

hand, structural heterogeneities (domains) are real (either alkyl groups or groups of ions), on the other hand, structural heterogeneities result from erroneous interpretations of experimental data. Structural heterogeneities are considered to determine all properties of IL as dissolution, solvation rate, self-diffusion, diffusion of substances dissolved in IL, electron transport etc. IL structures were investigated by SAXS and WAXS methods, by diffraction of synchrotron radiation and neutrons followed by interpretation of the radial distribution functions by molecular dynamic simulations. Structural model of IL is not available now in spite of the active research and great demand for such model. IL structure model shortly presented below is based on literature experimental data for imidazolium and tetraalkylammonium ILs with cation:anion ratio 1:1.

In accordance with the suggested model, 4 cations and 4 anions form an octupole and alkyl tails belonging to the neighbour octupoles are combined in pairs giving hydrocarbon domains. Octupoles and alkyl domains are two structural heterogeneities which construct IL structure. Octupoles are distributed in place of carbon atoms in the diamond structure and two diamond structures are inserted in one another with a shift for a half of the cubic cell dimension (diamond structure is friable so octupoles of one diamond structure fill the voids of another diamond structure). Alkyls are arranged along the C-C bond in diamond structure. Diamond-like cubic structure of IL can't help containing fragments of lonsdaleite structure and intermediate configurations. That is one of important reasons for the long range order absence.

Octupole combination of cations and anions is confirmed for alkylammonium (alkylphosphonium) IL. Nitrogen (phosphorous) atoms of four cations are distributed upon cube vertexes and three alkyl chains of each cation are situated above the face diagonal of the cube, i.e. pairs of alkyls are formed above one of two diagonals of any cubic face what means the alkyl domain existence. Four more vertexes of the cube are occupied with anions forming an octupole together with four cations. The fourth alkyl chain of each cation is oriented off the cube along the three-fold axis of octupole. The nearest octupoles combine such alkyls in pairs in the diamond-like (lonsdaleite-like) structures similarly to imidazolium IL. The suggested model is close to the structure of concentrated solutions of electrolytes.

Keywords: ionic, liquid, model

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The crystal engineering approach to design the pheromone releasing LMWG

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Gels are ubiquitous in nature and in everyday life. Starting from protoplasm to shaving cream, all are gel. It is a visco-elastic soft material comprising of a small amount of solid and a huge number of organic (organo gel) or aqueous (hydro gel) solvent(s). In a typical experiment, a relatively dilute solution of a gelator is heated and cooled bellow the critical temperature (sol-gel transition temperature), the immobilization of solvent occur by withstanding its own weight is termed as gel [1]. Under several kind of microscopic observation, it is found that, 1D self assembled fibrillar network (SAFIN) are cross linked among themselves via junction zones to form 3D matrix to arrest the flow of solvent. As SAFINs are the key to gel formation,

it is very important to investigate its molecular level self assembling by analyzing the crystal structure. It is not possible to obtain an x-ray crystal structure in its native state, as submicrometer size SAFINs are very poorly diffracting along with the scattering contribution of solvent molecules. Ab initio crystal structure determination of SAFIN using x-ray powder diffraction (XRPD) with very slow scan speed may be an alternative one but such a method of structure determination is not routine yet and requires high-intensity synchrotron beams, which are not readily accessible.

However, it was proposed by Shinkai nearly a decade ago that 1D hydrogen bonded networks promotes gelation whereas 2D and 3D networks either produce weak gels or no gelation at all. The fact that this hypothesis was indeed based on a logical foundation was most explicitly demonstrated by us by exploiting supramolecular synthons, which was first proposed by Desiraju in *Crystal Engineering*. We have identified and exploited some supramolecular synthones, namely Primary Ammonium Monocarboxylate (PAM), Primary ammonium Dicarboxylate (PAD), Secondary Ammonium Monocarboxylate (SAM) and Secondary Ammonium Dicarboxylate (SAD) synthons, which are robust enough to produce 1D hydrogen bonded network (HBN) with desired fictionalization.

