**Primary Objectives**

The primary objectives of the report were to self-assemble flat aromatic and C60 species into well defined 2D layers and 3d architectures via spontaneous directed assembly.

**Description of the work performed since the beginning of the project,**

The initial studies were two fold:- The first was aimed at the synthesis and C60 surfactants which upon dispersion at an air water interface would spontaneous assemble into 2D MONOLAYERS, similar in properties to graphene/graphene oxide. The focus of the research was the development of a synthetic route to polymer-C60 amphiphiles. The route choosen was to construct graphene-like



Unit: C60 (PEG)2

C60 (PEG)2 2D-surface

C60 2D-surface

a)



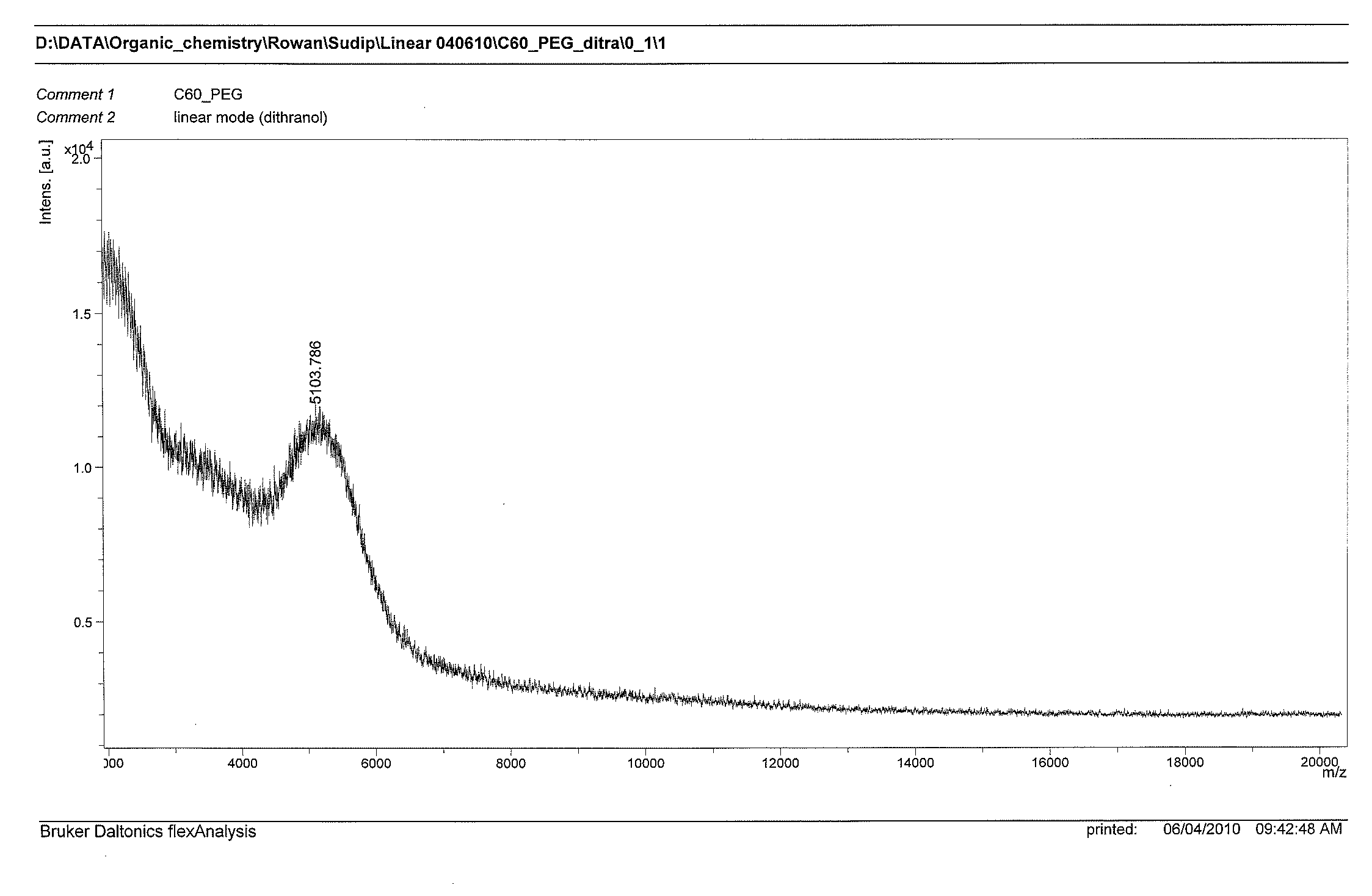
b)

**Figure1**: a) Schematic view of this project; blue circles represent C60 and black lines indicate polyethylene glycol chains. Two steps are involved (i) formation of monolayer and (ii) removal of PEG chains and subsequent polymerized C60 under gamma-ray. b)Synthesis of fullerene functionalized PEG.

