Electronic Supplementary Information *for*

Wavelength-Depending Multicolor Photochromism and Fluorescence Switch Based on an AIE-Acitive Skeleton by Regulating the Conjugation of Photoactive Unit

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1. Experimental Section

Synthesis of 5-(1,2,2-triphenylvinyl)thiophene-2-carbaldehyde (5-TPVTC). A mixture of 1-bromo-1,2,2-triphenylethylene (1.00 g, 3.0 mmol), 5-Formyl-2-thiopheneboronic acid (0.70 g, 4.5 mmol) and 2M potassium carbonate (4.5 mmol) in toluene and tetrahydrofuran (V:V=2:1), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) added under the protection of N_2, and the mixture was reacted at 80℃ for 20 h. After the reaction was completed, the mixture was poured into water and extracted three times with dichloromethane, and the organic layer was dried by $MgSO_4$. The solvent was removed by under reduced pressure and purified by silica gel column chromatography. The final crude product was recrystallized in ethanol to produce a bright yellow solid with a yield of 38.4%. Molecular formula: $C_{25}H_{18}OS$. ^1H NMR (600 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.40 (d, J = 3.9 Hz, 1H), 7.25 (dd, J = 5.3, 2.2 Hz, 4H), 7.19 – 7.14 (m, 5H), 7.13 – 7.11 (m, 2H), 7.07 – 7.05 (m, 3H), 6.96 (dd, J = 6.7, 3.1 Hz, 2H), 6.62 (d, J = 3.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 182.87, 157.01, 142.87, 142.36, 142.22, 135.63, 131.17, 130.89, 130.59, 130.50, 128.55, 128.07, 127.93, 127.71, 127.48, 127.09; HRMS (ESI) m/z: $[M+H]^+$, 367.1147, $[M+Na]^+$, 389.0962 (calcd. for $C_{25}H_{18}OS$, 366.11).

Synthesis of 4-(1,2,2-triphenylvinyl)thiophene-2-carbaldehyde (4-TPVTC). The synthesis of 4-TPVTC followed the procedure of 5-TPVTC by replacing 5-Formyl-2-thiopheneboronic acid with 4-bromothiophen-2-aldehyde. The crude product was finally acquired by recrystallization in ethanol to give a light yellow solid with a yield of 55.2%. Molecular formula: $C_{25}H_{18}OS$. ^1H NMR (600 MHz, $CDCl_3$) δ 9.64 (d, J = 1.2 Hz, 1H), 7.21 (t, J = 3.1 Hz, 4H), 7.16 – 7.14 (m, 4H), 7.12 (dd, J = 6.5, 2.2 Hz, 2H), 7.08 (q, J = 3.3 Hz, 5H), 6.99 (dd, J = 6.2, 2.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.10, 145.46, 143.26, 142.70, 142.45, 142.42, 142.28, 139.29, 135.40, 134.00, 131.06, 131.02, 130.74, 128.37, 128.06, 127.74, 127.33, 127.09, 126.79, HRMS (ESI) m/z: $[M+H]^+$,367.1154, $[M+Na]^+$, 389.0974 (calcd. for $C_{25}H_{18}OS$, 366.11).

Synthesis of (Z)-2-(4-(trifluoromethyl)phenyl)-3-(4-(1,2,2-triphenylvinyl) thiophen-2-yl)acrylonitrile (4-FTPVTA). A certain amounts of 4-(1,2,2-triphenylvinyl)thiophene-2-carbaldehyde (4-TPVTC) (1.01 g, 3.0 mmol), 4-trifluoromethylphenylacetonitrile (0.83 g, 4.5 mmol) and sodium ethanol (20% W/W) were dissolved in ethanol, and the mixtures were heated to reflux for 4h. After removing the solvent under reduced pressure, the residue was purified by silica gel chromatography using petroleum ether and ethyl acetate as eluent to obtain crude product, and then recrystallized with ethanol to obtain the final product as light yellow solid (yield 50.0%). Molecular formula: $C_{34}H_{22}F_3NS$. ^1H NMR (600 MHz, $CDCl_3$): δ7.68 – 7.63 (m, 4H), 7.49 (s, 1H), 7.25 – 7.20 (m, 3H), 7.18 – 7.13 (m, 5H), 7.09 (q, J = 3.2, 2.6 Hz, 5H), 7.07 (d, J = 1.3 Hz, 1H), 7.03 – 6.98 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$)：δ144.82, 142.56, 142.15, 137.42, 137.28, 136.30, 136.03, 134.06, 131.91, 131.10, 131.04, 130.74, 128.30, 127.98, 127.72, 127.22, 126.99, 126.73, 126.07, 126.04, 125.84, 106.08; HRMS (ESI) m/z: $[M+H]^+$,534.1501, $[M+Na]^+$,556.1325 (calcd. for $C_{34}H_{22}F_3NS$, 533.14).

Synthesis of (Z)-4-(1-cyano-2-(4-(1,2,2-triphenylvinyl)thiophen-2-yl)-vinyl)benzonitrile (4-CTPVTB). Synthesis of 4-CTPVTB followed the procedure of 4-FTPVTA by replacing 4-cyanophenylacetonitrile with 4-trifluoromethylbenzyl cyanide. The final crude product is yellow solid (yield 52.0%). Molecular formula: $C_{34}H_{22}F_3NS$.^1H NMR (600MHz, $CDCl_3$):δ 7.70 – 7.64 (m, 4H), 7.51 (s, 1H), 7.25–7.20 (m, 3H), 7.19 – 7.12 (m, 5H), 7.09 (q, J = 3.6 Hz, 6H), 7.04 (s, 1H), 6.99 (dd, J = 6.6, 3.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.00, 143.32, 142.50, 142.27, 138.34, 137.78, 136.92, 135.88, 133.93, 132.80, 132.51, 131.08, 131.01, 130.73, 128.32, 128.00, 127.72, 127.24, 127.03, 126.77, 126.01, 118.30, 117.15, 112.12, 105.62； HRMS (ESI) m/z: $[M+H]^+$, 491.1583, $[M+Na]^+$, 513.1398 (calcd. for

