Fluorescence in “Nonfluorescent” Polymers
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ABSTRACT: Recently, a great deal of research has been started on generating fairly strong photoluminescence from organic molecules without having any conjugated π-system or fluorophore. Discrete chromophores or auxochromophores termed as “subfluorophores” may undergo “space conjugation” via co-operative intramolecular conformation followed by intermolecular aggregation to generate fluorescence or sometimes phosphorescence emission. Polymeric materials are important in this regard as nonconjugated polymers self-assemble/aggregate in a moderately concentrated solution and also in the solid state, producing membranes, films, and so forth with good physical and mechanical properties. Therefore, promoting fluorescence in these commodity polymers is very much useful for sensing, organic light emitting diodes (OLED), and biological applications. In this perspective, we have discussed the aggregation-induced emission from four different types of architectures, for example, (i) dendrimers or hyperbranched polymers, (ii) entrapped polymeric micellar self-assembly, (iii) cluster formation, and (iv) stretching-induced aggregation, beginning with the genesis of fluorescence from aggregation of propeller-shaped small organic molecules. The mechanism of induced fluorescence of polymers with subfluorophoric groups is also discussed from the theoretical calculations of the energy bands in the aggregated state. Also, an attempt has been made to highlight some useful applications in the sensing of surfactants, bacteria, cell imaging, drug delivery, gene delivery, OLED, and so forth.

1. INTRODUCTION
Photoluminescence (PL) is one of the most intriguing natural phenomena responsible for the fascinating colors exhibited by various natural entities.1 Fluorescence and phosphorescence are two main categories of PL, which in a molecular level originates from electronic transitions from the singlet (S1) and triplet (T1) excited states to the singlet ground state (S0).2 Conjugated molecules most often contain aromatic carbocyclic/heterocyclic residues acting as fluorophores. These molecules are typically planar, and its π-conjugated systems provide appreciable rigidity in their structures. This perhaps allows efficient intramolecular excitonic recombination involving correlated excitonic states, and the molecular rigidity helps the suppression of vibrorotational motions as well as nonradiative relaxation pathways3 resulting in intense emission. Photoluminescent molecules offer a plethora of applications in optoelectronics,4,5 fluorescent bioprobes,6 photodynamic therapies,7 organic light-emitting diodes (OLEDs),8,9 molecular imaging,10,11 storage encryption,12 data security,13,14 anticounterfeiting materials, coatings, illuminants, displays, and so forth.15 In this respect, polymeric fluorescent materials have drawn significant attention because of their amplified signal response even after a minute perturbation due to the co-operative contribution from the chain segments, coupled with their intrinsic mechanical or viscoelastic properties.16,17 Polymeric photoluminescent materials are typically conjugated polymers or polymeric molecules having fluorophoric moieties attached to the chain.18–25 Despite the several advantages of nonthermoplastic nature, opacity, poor film-forming ability, nonbiodegradability or nonbiocompatibility, insolubility in aqueous media, poor flexibility of the chains, high cytotoxicity, acute inflammation, and serious immunogenicity impose difficulties during applications of the conjugated polymers.26–28 Irrespective of small molecular or polymeric fluorophores, quenching of PL in the aggregated state creates serious problems, particularly when their application in rather condensed states such as the gel state or thin film (application in LED, display, etc.) is desired.2,29–32 Therefore, attempts for designing fluorophoric materials having a lesser degree of quenching in the condensed state have been made with limited success.32 In this regard, a significant research impetus is observed in the last two decades after the discovery of Tang and his co-workers in 2001, which showed that the organics devoid
of contiguous \( \pi \)-systems may also generate rather strong PL in their aggregated states.\(^{30}\) Discrete chromophores or auxochromophores termed “subfluorophores” may undergo “space conjugation” in proper molecular conformations (intramolecular) and aggregation (intermolecular) generating fluorescence or even phosphorescence emission. Tang et al. termed such emissions as “aggregation-induced emission” (AIE) (Scheme 1).

Scheme 1. Different Types of AIEs in Subfluorophoric Polymeric Systems

and demonstrated very strong luminescence at 492 nm (being excited at 381 nm) from the nanoaggregates of 1-methyl-1,2,3,4,5-pentaphenylsilole in an EtOH/H\(_2\)O medium or in the solid state.

Aggregation of subfluorophoric groups is also noticed in linear or branched (dendrimers/hyperbranched) nonconjugated polymeric systems. Because of chain coiling, local abundance of such groups facilitates interactions between proximate subfluorophoric groups inducing “space conjugation”. This favors excitonic recombination involving correlated excitonic states, generating intense emission or recombination, which may also occur through radiative tunneling between localized excitonic states to generate rather weak fluorescence emission.\(^3\) Apart from the connectivity of subfluorophores in the aggregated state (clustering) via “space conjugation,” it also helps in the reduction of vibrational motion, hence decreasing the relaxation of the excited state of subfluorophoric groups through nonradiative pathways. This results in prominent radiative emissions from the subfluorophores. However, the excitation energy of individual subfluorophoric moieties is typically high; thus, emissions from them often fall in the UV region or in blue/green range of the visible region. Depending upon the heterogeneity of the aggregates and their local environment, excitation-dependent emission behavior is also expected from such systems.\(^{28,33,34}\) Aggregation can also be governed by self-assembly as in micelles or in vesicles or clustering of the subfluorophoric groups based on specific interactions. A few very interesting and detailed reviews are already published where cross-link-enhanced emission has been discussed for chemically or physically cross-linked nonconjugated polymer dots (PDs).\(^{35,36}\) However, the mechanism of such AIE is still in the infant stage. Therefore, a significant amount of research is presently going on for designing similar non-conjugated emissive polymer systems and exploration of their emission mechanism. The present perspective gives a concise account of various luminescent nonconjugated polymeric systems devoid of any conventional fluorophore, elucidation of their luminescence mechanism, and their applications including a short history of fluorescence from small organic nonfluorescent molecules based on the literature reports.\(^{1,30}\)

Figure 1. [(I(A–C))] Fluorescence emission spectra of DPM, s-TPE-TM, and s-TPE, respectively, in a THF/water mixture with different water fractions (\( f_w \)), (D) intramolecular through space conjugation between isolated phenyl rings. [(I(A))] Electron cloud distributions and energy levels of s-TPE-TM and s-TPE in the excited state, as calculated by TD-DFT B3LYP/6-31G(d), Gaussian 09 program. (B) Schematic definition of carbon atoms and phenyl rings in s-TPE-TM and s-TPE. (Reproduced with permission from J. Am. Chem. Soc. 2017, 139, 16264, copyright ACS, 2017.)
2. GENESIS OF AIE FROM PROPELLER-SHAPED SMALL ORGANIC MOLECULES

