Polymer Chemistry

ARTICLE

Benzo[5]helicene-based conjugated polymers: synthesis, photophysical properties, and application for the detection of nitroaromatic explosives

Li-Li Zhou,[a] Meng Li,[b] Hai-Yan Lu,*[a] and Chuan-Feng Chen*[b]

A series of conjugated polymers based on benzo[5]helicene have been synthesized by employing Sonogashira cross coupling, Suzuki–Miyaura cross coupling and Yamamoto homocoupling reactions. The photophysical properties of these polymers, and their fluorescence responses to the nitroaromatic compounds have then been investigated. Quantitative analysis of the fluorescence titration profiles of the polymers with nitroaromatics in solution exhibited that these electron-rich conjugated polymers could selectively detect the nitroaromatic explosives among the electron-deficient aromatic compounds, and the polymers displayed different responses to the nitroaromatics with similar structures. Moreover, the thin film of polymer **P2** also sensed the saturated vapors of nitroaromatics sensitively and selectively at room temperature, and the sensing process of the film was reproducible. The fluorescence intensity of **P2** revealed a reduction of 87% upon exposure to DNT vapor, and of 70% to TNT vapor in only 10 s. Thus, these new conjugated polymers can be excellent fluorescence sensory materials for detecting nitroaromatic explosives.

Introduction

Nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), picric acid (PA) and 4-nitrotoluene (NT) have drawn considerable attention owing to their threat to homeland security, perniciousness to the environment and toxicity in organisms.[1] To strengthen the protection of our society and improve the environment, various methods for their detection have been developed.[2] Although many physical instruments such as gas chromatography coupled with different detectors,[3] high performance liquid chromatography,[4] X-ray scanning[5] and surface-enhanced Raman spectroscopy[6] are available for the detection of the nitroaromatic compounds, they are expensive, complicated and unsuitable to operate in the field.[7] Thus, it is urgent to seek more reliable and practical detection methods. As a result, fluorescent sensing has been considered as one of the most effective methods because of its sensitivity, selectivity, ease of visualization, and low cost.[8] Especially, fluorescent conjugated

polymers are excellent candidates designed for the detection of nitroaromatic explosives because of the "molecular wire" effect in which excitons in the conjugated polymers extend over the repeat units and move along the chains.[9] The sensing mechanism can be explained that the photo-induced electron transfer from electron-rich conjugated polymers to electron-deficient nitroaromatics results in the fluorescence quenching of the polymers.[10] So far, several different kinds of fluorescent conjugated polymers, such as polyacetylenes,[11] poly(p-phenylenevinylenes),[12] poly(p-phenyleneethynylenes)[13] carbazole-based conjugated polymers,[14] and fluorene-based conjugated polymers[15] have been developed for the detection of nitroaromatic explosives. However, for the less-volatile nitroaromatics, the response time of most of the conjugated polymers for the vapors of the nitroaromatics is relatively long. To further improve the sensitivity and selectivity of the detection for the practical applications, it is still very attractive and meaningful tasks for further developing new fluorescent conjugated polymeric materials.

Helicenes are a kind of polycyclic aromatic compounds with unique helical structures.[16] It can be expected that the nonplanar screw-shaped polycyclic aromatic structures could make the helicene-based conjugated polymers exhibit strong emission in not only solution but also solid states.[17] Especially, the conjugated polymers based on electron-rich helicene skeletons could also be used as new and useful fluorescent materials for the detection of electron-deficient nitroaromatic explosives in both solution and solid states. However, to the best of our knowledge, no such examples have been reported so far. In this paper, we report the synthesis and photophysical

[a.] University of Chinese Academy of Sciences, Beijing 100049, China. E-mail: haiyanlu@ucas.ac.cn.

[b.] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: cchen@iccas.ac.cn.

† Electronic Supplementary Information (ESI) available: ¹H and ¹³C NMR spectra of compounds **2**, **3** and **4**, ¹H NMR and IR spectra of the polymers, AFM image of the film of **P2**, the fluorescence titration profiles of the polymers with the analytes in CDCl₃ along with their corresponding Stern-Volmer plots, and time-dependent fluorescence intensity of the film of **P2** upon exposure to the saturated vapors of the analytes. See DOI: 10.1039/x0xx00000x

properties of a new kind of conjugated polymers based on the benzo[5]helicene skeleton.[18] Especially, it is found that the conjugated polymers can detect selectively the nitroaromatic explosives among the electron-deficient aromatic compounds, and exhibit different fluorescent responses to the closely related nitroaromatics in chloroform solution. Moreover, the films of polymer **P2** also reveal rapid and selective responses upon exposure to the saturated vapors of the nitroaromatic explosives, and the sensing process of the film is reversible. The results indicate that these conjugated polymers based on the helicene skeleton can be utilized as effective fluorescent chemosensors for the nitroaromatic explosives.

