

FOCUS REVIEW

Recent advances in AIE polymers

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Aggregation-induced emission (AIE) polymers are a series of novel luminescent materials. These materials have experienced an exponential growth of research interests and are rapidly developing into an emerging field. AIE polymers boast high aggregated-state emissions, diverse structures and the use of various synthetic methods for preparation; they also demonstrate good solubility and processability compared with AIE small molecules. Furthermore, additional functionalities can be introduced into AIE polymers through a large number of simple and convenient synthetic strategies. Great progress has been made after the publication of a comprehensive review on AIE macromolecules. Herein, the newly developed AIE polymer systems are summarized, with an emphasis on the synthetic methods used to generate the polymers and their structures and applications. The structural design and synthetic approaches of a series of functional nonconjugated or conjugated AIE linear polymers with AIEgens on the side chains or main chains, as well as star-shaped or hyperbranched AIE polymers with AIEgens on the core or terminal parts are discussed. The advanced performance of AIE polymers in a series of practical applications, such as fluorescent sensors, stimuli-responsive materials, biological applications, porous materials and circularly polarized luminescence, is also introduced. The rapid development and large variety of potential applications of AIE polymers have demonstrated that this prosperous and promising field presents great opportunities.

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INTRODUCTION

Aggregation-induced emission (AIE) has attracted much attention since it was first reported in 2001.¹ This field is developing fast and ‘AIE characteristics and compounds’ were selected as one of the 100 top-ranked specialties in the sciences and social sciences by Thomson Reuters in both 2013 and 2015. The general principal of AIE compounds is that they are non-emissive or faintly emissive in solutions; however, when the molecules aggregate in certain solvents or in solids, bright emission is induced. This is in contrast to the well-known aggregation-caused quenching phenomenon of most traditional organic fluorophores, which provides a perfect solution for the notorious fluorescence-quenching problems of aggregates. Typical AIE compounds possess propeller-shaped structures with rotatable periphery phenyl rings, with representative examples being tetraphenylethene (TPE) and hexaphenylsilole. The widely accepted mechanism of AIE is through restriction of intramolecular motions (RIM), which include rotations and vibrations. In solution, the σ bonds connecting the periphery phenyl rings and the core structure are able to rotate. This intramolecular motion consumes the excited state energy and quenches the emission. In an aggregated state, such as nanoparticles and solid thin films/powders, the molecules are in a crowded neighborhood and these intramolecular motions are restricted, which diminish the nonradiative decay of the excited state energy and consequently induce strong emission. Based on the RIM principle, a large variety of AIE compounds have been developed over

the past decade. With the efficient aggregated-state emission of AIE materials, their utilization in a series of high-tech applications has been explored. For example, studies on optoelectronic devices, including organic light-emitting diodes, light-emitting liquid crystals, circularly polarized luminescence (CPL) and optical waveguides, together with luminescent sensors, including chemical sensors, biological probes and cellular, bacterial and tissue imaging, have been extensively reported.

Compared with AIE-active small molecules, polymer materials possess several advantages, such as processability, ease of functionalization, structural diversity and good thermal stability, endowing them with great potential in practical applications. Indeed, AIE polymers expand the application scope of AIE materials and exhibit relative potency in some widely investigated applications, such as fluorescent chemosensors. A few reviews have summarized the state of the art developments of AIE macromolecules, including their design, syntheses, structures, topologies, functionalities and applications.^{2,3} This young field is growing exponentially, and great progress has been made thus far. The development of a large number of nonconjugated and conjugated, star-shaped and hyperbranched AIE polymers has been reported with AIEgens on the side chains, main chains, center or periphery of the polymers. Significant progress has also been made on the development of applications that utilize AIE polymers, especially in biological applications and microporous materials.

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In this review, the up-to-date progress in AIE polymers will be summarized, providing the broad readership with an update on novel polymeric structures, synthetic methodologies, as well as the development of applications. It is expected that providing insight of materials design principles to this promising field will trigger new ideas to accelerate the development of additional AIE materials.

STRUCTURES OF AIE POLYMERS

The construction of a large variety of AIE polymers has been reported through the use of various synthetic strategies, incorporating typical AIEgens into polymer structures by either directly using AIEgen-containing monomers for homopolymerization or copolymerization or by modifying polymers with AIEgens through post-polymerization modification techniques. In addition, AIEgen-containing initiators are frequently used to produce polymers with AIE terminal groups.

Free radical polymerization, including reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP), is one of the most popular approaches used to construct nonconjugated AIE polymers. Meanwhile, transition metal-catalyzed coupling polymerizations, such as Yamamoto coupling, Suzuki coupling and Sonogashira coupling, are frequently used to build conjugated AIE polymers. New synthetic approaches such as ring-opening olefin metathesis and multicomponent tandem polymerizations (MCTPs) have also been used to construct AIE polymers. Moreover, various polymer architectures have been

generated using different combinations of monomers, initiators and polymerization reactions.

Nonconjugated linear AIE polymers

Nonconjugated AIE polymers, commonly prepared from free radical polymerization, are generally designed to incorporate additional functionalities, such as water solubility, biocompatibility, stimuli-responsive properties and mechanical properties (Figure 1). For example, TPE-containing polymers P1a–c with high molecular weights (M_n up to 648 000) could be readily prepared through free radical polymerization from acrylate monomers.⁴ P1a–c were non-emissive in THF, dichloromethane, chloroform or toluene solutions. However, pronounced emissions at ~468 nm were observed when nanoparticles formed on the addition of water, in which the materials exhibited poor solubility. The fluorescence quantum yields (Φ_F) of P1a–c in THF solutions were 0.09%, 0.07% and 0.06%, respectively, while their Φ_F in THF/water mixtures with 90 vol% water content were raised to 9.9%, 8.6% and 7.8%, respectively. Longer alkyl chain generally reduced the Φ_F values in both solutions and aggregated states, probably due to an increase in structural flexibility when the distance between the polymer main chain and the AIEgen increased. Polyhedral oligomeric silsesquioxane (POSS) is a well-known building block for the generation of porous materials and was also introduced to AIE polymers to increase their sensitivities for potential fluorescent sensor application.⁵ Free radical copolymerization of POSS-containing

