Electronic Supplementary Information

Tetraphenylfuran: Aggregation-Induced Emission or Aggregation-Caused Quenching?

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Experimental section

Materials and Instrumentation: All reagents was purchased from Alfa Aesar or Sigma-Aldrich and used without further purification. Tetrahydrofuran (THF) was distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. ^{1}H and ^{13}C NMR spectra were measured using a Bruker AV-300. Chemical shifts were expressed in parts per million (ppm), and splitting patterns are designated as s (singlet), d (doublet), m (multiplet) and br (broad). Coupling constants *J* are reported in Hertz (Hz). The elemental analyses were carried out on a ThermoFinnigan Flash EA 1112. The high-resolution mass spectra (HRMS) were recorded using a GCT premier CAB048 mass spectrometer operating in matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mode. Single-crystal X-ray diffraction data were collected at 100 K on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELXL suite of X-ray programs (version 6.10). The absorption spectra were recorded using a Shimadzu UV-1700 spectrometer. The emission spectra were obtained using a Horiba Fluoromax-4 spectrofluorometer. The photoluminescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-QY. Transient PL at room temperature was measured using Quantaurus-Tau fluorescence lifetime measurement system (C11367-03, Hamamatsu Photonics Co., Japan). All decay was evaluated on TCC900 mode with 340 nm LED excitation source.

Computational details: The geometry optimization and harmonic vibrational frequency calculations of ground state (S_0) were carried out at the level of density functional theory (DFT). Then for the first single excited state (S_1), the time-dependent density functional theory (TD-DFT) was applied. The B3LYP functional has been applied with 6-31G(d,p) basis set.[1] It was confirmed that all the frequencies obtained at the minima of S_0 and S_1 states are positive, namely, the optimized structures are stable. On the basis of optimized S_0 geometry, the single point energies

were calculated at the level of B3LYP/6-31++G(d,p). All these electronic structure calculations were performed with Gaussian 09 program package.[2] The reorganization energy was obtained through the DUSHIN program, with the total reorganization energy projected to the molecular structure parameters relaxation.[3]

Synthesis of tetraphenylfuran (TPF)[4]

Diphenylacetylene (0.89 g, 5 mmol), $Pd(OAc)_2$ (0.11 g, 0.5 mmol), and $ZnCl_2$ (0.14 g, 1 mmol) were added to an oven-dried Schlenck tube under air. The septum-sealed tube was evacuated and refilled with O_2 three times. *N*,*N*-Dimethylformamide (DMF) (2.5 mL) and perfluorodecalin (2.5 mL) were added via syringe. The reaction mixture was heated in an oil bath at 60 C for 24 h. After the reaction completed, 0.73g TPF (78% yield) was obtained by silica-gel column chromatography with petroleum ether as eluent. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.53–7.50 (m, 4H), 7.28–7.19 (m, 12H), 7.18–7.14 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 147.7, 133.1, 130.9, 130.4, 128.4, 128.3, 127.3, 127.1, 125.8, 125.1. Anal. calcd. for $C_{28}H_{20}O$ (%): C, 90.29; H, 5.14; found: C, 90.05; H, 5.35. HRMS (MALDI-TOF, *m*/*z*): $[M]^+$ calcd for $C_{28}H_{20}O$, 372.1514; found, 372.1506.

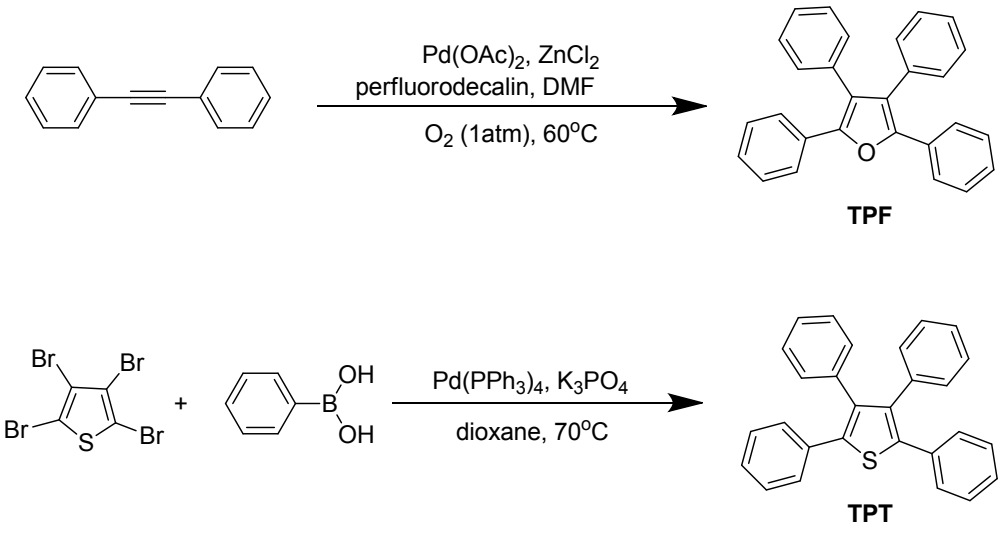
Synthesis of tetraphenylthiophene (TPT)[5]

