Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Multi-functional AIEgens with dark resonance energy transfer: tunable emission, circularly polarized luminescence and self-assembly

Hai-Tao Feng,[a‡] Xinggui Gu,[a, e‡] Jacky W. Y. Lam,[a] Yan-Song Zheng[b] and Ben Zhong Tang [a, c, d, *]

[a] *Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, Institute for Advanced Study, Division of Biomedical Engineering, and Division of Life Science, State Key Laboratory of Molecular Neuroscience and Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, China*

[b] *School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China*

[c] *HKUST Shenzhen Research Institute, No. 9 Yuexing 1st RD, South Area, Hi-tech Park, Nanshan, Shenzhen 518057, China*

[d] *NSFC center for Luminescence from Molecular Aggregates, SCUT-HKUST Joint Research Institute, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

[e] *Beijing Advanced Innovation Center for Soft Matter Science and Engineering (BAICAS), Beijing University of Chemical Technology, Beijing 100029, China*

**Email - tangbenz@ust.hk*

‡Dual Contribuotrs

Materials and Methods

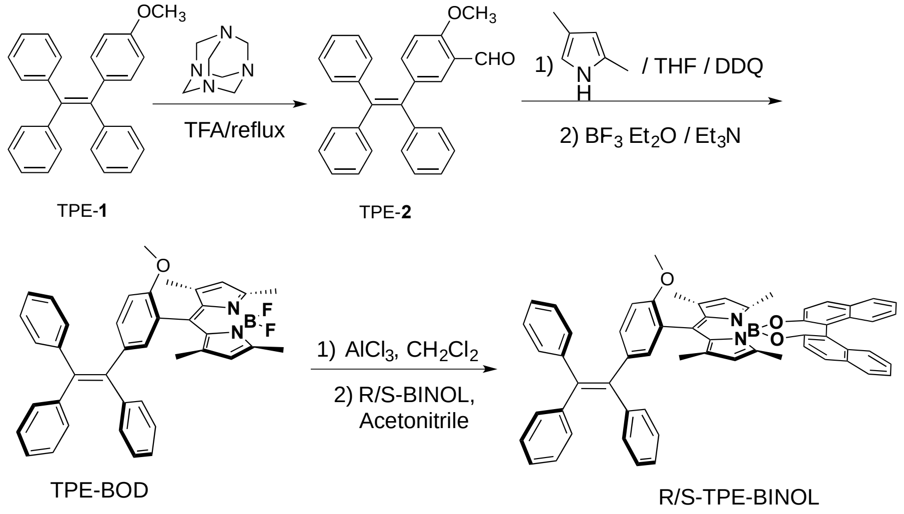
Materials: All reagents and solvents were chemical pure grade or analytical reagent grade and were used as received unless otherwise indicated.

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K. Absorption spectra were recorded on a Hewlett Packard 8453 UV–Vis spectrophotometer. High-resolution mass spectra (HRMS) were obtained on a GCT Premier CAB 048 mass spectrometer operated in MALDI-TOF mode. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. Solid state quantum yield was measured using a Hamamatsu C11347 Quantaurus-QY integrating sphere.

Calculation

The geometrical and electronic properties of *R*/*S*-TPE-BINOL were performed with the Amsterdam Density Functional (ADF) 2009.01 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functional) with the 6-31G (d) atomic basis set. Then the electronic structures were calculated at τ-HCTHhyb/6–311++G(d,p) level. Molecular orbitals were visualized using ADFview.

Synthesis of R/S-TPE-BINOL.



Synthesis of TPE-BOD: TPE-**1** and TPE-**2** were synthesized according to our previous literature.[1] TPE-**2** (0.5 g, 1.15 mmol) and 2, 4-dimethylpyrrole (0.47 g, 4.61 mmol) were dissolved in dry THF (15 mL) under a nitrogen atmosphere. Three drops of trifluoroacetic acid (0.20 mL) were added, and the mixture was stirred at room temperature overnight. After TLC showed complete disappearance of TPE-**2**, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.8 g, 3.45 mmol) in anhydrous THF (20 mL) was added. This mixture was further stirred for 3 h, and then triethylamine (3.3 g, 20.04 mmol) and $BF_3 \cdot OEt_2$ (3.3 g, 20.04 mmol) were successively added. After stirred overnight, the mixture was washed thoroughly with water and brine. The organic layer was dried over anhydrous Na_2CO_3, filtered, and evaporated under vacuum. The obtained crude compound was purified by silica gel column chromatography (petroleum ether/ethyl acetate =8:1, R_f = 0.25) to give a shiny orange powder (0.17 g, 24.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.43 (s, 6H), 2.51 (s, 6H), 3.68 (s, 3H), 5.92 (s, 2H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.96 – 6.99 (m, 4H), 7.06 – 7.10 (m, 12H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 154.85, 143.71, 143.45, 143.39, 142.49, 141.11, 139.86, 138.65, 137.42, 133.68, 132.16, 131.40, 131.15, 131.10, 127.92, 127.77, 127.63, 126.70, 126.50, 126.45, 123.48, 120.69, 110.56, 55.64, 14.55, 14.27. ESI$^+$ HRMS m/z calcd for $C_{40}H_{35}BF_2N_2O$ 609.2889 $[M+H]^+$, found 609.2852 $[M+H]^+$.

