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Supporting Information

Synthesis and Photoswitchable Amphiphilicity and Self-Assembly Properties of Photochromic Spiropyran Derivatives

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Table S1. Crystal and structure determination data of compound **1**.

Empirical formula	$2(C_{30}H_{30}N_2O_8)\bullet 2H_2O\bullet CHCl_3$
Formula weight	1248.52
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.0281(8) Å α = 82.245(3)°
	b = 16.7330(14) Å β = 75.706(3)°
	c = 18.4016(15) Å γ = 75.369(3)°
Volume	3174.3(4) $Å^3$
Z	2
Density(calculated)	1.306 mg m^{-3}
Absorption coefficient	0.217 mm^{-1}
F(000)	1308
Crystal size	0.130 × 0.120 × 0.100 mm
θ range for data collection	2.663 to 27.449°
Limiting indices	$-14 \le h \le 14$, $-21 \le k \le 21$, $-23 \le l \le 23$
Reflections collected / unique	69198 / 14457 [*R(int)* = 0.0496]
Completeness to θ = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.979 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14457 / 0 / 775
Goodness-of-fit on F^2	1.014
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0798, wR_2 = 0.2279
R indices (all data)	R_1 = 0.1444, wR_2 = 0.2822
Largest diff. peak and hole	0.951 and –0.517 e$Å^{-3}$

Table S2. The first ten singlet excited states (S_n) of **5** and **6** computed by TDDFT/CPCM using benzene as the solvent.

Compound	S_n	Excitation[a] (Coefficient)[b]	Vertical excitation wavelength / nm	f[c]
5	S_1	H–10→L (0.67)	305	0.000
Closed	S_2	H–3→L (0.67)	287	0.240
	S_3	H–3→L+1 (0.49)	276	0.022
		H–5→L (–0.31)		
	S_4	H–14→L (0.67)	269	0.000
	S_5	H–1→L (0.42)	267	0.175
		H–3→L+1 (–0.37)		
		H–1→L+1 (0.30)		
	S_6	H–1→L+1 (0.46)	252	0.069
	S_7	H–2→L+2 (0.56)	251	0.025
	S_8	H–5→L (0.48)	247	0.436
	S_9	H–1→L+3 (0.45)	244	0.053
	S_{10}	H→L+2 (0.61)	243	0.752
6	S_1	H–11→L (0.67)	305	0.000
Closed	S_2	H–3→L (0.67)	287	0.237
	S_3	H–3→L+1 (0.48)	276	0.021
		H–6→L (–0.31)		
	S_4	H–20→L (0.66)	269	0.000
	S_5	H–1→L (0.44)	268	0.172
		H–3→L+1 (–0.37)		
		H–1→L+1 (0.32)		
	S_6	H–1→L+1 (0.50)	252	0.065
		H–1→L (–0.30)		
	S_7	H–2→L+2 (0.55)	251	0.041
		H→L+7 (0.31)		
	S_8	H–6→L (0.48)	247	0.432
	S_9	H–1→L+3 (0.41)	244	0.200
		H→L+2 (0.41)		
	S_{10}	H→L+2 (0.49)	244	0.644
6	S_1	H–1→L (0.51)	467	0.950
Open		H→L (–0.47)		

S_2	H–4→L (0.65)	371	0.000
S_3	H→L (0.51)	335	0.008
	H–1→L (0.47)		
S_4	H–3→L (0.66)	319	0.177
S_5	H–11→L+1 (0.57)	308	0.000
	H–11→L (0.30)		
S_6	H–2→L (0.70)	297	0.004
S_7	H–1→L+1 (0.48)	297	0.515
	H→L+1 (–0.43)		
S_8	H–17→L+1 (0.60)	268	0.000
	H–17→L (0.33)		
S_9	H–7→L (0.57)	255	0.033
S_{10}	H–2→L+4 (0.45)	251	0.071

[a] Orbitals involved in the major excitation (H = HOMO and L = LUMO).

[b] The coefficients in the configuration interaction (CI) expansion that are less than 0.3 are not listed.

[c] Oscillator strengths.

Table S3. Cartesian coordinates of the optimized ground-state geometry of the closed form of **5**.

1	C	3.826870	1.398651	0.559989	54	C	-6.524732	-0.345626	0.940019
2	C	3.624675	2.206406	-0.570547	55	H	-5.009549	-1.766642	1.524129
3	C	3.321312	1.534996	-1.825639	56	C	-5.957956	1.082795	-0.924122
4	C	3.317781	0.204776	-1.907533	57	H	-4.034354	0.795974	-1.778351
5	H	4.215870	1.312895	2.664206	58	C	-6.878355	0.689071	0.050559
6	C	4.072984	1.966121	1.811705	59	O	-7.456916	-0.641903	1.882986
7	C	3.686435	3.586545	-0.433016	60	O	-6.156585	2.106751	-1.799205
8	H	3.081410	2.144563	-2.691332	61	O	-8.059112	1.368202	0.197670
9	H	3.071948	-0.297777	-2.835064	62	C	-7.145992	-1.641276	2.836278
10	C	3.945468	4.135460	0.813959	63	H	-6.979431	-2.613376	2.359923
11	C	4.136308	3.340970	1.940654	64	H	-6.260676	-1.372209	3.421981
12	H	3.531851	4.237982	-1.284204	65	C	-9.249751	0.625363	-0.052582
13	H	4.333266	3.809243	2.895964	66	H	-9.259071	0.234290	-1.076340
14	N	4.013579	5.582568	0.947248	67	H	-9.357018	-0.199020	0.654032
15	O	3.841697	6.261041	-0.057730	68	C	-7.433481	2.292100	-2.395827
16	O	4.239596	6.047407	2.056969	69	H	-7.866593	1.334651	-2.704878
17	O	3.771222	0.057132	0.494576	70	H	-8.124830	2.800574	-1.723284
18	C	3.660015	-0.692180	-0.755797	71	H	-7.262335	2.904592	-3.282662
19	C	3.263231	-2.810584	0.082433	72	H	-10.077608	1.324753	0.070863
20	C	4.647925	-2.747778	-0.087603	73	H	-8.009834	-1.706626	3.497129
21	C	2.664016	-3.850767	0.777254					
22	C	5.458071	-3.734043	0.437423					
23	C	3.494835	-4.843649	1.304489					
24	H	1.589909	-3.899135	0.921794					
25	C	4.873347	-4.792233	1.142134					
26	H	6.536126	-3.689822	0.312546					
27	H	3.048415	-5.665085	1.855809					
28	H	5.498591	-5.571761	1.564043					
29	N	2.654556	-1.706538	-0.535267					
30	C	4.982406	-1.529736	-0.926027					
31	C	6.218323	-0.762023	-0.463947					
32	H	6.334267	0.165820	-1.032766					
33	H	6.168504	-0.517487	0.597211					
34	H	7.113813	-1.365238	-0.635184					
35	C	5.163433	-1.967617	-2.390098					
36	H	6.001822	-2.665062	-2.455099					
37	H	4.273915	-2.476745	-2.769747					
38	H	5.382757	-1.113946	-3.037450					
39	C	1.294948	-1.333611	-0.209136					
40	H	1.063727	-1.568830	0.836571					
41	H	1.182167	-0.254120	-0.331444					
42	C	0.301921	-2.063420	-1.120147					
43	H	0.373804	-1.697119	-2.145369					
44	H	0.508140	-3.134317	-1.126267					
45	N	-1.065223	-1.892700	-0.662329					
46	C	-1.982422	-0.966778	-1.014623					
47	C	-3.067632	-1.228668	-0.206832					
48	H	-1.796466	-0.231585	-1.780793					
49	N	-1.536788	-2.680358	0.311936					
50	N	-2.741690	-2.287137	0.586888					
51	C	-4.374404	-0.564266	-0.127801					
52	C	-5.290906	-0.972718	0.846842					
53	C	-4.712472	0.457163	-1.003697					

Table S4. Cartesian coordinates of the optimized ground-state geometry of the closed form of **6**.

1	C	7.284652	1.070752	1.868299	54	C	-2.555575	-1.645150	-0.623502
2	C	6.933967	2.416435	1.674201	55	H	-0.808404	-2.824706	-1.084181
3	C	6.761250	2.870405	0.302263	56	C	-2.248448	0.750830	-0.688546
4	C	7.008685	2.057595	-0.724530	57	H	-0.298850	1.436743	-1.178263
5	H	7.683494	-0.501395	3.266751	58	C	-3.087993	-0.346768	-0.483941
6	C	7.420334	0.543548	3.153979	59	O	-3.425963	-2.655747	-0.367478
7	C	6.735508	3.228249	2.782855	60	O	-2.631074	2.045890	-0.513494
8	H	6.409661	3.883798	0.135125	61	O	-4.372867	-0.171807	-0.045677
9	H	6.861262	2.386144	-1.746130	62	C	-2.953626	-3.995685	-0.434443
10	C	6.887692	2.694042	4.053637	63	H	-2.581678	-4.211918	-1.444320
11	C	7.224745	1.358523	4.253246	64	H	-2.119967	-4.130744	0.266559
12	H	6.460683	4.269464	2.668154	65	C	-4.109113	-4.910430	-0.079581
13	H	7.330865	0.980501	5.261471	66	H	-4.930707	-4.729783	-0.782095
14	N	6.683351	3.553748	5.209326	67	H	-4.478356	-4.639479	0.915828
15	O	6.385856	4.724779	5.009112	68	C	-3.711240	-6.384477	-0.108489
16	O	6.819781	3.062458	6.322290	69	H	-3.327370	-6.641229	-1.104369
17	O	7.481197	0.231314	0.836862	70	H	-2.882475	-6.553828	0.591049
18	C	7.516053	0.656048	-0.561587	71	C	-4.865964	-7.320323	0.242683
19	C	7.531868	-1.406577	-1.607448	72	H	-5.694874	-7.151194	-0.457057
20	C	8.878965	-1.062042	-1.477710	73	H	-5.250938	-7.062743	1.238001
21	C	7.142938	-2.681485	-1.991129	74	C	-4.476277	-8.796554	0.217569
22	C	9.862948	-1.995289	-1.733729	75	H	-4.089374	-9.052654	-0.777690
23	C	8.148428	-3.618060	-2.247623	76	H	-3.647198	-8.964663	0.917656
24	H	6.097982	-2.957870	-2.083798	77	C	-5.629593	-9.734367	0.567016
25	C	9.491629	-3.287580	-2.121469	78	H	-6.459092	-9.567102	-0.133060
26	H	10.912596	-1.735544	-1.631052	79	H	-6.017236	-9.478774	1.562259
27	H	7.867479	-4.623376	-2.544973	80	C	-5.241173	-11.211294	0.542719
28	H	10.254511	-4.032322	-2.321390	81	H	-4.853826	-11.465952	-0.451700
29	N	6.723099	-0.301583	-1.298144	82	H	-4.412851	-11.377802	1.242633
30	C	8.974308	0.402772	-1.098812	83	C	-6.400343	-12.139977	0.892737
31	C	10.040568	0.718723	-0.053009	84	H	-7.229813	-12.017400	0.188788
32	H	9.978013	1.765092	0.261751	85	H	-6.095604	-13.189951	0.868164
33	H	9.944008	0.082594	0.826978	86	H	-6.785691	-11.928471	1.895403
34	H	11.034886	0.564256	-0.480310	87	C	-5.423507	-0.576511	-0.934375
35	C	9.236159	1.229529	-2.370045	88	H	-5.565799	0.203411	-1.694879
36	H	10.192530	0.928046	-2.803656	89	H	-5.145636	-1.505307	-1.436118
37	H	8.460637	1.065293	-3.122481	90	C	-6.686559	-0.770409	-0.119164
38	H	9.288076	2.298813	-2.146749	91	H	-7.471537	-1.127857	-0.796986
39	C	5.317493	-0.473750	-1.000134	92	H	-6.507382	-1.570615	0.608152
40	H	5.135648	-1.437673	-0.510214	93	C	-7.158664	0.491014	0.600499
41	H	5.002059	0.307594	-0.305180	94	H	-7.317907	1.290271	-0.136358
42	C	4.479953	-0.394527	-2.281062	95	H	-6.363214	0.839916	1.268248
43	H	4.484454	0.618879	-2.685401	96	C	-8.441183	0.278610	1.401470
44	H	4.882323	-1.065875	-3.040542	97	H	-9.235486	-0.075803	0.730839
45	N	3.104199	-0.792062	-2.042992	98	H	-8.281650	-0.524320	2.133236
46	C	2.032455	-0.035968	-1.722601	99	C	-8.916765	1.535117	2.127453
47	C	1.012758	-0.942822	-1.530881	100	H	-9.076067	2.338363	1.395642
48	H	2.080932	1.039347	-1.664771	101	H	-8.121750	1.888734	2.797199
49	N	2.784435	-2.091914	-2.042648	102	C	-10.197664	1.324596	2.931630
50	N	1.527192	-2.187418	-1.738747	103	H	-10.993157	0.970192	2.262390
51	C	-0.394395	-0.727194	-1.171785	104	H	-10.038824	0.522097	3.664353
52	C	-1.226572	-1.834212	-0.974004	105	C	-10.674165	2.581040	3.657639
53	C	-0.908889	0.553473	-1.028237	106	H	-10.833004	3.382391	2.925204

107	H	-9.879223	2.934428	4.326145
108	C	-11.954232	2.359778	4.458376
109	H	-12.273154	3.273657	4.967391
110	H	-12.774342	2.036774	3.808971
111	H	-11.813546	1.586156	5.220143
112	C	-3.894626	2.488880	-1.011439
113	H	-4.097533	2.008599	-1.977370
114	H	-4.691936	2.207152	-0.319117
115	C	-3.821665	3.995423	-1.169852
116	H	-3.551354	4.435295	-0.202920
117	H	-3.011968	4.242037	-1.865988
118	C	-5.138970	4.590075	-1.662767
119	H	-5.407392	4.137885	-2.626650
120	H	-5.944103	4.322458	-0.966013
121	C	-5.090131	6.108798	-1.816455
122	H	-4.823488	6.561542	-0.852535
123	H	-4.283584	6.376761	-2.511492
124	C	-6.404010	6.709462	-2.311151
125	H	-7.210273	6.439996	-1.616042
126	H	-6.670238	6.255374	-3.274933
127	C	-6.357472	8.227989	-2.465004
128	H	-6.091961	8.682995	-1.501392
129	H	-5.551120	8.498466	-3.159853
130	C	-7.670962	8.829831	-2.960319
131	H	-8.476014	8.559441	-2.265676
132	H	-7.935588	8.375042	-3.923097
133	C	-7.614084	10.347346	-3.110553
134	H	-8.565854	10.752046	-3.465911
135	H	-7.383240	10.829417	-2.155112
136	H	-6.838846	10.643815	-3.824494

Table S5. Cartesian coordinates of the optimized ground-state geometry of the open form of **6**.

