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A simple and rapid route to novel tetra(4-thiaalkyl)-ammonium bromides†

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A simple approach for the preparation of symmetrical quaternary ammonium bromides employing thiol–ene click chemistry is used to synthesize tetra(4-thiaalkyl)ammonium bromides. This approach allows the incorporation of a variety of alkyl moieties onto the nitrogen center with a one-step synthesis involving easy work-up, no side reactions and environmentally friendly reagents. To elucidate information regarding the behaviour of this novel class of compounds, comparisons to tetraalkylammonium analogues have been made. These include melting points, activity as phase-transfer catalysts, and conformational predictions from computational modelling. All results are consistent in indicating stronger bonding between the quaternary cation and the anion for the salts with 4-thiaalkyl chains as compared to those with *n*-alkyl chains.

Introduction

Quaternary ammonium salts or "quat salts" have been the mainstay of research and industrial use for phase transfer catalysis for over forty years beginning with the pioneering work of Starks,[1] Makosza[2] and Brandstrom.[3] In addition, the published literature since then has described a multitude of uses for quat salts,[4] including preparation of ionic liquids,[5] antimicrobial agents,[6] disinfectants,[7] surfactants,[8] fabric softeners,[9] antistatic agents,[10] wood preservation,[11] osmolytes,[12] chemical capacitors,[13] electrolytes for batteries,[14] capping agents for copper nanoparticles,[15] and plant growth retardants.[16]

Quaternary ammonium compounds are typically prepared by quaternization of tertiary amines with alkyl halides and by anion exchange reactions on commercially available salts.[17] Such a synthetic route poses a limit on the variety of quat salt structures based on availability of amines and alkyl halides. Under neutral or acidic environments, quat salts are generally stable up to 150 °C.[18] Conversely, under basic conditions, their susceptibility to Hofmann elimination and thermal decomposition at temperatures above 100 °C limit the utility of quat salts in applications requiring alkaline environments.[19]

Previous work in our group[20] described the thiol–ene click reaction with tetraallylammonium bromide and 1-thiogylcerol to prepare a polyhydroxylated tetra(4-thiaalkyl)ammonium bromide with subsequent metathesis to form the corresponding ionic liquid. The use of the thiol–ene reaction to add four alkyl appendages to the ammonium cation was modelled after the approach by Hawker *et al.* for the thiol–ene based assembly of functionalized dendrimers.[21]

Since the introduction of the principles of click chemistry by Kolb *et al.* in 2001,[22] researchers in the areas of synthetic and materials science have strived to incorporate these into drug discovery, and into syntheses of small molecules, polymers, and advanced materials. According to these guiding principles,[23] click chemistry includes syntheses that: (a) are modular, (b) have high yields, (c) have by-products that are removable by non-chromatographic processes, (d) are stereospecific, (e) are insensitive to oxygen or water, (f) can be accomplished with readily available starting materials and reagents, (g) can be performed without solvent or in environmentally benign media, and, (h) are wide in scope. Our intent was to incorporate as many of these principles as possible into a synthetic route for a new class of quaternary ammonium salts and to investigate their use as phase transfer catalysts.

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Experimental

Synthesis of tetra(4-thiaalkyl)ammonium bromides

For the present study, tetraallylammonium bromide was selected as the starting precursor due to its ease of synthesis from triallylamine with allyl bromide in a one-step process. As in our previous work,[20] we found methanol to be well-suited as the reaction solvent with a 1 : 0.5 : 2 equivalent ratio of alkene : photoinitiator : thiol being combined, followed by UV-irradiation at ambient temperature for 6–8 hours in a sealed quartz tube. The photochemical reactions were carried out without a nitrogen purge of the quartz tube before irradiation. The thiol–ene chemistry proceeded to completion *via* an anti-Markovnikov addition to the allyl moieties and without observation of any side reactions.[24]

The photoinitiator (2,2-dimethoxy-2-phenylacetophenone) and corresponding thiols were easily removed by washing with hexane or diethyl ether, in which none of the starting or product salts were soluble. No further purification was required to obtain the desired salts. All of the thiols employed for our studies were commercially available in high purity.

