

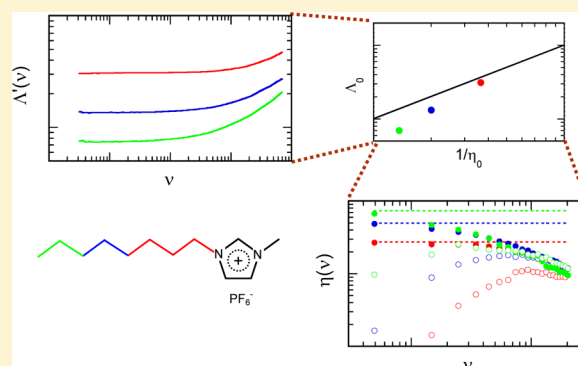
Interpretation of the Variation of the Walden Product of Ionic Liquids with Different Alkyl Chain Lengths in Terms of Relaxation Spectra

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Supporting Information

ABSTRACT: The shear relaxation spectra and the alternating-current (AC) conductivity of 1-alkyl-3-methylimidazolium hexafluorophosphate were measured in the MHz region, with the chain lengths varied from butyl to octyl. The relaxation times of both the conductivity and shear viscosity increased with increasing chain length approximately in proportion to the variation of the reciprocal molar conductivity. On the other hand, the increase in the shear viscosity was smaller than that of the relaxation time, which indicates that the high-frequency shear modulus decreases with the chain length. The decrease in the the Walden product with the chain length is thus ascribed to that of the high-frequency shear modulus.



1. INTRODUCTION

The Walden plot is the plot of molar conductivity against reciprocal shear viscosity, which is often employed in the analysis of ionic transport of ionic liquids.^{1–4} According to the position on the Walden plot relative to the so-called “ideal line”, which is determined with aqueous KCl solution, ionic liquids are classified into three categories. The first one, “good ionic liquid”, is for ionic liquids near the ideal line. The ionic liquids above the ideal line, that is, their ionic mobility is higher than that expected from the viscosity, are called “superionic liquids”. The ionic liquids below the ideal line are called “poor ionic liquids”.

The classification of the ionic liquids described above has been interpreted from two points of view. The first one is the ionic association, and the second one is the coupling between the ionic transport and the structural relaxation. The good ionic liquid is considered as an ideal state where ions are fully dissociated and the ionic transport is coupled to the structural relaxation. The poor ionic liquid is regarded as the ionic liquid whose ionic dissociation is incomplete. The superionic liquid is ascribed to the decoupling between the ionic transport and structural relaxation.

Measurement of the frequency dependence of the transport coefficients is a powerful tool to investigate the transport mechanism because the relaxation occurs at the frequency corresponding to the time scale of the microscopic motion coupled to the transport mechanism. The coupling between the viscosity and ionic conductivity also appears in the frequency-dependent viscosity and conductivity because the relaxation frequencies of both spectra agree with each other when the ionic mobility is coupled to the viscosity.

Šantić and co-workers performed a comparison between the conductivity and viscosity spectra of an ionic liquid near the glass transition temperature in order to understand the relationship between the temperature dependence of the conductivity and shear viscosity.⁵ We also compared these two spectra of another ionic liquid at the ambient condition to demonstrate the presence of the decoupling between frequency-dependent viscosity and conductivity.⁶

In this work, the relaxation measurement is applied to imidazolium-based ionic liquids with alkyl chains of different lengths. The viscosity of the ionic liquid increases with lengthening of the alkyl chain, while the molar conductivity decreases. The increase in the former is smaller than the decrease of the latter, so that the Walden product decreases with increasing chain length. The relationship between the molar conductivity and viscosity shall be analyzed here in terms of their relaxation spectra.

2. THEORETICAL BACKGROUND

The Walden plot is based on the Walden law, which states that the molar direct-current (DC) conductivity, Λ_0 , is reciprocally proportional to the steady-state shear viscosity, η_0 . The product of these two quantities, $\Lambda_0\eta_0$, is called the “Walden product”, and it is constant when the Walden law holds.

