Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Transformable fluorescent nanoparticles (TFNs) of amphiphilic block copolymers for visual detection of aromatic amines in water

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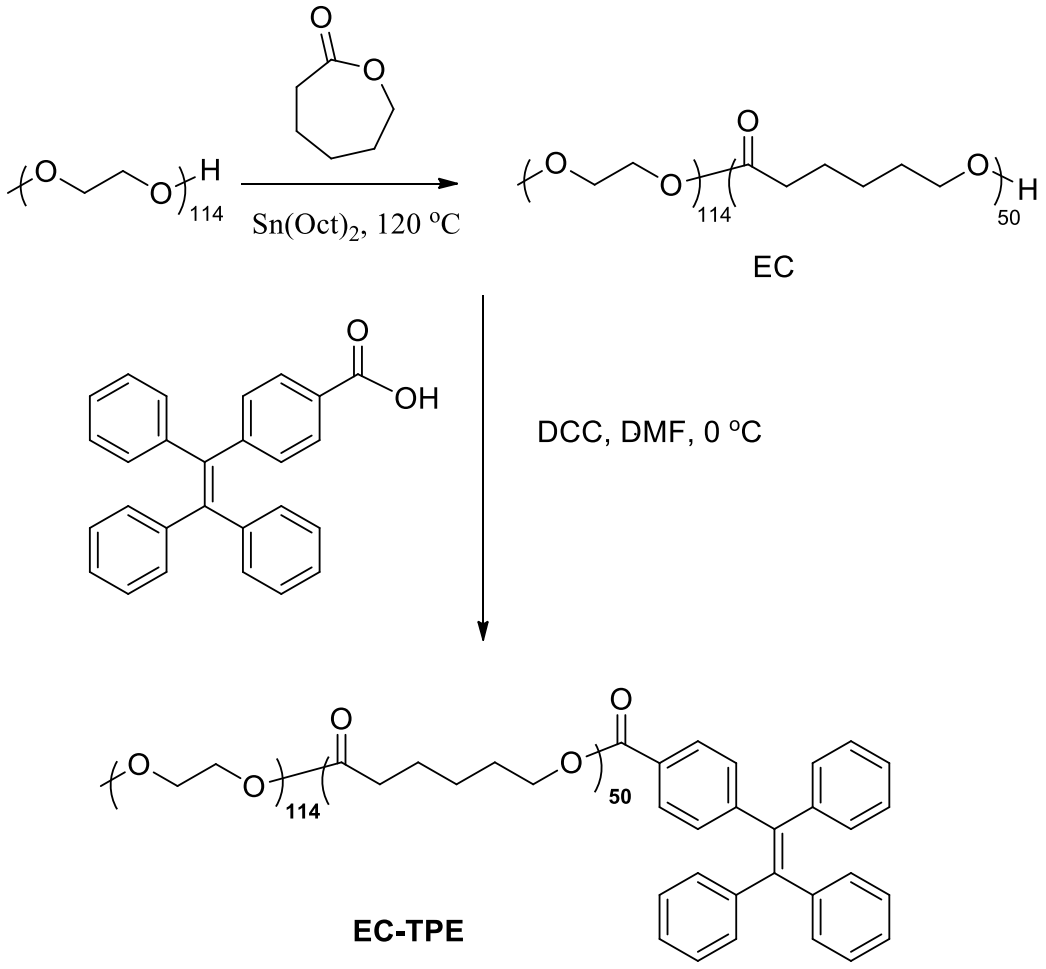


Scheme S1 Synthetic route for poly(ethylene glycol)-block-poly(caprolactone) mono-terminated with tetraphenylethene (EC-TPE).