1	C	-7.560439	3.841110	0.620360	54	H	7.829578	5.422192	-1.258674
2	C	-8.726722	3.090137	0.540810	55	H	7.734651	5.600827	0.483992
3	C	-7.567176	5.223773	0.700150	56	C	7.597234	7.460712	-0.597271
4	C	-9.955226	3.724698	0.547553	57	H	7.171242	7.826724	-1.540885
5	C	-8.811480	5.853139	0.706089	58	H	7.076801	8.005227	0.201756
6	H	-6.654159	5.805460	0.751829	59	C	9.085700	7.798466	-0.551215
7	C	-9.991074	5.117645	0.632138	60	H	9.606831	7.254194	-1.350174
8	H	-10.877681	3.155606	0.486999	61	H	9.512363	7.432624	0.392301
9	H	-8.855526	6.935136	0.767565	62	C	9.375380	9.291812	-0.688449
10	H	-10.946069	5.631448	0.637964	63	H	8.949030	9.656719	-1.631232
11	N	-6.454252	2.961707	0.602333	64	H	8.854814	9.834961	0.110145
12	C	-8.373922	1.619365	0.454451	65	C	10.865279	9.618340	-0.641250
13	C	-8.939902	0.861055	1.670260	66	H	11.404984	9.113775	-1.449158
14	H	-8.688400	-0.200018	1.641430	67	H	11.044742	10.692446	-0.741406
15	H	-8.559943	1.278683	2.605200	68	H	11.310045	9.293185	0.304805
16	H	-10.028870	0.950091	1.675871	69	C	4.667205	-0.360477	-0.918489
17	C	-8.888906	1.024127	-0.869241	70	H	4.292559	-1.136427	-1.600064
18	H	-9.977126	1.114784	-0.906801	71	H	4.729004	0.582388	-1.465380
19	H	-8.474059	1.557568	-1.727432	72	C	6.025325	-0.742065	-0.363588
20	H	-8.634624	-0.032131	-0.966471	73	H	6.728780	-0.793559	-1.203813
21	C	-5.071150	3.405427	0.656992	74	H	6.370403	0.067933	0.289378
22	H	-5.034299	4.361092	1.179961	75	C	6.032739	-2.064536	0.399917
23	H	-4.499874	2.693820	1.254701	76	H	5.668479	-2.864970	-0.258635
24	C	-4.451211	3.524904	-0.747353	77	H	5.321811	-2.000469	1.231039
25	H	-4.822228	2.720099	-1.385030	78	C	7.412598	-2.439228	0.935712
26	H	-4.699985	4.478503	-1.213133	79	H	8.124177	-2.498834	0.101188
27	N	-3.009208	3.430136	-0.691603	80	H	7.777662	-1.635282	1.588475
28	C	-2.266089	2.311808	-0.554416	81	C	7.425316	-3.758262	1.705174
29	C	-0.972328	2.771834	-0.475939	82	H	7.059452	-4.562250	1.052609
30	H	-2.692898	1.319165	-0.513056	83	H	6.713466	-3.697380	2.538950
31	N	-2.235382	4.527864	-0.693949	84	C	8.803407	-4.134658	2.244516
32	N	-1.005801	4.132325	-0.570325	85	H	9.516027	-4.195722	1.410992
33	C	0.262191	1.994067	-0.321994	86	H	9.169828	-3.331304	2.897610
34	C	1.506227	2.627447	-0.400222	87	C	8.816299	-5.453665	3.014501
35	C	0.192764	0.623893	-0.105275	88	H	8.450387	-6.255942	2.361601
36	C	2.667171	1.880786	-0.253644	89	H	8.104466	-5.391952	3.847079
37	H	1.539263	3.696211	-0.560398	90	C	10.197610	-5.820440	3.549461
38	C	1.357492	-0.132405	0.022173	91	H	10.178780	-6.767613	4.095833
39	H	-0.758311	0.108021	-0.020900	92	H	10.921930	-5.920426	2.734585
40	C	2.608385	0.486406	-0.052107	93	H	10.573325	-5.050338	4.230924
41	O	3.919814	2.408969	-0.270127	94	C	1.989426	-2.428443	-0.376845
42	O	1.179474	-1.458115	0.287314	95	H	2.170939	-2.110464	-1.411638
43	O	3.755458	-0.225674	0.179577	96	H	2.956880	-2.517806	0.124173
44	C	4.063438	3.815417	-0.416792	97	C	1.242131	-3.748135	-0.348604
45	H	3.627065	4.140145	-1.370461	98	H	1.006534	-3.992461	0.693755
46	H	3.526334	4.330364	0.390189	99	H	0.285241	-3.627508	-0.869821
47	C	5.544474	4.135209	-0.366940	100	C	2.042796	-4.884164	-0.981329
48	H	6.051279	3.583974	-1.167247	101	H	2.283925	-4.627968	-2.021427
49	H	5.951675	3.763558	0.579992	102	H	3.004533	-4.986776	-0.461794
50	C	5.821077	5.630527	-0.506148	103	C	1.307987	-6.222729	-0.950493
51	H	5.396580	5.995842	-1.450320	104	H	1.068814	-6.480072	0.089588
52	H	5.301645	6.175118	0.292950	105	H	0.344698	-6.119272	-1.466996
53	C	7.310020	5.967261	-0.459741	106	C	2.100867	-7.363646	-1.584091

107	H	3.065117	-7.465228	-1.068434
108	H	2.339175	-7.105600	-2.624590
109	C	1.368045	-8.702940	-1.551787
110	H	1.130215	-8.962085	-0.511471
111	H	0.403175	-8.601985	-2.066347
112	C	2.159425	-9.844867	-2.186223
113	H	3.123370	-9.945088	-1.671772
114	H	2.395990	-9.585695	-3.225817
115	C	1.418856	-11.178590	-2.148094
116	H	2.006373	-11.978010	-2.608313
117	H	1.198697	-11.477545	-1.118205
118	H	0.465733	-11.115313	-2.682929
119	C	-6.843598	1.672572	0.491407
120	C	-5.916930	0.637052	0.420149
121	H	-4.863939	0.871545	0.447032
122	C	-6.221503	-0.714936	0.324302
123	H	-7.265769	-1.013064	0.312079
124	C	-5.307603	-1.779665	0.245467
125	C	-5.838010	-3.091554	0.188483
126	C	-3.847897	-1.595367	0.225363
127	C	-5.017781	-4.181274	0.131425
128	H	-6.911425	-3.243476	0.193172
129	C	-3.045534	-2.806037	0.178672
130	C	-3.599725	-4.040936	0.131524
131	H	-1.969430	-2.668588	0.183900
132	H	-2.991062	-4.935763	0.093552
133	N	-5.597512	-5.501207	0.074255
134	O	-4.835769	-6.462473	0.025122
135	O	-6.821513	-5.605094	0.076491
136	O	-3.301719	-0.473947	0.245753

Table S6. Rate constants of compounds **1**–**8** in benzene solution at different temperatures.

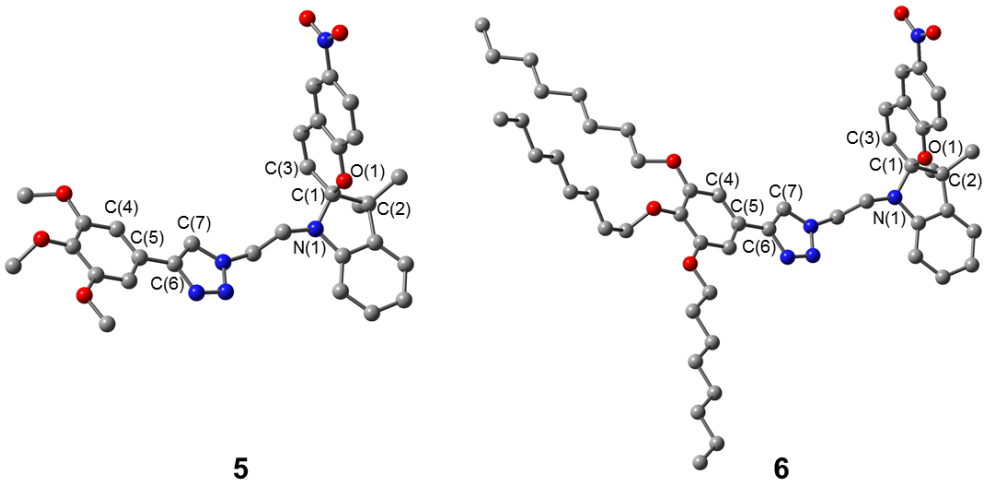
$k \times 10^2$ / s^{-1} in benzene						
Compound	T / K					
	288	293	298	303	308	313
1	1.6	2.6	4.4	7.3	11.8	19.0
2	1.9	3.2	5.3	8.5	13.9	23.2
3	2.7	4.1	6.6	10.7	16.2	26.2
4	2.7	4.1	7.7	10.8	17.4	28.3
5	3.7	6.1	10.6	17.8	25.6	38.9
6	6.4	11.6	17.9	29.0	49.4	71.5
7	4.8	8.7	15.0	24.4	40.3	66.7
8	4.2	7.7	11.3	20.2	40.7	76.9

Table S7. Cartesian coordinates of the ground-state geometry of the dimer of the open form of **6** optimized at the PBE0-D3(BJ) level.

1	C	7.577006	-4.981131	-1.624068	54	H	-6.853847	-7.697133	2.251739
2	C	8.757999	-4.243834	-1.622496	55	C	-8.940716	-7.465573	1.750088
3	C	7.543854	-6.350573	-1.841158	56	H	-9.541237	-7.213776	0.864181
4	C	9.968007	-4.881364	-1.837209	57	H	-9.128531	-6.660954	2.475983
5	C	8.769249	-6.982008	-2.056424	58	C	-9.433984	-8.786123	2.328167
6	H	6.619710	-6.917830	-1.846265	59	H	-9.245406	-9.590590	1.604583
7	C	9.964679	-6.261969	-2.054393	60	H	-8.843939	-9.035188	3.220384
8	H	10.901093	-4.325594	-1.836837	61	C	-10.914929	-8.752883	2.683978
9	H	8.787523	-8.053367	-2.228224	62	H	-11.525961	-8.533104	1.800986
10	H	10.902749	-6.780549	-2.223922	63	H	-11.255014	-9.708137	3.096135
11	N	6.508269	-4.102517	-1.363252	64	H	-11.122664	-7.975314	3.427881
12	C	8.441553	-2.790774	-1.351815	65	C	-4.646306	-0.921388	-3.738350
13	C	8.810927	-1.921324	-2.566804	66	H	-4.172765	-0.204208	-4.422300
14	H	9.886805	-1.994992	-2.745661	67	H	-4.507242	-1.929371	-4.149390
15	H	8.287070	-2.259998	-3.464345	68	C	-6.118017	-0.617410	-3.567479
16	H	8.561805	-0.871856	-2.394349	69	H	-6.586257	-0.670635	-4.559158
17	C	5.115852	-4.497462	-1.367569	70	H	-6.577305	-1.407802	-2.959039
18	H	5.050089	-5.566918	-1.173877	71	C	-6.386454	0.737737	-2.928556
19	H	4.612292	-3.993722	-0.541857	72	H	-5.865120	1.522799	-3.494597
20	C	4.453847	-4.131343	-2.699251	73	H	-5.948042	0.740516	-1.924185
21	H	4.792097	-3.149572	-3.034339	74	C	-7.868898	1.079305	-2.833927
22	H	4.702191	-4.861590	-3.471814	75	H	-8.287814	1.204902	-3.842049
23	N	3.017511	-4.065964	-2.557282	76	H	-8.411093	0.232574	-2.387925
24	C	2.221795	-2.977206	-2.603875	77	C	-8.125725	2.332166	-2.006414
25	C	0.948176	-3.478242	-2.409601	78	H	-7.587134	3.178938	-2.455195
26	H	2.615060	-1.978019	-2.708009	79	H	-7.688626	2.193550	-1.007289
27	N	2.307721	-5.176896	-2.329537	80	C	-9.597309	2.692153	-1.855692
28	N	1.057724	-4.827093	-2.238529	81	H	-10.042890	2.848717	-2.848404
29	C	-0.336086	-2.778804	-2.403864	82	H	-10.135528	1.842288	-1.411255
30	C	-1.465159	-3.413595	-1.883801	83	C	-9.820219	3.933367	-0.998358
31	C	-0.418617	-1.483214	-2.924408	84	H	-9.275138	4.778666	-1.440169
32	C	-2.687752	-2.746063	-1.898903	85	H	-9.371668	3.770384	-0.008827
33	H	-1.370418	-4.404478	-1.459567	86	C	-11.290799	4.296132	-0.841360
34	C	-1.643486	-0.814997	-2.930771	87	H	-11.422617	5.188211	-0.220983
35	H	0.465648	-1.015786	-3.338912	88	H	-11.753058	4.495310	-1.814702
36	C	-2.785964	-1.454648	-2.434022	89	H	-11.849621	3.478265	-0.372747
37	O	-3.847593	-3.244559	-1.421377	90	C	-0.777315	1.121040	-4.039980
38	O	-1.851768	0.435002	-3.409776	91	H	-0.261452	0.449791	-4.739735
39	O	-4.003580	-0.839918	-2.460655	92	H	-1.261322	1.902319	-4.633610
40	C	-3.851114	-4.511750	-0.774160	93	C	0.205271	1.750069	-3.066864
41	H	-3.567584	-5.299270	-1.486729	94	H	-0.350317	2.363714	-2.346981
42	H	-3.126566	-4.508692	0.050265	95	H	0.716631	0.974463	-2.484083
43	C	-5.268641	-4.698612	-0.278870	96	C	1.232751	2.601559	-3.807838
44	H	-5.943808	-4.530548	-1.127690	97	H	1.629743	2.034142	-4.661793
45	H	-5.484461	-3.906355	0.447837	98	H	0.737546	3.485399	-4.232798
46	C	-5.571358	-6.054697	0.342221	99	C	2.392331	3.029252	-2.920884
47	H	-5.364292	-6.853217	-0.383297	100	H	2.005627	3.542864	-2.030017
48	H	-4.911554	-6.235684	1.201465	101	H	2.900135	2.132028	-2.544097
49	C	-7.029632	-6.125528	0.783024	102	C	3.410021	3.925086	-3.614735
50	H	-7.670533	-5.889527	-0.078372	103	H	2.926439	4.863500	-3.921393
51	H	-7.218792	-5.331644	1.519244	104	H	3.753574	3.442747	-4.541118
52	C	-7.464511	-7.461798	1.368761	105	C	4.609629	4.232145	-2.727883
53	H	-7.272346	-8.262616	0.640737	106	H	4.257896	4.663029	-1.780316

