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Article

Generalizable Synthesis of Highly Fluorinated Ionic Liquids

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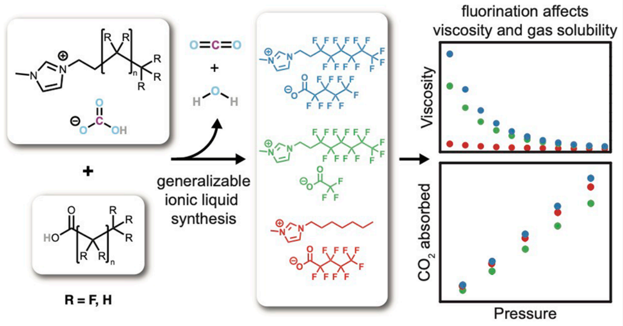
ABSTRACT: The unique chemistry of fluorocarbons (in particular, their weak intermolecular interactions and high degree of intrinsic free volume) makes them promising building blocks for ionic liquids with high gas capacities. Here, we report a generalizable method for the synthesis of fluorinated ionic liquids, which relies on the evolution of gaseous byproducts to drive product formation. This synthetic strategy overcomes solubility challenges that can hinder the synthesis of highly fluorinated ionic liquids via conventional methods and enables a systematic investigation of the effect of fluorination on ionic liquid viscosity and gas solubility.



INTRODUCTION

Fluorine (the most electronegative element) forms strong, polar bonds with carbon to yield rigid, weakly interacting molecules with unique solubility properties.[1,2] Fluorocarbon liquids are often immiscible with both hydrocarbons and water but are capable of absorbing higher densities of small gas molecules (such as H_2, O_2, N_2, and CO_2) than almost any other class of solvents.[3] These remarkably high gas solubilities have led to the investigation of fluorinated liquids for a wide range of applications, including as blood substitutes,[4] cell culture media,[5,6] electrolytes,[7] and solvents for bioreactors.[8]

As with molecular liquids, incorporating fluorine into ionic liquids can lead to increased gas solubilities,[9−12] providing opportunities for designing high-performance solvents for ion conduction, catalysis, and gas separation that feature negligible vapor pressures and tunable viscosities.[13] However, there are only limited examples of highly fluorinated ionic liquids,[14,15] which has limited systematic studies of the role of fluorination on gas solubility.[9−12,15] The lack of synthetic control for fluorinated ionic liquids contrasts with the structural diversity of neutral fluorocarbon liquids, in which adding other halides or utilizing aromatic instead of aliphatic carbon backbones has been shown to directly impact gas solubility.[16] Furthermore, these small chemical modifications can have a dramatic impact on other important liquid properties, including density, viscosity, miscibility, and biocompatibility,[4] but much remains to be understood about the influence of similar changes on the properties of fluorinated ionic liquids.

Ionic liquids with high degrees of fluorination in both the cation and anion are rare.[14,15] This is in part because conventional ionic liquid syntheses typically rely on solubility differences to drive an anion-exchange reaction from a halide salt to a tetrafluoroborate, hexafluorophosphate, or bis(trifluoromethane)sulfonimide salt.[17−19] However, the inclusion of heavily fluorinated functional groups complicates the solubility of both the halide salt and the desired product, especially when fluorination is present in both the cation and anion. Here, we report a synthetic route that overcomes these solubility challenges and affords ionic liquids with highly fluorinated cations and anions. Utilizing this strategy, we synthesize a series of imidazolium carboxylate-based ionic liquids that feature long perfluorocarbon chains. We then demonstrate the generalizability of this approach by synthesizing a fluorinated pyridinium carboxylate ionic liquid. To begin systematically exploring the effect of fluorination on ionic liquid properties, we report the thermal properties, densities, viscosities, and gas absorption capacities of select ionic liquids within our series, along with comparisons to their non-fluorinated analogues.

