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PAPER

Linearly Polarized Emission from Self-Assembled Microstructures of Mesogenic polythiophenes

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This work reports on linearly polarized photoluminescence and electroluminescence through spontaneous self assembly of mesogenic polythiophenes under ambient conditions. A systematic structural variation and different alkyl chain lengths leads to three series of closely related mesogenic polythiophenes viz; TPn, TNn and TVn. Polarized Light Emitting Diodes fabricated from TV12 by solution processing with configuration of ITO/PEDOT:PSS/Polymer/Al shows linearly polarized electroluminescence with dichroic ratio of 14.32 Spun thin films of TV12 elicited a dichroic ratio of 15.02 in photoluminescence. Studies using a range of techniques such as; Atomic Force Microscopy, Grazing Incidence X-Ray Diffraction, Fluorescence anisotropy, Linear dichroism, Fluorescence lifetime and Dynamic light scattering reveal that the presence of highly ordered self assembly was responsible for the dimensional confinement of optoelectronic properties. The ordering in thin film originates from vinyl groups in side chains in TV12 polymer. Further studies on device characteristics show higher charge carrier mobility in polymers with vinyl side chains. Solution processed PLEDs show a maximum brightness of 863 cd/m^2 for TP12 polymer and TV12 based LEDs show a maximum brightness of 524 cd/m^2.

Introduction

Dimensional confinement of optoelectronic properties in organic materials is an interesting facet of organic electronics. Organic materials with unique scope for robust design can be tuned for their desired property through control of aggregation. Careful engineering of molecular properties could result in properties such as anisotropic conductivity, polarized emission, chiral assembly to form interesting nanostructures.[1] Liquid crystals are an important class of materials with potential for such tuning of properties. Organic Light Emitting Diodes have been studied with columnar and nematic liquid crystals.[1, 2] However, nematic liquid crystals were most extensively studied for OLED applications and are found to show polarized electroluminescence.

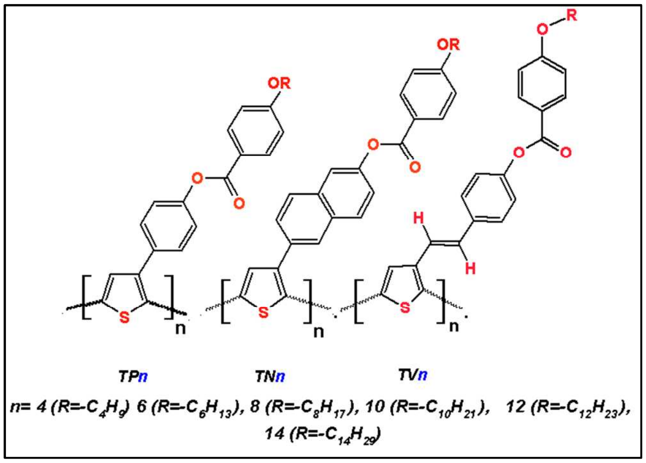

Chart 1. Structure of polymers under investigation.

Polarized light emission Light emitting diodes have attracted the interest of many researchers in recent times.[3, 4] Polarized Light Emitting Diodes (PLEDs) are important in development of efficient back lighting for display applications.[5] They can also be used for optical spintronics and optical information processing.[6, 7] The use of additional reflective polarizers or additional Liquid Crystaline (LC) layer reduces the efficiency of the back lighting in displays. Liquid crystalline conjugated polymers/oligomers are an integral part of the PLEDs.[8] Linearly polarized electroluminescence from thermotropic nematic mesomorphism is reported for monochromatic LEDs.[9, 10] White and full color electroluminescence with polarization is rapidly gaining research interest since it can result in highly efficient and wide view displays.[7, 11-13] As a common criterion, the uniaxial alignment of molecules is used for linearly polarized emission from organic luminogens.[7] Many methods used for polarized electroluminescence address the problem through preservation of uniaxial alignment. Different approaches for polarized electroluminescence are; Langimir-Blodgett technique,[14] mechanical rubbing/shearing,[15-18] orientation by pre-aligned substrate,[19, 20] precourser conversion on aligned substrate,[21] vapour phase epitaxy,[22] Friction transfer deposition,[23, 24] and by use of giant birefringent optical (GBO) reflective polarizers.[25] However polarized electroluminescence from spontaneous