An oven-dried Schlenck flask was charged with tetrabromothiophene (1.20 g, 3 mmol), phenylboronic acid (2.19 g, 18 mmol), $Pd(PPh_3)_4$ (0.42 g, 0.36 mmol) and powered, anhydrous K_3PO_4 (24 mmol, 5.09 g). The Schlenk flask was filled with nitrogen. The dioxane (60 mL) and distilled water (15 mL) were added by syringe. The reaction mixture was stirred and refluxed for 12 h at 60 ^{o}C. After cooling to room temperature, the product was extracted with chloroform (3× 100 mL), and the organic layer was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation under reduced pressure, the product was purified by silica-gel column chromatography using petroleum ether as eluent. TPT was obtained in a 43% yield (500 mg) after recrystallization from a mixture of chloroform/petroleum ether. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.25–7.17 (m, 10H), 7.15–7.08 (m, 6H), 6.98–

6.95 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 139.5, 138.5, 136.4, 134.2, 130.8, 129.2, 128.3, 127.8, 127.2, 126.6. Anal. calcd. for $C_{28}H_{20}S$ (%): C, 86.56; H, 5.19; found: C, 86.53; H, 5.12. HRMS (MALDI-TOF, *m*/*z*): $[M]^+$ calcd for $C_{28}H_{20}S$, 388.1286; found, 388.1270.

Preparation of nanoaggregates of TPF and TPT.

Stock THF solutions of TPF or TPT with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water fractions (0-99 vol%). Because TPF and TPT are soluble in THF but insoluble in water, the molecules must have aggregated into nanoaggregates when large amount water fractions are added. The PL spectra and quantum yields measurements of the resultant solutions were then performed immediately.



Scheme S1 Synthetic routes to tetraphenylfuran and tetraphenylthiophene.

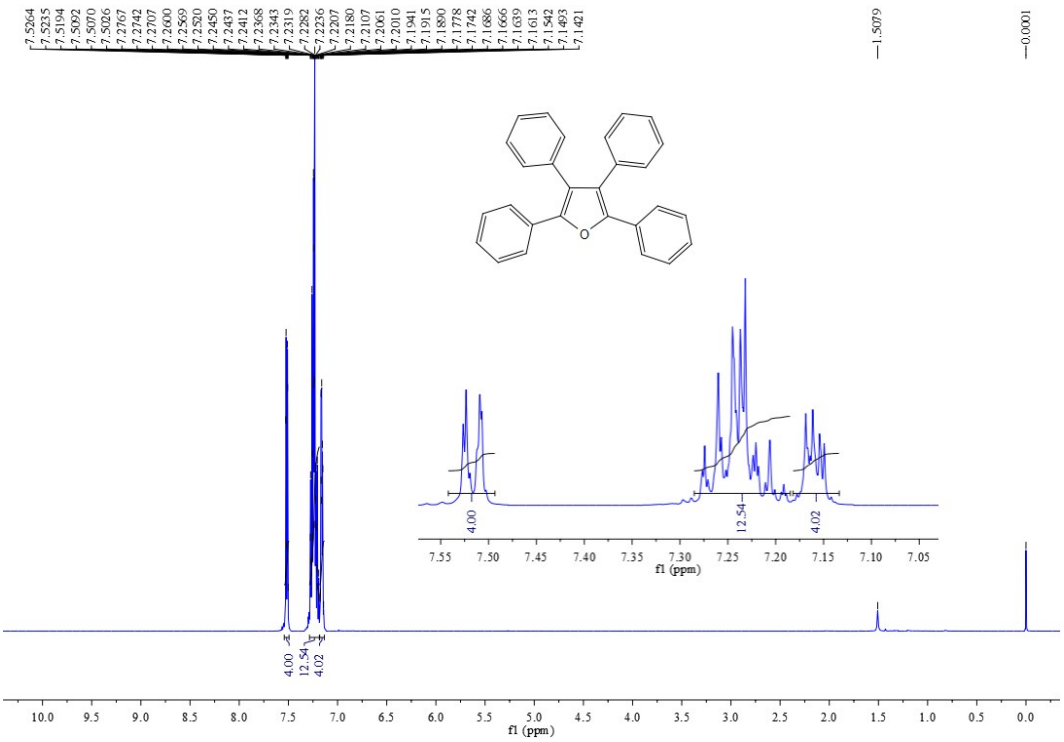


Fig. S1 ^{1}H NMR of TPF in $CDCl_3$.

