

AIEgens-lightened Functional Polymers: Synthesis, Properties and Applications

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Cite this article as:

Zhou Shi-Yuan, Wan Hai-Bo, Zhou Feng, Gu Pei-Yang, Xu Qing-Feng, Lu Jian-Mei. AIEgens-lightened Functional Polymers: Synthesis, Properties and Applications[J]. *Chinese J. Polym. Sci.*, 2019, 37(4): 302-326. doi: 10.1007/s10118-019-2217-0

View online: <https://doi.org/10.1007/s10118-019-2217-0>

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AI Egens-lightened Functional Polymers: Synthesis, Properties and Applications

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Abstract Recently, polymers with aggregation-induced emission (AIE) effects have attracted significant attention due to their broad applications in luminescence sensors, stimuli responsive materials, electroluminescence devices, *etc.* In this review, we summarize recent advances concerning AIE polymers. Four types of AIE polymers including end-functionalized polymers, side-chain polymers, main-chain polymers, and other polymers according to the location of AI Egens, are described. Their synthetic preparation, optical property, AIE effects, and applications are also illustrated in this review.

Keywords Aggregation-induced emission; Functional polymers; Synthetic method; Application

Citation: Zhou, S. Y.; Wan, H. B.; Zhou, F.; Gu, P. Y.; Xu, Q. F.; Lu, J. M. AI Egens-lightened functional polymers: Synthesis, properties and applications. *Chinese J. Polym. Sci.* 2019, 37, 302–326.

INTRODUCTION

Nowadays, amongst numerous applications of luminescent materials, the fabrication of solid samples allows for the tightening of intermolecular interactions and intensifies the π - π stacking of adjacent aromatic fluorescence moieties, but it often leads to fluorescence quenching. This phenomenon is called aggregation-caused quenching (ACQ).^[1,2] Tremendous efforts have been devoted to resolving this problem.^[3–5] It was not until 2001 that the Tang's group discovered that silole derivatives emitted weak fluorescence, which could be amplified dramatically upon aggregation,^[6] and such amplification was accompanied by a dramatic enhancement in quantum yield (QY). This abnormal phenomenon was termed as 'aggregation-induced emission' (AIE).^[7–10] Since this discovery, AIE effects have attracted the attention of chemical scientists all over the world, and a large number of luminogens with AIE characteristics (AI Egens) and innumerable AIE materials with different structures have been developed.^[11–18]

The early AI Egens possess spiral structures containing polyaryl-substituted moieties, such as hexaphenylsilole (HPS),^[17,19–21] tetraphenylethene (TPE),^[18,22–24] and distyreneanthracene (DSA),^[16,25,26] which are able to rotate freely in dilute solutions while restricted at aggregation state. According to these initial developments, AI Egen moieties have been considerably extended into numerous types. The major-

ity of the utilized AI Egens are shown in Chart 1(a). Currently, the generally accepted mechanism of the AIE phenomenon is called the restriction of intramolecular motions (RIM) theory, including restriction of intramolecular rotation (RIR) and restriction of intramolecular vibration (RIV).^[27] Moreover, structural rigidification (SR) and intramolecular charge-transfer (ICT) theories^[8,9,28,29] can also partially provide explanations for the AIE phenomena.

In addition to AIE small molecules, AIE polymers have received considerable interests due to their complex structures and intrinsic properties.^[30] AIE polymers possess much more complicated structures than those of small-molecule AIE dyes due to the different polymerization methods, monomers, and polymer components, *etc.* Moreover, polymers possess a number of outstanding intrinsic characteristics over small molecules, such as heat resistance, solvent resistance, ductility, plasticity, *etc.*^[31–33] Hence, incorporating AIE-active moieties into polymer chains may enrich the applications of both AI Egens and polymers.

In this paper, the discussion of AIE polymers is divided into four categories according to the location of AI Egens in polymer chains (Chart 1b): AI Egens anchored at the end of the polymer chains (end-functionalized AIE polymers), AI Egens located at the backbone of the polymer chains (main-chain AIE polymers), AI Egens attached to the side chain of the polymer chains (side-chain AIE polymers), and other functional polymers which are specially constructed, such as dendrimers, star-shaped polymers, hyperbranched polymers, *etc.* In each section, the design philosophy and synthetic approach of AIE-active polymers will be described, and their properties and potential applications will also be discussed.

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

Received October 28, 2018; Accepted December 25, 2018; Published online January 31, 2019

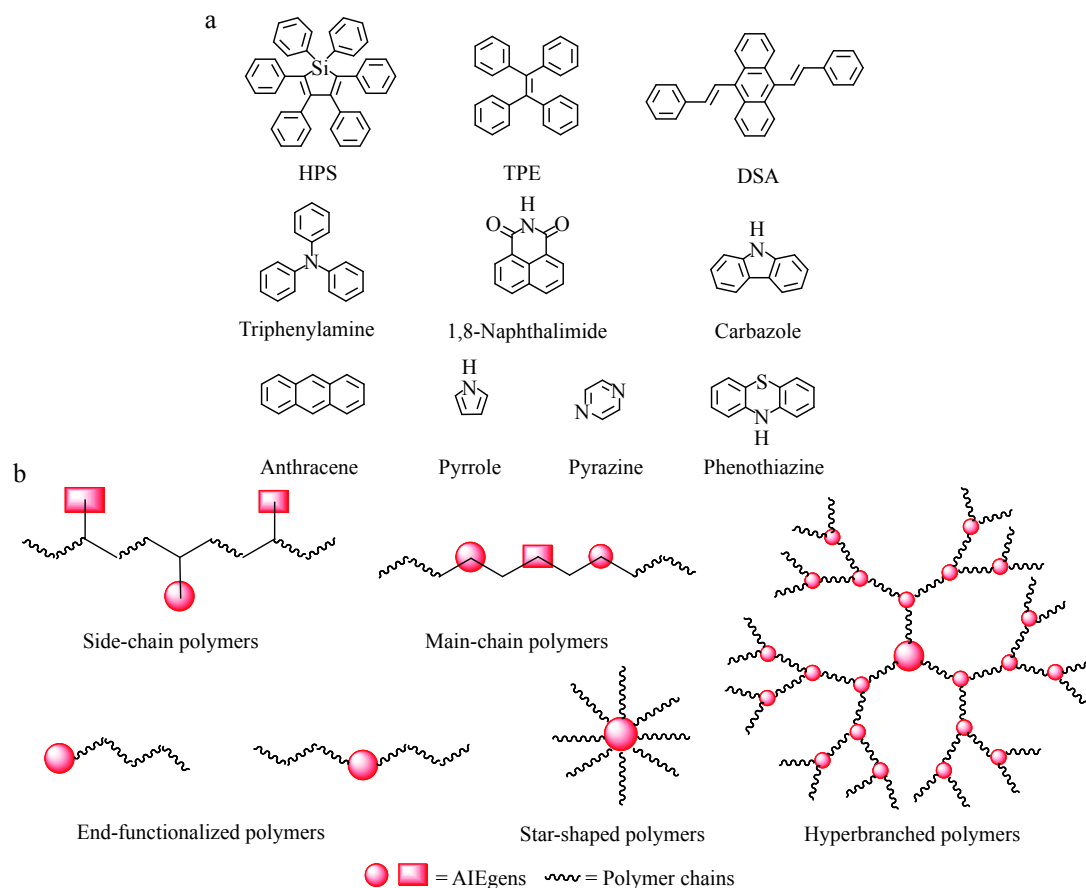


Chart 1 (a) Some typical AIE luminogens; (b) Schematic illustration of classification method according to the location of AIEgens in the polymer chains

SYNTHESIS AND PROPERTIES

End-functionalized Polymers

End-functionalized AIE polymers refer to polymers in which the end chain is functionalized by certain AIE moieties. Two different strategies are often employed for their synthesis: one utilizes initiators containing AIEgens to initiate common monomers, which endows them with AIE characteristics and preserves their intrinsic properties; the other relies on the introduction of certain polymer chains to the terminal ends of the AIE moieties, thus the obtained polymers will possess both an AIE-active skeleton and properties of the polymer chains.

Using an initiator-containing AIE moiety to initiate normal monomers is a useful strategy to endow polymers with AIE characteristics. For instance, in our previous work, we designed an initiator-containing naphthalene-pyrazoline moieties, which possessed intramolecular charge-transfer (ICT) and AIE dual photo-responsive properties.^[34] Common monomers, such as styrene (**2**), methyl methacrylate (**3**), and 2-hydroxyethyl methacrylate (**4**) (Fig. 1a), were polymerized using these initiators *via* atom transfer radical polymerization (ATRP) under moderate conditions to obtain the corresponding polymers **5**, **6**, and **7**, respectively. Therefore, these polymers possessed interesting photoluminescent properties.

These three α -end functionalized polymers could be dissolved in DMF and were almost non-emissive. With the addition of water or ethanol, the photoluminescent intensity

and quantum yield showed a sharp enhancement. Compared to the emission intensities in pure DMF solution, the maximum emission intensities of these three polymers in different mixtures were 155 (**5** in DMF-ethanol mixture), 65 (**6** in DMF/water mixture), and 10 times (**7** in DMF-water mixture) higher, respectively. Such emission enhancement can be primarily ascribed to two factors: (1) The strong wrapping of polymer chains when aggregated can segregate the initiator from solvent to avoid quenching; (2) The chromophore anchored at the end of the polymer chains can easily twist to form a configuration which is beneficial for emission. Owing to the introduction of an AIE-active initiator to the terminal of polymer chains, the regular polymers not only amplify the emission behavior, but also preserve the original properties of the polymer chains, for example, they retain the ease of fabrication and a flexible configuration. In addition, the quantum yield of polymer **5** in the film state prepared by spin-coating was unexpectedly high, approaching 48% (Fig. 1c).

More interestingly, by adding sulfuric acid to the DMF solution of **7**, its emission increased gradually and reached a maximum when pH = 1, whereas in the similar systems of **5** and **6**, only slight enhancements were observed. This could be mostly attributed to the poor solubility of the initiator in water, the lack of dimethyl amino groups on the particle surface, and the collapse of hydrogen bonding between the hydroxyl groups of 2-hydroxyethyl methacrylate and the water molecules in acid solution. Experiments carried out in simu-

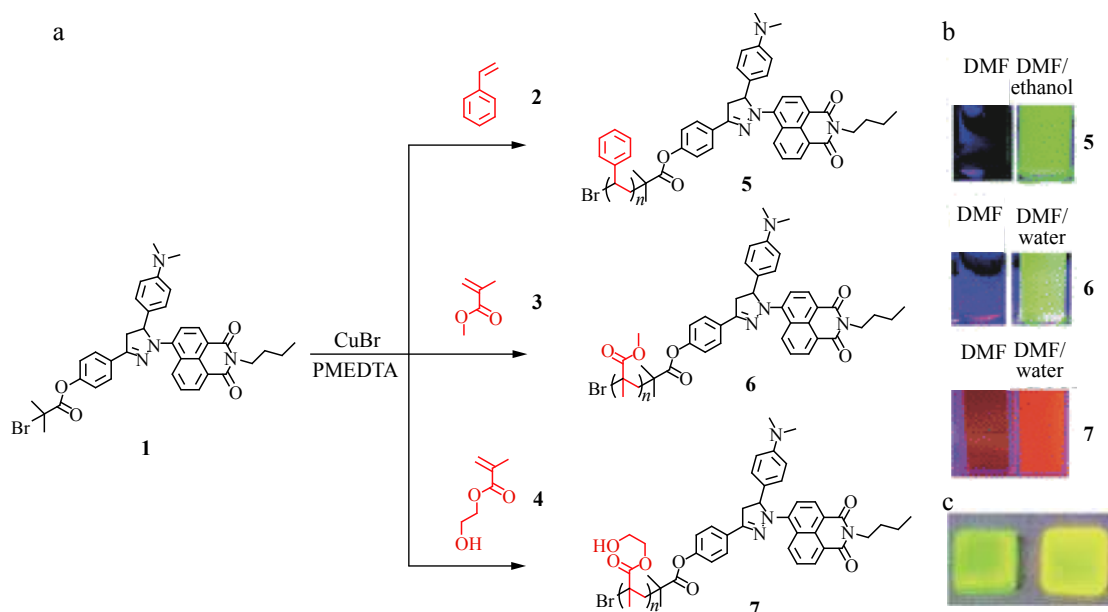


Fig. 1 (a) Synthetic approaches towards polymers **5–7** via ATRP; (b) Fluorescence photographs of their corresponding solutions and aggregates under a commercial 365 nm UV lamp; (c) Emission of polymer films (Adapted with permission from Ref. [34]; Copyright (2012) The Royal Society of Chemistry)

lated gastric juice solution revealed that **7** was a potential candidate as a fluorescence sensor for oral drug-delivery systems.

The end-functionalized polymers exhibit not only enhanced fluorescent properties but also the well-preserved functions derived from the monomeric units. For instance, using the above initiator **1**, polymer **9** containing *N*-isopropylacrylamide (NIPAM)[35] could be obtained via the ATRP

method (Fig. 2a). Polymer **9** dissolved well in cold water without emission but became turbid as the temperature increased, providing fluorescence ‘turn-on’ characteristics. When the temperature was above the lower critical solution temperature (LCST) of polymer **9**, the PL intensity was approximately 3 times higher than that at room temperature (Fig. 2c). This can mostly be attributed to the polymer chains being used as building blocks to reduce the intermolecular

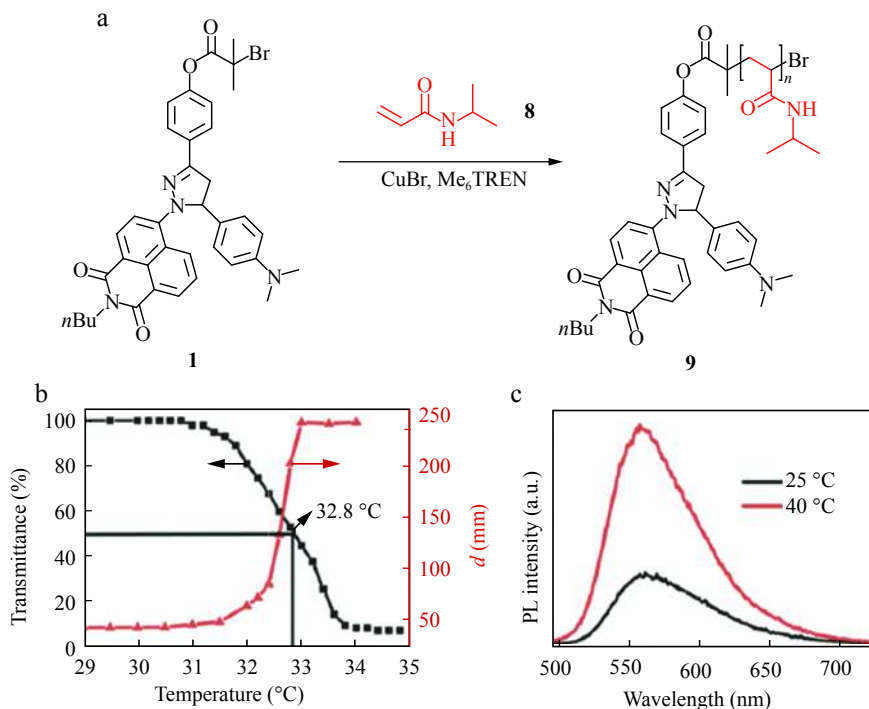


Fig. 2 (a) Synthetic approach towards polymer **9** via ATRP; (b) Effects of temperature on transmittance and particle size for the **9** aqueous solution (2 mg·mL⁻¹); (c) Emission spectra of the **9** aqueous solution at room temperature and at 40 °C (2 mg·mL⁻¹, λ_{ex} = 475 nm) (Adapted with permission from Ref. [35]; Copyright (2015) The Royal Society of Chemistry)

interactions between initiators. Therefore, polymer **9** can be considered as a type of ‘turn-on’ temperature-dependent photoluminescent material for fluorescence sensor.

