Silole-Core Phenylacetylene Dendrimers and Their Application in Detecting Picric Acid

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Silole-core phenylacetylene dendrimers were designed and synthesized, among them, the model compound (n = 0) and the first generation of the dendrimer (n = 1) were obtained by the reaction of 2,5dibromosilole with corresponding terminal alkynes, the second generation of the dendrimers (n = 2)was synthesized from 2,5-diiodosilole. These compounds indicated the absorptions of both phenylacetylene dendrons (250–350 nm) and silole core (400–500 nm). The first generation displayed efficient energy transfer from phenylacetylene dendrons to silole core, whose energy transfer efficiency was as high as 80%. These compounds were used as chemical sensors to probe explosive, for picric acid (PA), the Stern–Volmer constants of model compound and the first generation are 7120 and 5490 M^{-1} , respectively.

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INTRODUCTION

Siloles possess a unique silacyclopentadiene core structure and exhibit excellent photophysical and electronic properties. Some siloles have special and useful aggregation-induced enhanced emission (AIE) effect [1-2]. The characteristics of siloles allow them to function as organic electroluminescent devices, organic solar cells, pH sensors, ion monitors, and explosive detectors. Siloles may be used as efficient chemical sensors for nitroaromatic explosives because of the Lewis acid/base interactions between siloles and nitroaromatic explosives. And reliable detection of trace explosive materials becomes a focal point in the fields of humanitarian demining and security. On the other hand, phenylacetylene dendrimer is one of the ideal photon-harvesting systems. The stiff dendrimers exhibit high-energy transfer efficiency, which will be of potential applications in fabricating OLEDs [4,5], sensors [6-2], and membranes [9–2]. To our knowledge, phenylacetylene dendrimer with silole as the core, has not been reported.

In this work, we designed and synthesized a kind of silole-core dendrimers with rigid phenylacetylene dendrons and found that the energy transfer from the dendrons to the silole core occurred within the dendrimers. Their application in detecting picric acid was investigated as well.

RESULTS AND DISCUSSION

Synthesis. Phenylacetylene monodendrons **3c** and **4c** were synthesized analogous to the ref. 12 by repeating Sonogashira coupling (Scheme 1).

We selected 1,3,5-tribromobenzene as a key monomer for the synthesis of phenylacetylene monodendrons instead of 3',5'-dibromo-2-phenyl-1-(trimethylsilyl)acetylene. To improve the yields of **3a** and **4a**, we dropwised 2 equivmolar terminal alkyne to 1,3,5-tribromobenzene.

Scheme 1. Synthesis of phenylacetylene monodendrons. Reagents and conditions: (i) $Pd(PPh_3)_4$, CuI, Et₃N, Ar, 80°C, 5 h; (ii) 2-methylbut-3-yn-2-ol, $Pd(PPh_3)_4$, CuI, Et₃N, Ar, 80°C, 5 h; (iii) KOH, toluene, Ar, reflux, 3h; (iv) 2, $Pd(PPh_3)_4$, CuI, Et₃N, toluene, Ar, 90°C, 8 h; (v) 2-methylbut-3-yn-2-ol, $Pd(PPh_3)_4$, CuI, Et₃N, toluene, Ar, 90°C, 6 h.



During the reaction, some monosubstituted products were formed. However, these monosubstituted products could further react with 1 equivmolar terminal alkyne. During the reaction of 3c with 2, diacetylene would form due to Glaser coupling reaction. Rigorous de-oxy-

gen was necessary to suppress the formation of such diacetylene byproduct. Because the solubility of 4a and 4b was poor in Et_3N , toluene was added as cosolvent in Sonogashira coupling reaction. However, **6–8** are soluble fairly in common solvents such as CH_2Cl_2 .



Scheme 2. Synthesis of silole-core phenylacetylene dendrimers.

2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole 5a was synthesized according to the literature [13]. The parent compound **6** and silole-core phenylacetylene dendrimers **7–8** were synthesized by Negishi coupling (Scheme 2). Comparing to Sonogashira coupling system, diacetylene byproduct was not formed because of the absence of CuI. Dendrimers **6** and **7** were obtained conveniently with moderate yields (53 and 67%, respectively).

