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Stable and High Efficient Blue-Light Emitting Terphenyl-bridged Ladder Polysiloxane

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Measurements. Light scattering measurements were performed with a DLS-700 apparatus (Otsuka Electronic Co. Ltd.) equipped with He-Ne laser source (10 mW, λ = 632.8 nm). Determination of differential refractive index increment (dn/dc) was made with a RM-102 differential refractormeter (Otsuka Electronic Co. Ltd.) at a wavelength of 632.8 nm to give a value of dn/dc = 1.1361×10^{-4}. The FTIR measurement was performed with a Perkin-Elmer80 spectrometer, and the sample solution was dropped on KBr flake and dried before test. UV-vis spectra were obtained on a Shimadzu UV-vis spectrometer model UV-1601PC. Fluorescence spectra were recorded on a Hitachi F-4500. NMR spectra were obtained on a Bruker Avance DPS-400 (400 MHz) spectrometer. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex MALDI-TOF mass spectrometer.

X-ray diffraction (XRD) analysis was recorded on a Rigaku D/MAX 2400 diffractometer. Element analysis was measured with a Heraeus CHNRAPID DATEL System instrument. Thermal behavior was determined by using a Mettler Toledo Star-822 differential scanning calorimeter at a scanning rate of ± 10 ^{o}C min^{-1} under nitrogen atmosphere. Thermogravimetric analyses (TGA) were made using a 7 Series thermal analysis system (Perkin-Elmer). Samples were heated from 40 ^{o}C to 700 ^{o}C at a rate of 10 ^{o}C min^{-1} in a dynamic nitrogen atmosphere with a flow rate of 70 mL/min.

Synthesis of 4, 4′-di(N, N′-diallyl carbamoyl)-2′, 5′-didodecyloxy-(p)-terphenyl (2). To a 250 mL flask were added 100 mL chloroform, 3.08 g (18 mmol) of allylamine, and 3 mL (22 mmol) of triethylamine. Then, 4.34 g (6 mmol) of the acyl chloride of (1) was added intermittently into the flask over 3 h under stirring at 0 ^{o}C. The reaction mixture was stirred at room temperature for an additional 2 h. After removing chloroform, residual allylamine, and triethylamine by rotatory evaporation, a residual yellowish solid was obtained. The solid was washed with water and recrystallized twice in acetone to give a white needlelike crystal of compound (2) in 80% yield. R_f=0.8 (EtOAc/petroleum ether=1:5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ0.87 (t, J= 6 Hz, 6H), 1.24–1.34 (m, 36H), 1.64–1.71 (m, 4H), 3.90 (t, J= 4 Hz, 4H), 4.13 (t, J= 4 Hz, 4H), 5.20-5.32 (m, 4H), 5.94-6.01 (m, 4H), 6.19 (t, J= 4 Hz, 2H), 6.97 (s, 2H), 7.66 (d, J= 8 Hz, 4H), 7.82 (d, J= 8 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz)δ14.01, 22.67, 26.03, 29.25, 29.29, 29.34, 29.58, 29.63, 31.90, 42.46, 69.66, 116.02, 116.70, 126.58, 129.69, 130.25, 132.86, 134.24, 134.30, 141.64, 150.33, 167.12 ppm; MALDI-TOF MS m/z 764.3 M^{+}, 787.2$(M+Na)^{+}$. $C_{50}H_{72}N_2O_4$(765): Calcd. C, 78.49; H, 9.49; N 3.66%; Found: C, 78.51; H, 9.43; N, 3.70.

