Synthesis of Rod-coil Molecules bearing Oligo-Phenylene Vinylene Motifs: Effect of PEO Chain Lengths on the Evolution of Nanostructures Morphology and their Photophysical Properties

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Abstract

The applications of nano-dispersed organic conjugated active compounds or materials as well as current research is concerned mainly with optimization and control of the optical properties, by particle size and supramolecular structure of the particles. The aromatic macromolecules consisting of conjugated rigid rod segment and hydrophilic flexible chain as coil in aqueous solution can aggregate into a variety of supramolecular structures through mutual interaction between aromatic rod and hydrophilic chains of molecules and water. Here we report the synthesis of newer oligo phenylene vinylene (OPV) based rod-coil molecules with varying chain-length polyethylene oxide (PEO) repeating units (n = 8, 17, 45). Formation and photophysical properties of their nanostructures in water are studied comparatively. The nanostructures evolution of these molecules is observed with simple reprecipitation method. The stable nanostructures were formed without addition of any surfactants. The fabricated nanostructures ultimately give the materials with 'controlled' aggregation induced enhanced photophysical properties. The self-assembly of such OPV type rod molecules in water without adding any surfactants, therefore, can provide a strategy for the construction of well-defined and stable nanostructures with certain chemical functionalities and physical properties as advanced materials for photonic, electronic and biological applications. Copyright © VBRI Press.

Keywords: Rod-coil molecules, aggregation induced emission, fluorescence, nanostructures, PEO.

Introduction

The applications of nano-dispersed organic conjugated active compounds or materials as well as current research is concerned mainly with optimization and control of the optical properties, by particle size and supramolecular structure of the particles. The aromatic macromolecules consisting of conjugated rigid rod segment and hydrophilic flexible chain as coil in aqueous solution can aggregate into a variety of supramolecular structures through mutual interaction between aromatic rod and hydrophilic chains of molecules and water. Here we report the synthesis of newer oligo phenylene vinylene (OPV) based rod-coil molecules with varying chain-length polyethylene oxide (PEO) repeating units (n = 8, 17, 45). Formation and photophysical properties of their nanostructures in water are studied comparatively. The nanostructures evolution of these molecules is observed with simple reprecipitation method. The stable nanostructures were formed without addition of any surfactants. The fabricated nanostructures ultimately give the materials with 'controlled' aggregation induced enhanced photophysical properties. The self-assembly of such OPV type rod molecules in water without adding any surfactants, therefore, can provide a strategy for the construction of well-defined and stable nanostructures with certain chemical functionalities and physical properties as advanced materials for photonic, electronic and biological applications.

One of the fascinating subjects in areas such as materials science, nanochemistry, and biomimetic chemistry is concerned with the creation of supramolecular architectures with well-defined shapes and functions [1]. Organic nanoparticles have attracted much research interest because of their special properties which lie between the properties of molecules and those of bulk materials [2]. The electronic properties of organic nanoparticles differ fundamentally from those of inorganic ones because of weak intermolecular forces formed by the interactions of van der Waals type or hydrogen bonding [3]. Organic nanostructures allow much increased variability and flexibility in synthesis of materials in electronics and photonics [4, 5]. Organic nanoparticles are fascinating from a fundamental point of view because their optical properties on absorption and emission depend on their size [6-8]. Nakanishi and co-workers have done a pioneering work on this subject, particularly focusing on fabrication of nanocrystals and characterization of perylene [9-11] and other organic system [6, 12, 13]. Investigation on nanoparticles of several organic

compounds reveals that the emitted color can be tuned with either the particle size or the excitation wavelength and enhanced emission due to aggregation also has been reported for organic systems including CN-MBE, [7] *p*-BSP, [8] a silole derivative, [14, 15] PPB- an oligo-phenylenevinylene (OPV) derivative [16] and conjugated polymers [17]. This feature of aggregation-induced emission (AIE) is remarkable because intermolecular vibronic interactions generally induce nonradiative deactivation that produces quenching of emission [18]. The weak fluorescence intensity of CN-MBE in dilute solution is found to increase greatly in nanoparticles and UV spectral features of CN-MBE nanoparticles in absorption are red-shifted with respect to those of molecules in dilute solution. The enhanced fluorescence of CN-MBE nanoparticles was proposed to reflect both intra- and intermolecular effects [7]. In contrast, the planar DPST molecule constitutes an example of fluorescence quenching in nanoparticles with blue-shifted absorption [7].