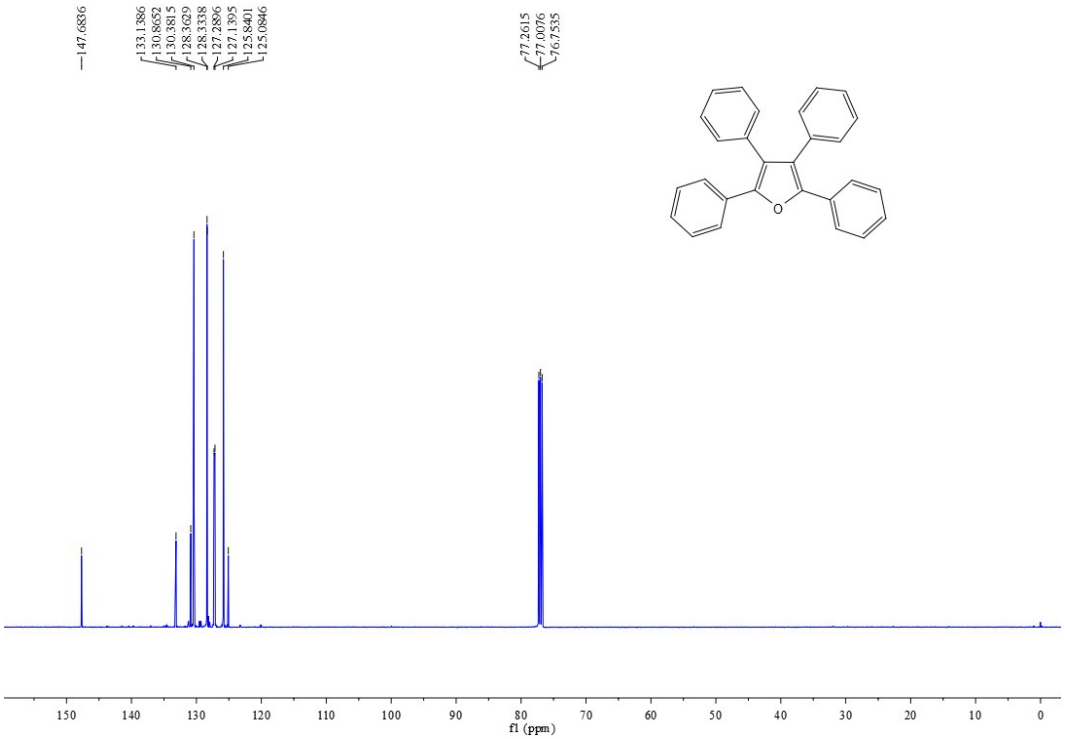


Fig. S2 ^{13}C NMR of TPF in $CDCl_3$.

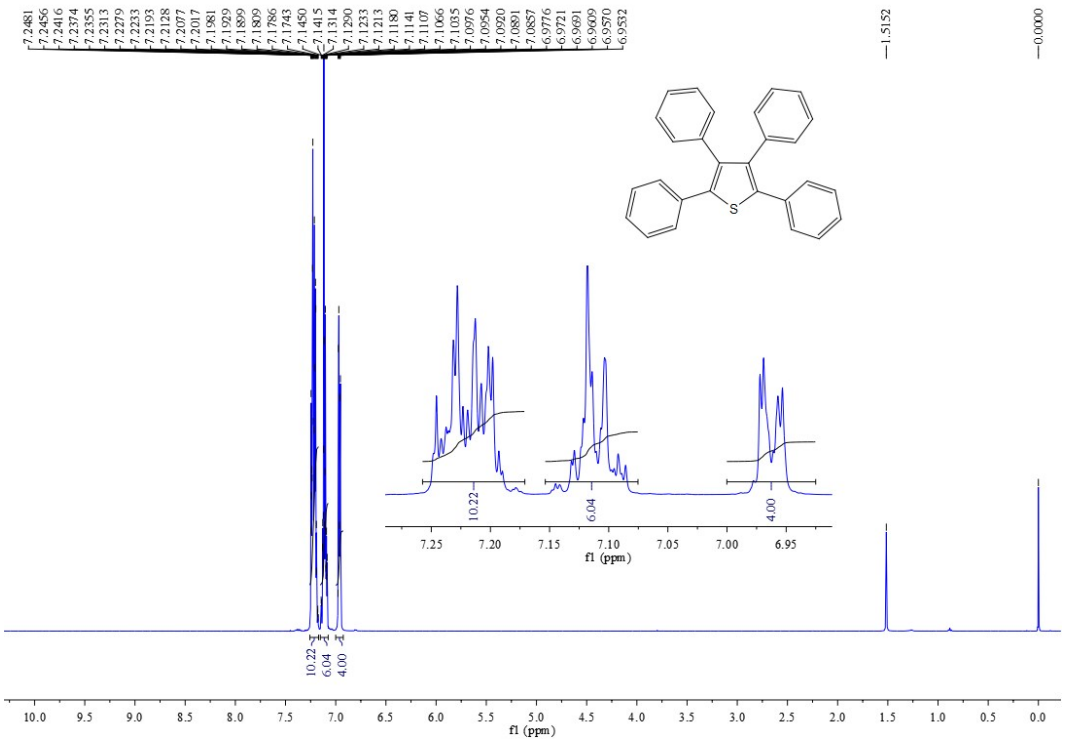


Fig. S3 ^{1}H NMR of TPT in $CDCl_3$.

