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PAPER

Conjugated poly(aryleneethynylenesiloles) and their application in detecting explosives

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Hyperbranched and linear conjugated polysiloles incorporating arylene ethynylene subunits (**6** and **7**) were synthesized by the Sonogashira reaction. The two polymers possess unusual phenomena of PL, with gradual addition of water in their THF solution, the intensity of PL firstly increased and then decreased, this may be due to the aggregate-enhanced emission (AEE) effect and aggregation-caused quenching (ACQ) effect. The polymers function as sensitive fluorescent chemosensors for the detection of explosives, such as picric acid (PA) and TNT. The quenching constants of **6** for PA and TNT were 4.7×10^{-2} ppm^{-1} and 4.6×10^{-3} ppm^{-1}, respectively. The quenching constants of **7** for PA and TNT were 8.6×10^{-2} ppm^{-1} and 6.5×10^{-3} ppm^{-1} respectively. The polymer **7** has more detective efficiency for PA and TNT than that of polymer **6**, this may be due to the less steric hindrance.

Introduction

Siloles have continued to receive much attention due to their potential application as a kind of novel π-electronic material. Siloles are five-membered aromatic rings, and possess unique optical and electrochemical characteristics because of their σ^*–π^* conjugation between the silicon atom and the butadiene moiety,[1] the σ^*–π^* conjugation structure lowers their lowest unoccupied molecular orbital energy levels and increases their electron affinities.[2] Another attractive aspect of siloles is the aggregation-induced emission (AIE) effect due to restricted intramolecular rotation (RIR).[3,4] Therefore, siloles have been used as electron-transporting[5–7] and light emitting layers[8–15] in the fabrication of highly efficient electroluminescence (EL) devices. In the recent years, great efforts have been made to incorporate siloles into polymers because polymers possess processing advantages over their small-molecule counterparts. Silole polymers have been found to show excellent photoluminescence (PL) and electroluminescence (EL) properties,[16–28] and many device applications have been demonstrated, such as light-emitting diodes,[19–23,26] photovoltaic cells,[20] and field effect transistors.[20,22]

Silole polymers have also been used to detect organic based explosives by a fluorescence quenching mechanism.[28–35] These polymers show excellent sensitivity towards quenching of their fluorescence by picric acid (PA) or 2,4,6-trinitrotoluene (TNT) in organic solution or in the solid state. The excited-state electron of the siloles can transfer into the nitroaromatic compounds when their frontier molecular orbital band gap matches the LUMO energies of the explosive analytes, the transmission results in the quenching of the emission intensity.[28–31,35–37]

The electronic and optical properties can be tuned by changing the *exo*-cyclic substituents at the 2,5 positions on the silole ring, these substituents can exhibit strong π-interactions with the silole core. On the other hand, the π-conjugated compounds containing C–C triple bonds facilitate electronic communication because of their structural rigidities;[38–40] moreover, unusually narrow band gaps are typically observed in alkyne-rich systems. The incorporation of both silole and arylene ethynylene structural motifs into π-conjugated compounds may render them with interesting and desirable properties and hence are of interest to us.

In this work, we synthesized a hyperbranched conjugated polysilole **6** and a linear polysilole **7** incorporating arylene ethynylene subunits. The polymers are very stable, and display narrow band gaps and a slight AIE effect with low extent of aggregation. We explored these polysiloles as fluorescent chemosensors for explosive detection.

Results and discussion

Synthesis

The synthetic procedures of the polymers are shown in Scheme 1 and Scheme 2. The compound **5** was synthesized according to the literature.[40] Theoretically speaking, the analogue of compound **5**, *i.e.* 2,5-diiodo-1,1-dimethyl-3,4-diphenylsilole or 2,5-dichloro-1,1-dimethyl-3,4-diphenylsilole could react with **2** and **4** to obtain the target compounds, but we found that 2,5-diiodo-1,1-dimethyl-3,4-diphenylsilole was unstable, when it was formed, it would decompose quickly at room temperature. Meanwhile, 2,5-dichloro-1,1-dimethyl-3,4-diphenylsilole was too inactive to prepare the polymer. When it reacted with **2** or **4**, the

