

Supporting Information

Self-Assembly Facilitated Visible Light-Driven Generation of Carbon Dots

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1. Experimental Section

Materials. TTC4L amphiphile was first synthesized in previous work of our laboratory.¹ TTC8L was synthesized in this work. Terthiophene (TT) was purchased from Puyang Huicheng Chemical Co., Ltd (98%). Rhodamine was purchased from Sinopharm Chemical Reagent Co., Ltd with A. R. grade. Mill-Q water was used to prepare all aqueous solution. The ethanol solvent was purchased from Beijing Tong Guang Fine Chemicals Co. with A. R. grade. All chemicals were used as received.

Preparation of carbon dots. The TTC4L-CDs were prepared by visible light irradiation TTC4L aqueous solution. In a typical preparation procedure, TTC4L aqueous solution with a concentration of 50 μM was irradiated by a daylight lamp (optical density=25 mW cm^{-2}). The reaction process was monitored by fluorescence spectra measurements. After the reaction reached equilibrium, the product was subjected to dialysis (500 kDa) to remove the residual TTC4L to get the pure TTC4L-CDs for further characterizations. TTC8L-CDs was also prepared with the same procedure. Increasing concentration of TTC4L or TTC8L does not affect the size and emission of the CDs, but longer irradiation time is required to reach equilibrium.

Fluorescence measurements. Fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrometer. The excitation wavelength was 365 nm. The slit for excitation was 2.5 nm and for emission was 5 nm. The scanning rate was 1200 nm min^{-1} . The scanning voltage of the Xe lamp was set at 700 V.

Fluorescence quantum yield measurements. The absolute fluorescence quantum yield was measured with the F-3018 Integrating Sphere on Nanolog FL3-2iHR fluorescence spectrometer (Horiba)^{2, 3}. The integrating sphere (Spectralon®) with a diameter of 102 mm which provide a reflectance >95% from 250 - 2500 nm. The sample was placed in the integrating sphere, and

excited with a monochromatic source of wavelength 365 nm. The sample absorbance, A , is

$$A = \frac{L_b - L_c}{L_b} \quad (1)$$

where L_b is the integrated excitation profile when the sample is diffusely illuminated by the integrating sphere's surface; and L_c is the integrated excitation profile when the sample is directly excited by the incident beam.

The quantum yield is photons emitted to photons absorbed:

$$\Phi_f = \frac{E_c - (1 - A) \cdot E_b}{L_a \cdot A} = \frac{E_c - E_a}{L_a - L_c} \quad (2)$$

where E_c is the integrated luminescence of the sample caused by direct excitation, and E_b is the integrated luminescence of the sample caused by indirect illumination from the sphere. The term L_a is the integrated excitation profile from an empty integrating sphere (without the sample, only a blank). E_a is the integrated luminescence from an empty integrating sphere (only a blank).

For integration of function L over the wavelength, λ , the integration limits can be from 10 nm below the excitation wavelength and 10 nm above the excitation wavelength.

The spectra recorded were background corrected, using a blank sample holder, and corrected for wavelength dependence of the spectrofluorometer and integrated sphere.

Fluorescence life measurements. The fluorescence lifetime measurement was performed on Delta flex ultrafast lifetime spectrometer (Horbia) with 355 nm laser source. The lifetime curves were fitted with the single exponential decay Equation 3 and three-exponential decay Equation 4 from DAS6 Software (Horbia) ⁴.

$$I_t = I_1 e^{-t/\tau_1} \quad (3)$$

$$I_t = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2} + I_3 e^{-t/\tau_3} \quad (4)$$

where I_t is the change in absorbance at time t , τ is the lifetime.

UV-Vis measurements. UV-Vis spectra were obtained with a spectrometer (Shimadzu, UV-1800) using a 10mm quartz cell in the range of 200 to 700 nm with a step size of 0.5 nm.

^1H NMR measurements. ^1H NMR spectra were acquired on Bruker Avance III 500 MHz NMR with 512 scanning times. The samples were prepared in an ethanol- d_6 and deuterium oxide mixed solvent with volume ratio of 1:1. The ethanol- d_6 was used to increase the concentration to 200 μM for better signal resolution.