Synthesis of *R*/*S*-TPE-BINOL: A mixture of TPE-BOD (0.1 g, 0.16 mmol) and aluminum chloride (0.055 g, 0.41 mmol) in dry CH_2Cl_2 (10 mL) was refluxed under nitrogen atmosphere until reaction completion (monitored by TLC). Then the mixture was cooled down to room temperature, and a solution of the *R*-BINOL (0.234 g, 0.82 mmol) in anhydrous acetonitrile (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for an additional 2 h, the mixture was washed with aqueous NaCl and dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate =4:1, R_f = 0.25) to afford *R*-TPE-BINOL as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.43 (d, *J* = 1.6 Hz, 6H), 1.55 (s, 3H), 1.71 (s, 3H), 3.72 (s, 3H), 5.69 (d, *J* = 2.0 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.98 – 7.03 (m, 6H), 7.06 – 7.14 (m, 14H), 7.18 – 7.23 (m, 3H), 7.27 (q, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.80 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 143.81, 143.55, 143.50, 142.24, 141.97, 141.05, 139.97, 138.34, 137.33, 133.85, 133.74, 133.60, 132.55, 132.26, 131.43, 131.18, 129.97, 129.70, 129.06, 128.96, 127.96, 127.85, 127.79, 127.64, 127.27, 127.08, 126.70, 126.50, 126.43, 125.07, 125.05, 124.13, 124.07, 123.77, 123.18, 123.12, 121.80, 121.01, 110.55, 55.65, 16.18, 15.72, 14.67, 14.48. MALDI-TOF HRMS m/z calcd for $C_{60}H_{47}BN_2O_3$ 855.3680 $[M+H]^+$, found 855.3671 $[M+H]^+$.

S-TPE-BINOL was afforded as an orange solid by following a similar route for *R*-TPE-BINOL. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.34 (d, *J* = 1.6 Hz, 6H), 1.41 (s, 3H), 1.57 (s, 3H), 3.68 (s, 3H), 5.64 (d, *J* = 2.0 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.91 – 7.11 (m, 20H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.20 (q, *J* = 6.8 Hz, 3H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.73 (dd, J_1 = 4.0 Hz J_2 = 8.0 Hz, 2H). ^{13}C NMR (CD_2Cl_2, 400 MHz) δ = 156.42, 155.01, 143.83, 143.68, 141.13, 140.04, 137.40, 133.79, 133.72, 133.61, 132.36, 131.30, 131.17, 131.07,130.03, 129.76, 129.12, 129.03, 127.96, 127.92, 127.86, 127.72, 127.60, 126.92, 126.78, 126.59, 126.49, 126.37, 125.10, 125.06, 124.10, 123.75, 123.67, 123.20, 123.12, 121.68, 110.63, 55.77, 15.77, 15.37, 14.45, 14.29. MALDI-TOF HRMS m/z calcd for $C_{60}H_{47}BN_2O_3$ 855.3680 $[M+H]^+$, found 855.3740 $[M+H]^+$.

[1] H.-T. Feng, X. Zhang, Y.-S. Zheng, *J. Org. Chem.*, **2015**, *80* (16), pp 8096–8101

Supporting Figures

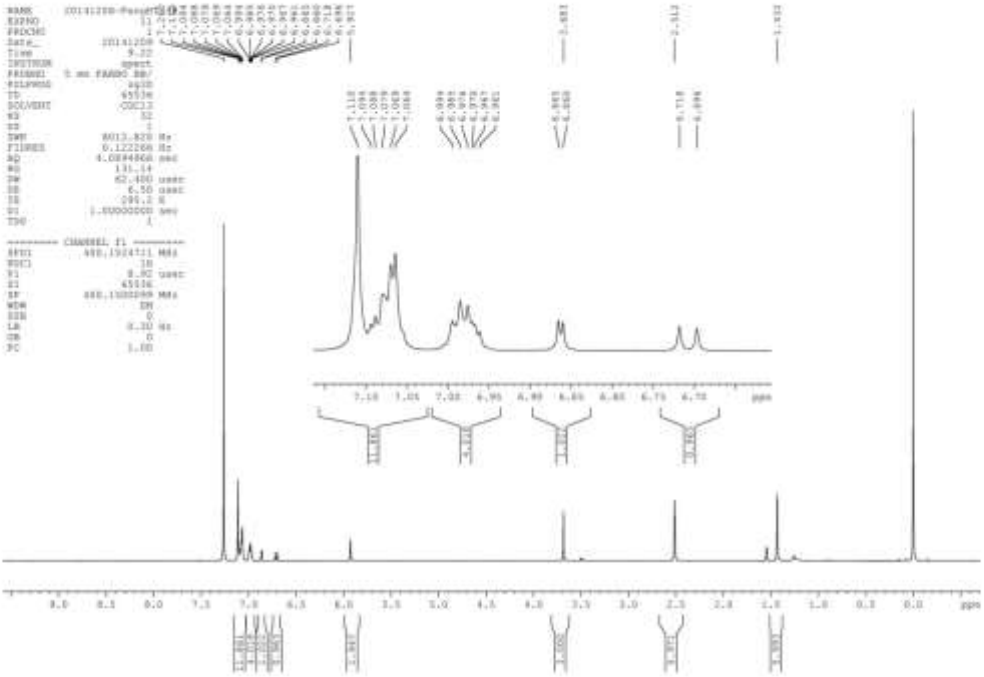


Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$.