The Walden law is derived from the Nernst–Einstein and the Stokes–Einstein relationships. For 1–1 salts composed of monovalent ions, the Nernst–Einstein relationship is described as⁷

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$$\Lambda_0 = \frac{F^2}{RT}(D_{0,+} + D_{0,-}) \quad (1)$$

where F , R , and T stand for the Faraday constant, the gas constant, and the absolute temperature, respectively, while $D_{0,+}$ and $D_{0,-}$ indicate the self-diffusion coefficients of the cation and anion, respectively. The basic assumption of the Nernst–Einstein relationship is the absence of the correlation between translational motions of different ions.^{8,9}

The Stokes–Einstein relationship is the relationship between the self-diffusion coefficient and the shear viscosity, and it is actually a combination of the Stokes and Einstein laws. The Einstein law is given by

$$D_{0,\alpha} = \frac{k_B T}{\zeta_{0,\alpha}} \quad (2)$$

where $\alpha \in \{+, -\}$ and k_B and $\zeta_{0,\alpha}$ mean the Boltzmann constant and the friction coefficient on the ion α , respectively. In the Stokes–Einstein relationship, the friction coefficient $\zeta_{0,\alpha}$ is replaced with that of the Stokes law, hydrodynamically derived as

$$\zeta_{0,\alpha} = f r_\alpha \eta_0 \quad (3)$$

In eq 3, r_α stands for the radius of ion α , and f is the coefficient determined by the hydrodynamic boundary condition. Because the Einstein law is an exact relationship based on the fluctuation–dissipation theorem,^{10,11} the basic assumption of the Stokes–Einstein relationship is the hydrodynamic treatment of the friction coefficient.

Equations 1–3 are combined to derive the Walden law, and its violation is ascribed to that of either the Stokes–Einstein or the Nernst–Einstein relationships. The conventional explanation for the poor ionic liquid is the breakdown of the Nernst–Einstein relationship through the introduction of the correlation between the motions of a cation and an anion due to the ionic association. The decoupling between the ionic motion and shear viscosity, which is an explanation for the superionic liquid, is regarded as the breakdown of the Stokes law.

The Stokes–Einstein and the Nernst–Einstein relationships can be extended to the frequency-dependent ones by replacing Λ_0 , η_0 , $D_{0,\omega}$, and $\zeta_{0,\alpha}$ to the respective frequency-dependent complex functions as $\Lambda(\nu)$, $\eta(\nu)$, $D_\alpha(\nu)$, and $\zeta_\alpha(\nu)$. The frequency-dependent Stokes–Einstein relationship has been used to analyze the origin of the decoupling between diffusion and viscosity of supercooled liquids in molecular dynamics simulations.^{12,13}

It is to be noted here that the extension of the Einstein law, $D_\alpha(\nu) = k_B T / \zeta_\alpha(\nu)$, is valid only in the diffusive limit where the effects of the inertial motion of ions are small. Because the dynamics studied in this work is slower than 1 GHz, we consider that the inertial effects can safely be neglected.

Both $\eta(\nu)$ and $\zeta_\alpha(\nu)$ can be described in terms of time correlation functions. According to the Kubo–Green formula for shear viscosity, $\eta(\nu)$ is related to the time correlation function of the shear stress tensor, $\Pi_{xz}(t)$, as^{10,11,14}

$$\eta(\nu) = \frac{V}{k_B T} \int_0^\infty dt e^{-2\pi i \nu t} \langle \Pi_{xz}(0) \Pi_{xz}(t) \rangle \quad (4)$$

where V stands for the volume of the system. On the other hand, the fluctuation–dissipation theorem relates $\zeta_\alpha(\nu)$ to the time correlation function of the Random force, $R_{\alpha,z}(t)$, as^{10,11,14}

$$\zeta_\alpha(\nu) = \frac{1}{k_B T} \int_0^\infty dt e^{-2\pi i \nu t} \langle R_{\alpha,z}(0) R_{\alpha,z}(t) \rangle \quad (5)$$

Therefore, $\zeta_\alpha(\nu)$ is expected to be proportional to $\eta(\nu)$ when the same microscopic dynamics is involved in both $\Pi_{xz}(t)$ and $R_{\alpha,z}(t)$. The comparison between $D_\alpha(\nu)$ and $\eta(\nu)$ thus tells us the relationship between the mechanisms of viscosity and ionic mobility. Although the spectrum of $\Lambda(\nu)$ may be different from that of $D_\alpha(\nu)$ due to the dynamic correlation between ions,^{15,16} we shall perform the comparison between $\Lambda(\nu)$ and $\eta(\nu)$, assuming that the effects of the dynamic correlation are small.

