

Electronic Supplementary Information (ESI)

Deciphering mechanism of aggregation-induced emission (AIE): Is *E*–*Z* isomerisation involved in an AIE process?

Nai-Wen Tseng,[†] Jianzhao Liu,[†] Jason C. Y. Ng, Jacky W. Y. Lam, Herman H. Y. Sung, Ian D. Williams, and Ben Zhong Tang*

[†] Equal contribution

*Correspondence: tangbenz@ust.hk

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Experimental Section

Materials and Instrumentations

All reagents were used as received from Sigma–Aldrich unless otherwise specified. THF was distilled under nitrogen from sodium/benzophenone immediately prior to use. All reactions were carried out under anhydrous conditions in an atmosphere of dry nitrogen unless otherwise indicated. Tris(4-methylphenyl)boroxin¹ and tetraphenylethene² were prepared according to published synthetic procedures.

¹H and ¹³C NMR spectra were recorded using Bruker AV 400 MHz spectrometers. ¹H NMR spectra were referenced to tetramethylsilane (TMS, 0 ppm) and ¹³C NMR spectra were referenced to CDCl₃ solvent (77 ppm). UV-vis absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yields (Φ_F) of DPDTE and stilbenes were calculated using quinine sulphate ($\Phi_F = 0.54$ in 0.1 M H₂SO₄) and *p*-terphenyl ($\Phi_F = 0.93$ in cyclohexane), respectively, as the standards.

High-quality single crystals of DPDTE were grown from a THF/methanol mixture at room temperature. X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo K α radiation. Processing of the intensity data was conducted using the SAINT and SADABS routines, and the structure and refinement were carried out using the SHELTL suite of X-ray programs (version 6.10).

Synthesis of Z-rich DPDTE

The TPE derivative with Z-rich conformation was prepared according to the synthetic route shown in Scheme 2.³ A mixture of 2 mL of water and 8 mL of DMF in a 100 mL two-neck round-bottom flask was purged with nitrogen and stirred for 10 min at 25 °C. Diphenylacetylene (89 mg, 0.5 mmol),

¹ Qu, D.-H.; Wang, Q.-C.; Ren, J.; He, T. *Org. Lett.* **2004**, *6*, 2085.

² Duan, X.-F.; Zeng, J.; Lu, J.-W.; Zhang, Z.-B. *J. Org. Chem.* **2006**, *71*, 9873.

³ Zhou, C.; Larock, R. C. *Org. Lett.* **2005**, *7*, 259.

4-iodotoluene (218 mg, 1.0 mmol), tris(4-methylphenyl)boroxin (120 mg, 0.34 mmol), and potassium carbonate (69 mg, 0.5 mmol) were added to the mixture and stirred at 100 °C for 10 min. To the solution was added Pd(PhCN)₂Cl₂ (5.8 mg, 0.015 mmol) and the resulting mixture was stirred at 100 °C for 16 h. The reaction mixture was then diluted with ethyl acetate, washed with water (×2) and brine (×2). The organic layer was dried over MgSO₄, filtered and concentrated in *vacuo*. Chromatography on silica gel using 5% dichloromethane in hexane as eluent ($R_f = 0.28$) gave Z-DPDTE (64 mg, 35%) as a white solid. Its spectral data matched with the previous reported characterization data.³ ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.11–7.04 (m, 6H), 7.03–6.98 (m, 4H), 6.91 and 6.89 (m, 8H), 2.26 and 2.24 (s, 6H). ¹³C NMR (75 MHz, CDCl₃), δ (CDCl₃, ppm): 144.1, 140.9, 140.4, 135.9, 131.3, 131.2, 128.4, 127.5, 126.2, 21.2.

Preparation of Nanoaggregates

A stock solution of Z-rich DPDTE in THF with a concentration of 10 mM was prepared. Aliquots (1 mL) of the stock solution were transferred to 10 mL volumetric flasks. After adding appropriate amounts of THF, water was added dropwise under vigorous stirring to furnish 10 μ M solutions with defined fractions of water ($f_w = 0$ –95 vol %). The dilute solutions or nanoaggregate suspensions of stilbenes were prepared in a similar fashion. Spectral measurements of the solutions or suspensions were performed immediately.