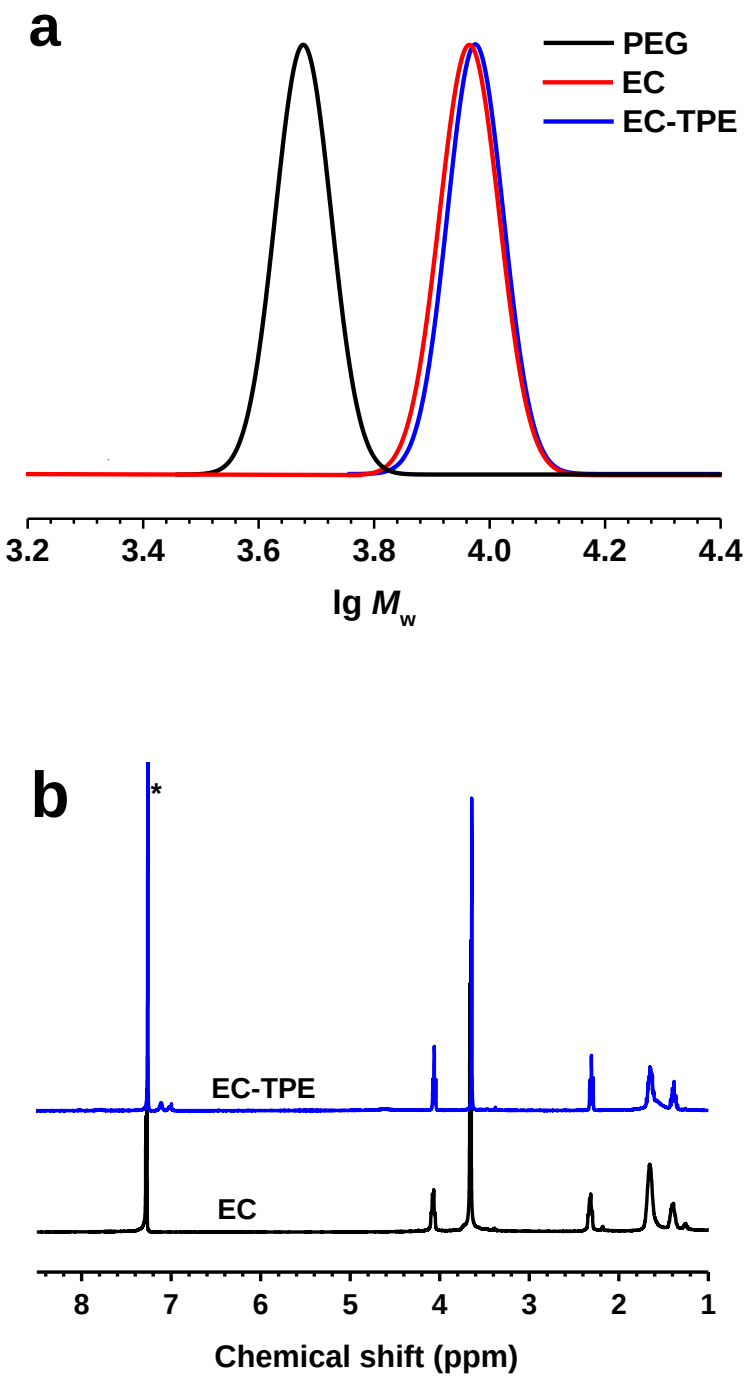


Fig. S1 (a) GPC traces of PEG, EC, and EC-TPE. (b) ^{1}H NMR spectra of EC-TPE using $CDCl_3$ as solvent. The solvent peak was marked with an asterisk.

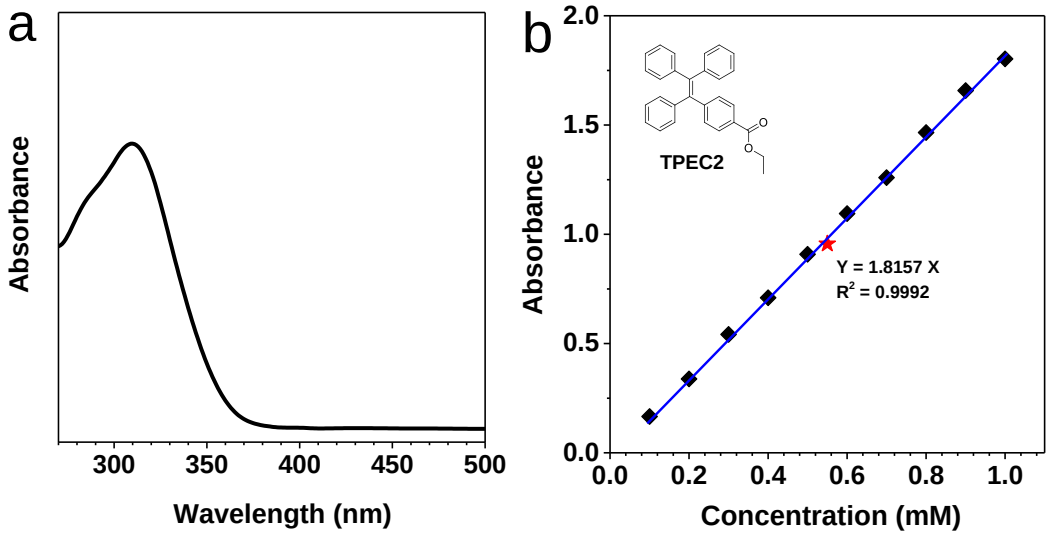


Fig. S2 (a) UV-vis spectrum of EC-TPE in THF (0.55 mM). (b) Plot of absorbance (312 nm) of TPEC2 in THF against TPEC2 concentration.

Calculation of the weight fraction of TPE in polymer based on ^{1}H NMR

The weight fraction of TPE (W_{TPE}) in the polymer was calculated as follows:

$W_{TPE} = M_{TPE}/M_{polymer} \times 100\%$

$= (331\ g\ mol^{-1}) / (11100\ g\ mol^{-1})$

$= 3.0$ wt%.

Calculation of the weight fraction of TPE in polymer using UV-vis spectra

The weight fraction of TPE molecules in polymer practically was calculated using the following fumula:

$W_{TPE} = A\ M_{TPEC2} / K / C / M_{polymer}$

= 0.956 ×404 g/mol /(1.8157 L/mmol) /0.55 mM / (11100 g/mol)

= 3.5 wt%.

M_{TPEC2} and $M_{polymer}$ are molecular weight of TPEC2 (404 g/mol) and EC-TPE (11100 g/mol), respectively. *A* is absorbance of EC-TPE/THF solution at 312 nm. *K* is the slope of calibration curve (1.8157 L/mmol, Fig. 5b). *C* is the concentration of EC-TPE/THF solutions.

The weight fraction of TPE in the polymer determined using UV-vis spectra (3.5 wt%) is close to that by ^{1}H NMR (3.0 wt%).

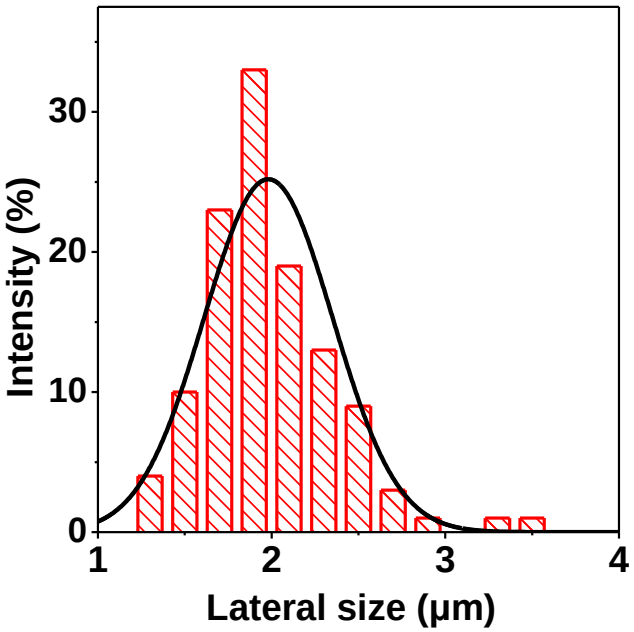


Fig. S3 Size distribution of EC-TPE nano-sheets in SEM images (about 50 nano-sheets were analysed).

