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"Dial-In" Emission from Unique Flexible Material with Polarization Tuneable Spectral Intensity

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ABSTRACT

The growth of an organic photoluminiscent material which could show a promising role as a catalyst, sensors, organic light-emitting diode, logic gate, etc is a major demand and challenge for the global scientific society. In context to this, we adopted a photoclick polymerization method for the growth of unique photoluminescent three dimensional (3D) polymer film E as a model system that showed emission tunability over the range 350-650 nm against excitation range 295-425 nm. The DFT analysis on energy calculation and pi stacking supported well to the spectroscopic observation for the material to exhibit broad range of emission due to newly formed chromophoric units within the film. Full polarization spectroscopic Mueller Matrix studies employed to extract and quantify the molecular orientational order of both the ground (excitation) and excited (emission) state anisotropies via a set of newly defined parameters, namely the fluorescence diattenuation and fluorescence polarizance. The information contained in the recorded fluorescence Mueller

matrix of the organic polymer material enabled a useful way to control the spectral intensity of emission using pre and post-selection of polarization states. The observation was on the assumption for the longer lifetime of the excited dipolar orientation attributed to compactness of the film.

Key Words: Thiol-alkene photoclick reaction, pi-pi interaction, crosslinked framework, pyrene, photoluminescent, anisotropy, polarization, molecular orientation order, Density Function Theory (DFT).

INTRODUCTION

A recent survey reports the global world to have overflown with photoluminescent molecules. Such luminescent molecules are either comprising of inorganic constituents or the organic – inorganic hybrid constituents.^[1] Though both inorganic, as well as hybrid organometallic luminescent material, show their dominance, however their limitations couldn't be overcome. New approaches are invoked with the input of modified organic-inorganic hybrid, but their prolonged efficiency remains one of the major concerns. Therefore with the focus onto such drawbacks, the field is slowly switching over to the growth of luminescent organic material. Extensive research is done on conjugated fluorophore based diode whereas reports on intact pi stacked 3D photoluminescent polymer film is limited.^[2-11] After thorough learning from the literature examples, we believed that with modification on the existing systems would provide superior material with excellent features related to sensing, the organic light-emitting diode (OLED), catalysis, etc. First, we wanted to adopt a simple and facile synthetic approach. Secondly, this approach should give an intact pi-stacked polymer film where chromophore constituents introduced should gain a static phase. The additional features that we expected to mold and incorporate within the modeled luminescent macromolecular film are flexibility, stability, insolubility, easy handling, and many more.

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Considering all these points, herein we report on the design, synthesis, and complete demonstration of a newly developed photoluminescent polymer material. We have utilized the thiol-alkene photo click polymerization reaction to grow such polymer material.^[13-15] The polymerization is two plane polymerization process, which gives rise to three dimensional (3D) polymer material in the form of film. This polymer film so grown via proposed photopolymerization technique is likely to be stable. Our proposed photopolymerization method has been highlighted in **Scheme** 2a.

Further, we have explored the fluorescence Mueller matrix spectroscopy technique for probing the polarization anisotropies of the film arising due to its cross-linked organization. The fluorescence polarization spectroscopy has shown its considerable promise for characterization of different chemical, biological, and complex physical systems. Traditionally fluorescence polarization anisotropy is quantified by the anisotropy parameter r= $(I_{\parallel}-I_{\perp})/(I_{\parallel}+2 I_{\perp})$ where I_{\parallel} and I_{\perp} are respectively the measured fluorescent intensities parallel to and perpendicular to the excitation linear polarization.^[16] The anisotropy parameter (r) contains information about the inherent depolarization associated with the fluorescence emission. Depolarization in case of fluorescence is caused due to the random orientation of fluorophores, radiationless energy transfer among fluorophores and extrinsic causes like multiple scattering effects, etc. Thus the resulting anisotropy parameter contains lumped information about all the contributing polarizing and depolarizing effects associated with the fluorescence scattering process. In addition to the intrinsic and extrinsic causes of depolarization, it is useful to capture and quantify exclusive information of the molecular orientation and organization of the fluorescent molecules. For this purpose, we have employed Mueller matrix (transfer function of an optical system) measurement for quantification of organizational anisotropies of both the excitation and emission states of the molecule. These anisotropies manifest themselves as differential excitation of fluorescence