Spectroscopic characterization

Characterization of the tetra(4-thiaalkyl)ammonium bromides using ^{1}H, ^{13}C and ^{19}F NMR was performed on a JEOL 500 MHz NMR with multi-nuclear capabilities using $CDCl_3$ as the deuterated solvent. Chemical shifts, provided as ESI† to this paper, are reported relative to TMS as the internal reference at 0.00 ppm for ^{1}H and ^{19}F NMR and 77.23 ppm (middle peak, $CDCl_3$) for ^{13}C NMR. ESI-MS analyses were performed by flow-injection on a Thermo Scientific mass spectrometer using HPLC grade acetonitrile. As our interest was in the cations of these salts, data was collected in positive ion mode.

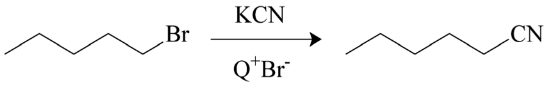
Differential scanning calorimetry

As part of the characterization of these novel quaternary salts, we have examined the thermal behaviour of tetra(4-thiadodecyl) ammonium bromide (entry 10, Table 1) and compared it with that of a tetraalkylammonium bromide of equivalent chain length, tetradodecylammonium bromide. The DSC curves were obtained using a TA Instruments Q2000 with sample sizes between 8 and 15 mg. Each compound was characterized using both a conventional DSC method (solid line) with a scan rate of 10 °C min^{-1} and modulated DSC utilizing a scan rate of 3 °C min^{-1} with a 1 °C amplitude modulation at a period of 60 seconds.

Phase-transfer catalysed reactions

For the purposes of this preliminary study, our goal was to establish that these tetra(4-thiaalkyl)ammonium bromides exhibit activity as phase-transfer catalysts and to compare the activity to that of a traditional tetraalkylammonium analog. For these reactions, we chose tetradodecylammonium bromide and its tetra(4-thiaalkyl)ammonium analogue (entry 10), having a sulfur atom replacing the fourth carbon from the nitrogen in each chain.

Table 1 Preparation of tetra(4-thiaalkyl)ammonium salts



Entry	R group	Yield^a (%)
1	$–C_2H_5$	71
2	$–C_3H_7$	54
3	$–C_3H_7$ (isopropyl)	66
4	$–C_4H_9$ (*n*-butyl)	51
5	$–C_4H_9$ (*tert*-butyl)	64
6	$–C_4H_9$ (isobutyl)	67
7	$–C_4H_9$ (anteisobutyl)	77
8	$–C_6H_{13}$	47
9	$–C_7H_{15}$	61
10	$–C_8H_{17}$	61
11	$–C_{14}H_{29}$	57
12	$–C_{18}H_{37}$	74
13	$–CH_2CH_2(CF_2)_7CF_3$	50
14	$–CH_2C_6H_5$ (benzyl)	98
15	$–C_6H_{11}$ (cyclohexyl)	56

[a] Isolated yield after purification and drying, no optimization.

Reactions were carried out in a 50 mL round-bottom flask containing 2.0 mL of a saturated aqueous solution of potassium cyanide (solid always visible), 10.00 mL of a 0.200 M solution of 1-bromopentane in toluene, and an amount of catalyst equal to 5.0 mol% of the amount of 1-bromopropane in the system. Temperature was controlled at 60 °C, and the system was stirred at 1400 rpm. Reaction analysis was carried out by taking periodic 1 μL samples of the organic layer and analysing by an Agilent 7820 gas chromatograph equipped with a thermal conductivity detector. Each reaction was performed at least three times with reproducible results.

Molecular modelling

Gas-phase geometry optimizations and the generation of electrostatic potential/isodensity surfaces were performed using Spartan '08 (Wavefunction, Inc., Irvine, CA). The isolated cations and cation/bromide complexes were optimized using the B3LYP density functional method[25] and the 6-31G** basis set.[26] All structures were confirmed as stable by computing analytic vibrational frequencies. The thiaalkyl-based cation required tighter convergence criteria than default values in order to eliminate all imaginary modes. The relative strength of binding of bromide or cyanide to one cation over another was estimated by computing ΔE of the gas-phase exchange: $\Delta E = E(\text{cation}_1) + E(\text{cation}_2\cdot\text{anion}) - (E(\text{cation}_2) + E(\text{cation}_1\cdot\text{anion}))$.