Another example is a naphthalene-imide-based end-functionalized polymer synthesized by Julien and coworkers.^[36] Naphthalene-imide-based AIE dye **10** was functionalized with *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]-nitroxide-based alkoxyamine **11** via an ester linkage to get **12**, and then further initiated the nitroxide-mediated polymerization of isoprene. By adjusting the ratio of isoprene and **12**, two polymers with different molecular weights, **13a** ($M_n = 2100 \text{ g}\cdot\text{mol}^{-1}$) and **13b** ($M_n = 3700 \text{ g}\cdot\text{mol}^{-1}$), were obtained. The optical behaviors of **13a** and **13b** were measured in a THF/water mixture system, which showed that the emission intensities of both systems started to increase dramatically when $f_w \geq 60\%$ (f_w represents the volume fraction of water in THF), and reached a maximum when $f_w = 99\%$ (Fig. 3b). The fluorescence intensity enhancements of **13a** and **13b** were almost 4–5 times (for $f_w = 90\%$), but lower than that of **12** (9.5 times). This might be attributed to the partially restricted intramolecular rotation of the naphthalene imide moiety of polymers **13a** and **13b** in pure THF, owing to the steric hinderance of the polymers. Moreover, as the fraction of water further increased to 99%, the enhancements in emission of **13a** and **13b** increased 6 and 9 folds, respectively. Obviously, the enhancement in fluorescence intensity of **13b** was much higher than that of **13a** due to the relatively long polymer chains of **13b**, thus **13b** could be chosen for the synthesis of prodrug nanoparticles. Cladribine-diglycolate-polyisoprene, a mature anticancer polymer prodrug, was then co-nanoprecipitated with **13b** to form AIE-active polymer prodrug nanoparticles. Owing to their easy fabrication and robust AIE characteristics, these polymer prodrug nanoparticles can be applied in living cell imaging and have potential usages in diagnostic testing.

Yang and coworkers reported the cyanostilbene derivative **14** (Fig. 4a) as an initiator to initiate the polymerization of ζ -caprolactone (**15**) and D,L-lactide (**16**) via ring-opening polymerization.^[37] Initiator **14** itself exhibited an AIE characteristic in THF/water mixture owing to the synergetic effect of intramolecular planarization and J-type aggregate formation. Both of the polymers showed AIE characteristics

compared to the initiator **14** in THF-water mixed systems and the PL intensities were enhanced 6 and 8 folds when the water fraction increased from 0% to 90%, respectively (Figs. 4b and 4c). This is due to the restriction of intramolecular motions of the luminogens at the end of polymer chains resulting from the rigid main-chain segments, thus leading to the emission enhancement.

Differing from the synthetic strategy of the end-functionalized polymers above, TPE-based AIE polymers provide another approach. For example, an end-functionalized polymer containing a TPE derivative and polydimethylsiloxane (PDMS) moieties was prepared utilizing covalent bonds.^[38] The PL intensity increased as the content of TPE increased, and a ratio of PDMS:TPE = 100:1 (*W:W*) was chosen for further studies. By introducing tetraethylorthosilicate into the polymer chains via condensation reaction and sol-gel reaction, the fluorescent elastomer **17** (Fig. 5a) was obtained. Elastomer **17** exhibited AIE characteristic in the THF/water system. The fluorescence emission increased progressively with the addition of water and reached a maximum without any shift in the λ_{max} when $f_w = 90\%$, which is 3.3-fold higher than that in pure THF. In addition, considering temperature as the variant, the PL intensity of **17** dropped linearly as temperature increased (Fig. 5b). Taking advantage of the soft and flexible polymer chains of PDMS and the AIE property of TPE, this end-functionalized TPE-based elastomer possessed the potential for use as temperature sensing materials.

Loh and coworkers introduced poly(ethylene glycol) into two ends of the TPE side chains to prepare the amphiphilic AIE oligomer **18** (Fig. 6a).^[39] The emission behavior of **18** was measured at different concentrations (ranging from $2.6 \times 10^{-3} \text{ mmol}\cdot\text{L}^{-1}$ to $2.6 \text{ mmol}\cdot\text{L}^{-1}$) and in the THF/water mixed system. At the concentration below the critical micelle concentration (CMC), the PL intensity changed slightly and peaked at 448 nm. The PL intensity started to enhance dramatically when the concentration was above CMC and reached a maximum ($2.6 \text{ mmol}\cdot\text{L}^{-1}$) with a red-shift of 26 nm (Figs. 6b and 6c). This phenomenon can be explained by RIM theory and the formation and aggregation of micelles. In the THF/water system, PL intensities were almost the same at $f_w < 90\%$. When $f_w > 90\%$, a sharp enhancement could be observed and a maximum value was reached when

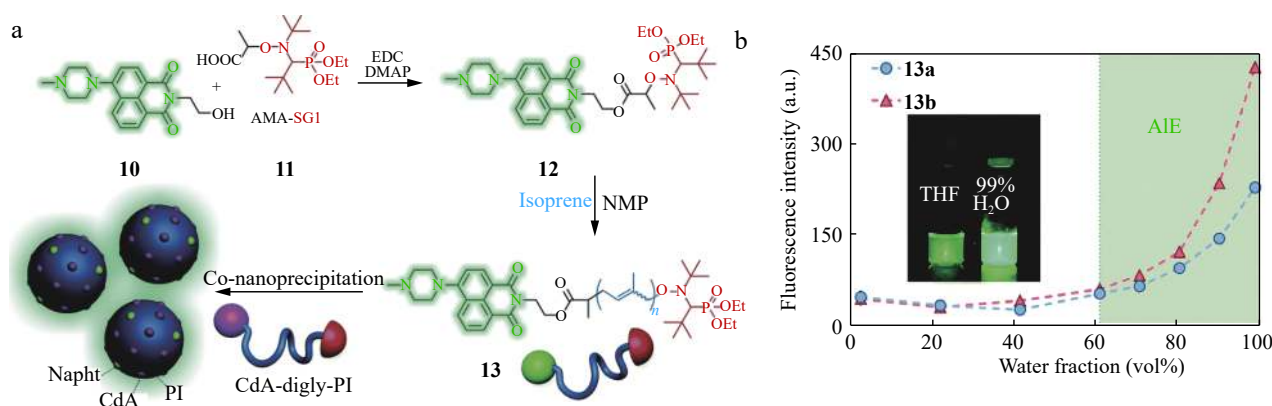


Fig. 3 (a) Synthetic routes towards polymer **13**; (b) Progressive enhancement of the fluorescence intensity of **13a** at 500 nm and **13b** at 490 nm with increasing water fraction in THF solution ($\lambda_{\text{ex}} = 420 \text{ nm}$, $10 \text{ mmol}\cdot\text{L}^{-1}$). Inset: photograph of **13b** in THF and in 99% water under a 365 nm UV lamp (Adapted with permission from Ref. [36]; Copyright (2017) The Royal Society of Chemistry)

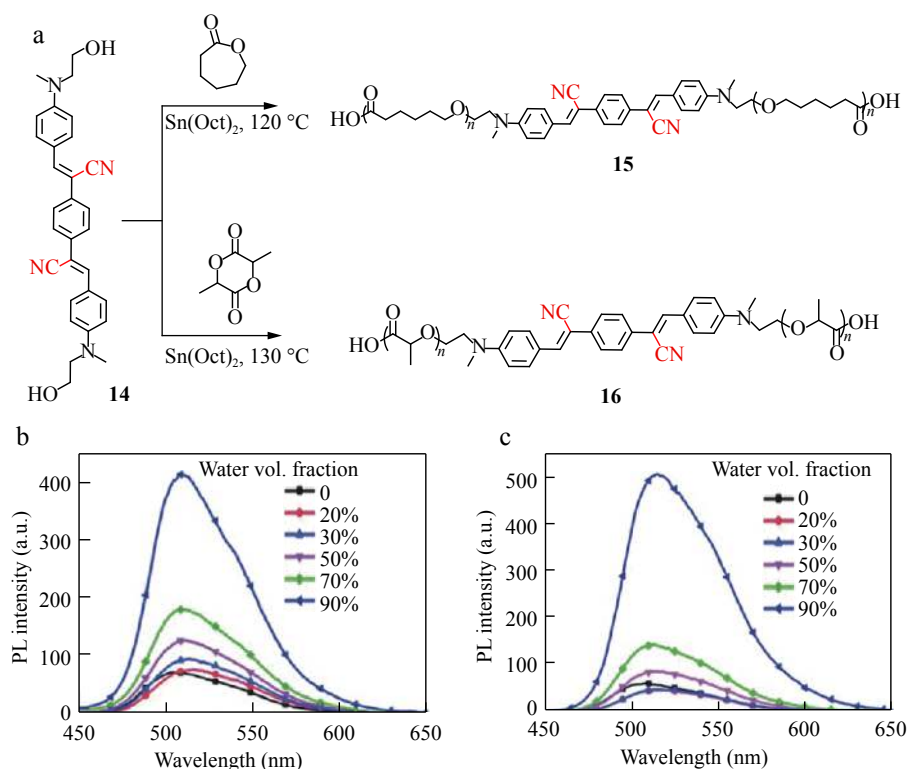


Fig. 4 (a) Molecular structure of initiator **14** and synthetic routes towards polymers **15** and **16**; PL intensity spectra changes of (b) **15** and (c) **16** in THF/water mixture with different water fractions ($10^{-5} \text{ mol} \cdot \text{L}^{-1}$) (Adapted with permission from Ref. [37]; Copyright (2014) The Royal Society of Chemistry)

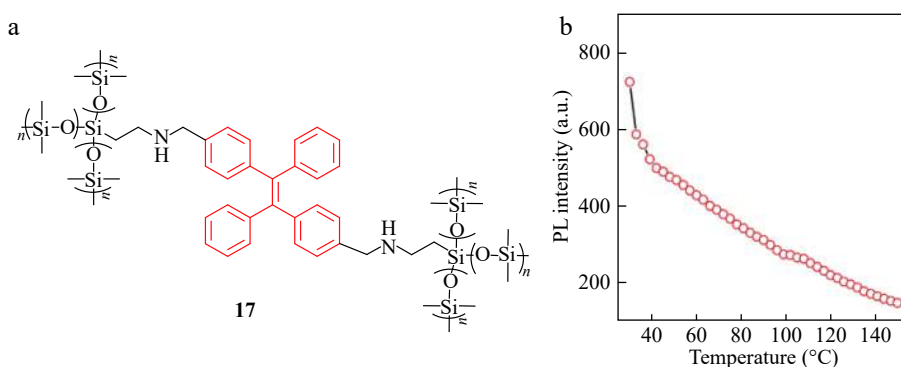


Fig. 5 (a) Molecular structure of TPE-based polymer **17**; (b) PL intensity varied with temperature of **17**, $\lambda_{\text{ex}} = 315 \text{ nm}$ (Adapted with permission from Ref. [38]; Copyright (2015) The Royal Society of Chemistry)

$f_w = 99\%$, which is nearly 8 times higher than that observed in pure THF solution. Moreover, following the addition of $4 \text{ mmol} \cdot \text{L}^{-1}$ α -cyclodextrin, the fluorescence intensity of **18** in solution increased 12 folds (Fig. 6d), thus forming a host-guest complex, which can be used in biological cell imaging due to its extraordinary AIE properties, low toxicity, and biocompatibility.

In order to obtain end-functionalized polymers emitting red fluorescence, new fluorogens ought to be chosen, for instance, cyanogen. Herein, two pyran-based and red-fluorescent initiators **19** and **20** (Fig. 7a) with different charge transfers (CT) were designed and prepared in our previous work.^[40] Initiator **19** showed an ACQ effect due to its relatively stronger intramolecular interactions, while **20** exhibited AIE characteristics. Three functional polystyrenes ini-

tiated with **19** and possessing different molecular weights ($M_n = 5320, 9220, \text{ and } 14740 \text{ g} \cdot \text{mol}^{-1}$, named **19a**, **19b**, and **19c**, respectively) were chosen to study the effect of different chain lengths on chromophore behavior; one polymer (**20d**) initiated by **20** was also prepared as a comparison. **19a**, **19b**, and **19c** shared almost the same tendency in variation for the absorption and emission behaviors in the THF/water mixture system. In pure THF, the absorption maximum of **19a** was 471 nm, and following the addition of water, the PL intensity first decreased slightly ($f_w < 20\%$) and then got amplified progressively. When $f_w = 90\%$, the emission maximum was blue-shifted to 591 nm with $\Phi_F = 18.5\%$ and the emission intensity was 1.85 times higher than that in pure THF solution. For **19b** and **19c**, the emission maximums were blue-shifted to 590 and 585 nm and the Φ_F s

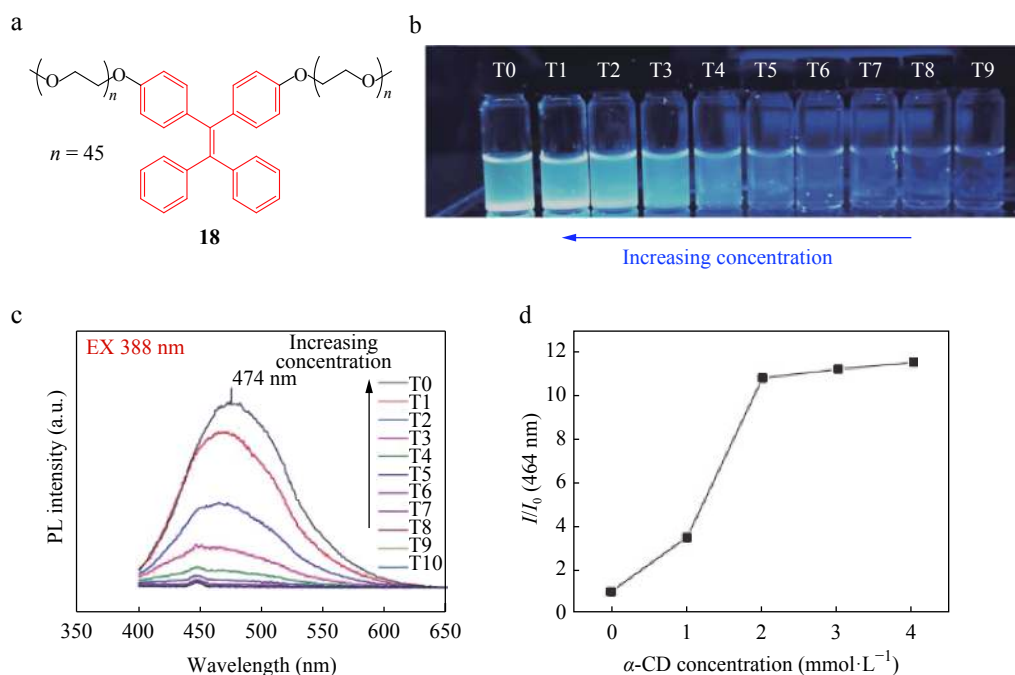


Fig. 6 (a) Molecular structure of polymer **18**; (b) Fluorescence emission spectra of **18** in aqueous solutions with various concentrations (2.6×10^{-3} – $2.6 \text{ mmol} \cdot \text{L}^{-1}$) at room temperature ($\lambda_{\text{ex}} = 388 \text{ nm}$); (c) Photograph of **18** in aqueous solutions with different concentrations under a 365 nm UV light; (d) Relative fluorescent intensity of $2.6 \text{ mmol} \cdot \text{L}^{-1}$ **18** before and after the addition of α -cyclodextrin (1 – $4 \text{ mmol} \cdot \text{L}^{-1}$) at room temperature ($\lambda_{\text{ex}} = 388 \text{ nm}$) (Adapted with permission from Ref. [39]; Copyright (2017) American Chemical Society)

