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Synthesis and properties of L-valine based chiral long alkyl chain appended 1,2,3-triazolium ionic liquids†

Roli Mishra, Shubha Pandey,* Shruti Trivedi, Siddharth Pandey* and Pramod S. Pandey*

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The increasing importance of ionic liquids (ILs) in various strata of chemical sciences is largely due to the fact that modification in the architecture of the cation and/or the anion imparts favorable and specific properties to an IL. Consequently, there is a need to develop new ILs with different functionalities. A series of L-valine based alkyl chain-appended 1,2,3-triazolium ILs (alkyl = hexyl, octyl, dodecyl, cetyl and octadecyl) with iodide and hexafluorophosphate anions, respectively, are synthesized and characterized. These new ILs show optical activity and hence are termed chiral ILs (CILs). All ten CILs are room temperature ILs (RTILs) as their melting points, obtained from differential scanning calorimetry (DSC), are found to be below ambient temperature. Thermogravimetric analysis indicates these CILs to have adequate thermal stability. The longer alkyl chain containing CILs exhibit facile self-aggregation when dissolved in ethanol. There is a hint of pre-micellar aggregation by short alkyl chain possessing CILs along with the long alkyl chain containing ones. These CILs demonstrate weak absorbance and emission of UV-Vis radiation and hence can be considered ideal solvents for photochemical applications. These CILs, consisting of different functionalities, possess interesting properties and have potential to be used in many areas of chemistry.

Introduction

Ionic liquids (ILs) have attracted increasing interest as versatile alternate substances in chemical sciences over the last decade and a half,[1–7] especially in synthesis, in catalysis, in separation processes, in biotechnology, as lubricant additives, as electrolytes, *etc.*[8–20] Various applications of ILs arise from the unique combination of properties they offer, such as, near nonvolatility, low toxicity, excellent thermal stability, high ionic conductivity, excellent reusability, good solubility, and a broad electrochemical stability window.[21–23] They are unique in the sense that they are organic salts composed entirely of ions that are liquid at ambient conditions (or below 100 °C).[24] As members of a subclass, the ILs that are liquid at ambient conditions, called room temperature ionic liquids (RTILs), are obviously more desirable and are better projected as solubilizing media.

ILs are called 'designer solvents' because their physicochemical properties can be tuned for a specific application by different combination of cations and anions.[22,24b,c] Structural changes/modifications in both cation and anion architecture are reported to result in widely varying properties of ILs.[3] Therefore, various functionalized ILs, termed 'task-specific ILs (TSILs)', may be obtained from a given parent structure by generating wide range of compounds by simply varying the cation, its substitution pattern and/or the anion.[25] Consequently, efforts on designing and developing ILs with modified functionalities have increased over the last few years. In this regard, ILs possessing one or more chiral centers on their cation or anion, called chiral ILs (CILs), are of special interest as chirality plays an important role in chemistry. Due to potential additional applications associated with CILs in analytical separation, in chiral discrimination, in asymmetric synthesis, in chiral chromatography, and as chiral solvents; a growing number of CILs have been designed, synthesized and utilized recently.[22,23] For synthesis of CILs, among others, amino acids offer a facile platform as amino acid-based CILs are not only biodegradable but are also biocompatible and less toxic.[22,23] It is proposed that amino acid-based 1,2,3-triazolium CILs may help enhance the greener aspects of these versatile substances.[26]

Application potential of ILs can be significantly enhanced by combining their interesting and useful aspects with surface-active properties. Subsequently, a subclass of ILs, where the anion or the cation of an IL consists of a charged hydrophilic head group and a long chain hydrophobic tail, shows some differences from common ILs and are coined surface-active ILs (SAILs).[27] These ILs possess surface-active properties similar to traditional surfactants and can assemble into various aggregates/

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi – 110016, India. E-mail: shubhapandey@hotmail.com; sipandey@chemistry.iitd.ac.in; pramod@chemistry.iitd.ac.in

† Electronic supplementary information (ESI) available: Spectral characterization data includes ^{1}H NMR, ^{13}C NMR, mass, UV-Vis absorbance and fluorescence emission spectra. See DOI: 10.1039/c4ra05037a

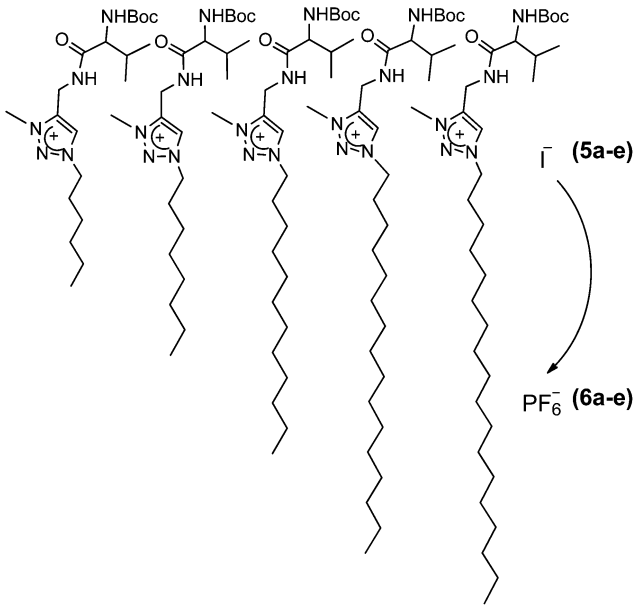


Fig. 1 Structures of the new CILs.

morphologies, such as, micelles, vesicles, bilayers, liquid crystals, *etc.*[28,29] In some instances, the SAILs have exhibited improved surface-active properties as compared to their more traditional counterparts having similar chain lengths.[29] As a result, there is a constant need to develop newer SAILs with better properties.

Among all classes of ILs, imidazolium cation containing ILs have dominated the field due to their high conductivity, low viscosity and wide liquid range deemed important for various applications.[21,30,31] Despite their wide applications, these ILs have some clear limitations. Apart from the minor toxicity issues,[26] 1,3-dialkylimidazolium salts undergo deprotonation at carbon-2 under strong basic conditions. 1,2,3-Triazolium-based compounds, in this regard, may turn out to be advantageous as they may not have hydrogen with such high acidity attached to ring-carbon flanked by two nitrogen atoms.[21,30a] Further, 1,2,3-triazoliumm-based compounds are highly desired as energy-rich materials and are alternative to many conventional materials used in explosive and propellant industry as molecular nitrogen is the primary decomposition product of 1,2,3-triazole ring rendering them as environmentally-acceptable alterantives.[31] In this paper, we report a class of new CILs synthesized starting from L-valine, an α-amino acid (Fig. 1). These CILs possess alkyl chains of variable length that may impart surface-active properties to these ILs, connected through 1,2,3-triazolium moiety. We have investigated thermal and optical properties of these new CILs. We also report the aggregation behavior of these CILs. These new long chain containing CILs may show extended applications in separation and chromatography as well as in colloid chemistry.