Highly emissive small molecules or polymers show a high degree of emission quenching, turning into weakly emissive systems in their films causing a major drawback in the fabrication of OLEDs.\(^{31,32}\) This possibly occurs due to the formation of less emissive excimers in the aggregated state.\(^{30}\) With this background, Tang and his co-workers have reported for the first time in 2001 a silole-type compound 1-methyl-1,2,3,4,5-pentamethylethylsilole (Figure 1), which is very poorly emissive in its dilute EtOH solution; however, as water is added to the system, a significant hike in the fluorescence emission quantum yield (\(\Phi\)) is noted due to the formation of nanoaggregates.\(^{30}\) Similarly, an increase in fluorescence emission intensity is also observed when solvent is dried off from the dilute ethanolic solution. Steric hindrance between the aromatic rings (particularly, in the ortho positions) restricts coplanarity of all the aromatic rings of the molecule. Hence, even in the aggregated state, co-facial alignment of molecules would not occur, which excludes the formation of emission-quenching excimers.\(^{30}\) In a subsequent paper, they carried out intense investigation of the phenomenon taking three different multiphenyl derivatives (2,4,5-trimethylphenyl)methane (DPM), 1,1,2,2-tetrais(2,4,5-trimethylphenyl)ethane (s-TPE-TM), and 1,1,2,2-tetraphenylethene (s-TPE).\(^{3}\) Evidently, all these three molecules do not have a continuous conjugated \(\pi\)-network. In dilute ethanolic or THF solutions, all these three molecules show similar absorption/emission behavior (\(\lambda_{\text{abs}} = 280 \text{ nm}\) and \(\lambda_{\text{em}} = 297 \text{ nm}\)), which is very similar to the individual phenyl rings present in the respective molecules. This suggests that in the ground state there is no resonance connection between phenyl rings in a molecularly dissolved state in THF or ethanol. However, as water molecules are added over 70% (f) into these solvents, a red shift in the emission position 390–400 nm for DPM and s-TPE-TM occurs with an increase of 140- and 170-fold of emission intensity, respectively [Figure 1(A–B)]. However, the s-TPE showed a relatively greater red-shifted emission (at \(\sim 460 \text{ nm}\)) and about 400-fold increase in emission intensity [Figure 1(C)]. In the solid state, s-TPE exhibited \(\sim 70\%\) quantum yield when excited at 365 nm. The analysis of the crystal structure and time-dependent density functional theory (TD-DFT) calculations indicate that intermolecular aggregations probably take part in increasing the rigidity, hence arresting the vibrorotational motions of these propeller-shaped molecules. The calculated distance of separation between the phenyl rings of different molecules in the aggregated state precludes any intermolecular “space conjugation”, and rather intramolecular space conjugation is observed in the excited state only [Figure 1II(A,B)]. The latter therefore accounts for the observed red shift in fluorescence emission. The intramolecular space conjugation is observed to be maximum in the case of s-TPE molecule, where the absence of methyl substituents helps the phenyl rings to attain a near parallel orientation, resulting in a significantly red-shifted emission. Hence, the increased intensity is attributed to the increased rigidity of the molecules due to aggregation. Apart from the reports of Tang et al., this field is experiencing a very fast growth, particularly, in view of the supramolecularly organized nonconjugated small molecular systems, which show very strong luminescence.\(^{36}\) However, a detailed discussion in this regard is beyond the scope of this contribution.

The common insolubility and difficulty in the processibility of conducting polymers and other chromophoric polymers deter them from diverse optoelectronic and biotechnological applications.\(^{37}\) Therefore, in the following sections, we shall discuss about the AIE of polymeric systems having no chromophoric groups but contains only sublumophores taking examples from different types of polymeric architectures and different modes of aggregation. The cooperative nature of the conformational change in the chain segments of different chains facilitates easier aggregation, forming effective space conjugation resulting in a substantial amount of emission. Furthermore, these polymeric systems are important because of their easy processibility, good mechanical property, good thermal stability, and good biocompatibility that make them useful for diverse optoelectronic and biotechnological applications.

3. AIE FROM DENDRIMERS OR HYPERBRANCHED POLYMERS

In 2004, Bard and co-workers while working on the electro-chemistry of previously reported fluorescent (\(\lambda_{\text{em}} = 450 \text{ nm}\)) polyamidoamine (PAMAM)-encapsulated Au\(_8\) nanoclusters astonishingly observed that hydroxy-terminated PAMAM dendrimers (G4-OH, G2-OH, or even G0-OH) exhibit the same emission profile upon oxidation with \(\text{NH}_4\text{H}_2\text{S}_2\text{O}_8\) (APS), without the presence of Au nanoclusters in the core (Figure 2).\(^{38}\) In an almost simultaneous work, Wang and Imae reported
strong fluorescence emission from the fourth generation (G-4) primary amine group-terminated PAMAM dendrimer (G4-NH$_2$), which shows remarkable pH dependence. Also, it is necessary to mention here that some other research groups have reported weaker fluorescence from PAMAM dendrimers and from carboxyl-terminated PAMAM dendrimers. Wang and Imae demonstrated a remarkable increase in fluorescence emission upon increase of molecular crowding in the (G4-NH$_2$) PAMAM dendrimer compared to that of (G2-NH$_2$) molecules. They found strong fluorescence emission irrespective of the hydroxyl- or carboxyl-terminated PAMAM dendrimers. In this respect, their explanation is in sharp contrast with that reported by Bard and co-workers, where the origin of emission is attributed particularly to the oxidation of terminal hydroxyl groups, irrespective of the backbone structure of the dendrimer molecules. In Scheme 2 an overview of a typical structure of PAMAM with hydroxy/amine-terminated molecules is presented for a better understanding. Wang and Imae have observed an increase in the PL intensity of (G4-NH$_2$) PAMAM dendrimer or (G5) polyethyleneimine (PEI) dendrimer as the medium pH is decreased. This has been attributed to the increased rigidity of the dendrimer structure as cationic centers are generated in the dendrimer interior due to protonation of tertiary amine moieties. Rigidity of “subfluorophores” inside the dendrimer reduces the rotational relaxation, thus improving the radiative decay. The poor fluorescence intensity observed with (G2-NH$_2$) PAMAM is also attributed to the lack of rigidity of the molecular system due to the poor degree of molecular crowding. Nevertheless, they have also reported an increase in fluorescence intensity for all the dendrimers (irrespective of the terminal groups present) upon oxidation. A few years later, in 2009, in a very interesting paper, Chu and Imae et al. demonstrated that instead of oxidation of the terminal functional groups, oxidation of the tertiary amine (R$_3$N) moieties present inside the dendrimers to the corresponding N-ox radicals (R$_3$N-O$_2$) is the principal reason for the increase in the fluorescence efficiency of PAMAM or PEI/PPI-based dendrimers. In 2005, Wu et al. reported fluorescent hyperbranched aminoester molecules, which are much easier to synthesize compared to dendrimers, and their biocompatibility is much improved than those of polyalkyl amines (PEI/PPI). The fluorescence emission observed in this work is attributed to the presence of both tertiary amine and ester carbonyl groups in the interior part of the molecular system. Oxidation of the hyperbranched polymer helps to increase the fluorescence intensity, but it is not responsible for the origin or position of the emission. Interestingly, tertiary amines up to tripropylamine show intense fluorescence emission in the gaseous phase due to the absence of the rotational relaxation effect, as is present in the nonemissive solution state. In this regard, it may be further mentioned that primary or secondary amines do not emit even in the gaseous phase because of their high predissociation rate. Wang and Imae attributed tertiary amine subfluorophores, which are present in