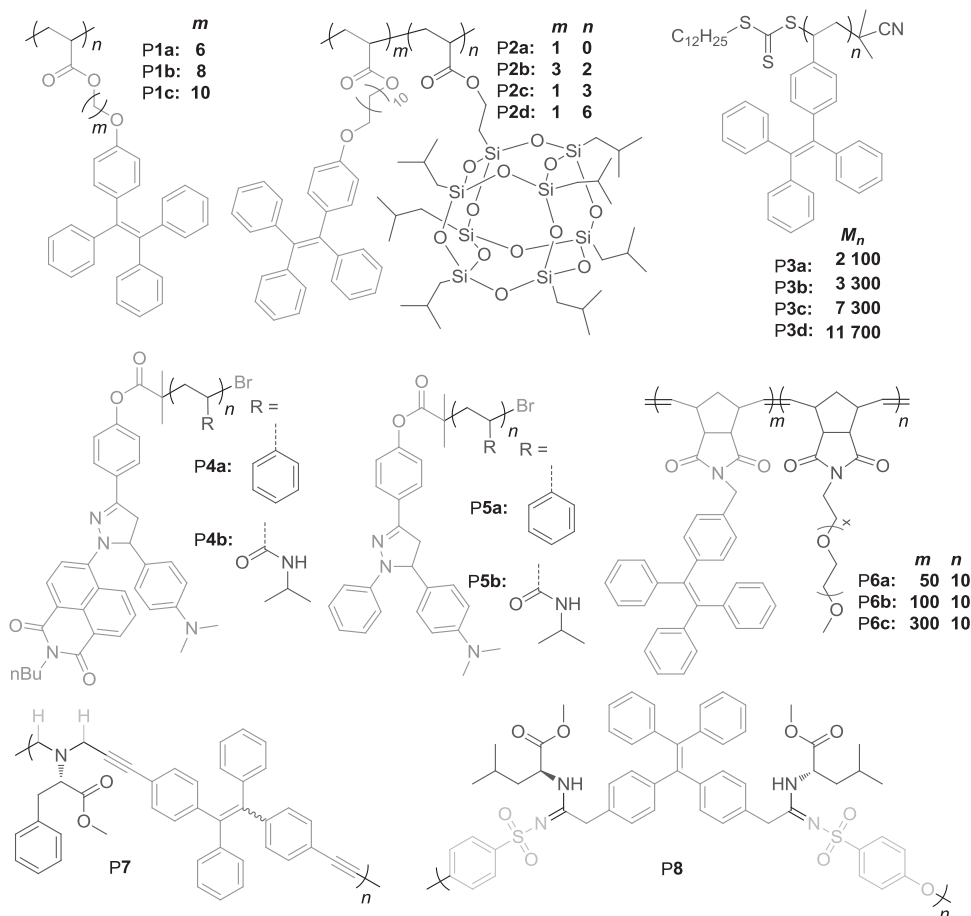


Figure 1 Chemical structures of nonconjugated AIE polymers. AIE, aggregation-induced emission. A full color version of this figure is available at *Polymer Journal* online.

acrylate and TPE-containing acrylate was used to prepare a series of POSS-based copolymers P2a–d with pronounced AIE effects.

RAFT polymerization and ATRP have been used to create AIE polymers with controlled degrees of polymerization. For example, a series of poly[(2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene]s P3a–d with various degrees of polymerization and M_w were synthesized using RAFT.⁶ Compounds P3a–d displayed no emissions in THF solutions and strong emissions in THF/water mixtures. In the nanoaggregates, the polymers with higher M_w s exhibited higher Φ_{FS} , which were reportedly due to an increase in hydrophobicity. An AIE initiator with a strong charge transfer (CT) effect and an aggregation-caused quenching initiator with a weak CT effect were also used in ATRP for the preparation of end-functionalized polystyrene (PS) (P4a and P5a) and poly(*N*-isopropylacrylamide) (PNIPAM) (P4b and P5b), respectively.⁷ Both terminal luminophores and the hydrophilicities of the polymers affected their photophysical properties: the CT effects of P4a and P5a were well-preserved, while their PL intensities increased compared with the initiator because the PS chains could separate the initiators from intermolecular interactions and restrict their intramolecular rotations. Due to the different polarity of PNIPAM, P4b exhibited strong CT and AIE effects; P5b exhibited weak CT and aggregation-caused quenching effects, similar to their corresponding initiators.

Recently, living ring-opening metathesis polymerization, a powerful controlled polymerization method with high efficiency that can be performed under mild conditions to form new C=C bonds for further post-functionalization, was used to prepare AIE polymers for the first time.⁸ In the presence of the third-generation Grubbs' catalyst, TPE-containing norbornene was copolymerized with a PEG-containing norbornene to synthesize a series of well-defined, AIE-active diblock copolymers P6a–c. These amphiphilic polymers could self-assemble in selective solvents, forming fluorescent nano-sized spherical micelles (P6a in THF/H₂O), cylindrical micelles (P6b in THF/H₂O) and vesicles (P6c in dioxane/H₂O) with emission maxima located at 480 nm and Φ_F values of 20–22%.

Multicomponent polymerization (MCP) is another powerful modern method that can be used for polymer synthesis, which enjoys a series of advantages such as high efficiency, high atom economy, environmental benefit and great structural diversity. A₃-polycoupling reactions of AIEgen-containing diynes, chiral amino esters and aldehydes catalyzed by CuCl were reported for the synthesis of soluble and structural regular poly(dipropargylamine)s P7 with high M_w s of up to 43 800 in high yields.⁹ Later, Cu-catalyzed polycoupling reactions of TPE-containing diyne, disulfonyl azide and optically active amino ester were reported to efficiently produce AIE-active poly(*N*-sulfonylamidine)s with high M_w s (up to 35 900).¹⁰ For example, the polymer main chain of P8 was able to helically rotate in a preferred screw sense induced by the chiral pendants, which was evidenced by the CD signals associated with the Cotton effect in the absorption region of the polymer backbone. Both MCPs generated AIE polymers with good thermal stabilities, excellent film-forming abilities and high refractive indices with small chromatic dispersions.

Conjugated linear AIE polymers

Compared with nonconjugated polymers, higher emission efficiencies can be expected from conjugated AIE polymers. Various polymerization reactions, such as Yamamoto polycoupling, Suzuki polycoupling and Sonogashira polycoupling reactions, have been utilized to synthesize conjugated AIE polymers (Figure 2).

Recently, Scherf and co-workers^{11,12} reported the development of a series of conjugated AIE polymers based on polytriphenylamines

P9–10 and polycarbazoles P11–12 with TPE as the side chains prepared by nickel-catalyzed Yamamoto polycoupling reactions. Polytriphenylamines and polycarbazoles with pronounced electron donor characteristics were designed to enhance the interactions between the polymers and electron-poor nitroaromatic compounds during the explosive detection process. Simultaneously, the TPE side groups could introduce AIE attributes to the polymers and maintained high emission efficiencies in aggregated states. Polytriphenylamines P9–10 possessed absorption maxima at 386 nm and 380 nm, respectively, and emission maxima at 511 nm and 495 nm, respectively. Polycarbazoles P11–12 generally blue shifted in the absorption spectra compared with P9–10. The Φ_{FS} of P9–12 lied in the range of 0.8–2.5% in dilute solutions and increased to 17–34% when they were in solid states.

Suzuki cross-coupling polymerization was used to prepare a series of copolymers P13 with fluorene, TPE and 9-benzylidene-fluorene with a dicarboxylate pseudo-crown as a Pb²⁺ receptor.¹³ The dual-mode-sensitive fluorescence detection of Pb²⁺ will be discussed below. Chujo *et al.*¹⁴ prepared a group of AIE polymers P14a–e with new AIE luminogens, namely boron di-iminates, using Suzuki polycouplings. The relationship between the substituents and their electronic structures was systematically investigated.¹⁴ P14a–e showed strong absorption at 374–407 nm and emitted from green to red with emission maxima of up to 628 nm and a solid-state Φ_F of up to 11%. P14d with an electron-withdrawing nitro group and P14e with a strong electron-donating dimethylamine group possessed emissions at 575 nm and 628 nm, respectively, which were significantly red-shifted compared with the emissions of P14a–c. Sonogashira polycoupling is another popular approach used to synthesize AIE polymers with C≡C bonds embedded in the main chains. For instance, a fluorescent sensory polymer P15 consisting of pentyptycene and TPE units linked by acetylene was generated for the direct detection of explosives in solution and air,¹⁵ and a series of 1,1'-binaphthyl and TPE-containing conjugated polymers P16–17 with main-chain chirality were prepared using Sonogashira polycoupling reactions.¹⁶

A novel MCTP reaction of alkynes was recently used to synthesize conjugated polymers. In MCTP reactions, multiple steps are combined in one synthetic operation, and the reactions occurred in a specific order without isolation of reactive intermediates. Consequently, they deliver compact and elegant syntheses of conjugated polymers in high yields and generate products with high M_w s and regio-/stereoselectivity. Through a one-pot three-component coupling-hydroamination sequential polymerization of a TPE-containing diyne, carbonyl chloride and a primary amine, nitrogen-substituted conjugated polymer P18 was generated with a high yield of up to 99%, high M_w of up to 46 100, 100% regioselectivity and stereoselectivity.¹⁷ Through an artful design of a newly formed intramolecular hydrogen bonding-linked six member ring in the polymer backbone, the structure of the *Z*-isomer was stabilized with 100% stereoselectivity. Such intramolecular hydrogen bonds also hamper the potential photo-induced energy transfer process and render the polymer emissive. Another one-pot three-component tandem polymerization based on the sequential coupling-addition-cyclization reaction of a TPE-containing diyne, carbonyl chloride and ethyl 2-mercaptoacetate proceeded efficiently in near quantitative yield, affording newly formed thiophene-containing conjugated polymer P19 with a high M_w of up to 156 000.¹⁸ P18–19 generally show aggregation-enhanced emissions: their solutions were weakly emissive, which turned to be emissive when nanoaggregates or thin films were formed.