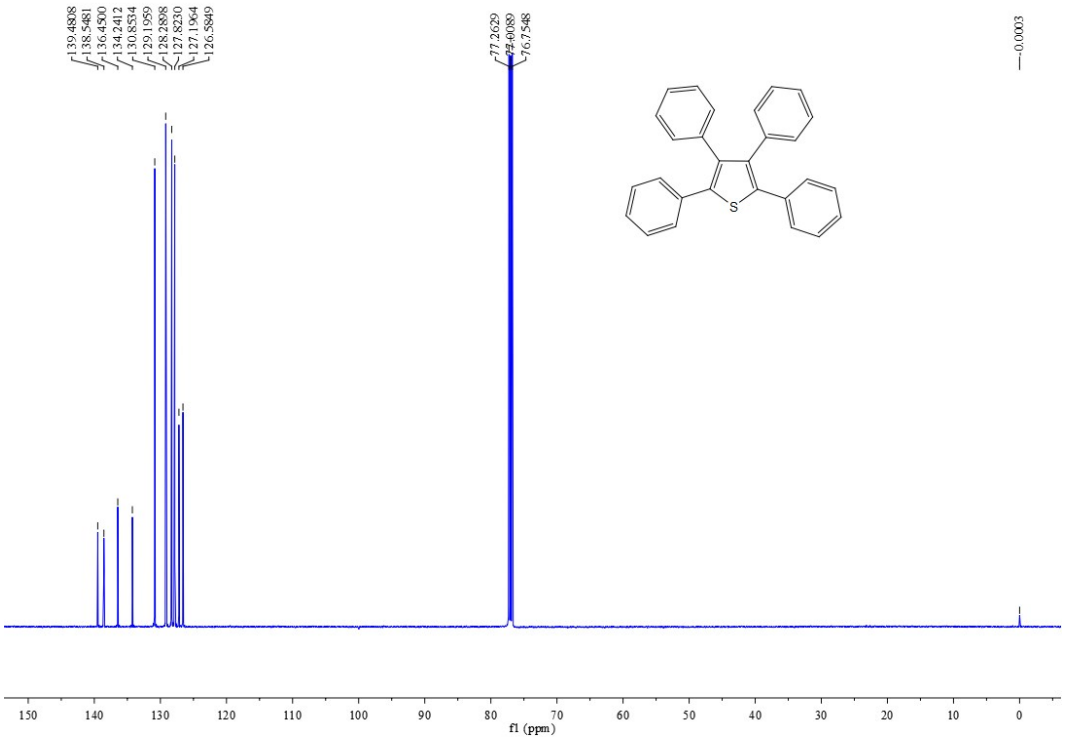


Fig. S4 ^{13}C NMR of TPT in $CDCl_3$.

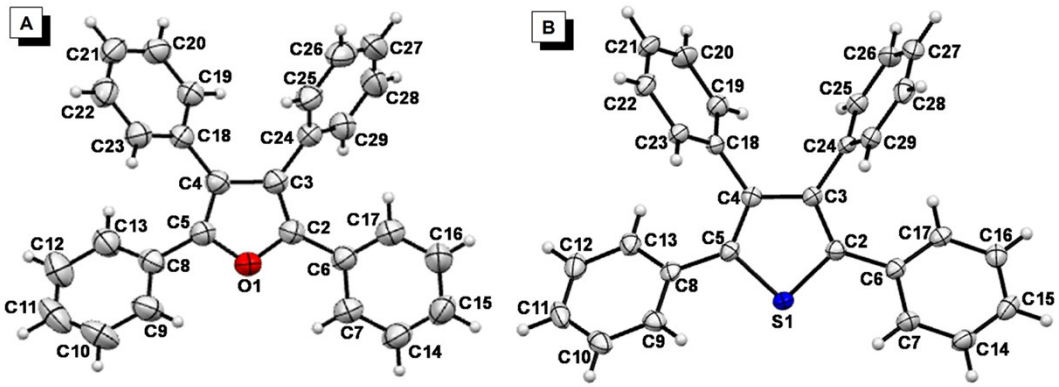


Fig. S5 ORTEP drawings of the crystal structures of (A) TPF and (B) TPT.