the backbone structure of such dendrimers or hyperbranched molecules, as the principal emitting species. This consideration is further supported by the fact that oxidation of tertiary amines in the gaseous phase similarly increases the emission intensity. Thus, analysis of the so far reported works indicates that the fluorescence emission in PAMAM dendrimers is primarily the result of subfluorophoric tertiary amine backbone structure and molecular rigidity. In contrast to the hyperbranched or dendrimeric polymers, PAMAM having a linear structure fails to emit.\textsuperscript{48} The emissive nature of tertiary amine moieties has been further established by Pan et al., when fluorescence emission quenching is observed for hyperbranched HPAMAM upon quaternization with MeI.\textsuperscript{49} The trialkyl amine moieties inside the HPAMAM experience a similar situation as in the gas phase due to reduced collisional relaxation events. Thus, strategically, it would be possible to increase the fluorescence emission intensity of PAMAM by increasing the molecular crowding through attachment of suitable moieties. Accordingly, in a very interesting report, attachment of mannose moieties with HPAMAM resulted in further increase in the intrinsic molecular fluorescence emission.\textsuperscript{33} Pan et al. have made a similar report on fluorescence emission, showing a quantum yield value of \( \sim 0.43 \) with hyperbranched poly(amino-ester) synthesized by Michael addition polymerization of tris(2-mercaptoethyl)amine and ethylene glycol diacrylate.\textsuperscript{33} The emitting species has been claimed to be the tertiary amine moieties whose emission intensity has similarly been found to increase with the molecular crowding due to the increase in the degree of branching and molecular weight of the hyperbranched polymer. In comparison with the linear molecular architecture or even by keeping the emissive tertiary amine centers toward the periphery instead of the hyperbranched polymer backbone results in much diminished quantum yield. This further sheds light on the issue of reduced rotational/collisional relaxation of tertiary amine moieties behind their emissive property. Oxidation of hyperbranched amine-ester polymers in this work similarly exhibits an increase in PL intensity. The increase in PL intensity is attributed to the formation of species such as \( \equiv N \rightarrow O \) formed via oxidation of the "N" atom attached to the methylene groups. This is in contrast with the oxygen-doped tertiary amine formed during the oxidation of PAMAM, as proposed by Chu and Imae,\textsuperscript{34} or the oxygen—amine “contact” donor—acceptor complex formed during the oxidation of aliphatic tertiary amines, as proposed by Halpern and Wryzykowska.\textsuperscript{50} Wang et al. have reported blue-light-emitting (in both the solution or film when excited at 365 nm) linear and hyperbranched PAMAM molecular systems by Michael-type polycondensation addition of \( N,N \)-bis-acrylamide and 1-(2-aminoethyl)piperazine (AP).\textsuperscript{51} These systems have also exhibited excitation-dependent red-shifted emission behavior. Upon conducting theoretical analysis, they found a variety of inter- and intra-chain clusters being formed by the isolated and periodic lone pair of electrons and delocalized \( \pi \) electrons in the polymer chain (Figure 3). The said lone pairs of electrons can delocalize through \( (n-\pi) \) and \( (\pi-\pi) \) interactions in the aggregates resulting in a relatively smaller band gap compared to those of the isolated subfluorophores. The increased intensity of emission is attributed to the suppression of the nonradiative deactivation pathway of excitons due to rigid conformations, which is obviously more apparent in the solid film compared to that in the solution. They have called the emitting species “cluster chromophores,” attributing to the excitation wavelength-dependent emission for the heterogeneity of clusters. Stiriba and co-workers have reported fluorescence emission from both the linear or hyperbranched PEI molecules in MeOH medium.\textsuperscript{33} Interestingly, their comparative studies reveal relatively intense emission from the linear PEI molecule compared to a hyperbranched system of comparable molecular weight. Furthermore, the emission is further modulated via N-capping methylation of free primary amine groups of PEI or adjusting the acidity of the polymer solution. The lowering of medium pH results in an increase in fluorescence intensity for the methanolic solution of PEI, and the genesis of emission is attributed to the formation of amine-rich nano-clusters and electron—hole recombination involving correlated localized excitonic states. In this regard, it may be mentioned that there are some exciting previous reports on silica-based organic/inorganic nanocomposite fluorescent gel where emission is observed in the absence of any conventional fluorophore in the system.\textsuperscript{52,53} Carlos et al. in 1999 proposed the origin of the observed luminescence as the electron—hole recombination process between strongly correlated excitonic states or even radiative tunneling between the localized states of electrons and holes.\textsuperscript{3} In a very interesting paper, Bekiari et al. reported the emission behavior of gel material prepared by connecting triethoxysilane groups with PEO/PPO chains through urea bridges (Ureasils).\textsuperscript{52} The observed luminescence is attributed to the delocalized electron—hole recombination where the local-
The delocalization of states depends on the \( \sigma \)-conjugation of the silicon network and interactions between (C=O) and (N\( \text{--} \)H) groups of urea bridges. The emissive centers are thus located on the surface of silica clusters, where an appreciable concentration of (C=O) and (N\( \text{--} \)H) groups is present. It was also observed that the larger clusters emit at larger wavelengths than that of smaller clusters. Polysiloxane-based PAMAM dendrimers or hyperbranched polymers containing plenty of carbonyl (C=O), (C=C), or NH\( \text{--} \)OH groups have been reported to show strong blue fluorescence either in the solid state or in the alcoholic solutions (Figure 4).\(^{54,55} \) In 2015, Feng et al. reported the synthesis of Si-PAMAM dendrimers by the alternate aza-Michael reaction and amidation reaction having 1,3-bis(3-aminopropyl) tetramethyldisiloxane (G0) as the core and branch point.\(^{56} \) Subsequently, in 2016, Niu et al. synthesized a hyperbranched polysiloxane compound via a one pot polycondensation reaction of triethoxyvinylsilane with excessive neopentyl glycol.\(^{55} \) The synthesized hyperbranched polymers contain a large number of hydroxyl and nonconjugated vinyl groups. The origin of blue emission in both these reports is attributed to the aggregation of vinyl/hydroxyl groups\(^{55} \) or carbonyl/amine groups.\(^{56} \) The developed aggregations may induce the electron-hole recombination involving correlated excitonic states or radiative tunneling due to the proximity of the groups. In both these works, interactions between heteroatom lone pairs (N and O atoms) and Si atoms of the polymer chains have played a key role behind the aggregate formation, as already claimed by Feng et al. for the Si-PAMAM system.\(^{54} \) This is further supported by the decrease in fluorescence emission intensity with pH lowering for Si-PAMAM in this work, which is in sharp contrast with the previously reported PAMAM systems. The decrease in the emission intensity observed in the Si-PAMAM system might have occurred due to the protonation of basic amino groups, and therefore, dismantling of the emissive aggregates.

