# Self-Assembly of Novel Fluorescent Silole Derivatives into Different Supramolecular Aggregates: Fibre, Liquid crystal and Monolayer

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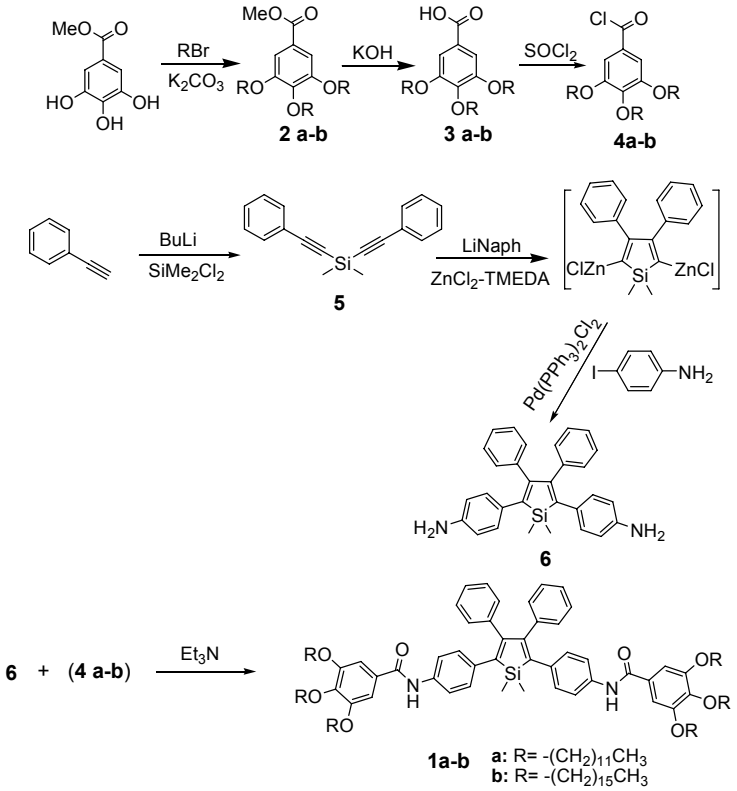



Scheme S1. The synthesis for **1a** and **1b**.

**Experimental Section**

**General methods**

All starting materials were obtained from commercial suppliers and used as received. Reagent grade solvents were dried and purified according to the following procedures: triethylamine ($Et_3N$), methylene chloride (MC) and N,N-dimethylformamide (DMF) were distilled over calcium hydride. THF was dried over sodium metal and distilled.

NMR spectra were recorded on a Bruker DPX 400 (1H NMR 400 MHz and $^{13}C$ NMR 100 MHz) spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a-cyano-4-hydroxycinnamic acid as the matrix on a Perseptive Biosystems Voyager DE-STR MALDI-TOF mass spectrometer. Elementary analysis data were obtained on an Elementar vario EL III (Germany). FT-IR spectra for the samples of xerogels and solid were measured on a Nicolet 5700 spectrometer. The luminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer (the path length of the quartz cell is 1 cm). The emission band-width was 3 nm. UV absorption spectra were obtained using a scinco S-3150 UV–vis spectrophotometer. DSC measurements were conducted by using Q-100 DSC instrument with a heating and cooling rate of $10^oC\ min^{-1}$. Liquid crystal images were recorded on an E600POL (Nikon Corp) with a heating and cooling rate of $3^oC\ min^{-1}$. FE-SEM images of xerogels were obtained using FEI Sirion-100 (Philips) with an accelerating voltage 25.0 KV. The samples were prepared by dropping the gels on a flat surface of cylindrical brass substrate and coated with Au. SAXS experiments were performed using SAXS equipment with a 2D detector (Bruker Histar) and were operated at 40 kV and 35 mA. The wavelength of the incident X-ray beam from Cu Kα radiation was $\lambda = 0.154$ nm. The distance between the sample and the detector was 27.25 cm, which was calibrated by Silver behenate. STM measurements were performed by using a Nanoscope IIIa (Veeco Metrology, USA) with mechanically formed Pt/Ir (80/20) tips. A droplet (2μL) of their 1-phenyloctane solutions was deposited on freshly cleaved HOPG surface and immediately observed by STM with constant current mode. The proposed models of molecular patterns were constructed using HyperChem. HOPG (grade ZYB) was purchased from Veeco Metrology (USA).

Methyl 3,4,5-Tris(n-alkan-1-yloxy)benzoate (**2a-b**), 3,4,5-Tris(n-alkan-1-yloxy)benzoic acids (**3a-b**) and 3,4,5-Tris(n-alkan-1-yloxy)benzoyl chlorides (**4a-b**) was synthesized as previously reported.[17]

Methyl 3,4,5-Tris(n-alkan-1-yloxy)benzoates (**3a**): $^1$H NMR (400Hz, $CDCl_3$):δ 7.25 (s, 2H), 4.03-3.99 (t, 6H), 3.89 (s, 3H), 1.83-1.72 (m, 6H), 1.49-1.26 (m, 54H), 0.90-0.87 (t, 9H). (n = 16). $^1$H NMR (400Hz, $CDCl_3$):δ 7.25 (s, 2H), 4.03-3.99 (t, 6H), 3.89 (s, 3H), 1.83-1.79 (m, 6H), 1.55-1.26 (m, 78H), 0.90-0.86 (t, 9H) ppm.

3,4,5-Tris(n-alkan-1-yloxy)benzoic acids (**3b**): $^1$H NMR (400Hz, $CDCl_3$):δ 7.34 (s, 2H), 4.07-4.01 (m, 6H), 1.86-1.72 (m, 6H), 1.50-1.21 (m, 54H), 0.90-0.86 (t, 9H). (n = 16). $^1$H NMR (400Hz, $CDCl_3$): δ 7.20 (s, 2H), 3.96-3.90 (m, 6H), 1.72-1.79 (m, 6H), 1.44-1.26 (m, 78), 0.89-0.86 (t, 9H) ppm.

