Aggregation effect on the one- and two-photon excited fluorescence performance of regioisomeric anthraquinone-substituted perylenediimide

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1. Experimental Section

1.1 Equipment and measurement conditions

Synthesis and characterization of the PDI derivatives. The PDI derivatives were synthesized using Suzuki-coupling protocols as detailed in Supplementary Information. Chemical structures were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy using a Brucker-Biosipin Avance 400 MHz spectrometer in $CDCl_3$ at room temperature.

UV-Vis absorption and fluorescence emission spectroscopy. UV-Vis absorption spectra and fluorescence emission spectra were determined with a Shimadzu UV-Vis-2600 spectrophotometer and a Shimadzu RF-6000 spectrophotometer.

Transient absorption spectroscopy. The fs-TA measurements were performed based on a femtosecond Ti: sapphire regenerative amplified Ti: sapphire laser system (Coherent, Astrella) and an automated data acquisition system (Ultra-fast Systems, HeliosFire). The half pulse width of output from amplifier is 80 fs. The probe pulse was obtained by using approximately 1 W of the amplified 800 nm output from the Spitfire to generate a white-light continuum (320-780 nm) in a sapphire plate or CaF_2 crystal. The maximum extent of the temporal delay was 8000 ps. The instrument response function was determined to be 200 fs. At each temporal delay, data were averaged for 2 s and collected by the acquisition system. The probe beam was split into two before passing through the sample. One probe beam traveled through the sample, the other was sent directly to the reference spectrometer that monitored the fluctuations in the probe beam intensity. Fiber optics was coupled to a multichannel spectrometer with a CMOS sensor that had a 1.5 nm intrinsic resolution. For the experiments described in this study, the sample solution was excited by a 525 nm pump beam which is obtained by using femtosecond TOPAS amplifier. The solutions were excited in a 2 mm path-length cuvette with a sample concentration of 0.2 mM throughout the data acquisition. The data were stored as three-

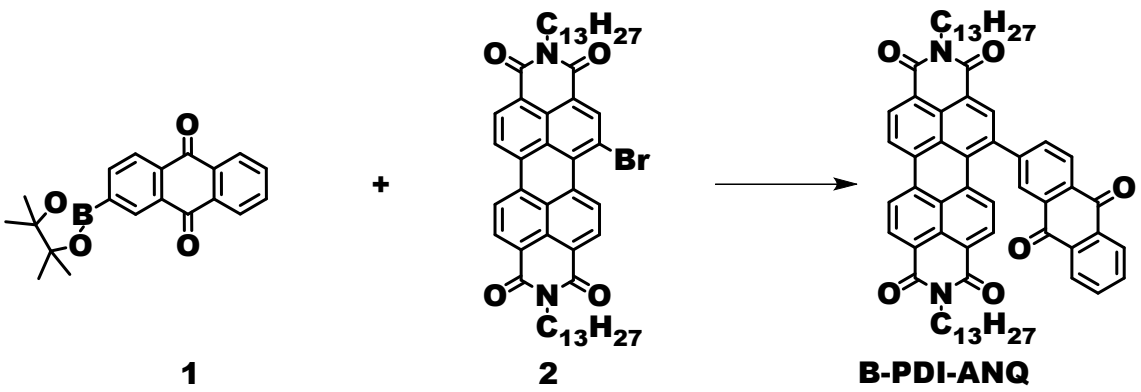
dimensional (3D) wavelength-time-absorbance matrices that were exported for use with the fitting software. Therefore, in order to remove the contributions of the solvent, the raw spectra of the sample were subtracted by the spectra of the solvent under the same conditions.

Kinetics fitting method. Equation 1 shows the exponential function for wavelength kinetics fitting. The wavelength kinetics fitting for B-PDI-ANQ and O-PDI-ANQ are fitted by

$$S(t) = e^{-(\frac{t-t_0}{t_p})^2} * \sum_i A_i e^{-\frac{t-t_0}{t_i}}, \quad t_p = \frac{IRF}{2\ln 2} \qquad \text{Equation 1}$$

Two-photon excited fluorescence spectroscopy. A homemade spectrofluorometer was used with a femtosecond pulsed laser (Chameleon Discovery NX, Coherent), with pulse duration, ≈140 fs (FWHM), 80 MHz repetition rate, 800 nm excitation source. 2PA measurements were performed in 10 mm spectrofluorometric quartz cuvettes with the dye concentrations of 5×10^{-5} M. Possible reabsorption of fluorescence emission was analyzed and taken into account. The quadratic dependence of two-photon induced fluorescence intensity on the excitation power was checked for the excitation wavelength. The reference is Rhodamine B with a concentration of 5×10^{-5} M solution in spectroscopic grade methanol. The samples are measured in spectroscopic grade THF. In the excitation wavelength of 800 nm, linear absorption could be neglected for all of the solutions.

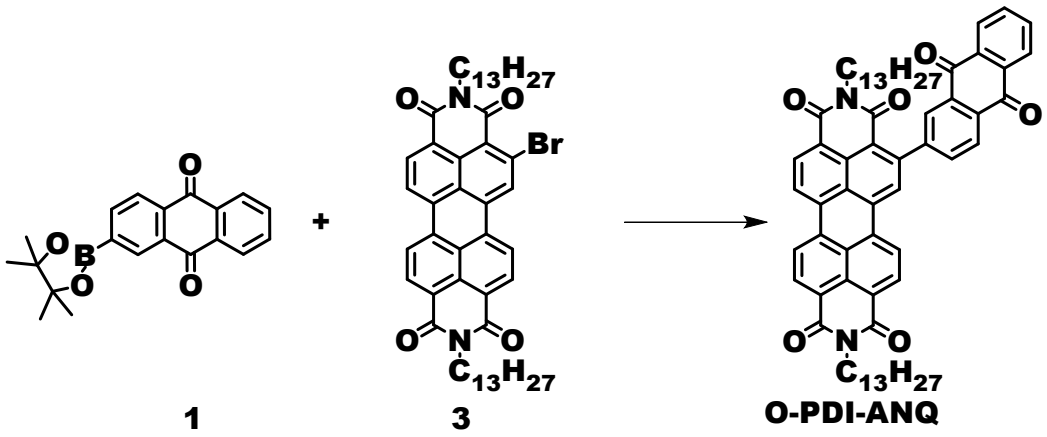
1.2 Synthesis of B-PDI-ANQ



Scheme S1. The synthetic route to B-PDI-ANQ.

Compounds **1** and **2** were synthesized according to the literature.[1] A mixture of **1** (192 mg, 0.57 mmol), **2** (400 mg, 0.48 mmol), $Pd(PPh_3)_4$ (55 mg, 0.047 mmol), K_2CO_3 (132 mg, 0.96 mmol), DMF (10 mL) was stirred at 80 °C under N_2 atmosphere for 24h. After cooling to room temperature, the solvent was removed under reduced pressure. Then the collected solid was redissolved in dichloromethane (100 mL) and washed with brine (100 mL) twice. The organic layer was dried over Na_2SO_4 and concentrated by the rotary evaporator in vacuum. The crude product was further purified by column chromatography (DCM/petroleum ether=16:1 to 4:1) to give the desired product as the dark purple solid (345 mg, 0.36 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.67 (m, 4H), 8.61-8.58 (d, 1H), 8.49-8.47 (d, 2H), 8.41-8.38 (d, 1H), 8.34-8.32 (d, 1H), 8.11-8.07 (m, 1H), 7.98-7.95 (d, 1H), 7.88-7.84 (m, 2H), 7.79-7.77 (d, 1H), 5.20-5.17 (m, 2H), 2.27-2.18 (m, 4H), 1.85-1.80 (m, 4H), 1.33-1.23 (m, 32H), 0.84-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.96, 182.87, 149.20, 140.46, 139.65, 135.62, 134.95, 134.85, 134.60, 133.98, 133.49, 130.76, 129.81, 129.32, 128.51, 128.01, 127.92, 124.24, 123.54, 55.35, 55.19, 32.82, 32.21, 32.17, 30.14, 29.67, 29.64, 27.36, 25.38, 23.04, 14.49.

1.3 Synthesis of O-PDI-ANQ



Scheme S2. The synthetic route to O-PDI-ANQ.