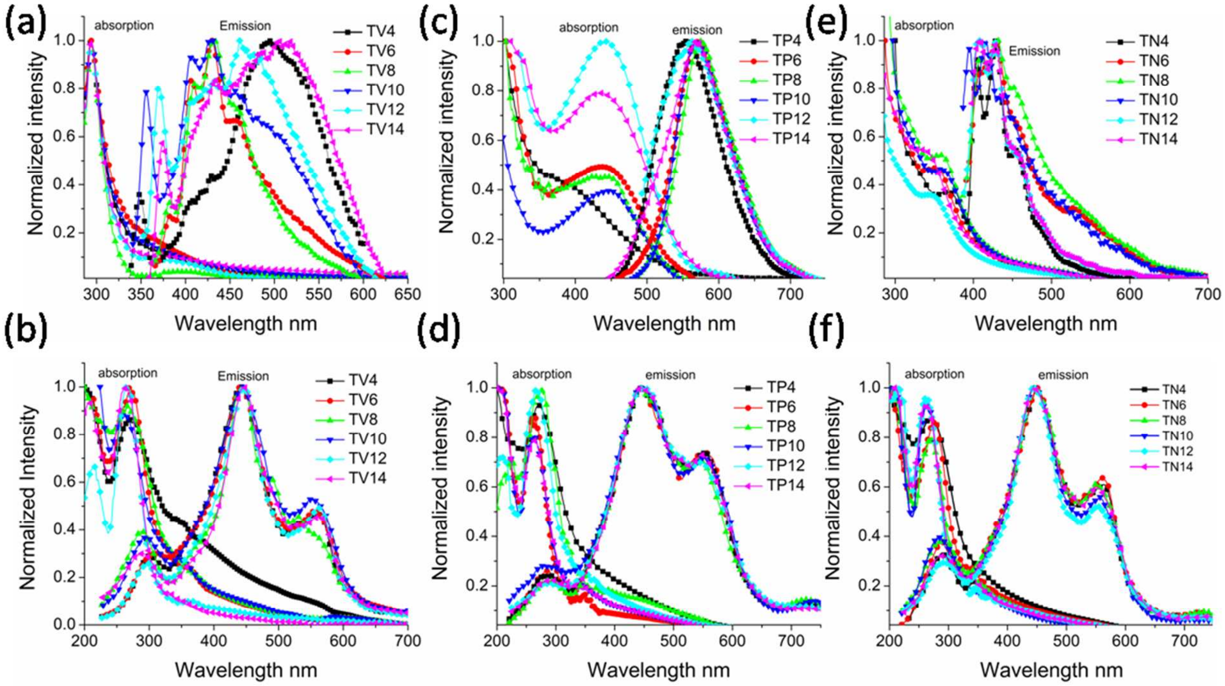

Figure 1. Absorption and Emission spectra of (a) TVn, (b) TPn and (c) TNn polymers in solution state; (d) TVn (e) TPn and (f) TNn polymers in thin film. Solution spectra of the polymers in THF medium were recorded with a uniform concentration of 4x10^{-4} g dl^{-1}. The excitation wavelength in solution and thin film are presented in supplementary information (Table S2†)

assembly is much better owing to its simplicity and robustness for device application over large area.

A survey of recent literature showed that circularly polarized electroluminescence was achieved by chiral substituents in the side chain.[26, 27] More interestingly Aggregation Induced Emission(AIE) luminogens with chiral substituents were reported with high Circularly polarized Light CPL dissymmetry factor.[28] AIE luminogens with Chiral side chains that have chiral sensing ability is also among the most recently reported high performance materials.[29] Nevertheless, a self assembled system with high Dichroic ratio of linearly polarized light is highly desirable but are seldom reported. In this work we present a comprehensive study of mesogenic polythiophenes shown in **Chart 1** to form self assembly with 1D orientation under ambient conditions through solution processing.

Experimental section

Materials and Methods

4-bromophenol, 6-bromonaphthalen-2-ol, N,N-dimethylcarbodiimide, 4-dimethylaminopyridine, 4-chloromethylphenyl acetate and all 4-alkoxybenzoic acids were purchased from Sigma-Aldrich and used as obtained without any further purification. ESI mass spectra were recorded on Thermo Finnigan LCQ Advantage MAX ESI-Mass Spectrometer; elemental analyses of monomers were done on Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer. ^{1}H and ^{13}C spectra were acquired on JEOL ECA 500 MHz NMR spectrometer with tetramethyl silane as standard with respective deuterated solvents for monomers and polymers. Photoluminescence (PL) spectra were measured on Varian Cary eclipse fluorescence spectrophotometer. UV-Visible absorption spectra were recorded on Varian Cary 50 Bio UV-Visible spectrophotometer. Cyclic voltammetry were done on CH instruments, CHI600D electrochemical work station with platinum working electrode by forming a thin films of the polymers on platinum disc working electrode, Ag/AgCl electrode as reference and platinum wire as counter electrode.

Differential scanning calorimetry (DSC) were recorded on TA instruments Q-200 Differential scanning calorimeter. Dynamic light scattering (DLS) experiments were done on Malvern instruments dynamic light scattering instrument, UK. Fluorescence lifetime (FLT) experiments were done on IBH Fluorescence Lifetime System (Picosecond resolution), exponential fitting of FLT data were done using Horiba–Jobin–Yvon decay analysis software. Atomic force micrographs were obtained on a Nova 1.0.26 RC1 Atomic force microscope with NT-MDT solver software for analysis, silicon cantilever (SII) with average frequency of 260–630 kHz with force constant of 28–91 N m^{-2} were used in semi contact mode. Charge carrier mobility of polymers were measured by space charge limited current method (SCLC) on devices fabricated by spin coating of polymer films onto pre-cleaned ITO coated glass substrates (polymer film thickness of 120–140 nm) from solution at a concentration of 1.0 mg mL^{-1} and aluminum (100–140 nm thickness) was coated over the polymer layer as cathode. The measurement by SCLC method was done on Keithley 2400 source meter.

Absolute fluorescence quantum yield of the polymer thin films were measured from spun polymer films on quartz substrates and were recorded using FLUOROLOG3 (model FL3-II) fluorescence spectrophotometer from Jobin-Yvon-Spex was

Table 1. Fluorescence anisotropy (FA), Linear dichroism (LD), Fluorescence lifetime (FLT) and Dynamic Light Scattering (DLS) data of polymers.[e]

