Supporting Information

Engineering Isomeric AIEgens Containing Tetraphenylpyrazine for Dual Memory Storage

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Experimental Section

Materials and Instruments: All the chemicals including 4-formylphenylboronic acid, $Pd(PPh_3)_4$, 4-pyridylacetonitrile, 3-pyridylacetonitrile and 2-pyridylacetonitrile were purchased from Energy Chemical and J&K Scientific, and used directly without further purification. THF was distilled from sodium benzophenone ketyl under nitrogen before use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer while $CDCl_3$ was used as solvent with tetramethylsilane as an internal reference. High-resolution mass spectra (HRMS) were performed on an LC/MS/MS consisting of a High Performance Liquid Chromatography (HPLC) system (Ultimate 3000 RSLC, Thermo Scientific, USA) and a Q Exactive Orbitrap mass spectrometer. UV-Vis spectra were carried out with a TU-1810PC/SPC spectrophotometer. The absolute quantum yield (Φ_F) was recorded on a Hamamatsu Quantaurus-QY C11347 spectrometer. The steady-state PL spectra was recorded on a EDINBURGH FS5 spectrofluorometer. The transient PL spectra was recorded on a EDINBURGH FLS 1000 spectrofluorometer. The dynamic light scattering was carried out with a NANO ZS at a fixed angle of 90º. Thermogravimetric analysis (TGA) was performed on a METTER TOLEDO TGA thermogravimetric analyzer under nitrogen at a heating rate of 10 ºC/min.

Synthesis of 2-(4-bromophenyl)-5,6-bis(4-methoxyphenyl)-3-phenylpyrazine (3): Into a 250 mL round bottom flask was added 4.7 g (17.3 mmol) of 1,2-bis(4-methoxyphenyl)ethane-1,2-diamine (**1**), 5.0 g (17.3 mmol) of 1-(4-bromophenyl)-2-phenylethane-1,2-dione (**2**) and 36 mL of acetic acid. The mixture was allowed to reflux for 12 h. Afterwards, the mixture was cooled down to room temperature and filtered. The crude products were washed with acetic acid several times. A white powder of 5.0 g (9.6 mmol) was obtained in a yield of 55.5%. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.65–7.62 (m, 6H), 7.55–7.53 (d, 2H), 7.47–7.45 (d, 2H), 7.38–7.36 (m, 3H), 6.90–6.88

(m, 4H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$), *δ* (ppm): 160.1, 147.9, 146.7, 146.6, 146.4, 138.3, 137.6, 131.5, 131.4, 131.2, 131.1, 130.9, 129.8, 128.7, 128.4, 123.0, 113.8, 55.3.

Synthesis of 4'-(5,6-bis(4-methoxyphenyl)-3-phenylpyrazin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (5): Into a 250 mL round bottom flask was added 5.0 g (9.6 mmol) of **3,** 1.72 g (11.5 mmol) of 4-formylphenylboronic acid (**4**), 12.8 mg (0.011 mmol) of Pd(PPh$_3$)$_4$, 150 mL of THF and 70 mL of K_2CO_3 aqueous solution (2 M) under nitrogen. The mixture was allowed for stir at 80 °C overnight. After cooled down to room temperature, the mixture was diluted with dichloromethane and washed with NH_4Cl aqueous solution. The collected organic phase was condensed and purified by a silica-gel column with DCM/petroleum ether (1:1 by volume) as eluent. A pale-yellow powder of 4.7 g (8.6 mmol) was obtained in a yield of 89.6%. ^{1}H NMR (400 MHz, CDCl$_3$), *δ* (ppm): 10.08 (s, 1H), 7.99-7.97 (d, 2H), 7.82–7.78 (t, 4H), 7.71–7.62 (m, 8H), 7.38-7.37 (m, 3H), 6.92–6.89 (m, 4H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$), *δ* (ppm): 192.0, 160.1, 147.8, 147.7, 146.8, 146.6, 139.6, 139.0, 138.6, 135.3, 131.3, 131.2, 131.0, 130.9, 130.6, 130.4, 130.0, 128.7, 128.4, 127.6, 127.2, 113.8, 55.4.

Synthesis of TPP-*p*-Py : Into a 250 mL round bottom flask was added 500 mg (0.91 mmol) of **5**, 0.305 mL (3.64 mmol) of 4-pyridylacetonitrile (**6**), 50 mL of 1,4-dioxane and 5 mL of KOH aqueous solution (4 M). The mixture was allowed for stir at 120°C for three days. After cooled down to room temperature, the mixture was condensed under reduced pressure, and then dissolved by ethyl acetate, washed with water and dry with anhydrous sodium sulfate. The collected organic phase was condensed and purified by a neutral alumina column with ethyl acetate /petroleum ether (1:2 by volume) as eluent. A yellow powder of 175 mg (0.27 mmol) was obtained in a yield of 29.7%. ^{1}H NMR (400 MHz, CDCl$_3$), *δ* (ppm): 8.75 (s, 1H), 8.64 (s, 1H), 8.08–8.06 (d, 1H), 7.81–7.54 (m, 14H), 7.39–7.32 (m, 5H), 6.92-6.89 (m, 4H), 3.87 (s, 6H). ^{13}C NMR (100 MHz,

$CDCl_3$), δ (ppm): 160.1, 150.6, 150.4, 147.8, 147.7, 146.9, 146.8, 144.7, 143.8, 143.6, 142.1, 141.7, 139.4, 139.1, 138.8, 138.6, 138.4, 133.5, 131.9, 131.2, 131.0, 130.6, 130.5, 129.9, 129.7, 128.7, 128.4, 127.7, 126.9, 126.8, 122.6, 120.3, 120.1, 117.1, 113.8, 108.8, 55.3. HRMS: *m*/*z* 649.2593 $[(M+1)^+$, calcd. for 649.2598].

Synthesis of TPP-*m*-Py:The synthetic method was similar to that of TPP-*p*-Py expect that the 4-pyridylacetonitrile was replaced by 3-pyridylacetonitrile (**7**). A yellow powder of 180 mg (0.28 mmol) was obtained in a yield of 30.8%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.00 (s, 1H), 8.68 (s, 1H), 8.07–8.03 (t, 3H), 7.80–7.77 (m, 4H), 7.73–7.63 (m, 9H), 7.49–7.46 (m, 1H) 7.39–7.37 (m, 3H), 6.92–6.89 (m, 4H), 3.87 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 160.1, 149.6, 147.7, 147.6, 146.8, 146.7, 143.4, 143.3, 139.5, 138.6, 133.8, 132.3, 131.2, 131.0, 130.9, 130.5, 130.1, 129.9, 128.7, 128.4, 127.6, 126.9, 123.9, 117.3, 113.8, 107.9, 55.3. HRMS: *m*/*z* 649.2596 $[(M+1)^+$, calcd. for 649.2598].