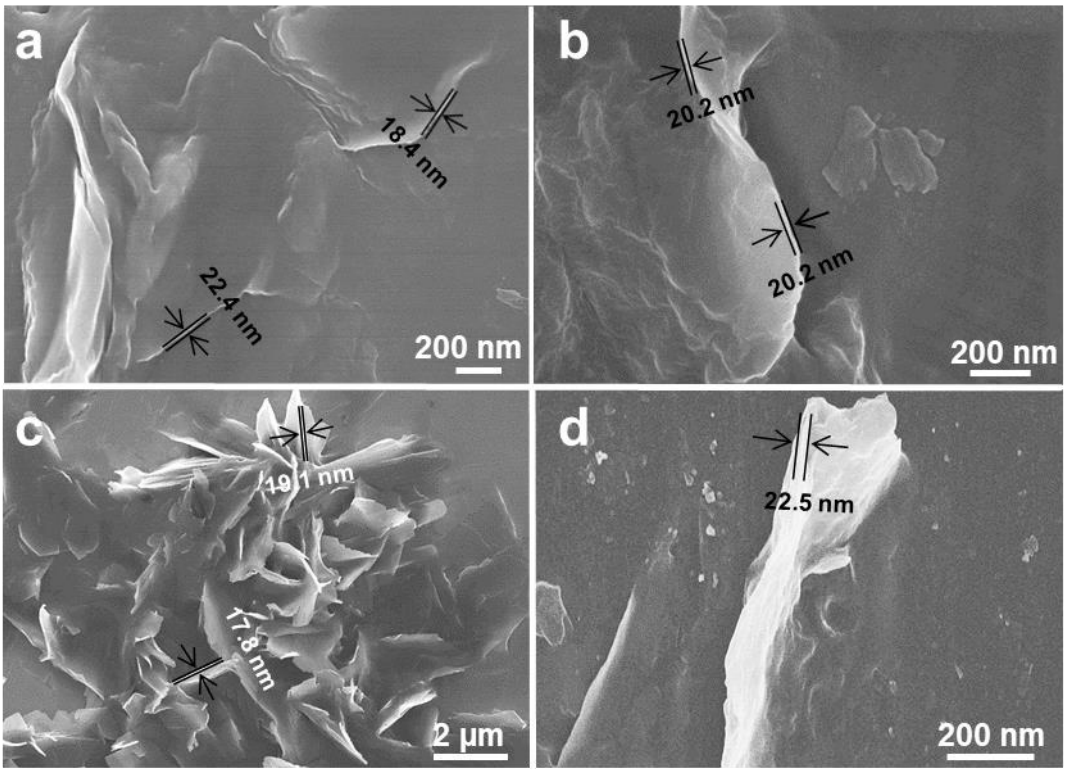


Fig. S4 Scanning electron microscopy (SEM) images of EC-TPE nano-sheets.

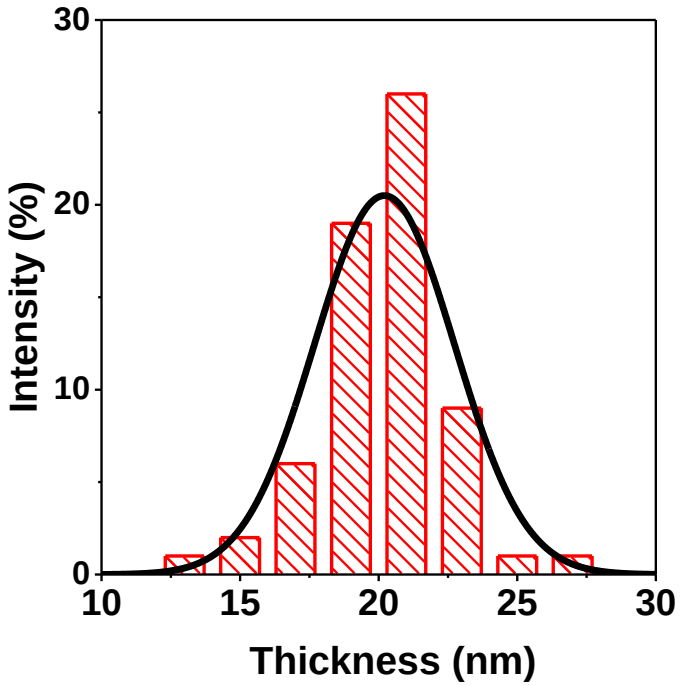


Fig. S5 Thickness distribution of EC-TPE nano-sheets in SEM images. About 65 nano-sheets were analysed.