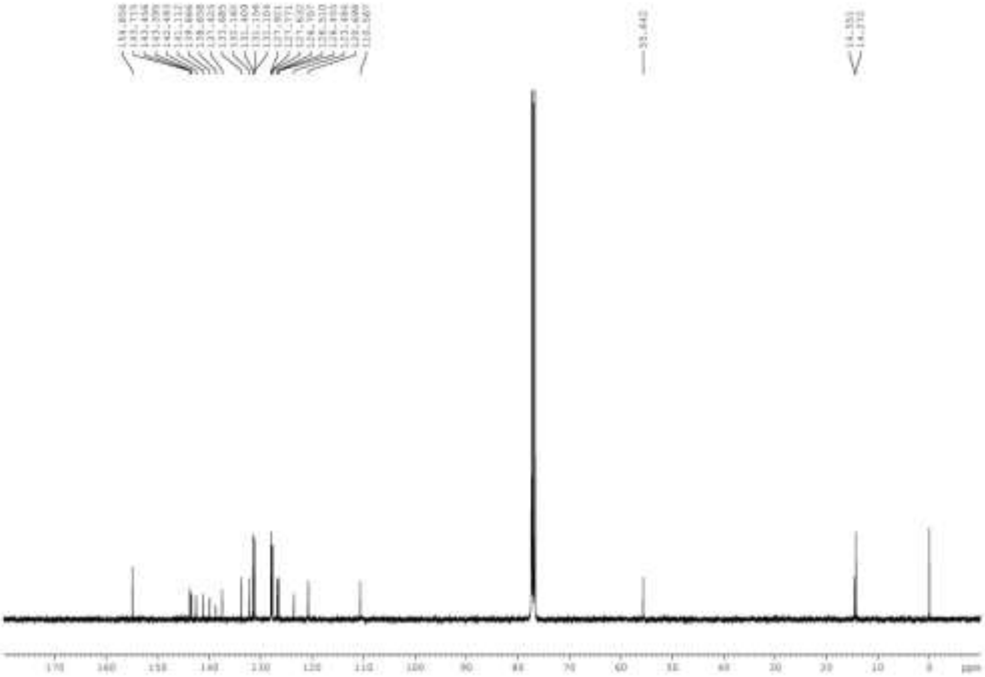
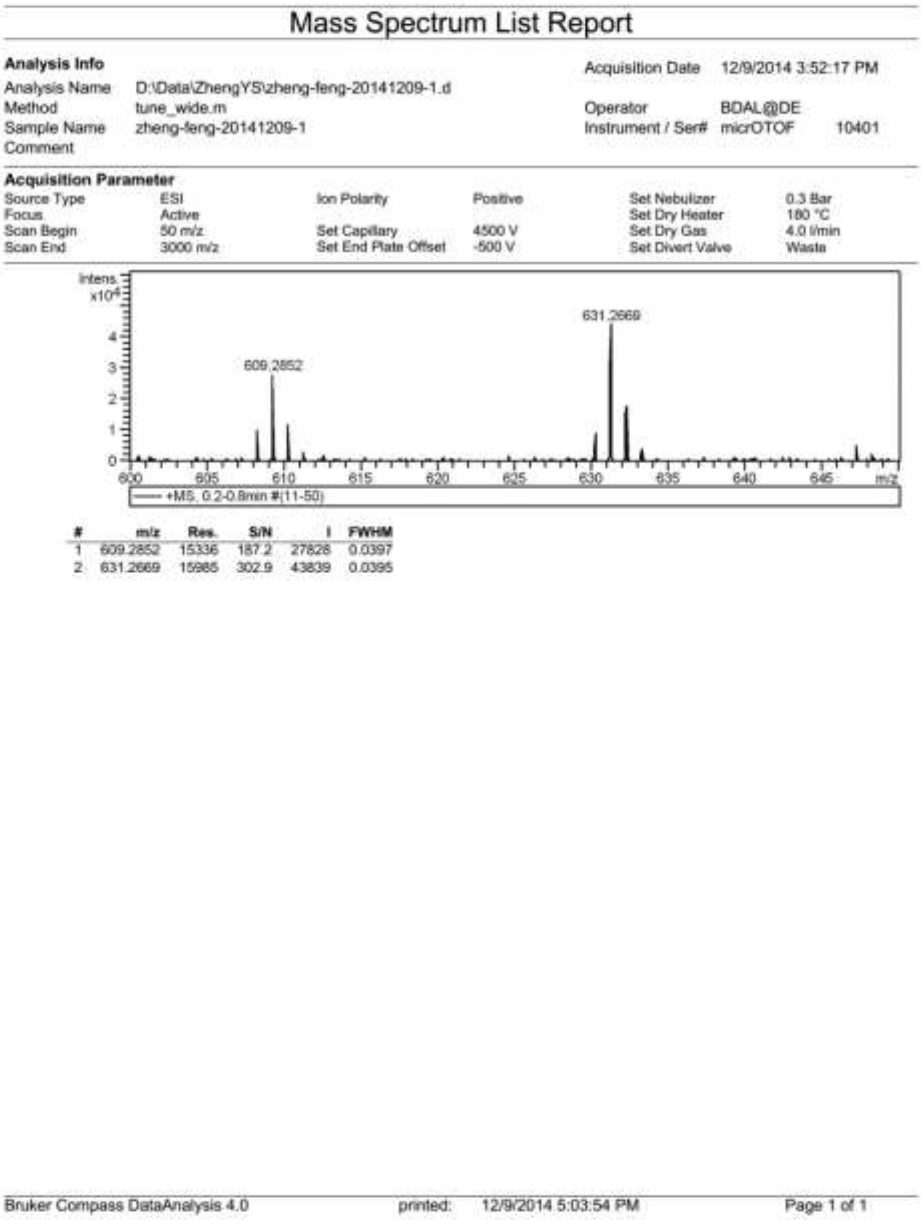


Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$.



Mass Spectrum List Report

Analysis Info

Analysis Name D:\Data\ZhengYS\zheng-feng-20141209-1.d
Method tune_wide.m
Sample Name zheng-feng-20141209-1
Comment
Acquisition Date 12/9/2014 3:52:17 PM
Operator BDAL@DE
Instrument / Ser# micrOTOF 10401

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

#	m/z	Res.	S/N	I	FWHM
1	609.2852	15336	187.2	27828	0.0397
2	631.2669	15985	302.9	43839	0.0395

Bruker Compass DataAnalysis 4.0 printed: 12/9/2014 5:03:54 PM Page 1 of 1

Figure S3. HRMS spectrum of **3**.