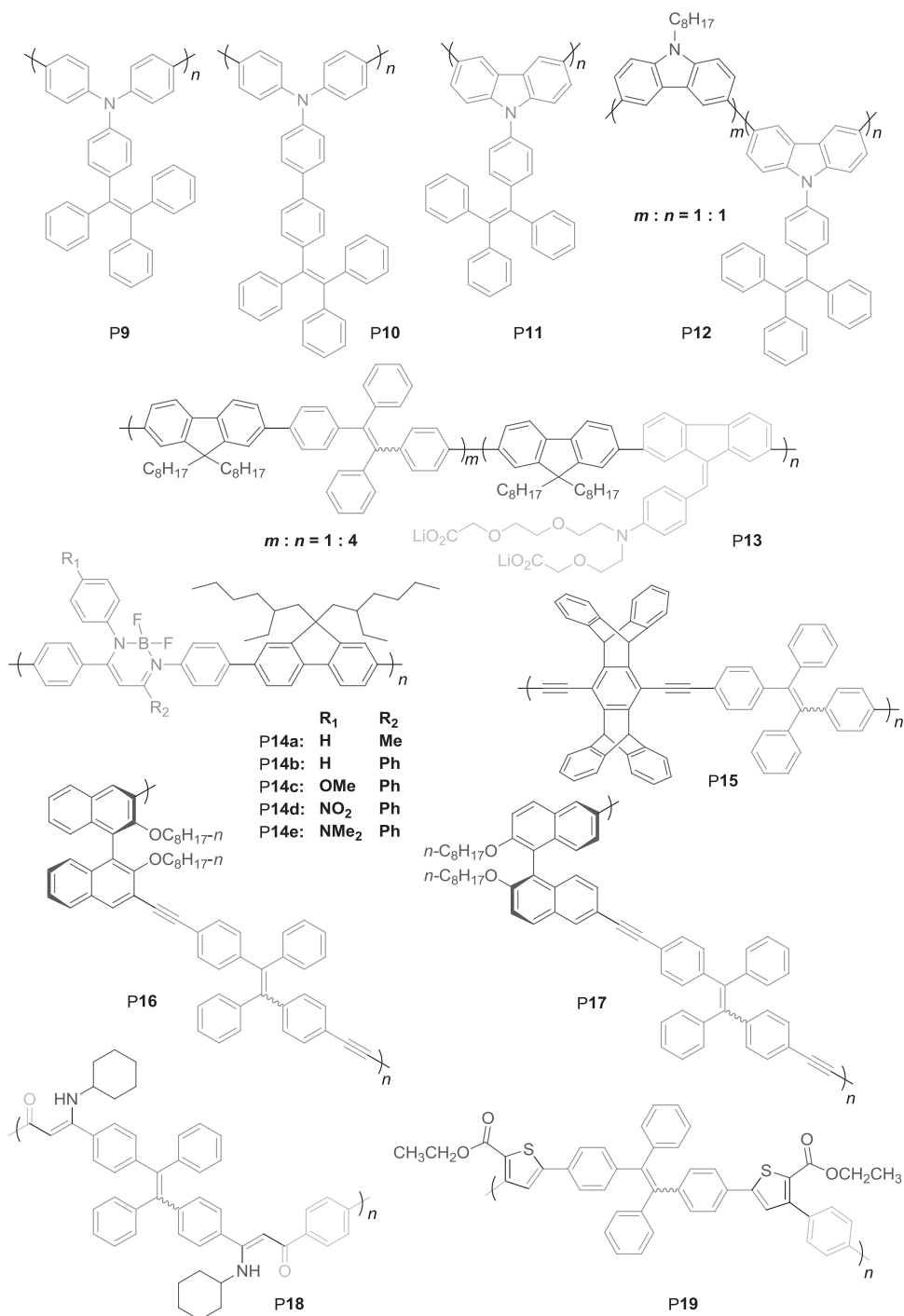


Figure 2 Chemical structures of conjugated AIE polymers. AIE, aggregation-induced emission. A full color version of this figure is available at *Polymer Journal* online.

Nonlinear AIE polymers

The syntheses of star-shaped, hyperbranched or cross-linked AIE polymers with AIEgens as the core or terminals have been frequently reported.^{19–21} A TPE derivative with four hydroxyl groups was reacted stoichiometrically with the lutetium alkyl moiety Lu-CH₂SiMe₃ of an *O,N,N,O*-tetradentate Salan lutetium alkyl complex to afford a TPE-labeled Lu-alkoxide counterpart **20** (Figure 3).²² Compound **20** then served as an efficient initiator for the ring-opening polymerization reaction with 500 equiv of *rac*-lactide to produce

polylactide **P20** with a M_w close to its theoretic value, indicating the induction of living polymerization. This type of methodology can be further extended to other cyclic esters and the ring-opening polymerizations of caprolactone and allyl or alkyne functionalized carbonates, and *rac*-butyrolactone to generate the corresponding syndiotactic products. The resulting star-shaped polymers were generally AIE active, and their fluorescence intensities in a THF/H₂O (1/9 v/v) mixture were more than 2850-fold stronger than that in THF.

