

Feature Article

AIE-active Polymers for Explosive Detection*

Yong-wei Wu^a, An-jun Qin^{a,**} and Ben Zhong Tang^{a, b,**}

^a Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices,
South China University of Technology, Guangzhou 510640, China

^b Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and
Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

Abstract Super-sensitive and ultra-selective detection of explosives plays a crucial role in anti-terrorism operations, homeland security, civilian safety and environment protection. Among the developed fluorescent probes, the polymers with aggregation-induced emission (AIE) characteristics have drawn much attention due to their bright emission in the aggregate and solid states. However, no review has summarized the development of AIE-active polymers for explosive detection. Herein, we reviewed the recent progress on using AIE-active polymers to detect explosives with super-amplification quenching effect. Moreover, the challenges and opportunities in this area were also briefly discussed.

Keywords Aggregation-induced emission; Polymer; Explosive; Fluorescent sensor; Super-amplification effect

INTRODUCTION

Explosive detection becomes an issue of international concern as the threat of global terrorism in recent years. Additionally, the extensive use of explosives for military purpose has also raised attention for the environmental contaminations and the public healthcare. Therefore, super-sensitive and ultra-selective detection of explosives plays a crucial role in anti-terrorism operations, homeland security, civilian safety and environment protection^[1, 2]. Typically, multi-nitro group-substituted aromatic compounds, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT), are the primary military explosives and also the principal components in the unexploded landmines worldwide. Nitramines and nitrate esters are the main components of the highly energetic plastic explosives. Current detection methods are mainly based on the ion mobility spectrometry (IMS)^[3], gas chromatography coupled with mass spectrometry (GC-MS)^[4], surface-enhanced Raman spectroscopy (SERS)^[5], plasma desorption mass spectrometry (PDMS)^[6], and energy dispersive X-ray diffraction (EDXRD)^[7], which all employ modern analytical instruments. Trained canines are another reliable method for the detection of explosives^[8]. These techniques provide high sensitivity and accuracy. However, they also suffer from several

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21525417 and 21490571), the Key Project of the Ministry of Science and Technology of China (No. 2013CB834702), the Natural Science Foundation of Guangdong Province (No. 2016A030312002), the National Program for Support of Top-Notch Young Professionals, the Fundamental Research Funds for the Central Universities (No. 2015ZY013) and the Innovation and Technology Commission of Hong Kong (No. ITC-CNERC14S01). A.J.Q. and B.Z.T. thank the support from Guangdong Innovative Research Team Program (No. 201101C0105067115).

** Corresponding authors: An-jun Qin (秦安军), E-mail: msqinaj@scut.edu.cn

Ben Zhong Tang (唐本忠), E-mail: tangbenz@ust.hk

Invited paper for special issue of “Opto-electronic Functional Polymer”

Received October 1, 2016; Revised October 17, 2016; Accepted October 18, 2016

doi: 10.1007/s10118-017-1882-0

disadvantages, especially the high cost and lack of portability.

Meanwhile, fluorescent sensor provides an attractive and promising alternative since it shares the advantages over aforementioned techniques, such as low-cost, fast response and good portability^[2, 9–15]. Fluorescent conjugated polymers (FCPs) represent the merits of fluorescent sensors and have bloomed over the past decade^[14, 15]. However, the analyte-induced polymer chain aggregation often deteriorates their sensing performance due to the emission quenching effect. In addition, the detection of explosives in aqueous solution is of paramount importance due to the extension of terrorism activities from land to marine environments, the location of underwater mine and the characterization of soil and groundwater contaminations^[16]. The inherent hydrophobic organic conjugated polymers will be unavoidable to aggregate in aqueous media, which will quench the light-emission of these polymers and diminish the performance of the sensors. Thus, the aggregation-caused quenching (ACQ) becomes a big challenge for the fluorescent sensors used to detect explosives.

Opposite to the ACQ effect, a phenomenon in which aggregation plays instructive instead of destructive role for the fluorescence was observed by our group^[9, 17–20]. Since the emission was induced by the aggregation, we thus coined it aggregation-induced emission (AIE). Recently, the AIE effect has attracted increasing interest and a large number of AIE systems have been designed and synthesized. Their applications were also fully explored in diverse areas. Thanks to its high fluorescence in the aggregate state, the AIE materials have been actively applied in the explosive detection. Among the developed AIE materials, the AIE-active polymers with linear or hyperbranched structures exhibit unique merits^[16, 20–26]. Compared to their small molecule congeners, they generally exhibit faster response, larger amplified signal at lower analyte concentration, and facile device fabrication. For example, as shown in Fig. 1, in sharp contrast to the performance of archityple AIE moiety of tetraphenylethene (TPE), whose emission is almost linearly quenched with increasing picric acid's (PA, the commercially available explosive) concentration, the Stern-Volmer plot of AIE-active poly(aroxycarbonyl-triazole)s (PACT) gives a nonlinear curve, which even bends upward at high PA concentration, manifesting a unique super-amplification quenching effect. However, to the best of our knowledge, there is no review that summarizes the development of AIE polymers for explosive detection. Herein, we intend to undertake the task, and introduce the developed AIE polymers and their performance for explosive detection in detail. Conclusions and perspectives are also presented and discussed.

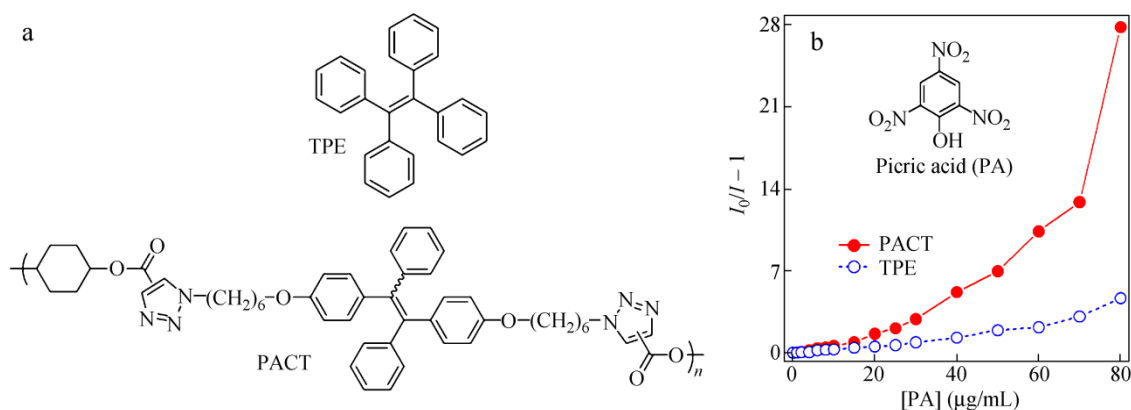


Fig. 1 (a) Molecular structures of tetraphenylethene (TPE) and polytriazole PACT; (b) Stern-Volmer plots of $(I_0/I - 1)$ versus PA concentration for PACT and TPE (I = peak intensity and I_0 = peak intensity at [PA] = 0 μg/mL) (Reproduced from Ref. [24] with permission from The Royal Society of Chemistry)

AIE POLYMER SYSTEMS FOR EXPLOSIVE DETECTION

Up to now, numerous AIE polymers have been developed and used for sensitively and selectively detecting explosives. According to their structural difference, we classified these AIE polymer systems into six groups.

Polyarylenes

Conjugated polymers have received increasing attention owing to their unique synergy effect, macroscopic processability, and fascinating photo-physical and optoelectronic properties. Among them, polyfluorene (PF) and its derivatives are considered as the promising materials for diverse applications due to their exceptionally high quantum yields in solutions, which make some specific functional PFs to be widely used as chemosensors. However, PFs tend to aggregate and bring about emission quenching, which have limited their practical utilizations. To solve this problem, Li and coworkers^[27] incorporated a TPE unit into the polymer main-chains and constructed a novel PF derivative **1** (Chart 1). Thanks to the TPE unit, compound **1** is AIE-active with the maximum emission peak at 503 nm in the aggregate state. Taking the advantage of the AIE effect, the nanoaggregates of **1** in THF/H₂O with water fraction (f_w) of 90 vol% could be used to detect explosives. When PA was added, fluorescence quenching happened, which could be recorded even at a PA concentration as low as 1.0 $\mu\text{g/mL}$. The fluorescence was completely quenched at a PA concentration of 50 $\mu\text{g/mL}$. Similarly, the PF derivative **2**, which contained a new AIE building block of di(naphthalen-2-yl)-1,2-diphenylethene, showed the unique aggregation-enhanced emission (AEE) characteristics. It could also be used to detect PA with high sensitivity in its aggregates^[28]. In addition, other AIE-active polyarylenes were also prepared and applied in PA detection with excellent performance^[29].