Bis(phenylethynyl)dimethylsilane was prepared by the reaction of dimethyldichlorosilane with lithium phenylacetylide, which was prepared using the reaction of phenylacetylene with n-BuLi. $^1$HNMR (400Hz, $CDCl_3$): δ 7.56-7.53 (m, 4H), 7.35-7.33 (m, 6H), 0.52 (s, 6 H) ppm.

2,5-Bis(4-aminophenyl)-1,1-dimethyl-3,4-diphenylsilole (**6**)

A mixture of lithium granular(0.014 g, 2 mmol) and naphthalene (0.26 g, 2 mmol) in THF (2 mL) was stirred at room temperature under argon for 20 min to form a deep green solution of lithium naphthalenide (LiNaph). A solution of bis(phenylethynyl)dimethylsilane (0.13 g, 0.5 mmol) was added to the solution of LiNaph dropwise over 1 min at room temperature. After stirred for 10 min, the mixture was cooled to 0$^o$C. Addition of solid $ZnCl_2$-TMEDA (0.5 g) to the mixture followed by the dilution with THF (5 mL) gave a black suspension. After stirring for 20 min at room temperature, 4-iodoaniline (0.22 g, 1 mmol) and $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol) were successively added. The mixture was heated to 70 $^o$C and stirred for 48 h. Water was added and the mixture was extracted with ether. The combined ether solution was washed with brine, dried over $MgSO_4$, and concentrated.

Chromatography on silica gel (petroleum ether/ethyl acetate gradient from 80:10 to 40:10) afford the pure product (62.5 mg, 28%).

$^{1}$H NMR (400 Hz, $CDCl_3$): δ 7.00 (s, 6H, ArH), 6.83-6.81 (m, 4H, ArH), 6.74-6.72 (m, 4H, ArH), 6.45-6.43 (m, 4H, ArH), 3.53 (s, 4H, NH), 0.45 (6H, $CH_3$) ppm. $^{13}$CNMR (100 Hz, $CDCl_3$): δ152.2, 144.0, 139.8, 130.2, 130.1, 127.5, 125.8, 114.8, -3.12 ppm. $^{29}$Si NMR ($CDCl_3$): δ 6.93 ppm.

Silole derivatives **1a** and **1b**

Compounds **1a** and **1b** were synthesized by the reaction of relative 3,4,5-Tris(n-alkan-1-yloxy)benzoyl chlorides with 2,5-Bis(4-aminophenyl)-1,1-dimethyl-3,4-diphenylsilole in 87% and 90% yield, respectively. Typically, 3,4,5-Tris(n-alkan-1-yloxy)benzoyl chlorides (0.28 mmol) in dry THF (2 mL) was added droppwise to a solution of 2,5-Bis(4-aminophenyl)-1,1-dimethyl-3,4-diphenylsilole (50 mg, 0.113 mmol) and triethylamine (0.04 mL, 0.282 mmol) in dry THF (5 mL) at 0 $^{o}$C under argon atmosphere. The mixture was stirred at room temperature for 1h and then filtered to remove triethylamine hydrochloride. The filtrate was evaporated in vacuo to dryness. The residue was chromatographed on silica gel pre-treated with triethylamine (petroleum ether/ethyl acetate?: 10/1 v/v) to afford the pure products.

**1a**: $^{1}$H NMR (400 HZ, $CDCl_3$): δ 7.86 (s, 2H, NH), 7.41-7.39 (d, 4H, ArH), 7.02-6.99 (d, 10H, ArH), 6.93-6.91 (d, 4H, ArH), 6.84-6.82 (m, 4H, ArH), 4.01-3.94 (t, 12H, OCH2), 1.80-1.28 (m, 120H, $CH_2$), 0.91-0.87 (t, 18H, $CH_3$), 0.5 (s, 6H, $CH_3$) ppm.$^{13}$C NMR (100 Hz, $CDCl_3$): 163.4, 153.8, 153.2, 140.8, 138.8, 136.0, 135.5, 130.0, 129.6, 127.5, 126.2, 119.6, 105.7, 73.5, 69.4, 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.0, 22.7, 14.1.-3.66 ppm. $^{29}$SiNMR ($CDCl_3$): 7.76 ppm. MALDI-TOF MS: molecular weight calcd for $C_{116}H_{180}N_2O_8Si$: m/z: 1758.7 Found: m/z: 1758.8. Elemental analysis calcd (%) for $C_{116}H_{180}N_2O_8Si$: C, 79.22; H, 10.32; N, 1.59. found: C, 79.45; H, 9.84; N, 1.57.

**1b**:$^{1}$H NMR (400 HZ, $CDCl_3$): δ 7.6 (s, 2H, NH), 7.39-7.37 (d, 4H, ArH), 7.03-6.99 (d, 10H, ArH), 6.94-6.92 (d, 4H, ArH), 6.83-6.82 (m, 4H, ArH), 4.03-4.00 (t, 12H, $OCH_2$), 1.80-1.28 (m, 168H, $CH_2$), 0.89-0.86 (t, 18H, $CH_3$), 0.49 (s, 6H, $CH_3$) ppm. $^{13}$C NMR (100 Hz, $CDCl_3$) : 165.5, 153.8, 153.2, 141.4, 140.8, 138.8, 136.0, 135.5, 130.0, 130.0, 129.6, 127.5, 126.2, 119.6, 105.6, 73.5, 69.4, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.0, 22.7, 14.1. -3.68 ppm. $^{29}$Si NMR ($CDCl_3$): 7.75 ppm. MALDI-TOF MS: molecular weight calcd for $C_{140}H_{228}N_2O_8Si$: m/z: 2095.4 Found: m/z: 2095.7. Elemental analysis calcd (%) for $C_{140}H_{228}N_2O_8Si$: C, 80.25; H, 10.97; N, 1.34. found: C, 79.58; H, 10.61; N, 1.33.