Because the zero-frequency values of η_0 and $\zeta_{0,\alpha}$ are given by the time integration of their respective correlation functions, its variation can be attributed to those of the relaxation times and amplitudes. Although the information on the zero-frequency value alone cannot resolve which is the principal reason for the variation, we can extract the information on the relaxation time from the relaxation spectra. In our previous work, we used the relationship that the normalized shear relaxation spectrum $\eta(\nu)/\eta_0$ is invariant as the function of $\eta_0 \nu$ when the relaxation time, τ_η , is responsible for the variation of η_0 .⁶ In the case of molar conductivity, the variation of Λ_0 is ascribed to that of the relaxation time, τ_Λ , when $\Lambda(\nu)/\Lambda_0$ does not change as the function of ν/Λ_0 .

3. EXPERIMENTAL SECTION

3.1. Samples. The ionic liquids used in this work are 1-alkyl-3-methylimidazolium hexafluorophosphates with changing lengths of the alkyl chains as butyl ([bmim][PF₆]), hexyl ([hmim][PF₆]), and octyl ([omim][PF₆]). [bmim][PF₆] and [omim][PF₆] were purchased from Tokyo Chemical Industry Co., Ltd., while [hmim][PF₆] was from Kanto Chemical Co., Inc. All of the samples were dried in vacuum at 60 °C prior to use. All of the measurements were performed at 25 °C. The densities of these liquids were taken from the literature.^{17–20}

3.2. Viscometry. The frequency-dependent shear viscosity was determined with shear impedance spectroscopy, which was described in detail elsewhere.^{21–23} The frequency range of the measurement was from 5 to 205 MHz. The $\eta(\nu)$ of [omim][PF₆] was taken from our previous work.²⁴ Those of [bmim][PF₆] and [hmim][PF₆] were measured in this work, and we confirmed that they were consistent with those in our previous work.⁶ The steady-state shear viscosity, η_0 , was taken from the literature.^{17–20}

3.3. Conductometry. Figure 1 shows the sample cell used to measure the alternating-current (AC) conductivity, $\sigma(\nu)$, of ionic liquids. An SMA panel receptacle was attached to the bottom of a hole in an aluminum block, and the hole was filled with the sample liquid. The impedance between the signal pin of the receptacle and the ground was determined by a vector network analyzer (VNA, ZVL3/03, Rhode & Schwarz) through the $S_{11}(\nu)$ measurement. The conductivity of the sample was calculated from the impedance by assuming the equivalent circuit described in our previous work.²² The parameters of the equivalent circuit were determined by measuring the impedance of air, water, and aqueous solutions of NaCl of various concentrations. The analysis with the equivalent circuit was described in detail in our previous paper.²² The temperature of the sample was controlled within ± 0.1 K by flowing the thermostatted water through the aluminum block. As we shall show later, $\sigma(\nu)$ of [bmim][PF₆] determined in this work agrees well with that calculated from the dielectric relaxation spectrum reported by Hunger and co-workers²⁵

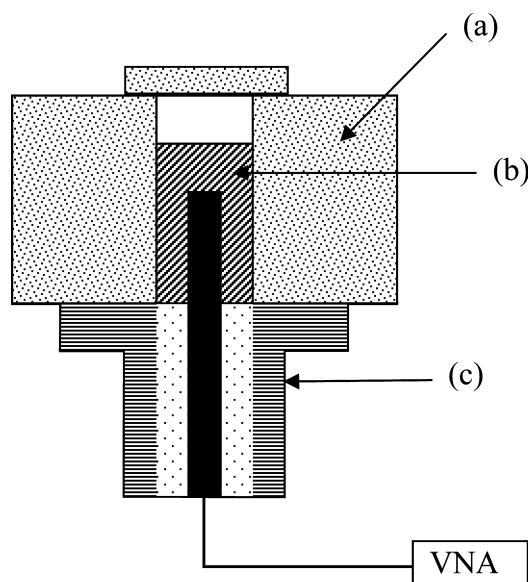


Figure 1. The schematic picture of the sample cell used for the frequency-dependent conductivity. (a) Aluminum block; (b) sample liquid; (c) SMA panel receptacle.