Results and discussion

Synthesis and characterization of P1-P5

The synthetic routes of the conjugated polymers **P1-P5** are depicted in Scheme 1. In consideration of the solubilities of the polymers, long alkyl chains were introduced into the helicene monomers. Starting from 2,15-dimethoxybenzo[5]helicene **1**,[18] compound **3** was conveniently obtained by the demethylation, etherification, and then bromination reaction, respectively. Then, by Sonogashira coupling reaction of **3** with trimethylsilyl-acetylene (TMSA), and then followed by hydrolysis, compound **4** was synthesized in 50% yield. It was found that both **3** and **4** showed good solubility in common organic solvents. Since aryl bromide and aryl acetylene are favored in coupling reactions with many functional groups, we then synthesized polymers **P1**-**P5** in good yields based on **3** and **4** as the monomers by Sonogashira cross coupling, Suzuki–Miyaura cross coupling and Yamamoto homo-coupling reactions, respectively.

The molecular weights and polydispersity indices (PDI) values of these polymers are listed in Table 1, and they were determined by Gel Permeation Chromatography (GPC) against polystyrene standards. The polymers exhibited a relatively narrow PDI of 1.35-1.97. Generally, the rigid structure of helicene prevents formation of the polymers with high molecular weights. However, **P4** (M_n=118.3kDa, M_w=163.3kDa) was an exception among them. It was found that **P4** displayed good solubilities only in chloroform and tetrahydrofuran at room temperature probably due to its high molecular weight, while the other polymers exhibited high solubilities in common organic solutions, such as chloroform, dichloromethane, tetrahydrofuran, toluene, and so on. Thermal stability of these polymers were measured by Thermogravimetric Analysis (TGA) (Fig. S12, ESI†), and their decomposition temperatures (T_d) under nitrogen are collected in Table 1. Clearly, the polymers exhibited high thermal stability with T_d values ranging from 268 to 330 °C under nitrogen.

Table 1. Molecular weights and thermal stability of the polymers

Polymer	$M_n{}^a$/kDa	$M_w{}^b$/kDa	PDI^c	T_d (in N$_2$)^d/°C
P1	12.3	16.6	1.35	268
P2	37.4	58.1	1.56	287
P3	17.9	35.2	1.97	311
P4	118.3	163.3	1.38	307
P5	11.0	15.4	1.39	330

$^a M_w$: the weight-average molecular weight. $^b M_n$: the number-average molecular weight. ^{c}PDI: polydispersity indices (M_w/M_n). $^d T_d$: the decomposition temperature at 5% weight loss occurs.
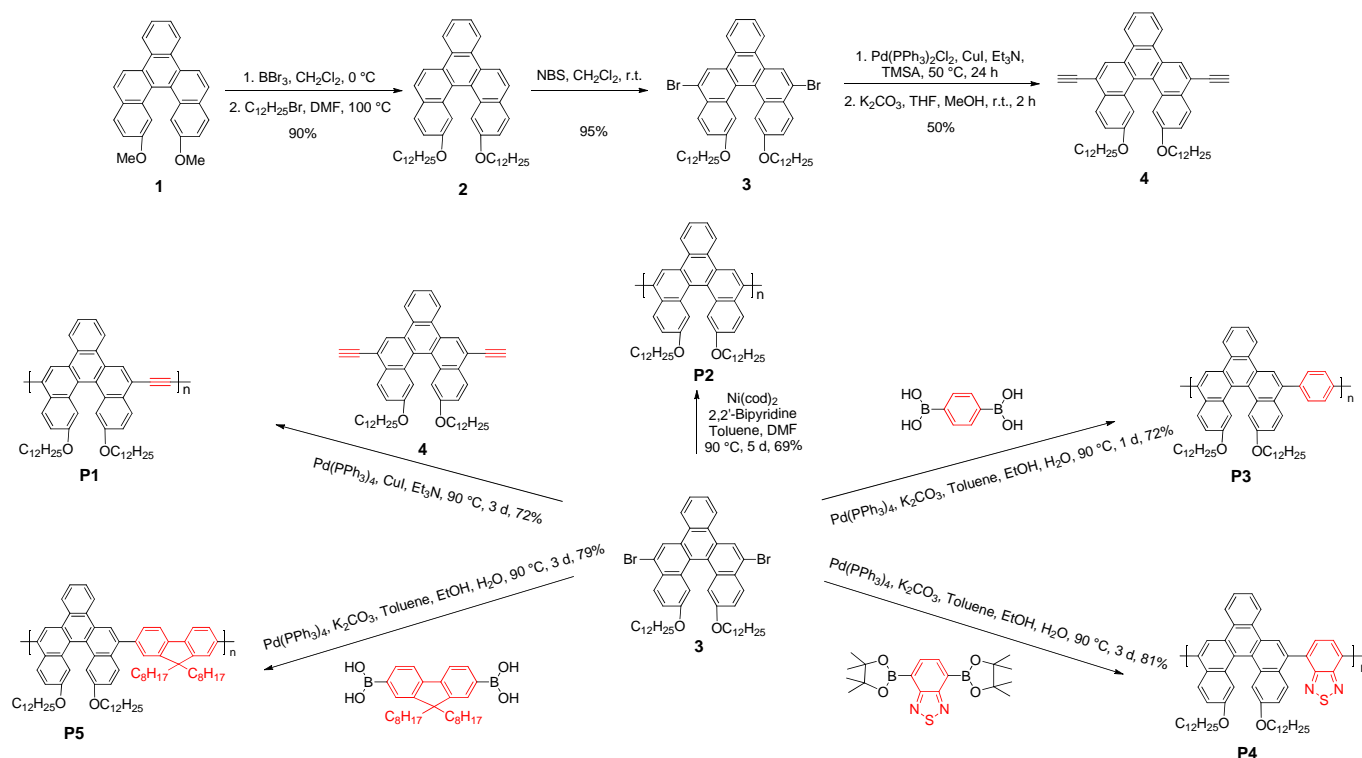
Scheme 1 Synthetic routes of conjugated polymers **P1**-**P5**.