Compound **3** were synthesized according to the literature.[2] A mixture of **3** (200 mg, 0.24 mmol), **1** (160 mg, 0.48 mmol), $Pd(PPh_3)_4$ (30 mg, 0.025 mmol), K_2CO_3 (66 mg, 0.48 mmol), DMF (30 mL) was stirred at 80 °C under N_2 atmosphere for 24h. After cooling, remove DMF with rotary evaporator. Then the collected solid was redissolved in dichloromethane (100 mL) and washed with brine (100 mL) twice. The organic layer was dried over Na_2SO_4 and concentrated by the rotary evaporator in vacuum. The residue was then purified by silica gel column chromatography (DCM/petroleum ether=16:1 to 4:1). A dark red solid of O-PDI-ANQ (70 mg, 0.07 mmol) was obtained in 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.58 (m, 6H), 8.34-8.25 (m, 3H), 8.07 (s, 2H), 7.78-7.76 (d, 1H), 7.64 (s, 2H), 5.22-4.93 (m, 2H), 2.27-2.07 (m, 4H), 1.88-1.67 (m, 4H), 1.33-1.23 (m, 32H), 0.84-0.80 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.39, 134.23, 133.89, 133.78, 133.49, 133.26, 132.36, 131.74, 130.35, 129.42, 127.02, 126.92, 126.68, 126.32, 126.19, 123.69, 123.19, 54.81, 32.40, 32.21, 31.77, 29.18, 29.18, 26.95, 26.93, 22.59.

2. Characterization Section

2.1 ^{1}H and ^{13}C NMR

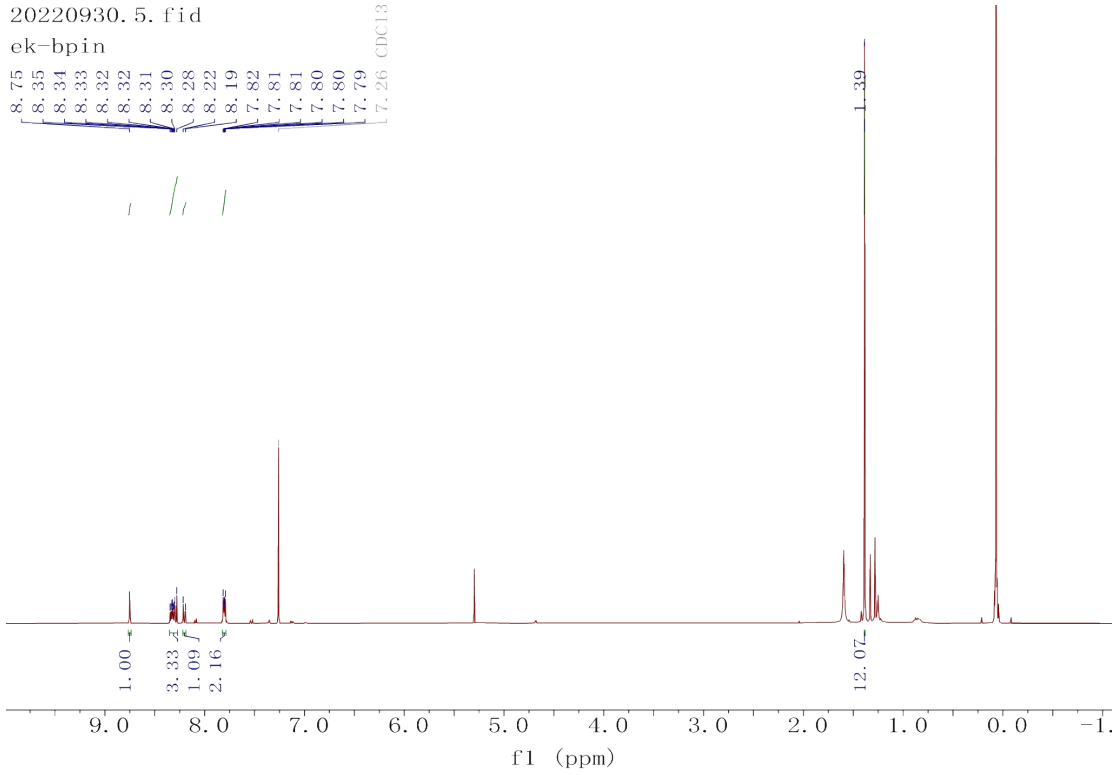


Figure S1-1. ^{1}H NMR of compound **1** in $CDCl_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.35-8.28 (m, 3H), 8.22-8.19 (d, 1H), 7.82-7.79 (m, 2H), 1.39 (s, 12H).

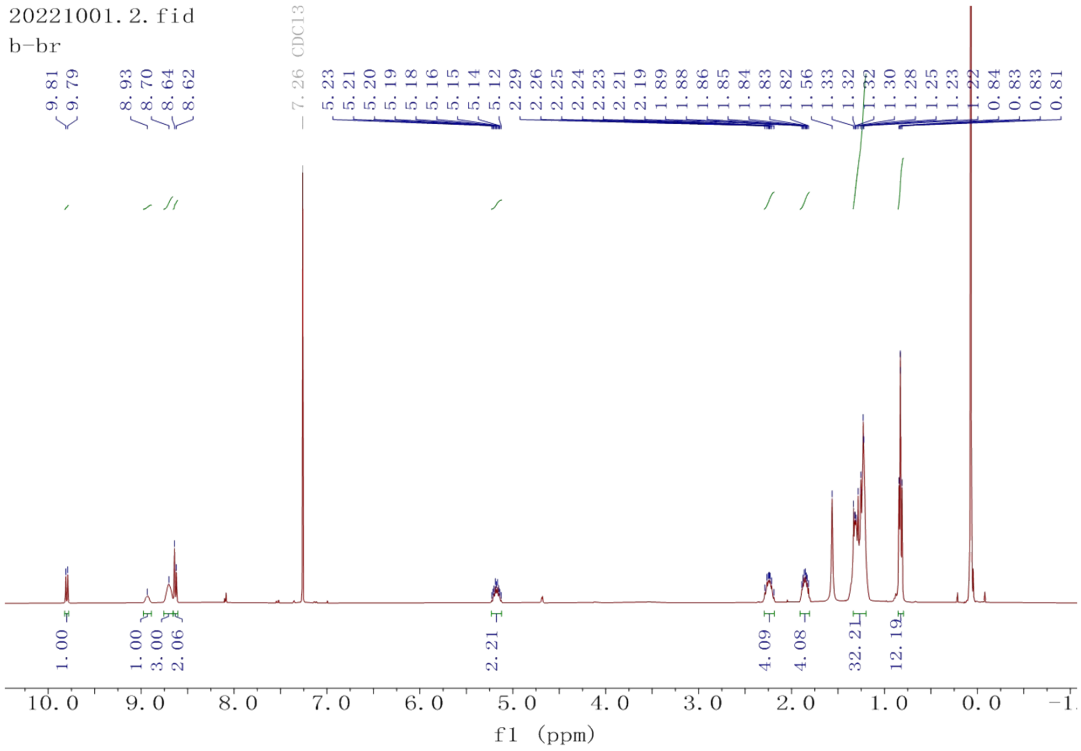


Figure S1-2. ^{1}H NMR of compound **2** in $CDCl_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81-9.79 (d, 1H), 8.93 (s, 1H), 8.70 (s, 3H), 8.64-8.62 (d, 2H), 5.23-5.12 (m, 2H), 2.29-2.19 (m, 4H), 1.89-1.82 (m, 4H), 1.33-1.22 (m, 32H), 0.84-0.81 (t, 12H).