Polymer	[a]FA	[b]LD	[c]T$_1$/T$_2$/T$_3$ (A$_1$/A$_2$/A$_3$)		[d]R$_h$ (I)
			Solution	Thin film	
TP4	0.09	0.01	1.56/-/- (100/-/-)	1.61/-/-	78.8/-/-(100/-/-)
TP6	0.11	0.04	2.94/-/- (100/-/-)	1.94/-/-	190/-/-(100/-/-)
TP8	0.08	0.03	1.41/-/- (100/-/-)	1.05/-/-	122/-/-(100/-/-)
TP10	0.10	0.09	2.27/-/- (100/-/-)	1.54/-/-	190/-/-(100/-/-)
TP12	0.12	0.05	1.08/-/- (100/-/-)	1.04/-/-	164/-/-(100/-/-)
TP14	0.06	0.05	2.18/-/- (100/-/-)	1.24/-/-	255/-/-(100/-/-)
TN4	0.06	0.02	5.35/1.11/- (97.2/2.8/-)	1.31/-/-	58.7/-/- (100/-/-)
TN6	0.08	0.08	4.77/1.12/- (98.6/1.4/-)	1.25/-/-	295.3/-/- (100/-/-)
TN8	0.09	0.06	5.36/1.19/- (97.3/2.7/-)	1.35/-/-	295/-/-(100/-/-)
TN10	0.13	0.04	5.84/1.22/- (99.1/1.9/-)	1.29/-/-	396/-/-(100/-/-)
TN12	0.09	0.05	5.27/1.20/- (96.8/3.2/-)	1.31/-/-	295/-/-(100/-/-)
TN14	0.10	0.06	5.52/1.22/- (99.3/0.7/-)	1.22/-/-	255/-/-(100/-/-)
TV4	0.29	0.11	1.06/5.04/- (80.7/ 19.3/-)	1.24/5.34/- (91.2/8.8/-)	615/ 105 (81.6/18.4)
TV6	0.31	0.13	0.84/3.44/-(99.2/0.8/-)	1.14/3.61/- (99.7/0.3/-)	396 (100/-)
TV8	0.30	0.15	1.15/4.86/- (95.3/4.7/-)	1.32/5.56/- (97.4/2.6/-)	531/58.7 (94.7/5.3)
TV10	0.34	0.16	1.18/5.09/- (91.8/8.2/-)	1.28/5.24/- (93.1/6.9/-)	955/58.7 (92.1/7.9)
TV12	0.38	0.19	0.61/1.48/6.45(0.7/86.0/13.3)	1.10/1.52/6.01 (1.2/91/7.8)	615/122.4 (88/12)
TV14	0.30	0.12	1.16/4.38/- (93.1/6.9/-)	1.11/5.02/- (96.0/4.0/-)	615.2/43.8 (93.2/ 6.8)

[a]FA, Fluorescence anisotropy data in THF solution;[b]LD, Linear dichroism in spun thin films;[c] T$_1$/T$_2$/T$_3$, Lifetime of different decay channels from FLT experiment in ns, A$_1$/A$_2$/A$_3$, % contribution of different decay channels;[d]R$_h$, Hydrodynamic radii in nm; I, % composition of different species with corresponding R$_h$ values; [e] concentration of solutions used for DLS and FLT are identical to those used for absorption and emission studies 4x10^{-4} g dl^{-1}.

instruments. S.A.Inc, USA, equipped with integrated sphere. The data treatment for absolute quantum yield measurement carried out using Horiba–Jobin–Yvon quantum yield and color calculator. The relative quantum yields of the polymers in solution state were measured by using quinine sulfate standard. GIXRD measurements were done on Bruker AXS D8 Advance X-ray diffractometer by using Cu-Kα wavelength.

Three series of polymers with systematic structural relationship were synthesized and their structures are presented in Chart 1. Detailed synthesis of intermediates, monomers and polymers are presented in supporting information along with ^{1}H and ^{13}C NMR, ESI mass, elemental analysis with interpretations.

Results and Discussion

Liquid crystalline polythiophenes are among the most interesting molecules for optoelectronic applications. A survey of literature showed that there is a renewed interest among the researcher from industry and academia in improving the properties of optoelectronic devices using the self assembling properties of liquid crystals.[30, 31] The presence of liquid crystalline property was found to improve the morphology in device state leading to better performance.[32] Three series of mesogenic polythiophenes were synthesized with different side chains with systematic variation for studying the effect of such change on the morphological property and electronic properties of the polymers. Accordingly homologous series of 3-substituted thiophenes viz.; of 4-(thiophen-3-yl)phenyl 4-(alkoxy)benzoate (TPAB), (6-(thiophen-3-yl)naphthalen-2-yl)methyl 4-(alkoxy)benzoate (6TNAB) and (E)-4-(2-(thiophen-3-yl)vinyl)phenyl 4-(alkoxy)benzoate (ETAB) with phenyl, naphthyl and vinylphenyl side chains respectively were synthesized with varying terminal alkyl side chains and polymerized to give corresponding polymers viz.; TPn, TNn and TVn (Chart 1). The detailed synthetic protocol of monomers and polymers are presented in Scheme S1 of supporting information.

Optical properties of the synthesized polymers were studied for the effect of systematic changes in the structure of polymers. The spectral properties in tetrahydrofuran solution are shown in **Figure 1.** The polymers showed some important but subtle variations in the solution absorption and emission properties within the homologous series and a significant variation of optical properties across the series of polymer. The TPn series polymers show a small bathochromic shift from TP4 to TP10 with increasing length of side chains and hypsochromic shift from TP10 to TP14. This change in behavior can be attributed to the predominance of steric hindrance over solvation effect in presence of longer side chains as observed in poly

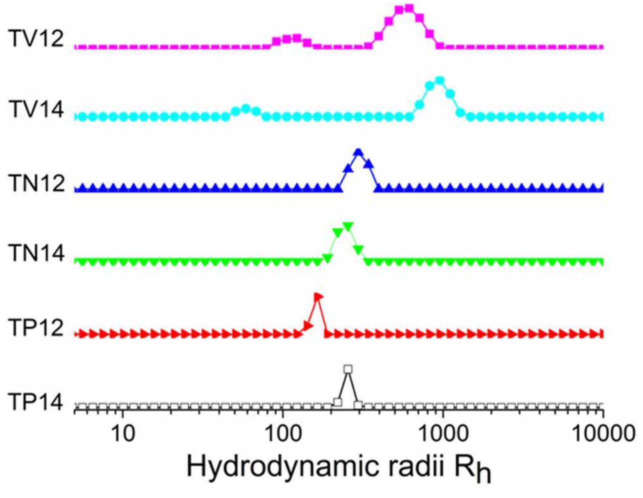

Figure 2 DLS traces of polymers in THF solution at concentration of $4x10^{-4}$ g dl^{-1}.

