Supporting Information

Efficient Near-Infrared Photosensitizer with Aggregation-Induced Emission Characteristics for Mitochondria-Targeted and Image-guided Photodynamic Cancer Therapy

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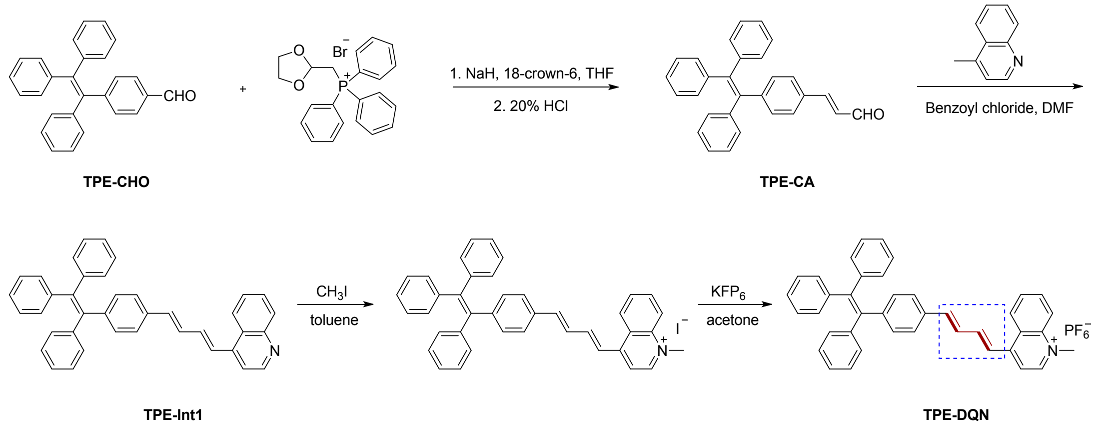
1. General Information

DMF was distilled over CaH_2, THF was distilled over Benzophenone and sodium. All other reagents and solvents were used directly from the corresponding supplier without further purification. All starting materials were purchased from Sigma, Energy, Accela and use directly. Analytical thin-layer chromatography (TLC) was carried out using commercial silica gel plated (GF254). Nuclear magnetic resonance spectra (^1H, ^{13}C NMR) were recorded on a Bruker Ascend 400 (^1H at 400 MHz, ^{13}C at 101 MHz) or a Bruker Ascend 600 (^1H at 600 MHz, ^{13}C at 151 MHz). The chemical shifts were reported as ppm and solvent residual peaks were shown as following: $CDCl_3$ δ H (7.26 ppm) and δ C (77.16 ppm). UV-visible absorption spectra were measured on Purkinje TU-1950 spectrometer. Fluorescence spectra were recorded on a Hitachi F-7000 spectrometer. Fluorescence quantum yields were measured using Hamamatsu C9920-02G. Single crystal was collected on Bruker CMOS PHOTON 100 detector. The fluorescence images were collected on Olympus FV1200. The fluorescence imaging in vivo was collected on IVIS Lumina III. Dynamic Light Scattering (DLS) measurement was carried out on Malvern Zetasizer Nano ZS90. High-resolution Mass spectra (HRMS) were obtained on a Bruker Maxis and Microflex and reported as m/z (relative intensity). Accurate masses are presented as molecular ion $[M–PF_6]^+$.

2. Reaction Procedure and Characterization Data



Scheme S2. Synthetic route of TPE-DQN.

TPE-CHO was prepared according to the previous literature.[S1]

TPE-CHO (600 mg, 1.67 mmol), (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (1429.5 mg, 3.33 mmol) and 18-crown-6 (8.8 mg, 0.033 mmol) were dissolved in THF under the atmosphere of N_2. The NaH (159.84 mg, 6.66 mmol) was added into above solution and the reaction was stirred for 2 h at room temperature before the second batch of NaH (159.84 mg, 6.66 mmol) was added. The resulted reaction mixture was stirred overnight. After the reaction was completed based on TLC, water was added to quench the reaction. The aqueous phase was extracted using CH_2Cl_2, and the combined organic phase was dried over Na_2SO_4. Removed the organic phase under reduced pressure. The residue was dissolved in THF, 20% HCl was added and the reaction stirred at room temperature for 2 h. Then, 10% NaOH was added and the aqueous phase was extracted using CH_2Cl_2. Combined organic phase was dried over Na_2SO_4. The solvent was removed and then purified by column chromatography on silica gel to give the desired product of TPE-CA (43% yield). ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm): 9.66 (d, 1H, J = 7.7 Hz, CHO), 7.38 (d, 1H, J = 15.9 Hz, vinyl CH), 7.31 (d, 2H, J = 8.2 Hz, Ar H), 7.14-7.09 (m, 11H), 7.06-7.03 (m, 6H), 6.66-6.62 (q, 1H); ^{13}C-NMR (151

MHz, $CDCl_3$) δ (ppm): 193.85, 152.71, 147.43, 143.37, 143.36, 143.24, 142.53, 140.02, 132.18, 132.05, 131.44, 131.43, 131.38, 128.25, 128.08, 128.01, 127.98, 127.82, 127.01, 126.88.

Benzoyl chloride (109.1 mg, 0.78 mmol) was slowly added into 5 mL DMF solution that contained Lepidine (111.1 mg, 0.78 mmol) under N_2. The resulted mixture was stirred at room temperature for 20 min. Then, the TPE-CA (300 mg，0.78 mmol) was added and the reaction was reacted at 160°C for 8 h. After the reaction was completed, the DMF was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the desired product of TPE-Int1 (47% yield).

TPE-Int1 (200 mg，0.39 mmol) and methyl iodide (233 mg, 2.35 mmol) were dissolved in 10 mL toluene. The reaction was refluxed for 1 h. After that, the toluene was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Then, the above product (100 mg, 0.153 mmol) and KPF_6 (281.6 mg, 1.53 mmol) were dissolved in 15 mL acetone. The reaction was stirred at room temperature for 5 h. After that, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the desired product of TPE-DQN (68% yield). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 9.27 (d, 1H, J = 6.6 Hz, CHO), 9.75 (d, 1H, J = 8.6 Hz, Ar H), 8.44-8.39 (m, 2H, Ar H), 8.26 (t, 1H, J = 7.3 Hz, Ar H), 8.06-7.96 (m, 2H, Ar H), 7.86 (d, 1H, J = 15.0 Hz, vinyl CH), 7.41 (d, 2H, J = 8.2 Hz, Ar H), 7.37-7.33 (m, 1H, Ar H), 7.20-7.08 (m, 10H, Ar H), 7.04-6.97 (m, 8H, Ar H), 4.51 (s, 3H, CH_3); ^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm): 151.84, 147.84, 144.54, 143.67, 143.08, 143.03, 142.89, 141.36, 140.48, 140.05, 138.76, 134.92, 134.17, 131.44, 130.78, 130.73, 130.67, 129.34, 128.77, 127.99, 127.95, 127.84, 126.94, 126.84, 126.75, 126.69, 125.96, 125.61, 123.44, 119.42, 115.76, 44.58. HRMS (ESI-

TOF) m/z: [M-PF_6^-]$^+$ calcd for $C_{40}H_{32}N^{2+}$, 526.2535, found, 526.2523.

3. Photoluminescence Properties

Aggregation-induced emission properties of target compound

Nanoaggregates preparation: 1 mM stock solutions of target compounds in DMSO were firstly prepared. Then aliquots of above stock solution were transferred into 5 mL volumetric flasks and appropriate amounts of water were added to obtain 10 μM solution with different water fractions (0 vol%, 10 vol%, 30 vol%, 50 vol%, 70 vol%, 80 vol%, 90 vol%, 95 vol%, 99 vol%). After that, the PL measurements of the resulting solutions were performed immediately.