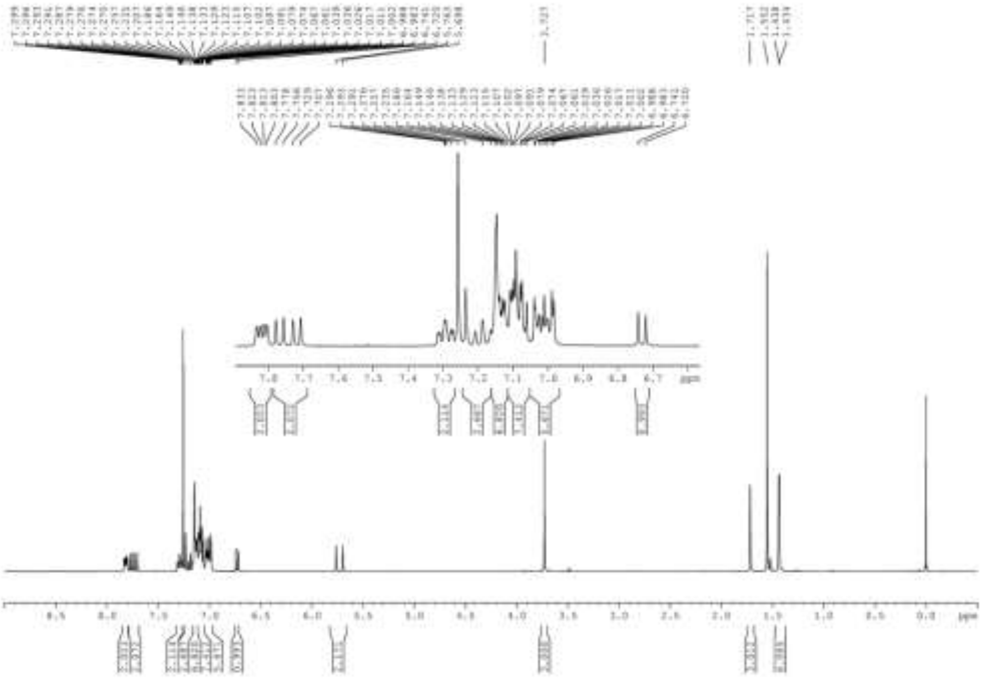


Figure S4. ^{1}H NMR spectrum of *R*-TPE-BINOL in CDCl$_3$

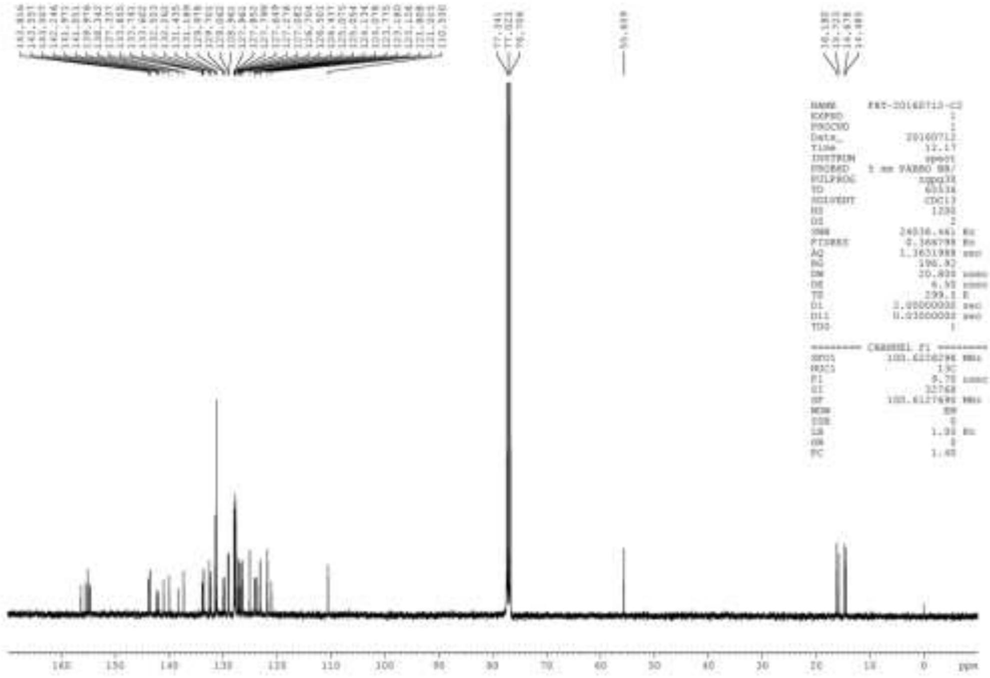


Figure S5. ^{13}C NMR spectrum of *R*-TPE-BINOL in CDCl$_3$.

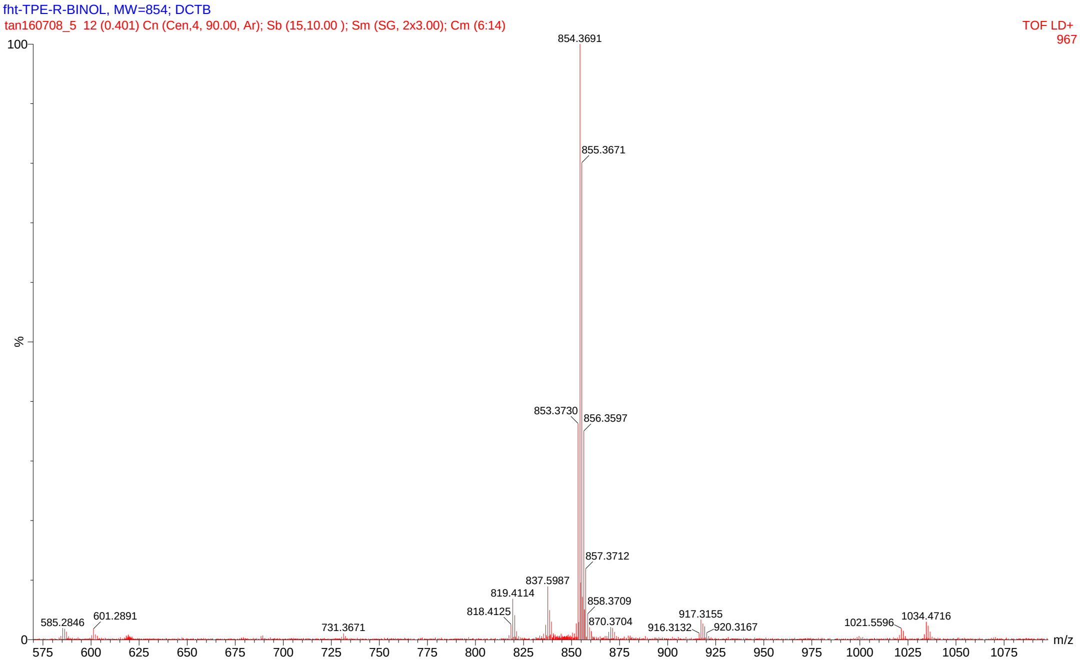


Figure S6. HRMS spectrum of *R*-TPE-BINOL.