Transmission electron microscope (TEM). The self-assembled structures before light irradiation were characterized by transmission electron microscope (FEI Tecnai G2 T20). Drops of samples were put onto 200 mesh copper grids coated with Formvar film. Excess water was removed followed by staining the film negatively with uranyl acetate. After removal of the excess staining liquid by filter paper, samples were then allowed to dry in ambient condition. The TEM morphology and high-resolution transmission electron microscope (HTEM) of carbon dots were recorded on FEI Tecnai F20. Drops of samples were put onto 200 mesh copper grids coated with ultrathin carbon film. Excess water was removed by filter paper and dry in ambient condition.

Atomic force microscope (AFM). AFM images were recorded in a Nanoscope scanning probe microscope (Bruker, Dimension Icon) with ScanAsyst mode under ambient condition. Drop of samples were put onto a silicon wafer with a spin coater to form a uniform film.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed with an X-ray Photoelectron Spectrometer (Kratos Analytical Ltd., AXIS Ultra). Several drops of samples were put onto a silicon wafer and were allowed to dry under ambient condition. With Al K_α ($h\nu=1486.7\text{eV}$) as X-ray source, the operating voltage is 15 kV and the emission current is 40 mA.

Raman scattering measurements. A Raman Imaging Microscope System (Horiba, HR800) excited with 514 nm laser was employed to acquire the Raman spectra of the CDs. Drop of samples were put onto a silicon wafer with a spin coater to form a uniform film.

FT-IR measurements. FT-IR spectra were measured with spectrometer (Thermo Scientific, NICOLET iN10 MX). Drops of samples were put onto diamond window plate and dry under ambient condition. The spectra were collected from 4000 to 600 cm⁻¹ with 16 scanning times with transmission mode.

Two-photon fluorescence (TPF) measurement. The excited source consists of a regeneratively amplified Ti and sapphire laser system (Spectra-Physics, SP-5 W, 80 fs, 80 MHz, adjustable from 700 to 880 nm). The TPF signal was collected at the right angles from excited solution placed in the 1cm fluorescence cuvette. The signal was guided into a monochromator (Zolix, Omni-λ300) and detected by a photomultiplier (Zolix, PMTH-S1C1-CR131).

Nanosecond time resolved transient absorption measurements. Time resolved transient absorption spectra were collected on a laser flash photolysis spectrometer (Edinburgh, LF900). Excitation of the TTC4L aqueous solution was accomplished using a Nd:YAG laser system from Continuum (Surelite I10 355nm) operating at 10 Hz. The probe light source was a Xe lamp (450 W) collected from 300 to 600 nm. Single wavelength kinetic traces were detected at 452 nm and fitted with Equation 5 (Edinburgh software LP920).

$$B_t = A + B_1 e^{-t/\tau_1} \quad (5)$$

where B_t is the differential absorption intensity at time t , τ is the lifetime.

Electron paramagnetic resonance measurements. The continuous-wave (cw) X-band electron paramagnetic resonance (EPR) experiments were performed on an EPR spectrometer (Bruker,

E500) operating at 9.85 GHz and with a modulation frequency at 100 kHz. Typical setting: center field at 3510.00 G, microwave power was 10.02 mW and modulation amplitude was 2.00 G. The irradiated source was a mercury lamp (100 W). The samples were prepared in a quartz tube with plasticine to seal. EPR spectrum was simulated using the Bruker Software Xepr.

Quantum chemistry calculation. Molecule modellings were calculated at restricted density functional theory level. The hybrid functional B3LYP and the 6-311+g(d,p) basis set were used. All calculations were performed using the Gaussian09 package.

2. Tab. S1

Tab.S1 Lifetime and FLQY of TTC4L and TTC4L-CDs.