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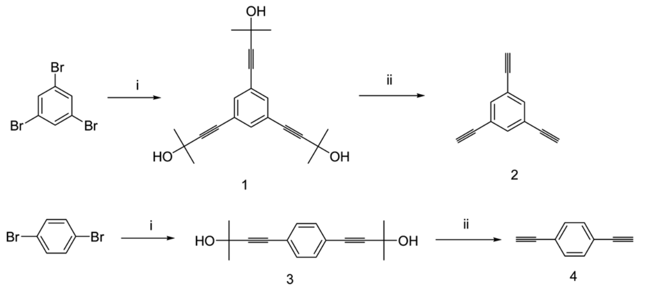
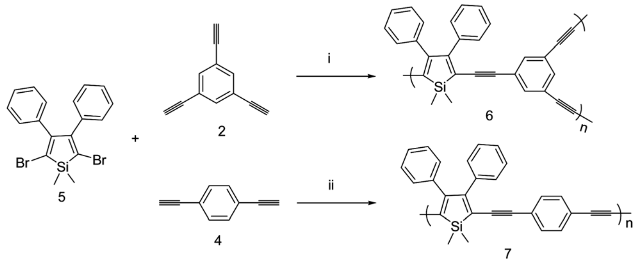


Scheme 1 Synthesis of monomers *via* 2-methyl-3-butyn-2-ol. (i) 2-Methyl-3-butyn-2-ol, $Pd(Ph_3P)_2Cl_2$, CuI, NEt_3, (ii) KOH, toluene at reflux.



Scheme 2 Synthesis of polysiloles by the Sonogashira reaction. (i) Pd $(Ph_3P)_4$, CuI, NEt_3, toluene. (ii) $Pd(Ph_3P)_2Cl_2$, CuI, NEt_3, toluene.

reaction did not happened, even after 100 h. Therefore we employed 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole (**5**) with moderate stability and activity to synthesize polymers **6** and **7**.

Generally speaking, $Pd(PPh_3)_2$ has a higher catalytic activity than that of $Pd(PPh_3)_2Cl_2$. At first, we tried used $Pd(PPh_3)_2Cl_2$ as the catalyst to prepare polymer **6**, however this failed. Then we used Pd $(PPh_3)_4$ which worked. The high steric hindrance of the hyperbranched polymer **6** may be the reason. Whereas the steric hindrance of the linear polymer **7** is smaller than that of polymer **6**, Pd $(PPh_3)_2Cl_2$ is OK for the synthesis of **7**. These two polymers were not obtained by using THF/triethylamine/$ZnCl_2$ as reaction systems, therefore, we conducted the reaction in toluene/triethylamine/CuI systems, and the two polymers were successfully prepared.

The two polymers were easily soluble in common organic solvents, such as THF, dichloromethane, chloroform and toluene. The molecular weight and the polydispersity index (PDI) were measured by GPC using THF as an eluent and polystyrene as the standard. The weight-averaged molecular weight (M_w) is 15 539 Da for polymer **6**, and 18 867 Da for polymer **7**, respectively. The number-average molecular weight (M_n) is 15 178 Da for polymer **6** and 8200 Da for polymer **7**, and the corresponding polydispersity index (PDI) is 1.02 for polymer **6** and 2.30 for polymer **7**, respectively. There is a large difference in the two M_n values and this gives rise to a difference in the polydispersity index between the two polymers, this difference was attributed to the different catalyst in the reactions and the different structures of the two polymers.

Thermal properties

Thermal properties of polymer **6** and **7** were tested by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

As shown in Fig. 1, when polymer **6** was heated to 207 °C, it lost 5% of the original weight, whereas polymer **7** lost 5% when it was heated to 151 °C. When the temperature was raised to 600 °C, polymer **6** and **7** demonstrated an 88% and 64% weight loss based on the initial weight, respectively.

As shown in Fig. 2, the thermal transitions were investigated by differential scanning calorimetry (DSC). Polymer **6** displayed an endothermic peak starting at 128 °C, while polymer **7** displayed an endothermic peak starting at 136 °C. Their glass transition temperatures were 171 °C and 164 °C for polymer **6** and **7**, respectively.

Photophysical properties

Fig. 3 shows the UV-Vis and PL spectra of polymer **6** and **7**. Polymer **6** and **7** show maximum absorption peaks at 456 nm and 462 nm, respectively.