UV Irradiation

Z-rich DPDTE was irradiated with UV light from a fluorescence spectrometer or a hand-held UV lamp. In the former case, a solution of Z-rich DPDTE in CDCl₃ in a quartz cell was irradiated repeatedly at a rate of 1 min/scan by the UV light in the Perkin-Elmer spectrofluorometer with an excitation wavelength of 290, 312 or 365 nm and a power of $\sim 52 \mu\text{W}/\text{cm}^2$ at 25 °C. In the latter case, a solution of Z-rich DPDTE in CDCl₃ in an NMR tube was irradiated with a hand-held Spectroline UV lamp with a wavelength of 254, 312 or 365 nm and a power of $\sim 1.1 \text{ mW}/\text{cm}^2$ at a distance of 8 cm at 25 °C in a dark room. After irradiation, the samples were protected from light by covering with aluminum

foil and the NMR spectra were measured immediately. The photoirradiation experiments of stilbenes were carried out in a similar manner.

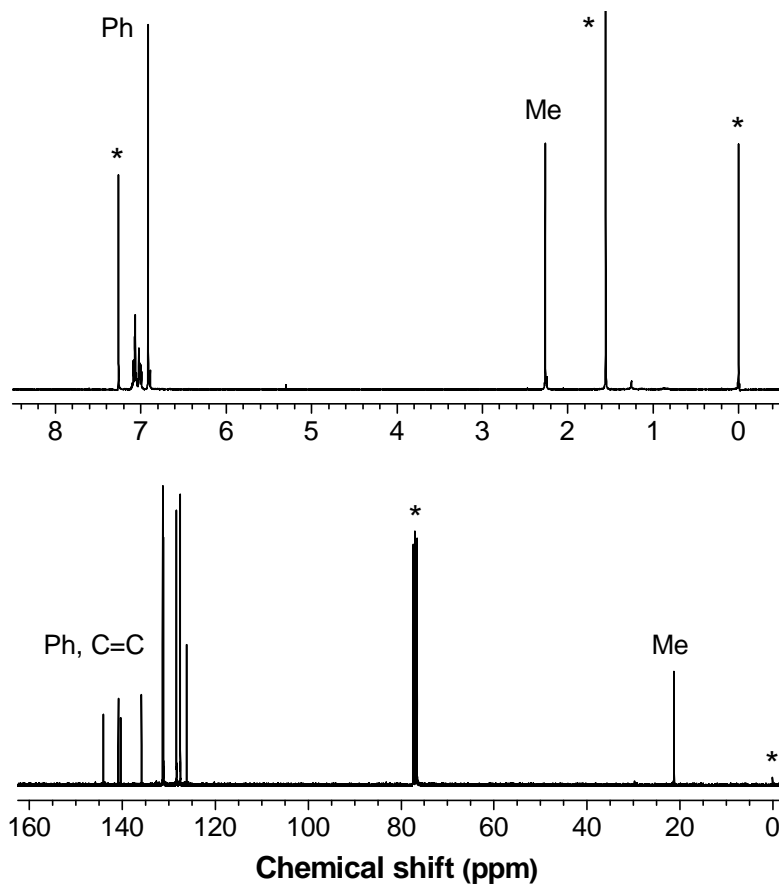


Figure S1. ¹H and ¹³C NMR spectra of Z-rich DPDTE in CDCl₃; peaks of solvent, water and reference (TMS) marked by asterisks (*).

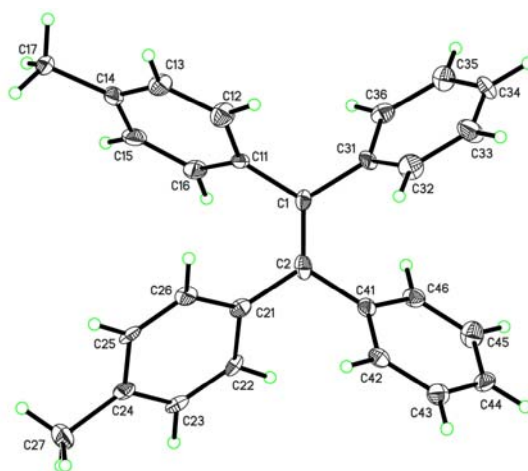


Figure S2. ORTEP drawing of (Z)-DPDTE at 30% probability (CCDC837495).

