Supporting Information for ja-2011-08883h

Click Synthesis, Aggregation-Induced Emission, *E–Z* Isomerization, Self-organization, and Multiple Chromisms of Pure Stereoisomers of a Tetraphenylethene-Cored Luminogen

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Measurement of Fluorescence Quantum Yield in the Solid State. The Φ_F values of *E* and *Z* isomers of BPHTATPE were measured with a calibrated integrating sphere on a time-resolved fluorescence spectroscopy, using eq 1 given below:[1]

$$\Phi_F = \frac{N_{em}}{N_{ab}} = \frac{\alpha \int \frac{\lambda}{hc} I_{em}(\lambda) d\lambda}{\alpha \int \frac{\lambda}{hc} [I_{ex}(\lambda) - I'_{ex}(\lambda)] d\lambda} \quad (1)$$

where N_{em} and N_{ab} are the numbers of emitted and absorbed photons, respectively, α is the calibration factor for the measurement setup, λ is the wavelength, *h* is the Plank's constant, *c* is the speed of light, $I_{em}(\lambda)$ is the emission intensity at λ, and $I_{ex}(\lambda)$ and $I'_{ex}(\lambda)$ are the intensities of the excitation laser beam with λ in the absence and presence of the sample, respectively. The measured Φ_F value is independent of sharp and thickness of sample and power of excitation laser.

(1) Kawamura, Y.; Sasabe, H.; Adachi, C. *Jpn. J. Appl. Phys.* **2004**, *43*, 7729–7730.

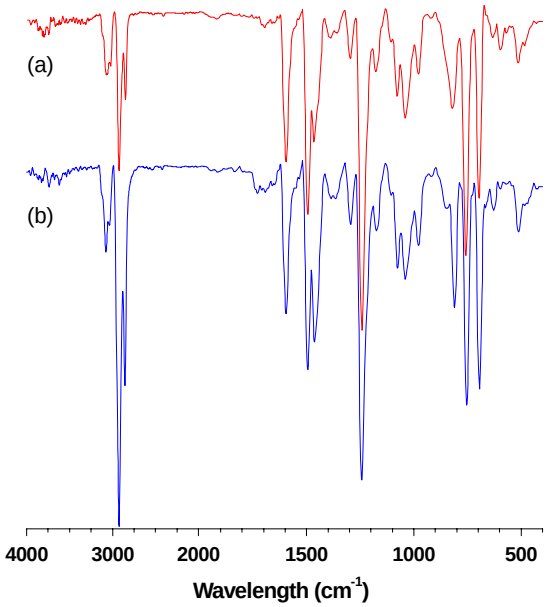


Figure S1. The IR spectra of (a) (*E*)- and (b) (*Z*)-BPHTATPE.

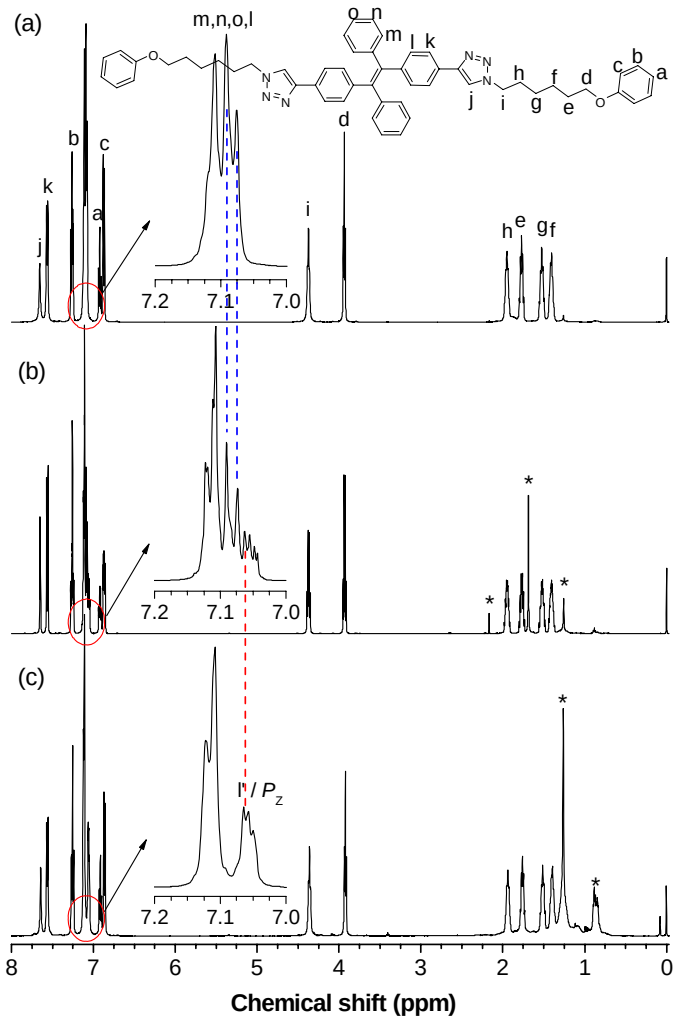


Figure S2. ^{1}H NMR spectra of (a) pure (*E*)-BPHTATPE, (b) (*E*)/(*Z*)-BPHTATPE mixture, and (c) pure (*Z*)-BPHTATPE in chloroform-*d*. The solvent peaks are marked with asterisks.

