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Combinatorial Library of Primaryalkylammonium Dicarboxylate Gelators: A Supramolecular Synthon Approach†

Pathik Sahoo,‡ N. N. Adarsh,‡ George E. Chacko,§ Srinivasa R. Raghavan,§ Vedavati G. Puranik,∥ and Parthasarathi Dastidar*,‡

‡Department of Organic Chemistry, Indian Association for the Cultivation of Science (IACS), 2A & 2B Raja S C Mullick Road, Jadavpur, Kolkata − 700032, West Bengal, India, §Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland 20742-2111 and ∥Center for Materials Characterization, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 400 008, India

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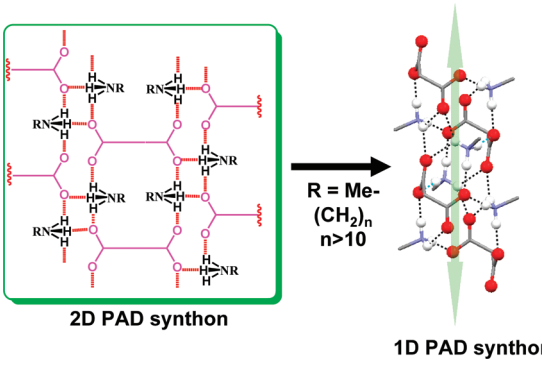
Following the supramolecular synthon approach, a combinatorial library comprising 35 organic salts derived from 7 dicarboxylic acids (malonic-, succinic-, adipic-, L-tartaric-, maleic-, phthalic-, and isophthalicacid) and 5 primaryalkyl amines Me-$(CH_2)_n$-NH_2 (n = 11−15) was prepared and scanned for gelation. About 66% of the salts in the combinatorial library were found to show moderate to good gelling ability in various polar and nonpolar solvents including commercial fuels such as petrol. The majority of the salts having a rigid, unsaturated anionic backbone (maleate, phthalate, and isophthalate) did not show gelation; only the corresponding hexadecylammonium salts showed gelation. Some of the representative gels were characterized by rheology, small-angle neutron scattering (SANS), optical microscopy (OM), and scanning electron microscopy (SEM). Single-crystal structures of two gelator and two nongelator salts were also discussed in the context of supramolecular synthon and structure−property correlation.

Introduction

Gels are ubiquitous in nature and in everyday life. Starting from protoplasm to shaving cream, all are gels. Immobilization of the solvent molecules within the supramolecular 3D network of the gelling agent is responsible for the solidlike appearance of the gel. Depending on the chemical structure of the gelling agents and its network formation, gels can be classified into two broad categories − polymeric and supramolecular or a physical gel, wherein the gel network is formed as a result of covalent bond formation and noncovalent interactions, respectively. Among the supramolecular gelling agents, low-molecular-mass organic gelators (LMOGs)—small organic compounds typically having a molecular mass of < 3000—are amazingly powerful in immobilizing organic solvents (organogel) and pure water and/or aqueous solvents (hydrogel) at very low gelator concentration.[1] In recent years, we have witnessed a surge of research dedicated to LMOGs because of their potential applications in sensors,[2] electrooptics/photonics,[3] structure-directing agents,[4] cosmetics,[5] art conservation,[6] drug delivery and biomedical applications,[7] and so forth. However, designing a gelling agent still remains a major challenge mainly because of the wide structural diversity of compounds known to impart gelation, lack of molecular-level information on the gel-formation mechanism, and unavailability of details on the gel-network/solvent interactions. Because self-assembled fibrilar networks (**SAFIN**s) are the key to gel formation, it is important to determine the supramolecular structure (crystal structure) of the meta-stable gel fiber, which is the

Scheme 1



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*Corresponding author. E-mail: parthod123@rediffmail.com; ocpd@iacs.res.in.

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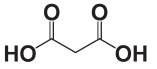
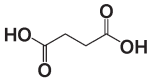
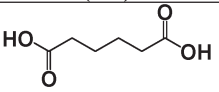
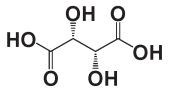
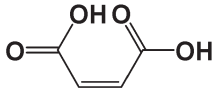
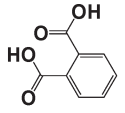
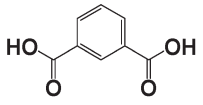
Table 1. Combinatorial Library

Amine / Acid	$A_n = Me\text{-}(CH_2)_n\text{-}NH_2$				
	Dodecylamine A_{11}	**Tridecylamine A_{12}**	**Tetradecylamine A_{13}**	**Pentadecylamine A_{14}**	**Hexadecylamine A_{15}**
 **Malonic acid (MA)**	$MA.2A_{11}$ Gelator	$MA.2A_{12}$ Gelator	$MA.2A_{13}$ Gelator	$MA.2A_{14}$ Gelator	$MA.2A_{15}$ Gelator
 **Succinic acid (SA)**	$SA.2A_{11}$ Gelator	$SA.2A_{12}$ Gelator	$SA.2A_{13}$ Gelator	$SA.2A_{14}$ Gelator	$SA.2A_{15}$ Gelator
 **Adipic acid (AA)**	$AA.2A_{11}$ Gelator	$AA.2A_{12}$ Gelator	$AA.2A_{13}$ Gelator	$AA.2A_{14}$ Gelator	$AA.2A_{15}$ Gelator
 **L-tartaric acid (TA)**	$TA.2A_{11}$ Gelator	$TA.2A_{12}$ Gelator	$TA.2A_{13}$ Gelator	$TA.2A_{14}$ Gelator	$TA.2A_{15}$ Gelator
 **Maleic acid (MAA)**	$MAA.2A_{11}$ Nongelator	$MAA.2A_{12}$ Nongelator	$MAA.2A_{13}$ Nongelator	$MAA.2A_{14}$ Nongelator	$MAA.2A_{15}$ Gelator
 **Phthalic acid (PA)**	$PA.2A_{11}$ Nongelator	$PA.2A_{12}$ Nongelator	$PA.2A_{13}$ Nongelator	$PA.2A_{14}$ Nongelator	$PA.2A_{15}$ Gelator
 **Isophthalic acid (IA)**	$IA.2A_{11}$ Nongelator	$IA.2A_{12}$ Nongelator	$IA.2A_{13}$ Nongelator	$IA.2A_{14}$ Nongelator	$IA.2A_{15}$ Gelator

sole ingredient of **SAFIN**s. It is not possible to use the standard single-crystal X-ray diffraction technique because of the fiber's submicrometer size; only an indirect method wherein the structure of the gel fiber is determined by comparing the X-ray powder diffraction (XRPD) patterns of the gel fibers and the simulated XRPD pattern of the gelator derived from its single-crystal data exists.[8] However, recording a good XRPD pattern of the gel fiber in its native (gel) form is difficult because of the scattering contribution of the solvent molecules and the less crystalline nature of the gel fibers. Ab initio crystal structure determination of the gel fiber in its native (gel) form using high-quality XRPD data may be an alternative;[9] however, such a method of structure determination is not yet routine and requires high-intensity synchrotron beams, which are not readily accessible.

It is reasonable to believe that there must be some anisotropic interactions of the gelator molecules that allow growth in one direction and lack such interactions in the other two dimensions, preventing lateral growth and resulting in 1D fibers. The tendency for the molecules to grow as a 1D fiber may favor **SAFIN** formation, resulting in a gel. Thus, it is logical to correlate supramolecular self-assembly patterns

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Table 2. Gelation Data[a]

	solvents												
salts	DMSO	DMF	methyl salicylate	Ph-NO_2	Ph-Cl	1,2-dichloro benzene	Ph-Me	*o*-xylene	*m*-xylene	*p*-xylene	petrol	MeOH	water
MA.2A$_{11}$	WG	4 (45)	VL	VL	VL	VL	VL	VL	VL	VL	P	VL	VL
MA.2A$_{12}$	WG	4 (45)	S	S	S	S	P	P	P	P	S	S	VL
MA.2A$_{13}$	4 (49)	2 (48)	VL	VL	S	WG	4 (34)	VL	VL	VL	WG	S	P
MA.2A$_{14}$	4 (53)	2.66 (49)	WG	WG	S	S	WG	VL	VL	VL	S	S	S
MA.2A$_{15}$	4 (55)	2.6 (60)	4 (58)	2.6*	S	S	WG	VL	4 (35)	VL	4 (33)	S	S
SA.2A$_{11}$	VL	WG	4 (79)	4 (79)	4 (57)	WG	WG	4 (69)	P	P	S	S	S
SA.2A$_{12}$	2.66(70)	2.66 (70)	2.66 (70)	2.66 (73)	WG	WG	WG	WG	WG	WG	WG	S	4 (50)
SA.2A$_{13}$	4 (78)	4 (74)	S	S	VL	4 (60)	P	4 (75)	4 (60)	4 (63)	4*	GP	WG
SA.2A$_{14}$	2.66 (80)	2.66 (58)	2.66 (77)	2.66 (77)	4 (54)	4 (60)	WG	4 (53)	4 (64)	4 (42)	4 (60)	GP	GP
SA.2A$_{15}$	4 (82)	2.66 (73)	1.33 (55)	2.08 (80)	1.33(51)	1.33 (65)	1.33((56)	2 (55)	2 (59)	2 (72)	2 (35)	P	P
AA.2A$_{11}$	4 (65)	4 (57)	VL	VL	VL	VL	VL	VL	VL	VL	S	S	S
AA.2A$_{12}$	4 (64)	4 (62)	S	S	S	S	P	P	P	P	S	S	S
AA.2A$_{13}$	2.66 (76)	2.66 (70)	2.66 (63)	2.66 (69)	WG	WG	4 (43)	4 (58)	4 (50)	WG	WG	S	S
AA.2A$_{14}$	2.66 (76)	2.66 (62)	4 (58)	4 (55)	VL	VL	P	WG	WG	WG	WG	S	S
AA.2A$_{15}$	2.66 (73)	2.66 (65)	2.66 (60)	2.66 (78)	4 (55)	S	4 (65)	4 (58)	4 (59)	4 (67)	S	S	P
TA.2A$_{11}$	3.2 (68)	VL	WG	WG	S	WG	WG	P	WG	WG	WG	GP	P
TA.2A$_{12}$	4 (65)	WG	P	WG	WG	S	WG	WG	WG	C	WG	GP	P
TA.2A$_{13}$	4 (71)	P	S	S	WG	S	WG	WG	WG	WG	4 (33)	4 (52)	P
TA.2A$_{14}$	4 (76)	4 (77)	WG	C	C	WG	4 (60)	WG	WG	4 (65)	P	WG	P
TA.2A$_{15}$	4 (79)	4 (73)	P	P	2.66 (67)	2.66 (58)	2.66 (56)	2.66 (70)	2.66 (68)	4 (59)	2*	4 (59)	P
MAA.2A$_{11}$	P	P	P	P	P	P	P	P	P	P	P	P	P
MAA.2A$_{12}$	P	P	P	P	P	P	P	P	P	P	P	P	P
MAA.2A$_{13}$	WG	S	WG	WG	WG	WG	4 (35)	WG	S	S	S	S	VL
MAA.2A$_{14}$	WG	WG	WG	S	S	S	S	S	S	S	S	S	P
MAA.2A$_{15}$	WG	WG	WG	WG	WG	WG	WG	4 (45)	WG	P	P	S	P
PA.2A$_{11}$	GP	GP	GP	GP	GP	VL	GP	GP	GP	GP	P	S	S
PA.2A$_{12}$	P	P	S	S	S	S	S	WG	WG	WG	S	S	P
PA.2A$_{13}$	WG	WG	WG	WG	VL	VL	WG	WG	WG	WG	S	S	S
PA.2A$_{14}$	GP	P	GP	WG	WG	WG	WG	WG	WG	WG	S	S	S
PA.2A$_{15}$	4 (58)	4 (62)	4 (57)	4 (52)	S	WG	VL	WG	WG	WG	S	S	S
IA.2A$_{11}$	S	S	S	S	S	S	S	S	S	S	S	S	VL
IA.2A$_{12}$	S	S	VL	VL	S	VL	S	S	S	S	S	S	VL
IA.2A$_{13}$	VL	VL	S	S	S	S	S	S	S	S	S	S	VL
IA.2A$_{14}$	WG	VL	S	S	S	S	P	P	S	P	P	S	P
IA.2A$_{15}$	4*	VL	4*	WG	P	P	P	P	P	P	P	S	P