with orthogonal polarization (both linear and circular) and differential emission of fluorescence for orthogonal polarization (both linear and circular). These anisotropies are quantified through the various elements of the recorded fluorescence Mueller matrix. Note that the Mueller matrix polarimetry is usually studied and well-explored for elastic scattering processes like reflection, refraction etc.^[17-18] Recent theoretical and experimental studies of our group and others have extended the Muller matrix measurement for inelastic scattering processes like fluorescence.^[19-20] The inverse analysis of fluorescence Mueller matrix has enabled us to quantify the excitation and emission state anisotropies via a set of newly defined polarimetry parameters, namely, the fluorescence diattenuation (differential excitation of fluorescence) and fluorescence polarizance (differential emission of fluorescence).^[21] These are then used to quantify the molecular orientational order of the organic polymer domain, and finally, the polarization anisotropies of fluorescence emission showed useful application involving polarization based tuning of spectral intensity.

Scheme a:



Scheme b:



Scheme c:





Scheme d:



Scheme 1(a-d). Synthesis of compounds - A, A', B and C

Results and Discussions



Scheme 2: (a) Synthesis of polymer E (sample). (b) and (c) respectively represent polymer E to exhibit flexibility and luminescence. (d) Represents a schematic of the experimental spectroscopic Fluorescence Mueller matrix setup. F: long-pass filter; P1 and P2: linear polarizers; Q1 and Q2: achromatic quarter-wave retarders. P1 and Q1 form the polarization state generator (PSG) unit. P2 and Q2 form the polarization state analyzer (PSA) unit. The inverse analysis of the recorded Fluorescence Muller matrix gives anisotropies of the ground and excited molecular states, namely fluorescence diattenuation, and polarizance respectively. The 4×4 fluorescence spectroscopic Mueller matrix R ($\lambda = 450-800$ nm) recorded from the gel sample. The first element (R_{11}) represents the polarization independent fluorescence spectra. The other three elements in the first row (blue colored) represent excitation anisotropy related to the ground molecular state while the three elements

in the first column (red colored) represent emission anisotropy related to the excited molecular state, respectively.

Photoluminescent material is a typical example for future utilization in a scientific and global society. With this into account, the need to work on up-gradation towards its efficiency in terms of tunability and mechanical properties has been invoked. We approached for the photopolymerization of the synthesized monomers B, and C, with the commercial monomer penterthritoltetrakis (3-mercaptopropionate) tetrathiol (4SH) to grow the photoluminescent 3D polymer film E (abbreviated as polymer E) as showed in Scheme 2a. To check the film formation, the non luminescent 3D polymer film D (abbreviated as polymer D) was synthesized first. The synthetic scheme for the polymer D is showed in supporting information, SI. The monomers required for the growth of polymer E is showed in Scheme 1. All the monomers were well characterized using NMR spectroscopy, mass spectrometer, and FTIR-ATR spectroscopy techniques (Figure S1-8, S13-16, S17, SI). The formation of Polymer D and E was characterized via NMR (Figure S9-S10, SI) and FTIR-ATR spectroscopy techniques (Figure S18, SI). The comparative ¹H NMR spectra confirmed the propagation of polymerization and product formation (Figure S11-12, SI). Comparative FTIR-ATR spectra supported well. The thiol (-SH) signal at 2535 cm⁻¹ disappeared for the polymers (Figure S18, SI). This confirmed thiolation to have occurred during photopolymerization process. The thermogravimetric analysis (TGA) curves for both the polymers D and E confirmed their thermal stability (Figure S20, SI). The morphology for the materials was observed too (Figure S22, SI). EDX and mapping for the respective polymers were analysed as well (Figure S23-24, SI). The observation supported the presence of elements- carbon; C, oxygen; O, nitrogen; N and sulphur; S. Comparative UV for the monomers were done as showed in **Figure** S19, SI. This confirmed only monomer C showing absorbance up to 350 nm. The physical observation under ultraviolet (UV) light reveals the