The λ_{max} value of polymer **7** (462 nm) is red shifted compared to that of polymer **6** (456 nm). It may be due to the higher extended π-conjugation in polymer **7**. Polymer **6** and **7** emit yellow-green fluorescence with maximum emission peaks at 520 nm and 545 nm, respectively. By calculating from the absorption onset wavelength, the band gaps of polymer **6** and **7** are 2.26 eV and 1.98 eV respectively.

As shown in Fig. 4, the photoluminescence intensity of polymer **6** and **7** are moderate in THF solution. When a small amount of water was added into the solutions, the PL intensity of both polymer **6** and **7** were enhanced. But, when a large amount of water was added into the solutions, the PL intensity of polymer **6** and **7** both decreased.

With the addition of a nonsolvent such as water into THF, the solution became turbid and macroscopically homogenous with no precipitate, the phenomenon became more pronounced when more H_2O was added. We have studied the UV-vis spectra of polymer **7** in THF/H_2O with the following ratios: 10 : 0, 3 : 7, and 1 : 9, the absorption maxima wavelength exhibited a bathochromic shift, and the absorbance band broadened. This is mostly because of the π–π stacking interactions between the

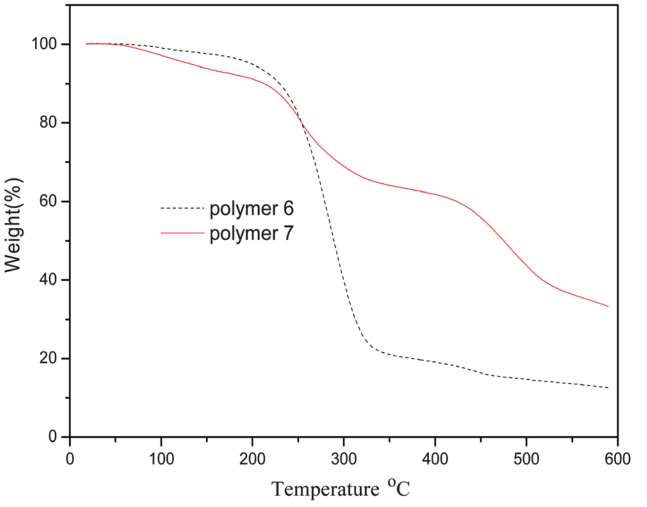


Fig. 1 TGA of polymer **6** and **7** in nitrogen at a heating rate of 10 °C min^{-1}.

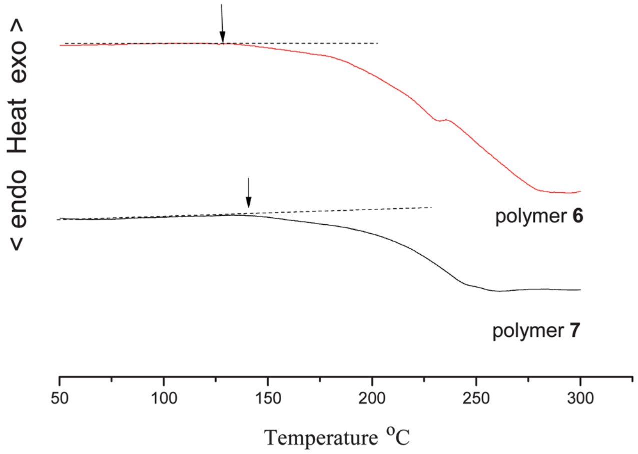


Fig. 2 DSC of polymer **6** and **7** in nitrogen at a scan rate of 10 °C min^{-1}.

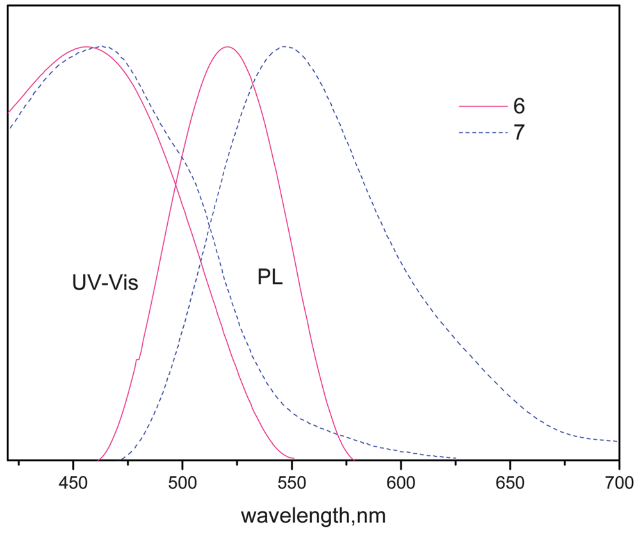


Fig. 3 Normalized UV-Vis and PL spectra of **6** and **7** in CH_2Cl_2 at room temperature. Concentration: 10 μg mL^{-1}.

polymer molecules, clearly suggesting the formation of an "aggregate" state.