4. AIE FROM ENTRAPPED POLYMERIC MICELLES

Apart from the dendrimeric or hyperbranched structures, an alternative way for increasing the proximity of the subfluorophoric groups is the formation of self-assembled micellar
aggregations. In this regard, there are two very interesting reports where subfluorophoric groups of amide moieties or PEI assembled either in a water-based micelle core or corona to emit bright blue or multicolor fluorescence, respectively. Liu et al. have demonstrated an amphiphilic polyetheramide (PEA) molecule on a hydrophilic PEO backbone. The aqueous solution of the amphiphilic polymer above its critical micellar concentration (cmc = 0.47 mg/mL) exhibits strong blue light
emission on excitation with 360 nm radiation. Interestingly, at a lower concentration of the solution (0.2 mg/mL), very low emission is noticed; however, when the solution concentration increases just above the cmc, a remarkable increase in fluorescence intensity was noted (Figure S5). The blue light emission becomes visible even to the naked eye at 2 mg/mL concentration on irradiation with $\lambda_{ex} = 360$ nm. The origin of this emission is attributed to the AIE by the H-bonded amide groups in the micelle core. On the other hand, Sun et al. have prepared biocompatible amphiphilic copolymers with hydrophilic PEI and hydrophobic poly(lactide) (PLA). The self-assembled micellar structure contains hydrophobic PLA chains in the micellar core, whereas aqueous soluble PEI remains in the corona. The proximity of PEI subfluorophores in the corona resulted in the generation of multicolored emissions. Interestingly, herein, the fluorescence emission shows significant dependence on the excitation wavelength and gets red-shifted as the excitation wavelength is increased, indicating the existence of different emitting species possibly formed due to the heterogeneous aggregation of PEI moieties in the micelle corona. Li et al. have reported the generation of blue fluorescence ($\lambda_{em} = 425$ nm, $\lambda_{ex} = 350$ nm, $\phi = 4\%$) from the block copolymer of polystyrene-b-polyacrylic acid (PS-b-PAA) having intermittently grafted 1H,1H,2H,2H-perfluoro-1-decanol (HFD) or higher homologues through ester linkages in their solid state or aqueous-based micelles. Theoretical analysis through DFT calculations indicates the interaction between the lone pair of electrons on “O” atoms of the free carboxylic acid groups (HOMO) and empty $\pi^*$ orbitals (LUMO) of the ester functional groups (Figure 6II(a,b)), and the origin of emission is attributed to the transitions between these two states. Aggregates in the solid state or aqueous micelle increase in the proximity of these groups, which favor emissive transitions. Furthermore, aggregation leads to the increased rigidity of the subfluorophores suppressing the nonradiative deactivations. This is further supported by the fact that in THF medium, the interactive moieties remain distinctly oriented due to the solvation factor, rendering a poor PL property ($\Phi = 1\%$). A distinct role of electron- withdrawing F atoms in increasing the interaction between the carbonyl “O” atoms and the ester carbonyl groups, and hence an increase in fluorescence intensity is observed when higher homologues of perfluoro alcohols such as 1H,1H,2H,2H-perfluoro-1-dodecanol (PFD) or 1H,1H-perfluoro-1-tetradecanol (PFTD) are anchored to the PAA backbone (Figure 6I). On the other hand, grafting of $n$-decanol (DA) on PAA significantly reduces the fluorescence emission intensity ($\lambda_{em} = 411$ nm, $\lambda_{ex} = 350$ nm, $\Phi = 2\%$), which is also consistent with relatively higher distance of separation between the transition centers (Figure 6II(c)). Thus, at this stage, it may be commented that greater interaction causes proximity and rigidity of the transition centers, facilitating improved correlation between the excitonic states. This would allow efficient excitonic recombination resulting in higher emission intensity. In a very interesting work, Nandi and his co-workers have reported for the first time fluorescence emission from a poly(vinylidene difluoride) (PVDF)-based graft copolymer in aqueous solutions. In this work, synthesis of PVDF-g-PDMAEMA (PVDM-1) is carried out at first using atom-transfer radical polymerization, and then the graft copolymer is fractionated to get a good water-soluble fraction. Subsequently, the product having tertiary amine groups of PDMAEMA-grafted chains is reacted with sulfone to obtain a water-soluble zwitterionic graft copolymer (PVDMS). In the aqueous medium, PVDM-1 and PVDMS self-assemble to form vesicles and multivesicular aggregates, respectively (Figure 7a), which are confirmed by dynamic light scattering and TEM studies. Their optoelectronic properties in aqueous solution show a relatively weak emission at 534 nm (\(\lambda_{em} = 390\) nm) for PVDM-1 and a strong blue emission at 438 nm (\(\lambda_{em} = 370\) nm) for PVDMS (Figure 7b,c). Theoretical calculations reveal that the origin of emission in the case of PVDM-1 is due to transition from the LUMO on the carbonyl group to the HOMO over the tertiary amine group. On the other hand, in the case of PVDMS, transition occurs between the LUMO situated on quaternary ammonium groups and the HOMO over sulfonate groups. Calculations also show that the proximity of the transitioning active groups in the case of latter is more than those of the former, which may be attributed to the improved electrostatic interactions between them. Thus, a better correlation among the excitonic energy states in PVDMS occurs resulting in improved electron—hole recombination, compared to the same between rather localized excitonic states in the case of PVDM-1. Apart from the hydrophobicity or crystallization effect leading to micelle formation, or imposing rigidity in the solution structure, which perhaps operated in the above report, PVDF also exerts a fluorous effect because of the presence of a large number of highly electron-withdrawing F atoms. Zhang et al. have observed excitation-dependent multicolor emission of an azide-grafted PVDF backbone polymer in the solid state or DMF solution. The observed fluorescence in the visible region is attributed to the electron-withdrawing effect of a large number of F atoms present in the PVDF chains, which lower the azide group energy states. Moreover, the intensity of emission...
Figure 9. CL originates from carbonyl group clustering of SA moieties only when their number per polymer chain is above a critical value. (Reproduced with permission from Macromol. Chem. Phys. 2008, 209, 900, copyright Wiley-VCH, 2008.)

Figure 10. (I) Chemical structures of PMP and OMAh4. (B) UV−vis spectra of PMP and OMAh4 in THF with a concentration of 0.01 M. (C) Photographs of PMP and OMAh4 in THF and their solids taken under (up) daylight and (down) 365 nm UV light irradiation. (D) PL spectra of PMP ($\lambda_{ex} = 365$ nm) and OMAh4 ($\lambda_{ex} = 365$ and 458 nm) in THF with a concentration of 0.01 M; (II(A)) Optimized conformation of OMAh4 at different views. (B) Optimized conformation of PMP (hydrogens on anhydride rings were omitted for the concise view). (C) The interaction types of carbonyl groups in OMAh4. (D) The proposed model of n → π* interaction; (III) process of cluster formation. (Reproduced with permission from J. Mater. Chem. C. 2017, 5, 4775, copyright RSC, 2017.)
increases with concentration in DMF medium, which indicates a relatively sluggish movement of PVDF chain segments, resulting in a local rigidity across the emissive azide groups (Figure 8). The excitation-dependent red shift of the emission indicates the differences in the local fluororesence effect as a result of inhomogeneity in the distribution of PVDF chains in relatively concentrated solutions.

5. AIE FROM CLUSTER FORMATION

This is another very important class of aggregation-induced luminescence. Herein, the π-chromophoric subfluorophores produce clusters because of the specific interactions and emissions originating from the newly created orbitals (energy bands). Such emissions are therefore termed “cluster luminescence” (CL). The formation of clusters is mostly reported to occur between carbonyl groups or phenyl/carbonyl groups. Ciardelli et al. in 2008 have reported the poly(isobutene succinic anhydride) (PIBSA) or poly(isobutene succinimide) (PIBSI) systems, which emit fluorescence in their neat form as well as in heptane solution, when the amount of functional groups per polymer chain is higher than a critical value (Figure 9).59 The observed luminescence is attributed to the aggregation of carbonyl groups of nonemissive molecules. The aggregates have caused a restricted vibrorotational motion reducing the nonradiative relaxation processes, resulting in an increased fluorescence quantum yield (Φ). It is further observed that the intensity of emission depends on the concentration (number) and nature of functional groups, for example, the fluorescence quantum yield (Φ) shows ~85% increase (from 0.02 in PIBSA to 0.037 in PIBSI) when more interactive succinimide (SI) functional groups are present in place of succinic anhydride (SA) groups. The generation of fluorescence emission is due to the clustering of carbonyl groups of SA moieties, which is studied in more detail by Zhou et al.50 For this purpose, they have studied the photophysical properties of two different polymers, one is oligo(maleic anhydride) (OMAh), where the carbonyl groups of SA units may easily form clusters, and the other is poly[maleic anhydride-co-(2,4,4-trimethyl-1-pentane)] (PMP), where the SA moieties are separated by intermittently placed bulky tert-butyl groups which hinder the SA carbonyl groups from clustering. A clear distinction in the photophysical behavior of OMahs and PMP is observed in respect of both absorption and emission spectra. The former shows two absorption signals at 365 and 458 nm along with a pair of emission peaks in the 430 and 500 nm region when >0.01 M concentration of the polymer in THF is taken (Figure 10I(B,D)). On the other hand, PMP shows no absorption over 300 nm, and it is nonemissive (Figure 10I(B,D)). Interestingly, a similar observation as in PMP is found in the case of dilute solution (~10 μM) of OMahs in THF solution. This definitely indicates noncovalent interactions between SA moieties as the origin behind the observed emission. DFT is applied for structural optimization, where a simplified model taking ten repeating units of OMAh and PMP has been considered. Simulation studies indicate that the distance of separation between adjacent SA units in OMAhs is ~2.84−3.18 Å, whereas the distance is much higher, ~4.90−5.37 Å, in the case of PMP (Figure 10II(B,C)). Thus, the distance between SA moieties in OMAhs is conducive to molecular clustering through intrachain noncovalent carbonyl interactions.61 The reason behind the red-shifted emission position also becomes apparent from the formation of low-energy LUMO via (n−π*) interaction between the carbonyl groups, as indicated by the
Carbonyl group interaction conformation in the OMAhs model. Similar interactions are not very uncommon\(^62\)−\(^65\) and occur most effectively following the Bürgi–Dunitz trajectory (Figure 10II(D)), when the donor oxygen atom and the acceptor carbon atom form a sub-van der Waals contact (\(d < 3.22 \text{ Å}\)). However, the absence of red-shifted absorption/emission of the OMAhs system in a dilute THF solution (where only intrachain interactions may operate) indicates the existence of thorough space interchain interactions. Such interactions help tight packing/clustering of the SA units to exert rigidity in the concentrated solution or condensed phase of OMAhs (Figure 10III) resulting in intense emission. However, this clustering fails because of steric hindrance imposed by the intermittent tert-butyl groups resulting in the nonemissive character of PMP. However, it cannot be denied that introduction of sterically congested groups introduces structural rigidity, which should be conducive for having an improved quantum yield (\(\Phi\)) of emission if space conjugation of subfluorophoric groups is not significantly hampered. On the other hand, it surely restricts the possibilities of longer wavelength emissions as well as the heterogeneous assembly of subfluorophores. This causes intense fluorescence emission with excitation wavelength-dependence. Therefore, it is often difficult to have longer wavelength emissions from such nonconventional luminogen systems. There are some very interesting reports in this regard, that is, Wang and co-workers have synthesized low-molecular weight poly(maleic anhydride-co-vinylpyrrolidone) copolymers, which emit a bright yellow light.\(^66\) Qiao and co-workers have reported poly(maleic anhydride-co-vinyl acetate) derivatives showing tunable emission from cyan to red when the copolymer is treated with an aqueous NaOH solution at different concentrations.\(^57\) The effect of increased chain flexibility is further demonstrated.

