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A silicon-cored fluoranthene derivative as a fluorescent probe for detecting nitroaromatic compounds

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Two fluoranthene derivatives, nonsilicon-cored 7,10-diphenylfluoranthene (DF) and silicon-cored bis(7,10diphenylfluoranthen-8-yl)diphenylsilane (BDS), were synthesized *via* the Knoevenagel/Diels–Alder method. The thermal properties and fluorescence quenching behavior of the derivatives with nitroaromatic compounds were investigated. Aside from its better thermal properties, BDS also showed lower detection limit, higher sensitivity, and higher quenching efficiency in detecting nitrobenzene and *m*dinitrobenzene than DF. The detection limits of BDS were 50 and 10 ppm toward nitrobenzene and *m*dinitrobenzene, respectively. Moreover, the Stern–Volmer plot of BDS swiftly curved upward, suggesting a super amplification effect. This result can be attributed to the special tetrahedral structure of BDS. Thus, BDS has great potential in the detection of explosives. This work may serve as a basis for designing new organic materials with great efficiency and sensitivity in fluorescence detection.

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Introduction

The serious environmental pollution in recent years has placed urgency in the design and preparation of chemical sensors for nitroaromatic compound detection.1-5 Nitrobenzene, dinitrotoluene (DNT), and trinitrotoluene (TNT) are the primary nitroaromatic compounds that can cause significant harm to humans. Aside from their explosive nature, nitroaromatic compounds severely pollute the environment and cause headaches, anemia, skin irritation, and eye and neurological damage to humans.6-10 Therefore, finding an efficient detection method for nitroaromatic compounds is crucial to protect humans and the environment. Gas chromatography-mass spectrometry, ion mobility spectroscopy, surface-enhanced Raman spectroscopy, and other spectroscopic techniques have been used to detect nitroaromatic explosives.11,12 However, the practical applications of these instrumental techniques are limited by their high cost, low selectivity, and low sensitivity. Thus, developing new techniques with efficient and sensitive detection capabilities is an important undertaking.

Fluorescence quenching has been recently found to be an efficient detection method for nitroaromatic explosives because of its high sensitivity, easy visualization, and short response time.^{8,13-25} The design and preparation of fluorescent materials are the key factors in this technique. Metal–organic frameworks (MOFs), particularly luminescent MOF sensors, have been widely used to detect nitroaromatic compounds because of their high selectivity and sensitivity.^{13,26-28} However, the preparation of MOFs is complicated and expensive, which limits the application of these materials.

Organic materials are suitable candidates in fluorescence quenching because of their abundance and flexible molecular design.²⁹⁻³² Among these organic materials, electron-rich aromatic compounds have a high quenching efficiency toward electron-deficient nitroaromatic compounds.^{31,32}

However, aromatic compounds have a serious disadvantage. That is, aromatic molecules demonstrate poor detection capacity because they easily aggregate and cause fluorescence quenching. The silicon-cored structure can improve the fluorescence efficiency of aromatic compounds in organic lightemitting devices.^{27,33–38} Silicon-cored aromatic derivatives have several advantages over common aromatic compounds. These advantages include well-defined structures, higher glass transition temperatures, thermal stability, and better fluorescent properties in solid films. Organic silicon compounds have been synthesized and applied as fluorescent probes. Therefore, silicon-cored compounds can be used in detecting applications to solve the fluorescence quenching problem of aromatic compounds.



