

Recent Progress in AIE-active Polymers

Hu Yu Bing, Lam Jacky W. Y., Tang Ben Zhong

Cite this article as:

Hu Yu Bing, Lam Jacky W. Y., Tang Ben Zhong. Recent Progress in AIE-active Polymers[J]. *Chinese J. Polym. Sci.*, 2019, 37(4): 289-301. doi: 10.1007/s10118-019-2221-4

View online: <https://doi.org/10.1007/s10118-019-2221-4>

Articles you may be interested in

[Recent Advances and Progress for the Fabrication and Surface Modification of AIE-active Organic-inorganic Luminescent Composites](#)

Chinese J. Polym. Sci. 2019, 37(4): 340 <https://doi.org/10.1007/s10118-019-2208-1>

[AIE-active Polymers for Explosive Detection](#)

Chinese J. Polym. Sci. 2017, 35(2): 141 <https://doi.org/10.1007/s10118-017-1882-0>

[Recent Progress in Fluorescent Vesicles with Aggregation-induced Emission](#)

Chinese J. Polym. Sci. 2019, 37(4): 352 <https://doi.org/10.1007/s10118-019-2204-5>

[具有聚集诱导发光特性的磷光聚合物的合成及性能研究](#)

Synthesis and Properties of Phosphorescent Polymers with Aggregation-induced Emission

高分子学报. 2019, 50(1): 27 <https://doi.org/10.11777/j.issn1000-3304.2018.18160>

[聚集诱导发光聚合物](#)

Polymers with Aggregation-induced Emission Characteristics

高分子学报. 2018(2): 132 <https://doi.org/10.11777/j.issn1000-3304.2018.17280>

[水溶性荧光增强共轭聚合物的合成及性能研究](#)

SYNTHESIS AND PROPERTIES OF A WATER-SOLUBLE AGGREGATION-INDUCED EMISSION ENHANCEMENT CONJUGATED POLYMER

高分子学报. 2012(4): 453 <https://doi.org/10.3724/SP.J.1105.2012.11322>

Recent Progress in AIE-active Polymers

Yu Bing Hu^{a,b}, Jacky W. Y. Lam^{a,b,c*}, and Ben Zhong Tang^{a,b,c*}^a HKUST-Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China^b Department of Chemistry, The Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction and Institute for Advanced Study, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China^c Center for Aggregation-Induced Emission, SCUT-HKUST Joint Research Institute, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

Abstract The demand for highly efficient solid-state luminophores is continuously growing due to their potential applications in optoelectrical devices, chemosensors, and biological applications. The discovery of luminogens with aggregation-induced emission (AIE) by Tang *et al.* in 2001 provides a good response to this demand. Among the exploited AIE luminogens, AIE-active polymers possess many advantages such as simple synthesis, convenient structure modifications, and good processability, which offer an extensive platform for scientists and engineers. Herein, the design principles and latest synthetic advancement of AIE-active polymers are summarized, including click polymerization and multicomponent polymerization. Non-conjugated heteroatom-rich polymers were *in situ* generated and demonstrated non-conventional clusteroluminescence. Advanced applications including fluorescent sensors, stimuli-responsive materials, biological applications, circularly polarized luminescence, and electroluminescence are then introduced in detail. AIE-active polymers display the signal-amplification effect for sensitive and selective response to chemo/bioanalytes or stimuli and enhanced photosensitization effect for cancer theranostics. Retrospecting the expansion of this field can further strengthen our belief that AIE-active polymers are promising for conceptual innovation and technological breakthroughs in the near future.

Keywords Aggregation-induced emission; Polymer synthesis; High-tech application

Citation: Hu, Y. B.; Lam, J. W. Y.; Tang, B. Z. Recent progress in AIE-active polymers. *Chinese J. Polym. Sci.* 2019, 37, 289–301.

INTRODUCTION

Since the first report in 2001, research on luminophores with aggregation-induced emission (AIE) characteristics has become a hot topic in the fields of chemistry and material science.^[1] AIE is exactly opposite to the aggregation-caused quenching (ACQ) effect observed in traditional luminophores and its discovery allows scientists to exploit the aggregation effect rather than against it. Over the past decades, considerable achievements have been reached in the development of AIE luminogens (AIEgens) and exploration of high-tech applications such as chemo/bio-sensing, biological imaging and therapy, and organic light-emitting diodes (OLEDs). In contrast to the conventional luminogens, AIEgens are generally propeller or shell in shape and are non-emissive or weakly emissive in dilute solution but emit intensely in the aggregate or solid state. It is widely accepted that the AIE phenomenon could be attributed to the restriction of intramolecular motions (RIM), including rotation and vibration. In dilute solution, AIEgens undergo active intramolecular motions, which consumes the energy of the excited state through a non-radiative decay pathway to

quench the emission. In the aggregate state, the restriction of intramolecular motions in a crowded environment blocks the pathway of non-radiative decay to prompt emission. Great progress has been made either in small molecular AIEgens or AIE-active polymers, which has been summarized in several review papers.^[2–5]

The first AIE-active polymers were reported in 2003, which inspired rapid development afterwards.^[6] Compared to small molecules, AIE-active polymers display more attractive advantages such as structure variation, multiple functionalization, high processability, and simple device fabrication. In this review, we present the progress in AIE-active polymers in last three years and illustrate it in two aspects: the synthetic strategies and applications. Herein, we classify the construction method of AIE-active polymers into five types according to the roles of AIEgens in the polymerizations. We then discuss the potential applications of AIE-active polymers including fluorescent sensors, stimuli-responsive materials, biological applications, and optoelectronic devices. From the discussion of this review, we hope to gain deeper insight for design principles and applications of AIE-active polymers to give an inspiration to the future innovation in this field.

CONSTRUCTION OF AIE-ACTIVE POLYMERS

The synthetic strategies of AIE-active polymers have been extensively broadened with the rapid development of AIE

* Corresponding authors: E-mail chjacky@ust.hk (J.W.Y.L.)

E-mail tangbenz@ust.hk (B.Z.T.)

Invited review for special issue of "AIE-active Polymer"

Received November 27, 2018; Accepted January 7, 2019; Published online February 2, 2019

research over the past decades. Incorporating or generating typical AIEgens such as tetraphenylethene (TPE) in polymer frameworks is critical for the construction of AIE-active polymers.^[7] Specifically, AIE-active polymers could be prepared by initiating with AIEgens, linking AIEgens-containing monomers, polymerizations of AIE-inactive precursors with *in situ* generation of AIEgens, post-polymerizations, and supramolecular self-assembly.

AIEgens as Polymerization Initiators

Polymerizations initiated by AIEgens have been established as simple and convenient methods to afford end/core-functionalized AIE-active polymers. Typically, they are referred as controlled free radical polymerizations including reversible addition fragmentation chain transfer (RAFT) polymerizations and atom transfer radical polymerizations (ATRP). It is fascinating that only one AIEgen moiety could endow the resulting polymers with intense fluorescence and AIE properties. For instance, the Cu-catalyzed ATRP of *t*-butyl acrylate monomers was initiated by tetraphenylthiophene derivatives, affording AIE-active polymers P1 with a number of repeating unit (n) of 21.65 (Fig. 1a).^[8] Wei's group reported a photo-initiated RAFT copolymerization of itaconic acid and styrene, in which TPE-based AIEgen worked as chain transfer agent and photo-iniferter agent (Fig. 1b).^[9] Copolymers P2 with a number-average molecular weight (M_n) of 8496 and a narrow polydispersity (PDI)

of 1.15 was obtained and could self-assemble into AIE-active nanoparticles (NPs) in aqueous medium due to the presence of both hydrophilic and hydrophobic units. Furthermore, initiators with two or more arms could construct core-functionalized branched or star polymers. A TPE derivative with two arms initiated the ATRP of *N*-isopropylacrylamide under the catalyst system of CuCl/Me₆TREN, yielding temperature-sensitive polymers P3 with $M_n = 32$ kDa and PDI = 1.9 (Fig. 1c).^[10] A TPE derivative with four arms was utilized as the initiator for synthesizing star polymers P4 with $M_n = 2.7 \times 10^4$ and PDI = 1.224 (Fig. 1d).^[11] All those polymers displayed enhanced emission in THF/water mixture with higher water fraction (f_w) or concentration-increased solutions, which proved the excellent inheritance of AIE properties from initiators.

AIEgens as Polymerization Monomers

Generally, AIEgens as monomers could be embedded into polymers either by free-radical polymerization such as RAFT and ATRP, or traditional metal-catalyzed coupling polymerizations such as Suzuki polycondensation, Sonogashira polycondensation, and McMurry polycondensation. Recently, a one-pot operation of multicomponent reactions (MCRs) and RAFT polymerization of monomers, amino-containing AIEgens, and mercaptoacetic acid, was designed and carried out (Fig. 2a).^[12] Thanks to the high efficiency of such a facile