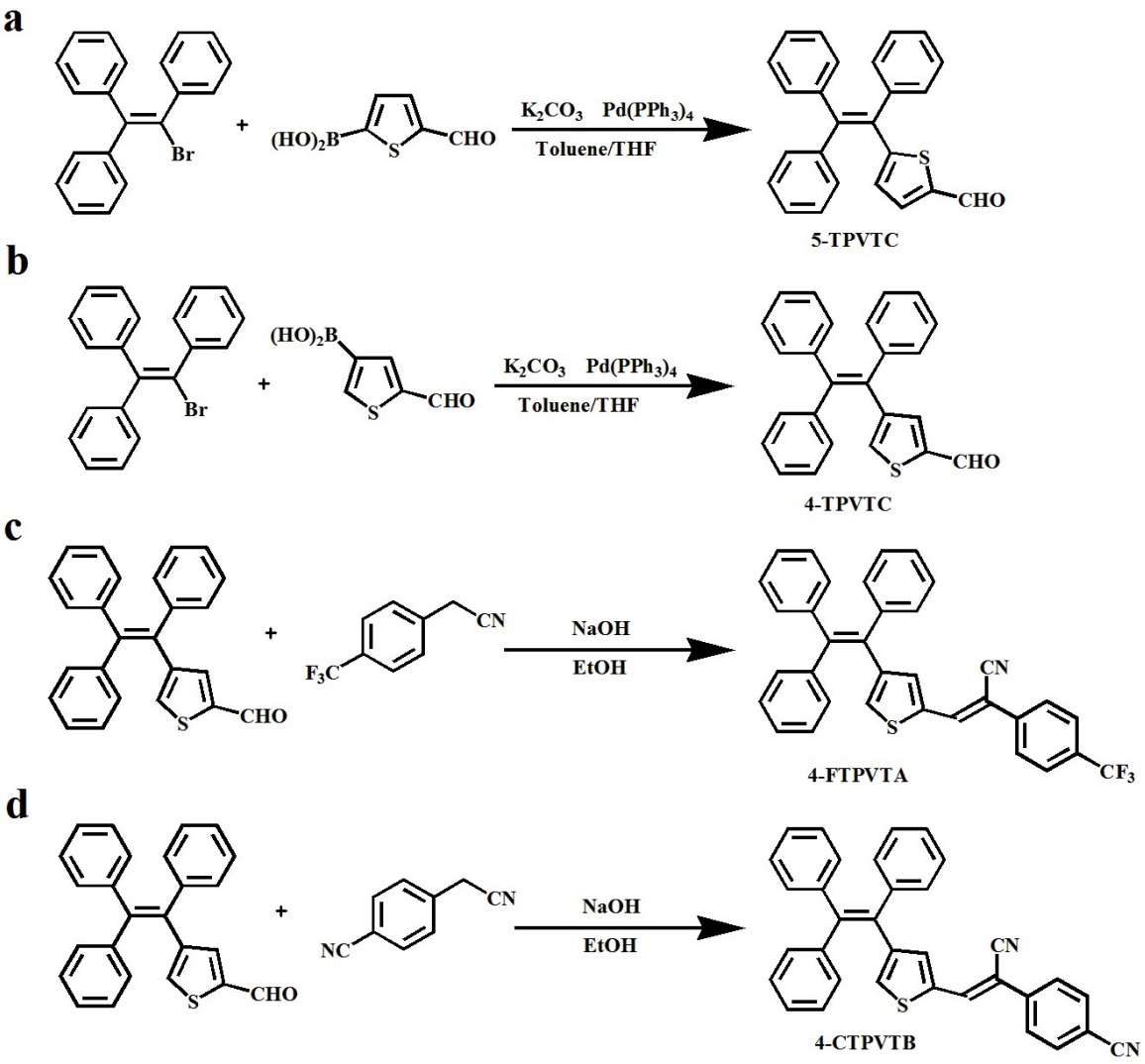
$C_{34}H_{22}F_3NS$, 490.15).

Characterization of UV-Visible and Fluorescence Properties of All Samples. UV−Vis absorption spectra were recorded using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder. Time-resolved fluorescence measurements were conducted with EPL-series lasers. The absolute PL quantum yields of all samples were determined using an integrating sphere equipped in FLS980 spectrophotometer for at least three times.

2. Computational Details

All the calculations were performed with density functional theory (DFT) and time-dependent density functional theory (TDDFT) implemented in Gaussian 09 program package.[1] The ground state equilibrium geometries and the normal modes of vibration of the single-molecules of 4-TPVTC, 4-FTPVTA and 4-CTPVTB were computed using density functional theory (DFT) with the hybrid B3LYP functional at 6-311+G(d,p) level.[2] Excitation energies and absorption maxima of all the four molecules and their *E*-products were calculated using M062X functional with 6-311+G(d,p) level based on the optimized structure in acetonitrile with SCRF.[3]

3. Supplementary Schemes and Figures



Scheme S1. Synthesis routes of 5-TPVTC, 4-TPVTC, 4-FTPVTA and 4-CTPVTB.

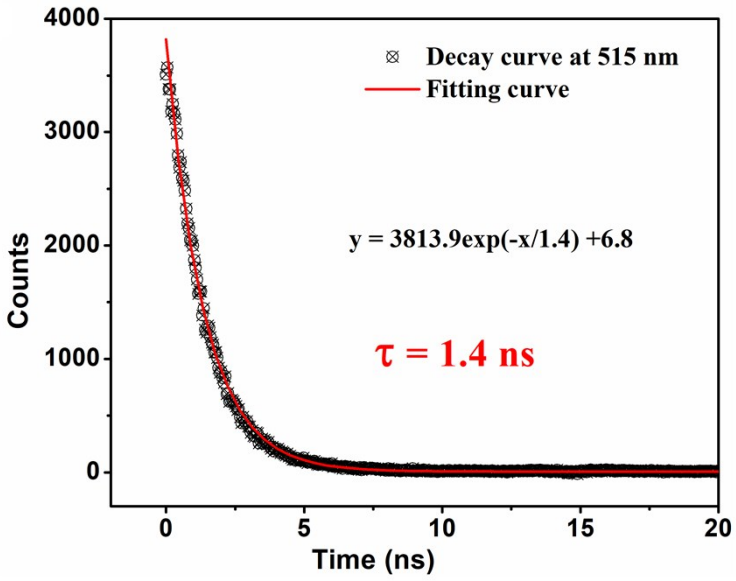


Figure S1. Time-resolved PL decay curve of 5-TPVTC in solid state.

