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## REVIEW

# Luminescent Polymers and Blends with Hydrogen Bond Interactions

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Organic luminogens with aggregation-induced emission (AIE) properties have unusual emission behaviour in respect that their non- or weakly- emissive solutions can be tuned to emit strongly in the solution aggregated and solid states. As restricted molecular rotation of luminogens is the main mechanism leading to AIE activity, hydrogen bond (H bond) interactions are therefore used in organic and polymeric luminogens to impose efficient rotational restriction and to intensify the emission intensity of the AIE-active luminogens. Luminescent polymers, containing H-bonding groups and luminescent blends, consisting of H-bond donors and acceptors, are therefore described in this review to evaluate the relationship between H bond interactions, rotational restriction and AIE-related emission intensity.

## Introduction

Traditional luminogens with disk-like, planar geometry (e.g. pyrene)<sup>1,2</sup> often experience strong  $\pi$ - $\pi$  interactions among the neighbouring molecules in the concentrated solution and solid states and upon photo-irradiation, the excited states of the aggregates therefore decay via non-radiative pathways, resulting in substantial weakening of the emission. This aggregation-caused quenching (ACQ)<sup>3-5</sup> in the condensed phase is notorious and limits the solid-state applications of the traditional luminogens. In contrast to ACQ, a series of non-coplanar luminogens were found to be non-luminescent in the solution state but highly emissive in the aggregated state. The aggregation-induced and -enhanced emission (AIE and AEE)<sup>6-11</sup> properties have been found in many organic and polymeric luminogens and have attracted intensive research interests due to the beneficial emission efficiency in the solid state.

Although an AIE process may mechanistically be associated with pathways like J-aggregate formation (JAF),<sup>2</sup> twisted intramolecular charge transfer (TICT),<sup>11-13</sup> and excited-state intramolecular proton transfer (ESIPT),<sup>14</sup> the intrinsic mechanism is actually due to the effective restriction on the intramolecular motions of the AIE-active luminogens. Study<sup>15</sup> on AIE-active luminogens of different molecular



Shih-Hung Huang

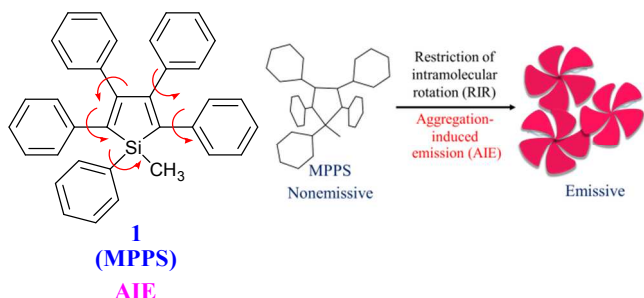
Shih-Hung Huang received his B.S. degree from Feng Chia University in 2012 before he joined the graduate program in the Department of Materials and Optoelectronic Science, National Sun Yat-Sen University at Kaohsiung. Currently, he is a Ph.D. candidate under the supervision of Prof. Y.-W. Chiang. His research interest at the present time is focused on the self-assembly of block copolymers in association with polymer photonic crystals, polymer crystallization and photoluminescent properties of fluorescence polymers.



Yeo-Wan Chiang

Yeo-Wan Chiang studied Polymer Science in the Department of Chemical Engineering, Chung-Hsing University in 1999. In 2004, he moved to National Synchrotron Light Source, Brookhaven National Laboratory and Department of Chemistry, Stony Brook University to study the synchrotron radiation in the characterization of polymer science. In 2007, he moved to Department of Material Science and Engineering, Massachusetts Institute of Technology in Cambridge (USA), as a visiting scientist in Pro. Edwin L. Thomas's group. He received his Ph.D. degree from the Department of Chemical Engineering, Tsing Hua University (Taiwan) under the supervision of Prof. R.-M. Ho in 2008. In 2010, he took a faculty position in the Department of Materials and Optoelectronic Science, National Sun Yat-Sen University (Taiwan) as an assistant professor. His current research focused on nanomaterials from self-assembly of block copolymers and supramolecules, polymer photonic crystals, crystallization of crystalline block copolymers and photoluminescent stereoregular polymers.

shapes has concluded that the restriction of intramolecular rotations and vibrations (RIR and RIV) are the main causes for the AIE phenomena observed in the propeller-shaped and shell-like luminogens, respectively. Most of the AIE-active luminogens are propeller-like molecules, so is the first discovered AIE-active molecule of 1-methyl-1,2,3,4,5-pentaphenylsilole (**1**, MPPS, Fig. 1).<sup>16,17</sup>



**Fig. 1** Chemical structure of first-discovered AIE luminogen of MPPS and the restriction of intramolecular rotation (RIR) involved in MPPS. Adapted from Ref. [16]

As similar to most of the propeller-like luminogens, MPPS is highly-emissive in the solution aggregated state and is non-luminescent in the dilute solution state. It is considered that the rotation- and vibration-coupled molecular interactions between **1** and solvent molecules prevail in the dilute solution state, resulting in nonradiative decay of the excited species and the final non-luminescence. The free molecular motion in the mobile solution state can however be hampered in the concentrated state; by dispersed in the solution aggregated state, the molecular rotations of the non-coplanar molecule **1** can be efficiently frozen by the constraints imposed by the crowded environment and the corresponding RIR process in the aggregated state reduces the possibility of non-radiative decay pathways and therefore, activates the radiative process to result in strong emission.



**Jin-Long Hong**

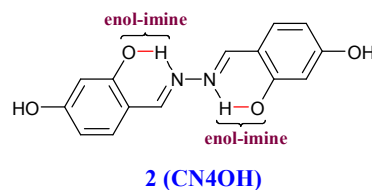
Jin-Long Hong completed a Ph.D in Polymer Chemistry at the University of Massachusetts, Amherst, and served as postdoctoral fellow at the Institute of Materials Science, University of Connecticut, Storrs, before joining National Sun Yat-Sen University, Kaohsiung as an associate professor. Currently, he is a full professor at department of Materials and Optoelectronic Science. His main research interests range from the synthesis

of organic and macromolecular systems, liquid crystals and liquid crystalline polymers, anode and cathode materials for lithium-ion battery, curing kinetics of polycyanurates, design and synthesis of conjugated polymers with conductivity, preparation and characterization of polymer blends as well as synthesis and characterization of luminogenic materials with aggregation-induced and -enhanced properties.

Emission responses<sup>18</sup> toward cooling, pressure and viscous matrix also indicate that RIR<sup>19,20</sup> is indeed the main mechanism controlling the AIE and AEE properties.

