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Study on the Self-Assembling Properties of a Chiral Oligo*p*-Phenyleneethynylene Derivative

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Abstract : *Supramolecular chirality plays a significant role in regulating the self-assembling as well as photophysical properties of molecules. Here, synthesis, characterization and supramolecular properties of an amide functionalized chiral oligo(p-phenyleneethynylene) molecule are described. The molecule was synthesized by multi-step synthetic pathway, which mainly based on palladium catalyzed Sonogashira-Hagihara coupling. The molecule was characterized using ^1H NMR, ^{13}C NMR, FT-IR spectroscopy and mass spectrometry. The aggregation behavior of this molecule was investigated in both chloroform and n-decane. The molecule shows high solubility in chloroform, whereas aggregation occurred in non-polar solvent such as n-decane. The aggregation behavior of the molecule was monitored by variable temperature UV/Vis and fluorescence spectroscopy. The molecule shows aggregation induced enhanced emission (AIEE) behavior. Chiroptical properties of molecule in the aggregated state were monitored by circular dichroism (CD) spectroscopy. Morphological characterization and mechanochromic properties were studied using fluorescence microscopy.*

Keywords: *Supramolecular, photophysical, Sonogashira-Hagihara, mechanochromic*

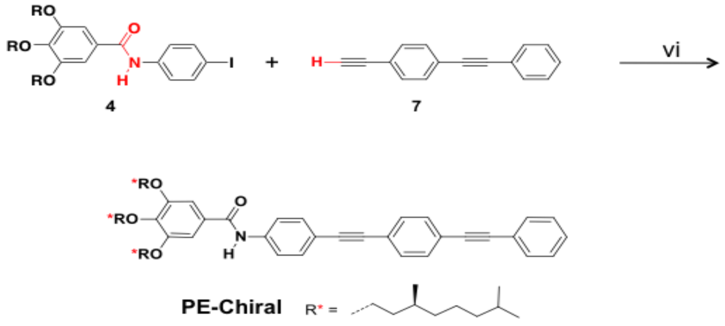
1.Introduction

Supramolecular chemistry is one of the new areas of chemistry that deals with secondary interactions rather than covalent bonds in molecules and focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components. [1-3]The forces responsible for the spatial organization may vary from weak intermolecular forces to strong covalent bonding.The weak intermolecular forces are Van der Waals forces, π-π interactions, hydrogen bonding, ionic interactions, metal coordination etc.Noncovalent interactions play a vital role in the development of supramolecular chemistry. They determine the structure of biomacromolecules such as DNA and proteins and are responsible for the molecular recognition process**.**The molecules can self-assemble in a particular solvent.Molecular self-assembly is the process by which molecules adopt a defined arrangement without external influences.[1-3]There are two types of self-assembly, intermolecular self-assembly and intra-molecular self-assembly. Self-assembly of rigid π-conjugated systems are potential candidates for applications in various fields of advanced materials. A large variety of linear π-conjugated polymers and oligomers of phenylenes, phenylenevinylenes, phenyleneethynylenes and thiophenes are used for this.[9-14]The electron and energy transport properties in these molecules are strongly influenced by the self-organization of the individual molecules. We have chosen the phenyleneethynylene back-bone due to their inherent optoelectronic properties and propensity for self-assembly.*p*-Phenyleneethynylene derivatives are molecules which consist of phenyl rings connected with triple bonds.[24] They are fully conjugated π-systems. Conjugated bonds play an important role in electron conduction because π-electrons are delocalized over a distance, called the length of conjugation. This type of system is capable to alter the mode of packing with respect to external stimuli. The alkyl or aryl chains linked to this type of system play vital role in determining its properties. We have designed molecule in such a way that, phenyleneethynylene molecule is linked with phenyl moiety bearing chiral hydrocarbon chains to bias the supramolecular helicity during the self-assembly (Scheme 1). The aromatic phenyleneethynylene moiety induces π-π stacking and the amide group allows self-assembly through hydrogen bonding.