[a] Numerical values indicate minimum gelator concentration in wt % (w/v); numerical values within parenthesis are the gel-to-sol dissociation temperature in °C; WG, weak gel; S, solution; VL, viscous liquid, GP, gelatenous precipitate; P, precipitate; C, crystals; *, gel only in the refrigerator, with phase separation occuring upon standing at room temperature.

of a molecule obtained from its single-crystal data with its gelling/nongelling behavior. The Shinkai group,[10] the van Esch and Feringa groups,[11] and the Hanabusa group[12] have all emphasized the importance of being 1D in gel formation. However, the fact that all the molecules having such anisotropic interactions do not display gelation ability and a gelator cannot gel all possible solvents clearly indicates the importance of other factors (such as gel-network/solvent interactions). Thus, the requirement for a molecule to self-assemble in one direction in order to be a gelator is an indispensable rather than sufficient condition. Thus, a working hypothesis that a 1D hydrogen-bonded network favors **SAFIN** and thus gel formation (under suitable conditions) can become quite handy in designing LMOGs. Direct correlation between single-crystal structures of molecules and their gelling/nongelling properties must be established in as many examples as possible before it can be accepted as a reasonable basis for designing new gelators. Our group remains the major contributor toward this goal and established this working hypothesis most explicitly in organic and organometallic salt-based gelators.[1a,13] Following this, we explored the supramolecular synthon[14] concept to design intriguing gelling agents.[1a] Recently,

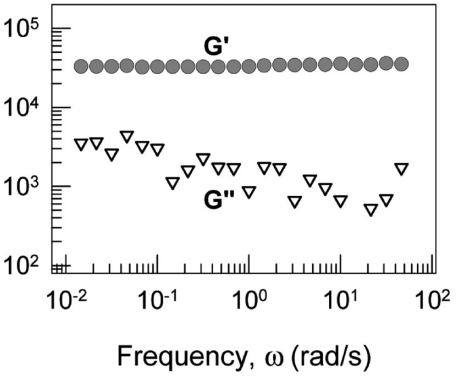

Figure 1. Dynamic rheology at 25 °C of a gel of 4 wt% **MA.2A$_{15}$** in deuterated DMSO. The elastic modulus G' and the viscous modulus G'' are shown as functions of the angular frequency ω. The strain used was 0.5%.

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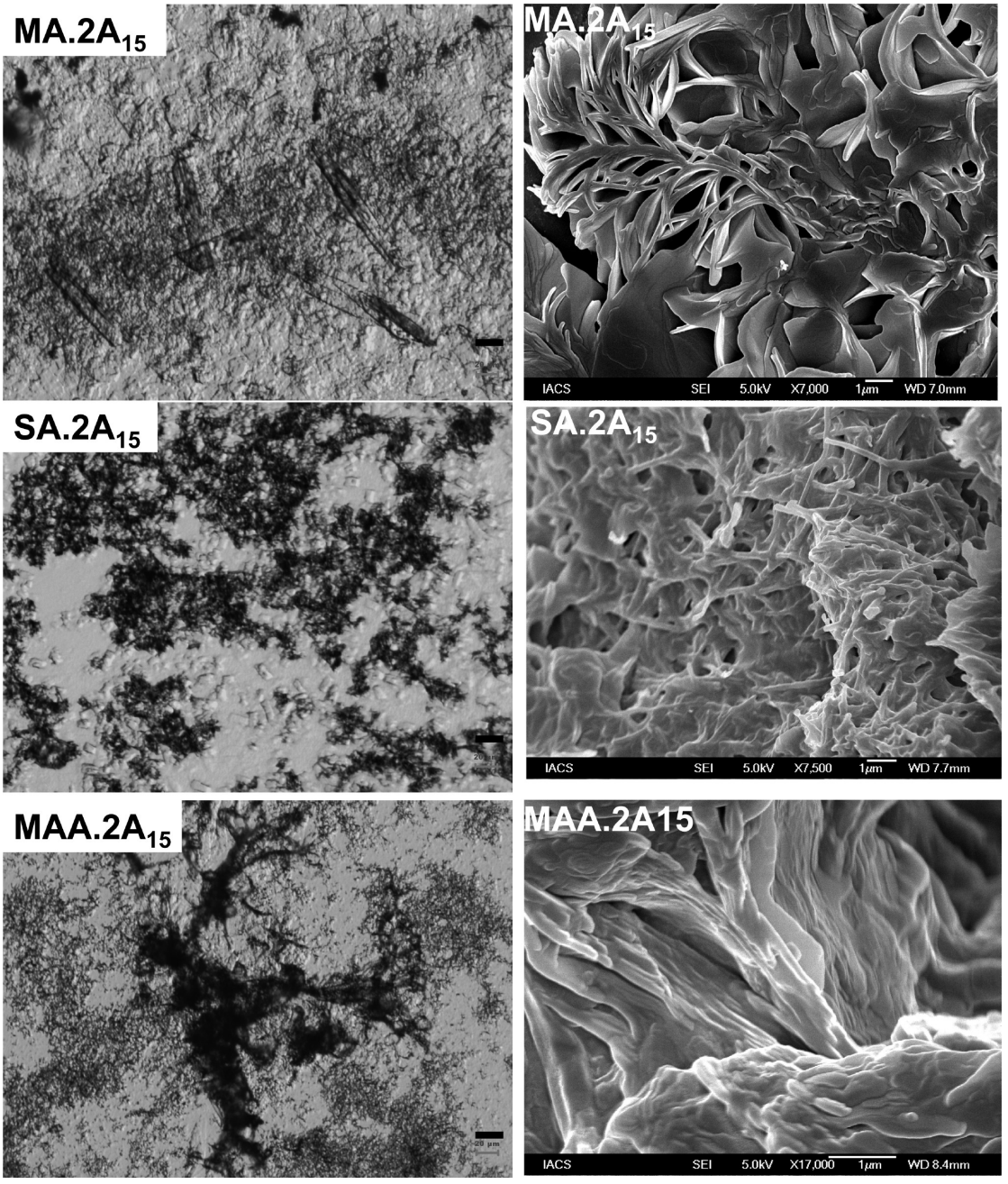

Figure 2. OM (230×, scale bar 20 μm) and SEM (scale bar 1 μm) of various dried gels of hexadecyammonium salts.

we showed how long-chain alkyl−alkyl interactions induced hydrogen bond isomerism in the primary ammonium dicarboxylate (PAD) synthon to generate a 1D nanotubular construct displaying gelling ability (Scheme 1).[15] Inspired by these results, we decided to explore this new 1D nanotubular synthon in searching for intriguing gelling agents in a series of PAD salts using a combinatorial library approach.[16] For this purpose, we synthesized a library of 35 PAD salts using 7 dicarboxylic acids and 5 alkyl amines $R(CH_2)_n$-NH_2 (n = 11−15) (Table 1); we deliberately restricted the chain length of the alkyl group to n = 11−15 because in our past experience with PAD salts[15] the salts having n > 10 showed gelation. About 66% of the salts of the combinatorial library were found to show moderate to good gelling ability in various polar and nonpolar solvents, including commercial fuels such as petrol. Some of the representative gels were characterized by rheology, small-angle neutron scattering (SANS), optical microscopy (OM), and scanning electron microscopy (SEM). Single-crystal structures of two gelator (**SA.2A$_{15}$** and **AA.2A$_{14}$**) and two nongelator (**PA.2A$_{14}$** and **IA.2A$_{14}$**) salts were also discussed in the context of supramolecular synthon and structure−property correlation.

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Results and Discussion

Gelation. All the 35 salts of the combinatorial library (Table 1) were scanned for gelation properties with 13 different solvents. Out of 35 salts, 23 were found to form moderate to good gels (Table 2).

Table 3. Crystallographic Data

crystal parameters	$IA.2A_{14}$	$SA.2A_{15}$	$PA.2A_{14}$	$AA.2A_{14}$
empirical formula	$C_{38}H_{74}N_2O_5$	$C_{18}H_{38}NO_2$	$C_{76}H_{144}N_4O_{10}$	$C_{36}H_{76}N_2O_4$
formula weight	638.99	300.49	1273.95	600.99
crystal size/mm^3	0.24 × 0.18 × 0.08	0.32 × 0.24 × 0.18	0.26 × 0.12 × 0.02	0.28 × 0.15 × 0.05
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.3702(4)	5.0630(11)	11.012(2)	5.7422(17)
b/Å	9.6182(4)	5.6437(12)	13.036(3)	10.188(3)
c/Å	23.4102(10)	35.086(7)	28.999(6)	33.233(10)
α/deg	80.173(2)	88.678(4)	84.282(3)	96.423(4)
β/deg	83.684(2)	87.339(4)	88.588(3)	94.766(4)
γ/deg	69.123(2)	81.574(4)	82.560(3)	101.674(4)
volume/Å^3	1939.62(14)	990.5(4)	4107.0(15)	1880.8(10)
Z	2	2	2	2
D_{calc}/g cm^{-3}	1.094	1.008	1.030	1.061
F(000)	712	338	1416	676
μ Mo Kα/mm^{-1}	0.071	0.064	0.067	0.067
temperature/K	100(2)	100(2)	100(2)	100(2)
R_{int}	0.0340	0.0605	0.0360	0.0465
range of h, k, l	−10/12, −12/12, −24/30	−6/6, −6/6, −41/41	−11/11, −14/14, −28/31	−6/6, −11/11, −38/39
Θ min/max/deg	0.88/27.99	1.75/25.00	0.71/22.50	0.62/24.80
reflns collected/unique/obsd [$I > 2\sigma(I)$]	20321/8292/5853	10399/3461/2432	23672/10681/6969	13270/6388/3759
data/restraints/ parameters	8292/0/418	3461/0/192	10681/0/808	6388/0/383
goodness of fit on F^2	1.024	1.173	1.084	0.939
final R indices [$I > 2\sigma(I)$]	R1 = 0.0473 wR2 = 0.1311	R1 = 0.1114 wR2 = 0.2372	R1 = 0.0882 wR2 = 0.2734	R1 = 0.0566 wR2 = 0.1446
R indices (all data)	R1 = 0.0737 wR2 = 0.1494	R1 = 0.1538 wR2 = 0.2555	R1 = 0.1194 wR2 = 0.3058	R1 = 0.1056 wR2 = 0.1847