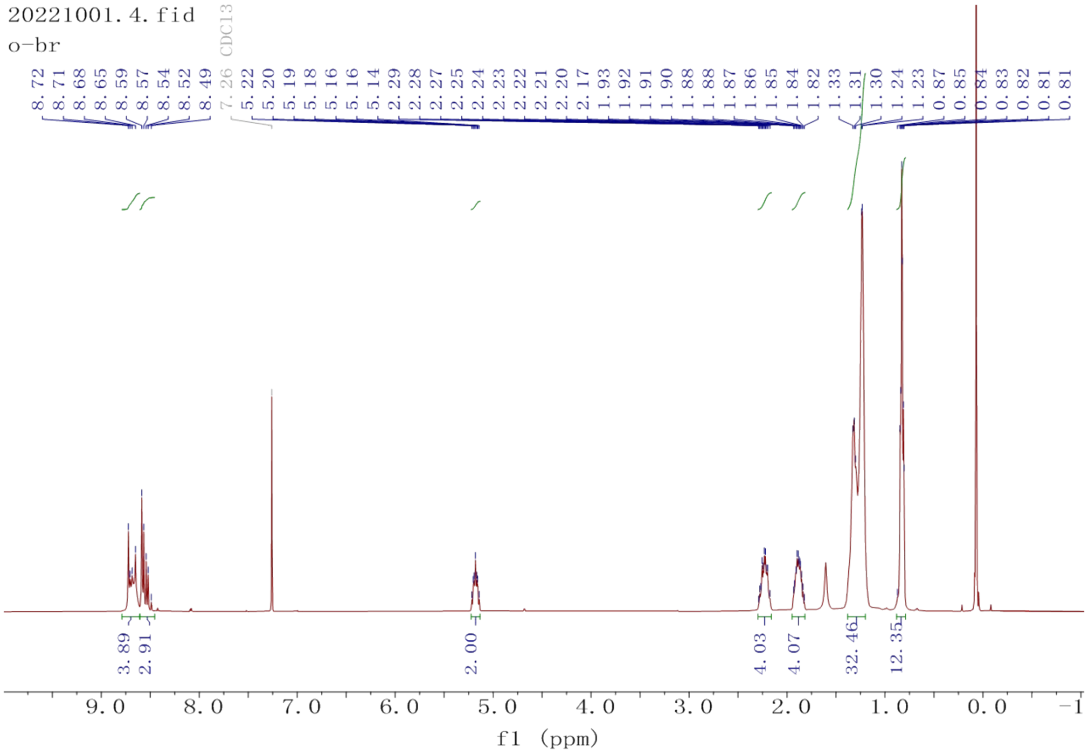


Figure S1-3. ^{1}H NMR of compound **3** in $CDCl_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.65 (m, 4H), 8.59-8.49 (m, 3H), 5.22-5.14 (m, 2H), 2.29-2.17 (m, 4H), 1.93-1.82 (m, 4H), 1.33-1.23 (m, 32H), 0.87-0.81 (m, 12H).

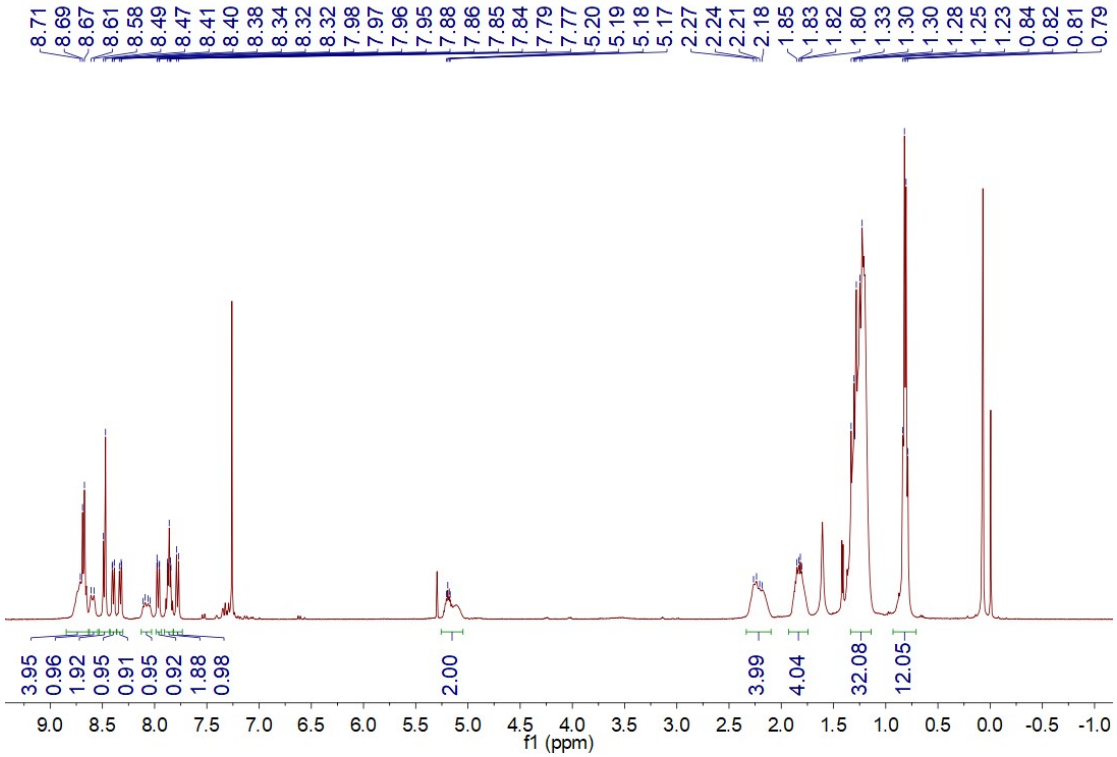


Figure S2. ^{1}H NMR of compound B-PDI-ANQ in $CDCl_3$

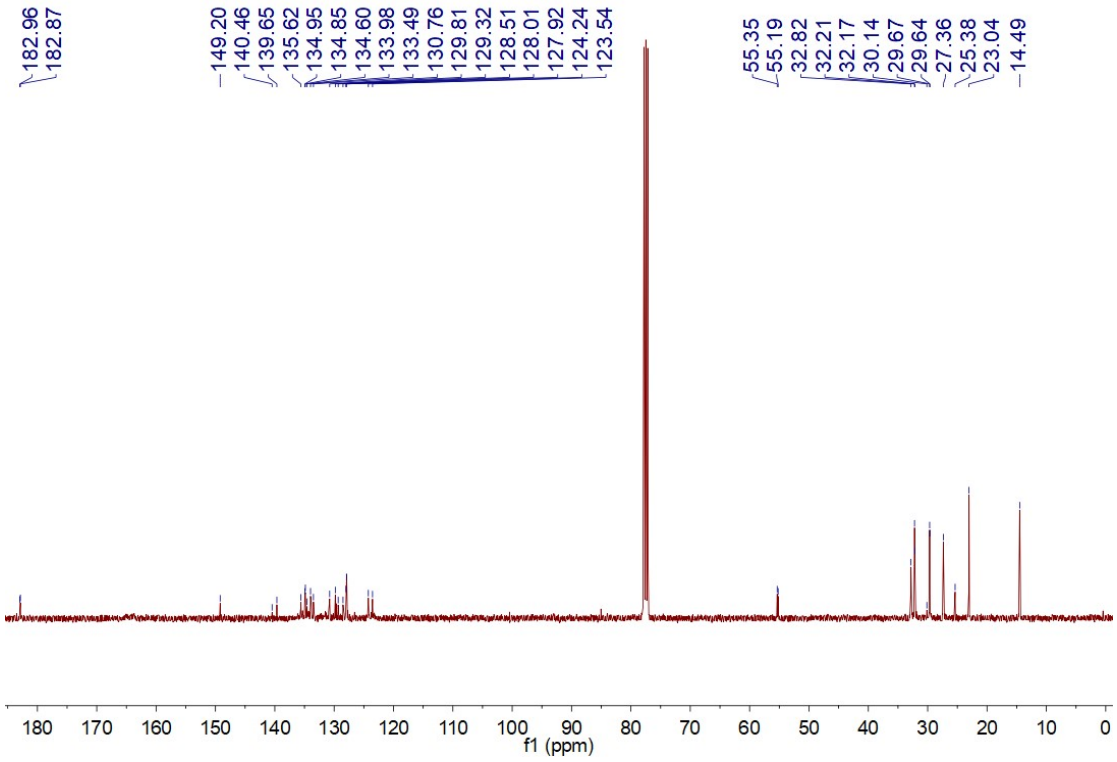


Figure S3. ^{13}C NMR of compound B-PDI-ANQ in $CDCl_3$.

