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Electronic Supplementary Information

Diethylamino functionalized tetraphenylethenes: structural and electronic modulation of photophysical properties, implication for CIE mechanism and application to cell imaging†

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Fig. S8 Size distribution, D_m and PD of DEATPE suspensions in 10/90 THF/water mixture at different time after being freshly prepared.

Fig. S9 D_m of DEATPE suspensions in THF/water mixtures with f_w of (A) 80% and (B) 90% at different time after being freshly prepared.

Fig. S10 TEM images and ED patterns of DEATPE suspensions in 20/80 THF/water mixture: (A) freshly prepared; (B) standing for 12 h.

Fig. S11 TEM images and ED patterns of DEATPE suspensions in 10/90 THF/water mixture: (A and B) freshly prepared; (C) standing for 12 h.

Fig. S12 (A) Emission spectra and (B) fluorescent photographs of DFDEATPE in DMF with varying water fractions. Concentration = 40 μM; excitation wavelength = 365 nm.

Fig. S13 Normalized emission spectra of DEATPE and DFDEATPE crystals.

Fig. S14 Normalized emission spectra of DFDEATPE in varying solvents. Concentration = 40 μM.

Fig. S15 XRD patterns of as prepared DEATPE and DFDEATPE solids.

Fig. S16 Photographs of (A) as prepared and (B) ground solids of TPE taken under 365-nm UV illumination. (C) XRD patterns and (D) emission spectra of as prepared and ground solids of TPE.

Experimental section

Materials. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine (TEA) was distilled and dried over potassium hydroxide. Dichloroform (DCM) was distilled over calcium hydride under nitrogen before use. Other solvents, such as pyridine, *n*-hexane, dimethyl formamide (DMF), and ethyl ether, are of high purities and were used as received. 4,4′-bis(diethylamino)benzophenone (**1**), benzophenone (**2a**), 4,4′-difluorobenzophenone (**2b**), 4-bromobenzonitrile (**4**), dichlorobis(triphenylphosphine)palladium(II) [$Pd(PPh_3)_2Cl_2$], copper(I) iodide (CuI), triphenylphosphine (PPh_3), zinc dust (Zn), titanium tetrachloride ($TiCl_4$), potassium carbonate (K_2CO_3), and anhydrous sodium sulfate (Na_2SO_4) were purchased from Aldrich and used without further purification. 1,1-Bis[4-(diethylamino)phenyl]-2-(4-ethynylphenyl)-2-phenylethylene (**3**) was prepared according to our previous procedures.[1]

Instruments. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 spectrometer using chloroform-*d* ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) high-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 (DEATPE and DFDEATPE) mass spectrometer and a Bruker solariX FTICR mass spectrometer (CNDEATPE). Absorption spectra were taken on a Milton Roy Spectronic 3000 Array spectrometer. Emission spectra were taken on Perkin-Elmer spectrofluorometer LS 55. XRD data were obtained on a Rigaku Corporation, Japan D/max-2200/PC. Single crystal X-ray diffraction intensity data were collected on a Bruker-Nonices Smart Apex CCD diffractometer at 100 K with graphite monochromated Cu-Kα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). The mean diameter (D_m) and polydispersity (PD) of the suspensions were determined on a Malvern Zetasizer nano ZS90 instrument at room temperature. Transmission electron microscopy (TEM) and electron diffraction (ED) patterns were obtained on a JEOL Ltd. JEM-2010 TEM instrument.

Luminogens preparation. DEATPE, DFDEATPE and CNDEATPE luminogens were prepared according to the synthetic routes shown in Scheme 1 (**see main text**). The detailed synthetic procedures and characterization data are given below.