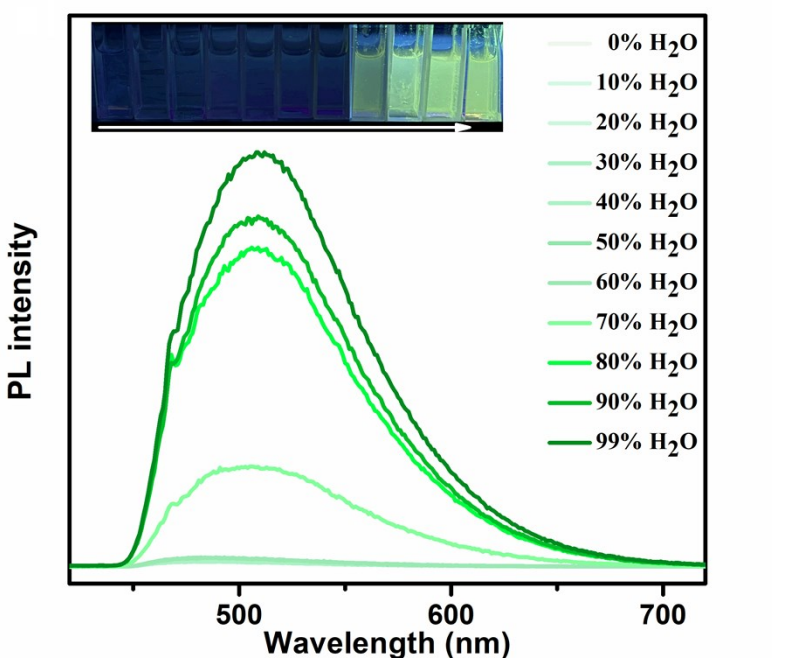


Figure S2. PL spectra of 5-TPVTC in THF with addition of different amount of water.

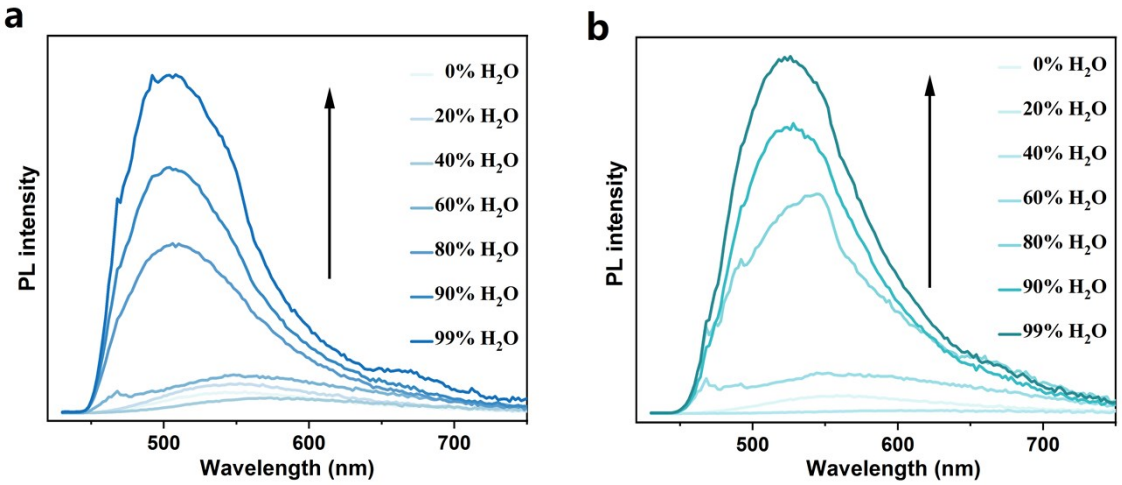


Figure S3. PL spectra of 4-FTPVTA (a) and 4-CTPVTB (b) in THF with addition of different amount of water.

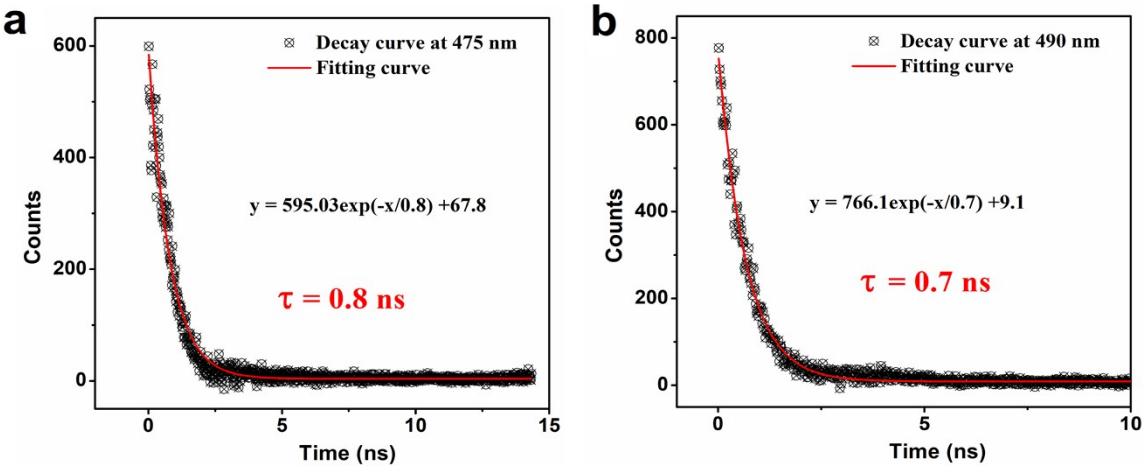


Figure S4. Time-resolved PL decay curves of 4-FTPVTA (a) and 4-CTPVTB (b) in solid.

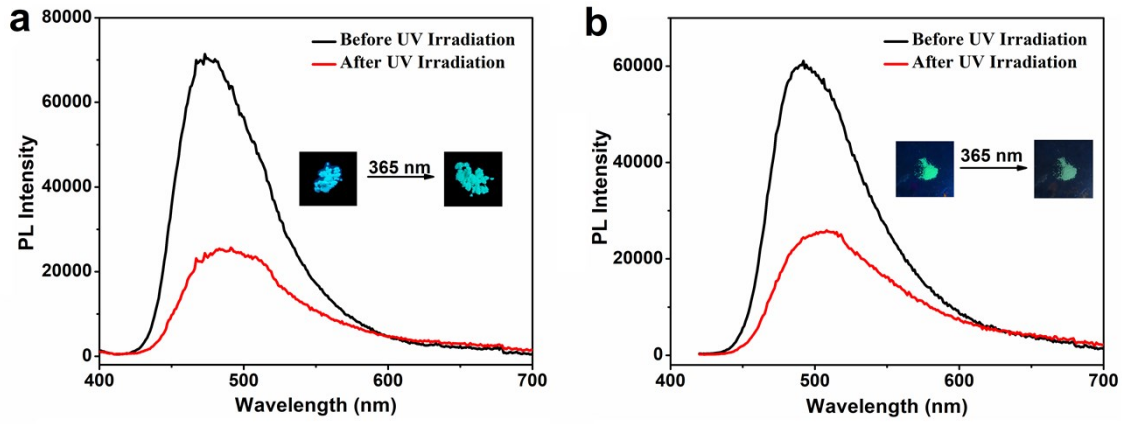


Figure S5. Changes of PL spectra and images of 4-FTPVTA (a) and 4-CTPVTB (b) in solid after 3 min of UV irradiation at 365 nm.

