Supporting Information

Discovery and Insight into One-photon and Two-photon Excited ACQ-to-AIE Conversion via Positional Isomerization

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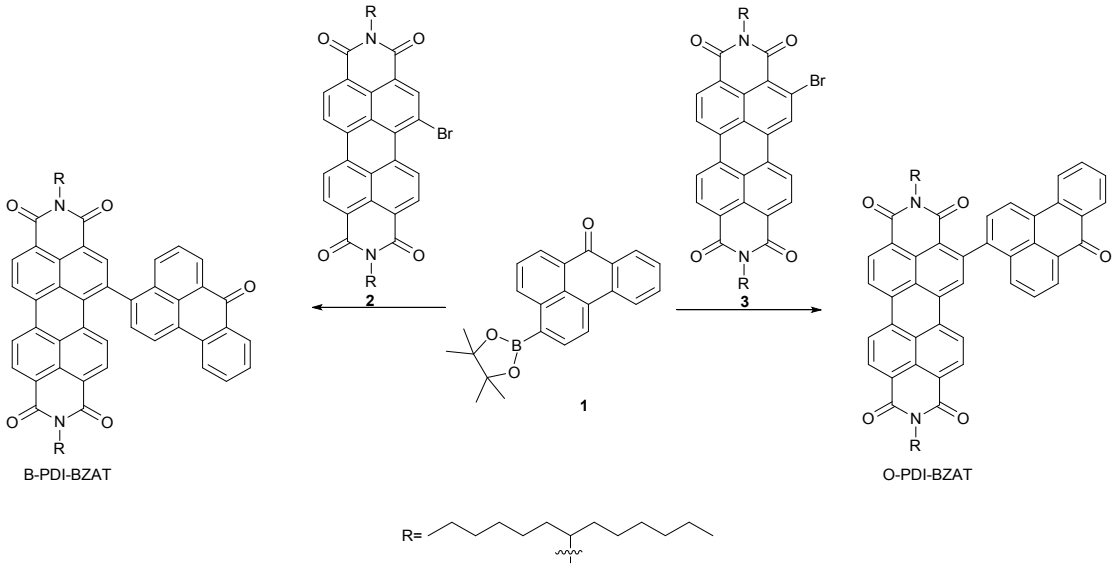
1. Synthesis



Scheme S1 The synthetic routes of B-PDI-BZAT and O-PDI-BZAT.

Synthesis of B-PDI-BZAT

Compound 1, 2 and 3 were synthesized according to the literature.[1] A mixture of 1 (1.72 g, 4.82 mmol), 2 (2.01 g, 2.41 mmol), $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), K_2CO_3 (0.67 g, 4.82 mmol), DMF (50 mL) was stirred at 80 °C under N_2 atmosphere for 24h. After cooling, DMF was removed by rotary evaporator. The residue was then purified by column chromatography (petroleum ether: DCM = 6:1 to 1:1). A dark red solid of B-PDI-BZAT (1.71 g, 1.74 mmol) was obtained in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81-8.74 (m, 3H), 8.70-8.68 (d, 2H), 8.64-8.62 (d, 2H), 8.58-8.56 (d, 1H), 8.45-8.43 (d, 1H), 8.07-8.05 (d, 1H), 7.88-7.82 (m, 2H), 7.79-7.78 (d, 1H), 7.69-7.61 (m, 3H), 5.19-5.04 (m, 2H), 2.25-2.12 (m, 4H), 1.86-1.76 (m, 4H), 1.33-1.16 (m, 32H), 0.84-0.77 (m, 12H). ^{13}C NMR

(125 MHz,$CDCl_3$) δ 182.58, 141.68, 137.24, 134.61, 132.69, 130.85, 130.09, 129.59, 128.99, 128.26, 128.14, 128.11, 128.04, 127.96, 127.92, 127.34, 126.86, 126.81, 126.26, 126.18, 123.78, 122.66, 122.29, 121.94, 53.87, 31.33, 31.21, 30.74, 30.67, 28.67, 28.19, 28.12, 25.90, 25.81, 21.57, 21.51, 13.03, 12.99. Mol. Wt 983.28, MALDI-TOF 983.298 Anal. Calcd for $C_{67}H_{70}N_2O_5$, C, 81.84; H, 7.18; N, 2.85; Found C, 81.81; H, 7.20; N, 2.86.