Synthesis of TPP-*o*-Py: The synthetic method was similar to that of TPP-*p*-Py expect that the 4-pyridylacetonitrile was replaced by 2-pyridylacetonitrile (**8**). A yellow powder of 200 mg (0.31 mmol) was obtained in a yield of 34.1%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.71–8.70 (d, 1H), 8.62 (s, 1H), 8.14–8.12 (d, 2H), 7.90–7.63 (m, 14H), 7.39–7.35 (m, 4H), 6.92–6.89 (m, 4H), 3.87 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 160.1, 151.0, 149.4, 147.7, 147.6, 146.9, 145.0, 143.3, 139.7, 138.6, 138.5, 137.8, 132.4, 131.2, 131.0, 130.7, 130.5, 129.9, 128.7, 128.4, 127.5, 126.9, 123.6, 121.5, 117.9, 113.8, 55.3. HRMS: *m*/*z* 649.2595 $[(M+1)^+$, calcd. for 649.2598].

Calculation details: All quantum mechanical calculations carried out using the Gaussian 09 package[1]. The structures of molecules were optimized by the density functional theory at the B3LYP/6-31G(d,p) level[2]. Grimme's D3 dispersion correction[3] was applied to structure optimizations.

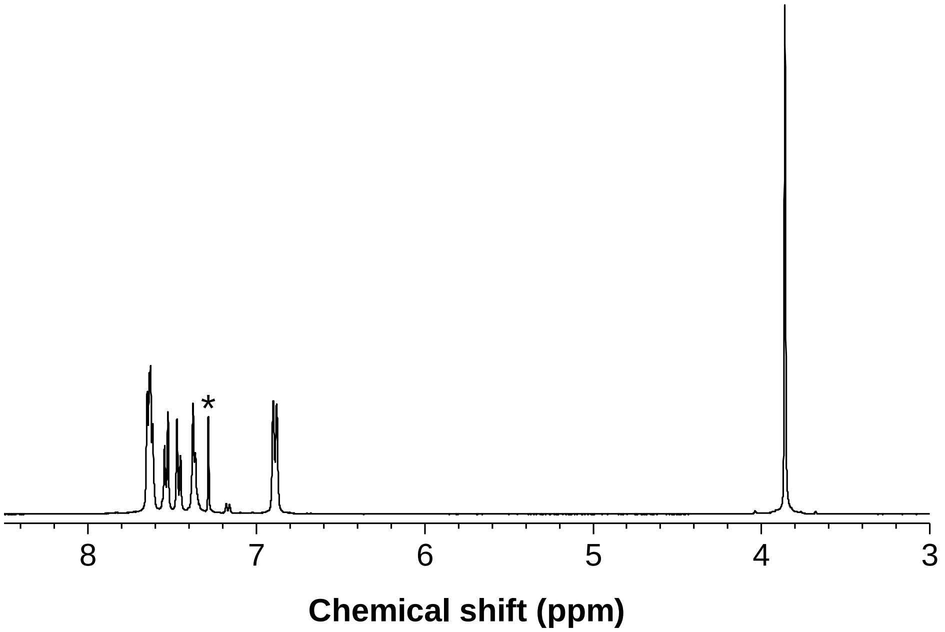


Figure S1. ^{1}H NMR spectra of **3** in $CDCl_3$. The solvent peak is marked with an asterisk.

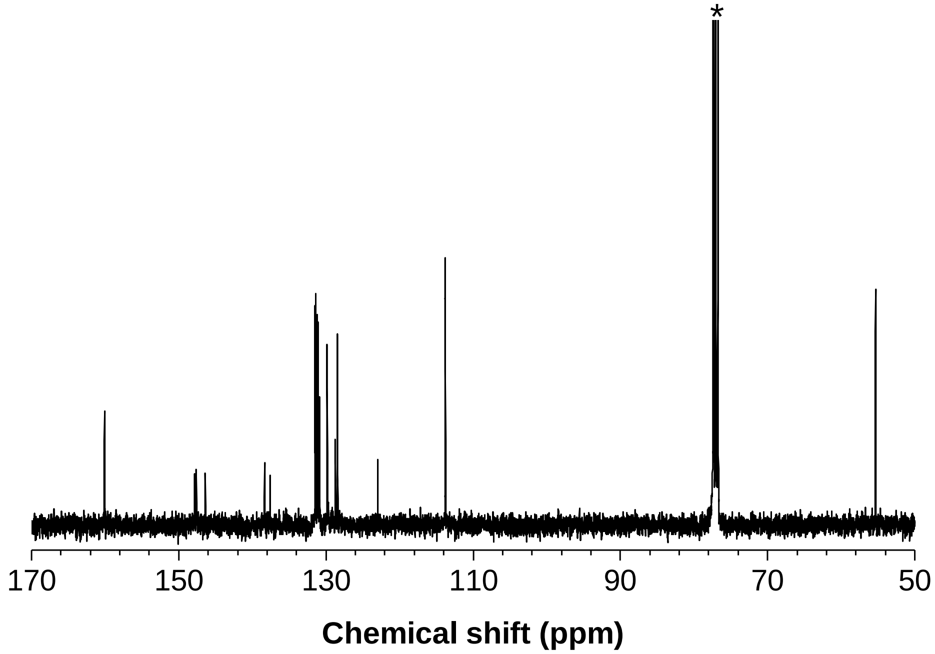


Figure S2. ^{13}C NMR spectra of **3** in $CDCl_3$. The solvent peaks are marked with an asterisk.

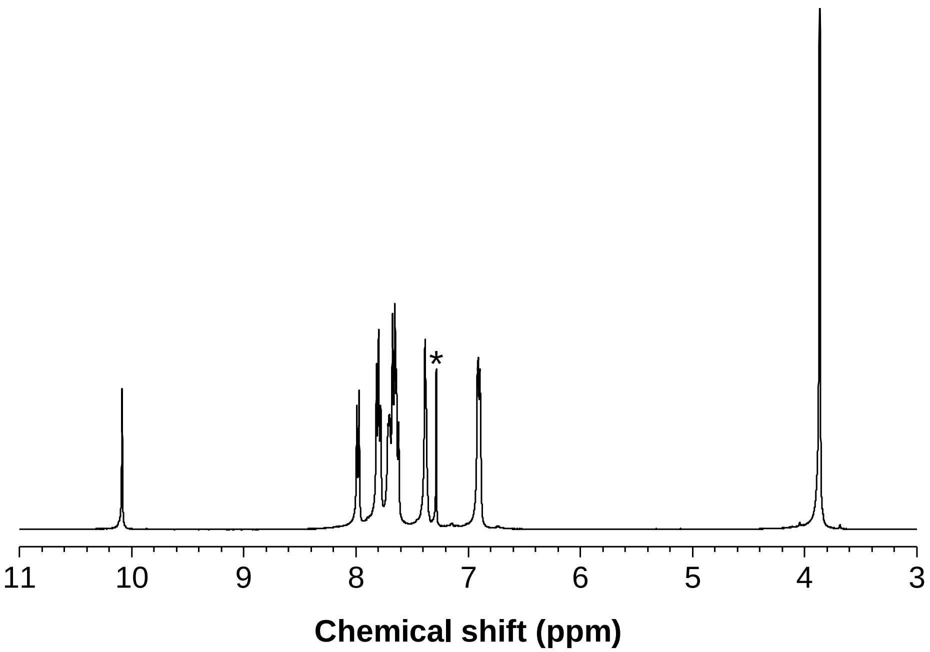


Figure S3. ^{1}H NMR spectra of **5** in $CDCl_3$. The solvent peak is marked with an asterisk.

