Electronic Supporting Information

Dissipative Aggregation-Induced Emission Behaviour of an Amino-functionalized Tetraphenylethene using a pH Oscillator

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1. Materials
Trityl chloride (97%), benzophenone (99.5%), zinc powder (99.9%) fuming nitric acid, Raney Ni and tetrahydrofuran (THF) were obtained from Adamas Reagent Co., Ltd (Shanghai, China). Acetic acid (glacial), dichloromethane and ethyl acetate were obtained from Tansoole (Shanghai, China). THF was purified by distillation from sodium benzophenone under nitrogen immediately prior to us. All chemicals were used without purification unless otherwise noted.

2. Characterisations
$^1$H spectra were recorded on a 400 MHz Bruker Avance-400 NMR spectrometer. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer and the FL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer with a Xenon discharge lamp excitation. Samples for absorption and emission measurements were carried out in 1 cm × 1 cm quartz cuvettes. Average hydrodynamic diameter (Dh) of polymer aggregates was determined using a dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern Instrument Ltd., UK) instrument. The morphology was observed using a Hitachi S-4800 scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) analyzer. The dispersed samples in solution dried on a carbon-coated copper grid without any metal coating. A PHSJ-3F pH meter (Shanghai REX, China) was used to record the pH-time curve using the REX DC1.0 data collection software package (Shanghai REX, China). A ZDJ-4A automatic titrator (Shanghai REX, China) was used to determine the pKa value by potentiometric acid-base titration. The reactor for the pH oscillating system was fed by a Longer Dispensing Peristaltic Pump (BT100-1F, China). The laser beam was produced by a stabilized laser source MRLIII-655L (Changchun New Industries Optoelectronics Technology Co., Ltd., China). The intensity of the scattering light was measured by a Maya 2000 pro micro fibre spectrometer. Movies and pictures were obtained by a Canon IXUS 130 digital camera. Millipore water was used to prepare all aqueous solutions. All experiments were performed at room temperature (~25 °C) unless otherwise specified.
3. Synthesis

3.1 Synthesis of tetraphenylethene (A)\(^{[1]}\)

Tetraphenylethene was synthesized according to the standard procedure. A suspension of benzophenone (5 g, 30 mmol) and zinc (5.9 g, 90 mmol) in 300 mL dried THF was stirred under nitrogen at 0 °C. TiCl\(_4\) (5 mL, 60 mmol) was injected slowly over a period of 30 min. The ice-water-bath was removed and the mixture was stirred at 70 °C for 12 h. The reaction was quenched by aqueous solution of potassium carbonate and extracted with ethyl acetate (2 × 200 mL). The organic phase was combined, washed with brine, and dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated under vacuum to afford A as a white solid (5 g, 98%) \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.02 (m, 8H), 7.09-7.11 (m, 12H).\)

3.2 Synthesis of 1,1,2,2-tetrakis(4-nitrophenyl)ethene (B)\(^{[2]}\)

A (5 g, 15 mmol) was dissolved in a mixed solvent of acetic acid and dichloromethane (30 mL/60 mL). 30 mL fuming nitric acid was added slowly to the reaction mixture, and the mixture was stirred for 16 h at room temperature. The reaction mixture was extracted with dichloromethane (2 × 200 mL), and the combined organic phase was washed with water, and dried over anhydrous Na\(_2\)SO\(_4\). After filtration, the filtrate was concentrated to afford crude product, which was recrystallized from 1,4-dioxane to give B as a light yellow solid (4.6 g, 60%). \(^{1}\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta: 8.12 (d, J = 8.7 Hz, 8H), 7.35 (d, J = 8.7, 8H).\)

3.3 Synthesis of 4,4',4''',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (TPE-4N)\(^{[2]}\)

B was dissolved in 10 ml ethanol. Raney nickle (~2 g) and hydrazine monohydrate (670 mg, 13.4 mmol) were added to the solution carefully and the reaction mixture was heated to reflux for 2 hours. After the reaction mixture was cooled to room temperature, the nickle was filtered off and the solvent was evaporated under reduced pressure to get light yellow solid in 84 % yield. \(^{1}\)H NMR (400 MHz, DMSO -d\(_6\)) \(\delta: 6.60 (d, J = 8.5 Hz, 8H), 6.27 (d, J = 8.5 Hz, 8H), 4.97 (s, 8H).\)
4. pH-responsive AIE

Fig. S2 (a) Absorption spectra and (b) PL spectra of TPE-4N in aqueous solutions (c=3.6×10^{-4} M) with different pH values, respectively (λ_{ex}=365 nm). (c) The maximum absorption wavelength (λ_{max}) and the maximum PL intensity (I_{max}/I_0) of the suspensions as a function of pH. (I_0 and I_{max} are the maximum PL intensity of the suspension with pH of 3.66 and different pH values, respectively) (d) Hydrodynamic size distributions at pH 3.66 and 8.31 for TPE-4N.
Fig. S3 Tyndall effect of the TPE-4N at pH 3.66 and 8.31, respectively

Fig. S4 SEM images of TPE-4N in water formed from solutions with different pH
5. Determination of pKa value

The pH profile of TPE-4N was determined by potentiometric acid-base titration. In 150 mM of NaCl aqueous solution (10 ml) saturated with nitrogen gas, 0.25 mmol TPE-4N were dissolved. The pH of all solutions were set to 2 with 1 M HCl prior to titration. Subsequently, potentiometric titration was carried out with 0.1 M NaOH using an automatic titrator. pKa values were obtained according to the plateau values of the titration curves (Fig. S6). The plateau values indicated that the pKa value of TPE-4N was 4.6.

6. The construction of an oscillating system

A. Reactor
The pH oscillating system used in our studies was based on the sulfur oscillatory mechanism under a continuously stirred tank reactor (CSTR) \cite{3}. The CSTR is a cylindrical-shaped glass reactor with a liquid volume of 24 mL with two input tubes and one output tube, as shown in Figure S7. A combination pH meter and a thermometer were connected to a computer.

![Illustration of the CSTR](image)

Fig.S7(a) The illustration of the CSTR for sustainable oscillations and (b) the experimental setup.

**B. Procedures**

The mixed solution of Sodium dithionite (7.5 mmol/L) (Na$_2$S$_2$O$_4$) and TPE-4N (0.36mmol/L) with pH 12 and hydrogen peroxide (23 mmol/L) (H$_2$O$_2$) solutions were prepared separately using deionized water in 250 mL volumetric flasks. Throughout the experiments, the solution of sodium dithionite in its reservoir was bubbled with nitrogen gas to prevent autoxidation. The experimental setup for the pH oscillator was shown in Figure S8. The oscillating reactions were carried out at different temperatures in the CSTR. Reactant solutions were pumped into the reactor through the inlet tubes by means of a Longer Dispensing Peristaltic Pump (BT100-1F, China). The excess reaction mixture was removed through an outlet tube. A magnetic stirrer at a constant stirring rate was used to ensure uniform mixing. The maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered to the desired value. The reactions in the batch system were initiated by the addition of the H$_2$O$_2$ solution. The pH-time data was monitored by a pH meter connected to a computer using a REXDC 1.0 data collection software package.
Fig.S8 pH-time series measured in a CSTR at T=21.5°C

7. References