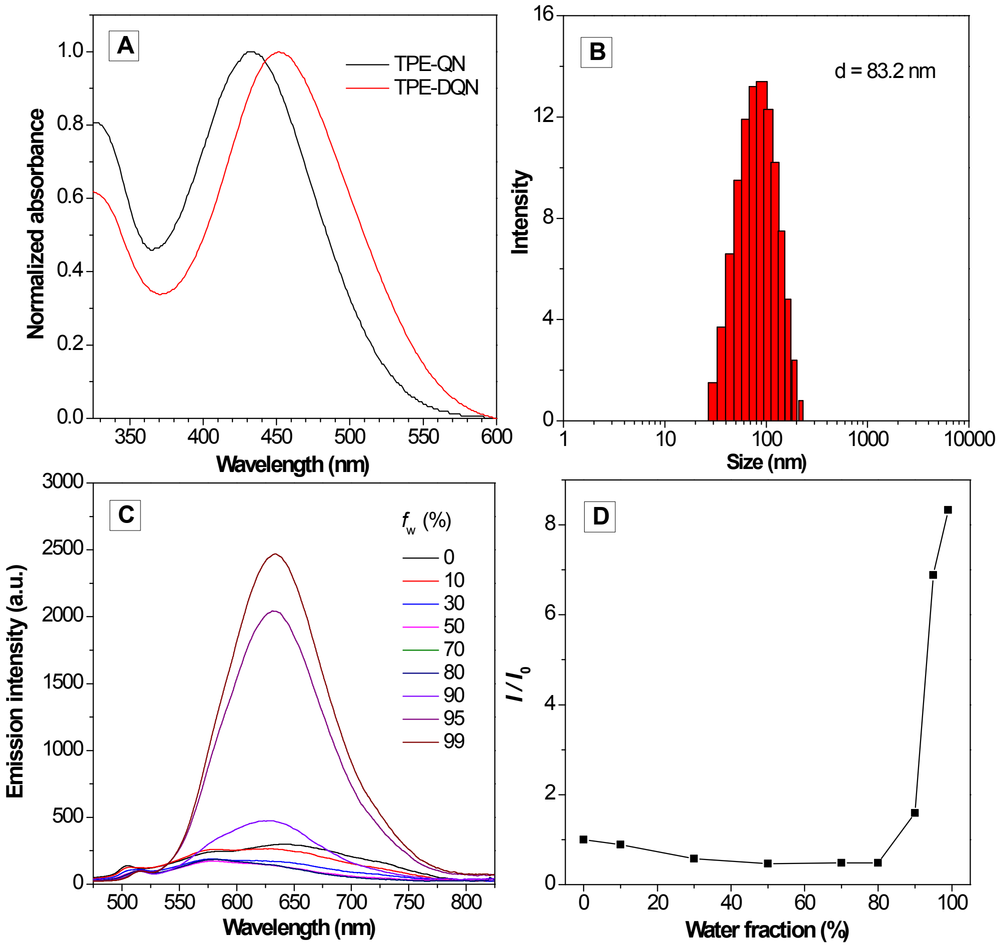


Fig. S1 (A) Normalized UV-Vis spectra of TPE-QN (10 μM) and TPE-DQN (10 μM) in DMSO (B) Particle size distributions of TPE-DQN at f_w of 99% (PDI value is 0.221). (C) Emission spectra of TPE-DQN in DMSO/water mixture with different f_w. (D) The plot of I/I_0 with different f_w. I_0 represents the emission intensity at 635 nm in pure DMSO solution. The excitation wavelength of TPE-QN is 435 nm.

Table S1. Optical summary of TPE-QN and TPE-DQN.

AIEgens	Solution[a]				Aggregation[b]		Solid[c]	
	λ_{abs} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{em} [nm]	$Ø_f$ [%][d]	λ_{em} [nm]	$Ø_f$ [%][d]	λ_{em} [nm]	$Ø_f$ [%][d]
TPE-QN	435	15668	633	2.7	630	8.3	589	29.2
TPE-DQN	450	28044	660	1.8	650	6.6	651	38.4

[a]In DMSO solution (10 μM); [b]In DMSO/water mixtures with f_w of 0 and 99%; [c]Solid state; [d]Absolute fluorescence quantum yield measured using the calibrated integrating sphere system

4. Theoretical Calculation and X-ray Single Crystal Data

Table S2. Cartesian Coordinates of Optimized TPE-QN Structures.[S2]

Atom	S_0			S_1			T_1		
	X	Y	Z	X	Y	Z	X	Y	Z
C	6.020658	1.411391	-0.48851	-5.96616	-1.58835	-0.05128	5.340291	-2.02126	-1.0618
C	5.121437	0.690422	0.304271	-4.98787	-0.74617	0.511323	4.300925	-1.06801	-1.10548
C	5.595296	0.086694	1.47292	-5.30408	-0.05218	1.694729	4.041568	-0.44464	-2.34388
C	6.933052	0.186754	1.829128	-6.54986	-0.18731	2.281867	4.757917	-0.77922	-3.48011
C	7.82179	0.886675	1.02073	-7.51394	-1.00482	1.696644	5.769448	-1.73382	-3.41698
C	7.361559	1.497963	-0.14017	-7.21896	-1.70115	0.526745	6.059525	-2.34497	-2.2001
H	5.663601	1.90273	-1.38768	-5.74061	-2.1281	-0.96398	5.604772	-2.47908	-0.11637
H	4.907426	-0.46248	2.105869	-4.55284	0.573582	2.161949	3.254581	0.299109	-2.41032
H	7.282186	-0.2824	2.743001	-6.77148	0.340789	3.202709	4.528681	-0.29209	-4.42207
H	8.868043	0.961132	1.298007	-8.49242	-1.10305	2.154324	6.334819	-1.99092	-4.30615
H	8.047771	2.049783	-0.77402	-7.96988	-2.33372	0.06635	6.862771	-3.07145	-2.13566
C	3.681545	0.62196	-0.07186	-3.6597	-0.63392	-0.10803	3.546963	-0.68856	0.075844
C	3.079512	1.923463	-0.47944	-3.06771	-1.87568	-0.62075	3.342694	-1.55687	1.220261
C	3.238015	3.057224	0.32492	-3.2586	-3.09044	0.065253	3.363697	-2.96409	1.106923
C	2.394053	2.053166	-1.69054	-2.34602	-1.89904	-1.8299	3.073122	-1.01345	2.495303
C	2.691569	4.275758	-0.05316	-2.73076	-4.27273	-0.42587	3.15271	-3.77354	2.210923
H	3.795011	2.976332	1.252693	-3.80368	-3.09113	1.002332	3.516974	-3.41806	0.135398
C	1.860999	3.276459	-2.0766	-1.84331	-3.0861	-2.32933	2.873324	-1.82807	3.595962
H	2.291379	1.18836	-2.3374	-2.20371	-0.97879	-2.38346	3.040598	0.063895	2.618422
C	2.001277	4.389344	-1.2559	-2.02659	-4.27624	-1.62661	2.914575	-3.214	3.463164
H	2.814915	5.142863	0.587361	-2.86861	-5.19526	0.127285	3.166084	-4.85199	2.092063
H	1.342979	3.362229	-3.02632	-1.30736	-3.08919	-3.27201	2.685864	-1.38072	4.566517
H	1.587085	5.345646	-1.55792	-1.62222	-5.20424	-2.01634	2.755196	-3.8514	4.326108
C	2.977309	-0.5386	-0.06775	-2.98466	0.590303	-0.17433	2.971302	0.685538	0.115172

C	1.501148	-0.58209	-0.23195	-1.51788	0.648455	-0.32951	1.569155	0.850567	0.127743
C	0.909546	-1.55779	-1.04593	-0.92819	1.542426	-1.23758	0.929702	2.053576	0.558503
C	0.653452	0.29568	0.466957	-0.66906	-0.18373	0.416921	0.709961	-0.23356	-0.23871
C	-0.4629	-1.62835	-1.18498	0.443823	1.585083	-1.40038	-0.43277	2.160216	0.58929
H	1.542584	-2.26081	-1.57494	-1.55897	2.192213	-1.8348	1.53501	2.878316	0.911579
C	-0.71631	0.217649	0.34136	0.701672	-0.12906	0.263559	-0.64877	-0.11263	-0.22563
H	1.090157	1.043189	1.117633	-1.09678	-0.87878	1.13073	1.1602	-1.16529	-0.5591
C	-1.30924	-0.7455	-0.49516	1.297478	0.759777	-0.64987	-1.27785	1.091979	0.191434
H	-0.89674	-2.38207	-1.83583	0.873961	2.278296	-2.11648	-0.88718	3.080723	0.943407
H	-1.33295	0.912029	0.901615	1.319109	-0.79548	0.854614	-1.25028	-0.95718	-0.54145
C	3.623827	-1.87711	0.079464	-3.68554	1.869878	-0.07919	3.911108	1.805593	0.152768
C	3.159413	-2.78899	1.03242	-3.07339	2.969806	0.557081	3.643268	3.028799	-0.48825
C	4.671652	-2.26386	-0.76001	-4.95505	2.059718	-0.66607	5.151911	1.651822	0.79653
C	3.743474	-4.04224	1.160429	-3.72048	4.189613	0.638135	4.566171	4.062241	-0.45789
H	2.338592	-2.50784	1.68537	-2.0984	2.842003	1.011493	2.724522	3.149157	-1.05081
C	5.250115	-3.52047	-0.6386	-5.58382	3.288573	-0.60649	6.062621	2.693792	0.841162
H	5.036951	-1.5686	-1.50794	-5.42467	1.239149	-1.19424	5.386776	0.708302	1.276643
C	4.791052	-4.41207	0.324231	-4.97466	4.355068	0.053823	5.773252	3.903311	0.215529
H	3.379666	-4.73214	1.9149	-3.24838	5.017675	1.154892	4.349238	4.991907	-0.97297
H	6.062594	-3.80384	-1.29948	-6.54994	3.423413	-1.07981	7.006602	2.561321	1.358491
H	5.245965	-5.39223	0.420842	-5.4749	5.316021	0.106823	6.493265	4.714245	0.239789
C	-2.73471	-0.87601	-0.67712	2.736882	0.864062	-0.84937	-2.68668	1.275665	0.245351
H	-3.02281	-1.65715	-1.37707	3.036459	1.502527	-1.67511	-2.99768	2.260683	0.581874
C	-3.71218	-0.16643	-0.05908	3.689957	0.277445	-0.0798	-3.64951	0.352076	-0.07619
H	-3.42419	0.573492	0.674815	3.356863	-0.29253	0.779336	-3.31457	-0.62132	-0.40507
C	-5.1178	-0.34395	-0.30157	5.106365	0.342291	-0.29211	-5.05222	0.569436	-0.00752
C	-6.11271	0.196675	0.591934	6.052154	-0.10205	0.707088	-6.00464	-0.46555	-0.36392
C	-5.59514	-1.0291	-1.42597	5.647702	0.826333	-1.50405	-5.6037	1.797664	0.410817
C	-5.77203	0.877605	1.784452	5.6643	-0.568	1.979814	-5.60712	-1.74715	-0.80438
C	-7.49348	0.038412	0.299175	7.449051	-0.06427	0.428909	-7.39873	-0.21181	-0.27701
C	-6.94032	-1.1636	-1.65686	6.990233	0.851888	-1.72397	-6.95398	1.987531	0.474961
H	-4.91739	-1.43711	-2.16231	5.000249	1.155483	-2.30516	-4.97229	2.627061	0.694708
C	-6.73143	1.388586	2.619252	6.582784	-0.99816	2.913038	-6.52102	-2.71606	-1.13695
H	-4.73128	0.987203	2.055678	4.615114	-0.57732	2.243219	-4.55491	-1.98168	-0.88558
C	-8.47027	0.571048	1.160882	8.374059	-0.50531	1.384498	-8.32744	-1.21059	-0.61905
H	-7.30892	-1.68421	-2.53195	7.409446	1.207976	-2.65579	-7.3725	2.932626	0.797558
C	-8.08985	1.238165	2.299484	7.944698	-0.97189	2.612076	-7.89167	-2.44384	-1.04247
H	-6.4426	1.904065	3.527682	6.245278	-1.34986	3.881306	-6.18201	-3.68948	-1.47173
H	-9.522	0.458825	0.9377	9.433659	-0.48233	1.170709	-9.38911	-1.01812	-0.55252
H	-8.84925	1.644761	2.95799	8.673392	-1.30882	3.340565	-8.61705	-3.20617	-1.3037
C	-9.29144	-0.82704	-1.16855	9.312434	0.469738	-1.10254	-9.27647	1.316908	0.246524
H	-9.79558	-1.38001	-0.37479	9.838281	1.110939	-0.39069	-9.75283	1.216886	-0.7304
H	-9.76999	0.143995	-1.30305	9.750611	-0.53101	-1.0728	-9.75268	0.638115	0.956267
H	-9.36909	-1.39046	-2.09566	9.444769	0.878067	-2.10257	-9.40648	2.338544	0.597064