Results and discussion

Synthesis

In all but two salts, the new tetra(4-thiaalkyl)ammonium bromides were isolated as solids, while viscous liquids were obtained for entries 7 and 14 as shown in Table 1. The range of alkyl thiols employed shows the versatility of the thiol–ene reaction. Alkyl chains of various lengths ranging from ethyl to octadecyl were incorporated, as well as branched and cyclic groups and even perfluorinated chains. Entry 14 employs benzyl mercaptan as the thiol and provides an opportunity for incorporation of aryl rings into the quaternary framework as well as future substitution at the *ortho*, *meta* and *para* positions. According to NMR analysis, the reactions proceeded to completion, and the losses resulting in reported yields result from a work-up method that has not been optimized.

Entries 4 through 7 in Table 1 provide an interesting series, based on the differences in structure of the butyl chains as part of the overall thioether chain. The salts of entries 4, 5 and 6 yielded solids while entry 7 was isolated as a viscous liquid. As we have shown in previous work with ionic liquids,[27] a perturbation in the alkyl chain leads to lower packing efficiency and lower surface area contact[28] for entry 7 and thus to an increased fluidity – most probably as an entropy-dominated effect.

Spectroscopic characterization

The ^{1}H and ^{13}C NMR of each new salt fully comport with its proposed structure and formulation. Both ^{1}H and ^{13}C NMR spectra of entries 1–15 unambiguously show complete removal of the photoinitiator and thiols with complete thiolation, which is readily ascertained on the basis of peak integration (^{1}H) and the disappearance of the olefinic peaks (^{1}H, ^{13}C) of the starting tetraallylammonium bromide. Of interest is the ^{19}F NMR of entry 13, which yielded peaks in the -80 to -126 ppm region for the presence of the C–F bonds[29] for the fluorinated tether.

Further elucidation of entries 1–15 using ESI-MS yielded interesting results with fragmentation of the salts, though the expected parent ions were not seen. As a representative example, entry 10, having four dodecyl chains (m/z = 763), produces a high-mass ion with m/z = 471, consistent with a structure in which two of the four dodecyl chains have been cleaved, leaving two intact while re-generating two of the original *N*-tethered allyl moieties. This retro-thiolation is likely promoted by severe steric crowding around the central nitrogen of these ions. This type of fragmentation pattern was observed in our previous work.[20]

Differential scanning calorimetry

The curves obtained using differential scanning calorimetry are provided in Fig. 1. The most prominent features of each curve are the sharp melting points, which are followed by broad thermal decomposition. For the tetradodecylammonium bromide, the melting point as measured by the transition onset from the modulated DSC scan was 86.3 °C. This value is in good agreement with a previously reported melting point (89 °C),[30] as are the two lower temperature solid/solid mesophase transitions.[31] For the tetra(4-thiadodecyl)ammonium bromide, the melting point is significantly higher, 234 °C from the modulated scan and 238 °C from the traditional scan. This range is consistent with visual determination of the melting point of 234–235 °C.

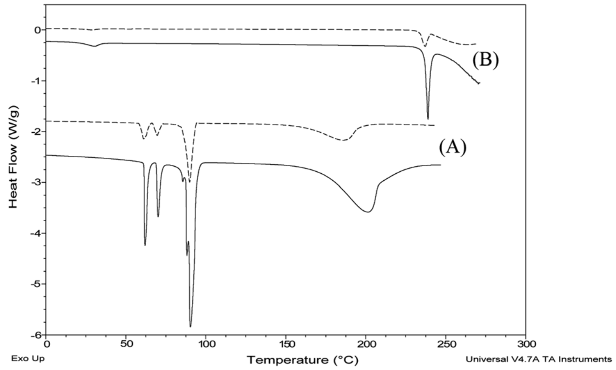


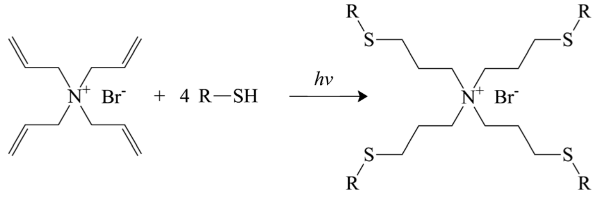
Fig. 1 DSC curves for (A) tetradodecylammonium bromide and (B) tetra(4-thiadodecyl)ammonium bromide (entry 10). The solid lines were obtained using at simple temperature ramp and the dashed lines were obtained using modulated DSC. The curves are offset on the *y*-axis to distinguish them from one another, but are not scaled.

