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Electronic Supplementary Information

Development of phenazine-2,3-diol-based photosensitizers: effect of substitution of cyano group for nitro group on singlet oxygen generation

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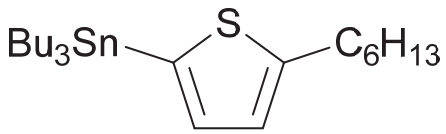
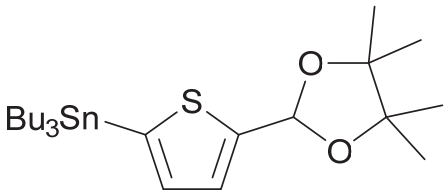
1. Synthesis



S1

S1 was synthesized by the method in our previous work.[1]



S2

S2 was synthesized by the method in our previous work.[2]

Reference

1. K. Imato, K. Ohira, M. Yamaguchi, T. Enoki and Y. Ooyama, *Mater. Chem. Front.*, 2020, **4**, 589−596.

2. K. Ohira, K. Imato and Y. Ooyama, *Mater. Chem. Front.*, 2021, **5**, 5298−5304.

2. NMR Spectra

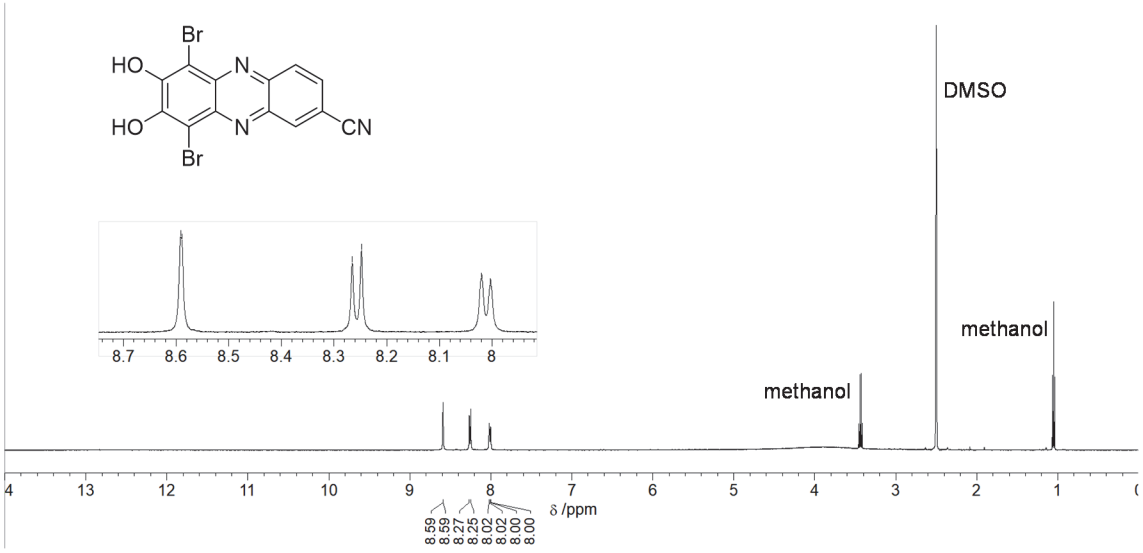


Fig. S1 ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

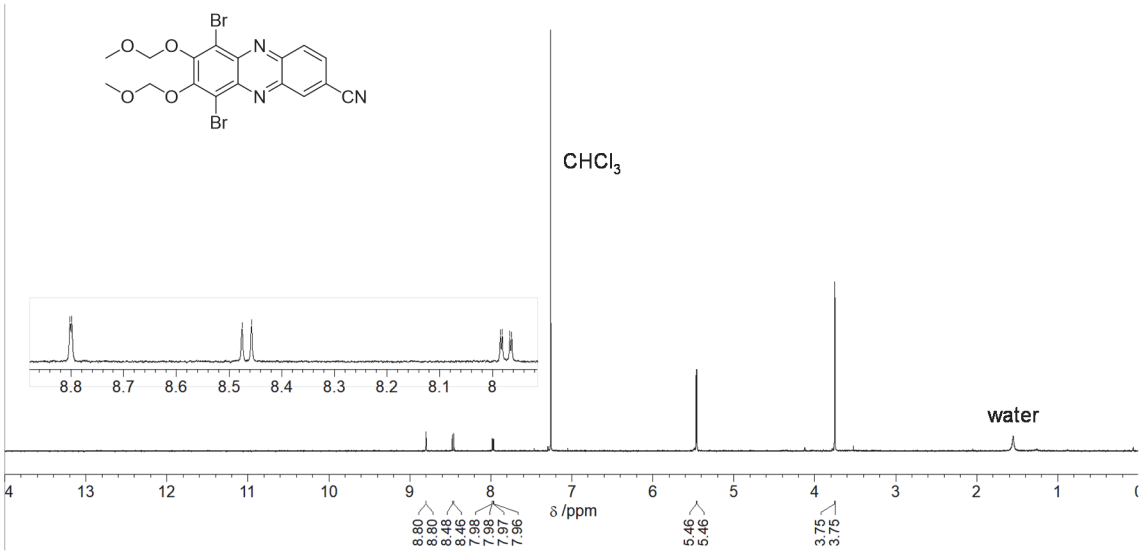


Fig. S2 ^{1}H NMR spectrum of compound **2** in chloroform-d_1.

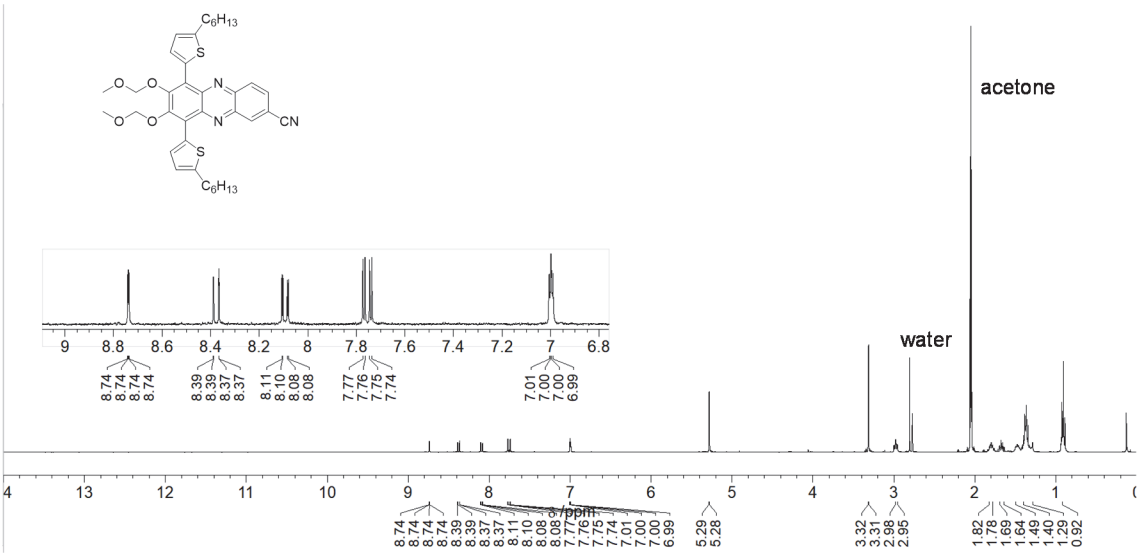


Fig. S3 ^{1}H NMR spectrum of compound **3** in Acetone-d_6.

