Electronic Supplementary Information

Influence of number and substitution position of phenyl groups on the aggregation-induced emission of benzene-cored luminogens

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Experimental Section

Materials: 1,3,5-triphenyl benzene, 1,2,4-triphenyl benzene, 1,2,4,5-tetraphenyl benzene, Phenyl boronic acid, *p*-terphenyl, hexaphenyl benzene and phenylacetylene were purchased from J&K. 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone and *m*-terphenyl were purchased from TCI. Diphenylether was purchased from Alfa. $Pd(PPh_3)_4$ was purchased from J&K and used as received without further purification. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

Instrumentation: ^1H and ^{13}C NMR spectra were measured on a Mercury plus 400MHz NMR spectrometer in $CDCl_3$ using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. UV-visible absorption spectra were measured on a Varian CARY 100 Biospectrophotometer. Single crystal X-ray diffraction intensity data for 1,3,5-TPB was collected on an Xcalibur, Sapphire 3, Gemini ultra diffractometer with graphite monochromated Cu-Ka X-ray radiation. Thermalgravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (TAQ50) under nitrogen atmosphere at a heating rate of 10 ^oC/min. Absolute PL quantum yield spectrometer was tested on Hamamatsu C11347.

Synthesis of 1,3,5-triphenyl benzene (1,3,5-TPB): 1,3,5-tribromobenzene (629.6 mg, 2 mmol), phenylboronic acid (878.06 mg, 7.2 mmol), and $Pd(PPh_3)_4$ (115.6 mg, 0.2 mmol) were added into a 100 mL two necked round flask. The flask was evacuated under vacuum and flushed with dry nitrogen three times. THF (20 mL) and potassium carbonate solution (2 M, 10 mL) were injected into the flask and the mixture was stirred at 74 ^oC, after refluxed for 8 h, the solution was poured into water and extracted with DCM. The organic layer was washed with brine and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography using PE as eluent. White product was obtained

in 68.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 7.82 (s, 2H), 7.75 (d, 6H), 7.52 (t, 6H) 7.43 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 142.33, 141.14, 128.84, 127.54, 127.35, 125.17. HRMS (MALDI-TOF): *m*/*z* 306.1400 ($[M]^+$); calcd for $C_{24}H_{18}$ 306.1409.

Synthesis of 1,2,4-triphenyl benzene (1,2,4-TPB): The synthetic procedure is similar to that of 1,3,5-TPB. White solid was obtained in 92.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 7.68 (m, 4H), 7.52 (d, 1H), 7.47 (t, 2H), 7.38 (t, 1H), 7.22 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 141.5, 141.7, 141.0, 140.6, 139.6, 131.2, 130.0, 129.9, 129.5, 128.9, 127.5, 127.2, 126.7, 126.6, 126.2. HRMS (MALDI-TOF): *m*/*z* 306.1407 ($[M]^+$); calcd for $C_{24}H_{18}$ 306.1409.

Synthesis of 1,2,4,5-tetraphenyl benzene (1,2,4,5-TPB): the synthetic procedure is similar to that of 1,3,5-TPB. White solid was obtained in 77.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 7.55 (s, 2H), 7.25 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 140.9, 139.6, 133.0, 129.9, 128.05, 126.6. HRMS (MALDI-TOF): *m*/*z* 382.1707 ($[M]^+$); calcd for $C_{30}H_{22}$ 382.1722.

Synthesis of pentaphenylbenzene (PPB): 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (384.5 mg, 1 mmol) and phenylacetylene (204.1 mg, 2 mmol) were dissolved in diphenylether (20 mL) under N_2. The mixture was stirred at 110 ^{o}C overnight. Afterwards, diphenylether was removed by reduced pressure distillation. The residue was purified by silica gel column chromatography using PE/DCM=20:1 as eluent. White product was obtained in 77.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 7.60 (s, 1H), 7.18 (m, 10H), 6.95 (m, 6H), 6.88 (m, 7H), 6.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 141.8, 141.7, 146.8, 140.0, 139.3, 131.6, 131.5, 131.4, 130.0, 127.6, 127.0, 126.3, 125.6, 125.4. HRMS (MALDI-TOF): *m*/*z* 458.2020 ($[M]^+$); calcd for $C_{36}H_{26}$ 458.2035.