Results and discussion

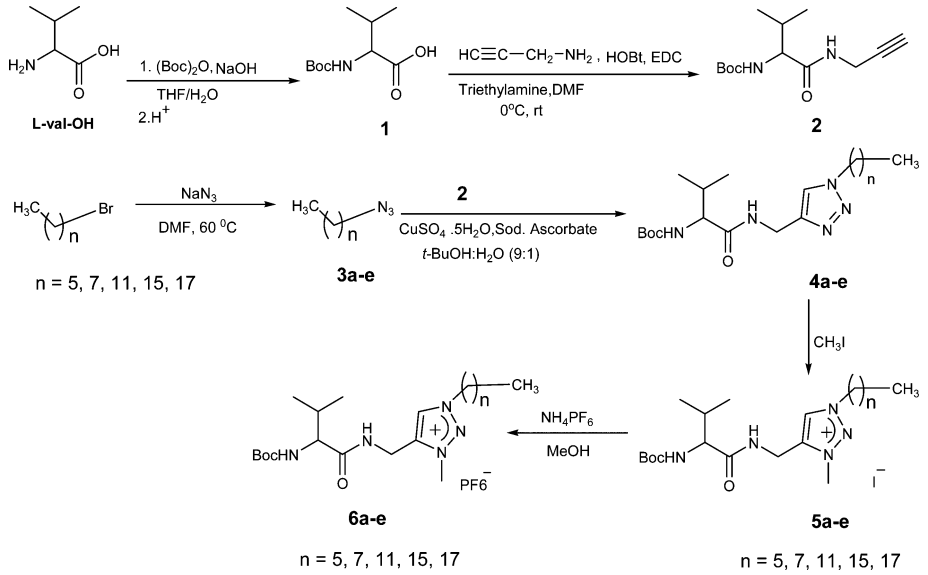
Synthesis and characterization of novel CILs

Starting materials, **1** [*N*-(*tert*-butoxycarbonyl)-L-valine] and **2** [*N*-(*tert*-butoxycarbonyl)-L-valine *N*′-propargylamide] were synthesized from L-valine amino acid according to reported literature procedures (Scheme 1).[32,33] Alkylazides of hexyl, octyl, dodecyl, cetyl and octadecyl (**3a–e**), respectively, were synthesized from stirring their bromides with sodium azide in DMF at 60 °C.[34] Click reaction[35] of compound **2** with various azides (**3a–e**) in equimolar amounts resulted in their 1,2,3-triazole derivatives (Boc-val-alkyl-Tr): *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-hexyl-1,2,3-triazole (**4a**), *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-octyl-1,2,3-triazole (**4b**), *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-dodecyl-1,2,3-triazole (**4c**), *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-cetyl-1,2,3-triazole (**4d**) and *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-octadecyl-1,2,3-triazole (**4e**) in good yields (Scheme 1). Methylation of Boc-val-alkyl-Tr compounds (**4a–e**) with methyl iodide resulted in triazolium-based chiral ionic liquids (CILs) (Boc-val-[C_n-Tr][I], **5a–e**) in nearly quantitative yields and high purity.[36] To understand the effect of anion on the properties of CILs, anion exchange reactions using ammonium hexafluorophosphate on compounds **5a to 5e** were performed to achieve desired CILs with hexafluorophosphate anion (Boc-val-[C_n-Tr][PF_6], **6a–6e**).[37] As the PF_6 anion based ILs can hydrolyze and form HF over the time,[38] we have used freshly prepared **6a–6e** in all subsequent work reported in this paper. All synthesized CILs (**5a–e** and **6a–e**) are yellowish-orange, highly viscous liquids at room temperature except dodecyl CILs (**5c** and **6c**) that are light yellow in color. The fact that all the ILs synthesized are chiral in nature is confirmed by measuring their optical rotation (see Experimental section). They all show appreciable optical rotation in accordance with the values reported for L-valine and related compounds in the literature (*vide infra*).[33a]

The structures of the synthesized CILs (Boc-val-[C_n-Tr][X]) as well as azides (**3a–e**) and triazoles (**4a–e**) were established by the analysis of their ^{1}H and ^{13}C NMR spectra, and IR and mass spectra (Fig. S1 to S45, ESI†). For example, in the IR spectrum of **4d** the formation of 1,2,3-triazole ring was confirmed by appearance of characteristic peaks of –N=N– and –C=C– at 1526 cm^{-1} and 1468 cm^{-1}, respectively, as well as disappearance of alkyne peak of **2** at 2117 cm^{-1} and azide peak of **3d** at 2092 cm^{-1} (please refer to ESI†). The formation of 1,2,3-triazole ring was further confirmed by appearance of a new peak of triazole ring proton at 7.47 ppm in ^{1}H NMR spectrum and two peaks at 139 and 144 ppm in ^{13}C NMR spectrum of **4d**. As soon as **3d** was converted to its 1,2,3-triazole derivative, the peak at 2.21 ppm which corresponded to the alkyne proton in the ^{1}H NMR spectrum of **3d**, completely disappeared from ^{1}H NMR of **4d**. When **4d** was converted to its triazolium derivative **5d**, a distinct downfield shift in the triazole ring proton from 7.47 ppm to 8.85 ppm was observed along with the appearance of a new peak of methyl proton ($–N^+–CH_3$) at 4.28 ppm as singlet indicating the methylation of 1,2,3-triazole ring (Fig. 2). Further, anion exchange of **5d** with hexafluorophosphate caused 1,2,3-triazolium ring proton to again shift upfield from 8.85 to 8.57 ppm in the ^{1}H NMR spectrum of **6d** (Fig. 2).

Thermal properties of CILs

One of the most crucial aspects of an IL is its thermal stability. Thermal stabilities of the ten newly synthesized CILs (**5a–e** and



Scheme 1 Details of the synthesis of triazolium-based CILs.

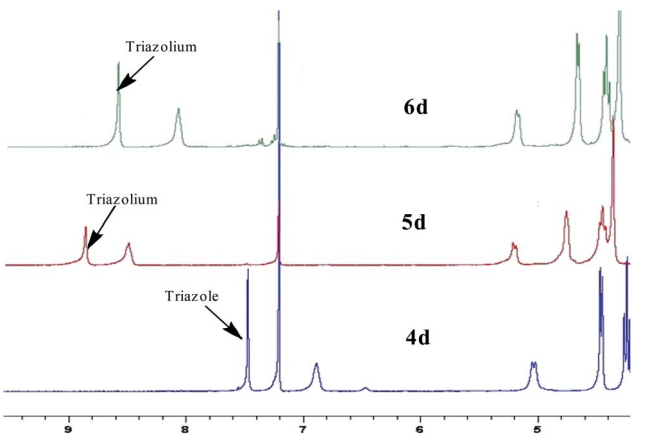


Fig. 2 Partial ^{1}H NMR spectra of compounds **4d**, **5d** and **6d** showing shifting in triazole and triazolium group protons.

Table 1 Thermal properties of Boc-val-[C_n-Tr][X] CILs determined from TGA and DSC analysis

CIL	$T_{dcp}{}^a$/°C	$T_{dcp}{}^b$/°C	T_m/°C
Boc-val-[C_6-Tr][I]	93	132	−9
Boc-val-[C_6-Tr][PF_6]	90	142	−5
Boc-val-[C_8-Tr][I]	91	157	−7
Boc-val-[C_8-Tr][PF_6]	80	120	−6
Boc-val-[C_{12}-Tr][I]	93	130	+7
Boc-val-[C_{12}-Tr][PF_6]	102	129	−9
Boc-val-[C_{16}-Tr][I]	110	180	−6
Boc-val-[C_{16}-Tr][PF_6]	210	226	+18
Boc-val-[C_{18}-Tr][I]	90	164	−5
Boc-val-[C_{18}-Tr][PF_6]	110	213	−10

[a] T_{dcp} is the temperature obtained from the TGA traces at which 10% total weight loss had occurred. [b] Is the temperature obtained from TGA at which 19% total weight loss, corresponding to the loss of BOC protecting group, had occurred.

6a–e) are investigated using thermogravimetric analysis (TGA). The thermal decomposition temperature (T_{dcp}) for each CIL is obtained at the onset of the decomposition defined by 10% weight loss. The T_{dcp} thus obtained are reported in Table 1. A careful examination of the data reveals that among all CILs, interestingly, the two cetyl chain containing CILs exhibit better thermal stability (Fig. 3). Further, Boc-val-[C_{16}-Tr][PF_6] not only shows highest thermal stability among all ten CILs (T_{dcp} nearing 210 °C) but it also shows well-behaved mass loss profile occurring in a single step. Further, except for cetyl CILs, the thermal stabilities of the other CILs appear to be not too affected by the identity of the anion – T_{dcp} of Boc-val-[C_{16}-Tr][PF_6] is almost double that of Boc-val-[C_{16}-Tr][I]. Thermal stabilities of higher chain length (octadecyl) as well as lower chain length (hexyl, octyl, and dodecyl) containing CILs are clearly not as good as that of Boc-val-[C_{16}-Tr][PF_6]. It is generally observed that ILs with bulkier anions (BF_4, PF_6, TF_2N) show higher thermal stability than ILs with iodide and TFO^- anions.[36,39] Considering the fact that BOC is a good leaving group, T_{dcp} is also estimated at 19% mass loss which corresponds to the loss of the protective BOC group (Table 1). It is interesting to note that our CILs when functionalized with free amine show considerably improved thermal stabilities as compared to the BOC-protected CILs.[40] The thermal stabilities of the free amine functionalized CILs may be considered significant.