METHODS

Ionic Liquid Synthesis. All highly fluorinated ionic liquids were synthesized according to the same general procedure: (1) formation and purification of a halide salt of the desired cation;

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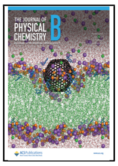

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(2) anion exchange to form a bicarbonate salt; and (3) anion metathesis with an acid of the desired anion. Note that all purification of organic precursors must occur before the formation of the bicarbonate salt, as this salt cannot be isolated from water. Detailed synthetic procedures for each highly fluorinated ionic liquid are included in the Supporting Information. All ionic liquid samples used for viscosity or gas sorption measurements were dried at elevated temperatures (>50 °C) for at least 12 h.

Thermal Characterization. A Discovery 2500 DSC with an RCS 90 cooling system (TA Instruments) was used to measure the melting temperatures for all compounds. The DSC baseline and cell thermal parameters were calibrated using sapphire disks. The temperature and cell constant were calibrated using an indium standard. All DSC samples were prepared under a nitrogen atmosphere using approximately 10 mg of sample and were hermetically sealed in Al pans (purchased from TA Instruments). Heating and cooling rates of 2.5 °C/min were used with a 50 mL/min N_2 flow. An empty, hermetically sealed Al pan was used as a reference. Melting temperatures (T_m) and glass transition temperatures (T_g) are reported as the extrapolated onset as described in a previous publication.[20]

Viscosity Measurements. An electromagnetically spinning viscometer (EMS-1000S, Kyoto Electronics Manufacturing Co LTD) was used to measure variable-temperature viscosities. A glass sample tube was equipped with a 2 mm Al ball, and enough sample was added to fully cover the ball. The Al ball was rotated at 1000 Hz, and its movement was traced with a red laser. The viscosity of the sample was determined by the reduction in rotational speed. All measurements were performed on samples dried for >5 h at a temperature of at least 50 °C and stored in a nitrogen-filled glovebox before being loaded into the viscosity tube, which was then capped and taped. The reported viscosities are an average of 10 individual measurements.

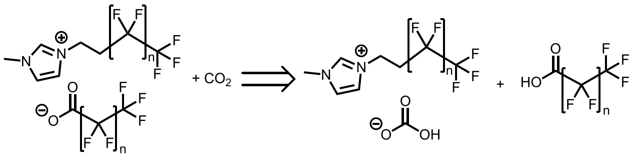
Gas Solubility Measurements. All samples were dried under vacuum at elevated temperature with stirring using a Schlenk line for >5 h prior to storage in a nitrogen-filled glovebox. Samples were then loaded into round-bottomed sample tubes equipped with a Teflon-coated SmCo stir bar (VWR part number 89030-550). Sample tubes were removed from the glovebox and attached to a Micromeritics SmartVacPrep without exposure to air. Samples were further activated using a turbomolecular vacuum pump at elevated temperature (minimum of 50 °C) overnight before transferring to a Micromeritics 3Flex 3500 for analysis. Multiple activations at elevated temperature with stirring, including the use of a turbomolecular pump, were undertaken in order to remove as much water and dissolved gas from the samples as possible.

Absorption experiments for ionic liquids were performed as described previously.[12] Briefly, each set of isotherm measurements was preceded by 3−5 independent free space measurements that were averaged to obtain the free space volume. Each isotherm used an equilibration interval of 600 s, which corresponds to a total equilibration time of at least 1.7 h for each data point. The samples were stirred at 200 rpm throughout the measurement. The reported data were obtained by subtracting the absorption on a blank tube (see Supporting Information) and averaging at least 3 independent isotherms.

RESULTS AND DISCUSSION

In an effort to design a generalizable synthetic route to highly fluorinated ionic liquids, we hypothesized that challenges associated with the solubility of fluorinated cations and anions could be overcome by driving the formation of an ionic liquid through the evolution of a gaseous byproduct. In particular, we targeted the reaction of the bicarbonate salt of a fluorinated cation with a fluorinated Brønsted acid to afford a doubly fluorinated ionic liquid with concomitant formation of H_2O and CO_2 (Scheme 1). This approach contrasts with the more typical ionic liquid synthesis route that relies on solubility differences to drive liquid−liquid phase separation of the desired ionic liquid from the reaction solvent or precipitation of a metal halide salt after an anion metathesis reaction. This conventional approach is unreliable for highly fluorinated systems because of their different solubility and miscibility, which can make it challenging to isolate the fluorinated ionic liquid from halide-based reaction byproducts and to drive synthesis reactions to completion (see Supporting Information). Thus, instead of relying on the conventional halide anion as an intermediate,[21] we hypothesized that using bicarbonate as an intermediate anion would dramatically improve the outcome of fluorinated ionic liquid syntheses by driving the reaction through the evolution of CO_2. We note that imidazolium hydroxides have also been employed as intermediates to circumvent ionic liquid synthesis issues caused by metal halide impurities.[22]