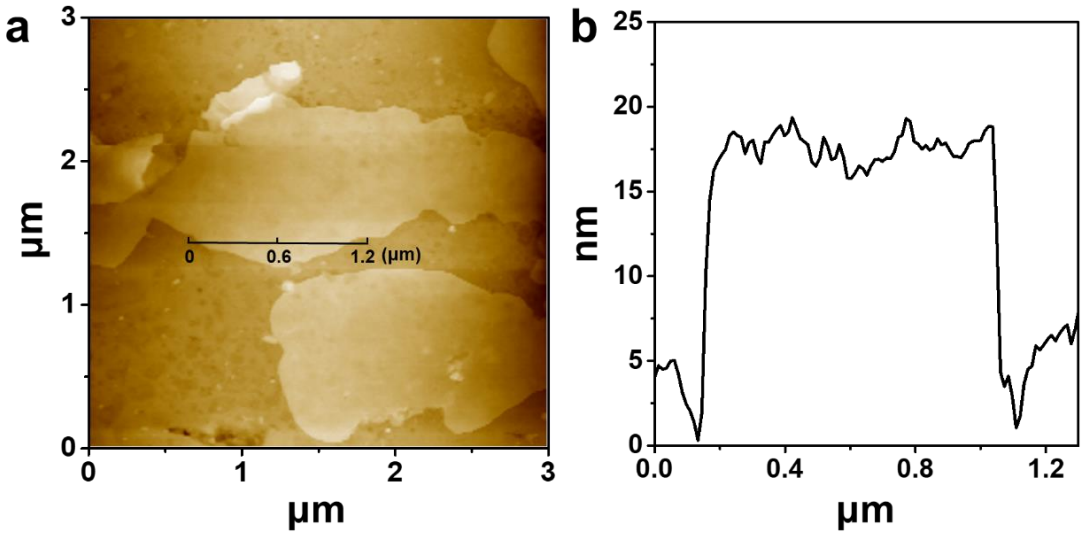


Fig. S6 Tapping mode atomic force microscope (AFM) height images (a) and the cross-sectional profile (b) of EC-TPE nano-sheets.

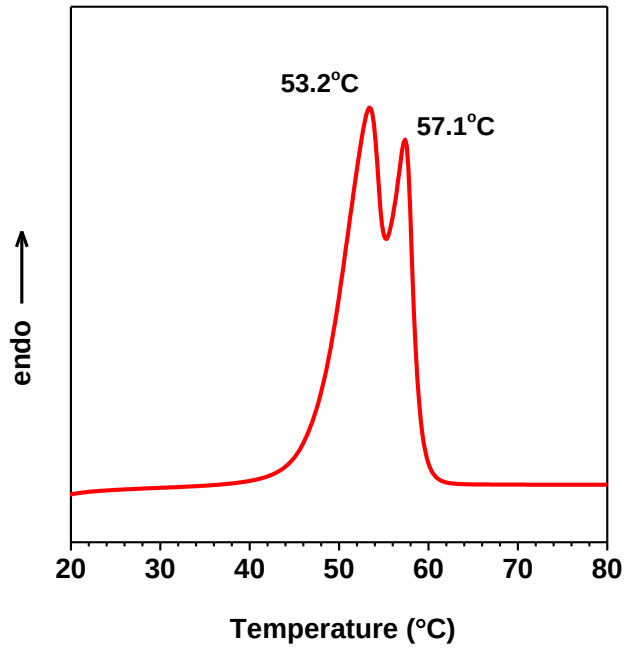


Fig. S7 DSC heating traces of EC-TPE.

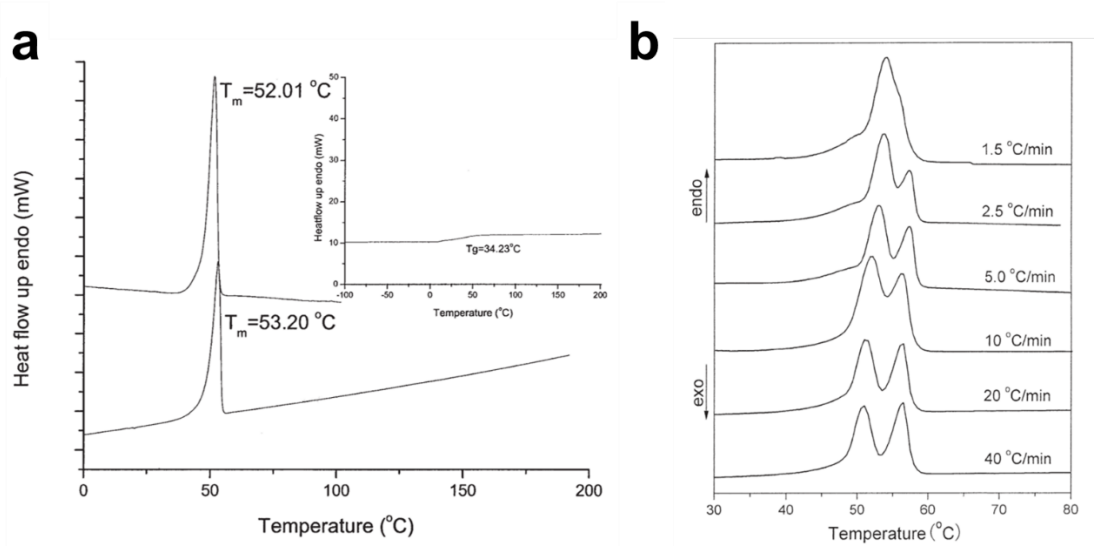


Fig. S8 (a) DSC heating scans of PEG (M_n=5000 g/mol) reported in reference.[1] (b) DSC heating scans of PCL-PEG-PCL triblock copolymers reported in reference.[2]

Calculation of folding number of PCL

The length of fully extended polycaprolactone (PCL) chains was estimated to be 0.86·DP nm using ChemDraw 7.5 (DP was the number of repeating units of PCL).

The folding number of PCL in EC-TPE was determined to be the integer of 0.86·DP/*l* -1, where *l* was the thickness of EC-TPE lamellae.