The compound is observed to decompose upon melting, and samples were observed to change colour from white to brown after scans at temperatures higher than 210 °C, even when the melting point was not reached. Because of this, the scans shown in Fig. 1 were each performed using separate samples. This decomposition temperature is significantly higher than that of the tetraalkyl analogue, which can be seen to exhibit endothermic degradation beginning at around 160 °C.

The higher melting point of tetra(4-thiadodecyl)ammonium bromide relative to tetradodecylammonium bromide is indicative of greater cation–anion interactions in the sulfur-containing salt. It is unclear whether the phase transition, which certainly disrupts solid-phase interactions between ion pairs, additionally disrupts internal ion-pair interactions or interactions between a bromide of one ion pair and a hydrogen alpha to the sulfur on another ion pair. Regardless, the higher melting point is consistent with other measurements and calculations in this work indicating enhanced interactions between the ions, including the predictions made using quantum-based computational methods and the experimentally-observed reduction of reaction rate. Furthermore, the greater thermal stability may be due to the sulfur's proximity to the central nitrogen, electronically or sterically preventing degradation reactions. We are currently investigating the thermal behaviour of these salts in greater detail.

Phase-transfer catalysed reactions

For the novel quaternary ammonium salts, phase-transfer catalysis (PTC) offers both a potential application and a tool for evaluating behaviour. Because the mechanism of the PTC cycle is generally well understood,[32] the activity of these salts compared to their traditional analogues provides a means of characterizing them. A commonly used reaction for screening the activity of phase transfer catalysts is the nucleophilic substitution of cyanide for bromide.[33] In this work, we have chosen as a model reaction the cyanide displacement on 1-bromopentane:



This reaction takes place by a well-established mechanism in which the Q^+ exchanges the Br^- for the CN^- in the aqueous phase, transfers it to the organic phase where a second-order nucleophilic substitution takes place, generating the product and regenerating the Q^+Br^-, which partitions back into the aqueous phase to restart the cycle.[34]

As shown in Fig. 2, results indicate that the quaternary ammonium salts containing sulfur yield slower reaction rates than those without. However, the reaction rate is significantly increased compared to that without a catalyst present. With no catalyst, approximately 3% conversion of the 1-bromopentane was achieved in a 24 hour period.

According to the established mechanism for this reaction, the rate law should be

$$\text{rate} = k_2[Q^+CN^-]_{org}[C_5H_{11}Br]$$

Because the catalyst concentration is constant, pseudo-first-order reaction kinetics are expected:

$$\text{rate} = k_1'[C_5H_{11}Br]$$

In this pseudo-first-order rate law, a constant catalyst concentration has been factored into the rate constant.

The relevant plots for the integrated form of the pseudo-first-order rate expression are provided in Fig. 3. The linearity of these plots is consistent with the mechanistic prediction. Rate constants, evaluated using the slope of the best linear fit lines in Fig. 3, are shown in Table 2. The rate constant for the tetra(4-thiadodecyl)ammonium bromide (entry 10) is less than that for tetradodecylammonium bromide, but is of the same order of magnitude. As the rate-limiting step involves the attack of the cyanide ion on the 1-bromopentane, the rate of reaction depends upon the nucleophilicity of the cyanide ion. We believe that a tighter ion pairing reduces the charge density on the cyanide anion, rendering it less nucleophilic and thus reducing the reaction rate. This is consistent with the results of preliminary quantum calculations performed on the smaller pentyl and 4-thiapentyl model systems shown in Fig. 4 and discussed below.