Silole monomers are AIE luminogens and emit weakly in the dilute solutions of their good solvents. Silole polymers, however, are somewhat luminescent in their THF solutions, as exemplified by the fluorescent image of the polymer **6** and **7** solution shown in Fig. 4. The silole units are located within the stiff polymer spheres, which limit their intramolecular rotations to some extent and thus render the polymers somewhat luminescent in the solution state.[29]

As shown in Fig. 5, the PL intensity of polymer **7** firstly increased and then decreased when its solution was thickened from 10 to 600 μg mL^{-1}. These results are similar to the PL intensity of polymer **6** in THF/H_2O solution.

Polymer **6** and **7** are insoluble in water, and the molecules will aggregate in the THF/water mixtures. In polymers **6** and **7**, the phenyl rings on the 2,5-positions are connected to the silole core by alkynes, and the phenyl rings on the 3,4-positions are connected to the silole core by a single-bond. In the THF/water mixtures, the molecules of the polymers will aggregate. Therefore, the intramolecular rotation of the phenyl rings on the 3,4-position will be restricted. It will limit the nonradiative route and increase the radiative excitons, these will cause the aggregate-enhanced emission (AEE) effect.[3] On the 2,5-position, the aggregate of phenyl rings will induce the formation of nonradiative species such as excimers and exciplexes, these will cause an aggregation-caused quenching (ACQ) effect. To polymer **6**, with low fractions of water in the mixture (10%, 20%, 30%), the AEE effect is more powerful than the ACQ effect, so the PL intensity of polymer **6** goes up. With high fractions of water in the mixtures (40%, 50%, 60%, 70%), the ACQ effect is more powerful than the AEE effect, so the PL intensity of polymer **6** goes down. For polymer **7**, the AEE effect is stronger than the ACQ effect in the mixtures with low fractions of water (10%, 20%), so the PL intensity of polymer **7** goes up. With high fractions of water in the mixtures (30%, 40%, 50%, 60%), the ACQ effect is stronger than the AEE effect, so the PL intensity of polymer **7** goes down. The I/I_0 value of polymer **6** is higher than polymer **7** at the same fraction of water; this suggests that polymer **6** has a greater proportion of silole units than that of polymer **7**.

Explosive detection

We studied the change of the emission intensity of the polymers responding to PA and TNT with different quantities in the CH_2Cl_2 solution. The polysiloles exhibit attractive fluorescence quenching characteristics in the presence of the explosives. As shown in Fig. 6, with gradual addition of PA or TNT, the emission intensity of polymers **6** and **7** both weakened. This is expected due to the favorable energy matching between the emitting polysilole materials and the nonaromatic explosives with high-energy LUMOs. As shown in Fig. 7, the excited-state electron can transfer from the polysiloles (polymer **7**) fluorophore to the lowest unoccupied molecular orbital (LUMO) of the nitroaromatic explosive materials.[35] This transmission results in the quenching of the emission intensity.[28–31,35–37] The excited state electron transfer process is also improved by Lewis acid/base interactions between the nitro groups of the explosives and the silacycle core of the silole fluorophores.

The data of the fluorescent quenching is consistent to the Stern–Volmer equation:

$$I_0/I = K_{sv}[\text{analyte}] + 1 \tag{1}$$

Where I is the PL intensity at the analyte concentration ([A]). I_0 is the intensity at [A] = 0, and K_{sv} is the Stern–Volmer quenching constant.

The Stern–Volmer plot of polymer **6** and **7** affected by the nitroaromatic compounds are shown in Fig. 8.

