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Molecular "Pincer" from a Diimidazolium Salt: A Study of Binding Ability

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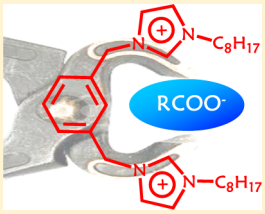
Supporting Information

ABSTRACT: The anion recognition ability of the dicationic imidazolium salt 3,3′-di-*n*-octyl-1,1′-(1,3-phenylenedimethylene)diimidazolium 1,5-naphthalenedisulfonate ([*m*-Xyl-(oim)$_2$][1,5-NDS]) was investigated in acetonitrile solution by means of proton NMR titrations. A wide range of anions, comprising simple inorganic ions, halides, and mono- and dicarboxylates was taken into account. The study showed that this receptor binds carboxylate anions more strongly than halides. Moreover [*m*-Xyl-(oim)$_2$][1,5-NDS] displays selectivity for di- over monocarboxylate anions. The complex stability was mainly affected by the anion basicity in the presence of monocarboxylates, whereas the flexibility of the alkyl chain linking the two carboxylate moieties appeared to play a major role in the presence of dicarboxylate anions.



INTRODUCTION

The study and design of anion binding hosts make up a major branch in present-day supramolecular chemistry because of the large number of applications ranging from catalysis to environmental and biological processes.[1−9] In this context, after the seminal papers by Sato,[10] Alcalde,[11] and Kim,[12] imidazolium-based hosts have recently been the subject of an increasing amount of interest, as witnessed by recent reviews of this topic.[13−15] Imidazolium salts are characterized by a thick network of hydrogen bonds, which alongside Coulombic, $\pi-\pi$, and π−quadrupole interactions imparts them a high degree of structural order that is retained to a significant extent also in the solution state.[16] Imidazolium cations provide both positively charged heterocyclic rings and relatively acidic C(2)−H protons; as a result, they can interact with anionic species by means of $(C-H)^+-X^-$ type ionic hydrogen bonds with a dominating charge−charge electrostatic interaction.[15] Since hydrogen bonding is one of the major interactions involved in anion binding, this feature has been successfully exploited for the synthesis of a number of receptors containing two or more imidazolium moieties embedded in podand-like as well as (macro)cyclic-like receptors.[17−28] Moreover, because of their peculiar features, low-molecular-weight imidazolium salts can display anionophoric properties, with potential applications in medicinal chemistry.[29] The selectivity and versatility often displayed by imidazolium-based hosts has allowed their application field to be expanded to the detection and sensing of nucleic acids like DNA[30] and RNA[31] and biologically important anions such as ATP[32] and GTP.[33] Moreover they have also proved to be valuable tools for the synthesis of nanoassembled structures[34] and mechanically interlocked assemblies.[35]

In the framework of our interest in ionic liquids, we recently investigated the structural features and the behavior as reaction media of some dicationic imidazolium salts in which a rigid spacer is interposed between the two cationic heads.[36−38] These compounds proved to possess a higher degree of structural order in comparison with common monocationic imidazolium salts. More recently, diimidazolium salts such as 3,3′-di-*n*-octyl-1,1′-(1,4-phenylenedimethylene)diimidazolium 1,5-naphthalenedisulfonate and 3,3′-di-*n*-octyl-1,1′-(1,4-phenylenedimethylene)diimidazolium 2,6-naphthalenedisulfonate proved to be promising gelling agents.[39,40] Bearing this in mind, we turned our attention to the study of the anion recognition ability of 3,3′-di-*n*-octyl-1,1′-(1,3-phenylenedimethylene)diimidazolium 1,5-naphthalenedisulfonate ([*m*-Xyl-(oim)$_2$][1,5-NDS] (Chart 1). This was partly motivated by the unexpected poor yields and difficulties we encountered in carrying out the anion exchange on [*m*-Xyl-(oim)$_2$]$^{2+}$ halides by using a classic metathesis protocol. We hypothesized that this sluggish exchange process might be caused by stronger binding between the [*m*-Xyl-(oim)$_2$]$^{2+}$ cation and halide anions compared with the corresponding monocationic salts. Indeed, in this compound the spatial arrangement of the two cationic groups may be suitable for anion recognition, as the binding sites could in principle "converge" on the anion in a pincerlike fashion, although other binding modes may be possible. In this regard, computational evidence has revealed that a pincer or tweezer shape is beneficial for anion binding hosts, as anions require a large vacant space around them to stabilize their excess electron.[41,42] This cannot be achieved with a full spherical coordination because of strong confinement of the excess electron. Most of the imidazolium-based receptors reported in the literature to date bear noncoordinating monoanions such as PF_6^- and ClO_4^-. To the best of our knowledge, this is the first report dealing with a non-macrocyclic imidazolium-based receptor