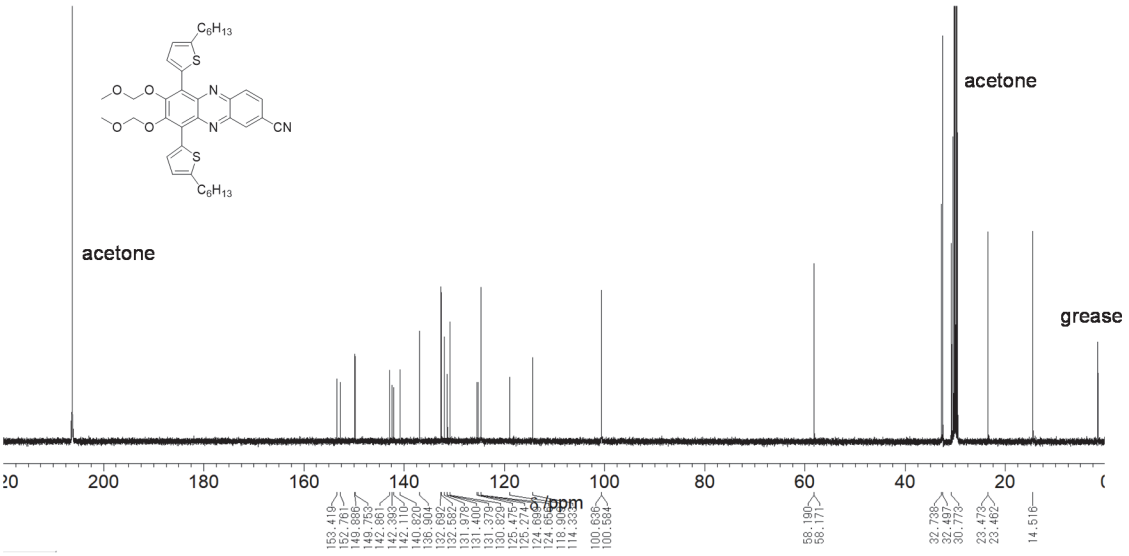


Fig. S4 ^{13}C NMR spectrum of compound **3** in Acetone-d_6.

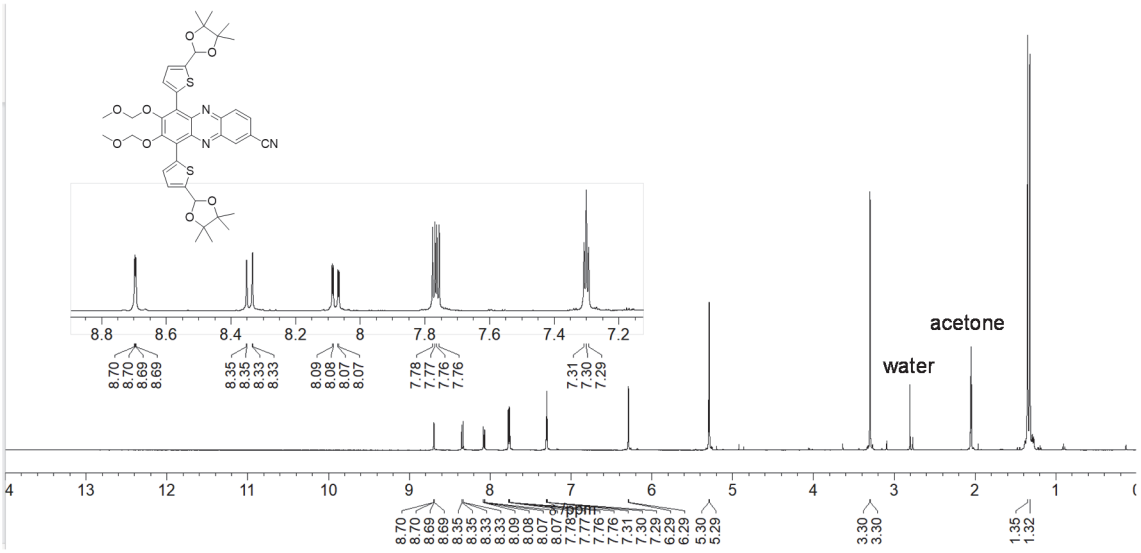


Fig. S5 ^{1}H NMR spectrum of compound **4** in Acetone-d_6.

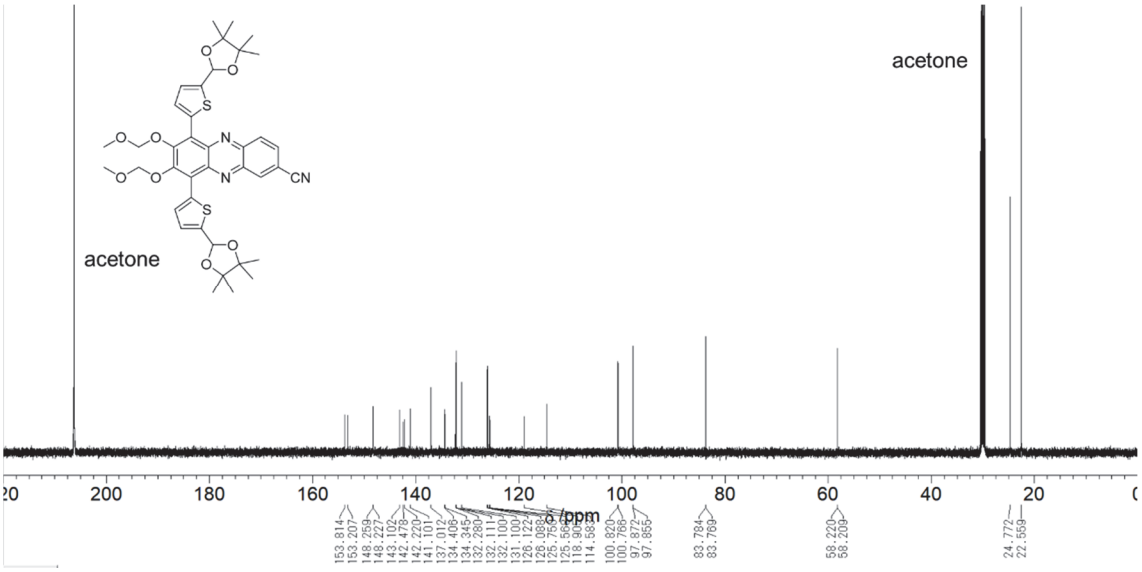


Fig. S6 ^{13}C NMR spectrum of compound **4** in Acetone-d_6.