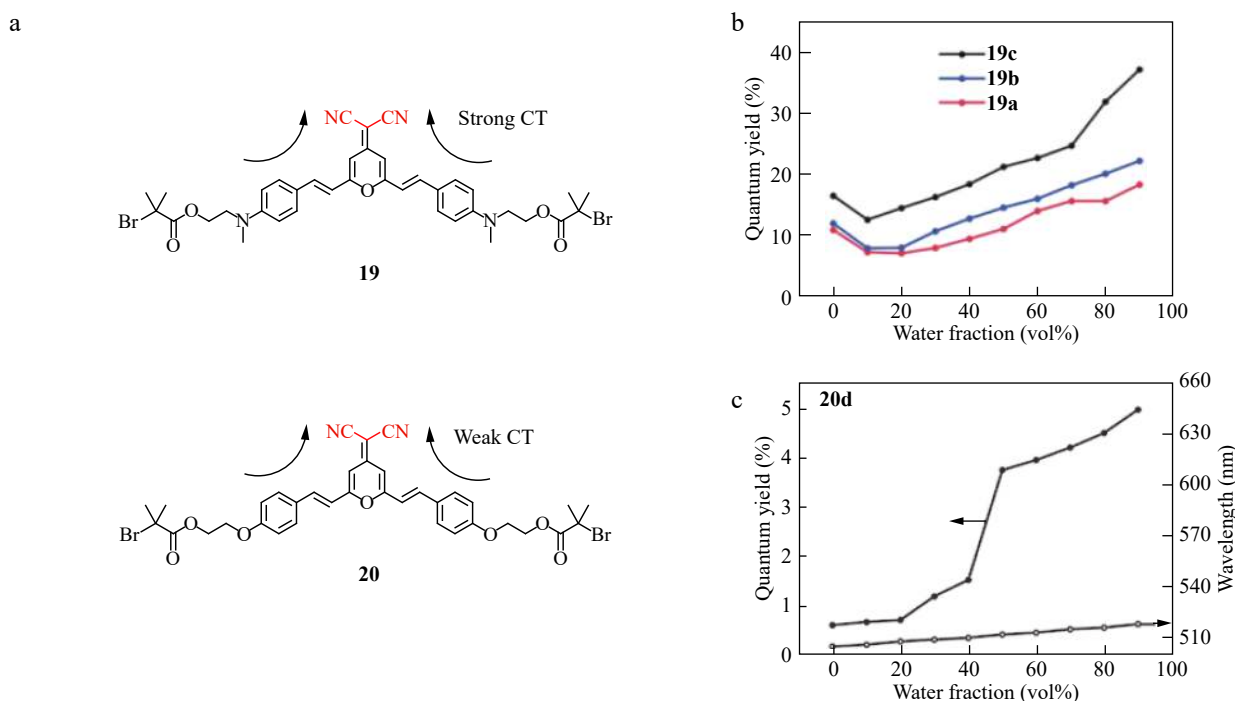


Fig. 7 (a) Molecular structures of cyanogen-containing initiators **19** and **20**; (b) Spectra of quantum yields of **19a**, **19b**, and **19c** with different water fractions in THF/water mixtures ($10 \text{ mmol} \cdot \text{L}^{-1}$, $\lambda_{\text{ex}} = 479 \text{ nm}$); (c) Spectra of quantum yield and maximum wavelength of **20d** with different water fractions in THF/water mixtures ($10 \text{ mmol} \cdot \text{L}^{-1}$, $\lambda_{\text{ex}} = 415 \text{ nm}$) (Adapted with permission from Ref. [40]; Copyright (2014) The Royal Society of Chemistry)

increased to 22.39% and 37.36%, respectively, revealing that the longer chain length hindered the intramolecular interactions and conducted to a higher quantum yield (Fig. 7b). The aggregation behavior of **20d** was similar to its initiator **20**

and its PL intensity was enhanced dramatically with a Φ_F of 4.98% when $f_w = 90\%$; this was in stark contrast to the result of $\Phi_F = 0.67\%$ in pure THF (Fig. 7c). However, **20d** only emitted a green light upon aggregation.

Initiator **19** (Fig. 8a), possessing strong charge transfer, could be employed for the polymerization of three regular monomers, *tert*-butyl methacrylate (**21**), methyl methacrylate (**3**), and hydroxyethyl methacrylate (**22**), using an ATRP method under moderate conditions.^[41] All of these polymers, including the copolymer **26**, showed AIE properties in the DMF/water mixture systems. Contact angle experiments revealed that polymers **23** (with a contact angle of 109°) and **25** (99°) were hydrophobic, while **26** (68°), **27** (59°), and **24** (53°) were hydrophilic (Fig. 8b). For the hydrophobic polymer **23**, its Φ_F in pure DMF was 0.79% and the λ_{em} peak located at 629 nm. When the water fraction was increased to 50%, the λ_{em} peak was blue-shifted to 598 nm and Φ_F increased to 15.45%, which was 19.56 times higher than that in pure DMF solution. This might be due to the effective protection of the chromophore provided by polymer side chains in the aggregated state and hindrance of the intramolecular charge transfer effect which can cause emission quenching. As the water fraction increased sequentially, the PL intensity decreased gradually owing to the increase of solvent polarity, which is beneficial to an intramolecular charge transfer state. For polymer **25** containing hydrophobic side chains, its Φ_F reached a maximum value (12.87%) when the water fraction was 70%. Compared with the quantum yield in pure DMF, its maximum Φ_F increased by 7.44 folds. The remainder of the three hydrophilic polymers (**24**, **26**, and **27**) all tended to reach the maximum emission intensities in a 90% DMF/water mixture and possessed relatively low quantum yields.

Xing and coworkers reported a simple strategy to synthesize DSA-based end-functionalized supramolecular polymers **29** (Fig. 9a) by mixing 9,10-bis((*E*)-2-(pyridin-4-yl)vinyl) anthracene **28** and cucurbit[8]uril (CB[8]) in aqueous solutions.^[42] When the naphthyl groups of **28** were encapsulated by CB[8], the emission of polymer **29** increased a lot in dilute solutions. This is mainly attributed to the host-guest in-

teractions between naphthyl groups of **28** and CB[8], which would restrict the intramolecular motions and the non-radiative relaxation channels. Additionally, by gradually adding sulfo-cyanine5 carboxylic acid (Cy5) into the dilute solution of **29**, the donor emission (**29**) decreased while the acceptor emission (Cy5) increased, indicating the Forster energy transfer from **29** to Cy5. Therefore, an efficient light-harvesting system has been built up and shows potential applications in photocatalysis, light-emitting devices, and optical sensors.

Side-chain Polymers

Side-chain AIE polymers can be obtained by using monomers such as styrene and acrylic acid derivatives with AIE moieties. In our previous works, 1,8-naphthalimide (NI) was once employed as the AIEgen in side-chain polymers. For example, the monomer **30** (Fig. 10a) containing a pyrazoline ring system, an NI electron acceptor, and diethylamino electron donor moieties was prepared.^[43] Its homopolymer **31** was synthesized *via* ATRP method. The AIE property of **31** was observed in three different systems: THF/cyclohexane mixture, THF/ethanol mixture, and DMF/ethanol mixture. In the THF/cyclohexane mixture, the PL intensity increased progressively as the cyclohexane fraction increased and λ_{max} was red-shifted because of the decreased polarity of the solution and the formation of nanoaggregates. In the THF/ethanol mixture, the emission behavior was different: it decreased when $f_e \leq 50\%$ (f_e : ethanol fraction) owing to the ICT effect, and then increased when $f_e \geq 60\%$. The emission behavior of **31** in a DMF/ethanol mixture was almost the same as that of the THF/ethanol mixture. The PL intensity of **31** ($f_e = 99\%$) in the THF/ethanol mixed system was 2.83 times higher than that in pure THF, while it was 4.12 times higher in the DMF/ethanol mixture system. Moreover, the emission behavior of the polymer in the film state was also measured and showed a QY of 9%.

In addition, the two-photon fluorescence (TPF) and two-

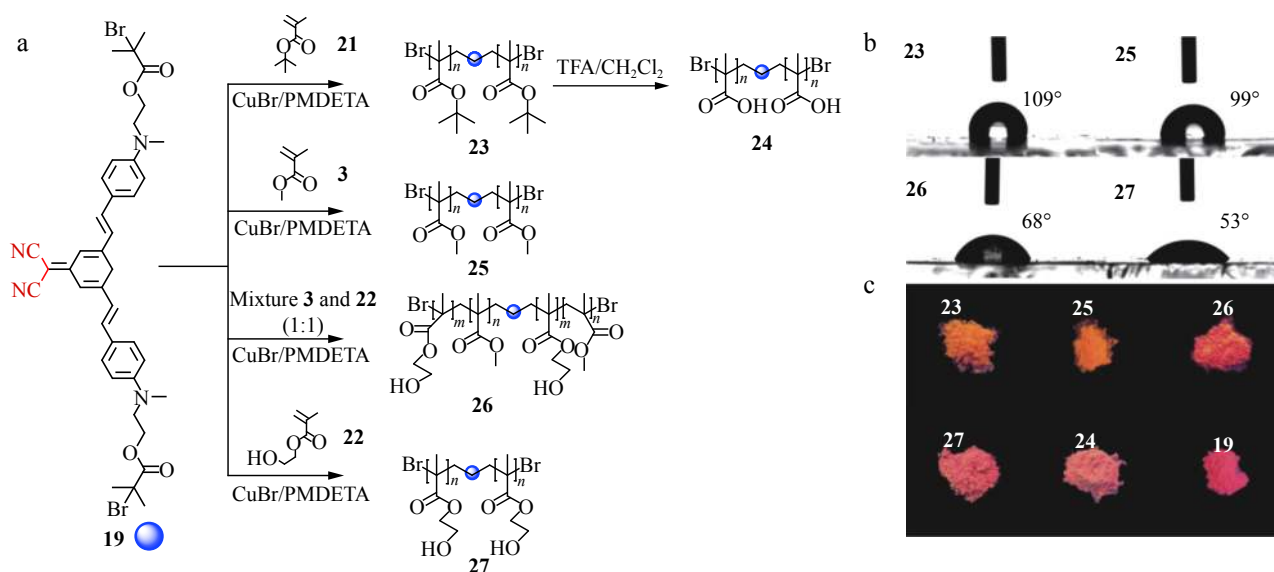


Fig. 8 (a) Molecular structure of cyanogen-containing initiator **19** and synthetic routes towards polymers **23**–**27**; (b) Contact angles of polymers **23**, **25**–**27**; (c) Photographs of the solid fluorescence of polymers **23**–**27** and initiator **19** under a 365 nm UV lamp (Adapted with permission from Ref. [41]; Copyright (2018) The Royal Society of Chemistry)

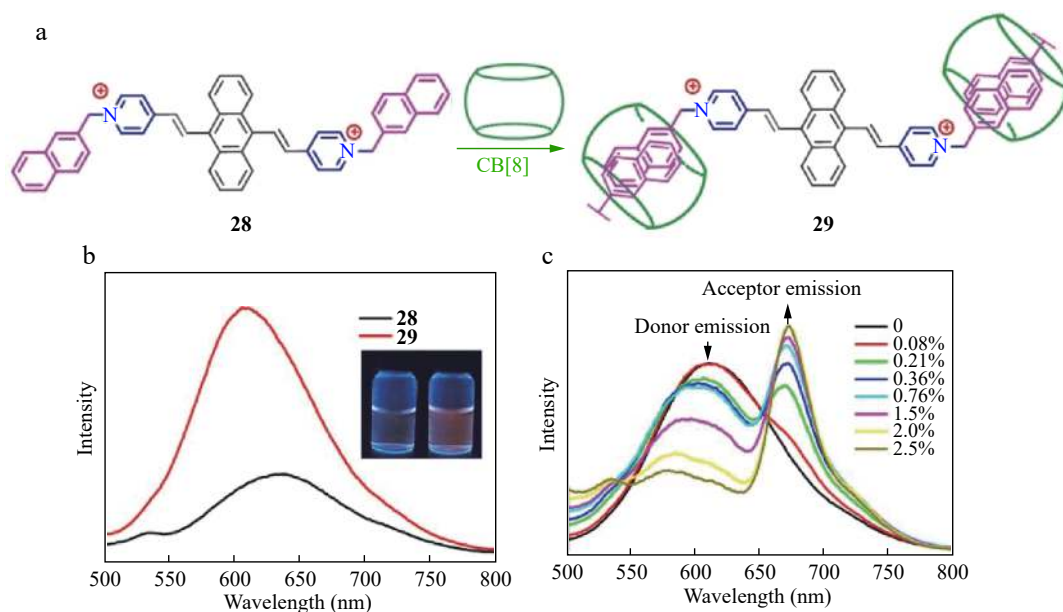


Fig. 9 (a) Molecular structures of supramolecular polymers **28** and **29**; (b) Fluorescence spectra of **28** ($60.2 \text{ mmol} \cdot \text{L}^{-1}$, black) and **29** ($60.2 \text{ mmol} \cdot \text{L}^{-1}$, red). Inset: Photographs of the corresponding fluorescence changes of **28** and **29** under a 365 nm UV lamp; (c) Fluorescence spectra of **29** in aqueous solution with different concentrations of Cy5; $\lambda_{\text{ex}} = 450 \text{ nm}$ (Reprinted from Ref. [42]; Copyright (2018) with permission from Elsevier)

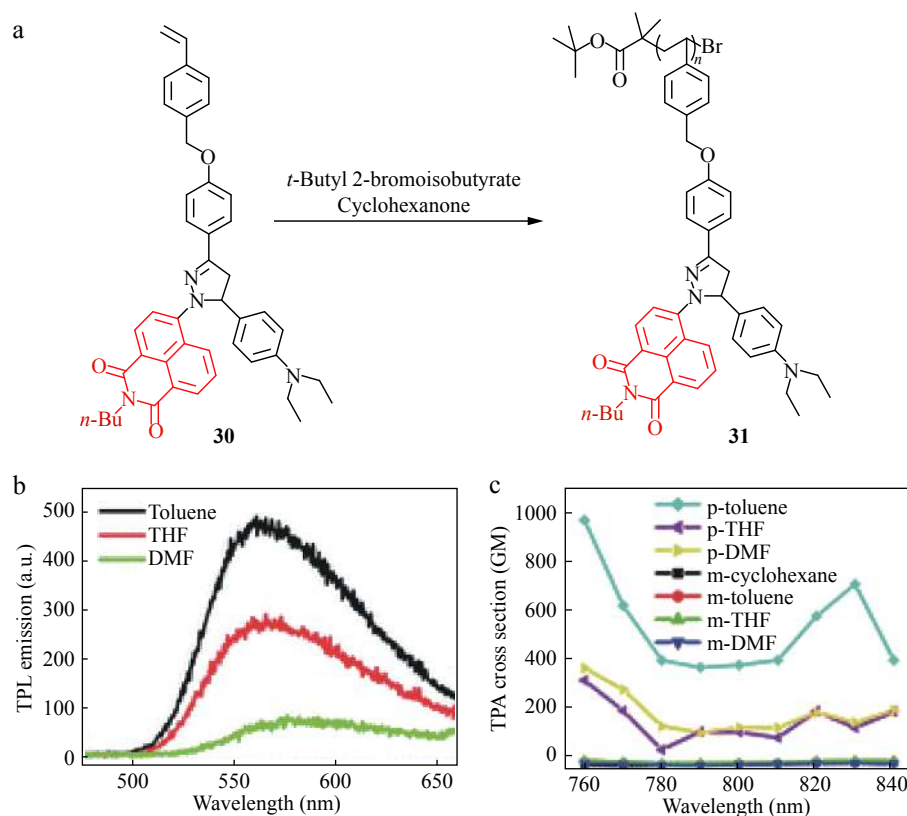


Fig. 10 (a) Synthetic approach to polymer **31** via ATRP; (b) TPF spectra of **31**; (c) TPA spectra of **30** and **31** in different solutions at the same concentration (m represents monomer **30**, p represents polymer **31**) (Adapted with permission from Ref. [43]; Copyright (2013) The Royal Society of Chemistry)

photon absorption (TPA) of **31** were also measured. Figs. 10(b) and 10(c) show the TPF spectra and TPA cross-sections, and one-photon fluorescence (OPF). The monomer **30** showed weak emission in the TPF spectrum and a lower

TPA cross-section in different polar solvents, which is similar to its OPF behavior. However, the emission band of polymer **31** exhibited a larger Stokes shift and got significantly amplified in emission intensity. Moreover, the TPA cross-

section of **31** in toluene was 983 GM per molecule (40 GM per repeat unit); this value was much higher than that of **30** in the same solvent (22 GM).