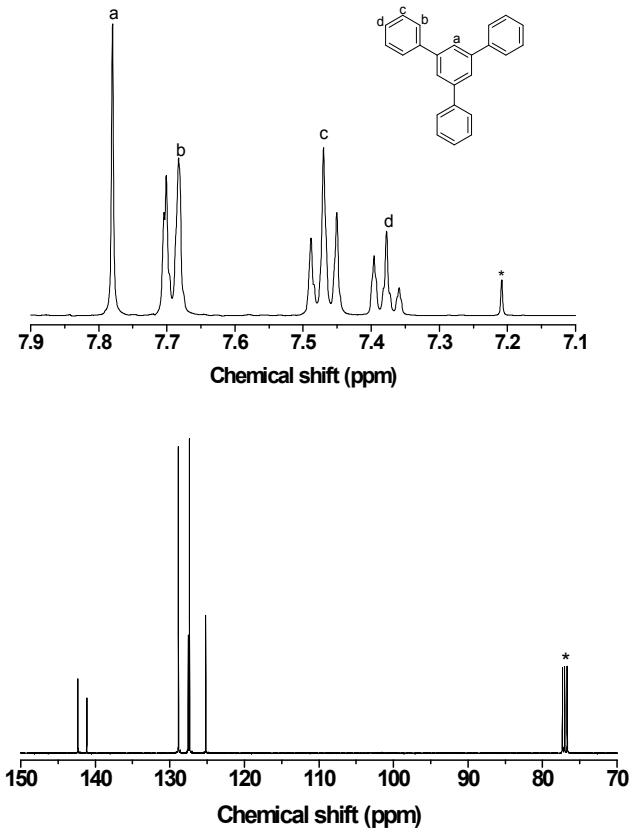

Figure S1. ^{1}H and ^{13}C NMR spectra of 1,3,5-triphenylbenzene (1,3,5-TPB) in $CDCl_3$. The solvent peaks are marked with asterisks.

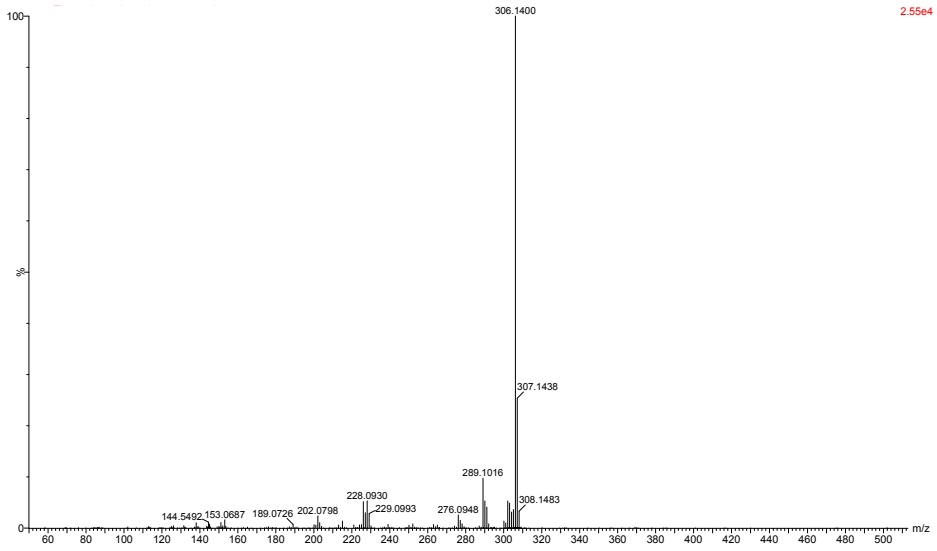

Figure S2. HRMS spectrum of 1,3,5-TPB.

