Electronic Supplementary Information

Synthesis and optical properties of phenazinone-based photosensitizers for singlet oxygen generation

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1. NMR Spectra

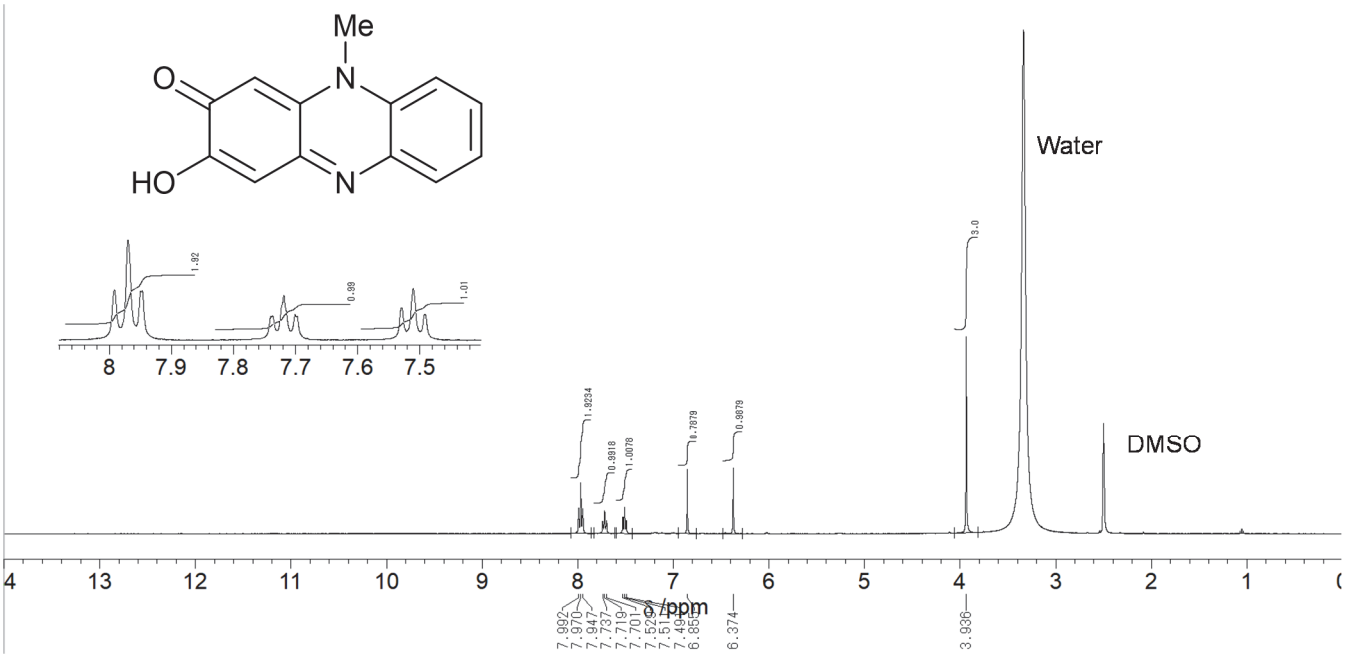


Fig. S1 ^{1}H NMR spectrum of **PZ1** in DMSO-d_6.

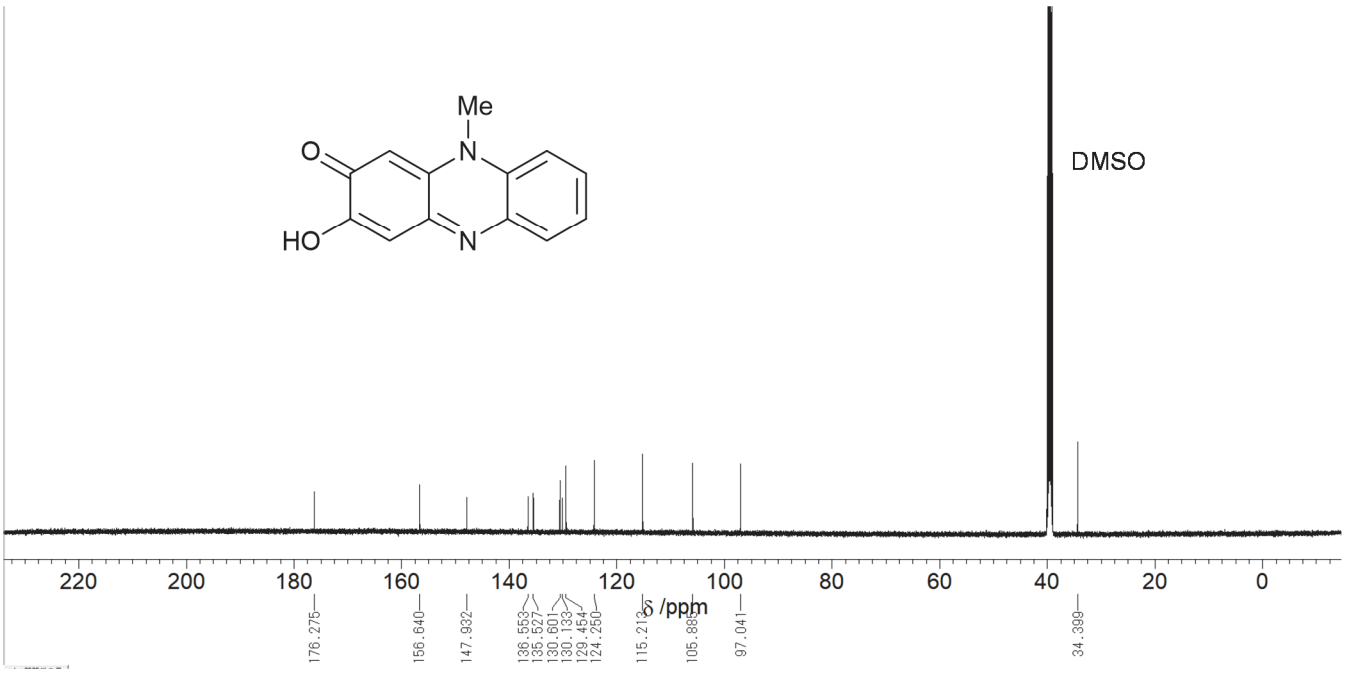


Fig. S2 ^{13}C NMR spectrum of **PZ1** in DMSO-d_6.

Fig. S3 ^{1}H NMR spectrum of **PZ2** in Acetone-d_6.