Scheme 1. Retrosynthesis of Highly Fluorinated Ionic Liquids



To begin evaluating this approach, we aimed to synthesize $[\text{F-omim}][CF_3(CF_2)_7CO_2]$ (F-omim = 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium), which has six perfluorinated carbons in the cation chain and eight perfluorinated carbons in the anion chain (Figure 1a) and is a combination of the fluorinated cation and anion used in two previously studied ionic liquids that have high O_2 solubilities (Figure 1d).[12] To form $[\text{F-omim}][CF_3(CF_2)_7CO_2]$, we first reacted imidazole with a fluorinated alkyl halide, then methylated with CH_3I to afford a fluorinated methylimidazolium iodide (Figure 1a). Using an anion−exchange column loaded with $KHCO_3$, iodide was exchanged for bicarbonate to form a fluorinated imidazolium bicarbonate, which was soluble in water. The addition of a fluorinated carboxylic acid forms H_2CO_3 in solution, which decomposes to produce CO_2. Subsequent lyophilization to remove water afforded the desired highly fluorinated ionic liquid.

Though $[\text{F-omim}][CF_3(CF_2)_7CO_2]$ is a solid at room temperature (T_m = 62 °C), a series of room-temperature ionic liquids could be produced by using shorter fluorinated carboxylic acids in the last reaction step (Figure 1b, Table S1). These highly fluorinated ionic liquids contain the same [F-omim] cation and cover a wide range of anion fluorocarbon chain lengths, allowing the influence of anion fluorination on ionic liquid properties to be directly studied. For instance, the degree of anion fluorination is correlated with ionic liquid