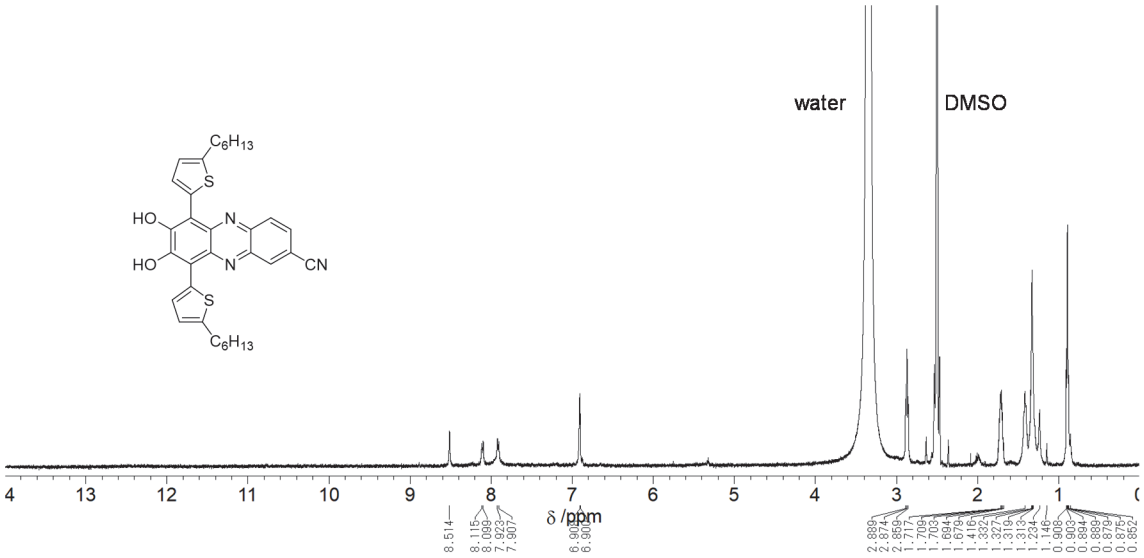


Fig. S7 ^{1}H NMR spectrum of **YC-1** in DMSO-d_6.

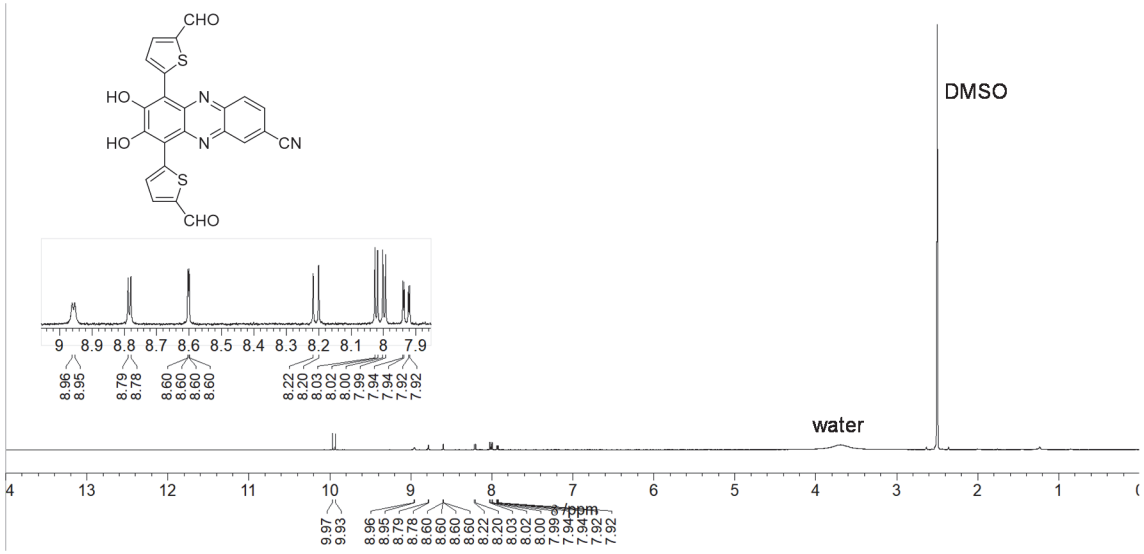
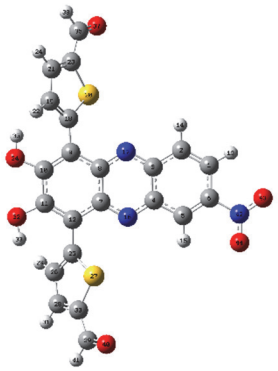


Fig. S8 ^{1}H NMR spectrum of **YC-2** in DMSO-d_6.

3. Theoretical calculation

Table S1 The cartesian coordinates of S_0 state geometry of **KI-3** optimized by DFT at the B3LYP/6-31G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
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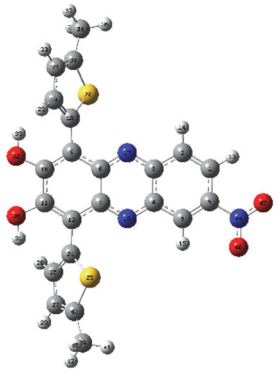
4	C	-0.8813	1.851643	0.042748
5	C	-1.77148	2.955123	0.116823
6	C	-1.25572	4.222542	0.007386
7	C	-0.51524	-0.41524	0.072715
8	C	0.90848	-0.17849	-0.10604
9	C	1.819375	-1.29201	-0.18155
10	C	1.304481	-2.57256	-0.0639
11	C	-0.11251	-2.80908	0.099313
12	C	-1.01575	-1.76425	0.184146
13	H	0.467826	5.505281	-0.25473
14	H	2.064464	3.581397	-0.38806
15	H	-2.83105	2.785091	0.255635
16	N	-1.37184	0.600177	0.147184
17	N	1.390189	1.059852	-0.2124
18	C	3.266503	-1.10438	-0.37266
19	C	4.073298	-1.78289	-1.27626
20	S	4.212494	-0.02416	0.619144
21	C	5.441831	-1.44116	-1.16989
22	H	3.681133	-2.46672	-2.02104

Tag	Symbol	X	Y	Z
23	C	5.683693	-0.50717	-0.18344
24	H	6.222294	-1.85333	-1.79949
25	C	-2.44581	-2.05075	0.378662
26	C	-2.9908	-2.93379	1.30129
27	S	-3.6894	-1.35622	-0.62955
28	C	-4.39608	-3.05502	1.196384
29	H	-2.39895	-3.43773	2.057335
30	C	-4.92595	-2.2713	0.191837
31	H	-5.00203	-3.68366	1.838975
32	O	-0.44654	-4.11233	0.149021
33	H	-1.41544	-4.19293	0.177018
34	O	2.04717	-3.69382	-0.08076
35	H	2.98899	-3.45267	-0.11704
36	C	6.966984	0.073277	0.182057
37	O	7.1249	0.916024	1.054704
38	H	7.822833	-0.31704	-0.40442
39	C	-6.3274	-2.14521	-0.17903
40	O	-6.74704	-1.42071	-1.07097
41	H	-7.01261	-2.77566	0.422478
42	N	-2.17525	5.364787	0.083375
43	O	-1.69468	6.495729	-0.01609
44	O	-3.37563	5.137745	0.242264