107	H	5.106140	3.289453	-2.458436	160	N	-1.256011	-2.806363	1.286295
108	C	5.629166	5.175847	-3.351762	161	C	-1.776731	-0.384744	0.982732
109	H	5.135994	6.122338	-3.610715	162	C	-3.143098	-0.558559	0.744057
110	H	5.989073	4.750853	-4.298487	163	C	-1.264800	0.889335	1.227842
111	C	6.808817	5.449060	-2.427421	164	C	-3.997768	0.542017	0.743399
112	H	7.534835	6.128416	-2.885546	165	H	-3.515493	-1.552263	0.532430
113	H	6.475567	5.899728	-1.485732	166	C	-2.114283	1.990705	1.201713
114	H	7.331764	4.520695	-2.171882	167	H	-0.223968	1.025711	1.505271
115	C	6.927403	-2.838667	-1.183206	168	C	-3.480981	1.837687	0.947858
116	C	6.014029	-1.810248	-0.919156	169	O	-5.339309	0.458031	0.575245
117	H	4.957101	-2.039921	-0.881354	170	O	-1.604448	3.222001	1.508103
118	C	6.341158	-0.496972	-0.647826	171	O	-4.299941	2.927935	0.979900
119	H	7.386570	-0.197992	-0.667120	172	C	-5.888808	-0.853152	0.482468
120	C	5.434659	0.531530	-0.293020	173	H	-5.527668	-1.334364	-0.434930
121	C	5.989364	1.778084	0.056532	174	H	-5.543340	-1.449997	1.338763
122	C	3.975075	0.349147	-0.252879	175	C	-7.397587	-0.757098	0.504835
123	C	5.186690	2.832993	0.426128	176	H	-7.741595	-0.146908	-0.337388
124	H	7.065456	1.917097	0.031600	177	H	-7.712624	-0.244382	1.422101
125	C	3.203396	1.508399	0.135793	178	C	-8.018637	-2.147310	0.439381
126	C	3.776718	2.697714	0.459463	179	H	-7.693450	-2.647960	-0.482953
127	H	2.124791	1.394012	0.164683	180	H	-7.623568	-2.754822	1.265897
128	H	3.177302	3.547795	0.760721	181	C	-9.540233	-2.163405	0.506526
129	N	5.778392	4.093026	0.744796	182	H	-9.955094	-1.611140	-0.348537
130	O	5.029647	5.051437	0.942219	183	H	-9.872836	-1.629342	1.407576
131	O	7.003566	4.177240	0.797769	184	C	-10.094355	-3.583660	0.525333
132	O	3.405453	-0.730387	-0.544358	185	H	-9.753303	-4.117505	-0.373313
133	C	5.022705	-4.366768	2.371148	186	H	-9.657376	-4.124463	1.376801
134	C	6.258042	-3.846984	2.751250	187	C	-11.612843	-3.663903	0.612183
135	C	4.874146	-5.637984	1.835199	188	H	-12.059093	-3.156377	-0.254939
136	C	7.402585	-4.608905	2.589772	189	H	-11.957872	-3.111779	1.498139
137	C	6.038305	-6.389993	1.661436	190	C	-12.127924	-5.097812	0.681649
138	H	3.907901	-6.034451	1.541118	191	H	-11.772517	-5.650898	-0.198596
139	C	7.285503	-5.883894	2.026336	192	H	-11.680537	-5.597960	1.551128
140	H	8.375503	-4.229160	2.888223	193	C	-13.645715	-5.187876	0.764838
141	H	5.966531	-7.382088	1.227350	194	H	-14.116950	-4.727905	-0.111010
142	H	8.174934	-6.485318	1.869746	195	H	-13.984803	-6.227328	0.818714
143	N	4.037750	-3.387548	2.589122	196	H	-14.022550	-4.667853	1.652738
144	C	6.054671	-2.461404	3.323268	197	C	-4.816357	3.327626	-0.295270
145	C	6.213241	-2.514283	4.859484	198	H	-3.980974	3.618003	-0.948261
146	H	5.994471	-1.538792	5.301778	199	H	-5.338434	2.486054	-0.759754
147	H	5.543871	-3.257280	5.300765	200	C	-5.756842	4.490468	-0.075795
148	H	7.243660	-2.787115	5.102582	201	H	-6.214478	4.740202	-1.041279
149	C	2.624086	-3.631205	2.375884	202	H	-6.574335	4.160929	0.579067
150	H	2.415095	-4.661306	2.671160	203	C	-5.080680	5.722054	0.513038
151	H	2.063076	-2.986559	3.053998	204	H	-4.282843	6.054493	-0.166737
152	C	2.179087	-3.366050	0.926976	205	H	-4.588183	5.446547	1.453810
153	H	2.813854	-2.603496	0.467627	206	C	-6.047902	6.873017	0.757891
154	H	2.203978	-4.275045	0.321410	207	H	-6.543975	7.139861	-0.186342
155	N	0.835881	-2.837117	0.908653	208	H	-6.846431	6.537756	1.435035
156	C	0.486146	-1.547913	0.745040	209	C	-5.375896	8.109214	1.342960
157	C	-0.871649	-1.531520	0.992588	210	H	-4.577623	8.443435	0.664932
158	H	1.211726	-0.803788	0.455299	211	H	-4.878969	7.839248	2.285678
159	N	-0.218514	-3.592411	1.241910	212	C	-6.340364	9.262106	1.593250

213	H	-6.837303	9.532206	0.650385	266	H	7.019690	-0.494465	3.236194
214	H	-7.138919	8.927852	2.271095	267	H	8.049068	-1.849522	2.814805
215	C	-5.668355	10.498662	2.179450	268	H	6.824911	-1.287925	1.663463
216	H	-4.870513	10.830514	1.501410	269	C	9.169185	-2.323488	-0.083319
217	H	-5.172246	10.226714	3.120892	270	H	8.955263	-1.279407	0.152660
218	C	-6.640986	11.644618	2.425530	271	H	8.889409	-2.942333	0.771567
219	H	-6.135945	12.519926	2.846041	272	H	10.246929	-2.419062	-0.238773
220	H	-7.126669	11.955363	1.493673					
221	H	-7.430566	11.347124	3.124723					
222	C	-1.391597	4.106932	0.403757					
223	H	-1.524572	3.560194	-0.538218					
224	H	-2.143799	4.905035	0.437568					
225	C	0.009043	4.673177	0.497533					
226	H	0.125769	5.156210	1.476136					
227	H	0.721767	3.839017	0.475659					
228	C	0.335811	5.665159	-0.610064					
229	H	0.261822	5.164902	-1.586192					
230	H	-0.411852	6.470294	-0.622163					
231	C	1.727392	6.266146	-0.451251					
232	H	1.781200	6.805021	0.505262					
233	H	2.468480	5.458402	-0.380203					
234	C	2.122982	7.200693	-1.586371					
235	H	1.381054	8.007057	-1.674983					
236	H	2.086473	6.648177	-2.536139					
237	C	3.511165	7.803181	-1.409713					
238	H	3.545173	8.373844	-0.470665					
239	H	4.244380	6.992994	-1.295226					
240	C	3.931941	8.705128	-2.563883					
241	H	3.218655	9.535513	-2.653553					
242	H	3.859406	8.142185	-3.504622					
243	C	5.344053	9.252710	-2.404537					
244	H	5.623133	9.901801	-3.240514					
245	H	5.437870	9.836928	-1.482217					
246	H	6.075987	8.438746	-2.354389					
247	C	4.576244	-2.225234	3.014746					
248	C	3.808955	-1.066690	3.143141					
249	H	2.760287	-1.088015	2.871749					
250	C	4.314271	0.164694	3.522804					
251	H	5.362573	0.234848	3.795190					
252	C	3.615761	1.390768	3.556391					
253	C	4.367122	2.552652	3.814371					
254	C	2.180193	1.505605	3.252665					
255	C	3.782010	3.798290	3.777661					
256	H	5.430543	2.476921	4.018020					
257	C	1.630043	2.849402	3.260444					
258	C	2.395123	3.947201	3.504109					
259	H	0.574268	2.947617	3.025362					
260	H	1.975436	4.946788	3.481034					
261	N	4.584597	4.959513	3.996088					
262	O	4.032820	6.058858	3.982383					
263	O	5.791784	4.816762	4.188315					
264	O	1.462407	0.519830	2.989317					
265	C	7.034687	-1.454304	2.719229					



5

C(1)–O(1)	1.462
O(1)–C(1)–C(2)	107.53
O(1)–C(1)–C(3)	111.58
O(1)–C(1)–N(1)	106.39
C(4)–C(5)–C(6)–C(7)	4.037

6

C(1)–O(1)	1.462
O(1)–C(1)–C(2)	107.56
O(1)–C(1)–C(3)	111.56
O(1)–C(1)–N(1)	106.38
C(4)–C(5)–C(6)–C(7)	3.048

Figure S1. The ground-state geometries of the closed forms of compounds **5** and **6** optimized at the CAM-B3LYP/6-31G(d,p) level, with selected structural parameters. The bond lengths and bond angles are in angstroms and degrees, respectively. All hydrogen atoms are omitted for clarity.

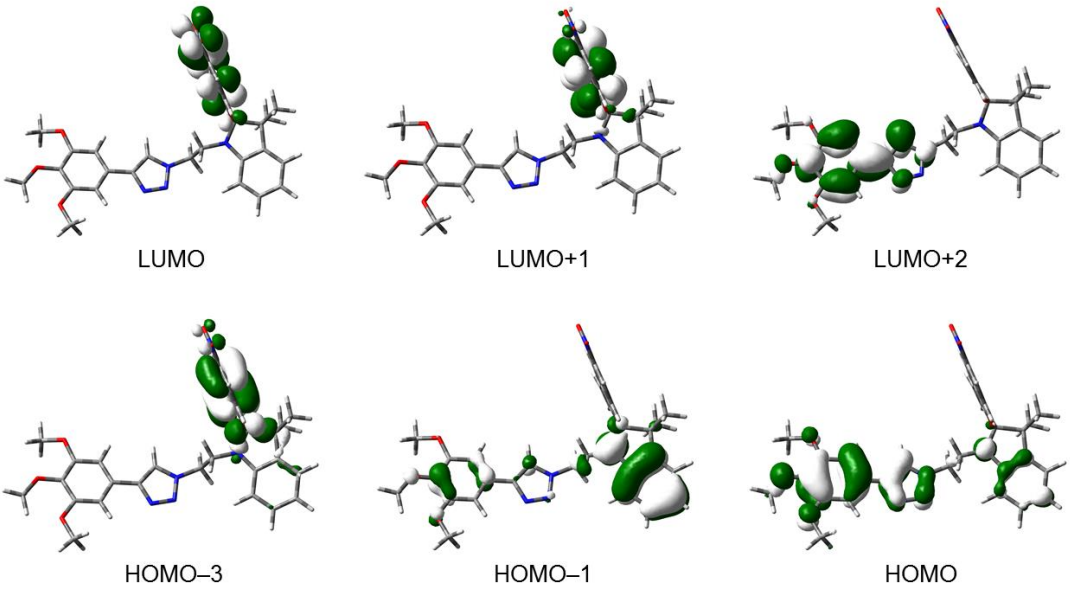


Figure S2. Spatial plots (isovalue = 0.03) of selected molecular orbitals of the closed form of **5** at the ground-state geometry optimized at the CAM-B3LYP level.

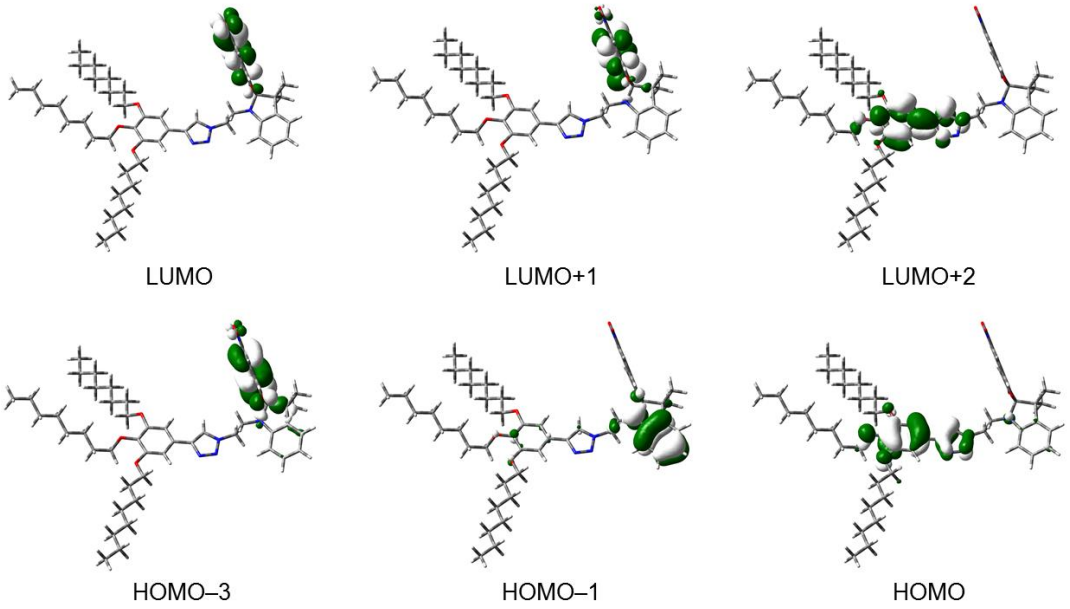


Figure S3. Spatial plots (isovalue = 0.03) of selected molecular orbitals of the closed form of **6** at the ground-state geometry optimized at the CAM-B3LYP level.

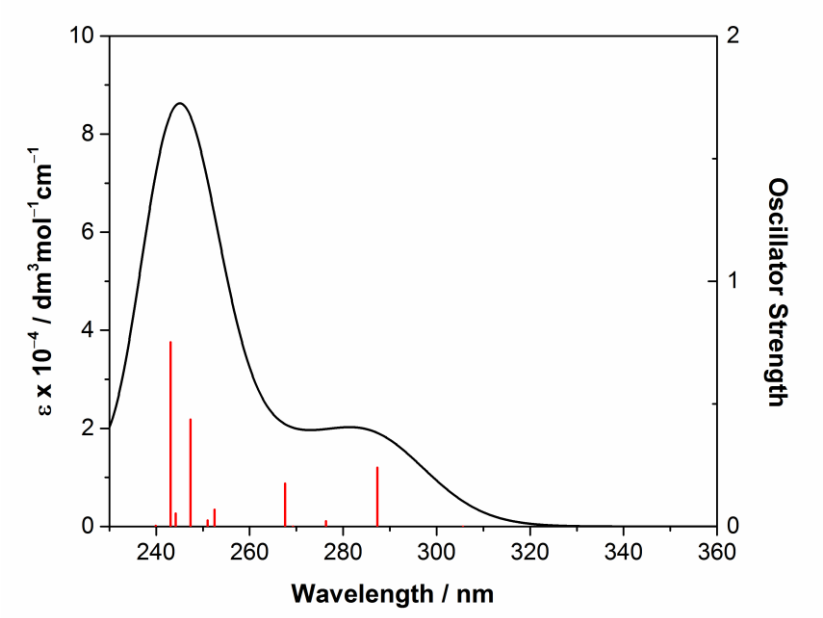


Figure S4. Simulated UV-vis spectrum of the closed form of **5** computed by TDDFT/CPCM using benzene as the solvent.

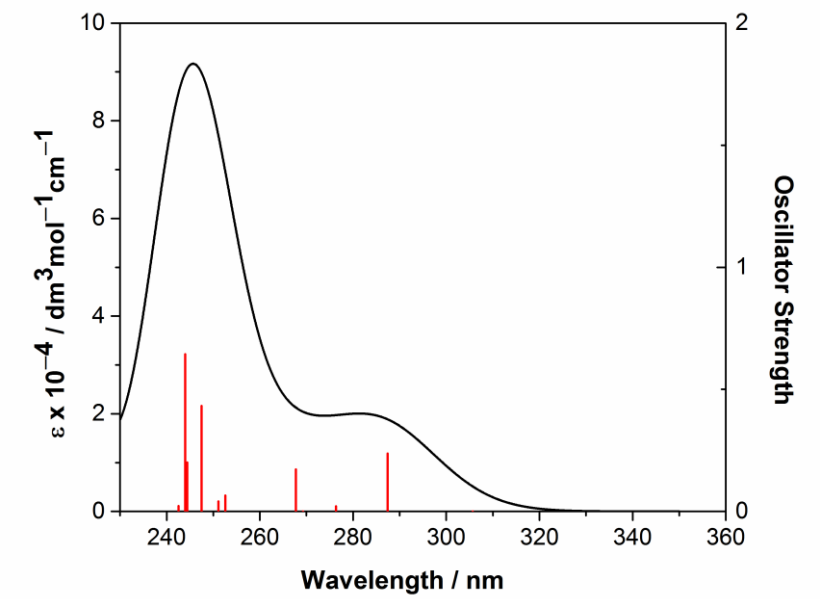


Figure S5. Simulated UV-vis spectrum of the closed form of **6** computed by TDDFT/CPCM using benzene as the solvent.