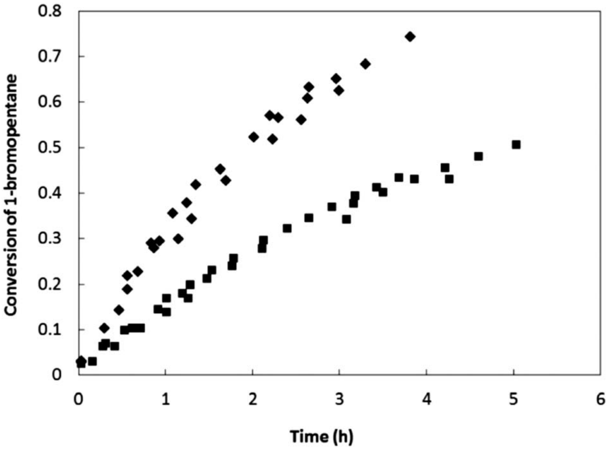


Fig. 2 Conversion of 1-bromopentane to hexanenitrile at 60 °C using (◆) tetradodecylammonium bromide and (■) tetra(4-thiadodecyl)ammonium bromide (entry 10) as phase-transfer catalysts.

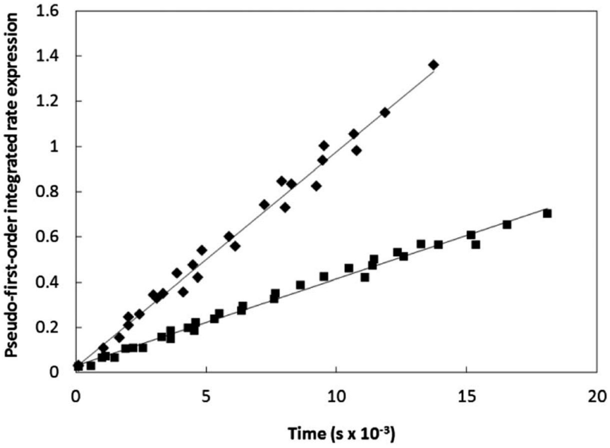


Fig. 3 Pseudo-first-order integrated rate expression [ln(1/1 − X)] (X = conversion) for the reaction of 1-bromopentane to hexanenitrile at 60 °C using (◆) tetradodecylammonium bromide and (■) tetra(4-thiadodecyl)ammonium bromide (entry 10) as phase-transfer catalysts.

Table 2 Rate constants for the reaction of 1-bromopentane to hexanenitrile at 60 °C using tetradodecylammonium bromide and tetra(4-thiadodecyl)ammonium bromide (entry 10) as phase-transfer catalysts. The second order constants (k_2) are evaluated by accounting for the concentration of catalyst that is factored into the pseudo-first order constants (k_1')

Catalyst	k_1' (s^{-1})	k_2 ($L\ mol^{-1}\ s^{-1}$)
Tetradodecylammonium bromide	9.5×10^{-5}	9.5×10^{-3}
Tetra(4-thiadodecyl)ammonium bromide	3.9×10^{-5}	3.9×10^{-3}

We conclude that while the reactions employing the 4-thiaalkylammonium salts as phase-transfer catalysts are slower than those with the traditional quat salts, the reduction in rate is not significant enough to disqualify compounds of this novel class as candidates for PTC. There may be cases where their increased stability makes them more attractive, or examples where the increased binding can be manipulated to control reaction selectivity. Using the insight gained in this study, we are continuing to explore potential applications exploiting both their reactivity in exchange reactions and their stability relative to traditional quat salts.

Molecular modelling

Molecular modelling was performed using the model cations tetrapentylammonium and tetra(4-thiapentyl)ammonium. The