Synthesis of 4, 4′-di[N, N′-di(3-methyldiethoxylsilylpropyl) carbamoyl]-2′, 5′-didodecyloxy-(p)-terphenyl (M1). To a 100 mL Schlenk flask were added 3.82 g (5 mmol) of compound (2) and 3 mg of catalyst Cp_2PtCl_2. The reaction system was vacuumed and refilled with argon, and this process was repeated three times. Under

the argon atmosphere, 50 mL of THF and 2.3 mL (15 mmol) of methyldiethoxysilane were injected into the system. The reaction mixture was stirred under reflux for 12 h. After removing THF and residual methyldiethoxylsilane at room temperature by vacuum distillation, a pale yellow cream-like solid was obtained. The product was isolated by chromatography on a silica gel column (CH_2Cl_2/THF=100/1). Yield, 85%; R_f=0.6 (THF/petroleum ether=1:3); ^{1}H NMR (d_6-acetone, 400 MHz) δ 0.089 (s, 6H), 0.69 (t, J = 8 Hz, 4H), 0.86 (t, J = 4 Hz, 6H),1.17 (t, J = 8 Hz, 12H), 1.26-1.38 (m, 34H), 1.69 (m, 8H), 3.40-3.41 (m, 4H), 3.73-4.00 (q, J = 8 Hz, 8H), 4.02 (t, J= 4 Hz, 4H), 7.11 (s, 2H), 7.69-7.75 (m, 6H), 7.94 (d, J= 8 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz) δ -5.65, 11.42, 14.10, 18.40, 22.67, 26.03, 29.25, 29.29, 29.34, 29.58, 29.63, 31.90, 42.46, 58.26, 69.64, 116.02, 116.04, 126.55, 129.59, 130.26, 133.29, 141.38, 150.32, 167.27 ppm; ^{29}Si NMR (59.6 MHz) δ-6.02 ppm; $C_{60}H_{100}N_2O_8Si_2$(1033.6): Calcd. C, 69.72; H, 9.75; N 2.71% ; Found: C, 69.57; H, 9.49; N, 2.68.

Synthesis of M2. To a solution of M1 (4.13g, 4 mmol) in THF (300 mL), 4 mL water and two drops of 0.5 M HCl was added with stirring at 0 °C. After 20 mins, 80 mL ether and 80 mL water was added. The ethereal layer was separated out, washed with three 25 mL portions of water and dried over sodium sulfate. The filtrate was condensed to ca. 20 mL; then 50 mL of CH_2Cl_2 was added under stirring followed by filtration. The filter cake was dried under vacuum at room temperature and white power was obtained. Yield, 85%; R_f = 0.5 (CH_2Cl_2/MeOH = 9/1); ^{1}H NMR (d_6-acetone, 400 MHz) δ 0.06 (s, 6H), 0.56 (t, J = 8 Hz, 4H), 0.87 (t, J = 4 Hz, 4H) 1.26–1.37 (m, 38H), 1.63-1.67 (m, 8H), 3.37-3.42 (m, 4H), 3.91-3.94 (t, 8 Hz, 4H), 5.14 (s, 4H), 7.04 (s, 2H), 7.62 (d, J = 8 Hz, 4H), 7.74 (s, 2H) 7.88 (d, J = 8 Hz, 4H) ppm; ^{13}C NMR (d_8-THF, 400 MHz)δ-2.14, 13.49, 13.75, 22.60, 26.03, 29.29, 29.34, 29.62, 31.90, 42.23, 69.16, 115.77, 126.59, 128.98, 130.23, 133.77, 140.95, 150.40, 166.00 ppm; ^{29}Si NMR (59.6 MHz) δ-8.739 ppm; $C_{52}H_{84}N_2O_8Si_2$ (921.4): Calcd. C, 67.78; H, 9.19; N 3.04%; Found: C, 67.54; H, 9.22; N, 3.04.