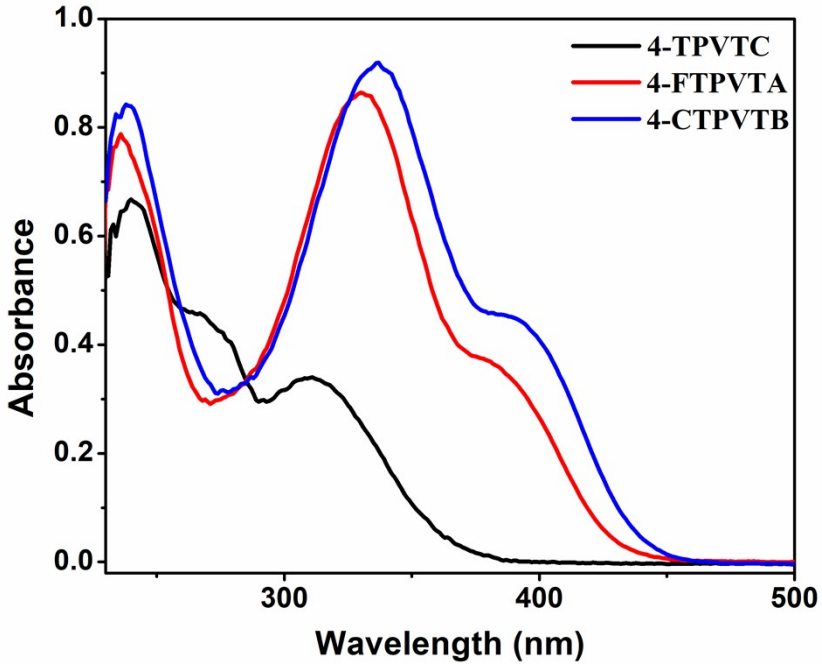


Figure S6. UV-visible spectra of 4-TPVTC, 4-FTPVTA and 4-CTPVTB in THF at 25.0 μM.

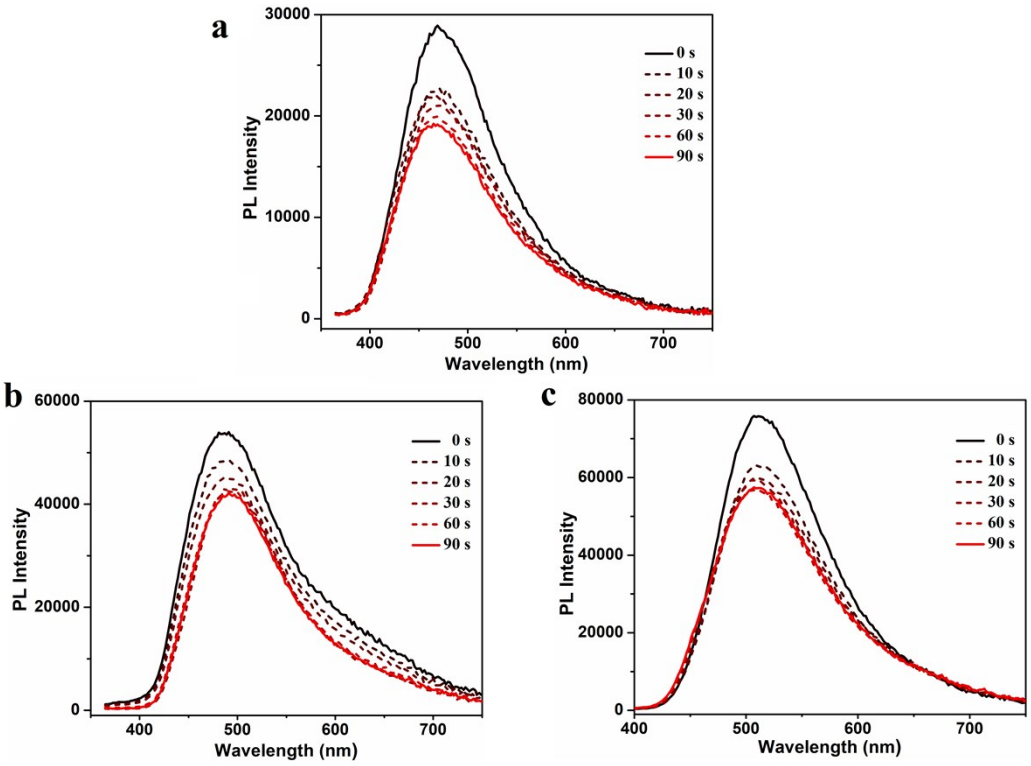


Figure S7. Time-resolved PL spectra of 4-TPVTC (a), 4-FTPVTA (b) and 4-CTPVTB (c) in film under continuous UV light irradiation.

4. Supplementary Tables

Table S1. Experimental and computational data for $S_0 \rightarrow S_1$ absorption maxima of 4-TPVTC, 4-FTPVTA, 4-CTPVTB and their cyclized forms

Compounds		$\lambda_{ab}{}^{a}$ (nm)	$\varepsilon_{ab}{}^{a}$ ($L \cdot mol^{-1} \cdot cm^{-1}$)	$\lambda_{ab}{}^{b}$ (nm)	f^{b}
4-TPVTC	The open form	310	13596	309	0.1006
	The closed form	512	-	548	0.1980
4-FTPVTA	The open form	378	14236	376	0.2879
	The closed form	565	-	546	0.4672
4-CTPVTB	The open form	390	12092	408	0.2913
	The closed form	570	-	561	0.5494

[a] The experimental data in THF. [b] The calculated values with M062X functional. λ_{ab}, ε_{ab} and f represent absorption maximum, molar absorption coefficient and oscillator strength respectively.