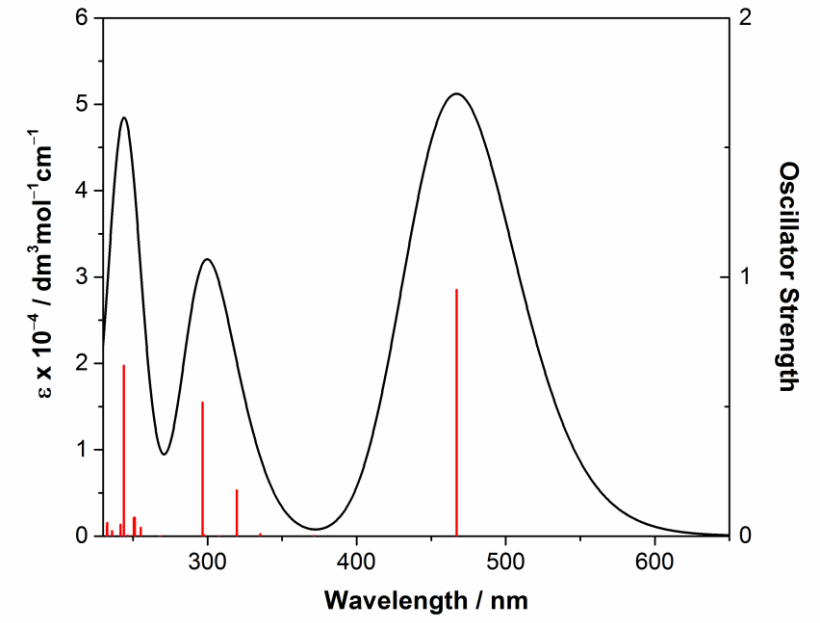


Figure S6. Simulated UV-vis spectrum of the open form of **6** computed by TDDFT/CPCM using benzene as the solvent.

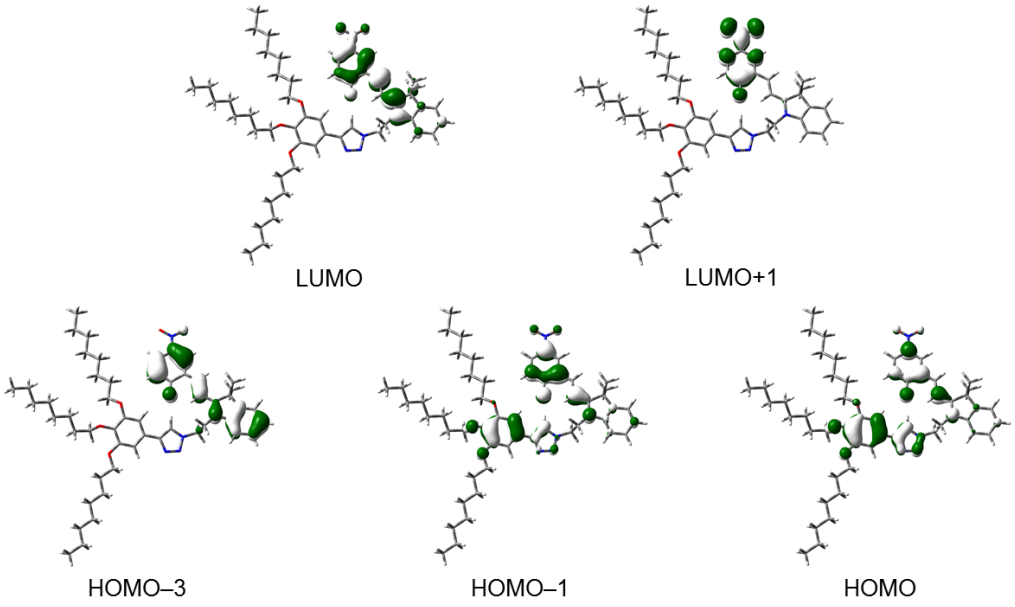


Figure S7. Spatial plots (isovalue = 0.03) of selected molecular orbitals of the open form of **6** at the ground-state geometry optimized at the CAM-B3LYP level.

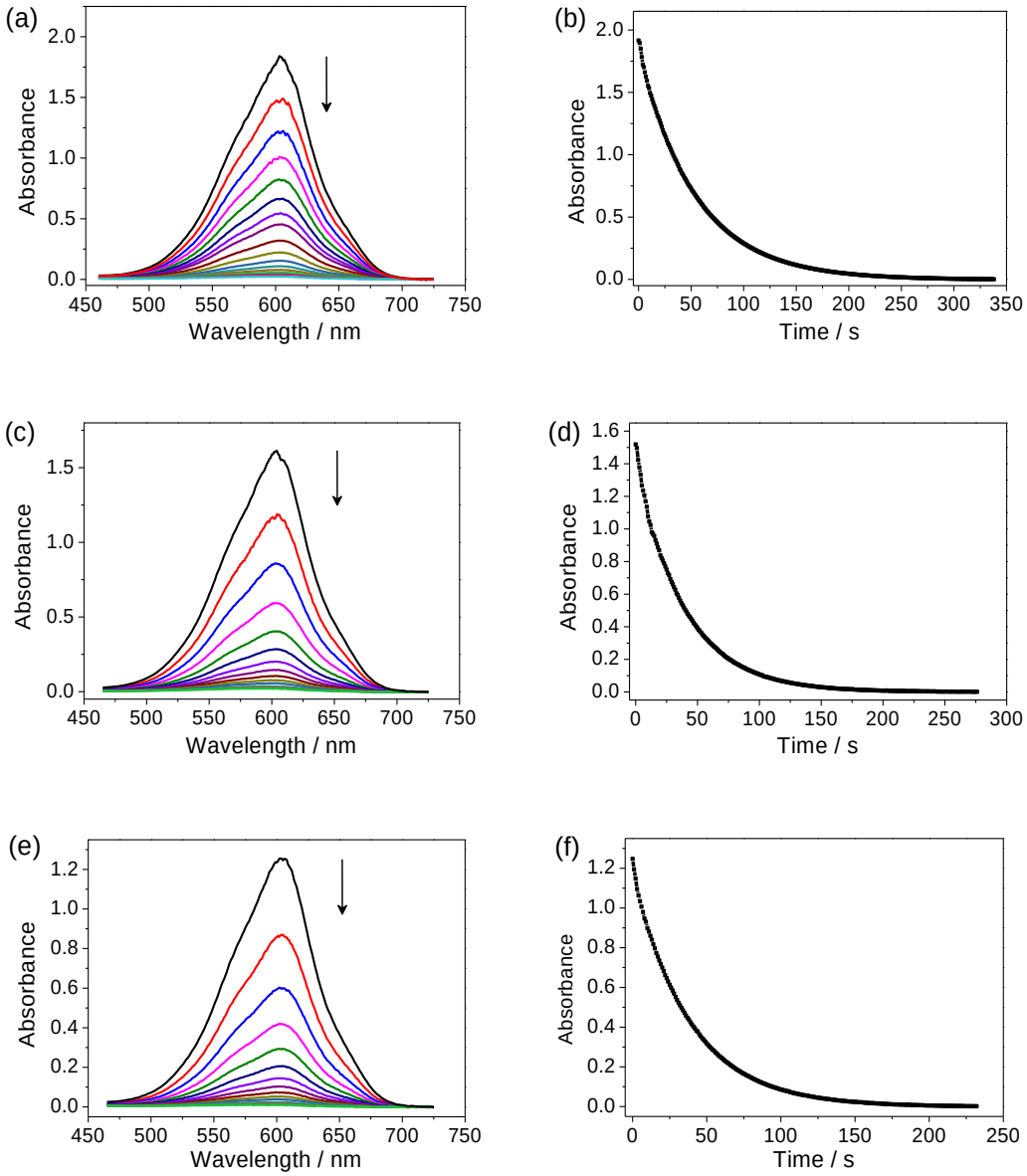


Figure S8. (a) Time-dependent UV-vis absorption spectral changes of the open form and (b) the decay trace at the absorption maximum at 603 nm with time of compound **2**. (c) Time-dependent UV-vis absorption spectral changes of the open form and (d) the decay trace at the absorption maximum at 603 nm with time of compound **3**. (e) Time-dependent UV-vis absorption spectral changes of the open form and (f) the decay trace at the absorption maximum at 603 nm with time of compound **4** in benzene solution at 288 K after excitation at 365 nm (at time intervals of 10 s). The arrows indicate the spectral changes with time ($c = 8\times10^{-5}$ M).

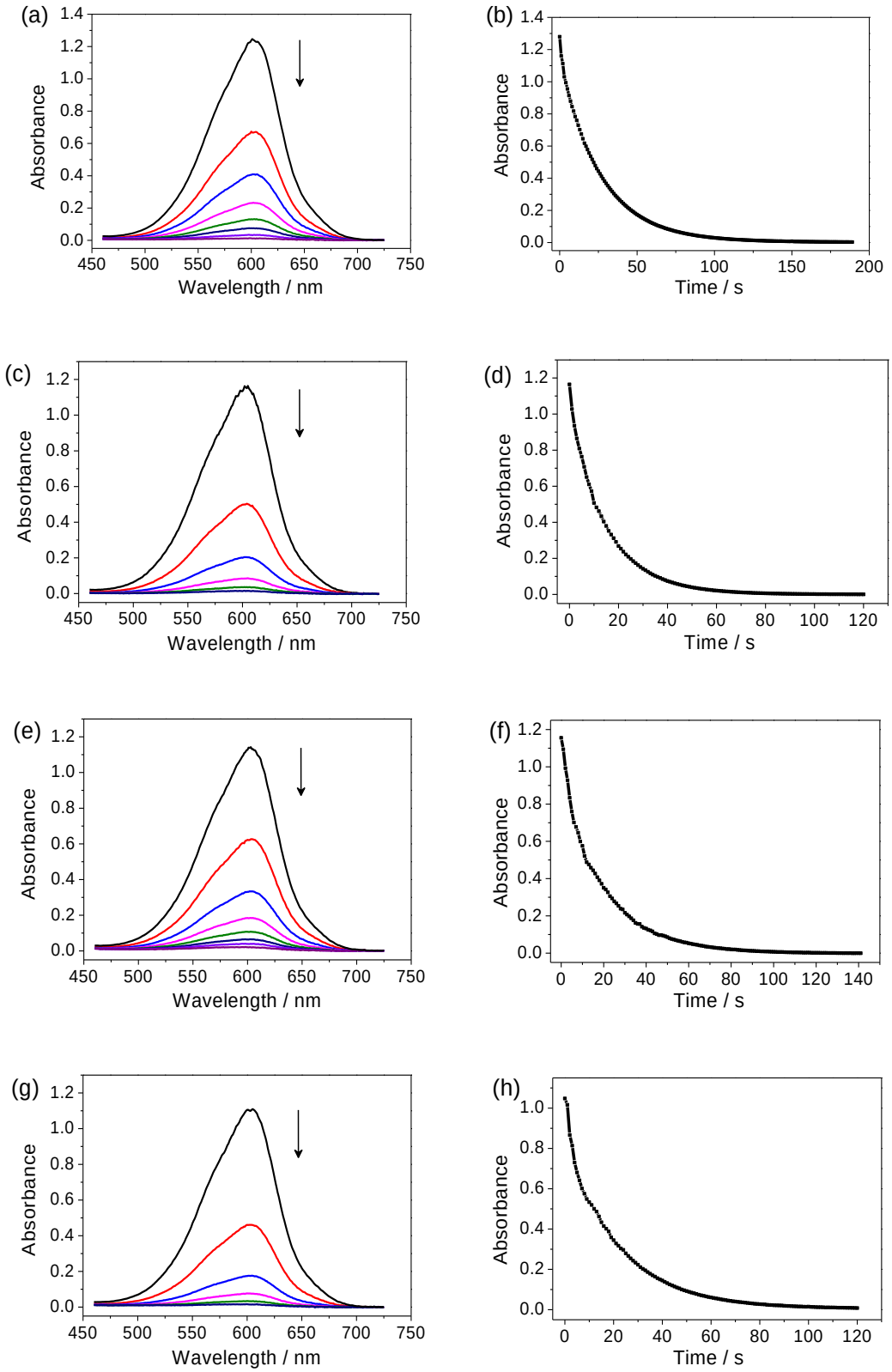


Figure S9. (a) Time-dependent UV-vis absorption spectral changes of the open form and (b) the decay trace at the absorption maximum at 603 nm with time of compound **5**. (c) Time-dependent UV-vis absorption spectral changes of the open form and (d) the decay trace at the absorption

maximum at 603 nm with time of compound **6**. (e) Time-dependent UV-vis absorption spectral changes of the open form and (f) the decay trace at the absorption maximum at 603 nm with time of compound **7**. (g) Time-dependent UV-vis absorption spectral changes of the open form and (h) the decay trace at the absorption maximum at 603 nm with time of compound **8** in benzene solution at 288 K after excitation at 365 nm (at time intervals of 10 s). The arrows indicate the spectral changes with time ($c = 8\times10^{-5}$ M).

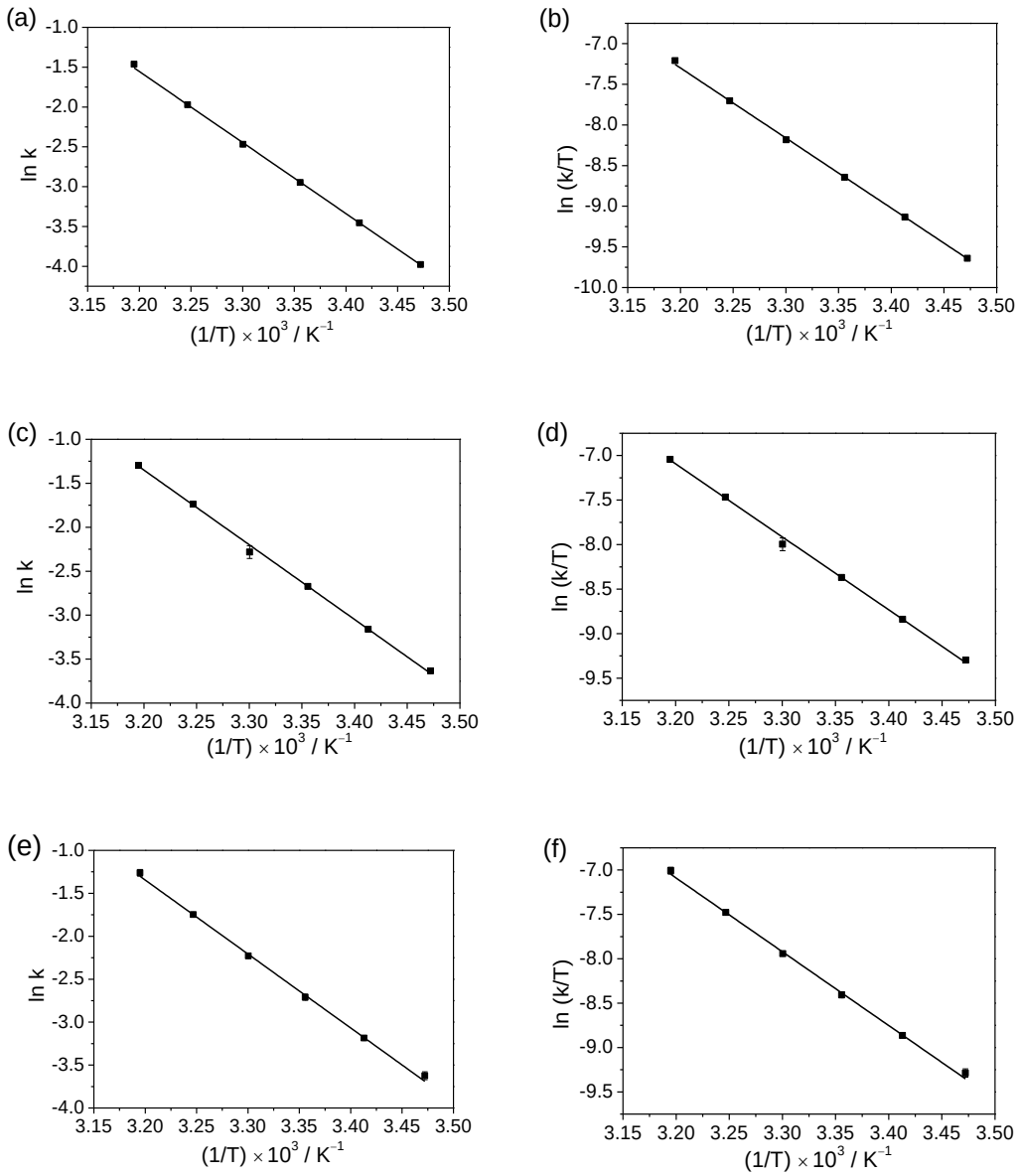


Figure S10. (a) Arrhenius and (b) Eyring plots for the thermal bleaching reaction of compund **2**. (c) Arrhenius and (d) Eyring plots for the thermal bleaching reaction of compund **3**. (e) Arrhenius and (f) Eyring plots for the thermal bleaching reaction of compund **4** in benzene solution ($c = 8\times10^{-5}$ M).