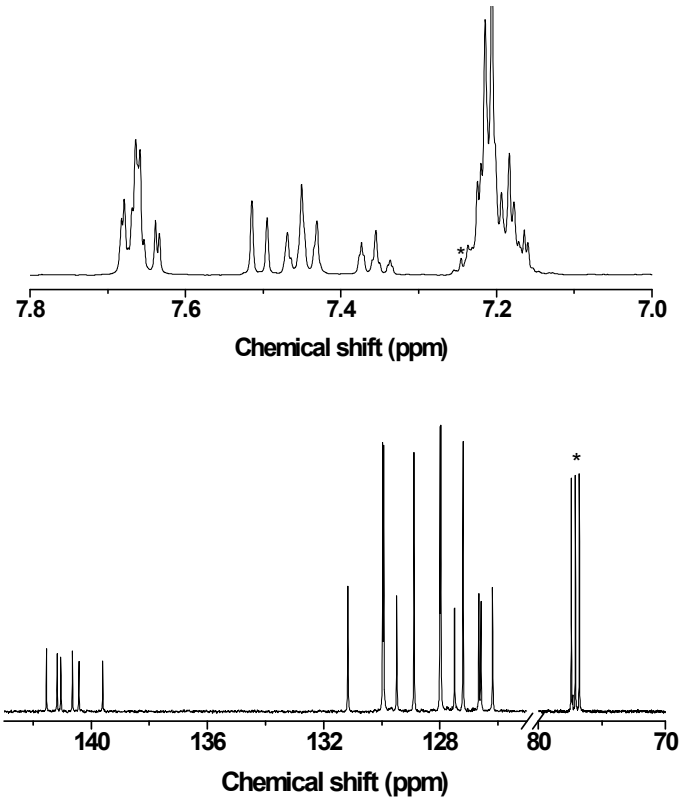

Figure S3. ^{1}H and ^{13}C NMR spectra of 1,2,4-triphenylbenzene **(**1,2,4-TPB**)** in $CDCl_3$. The solvent peaks are marked with asterisks.

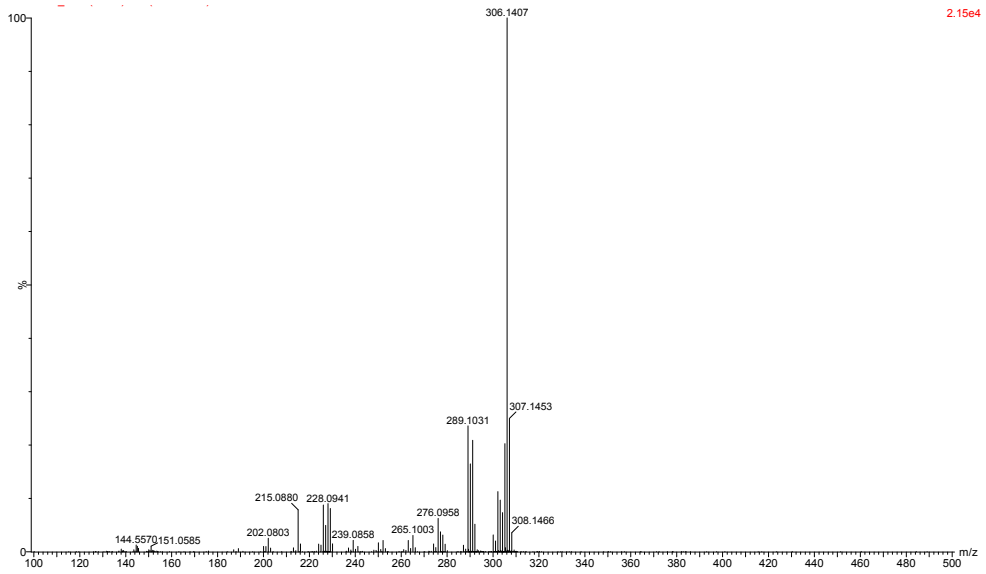

Figure S4. HRMS spectrum of 1,2,4-TPB.