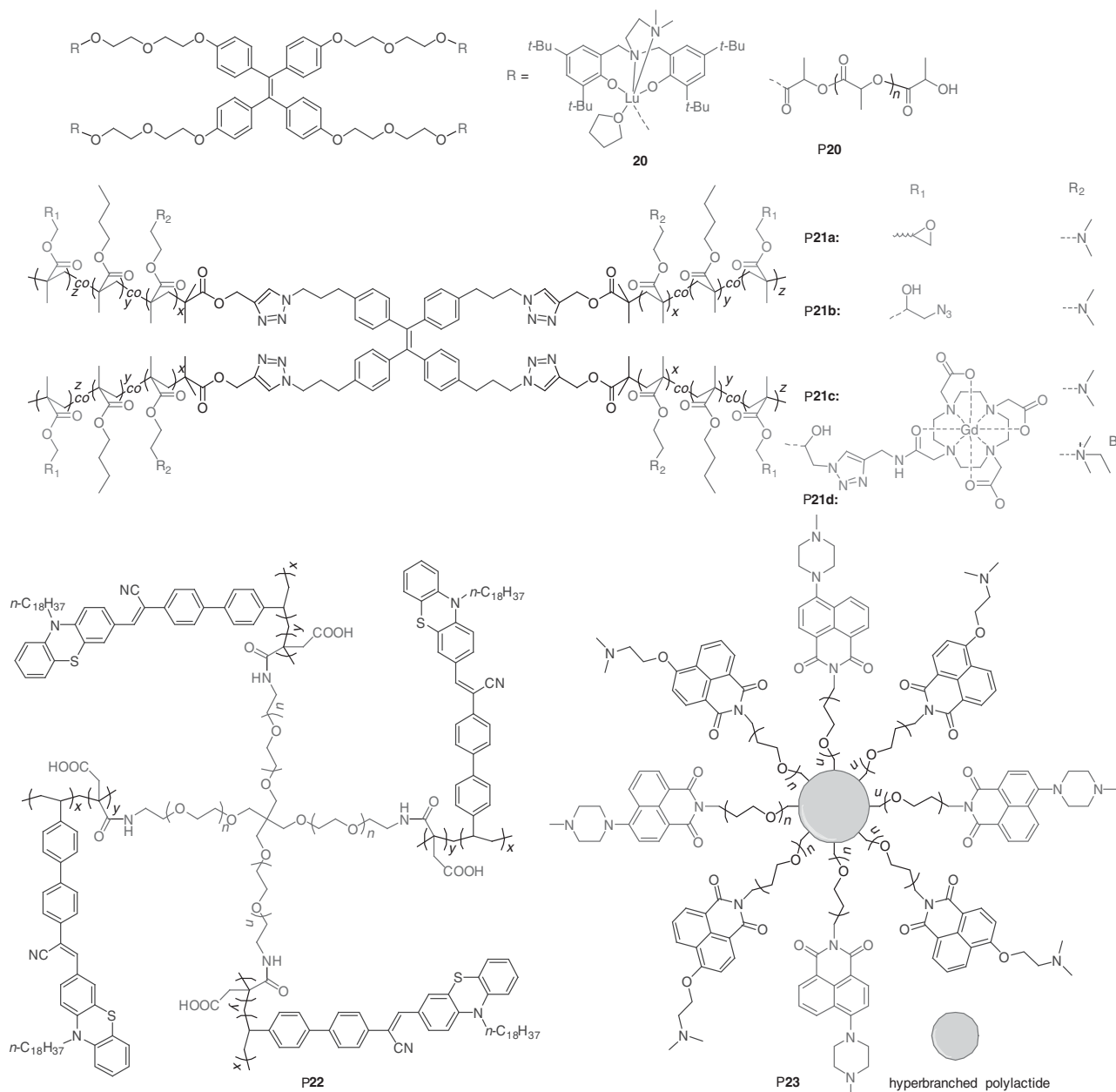


Figure 3 Chemical structures of nonlinear AIE polymers. AIE, aggregation-induced emission. A full color version of this figure is available at *Polymer Journal* online.

Another amphiphilic star-shaped copolymer **P21c**, TPE-*star*-P (DMA-*co*-BMA-*co*-Gd), consisting of a TPE core with amphiphilic/cationic P(DMA-*co*-BMA-*co*-Gd) arms, where DMA, BMA and Gd are 2(dimethylamino)ethyl methacrylate, butyl methacrylate and T1-type magnetic resonance (MR) imaging contrast agent, DOTA-Gd, respectively,²³ was synthesized by combining ATRP and the successive post-modification reactions. Alkynyl-terminated terpolymers, alkynyl-P(DMA-*co*-BMA-*co*-GMA), were prepared via ATRP, which were then covalently conjugated onto azide-functionalized TPE via click reactions to afford the star-shaped polymer **P21a**. The pendent epoxy moieties of the GMA residues were reacted with NaN₃ to yield TPE-*star*-P(DMA-*co*-BMA-*co*-N₃) **P21b**, which was then linked with an alkynyl-functionalized DOTA-Gd complex via a click reaction to

afford **P21c**. A quaternization reaction of the *N,N*-dimethylamine groups of **P21c** with bromoethane then introduced ammonium ions to the polymers as positive charges to afford **P21d**.

Other nonlinear AIE polymers with terminal AIEgens have also been studied.²⁴ For example, a cross-linked fluorescent polymer **P22** was prepared through radical copolymerization of AIEgen-containing vinyl monomers and itaconic anhydride, followed with the ring-opening PEGylation of an anhydride with a four-arm PEG amine. **P22** could self-assemble into uniform fluorescent nanoparticles with diameters ranging from 50 to 80 nm, which showed bright yellow fluorescence and high water dispersibility.²⁵ An amphiphilic hyperbranched polymer-based fluorescent pH nanosensor **P23** was prepared by grafting a hyperbranched poly(lactide) with PEG through

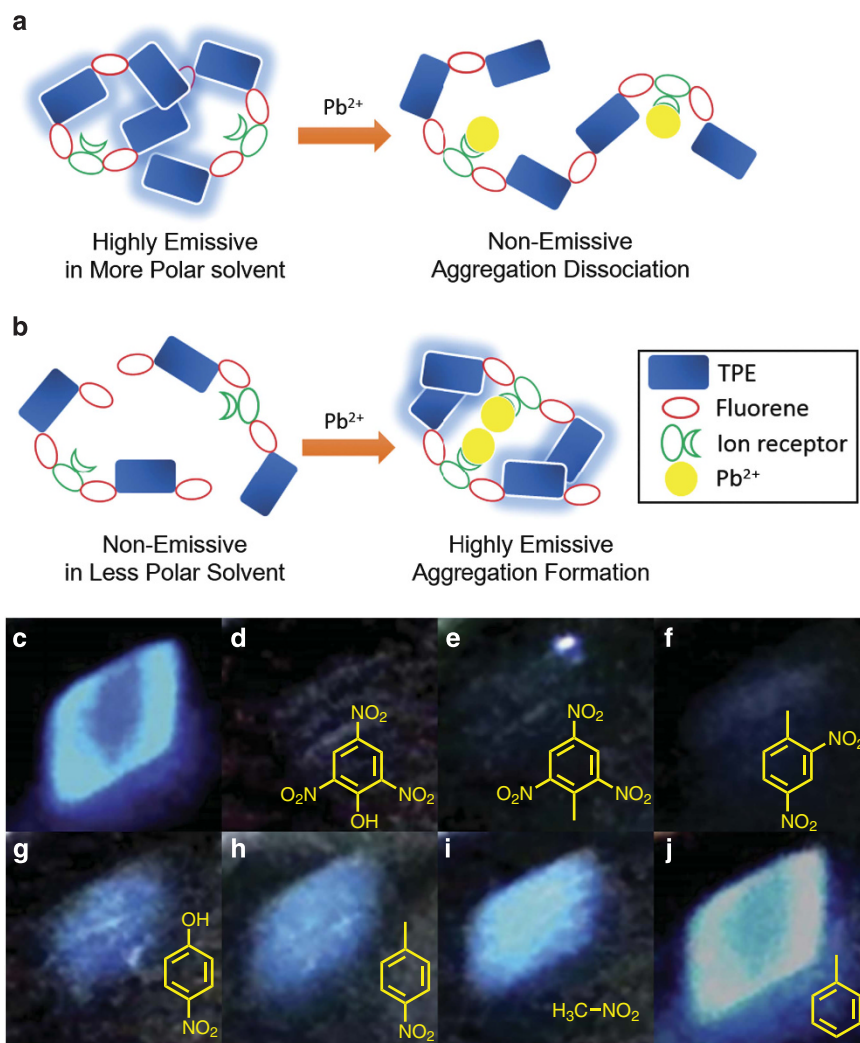


Figure 4 Fluorescence detection of Pb^{2+} using **P13** through (a) 'turn-off' mode in a THF/water mixture with 90 vol% water content and (b) 'turn-on' mode in a THF/water mixture with 20 vol% water content. Fluorescence photos of (c) the thin film of **P1a** in the presence of 50 p.p.m. of (d) picric acid, (e) 2,4,6-trinitrotoluene, (f) 2,4-dinitrotoluene, (g) 4-nitrophenol, (h) 4-nitrotoluene, (i) nitromethane and (j) toluene. All photos were taken under ultraviolet illumination. Reproduced with permission.⁴ Copyright 2014, Royal Society of Chemistry.

esterification, and by subjecting the material to subsequent functionalization with a pH-sensitive green emissive naphthalimide-based dye and a blue emissive naphthalimide-based dye.²⁶ **P23** showed strong emissions in aqueous solutions and exhibited excellent sensing properties for the intracellular pH, which is discussed below.