Calculation of the aggregation number of EC-TPE nano-sheets

Based on the lamellar morphology EC-TPE micelles, the aggregation number, *N*, of EC-TPE micelles were estimated from the following formula:

$N=N_A \cdot d \cdot V/M$

where N_A is Avogadro's number (6.02×10^{23}), M is molecular weight of EC-TPE (11,100 g/mol), d is density of EC-TPE, estimated using $d=W_{TPE}\cdot d_{TPE}+W_{PCL}\cdot d_{PCL}+W_{PEG}\cdot d_{PEG}$ = (331×1/11100)×1.088 g/cm^3 + (5700/11100) × 1.145 g/cm^3 + 5000/11100×1.270 g/cm^3 =1.192 g/cm^3. (d_{PCL} is density of PCL, 1.145 g/cm^3, http://en.wikipedia.org/wiki/Polycaprolactone. d_{TPE} is density of TPE, 1.088 g/cm^3, http://en.wikipedia.org/wiki/Tetraphenylethylene. d_{PEG} is density of TPE, 1.270 g/cm^3, http://en.wikipedia.org/wiki/Polyethylene glycol). W' is weight fraction of TPE, PCL and PEG respectively. V is volume of each micelle, calculated using $V=A^2H$ (A is the side length of the lamellar, 2000 nm. H is the height the lamellar, 20 nm).

$N=N_A\cdot d\cdot V/M$

$=6.02\times10^{23}$/mol ×1.192 g/ cm^3 ×2000×2000×20×$(10^{-7})^3$ cm^3 /(11100 g/mol)

$=5.2\times10^6$

Calculation of the aggregation number of EC-TPE nano-spheres

Based on the spherical morphology EC-TPE micelles, the aggregation number, N, of EC-TPE micelles were estimated from the following formula:

$N=N_A\cdot d\cdot V/M$

where N_A is Avogadro's number (6.02×10^{23}), M is molecular weight of EC-TPE (11,100 g/mol), d is density of EC-TPE, estimated using $d=W_{TPE}\cdot d_{TPE}+W_{PCL}\cdot d_{PCL}+W_{PEG}\cdot d_{PEG}$ = (331×1/11100)×1.088 g/cm^3 + (5700/11100) × 1.145 g/cm^3 + 5000/11100×1.270 g/cm^3 =1.192 g/cm^3. (d_{PCL} is density of PCL, 1.145 g/cm^3,

http://en.wikipedia.org/wiki/Polycaprolactone. d_{TPE} is density of TPE, 1.088 g/cm^3, http://en.wikipedia.org/wiki/Tetraphenylethylene. d_{PEG} is density of TPE, 1.270 g/cm^3, http://en.wikipedia.org/wiki/Polyethylene glycol). W' is weight fraction of TPE, PCL and PEG respectively. V is volume of each micelle, calculated using $V=4/3\pi(D/2)^3$ (D is diameter of the micelle, 66 nm).

$N=N_A \cdot d \cdot V/M$

$=6.02\times10^{23}$/mol × 1.192 g/ cm^3 $\times 4/3\pi\times(66/2\times10^{-7}$ cm$)^3$ /(11100 g/mol)

$=9.8\times10^3$

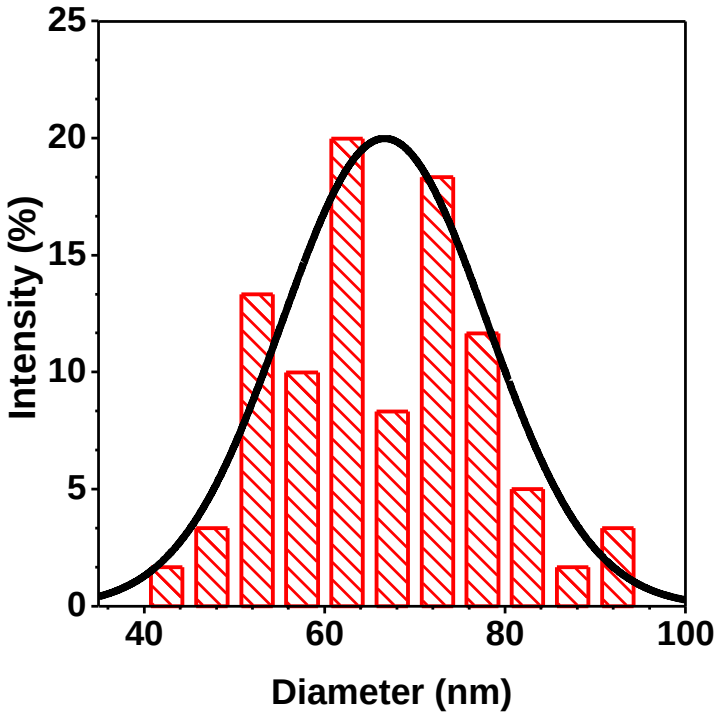
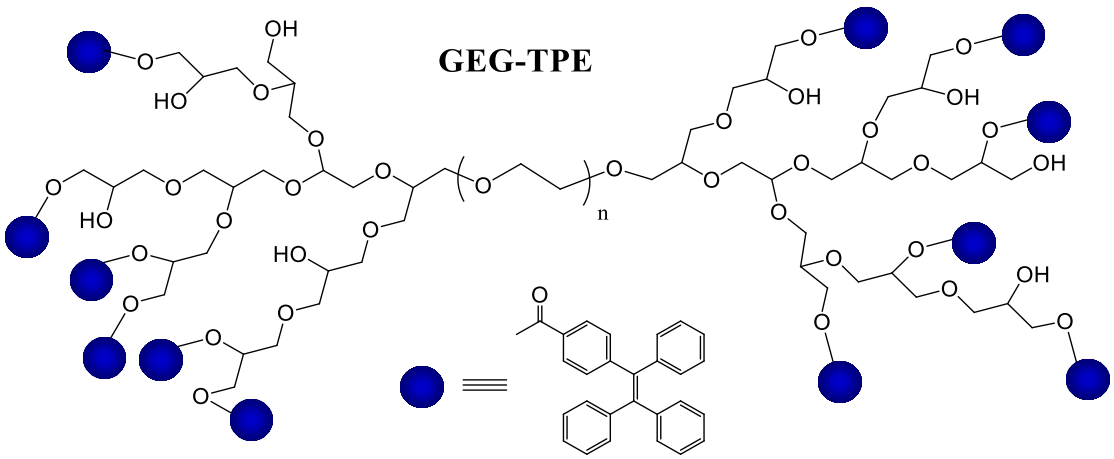


Fig. S9 Diameter distribution of EC-TPE nanoparticles in SEM and TEM images.