We tried to synthesize dendrimer **8** by using the same synthetic procedure as **6** and **7**; however, no products formed even if the reaction time was extended to longer than 48 h. It might imply that molecule **4c** was so large that its reactivity not enough to react with 2,5-dibromosilole. Therefore, we used 2,5-diiodosilole instead of 2,5-diiodosilole by the reaction of corresponding dilithiosilole with 1,2-diiodoethane. Pagenkopf *et al.* [13] had synthesized chloroiodosilole by the reaction of 2-chloro-5-metallosilole with I₂, they found that chloroiodosilole was very unstable and should be used in the next step without purifi-

cation. We speculate that 2,5-diiodosilole is also unstable, therefore, we synthesized 2,5-diiodosilole analogous to dibromosilole except using I₂ instead of NBS, and the resulting mixture was reacted with alkyne **4c** directly because of the instability of 2,5-diodosilole. In the beginning, the reaction was conducted at 40°C for 12 h; it was found that no products formed during the reaction. So the reaction was carried out at 65°C. After reaction for 12 h, some products appeared. Dendrimer **8** was obtained after separation from the reaction mixture. However, **8** was not so stable that decomposed slowly even keeping in dark. When exposed to ultraviolet light, it would be decomposed rapidly. The yield of **8** was extremely low (<10%). Perhaps **8** would decompose once it formed in the reaction, and this was confirmed by TLC experiments in the later.

Absorption and fluorescence spectra. The photophysical properties of silole-core phenylacetylene dendrimers 7-8 and their parent compound 6 were studied by UV-vis and fluorescence spectroscopies. Their photophysical data in dichloromethane are summarized in

Compounds	Absorption ^a		Fluorescence ^a	
	λ_{max} (nm)	$\epsilon (10^4 \text{ cm}^{-1} M^{-1})$	$\lambda_{FLmax} (nm)^b$	Φ_{ET} (%)
6	269, 308, 435	2.40, 1.36, 0.98	362, 521	_c
7	292, 308, 431	3.94, 3.27, 1.10	361, 520	80
8	293, 310, 434	13.83, 13.75, 1.54	370, 501	_c

 Table 1

 Photophysical properties of silole-core dendrimers 6–8.

^a In CH₂Cl₂.

^bExcited at 310 nm.

^c Not available.

Table 1, the absorption and fluorescence spectra of **7–8** are shown in Figures 1 and 2, respectively. In Figure 1, the absorptions between 250 and 350 nm are due to the phenylacetylene monodendrons, the absorptions between 350 and 500 nm are due to the silole core. From the absorption spectra, we find that dendrimer **8** possesses the absorption of phenylacetylene monodendrons and silole core. The molar extinction coefficient of phenylacetylene monodendrons. The change of the molar extinction coefficient of silole group is very small, which is coincide with their structures.

The emission spectra of **6** and **7** excited at 310 nm are almost the same. Both compounds display an intense emission around 520 nm, which could be attributed to the silole core and negligible emission around 360 nm, which could be attributed to the phenylacetylene dendrons. For the intensity, these compounds have no apparent AIE effect. Obviously, there exists efficient energy transfer from the phenylacetylene dendrons to the silole core in dendrimer **7** and the parent compound **6**. The energy transfer efficiency (Φ_{ET}) of the model compound **6** was not estimated analogous to the literature [15,16].



Figure 1. UV–vis absorption spectra of 6–8 in CH₂Cl₂, the spectra are normalized to 1.0×10^{-5} M concentration.

The energy transfer efficiency was estimated by a comparison of the absorption spectra and the excitation spectra of 7 by monitoring the emission of silole core (520 nm). The $\Phi_{\rm ET}$ of 7 was as high as 80%, which was in the range of $\Phi_{\rm ET}$ values (54–95%) of peryleneterminated phenylacetylene dendrimers reported by Moore et al. [16] However, in the emission spectra of 8 excited at 310 nm, we find intense emission around 370 nm and moderate emission of silole core (\sim 500 nm). This clearly indicates that the energy transfer occurred within dendrimer 8. However, due to the poor stability of 8, the energy transfer efficiency was not estimated. Moore et al. have reported that the emission around 370 nm was due to the phenylacetylene dendrons [16]. Hence, from the absorption and emission spectra of dendrimer 8, we suppose that the emission around 370 nm is due to the product formed by the decomposition of silole ring in dendrimer 8. The huge rigid phenylacetylene dendrons at 2,5-positions of silole ring probably is the main cause of the instability of 8. The steric effect between the two phenylacetylene dendrons or phenylacetylene dendrons and phenyls at 3,4-positions probably was too strong to sustain the silole ring.



Figure 2. Fluorescence spectra of 6-8 in CH₂Cl₂ excited at 310 nm, the fluorescence intensities were normalized in the molar concentration.