Tang and coworkers introduced a small amount of a fluorogen unit, based on TPE, into poly(*N*-isopropylacrylamide) (PNIPAM) chains with the ratio $m/n = 372/1$ by direct copolymerization of two monomers *via* AIBN-initiated free radical polymerization.^[44] The introduction of a TPE-based fluorogenic label not only preserved the original properties of the PNIPAM chains, but also endowed PNIPAM with AIE characteristics. In pure THF, copolymer **32** was non-emissive; however, the fluorescence intensity started rising dramatically to make the polymer visible at $f_w \geq 70\%$ and reached a maximum when $f_w = 100\%$ (Fig. 11b). In addition, the temperature-dependent PL intensity spectrum ranging from 14 °C to 51 °C shows that the PL intensity first increased and then decreased, peaking at 34.2 °C. Heating and cooling experiments provided a similar spectrum. This indicates that the thermal transitions of **32** (Fig. 11a) were tunable. Hence, the TPE-based fluorogenic label could be used as a probe to monitor the thermal variation in **32** aqueous solution. By changing the degree of labelling, the working mode could be tuned between non-monotonic (with small amounts of TPE fluorogens) and monotonic (with a large number of TPE fluorogens).

The reversible addition fragmentation chain transfer polymerization (RAFT) method was also used in the synthesis of AIE copolymers, as reported by Zhang and coworkers.^[45] TPE-based fluorogen was first copolymerized with an equivalent amount of styrene and then copolymerized with 150 equiv. of 4-vinylpyridine using AIBN and EDMAT as the radical initiator and chain transfer agent, respectively. Next, the resulting copolymer was treated with excess iodomethane in DMSO to give the copolymer **33**. The ¹H-NMR data showed that the ratio of $m:n:p:q$ was 15:15:28:102. Deionized water was slowly added into the DMF solution of **33** under vigorous stirring, followed by dialysis for 72 h to afford the fluorescent micelles. Compared with the fluorescence intensity of **33** in DMSO/water (5/95, *V/V*) mixture, that of the polymeric micelles in DMF was much stronger with a QY of 12%, which was 4 times higher than that in the DMSO/wa-

ter (5/95, *V/V*) mixture. This could be primarily attributed to the aggregation of TPE moiety in the hydrophobic core of polymeric micelles that restricted the intramolecular free rotation. Moreover, the PL intensity of such micelles in aqueous solution decreased progressively as the temperature increases, but could recover when cooled to room temperature, most likely due to alteration of the micelle structure.

Differing from the synthetic strategy of the previous copolymer examples, the AIEgen was also introduced into a polymer using a post-functionalization process, as reported by Tang and coworkers.^[46] During the synthetic procedure, cholesterol derivative **34** was first reacted with the polymer **35** in freshly distilled toluene, and then the solution of TPE-based fluorogen **36** in dry toluene was injected into the reaction mixture under nitrogen to give the final copolymer **37**. The emission behavior of **37** was measured in a DMF/water system. Copolymer **37** was non-emissive in pure DMF, whereas upon addition of water, the fluorescence intensity increased continuously and reached the maximum when $f_w = 99\%$. Particle aggregation in the solution with high water content could be tuned with diameters ranging from 2 μm to 50 nm. Additionally, the surface of the aggregates tended to be smoother.

A series of side-chain AIE polymers containing PDMA (poly(*N,N*-dimethylaminoethyl methacrylate), BzMA (benzyl methacrylate), and TPE moieties were synthesized by Yuan and coworkers *via* RAFT method.^[47] The feed ratio of PDMA/BzMA was 1/*x* (*x* = 120, 240, and 360, named **38a**, **38b**, and **38c**, respectively), while the ratio of TPE/PDMA was 1/20 for all of these polymers. In THF/water mixtures, **38a**, **38b**, and **38c** tended to self-assemble into spherical micelles, worm-like micelles, and vesicles, respectively. As shown in Fig. 12(b), the emission intensity increased in the order of vesicles > worm-like micelles > spherical micelles. Such structure-correlated optical behavior was mainly attributed to the stress variation of core-forming chains in the aggregates. Therefore, this work provided a new strategy for controlling the morphology of polymers and more clear understandings of the nanostructures and evolution process of polymer self-assemblies.

Click chemistry is a concept that was first proposed by K.

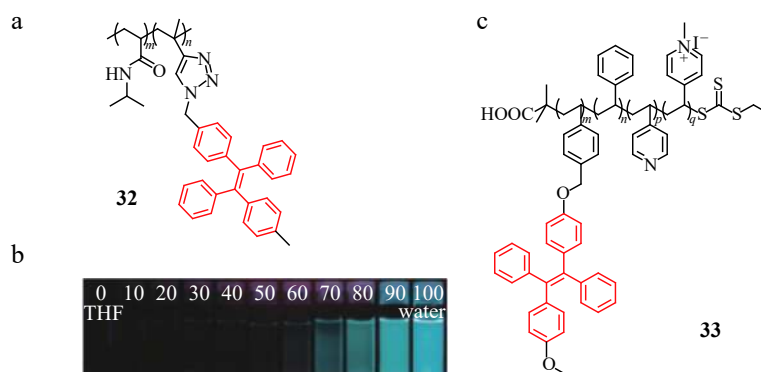


Fig. 11 Molecular structures of polymers (a) **32** and (c) **33**; (b) Photographs of polymer **32** (1 mg·mL⁻¹) in THF/water mixtures with different water fractions (17 °C, $\lambda_{\text{ex}} = 322$ nm) under a 365 nm UV light (Adapted with permission from Ref. [44]; Copyright (2009) The Royal Society of Chemistry)

Barry Sharpless in 2001, which includes a series of efficient chemical reactions.^[48] Among them, the most representative reaction is the copper-catalyzed azide-alkyne cycloaddition, which provides advantages of high efficiency and relatively mild reaction conditions.^[49] Hong and coworkers reported the preparation method of azide-functionalized compound **40**, containing a fluorescent 2,4,6-triphenylpyridine pendant group, together with vinyl polymer **39**, containing acetylene pendant groups, *via* the above-mentioned copper-catalyzed azide-alkyne cycloaddition to give **41**.^[50] Two different molecular weights (**41a**: $M_n = 5.254 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ and **41b**: $M_n = 3.73 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$) of polymer **41** were selected for further studies. The fluorogen compound **40** itself was non-emissive in pure THF, but showed blue emission when $f_w = 90\%$. Polymer **41b** possessed typical AIE characteristic

emission which was weak in pure THF while enhanced progressively by adding deionized water and reached maximum when $f_w = 80\%$, after which precipitation occurred. However, the emission behavior of polymer **41a** was not obvious. Since it showed strong blue emission in pure THF, only a slight enhancement could be observed when $f_w = 60\%$ (Fig. 13c). The QY of polymer **41b** increased from 25% to 78%, while that of polymer **41a** increased from 82% to 84%. Computational simulations revealed that polymer **41b** contained a linear framework which could isolate fluorogens, leading to weak emission in pure THF. Conversely, following the addition of water, densely-packed fluorogen aggregates started to form, resulting in emission enhancement. On the other hand, polymer **41a** possessed a longer chain, more aggregated domains, and a coil-like framework, thus few

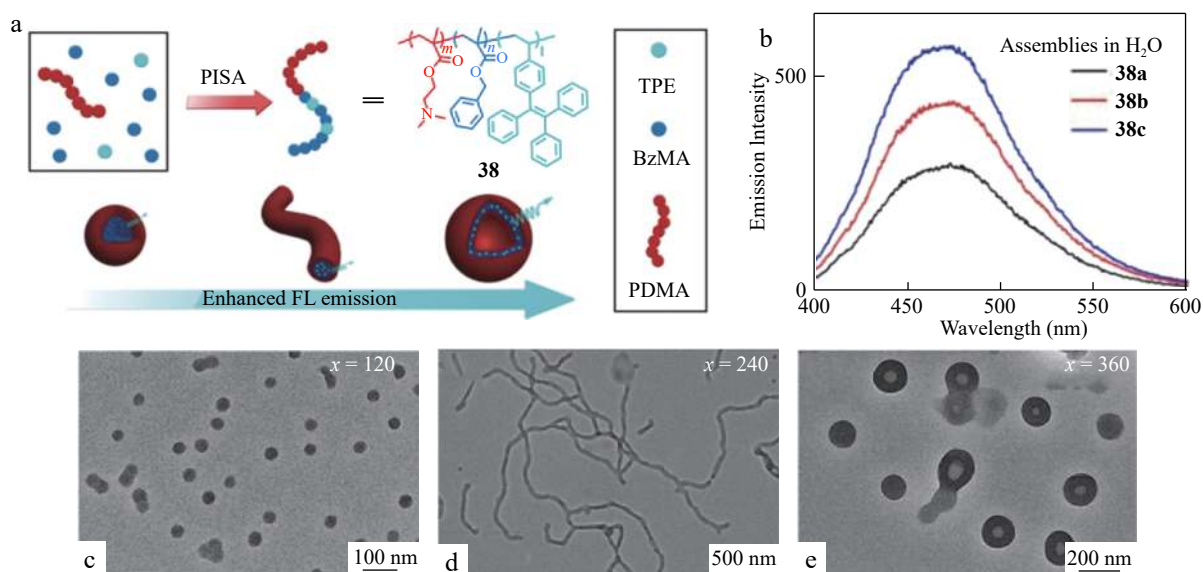


Fig. 12 (a) Molecular structures of polymers **38**; (b) Fluorescence intensity of **38a**, **38b**, and **38c** assemblies in water (the concentration of TPE group for all the samples is $2.5 \mu\text{g}\cdot\text{mL}^{-1}$); TEM images of (c) **38a**, (d) **38b**, (e) and **38c** assemblies in water (Adapted with permission from Ref. [47]; Copyright (2017) American Chemical Society)

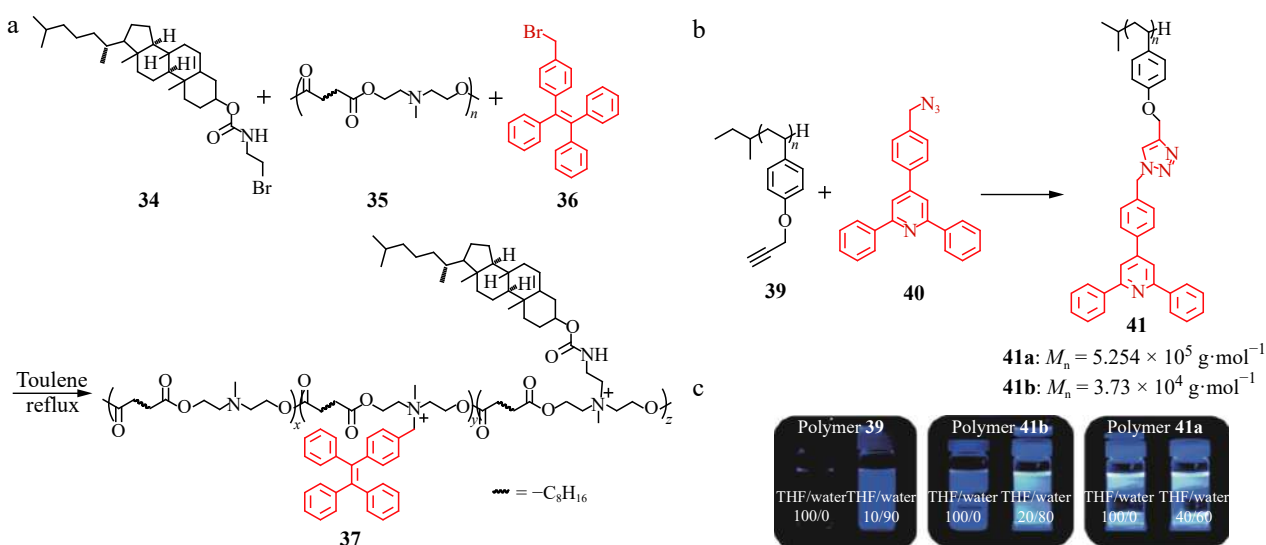


Fig. 13 (a) Synthetic approach towards polymer **37**; (b) Synthetic route towards polymer **41** *via* copper-catalyzed azide-alkyne cycloaddition; (c) Fluorescent photographs of polymers **39**, **41b**, and **41a** in THF/water mixture with different water fractions under a 365 nm UV lamp (Adapted with permission from Ref. [50]; Copyright (2012) The Royal Society of Chemistry)

changes were observed as the water fraction increased.

Main-chain Polymers

Main-chain polymers represent those with AIEgens, such as TPE and siloles, on the backbone. Tang and coworkers reported two different polytriazoles (**44a**, **44b**), using TPE as the backbone, *via* a 1,3-dipolar polycycloaddition between diyne (**42**) and diazide (**43a**, **43b**) monomers (Fig. 14a).^[51] Polymer **44b** ($M_w = 1.21 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$) could only be partially dissolved in THF while could be completely dissolved in polar solvents, for example, DMF and DMSO. On the contrary, its counterpart **44a** ($M_w = 3.66 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$), bearing longer polymer chains, was soluble in THF and other organic solvents. The emission behavior of these two polytriazoles was measured in a THF/water system. Both of these polymers were non-emissive when molecularly dissolved in pure THF. Upon addition of large amounts of water (> 60 vol%), **44a** exhibited strong PL peaks at 480.5 nm, indicating the formation of aggregates (Fig. 14b). However, triggering of the activation state for **44b** required much less water (10 vol%) owing to its relatively low solubility in THF. The QY measurement further proved the formation of aggregates. When $f_w = 90\%$, the Φ_F of **44a** and **44b** both reached a maximum (16.9% and 17.8%, respectively), which were 94 and 110 times higher than those in pure THF, respectively. The excellent AIE characteristic and thermal

stability made these polytriazoles potential candidates for the application in explosive chemosensors.^[52]

He and coworkers synthesized TPE-based AIE polymers with azobenzene pendants through a post-polymerization azo-coupling method, and the degrees of functionalization (DFs) of azobenzene chromophores could be controlled only by adjusting the feed ratios.^[53] The precursor polymer **45** (Chart 2) showed typical AIE effect in the DMF/water mixtures and the PL intensity reached the maximum when $f_w = 90\%$. However, it started to decline significantly once incorporating azobenzene moiety, and when DFs was higher than 21%, fluorescence quenching could be observed. This was mainly attributed to the fluorescence resonance energy transfer process—the excited energy of TPE moiety could be transferred to the azobenzene chromophores, thus leading to the fluorescence quenching. Interestingly, upon treatment with hydrazine hydrate at room temperature, the azobenzene chromophores could be reduced to hydrazobenzene, so the strong emission would be recovered. Therefore, a redox triggered fluorescence “ON/OFF” system was established.