N	-7.87227	-0.65181	-0.84124	7.889106	0.419759	-0.79888	-7.84461	1.031974	0.148714

Table S3. Cartesian Coordinates of Optimized TPE-DQN Structures.[S2]

Atom	S_0			S_1			T_1		
	X	Y	Z	X	Y	Z	X	Y	Z
C	6.914513	1.506424	-0.50132	6.765512	1.798345	-0.16129	-6.70883	1.832339	0.14836
C	6.035127	0.785791	0.31352	5.853468	0.937499	0.477701	-5.81807	0.959371	-0.49592
C	6.520736	0.247661	1.508883	6.225572	0.364471	1.707842	-6.21907	0.367345	-1.70359
C	7.851128	0.410434	1.87012	7.461843	0.634078	2.268229	-7.46689	0.634882	-2.24239
C	8.720816	1.109407	1.040591	8.361581	1.468725	1.609319	-8.34691	1.486472	-1.58047
C	8.248368	1.656183	-0.14731	8.010424	2.046528	0.391816	-7.96535	2.081389	-0.38247
H	6.54716	1.948066	-1.42193	6.496633	2.246476	-1.11115	-6.41554	2.3001	1.081622
H	5.847617	-0.30066	2.1583	5.524702	-0.27586	2.230174	-5.53801	-0.29452	-2.22548
H	8.209146	-0.00883	2.804629	7.726184	0.197308	3.224977	-7.7551	0.179374	-3.18358
H	9.761297	1.23332	1.321995	9.333264	1.672175	2.046378	-9.32664	1.688584	-2.00012
H	8.919403	2.206994	-0.79816	8.710941	2.692581	-0.12585	-8.64819	2.743689	0.138606
C	4.601212	0.649973	-0.0694	4.531479	0.683823	-0.11368	-4.47797	0.711857	0.067539
C	3.953118	1.915191	-0.51962	3.854346	1.836156	-0.72379	-3.79538	1.874833	0.666137
C	4.068142	3.078859	0.248461	3.951843	3.111637	-0.13615	-3.83754	3.128604	0.035146
C	3.266509	1.982328	-1.73508	3.140724	1.710502	-1.93084	-3.13185	1.767993	1.898595
C	3.480136	4.264768	-0.16907	3.33852	4.208524	-0.71779	-3.20451	4.225338	0.599133
H	4.624362	3.047437	1.179736	4.492754	3.226525	0.796297	-4.35675	3.229868	-0.91141
C	2.690893	3.172846	-2.16041	2.550742	2.813501	-2.52085	-2.51857	2.871924	2.470245
H	3.194664	1.094164	-2.35376	3.074111	0.741709	-2.41106	-3.12134	0.815207	2.415477
C	2.789462	4.315772	-1.37572	2.640328	4.064791	-1.91371	-2.5454	4.101169	1.818971
H	3.570648	5.155354	0.444229	3.405113	5.179633	-0.23961	-3.23042	5.182538	0.089554
H	2.171466	3.20914	-3.11257	2.021114	2.702284	-3.46058	-2.02504	2.775782	3.431366
H	2.341831	5.246507	-1.70845	2.169588	4.926571	-2.37459	-2.06282	4.963895	2.265886
C	3.941697	-0.53511	-0.03113	3.946586	-0.5853	-0.08483	-3.90244	-0.56179	0.075328
C	2.468684	-0.64071	-0.20492	2.497147	-0.77061	-0.24347	-2.4847	-0.77775	0.229588
C	1.922931	-1.65281	-1.00568	1.987229	-1.82972	-1.01536	-1.98882	-1.97186	0.828897
C	1.582841	0.214439	0.471973	1.572486	0.08268	0.38676	-1.51189	0.143259	-0.26262
C	0.555106	-1.78058	-1.15335	0.626154	-2.00224	-1.17219	-0.65045	-2.19959	0.964413
H	2.587586	-2.33982	-1.51704	2.67368	-2.50331	-1.51667	-2.6962	-2.69362	1.218894
C	0.217375	0.079936	0.337788	0.214305	-0.10655	0.247712	-0.17433	-0.09848	-0.16035
H	1.98489	0.989492	1.112987	1.935248	0.891976	1.009948	-1.84879	1.039399	-0.76778
C	-0.33015	-0.91959	-0.48592	-0.29918	-1.14983	-0.54591	0.324015	-1.27832	0.473725
H	0.155463	-2.56238	-1.7927	0.259316	-2.81496	-1.79119	-0.30482	-3.10037	1.460949
H	-0.43276	0.754587	0.884033	-0.46119	0.563095	0.76725	0.518509	0.619157	-0.5827
C	4.636206	-1.84199	0.170795	4.745505	-1.80107	0.113839	-4.75076	-1.77537	-0.0631
C	4.190557	-2.73824	1.147254	4.240893	-2.86296	0.888465	-4.39739	-2.79185	-0.95942
C	5.711706	-2.21708	-0.63844	6.00288	-1.95988	-0.50008	-5.89947	-1.94006	0.719606

C	4.81944	-3.96295	1.327998	4.980615	-4.01895	1.070722	-5.18118	-3.9309	-1.08289
H	3.348032	-2.46695	1.776159	3.274743	-2.75652	1.36771	-3.51119	-2.67586	-1.57493
C	6.335043	-3.44578	-0.46456	6.726162	-3.12719	-0.33651	-6.67287	-3.08551	0.606653
H	6.062742	-1.53451	-1.40463	6.393089	-1.16657	-1.1262	-6.18076	-1.16504	1.424067
C	5.89417	-4.32085	0.521597	6.222689	-4.15693	0.456312	-6.31906	-4.08155	-0.29837
H	4.468858	-4.64018	2.100043	4.589379	-4.8173	1.691559	-4.90288	-4.70213	-1.79315
H	7.168365	-3.72032	-1.1029	7.68467	-3.24089	-0.83065	-7.55498	-3.20246	1.226916
H	6.38398	-5.27911	0.659145	6.79633	-5.06766	0.590595	-6.92917	-4.97372	-0.39078
C	-1.7495	-1.10676	-0.66844	-1.72233	-1.38598	-0.7391	1.692711	-1.57646	0.632254
H	-2.02397	-1.92355	-1.33531	-1.97368	-2.23672	-1.36867	1.933656	-2.51346	1.12734
C	-2.76458	-0.39444	-0.11405	-2.74092	-0.65969	-0.21685	2.754172	-0.78166	0.212831
H	-2.55956	0.432348	0.559393	-2.52377	0.197961	0.416184	2.536778	0.161671	-0.28382
C	-4.12408	-0.70171	-0.3902	-4.12117	-0.94454	-0.44202	4.101947	-1.10127	0.379795
H	-4.29075	-1.53491	-1.06918	-4.34204	-1.80127	-1.07267	4.338678	-2.03833	0.873853
C	-5.18626	-0.03187	0.143251	-5.13269	-0.19686	0.097733	5.114954	-0.25875	-0.06794
H	-4.95572	0.7797	0.820699	-4.82395	0.636748	0.718585	4.780218	0.653634	-0.54987
C	-6.56148	-0.31971	-0.11854	-6.53	-0.4034	-0.07306	6.502516	-0.46633	0.037449
C	-7.62725	0.398666	0.544451	-7.51943	0.441263	0.567879	7.477044	0.489203	-0.47389
C	-6.95719	-1.30841	-1.03418	-7.03191	-1.45014	-0.88429	7.032412	-1.62995	0.653015
C	-7.38168	1.413775	1.497917	-7.17875	1.519531	1.408873	7.110203	1.690322	-1.10922
C	-8.98281	0.092511	0.251457	-8.9063	0.19537	0.360458	8.865096	0.224248	-0.34022
C	-8.27952	-1.56472	-1.27743	-8.36657	-1.64577	-1.05037	8.372413	-1.83352	0.754818
H	-6.22973	-1.8902	-1.58164	-6.35955	-2.12266	-1.39845	6.37805	-2.38848	1.058848
C	-8.40462	2.085723	2.116088	-8.13335	2.311716	2.008131	8.046044	2.580857	-1.58628
H	-6.36366	1.67038	1.754827	-6.13614	1.737616	1.596526	6.062365	1.930751	-1.23162
C	-10.0252	0.788602	0.890773	-9.87013	1.007948	0.97443	9.812489	1.136593	-0.82929
H	-8.58058	-2.32587	-1.98642	-8.75149	-2.4447	-1.67077	8.77676	-2.72105	1.224295
C	-9.73591	1.769935	1.807305	-9.48737	2.054742	1.788824	9.406769	2.301195	-1.44497
H	-8.18508	2.85877	2.843129	-7.83062	3.131983	2.648942	7.724686	3.496031	-2.07025
H	-11.0576	0.558265	0.668227	-10.9232	0.821357	0.81568	10.86973	0.93412	-0.72766
H	-10.5462	2.300577	2.294601	-10.2451	2.673361	2.256272	10.15013	2.99671	-1.81792
C	-10.6656	-1.23514	-0.99094	-10.7157	-1.1284	-0.67959	10.70902	-1.23957	0.427442
H	-11.1882	-1.57862	-0.0969	-11.2212	-1.35483	0.262493	11.19273	-1.30346	-0.5499
H	-11.1781	-0.36569	-1.40539	-11.2046	-0.27199	-1.15066	11.20107	-0.46717	1.022847
H	-10.6714	-2.03282	-1.73043	-10.8092	-1.98855	-1.33971	10.82163	-2.19541	0.935149
N	-9.275	-0.90076	-0.67025	-9.30209	-0.85864	-0.45583	9.287279	-0.94965	0.28087

Table S4. Crystallographic data of TPE-DQN.