The quenching constants about PA for the solutions of polymer **6** and **7** are 4.7×10^{-2} ppm^{-1} (or 8.13×10^3 M^{-1}) and 8.6×10^{-2} ppm^{-1} (or 1.49×10^4 M^{-1}), respectively, which are much higher than the value (1500 M^{-1}) reported in the literature.[12] About TNT, the quenching constants for **6** and **7** are 4.6×10^{-3} ppm^{-1}(or 7.88×10^2 M^{-1}) and 6.5×10^{-3} ppm^{-1} (or 1.11×10^3 M^{-1}), respectively, which are higher than those (1–185 M^{-1}) reported in the literature for the linear conjugated

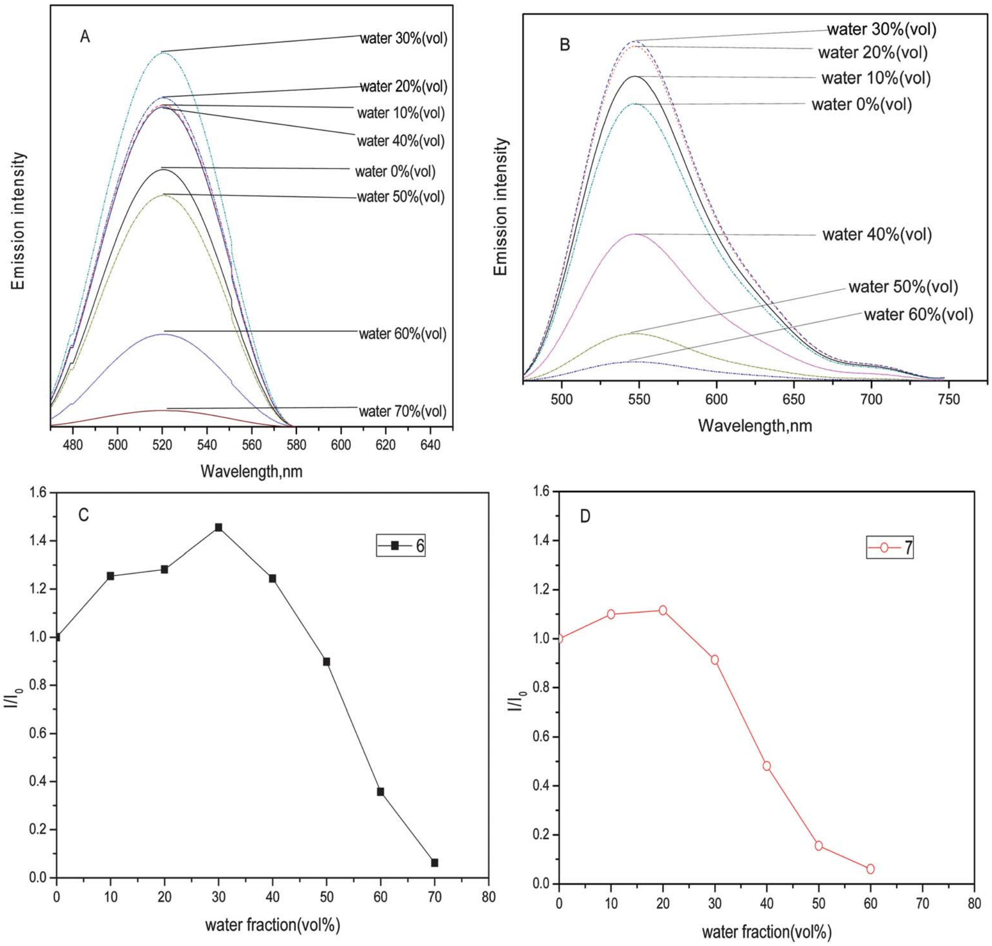


Fig. 4 (A) PL spectra of polymer **6** in THF/water mixtures with different fractions of water. Concentration: 10 μg mL^{-1}. Excitation wavelength: 466 nm. (B) PL spectra of polymer **7** in THF/water mixtures with different fractions of water. Concentration: 10 μg mL^{-1}. Excitation wavelength: 472 nm. (C) I/I_0 plot of polymer **6** in THF/water mixtures with different fractions of water. (D) I/I_0 plot of polymer **7** in THF/water mixtures with different fractions of water.