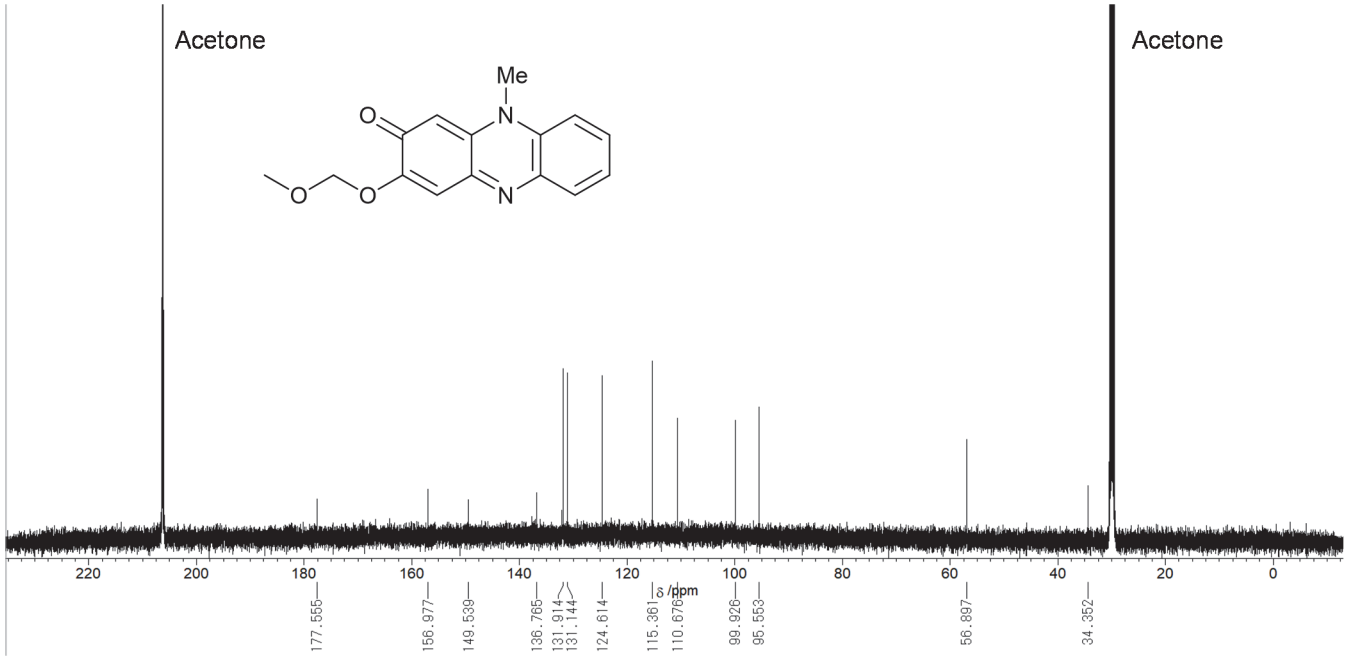


Fig. S4 ^{13}C NMR spectrum of **PZ2** in Acetone-d_6.

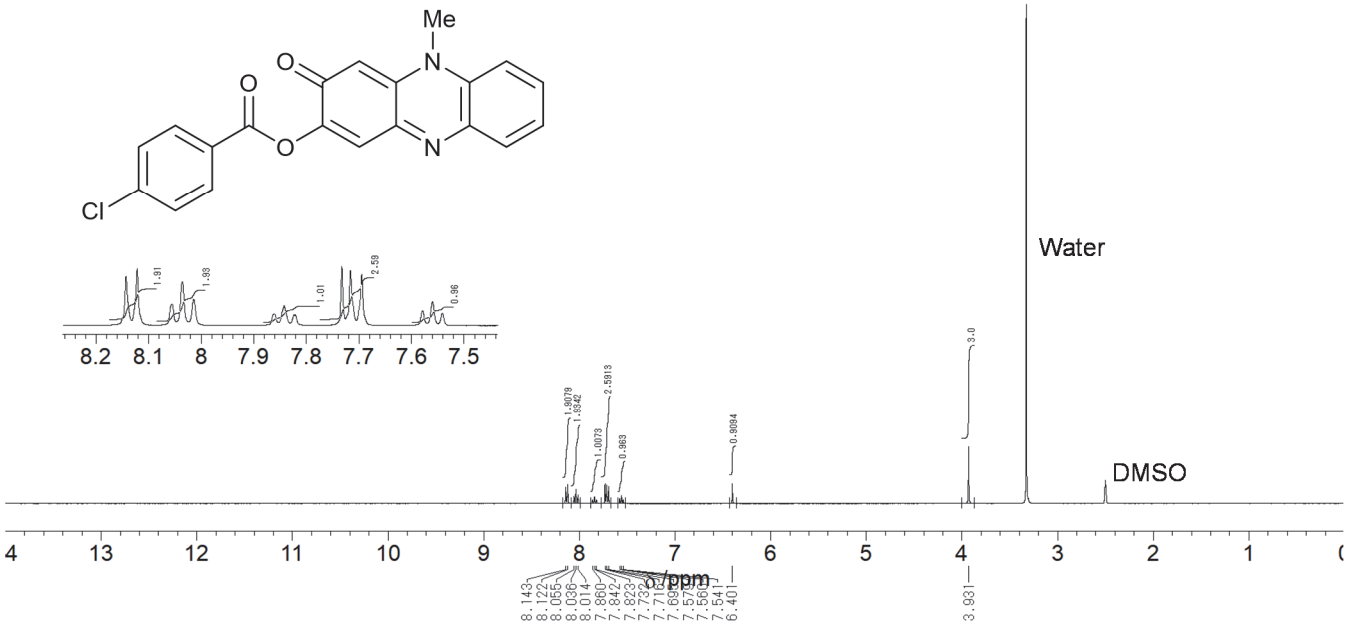


Fig. S5 ^{1}H NMR spectrum of **PZ3** in DMSO-d_6.