Using FT-IR, ^{1}H-NMR and ^{29}Si-NMR to follow the progress of the hydrolysis and condensation reaction. FT-IR spectroscopy of the monomer **M1** shows strong peaks at 1103, 1078 and 1017 cm^{-1}, which is attributed to the asymmetric Si-O-C stretch for the ethoxy group; and the symmetric Si-O-C stretch falls at 800 cm^{-1}. In the FT-IR spectroscopy of **M2**, however, the peaks in the 1000 to 1100 cm^{-1} region disappear, and a large peak at 3289 cm^{-1}, which corresponds to the hydrogen-bonded silanols, is observed. (The N-H stretching vibration of amide was suppressed in this region) In addition, the peak at 854 cm^{-1} originates from the Si-O stretching vibration of Si-OH group in **M2**. As for the FT-IR spectrum of the polymer **TBLP**, the characterizing absorption of Si-OH group disappears (i.e. 3289 & 854 cm^{-1}) and two strong peaks at 1000-1100 cm^{-1}, which corresponds to asymmetric Si-O-Si stretching vibration respectively, comes forth. (**Figure S1**)

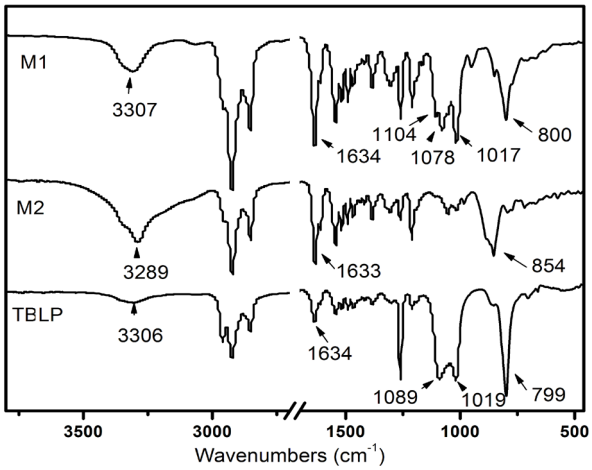

Figure S1. FT-IR spectra of **M1**, **M2** and **TBLP** (These are portion of spectra).

The ^{1}H-NMR also records the group change during the process of hydrolization and condensation. As shown in **Figure S2**, the protons of Si-OEt [δ=3.77 (8H, q) ppm] disappear and the protons of Si-OH [δ=5.09 (4H, s) ppm] emerge as **M2** hydrolized to be **M1**. The completion of the condensation reaction was indicated by the disappearance of the protons of Si-OH in ^{1}H-NMR spectrum.