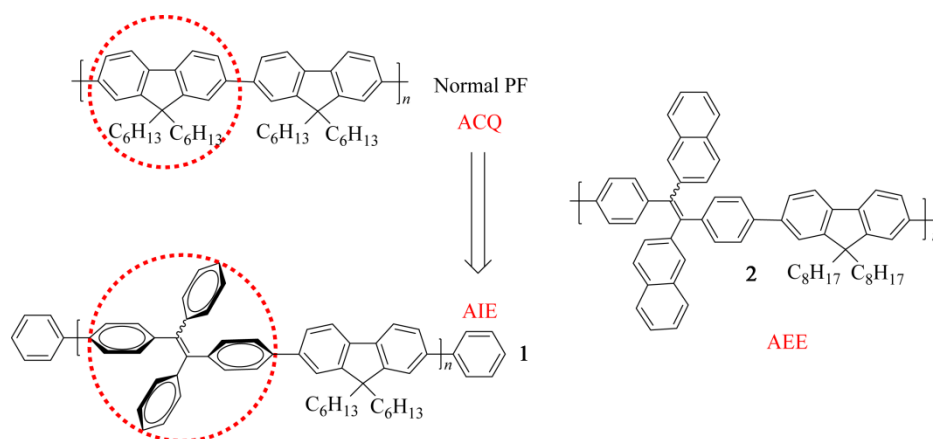


Chart 1 Molecular structures of polyfluorene derivatives **1** and **2**

Determination of the chemical compositions of explosives is crucial for tracking their source and terrorist provenance. For example, the discrimination of TNT and PA is still a challenge because both of them are extremely strong electron acceptors. In view of this, Tong and coworkers designed and prepared the TPE-containing PF derivatives **3–5** (Chart 2)^[30]. These polymers are AIE-active. Polymer **3** contains an electron accepting group of 2,1,3-benzothiadiazole (BT) in its backbone and electron donating dimethylamino groups on the TPE units. Whereas, polymers **4** and **5** contain only electron donating groups. These polymers are AIE-active because of TPE units. The fluorescence quenching of **3**, **4** and **5** could be observed upon addition of PA and TNT in their aqueous solutions. TNT exhibited a much higher quenching constant than that of PA for **3**, whereas contrary results were observed for **4** and **5**. From the Stern-Volmer plots of **3**, the quenching constant (K_{SV}) of TNT (1.2×10^5 L/mol) is deduced, which is almost 2 orders higher than that of PA (1.8×10^3 L/mol). While, polymer **5** could selectively detect PA with a limitation of 2 $\mu\text{g/L}$ and a K_{SV} constant of 2.8×10^4 L/mol. Generally, PA exhibited higher quenching efficiencies than TNT for the conjugated polymer sensors because its lowest unoccupied molecular orbital (LUMO) energy level was lower. The D-A structure of polymer **3** enables it to have a substantial intra-chain charge transfer from dimethylamino groups to BT units. Since PA could easily form a negative charged anion in aqueous solution, an electrostatic repulsion interaction between the BT unit and PA would block the efficient electron transfer. However, this phenomenon would not happen for TNT due to its neutral form.

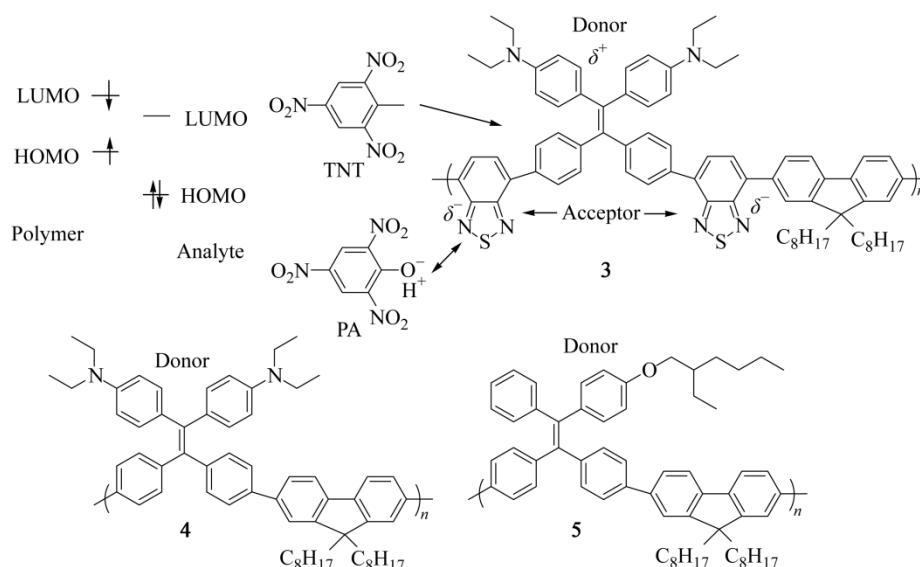


Chart 2 Molecular structures of TPE-containing polymers and electron-transfer fluorescence quenching process of **3–5**

Comparing to their linear analogues, hyperbranched polymers often exhibit improved sensing ability because of their multiple exciton migration channels and diffusion pathways *via* numerous branches in the 3D architectures (Fig. 2). Accordingly, a large number of AIE-active hyperbranched polyarylenes were developed, and their applications in sensitively detecting explosives were fully explored^[31–38]. For example, poly(silylenephénylene) **6** was synthesized by the polycyclotrimerization of aromatic diynes. It exhibited the AEE effect, and possessed a 3D topological structure with numerous molecular cavities or voids. The polymer could work as an excellent fluorescent sensor for nitroaromatic explosives, such as PA^[31]. When PA was gradually added, the fluorescence of the nanoaggregates of **6** in THF/water mixture was progressively quenched. The emission quenching could be clearly discerned at a PA concentration as low as 1 $\mu\text{g/mL}$. The quenching was determined to be static process when PA was present or absent through measuring the emission life time of the sensing system. Compared with that of the conventional conjugated polymers, the Stern-Volmer plot of **6** bent upward when large amount of PA was added (Fig. 3), demonstrating a super-amplification quenching effect. This phenomenon can be rationalized as that the aggregates have more cavities to interact with more quenchers and provide additional inter-branch diffusion pathways for exciton migration. This new type of chemosensor undoubtedly will shine light on the reliable and effective detection of explosives and other chemicals.

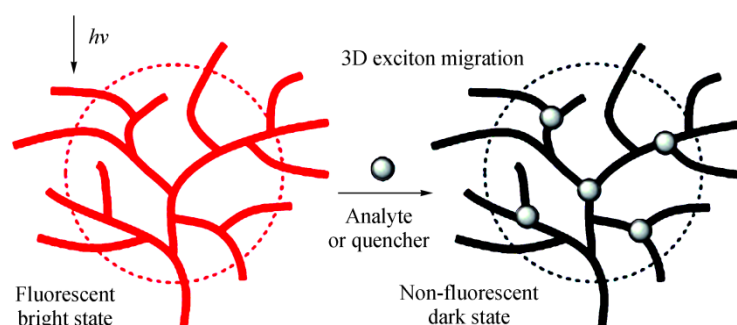


Fig. 2 Schematic illustration of the quenching processes of the fluorescence from 3D hyperbranched polymers by the analytes (Reproduced from Ref. [31] with permission from The Royal Society of Chemistry)

Besides the partially conjugated hyperbranched polymers, the explosive detection performance of fully conjugated ones has been also explored. It is worth noting that the extended electronic communication in fully

conjugated polymers can greatly enhance the detection sensitivity. Thus, the fully conjugated hyperbranched polyarylenes usually demonstrate lower detection limits. For example, polymer **7** (Chart 3), a fully conjugated hyperbranched polyarylene, has a detection limit as low as $0.33 \mu\text{g/mL}$ [35].