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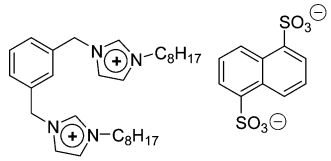
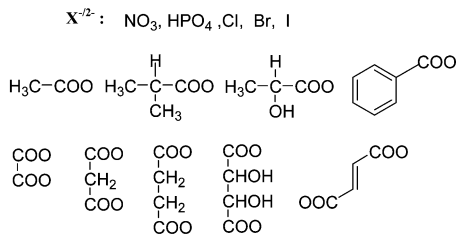
Chart 1. Structures of the Host [*m*-Xyl-(oim)$_2$][1,5-NDS] and the Guest Anions of Tetrabutylammonium Salts



[*m*-Xyl-(oim)$_2$][1,5-NDS]



[N(C$_4$H$_9$)][X]

featuring an aromatic dianion. The presence of an aromatic anionic counterpart can substantially influence the structural organization of a given imidazolium salt. Indeed, on the grounds of computational evidence previously reported in the literature,[39] the presence of a rigid aromatic dianion like 1,5-NDS could provide further preorganization to the host system by means of $\pi-\pi$ interactions between the anion naphthyl ring and the phenyl ring on the cation. The study has been carried out by means of ^{1}H NMR titrations of acetonitrile solutions containing a fixed concentration of the host and increasing amounts of tetrabutylammonium salts [N(C$_4$H$_9$)$_4$]X containing anions that differ in size, symmetry, charge, and coordinating ability. Although similar dicationic xylylene-bridged non-macrocyclic imidazolium receptors have been reported in the literature,[10,43,44] herein we have considered a significantly wider range of anions. In particular, halides (Br^-, Cl^-, I^-) and other inorganic monoanions have been taken into account as well as carboxylate anions. The importance of carboxylate anion recognition stems from their involvement in many biological and physiological processes. Not surprisingly, carboxylate groups constitute a key feature in a number of pharmaceutically active compounds. This has led to increasing interest in carboxylate recognition and sensing by supramolecular systems.[45] Bearing all of this in mind, we investigated the binding between the host and mono- and dicarboxylate anions characterized by different basicities, molecular geometries, and steric requirements (Chart 1).

RESULTS AND DISCUSSION

Upon the addition of the anions (as their tetrabutylammonium salts) to solutions of the host in acetonitrile, the signal of the C(2)−H protons in the imidazolium moieties shifted downfield, whereas the position of the other signals underwent only minor or no changes. This indicates that these protons are the portion of the host molecule that is actually involved in interactions with anions. In all of the measurements performed, a single set of signals was detected for the host molecule, indicative of fast exchange relative to the time scale of the NMR experiment. Stacked ^{1}H NMR spectra obtained for a typical titration are reported in Figure 1 in the Supporting Information. It has been reported in the literature that imidazolium cations can be deprotonated by carboxylate anions at high temperatures and in polar solvents, yielding the corresponding carbenes.[46] However, examination of the NMR spectra ruled out the possibility that such a process took place to any appreciable extent under our experimental conditions. Association constant (K) values were obtained by nonlinear least-squares fitting using the WINEQNMR2 software package.[47] In the presence of iodide and tartrate anions, ^{1}H NMR titrations did not allow the binding constant value to be determined with an acceptable degree of uncertainty. Particularly in the case of iodide, the change in the chemical shift was so small that the K value could only be estimated as $K < 10$. Conversely, in the instance of tartrate, the binding association constant fell beyond the upper limit of measurement by WINEQNMR2 (10 000 M^{-1}), and consequently, only a value of $K > 10\,000$ M^{-1} could be estimated. Moreover, the presence of nitrate induced no observable chemical shift change over the investigated concentration range. Finally, it was not possible to carry out a titration in the presence of monohydrogen phosphate and malonate, as addition of their tetrabutylammonium and bis(tetrabutylammonium) salts to the acetonitrile solution of the host resulted in formation of white precipitates.