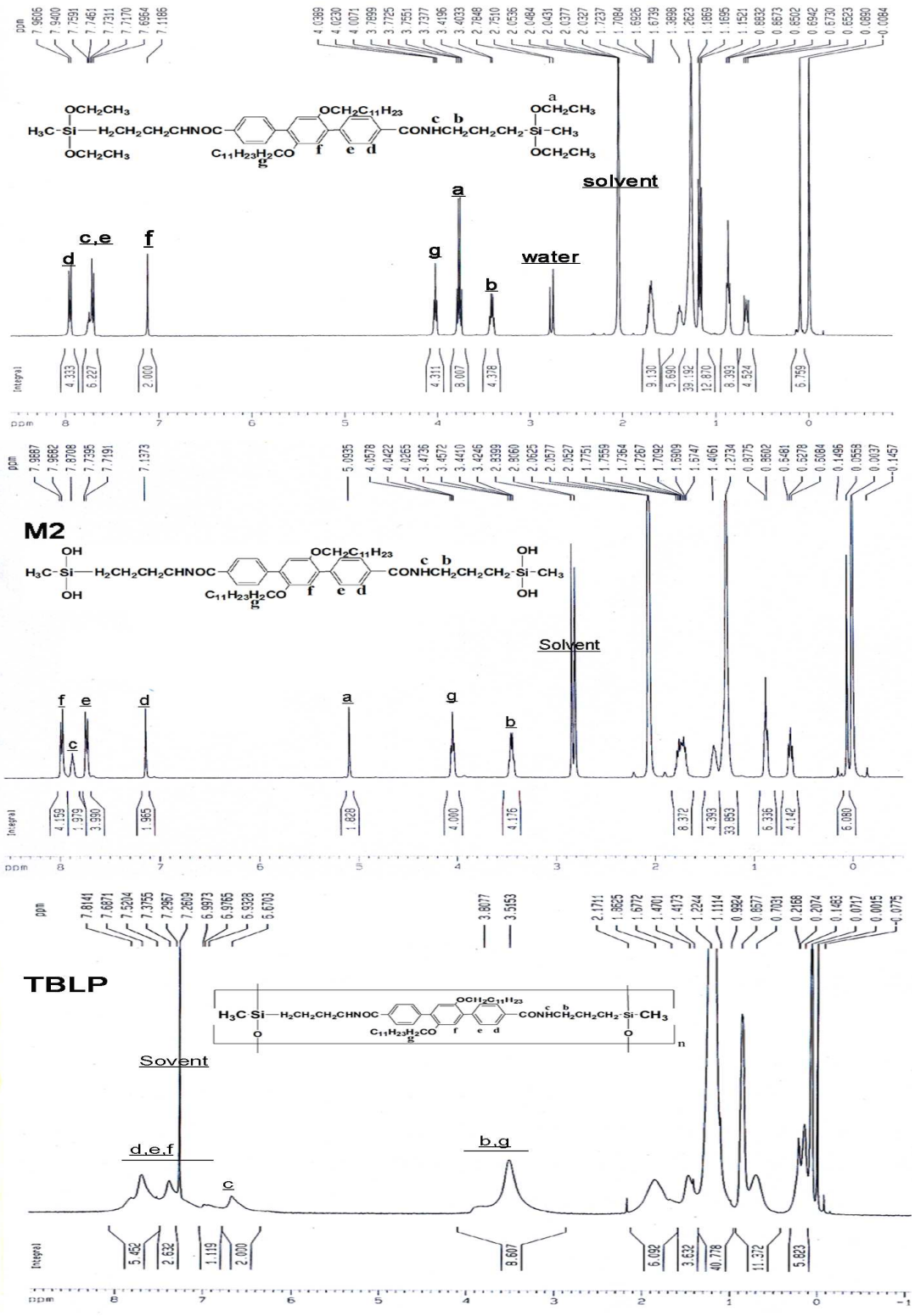

Figure S2. ^{1}H NMR of **M1**, **M2** and **TBLP.**

The difference of chemical shift in ^{29}Si-NMR spectroscopy of **M1** (δ=-6.03 ppm), **M2** (δ=-8.74 ppm) and **TBLP** (δ=-22.35 ppm) also reflects the development of hydrolysis and condensation as depicted in **Figure S3**.