Crystal	**TPE-DQN**
formula	$C_{40}H_{32}NF_6P$
crystal system	monoclinic
space group	I 2/a
a [Å]	14.3546 (2)
b[Å]	11.3528 (2)
c[Å]	49.0547 (7)
β [deg]	97.669 (1)
V [Å^3]	7922.7 (2)
Z	8
μ [mm^{-1}]	1.135
T [K]	150
θ_{min}-θ_{max} [deg]	4.2230-71.3480
R	0.072
wR_2	0.2108
GOOF	1.034
grow condition	CH_2Cl_2/acetone
diffraction radiation type	CuK\a
diffraction measurement method	w scans
CCDC number	1975428

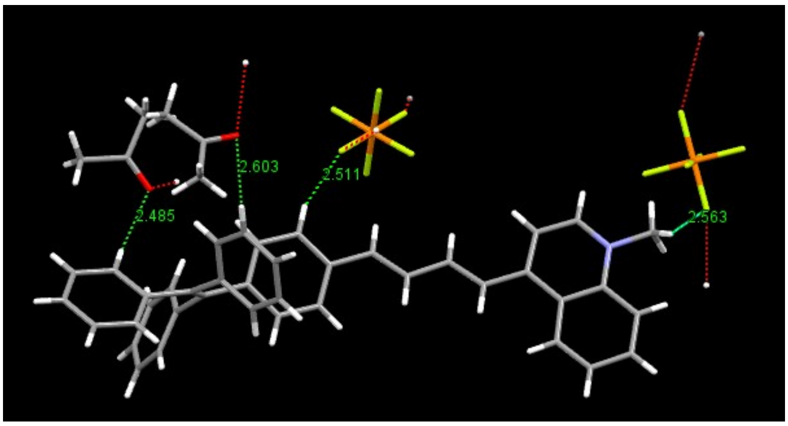


Fig. S2 Intermolecular interactions as well as short contacts of TPE-DQN.

5. Cell Imaging and Photodynamic Therapy of Cancer Cell

Cell culture and imaging

Both cancer (HeLa or CT26) and normal (CHO) cells were cultured in DMEM containing 10% FBS, and incubated at 37°C in a 5% CO_2 atmosphere. Cells were seeded onto 35 mm glass-bottom dishes and allowed to grow until the confluence reached of 80%. Prior to experiments, the medium was removed and the adherent cells were washed with PBS buffer to remove the remnant growth medium. The TPE-QN or TPE-DQN stock solution (2 mM) and MitoTracker Green (MTG, 1mM) were added into the cell plates in DMEM to give the final concentration of 2 μM (TPE-QN or TPE-DQN) and 100 nM (MTG), respectively. Then the cells were incubated for 30 min at 37°C, followed by PBS washing (two times) and used for bio-imaging subsequently. Under CLSM, TPE-QN or TPE-DQN was excited at 488 nm and the emission was collected at 600–700 nm, MTG was excited at 488 nm and the emission was collected at 500–550 nm. No background fluorescence of cells was detected under the setting condition.

Photo-stability measurement

The HeLa cells were stained with 2 μM TPE-QN (or TPE-DQN) and 100 nM MTG for 30 min at 37°C. The images of pre-stained cells were collected by continuous laser excitation and sequential images collection. Scanning times: 300 times. Excitation: 488 nm for TPE-QN, TPE-DQN and MTG with the same laser power of 2.0 %.

Washing-free staining experiments

The HeLa cells were seeded on the 35 mm glass-bottom culture dishes in DMEM containing 10% FBS at 37°C in a 5% CO_2 atmosphere. The resulted cells were allowed to grow until the cell confluence reached to 50%. The cells were then incubated with either TPE-QN (2 μM) or TPE-DQN (2 μM) for 30 min at 37^{o}C under 5% CO_2 and collected CLSM images directly.

Extracellular ROS detection

The ROS generation was measured using DCF-DA as an indicator since the emission of DCF-DA increases upon reaction with ROS. For ROS detection, the DCF-DA (5 μM) was mixed with TPE-QN or TPE-DQN (10 μM) in DMSO/PBS buffer (1:99, v/v) and exposed to white light irradiation (25 mW cm^{-2}). The oxidized DCF was monitored by the emission increase at 525 nm.

Extracellular $^1O_2$ detection

The $^1O_2$ generation was measured using 9,10-anthracenediyl bis-(methylene)-dimalonic acid (ABDA) as an indicator since the absorbance of ABDA decreases upon reaction with $^1O_2$. For $^1O_2$ detection, the ABDA (100 μM) was mixed with the TPE-QN or TPE-DQN (10 μM) in DMSO/water (1:99, v/v) and exposed to white light irradiation (25 mW cm^{-2}). The decomposition of ABDA was monitored by the absorbance decrease at 378 nm.

$^1O_2$ generation efficiency measurement

The $^1O_2$-sensitive indicator 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) was used as the $^1O_2$ indicator, and Rose Bengal (RB) was employed as the standard photosensitizer. In these experiments, ABDA solution was added into the sample solution (100 μM), and white light (25 mW cm^{-2}) was used as the irradiation source. The absorbance of ABDA at 378 nm was recorded at different irradiation times to obtain the decay rate of the photosensitizing process. The $^1O_2$ generation efficiency of the AIEgens was calculated using the following equation (Eq. 1):

$$\Phi_{PS} = \Phi_{RB} (K_{PS} \bullet A_{RB}) / K_{RB} \bullet A_{PS} \qquad \text{Eq. 1}$$

Where K_{PS} and K_{RB} are the decomposition rate constants of ABDA by the TPE-QN, TPE-DQN, and RB, respectively. A_{PS} and A_{RB} represent the light absorbed by the TPE-QN, TPE-DQN or RB, respectively, which are determined by integration of the areas under the absorption bands in the wavelength range of 400–600 nm. Φ_{RB} is the $^1O_2$ generation efficiency of RB, which is 0.75 in water.

Intracellular ROS detection

Intracellular ROS generation under white light irradiation was detected using DCF-DA as an indicator. CT26 cells were cultured in DMEM with 10% FBS at 37°C under 5% CO_2 atmosphere. After cells reached 80% confluence, the culture medium was removed and cells were washed with PBS buffer. The resulted cells were treated with DCF-DA (20 μM) for 15 min under dark and washed once with PBS buffer. Then the cells were incubated with TPE-QN or TPE-DQN (2 μM) for 30 min under dark. After that, the cells were washed twice with PBS buffer and exposed to white light irradiation (25 mW cm^{-2}) for different time.

For control experiment, the cells were only incubated with DCF-DA (20 μM) for 15 min, then cells were washed once with PBS buffer and exposed to white light irradiation (25 mW cm^{-2})

for different time. Under CLSM, DCF-DA was excited at 488 nm and the emission was collected at range of 500–550 nm. No background fluorescence of cells was detected under the setting condition.

Photo-toxicity measurement

To determine the cytotoxicity induced by PDT process, a MTT based cell viability assay was performed in 96 well plates. CHO or CT26 cells were seeded at a density of 10000 cells per well and then incubated for 24 h. The TPE-DQN were dissolved in DMSO solution to give a 20 mM stock solution. After 24 h, adding specific amount of above stock solution into cell culture medium to give desired concentration and incubated for 30 min. Then the medium was replaced by fresh DMEM and selected wells were exposed to white light irradiation (25 mW cm^{-2}, 30 min). After that, the cells were further cultured for 2 h under dark (In the parallel experiment, both cell lines were treated with fresh DMEM for 2.5 h in the dark). Then, the cells were incubated with MTT for 4 h. The formed formazan crystals were solubilized in 100 μL of lysate buffer. Absorbance at 570 nm of each well was measured on a Spectra Max M384 (Molecular Devices) and the data was recorded using Softmax Pro 6.4 software. The IC_{50} of the compounds were calculated by using Graphpad Prism 5.

Cell apoptosis detection

Annexin V-FITC and PI were used as indicators to detect the cell apoptosis process in living cells. The CT26 cells were seeded on the 35 mm glass-bottom culture dishes in DMEM containing 10% FBS at 37°C in a 5% CO_2 atmosphere and allowed to grow until the cell confluence reached to 50%. The cells were firstly incubated with TPE-DQN (2 μM) for 30 min and then exposed to the white light irradiation (25 mW cm^{-2}) for 30 min. The resulted cells were stained with both Annexin V-FITC and PI following the protocols of the manufacturer (Life Technologies) and collected CLSM images with the elapse of time. For control group, similar procedure was performed except remove of the white light irradiation. Annexin V-FITC was excited at 488 nm and the emission was collected at range of 500-550 nm, PI was excited at 559 nm and the emission was collected at range of 570–670 nm.