alkylthiophenes.[33, 34] The reverse trend wherein there was a blue shift from TN4 to TN10 was observed and a bathochromic shift is observed from TN10 to TN14 which is similar to that observed in bithiophene systems due to predominant solvation in higher chain lengths.[35] TVn series polymers showed no significant change in the absorption maxima from TV4 to TV14 while there was a significant change in the long wavelength shoulder which had relatively low intensity. The presence of long wavelength shoulders showed that there is a considerable amount of planarization in thiophene backbone.[36] A random change in the position of low energy shoulders can be attributed to the intermediate behavior of TVn polymers (also see Table S2 support information). Interestingly the absorption maxima in the solution state completely changed in thin film. It is possible to explain the mode of aggregation based on relative positions of absorption bands in solution and thin film. TNn polymers exhibited a hypsochromic shift of about ~90nm while for TPn polymers it was found to be as high as ~170nm. In sharp contrast to the above observation, TVn series polymers elicited comparitively small blue shift (maximum of 20 nm) along with the appearance of more prominent low energy shoulders and a significant red shift of absorption onset of thin films than solution state. The above observations showed that there is a significant variation in the mode of aggregation of polymers upon simple variation of the structural segments in side chain and that TVn series of polymers elicit a J-type aggregation upon evaporation of solvent in contrast to other polymers.

Emission spectra of conjugated polymers can be used as a sensitive tool to study the intermolecular interactions in solution and solid states. The emission spectra of the polymers are presented in Figure 1. A close inspection of emission spectra of the polymers can reveal many subtle changes that happen upon aggregation and it can also serve as an additional evidence for the inferences drawn from absorption spectra. The change in emission spectra of polymers can be interpreted with respect to alkyl side chains within a series and across the series. TPn series of polymers showed featureless emission pattern with small change (with maximum variation of 19nm) in λ^{emi}_{max} upon changing the side chain of the polymers. TNn polymers showed prominent vibronic features in the emission spectra which clearly indicates single chain packing by intra chain interaction which is a precursor for H-aggregate formation.[36] The change in wavelength of emission in TNn polymers with the alkyl chain length is relatively smaller than that observed for TPn polymers (with maximum difference of 13 nm). TVn polymers exhibit a mixed character wherein a featureless emission spectrum was observed for TV4 and TV14 polymers. TV6, TV8 and TV10 exhibit strong vibronic features in the emission spectra. TV12 exhibited emission maxima at 461 nm with a high energy shoulder at 409 nm. The vibronic features in the emission spectra are very sensitive to the aggregation due to intermolecular interactions.[37, 38]Thus, the change in alkyl side chains of TVn polymers resulted in different mode of solvation. The presence of vibronic features indicate a single chain interaction in TV6-TV10, while a largely red shifted emission in EV4, EV12 and TV14 indicate the presence of aggregates with high ordering.[37, 38]

Interestingly thin film state of all polymers showed two prominent emission peaks irrespective of their structure across the series. The above observation is a clear indication that the solvation effects was responsible for the variations observed in solution state and are absent in thin film state. However the ratio of intensities of the peak at ~440nm and ~550nm changed with change in structure of the polymers. The change in ratio of intensities between long and short wavelength emissions revealed that there is a change in packing pattern of the polymer chains in the solid state caused by steric factors and solubility of polymers. The featureless emission spectra in all polymers show that there is extensive aggregation in thin film state.[39, 40]

The anomaly in the spectral behavior was also observed when quantum yield of the polymers in solution and solid state are compared. The quantum yields of the polymers are listed in Table S2 in supporting information. It is clear that the quntum yield of TPn and ENn polymers were reduced in thin film state while a marginal enhancement in the quantum yield was observed in the case of TVn polymers in solid state. The enhancement in emission of thin film is a clear indication of J-aggregate formation in TVn polymers.[41]

Aggregation and excited state dynamics

The polymers were studied using fluorescence lifetime measurements to understand their excited state decay dynamics. The decay of excited states strongly depend on the medium and consequent intermolecular interactions. We have recently reported on the modes of intermolecular interactions using Fluorescence Lifetime (FLT) and Dynamic Light Scattering (DLS).[42] The aggregation of fluorescent conjugated polymer in solution states is manifested in the form of multiple decay channels of excited states and such techniques are used for polymeric systems also.[38, 43] In the present study the solutions used for studying the absorption and emission spectra were used to study their lifetime and hydrodynamic radii so that it is possible to understand the decay channels in terms of aggregation.[44] The number of decay channels can be directly correlated with the different types of aggregates that exist in solution.[45] Dynamic light scattering (DLS) can also be used to study the aggregation of conjugated polymers and is a complimentary technique to understand bulk aggregation