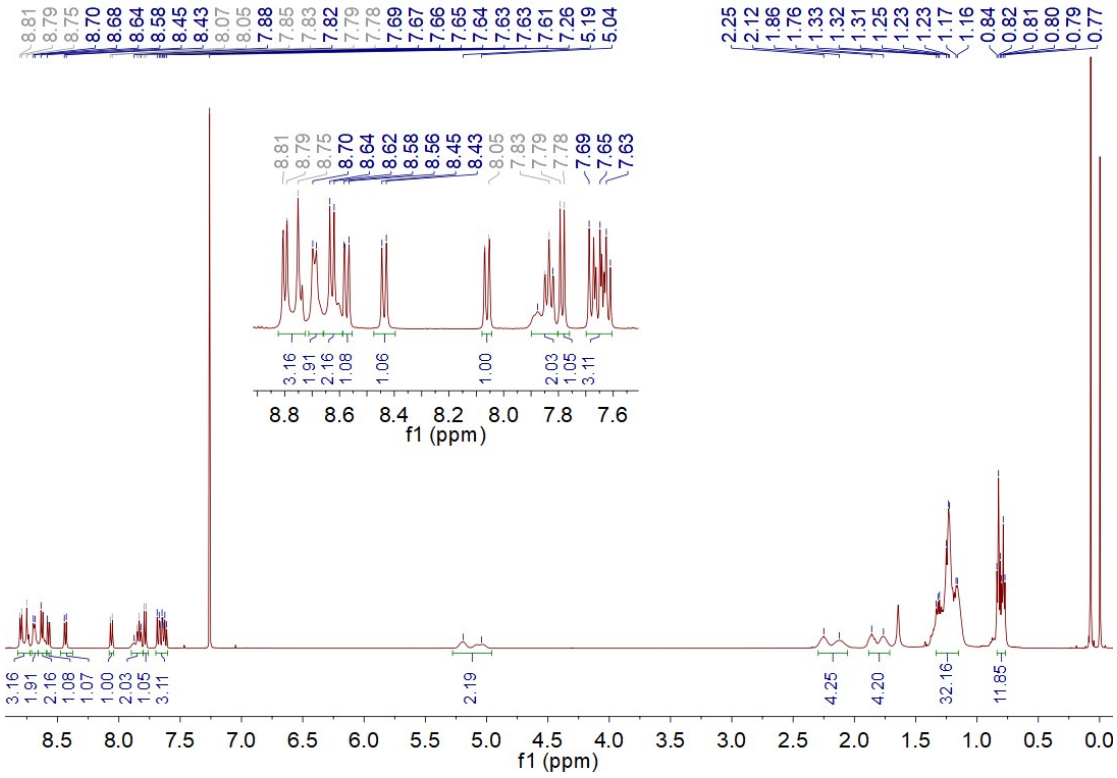


Figure S1 ^{1}H NMR of compound B-PDI-BZAT in $CDCl_3$.