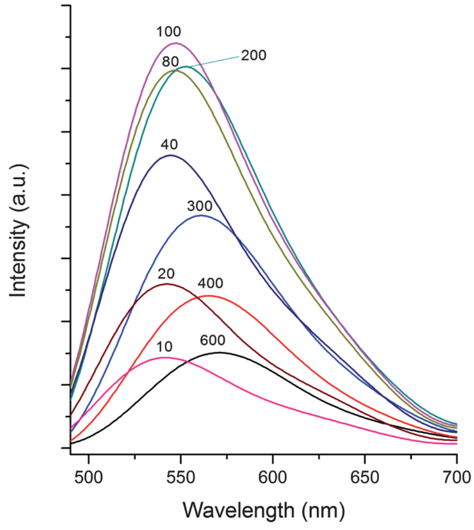


Fig. 5 Concentration-dependent PL spectra of polymer **7** in THF solutions, the numbers near the curves are the concentration (μg mL^{-1}). Excitation wavelength: 472 nm.

iptycene-containing poly(*p*-phenylenebutadiynylene)s and poly(*p*-phenylene ethynylene)s.[41] We found that the efficiency of polymer **7** detecting PA or TNT is higher than that of polymer **6**. It may be due to the smaller steric hindrance of polymer **7** than that of polymer **6**, because the big steric hindrance prevented the interaction between siloles and the nitroaromatic explosives. It means that the binding interaction between the silole core with the PA or TNT more easily occurred in the linear polymer **7** than that of the hyperbranched polymer **6**.

Conclusions

We synthesized the hyperbranched polymer **6** and linear polymer **7** successfully. These polymers show unusual photophysical phenomena due to the AEE effect and the ACQ effect. With a low fraction of water in the mixture, the emission intensity of the polymers slightly increased. The PL intensity of polymers drops with a high fraction of water in the mixture. The polymers are used to detect picric acid and TNT successfully, and they have higher sensitivity of quenching efficiencies for PA than TNT. Because of the less steric hindrance, polymer **7** has more detective efficiency for PA and TNT than those of polymer **6**.