Table S1. Crystal Data and Structure Refinement for Z-DPDTE (CCDC837495)

Empirical formula	C ₂₈ H ₂₄
Formula weight	360.47
Temperature	143.0 K
Wavelength	0.7107 Å
Crystal system	Trigonal
Space group	P 32
Unit cell dimensions	a = 29.9106(3) Å α = 90°. b = 29.9106(3) Å β = 90°. c = 5.97140(10) Å γ = 120°.
Volume	4626.55(10) Å ³
Z	9
Density (calculated)	1.164 Mg/m ³
Absorption coefficient	0.066 mm ⁻¹
F(000)	1728
Crystal size	0.40 x 0.15 x 0.13 mm ³
Theta range for data collection	2.7184 to 28.9808°
Index ranges	-27 ≤ h ≤ 40, -40 ≤ k ≤ 24, -7 ≤ l ≤ 8
Reflections collected	31922
Independent reflections	6052 [R(int) = 0.0332]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.90768
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6052 / 1 / 764
Goodness-of-fit on F ²	1.018
Final R indices [I > 2σ(I)]	R1 = 0.0538, wR2 = 0.1339
R indices (all data)	R1 = 0.0544, wR2 = 0.1342
Absolute structure parameter	-10(10)
Largest diff. peak and hole	0.356 and -0.223 e.Å ⁻³

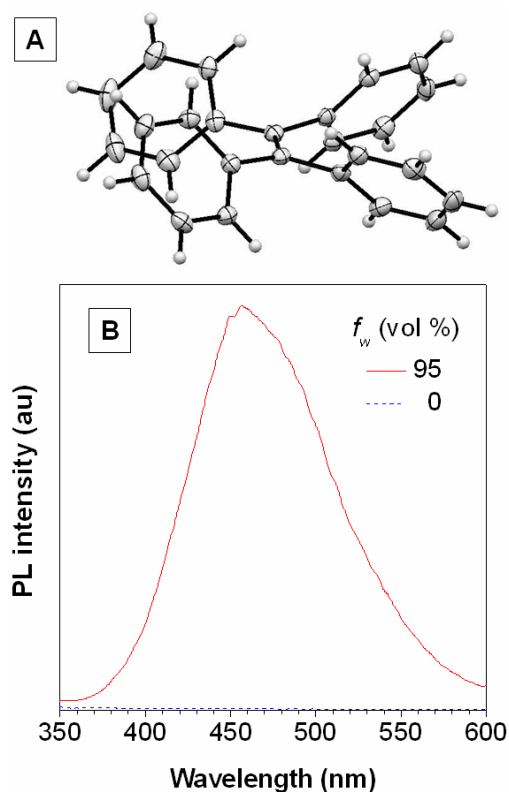


Figure S3. (A) Crystal structure of TPE and (B) its emission spectra in THF and a THF/water mixture with 95% water fraction (f_w). TPE concentration: 10 μ M; excitation wavelength: 310 nm.