Scheme S2 Chemical structure of GEG-TPE.

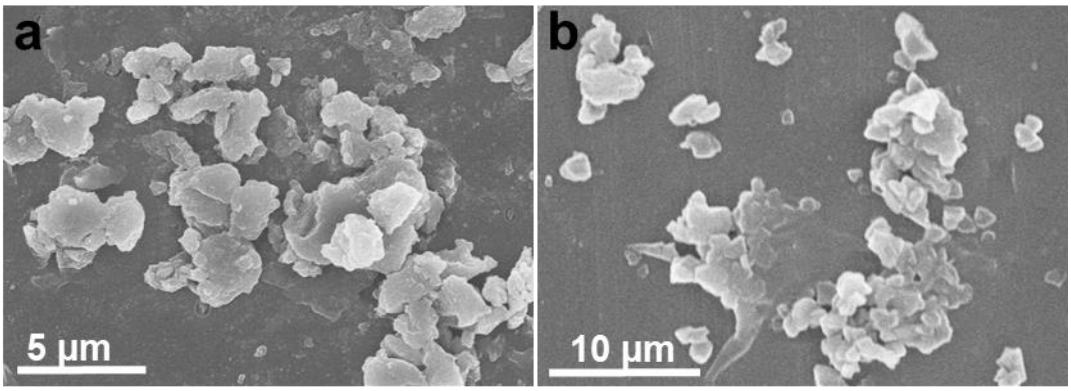


Fig. S10 Scanning electron microscopy (SEM) images of (a) EC/TPE blends and (b) TPE aggregates in water.

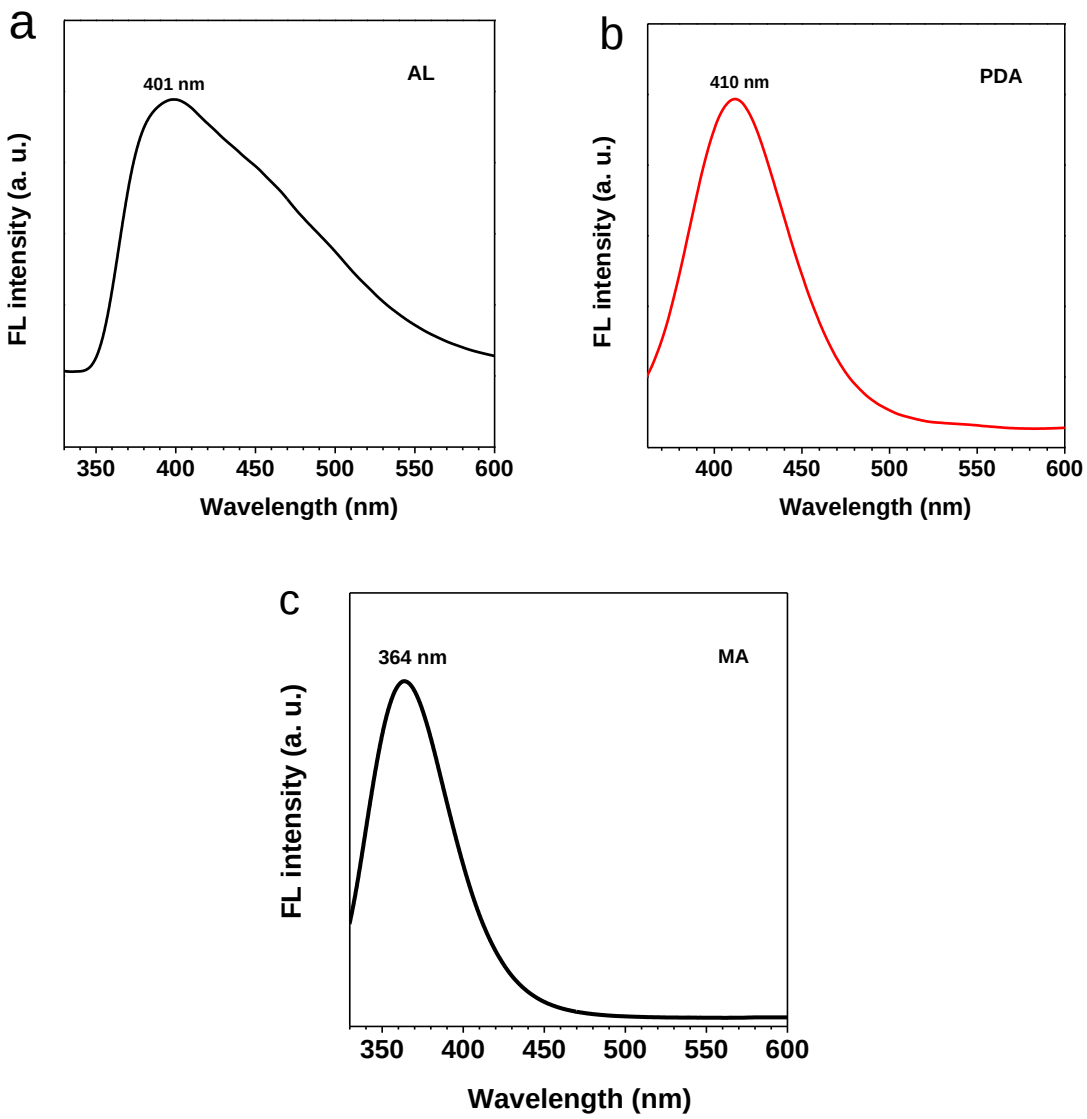
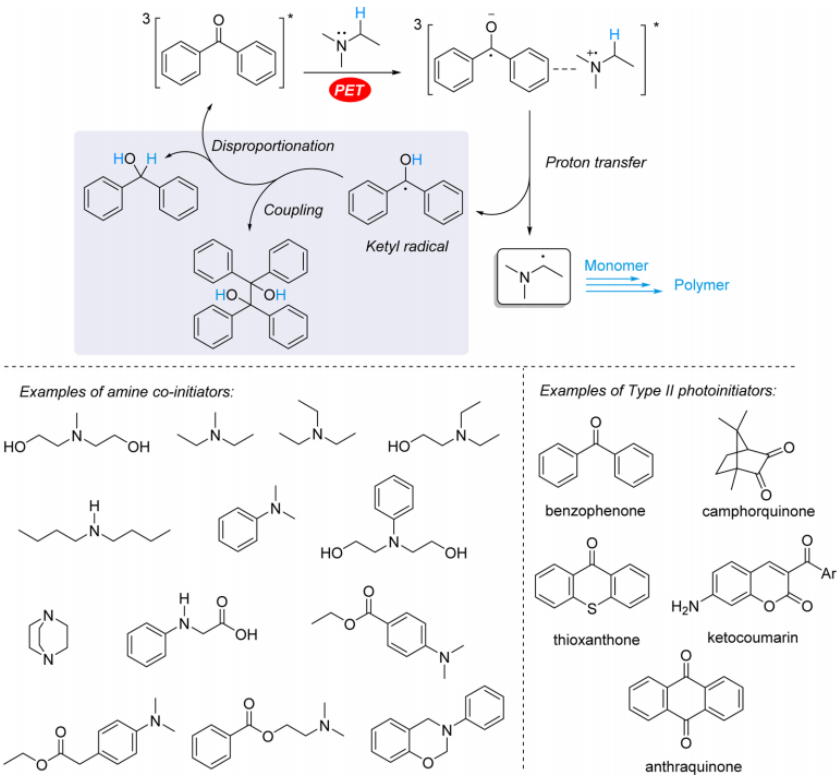