As per the general rule based on a molecular exciton model [19, 20], a parallel alignment of transition dipole moments, known as *H*-aggregation, shifts absorption to the blue and diminishes emitted intensity, whereas head-to-tail alignment, *J*-aggregation, shifts absorption to the red and enhances the emission. The observed enhanced fluorescence of CN-MBE and fluorescence quenching in DPST is then readily explicable according to this exciton model. Our earlier work on 1,4-di[(*E*)-2-phenyl-1-propenyl]-benzene (PPB) [16], an OPV derivative showed a feature with weak emission in solution but exhibited blue-shifted absorption and strong emission as nanoparticle aggregates; making PPB an outstanding exception to a well-established rule based on the molecular exciton model.

XRD studies of PPB nanocrystals showed long-range packing structures of two types. Self-assembly of molecules through non-covalent forces including hydrophobic and hydrophilic effects, electrostatic interactions, hydrogen bonding, microphase segregation, and shape effects has the great potential for creating supramolecular structures [21-25]. Rod-coil block copolymers have both rigid rod and block copolymer characteristics. The formation of liquid crystalline nematic phase is characteristic of rigid rod, and the formation of various nanosized structures is a block copolymer characteristic. Supramolecular chemistry in particular has been actively applied to the development of such materials and among various types of supramolecular building blocks, rod–coil molecules are well-suited for tailoring nanostructural properties such as size and shape [26]. Apart from the wide range of different supramolecular structures in nanoscale dimensions, another unique characteristic is that rod segments can endow various functionalities such as photophysical and electrochemical properties to the supramolecular materials [1, 2, 21-23].

The emphasis in the application of nano-dispersed organic active compounds and effect materials as well as current research and development targets is concerned mainly with the optimization and control of the optical properties, by particle size and supramolecular structure of the particles.

Photoluminescence emission and excitation studies showed that the photophysical properties strongly depend on the supramolecular structure of π–conjugated rod segments [12]. Previous research efforts have led to the synthesis of many conjugated polymers, particularly derivatives of poly(phenylene vinylene) (PPV), soluble in organic solvents and easily processed into films with great promise as organic electronic materials [27-29]. Controlling the nanoscale structure of rod-like conjugated polymers has been proven to be difficult. However, supramolecular order plays a critical role in device performance, as both charge mobility and luminescent efficiency are influenced by molecular aggregation and structural defects [30-34]. Aromatic rigid rod molecules consisting of hydrophilic flexible chains, in aqueous solution can self-assemble into a variety of supramolecular structures through mutual interactions between aromatic rod molecules and water. These mainly include hydrophobic and hydrophilic interactions and π–π interaction [35]. An extensive work has been carried out by Tang's group on these AIE molecules and that has been published recently as comprehensive reviews [36, 37] with a focus on recent advances in science and application of AIE molecules, including new mechanistic understanding, new AIE molecules for sensing and imaging, stimuli-responsive AIE molecules and applications of AIE molecules for OLEDs.