Different scanning calorimetry (DSC) is perhaps the most appropriate and used technique to obtain quantitative information regarding important phase transitions, such as, glass transition, melting/freezing, crystallization/recrystallization, *etc.* The DSC traces of the ten CILs, in general, do not show any glass transition within the temperature range of investigation (−80–150 °C). In order to find whether our CILs can be classified as RTILs as opposed to just ILs, we estimated the

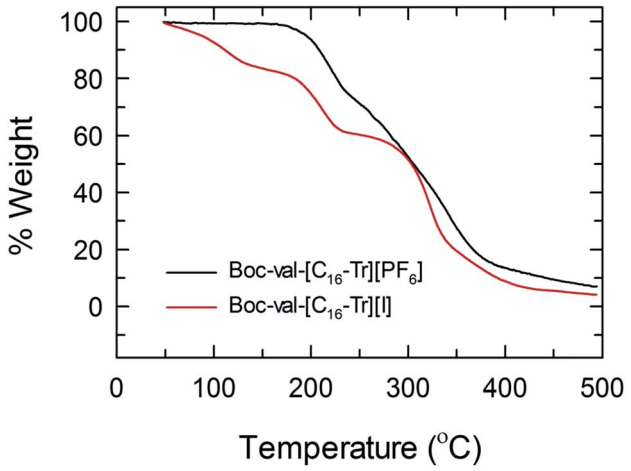


Fig. 3 TGA profile of Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6] under nitrogen at a scanning speed of 10 °C min^{-1}.

melting points (T_m) of the ten Boc-val-[C_n-Tr][X] CILs using DSC. The T_m values are summarized in Table 1. A careful examination of the T_m of all ten CILs reveals them all to be RTILs as all the CILs have melting points below ambient temperature of 25 °C. The CIL Boc-val-[C_{16}-Tr][PF_6], which is the most stable thermally, is observed to have the highest T_m. Except for Boc-val-[C_{16}-Tr][PF_6] (T_m = +18 °C) and Boc-val-[C_{12}-Tr][I] (T_m = +7 °C), all other CILs have fairly similar T_m values that vary from −10 °C to −5 °C. This is surprising as it is usually conceived that more energy is required to overcome increased van der Waals interactions as the mass and chain length of the compound is increased.[31] We believe the complexity of the interactions present in our CILs translates into observation of no clear-cut trend in the melting point of our CILs as the appended chain length is increased. The extent of coiling of alkyl chain may contribute to the observed melting behavior. The similar melting points may imply the L-valine along with the 1,2,3-triazolium functionalities to control the interactions within the CILs as opposed to the alkyl carbon chains as far as phase transition involving melting is concerned. The inherent complexity of the interactions presents in our CIL system on molecular level is revealed nonetheless.

Self-aggregation of CILs

Many such long alkyl chain appended ILs have gained additional popularity due to their surface active properties. As mentioned earlier, the SAILs show conventional surfactant like behavior.[27,28] However, selected properties of some of the SAILs are found to be superior to the conventional surfactants.[29] Many such SAILs are known to form various self-aggregated assemblies, such as, normal micelles, reverse micelles, bilayers, microemulsions, *etc.*[28] Effective coupling of conventional advantages of RTILs with their surface-active capabilities enhances the overall applications of such SAILs. In order to explore whether our CILs self-aggregate at ambient conditions and what are the roles of the alkyl chain length as well as the counter ion (*i.e.*, the anion of the CIL), we chose a short alkyl chain containing CIL, Boc-val-[C_8-Tr][I], and two long alkyl chain appended CILs, Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6]. Due to the fact that our CILs are only sparingly soluble in water, we investigated their self-aggregation behavior, if any, when dissolved in ethanol. Self-aggregation of surfactants in non-aqueous media is a topic of active research as water is not always the media of interest in several applications.[41] We investigated concentration-dependent behavior of the three aforementioned CILs dissolved in ethanol at ambient conditions using fluorescence response of pyrene, a well-known fluorescence solvatochromic probe.

Molecular fluorescence from an appropriate fluorophore is well-suited to furnish information regarding self-aggregation of long-chain molecules owing to the higher sensitivity and orthogonality of information inherent to fluorescence techniques.[42] Pyrene is one of the most widely used neutral fluorescence probes for polarity studies.[43–45] The pyrene solvent polarity scale (Py I_1/I_3) is defined by its I_1/I_3 emission intensity ratio, where I_1 is the intensity of the solvent-sensitive band arising from the $S_1(v = 0) \rightarrow S_0(v = 0)$ transition and I_3 corresponds to the solvent-insensitive $S_1(v = 0) \rightarrow S_0(v = 1)$ transition. The I_1/I_3 ratio increases with increasing solvent dipolarity and is a function of both the solvent dielectric (ε) and the refractive index (n) *via* the dielectric cross term, $f(\varepsilon, n^2)$. In ethanol, in the absence of any self-assembling moieties, the Py I_1/I_3 is fairly high due to the high polarity of ethanol. As self-assembling molecules are added to ethanol the I_1/I_3 starts to decrease rapidly till the critical aggregation concentration (cac) is reached after which the decrease in I_1/I_3 is not so rapid anymore Fig. 4. Once the aggregates are formed, non-polar pyrene partitions into the aggregates resulting in gradual decrease in I_1/I_3. The inflection point is considered to be the cac. Pyrene I_1/I_3 as a function of CIL concentration is presented in Fig. 5. While pyrene I_1/I_3 in the higher concentration regime do not show any inflection point for Boc-val-[C_8-Tr][I], the short alkyl chain CIL; for Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6], the inflection points are clearly present. From the inflection points, the cac for Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6] are estimated to be 12.5(±1.5) mM and 8.7(±1.2) mM, respectively. It is clear that these CILs self-aggregate at fairly low cac values in ethanol. The lower cac for Boc-val-[C_{16}-Tr][PF_6] as compared to that for Boc-val-[C_{16}-Tr][I] implies more efficient and favorable aggregation for the cetyl chain appended compounds when $[PF_6]^-$ as opposed to $[I]^-$ is the counter ion. These cac values are similar to those reported for similar alkyl chain containing conventional cationic surfactants dissolved in ethanol.[41e,f] It is clear that while the short alkyl chain appended CIL does not self-aggregate within ethanol at higher concentrations, the long alkyl chain containing CILs do, and thus, can effectively be called SAILs.