Tang and coworkers reported that a chiral polytriazole using TPE and alanine as the backbone could be prepared *via* a Cu(I)-catalyzed click polymerization by introducing a chiral amino acid pendant (monomer **48**) into the AIE scaffold (monomer **47**).^[54] The resulting polymer, **49** (Fig. 15), ex-

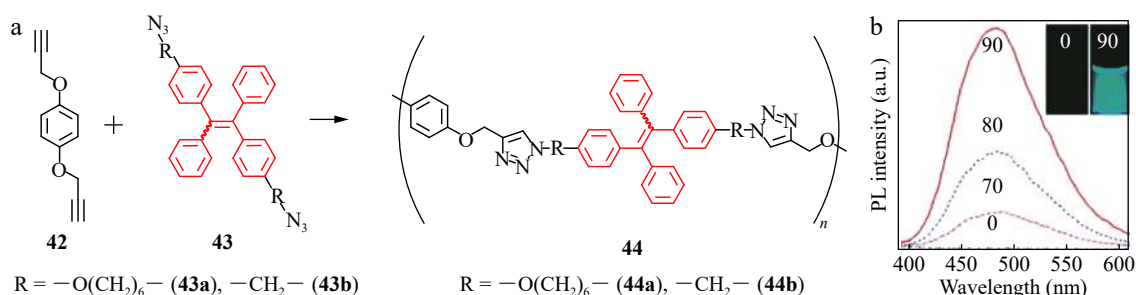


Fig. 14 (a) Synthetic route towards polymer **44** *via* a click reaction; (b) PL spectra of **44a** in the THF/water mixture with different water fractions ($10 \mu\text{mol} \cdot \text{L}^{-1}$; $\lambda_{\text{ex}} = 326 \text{ nm}$). Inset: fluorescence photographs of **44a** solutions with water fractions of 0% (left) and 90% (right) (Adapted with permission from Ref. [51]; Copyright (2009) American Chemical Society)

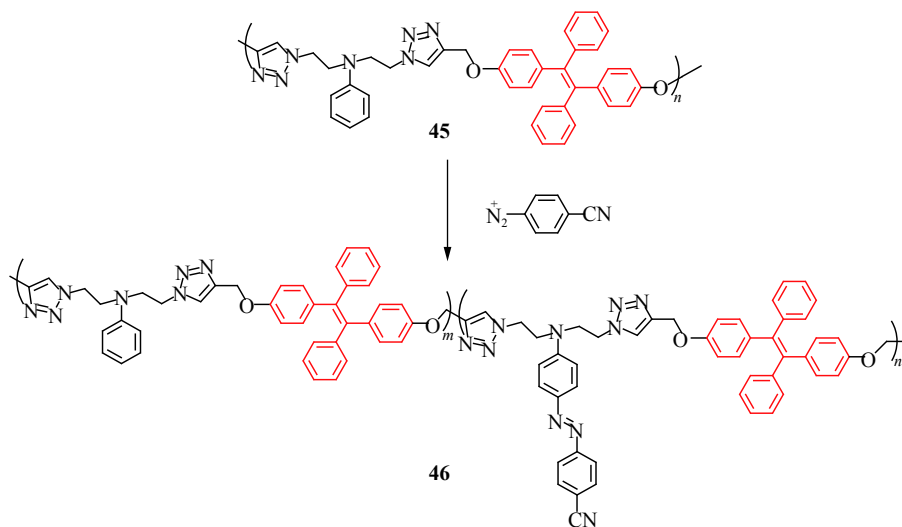


Chart 2 Molecular structures of polymers **45** and **46**

hibited typical AIE characteristic in a THF/water system. It showed weak emission peaking at 463 nm in pure THF and almost no emission enhancement could be observed when $f_w \leq 40\%$. However, when $f_w \geq 50\%$, the PL intensity increased dramatically and $\lambda_{\max}$ was red-shifted to 493 nm. The PL intensity reached the maximum when $f_w = 80\%$, which was 15-fold higher than that in pure THF. When $f_w > 80\%$, the PL intensity started to decrease owing to the formation of precipitation. Photographs of polymer **49** in different solutions under a UV lamp (Fig. 15) displayed such changes clearly in fluorescence. Interestingly, a different nano mor-

phology could be obtained by adjusting the water fraction of the polymer solution, providing an important strategy for designing fluorescent building blocks with desirable architectures.

To understand the structure-property relationship of the polymers constructed from the AIE monomers, Tang and coworkers designed and synthesized two different polytriazoles, **52a** and **52b** (Fig. 16a), containing 2,3-dicyano-5,6-diphenylpyrazine (DCDPP) and tetraphenylpyrazine (TPP) moieties, respectively, *via* copper-catalyzed azide-alkyne click polymerization.^[55] Polymer **52b** showed AIE

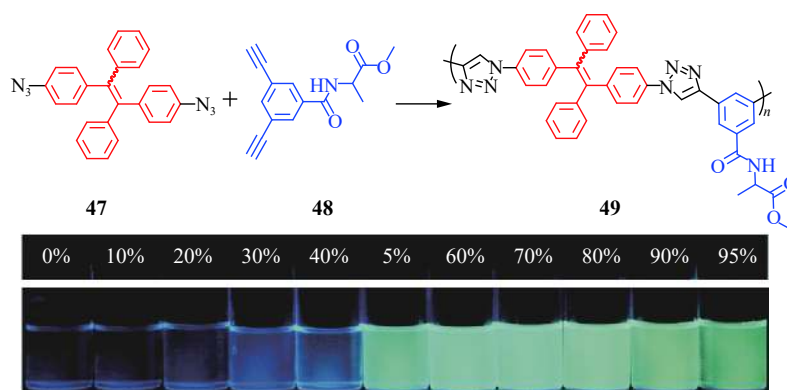


Fig. 15 Synthetic route towards polymer **49** *via* a click reaction and fluorescence photographs of solutions of **49** with different water contents under a commercial 365 nm UV lamp (Adapted with permission from Ref. [54]; Copyright (2018) The Royal Society of Chemistry)

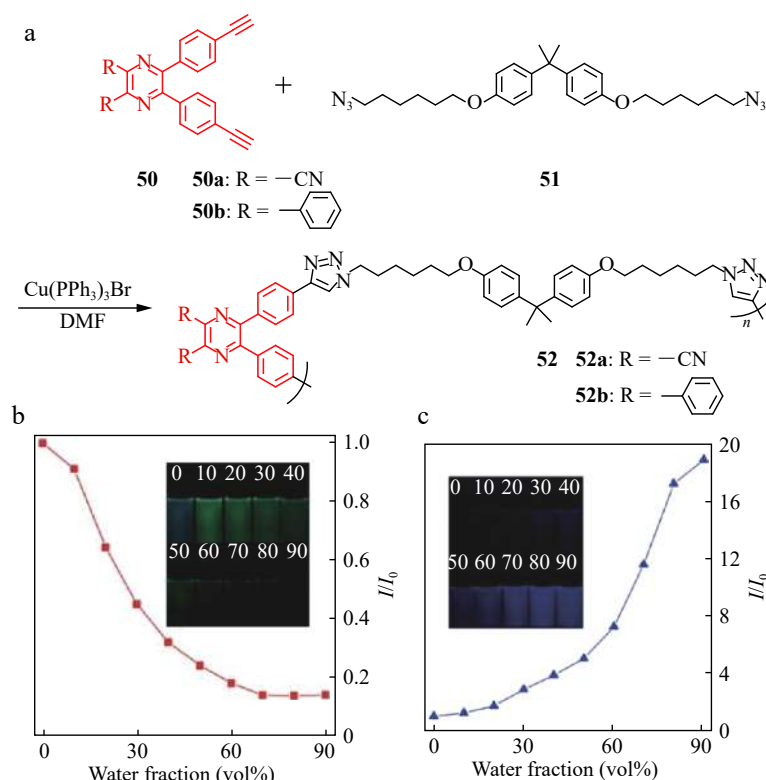


Fig. 16 (a) Synthetic route towards polymer **52** *via* a copper-catalyzed azide-alkyne click polymerization; Plots of relative intensity (I/I_0) versus water fraction of the THF/water mixtures of (b) **52a** and (c) **52b**. I_0 is the PL intensity in pure THF. Inset: photographs of (b) **52a** and (c) **52b** in THF/water mixtures with water fraction increasing from 0 to 90% under 365 nm UV light (Adapted with permission from Ref. [55]; Copyright (2018) American Chemical Society)

characteristic in THF/water mixtures, and PL intensity reached the maximum when $f_w = 90\%$, which was 18-fold higher than that in pure THF solution. Differing from the emission behavior of polymer **52b**, polymer **52a** suffered from the ACQ effect, which was mainly attributed to the strong packing of the DCDPP moiety in its backbones caused by their partially planar structure. On the contrary, no such interaction could be observed in the structure of polymer **52b**, thus endowing **52b** with AIE characteristics. In general, this work provided an effective strategy for the design of AIE polymers' construction by direct polymerization of AIE-active monomers.

Fluorene possesses an ACQ characteristic; however, once it is incorporated into an AIE-active skeleton, an unexpected AIE phenomenon can be observed in the obtained nanoparticles upon aggregation. For example, Dong and coworkers prepared a series of TPE-based copolymers containing a fluorene moiety *via* standard Suzuki cross-coupling polymerization.^[56] By adjusting the feed ratio of TPE-based monomer **53** (Fig. 17), dibromofluorene **54**, and diboronate ester fluorene **55**, copolymers **56a–56f** could be obtained. Fig. 17 shows the fluorescence photographs of such copolymers in solution, aggregates, and in the film states under

365 nm UV illumination. Polyfluorene (**56f**) showed an obvious ACQ characteristic; however, following the introduction of TPE units, a clear transformation from ACQ to AIE was observed. Moreover, copolymers **56c–56e** possessed dual-channel fluorescence response (DCFR) properties—emission in solution was quenched, whereas in aggregated and film states increased dramatically. Further experiments revealed that the best ratio of TPE:fluorene was 3:7 or 2:8 owing to their high sensitivity at certain aggregation levels. Hence, a possible method for the conversion of regular ACQ polymers into AIE polymers relies on incorporation of AIE units into traditional polymer structures.

Similarly, in order to improve the emission behavior, Cao and coworkers incorporated siloles into the chains of polyfluorene *via* a Suzuki coupling polymerization.^[57] Silole monomer **57** (Chart 3) was copolymerized with dibromofluorene **58** and diboronate ester fluorene **59** at feed ratios of 1%, 10%, and 20% to give copolymers **60a**, **60b**, and **60c**, respectively. The PL spectrum of **60a** in THF showed only two blue emission peaks (418 nm, 440 nm) owing to the relatively large number of polyfluorene units. However, as the HPS content increased, a new emission peaked at 506 nm emerged and increased progressively, and the intensity ra-

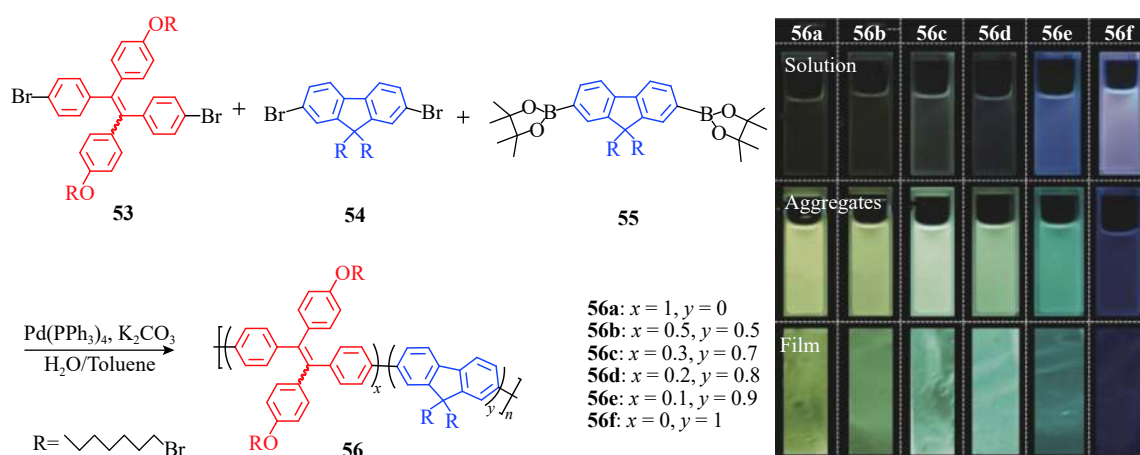


Fig. 17 Synthetic route towards polymer **56** and fluorescence photographs of **56a–56f** in THF solution, as aggregates in THF/water mixture ($f_w = 99\%$), and as films under a 365 nm UV lamp (Adapted with permission from Ref. [56]; Copyright (2012) The Royal Society of Chemistry)

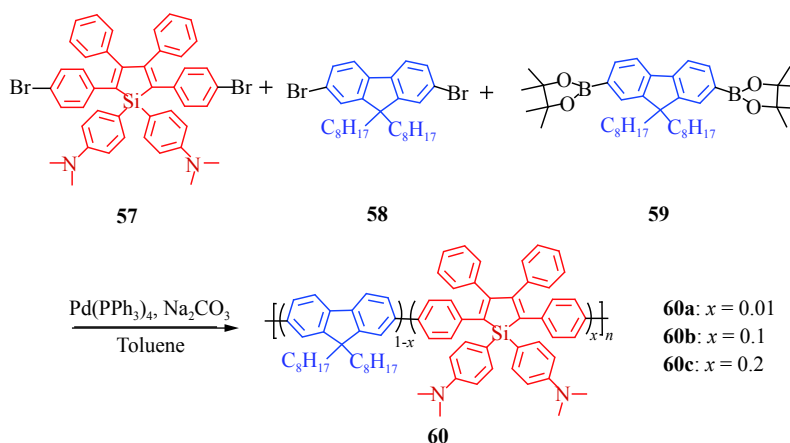


Chart 3 Synthetic route towards polymer **60**

tios of the silole peak to the fluorene signal were 30% and 60% for copolymers **60b** and **60c**, respectively. In addition, in the thin solid film state, the blue emission peak (from the fluorene moiety) in the PL spectrum of **60a** was slightly red-shifted, but the relative intensity of green emission band (from the silole moiety) to the former blue emission peak reached 75%. For **60b**, the green emission band became predominant and the blue emission peak declined at the same time. As for **60c**, the emission peak from the fluorene segment almost disappeared. This method provided another strategy for transforming ACQ polymers to AIE polymers by introducing AIE units into the backbone of regular polymers.

Other Polymers

In this section, several examples of AIE polymers bearing special structures, such as dendrimers, star-shaped polymers, hyperbranched polymers, and microporous polymers, will be introduced. For instance, benzene-tricarboxamide-cored triphenylamine dendrimers, **61a** and **61b** (Chart 4), were reported by Ho and coworkers.^[58] These dendrimers consisted of an electron-deficient aromatic core, a hydrogen bond array, and an electron-rich outer-shell, of which an electronic-gradient could be established. By dropwisely adding deionized water into the THF solutions, nanoparticles of **61a** and **61b** with average diameters of (60 ± 20) and (80 ± 20) nm, respectively, were easily formed. At room temperature, the QYs of **61a** and **61b** increased to 2.6% and 4.8% in the THF/water mixture when $f_w = 90\%$, in comparison to their original values of 0.11% and 0.27% in THF, respectively.

Another series of conjugated dendrimers **62a–62c** (Fig. 18a) were reported by Tian and coworkers.^[59] These dendrimers consisted of a twisted divinylanthracene-based core, which was linked to an electron-donating triphenylamine outer-shell by alkenes. In dilute solutions, the conformation of these dendrimers was twisted, and the free intramolecular rotational motion in solution enhanced the fluorescence quenching. Conversely, in the aggregation state,

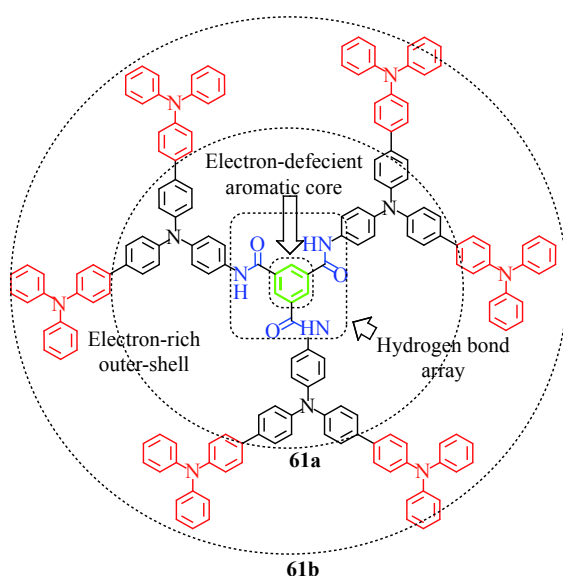


Chart 4 Molecular structure of dendrimer **61**

the intramolecular rotations were firmly restricted, and these dendrimer molecules were considerably more planarized due to their stacking forces and intramolecular interactions, resulting in the enhancement of emission intensity. As the fraction of water increased, the amplitude of QY enhancement for these dendrimers varied. For example, QY of **62c** could reach 85% when the water content increased to 80% (Fig. 18b).