Fig. S11 Fluorescence spectra of AL (a), PDA (b) and MA (c) in water. Concentration: 1 mM. Excitation: 310 nm.



Scheme S3 Schematic representation of a photoinitiation with benzophenone as an example of ketone-based photoinitiator and a tertiary amine co-initiator.[3]

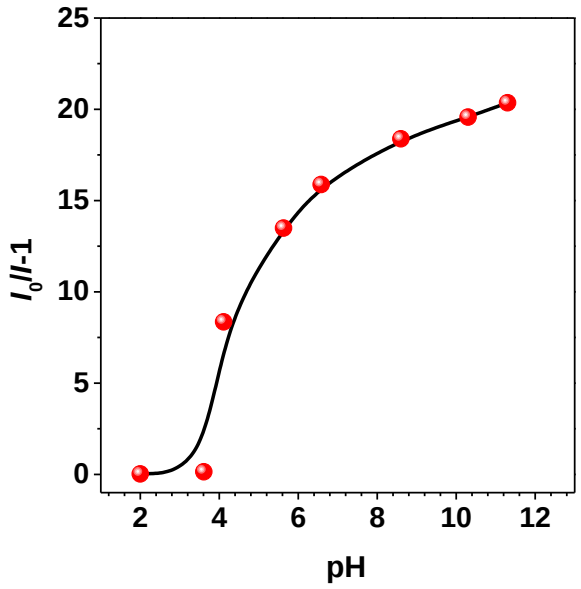


Fig. S12 Fluorescence response of EC-TPE nanosheets to AL at various pH. EC-TPE concentration: 0.1 mg/mL, AL concentration: 10 mg/L.

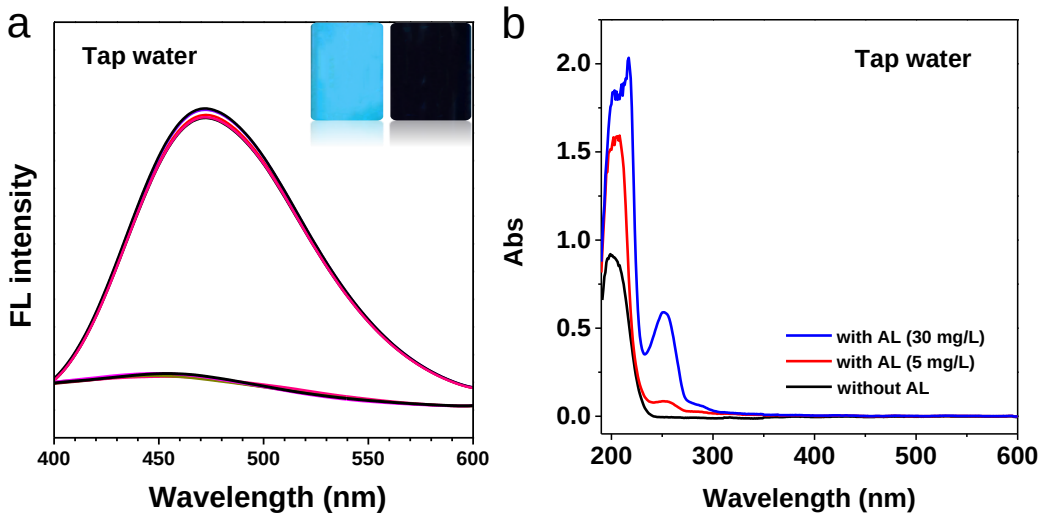


Fig. S13 Detection of AL in tap water. (a) Fluorescence spectra of EC-TPE nano-sheet aqueous suspensions in the absence and presence of AL (5 mg/L). (b) UV-vis spectra of tap water in the absence and presence of AL.