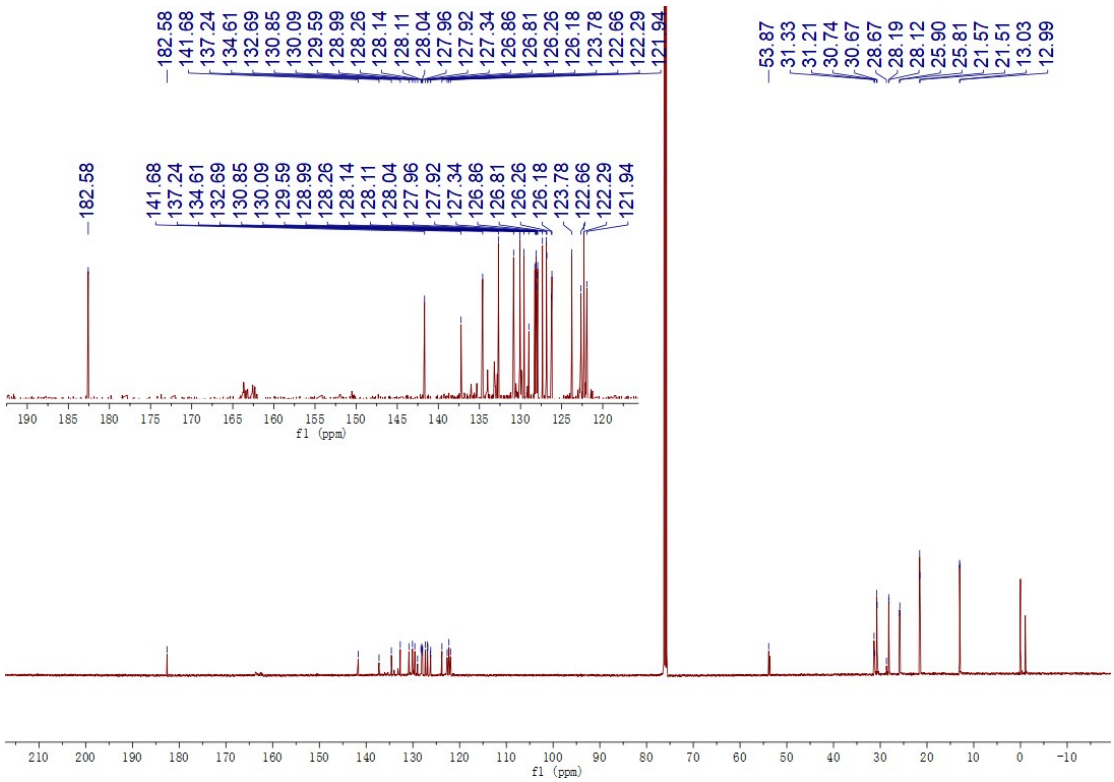


Figure S2 ^{13}C NMR of compound B-PDI-BZAT in $CDCl_3$.

Synthesis of O-PDI-BZAT

A mixture of 1 (0.59 g, 1.66 mmol), 3 (0.69 g, 0.83 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol), K_2CO_3 (0.23 g, 1.66 mmol), DMF (30 mL) was stirred at 80°C under N_2 atmosphere for 24h. After cooling, DMF was removed by rotary evaporator. The residue was then purified by silica gel column chromatography (petroleum ether: DCM=6:1 to 1:1). A dark red solid of O-PDI-BZAT (0.20 g, 0.2 mmol) was obtained in 25% yield. ^1H NMR (500MHz, $CDCl_3$) δ 8.79-8.68 (m, 5H), 8.59-8.50 (m, 5H), 8.38-8.37 (d, 1H), 7.90-7.88 (d, 1H), 7.78-7.75 (t, 1H), 7.69-7.67 (d, 1H), 7.62-7.53 (m,2H), 5.19 (s, 1H), 4.79 (m, 1H), 2.25 (s, 2H), 1.87 (s, 2H), 1.73 (s, 4H), 1.33-1.21 (m, 32H), 0.83-0.81 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.88, 163.52, 142.92, 136.19, 134.56, 133.45, 132.03, 131.04, 130.93, 130.30, 129.79, 129.50, 128.99, 128.37, 128.12, 128.00, 127.60, 126.71, 126.47, 124.03, 123.44, 123.30, 123.24, 123.06, 54.82, 31.75, 31.44, 30.19, 29.70, 29.21, 26.94, 22.58, 14.04. Mol. Wt 983.28, MALDI-TOF 983.387 Anal. Calcd for $C_{67}H_{70}N_2O_5$, C, 81.84; H, 7.18; N, 2.85; Found C, 81.79; H, 7.19; N, 2.88.