It may be noted from Table 1 that all of the salts derived from dicarboxylic acids having saturated backbones (malonic to tartaric acid) irrespective of the alkyl chain length of the ammonium moiety showed gelation. However, salts derived from dicarboxylic acids having rigid, unsaturated backbones (maleic to isophthalic acid) did not show gelation except for the ones having an ammonium moiety with n = 15. These results clearly indicated the importance of the acid backbone on gelation. An examination of the gelation data (Table 2) indicated that most of the gelators were able to gel polar solvents such as DMSO, DMF, methylsalicylate, and nitrobenzene but were not as efficient at gelling nonpolar solvents such as halobenzenes and xylenes. Some of the gelators were also capable of gelling commercial fuels such as petrol. It is interesting that salt **SA.2A$_{12}$** was found to be an ambidextrous gelator capable of gelling both organic and aqueous solvents. The minimum gelator concentration (MGC) and gel−sol dissociation temperature (T_{gel}) were within the range of 1.33−4 wt % and 33−82 °C, respectively, indicating a moderate to good gelation ability of these salts.

Rheology. Selected gels were also studied using dynamic rheology. The characteristic gel-like response was typically found, and this is illustrated in Figure 1 for a gel of 4 wt % **MA.2A$_{15}$** in deuterated DMSO. Here, the elastic modulus G' and the viscous modulus G'' are plotted as functions of the angular frequency ω. Note that G' is independent of frequency and considerably higher than G'' over the range of frequencies. The gel modulus (value of G') is a measure of the gel stiffness. For the above 4% **MA.2A$_{15}$** sample, its value is 35 kPa, which is very high and shows that the sample is a stiff gel. For comparison, a 4% gel of **SA.2A$_{15}$** in the same solvent has a modulus of 2 kPa, and a 4% gel of **AA.2A$_{15}$** has a modulus of only 120 Pa. Thus, it appears that with the increase in the number of the backbone $>CH_2$ moieties of the anionic counterpart in these salts, gel stiffness seems to be decreasing.

Optical and Scanning Electron Microscopy. Optical and scanning electron microscopy (OM and SEM) were recorded for dried thin layers of DMSO gels (0.5 wt %, w/v in DMSO) smeared over a glass slide and DMSO xerogels (2 wt %, w/v) of the hexadecylammonium gelators salts (column 6, Table 1), respectively (Figure 2); the appearance of scattered colonies of small crystallites displaying microthin plate-type morphology in some cases (e.g., **MA.2A$_{15}$** and **SA.2A$_{15}$**), a highly entangled gel network along with microthin platelike crystallites in **MAA.2A$_{15}$** in OM, and a fibrous network in the corresponding SEM micrographs are clear indications of the metastable nature of the gels. The kinetically slow, concentration-dependent process of hierarchical self-assembly of primary gel fibers into a larger assembly to sustain a gel-forming network is revealed here. The gel-forming network collapsed under fast evaporation conditions of the highly diluted solutions on the glass slides giving rise to thermodynamically more stable neat crystallites having microthin platelike morphology. OM and SEM of other

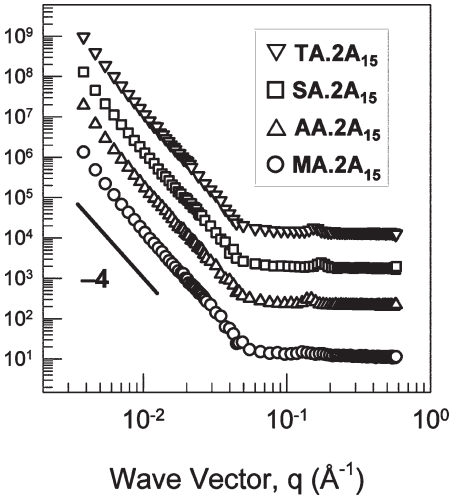

Figure 3. SANS data (I vs q) at 25 °C for 4 wt % gels of various gelators in deuterated DMSO. Successive curves are offset by factors of 10 for clarity.

hexadecylammonium salt gelators showed similar results (Figure S1, Supporting Information). It is worth mentioning here that the formation of microcrystals directly from gel samples has recently been observed by us[17] and others.[18] It is also noted here that in the SEM micrographs the salts derived from saturated acids displayed 1D fibrous morphology whereas salts derived from unsaturated acids showed platetype morphology.

Small-Angle Neutron Scattering (SANS). SANS experiments were also conducted on selected samples of the gelators in deuterated DMSO. The deuteration of the solvent ensured good contrast between the gelator aggregates and the continuous phase. In all cases, the intensity I follows the Porod law (i.e., $I \approx q^{-4}$, which is indicative of sharp interfaces in the sample (Figure 3)). On the basis of the SEM micrographs above, we can conclude that these structures are crystallites of the gelator molecules, arranged either as thin plates or as rods. Similar SANS data were also reported by us for gels of secondary ammonium salts of various bile acids.[16a]

Single-Crystal X-ray Diffraction. To correlate the single-crystal structures with the gelling/nongelling properties of the salts, we tried to crystallize as many salts as possible. Despite our best efforts, we have been successful in crystallizing two gelator salts, namely, **AA.2A$_{14}$** and **SA.2A$_{15}$**, and two nongelator salts, namely, **PA.2A$_{14}$** and **IA.2A$_{14}$** (Table 3). Single-crystal structures of these salts revealed intriguing results.

Gelator salt **AA.2A$_{14}$** crystallized in the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit contains one dicarboxylate moiety and two ammonium moieties. In the crystal structure, the dicarboxylate moiety is involved in hydrogen bonding with two ammonium moieties via N−H···O interactions (N···O = 2.684(2)−2.729(2) Å; ∠N−H···O = 162.7−164.5°). This 1:2 (acid/amine) salt unit is further self-assembled with the crystallographically equivalent salt unit via N−H···O hydrogen bonding interactions (N···O = 2.723(2)−2.732(3) Å; ∠N−H···O = 160.1−170.6°), resulting in a 1D network. Two such 1D networks are further assembled centrosymmetrically via N−H···O interactions (N···O = 2.803(2)−2.897(2) Å; ∠N−H···O = 156.0−158.4°), giving rise to a 1D columnar network. Thus, in this structure, the generally expected 2D PAD synthon (Scheme 1) is absent; instead, a hydrogen bonding isomerism has taken place, resulting in the formation of a 1D columnar network similar to what is depicted in Scheme 1. The 1D networks displayed noninterdigited parallel packing (Figure 4).

Gelator salt **SA.2A$_{15}$** also crystallized in the centrosymmetric triclinic space group $P\bar{1}$. In the asymmetric unit, a full molecule of the hexadecylammonium cation and half a molecule of the succinate anion were located. The anionic moiety was found be located on a center of symmetry at 0, 1/2, 1/2. The cationic moiety was found to be hydrogen bonded to the carboxylate O atoms of two neighboring anionic moieties (N−H···O = 2.756(4)−2.990(4) Å; ∠N−H···O = 129.7−171.4°). In the crystal structure, each anionic moiety is hydrogen bonded to six cationic moieties. The overall hydrogen bonding network can be best described as 2D sheet-type architecture wherein the long chains of the ammonium cations are protruding out of the sheet in a manner similar to that expected in PAD salts (Scheme 1). The sheets are further packed in a noninterdigited fashion (Figure 5).

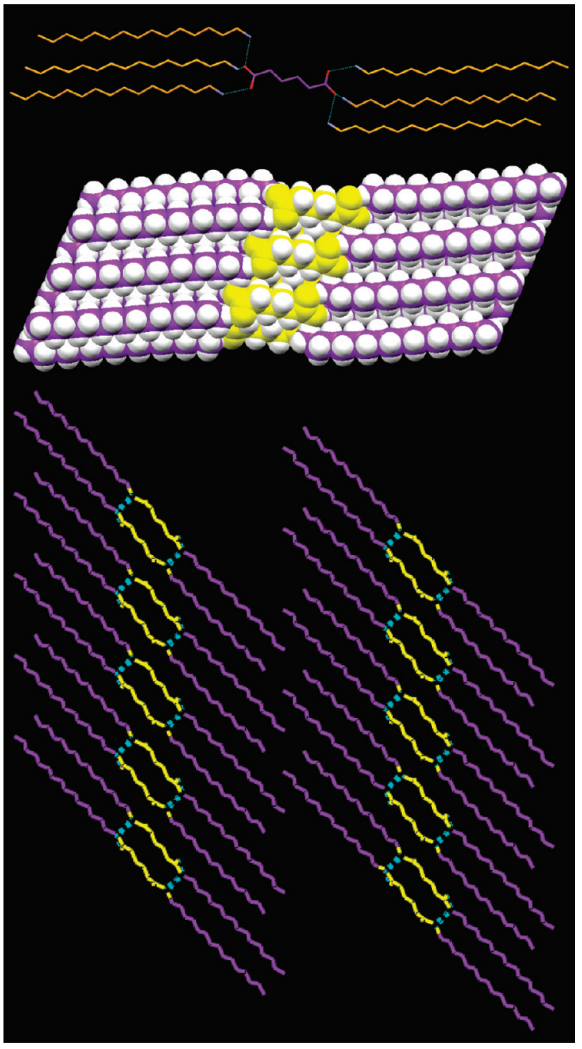

Figure 4. Illustration of the single-crystal structure of gelator salt **AA.2A$_{14}$**. (Top) Hydrogen bonding interactions involving anionic and cationic moieties. (Middle) One-dimensional columnar hydrogen-bonded network in a space-filling model displaying intranetwork alkyl−alkyl interactions. (Bottom) Noninterdigited parallel packing of the 1D network.

However, nongelator salt **PA.2A$_{14}$** also crystallized in the same space group ($P\bar{1}$). The asymmetric unit is composed of two salt units and some disordered water molecules. An alkyl chain of one of the ammonium moieties and one oxygen atom of one of the carboxylate moieties are also found to be disordered. In the crystal structure, the salt moieties are hydrogen bonded via N−H···O interactions involving carboxylate, ammonium, and disordered water molecules (N···O = 2.737(5)−3.024(4) Å; ∠N−H···O = 128.4−170.5°), resulting in a 2D sheet type of hydrogen-bonded network (similar to what is expected in the PAD salt, Scheme 1), wherein the long alkyl chains are protruding out of the sheet structure. Parallel packing of the sheets maximizes the alkyl−alkyl interactions via a high degree of interdigitation of the alkyl chains (Figure 6).