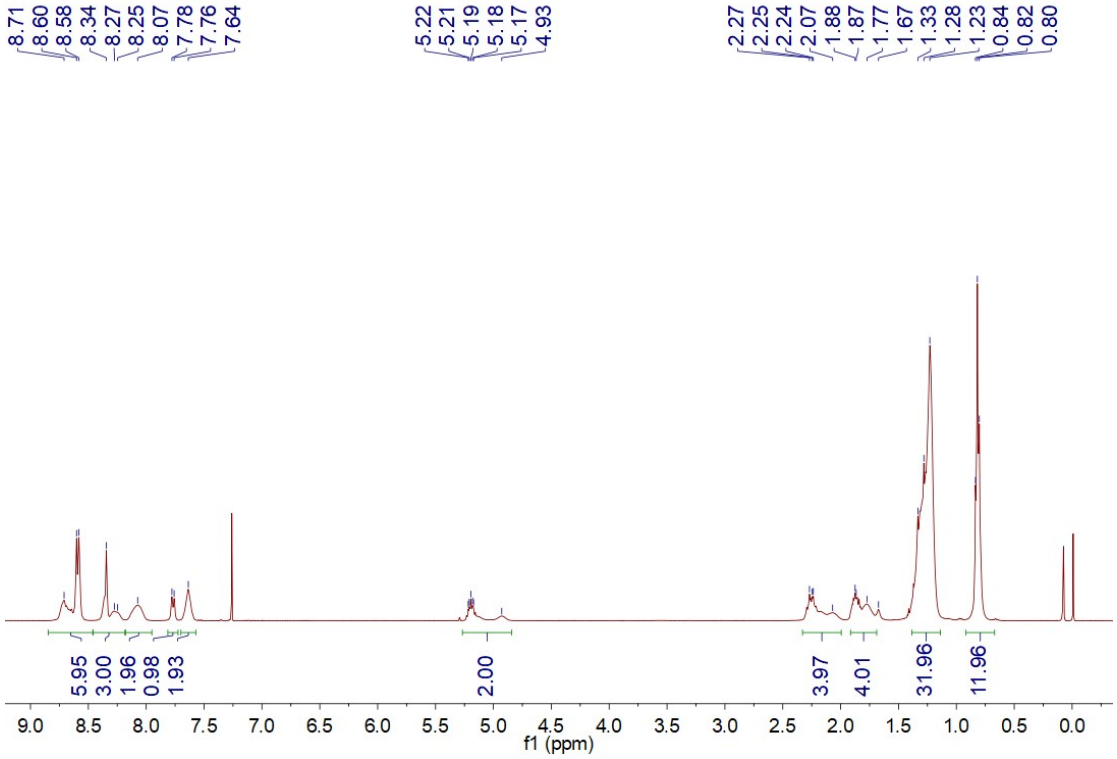


Figure S4a. ^{1}H NMR of compound O-PDI-ANQ in $CDCl_3$.

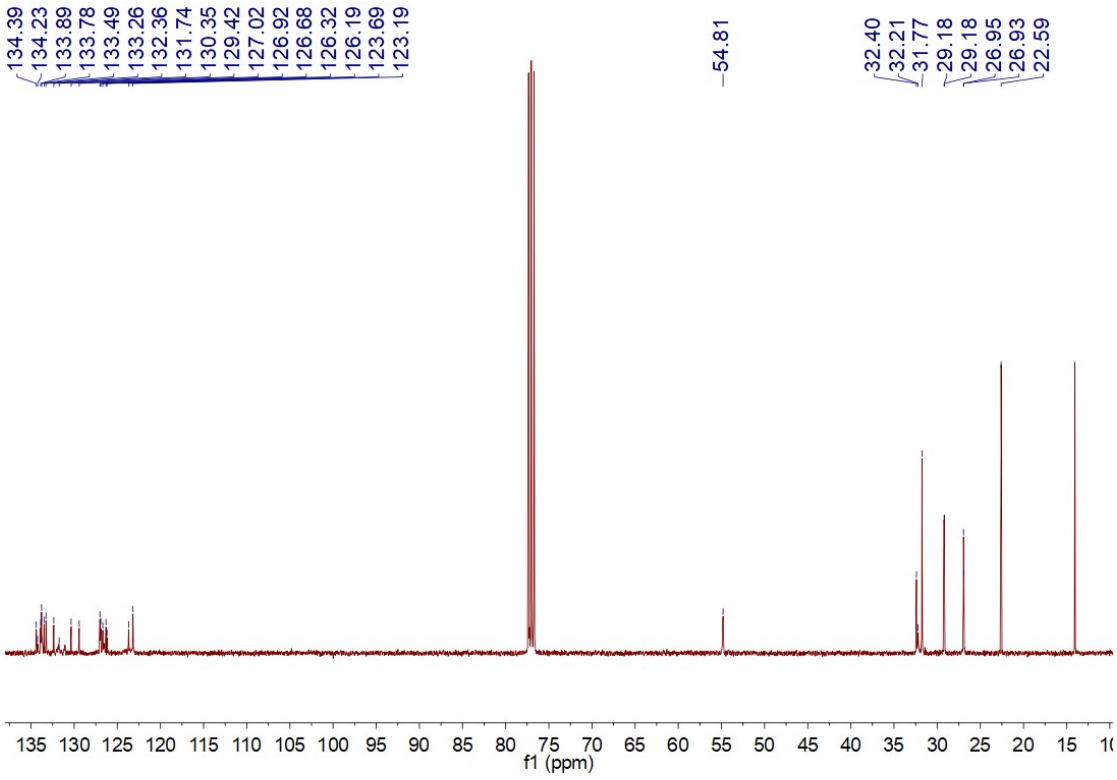


Figure S4b. ^{13}C NMR of compound O-PDI-ANQ in $CDCl_3$.

2.2 The optimized S_0 and S_1 of B-PDI-ANQ and O-PDI-ANQ

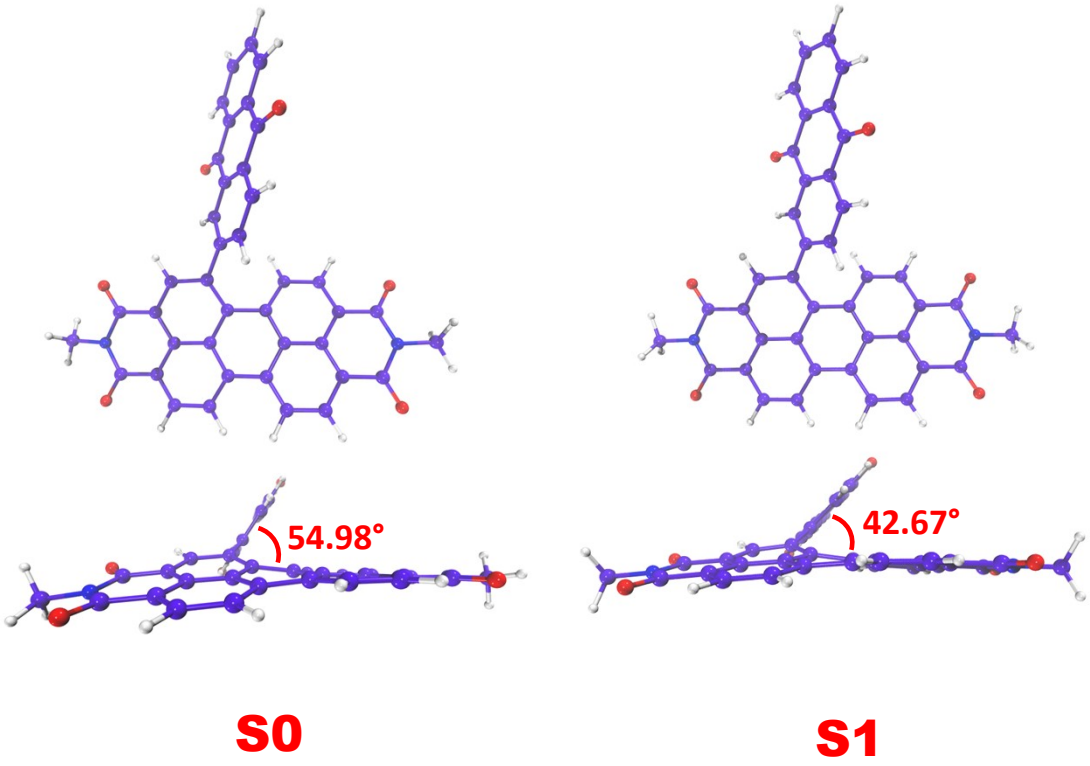


Figure S5. The optimized S_0 and S_1 of B-PDI-ANQ in vacuum.