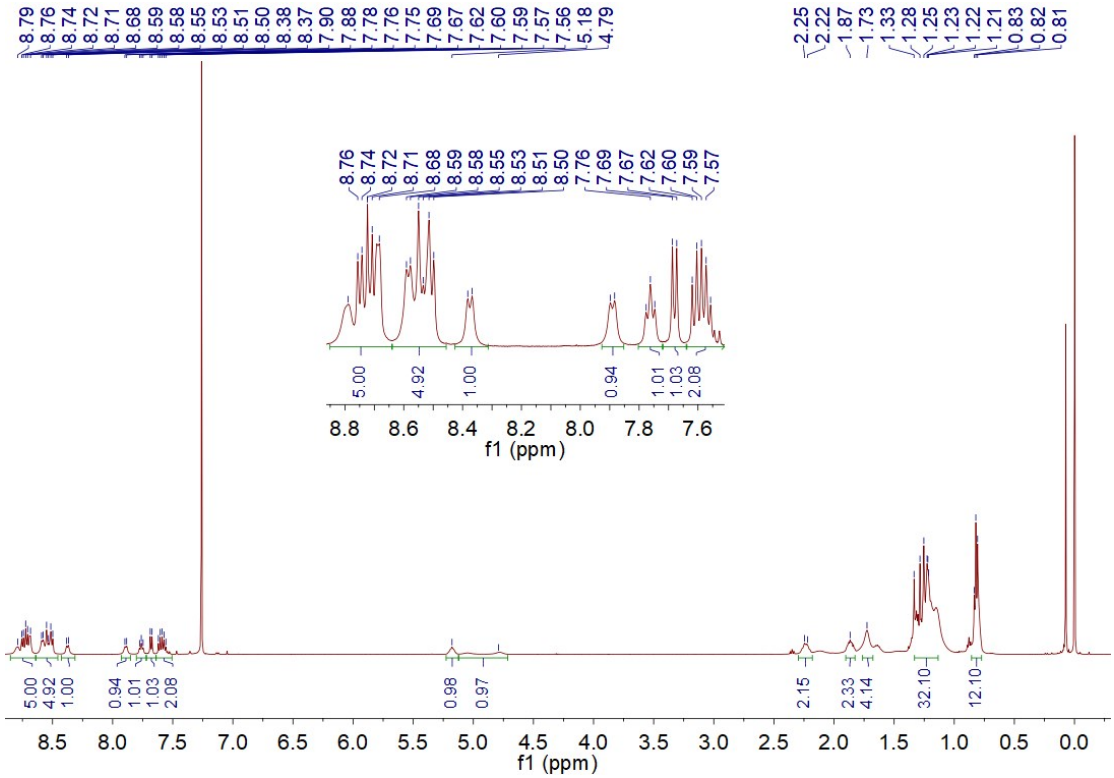


Figure S3 ^{1}H NMR of compound O-PDI-BZAT in $CDCl_3$.