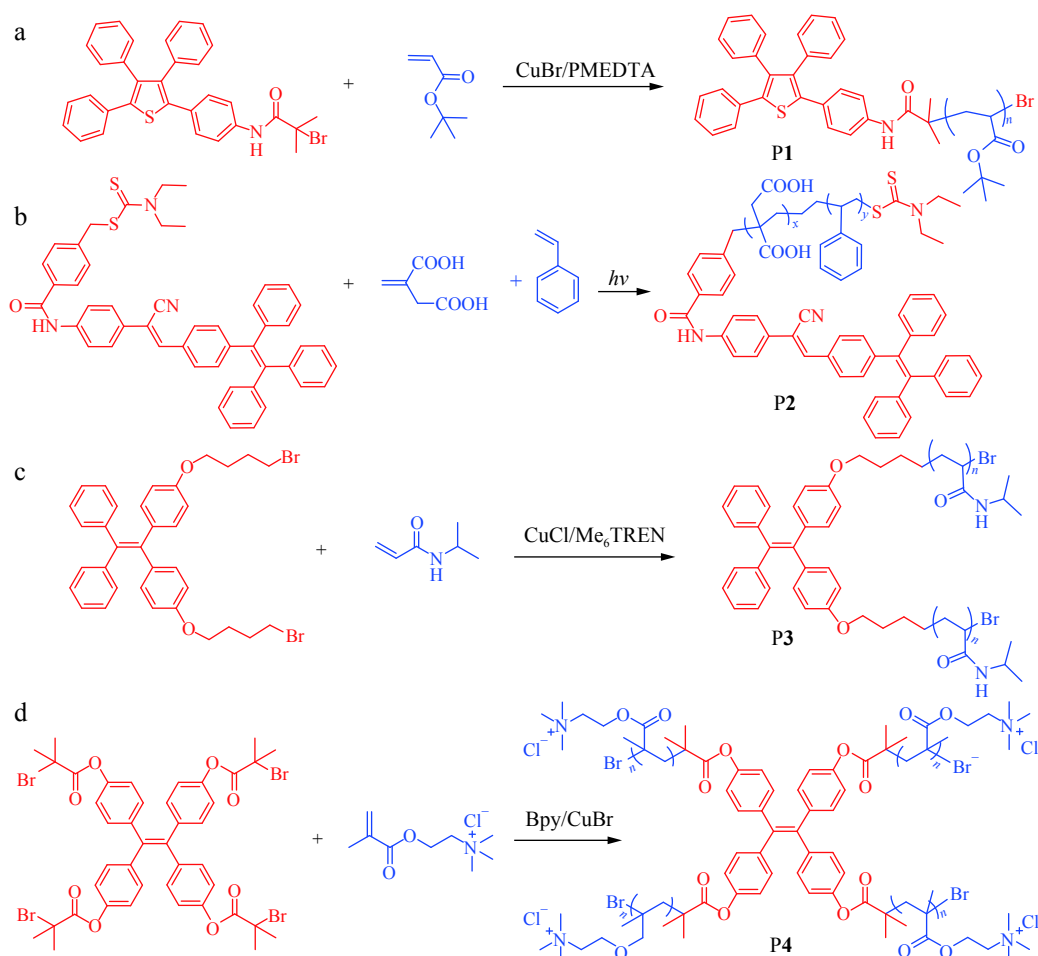


Fig. 1 Synthetic routes to AIE-active P1–P4 by AIEgen-initiated polymerizations

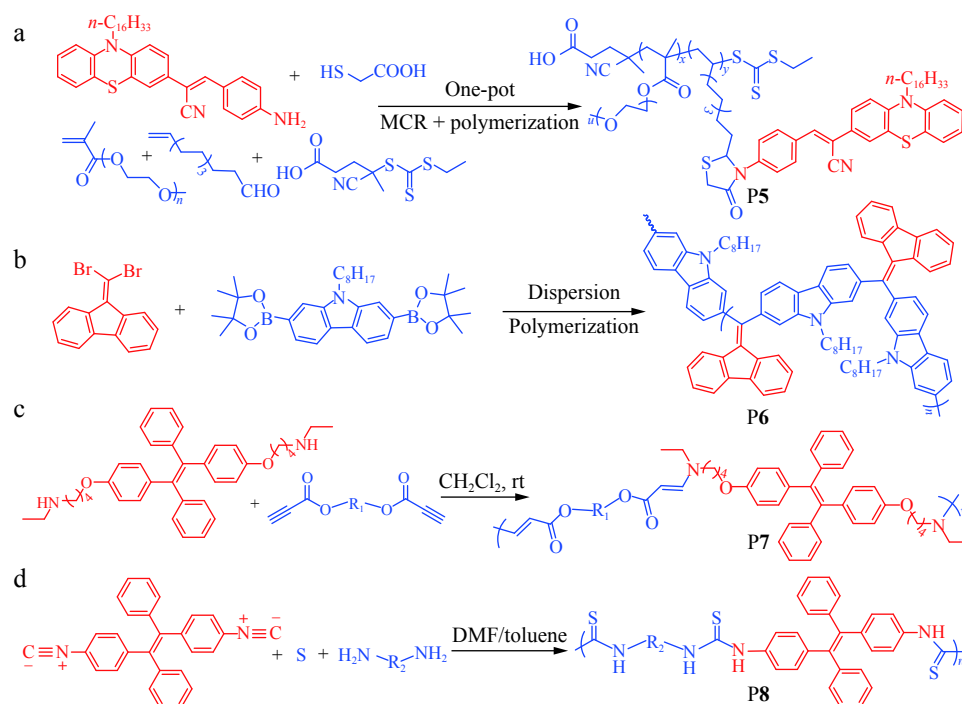


Fig. 2 Synthetic routes to AIE-active P5–P8 from AIEGen-containing monomers

method, the resulting amphiphilic polymers P5 with AIE-active pendants would self-assemble into NPs in aqueous solution with intense fluorescence. Zhu and his coworkers reported dispersion polymerization *via* geminal Suzuki cross-coupling reaction of dibromides and bis(pinacolato)diborons to prepare the mono-dispersed NPs of AIE-active conjugated polymer P6 (Fig. 2b).^[13] The resulting NPs of P6 possessed well-defined spheric structure with tunable size (mean particle diameter: 229–958 nm) and demonstrated increased emission in particle form compared to dissolved form. Click polymerization has firmly grasped the attention of polymer scientists for its high efficiency and mild reaction conditions. Considering metal catalysts as residues in traditional click polymerization such as azide-alkyne cycloaddition,^[14] Tang's group developed a novel spontaneous amine-yne click polymerization for efficient preparation of regio- and stereospecific poly(enamine)s P7 (Fig. 2c).^[15] Without external catalyst, regio- and stereospecific P7 were obtained with high weight-average molecular weight (M_w , up to 6.44×10^4) in high yields (up to 99%). By incorporating TPE derivatives in polymer chain, P7 showed AIE behavior in THF/H₂O mixture. Multicomponent polymerizations (MCPs) with fascinating characters, such as high efficiency, simple operation, and broad structural diversity, provide a wonderful platform for the construction of AIE-active polymers. The efficient and atom-economical synthesis of polythioureas P8 from sulfur, diamines, and diisocyanides has been completed by a catalyst-free MCPs (Fig. 2d).^[16] TPE-containing diisocyanides were utilized for preparation of AIE-active P8 and exploration of mercury detection and removal.

In Situ Generation of AIE-active Polymers

To acquire AIE-active polymers without previous time-consuming synthesis of AIEgens, a simple and straightfor-

ward *in situ* generation strategy by AIE-inactive starting materials was proposed by Tang's group in 2015.^[17] Poly-coupling of AIE-inactive diyne, diiodobenzene, and phenyl boronic acid was catalyzed by palladium and sodium fluoride, which *in situ* generated poly(tetraarylethene) P9 with typical AIE behavior (Fig. 3a). Tang's group continued to explore such a convenient and efficient polymerization method. In 2016, poly(triphenylacrylonitrile) P10 with high M_w (up to 2.23×10^5) was prepared by palladium-catalyzed polymerization of AIE-inactive diyne, dibromobenzene, and potassium ferrocyanide (Fig. 3b).^[18] The *in situ* generated triphenylethene chromophore imparted the resulting polymer P10 with strong solid-state emission due to the restricted rotation of the phenyl rings.

Our group first proposed the cluster-triggered emission mechanism to explain the unconventional solid-state emission of nonconjugated heteroatom-rich synthetic polymers in 2014.^[19] In 2015, Zhu's group synthesized linear and hyperbranched aliphatic poly(amido amine)s, P11 and P12, by Michael-type polycondensation in DMF and water, respectively (Fig. 3c). The resulting water-soluble polymers showed enhanced emission when increasing the solution concentration from 0.1 mg/mL to 20 mg/mL and red-shifted emission at higher excitation wavelength. Such a phenomenon was understandable due to the formation of cluster formation with extended electronic delocalization and conformation rigidification.^[20] In 2018, our group synthesized azetidine-containing polymers P13, which exhibited red-shifted and enhanced emission from solution to aggregate or solid state and showed an obvious excitation-dependent emission behavior (Fig. 3d).^[21] Such an unconventional phenomenon promoted the mechanism study by theoretical calculation. Results showed that heteroatom cluster formation and through-space conjugation were beneficial to the conformational rigidifica-

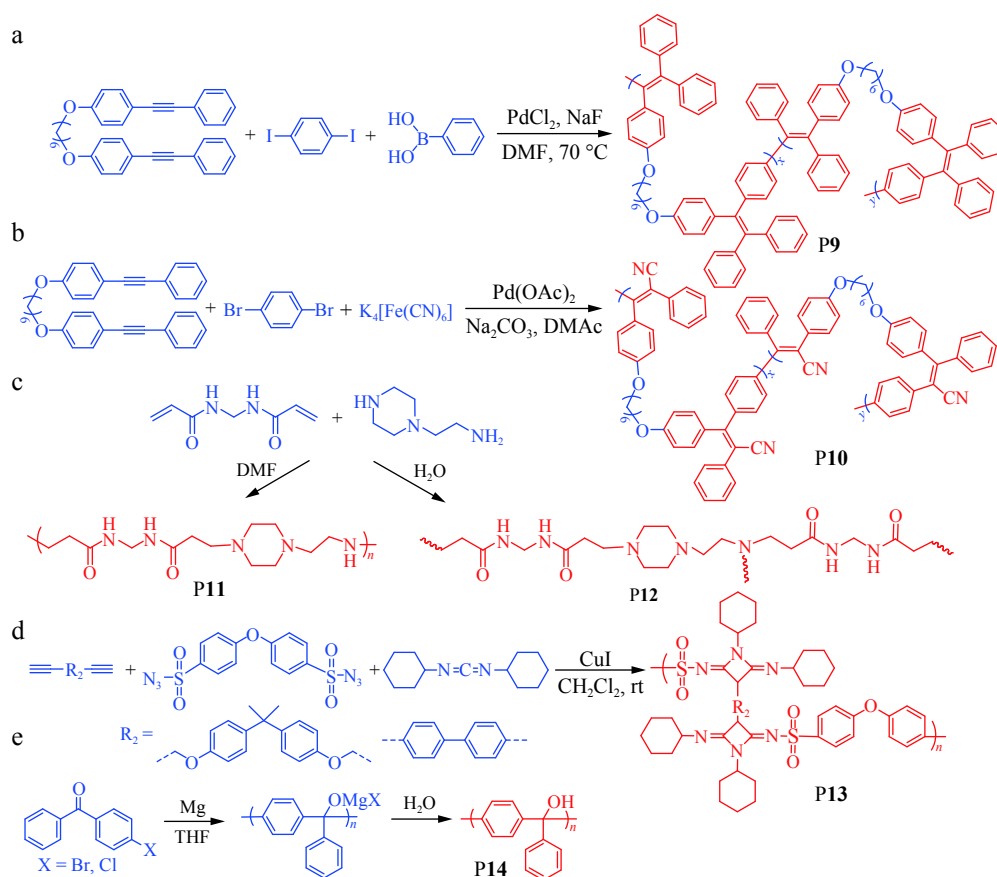


Fig. 3 Synthetic routes to *in situ* generated AIE-active polymers P9–P14

tion to restrict intramolecular motions in the aggregate state. Also, Wan's group successfully developed Barbier reaction into one-pot polyaddition of halide and benzoyl-containing monomers, yielding *para*-phenylmethanol group containing polymers **P14** without typical AIEgen as a structural unit, which showed non-conventional AIE-active luminescence and thermoresponsive behavior (Fig. 3e).^[22]