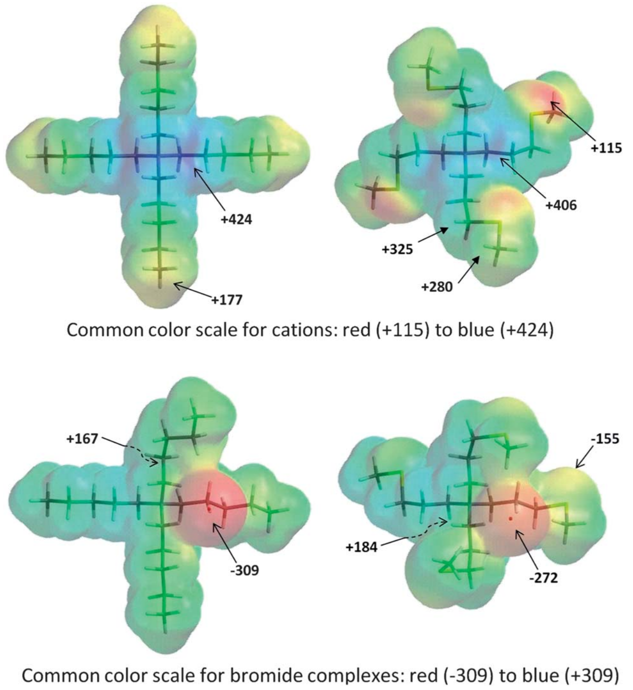


Fig. 4 Optimized geometries and electrostatic potential energy maps of model pentyl- and 4-thiapentyl-based quaternary ammonium cations (top) and bromide salts (bottom). Minima, maxima, and other selected values of the electrostatic potential energy (kJ mol^{-1}) are indicated. Maxima for the bromide complexes are located on the backside surfaces.

lowest-energy conformations of these model cations and their bromide complexes are shown in Fig. 4. At the left side of Fig. 4 are the tetrapentylammonium cation (top) and its bromide complex (bottom). At right are the tetra(4-thiapentyl)ammonium cation (top) and its bromide complex (bottom). The depictions of the isolated cations show a quasi-tetrahedral arrangement of the pentyl (or 4-thiapentyl) chains about the nitrogen center. As expected, there is a gradual falling off of positive charge along the pentyl chains. In contrast, the electronegative sulfur atom of the thiapentyl chains causes the C3 methylene and terminal C5 methyl regions to be far more positive than their alkyl counterparts; the conformation about the C2–C3 bonds (d(C1–C2–C3–S) = 70°) allows each sulfur atom to interact with a C2 hydrogen of a neighbour thialkyl chain.

The bottom images of Fig. 4 indicate substantial differences between the corresponding bromide complexes. On the left, the bromide ion is electrostatically bound to the most positive region of the pentyl-based cation, contacting two C1 and one C2 hydrogens; one pentyl moiety has what is usually a higher-energy rotational conformation about its C2–C3 bond to achieve contact between a C4 hydrogen and the bromide ion. Higher-quality calculations (B3LYP/6-311+g(d,p)) indicate that this conformation is only slightly more favorable ($<$0.05 kcal mol^{-1}) than the typical straight chain. The bromide ion is positioned at a similar site on the tetra(4-thiapentyl)ammonium cation at right. However, two of the thiapentyl moieties adopt conformations about the C2–C3 bond so that their terminal methyls can approach the bromide ion; the rotational flexibility of the C–S bonds permits these hydrogen–bromide contacts and yet another hydrogen–bromide contact from the terminal methyl group at right. At the same time, the sulfur lone pair regions are directed away from the bromide ion. The resulting charge delocalization of the bromide ion is far more pronounced in this complex, wherein the sulfur atoms serve as sinks for the anion's negative charge, conveyed through several contacting thiaalkyl hydrogens.

Our calculations show that the bromide ion binds more favorably to the model 4-thiapentyl cation than to the pentyl cation by 2.5 kcal mol^{-1}. The stronger thiaalkyl–anion interaction explains the significantly higher melting point of tetra(4-thiadodecyl) ammonium bromide over that of tetradodecylammonium bromide. Follow-up model calculations in which cyanide is the complexed counter-ion yield completely analogous results, again with greater charge delocalization of the anion in the 4-thiapentyl complex as compared to the pentyl complex, and stronger binding by 3.8 kcal mol^{-1}. The observed reduction in the intrinsic reaction rate for the phase-transfer catalyzed displacement reaction is explained both by the tighter binding of cyanide and the reduced negative charge on cyanide accomplished by the thiaalkyl groups, which result in a weakening of cyanide's nucleophilicity.

Conclusions

In conclusion, we have demonstrated a rapid and simple approach for the construction of symmetrical tetra(4-thiaalkyl)-ammonium bromides using the thiol–ene click reaction, which offers considerable promise as a means to fabricate structurally elaborate quat salts. The reactions proceed quickly and cleanly, and provide acceptable yields of products without optimization. Based on the observed thermal behaviour, the PTC activity, and our quantum-based computations, the tetra(4-thiaalkyl)ammonium cations exhibit stronger interactions with their associated anions than do their tetraalkylammonium counterparts. Further studies involving the thermal stability of these novel salts, their partitioning between aqueous and organic phases, and their utility in various applications are ongoing in our laboratories.

Acknowledgements

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