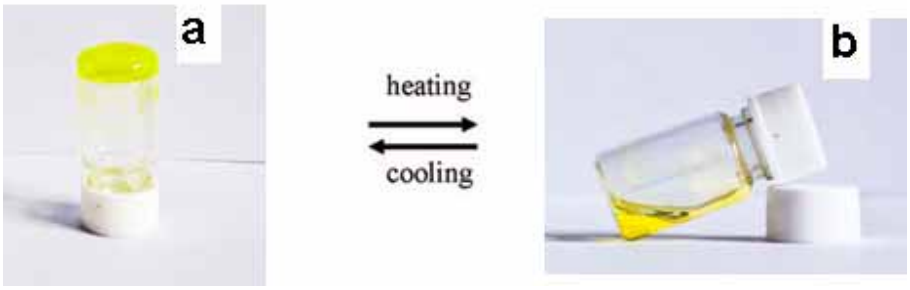



Fig. S1.The photo images (a) and (b) show the thermoreversible transition between sol and gel of **1a** in cyclohexane (8 mg/ml).

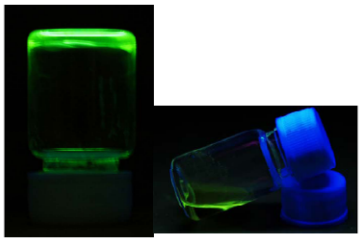


Fig. S2. The photo images of **1b** gel and $CH_2Cl_2$ solution observed upon UV irradiation at 365 nm.

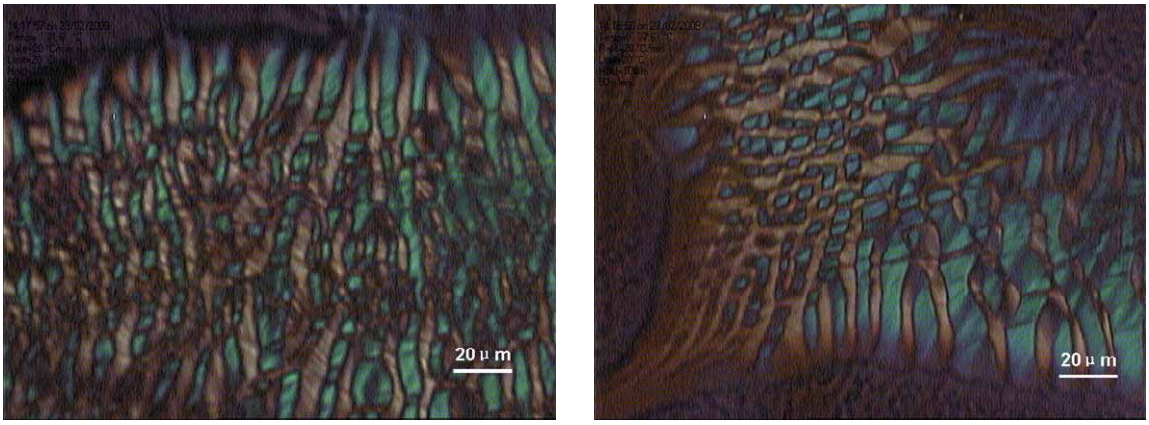



Fig. S3. POM images of xerogel formed from **1a** in n-Decane (14 mg/mL).

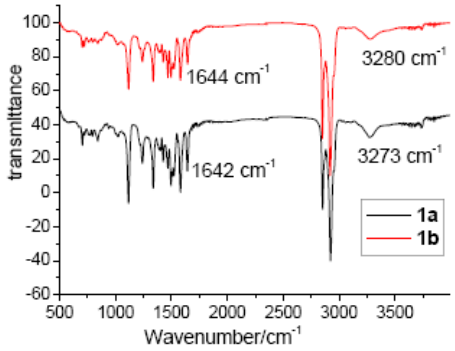



Fig. S4. FT-IR spectra of xerogels of **1a** and 1**b**.

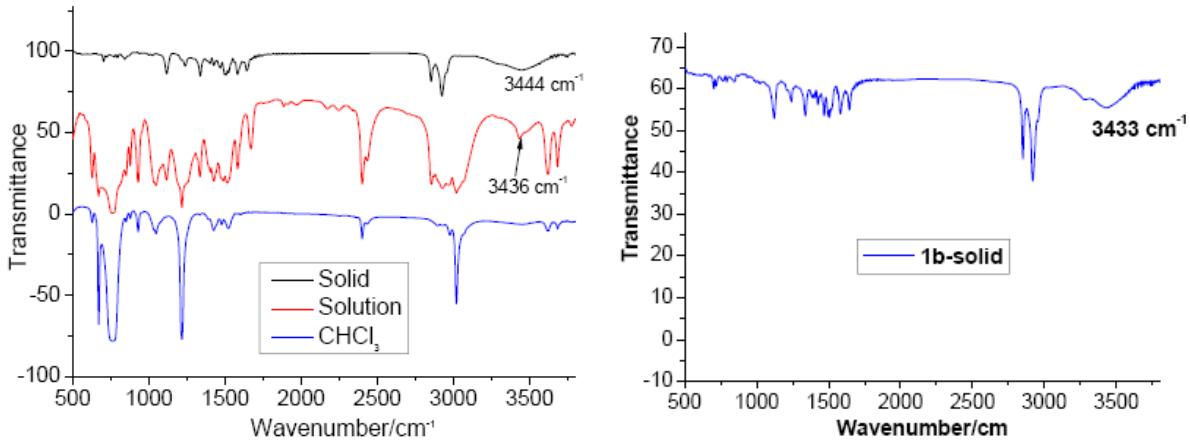



Fig. S5. FT-IR spectra of **1a** in solid and solution of $CHCl_3$ (0.01mol/L) (left), FT-IR spectra of **1b** in solid (right).