Interestingly, a careful examination of the data presented in Fig. 5 reveals presence of inflection points for all three CILs at much lower concentrations as well. The conventional cationic surfactants of similar chain lengths are not known to self-aggregate in nonaqueous media at such low concentrations.[41] In general, amphiphilic molecules are known to form aggregates above a well-defined critical aggregation concentration

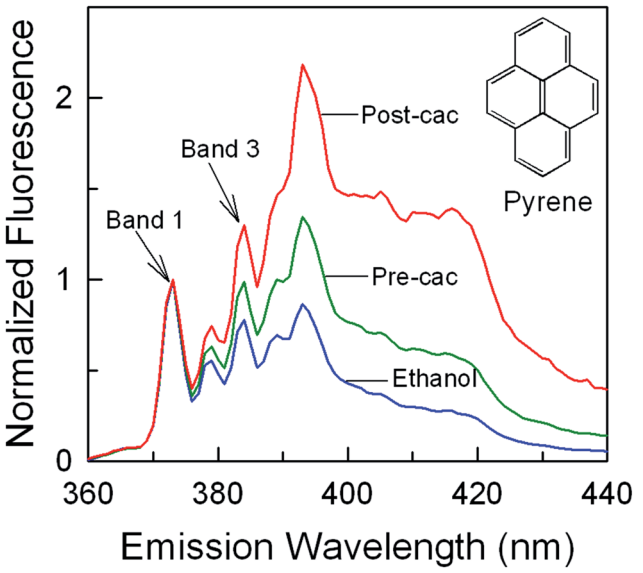


Fig. 4 Normalized fluorescence spectra of pyrene (10 μM) dissolved in Boc-val-[C_{16}][PF_6] solution in ethanol at ambient conditions. $\lambda_{ex} = 337$ nm, slits = 1/1, spectrum in ethanol is in the absence of Boc-val-[C_{16}][PF_6], pre-cac is 4.0 mM Boc-val-[C_{16}][PF_6], and post-cac is 9.4 mM Boc-val-[C_{16}][PF_6].

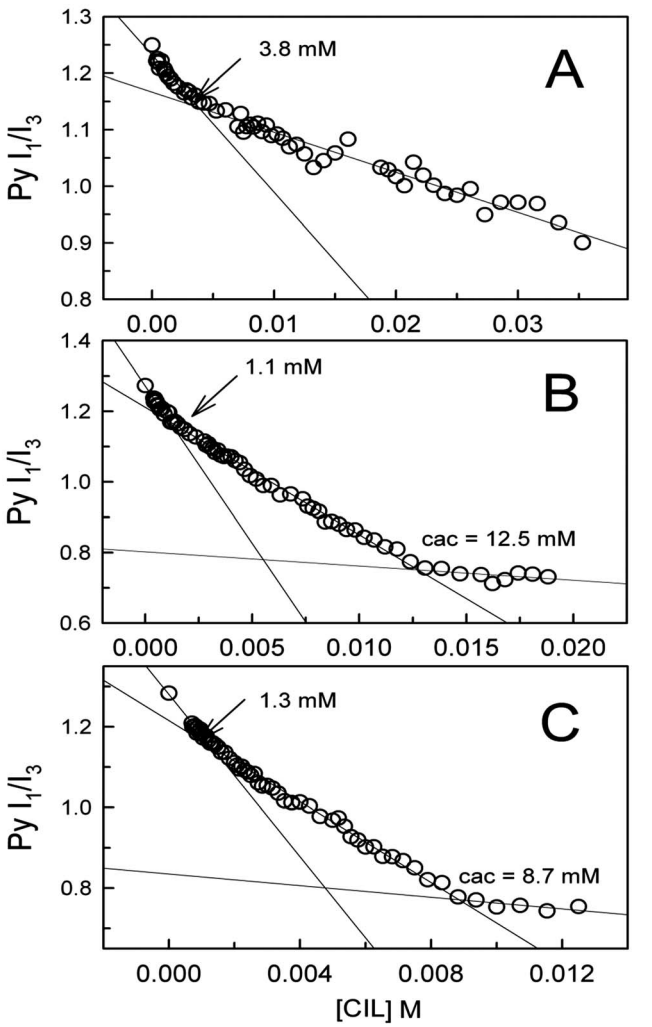


Fig. 5 Pyrene (10 μM) band 1-to-band-3 emission intensity ratio (Py I_1/I_3) within CILs dissolved in ethanol at ambient conditions: Boc-val-[C_8-Tr][I] (panel A); Boc-val-[C_{16}-Tr][I] (panel B); Boc-val-[C_{16}-Tr][PF_6] (panel C).

(cac). However, during the years, there have been several experimental indications, as well as theoretical ones, for the appearance of aggregates at concentrations well below the cac – a phenomenon referred to as premicellar aggregation. Presence of premicellar aggregates has been confirmed, in particular, by fluorescence correlation spectroscopy (FCS) experiment, which appears to have afforded direct observation of premicellar aggregates at concentrations four times lower than the macroscopically determined cac.[46] Such premicellar aggregates are considered metastable and are rather short-lived. There is ample evidence of the presence of premicellar aggregates in several cases in current literature.[46] It appears our CILs, including the short chain containing Boc-val-[C_8-Tr][I] which does not show cac, form premicellar aggregates as evident by the inflection in the pyrene I_1/I_3 at much lower concentrations (Fig. 5A). For, Boc-val-[C_8-Tr][I], Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6], the concentrations for the onset of the premicellar aggregation is estimated to be 3.8(±0.5) mM, 1.1(±0.3) mM, and 1.3(±0.3) mM, respectively. While these concentrations are similar for the cetyl containing CILs, it is relatively higher for the short octyl chain containing CIL. The presence of L-valine functionality may tentatively be proposed to be the reason for the formation of premicellar aggregates in ethanol by our CILs.

UV-Vis absorbance and fluorescence of CILs

Unwanted absorbance and, in some cases, subsequent undesired emission of radiation are associated to certain class of ILs in the current literature.[47] The inherent ability of an IL to absorb and/or emit UV-Vis radiation mostly hampers its application potential. We measured UV-Vis absorbance spectra of Boc-val-[C_8-Tr][I], Boc-val-[C_8-Tr][PF_6], Boc-val-[C_{16}-Tr][I], and Boc-val-[C_{16}-Tr][PF_6] dissolved in two different solvents – ethanol (polar-protic) and chloroform (chlorinated relatively nonpolar) – representing two major classes of solvents. The UV-Vis absorbance spectra of aforementioned CILs are presented in Fig. S46 and S47† and a representative spectrum for Boc-val-[C_{16}-Tr][PF_6] dissolved in ethanol is depicted in Fig. 6. It is clear from the absorbance spectra that CILs weakly absorb UV-Vis radiation and exhibit two bands as shown by all four CILs irrespective of the solvent. The higher energy band maxima appears in the range 282–292 nm, whereas the lower energy band maxima appears in the vicinity of 360(±4) nm. The band at lower energy can be tentatively assigned to the Boc-NH- and/or L-val functionalities, while the 1,2,3-triazolium moiety can be held responsible for the higher energy absorbance feature. These absorbance spectral features are in good agreement with those reported in the literature for cationic triazolium macrocycles.[48] Due to the nature of the functionalities involved, the associated molar absorptivities of our CILs are not too high. The low molar absorptivities of our CILs are advantageous as lower UV cut-offs of solvent media are preferred in most chemical analyses.

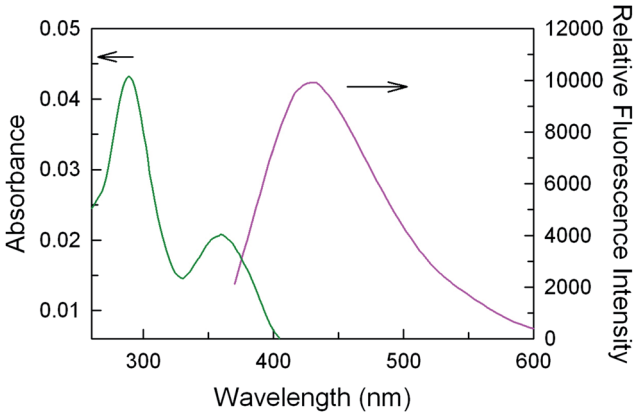


Fig. 6 UV-Vis absorbance (green, 100 μM) and fluorescence emission spectra (pink, 25 μM) of Boc-val-[C_{16}-Tr][PF_6] dissolved in ethanol at ambient conditions [slits: 3/3, $\lambda_{ex} = 360$ nm].

