Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

A simple functionalized silica microsphere for fast PETN vapor detection based on fluorescence color changing via catalyzed oxidation process

Yixun Gao[a*,b], Dehai Mu[b], Peng Guan[b,c], Pengran Guo[b*] and Huacan Song[a,b*]

[a] School of Chemical Engineering and Technology, Sun Yat-Sen University, Guangzhou 510275, China. Email: bet.phoenix@163.com; songhc2007@163.com.

[b] Guangdong Provincial Public Laboratory of Analysis and Testing Technology, China National Analytical Center Guangzhou, 100 Xianlie Middle Road, Guangzhou 510070, China. Email: prguo@fenxi.com.cn.

[c] College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, China.

1. Materials and Instruments

All chemicals and solvents were obtained from commercial sources and used as received without further purification. Polyhedral octavinylsilsesquioxane (POVS) was bought from Aladdin Industrial Corporation. UV-Vis absorption and fluorescence analysis were obtained by HORIBA Fluoromax Plus spectrometer with CCD device. IR spectroscopy were carried out by NICOLET iS50 FT-IR spectrometer. Thermogravimetric analysis were carried out by Pyris Diamond TG/DTA, Perkin Elmer. SEM spectroscopy were carried out by S-3700N Ultra Large VP, Hitachi.

2. Synthesis

2.1 Synthesis of SiO microsphere

Solution consisting of NH_4OH (5.6 g, 25%) and water (4.5 g) in 50 ml of EtOH was firstly prepared.

A 1:1 (w/w) ethanol solution of Tetraethoxysilane (TEOS) was added suddenly. During vigorous stirring under 40 ℃ for 30 min, Vinyltriethoxysilane (VTEOS) was added after the reaction mixture started to become turbid (after about 5 min). The amount of VTEOS was so that to obtain samples with different TEOS/VTEOS molar ratios including 2:1, 1:1 and 1:2. Finally, the white precipitates was separated by centrifugation at 3500 rpm for 15 min and then washed with water and EtOH for several times. The final product was dried for 12 h under reduced pressure with a yield of 90-95% depending on TEOS/VTEOS molar ratios used.

2.2 Synthesis of **21F**, **11F** and **12F**

2-bromofluorene in over-dose(300 mg, 1.2 mmol), $Pd_2(dba)_3$ (12 mg, 0.013 mmol) and SiO microsphere of different ratio (0.4 g) were respectively placed in an oven-dried round bottom Schlenk flask. A mixture of freshly dried dioxane (20 mL), N,N-dicyclohexylmethylamine (7.1 mmol, 1.5 mL) and Tri-*tert*-butylphosphine tetrafluoroborate (12 mg, 0.04 mmol) was added to the degassed flask. The reddish brown mixture was stirred at 90 ℃ for 48 hrs. After cooling to room temperature, precipitates was separated by centrifugation at 3500 rpm for 15 min and then washed with THF and EtOH for several times. The final light grey powder was dried for 12 h under reduced pressure with a yield of 87%.

2.3 Synthesis of **PF**

Polyhedral octavinylsilsesquioxane (**POVS**) (0.32 g, 0.5 mmol), 2-bromofluorene (1.25 g, 5 mmol), and $Pd_2(dba)_3$ (0.25 g, 0.28 mmol) were placed in an oven-dried round bottom Schlenk flask. A mixture of freshly dried dioxane (30 mL), N,N-dicyclohexylmethylamine (65 mmol, 14 mL) and Tri-*tert*-butylphosphine tetrafluoroborate (200 mg, 0.66 mmol) was added to the degassed flask. The reddish brown mixture was stirred at 85 ℃ for 48 hrs. After cooling to room temperature, it was then filtered and the filtrate was poured into methanol. The precipitate was collected and purified by column chromatography using dichloromethane and petroleum ether as eluent with a ratio of 1:4. After drying, 0.52 g light yellow powder **PF** was obtained in a yield of 44%. ^1H NMR (500M, $CDCl_3$, ppm): δ 7.670 (s, 8H), 7.529-7.407 (m, 12H), 7.312 (d, 12H, J=7.5 Hz), 6.389-6.164 (m, 10H), 3.738 (t, 6H, 7.5 Hz), 1.846 (t, 6H, 5 Hz), 1.643 (s, 2H). ^{13}C NMR (500M, $CDCl_3$, ppm): 151.18, 149.76, 142.28, 140.63, 137.05, 136.36, 129.10, 127.30, 126.79, 126.37, 122.90, 121.09, 121.00, 119.87, 119.72, 116.36, 71.84, 55.06, 40.41, 29.19, 23.72, 22.57. MALDI-MS calcd. for $C_{120}H_{88}O_{12}Si_8$: 1944.1; found: 1780, 1944.