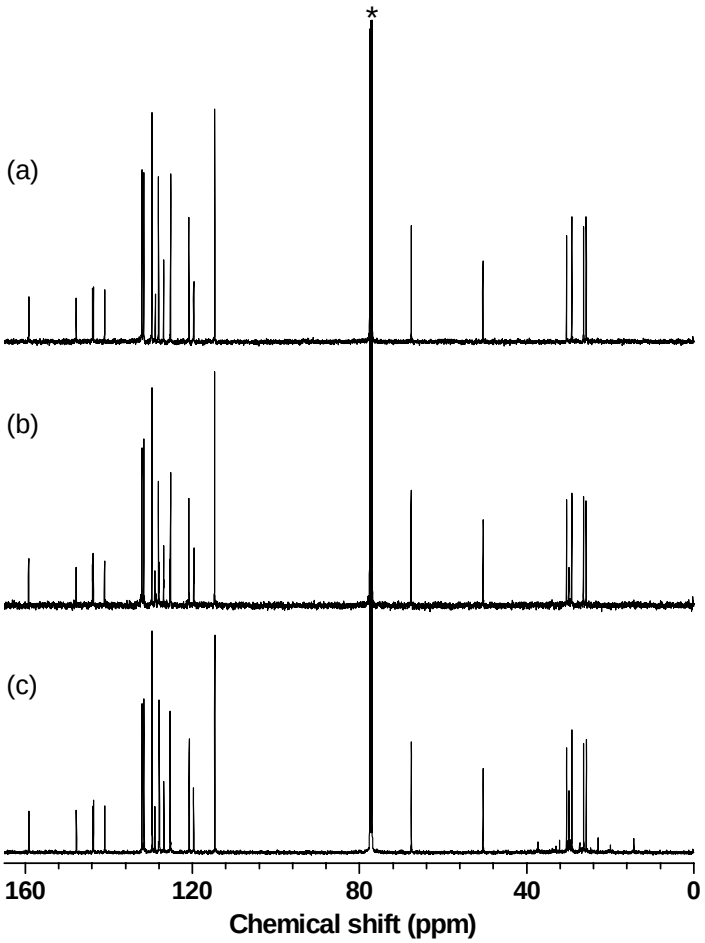
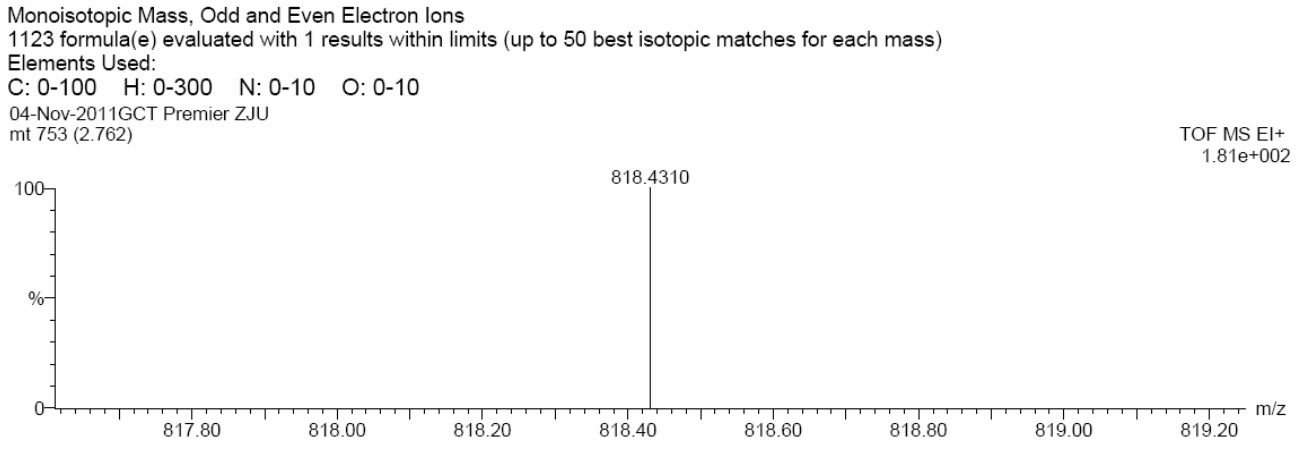
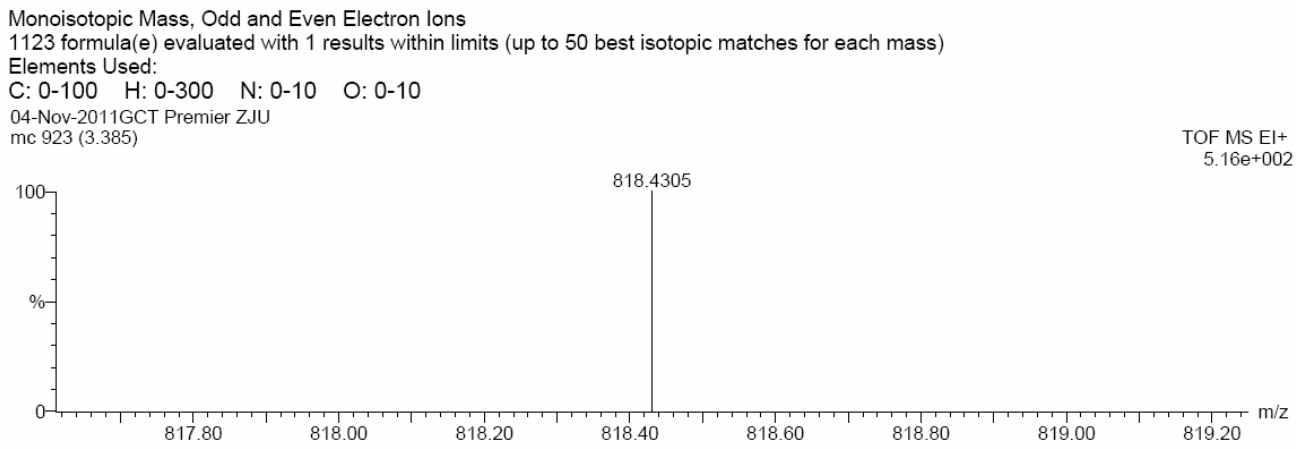


Figure S3. ^{13}C NMR spectra of (a) pure (*E*)-BPHTATPE, (b) (*E*)/(*Z*)-BPHTATPE mixture, and (c) pure (*Z*)-BPHTATPE in chloroform-*d*. The solvent peaks are marked with asterisks.



Minimum:				-1.5		
Maximum:		1.0	0.8	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
818.4310	818.4308	0.2	0.2	31.0	5546112.5	C54 H54 N6 O2

Figure S4. High resolution mass spectrum of (*E*)-BPHTATPE.



Minimum:				-1.5		
Maximum:		1.0	0.8	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
818.4305	818.4308	-0.3	-0.4	31.0	5546280.0	C54 H54 N6 O2

Figure S5. High resolution mass spectrum of (*Z*)-BPHTATPE.

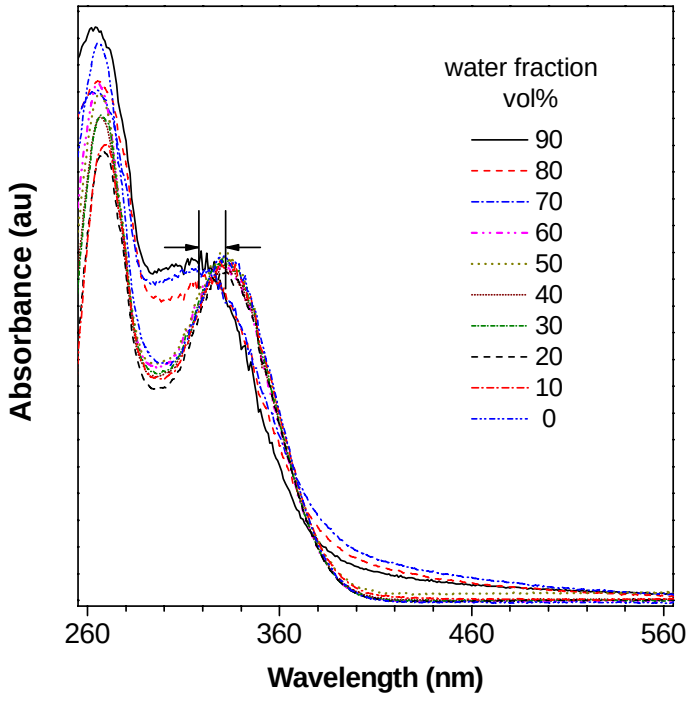


Figure S6. Absorption spectra of (*E*)-BPHTATPE in THF/water mixtures with different fractions of water; c = 10 μM.

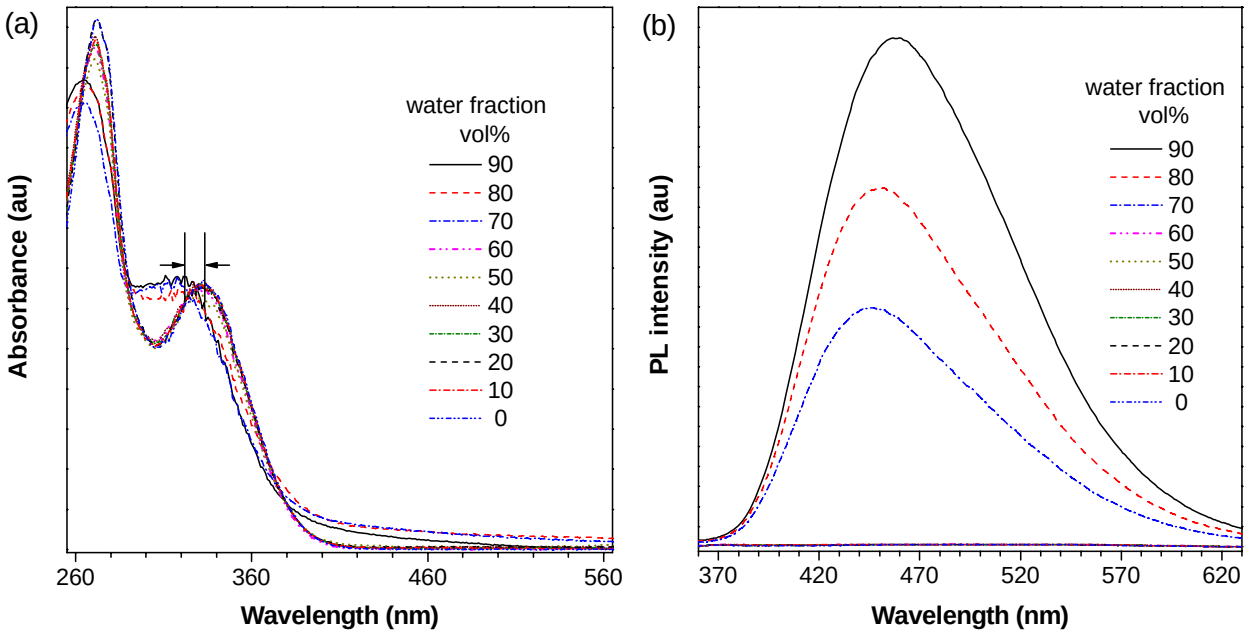


Figure S7. (a) Absorption and (b) emission spectra of (*Z*)-BPHTATPE in THF/water mixtures with different fractions of water; λ_{ex} = 332 nm, *c* = 10 μM.

