

Development of Fluorescent Carbon Dots from Disposable Cups and as a Sensor to Detect Toxic Metal Ions from Contaminated Water

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Abstract—Our daily use paper cups, which were coated by ethylene molecule, were considered as the source to prepare Carbon dots(C-dot) using the environment friendly and greener solvent (IL) Imidazolium based Ionic Liquids. The hydrothermal method was adopted to prepare the fluorescent natured C-dots from this paper cups. The prepared fluorescent nature CQDs act as a promising probe for food quality detection and helps to find some hazardous impurities present in food materials and to detect toxic metals from the contaminated water through fluorescence quenching mechanism. The prepared C-dots were characterized using IR, UV, PL, and XRD.

Index Terms—paper cup, Hydrothermal method, Imidazolium based IL, Carbon Dot, fluorescent nature.

I. INTRODUCTION

Metal-based quantum dots, a new class of nano-materials, though it possess much interesting properties, such as high optical absorptivity, chemical stability, biocompatibility, and low toxicity [1], it also possess some limitations such as poor quantum yield, unable to tune their most of the emissions in NIR region and some toxicity towards biological functions. To eliminate such pitfalls, carbon-based materials in nano regime with same dimension (1-10nm), other than metals are considered as carbon dots (CQDs) were used in the most of scientific applications. These CQDs have the desired advantages over metal based QDs, as they have their comparable optical properties, low toxicity, environmental friendliness, low cost and can be prepared by simple synthetic and greener ways. Ever since the CQDs were invented, their applications and utility go in an enormous manner. During recent time many scientists concentrate to prepare CQDs

from carbon based raw materials including most of the waste materials. A number of research groups have endeavoured even to convert lower quality waste paper into valuable products [2-4]. However, many of them overlooked or ignored our day-to-day use of paper cups as a carbon source. These paper cups are lined inside with wax or a plastic lining to be waterproof, and that lining is made up of polyethylene from petroleum [5]. These paper cups are not mostly recycled, since they contain only limited (10%) recycled content[6]. But on economic and environmental benefits, paper recycling rates have increased now-a-days by nearly 20% within the last few decades [7-9]. In this regard, the present work concentrates to convert the paper from paper cups along with wax (polymer) material present in paper cups to fluorescent carbon dots as a value added material in food quality and safety detection.

Ionic liquids (ILs), such as organic and organo element salts, have recently gained attention in both academia and industry for their ability to dissolve cellulose and wax derivatives, such as fibers, papers, and membranes.[10-13] Compared to the conventional solvents, ILs are environmentally friendly and more effective alternatives due to the chemical and thermal stability, miscibility, and negligible vapor pressure over a wide temperature range with nonflammable nature.[12-14].

This environment friendly and greener solvent (IL) has unique properties, since it can be easily recovered and recycled after dissolving polymer like material, such as cellulose through a simple purification step[15,16]. These unique properties make IL as ideal solvents for many applications. Most notably, ILs can be easily recovered and recycled after dissolving wax through a

simple purification step with consistent, strong wax dissolving capacity.

Hence, the present work concentrates to prepare imidazolium based ionic liquids assisted fluorescent CQDs from paper cups using Hydrothermal method in a greener and eco-friendly way. This study will also demonstrate the potential use of the prepared CQDs as promising fluorescent probes or sensors to detect quality of food materials, and some hazardous impurities present in food materials through fluorescence quenching mechanism.

1.1 The main Objective of the present Study

- In the present study, polyethylene (PE) of paper cups has been chosen as a precursor.
- PEs present in paper cups creates the most carcinogenic health issues for humans and the environment.
- PEs in the paper cups, though contain 5%, in the entire content of paper cups, when it's been served in hot condition, it emits 25000 micro plastics, and hence, these PEs are considered as the most toxic to humans and using this paper cups only create cancer like disease to humans.
- The PE-coated paper cups also contain trace amounts of nitrates, fluorides, chlorides, and sulphates, which are also toxic to humans.
- The non-recyclability and non-degradable nature of these PEs also harm the environment severely, and do not allow the water level in uniform on the earth's surface.
- The non-degradable PEs also hinders the flow rate of rainwater on Earth's surface and reduces the uptake of water from the ground.
- To reduce the PEs present in paper cups, the present study aims to convert this non-degradable and distressing PEs into a value-added material.
- Hence, in the present work, C-dots from this PEs were prepared through a greener hydrothermal method using eco-friendly Ionic liquids as solvents, so as to minimize their harmfulness to society.
- The greener and eco-friendly solvents ILs used in the present study are imidazolium-based ILs.
- The prepared C-dots from PEs were used to find the adulteration present in the food materials.

- The C-dots from PEs mainly help to find toxic metals present in the contaminated water as well as in food materials.

II. METHODOLOGY ADAPTED IN THE PRESENT STUDY

2.1 Preliminary procedure adapted to prepare C-dots from PEs of paper Cups.

- Collected waste paper cups (PCs) were washed to eliminate filth present on the surface and then dried in a hot air oven.
- After that, these paper cups were cut into small pieces and dipped into hot water (temperature 60-70°C) for 3-4 hours.
- The thin lining made up of polyethylene (PE) was separated from the paper part [17].
- Then these wet paper clumps were removed from hot water and again dried in a hot air oven at 105°C for 24h.
- The dried material was ground and sieved with a 0.25 mm sieve.
- Then, 30 g of grounded material was added to the FeCl₃ solution (15g FeCl₃ + 150 mL distilled water).
- The mixture was kept on a magnetic stirrer (model no. 1MLH, REMI, India) and stirred for four hours.
- The material was then filtered and kept overnight in an oven for drying.
- After drying, the material was kept in a muffle furnace at 500°C for two hours, after that the material was crushed by mortar pestle to change it into powder form and was washed with deionized water 2-3 times.
- Then it was oven dried overnight to remove any unwanted impurities, and then it was used to prepare C-dots from the Hydrothermal method. [17]
- The obtained paper clumps prepared from paper cups (a) and the C-dots from PEs of paper cups (b) are shown in Fig-1

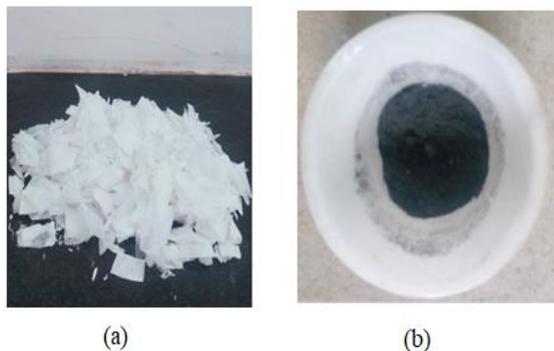


Fig-1 Paper clumps prepared from paper cups (a) and the C-dots from PEs of paper cups (b)

2.2 Preparation of CQDs from paper cups using IL through Hydrothermal method.

In a typical procedure, paper cups (2g) will first be dispersed in imidazolium-based ILs (50 ml). The contents will be refluxed for about 6-8 hrs. The obtained solution will be transferred to a Teflon reaction vessel and will be hydrothermally treated for 100 min at different temperatures (160, 200, or 250 °C). The large particles in the resulting suspension will then be removed by vacuum filtration through a filter paper (2.5 μm) and a micro-porous membrane (0.22 μm). The suspension of the CDs will be obtained by dialysis against Milli-Q water with a cellulose ester membrane bag (Mw = 3500). The obtained CDs were then concentrated by freeze-drying under vacuum for further characterization.

2.3 The importance and uniqueness of ionic Liquids as a solvent for soluble C-dots from polymer sources.

The highly fascinating complex phenomenon, ionic natured ionic Liquids (IL) with very low melting point, below 100°C, with the ability to undergo intermolecular interactions, and are able to form strong and unique structure-property relationships, are considered as efficient solvents in the existing solvents [18,19].

The competent nature of these ILs, due to their non-volatile, speedy reaction rate acceleration with high thermal stability, enables them to form a homogeneous mixture with all types of reactants and will be separated from the reaction mixture when the reactions are over.

ILs are also used as biphasic catalysts, or “immobilized catalysts”, in most of the systems, and

hence can dissolve polymers and long-chain moieties in an effortless manner.

Both IR and Raman spectral techniques provide detailed and exhaustive ILs structure-property relationships of ionic interaction with the prescribed reagents. Paschoal et al [20] suggest that ILs in the mid- and low-frequency range of IR and Raman accomplish excellent phase transfer by simply varying temperature and pressure.

Wang, et al [21] found, among the existing ILs, imidazolium based ILs, express highest chemical stability, and low rate of thermal decomposition and hydrolysis. These imidazolium-based ILs are also able to form an efficient, stable, and strong bond with nucleophilic reactions of anions under distinctive reaction conditions, such as even at higher temperatures and the presence of water, air, or even with various gases. The distinctive nature of these imidazolium-based anions also excels in polymer solubility, without harming the environment. This imidazolium-based ILs also act as a solvent as well as a catalyst in most of the reactions.

The wonderful and unique characteristics of these imidazolium-based ILs have been chosen in the present study as a medium as well as a solvent to solve the polyethylene (PE) present in the inner surface of paper cups.

The present study aims to solubilize PE present in the inside of paper cups using Imidazolium-based ILs under a greener method by adopting Hydrothermal, Microwave, and refluxing methods.

In the present study, the two imidazolium-based cations used are

- 1-ethylimidazole and
- 2-methylimidazole.

The various anions with lower viscosities that are preferred and used in the present study are,

- i) Chloride
- ii) Allyl chloride
- iii) Tetrafluoroborate (BF₄)
- iv) Hexafluorophosphate (PF₆)

The general Methodology adapted to synthesize Imidazolium-based ILs is

- Reflux method
- Hydrothermal method

The reflux method was adapted to synthesize imidazolium-based.

2.4 General procedure to Synthesis alkylimidazolium Chlorides

2.4.1 General Procedure to synthesis [2-methylimidazoliumchloride & 1-ethylimidazoliumchloride {[MIM]Cl } & {[EIM]Cl}

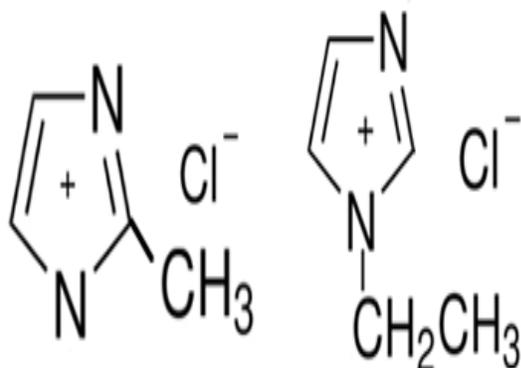


Fig-2 Chemical structures of [MIM]Cl & [EIM]Cl

- The alkyl imidazolium chloride chosen in the present study is 2-methylimidazolium chloride & 1-ethylimidazolium chloride
- In a 50 ml flat-bottomed round flask, 10 ml of (alkylimidazoles such as, 2-methylimidazole & 1-ethylimidazole) were dissolved in 20 ml of ethanol separately and stirred the contents at 40°C for half an hour.
- After half an hour, to the reaction mixture, 10 mL of con.HCl was added in a drop-by-drop manner in the respective flasks, and the resulting contents were stirred for 8 hours at 40°C.
- After 8 hours, the appearance of slight viscosity of the above two solutions confirmed the completion of the reactions.
- To get pure alkylimidazolium chlorides (2-methylimidazolium chloride, and 1-ethylimidazolium chloride) the above contents were evaporated through a vacuum distillation process to remove excess ethanol from each of the reaction mixtures.
- The obtained 2-methylimidazolium chloride and 1-ethylimidazolium chloride were collected separately and stored for further analysis.