Figure 12. (A) HOMO is the \(\pi\) MO located in the benzene ring and LUMO is the \(\pi^*\) located in the benzene ring and the neighboring carbonyl. (B) Fluorescent properties of phenyl-containing polymers with and without a side carbonyl unit. (C) Calculated distances between the benzene ring and its neighboring carbonyl group for a different number of polymerization units. (Reproduced with permission from Adv. Mater. 2012, 24, 5617, copyright Wiley-VCH, 2012.)
by the photophysical studies of poly(itaconic anhydride) (PITA) and poly[(1-octene)-co-((itaconic anhydride)] (POITA). The increased fluorescence intensity and red-shifted emission of POITA compared to those of PITA is indicative of improved chain flexibility of the former. The presence of poly(maleic anhydride) (PMAh) chain segment in the copolymer induces greater restrictions to the entire chain mobility compared to that of PITA segment, as the latter remains attached with the polymer chain only with one carbon atom. Therefore, a greater degree of chain flexibility is expected with the PITA chains. Keeping this in mind, Shang et al. have synthesized poly[ITA-co-N-vinylpyrrolidone] (PIVP) or poly-[ITA-co-vinylcaprolactum] (PIVC), which exhibited a maximum emission wavelength in the orange-red region (627 and 611 nm) and white emission under 365 nm UV irradiation. In another very interesting work, Zhao et al. have reported the fluorescence and solvatochromic behavior from the random copolymer of maleic anhydride (MAH) and vinyl acetate (PMV) (Figure 11). Simulation studies on PMAh indicated a helical arrangement of SA units with an interunit dihedral angle of (Figure 11).69 These conditions are undoubtedly very much favorable for the generation of π−π interactions leading to the formation of emissive carbonyl clusters. It has also been found that VAc units in the PMV polymer have no role in generating emission, but the differential interaction of SA, VAc, and different solvent molecules leads to the observed solvatochromic effect (Figure 11A,B). The steric hindrance imposed by the pair of carbonyl groups in SA moieties induces restriction in the rotation of the (C−C) bond, hence significant rigidity is introduced in the SA aggregates. This structural rigidity exerts significant influence on the luminescence intensity of carbonyl aggregates due to reduced vibrorotational relaxations. This is apparent from the fact that in the aqueous solution of PMV, as the hydrolysis of the anhydride moieties proceeds with time, fluorescence intensity shows a gradual decrease.

Apart from the aggregation of only the carbonyl groups, emissive clustering may also occur between carbonyl groups and the phenyl ring or similar nonemissive or weakly emissive aromatic chromophores. In this respect, Yan et al. have observed blue fluorescence during the radical addition fragmentation transfer (RAFT) polymerization of NIPAM mediated by poly(trithiocarbonate) (PTTC, Mw ~ 2000).70 The blue PL emission is observed first after 6 h of polymerization, and emission intensity increases with polymerization time, that is, with the increase in the polymer molecular weight. Further works reveal similar genesis of fluorescence during polymerization of methyl acrylate, dimethyl acrylamide, or styrene. A more detailed analysis indicates that the emission is not observed if NIPAM is polymerized with AIBN only or PTTC is replaced by 2-dodecylsulfonylthiocarbonysulfanyl-2-methylpropionic acid. On the other hand, the fluorescence is retained if trithiocarbonate residues are removed from PTTC-mediated RAFT-polymerized PNIPAM. The random copolymer of chlorotrifluoroethene and butylvinylether synthesized using S-benzyl O-ethyl dithiocarbonate does not exhibit similar fluorescence, apart from a weak emission at ~300 nm for the phenyl rings. However, PNIPAM synthesized by the same protocol exhibited strong emission at 400 nm. Thus, the presence of phenyl ring as well as carbonyl groups seems to be a prerequisite for the origin of such emission. Theoretical analysis also indicates that phenyl rings constitute the HOMO and a strong interaction between the π-residues of the phenyl ring and proximate carbonyl groups constitutes the LUMO (Figure 12).70 In their proposed model, with increasing polymer chain length, the π-stacked domains are tightly wrapped up by the coiled polymer chains generating discrete nanodomains. Furthermore, such a model explains the rigidity of π-stacked moieties resulting in an increase in the fluorescence intensity. The poly[NIPAM-b-oligoethylene glycol acrylate (OEGA)] synthesized using the PTTC-mediated RAFT polymerization shows much stronger emission compared to that of POEGA alone. This multiblock copolymer shows remarkable biocompatibility, poor cytotoxicity, and remarkable photostability being comparable with the quinine sulfate. This diblock copolymer is, therefore, successfully used in cell labeling. A similar space conjugation between the carbonyl groups of maleic anhydride (MA) units and/or aryl units in different random polymeric materials of poly(maleic anhydride) with styrene, α-methylstyrene, vinyl carbazole, vinyl acetate, pentene, and so forth are demonstrated by Qiao and co-workers.15 Interestingly, they have reported fluorescence (type-A polymer) as well as phosphorescence (type-B polymer) for compounds containing aromatic ring substituents (Figure 13I). Theoretical analysis of

Figure 13. ([A]) General structure of fluorescent copolymers; (B) general structure of phosphorescent copolymers; (II) luminous unit and its molecular orbitals in MASL. (Reproduced with permission from Polym. Chem. 2016, 7, 6250, copyright RSC, 2016.)

the PMAh-alt-P(α-methylstyrene) polymer indicated that the HOMO placed on benzene rings and the (π−π) interaction between the carbonyl group and the neighboring benzene ring constitute the LUMO (Figure 13II).

Zhou et al. have reported a blue emission at λmax = 405 nm (λex = 348 nm) of a relatively concentrated solution (0.05 M) of polyacrylonitrile (PAN) in DMF or DMSO solvent or an even more intense emission in the solid state.29 The observed emission is attributed to the clustering of nitrile (−CN) groups in the highly entangled PAN chains from the overlap between lone pairs of nitrile group of the “N” atom and π electrons, together with dipole−dipole interactions and (n−π) interactions (Figure 14I). The clustering of nitrile groups through intermolecular interactions is further apparent from the gradual increase in the fluorescence quantum yield (Φ) value from dilute N-methyl-2-pyrrolidone (NMP) solution (1.25 × 10−4 M, Φ = 0.9%) to a relatively concentrated solution (2 M, Φ = 6.7%), and finally Φ = 16.9% is achieved for the solid powder. The intense blue emission is observed in the solid state or in the DFM-casted film of pure PAN (Figure 14II) or PAN/PMMA mixtures. It may be attributed in part to the semicrystalline nature of PAN chains which helps in the rigidification of the subfluorophoric
nitrile groups in the polymer chain matrix. This issue was also commented by Nandi and co-workers while working on the emission properties of semicrystalline PVDF-based graft copolymers.\textsuperscript{58} Thus, the observed intense emission in films promises their potential application during fabrication of OLEDs or light-conversion films.\textsuperscript{15} Apart from the fluorescence emissions, triplet emissions (phosphorescence) from PAN are achieved in the solid state (Figure 14III). The observed phosphorescence has been attributed to the "N" atom's lone pairs within the clusters, which promote spin–orbit coupling, facilitating the intersystem crossing (ISC). In another very interesting and recent report, Zhou et al. have shown clustering-triggered emission due to the molecular packing of the nonconventional luminophores comprising only oxygen functionalities devoid of any \(\pi\)-bonding such as D-(+)-xylose, pentaerythritol, D-fructose, and D-galactose.\textsuperscript{71} Concentrated solutions or crystals of these molecules at 77 K or even under ambient conditions exhibit remarkable multicolor phosphorescence afterglows in response to varying excitation wavelengths. This has been attributed to the formation of various

