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Synthesis of Perylene Diimide Modified by POSS and its Assembly Behavior in Solution and SBS Matrix

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Abstract:- In this work, Perylene diimide derivatives 1,7-POSS-PDI-C_{12} (PPC) were synthesized using 1,7-Br-PDI-C_{12}, 18-crown-6 ether as phase transfer agent, K_2CO_3 as catalyst and THF as solvent in a reaction system. Subsequently, the POSS-SH group was successfully introduced into the perylene imide bay site in high yield. The chemical structure and molecular weight of the products were characterized by ^{1}H-NMR, ^{13}C-NMR, MALDI-TOF MS and FT-IR. The self-assembly behavior in different solvents was studied using the research solution self-assembly method. PPC remained in a single monomolecular state due to the bulky POSS group, which introduced large steric hindrance in the molecular packing, leading to the weakening of the π–π interactions. Then, the Composite thin films containing PPC in SBS was prepared. PPC do not exhibit significant force-chromic behavior owing to the dispersion of single-molecule states. This shows that in the construction of mechanochromic materials, chromophore molecules need to have a certain degree of aggregation in the matrix, but the aggregation degree should not be too high.

***Keywords:-** Perylene Diimide; Bay POSS Synthesis; Self-Assembly; Thin Film.*

I. INTRODUCTION

Perylene diimide (PDI) has a dense aromatic hydrocarbon structure with strong fluorescence[1, 2]. Its nucleus is formed by two naphthalene molecules through SP^2 hybridization, forming a large π-conjugated system. The delocalization of electrons through conjugation results in a polarizable π-electron cloud, causing the perylene imide molecules to display a remarkably high fluorescence quantum yield[3]. However, the strong conjugation also contributes to the poor solubility of perylene imide owing to its large lattice energy. Despite this, Friedlander synthesized perylene compounds in 1913 and used them in the dye and coating industry because of their good photothermal stability and strong coloring. It was only in the 1950s that the solubility of perylene compounds in organic solvents was significantly improved through modification and introduction of soluble groups in the side chain. This improvement further revealed their high fluorescence quantum yield and light stability, leading to their study in the fields of photoinduced energy, electron transfer, laser dyes[4], and fluorescence. Furthermore, perylene imide, a typical n-type semiconductor material, exhibits a high electron nucleophilic potential and strong electron absorption capacity. In recent years, the modification of perylene imides has led to the synthesis of numerous derivatives that have been widely applied in the fields of organic solar cells[3], fluorescence imaging[5], and biofluorescence probe molecules[6].

The strong π-π interaction among the perylene rings leads to the formation of a densely packed structure, resulting in fluorescence quenching and impacting the photoelectric performance of perylene. Additionally, this strong intermolecular force contributes to its poor solubility, which limits its application and poses challenges for modifying perylene imide compounds through solvent dissolution.

Currently, two main modifications have been made to perylene diimide for enhanced applications[7]. One approach involves the introduction of solubilizing substituents at the nitrogen atom of the amide site[8, 9], while the other involves the incorporation of solubilizing substituents at the perylene bay site. Researchers have demonstrated that modifying amide substituents significantly improves the solubility of perylene imides without substantially affecting their optical properties. On the other hand, modifying the bay position not only alters the solubility, but also has a significant impact on its electron cloud characteristics[10-14] [15].

Polyhedral oligomeric silsequioxanes (POSS) are nano-sized cage compounds containing a hard, well-organized molecular structure with various surface functional groups. The inflexible conformation of POSS provides molecular shape stability, and its peripheral groups allow it to dissolve in various organic solvents. POSS has been widely employed in polymer nanocomposites to enhance their stability and mechanical properties via reactive or physical blending. Previous research has shown that the photophysical properties and assembly behavior of PDI in a condensed state are changed after introducing POSS into the imide site of PDI[16], and strong fluorescence emission and special dimer assembly appear. However, the existing researches have not reported the introduction of POSS for the bay site, and the combination of large steric resistance and changing the conjugated structure of PDI has academic research significance for the change of its molecular photophysical properties and fluorescence.