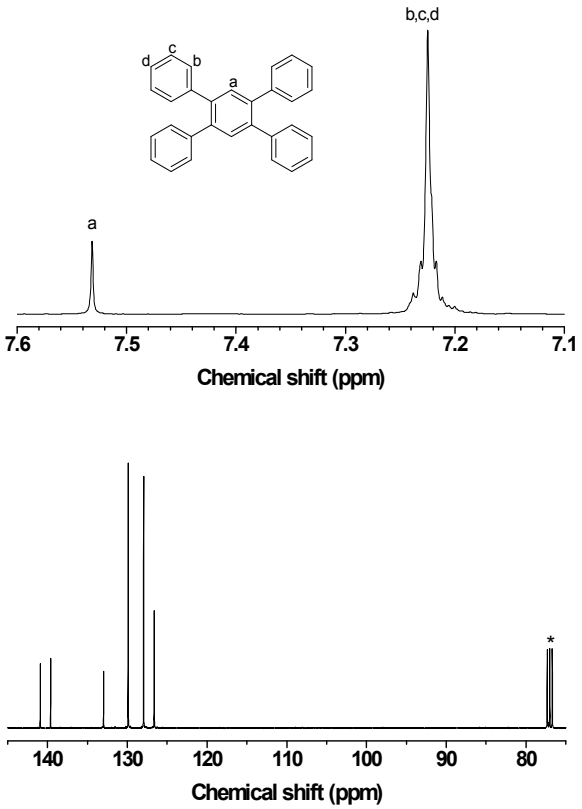

Figure S5. ^{1}H and ^{13}C NMR spectra of 1,2,4,5-tetraphenylbenzene (1,2,4,5-TPB) in $CDCl_3$. The solvent peaks are marked with asterisks.

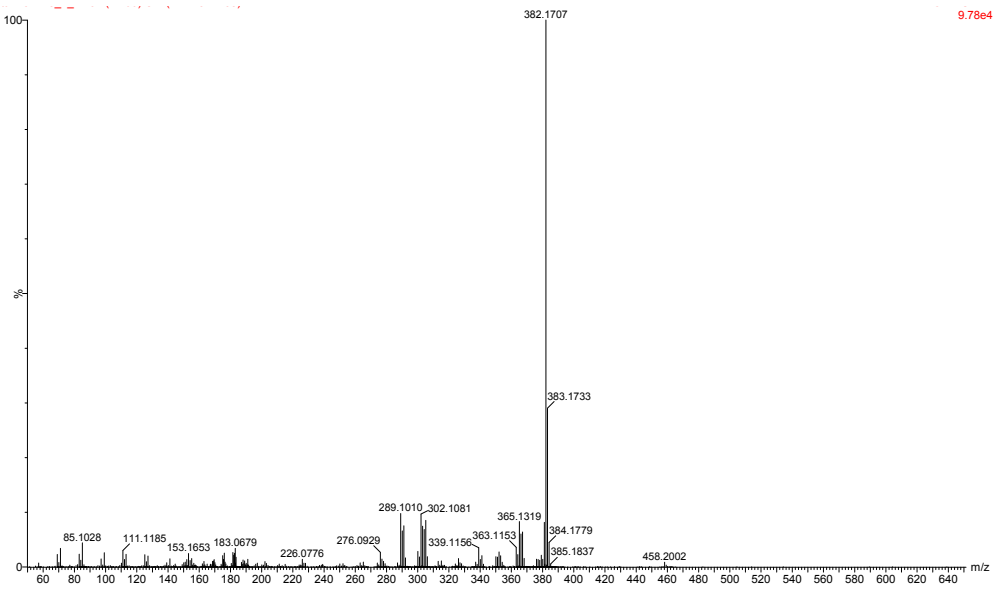

Figure S6. HRMS spectrum of 1,2,4,5-TPB.