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polymer E contained with chromophore C emits white light against excitation at a wavelength of 365 nm (**Scheme** 2c). The basic principle that governs photoluminescence in devices is a combination of charge injection (CI) and charge recombination (CR) i.e., back electron transfer (BET).^[22] Based on this, prolonged analysis has been undertaken to check the tunability of the polymer E. During the process towards growth of pyrene based polymer E, the reaction mixture was allowed to stabilize. The reorientation and interlocking due to pi stacking occurred within the reaction mixture. The polymer E as film so grown was flexible, transparent and compressible (**Scheme** 2b). The probable mechanism to formation of polymer E has been showed in **Figure** S21, SI.



Figure 1: *a*) represent UV spectrum, *b*) represent fluorescence spectrum for excitation at 355 nm, *c*) represents CIE coordinate diagram, *d*) represents tunability to emission with switch in excitation energy, *e*) represent computed absorption spectra of aggregated pyrene derivative, and *f*) represents lifetime decay for the polymer E with lifetime of 17.7 μ s.

The proposed mechanism has been highlighted for single thiol-alkene moiety. The thiol radical (-S^o) generated in step1 reduces the alkenes B, and C in substages. The free radical crosslinking proceed repeatedly unless the saturation and the randomness of the monomers ceases. The polymer E with white light emission was analysed using solid state ultraviolet

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(UV) and Fluorescence spectroscopy. The solid-state UV and fluorescence spectroscopic analysis supported our physical observation. UV curve reflects the polymer E to cover the range over 250-600 nm, whereas the emission spectrum covered the range for red, green, and blue (RGB) (**Figure** 1a-b). To value the white color and emissive property, Commission International de I'Eclairage (CIE) chromaticity coordinates (x,y) were calculated.^[23-25] The color co-ordinate was 0.34 and 0.37, falling in range of white light CIE coordinates (x = 0.33, y = 0.33). The correlated color temperature, Tcp for the polymer E is 4936 K. The Tcp value is around light source of a cool compact fluorescent lamp (CFL).

Further to check the emission tunability, emission spectra over range 400 - 650 nm for excitation over range 295-425 nm was observed. The lifetime decay for the polymer E was found to be 17.8 μ s (**Figure** 1f). The emission tunability can now be attributed to the formation of pi stacked pyrene units within the polymer E. To support the growth of pi stacked energy states in polymer E responsible to emission tunability, theoretical analysis on pi stacking was undertaken.

We performed quantum computation in density functional approach using Gaussian 09^[26] package for molecular-level understanding of the observed absorption phenomenon of our polymer E. It is previously reported that pyrene or pyrene derivatives show fluorescence due to the formation of excimer.^[27-30] In recent time it is reported that intermolecular photoinduced electron transfer (PET) and BET is also possible for pyrene which causes intense fluorescence. ^[31] But, in all these cases, emission occurs in the blue region. At the same time, it is believed that the formation of excimer is not possible in polymer E. There are possibilities of electron transfer from the pyrene unit to any other unit. Similarly, it is expected in both the units exist in our pyrene based polymer film E. To test these possibilities we compute absorption spectra of compounds formed from unit-c (pyrene derivative) with unit-b, unit-c with unit-a separately and unit-c with both unit-a and unit-b. Computed results