Since molecular rotations of organic luminogens can be controlled internally or externally, several chemical and physical methods were therefore attempted previously, with the purpose to hamper molecular rotation and to achieve the goal of enhance AIE-related emission. Internally, chemically-linked bulky substituents<sup>21-26</sup> should inherently raise the rotation energy barrier of the single bonds in the propeller-like molecules, leading to the desired AIE-activity. Externally, molecular rotation of the luminogens should be strongly affected by the surrounding environment; for example, molecular rotation of the luminogens in viscous polymer matrix is considerably hampered and the corresponding emissions should be largely enhanced compared to when they are in the mobile solution state.

Hydrogen bonds (H bonds)<sup>27</sup> can be used to help formation of self-assembled structures in organic molecules and polymers. Unlike the isotropic electrostatic interaction forces, H bonds are oriented dependent on the direction of the paired interaction and molecules physically connected by H bonds can be treated as a structural assembly in which the rotation of the constituent molecules can be efficiently locked. Among them, intramolecular H bond interactions are internal forces constantly practiced in building effective rotational restriction required for the AIE-active materials. In respect to intramolecular H bond interaction, the salicylideneazine derivative of **2** (CN4OH, Fig. 2), containing two six-membered enolimine rings bridged by intramolecular H bonds, is the most widely studied system. The C=N isomerization in the excited state is considered to be the predominant decay pathway for imine dyes with unbridged C=N bond but for the bridged CN4OH, decay of its excited state actually involves an excited-state intramolecular proton transfer (ESIPT)<sup>6,33-39</sup> process. Upon photoexcitation, fast transfer of hydroxyl proton to imine nitrogen quickly converts the excited enol (E\*) into the excited keto (K\*), giving rise to emission band with large Stoke shift. When in the solution state, luminogen **2**<sup>30</sup> (CN4OH) emits weakly due to the efficient radiativeless decay process of the twisted ketonic excited state; in the aggregated state, a planar dimer structure, with the molecular rotations of the two aromatic rings effectively locked by the intramolecular H bonds in the enolimine rings, results in strong AEE-related emission.

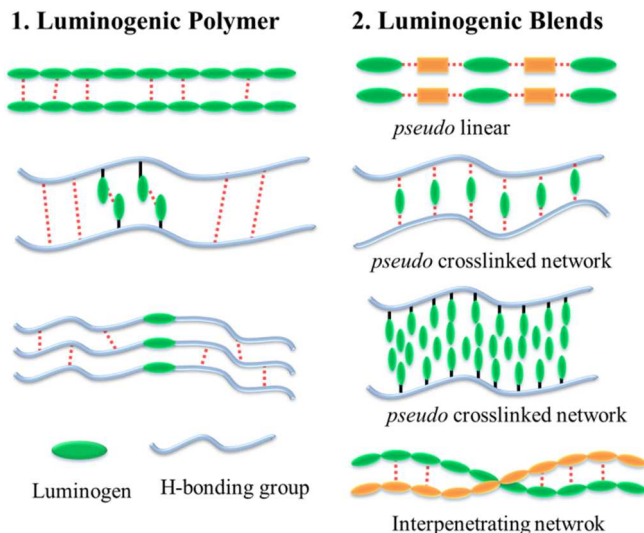


**Fig. 2** A salicylideneazine derivative of **2** (CN4OH) containing two six-membered enolimine rings. (Reprinted with permission from Ref. [30]. Copyright 2009, American Chemical Society.)

A large salicylideneaniline-based molecule<sup>40</sup> with the same enolimine ring is also an AEE-active luminogen. In addition, organogelators containing hydrazine (12b)<sup>41</sup>, benzoxazole (12c)<sup>42</sup>, acrylamido<sup>43</sup>, and naphthalide<sup>44</sup> moieties were also reported to be AEE-active materials due to the rotational restriction imposed by the inherent intramolecular H bond

interactions. Theoretically, the intramolecular H bond interactions preferentially lock the molecular conformations and the resulting RIR of the rigid conformers contributes to the high emission of the organogelators.

Besides intramolecular H bonds mentioned above, intermolecular H bond interactions involving several molecular species are other resources available for the purpose of imposing rotational restriction required for AIE system and are therefore the main focus of this review.



**Fig. 3** Intermolecular H bond interactions involved in (1) polymers with multiple or single luminogenic unit and (2) luminogens blends containing H bond donors and acceptors.

As illustrated in Fig. 3, the intermolecular H bond interactions existing in luminogenic polymers and luminogenic blends can be briefly illustrated below. 1) Luminogenic polymers may contain single or multiple luminogenic units connecting by H-bonding groups (such as amine, amide and hydroxyl groups etc.). The intermolecular H bond interactions among the multiple H-bonding sites provide efficient rotational restriction on the luminogenic units in the polymer chains, thereby, the luminogenic units are supposed to emit strongly with efficient RIR process. Besides the beneficial intermolecular H bond interactions, chain conformation of the copolymers containing hydrophobic and hydrophilic segments is also affected by the H-bonding interactions; that is, the hydrophobic luminogens may associate together to form aggregated phase separated from the hydrophilic H-bonding segments. Surrounding environment will affect the extent of aggregation and the molecular motion of the hydrophobic luminogens in the aggregated phase. High extent of aggregation leads to efficient rotational restriction and the enhanced emission of the aggregated luminogenic units. 2) For the blend system, two components with the respective H-bond donating and accepting groups are required. Therefore, organic or polymeric luminogens containing H-bond donating and accepting groups are used to inter-react with each other through the facile H bond interactions, to result in molecular architectures such as *pseudo* linear, *pseudo* crosslinked network and interpenetrating network. Molecular rotation of the luminogenic units in the vast entities of the assembled *pseudo* structures is supposed to be effectively restricted to

and strong emission of the H-bonded blends is therefore expected.

Above systems illustrate the generation of new AIE systems by intermolecular H bond interactions. Several examples already disclosed will be given and various factors, from chemical structure and environment (e.g. solvent, temperature), controlling the H bond interactions, the restricted molecular rotation and therefore the AIE-related emission behaviour will be illustrated case by case below.