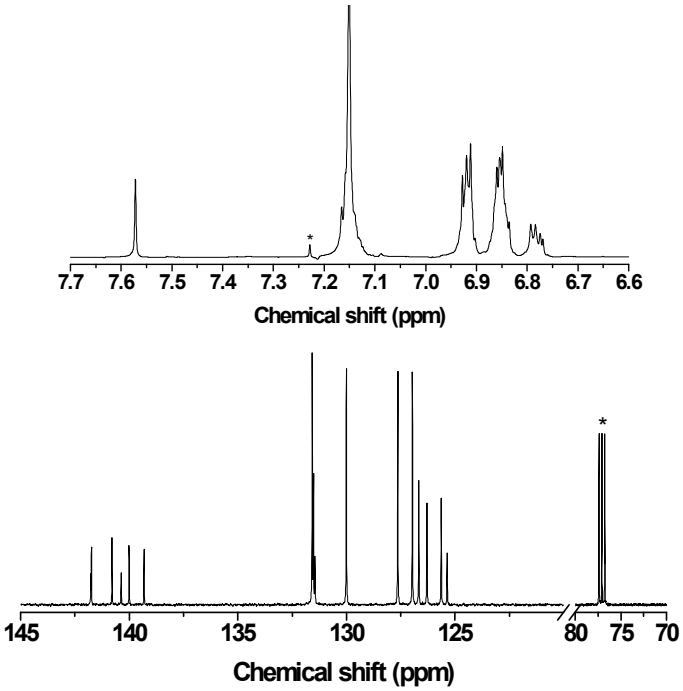

Figure S7. ^{1}H and ^{13}C NMR spectra of pentaphenylbenzene (PPB) in $CDCl_3$. The solvent peaks are marked with asterisks.

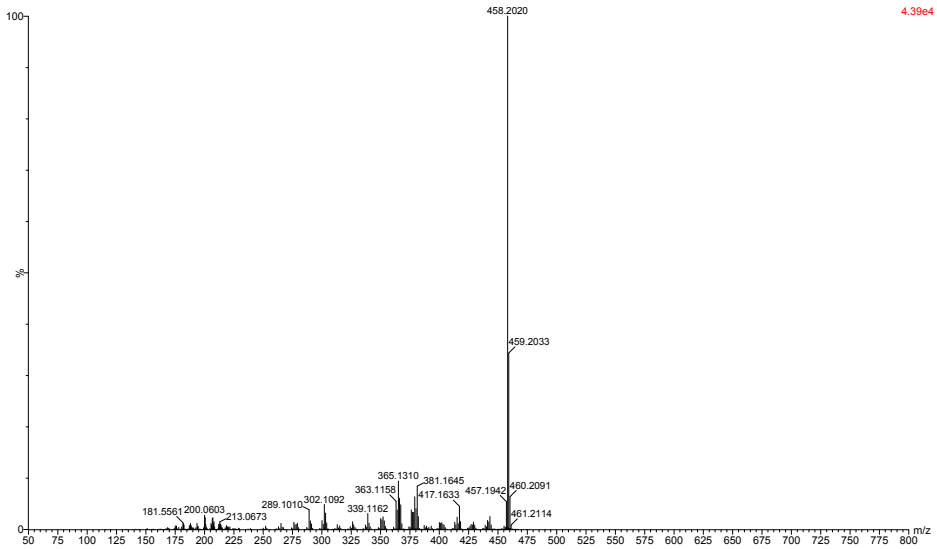

Figure S8. HRMS spectrum of PPB.

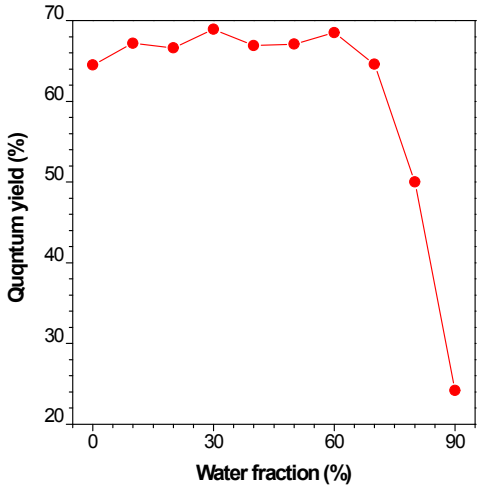

Figure S9. The changes of absolute quantum yields of *p*-terphenyl in THF/water mixtures with different water fractions. Concentration: 10 μM, λ_{ex} = 275 nm.