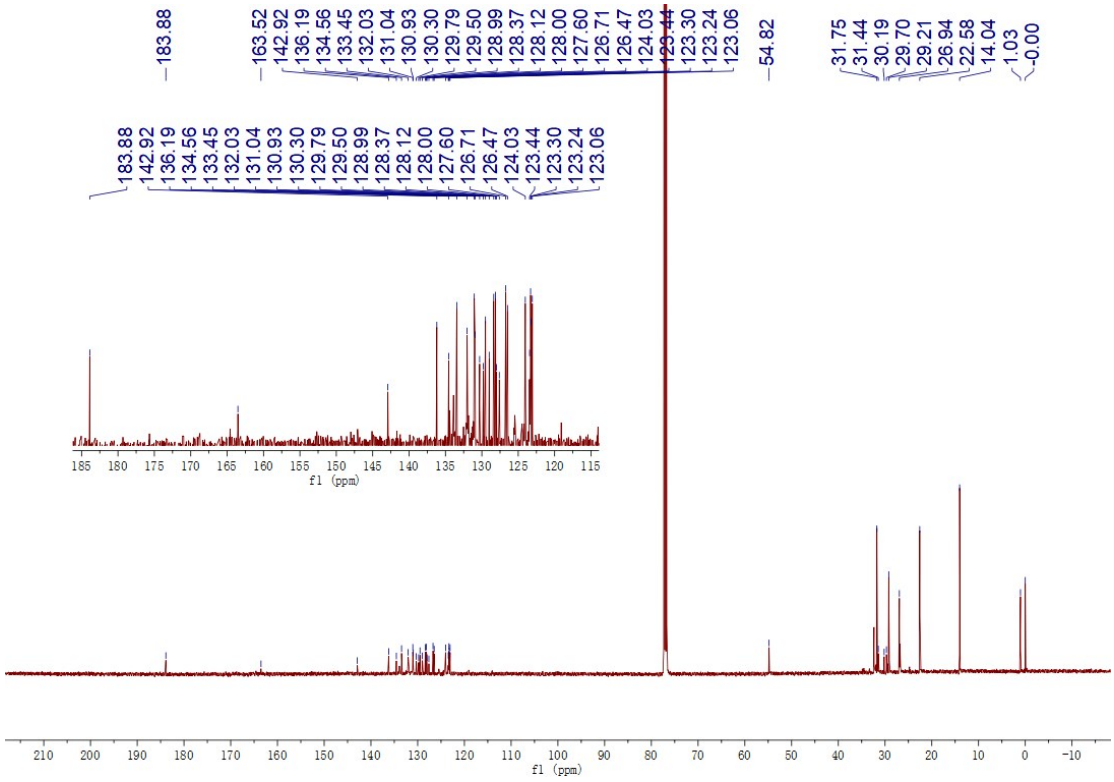


Figure S4 ^{13}C NMR of compound O-PDI-BZAT in $CDCl_3$.