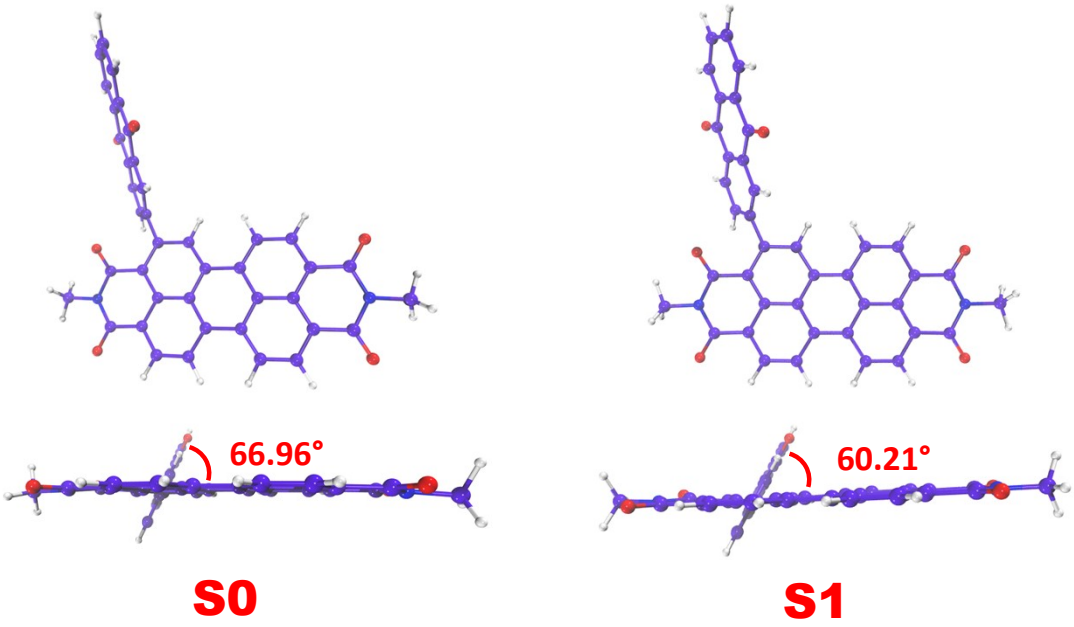


Figure S6. The optimized S_0 and S_1 of O-PDI-ANQ in vacuum.

2.3 The optimized XYZ coordinates

S_0 of B-PDI-ANQ

C	-4.99408	0.28042	-0.03649
N	-5.63792	-0.95255	0.1353
C	-4.96566	-2.12082	0.49494
C	5.09764	-2.04989	0.47018
N	5.74046	-0.97232	-0.13908
C	5.05573	0.11663	-0.6987
O	-5.56221	-3.14766	0.76439
O	-5.62775	1.30004	-0.23969
O	5.71751	-3.00512	0.90244
O	5.65088	1.00263	-1.28499
C	7.2246	-0.94945	-0.29437
C	-7.12208	-0.93144	-0.02396
C	-7.6906	-2.1235	-0.79996
C	-7.83774	-0.63484	1.30135
C	8.00295	-1.32002	0.97121
C	7.67471	-1.68759	-1.5637
C	-3.48155	-2.07779	0.52302
C	-3.51274	0.29724	0.0228
C	-2.78394	-0.88128	0.26791
C	-2.78222	-3.22465	0.81306
C	-1.38511	-3.19887	0.86297
C	-0.66468	-2.04184	0.6146
C	-1.36828	-0.84743	0.27412
C	-0.68598	0.37641	-0.02228
C	-1.43704	1.55481	-0.11267
C	-2.84647	1.48526	-0.12112
C	3.61681	-2.00051	0.57182
C	3.58174	0.15467	-0.552
C	2.89054	-0.89847	0.07864
C	1.47799	-0.86288	0.18776
C	0.80196	-2.0084	0.69349
C	1.5497	-3.06531	1.18632
C	2.94813	-3.05855	1.14096
C	2.87595	1.20961	-1.07679
C	1.4855	1.27945	-0.92267
C	0.77229	0.29858	-0.25052
C	-7.03485	-2.36011	-2.15908
C	-7.77381	-1.69041	2.40464
C	-8.59849	-1.28633	3.62655
C	-7.7216	-3.46812	-2.95582
C	-8.54785	-2.31259	4.7562
C	-9.37911	-1.91658	5.97527
C	-7.06245	-3.74397	-4.30549

C	-7.74379	-4.85905	-5.09671
C	-9.32191	-2.94834	7.0982
C	-7.07535	-5.13315	-6.44108
C	7.48147	-3.20247	-1.62642
C	7.60787	-0.50825	2.20332
C	8.04988	-3.79843	-2.91389
C	8.53471	-0.75389	3.39259
C	8.15209	0.04707	4.63515
C	7.84737	-5.30856	-3.01788
C	8.41093	-5.91269	-4.3026
C	9.08769	-0.18604	5.81987
C	8.70023	0.6216	7.05483
C	8.19965	-7.42128	-4.39542
H	7.42376	0.10559	-0.48261
H	-7.27816	-0.04954	-0.64631
H	-8.75189	-1.88924	-0.95685
H	-7.6488	-3.03798	-0.20895
H	-8.89029	-0.44754	1.04977
H	-7.44861	0.31692	1.68275
H	9.05557	-1.11334	0.73588
H	7.92616	-2.38471	1.19026
H	8.74143	-1.46023	-1.69221
H	7.16602	-1.22079	-2.41624
H	-3.33252	-4.13783	1.00817
H	-0.86614	-4.12058	1.09453
H	-3.42924	2.39293	-0.23173
H	1.05662	-3.92989	1.61327
H	3.52329	-3.89336	1.52448
H	3.4148	1.99122	-1.59988
H	0.97062	2.12757	-1.34888
H	-5.98005	-2.62715	-2.02129
H	-7.04408	-1.42936	-2.74306
H	-6.73445	-1.85675	2.70821
H	-8.13115	-2.65522	2.02739
H	-9.64401	-1.13055	3.32547
H	-8.24503	-0.31563	4.00187
H	-8.77634	-3.20399	-3.11383
H	-7.72512	-4.3901	-2.35894
H	-7.50367	-2.46454	5.06315
H	-8.89631	-3.28444	4.37993
H	-10.42231	-1.76626	5.66765
H	-9.03069	-0.94543	6.35079
H	-6.00702	-4.00598	-4.14727
H	-7.05935	-2.82349	-4.90557

H	-8.79763	-4.59654	-5.25725
H	-7.74811	-5.77718	-4.49497
H	-9.92571	-2.64099	7.95799
H	-8.29376	-3.09407	7.44797
H	-9.69523	-3.92107	6.75902
H	-7.58243	-5.93576	-6.98576
H	-6.02907	-5.43011	-6.308
H	-7.08613	-4.24074	-7.07653
H	6.41696	-3.45022	-1.5567
H	7.95505	-3.68136	-0.76223
H	6.58013	-0.75608	2.49593
H	7.60979	0.56262	1.95644
H	9.12282	-3.57045	-2.98052
H	7.58302	-3.30936	-3.78029
H	9.5661	-0.50625	3.10597
H	8.53541	-1.82508	3.63541
H	7.1244	-0.20664	4.9298
H	8.14091	1.11789	4.38854
H	6.77446	-5.53618	-2.95134
H	8.3137	-5.79825	-2.15199
H	9.48334	-5.68731	-4.36821
H	7.94455	-5.42281	-5.16722
H	10.11413	0.06592	5.52396
H	9.09727	-1.25525	6.06795
H	9.38625	0.4367	7.88713
H	7.69018	0.36588	7.3925
H	8.71434	1.6964	6.84355
H	8.61172	-7.82901	-5.32381
H	7.13366	-7.67274	-4.36519
H	8.68366	-7.93927	-3.56021
C	-0.86769	2.93281	-0.10715
C	-1.22065	3.85913	-1.08499
C	-0.04065	3.34749	0.94699
C	-0.74404	5.16718	-1.03095
H	-1.86414	3.58276	-1.91384
C	0.43271	4.64548	1.00804
H	0.22616	2.63717	1.72269
C	-1.1396	6.12161	-2.10632
C	0.08843	5.56521	0.01859
H	1.07091	4.97616	1.81969
C	-0.62304	7.51442	-2.01389
C	0.6107	6.95688	0.10848
C	-0.98036	8.43218	-2.99858
C	0.21094	7.91164	-0.96078

C	-0.5113	9.73633	-2.93522
H	-1.62684	8.0996	-3.80276
C	0.67893	9.22191	-0.90372
C	0.31885	10.13114	-1.88787
H	-0.7919	10.44987	-3.7034
H	1.32304	9.5031	-0.07824
H	0.68465	11.15188	-1.84106
O	1.33644	7.29721	1.02606
O	-1.8574	5.76946	-3.02538