In this study, polyhedral oligomeric silsequioxanes (POSS) were introduced into the bay side of perylene imide to synthesize new perylene imide derivatives, 1,7-POSS-PDI-C_{12}. The introduction of polyhedral oligomeric silsequioxanes (POSS) at the bay side changed the molecular structure of the perylene imide, disrupting the planarity of the perylene core and weakening its strength. In our previous research,[16] we successfully incorporated POSS into the imide side of a perylene imide, leading to the formation of POSS-PDI-POSS. The PPP molecules in both their crystal and powder states exhibit discontinuous dimeric packing rather than continuous π-π stacking owing to steric hindrance caused by the bulky POSS units. As a result, less well-defined packing led to a higher possibility of non-fluorescence relaxation interaction forces within the perylene ring. Consequently, this modification affects the assembly behavior of the molecule. Then, explore the photophysical properties and self-assembly behavior both in the solution phase and in the solid phase.

➢ *Experimental Section*

- *Experimental Raw Materials and Reagent*

All the reagents were purchased from GENERAL-REAGENT (China) and used as received. Styrene Butadiene Styrene (SBS) was purchased from KRATON D1102 K Polymer (North America) in the form of dusted porous pellets. The product has a polystyrene (PS) content of 28% and a bulk density of 28 *Ibs/ft3*. Unless otherwise stated, reagents and solvents were procured as reagent grade and used without further purification. All reactions were conducted using standard glassware under an inert nitrogen atmosphere.

- *Film Preparation*

2.7 g of SBS dissolved in 15 ml chloroform at room temperature. The mixture was stirred using physical mixing until all the SBS pellets had fully dissolved in chloroform. Then, the proper amount of PPC (0.05-1.5 wt.%) was added to prepared their respective blends, which were then left to stir for 24 h. The colored solution was then applied to the glass plate under a hood to facilitate the evaporation of the solvent. After some time, the film was removed from the plate and allowed to reach room temperature.

- *Instrument and Characterization*

The Ultraviolet and visible (UV-vis) spectra (1×10^{-5} to 3.2×10^{-4}) were recorded on GENESYS 50. The fluorescence spectra (FL) of the samples were recorded on a FluoroMax Plus. The NMR spectra was recorded on a Swiss Bruker (Avance 600). The Mass spectroscopy was recorded on UltrafleXtreme, and Fourier Transform Infrared Spectroscopy (FT-IR) was recorded on NICOLET 6700. Solid-state drawing was carried out at room temperature.

- *Synthesis of Target Compound 1,7-POSS-PDI-C_{12}*

PTCDA-Br was prepared according to the literature procedure[17]. The prepared PTCDA-Br 0.50 g (0.91 mmol) and 15.00mL 1-methyl-2-pyrrolidone (NMP) were successively added to a 100mL three-neck flask, which was then stirred at 25 °C for 1 h. Subsequently, dodecylamine 0.84 g (4.54 mmol) was added, followed by the addition of acetic acid 16.80 g (280.00 mmol). The reaction mixture was heated to a temperature of 85~90°C and continued under N_2 protection for 7 hours. The mixture was then cooled to room temperature, 120.00 mL methanol was added, and the mixture was allowed to stand overnight. The product was filtered, and the resulting red solid was dried under vacuum. The crude product was purified by silica gel column chromatography (mobile phase: chloroform/n-hexane = 1:1, R_f=0.3) to obtain a red solid, 1,7-Br-PDI-C_{12} (75%). Add more long crystals to remove the inclusion 1,6-Br-PDI-C_{12} to get a pure 1,7-Br-PDI-C_{12} sample. ^{1}H NMR (600 MHz, $CDCl_3$): δ=9.50 (d, 2H, ArH), 9.00 (s, 2H, ArH), 8.73 (d, 2H, ArH), 4.23 (m, 4H, N-CH^*_2), 1.76 (t, 4H, N-CH_2-CH^*_2), 1.43~1.38 (t, 36H, CH_3-$(CH^*_2)_9$), 0.90 (t, 6H, CH^*_3). ^{13}C NMR (400 MHz, $CDCl_3$): δ(ppm) = 162.9, 138.0, 132.8, 129.3, 126.9, 123.2, 122.8, 120.8, 40.8, 29.6, 29.4, 28.1, 27.1, 22.7,14.1