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Accordingly, this study designed and synthesized two fluoranthene derivatives, nonsilicon-cored 7,10-diphenylfluoranthene (DF) and silicon-cored bis(7,10-diphenylfluoranthene-8-yl)diphenylsilane (BDS). Fluoranthene is an excellent fluorescent material that has attracted increasing attention in recent years. Wudl reported that modifying a fluoranthene derivative with a phenyl group can effectively reduce fluorescence quenching.39 Meanwhile, Patil et al. detected nitroaromatics using fluoranthene derivatives.40 These derivatives exhibit excellent detection capability for nitroaromatic compounds. In the present report, we added a silicon atom into a fluoranthene derivative to form a tetrahedral structure. We previously investigated the optical properties of the silicon-cored derivative in solution and the solid state.41 Our results showed that the silicon-cored derivative exhibits better fluorescent properties than diphenylfluoranthene. In the present study, we explored the fluorescence quenching behavior of the silicon-cored derivative toward nitrobenzene and *m*-dinitrobenzene to further elucidate its fluorescent properties and applications. We hope that this method can retain the excellent fluorescent properties of fluoranthene while improving its thermodynamic properties, sensitivity, and response time in detecting nitroaromatic compounds. The thermodynamic properties and fluorescence quenching behavior of the derivatives with nitroaromatic compounds were also investigated. Compared with DF, BDS exhibited better thermal stability and detection capability. Both showed a special curve relationship between their emission intensity and nitroaromatic compound concentration, and were sensitive to the presence of nitroaromatic compounds. BDS showed a lower detection limit to nitroaromatic compounds than DF. Compared with DF, BDS exhibited better thermal properties, higher sensitivity, and higher quenching efficiency in detecting nitrobenzene and m-dinitrobenzene. Therefore, BDS has great potential in detecting nitroaromatic compounds.

Experimental section

Materials and methods

Dichloromethane and ethanol were purchased from Tianjin Fuyu Chemical Engineering Company. Acenaphthenequinone and 1,3-diphenyl-propan-2-one were purchased from Shanghai Chemical Reagent Company.

¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer. Elemental analyses (C, H and N) were carried out on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. The UV-visible spectra were recorded with a TU-1901 double-beam UV-visible spectrophotometer. The fluorescence spectra were recorded with a Hitachi F-7000 spectrophotometer. Thermal gravimetric analyses (TGA) were performed with a Mettler Toledo SDTA-854 TGA system in nitrogen at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurement was performed with a Mettler Toledo DSC-822 system in nitrogen at a heating rate of 10 °C min⁻¹. The fluoranthene derivatives were synthesized *via* the Knoevenagel/Diels–Alder method from acenaphthenequinone and 1,3-diphenylpropan-2-one. The synthesis routes are shown in Scheme 1.

1. 7,9-Diphenyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one (DCA). synthesized from acenaphthenequinone and was DCA 1,3-diphenylpropan-2-one according to a literature method.⁴² A three-necked 250 mL round bottom flask was equipped with a reflux condenser and ethanol (60 mL). Then acenaphthenequinone (5.47 g, 0.03 mol) and 1,3-diphenylpropan-2-one (6.3 g, 0.03 mol) were added, heated and stirred. When the solution mixture began to reflux, ethanol solution (5 mL) of KOH (0.8 g) was added dropwise to the slightly boiling solution via a drop funnel. The reaction mixture immediately became black and formed a black precipitate. After the dropwise addition of the ethanol solution, the reaction was allowed to continue for 2 h. The above solution was cooled to room temperature, and was filtered to obtain the crude product. Then the product was washed with ethanol several times. The pure product was obtained as a purpleblack solid powder with a yield of 90% (10.7 g). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.08 (d, 2H), 7.86 (m, 6H), 7.61 (dd, 2H), 7.54 (dd, 4H), 7.42 (t, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 154.2, 132.1, 131.5, 131.4, 129.0, 128.6, 128.3, 127.8, 121.7, 120.9.