Table 2 Photophysical data of **P1**-**P5**

Polymer[a]	UV-Vis $\Lambda_{max}{}^b$/nm		Log ε	PL Λ^c/nm		Stokes shift/nm		$\Phi_f{}^d$/%	Life time τ/ns	
	Sol	Film		Sol	Film	Sol	Film		Sol	Film
P1	457	471	4.29	507	561	57	90	59.3	1.02	0.59
P2	393	394	4.21	464	490	71	96	70.8	1.34	0.91
P3	383	385	4.34	450	451	67	66	13.7	1.42	0.53
P4	430	428	4.02	558	556	128	128	36.7	6.47	1.19
P5	384	385	4.49	457	472	73	87	20.1	1.12	0.52

[a]Photophysical properties date in chloroform solution are recorded at room temperature (c = 1.0 × 10^{-6} M). [b]Only the longest absorption maxima are shown. [c]Excited at the longest absorption maxima. [d]Absolute fluorescence quantum yield in solution.
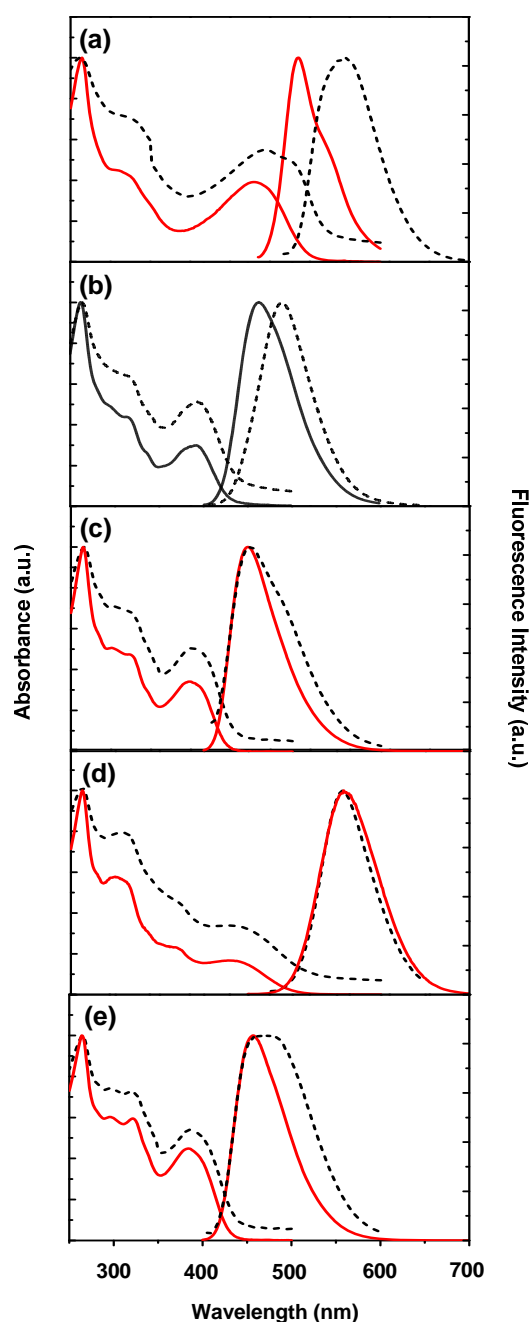

Fig. 1 The absorption and fluorescence spectra of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4** and (e) **P5** in chloroform at 1.0 × 10^{-6} M (solid lines) and in spin-cast films (dotted lines).

Photophysical properties of the conjugated polymers

The photophysical properties of the conjugated polymers **P1**-**P5** were characterized in both chloroform solution at a concentration of 1 × 10^{-6} M and solid states, and the results are shown in Fig. 1 and Table 2. It was found that the polymers exhibited similar absorption and emission spectra between the solution and the solid states. The maximum absorption band of these polymers displayed a large red shift compared to compound **2** (350 nm) in solution due to the large conjugated π-system of the polymers (Fig. S49, ESI†). As the electron-deficient moiety, 2,1,3-benzothiadiazole in the polymer leaded to strong charge transfer, so the stokes shift of **P4** was even up to 128 nm. In the fluorescent spectra, the maximum emission wavelength of **P4** was longer than that of the other four polymers in solution which might also be attributed to the strong charger transfer. When the acetylenyl group was introduced, the maximum absorption of **P1** displayed a large red shift compared to the other four polymers. The large red shifts of absorption and emission spectra of **P1** in solid states relative to its solution indicates that there might exist weak chain aggregations in solid states. The fluorescence lifetimes of the polymers fall into the nanosecond region. Especially, the fluorescence lifetime of **P4** was found to be about 6 times longer than that of the other four polymers in chloroform. It was also observed that the polymers have good photoluminescence capabilities with Φ_f values between 0.14 and 0.71 in chloroform.