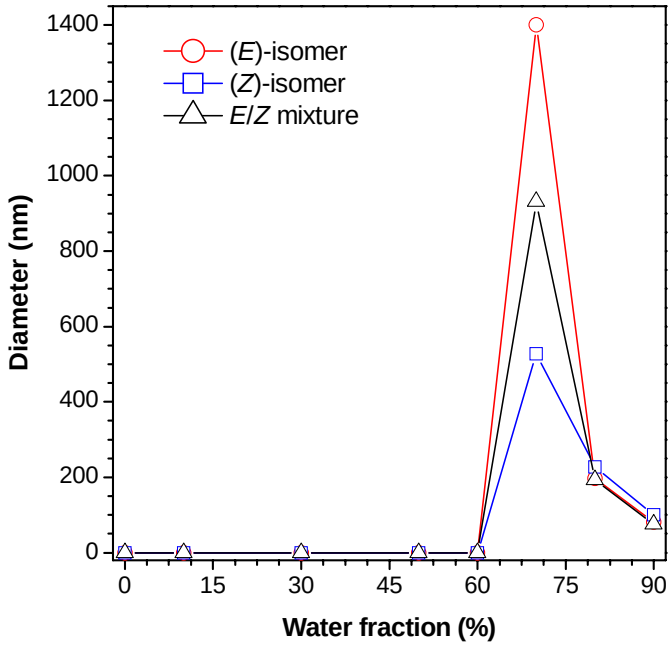


Figure S8. Variation in the sizes of aggregates of (*E*)- and (*Z*)-isomers and an *E*/*Z* mixture (1:1) of BPHTATPE with water fractions in THF/water mixtures.

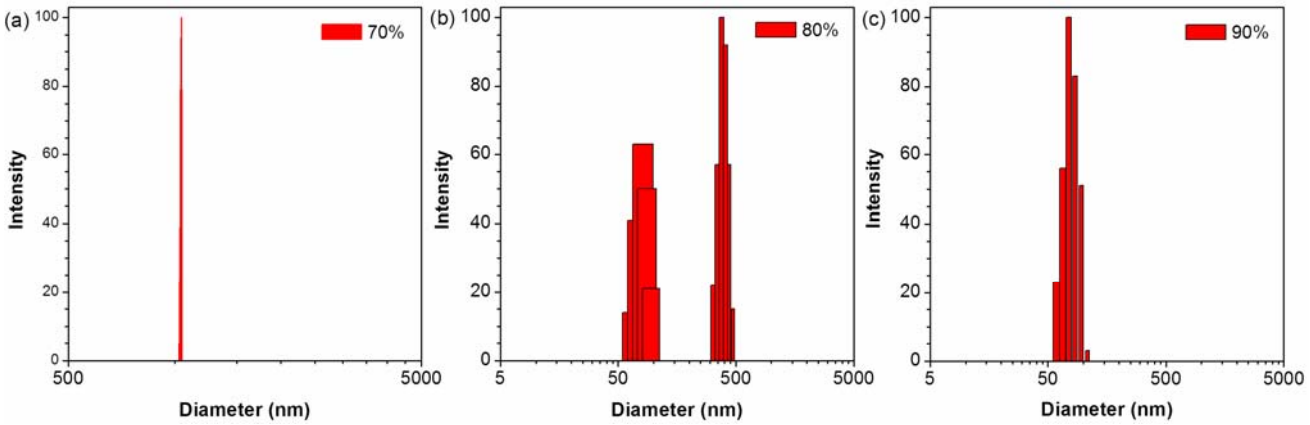


Figure S9. Particle size distributions of (*E*)-BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%.

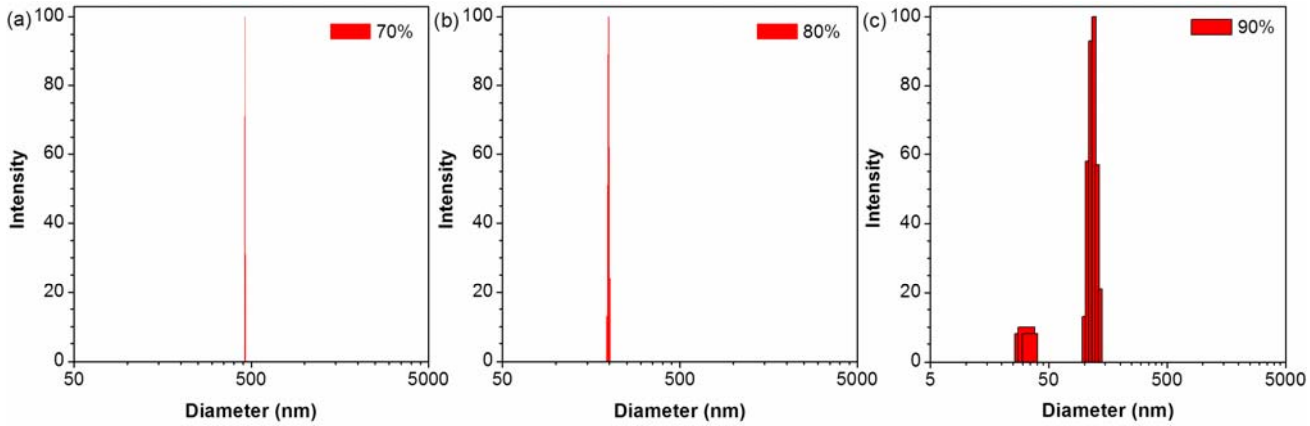


Figure S10. Particle size distributions of (*Z*)-BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%.

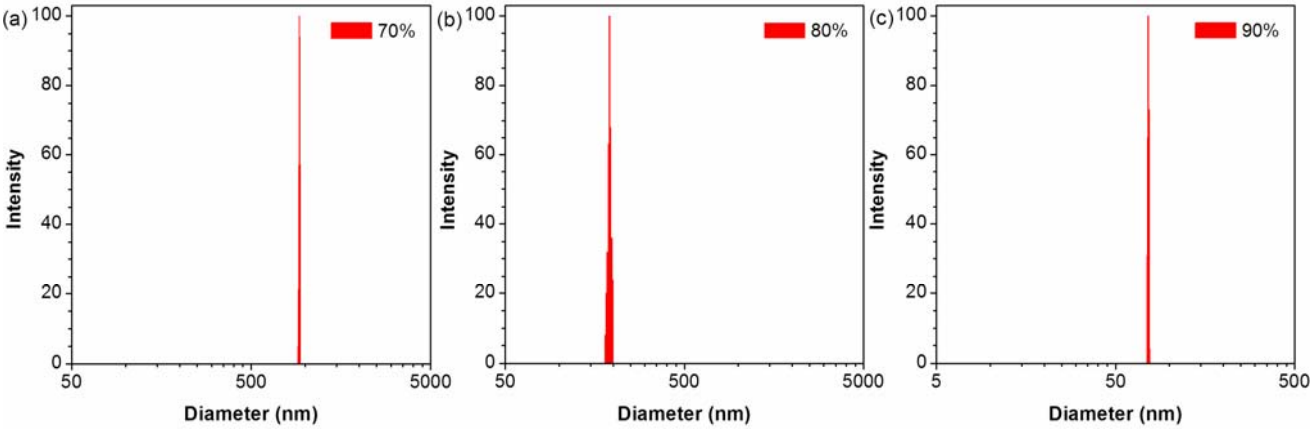


Figure S11. Particle size distributions of an *E*/*Z* mixture (1:1) of BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%.