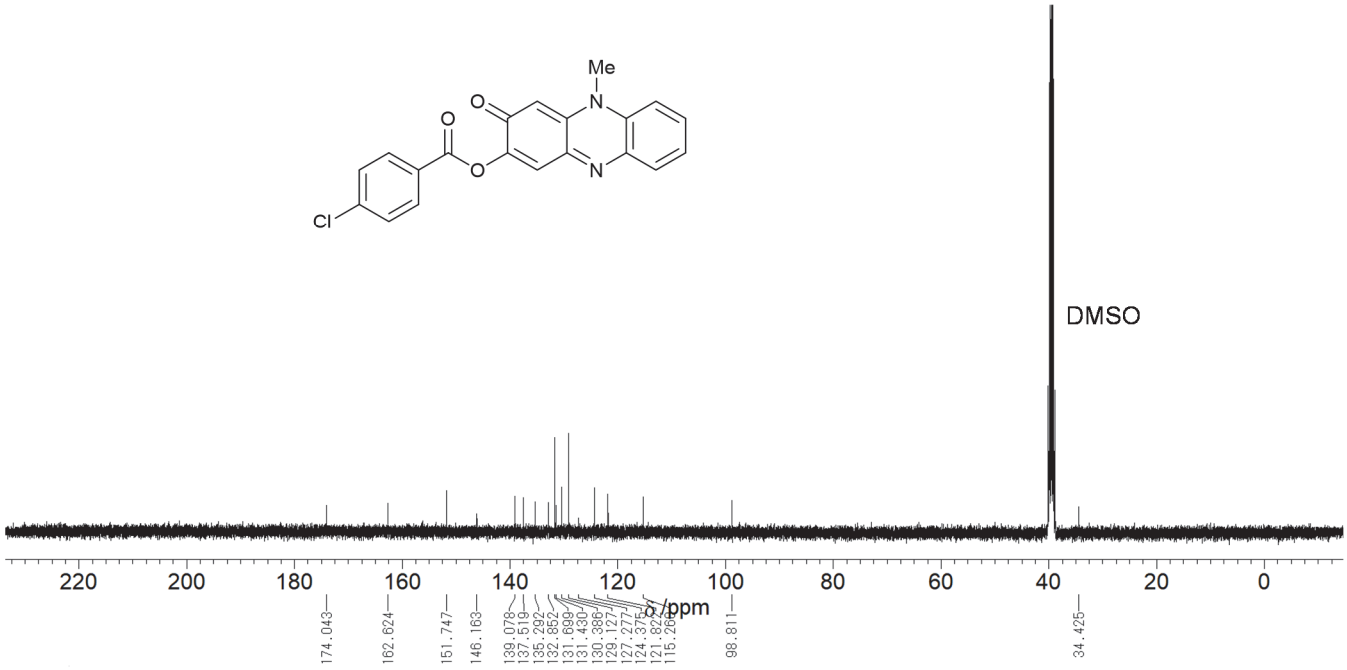


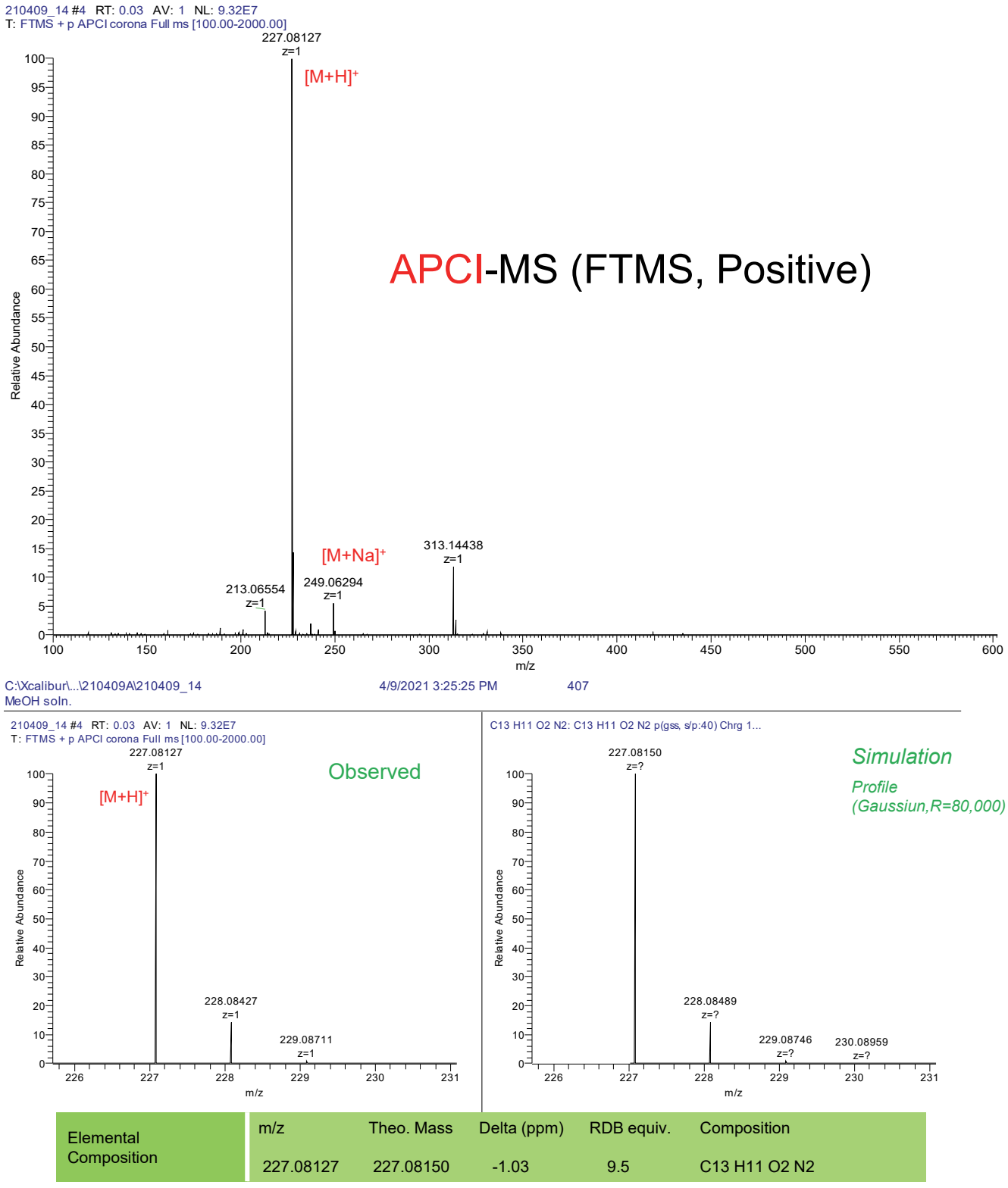
Fig. S6 ^{13}C NMR spectrum of **PZ3** in DMSO-d_6.

2. X-ray crystallographic analysis

Table S1 Crystal data and structure refinement parameters for **PZ1** (CCDC 2194829), **PZ2** (CCDC 2194831), and **PZ3** (CCDC 2194832).

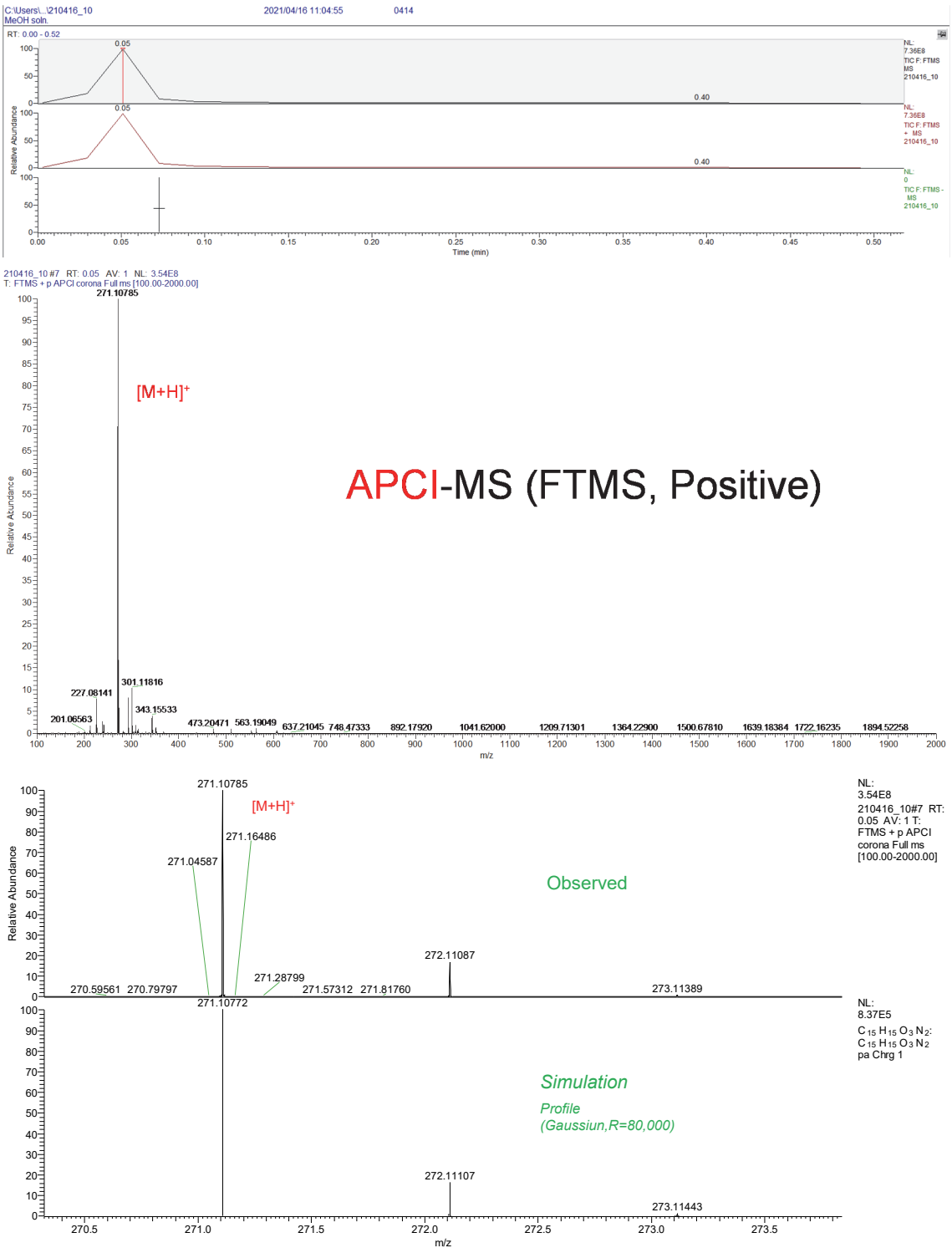
Conpound	**PZ1**	**PZ2**	**PZ3**
Molecular formula	$C_{13}H_{10}N_2O_2$	$C_{15}H_{14}N_2O_3$	$C_{20}H_{13}ClN_2O_3$
Formula weight	226.23	270.28	364.77
Number of reflection used for unit cell determination (2θ range/°)	4448(3.73-57.1)	6956(3.78-57.0)	12633(3.88-58.0)
Temperature/K	100(2)	100(2)	100(2)
Crystal System	monoclinic	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/c
a/Å	6.7461(17)	10.8605(18)	12.9125(8)
b/Å	6.8315(18)	11.1311(18)	17.0395(10)
c/Å	21.892(6)	10.3566(17)	7.2712(4)
α/°	90	90	90
β/°	93.503(3)	96.649(2)	93.9830(10)
γ/°	90	90	90
V/Å^3	1007.0(4)	1243.6(4)	1595.96(16)
Z	4	4	4
D_c/g cm^{-3}	1.492	1.444	1.518
F(000)	472	568	752
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)
Crystal size/mm^3	0.13×0.08×0.08	0.18×0.15×0.05	0.17×0.14×0.08
Range of induces h; k; l	-8, 8; -9, 8; -28, 28	-14, 14; -14, 14; -13, 13	-16, 17; -22, 22; -9, 9
Reflections collected (unique)	2397	2984	3827
Reflection observed with $I_0>2\sigma I_0$	1714	2449	3316
Number of parameters	156	183	236
Final R indexes [$I_0>2\sigma I_0$]	R_1 = 0.0434, wR_2 = 0.1073	R_1 = 0.0389, wR_2 = 0.0965	R_1 = 0.0341, wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.0656, wR_2 = 0.1197	R_1 = 0.0495, wR_2 = 0.1037	R_1 = 0.0410, wR_2 = 0.0935
Goodness-of-fit on F^2	1.055	0.998	1.025
Max. Shift/Error in final cycle	0.00	0.00	0.00
Max. peak in final diff. map/e Å^{-3}	0.338	0.332	0.359
Min. peak in final diff. map/e Å^{-3}	-0.258	-0.235	-0.281