Tap water was taken in our laboratory and used without further purification.

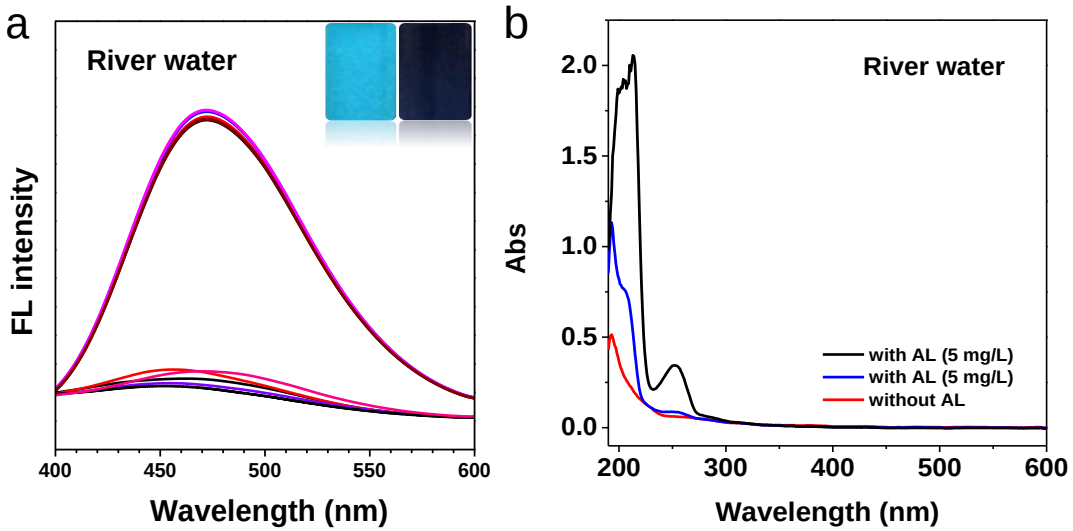


Fig. S14 Detection of AL in river water. (a) Fluorescence spectra of EC-TPE nano-sheets aqueous suspensions in the absence and presence of AL (5 mg/L). (b) UV-vis spectra of river water in the absence and presence of AL.

The river water was taken from Pearl River (Zhongda dock) and passed through a filter of 220 nm to remove insoluble impurities.

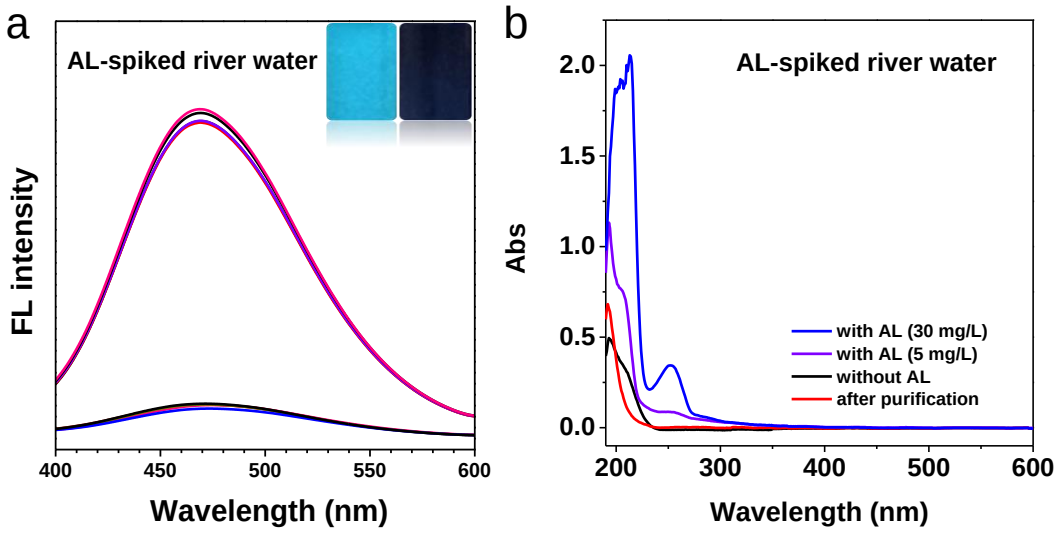


Fig. S15 Detection of AL in river water. (a) Fluorescence spectra of EC-TPE nano-sheets aqueous suspensions in the absence and presence of AL (5 mg/L). (b) UV-vis spectra of river water before and after purification using activated carbon.

The AL-spiked river water was used as simulated polluted water for AL detection. the AL-spiked river water was purified using activated carbon to remove AL but leave salt ions in the solution for preparation of reference samples. 10 mL of AL-spiked river water was added 2 g of activated carbon powder. The mixture was stirred for 10 min. The activated carbon powders were filtered off. The filtrate was used to prepare reference samples.

Notes and references

1. F. Hua, X. Yang, B. Gong and E. Ruckenstein, *J Polym Sci Pol Chem*, 2005, **43**, 1119-1128.

2. Z. Wei, F. Yu, G. Chen, C. Qu, P. Wang, W. Zhang, J. Liang, M. Qi and L. Liu, *J Appl Polym Sci*, 2009, **114**, 1133-1140.

3. S. Dadashi-Silab, S. Doran and Y. Yagci, *Chem Rev*, 2016, **116**, 10212-10275.