\square	τ	ratio	χ^2	FLQY
TTC4L	0.32ns	82%	1.35	2.55%
	2.62ns	18%		
TTC4L-CDs	2.51ns	100%	1.31	87.04%

Two lifetime means the monomeric state and the aggregated state of TTC4L, respectively.¹

3. Fig. S1-Fig. S1

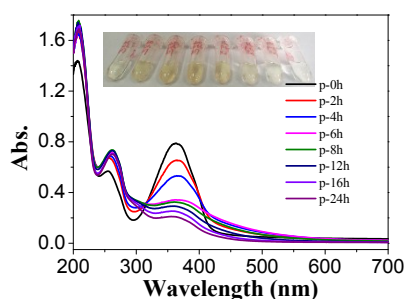


Fig. S1. UV-vis spectra of the 50 μ M TTC4L aqueous solution under different photo irradiation time.

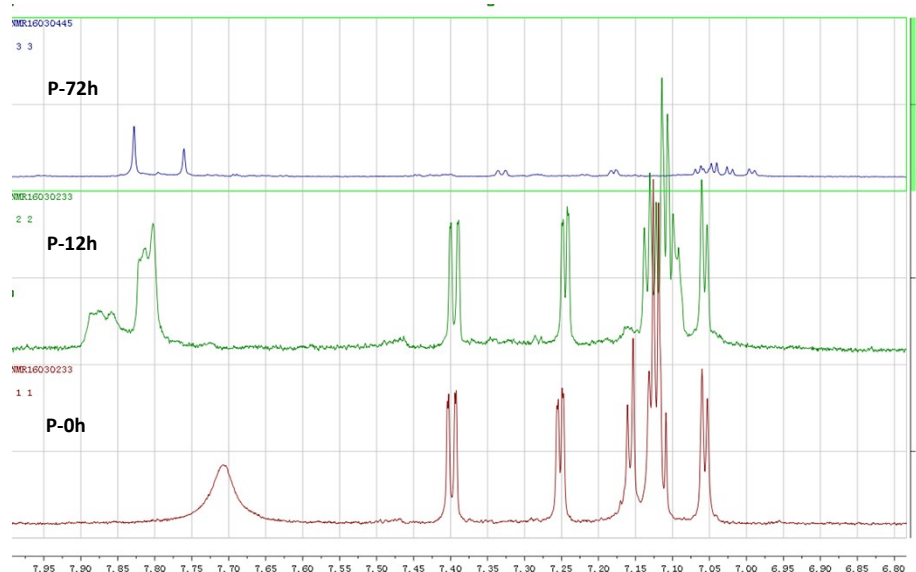


Fig. S2 ^1H NMR spectra of TTC4L with different irradiation time. TTC4L samples (solvent: ethanol- d_6 : deuterium oxide=1:1) were exposed to a daylight lamp with the intensity of 15 mW cm^{-2} . The disappearance of terthiophene group peaks with the increase of irradiation time was observed.

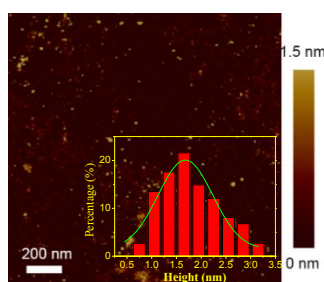


Fig. S3 AFM image and height distribution (inset) of TTC4L-CDs.

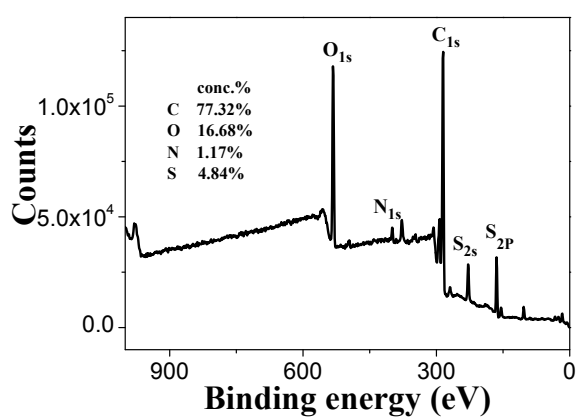


Fig. S4 XPS spectrum of TTC4L without light irradiation.