Synthesis of 4,4'-(2,2-diphenylethene-1,1-diyl)bis(N,N-diethylaniline) (DEATPE). Into a 250 mL two-necked round-bottom flask equipped with a reflux condenser was placed 0.507 g (7.6 mmol) of zinc dust. The flask was evacuated under vacuum and flushed with dry nitrogen three times, after which 80 mL of THF was added. The mixture was cooled to around 5 ℃, to which 0.42 mL of $TiCl_4$ was added. The mixture was slowly warmed to room temperature and stirred for 0.5 h and then refluxed for 2.5 h. The mixture was again cooled to around 5 ℃, charged with 0.16 mL of pyridine and stirred for 10 min. Then 20 mL of THF solution containing benzophenone (**2a**; 0.547 g, 3 mmol) and 4,4′-bis(diethylamino)benzophenone (**1**; 1.07 g, 3.3 mmol) was slowly added. The mixture was refluxed overnight. The reaction was quenched with a 10% K_2CO_3 solution. A large amount of water was added until the solid is turned to white. The mixture was then extracted with DCM three times and the combined organic layer was washed by brine twice. The mixture was dried over 5 g of anhydrous Na_2SO_4 for 4 h. The crude product was condensed and purified on a silica-gel column using gradient eluent from hexane to DCM/hexane (1/1 by volume). A yellow solid was obtained in 67% yield. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.09, 7.07, 7.06, 7.05, 7.04, 7.03 (10H, aromatic protons), 6.87 (d, 4H), 6.40 (d, 4H), 3.27 [m, 8H, $–(NCH_2)_4$], 1.11 [t, 12H, $–(CH_3)_4$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 146.27, 145.56, 141.48, 136.08, 132.79, 131.57, 131.25, 127.46, 125.25, 110.76, 44.15 ($–NCH_2$), 12.62 ($–CH_3$). HRMS (MALDI-TOF): Calcd. for $C_{34}H_{38}N_2$: 474.3035. Found: 474.3039 [M^+].

Synthesis of 4,4'-[2,2-bis(4-fluorophenyl)ethene-1,1-diyl]bis(N,N-diethylaniline) (DFDEATPE). The synthetic procedure of DFDEATPE is similar to that of DEATPE described above. Light yellow solid, yield: 70%. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 6.98, 6.96 (m, 4H), 6.82 (d, 4H), 6.78 (t, 4H), 6.41 (d, 4H), 3.27 [m, 8H, $–(NCH_2)_4$], 1.11 [t, 12H, $–(CH_3)_4$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 162.11, 159.72, 146.35, 141.91, 136.02, 132.96, 132.71, 130.73, 114.35, 110.74, HRMS (MALDI-TOF): Calcd. for $C_{34}H_{36}F_2N_2$: 510.2847. Found: 510.2916 [M^+].

Synthesis of 4-{{4-{2,2-bis[4-(diethylamino)phenyl]-1-phenylvinyl}phenyl}ethynyl}benzonitrile (CNDEATPE). Into a 100 mL two-necked flask were added 11.6 mg of $PdCl_2(PPh_3)_2$, 2 mg of CuI, 6 mg of PPh_3, 97 mg of 4-bromobenzophenone (**4**), and 250 mg of 1,1-bis[4-(diethylamino)phenyl]-2-(4-ethynylphenyl)-2-phenylethylene (**3**). The flask was evacuated under vacuum and flushed with dry nitrogen three times, after which 60 mL of TEA was added. The mixture was stirred at 60 ^{o}C for 24 h. The formed solid was removed by filtration and washed with diethyl ether. The filtrate was concentrated by a rotary evaporator. The crude product was purified on a silica-gel column with DCM as eluent. A brown solid was obtained in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.60 (d, 2H, aromatic protons meta to –CN), 7.56 (d, 2H, aromatic protons ortho to –CN), 7.25 (2H, overlapped with $CDCl_3$ signal, aromatic carbons ortho to –C≡), 7.11, 7.10, 7.06, 7.05, 7.04, 7.03 (m, 7H, aromatic protons), 6.87 (t, 4H), 6.40 [t, 4H, aromatic protons ortho to $–N(CH_2CH_3)_2$], 3.29 [m, 8H, $–(NCH_2)_4$], 1.12 [t, 12H, $–(CH_3)_4$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 147.14, 146.59, 146.47, 145.12, 142.90, 135.03, 132.95, 132.87, 132.00, 131.91, 131.76, 131.66, 131.04, 130.76, 130.72, 128.62, 127.66, 125.57, 118.63, 118.45, 111.07, 110.76, 110.64, 94.84, 87.51, 44.15, 12.64. HRMS (MALDI-TOF): Calcd for $C_{43}H_{41}N_3$: 599.3300. Found: 599.3286 [M^+].

Sample preparation for AIE measurement. Stock solutions of the luminogens in THF or DMF with a concentration of 400 μM were prepared. An aliquot (1 mL) of the stock solution was transferred to 10 mL volumetric flask. After appropriate amount of THF was added, water was added dropwise under vigorous stirring to furnish 40 μM solution with different water fractions (0~90 vol%). Photoluminescence (PL) measurement of the resultant samples was performed immediately.

Cell culture and imaging. HeLa cells were cultured in the minimum essential medium (MEM) containing 10% fetal bovine serum and antibiotics (100 units mL^{-1} penicillin and 100 μg mL^{-1} streptomycin) in a 5% CO_2 humidity incubator at 37 ^{o}C. The HeLa cells were grown overnight on a plasma-treated 25 mm round cover slip mounted to the bottom of a 35 mm petri dish with an observation window. The living cells were stained with 10 μM (by adding 1 μL of a 10 mM stock solution of the luminogens in DMSO to 1 mL culture) for 45 min. The stained cells were imaged under an inverted FL microscope (Nikon Eclipse TE2000-U). The images of the cells were captured using a computer-controlled SPOT CCD camera (Spot RT SE 18 Mono).