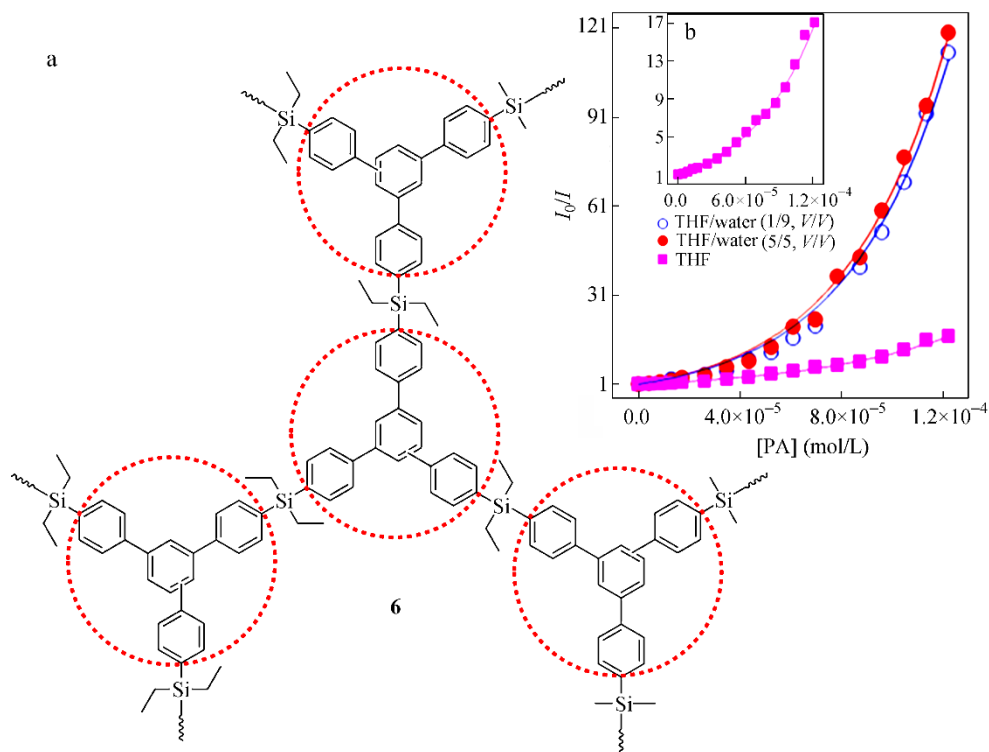


Fig. 3 (a) Molecular structure of **6**; (b) Stern-Volmer plots of I_0/I versus PA concentration in THF and THF/water mixtures with f_w of 50 vol% and 90 vol%; I_0 = PL intensity in the absence of PA (Inset: enlarged plot in the THF solution) (Reproduced from Ref. [31] with permission from The Royal Society of Chemistry)

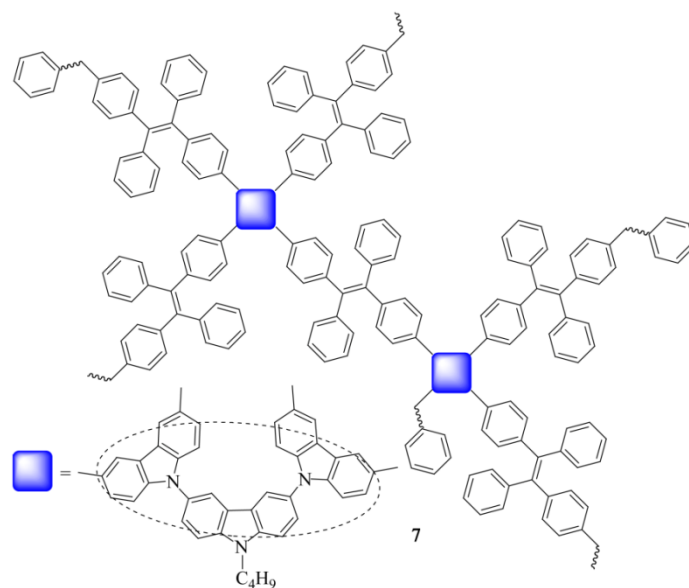


Chart 3 Molecular structure of **7**

Polytriazoles

The azide-alkyne cycloaddition has attracted considerable attention since the introduction of the concept of “click chemistry” and the discovery of Cu(I) catalysts by Sharpless and coworkers^[39–41]. This highly efficient reaction has been introduced into the polymer science, and fostered into a new polymerization technique, *i.e.* click polymerization. A series of linear and hyperbranched polytriazoles with high molecular weights have been synthesized by the Cu(I)-catalyzed and metal-free azide-alkyne click polymerizations^[42–50]. With elaborate design, the polytriazoles with AIE or AEE characteristics were also obtained. Thanks to their efficient emissions in the aggregate states, these polytriazoles were also applied in the explosive detection^[42–44, 51, 52]. For instance, polytriazoles **8a** and **8b** (Chart 4) were not emissive when dissolved in a good solvent, but emitted intensely in their aggregate states, showing the typical AIE characteristics^[43]. The aggregates of **8** formed in the THF/H₂O mixture with f_w of 90 vol% were used as the probes for the explosive detection. The emission of the aggregates was gradually quenched with addition of PA. The quenching effect was recorded even at a PA's concentration as low as 0.1 $\mu\text{g/mL}$, and a super-amplification effect was also observed. When the concentrations of PA are below 10 and 30 $\mu\text{g/mL}$, the Stern-Volmer quenching constants of **8a** and **8b** are deduced to be as high as 0.987×10^5 and 1.10×10^5 L/mol, respectively. Moreover, prototype devices were fabricated by adsorbing **8a** onto the filter papers, which displayed strong emission upon photo-excitation and became non-emissive after dipping into the PA solution. This result demonstrates the potential of AIE sensors for detecting explosives in real-world applications (Fig. 4).



Chart 4 Molecular structures of **8a** and **8b**

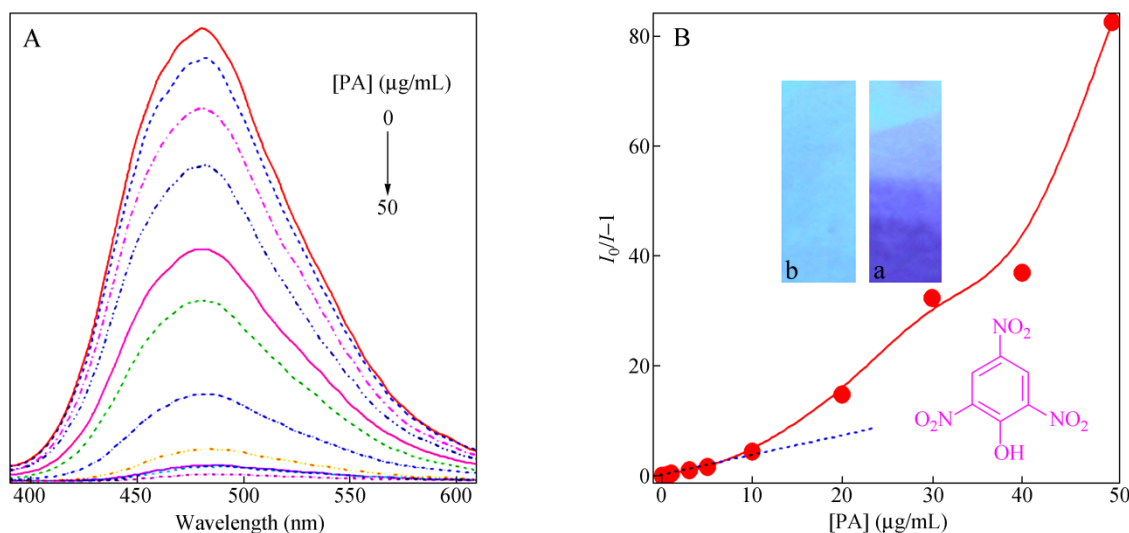


Fig. 4 (A) PL spectra of **8a** in the THF/water mixture (1/9, V/V) containing different amounts of picric acid (PA), polymer concentration: 10 $\mu\text{mol/L}$, excitation wavelength: 326 nm; (B) Plot of $(I_0/I - 1)$ versus PA concentration (where I = peak intensity, I_0 = peak intensity at $[\text{PA}] = 0$ $\mu\text{g/mL}$; inset: fluorescence images of **8a** samples adsorbed on the filter papers before (b) and after (a) being partially dipped into 50 $\mu\text{g/mL}$ PA-toluene solution) (Reproduced with permission from Ref. [43]; Copyright (2009) American Chemical Society)

AIE-active hyperbranched polytriazoles were also prepared and well applied in the explosive detection. According to above discussion, the hyperbranched polymers are promising to show more outstanding performance than their linear congeners on the detection of explosives. Taking the strategy of introducing spring-like architectures into the polymer chains, the resultant hyperbranched polytriazoles **9a** and **9b** exhibited typical AIE feature and their aggregates could be used to sensitively detect PA and TNT (Fig. 5a)^[44]. The fluorescence of the aggregates of **9a** in the THF/water mixture with f_w of 90 vol% was progressively quenched with the sequential addition of PA, and the super-amplification quenching effect was also observed. When the concentration of PA was below 0.09 mmol/L, a linear curve of Stern-Volmer plot was obtained, and the quenching constant was deduced to be 56848 L/mol. It is worth noting that this value is much higher than that of **8a** or **8b**, further confirming the outstanding performance of AIE-active hyperbranched polymers.