Results and discussion

DSB (highly fluorescent in solution) and PPV (non-fluorescent in solution) have almost similar molecular structure, but behave differently in solution and as nanoaggregates. So, it was our interest to see the effect of different PEO chain-lengths, from the fundamental point of view, on the morphology and photophysical properties of these similar structrures.
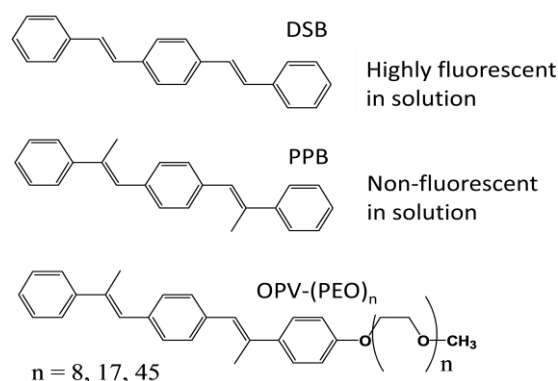

Chart 1. Chemical Structures of DSB, PPB and OPV-(PEO)ₙ

To see the effect of varying chain-lengths of polyethylene oxide (PEO) on the structure formation and on the optical properties of PPB, we synthesized oligophenylene vinylene (OPV) derivatives with different polyethylene oxide (PEO) repeating units (n = 8, 17, 45) *via* Heck coupling reactions and their photophysical properties in THF and water were also studied. Chung Feng et al [38] carried out the self-assembly studies of the molecules containing dihexyloxy-phenylene vinylene block (OHPV)

connected to a series of poly(ethylene glycol) (PEG) chains of different average lengths (12, 45 and 115 PEG units). The molecules studied by them are different and moreover their OHPV block copolymer unit contains dihexyloxy as flexible chain component, so it cannot be a rigid rod like segment that our molecules have.
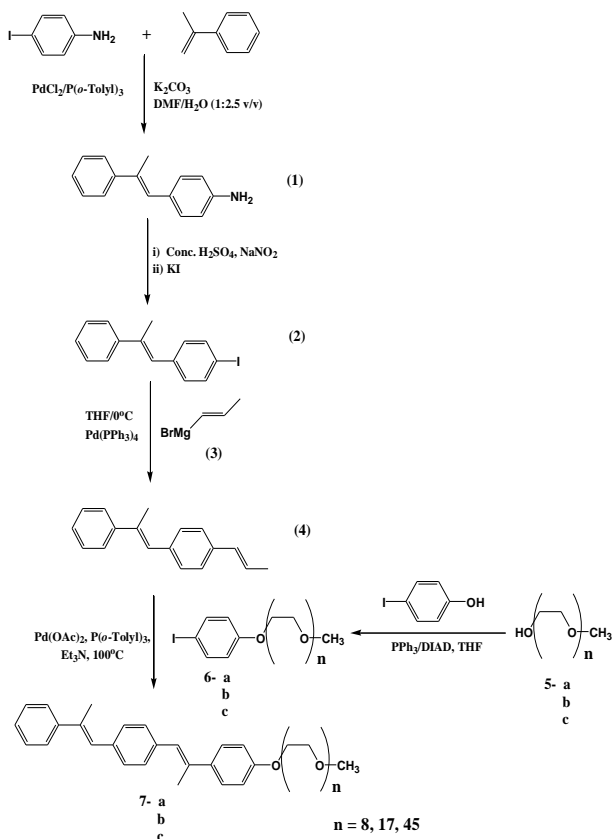
Scheme 1. Synthesis of OPV rod-coil molecules with varying length of PEO chains.

The supramolecular architecture in water can be manipulated by variation of the shape of the rigid rod and flexible coil segments of varying length, as well as the relative volume fraction of the flexible segment. The synthetic scheme of these OPVs is outlined in the scheme 1 and their corresponding ^{1}H NMR spectra are shown in the **Fig. 1(a, b, c)**.
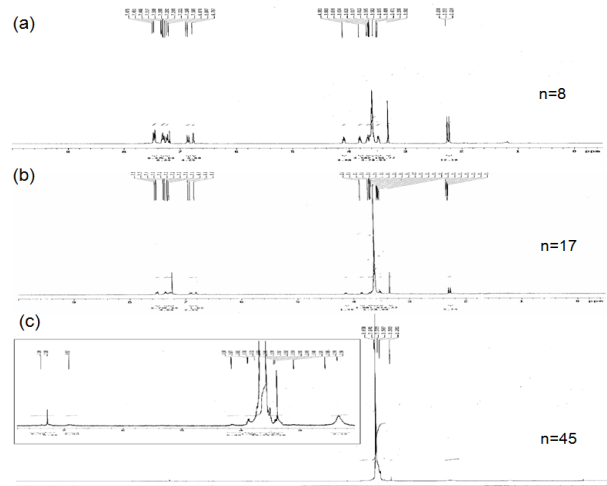