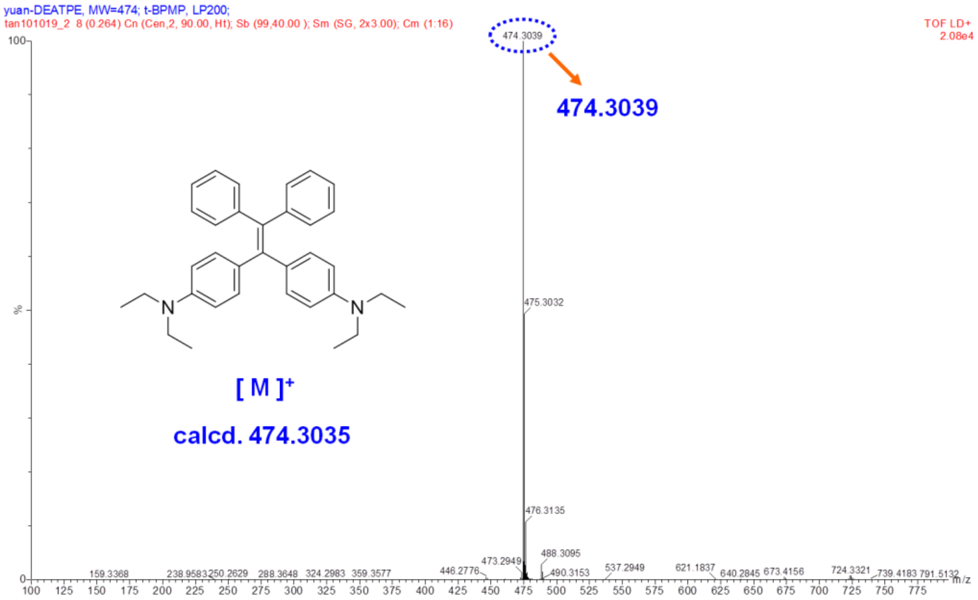

Fig. S1 HRMS spectrum of DEATPE.

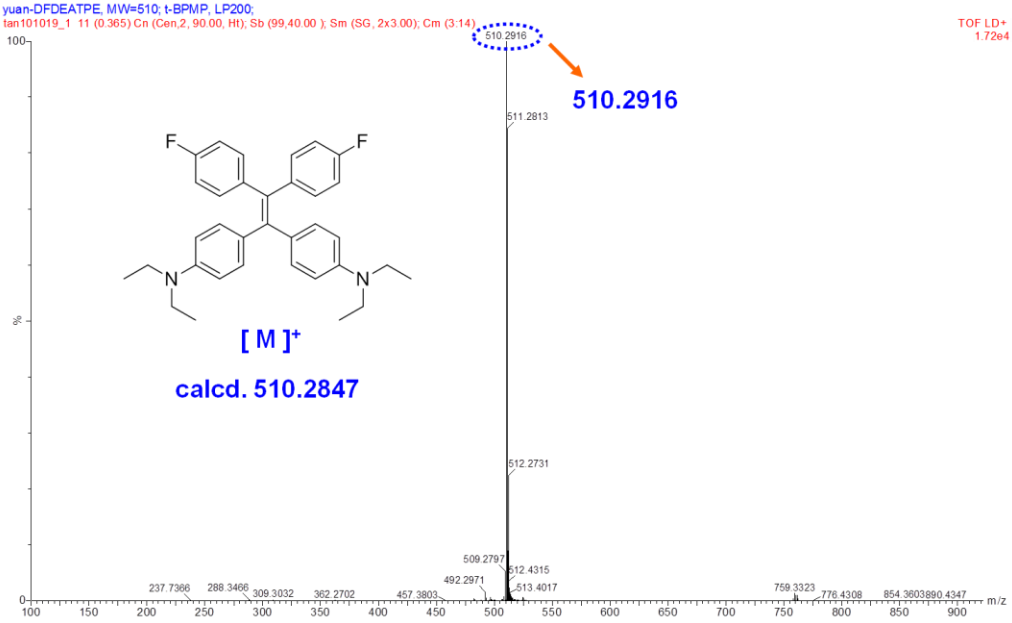

Fig. S2 HRMS spectrum of DFDEATPE.