2. (7,10-Diphenylfluoranthen-8-yl)trimethylsilane (DFTS). Under an argon atmosphere, 1.48 g (15 mmol) ethynyltrimethylsilane and 3.44 g (10 mmol) DCA were dissolved in 30 mL xylene in a sealed stainless steel reactor, and the reaction mixture was heated at 230 °C for 20 h. Then xylene was removed under reduced pressure. The crude product was precipitated in a large amount of methanol and purified by silica gel column chromatography. Finally, the pure product was obtained as a yellow solid powder with a yield of 55% (2.32 g). ¹H NMR (DMSO, 400 MHz, ppm): δ 0.02 (s, 9H), 6.30 (d, 1H), 7.35 (t, 1H), 7.46–7.68 (m, 13H), 7.82–7.89 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 1.07 (Si–CH3), 123.2, 123.3, 127.3, 127.8, 128.3, 128.5, 128.7, 129.1, 129.3, 129.4, 129.9, 130.1, 132.4, 135.5, 135.6, 136.4, 136.6, 137.0, 137.2, 138.7, 140.8, 141.4.

3. 7,10-Diphenylfluoranthene (DF). 2.00 g (4.6 mmol) **DFTS** and concentrated hydrochloric acid (4 mL) were dissolved in 30 mL THF solution. The mixture was refluxed for 10 h. And then the solvent was removed. The crude product was precipitated in



Scheme 1 The synthesis routes towards the fluoranthene derivatives.

Paper

a large amount of methanol and purified by silica gel column chromatography. Finally, the pure product was obtained as a yellow crystal with a yield of 90% (1.46 g). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.24 (d, 2H), 7.29 (s, 2H), 7.37 (t, 2H), 7.52–7.60 (m, 6H), 7.67 (m, 4H), 7.78 (d, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 123.0, 126.7, 127.6, 127.8, 128.7, 129.1, 129.8, 132.8, 136.3, 136.8, 138.0, 141.0. Anal. calcd for C₂₈H₁₈: C 94.88%, H 5.12%. Found: C 94.83%, H 5.17%.

4. Diethynyldiphenylsilane (DDS). Under an argon atmosphere, 2.4 g (100 mmol) magnesium powder and anhydrous THF (20 mL) were added to a 100 mL three-necked round bottle. Under stirring, THF solution (25 mL) of 10.9 g (100 mmol) ethyl bromide was slowly added dropwise into the flask. After all the magnesium powder disappeared, the reaction mixture was allowed to boil for 2 h. After cooling to room temperature, the bromoethane Grignard reagent was obtained.

First, the acetylene gas, which was cooled at -78 °C, was bubbled into dry 150 mL THF for 1 h to obtain the acetylene saturated solution. Then the bromoethane Grignard reagent was added into the acetylene saturated solution. In this process, acetylene was always kept bubbling into the mixture for 0.5 h. The reaction was kept for 2 h after the dropping of the bromoethane Grignard reagent was completed. Then the acetylene Grignard reagent was obtained. A 500 mL three-necked, round bottom flask was equipped with a reflux condenser and a stirrer. The flask was charged with the acetylene Grignard reagent obtained in the last step.

In an ice water bath, 20.26 g (80 mmol) diphenyldichlorosilane and THF (30 mL) were added drop-wise to the well stirred reaction mixture over 0.5 h. It was quenched by the addition of methanol (10 mL). The organic layer was washed with water, dried with anhydrous MgSO₄, filtered, and concentrated at reduced pressure. The product was purified by silica gel column chromatography. The pure product was obtained as a straw yellow crystal with a yield of 70% (13 g) and petroleum ether as an eluent. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.75 (m, 4H, ArH), 7.26–7.50 (m, 6H, ArH), 2.75 (s, 2H, –C=CH).