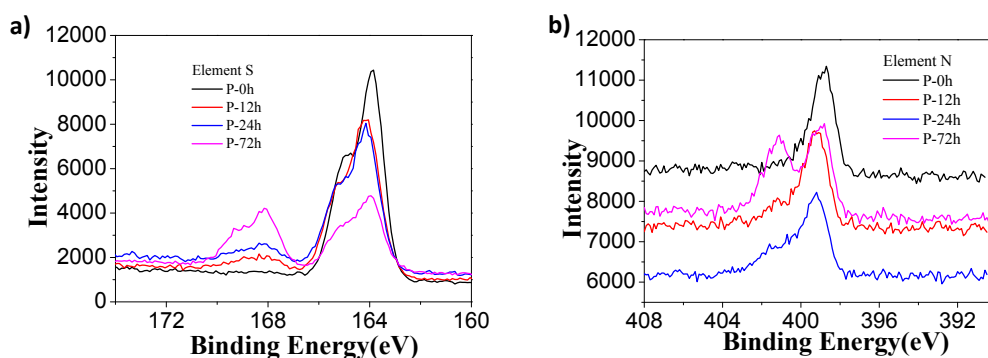


Fig. S5 a) Variation of the XPS signal for the S element in TTC4L aqueous solution with different irradiation time. b) Variation of the XPS signal for the N element in TTC4L aqueous solution with different irradiation time (a daylight lamp with the intensity of 15 mW cm^{-2}).

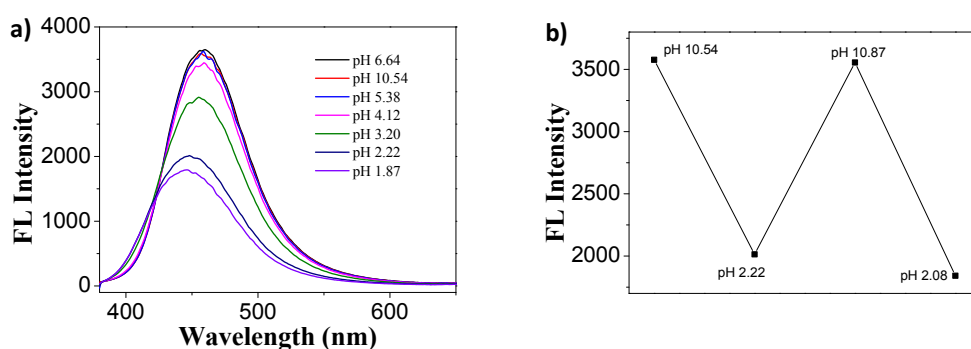


Fig. S6. pH responsive and reversibility of the fluorescence of TTC4L-CDs. a) Fluorescence spectra of TTC4L-CDs at various pH. b) The reversibility of the fluorescence intensity of TTC4L-CDs in acidic or alkaline condition.

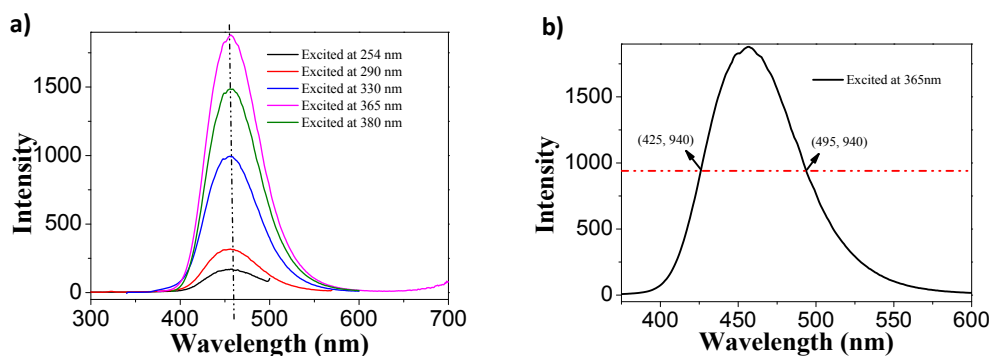


Fig. S7 Excitation-independent emission property of TTC4L-CDs and the FWHM of TTC4L-CDs fluorescence spectrum. a) Fluorescence spectra of TTC4L-CDs at different excitation wavelength; b) The FWHM of fluorescence spectrum of TTC4L-CDs excited at 365 nm.