CT26 tumor beared mice model

The 5 weeks female BALB/c mice were housed at 25°C with 50-60% humidity and subjected to 12 h light/12 h dark cycles. Mice were fed with distilled water and ordinary solid diet. The status of mice was checked every day. Mice were used for experiment after acclimatized for one week. During the imaging and treatment, mice were anesthetized with 0.5 L/min oxygen/isoflurane stream. At the end of this research, mice were sacrificed by diethyl ether inhalation. All animal experiments were carried out with the approval of the science ethics specialized committee, Shaanxi Normal University.

100 μL of CT26 cells (5×10^6) in saline suspension was injected into BALB/c (female) mice subcutaneously. The mice were used for fluorescent imaging when the volume of tumor reached up to 1000 mm^3. Mice were utilized to PDT treatment when the volume of tumor reached to 150 mm^3.

***In vivo* fluorescent imaging**

BALB/c (female) mice bearing CT-26 tumor were intratumorally injected with 100 μL of TPE-DQN saline solution (5 mM). Fluorescent images were captured at 0, 0.5, 1, 2, 6, 24 hours after injections, using IVIS Lumina III *in vivo* imaging system (PerkinElmer). The mice were sacrificed on 24 h and major organs and tumors were separated and photographed. The excitation wavelength was 480 nm and the emission was collected at 670 nm. The IVIS Lumina Living Image software was employed to quantify the imaging results.

***In vivo* anti-tumor efficiency**

BALB/c (female) mice bearing CT26-colon-tumor were randomly divided into four groups (three mice each). The fore groups were further separately treated with saline (w/o light irradiation), saline (w light irradiation), TPE-DQN (w/o light irradiation) and TPE-DQN (w light irradiation). For the groups treated with TPE-DQN, 100 μL of TPE-DQN saline solution (5 mM) was intratumorally injected into mice on day 0, day 3 and day 6. For the groups treated with saline, 100 μL of saline solution was intratumorally injected into mice on day 0, day 3 and day 6. For the groups with light irradiation, the mice were exposed to white light (100 mW cm^{-2}) for 10 min after 6 hours of post-injection. For the groups w/o light irradiation, mice were kept in the dark after 6 hours of post-injection. After treatment, the tumor size and body weight of each mouse was measured daily by using a caliper, and the tumor volume was calculated according to the following equation: volume = $W^2 \times L/2$. (L and W were the longer diameter and shorter diameter of the tumor, respectively). The mice in different groups were sacrificed on day 10, tumors were separated and photographed.

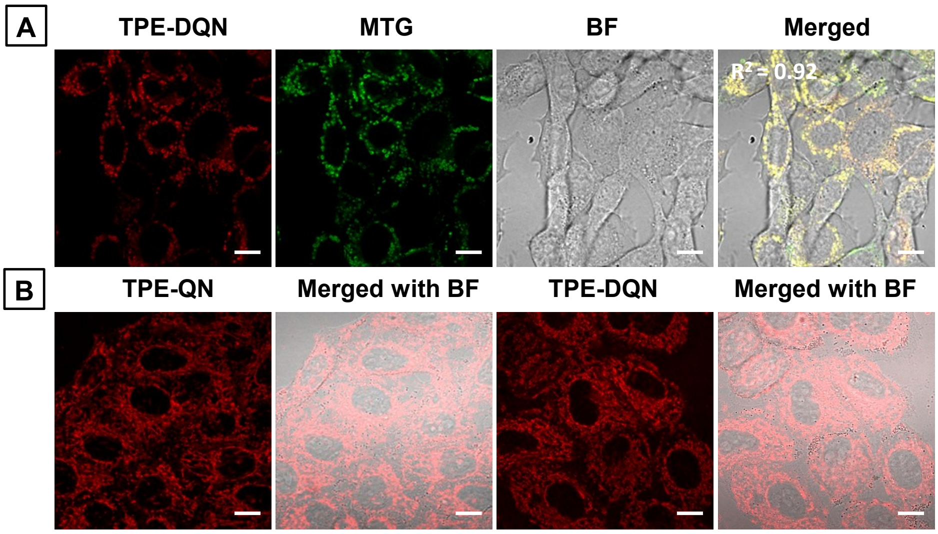


Fig. S3 (A) CLSM images of CT26 cells after stained with TPE-DQN (2 μM) and MTG (100 nM), respectively. (B) CLSM images of HeLa cells stained with TPE-QN or TPE-DQN (2 μM) in absence of washing procedure. λ_{ex} for TPE-QN (or TPE-DQN): 488 nm, λ_{ex} for MTG: 488 nm. Scale bar: 10 μm.

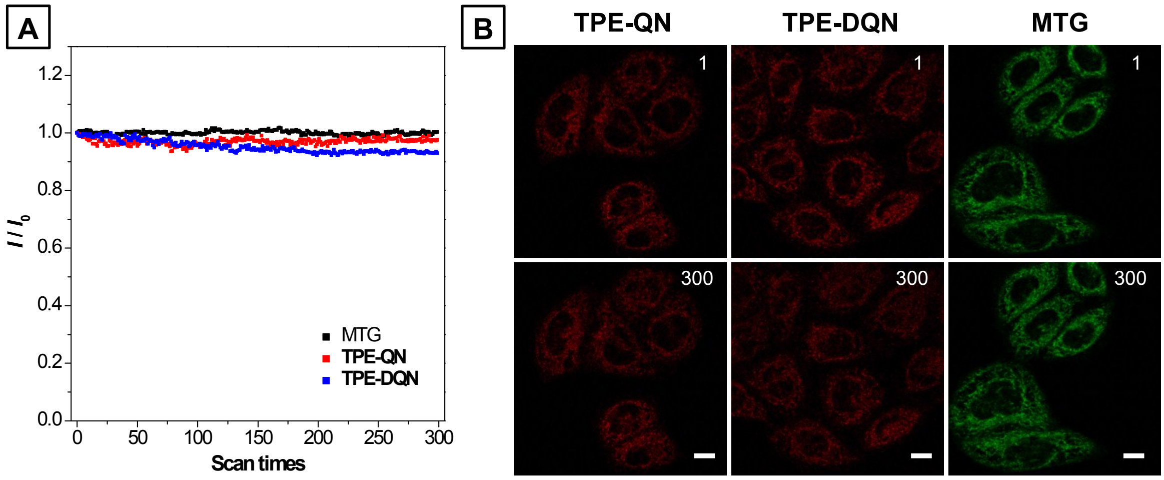


Fig. S4 (A) Loss in fluorescent signal of HeLa cells stained with TPE-QN (2 μM), TPE-DQN (2 μM) and MTG (100 nM) with the number of scans after laser irradiation. (B) CLSM images of HeLa cells stained with different probes after 1 and 300 scans. Scale bar: 10 μm.

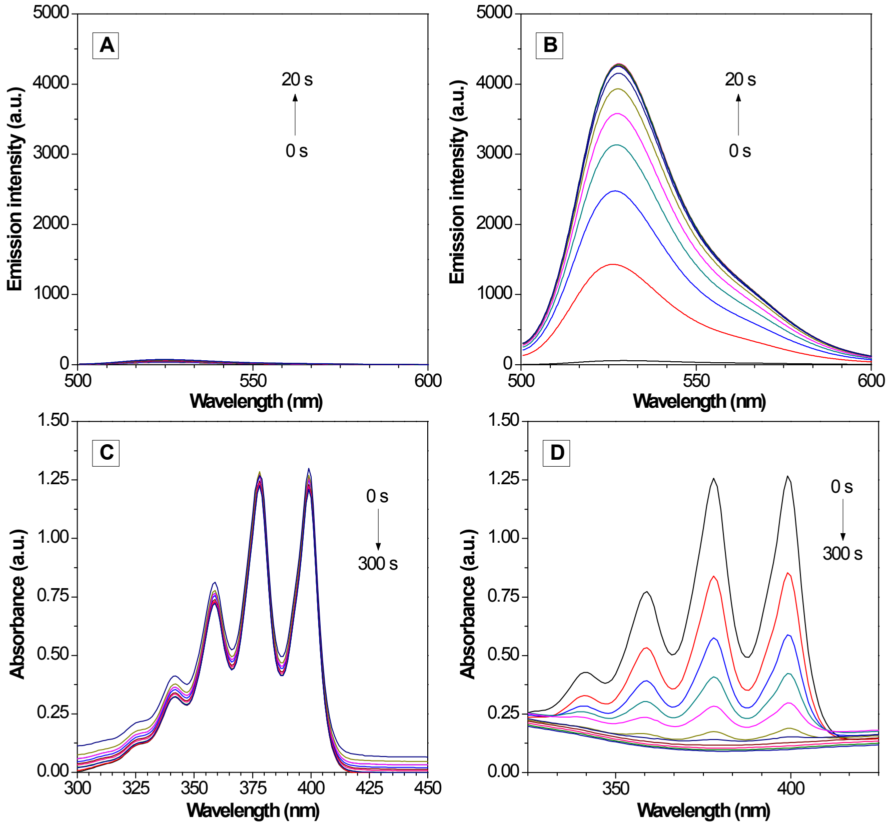


Fig. S5 Emission spectra change of DCF-DA (5 μM) (A) without TPE-QN (B) in the presence of TPE-QN (10 μM) in PBS (containing 1% DMSO) after different durations under white light irradiation. Absorption spectra change of ABDA (100 μM) (C) without TPE-QN (D) in the presence of TPE-QN (10 μM) at f_w of 99% after different durations under white light irradiation.