Figure 14. (I) Schematic illustration of PAN molecules in (a) isolated and (b) aggregated states. (c) Cyano clusters in the aggregated states. Possible intra- and intermolecular interactions within cyano clusters: (d) electron overlap between lone pairs and \(\pi\) electrons, (e) dipole–dipole interactions, and (f) \(n\)–\(\pi\) interactions. (II) Photographs of (a) solid powders, (b) solution-cast films of PAN obtained under 365 nm UV light or room light. (III(a)) Chemical structure of PAN and its Jablonski diagrams in (b) dilute solution, (c) concentrated solution, and (d) solid powder states. (Reproduced with permission from Small 2016, 12, 6586, copyright Wiley-VCH, 2016.)

Figure 15. (A) Example of protein structure and the chemical structure of three aromatic amino acids. (B) GFP structure and its chromophore p-HOBDI. (C) Representative nonaromatic amino acids and poly(amino acids). (D) BSA structure with partial aromatic and nonaromatic amino acid residues shown in different colors. (Reproduced with permission from Angew. Chem., Int. Ed. 2019, 58, 12667 copyright Wiley-VCH, 2019.)
molecular clusters with sufficient rigidity led by inter- and intramolecular (O···O) interactions and H-bonding interactions, which is illustrated by single-crystal and theoretical analyses. Zhao et al. have also demonstrated cluster-triggered emission from sulfur-containing polythioether or their corresponding oxidation products such as sulfoxides or sulfones.72 The concerned molecules are synthesized by Michael polyaddition between 1,4-butanedithiol and 1,4-butanediol diacrylate. Subsequently, the polyethers are oxidized by H₂O₂ in the presence of sulfamic acid to get corresponding sulfoxide or sulfone derivatives. The synthesized polymers show emission at 435 nm (Φ = 3.9%) with a couple of shoulders at 454 nm and 483 nm (λₑₓ = 365 nm), only when a high concentration of it (100 mg/mL) in DMF solution is used. The observed fluorescence emission is attributed to be triggered by clustering of sulfophoric groups due to multiple inter- and intramolecular interactions such as C=O···O (n-π*), S···C=O (n-π*), O=O···O (dipole–dipole), and O···O short contacts. The larger size of sulfur atoms, higher polarizability than oxygen atoms, and electron-rich nature help such cluster formation. The oxidized sulfoxide or sulfone derivatives at similar concentrations show emission properties in DMF at somewhat red-shifted region due to the improved clustering-based conjugation of S=O or (O=S=O) groups. The aggregations are further improved in their solid states showing increase in the quantum yield for all of the polythioether (Φ = 4.5%), sulfoxide (Φ = 7%), and sulfone (Φ = 12.8%) derivatives. Along with improved fluorescence emission intensity, all these polymers in their solid state exhibit green phosphorescence after stopping UV irradiation (at 365 nm) upon cooling to 77 K. The increased rigidity of aggregated chains in the solid state at low temperatures and spin–orbit coupling at the n-electron-rich clusters facilitating ISC account for the occurrence of green phosphorescence.

The fluorescence emission of protein molecules is very much valuable in understanding photochemical reactions in proteins, pH sensors, bioimaging, autofluorescent tissues, and protein conformation indicators.73 It is worth mentioning that the Nobel Prize winning work on Green Fluorescent Proteins (GFP) from the jellyfish Aequorea victoria74–76 has revolutionized and made a remarkable advancement in evolutionary biology. This unique emission, however, originates from the chromophore p-hydroxybenzylidene-2,3-dimethylimidazolone (p-HOBDI) remaining in the protective β-barrel (Figure 15B). The aromatic residues present in tyrosine (Tyr), tryptophan (Trp), or phenylalanine (Phe) (Figure 15A) are attributed to the luminescence observed in the near-UV region of protein molecules. Inspired from the emission behavior of nonaromatic amino acids or polypeptides in their highly concentrated solutions,77–79 Yuan and co-workers revisited the fluorescence emission behavior of bovine serum albumin (BSA) (Figure 15A,C).73 It is important to mention here that nonaromatic amino acid residues are mostly populated in most of the protein structures, causing emission behavior under
appropriate conditions. These workers have found that a concentrated aqueous solution (100 mg/mL) of BSA exhibits blue emission (in the visible region) when excited at 365 nm. However, in dilute solutions (<0.1 mg/mL), BSA shows relatively much weak emission signal at 348 nm (in the near-UV region) when excited at 300 nm. Such emissions in the near-UV region are typically observed from the aqueous solution of BSA or other protein molecules, which originate from different aromatic residues present in the protein molecule.\textsuperscript{80,81} At higher BSA concentrations (20 mg/mL), a very strong emission is observed at 442 nm (\(\lambda_{\text{ex}} = 365\) nm), which is far beyond the absorption of aromatic residues.\textsuperscript{80} The development of such emission is attributed to the entanglement of BSA chains at higher concentrations, where in the aggregated state, clustering occurs between C\(=\text{O}\) and N–H/H–O–H groups through their n\π and \π electrons. These interactions along with H-bonding interactions within the nonconjugated backbone of peptide chains provide rigidity to the protein molecular conformations, which is conducive for such emissions. The concentration-dependent emission or AIE of aqueous BSA solution is further apparent from the increase in quantum yield with increasing solution concentrations (\(\Phi = 0, 3.9,\) and \(5\%\) for \(0.01, 10,\) and \(20\) mg/mL, respectively). Increased aggregation and rigidity in the amorphous solid BSA powder results in increased quantum yield (\(\Phi = 7\%\)) compared to \(5.3\%\) in 20% aqueous solution. Subsequently, formation of tablets upon pressurization of amorphous BSA powder shows further increase in quantum yield (\(\Phi = 10.2\%\)). The concentrated aqueous solution (20 mg/mL) of BSA as well as the solid state exhibit the excitation-dependent emission, which is attributed to the heterogeneous clustering of functional groups. Concentrated solution or the solid state of BSA shows persistent room-temperature phosphorescence at 444 and 481 nm after ceasing the UV excitation at 312 and 365 nm. This is in sharp contrast with the low-temperature phosphorescence by Trp residues of BSA at 435 nm. The observed phosphorescence in the case of concentrated aqueous solution or solid state of BSA results from the aggregation and presence of plentiful n electrons favoring spin–orbit coupling which assists the occurrence of intersystem crossing (ISC).