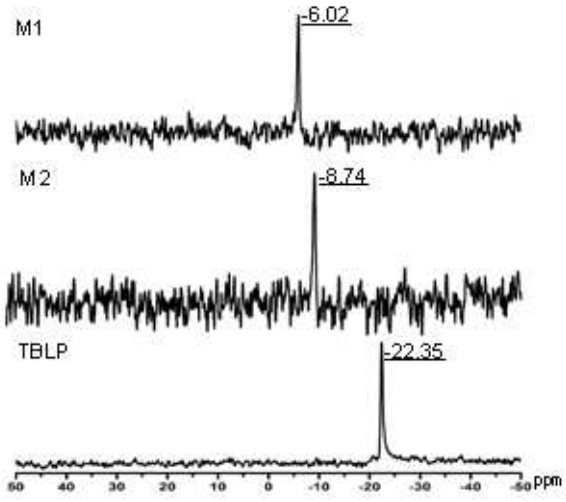

Figure S3. ^{29}Si NMR of **M1**, **M2** and **TBLP.**

Effect of the Sampling Method on XRD Signal

Sample preparing method affected the XRD signal of **TBLP** to some extent, especially the signal of the thickness (d2). Two sample preparing methods were discussed here, i.e. the film casting from the THF solution (10 mg/mL) of **TBLP**, and the powder precipitated by MeOH from its THF solution. As shown in Figure S4, when the sample is a thin film (ca. 3 um), the signal on the XRD spectrum is d1=2.87 nm and d2=1.47 nm; for the thick film (ca. 15 um), however, the signal at 2.87 nm shifted to 2.60 nm and the signal at 1.47 nm even shifted to 0.95 nm; and for the powder, the two signals further shifted to the wide angle region (d1=2.31 nm and d2= 0.72 nm). We considered that the thicker film spends more time on the film-forming process, and the corresponding chains (especially the soft part on the molecule, i.e. the alkoxy chain, alkyl bridge linking to terphenyl) have more time to adjust its conformation to pack tightly. This kind of chain adjustment would not only affect the thickness of **TBLP** (d2) remarkably, but also affect the width of **TBLP** (d1) to some extent on the XRD spectrum. As to the powder **TBLP**, because the high-polar MeOH

suppresses the extension of the above-mentioned soft part and makes them pack more tightly during the precipitation process, the two signals further shifted to the wide angle region.

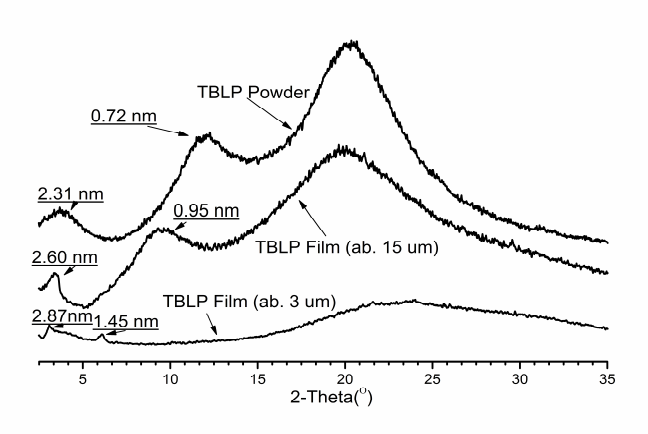

Figure S4 XRD spectra of **TBLP**. The sample was thin (ca. 3 um, bottom) and thick film (ca. 15 um, medium) casting from its THF solution (10 mg/mL) and powder (top) precipitated by MeOH from its THF solution, respectively.

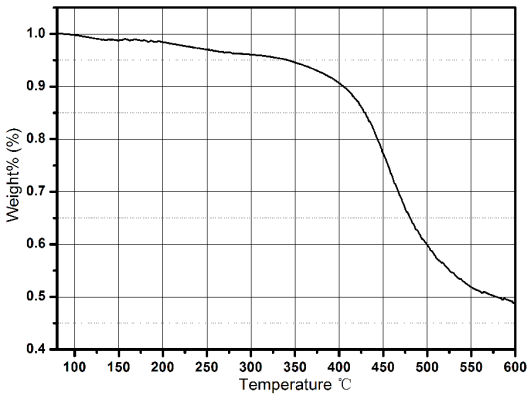

Figure S5. TGA curve of **TBLP.**

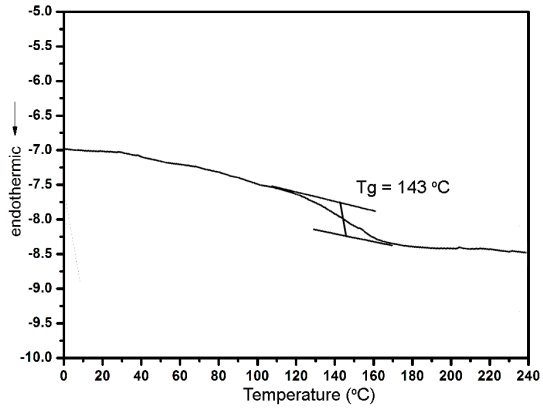

Figure S6. **DSC** curve of **TBLP.**