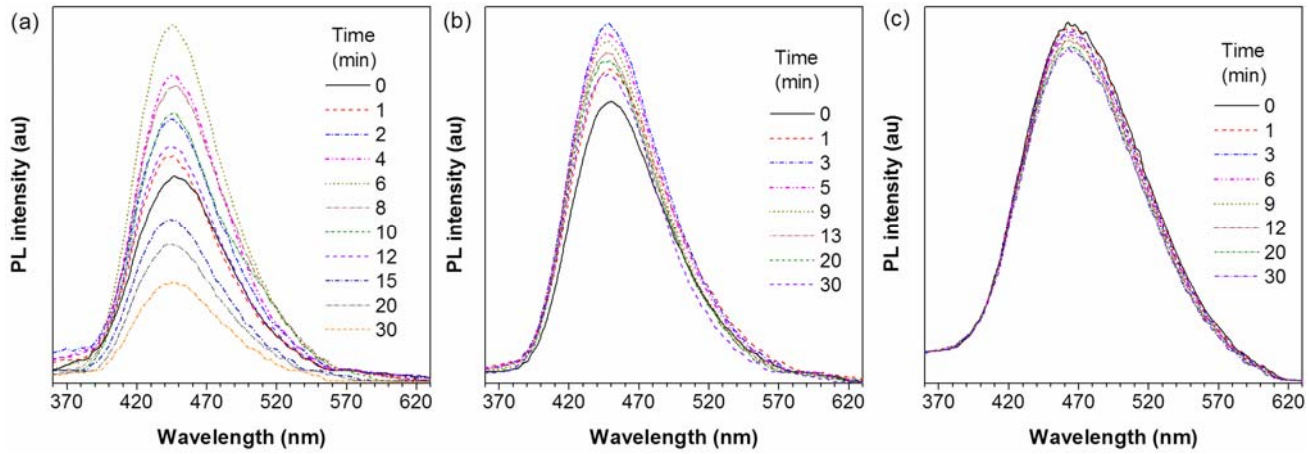


Figure S12. Time dependences of PL spectra of (*E*)-BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%; λ_{ex} = 332 nm, c = 10 μM.

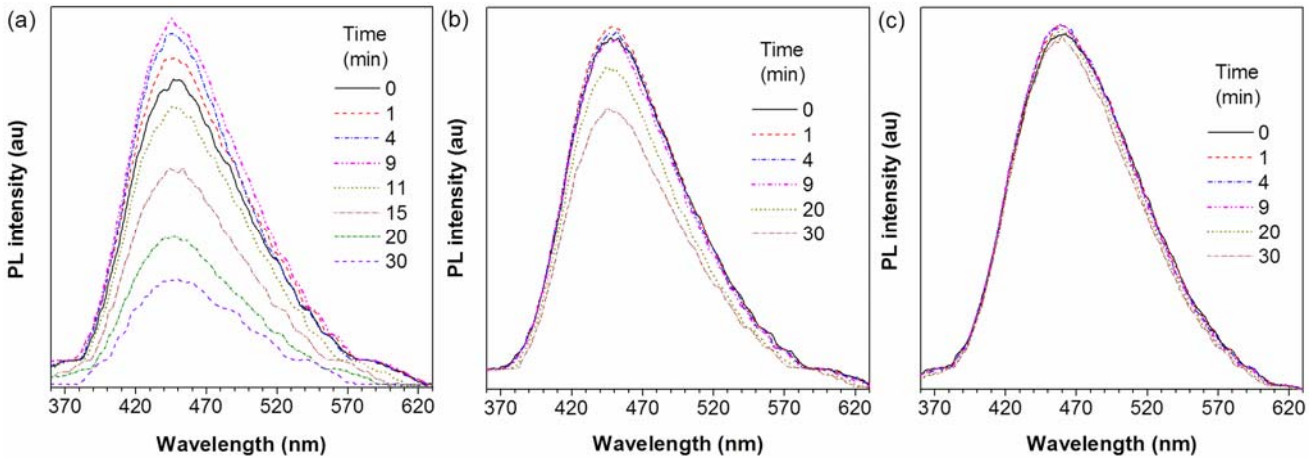


Figure S13. Time dependences of PL spectra of (*Z*)-BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%; λ_{ex} = 332 nm, c = 10 μM.

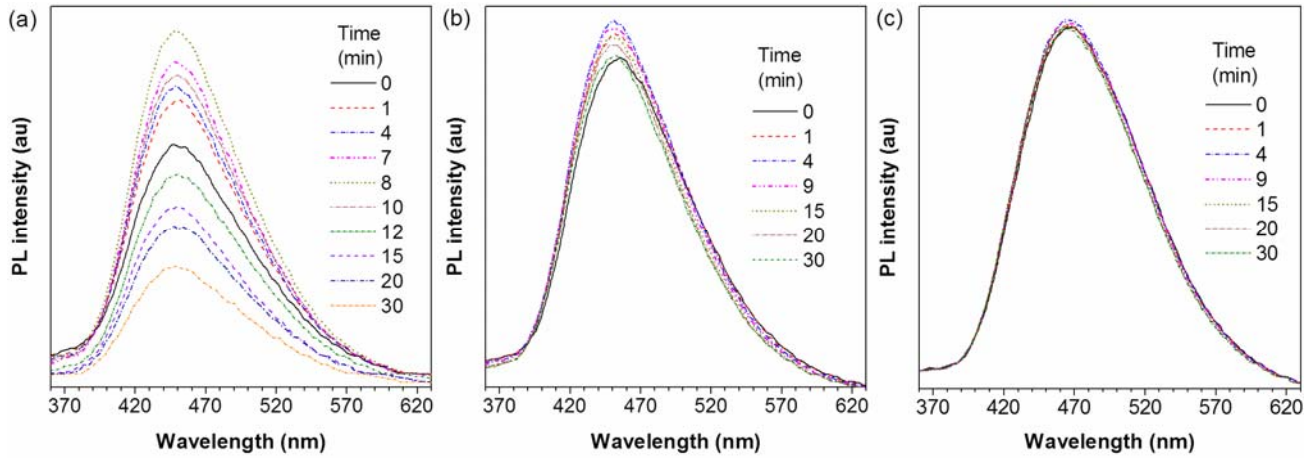


Figure S14. Time dependences of PL spectra of an *E*/*Z* mixture (1:1) of BPHTATPE in THF/water mixtures with water fractions of (a) 70%, (b) 80%, and (c) 90%; λ_{ex} = 332 nm, c = 10 μM.