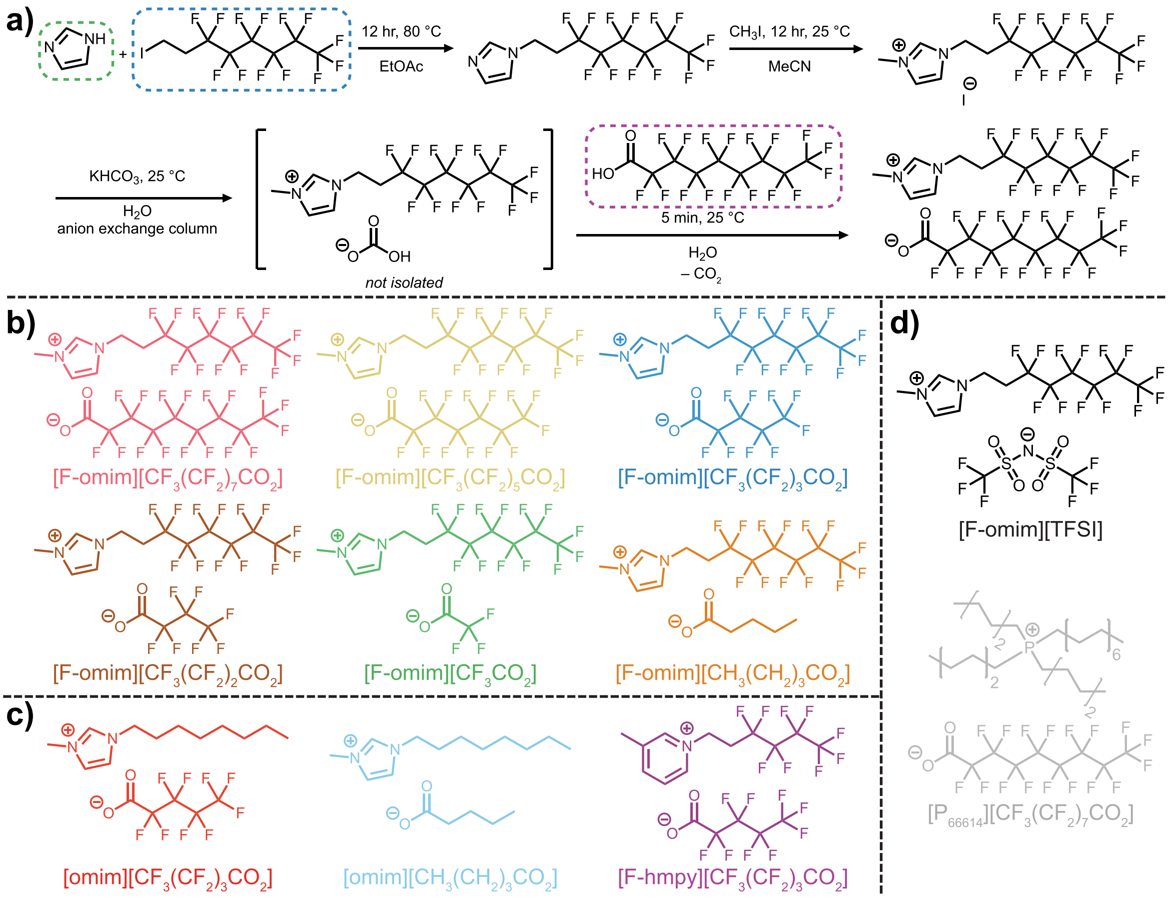


Figure 1. (a) Representative synthetic route to produce highly fluorinated ionic liquids via CO_2 evolution. (b) Chemical structures and abbreviations for the series of highly fluorinated ionic liquids based on the [F-omim] cation studied in this work. (c) Chemical structures and abbreviations for other fluorinated ionic liquids produced by the same synthetic route. (d) Previously reported ionic liquids with partial fluorination that were also studied in this work.

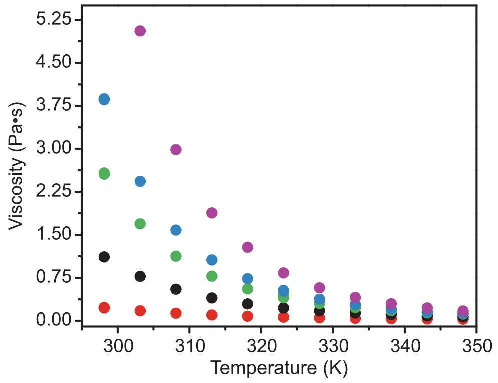


Figure 2. Viscosity as a function of temperature for [F-hmpy][$CF_3(CF_2)_3CO_2$] (purple), [F-omim][$CF_3(CF_2)_3CO_2$] (blue), [F-omim][CF_3CO_2] (green), [F-omim][TFSI] (black), and [omim][$CF_3(CF_2)_3CO_2$] (red).

viscosity (Figure 2), with [F-omim][$CF_3(CF_2)_3CO_2$] having the highest viscosity and the longest fluorocarbon chain on the anion. The ionic liquid with the shortest fluorinated anion ([F-omim][CF_3CO_2]) is 34% less viscous at 25 °C, while replacing the fluorocarbon carboxylate anion with a bis(trifluoromethane)sulfonimide leads to a 71% reduction in viscosity (Figure 1d). These changes in viscosity are consistent with the observed increase in viscosity as a function of chain length for neutral perfluorocarbon liquids.[23]

In addition to applying this synthetic strategy to tune the length of the fluorocarbon chain on the carboxylate anion, we were also able to access hydrocarbon analogues of the imidazolium cation by changing the precursor alkyl halide (Figure 1a, blue), resulting in several additional room-temperature ionic liquids (Figure 1c). These ionic liquids enable comparisons between fluorocarbon and hydrocarbon analogues and also highlight the generalizability of driving ionic liquid syntheses by bicarbonate decomposition. For example, the fluorinated liquid [F-omim][$CF_3(CF_2)_3CO_2$] is more viscous than its hydrocarbon analogue [omim][$CF_3(CF_2)_3CO_2$] (Figure 2, Table S2), which is consistent with an increased viscosity for fluorocarbons compared to hydrocarbons.[23,24] However, somewhat surprisingly, [omim][$CF_3(CF_2)_3CO_2$] has a slightly lower viscosity at 25 °C (220 mPa·s) than conventional nonfluorinated ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate (270 mPa·s).[25] The longer alkyl chain present in [omim][$CF_3(CF_2)_3CO_2$] would be expected to increase the viscosity of the liquid (based on typical trends for hydrocarbon viscosities as a function of chain length[24]) so the slightly lower viscosity suggests that there is convolution of factors (including chain length, degree of fluorination, and differences in cation and anion size and electrostatics) that influence viscosity and demonstrate that low-viscosity ionic liquids can still be realized when long alkyl chains are present.