### 1. Polymers with multiple or single luminogenic units

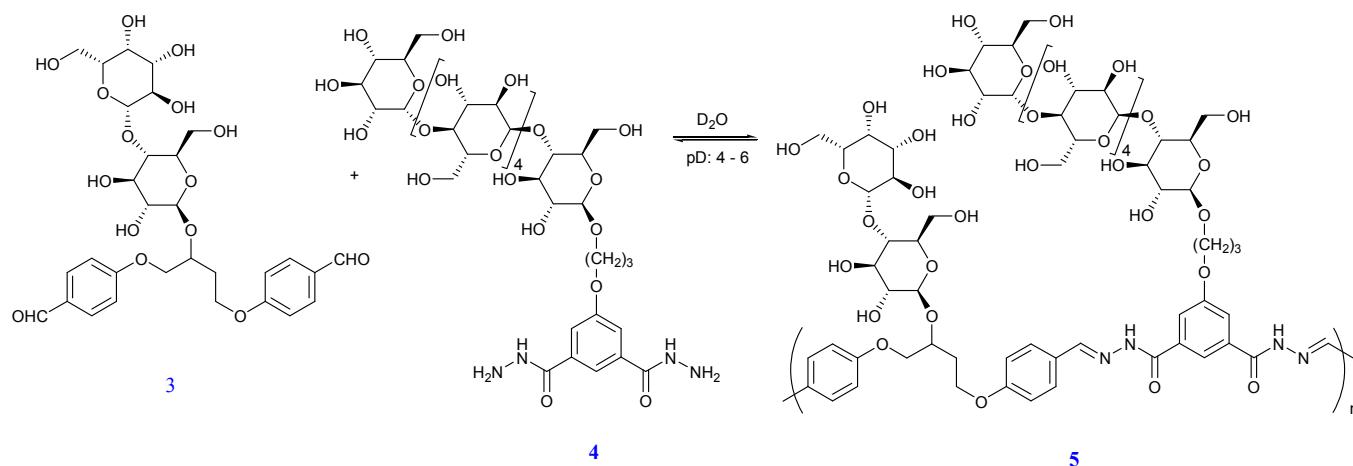
For polymers containing H-bonding groups, the molecular motions of the luminogenic units are effectively restricted by the long, viscous polymer chain and the multiple H-bonding sites and the emission properties of the luminogenic units are correlated to the self-assembled structures formed in different solvents. The resulting AIE-related emission is strongly affected by the rotational restriction of the aggregated segments in the assembled structures and several examples given below thereby illustrate it.

Constitutional dynamic chemistry (CDC)<sup>45</sup> involves the implementation of reversible chemical connections of either a covalent or non-covalent nature to link the components of a molecular or supramolecular entity. As a consequence, continuous modification of the constitutional dynamic entities is possible through assembly/disassembly of their building blocks<sup>46-49</sup>. In materials science, the interconvertible building process can generate dynamic polymers (dynamers) from the reversible connection of monomers through covalent or noncovalent linkages.<sup>50-59</sup> Lehn and co-workers therefore extended the dynamer research to biopolymers containing oligosaccharide residues.<sup>60,61</sup> By polycondensation of oligosaccharide-containing aromatic dialdehyde **3** and bishydrozide **4** (Fig. 4), a high Mw glycodynamer **5** with a  $M_n$  of 511,000 was prepared and was found to be soluble in water due to extensive H bond interaction between the oligosaccharide and water.

Despite the starting monomers **3** and **4** are non-luminescent in D<sub>2</sub>O, the resulting glycodynamer **5** are highly luminescent due to the restricted molecular rotation of the fluorescent hydrazine units in the polymer. By linking to the large oligosaccharide side chains, the fluorescent hydrazine units are rather clumsy in rotational motion, rendering in the observed high luminescence. The same polycondensation was also applied to different monomers and all the resulting glycodynamers are good emitters with strong emissive light from blue to red dependent on the monomer counterparts and this result illustrates the dynamic equilibrium nature of the glycodynamer constituent.

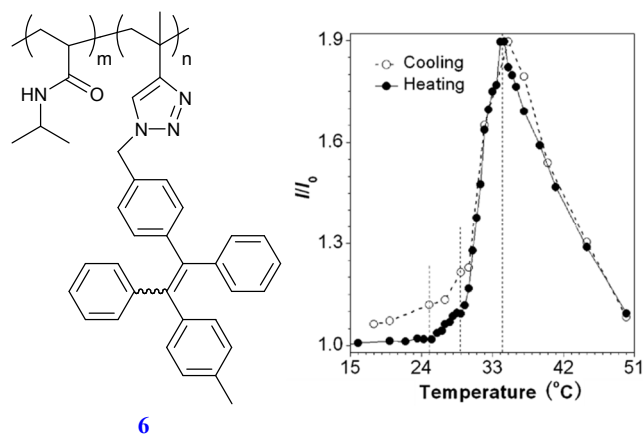
Thermoresponsive water-soluble poly(*N*-isopropylacrylamide) (PNIPAM) in water displays a lower critical solution temperature (LCST)<sup>62-78</sup> and some possible models have been portrayed to account for the coil-to-globule collapse of PNIPAM in water. This temperature-driven conformational transformation of the single PNIPAM chain and the following macroscopic phase separation reflect rather subtle changes in polymer/water H-bonded interactions. At temperature below LCST, the facile H bond interaction between the amide groups of PNIPAM and water makes the homogeneous dispersion of the polymer in water; however, dissociation of H bonds occurs when heated to the LCST around 32 °C, polymer chains results in conformational transformation from hydrated coil to dehydrated globule.





**Fig. 4** Preparation of glycodynamer **5** from polycondensation of dialdehyde **3** and bishydrozide **4**. (Reprinted with permission from Ref. [61]. Copyright 2010, American Chemical Society.)

Based on PNIPAM polymer, Tang and coworkers<sup>79</sup> developed a fluorescent thermometer labelled with AIE-active luminogens of tetraphenylethene (TPE) (Fig. 5). A representative PNIPAM polymer of **6** containing 0.27% TPE unit was demonstrated to be AIE-active by the solution emission behavior in THF/water mixture.