2.Results and Discussion

Synthesis of PE-Chiral

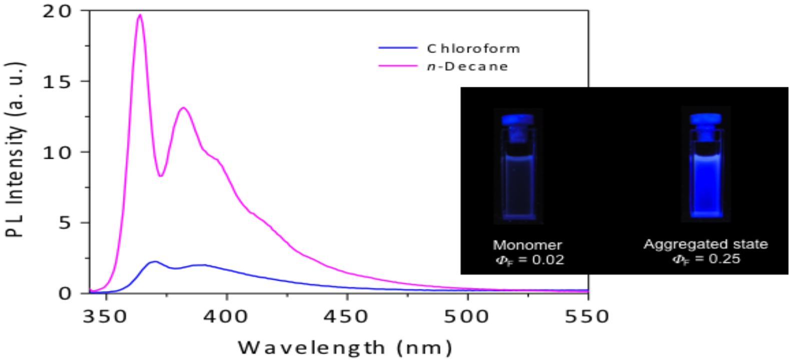
We designed and synthesized a chiral oligo*p*-phenyleneethynylene derivative and PE-Chiral having the structure as shown in Scheme 1. In this molecule, the triple bonded linear aromatic π-backbone is the fluorescent core, which is connected to a bulky end group through an amide bond. The bulky terminal group is composed of flexible chiral side chains. The amide linkage provides hydrogen bonds that can control the molecular assembly. This molecule was synthesized using multistep synthetic procedures using palladium-catalyzed Sonogashira–Hagihara cross coupling reactions.



Scheme 1. Reagents and conditions**:** (vi) $PdCl_2(PPh_3)_2$, CuI, Et_3N, dry THF, N_2, rt., 12 h, 60%.

Aggregation Studies

Recently, aggregation induced enhanced emission (AIEE) has become an attractive research object for researchers interested in the photophysical properties of organic and organometalliccompounds and their applications.[22,23] For AIEE active compounds emission intensity is enhanced upon aggregation. Theoretical works that have provided solid proof to the three main hypotheses for the mechanistic causes of the AIEE effects are restriction of intramolecular rotations (RIR), restriction of intramolecular vibrations (RIV), and restriction of intramolecular motions (RIM).The emission studies of PE-Chiral have been carried out in chloroform and *n*-decane at 1×10^{-4} M concentration (λ_{ex} = 340 nm). In chloroform, the emission maximum for PE-Chiral was centered at 370 nm with a broad feature and in *n*-decane the spectrum looks structured with maxima at 360and 380 nm with a small enhancement in intensity (Figure 1). This observation is a special case; usually the emission intensity will decrease during the aggregation. But in the case of PE-Chiral, the intensity of emission spectrum in chloroform was weak (quantum yield, $\Phi_F = 0.02$), whereas in *n*-decane the molecule exhibited 8 times enhanced fluorescence (quantum yield, $\Phi_F = 0.25$) indicating aggregation induced enhanced emission (AIEE) behavior .



Chiro-Optical Studies

Supramolecular chirality of the aggregates was investigated using circular dichroism (CD) spectropolarimeter. The PE-Chiral molecule is found to be CD silent in chloroform, due to the lack of aggregate formation (Figure 10). However, in *n*-decane PE-Chiral was CD active and showed an exciton couplet circular dichroic spectrum of with a positive signal at 390 nm followed by a negative signal at 310 nm with a zero cross over at 330 nm, indicating of the formation of right handed helical arrangement of chromophoric units (Figure 10).

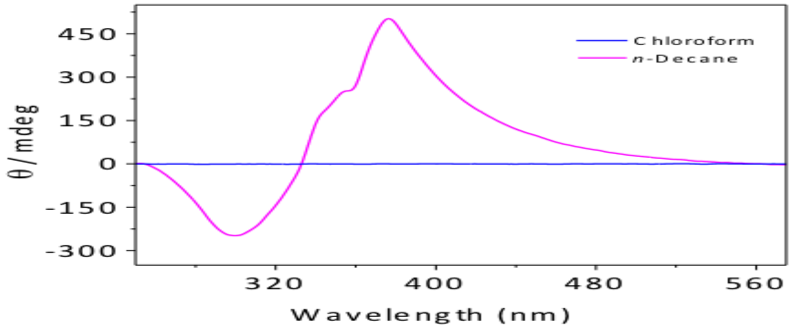


Figure 2.CD spectra of PE-Chiral in chloroform and *n*-decane ($c = 5 \times 10^{-4}$ M).

Fluorescence microscopyanalysis was carried out in order to get insight into the supramolecular morphology of PE-chiral in the gel state. Samples for the analysis were prepared by drop casting *n*-decane solution ($c = 5 \times 10^{-5}$ M) on a glass plate and the solvent was removed by keeping it under vacuum. The fluorescence microscopy images show the formation of blue-emitting micrometer long helical fibers (Figure 3).