Easy access to a class of chiral gelators has been achieved by exploiting primary ammonium monocarboxylate (PAM), a supramolecular synthon. A combinatorial library comprising of 16 salts, derived from 5 lamino acid methyl esters and 4 cinnamic acid derivatives, has been prepared and scanned for gelation. Remarkably, 14 out of 16 salts prepared (87.5% of the salts) show moderate to good gelation abilities with various solvents. Anti-solvent induced instant gelation at room temperature has been achieved in all the gelator salts, indicating that the gelation process is indeed an aborted crystallization phenomenon. Rheology, optical and scanning electron microscopy, small angle neutron scattering, and X-ray powder diffraction have been used to characterize the gels. A structure-property correlation has been attempted, based on these data, in addition to the single-crystal structures of 5 gelator salts. Analysis of the FT-IR and ¹H NMR spectroscopy data reveals that some of these salts can be used as supramolecular containers for the slow release of certain pest sex pheromones. The present study clearly demonstrates the merit of crystal engineering and the supramolecular synthon approach in designing new materials with multiple properties.

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Keywords: crystal engineering, supramolecular synthon, sex pheromones

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Structure of a new μ -oxalic acid- μ -oxalato -dicaesium, Cs₂(H₂C₂O₄)(C₂O₄) at 100K

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As a part of our study concerning the polymeric metallic dicarboxylates, their supramolecular features and their fascinating and attractive architectures, several oxalato-based alkali metal have been obtained as monometallic as well as bimetallic single crystals with Rb [1], [2], Li and Cs atoms. For the two first alkali metals, the structural investigations have conclude that the corresponding compounds have the specificities of coordination polymers .

Concerning the Cs atom, two oxalato-based compounds have been previously reported, one formed with the partially deprotonated acid CsHC₂O₄ [3] and the other containing both partially deprotonated

and totally protonated acid $\text{Cs}(\text{H}_2\text{C}_2\text{O}_4)(\text{HC}_2\text{O}_4)(\text{H}_2\text{O})_2$ [4]. We focus here on the structural reinvestigation of a caesium oxalate at 100 K. The structure is resolved in the space group $P2_1/c$, with the lattice parameters consistent with the data reported in [3], ($a=10.3677(10)\text{\AA}$, $b=6.7050(15)\text{\AA}$, $c=6.5849(8)\text{\AA}$, $\alpha=93.552(4)^\circ$). However, the new XRD structural study shows that instead of the chemical formula suggested in [3], the compound contains both the acid and the dianion: $\text{Cs}_2(\text{H}_2\text{C}_2\text{O}_4)(\text{C}_2\text{O}_4)$.

The asymmetric unit contains one Cs atom, one half oxalate dianion $(\text{C}(1)\text{O}(1)\text{O}(2))$ and one half oxalic acid molecule $[\text{C}(2)\text{O}(3)\text{O}(4)\text{H}]$. The nine-coordinated caesium atom is surrounded by four centrosymmetrical $\text{H}_2\text{C}_2\text{O}_4$ molecules, acting in unidentate fashion, and four oxalato ligands. The dianion is involved in a chelation by one function and in unidentate mode by the second function. The 2D structure consists of double files of CsO_6 polyhedra, running along [001] and [010] directions. In the two kinds of files, each polyhedron is sharing one edge with its nearest neighbours forming layers of double files. Within the layers, the deprotonated ligands link the files, while the other ligands connect the double file layers.

The single H atom has been localized in the difference Fourier map. In this structure, it is noteworthy to point out that, in each kind of ligand, it occurs a distance C-OH longer than the others C-O distances, implying a vicinity of the proton near the O1 or O4 atom. Strong H-bonds involving O4 and/or O1, occur between acid molecules and oxalate anions, leading to files extending along [100] direction. Further studies should concern the H motion, eventually by H RMN and electrical conductivity.

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Key-words: oxalate, polymeric structure, static disordered H atoms

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Carbon nanotubes as nucleation agents in polypyrrole-carbon nanotube nanocomposites

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A nanocomposite has been synthesized by *in-situ* chemical polymerization using pyrrole (Py) as a monomer and single wall carbon nanotube (SWNT) as an additive component. Experiments show that PPy growth on the surface of SWNTs in the spherical and cylindrical core-shell structures. As a result of strong bonds with carbon nanotubes (CNTs) [1, 2], the radical monomers and oligomers forming during the polymerization are adsorbed and anchored on amorphous carbon and SWNT surfaces which act as preferable sites for nucleation and growth of PPy. Depending on the anchoring sites the growth modes give rise to different morphologies. Wide-angle X-ray diffraction patterns indicate a change in the crystallinity of PPy in the composite.