APPLICATIONS OF AIE POLYMERS

A large number of applications of AIE polymers have been summarized in previous literature reports, including fluorescent sensors, stimuli-responsive materials, biological probes and imaging, optoelectronic devices and fluorescent photopatterning applications.^{2,3} Great progress has been made recently with the development of the examples that are introduced below.

Fluorescent chemosensors

AIE polymers present many advantages for use in fluorescent sensory applications, such as their high emission efficiencies in aggregated states, high sensitivities, as well as possible 'turn-on' or 'turn-off' detection modes. A large variety of analytes, such as gases (for example, CO_2 , NH_3 and NH_2NH_2), metal ions (for example,

Cu^{2+} , Ru^{3+} and Fe^{3+}) and protons, have been detected using AIE polymer-based fluorescent sensors.^{27–30} The scope of these sensors has been further extended. For example, the previously mentioned compound **P13**, which had a TPE fluorophore and a dicarboxylate pseudo-crown (DP) as an ion receptor, demonstrated the unique dual-mode selective detection of Pb^{2+} in water.¹³ 'Turn-off' mode could be achieved in a THF/water mixture with a 90 vol% water content, and the original polymer was highly emissive due to aggregation of the TPE units. On the addition of Pb^{2+} , the ionic interactions between the DP- Pb^{2+} complexes could alter the polymer chain folding and dissociation processes of the aggregates of TPE segments, which led to a significant decrease in fluorescence by over 90% at a Pd^{2+} concentration of $6 \times 10^{-7} \text{ M}$ (Figure 4a). 'Turn-on' mode was achieved in a less polar THF/water mixture with a 20 vol% water content, and **P13** was well-dissolved and thus exhibited no emissions. On the addition of Pb^{2+} , the strong ionic interactions resulted in a less soluble ionic DP- Pb^{2+} complex and caused chain folding and aggregation of the TPE segments, which led to an increase in the observed fluorescence (Figure 4b). The fluorescent sensor demonstrated high selectivity towards Pb^{2+} compared with a series of different alkali,

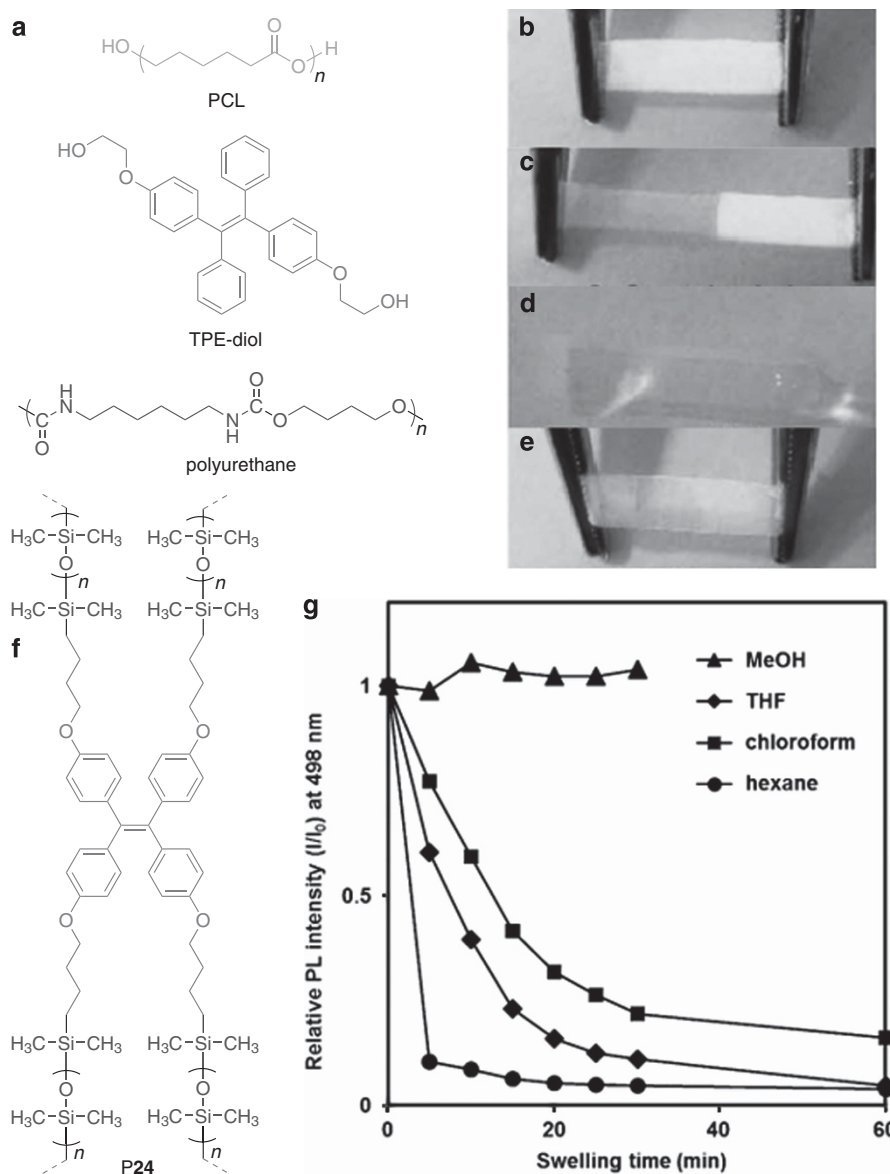


Figure 5 (a) Chemical structures of the three components that produce shape memory polyurethane with AIE characteristics. Photos of a shape memory polymer in its (b) original form, (c) stretched form, after (d) immersion in acetone and (e) removal from acetone and after drying. (f) Chemical structure of AIE elastomer P24, and (g) time-course fluorescence intensity of P24 in various solvents. Excitation wavelength, 350 nm. Reproduced with permission.^{42,43} Copyright 2014, Wiley-VCH; Copyright 2014, American Chemical Society. AIE, aggregation-induced emission. A full color version of this figure is available at *Polymer Journal* online.

alkaline earth, transition metal and heavy metal ions, such as K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} .

Among the various AIE polymer-based sensory applications, explosive detection has been extensively investigated.^{31–33} It is generally believed that electron-donor/acceptor interactions cause energy transfer from the AIE polymers to electron-deficient nitro-containing explosives through a static quenching mechanism. On the addition of explosive analytes, the strong fluorescence of AIE polymers is quenched significantly and exhibits a superamplification effect in many cases.³⁴ Calculated from the Stern–Volmer curve, which is defined as the PL intensity ratio ($I_0/I - 1$) versus the concentration of the analyte, the quenching constant could achieve a value of up to $1.09 \times 10^6 M^{-1}$, revealing the high sensitivity of the material.³⁵ The detection of various explosives with high selectivity is currently being pursued. For example, the quenching constants of P1a–c in picric acid

detection and P12 in trinitrobenzene detection were found to be 9.72×10^4 , 6.98×10^4 , 4.27×10^4 and $1.26 \times 10^6 M^{-1}$.^{4,12} Fluorescent polymer thin films were also fabricated for the convenient detection of explosive vapors. As shown in Figures 4c–j, the thin film of P1a exhibited strong fluorescence. When the polymer was treated with explosive analytes by mixing and drop casting, the fluorescence of the resultant thin films was almost completely quenched. The fluorescence-quenching efficiencies occurred in the following order: picric acid > 2,4,6-trinitrotoluene > 2,4-dinitrotoluene > 4-nitrophenol > 4-nitrotoluene. Within 1 min, the fluorescence of the porous thin film of P2 was quenched by 15% in the presence of TNT vapor.⁵ Similarly, in the presence of trinitrobenzene vapor, the fluorescence of the thin films of P9 and P10 were quenched by 50% and 63% in 1 min, respectively.¹¹ The fluorescence of a thin film of P15 was quenched by 70% in the presence of DNT vapor in merely