below 700 MHz, and we use $\sigma(\nu)$ between 300 kHz and 700 MHz for analysis. The DC conductivities were determined from the plateau of the real part of $\sigma(\nu)$, denoted as $\sigma'(\nu)$, around 1 MHz, and they agree with the values in the literature measured with conductance bridges within $\pm 5\%$.^{26–29}

4. RESULTS AND DISCUSSION

Figure 2 shows the Walden plot of the ionic liquids investigated in this work. The molar conductivity decreases with increasing

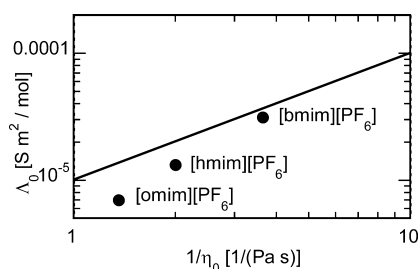


Figure 2. The molar conductivity, Λ_0 , of ionic liquids studied in this work is correlated with the reciprocal viscosity, $1/\eta_0$. The straight line is the so-called ideal line, whose slope is unity and whose intercept is determined from the Walden product of aqueous KCl solution.

chain length, while the shear viscosity increases. The decrease in Λ_0 is larger than the increase in η_0 , which leads to the decrease in the Walden product. The positions of these ionic liquids on the Walden plot are slightly lower than the ideal line, and the deviation from the ideal line increases with lengthening alkyl chain. The tendency described above was already reported in the literature for various ionic liquids including PF_6^- salts studied here.^{30,31}

Figure 3 demonstrates the real part of the molar AC conductivity, $\Lambda'(\nu)$, as the function of frequency. Here, $\Lambda(\nu)$ is defined as the ratio of $\sigma(\nu)$ to the molar density of the liquid. The spectrum of $[\text{bmim}][\text{PF}_6]$ reported by Hunger and co-workers as the dielectric relaxation²⁵ is plotted also for comparison. Both spectra agree with each other well. The

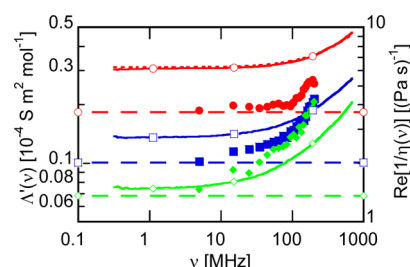


Figure 3. The real part of the molar AC conductivity, $\Lambda'(\nu)$ (solid curves), and that of the reciprocal viscosity, $\text{Re}[1/\eta(\nu)]$ (filled symbols), are plotted as the functions of the frequency. Both axes are on the log scale. The red symbols with circles, blue ones with squares, and green ones with diamonds indicate the data of $[\text{bmim}][\text{PF}_6]$, $[\text{hmim}][\text{PF}_6]$, and $[\text{omim}][\text{PF}_6]$, respectively. The horizontal lines show the reciprocal values of the zero-frequency viscosity, $1/\eta_0$. The red dotted curve exhibits $\Lambda'(\nu)$ calculated from the dielectric relaxation spectrum reported by Hunger and co-workers,²⁵ which almost overlaps with our data shown by the solid curve.

molar AC conductivities, $\Lambda'(\nu)$, become constant below 1 MHz, and the constant values agree with the respective DC values in the literature, which indicates that the translational motion of ions is Markovian on the time scale of microseconds. The AC conductivities show a relaxation, that is, an increase with frequency above 100 MHz. The relaxation frequency of liquids with a longer alkyl chain is lower, which is in harmony with the lower ionic mobility.

The real part of the frequency-dependent reciprocal viscosity, $\text{Re}[1/\eta(\nu)]$, is also exhibited in Figure 3 for comparison with the molar AC conductivity. The frequency dependence of $\text{Re}[1/\eta(\nu)]$ is qualitatively similar to that of $\Lambda'(\nu)$. A relaxation is observed in the 100 MHz region, and $\eta(\nu)$ converges to η_0 below 1 MHz. However, the relaxation of the shear viscosity is slower than that of the AC molar conductivity in cases of all liquids. The slower relaxation of the shear viscosity than that of the conductivity was reported by Šantić and co-workers for an ionic liquid near the glass transition temperature,⁵ and we have already shown the decoupling for $[\text{bmim}][\text{PF}_6]$.⁶ Because the amount of the decoupling is comparable with the deviation from the ideal line, it should be taken into consideration in the discussion on the position in the Walden plot relative to the ideal line.