S_1 of B-PDI-ANQ

C	-0.73658700	5.02492700	-0.19409400
N	-1.90123200	5.78864900	-0.09901500
C	-3.18187700	5.27019900	0.07440700
C	-4.22483900	-4.69039900	0.05622800
N	-3.13831900	-5.44018100	-0.38586400
C	-1.89686200	-4.91220300	-0.74656500
O	-4.14223700	6.01640600	0.16417300
O	0.35829400	5.54617200	-0.32357600
O	-5.27489900	-5.23836800	0.34860400
O	-0.99026800	-5.62782900	-1.13929800
C	-3.34127100	-6.88349700	-0.47683500
C	-1.79408100	7.24364300	-0.16341400
C	-3.31163800	3.80181600	0.14155000
C	-0.90490400	3.55986300	-0.13225600
C	-2.18443200	2.98119400	0.03194400
C	-4.57924300	3.23820200	0.30968500
C	-4.72459800	1.87123500	0.36406200
C	-3.61286800	1.00295200	0.24375300
C	-2.31733000	1.56323800	0.06824600
C	-1.16188200	0.74353000	-0.08437200
C	0.13927200	1.37070000	-0.04537100
C	0.22200500	2.75951900	-0.14417500
C	-4.04252000	-3.22937500	0.14389600
C	-1.74117200	-3.45081200	-0.62224100
C	-2.80851800	-2.64256100	-0.17824000
C	-2.64008900	-1.23141900	-0.06815800
C	-3.75614600	-0.42925700	0.28206300
C	-4.97910500	-1.06383400	0.60796300
C	-5.11395700	-2.43380100	0.55099100
C	-0.53579200	-2.86417300	-0.99510500
C	-0.34678300	-1.50355700	-0.85954100

C	-1.36078200	-0.65890100	-0.32598200
H	-2.42151400	-7.32336000	-0.85327300
H	-0.75054200	7.49041300	-0.34092900
H	-5.43144800	3.90328100	0.38707900
H	-5.71890200	1.45785200	0.47341000
H	1.18706100	3.25324700	-0.14699900
H	-5.82791800	-0.46959000	0.92130500
H	-6.04773100	-2.92162000	0.80577200
H	0.24318000	-3.50016100	-1.39941600
H	0.57761900	-1.06886200	-1.21009500
C	1.38132500	0.64552400	0.25364300
C	2.58410100	0.99101600	-0.37645800
C	1.40978700	-0.37444900	1.22809600
C	3.76699400	0.33789200	-0.06429500
H	2.61422400	1.75572200	-1.14486500
C	2.59229900	-1.01386200	1.55367100
H	0.49781700	-0.63319400	1.75384300
C	5.01244500	0.72605900	-0.78775400
C	3.77863500	-0.67175100	0.90964700
H	2.62252400	-1.78737300	2.31282800
C	6.26711200	0.01550000	-0.42202300
C	5.03377400	-1.38146200	1.27345600
C	7.44894300	0.35986300	-1.07372800
C	6.27728600	-0.98653800	0.55774700
C	8.63286500	-0.28807800	-0.75272600
H	7.41350800	1.13825000	-1.82763000
C	7.46952900	-1.63307900	0.87449000
C	8.64302800	-1.28485000	0.22160700
H	9.55244200	-0.01766500	-1.26186100
H	7.44998800	-2.40494800	1.63561900
H	9.57061000	-1.79044500	0.47057200
O	5.03916000	-2.25261900	2.12634900
O	4.99639300	1.59143500	-1.64489700
H	-2.13617400	7.68410800	0.77562300
H	-2.42415500	7.62275300	-0.96973600
H	-3.58412700	-7.28606100	0.50834700
H	-4.17392800	-7.09729800	-1.14917700

S_0 of O-PDI-ANQ

C	-5.93540500	-0.26702500	-0.12079100
N	-6.59936500	-1.47415000	-0.33630200
C	-5.93985100	-2.66359400	-0.67692800

C	4.13645700	-2.75238900	-0.54821200
N	4.81075600	-1.57773400	-0.23624900
C	4.16803200	-0.34224000	-0.06569200
O	-6.56275400	-3.67558300	-0.94371300
O	-6.54025800	0.77176800	0.07460400
O	4.72605100	-3.79280300	-0.78095100
O	4.82513800	0.67783900	0.03202400
C	6.30117000	-1.54736800	-0.15053200
C	-4.45791900	-2.65330800	-0.68617400
C	-4.45039700	-0.28980700	-0.12249400
C	-3.74053900	-1.47555100	-0.39750600
C	-3.77789400	-3.81304700	-0.97034800
C	-2.37870600	-3.82978000	-0.96521800
C	-1.63474200	-2.69684400	-0.67882100
C	-2.32278800	-1.48231700	-0.38882000
C	-1.62805500	-0.27375300	-0.09153000
C	-2.36333200	0.87271600	0.15935100
C	-3.76260700	0.86948400	0.14391000
C	2.65622900	-2.69236500	-0.58831400
C	2.68112800	-0.32253600	-0.00069100
C	1.95470000	-1.49905700	-0.31205900
C	0.53559900	-1.50170400	-0.34505200
C	-0.16190900	-2.70539800	-0.66073200
C	0.57200900	-3.84666600	-0.93273100
C	1.96828400	-3.84189700	-0.89550900
C	1.99173200	0.84233500	0.30646700
C	0.58431800	0.82868200	0.26233300
C	-0.15589300	-0.29097700	-0.05824800
H	-4.34494300	-4.70960900	-1.19308400
H	-1.88476500	-4.76611300	-1.19137600
H	-1.86326500	1.80828800	0.37514200
H	-4.32402200	1.77491700	0.34349400
H	0.07368300	-4.77578900	-1.17776100
H	2.53529300	-4.74206900	-1.10256300
H	0.08569200	1.75609700	0.51264000
C	2.61441100	2.13096300	0.72740600
C	3.27883400	2.24124900	1.95454400
C	2.43893000	3.26932400	-0.04997200
C	3.76948200	3.46079400	2.38246500
H	3.41181400	1.35754000	2.57039600
C	2.94184000	4.49900800	0.36881600
H	1.92278200	3.22445100	-1.00288200
C	3.61048500	4.59846800	1.59182500
H	4.28577500	3.55987400	3.33055900

C	2.74351000	5.68997200	-0.50240400
C	4.15705500	5.89705400	2.07108800
C	3.31165100	6.98512200	-0.03709800
C	3.98461200	7.08391100	1.18719400
C	3.16508100	8.11315000	-0.84000000
C	4.50425100	8.30946400	1.59569800
C	3.68720700	9.33082100	-0.42829800
H	2.63898400	8.00928100	-1.78231300
C	4.35708400	9.42903100	0.78994100
H	5.01966600	8.35815400	2.54834000
H	3.57334100	10.20801300	-1.05687800
H	4.76479500	10.38278700	1.10966200
O	2.13847200	5.60734800	-1.55701800
O	4.72573700	5.98601600	3.14554200
H	6.59634711	-1.07355421	0.76230477
H	6.68010965	-2.54779275	-0.17186396
H	6.69506711	-0.99899710	-0.98061297
C	-8.06479396	-1.55815637	-0.25654677
H	-8.47062650	-1.65530843	-1.24181903
H	-8.34188674	-2.40984006	0.32890561
H	-8.44854097	-0.67046806	0.20132623

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C	5.33971300	-3.72842300	0.20409200
N	6.67597500	-3.33940300	0.13919700
C	7.11857600	-2.02091600	0.03586200
C	0.16265200	5.19095500	-0.31245100
N	-1.17169400	4.81575500	-0.28665500
C	-1.63545600	3.50017100	-0.19040300
O	8.30659800	-1.74784900	-0.02038700
O	5.04470400	-4.90941400	0.28908200
O	0.47788800	6.36670700	-0.40950200
O	-2.83011700	3.26541700	-0.26408500
C	-2.14732000	5.89466900	-0.42393000
C	7.66592200	-4.41238000	0.17969600
C	6.07709500	-0.97590900	-0.00130000
C	4.32708200	-2.65919900	0.16646100
C	4.71218400	-1.30997900	0.06563300
C	6.46603600	0.36062300	-0.10487000
C	5.51955100	1.35987200	-0.14465100
C	4.13086100	1.07165100	-0.08030300