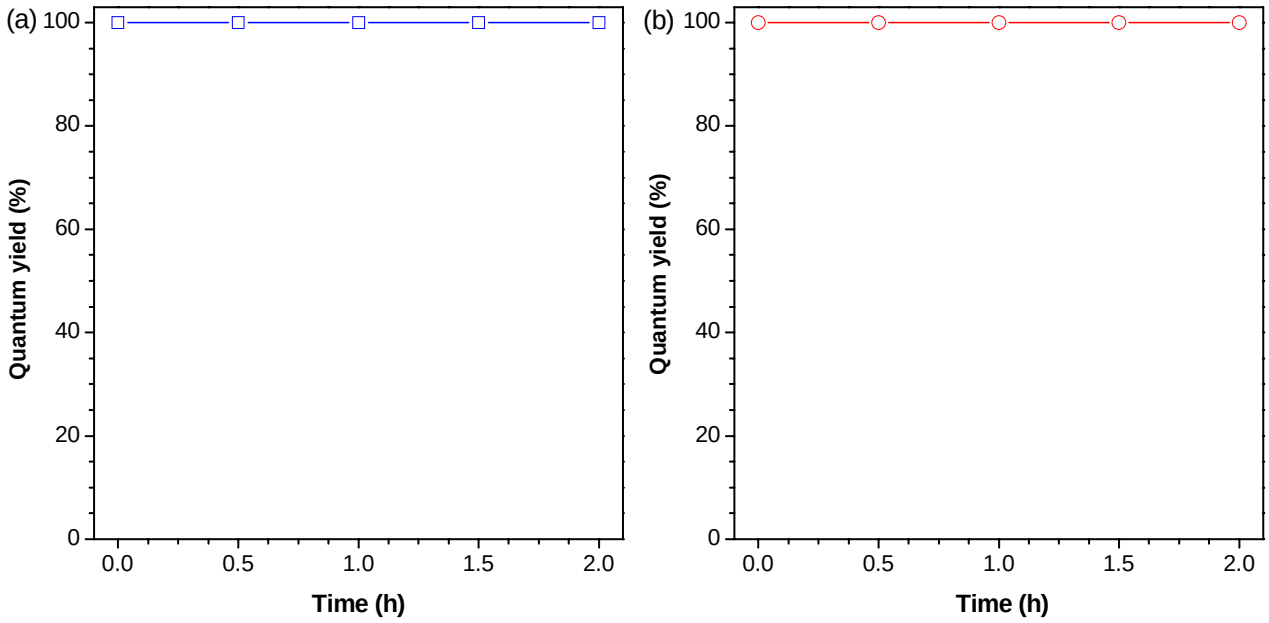


Figure S15. Variations in the solid-state quantum yields of (a) (*E*)- and (b) (*Z*)-BPHTATPE with time.

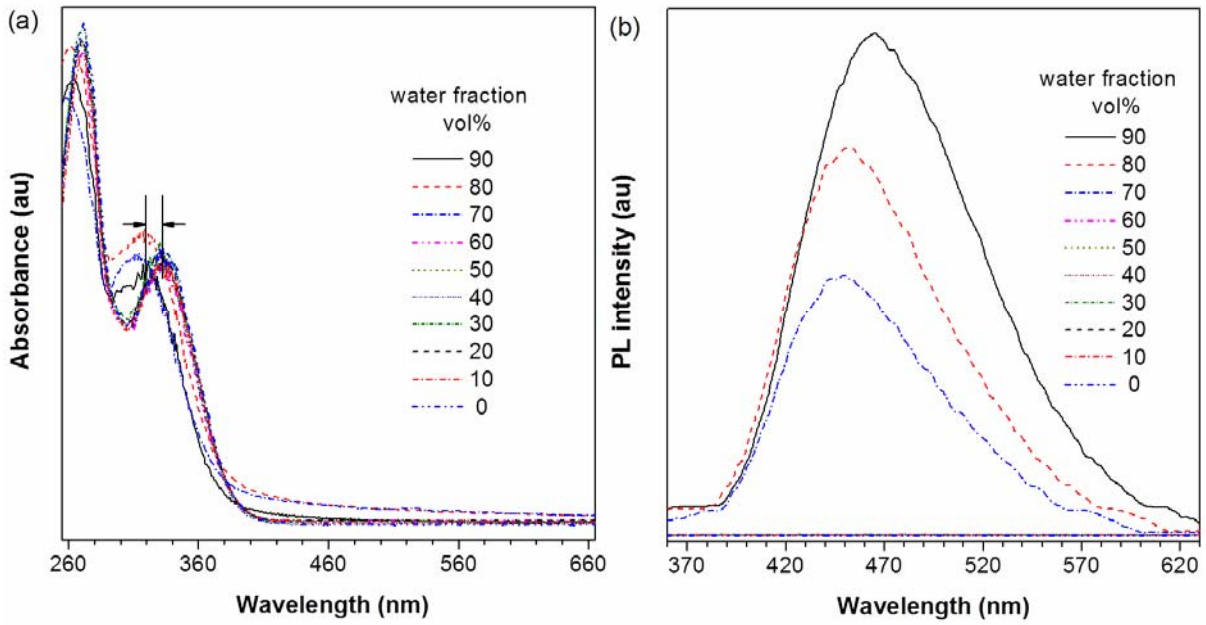


Figure S16. (a) Absorption and (b) emission spectra of an *E*/*Z* mixture (1:1) of BPHTATPE in THF/water mixtures with different fractions of water; λ_{ex} = 332 nm, *c* = 10 μM.

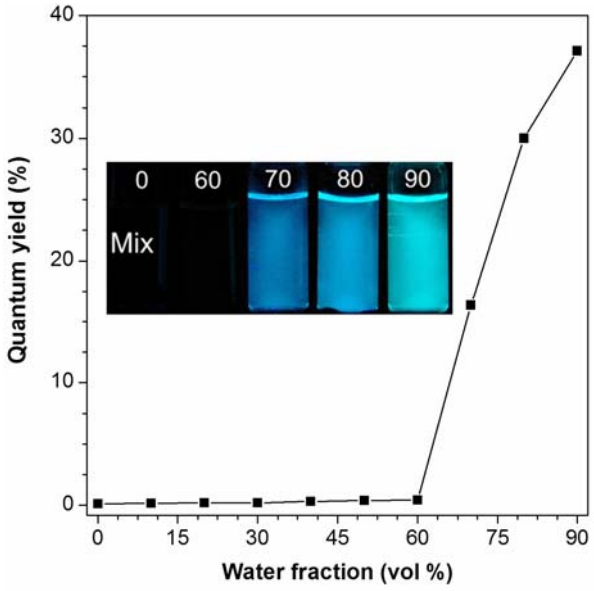


Figure S17. Variation in the quantum yield (Φ_F) of an *E*/*Z* mixture (1:1) of BPHTATPE with water fractions in THF/water mixtures. Φ_F values estimated using quinine sulfate in 0.05 mol/L H_2SO_4 (Φ_F = 54.6%) as standard. Inset: fluorescent images of the solution in THF and the suspensions in THF/water mixtures (f_w = 60–90%).

Table S1. Photo[a]- and thermo[b]-induced *E*–*Z* isomerizations of (*E*)-BPHTATPE

no.	time (min)	integral quantity of peak *Z*[b]	f_Z (%)[c]	
			(from peak *Z*)[c]	(from triazole)[d]
		photoisomerization		
1	2	0.04	1.0	
2	6	0.16	4.0	
3	11	0.28	7.0	
4	20	0.58	14.5	
5	30	1.00	25.0	
6	50	1.40	35.0	35.1
7	70	1.68	42.0	41.8
8	90	1.80	45.0	44.3
9	120	1.94	48.5	47.9
10	150	2.02	50.5	50.3
		thermoisomerization		
11	5	0.12	3.0	
12	10	0.24	6.0	
13	20	0.40	10.0	
14	30	0.56	14.0	
15	45	1.00	25.0	
16	60	1.38	34.5	34.7
17	90	1.76	44.0	43.5
18	120	1.86	46.5	46.1
19	150	1.92	48.0	47.5

[a] For photoisomerization, solutions of (*E*)-BPHTATPE in chloroform-*d* were exposed to a UV light of 365 nm at room temperature; for thermoisomerization, powders of (*E*)-BPHTATPE were heated to 203 °C under nitrogen. [b] Set the integral quantity of the peaks lying between 7.2 and 7.0 ppm in ^{1}H NMR as 14 when quantifying the quantity of peak *Z*. [c] Fraction of *Z*-conformer calculated from peak *Z*. [d] Fraction of *Z*-conformer calculated by fitting the two peaks corresponding to the hydrogen of triazole groups of *E* (7.654 ppm) and *Z* (7.645 ppm) isomers.