Figure 1. ^{1}H NMR spectra of OPV-PEO$_n$ with (a) n=8, (b) n=17 and (c) n=45.

In short, appropriate poly(ethylene glycol methyl ether) with ethylene glycol repeat units n = 8, 17, 45 were reacted by Mitsunobu reaction with *p*-iodophenol to get respective iodobenzene-PEG (n = 8, 17, 45) i.e. compounds 6a-c. These compounds in turn reacted with 1-[(*E*)-2-phenyl-1-propenyl]-4-[(*E*)-1-propenyl]benzene (4) to get desired OPV-PEO rod-coil molecules 7a, b and c by Heck coupling. Formation of compounds 1-Iodo-4-[(*E*)-2-phenyl-1-propenyl]benzene (2) and 1-[(*E*)-2-phenyl-1-propenyl]-4-[(*E*)-1-propenyl]benzene (4) was confirmed additionally by EI-MS spectroscopy (see Supporting Information). The detailed synthetic procedures are given in the experimental section at the end.
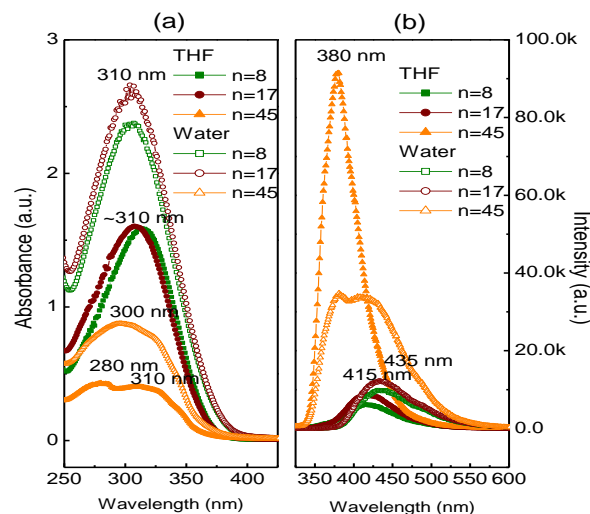

Fig. 2. UV-Visible absorption spectra (a) and the corresponding emission spectra (b) of 7a-c in molecular solutions of THF and their dispersions in water.

Steady-state absorption/emission spectra

UV-visible absorption spectra and the corresponding emission spectra of 7a-c in molecular solutions of THF and their dispersions in water are shown in **Fig. 2**, parts a and b, respectively. The absorbance of 7-a, b and c dispersions in water was increased than that compared to their corresponding THF solutions. There was observed a blue shift in a band position for 7a that showed λ_{max} at 317 nm in THF and 305 nm in water. OPV 7b did not show any change in a band position in THF as well as in water dispersions; with λ_{max} at 305 nm. UV absorption spectrum of 7a dispersions in water shows a distinct blue shift, which typically indicates formation of H-type aggregates [**19**]. This was in agreement with our previous results related to PPB[16] molecule that belongs to the family of oligophenylenevinylenes (OPV) with two methyl groups added to the 1,4-distyrylbenzene (DSB) skeleton. OPV-(PEO)$_8$ and OPV-(PEO)$_{17}$ exhibit weak emission in dilute solution, but increased absorption and red-shifted emission in nanodispersions. However, the case of OPV 7-c was different. Figure 7c in THF showed a band splitting at 280 and 310 nm, whereas it showed an increase in the absorbance in water with λ_{max} at 295 nm and a less prominent shoulder at about 324 nm. Photoluminescence of 7a and 7b in THF showed increasing trend in their intensities. This trend remained the same in nanodispersions in water with comparative increase in the PL intensities than their