Post-functionalization

Modification to synthetic or natural polymers can be another way to achieve AIE-active polymers. Usually, AIEgens are attached to polymers as pendants or connectors *via* polymer reactions such as aldimine condensation and click reaction. For example, TPE molecules were grafted onto the polymer side-chains *via* pH-cleavable hydrazone bonds by the reaction of benzaldehyde groups and hydrazine groups (Fig. 4a).^[23] The resulting AIE-active copolymer **P15** could self-assemble into micelles and swell under pH = 5.0 after bond cleavages, for applications in bio-imaging and pH-responsive drug delivery. In 2017, Wei's group post-polymerized an amino-containing polymer by its Kabachnik-Fields reactions with benzaldehyde group and diethyl phosphate, which rendered AIE-active polymeric nanoparticle **P16** under microwave irradiation for 5 min (Fig. 4b).^[24] For another aspect, functionalization of natural polymers such as glucan,^[25] chitosan,^[26] and starch^[27] has been performed to give biomacromolecules with good water dispersity, excellent biocompatibility and stability, and strong solid-state emission. For instance, aldehyde-containing TPE and glucan

were connected by 3-aminobenzeneboronic acids *via* Schiff base and phenyl borate bonds, generating AIE-active green emissive polymers **P17** (Fig. 4c).^[25] As shown in Fig. 4(d), sodium alginate from marine seaweeds was oxidized first to acquire aldehyde groups followed by Schiff base condensation with amino-containing AIEgens, giving AIE-active red-emissive polymers **P18**.^[28]

Supramolecular Polymers

Unlike conventional polymers discussed above, supramolecular polymers are formed by connecting AIE-active monomers *via* strongly directive and reversible non-covalent interactions such as hydrogen bonding, host-guest interaction, and metal-coordination bonds. In 2017, our group incorporated ureidopyrimidinone (UPy) with TPE to prepare TPE-UPy with strong binding strength (Fig. 5a).^[29] (*Z*)- and (*E*)-TPE-UPy were successfully separated by column chromatography and both showed evident AIE feature in THF/water mixture but different aggregate-state emissions. Through isodesmic polymerization, supramolecular polymers **P19** were formed by (*E*)-TPE-UPy in dilute solution and confirmed by viscosity experiments. Sun's group synthesized two TPE-derivatives with dibenzo-24-crown-8 (DB24C8) and benzylamino moieties as host-guest molecules and reversible acid/base-induced turn-on/turn-off behaviors (Fig. 5b).^[30] Jiang's group obtained AIE-active coordination polymers **P21** of Ag⁺ and TPE-containing thiol ligand, connected by the *in situ* formed Ag–S bonds and Ag⁺⋯Ag⁺

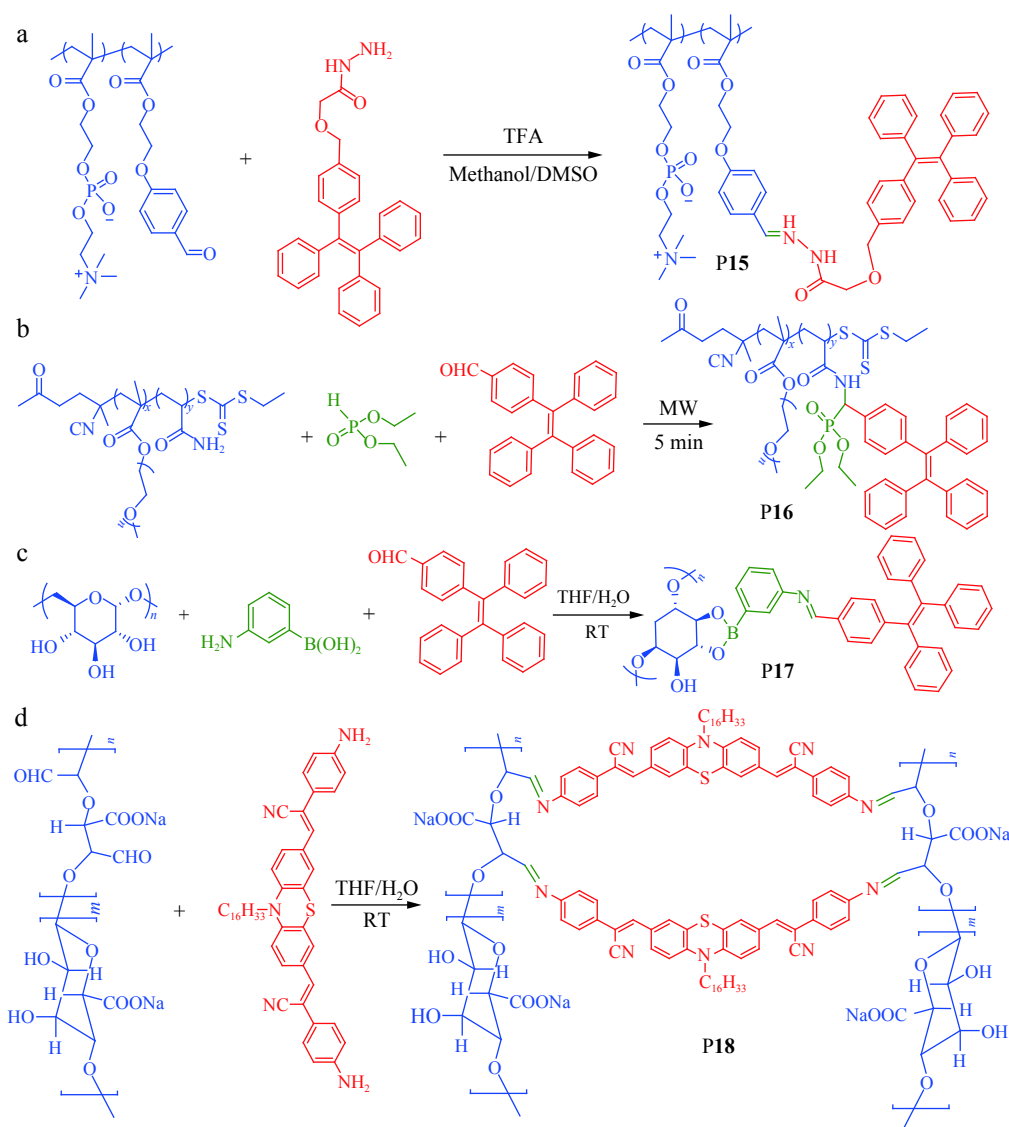


Fig. 4 Synthetic routes to AIE-active polymers P15–P18 by post-polymerizations with AIEgens

interaction (Fig. 5c).^[31] Furthermore, supramolecular polymers with two or more non-covalent interactions offer a simple and convenient way to construct different topologies from linear to branched and hyperbranched. For instance, hyperbranched supramolecular polymers P22 were linked by the metal-ligand coordination interactions of terpyridine/Zn and host-guest interactions of DB24C8/benzylamino salts (Fig. 5d).^[32] The formation of hyperbranched structures would restrict the intramolecular motions of TPE moieties to enhance the fluorescence.

APPLICATION OF AIE-ACTIVE POLYMERS

Since the first report on AIE-active polymers in 2003,^[6] numerous research interests from academic and technological areas have been devoted to this field. Many exciting results were generated and summarized in recent reviews. From the synthetic perspective, various polymerizations offer a broad monomer scope to afford polymers with considerable structure diversity and multifunctional applications. The incorporation of attractive AIE effect to polymers will lead to

materials with strong light emission in the aggregate state and amplification effect, which demonstrate obvious advantages in sensing and biological areas. As the use of AIE concept in polymer science is rich and the development of AIE-active polymers is rapid, we are not able to include all the applications of AIE-active polymers in this review but would like to introduce their use in fluorescent sensors, biological imaging and therapy, stimuli-responsive materials, and devices with circularly polarized luminescence in the past three years.