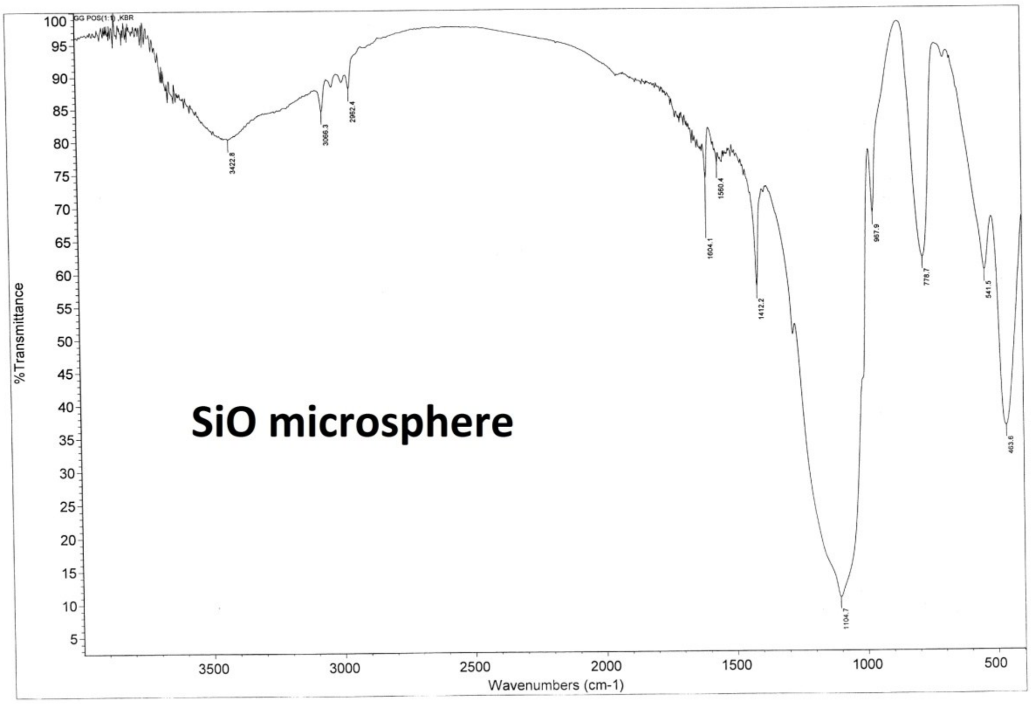
2.4 Synthesis of 2-bromo-9,9'-dihexylfluorene