6. STRETCHING-INDUCED AIE RESULTS IN POLARIZED LIGHT EMISSION

Materials emitting polarized light are drawing increasing attention as active materials for next-generation display materials having high brightness and low power consumption. Conjugated polymers or oligomers emitting polarized light are very much useful in optoelectronic applications such as in the fabrication of OLEDs. However, insolubility of conjugated polymers in most of the solvents and their insufficiency impose difficulty in their processability. Therefore, practically, alignment of conjugated polymer chains has to be made mechanically through a series of difficult steps, which is infeasible for a large-scale preparation. In this respect, nonconjugated polymers should be preferable; however, most of them lack emission properties because of their remarkable chain flexibility making the alignment of polymer chains pretty difficult. In this background, Liao et al. have recently reported a very interesting work where polarized light emission is observed from a nonconjugated polymer such as PAN.\textsuperscript{82} This polymer system shows luminescence properties because of clustering of the nitrile groups in a highly concentrated solution or in the solid state. This polymer is well soluble in different solvents; therefore, fabrication of PAN fibers is carried out via electrospinning, subsequently the electrospun PAN fibers are subjected to heat stretching keeping the temperature over the \(T_g\) of PAN to obtain remarkably aligned nanoribbons (SR-ENR) (Figure 16I). Heat-stretched electrospun fibers (SR-ENR) exhibit polarized deep blue luminescence (quantum yield, \(\Phi = 32\%\)) at \(\sim 410\) nm (\(\lambda_{\text{ex}} = 340\) nm) with an anisotropy factor of \(0.37\). In addition, they also show room-temperature green phosphorescence with a lifetime of about 200 ms (Figure 16II(a,b)) as well as delayed deep blue emission which is attributed to the triplet–triplet annihilation (noncoherent photon up-conversion). Analysis by wide-angle X-ray scattering and small-angle X-ray scattering has shown nearly uniaxial orientation of the heat-stretched electrospun fibers within the fabricated ribbons. The mechanical strength and toughness are also reported to be quite high (\(534 \pm 28\) MPa) and (\(79 \pm 7\) J/g), respectively. The observed mechanical properties probably originate from the high \(T_g\) of PAN and inter-/intrachain interactions between the highly polar nitrile groups (which are also responsible for the emissive property), probably acting as physical cross-linking sites (Figure 16I). Analysis of the emission spectra show that upon excitation with plane-polarized UV radiation at 340 nm, the PAN film or as-electrospun PAN fibers show a signal almost at the same position (394–388 nm); however, heat-stretched ENR shows a broad signal at somewhat red-shifted \(\sim 410\) nm (Figure 16II(c)). Furthermore, a remarkable effect on the emission profile is observed when excitation with a plane polarized light at 337 nm is done parallel to the long axis of SR-ENRs (having anisotropy \(r = 0.37\) and degree of polarization \(P = 0.47\)) for the emission) or perpendicular to it (Figure 16II(e)). In the former case, an anisotropy \(r = 0.37\) and degree of polarization \(P = 0.47\) are observed which are not, however, observed during similar excitation perpendicular to the long axis of SR-ENR. On the other hand, as-spun NRs do not show any dependence of the emission intensity on the position of the analyzer (Figure 16II(d)). Here, the emission occurs due to contribution from n\(\rightarrow\pi^*\) transitions from the nitrogen atoms of cyano groups in the aligned rigid state, and ISC also occurs forming highly mobile triplet states, which yield delayed fluorescence via triplet–triplet annihilation and also yield green phosphorescence. Thus, in order to obtain polarized emission in nonconjugated polymers, (i) electrospinning of the polymer into nanofibers, (ii) heat-stretching above \(T_g\) for an aligned crystal arrangement, and (iii) use of polymers having interacting functional groups in the adjacent groups forming a highly extended \pi-conjugation are indispensable.

7. APPLICATIONS

Fluorescent polymers, capable of interacting with biomolecules, are of significant interest in respect of bioimaging, drug/gene delivery or imaging-guided drug delivery, bacterial detection, explosive detection, sensor applications, and so forth (Scheme 3). However, fluorescent polymers with aromatic repeating units are not desirable in these applications as they are typically hydrophobic, nonbiodegradable, potentially carcinogenic, or toxic. On the other hand, polymers/nanoparticles doped with fluorescent organic dyes suffer from poor photostability or significantly high cytotoxicity.\textsuperscript{28,57,84} In this regard, luminescent polymers without conventional fluorophoric moieties such as aromatic or conjugated residues are superior because of their relatively better hydrophilicity, structural flexibility, biocompatibility, and biodegradability. In this respect, autofluorescent
PAMAM systems are most promising in view of their biodegradability, low cytotoxicity, and high transfection efficiency.84–86

Yang et al. have used hyperbranched polyamidoamine (HPAMAM) with mannose groups on their surface (M-HPAMAM) for efficient bacterial detection.28 The attachment of mannose moieties on the HPAMAM surface increases the fluorescence emission intensity because of molecular crowding. Furthermore, mannose moieties show strong interactions with bacteria.87 Incubation of M-HPAMAM with Escherichia coli for 30 min in PBS solution resulted in the formation of lots of visible clusters, which are perhaps formed due to the assembly of bacterial aggregates with M-HPAMAM. The fluorescence images of these aggregates under a laser confocal fluorescence microscope when excited at 800, 480, and 543 nm are given in Figure 17.

Sun et al. have demonstrated imaging-guided delivery of paclitaxel (PTX) drug through the self-assembled amphiphilic copolymer-based vehicles containing hydrophilic PEI and hydrophobic PLA.56 The hydrophobic PLA core functions as the hydrophobic PTX drug-loading center. The drug molecules have been encapsulated in the hydrophobic core of the micellar PD in aqueous medium through a modified emulsion/evaporation method. The micellar PDs have shown a broad proton-buffering ability (specifically, in the pH range 5.1−7.4), which should allow PDs to escape easily from endosomes/lysosomes prior to their delivery into the cell cytoplasm. Drug release experiments have indicated sustained release of the drug from the PD vehicle at the physiological pH 7.4. It has been observed that the growth rate of MCF-7 tumors in mice is much lower with PTX-loaded PDs than with free PTX (Figure 18c,d). In vivo images of PDs injected into mice subcutaneously and intramuscularly are presented in the figure (Figure 18c,d). The PTX-loaded PDs exhibit significantly higher antitumor activity than that of free PTX.

Tsai et al. have successfully used blue fluorescent amino-terminated PAMAM for the evaluation of gene delivery and transfection toward rat C6 glioma cell lines.88 They have used three antisense oligonucleotides (AS-ODN) p75, NGF1, and NGF2 for knocking down specific protein expressions. These oligonucleotides are attached at various N/P ratios with amine-terminated PAMAM exploiting electrostatic interactions. The fluorescent PAMAM dendrimers have shown much lower cytotoxicity than pristine PAMAM or hyperbranched PEI. Therefore, cell transfection with a higher N/P ratio could have been possible. Furthermore, intrinsic fluorescence has helped in directly analyzing the cellular uptake behavior by fluorescence microscopy and flow cytometry. Apart from these, several applications of non-conventional fluorescent polymers have been reported in cell imaging or detection of ionic surfactants.57,58,89

Relatively poor degree of conjugation between the subfluorophoric groups in nonconjugated polymers compared to the conventional fluorophoric systems results in blue light emission. This problem may, however, be alleviated by increasing the subfluorophoric electronic conjugation via increasing the polymer chain flexibility. In this regard, Shang et al. have synthesized PIVP and PIVC copolymers (discussed above), which exhibit concentration-dependent fluorescence, from blue to orange with increasing polymer concentration. Furthermore, they exhibit excitation-dependent emission and emit dark red light on excitation with red light, but in the solid state, they emit white light under 365 nm radiation.60 Zhao et al. have shown very interesting applications of their synthesized polyether molecules in explosive detection.72 The concentrated solution of polythioether in DMF (50 mg/mL) has shown quenching in the fluorescence emission intensity of the signal at 435 nm upon addition of electron-deficient picric acid (PA) (an explosive) because of the excitonic transfer from the polymer to PA. A detectable extent of PL intensity decay is observed upon addition of 3.71 ppm PA, which subsequently shows a gradual decrease upon incremental addition of PA. Finally, no detectable PL intensity is observed when 30.59 ppm PA is added. The relevant emission signal with incremental addition of PA and the corresponding Stern−Volmer plot are presented in Figure 19A,B. The unique PL properties of solid BSA, as demonstrated by Yuan and co-workers73 make it potential for useful applications in optoelectronics. The artwork painted on a filter paper by solid BSA becomes prominent upon UV irradiation.