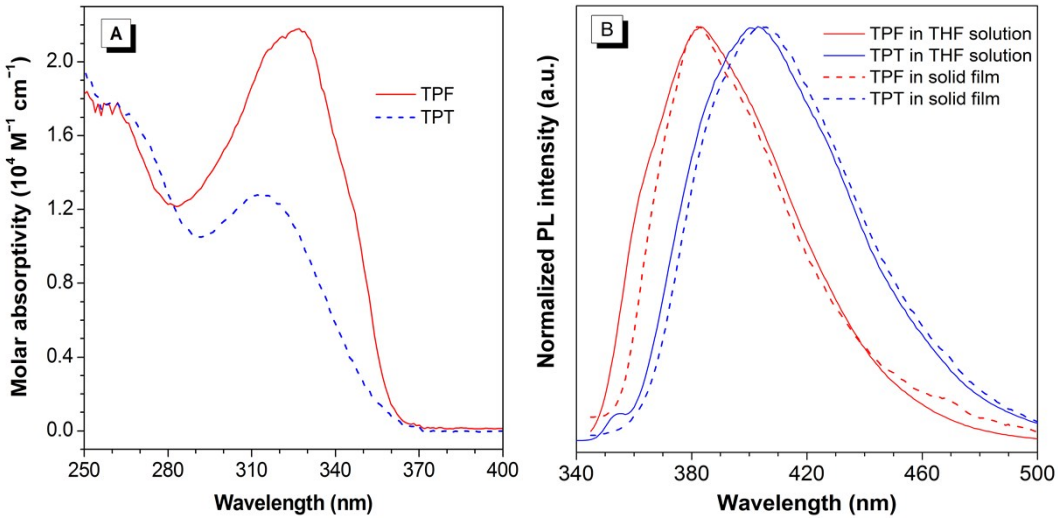


Fig. S6 (A) UV absorption spectra of TPF and TPT in THF solutions. (B) PL spectra of TPF and TPT in THF solutions (10 μM) and in solid films, excitation wavelengths: 327 nm for TPF and 320 nm for TPT.

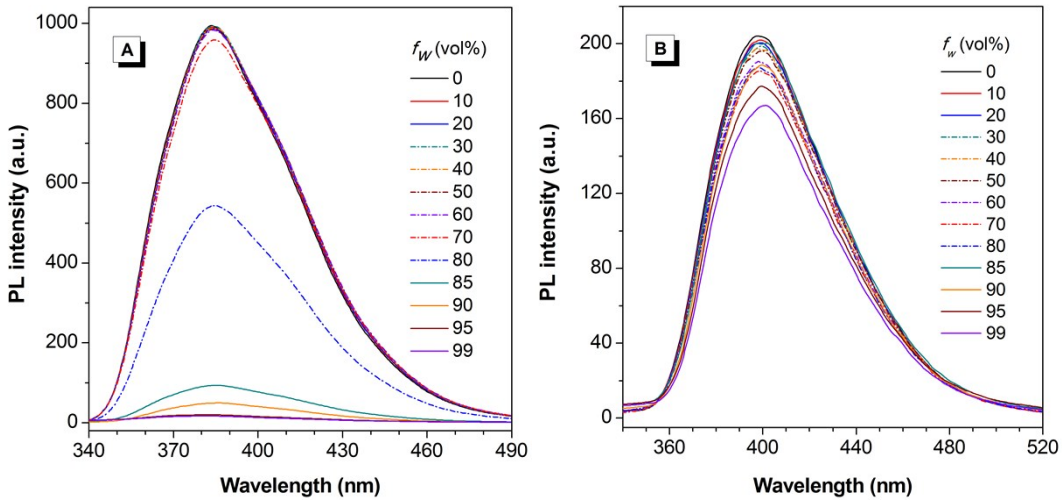


Fig. S7 PL spectra of (A) TPF and (B) TPT in THF/water mixtures with different water fractions (f_w). Concentration: 10 μM; excitation wavelengths: 327 nm for TPF and 320 nm for TPT.

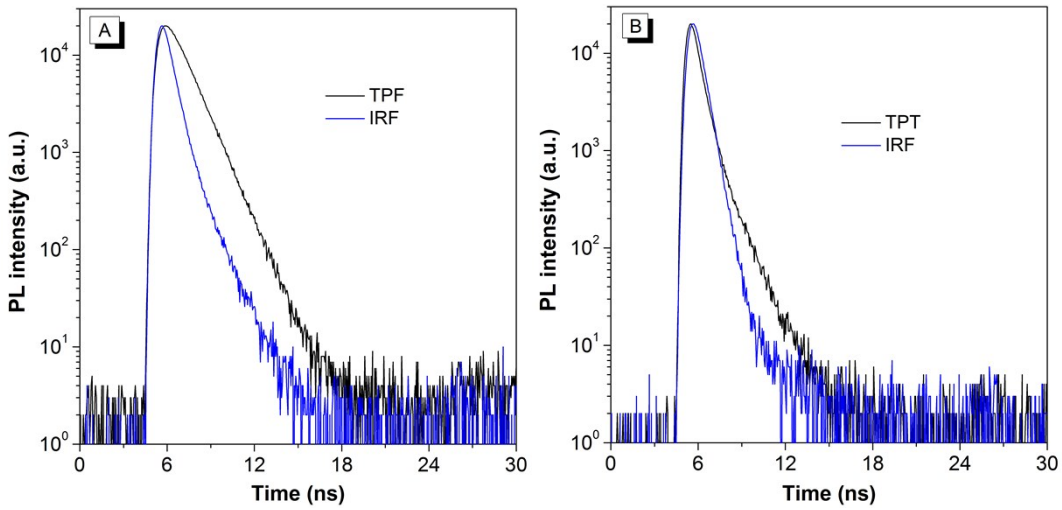


Fig. S8 Transient PL decay curves of (A) TPF and (B) TPT in THF solutions (10 μM). Excitation wavelengths: 340 nm. Blue curves are instrument response factor (IRF) data.