We also collected the fluorescence emission spectra of CILs Boc-val-[C_8-Tr][I], Boc-val-[C_8-Tr][PF_6], Boc-val-[C_{16}-Tr][I] and Boc-val-[C_{16}-Tr][PF_6] dissolved in ethanol and chloroform, respectively. As in case of UV-Vis absorbance, the fluorescence emission characteristics of the CILs are found to be independent of the nature of the solvent. The fluorescence emission spectrum of Boc-val-[C_{16}-Tr][PF_6] dissolved in ethanol is included in Fig. 6 (the emission spectra of all four CILs are presented in Fig. S48†). Most importantly, the emission signal from the CILs are found to be very weak implying them to possess very low fluorescence quantum yields. This is again advantageous and preferred of a medium as low fluorescence background renders a solvent useful in chemical applications where various optical spectroscopic techniques are to be employed. Weak UV-Vis radiation absorbing and emitting ability makes our CILs useful solvents in chemical analyses where low background signals are desired.

Conclusions

We have successfully synthesized a series of new L-valine based chiral alkylated-1,2,3-triazolium ILs consisting of two different anions (iodide and hexafluorophosphate). These long chain triazolium-based CILs show adequate thermal stability and they are all in liquid state at room temperature hence can be classified as RTILs. Due to the presence of long alkyl chains, they easily self-aggregate and show surface-active behavior and can thus be assigned to the SAIL family. They absorb and emit UV-Vis radiation very weakly and hence are desirable as solvents in photochemical applications. This new class of CILs with several interesting and useful properties is bound to find use in various applications in chemistry.

Experimental section

Materials and methods

Starting materials, amino acid L-valine, Boc-anhydride, 1-hydroxylbenzotriazole (HOBt), sodium azide, propargylamine, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), triethylamine, and alkyl bromides (hexyl, octyl, dodecyl, cetyl and octadecyl) were purchased from Aldrich Chemical Company. Fluorescence probe pyrene (Py) was purchased from Sigma-Aldrich in the highest purity possible. ACS spectrophotometric grade chloroform (≥99.8%) was purchased from Sigma-Aldrich. Ethanol (99.9%) was obtained from Merck Ltd. All other reagents used in the study were purchased from Sigma-Aldrich or Merck and were chemically pure. All chemicals were obtained in the highest purity grade possible and were used as received unless otherwise stated. All synthesized compounds were dried under high vacuum at 60 °C for 48 hours to remove water.

The solvents used were dried and distilled. HPLC grade solvents were used for fluorescence spectroscopy and UV-Vis spectroscopic studies. Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. The eluting solvent indicated in parentheses for each purification was determined by TLC that was performed on pre-coated silica gel on aluminum sheets (kieselgel 60, F254, Merck). TLC plates were visualized in an iodine chamber. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker DPX 300 instrument at room temperature using tetramethylsilane (TMS) at 0.00 as an internal standard. Mass spectra were acquired on a triple-quadrupole Finnigan TSQ7000 mass spectrometer equipped with electrospray ionization (ESI) in both positive and negative ion modes. The Infrared spectra were recorded on a Agilent Technology Cary 600 series FTIR Spectrometer and band positions were given in reciprocal centimeters (cm^{-1}). Decomposition temperature was measured using model TGA Q50 from TA Instruments, Inc. at a ramp rate of 10 °C min^{-1}. Melting points were measured with model DSC Q200 instrument purchased from TA Instruments. Optical rotation (α) were measured on Rudolph Research Polarimeter Model Autopol-V Analytical at 25 °C with concentration (g per 100 cm^3 of $CHCl_3$). A UV-Vis double beam spectrophotometer (model UV-2450, Shimadzu) with variable band width was used for acquisition of the UV-Vis absorbance spectra. Fluorescence spectra were acquired on a model FL 3-11 Fluorolog-3 modular spectrofluorometer (Horiba-Jobin Yvon, Inc.) with single Czerny-Turner grating excitation and emission monochromators as wavelength selection devices, a 450 W Xe-arc lamp as the excitation source, and a PMT as the detector. Fluorescence spectra of the probes pyrene (Py) were collected with the following excitation/emission slit widths (in nm): Py: 1/1 excited at 337 nm and CILs: 3/3 excited at 360 nm. All reported spectroscopic values were averages based on performing triplicate measurements on independently prepared samples. The spectral responses from appropriate blanks were subtracted before data analysis in each case. All absorbance and fluorescence data were acquired using 10.0 mm pathlength quartz cuvettes. All data analysis was performed using SigmaPlot v12.0 software.

Requisite amounts of materials were weighed on a Mettler-Toledo AB104-S balance with a precision of ±0.1 mg. Stock solution of pyrene and CILs were prepared in ethanol and stored in pre-cleaned amber glass vial at 4 ± 1 °C. To acquire the fluorescence emission spectra of pyrene in CILs dissolved in ethanol, appropriate aliquot of the probe was taken from the

stock and ethanol was added to achieve the desired final concentration. These solutions contained 10 μM pyrene such that the pyrene concentration remained constant during the titrations. Solutions of different CILs were prepared separately in chloroform and ethanol. Solutions thus prepared were subjected to fluorescence and UV-Vis absorbance spectroscopic acquisitions.

Synthesis of various compounds

Boc-L-val-OH (1). A solution of L-valine (2.34 g, 20 mmol) in a mixture of THF (30 mL), water (15 mL) and 1 M NaOH (20 mL) was stirred and cooled in an ice bath. Afterwards di-*tert*-butyl-pyrocarbonate (4.8 g, 22 mmol) was added and reaction mixture was further stirred for 12 h at room temperature. It was then acidified with 1 M HCl and extracted with ethyl acetate (3 × 100 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to give a gummy mass, yield 95%, ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.92–0.89 (m, 6H, CH(CH_3)$_2$), 1.44 (s, 9H, (CH_3)$_3$), 2.07–2.10 (m, 1H, β-C*H*), 4.19–4.23 (m, 1H, α-C*H*), 8.10 (br s, 1H, N*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 17.42, 18.99, 28.27, 31.01, 58.39, 80.00, 155.85, 176.63.

Boc-L-valine-propargylamide (2). Boc-L-val-OH (**1**) (1.086 g, 5 mmol) was dissolved in CH_2Cl_2 (10 mL). To this solution, 1-hydroxy benzotriazole (HOBt) (743 mg, 5.5 mmol, 1.1 equiv.), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (1.054 g, 5.5 mmol, 1.1 equiv.) was added and the resulting mixture was stirred at 0 °C for 20 minutes. Propargylamine (0.352 mL, 5.5 mmol) and triethylamine (1.53 mL, 11 mmol, and 2.5 equiv.) were subsequently added. The reaction mixture was allowed to stir overnight at 25 °C. Reaction mixture was extracted with ethyl acetate and subsequently washed with 5% cold HCl, saturated aq. $NaHCO_3$, water and brine. The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography. Solid, yield 90%, $[\alpha]_D^{20}$ −13.3 (c 1.0, $CHCl_3$), (lit[33a] $[\alpha]_D^{22}$ −11.4 (c 1.5, $CHCl_3$)), ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.91–0.97 (m, 6H, CH(CH_3)$_2$), 1.44 (s, 9H, (CH_3)$_3$), 2.09 (m, 1H, β-C*H*), 2.19 (t, J = 2.4 Hz, 1H, *H*C≡), 3.96–4.12 (m, 3H, CH_2, α-C*H*), 5.28 (d, 1H, J = 9 Hz, N*H*CH), 6.90 (br, s, 1H, N*H*CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 18.0, 18.9, 28.1, 28.6, 29.1, 29.4, 31.1, 59.5, 71.1, 79.5, 79.8, 155.8, 171.1; HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{22}N_2O_3$ (M + Na)$^+$ 277.1528, found 277.1528.

General synthetic procedure for alkylazides (3a–e). To a solution of alkyl bromides in DMF, solid NaN_3 was added. The solution was stirred at room temperature for overnight before it was quenched with excess amount of water. It was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the colorless liquid.

Hexyl azide (3a). Colorless liquid, yield 87%, IR (ATR, ν^{max}/cm^{-1}); 2959, 2931, 2098, 1464, 1253, 720; ^{1}H NMR (300 MHz; $CDCl_3$, δ in ppm); 0.83 (t, J = 6.6 Hz, 3H), 1.16–1.35 (m, 6H), 1.47–1.57 (m, 2H), 3.17 (t, J = 6.9 Hz, 2H).