The detection of nitroaromatics by the polymers in solution

With the conjugated polymers in hand, we first applied them for detecting the nitroaromatics in solution. Considering that nitroaromatics are strong electron acceptors owing to the electron-withdrawing nitro groups, the conjugated polymers as electron donors can interact with the explosives with their fluorescence being quenched. Generally, there are mainly two mechanistic pathways: static quenching and dynamic quenching. Static quenching mainly results from the formation of a non-emissive bound complex, while the dynamic quenching is based on a bimolecular collision at the excited state.[19] The nitroaromatics used in our study were TNT, DNT, PA, and NT. To explore the selectivity, benzophenone (BP) which is a non-nitrated and high electron affinity aromatic compound was used as a control. The concentration of the

polymers was fixed at 1.0×10^{-6} M. As depicted in Fig. 2, after adding the analyte to the solution, the fluorescence intensity of the polymers was quenched gradually. In order to evaluate the quenching efficiencies of the polymers in response to the nitroaromatics in solution, according to the previous studies, the Stern–Volmer equation was used to quantify quenching efficiencies:

$$I_0/I = 1 + K_{sv}[M]$$

In this equation, I_0 is the initial fluorescence intensity without the analyte; I is the fluorescence intensity after adding the analyte of concentration [M]; K_{sv} is the Stern–Volmer constant which can be calculated. It was exhibited that all the Stern–Volmer plots of these polymers presented a linear relationship at lower concentration of nitroaromatics. The linear relationship means that the fluorescence quenching might involve a static mechanism.[8a,20]

The Stern–Volmer constants of the polymers in response to the analytes are listed in Table 3, which were quantitatively measured. Although BP has a suitable electron affinity, the polymers showed much stronger fluorescence quenching to nitroaromatics than BP, which suggested that the polymers could selectively detect the nitroaromatics explosives. It was inferred that stronger dipolar or electrostatic interaction between the nitroaromatics and the polymers resulted in the higher fluorescence quenching.[20a,20c] The fluorescence quenching efficiencies of the polymers for nitroaromatics were generally in the order of PA>TNT>DNT>NT, which was in accordance with the electron deficient property of these nitroaromatics. Higher electron deficiency of the nitroaromatics resulted in stronger interaction with the conjugated polymers, which caused higher sensitivity in detection. The selected polymers showed different fluorescence quenching responses to various nitroaromatics, which could be applied to discriminate the semblable nitroaromatics. It was also observed that different polymers displayed distinct fluorescence quenching efficiencies to the same nitroaromatics, and the fluorescence quenching efficiencies of these polymers were mainly in the order of **P3**≈**P5**>**P2**>**P1**≈**P4**. The poor quenching response of **P4** towards nitroaromatics was due to the fact that the electron-withdrawing 2,1,3-benzothiadiazole groups in the helicene backbones made **P4** less electron donating resulting in weaker interaction between the polymer and the nitroaromatics. In addition, due to overlap of the fluorescence spectra between TNT and **P4**, the fluorescence of TNT interfered the fluorescence of **P4** to prevent detecting TNT. On the contrary, the introduction of electron-rich phenyl ring and fluorene into the polymers increased the electron donating ability of the polymers, and thus improved their sensitivity to nitroaromatics. The poor fluorescence quenching response of **P1** to the nitroaromatics might result from the weak electron donating ability of the acetylenyl groups. Based on the observation, it is concluded that the electron donating ability of the polymers greatly impact the sensitivity of the polymers and the helicene-based polymers can be used as chemosensing materials for the detection of nitroaromatics.
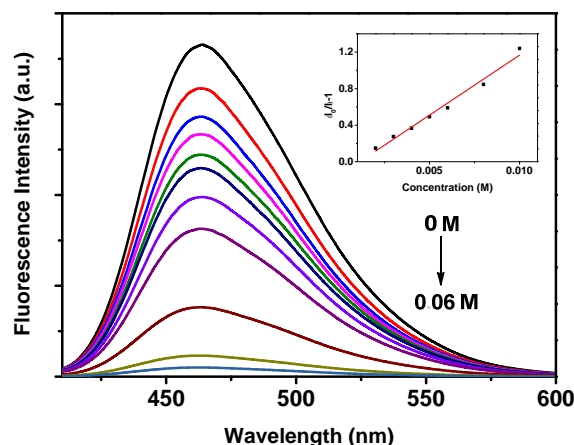

Fig. 2 Fluorescence titration profiles of **P2** with gradual addition of DNT in chloroform (inset: Stern-Volmer plot of **P2**).