3. HRMS Spectra



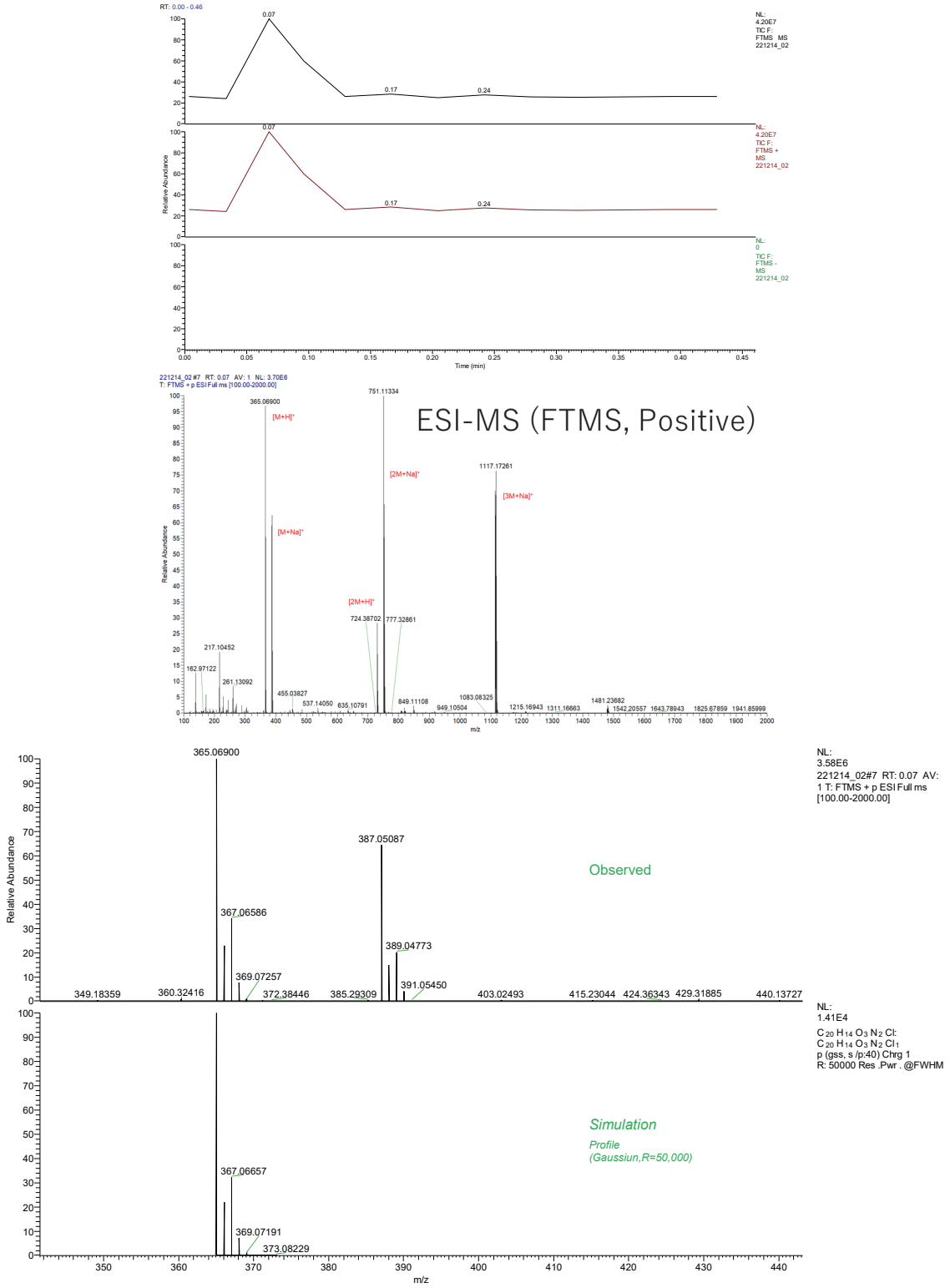
Elemental Composition	m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
	227.08127	227.08150	-1.03	9.5	C13 H11 O2 N2

Fig. S7 HRMS spectrum of **PZ1**.



Elemental Composition	m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
	271.10785	271.10772	0.48	9.5	$C_{15}H_{15}O_3N_2$

Fig. S8 HRMS spectrum of **PZ2**.



Elemental Composition	m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
	365.06900	365.06875	0.69	14.5	C20 H14 O3 N2 Cl

Fig. S9 HRMS spectrum of **PZ3**.

4. $^1O_2$ quantum yield

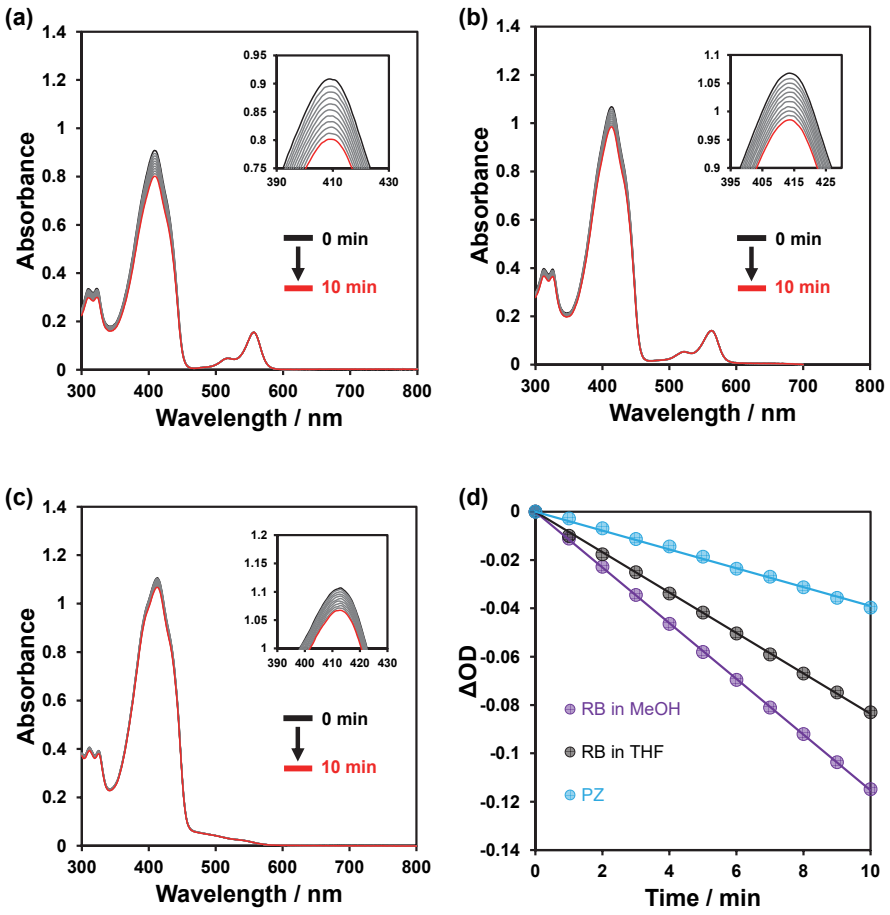
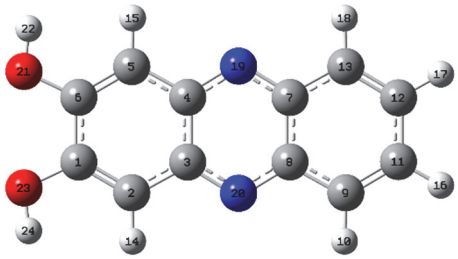


Fig. S10 Photoabsorption spectra of DPBF (5×10^{-5} M) in the presence of (a) **RB** in MeOH, (b) **RB**, and (c) **PZ** (abs. @509 nm = ca. 0.03) upon irradiation with monochromatic light (509 nm, 300 μW cm^{-2}) in THF. Insets are magnifications of peak tops in the spectra around 410 nm. (d) Plots of ΔOD of DPBF at 413 nm against photoirradiation time (509 nm, 300 μW cm^{-2}) in the presence of **RB** (in MeOH), **RB**, and **PZ** in THF.