Tang and coworkers reported a star-shaped oligomer **63** (Fig. 19a) with a triphenylamine core, which was connected to a 1,1,2,3,4,5-hexaphenylsilole outer-shell *via* alkyne linkers.^[60] This oligomer showed nearly no emission in pure THF ($\Phi_F = 0.81\%$). However, as the fraction of water increased, fluorescence enhancement could be clearly observed, as shown in Fig. 19(b), which was due to the intramolecular rotational restriction and the blocking of nonradiative pathways.

TPE can also be an AIEgen for star-shaped oligomers. For example, a star-shaped oligomer **64** (Fig. 19c), with a cyclohexanehexone core bearing six TPE moieties, was reported by Bhosale and coworkers.^[61] Likewise, this oligomer was also nearly non-emissive in THF. However, the intensity in emission increased dramatically following the addition of water and the emission enhancement from pure THF to aggregation ($f_w = 90\%$) was 218 folds.

Another similar example was recently reported by Zhu and coworkers—two different oligomers,^[62] **65** and **66** (Chart 5), using triazine as the acceptor core, spirotriphenylamine as the donor moiety, and TPE as the AIEgen, were designed and synthesized. For **66**, when $f_w = 90\%$, the fluorescence intensity reached the maximum at 482 nm, which was 71 times higher than that in pure THF. For **65**, the fluorescence intensity increased by 41 folds.

Interestingly, according to their fluorescent properties, some specific star-shaped gelators can exhibit a high selectivity towards particular anions. For example, Zhou and coworkers synthesized a new star-shaped gelator **67** (Fig. 20a) using carbazole as the backbone and amide groups as the connector to joint aromatic rings.^[63] In the emission spectra of **67** in DMSO at 299 nm versus different concentrations, only one emission peak at 358 nm could be observed with the concentration of $1.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$. As the concentration increased ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$), a new emission band at 460 nm emerged and became increasingly stronger until it exceeded the original single emission peak, revealing the existence of the aggregated species. Furthermore, in the temperature-dependent fluorescence spectrum with excitation at 299 nm (Fig. 20b), the emission of **67** increased nearly 40 folds from hot DMSO solution to the gel phase. This phenomenon could be attributed to the synergetic effect of J-aggregate formation in the gel state and associated restricted molecular motion. By using tetrabutylammonium salts as the source, the effect of anions, including F^- , Cl^- , Br^- , I^- , and AcO^- , on the gelation capability was studied. The results showed that this gel exhibited high selectivity towards F^- (Fig. 20c) due to the formation of $\text{N}-\text{H} \cdots \text{F}^-$ bonds. Hence, this gel could be destroyed to provide emission enhancement.

A conjugated hyperbranched polymer **68** (Chart 6), bear-

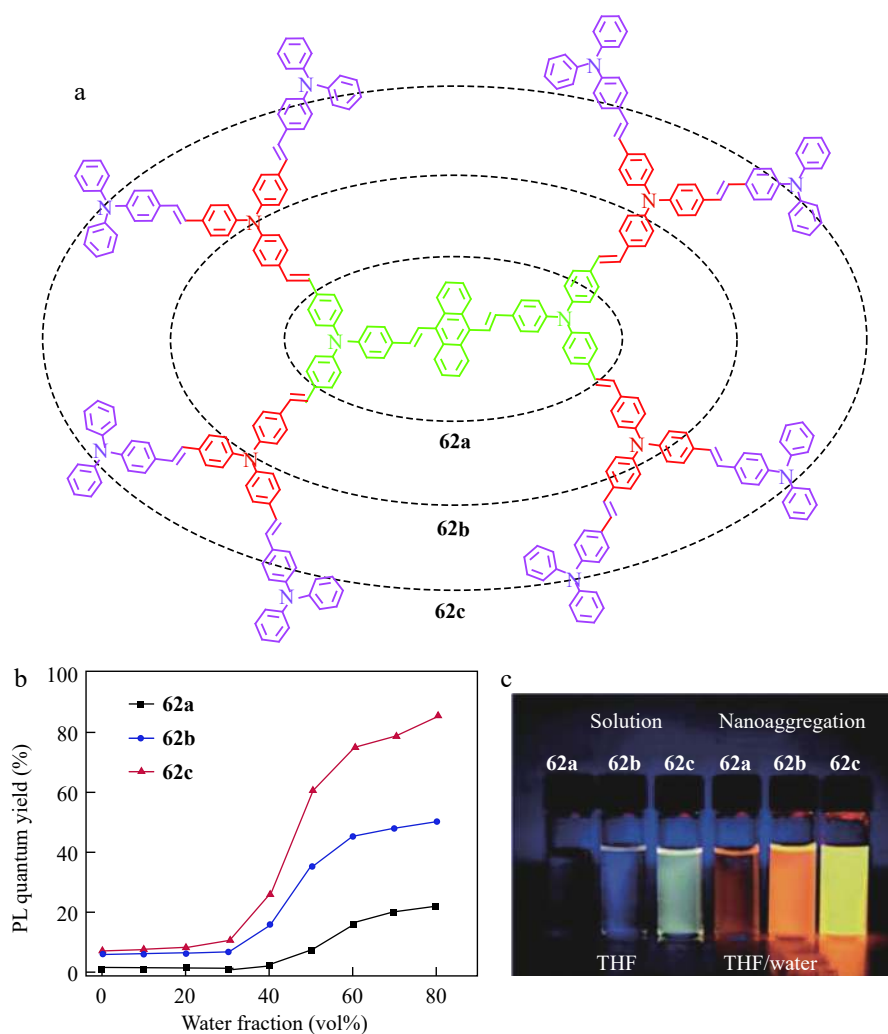


Fig. 18 (a) Molecular structure of dendrimer **62**; (b) QYs of dendrimers **62a–62c** with different water fractions in THF; (c) The fluorescence photographs of dendrimers **62a–62c** in THF and THF/water mixture ($f_w = 80\%$) nanoaggregate suspension ($2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) under a 365 nm UV light (Adapted with permission from Ref. [59]; Copyright (2014) The Royal Society of Chemistry)

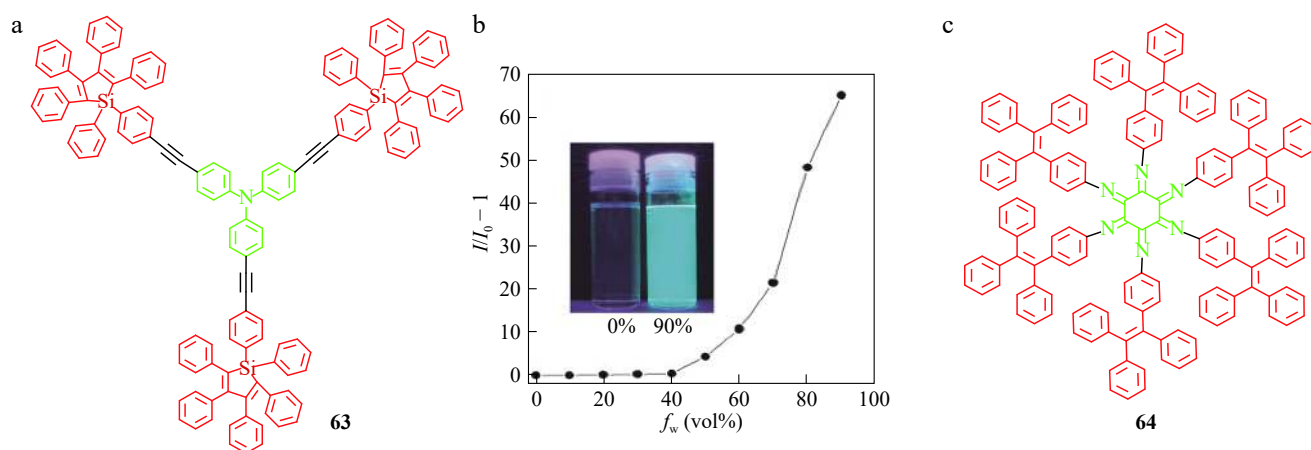


Fig. 19 Molecular structure of polymers (a) **63** and (c) **64**; (b) Plots of $(I/I_0 - 1)$ values of **63** with different water fractions in THF/water mixtures (I_0 : the PL intensity in pure THF) (Reprinted with permission from Ref. [60]; Copyright (2011) Elsevier)

ing carbazole moieties and TPE units, was reported by Li and coworkers.^[64] The polymer was synthesized through an “ $A_2 + B_4$ ” approach *via* Suzuki polycondensation reactions. By adding deionized water into THF solution of **68** under

vigorous stirring, the obtained mixtures were transparent and homogenous, but upon excitation at 360 nm, the fluorescence intensity increased significantly. In pure THF, **68** showed weak emission, while as the water fraction in-

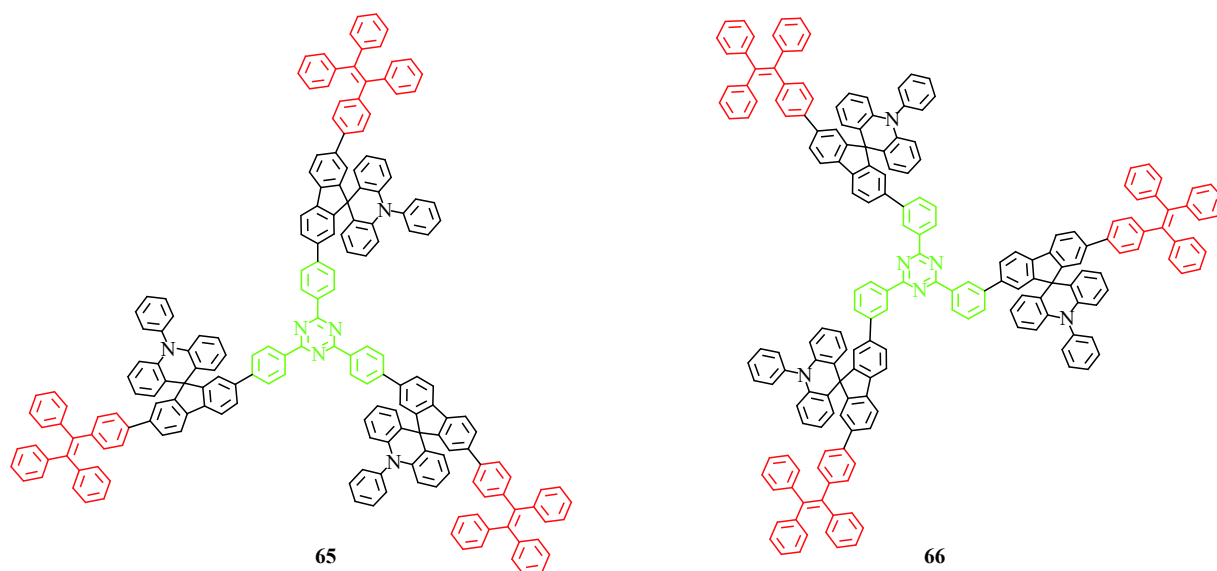
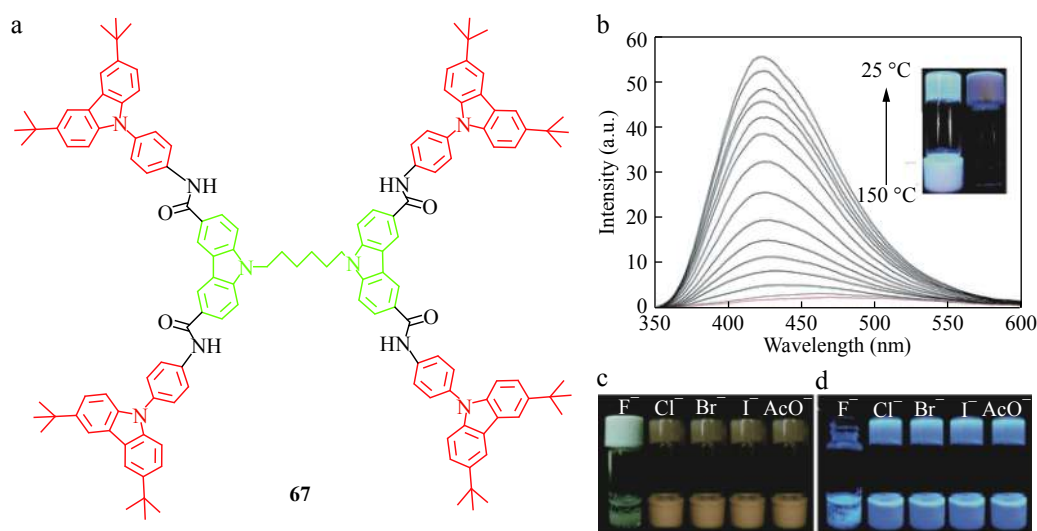
Chart 5 Molecular structures of polymers **65** and **66**

Fig. 20 (a) Molecular structure of polymer **67**; (b) Fluorescence emission spectra of **67** in DMSO (black line) ($8.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $\lambda_{\text{ex}} = 299 \text{ nm}$) and in THF (red line, $8.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, 25°C) versus different temperatures. Inset: photograph of the DMSO gel and sol under a 365 nm UV light; Photographs of DMSO gels of **67** under (c) daylight and (d) a 365 nm UV light by adding 4 equiv. of different anions (Adapted with permission from Ref. [63]; Copyright (2011) The Royal Society of Chemistry)

creased, an intense PL peak at 510 nm emerged. When $f_w = 90\%$, QY increased to 29.6%, which was 27 times higher than that in pure THF. In addition, due to the good hole injection and transporting properties, **68** is a potential candidate for polymer light-emitting diodes (PLEDs) devices.

Yin and coworkers synthesized a novel hyperbranched supramolecular polymer with AIE characteristic by the orthogonal self-assembly of terpyridine-based metal-ligand interactions and crown ether-based host-guest interactions.^[65] By simply mixing monomers **69**, **70** (Fig. 21), and $\text{Zn}(\text{OTf})_2$ in a 4:1:2 molar ratio, hyperbranched supramolecular polymer **71** could be obtained. The formation of hyperbranched supramolecular polymer **71** needed relatively high concentration and brought about an increasing density of TPE units, leading to more restriction of intramolecular motions of AIE-

gens. Therefore the emission of polymer **71** increased dramatically compared to monomers **69** and **70**. Additionally, because of the abundant stimuli-responsiveness of dibenzo-24-crown-8/dibenzylammonium salts and the terpyridine/Zn recognition motifs, polymer **71** could respond to several stimuli including cyclen, triethylamine, K^+ , Cl^- , and heating with fluorescence decrease. Therefore, hyperbranched supramolecular polymer **71** can be potentially used as a smart and adaptive luminescent material.