The pure 1, 7-Br-PDI-C_{12} is successfully obtained. In this process, the bromine atom is substituted with POSS-SH groups, as shown in Fig. (2-2). 1, 7-Br-PDI-C12 (0.11 mmol, 100 mg) was added to a round-bottomed flask and dissolved in 20 mL of THF. Then, 60.80 mg of K_2CO_3 (0.44 mmol) and 108.48 mg of 18-crown-6 ether (0.44 mmol) were added, followed by a slightly excessive amount of POSS-SH 0.45 mg (0.50 mmol). Upon observation, the solution rapidly turned purple. The mixture was then stirred at room temperature for 2 h. The liquid was extracted with water and chloroform and subsequently separated by column chromatography (petroleum ether/DCM =200:3, Rf=0.3). The second separation band corresponded to the purple-red target compound 1,7-POSS-PDI-C_{12} (162 mg, 57%).

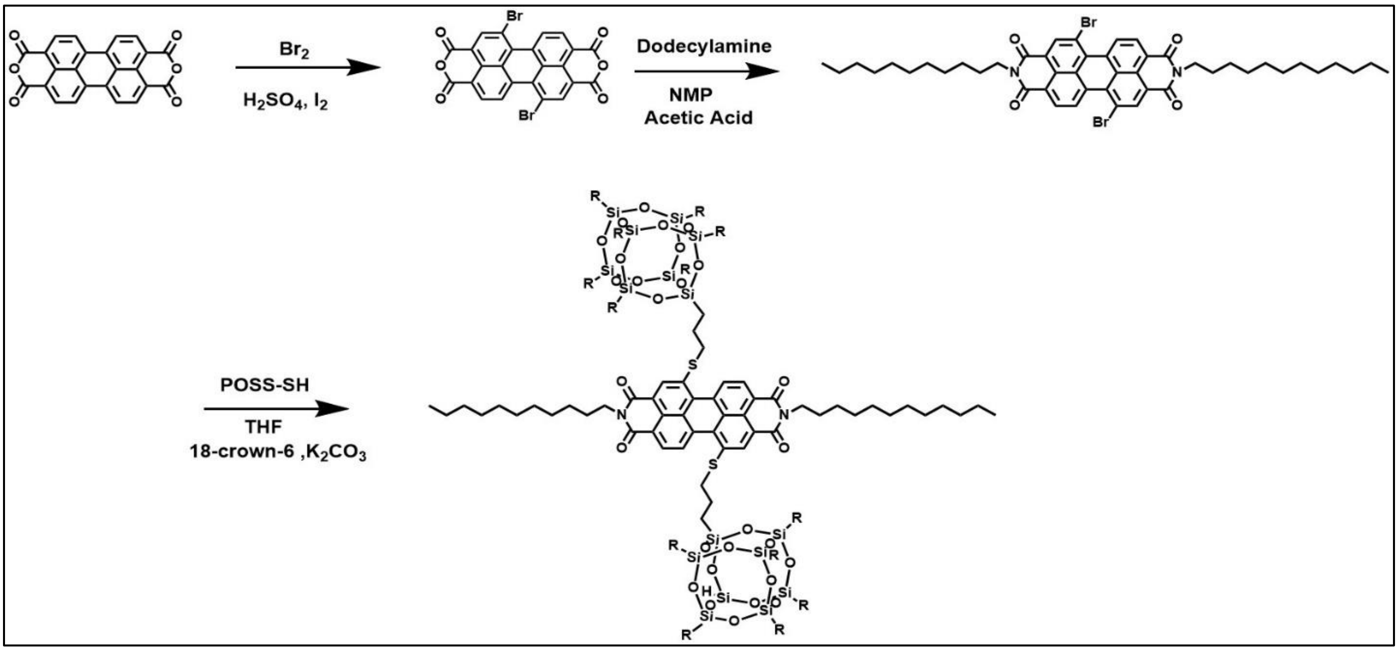

Fig 1 The Synthesis Route of PPC

1H NMR, 13C-NMR, and FTIR analyses showed that the target product was successfully synthesized. 1H NMR (600 MHz, CDCl3) δ 8.89 (d, *J* = 8.1 Hz, 1H), 8.78 (s, 1H), 8.70 (d, *J* = 8.1 Hz, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.76 (m, 6H), 1.27 (d, *J* = 17.3 Hz, 16H), 0.98 – 0.85 (m, 46H), 0.65 – 0.53 (m, 14H); 13C NMR (151 MHz, CDCl3): δ (ppm)= 25.68, 23.85, 22.71, 22.45, 22.38; MALDI-TOF Ms (m/z): Calculated Mass: 2544.67; found: 2506.10.