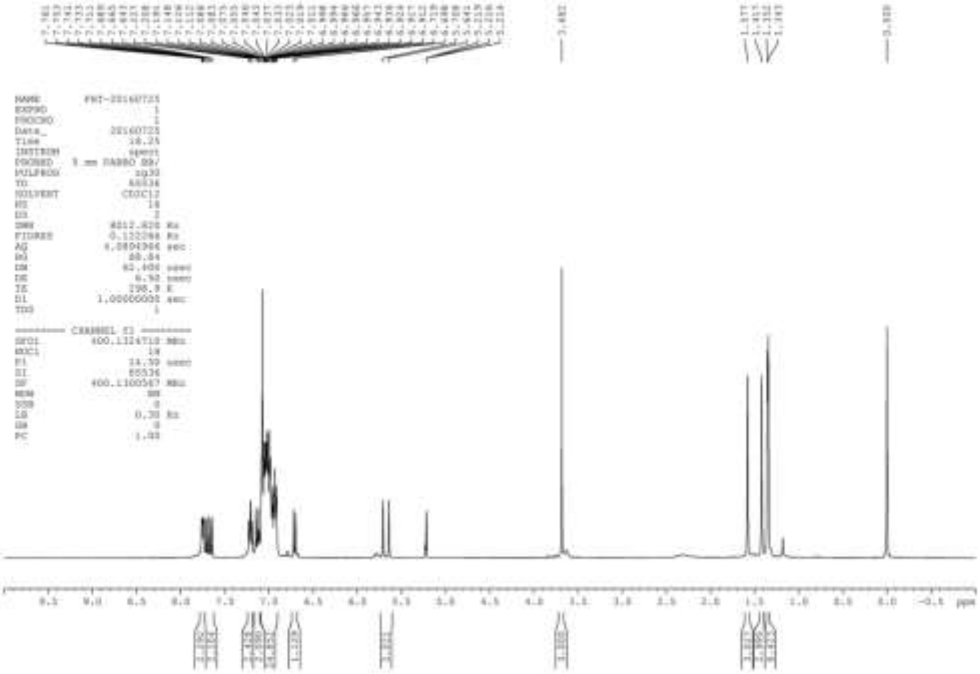
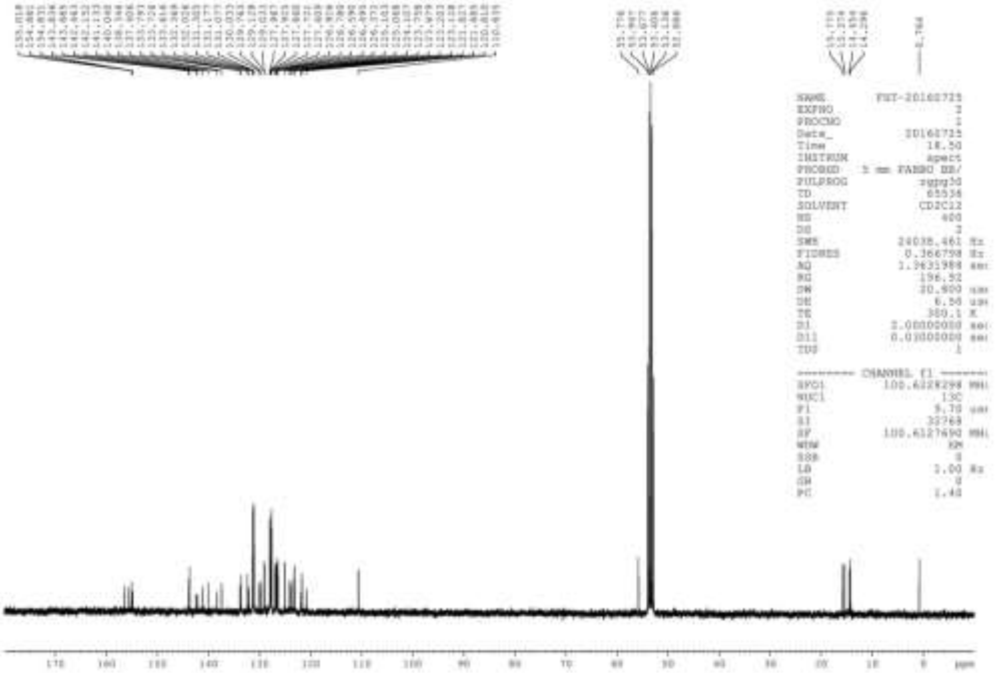