Nongelator salt **IA.2A$_{14}$** crystallized in the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit

(17) Ballabh, A.; Adalder, T. K.; Dastidar, P. *Cryst. Growth Des.* **2008**, *8*, 4144.
(18) Moffat, J. R.; Smith, D. K. *Chem. Commun.* **2008**, 2248–2250.

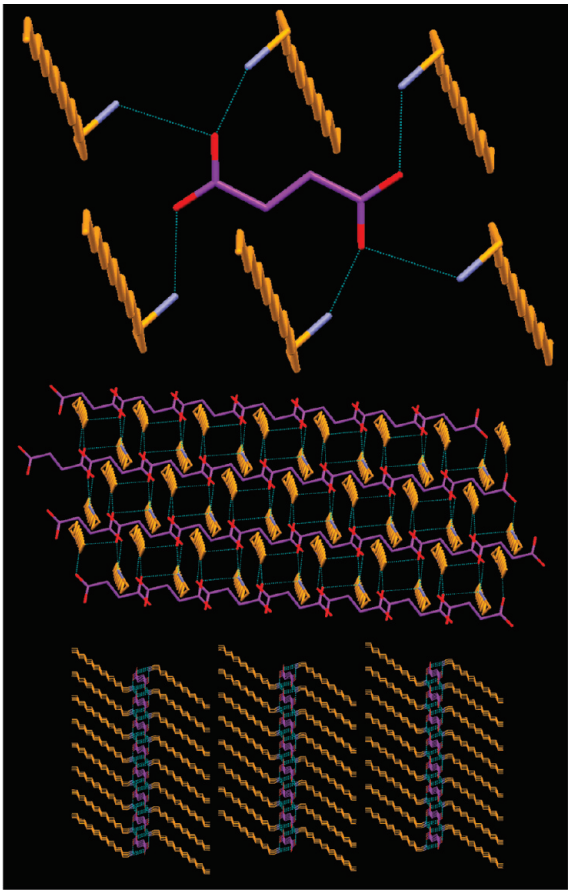

Figure 5. Illustration of the single-crystal structure of gelator salt **SA.2A$_{15}$**. (Top) Hydrogen bonding interactions involving anionic and cationic moieties. (Middle) Two-dimensional hydrogen-bonded sheet structure. (Bottom) Noninterdigited packing of the sheet structures.

contains one isophthalate dianion, two pentadecylammonium cations, and one water molecule of solvation, all located in general positions. In the crystal structure, the anionic moiety is hydrogen bonded to six cationic moieties via N−H···O interactions (N···O = 2.7819(15)−2.8754 (15) Å;∠N−H···O = 162.9−177.7°) and two water molecule of solvation via O−H···O interactions (O···O = 2.7804(15)−2.8437(14) Å; ∠O−H···O = 146(2)−167.0 (19)°). The overall hydrogen-bonded network may be best described as 2D sheet architecture, similar to what is expected in the PAD salt (Scheme 1) except that the water molecules of solvation are also part of the network. The 2D sheets are packed parallel, maximizing alkyl−alkyl interactions via interdigitation (Figure 7).

To determine if the single-crystal structures truly represent the bulk solid and xerogel of these gelators, namely, **AA.2A$_{14}$** and **SA.2A$_{15}$**, various X-ray powder diffraction patterns obtained from the bulk and the xerogel were compared with the simulated pattern obtained from the corresponding single-crystal data (Figure 8). Figure 8a clearly showed that the major peaks of the simulated pattern and bulk solid of salt **AA.2A$_{14}$** matched well whereas the corresponding pattern obtained from the DMSO xerogel did not match these patterns. These results indicated the formation of a new crystalline phase or a mixture of crystalline phases in the xerogel. However, in the case of salt **SA.2A$_{15}$**, all of the corresponding patterns were found to be in good agreement, meaning that the single-crystal

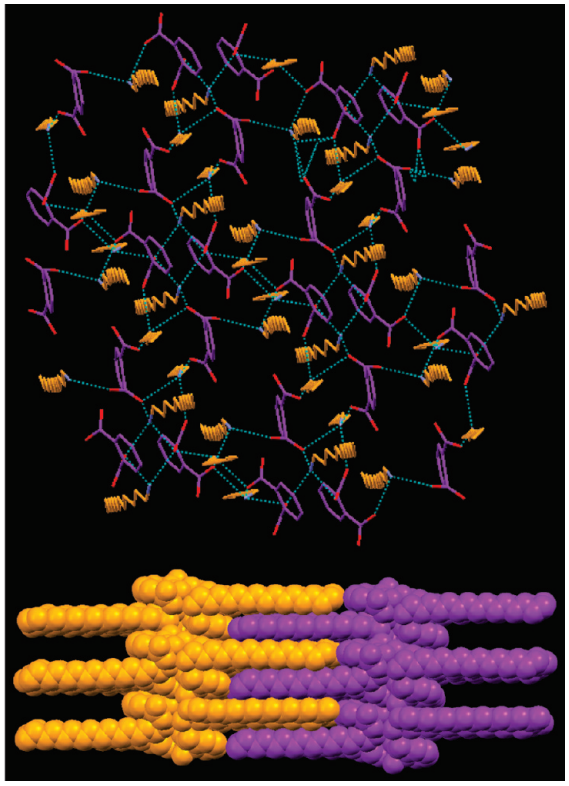

Figure 6. Illustration of single-crystal structure of nongelator salt **PA.2A$_{14}$**. (Top) Two-dimensional hydrogen-bonded network (disordered solvents not shown). (Bottom) Interdigited packing of the 2D network displaying a high degree of alkyl−alkyl interactions (interacting 2D networks are shown in purple and orange).

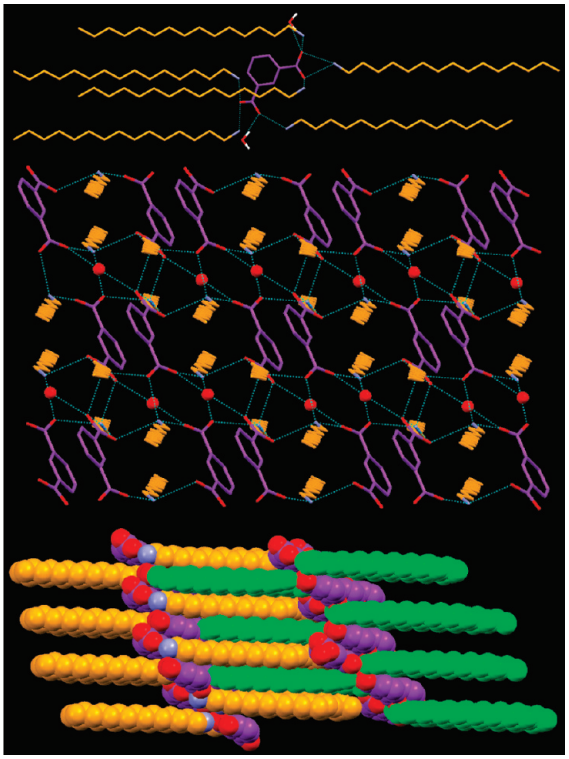

Figure 7. Illustration of the single-crystal structure of nongelator salt **IA.2A$_{14}$**. (Top) Hydrogen bonding interactions involving anionic and cationic moieties. (Middle) Two-dimensional hydrogen-bonded network involving the cationic and anionic species and water molecules of solvation (red ball). (Bottom) Interdigited packing of the 2D network displaying a high degree of alkyl−alkyl interactions.

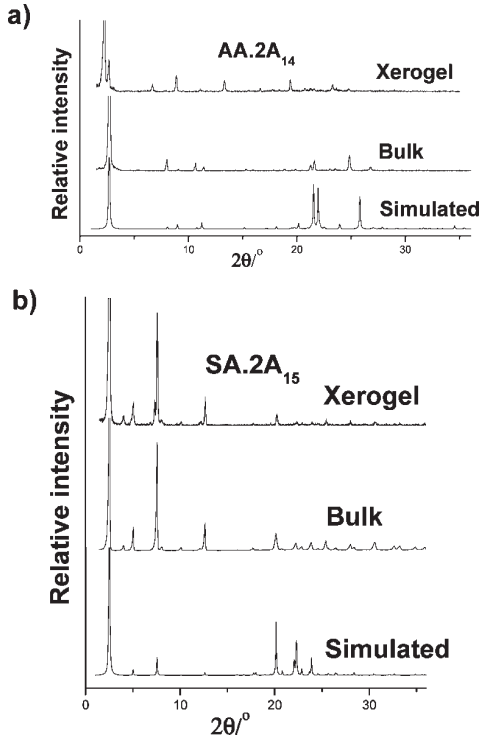

Figure 8. XRPD patterns under various conditions for salts (a) **AA.2A$_{14}$** and (b) **SA.2A$_{15}$**.

structure of this salt truly represents the bulk solid as well as the xerogel.

Thus, the 1D columnar supramolecular PAD synthon is observed in gelator salt **AA.2A$_{14}$**, whereas the generally expected 2D supramolecular PAD synthon is found in gelator salt **SA.2A$_{15}$** (Scheme 1). Interestingly, both nongelator salts (**PA.2A$_{14}$** and **IA.2A$_{14}$**) displayed a 2D hydrogen-bonded network similar to that generally obtained in PAD salts (Scheme 1) except that occluded water molecules are also part of the network in these cases. Because the alkyl chain length of the cationic moieties is nearly the same in all of these crystal structures, the anionic backbone may be attributed to the different supramolecular synthons (1D in **AA.2A$_{14}$** and 2D in **SA.2A$_{15}$**, **PA.2A$_{14}$**, and **IA.2A$_{14}$**) observed in these salts. The fact that **AA.2A$_{14}$**, which displayed a 1D columnar network, showed gelation and **PA.2A$_{14}$** and **IA.2A$_{14}$** having 2D sheet architecture failed to show gelation is quite intriguing and agrees well with the earlier reported results (i.e., a 1D network is important for gelation).[1a,10] However, **SA.2A$_{15}$** showed a 2D hydrogen-bonded network despite being a gelator. This observation is also in good agreement with the earlier reported results.[10] It may be noted that direct correlation with the network dimensionality as seen in the neat crystal structure and the morphology of the gel fiber may not be possible because gel fiber formation is a complicated crystallization process that leads to the formation of a meta-stable network of gel fibers (i.e., SAFIN). For example, we have reported that the imidazolium hydrogen cyclobutane-1,1-dicarboxylate salt displayed a 1D fibrous network in both SEM (in xerogel) and OM (in gel) and a 3D hydrogen-bonded network structure in its single crystals.[19] Thus, the fact that **SA.2A$_{15}$** displayed a 2D network structure in its single-crystal form and a 1D fibrous network in SEM is not surprising.