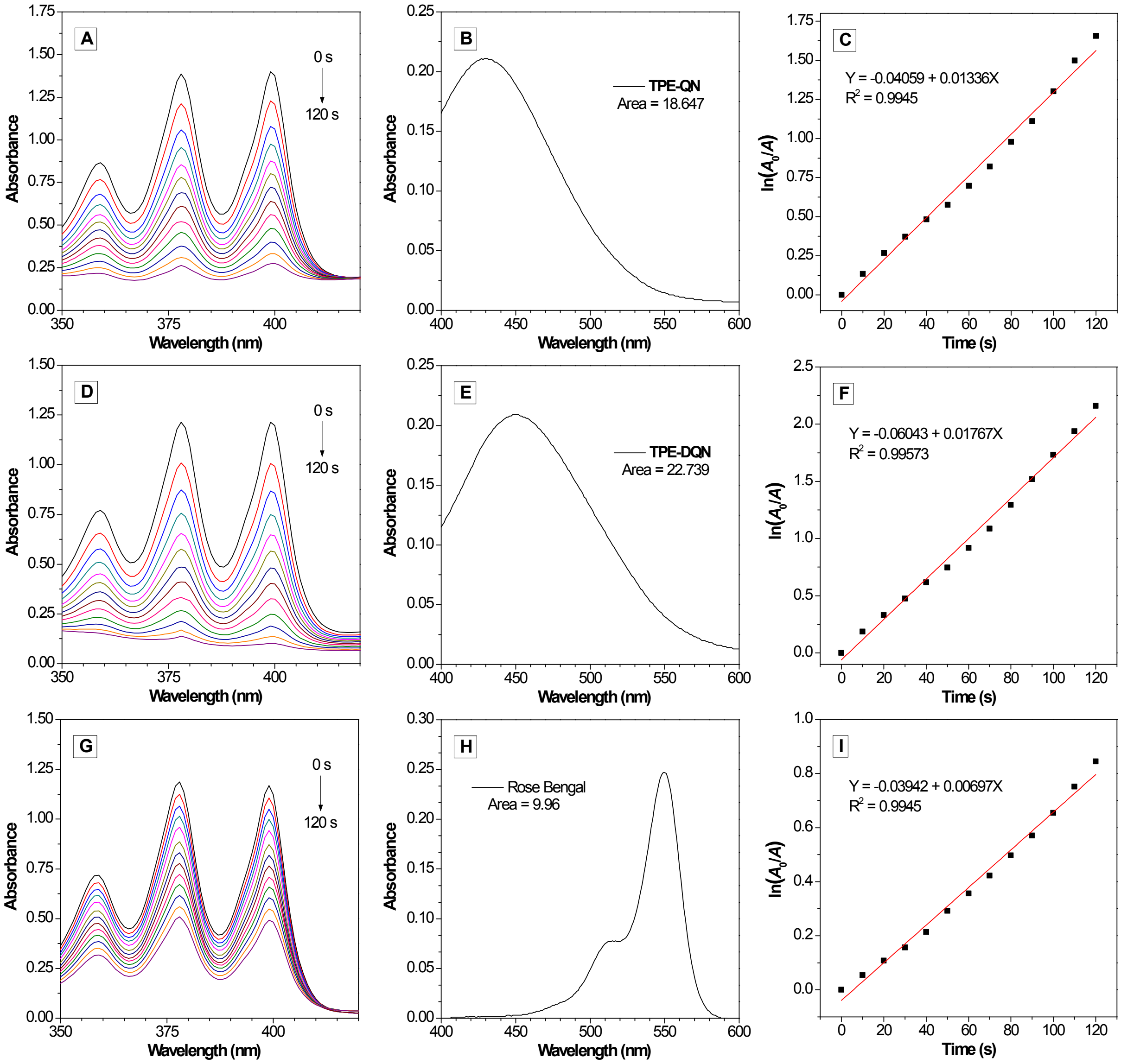


Fig. S6 Photodegradation of ABDA with TPE-QN (A), TPE-DQN (D) and RB (G). The absorption peak area of TPE-QN (B), TPE-DQN (E) and RB (H). The decomposition rate constants of ABDA by TPE-QN (C), TPE-DQN (F) and RB (I). To eliminate the inner-filter effect, the absorption maxima were adjusted to ~0.2 OD.

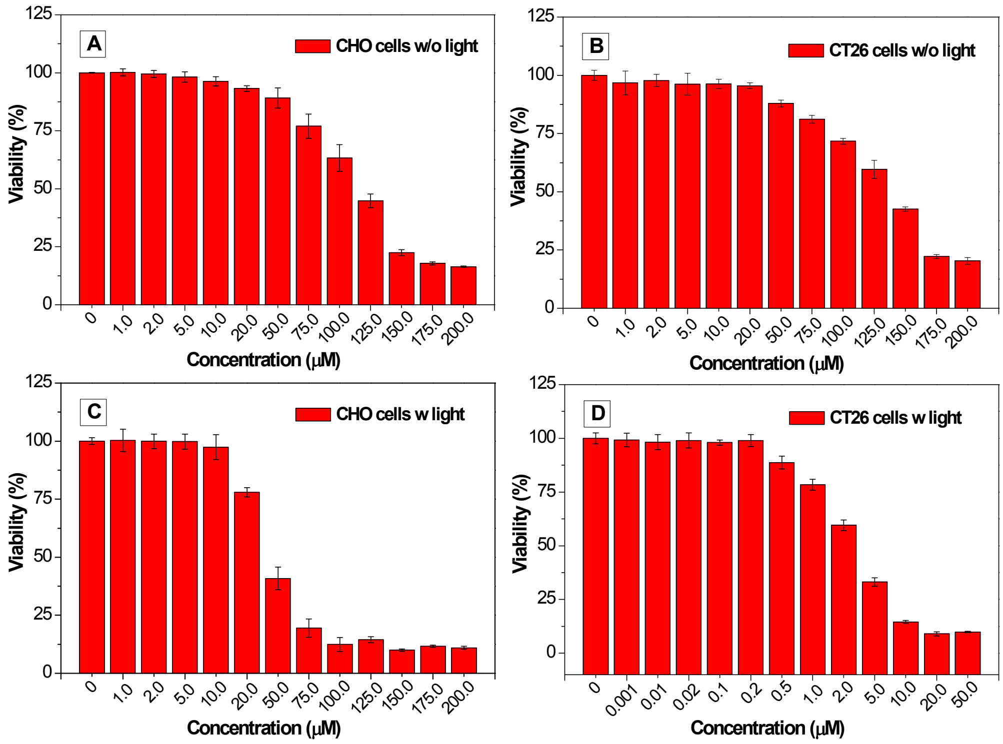


Fig. S7 The dark-toxicity of TPE-DQN towards (A) CHO cells and (B) CT26 cells. The photo-toxicity of TPE-DQN towards (C) CHO cells and (D) CT26 cells under white light irradiation (25 mW cm^{-2}, 30 min). Error bars: mean ± SD (n = 6).

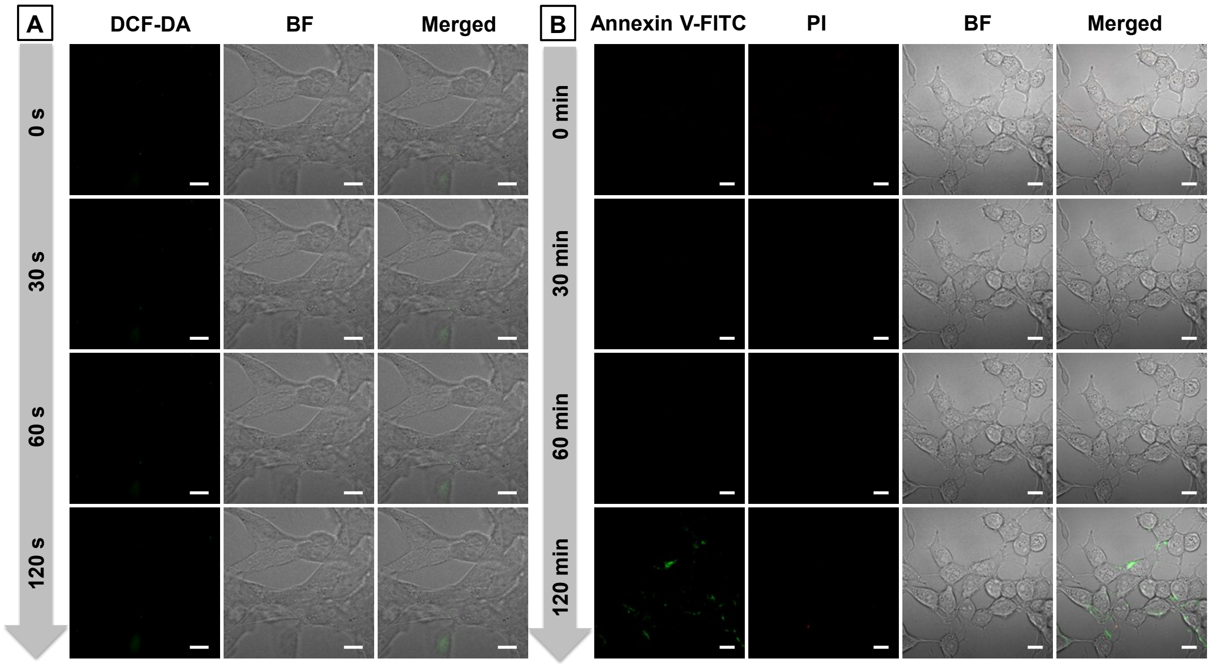


Fig. S8 (A) Intracellular ROS detection by CLSM after CT26 cells were stained with DCF-DA (20 μM) in the absence of TPE-DQN under white light illumination (25 mW cm^{-2}) for different time. (B) Apoptosis observation of CT-26 cells by CLSM after treated with TPE-DQN (2 μM) under dark. Scale bar: 10μm