5. NMR and HRMS Spectra of Compounds

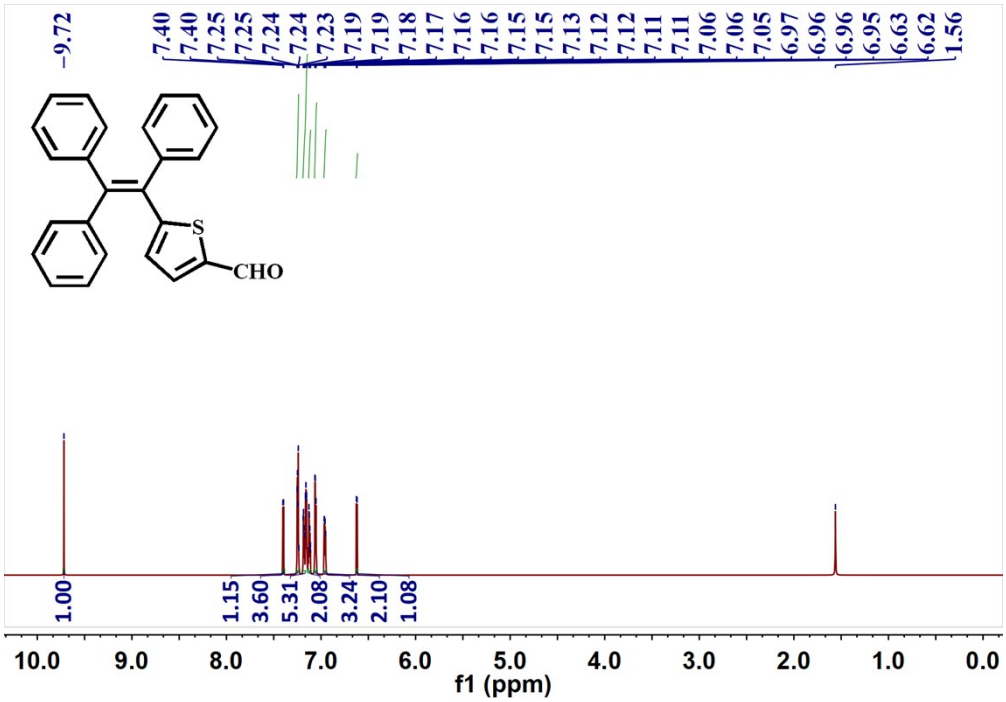


Figure S8. ^{1}H NMR spectrum of 5-TPVTC in $CDCl_3$

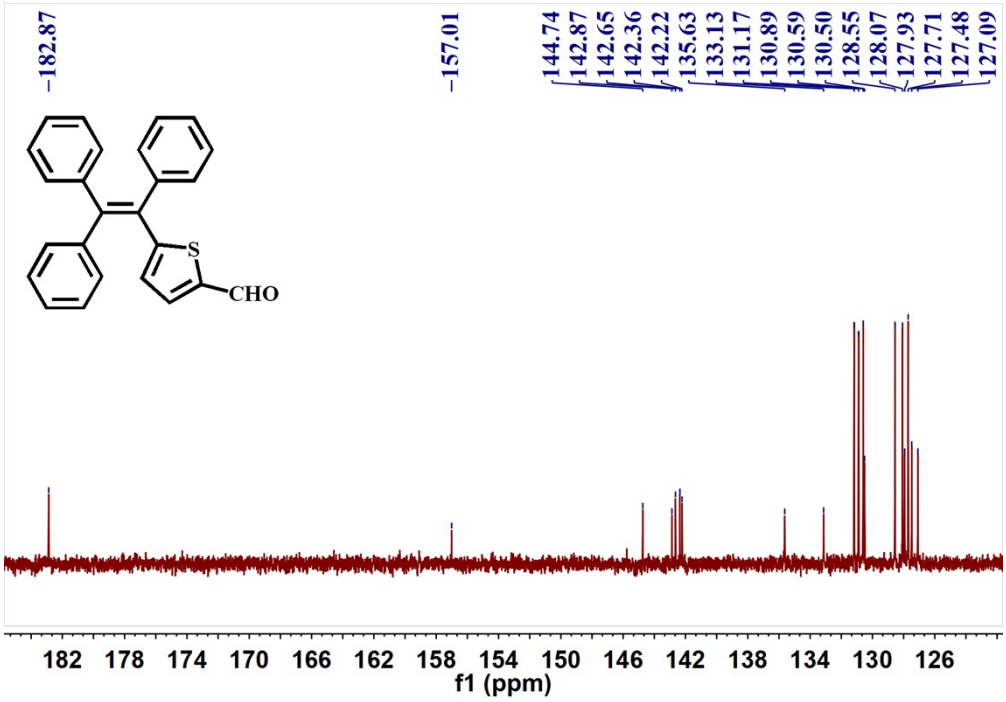


Figure S9. ^{13}C NMR spectrum of 5-TPVTC in $CDCl_3$.