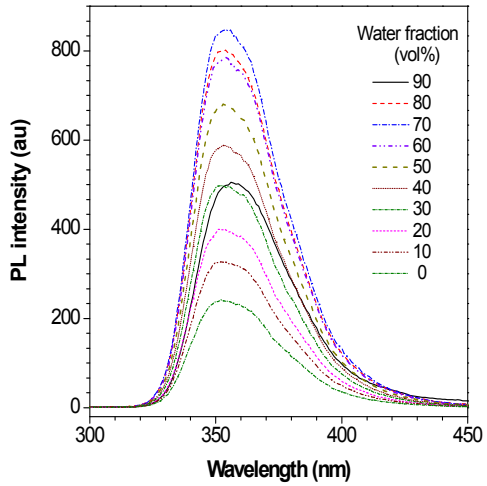

Figure S10. PL spectra of 1,3,5-TPB in THF/water mixtures with different water fractions. Concentration: 10 μM, λ_{ex} = 253 nm.

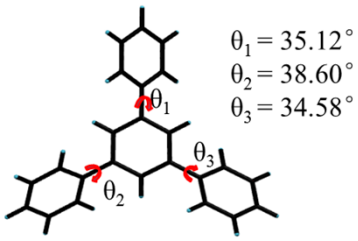

Figure S11. Torsion angles obtained from the single crystal of 1,3,5-TPB.

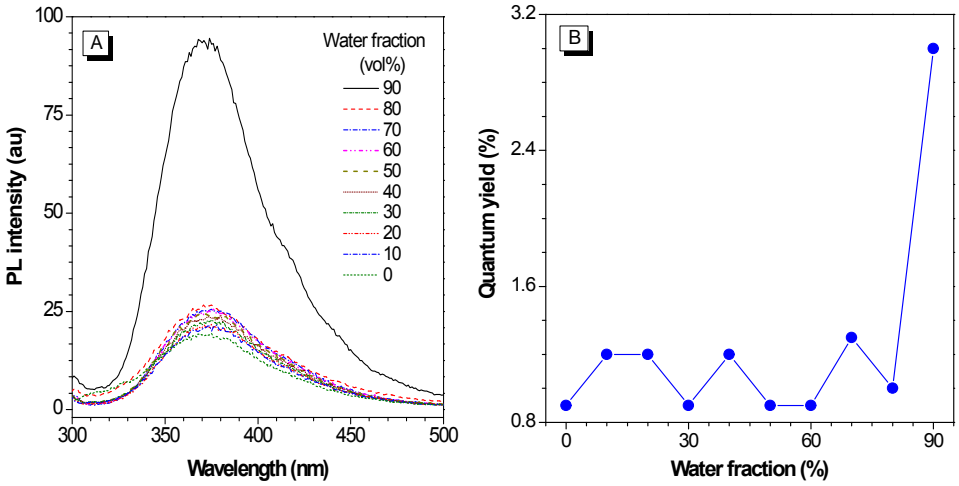

Figure S12. (A) PL spectra of 1,2,4-TPB in THF/water mixtures with different water fractions. λ_{ex} = 273 nm (B) Changes of absolute Φ_F of 1,2,4-TPB versus water fraction in THF/water mixtures. λ_{ex} = 275 nm. Concentration: 10 μM.

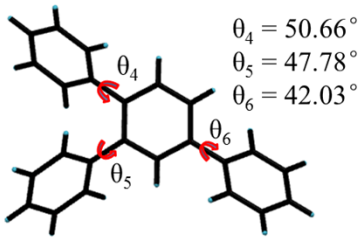

Figure S13. Torsion angles obtained from the single crystal of 1,2,4-TPB.

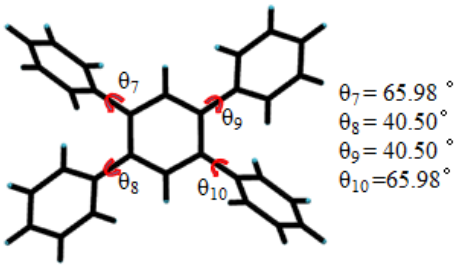

Figure S14. Torsion angles obtained from the single crystal of 1,2,4,5-TPB.