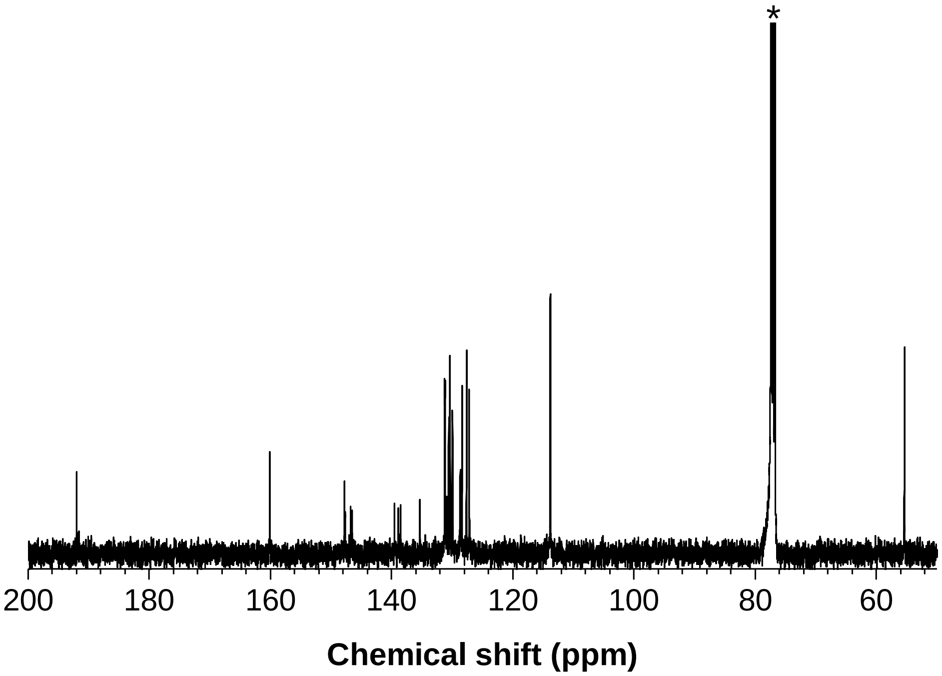


Figure S4. ^{13}C NMR spectra of **5** in $CDCl_3$. The solvent peaks are marked with an asterisk.

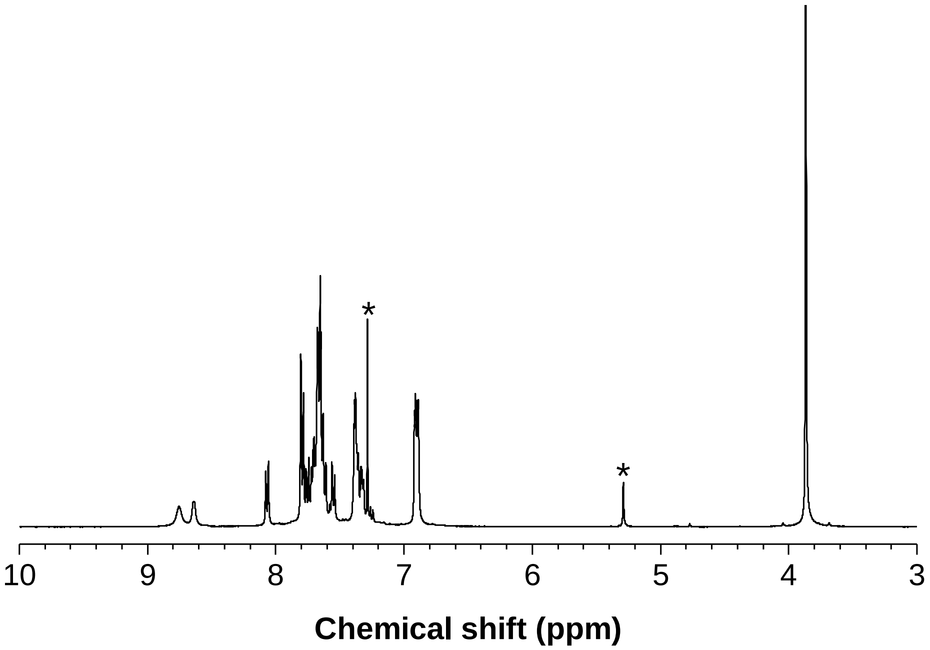


Figure S5. ^{1}H NMR spectra of TPP-*p*-Py in $CDCl_3$. The solvent peaks are marked with asterisks.

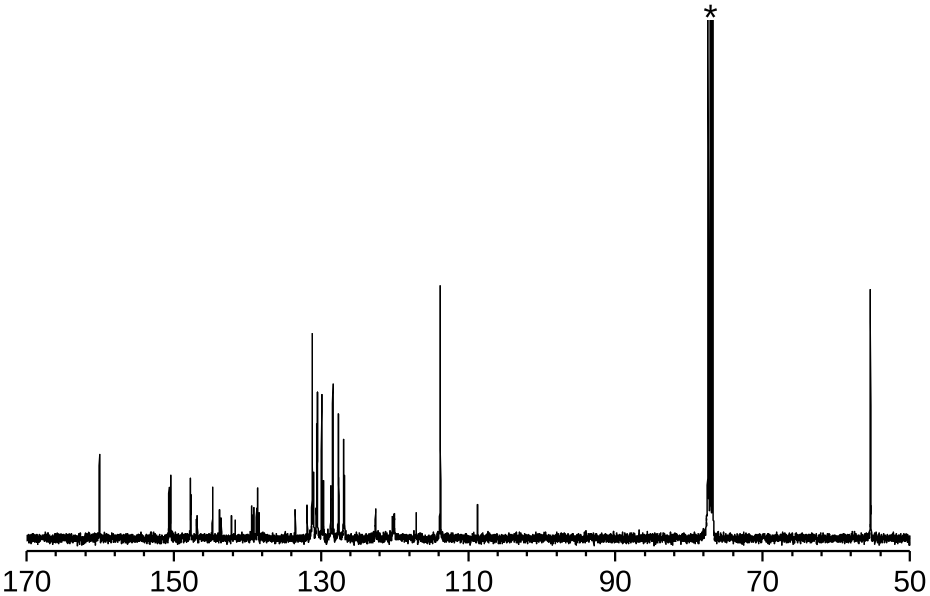


Figure S6. ^{13}C NMR spectra of TPP-*p*-Py in $CDCl_3$. The solvent peaks are marked with an asterisk.