- The schematic representation of the reflux method adapted in the present study is shown in Fig-3



Fig-3 The schematic representation of reflux method adapted in the present study

2.5 General Procedure to synthesis allyl-alkylimidazolium chlorides

10.5.1 General Procedure to synthesis 1-ethyl-2-allylimidazolium chloride {[AEIM]Cl} and 2-methyl-1-allylimidazolium chloride {[AMIM]Cl} & {[AEIM]Cl} & {[AMIM]Cl}

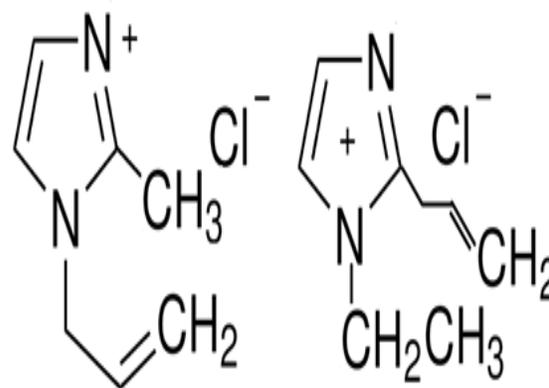


Fig-4 Chemical structures of [AEIM]Cl & [AMIM]Cl

- In a 50 ml flat RB, 20 ml of allyl chloride and 10 ml of alkyl imidazolium chlorides in a 2:1 molar ratio were taken in two separate flasks and refluxed for 8 hours at 55 °C with constant stirring.
- After 8 hours, the unreacted reagents and impurities were removed by vacuum distillation, and the obtained products (1-allyl-2-

methylimidazolium chloride and 2-allyl-1-ethyl imidazolium chloride) appeared in amber colour and were separated carefully from both the flasks and stored safely

2.6 Synthesis of -allyl-alkylimidazolium tetra fluoroborates

2.6.1 Synthesis of 1-allyl-2-methylimidazolium tetra fluoroborate and 2-allyl-1-ethylimidazolium tetra-fluoroborate

{[AMIM]BF₄} & {[AEIM]BF₄}

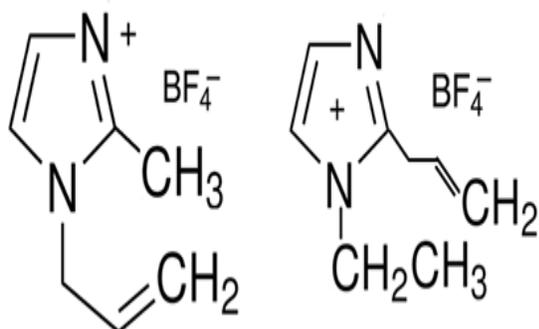


Fig-5 Chemical structures of {[AMIM]BF₄} and {[AEIM]BF₄}

- In two different 50 ml three-necked flasks, alkyl imidazoles (1-ethyl imidazole in DCM and 2-methyl imidazole in DMF) and the sodium salt of tetrahydroborate, each 0.05 mol, were taken and refluxed in the above mixtures separately at 80°C for 5 hours.
- Upon completion of the reactions, the mixtures were diluted separately with 50 mL of acetonitrile, at once it forms slight yellow and brown coloured precipitate of borate salt of 2-allyl- 1-ethylimidazolium and 1-allyl- 2-methylimidazolium based ILs, respectively.
- The formed precipitates were filtered through a pad of celite to remove the residual halide salts and concentrated the respective ILs using to rotary evaporator to form pale yellow and brown liquids for 2-allyl-1-ethylimidazole-based borates and 1-allyl-2-methylimidazole-based borates, respectively.
- The formed ILs was further dried under high vacuum at 80°C for 6 hours to remove the unwanted impurities.

2.7 Synthesis of allyl-alkylimidazolium hexafluoro phosphate

2.7.1 Synthesis of 1-allyl-2-methylimidazolium hexa fluorophosphate and 2-allyl-1-ethylimidazolium hexa fluorophosphate

[AMIM][PF₆]& [AEIM][PF₆]

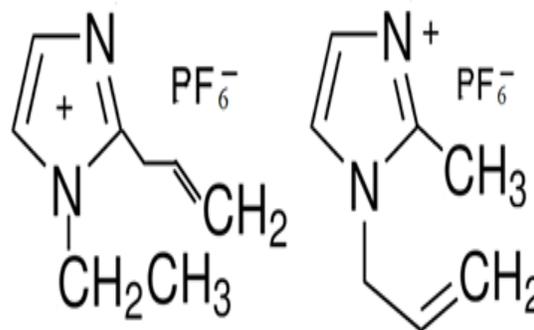


Fig-6 Chemical structures of [AEIM][PF₆] and [AMIM][PF₆]

- In a 50 ml three-necked flask, alkyl imidazoles (2-methyl imidazole in DCM & 1-ethyl imidazole in DMF) and potassium salt of hexafluoro phosphate, each 0.05 mol, were taken, and the above mixture was heated at 80°C for 5 hours.
- Then, 10 ml of water was added to the above mixtures separately and the bi-phase of water/ionic liquids was formed.
- The immiscible IL layers formed from each of the flasks were separated from the water phase, and then it was extracted with diethyl ether using reparatory funnel to extract the organic IL layer from the respective aqueous layers.
- The formed ILs in both the flasks as 1-ethyl-2-allyl imidazolim tetrafluoro borates and 2-methyl-1-allyl imidazolim tetrafluoro borates were dried separately in a vacuum at 120°C for 2 hrs, and the formed respective ILs were in pale yellow and pale black colour with the approximate yields of 60% were collected separately and stored carefully for further analysis.

2.8 Synthesis of C-dots Incorporated Ionic Liquids

- To synthesize C-dots incorporated ILs, the hydrothermal method was adapted.

- 0.5 g of C-dots prepared from PEs of paper cups were mixed with 10 ml of the respective ILS, and the contents were stirred at approximately 60° C for 3 to 4 hrs.
- Then the mixture was transferred to a 50 ml Teflon flask and kept in a 50 ml autoclave.
- Then this autoclave was kept in a Muffle furnace above 500°C (depending on the nature of ILs for 3 hrs).
- After 24 hours, the formed C-dots incorporated ILs were collected and used for further analysis.



Fig-7 The schematic representation of C-dots Incorporated ILs preparation Method

III. RESULTS AND DISCUSSIONS

3.1 FTIR spectral analysis of C-dots, IL, and IL incorporated C-dots

To find the nature of functional groups present on the surface of prepared C-dots from PEs, also known as p-dots of disposable paper cups, ionic liquids used in the present study, and IL-incorporated C-dots were analyzed by recording their FTIR spectral studies.

Hence, in the following section, each of the prepared C-dots (from PES of paper cups) ILs prepared in the present study, and Soluble C-dots incorporated ILs were recorded.

The main objective of the present study is, the non-degradable PEs from paper cups should be made degradable and to solubilize them using imidazolium-based Ionic Liquids.

The chosen ILs list was given in the experimental section itself.

To characterize the solubility of C-dots in the respective ILs, in the following section, each of the prepared C-dots from PEs, the ionic liquid used for the corresponding study, and the soluble C-dots in the respective ILs were separately taken, and each of the above materials FTIR were recorded and compared in a single graph to find the solubility of C-dots in IL, and also the nature of functional groups present on the surface of each of the components.

3.1.1 FTIR spectral analysis of C-dot, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride

In the first series, C-dots from PEs, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride were taken as shown in Fig. 1 and compared their properties and functional groups present on them.

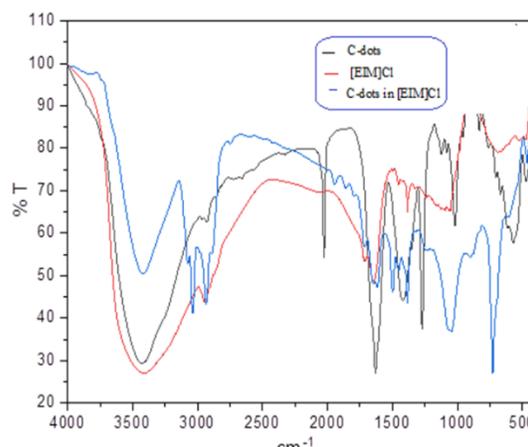


Fig.1 FTIR spectra of C-dot, 1-ethylimidazoliumchloride, and solubilized C-dots in 1-ethylimidazolium chloride

In Fig. 1, out of the three spectra, the C-dot solubilized 1-ethylimidazolium chloride exhibits sharp and strong peaks in all frequencies, confirming that the maximum solubility of C-dots of PE in the respective IL. Apart from that, the prepared C-dots are completely soluble

in the IL chosen, confirming the appearance of a sharp peak in this case.

The appearance of a peak around 3400 cm^{-1} in all the cases reveals that the bare C-dots and IL exhibit broad peaks, whereas the C-dots incorporated or solubilized in ILs exhibit sharp peaks.

The appearance of broad bands in both cases around 3400 cm^{-1} confirms the presence of hydroxyl groups on its surface in larger quantities. Whereas, the soluble C-dots in IL sharply exhibit the same peak, confirming the lesser amount of hydroxyl groups present on its peripheral surface.

Similarly, the peaks around 3000 cm^{-1} confirm the presence of $-\text{CH}_2$ and $-\text{CH}_3$ alkyl and aliphatic functional groups on its surfaces. These aliphatic groups are responsible for the hydrophobic nature of these bare C-dots. Hence, it produced, broad peak, whereas the IL and C-dots incorporated IL produced a sharp peak, confirming their ability to solubilize.

The presence of C-O and C=O carbonyl groups in all the cases around 1400 to 1650 cm^{-1} confirms the organic moiety present on its surface. Besides, peaks around 1587 cm^{-1} [22] in all cases confirms the presence of $-\text{NH}_2$ stretch, and the appearance of sharp strong peaks around 1200 cm^{-1} in all these cases again confirms the presence of C-N aromatic amines in each cases and the presence of some feable peaks around 500 cm^{-1} confirms the presence of COO carboxyl groups on its surfaces.