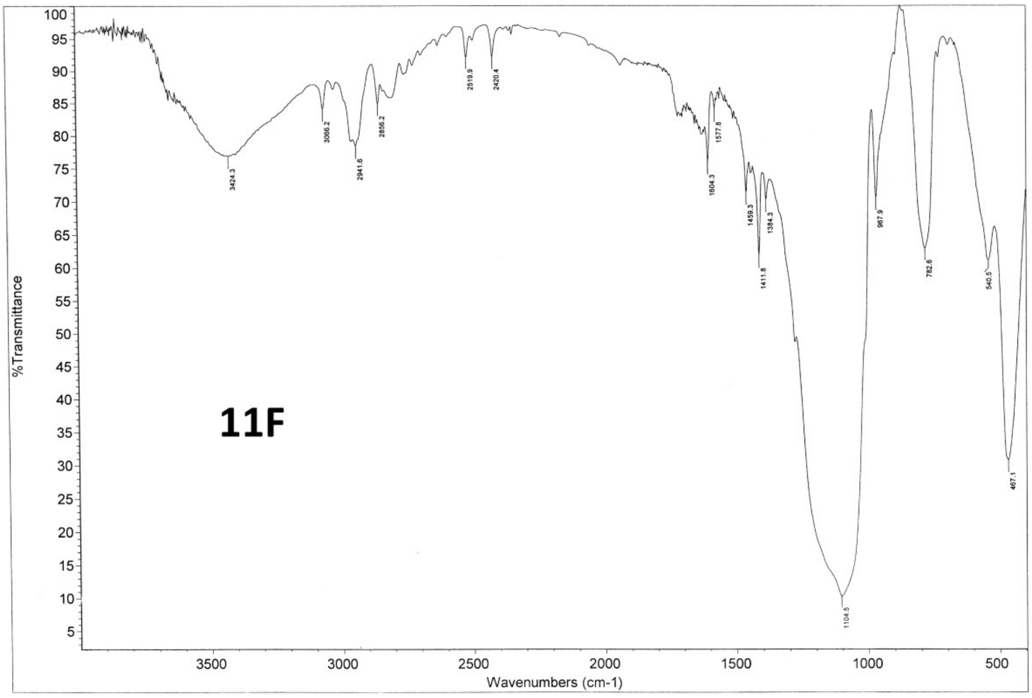
2-bromofluorene (20 mmol, 4.88 g) and tetrabutylammonium bromide (1.25 mmol, 0.4 g) were added to a flask with DMSO (40 mL) and 50% aqueous solution of NaOH (25 mL). Then 1-bromohexane (100 mmol, 16.5 g) was slowly added to the mixture. After stirred at 100 ℃ for 12 hrs, the mixture was extracted by dichloromethane and water to obtain colorless oily 2-bromo-9,9'-dihexylfluorene (4.68 g) in a yield of 57%. ^{1}H NMR (500M, $CDCl_3$, ppm): δ 7.655 (t, 1H, J=7 Hz), 7.544 (d, 1H, J=7.5 Hz), 7.448 (d, 2H, J=5 Hz), 7.311 (s, 3H), 1.925 (q, 4H, J=10 Hz), 1.113-1.025 (m, 12H), 0.761 (t, 6H, J=14 Hz), 0.599 (s, 4H). ^{13}C NMR (500M, $CDCl_3$, ppm): 151.04, 147.16, 141.14, 140.23, 133.11, 130.62, 129.59, 126.78, 122.91, 121.15, 119.93, 52.27, 43.78, 43.69, 31.87, 29.91, 29.17, 24.42, 22.67, 14.06.

2.5 Synthesis of **SiO-DHF** and **SiO-FO**

2-bromo-9,9'-dihexylfluorene and 2-bromo-9-fluorenone in over-dose(500/320 mg, 1.2 mmol), $Pd_2(dba)_3$ (12 mg, 0.013 mmol) and SiO microsphere of different ratio (0.4 g) were respectively placed in oven-dried round bottom Schlenk flasks. A mixture of freshly dried dioxane (20 mL), N,N-dicyclohexylmethylamine (7.1 mmol, 1.5 mL) and Tri-*tert*-butylphosphine tetrafluoroborate (12 mg, 0.04 mmol) was added to the degassed flask. The reddish brown mixture was stirred at 90 ℃ for 48 hrs. After cooling to room temperature, precipitates were separated respectively by centrifugation at 3500 rpm for 15 min and then washed with THF and EtOH for several times. The final light grey powder was dried for 12 h under reduced pressure with a yield of about 85%.