In general, the plots of the C(2)−H chemical shift as a function of the anion/host ratio displayed saturation curves consistent with the formation of complexes characterized by 1:1 stoichiometry (Figure 1). This was further supported by

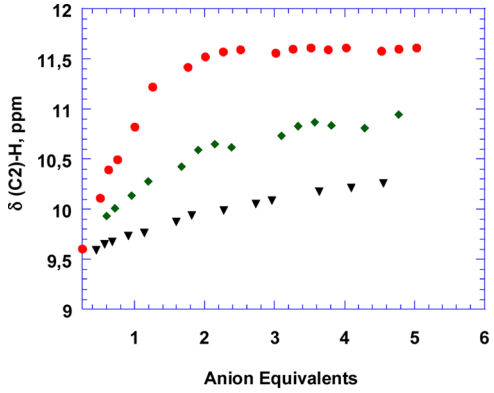


Figure 1. Plots of C(2)−H chemical shifts of the host imidazolium moieties as functions of anion equivalents in acetonitrile solution in the presence of tetrabutylammonium salts of chloride (▼), acetate (◆), and oxalate (●).

approximations of Job plots obtained from the NMR titration data by plotting $\chi_H \cdot \Delta\delta_H$ as a function of χ_H, where χ_H is the host mole fraction and $\Delta\delta_H$ the difference between the chemical shift of the C(2)−H protons in the solution under examination and that of the free host (Figure 2a). A similar approach was reported in the literature by Beer and co-workers.[24,48] All of these plots indicated a 1:1 stoichiometry for the complexes formed between the host and the considered anions. In the case of chloride, the approximated Job plot did not allow a clear-cut assessment of the binding stoichiometry because of the broad maximum of the resulting curve (Figure 2 in the Supporting Information).

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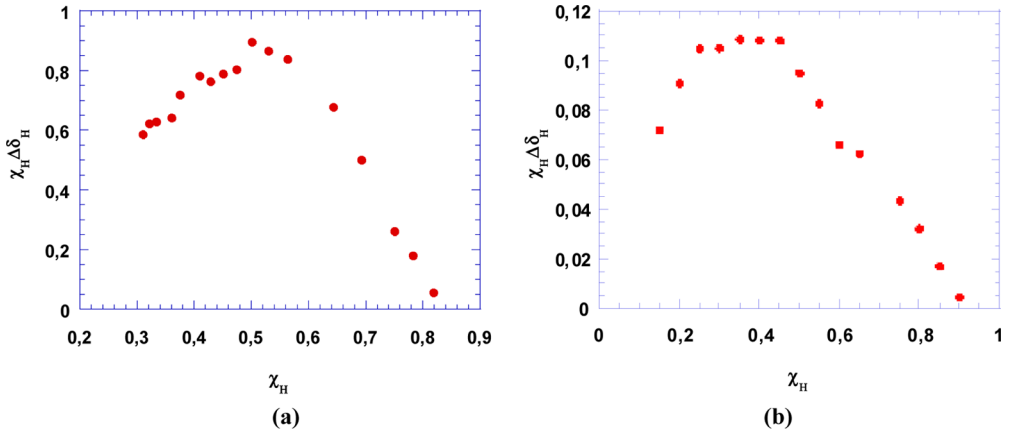

Figure 2. (a) Approximated Job plot obtained from NMR titration data in the presence of bis(tetrabutylammonium) succinate. (b) Job plot obtained in the presence of tetrabutylammonium chloride at a total concentration of 8×10^{-3} M.

