**Electronic Supplementary Information (ESI)** 

# Unanticipated Bright Blue Fluorescence Produced from Novel Hyperbranched Polysiloxanes Carrying Unconjugated Carbon-Carbon Double Bonds and Hydroxyl Groups

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### 1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of raw materials

NPG

<sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 4.02 (d, J = 1.0 Hz, 1H), 3.40 (s, 2H), 0.84 (s, 3H).

<sup>13</sup>C NMR (101 MHz, Chloroform-d) δ 70.50 , 36.44 , 21.32.

A-151



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.05 (dd, *J* = 14.3, 4.6 Hz, 1H), 5.94 (dd, *J* = 20.6, 4.6 Hz, 1H), 5.82 (dd, *J* = 20.6, 14.3 Hz, 1H), 3.83 – 3.71 (m, 6H), 1.16 (dd, *J* = 7.8, 6.5 Hz, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.97, 136.71, 136.30, 136.24, 136.19, 129.89, 129.82, 129.23, 128.65, 77.39, 77.27, 77.07, 76.75, 60.42, 58.96, 58.50, 58.32, 58.28, 58.12, 57.86, 19.73, 18.19, 18.15, 18.11, 18.01, 17.96, 17.91, 17.84, 15.12.



## 2 The predicted <sup>29</sup>Si NMR spectra of A-151 and P1

Fig. S1 The printscreen of the software MestReNova v10.0.2



Fig. S2 The predicted <sup>29</sup>Si NMR of A-151 by the software MestReNova v10.0.2



Fig. S3 The predicted <sup>29</sup>Si NMR of the hyperbranched polymer by the software MestReNova v10.0.2



### 3 Absolute fluorescence quantum yield and lifetime of P1

**Fig. S4** The printscreen of absolute fluorescence quantum yield of P1 from a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).



**Fig. S5** The printscreen of transient photoluminescence decay curve of P1 from a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).

## 4 Hyperbranched polysiloxanes and their fluorescence images

Synthesis of Polymer A: In this polymerization,  $-OC_2H_5$  is excess compared to -OH. The mole ratio of A-151 and NPG is 1:1.36, that is, the mole ratio of  $-OC_2H_5$  and -OH is 3:2.72. The polymer A was obtained using 0.5920 mol A-151 (116.1473 g), 0.8051 mol NPG (83.8527 g) and 0.04 g *p*-TSA based on the synthesis process. of **polymer B (P1)**.



Fig. S6 Hyperbranched polysiloxanes respectively with excessive A)  $-OC_2H_5$  and B) -OH groups and their fluorescent photos under UV ( $\lambda = 365$  nm) irradiation. The polymer B is P1.



Fig. S7 UV-vis absorption spectra of polymer A and B in ethanol at the concentration of 40 mg/mL.



Fig. S8 Fluorescence spectra of polymer A and B in ethanol at the concentration of 40 mg/mL: excitation (Ex) spectra (monitored at  $\lambda em = 432$  nm) and emission (Em) spectra (excited at  $\lambda ex = 355$  nm) measured at room temperature.

#### Synthesis of Polymer C and D:

(1) 1.08 mol TEOS (99.5%, 226.13 g), 3.47 mol NPG (361.76 g), and 1.18 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. N2 protection was provided by supplying N2 gas through the gas inlet. Then the reaction mixt. 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 mixt. to about 160 °C and keep the temperature of the distillate at 78±2 °C. The reaction mixt. was maintained at 160 °C till the distillate temperature dropped below 55 °C. Finally, the silicone-based polymer terminated with hydroxyl groups

(C) was prepared;

(2) 2.57 mol TBAA (98.5%, 412.11 g) was further added to the reaction mixt. after its temperature was dropped below 100 °C. Then the reaction mixt. was heated to about 120°C, and kept at this temperature till some distillate was distilled off. After that, the temperature of the reaction mixt. 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 (**D**) was obtained



Fig. S9 Synthetic routes to different hyperbranched polymers and their fluorescent photos under UV ( $\lambda$  = 365 nm) irradiation. C) hyperbranched polysiloxane only containing hydroxyl groups (solid at room temperature) and D) acetoacetyl-terminated hyperbranched polysiloxane.



Fig. S10 UV-vis absorption spectra of polymer C and D in ethanol at the concentration of 40 mg/mL.



Fig. S11 Fluorescence spectra of polymer C and D in ethanol at the concentration of 100 mg/mL: excitation (Ex) spectra (monitored at  $\lambda em = 432$  nm) and emission (Em) spectra (excited at  $\lambda ex = 355$  nm) measured at room temperature.