3. IR spectrum


GG POS(1:1) ,KBR
SiO microsphere
%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
3422.8
3066.3
2962.4
1604.1
1560.4
1412.2
1104.7
967.9
778.7
541.5
463.6
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


11F
%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
3424.3
3066.2
2941.6
2856.2
2519.9
2420.4
1604.3
1577.8
1459.3
1384.3
1411.8
1104.5
967.9
782.6
540.5
467.1
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

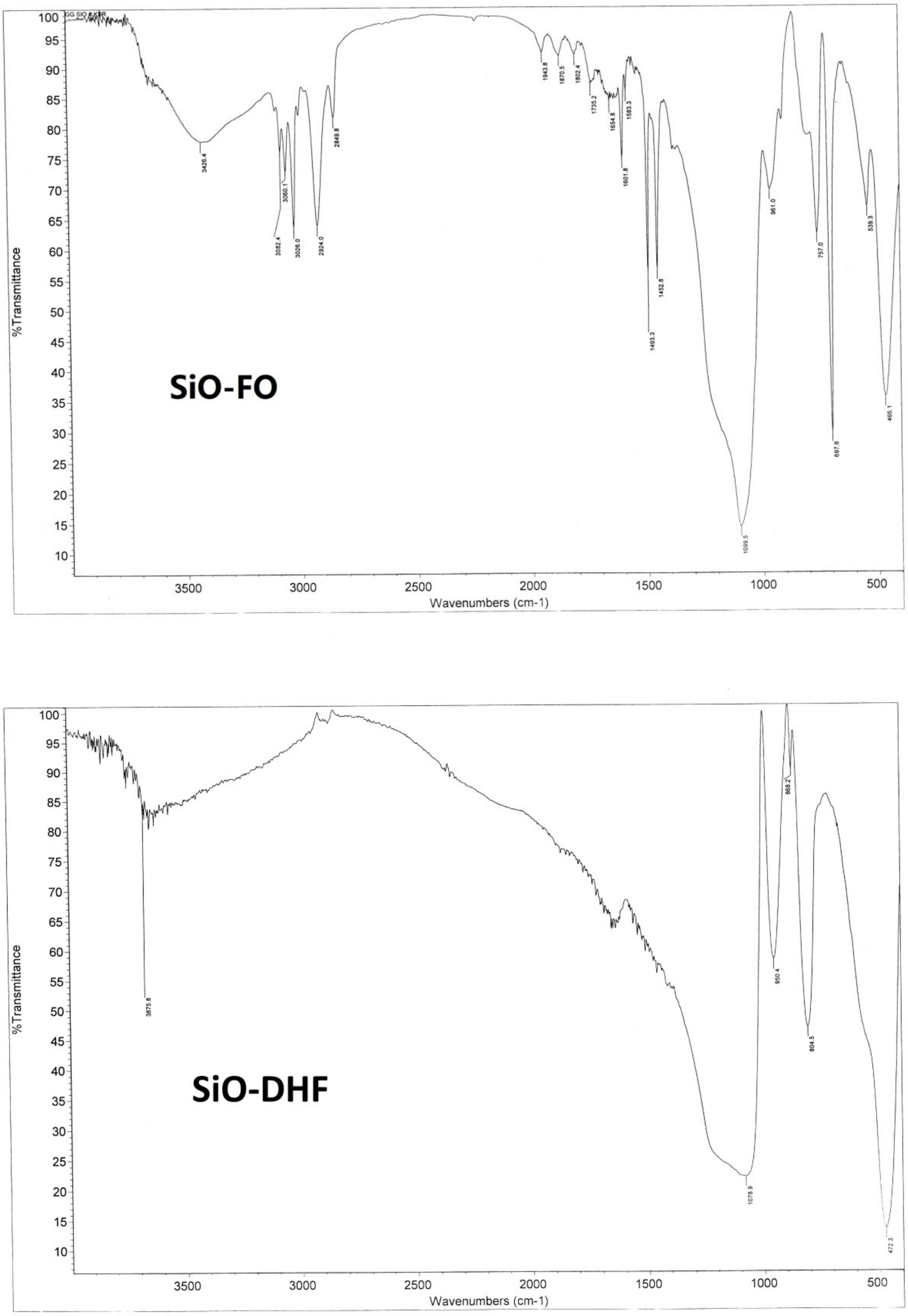


Fig. S1 IR spectrum of SiO microsphere, **11F**, **SiO-FO** and **SiO-FO**.