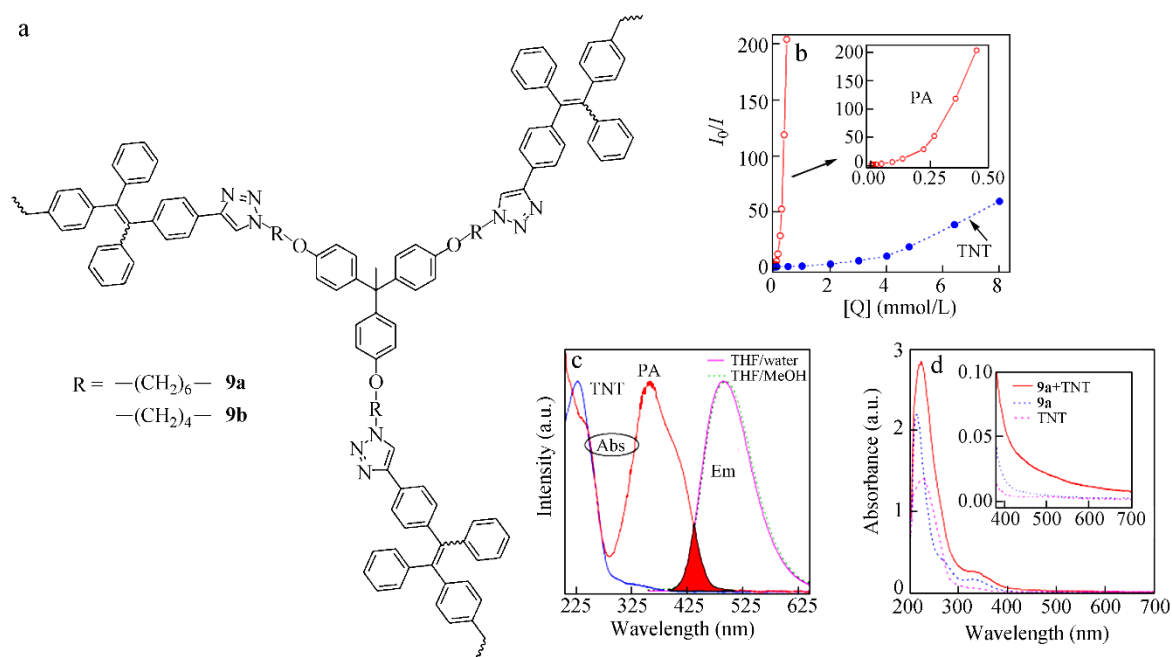


Fig. 5 (a) Molecular structures of **9a** and **9b**; (b) Stern-Volmer plots of I_0/I versus PA concentration in THF/water with $f_w = 90$ vol% and TNT concentration in THF/methanol with the fraction of methanol of 90 vol% (Inset: enlarged plot of I_0/I versus PA concentration; $[Q]$ represents the concentration of PA and TNT); (c) Normalized absorption spectra of TNT and PA, as well as the PL spectrum of **9a** in THF/methanol ($f_m = 90$ vol%) and THF/water ($f_w = 90$ vol%); (d) Absorption spectra of TNT, **9a**, and their mixture in THF/methanol ($f_m = 90$ vol%) (Inset: enlarged UV spectra of TNT, **9a**, and their mixture in the range of 380–700 nm) (Reproduced from Ref. [44] with permission from The Royal Society of Chemistry)

Interestingly, the fluorescence quenching of the aggregates **9a** was more sensitive to PA than to TNT (Fig. 5b). To understand the quenching process, the UV-Vis spectra of explosives and photoluminescence (PL) spectra of polymers were systematically investigated (Fig. 5c). The obvious spectral overlap between the absorption of PA and the emission of **9a** in the range of 390 nm to 500 nm suggests that energy-transfer mechanism is involved in the quenching process of PA detection. In contrast, there is no discernible spectral overlap of the absorption of TNT and emission of **9a**, indicating that the energy-transfer plays an eligible role in the fluorescence quenching. Further surveying the absorption spectra of **9a**, TNT and the mixture of **9a** and TNT, we found a tail absorption at longer wavelength in the mixture of **9a** and TNT (Fig. 5d). This result demonstrates the existence of charge-transfer in the quenching process. Therefore, we could conclude that, for PA, energy-transfer was mainly responsible for the fluorescence quenching process, whereas for TNT, energy-transfer could be neglected and charge-transfer played a main role. It is well known that the energy-transfer is a long-range process whereas the charge-transfer is a short-range one. Thus the aggregates of **9a** showed more

sensitive response to PA than to TNT. Above mechanism could also be employed to decipher the specific quenching effect of PA to the AIE-active cross-linked poly(tetraphenylethylene-*co*-cyclotriphosphazene) (TPE-CP) even in the presence of TNT^[53]. These results manifest that the AIE-based chemosensors for a specific explosive could be developed under elaborate design.

Polysilylenevinylenes

As an important kind of heteroatom-containing polymer, the silicon-containing polysilylenevinylenes may exhibit unique optoelectronic properties due to the $\sigma^*-\pi^*$ conjugation between the σ orbitals of the silicon atoms and the π orbitals of the double bonds. During the course of developing new polymerization reactions based on triple-bond building blocks, we designed and synthesized polysilylenevinylenes by the polyhydrosilylation of alkynes^[54–56]. When TPE or silole units were incorporated, the resultant polysilylenevinylenes exhibited much higher emission efficiency in the aggregate and solid states than in their solution state, *i.e.* they were AIE/AEE-active. According to the literature, incorporating hard Lewis acid centers, such as silicon, in a delocalized polymer chain could lead to the binding of lone pairs on both oxygen and nitrogen atoms in nitroaromatic explosives to the silicon centers through a Lewis acid-base interaction, which would help to improve the sensing performance^[57]. Thus, the aggregates of these AIE-active polysilylenevinylenes suspended in the THF/H₂O mixture with f_w of 90 vol% were adopted as the explosive probes to check their performance. The PL spectrum of the aggregate **10** was progressively weakened when increasing the amount of PA in the aqueous solution (Fig. 6)^[55]. This quenching process could be clearly discerned at a PA concentration as low as 1 $\mu\text{g/mL}$. The Stern-Volmer plot is composed of two linear stages divided at a PA's concentration of 0.12 mmol/L. These two stages both possess higher K_{SV} than those of the polysiloles and polygermoles, suggesting that **10** is a highly sensitive probe for the explosive detection.