The FTIR and Raman spectra of PPy/SWNTs composites consist of a broad adsorption band in the special domain between 4000 and 2500 cm^{-1} , which is commonly assigned for the adsorption band of O-H, C-H, N-H groups. However, due to the intensity of this adsorption band relatively increases with the laser excitation intensity, a portion of the 3000-3500 cm^{-1} band is speculated as the photoluminescence arising from transitions between valence band to polaron or to bipolaron levels [3]. Charge transfer interaction between composite components likely brings

more new polaron and bipolaron levels into the band gap of PPy.

The Raman spectra of the composite show the change in 1590, 1280 cm^{-1} and 940 cm^{-1} peaks. The band located at about 940 cm^{-1} is assigned to the ring deformation associated with radical cation (polaron state) while the band around 1590 cm^{-1} is the tangential mode (G-band) associated with sp^2 -hybridized carbon atoms (C=C bond) of SWNTs and PPy. The 1280 cm^{-1} band in PPy/SWNTs is assumed to be the superposition of both 1310 and 1253 cm^{-1} bands which stand for the bipolaron state of PPy [4, 5]. The decline of 940 cm^{-1} band and the emergence of 1280 cm^{-1} band in Raman spectra then indicate the transition from polaron to bipolaron state, i.e., indicate an increase in conductivity of PPy.

The UV-Vis spectra of PPy and PPy/SWNTs show two major peaks centering around 340 nm and 460 nm. The 340 nm adsorption band stands for $\pi^*-\pi$ transition while the 460 nm adsorption band represents the bipolaronic transition in PPy relating to the oxidized levels. The 340 nm band is intensified and undergoes a redshift while the 460 nm band exhibits a blueshift when SWNTs are doped. The change in the intensity and position of these adsorption bands indicates a strong modification in electronic structure and polaron levels in PPy bandgap.

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Keywords: PPy, SWNTs, nanocomposite

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Molecular structure of binuclear Ag (I) complex of phenyl bis(2-pyridyl)phosphine

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The design of silver (I) complexes has attracted particular attention due to their interesting structures, photoluminescent, biological and pharmacological activities, such as anticancer and antifungal properties [1] we describe synthesis, spectroscopic studies and crystal structure of Ag(I) complex of phenyl bis(2-pyridyl)phosphine. This complex was synthesized by reacting 2-lithiopyridine and dichlorophenyl phosphine in Et_2O [2] $(\text{PhP}(2\text{-py})_2)$ followed by treating with AgNO_3 in water. Single-crystal X-ray analysis reveals that mentioned complex crystallizes in monoclinic system, with $P2_1/n$ space group. The structure of this complex consists of two silver atoms, two molecules of ligand that act as tridentate beside two nitrate ions. The $\text{Ag}\cdots\text{Ag}$ distances is 3.216 (9) \AA , which is shorter than the sum of the van der Waals radii of two silver atoms (3.44 \AA), suggesting the existence of metal-metal interaction between the silver atoms. The free oxygen atoms of nitrate ligands interact with hydrogen atoms of the pyridyl groups to form hydrogen bonding. The separations for $\text{C}(2)\cdots\text{O}(3)$, $\text{C}(3)\cdots\text{O}(2)$, $\text{C}(8)\cdots\text{O}(1)$ and $\text{C}(10)\cdots\text{O}(3)$ (symmetry code: $1/2+x, 3/2-y, 1/2+z, 5/2-x, -1/2+y, 3/2-z$ and $-1+x, y, z$) are 3.369(8), 3.355(8), 3.313(8) 3.332(8) \AA .

In order to verify presence of silver-silver intra-molecular bonding the electron density of the synthesized complex was studied in the context of Quantum Theory of Atoms in Molecules, QTAIM[3]. The electron density of the complex was obtained from a single point energy calculation on the X-ray resolved crystal structure by Win-GAMESS.08 suit of programs at the B3LYP combined with three different basis sets for different elements; 6-31G for carbon and hydrogen atoms, 6-31+G(d) for nitrogen, oxygen and phosphorus and DZVP (DFT orbitals)