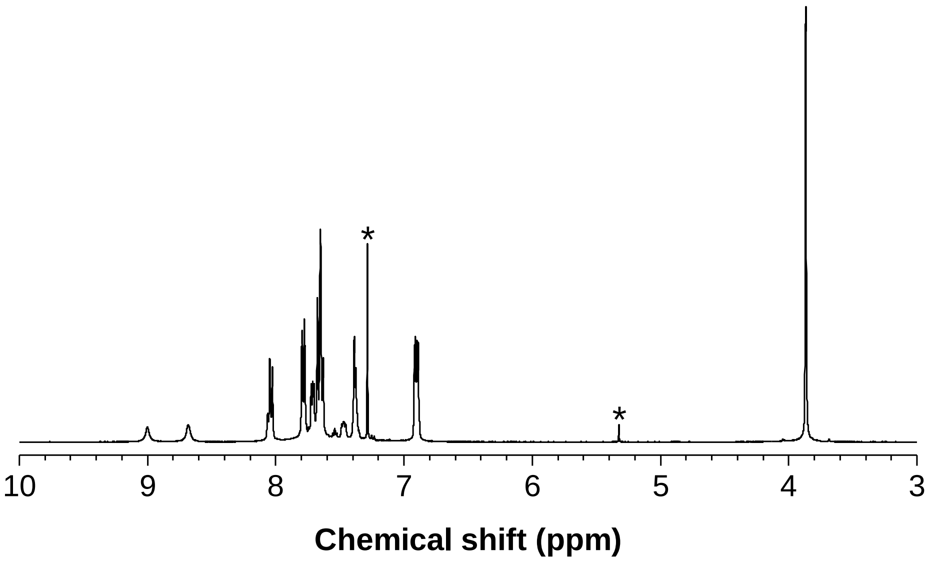


Figure S7. ^{1}H NMR spectra of TPP-*m*-Py in $CDCl_3$. The solvent peaks are marked with asterisks.

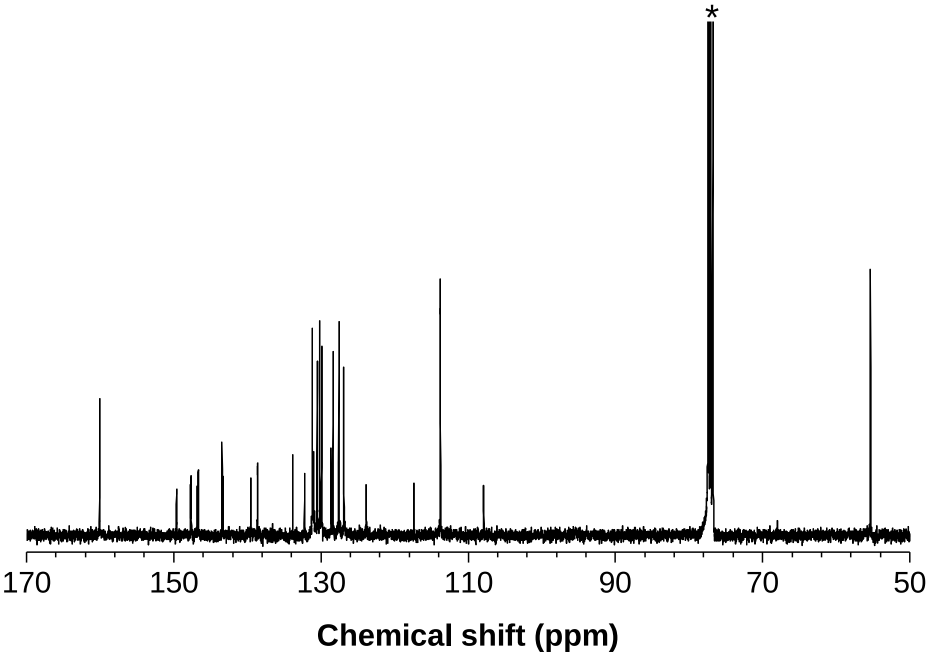


Figure S8. ^{13}C NMR spectra of TPP-*m*-Py in $CDCl_3$. The solvent peaks are marked with an asterisk.

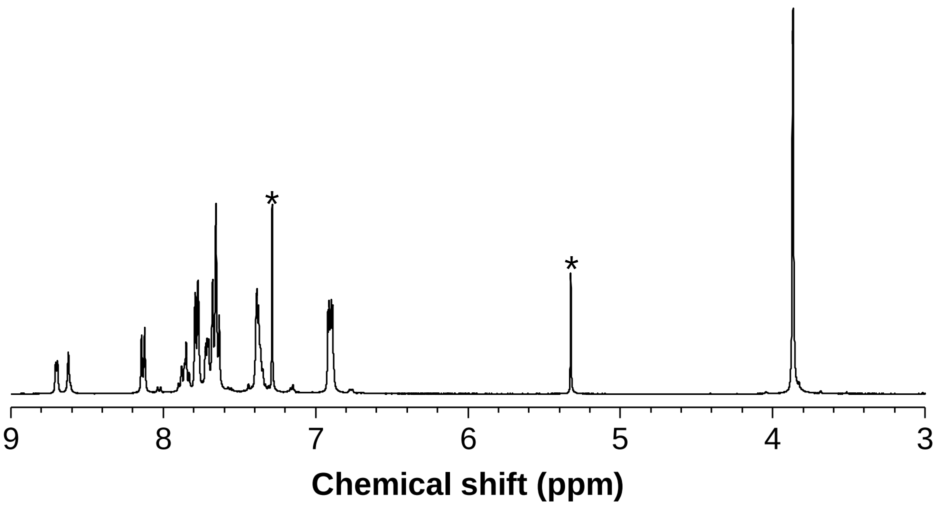


Figure S9. ^{1}H NMR spectra of TPP-*o*-Py in $CDCl_3$. The solvent peaks are marked with asterisks.

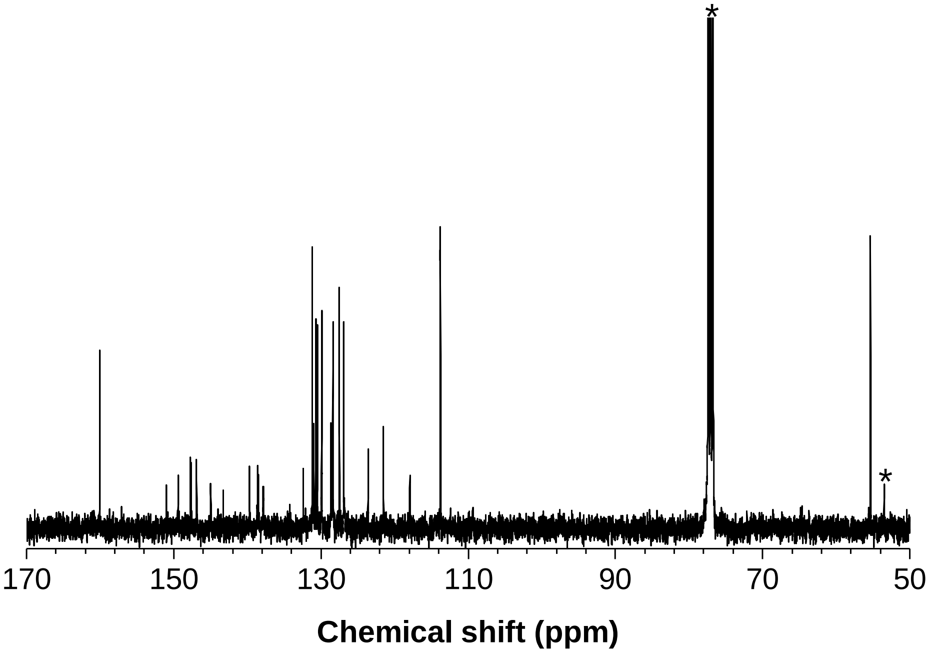


Figure S10. ^{13}C NMR spectra of TPP-*o*-Py in $CDCl_3$. The solvent peaks are marked with asterisks.