respective THF solutions. Both these rod-coil molecules showed maximum wavelength λ_{max} at about 415 nm in their THF solutions. Also the corresponding nanodispersions in water showed increase in photoluminescence intensity. Enhanced emission due to aggregation has been reported for organic systems including CN-MBE [7], HPS [15] PPB [16], CN-DSB [39] and conjugated polymers [17]. We speculate the enhanced emission of water dispersions of OPV molecules, 7a-b, may be due to the combined effects of a planar conformation and the formation of herringbone-type aggregates with an edge-to-face feature as is in the case of PPB [16]. Rod-coil molecule with n = 45 (7c), however, showed different results. 7c in THF solution showed significantly higher photoluminescence intensity compared to dispersions of 7-a and b in water as well as in THF, with a blue shift having λ_{max} at 380 nm. Its photoluminescence intensity decreased in water dispersions drastically with a development of a new prominent band at 415 nm. This band splitting indicates the simultaneous formation of two structural entities within the nanodispersions of 7c in water; one is similar to that in its THF solution and other one because of the larger microstructures formation which decreases photoluminescence intensity. This decrease may be due to larger microparticles formation in water. The increase in PL in THF solvent can be explained as: the conjugated OPV rod segment is coiled with PEO chains with limited extent, causing aggregation of rods attached with free moving PEO segments. This aggregation may be in a 'controlled' way that might have led to 'aggregation induced' emission enhancement of 7c in the THF solvent. The so called nanodispersions of 7c in water led to the formation of larger aggregates with varied particle size distribution as evident from scanning electron microscopy image in Fig. 3c. The increase in relative volume fraction of the flexible segment of PEO might have also contributed to this.

Evolution of Nanostructures and Scanning Electron Microscopy (SEM)

Nanoparticles of OPV rod-coil molecules were formed after making their dispersions in water by simple reprecipitation method. All the dispersions were stirred for one hour prior to measurements. The concentrations of all solutions were 1.35×10^{-5} M after injecting into water. Formation of nanoparticles took place as the best solvent (THF) was replaced by the non-solvent (water) and dispersed in bulk water. The size of the nanoparticles increased with length of the coil. The scanning electron microscopy images are shown in **Fig. 3**.
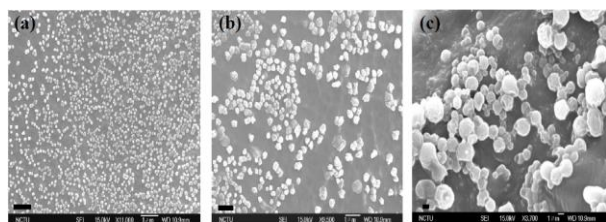

Fig. 3. Scanning electron microscopy images of **7** with ethylene glycol repeating units (a) 8, (b) 17 and (c) 45; in their dispersions in water. (Scale bar = 1 μm)

The average diameter of the particles of 7a was about 150 nm and that for 7b was about 300 nm. These nanoparticles were quite uniformly distributed. This uniformity in distribution of nanoparticles is because of the small chain length of the PEO moieties (n = 8, 19) and observed spherical shape of nanoparticles of these molecules (7a, b) likely results from minimization of interfacial energies between them and non-solvent water [8]. However, as the PEO chain length increased (OPV molecule with n = 45), the molecules aggregated to larger structures- microparticles (1-3 μm) with a small groove on the surface. It shows the entanglement of these longer PEO chains takes place on larger scale leaving OPV rods to aggregate in a 'controlled' fashion. So, although the overall particle aggregation is on micrometer scale, 'controlled' nano-aggregates of the OPV rods could lead to emission enhancement in 7c. This formation of peculiar microparticles likely reflects a competition between anisotropic growth and spherical aggregation. The studies on self-assembly of oligo(*p*-phenylenevinylene)-*block*-poly(ethylene oxide) in polar media and solubilisation of an oligo(*p*-phenylenevinylene) homooligomer inside the assembly by Takeshi Mori et al[40], showed cylindrical and distorted spherical aggregates at 62 and 79 wt % of PEO weight fractions in THF/water system.