To have a clearer indication of the actual complex stoichiometry, in this case we carried out a continuous variations measurement, obtaining the Job plot reported in Figure 2b. This plot is practically analogous to that obtained by using the titration data; the broadening of the curve in the vicinity of the maximum could be a consequence of the moderate stability of the complex. As reported in the literature, this latter factor can lead to an ill-defined maximum in the Job plot.[49] Moreover, fitting of the NMR titration data gave statistically significant results only when formation of a 1:1 complex was taken into account, whereas it failed when complexes with different stoichiometry were considered. On these grounds, and bearing in mind literature reports dealing with closely related receptors,[10,43,44] we hypothesized a 1:1 stoichiometry for this complex. To further support this hypothesis, we carried out a titration experiment using a different concentration of the host. It is indeed known that the constancy of the binding constant obtained by measurements performed at different concentrations can be a reliable indicator of the suitability of a given stoichiometric model to explain the experimental results.[50]

Toward this aim, we carried out a titration using a host concentration of 5.2×10^{-3} M. The values obtained at the two different concentrations (K = 38 and 43 M^{-1} for host concentrations of 8.0×10^{-3} and 5.2×10^{-3} M, respectively) are comparable within the experimental uncertainty. It is worth mentioning that also in this case, fitting of the data was successful only when a 1:1 stoichiometry was considered, whereas it failed to yield statistically significant parameters when different stoichiometries were taken into account. On the grounds of all the above considerations, we propose that the stoichiometry of the complex formed by the host in the presence of chloride anion is 1:1 under the experimental conditions considered. Values of 1:1 association constants K are reported in Table 1, while plots of the NMR titrations are reported in Figures 3−14 in the Supporting Information.

As far as halide ions are concerned, the binding strength increases in the order $I^- < Br^- < Cl^-$, parallel to the increasing charge density and hydrogen-bond acceptor ability as estimated by the Kamlet−Taft β parameter of monocationic imidazolium salts[52] (β = 0.75, 0.87, and 0.95 for [bmim][I], [bmim][Br], and [bmim][Cl], respectively) or by IR measurements on anion solutions in the presence of water as a hydrogen-bond donor ($\Delta\nu_{HOD}$ = 30, 277, and 326 cm^{-1} for I^-, Br^-, and Cl^- respectively).[53] A higher range of binding constants was

Table 1. Association Constants Calculated for [*m*-Xyl-(oim)$_2$]$^{2+}$ and Anions in Acetonitrile at 298 K

entry	anion	K (M^{-1})[a]	pK_a (pK_{a2}[b])
1	$[Cl]^-$	38	
2	$[Cl]^-$	43[c]	
3	$[Br]^-$	27	
4	$[I]^-$	<10	
5	$[CH_3COO]^-$	130	4.76
6	$[CH_3COCOO]^-$	21	2.39
7	(±)-$[CH_3-CH(OH)-COO]^-$	80	3.86
8	$[C_6H_5COO]^-$	130	4.19
9	$[(CH_3)_2CHCOO]^-$	110	4.86
10	*trans*-$[OOC-CH=CH-COO]^{2-}$	150	3.02 (4.44)
11	$[(COO)_2]^{2-}$	1000	1.23 (3.18)
12	$[OOC-(CH_2)_2-COO]^{2-}$	8000	4.19 (5.61)
13	(±)-$[OOC-(CHOH)_2-COO]^{2-}$	>10000	2.98 (4.34)
14	$[NO_3]^-$	no binding	
15	$[HPO_4]^{2-}$	–[d]	
16	$[OOC-CH_2-COO]^{2-}$	–[d]	

[a]Association constant values were reproducible within 15%. [b]pK_a values in water from ref 51. [c]Host concentration 5.2×10^{-3} M. [d]Formation of white precipitates.

observed in the presence of carboxylate anions. For the sake of simplicity, the binding of [*m*-Xyl-(oim)$_2$]$^{2+}$ to mono- and dicarboxylate anions will be treated separately. We first tried to explain the observed binding strength trend on the grounds of the different basicities of the considered anions. A plot of ln K versus aqueous pK_a for the monocarboxylic conjugate acids (Figure 3) evidenced a partial correlation, showing that although anion basicity is an important factor, it is not the only parameter affecting complex stability.