Jiang and coworkers reported a light-emitting conjugated microporous polymer^[66] using TPE as the building block; the TPE moieties are connected to the tetrakis(4-bromophenyl)-ethene by covalent bonds. A Yamamoto coupling reaction was used to construct an interlocked network. Yamamoto reactions with different reaction time were carried out to mon-

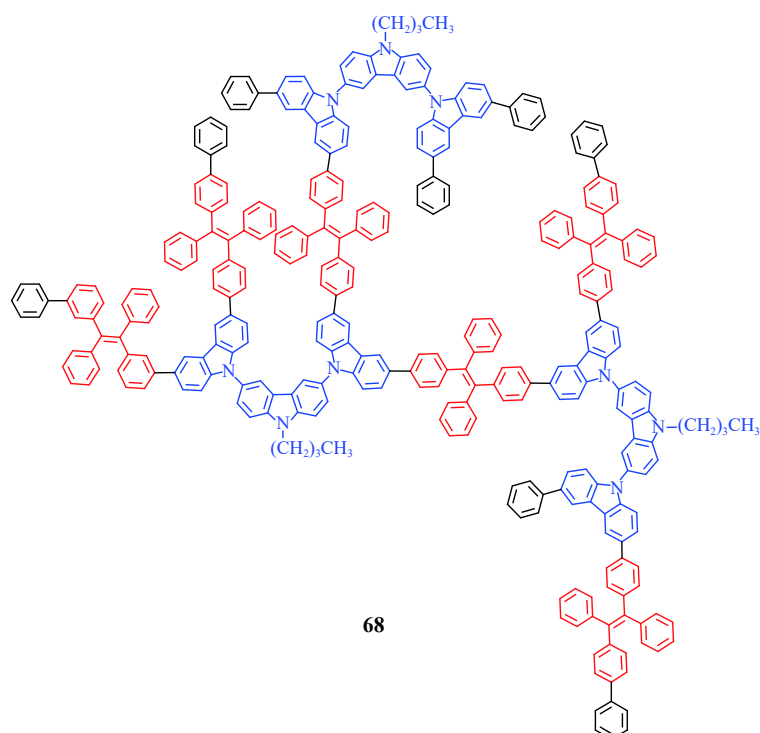


Chart 6 Molecular structure of polymer **68**

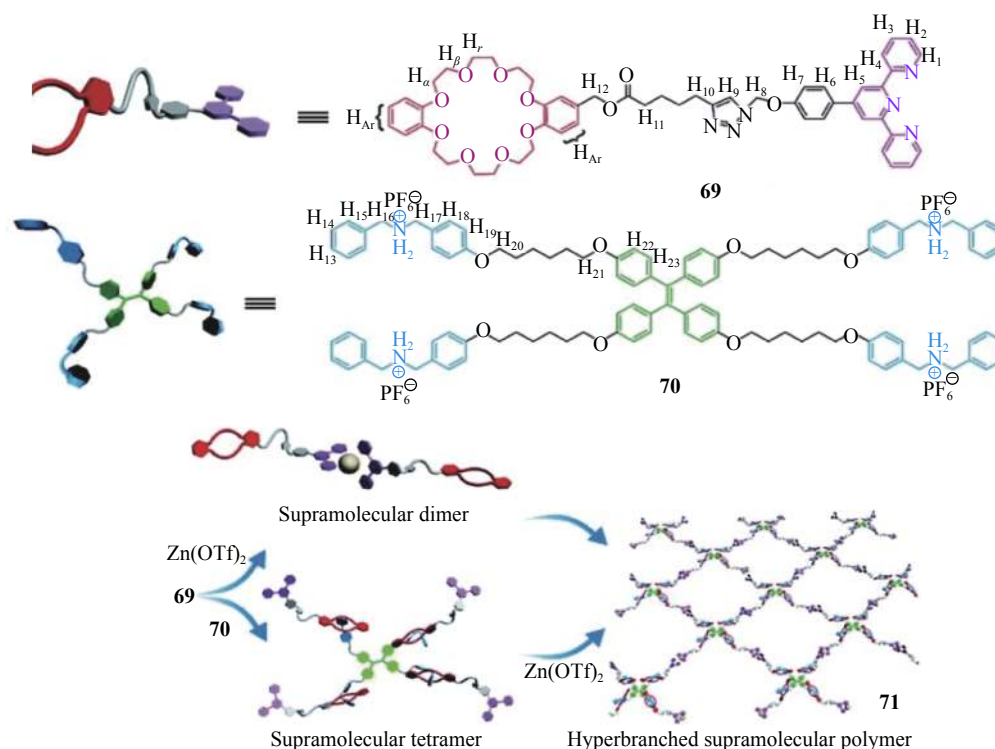


Fig. 21 Cartoon representation of the formation of hyperbranched fluorescent supramolecular polymer **71** (Adapted with permission from Ref. [65]; Copyright (2016) The Royal Society of Chemistry)

itor the development of the porous network. Results showed that as the reaction time increased from 2 h to 72 h, the average size of **73** (Fig. 22) platelets increased from 25 nm to 255 nm, the absorption band was red-shifted from 342 nm to 368 nm, and the emission band was red-shifted from 538 nm to 551 nm. The QY of **72** and TPE in THF at room tempera-

ture was only 0.16% and 0.20%, respectively, and Φ_F of **74** (72 h) was only 0.65%. Conversely, **73** (2 h) showed a high Φ_F , which reached 40% under the same conditions. All the **73** polymers prepared at different reaction time exhibited similarly high Φ_F values, indicating that the interwoven conjugated microporous polymer (CMP) skeleton could greatly

enhance luminescence activity. The three-dimensional interlocked network successfully hindered the rotation of TPE backbone, promoted π -electronic conjugation, facilitated exciton migration, and enhanced luminescence properties.

Another microporous organic polymer was designed and synthesized by Son and coworkers (Fig. 23).^[67] This polymer consisted of a TPE-containing microporous network (**75**) whereby poly(vinylpyrrolidone) (PVP) was entrapped to form materials with excellent water compatibility (**76**). SEM analysis revealed that **75** lacking PVP showed irregular and relatively large sizes in the region of 300–1000 nm, whereas the **76** materials showed nanoparticulate morphologies with an average diameter of (136 ± 18) nm owing to the efficient hindrance of network growth by PVP. Besides, **76** could be well dispersed in water showing the maximum emission at

545 nm and excitation at 410 nm with $\Phi_F = 7.3\%$, while **75** could not be dispersed in water even under sonication (Fig. 23b). On account of the excellent water compatibility and the fluorescence properties, **76** can be applied to sense nitrophenol, which is one of the major pollutants in water discharged from modern chemical manufacturing. Emission quenching could be observed as the concentration of nitrophenol increased, and the sensitivity K_{SV} values ranged from $1.26 \times 10^4 \text{ L} \cdot \text{mol}^{-1}$ to $3.37 \times 10^4 \text{ L} \cdot \text{mol}^{-1}$.

APPLICATIONS

Fluorescence Sensors

Due in large part to the work of Tang and coworkers on fluorescence biosensors, a variety of AIE biosensors with

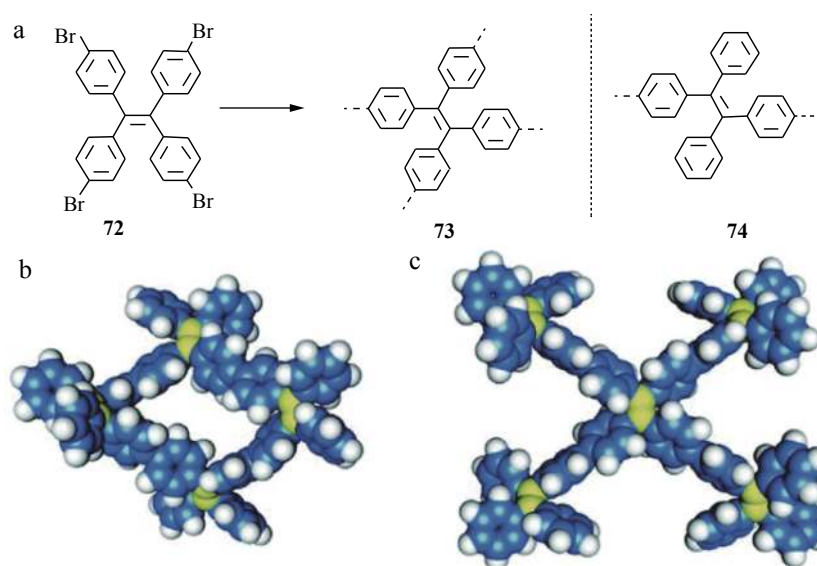


Fig. 22 (a) Synthetic route towards polymer **73** and its linear analogue **74**; (b) Closed tetragonal skeleton and (c) open framework of the **73** segments simulated by DFT calculations at the B3LYP 6-31G* level (phenyl, blue; ethene, yellow; H, white) (Adapted with permission from Ref. [66]; Copyright (2011) American Chemical Society)

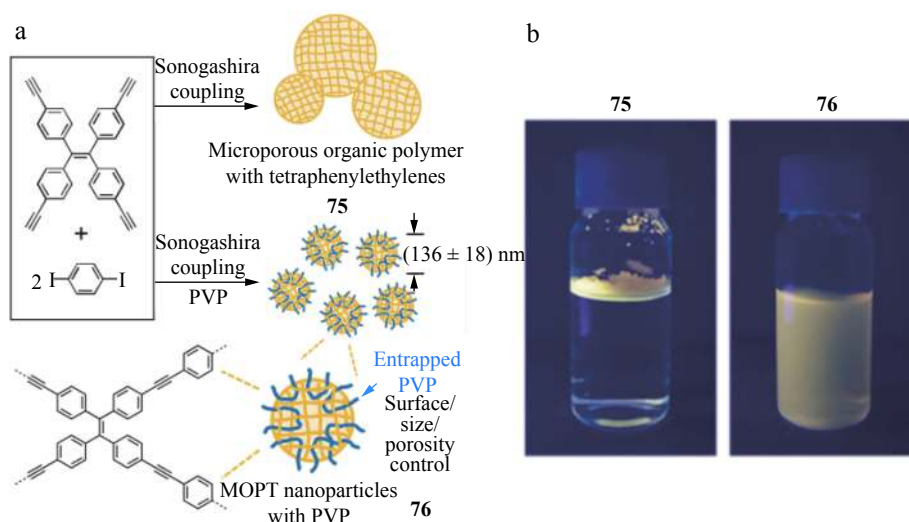


Fig. 23 (a) Synthetic routes toward polymers **75** and **76**; (b) Photographs of **75** and **76** ($0.050 \text{ mg} \cdot \text{mL}^{-1}$ in water, $\lambda_{\text{ex}} = 410 \text{ nm}$) (Adapted with permission from Ref. [67]; Copyright (2018) American Chemical Society)

high selectivity and sensitivity have been designed and fabricated, and successfully applied in various fields such as molecular sensing, cell imaging, biological probes, etc.^[68,10] The following section on fluorescence sensors will introduce several examples of “turn on” or “turn off” detection systems.

For instance, based on the mercury ion-promoted deprotection reaction of thioketals, Ruan *et al.* designed and synthesized a polymer containing TPE moiety as an efficient fluorescent probe for Hg^{2+} .^[69] Polymer **78** exhibited obvious AIE property in a THF/water system and was almost non-emissive in pure THF. The PL intensity increased progressively by adding water slowly and reached the maximum when $f_w = 98\%$ (Fig. 24b). Polymer **77** showed a similar AIE characteristic when $f_w \leq 80\%$. However, following the addition of more water, its PL intensity decreased swiftly and reached the minimum when $f_w = 98\%$, which was unexpectedly lower than that in pure THF. This could be mainly attributed to the formation of precipitates when $f_w = 98\%$ and the efficient energy transfer from TPE moiety to an additional fluorophore (the nitrobenzene moiety). Hence, an obvious distinction in fluorescent intensity under a 365 nm UV light could be observed by adding mercury ions into the THF/water (2/98, *V/V*) mixture, proving the potential application of **77** as a “turn on” fluorescence sensor for the detection of Hg^{2+} . Further experiments revealed an excellent selectivity towards Hg^{2+} with the detection limit being as low as $2.3 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$.

Wang and coworkers designed and synthesized a novel polymer **79** using TPE as the backbone that incorporated a thiazole moiety prepared *via* a Pd-catalyzed Sonogashira coupling reaction.^[70] In the THF/water system, **79** exhibited an obvious AIE characteristic—the PL intensity increased gradually by slowly adding water and reached the maximum when $f_w = 90\%$, which is 4.07 times higher than that in pure THF. Therefore, a THF/water (10/90, *V/V*) mixture was chosen for metal ion detection experiments. Upon the addition of Hg^{2+} , a dramatic decline in PL intensity was observed owing to the reduction of π -conjugated system in **79** induced by the metal coordination with the thiazole groups. The maximum fluorescence quenching was up to 88% when 100 equiv. of Hg^{2+} was added to the solution (Fig. 25b). Fluorescence quenching for Ag^+ was 91.5% when the concentration of silver ion was 40 equiv. (Fig. 25c). A visual color change from bright yellow to practically non-emissive could be clearly observed under a 365 nm UV lamp, thus endowing **79** with the ability to be a “turn-off” fluorescence sensor for Hg^{2+} and Ag^+ .

Cao and coworkers designed and synthesized an electron donor-accepter polymer **80** (Fig. 26a) containing diketopyrrolopyrrole unit as an electron acceptor and triphenylamine moiety as an electron donor.^[71] Polymer **80** showed AIE effect in the DMF/water mixtures and the PL intensity reached the maximum when $f_w = 90\%$, which was 7 times higher than that in pure DMF solution. Interestingly, upon the addition of water into THF solution of polymer **1**, its emission started to

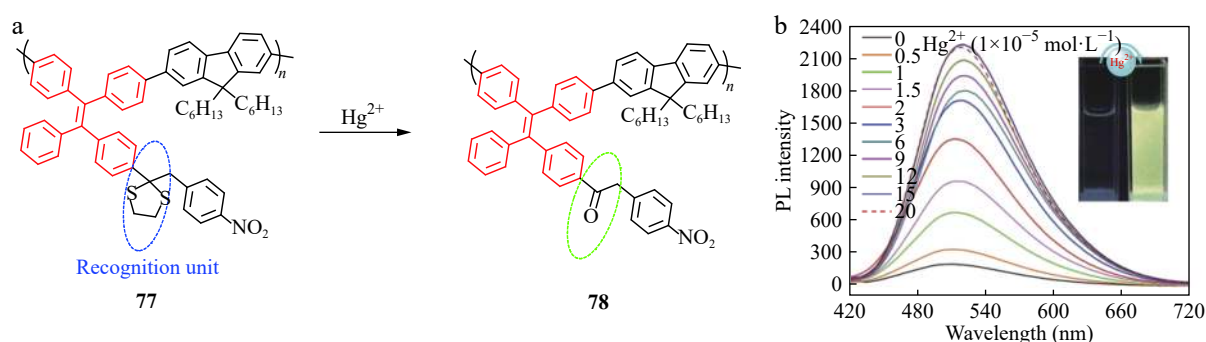


Fig. 24 (a) Schematic showing transition of polymer **77** to **78** following the addition of mercury ions; (b) PL spectra of **78** ($20 \mu\text{mol} \cdot \text{L}^{-1}$) with different concentrations of Hg^{2+} in THF/ H_2O system with $f_w = 98\%$ ($\lambda_{\text{ex}} = 368 \text{ nm}$). Inset: fluorescence photographs of **78** before and after reaction with Hg^{2+} ($1.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) (Reprinted with permission from Ref. [69]; Copyright (2018) Elsevier)

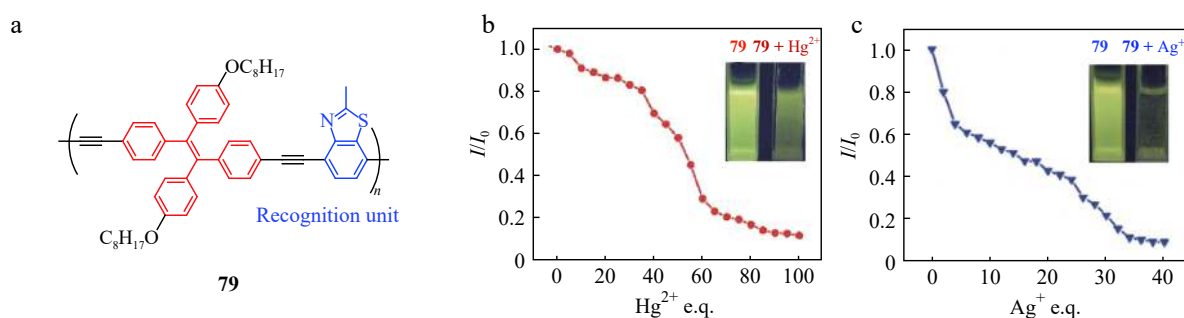


Fig. 25 (a) Molecular structure of polymer **79**; PL quenching efficiencies (I/I_0) of **79** with different concentrations of (b) Hg^{2+} and (c) Ag^+ at 525 nm (I_0 : fluorescence intensity without Hg^{2+} or Ag^+). Inset: fluorescence photographs of the polymer solution before (left) and after (right) the addition of 100 equiv. of Hg^{2+} or 40 equiv. of Ag^+ under 365 nm UV light (Reprinted with permission from Ref. [70]; Copyright (2018) Elsevier)

decrease, and when the water fraction reached 10%, completely fluorescence quenching could be observed. This was mainly due to the synergism of the solvent polarity and ICT effect. Moreover, the detection limit of polymer **80** for water in THF was 0.005%. Therefore, a fluorescence “turn-off” sensor for detection of trace water in organic solvents has been successfully fabricated.