Experimental

Nuclear Magnetic Resonance (NMR)

^{1}H NMR spectra were recorded on Unity-300 spectrometer at 300 MHz for samples in $CDCl_3$, *d*-Acetone, *d*-Methanol solutions.

Steady State UV/visible Absorption and Photoluminescence (PL) spectra

UV-Visible absorption spectra were recorded on Hewlett-Packard HP8453 spectrophotometer and Cary 50, Varian and fluorescence spectra on F4500 Hitachi and SpectraPro-150 (with Muller SVX 1450 xenon lamp) spectrophotometers in standard manners.

Scanning Electron Microscopy (SEM)

Images were acquired on a field-emission scanning electron microscope-JSM-6500 F, JEOL. To enhance the conductivity of the specimen, a layer of platinum was sputtered (current 30 mA, pressure 4 Pa, duration 30 s).

Synthesis of OPV Rod-coil Molecules

The synthesis of rod-coil molecules containing poly(ethylene oxide)s with various degrees of polymerization was performed as outlined in the Scheme 1. The appropriate poly(ethylene oxide) reacted with *p*-iodo phenol (Mitsunobu Reaction) to produce an intermediate which in turn reacted with 1-[(*E*)-2-phenyl-1-ethenyl]-4-vinylbenzene to give oligophenylene vinylene (OPV) derivative as a rod segment and poly(ethylene oxide)s as coil segment.

4[(*E*)-2-phenyl-1-propenyl] aniline (**1**): *p*-iodoaniline (5 g, 22.8 mmols), α-methyl styrene (4.04 g, 34.2 mmols), $PdCl_2$ (0.04 g, 1 mol%), P(*o*-tolyl)$_3$

(0.277 g, 0.912 mmols), K_2CO_3 (4.72 g, 34.2 mmols) were taken in a three-necked round bottom flask. N, N-Dimethylformamide (DMF) and water in proportion of 1:2.5 by volume was used as solvent system. The mixture was heated at about 100°C for one day. The black solution formed was extracted with ethyl acetate, water, saturated NaCl and organic layer was dried over $MgSO_4$. The solvent was removed on rotavap to get solid crude. The product was purified by the recrystallization of the crude from ethyl acetate/hexane mixture. Brownish crystals were formed (Yield- 85%).

^{1}H-NMR(300 MHz, CDCl$_3$, δ, ppm) : 7.50-7.47 (m, 2H, Ar-H), 7.36-7.30 (m, 2H, Ar-H), 7.26-7.21 (m, 3H, Ar-H), 7.17-6.62 (m, 2H, Ar-H *ortho* to –NH$_2$, 1H, *ortho* to –CH), 3.90-3.40 (s, 2H, -NH$_2$), 2.26 (d, 3H, -CH$_3$).

1-Iodo-4-[(E)-2-phenyl-1-propenyl]benzene (**2**): Compound 1 (4.0 g, 19.2 mmols) was taken in a round bottom flask and dissolved in concentrated H_2SO_4 (5.6 g, 57.36 mmols), stirred for some time and kept in ice bath. Then was added cooled solution of $NaNO_2$ (1.70 g, 24.8 mmols) in water to the above mixture to form the diazonium salt of the compound. The clear solution was obtained and bubbling was observed. The aqueous solution of KI (4.11 g, 4.11 mmols) was then added dropwise. Stirring continued for an hour. The mixture was then heated at about 65°C for one hour, cooled down and treated with aqueous $Na_2S_2O_3$ to neutralize excess KI, extracted with ethyl acetate, water, saturated NaCl, dried over $MgSO_4$ and filtered. After removing solvent on rotar red solid crude was obtained. The product was purified by column chromatography using hexane as an eluent. White solid was obtained (Yield= 54%).