Figure 3. Fluorescence quenching of 6 in CH₂Cl₂ by picric acid (PA); [6] = $1 \times 10^{-5}M$, $\lambda_{ex} = 310$ nm.

Explosives detection. Because of the commercial unavailability of explosives such as 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT), we used picric acid (PA; a derivative of TNT). We investigated the photoluminescence (PL) responses of 6 and 7 to PA by adding PA solutions successively. Figures 3 and 4 showed fluorescence quenching of 6 and 7 in CH_2Cl_2 solution by PA, respectively. The fluorescence quenching effect by PA is significant. For both 6 and 7, the detection limit reaches as low as 1 µM. Hence, the larger phenylacetylene dendrons at 2,5-positions have no effect on the detection limit, because that they have little block effect on the detection sites (silicon atoms). Trogler et al. have reported that less steric encumbrace surrounding silicon atoms, which caused by the substituent at 1,1-postions could lead to better detection limits





Figure 5. Stern–Volmer plots for fluorescence quenching of 6 and 7 by PA.

[17]. The quenching constants are determined by the Stern–Volmer equation:

$$I_0/I - 1 = K_{\rm sv}[A]$$

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

Figure 5 shows Stern–Volmer plots for fluorescence quenching of 6 and 7 by PA. The Stern–Volmer constants of 6 and 7 are 7120 and $5490M^{-1}$, respectively. Dendrimer 8 was not investigated because of the poor stability.

CONCLUSIONS

Silole-core phenylacetylene dendrimers were synthesized. The parent compound 6 and dendrimer 7 were synthesized by the reaction of 2,5-dibromosilole with corresponding terminal alkynes, the second generation 8 was obtained by the reaction of more reactive 2,5-diiodosilole with corresponding alkyne. Dendrimer 8 was unstable. Their photophysical properties were investigated. All of the compounds possess the absorption of phenylacetylene dendrons (250-350 nm) and silole core (400-500 nm). When excited at 310 nm, compounds 6 and 7 mainly display an emission at about 520 nm from the silole core. The energy transfer efficiency of 7 is as high as 80%. Dendrimer 8 displays an intense emission at about 370 nm, which probably caused by the decomposed product. Their use in explosives detection was investigated. When quenched by PA, the Stern-Volmer constants of 6 and 7 are 7120 and $5490M^{-1}$, respectively.

EXPERIMENTAL

Figure 4. Fluorescence quenching of 7 in CH₂Cl₂ by picric acid (PA); $[7] = 1 \times 10^{-5} M$, $\lambda_{ex} = 310$ nm

Instruments and materials. ¹H-NMR spectra were obtained on a Bruker 500 or 400 MHz spectrometer. Mass spectra were recorded using an LCQ Advantage mass spectrometer. Absorption spectra were measured with a CARY 100 Conc UV–vis spectrophotometer. Fluorescence spectra were recorded with a CARY Eclipse fluorescence spectrophotometer in a 1-cm quartz cell. All reagents were purchased from commercial sources and distilled or dried when necessary using the standard procedures. All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification unless mentioned below. Triethylamine was distilled from calcium hydride. Reactions were carried out under an inert atmosphere (dry argon) when necessary.

Synthesis. The synthetic route is shown in Schemes 1 and 2.

4,4'-(5-Bromo-1,3-phenylene)bis(ethyne-2,1-diyl)bis(tertbutylbenzene) (3a). A flask with 30-mL degassed Et₃N was charged with compound 2 (1.5 g, 4.8 mmol, 1 eq.), CuI (18 mg, 0.095 mmol, 0.02 eq.) and Pd(PPh₃)₄ (110 mg, 0.095 mmol, 0.02 eq.) under a stream of Ar. Compound 1 (1.65 g, 10.5 mmol, 2.2 eq.) dissolved in 10-mL degassed Et₃N was dropwised more than 1 h at 80°C. After that, the solution was stirred for 4 h. Then, the mixture was diluted with dichloromethane, washed with water, dried by MgSO₄, and filtered. The concentrated product was purified by flash chromatography, eluting with petroleum ether to give **3a** as white powder (1.452 g, 64.4%). ¹H NMR (CDCl₃, 500 MHz) δ : 1.35 (s, 18 H), 7.39 (d, J = 8.3 Hz, 4 H), 7.46 (d, J = 8.3 Hz, 4 H), 7.61 (s, 3H). MS(EI): m/z 468.1 [M]⁺ (calcd for C₃₀H₂₉Br 468.1).