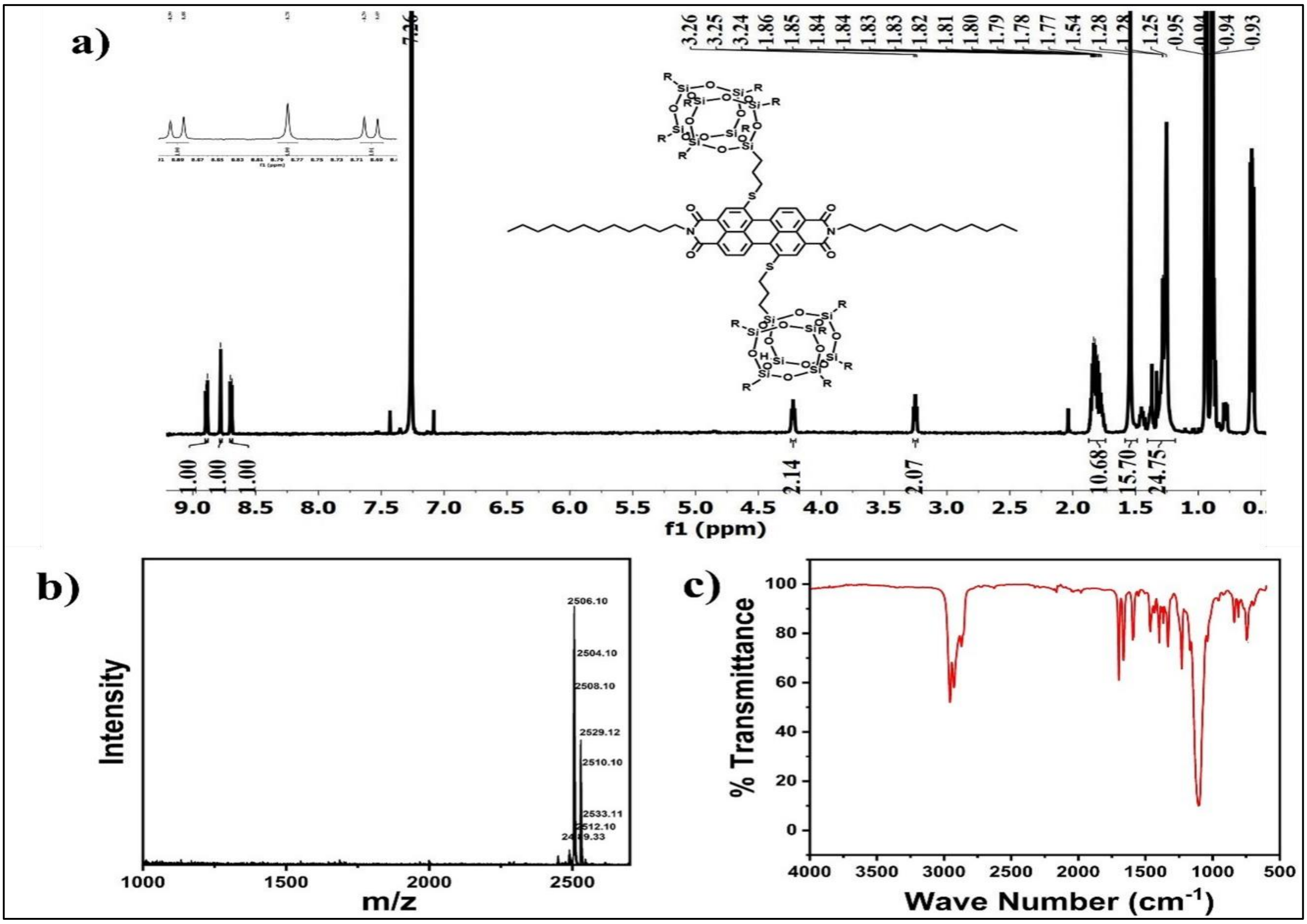

Fig 2 (a) ^{1}HNMR Spectra; (b) MS and; (c) FT-IR

II. RESULT AND DISCUSSION

➢ *Photophysical Properties in Solution*

When molecules were aggregated under the π–π interaction in the same solvent, the peak shape of the UV absorption spectrum typically changes, often resulting in a reversal of the peak pattern. Similarly, the fluorescence emission spectrum can also directly reflect the aggregation phenomenon caused by changes in concentration or solvent polarity. Therefore, the self-assembly behavior of the compounds in solution can be observed using both the UV-vis absorption and fluorescence spectra. Perylene imide derivatives have good solubility in chloroform; therefore, chloroform was chosen as the single solvent to study and check the self-assembly behavior of 1,7-POSS-PDI-C_{12} in different solvents as well. Figure 3 (a) and (b) shows the UV-vis absorption and fluorescence spectra of the PPC. When a large bulky POSS group was introduced into the bay side of the perylene imide, it caused steric hindrance, which altered the intermolecular interactions, size, and shape of the structure. The spectra show considerable band broadening and a less pronounced vibrionic structure of PDI owing to the greater tilt angle between the POSS and perylene core, which disrupts the planarity of the perylene core and weakens the strong π–π interaction force.