Octyl azide (3b). Colorless liquid, yield 92%, IR (ATR, ν^{max}/cm^{-1}); 2925, 2856, 2090, 1464, 1258, 723; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.87–0.89 (m, 3H), 1.29 (br, s, 10H), 1.48–1.62 (m, 2H), 3.25 (t, J = 6.9 Hz, 2H).

Dodecyl azide (3c). Colorless liquid, yield 89%, IR (ATR, ν^{max}/cm^{-1}); 2921, 2852, 2092, 1465, 1257, 721; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.85–0.88 (m, 3H), 1.29 (br, s, 18H), 1.58 (t, J = 6.9 Hz, 2H), 3.23 (t, J = 6.9 Hz, 2H).

Cetyl azide (3d). Colorless liquid, yield 90%, IR (ATR, ν^{max}/cm^{-1}); 2921, 2852, 2092, 1465, 1257, 721; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.88 (t, J = 6.9 Hz, 3H), 1.06–1.26 (m, 26H), 1.45–1.61 (m, 2H), 3.24 (t, J = 7.2 Hz, 2H).

Octadecyl azide (3e). Colorless liquid, yield 89%, IR (ATR, ν^{max}/cm^{-1}); 2921, 2852, 2092, 1465, 1257, 894, 721; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.88–0.90 (m, 2H), 1.28–1.37 (s, 30H), 1.59–1.64 (m, 2H), 3.27 (t, J = 6.9 Hz, 1H).

General procedure for synthesis of *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-alkyl-1,2,3-triazole (Boc-val-C$_n$-Tr) (4a–e). To a solution of corresponding azides (**3a–e**, 1 mmol) and compound 2 (1 mmol) in *t*-BuOH–H_2O (9 : 1), sodium ascorbate (40 mg, 20 mol%), $CuSO_4$ (24 mg, 10 mol%) were added. The solution was stirred at 60 °C for 24 h. The solution was evaporated under reduced pressure. The residue was washed with ethyl acetate to remove the starting material. The combined organic layers were washed with brine (25 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica-gel (ethyl acetae/hexane) to give respective compounds (**4a–e**).

***N*-(*tert*-Butoxycarbonyl)-L-valinyl-4-aminomethyl-1-hexyl-1,2,3-triazole (Boc-val-C$_6$-Tr) (4a).** Off-white solid, yield 82%, mp 68 °C, IR (KBr, ν^{max}/cm^{-1}); 3443, 3337, 2959, 2931, 1682, 1649, 1523, 1465, 1368, 1248; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 0.77–0.83 (m, 9H, CH(CH_3)$_2$, CH_3 (hex)), 1.18–1.22 (m, 6H, CH_2), 1.33 (s, 9H, (CH_3)$_3$), 1.79 (m, 2H, CH_2), 2.02–2.13 (m, 1H, β-C*H*), 3.95 (br, s, 1H, α-C*H*), 4.23 (t, J = 6.9 Hz, 2H, CH_2) 4.43 (s, 2H, CH_2), 5.40 (d, J = 7.2 Hz, 1H, N*H*CH), 7.55 (s, 1H, N*H*CH_2), 7.70 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz; $CDCl_3$, δ in ppm); 13.4, 17.2, 18.8, 21.9, 25.6, 27.8, 29.2, 29.7, 30.6, 30.6, 34.3, 49.9, 59.3, 79.3, 155.4, 171.6; HRMS (ESI) *m*/*z*: calcd for $C_{19}H_{35}N_5O_3$ [M + Na]$^+$ 404.2632, found 404.2640.

***N*-(*tert*-Butoxycarbonyl)-L-valinyl-4-aminomethyl-1-octyl-1,2,3-triazole (Boc-val-C$_8$-Tr) (4b).** Pale yellow solid, yield 89%, mp 84 °C, IR (KBr, ν^{max}/cm^{-1}); 3350, 2956, 2925, 1679, 1656, 1523, 1466, 1370, 1303, 1246; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.70–0.98 (m, 6H, CH(CH_3)$_2$), 1.01–1.34 (m, 10H, CH_2), 1.43 (s, 9H, (CH_3)$_3$), 1.78–1.97 (m, 2H, CH_2), 2.00–2.83 (m, 1H, β-C*H*), 3.88–3.97 (m, 1H, α-C*H*), 4.03–4.26 (m, 2H, CH_2), 4.44–4.94 (m, 2H, CH_2), 5.06 (d, 1H, N*H*CH), 6.99 (br, s, 1H, N*H*CH_2), 7.48 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.8, 17.5, 19.0, 22.3, 26.2, 28.1, 28.7, 28.8, 29.1, 29.4, 30.0, 31.0 31.4, 31.6, 34.5, 50.1, 59.5, 79.3, 122.2, 155.7, 172.0; HRMS (ESI) *m*/*z*: calcd for $C_{21}H_{39}N_5O_3$ [M + Na]$^+$ 432.2945, found 432.2945.

***N*-(*tert*-Butoxycarbonyl)-L-valinyl-4-aminomethy-1-dodecyl-1,2,3-triazole (Boc-val-C$_{12}$-Tr) (4c).** Pale yellow solid, yield 88%, mp 87–89 °C, IR (KBr, ν^{max}/cm^{-1}); 3364, 2956, 2918, 2850, 1679, 1658, 1448, 1371, 1300; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.85–0.876 (m, 9H, CH(CH_3)$_2$, CH_3 (dodecyl)), 1.25–1.34 (m, 18H, CH_2), 1.43 (s, 9H, (CH_3)$_3$), 1.84–1.86 (m, 2H, CH_2), 2.07–2.10 (m, 1H, β-C*H*), 4.03 (d, J = 6 Hz, 1H, α-CH), 4.30 (t, J = 6 Hz,

2H, CH_2), 4.51 (d, J = 3 Hz, 2H, CH_2), 5.52 (d, J = 9 Hz, 2H, NHCH), 7.62 (d, J = 6 Hz, 1H, NHCH_2), 7.86 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.8, 17.5, 19.0, 22.4, 26.2, 28.7, 29.0, 29.1, 29.2, 29.3, 30.0, 31.0, 31.6, 34.5, 50.0, 59.5, 79.2, 122.2, 144.6, 155.7, 172.0; HRMS (ESI) calcd for $C_{25}H_{47}N_5O_3$ [M + Na]$^+$ 488.3571, found 488.3571.

***N*-(*tert*-Butoxycarbonyl)-L-valinyl-4-aminomethyl-1-cetyl-1,2,3-triazole (Boc-L-val-C$_{16}$-Tr) (4d).** Orange solid, yield 85%, mp 78 °C, IR (KBr, ν^{max}/cm^{-1}); 3343, 3295, 2920, 2957, 2849, 1688, 1651, 1526, 1468, 1301, 1247; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.77–0.80 (m, 9H, CH(CH_3)$_2$, CH_3 (cetyl)), 1.18 (m, 26H, CH_2), 1.33 (s, 9H, (CH_3)$_3$), 1.79–1.97 (m, 2H, CH_2), 2.05–2.11 (m, 1H β-CH), 3.88 (br, s, 1H, α-CH), 4.24 (t, J = 6 Hz, 2H, CH_2), 4.45 (d, J = 6 Hz, 2H, CH_2), 5.03 (m, 1H, NHCH), 6.88 (s, 1H, NHCH_2), 7.47 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.9, 17.5, 19.0, 22.4, 26.3, 28.1, 28.8, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 30.0, 31.0, 31.7, 33.6, 34.5, 50.1, 59.6, 79.3, 113.9, 122.2, 139.0, 144.6, 155.7, 172.0; HRMS (ESI) *m*/*z*: calcd for $C_{29}H_{55}N_5O_3$ (M + Na)$^+$ 544.4197, found 544.4210.