C	3.72242500	-0.28490700	0.03045300
C	2.34972000	-0.64310900	0.10566100
C	2.00888200	-2.01803400	0.19775500
C	2.97496600	-2.99915200	0.22731000
C	1.15389900	4.10731200	-0.23618400
C	-0.62092700	2.43762900	-0.00661800
C	0.75475600	2.76392900	-0.09565800
C	1.75800900	1.74976000	-0.04384600
C	3.13205900	2.10569800	-0.12788200
C	3.47555000	3.47559300	-0.25831700
C	2.50625700	4.44818000	-0.31147900
C	-1.00606800	1.09081100	0.18413500
C	-0.02297600	0.11523200	0.20921200
C	1.35629400	0.39609800	0.08369800
H	-3.13928500	5.45626000	-0.36483700
H	8.65094300	-3.95400500	0.15560800
H	7.52541200	0.58391800	-0.15347400
H	5.85607600	2.38488600	-0.22545500
H	0.96953600	-2.31656100	0.23653600
H	2.71221800	-4.04838200	0.29676600
H	4.51365200	3.77288700	-0.32310200
H	2.75938000	5.49688800	-0.41441600
H	-0.34722600	-0.90459600	0.36722600
C	-2.40172600	0.62063800	0.41554800
C	-3.14211300	1.06009900	1.52059700
C	-2.94210400	-0.36085000	-0.40730900
C	-4.39246000	0.53525700	1.78581900
H	-2.72703500	1.82080500	2.17286000
C	-4.20628800	-0.88737300	-0.15232700
H	-2.40016400	-0.72738800	-1.27238000
C	-4.93794800	-0.43919900	0.95025000
H	-4.97311400	0.86605200	2.63938000
C	-4.74540200	-1.93246200	-1.06537300
C	-6.28887900	-0.98270300	1.25416400
C	-6.10500000	-2.46481600	-0.77379800
C	-6.83958500	-2.01281700	0.32974700
C	-6.64609200	-3.43130200	-1.61784600
C	-8.10780300	-2.53164800	0.57729500
C	-7.91082700	-3.94332400	-1.36627100
H	-6.05597500	-3.76431100	-2.46424500
C	-8.64195000	-3.49323600	-0.26839300
H	-8.65460500	-2.16475400	1.43864000
H	-8.33086300	-4.69571000	-2.02628800
H	-9.63122500	-3.89522400	-0.07373100

O	-4.09607100	-2.33878500	-2.01370800
O	-6.92129800	-0.59992700	2.22312400
H	-2.01061100	6.39906700	-1.38243100
H	7.53518700	-4.99921200	1.09022400
H	7.53111400	-5.07441900	-0.67781500
H	-1.99641300	6.62551800	0.37187100

2.4 Nanosecond transient absorption spectra and kinetics fitting of B-PDI-ANQ and O-PDI-ANQ in THF

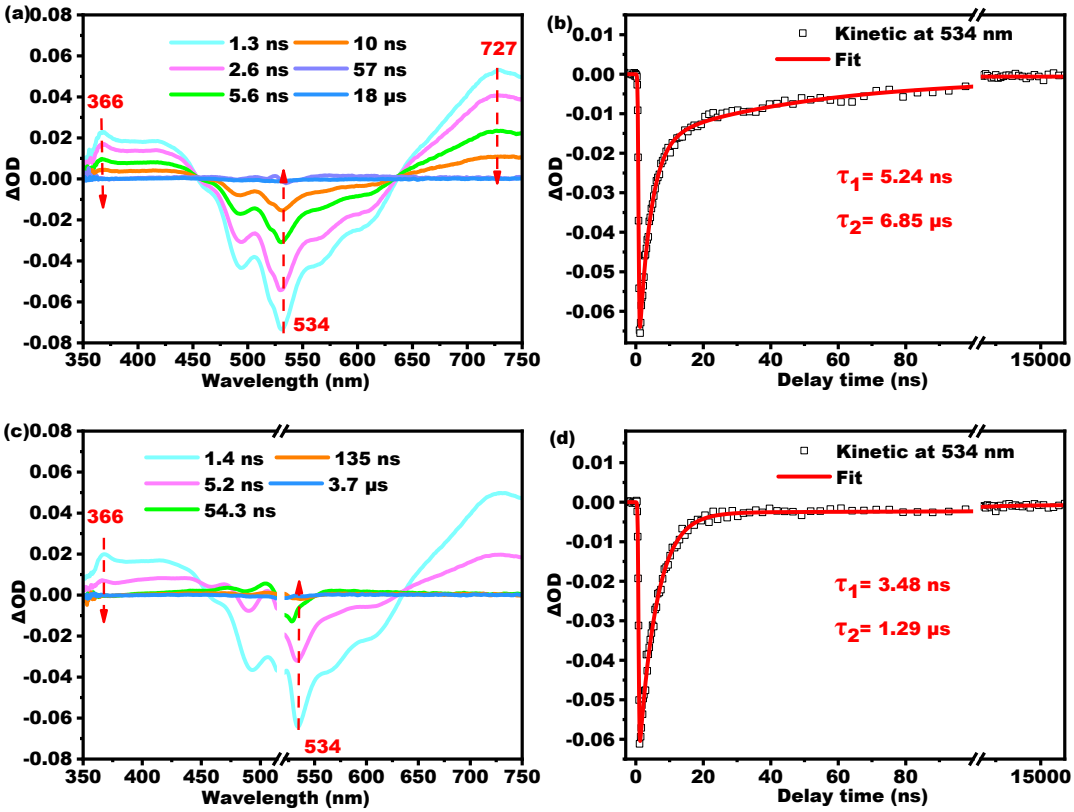
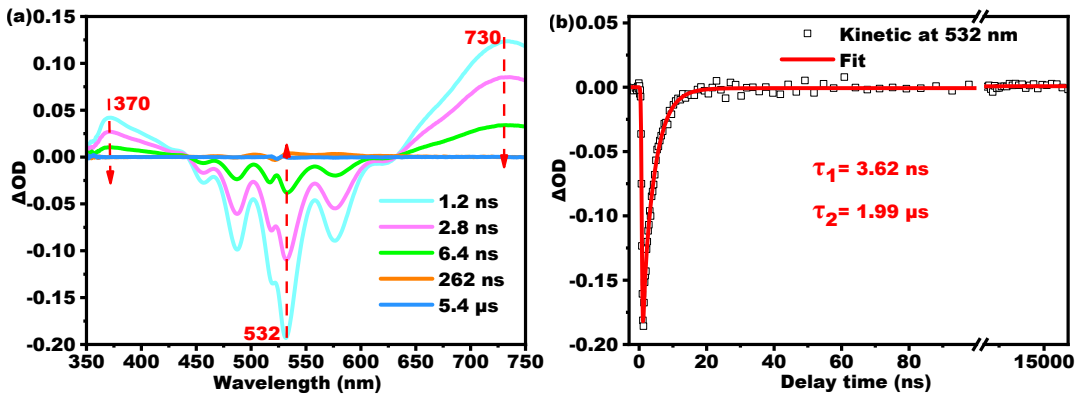


Figure S7. Ns-TA spectra and kinetics of B-PDI-ANQ in THF purged with (a, b) N_2 or (c, d) O_2



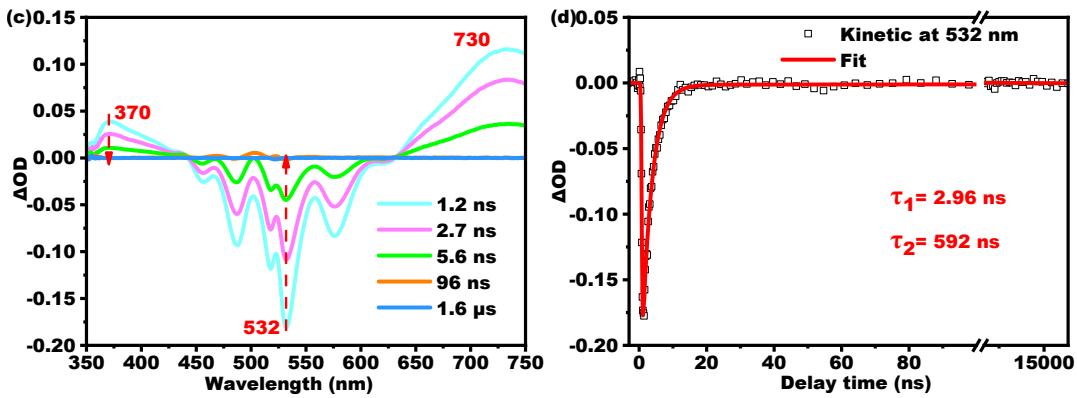


Figure S8. Ns-TA spectra and kinetics of O-PDI-ANQ in THF purged with (a, b) N_2 or (c, d) O_2

The triplet excited state of the bay- and ortho-substituted PDI derivatives are studied with the nanosecond transient absorption spectroscopy. Figure S7a shows the ns-TA spectrum of B-PDI-ANQ in deoxygenated THF. The kinetic fitting at 534 nm (Figure S7b) shows that B-PDI-ANQ has a short lifetime of τ_1=5.24 ns and a long lifetime of τ_2=6.85 µs. To confirm that the long lifetime transient state is a triplet state of B-PDI-ANQ, the solution is purged with oxygen (Figure S7c and 7d). The long lifetime transient state is quenched by the oxygen and the lifetime drops to 1.29 µs. This demonstrates that the long lifetime transient state of B-PDI-ANQ has a triplet-state nature. Therefore, ns-TA quenching experiments demonstrates that B-PDI-ANQ undergoes ISC to produce the triplet state after excitation at 525 nm. As shown in Figure S8, for O-PDI-ANQ, the main GSB peak at 532 nm gradually decreases with a lifetime of 1.99 µs in a nitrogen-saturated solution and with a much shorter lifetime of 592 ns in an oxygen-saturated solution. Thus, the triplet-state lifetime observed for B-PDI-ANQ (6.85 µs) is much longer than that of O-PDI-ANQ (1.99 µs).