Using proper design, fullerene functionalized PEG (polyethylene glycol) having C60 as head (hydrophobic part) and PEG chains as tails (hydrophilic part) was synthesized and it was expecting to form monolayer on air/water interface. Initial studies aimed at functionalizing the C60 with acetylenes and attaching a single azide functionalized PEG chain. These studies revealed that a single chain was too small to give a well defined surface and hence a new route was developed in which two chains were added to the C60 giving well defined monolayers. As shown in Figure 2, the results have indicated the successful synthesis of fullerene functionalized PEG having long(MW-5000) and short PEG (MW-2000) chains. Subsequently, dilute solution of fullerene functionalized PEG was dropped at the water surface on Langmuir trough. Upon compression, the measured surface pressure vs area plots have indicated formation of monolayer (Figure4a). Using Langmuir-Blodgett technique, we were able to transfer the monolayer on the glass surface and subsequent AFM investigations have revealed the formation of monolayer of fullerene (Figure 3).



a



b

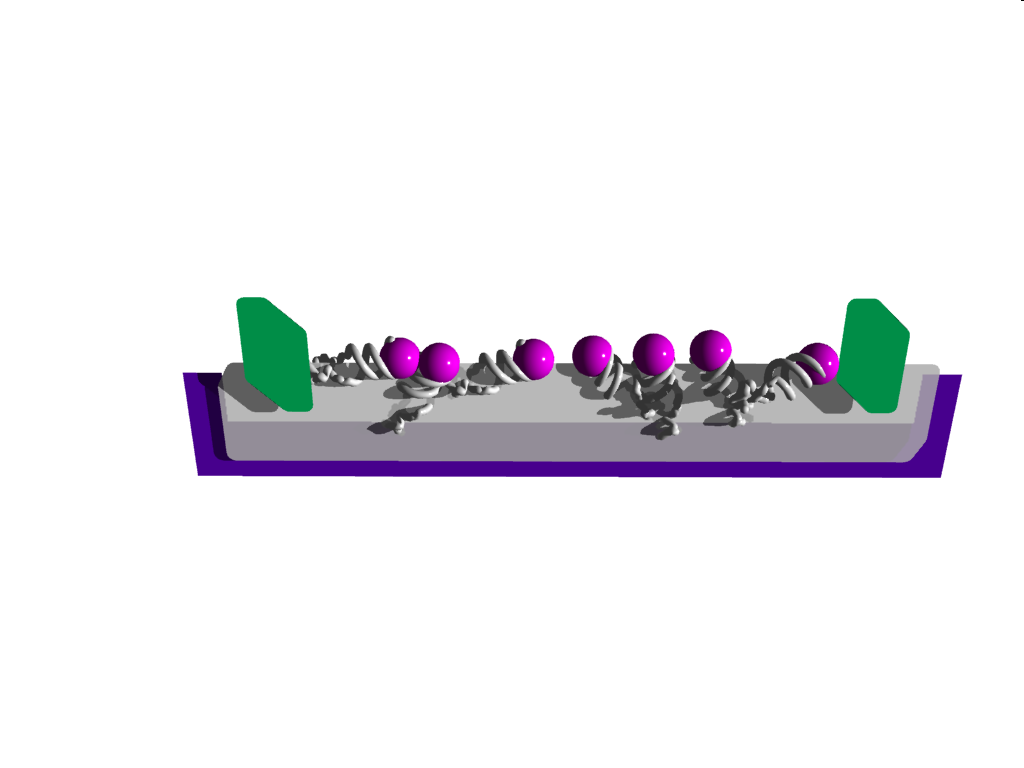
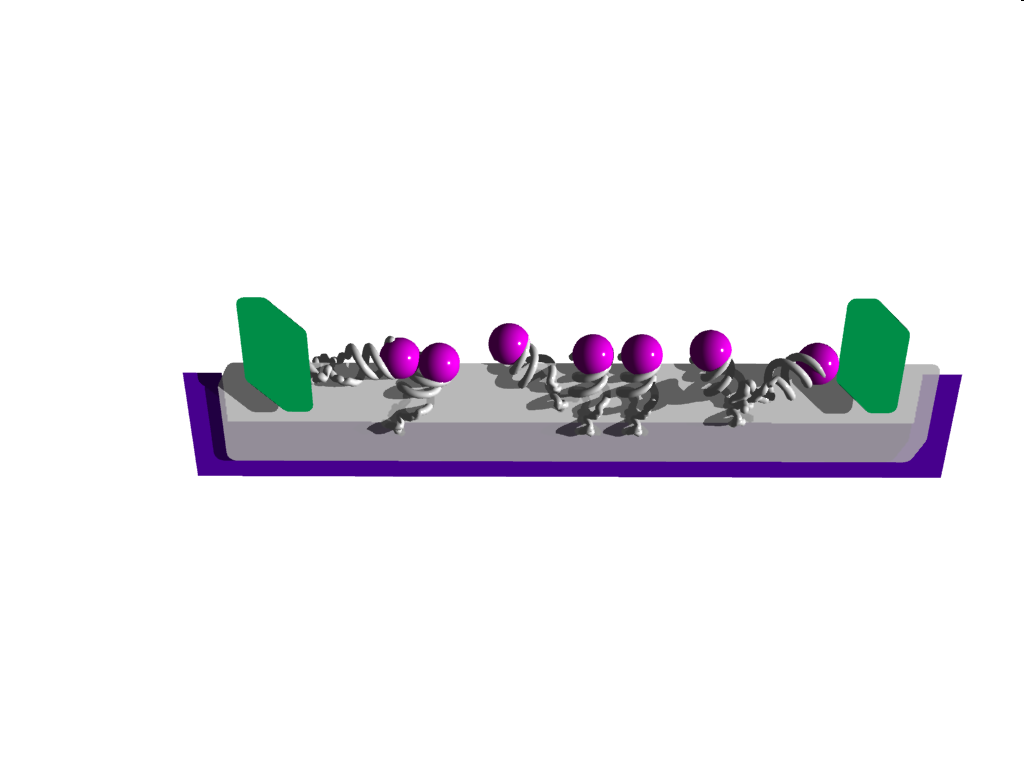
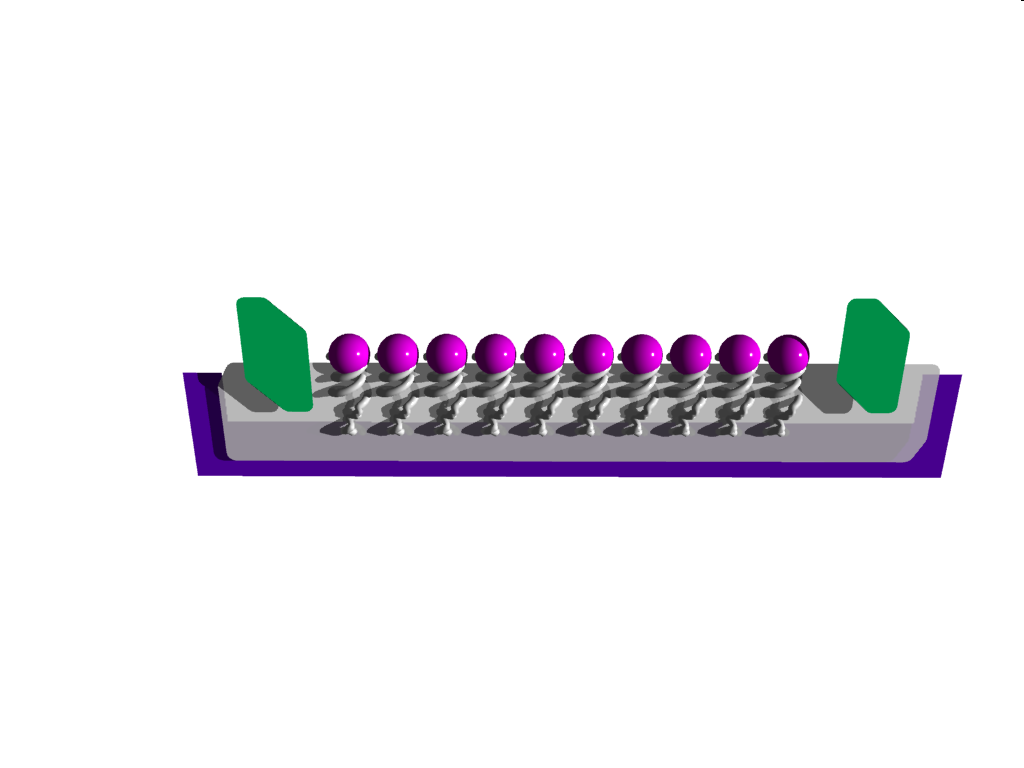


c

**Figure 2**: Characterization results (a) 13C-NMR of PEG derivatives, (b) MALDI-TOF results of C60(PEG)2\_5000 and (c) FT-IR data of C60(PEG)2\_5000 (disappearance of characteristic vibration of C≡C at 2110 cm-1).