***N*-(*tert*-Butoxycarbonyl)-L-valinyl-4-aminomethyl-1-octadecyl-1,2,3-triazole (Boc-val-C$_{18}$-Tr) (4e).** Light yellow solid, yield 86%, mp 86 °C, IR (ν^{max}/cm^{-1}); 3339, 3293, 2956, 2925, 2853, 1689, 1656, 1651, 1526, 1469, 1366, 1247, 1178; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.85–0.97 (m, 9H CH(CH_3)$_2$, CH_3 (octadecyl)), 1.24 (m, 30H, CH_2), 1.42 (s, 9H, (CH_3)$_3$), 1.70 (s, 2H, CH_2), 1.87 (t, J = 6.0 Hz, 1H, β-CH), 3.96 (t, J = 6.0 Hz, 1H, α-CH), 4.27 (m, 2H, CH_2) 4.30 (t, J = 6.0 Hz, 2H, CH_2), 4.52 (d, J = 5.7 Hz, 2H, CH_2), 5.03 (br, s, 1H, NHCH), 6.72 (br, s, 1H, NHCH_2), 7.51 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 14.0, 17.5, 19.2, 22.6, 26.4, 28.2, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 30.2, 31.9, 34.7, 50.3, 59.7, 79.7, 122.1, 144.5, 155.8, 171.8; HRMS (ESI) *m*/*z*: calcd for $C_{31}H_{60}N_5O_3$ (M + H)$^+$ 550.4691, found 550.4704.

General procedure for methylation of *N*-(*tert*-butoxycarbonyl)-L-valinyl-4-aminomethyl-1-alkyl-1,2,3-triazole (5a–e). The solution of Boc-val-alkyl-triazole (**4a–e**) (0.1 mol) and MeI (0.6 mol) was stirred overnight at 80 °C. The reaction mixture was evaporated under reduced pressure. The residue was diluted with $CHCl_3$ and washed with H_2O, dried over Na_2SO_4 and evaporated under reduced pressure to give **5a–e** in quantitative yield.

Boc-val-[C$_6$-Tr][I] (5a). Yellow liquid, $[\alpha]_D^{20}$ + 3.3 (c 0.73 in $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3435, 3258, 2960, 2929, 1667, 1500, 1458, 1365, 754, 640; ^{1}H NMR (300 MHz; $CDCl_3$, δ in ppm); 0.77–0.96 (m, 9H, CH(CH_3)$_2$), CH_3 (hexyl), 1.15–1.27 (m, 6H, CH_2), 1.33 (s, 9H, (CH_3)$_3$), 1.92–1.97 (m, 2H, CH_2), 2.05–2.09 (m, 1H, β-CH), 3.90–3.95 (m, 1H, α-CH), 4.35 (s, 3H, CH_3), 4.44–4.47 (m, 2H, CH_2), 4.73–4.76 (m, 2H, CH_2), 5.18–5.23 (m, 1H, NHCH), 8.52 (br, s, 1H, NHCH_2), 8.87 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz; $CDCl_3$, δ in ppm); 13.3, 17.5, 18.9, 21.7, 25.2, 27.8, 28.7, 29.0, 30.3, 31.9, 39.1, 53.8, 56.4, 59.6, 79.1, 130.0, 141.3, 155.4, 172.7; HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{38}N_5O_3$ 396.2969 [M − I]$^+$, found 396.2969.

Boc-val-[C$_8$-Tr][I] (5b). Yellow liquid, $[\alpha]_D^{20}$ + 2.6 (c 0.53 in $CHCl_3$), IR (ATR, cm^{-1}); 2959, 2927, 2856, 1702, 1668, 1499, 1365, 1162, 729, 641; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.851–0.97 (m, 9H, CH(CH_3)$_2$), CH_3 (octyl), 1.26–1.33 (m, 10H, CH_2), 1.42 (s, 9H, (CH_3)$_3$), 1.98–2.05 (m, 2H, CH_2), 2.13–2.18 (m, 1H, β-CH), 3.99 (t, J = 6.3 Hz, 1H, α-CH), 4.42 (s, 3H, CH_3), 4.51 (t, J = 7.3 Hz, 2H, CH_2), 4.80–4.81 (m, 1H, CH_2), 5.23–5.26 (d, J = 7.2 Hz, 1H, NHCH), 8.53 (br, s, 1H, NHCH_2), 8.92 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.8, 17.7, 19.2, 22.2, 25.8, 28.1, 28.5, 28.6, 29.0, 29.3, 30.6, 31.3, 32.2, 39.3, 54.1, 59.9, 79.5, 130.3, 141.7, 155.7, 173.0; HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{48}N_5O_3$ 424.3282 [M − I]$^+$, found 424.3294.

Boc-val-[C$_{12}$-Tr][I] (5c). Pale yellow liquid, $[\alpha]_D^{20}$ + 2.2 (c 0.56, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3433, 3230, 2893, 2859, 1687, 1478, 1368, 1257, 1165, 743; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.89–0.97 (m, 9H, CH(CH_3)$_2$, CH_3 (dodecyl)), 1.25–1.34 (m, 18H, CH_2), 1.43 (s, 9H, (CH_3)$_3$), 2.04 (s, 2H, CH_2), 2.17 (m, 1H, β-CH), 4.01 (s, 1H, α-CH), 4.45 (s, 3H, CH_3), 4.53 (s, 2H, CH_2), 4.83 (s, 2H, CH_2), 5.29 (br, s, 1H, NHCH), 8.54 (s, 1H, NHCH_2), 8.93 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.9, 17.8, 19.3, 22.4, 25.9, 28.2, 28.6, 28.8, 29.1, 29.3, 30.6, 31.7, 32.3, 39.4, 54.1, 60.0, 79.5, 130.3, 141.8, 155.8, 173.1; HRMS (ESI) *m*/*z*: calcd for $C_{26}H_{50}N_5O_3$ 480.3908 [M − I]$^+$, found 480.3926.

Boc-val-[C$_{16}$-Tr][I] (5d). Yellow liquid, $[\alpha]_D^{20}$ + 2.4 (c 1.0, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3435, 3227, 2923, 2853, 1703, 1668, 1499, 1464, 1365, 1240, 1164, 731; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.78–0.98 (m, 9H, CH(CH_3)$_2$, CH_3 (cetyl)), 1.01–1.29 (m, 26H, CH_2), 1.35 (s, 9H, (CH_3)$_3$), 1.79–1.82 (m, 2H, CH_2), 2.09–2.14 (m, 1H, β-CH), 3.93 (m, 1H, α-CH), 4.44 (s, 3H, CH_3), 4.46 (d, J = 5.4 Hz, 2H, CH_2), 5.20 (m, 1H, NHCH), 8.48 (br, s, 1H, NHCH_2), 8.85 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.6, 17.6, 19.0, 22.2, 25.7, 27.9, 28.4, 28.8, 29.0, 29.1, 29.2, 29.8, 30.4, 31.4, 32.1, 39.1, 53.9, 59.7, 79.2, 130.1, 141.4, 155.5, 172.8; HRMS (ESI) *m*/*z*: calcd for $C_{30}H_{58}N_5O_3$ 536.4534 [M − I]$^+$, found 536.4540.

Boc-val-[C$_{18}$-Tr][I] (5e). Yellow liquid, $[\alpha]_D^{20}$ + 2.5 (c 0.55, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3435, 3232, 2922, 2852, 1703, 1668, 1499, 1464, 1365, 1164, 729; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.86–0.98 (m, 9H, CH(CH_3)$_2$, CH_3 (octadecyl)), 1.25–1.35 (m, 30H, CH_2), 1.43 (s, 9H, (CH_3)$_3$), 1.64–1.99 (m, 2H, CH_2), 2.01–2.22 (m, 1H, β-CH), 4.00 (t, J = 6.4 Hz, 1H, α-CH), 4.43 (s, 3H, CH_3), 4.52 (t, J = 7.2 Hz, 2H, CH_2), 4.82 (d, J = 5.7 Hz, 1H, CH_2), 5.25 (d, J = 7.2 Hz, 1H, NHCH), 8.53 (br, s, 1H, NHCH_2), 8.94 (s, 1H, Tr-CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 14.1, 18.0, 19.4, 22.6, 26.1, 28.3, 28.7, 29.2, 29.3, 29.4, 29.5, 29.6, 30.5, 31.9, 32.4, 39.1, 54.3, 60.5, 79.9, 130.6, 142.5, 156.0, 173.4; HRMS (ESI) *m*/*z*: calcd for $C_{32}H_{62}N_5O_3$ 564.4847 [M − I]$^+$, found 564.4847.