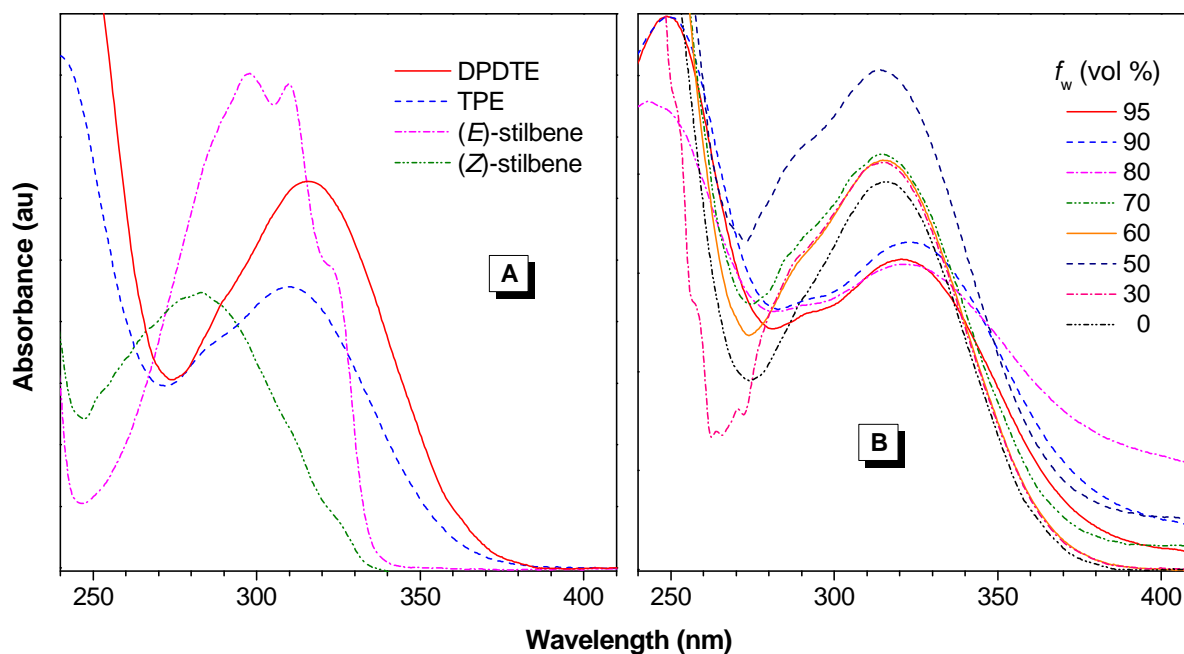


Figure S4. Absorption spectra of (A) Z-rich DPDTE, TPE and (E)- and (Z)-stilbenes in THF and (B) Z-rich DPDTE in THF/H₂O mixtures with different fractions of water (f_w); $c = 10 \mu$ M.