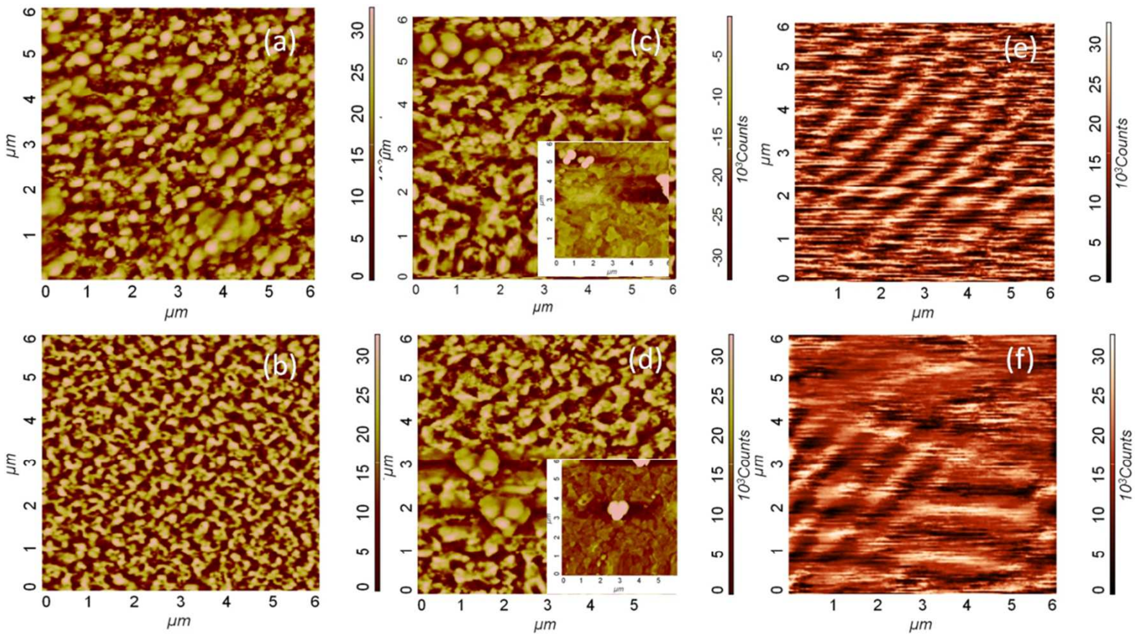

Figure 3 AFM micrograph of (a) TP14, (b) TP12, (c) TN14, (inset with terraced morphology without local equalization) (d)TN12 (inset with terraced morphology without local equalization) (e) TV12 and (f) TV14 spin coated on indium tin oxide (ITO) substrate.

properties of polymers in solution.[46] Further the shape and size of these aggregates can greatly contribute to different decay channels owing to different intermolecular interactions in them.[47] The Fluorescence lifetime (FLT) and Dynamic Light Scattering (DLS) data are presented in **Table 1**. The fluorescence decay analysis of the polymer solution under identical concentrations reveal that there are clearly different decay channels in solution state and divulge inner details on extent of aggregation. The ratio of long and short decay channels of excited states can be correlated with the presence of non aggregated and aggregated species respectively.[48] The TPn series polymers showed mostly single exponential decay of excited states with lifetime ranging between 1.08-2.94 ns which is consistant with the DLS measurement that show presence of one type of interaction in solution. The unimodal distribution in DLS however changed in size upon variation of the alkyl side chains. TP4 showed a lowest Rh value of 78.8 nm while TP14 showed highest size of aggregates in the series with Rh values of 255 nm (**Figure 2**). The increase in the size of aggregates with the change in alkyl side chain indiacate that the steric hindrance and by phillic-phobic interactions imparted by alkyl side chains.[49] Presence of steric effect due to long aliphatic chains as inferred from fluorescence lifetime and DLS measurements are consistent with the conclusions drawn from the absorption and emission studies in solution state. Further the unimodal distribution of the DLS peaks for TPn polymers point to the existence of aggregates with nearly spherical shape.[42, 50] TNn polymers showed biexponential decay in FLT which is in contrast to TPn polymers. The two decay channels observed in the case of TNn polymers exhibited lifetime of 4.77-5.94 and 1.11-1.22 ns respectively. The short lived components can be attributed to the presence of aggregated molecules along with solvated clusters of polymer chains which elicit a delayed decay channel as proposed earlier for fluorenone based systems.[42] Presence of predominant long lived channel in TNn polymers and vibronic features in the emission spectrum underpin the presence of solvated polymer chains as clusters. The DLS studies of the TNn polymers showed unimodal distribution which is also consistent with the above conclusions. Interestingly TN4 polymer showed a R_h value of 58.7 nm while other polymer of the series showed higher R_h values that can only accounted for by presence of solvated clusters.[41]

Fluorescence lifetime studies and DLS measurements show a distinct character in the case of solutions of TVn polymers. Presence of dual decay channels for TVn polymers in FLT showed that there is presence of aggregated and solvated polymer chains in solution state. The decay channels showed lifetime of 3.44-5.09 ns and 0.84-1.18 ns respectively. However, in sharp contrast to other series of polymers the short lived component showed predominance in TVn polymers. Short decay channels present in predominant proportions signify the presence of innate self assembly by aggregation in TVn polymers that is engendered by fast vibrational relaxation through torsional relaxation.[51] TV12 polymer showed a tricomponent decay character in FLT albeit the short lived component with lifetime of 0.61 ns had a negligible contribution. Apart from three component decay TV12 showed a higher contribution from the short lived component. The DLS measurements of TV12 and TV14 showed bimodal distribution of aggregates (**Figure 2**) consistent with FLT studies in contrast to other polymers. Further the Short lived components with lifetime of 0.84-1.18 ns closely correlated with the composition of aggregates with large hydrodynamic radii. Thus it is clear from the above observations that TVn polymers predominantly existed as aggregates in solution state. Further, such trimodal distribution in FLT with relatively less contribution of one of the decay channels was already observed in thienylene vinylene polymers that exhibit hierarchical super twisted assembly.[38] Further the

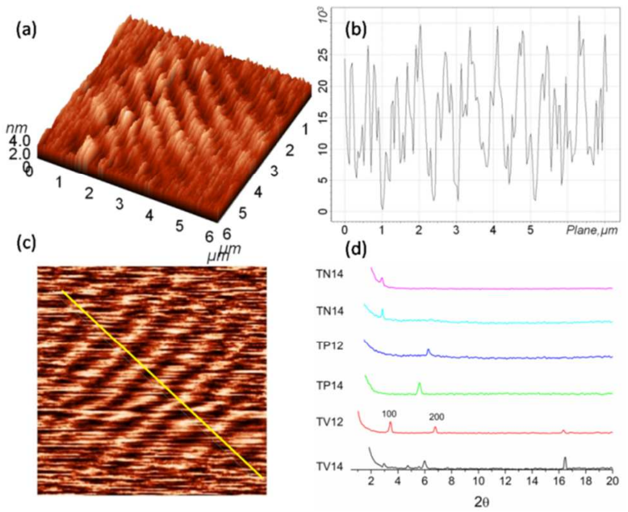

Figure 4 (a) 3D AFM micrograph of TV12 on ITO substrate, (b) Line profile along the line indicated in (c), (d) GIXRD traces of polymer films spin coated on ITO substrate.

multi component decay channel is TVn polymers was also preserved in thin film state thus pointing to similar kind of aggregates. Fluorescence anisotropic studies were carried out on the same solutions since it can offer an insight into the ordering of polymer chains in aggregates present in solution state and have been used to study polythiophenes.[52] The fluorescence anisotropy values of TVn polymers were found to be about 4 times higher than that of TPn and TNn polymers indicating the high ordering of polymer chains in the aggregates of TVn polymers.[53] It is interesting to note that TV12 showed the highest fluorescence anisotropy value of 0.38 which is close to that reported by us in case of thienylene vinylene with highly ordered morphology.[42]

Formation of nano and mocrostructures under device conditions.