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are presented in Figure-S25, ESI. We observe that all lowest energy absorption peaks are located near 338 nm where the lowest absorption peak of unit-c exists. Thus, emission of white light is not due to intramolecular charge transfer. There is only one possibility left which may be responsible for white light emission- pi-pi stacking of pi-electron of pyrene rings which exist in parallel orientation within the polymer film E. To test this possibility, we compute absorption spectra of aggregated form of unit-c. We studied dimer, tetramer and hexamer of unit-c. A computed spectrum is presented in Figure 1e. Absorption spectra of monomer of pyrene derivative i.e. unit-c consists of three different peaks located at 338 nm, 266 nm and 225 nm. Here lowest energy transition (338 nm) occurs for HOMO to LUMO electron transition. Both HOMO and LUMO are located over pyrene ring (Figure S26, ESI). Thus, derivatization of pyrene doesn't help to shift of absorption spectra. Transitions correspond to the other two peaks (266 nm and 225 nm) are dominated by HOMO-1 to LUMO and HOMO-1 to LUMO+2 electron transfer. All these MOs are also located on the pyrene ring (Figure S26, SI). Thus, other peaks also don't change due to derivatization. But, peaks shifted due to aggregation. It is observed that with an increase of aggregation, peaks merge into two peaks for dimer and tetramer. It further reduces to one peak for hexamer. In hexamer, only one broad peak appears which shows very good absorbance (more than 5000) in the visible region (400 nm to 650 nm). Thus, it would emit white light. To understand the redshift of spectra on aggregation, we studied key electron transitions of the hexamer. It is observed that the electron transition for the lowest energy absorption (710 nm) which is in the red color zone, is dominated by HOMO-1 to LUMO+6. This is, in fact, the charge transfer from one pyrene ring to its nearest pyrene ring (Figure S27-Y1, SI). The key absorption in the green color zone (542 nm) is dominated by HOMO to LUMO+14 electron transfer. This transition is the charge transfer from the pyrene ring to the carbonyl pi-electron (Figure S27-Y2, SI). Absorption in the blue color zone (399 nm) is also due to pyrene ring electron

transfer but it is quite complicated. Here, the pi-electron cloud of two closest pyrene rings is transferred to their nearest pyrene ring simultaneously (**Figure** S27-Y3, SI). The important nature of these transitions is that they depend on aggregation and the compactness of aggregation.

With the theoretical analysis parallel the spectroscopic observation, the concern we looked for was the flexibility for the polymer E. To analyze the material strength, the polymer E was mounted onto the Universal Testing Machine (UTM). The respective length (l), breadth (b) and height (h) of the material were monitored (l=7.01 mm, b=6.9 mm, h=3.09 mm). The compression curve revealed quality strength and elasticity for the film. The release of compressed pressure allowed the film to gain its usual form. The compression was performed over cycles to analyse the existence of elasticity. The polymer material tends to retain its linear elasticity over cycles as shown in **Figure** 2. This promising property makes it as a potential model system towards growth of organic photoluminiscent material that is easy to handle and can be applied to application such as catalysis, OLED, etc.



Figure 2: Compression analysis for the polymer film E over cycles; Cn.

Further, during our experimental fluorescence Mueller matrix measurement, we selected wavelength λ = 405 nm beams and excited the polymer E which is close to the absorption band maxima at λ = 399 nm. The fluorescence is found to be highly anisotropic both during

excitation and emission. In this situation, the polymer E likely undergoes HOMO-1 to LUMO+27 transition with negligible contribution from HOMO to LUMO+14 and HOMO-1 to LUMO+6 transitions (see supplementary for the anisotropic configuration obtained using DFT calculations). This is the reason for the ground state (during excitation) anisotropy of the fluorescence which is manifested as the fluorescence diattenuation (differential excitation of fluorescence by orthogonal polarizations). We also saw higher anisotropy during emission of fluorescence at the excited state of the molecule manifesting as the fluorescence polarizance (differential emission of fluorescence with orthogonal linear polarization)

Experimental Fluorescence Mueller Matrix studies:

A schematic representation of our home built comprehensive experimental Mueller Matrix Fluorescence Spectroscopy platform has been introduced in Scheme 2d. The system is calibrated using a robust Eigenvalue calibration method.^[32-33] The specifics of the system and various steps of this method can be found elsewhere.^[34] Recorded spectroscopic 4 x 4 fluorescence Mueller matrix (R) from the polymer E has been highlighted in Scheme 2d. Ground and excited states anisotropic information is extracted from recorded R (λ).