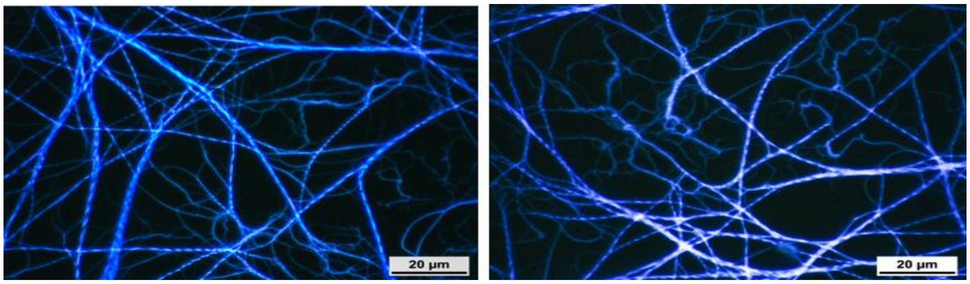


Figure 3. Fluorescence microscopy images of PE-Chiral in *n*-decane ($c = 5 \times 10^{-4}$ M).

[12] Supramolecular chirality has a role in the mechanoresponsive properties of self-assembled systems in switching its luminescent properties by fluctuating the mode of packing. The PE-Chiral molecule self assembles in *n*-decane, by means of noncovalent interactions and form blue emitting gel. The xerogel film can be prepared by casting the gel on glass slide also shows similar kind of blue fluorescence. As we applied pressure on this film there occur emission color changes from blue to cyan due to rearrangement of chiral packing of the molecules (Figure 4). Furthermore, upon application of heat the cyan emission of the film reverted back to the original emission color, which shows the reversibility of the system.

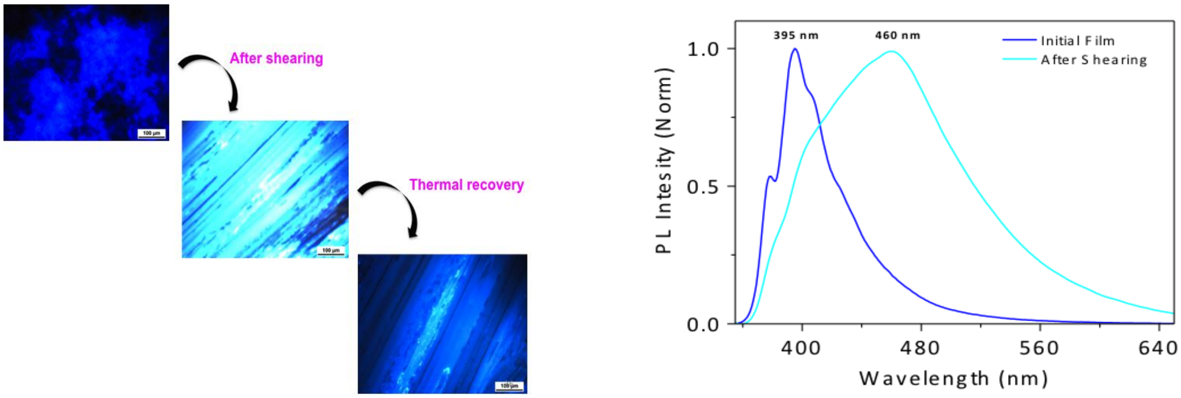


Figure 4. Fluorescence microscopy images and emission spectra of **PE-Chiral***n*-decanexerogel film before and after shearing.

3.Conclusion

A chiral *p*-phenyleneethynylenederivative, PE-Chiral was synthesized through multistep synthesis involving Sonogashira-Hagiharacoupling and completely characterized by various spectroscopic techniques. The aggregation property of the molecule in nonpolar solvent like *n*-decane is probed with the help of UV/Vis absorption, emission and CD spectroscopy. The aggregation induced enhanced emission (AIEE) behavior of the molecule is evident from the emission studies. . Due to the presence of chiral chain, it can fluctuate the mode of packing and show mechanochromism.The detailed spectroscopic as well as morphological studies revealed that the PE-Chiral in *n*-decane form right-handed helical one-dimensional fibers, which is characterized by a CD signal with a positive followed by a negative cotton effect.

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