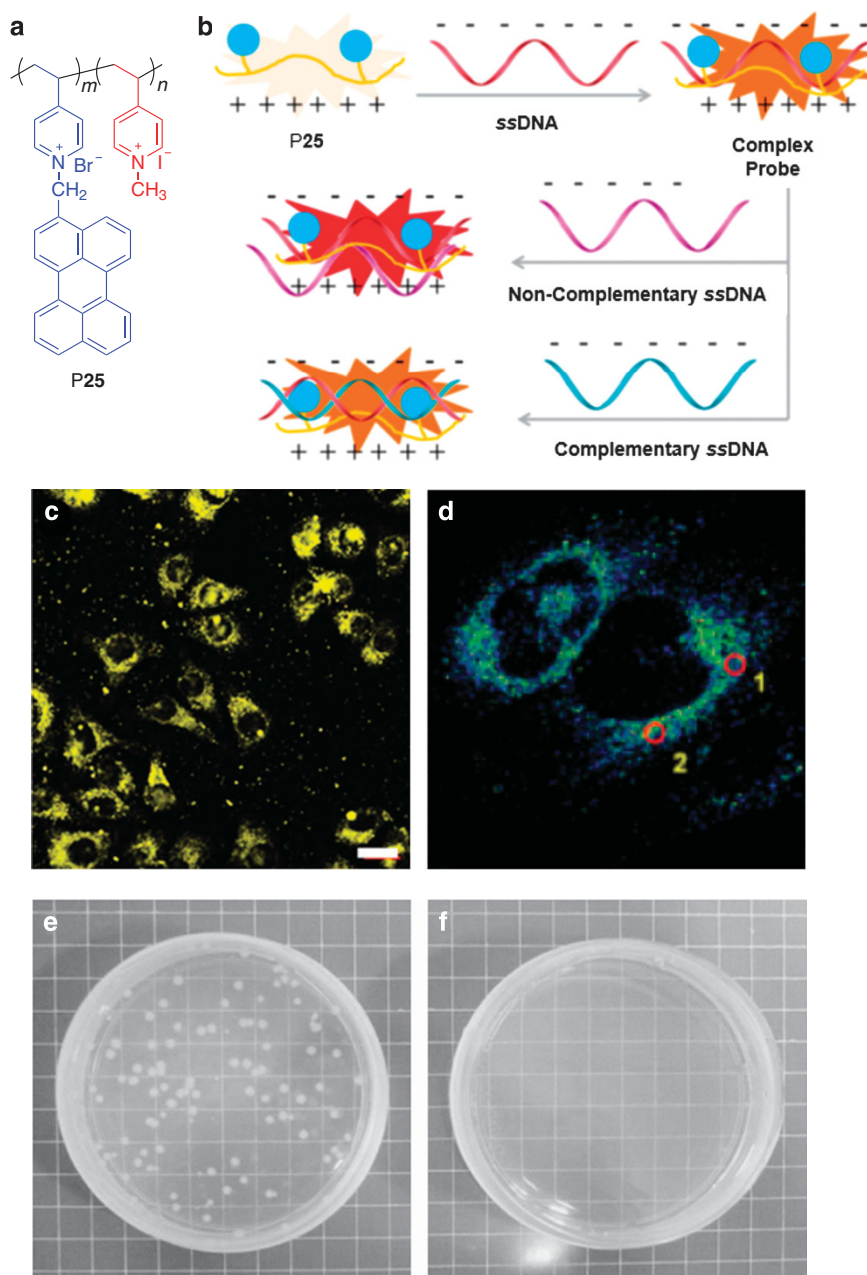


Figure 6 (a) Chemical structure of P25. (b) Conceptual illustration of the complex probe formation and label-free DNA detection based on AIE and DNA hybridization. (c) CLSM image of A549 cells incubated with $10 \mu\text{g ml}^{-1}$ of P22 for 3 h and excitation with a 405 nm laser. (d) pH map of HeLa cells with P23. Antibacterial tests with *Escherichia coli* strains in the (e) absence and (f) presence of P21d. Reproduced with permission.^{23,25,26,47} Copyright 2014, Wiley-VCH; Copyright 2015, Royal Society of Chemistry; Copyright 2015, American Chemical Society; Copyright 2014, American Chemical Society. AIE, aggregation-induced emission.

30 s.¹⁵ These updated studies indicate the good selectivity of the polymers against various electron-deficient nitro compounds.

Stimuli-responsive materials

AIE polymers and their unique fluorescence sensitivities toward subtle environmental changes show great potential for use in stimuli-responsive polymers. Due to their distinct ability to respond to temperature, pH, light, forces or solvents,³⁶ stimuli-responsive AIE polymers have been developed.^{37–39} For example, the color and emission of a thin film of P14e could be reversibly tuned through acid–base interactions in a facile manner. When the thin film was

placed in a saturated trifluoroacetic acid vapor environment, the fumed film showed decreased absorption at $\sim 500 \text{ nm}$ and increased absorption at $\sim 400 \text{ nm}$.¹⁴ The strong donor–acceptor interactions between the amino groups and the boron chelating rings could be suppressed by protecting the amino group, which changed the color of the thin film from orange to yellow and changed the emission color from red to yellow. The optical properties of this trifluoroacetic acid-exposed film could be converted back to the original state by exposing it to triethylamine vapor.

Shape memory polymers are one of the most widely investigated smart materials because of their great potential to be used in different