2. Femtosecond and Nanosecond Transient Absorption experiments

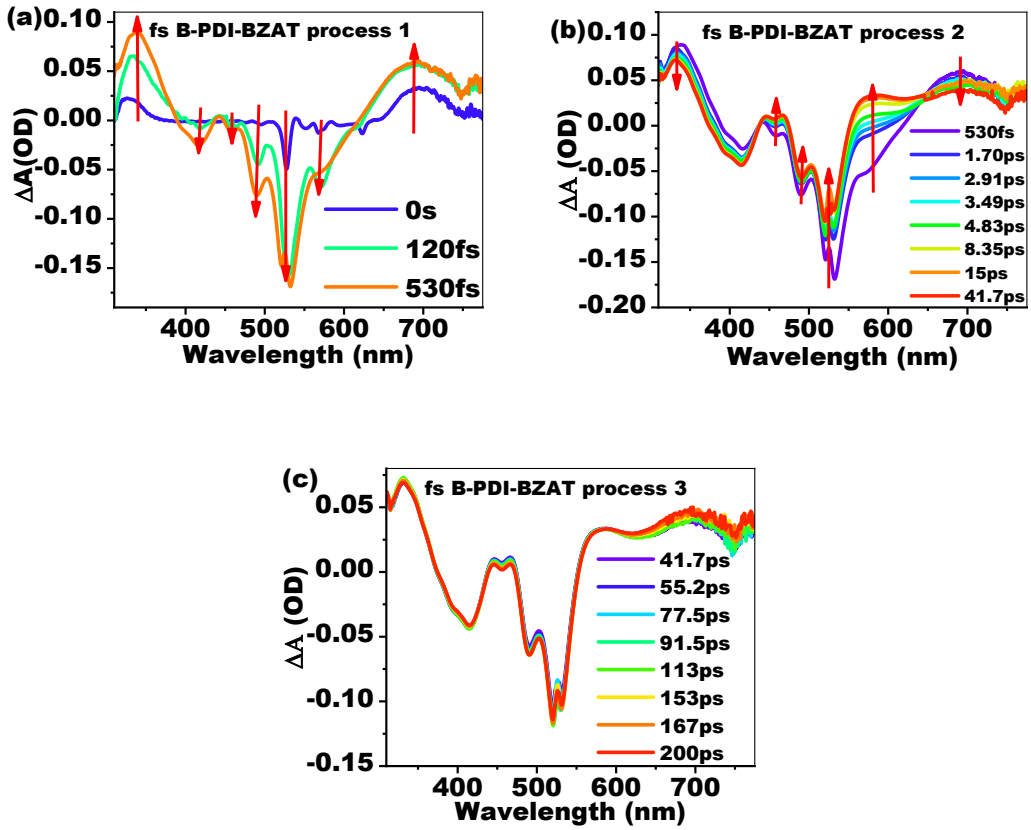


Figure S5 Parts of the fs-TA spectra of B-PDI-BZAT

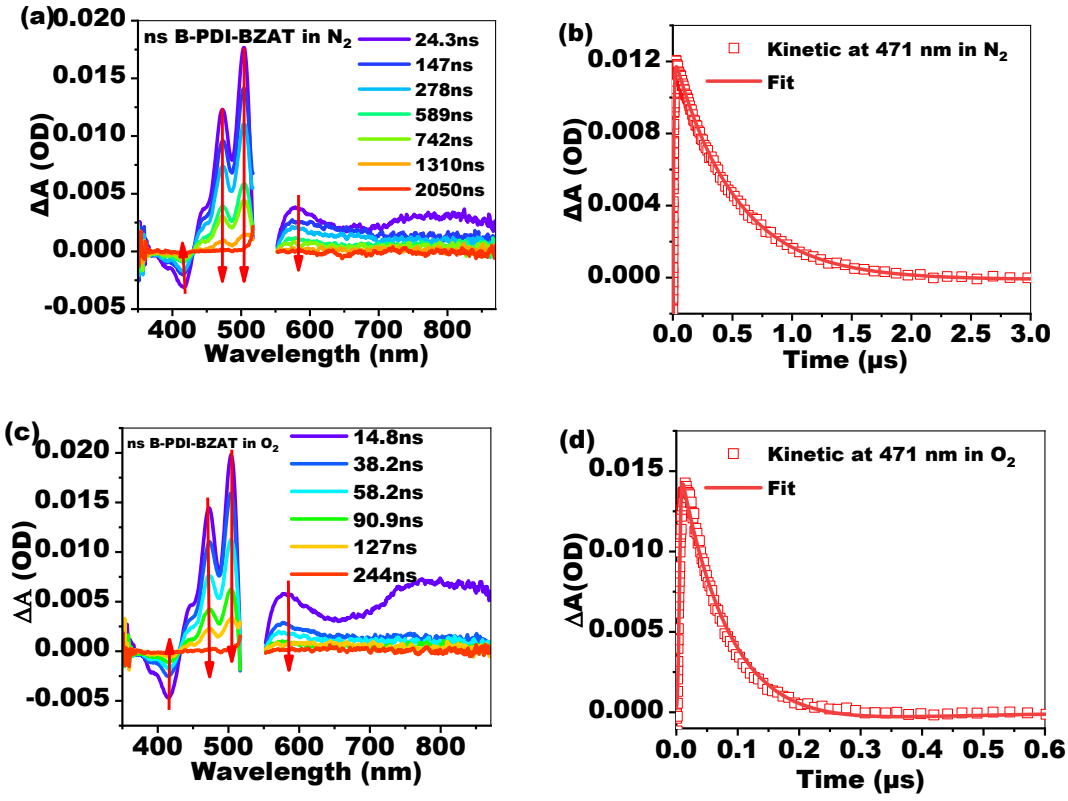


Figure S6 Ns-TA spectra and kinetics of B-PDI-BZAT in THF purged with N_2 or O_2

Table S1 Kinetic fitting decay lifetimes of the corresponding wavelengths for B-PDI-BZAT measured by fs-TA and ns-TA (in N_2 and O_2)

	λ(nm)	A_1	τ_1	A_2	τ_2	A_3	τ_3	A_4	τ_4
Fs	491	0.105	0.437ps	0.0634	3.68ps	0.135	280ps	0.548	7260ps
Ns in N_2	471	0.366	0.511us						
Ns in O_2	471	0.5	0.108us						