Fluorescent Sensors

In 2007, Swager *et al.* reported the signal amplification of conjugated polymers (CPs) due to the efficient electron communication and energy migration along the polymer backbone under excitation.^[33] However, conventional CPs would suffer from severe aggregation-caused quenching (ACQ) effect due to strong π - π interactions, which led to weak fluorescence and limited their applications. To solve the ACQ problem, AIE-active polymeric sensory systems were designed and developed. Furthermore, AIE-active

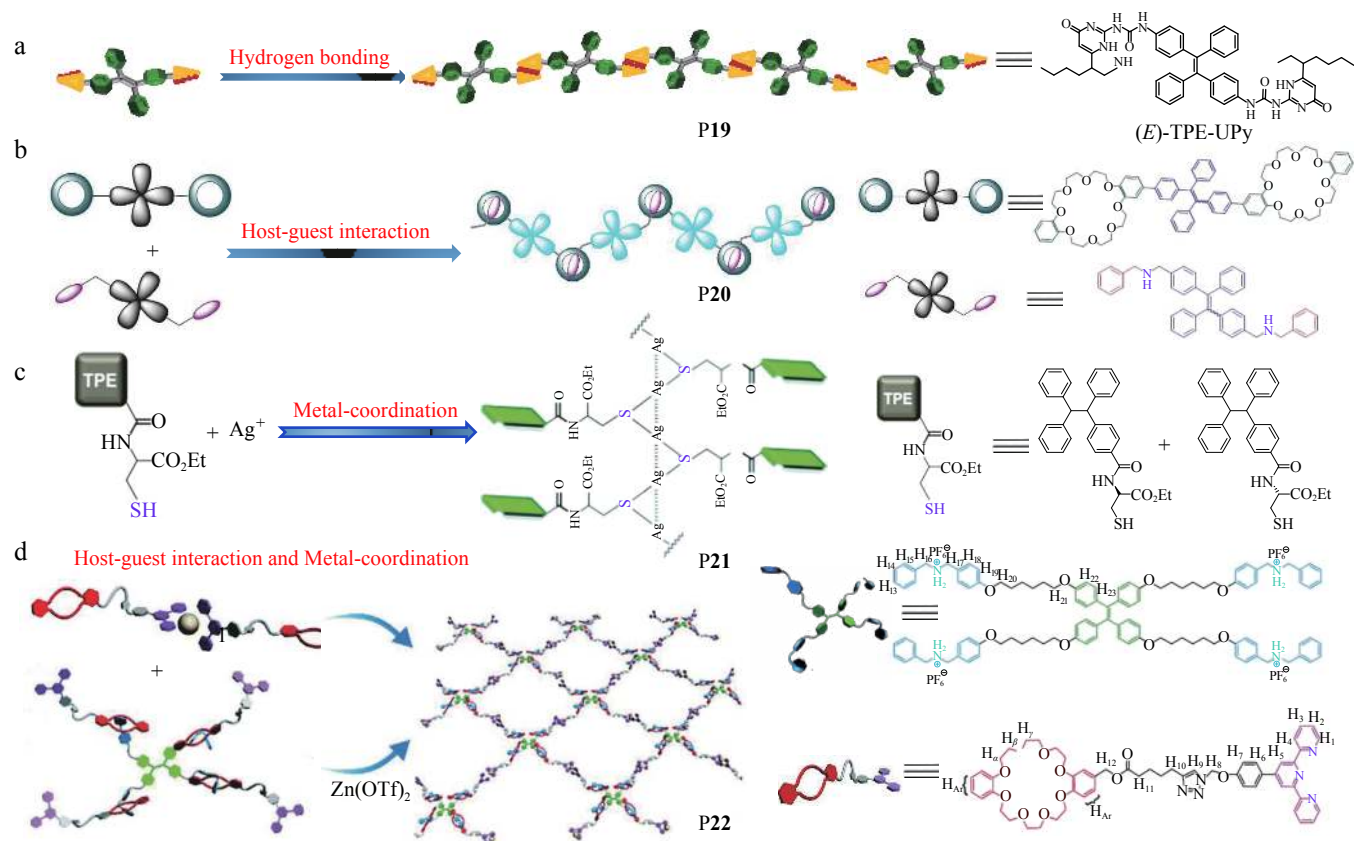


Fig. 5 Synthetic routes to AIE-active supramolecular polymers P19–P22 (Reproduced with permission from Refs. [29–32]; Copyright (2017) American Chemical Society, Copyright (2015) (2017) (2016) The Royal Society of Chemistry)

polymers usually contain many phenyl groups with a high degree of rotational freedom. This prevents close molecular packing and increases the chance to react with analytes, thus realizing “super-amplification” effect.^[34] Up to now, fluorescent sensors based on AIE-active polymers for detecting explosives,^[34] ions (Hg^{2+} , Ag^+ , Cd^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , Al^{3+} , CN^-),^[16,35–40] vapor (solvent, CO_2),^[41–43] pH,^[44] temperature,^[45] and biomolecules (BSA)^[46] have been developed.

Ion detection, especially heavy metal, is of great significance to environmental and health issues. The principle of ion detection is mainly based on molecular recognition. Thus, the main design strategy is incorporating AIE-active moieties and recognition units into polymers. In 2016, our group developed a highly selective and sensitive polymer-based detector of Al^{3+} synthesized by click polymerization of water-soluble units and AIEgens (Fig. 6a).^[35] Experiments showed that only Al^{3+} could largely increase the emission of polymer with a detection limit of as low as 31 ppb. Such a value is much lower than that (200 ppb in drinking water) proposed by the U.S. Environmental Protection Agency (Fig. 6b). Mechanistic study suggested that Al^{3+} could coordinate with sulfonic group and nitrogen of the triazole ring in two different polymer chains. This partially restricted the polymer chains to result in emission generation. In 2018, polythioureas with AIEgens were fabricated for “turn-off” detection and removal of Hg^{2+} due to the strong binding ability of thioureas for heavy metal ions (Fig. 6c).^[16] Compared to various metal ions, polythioureas displayed specific fluor-

escence quenching effect to Hg^{2+} with a detection limit of 0.1 ppm. Moreover, the poor solubility of polythioureas- Hg^{2+} complex was utilized to eliminate Hg^{2+} with high removal efficiency (up to 99.99%) (Fig. 6d). Specifically, polythioureas could effectively reduce $[\text{Hg}^{2+}]$ from 10 mg/L to 0.8 $\mu\text{g/L}$ in 2 mL of HgCl_2 solution.

TPE-containing four-armed star polymer P24 could serve as a fluorescent sensor for CO_2 and also demonstrated pH-tunable thermoresponsive property (Fig. 6e).^[41] As shown in Fig. 6(f), the dilute (1.0 g/L) aqueous solution of P24 was a transparent and weakly emissive solution, which transformed into a turbid solution with strong emission when the solution temperature was raised above the lower critical solution temperature (LCST). Because the amidine groups in P24 could react with CO_2 to form charged amidinium bicarbonate, the fluorescence of P24 remarkably decreased with the increasing volume of CO_2 added (Fig. 6g). A linear relationship between the relative fluorescence (I_0/I , where I_0 was the emission intensity of the blank solution) and the volume of CO_2 proved the successful construction of CO_2 fluorescent sensor.

Stimuli-responsive Materials

Stimuli-responsive materials showing dramatic responses to subtle environmental stimuli are of both scientific and industrial interests.^[47] As their emission is highly sensitive to environmental change, a large variety of AIE-active polymers were developed into stimuli-responsive systems such as mechanical, temperature, light, and pH. For example, Chi

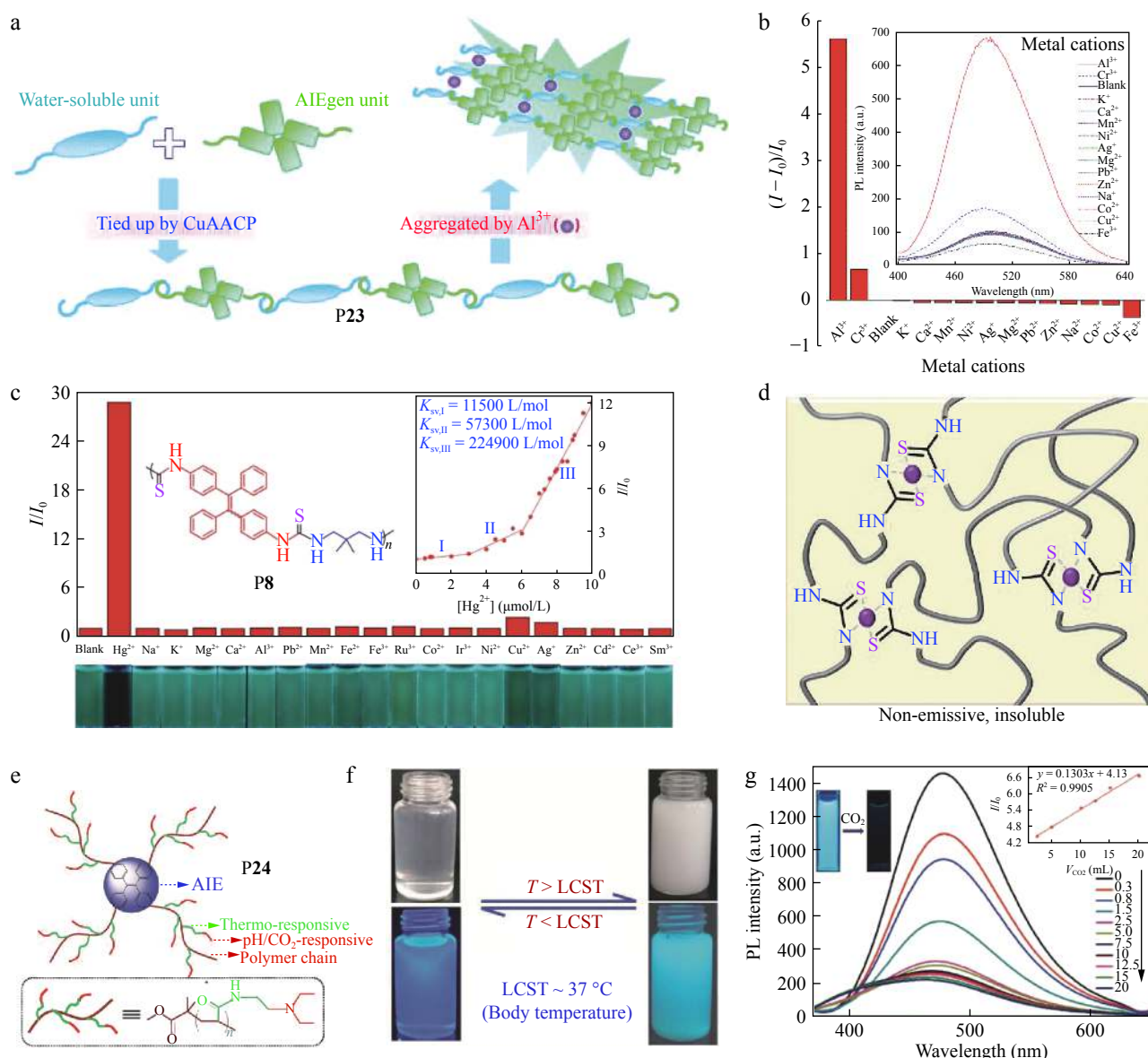


Fig. 6 (a) Proposed schematic sensing mechanism of P23 for Al^{3+} ; (b) Fluorescence detection of metal cations in DMSO/water mixture; (c) Fluorescence detection of mercury ion with polythiourea P8; (d) The proposed mechanism for mercury removal with P8; (e) Structure of four-arm star polymer P24; (f) Photographs of P24 at (left) 25 °C and (right) 40 °C under visible light and UV light; (g) Fluorescence spectra of P24 at different CO_2 volumes. Inset: plot of relative fluorescence intensity (I/I_0) versus CO_2 volume (Reproduced with permission from Refs. [35], [16], and [41]; Copyright (2016) The Royal Society of Chemistry, Copyright (2018) American Chemical Society, and Copyright (2018) Wiley-VCH)

and his coworkers reported the solid-state mechano-fluorochromism from a single-component polymer P25 in 2017 (Fig. 7a).^[48] The polymer was constructed by linking TPE groups as pedants to a conjugated and rigid mechanochromic backbone, which showed 5-fold enhanced emission in THF/water mixtures with 95% water fraction than that in THF. The emission color of the polymer changed from yellow to red as the emission maximum shifted from 541 nm to 602 nm after grinding or shearing. XRD analysis proved that this mechanochromism was related to the transformation of crystalline state to amorphous state. Thereafter, AIE-active mechano-responsive materials have been extended from small molecules to polymers.