(19) Ballabh, A.; Trivedi, D. R.; Dastidar, P. *Chem. Mater.* **2003**, *15*, 2136.

Conclusions. On the basis of the supramolecular synthon rationale, a new class of LMOGs derived from a combinatorial library of 35 organic salts generated by reacting various dicarboxylic acids and *n*-alkylprimary amines was synthesized. About 66% of the salts (i.e., 23 out of 35 salts prepared) were found to be moderate to good gelling agents of various polar and nonpolar organic solvents including commercial fuel such as petrol. Interestingly, salts derived from dicarboxylic acids having saturated backbones were all gelators whereas the corresponding salts derived from rigid and unsaturated dicarboxylic acids were found to be nongelators except for the one containing the ammonium moiety with $n = 15$. Interestingly, one gelator salt, namely, **SA.2A$_{12}$** displayed ambidextrous behavior. The formation of platelike crystallites in the gel samples as revealed by OM and SEM indicated the metastable nature of the gel fibers. SANS data on some of the hexadecylammonium salts followed Porod's law (i.e., $I \approx q^{-4}$), which indicated the presence of sharp interfaces in the sample. The 1D network observed in gelator salt **AA.2A$_{14}$** and the 2D network observed in nongelator salts **PA.2A$_{14}$** and **IA.2A$_{14}$** emphasized the importance of the 1D network in gelaton. Although the 1D network was found to be important in gelation, the 2D network as observed in gelator salt **SA.2A$_{15}$** occasionally induced gelation. In the absence of the crystal structures of the rest of the salts, it is not possible to make general comments on the plausible supramolecular synthons of the gelator and nongelator salts in the combinatorial library. However, a reasonably good success rate of about 66% salts being gelators and the presence of 1D and 2D hydrogen-bonded networks in the gelator and nongelator salts, respectively, highlighted the merit of the supramolecular synthon approach in designing a new class of gelators.

Experimental Section

Materials and Methods. All of the chemicals (Aldrich) and solvents are (A.R. grade, SD, Fine Chemicals, India) commercially available and used without any further purification. Petrol used in the gelation experiments have been purchased from the local market. Microanalyses are performed on a Perkin-Elmer elemental analyzer 2400, series II. FT-IR spectra are recorded using a Perkin-Elmer spectrum GX. Powder X-ray patterns are recorded on an XPERT Philips (Cu Kα radiation, λ = 1.5418Å) diffractometer. Scanning electron microscopy (FT-SEM) is performed on a JEOL (JSM-6700F). Single-crystal X-ray spectra were recorded on a Bruker AXS, Smart Apex II.

Preparation of Salts. Salts were prepared by mixing several dicarboxylic acids with the corresponding amines according to Table 1 in a 1:2 molar ratio acid:amine in MeOH in a beaker. The resultant mixture was subjected to sonication for a few minutes to ensure the homogeneous mixing of the two components. A white precipitate was obtained after complete dryness of MeOH at room temperature, which was subjected to various physicochemical analyses (Supporting Information) and a gelation test (Table 2).

Rheological Studies. Dynamic rheological experiments were performed on an AR2000 stress-controlled rheometer (TA Instruments). Samples were run at 25 °C on cone-and-plate geometry (40 mm diameter, 2° cone angle). Frequency sweeps were conducted in the linear viscoelastic regime of each sample, as determined previously by stress-sweep experiments.

Small-Angle Neutron Scattering (SANS). SANS experiments were carried out on the NG-7 (30 m) beamline at NIST in Gaithersburg, MD. Neutrons with a wavelength of 6 Å were selected. Three sample−detector distances were used to obtain

data over a range of wave vectors from 0.004 to 0.4 $Å^{-1}$. Samples were studied in 2 mm quartz cells at 25 °C. Scattering spectra were corrected and placed on an absolute scale using NIST calibration standards. The data are shown as plots of the absolute intensity I versus the wave vector $q = (4\pi \sin(\theta/2))/\lambda$, where λ is the wavelength of incident neutrons and θ is the scattering angle.

Acknowledgment. P.S. and N.N.A. thank CSIR and IACS for SRF fellowships, respectively.

Supporting Information Available: Physicochemical data for the salts. OM and SEM of the gelator salts. CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

SUPPORTING INFORMATION

A Combinatorial Library of Primaryalkylammonium Dicarboxylate Gelators – A Supramolecular Synthon Approach

Pathik Sahoo,[a] N. N. Adarsh,[a] George E. Chacko,[b] Srinivasa R. Raghavan,[b] Vedavati G. Puranik,[c] Parthasarathi Dastidar*,[a]

[a]*Department of Organic Chemistry, Indian Association for the Cultivation of Science (IACS),*
2A & 2B Raja S C Mullick Road, Jadavpur, Kolkata – 700032, West Bengal, India

[b]*Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111*

[c]*Center for Materials Characterization,National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 400 008,* India

e-mail: parthod123@rediffmail.com; ocpd@iacs.res.in

Physico-chemical data for the salts

1. **Di-dodecylammoniummalonate**: m.p.140°C. Anal. Calc. for$C_{27}H_{58}N_2O_4$: C, 68.31; H, 12.31; N, 5.90. Found: C, 68.40; H, 12.79; N, 5.87 %. FT-IR (KBr): 3336, 2958, 2921, 2852, 2361, 2184, 1567, 1468, 1434, 1394, 1333, 1249, 1205, 1167, 1123, 1052, 977, 954, 923, 817, 761, 722, 697, 646, 588, 518, 455, 419cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.06 (br, N-H), 3.04 (s, 2H, $C\underline{H_2}(COO^-)_2$), 2.86 (t, J = 7.33 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_9CH_3$), 1.64 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_9CH_3$), 1.24 (brS, 36H, $^+NH_3CH_2CH_2(C\underline{H_2})_9CH_3$), 0.87 (t, J = 6.36 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_9C\underline{H_3}$).
2. **Di-tridecylammoniummalonate**: m.p.136°C. Anal. Calc. for$C_{29}H_{62}N_2O_4$: C, 69.27; H, 12.43; N, 5.57. Found: C, 69.52; H, 12.74; N, 6.69 %. FT-IR (KBr): 3427, 2922, 2853, 2364, 2147, 1570, 1469, 1441, 1353, 1244, 1165, 1124, 1058, 1030, 993, 957, 927, 901, 815, 721, 692, 600, 465cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.11 (br, N-H), 3.04 (s, 2H, $C\underline{H_2}(COO^-)_2$), 2.90 (t, J = 6.6 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{10}CH_3$), 1.68 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{10}CH_3$), 1.25 (brS, 40H, $^+NH_3CH_2CH_2(C\underline{H_2})_{10}CH_3$), 0.87 (brS, 6H, $^+NH_3CH_2CH_2(CH_2)_{10}C\underline{H_3}$).
3. **Di-tetradecylammoniummalonate**: m.p.157°C. Anal. Calc. For$C_{31}H_{66}N_2O_4.2CH_3OH$: C, 66.62; H, 12.54; N, 4.71. Found: C, 66.93; H, 12.73; N, 4.83 %. FT-IR (KBr): 3782, 2921, 2852, 2364, 1637, 1567, 1468, 1439, 1396, 1329, 1167, 1121, 1028, 978, 922, 726, 697, 648, 590cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.80 (br, N-H), 3.07 (s, 2H, $C\underline{H_2}(COO^-)_2$), 2.92 (t, J = 7.0 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{11}CH_3$), 1.48 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{11}CH_3$), 1.24 (brS, 44H, $^+NH_3CH_2CH_2(C\underline{H_2})_{11}CH_3$), 0.87 (t, J = 6.1Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{11}C\underline{H_3}$).
4. **Di-pentadecylammoniummalonate**: m.p.141°C. Anal. Calc. For$C_{33}H_{70}N_2O_4$: C, 70.91; H, 12.62; N, 5.01. Found: C, 69.93; H, 13.06; N, 5.76 %. FT-IR (KBr): 3782, 3407, 2921, 2851, 2363, 2121, 1627, 1554, 1468, 1381, 1342, 1246, 1168, 1055, 1002, 968, 926, 814, 723, 697, 652, 590, 477cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.91 (br, N-H), 3.08 (s, 2H, $C\underline{H_2}(COO^-)_2$), 2.93 (t, J = 7.2 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{12}CH_3$), 1.70 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{12}CH_3$), 1.24 (brS, 48H, $^+NH_3CH_2CH_2(C\underline{H_2})_{12}CH_3$), 0.87 (t, J = 6.0Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{12}C\underline{H_3}$).
5. **Di-hexadecylammoniummalonate**: m.p.140°C. Anal. Calcd. for $C_{35}H_{74}N_2O_4.1/2H2O$: C, 70.53; H, 12.68; N, 4.70. Found: C, 70.44; H, 12.92; N, 5.09 %. FT-IR (KBr): 3786, 2920, 2851, 2360, 1574, 1468, 1341, 1248, 1173, 1054, 724, 588cm^{-1} NMR ($CDCl_3$, 300MHz) δ = 5.16 (br, N-H), 3.03 (s, 2H, $C\underline{H_2}(COO^-)_2$), 2.91 (t, J = 9 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{13}CH_3$), 1.58 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{13}CH_3$), 1.25 (brS, 52H, $^+NH_3CH_2CH_2(C\underline{H_2})_{13}CH_3$), 0.87 (t, J = 6.0Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{13}C\underline{H_3}$).
6. **Di-dodecylammoniumsuccinate**: m.p.116°C. Anal. Calc. For$C_{28}H_{60}N_2O_4$: C, 68.80; H, 12.37; N, 5.73. Found: C, 68.79; H, 12.50; N, 6.45 %. FT-IR (KBr): 3436, 3139, 2920, 2851, 2205, 1658, 1527, 1465, 1377, 1315, 1234, 1170, 1052, 923, 841, 806, 721, 662, 519, 473cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.11 (br, N-H), 2.88 (t, *J* = 7.37Hz, 4H, $^-OOC(C\underline{H_2})_2COO^-$), 2.36 (m, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_9CH_3$), 1.67 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_9CH_3$), 1.24 (brS, 36H, $^+NH_3CH_2CH_2(C\underline{H_2})_9CH_3$), 0.87 (t, J = 5.94 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_9C\underline{H_3}$).