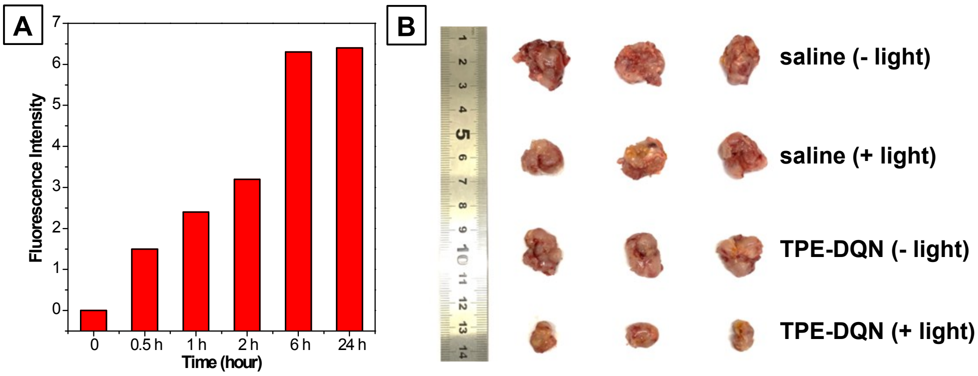
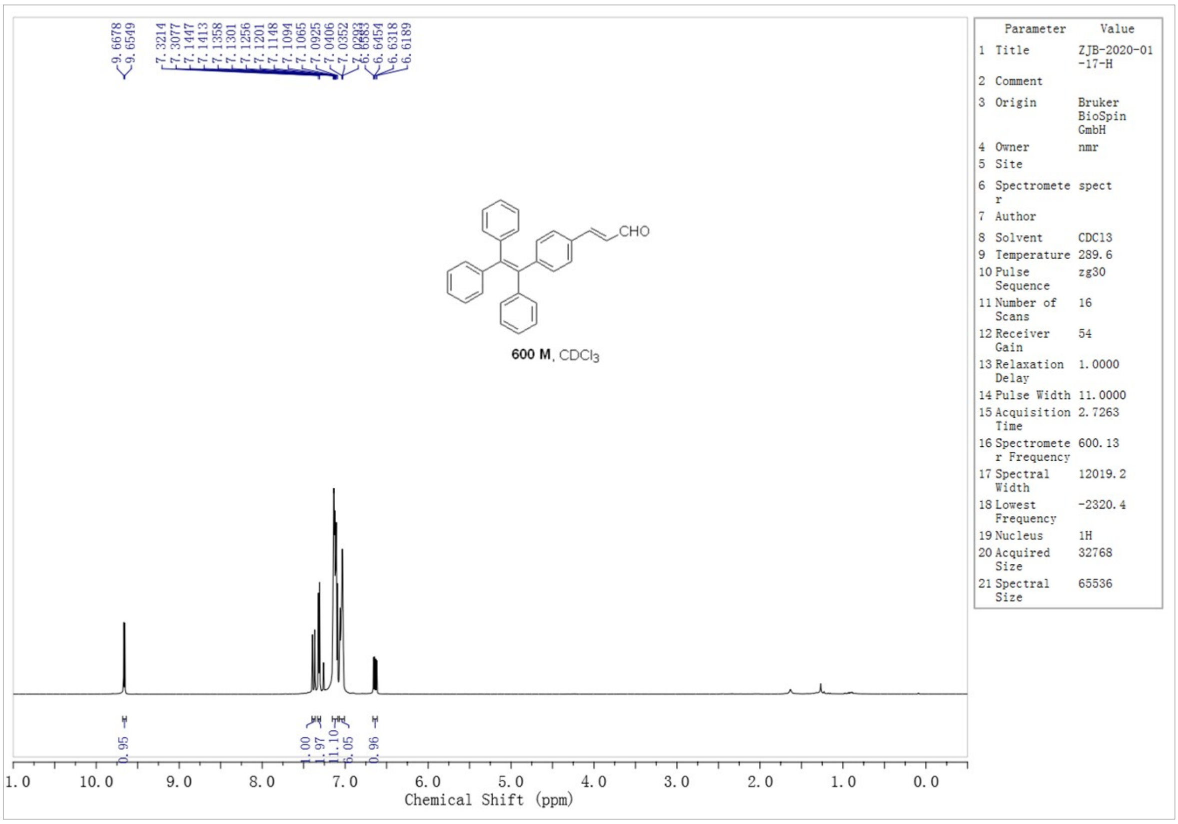


Fig. S9 (A) Fluorescence intensity change at different times after intratumorally injected with 100 μL of TPE-DQN saline solution (5 mM). (B) Tumor pictures after 10 days *in vivo* antitumor treatments at different conditions.

6. NMR Spectra



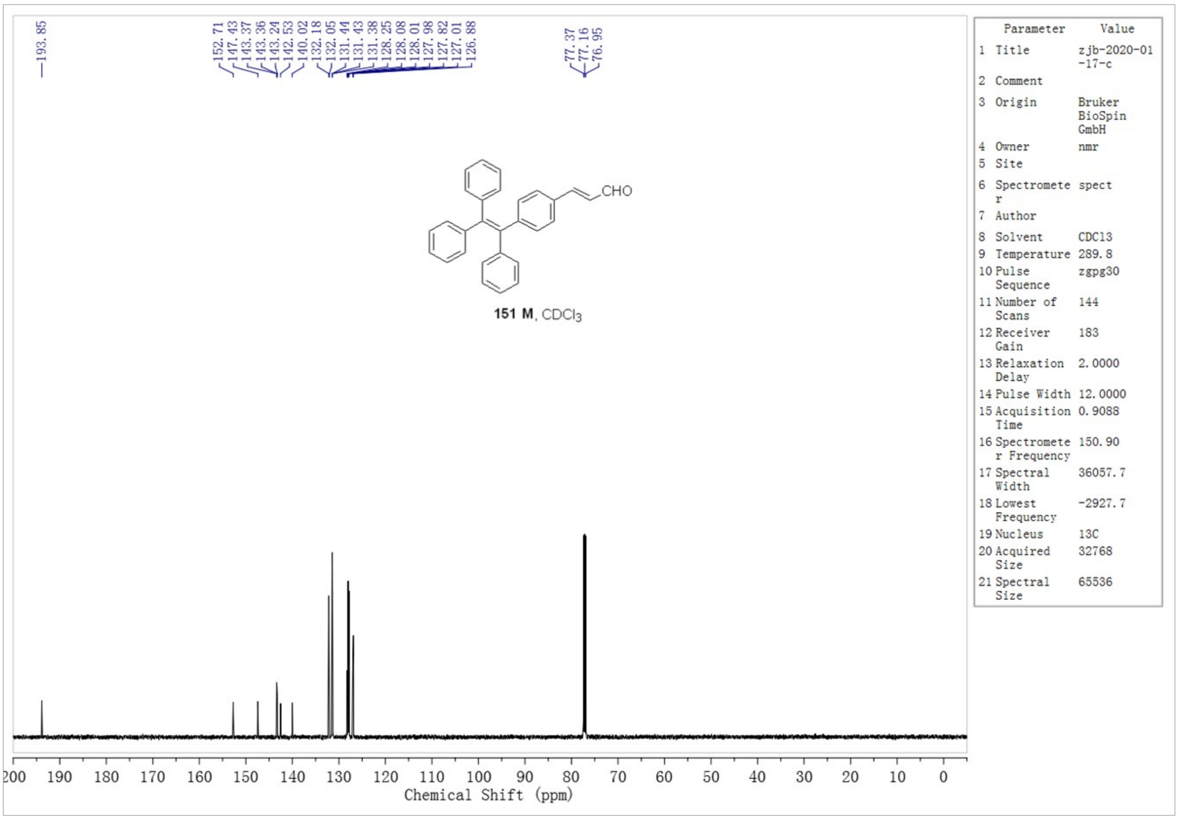
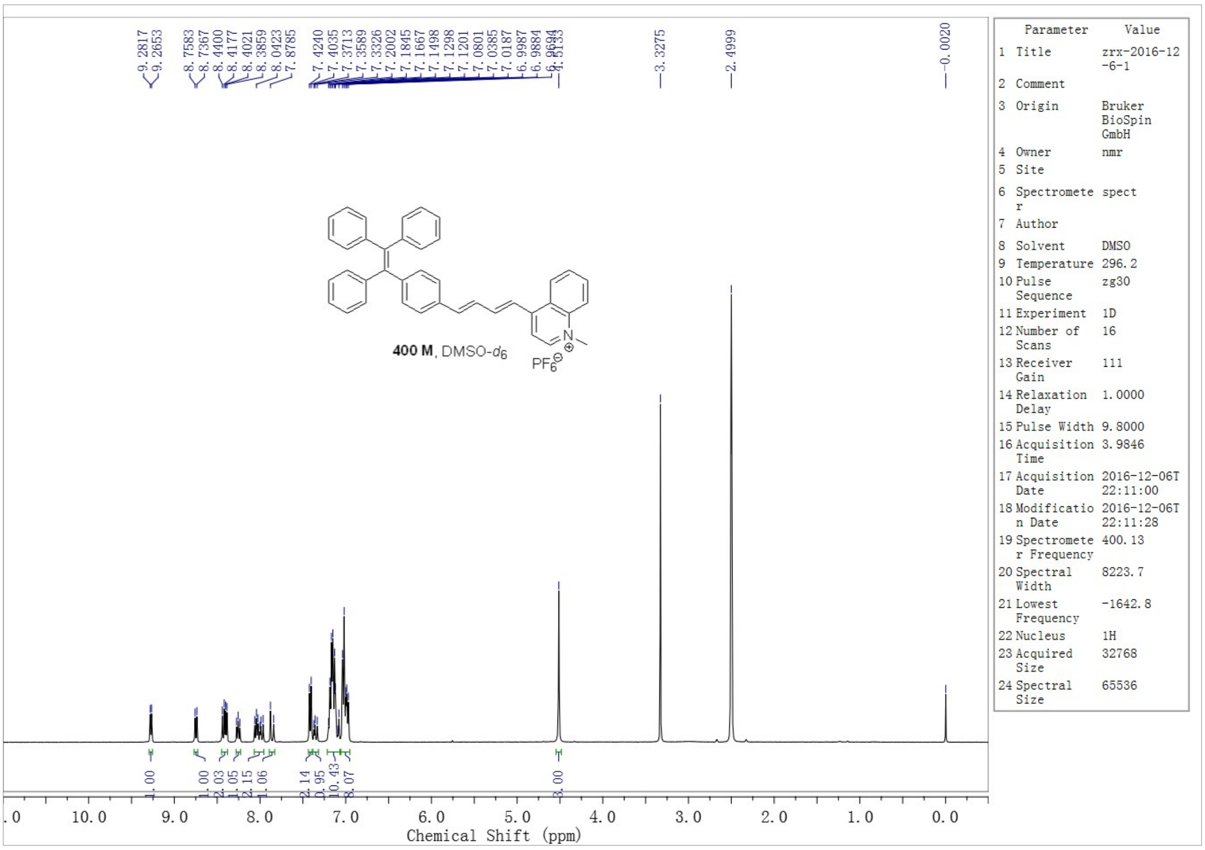


