Supporting information

Experimental section

Instrumentation

Fourier transform infrared (FTIR) spectra were recorded using a NICOLET spectrophotometer in the range of 400-4000cm⁻¹.

¹H and ²⁹Si nuclear magnetic resonance spectra were obtained with a Bruker DX300 spectrometer at 300 MHz and 59.6 MHz at room temperature respectively. For ²⁹Si- and ¹H-NMR measurements tetramethylsilane was used as the reference. Electron spray ionization (ESI) mass spectra were obtained with a Shimadzu LCMC-2010 spectrometer.

X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2400 diffractometer with Cu Kα radiation. The preparation of H-LS sample: ladder superstructure (H-LS) formed in monomer solution was lyophilized to form a thin layer on glass slides by quickly freezing the solution with liquid nitrogen followed by the removal of solvent under vacuum.

UV-vis spectra of IPC, H-DLPS and DAC complex were measured on a UV-1601PC spectrometer in toluene and 1, 4-dioxane (1:1) with a concentration of 3.25×10⁻⁴mol/l at 0°C.

UV-vis spectra of H-I were measured on a UV-1601PC spectrometer in toluene and 1, 4-dioxane (1:1) with different concentrations.

The DSC investigation was carried out on a Mettler Toledo Star 822 differential scanning calorimeter with heating rate 10°C/min in nitrogen atmosphere.
Vapor pressure osmometry (VPO) analysis was conducted in dry toluene at 40°C on a Knauner VPO instrument.

Elemental analysis was conducted by Flash EA 1112.

Laser light scattering (LLS) measurements were performed on a commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne Laser ($\lambda_0 = 632.8$ nm) as the light source. The spectrometer has a high coherence factor of $\beta \sim 0.95$ because of a novel single-mode fiber optical coupled with an efficient avalanche photodiode. The LLS cell was held in a thermostat index matching vat filled with purified and dust-free THF, with the temperature controlled to within ± 0.02 °C. The details of the LLS instrumentation and theory can be found elsewhere.[1]

Solid-state cross-polarization/magic angle spinning (CP/MAS) $^{29}$Si nuclear magnetic resonance (NMR) spectra were obtained at 298K on an AVANCE III 400 spectrometer equipped with wide-bore magnets (triple-axis pulsed field gradient double resonance probes). The samples were packed into 4 mm rotors and scan times was 4096. The chemical shifts were determined in ppm relative to a TMS external standard.

Materials

All reagents were obtained from commercial sources and without further purification. Toluene, 1,4-dioxane and tetrahydrofuran were distilled over sodium and benzophenone. Triethylamine was distilled over sodium before use. Cp$_2$PtCl$_2$ catalyst
was preparation according to a literature method.[2]

**Synthesis**

*Preparation of isophthalyl dichloride (IPC):* A mixture of m-phthalic acid (6.64g, 40mmol), Thionyl chloride (21.6g, 160mmol) and 300ml of THF were heated reflux for 12h. The solution was removed and recrystallized with n-hexane to give the white crystal product (7.88g, 97%). $^1$H-NMR (400MHz, d$_6$-acetone) δ 8.77(s, 1H), 8.53(d, 2H), 7.95(t, 1H). Elem. Anal. Calcd.: for C$_8$H$_4$O$_2$Cl$_2$: C, 47.33; H, 1.99; Cl, 34.93. Found C, 47.18; H, 2.00; Cl, 34.80.

*Preparation of 1,5-dinitro-2,4-bis(octyloxy)benzene*[3]: A mixture of 1-octanol (10.50g, 80.4mmol), triethylamine (8.25g, 81.5mmol) and 1,5-difluoro-2,4-dinitrobenzene (8.00g, 39.2mmol) was stirred at room temperature for 2h. The mixture was dissolved in ethyl acetate and washed with water, dried over anhydrous sodium sulfate, removal of the solvent and recrystallized with ethanol to give the yellow crystal product (14.96g, 90%). $^1$H-NMR (400MHz, d$_1$-chloroform) δ 8.73(s, 1H), 6.56(s, 1H), 4.16(t, 4H), 1.88(m, 4H), 1.50(m, 4H), 1.35-1.20(m, 16H), 0.89(m, 6H).

*Preparation of 4,6-bis(octyloxy)benzene-1,3-diamine:* A mixture of 1,5-dinitro-2,4-bis(octyloxy)benzene (7.32g, 17.5mmol), Diamine hydrate(9.2g, 190mmol), 0.5g 5% Pd-C and 180ml of ethanol were heated reflux for 4h under Argon atmosphere. Pd-C was removed by filtering under Argon atmosphere. The solution was dried over anhydrous sodium sulfate and removed the solvent to give the product (5.46g, 85%). $^1$H-NMR (400MHz, d$_1$-chloroform) δ 6.44(s, 1H), 6.21(s, 1H),...
3.96(t, 4H), 1.75(m, 4H), 1.44(m, 4H), 1.42-1.25(m, 16H), 0.88(m, 6H). $^{13}$C-NMR (100.5MHz, d$_1$-chloroform) δ 139.3, 130.7, 104.3, 102.2, 69.9, 31.8, 29.6, 29.4, 29.3, 26.1, 22.6, 14.1. MS (ESI) m/z, Calcd.: for C$_{22}$H$_{40}$N$_{2}$O$_{2}$ 364.31, Found 364.4.