7. **Di-tridecylammoniumsuccinate**: m.p.120°C. Anal. Calc. For$C_{30}H_{64}N_2O_4$: C, 69.72; H, 12.48; N, 5.42. Found: C, 70.14; H, 12.87; N, 6.39 %. FT-IR (KBr): 3139, 2920, 2851, 2748, 2205, 1659, 1529, 1464, 1394, 1377, 1311, 1235, 1171, 1086, 1053, 1026, 924, 845, 806, 721, 662, 519, 471, 428cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.72 (br, N-H), 3.08 (t, J = 7.01Hz, 4H, $^-$OOC($C\underline{H_2}$)$_2$COO$^-$), 2.38 (m, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_{10}$CH$_3$), 1.70 (brS, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_{10}$CH$_3$), 1.24 (brS, 40H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_{10}$CH$_3$), 0.87 (t, J = 6.24 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_{10}C\underline{H_3}$).
8. **Di-tetradecylammoniumsuccinate**: m.p.116°C. Anal. Calc. For$C_{32}H_{68}N_2O_4$: C, 70.54; H, 12.58; N, 5.14. Found: C, 70.64; H, 12.59; N, 4.86 %. FT-IR (KBr): 3138, 2920, 2851, 2752, 2364, 2204, 1657, 1528, 1464, 1378, 1315, 1235, 1170, 1086, 1054, 1028, 999, 923, 886, 840, 806, 721, 662, 578, 518, 475cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.41 (br, N-H), 2.88 (t, J = 7.48Hz, 4H, $^-$OOC($C\underline{H_2}$)$_2$COO$^-$), 2.37 (m, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_{11}$CH$_3$), 1.66 (m, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_{11}$CH$_3$), 1.25 (brS, 44H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_{11}$CH$_3$), 0.87 (t, J = 6.39 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_{11}C\underline{H_3}$).
9. **Di-pentadecylammoniumsuccinate**: m.p.116°C. Anal. Calc. For$C_{34}H_{72}N_2O_4$: C, 71.27; H, 12.67; N, 4.89. Found: C, 71.43; H, 12.95; N, 5.23 %. FT-IR (KBr): 3435, 3140, 2920, 2851, 2361, 2203, 1657, 1529, 1463, 1378, 1234, 1170, 1053, 925, 806, 721, 662cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 4.12 (br, N-H), 2.84 (t, J = 7.38Hz, 4H, $^-$OOC($C\underline{H_2}$)$_2$COO$^-$), 2.32 (m, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_{12}$CH$_3$), 1.62 (m, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_{12}$CH$_3$), 1.18 (brS, 48H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_{12}$CH$_3$), 0.81 (t, J = 6.50 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_{12}C\underline{H_3}$).
10. **Di-hexadecylammoniumsuccinate**: m.p.118°C. Anal. Calc. For$C_{36}H_{76}N_2O_4$: C, 71.94; H, 12.75; N, 4.66. Found: C, 72.01; H, 12.96; N, 4.63 %. FT-IR (KBr): 3439, 3138, 2920, 2851, 2358, 2203, 1656, 1528, 1465, 1379, 1234, 1171, 1054, 924, 806, 721, 662cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 3.48 (br, N-H), 2.86 (t, J = 7.53Hz, 4H, $^-$OOC($C\underline{H_2}$)$_2$COO$^-$), 2.33 (m, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_{13}$CH$_3$), 1.63 (m, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_{13}$CH$_3$), 1.17 (brS, 52H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_{13}$CH$_3$), 0.80 (t, J = 6.50 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_{13}C\underline{H_3}$).
11. **Di-dodecylammoniumadipate**: m.p.136°C. Anal. Calc. For$C_{30}H_{64}N_2O_4$.4/3CH_3OH: C, 67.26; H, 12.49; N, 5.01. Found: C, 66.95; H, 12.73; N, 5.13 %. FT-IR (KBr): 2953, 2917, 2851, 2577, 2364, 2200, 1661, 1630, 1572, 1512, 1396, 1328, 1287, 1210, 1179, 1126, 1050, 1025, 984, 917, 835, 718, 640, 515, 451, 429cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.38 (br, N-H), 2.61 (t, J = 7.30Hz, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_9$CH$_3$), 1.93(brS, 4H, $^-$OOC $C\underline{H_2}$CH$_2$CH$_2C\underline{H_2}$COO$^-$), 1.44 (m, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_9$CH$_3$), 1.32 (m, 4H, $^-$OOC CH$_2$C$\underline{H_2}$C$\underline{H_2}C$H$_2$COO$^-$), 1.02 (brS, 36H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_9$CH$_3$), 0.65 (t, J = 6.43 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_9C\underline{H_3}$).
12. **Di-tridecylammoniumadipate**: m.p.141°C. Anal. Calc. For $C_{32}H_{68}N_2O_4$: C, 70.54; H, 12.58; N, 5.18. Found: C, 71.09; H, 12.91; N, 6.04 %. FT-IR (KBr): 3447, 2955, 2921, 2851, 2510, 2162, 1648, 1587, 1525, 1465, 1406, 1323, 1270, 1208, 1134, 1077, 1046, 989, 948, 915, 854, 814, 750, 723, 697, 648, 592, 521, 472, 435cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.28 (br, N-H), 2.60 (t, J = 7.59 Hz, 4H, $^+$NH$_3C\underline{H_2}$CH$_2$(CH$_2$)$_{10}$CH$_3$), 1.91(brS, 4H, $^-$OOC$C\underline{H_2}$CH$_2$CH$_2C\underline{H_2}$COO$^-$), 1.43 (m, 4H, $^-$OOCCH$_2$C$\underline{H_2}$C$\underline{H_2}C$H$_2$COO$^-$), 1.31 (m, 4H, $^+$NH$_3$CH$_2C\underline{H_2}$(CH$_2$)$_{10}$CH$_3$), 1.01 (brS, 40H, $^+$NH$_3$CH$_2$CH$_2$($C\underline{H_2}$)$_{10}$CH$_3$), 0.64(t, J = 6.45 Hz, 6H, $^+$NH$_3$CH$_2$CH$_2$(CH$_2$)$_{10}C\underline{H_3}$).

13. **Di-tetradecylammoniumadipate**: m.p.141°C. Anal. Calc. For $C_{34}H_{72}N_2O_4$: C, 71.27; H, 12.67; N, 4.89. Found: C, 71.45; H, 12.82; N, 5.12 %. FT-IR (KBr): 2953, 2917, 2851, 2193, 1664, 1625, 1574, 1509, 1472, 1423, 1395, 1329, 1209, 1177, 1126, 1054, 996, 959, 917, 870, 718, 640, 577, 519, 479, 437, 406cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.33 (br, N-H), 2.85 (t, J = 7.58 Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{11}CH_3$), 2.17 (brS, 4H, $^-OOC\ C\underline{H_2}CH_2CH_2C\underline{H_2}COO^-$), 1.68 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{11}CH_3$), 1.56 (m, 4H, $^-OOCCH_2C\underline{H_2}C\underline{H_2}CH_2COO^-$) 1.26(brS, 44H, $^+NH_3CH_2CH_2(C\underline{H_2})_{11}CH_3$), 0.89(t, J = 6.43 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{11}C\underline{H_3}$).
14. **Di-pentadecylammoniumadipate**: m.p.146°C. Anal. Calc. For$C_{36}H_{76}N_2O_4$: C, 71.94; H, 12.75; N, 4.66. Found: C, 72.26; H, 13.01; N, 4.37 %. FT-IR (KBr): 3435, 2920, 2851, 2167, 1647, 1526, 1466, 1406, 1323, 1269, 1244, 1208, 1133, 1077, 915, 887, 847, 810, 747, 723, 697, 648, 591, 523, 480, 406cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.16 (br, N-H), 2.85 (m, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{12}CH_3$), 2.16 (brS, 4H, $^-OOCC\underline{H_2}CH_2CH_2C\underline{H_2}COO^-$), 1.66 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{12}CH_3$), 1.55 (m, 4H, $^-OOCCH_2C\underline{H_2}C\underline{H_2}CH_2COO^-$) 1.24(brS, 48H, $^+NH_3CH_2CH_2(C\underline{H_2})_{12}CH_3$), 0.87(t, J = 6.39 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{12}C\underline{H_3}$).
15. **Di-hexadecylammoniumadipate**: m.p.147°C. Anal. Calc. For$C_{38}H_{80}N_2O_4$: C, 72.55; H, 12.82; N, 4.45. Found: C, 72.86; H, 13.08; N, 4.09 %. FT-IR (KBr): 2917, 2850, 2571, 2193, 1663, 1624, 1547, 1509, 1471, 1424, 1395, 1329, 1208, 1177, 1127, 1056, 976, 917, 825, 767, 717, 577, 519, 483, 430cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.35 (br, N-H), 2.64 (t, J = 7.52Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{13}CH_3$), 1.96 (brS, 4H, $^-OOCC\underline{H_2}CH_2CH_2C\underline{H_2}COO^-$), 1.45 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{13}CH_3$), 1.35 (m, 4H, $^-OOCCH_2C\underline{H_2}C\underline{H_2}CH_2COO^-$) 1.03 (brS, 52H, $^+NH_3CH_2CH_2(C\underline{H_2})_{13}CH_3$), 0.66(t, J = 6.48 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{13}C\underline{H_3}$).
16. **Di-dodecylammoniummaleate**: m.p.181°C. Anal. Calc. For$C_{28}H_{58}N_2O_4.CH_3OH$: C, 67.14; H, 12.05; N, 5.40. Found: C, 67.48; H, 12.27; N, 5.49 %. FT-IR (KBr): 2959, 2922, 2851, 2119, 1629, 1601, 1543, 1466, 1421, 1382, 1339, 1300, 1234, 1204, 1156, 1121, 1095, 1060, 1028, 970, 944, 893, 857, 769, 722, 656, 627, 518, 455, 433cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.82 (br, N-H), 6.08 (s, 2H, $^-OOCC\underline{H}=C\underline{H}COO^-$), 2.80 (t, J = 7.17Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_9CH_3$), 1.58 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_9CH_3$), 1.15 (brS, 36H, $^+NH_3CH_2CH_2(C\underline{H_2})_9CH_3$), 0.78(t, J = 6.47 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_9C\underline{H_3}$).
17. **Di-tridecylammoniummaleate**: m.p.182°C. Anal. Calc. For$C_{30}H_{62}N_2O_4.CH_3OH$: C, 68.08; H, 12.16; N, 5.12. Found: C, 68.79; H, 11.68; N, 5.20 %. FT-IR (KBr): 3365, 2922, 2852, 2361, 2142, 1643, 1569, 1508, 1470, 1423, 1397, 1306, 1192, 1169, 1123, 1086, 1057, 1029, 991, 948, 891, 850, 753, 720, 673, 621, 562, 519, 468, 433cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.36 (br, N-H), 6.15 (s, 2H, $^-OOCC\underline{H}=C\underline{H}COO^-$), 2.88 (t, J = 7.62Hz, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{10}CH_3$), 1.65 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{10}CH_3$), 1.24 (brS, 40H, $^+NH_3CH_2CH_2(C\underline{H_2})_{10}CH_3$), 0.87(t, J = 6.43 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{10}C\underline{H_3}$).
18. **Di-tetradecylammoniummaleate**: m.p.185°C. Anal. Calc. For$C_{32}H_{66}N_2O_4$: C, 70.80; H, 12.25; N, 5.16. Found: C, 70.53; H, 12.54; N, 5.75 %. FT-IR (KBr): 3182, 2921, 2851, 2357, 2116, 1630, 1540, 1469, 1422, 1383, 1300, 1224, 1201, 1158, 1060, 1031, 970, 945, 892, 857, 770, 724, 627, 540, 433cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.53 (br, N-H), 6.16 (s, 2H, $^-OOCC\underline{H}=C\underline{H}COO^-$), 2.88 (t, J = 7.44Hz, 4H,

$^{+}NH_3C\underline{H_2}CH_2(CH_2)_{11}CH_3$), 1.66 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{11}CH_3$), 1.24 (brS, 44H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{11}CH_3$), 0.87(t, J = 6.40 Hz, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{11}C\underline{H_3}$).