Our group designed and prepared water-soluble thermo-

responsive polymers P26 by free radical polymerization of temperature-sensitive *N*-isopropyl acrylamide, hydrophilicity-tunable methyl methacrylate or oligo(ethylene glycol) methacrylate, and TPE derivatives.^[49] With different monomer ratios, the resulting polymers P26 exhibited variable hydrophilicity, tunable LCST, and temperature-dependent ranges as depicted in the contact angle measurement (Fig. 7b). During the repeatable and reversible heating-cooling cycle, P26 in aqueous solution performed enhanced emission with increased temperature (Fig. 7c). The linear temperature-responsive ranges of P26 could be modulated continuously from 23 °C to 47 °C and the biological temperature range. Lin and his coworkers combined TPE and photo-switchable diarylethenes (DAE) through protonable

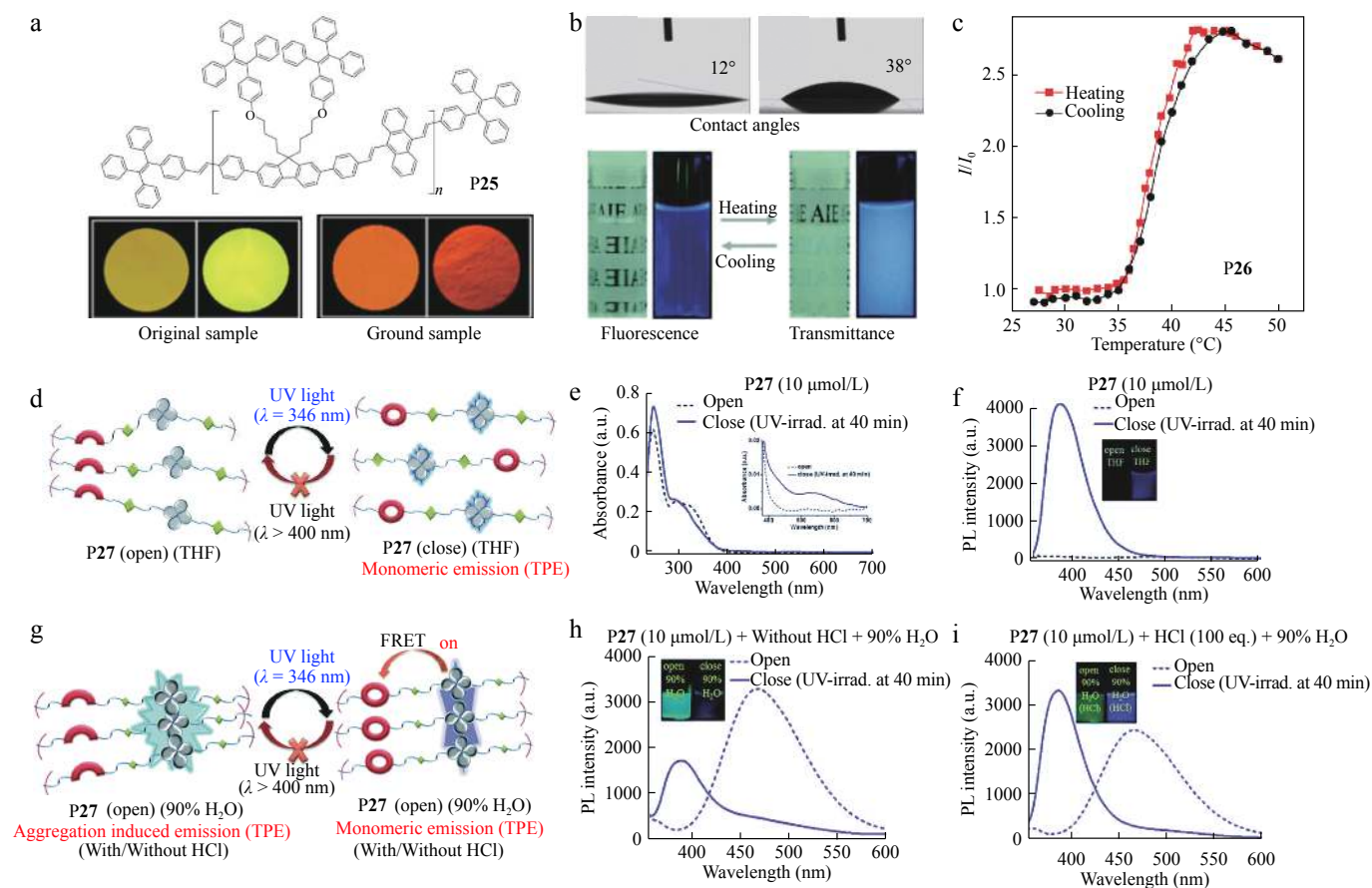


Fig. 7 (a) Structure of mechanoresponsive polymer **P25** and photographs of **P25** power before/after grinding under daylight and UV irradiation; (b) Photographs of contact angle with thin films and aqueous solution of thermoresponsive polymer **P26** upon heating and cooling taken under daylight and UV irradiation; (c) Temperature-dependent fluorescence of aqueous solution of **P26** in a heating-cooling cycle; **P27** in THF before and after UV-irradiation: (d) Pictorial diagram of **P27** (open to close), (e) UV-Vis spectral changes, and (f) PL spectral changes; **P27** at 90% aqueous mixture before and after UV-irradiation; (g) Pictorial diagram of **P27** (90% H₂O) from open to closed forms upon UV-irradiation; (h, i) PL spectral changes in **P27** with HCl (100 equiv.) (Reproduced with permission from Refs. [48–50]; Copyright (2017) Chinese Academy of Sciences and Springer-Verlag Berlin Heidelberg, Copyright (2016) The Royal Society of Chemistry, and Copyright (2017) The Royal Society of Chemistry)

flexible triazole linkers *via* click polymerization, giving the first example of photo-switchable polymers.^[50] As shown in the mechanistic scheme (Figs. 7d and 7g), the polymer **P27** showed various fluorescence changes when photocyclized in the presence of UV-irradiation under different conditions. In THF solution, the cycle-closed polymers showed TPE monomeric emission with the emission maximum at 385 nm (Figs. 7e and 7f). In semi-aqueous THF/water mixture, the polymers exhibited an AIE feature with the emission maximum at 466 nm but gradually transformed into monomeric emission due to energy transfer from TPE to cyclized DAE units after cyclization (Fig. 7h). Similar results were observed for polymers with protonated triazole under acidic conditions (Fig. 7i).

Biological Applications

In contrast to conventional fluorophores with ACQ, AIE-active polymers have numerous advantages, such as superior photostability, low background noise, high fluorescence efficiency, tunable water solubility/dispersibility, and good biocompatibility.^[51] Thanks to great endeavors from scientists, AIE-active polymers are developed from biological

imaging and diagnosis^[52] to fluorescence image-guided therapy.^[53–55] For example, Jin's groups reported an AIE-active image-guided chemotherapy by encapsulating doxorubicin (DOX) into pH-responsive zwitterionic polymer **P15** (Fig. 8a).^[23] When the self-assembled spherical micelles were incubated under endo/lysosomal acidic conditions (pH = 5), the hydrazine groups connected to TPE units would be cleaved to disassemble the micelles and release DOX drug. From the *ex vivo* fluorescence images, the polymeric micelles possessed the increased accumulation than free DOX, showing great potential for cancer theranostics.

Another thrilling therapeutic technique in the field of AIE-active polymer is photodynamic therapy (PDT), in which photosensitizers could ablate cancer cells by their ability to generate singlet oxygen (¹O₂) under light irradiation. In 2018, Wu reported the polymerization-enhanced photosensitization effect, which illustrated that the conjugated polymers showed higher photo-sensitization efficiency by up to 5.07-fold than their small molecular counterparts (Fig. 8b).^[56] The possible mechanism was deduced as that the numerous repeat units in conjugated polymers would introduce more channels for intersystem crossing (ISC) and