Accordingly, analysis of the results reported in Table 1 shows that among monocarboxylate anions, the weakest binding was detected in the presence of pyruvate and lactate; however, the host displays selectivity for the latter over the former (entries 6 and 7 in Table 1). This finding could be rationalized by considering the higher basicity of the lactate anion, as estimated by aqueous pK_a values (pK_a = 2.39 and 3.86 at 298 K for pyruvic and lactic acid, respectively).[51] For the other monocarboxylate anions (acetate, isobutyrate, and benzoate), nearly identical K values were determined despite their significantly different structural characteristics, basicities, and bulkiness. This finding suggests that the carboxylate moiety is

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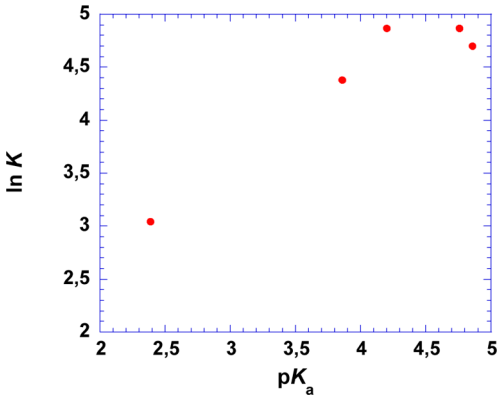

Figure 3. Plot of ln K in acetonitrile vs aqueous pK_a[51] for the conjugate acids of the considered anions at 298 K.

the portion of the anion that is actually involved in the interaction with the host. In general, we could represent all of these monocarboxylate anions in the form R−Y−COO^-, where R is an alkyl or phenyl group and Y the substituted carbon atom directly bound to the carboxylic group. According to this representation Y is CHOH for lactate, C═O for pyruvate, and absent for the other monocarboxylates. Comparison of the association constants determined in the presence of these anions shows that the presence of a Y group significantly influences the complex stability, exerting a detrimental effect. A more electron-attracting Y is associated with a lower K value, in agreement with the aforementioned partial correlation between complex stability and anion basicity. Conversely, when Y is absent (entries 5, 8, and 9 in Table 1) comparable constants are obtained, irrespective of the aliphatic or aromatic nature of R. In particular, no observable gain in binding strength is associated with the presence of the phenyl ring in the benzoate anion, showing that no $\pi-\pi$ interactions with the imidazolium rings in the host are operative in complex formation or that they play a negligible effect on the stability of the complex.

In the case of dicarboxylate anions, the host, though very simple in its design, displays a more articulate behavior in terms of anion binding selectivity. In general, with only the exception of fumarate, the K values obtained were much higher than those for formation of complexes between monocarboxylate anions and the host. In particular, the data reported in Table 1 show that the affinity of the host toward dicarboxylate anions increases in the order fumarate < oxalate < succinate < tartrate. As already mentioned, for the complex formed in the presence of tartrate, a value for the association constant could not be determined because the chemical shift variation of the C(2)−H proton was so high that the association constant value fell beyond the upper limit of reliable measurement by NMR. Consequently, only a K value of >10 000 M^{-1} could be estimated. Also in this case we tried to correlate the obtained association constants to the basicities of the dicarboxylate anions by plotting ln K as a function of the aqueous pK_{a2} values of the conjugate acids. Comparison of the trends displayed by the K values as functions of pK_{a1} and pK_{a2} shows that no such correlation could be observed. It is worth noting that in the instance of fumarate, the presence of a further carboxylate moiety does not provide any significant binding enhancement. Indeed, the association constant barely exceeded those determined in the presence of acetate and benzoate. This may indicate that the relative rigidity of the linker between the two charged ends in the fumarate anion prevents the second COO^- group from reaching the binding sites; consequently, what the host experiences is not significantly different from the interactions for a monocarboxylate anion. As a comparison, in the presence of the simplest dicarboxylate anion, oxalate, the observed association constant is almost seven times higher (entry 11 vs 10 in Table 1). In this case the host can interact with two carboxylate groups at the same time, causing a significant increase in the anion binding strength. We are aware that in this regard, the measurement of the complexation ability of the host toward the isomeric maleate anion could provide useful insight. Unfortunately, solubility issues prevented this determination, as the addition of bis(tetrabutylammonium) maleate to the host solution resulted in the formation of white precipitates. Nonetheless, this finding could highlight a significant difference in the extent of interaction between the host and these anions. A more dramatic increase in the binding affinity is found when the host interacts with succinate and tartrate anions. Once again, flexibility of the alkyl spacer between the carboxylate groups appears to be an important factor favoring the binding of dicarboxylate anions by the host. A similar result was reported by Yoon and co-workers using an imidazolium-functionalized cavitand as the host.[54] This can be rationalized by considering that a more flexible anion can adopt more easily an optimal conformation in order to maximize the interactions with the dicationic host. Finally, it may be useful to assess the selectivity for dicarboxylates over monocarboxylates of [*m*-Xyl-(oim)$_2$][1,5-NDS] with respect to that of related receptors reported in the literature. In this regard, the ratio of the stability constants measured in the presence of succinate and acetate (K_{succ}/K_{acet}) may provide a useful comparison. For example, K_{succ}/K_{acet} amounts to 65 for [*m*-Xyl-(oim)$_2$][1,5-NDS] and to 20 for Yoon's tetracationic cavitand in the same solvent.[54] Moreover, the selectivity for dicarboxylates shown by a diimidazolium-functionalized calixarene, as expressed by the ratio of constants for the complex formed in the presence of malonate and acetate (K_{mal}/K_{acet}) in acetonitrile is 20, although in this case the dicarboxylate anion is different and the comparison is therefore less reliable.[55] Notwithstanding the extensive work devoted to the study of imidazolium-based anion receptors, few reports have appeared in the literature dealing with the recognition of mono- and dicarboxylates by the same host, so no other comparisons could be made. Overall the selectivity "performance" displayed by the simple receptor [*m*-Xyl-(oim)$_2$][1,5-NDS] appears to be well in line with those of macrocyclic imidazolium-based hosts for anions.

