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Supplementary Information

Aggregation-induced emission (AIE) characteristic of water-soluble tetraphenylethene (TPE) bearing four sulfonate salts

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Experimental Section:

General: IR spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer by ATR method. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-400 or Varian-500 FT NMR spectrometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Absorption spectra of solution were observed with a HITACH U-2910 spectrophotometer and absorption spectrum of the solid was recorded by a Shimadzu UV-3600 plus spectrophotometer with a calibrated integrating sphere system. fluorescence spectra were measured with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere system. The water-organic solvent mixture containing **WS-TPE** was made by weight percent (wt%) for water. The determination of water in 1,4-dioxane, THF and acetonitrile was done with a MKC-610 Karl Fischer moisture titrator (Kyoto Electronics manufacturing Co., Ltd.) based on Karl Fischer coulometric titration for samples below ca. 10.0 wt% water fraction. The dynamic light scattering (DLS) measurements was done with a Malvern Zetasizer Nano (Malvern, ZEN3600) analyzer. The solid 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.

Preparation of tetra(4-sulfophenyl)ethene (TPE-SO_3H)

To conc. H_2SO_4 (10 ml) heated at 115 ºC was added tetraphenylethene (0.51 g, 1.5 mmol) and the solution was stirred for 4 h at 115 ºC. To ethyl acetate at 0 ºC was very slowly added dropwise the reaction mixture, which is key point to successfully obtain **TPE-SO_3H**. The resulting precipitate was filtered and was chromatographed on reverse-phased silica gel (methanol as eluent) to give **TPE-SO_3H** (0.89 g, yield 90 %) as a gray solid; FT-IR (ATR): $\tilde{\nu}$ = 1159, 1107, 1030, 999 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ = 7.23 (d, J = 8.4 Hz, 8H), 7.54 (d, J = 8.4 Hz, 8H); ^{13}C NMR (125 MHz, D_2O, DSS as standard) δ = 125.92, 132.49, 141.72, 141.89, 146.30 ppm; HRMS (ESI): m/z (%):[M–4H$^-$] calcd for $C_{26}H_{16}O_{12}S_4$, 161.98866; found 161.98901.

Preparation of tetra(4-sulfophenyl)ethene sodium salt (WS-TPE)

A solution of **TPE-SO_3H** (0.11 g, 0.16 mmol) in water was neutralized with aqueous NaOH and the solution was concentrated under reduced pressure. The residue was dissolved in water, and vapor diffusion method by acetone was performed to afford **WS-TPE** (0.072 g, yield 61 %) as a yellow solid; FT-IR (ATR): $\tilde{\nu}$ = 1175, 1123, 1036, 1009 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ = 7.26 (d, J = 8.0 Hz, 8H), 7.57 (d, J = 8.0 Hz, 8H); ^{13}C NMR (125 MHz, D_2O, DSS as standard) δ = 127.79 (127.86), 134.39 (134.42), 143.62, 143.75, 148.14 ppm; HRMS (ESI): m/z (%):[M–4H$^-$] calcd for $C_{26}H_{16}O_{12}S_4$, 161.98866; found 161.98898.