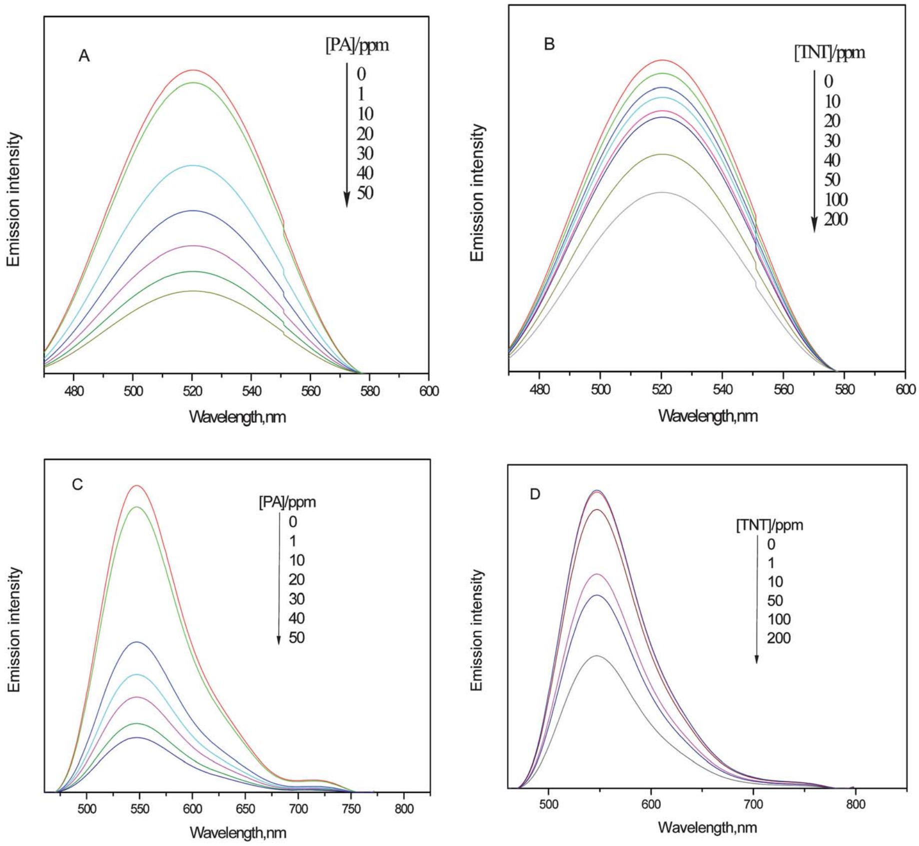


Fig. 6 (A) Effect of the picric acid on the emission of **6** in CH_2Cl_2, [**6**] = 10 μg mL^{-1}, $\lambda_{ex} = 466$ nm. (B) Effect of the TNT on the emission of **6** in CH_2Cl_2, [**6**] = 10 μg mL^{-1}, $\lambda_{ex} = 466$ nm. (C) Effect of the picric acid on the emission of **7** in CH_2Cl_2, [**7**] = 10 μg mL^{-1}, $\lambda_{ex} = 472$ nm. (D) Effect of the TNT on the emission of **7** in CH_2Cl_2, [**7**] = 10 μg mL^{-1}, $\lambda_{ex} = 472$ nm.

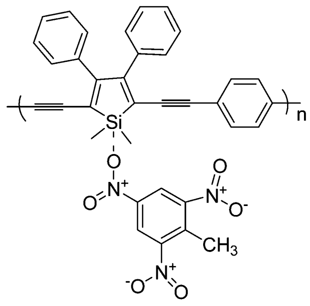


Fig. 7 The interaction between polymer **7** and TNT.

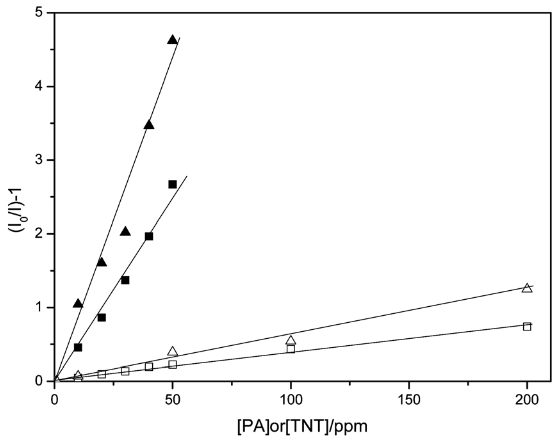


Fig. 8 (▲) Stern–Volmer plot of the effect of PA on **6**. (△) Stern–Volmer plot of the effect of TNT on **6**. (■) Stern–Volmer plot of the effect of PA on **7**. (□) Stern–Volmer plot of the effect of TNT on **7**.

These polymers are expected to be used in the area of explosive detection.

Experimental

All solvents and reagents were purchased from commercial sources. Triethylamine (Et_3N, AR grade) was dried over calcium hydride and distilled prior to use. Tetrahydrofuran (THF, AR grade) was dried over sodium and distilled prior to use. Zinc chloride ($ZnCl_2$, AR grade) was dried over sulfurous oxychloride prior to use. Dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, and other chemicals and solvents were all purchased from Sinopharm Chemical Reagent Co. Ltd (SCRC) and used as received without further purification. All reactions were carried out under an atmosphere of dry argon gas, and the reactions were protected from light by wrapping with aluminium foil when necessary. The polymerization reaction required an anaerobic reaction condition. NMR data were taken on a Brück AM-400 spectrometer. GPC data were obtained by a WATERS 1515 GPC. UV-vis spectra were obtained with the use of a VARIAN-Cary 500 UV-Vis spectrophotometer. Fluorescence emission spectra were obtained with the use of a VARIAN Cary Eclipse luminescence spectrometer.

1,3,5-Tris(2-methyl-2-hydroxy-3-butynyl)-benzene (1)

1,3,5-Tribromobenzene (2 g, 6 mmol), CuI (102 mg, 0.5 mmol), $Pd(PPh_3)_4$ (350 mg, 0.5 mmol) and 2-methylbut-3-yn-2-ol (2.4 g, 28 mmol) were vigorously refluxed for 4 h (monitored by TLC) in Et_3N (30 mL) under argon, then filtered, removing the solvent in the filtrate. The residue was purified by flash chromatography on a silica gel column, eluting with hexane/ethyl acetate (1 : 1), providing **1** as a pale yellow solid (1.62 g, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 18H), 7.39 (s, 3H).

1,3,5-Triethynylbenzene (2)

To a solution of **1** (1 g, 3 mmol) in toluene (20 mL) finely powdered KOH (504 mg, 9 mmol) was added. The mixture was refluxed for 3 h until no acetone escaped from the reaction mixture, cooled to room temperature, filtered, and the solvent removed in the filtrate. The residue was purified by flash chromatography on a silica gel column, eluting with hexane, providing **2** as a colorless solid (324 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ 3.15 (s, 3H), 7.57 (s, 3H).