■ CONCLUSIONS

The study of the anion binding ability of the dicationic imidazolium salt [*m*-Xyl-(oim)$_2$][1,5-NDS] in acetonitrile solutions evidenced that this simple receptor shows affinity for mono- and dicarboxylate anions. The parameters affecting the binding strength appear to be different in the two cases: in particular, binding of monocarboxylates seems to be mainly influenced by the anion basicity, while in the presence of dicarboxylate anions this parameter plays a marginal role. On the contrary, flexibility of the alkyl chain linking the two carboxylate anions is found to be a key feature affecting complex stability. Finally, comparison with data previously reported in the literature for imidazolium-based receptors highlights that the molecular "pincer" used in this work shows a higher selectivity for dicarboxylates over monocarboxylates.

EXPERIMENTAL SECTION

Materials. Commercially available anhydrous acetonitrile, tetrabutylammonium hydroxide 30-hydrate, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium iodide, and tetrabutylammonium nitrate were used without further purification. Tetrabutylammonium pyruvate and (±)-lactate were prepared according to a reported procedure.[56] Tetrabutylammonium salts of the other carboxylate anions were synthesized by following the previously reported procedure.[57] The synthesis of 3,3′-di-*n*-octyl-1,1′-(1,4-phenylenedimethylene)diimidazolium 1,5-naphthalenedisulfonate was carried out as previously described in the literature.[39]

NMR Titrations. ^{1}H NMR spectra were recorded on a 250 MHz spectrometer. Typical samples for NMR titrations were prepared by mixing suitable amounts of stock solutions of host and TBA salts of the anions in acetonitrile. In each resulting solution, the host concentration was kept constant (8×10^{-3} M) while the anion concentration ranged from 8×10^{-4} to 4×10^{-2} M. In general, we used the maximum concentration range allowed by the solubility of the formed complex, the upper limit being reached when further addition of anion solution led to the occurrence of a turbid mixture. Each solution was left to equilibrate overnight and then transferred in an NMR tube equipped with a sealed coaxial capillary tube loaded with DMSO-d_6 for the external lock of the NMR field/frequency, and its signal was used as the ^{1}H NMR external reference at 2.56 ppm. The chemical shift of the imidazolium C(2)−H protons was monitored. Each titration was performed in duplicate to verify the consistency of the calculated association constant values. Data analysis was carried out using the WINEQNMR2 software.[47]

ASSOCIATED CONTENT

Supporting Information

Stacked plot of proton NMR spectra obtained for a typical titration and NMR titrations plots in acetonitrile. 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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