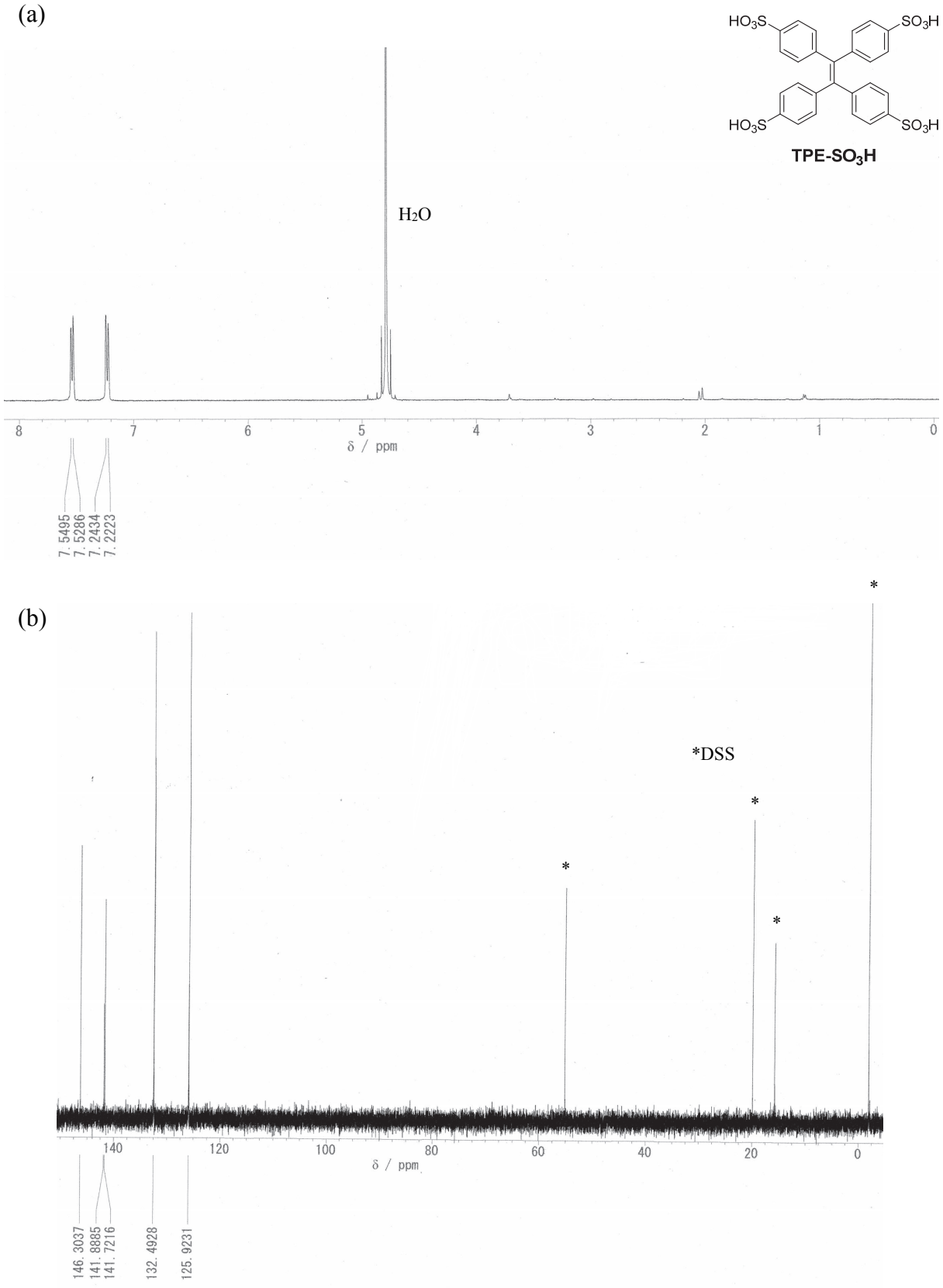

Fig. S1 (a) ^{1}H HMR (400 MHz) and (b) ^{13}C HMR (125 MHz) of **TPE-SO_3H** in D_2O.