Table 3 Stern–Volmer quenching constants[a]

Polymer	TNT	DNT	PA	NT	BP
P1	44	54	117	13	0
P2	213	131	381	77	0.94
P3	331	199	667	118	12
P4	-	27	134	2	0
P5	299	209	634	113	15

[a]All quenching constants were determined in chloroform by fitting the experimental date to equation.

The detection of nitroaromatics by the polymers in solid states

It is significant for the materials to detect the nitroaromatics in solid states, taking the stability, reusability and suitability for field test into consideration. For **P2** with more excellent fluorescence behavior than the other four polymers in solid states, we then investigated the films of **P2** in response towards the saturated vapors of the nitroaromatics.

The films were prepared by spin-coating the chloroform solution of **P2** (0.5 mg/mL) onto a quartz substrate (15 mm × 15 mm) at a spin rate of 3000 rpm and the average value for thickness of films was around 8 nm measured by Atomic Force Microscopy (AFM). The fluorescence intensities of the films of **P2** upon exposure to the saturated vapors of TNT (5.8×10^{-6} Torr), DNT (1.1×10^{-4} Torr), NT (1.6×10^{-1} Torr), PA (5.8×10^{-9} Torr) and BP (1.6×10^{-3} Torr) were obtained by putting the films into glass vials (10 mL) containing nitroaromatics and cotton gauze, which could prevent the analytes from directly contacting the film of **P2** and help maintain a constant saturated vapor pressure.[13a] After the films were put into the vials with the saturated vapors of the analytes for a certain period, the fluorescence spectra were recorded immediately at the excitation wavelength (394 nm).

The films were exposed to the nitroaromatics vapors at different time, and the corresponding quenching efficiencies are shown in Fig. 3. It was observed that the films presented high sensitivity and selectivity towards nitroaromatics, and the fluorescence responses of **P2** towards the nitroaromatics in solid states were quite different from that in solution, since
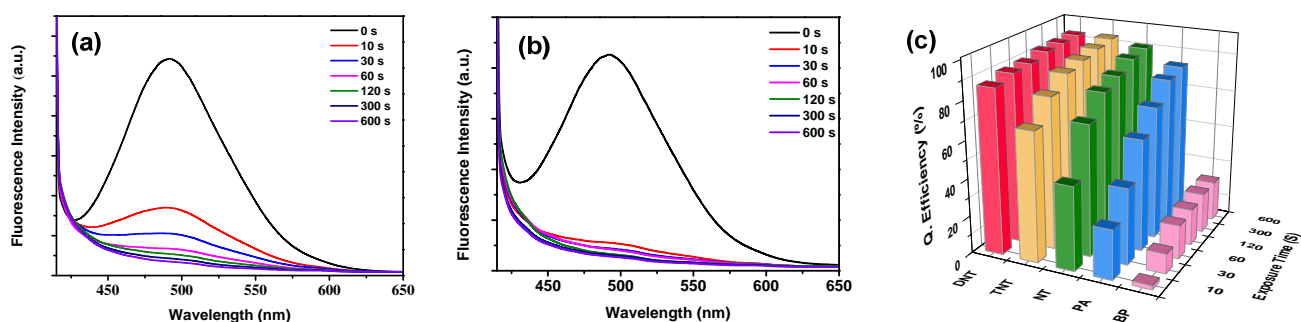
Fig. 3 (a) Fluorescence behavior of the film of **P2** upon exposure to saturated vapor of TNT at different time interval. (b) Fluorescence behavior of the film of **P2** upon exposure to saturated vapor of DNT at different time interval. (c) Fluorescence quenching efficiency of the film of **P2** upon exposure to saturated vapor of analytes at different time interval.

factors can affect the sensing process, such as the vapor pressure and redox potential of the nitroaromatics.[13a,20a] On the whole, the quenching efficiency of the films for the vapors of analytes followed the order of DNT>TNT>NT>PA>BP. The film exhibited better fluorescence quenching to the nitroaromatics than BP, just the same as that in solution. To our amazement, **P2** showed nearly 70% quenching of the fluorescence in 10 s upon exposure to TNT vapor, which was much higher than most reported conjugated polymers (**PPE**: 30%,[13a] **PPV**: 38%[12a]). And it also reached 87% quenching efficiency to DNT vapor in 10 s, 26% to PA vapor, and 45% to NT vapor. Although NT has a much lower redox potential than PA, the faster quenching response of NT resulted from the higher vapor pressure. It could also explain that the higher quenching efficiency was found for DNT than TNT and PA. Furthermore, the different fluorescence quenching of the film of **P2** in response to the nitroaromatics with similar structures provided a method to distinguish the nitroaromatics. The high quenching efficiency of the film of **P2** is probably attributed to the fact that **P2** is an excellent electron donor due to the electron-rich π-conjugated system, which increases the interaction between the polymer and the nitroaromatics and tends to form strong charge-transfer complex with the nitroaromatics, and the rigid helical structure of the helicene skeleton and the long alkyl chains increase the diffusion rate of the nitroaromatics vapor into the films.[21] Notably, the rapid fluorescence response rate of the films of **P2** upon exposure to the saturated vapor of the nitroaromatics demonstrates that the conjugated polymer **P2** is an outstanding material to sense the nitroaromatics.