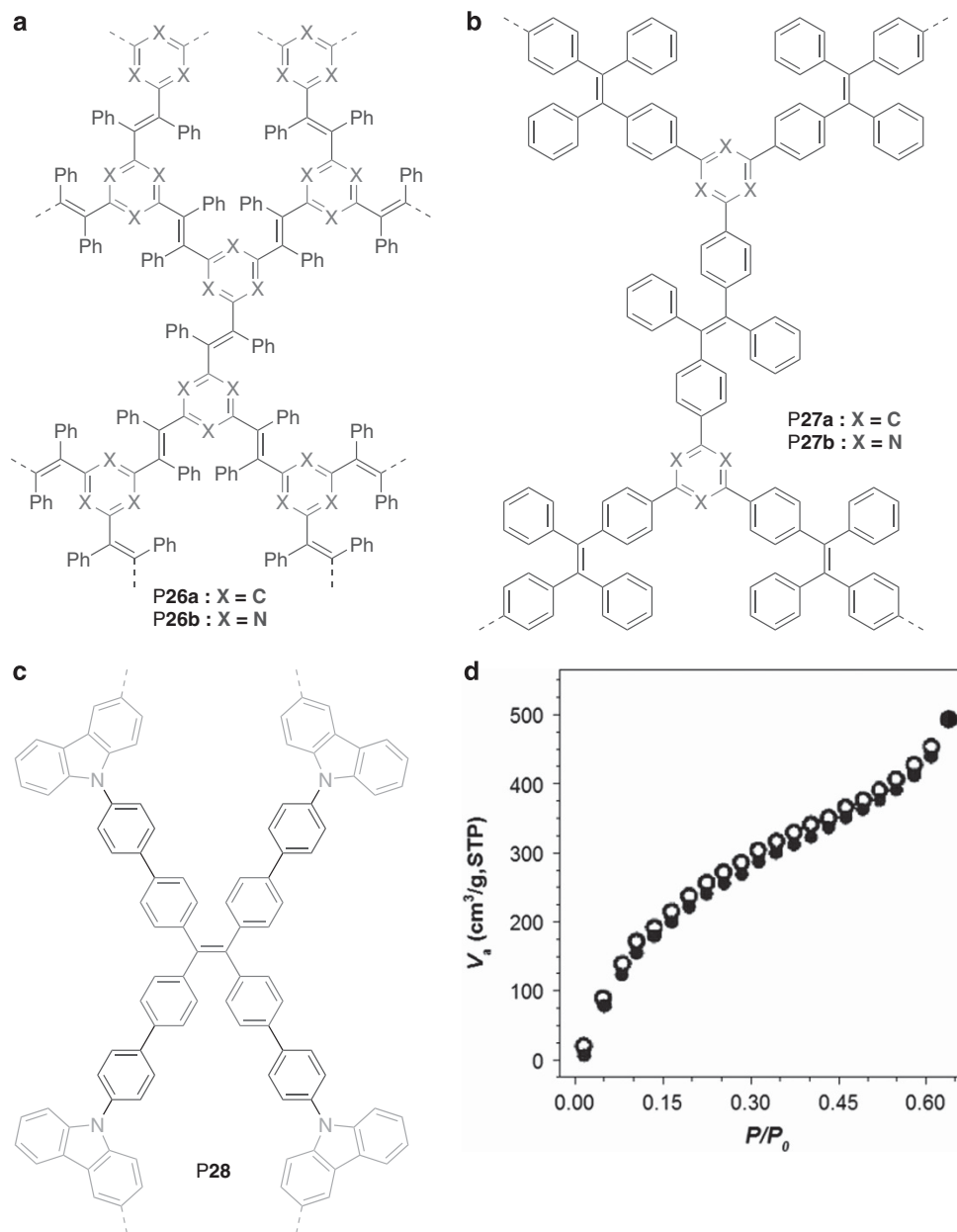


Figure 7 Chemical structures of conjugated microporous AIE polymers (a) P26a–b, (b) P27a–b and (c) P28. (d) Kr sorption isotherm curves for a thin film of P28 at 77 K (filled circles, adsorption; open circles, desorption; STP, standard temperature and pressure). Reproduced with permission.⁵⁶ Copyright 2015, Wiley-VCH. AIE, aggregation-induced emission. A full color version of this figure is available at *Polymer Journal* online.

applications such as sensors, actuators, biomedical devices and textiles.^{40,41} The first development of an AIE-active shape memory polymer was reported recently (Figure 5a).⁴² To obtain biocompatibility, biodegradability and a glass transition temperature close to body temperature, oligo(*ε*-caprolactone)diol was chosen to act as a soft segment in the shape memory polymer. In this method, 25% of polyurethane served as a hard segment to guarantee high recovery of stress and to ease the phase separation. In addition, 0.1 wt% of TPE units covalently connected to PCL served as net points to afford the chromic polymer. The thin film emitted at 479 nm, which blue shifted to 468 nm in the stretched state and was accompanied by a 30% decrease in PL intensity (Figure 5c). Moreover, immersing the polymer in acetone also reduced the fluorescence because acetone was a good solvent for TPE and the soft segment (Figure 5d). After the

sample was removed from the solvent and dried, both the shape and fluorescence were recovered (Figure 5e).

Elastomers are known to be rubbery materials consisting of soft and flexible polymer chains and cross-linking points. A series of AIE elastomers P24 were prepared via hydrosilylation modifications of a tetravinyl TPE compound with H-terminated polysiloxanes in the presence of Karstedt's catalyst (Figure 5f).⁴³ A tensile test of the obtained sample strips showed archetypal elastomeric behavior, while the chain length of polydimethylsiloxane was shown to affect the mechanical properties of the materials, such as their Young's moduli and maximum strains. With the AIE feature, the fluorescence of P24 was found to be stimuli-sensitive against the employed organic solvents because the swelling behaviors of elastomers were influenced by solvent reversibly. When P24 was immersed in high solubility

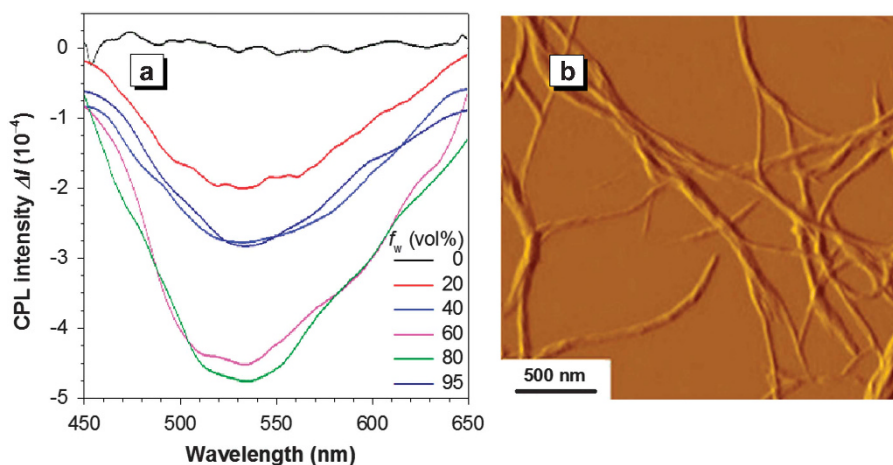


Figure 8 (a) CPL spectra of P16 in THF/water mixtures with different water contents. Solution concentration: $1.0 \times 10^{-5} \text{ mol l}^{-1}$. (b) AFM image of P16 obtained from a THF/water mixture with 60 vol% water content. Solution concentration: 0.01 mg ml^{-1} . Reproduced with permission.¹⁶ Copyright 2015, Royal Society of Chemistry. AFM, atomic force microscopy; CPL, circularly polarized luminescence.

solvents such as THF, hexane and chloroform, the fluorescence was readily quenched to $<20\%$ without any changes in their fluorescence profiles. In contrast, the non-compatible solvent, methanol, did not induce a similar quenching effect (Figure 5g).

Biological applications

The development and use of AIE polymers have resulted in impressive progress for biological applications from a molecular level to a cellular level and even to a microorganism level. Much effort has been made to develop water soluble AIE polymer bioprobes.^{44–46} For example, a water soluble perylene-functionalized nonconjugated polycation P25 was prepared through quaternization of poly(4-vinylpyridine) with bromomethyl perylene and methyl iodide (Figure 6a).⁴⁷ The non-emissive aqueous solution of P25 turned emissive in a water/THF mixture when the mixture contained $>20 \text{ vol\%}$ of THF. Based on the AIE characteristics of P25 and complex formation between the polycation P25 and polyanion single-stranded DNA (ssDNA), DNA hybridization could be detected (Figure 6b). In the presence of polycation P25 and ssDNA, on addition of noncomplementary ssDNA, the fluorescence of the complex probe increased due to the AIE effect; when complementary ssDNA was added, the fluorescence changed a little due to the combined effects of AIE and duplex-quenching caused by the intercalation of perylene into the DNA duplexes. This AIE-based strategy for the detection of DNA hybridization provides a valuable direction for the utilization of AIE polymers in bioassays.