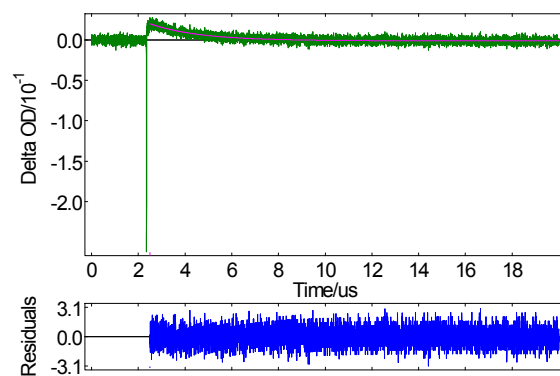


Fig. S8 Lifetime decay of TTC4L triplet at 452 nm. Fitting results: $\tau_1=2.12 \mu\text{s}$, $B_1=0.021$, $A=-0.001$, $\chi^2=0.71$

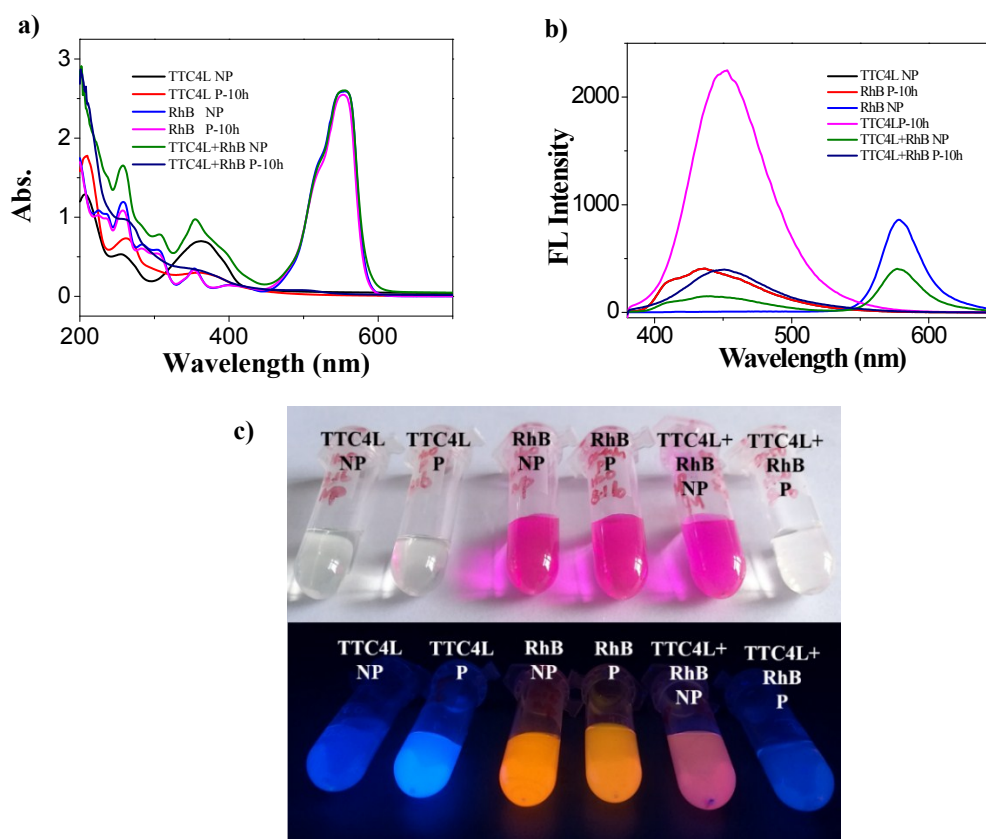


Fig. S9 Variation of the fluorescence on TTC4L (50 μM)-RhB(50 μM) system under visible light irradiation (a daylight lamp with optical intensity of 25mW cm^{-2}). **a)** UV-visible spectra of TTC4L-RhB system before and after light irradiation with an effective removal efficiency of 98.85%. **b)** Fluorescence spectra of TTC4L-RhB system. **c)** Daylight photo and fluorescence photo (under 365 nm UV lamp) of TTC4L-RhB. **Abbreviations:** NP: no photo irradiation; P: photo irradiation; RhB: rhodamine B