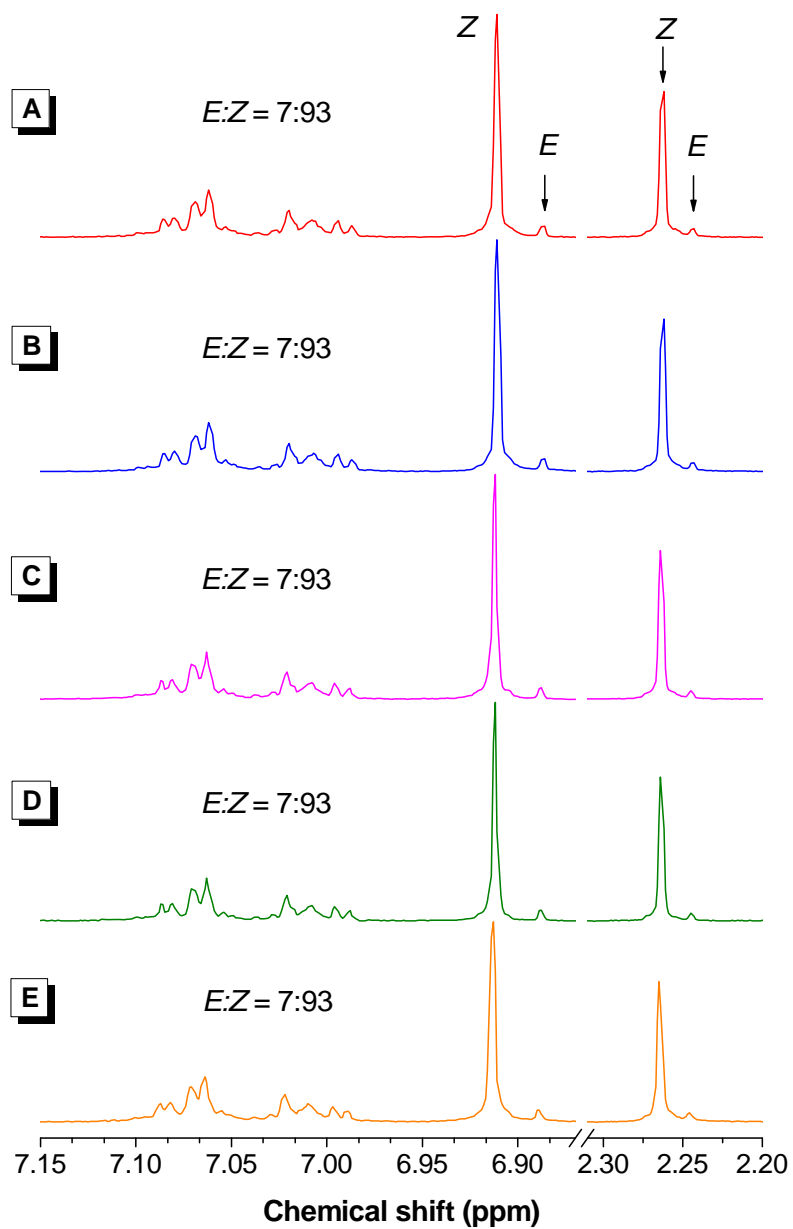


Figure S5. ¹H NMR spectra of Z-rich DPDTE (Z = 93 mol %) in CDCl₃ after exposure to UV light in a standard spectrofluorometer for (A) 5, (B) 8, (C) 11, (D) 14, and (E) 29 min. DPDTE concentration: 3.5 mM; excitation wavelength: 312 nm.