The decoupling between the structural relaxation and the ionic mobility has been considered as the characteristic of the superionic liquid, as was described in the Introduction. Provided that the decoupling between the shear relaxation and ionic mobility is observed in the three ionic liquids investigated in this work, it can cause the superionic deviation of these ionic liquids from the ideal line, though they are positioned below the ideal line in the Walden plot.

The discrepancy between the classifications based on the Walden plot and the relaxation spectra can be ascribed partly to the choice of the ideal line. Although the ideal line has been determined conventionally from the Walden product of the aqueous solution of KCl, many researchers have doubted the validity of the use of the KCl solution because there is no reason to assume that the Walden product of the ideal ionic liquid is the same as that of KCl solution under the given particular condition.^{32,33} The superionic behavior of the relaxation spectra of the ionic liquids in this work may suggest that the position of the ideal line is in fact lower than that of the conventional one. We consider that the collection of the

relaxation spectra of various ionic liquids shall help in examining the possibility to provide a better method to determine the ideal line for ionic liquids.

An important point to understand the mechanism of ionic transport in an ionic liquid is the reason why the relaxation of the AC conductivity is decoupled from the shear relaxation. In our previous work, the shear relaxation spectra of some ionic liquids are compared with the structural relaxation determined by the inelastic neutron scattering spectroscopy, and we demonstrated that the shear relaxation is slower than the relaxation of the main peak of the static structure factor.²⁴ We expect that a similar comparison between the neutron spectroscopy and the AC conductometry can be used to resolve the origin of the decoupling between $\Lambda(\nu)$ and $\eta(\nu)$. It is the plan of our next work on the dynamics of ionic liquids, and the analyses with molecular dynamics simulation and mode-coupling theory (MCT)^{15,16} will be combined there.

The relaxation of the conductivity is assigned to the frequency dependence of the translational mobility of ions in this work. However, it should be commented that the conventional assignment of the relaxation in the dielectric spectroscopy is the reorientational relaxation of cations, under the assumption that the translational mobility of ions is Markovian in the frequency range studied here.^{34–37} There have been many simulation studies on ionic liquids that the self-diffusion of ions is non-Markovian in this frequency range,^{16,38–41} which is enough of a reason to suspect the existence of the frequency dependence of the translational mobility of ions. We have also demonstrated with MCT that the dielectric relaxation of a model ionic liquid is mainly assigned to the translational mode.¹⁵ The presence of the shear relaxation in the frequency region also suggests the frequency-dependent conductivity according to the frequency-dependent Walden law.¹⁶ Therefore, we cannot accept the conventional assignment in the dielectric spectroscopy that the relaxation is assigned exclusively to the reorientational relaxation of the cation. On the other hand, we cannot exclude the contribution of the reorientational mode to the relaxation. MD simulation studies performed by Schröder and co-workers show that the contributions of the reorientation and translation are comparable.^{42,43} Because the contribution of the reorientational relaxation should be subtracted from $\Lambda(\nu)$ in the discussion on the translational mobility of ions, the relaxation of the translational mobility would be weaker, and the decoupling would be larger than that observed in Figure 3 after the subtraction of the contribution of the reorientational mode.

Now, we are going to analyze the mechanism of the decrease in the Walden product with lengthening alkyl chain from the view of the relaxation spectra. We shall at first clarify the role of the relaxation time in the variation of Λ_0 and η_0 .

We have already shown in our previous work that the increase in τ_η with increasing chain length is larger than the increase in η_0 . The variation of η_0 is explained by cancellation between the increase in τ_η and the decrease in the high-frequency shear modulus, G_∞ .⁶ The same analysis is performed again with $\eta(\nu)$ exhibited in Figure 3, and the conclusion above is confirmed, although the results are not shown for brevity.