5. Bis(7,10-diphenylfluoranthen-8-yl)diphenylsilane (BDS). Under an argon atmosphere, a three-necked 100 mL round bottom flask was equipped with a reflux condenser and a thermometer and charged with 306.5 mg (0.86 mmol) 7,9diphenyl-8H-cyclopenta[a]acenaphthylen-8-one and 100 mg (0.43 mmol) diethynyldiphenylsilane. A minimal amount (7 mL) of diphenyl ether was added. The reaction mixture was heated at 230 °C for 8 h with vigorous stirring, with a color of heterogeneous solution varying from purple-black to homogeneous and transparent black-red. The reaction mixture was cooled for a while and poured into a large amount of methanol (150 mL) to precipitate the crude solid product, which was obtained by filtration and washed with copious amounts of methanol. What is more, the above steps were repeated several times and finally the pure product was obtained as a canary yellow solid powder with a yield of 30% (114 mg). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 6.04 (d, 2H), 6.94 (d, 8H), 7.08 (t, 4H), 7.15-7.25 (m, 10H), 7.32-7.40 (m, 4H), 7.50-7.67 (m, 6H), 7.64-7.68 (m, 8H), 7.75 (d, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 123.19, 123.42, 126.27, 126.96, 127.14, 127.30, 127.41, 127.61, 127.69, 127.96, 128.28,

128.56, 129.26, 129.66, 130.06, 132.87, 133.88, 135.96, 135.99, 136.45, 136.57, 136.85, 137.55, 138.39, 139.00, 140.56, 141.13, 144.43. ²⁹Si NMR (CDCl₃, 80 MHz, ppm): δ –14.71. Anal. calcd for C₆₈H₄₄Si: C 91.85%, H 4.99%. Found: C 91.24%, H 4.87%.

Results and discussion

Optical properties

The absorption spectra of the two compounds in THF solution are shown in Fig. 1(a). **DF** exhibited two absorption peaks centered at 371 and 326 nm, originating from the π - π * transitions. The silicon-cored fluoranthene derivative showed a similar absorption spectrum to **DF**. **BDS** exhibited two absorption peaks centered at 372 and 328 nm, and only showed a slight bathochromic shift compared with **DF**. In other words, the silicon-cored structure only slightly influenced the conjugated degree and absorption spectra of diphenylfluoranthene.

Fig. 1(b) shows the fluorescent emission spectra of **DF** and **BDS** in THF solution and in the solid thin film. The maximum emission peaks of **DF** and **BDS** appeared at 446 and 453 nm in solution, respectively. The emission spectra of the two compounds were similar. The fluorescence of **BDS** showed only a slight bathochromic shift to **DF**. This phenomenon also indicated that the silicon-cored structure only slightly influenced the conjugation degree of diphenylfluoranthene. However, the emission spectra of the silicon-cored derivative showed shorter wavelengths of red shift than that of diphenylfluoranthene. It indicated that the silicon-cored structure could prevent the close-packing of molecules and thus effectively restrain the intermolecular interactions.

Thermal properties

The thermal properties of **DF** and **BDS** were studied by both differential scanning calorimetry and thermogravimetric analysis (Fig. 2 and Table 1).

Table 1 shows that the glass transition temperature (T_g) of **BDS** was 250 °C, which was 190 °C higher than that of **DF**. This result can be attributed to the molecular tetrahedral configuration formed by the silicon-cored structure. Meanwhile, the melting temperatures (T_m) of **DF** and **BDS** were 165 °C and 350 °C, respectively. The better stability of **BDS** than **DF** when they were prepared into solid films can be attributed to the higher T_g and T_m of the former than the latter. **BDS** also showed higher



Fig. 1 Absorption and emission spectra of DF and BDS.



Fig. 2 The differential thermogravimetric curves of DF and BDS.

Table 1 Thermal properties of DF and BDS; T_g : glass transition; T_m : melting temperature; T_d : decomposition temperature

Compound	$T_{ m g} \left(^{\circ} { m C} \right)$	$T_{\rm m}$ (°C)	$T_{\rm d}$ (°C)
DF	60	165	298
BDS	250	350	444

decomposition temperatures (corresponding to 5% weight loss) than **DF**. This result may be attributed to the H of **BDS** in the C-8 position.⁴¹

Fluorescence quenching of nitroaromatic compounds in solution

The fluorescence spectra of **DF** and **BDS** immersed in different organic solvents, such as acetone, methanol, ethanol, acetonitrile, DMF, CH_2Cl_2 , $CHCl_3$, and nitrobenzene, were tested. As shown in Fig. 3(a) and (b) for **DF** and **BDS**, all the emission spectra of **DF** and **BDS** revealed linker-based emission with the same broad maximum at 446 and 453 nm, respectively. A significant fluorescence quenching effect was observed for nitrobenzene (Fig. 3).