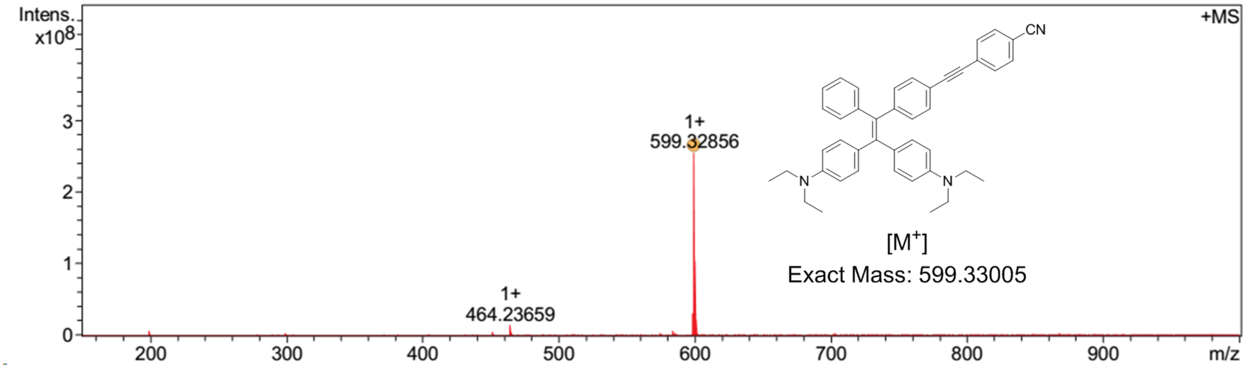

Fig. S3 HRMS spectrum of CNDEATPE.

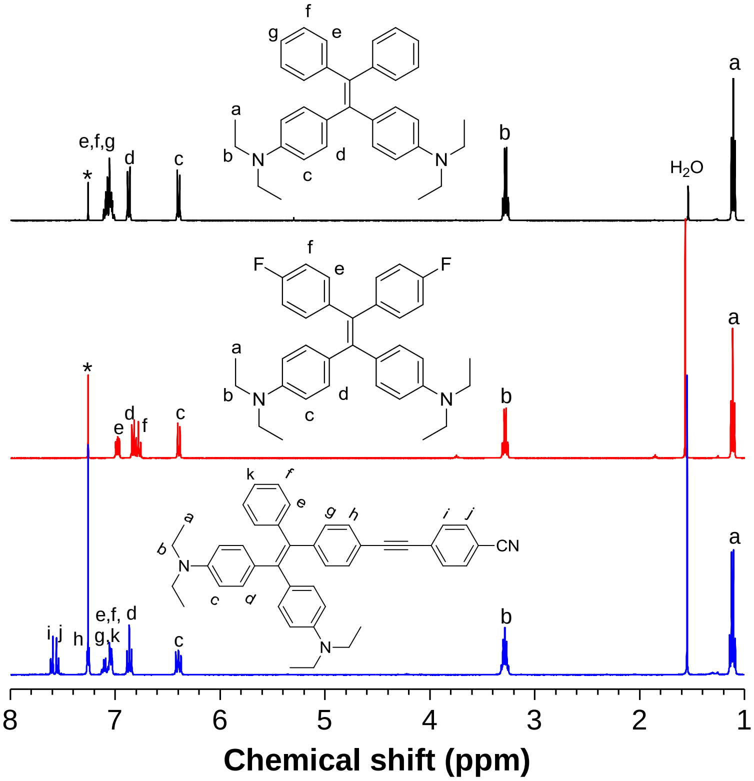

Fig. S4 ^{1}H NMR spectra of DEATPE, DFDEATPE and CNDEATPE in $CDCl_3$. The $CDCl_3$ peaks are marked with asterisks.

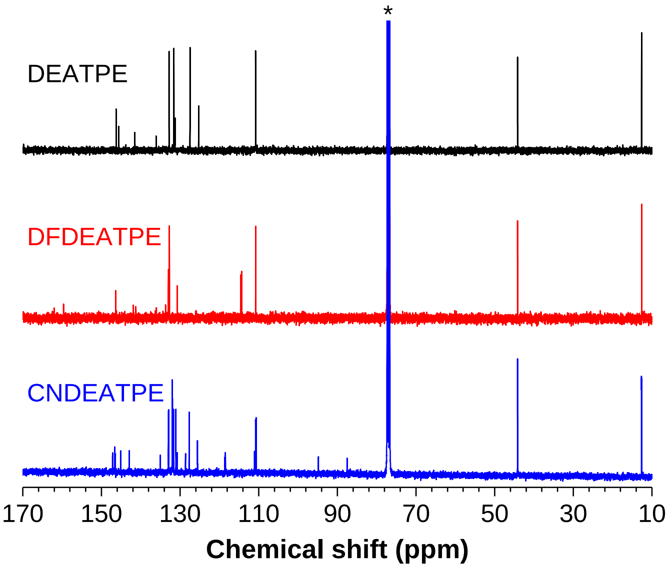

Fig. S5 ^{13}C NMR spectra of DEATPE, DFDEATPE and CNDEATPE in $CDCl_3$. The $CDCl_3$ peaks are marked with asterisks.