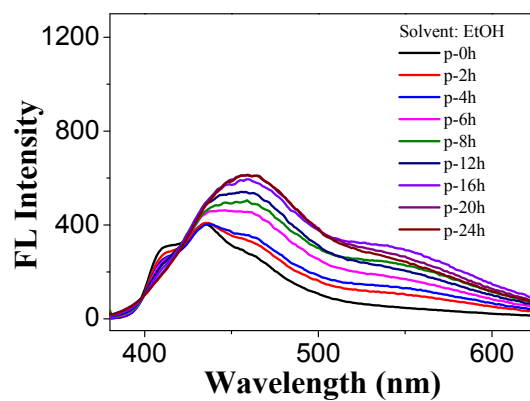


Fig. S10 Fluorescence intensity for 50 μM TTC4L in ethanol with increasing irradiation time (a daylight lamp with optical intensity of 25mW cm^{-2}).

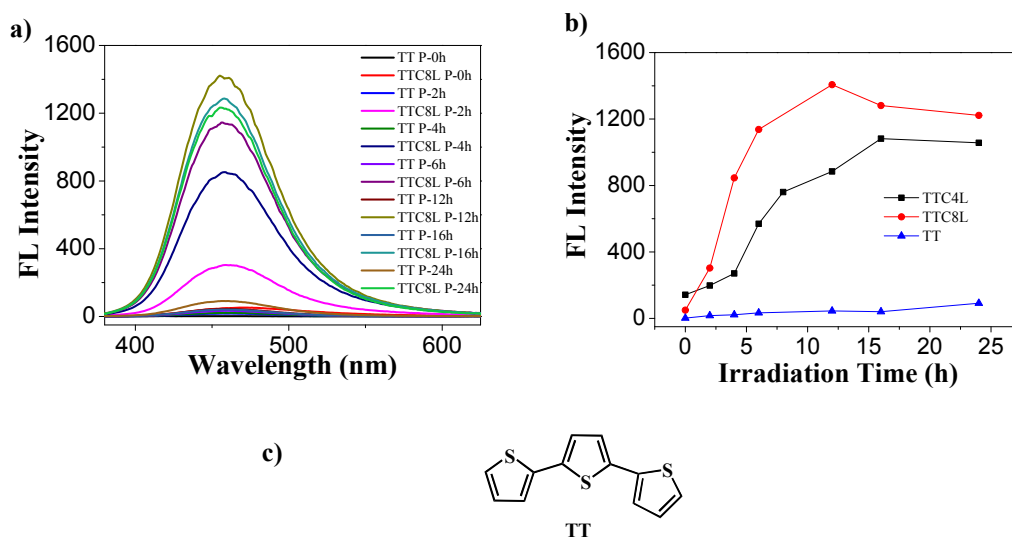


Fig. S11 Fluorescence intensity of TTC8L and TT with different light irradiation time (a daylight lamp with optical intensity of 25mW cm^{-2}). **a)** Fluorescence spectra of TTC8L and TT with different irradiation time. **b)** Fluorescence intensity of TTC4L, TTC8L and TT with increase of light irradiation time. TT represents the terthiophene compound. **c)** Molecular structure of terthiophene (TT).