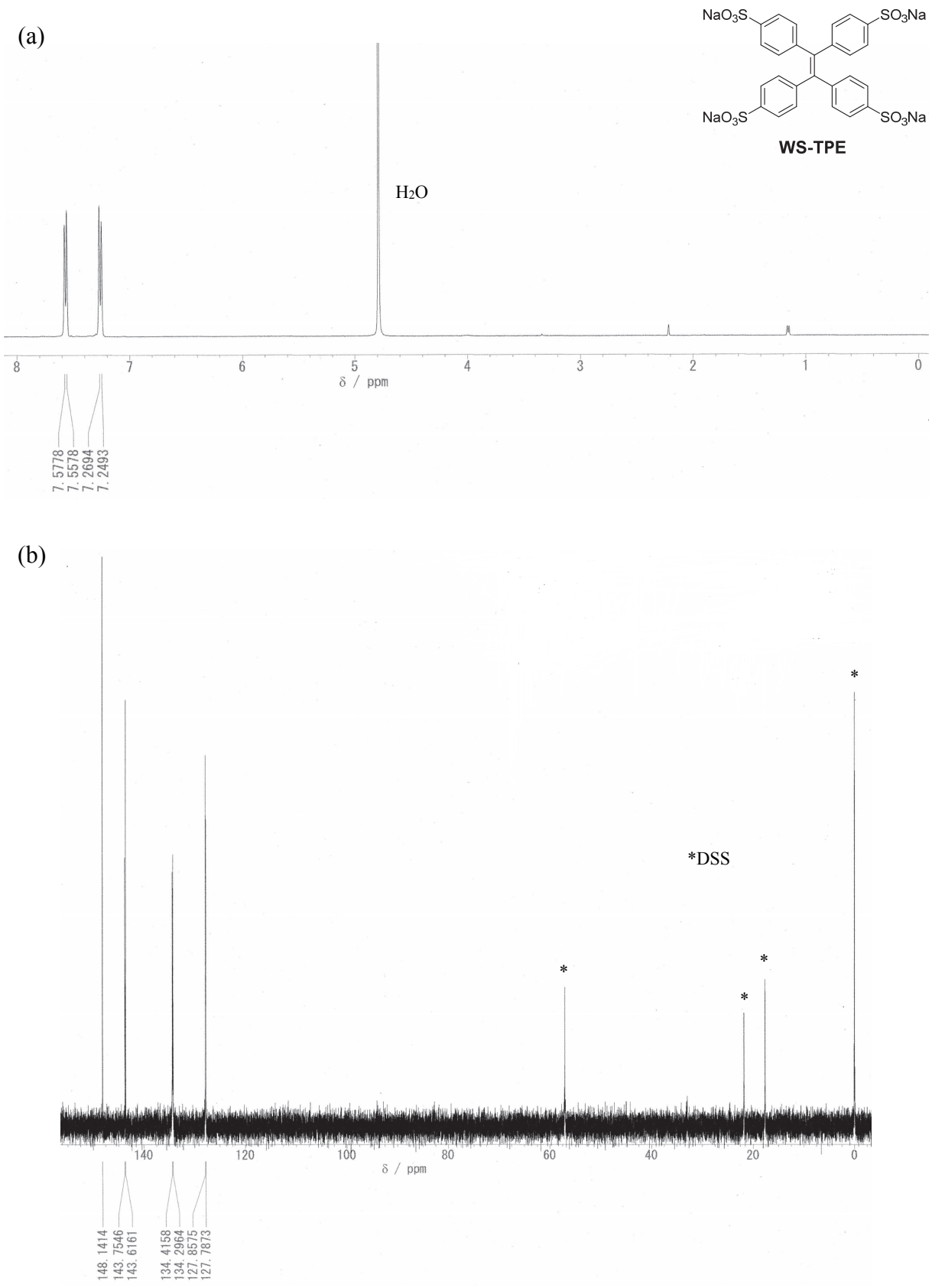

Fig. S2 (a) ^{1}H HMR (400 MHz) and (b) ^{13}C HMR (125 MHz) of **WS-TPE** in D_2O.

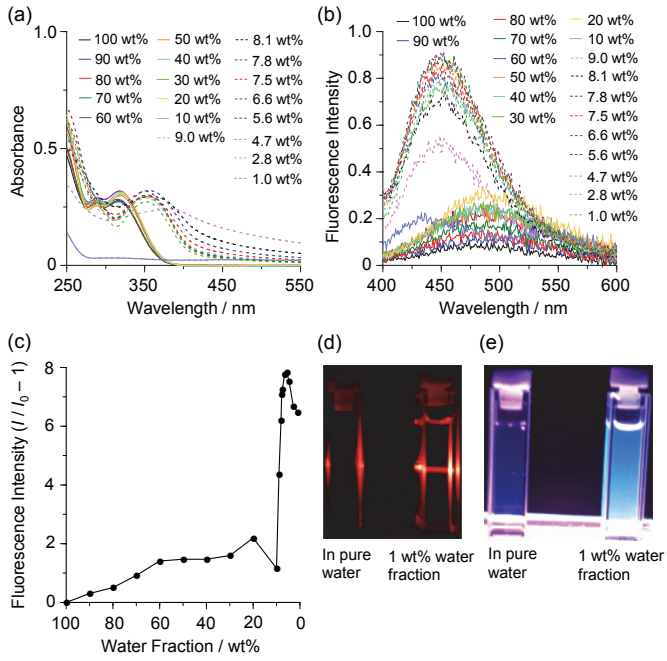

Fig. S3 (a) Absorption and (b) fluorescence spectra (λ_{ex} = 315–360 nm) of **WS-TPE** (c = 2.0×10^{-5} M) in water-1,4-dioxane mixture (1–100 wt% for 1,4-dioxane fraction). (c) The plot of fluorescence intensity (I/I_0–1) against the 1,4-dioxane fraction. (d) Tyndall scattering and fluorescence color images of **WS-TPE** in pure water and the water-1,4-dioxane mixture with 1 wt% water fraction.

