

## *Supporting Information for*

# **Hydrosoluble aliphatic tertiary amine-containing hyperbranched polysiloxanes with bright blue photoluminescence**

Song Niu\*, Hongxia Yan\*, Zhengyan Chen, Yuqun Du, Wei Huang, Lihua Bai and Qing Lv

*Key Laboratory of Polymer Science and Technology, Shaanxi Province, School of Natural and Applied Sciences, Northwestern Polytechnical University, Xi'an 710129, People's Republic of China*

*Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Natural and Applied Sciences, Northwestern Polytechnical University, Xi'an 710129, People's Republic of China*

\*Corresponding author, Tel.: +862988431657.

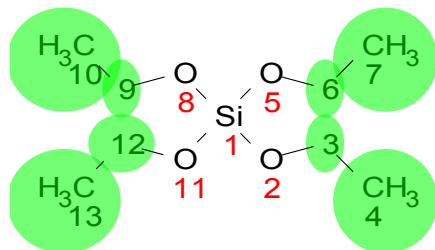
E-mail: niusong84@163.com (S. Niu), hongxiayan@nwpu.edu.cn (H. Yan).

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## 1. Spectral characteristics for raw materials

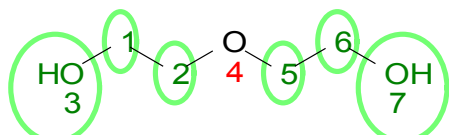
### TEOS



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.76 (qd,  $J = 6.9, 1.1$  Hz, 2H), 1.15 (td,  $J = 6.9, 1.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  58.96, 17.91.

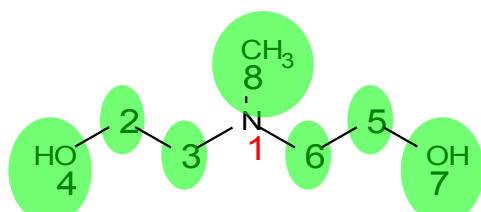
### DEG



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.68 (d,  $J = 1.6$  Hz, 5H), 3.58 – 3.51 (m, 9H), 3.46 – 3.36 (m, 9H), 3.35 – 3.29 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  72.15, 63.31, 61.18.

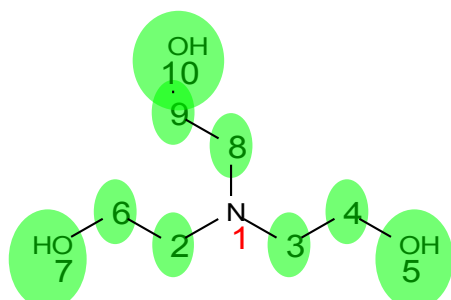
### NMDEA



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.47 (s, 2H), 3.49 – 3.41 (m, 4H), 2.42 – 2.34 (m, 4H), 2.11 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  59.51, 58.90, 42.08.

### TEA

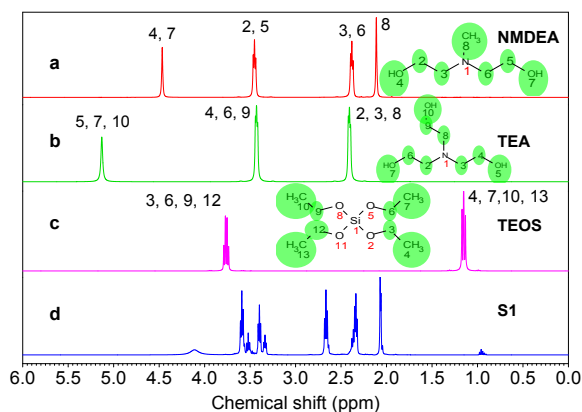


$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  5.13 (s, 1H), 3.47 – 3.39 (m, 2H), 2.45 – 2.37 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  59.28, 56.99.

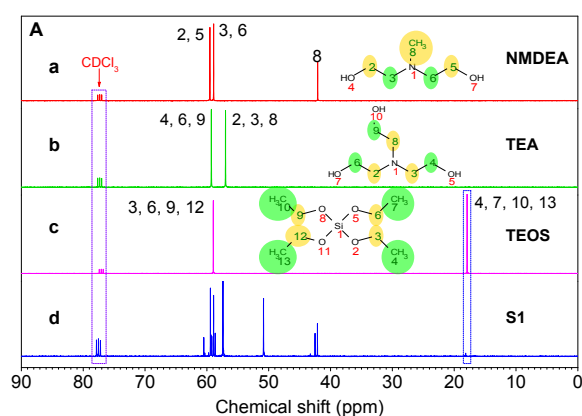
## 2. The $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of TEOS, TEA, NMDEA and DEG

The molecular structures of raw materials and the resultant polymer S1 were proved using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. Fig. S1 presents the  $^1\text{H}$  NMR spectra of NMDEA (a), TEA (b), TEOS (c) and S1 (d). In Fig. S1a, the proton peaks marked with 4 & 7 at 4.47 ppm, 2 & 5 at 3.45 ppm, 3 & 6 at 2.38 and 8 at 2.11 ppm are, respectively, attributed to hydroxyl group (–OH), methylene group connected with oxygen atom (HO–CH<sub>2</sub>–), methylene group linked to nitrogen atom (–CH<sub>2</sub>–N) and methyl group (–CH<sub>3</sub>). From Fig. S1b, we can find that the signals centered at 5.13, 3.43 and 2.41 ppm are, respectively, corresponding to hydroxyl group (–OH, 5 & 7 & 10), methylene group linked to oxygen atom (–CH<sub>2</sub>–OH, 4 & 6 & 9) and methylene group connected with nitrogen atom (–CH<sub>2</sub>–N, 2 & 3 & 8). In Fig. S1c, the proton peaks marked with 3 & 6 & 9 & 12 at 3.76 ppm and 4 & 7 & 10 & 13 at 1.15 ppm are, respectively, attributed to methylene group (–CH<sub>2</sub>–) and methyl group (–CH<sub>3</sub>). Fig. S1d displays the  $^1\text{H}$  NMR spectrum of S1, however, to characterize the S1 structure in detail, a single spectrum is provided in Fig. 2 of the main text.



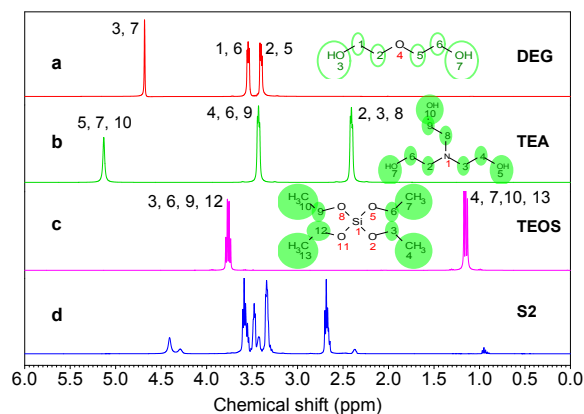
**Fig. S1**  $^1\text{H}$  NMR spectra of a) NMDEA, b) TEA, c) TEOS and d) S1.

Fig. S2 shows the  $^{13}\text{C}$  NMR spectra of NMDEA (a), TEA (b), TEOS (c) and S1 (d). Fig. S2a shows the  $^{13}\text{C}$  NMR spectrum of NMDEA, and we can see that the carbon signals at 59.51, 58.90 and 42.08 ppm are, respectively, correlated with the methylene group connected with oxygen atom ( $\text{HO}-\text{CH}_2-$ , C2 & 5), the methylene group coupled with nitrogen atom ( $-\text{CH}_2-\text{N}$ , C3 & 6) and methyl group ( $-\text{CH}_3$ , C8). In Fig. S2b, the carbon signals at 59.28 and 56.99 ppm correlating to  $\text{HO}-\text{CH}_2-$  and  $\text{N}-\text{CH}_2-$  are, respectively, observed at peak 4 & 6 & 9 and 2 & 3 & 8. From Fig. S2c, we can see that the signals at 58.96 and 17.92 ppm are, respectively, assigned to methylene group ( $-\text{CH}_2-$ , C3 & 6 & 9 & 12) and methyl group ( $-\text{CH}_3$ , C4 & 7 & 10 & 13) of TEOS. Fig. S1d displays the  $^{13}\text{C}$  NMR spectrum of S1, however, to characterize the S1 structure in detail, a single spectrum is provided in Fig. 3 of the main text.



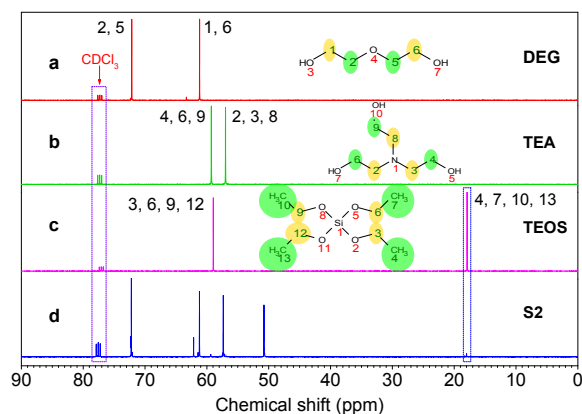
**Fig. S2**  $^{13}\text{C}$  NMR spectra of a) NMDEA, b) TEA, c) TEOS and d) S1.

Fig. S3 shows the  $^1\text{H}$  NMR spectra of DEG (a), TEA (b), TEOS (c) and S2 (d). The  $^1\text{H}$  NMR spectra of TEA (Fig. S3b) and TEOS (Fig. S3c) have been presented in the above analysis. Fig. S3a shows the proton signals of hydroxyl group ( $-\text{OH}$ , 3 & 7) at 4.68 ppm, methylene group coupled with hydroxyl group ( $-\text{CH}_2-\text{OH}$ , 1 & 6) at 3.58 ppm and methylene group connected with oxygen atom ( $-\text{CH}_2-\text{O}-$ , 2 & 5) at 3.46 ppm. Fig. S3d displays the  $^1\text{H}$  NMR spectrum of S2, however, to characterize the S2 structure in detail, a single spectrum is provided in Fig. 4 of the main text.



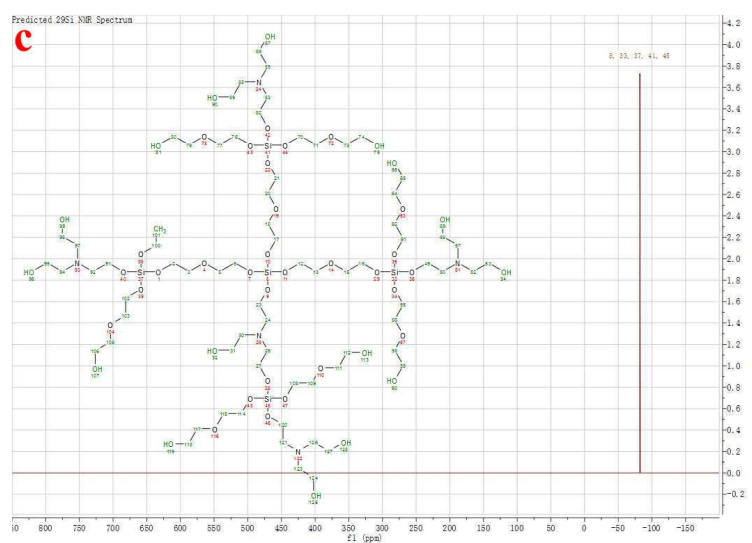
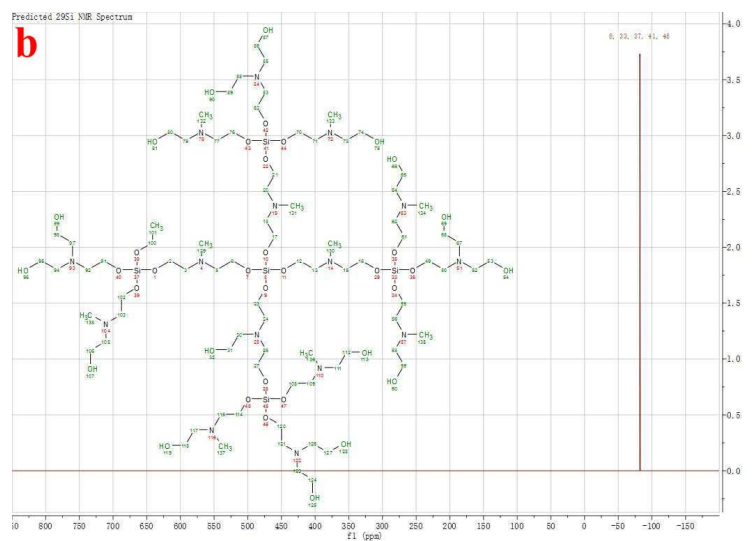
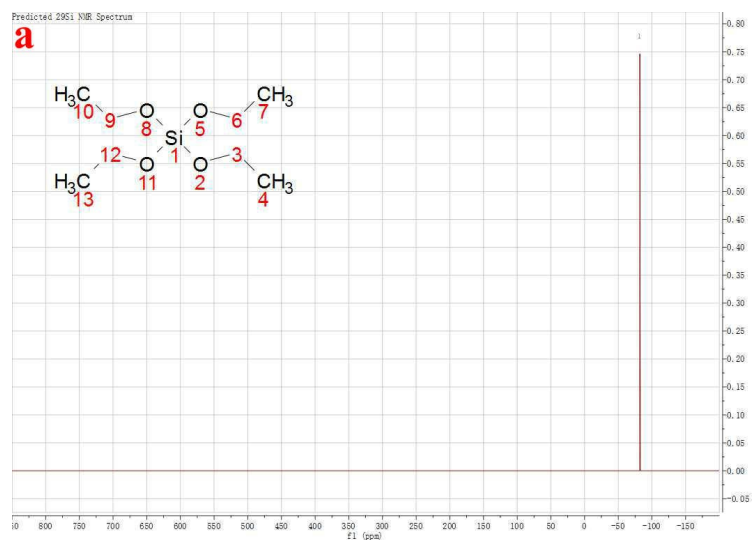
**Fig. S3**  $^1\text{H}$  NMR spectra of a) DEG, b) TEA, c) TEOS and d) S2.

Fig. S4 indicates the  $^{13}\text{C}$  NMR spectra of DEG (a), TEA (b), TEOS (c) and S2 (d), and those of the TEA (Fig. S4b) and TEOS (Fig. S4c) have been discussed in the above analysis. In Fig. S4a, the carbon peaks marked by 2 & 5 and 1 & 6 associated with methylene group linked with hydroxyl group ( $\text{HO}-\text{CH}_2-$ ) and methylene group connected with oxygen atom ( $-\text{CH}_2-\text{O}-$ ) are, respectively, observed at 72.16 and 61.18 ppm. Fig. S4d presents the  $^{13}\text{C}$  NMR spectrum of S2, however, to characterize the S2 significantly, a single spectrum is plotted in Fig. 5 of the main text.



**Fig. S4**  $^{13}\text{C}$  NMR spectra of a) DEG, b) TEA, c) TEOS and d) S2.

### 3. The printscreen of the predicted $^{29}\text{Si}$ NMR of TEOS, S1 and S2

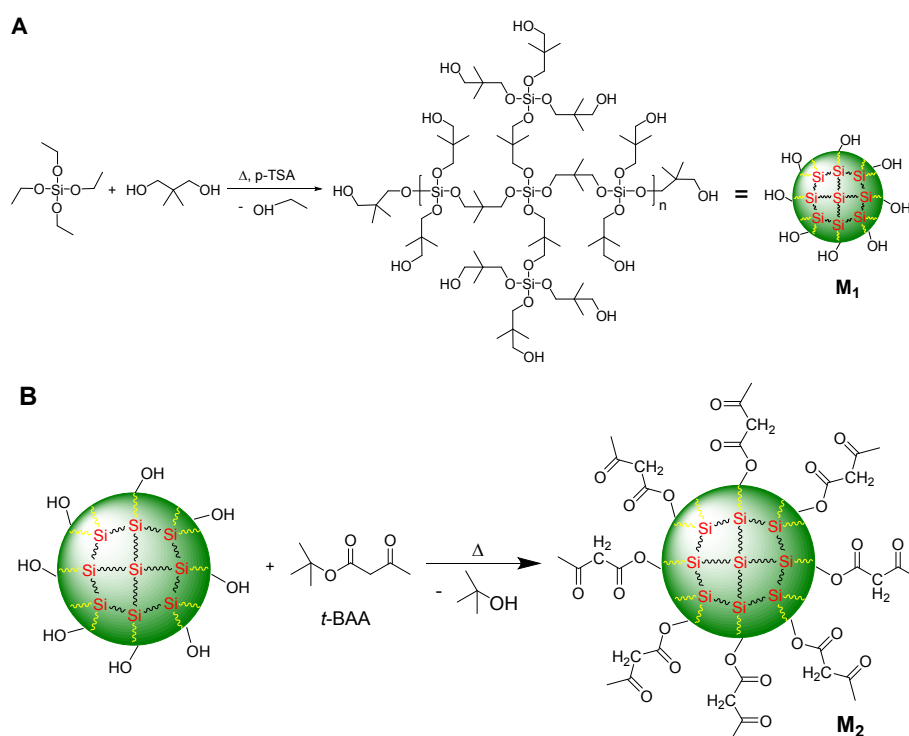


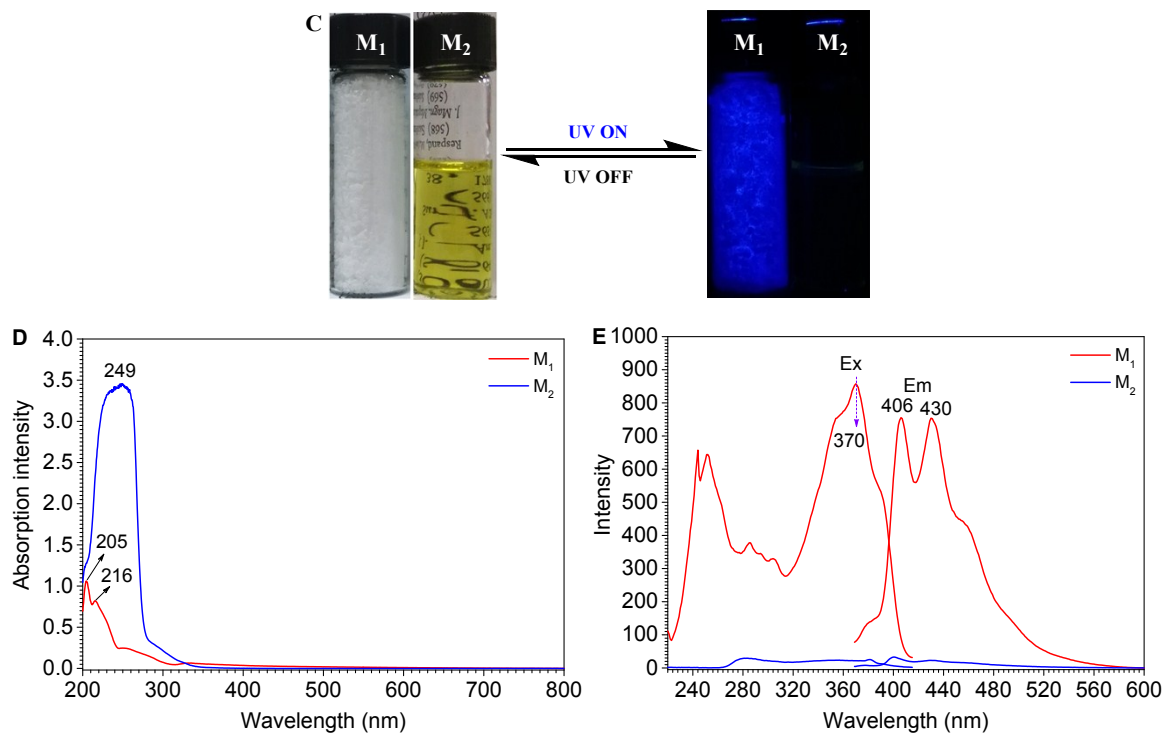
**Fig. S5** The printscreen pictures of the predicted  $^{29}\text{Si}$  NMR of a) TEOS, b) S1 and c) S2.

#### 4 Model polymers $M_1$ and $M_2$

(1) 0.27 mol TEOS (99.5%, 56.53 g), 0.87 mol NPG (90.44 g), and 0.05 g *p*-TSA were charged into a four-necked flask equipped with a thermometer, a top stirrer, a gas inlet, and a distilling setup at room temperature.  $N_2$  protection was provided by supplying  $N_2$  gas through the gas inlet. Then the reaction mixture was heated to about 110 °C, and kept at this temperature till some distillate was distilled off. Thereafter the heating was continued to raise the temperature of the reaction mixture to about 160 °C and keep the temperature of the distillate at  $78 \pm 2$  °C. The reaction mixture was maintained at 160 °C till the distillate temperature dropped below 55 °C. Finally, the silicone-based polymer terminated with hydroxyl groups ( $M_1$ ) (Fig. S6A) was prepared;

(2) 0.643 mol TBAA (98.5%, 103.027 g) was further added to the reaction mixture after its temperature was dropped below 100 °C. Then the reaction mixture was heated to about 120 °C, and kept at this temperature till some distillate was distilled off. After that, the temperature of the reaction mixture was raised to about 160 °C while the temperature of the distillate was kept at  $82 \pm 2$  °C. The reaction temperature was kept at 160 °C till the distillate temperature dropped below 55 °C. Finally, the silicone-based polymer containing acetoacetyl groups ( $M_2$ ) (Fig. S6B) was obtained.

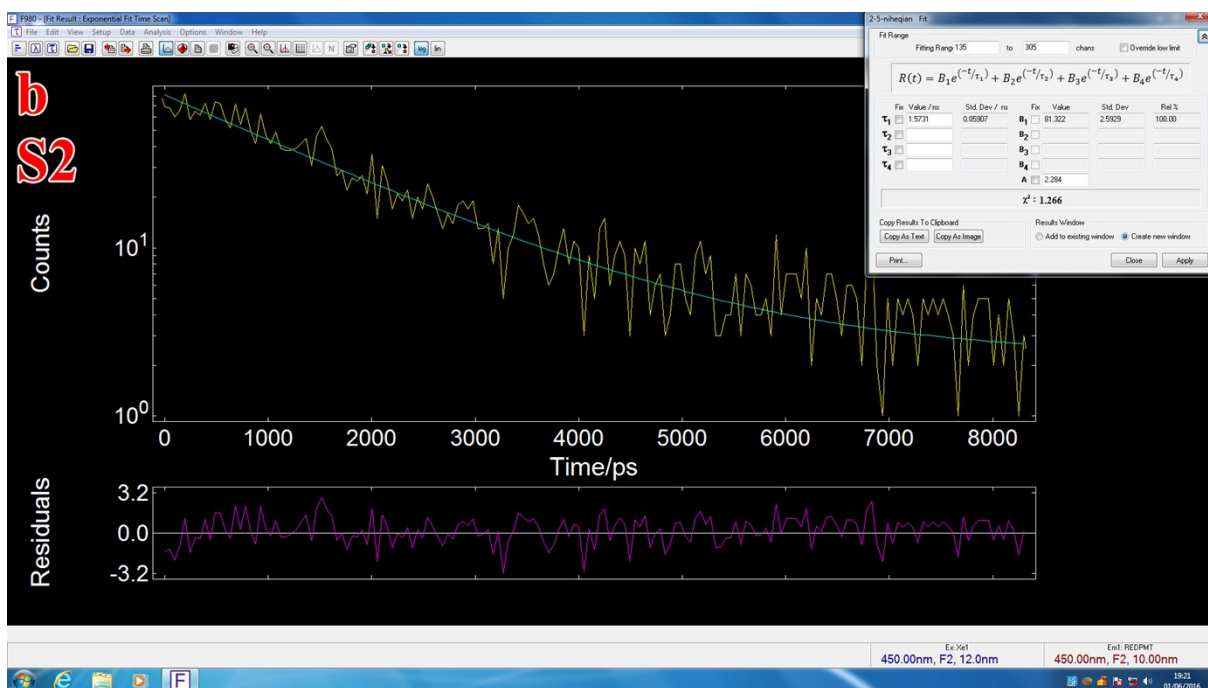
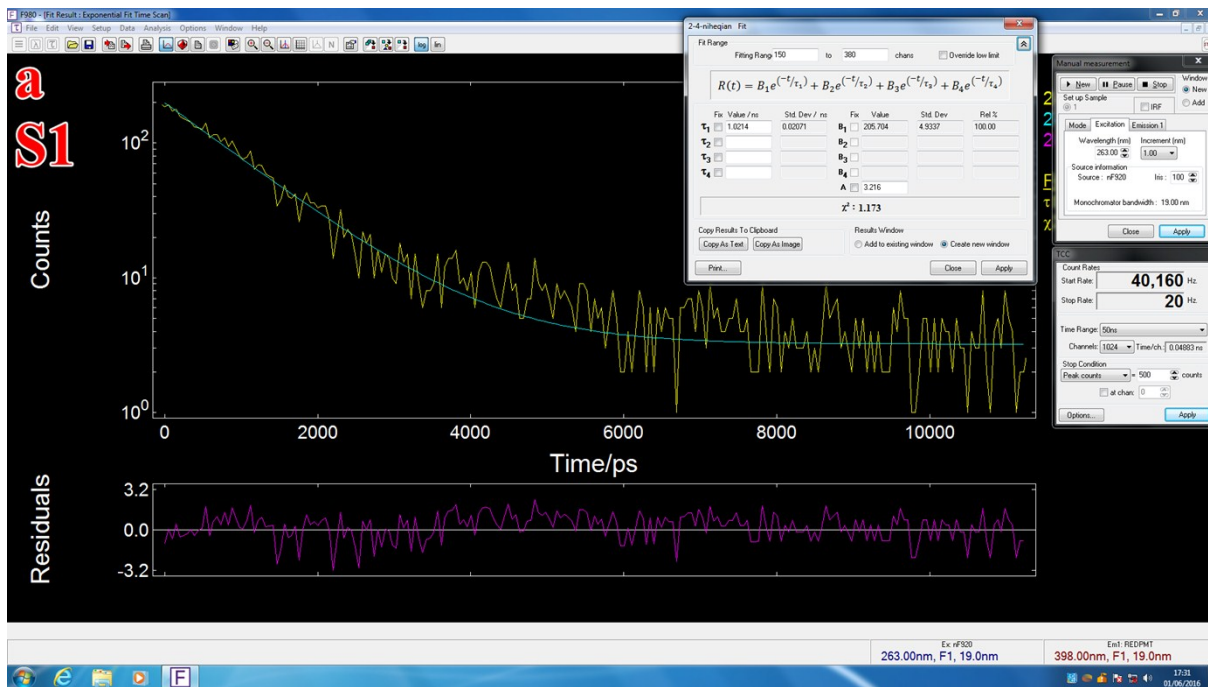




**Fig. S6** (A) Hyperbranched polysiloxanes terminated with  $\text{-OH}$  groups  $\mathbf{M}_1$ ; (B) hyperbranched polysiloxanes terminated with acetoacetyl groups  $\mathbf{M}_2$ ; (C) Fluorescence images of the polymer  $\mathbf{M}_1$  and  $\mathbf{M}_2$  excited under 365 nm UV light; (D) UV-vis spectra of the polymer  $\mathbf{M}_1$  and  $\mathbf{M}_2$ , and (E) Excitation (excited at  $\lambda_{em} = 432$  nm) and emission (monitored at  $\lambda_{ex} = 355$  nm) spectra of the polymer  $\mathbf{M}_1$  and  $\mathbf{M}_2$  with the concentration of 40 mg/mL in ethanol at room temperature.

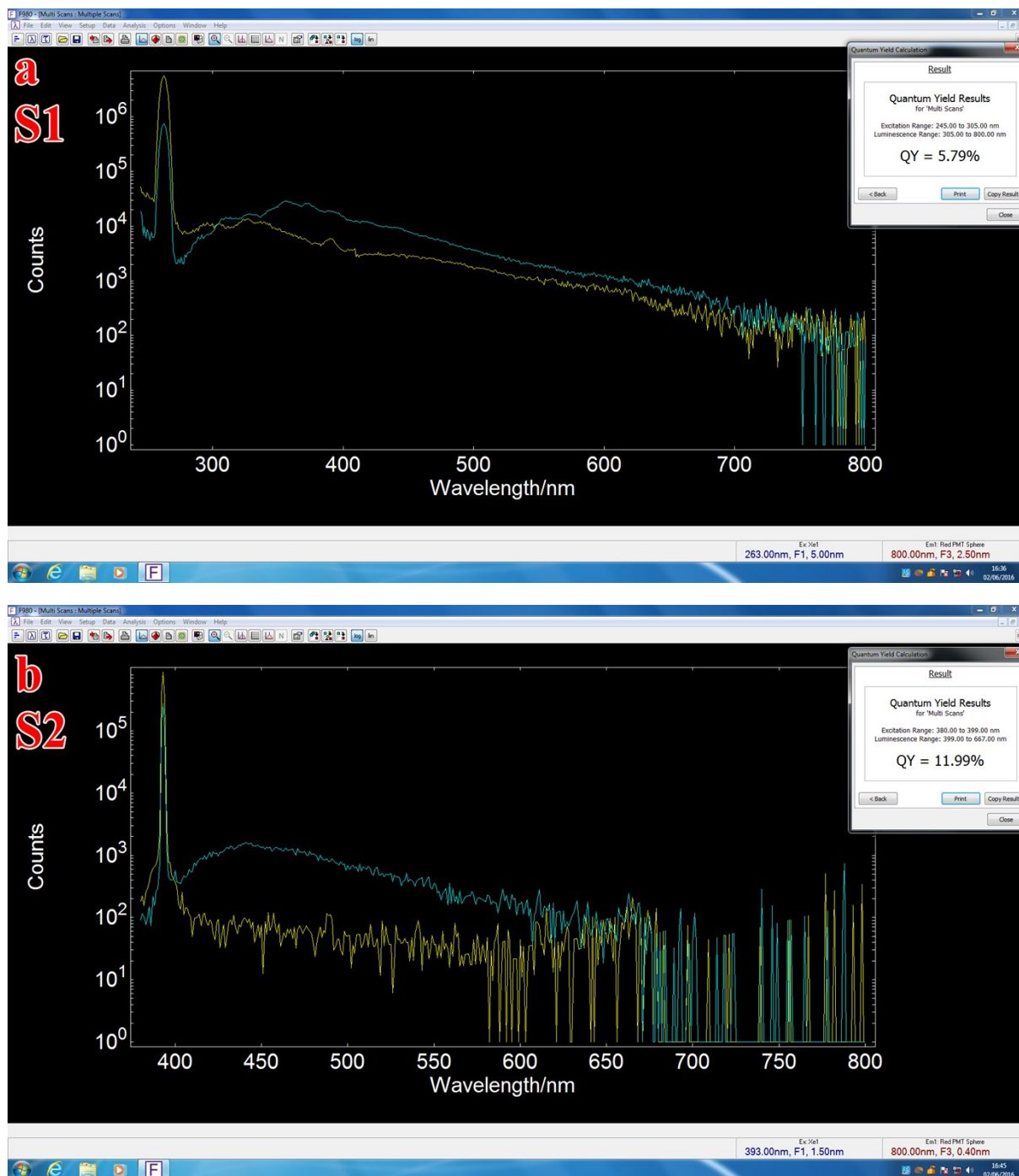
## 5 The fluorescent lifetimes of S1 and S2





**Fig. S7** The printscreen of transient photoluminescence decay curves of S1 and S2 by a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).

## 6 The absolute fluorescence quantum yields of S1 and S2



**Fig. S8** The printscreen of absolute fluorescence quantum yields of S1 and S2 by a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).

## 7 The CIE coordinates (x, y) of S1 and S2 water solutions

**Table S1** The calculated CIE chromaticity coordinates (x, y) of S1 and S2.

| Polymer   | Excitation wavelength (nm) | CIE x  | CIE y  | Peak | Peak intensity |
|-----------|----------------------------|--------|--------|------|----------------|
| <b>S1</b> | 310                        | 0.159  | 0.1345 | 388  | 70.571         |
|           | 330                        | 0.1576 | 0.1158 | 396  | 93.651         |
|           | 350                        | 0.1553 | 0.1121 | 402  | 97.087         |
|           | 370                        | 0.1542 | 0.1253 | 428  | 81.895         |
|           | 390                        | 0.1536 | 0.1476 | 452  | 61.815         |
|           | 410                        | 0.1539 | 0.1923 | 457  | 43.725         |
|           | 430                        | 0.1586 | 0.3128 | 479  | 32.493         |
|           | 450                        | 0.1836 | 0.504  | 499  | 22.948         |
|           | 470                        | 0.2332 | 0.6407 | 513  | 17.8           |
|           | 490                        | 0.2861 | 0.6733 | 527  | 13.136         |
| <b>S2</b> | 310                        | 0.1571 | 0.1305 | 349  | 97.454         |
|           | 330                        | 0.1565 | 0.1194 | 373  | 110.378        |
|           | 350                        | 0.1546 | 0.1138 | 401  | 94.432         |
|           | 370                        | 0.1535 | 0.1228 | 428  | 73.631         |
|           | 390                        | 0.1526 | 0.14   | 453  | 56.641         |
|           | 410                        | 0.1526 | 0.1711 | 448  | 45.357         |
|           | 430                        | 0.1539 | 0.2586 | 469  | 36.275         |
|           | 450                        | 0.1785 | 0.4762 | 496  | 19.967         |
|           | 470                        | 0.2343 | 0.6351 | 507  | 14.378         |
|           | 490                        | 0.2822 | 0.6734 | 525  | 11.462         |