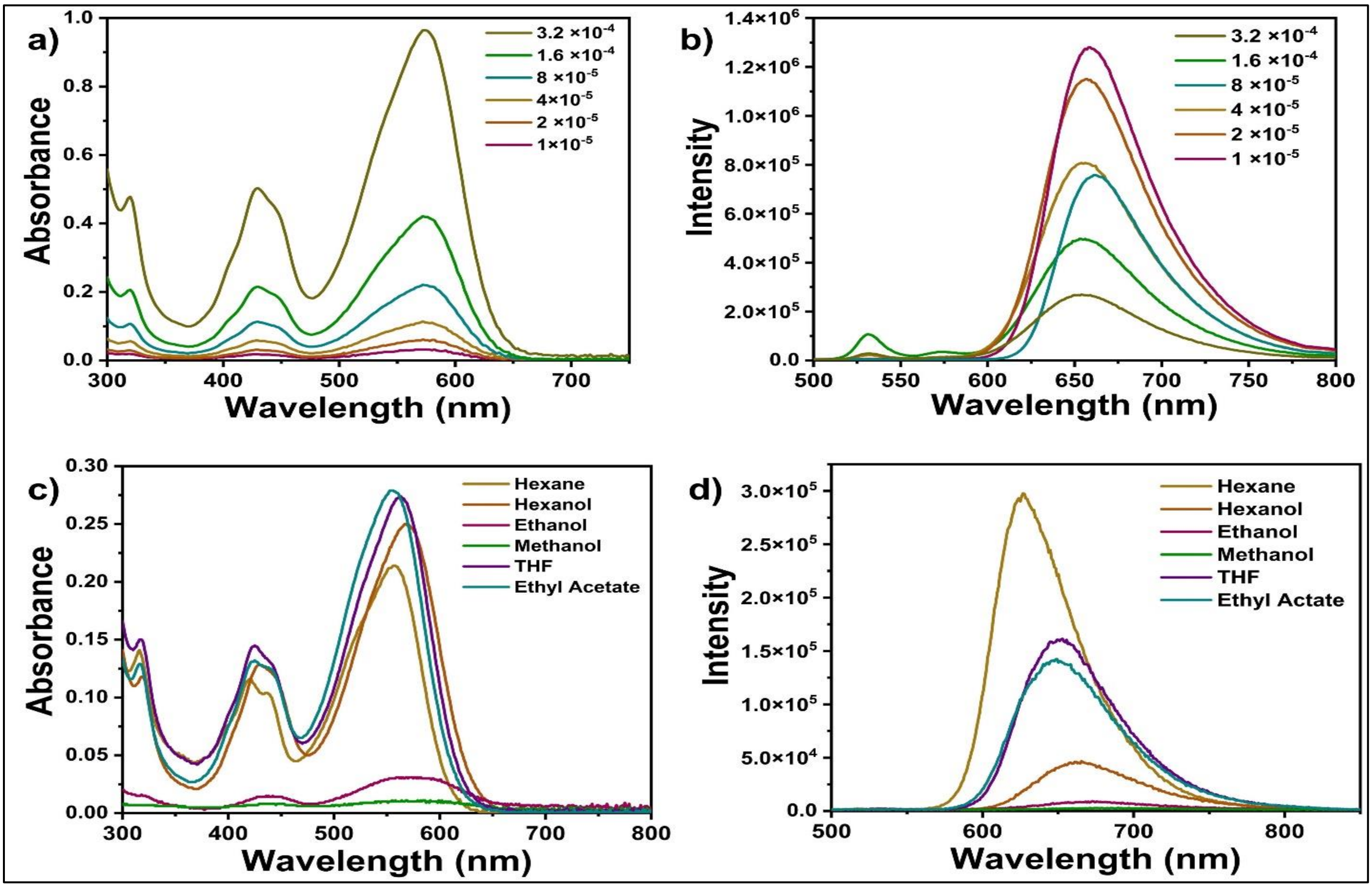

Fig 3 (a) UV-vis Absorption Spectra; (b) Fluorescence Spectra of PPE in TCM; (c) UV-vis Absorption Spectra; (d) Fluorescence Spectra of PPC in Different Solvents

Figure 3 (c) and (d) shows the UV-vis absorption and fluorescence spectra of PPC in various solvents. In contrast to the absorption spectra of TCM, the absorption spectra were influenced by the polarity of the solvent. In Ethyl acetate, THF, Hexanal, and Hexane, characteristic absorption peaks at different wavelengths were observed, indicating that PPC can fully interact with solvent molecules to form a single-molecule solution. With increasing solvent polarity, the aggregation propensity also increased, and the aggregation band redshifted, accompanied by peak quenching, especially in the case of ethanol and methanol. The corresponding fluorescence spectra were similarly affected by the solvent polarity, with the highest emission peak observed in hexane. Furthermore, an increase in solvent polarity enhanced the aggregation behavior, as evidenced by decreased in peak intensity and fluorescence quenching, particularly in ethanol and methanol.

The result reveals that the PPC molecules began aggregating, it was found to be at 8×10^{-5}M and remained in a single monomolecular state due to the bulky POSS group, which introduced large steric hindrance in the molecular packing, leading to weakening of the π–π interactions.

➢ *Photophysical Properties in Solid Thin Film*

Perylene diimide dyes are widely known for their excellent thermal and chemical stabilities, high photostability, and strong absorption in the visible region.

Styrene-butadiene-styrene (SBS) is a thermoplastic elastomer with a unique block copolymer structure that offers flexibility and toughness. When combined, PDI dyes and SBS polymers can form composite thin films with enhanced optical and mechanical properties. So, here we explore the fabrication and characterization of four different PDI derivatives in styrene–butadiene–styrene (SBS), a matrix, with a particular focus on the additional π–π interaction between the dye and the polymer, which enhances the sensitivity of the mechanical simulation.