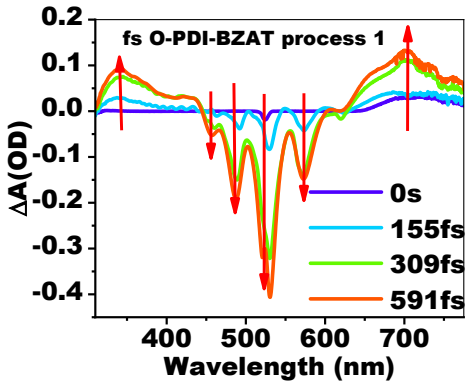


Figure S7 Parts of the fs-TA spectra of O-PDI-BZAT

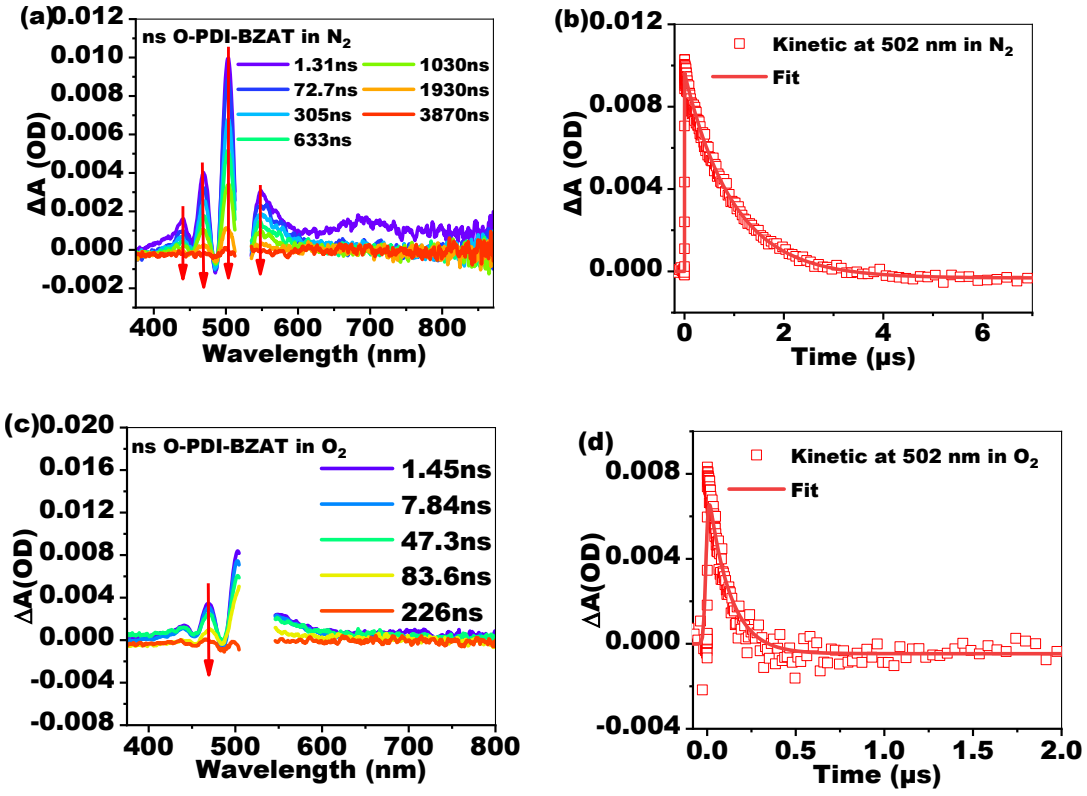


Figure S8 Ns-TA spectra and kinetics of O-PDI-BZAT in THF purged with N_2 or O_2

Table S2 Kinetic fitting decay lifetimes of the corresponding wavelengths for O-PDI-BZAT measured by fs-TA and ns-TA (in N_2 and O_2)

	λ(nm)	A1	τ1	A2	τ2	A3	τ3	A4	τ4
Fs	502	0.125	0.118ps	0.213	3.09ps	0.474	13.4ps	0.0434	147ps
Ns in N_2	502	0.969	0.979us						
Ns in O_2	502	0.949	0.121us						

Figure S6 shows that the signals (471 and 505 nm) generated by ISC are gradually decreased to the baseline from 24.3 ns to 2.05 μs. The kinetic fitting at 471 nm shows that B-PDI-BZAT has a long lifetime of τ_1 = 0.511 μs. When the solution is purged with oxygen, the long-lifetime transient state is significantly quenched by the oxygen and the lifetime drops down to 0.108 μs. This demonstrates that the long-lifetime transient state with main peaks at 471 and 505 nm of B-PDI-BZAT has a triplet-state nature. Similar ns-TA quenching results are also observed for O-PDI-BZAT (Figure S8). The major triplet state located at 469 and 502 nm gradually decay with a lifetime of 0.979 μs in a nitrogen-saturated solution and with a much shorter lifetime of 0.121 μs in an oxygen-saturated solution.