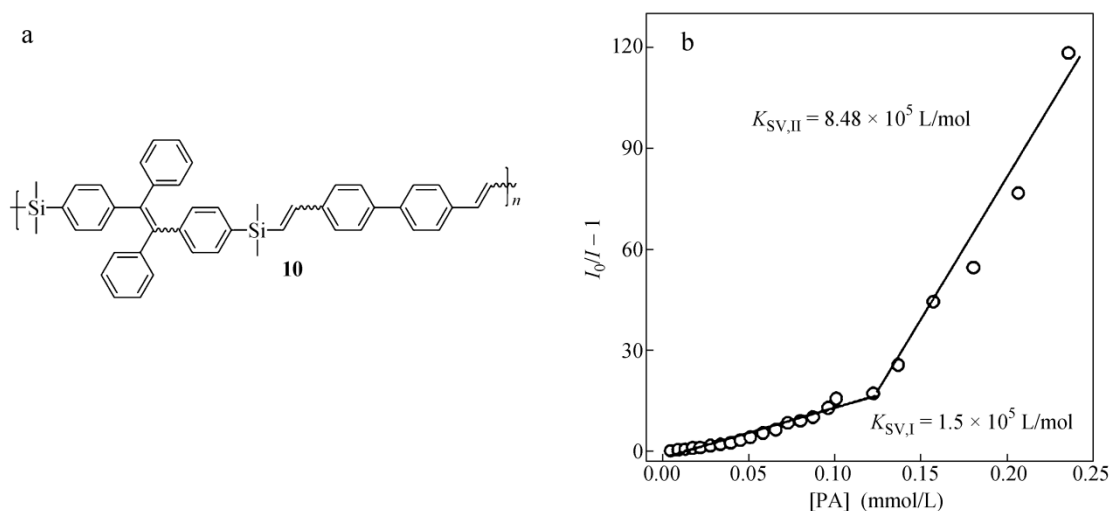
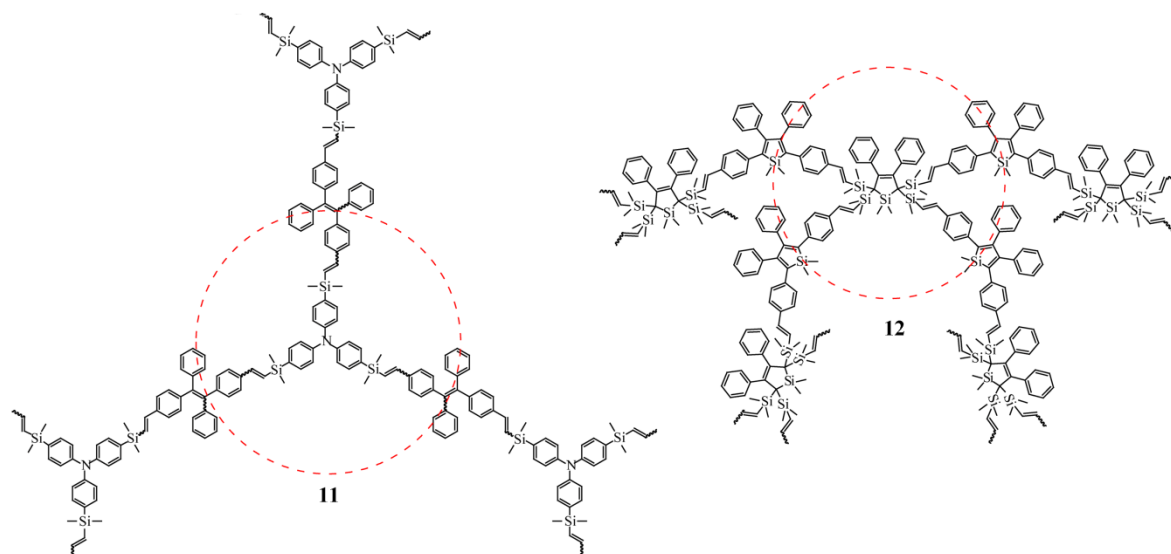


Fig. 6 (a) Molecular structure of **10**; (b) Stern-Volmer plots of $(I_0/I - 1)$ versus PA concentration in THF/water with $f_w = 90$ vol% (Reproduced with permission from Ref. [55]; Copyright (2011) American Chemical Society)

Similar with the AIE-active hyperbranched polytriazoles, TPE or silole-containing hyperbranched poly(silylenevinylene)s **11**^[54] and **12**^[56] also showed high performance in explosive detection (Chart 5). The emissions of the aggregates of **11** and **12** were progressively quenched with the addition of PA. The emission quenching of them could be clearly discerned at a PA concentration as low as 1 $\mu\text{g/mL}$. The Stern-Volmer plots showed that **11** and **12** gave swiftly upward-bending curves rather than linear lines at higher PA concentration, revealing a super-amplification quenching effect. Furthermore, the sensing ability of them was much higher than that of silole-containing linear polysilylenevinylenes as revealed by the deduced quenching constants.

Chart 5 Molecular structures of **11** and **12**

Polymers with AIE Units at Their Side Chains

Besides AIE units in the main-chains, the polymers bearing AIE-units at their side-chains could also function as the sensitive probes to detect explosives^[58, 59]. For example, the TPE-functionalized polyacetylene **13** is AIE-active and shows strong yellow emission with maximum wavelength at 558 nm in its aggregate state, which can be used to detect explosives (Fig. 7a)^[58]. When PA was gradually added into the aqueous solution containing the aggregates of **13**, the PL intensity was progressively decreased. The quenching could be observed at a PA concentration as low as 0.17 $\mu\text{g/mL}$. Similar to with that of other AIE-active polymers, the Stern-Volmer plot of **13** also shows upward bent curve (Fig. 7b) at high PA concentrations, suggesting that the super-amplification effect is a universal phenomenon for AIE-active polymers.

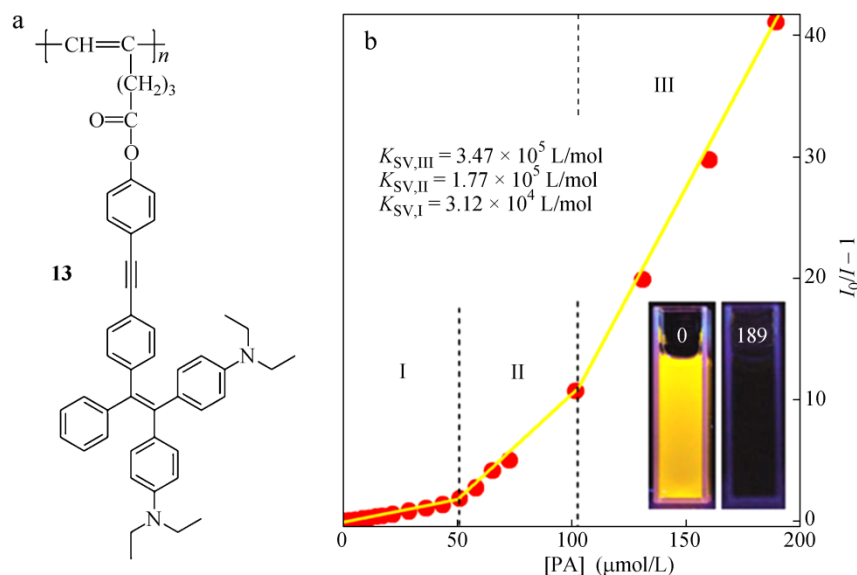


Fig. 7 (a) Molecular structure of **13**; (b) Stern-Volmer plots of $(I_0/I - 1)$ versus PA concentration in THF/water with $f_w = 90$ vol% (Reproduced with permission from Ref. [58]; Copyright (2009) American Chemical Society)

Moreover, the flexible main-chain polyolefins bearing TPE units as its pendant were also synthesized and

their performance as effective explosive sensor was carefully explored^[60, 61]. For example, Xu and coworkers designed and synthesized porous copolymer **14** *via* free-radical copolymerization of polyhedraloligomeric-silsesquioxane (POSS) and TPE-containing acrylate monomers (Chart 6)^[60]. This POSS-based copolymer could be facilely fabricated into thin films with large surface area and thanks to the AIE activity, it could sensitively detect DNT vapor with the emission quenching rate reaching 52% in 30 s, 79% in 90 s and 90% in 4 min, respectively. Although these films with the thickness as high as (560 ± 60) nm, they exhibited an approximately 9-fold increment in response to explosive vapors compared to the dense films. Moreover, the emission of the films could be recovered by exposure to hydrazine vapor, and reused to detect explosives. Such a detection system provides a new avenue to portable, cost-effective AIE-based sensing devices for real world application.

The polymers with rigid backbones and AIE-active pendants were also prepared and used to detect explosives. For example, the rigid polycarbazole **15** bearing TPE unit at its side chains was prepared by nickel-catalyzed Yamamoto polycondensation with the assistance of microwave (Chart 7)^[62]. This polymer displays a pronounced AIE feature, and their aggregates are highly fluorescent with bluish-green emission at ~ 495 nm. The electron-rich nature of **15** is beneficial to the interaction with electron-deficient trinitrobenzene. The aggregates of **15** in the THF/H₂O mixture with f_w of 90 vol% was chosen as the probe to detect 1,3,5-trinitrobenzene (TNB). Similar to other AIE polymers, the fluorescence decreased progressively upon gradual addition of TNB, and the onset of PL quenching was recorded to be as low as 50 nmol/L. The quenching mechanism could be ascribed to the charge-transfer from the electron-rich TPE-substituted polycarbazole to the electron-deficient TNB, which was confirmed by the cyclic voltammetry measurement. Moreover, strips covering **15** also showed obvious PL quenching, both towards TNB vapor or solution, suggesting a promising utility of this polymer for the practical application.