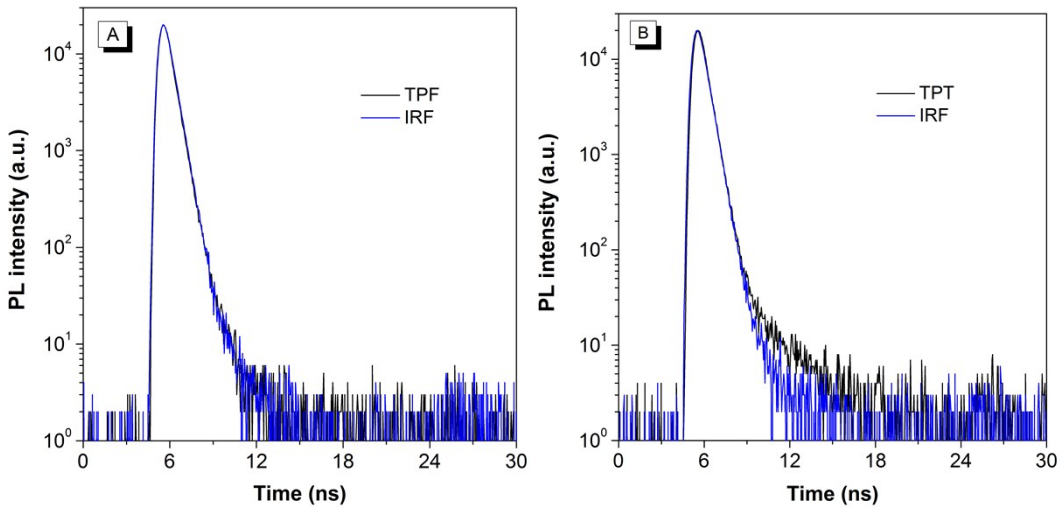


Fig. S9 Transient PL decay curves of (A) TPF and (B) TPT in solid films, excitation wavelengths: 340 nm. Blue curves are instrument response factor (IRF) data.

Table S1 Calculated Absorption and Emission Data for TPF and TPT

	Electronic state transition	Vertical excitation energy [eV (nm)]	Oscillator strength *f*	Main configuration (%)
		Absorption		
TPF	$S_0 \rightarrow S_1$	3.71 (334)	0.47	HOMO→LUMO (99)
TPT	$S_0 \rightarrow S_1$	3.85 (322)	0.33	HOMO→LUMO (98)
		Emission		
TPF	$S_1 \rightarrow S_0$	3.12 (397)	0.46	LUMO→HOMO (99)
TPT	$S_1 \rightarrow S_0$	2.80 (416)	0.43	LUMO→HOMO (99)

Table S2 Transient PL Decay Data for TPF and TPT[a]

	state	CHI	$\langle\tau\rangle$ (ns)	τ_1 (ns)	τ_2 (ns)	A_1	A_2
TPF	solution	1.80	0.68	0.048	0.98	19204	1939
TPT	solution	1.53	0.24	0.12	1.25	9676	106
TPF	film	1.12	0.06	0.08	0.22	14605	-695
TPT	film	1.29	0.11	0.10	3.08	12323	2

[a] The transient PL decay data were fitted by double-exponential function and the average fluorescence lifetimes ($\langle\tau\rangle$) were calculated by $\langle\tau\rangle = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, where A_i is the pre-exponential for lifetime τ_i.

Table S3 Crystallographic Data for TPF and TPT

	TPF	TPT
chemical formula	$C_{28}H_{20}O$	$C_{28}H_{20}S$
formula weight	372.44	388.50
crystal system	monoclinic	monoclinic
space group	I 2/c	I 1 2 1
Z	8	4
a [Å]	21.710(7)	15.4081(5)
b [Å]	8.1600(15)	6.0485(2)
c [Å]	24.855(8)	22.1271(7)
α [deg]	90	90
β [deg]	113.396(19)	102.299(3)
γ [deg]	90	90
V [Å^3]	4041(2)	2014.83(11)
density [g/cm^3]	1.224	1.281
μ [mm^{-1}]	0.073	1.489
F(000)	1568.0	816.0
crystal size [mm]	0.31 × 0.27 × 0.25	0.35 × 0.04 × 0.02
temperature [K]	293(2)	173(3)
radiation (λ), [Å]	0.71073	1.54178
no. of collected reflns.	16508	5771
no. of independent reflns. (R^{int})	3987 (0.0270)	2833 (0.0361)
R_1, wR_2 (all data)	0.0489, 0.1095	0.0378, 0.0851

Table S4 Coordinate of TPF in ground state[a]

atom	x	y	z
O	0.00002400	-1.79707200	-0.00002500
C	2.39251400	-1.70785300	0.05954000
C	-1.48446700	2.51707900	-0.94586100
H	-0.76220200	2.39676400	-1.74705900
C	1.59143900	1.52213100	-0.03925700
C	1.48446900	2.51707200	0.94590800
H	0.76224500	2.39670500	1.74713500
C	1.11286800	-1.00044600	0.01009100
C	-2.29564400	3.65061800	-0.90408100
H	-2.20040900	4.40812300	-1.67670500