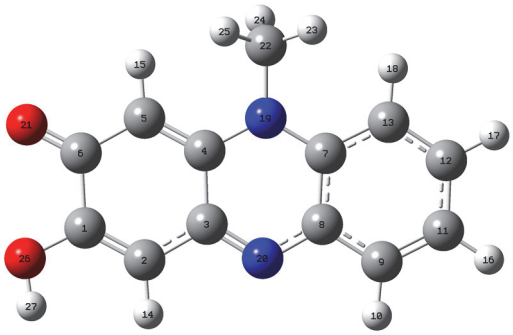
5. Theoretical calculations

Table S2 Cartesian coordinates of **PZ**.



Tag	Symbol	X	Y	Z
1	C	-2.86969	-0.7225	0
2	C	-1.68854	-1.40896	0
3	C	-0.43902	-0.72308	0
4	C	-0.43902	0.723078	0
5	C	-1.68854	1.408956	0
6	C	-2.86969	0.722496	0
7	C	1.845435	0.720318	0
8	C	1.845435	-0.72032	0
9	C	3.09172	-1.41073	0
10	H	3.063222	-2.49376	0
11	C	4.268012	-0.71202	0
12	C	4.268012	0.712019	0
13	C	3.09172	1.410729	0
14	H	-1.66691	-2.49346	0
15	H	-1.66691	2.493455	0
16	H	5.213998	-1.24156	0
17	H	5.213998	1.24156	0
18	H	3.063222	2.493756	0
19	N	0.698276	1.420527	0
20	N	0.698276	-1.42053	0
21	O	-4.09472	1.301959	0
22	H	-3.98798	2.259638	0
23	O	-4.09472	-1.30196	0
24	H	-3.98798	-2.25964	0

Table S3 Cartesian coordinates of **PZ1**.



Tag	Symbol	X	Y	Z
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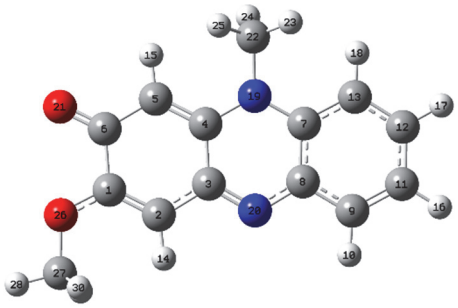
2	C	-1.84401	-1.53534	0.071829
3	C	-0.57355	-0.86255	0.057195
4	C	-0.56729	0.608948	0.011604
5	C	-1.74836	1.296425	-0.07371
6	C	-3.04102	0.64152	-0.08469
7	C	1.846161	0.468344	0.013246
8	C	1.729849	-0.94733	0.032746
9	C	2.893695	-1.73684	-0.00441
10	H	2.757881	-2.81103	0.020344
11	C	4.145401	-1.15814	-0.07638
12	C	4.252973	0.237572	-0.1212
13	C	3.125781	1.043896	-0.07993
14	H	-1.80716	-2.61885	0.121194
15	H	-1.79361	2.372707	-0.15256
16	H	5.034878	-1.77544	-0.10749
17	H	5.228797	0.703061	-0.19785
18	H	3.249121	2.115371	-0.14571
19	N	0.675988	1.217426	0.082158
20	N	0.514998	-1.58226	0.082579
21	O	-4.10397	1.243801	-0.16789
22	C	0.72866	2.67241	0.201816
23	H	1.664235	2.971053	0.66527
24	H	0.63195	3.159445	-0.77349
25	H	-0.08659	3.003575	0.843655
26	O	-4.23222	-1.42255	0.012843
27	H	-4.13687	-2.38075	0.072895

Table S4 Cartesian coordinates of **PZ2**.



Tag	Symbol	X	Y	Z
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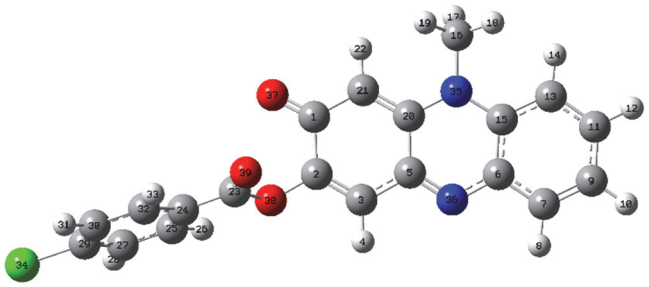
2	C	1.726784	-1.13691	-0.0528
3	C	0.380505	-0.62831	-0.04508
4	C	0.181064	0.829225	-0.00949
5	C	1.262255	1.664119	0.074815
6	C	2.628768	1.181763	0.093926
7	C	-2.19363	0.376159	-0.01688
8	C	-1.89339	-1.0121	-0.02595
9	C	-2.94439	-1.94616	0.01383
10	H	-2.66961	-2.99364	-0.00284
11	C	-4.26145	-1.53532	0.078203
12	C	-4.55043	-0.16554	0.11264
13	C	-3.53755	0.780571	0.068778
14	H	1.812389	-2.21369	-0.09627
15	H	1.167852	2.737776	0.146768
16	H	-5.06281	-2.26332	0.111218
17	H	-5.5789	0.169258	0.18318
18	H	-3.79951	1.827339	0.126614
19	N	-1.13059	1.270781	-0.08815
20	N	-0.60547	-1.48343	-0.06829
21	O	3.600497	1.921824	0.177376
22	C	-1.37126	2.705523	-0.218
23	H	-2.33606	2.877186	-0.68608
24	H	-1.34211	3.207746	0.754012
25	H	-0.60346	3.135617	-0.85981
26	O	4.085293	-0.68396	0.01216
27	C	4.381266	-2.0752	-0.06033
28	H	5.46668	-2.14726	-0.04881
29	H	3.966345	-2.61087	0.799762
30	H	3.991392	-2.51271	-0.98528

Table S5 Cartesian coordinates of **PZ3**.



Tag	Symbol	X	Y	Z	Tag	Symbol	X	Y	Z
1	C	0.253187	1.376457	-0.38198	21	C	1.655544	1.738521	-0.38233
2	C	-0.04048	-0.05977	-0.10506	22	H	1.852983	2.781825	-0.58004
3	C	0.92687	-0.97717	0.060376	23	C	-2.21069	0.102433	0.800192
4	H	0.70213	-2.02282	0.225608	24	C	-3.63401	-0.07655	0.41994
5	C	2.320106	-0.60023	0.009413	25	C	-4.02388	-0.57611	-0.82634
6	C	4.543692	-1.1951	0.069657	26	H	-3.27072	-0.84631	-1.55374
7	C	5.500031	-2.22408	0.148837	27	C	-5.37182	-0.71716	-1.13468
8	H	5.1258	-3.23279	0.272161	28	H	-5.68307	-1.09989	-2.09772
9	C	6.84958	-1.94721	0.065245	29	C	-6.32457	-0.35473	-0.18708
10	H	7.579547	-2.74499	0.12427	30	C	-5.95703	0.148488	1.058401
11	C	7.26578	-0.62061	-0.10875	31	H	-6.71633	0.426952	1.777236
12	H	8.322037	-0.3932	-0.19494	32	C	-4.6081	0.286583	1.355523
13	C	6.349169	0.416398	-0.18429	33	H	-4.29082	0.679607	2.313187
14	H	6.711108	1.421298	-0.34702	34	Cl	-8.02934	-0.5328	-0.57192
15	C	4.971476	0.151726	-0.08213	35	N	3.99944	1.143017	-0.12732
16	C	4.372999	2.555743	-0.14581	36	N	3.217409	-1.53629	0.139674
17	H	4.400021	2.949867	-1.16634	37	O	-0.6569	2.166674	-0.60917
18	H	5.345008	2.686871	0.32023	38	O	-1.36155	-0.43697	-0.14699
19	H	3.642773	3.120552	0.432054	39	O	-1.81558	0.595192	1.819729
20	C	2.650911	0.819761	-0.18202					