2.5 Femtosecond transient absorption spectra of B-PDI-ANQ and O-PDI-ANQ in THF-H_2O with different f_w.

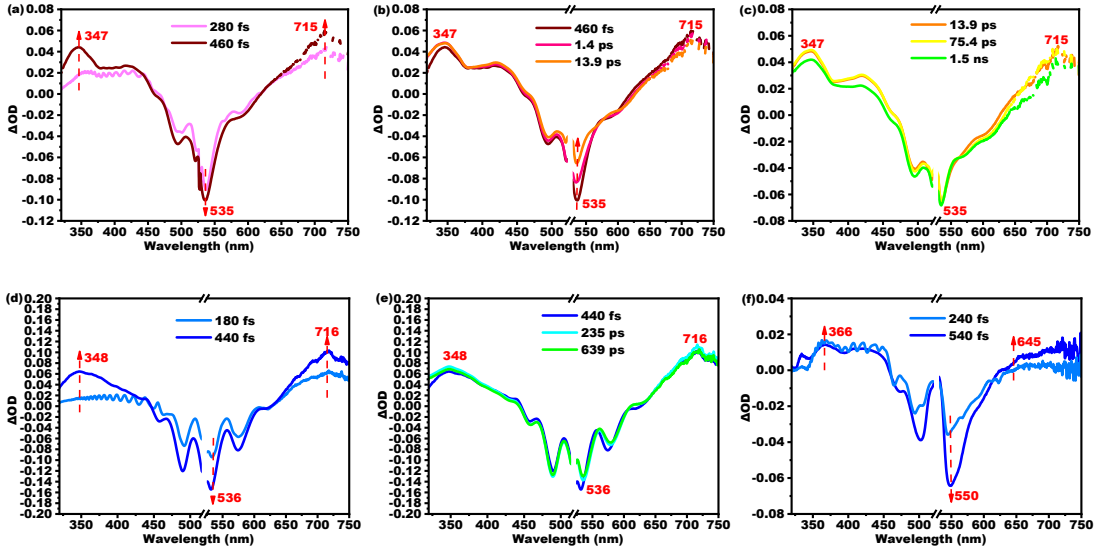


Figure S9. Fs-TA spectra of B-PDI-ANQ in (a, b, c) THF/H_2O (f_w = 30 %) and O-PDI-ANQ in (d, e) THF/H_2O (f_w = 30%) and (f) THF/H_2O (f_w = 70%).

2.6 The concentration calibration of B-PDI-ANQ and O-PDI-ANQ in THF

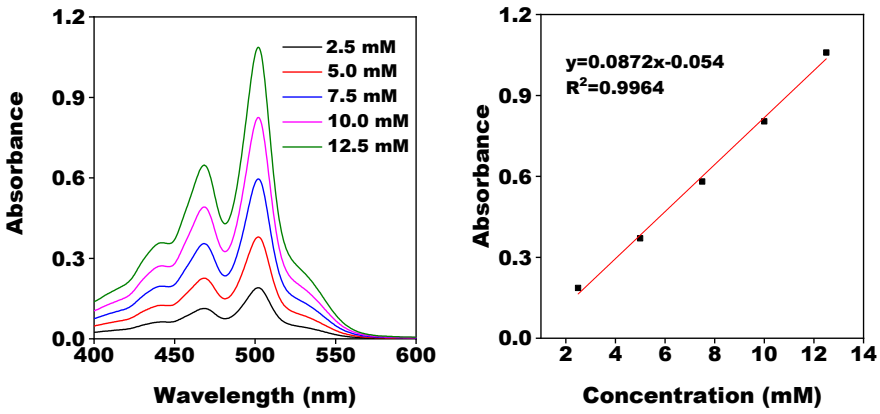


Figure S10. The concentration calibration of B-PDI-ANQ in THF.

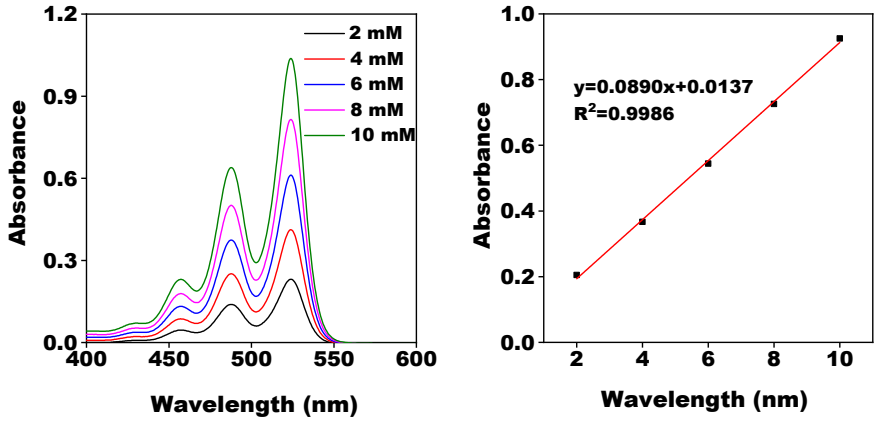


Figure S11. The concentration calibration of O-PDI-ANQ in THF.

2.7 The dynamic light scattering (DLS) study on nanoparticle size distribution of B-PDI-ANQ and O-PDI-ANQ

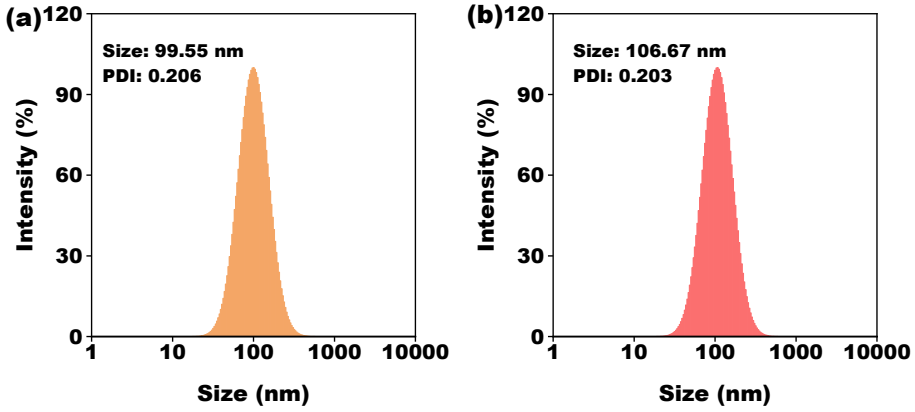


Figure S12. The DLS study on nanoparticle size distribution of (a) B-PDI-ANQ and (b) O-PDI-ANQ in the cellular imaging test.

3. Supplementary References

1. (a) Xu, L.; Li, Y.; Jiang, R.; Qin, Z.; Li, Y., 2,6-Anthracenyl(anthraquinonyl)-substituted difluoroboron dipyrromethenes: Synthesis, spectroscopy, electrochemistry and quantum chemical calculations. *Dyes Pigm.* **2014,** *107*, 90-96; (b) Holman, M. W.; Liu, R.; Adams, D. M., Single-Molecule Spectroscopy of Interfacial Electron Transfer. *J. Am. Chem. Soc.* **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. *J. Mater. Chem. C* **2016,** *4* (35), 8270-8275.

2. (a) Teraoka, T.; Hiroto, S.; Shinokubo, H., Iridium-Catalyzed Direct Tetraborylation of Perylene Bisimides. *Org. Lett.* **2011,** *13* (10), 2532-2535; (b) 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 Appl. Mater. Interfaces* **2019,** *11* (7), 6970-6977.