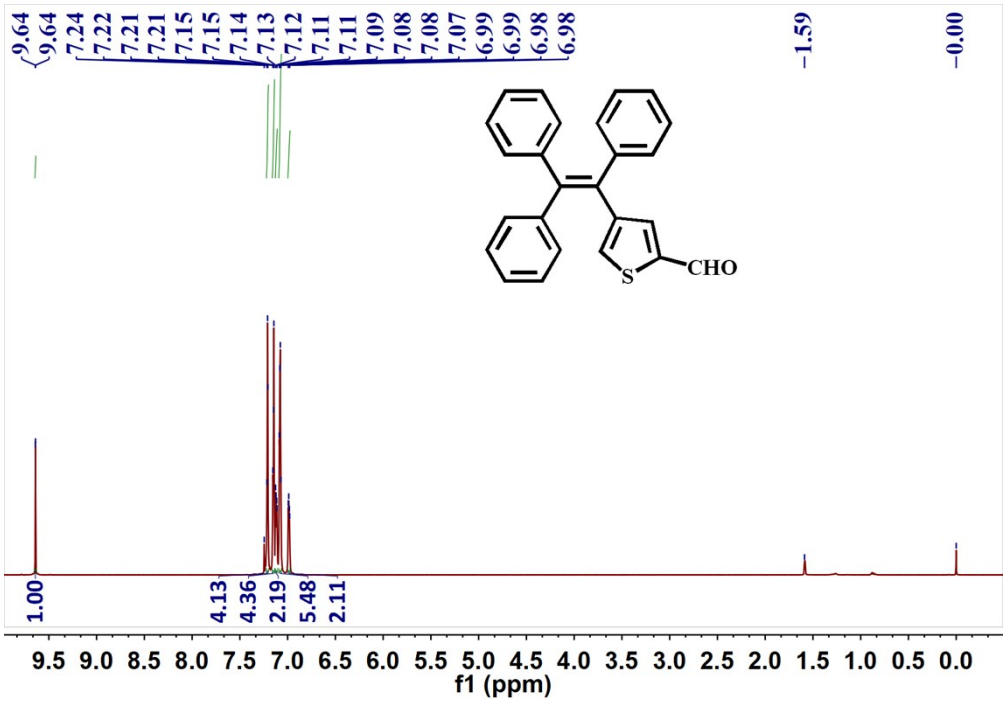


Figure S10. ^{1}H NMR spectrum of 4-TPVTC in $CDCl_3$

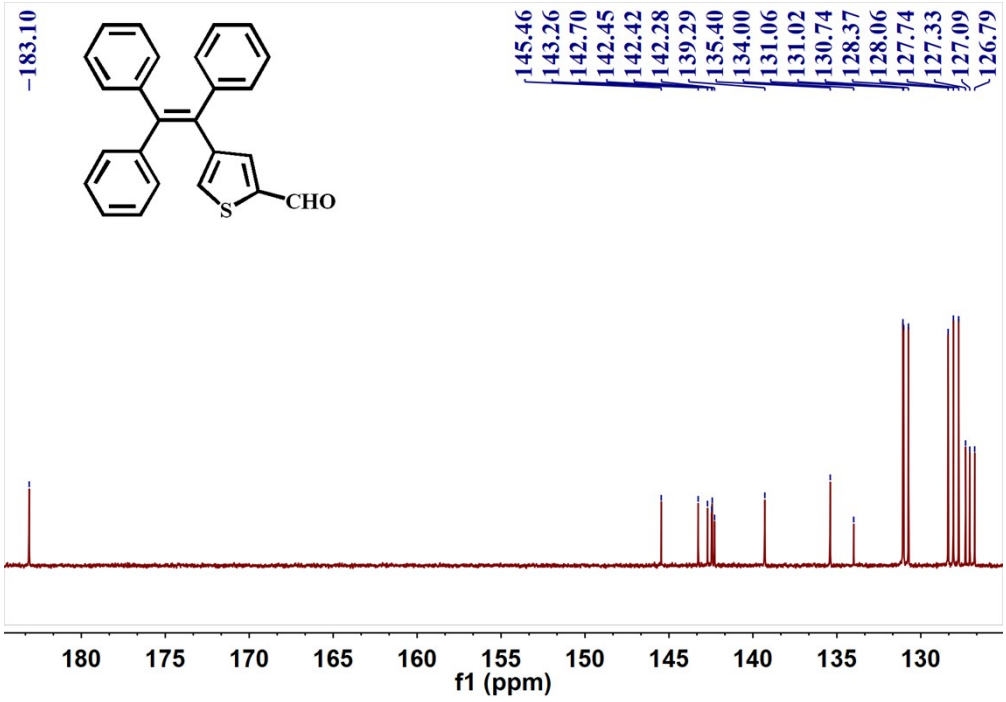


Figure S11. ^{13}C NMR spectrum of 4-TPVTC in $CDCl_3$.

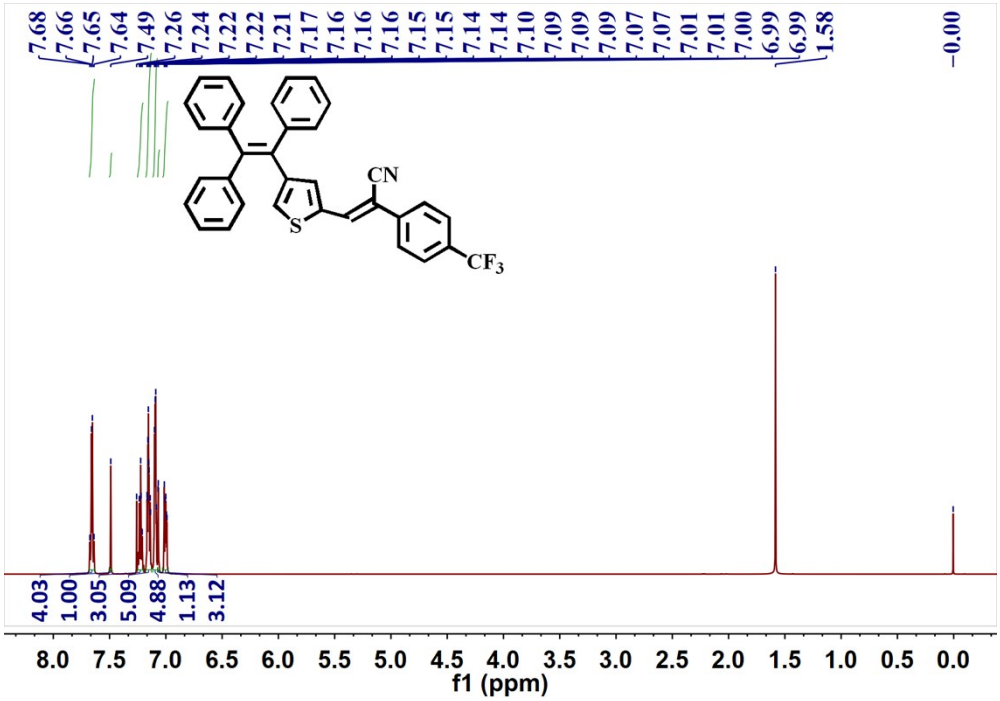


Figure S12. ^{1}H NMR spectrum of 4-FTPVTA in $CDCl_3$.

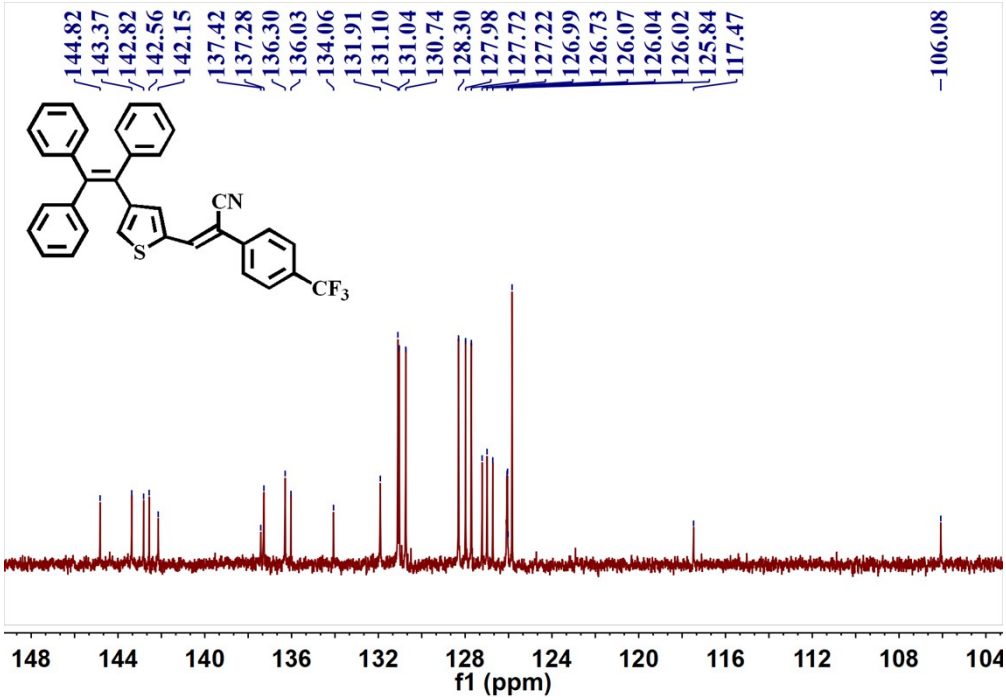


Figure S13. ^{13}C NMR spectrum of 4-FTPVTA in $CDCl_3$.