Table S1. Single crystal data of DEATPE.

Chemical formula	$C_{34}H_{38}N_2$
Formula Mass	474.66
Crystal system	Monoclinic
a/Å	12.6244(2)
b/Å	14.8163(3)
c/Å	14.6426(3)
α/ °	90.00
β/ °	91.253(2)
γ/ °	90.00
Unit cell volume/Å^3	2738.20(9)
Temperature/K	173(2)
Space group	$P2(1)/n$
No. of formula units per unit cell, Z	4
No. of reflections measured	9702
No. of independent reflections	4832
R_{int}	0.0506
Final R_1 values ($I > 2\sigma(I)$)	0.0503
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1419
Final R_1 values (all data)	0.0600
Final $wR(F^2)$ values (all data)	0.1470

Table S2. Single crystal structure of DFDEATPE.

Chemical formula	$C_{34}H_{36}F_2N_2$
Formula Mass	510.65
Crystal system	Triclinic
a/Å	9.6825(4)
b/Å	10.7418(5)
c/Å	14.3568(7)
α/ °	73.476(4)
β/ °	76.694(4)
γ/ °	88.074(4)
Unit cell volume/Å^3	1392.30(11)
Temperature/K	173(2)
Space group	P-1
No. of formula units per unit cell, Z	2
No. of reflections measured	8337
No. of independent reflections	5015
R_{int}	0.0278
Final R_1 values ($I > 2\sigma(I)$)	0.0403
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1160
Final R_1 values (all data)	0.0470
Final $wR(F^2)$ values (all data)	0.1196

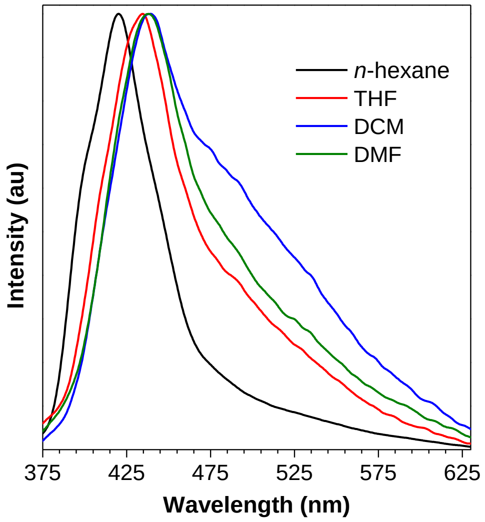

Fig. S6 Emission spectra of DEATPE in varying solvents. Concentration = 40 μM.