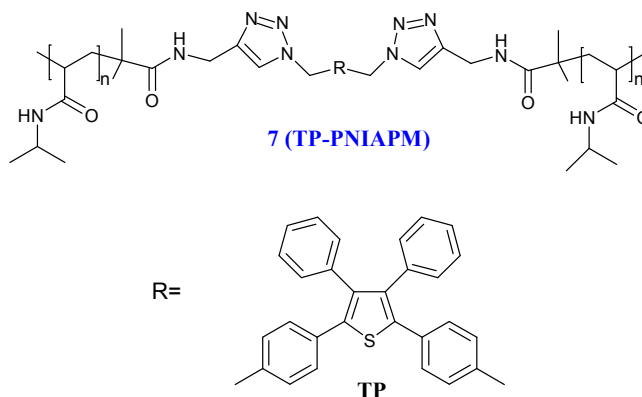


**Fig. 5** A TPE-labelled PNIPAM **6** (left) and variation of solution emission intensity at different temperatures (right). Adapted from Ref. [79]

In pure water, polymer **6** shows interesting emission response toward heating. The aqueous solution of **6** shows a major emission jump from 29 to 34.2 °C but further heating leads to a gradual decrease in the luminescence intensity. At temperature lower than 25 °C, the hydrophobic TPE labels may have been loosely encompassed by the polymer coils or aggregated into tiny particles, within which the motions of the phenyl rings are effectively restricted, making the polymer luminescent. Heating at the temperature region of 29–34 °C weakens the intermolecular H bond interactions to water and therefore, polymer chains start to dehydrate, forming compact aggregates with high emission intensity. At temperatures above 34 °C, the compact aggregates may associate with each other into big aggregate and within it, the TPE labels may have been isolated from each other by the PNIPAM chains,

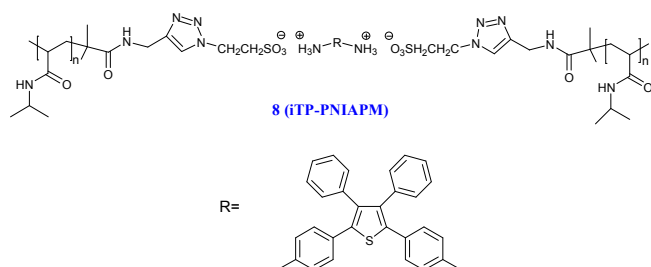
resulting in the emission quenching due to the loss of aggregated structures. Meanwhile, the elevated temperature may activate the motions of the phenyl rings. These two effects collectively make the system less emissive.

The temperature-driven conformational transformation and phase separation behavior also reflects in the PNIPAM polymer **7**<sup>80</sup> with an AIE-active tetraphenylthiophene (TP) label (Fig. 6). In water, polymer **7** self-assembles into core-shell micelles containing the hydrophilic PNIPAM shell, interacting with surrounding water molecules through intermolecular H bond interactions, and the hydrophobic TP core encompassed by the polymeric segments of the PNIPAM outer shell. Below LCST, molecular rotation of the aggregated TP units is effectively restricted in the compact core and the aqueous solution of **7** therefore emits strongly; however, heating dissociates the H bond interactions between PNIPAM segments and water and the collapsed micelles further coalesce to form macroscopic aggregates at temperature higher than LCST. Inside the macroscopic aggregates, the fluorescent TP units are all isolated by the retracted PNIPAM chains and are therefore non-luminescent due to the loss of aggregated structure. The emission quenching of polymer **7** at high temperature can therefore be used to locate LCST.



**Fig. 6** Chemical structure of polymer **7** (TP-PNIPAM) with an AIE-active tetraphenylthiophene (TP) center. (Reproduced with permission from Ref. [80]. Copyright 2011, American Chemical Society.)

Instead of covalent bond used in polymer **7**, the luminogenic TP unit can also bind to PNIPAM chain by ionic bond as illustrated in the ionic complex **8** (iTP-PNIPAM).<sup>81,82</sup> Complex **8** was prepared from the acid-base reaction between a cationic ammonium-functionalized TP and an anionic sulfate terminal of PNIPAM chain. In water, polymer **8** forms micelles with the architecture that the interior TP core is surrounded by the outer PNIPAM shell through the ionic ammonium sulfonate bonds. Here, the ionic bonds connecting the TP core and the PNIPAM shell are sensitive to acid, base and metal ions. Under the reaction of the externally-added acid, base and metal ions, the ammonium sulfonate bonds will dissociate, resulting in the rupture of the micelles<sup>82</sup> and the emission quenching due to the precipitation of the hydrophobic TP molecules from the water matrix.



**Fig. 7** Chemical structure of ionic polymer **8** (iTP-PNIPAM). (Reproduced with permission from Ref. [82]. Copyright 2012, American Chemical Society.)

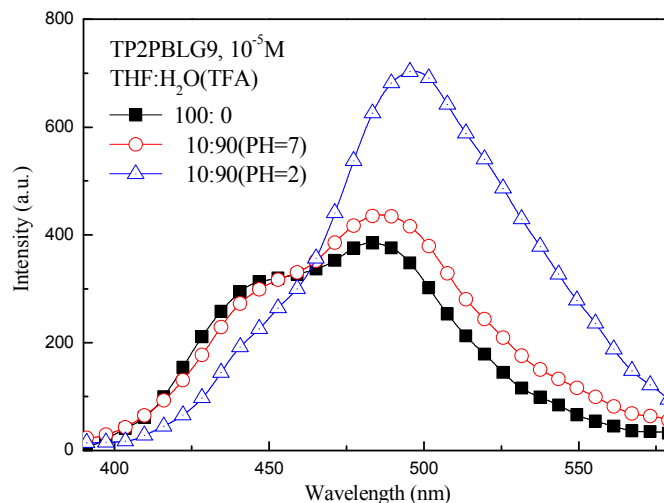
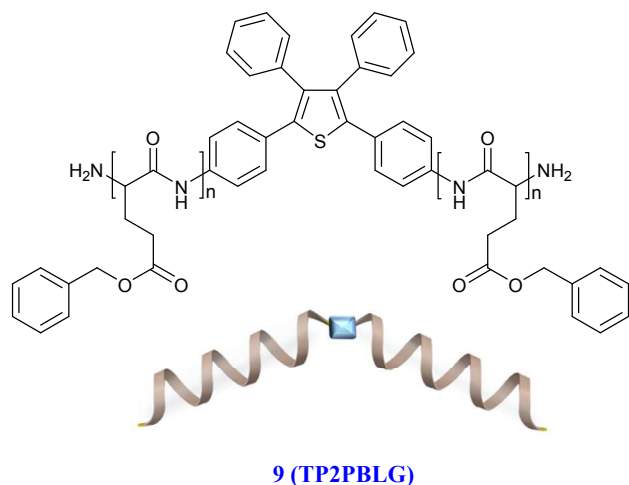
Emission responses of polymer **8** (iTP-PNIPAM) toward concentration and temperature can be used to probe the critical micelles concentration (CMC) and LCST, respectively. When concentration of polymer **8** in water is low, the aqueous solution of iTP-PNIPAM is non-emissive due to the failure in forming micelles with aggregated TP core. With increasing concentration to approach CMC, chains start to self-assemble into emissive micelles with the aggregated TP core. Micelles formed at this stage can be further heated to locate LCST; however, in contrast to the emission quenching observed in the covalently-bonded polymer **7** (TP-PNIPAM, Fig. 6), emission of the ionic **8** was further intensified at temperature above LCST. The peculiar emission enhancement at high temperature can be attributed to the ammonium sulfonate bonds, as the ionic insulation layer in between the TP2NH<sub>3</sub><sup>+</sup> core and the PNIPAM shell, and the involving long-range electrostatic stabilization forces. It is suggested that the strong electrostatic interactions still persist at high temperature and function to keep the aggregated TP2NH<sub>3</sub><sup>+</sup> phase remained intact and isolated from the PNIPAM chains. During the coil-to-globule collapse process, the PNIPAM chains contracted to considerably compact the phase-separated TP2NH<sub>3</sub><sup>+</sup> aggregates, resulting in further emission enhancement at high temperatures. The varied emission responses between polymers **7** and **8** therefore reside on the nature of linking groups (covalent or ionic) connecting the luminescent core and the PNIPAM shell.