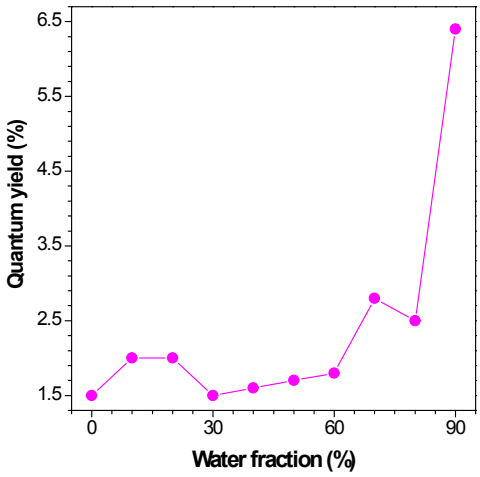

Figure S15. Changes of absolute Φ_F of 1,2,4,5-TPB versus water fraction in THF/water mixtures. Concentration: 10 μM. λ_{ex} = 275 nm.

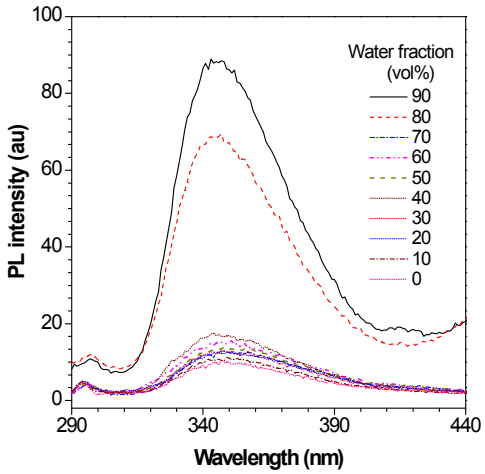

Figure S16. PL spectra of PPB in THF/water mixtures with different water fractions. Concentration: 10 μM, λ_{ex} = 249 nm.

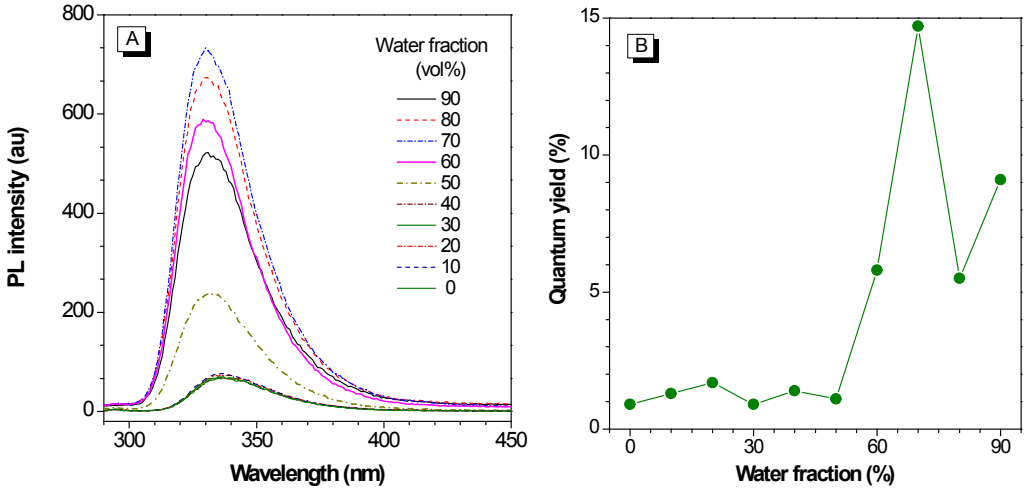

Figure S17. (A) PL spectra of HPB in THF/water mixtures with different water fractions. λ_{ex} = 274 nm. (B) Changes of absolute Φ_F of HPB versus water fraction in THF/water mixtures. λ_{ex} = 275 nm. Concentration: 10 μM.