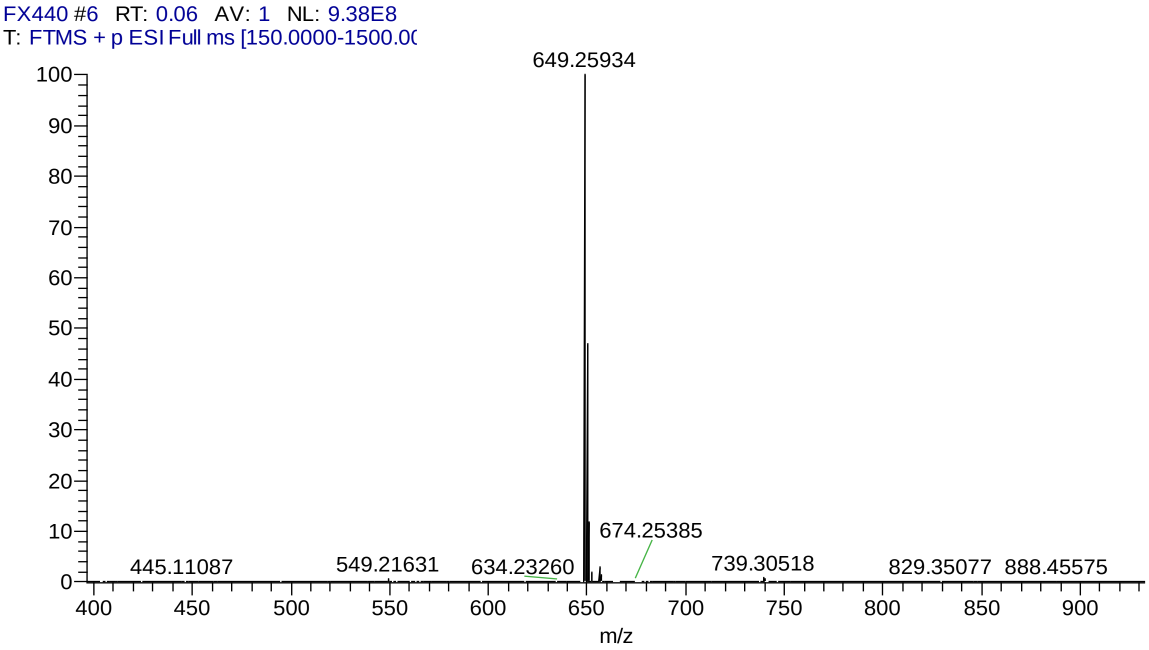


Figure S11. HRMS of TPP-*p*-Py.

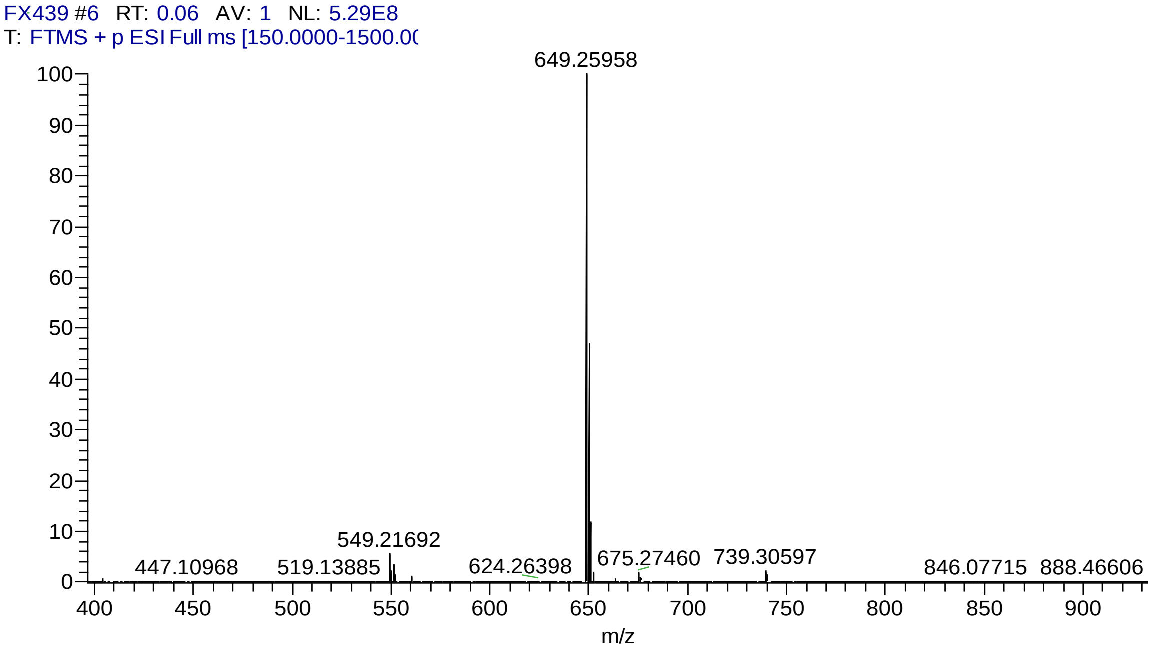


Figure S12. HRMS of TPP-*m*-Py.

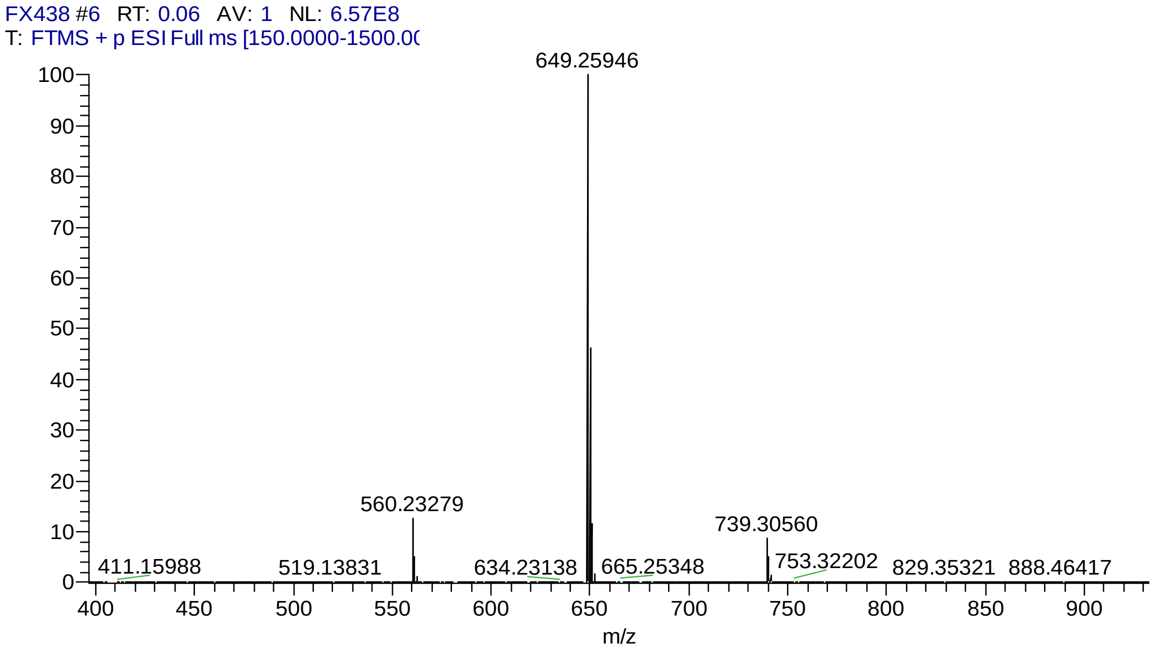


Figure S13. HRMS of TPP-*o*-Py.