Study on synthetic polypeptides such as poly( $\gamma$ -benzyl-L-glutamate) (PBLG)<sup>83-89</sup> provides information regarding the fundamental secondary structures such as  $\alpha$ -helical rod, which can be considered as structure stabilized through

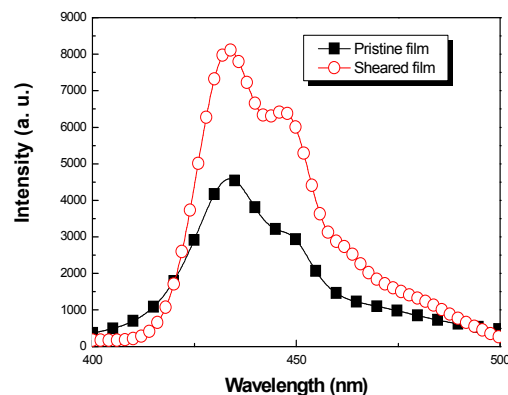
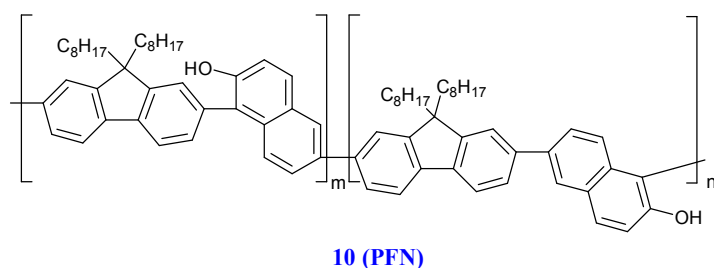
intramolecular H bonds, and  $\beta$ -sheet stabilized by intermolecular H-bonds and the random coil of the peptide chains. Conformation and aggregation structures of PBLG can be varied by external factors, for example, the rigid  $\alpha$ -helical conformation of PBLG<sup>92-94</sup> is the predominant form existing in N,N-dimethylformamide or *m*-cresol whereas random-coil conformation is the major form when PBLG is dissolved in dichloroacetic and trifluoroacetic acid. This results illustrate the transformation of intra and intermolecular H bonding modes by the surrounding solvent media. Previously, fluorescence spectroscopy had been shown to be a powerful tool for detecting peptide conformation and by connecting traditional fluorescent probes<sup>95-97</sup> to PBLG, conformation of polypeptides can be evaluated by the corresponding emission behavior, for example, the emission spectrum of a pyrene-based PBLG block copolymer<sup>96</sup> contains no excimer emission, which indicates the pyrene groups in the copolymer are separated from each other in the self-assembled structure.

Instead of using traditional planar luminogens, the AIE-active luminogen of tetraphenylthiophene (TP) was used as probe for PBLG and the emission behavior of the resulting polypeptide **9** (TP2PBLG, Fig. 8)<sup>98</sup> is correlated with the peptide chain conformation. It is envisaged that intermolecular aggregation of the central TP unit in the disubstituted TP2PBLG is sterically blocked by the large  $\alpha$ -helical PBLG chains, leading to weak emission of the aggregated solution. The strong intramolecular H bonds involved in the  $\alpha$ -helical chains of TP2PBLG, however, can be ruptured by the externally-added triflic acid (TFA) and the corresponding helix-to-coil transformation induced by the acidic TFA results in the enhanced emission. Suggestively, the TP centers connected to the flexible coil-like chains can be easily approached by each other and the feasible intermolecular aggregation leads to the enhanced emission of the acidic TP2PBLG solution. The helix-to-coil transformation induced by TFA also refers to the conversion of the H-bonding pattern from the intra to the intermolecular manner; therefore, this study illustrated the important role of H bond interactions on the AEE-related emission behavior. Compared to the neutral solution, the acidic TFA solution emits at longer wavelengths, presumably due to the formation of more coplanar TP unit in the coil chain segments.

The hydroxyl groups also provide enriched sources for generating the desired H bonding interactions as illustrated in the luminogenic polymer of PFN (**10**, Fig. 9).<sup>99</sup> For PFN, the intermolecular H bond interactions among the inherent hydroxyl groups of the naphthol units impose effective restrictions on the molecular rotations of the neighboring fluorene rings, and this effective rotational restriction is responsible for the strong emission of polymer **10** in the concentrated solution and solid film states. The emissive behavior of the solid films deserves more discussion since the solid films cast from different procedures show varied emission behavior. When unidirectional shearing force was applied during the solution-casting step, the resulting film emits with intensity higher than film without shearing. External shearing is supposed to align the polymer chains, resulting in more intimately-packed chains with the chain mobility effectively frozen by the prevalent intermolecular H bonds among the aligned polymer segments. The enhanced H bond interactions therefore contributed to the enhanced emission of the sheared film.



**Fig. 8** Polypeptide **9** with an AIE-active TP center (left) and its solution emission spectra with and without the presence of TFA. Adapted from Ref. [98]



**Fig. 9** Alternative copolymer of poly(fluorene-*alt*-naphthol) (**10**, PFN) (left) and the solid state emission spectra of the pristine and the sheared films (right). (Reprinted with permission from Ref. [99]. Copyright 2011, American Chemical Society.)