3.1.2. FTIR spectral analysis of C-dot, 2-methylimidazolium chloride, and the solubilized C-dots in 2-methylimidazolium chloride.

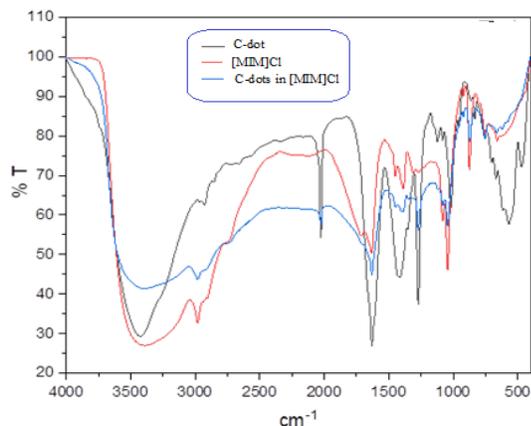


Fig-2 FTIR spectra of C-dot, 2-methylimidazolium chloride, and solubilized C-dots in 2-methylimidazolium chloride

In Fig. 2, as in the previous case, the C-dot incorporated 2-methylimidazolium chloride exhibits a sharper, stronger peak than the other two spectra, such as bare C-dots and 2-methylimidazolium chloride. All the peaks corresponding to hydroxyl, alkyl, and NH_2 appear in the same regions with slight deviations. The existence of slight deviation with strong, sharp peaks in the present case may be due to the presence of the methyl group in the second position of imidazole, rather than the ethyl group present in the 1-position of ethylimidazolium.

Generally, ILs with low alkyl chains have a more hydrophilic nature. Hence, 2-methylimidazolium chloride, the imidazole cation contains small alkyl group methyl, that too at the second position enhance hydrophilicity in larger amount and hence to soluble the C-dots from PEs in a higher manner, than the 1-ethyl imidazole, which contains ethyl group a bulky group at the first position induce hydrophobicity and viscosity, hence, their soluble nature towards C-dots from PEs are little bit less compared to 2-methylimidazolium chlorides.

3.1.3. FTIR spectral analysis of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2-methylimidazolium chloride.

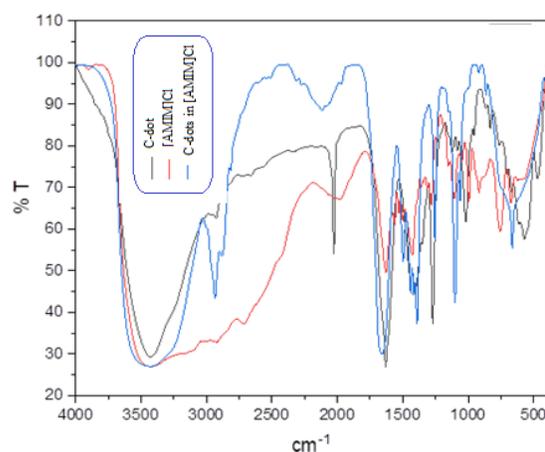


Fig. 3 FTIR spectra of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2-methylimidazolium chloride.

In Fig. 3, as in the previous case, the C-dot incorporated 1-allyl-2-methylimidazolium chloride exhibits a sharper, stronger peak than the other two spectra, such as bare C-dots and the solvent 1-allyl-2-methylimidazolium chloride.

All the peaks corresponding to hydroxyl, alkyl, and NH_2 appear in the same regions with slight deviations. The existence of slight deviation with strong, sharp peaks in the present case may be due to the presence of a methyl group in the second position of the imidazole ring, in which the allyl group is present in the first position. The influence of the inductive effect of the allyl group over the methyl group in the second position results in the higher solubility of C-dots from PEs of paper cups, and hence these peaks appear in a very strong and sharp manner.

The appearance of C=C stretching frequency in the range of $1580\text{--}1650\text{ cm}^{-1}$ and the presence of C-H out-of-plane bending vibrations around 930 cm^{-1} confirm the characteristic peak of the allyl group and confirm the presence of in the ILs of 1-allyl-2-methylimidazolium chloride. The appearance of a sharp, strong peak around 1490 cm^{-1} and a broad peak with the ring bending vibrations at 750 cm^{-1} confirms the presence of imidazole ring skeleton vibrations. The appearance of asymmetric and symmetric stretches around 2900 cm^{-1} and 2875 cm^{-1} respectively, authenticates the presence of a methyl group in the imidazolium skeleton.

3.1.4. FTIR spectral analysis of C-dot, 2-allyl-1-ethylimidazolium chloride, and the solubilized C-dots in 2-allyl-1-ethylimidazolium chloride.

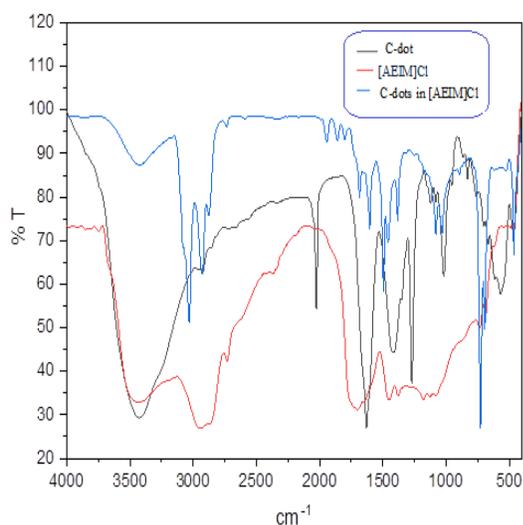


Fig- 4 FTIR spectra of C-dot, 2-allyl-1-ethylimidazolium chloride, and and the solubilized C-dots in 2-allyl-1-ethylimidazolium chloride.

The appearance of two sharp peaks at 2790 and 2990 cm^{-1} in the present cases reveals the authentication of an ethyl group in the imidazolium skeleton of 2-allyl-1-ethylimidazolium chloride based ILs.

All the peaks corresponding to hydroxyl, alkyl, and NH_2 appear in the same regions with slight deviations as in the previous case of ILs. The existence of slight deviation with strong, sharp peaks in the present case may be due to the presence of an ethyl group in first position of the imidazole ring, which has strong electron delocalization with the allyl group present in the second position, leading to higher solubility of the prepared C-dots, this implies the sharp appearance of a doublet at 2790 and 2990 cm^{-1} region.

The appearance of C=C stretching frequency in the range of 1580 cm^{-1} and the presence of C-H out-of-plane bending vibrations around 930 cm^{-1} confirm the characteristic peak of the allyl group and confirm the presence in the ILs of 2-allyl-1-ethylimidazolium chloride. The appearance of a sharp, strong peak around 1490 cm^{-1} and a broad peak with the ring bending vibrations at 450 cm^{-1} confirms the presence of imidazole ring skeleton vibrations, authenticating the presence of a methyl group in the imidazolium skeleton.

3.1.5 FTIR spectral analysis of C-dot, 2-allyl-1-ethylimidazolium Borate and the solubilized C-dots in 2-allyl-1-ethylimidazolium Borate

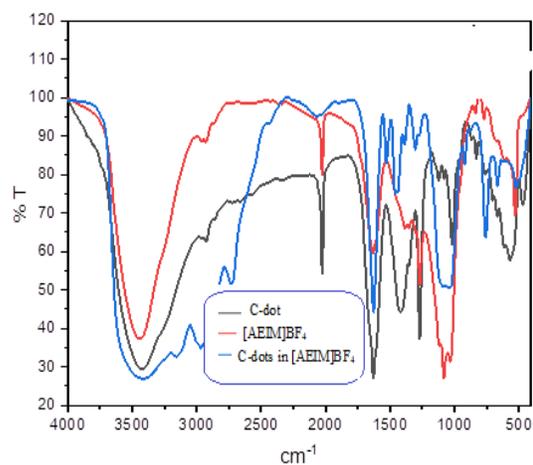


Fig-5 FTIR spectra of C-dot, 2-allyl-1-ethylimidazolium Borate and and the solubilized C-dots in 2-allyl-1-ethylimidazolium Borate.

Borate-based ILs are one of the most widely studied ionic liquids. In the present case, the IL incorporated C-dots exhibit a sharp, strong peak compared to the bare C-dots and the pure solvent (IL-2-allyl-1-ethylimidazolium Borate).

The asymmetric stretching vibrations of borates present in IL are due to the stretching of the B-O bond in trigonal BO_3 units, and in the present case, the B-O absorption band appears around 700 to 1550 cm^{-1} . In borate-based IL, the B-O bonds in borate are a key structural element, and their stretching vibrations are the most prominent in the IR spectra, as well as their solubility to C-dots from PEs is also excellent.

The appearance of peaks at 1100 and 1700 cm^{-1} and their sharpness indicate the maximum solubility of C-dots in this solvent, due to the formation of strong H-bonds between the oxygen of B-O to the hydroxyl groups present on the surface of the C-dots.

The borate's exclusive peaks were absent in the pure C-dots, confirming the influence of borate-based IL on the solubility of C-dots. Compared to methyl, the ethyl group present here influences the solubility through the inductive effect.

3.1.6. FTIR spectral analysis of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2- methylimidazolium Borate

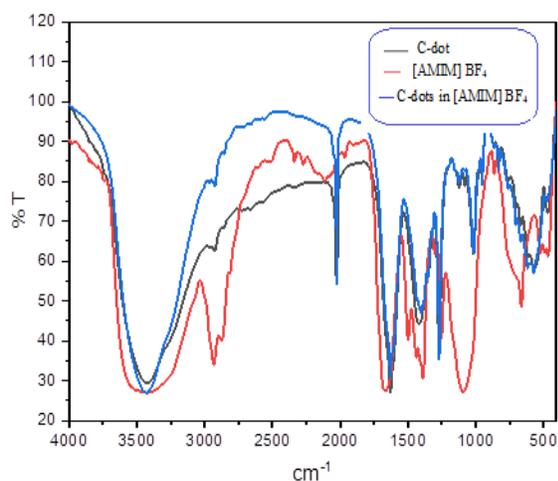


Fig-6 FTIR spectra of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2- methylimidazolium Borate.

Borate-based ILs are one of the most widely studied ionic liquids. In the present case, the IL incorporated C-dots also exhibit a sharp, strong peak compared to

the bare C-dots and the pure solvent (IL-1-allyl-2-methylimidazolium Borate).

The asymmetric stretching vibrations of borates present in IL are due to the stretching of the B-O bond in trigonal BO_3 units, and in the present case, the B-O absorption band appears around 700 to 1550 cm^{-1} . In borate-based IL, the B-O bonds in borate are a key structural element, and their stretching vibrations are the most prominent in the IR spectra, as well as their solubility to C-dots from PEs is also excellent.