This phenomenon can be attributed to the electron transfer from the benzene rings of **DF** and **BDS** to electron-deficient nitrobenzene and their interactions with nitrobenzene molecules. These results demonstrate that **DF** and **BDS** exhibit high selectivity for nitrobenzene compared with other small molecules. Therefore, **DF** and **BDS** can be used as fluorescent sensors for nitrobenzene detection.

To examine the sensing ability and monitor the fluorescent response of **DF** and **BDS** toward nitrobenzene, the two compounds were dispersed in THF solution with gradually increasing nitrobenzene content.

As shown in Fig. 4(a) and (b) for **DF** and **BDS**, the emission intensity gradually decreased with increasing nitrobenzene



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Fig. 4 The fluorescent emission spectra of DF (20 μ M) and BDS (10 μ M) (upon addition of nitrobenzene in THF solution and the obtained Stern–Volmer curve with nitrobenzene (0–1500 ppm)).

content. In addition, fluorescence quenching was obvious. When the nitrobenzene content was up to 1500 ppm, the fluorescence quenching efficiencies of **DF** and **BDS** were 71% and 80%, respectively.

Interestingly, the I_0/I -C plots of **DF** and **BDS** swiftly curved upward, suggesting a super amplification effect. Therefore, **DF** and **BDS** had high fluorescence sensitivity for nitrobenzene detection, with detection limits of 100 and 50 ppm, respectively. When the nitrobenzene content was up to 200 ppm, the fluorescence quenching efficiencies of **DF** and **BDS** were 20% and 31.19%, respectively.

The difference in detection degree and fluorescence quenching efficiency of the two compounds may be attributed to their molecular structures. **DF** showed a plane molecular structure with two phenyl groups twisting out of the core, whereas **BDS** possessed a "V" structure that connects two 7,10-diphenylfluoranthene groups.⁴¹ The two 7,10-diphenylfluoranthene units were significantly twisted against each other because of the tetrahedral environment of the central silicon core, resulting in a noncoplanar configuration.⁴¹ This special tetrahedral structure enhanced the π - π interaction between **BDS** and nitrobenzene. As shown in Fig. 5, one nitrobenzene molecule can intermolecularly interact with one **DF** molecule because of the plane structure. However, one nitrobenzene molecule can simultaneously influence two fluorescent groups because of the "V" structure of **BDS**.

We further examined the detection capabilities of **DF** and **BDS** to *m*-dinitrobenzene. The results are shown in Fig. 6(a) and (b) for **DF** and **BDS**. The $I_0/I-C$ plots of the two compounds swiftly curved upward, suggesting a super amplification effect. This trend was similar to that observed in nitrobenzene detection. Furthermore, the fluorescence quenching response of **BDS** was observed at a low *m*-dinitrobenzene concentration of 10



Fig. 3 The fluorescent emission spectra of DF and BDS in different solvents (DMF = N,N-dimethylformamide).



Fig. 5 Diagram of DF and BDS with nitrobenzene producing interaction.



Fig. 6 The fluorescent emission spectra of DF (20 μ M) and BDS (10 μ M) upon addition of *m*-dinitrobenzene in THF solution and the obtained Stern–Volmer curve with *m*-dinitrobenzene (0–500 ppm) (*m*-DNB = *m*-dinitrobenzene).

ppm. The silicon-cored derivative had a lower detection degree than the nonsilicon-cored one. When the *m*-dinitrobenzene content was up to 500 ppm, the fluorescence quenching efficiencies of **DF** and **BDS** were 58% and 68%, respectively. The silicon-cored derivative also exhibits excellent sensing properties for compounds that contain multiple nitro groups. Therefore, **BDS** had higher sensitivity and higher quenching efficiency in detecting *m*-dinitrobenzene than **DF**.