## 2. Blends containing H-bond donating and accepting components

The H-bond donating (or accepting) groups can be chemically linked to AIE-active molecules to generate functionalized luminogens. These functionalized luminogens were then blended with either monomers or polymers containing the opposite H-bond accepting (or donating) groups to prepare AIE-active blend systems with preferable intermolecular H bond interactions among the H-bonding groups of the opposite characters. With the intermolecular H bond interactions, physical blends with the hypothetical *pseudo* linear, *pseudo* crosslinked network or interpenetrating network structures can be conveniently prepared and characterized. The luminogenic units inside the *pseudo* structures are supposed to be clumsy in rotation due to mobility restriction imposed by the neighboring H-bonded molecules inside the vast entities of the *pseudo* structure. The relationship between H bond interactions and the restricted molecular rotations in the blends are therefore illustrated in the following examples.

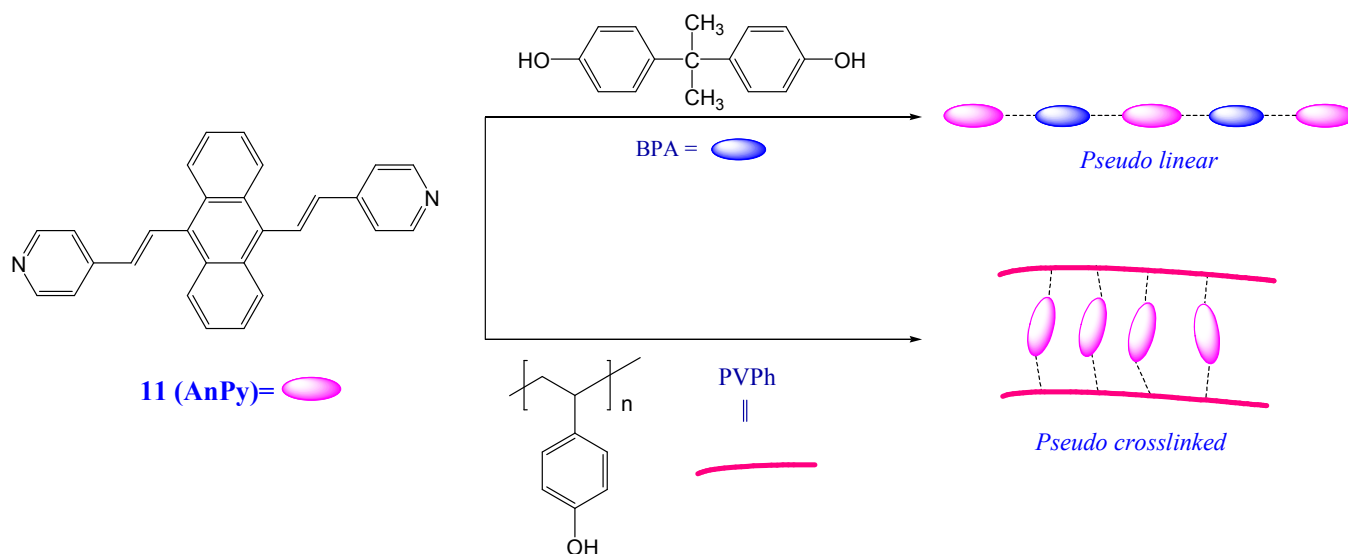
An AIE-active luminogen of **11** (An2Py, Fig. 10)<sup>100</sup> was prepared and blended with organic bisphenol A (BPA) and polymeric poly(vinyl phenol) (PVPh) to prepare the *pseudo* linear An2Py/BPA and the *pseudo* crosslinked An2Py/PVPh blends, respectively. As the H-bond accepting groups, the two pyridine rings of An2Py can readily H-bond to the donating

hydroxyl groups in BPA and PVPh, resulting in homogeneous blends of different compositions. Molecular rotations of An2Py are efficiently restricted in the H-bonded blend systems and the resulting solid blends, with less content of luminescent An2Pys, are all higher in emission than the pure An2Py itself. The WAXD spectra of the selected An2Py/BPA blends show the presence of new crystalline diffraction peaks at positions essentially different from those in the spectra of pure An2Py and BPA. New crystalline structure should form in the An2Py/BPA blends and the results from the emission spectra indicate that increasing BPA content enhances the crystallinity and the corresponding emission intensity of the An2Py/BPA blends. The coherent response between crystallinity and emission intensity indicate the interesting crystallinity-enhanced emission (CEE)<sup>101-106</sup> behavior. Suggestively, crystalline lattices contain less defects and molecular voids and molecular motions of the luminogens in the intimately-packed crystalline lattices are considered to be sluggish, resulting in the enhanced emission of the An2Py/BPA blends. The *pseudo* crosslinked AnPy/PVPh blends are also crystalline materials for the blends with lower PVPh content but increasing PVPhs in the blends results in the loss of the crystalline structure. Therefore, we may not give conclusion for the AnPy/PVPh blends.

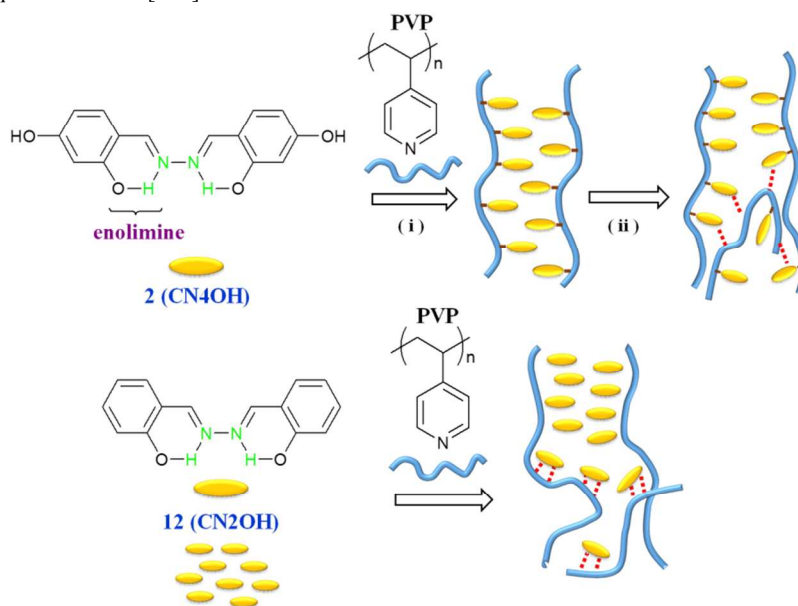
Pyridine and triphenylamine (TPA) were also incorporated with the tetraphenylthiophene (TP)<sup>107</sup> moiety to prepare AIE-active luminogens for the convenient blending with PVP and poly(vinyl alcohol) (PVA), respectively. The resulting blends also show enhanced emissions compared to the pure luminogens, therefore, effective rotational restriction for the luminogens in the blends is the key controlling the emission efficiency of the AIE-active blends.