Fig. S10 ^{1}H and ^{13}C NMR spectra of TPE-CA in $CDCl_3$.



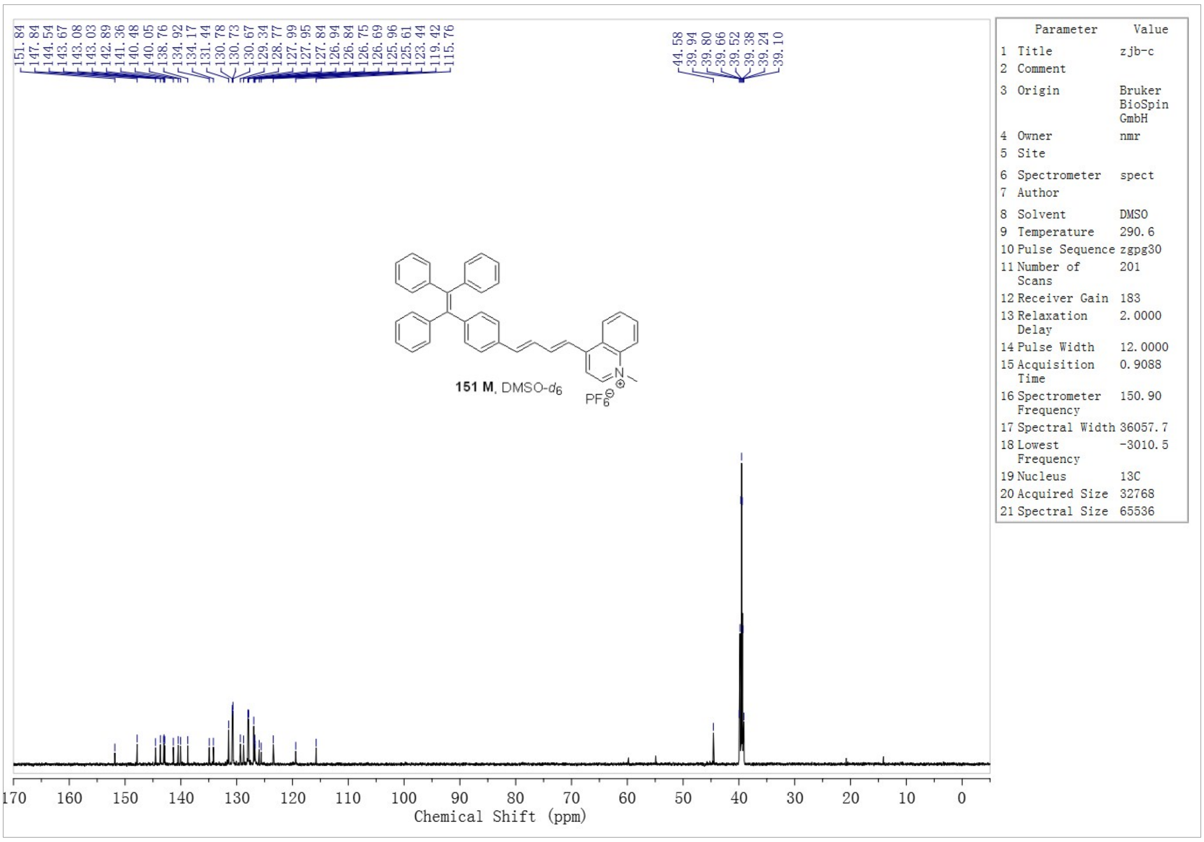


Fig. S11 ^{1}H and ^{13}C NMR spectra of TPE-DQN in DMSO-d_6.

Display Report

Analysis Info

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Acquisition Parameter

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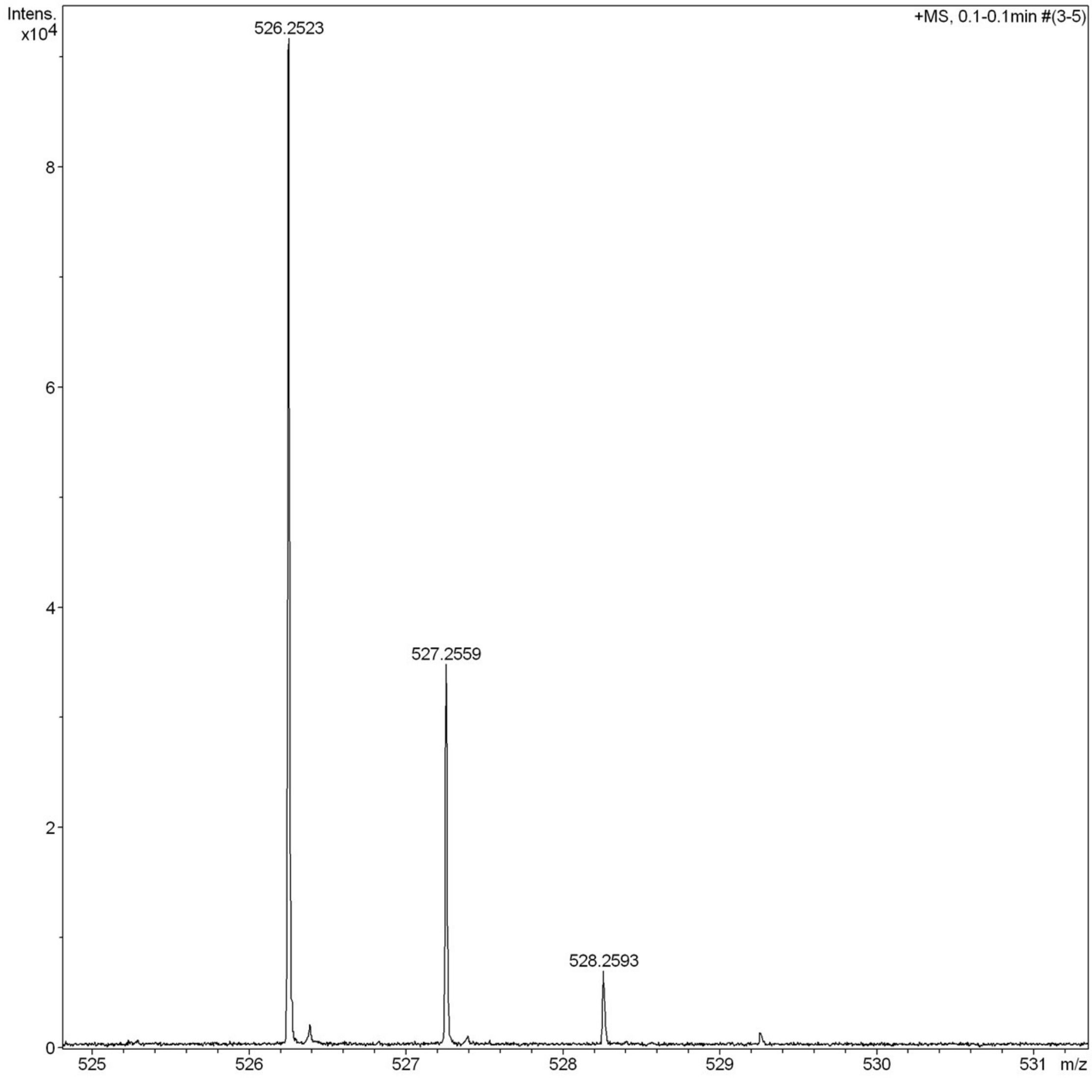

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Fig. S12 High-resolution mass spectra of TPE-DQN.

Reference

[S1] Zhang, R. X.; Li, P. F.; Zhang, W. J.; Li, N.; Zhao, N. *J. Mater. Chem. C* **2016**, *4*, 10479−10485.

[S2] 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.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, 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, J.; 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 09, Revision A.1, Gaussian, Inc.: Wallingford CT, **2009**.