

## Supporting Information

### Uncovering a broad class of fluorescent amine-containing compounds by heat treatment

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#### Materials

All reagents were purchased from Aladdin Chemical Reagent Co., Ltd. and used without further purification.

#### Instruments

Absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Excitation-emission matrices and fluorescence measurement were performed on a Hitachi F-7000 and the slit width of excitation and emission were fixed at 2.5 and 5 nm, respectively. All absorption and fluorescence spectra were collected at 25 °C.

Fourier transform-infrared absorption spectra were recorded using a Bruker Tensor 27 spectrometer. KBr pellets of powders were used in measurement.

Measurements of the fluorescence lifetimes were performed with standard time-correlated single-photon counting method. The exciting light was a portable diode laser (EPL-375, Edinburgh Instruments), the 379 nm (69 ps, 0.10 mW) laser beam was guided into the samples, and fluorescence was detected at the emission maximum of a sample. The bandwidth for excitation as well as for emission was < 2 nm.

Microscopic images photographed using a Zeiss HBO 50/AC microscope with an Olympus DP72 digital camera. The onion sample was first soaked in a water solution of sucrose (1 mol L<sup>-1</sup>) on a microscope slide for 5 min to separate the cell membrane from their wall, then in a solution of fluorescent amine-containing compounds for 10 min to stain, and rinsed with the same solution of sucrose many times before microscopic observation.

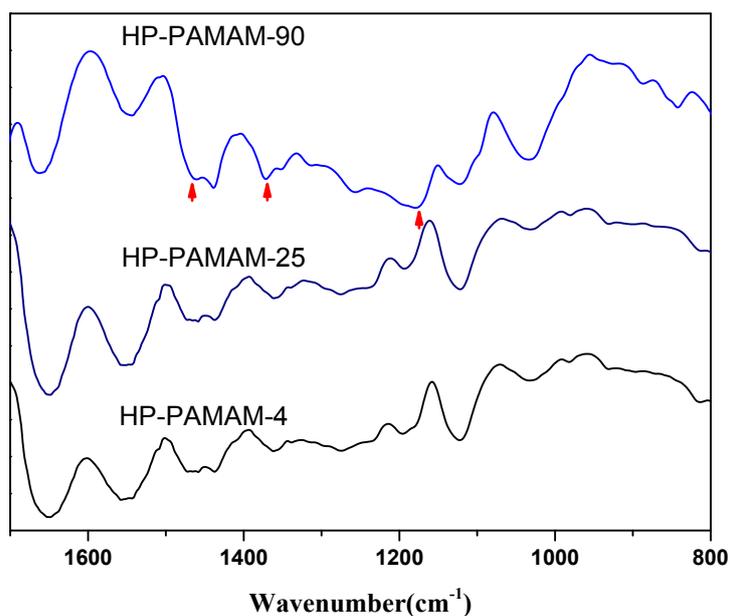
The data of gel permeation chromatography of HP-PAMAM were collected using Agilent 1260 Infinity with a column of PL aquagel-OH MIXED-H. The mobile phase used was water

and the flow rate adjusted to 1.0 mLmin<sup>-1</sup>. The eluting polymers were detected using a RID ( Agilent 1362A ) detector.

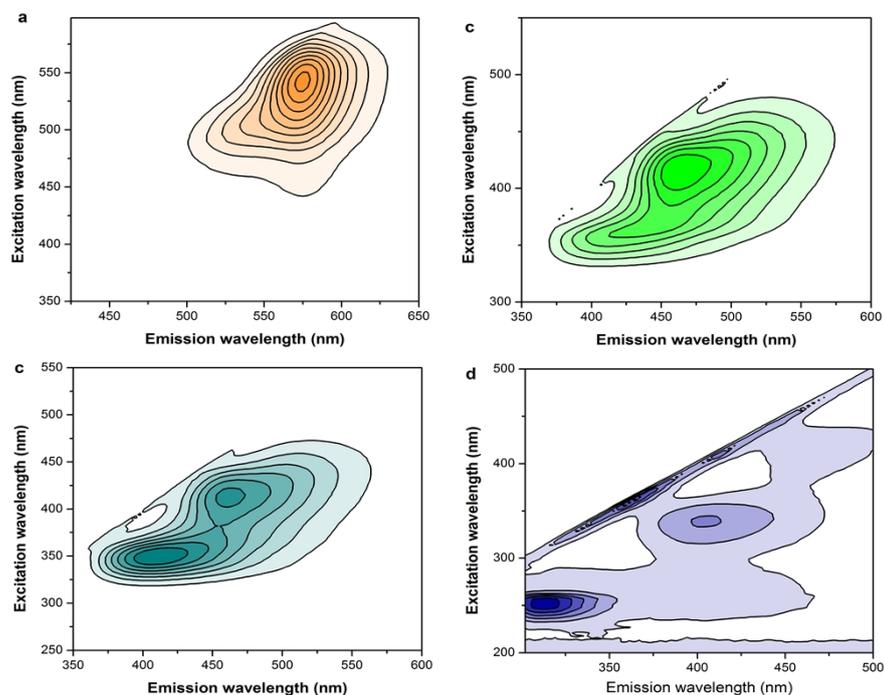
## **Experiments**

**Synthesis of HP-PAMAM:** HP-PAMAM was prepared by ethane diamine (EDA) and methyl acrylate using one-pot method at around 25°C. To a 100ml conical flask was added 0.2mol EDA in 0.2mol of the methanol. Then 0.2mol methyl acrylate was added dropwise into the reaction system. The mixture was stirred at room temperature for 7 days in conical flask. The obtained product was dried under vacuum condition at 35°C for about 3 days, and then kept in refrigerator. The as-prepared materials were used directly without further purification.

**Heat treatment of amine-containing compounds:** In a typical heat treatment, sample was added into a 250ml four-necked, round-bottomed flask equipped with a water jacket in electric heating mantle and heated at controlled temperatures for a certain period of time.



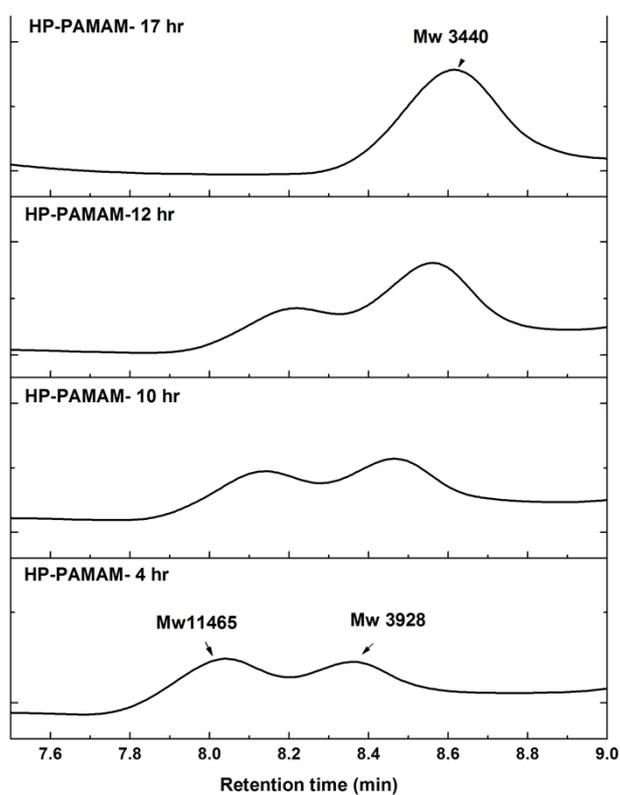
**Fig. S1:** IR spectra of the HP-PAMAM samples treated at different temperatures: 4, 25 and 90 °C, respectively. The IR data were collected at the seventh day after preparation. The characteristic N→O absorption bands at 1180, 1365 and 1464 cm<sup>-1</sup> (indicated by red arrows) are clearly observed for the sample treated at 90 °C, which correlate with the results in Ref. 8b. In addition, this result also supports the suggestion that the high temperature accelerates the formation of oxidized amine groups.



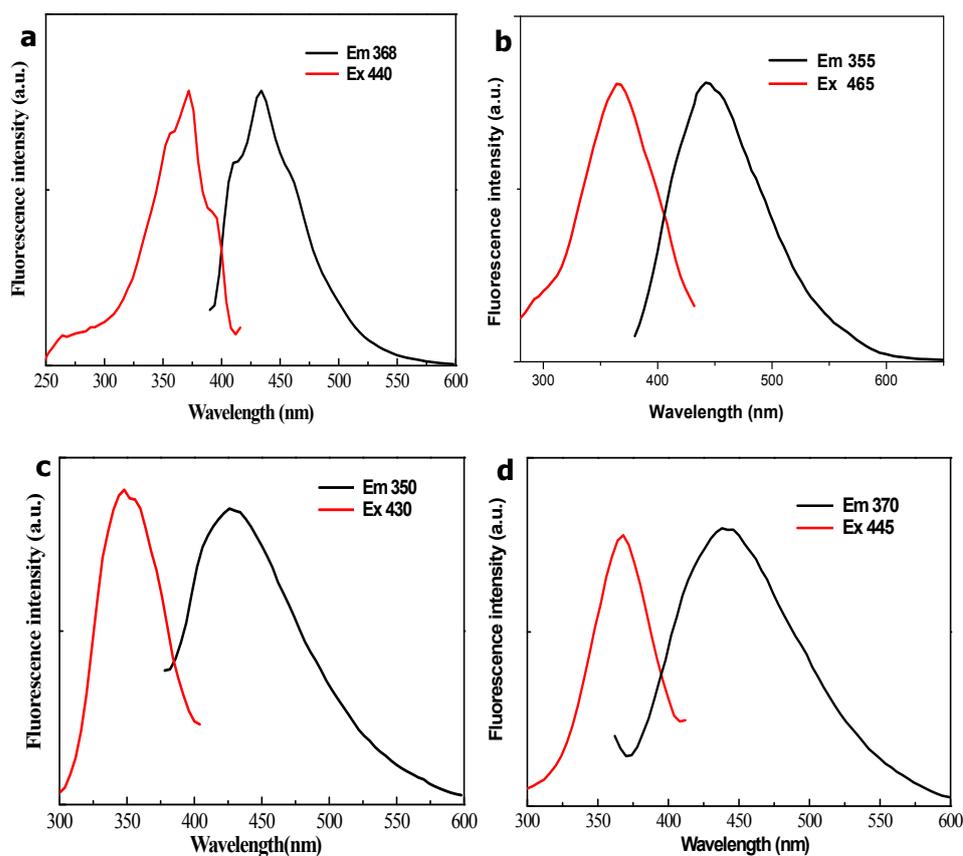
**Fig. S2:** Change in fluorescence of heat-treated HP-PAMAM in a process of dilution. a)–d), Contour plot for the EEMs of thermal-treated HP-PAMAM measured at different concentration in methanol: 640, 44, 5 and 0.3 mg ml<sup>-1</sup>, respectively. The change of fluorescent properties in the process of dilution is almost a reverse process of the heat treatment as shown in Fig. 1.

**Table S1.** Data of fluorescence lifetimes of EDA-HP-PAMAM measured at different times in the process of heat treatment, corresponding to samples in Fig.1.

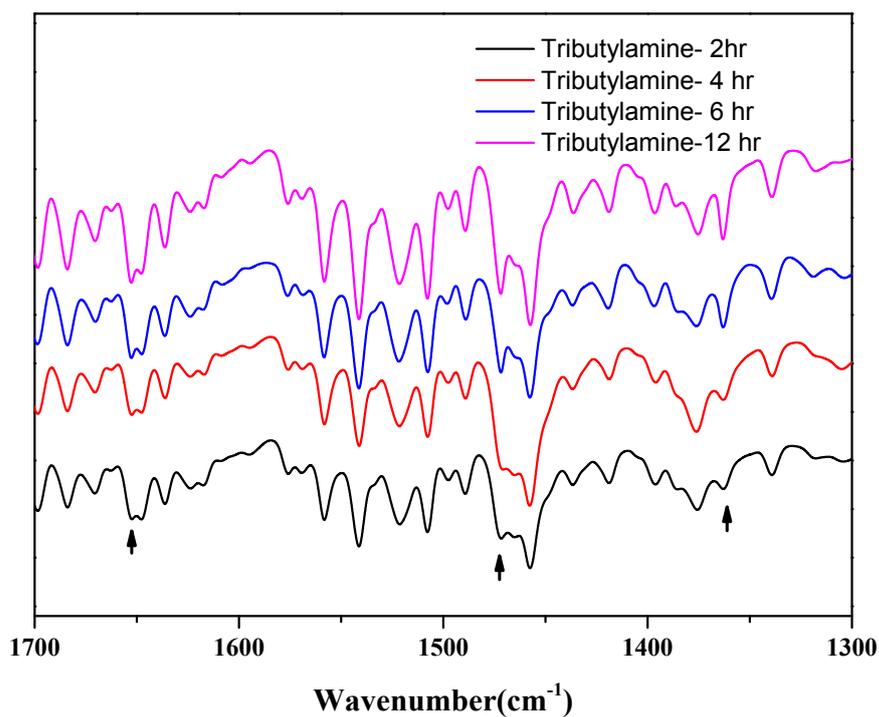
Reaction time (hour)	Excited state lifetime [ns], relative amplitude [%]			
	$\tau_1$	$\tau_2$	$\tau_3$	$\chi^2$
<b>HP-PAMAM-0h</b>	0.30 (82.87%)	2.20(10.74%)	8.30(6.39%)	1.151
<b>HP-PAMAM-4h</b>	1.25(35.91%)	3.73(55.99%)	13.13(8.11%)	1.070
<b>HP-PAMAM-8h</b>	1.27(38.95%)	4.08(50.55%)	13.34(10.50%)	1.036
<b>HP-PAMAM-12h</b>	1.37(24.72%)	4.43(61.75%)	12.40(13.53%)	1.052
<b>HP-PAMAM-14h</b>	1.72(19.67%)	5.37(67.32%)	14.17(13.00%)	1.039



**Fig. S3:** The data of gel permeation chromatography of HP-PAMAM measured at different times in heating process at 90 °C: 4, 10, 12 and 17 hrs, respectively. It is obvious that the weight-average of molecular weight of HP-PAMAM kept above 3000 throughout the heating process, although the variation of molecular weight distribution was observed, possibly as a result of the chemical decomposition.



**Fig. S4:** Fluorescent excitation and emission spectra of several typical amine-containing compounds after heat treatment. a) Dodecylamine after heat treatment of reflux for 36 hr. Fluorescent measurement was performed at 30°C (above its melting point). b) Diethylamine after heat treatment at 100°C for 48 hr in a hydrothermal synthesis reactor, due to its low temperature of the boiling point under ambient pressure. c) Triethylamine after thermal treatment of reflux for 36 hr. d) Triethanolamine after thermal treatment at 100°C for 36 hr. In a)–d), “Em xxx” indicates an emission spectrum at xxx nm excitation. Similarly, “Ex xxx” stands for an excitation spectrum at xxx nm detection. Herein, we show the fluorescent emission from some examples containing primary, secondary and tertiary amine groups.



**Fig. S5:** IR spectra of Tributylamine measured at different times in a heating process at 150 °C: 2, 4, 6 and 12 hr, respectively. The intensity of the bands at 1362, 1472 and 1650 cm<sup>-1</sup> (indicated by black arrows) increased gradually in the heating process, and the former two bands correlate with that of HP-PAMAM. This result indicates the formation of N→O chromophore in the cases of small amine molecules in the process of heat-treatment.