Table S2 The cartesian coordinates of S_0 state geometry of **KI-5** optimized by DFT at the B3LYP/6-31G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
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3	C	0.255775	2.148644	-0.12921
4	C	-1.10876	1.732538	0.035403
5	C	-2.13395	2.711869	0.104818
6	C	-1.78715	4.037197	0.00741
7	C	-0.45496	-0.46879	0.055373
8	C	0.932488	-0.04732	-0.09459
9	C	1.980137	-1.03078	-0.14623
10	C	1.630089	-2.36779	-0.05253
11	C	0.254491	-2.78705	0.071587
12	C	-0.77998	-1.87069	0.138821
13	H	-0.24059	5.533482	-0.22937
14	H	1.591831	3.832089	-0.35194
15	H	-3.16404	2.40487	0.230095
16	N	-1.43739	0.42764	0.123936
17	N	1.251572	1.245384	-0.19076
18	C	3.400212	-0.66529	-0.28485
19	C	4.304353	-1.14786	-1.20699
20	S	4.214268	0.413801	0.836522
21	C	5.63052	-0.65605	-1.02174
22	H	4.01814	-1.80464	-2.02212
23	H	6.463271	-0.92023	-1.66411

Tag	Symbol	X	Y	Z
24	C	-2.16403	-2.35075	0.283723
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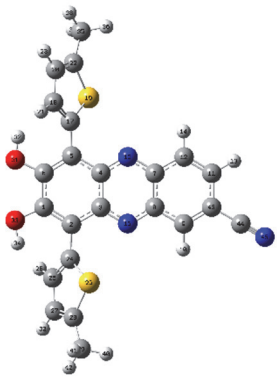
26	S	-3.44824	-1.89288	-0.8233
27	C	-4.02285	-3.57868	1.028994
28	H	-2.03806	-3.65032	2.014715
29	H	-4.56657	-4.26174	1.672155
30	O	0.079256	-4.12314	0.109977
31	H	-0.87812	-4.30191	0.141977
32	O	2.522569	-3.37576	-0.06395
33	H	3.416015	-2.98854	-0.10818
34	C	6.98569	0.905096	0.527886
35	H	7.238872	0.624877	1.556121
36	H	6.862553	1.993226	0.505932
37	H	7.834424	0.64794	-0.11092
38	C	5.756555	0.196314	0.043271
39	C	-6.0274	-3.0153	-0.50018
40	H	-6.09348	-3.37704	-1.53199
41	H	-6.52618	-2.04087	-0.46225
42	H	-6.58602	-3.70611	0.136427
43	C	-4.6069	-2.93153	-0.02795
44	N	-2.84715	5.048124	0.076699
45	O	-2.51821	6.233602	-0.01281
46	O	-4.01066	4.66713	0.220452

Table S3 The cartesian coordinates of S_0 state geometry of **YC-1** optimized by DFT at the B3LYP/6-31G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
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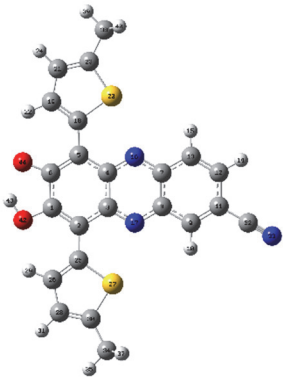
4	C	0.817933	0.06147	-0.08649
5	C	1.704009	-1.07108	-0.14319
6	C	1.155147	-2.33922	-0.05218
7	C	0.48268	2.335107	-0.11712
8	C	-0.9284	2.132397	0.04943
9	C	-1.79193	3.257504	0.120127
10	H	-2.85527	3.089095	0.247205
11	C	0.14252	4.737187	-0.14648
12	C	0.989996	3.664019	-0.21476
13	H	0.522862	5.749812	-0.21906
14	H	2.059124	3.795015	-0.34217
15	N	1.329605	1.290613	-0.18099
16	N	-1.45119	0.892734	0.137875
17	C	3.162671	-0.92533	-0.28588
18	C	3.981231	-1.54412	-1.20667
19	S	4.133924	0.023431	0.82833
20	C	5.367131	-1.25846	-1.02612
21	H	3.596698	-2.15348	-2.01816
22	C	5.62361	-0.4297	0.034055
23	H	6.148635	-1.64912	-1.66842
24	C	-2.59093	-1.74546	0.291243
25	C	-3.20314	-2.56376	1.216981
26	S	-3.79007	-1.11213	-0.82532
27	C	-4.61349	-2.67873	1.037821
28	H	-2.66289	-3.03696	2.030596
29	C	-5.09234	-1.96116	-0.02638
30	H	-5.25398	-3.26895	1.683837
31	O	1.88355	-3.47283	-0.06942
32	H	2.825318	-3.22593	-0.11326
33	O	-0.64644	-3.83678	0.111875
34	H	-1.61978	-3.86549	0.148548
35	C	6.947233	0.088018	0.511586
36	H	6.991436	1.18198	0.478921
37	H	7.15667	-0.21741	1.542464
38	H	7.745827	-0.30155	-0.1249
39	C	-6.50816	-1.83798	-0.5041
40	H	-6.86043	-0.80144	-0.46829
41	H	-6.62211	-2.18704	-1.53609
42	H	-7.16384	-2.43983	0.130301
43	C	-1.26577	4.532153	0.023415
44	C	-2.1349	5.669934	0.091732
45	N	-2.83181	6.600554	0.145593

Table S4 The cartesian coordinates of S_0 state geometry of **YC-1P** optimized by DFT at the B3LYP/6-31+G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
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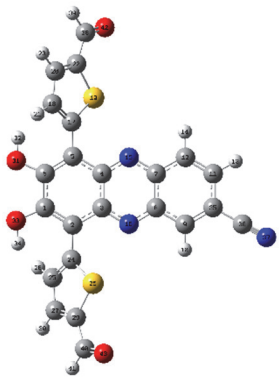
4	C	0.86745	-0.12118	0.001954
5	C	1.773117	-1.22659	-0.00062
6	C	1.194518	-2.52231	-0.00168
7	C	0.532879	2.179496	0.002671
8	C	-0.88483	1.990278	0.004093
9	C	-1.74567	3.110349	0.004871
10	H	-2.81822	2.94842	0.006154
11	C	-1.21005	4.393981	0.004314
12	C	0.206697	4.590058	0.003013
13	C	1.0528	3.507337	0.002232
14	H	0.60229	5.600163	0.002675
15	H	2.129898	3.639281	0.001213
16	N	1.366934	1.122309	0.001583
17	N	-1.40721	0.736852	0.00535
18	C	3.229401	-1.06883	-0.0028
19	C	4.185011	-2.0743	-0.00634
20	S	4.059364	0.503734	-0.00027
21	C	5.532035	-1.60731	-0.00675
22	H	3.902633	-3.11647	-0.00838

Tag	Symbol	X	Y	Z
23	C	5.644714	-0.24138	-0.00359
24	H	6.391857	-2.27126	-0.00932
25	C	-2.64473	-1.8618	0.011031
26	C	-3.30905	-3.07852	0.03845
27	S	-3.84796	-0.55753	-0.02589
28	C	-4.72979	-2.97407	0.028642
29	H	-2.7876	-4.02295	0.064697
30	C	-5.18686	-1.68234	-0.00752
31	H	-5.38947	-3.83636	0.047906
32	C	-2.07862	5.530813	0.005103
33	N	-2.77773	6.464354	0.005731
34	C	-6.60716	-1.19625	-0.02644
35	H	-7.29071	-2.05037	-0.00746
36	H	-6.83523	-0.56313	0.839284
37	H	-6.82735	-0.60872	-0.9257
38	C	6.893147	0.592838	-0.00294
39	H	7.773116	-0.05783	-0.00577
40	H	6.954364	1.243387	-0.88398
41	H	6.956558	1.238654	0.881434
42	O	-0.62878	-3.96948	0.001203
43	H	0.273641	-4.40565	-0.00343
44	O	1.811527	-3.64265	-0.00597

Table S5 The cartesian coordinates of S_0 state geometry of **YC-2** optimized by DFT at the B3LYP/6-31G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
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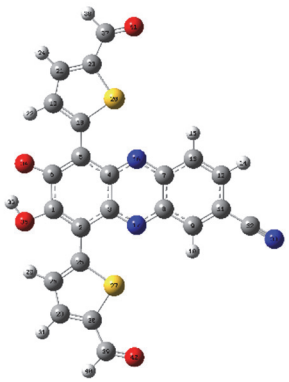
3	C	0.623407	-0.13962	-0.08357
4	C	-0.81411	-0.01748	0.09193
5	C	-1.63496	-1.20062	0.168472
6	C	-1.01894	-2.43551	0.045834
7	C	-0.60957	2.272156	0.120541
8	C	0.808988	2.150146	-0.05814
9	C	1.608097	3.32166	-0.13247
10	H	2.67822	3.214569	-0.26799
11	C	-0.40685	4.687464	0.149841
12	C	-1.19252	3.568594	0.223088
13	H	-0.84317	5.676875	0.226353
14	H	-2.26616	3.638778	0.358621
15	N	-1.39212	1.179051	0.192928
16	N	1.396801	0.941202	-0.15815
17	C	-3.09149	-1.12873	0.363359
18	C	-3.84555	-1.90256	1.23689
19	S	-4.11783	-0.08048	-0.58232
20	C	-5.23561	-1.66142	1.141206
21	H	-3.40379	-2.58393	1.955694
22	C	-5.54796	-0.70853	0.193203

Tag	Symbol	X	Y	Z
23	H	-5.98232	-2.15677	1.75151
24	C	2.679554	-1.6156	-0.3797
25	C	3.298716	-2.45937	-1.29253
26	S	3.858808	-0.81476	0.627398
27	C	4.70859	-2.46672	-1.18055
28	H	2.753348	-3.01515	-2.04729
29	C	5.168992	-1.63483	-0.18043
30	H	5.36598	-3.04985	-1.81558
31	O	-1.66884	-3.61422	0.053038
32	H	-2.6273	-3.45004	0.073582
33	O	0.850133	-3.83036	-0.15994
34	H	1.822487	-3.83288	-0.181
35	C	1.009643	4.563136	-0.02997
36	C	1.810705	5.749929	-0.10354
37	N	2.451168	6.719708	-0.16207
38	C	-6.87106	-0.2113	-0.15079
39	H	-7.69492	-0.69036	0.415409
40	C	6.553775	-1.3931	0.194677
41	H	7.290163	-1.97243	-0.39766
42	O	-7.09246	0.654373	-0.9867
43	O	6.910174	-0.62861	1.080904

Table S6 The cartesian coordinates of S_0 state geometry of **YC-2P** optimized by DFT at the B3LYP/6-31+G(d,p)/THF-IEFPCM level.



Tag	Symbol	X	Y	Z
1	C	-0.40748	-2.7079	-0.00533
2	C	-1.26442	-1.62397	-0.00119
3	C	-0.61066	-0.32344	-0.00215
4	C	0.855018	-0.2022	-0.0037
5	C	1.713047	-1.35498	-0.00537
6	C	1.080216	-2.62723	-0.00785
7	C	0.628157	2.108963	-0.00281
8	C	-0.79446	1.98434	-0.00207
9	C	-1.60465	3.142641	-0.00166
10	H	-2.68347	3.031253	-0.00113
11	C	-1.00705	4.397112	-0.00191
12	C	0.416415	4.527684	-0.0025
13	C	1.212413	3.407204	-0.00293
14	H	0.858139	5.518262	-0.00263
15	H	2.294314	3.488022	-0.00344
16	N	1.412098	1.00962	-0.00363
17	N	-1.37179	0.754872	-0.00155
18	C	3.163373	-1.25421	-0.00403
19	C	4.071615	-2.32456	-0.00569
20	S	4.041627	0.278136	0.002336
21	C	5.417894	-1.92879	-0.00123
22	H	3.733504	-3.3492	-0.00958
23	C	5.587971	-0.55038	0.003904
24	H	6.250873	-2.62526	-0.00138
25	C	-2.72086	-1.77572	0.003592
26	C	-3.43428	-2.97961	0.013727
27	S	-3.83828	-0.4127	-0.00317
28	C	-4.83064	-2.81401	0.015384
29	H	-2.94965	-3.94271	0.020024
30	C	-5.22151	-1.48461	0.006367
31	H	-5.53533	-3.63945	0.023065
32	C	-1.82031	5.576108	-0.00153
33	N	-2.47172	6.54259	-0.00124
34	O	1.638805	-3.77086	-0.01147
35	O	-0.81133	-3.982	-0.00737
36	H	0.065819	-4.46735	-0.01032
37	C	6.847064	0.143161	0.010639
38	H	7.729817	-0.52793	0.010346
39	C	-6.58345	-1.00593	0.006057
40	H	-7.34393	-1.81219	0.013108
41	O	7.005998	1.370334	0.016758
42	O	-6.93526	0.176534	-0.00117

Table S7 Excitation energy, oscillator strength, main transition orbital, and their contribution for singlet states of **KI-3**, **KI-5**, **YC-1**, and **YC-2** at B3LYP/6-31G(d,p)/THF-IEFPCM level, and **YC-1P** and **YC-2P** at B3LYP/6-31G+(d,p)/THF-IEFPCM level.

PS	State	Excitation energy / eV	Oscillator strength	Main transition orbital	Contribution	Transition
KI-3	S1	2.49	0.0974	HOMO→LUMO	0.99	ππ*
	S2	2.98	0.0019	HOMO-2→LUMO	0.88	nπ*
	S3	3.08	0.1321	HOMO-1→LUMO	0.71	ππ*
KI-5	S1	2.23	0.0539	HOMO→LUMO	0.99	ππ*
	S2	2.77	0.0321	HOMO-1→LUMO	0.92	ππ*
	S3	2.94	0.0013	HOMO-3→LUMO	0.72	nπ*
YC-1	S1	2.42	0.0806	HOMO→LUMO	0.99	ππ*
	S2	2.97	0.036	HOMO-1→LUMO	0.92	ππ*
	S3	3.07	0.0017	HOMO-4→LUMO	0.38	ππ*
				HOMO-3→LUMO	0.45	nπ*
YC-2	S1	2.62	0.1722	HOMO→LUMO	0.98	ππ*
	S2	3.07	0.0044	HOMO-2→LUMO	0.88	nπ*
	S3	3.23	0.2277	HOMO-1→LUMO	0.72	ππ*
YC-1P	S1	1.88	0.0696	HOMO→LUMO	0.97	ππ*
	S2	2.72	0.1078	HOMO-1→LUMO	0.82	ππ*
	S3	3.06	0.5963	HOMO→LUMO+1	0.83	ππ*
YC-2P	S1	2.18	0.2028	HOMO→LUMO	0.94	ππ*
	S2	2.66	0.5482	HOMO→LUMO+1	0.93	ππ*
	S3	2.98	0.5275	HOMO-1→LUMO	0.73	ππ*

Table S8 Excitation energy, oscillator strength, main transition orbital, and their contribution for triplet states of **KI-3**, **KI-5**, **YC-1**, and **YC-2** at B3LYP/6-31G(d,p)/THF-IEFPCM level, and **YC-1P** and **YC-2P** at B3LYP/6-31G+(d,p)/THF-IEFPCM level.

PS	State	Excitation energy / eV	Main transition orbital	Contribution	Transition
KI-3	T_1	1.77	HOMO→LUMO	0.81	ππ*
	T_2	2.34	HOMO-1→LUMO	0.80	ππ*
	T_3	2.48	HOMO→LUMO+1	0.45	ππ*
	T_4	2.61	HOMO-2→LUMO	0.72	nπ*
KI-5	T_1	1.68	HOMO→LUMO	0.77	ππ*
	T_2	2.29	HOMO-1→LUMO	0.66	ππ*
	T_3	2.59	HOMO-3→LUMO	0.59	nπ*
	T_4	2.64	HOMO-4→LUMO	0.46	ππ*
YC-1	T_1	1.75	HOMO→LUMO	0.83	ππ*
	T_2	2.38	HOMO-1→LUMO	0.71	ππ*
	T_3	2.66	HOMO-3→LUMO	0.44	nπ*
	T_4	2.72	HOMO-4→LUMO	0.36	nπ*
YC-2	T_1	1.80	HOMO→LUMO	0.88	ππ*
	T_2	2.37	HOMO-1→LUMO	0.85	ππ*
	T_3	2.48	HOMO→LUMO+1	0.55	ππ*
	T_4	2.65	HOMO→LUMO+2	0.35	ππ*
	T_5	2.67	HOMO-2→LUMO	0.74	nπ*
YC-1P	T_1	1.43	HOMO→LUMO	0.93	ππ*
	T_2	1.89	HOMO-1→LUMO	0.87	ππ*
	T_3	2.36	HOMO→LUMO+1	0.72	ππ*
	T_4	2.78	HOMO→LUMO+2	0.31	ππ*
YC-2P	T_1	1.62	HOMO→LUMO	0.93	ππ*
	T_2	1.91	HOMO-1→LUMO	0.87	ππ*
	T_3	2.06	HOMO→LUMO+1	0.72	ππ*
	T_4	2.47	HOMO→LUMO+2	0.31	ππ*

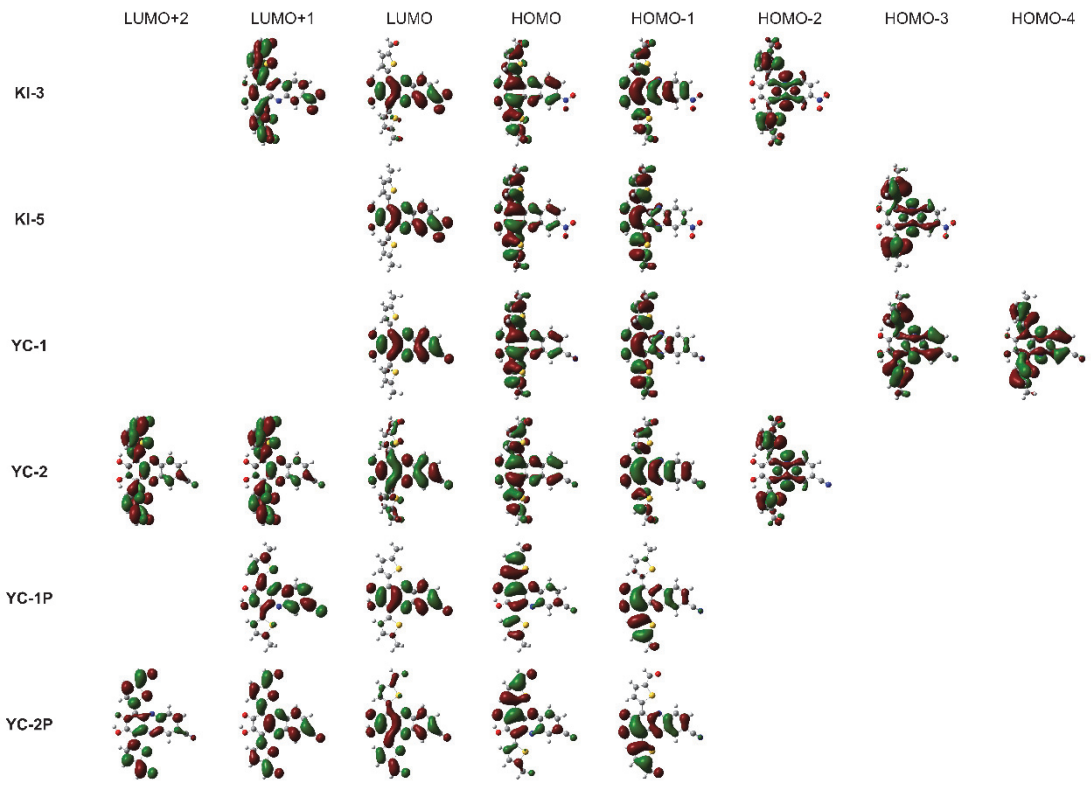


Fig. S9 Molecular orbitals of **KI-3**, **KI-5**, **YC-1**, and **YC-2** at B3LYP/6-31G(d,p)/THF-IEFPCM level, and **YC-1P** and **YC-2P** at B3LYP/6-31G+(d,p)/THF-IEFPCM level.

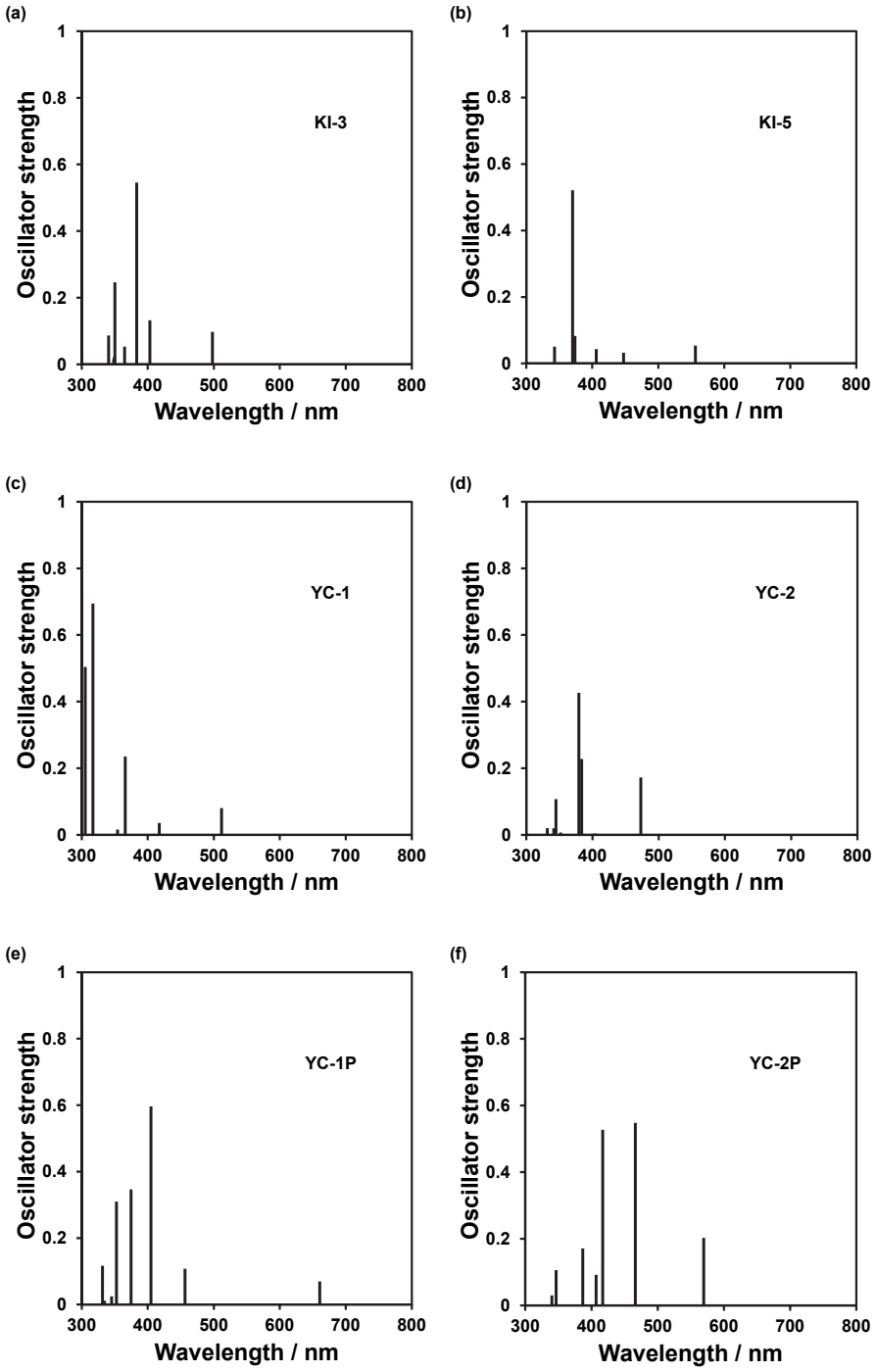


Fig. S10 Calculated oscillator strength of (a) **KI-3**, (b) **KI-5**, (c) **YC-1**, and (d) **YC-2** derived from TDDFT calculations at B3LYP/6-31G(d,p)/THF-IEFPCM level, and (e) **YC-1P** and (f) **YC-2P** at B3LYP/6-31+G(d,p)/THF-IEFPCM level.

4. Optical properties

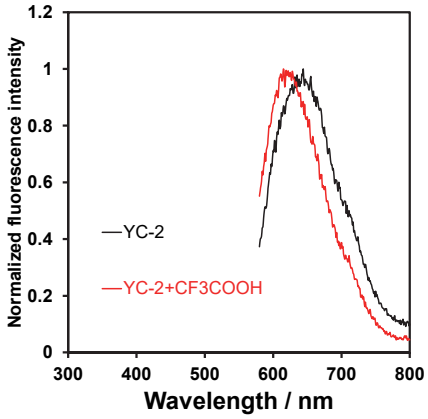


Fig. S11 Fluorescence spectra (λ_{ex} = 448 nm) of **YC-2** in THF with and without trifluoroacetic acid (TFA) (50 eq.).

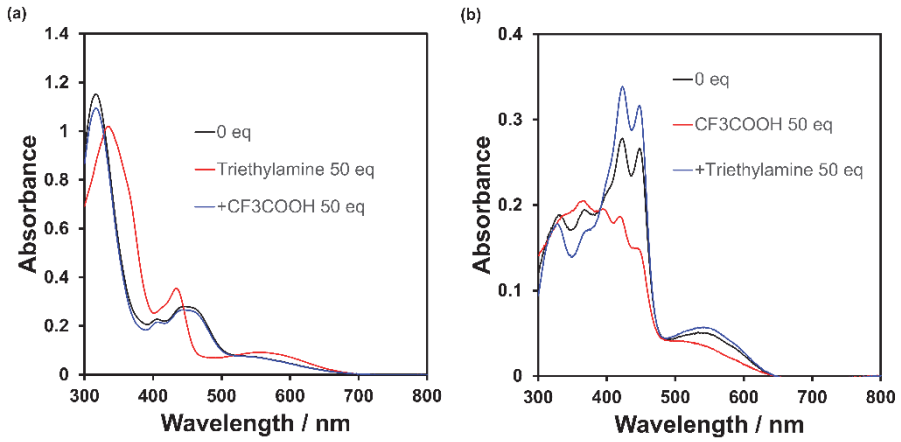


Fig. S12 (a) Photoabsorption spectra of **YC-1** in THF with and without triethylamine (TEA), and after addition of trifluoroacetic acid (TFA) to THF solution of **YC-1** containing TEA. (b) Photoabsorption spectra of **YC-2** in THF with and without TFA, and after addition of TEA to THF solution of **YC-1** containing TFA.