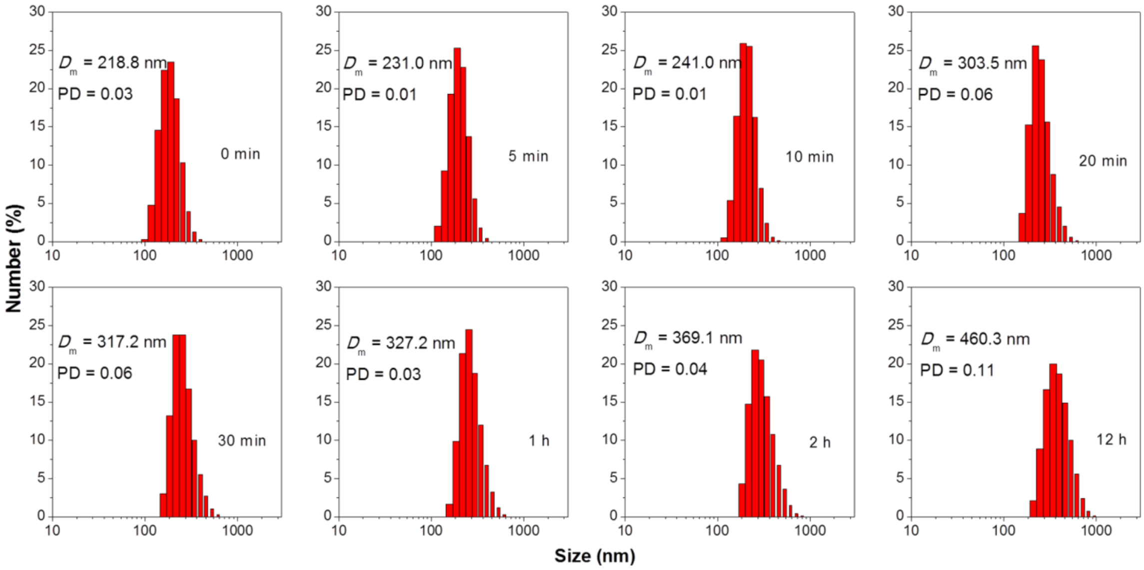

Fig. S7 Size distribution, D_m and PD of DEATPE suspensions in 20/80 THF/water mixture at different time after being freshly prepared.

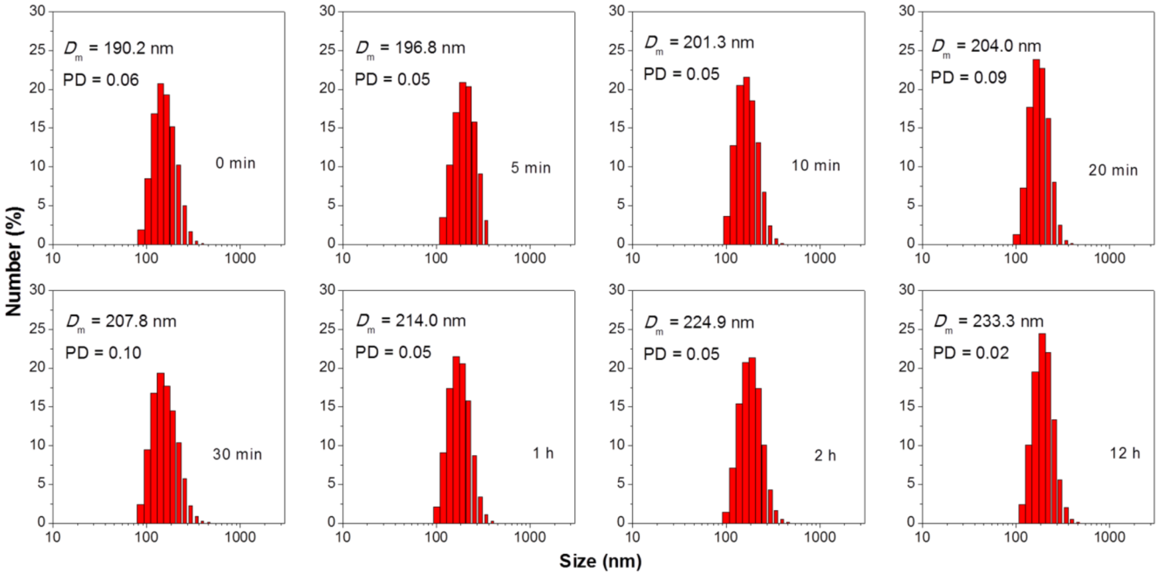

Fig. S8 Size distribution, D_m and PD of DEATPE suspensions in 10/90 THF/water mixture at different time after being freshly prepared.

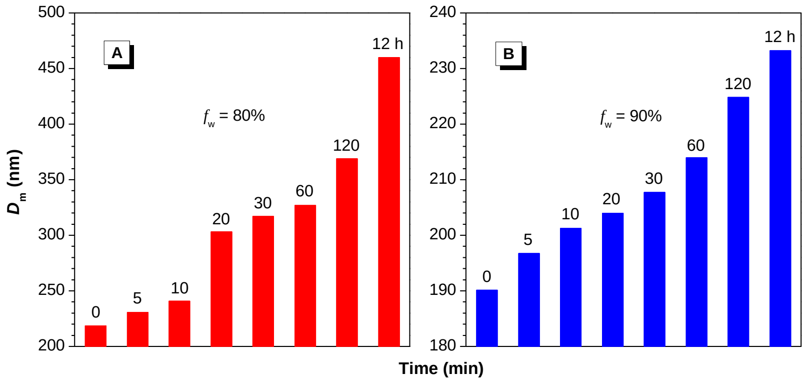

Fig. S9 D_m of DEATPE suspensions in THF/water mixtures with f_w of (A) 80% and (B) 90% at different time after being freshly prepared.