As described earlier, the C=N isomerization in the excited state was known as the predominant decay pathway for imine dyes with unbridged C=N bond<sup>28-32</sup> and study on salicylaldehydeazine derivative of molecule 2 (CN4OH, Fig. 2) gives example on how the C=N isomerization can be effectively inhibited by the intramolecular H bonds within the enolimine rings. Besides two *o*-hydroxyl groups held by the intramolecular H bonds, CN4OH also contains two *p*-hydroxyl

groups, which can be used to bind to other H-bond accepting group through favorable intermolecular H bonds. In contrast to the stable *o*-hydroxyl groups, the less-hindered *p*-hydroxyl groups of CN4OH will preferably react with pyridine ring of poly(vinyl pyridine) (PVP) (Fig. 11). Therefore, when the pyridine rings of PVP is less than the *p*-hydroxyl groups of CN4OH, the corresponding blends emit efficiently with intensity higher than the pure CN4OH itself. Nevertheless, excess pyridine rings loaded in the blends start to H-bond to the *o*-hydroxyl groups of CN4OH and ruptured certain fractions of the intramolecular H bonds in the enolimine rings and this caused the C=N isomerization and reduced the emission of the highly PVP-loaded blends. For the CN2OH/PVP blends, the loaded PVPs can only H-bond to the *o*-hydroxyl groups of CN2OH; therefore, the CN2OH/PVP blends all emit with lower intensity than pure CN2OH itself.

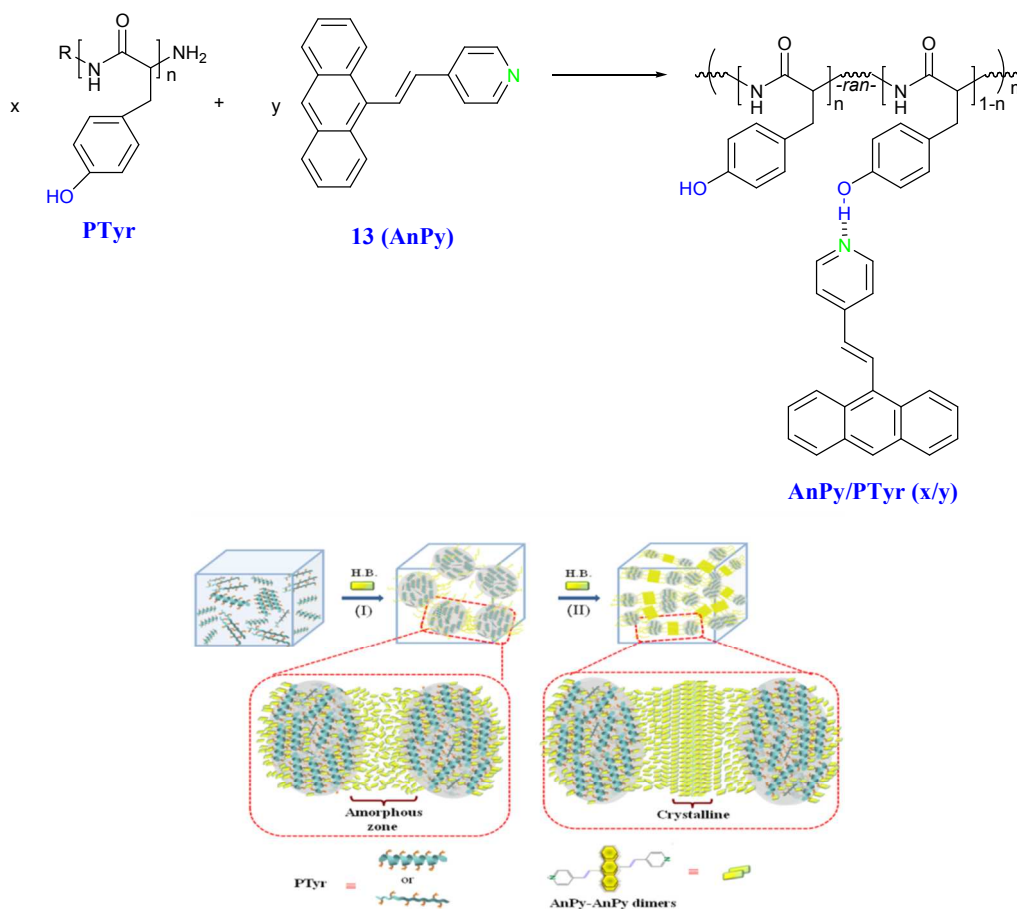


**Fig. 10** Blends of AIE-active **11** (AnPy) with BPA and PVPh to generate the *pseudo* linear and the *pseudo* crosslinked network systems, respectively. Adapted from Ref. [100]



**Fig. 11** Salicylideneazine derivatives of molecules **2** (CN4OH) and **12** (CN2OH) and the corresponding variations on chain conformations upon blending with PVP. Adapted from Ref. [107]





**Fig. 12** H bond interactions between AnPy and polytyrosine (PTyr) (upper) and variations of the chain conformations (TPyr) upon increasing the AnPy content in the blends (lower). Adapted from Ref. [110]

The preferable H bond interactions between the less-hindered *p*-OH groups of CN4OH and the pyridine rings of the PVP chains result in crystalline blends, too. Presumably, the polymeric PVPs serve as templates to anchor the crystalline CN4OHs packed in nearly-parallel fashion. Molecular rotation of the CN4OHs in the closely-packed crystalline lattices was supposed to be effectively restricted, leading to highly-emissive blends (a highest quantum yield ( $\Phi_f$ ) of 88% can be achieved). Nevertheless, extra PVPs loaded in the blends inevitably bind to the lateral *o*-hydroxyl groups of CN4OH, interfering the parallel packing of the CN4OHs and reducing the crystallinity and the emission efficiency of the corresponding CN4OH/PVP blends. All the results suggest that luminescence of the blends is actually governed by crystallization. Increasing crystallinity of the blends directly leads to the enhanced emission efficiency. Once again, the emission behavior of the CN4OH/PVP blends correlates with the CEE<sup>101-106</sup> property.