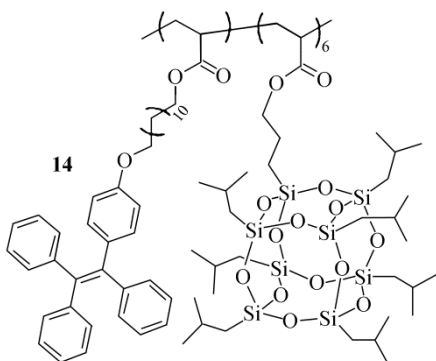


Chart 6 Molecular structures of copolymer **14**

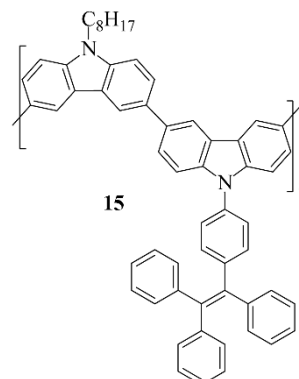


Chart 7 Molecular structures of **15**

AIE Unit End-capped Polymers

Besides incorporating the AIE units in the polymer main-chains or at side-chains, the AIE moieties were also decorated as the terminal groups. The resultant AIE-polymers also exhibited excellent performance for explosives detection^[63–69]. One of the examples is the TPE-containing poly(ϵ -caprolactone) (PCL) **16**, a kind of crystalline polymer (Fig. 8)^[68]. Polymer **16** exhibits the typical AIE behavior. During crystallization of the polymer, the TPE units were expelled out of lamellar crystals and finally located on the surface of the nanosheets, which could be used to detect explosives. The strong fluorescence of nano-sheets of **16** was gradually quenched by the addition of PA. As shown in Fig. 8, the quenching process gives a linear relationship between I_0/I value and PA concentration when it is lower than 200 $\mu\text{mol/L}$. The quenching constant deduced from Stern-Volmer plot is 3.8×10^5 L/mol, which is one order larger than that of the bare TPE (4.9×10^4 L/mol). This high quenching constant may be related to the novel structure of nanosheets where the effective TPE moieties are coated on their surface. Thus, this example provides another new insight to fabricate functional

AIE-active nano-materials for explosive detection.

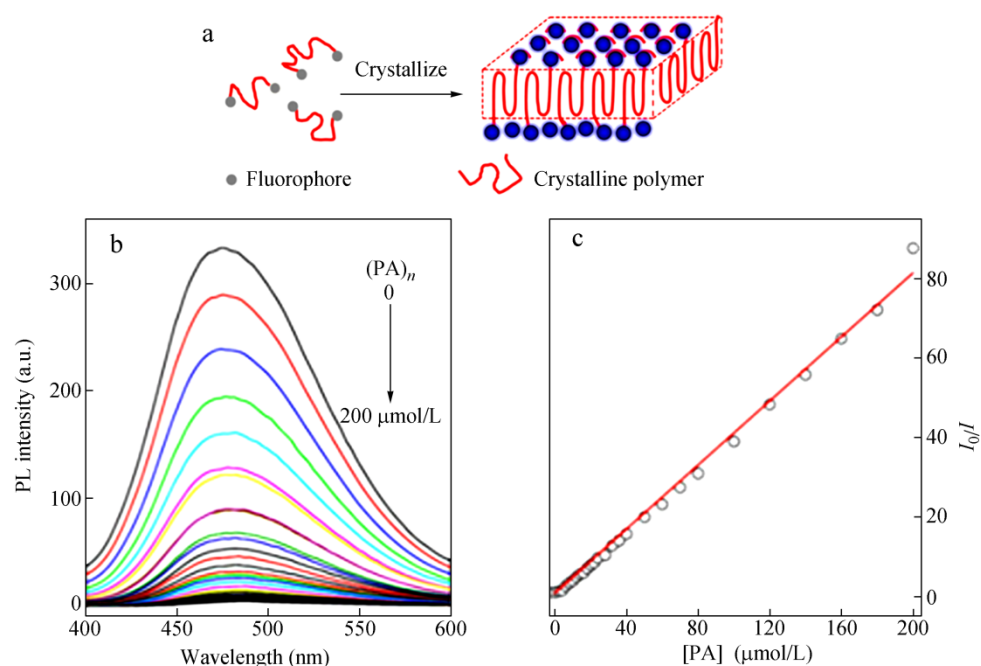


Fig. 8 (a) Schematic illustration of crystallization-induced nanosheets of **16**; (b) PL spectra of **16** nanosheets suspension containing various amount of PA in aqueous solution; (c) Stern-Volmer plot of I_0/I values versus PA concentrations of the **16** suspension in aqueous solution (Reproduced with permission from Ref. [68]; Copyright (2014) American Chemical Society)

MOFs Bearing AIE Units

Generally, the detection of explosives is based on the fluorescence turn-off model. Recently, an intriguing fluorescent turn-on sensor based on organic-inorganic hybrid materials was reported. One-dimensional metal-organic frameworks (MOFs) were facily prepared by the coordination of AIE-active carboxylic acid derivative **17** with Mg^{2+} , Ni^{2+} , and Co^{2+} , respectively (Fig. 9)^[70]. Interestingly, no emission was observed for **17**- Co^{2+} -MOF due to the strong ligand-to-metal charge transfer (LMCT) transitions, which readily makes **17**- Co^{2+} -MOF serve as an effective fluorescence turn-on sensor to detect five-membered-ring energetic heterocyclic compounds (5MR-EHCs), such as 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO).

Such explosives possess the unique molecular structures, and share one common feature that the containing $\text{C}=\text{N}$ and/or $\text{N}=\text{N}$ bonds can dissociate the coordination bonds between carboxylate groups and metal ions in MOFs through competitive coordination substitution. Thus, once the AIE-active **17** was dissociated and released, fluorescent aggregates will be generated. As reported, a rapid and quantitative detection of NTO by **17**- Co^{2+} -MOF in THF/hexane with the concentration range of 4.0×10^{-8} mol/L to 1.0×10^{-3} mol/L could be achieved. In spot testing, the minimum naked-eye-readable detection amount of NTO was as low as 10 μL , corresponding to a visible detection limitation about 6.5 ng/cm². This MOF sensor also holds high selectivity since except the 5MR-EHCs, no obvious fluorescence changes were detected for common organic molecules and nitroaromatic compounds, such as hexane (Hex), DMF, triethylamine (Et_3N), aniline (AN), toluene (PhMe), acetonitrile (MeCN), DCM, acetone (DMK), THF, ethyl acetate (EtOAc), and TNT. The MOF sensing system with high sensitivity and selectivity shines light on developing AIE-active fluorescent turn-on sensors for the explosive detection.