Inverse Analysis of fluorescence Mueller matrix for determination of Molecular Orientation:

When light interact with an optical medium, the output light is characterised by its stoke vector $S_{out} = RS_{In}$ where S_{in} and S_{out} are the input and out stokes vector, and R is the transfer function (Mueller Matrix) of the medium which contains all the polarization information of the system under study. There are several decomposition methods which may decouple the contributing polarization information from a recorded Mueller Matrix. These, polarization information have been successfully extracted using several decomposition methods are not

valid for inelastic scattering process such as fluorescence. Recent studies of our group and others have shown that for complex processes such as fluorescence the polarization information can be extracted from a recorded Mueller matrix as $R = M_1 M_d M_0$ where M_d represents the depolarization effects occurs due to random orientation of the fluorophores and other extrinsic causes, $M_0 \& M_1$ represents the amplitude anisotropies of the ground and excited states of fluorophore molecules (**Figure** S28, SI)³⁴. Finally, florescence anisotropy parameters can be obtained from the recorded fluorescence Mueller matrix (R) as:

$$\alpha_{T} = \frac{\sqrt{R_{12}^{2} + R_{13}^{2} + R_{14}^{2}}}{R_{11}}; \qquad \alpha_{L} = \frac{\sqrt{R_{12}^{2} + R_{13}^{2}}}{R_{11}}; \qquad \alpha_{C} = \frac{R_{14}}{R_{11}};$$
$$\beta_{T} = \frac{\sqrt{R_{21}^{2} + R_{31}^{2} + R_{41}^{2}}}{R_{11}}; \qquad \beta_{L} = \frac{\sqrt{R_{21}^{2} + R_{31}^{2}}}{R_{11}}; \qquad \beta_{C} = \frac{R_{41}}{R_{11}}; \qquad \dots \dots (1)$$

Where, α_T , α_L , and α_C are the total, linear, and circular fluorescence diattenuation, respectively and β_T , β_L , and β_C are the total, linear and circular polarizance, respectively. Anisotropy parameters contain information about the molecular orientation of the samples. Mueller Matrix elements R_{13}/R_{12} and R_{31}/R_{21} represent average fluorescent dipolar orientation angles for the ground (θ_{ex}) and the excited (θ_{em}) molecular states and can be expressed in terms of recorded spectral Mueller Matrix^[35] as

Here we define a molecular angular distribution function $f(\theta) = e^{-(\theta - \theta_{ex/em})^2} / 2\Delta \theta_{ex/em}^2$ with width $\Delta \theta$ around the average fluorescent dipolar orientation angle (θ_{ex} and θ_{em}) which contains information on the distribution of the orientation angles of the molecules. Hence, the measured fluorescence intensity for excitation with a given polarization vector **E** can be written as:

$$I_{\eta} = \int_{\theta}^{\pi} \left| \boldsymbol{\mu} \cdot \boldsymbol{E}_{\eta} \right|^{2} f(\theta) d\theta = (1 - \eta) \int_{\theta}^{\pi} \cos^{2}(\theta) f(\theta) d\theta + \eta \int_{\theta}^{\pi} \sin^{2}(\theta) f(\theta) d\theta ; \text{ where, } \eta = \begin{cases} 0, \text{ for } H \\ 1, \text{ for } V \end{cases}$$
$$I_{P/M} = \int_{\theta}^{\pi} \left| \boldsymbol{\mu} \cdot \boldsymbol{E}_{P/M} \right|^{2} f(\theta) d\theta \mu \int_{\theta}^{\pi} \cos^{2}(\theta \pm \pi / 4) f(\theta) d\theta$$