Zhang and coworkers fabricated a series of new porous fibers based on AIE polymer **6** using an electrospinning tech-

nique.^[72] Due to the large surface area ($41.1234 \text{ m}^2 \cdot \text{g}^{-1}$) and extraordinary fluorescence characteristics, such porous fibers exhibited excellent oil adsorption capability. Fig. 27(b) shows the PL intensity of the porous fibers before and after oil adsorption with obvious fluorescence quenching phenomenon. Such quenching arose from the different intramolecular rotation states which are shown in Fig. 27(c). The intramolecular rotations of **6** in an aggregate state were restricted by the PMMA chains; however, penetration of oil

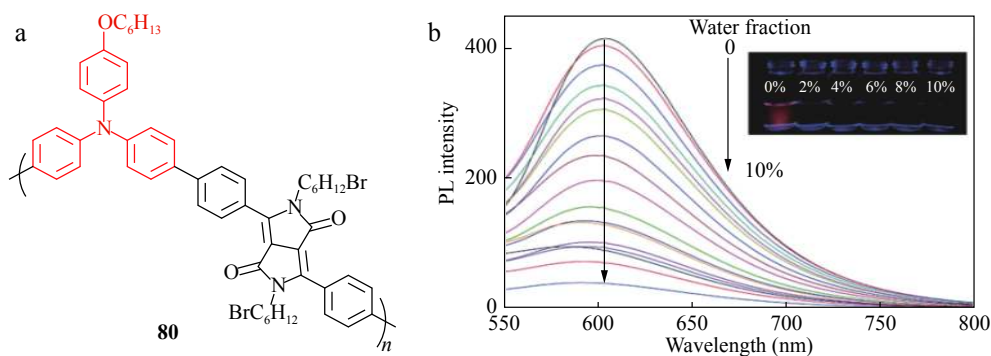


Fig. 26 (a) Molecular structure of polymer **80**; (b) Fluorescent spectra of polymer **80** ($10 \text{ mmol} \cdot \text{L}^{-1}$) in THF/water mixtures ($\lambda_{\text{ex}} = 500 \text{ nm}$) versus water fractions (Adapted with permission from Ref. [71]; Copyright (2016) The Royal Society of Chemistry)

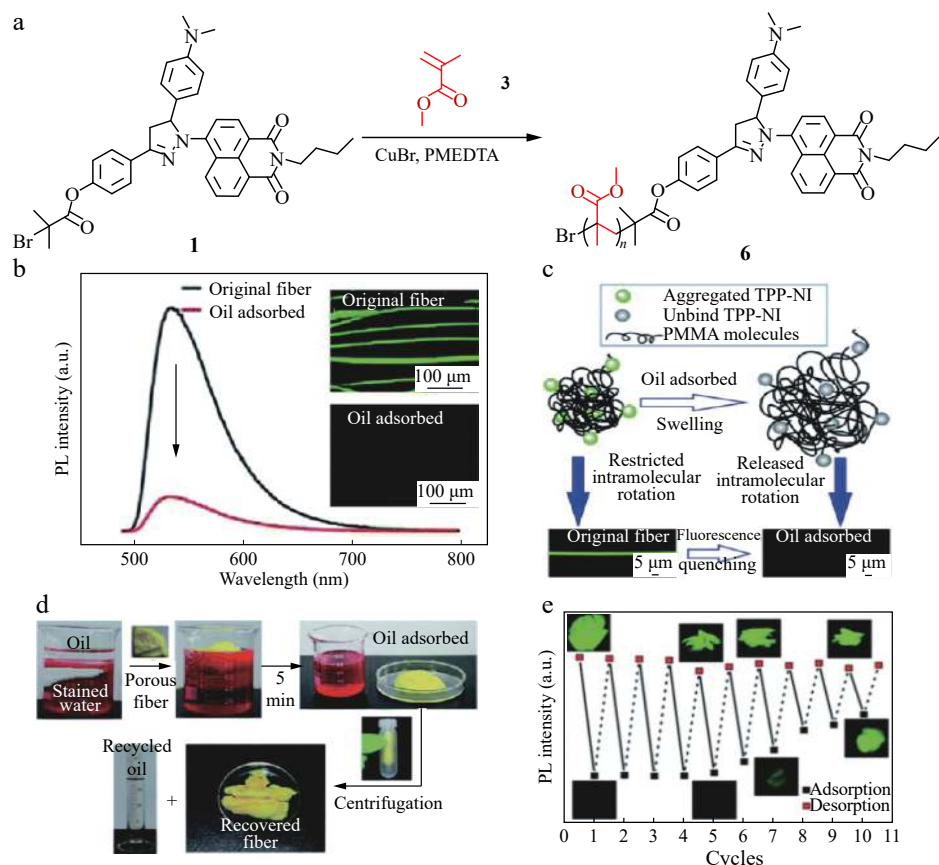


Fig. 27 (a) Synthetic route towards polymer **6**; (b) PL spectra of the PMMA porous fibers before and after silicon oil adsorption as monitored under a fluorescence microscope; (c) Mechanism of fluorescence quenching of the porous fibers by adding oil; (d) Photographs of the oil adsorption and desorption for PMMA porous fibers; (e) PL intensity and corresponding fluorescence photographs of PMMA porous fibers with 10 cycles including oil adsorption and desorption (Adapted with permission from Ref. [72]; Copyright (2014) The Royal Society of Chemistry)

molecules provided more unoccupied space for the unbinding of intramolecular rotations. Thus, energy was converted from photo energy to kinetic leading to fluorescence quenching. Moreover, the oil adsorption capacity and porous structure of the porous fibers could undergo at least 4 adsorption-desorption cycles when squeezed by centrifugal force, as shown in Figs. 27(d) and 27(e). However, the oil adsorption of the porous fibres started to decrease gradually after 5 cycles owing to the damage of porous structure caused by the multiple centrifugation processes. In summary, a potential “turn-off” fluorescent porous fiber material has been successfully prepared and shows promising potential applications in the detection of oil adsorption.

Stimuli-responsive Materials

Some AIE polymers can respond to stimuli from various surrounding elements, for example, heat and light.^[73,74] For example, Nikos and coworkers designed and synthesized a series of temperature and pH-dual responsive miktoarm star copolymers with a TPE-based AIE-active core **81** (Fig. 28a) and different arms including polyethylene (PE), poly(methacrylic acid) (PMAA), and poly(*tert*-butyl methacrylate) (PtBMA) units *via* ATRP method.^[75] The feed ratio of PE and PtBMA selected for further experiments was 19.4:14.5. Star polymer **83** (Fig. 28b) showed typical AIE characteristics in THF/hexane mixtures and its PL intensity reached the maximum when the hexane fraction increased to 90%, which was 11-fold higher than that in a pure THF solution. When the temperature decreased from 55 °C to 5 °C, the PL intensity of **83** increased due to the shrinkage of the shell which restricted the motions of TPE molecules in the core. Moreover, the PL intensity exhibited changes in the

pH-responsive experiment with pH value ranging from 1.1 to 13.3 due to the existence of hydrophilic PMAA arms and the different aggregation states of TPE-based cores. In general, such miktoarm star copolymers can be potentially applied in areas from the porous membranes to vehicles for drug delivery and pH-responsive nanofilms.

A series of AIE supramolecular polymer gels were synthesized by Yang and coworkers through hierarchical self-assembly involving coordination and host-guest interactions.^[76] Based on the structure of dipyrindyl donor **84a** (Fig. 29a) containing a TPE scaffold and two pillar[5]arene units, a rhomboidal metallacycle **84b** with four pillar[5]arene units and a hexagonal metallacycle **84c** with six pillar[5]arene units were successfully prepared. **84a**, **84b**, and **84c** all showed AIE characteristics in acetone/water mixtures ($20 \mu\text{mol}\cdot\text{L}^{-1}$), and when $f_w = 90\%$, the PL intensities reached the maximum, which were 48, 18, and 50 times higher than those in pure acetone solutions, respectively. When the concentrations increased to $45.2 \text{ mmol}\cdot\text{L}^{-1}$ (**84b**) and $40.1 \text{ mmol}\cdot\text{L}^{-1}$ (**84c**), supramolecular polymer gels with AIE characteristics could be obtained due to the restrictions of TPE intramolecular motions within three-dimensional polymeric networks. Upon the addition of 1.0 equiv. adiponitrile, the gel collapsed immediately and led to fluorescence quenching. Moreover, upon addition of 2.0 equiv. of tetrabutyl-ammonium bromide (TBABr), the gel gradually collapsed and finally became a turbid solution, and the fluorescence colour changed from light green to blue under a 365 nm UV light.

Electroluminescence Devices

Conjugated polymers usually show light-emitting perform-

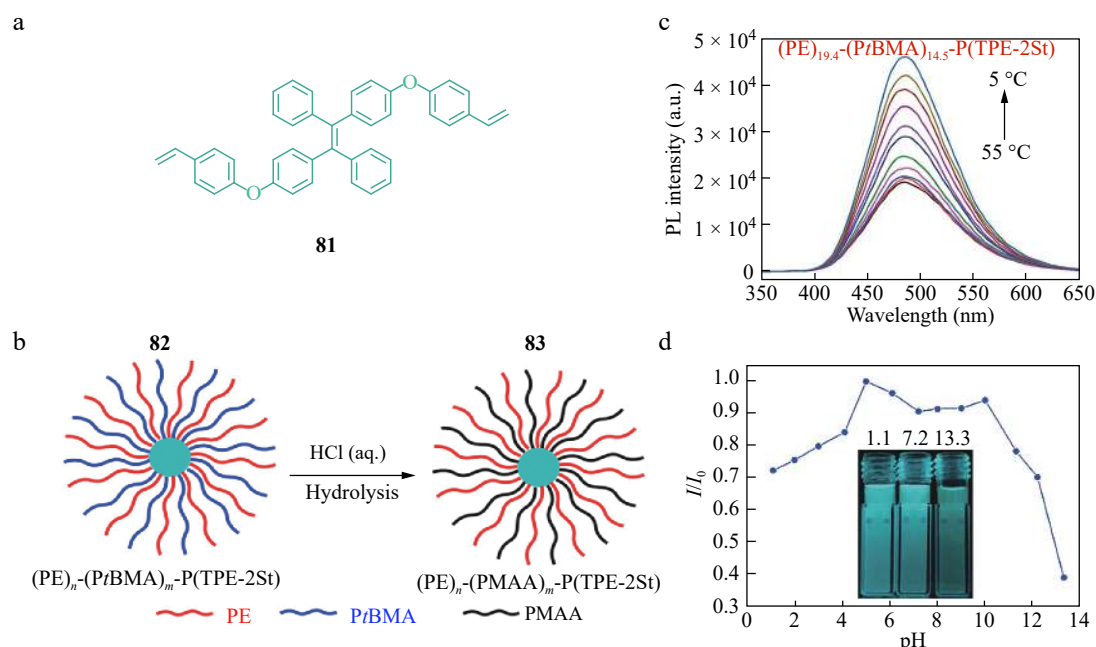


Fig. 28 (a) Molecular structure of TPE-based AIE-active core **81**; (b) Structures of star-copolymers **82** and **83** with different arms; (c) PL spectra of **83** ($0.1 \text{ g}\cdot\text{L}^{-1}$) in THF/hexane mixture (50/50, *V/V*) with temperature decreasing from 55 °C to 5 °C by a step size of 5 °C; (d) Plot of I/I_0 versus pH value, where I_0 is PL intensity of **83** ($0.05 \text{ g}\cdot\text{L}^{-1}$) in THF/buffer mixture (10/90, *V/V*) at pH 5.0; Inset: fluorescence photographs of **83** in THF/buffer mixture when pH = 1.1, 7.2, and 13.3 under a 365 nm UV lamp (Adapted with permission from Ref. [75]; Copyright (2018) American Chemical Society)

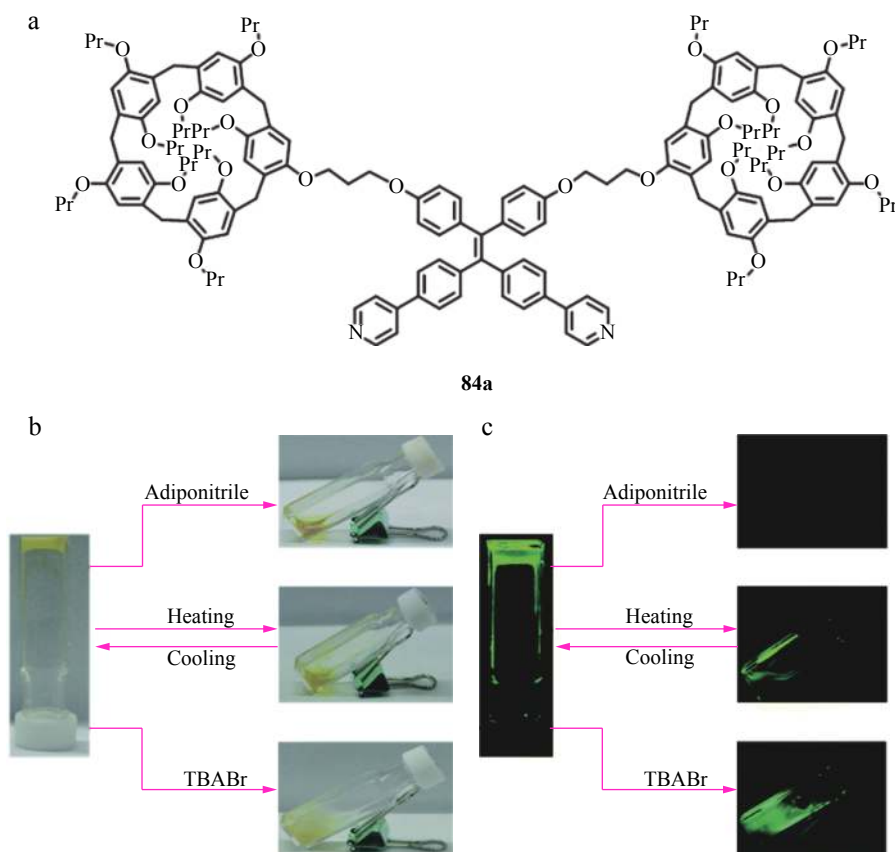


Fig. 29 (a) Molecular structure of supramolecular polymer gel **84a**; Sol-gel transition of supramolecular polymer gel **84c** triggered by various stimuli under (b) natural light and (c) 365 nm UV light (Adapted with permission from Ref. [76]; Copyright (2018) The Royal Society of Chemistry)

ance once they are fabricated into LED devices.^[77–79] The hyperbranched polymer **68** not only is a conjugated polymer, but also possesses AIE properties, so its electroluminescence (EL) can be measured.^[64] Using **68** as the emitting layer, a PLEDs device was prepared consisting of ITO/PEDOT: PSS (25 nm)/Poly-TPD (25 nm)/polymer **68** (32 nm)/TPBI (35 nm)/Cs₂CO₃ (8 nm):Ag (100 nm). The EL properties of polymer **68** were much better than its linear counterpart. The turn-on voltage of this PLEDs device was only 5.2 V, and the maximum luminescence was 5914 cd·m⁻². More significantly, **68** exhibited a high luminescence efficiency (2.13 cd·A⁻¹), which was two times higher than that of its linear analogue, and might even be one of the highest values ever reported for conjugated hyperbranched polymers. The extraordinary EL performance of **68** could be attributed to its AIE properties and the excellent hole-transport characteristics of its B₄-type carbazole-based core.

CONCLUSIONS AND PERSPECTIVES

In general, we have reviewed a variety of AIE polymers. Our focus mainly concerned polymer synthesis, applications, and AIE properties. An increasingly large number of AIE polymers have been designed and synthesized. AIE polymers provide significant advantages in various applications such as in sensors, drug delivery systems, stimuli-responsive

devices, and OLEDs. In the near future, synthetic approaches to AIE polymers are most likely to involve novel polymerization methods and surface modification. Multifunctional AIE polymers will undoubtedly attract an increasing amount of interests.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21776190, 21336005, and 51773144) and PAPD in Jiangsu Province.

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