19. **Di-pentadecylammoniummaleate**: m.p.188°C. Anal. Calc. For$C_{34}H_{70}N_2O_4.CH_3OH$: C, 69.72; H, 12.37; N, 4.65. Found: C, 70.01; H, 12.52; N, 5.19 %. FT-IR (KBr): 3747, 2920, 2851, 2364, 1559, 1469, 1388, 1302, 1169, 853, 721, 666cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 6.15 (s, 2H, $^{-}OOCC\underline{H}=C\underline{H}COO^{-}$), 3.63 (br, N-H), 2.87 (t, J = 6.97Hz, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{12}CH_3$), 1.69 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{12}CH_3$), 1.25 (brS, 48H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{12}CH_3$), 0.87(t, J = 6.39 Hz, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{12}C\underline{H_3}$).
20. **Di-hexadecylammoniummaleate**: m.p.188°C. Anal. Calc. For$C_{36}H_{74}N_2O_4$: C, 72.19; H, 12.45; N, 4.68. Found: C, 71.88; H, 12.67; N, 4.39 %. FT-IR (KBr): 3182, 2920, 2851, 2559, 2117, 1629, 1541, 1469, 1423, 1383, 1301, 1215, 1158, 1090, 1060, 1006, 973, 944, 858, 770, 723, 628, 539, 433cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 5.86 (s, 2H, $^{-}OOCC\underline{H}=C\underline{H}COO^{-}$), 4.01 (br, N-H), 2.61 (t, J = 7.52Hz, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{13}CH_3$), 1.39 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{13}CH_3$), 1.03 (brS, 52H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{13}CH_3$), 0.66(t, J = 6.48 Hz, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{13}C\underline{H_3}$).
21. **Di-dodecylammoniumphthalate**: m.p.149°C. Anal. Calc. For$C_{32}H_{60}N_2O_4.H_2O$: C, 69.27; H, 11.26; N, 5.05. Found: C, 69.36; H, 11.59; N, 5.08 %. FT-IR (KBr): 3411, 2922, 2853, 2364, 2124, 1603, 1547, 1465, 1440, 1408, 1148, 1084, 1037, 857, 830, 750, 723, 693, 650, 425cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.52 (m, 2H, 3,6-H of $C_6H_4(COO^{-})_2$, 7.27 (m, 2H, 4,5-H of $C_6H_4(COO^{-})_2$, 2.61 (t, J = 7.62Hz, 4H, $^{+}NH_3C\underline{H_2}(CH_2)_{10}CH_3$), 1.25 (m, 40H, $^{+}NH_3CH_2(C\underline{H_2})_{10}CH_3$), 0.89(t, J = 6.29 Hz, 6H, $^{+}NH_3CH_2(CH_2)_{10}C\underline{H_3}$).
22. **Di-tridecylammoniumphthalate**: m.p.140°C. Anal. Calc. For$C_{34}H_{64}N_2O_4.CH_3OH$: C, 70.42; H, 11.48; N, 4.69. Found: C, 70.87; H, 12.04; N, 4.93 %. FT-IR (KBr): 3401, 2924, 2854, 2121, 1603, 1555, 1466, 1440, 1407, 1387, 1257, 1148, 1084, 1037, 952, 856, 830, 750, 723, 693, 651, 582, 428cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.55 (m, 2H, 3,6-H of $C_6H_4(COO^{-})_2$, 7.28 (m, 2H, 4,5-H of $C_6H_4(COO^{-})_2$, 2.62 (t, J = 7.71Hz, 4H, $^{+}NH_3C\underline{H_2}(CH_2)_{11}CH_3$), 1.24 (m, 44H, $^{+}NH_3CH_2(C\underline{H_2})_{11}CH_3$), 0.89(t, J = 6.56 Hz, 6H, $^{+}NH_3CH_2(CH_2)_{11}C\underline{H_3}$).
23. **Di-tetradecylammoniumphthalate**: m.p.125°C. Anal. Calc. For$C_{36}H_{68}N_2O_4$: C, 72.92; H, 11.56; N, 4.72. Found: C, 71.42; H, 11.53; N, 4.74 %. FT-IR (KBr): 3500, 2920, 2851, 2103, 1649, 1556, 1471, 1442, 1405, 1379, 1167, 1085, 1036, 954, 833, 749, 722, 695, 520, 484, 431cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.55 (m, 2H, 3,6-H of $C_6H_4(COO^{-})_2$, 7.28 (m, 2H, 4,5-H of $C_6H_4(COO^{-})_2$, 2.62 (brS, 4H, $^{+}NH_3C\underline{H_2}(CH_2)_{12}CH_3$), 1.24 (m, 48H, $^{+}NH_3CH_2(C\underline{H_2})_{12}CH_3$), 0.87(t, J = 6.52 Hz, 6H, $^{+}NH_3CH_2(CH_2)_{12}C\underline{H_3}$).
24. **Di-pentadecylammoniumphthalate**: m.p.115°C. Anal. Calc. For$C_{38}H_{72}N_2O_4$: C, 73.50; H, 11.69; N, 4.51. Found: C, 71.9; H, 12.18; N, 4.24 %.FT-IR (KBr): 2921, 2851, 2110, 1557, 1471, 1404, 1380, 1168, 1085, 1037, 952, 832, 753, 723, 693, 652, 580, 429cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.53 (m, 2H, 3,6-H of $C_6H_4(COO^{-})_2$, 7.26 (m, 2H, 4,5-H of $C_6H_4(COO^{-})_2$, 2.60 (t, J = 7.54, 4H, $^{+}NH_3C\underline{H_2}(CH_2)_{13}CH_3$), 1.24 (m, 52H, $^{+}NH_3CH_3(C\underline{H_2})_{13}CH_3$), 0.87(t, J = 6.42 Hz, 6H, $^{+}NH_3CH_2(CH_2)_{13}C\underline{H_3}$).
25. **Di-hexadecylammoniumphthalate**: m.p.125°C. Anal. Calc. For$C_{40}H_{76}N_2O_4$: C, 74.02; H, 11.80; N, 4.32. Found: C,73.42; H, 11.90; N, 4.1 %.FT-IR (KBr): 3494, 3058, 2950, 2918, 2848, 1645, 1600, 1556, 1506, 1471, 1438, 1406, 1379, 842, 752,

719, 700cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 7.60 (m, 2H, 3,6-H of $C_6H_4(COO^-)_2$, 7.32 (m, 2H, 4,5-H of $C_6H_4(COO^-)_2$, 2.65 (t, J = 7.40, 4H, $^+NH_3C\underline{H_2}(CH_2)_{14}CH_3$), 1.27 (m, 56H, $^+NH_3CH_3(C\underline{H_2})_{14}CH_3$), 0.89(t, J = 6.42 Hz, 6H, $^+NH_3CH_2(CH_2)_{14}C\underline{H_3}$).

26. **Di-dodecylammoniumisophthalate**: m.p.143°C. Anal. Calc. For $C_{32}H_{60}N_2O_4.1/3CH_3OH$: C, 70.16; H, 11.29; N, 5.06. Found: C, 70.44; H, 11.54; N, 5.16 %. FT-IR (KBr): 3425, 2923, 2853, 2360, 2159, 1607, 1559, 1470, 1423, 1365, 1267, 1154, 1073, 936, 909, 816, 747, 710, 508, 456 cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 8.35 (s, 1H, 2-H of $C_6H_4(COO^-)_2$, 7.95 (d, J = 7.39Hz, 2H, 4,6-H of $C_6H_4(COO^-)_2$, 7.27 (m,1H, 5-H of $C_6H_4(COO^-)_2$, 2.81 (brS, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_9CH_3$), 2.52 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_9CH_3$), 1.23 (m, 36H, $^+NH_3CH_2CH_2(C\underline{H_2})_9CH_3$), 0.87(t, J = 5.811 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_9C\underline{H_3}$).
27. **Di-tridecylammoniumisophthalate**: m.p.120°C. Anal. Calc. For$C_{34}H_{64}N_2O_4$: C, 72.29; H, 11.42; N, 4.96. Found: C,; H,; N, %. FT-IR (KBr): 3403, 2920, 2852, 2160, 1603, 1562, 1470, 1423, 1362, 1266, 1153, 1121, 1093, 1073, 1026, 991, 937, 902, 816, 746, 711, 657, 508cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ = 8.35 (s, 1H, 2-H of $C_6H_4(COO^-)_2$, 7.94 (d, J = 6.54Hz, 2H, 4,6-H of $C_6H_4(COO^-)_2$, 7.25 (m,1H, 5-H of $C_6H_4(COO^-)_2$, 2.81 (brS, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{10}CH_3$), 2.51 (brS, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{10}CH_3$), 1.22 (m, 40H, $^+NH_3CH_2CH_2(C\underline{H_2})_{10}CH_3$), 0.85(t, J = 6.44 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{10}C\underline{H_3}$).
28. **Di-tetradecylammoniumisophthalate**: m.p.159°C. Anal. Calc. For $C_{36}H_{68}N_2O_4$: C, 72.96; H, 11.56; N, 4.72. Found: C, 72.32; H, 12.16; N, 4.77 %. FT-IR (KBr): 3405, 2919, 2851, 2160, 1630, 1603, 1562, 1470, 1423, 1389, 1360, 1266, 1230, 1154, 1092, 1072, 1031, 997, 958, 937, 903, 873, 817, 746, 711, 656, 507cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 8.33 (s, 1H, 2-H of $C_6H_4(COO^-)_2$, 7.95 (d, J = 6.54Hz, 2H, 4,6-H of $C_6H_4(COO^-)_2$, 7.28 (m,1H, 5-H of $C_6H_4(COO^-)_2$, 4.98 (br,N-H), 2.78 (m, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{11}CH_3$), 1.49 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{11}CH_3$), 1.25 (m, 44H, $^+NH_3CH_2CH_2(C\underline{H_2})_{11}CH_3$), 0.88(t, J = 6.65 Hz, 6H, $^+NH_3CH_2CH_2(CH_2)_{11}C\underline{H_3}$).
29. **Di-pentadecylammoniumisophthalate**: m.p.160°C. Anal. Calc. For $C_{38}H_{72}N_2O_4.CH_3OH$: C, 71.73; H, 11.73; N, 4.29. Found: C, 72.44; H, 12.14; N, 4.55 %. FT-IR (KBr): 3402, 2919, 2851, 2160, 1603, 1562, 1471, 1424, 1363, 1267, 1154, 1124, 1093, 1073, 1003, 968, 931, 903, 818, 746, 711, 657, 508cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ =8.535 (s, 1H, 2-H of $C_6H_4(COO^-)_2$, 8.01 (d, J = 7.50 Hz, 2H, 4,6-H of $C_6H_4(COO^-)_2$, 7.38 (t, J = 7.65, 1H, 5-H of $C_6H_4(COO^-)_2$, 2.91 (t, J = 7.65, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{12}CH_3$), 1.63 (d, J = 6.60, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{12}CH_3$), 1.30 (brS, 48H, $^+NH_3CH_2CH_2(C\underline{H_2})_{12}CH_3$), 0.89(m, 6H, $^+NH_3CH_2CH_2(CH_2)_{12}C\underline{H_3}$).
30. **Di-hexadecylammoniumisophthalate**: m.p.160°C. Anal. Calc. For $C_{40}H_{76}N_2O_4.CH_3OH$: C, 74.02; H, 11.80; N, 4.32. Found: C, 73.79; H, 12.33; N, 4.15 %. FT-IR (KBr): 3412, 2918, 2851, 2162, 1634, 1604, 1555, 1472, 1430, 1367, 1266, 1156, 1091, 1059, 975, 938, 900, 817, 742, 716, 655, 508, 461cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ = 8.54 (s, 1H, 2-H of $C_6H_4(COO^-)_2$, 8.02 (m, 2H, 4,6-H of $C_6H_4(COO^-)_2$, 7.38 (t, J = 7.65, 1H, 5-H of $C_6H_4(COO^-)_2$, 2.90 (t, J = 7.66, 4H, $^+NH_3C\underline{H_2}CH_2(CH_2)_{13}CH_3$), 1.61 (m, 4H, $^+NH_3CH_2C\underline{H_2}(CH_2)_{13}CH_3$), 1.29 (brS, 52H, $^+NH_3CH_2CH_2(C\underline{H_2})_{13}CH_3$), 0.92(m, 6H, $^+NH_3CH_2CH_2(CH_2)_{13}C\underline{H_3}$).