Figure S7. ^{1}H NMR spectrum of *S*-TPE-BINOL in CD_2Cl_2.



```
NAME        FHT-20160725
EXPNO                  2
PROCNO                 1
Date_           20160725
Time               18.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                   400
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                196.92
DW                20.800 usec
DE                  6.50 usec
TE                 300.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.70 usec
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S8. ^{13}C NMR spectrum of *S*-TPE-BINOL in CD_2Cl_2.

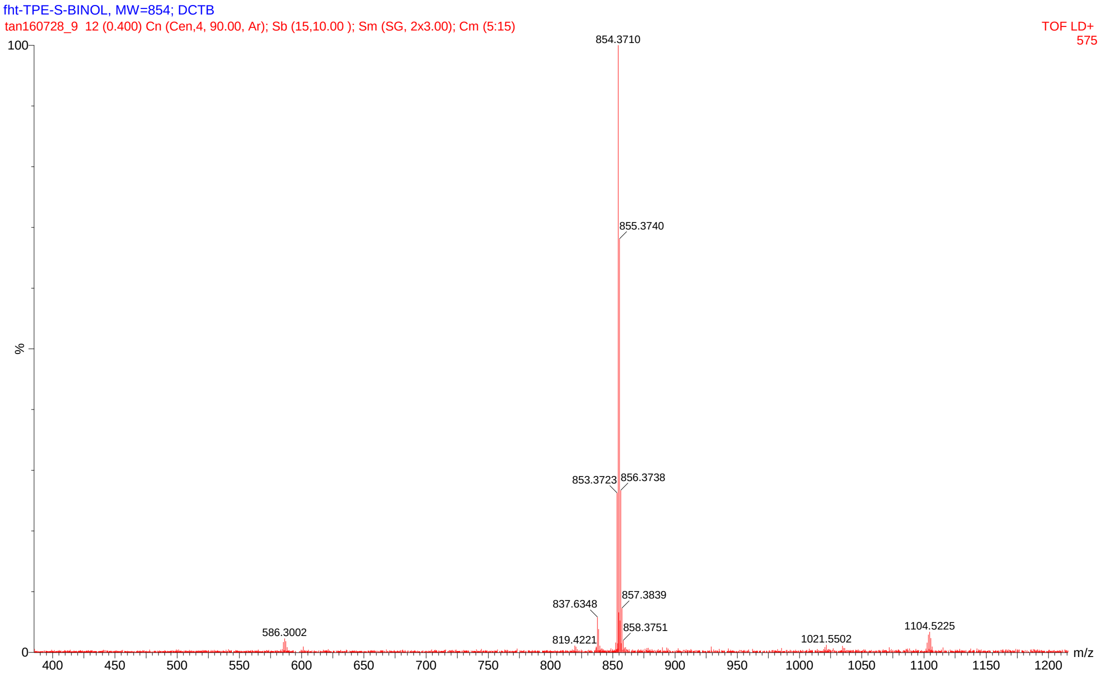


Figure S9. HRMS spectrum of *S*-TPE-BINOL.

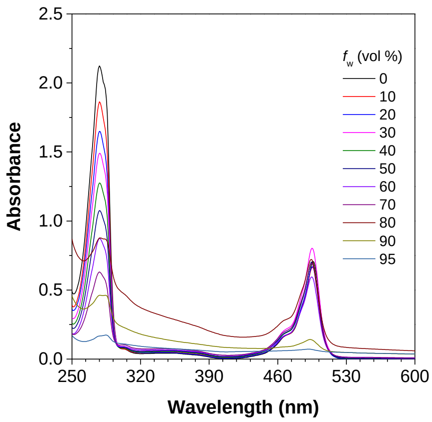


Figure S10. Absorption spectra of BODIPY in THF/water mixture, [BODIPY] =1.0 ×10^{-5} M.

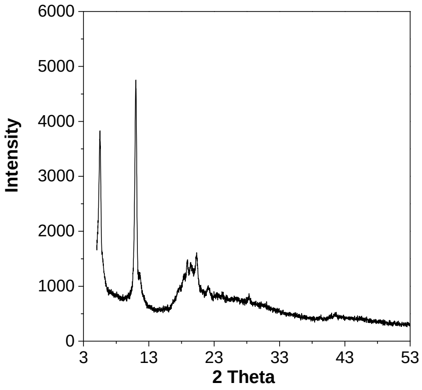


Figure S11. Powder XRD pattern of *R*-TPE-BINOL.

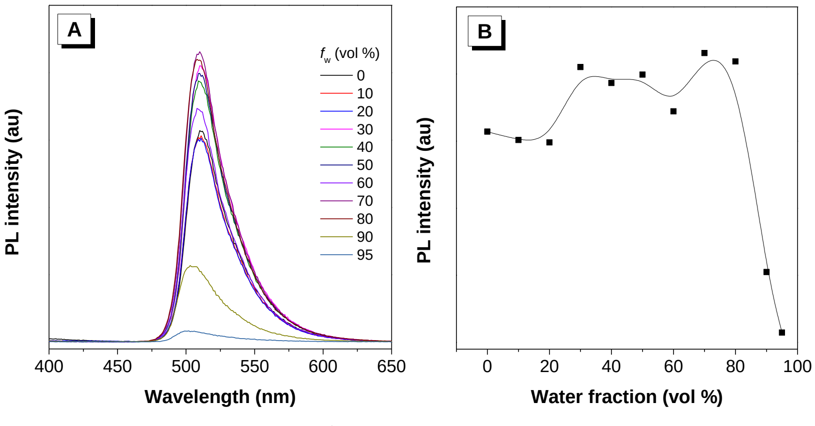


Figure S12. (A) Fluorescence spectra of BODIPY in THF/water mixture with different water fractions. (B) Dependent of the fluorescence intensity on the water fraction. Excitation wavelength: 350 nm, [BODIPY] =1.0 ×10^{-5} M.