In addition to investigating the role of fluorination, we used our synthetic route to further explore the impact of the cation core on ionic liquid properties. Specifically, using 3-methylpyridine instead of imidazole as a precursor (Figure 1a, green) affords the fluorinated pyridinium ionic liquid [F-hmpy][$CF_3(CF_2)_3CO_2$] (F-hmpy = 1-(3,3,4,4,5,5,6,6,6,-nonafluorohexyl)-3-methylpyridinium), Figure 1c) and demonstrates that our synthetic route can be generalized to a diverse range of cations. Moreover, the pyridinium cation has a large impact on the ionic liquid viscosity, with [F-hmpy][$CF_3(CF_2)_3CO_2$] exhibiting the highest viscosity of any of the ionic liquids studied in this work despite having the shortest fluorocarbon chain. This result is consistent with previous reports that pyridinium-based ionic liquids have higher viscosities than imidazolium-based ionic liquids, perhaps due to the larger size of the pyridinium cation.[26]

Beyond viscosity, this series of highly fluorinated ionic liquids provides opportunities to understand trends in gas solubility. Indeed, the unusual solubility properties of fluorinated compounds (particularly the high solubility of gases in neutral perfluorocarbon solvents) has led to several attempts to understand the effects of fluorination on gas solubility in ionic liquids.[9−12] However, without a controlled series of similar fluorinated ionic liquids and hydrocarbon analogues, the role of fluorination in influencing liquid structure and gas solubility has been difficult to establish.

First, we investigated the effect of different anions on O_2 and CO_2 solubility at 25 °C by comparing [F-omim][$CF_3(CF_2)_3CO_2$], [F-omim][CF_3CO_2], and [F-omim][TFSI], all of which contain the same fluorinated imidazolium cation (Figure 3, Tables S4 and S5). Similar to the trend of increasing solubility with chain length observed for neutral fluorocarbons,[3] the more heavily fluorinated anion [$CF_3(CF_2)_3CO_2$]$^-$ leads to a higher O_2 and CO_2 solubility compared to the less fluorinated [CF_3CO_2]$^-$ anion. However, the anion effect is more complicated when comparing fluorinated to non-fluorinated anions. Specifically, [F-omim][$CF_3(CF_2)_3CO_2$] has a higher O_2 solubility but a lower CO_2 solubility than [F-omim][TFSI]. This result suggests that increased fluorination has a larger impact on O_2 solubility than on CO_2 solubility, which could be the result of an interplay between how anion fluorination affects free volume and the strength of interactions between the ionic liquid and solubilized gas, the latter of which has a bigger impact on the absorption of more polarizable gases like CO_2.[27,28]

In addition to the anion effect on gas solubility, we observe that the degree of fluorination of the cation is directly correlated to both O_2 and CO_2 solubility. Specifically, the ionic liquid [F-omim][$CF_3(CF_2)_3CO_2$] has a higher O_2 and CO_2 solubility than its hydrocarbon cation analogue, [omim][$CF_3(CF_2)_3CO_2$]. Interestingly, the ionic liquid [P_{66614}][$CF_3(CF_2)_7CO_2$], which contains the longest fluorinated anion studied here, has a higher O_2 solubility and lower CO_2 solubility than [F-omim][$CF_3(CF_2)_3CO_2$] and [omim][$CF_3(CF_2)_3CO_2$]. This result suggests that there may be interesting differences in the free volume and gas absorption affinity between each of these ionic liquids.