Scheme 3. Various Applications of Nonconventional Fluorescent Polymer Systems

Figure 17. Laser confocal fluorescence microscopy images of E. coli strain at OD1.0 with M-HPAMAMs at excitation wavelengths of 800 (a), 488 (b), and 543 nm (c). (Reproduced with permission from Biomacromolecules 2010, 11, 1840, copyright ACS, 2010.)
irradiation has ceased when protected by a polymer. Plots of polymers having discrete chromophores or auxochromophores in a polymer matrix show that the AIE of such systems can be very strong. In summary, here we have discussed the rapid growth of AIE of non-linear polymer systems containing subfluorophores of various types of architectures: (i) dendrimers or hyperbranched polymers, (ii) entraped polymeric micellar self-assembly, (iii) cluster formation, and (iv) stretching-induced aggregation, are discussed. In architecture (i), the first example is hydroxy-terminated polyamidoamine (PAMAM) dendrimers (G4-OH, G2-OH, or even G0-OH) exhibiting emission upon oxidation of terminal hydroxyl groups; however, some other works indicate that oxidation of tertiary amine (R3N) moieties present inside the dendrimers to N-oxy radicals (R3N-O2) is the principal reason. The rigidity of dendrimers causes the suppression of nonradiative deactivation pathway of excitons causing fluorescence. In architecture (ii), the amphiphilic polymer polyetheramide (PEI) in the micellar aggregate or triblock copolymer PLA-PEI-PLA exhibits fluorescence due to aggregation-induced rigidity resulting in emission. In the zwitterionic graft copolymer (PVDMS), multivesicular aggregates are produced showing a strong blue fluorescence due to the electronic transition between the HOMO over the phenyl ring or from a similar nonemissive or weakly emissive aromatic chromophore; a good example of this type is poly[(N-isopropyl acrylamide, NIPAM)-b-oligoethylene glycol acrylate (OEGA)] synthesized using poly(trithiocarbonate) (PTTC)-mediated RAFT polymerization showing much strong emission. PAN in DMF or DMSO or even in the solid state shows more intense emission because of the clustering of nitrile (–CN) groups in PAN in DMF or DMSO or even in the solid state shows more intense emission because of the clustering of nitrile (–CN) groups in the highly entangled PAN chains. The dilute solution of BSA does not exhibit any fluorescence, but at higher BSA concentrations (20 mg/mL), very strong emission is observed due to triplet quenching. This makes solid BSA powder promising for application in anti-counterfeiting or as an O2 sensor.

8. SUMMARY AND FUTURE SCOPE

In summary, here we have discussed the rapid growth of AIE of polymers having discrete chromophores or auxochromophores termed "subfluorophores," originating from "space conjugation" via co-operative intramolecular or intermolecular aggregation. Herein, the main focus is given to nonconjugated nonfluorescent polymers that self-assemble/aggregate in moderately concentrated solutions and also in solid state. A brief history of the genesis of PL of subfluorophores from the aggregation of propeller-shaped small organic molecules is discussed with 1-methyl-1,2,3,4,5-pentamethylsilole, which is very poorly emissive in dilute EtOH solution, but on adding water, a significant hike in the fluorescence emission and quantum yield (Φ) is noted because of the intermolecular aggregate formation arresting vibrorotational motions and hence enhancing the emission. Then, the AIE of polymeric systems containing subfluorophores of four types of architectures, for example, (i) dendrimers or hyperbranched polymers, (ii) entraped polymeric micellar self-assembly, (iii) cluster formation, and (iv) stretching-induced aggregation, are discussed. In architecture (i), the first example is hydroxy-terminated polyamidoamine (PAMAM) dendrimers (G4-OH, G2-OH, or even G0-OH) exhibiting emission upon oxidation of terminal hydroxyl groups; however, some other works indicate that oxidation of tertiary amine (R3N) moieties present inside the dendrimers to N-oxy radicals (R3N-O2) is the principal reason. The rigidity of dendrimers causes the suppression of nonradiative deactivation pathway of excitons causing fluorescence. In architecture (ii), the amphiphilic polymer polyetheramide (PEI) in the micellar aggregate or triblock copolymer PLA-PEI-PLA exhibits fluorescence due to aggregation-induced rigidity resulting in emission. In the zwitterionic graft copolymer (PVDMS), multivesicular aggregates are produced showing a strong blue fluorescence due to the electronic transition between the LUMO on quaternary ammonium groups and the HOMO over sulfonate groups. In architecture (iii), the π-π chromophoric subfluorophores forming clusters between carbonyl groups or phenyl/carbonyl groups restrict the vibrorotational motion and reduces the nonradiative relaxation resulting in an increased fluorescence quantum yield. Such examples are oligo(maleic anhydride) (OMAh), which forms clusters with carbonyl groups of succinic acid (SA), a random copolymer of maleic anhydride (MAh) and vinyl acetate (PMV), where the π–π interaction leads to the formation of emissive carbonyl clusters. Also, emissive clustering is generated between carbonyl groups and the phenyl ring or from a similar nonemissive or weakly emissive aromatic chromophore; a good example of this type is poly[(N-isopropyl acrylamide, NIPAM)-b-oligoethylene glycol acrylate (OEGA)] synthesized using poly(trithiocarbonate) (PTTC)-mediated RAFT polymerization showing much strong emission. PAN in DMF or DMSO or even in the solid state shows more intense emission because of the clustering of nitrile (–CN) groups in the highly entangled PAN chains. The dilute solution of BSA does not exhibit any fluorescence, but at higher BSA concentrations (20 mg/mL), very strong emission is observed at 442 nm (λem = 365 nm), which is attributed to the entanglement of BSA chains at higher concentrations, where in...
the aggregated state, clustering occurs between C==O and N–H/O–H groups through their n and π electrons. These additional H-bonding interactions within the nonconjugated backbone of peptide chains provide rigidity to the BSA molecular conformations, which is responsible for such emissions. In type (iv), stretching-induced aggregation emitting polarized light is discussed with ENRs when subjected to heat stretching over the $T_d$ of PAN yield remarkably aligned nanoribbons (SR-ENR) which emit polarized deep blue luminescence (quantum yield, $\Phi = 32\%$) at $\lambda_{em} = 340\ nm$ with an anisotropy factor of 0.37. Additionally, they also show room-temperature green phosphorescence with a lifetime of about 200 ms. The mechanism of different types of aggregation-induced fluorescence has also been discussed by some workers from the theoretical calculations of energy bands in the aggregated state. Most important applications of induced fluorescence in nonfluorescent polymers are discussed; for example, detection of E. coli bacteria in vitro bioimaging-guided drug delivery, gene delivery, oxygen sensor, explosive sensor, white light emission, and so forth.

Like small molecules, photoluminescent polymers can offer a plethora of applications in optoelectronics, fluorescent bioprobes, molecular imaging, photodynamic therapies, OLEDs, storage data security, encryption, anticounterfeiting materials, coating illuminants, displays, and so forth. In this regard, the polymeric fluorescent materials have drawn significant attention because of their amplified signal response even after a minute perturbation because of co-operative conformational effects of its chain segments. This is also beneficial from their excellent viscoelastic and mechanical properties helping in the fabrication of devices and external applications, respectively. Thus, there is an immense importance of aggregation-induced fluorescence in nonfluorescent polymers, mainly for sensing, OLED, and biological applications, and further work can be initiated aiming at targeted applications such as the sensing of surfactants, bacteria, viruses, proteins, nucleic acids; biotechnological applications such as cell imaging, drug delivery, gene delivery, and so forth. Stretching-induced and thermally treated aggregation of polymers emit polarized light which is very important as active materials for next-generation display materials having high brightness and fabrication of OLEDs. Attempts should be made to increase the quantum yield by changing the environmental and physical conditions of these systems. These future works would be very important as the nonaromatic polymers are less toxic and biocompatible, and in some cases, they are biodegradable. Further scope also remains from the technology viewpoint, for example, fabrication of OLEDs, storage data security, anticounterfeiting materials, coating illuminants, displays, and so forth. Besides, on the theoretical side, the mechanism of the origin of fluorescence in the subfluorophores is not yet fully exploited as the influence of substituents, molecular weight, and polydispersity of polymers is the key factor governing the self-assembly, and hence the fluorescence property of the systems. In a word, there is an immense scope for future work in this important new field of inducing fluorescence in nonfluorescent polymers both from academic and technology viewpoints because there are plenty of nonfluorescent polymers with a myriad of properties, which can promote many targeted applications.

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Notes

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