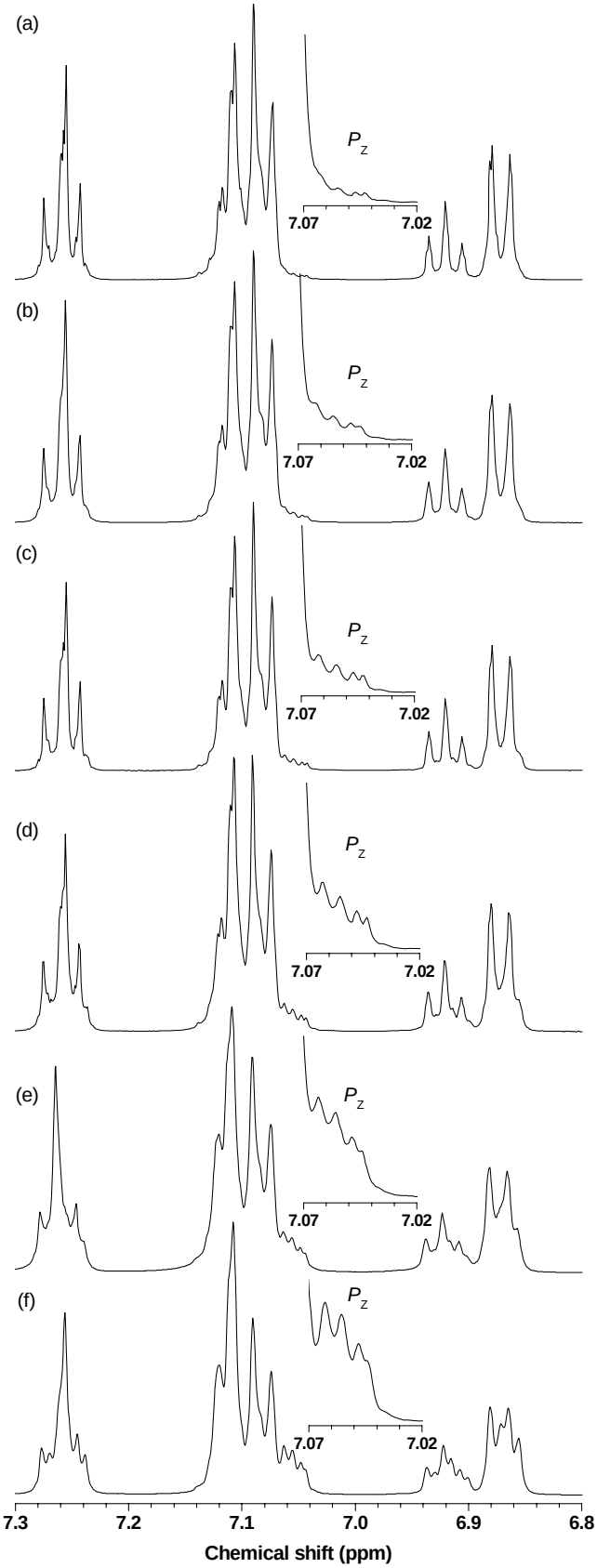


Figure S18. ^{1}H NMR spectra of (*E*)-BPHTATPE exposed to UV lamp (365 nm) for (a) 2, (b) 6, (c) 11, (d) 20, (e) 30, and (f) 50 min in $CDCl_3$. Insets: enlarged spectra. P_Z: peaks for *Z*-conformer.

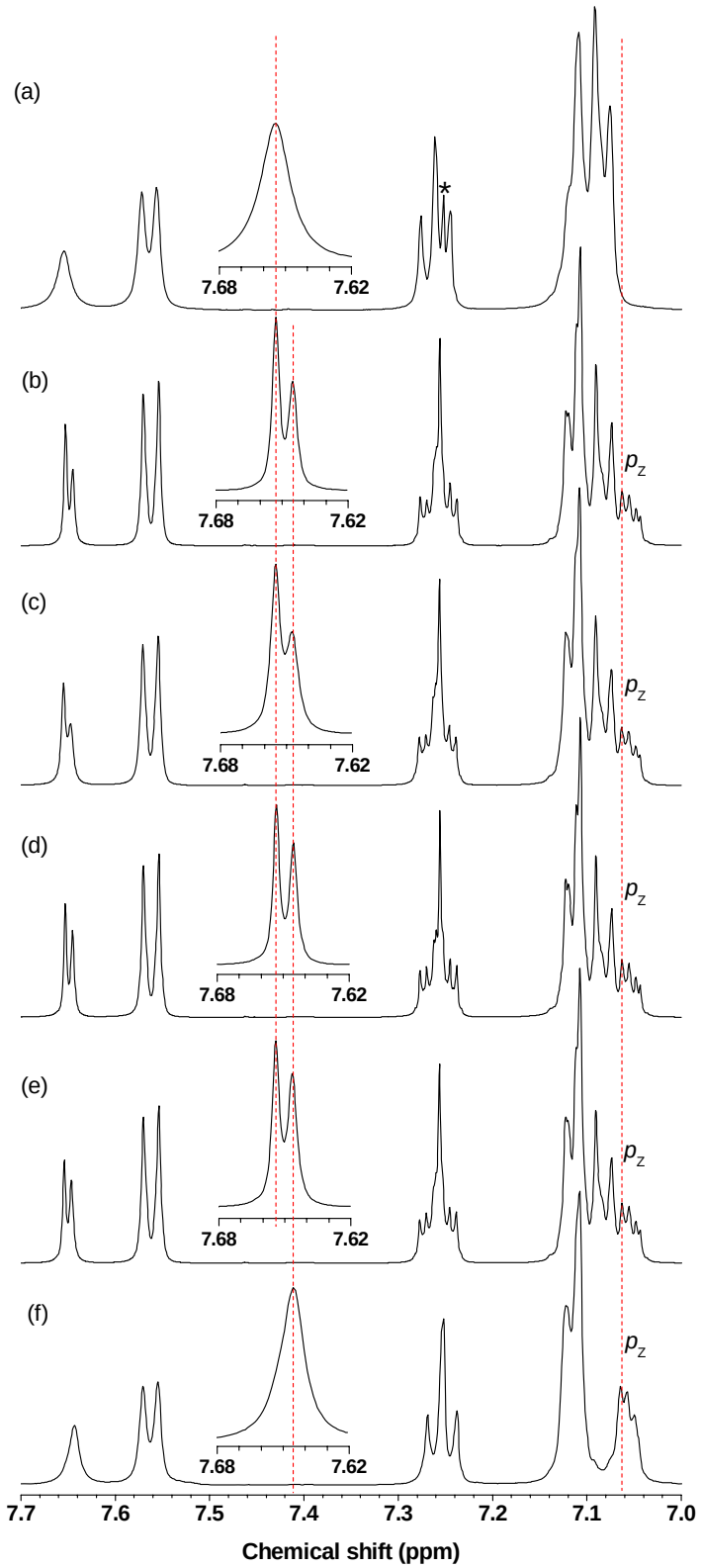


Figure S19. ^{1}H NMR spectra of (a) pure (*E*)-BPHTATPE and its solutions in $CDCl_3$ exposed to a UV lamp (365 nm) for (b) 70, (c) 90, (d) 120, and (e) 150 min, and (f) pure (Z)-BPHTATPE . Insets: enlarged spectra. P_Z: peaks for *Z*-conformer.

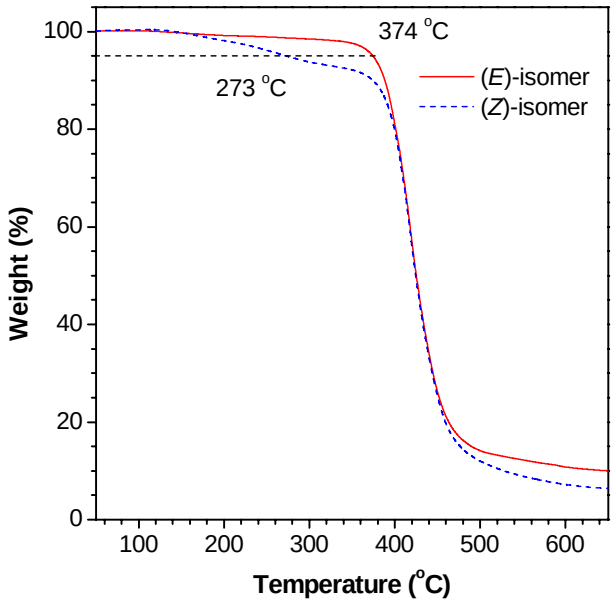


Figure S20. TGA thermograms of (*E*)- and (*Z*)-BPHTATPE recorded under nitrogen at a heating rate of 20 °C/min.