Polytyrosine (PTyr)<sup>108,109</sup> containing phenol side groups can be used as H-bond donating groups for the convenient reaction with pyridine ring of an AIE-active luminogen **12** (AnPy, Fig. 12)<sup>110</sup> to prepare AnPy/PTyr blends of different AnPy contents. Increasing AnPy content in the blends causes the conformation changes on both PTyr and AnPy components, which in turn change the degree of restriction forces on the molecular rotation of the AnPy. The varied restriction forces also generate blends of different emission behaviour. Primary investigation on the DSC thermograms

indicates the presence of amorphous phase, representative of the aggregated H-bonded PTyr chains, in the blends containing low AnPys and the crystalline phase, representative of organic AnPy molecules, in the blends containing high AnPys. The DSC thermograms plus the results from WAXD spectra indicate that chain conformation of the blends undergoes a two-step transformation process with increasing AnPy content in the blends.

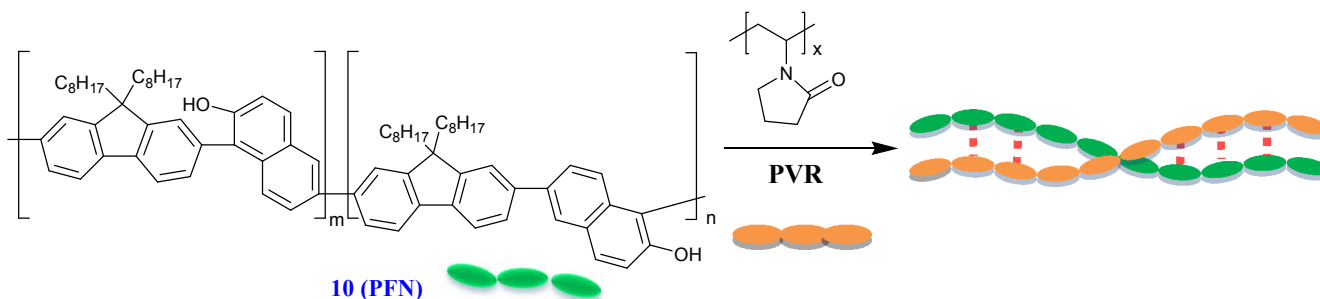
Initially (step I, Fig. 12), the intimately-packed  $\beta$ -sheet secondary structure of PTyr was open by the implanted AnPys, transforming into rigid  $\alpha$ -helical chains with distant phenol rings for the accommodation of the AnPy molecules. The anchored AnPys over the rigid helical chains of PTyr are sluggish in rotation and therefore, emit strongly with prevalent effect of RIR. In this stage, the fundamental feature of the blends is the coexisting peptide aggregates and the amorphous AnPy zone in between the peptide aggregates. To accommodate the implanted AnPys, the peptide aggregates will reduce the size, resulting in the observed reduced glass transitions, upon increasing AnPy content in the blends.

Step II, involving in the highly AnPy-loaded blends, basically relates to the formation of new AnPy crystals. With fewer PTyr templates available, extra AnPys in the blends will form new crystals separate from the amorphous PTyr aggregates. In the middle region between the amorphous PTyr aggregates, AnPy dimers in near parallel geometry exclusively develop through stepwise orientation adjustments of the dimers. According to the

WAXD spectra, the parallel AnPy dimers contain closed-packed anthracene pair with a short inter-ring distance of 3.47 Å. The near parallel dimers in the crystalline blends are considered to be rather clumsy in rotation due to the short inter-ring distance; therefore, the crystalline blends emit with higher intensity than the amorphous blends with lower AnPy content (step i). In addition, the excimer emission of the crystalline blends is at 545 nm, which is comparatively higher in wavelength than the monomer emission at 506 nm.

The hydroxyl groups of polymer **10** (PFN, Fig. 13), as described earlier,<sup>99</sup> was also used as H-bond donating groups to bind to the carbonyl groups of poly(vinylpyrrolidone) (PVR). Conceptually, the resulting PFN/PVR blends<sup>111</sup> are system with the hypothetical interpenetrating network (IPN) structure. With the mutual H bond interactions, all the PFN/PVR blends are

homogenous materials with one single glass transition according to the DSC thermograms. The quantum yields ( $\Phi_F$ ) of the solid PFN/PVR blends are all higher than that of the pure PFN ( $\Phi_F = 0.61$ ). As the blend containing the lowest amounts (2.33 wt %) of the luminescent PFNs, the solid PFN/PVR(1/200) actually emits with the highest  $\Phi_F$  value of 0.93 among all solid blends. In the PFN/PVR(1/200) blend, the luminescent PFNs should be well isolated by the overwhelming PVR chains and molecular rotations of the luminescent units are considered to be highly restricted by the H-bonds imposed by the surrounding PVR chain matrix. Because that aggregation of the luminogens in the blend (i.e. PFN/PVR91/200) full of PVR is rather difficult, it is then reasonable to suggest that the key for the enhanced emission is the restricted molecular rotation rather than the degree of aggregation.



**Fig. 13** Blending of polymer **10** (PFN) with PVR to result in interpenetrating network system with intense emissions. (Reproduced with permission from Ref. [111]. Copyright 2011, American Chemical Society.)

## Conclusions

Intermolecular H bond interactions are the versatile sources efficient in imposing rotational restriction required for the AIE-active polymers and blends. By appropriate choices of H bonding sites, or H bond donating and accepting groups, large amounts of AIE-, AEE- and CEE-active luminogenic polymers and blends can be conveniently created. Inside the H-bonded assembled body, molecular motion of the luminogens is considered to associate with movements of the neighbouring groups and therefore, should be rather sluggish. The rotational restriction of the luminogens with prevalent H bond interaction is therefore so effective that high emissive polymers and blends can be conveniently prepared.

For polymers containing multiple luminogenic units, viscous polymer chains and the multiple, intermolecular H bonding sites offer effective rotational restriction on the inherent luminogens. Strong emission efficiency is a general character of this system. For hydrophilic polymers containing single luminogen, easy aggregation of the hydrophobic luminogen from the phase-separated H-bonding sites reinforces the beneficial rotational restriction to result in an AIE system with intense luminescence. For luminogenic blends consisting of H bond donors and acceptors, the preferable intermolecular H bond interactions effectively hamper the motion of the constituent components. Appropriate selections of H bond donating and accepting components provide versatile sources for the generation of AIE-active blends with strong emission intensity.

With effective intermolecular H bond interactions, the blend systems are emitters with emission intensity higher than the pure

luminogens without any H bond interactions. Therefore, it is the effective rotational restriction, rather than the amounts of luminogens loaded in the blends, controls the final AIE-related emission intensity.

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## Notes and references

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