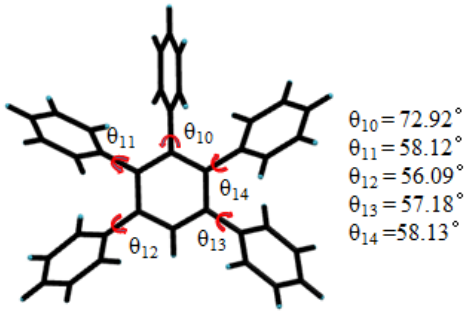

Figure S18. Torsion angles obtained from the single crystal of PPB.

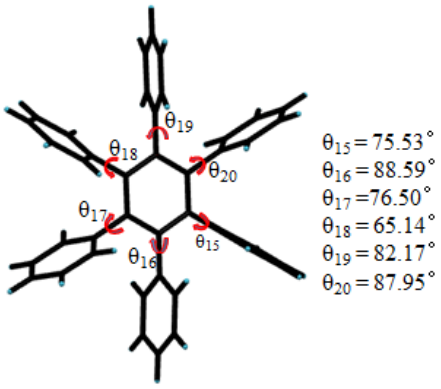

Figure S19. Torsion angles obtained from the single crystal of HPB.

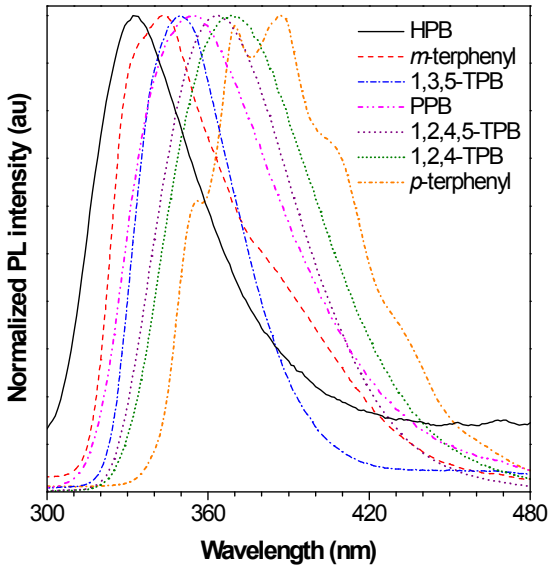

Figure S20. PL spectra of polyphenyls in their thin film states.

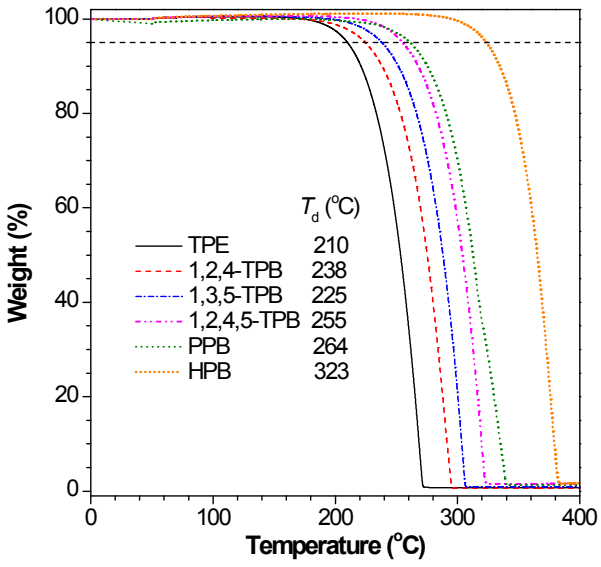

Figure S21. TGA curves of polyphenyls under nitrogen at a heating rate of 10 °C/min.

Table S1. Absolute quantum yields of polyphenyls in their film states.

polyphenyl	quantum yield (%)	λ_{em} (nm)
p-terphenyl	45.2	279
1,2,4-TPB	3.8	273
1,2,4,5-TPB	20.9	275
HPB	13.2	274

Table S2. Maximum emission peaks of polyphenyls in solution and thin film states.

polyphenyl	$\lambda_{em,soln}$ (nm)	$\lambda_{em,film}$ (nm)
p-terphenyl	350	387
m-terphenyl	341	343
1,3,5-TPB	354	350
1,2,4-TPB	375	369
1,2,4,5-TPB	380	363
PPB	347	355
HPB	337	332