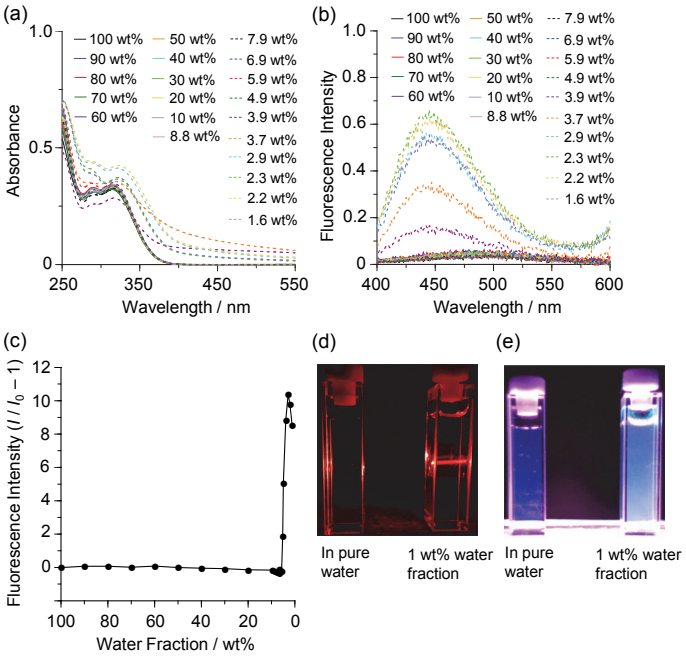

Fig. S4 (a) Absorption and (b) fluorescence spectra (λ_{ex} = 315–320 nm) of **WS-TPE** (c = 2.0×10^{-5} M) in water-acetonitrile mixture (1–100 wt% for acetonitrile fraction). (c) The plot of fluorescence intensity (I/I_0–1) against the acetonitrile fraction. (d) Tyndall scattering and fluorescence color images of **WS-TPE** in pure water and the water-acetonitrile mixture with 1 wt% water fraction.

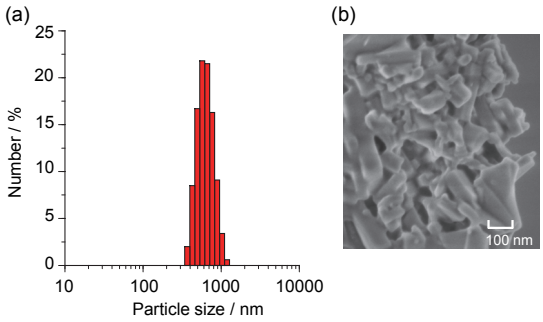

Fig. S5 (a) DLS of **WS-TPE** in the 1,4-dioxane solution with 1 wt% water fraction. (b) SEM images of the substance of **WS-TPE** obtained from the 1,4-dioxane solution with 1 wt% water fraction.

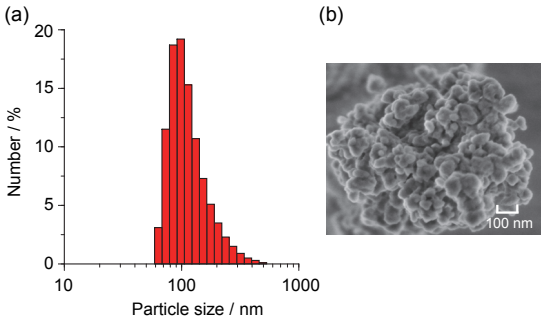

Fig. S6 (a) DLS of **WS-TPE** in the acetonitrile solution with 1 wt% water fraction. (b) SEM images of the substance of **WS-TPE** obtained from the acetonitrile solution with 1 wt% water fraction.