The observed anisotropy in absorption is a clear indication of the fact that the polymer chains are highly oriented in thin film state.[54] Linear dichroism values of all polymers were measure on spin coated thin film over quartz substrates and are listed in Table 1. It is interesting to note that the TVn polymers exhibit higher linear dichroism values compared to other polymers and hinting that the structural component in the side chain played a crucial role in deciding intermolecular interactions.

Ordering in solution state is transferred to the thin film due to the memory effect.[55] Thus, the control of morphology under device conditions can be acomplished by controlling the aggregates in the solution state. Isolated conjugated polymer chains show a quick diffusion of charge by coherent transfer within the polymer chains.[56] Whereas in a condensed state such as a neat film they tend to lose the property due to formation of inter chain species that act as low energy traps and higher disorder arising from chaiotic packing of polymer chains.[57] The ordering of conjugated polymers have gained ever growing interest due to enhancement of optoelectronic properties.[58] The orientation of conjugated polymers can be achieved by introducing liquid crystalline groups in the side chain.[59] The angle between the polymer backbone director and the transition dipole moment plays a key role in high electroluminescence Dichroic ratio.[60] The polymer thin films were analysed for supramolecular ordering using Atomic Force Microscopy (AFM), Grazing Incidence X-ray Diffraction (GIXRD) to understand the mode of orientation.

All the polymers were spin coated on plasma cleaned ITO substrates and studied by AFM and GIXRD to ascertain the extent of ordering in the thin films. It is clear from the AFM micrograph that TV12 showed a well ordered morphology where lamellar structures are aligned normal to the surface (**Figure 3, Figure S12**). Further the lamellar structures as observed in the 3D AFM micrograph of TV12 are periodically arranged in a one dimensional order along with directional order (**Figure 4**). The profile diagram in Figure 4 (b) indicate that the lamellae are arranged with some slippage leading to staircase like profile. The overall morphology closely resembled to the 1 dimensional alignment of liquid crystalline polymers by physical process and liquid crystalline polymers with non-interdigitated side chain using a flow field.[61, 62] AFM micrograph of TV14 showed a orientational ordering of the lamellae. However, the positional ordering of lamellar structure is disturbed. TV4 and TV6 polymers also showed lamellar structures but positional ordering was not observed. However, TV8 and TV10 showed some positional ordering of lamellae albeit in a distorted manner (Figure S9, supporting information). TP14 and TP12 showed morphology with more lamellar and spherical structure with no ordering similar to earlier reported for un-annealed thin films of 3-substituted polythiophene system (Figure 3).[63] TN12 and TN14 polymer showed lamellar terraced morphology (Figure 3 (c) and (d) inset) where the lamellar structures are aligned parallel to the substrate as reported for thiophene based systems.[64]

GIXRD traces of polymer films spin coated from THF solutions on to ITO substrates were studied to ascertain the orientational ordering of polymer chains (Figure 4). TV12 showed crystalline peaks indicating well ordered thin film. The peak at 2θ=3.4° (25.22 Å) and second order reflection at 2θ=6.8° (12.80 Å) correspond to the interchain lamellar spacing.[65] It is interesting to note that these values are closely matching with that previously observed for 3-(phenylvinyl)thiophene polymer.[66]The above value of interchain lamellar spacing is very close to our previously reported value for similar system with azomethine liked side chain.[54] Another peak at 2θ=16.36° (5.4 Å) is attributed to the π-π stacking interaction between the chains and is higher than that (3.9 Å) reported for simple alkyl substituted thiophenes.[63] The higher π-π stacking distance indicate reduced side chain interdigitation due to vinyl units in the side chain. Lowering of interdigitation was recently proposed as an effective strategy for better dimensional confinement of optical and electronic properties.[62] In the case of TV12 the results indicate the lower interdigitation has caused better orientation. TV14 in contrast showed very weak reflections at 2θ=16.55° (5.35 Å) and 2θ=5.9° (14.96 Å) clearly indicating the absence of hierarchical ordering found in TV12. TP12 and TP14 show only one reflections each at 2θ=6.33° and 6.67° respectively consistent with unordered morphology in AFM. TN12 and TN14 showed one reflection indicating absence of ordered assembly of polymer chains as in TV12.