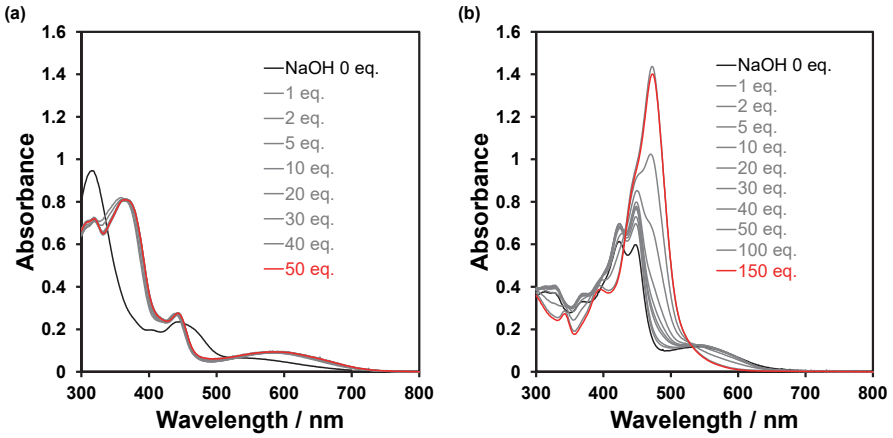


Fig. S13 Photoabsorption spectra of (a) **YC-1** and (b) **YC-2** upon the addition of NaOH in THF.

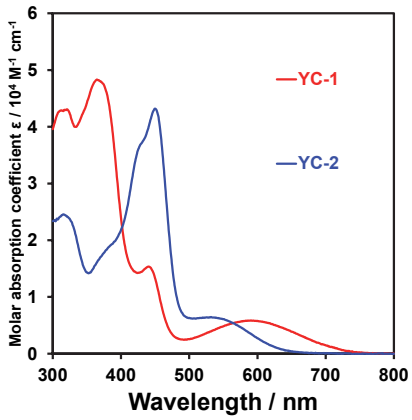


Fig. S14 Photoabsorption spectra of **YC-1** and **YC-2** in DMSO.

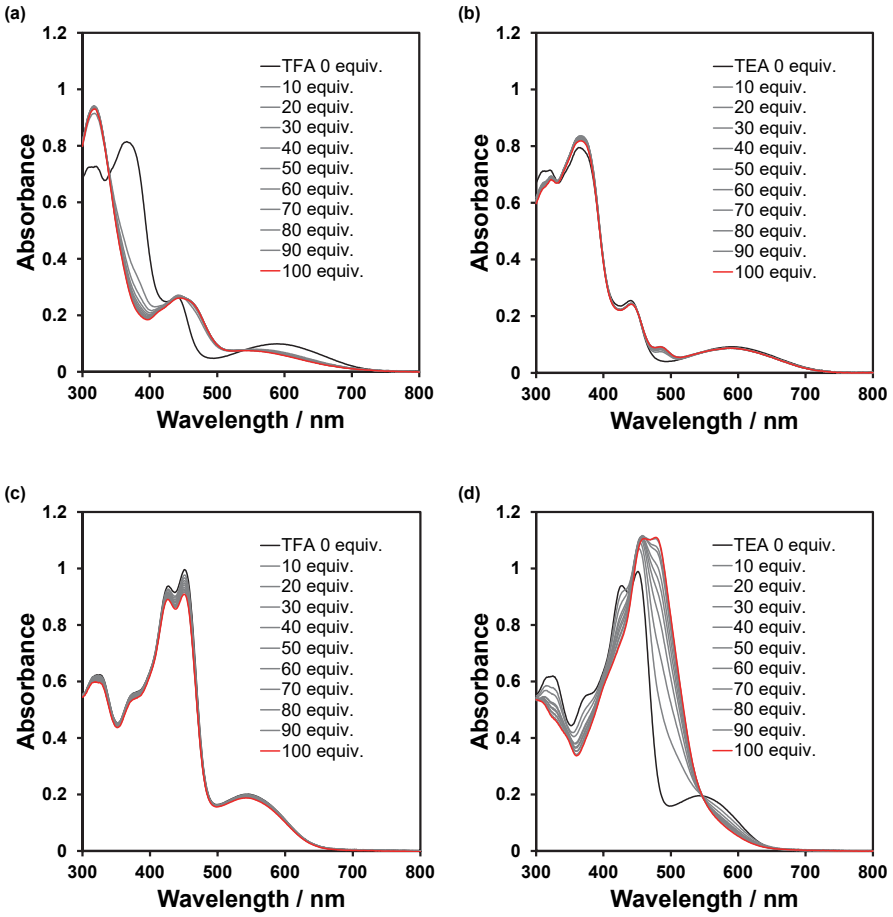


Fig. S15 Photoabsorption spectra of (a) **YC-1** and (c) **YC-2** upon the addition of trifluoroacetic acid (TFA) in DMSO, and (b) **YC-1** and (d) **YC-2** upon the addition of triethylamine (TEA) in DMSO.

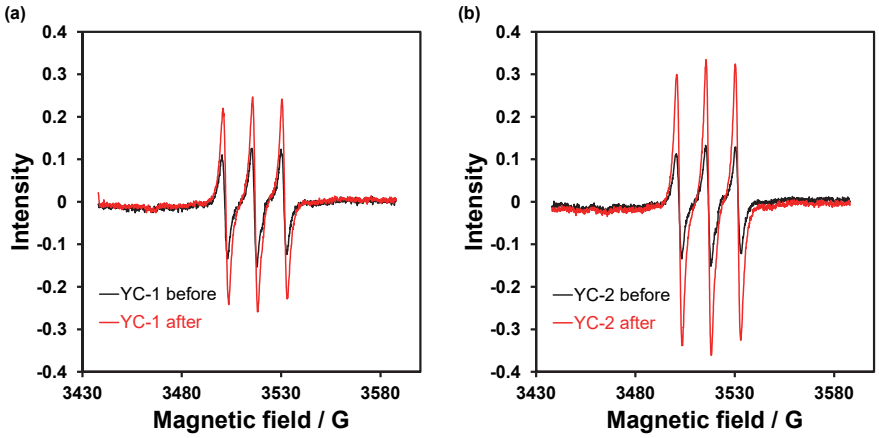


Fig. S16 EPR spectra of air-saturated THF solutions containing 4-oxo-TEMP (50 mM) and (a) **YC-1** or (b) **YC-2** (5 μM) before and after exposure to continuous visible light (>510 nm, and 30 mW cm^{-2}) for 60 min. The characteristic 1:1:1 triplet signal originates from a stable nitroxide radical (4-oxo-TEMPO) formed by the reaction of 4-oxo-TEMP with $^1O_2$.