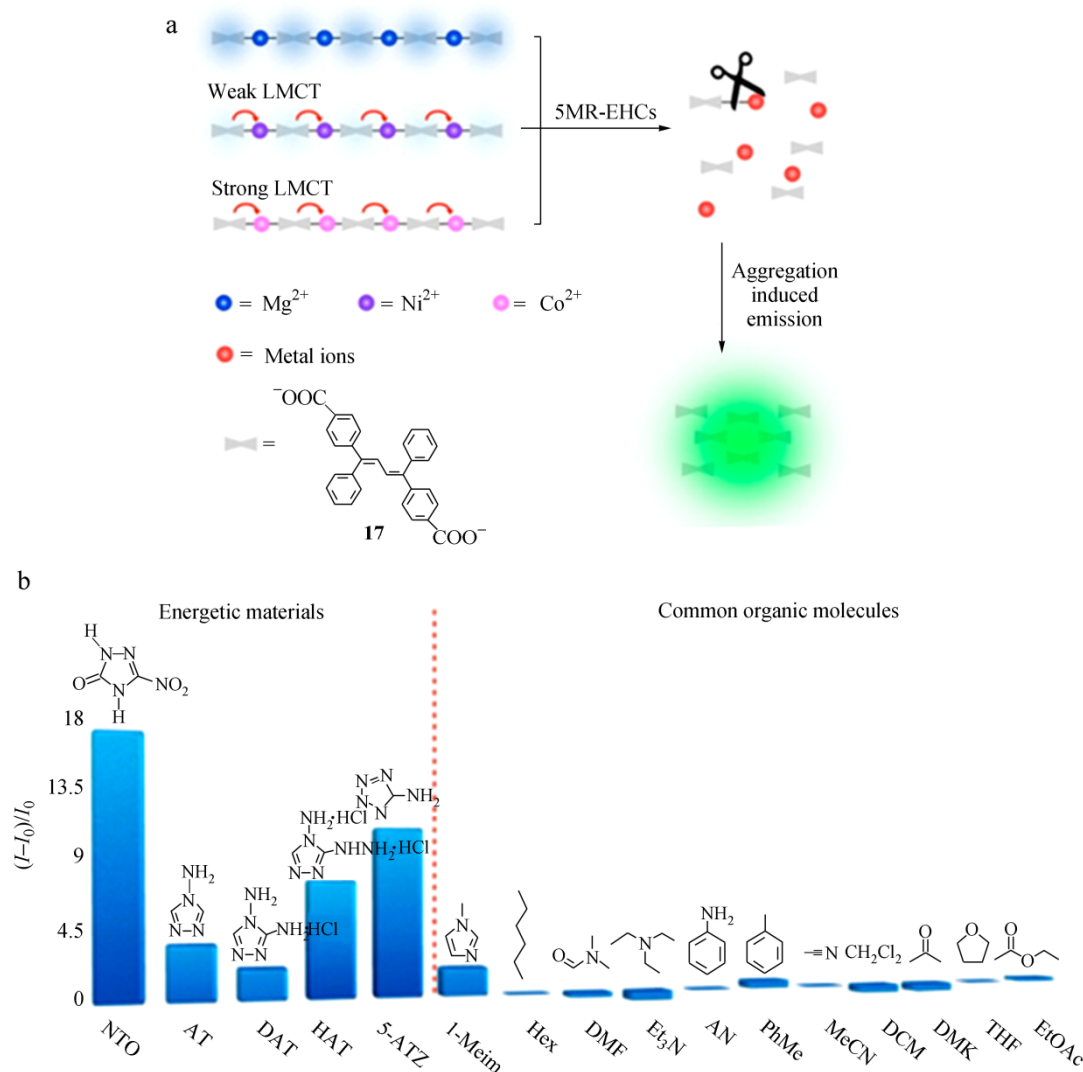


Fig. 9 (a) Schematic representation of detection of energetic heterocyclic compounds by the **17**- Co^{2+} -MOF; (b) Fluorescence enhancement efficiencies $[(I - I_0)/I_0]$ obtained from different analytes by **17**- Co^{2+} -MOF (Reproduced with permission from Ref. [70]; Copyright (2014) American Chemical Society)

CONCLUSIONS AND PERSPECTIVES

In this review, we have mainly summarized the progress on detection of explosives by the AIE-active polymers. Thanks to their intense emission in the practically useful aggregate or film states and synergy effect, the AIE-active polymers could easily be used to detect explosives with super-amplification quenching effect. It is worth noting that the AIE-active hyperbranched polymers generally show higher performance than their linear congener on the explosive detection due to the 3D architectures, which offer multiple exciton migration channels and diffusion pathways *via* numerous branches. Meanwhile, MOFs containing AIE units have been developed for the detection of 5MR-EHCs with rarely reported fluorescent turn-on model. More importantly, sensitive detection for explosives was realized using prototype devices fabricated by coating the AIE-active polymers on the filter papers and thin layer chromatography (TLC) plates, which offer tremendous potential for portable and *in situ* detection.

Although remarkable progress has been made in this area, the use of AIE-active polymers to detect explosive is full of challenges. On one hand, the advantages of using AIE-active polymers for the explosive

detection should be further demonstrated. On the other hand, the currently investigated explosives are mainly based on nitroaromatic compounds, such as TNT, DNT and PA; other explosives like nonaromatic nitramine and nitrate esters have rarely been reported. Meanwhile, the detection performance of the AIE-active polymers should be further improved through elaborative molecular design. Moreover, fluorescence enhancement is a more sensitive technique with little influence on the background, thus, new sensing systems based on AIE-active polymers performing in a “turn-on” mode is another challenge. In addition, the portable, sensitive and fast responsive devices for the explosive detection based on AIE-active polymers are the ultimate aim in this area.

REFERENCES

- 1 Salinas, Y., Martinez-Manez, R., Marcos, M.D., Sancenon, F., Costero, A.M., Parra, M. and Gil, S., *Chem. Soc. Rev.*, 2012, 41: 1261
- 2 Sun, X., Wang, Y. and Lei, Y., *Chem. Soc. Rev.*, 2015, 44: 8019
- 3 Eiceman, G. and Stone, J., *Anal. Chem.*, 2004, 76: 390 A
- 4 Walsh, M.E., *Talanta*, 2001, 54: 427
- 5 Sylvia, J.M., Janni, J.A., Klein, J. and Spencer, K.M., *Anal. Chem.*, 2000, 72: 5834
- 6 Håkansson, K., Coorey, R.V., Zubarev, R.A., Talrose, V.L. and Håkansson, P., *J. Mass Spectrom.*, 2000, 35: 337
- 7 Luggar, R., Farquharson, M., Horrocks, J. and Lacey, R., *X-Ray Spectrom.*, 1998, 27: 87
- 8 Furton, K.G. and Myers, L.J., *Talanta*, 2001, 54: 487
- 9 Mei, J., Hong, Y., Lam, J.W.Y., Qin, A., Tang, Y. and Tang, B.Z., *Adv. Mater.*, 2014, 26: 5429
- 10 Guan, W., Zhou, W., Lu, J. and Lu, C., *Chem. Soc. Rev.*, 2015, 44: 6981
- 11 Hu, Z., Deibert, B.J. and Li, J., *Chem. Soc. Rev.*, 2014, 43: 5815
- 12 Daly, B., Ling, J. and de Silva, A.P., *Chem. Soc. Rev.*, 2015, 44: 4203
- 13 Jung, H.S., Verwilt, P., Kim, W.Y. and Kim, J.S., *Chem. Soc. Rev.*, 2016, 45: 1242
- 14 McQuade, D.T., Pullen, A.E. and Swager, T.M., *Chem. Rev.*, 2000, 100: 2537
- 15 Thomas, S.W., Joly, G.D. and Swager, T.M., *Chem. Rev.*, 2007, 107: 1339
- 16 Toal, S.J., Magde, D. and Trogler, W.C., *Chem. Commun.*, 2005, 5465
- 17 Luo, J., Xie, Z., Lam, J.W.Y., Cheng, L., Chen, H., Qiu, C., Kwok, H.S., Zhan, X., Liu, Y., Zhu, D. and Tang, B.Z., *Chem. Commun.*, 2001, 1740
- 18 Liu, J., Lam, J.W.Y. and Tang, B.Z., *J. Inorg. Organomet. Polym. Mater.*, 2009, 19: 249
- 19 Hong, Y., Lam, J.W.Y. and Tang, B.Z., *Chem. Soc. Rev.*, 2011, 40: 5361
- 20 Mei, J., Leung, N.L.C., Kwok, R.T.K., Lam, J.W.Y. and Tang, B.Z., *Chem. Rev.*, 2015, 115: 11718
- 21 Qin, A., Lam, J.W.Y. and Tang, B.Z., *Prog. Polym. Sci.*, 2012, 37: 182
- 22 Hu, R., Leung, N.L.C. and Tang, B.Z., *Chem. Soc. Rev.*, 2014, 43: 4494
- 23 Li, H., Mei, J., Wang, J., Zhang, S., Zhao, Q., Wei, Q., Qin, A., Sun, J. and Tang, B.Z., *Sci. China Chem.*, 2011, 54: 611
- 24 Li, H., Wang, J., Sun, J.Z., Hu, R., Qin, A. and Tang, B.Z., *Polym. Chem.*, 2012, 3: 1075
- 25 Sohn, H., Sailor, M.J., Magde, D. and Trogler, W.C., *J. Am. Chem. Soc.*, 2003, 125: 3821
- 26 Sanchez, J.C., DiPasquale, A.G., Rheingold, A.L. and Trogler, W.C., *Chem. Mater.*, 2007, 19: 6459
- 27 Wu, W., Ye, S., Tang, R., Huang, L., Li, Q., Yu, G., Liu, Y., Qin, J. and Li, Z., *Polymer*, 2012, 53: 3163
- 28 Gao, M., Wu, Y., Chen, B., He, B., Nie, H., Li, T., Wu, F., Zhou, W., Zhou, J. and Zhao, Z., *Polym. Chem.*, 2015, 6: 7641
- 29 Hu, R., Luis Maldonado, J., Rodriguez, M., Deng, C., Jim, C.K.W., Lam, J.W.Y., Yuen, M.M.F., Ramos-Ortiz, G. and Tang, B.Z., *J. Mater. Chem.*, 2012, 22: 232
- 30 Xu, B., Wu, X., Li, H., Tong, H. and Wang, L., *Macromolecules*, 2011, 44: 5089
- 31 Liu, J., Zhong, Y., Lu, P., Hong, Y., Lam, J.W.Y., Faisal, M., Yu, Y., Wong, K.S. and Tang, B.Z., *Polym. Chem.*, 2010, 1: 426
- 32 Hu, R., Lam, J.W.Y., Liu, J., Sung, H.H.Y., Williams, I.D., Yue, Z., Wong, K.S., Yuen, M.M.F. and Tang, B.Z., *Polym. Chem.*, 2012, 3: 1481