^{1}H-NMR(300 MHz, CDCl$_3$, δ, ppm) : 7.68-7.65 (t, 2H, Ar-H), 7.49-7.47 (t, 2H, Ar-H), 7.35-7.32 (m, 4H, Ar-H), 7.09-7.06 (d, 1H, Ar-H), 6.70 (s, 1H, -CH), 2.23 (d, 3H, -CH$_3$).

1-[(*E*)-2-phenyl-1-propenyl]-4-[(*E*)-1-propenyl]benzene (**4**):

Compound 2 (1.0 g, 4.27 mmols) was reacted with isopropenylmagnesium bromide (3) (9 mL in 0.5 M THF) under absolutely dry conditions. $PdCl_2$ (0.015 g, 0.084 mmols) was used in catalytic amount. Dry THF was used as a solvent. The reaction was carried out at 0°C under nitrogen atmosphere. Isopropenylmagnesium bromide was added very slowly. Monitored the reaction by TLC and stirred for about 5 hours. After 5 hours, the reaction was quenched by adding few drops of water. THF was removed on rotar, extracted with CH_2Cl_2, water, saturated NaCl, dried over $MgSO_4$ and filtered. After removing solvent on rotavap, reddish solid crude was obtained. The product was separated on column by hexane. The white solid product was obtained (Yield= 40%).

^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.54-7.47 (m, 4H, Ar-H), 7.46-7.32 (m, 5H, Ar-H), 6.82 (s, 1H, -CH), 5.41 (d, 1H, -CH), 5.08-5.09 (d, 1H, -CH), 2.35-2.25 (t, 3H, -CH$_3$), 2.20-2.15 (t, 3H, -CH$_3$).

Iodobenzene-PEO (n = 8, 17, 45) (**6a-c**): Iodophenol (6 g, 27.2 mmols), poly(ethyleneglycol methyl ether) with ethylene glycol repeat units n = 8 (5a) (11.5 g, 30.0 mmols), PPh$_3$ (8.6 g, 32.7 mmols)

were taken in a round bottom flask. To it was added about 40 mL dry THF and stirred in an ice-bath. To this solution was added diisopropyl azodicarboxylate (DIAD) (7.2 g, 35.4 mmols) slowly. Then after removing ice-bath, stirred the reaction mixture overnight. THF was removed on rotavap. Added little EA and hexane and triturated and kept for cooling in the refrigerator. The solid formed may be of oxide of PPh$_3$ and discarded. Repeated this procedure of crystallization several times to get the filtrate, concentrated it and kept under high vacuum to finally yield the desired compound 6a. The similar procedure was followed for the reactions involving poly(ethylene glycol methyl ether) with repeat units n = 17 (5b) and 45 (5c). The compounds 6a and 6b were liquid, yellow and brownish respectively; whereas 16c was solid.

6a: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.47-7.44 (d, 2H, Ar-H), 6.63-6.60 (d, 2H, Ar-H), 4.02-3.63 (m, 32 H, -CH$_2$-CH$_2$-O), 3.29 (s, 3H, -CH$_3$).

6b: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.55-7.52 (d, 2H, Ar-H), 6.71-6.68 (d, 2H, Ar-H), 4.10-3.53 (m, 68 H, -CH$_2$-CH$_2$-O), 3.38 (s, 3 H, -CH$_3$).

6c: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.52-7.49 (d, 2H, Ar-H), 6.68-6.65 (d, 2H, Ar-H), 4.06-3.50 (m, 180 H, -CH$_2$-CH$_2$-O), 3.30 (s, 3H, -CH$_3$).