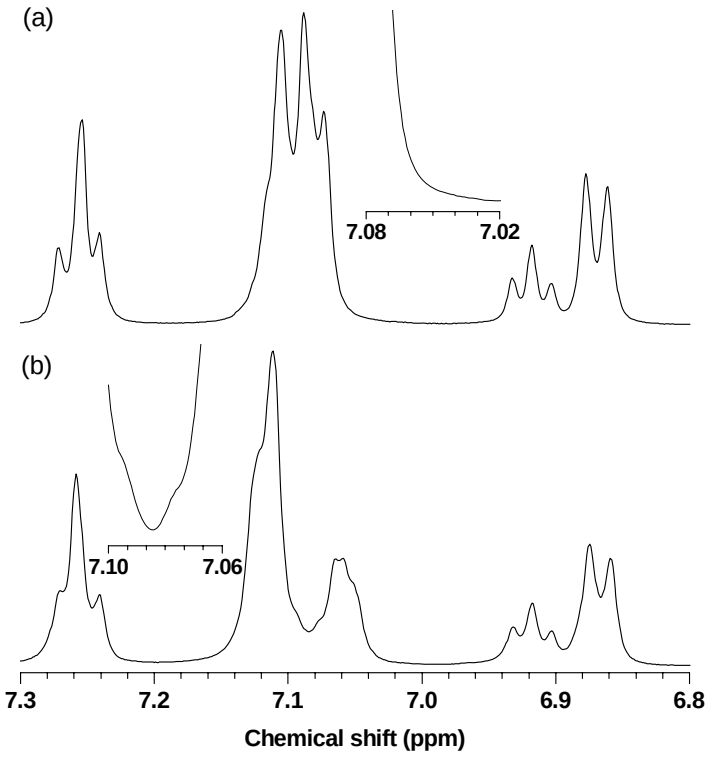


Figure S21. ^{1}H NMR spectra of (a) (*E*)-BPHTATPE heated at 180 °C and (b) (*Z*)-BPHTATPE heated at 165 °C for 30 min.

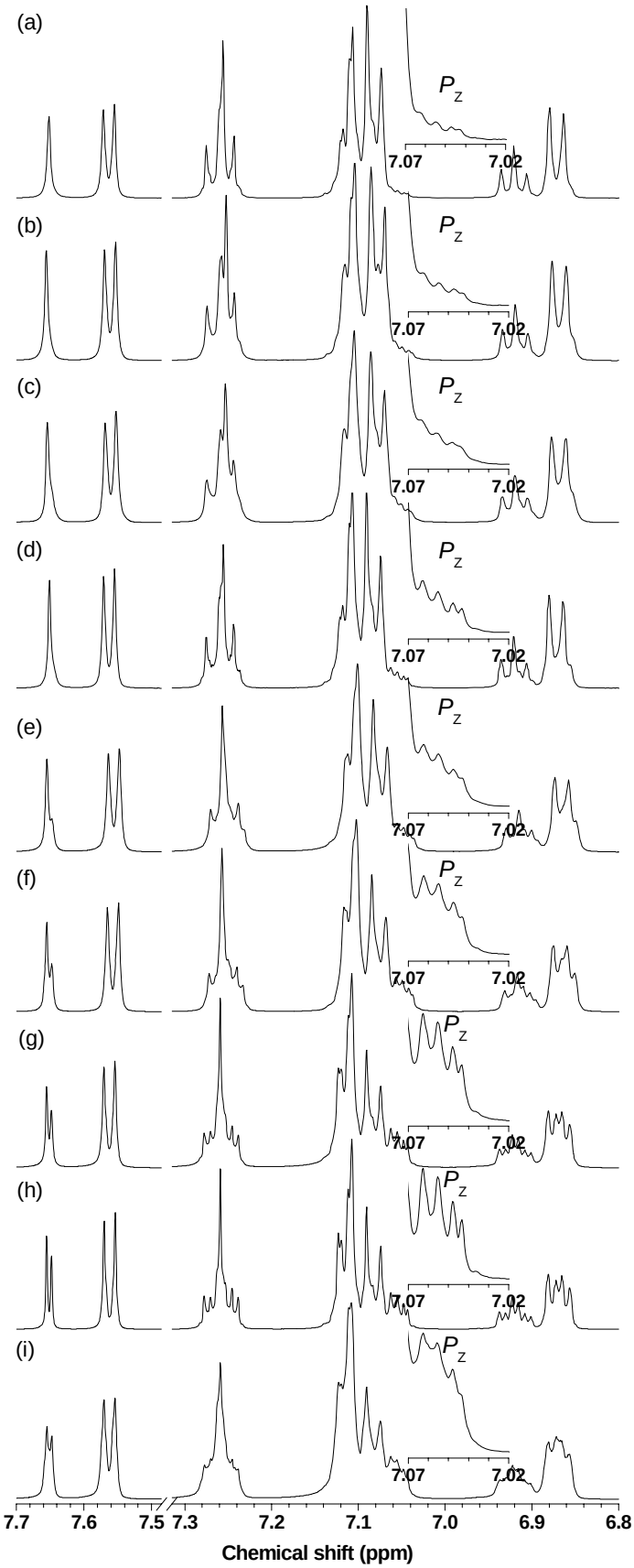


Figure S22. ^{1}H NMR spectra of (*E*)-BPHTATPE heated at 203 °C for (a) 5, (b) 10, (c) 20, (d) 30, (e) 45, (f) 60, (g) 90, (h) 120, and (i) 150 min in chloroform-*d*. Insets: enlarged spectra. P_Z: peaks for *Z*-conformer.

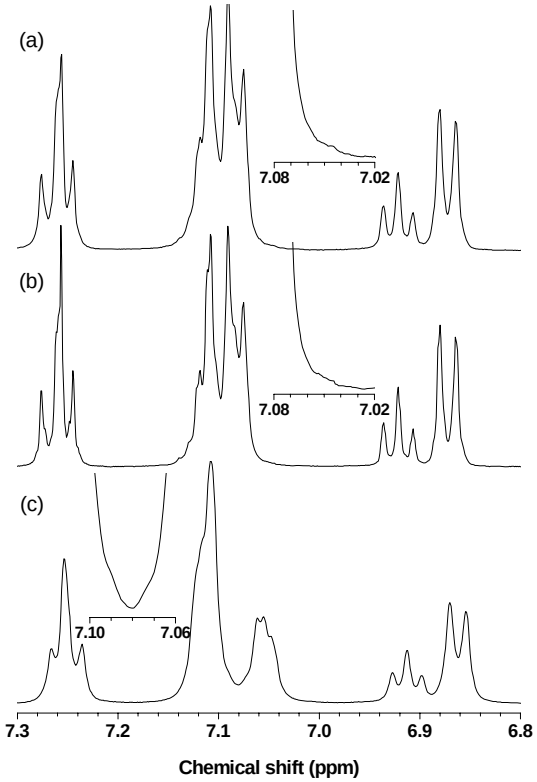


Figure S23. [1]H NMR spectra of (a, b) (*E*)- and (c) (*Z*)-BPHTATPE irradiated by the excitation light in a spectrofluorometer for 30 min with a wavelength of (a, c) 332 or (b) 254 nm. Insets: enlarged spectra.