The appearance of peaks at 1100 and 1700 cm^{-1} and their sharpness indicate the maximum solubility of C-dots in this solvent, due to the formation of strong H-bonds between the oxygen of B-O to the hydroxyl groups present on the surface of the C-dots.

The borate's exclusive peaks were absent in the pure C-dots, confirming the influence of borate-based IL on the solubility of C-dots. Here the the electron-withdrawing methyl present at the second position to the allyl group, enhances the inductive effect of these borate-based IL towards the solubility of C-dots. Apart from the inductive effect of these allyl-based imidazolium-based cations, the anion borate also helps to solubilize the C-dots to their full extent, without the influence of any external energy, such as heat or any other sources.

3.1.7 FTIR spectral analysis of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2- methylimidazolium hexa fluoro phosphate.

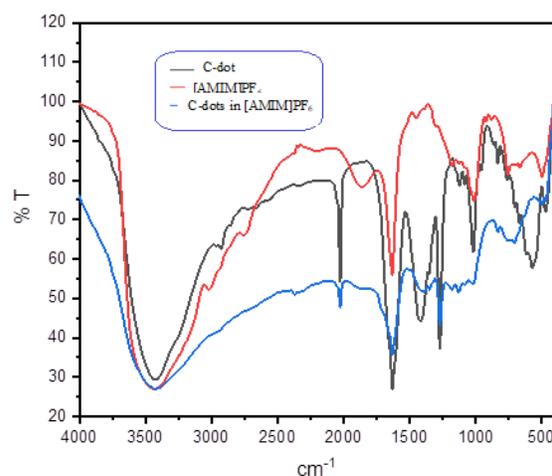


Fig-7 FTIR spectra of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2- methylimidazolium hexa fluoro phosphate

The existence of stretching vibration frequencies around 700-1000 cm^{-1} a characteristic stretch frequency confirms the presence of 1-allyl-2-methylimidazolium cation is associated with the imidazolium ring. The appearance of feeble frequencies from 600 to 1300 cm^{-1} , includes the vibrations responsible for the C-H, C=C, and C-N bonds present in the imidazolium-based cations.

The hexafluoro phosphate anion (PF_6^-) present as anions in the present case also contributes stretch frequencies due to its P-F bonds. These frequencies are typically observed in the higher wavenumber region (around 1100 cm^{-1}) and the lower wavenumber region (around 700 cm^{-1}).

The interaction between the cation and anion, particularly through electrostatic forces, can also slightly shift and modify the observed stretching frequencies. For both the solvent 1-allyl-2-methylimidazolium hexafluoro phosphate (IL) and the C-dot solubilized 1-allyl-2-methylimidazolium hexafluoro phosphate (IL) confirms the presence of the synthesized IL in the system. The stretching frequency appeared in this limit is due to the presence of 1-allyl-2-methylimidazolium cation and the hexafluoro phosphate anion present in the prepared IL. The corresponding stretching frequency range were absent in the bare C-dots again confirm the presence of IL in the present system.

Some specific bands may be assigned to the stretching vibrations of the C-dots present in the IL and the normal functional groups, such as NH_2 , and Carbonyl groups present on the surface of the C-dots. The interaction of C-dots while soluble in 1-allyl-2-methylimidazolium hexafluoro phosphate will interact with both the imidazole based cation and PF_6^- based anion, due to this interaction, the shift of C-dots incorporated 1-allyl-2-methylimidazolium hexafluoro phosphate frequencies may slightly shift from the original IL solvent 1-allyl-2-methylimidazolium hexafluoro phosphate.

3.1.8 FTIR spectral analysis of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate .

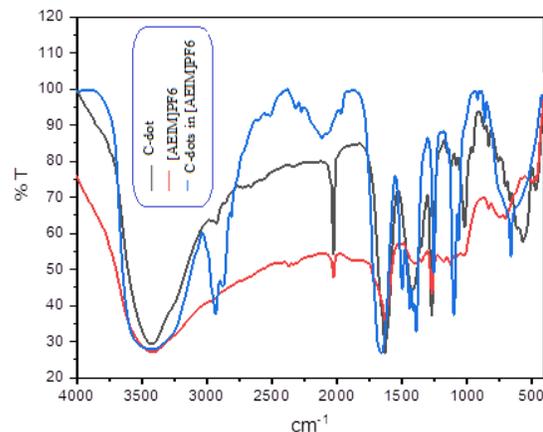


Fig-8 FTIR spectra analysis of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate.

The existence of stretching vibration frequencies around 3122 cm^{-1} for both the solvent 2-allyl-1-ethylimidazolium hexafluoro phosphate (IL) and the C-dot incorporated 2-allyl-1-ethylimidazolium hexafluoro phosphate (IL) confirms the presence of the synthesized IL in the system. The stretching frequency that appeared in this limit is due to the presence of 2-allyl-1-ethylimidazolium cation and the hexafluorophosphate anion present in the prepared IL. The corresponding stretching frequency range was absent in the bare C-dots, again confirming the presence of IL in the present system.

The presence of C-H stretch in both $-\text{CH}_3$ (methyl group) and $-\text{CH}_2-$ (methylene group) appears around 2997 cm^{-1} and 2952 cm^{-1} , respectively confirms the presence of ethyl group in the 1st position of imidazole moiety.

In summary, While specific frequencies for the 2-allyl-1-ethylimidazolium hexafluorophosphate contain stretching frequencies in the typical range, such as from 2200 to 2100 cm^{-1} , containing functional groups such as C-H, C-C, and C=C stretches in similar molecules can help predict its spectral features.

3.2 UV spectral analysis of C-dots, IL, and IL incorporated C-dots

To find the absorption ability of the functional groups present on the surface of prepared C-dots from PEs, also known as p-dots of disposable paper cups, ionic

liquids used in the present study, and IL-incorporated C-dots were analyzed by recording their UV-Visible spectral studies.

Hence, in the following section, each of the prepared C-dots (from PES of paper cups) ILs prepared in the present study, and soluble C-dots incorporated ILs' UV-Visible spectra were recorded.

The main objective of the present study is, the non-degradable PEs from paper cups should be made degradable and to solubilize them using imidazolium-based Ionic Liquids, and by recording their UV, we can find their optical properties, which helps to understand the absorption properties of the C-dots.

To characterize the absorption ability of C-dots in the respective ILs, in the following section, each of the prepared C-dots from PEs, the ionic liquid used for the corresponding study and the soluble C-dots in the respective ILs were separately taken, and each of the above materials UV were recorded and compared in a single graph to find the absorption ability of C-dots in IL and also the nature of functional groups present on the surface of each of the components.

The UV-vis absorption and luminescence spectral studies of the prepared Imidazolium-based ILs and the prepared C-dots from PEs and the Imidazolium-based ILs incorporated C-dots were studied to measure the polarity or solvent strength of these ionic liquids [23-27].

The literature survey reveals that imidazolium-based ILs generally exhibit mostly optically transparent absorption, and their UV region is usually in the visible region [28-30]. According to Lancaster[9], imidazolium-based ionic liquids are generally transparent above 240 nm.

The presence of the imidazolium ring and its associated structure in this type of ILs influences the UV absorption in the far- and deep-ultraviolet regions. The electronic states and the interaction of these imidazolium rings and the associated functional groups influence the shift in absorption peaks due to the unique electronic states of these imidazolium-based ILs and their interaction with the neighbouring atoms. Many studies reveal that the peak wavelengths and intensities are influenced by factors like the alkyl chain length, the type of anion, and the presence of solvents.

The absorption characteristics of these imidazolium-based ILs generally exhibit strong absorption in the

UV region, with a long tail extending into the visible region.

UV absorption studies of these imidazolium-based ILs can help to elucidate the solubility and association behavior of imidazolium-based ILs in different solvents.

3.2.1 UV spectral analysis of C-dot, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride

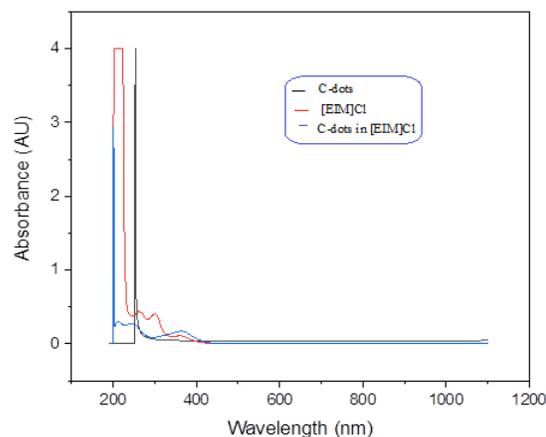


Fig-9 UV spectra of C-dot, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride

In the first series, C-dots from PEs, 1-ethylimidazolium chloride, an IL, and the solubilized C-dots in 1-ethylimidazolium chloride were taken as shown in Fig. 9 and compared their optical properties. UV-Vis spectroscopy is a valuable technique for characterizing carbon dots (C-dots), as it reveals information about their optical properties and electronic structure. C-dots prepared from PEs of paper cups typically exhibit strong absorption in the UV region, with absorption peaks that can be attributed to various electronic transitions, such as $n-\pi^*$ and $\pi-\pi^*$ transitions. These peaks provide insights into the presence of different functional groups and the overall structure of the C-dots.

C-dots generally display characteristic absorption peaks in the UV-Vis spectrum. In the present case, a peak around 260 nm indicates that $\sigma-\sigma$ transitions.

The presence of various functional groups on the surface of the prepared C-dots also influences the shift in the absorption spectrum. The presence of carbonyl groups and NH_2 on the surface may induce some

defects on its surface, and it may significantly affect the optical properties of these C-dots.

The UV absorption study of 1-ethylimidazolium chloride (IL) and C-dots incorporated 1-ethylimidazolium chloride (IL) exhibits their absorption in the range of 230 and 200 nm, respectively.

The existence of a blue shift of the IL incorporated C-dots, compared to the pure ILs and the C-dots, indicates the solubility of C-dots in IL. The absorption of the C-dots incorporated IL's optical properties reveals that maximum absorption ability indicates their ability to sense optical materials.

3.2.2 UV spectral analysis of C-dot, 2-methylimidazolium chloride, and the solubilized C-dots in 2-methylimidazolium chloride.

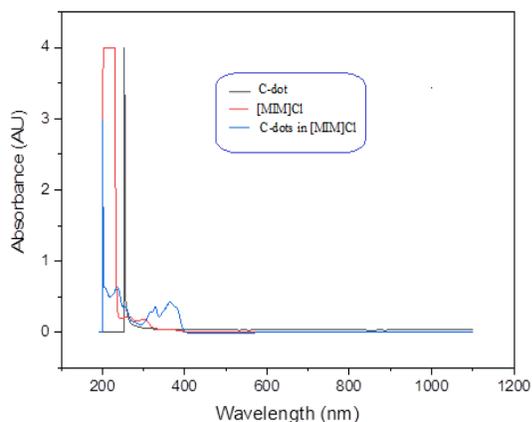


Fig-10 UV spectra of C-dot, 2-methylimidazolium chloride, and the solubilized C-dots in 2-methylimidazolium chloride.