General procedure for synthesis of Boc-val-[C$_n$-Tr][PF$_6$] (6a–e). A solution of triazolium salts (**5a–e**; 100 mg in 5 mL MeOH) was added to saturated methanolic solution of NH_4PF_6 (3 mL) and stirred for 2 h. White precipitate of product obtained was filtered and washed with methanol and then dried under reduced pressure followed by vacuum in desiccators over P_2O_5 and KOH Pellets, yield 85–90%.

Boc-val-[C$_6$-Tr][PF$_6$] (6a). Yellow colored liquid, $[\alpha]_D^{20}$ + 1.48 (c 1.08, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3421, 3298, 2962, 2931, 1671, 1500, 1366, 1162, 840; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.81–0.89 (m, 9H, CH(CH_3)$_2$), CH_3 (hexyl), 1.18–1.26 (m, 15H, (CH_3)$_3$, CH_2), 1.92 (s, 2H, CH_2), 2.06–2.08 (m, 1H, β-CH), 3.92 (t, J = 6 Hz, 1H, α-CH), 4.30 (s, 3H, CH_3), 4.40–4.45 (m, 2H, CH_2), 4.65 (m, 2H, CH_2), 5.19 (m, 1H, NHCH), 8.04 (br, s, 1H, NHCH_2),

8.57 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz; $CDCl_3$ δ in ppm); 13.8, 17.8, 19.3, 22.2, 25.7, 28.2, 29.0, 29.6, 30.5, 30.8, 32.2, 38.6, 54.2, 60.4, 80.0, 130.0, 142.2, 156.1, 173.4; HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{38}N_5O_3$ 396.2969 $(M - PF_6)^+$, found 396.2969.

Boc-val-[C_8-Tr][PF_6] (6b). Yellow color liquid, $[\alpha]_D^{20}$ + 2.0 (c 0.70, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3425, 3237, 2961, 2928, 1671, 1499, 1465, 1366, 1241, 1162, 842; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.79–0.87 (m, 9H, $CH(CH_3)_2$, CH_3 (octyl)), 1.91–1.25 (m, 10H, CH_2), 1.34 (s, 9H, $(CH_3)_3$), 1.91–2.03 (m, 2H, CH_2), 2.05–2.09 (m, 1H, β-C*H*), 3.91 (t, J = 6 Hz, 1H, α-C*H*), 4.32 (s, 3H, CH_3), 4.45 (t, J = 6.9 Hz, 2H, CH_2), 4.64 (d, J = 4.5 Hz, 2H, CH_2), 5.26 (d, J = 6 Hz, 1H, N*H*CH), 8.14 (s, 1H, N*H*CH_2), 8.59 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.9, 17.8, 19.3, 22.4, 26.0, 28.2, 28.6, 28.8, 29.1, 29.5, 30.6, 31.5, 31.8, 32.1, 33.7, 38.8, 54.1, 60.1, 79.8, 129.9, 141.8, 155.9, 173.2; HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{42}N_5O_3$ 424.3282 $(M - PF_6)^+$, found 424.3298.

Boc-val-[C_{12}-Tr][PF_6] (6c). Yellow color liquid, $[\alpha]_D^{20}$ + 1.6 (c 0.93, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3420, 3239, 2966, 2923, 1678, 1490, 1463, 1364, 1240, 1159, 840; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.85–0.96 (m, 9H, $CH(CH_3)_2$, CH_3(dodecyl)), 1.20–1.42 (m, 18H, CH_2), 1.43 (s, 9H, $(CH_3)_3$), 1.99 (t, J = 6.2 Hz, 2H, CH_2), 2.01–2.16 (m, CH, β-C*H*), 3.96 (t, J = 6.9 Hz, 1H, α-C*H*), 4.39 (s, 3H, CH_3), 4.51 (t, J = 7.2 Hz, 2H, CH_2), 4.73 (d, J = 7.2 Hz, 2H, CH_2), 5.32 (d, J = 9 Hz, 1H, N*H*CH), 8.22 (br, s, 1H, N*H*CH_2), 8.67 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.8, 17.7, 19.1, 22.4, 25.8, 28.1, 28.6, 28.9, 29.0, 29.2, 29.3, 30.5, 31.6, 32.0, 38.7, 53.9, 60.0, 79.6, 129.8, 141.7, 155.8, 173.1; HRMS (ESI) *m*/*z*: calcd for $C_{26}H_{50}N_5O_3$ 480.3908 $(M - PF_6)^+$, found 480.3914.

Boc-val-[C_{16}-Tr][PF_6] (6d). Yellow viscous liquid, $[\alpha]_D^{20}$ + 2.05 (c 0.76, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3435, 2922, 2852, 1706, 1677, 1503, 1365, 1169, 838; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.82–0.93 (s, 9H, $CH(CH_3)_2$, CH_3 (cetyl)), 1.13–1.30 (m, 26H, CH_2), 1.39 (s, 9H, $(CH_3)_3$), 1.93–1.97 (m, 2H, CH_2), 2.06–2.17 (m, 1H, β-C*H*), 3.90 (m, 1H, α-C*H*), 4.30 (s, 3H, CH_3), 4.41–4.44 (m, 2H, CH_2), 4.44–4.66 (m, 2H), 5.16–5.18 (m, 1H, N*H*CH), 8.06 (br, s, 1H, N*H*CH_2), 8.57 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 13.9, 17.7, 19.2, 22.4, 25.9, 28.1, 28.6, 29.0, 29.1, 29.3, 29.4, 29.5, 30.5, 31.7, 32.0, 38.6, 54.0, 60.1, 79.7, 129.8, 141.9, 155.8, 173.1; HRMS (ESI) *m*/*z*: calcd for $C_{30}H_{58}N_5O_3$ 536.4534 $(M - PF_6)^+$, found 536.4534.

Boc-val-[C_{18}-Tr][PF_6] (6e). Yellow viscous liquid, $[\alpha]_D^{20}$ + 1.04 (c 0.48, $CHCl_3$), IR (ATR, ν^{max}/cm^{-1}); 3420, 2922, 2852, 1669, 1501, 1465, 1366, 1164, 841; ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm); 0.83–0.87 (m, 6H, $CH(CH_3)_2$), 0.92–0.94 (m, 3H, CH_3), 1.23–1.31 (m, 30H, CH_2), 1.40 (s, 9H, $(CH_3)_3$), 1.96 (m, 2H, CH_2), 2.14 (m, 1H, β-C*H*), 3.95 (m, 1H, α-C*H*), 4.36 (s, 3H, CH_3), 4.47 (t, J = 7.2 Hz, 2H, CH_2), 4.71 (d, J = 4.8 Hz, 2H, CH_2), 5.24 (m, 1H, N*H*CH), 8.31 (br, s, 1H, N*H*CH_2), 8.63 (s, 1H, Tr-C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm); 14.0, 17.8, 19.2, 22.5, 26.0, 28.2, 28.7, 29.0, 29.1, 29.2, 29.4, 29.5, 30.5, 31.8, 32.1, 38.7, 54.1, 60.2, 79.8, 129.9, 142.0, 155.9, 173.2; HRMS (ESI) *m*/*z*: calcd for $C_{32}H_{62}N_5O_3$ 564.4847 $(M - PF_6)^+$, found 564.4848.

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