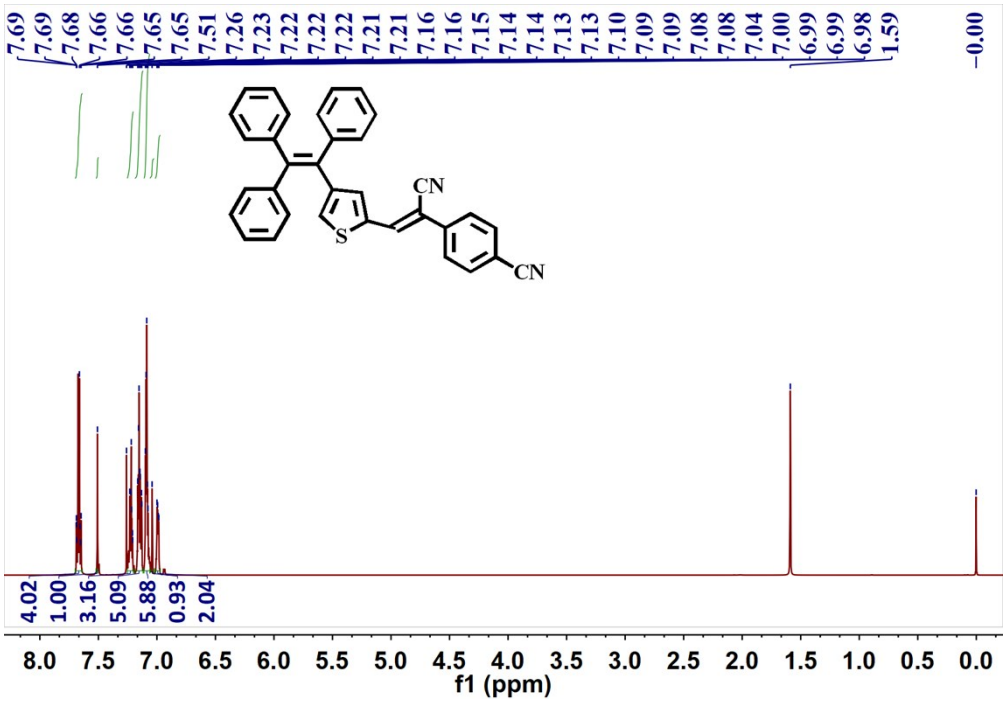


Figure S14. ^{1}H NMR spectrum of 4-CTPVTB in $CDCl_3$.

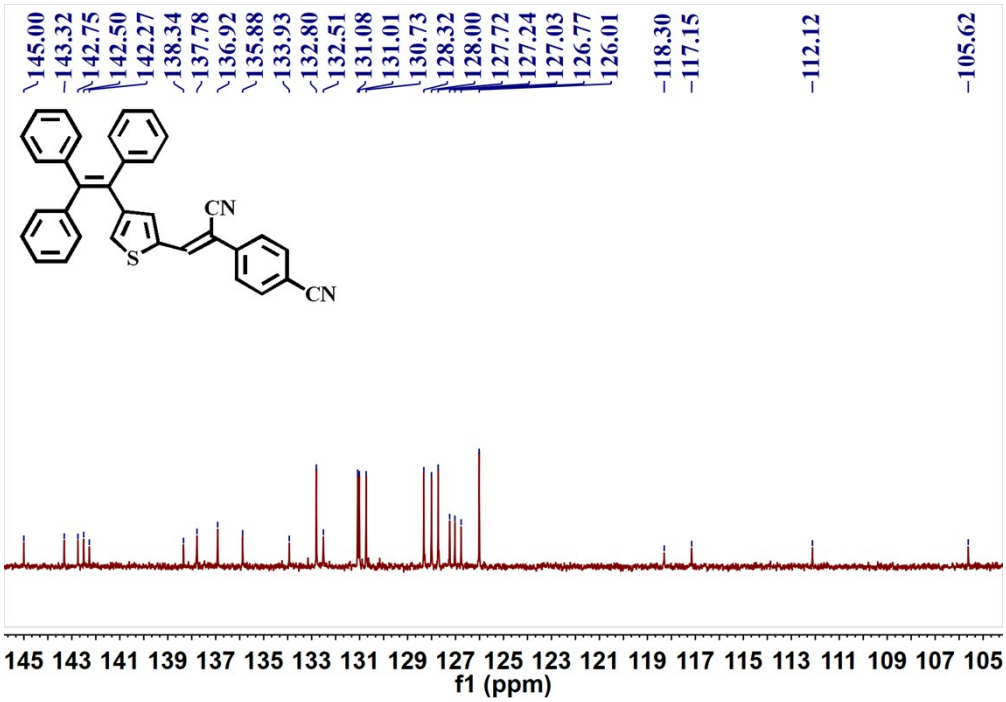


Figure S15. ^{13}C NMR spectrum of 4-CTPVTB in $CDCl_3$.

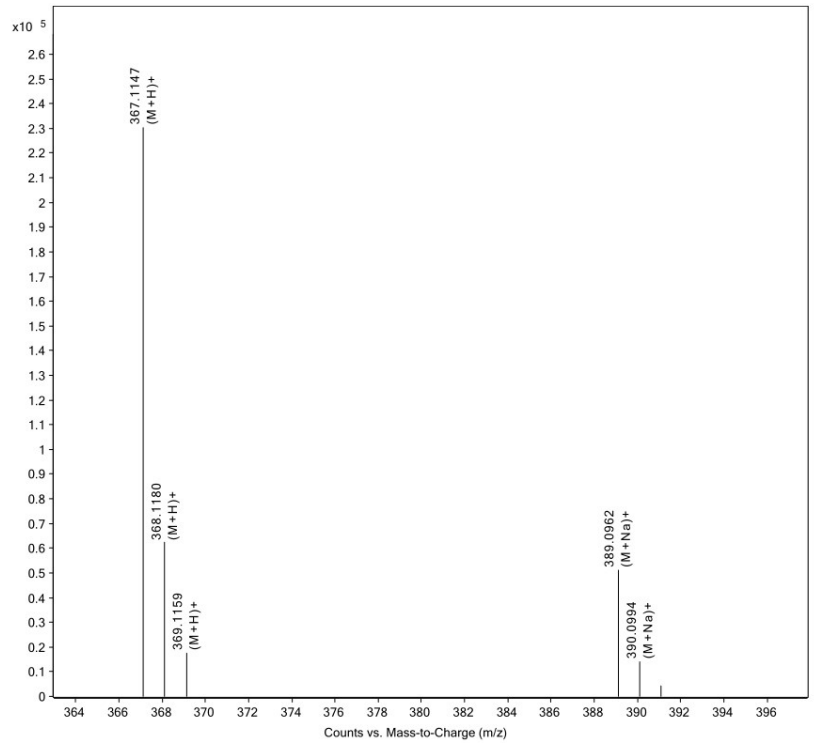


Figure S16. High-resolution mass spectrum of 5-TPVTC.