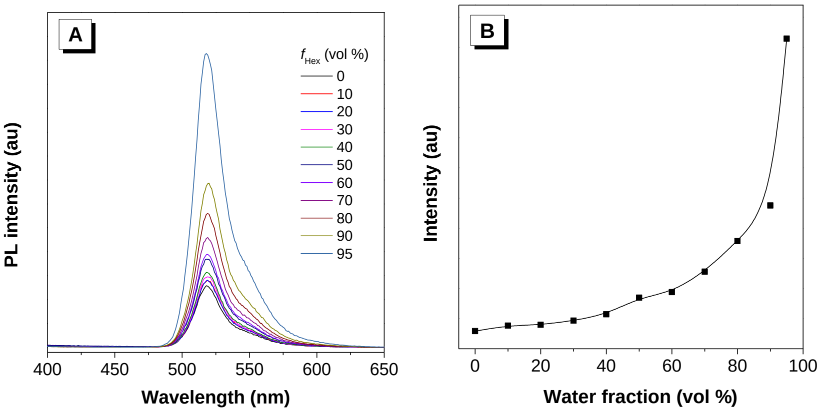


Figure S13. (A) Fluorescence spectra of *R*-TPE-BINOL in THF/hexane mixtures with different hexane fractions (excitation wavelength: 350 nm). (B) Dependent of the fluorescence intensity on the water fraction. [*R*-TPE-BINOL] =1.0 ×10^{-5} M.

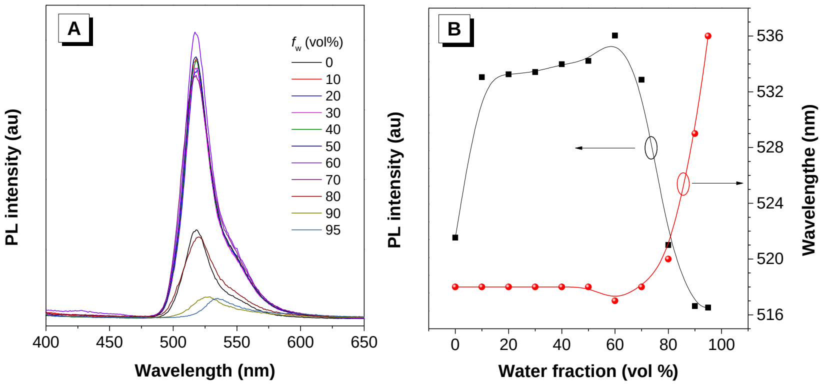


Figure S14. (A) Fluorescence spectra of *R*-TPE-BINOL in THF/water mixture with different water fractions (excitation wavelength: 350 nm). (B) Dependent of the fluorescence intensity and wavelength on the water fraction. [*R*-TPE-BINOL] =1.0 ×10^{-5} M.

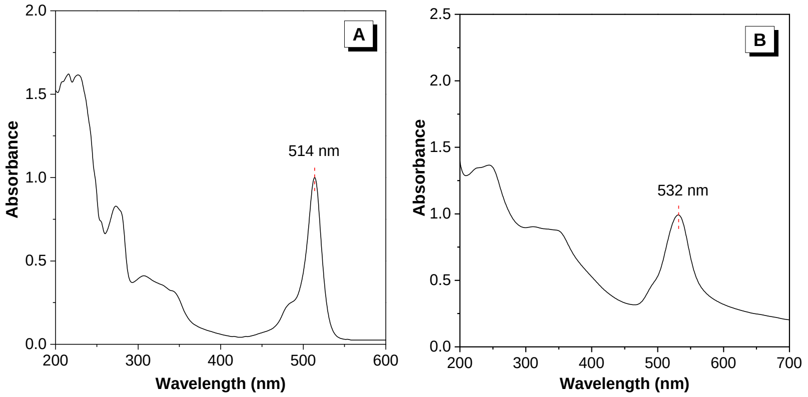


Figure S15. Absorption spectra of *R*-TPE-BINOL in THF (A) and 90% THF/water (B), [*R*-TPE-BINOL] =1.0 ×10^{-4} M.

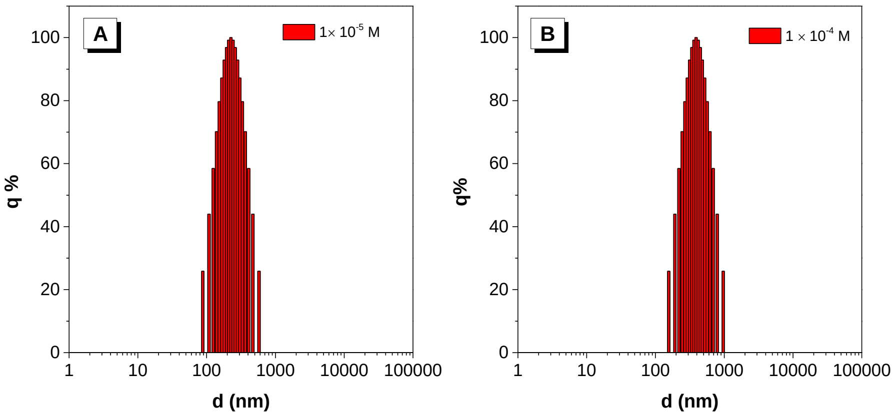


Figure S16. Dynamic light scattering (DLS) diagram of *R*-TPE-BINOL with different concentration: (A) [*R*-TPE-BINOL] = 1.0 × 10^{-5} M and (B) [*R*-TPE-BINOL] = 1.0 × 10^{-4} M in THF/H_2O mixture (v/v, 5/95).

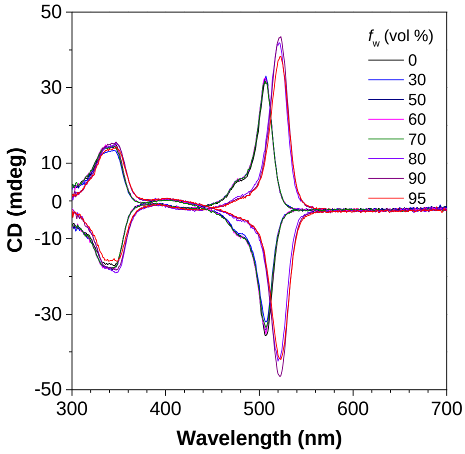