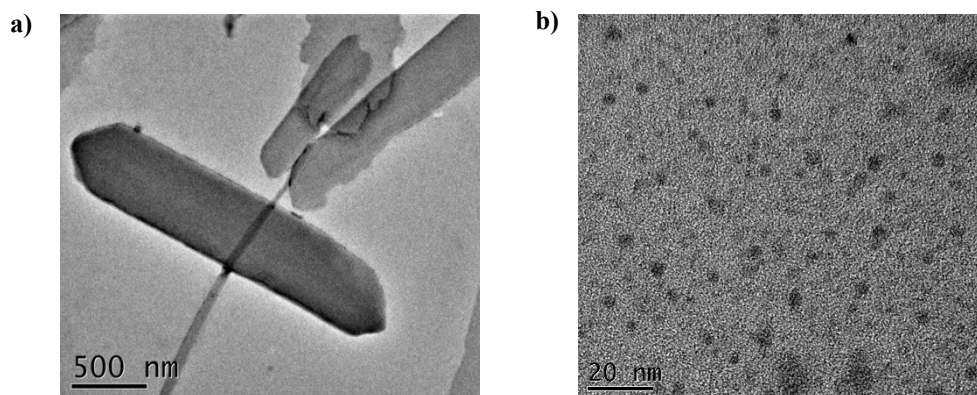
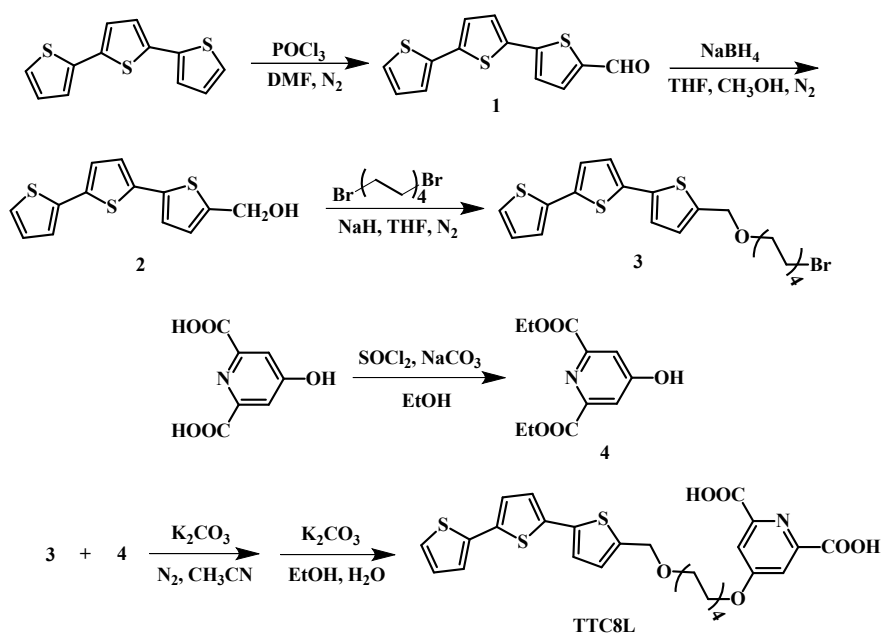


Fig. S12 TEM images for the Self-assembled structure of **a)**, TTC8L and **b)**, TTC8L-CDs.

4. Synthesis of TTC8L

TTC8L was synthesized in this work according to the synthetic method of TTC4L.¹



Scheme S1 Synthetic route of TTC8L

The product TTC8L occurred as yellowish green solid: ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.64 (s, 2H), 7.52 (d, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.24 (q, *J* = 3.8 Hz, 2H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 4.60 (s, 2H), 4.22 (t, *J* = 6.3 Hz, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 1.74 (m, 2H), 1.52 (m, 2H), 1.40-1.26 (m, 8H); FT-MS (*m/z*): 570.10593 (M⁺) (Fig. S12). Anal. Calcd for C₂₈H₂₉NO₆S₃ (%), C, 58.82; H, 5.11; N, 2.45. Found: C, 59.61; H, 4.86; N, 2.37.