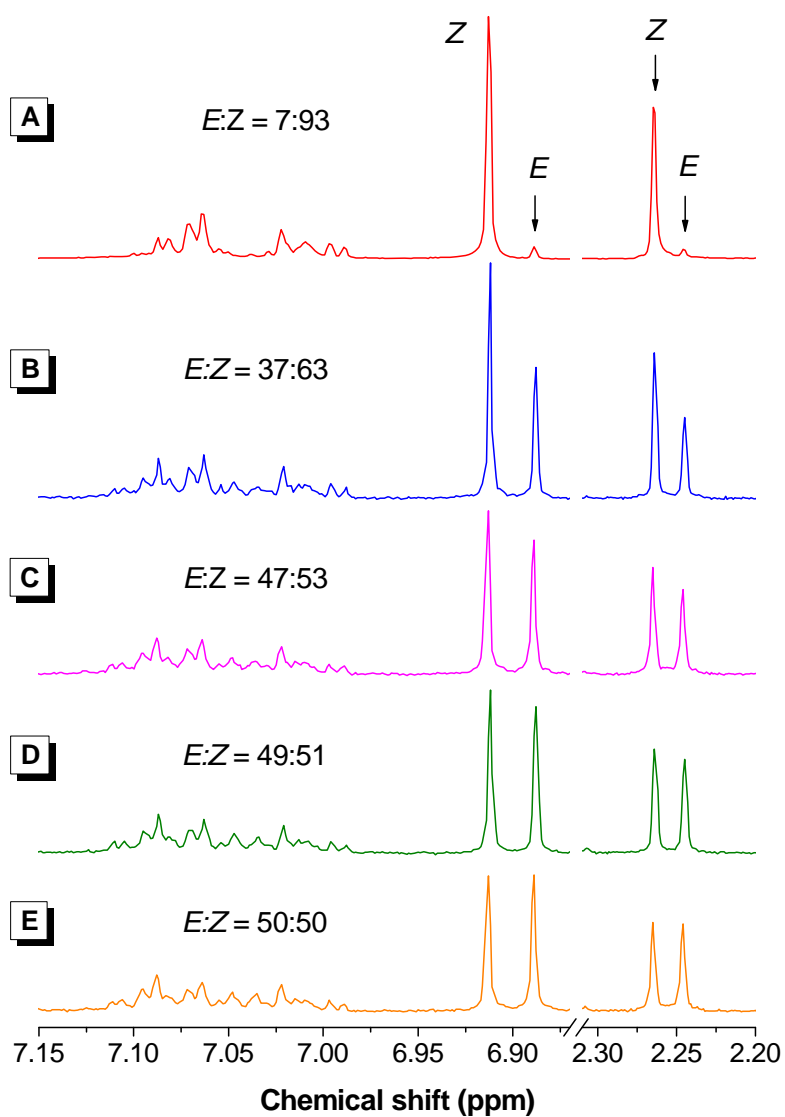


Figure S6. Time course study of the isomerisation of Z-rich DPDTE ($Z = 93$ mol %) in $CDCl_3$ induced by photoirradiation with a hand-held UV lamp. Exposure time: (A) 0, (B) 5, (C) 8, (D) 11, and (E) 14 min. DPDTE concentration: 3.5 mM; excitation wavelength: 312 nm.

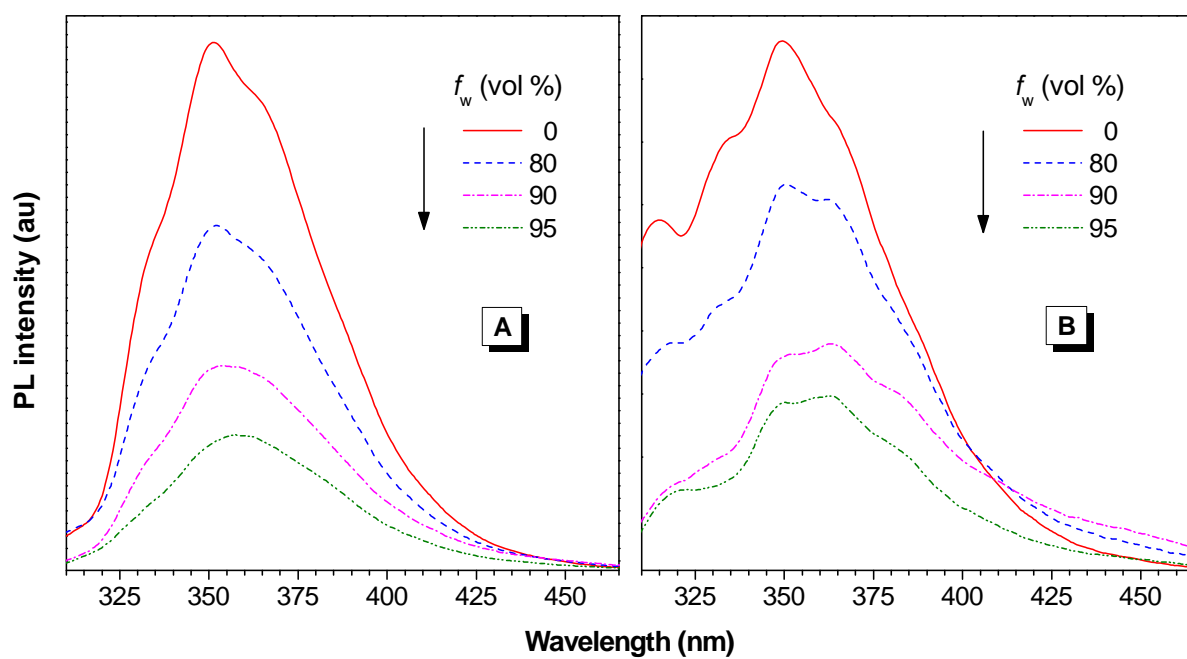


Figure S7. (A) PL spectra of (A) (*E*)- and (B) (*Z*)-stilbenes in THF/water mixtures with different fractions of water (f_w). Stilbene concentration: $\sim 2.5 \mu\text{M}$; excitation wavelength: 290 nm.