Figure 4 shows the UV-vis absorption and fluorescence spectra of the PPC/SBS film in TCM. The absorption spectra display the same monomolecular state as that observed in the single solvent chloroform in the spectra in Fig. (3-1), with an increase in the concentration. The corresponding fluorescence spectra displayed continued monomeric emission from 0.05% to 0.5%. However, at a very high concentration of 1.0%, a significant fluorescence quenching effect was observed, resulting in the formation of a new red-shifted peak, indicative of aggregation.

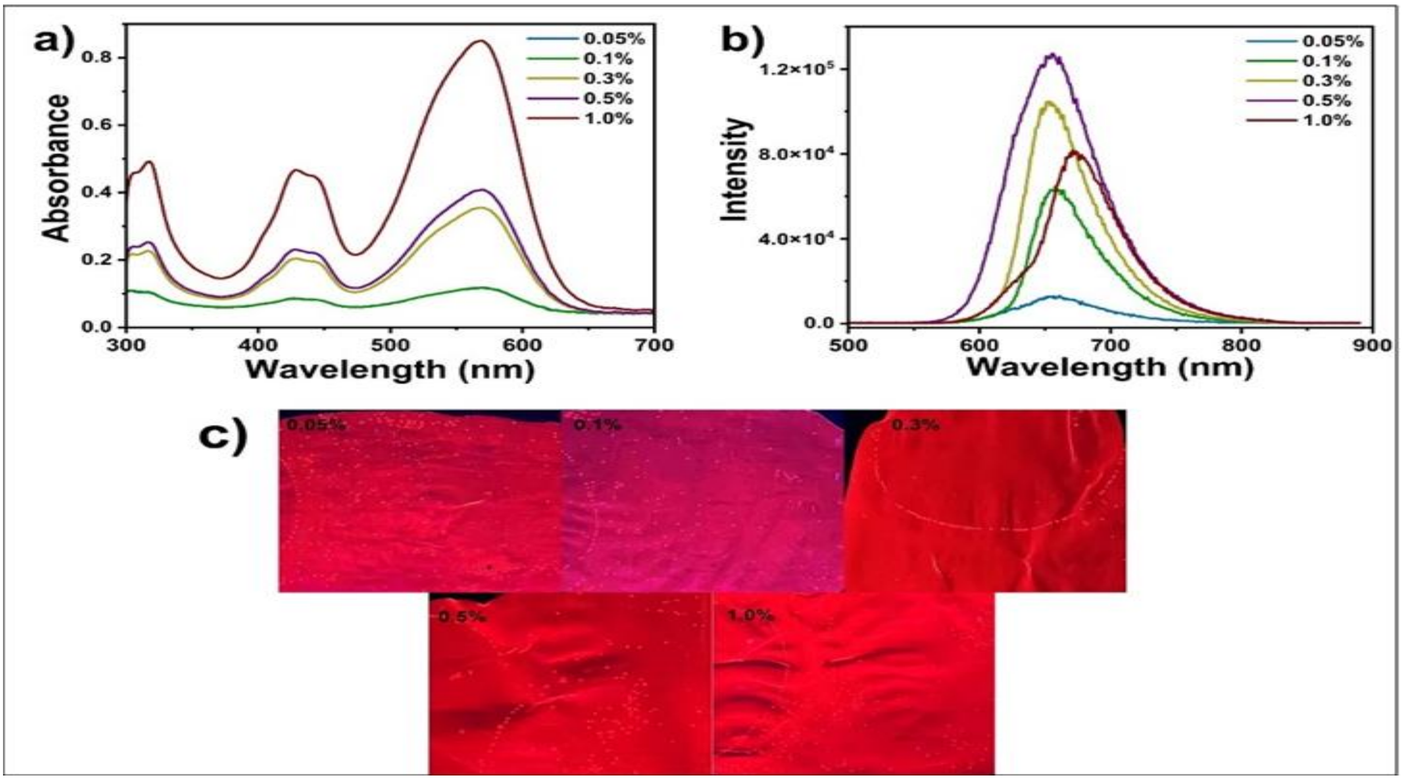

Fig 4 (a) UV-vis Absorption; (B) Fluorescence Spectra of PPC/SBS Film; (c) Fluorescence Microscope Images of Film with Different Concentrations

Figure 4 illustrate the mechanical deformation fluorescence spectra of the PPC/SBS films at a 0.3% concentration. As the deformation level increased from normal to 100%, the excimer emission increased, with no shift in the peaks. PPC exhibited monomeric behavior because of the large bulky POSS group on the bay side, which disrupted the planarity of the perylene core.