4-(3,5-Bis((4-tert-butylphenyl)ethynyl)phenyl)-2-methylbut-3yn-2-ol (3b). A flask with 20-mL degassed Et₃N was charged with compound **3a** (357 mg, 0.76 mmol, 1 eq.), 2-methylbut-3-yn-2-ol (128 mg, 1.52 mmol, 2 eq.), CuI (3 mg, 0.015 mmol, 0.02 eq.), and Pd(PPh₃)₄ (18 mg, 0.015 mmol, 0.02 eq.) under a stream of Ar. The solution was stirred about 5 h at 80°C. Then the mixture was diluted with dichloromethane, washed with water, dried by MgSO₄, and filtered. The concentrated product was purified by flash chromatography, eluting with 15% EtOAc/petroleum ether to give **3b** as white powder (274 mg, 76.3%). ¹H NMR (CDCl₃, 500 MHz) δ : 1.36 (s, 18 H), 1.64 (s, 6H), 7.39 (d, J = 8.4 Hz, 4 H), 7.46 (d, J = 8.4Hz, 4 H), 7.53 (s, 2H), 7.64 (s, 1 H). MS(EI): m/z 472.3 [M]⁺ (calcd for C₃₅H₃₆O 472.3).

4,4'-(5-Ethynyl-1,3-phenylene)bis(ethyne-2,1-diyl)bis(tertbutylbenzene) (3c). Compound 3b (274 mg, 0.58 mmol), KOH (0.1 g, 1.8 mmol), and 15-mL toluene were added into a flask and protected by Ar. The solution was stirred about 3 h at reflux. Then, the mixture was diluted with dichloromethane, washed with water, dried by MgSO₄, and filtered. The concentrated product was purified by flash chromatography, eluting with petroleum ether to give **3c** as colorless oil (225 mg, 93.6%). ¹H NMR (CDCl₃, 500 MHz) δ : 1.36 (s, 18 H), 3.10 (s, 1 H), 7.38 (d, J = 8.2 Hz, 4 H), 7.46 (d, J = 8.2 Hz, 4 H), 7.58 (s, 2 H), 7.66 (s, 1 H). MS(EI): *m*/z 414.2 [M]⁺ (calcd for C₃₂H₃₀ 414.2).

4,4',4",4"'(5,5'-(5-Bromo-1,3-phenylene)bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl))tetrakis(ethyne-2,1-diyl)tetrakis(tertbutylbenzene) (4a). Compound 4a was synthesized analogous to compound 3a except that toluene was added as cosolvent. The product was purified by flash chromatography, eluting with 10% CH₂Cl₂/petroleum ether to give 4a as white powder (256 mg, 40.8%). ¹H NMR (CDCl₃, 500 MHz) δ : 1.35 (s, 36 H), 7.39 (d, J = 8.3 Hz, 8 H), 7.47 (d, J = 8.3 Hz, 8 H), 7.62–7.68 (m, 9 H). MS(ESI): m/z 981.4 [M+H]⁺ (calcd for C₇₀H₆₁Br + H 981.4). 4-(3,5-Bis((3,5-bis((4-tert-butylphenyl)ethynyl)phenyl)ethynyl)phenyl)-2-methylbut-3-yn-2-ol (4b). Compound 4b was synthesized analogous to compound 3b except that toluene was added as co-solvent. The product was purified by flash chromatography, eluting with 50% CH₂Cl₂/petroleum ether to give 4b as white powder (106 mg, 54%). ¹H NMR (CDCl₃, 500 MHz) δ: 1.36 (s, 36 H), 1.64 (s, 6H), 7.40 (d, J = 8.4 Hz, 8 H), 7.47 (d, J = 8.4 Hz, 8 H), 7.56–7.58 (m, 2 H), 7.62–7.64 (m, 5 H), 7.66–7.68 (m, 2 H). MS(ESI): m/z 985.5 [M+H]⁺ (calcd for C₇₅H₆₈O+H 985.5).