1,4-Di(2-methyl-2-hydroxy-3-butynyl)-benzene (3)

1,4-Dibromobenzene (2 g, 8 mmol), CuI (91 mg, 0.48 mmol), $Pd(PPh_3)_4$ (337 mg, 0.48 mmol) and 2-methylbut-3-yn-2-ol (2 g, 24 mmol) were vigorously refluxed in Et_3N (30 mL) for 4 h (monitored by TLC) and then filtered, removing the solvent in the filtrate. The residue was purified by flash chromatography on a silica gel column, eluting with hexane/ethyl acetate (1 : 1), providing **3** as a light yellow solid (1.84 g, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.61 (s, 12H), 2.05 (s, 2H), 7.34–7.35 (m, 4H).

1,4-Diethynylbenzene (4)

To a solution of **1** (1.5 g, 6 mmol) in toluene (20 mL) finely powdered KOH (672 mg, 12 mmol) was added. The mixture was refluxed for 3 h until no acetone escaped from the reaction mixture, cooled to room temperature, filtered, and the solvent removed in the filtrate. The residue was purified by flash chromatography on a silica gel column, eluting with hexane, providing **4** as a colorless solid (743 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 2H), 7.42 (s, 4H).

2,5-Dibromo-1,1-dimethyl-3,4-diphenyl-silole (5)

Compound **5** was prepared according to the literature.[40] MS(EI): m/z 419.9 $[M]^+$ (calcd. for $C_{30}H_{29}Br_2Si$ 420.2).

Hyperbranched conjugated polysilole (6)

1,3,5-Triethynylbenzene (120 mg, 0.8 mmol), CuI (14 mg, 0.072 mmol), $Pd(PPh_3)_4$ (83 mg, 0.072 mmol) and 2,5-dibromo-1,1-dimethyl-3,4-diphenyl-silole (520 mg, 1.2 mmol) were stirred for 3 h at 60 °C in 4 mL Et_3N and 15 mL toluene under argon, a solution of phenylacetylene (12 mg, 0.12 mmol) in 5 mL of dried toluene was added into the mixture. The reaction was conducted for another 72 h at 60 °C under argon. The reaction mixture was poured into 30 mL of chloroform and washed with water (20 mL × 2) and brine (20 mL × 2), dried over anhydrous magnesium sulfate, filtered and concentrated the solution and precipitated with 30 mL of methanol. The precipitation procedure was repeated three times to remove low molecular weight oligomers. A red solid was obtained (223 mg, 52%). ^1H NMR (400 MHz, $CDCl_3$) δ 0.55–0.82 (m, $-CH_3$), 7.00–7.17 (m, Ph–H), 7.29–7.45 (m, Ph–H), 7.49–7.68 (m, Ph–H). GPC (THF): M_w = 15 539, M_n = 15 178.

Linear conjugated polysilole (7)

1,4-Diethynylbenzene (157 mg, 1.2 mmol), CuI (14 mg, 0.072 mmol), $Pd(PPh_3)_2Cl_2$ (51 mg, 0.072 mmol) and 2,5-dibromo-1,1-dimethyl-3,4-diphenyl-silole (523 mg, 1.2 mmol) were stirring at 60 °C in 4 mL Et_3N and 15 mL toluene for 3 h. After that, a solution of phenylacetylene (12 mg, 0.12 mmol) in 5 mL of dried toluene was added into the mixture. The reaction was conducted for another 12 h at 60 °C under an argon atmosphere. Then the reaction mixture was poured into 30 mL of chloroform and washed with water (20 mL × 2) and brine (20 mL × 2), dried over anhydrous magnesium sulfate concentrated the solution and precipitated with 30 mL of methanol. The precipitation procedure was repeated three times to remove low molecular weight oligomers. A red solid was collected by vacuum filtration (103 mg, 22%). ^1H NMR (400 MHz, $CDCl_3$) δ 0.48–0.88 (m, $-CH_3$), 7.05–7.15 (m, Ph–H), 7.20–7.45 (m, Ph–H). GPC (THF): M_w = 18 867, M_n = 8200.

Acknowledgements

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