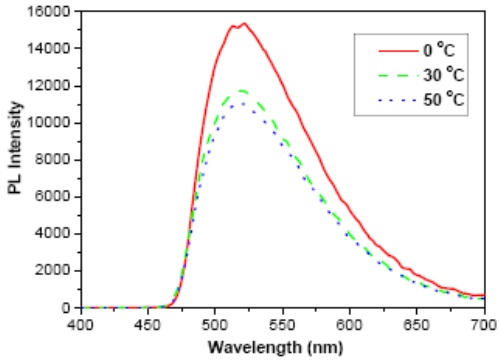



Fig. S6. Variable-temperature fluorescence spectra of the hexane gel of **1a** (excitated at 365 nm).

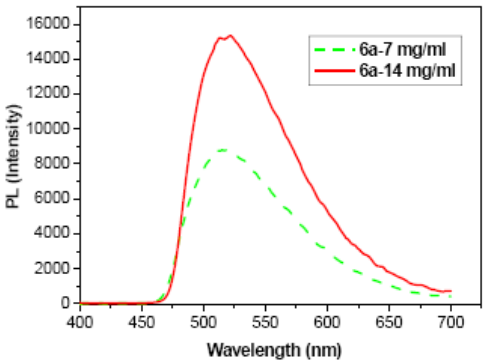



Fig. S7. Variable-concentration fluorescence spectra of the hexane gel of 1**a** (excitated at 365 nm).

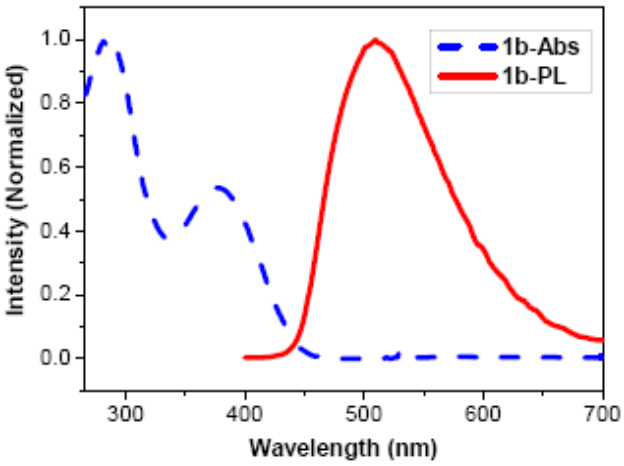



Fig. S8. The absorption and fluorescrnce spectra of **1b** in solution.

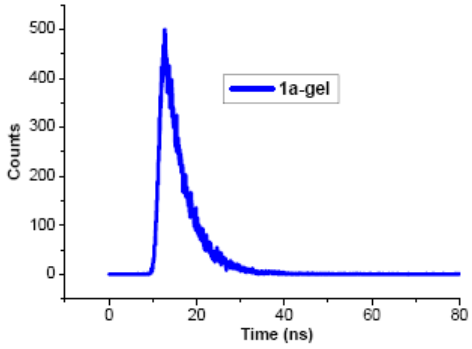



Fig. S9**.** Decaying lifetime of gel for **1a** in hexane (14 mg/ml) measured at 518nm.