1.17 mg/ml

1.08 mg/ml



a

Transfer ratio

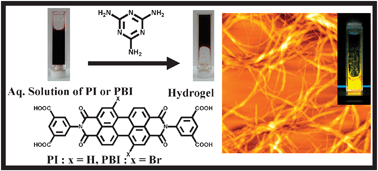
**Figure 3**: (a) Langmuir isotherm of two composites, it confirms the formation of monolayer at water/air interface. Transfer ratio indicates that glass surface is better than silica or mica surface

**Conclusion**: Successful design and synthesis of fullerene functionalized PEG have achieved within first year of this project. Monolayer of these derivatives has been nicely fabricated on the glass surface. Temperature, salt and surface dependence studies were critically observed.

**Future Plan**: (a) Electron density mapping using GIXD to get insight of packing of C60 (fcc or hexagonal geometry) upon formation of monolayer, and crosslinking with gamma irradiation

In the second part of the project the self assembly of a perylene dimide derivatives with melamine into luminescent hydrogels was studied**.**The study of molecular gels has recently become an area of great interest in the fields of supramolecular chemistry and material science. Small molecules are held together by non-covalent interactions such as hydrogen bonds, π–π interactions, dipole–dipole interactions, van der Waals forces, solvophobic interactions *etc.* These weak interactions are advantageous for the creation of smart materials due to their dynamic character.

Perylenediimide dyes are an interesting class of chromophores and fluorophores due to their enhanced stability, good optical properties and pronounced capabilities of self-assembly by means of π–π stacking. These are also the basic materials of numerous organic electronics for light emitting diodes, field effect transistors and photovoltaic cells. As a consequence there has been tremendous efforts directed towards the design and synthesis of perylene assemblies as light harvesting organogels, super organogelator from perylene derivatives with J-type aggregation, even, stimuli responsive supramolecular gels of perylenes.



**Figure 1.** Typically, hydrogels are prepared by mixing of the solution of PI in water (2 × 10−2 M) with the solution of MM in water (4 × 10−2 M) at equal volume ratio. Spontaneous gel is formed for PI at low concentration (0.9% w/v). Upon excitation these gels exhibit an exceptionally high fluorescence emission, which is normally fully quenched in water.

Their application as biomedical materials is absent due to their extremely hydrophobic nature. Utilizing a rational design, herein we report an extremely rare two-component based super-hydrogelation of perylene derivatives with melamine (MM).

These modeling studies reveal the molecular cooperativity within these fibers. The perylenes stacks are glued together by the melamine, and the resulting bundles are coated with water soluble carboxylic acids.The addition of MM affects the packing of the PI molecules within the columns in multiple ways, which have dramatic impact on the luminescent properties of the gels. MD studies reveal that MM molecules can be inserted into the columns thus not only preventing direct quantum-mechanical coupling between PI molecules and hence excimer formation but also slowing down energy migration to weakly emissive excimer sites. Most importantly, MM molecules form a continuous belt of H-bonds cross-linking the PI stacks and preventing close contacts (below 3.3 Å) between adjacent PI molecules in the excited state (the excited-state potential is modeled here by adding partial charges on adjacent PI cores to mimic possible excimer formation). As a result, exciton emission (optically allowed as a result of the finite angle between neighboring molecular transition dipoles and energetic/positional disorder along the columns) is favored over excimer emission (necessitating short intermolecular distances) in the presence of MM.

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**Figure 2** (a and b) Charge-transfer character, electronic excitation energy and radiative lifetime for PI dimers *versus* the intermolecular spacing *z*, as calculated at the INDO/SCI level. (c) Simulated distribution of the intermolecular spacing for a couple of oppositely charged PIs inside a stack, in the presence and absence of MM. (d and e) Two MD snapshots showing the intercalation and the wrapping of MM around a PI stack.

In conclusion, we report the first example of perylene based hydrogels formed spontaneously upon mixing of a simple perylene diimide derivative with melamine. These gels exhibit highly intense fluorescence visible to the naked eye. The resulting gel network consists of inner core of H-stacked perylenes cross-linked by MMs and a water-soluble carboxylic acid at the outer surface. The observation that the perylene derivative forms gel in aqueous medium is novel and will encourage the design of perylene based gelators aiming for a biological environment.

**Expected final results and their potential impact and use (including the socio-economic impact and the wider societal implications of the project so far).**

The development of a cheap and conductive monolayer is of considerable industrial interest, since it would lead to cheap conductive paints and coatings, with numerous potential applications.

The latter topic of a fluorescent hydrogel is of considerable interest as a biological matrix, which reports on protein/gel interactions.

Both applications are aimed at cheap and cost effective self-assembly processes, for large scale coatings and sensors, which will have societal implications, in the fields of consumer electronic and medical diagnostic kits.