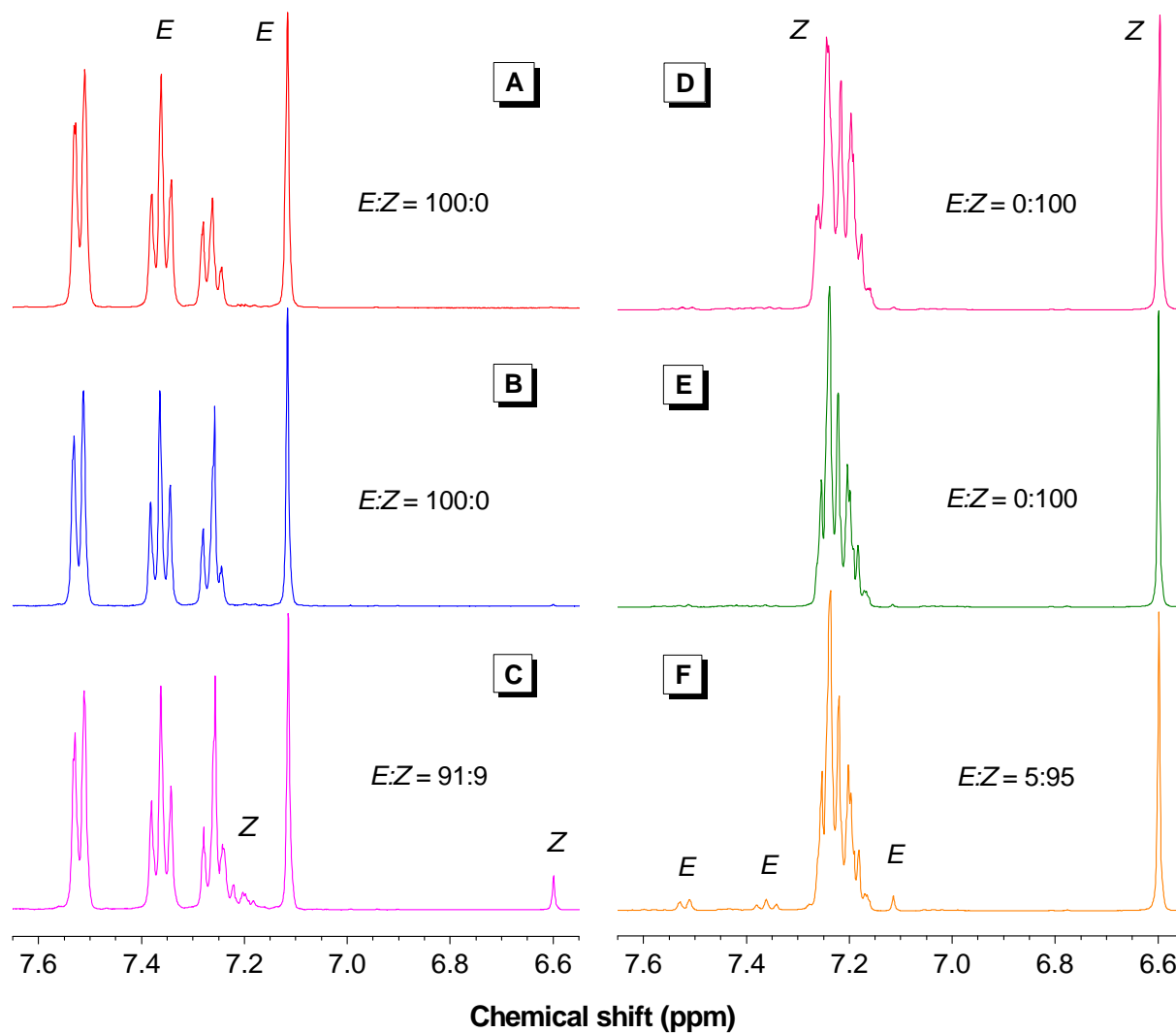


Figure S8. ^1H NMR spectra of (A–C) (*E*)- and (D–F) (*Z*)-stilbenes in CDCl_3 (A, D) before and (B, C, E, F) after exposure to UV light (B, E) in a standard spectrofluorometer and (C, F) from a handheld UV lamp for 30 min. Stilbene concentration: 50 mM; excitation wavelength: (B) 290, (E) 280, (C, F) 254 nm.