4,4',4",4"',4'''-(5,5'-(5-*Ethynyl-1*,3-*phenylene*)*bis*(*ethyne-2*,1-*diyl*)*bis*(*benzene-5*,3,1-*triyl*))*tetrakis*(*ethyne-2*,1-*diyl*)*tetrakis*(*tertbutylbenzene*) (4c). Compound 4c was synthesized analogous to compound 3c. The concentrated product was purified by flash chromatography, eluting with 10% CH₂Cl₂/petroleum ether to give 4c as white powder (76 mg, 82%). ¹H NMR (CDCl₃, 500 MHz) δ : 1.34 (s, 36 H), 3.15 (s, 1 H), 7.39 (d, J = 8.4 Hz, 8 H), 7.48 (d, J = 8.4 Hz, 8 H), 7.62–7.65 (m, 6 H), 7.66–7.68 (m, 3 H). MS(ESI): *m*/*z* 927.5 [M+H]⁺ (calcd for C₇₂H₆₂+H 927.5).

2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole (5a). Compound **5a** was synthesized according to the literature [13]. yield: 64.0%. m.p. 162–163°C. MS(EI): m/z 419.9 [M]⁺ (calcd for C₁₈H₁₆Br₂Si 420.2).

2,5-Bis((4-tert-butylphenyl)ethynyl)-1,1-dimethyl-3,4-diphenylsilole (6). A flask was charged with 5a (200 mg, 0.478 mmol, 1 eq.), compound 1 (107 mg, 1.05 mmol, 2.2 eq.), ZnCl₂ (40.8 g, 0.3 mmol), Pd(PPh₃)₄ (12 mg, 0.01 mmol), 5-mL Et₃N and 20-mL THF, then degassed by Ar. The resulting mixture was placed in a 65°C oil bath for 7 h. Upon completion, the mixture was diluted with petroleum ether and filtered through a thin pad of silica (50% CH₂Cl₂/petroleum ether). The concentrated product was purified by flash chromatography, eluting with 10% CH₂Cl₃/petroleum ether to give **6** as yellow powder (186 mg, 67.5%).¹H NMR (CDCl₃, 400 MHz) δ : 0.55 (s, 6 H), 1.30 (s, 18 H), 7.20 (s, 10 H), 7.24 (d, J = 8.8 Hz, 4 H), 7.29 (d, J = 8.8 Hz, 4 H). MS(EI): m/z574.3 [M]⁺ (calcd for C₄₂H₄₂Si 574.3).

2,5-Bis((3,5-bis((4-tert-butylphenyl)ethynyl)phenyl)ethynyl)-1,1-dimethyl-3,4-diphenylsilole (7). Compound 7 was synthesized analogous to compound 6. The concentrated product was purified by flash chromatography, eluting with 15% CH₂Cl₂/ petroleum ether to give 7 as yellow powder (84 mg, 53.2%). ¹H NMR (CDCl₃, 400 MHz) δ : 0.52 (s, 6 H), 1.26 (s, 36 H), 7.11–7.18 (m, 10 H), 7.31 (d, J = 8.8 Hz, 12 H), 7.39 (d, J =8.4 Hz, 8 H), 7.49 (t, J = 1.6 Hz, 2H). MS(ESI): *m*/*z* 1125.6 [M+K]⁺ (calcd for C₈₂H₇₄Si+K 1125.6).

2,5-Bis((3,5-bis((4.5-bis((4-tert-butylphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,1-dimethyl-3,4-diphenylsilole (8). Compound **5b** was synthesized analogous to compound **5a** except using I_2 instead of NBS. After concentration, the mixture was used in the next step directly without purification. Compound **4c** (260 mg, 0.28 mmol), mixture with **5b**, ZnCl₂ (10 mg, 0.07 mmol), Pd(PPh₃)₄ (24 mg, 0.02 mmol), 40-mL THF and 8-mL Et₃N were charged in a flask, then degassed by Ar. The resulting mixture was placed in a 40°C oil bath for 12 h. However, when checked by TLC, there were lots of unreacted **4c** and no products and temperature was raised to 65°C. After 12 h, the mixture was diluted with petroleum ether and filtered through a thin pad of silica (50% CH₂Cl₂/petroleum ether). The concentrated product was purified by flash chromatography, eluting with 10% CH₂Cl₂/petroleum ether to give **8** as yellow powder (15 mg). When based on the starting material dimethylbis(phenylethynyl)silane, the yield was below 1%. ¹H NMR (CDCl₃, 400 MHz) δ : 0.53 (s, 6 H), 1.27 (s, 72 H), 7.15 (s, 10 H), 7.32 (d, J = 8.4 Hz, 16 H), 7.41 (d, J = 8.4 Hz, 16 H), 7.52–7.60 (m, 18 H). MS(ESI): *m/z* 2113.9 [M+H]⁺ (calcd for C₁₆₂H₁₃₈Si+H 2113.9).

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