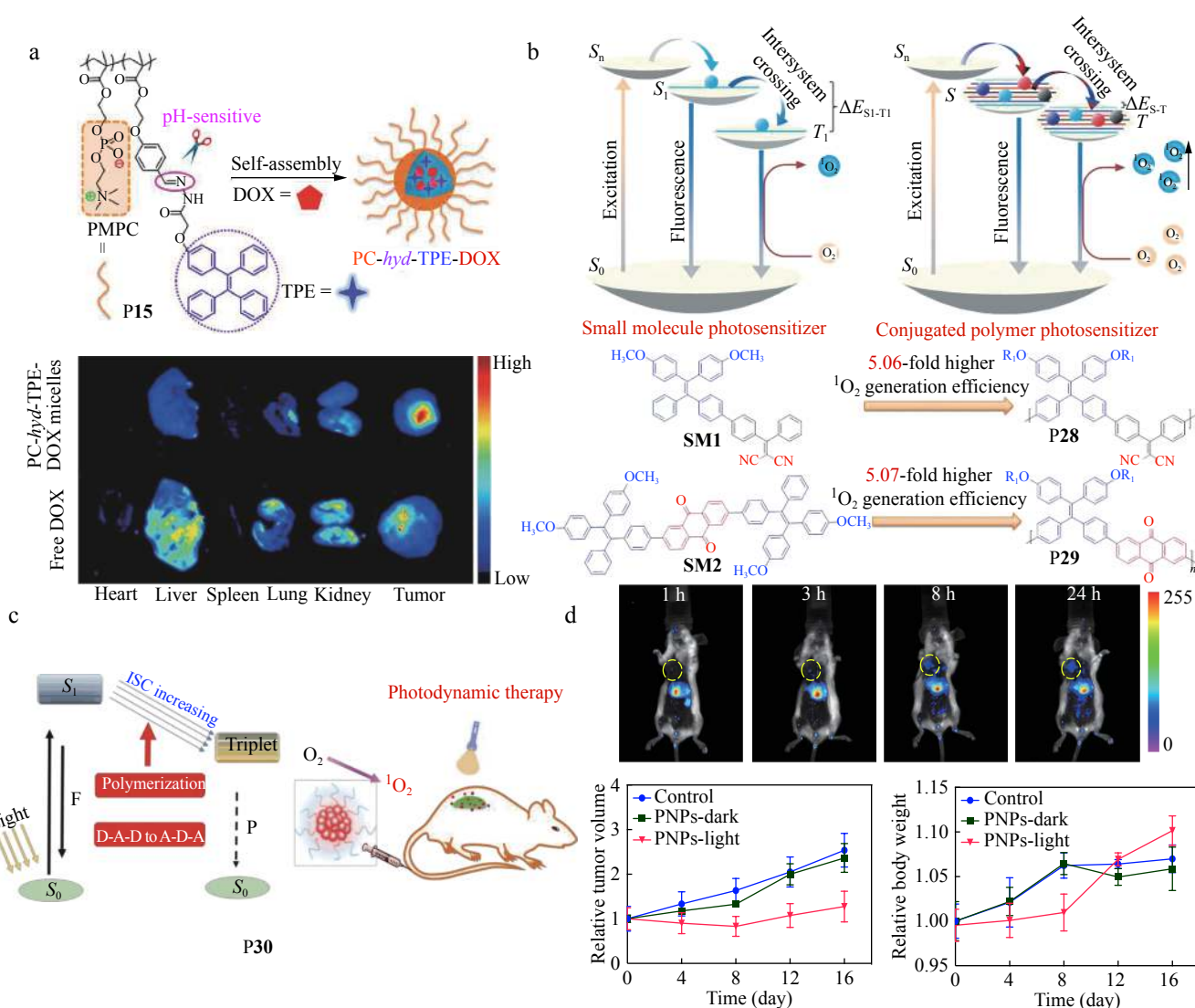


Fig. 8 (a) Schematic of pH-responsive zwitterionic polymeric micelles self-assembled by P15 and fluorescence images of excised tissues at 6 h post-injection of polymeric micelles and free DOX; (b) The different photosensitization processes of small-molecule and conjugated-polymer photosensitizers; (c) Enhanced photosensitization for application in PDT; (d) Tumor imaging of mouse after intravenous injection of PNPs at different time, as well as tumor growth curves and body weight changes of mice in different treatment groups (Reproduced with permission from Refs. [23], [56], and [57]; Copyright (2016) American Chemical Society, Copyright (2018) Elsevier B.V., and Copyright (2018) Wiley-VCH)

improve the light-harvesting ability. Recently, our group proposed two efficient strategies to acquire higher 1O_2 generation efficiency: polymerization and donor (D)-acceptor (A) even-odd effect. Generally, photosensitizers (PSs) with A-D-A structures behaved better than their D-A-D cousins (Fig. 8c).^[57] Theoretical analyses illustrated that the extended conjugation length could facilitate the ISC process from the lowest singlet excited state to the low-lying triplet excited states. Among those PSs, triphenylamine and benzothiadiazole were employed to construct P30 with enhanced 1O_2 generation efficiency of 14%. The image-guided PDT was conducted by P30 nanoparticles in xenograft 4T1 tumor-bearing balb/c mice, and the results are shown in Fig. 8(d). The treatment of P30 nanoparticles under light irradiation could efficiently inhibit the growth of tumor and promote the growth of body weight, indicating an effective PDT effect.

Circularly Polarized Luminescence and Electroluminescence

With efficient solid-state emission, simple preparation, and mechanical flexibility, AIE-active polymers have emerged for the fabrication of high-tech optoelectronic devices showing circularly polarized luminescence (CPL) and electroluminescence (EL).^[58] Recently, an AIE-active chiral polytriazole P31 with alanine pendants was synthesized and its controlled self-assembling behaviors and optical properties were investigated (Fig. 9a).^[59] AFM, TEM, and SEM analyses and fluorescence microscopy were utilized to observe the morphological transition from vesicles, “pear-necklace” to helical nano/micro fibers of P31 by tuning the polymer concentration or water fraction in the THF/water mixture (Fig. 9b). The detailed study on the self-assembly architectures in aggregate state depicted the formation of helical conformation triggered by cooperative effect of

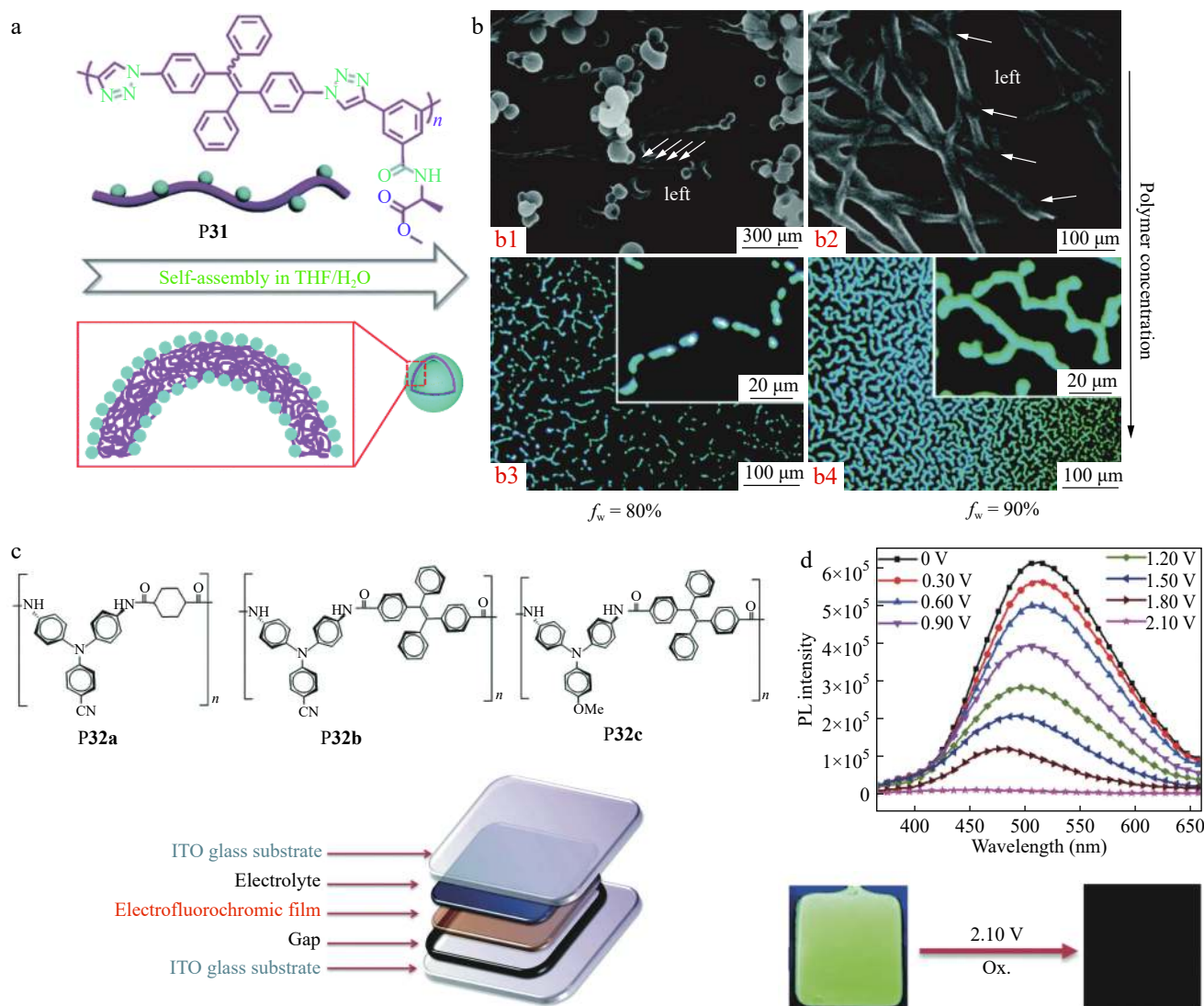


Fig. 9 (a) Schematic representation of the structure and self-assembly process of P31; (b) (b1, b2) TEM images of P31 in THF/water with water fraction (f_w) of 80% and 90% (10^{-5} mol/L), and (b3, b4) fluorescence images of P31 in THF/water with f_w of 80% and 90% (10^{-4} mol/L); (c) Chemical structures of polyamides P32 and schematic diagram of EFC devices based on P32; (d) Diagrams of applied voltage versus PL intensity of EFC devices based on thin films of P32b (Reproduced from Refs. [59] and [61]; Copyright (2018) The Royal Society of Chemistry)

noncovalent interactions. Such self-assembly may enable the polymer to find possible application in nano/micro devices and functional coating materials.