In summary, **DF** and **BDS** showed excellent detection capabilities for nitroaromatic compounds. **BDS** exhibited lower detection limit and higher sensitivity than **DF**, suggesting the better properties and development potential of the former than the latter.

Fluorescence quenching of nitrobenzene vapor in the solid state

We further investigated the nitrobenzene detection behavior of **DF** and **BDS** in thin films.

A solid-state fluorescence quenching experiment was performed toward nitrobenzene vapor using thin films of **DF** and **BDS**. The films were prepared by dropwise addition of the THF solutions of **DF** and **BDS** onto TLC strips, followed by vacuum drying.

Then, the TLC strips were placed in a sealed bottle filled with saturated nitrobenzene vapor. As shown in Fig. 7, the thin films of both DF and BDS exhibited strong fluorescence without being exposed to nitrobenzene vapor. Exposure of the DF thin film to saturated nitrobenzene vapor for 120 s partly quenched the fluorescence. However, weak fluorescence was still observed. When the exposure time was prolonged to 180 s, the fluorescence was completely quenched. However, the BDS thin film showed a different phenomenon. The fluorescence of the BDS thin film was completely quenched after exposure to saturated nitrobenzene vapor for 120 s. This result indicated that the BDS thin film was more efficient and faster in responding to nitrobenzene vapor compared with DF. Patil et al. also reported that exposing the thin films of fluoranthene derivatives to saturated PA vapor for 210 s decreases the fluorescence intensity by 91%.40 This result may be attributed to the special tetrahedral structure of BDS molecules that complicates their aggregation. The nitrobenzene vapor was rapidly diffused into the BDS film. Meanwhile, the low sensitivity of the DF thin film can be attributed to the easy aggregation of DF molecules and the poor



Fig. 7 Photographs of the fluorescence quenching (under 365 nm UV light) of the thin film of **DF** (up) and **BDS** (below) upon exposure to the saturated vapor of nitrobenzene at different times for the visual detection. (a) Without exposure to nitrobenzene vapor; (b) exposure to nitrobenzene vapor for 120 s; (c) exposure to nitrobenzene vapor for 180 s.

diffusion of nitrobenzene vapor into the molecules. The presence of $T_{\rm g}$ indicated the amorphous fractions of the solid thin film. The $T_{\rm g}$ values of **DF** and **BDS** were 60 °C and 250 °C, respectively. The special tetrahedral structure of **BDS** can resist crystallization and form an amorphous thin film through steric hindrance. The reduction in fluorescence intensity can be ascribed to the charge transfer between electron-deficient nitrobenzene and electron-rich fluorescent molecules, producing π - π interactions. Energy transfer is a long-range process, whereas charge transfer is a short-range one.¹⁹ Therefore, the response time of the fluorescence probe for nitrobenzene detection was very short. Overall, the **BDS** thin film exhibited shorter fluorescence quenching response time toward nitroaromatics compared with the **DF** thin film.

Conclusions

In this study, we synthesized nonsilicon-cored DF and siliconcored **BDS**. The thermal properties and fluorescence quenching behavior of these derivatives with nitroaromatic compounds were investigated. Aside from its better thermal properties, BDS also had higher sensitivity and higher quenching rate in detecting nitroaromatic compounds than DF. Fluorescence quenching can be attributed to the electron transfer from the benzene rings of DF and BDS to the electron-deficient nitrobenzene and their interactions with nitrobenzene molecules. The detection limits of BDS toward nitrobenzene and m-dinitrobenzene were 50 and 10 ppm, respectively. The special tetrahedral structure of BDS enhanced the π - π interaction. Furthermore, the Stern-Volmer plot curved upward. Thus, BDS has great potential in detecting explosives. This work may serve as a basis for designing new organic materials with great efficiency and sensitivity in fluorescence detection. The design and synthesis of high-performance fluorescent probes are still in progress.

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