C	2.47131800	-3.04233700	-0.38179300
H	1.58089600	-3.52532600	-0.76879900
C	-2.52660100	1.69970900	1.07255700
H	-2.61210300	0.94165900	1.84514200
C	0.72325800	0.32261800	-0.00285500
C	-0.72324300	0.32260600	0.00285100
C	-1.59145300	1.52209700	0.03926200
C	-3.33851900	2.83246000	1.11210500
H	-4.05578600	2.95192800	1.91909200
C	-2.39247200	-1.70787700	-0.05955300
C	2.52652900	1.69981400	-1.07259300
H	2.61201500	0.94179900	-1.84521400
C	-1.11283000	-1.00046200	-0.01011000
C	-2.47127500	-3.04235700	0.38179000
H	-1.58085200	-3.52534400	0.76879700
C	3.55481800	-1.09741800	0.56546100
H	3.51065200	-0.07983600	0.93463200
C	-3.22633800	3.81188500	0.12344000
H	-3.85743800	4.69523200	0.15543500
C	2.29561100	3.65063600	0.90413500
H	2.20039100	4.40810800	1.67679300
C	4.82723400	-3.11823200	0.16323300
H	5.76717900	-3.66071700	0.20183900
C	-4.75786700	-1.79716200	-0.61023200
H	-5.64378400	-1.30966700	-1.00683900
C	3.33841200	2.83259100	-1.11213500
H	4.05563500	2.95211200	-1.91915400
C	4.75790600	-1.79714100	0.61023400
H	5.64382100	-1.30964700	1.00684600
C	-3.55477700	-1.09744000	-0.56546700
H	-3.51060900	-0.07985600	-0.93463400
C	3.67656900	-3.73725300	-0.32864400
H	3.71745200	-4.76537800	-0.67679400
C	-3.67652600	-3.73727300	0.32864800
H	-3.71741100	-4.76539700	0.67680300
C	3.22625100	3.81197200	-0.12342500
H	3.85732300	4.69533900	-0.15541500
C	-4.82719300	-3.11825200	-0.16322800
H	-5.76713900	-3.66073500	-0.20182700

[a] Absolute energy = -1154.28926402 Hartree

Table S5 Coordinate of TPF in first singlet excited state[a]

atom	x	y	z
O	0.03405100	-1.82295500	-0.06096500

C	-2.34129900	-1.72591100	-0.12169400
C	1.32454400	2.72869200	0.60605700
H	0.51859900	2.74976300	1.33118100
C	-1.62387400	1.48960600	0.16487100
C	-1.68005400	2.44383400	-0.86509900
H	-1.05428800	2.31582700	-1.74223000
C	-1.09878800	-1.02560200	-0.00530800
C	2.13747700	3.84330500	0.44883900
H	1.95164900	4.72886100	1.05002500
C	-2.33984000	-3.15118100	-0.06936200
H	-1.40061000	-3.67037100	0.07736900
C	2.63137800	1.55273100	-1.06701600
H	2.81189900	0.67079900	-1.67224100
C	-0.71317400	0.32762000	0.07119900
C	0.70138500	0.37263300	-0.01010100
C	1.54842800	1.55353500	-0.14912200
C	3.43444600	2.67866000	-1.22382500
H	4.24960900	2.65621000	-1.94186500
C	2.39567500	-1.63732400	0.14070700
C	-2.43803800	1.66853000	1.29697700
H	-2.39849300	0.93806300	2.09953300
C	1.14132500	-0.99379000	-0.01131300
C	2.50183300	-3.04837800	-0.08841300
H	1.61937800	-3.59699400	-0.39749500
C	-3.58966100	-1.06822600	-0.31067600
H	-3.62430400	0.01042700	-0.38397800
C	3.19913400	3.82946900	-0.46828700
H	3.83301100	4.70302800	-0.58595300
C	-2.53005700	3.54392500	-0.76493700
H	-2.56519300	4.27026600	-1.57163900
C	-4.74216700	-3.20145900	-0.36070200
H	-5.66540900	-3.76548400	-0.45131000
C	4.78073300	-1.61470800	0.68515000
H	5.66273200	-1.06809200	1.00780500
C	-3.28383600	2.77224700	1.39594300
H	-3.90314500	2.89779900	2.27931500
C	-4.76012800	-1.80009600	-0.42659400
H	-5.70033200	-1.27782300	-0.57812600
C	3.57987000	-0.93751000	0.54999000
H	3.52391700	0.11427300	0.79535800
C	-3.52239100	-3.86542300	-0.18363900
H	-3.49793800	-4.95029500	-0.13338100
C	3.71353900	-3.69753300	0.04866900
H	3.77253200	-4.76542300	-0.14326900

C	-3.33362900	3.71324500	0.36474600
H	-3.99411300	4.57186300	0.44106200
C	4.86906300	-2.99086400	0.43086100
H	5.81674400	-3.50921200	0.54003900