- 33 Liu, J., Zhong, Y., Lam, J.W.Y., Lu, P., Hong, Y., Yu, Y., Yue, Y., Faisal, M., Sung, H.H.Y., Williams, I.D., Wong, K.S. and Tang, B.Z., *Macromolecules*, 2010, 43: 4921
- 34 Wu, W., Tang, R., Li, Q. and Li, Z., *Chem. Soc. Rev.*, 2015, 44: 3997
- 35 Wu, W., Ye, S., Huang, L., Xiao, L., Fu, Y., Huang, Q., Yu, G., Liu, Y., Qin, J., Li, Q. and Li, Z., *J. Mater. Chem.*, 2012, 22: 6374
- 36 Wu, W., Ye, S., Yu, G., Liu, Y., Qin, J. and Li, Z., *Macromol. Rapid Commun.*, 2012, 33: 164
- 37 Wu, W., Ye, S., Huang, L., Yu, G., Liu, Y., Qin, J. and Li, Z., *Chinese J. Polym. Sci.*, 2013, 31: 1432
- 38 Shu, W., Guan, C., Guo, W., Wang, C. and Shen, Y., *J. Mater. Chem.*, 2012, 22: 3075
- 39 Kolb, H.C., Finn, M. and Sharpless, K.B., *Angew. Chem. Int. Ed.*, 2001, 40: 2004
- 40 Rostovtsev, V.V., Green, L.G., Fokin, V.V. and Sharpless, K.B., *Angew. Chem. Int. Ed.*, 2002, 41: 2596
- 41 Tornøe, C.W., Christensen, C. and Meldal, M., *J. Org. Chem.*, 2002, 67: 3057
- 42 Qin, A., Tang, L., Lam, J.W.Y., Jim, C.K.W., Yu, Y., Zhao, H., Sun, J. and Tang, B.Z., *Adv. Funct. Mater.*, 2009, 19: 1891
- 43 Qin, A., Lam, J.W.Y., Tang, L., Jim, C.K.W., Zhao, H., Sun, J. and Tang, B.Z., *Macromolecules*, 2009, 42: 1421
- 44 Wang, J., Mei, J., Yuan, W.Z., Lu, P., Qin, A., Sun, J.Z., Ma, Y. and Tang, B.Z., *J. Mater. Chem.*, 2011, 21: 4056
- 45 Qin, A., Jim, C.K.W., Lu, W., Lam, J.W.Y., Häussler, M., Dong, Y., Sung, H.H., Williams, I.D., Wong, G.K. and Tang, B.Z., *Macromolecules*, 2007, 40: 2308
- 46 Qin, A., Lam, J.W.Y. and Tang, B.Z., *Macromolecules*, 2010, 43: 8693
- 47 Qin, A., Lam, J.W.Y. and Tang, B.Z., *Chem. Soc. Rev.*, 2010, 39: 2522
- 48 Wang, Q., Li, H., Wei, Q., Sun, J.Z., Wang, J., Zhang, X.A., Qin, A. and Tang, B.Z., *Polym. Chem.*, 2013, 4: 1396
- 49 Wu, H., Li, H., Kwok, R.T.K., Zhao, E., Sun, J.Z., Qin, A. and Tang, B.Z., *Sci. Rep.*, 2014, 4: 5107
- 50 Li, H., Sun, J.Z., Qin, A. and Tang, B.Z., *Chinese J. Polym. Sci.*, 2012, 30: 1
- 51 Li, H., Wu, H., Zhao, E., Li, J., Sun, J.Z., Qin, A. and Tang, B.Z., *Macromolecules*, 2013, 46: 3907
- 52 Wang, Q., Chen, M., Yao, B., Wang, J., Mei, J., Sun, J.Z., Qin, A. and Tang, B.Z., *Macromol. Rapid Commun.*, 2013, 34: 796
- 53 Hu, X., Chen, Q., Zhou, D., Cao, J., He, Y. and Han, B., *Polym. Chem.*, 2011, 2: 1124
- 54 Lu, P., Lam, J.W.Y., Liu, J., Jim, C.K.W., Yuan, W., Xie, N., Zhong, Y., Hu, Q., Wong, K.S., Cheuk, K.K.L. and Tang, B.Z., *Macromol. Rapid Commun.*, 2010, 31: 834
- 55 Lu, P., Lam, J.W.Y., Liu, J., Jim, C.K.W., Yuan, W., Chan, C.Y.K., Xie, N., Hu, Q., Cheuk, K.K.L. and Tang, B.Z., *Macromolecules*, 2011, 44: 5977
- 56 Zhao, Z., Guo, Y., Jiang, T., Chang, Z., Lam, J.W.Y., Xu, L., Qiu, H. and Tang, B.Z., *Macromol. Rapid Commun.*, 2012, 33: 1074
- 57 Sanchez, J.C., DiPasquale, A.G., Mrse, A.A. and Trogler, W.C., *Anal. Bioanal. Chem.*, 2009, 395: 387
- 58 Yuan, W.Z., Zhao, H., Shen, X.Y., Mahtab, F., Lam, J.W.Y., Sun, J.Z. and Tang, B.Z., *Macromolecules*, 2009, 42: 9400
- 59 Chan, C.Y.K., Lam, J.W.Y., Deng, C., Chen, X., Wong, K.S. and Tang, B.Z., *Macromolecules*, 2015, 48: 1038
- 60 Zhou, H., Ye, Q., Neo, W.T., Song, J., Yan, H., Zong, Y., Tang, B.Z., Hor, T.S.A. and Xu, J., *Chem. Commun.*, 2014, 50: 13785
- 61 Mukundam, V., Kumar, A., Dhanunjayarao, K., Ravi, A., Peruncheralathan, S. and Venkatasubbaiah, K., *Polym. Chem.*, 2015, 6: 7764
- 62 Dong, W., Fei, T., Palma-Cando, A. and Scherf, U., *Polym. Chem.*, 2014, 5: 4048
- 63 Zhang, L., Jiang, T., Wu, L., Wan, J., Chen, C., Pei, Y., Lu, H., Deng, Y., Bian, G., Qiu, H. and Lai, G., *Chem. Asian J.*, 2012, 7: 1583
- 64 Yuan, W.Z., Hu, R., Lam, J.W.Y., Xie, N., Jim, C.K.W. and Tang, B.Z., *Chem. Eur. J.*, 2012, 18: 2847
- 65 Ghosh, K.R., Saha, S.K. and Wang, Z.Y., *Polym. Chem.*, 2014, 5: 5638
- 66 He, G., Peng, H., Liu, T., Yang, M., Zhang, Y. and Fang, Y., *J. Mater. Chem.*, 2009, 19: 7347
- 67 Martinez, H.P., Grant, C.D., Reynolds, J.G. and Trogler, W.C., *J. Mater. Chem.*, 2012, 22: 2908
- 68 Liang, G., Weng, L.T., Lam, J.W.Y., Qin, W. and Tang, B.Z., *ACS Macro Lett.*, 2014, 3: 21
- 69 Fan, Z., Zhao, Q., Wang, S., Bai, Y., Wang, P., Li, J., Chu, Z. and Chen, G., *RSC Adv.*, 2016, 6: 26950
- 70 Guo, Y., Feng, X., Han, T., Wang, S., Lin, Z., Dong, Y. and Wang, B., *J. Am. Chem. Soc.*, 2014, 136: 15485