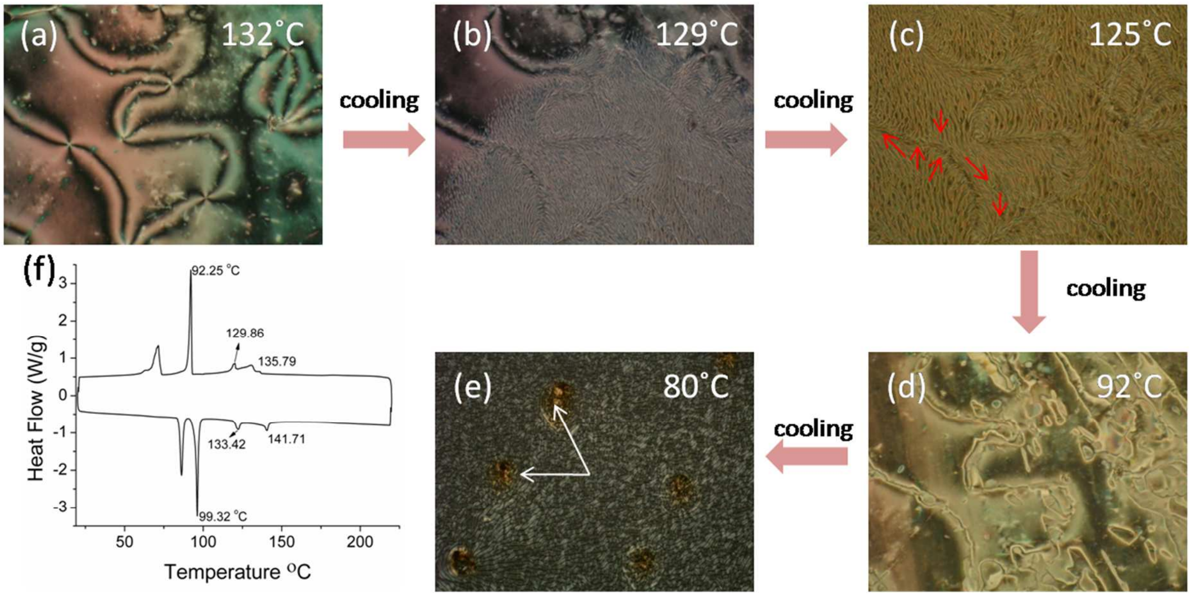

Figure 5(a-e) Optical polarizing micrograph of TV12 at different temperatures on cooling at 10 ˚C/min and (f) DSC of TV12 polymer at 10 °C/min.

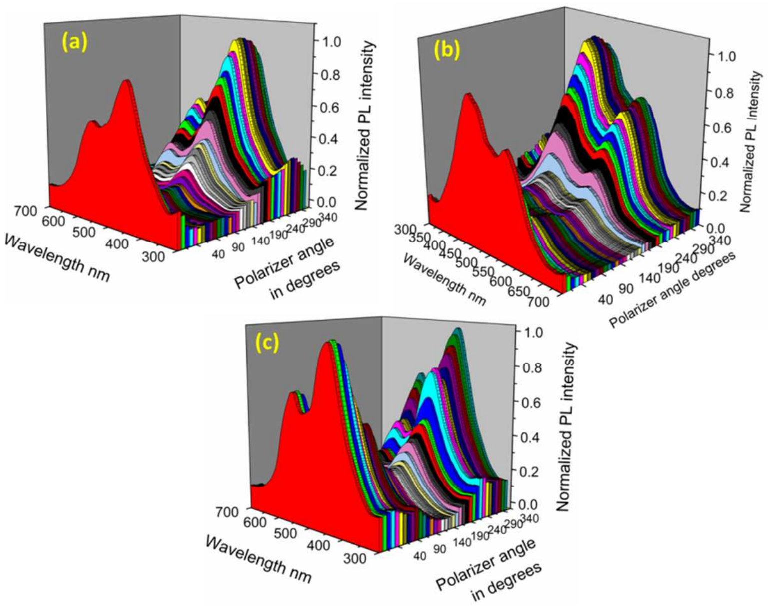

Figure 6 Polarized photoluminescence in thin film of (a) TP12, (b) TN12 and (c) TV12.

Dimensional Confinement of properties.

The presence of ordering in the polymers can be attributed to the liquid crystallinity of polymers. All polymers were studied under optical polarizing microscope and Differential scanning caloriemetry. The polymers exhibited liquid crystalline property as evident from the OPM micrographs (**Figure S7)** and DSC traces **(Figure S8)** in support information. The TPn and TNn polymers exhibited nematic phase on both heating and cooling. Nematic phase was observed for TV4, TV6 and TV8 polymers. However, TV10, TV12 and TV14 polymers exhibited an additional smectic phase as shown in **Figure S7 and Table S3**. It is interesting to notice that TV12 retained the surface orientation from the smectic phase after crystallization as shown in **Figure 5.** The smectic phase of TV12 is interesting since the nematic phase at higher temperature with threads transformed into smectic phase with number of disclinations traced along nematic threads as indicated by change in director of orientation in **Figure 5(c)** due to focal conic defects**.**[67] The disclinations with point defectd in smectic phase appeared as bright colored spot after crystallization as indicated by arrow in **Figure 5(d).** The polymers were also examined for linearly polarized light emission. The orientational ordering in thin film can be manifested in the form of polarized emission. Since these polymers were spin coated on substrate (quartz) for this study, the intensity of fluorescence was measured as a function of angle of polarizer from 0 to 350 degrees to know the extent of polarization of photoluminescence (**Figure 6)**.TV12 elicited the highest dichroic ratio of 15.02 (Table 2) consistent

Table 2. Electrochemical properties of polymers and characteristics of OLEDs fabricated from polymers.$^{k)}$