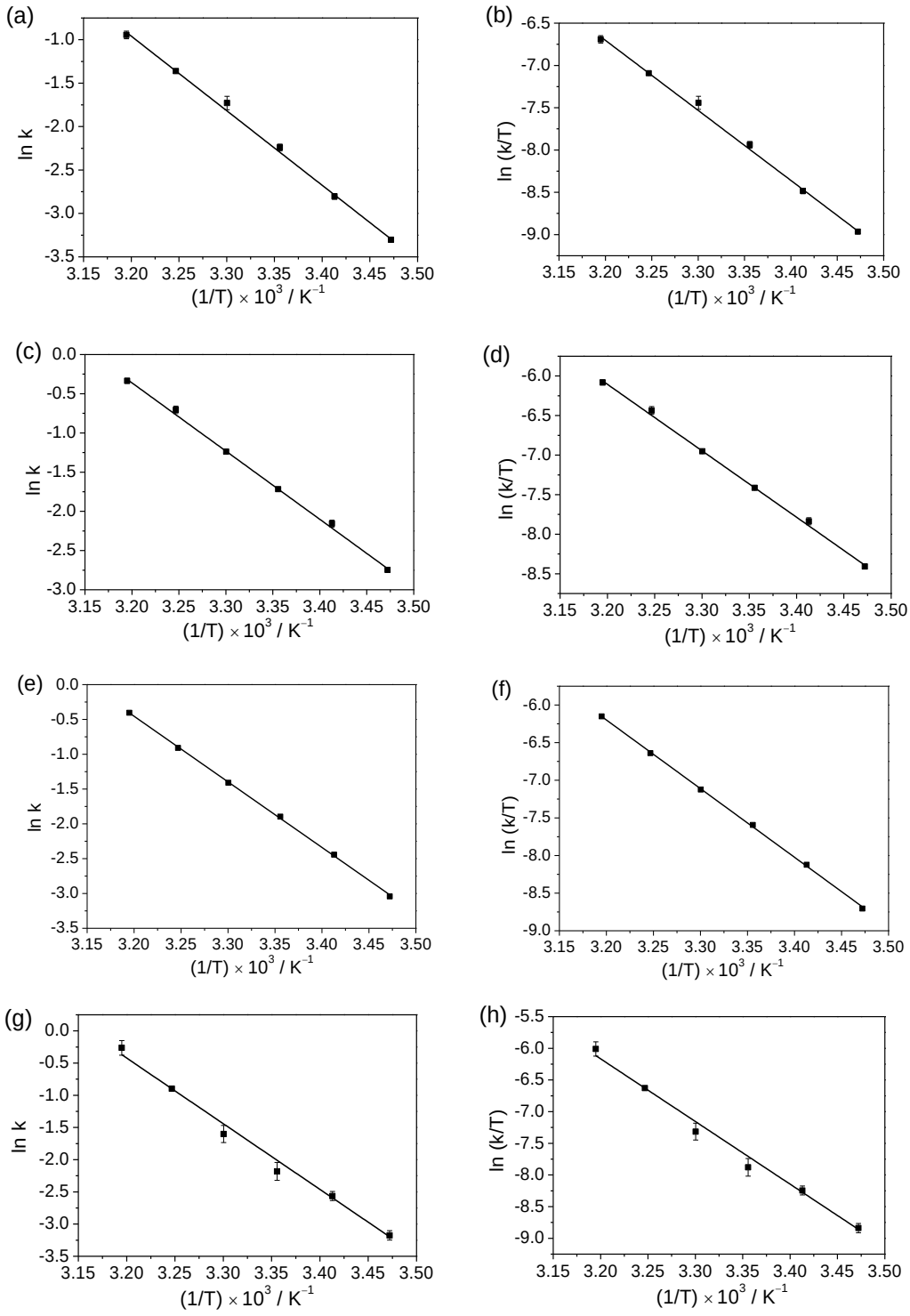


Figure S11. (a) Arrhenius and (b) Eyring plots for the thermal bleaching reaction of compund **5**. (c) Arrhenius and (d) Eyring plots for the thermal bleaching reaction of compund **6**. (e) Arrhenius and (f) Eyring plots for the thermal bleaching reaction of compund **7**. (g) Arrhenius and (h) Eyring plots for the thermal bleaching reaction of compund **8** in benzene solution ($c = 8\times10^{-5}$ M).

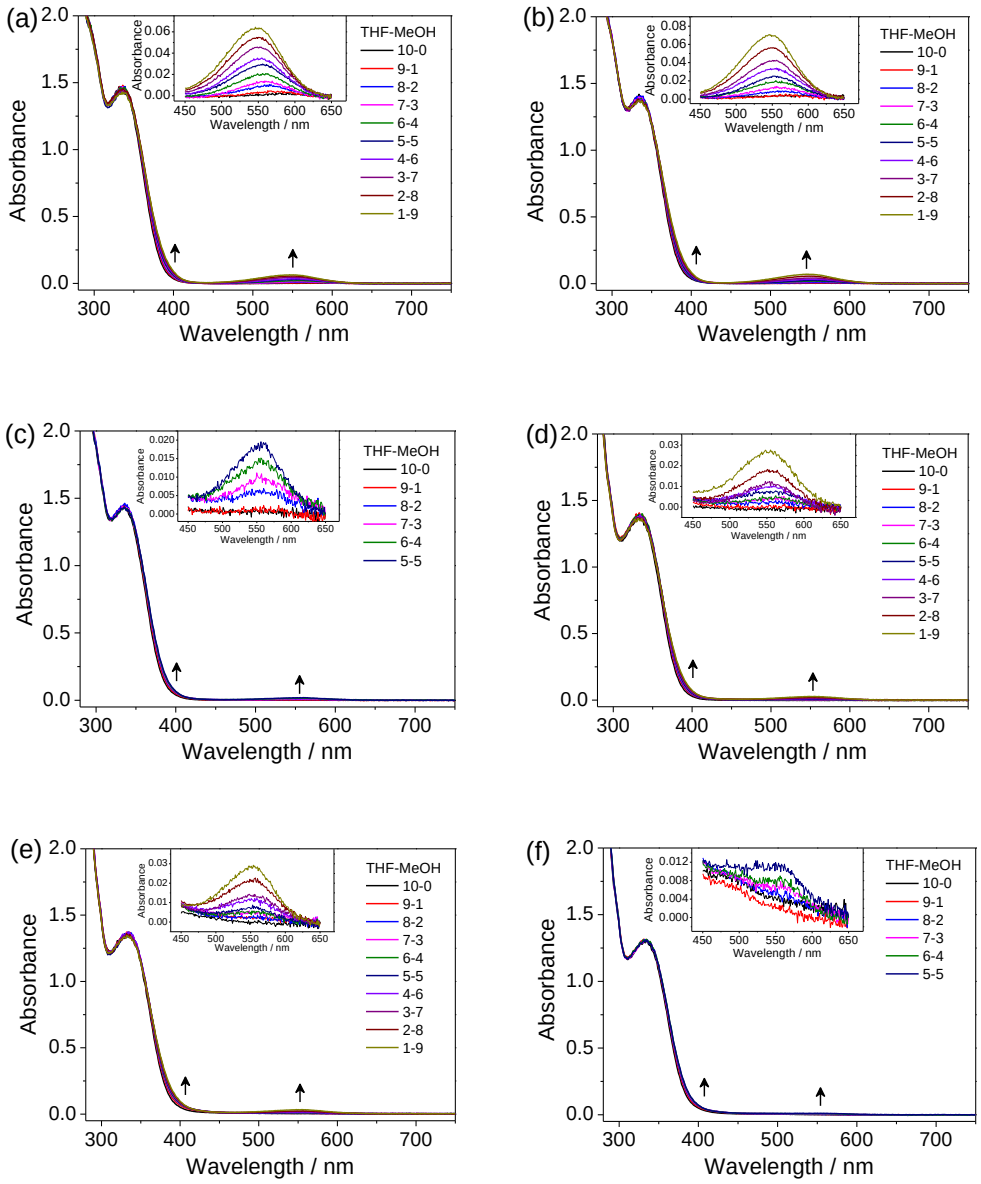


Figure S12. UV−Vis absorption spectral changes of compounds (a) **1**, (b) **2**, (c) **4**, (d) **6**, (e) **7** and (f) **8** in THF solutions upon increasing MeOH content at a concentration of 1.5×10^{-4} M. Inset: Expanded spectral changes at the lowest-energy absorption band from 450 nm to 650 nm.

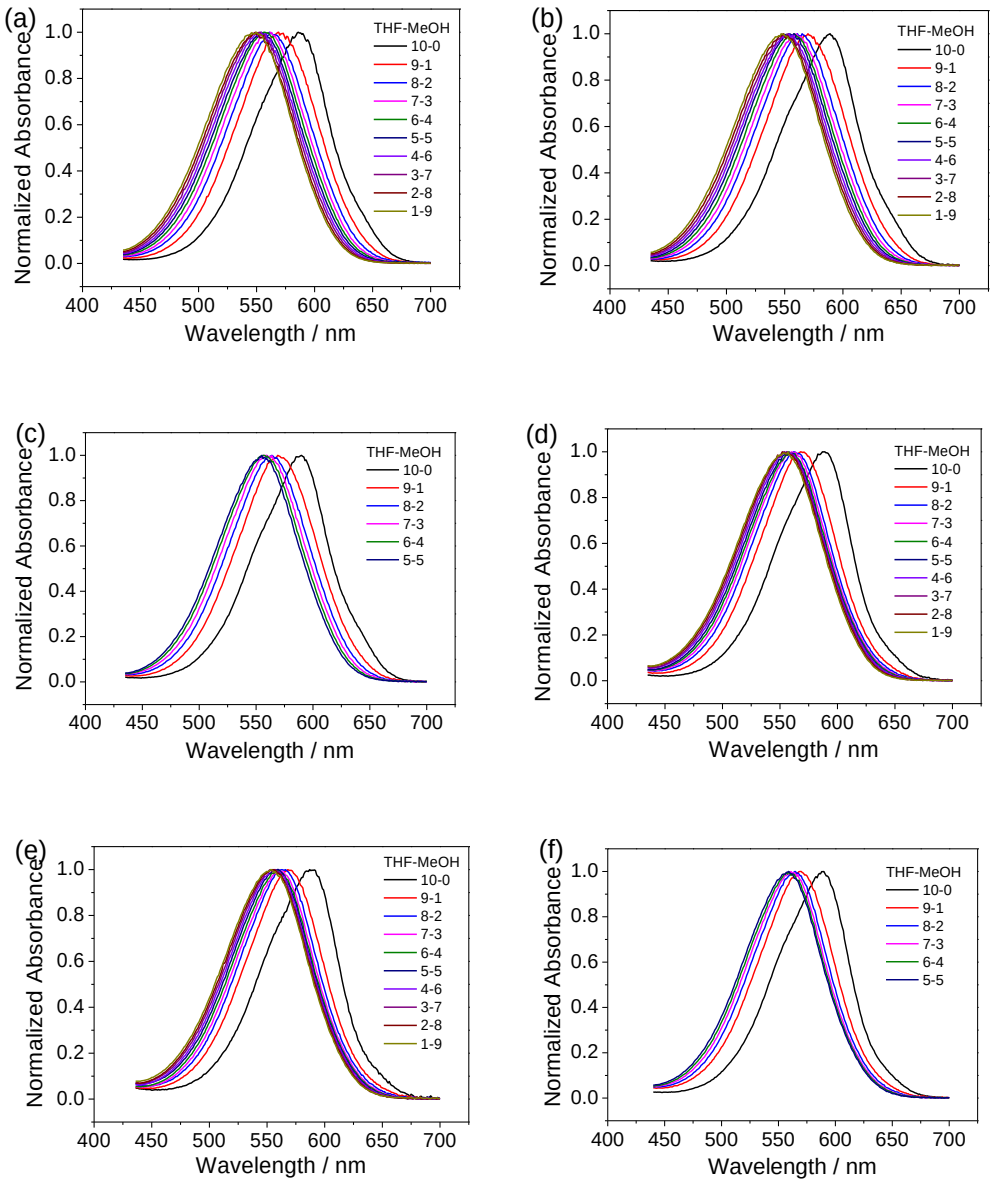


Figure S13. Normalized UV-vis absorption spectra of compounds (a) **1**, (b) **2**, (c) **4**, (d) **6**, (e) **7** and (f) **8** in mixed THF–MeOH solutions after UV light irradiation.

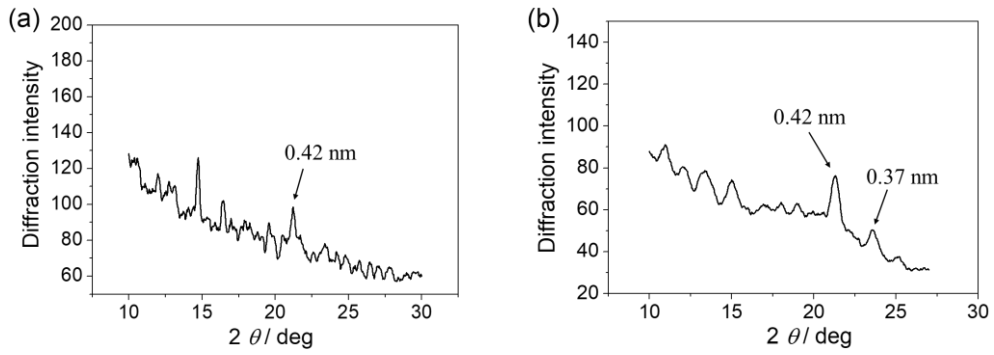


Figure S14. Powder XRD patterns of (a) compound **3** prepared from a THF–MeOH (1 : 9 v/v) solution after UV irradiation and (b) compound **4** prepared from a THF–MeOH (1 : 1 v/v) solution after UV irradiation.

