F.A.C. and H.Y. synthesized the three ILs. Y.S. and D.K. measured the basic properties of the ILs. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interests.

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