In the present case, C-dots from PEs, 2-methylimidazolium chloride, an IL, and the solubilized C-dots in 2-methylimidazolium chloride were taken as shown in Fig. 2 and compared their optical properties.

The UV absorption study of 2-methylimidazolium chloride (IL) and C-dots incorporated 2-methylimidazolium chloride (IL) exhibits their absorption in the range of 240 and 210 nm, respectively. This absorption peaks reveals that, due to the methyl group in the 2nd position shifts its absorption in the red region to the absorption peaks of 1-ethylimidazolium chloride and its C-dots counterpart. The shift in absorption in the present case

denotes their ability to exhibit optical properties in a considerable manner.

3.2.3 UV spectral analysis of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2-methylimidazolium chloride.

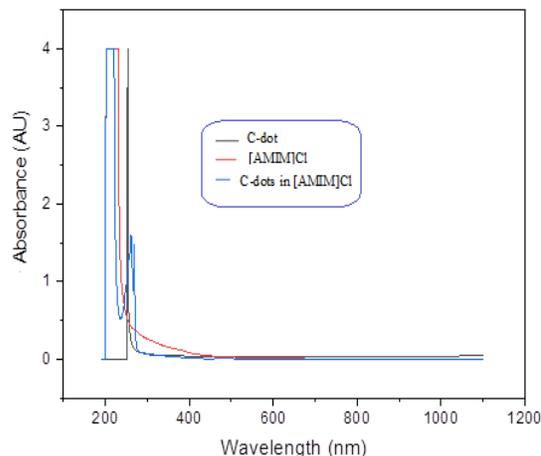


Fig-11 UV spectral analysis of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2-methylimidazolium chloride.

In the present case, C-dots from PEs, 1-allyl-2-methylimidazolium chloride, an IL, and the solubilized C-dots in 1-allyl-2-methylimidazolium chloride were taken as shown in Fig. 3 and compared their optical properties.

1-allyl-2-methylimidazolium chloride, also known as AMIMCl, is an ionic liquid that exhibits UV spectral properties. Its UV absorption spectrum typically displays a peak around 270 nm and potentially another feature around 260 nm, according to the literature study. This peak is attributed to the imidazolium ring, and its presence, or the lack thereof, can be used to identify and quantify its ability to solubilize [AMIM]Cl C-dots and enhance their optical properties.

The intensity of this peak can be used to determine the concentration of C-dots in [AMIM]Cl solutions.

The presence and nature of substituent groups on the imidazolium ring can affect the wavelength and intensity of the UV absorption peak.

The UV absorption spectrum can also reveal information about the interaction of [AMIM]Cl with other molecules, such as polymers or surfactants, through shifts in the absorption peak

3.2.4 UV spectral analysis of C-dot, 2-allyl-1-ethylimidazolium chloride, and the solubilized C-dots in 2-allyl-1-ethylimidazolium chloride.

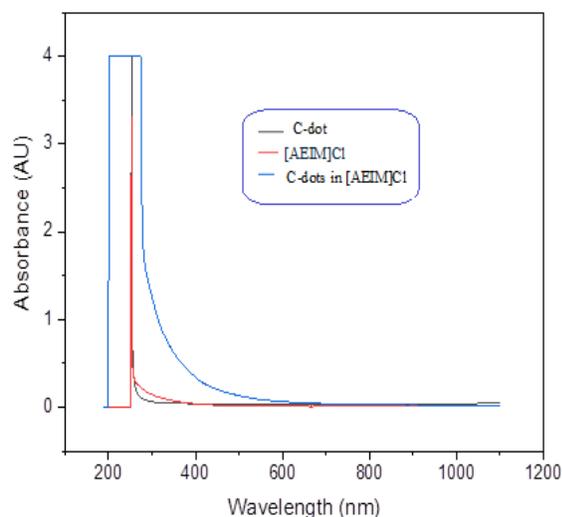


Fig-12 UV spectra analysis of C-dot, 2-allyl-1-ethylimidazolium chloride, and the solubilized C-dots in 2-allyl-1-ethylimidazolium chloride.

2-allyl-1-ethylimidazolium chloride consists of an imidazolium ring (a five-membered aromatic ring) and an allyl group (a vinyl group).

UV spectral analysis of 2-allyl-1-ethylimidazolium chloride would primarily focus on the electronic transitions of the imidazolium ring and the allyl group, particularly in the UV region (around 200-350 nm). The spectra might show bands associated with the π -electron system of the imidazolium ring and the double bond in the allyl group, potentially influenced by the chloride counter ion.

The imidazolium ring, being aromatic, is expected to exhibit characteristic UV absorption bands, typically around 200-250 nm and potentially weaker bands in the 250-300 nm range.

The allyl group, with its double bond, will also contribute to UV absorption. A typical absorption band for a double bond is expected to be around 200-250 nm.

The presence of the chloride counterion can influence the UV absorption through electrostatic interactions, potentially shifting or modifying the absorption bands. UV spectral analysis of 2-allyl-1-ethylimidazolium chloride would involve measuring its UV absorbance across a range of wavelengths and analyzing the

resulting spectrum to identify characteristic absorption peaks and bands related to the imidazolium ring and the allyl group. The influence of the chloride counterion on these bands would also be examined.

3.2.5 UV spectral analysis of C-dot, 2-allyl-1-ethylimidazolium Borate and the solubilized C-dots in 2-allyl-1-ethylimidazolium Borate

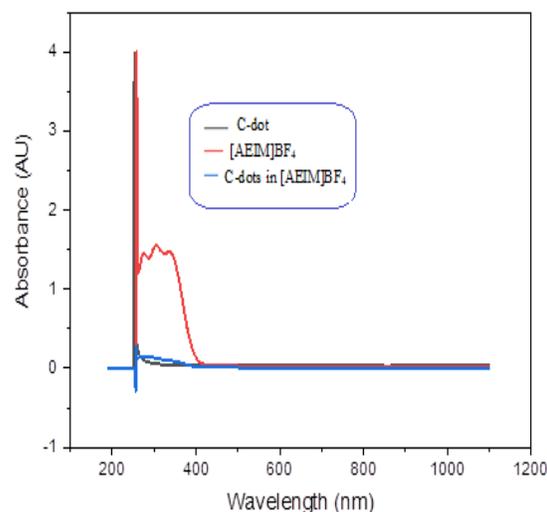


Fig-13 UV spectra of C-dot, 2-allyl-1-ethylimidazolium Borate and the solubilized C-dots in 2-allyl-1-ethylimidazolium Borate

UV-Vis spectroscopy can be used to analyze 2-allyl-1-ethylimidazolium borate. The molecular structure of the compound will influence the UV-Vis spectrum, particularly the presence of π -electron systems (like the double bonds in the allyl group) and the effects of the borate.

In the present case, all three C-dots, IL, and IL incorporated C-dots all exhibit the same absorbance region around 280nm, indicating the highest solubility of C-dots in the IL 2-allyl-1-ethylimidazolium borate. The highest solubility is due to the $n-\pi^*$ interaction of the allyl group of IL with the carbonyl group present on the surface of the C-dots. It has $\pi-\pi^*$ $\pi-\pi^*$ interaction between the allyl group and the ethyl group; altogether, it produces strong solubility of C-dots, and all these enhance the optical absorption considerably.

3.2.6 UV spectral analysis of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2-methylimidazolium Borate

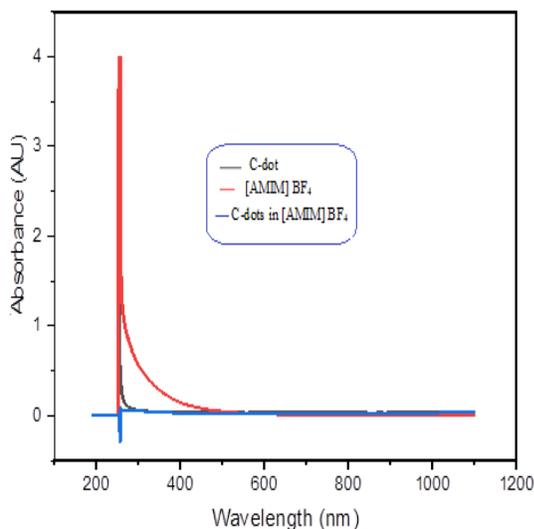


Fig-14 UV spectra of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2-methylimidazolium Borate

UV-Vis spectroscopy can be used to analyze 1-allyl-2-methylimidazolium borate, C-dot, and C-dot incorporated 1-allyl-2-methylimidazolium borate.

1-allyl-2-methylimidazolium borate, as an ionic liquid, will likely exhibit characteristic UV-Vis absorption bands related to the imidazolium ring and the allyl group. The borate anion may also contribute to absorption features.

The UV-Vis spectrum of these compounds exhibits the characteristic absorption bands in the UV region, potentially with a band in the 280 nm region.

The spectral analysis can provide information about the complete solubility of C-dots in the respective IL, and shows transitions involving the excitation of non-bonding (n) electrons on atoms like oxygen or nitrogen of the surface of C-dots to the π^* orbitals of nearby π bonds of the allyl group of IL.

The molecular structure of the IL influences the UV-Vis spectrum, particularly the presence of π -electron systems (like the double bonds in the allyl group), and the effects of the borate enhance the absorption in a more pronounced manner.

3.2.7 UV spectral analysis of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2-methylimidazolium hexa fluoro phosphate.

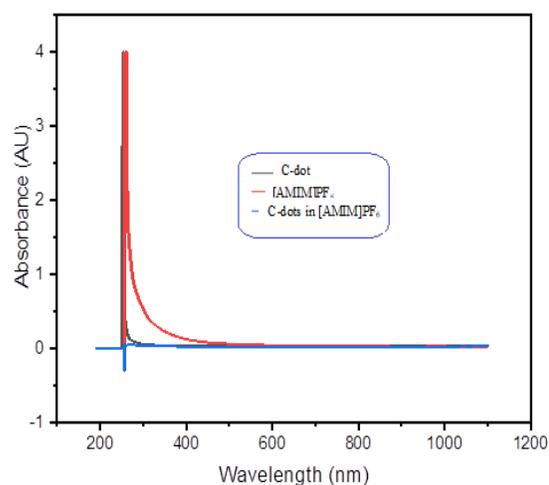


Fig-15 UV spectra of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2-methylimidazolium hexa fluoro phosphate.