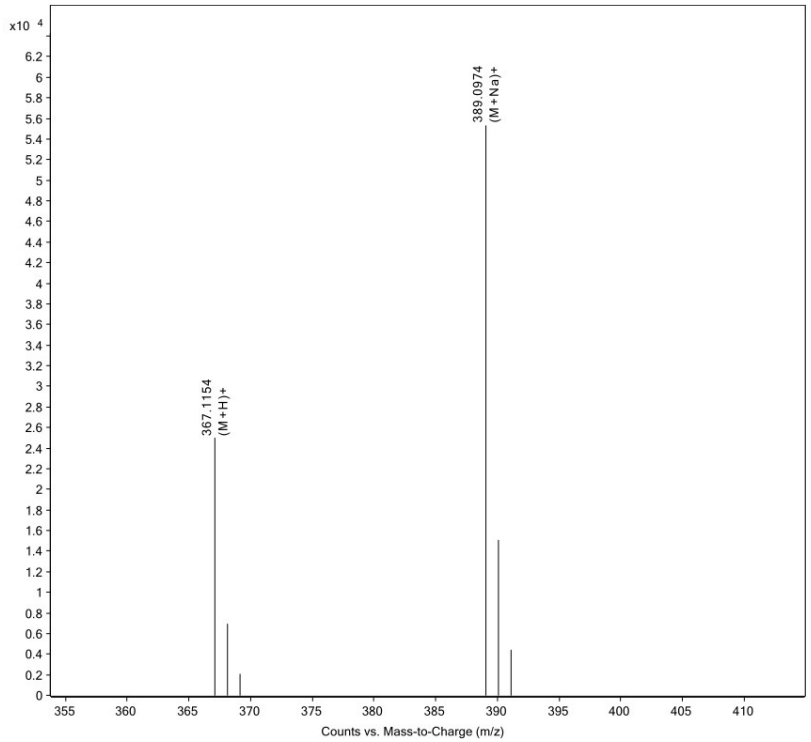


Figure S17. High-resolution mass spectrum of 4-TPVTC.

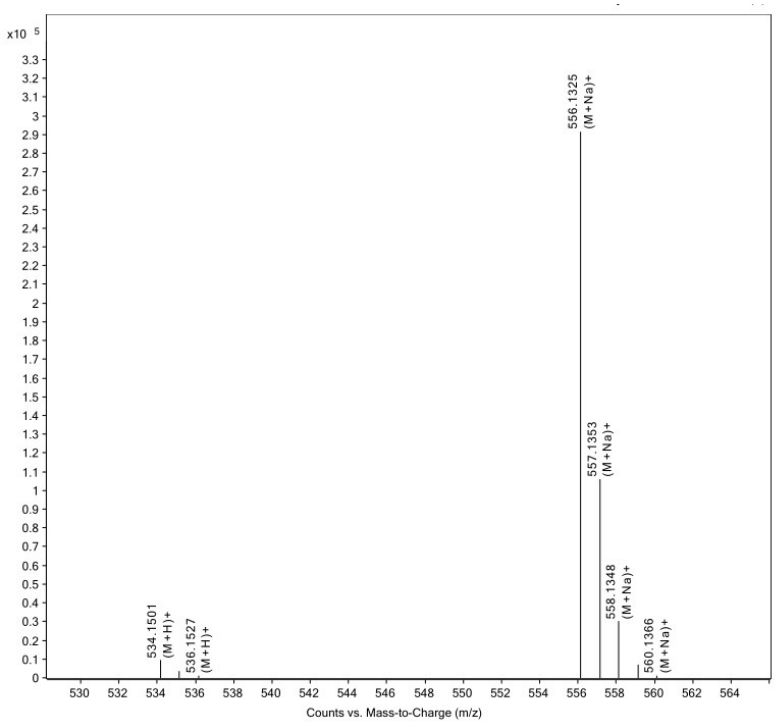


Figure S18. High-resolution mass spectrum of 4-FTPVTA.

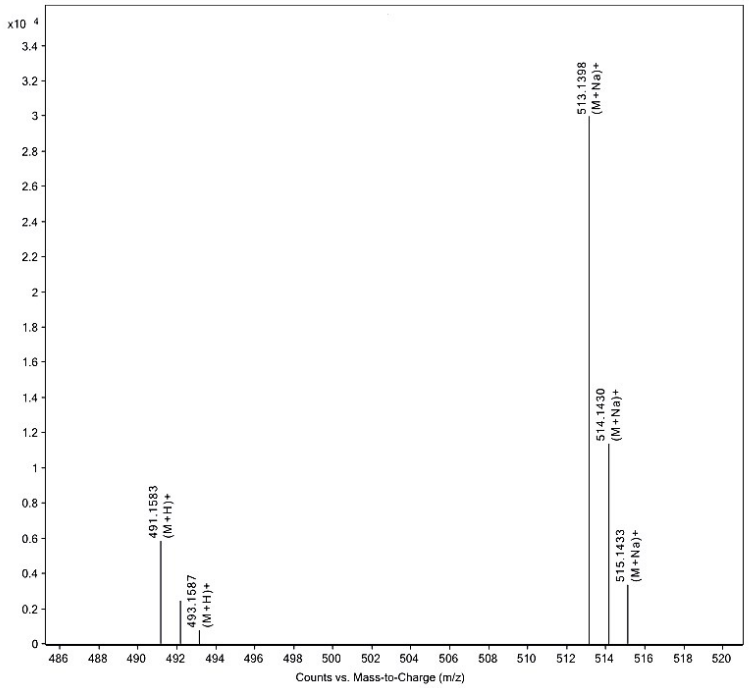


Figure S19. High-resolution mass spectrum of 4-CTPVTB.

6. 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.; Nakajiama, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Borthers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Rahavachari, 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, Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc. Wallingford CT, 2009.

(2) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(3) Adamo, C.; Jacquemin, D. The calculations of excited-state properties with time-dependent density functional theory. *Chem. Soc. Rev.* **2013**, *42*, 845−856.