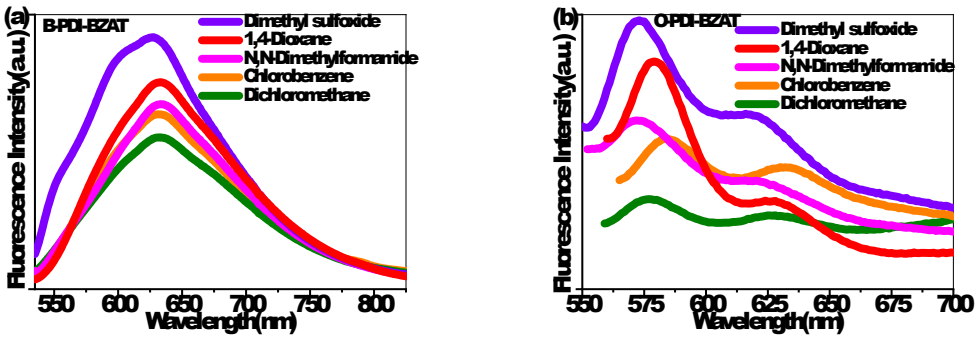


Figure S9 The fluorescence emission behaviors of B-PDI-BZAT (a) and O-PDI-BZAT (b) in five good solvents with different viscosities. The excitation wavelength of fluorescence emission spectra for B-PDI-BZAT and O-PDI-BZAT is 525 nm

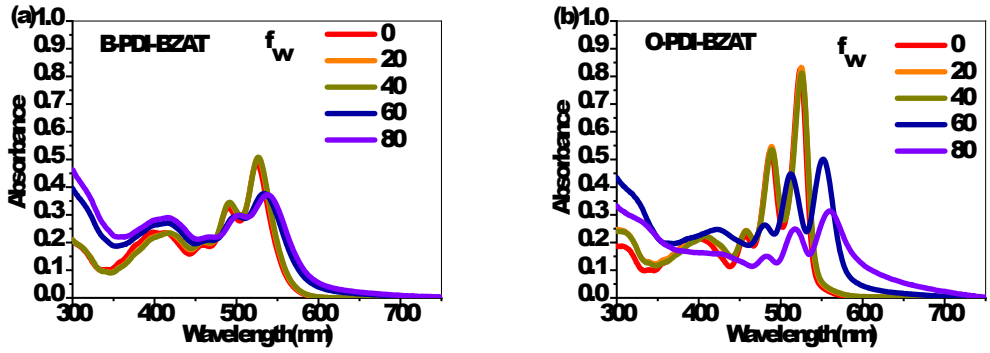


Figure S10 The UV-vis absorption changes of B-PDI-BZAT (a) and O-PDI-BZAT (b) upon the addition of non-solvent water

References

1. (a) Cao, L.; Zhang, D.; Xu, L.; Fang, Z.; Jiang, X.-F.; Lu, F., Perylenediimide–Benzanthrone Dyad: Organic Chromophores with Enhanced Third-Order Nonlinear-Optical Activities. *European Journal of Organic Chemistry* **2017,** *2017* (17), 2495-2500; (b) Holman, M. W.; Liu, R.; Adams, D. M., Single-Molecule Spectroscopy of Interfacial Electron Transfer. *Journal of the American Chemical Society* **2003,** *125* (41), 12649-12654; (c) Davis, N. J. L. K.; MacQueen, R. W.; Roberts, D. A.; Danos, A.; Dehn, S.; Perrier, S.; Schmidt, T. W., Energy transfer in pendant perylene diimide copolymers. *Journal of Materials Chemistry C* **2016,** *4* (35), 8270-8275; (d) Horinouchi, H.; Sakai, H.; Araki, Y.; Sakanoue, T.; Takenobu, T.; Wada, T.; Tkachenko, N. V.; Hasobe, T., Controllable Electronic Structures and Photoinduced Processes of Bay-Linked Perylenediimide Dimers and a Ferrocene-Linked Triad. *Chemistry – A European Journal* **2016,** *22* (28), 9631-9641; (e) Teraoka, T.; Hiroto, S.; Shinokubo, H., Iridium-Catalyzed Direct Tetraborylation of Perylene Bisimides. *Organic Letters* **2011,** *13* (10), 2532-2535; (f) Han, H.; Ma, L.-K.; Zhang, L.; Guo, Y.; Li, Y.; Yu, H.; Ma, W.; Yan, H.; Zhao, D., Tweaking the Molecular Geometry of a Tetraperylenediimide Acceptor. *ACS Applied Materials & Interfaces* **2019,** *11* (7), 6970-6977.