AIE fluorescent polymeric nanoparticles exhibit a series of superior characteristics in cell imaging applications, such as the ability to detect stable morphologies in dilute physiological solutions, good water dispersibility, strong fluorescence, excellent biocompatibility, high cell permeability and labeling performance.⁴⁸ Wei and Zhang *et al.*^{49–54} made a great effort to develop fluorescent nanoparticles based on AIE polymers and to utilize them in cell imaging applications. For example, the cross-linked fluorescent amphiphilic AIE polymer P22 was shown to self-assemble into nanoparticles with hydrophobic AIEgens as the core and hydrophilic PEG groups on the surface. The nanoparticles exhibited strong orange fluorescence at 580 nm with a high Φ_F of $\sim 38\%$, enhanced water dispersibility, excellent biocompatibility and levels of cellular uptake.²⁵ As shown in Figure 6c, the fluorescent nanoparticles localized in the cytoplasm of A549 cells could be clearly observed after being incubated for 3 h. This facile

strategy of combining a PEG amine, anhydride and AIEgen provides a new approach for preparing novel biocompatible and robust cross-linked fluorescent polymeric nanoparticles, which may afford a multifunctional platform and expand the scope of their biomedical applications. Furthermore, cell imaging and simultaneous intracellular pH mapping have been realized using the hyperbranched polymer P23 described above, which was functionalized with pH-sensitive green emissive naphthalimide-based dyes and nonresponsive blue emissive naphthalimide-based dyes as references.²⁶ When the pH value of the solution decreased from 8.1 to 5.0, the blue emission at 450 nm remained unchanged, but the green emission at 520 nm increased because the photo-induced electron transfer process was inhibited. The ratio channel obtained from the green and blue channels could produce a characteristic pH-dependent signal, affording a calibration curve. This is the first ratiometric fluorescent sensor based on AIE hyperbranched polymers for the quantitative detection of intracellular pH values. Intracellular calibration in HeLa cells showed that the green emission increased dramatically with a reduction in pH, whereas the blue emission changed slowly. Based on this calibration, the pH values of spots 1 and 2 in cells were determined to be ~ 6.0 and 5.2 , respectively, corresponding to acidic organelles, such as endosomes and lysosomes (Figure 6d). In addition, the cell imaging studies and MTT assays indicated its low cytotoxicity and good biocompatibility.

The first bacterial detection and inhibition platform based on star-shaped AIE polymer P21d with a TPE core, bacteria binding and amphiphilic arms, and a T1-type MR imaging contrast agent was recently reported by Liu *et al.*²³ The electrostatic complexes were formed on contact with negatively charged bacterial surfaces, which restricted the intramolecular rotation of the TPE cores and tumbling mobility of the anchored Gd moieties, leading to synergistic fluorescence emission turn-on and an enhancement of the MR longitudinal relaxation rate. With the addition of *Escherichia coli* cells, the fluorescence intensity of P21d constantly increased with a linear relationship against the bacterial concentration. Furthermore, after incubation of HeLa cells with P21d for 4 h, the bacteria were sterilized, demonstrating a 'sensing/killing' bifunctional system that could be used for bacterial prevention/prohibition (Figures 6e and f).

Microporous materials

Combinations of conjugated microporous polymers (CMP) and AIE attributes are of great interest because of their high surface areas,

chemical stabilities and fluorescence responses. Based on previously reported AIE-active CMPs, recent efforts have focused on improving fluorescence efficiencies and porosities. For example, porous polymer networks **P26a–b** and **P27a–b** were prepared via reductive polyolefination processes, which exhibited intense yellow photoluminescence at ~ 560 nm, a remarkably high Φ_F of up to 25.3% and a moderately high Brunauer–Emmett–Teller surface area of $475 \text{ m}^2 \text{ g}^{-1}$ (Figures 7a and b).⁵⁵

Poor processability is one of the major obstacles in the field of CMPs. To prepare highly emissive porous polymer films, Jiang and co-workers⁵⁶ developed a high-throughput and facile synthetic method for the direct synthesis of large-area porous thin films at the liquid–electrode interface. TPE monomers with multiple peripheral carbazole units were used to enable site-specific electropolymerization, and phenylene linkers were used to introduce twists for the electrochemical synthesis of three-dimensional porous skeleton **P28** (Figure 7c). Polymer films with smooth surface morphologies were produced on electrodes through multicycle cyclic voltammetry of the monomer. The shapes and thicknesses of the films could be precisely controlled according to the electrode and the number of CV cycles, respectively. The Brunauer–Emmett–Teller surface area of **P28** was $1020 \text{ m}^2 \text{ g}^{-1}$, representing the highest value among the reported conjugated microporous AIE polymers (Figure 7d). Furthermore, the porous films exhibited green emission at 524 nm with a high Φ_F of $\sim 40\%$, irrespective of film thickness, which was much larger than that of the solution ($\Phi_F = 5\%$) and spin-coated thin film ($\Phi_F = 21\%$) of the monomer, representing one of the most emissive AIE porous materials developed to date.

Circularly polarized luminescence

CPL is another promising application for AIE polymers because of their tunable structures, optoelectronic properties and ease of fabrication.^{57–59} Most importantly, unlike common chiral conjugated polymers, the luminescence of AIE polymers does not quench when the polymers are in aggregated or solid states. The CPL performance of a material is characterized by the emission dissymmetry factor g_{lum} , which is defined as $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the emission intensities of left and right circularly polarized light, respectively.⁶⁰ Zhu and co-workers⁶¹ previously reported the development of an AIE-active conjugated polymer with side-chain chirality, which exhibited CPL behavior and a high g_{lum} value of 0.44. Recently, the authors synthesized a series of conjugated AIE polymers with main-chain chirality and observed an aggregation-induced CPL signal from the luminescent nanoaggregates of **P16**.¹⁶ The CPL signal was not observed in a THF solution of **P16** or in the nanoaggregates of other similar polymers, such as **P17**. Furthermore, the CPL intensity of **P16** could be tuned by adjusting the water content in the aqueous mixture, indicating a possible relationship between CPL properties and the microstructures of the nanoaggregates (Figure 8a). The CPL signals were gradually enhanced until an 80 vol% of water was added and the g_{lum} value of **P16** reached approximately -1.6×10^{-3} in the 80 vol% aqueous mixture, corresponding to the right-handed helical structure. Transmission electron microscopy and atomic force microscopy studies suggested that **P16** self-assembled into helical nanofibers during the aggregation process (Figure 8b).

CONCLUSION

In this focus review, recent progress in the field of AIE polymers was introduced, including the newly reported structures of AIE polymers and their updated performances in various applications. New synthetic methods and techniques have been utilized to prepare AIE polymers,

such as olefin metathesis ring-opening polymerization and MCTP, as well as electrochemical synthesis of AIE porous films. In particular, the use of AIEgen-containing initiators and living polymerization to build functional AIE polymers with defined chain lengths has become popular. With such synthetic approaches, the chemical and topological structural scope of AIE polymers has been expanded and places an emphasis on the addition of functional groups, which has resulted in enhancements of their water solubilities, biocompatibilities, porosities and stimuli responsiveness. Great progress has also been made in the application of AIE polymers such as explorations in shape memory AIE materials, the use of AIE probes for bacterial imaging and inhibition, and the development of AIE-CMPs.

The current trend of AIE polymers combines properties of well-documented traditional functional polymers with AIE features to endow the materials with both AIE characteristics and specific functionalities, such as stimuli-responsive properties, porosity, chirality, water solubility and MR, to achieve new fluorescence-based applications. Most of the reported AIE polymers are based on TPE structures because of their synthetic feasibility. There is an urgent need to develop new AIE systems with improved luminescence properties, such as red/near infrared emission and high emission efficiency, which may be able to significantly improve their performances in various applications, especially in biological applications. It is hoped that the continuous effort of scientists from all over the world and the rapid development of this field will result in breakthroughs in synthetic approaches, polymer structures, functionalities and applications of AIE polymers in the near future.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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