For practical application, easy regeneration of the films after use is highly desirable. As a result, the reversibility of the film of **P2** toward the exposure of DNT was examined. The film was exposed to the saturated vapors of DNT for 60 s at room temperature. Then the fluorescence intensity of the film was recorded immediately. Later, the film was washed with methanol for several times and dried in hot air. And the process was repeated five times. As shown in Fig. 4, after five times of quenching-regeneration cycles, the fluorescence intensity of the film was only a little lower relative to the initial state. Therefore, the quenching process of the **P2** film response to DNT vapor exhibits great reversibility.
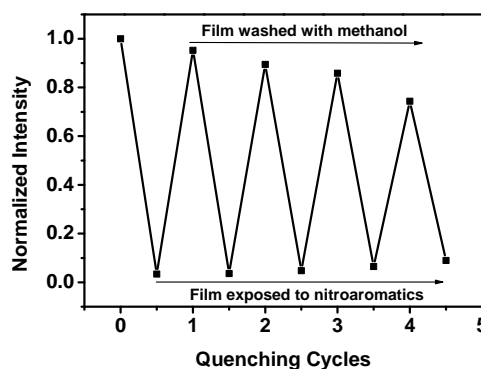

Fig. 4 Reversibility of sensing ability of the **P2** film to the saturated vapor of DNT.

Conclusions

In summary, we have successfully constructed a new series of conjugated polymers based on benzo[5]helicene skeleton by Sonogashira cross coupling, Suzuki–Miyaura cross coupling and Yamamoto homocoupling reactions. We have also investigated the photophysical properties of the polymers in both solution and solid states, and found that these polymers could act as efficient fluorescent chemosensors for the nitroaromatic explosives. The polymers exhibit high selectivity towards the nitroaromatic explosives in solution. Moreover, the 8 nm-film of **P2** also senses the saturated vapor of the nitroaromatics sensitively and selectively at room temperature, and the sensing process of the films is reversibility. The film shows about 70% quenching of the fluorescence upon exposure to TNT vapor and 87% to DNT vapor only in 10 s, which are higher than most of those reported conjugated polymers. The preeminent performance might be attributed to the following factors: first, the "molecular wire" effect amplifies the quenching; second, in solid states the twisted structure of the helicene and the long chains increase the diffusion rate of the nitroaromatics vapors into the films; third, these helicene units in the macromolecules extend π-conjugation and thus increases the interaction between the polymers and the nitroaromatics. The results presented in this paper indicate that the conjugated polymers based on the helicene can be used as a new class of candidates of efficient sensors and found practical applications for the detection of nitroaromatic explosives.

Experimental

General

All the reactants were commercial and used without further purification. Melting points were recorded on an electrothermal melting point apparatus and were uncorrected. Absorption spectra were measured on a UV–Vis spectrophotometer (Lambda 950 spectrophotometer) in chloroform of HPLC grade. Infrared spectra were measured by Nicolet 6700 FT-IR Spectrometer. Fluorescence spectra were recorded on Hitachi F-7000 fluorometer with the Xenon lamp as excitation source. The absolute fluorescence quantum yield were obtained by Edinburgh FLS920 at room temperature. Fluorescence lifetimes were obtained by Edinburgh Lifespec-Red. ^{1}H and ^{13}C NMR spectra were measured by a Bruker DMX300/500 NMR. APCI mass spectra were obtained with an FTICR mass spectrometer. Elemental analyses were performed by a Flash EA 1112 micro-analyzer. The thermogravimetric analysis (TGA) of the polymer samples were determined by a Perkin Elmer's Pyris1 TGA analyzer running from 30 °C to 780 °C at a heating rate of 10 °C/min. The molecular weights of the polymers were determined by Waters alliance 2000 gel permeation chromatography (GPC) relative to polystyrene standards using THF at ambient temperature.

Synthesis of compound 2

Compound **1** (388 mg, 1 mmol) was treated with boron tribromide (0.94 mL, 10 mmol) in dry dichloroethane (30 mL) for 7 h at 0 °C, and then the reaction was quenched with water (30 mL). The organic phase was extracted with ethyl acetate, dried over MgSO$_4$ and concentrated under vacuum. To a solution of the residue in dried DMF (15 mL) was added C$_{12}$H$_{25}$Br (525 mg, 2.1 mmol) and K$_2$CO$_3$ (552 mg, 4 mmol), and the mixture was stirred under argon for 12 h at 100°C. After the mixture was cooled to room temperature, water was added and then collected by filtration to give compound **2** (627 mg, 90%) as pale white powder. m.p.: 94-96 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.77–8.67 (m, 2H), 8.59 (d, J = 8.7 Hz, 2H), 8.01 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.73–7.65 (m, 2H), 7.37 (d, J = 2.3 Hz, 2H), 7.13 (dd, J = 8.8, 2.4 Hz, 2H), 3.54 (t, J = 6.6 Hz, 4H), 1.60 (m, 4H), 1.37–1.20 (m, 36H), 0.89 (t, J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 156.5, 131.8, 130.5, 129.9, 129.3, 127.6, 127.5, 127.4, 125.2, 123.7, 118.6, 118.3, 110.6, 67.8, 32.1, 29.89, 29.85, 29.8, 29.6, 29.4, 29.2, 26.2, 22.9, 14.3. HR-MS (APCI): m/z calcd for [M + H]$^+$ C$_{50}$H$_{65}$O$_2$: 697.4979, found 697.4970. Anal. calcd for C$_{50}$H$_{64}$O$_2$: C, 86.15; H, 9.25. Found: C, 85.88; H, 9.30.