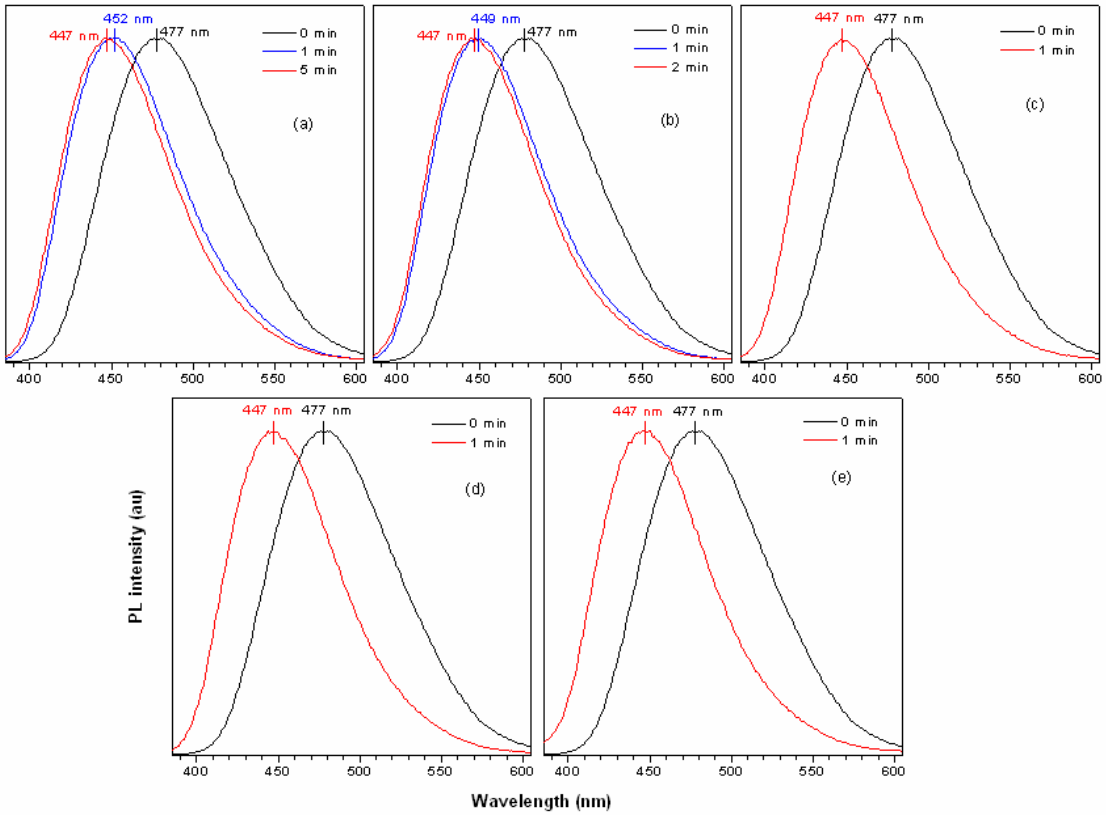


Figure S24. PL spectra of ground (*E*)-BPHTATPE heated at (a) 100, (b) 110, (c) 120, (d) 140 and (e) 160 °C for different time; λ_{ex} = 332 nm.

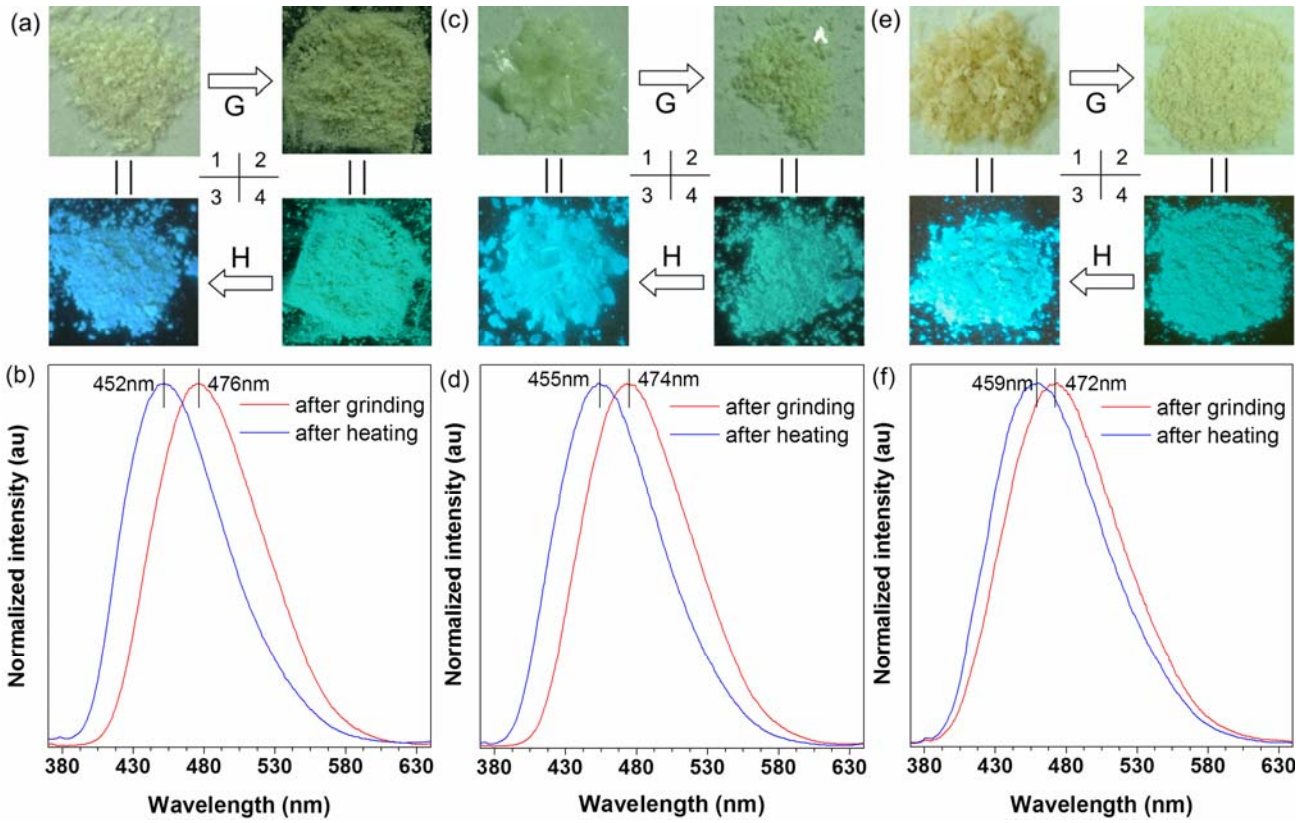


Figure S25. Mechanochromic processes of (*E*)/(*Z*)-BPHTATPE mixtures with mole ratios of (a) 8:2, (c) 5:5, and (e) 2:8. G and H represent the procedures of grinding and heating at 120 °C for 1 min. The corresponding PL spectra of the mixtures after grinding and then heating at 120 °C for 1 min are shown in panels (b), (d) and (f).

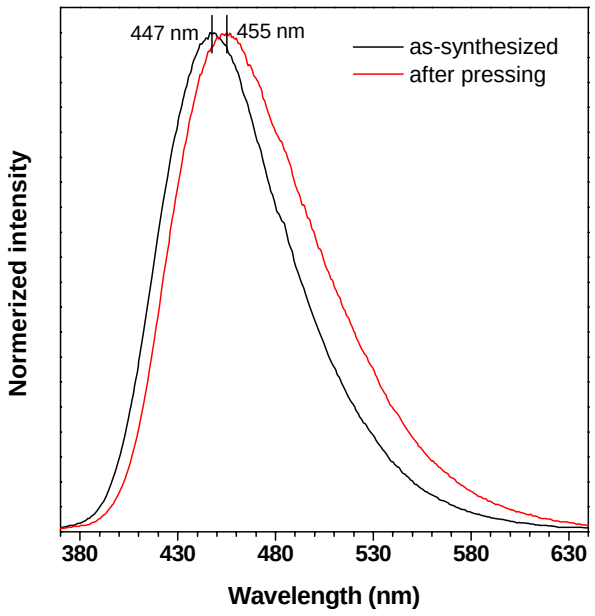


Figure S26. PL spectra of (*E*)-BPHTATPE before and after pressing; λ_{ex} = 332 nm.