OPV-PEO (n = 8, 17, 45) (**7a-c**):
Compounds 7a-c were obtained by Heck coupling. Typically, compounds 4 (0.4 g, 0.8 mmols), 6a (1, 0.7 mmols), Pd(OAc)$_2$ (0.003 g, 0.007 mmols), P(*o*-tolyl)$_3$ (0.008 g, 0.014 mmols) were mixed in triethylamine (about 3.5 mL) solution and stirred in a screw-capped hard glass tube at around 85°C. Within an hour solution became greenish in color. Stopped heating after 2.5 days. Triethylamine was removed on rotar, extracted the mixture with Ethyl acetate (EA), water, saturated NaCl, dried over $MgSO_4$ and filtered. EA was removed on rotar to get yellow viscous liquid which under high vacuum solidified. It was heated in EA/hexane. After decantation and cooling several times desired (7a) pale white solid was formed (Yield = 55%). The similar procedure was followed for the compounds 7b-c using 6b-c.

7a: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.50-7.47 (m, 4H, Ar-H), 7.35-7.25 (m, 5H, Ar-H), 7.25-7.20 (m, 4H, Ar-H), 6.90-6.85 (d, 1H, vinyl –CH), 6.76 (s, 1H, vinyl –CH), 4.15-3.50 (m, 32 H, -CH$_2$-CH$_2$-O), 3.30 (d, 3H, O–CH$_3$), 2.25-2.20 (s, 6H, vinyl –CH$_3$).

7b: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.52-7.48 (m, 4H, Ar-H), 7.40-7.32 (m, 5H, Ar-H), 7.32-7.25 (m, 4H, Ar-H), 6.90-6.85 (d, 1H, vinyl –CH), 6.82 (s, 1H, vinyl –CH), 4.15-3.50 (m, 68 H, -CH$_2$-CH$_2$-O), 3.35 (d, 3H, O–CH$_3$), 2.35-2.25 (s, 6H, vinyl –CH$_3$).

7c: ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm) : 7.58-7.50 (m, 4H, Ar-H), 7.45-7.35 (m, 5H, Ar-H), 7.35-7.20 (m, 4H, Ar-H), 6.95-6.90 (d, 1H, vinyl –CH), 6.85 (s, 1H, vinyl –CH), 4.20-3.45 (m, 180 H, -CH$_2$-CH$_2$-O), 3.38 (d, 3H, O–CH$_3$), 2.60-2.18 (s, 6H, vinyl –CH$_3$).

Nanostructures formation of OPV-PEO Derivatives

Typically, stock solutions of the compounds 7a, 7b and 7c were made and certain amount of stock solution was injected in the water while stirring and made its dispersions in water. All the dispersions were stirred for

one hour prior to measurements. The concentrations of all solutions were 1.35×10^{-5} M after injecting into THF or water.

Conclusion

In summary, we have demonstrated the preparation of oligophenylene vinylene rod-coil molecules with varying PEO chain lengths and shed a light on the nanostructures evolution of these molecules by simple reprecipitation method. The self-assembly of such OPV type rod molecules in water without adding any surfactants, therefore, can provide a strategy for the construction of well-defined and stable nanostructures with certain chemical functionalities and physical properties as advanced materials for photonic, electronic and biological applications. The chain length dependent photophysical properties can be utilized to optimize the nanostructures formation, fabrication parameters, etc. Presently, neither the exact nature of the aggregates nor their aggregation behavior in THF and water is accessible by our experiments. Further experimental work is needed to establish a more complete picture. Introducing useful functionality or bulky functional groups in OPV segment should change photophysical properties. Thus, we have successfully synthesized these OPV rod-coil molecules with varying PEO chain lengths and studied their nano/microstructures formation and 'controlled' aggregation induced photophysical properties and these results could lead to synthesis of newer organic macromolecules with desired functionality and fabrication of their nanostructures, ultimately giving the materials with 'controlled' aggregation induced enhanced photophysical properties. The length of the PEO chains affects the packing of the OPV core, leading to different morphologies with different photophysical characteristics.

Acknowledgements

Author's contributions

Conceived the plan: CJB; Performed the experiment: YP, RC: Wrote the paper: CJB. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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