**Preparation of N,N'-bis(dimethylsilyl)-4,6-bis(octyloxy)benzene-1,3-diamine:** A mixture of 4,6-bis(octyloxy)benzene-1,3-diamine (3.8g, 8mmol), triethylamine (1.62g 16mmol) and 50ml anhydrous toluene were added dropwise into a three-neck flask containing 50ml toluene and dimethylchlorosilane (1.51g, 16mmol) under Argon atmosphere over 5h at 0°C. The reaction was continued for a further 2h at the same temperature after addition. The solution was removed the solvent and recrystallized with ethyl acetate to give the white crystal product. (4.12g, 87%) $^1$H-NMR (400MHz, d$_1$-chloroform) δ 6.47(s, 1H), 6.25(s, 1H), 4.75(s, 2H), 3.91(t, 4H), 3.39(s, 2H), 1.75(m, 4H), 1.44(m, 4H), 1.42-1.25(m, 16H), 0.88(m, 6H), 0.33(s, 6H). $^{29}$Si-NMR (59.6MHz, Toluene) δ -15.8 ppm.

**Preparation of H-DLPS:** 4,6-bis(octyloxy)benzene-1,3-diamine (5.5g, 15mmol), triethylamine (3.03g 30mmol) and 80ml toluene were added dropwise into a three-neck flask containing 80ml toluene and trichlorosilane (4.1g, 30mmol) under Argon atmosphere over 10h at -15°C. After that, 40ml toluene, 30ml 1,4-dioxane, water (0.27g, 15mmol) and triethylamine (6.06g, 60mmol) were added for 12h at -15°C. Then, the reaction was heated to 40°C for 6h. To end-cap the possible terminal Si-OH group, 0.2ml trimethylchlorosilane was added over 4h at 40°C. The sediment was filtered and the solvent was removed to give 5.17g H-DLPS (82%). FTIR(cm$^{-1}$): 3340 (N-H); 2931,2854 (-C$_8$H$_{17}$) ; 2250 (Si-H) ; 1523 (Si-N) ; 1430, 1260 (Si-CH$_3$) ;
1070 (Si-O-Si). $^1$H-NMR (400MHz, $d_1$-chloroform) $\delta$ 6.46 (s, 1H), 6.3 (s, 1H), 4.6 (2H), 4.1 (2H), 3.96 (t, 4H), 1.75 (m, 4H), 1.44 (m, 4H), 1.42-1.25 (m, 16H), 0.88 (m, 6H).

**Preparation of H-LPSQ**: 5.48g H-DLPS (10mmol of one unit) and 150ml toluene were placed into a three-necked flask equipped with Argon atmosphere. Firstly, 0.68g isophthalyl dichloride (3.3mmol, one third of total) and 20ml toluene were added over 2h at R.T. The reaction was continued for 10h at R.T. Secondly, 0.03g water (1.67mmol, one third of total), 0.17g triethylamine (1.67mmol, one third of total), 5ml toluene and 15ml 1,4-dioxane were added dropwise over 2h at R.T. The reaction was continued for 10h at 40°C. The above-mentioned procedure was repeatedly carried for another two times. After that, the sediment was separated by filtering and washed by chloroform to give H-LPSQ. (0.62g, 58%). FTIR (cm$^{-1}$): 2967, 2925, 2854 (Capped -CH$_3$); 2250 (Si-H); 1070 (Si-O-Si); 826 (Si-H, Si-CH$_3$). $^1$H-NMR (400MHz, $d_8$-THF), $\delta$ 4.6 (Si-H). Elem. Anal. Calcd.: for HSiO$_3$/2: C, 0; N, 0; H, 1.88. Found: C, <0.3%; N, <0.3%; H, 1.86.

**Preparation of Ch-LPSQ**: 2.65g H-LPSQ (25mmol of one unit), 5mg Cp$_2$PtCl$_2$, 4.1g cyclohexylene (50mmol) and 100ml THF were placed into a three-necked flask equipped with Argon atmosphere. The mixture was heated to 60°C for 60h. The solvent was evaporated to give 6.41g Ch-LPSQ (95%). FTIR (cm$^{-1}$): 2920, 2840 (-C$_6$H$_{11}$); 1440, 1260 (Si-C); 1020 (Si-O-Si); 880 (Si-CH$_3$). $^1$H-NMR (400MHz, $d_6$-acetone), $\delta$ 2.1-1.96 (4H), 1.9-1.8 (4H), 1.8-1.7 (2H), 1.57-1.5 (2H), 1.4-1.22 (10H).

**Supporting figures**
Figure S1. UV spectra of H-LS with different concentration (a) $9.2 \times 10^{-3}$; (b) $3.1 \times 10^{-3}$; (c) $1.0 \times 10^{-3}$ and (d) $5.0 \times 10^{-4}$.

Figure S2. XRD patterns of (a) H-DLPS; (b) Ladder superstructure (H-LS)
Figure S3, DSC curve of **H-DLPS**

Figure S4, XRD patterns of (a) **H-LPSQ** and (b) **Ch-LPSQ**
Figure S5, DSC curve of Ch-LPSQ

Figure S6, IR Spectrum of H-LPSQ
Figure S7, IR Spectrum of Ch-LPSQ

Figure S8, $^1$H-NMR of H-LPSQ
Figure S9, $^1$H-NMR of Ch-LPSQ

Reference