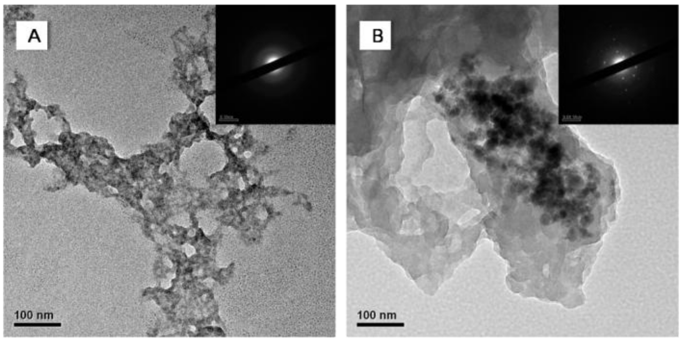

Fig. S10 TEM images and ED patterns of DEATPE suspensions in 20/80 THF/water mixture: (A) freshly prepared; (B) standing for 12 h.

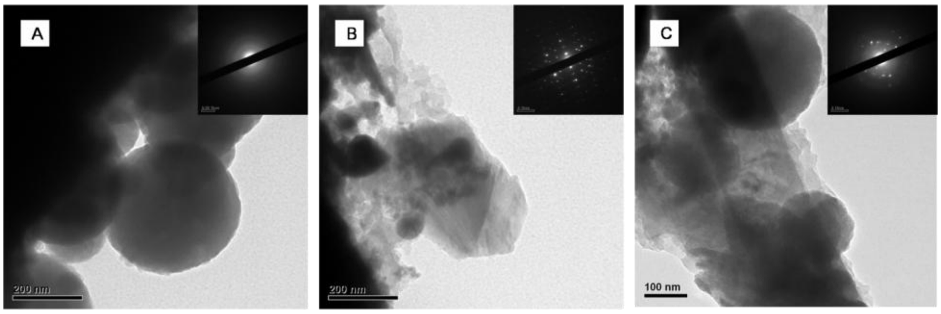

Fig. S11TEM images and ED patterns of DEATPE suspensions in 10/90 THF/water mixture: (A and B) freshly prepared; (C) standing for 12 h.

During our experiments, it is found that the freshly prepared DEATPE suspensions in 80% and 90% aqueous mixtures are essentially amorphous (Fig. S10A and S11A). And only a small fraction of crystalline aggregates are observed (Fig. S11B). These crystalline aggregates might be formed when they are freshly prepared or during the preparation process for the TEM sample. However, after standing for 12 h, both samples become crystalline with much larger sizes (Fig. S10B and S11C). These results are consistent with the DLS data and definitively indicate that the DEATPE aggregates have undergone molecular rearrangement from disordered amorphous state into well-ordered crystal lattice.

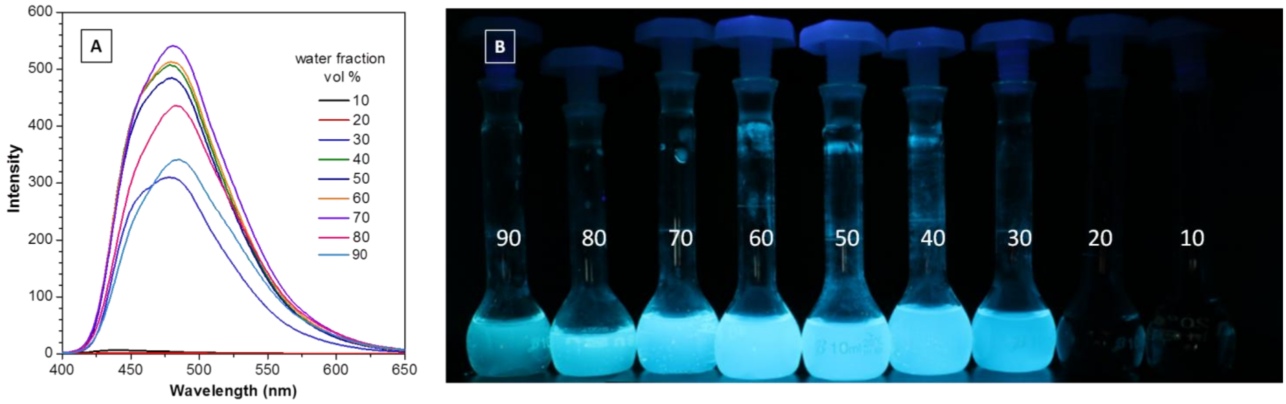

Fig. S12 (A) Emission spectra and (B) fluorescent photographs of DFDEATPE in DMF with varying water fractions. Concentration = 40 μM; excitation wavelength = 365 nm.