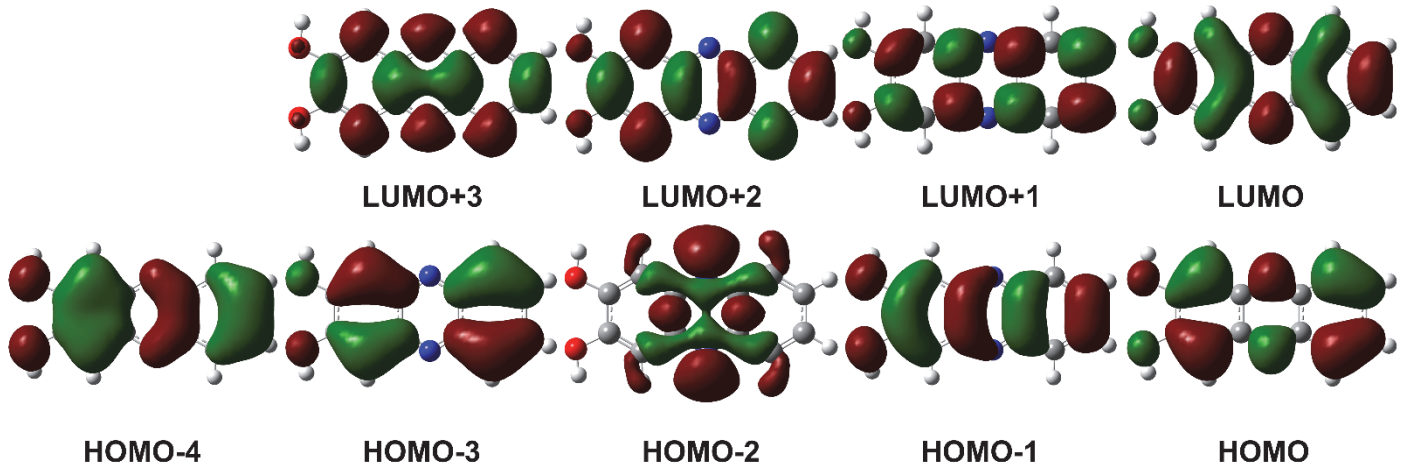


Fig. S11 Plots of visualized orbitals based on the optimized geometry of **PZ** derived from DFT calculations at B3LYP/6-311G(d,p) level.

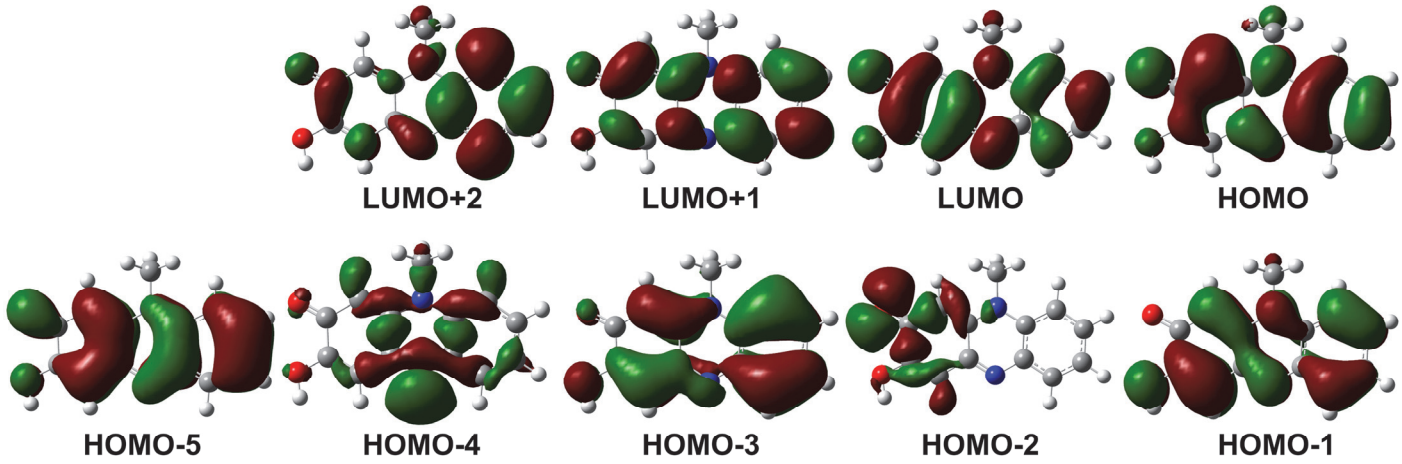


Fig. S12 Plots of visualized orbitals based on the optimized geometry of **PZ1** derived from DFT calculations at B3LYP/6-311G(d,p) level.

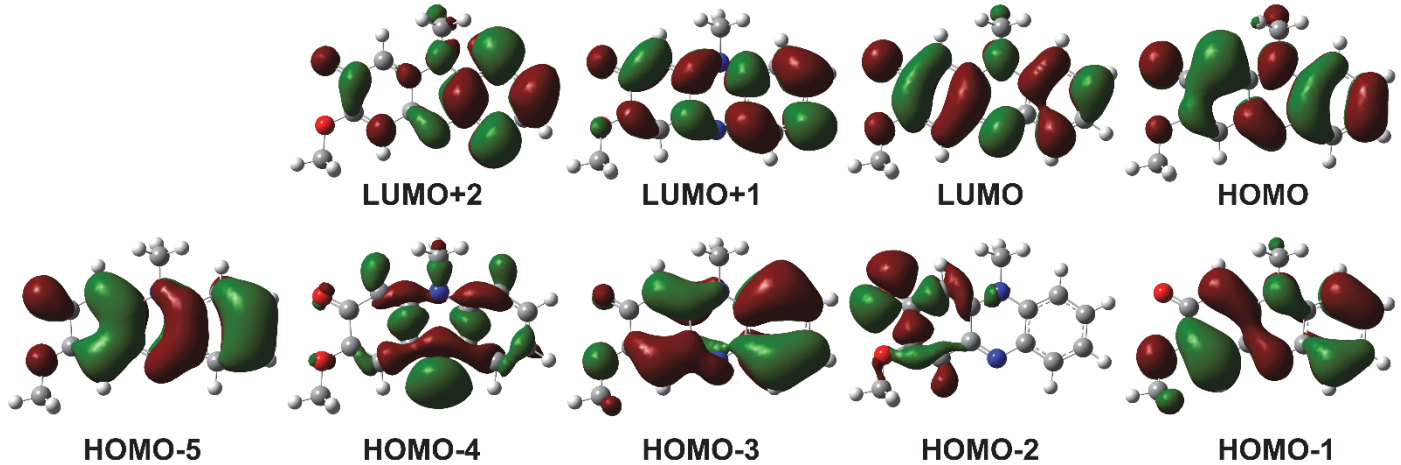


Fig. S13 Plots of visualized orbitals based on the optimized geometry of **PZ2** derived from DFT calculations at B3LYP/6-311G(d,p) level.