More broadly, these gas absorption isotherms indicate that fluorination has only a limited effect on the gas solubility of ionic liquids, particularly for O_2. The difference in the amount of O_2 absorbed across the series of fluorinated and nonfluorinated ionic liquids reported here is only 1.0 ± 0.3 mmol/L, which is a far smaller effect than is observed for neutral liquids. For example, exchanging the hydrocarbon [omim] cation for the fluorocarbon [F-omim] cation results in only a 5% increase in O_2 solubility, while perfluorohexane has a 40% higher O_2 solubility compared to hexane.[3] This is likely due to a limit in how much fluorination can increase free volume when attractive electrostatic interactions also exist between solvent molecules.

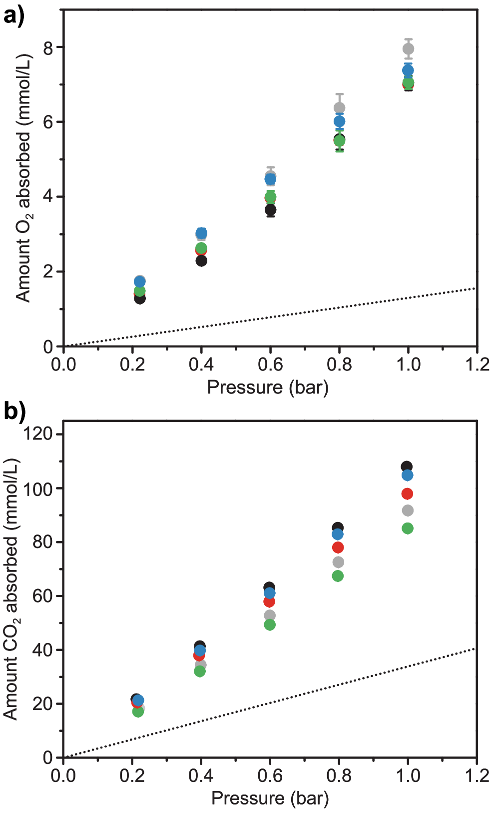


Figure 3. (a) Amount of O_2 absorbed in terms of mmol of O_2 per L of ionic liquid as a function of pressure at 25 °C. (b) Amount of CO_2 absorbed in terms of mmol of CO_2 per L of ionic liquid as a function of pressure at 25 °C. As a reference, the O_2 and CO_2 solubilities of H_2O are shown as dotted black lines. Dark blue, green, red, gray, and black circles represent the absorption isotherm data for [F-omim][$CF_3(CF_2)_3CO_2$], [F-omim][CF_3CO_2], [omim][$CF_3(CF_2)_3CO_2$], [P_{66614}][$CF_3(CF_2)_7CO_2$], and [F-omim][TFSI], respectively. Error bars represent the standard deviation of blank measurements. Note that the error bars are smaller than the size of the data point in some cases.

Despite the limited impact of fluorination on gas solubility, to the best of our knowledge, the ionic liquids evaluated here feature some of the highest O_2 solubilities ever directly measured for an ionic liquid. In particular, the relatively low viscosity and high gas solubility of the new partially fluorinated [omim][$CF_3(CF_2)_3CO_2$] make this ionic liquid the most promising of our series for further exploration in applications where low vapor pressure and high gas solubility are required. For example, [omim][$CF_3(CF_2)_3CO_2$] offers a 2.4-fold enhancement in O_2 solubility and 1.9-fold decrease in viscosity compared to the nonfluorinated ionic liquid [MTBDH][beti] (MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, beti = bis(perfluoroethylsulfonyl)imide), which has received attention as an electrolyte for the oxygen reduction reaction.[29,30]

More generally, while this work focused on the synthesis and physical properties of highly fluorinated ionic liquids, it is important to acknowledge that some of the anions used in these liquids (particularly the perfluorooctanoate ($[CF_3(CF_2)_7CO_2]^-$) anion) persist in the environment and lead to undesirable health effects that need to be considered when evaluating the safety of these compounds for new applications.[31] Notwithstanding these concerns, the diverse range of highly fluorinated ionic liquids that can be accessed through the new synthetic route reported in this work should offer opportunities for high-performance media for fluorocarbon gas capture,[32] oxygen therapeutics,[33] and electrocatalysis.[15]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.2c08374.

Synthesis procedure, NMR data, and additional experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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