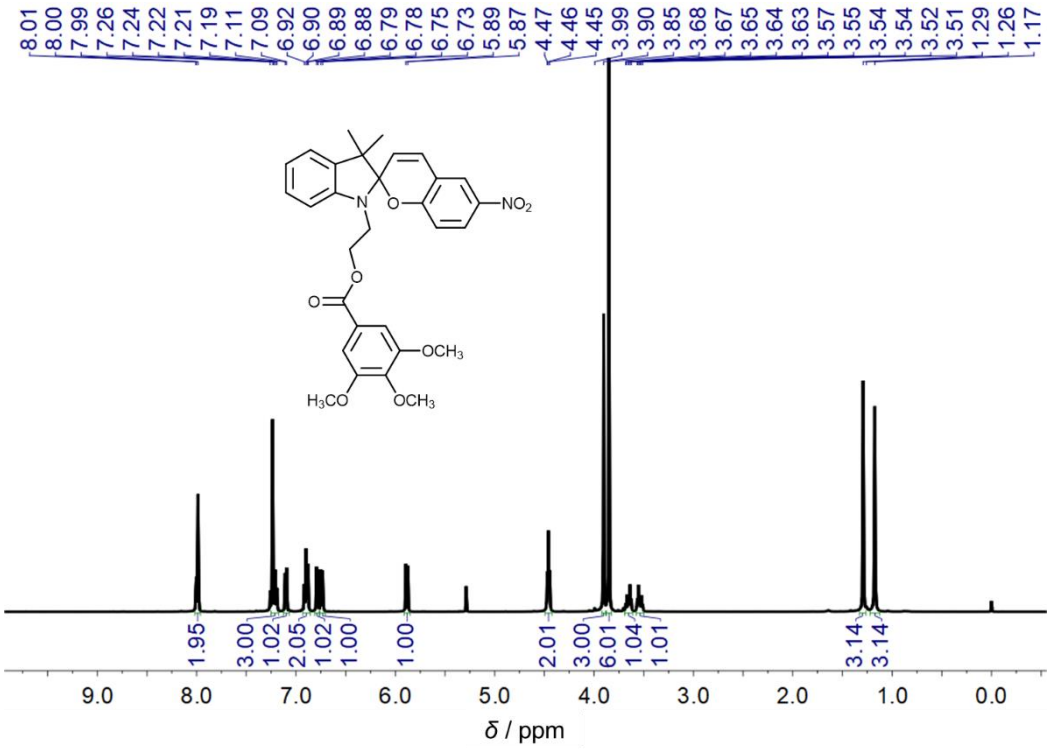


Figure S15. ^{1}H NMR of compound **1** in $CDCl_3$ at room temperature.

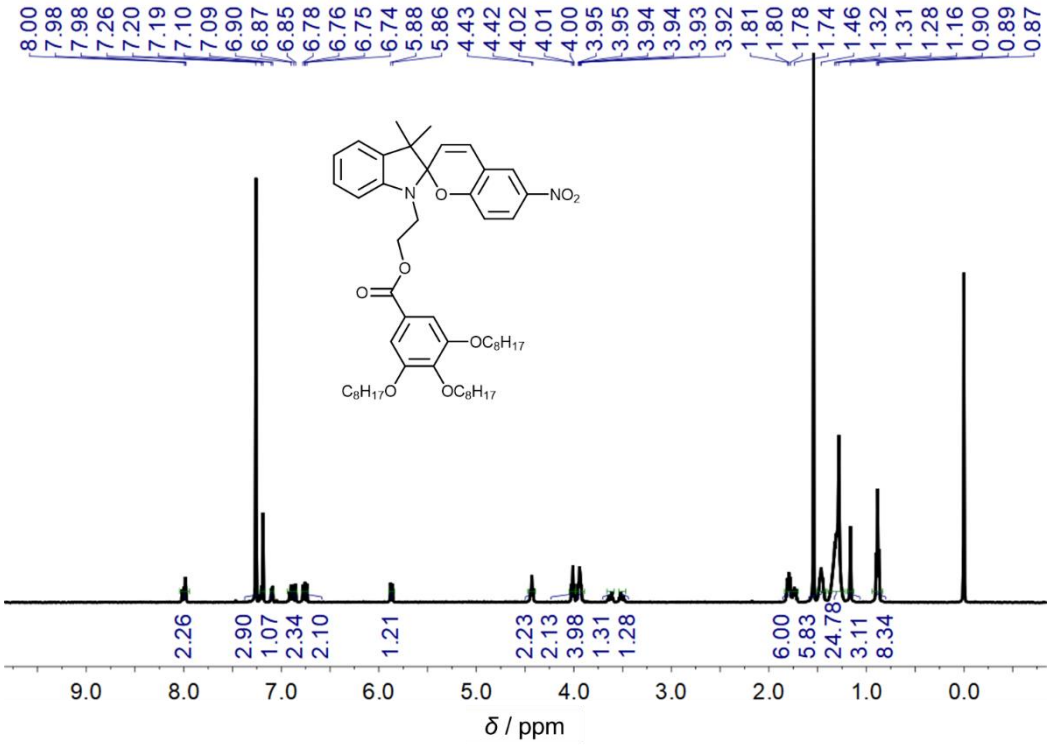


Figure S16. ^{1}H NMR of compound **2** in $CDCl_3$ at room temperature.

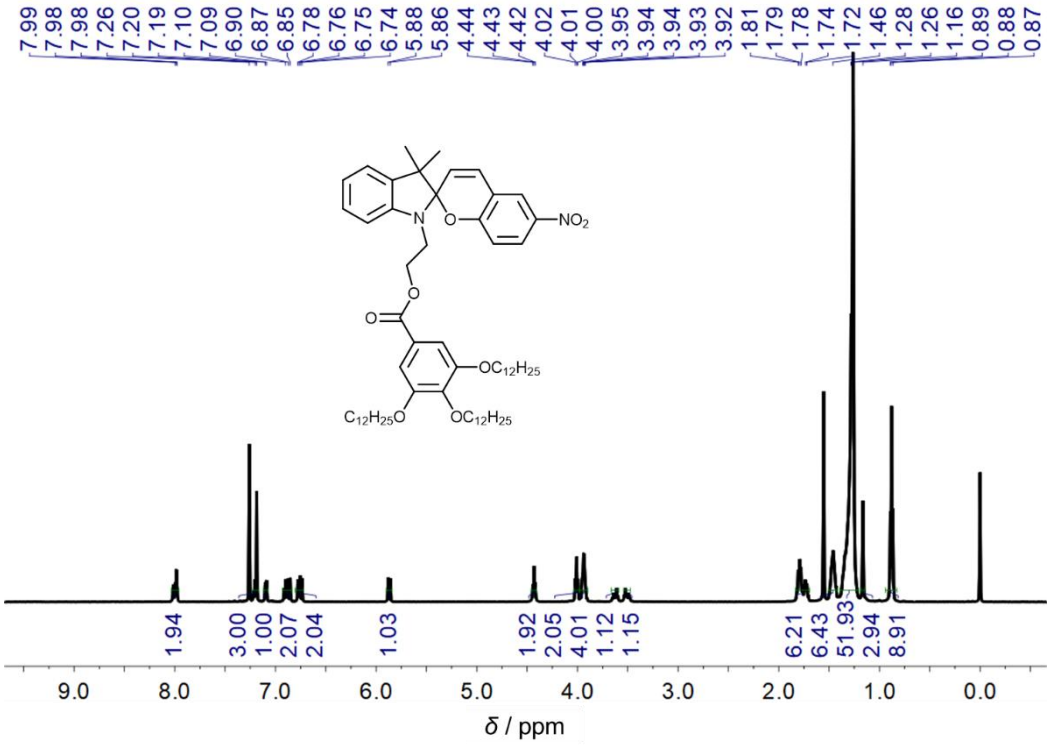


Figure S17. ^{1}H NMR of compound **3** in $CDCl_3$ at room temperature.

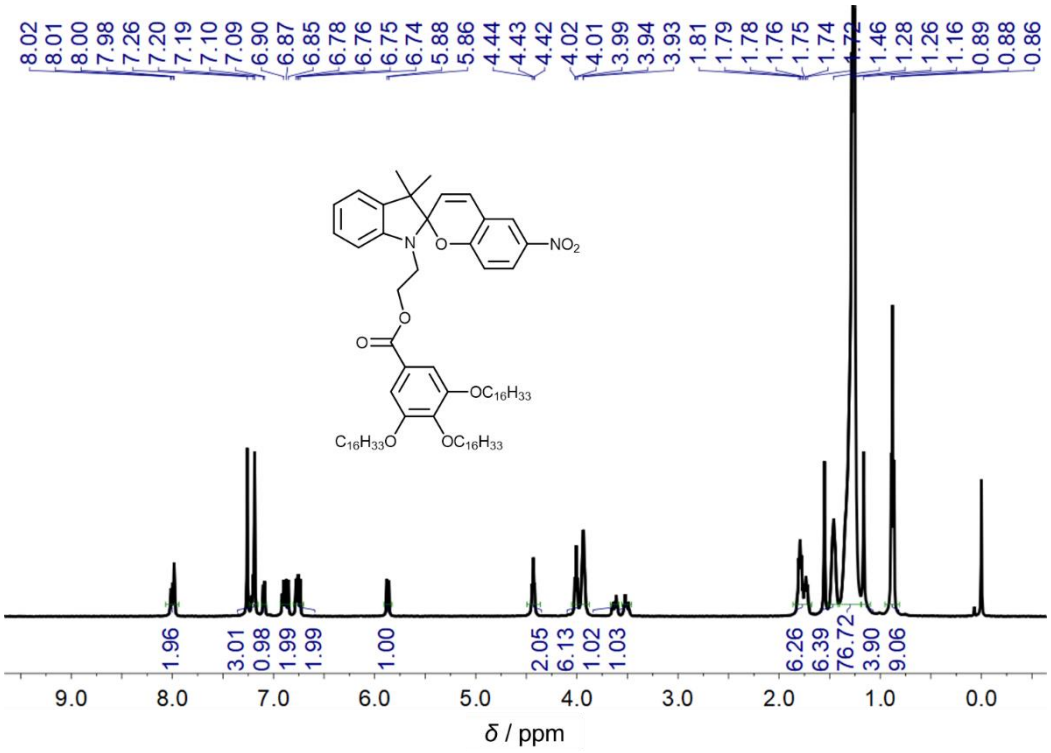


Figure S18. ^{1}H NMR of compound **4** in $CDCl_3$ at room tempearture.

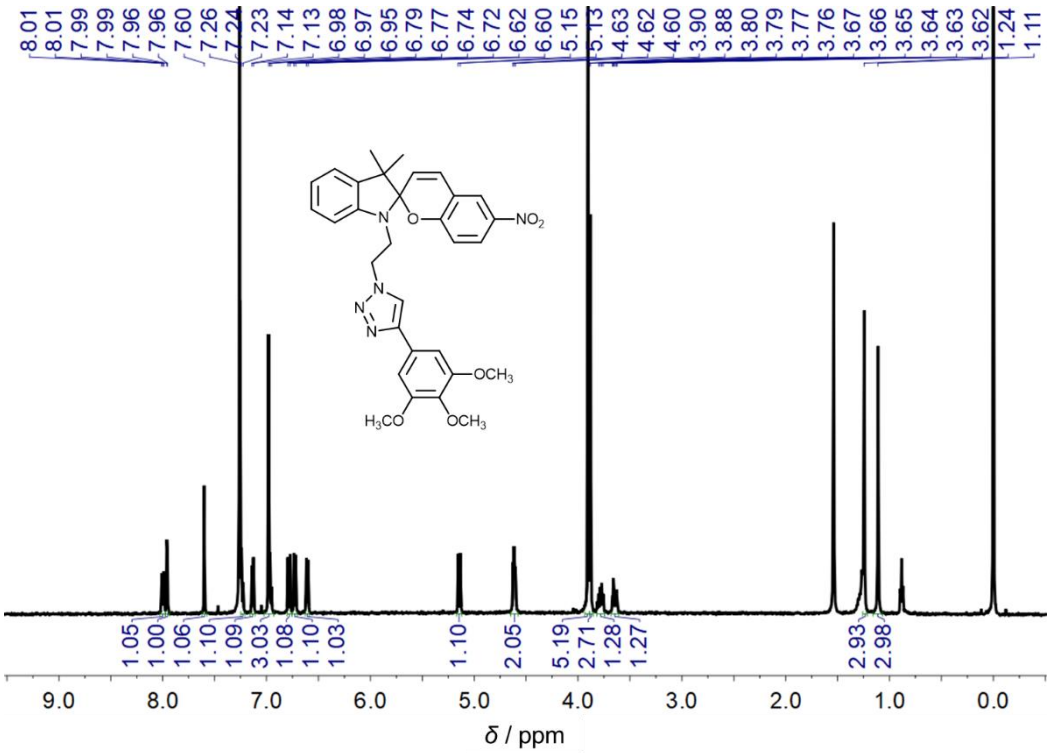


Figure S19. ^{1}H NMR of compound **5** in $CDCl_3$ at room temperature.

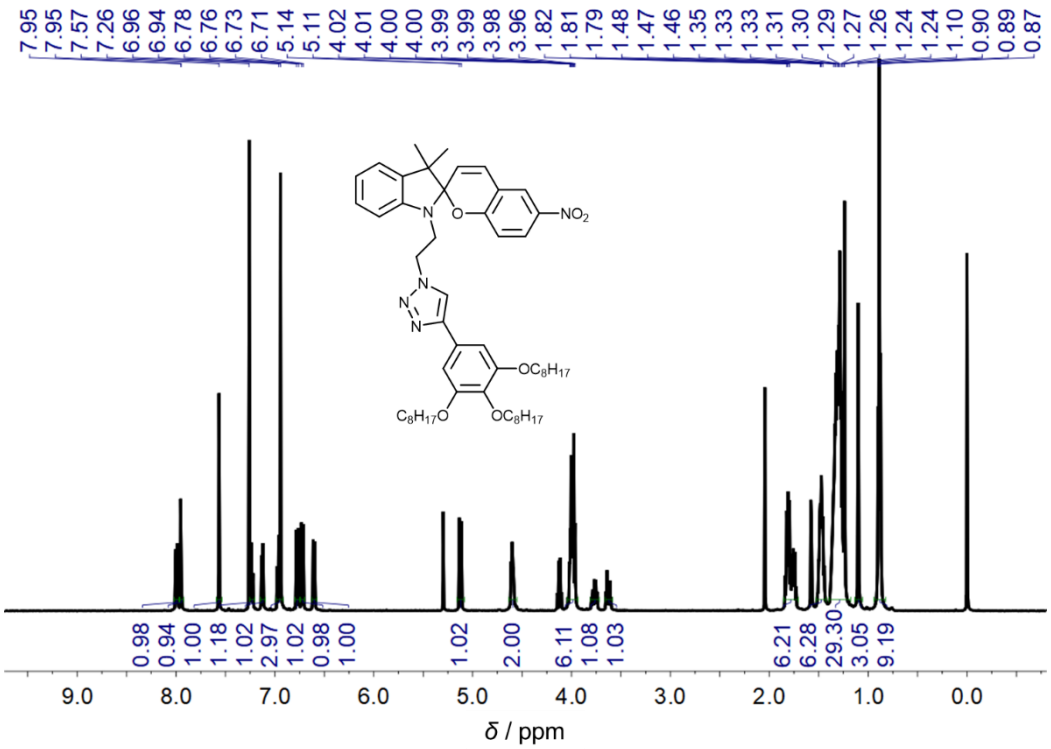


Figure S20. ^{1}H NMR of compound **6** in $CDCl_3$ at room temperature.