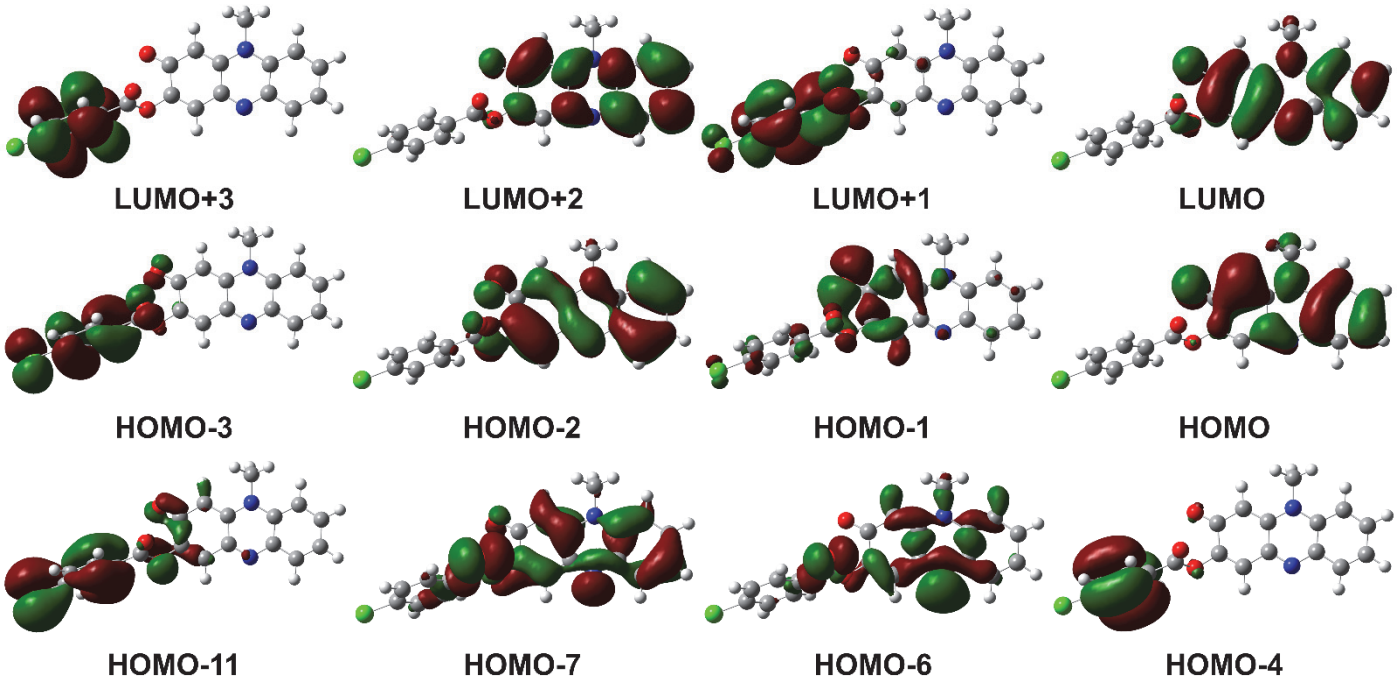


Fig. S14 Plots of visualized orbitals based on the optimized geometry of **PZ3** derived from DFT calculations at B3LYP/6-311G(d,p) level.

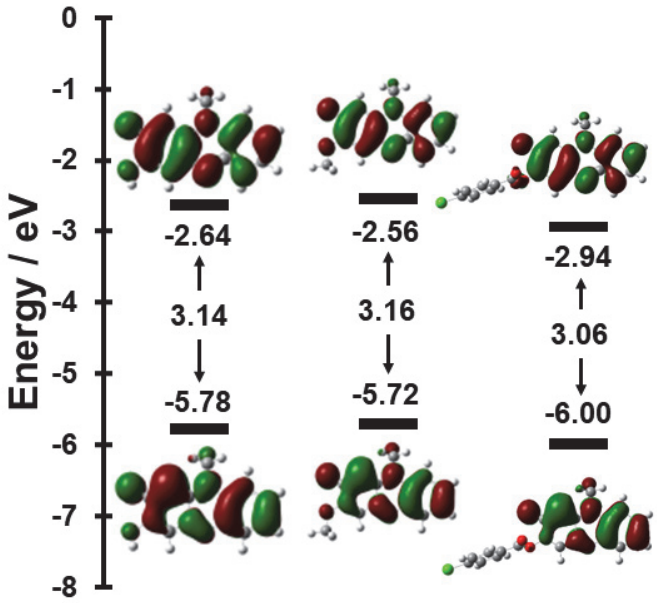


Fig. S15 Energy level diagram, HOMO and LUMO of **PZ1**–**3** from DFT calculations at B3LYP/6-311G(d,p) level.

Table S6 Excitation energy, oscillator strength, main transition orbital, and their contribution calculated for singlet states of **PZ**, **PZ1**–**3** derived from TD-DFT calculations at B3LYP/6-311G(d,p) level.

Dye	State	Excitation energy / eV	Oscillator strength	Main transition orbital	Contribution	Transition
PZ	S_1	3.22	0.025	HOMO→LUMO	0.98	ππ*
	S_2	3.22	0.0012	HOMO-2→LUMO	0.99	nπ*
	S_3	3.62	0.25	HOMO-1→LUMO	0.84	ππ*
				HOMO→LUMO+1	0.16	ππ*
PZ1	S_1	2.86	0.119	HOMO-2→LUMO	0.09	nπ*
				HOMO-1→LUMO	0.21	ππ*
				HOMO→LUMO	0.68	ππ*
	S_2	2.90	0.01	HOMO-2→LUMO	0.88	nπ*
				HOMO-1→LUMO	0.02	ππ*
				HOMO→LUMO	0.07	ππ*
	S_3	3.40	0.2879	HOMO-1→LUMO	0.71	ππ*
				HOMO-1→LUMO+1	0.02	ππ*
				HOMO→LUMO	0.2	ππ*
				HOMO→LUMO+1	0.05	ππ*
PZ2	S_1	2.87	0.122	HOMO-2→LUMO	0.11	nπ*
				HOMO-1→LUMO	0.20	ππ*
				HOMO→LUMO	0.66	ππ*
	S_2	2.91	0.017	HOMO-2→LUMO	0.85	nπ*
				HOMO-1→LUMO	0.03	ππ*
				HOMO→LUMO	0.09	ππ*
	S_3	3.37	0.30	HOMO-1→LUMO	0.72	ππ*
				HOMO-1→LUMO+1	0.02	ππ*
				HOMO→LUMO	0.20	ππ*
				HOMO→LUMO+1	0.05	ππ*
PZ3	S_1	2.73	0.19	HOMO-2→LUMO	0.08	ππ*
				HOMO→LUMO	0.89	ππ*
	S_2	2.86	0.00010	HOMO-2→LUMO	0.04	ππ*
				HOMO-1→LUMO	0.93	nπ*
	S_3	3.54	0.33	HOMO-2→LUMO	0.78	ππ*
				HOMO-1→LUMO	0.03	nπ*
				HOMO→LUMO	0.06	ππ*
				HOMO→LUMO+2	0.08	ππ*

Table S7 Excitation energy, oscillator strength, main transition orbital, and their contribution calculated for triplet states of **PZ**, **PZ1**–**3** derived from TD-DFT calculations at B3LYP/6-311G(d,p) level.

Dye	State	Excitation energy / eV	Main transition orbital	Contribution	Transition
PZ	T_1	2.02	HOMO-3→LUMO+2	0.030	ππ*
			HOMO-1→LUMO+1	0.021	ππ*
			HOMO→LUMO	0.950	ππ*
			HOMO←LUMO	0.023	ππ*
	T_2	2.66	HOMO-1→LUMO	0.982	ππ*
	T_3	2.75	HOMO-2→LUMO	0.958	nπ*
			HOMO-2→LUMO+3	0.033	nπ*
	T_4	3.27	HOMO-3→LUMO	0.754	ππ*
			HOMO-3→LUMO+3	0.023	ππ*
			HOMO→LUMO+2	0.203	ππ*
	T_5	4.14	HOMO-4→LUMO+1	0.021	ππ*
			HOMO-3→LUMO+2	0.033	ππ*
			HOMO-1→LUMO+1	0.864	ππ*
			HOMO→LUMO	0.035	ππ*
			HOMO→LUMO+3	0.024	ππ*
PZ1	T_1	1.65	HOMO-1→LUMO	0.041	ππ*
			HOMO→LUMO	0.95	ππ*
			HOMO←LUMO	0.026	ππ*
	T_2	2.34	HOMO-1→LUMO	0.91	ππ*
			HOMO→LUMO	0.038	ππ*
	T_3	2.52	HOMO-2→LUMO	0.93	nπ*
			HOMO-2→LUMO+2	0.02	nπ*
	T_4	3.34	HOMO-4→LUMO	0.85	nπ*
			HOMO-3→LUMO	0.09	ππ*
	T_5	3.44	HOMO-5→LUMO	0.075	ππ*
			HOMO-5→LUMO+1	0.02	ππ*
			HOMO-4→LUMO	0.07	nπ*
			HOMO-3→LUMO	0.26	ππ*
			HOMO-3→LUMO+2	0.052	ππ*
			HOMO-1→LUMO+2	0.092	ππ*
			HOMO→LUMO+1	0.38	ππ*
PZ2	T_1	1.67	HOMO-1→LUMO	0.032	ππ*
			HOMO→LUMO	0.96	ππ*
			HOMO←LUMO	0.025	ππ*
	T_2	2.36	HOMO-1→LUMO	0.91	ππ*