In 2006, Audebert's groups successfully prepared redox-active fluorescent compounds and their devices displayed emission change during the electrochemical switching.[60] To improve the emission contrast, Liou and his coworkers developed a series of AEE-active polyamides P32 from triphenylamine or TPE-based monomers to embed electro-active and strong-emissive properties in 2018 (Fig. 9c).[61] The solid films of P32a, P32b, and P32c with the high quantum yield of 46%, 16%, and 5% as well as emission maximum at 471, 510, and 554 nm were fabricated into electrofluorochromic devices (EFC). The EFC devices of P32 displayed reversible, fast-responsive, dual-switching electrochromic, and electrofluorescent behavior at low trigger voltage (Fig. 9d). The EFC devices based on TPE-containing P32

showed shorter switching response time (less than 4.9 s), stronger solid-state emission, and broader emission of full width at half maximum (up to 130 nm). Furthermore, Cheng *et al.* combined CPL and EL to design the first circularly polarized OLEDs from AIE-active main-chain chiral polymers, which showed doping-free circularly polarized electroluminescence with dissymmetric factor (g_{EL}) up to 0.024.[62]

CONCLUSIONS AND PERSPECTIVE

Over the past 17 years, the establishment of AIE concept has evoked the conceptual and technical revolution of fluorescence research. It has been qualified as a creative and extensive platform for exploration of new luminogens and high-tech applications. On the "big tree" of AIE, polymer-based materials display their advantages in accessible synthetic routes, structure diversity, multi-functional properties, and applications. The AIE-active polymers could be cons-

tructured by incorporating typical AIEgens in polymer skeletons through multiple synthetic techniques such as AIEgen-initiated RAFT or ATRP, *in situ* generation of AIEgens, and non-covalent bonding supramolecular polymerization. Newly developed small molecular AIEgens are encouraged to be combined with polymer science, which might inspire unique optoelectrical properties and exciting applications. Particularly, multicomponent polymerizations and post-polymerizations provide the highly efficient, straightforward, and convenient synthetic methods to AIE-active polymers. The non-conventional luminescence from non-conjugated heteroatom-rich polymers appears as the tip of the iceberg and more secrets are waiting for exploration. Studying the luminescent mechanism of natural and synthetic polymers through direct experimental results, such as the cluster formation induced by through-space conjugation, could be helpful for understanding the non-conventional luminescence.

In the field of AIE, aggregation plays a constructive role rather than a destructive one, which benefits various high-tech applications in the aggregate or solid state. Numerous efforts have been devoted to the applications of AIE-active polymers such as broader analytes for fluorescent sensors, novel mechano/photo-responsive materials, fluorescence image-guided therapy, and circularly polarized OLEDs. Remarkably, polymerization-enhanced photosensitization effect is promising to arouse the evolution of photodynamic therapy and cancer theranostics. The facile and efficient construction of high-performance circularly polarized OLEDs with high g_{EL} value by AIE-active polymers that possessed well-defined structures and precise-controlled chirality is still challenging. The continuous development of polymerization methodology is fundamentally important to obtain specific functional polymers. With so much challenges and opportunities, we believe that our passionate and earnest scientists will realize the bright future of AIE research.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21788102, 21490570, and 21490574), the Research Grant Council of Hong Kong (Nos. 16308116, 16303815, C2014-15G, C6009-17G, and A-HKUST605/16), the Science and Technology Plan of Shenzhen (Nos. JCYJ20160229205601482, JCY20170307173739739, and JCYJ20170818113602462), and the Innovation and Technology Commission (Nos. ITC-CNRC149C01 and ITS/254/17).

REFERENCES

- Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.* **2001**, 1740–1741.
- Hong, Y.; Lam, J. W.; Tang, B. Z. Aggregation-induced emission. *Chem. Soc. Rev.* **2011**, *40*, 5361–5388.
- Hu, R.; Kang, Y.; Tang, B. Z. Recent advances in AIE polymers. *Polym. J.* **2016**, *48*, 359.
- Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Aggregation-induced emission: Together we shine, united we soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- Qiu, Z.; Liu, X.; Lam, J. W.; Tang, B. Z. The marriage of aggregation-induced emission with polymer science. *Macromol. Rapid Commun.* **2018**, 1800568.
- Chen, J.; Xie, Z.; Lam, J. W.; Law, C. C.; Tang, B. Z. Silole-containing polyacetylenes. Synthesis, thermal stability, light emission, nanodimensional aggregation, and restricted intramolecular rotation. *Macromolecules* **2003**, *36*, 1108–1117.
- Hu, R.; Leung, N. L.; Tang, B. Z. AIE macromolecules: Syntheses, structures and functionalities. *Chem. Soc. Rev.* **2014**, *43*, 4494–4562.
- Yang, D. J.; Lin, L. Y.; Huang, P. C.; Gao, J. Y.; Hong, J. L. Tetraphenylthiophene-terminated poly(acrylic acid) as pH- and bio-sensors by the aggregation-induced emission property. *React. Funct. Polym.* **2016**, *108*, 47–53.
- Jiang, R.; Liu, M.; Huang, Q.; Huang, H.; Wan, Q.; Wen, Y.; Tian, J.; Cao, Q. Y.; Zhang, X.; Wei, Y. Fabrication of multifunctional fluorescent organic nanoparticles with AIE feature through photo-initiated RAFT polymerization. *Polym. Chem.* **2017**, *8*, 7390–7399.
- Wang, Z.; Yong, T. Y.; Wan, J.; Li, Z. H.; Zhao, H.; Zhao, Y.; Gan, L.; Yang, X. L.; Xu, H. B.; Zhang, C. Temperature-sensitive fluorescent organic nanoparticles with aggregation-induced emission for long-term cellular tracing. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3420–3425.
- Guan, X.; Zhang, D.; Jia, T.; Zhang, Y.; Meng, L.; Jin, Q.; Ma, H.; Lu, D.; Lai, S.; Lei, Z. Intriguingly tuning the fluorescence of AIEgen using responsive polyelectrolyte microspheres. *RSC Adv.* **2016**, *6*, 107622–107627.
- Wan, Q.; Jiang, R.; Mao, L.; Xu, D.; Zeng, G.; Shi, Y.; Deng, F.; Liu, M.; Zhang, X.; Wei, Y. A powerful “one-pot” tool for fabrication of AIE-active luminescent organic nanoparticles through the combination of RAFT polymerization and multicomponent reactions. *Mater. Chem. Front.* **2017**, *1*, 1051–1058.
- Chen, T.; Yin, H.; Chen, Z. Q.; Zhang, G. F.; Xie, N. H.; Li, C.; Gong, W. L.; Tang, B. Z.; Zhu, M. Q. Monodisperse AIE-active conjugated polymer nanoparticles *via* dispersion polymerization using geminal cross-coupling of 1,1-dibromoolefins. *Small* **2016**, *12*, 6547–6552.
- Chen, M.; Li, L.; Wu, H.; Pan, L.; Li, S.; He, B.; Zhang, H.; Sun, J. Z.; Qin, A.; Tang, B. Z. Unveiling the different emission behavior of polytriazoles constructed from pyrazine-based AIE monomers by click polymerization. *ACS Appl. Mater. Interfaces* **2018**, *10*, 12181–12188.
- He, B.; Su, H.; Bai, T.; Wu, Y.; Li, S.; Gao, M.; Hu, R.; Zhao, Z.; Qin, A.; Ling, J. Spontaneous amino-yne click polymerization: A powerful tool toward regio- and stereospecific poly(β -aminoacrylate)s. *J. Am. Chem. Soc.* **2017**, *139*, 5437–5443.
- Tian, T.; Hu, R.; Tang, B. Z. Room temperature one-step conversion from elemental sulfur to functional polythioureases through catalyst-free multicomponent polymerizations. *J. Am. Chem. Soc.* **2018**, *140*, 6156–6163.
- Liu, Y.; Roose, J.; Lam, J. W.; Tang, B. Z. Multicomponent polycoupling of internal diynes, aryl diiodides, and boronic acids to functional poly(tetraarylethene)s. *Macromolecules* **2015**, *48*, 8098–8107.
- Qiu, Z.; Han, T.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Pol-