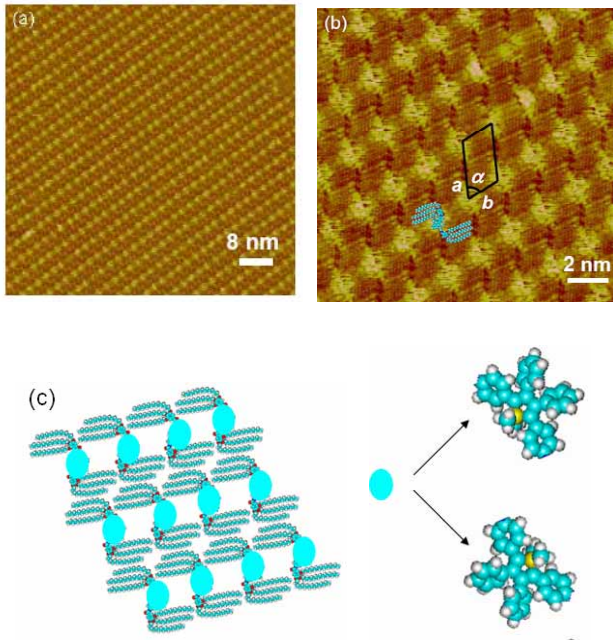
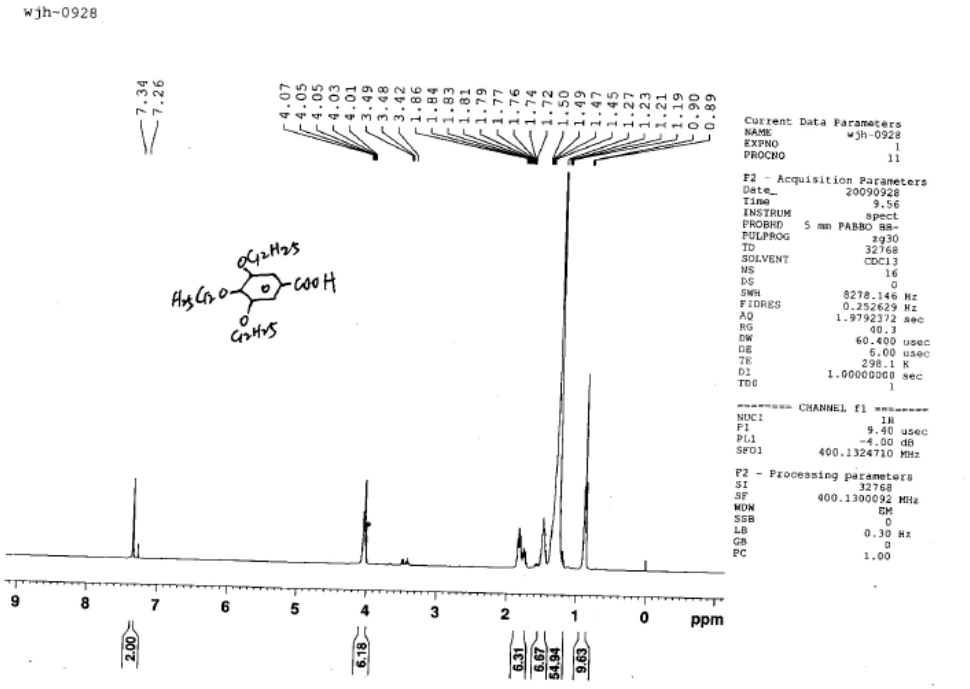
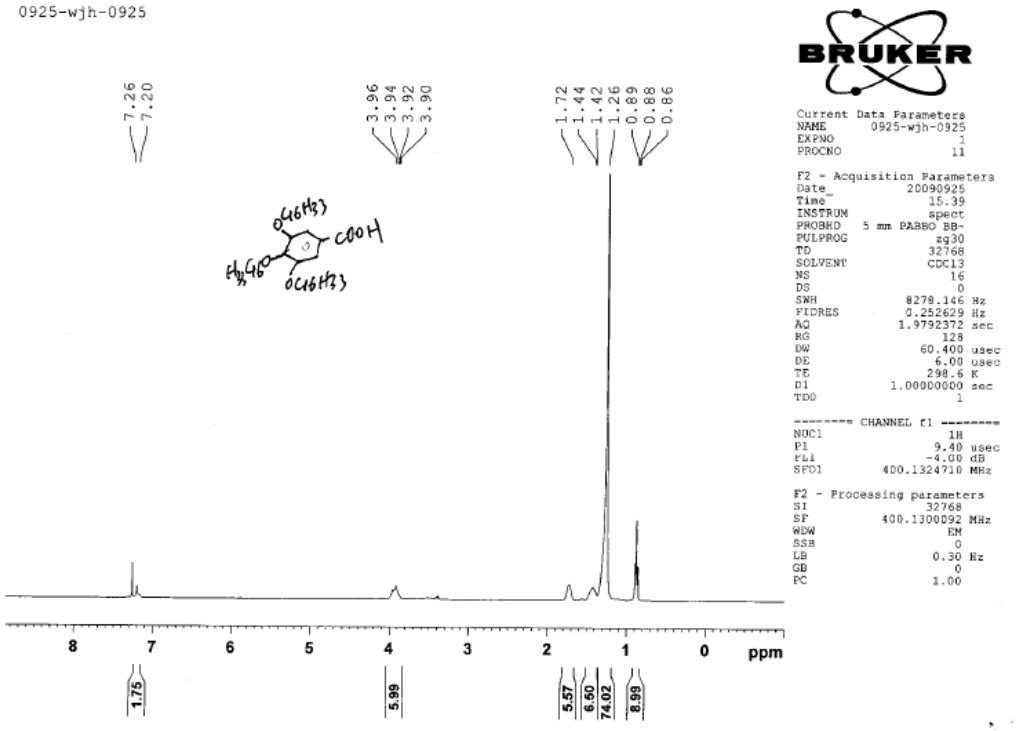



Fig. S10. (a) Large-scale STM image (81.6 nm × 81.6 nm) of 1**b**. (b) A high-resolution STM image (22.1 nm × 22.1 nm) of **1b**. (c) Proposed structural model of the ordered array (The green circles in (c) were specified to 2,3,4,5-tetraphenylsilole moieties), lattice parameters: $a$ = (4.1 ± 0.2) nm, $b$ = (2.6 ± 0.2) nm, and $\alpha$ = (60 ± 2)°