Figure 3: (a) Normalized fluorescence spectroscopic Mueller matrix; (b) The fluorescence diattenuation and polarizance parameters; (c) Wavelength variation of the average fluorescent dipolar orientation angles for the ground (θ_{ex} , blue dashed line) and the excited (θ_{em} , solid red line) molecular states. (d) The derived molecular angular distribution function for the ground ($f_{ex}(\theta)$, blue dashed line) θ_{ex} and the excited ($f_{em}(\theta)$, solid red line) molecular states of the fluorescent molecule. Inverse calculations were performed on the

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Mueller matrix-derived α_L and β_L parameters to extract this information. The estimated standard deviations of the orientation angle distribution for the ground and excited states were found to be $\Delta \theta_{ex} = 0.02614$ rad and $\Delta \theta_{em} = 0.05397$ rad, respectively. The vertical lines mark the center positions of the distribution functions.

Figure 3a shows the recorded experimental normalized fluorescence Muller matrix, Figure 3b shows the extracted fluorescence linear (β_L) and circular (β_C) polarizance parameter and fluorescence linear (a_L) and circular (a_C) diattenuation using equation (1), Figure 3c shows wavelength variation of the average fluorescent dipolar orientation angles for the ground (θ_{ex} , blue dashed line) and the excited ($\theta_{\rm em}$, red solid line) molecular states using equation (2) , Figure 3d shows the derived molecular angular distribution function for the ground ($f_{ex}(\theta)$ blue solid line) θ_{ex} and the excited ($f_{em}(\theta)$, red dashed line) molecular states of the fluorescent molecule. Several interesting trends can be obtained from these figures. First element (R_{II}) of recorded experimental normalized fluorescence Muller matrix represents total fluorescence intensity. The elements in first row colored in blue represents the intrinsic anisotropic properties of the ground molecular states. Similarly, elements in first column of MM highlighted in red color represent emission state anisotropy of the molecules in excited state. The diagonal elements of MM are related to the depolarization effect associated with the fluorescence process. Elements R_{23} , R_{24} ; R_{34} , R_{32} , R_{42} , R_{43} are related with the phase anisotropy effect associated with the fluorescence process which is negligible (close to zero) in case of fluorescence scattering. In Figure 3(b) we have shown the linear and circular anisotropy of the polymer E. The linear anisotropy of the excited molecular state is higher compared to that of the ground molecular state which means the excited molecular state is more organized compared to the ground molecular state. However, the circular anisotropy has

negligible value implying the fact that molecules possess no chirality in it, which is also confirmed using DFT simulation. The ground and excited-state molecular orientation angles are plotted in **Figure** 3(c). We have plotted the distribution function to infer about the molecular orientation. As excited molecular state anisotropy parameter (β_L) is significantly larger compared to ground state anisotropy parameter (α_L), the excited molecular states are more organised than ground states, accordingly standard deviation $\Delta \theta_{ex}$ is larger than $\Delta \theta_{em}$. Molecular distribution function $f_{ex}(\theta)$ and $f_{em}(\theta)$ were calculated near the peak of the fluorescence intensity (520 nm). Note that Pi-Pi stacking of Pyrene moieties and thiol-alkene photo-click radical polymerization reaction in the norbornene monomers generated a single one product material within the cross-linked framework. This leads to preferential linear organization of the fluorescent molecular dipoles (of Pyrene units), which appears to be the underlying reason for considerably high magnitudes of the fluorescence anisotropy, α_L and β_L parameters.

Polarization controlled tuning of Fluorescence spectra:



Figure 4: Comparison of polarization projected intensity using different pre and post selected states: the polarization independent fluorescence spectra is shown by the black dashed line, the recorded fluorescence intensity for input horizontal pre-selection and horizontal (vertical) post-selection state is shown by the red(blue) solid curve. The inset shows spectral variations of area normalized the projected intensities for the same. The vertical line in each curve corresponds to the maximum position of the corresponding intensity.

The strong polarization anisotropy of fluorescence of the crosslinked polymer E provides a useful handle to control the emitted spectral intensity of fluorescence by using a proper set of pre- and post-selection of the polarization states. To get desirable control over emitted fluorescence intensity without changing the physical or chemical properties of the polymer matrix, we have thus used a general recipe using polarization state projection on the recorded fluorescence Mueller Matrix $(I(\lambda) = \frac{1}{2} \mathbf{S}_{out}^T M(\lambda) \mathbf{S}_{in})$. The fluorescence intensity can be desirably enhanced or suppressed by orders of magnitude using different pre- and postselected polarization states, as illustrated in Figure 4. This also leads to systematic changes in the spectral line shape of the emission (shown in the inset, where the area normalized spectral line shapes are displayed). The emitted fluorescence spectra with horizontal input and detection with horizontal and vertical post-selection are shown by red and solid blue curves, respectively. Using horizontal pre- and post-selection, the emitted fluorescence signal is observed to be considerably enhanced for unpolarized fluorescence intensity, which is accompanied by subtle changes in the line shape. For detection with vertical post-selection for horizontal pre-selection leads to more apparent shifts in the peak position (~ 5 nm) and a more drastic reduction in the intensity of emission. The fluorescence anisotropy properties, namely, linear fluorescence diattenuation (differential excitation of fluorescence by

orthogonal linear polarizations) and the fluorescence polarizance (differential emission of fluorescence with orthogonal linear polarization) properties of the OLED sample are responsible for such differential spectral intensity profiles for different linear polarizations. Thus, in this intrinsically anisotropic systems, pre and post selection of polarization states provides a unique handle to desirably control both the intensity and the spectral line shape of emission without changing the chemical composition or molecular organization of the sample. This remarkable feature of the polymer E may find useful application for developing polarization control tuneable devices such as diagnostics and imaging, apollo sensors, and logic gates.^[36-38]

Conclusions

To summarize, in this article, we have successfully demonstrated emission properties of the newly synthesized photoluminescent 3D polymer film E covering the wide range over RGB range from spectroscopic analysis. This synthesized polymer E exhibiting physical properties such as flexibility and mechanical strength in context to compressibility could be useful as an efficient organic spin-optical device.

Moreover the theoretical analysis confirms its pi-pi stacking via formation to dimer, trimer, tetramer, pentamer, and so on which has covered the region of our interest. Also, we have quantified the excited and emission state anisotropies arising from the orientation and organization of organic polymer film E via the fluorescence diattenuation and fluorescence polarizance parameters. These parameters are further used to quantify the molecular orientational order of the organic LED sample. Finally, the information contained in the fluorescence Mueller matrix is exploited for polarization controlled tuning of spectral intensity of emission. Thus the modeled organic polymer E holds considerable promise and which can turn out to be a potential candidate for devices related to catalysis, sensing,

diagnostic and imaging, light emission as OLED, etc. Particularly the polarization controlled tuning of the intensity may also have useful application in this domain.

Associate contents

The Supporting Information (SI) contains - Synthetic scheme for polymer D. Synthetic procedures for A, A', B, C, polymer D, and E. ¹H NMR and ¹³C NMR for A, A', B, and C, ¹H NMR for the polymer D and E. Comparative ¹H NMR for polymer D and E. ESI-MS for the synthesized monomers A, A', B and C. TGA analysis for polymer D and E. ATR-FTIR curves of 4SH, monomer B, monomer C, polymer D and E. Comparative UV analysis of 4S, monomer B and monomer C. Mechanism to formation of pyrene crosslinked polymer E. HOMO-LUMO energy state calculation. Muller Matrix analysis. FE SEM, EDX and Mapping analysis for polymer D and E.

Author's contributions

The project is an outcome of effort from all the authors.

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