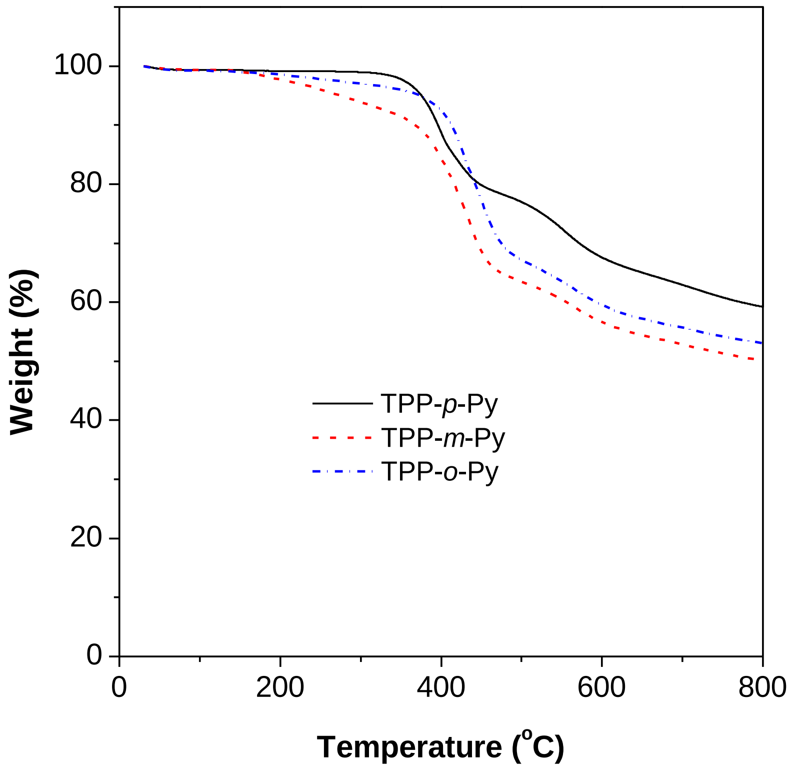


Figure S14. TGA curves of AIEgens under nitrogen at a heating rate of 10 ºC/min.

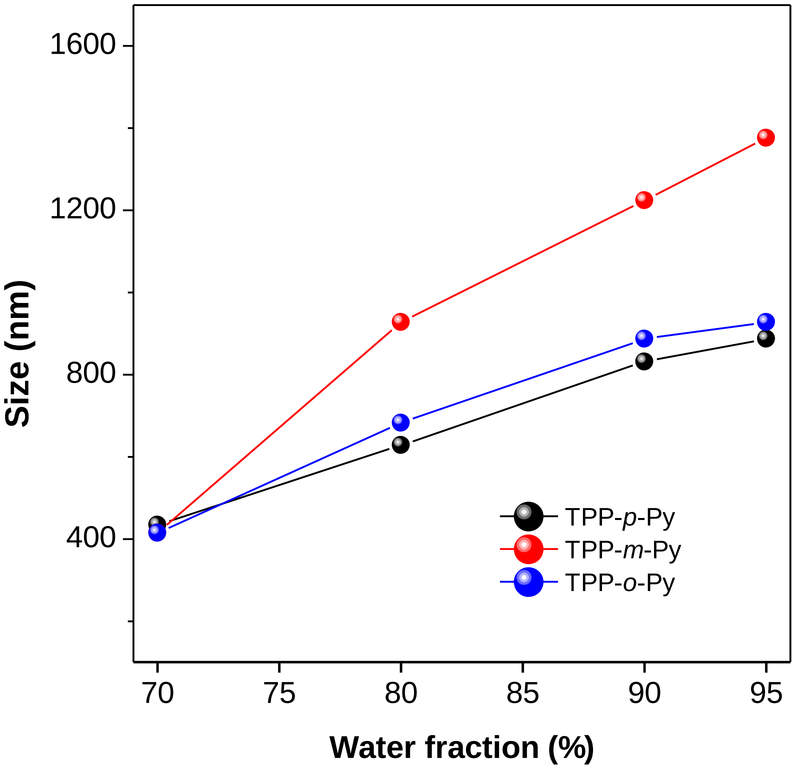
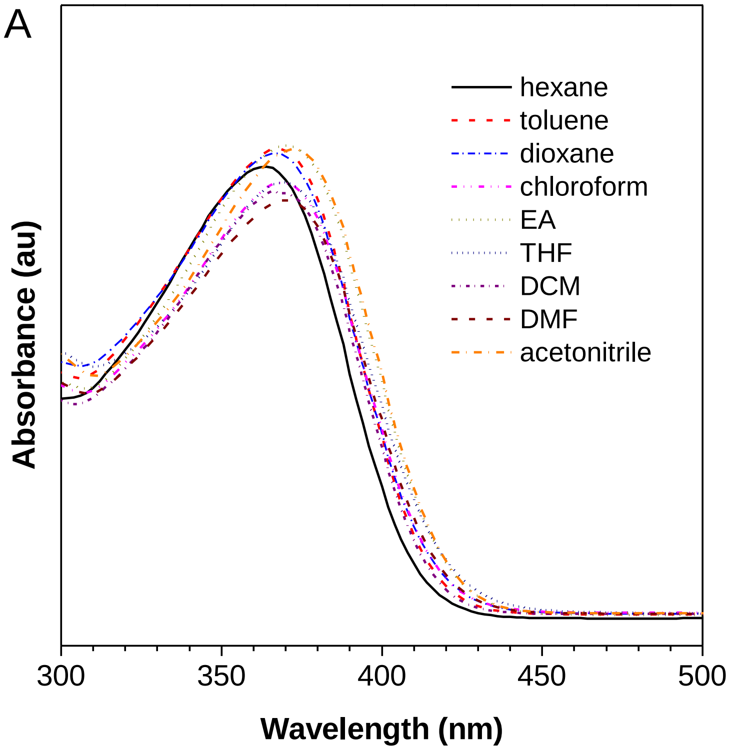


Figure S15. Size of aggregates formed in THF/water mixtures with water fractions from 70%-95% as monitored by the dynamic light scattering.