UVspectral analysis of 1-allyl-2-methylimidazolium hexafluorophosphate involves measuring its absorption and transmission of ultraviolet light to determine characteristic UV absorption bands. 1-methylimidazole in [AMIM]PF₆ using UV measurements, revealing an absorption feature at 270 nm for 1-methylimidazole and 260 nm for imidazole cation. Absorption at 280 nm scales with 1-methylimidazole mole fraction, and changes in absorption around 240 nm are attributed to intermolecular interactions.

3.2.8 UV spectral analysis of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate

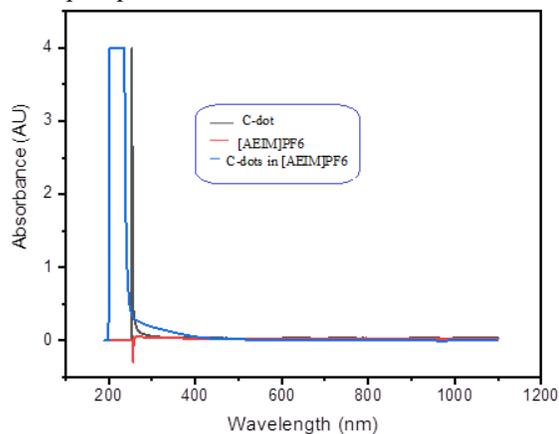


Fig- 16 UV spectra of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate

2-Allyl-1-ethylimidazolium hexafluorophosphate, often abbreviated as [AEIM][PF₆], exhibits UV absorption primarily in the ultraviolet region, with absorption maxima typically observed around 260 nm. This absorption is due to the presence of the conjugated allyl group and the imidazolium ring system.

The UV absorption of [AEIM][PF₆] arises from electronic transitions within the molecule, specifically involving the π electrons of the conjugated double bond in the allyl group and the aromatic system of the imidazolium ring.

The UV absorption spectrum typically shows a peak around 260 nm, indicating the most intense absorption at that wavelength. This peak is associated with the π to π^* electronic transition in the conjugated systems

- Conjugation Effects:

The allyl group, being a conjugated system, contributes to the UV absorption by extending the π electron system and allowing for electronic transitions at longer wavelengths than would be observed for a purely saturated alkyl chain.

- Imidazolium Ring:

The imidazolium ring also contributes to the UV absorption, with its characteristic absorption bands. The combined effect of the allyl and imidazolium systems leads to the overall UV absorption pattern of [AEIM][PF₆].

- Factors Affecting Absorption:

The specific UV absorption characteristics of [AEIM][PF₆] can be influenced by the solvent used for the measurements, as well as the presence of any impurities or other substances in the sample.

3.3. Photoluminescence spectroscopy of C-dots ILs and the C-dots incorporated IL

Photoluminescence spectroscopy of carbon dots (C-dots) involves to study about the light emitted by these nanomaterials when they are excited by light. C-dots exhibit fluorescence, meaning they absorb light and then emit light at a longer wavelength. This property

makes them useful for various applications, including biomedical imaging and sensing [31-34].

Key aspects of photoluminescence spectroscopy of C-dots:

- Photoluminescence spectra of carbon dots often exhibit a broad asymmetrical band, with emission maximum and intensity varying with excitation wavelength.
- The spectra are also influenced by the C-dot environment, with shifts in the emission peak position observed between colloidal solution and C-dots embedded in a matrix.
- C-dots typically show a broad PL emission band rather than a sharp line, indicating a distribution of energy levels or surface states contributing to luminescence.
- The PL spectra can also be influenced by the composition and structure of the C-dots.
- The PL spectrum can shift significantly with excitation wavelength, with longer wavelengths causing a red shift in the emission.
- Surface defects and surface-modified functional groups can affect the emission and act as trapping or emission sites.

C-dots typically show good PL quantum yields and present a characteristic shift in their emission spectrum with excitation wavelength: longer excitation wavelengths shift the PL spectrum towards the red, in an apparent break of Kasha's rule. This behaviour is easily identified in an Excitation-Emission Map (EEM) of the sample's photoluminescence. Several hypotheses have been proposed to explain the wavelength dependent emission spectrum of C-dots. One is the effect of carbon dot size, which is similar in semiconductor quantum dots. As the carbon particle decreases in size, quantum confinement takes place meaning that the particle is smaller than the de Broglie wavelength of the electron in the dot, creating a deviation from bulk properties.

This confinement creates a quantisation of the energy into discrete levels in the conduction and valence bands, so the C-dot can be understood as a "virtual atom". The emission energy depends on the radius of the particle so that as the particle gets smaller, both the excitation and emission spectrum shift to shorter wavelengths. In a distribution of C-dots with varying sizes, different subsets get preferentially excited as the

excitation wavelength varies. As C-dots of different size are excited, the emission spectrum shifts with excitation wavelength. Although size-dependent PL of C-dots has been reported, it is not the only factor affecting the emission spectrum and in practice it is difficult to obtain a distribution with a narrow PL spectrum. Another potential explanation for the PL behaviour of carbon dots is the existence of different emissive sites on the surface of the dot.[13] These sites are related to different defects on the surface, which are selectively excited depending on the wavelength used. Despite the large volume of research in this field, the mechanism of PL in C-dots remains uncertain. This is partly due to the lack of strategies to selectively produce just one type of C-dot structure. New synthetic approaches to control the degree of crystallinity and functionalization of C-dots are needed.

3.3.1 PL spectral analysis of C-dot, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride

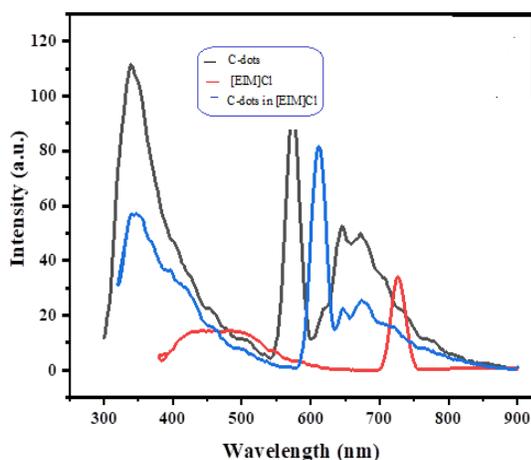


Fig-17 PL spectra of C-dot, 1-ethylimidazolium chloride, and the solubilized C-dots in 1-ethylimidazolium chloride

Imidazolium-based Ionic liquids can act as new benign media for liquid sensing systems. The present study involves studying the emission properties of the prepared C-dots from PEs of Pare cups and the corresponding Ionic Liquids as a solvent used in the present study. Correspondingly, the solubilized C-dots in the respective ILs' emission properties were also studied, to find the optical properties, and with the

help of these PL studies, we can analyze the sensing ability of the prepared C-dots. Initially PL of each of the sets was recorded and their results. Then, each set of metal sensing abilities has also been studied.

In the first case, the PL spectra of C-dots from PEs, 1-ethylimidazolium chloride, and IL, and the solubilized C-dots in 1-ethylimidazolium chloride were taken as shown in Fig. 1 and compared their optical properties. In the figure, the C-dot exhibits three prominent excitation peaks with nearly sharp in the range of 350, 580, and 700 nm. The prepared C-dots extend their emission till the red region, confirming their utility as a sensor in biological imaging and food adulteration.

The PL of 1-ethylimidazolium chloride, an IL, exhibits a feeble and structureless peak from 400- 650 nm and exhibits a low intensity emission peak around 720 nm in the red region, indicating the influence of the imidazolium cation in the emission spectra. The presence of ethyl groups on the side chain of the imidazolium moiety, due to its higher inductive effect, influences the photoluminescence properties of this IL as broad and structureless emission.

The PL of C-dots incorporated exhibit emission peaks broad and sharp peaks around 350 and 620 nm, respectively, and also in the red region, indicating the complete solubility of C-dots in IL and also their ability to act as sensors in both bio and other fields.

3.3.2 PL spectral analysis of C-dot, 2-methylimidazolium chloride, and the solubilized C-dots in 2-methylimidazolium chloride.

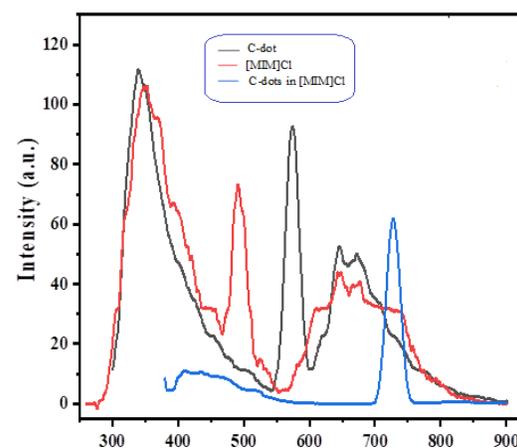


Fig-18 depicts PL spectral analysis of C-dot, 2-methylimidazolium chloride, and the solubilized C-dots in 2-methylimidazolium chloride.

Here, C-dots PL emissions are discussed as in the previous case. The PL emission of 2-methylimidazolium chloride is almost in the C-dot region, indicating that their maximum optical properties. Whereas, the C-dots incorporated 2-methylimidazolium chloride IL exhibits, very sharp emission peak at 740 nm in the red region, indicating that their maximum emission as well as solubility nature. The appearance of a narrower FWHM of these C-dots incorporated 2-methylimidazolium chloride indicates a more homogeneous nature and confirms their maximum solubility and emission properties, and are considered the best sensor for most of the bio-related studies.

3.3.3 PL spectral analysis of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2- methylimidazolium chloride.

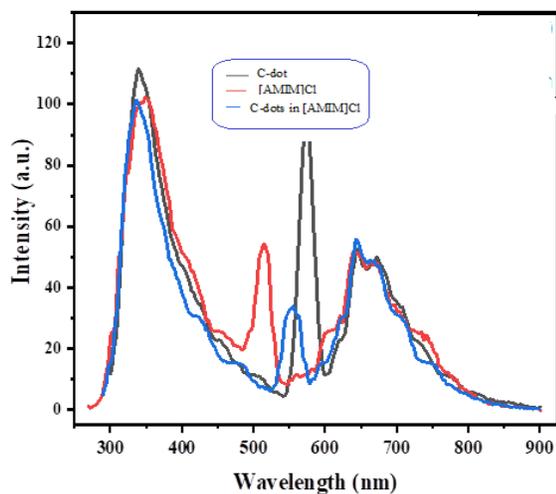


Fig- 19 PL spectral analysis of C-dot, 1-allyl-2-methylimidazolium chloride, and the solubilized C-dots in 1-allyl-2- methylimidazolium chloride.

The imidazolium [Amim][Cl] based ILs can demonstrate their photoluminescence property, due to the presence of the imidazole ring and the allyl groups present in them, which may contribute to the electronic transitions that result in light emission.