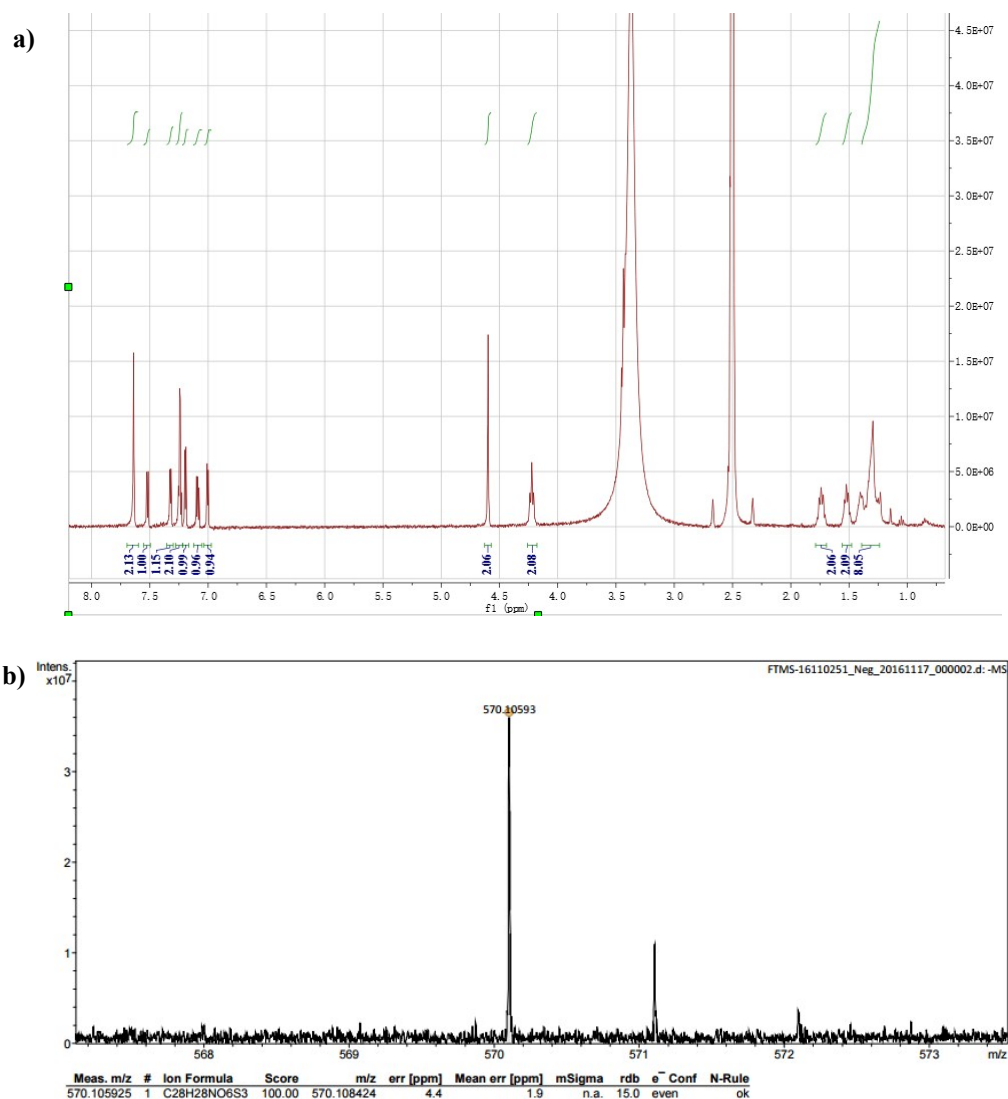


Fig. S12 Characterizations of synthesized TTC8L. **a** ^1H NMR spectrum of TTC8L. **b** FT-MS spectrum of TTC8L.

5. Supplementary references

- 1 L. Zhao, X. Cheng, Y. Ding, Y. Yan and J. Huang, *Soft Matter*, 2012, **8**, 10472-10478.
- 2 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230-232.
- 3 L. Porres, A. Holland, L.-O. Pålsson, A. P. Monkman, C. Kemp and A. Beeby, *Journal of Fluorescence*, 2006, **16**, 267-273.
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