Synthesis of compound 3

To a solution of compound **2** (350 mg, 0.5 mmol) in dried dichloromethane (50 mL) was added NBS (223 mg, 1.25 mmol). The mixture was stirred for 8 h at room temperature and then performed by filtration. The filtrate was concentrated under reduced pressure to give a residue which was purified by flash column chromatography with dichloromethane : petroleum ether (1:3, v/v) as eluent to afford compound **3** (406 mg, 95%) as white powder. m.p.: 74-76°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ

8.82 (s, 2H), 8.66–8.50 (m, 2H), 8.27 (d, J = 9.0 Hz, 2H), 7.83–7.63 (m, 2H), 7.27 (d, J = 2.4 Hz, 2H), 7.20 (dd, J = 9.1, 2.4 Hz, 2H), 3.77–3.19 (m, 4H), 1.59 (m, 4H), 1.28 (s, 36H), 0.97–0.77 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 157.1, 132.9, 130.5, 129.5, 128.8, 128.0, 125.8, 124.6, 123.6, 122.8, 122.4, 119.6, 110.7, 67.9, 32.1, 29.89, 29.85, 29.81, 29.78, 29.6, 29.4, 29.1, 26.1, 22.9, 14.3. HR-MS (APCI): m/z calcd for [M + H]$^+$: 855.3174, found 855.3152. Anal. calcd for C$_{50}$H$_{62}$Br$_2$O$_2$: C, 70.25; H, 7.31. Found: C, 70.02; H, 7.20.

Synthesis of compound 4

Under an atmosphere of argon, ethynyltrimethylsilane (176 mg, 1.8 mmol) was added to a 100-mL Schlenk flask containing a solution of compound **3** (256 mg, 0.3 mmol), PdCl$_2$(PPh$_3$)$_2$ (11 mg, 0.016 mmol) and CuI (2 mg, 0.011 mmol) in dry triethylamine (30 mL). The mixture was stirred under argon for 12 h at 50°C, cooled to room temperature and then added chloroform (50 mL) and water (50 mL). The organic phase was collected and concentrated under reduced pressure. To a solution of the residue in THF (20 mL) and methanol (60 mL) was added K$_2$CO$_3$ (248 mg, 1.8 mmol). The mixture was vigorously stirred for another 2 h at room temperature and the solvent was removed under reduced pressure. The reaction mixture was diluted with dichloromethane and washed with water. Then the organic phase was collected, dried over MgSO$_4$ and concentrated under reduced pressure give a residue, which was purified by flash column chromatography with dichloromethane : petroleum ether (1:10, v/v) as eluent to afford compound **4** (112 mg, 50%) as pale yellow solid. m.p.: 90-92°C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.84 (s, 2H), 8.72–8.57 (m, 2H), 8.38 (d, J = 9.0 Hz, 2H), 7.82–7.65 (m, 2H), 7.28 (d, J = 2.4 Hz, 2H), 7.20 (dd, J = 9.0, 2.4 Hz, 2H), 3.60 (s, 2H), 3.57–3.43 (m, 4H), 1.60 (m, 4H), 1.36–1.19 (m, 36H), 0.88 (t, J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 157.0, 131.8, 129.8, 129.7, 127.9, 127.6, 127.0, 125.6, 124.0, 123.6, 119.4, 119.3, 110.7, 82.5, 82.4, 67.8, 32.1, 29.9, 29.8, 29.80, 29.78, 29.6, 29.4, 29.1, 26.1, 22.9, 14.3. HR-MS (APCI): m/z calcd for [M + H]$^+$: 745.4979, found: 745.4968. Anal.calcd for C$_{54}$H$_{64}$O$_2$: C, 87.05; H, 8.66. Found: C, 86.88; H, 8.75.

Synthesis of polymer P1

Under an atmosphere of argon, dry triethylamine (5 mL) was added to a 25-mL Schlenk flask containing compound **3** (77 mg, 0.09 mmol), compound **4** (67 mg, 0.09 mmol), CuI (3 mg, 0.016 mmol) and Pd(PPh$_3$)$_4$ (7mg, 0.006 mmol). The mixture was stirred under argon for 3 days at 90°C, cooled to room temperature and then added chloroform (50 mL) and water (50 mL). The organic phase was dried over MgSO$_4$ and concentrated under reduced pressure to give a residue, which was dissolved in chloroform (3 mL) and reprecipitated in methanol (60 mL) for three times to afford **P1** (95 mg, 72%) as orange red powder. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.19–8.15 (m, br, 4H), 7.99–7.74 (m, br, 2H), 7.74–7.61 (m, br, 1H), 7.61-7.50 (m, br, 1H), 7.50–7.30 (m, br, 3H), 7.24–7.15 (m, br, 1H), 3.91–3.25 (m, br, 4H), 1.79-1.61 (m, br, 4H), 1.52-1.00 (m, br, 55H), 0.95-0.73 (m, br, 13H).