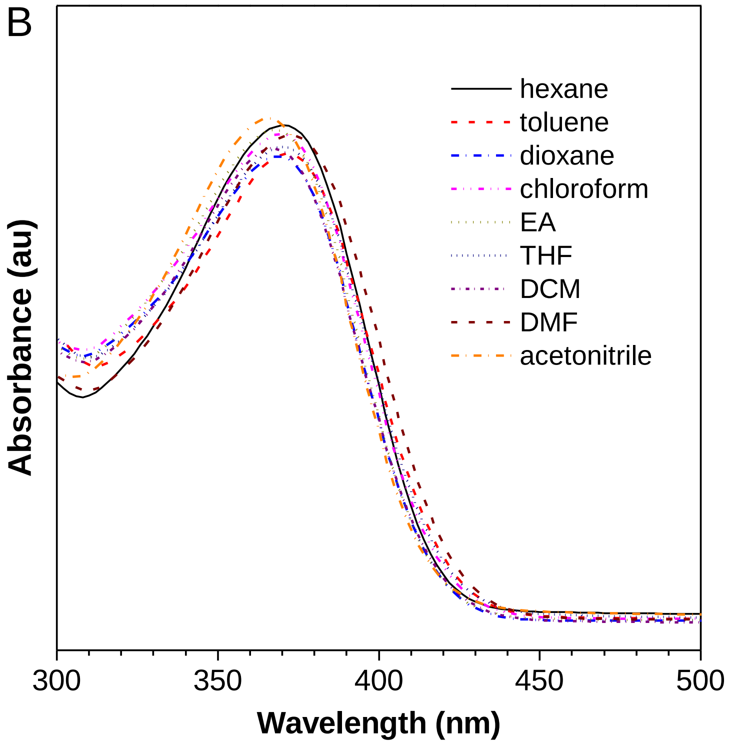
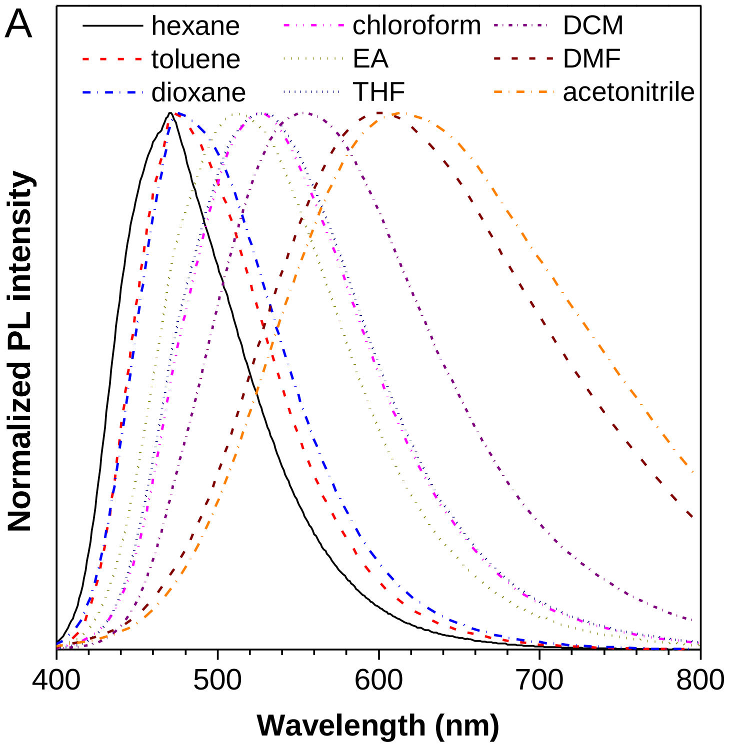


Figure S16. UV-Vis spectra of (A) TPP-*m*-Py and (B) TPP-*o*-Py in different solvents.



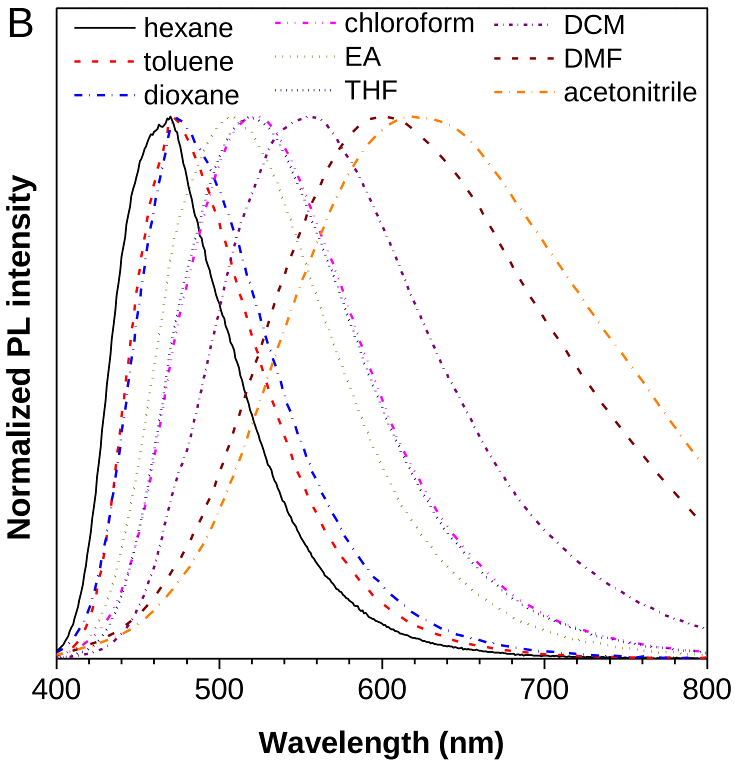
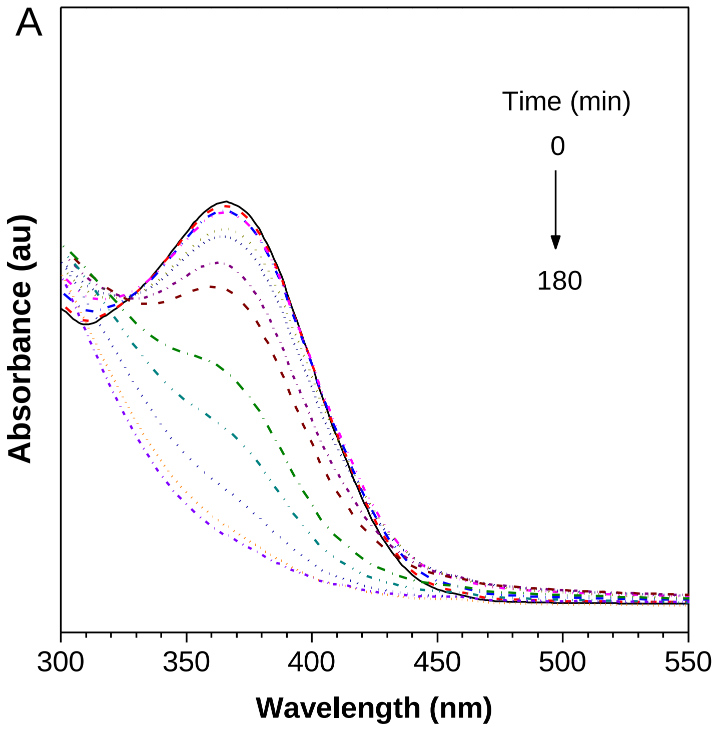


Figure S17. PL spectra of (A) TPP-*m*-Py and (B) TPP-*o*-Py in different solvents.