A similar analysis is performed in Figure 4 for molar conductivity by plotting $\Lambda'(\nu)/\Lambda_0$ against ν/Λ_0 . The three normalized conductivity spectra overlap with each other well, suggesting that the relaxation time, τ_Λ , is inversely proportional to Λ_0 . The mobility of an ion, $D_{0,\omega}$, is reciprocally proportional to the zero-frequency friction, $\zeta_{0,\omega}$, which is in turn described as

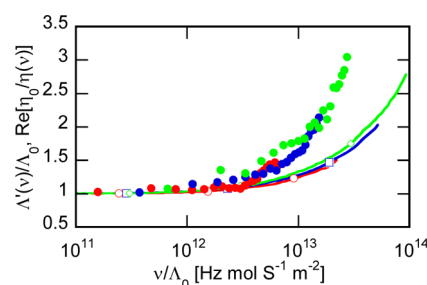


Figure 4. The real part of the normalized molar AC conductivity, $\Lambda'(\nu)/\Lambda_0$, and that of the normalized reciprocal viscosity, $\text{Re}[\eta_0/\eta(\nu)]$, are plotted as the functions of ν/Λ_0 . Both axes are on the log scale. The meanings of the symbols are the same as those in Figure 3.

the product of the amplitude and the relaxation time of the time correlation function of the random force. Therefore, the proportionality between Λ_0 and τ_Λ indicates that the variation of the latter is mainly responsible for that of the former, and the effects of the change in the amplitude of the time correlation function of the random force are marginal.

In Figure 4, the real part of the normalized reciprocal viscosity, $\text{Re}[\eta_0/\eta(\nu)]$, is also plotted against the same reduced frequency. Surprisingly enough, the shear relaxation spectra also overlap with each other fairly well, which indicates that the relaxation time associated with the shear viscosity, τ_η , is proportional to τ_Λ . Therefore, we consider that there are some relationships between the mechanisms of shear viscosity and ionic mobility, although the absolute values of their relaxation times are different.

Given that τ_η , τ_Λ , and $1/\Lambda_0$ are proportional to each other, the Walden law would hold if η_0 were proportional to τ_η . As we have shown in our previous work,⁶ however, the increase in η_0 with lengthening alkyl chain is smaller than that in τ_η due to the decrease in the high-frequency shear modulus, G_∞ , which explains the decrease in the Walden product. In short, the decrease in G_∞ is the reason for the violation of the Walden law as a function of the alkyl chain length. The Walden law is the relationship between the shear viscosity and the molar conductivity. Both of these two quantities can thus be a reason for its violation in principle. Although the deviation from the Walden law has been discussed in terms of the mechanism of ionic conduction, it is the shear viscosity that is responsible for the violation of the Walden law in this work.

One may consider that the increase in the size of the cation is the reason for the decrease in the Walden product because the effective radius, r_+ , is involved in the Stokes law, eq 3. On the basis of the extension of the Stokes law to the frequency-dependent one, the role of the increase in r_+ is to amplify the friction spectrum without changing the shape of the spectrum. Because Λ_0 is inversely proportional to τ_Λ in our experiment, it cannot be explained in terms of the effective size. The explanation with the degree of ionic association is not in harmony with our relaxation spectra either. The ionic association reduces the effective concentration of ions, which works in the Nernst–Einstein relationship, eq 1, as a prefactor of the right-hand side. Therefore, it also modifies the amplitude of $\Lambda(\nu)$ without changing the frequency dependence, in contradiction with our experiment.

5. CONCLUSION

The frequency-dependent conductivities of ionic liquids, 1-alkyl-3-methylimidazolium hexafluorophosphates, were deter-

mined between 300 kHz and 700 MHz, and the variation of the relaxation time with lengthening alkyl chain was compared with that of the DC molar conductivity, Λ_0 . The relaxation time, τ_Λ , was proportional to $1/\Lambda_0$, which means that the decrease in Λ_0 with the chain length is ascribed to the increase in the relaxation time.

The conductivity spectra were compared with the shear relaxation spectra. The relaxation time of the shear relaxation, τ_η , is also proportional to τ_Λ , although the absolute value of the former is larger than that of the latter. The increase in the steady-state shear viscosity, η_0 , is smaller than that of τ_η due to the decrease in the high-frequency shear modulus, G_∞ , which is the reason for the decrease in the Walden product with lengthening alkyl chain.

■ ASSOCIATED CONTENT

Supporting Information

The numerical values of shear and conductivity relaxation spectra are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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