31. **Di-dodecylammoniumtartarate**: m.p.207°C. Anal. Calc. For $C_{28}H_{60}N_2O_6$: C, 64.58; H, 11.61; N, 5.38. Found: C, 64.61; H, 11.40; N, 5.93 %. FT-IR (KBr): 3308, 3128,

2921, 2852, 2095, 1633, 1579, 1467, 1359, 1239, 1202, 1171, 1112, 1059, 1022, 978, 932, 910, 884, 832, 790, 757, 720, 700, 611, 541, 456cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ = 4.87 (s, $^{-}OOC(CHO\underline{H})_2COO^{-}$), 4.30 (s, 2H, $^{-}OOC(C\underline{H}OH)_2COO^{-}$), 2.90 (t, J = 7.63Hz, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_9CH_3$), 1.62 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_9CH_3$), 1.29 (brS, 36H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_9CH_3$), 0.89 (t, J = 6.48, 6H, $^{+}NH_3CH_2CH_2(CH_2)_9C\underline{H_3}$).

32. **Di-tridecylammoniumtartarate**: m.p.212°C. Anal. Calc. For $C_{30}H_{64}N_2O_6$: C, 65.65; H, 11.75; N, 5.70. Found: C, 65.93; H, 11.87; N, 5.39 %. FT-IR (KBr): 2922, 2851, 2113, 1634, 1581, 1462, 1359, 1200, 1169, 1111, 1058, 987, 949, 909, 844, 807, 722, 701, 613, 542, 468, 433cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ = 4.87 (s, $^{-}OOC(CHO\underline{H})_2COO^{-}$), 4.29 (s, 2H, $^{-}OOC(C\underline{H}OH)_2COO^{-}$), 2.90 (t, J = 7.63Hz, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{10}CH_3$), 1.62 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{10}CH_3$), 1.28 (brS, 40H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{10}CH_3$), 0.89 (t, J = 6.54, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{10}C\underline{H_3}$).
33. **Di-tetradecylammoniumtartarate**: m.p.211°C. Anal. Calc. For $C_{32}H_{68}N_2O_6$: C, 66.62; H, 11.88; N, 4.86. Found: C, 67.09; H, 12.39; N, 5.03 %. FT-IR (KBr): 2920, 2850, 2361, 2115, 1634, 1591, 1522, 1461, 1424, 1358, 1200, 1169, 1111, 1058, 1029, 990, 954, 910, 886, 790, 723, 701, 615, 542, 501cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ = 4.30 (s, 2H, $^{-}OOC(C\underline{H}OH)_2COO^{-}$), 2.87 (brS, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{11}CH_3$), 1.67 (brS, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{11}CH_3$), 1.25 (brS, 44H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{11}CH_3$), 0.88 (t, J = 6.17, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{11}C\underline{H_3}$).
34. **Di-pentadecylammoniumtartarate**: m.p.209°C. Anal. Calc. For $C_{34}H_{72}N_2O_6$: C, 67.50; H, 12.00; N, 4.63. Found: C, 67.38; H, 11.98; N, 5.67 %. FT-IR (KBr): 2920, 2850, 2363, 1634, 1580, 1523, 1461, 1358, 1198, 1168, 1112, 1059, 1001, 911, 886, 842, 778, 723, 701, 614, 542, 479, 420cm^{-1}. ^{1}H NMR ($CDCl_3$) (300MHz) δ =^{1}H NMR (CD_3OD) (300MHz) δ = 4.18 (s, 2H, $^{-}OOC(C\underline{H}OH)_2COO^{-}$), 2.77 (t, J = 7.50, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{12}CH_3$), 1.51 (brS, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{12}CH_3$), 1.15 (brS, 48H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{12}CH_3$), 0.76 (t, J = 6.30, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{12}C\underline{H_3}$).
35. **Di-hexadecylammoniumtartarate**: m.p.207°C. Anal. Calc. For $C_{36}H_{76}N_2O_6$: C, 68.31; H, 12.10; N, 4.43. Found: C, 67.13; H, 12.10; N, 4.46 %. FT-IR (KBr): 3401, 2918, 2851, 2364, 1640, 1567, 1471, 1360, 1215, 1164, 1122, 1071, 898, 717, 645, 522, 488, 423cm^{-1}. ^{1}H NMR (CD_3OD) (300MHz) δ =^{1}H NMR (CD_3OD) (300MHz) δ = 4.18 (s, 2H, $^{-}OOC(C\underline{H}OH)_2COO^{-}$), 2.77 (t, J = 7.50, 4H, $^{+}NH_3C\underline{H_2}CH_2(CH_2)_{13}CH_3$), 1.66 (m, 4H, $^{+}NH_3CH_2C\underline{H_2}(CH_2)_{13}CH_3$), 1.30 (brS, 52H, $^{+}NH_3CH_2CH_2(C\underline{H_2})_{13}CH_3$), 0.89 (t, J = 6.6, 6H, $^{+}NH_3CH_2CH_2(CH_2)_{13}C\underline{H_3}$).

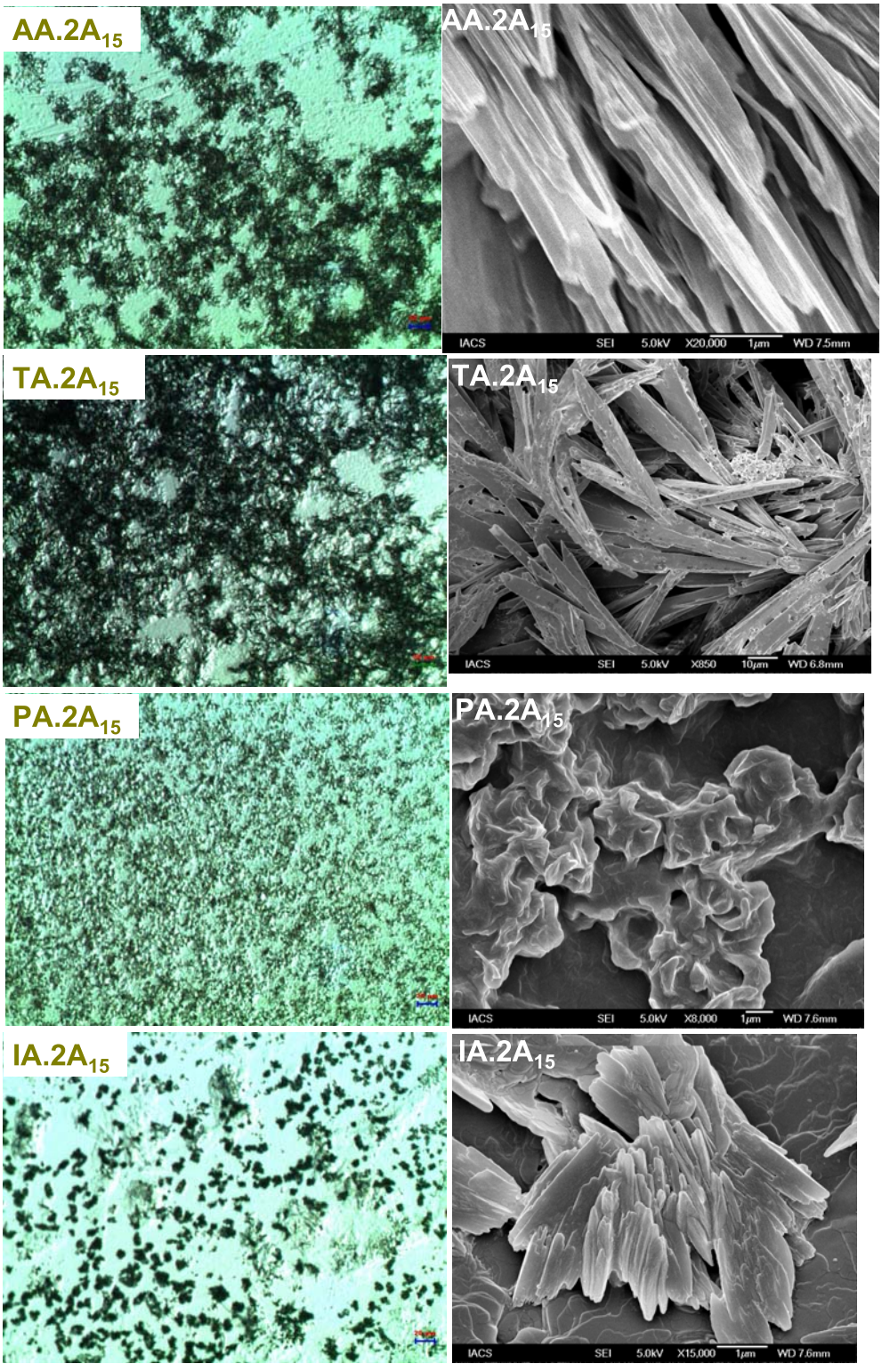

Figure S1: OM (230x, bar = 20 μm) and SEM (bar = 10 μm for **TA.2A$_{15}$** and 1 μm for the rest of the salts) of the gelator salts.