Here, the bare C-dots, IL, and IL incorporated C-dots all exhibit almost similar emission in the range of 350 nm in the blue region. Here the the C-dots solubilized IL exhibit two broad peaks in the range of 350 and 690 nm belonging to the violet and red regions. The existence of a third emission peak around 550 nm in

the green region confirms that their emissions are attributed to π - π^* electronic transitions involving the entire electronic system of the compounds. This may lead to sense most of the biological systems.

3.3.4 PL spectral analysis of C-dot, 2-allyl-1-ethylimidazolium chloride, and the solubilized C-dots in 2-allyl-1- ethylimidazolium chloride.

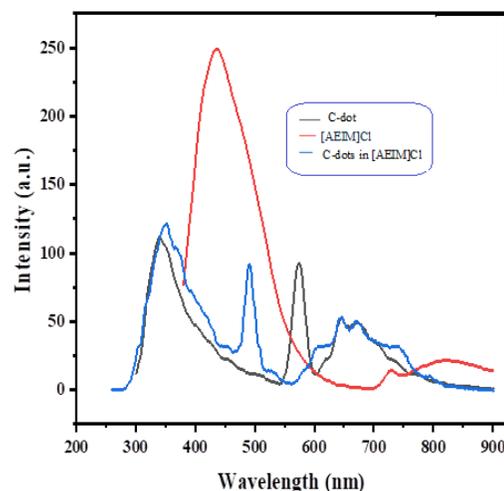


Fig-20 PL spectra of C-dot, 2-allyl-1-ethylimidazolium chloride, and the solubilized C-dots in 2-allyl-1- ethylimidazolium chloride.

The imidazolium [Emim][Cl] based ILs can demonstrate their photoluminescence property, due to the presence of the imidazole ring and the allyl and ethyl groups present in them, which may contribute to the electronic transitions that result in light emission. In this case, the IL exhibits broad peaks in the 500 nm green region, compared to its methyl counterpart. The reason for this emission scenario is due to the longer alkyl chain of ethyl groups compared to the methyl group, and hence able to undergo maximum electronic transition between the ethyl and allyl groups.

The solubility of C-dots with this IL is also good, and their emission properties are also quite acceptable. Hence, the IL used in the present study exhibits potential applications in areas such as optoelectronics or sensing technologies.

3.3.5 PL spectral analysis of C-dot, 2-allyl-1-ethylimidazolium Borate and the solubilized C-dots in 2-allyl-1- ethylimidazolium Borate

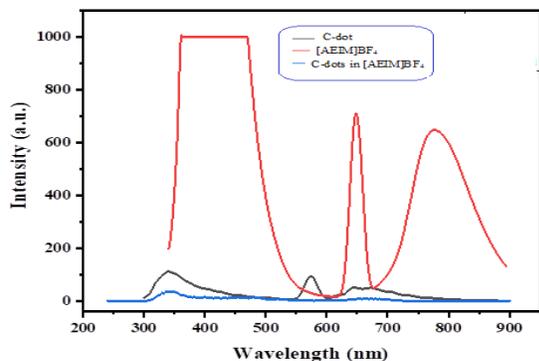


Fig-21 depicts the PL spectral analysis of C-dot, PL spectral analysis of C-dot, 2-allyl-1-ethylimidazolium Borate and the solubilized C-dots in 2-allyl-1-ethylimidazolium Borate

Borate compounds, including those with imidazolium cations, are recognized for their diverse structural chemistry and luminescent properties.

For instance, 2-allyl-1-ethylimidazolium Borate reveals strong blue-light emission maxima at 489 and 491 nm, respectively. The occurrence of intramolecular charge transfer (ICT) excited states, with significant contributions from $\pi-\pi^*$ transitions of the allyl group present in the imidazole cation and borate anions, reveals their maximum electron transfer and hence exhibits maximum and broad structureless emissions. Whereas the C-dots incorporated IL could not emit light, and their emission intensities are also very very minimum, indicating that the solubility of C-dots in this IL and their sensor abilities are not possible.

3.3.6 PL spectral analysis of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2-methylimidazolium Borate

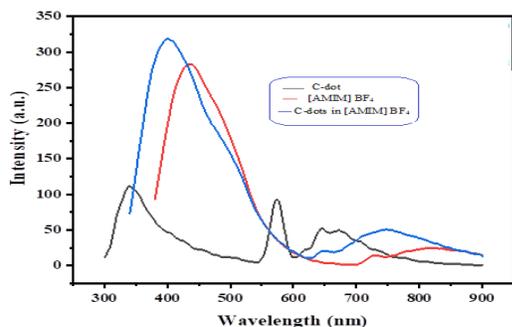


Fig-22 PL spectral analysis of C-dot, 1-allyl-2-methylimidazolium Borate and the solubilized C-dots in 1-allyl-2-methylimidazolium Borate

The same scenario has been taken place for 1-allyl-2-methylimidazolium Borate. Here also the C-dots incorporated ILs could not exhibit maximum emission and could not able to use in sensor studies.

3.3.7 PL spectral analysis of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2-methylimidazolium hexa fluoro phosphate.

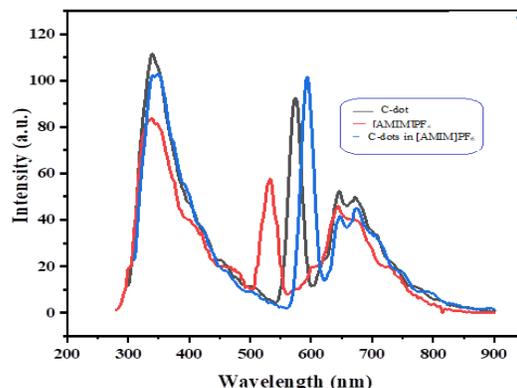


Fig- 23 PL spectra of C-dot, 1-allyl-2-methylimidazolium hexa fluoro phosphate and the solubilized C-dots in 1-allyl-2-methylimidazolium hexa fluoro phosphate.

The photoluminescence of [AMIM][PF₆] behavior suggests that [AMIM][PF₆] based ILs exhibit tunable photoluminescent properties. The structural features of the cation, such as the allyl group and the methyl substitution, could influence its electronic interactions and, consequently, its emission characteristics. The characteristic photoluminescence of [AMIM][PF₆] explores its potential applications in optoelectronic devices.

In the present case, the C-dots are completely soluble in the PF₆-based IL and exhibit two strong emission peaks around 560 and 620 nm in the green and red regions, respectively. Hence, these C-dots involved in IL can be used for most of the bio-related sensor applications.

3.3.8 PL spectral analysis of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate.

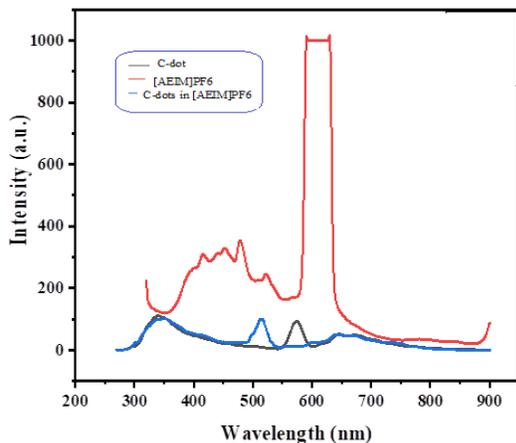


Fig-24 PL spectra of C-dot, 2-allyl-1-ethylimidazolium hexa fluoro phosphate and the solubilized C-dots in 2-allyl-1-ethylimidazolium hexa fluoro phosphate.

The photoluminescence of [AEIM][PF₆] behavior compared to [AMIM][PF₆] suggests that, this [AEIM][PF₆] based IL's structural features of the cation, such as the allyl group and the ethyl substitution, could diminishes its electronic interactions and, consequently, its emission characteristics. The characteristic photoluminescence of [AEIM][PF₆] could not be explored for its potential applications in optoelectronic devices.

In the present case, the C-dots are partially soluble in the [AEIM][PF₆] based IL and exhibit feeble emission peaks around 350 nm in the violet region. Hence, these C-dots involved IL could not be used for most of the bio-related sensor applications.

3.4. XRD – Spectral Analysis of C-dots prepared from PEs of Paper cups.

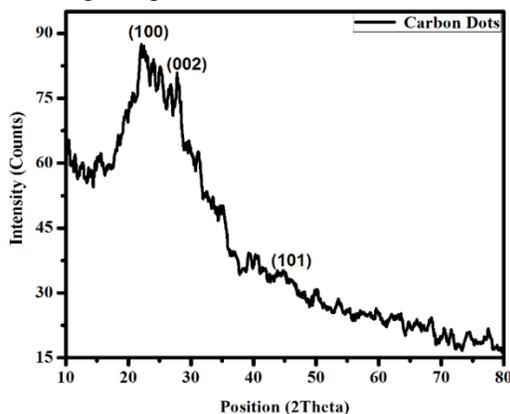


Fig- 25 The XRD spectra of Carbon dots.

The powders XRD of the prepared C-dots from PEs of paper cups were recorded using a Bruker D8 ADVANCE instrument with a scanning rate of 2° per minute from 10° -80°.

The appearance of a broad peak near $2\theta = 26.6^\circ$ and 33° corresponds to (001) & (002) planes with the d-spacing of 0.34 nm and 0.42 nm respectively, typically indicates the presence of carbon particles in the size range of 15-25nm with a monoclinic system. The appearance of broader peaks in both cases confirms their disordered or amorphous nature of the prepared C-dots from PEs of paper cups with the higher layer of interlayer spacing, confirming the presence of oxygen-containing functional groups present on the periphery of C-dots and their nanosize nature.

IV. FLUORESCENCE QUENCHING (ON-OFF) TO DETECT TOXIC METALS PRESENT IN CONTAMINATED WATER OR FOOD MATERIALS

- The functional groups on the surface of C-Dots generally exhibit distinct affinities to diverse target ions, resulting in the specific interaction between C-Dots and the respective metal ions based on the high selectivity to these ions, as well as the quenching of PL intensity via an energy or electron transfer process. The surface of the prepared CQDs from paper cups contain appreciable functional groups, such as NO₂, -NH₂, or -COOH groups can interact with the metal ions present in the medium.
- The sensing ability of the prepared CQDs will be based on the fluorescence quenching mechanism, induced by the surface states in the C-Dots. The prepared C-QDs will serve as a sensing platform for multifunctional detection of Fe³⁺, Ag⁺, Hg²⁺ apart from that, pH values based on their distinctive fluorescence influence on the system may also be detected.

V. ILS SOLUBILIZED C-DOTS AS A SENSOR TO DETECT TOXIC METALS PRESENT IN CONTAMINATED WATER

The primary objective of the present work is to investigate the efficiency of C-dots from PEs of paper cups in removing the most toxic and heavy or bulky

metals, such as Pb, Hg and, Cd from contaminated water. This water contains these toxic metals and produces hazardous pollution to humans and the environment.