Polymer	$^{a)}E^{HOMO}$	$^{b)}E^{LUMO}$	$^{c)}E^{ele}$	$^{d)}E^{opt}$	$^{e)}\mu^{SCLC}$	$^{f)}$Dichroic ratio		$^{i)}$Brightness	$^{j)}(x,y)^{EL}$
						$^{g)}$EL	$^{h)}$PL		
TP4	-6.03	-3.87	2.15	2.19	$7.80X10^{-5}$	6.03	5.24	647	0.27,0.34
TP6	-6.05	-3.87	2.17	2.24	$6.26X10^{-4}$	5.92	6.12	816	0.27,0.33
TP8	-6.02	-3.88	2.14	2.17	$3.17X10^{-4}$	6.21	6.19	754	0.27,0.32
TP10	-5.96	-3.84	2.12	2.14	$4.27X10^{-5}$	6.31	6.28	798	0.27,0.32
TP12	-5.93	-3.90	2.02	2.10	$1.28X10^{-4}$	6.38	6.55	863	0.27,0.32
TP14	-6.02	-3.88	2.14	2.19	$3.19X10^{-4}$	6.79	6.81	833	0.28,0.32
TN4	-6.29	-4.05	2.24	2.32	$2.60X10^{-5}$	4.35	3.21	787	0.27, 0.32
TN6	-6.16	-4.08	2.08	2.21	$2.30X10^{-5}$	4.65	4.34	648	0.25,0.30
TN8	-6.16	-4.07	2.08	2.18	$1.71X10^{-5}$	4.71	4.25	679	0.24,0.30
TN10	-6.15	-4.08	2.07	2.15	$1.67X10^{-6}$	4.96	4.83	521	0.24,0.29
TN12	-6.14	-4.08	2.05	2.17	$2.39X10^{-5}$	4.87	4.76	511	0.25,0.29
TN14	-6.12	-4.08	2.04	2.13	$1.07X10^{-5}$	4.98	4.86	534	0.24,0.30
TV4	-6.03	-3.88	2.14	2.24	$8.95X10^{-4}$	7.95	7.26	487	0.27,0.29
TV6	-6.09	-3.87	2.21	2.36	$6.42X10^{-4}$	7.92	7.98	456	0.26,0.28
TV8	-6.01	-3.90	2.11	2.31	$1.74X10^{-4}$	8.02	8.24	529	0.26,0.28
TV10	-5.91	-3.87	2.04	2.18	$2.17X10^{-3}$	11.63	12.01	531	0.27,0.32
TV12	-6.02	-3.87	2.14	2.19	$3.90X10^{-3}$	15.02	14.32	524	0.27,0.34
TV14	-6.04	-3.87	2.16	2.16	$1.85X10^{-3}$	10.12	10.10	539	0.24,0.29

$^{a)}E^{HOMO}$, Energy Highest Occupied Moleecular Orbital;$^{b)}E^{LUMO}$, Energy of Lowest Unoccupied Molecular Orbital in eV;$^{c)}E^{ele}$, Electrochemical band gap found from cyclic voltammetry;$^{d)}E^{opt}$, optical band gap found from absorption edge; $^{e)}\mu^{SCLC}$, Charge carrier mobility found by Space Charge Limited Current (SCLC) method incm^2 V^{-1} S^{-1};$^{f)}$Dichroic ratio, found by the ratio between maximum intensity and minimum intensity of EL or PL;$^{g)}$EL, Electroluminescence:$^{h)}$PL, photoluminescence;$^{i)}$Brightness, in cd/m^2;$^{j)}$(x,y)EL, Commission internationale de l'Eclairage (CIE) 1931 color coordinates from electroluminescence;$^{k)}$ all energy are represented in eV.

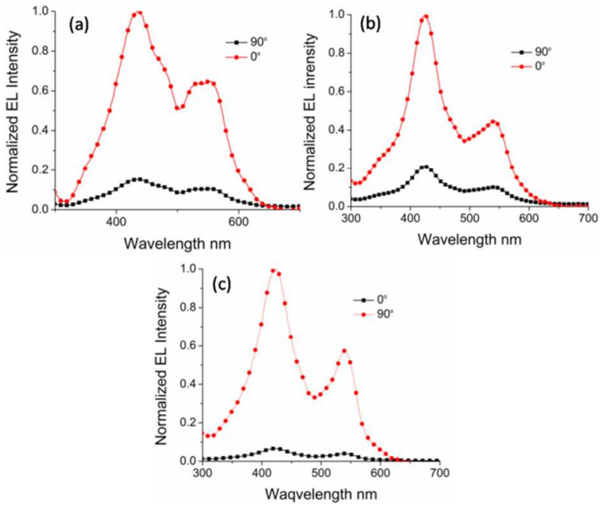

Figure 7 Polarized electroluminescence from (a) TP12, (b) TN12 and (c) TV12

with the observations made using AFM and GIXRD studies.

Further to demonstrate the applicability of the above polymers for polarized electroluminescence, light emitting diodes were constructed with device configuration of ITO/PEDOT:PSS/polymer/Al were fabricated. TV12 also showed a dichroic ratio of 14.32 (Figure 7) and a charge carrier mobility of 3.9x10^{-3} cm^{2}V^{-1}s^{-1} highest among all three series of polymers (Table 2). The high charge carrier mobility is attributed to the ordering of the polymer chains. TV14 showed a charge carrier mobility that is slightly lesser than that of TV12 due to the absence of long range ordering in thin film. The LEDs fabricated from the polymers elicited electroluminescence almost in the same wavelength region albeit with difference in polarization. TP12 showed a EL dichroic ratio of 6.55, while that of was observed to be 4.76.

Conclusions

Liquid crystalline polymers with systematic structural variation and aromatic side chains were synthesized and their orientational characteristics were studied using UV-Visible absorbance, emission, fluorescence lifetime, Dynamic Light Scattering, GIXRD and AFM. TV12 polymer showed a high photoluminescence dichroic ratio of 15.02 which is close to that achieved by mechanical alignment.[62] The smectic phase as elicited by TV12 with good surface orientation are of great interest in semiconductor industry and lithography for surface patterning.[68] The reason for good orientation can be attributed to optimal side chain that prevented chain interdigitation which locks up the polymer chains along the thickness direction. A high dichroic ratio was achieved by simple spin coating at room temperature. The OLEDs fabricated from the TV12 polymer also showed a dichroic ratio of 14.32. It is worthwhile to recall that these OLEDs exhibited two emission maxima corresponding to complimentary colours and the emission covered almost all of visible region. The CIE coordinates of these polymers indicate a near white colour emission (Table 2). The device performance can further be improved by optimizing the parameters for fabrication. The mesogenic polymers reported here showed better homogeniety and lower melting point.[69]

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Notes and references

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Graphical abstract

Polarized Electroluminescence from ordered mesogenic polythiophenes.