Figure S17. CD spectra of *R*-TPE-BINOL (negative Cotton effect) and *S*-TPE-BINOL (positive Cotton effect) in THF/water mixture with different f_w, [*R*/*S*-TPE-BINOL] =1.0 ×10^{-5} M.

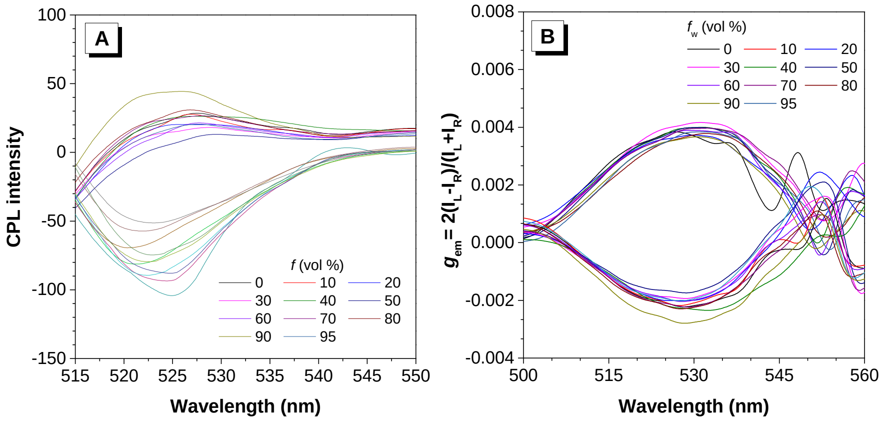


Figure S18. CPL spectra (A) and CPL dissymmetry factor g_{em} (B) of *R*-TPE-BINOL (upper) and *S*-TPE-BINOL (lower) in THF/hexane mixtures with different hexane fractions, [*R*/*S*-TPE-BINOL] =1.0 ×10^{-4} M.

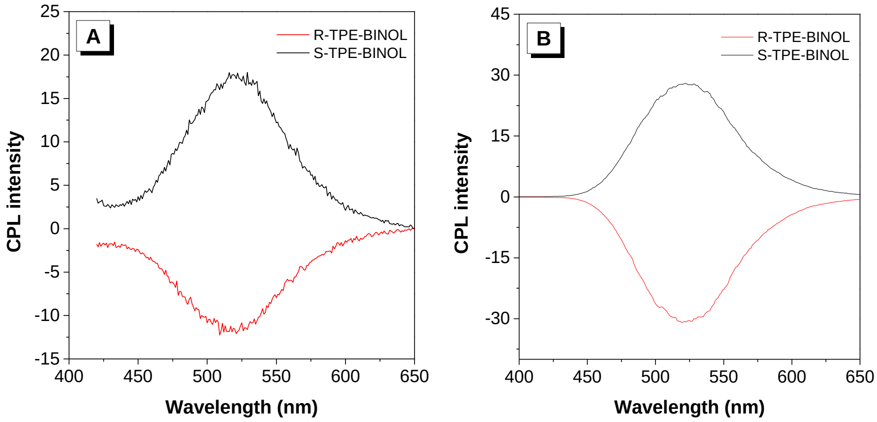


Figure S19. CPL spectra of *R*/*S*-TPE-BINOL in (A) THF/water (v/v, 50/50) and (B) THF/water (v/v, 10/90) mixture, [*R*/*S*-TPE-BINOL] =1.0 $\times 10^{-4}$ M.

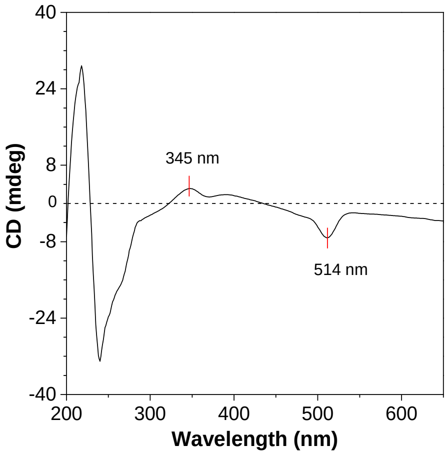


Figure S20. CD spectrum of PS film containing 0.1 wt % *R*-TPE-BINOL.

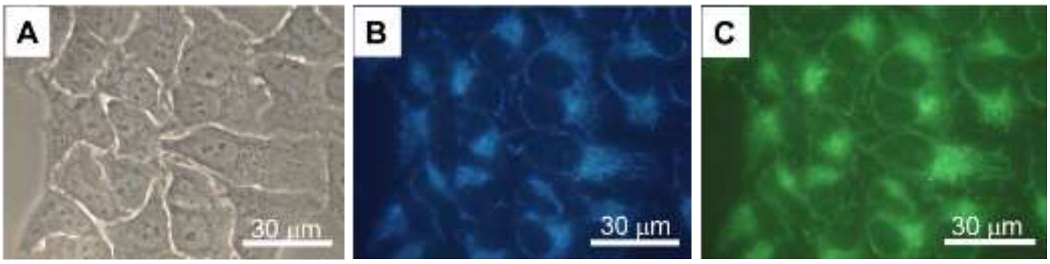


Figure S21. (A) Bright-field; (B) fluorescent images of HeLa cells stained with 10 μM of *R*-TPE-BINOL for 30 min, Excitation wavelength: 330-385 nm; (C) Excitation wavelength: 400−440 nm.

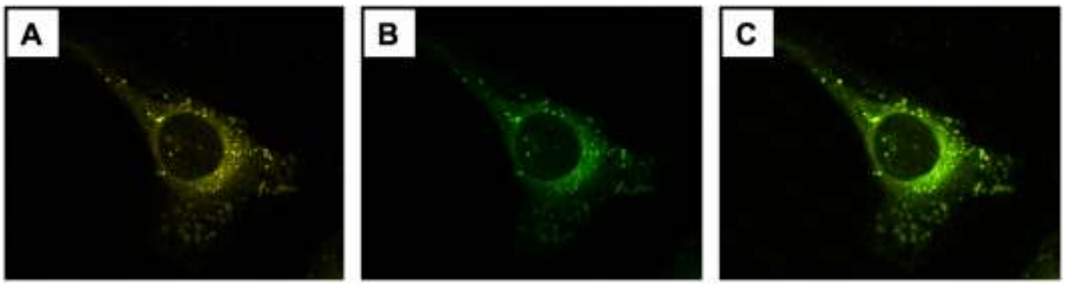


Figure S22. Fluorescent images of a HeLa cell incubated with (A) TPE-BOD (10 μM) and (B) BODIPY (100 nM) for 30 min at 37 °C, and (C) their merged picture.