Hence, the present work involves removing these toxic metal ions using the prepared C-dots from the paper cups' PEs.

The incorporation of prepared C-dots from PEs of paper cups with different ILs was prepared to fetch these toxic metal ions smoothly and effectively. Since the presence of hydroxyl and amino groups on C-dots can form bonds with these metals.

Further, utilization of the prepared C-dots from PEs of paper cups, due to the presence of specific functional groups present on the CDs surface, enhances the metal ions removal process effectively as well as efficiently, after solubilizing into the respective ILs

In the present case PL spectra of the prepared C-dots from PEs of paper cups with different ILs solubilize with specific concentration of the toxic metal ion such as Cd and Pb, involved solutions were prepared and their PL spectra were recorded to find the quenching effect of these C-dots from PEs of paper cups with different ILs to the respective metals, and the recorded PL spectra were recorded and shown in Fig-26

Further, here the metal ions which have to be removed, such as cadmium and lead, were prepared with the corresponding anions (carbonates), which helps to remove the respective metals effectively.

Many literature survey reveals that, fluorescent properties of C-dots, when it is incorporated into any material, it were widely employed to detect metal ions, molecules, and many toxins by altering the parameters such as temperature, pH, duration, concentration and etc. In particular, several researchers utilized C-dots as a tool for the quantitative and qualitative detection agents.

5.1.ILs solubilized C-dots as a sensor to detect toxic cadmium present in contaminated water.

The C-dots prepared from PEs of paper cups were mixed with the respective Ionic Liquids used in the present study, and are shown as follows,

- 2-methylimidazolium chloride,
- 1-allyl-2-methylimidazoliumchloride
- 1-allyl-2-methylimidazoliumtetrafluoroborate and
- 1-allyl-2-methylimidazolium hexafluorophosphate.

In the first case, C-dots solubilized ILs were used to remove cadmium ions from the prepared cadmium carbonate solution with a constant concentration of 0.5N. The cadmium ions incorporated C-dots solubilized ILs (4 ILs, so 4 solutions were prepared), and the prepared solutions were kept in the orbital shaker at 450 rpm for 3 hours.

After shaking all the contents from each shaker bottle were collected and immediately their PL spectra were recorded and the quenching effect of this C-dots influence over cadmium ions was recorded, and the corresponding PL spectra are shown in Fig. 26.

From the results, we found that maximum quenching was observed for C-dots with 1-allyl-2-methylimidazolium chloride. Hence, the C-dots in 1-allyl-2-methylimidazolium chloride exhibit maximum quenching results, as they have a higher ability to remove cadmium ions compared to the other ILs. Hence, these IL-solubilized C-dots can be used as a sensor to detect toxic metals effectively.

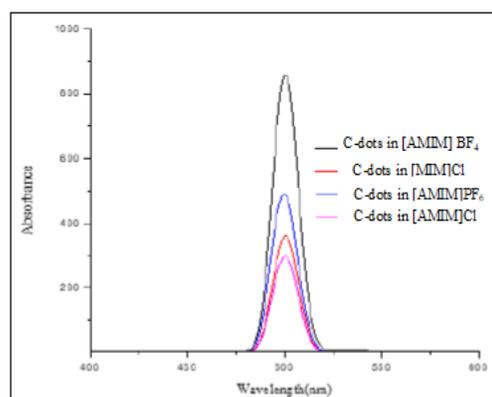


Fig- 26 PL spectra of C-dots solubilized 2-methylimidazolium chloride, 1-allyl-2-methylimidazoliumchloride, 1-allyl-2-methylimidazoliumtetrafluoroborate and 1-allyl-2-methylimidazolium hexafluoro phosphate and cadmium carbonate solution to remove cadmium.

The similar experiments were done using 1- ethyl imidazolium based ILs. The similar scenario has been obtained for 1-ethyl imidazolium based ILs with cadmium solutions as 2- methyl imidazolium ILs. Here also, from the PL studies,(Fig- 27) the results of quenching of the C-dots with 1-ethyl imidazolim ILs , exhibit, maximum quenching activity of 2-allyl-1-ethylimidazolium chloride. This 2-allyl-1-ethylimidazolium chloride has higher ability to

remove cadmium ions compared to the other ILs. Hence, these IL-solubilized C-dots can be used as a sensor to detect toxic metals effectively.

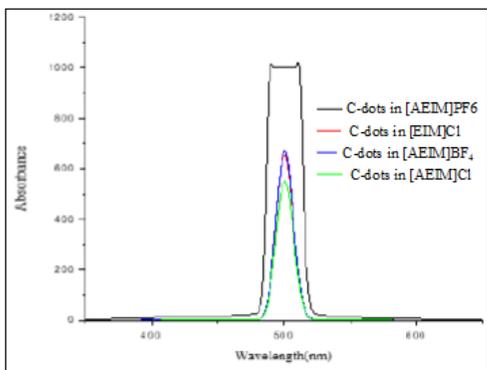


Fig-27 1-ethylimidazolium chloride, 2-allyl-1-ethylimidazoliumchloride, 2-allyl-1-ethylimidazoliumtetrafluoroborate and 2-allyl-1-ethylimidazolium hexafluoro phosphate to remove Cadmium ions

5.2 ILs solubilized C-dots as a sensor to detect toxic lead present in contaminated water.

In the first case, C-dots solubilized ILs were used to remove lead ions from the prepared lead carbonate solution with a constant concentration of 0.5N. The lead ions incorporated C-dots solubilized ILs (4 ILs, 2 sets, methyl imidazolium based and ethyl imidazolium based ILs, so totally 8 solutions were prepared), and the prepared solutions were kept separately in the orbital shaker at 450 rpm for 3 hours.

After shaking all the contents from each shaker bottle were collected and immediately their PL spectra were recorded and the quenching effect of this C-dots influence over lead ions was recorded, and the corresponding PL spectra of each of ILs – methyl imidazolium and ethyl imidazolium based ILs are shown in Fig. 28 and Fig 29 respectively.

From the results, we found that maximum quenching was observed for C-dots with 1-allyl-2-methylimidazolium borate for methyl imidazolium based ILs and 2-allyl-1-ethyl imidazolium chloride for ethyl imidazolium based ILs respectively.

Hence, the C-dots in 1-allyl-2-methylimidazolium borate exhibit maximum quenching results among methyl imidazolium based ILs and 2-allyl-1-ethyl imidazolium chloride among ethyl imidazolium based

ILs as they have a higher ability to remove lead ions compared to the other ILs. Hence, these IL-solubilized C-dots can be used as a sensor to detect toxic metals effectively.

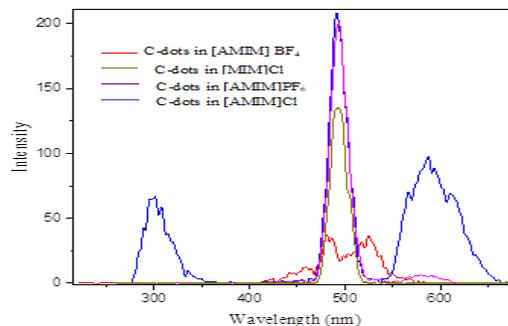


Fig-28 PL spectra of C-dots solubilized 2-methylimidazolium chloride, 1-allyl-2-methylimidazoliumchloride, 1-allyl-2-methylimidazoliumtetrafluoroborate and 1-allyl-2-methylimidazolium hexafluoro phosphate and cadmium carbonate solution to remove lead

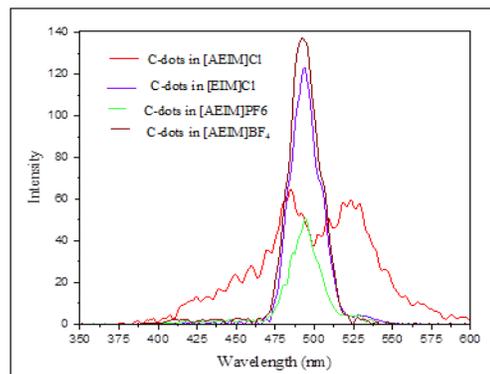


Fig-29 1-ethylimidazolium chloride, 2-allyl-1-ethylimidazoliumchloride, 2-allyl-1-ethylimidazoliumtetrafluoroborate and 2-allyl-1-ethylimidazolium hexafluoro phosphate to remove lead ions

VI. CONCLUSION

- The present paper involves preparing C-dots from PEs, which are present in a disposable cup, using Greener Solvent (IL) by a simple Hydrothermal method.
- The prepared C-dots from PEs of paper cups, FTIR, UV, PL and XRD studies were done to

find, the functional groups, optical activities, and amorphous nature .

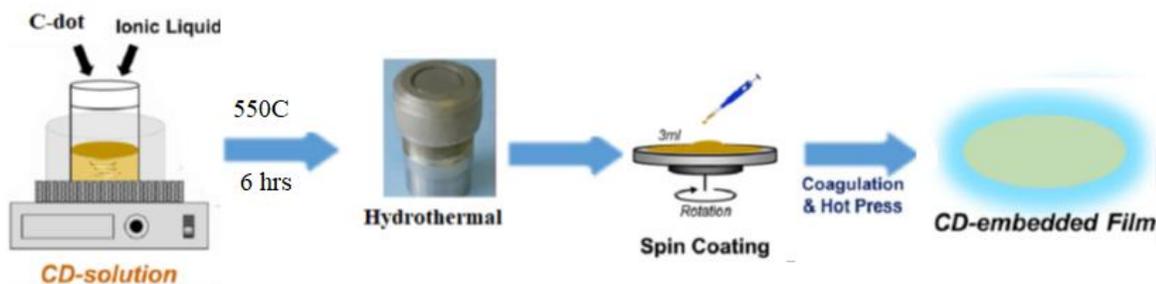
- From the C-dot's optical properties of PE of paper cup, it is found that fluorescent carbon dots act as a value-added material to detect toxic metals from the contaminated water and food quality and safety detection.
- The C-dots solubilized ILs, Pls, were also studied to detect toxic metal ions present in contaminated water through Quenching mechanisms.
- The non-recyclability and non-degradable nature of these PEs are converted into soluble and degradable form using greener Ionic Liquid solvents and by a simple greener Hydrothermal method.

- By solubilizing PEs of paper cups, we can minimize their harmfulness to society and human beings.

VII. SCOPE OF THE FUTURE WORK

- In the future, the solubilized C-dots-based coating (through thin film formation) will be employed to prepare paper cups, so as to reduce harm to the environment and humans.
- In the future, other than PEs will be found from natural sources, and these materials will be coated over paper cups, so as to reduce the harm to humans and also make these paper cups degradable.

The schematic diagram for the preparation of thin films using C-dots are shown in Fig-30.



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