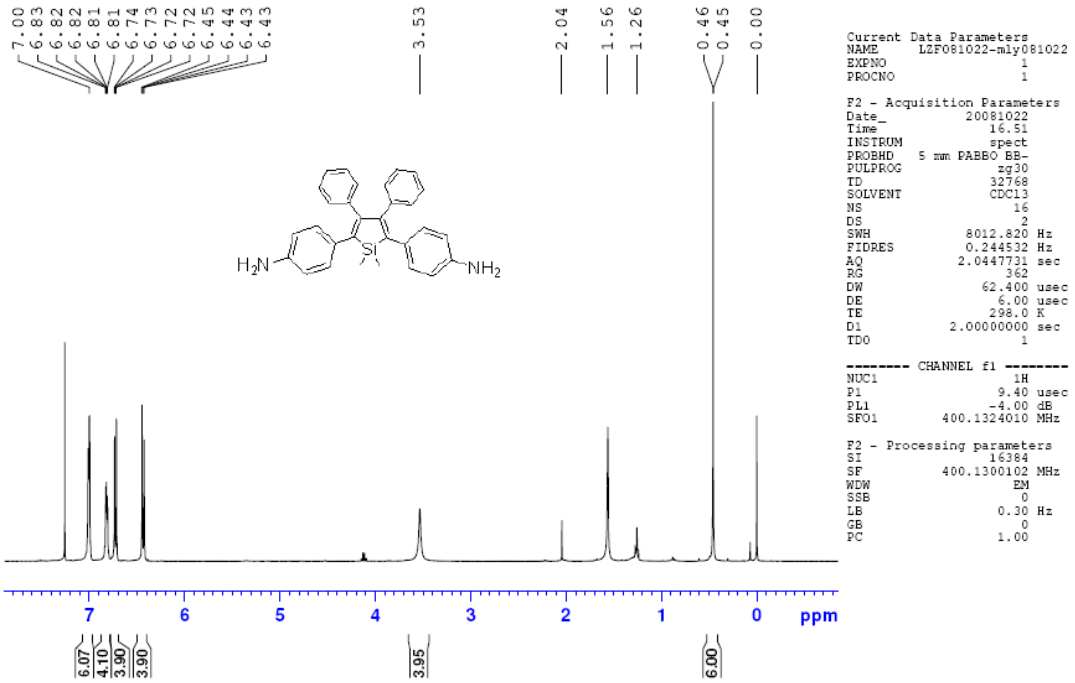
**The NMR spectra:**

The [1]HNMR spectrum of 3,4,5-Tris(n-alkan-1-yloxy)benzoic acids:

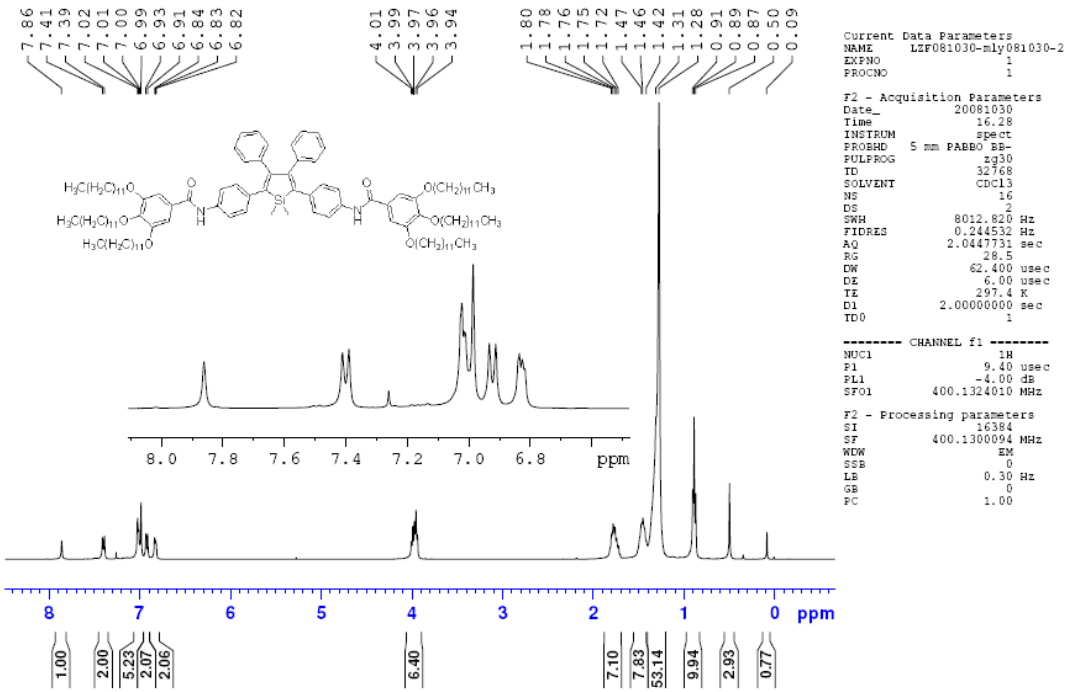




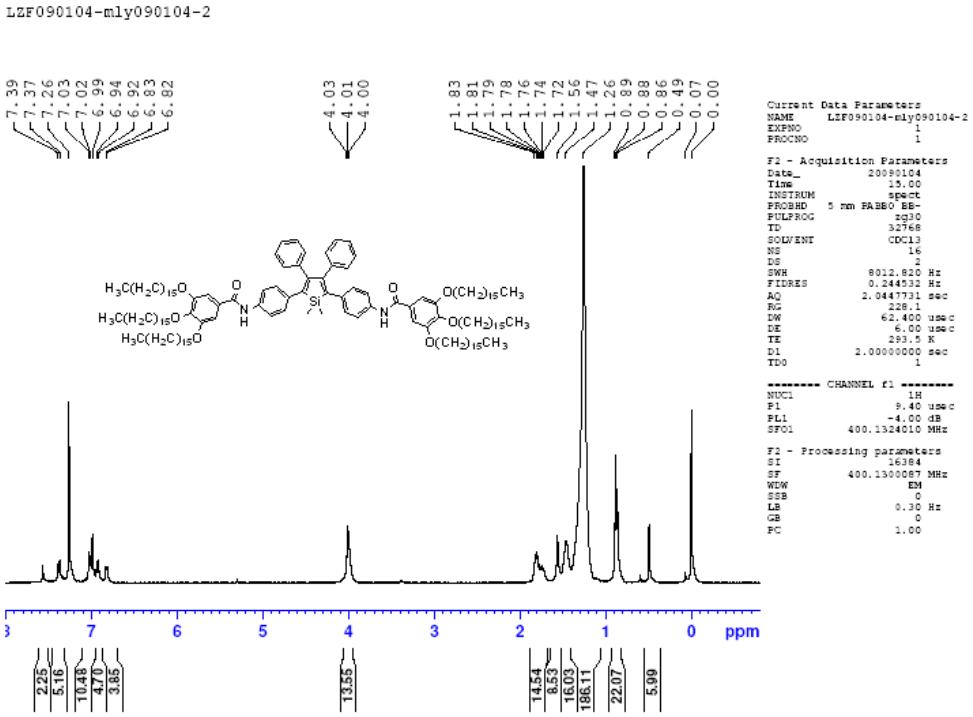

The [1]HNMR spectrum of 2,5-bis(4-amidophenyl)-3,4,--diphenylsilole:



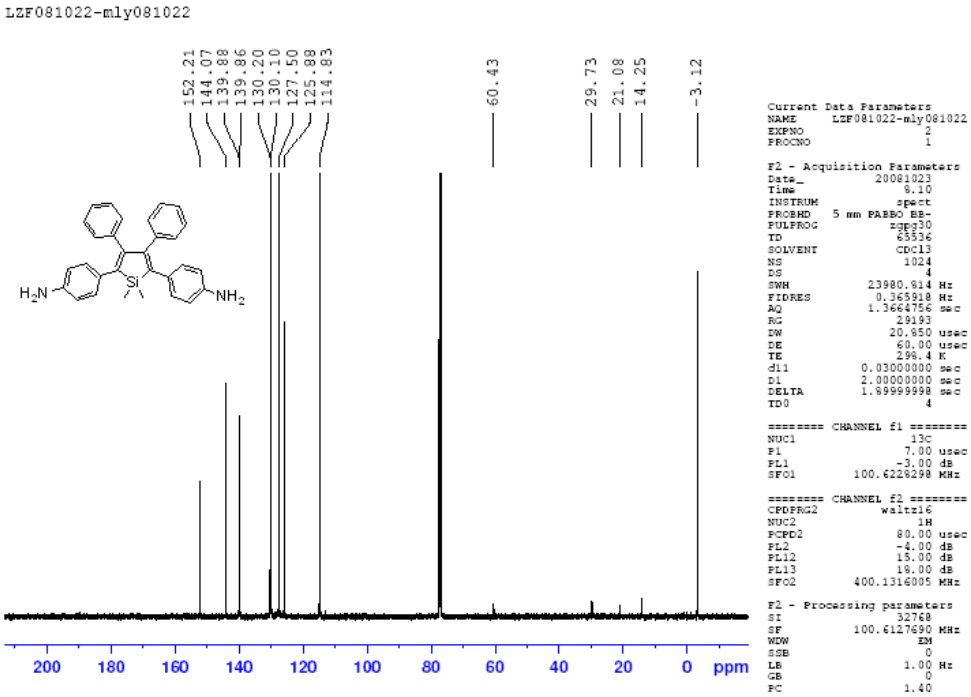

[1]H NMR spectrum of **1a**:



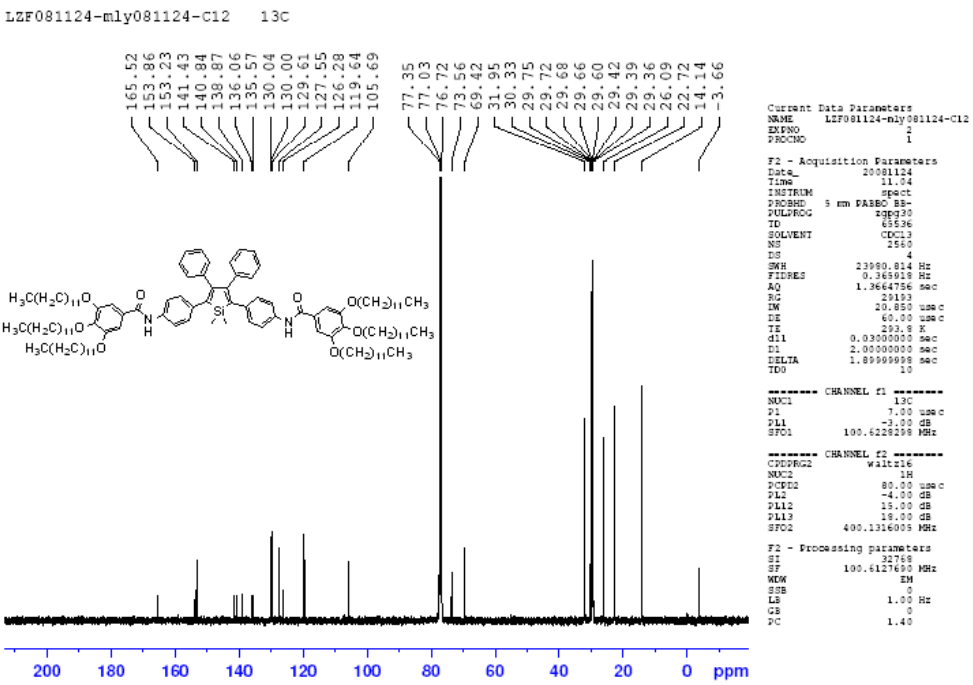

$^{1}$H NMR spectrum of **1b**:



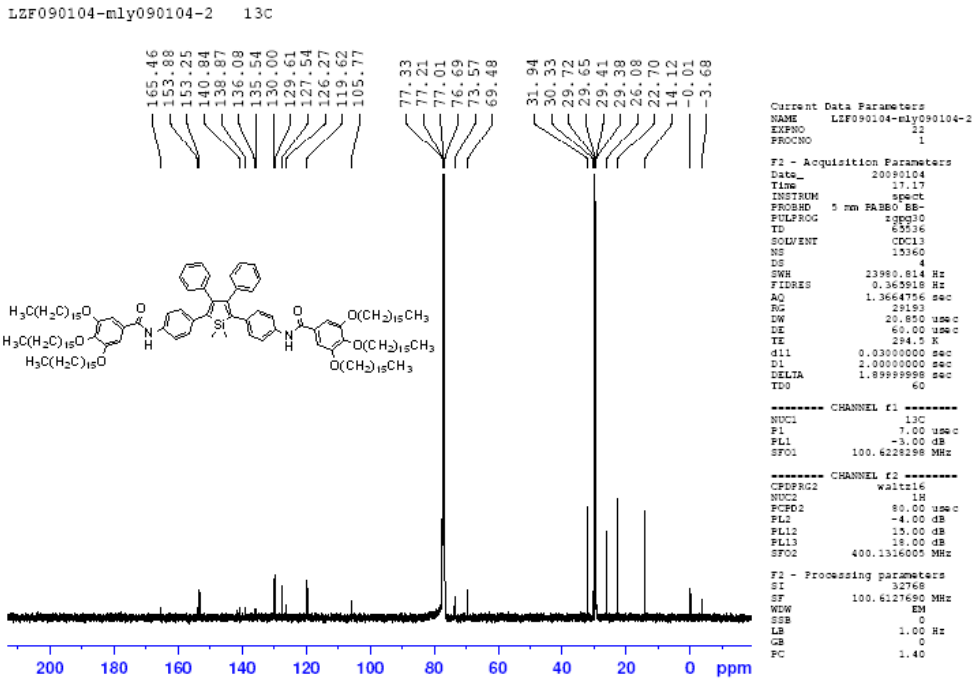
$^{13}$C NMR spectrum of 2,5-bis(4-amidophenyl)-3,4,--diphenylsilole:



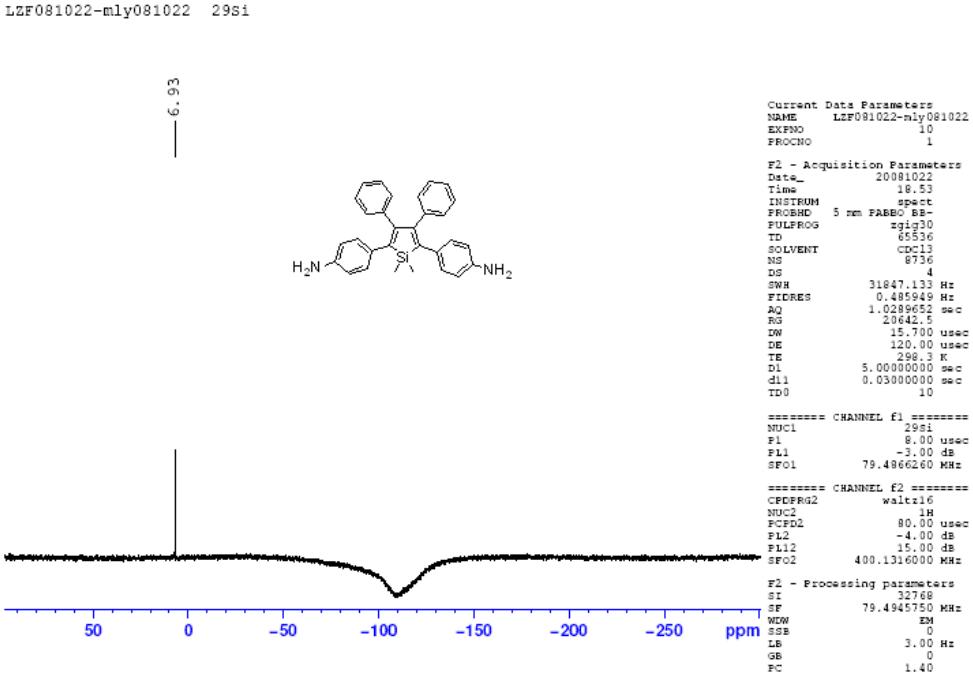

$^{13}$C NMR spetrum of 1**a**:



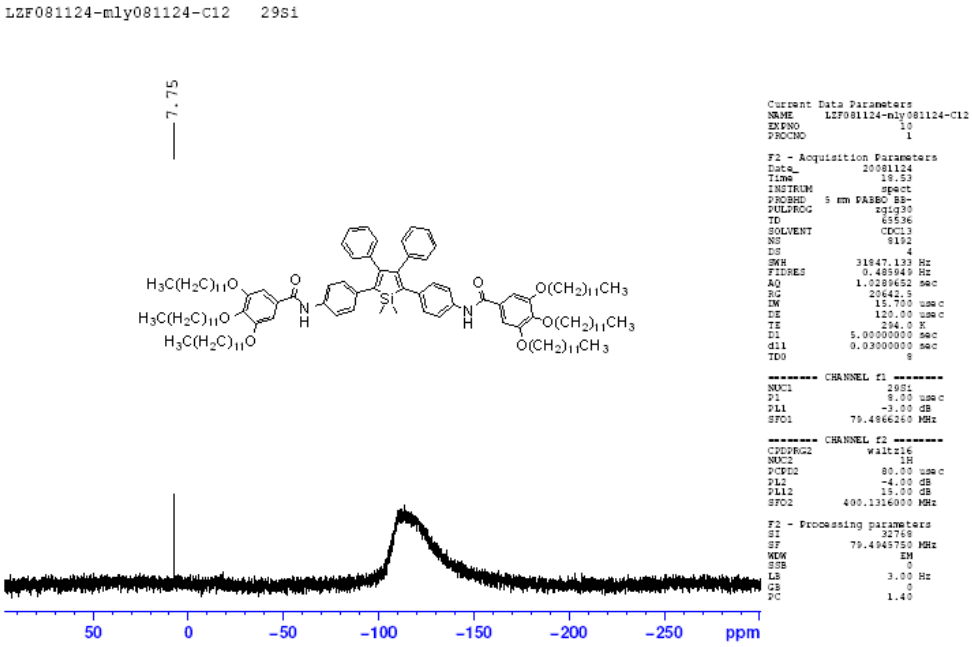
$^{13}$C NMR spetrum of 1**b**:




$^{29}$Si NMR spetrum of 2,5-bis(4-amidophenyl)-3,4,--diphenylsilole:



$^{29}$Si NMR spetrum of **1a**:




$^{29}$Si NMR spetrum of **1b**: