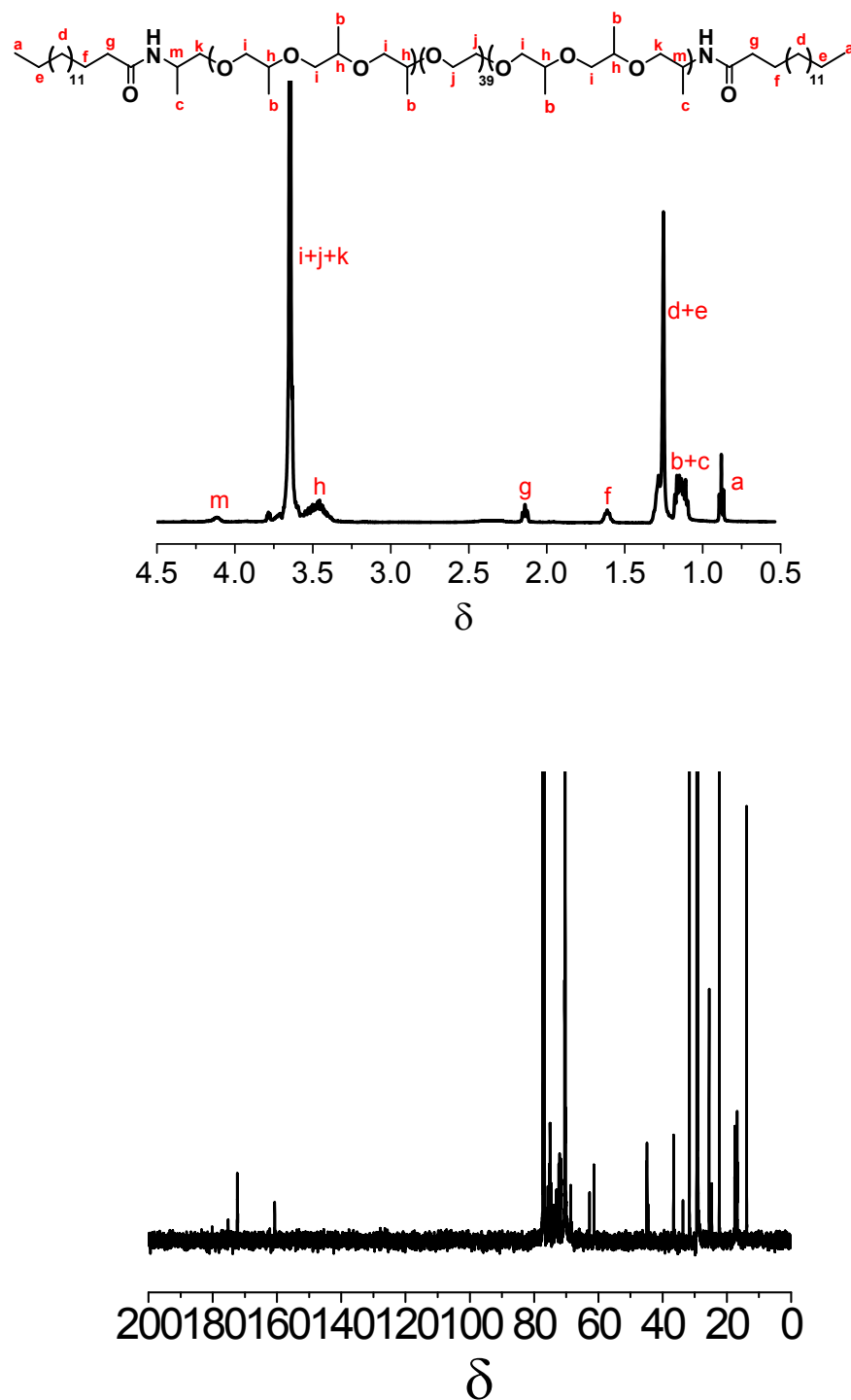


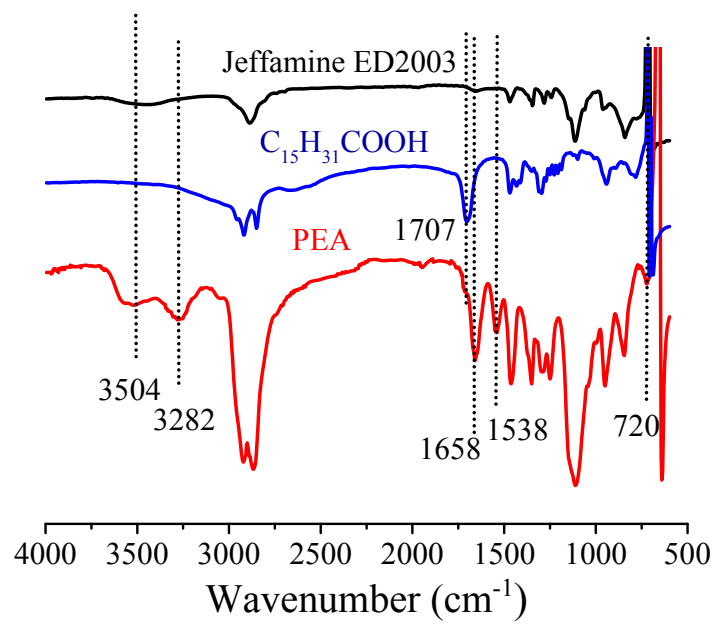
Autofluorescent Micelles Self-assembled from an AIE-active Luminogen Containing Intrinsic Unconventional Fluorophore

Chunyan Liu,* Qingbao Cui, Jing Wang, Yang Liu and Jing Chen

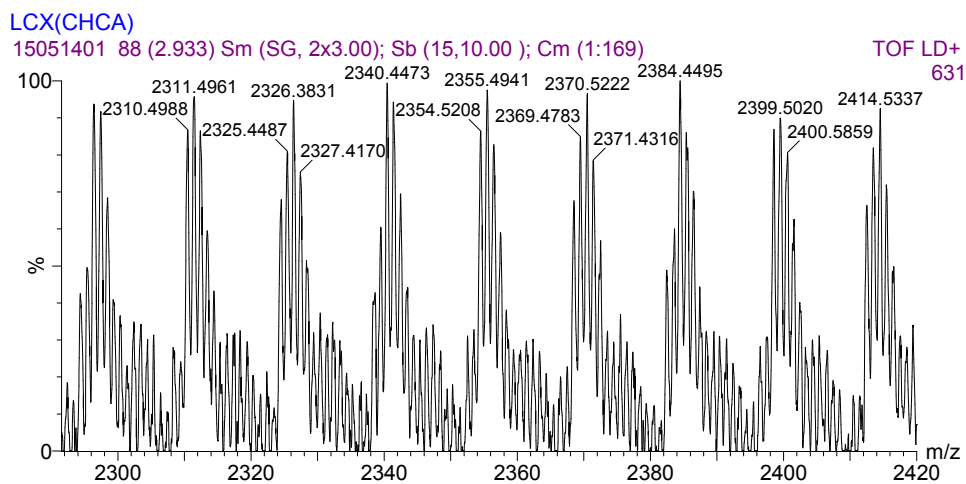
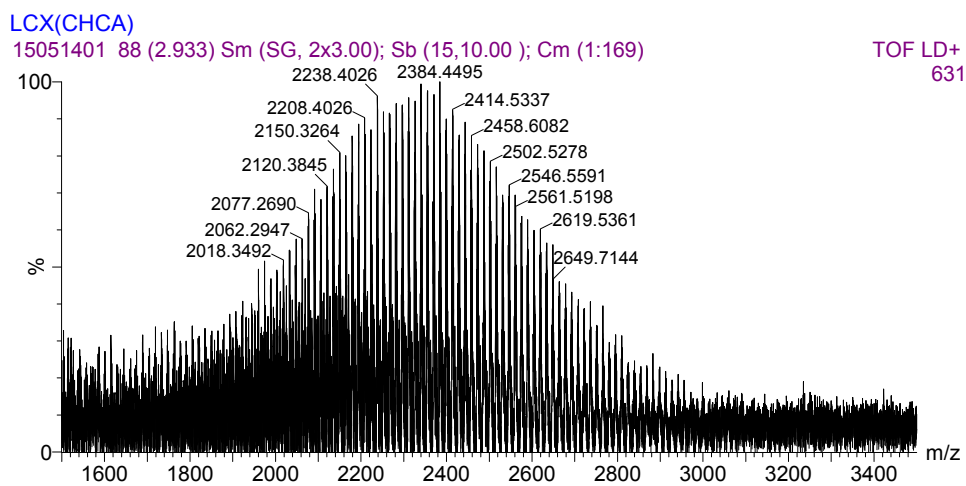
Fig. S1 a) ^1H NMR spectrum and ^{13}C NMR spectrum. b) IR spectra. c) Mass spectra



(a)



(b)



(c)

Fig. S2 Plot of surface tension (γ) versus PEA concentration.

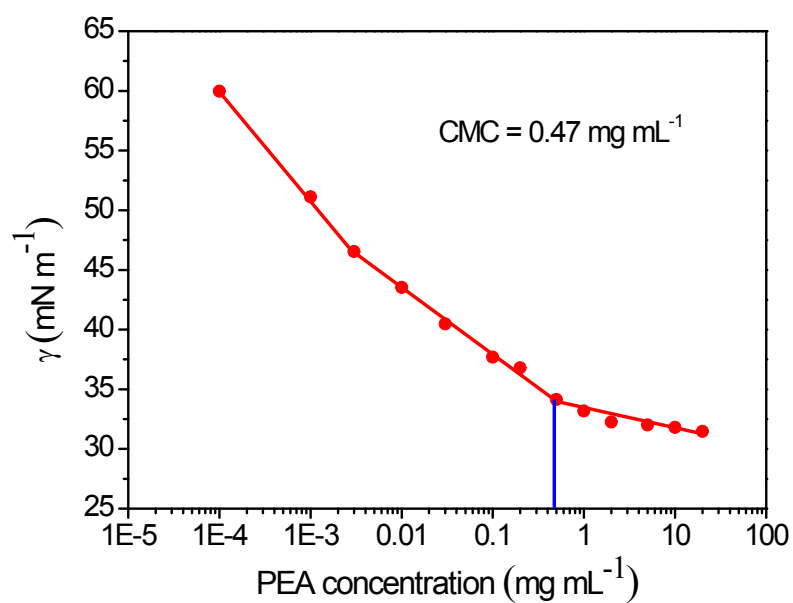


Fig. S3 Time-resolved emission-decay curve of PEA micelles solution.

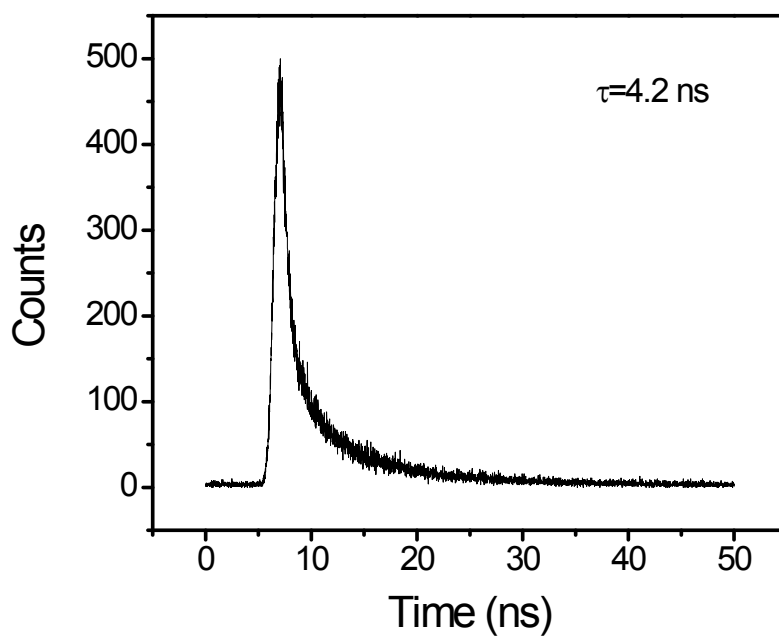
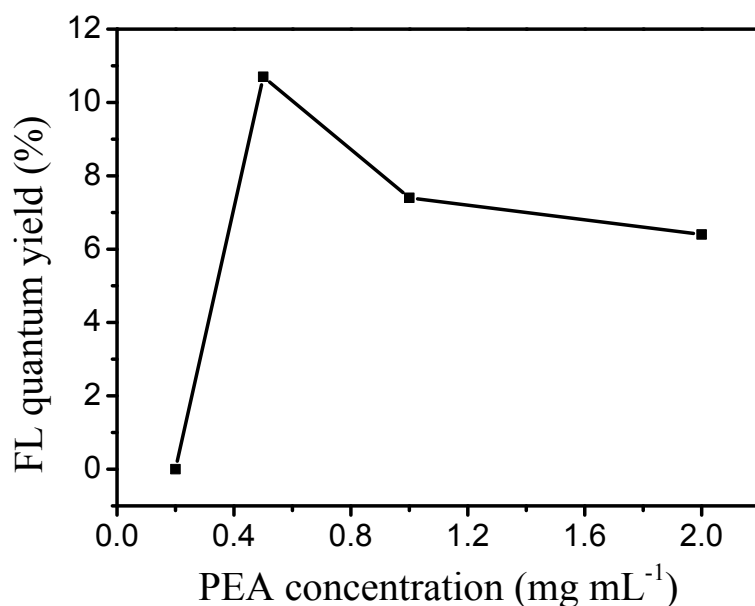


Fig. S4 FL quantum yields of PEA in the solution and aggregated micelles solutions.



Experimental Section

Materials: Palmitic acid and Petroleum ether were purchased from Sinopharm Chemical Reagent Co. Ltd. O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (trade name Jeffamine ED2003 (XTJ-502), average $M_n \sim 1900 \text{ g mol}^{-1}$) was supplied by Sigma-Aldrich. Deionized water was obtained using a Milli-Q water purification system. All agents were used directly without further purification.

Measurements: The FT-IR spectra were recorded on a Bruker-AXS TENSOR 27 FT-IR spectrometer. The sample for infrared analysis was prepared by casting a film onto a potassium bromide (KBr) window from a 2 mg mL^{-1} PEA micelles solution. After evaporation of the majority of the solvent at room temperature the sample was placed under vacuum in an oven at 100°C to remove residual water. NMR spectra were carried out on a Bruker AC-80 NMR instrument, operating at 500 MHz. Mass spectra were obtained on a MALDI TOF Mass Spectrometer (Waters Corp., USA). Equilibrium surface tensions were measured using the lifting circle method on a K100C tensiometer (Krüss, Germany). The measuring accuracy of the device as reported by the manufacturer is $\pm 0.1 \text{ mN m}^{-1}$. Each reported value of surface tension was the average of three measurements that were taken after allowing each of the solutions to equilibrate in the instrument fixed at 20°C . The sizes of micelles in water were determined by Malvern Zetasizer Nano-ZS dynamic light scattering (DLS) equipped with 633 nm He-Ne laser source at room temperature. Transmission electron microscopy (TEM) images were recorded on a Hitachi H-600 electron microscope operated at 120 kV. The samples for TEM measurements were prepared by dropping a drop of 2 mg mL^{-1} PEA micelle solution onto a copper grid and allowed to dry. SEM images were taken on a Hitachi SU8010 microscope. UV-visible absorption spectra were recorded at room temperature on a UV/Vis lambda 35 spectrometer using quartz cuvettes of 1 cm path length. Fluorescence spectra were measured at room temperature on a Hitachi F-7000 Fluorescence (FL) Spectrophotometer with a slit width of 5 nm for both excitation and emission. Weight percentages of carbon, hydrogen, and nitrogen atoms in product were assessed by elemental analysis using a PE 2400CHN elemental analyzer.

Synthesis of PEA: A mixture of Jeffamine ED2003 and palmitic acid (molar ratio is 1:2.1) was heated at 180 °C for 7~8 h. The reaction mixture was then cooled to room temperature. A brown solid product (named PEA, O,O'-Bis(2- palmitamidopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol) was obtained, after filtration and washing with petroleum ether, and dried overnight in an oven at 100 °C. ¹H NMR (500 MHz, CDCl₃): δ 0.88 (t, *J* = 6.75 Hz, 6H; CH₃-CH₂), 1.09~1.18 (m, 21H; CH₃-CH), 1.25~1.28 (m, 48H; CH₂-alkyl chain), 1.61 (m, 4H; CH₂ in β of CO group), 2.14 (t, *J* = 8.45 Hz, 4H; CH₂ in α of CO group), 3.38~3.55 (m, 5H; CH-OCH₂), 3.60~3.69 (m, 170H; CH₂O), 4.11 (m, 2H; CH-NH).

From FT-IR spectroscopy of PEA, both the free and the hydrogen-bonded N-H stretching bands located at 3504 cm⁻¹ and 3282 cm⁻¹, respectively, and C=O stretching (amide I) band located at 1658 cm⁻¹ from the amide groups were found. Stretching vibration of C=O shifts from 1707 cm⁻¹ (in COOH) to 1658 cm⁻¹ (in CONH). The scissoring vibration of N-H located at 1538 cm⁻¹ and scissoring vibration of alkyl chain [-(CH₂)_n, n ≥ 4] located at 720 cm⁻¹ were also observed.

Elemental analysis calculated (%) for C₁₃₁H₂₆₂N₂O₄₇: C 60.14, H 10.02, N 1.07; found: C 59.68, H 10.04, N 1.08.