- arylcyanation of diyne: A one-pot three-component convenient route for in situ generation of polymers with AIE characteristics. *Macromolecules* **2016**, *49*, 8888–8898.
- 19 Zhao, E.; Lam, J. W.; Meng, L.; Hong, Y.; Deng, H.; Bai, G.; Huang, X.; Hao, J.; Tang, B. Z. Poly[(maleic anhydride)-*alt*-(vinyl acetate)]: A pure oxygenic nonconjugated macromolecule with strong light emission and solvatochromic effect. *Macromolecules* **2014**, *48*, 64–71.
- 20 Wang, R. B.; Yuan, W. Z.; Zhu, X. Y. Aggregation-induced emission of non-conjugated poly(amido amine)s: Discovering, luminescent mechanism understanding and bioapplication. *Chinese J. Polym. Sci.* **2015**, *33*, 680–687.
- 21 Han, T.; Deng, H.; Qiu, Z.; Zhao, Z.; Zhang, H.; Zou, H.; Leung, N. L.; Shan, G.; Elsegood, M. R.; Lam, J. W. Facile multicomponent polymerizations toward unconventional luminescent polymers with readily openable small heterocycles. *J. Am. Chem. Soc.* **2018**, *140*, 5588–5598.
- 22 Sun, X. L.; Liu, D. M.; Tian, D.; Zhang, X. Y.; Wu, W.; Wan, W. M. The introduction of the Barbier reaction into polymer chemistry. *Nat. Commun.* **2017**, *8*, 1210.
- 23 Chen, Y.; Han, H.; Tong, H.; Chen, T.; Wang, H.; Ji, J.; Jin, Q. Zwitterionic phosphorylcholine-TPE conjugate for pH-responsive drug delivery and AIE active imaging. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21185–21192.
- 24 Cao, Q. Y.; Jiang, R.; Liu, M.; Wan, Q.; Xu, D.; Tian, J.; Huang, H.; Wen, Y.; Zhang, X.; Wei, Y. Microwave-assisted multicomponent reactions for rapid synthesis of AIE-active fluorescent polymeric nanoparticles by post-polymerization method. *Mater. Sci. Eng. C* **2017**, *80*, 578–583.
- 25 Wan, Q.; Liu, M.; Xu, D.; Huang, H.; Mao, L.; Zeng, G.; Deng, F.; Zhang, X.; Wei, Y. Facile fabrication of amphiphilic AIE active glucan *via* formation of dynamic bonds: Self assembly, stimuli responsiveness and biological imaging. *J. Mater. Chem. B* **2016**, *4*, 4033–4039.
- 26 Wan, Q.; Liu, M.; Xu, D.; Mao, L.; Tian, J.; Huang, H.; Gao, P.; Deng, F.; Zhang, X.; Wei, Y. Fabrication of aggregation induced emission active luminescent chitosan nanoparticles *via* a “one-pot” multicomponent reaction. *Carbohydr. Polym.* **2016**, *152*, 189–195.
- 27 Huang, Z. F.; Zhang, X. Q.; Zhang, X. Y.; Yang, B.; Wang, K.; Wang, S. Q.; Yuan, J. Y.; Tao, L.; Wei, Y. Synthesis of starch-based amphiphilic fluorescent nanoparticles and their application in biological imaging. *J. Nanosci. Nanotechnol.* **2018**, *18*, 2345–2351.
- 28 Wan, Q.; Jiang, R.; Guo, L.; Yu, S.; Liu, M.; Tian, J.; Liu, G.; Deng, F.; Zhang, X.; Wei, Y. Novel strategy toward AIE-active fluorescent polymeric nanoparticles from polysaccharides: Preparation and cell imaging. *ACS Sustain. Chem. Eng.* **2017**, *5*, 9955–9964.
- 29 Peng, H. Q.; Zheng, X.; Han, T.; Kwok, R. T.; Lam, J. W.; Huang, X.; Tang, B. Z. Dramatic differences in aggregation-induced emission and supramolecular polymerizability of tetraphenylethene-based stereoisomers. *J. Am. Chem. Soc.* **2017**, *139*, 10150–10156.
- 30 Bai, W.; Wang, Z.; Tong, J.; Mei, J.; Qin, A.; Sun, J. Z.; Tang, B. Z. A self-assembly induced emission system constructed by the host-guest interaction of AIE-active building blocks. *Chem. Commun.* **2015**, *51*, 1089–1091.
- 31 Tao, D. D.; Wang, Q.; Yan, X. S.; Chen, N.; Li, Z.; Jiang, Y. B. Ag⁺ coordination polymers of a chiral thiol ligand bearing an AIE fluorophore. *Chem. Commun.* **2017**, *53*, 255–258.
- 32 Zhang, J.; Zhu, J.; Lu, C.; Gu, Z.; He, T.; Yang, A.; Qiu, H.; Zhang, M.; Yin, S. A hyperbranched fluorescent supramolecular polymer with aggregation induced emission (AIE) properties. *Polym. Chem.* **2016**, *7*, 4317–4321.
- 33 Thomas, S. W.; Joly, G. D.; Swager, T. M. Chemical sensors based on amplifying fluorescent conjugated polymers. *Chem. Rev.* **2007**, *107*, 1339–1386.
- 34 Wu, Y. W.; Qin, A. J.; Tang, B. Z. AIE-active polymers for explosive detection. *Chinese J. Polym. Sci.* **2017**, *35*, 141–154.
- 35 Dong, W.; Wu, H.; Chen, M.; Shi, Y.; Sun, J.; Qin, A.; Tang, B. Z. Anionic conjugated polytriazole: direct preparation, aggregation-enhanced emission, and highly efficient Al³⁺ sensing. *Polym. Chem.* **2016**, *7*, 5835–5839.
- 36 Wan, H.; Gu, P.; Zhou, F.; Wang, H.; Jiang, J.; Chen, D.; Xu, Q.; Lu, J. M. Polyacrylic esters with “one-is-enough” effect and investigation of their AIEE behaviours and cyanide detection in aqueous solution. *Polym. Chem.* **2018**, *9*, 3893–3899.
- 37 Qian, Y.; Liu, H.; Tan, H.; Yang, Q.; Zhang, S.; Han, L.; Yi, X.; Huo, L.; Zhao, H.; Wu, Y. A novel water-soluble fluorescence probe with wash-free cellular imaging capacity based on AIE characteristics. *Macromol. Rapid Commun.* **2017**, *38*, 1600684.
- 38 Wei, G.; Jiang, Y.; Wang, F. A novel AIEE polymer sensor for detection of Hg²⁺ and Ag⁺ in aqueous solution. *J. Photochem. Photobiol. A* **2018**, *358*, 38–43.
- 39 Morishima, K.; Ishiwari, F.; Matsumura, S.; Fukushima, T.; Shibayama, M. Mesoscopic structural aspects of Ca²⁺-triggered polymer chain folding of a tetraphenylethene-appended poly(acrylic acid) in relation to its aggregation-induced emission behavior. *Macromolecules* **2017**, *50*, 5940–5945.
- 40 Yang, D.; Li, F.; Luo, Z.; Bao, B.; Hu, Y.; Weng, L.; Cheng, Y.; Wang, L. Conjugated polymer nanoparticles with aggregation induced emission characteristics for intracellular Fe³⁺ sensing. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 1686–1693.
- 41 Guan, X.; Meng, L.; Jin, Q.; Lu, B.; Chen, Y.; Li, Z.; Wang, L.; Lai, S.; Lei, Z. A new thermo-, pH- and CO₂-responsive fluorescent four-arm star polymer with aggregation-induced emission for long-term cellular tracing. *Macromol. Mater. Eng.* **2018**, 1700553.
- 42 Wang, K.; Lu, H.; Liu, B.; Yang, J. Multi-stimuli-responsive fluorescence of AEE polyurethane films. *Eur. Polym. J.* **2018**, *101*, 225–232.
- 43 Minei, P.; Pucci, A. Fluorescent vapochromism in synthetic polymers. *Polym. Int.* **2016**, *65*, 609–620.
- 44 Zhao, Y.; Zhu, W.; Ren, L.; Zhang, K. Aggregation-induced emission polymer nanoparticles with pH-responsive fluorescence. *Polym. Chem.* **2016**, *7*, 5386–5395.
- 45 Zhang, Z.; Bilalis, P.; Zhang, H.; Gnanou, Y.; Hadjichristidis, N. Core cross-linked multiarm star polymers with aggregation-induced emission and temperature responsive fluorescence characteristics. *Macromolecules* **2017**, *50*, 4217–4226.
- 46 Wang, L.; Yang, L.; Li, L.; Cao, D. The synthesis and highly sensitive detection of water content in THF using a novel solvatochromic AIE polymer containing diketopyrrolopyrrole and triphenylamine. *New J. Chem.* **2016**, *40*, 6706–6713.
- 47 Liu, F.; Urban, M. W. Recent advances and challenges in designing stimuli-responsive polymers. *Prog. Polym. Sci.* **2010**, *35*, 3–23.
- 48 Chen, J. R.; Zhao, J.; Xu, B. J.; Yang, Z. Y.; Liu, S. W.; Xu, J. R.; Zhang, Y.; Wu, Y. C.; Lv, P. Y.; Chi, Z. G. An AEE-active polymer containing tetraphenylethene and 9,10-distyrylanthracene moieties with remarkable mechanochromism. *Chinese J.*

- Polym. Sci.* **2017**, *35*, 282–292.
- 49 Li, T.; He, S.; Qu, J.; Wu, H.; Wu, S.; Zhao, Z.; Qin, A.; Hu, R.; Tang, B. Z. Thermoresponsive AIE polymers with fine-tuned response temperature. *J. Mater. Chem. C* **2016**, *4*, 2964–2970.
- 50 Singh, R.; Wu, H. Y.; Dwivedi, A. K.; Singh, A.; Lin, C. M.; Raghunath, P.; Lin, M. C.; Wu, T. K.; Wei, K. H.; Lin, H. C. Monomeric and aggregation emissions of tetraphenylethene in a photo-switchable polymer controlled by cyclization of diarylethene and solvent conditions. *J. Mater. Chem. C* **2017**, *5*, 9952–9962.
- 51 Zhan, R.; Pan, Y.; Manghnani, P. N.; Liu, B. AIE polymers: Synthesis, properties, and biological applications. *Macromol. Biosci.* **2017**, *17*, 1600433.
- 52 Yan, L.; Zhang, Y.; Xu, B.; Tian, W. Fluorescent nanoparticles based on AIE fluorogens for bioimaging. *Nanoscale* **2016**, *8*, 2471–2487.
- 53 Gao, M.; Tang, B. Z. Aggregation-induced emission probes for cancer theranostics. *Drug Discovery Today* **2017**, *22*, 1288–1294.
- 54 Yuan, Y.; Liu, B. Visualization of drug delivery processes using AIEgens. *Chem. Sci.* **2017**, *8*, 2537–2546.
- 55 Liang, J.; Liu, B. ROS-responsive drug delivery systems. *Bioeng. Transl. Med.* **2016**, *1*, 239–251.
- 56 Wu, W. High-performance conjugated polymer photosensitizers. *Chem* **2018**, *4*, 1762–1764.
- 57 Liu, S.; Zhang, H.; Li, Y.; Liu, J.; Du, L.; Chen, M.; Kwok, R.; Lam, J.; Phillips, D. L.; Tang, B. Z. Strategies to enhance the photosensitization: Polymerization and D/A even-odd effect. *Angew. Chem.* **2018**, *130*, 15409–15413.
- 58 Roose, J.; Tang, B. Z.; Wong, K. S. Circularly-polarized luminescence (CPL) from chiral AIE molecules and macrostructures. *Small* **2016**, *12*, 6495–6512.
- 59 Liu, Q.; Xia, Q.; Wang, S.; Li, B. S.; Tang, B. Z. *In situ* visualizable self-assembly, aggregation-induced emission and circularly polarized luminescence of tetraphenylethene and alanine-based chiral polytriazole. *J. Mater. Chem. C* **2018**, *6*, 4807–4816.
- 60 Kim, Y.; Kim, E.; Clavier, G.; Audebert, P. New tetrazine-based fluoro-electrochromic window; modulation of the fluorescence through applied potential. *Chem. Commun.* **2006**, *34*, 3612–3614.
- 61 Cheng, S. W.; Han, T.; Huang, T. Y.; Tang, B. Z.; Liou, G. S. High-performance electrofluoro-chromic devices based on aromatic polyamides with AIE-active tetraphenylethene and electro-active triphenylamine moieties. *Polym. Chem.* **2018**, *9*, 4364–4373.
- 62 Yang, L.; Zhang, Y.; Zhang, X.; Li, N.; Quan, Y.; Cheng, Y. Doping-free circularly polarized electroluminescence of AIE-active chiral binaphthyl-based polymers. *Chem. Commun.* **2018**, *54*, 9663–9666.