[a] Absolute energy = -1154.16390246 Hartree

Table S6 Coordinate of TPT in ground state[a]

atom	x	y	z
S	-0.00009500	-2.31882800	-0.00036700
C	-1.26294200	-1.11272500	-0.01225400
C	-0.72373800	0.16141000	-0.00876200
C	0.72369900	0.16135900	0.00860300
C	1.26282000	-1.11280500	0.01209700
C	-2.66950400	-1.55810300	0.03409600
C	-3.09890100	-2.64835200	-0.74381700
H	-2.39565600	-3.13557800	-1.41285600
C	-4.41697000	-3.09710700	-0.68040100
H	-4.72707900	-3.93905700	-1.29255300
C	-4.92140300	-1.38041500	0.93613900
H	-5.62599200	-0.88542300	1.59822700
C	-3.60335700	-0.93364900	0.88052800
H	-3.28741000	-0.10250800	1.50067300
C	-1.54687500	1.40160300	-0.03475100
C	-2.46588300	1.62723100	-1.07202700
H	-2.56665800	0.88774600	-1.86035900
C	-3.24430700	2.78384000	-1.09672000
H	-3.94880200	2.94055200	-1.90858200
C	-3.11774200	3.73711800	-0.08505700
C	-2.20492400	3.52637800	0.94976100
H	-2.09851500	4.26304000	1.74093900
C	-1.42509800	2.37072600	0.97420700
H	-0.71508400	2.21453900	1.78017500
C	1.54694100	1.40147900	0.03468100
C	2.46602500	1.62690500	1.07193400
H	2.56677300	0.88732100	1.86017600
C	3.24455600	2.78344000	1.09671400
H	3.94910700	2.93999800	1.90855700
C	3.11803100	3.73683800	0.08515900
C	2.20515000	3.52629100	-0.94964300
H	2.09877700	4.26304500	-1.74074100
C	1.42521800	2.37071300	-0.97417700
H	0.71515500	2.21467400	-1.78013100
C	2.66937100	-1.55822500	-0.03408800
C	3.09860000	-2.64866800	0.74364500
H	2.39521900	-3.13604700	1.41243200

C	4.41667400	-3.09743000	0.68037200
H	4.72665200	-3.93953500	1.29237400
C	5.33492500	-2.46356800	-0.15730900
C	4.92145100	-1.38032900	-0.93562900
H	5.62618100	-0.88517000	-1.59744200
C	3.60340000	-0.93355900	-0.88016500
H	3.28758800	-0.10223900	-1.50014100
C	-5.33504900	-2.46344300	0.15761800
H	-3.72379600	4.63823800	-0.10407900
H	3.72417000	4.63789900	0.10424800
H	6.36270500	-2.81104400	-0.20522600
H	-6.36282300	-2.81092000	0.20565200

[a] Absolute energy = -1477.25694141 Hartree

Table S7 Coordinate of TPT in first singlet excited state[a]

atom	x	y	z
S	-0.00009300	-2.35048000	-0.00120000
C	-1.27161900	-1.10217000	-0.03291200
C	-0.70386800	0.21095000	-0.06248900
C	0.70381900	0.21081100	0.06225100
C	1.27149500	-1.10214400	0.03206800
C	-2.63165600	-1.53120300	0.10344800
C	-2.98950400	-2.87700700	-0.22119200
H	-2.24387800	-3.53344700	-0.65884900
C	-4.28396500	-3.34065100	-0.04706100
H	-4.52496100	-4.36492000	-0.31732600
C	-4.95377800	-1.17527800	0.79444600
H	-5.71407900	-0.51828800	1.20734000
C	-3.66660300	-0.69323000	0.62254100
H	-3.43240300	0.31708000	0.92870400
C	-1.52886100	1.42665600	-0.21969000
C	-2.42502200	1.53734900	-1.30280000
H	-2.49236700	0.72324000	-2.01759000
C	-3.20850100	2.67677100	-1.46782600
H	-3.88467800	2.74477100	-2.31522600
C	-3.12944500	3.72545100	-0.54806200
C	-2.25452600	3.62375800	0.53770100
H	-2.19277900	4.42978200	1.26331900
C	-1.46120900	2.49101300	0.70105200
H	-0.78902200	2.41823100	1.54908700
C	1.52896300	1.42653400	0.21952800
C	2.42366900	1.53796800	1.30367600

H	2.48996700	0.72443400	2.01922600
C	3.20719500	2.67737800	1.46868100
H	3.88233000	2.74600300	2.31686000
C	3.12948100	3.72525900	0.54789000
C	2.25592700	3.62281000	-0.53887000
H	2.19520300	4.42824100	-1.26523000
C	1.46261000	2.49003200	-0.70222400
H	0.79136700	2.41661900	-1.55096100
C	2.63165400	-1.53131200	-0.10345100
C	2.98900900	-2.87728700	0.22084900
H	2.24296000	-3.53379400	0.65767600
C	4.28353900	-3.34109500	0.04744400
H	4.52414700	-4.36553000	0.31742700
C	5.28074200	-2.49787100	-0.45750400
C	4.95428800	-1.17548100	-0.79261600
H	5.71499600	-0.51842000	-1.20464500
C	3.66707100	-0.69329900	-0.62138600
H	3.43329800	0.31724200	-0.92712500
C	-5.28069400	-2.49745200	0.45895500
H	-3.74642400	4.61039000	-0.67229500
H	3.74646300	4.61019500	0.67214100
H	6.29401200	-2.86412200	-0.59118700
H	-6.29393400	-2.86359100	0.59316600

[a] Absolute energy = -1477.13360240 Hartree

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