			HOMO→LUMO	0.030	ππ*
			HOMO→LUMO+1	0.021	ππ*
	T_3	2.54	HOMO-2→LUMO	0.93	nπ*
			HOMO-2→LUMO+2	0.020	nπ*
	T_4	3.35	HOMO-4→LUMO	0.84	nπ*
			HOMO-3→LUMO	0.10	ππ*
	T_5	3.44	HOMO-5→LUMO	0.072	ππ*
			HOMO-5→LUMO+1	0.023	ππ*
			HOMO-4→LUMO	0.071	nπ*
			HOMO-3→LUMO	0.21	ππ*
			HOMO-3→LUMO+2	0.053	ππ*
			HOMO-1→LUMO+2	0.079	ππ*
			HOMO→LUMO+1	0.43	ππ*
PZ3	T_1	1.63	HOMO-2→LUMO	0.039	ππ*
			HOMO→LUMO	0.95	ππ*
			HOMO←LUMO	0.022	ππ*
	T_2	2.43	HOMO-2→LUMO	0.76	ππ*
			HOMO-1→LUMO	0.11	nπ*
			HOMO→LUMO	0.037	ππ*
	T_3	2.53	HOMO-2→LUMO	0.12	ππ*
			HOMO-1→LUMO	0.80	nπ*
	T_4	3.24	HOMO-7→LUMO	0.15	nπ*
			HOMO-6→LUMO	0.78	nπ*
	T_5	3.40	HOMO-11→LUMO+1	0.020	ππ*
			HOMO-4→LUMO+3	0.15	ππ*
			HOMO-3→LUMO	0.038	ππ*
			HOMO-3→LUMO+1	0.71	ππ*
			HOMO-1→LUMO+1	0.035	nπ*

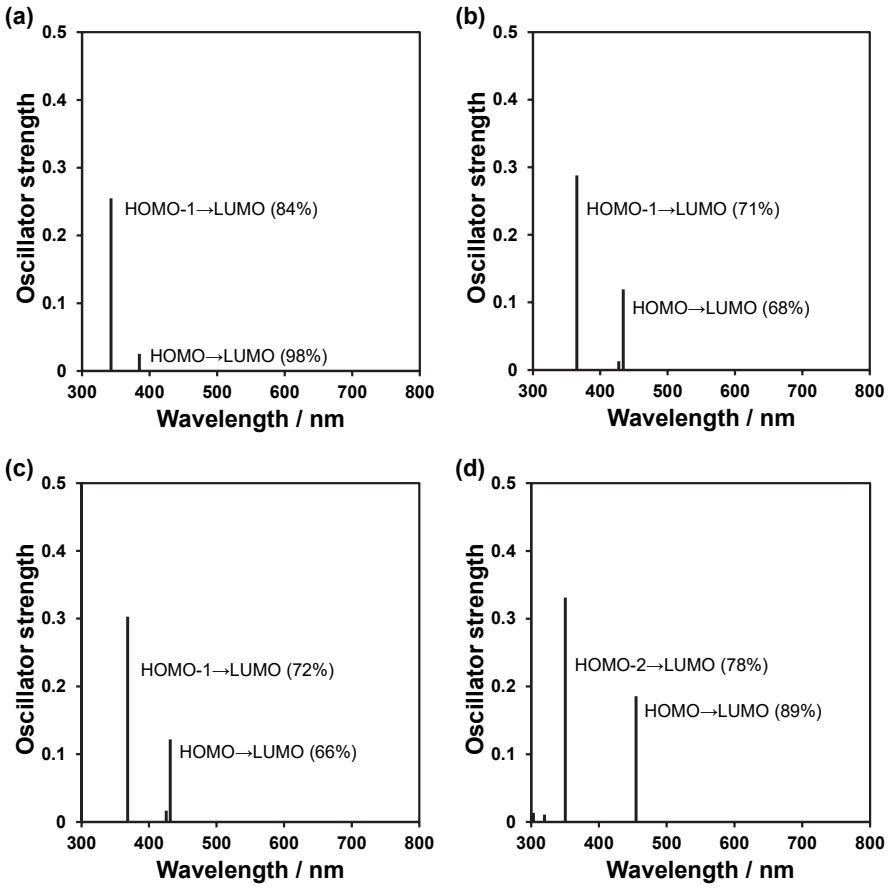


Fig. S16 Calculated oscillator strength and the contributions of (a) **PZ**, (b) **PZ1**, (c) **PZ2**, and (d) **PZ3** derived from TD-DFT calculations at B3LYP/6-311G(d.p) level.

Table S8 Optical energy gaps (E_g^{opt}) and energy levels of S_1 of **PZ1**, **PZ2**, and **PZ3**.

	λ(0,0) / nm	E_g^{opt} / eV	Energy level / eV
PZ1	526	2.36	2.86
PZ2	542	2.29	2.87
PZ3	568	2.18	2.73

E_g^{opt} were determined from the intersection of photoabsorption and fluorescence spectra (Fig. 3) in THF.

Table S9 Energy difference between S_1 and T_3 of **PZ**, **PZ1**, **PZ2**, and **PZ3** derived from TD-DFT calculations.

	$\Delta E(S_1,T_3)$ / eV
PZ	-0.47
PZ1	−0.34
PZ2	−0.33
PZ3	−0.20

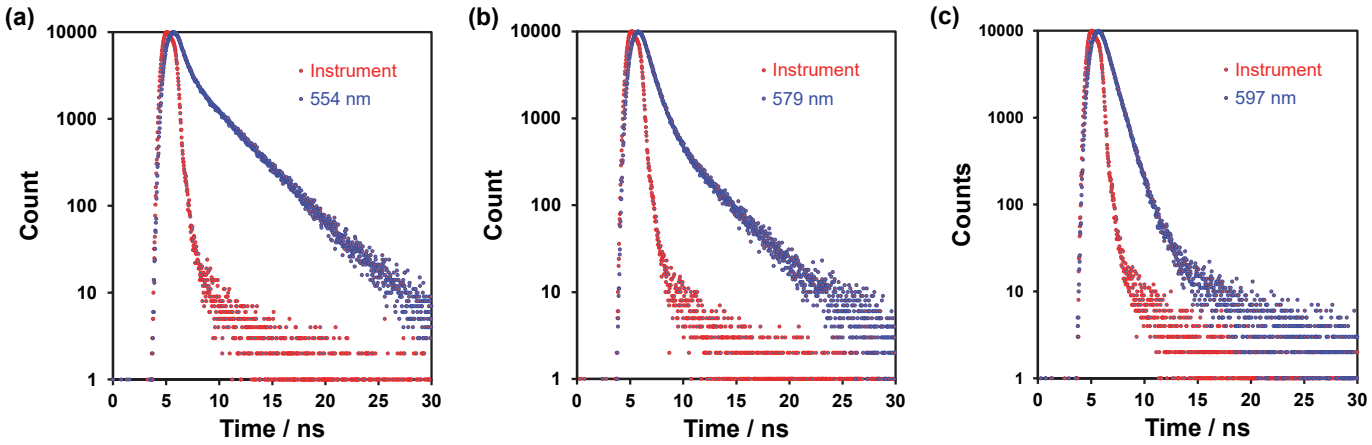


Fig. S17 Instrument profiles (red dots) and fluorescence decay profiles (blue dots) of (a) **PZ1** (λ_{ex} = 451 nm), (b) **PZ2** (λ_{ex} = 451 nm), and (c) **PZ3** (k: λ_{ex} = 451 nm).