Synthesis of polymer P2

A mixture of bis(1,5-cyclooctadiene)nickel(0) (191 mg, 0.736 mmol), 1,5-cyclooctadiene (81 mg, 0.736 mmol), 2,2'-bipyridine (108 mg, 0.736 mmol) and compound **3** (200 mg, 0.23 mmol) was added into a 25-mL Schlenk flask in glove box and then dried toluene (3.9 mL) and DMF (1.3 mL) were added to the mixture with syringe under argon. The mixture was stirred for 5 d at 90 °C, treated with water and extracted with chloroform. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give a residue, which was dissolved in chloroform (3 mL) and reprecipitated in methanol (60 mL) for three times to give **P2** (110 mg, 69%) as yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48–8.44 (m, br, 4H), 8.16–7.40 (m, br, 6H), 7.25–6.95 (m, br, 2H), 3.77 (m, br, 4H), 1.80-1.59(m, br, 4H), 1.26(m, br, 48H), 0.84 (m, br, 12H).

Synthesis of polymer P3

To a mixture of compound **3** (145 mg, 0.17 mmol), 1,4-benzenediboronic (34 mg, 0.20 mmol) and K_2CO_3 (140 mg, 1.02 mmol) in toluene (3 mL), ethanol (2 mL) and H_2O (1 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_4$ (14 mg, 0.012 mmol). The mixture was stirred at 90 °C for 24 h under argon, cooled to room temperature and then poured into chloroform (50 mL) and water (50 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under reduced pressure to give a residue which was dissolved in chloroform (3 mL) and reprecipitated in methanol (60 mL) for three times to give **P3** (94 mg, 72%) as yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18–8.51 (m, br, 4H), 8.33–7.91 (m, br, 5H), 7.91–7.53 (m, br, 6H), 7.18–6.73 (m, br, 2H), 3.96–3.29 (m, br, 4H), 1.7 (m, br, 4H), 1.29 (m, br, 35H), 0.85 (m, br, 6H)

Synthesis of polymer P4

To a mixture of compound **3** (145 mg, 0.17 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (79 mg, 0.20 mmol) and K_2CO_3 (140 mg, 1.02 mmol) in toluene (3 mL), ethanol (2 mL) and H_2O (1 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_4$ (14 mg, 0.012 mmol). The mixture was stirred at 90 °C for 3 d under argon, and cooled to room temperature. The workup procedure was similar to that described for the preparation of **P3** to afford **P4** (118 mg, 81%) as orange powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.27–8.56 (m, 4H), 8.44–7.89 (m, br, 4H), 7.89–7.54 (m, br, 4H), 7.23–6.95 (m, br, 2H), 4.30–3.11 (m, br, 4H), 1.80–1.58 (m, br, 4H), 1.26 (m, br, 41H), 0.86 (m, br, 8H).

Synthesis of polymer P5

To a mixture of compound **3** (145 mg, 0.17 mmol), 9,9-di-n-octylfluorene-2,7-diboronic acid (95 mg, 0.20 mmol) and K_2CO_3 (140 mg, 1.02 mmol) in toluene (3 mL), ethanol (2 mL) and H_2O (1 mL) under argon atmosphere was added catalytic amount of $Pd(PPh_3)_4$ (14 mg, 0.012 mmol). The mixture was stirred at 90 °C for 3 d under argon, and cooled to room temperature. The workup procedure was similar to that described for the preparation of **P3** to give **P5** (127 mg, 79%) as yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00–8.78 (m, br, 2H), 8.78–8.63 (m, br, 2H), 8.18–7.96 (m, br, 4H), 7.93–7.64 (m, br, 8H), 7.59–7.33 (m, br, 2H), 7.24–7.04 (m, br, 2H), 3.85–3.35 (m, br, 4H), 2.55–1.95 (m, br, 4H), 1.77–1.55 (m, br, 6H), 1.43-1.09(m, br, 72H), 0.94-0.71(m, br, 18H).

Acknowledgements

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Benzo[5]helicene-based conjugated polymers: synthesis, photophysical properties, and application for the detection of nitroaromatic explosives

Li-Li Zhou, Meng Li, Hai-Yan Lu,* and Chuan-Feng Chen*
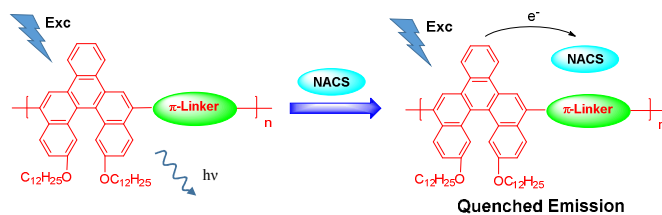
Benzo[5]helicene-based conjugated polymers were synthesized and demonstrated as fluorescent chemosensors for the high selective and sensitive detection of nitroaromatic explosives.