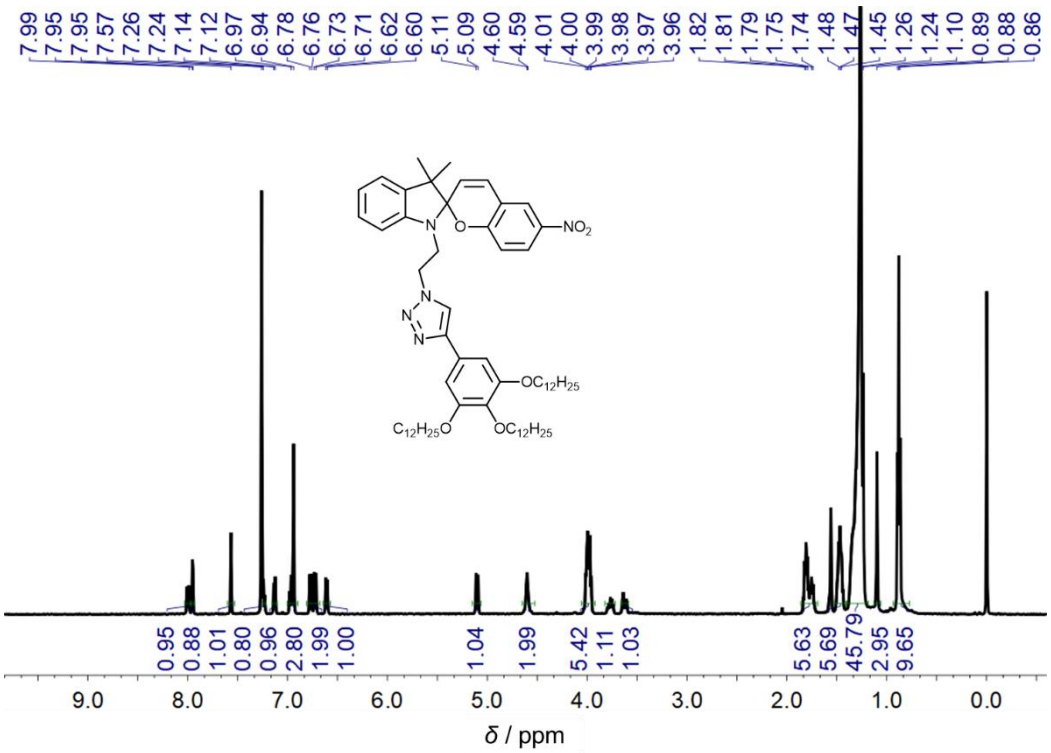


Figure S21. ^{1}H NMR of compound **7** in $CDCl_3$ at room temperature.

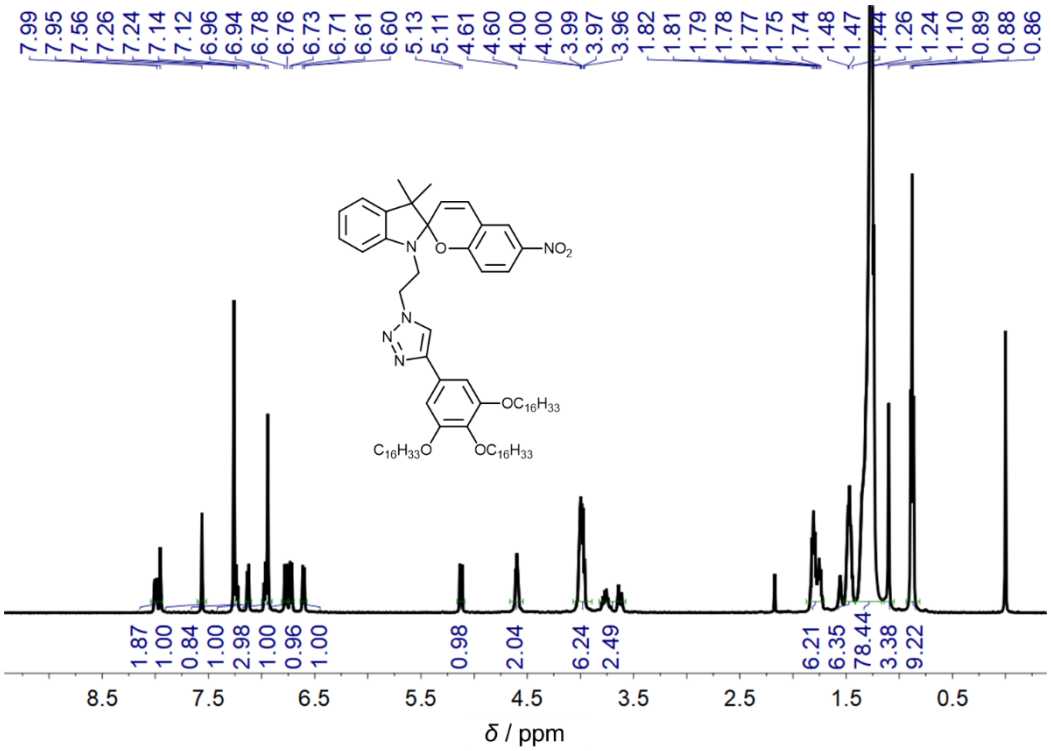
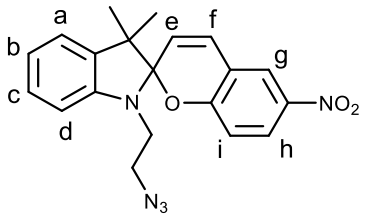


Figure S22. ^{1}H NMR of compound **8** in $CDCl_3$ at room temperature.

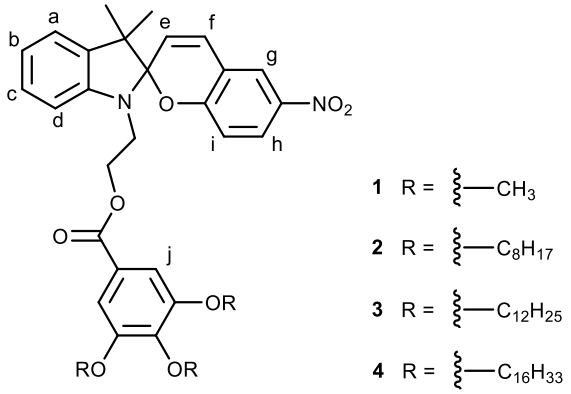
Experimental section

Materials and reagents: 3,4,5-Trimethoxybenzoic acid, 4-dimethylaminopyridine (DMAP), *N*,*N*'-dicyclohexylcarbodiimide (DCC) and sodium ascorbate were purchased from Energy Chemical Co, Ltd. Sodium azide (NaN_3), copper(II) sulfate pentahydrate ($CuSO_4$•$5H_2O$), *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM) and sodium sulphate (Na_2SO_4) were the products of Beijing Chemical Reagent Company. All commercially available reagents were of analytical grade and were used as received. All solvents were purified and distilled using standard procedures before use. 2-(3',3'-Dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol (SP-OH),[1] 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl 4-methylbenzenesulfonate (SP-OTs),[2] 3,4,5-tris(octyloxy)benzoic acid (C_8-COOH),[3] 3,4,5-tris(dodecyloxy)benzoic acid (C_{12}-COOH),[3] 3,4,5-tris(hexadecyloxy)benzoic acid (C_{16}-COOH),[4] 5-ethynyl-1,2,3-trimethoxybenzene,[5] 5-ethynyl-1,2,3-tris(octyloxy)benzene (C_8-alkyne),[6] 5-ethynyl-1,2,3-tris(dodecyloxy)benzene (C_{12}-alkyne)[6] and 5-ethynyl-1,2,3-tris(hexadecyloxy)benzene (C_{16}-alkyne)[7] were synthesized recording to the literature with slight modifications.

Synthesis and characterization



1'-(2-Azidoethyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline] (SP-N_3). NaN_3 (410 mg, 6.3 mmol) was added to a *N*,*N*-dimethylformamide (50 mL) solution containing SP-OTs (640 mg, 1.26 mmol). The mixture was stirred for 2 days at room temperature under nitrogen atmosphere. The reaction mixture was then poured into deionized water (100 mL). A yellow solid was precipitated, filtered and washed with deionized water for three times. Yield: 400 mg, 84 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si) : δ/ppm = 8.06–7.96 (m, 2H; H_h, H_g), 7.21 (t, J = 7.1 Hz, 1H; H_c), 7.11 (d, J = 7.1 Hz, 1H; H_a), 6.98–6.88 (m, 2H; H_b, H_f), 6.76 (d, J = 8.7 Hz, 1H; H_i), 6.62 (d, J = 7.1 Hz, 1H; H_d), 5.95 (d, J = 10.3 Hz, 1H; H_e), 3.60–3.40 (m, 2H; –CH_2O–), 3.39–3.29 (m, 2H; –NCH_2–), 1.29 (s, 3H, CH_3), 1.20 (s, 3H, CH_3). Elemental analysis calcd (%) for $C_{20}H_{19}N_5O_3$: C 63.65, H 5.07, N 18.56; found: C 63.75, H 5.02, N 18.12.



Compound **1**. To a degassed mixture of SP-OH (960 mg, 2.75 mmol), 3,4,5-trimethoxybenzoic acid (700 mg, 3.30 mmol) and a catalytic amount of DMAP (37.5 mg, 0.31

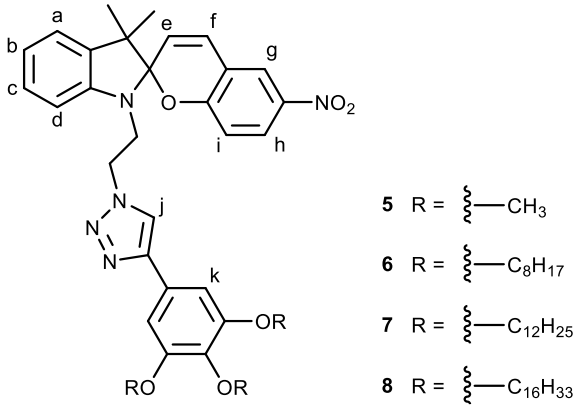
mmol) in dry dichloromethane (60 mL) was added DCC (684 mg, 3.32 mmol). The resulting solution was allowed to stir at room temperature for 36 h under nitrogen atmosphere. After filtering out the resulting 1,3-dicyclohexylurea (DCU), the solvent was removed under reduced pressure to obtain the residue, which was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether-ethyl acetate (10:1, v/v) as the eluent. Subsequent recrystallization from dichloromethane-methanol gave the pure product as a solid with a pale green tint. Yield: 830 mg, 55 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.02–7.96 (m, 2H; H_h, H_g), 7.25–7.17 (m, 3H; H_c, H_j), 7.10 (d, J = 7.2 Hz, 1H; H_a), 6.94–6.86 (m, 2H; H_b, H_f), 6.79 (d, J = 7.2 Hz, 1H; H_d), 6.74 (d, J = 8.5 Hz, 1H; H_i), 5.88 (d, J = 10.3 Hz, 1H; H_e), 4.46 (t, J = 6.2 Hz, 2H; –CH_2O–), 3.90 (s, 3H; –OCH_3), 3.85 (s, 6H; –OCH_3), 3.69–3.61 (m, 1H; –NCH_2–), 3.58–3.50 (m, 1H; –NCH_2–), 1.29 (s, 3H; –CCH_3), 1.17 (s, 3H; –CCH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 166.08, 159.37, 152.97, 146.79, 142.38, 141.12, 135.77, 128.42, 127.89, 126.00, 124.83, 122.79, 121.89, 121.68, 119.97, 118.39, 115.59, 106.84, 106.74, 106.50, 63.14, 60.94, 56.24, 52.84, 42.44, 25.91, 19.83. MALDI-TOF MS: *m/z*: 546.9 $[M+H]^+$. Elemental analysis calcd (%) for $C_{30}H_{30}N_2O_8$: C 65.92, H 5.53, N 5.13; found: C 66.13, H 5.42, N 5.05.

Compound **2**. This was prepared from a similar procedure as that of compound **1**, except C_8-COOH (470 mg, 0.93 mmol) was used instead of 3,4,5-trimethoxybenzoic acid. Yield: 203 mg, 31 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.04–7.94 (m, 2H; H_h, H_g), 7.23–7.17 (m, 3H; H_c, H_j), 7.10 (d, J = 7.1 Hz, 1H; H_a), 6.94–6.84 (m, 2H; H_b, H_f), 6.79–6.72 (m, 2H; H_i, H_d), 5.87 (d, J = 10.3 Hz, 1H; H_e), 4.43 (t, J = 6.2 Hz, 2H; –CH_2O–), 4.01 (t, J = 6.6 Hz, 2H; CH_2), 3.94 (t, J = 6.6 Hz, 4H; CH_2), 3.67–3.45 (m, 2H; –NCH_2–), 1.84–1.70 (m, 6H; CH_2), 1.51–1.41 (m, 6H; CH_2), 1.40–1.22 (m, 27H; CH_2, –CCH_3), 1.16 (s, 3H; –CCH_3), 0.88 (t, J = 6.3 Hz, 9H; –CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 166.30, 159.38, 152.86, 146.80, 142.59, 141.12, 135.74, 128.35, 127.89, 125.99, 124.33, 122.77, 121.84, 121.75, 119.94, 118.39, 115.58, 108.01, 106.75, 106.52, 73.53, 69.19, 62.94, 52.81, 42.51, 31.90, 31.84, 30.34, 29.51, 29.36, 29.31, 29.29, 26.10, 26.05, 25.91, 22.68, 19.84, 14.10. MALDI-TOF MS: *m/z*: 841.4 $[M+H]^+$. Elemental analysis calcd (%) for $C_{51}H_{72}N_2O_8$: C 72.82, H 8.63, N 3.33; found: C 72.91, H 8.52, N 3.24.

Compound **3**. This was prepared from a similar procedure as that of compound **1**, except C_{12}-

COOH (580 mg, 0.85 mmol) was used instead of 3,4,5-trimethoxybenzoic acid. Yield: 380 mg, 51 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.04–7.96 (m, 2H; H_h, H_g), 7.23–7.16 (m, 3H; H_c, H_j), 7.09 (d, J = 7.2 Hz, 1H; H_a), 6.93–6.84 (m, 2H; H_b, H_f), 6.79 – 6.72 (m, 2H; H_i, H_d), 5.87 (d, J = 10.3 Hz, 1H; H_e), 4.43 (t, J = 6.1 Hz, 2H; –CH_2O–), 4.01 (t, J = 6.5 Hz, 2H; CH_2), 3.98–3.90 (m, 4H; CH_2), 3.67–3.45 (m, 2H; –NCH_2–), 1.83–1.69 (m, 6H; CH_2), 1.52–1.40 (m, 6H; CH_2), 1.40–1.22 (m, 51H; CH_2, –CCH_3), 1.16 (s, 3H; –CCH_3), 0.88 (t, J = 6.8 Hz, 9H; –CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 166.30, 159.38, 152.87, 146.80, 142.59, 141.12, 135.74, 128.35, 127.90, 125.99, 124.33, 122.78, 121.84, 121.74, 119.94, 118.39, 115.58, 108.01, 106.75, 106.52, 73.53, 69.18, 62.95, 52.81, 42.52, 31.94, 30.35, 29.74, 29.72, 29.68, 29.66, 29.58, 29.42, 29.41, 29.38, 29.33, 26.11, 26.07, 25.91, 22.71, 19.84, 14.13. MALDI-TOF MS: *m/z*: 1010.1 $[M+H]^+$. Elemental analysis calcd (%) for $C_{63}H_{96}N_2O_8$: C 74.96, H 9.59, N 2.78; found: C 74.85, H 9.49, N 2.63.