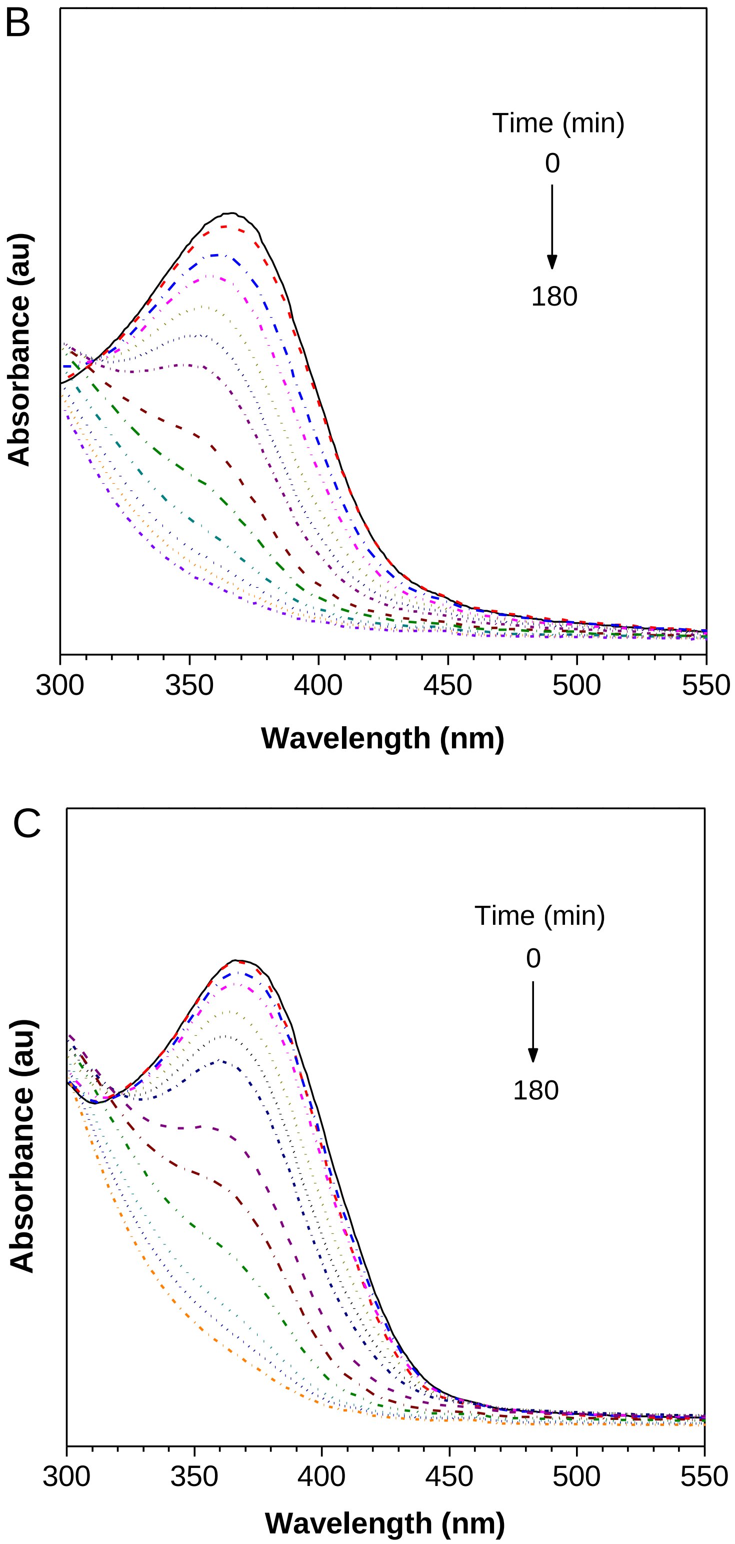


Figure S18. UV-Vis spectra of aggregates of (A) TPP-*p*-Py, (B) TPP-*m*-Py and (C) TPP-*o*-Py formed in THF/water mixtures with f_w = 90% under continuous 356 nm UV light irradiation.

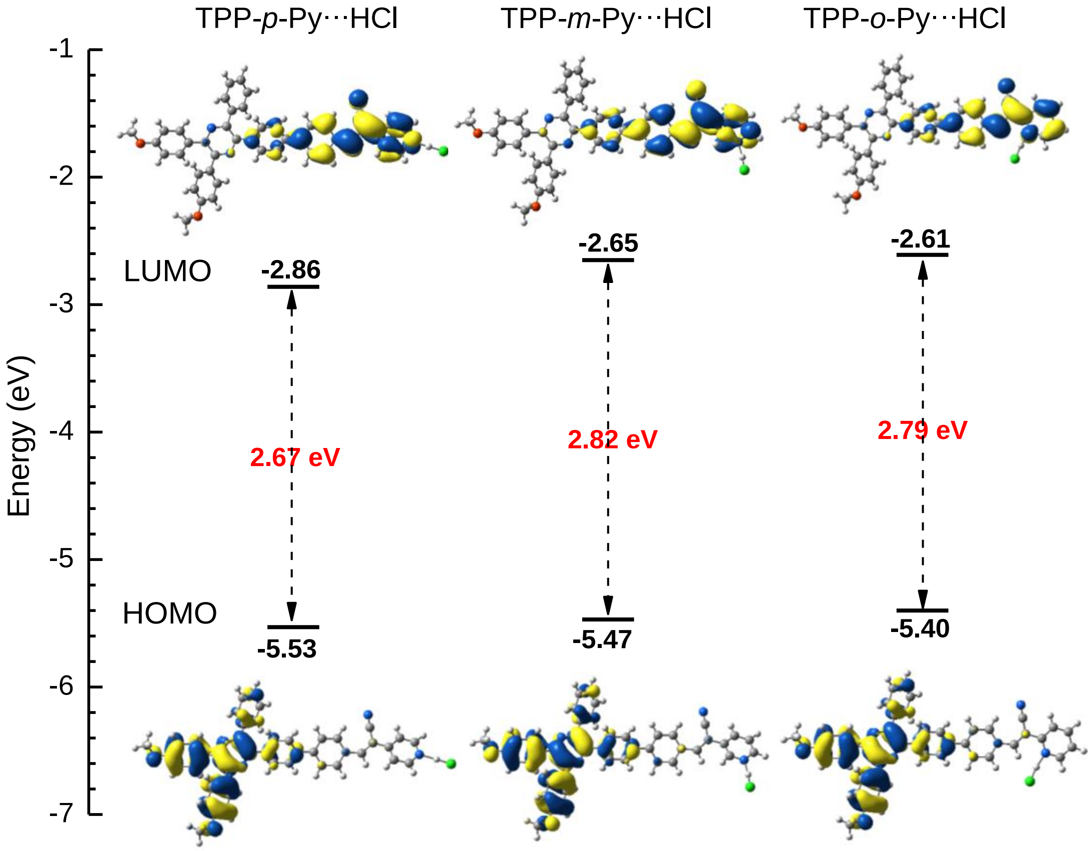


Figure S19. Electronic structures of protonated AIE isomers based on B3LYP/6-31G (d, p) set.

Reference

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R. C.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*. **2009**, Revision E.01 Gaussian Inc., Wallingford CT.

[2] Becke, A. D. A New Mixing of Hartree–Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[3] Grimme, S,Antony, J,Ehrlich, S,Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.