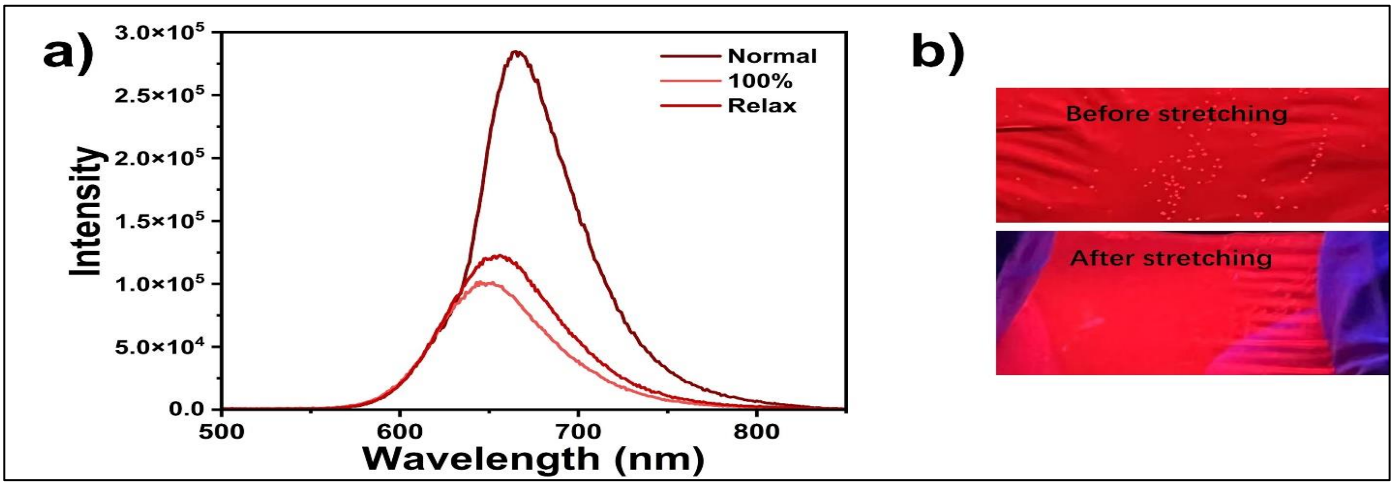

Fig 5 (a) Fluorescence Spectra of PPC/SBS Films at 0.3% Concentration; (b) Fluorescence Microscope Images of before and after Stretching

III. CONCLUSION

In this work, Perylene diimide derivatives 1,7-POSS-PDI-C_{12} (PPC) were synthesized using 1,7-Br-PDI-C_{12} and , 18-crown-6 ether as phase transfer agent, K_2CO_3 as catalyst and THF as solvent in a reaction system. Subsequently, the POSS-SH group was successfully introduced into the perylene imide bay site in high yield. The chemical structure and molecular weight of the products were characterized by ^{1}H-NMR, ^{13}C-NMR, MALDI-TOF MS and FT-IR. The self-assembly behavior in different solvents was studied using the research solution self-assembly method. PPC remained in a single monomolecular state due to the bulky POSS group, which introduced large steric hindrance in the molecular packing, leading to the weakening of the π–π interactions. Then, the Composite thin films containing PPC in SBS was prepared. PPC do not exhibit significant force-chromic behavior owing to the dispersion of single-molecule states. This shows that in the construction of mechanochromic materials, chromophore molecules need to have a certain degree of aggregation in the matrix, but the aggregation degree should not be too high.

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