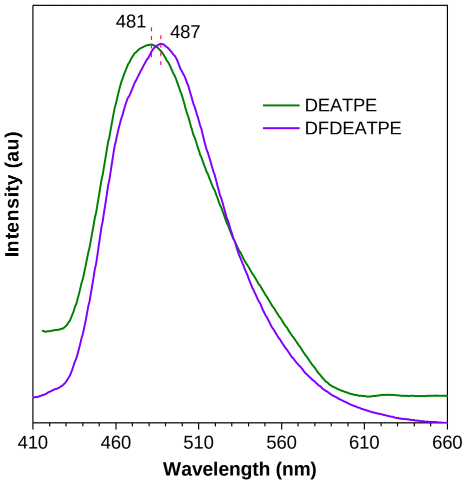

Fig. S13 Normalized emission spectra of DEATPE and DFDEATPE crystals.

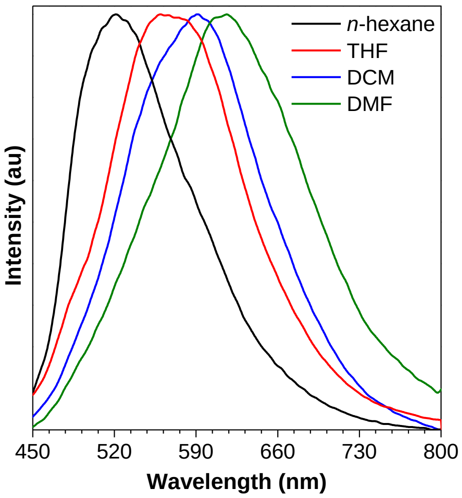

Fig. S14 Normalized emission spectra of DFDEATPE in varying solvents. Concentration = 40 μM.

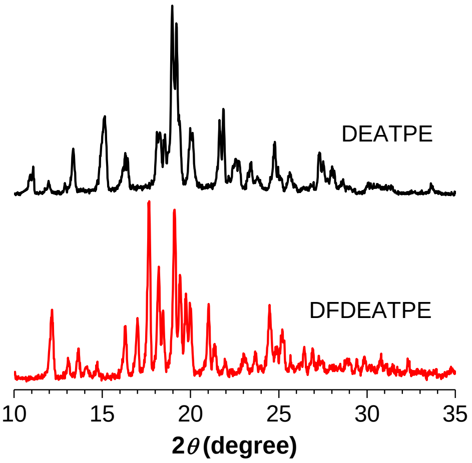

Fig. S15 XRD patterns of as prepared DEATPE and DFDEATPE solids.

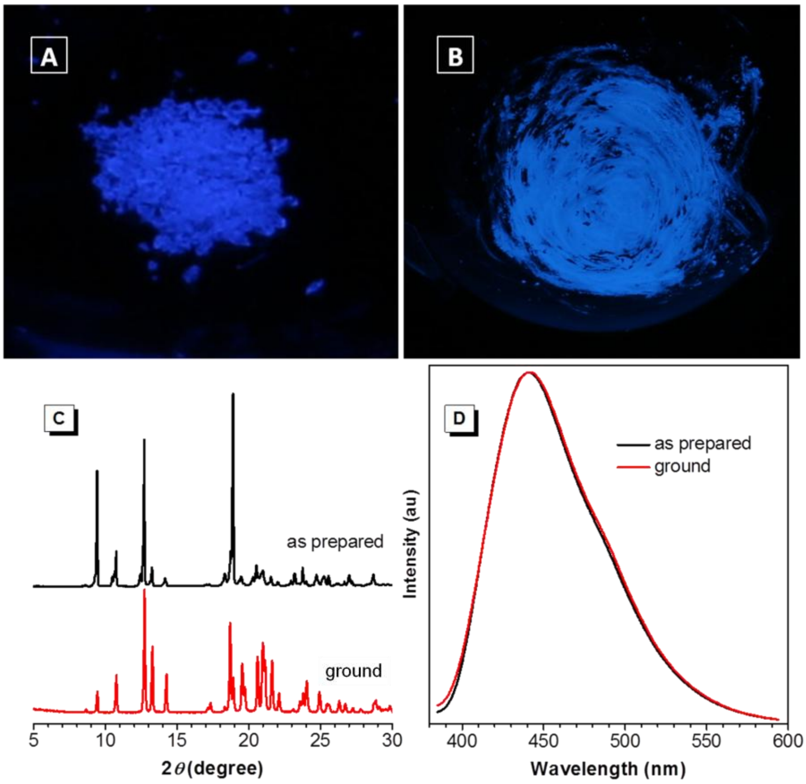

Fig. S16 Photographs of (A) as prepared and (B) ground solids of TPE taken under 365-nm UV illumination. (C) XRD patterns and (D) emission spectra of as prepared and ground solids of TPE.