Compound **4**. This was prepared from a similar procedure as that of compound **1**, except C_{16}-COOH (490 mg, 0.58 mmol) was used instead of 3,4,5-trimethoxybenzoic acid. Yield: 250 mg, 36 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.04–7.96 (m, 2H; H_h, H_g), 7.23–7.15 (m, 3H; H_c, H_j), 7.09 (d, J = 7.0 Hz, 1H; H_a), 6.92–6.84 (m, 2H; H_b, H_f), 6.80 – 6.70 (m, 2H; H_i, H_d), 5.87 (d, J = 10.4 Hz, 1H; H_e), 4.43 (t, J = 6.1 Hz, 2H; –CH_2O–), 4.01 (t, J = 6.5 Hz, 2H; CH_2), 3.98–3.90 (m, 4H; CH_2), 3.67–3.45 (m, 2H; –NCH_2–), 1.87–1.67 (m, 6H; CH_2), 1.51–1.40 (m, 6H; CH_2), 1.39–1.19 (m, 75H; CH_2, –CCH_3), 1.16 (s, 3H; –CCH_3), 0.88 (t, J = 6.8 Hz, 9H; –CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 166.30, 159.38, 152.87, 146.80, 142.59, 141.12, 135.74, 128.35, 127.90, 125.99, 124.33, 122.77, 121.84, 121.74, 119.94, 118.39, 115.58, 108.01, 106.76, 106.51, 73.53, 69.19, 62.96, 52.81, 42.52, 31.95, 30.36, 29.73, 29.69, 29.67, 29.59, 29.43, 29.39, 29.33, 26.12, 26.08, 25.92, 22.71, 19.84, 14.13. MALDI-TOF MS: *m/z*: 1178.3 $[M+H]^+$. Elemental analysis calcd (%) for $C_{75}H_{120}N_2O_8$: C 76.48, H 10.27, N 2.38; found: C 76.21, H 9.98, N 2.26.



Compound **5**. This was prepared according to a modification of the procedures for azide-alkyne click reaction in the literature.[8] To a solution of SP-N_3 (315 mg, 0.83mmol) and 5-ethynyl-1,2,3-trimethoxybenzene (200 mg, 1.04 mmol) in dichloromethane (30 mL) were added sodium ascorbate (100 mg, 0.50 mmol) and $CuSO_4$•$5H_2O$ (253 mg, 1.01 mmol) in deionized water (20 mL). The mixture was stirred at room temperature under nitrogen atmosphere overnight. The organic phase was separated and washed with deionized water, and was dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1, v/v) as the eluent to give the product as a solid with a pale blue tint. Yield: 300 mg, 62 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.03–7.93 (m, 2H; H_h, H_g), 7.60 (s, 1H; H_j), 7.23 (t, J = 7.1 Hz, 1H; H_c), 7.13 (d, J = 7.1 Hz, 1H; H_a), 7.00–6.93 (m, 3H; H_b, H_k), 6.78 (d, J = 10.4 Hz, 1H; H_f), 6.73 (d, J = 8.9 Hz, 1H; H_i), 6.61 (d, J = 7.1 Hz, 1H; H_d), 5.14 (d, J = 10.4 Hz, 1H; H_e), 4.62 (t, J = 4.8 Hz, 2H; –NCH_2–), 3.90 (s, 6H; CH_3), 3.88 (s, 3H; CH_3), 3.83–3.73 (m, 1H; –CH_2O–), 3.69–3.60 (m, 1H; –CH_2O–), 1.24 (s, 3H; –CCH_3), 1.11 (s, 3H; –CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 158.91, 153.72, 147.61, 145.90, 141.26, 138.24, 136.14, 128.82, 128.01, 125.98, 122.81, 122.25, 120.76, 120.66, 120.58, 118.36, 115.51, 106.45, 106.37, 102.87, 60.96, 56.25, 52.70, 48.84, 44.46, 25.75, 19.84. MALDI-TOF MS: *m/z*: 570.0 $[M+H]^+$. Elemental analysis calcd (%) for $C_{31}H_{31}N_5O_6$: C 65.37, H 5.49, N 12.30; found: C 65.48, H 5.47, N 12.12.

Compound **6**. This was prepared from a similar procedure as that of compound **5**, except C_8-alkyne (340 mg, 0.73 mmol) was used instead of 5-ethynyl-1,2,3-trimethoxybenzene. Yield: 340 mg, 39 %. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.03–7.92 (m, 2H; H_h, H_g), 7.57 (s, 1H; H_j), 7.25–7.20 (m, 1H; H_c), 7.15–7.10 (m, 1H; H_a), 6.99–6.92 (m, 3H;

H_b, H_k), 6.77 (d, J = 10.3 Hz, 1H; H_f), 6.72 (d, J = 9.0 Hz, 1H; H_i), 6.61 (d, J = 7.1 Hz, 1H; H_d), 5.12 (d, J = 10.3 Hz, 1H; H_e), 4.63–4.55 (m, 2H; $-CH_2O-$), 4.04–3.93 (m, 6H; CH_2), 3.81–3.73 (m, 1H; $-NCH_2-$), 3.66–3.58 (m, 1H; $-NCH_2-$), 1.85–1.71 (m, 6H; CH_2), 1.53–1.42 (m, 6H; CH_2), 1.40–1.18 (m, 27H; CH_2, $-CCH_3$), 1.10 (s, 3H; $-CCH_3$), 0.89 (t, J = 6.6 Hz, 9H; $-CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 158.91, 153.61, 147.87, 145.92, 141.29, 138.53, 136.17, 128.82, 127.99, 125.97, 125.41, 122.82, 122.24, 120.64, 120.58, 118.37, 115.50, 106.46, 106.36, 104.37, 77.28, 77.03, 76.77, 73.55, 69.30, 52.69, 48.78, 44.50, 31.92, 31.85, 30.36, 29.57, 29.44, 29.39, 29.31, 26.13, 26.11, 25.75, 22.71, 22.69, 19.84, 14.11. MALDI-TOF MS: *m/z*: 864.1 $[M+H]^+$. Elemental analysis calcd (%) for $C_{52}H_{73}N_5O_6$: C 72.27, H 8.51, N 8.10; found: C 72.49, H 8.25, N 8.07.

Compound **7**. This was prepared from a similar procedure as that of compound **5**, except C_{12}-alkyne (833 mg, 1.32 mmol) was used instead of 5-ethynyl-1,2,3-trimethoxybenzene. Yield: 510 mg, 47 %. ^1H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.04–7.92 (m, 2H; H_h, H_g), 7.57 (s, 1H; H_j), 7.23 (t, J = 7.1 Hz, 1H; H_c), 7.13 (d, J = 7.1 Hz, 1H; H_a), 7.00–6.90 (m, 3H; H_b, H_k), 6.77 (d, J = 10.3 Hz, 1H; H_f), 6.72 (d, J = 9.0 Hz, 1H; H_i), 6.61 (d, J = 7.1 Hz, 1H; H_d), 5.10 (d, J = 10.3 Hz, 1H; H_e), 4.65–4.53 (m, 2H; $-CH_2O-$), 4.05–3.93 (m, 6H; CH_2), 3.82–3.72 (m, 1H; $-NCH_2-$), 4.00–3.92 (m, 1H; $-NCH_2-$), 1.86–1.70 (m, 6H; CH_2), 1.53–1.42 (m, 6H; CH_2), 1.40–1.29 (m, 51H; CH_2, $-CCH_3$), 1.10 (s, 3H; $-CCH_3$), 0.88 (t, J = 6.9 Hz, 9H; $-CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 158.92, 153.62, 147.86, 145.93, 141.27, 138.51, 136.15, 128.80, 128.00, 125.95, 125.43, 122.80, 122.22, 120.63, 118.38, 115.49, 106.46, 106.37, 104.35, 73.54, 69.29, 52.68, 48.79, 44.50, 31.96, 31.95, 30.38, 29.78, 29.76, 29.73, 29.72, 29.68, 29.64, 29.46, 29.41, 29.39, 26.16, 26.14, 25.76, 22.71, 19.84, 14.13. MALDI-TOF MS: *m/z*: 1032.7 $[M+H]^+$. Elemental analysis calcd (%) for $C_{64}H_{97}N_5O_6$: C 74.45, H 9.47, N 6.78; found: C 74.62, H 9.37, N 6.70.

Compound **8**. This was prepared from a similar procedure as that of compound **5**, except C_{16}-alkyne (680 mg, 0.81 mmol) was used instead of 5-ethynyl-1,2,3-trimethoxybenzene. Yield: 480 mg, 50 %. ^1H NMR (500 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ/ppm = 8.03–7.93 (m, 2H; H_h, H_g), 7.56 (s, 1H; H_j), 7.23 (t, J = 7.2 Hz, 1H; H_c), 7.13 (d, J = 7.2 Hz, 1H; H_a), 7.00–6.90 (m, 3H; H_b, H_k), 6.77 (d, J = 10.3 Hz, 1H; H_f), 6.72 (d, J = 9.0 Hz, 1H; H_i), 6.60 (d, J = 7.2 Hz, 1H; H_d), 5.12 (d, J = 10.3 Hz, 1H; H_e), 4.67–4.52 (m, 2H; $-CH_2O-$), 4.07–3.89 (m, 6H; CH_2),

3.82–3.57 (m, 2H; –NCH_2–), 1.87–1.71 (m, 6H; CH_2), 1.52–1.42 (m, 6H; CH_2), 1.41–1.17 (m, 75H; CH_2, $–CCH_3$), 1.10 (s, 3H; $–CCH_3$), 0.88 (t, J = 6.7 Hz, 9H; $–CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ/ppm = 158.92, 153.62, 147.86, 145.93, 141.27, 138.51, 136.15, 128.80, 128.00, 125.95, 125.43, 122.80, 122.22, 120.63, 118.38, 115.49, 106.46, 106.37, 104.35, 73.54, 69.29, 52.68, 48.79, 44.50, 31.96, 31.95, 30.38, 29.78, 29.76, 29.73, 29.72, 29.68, 29.64, 29.46, 29.41, 29.39, 26.16, 26.14, 25.76, 22.71, 19.84, 14.13. MALDI-TOF MS: *m/z*: 1200.9 $[M+H]^+$. Elemental analysis calcd (%) for $C_{76}H_{121}N_5O_6$: C 76.02, H 10.16, N 5.83; found: C 76.23, H 10.07, N 5.73.

Physical measurements and instrumentation

^1H NMR (500 MHz) and $^{13}C\{^1H\}$ NMR (125 MHz) spectra were obtained on a Bruker DRX 500 (500 MHz) spectrometer at 298 K with chemical shifts reported relative to tetramethylsilane (Me_4Si). All MALDI-TOF mass spectra were recorded on a Bruker Autoflex speed TOF. Elemental analysis was carried out on a Flash EA1112 analyzer from ThermoQuest Italia S.P.A. The single crystal structure was obtained on a R-AXIS RAPID X-ray single crystal diffractometer. UV-Vis absorption spectra were recorded using a Varian Cary 50 UV-vis spectrophotometer. Steady-state excitation and emission spectra at room temperature were obtained on an Edinburgh Instruments FS5 spectrofluorometer. The kinetics experiments of the thermal backward reaction of the open form of all the compounds at various temperatures were carried out by using a Varian Cary 50 UV-vis spectrophotometer with a single cell Peltier thermostat. Transmission electron microscopy (TEM) experiments were recorded on a Philips Tecnai G2 20 S-TWIN or on a Philips CM100 Transmission Electron Microscope with an accelerating voltage of 200 kV. Dynamic light scattering (DLS) measurements were performed at 25 °C using Malvern (UK) Zetasizer 3000HSA with internal HeNe laser (λ_0 = 632.8 nm). Atomic force microscope (AFM) measurements were carried out on a Bruker FastScan atomic force microscope. Powder X-ray diffraction (XRD) data were recorded on a Rigaku X-ray diffractometer using Cu-Kα radiation at a wavelength of 1.542 Å.

Thermal bleaching kinetics measurement

The thermal bleaching reaction of spiropyrans is known to follow first order kinetics at

various temperatures. The kinetics for the bleaching reaction were determined by measurement of the UV-vis spectral changes at various temperatures by use of a Varian Cary 50 UV-vis spectrophotometer, with the temperature controlled by a Varian Cary single cell Peltier thermostat. The first-order rate constants were obtained by taking the negative value of the slope of a linear least-squares fit of ln $[(A - A_\infty)/(A_0 - A_\infty)]$ against time according to Equation(1),

$$\ln [(A - A_\infty)/(A_0 - A_\infty)] = -kt \quad (1)$$

where A, A_0, and A_∞ are the absorbances at the absorption wavelength maximum of the photomerocyanine at times t, 0 and infinity, respectively, and k is the rate constant of the reaction. The kinetics parameters were obtained by a linear least-squares fitting of ln (k/T) against $1/T$ according to the linear expression of the Eying equation (2), ln k against $1/T$ according to the Arrhenius equation (3), and the change in Gibbs free energy of activation ($\Delta G^{\neq}$) at 298 K were determined according to equation (4),

$$\ln (k/T) = -(\Delta H^{\neq}/R)(1/T) + \ln (k_B h^{-1}) + (\Delta S^{\neq}/R) \quad (2)$$

$$\ln (k) = -E_a/RT + \ln A \quad (3)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (4)$$

where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the changes in activation enthalpy and entropy, respectively, T is the temperature, and k_B, R, h, and A are the Boltzmann's constant, the universal gas constant, the Planck constant and the frequency factor, respectively.

Sample preparation

The samples for TEM measurements were prepared by adding a few drops of solutions onto a carbon-coated copper grid. They were then dried in air until the solvent was completely evaporated off in the dark. The sample preparation for AFM measurements was the same as that for TEM except that 10 μL of solution was dropped onto a silicon wafer. Samples for XRD experiments were prepared by drop-casting 10 μL of self-assembly solution onto a silicon wafer followed by drying at room temperature, and this procedure was repeated for ten times to accumulate enough samples for obtaining XRD signals.

Computational Details

All the calculations were performed using the Gaussian 09 suite of programs.[9] By density functional theory (DFT), the ground-state (S_0) geometries of the closed forms of compounds **5**

and **6**, as well as the open form of compound **6**, were fully optimized in benzene with the long range corrected B3LYP functional using the Coulomb-attenuating method (CAM-B3LYP),[10] in conjunction with the conductor-like polarizable continuum model (CPCM).[11,12] Time-dependent DFT (TDDFT)[13–15] calculations at the same level of theory associated with CPCM (benzene) have been performed based on the optimized S_0 geometries for the computation of the singlet–singlet transitions in the electronic absorption spectra of compounds **5** and **6**. To investigate the noncovalent interactions in the dimeric form, geometry optimization on the dimer of the open merocyanine form of compound **6** has been performed with the PBE0-D3(BJ) functional in methanol, and noncovalent interactions (NCI) analysis has been carried out on the optimized geometry. Vibrational frequency calculations have been carried out based on the optimized S_0 geometries. All stationary points were verified to be minima on the potential energy surface, as no imaginary frequencies were observed (NIMAG = 0), except the dimer of the open form of **6** in which a small imaginary frequency of 2i cm^{-1} was found. For all the calculations, the 6-31G(d,p) basis set[16–19] was employed to describe all the atoms. All the DFT and TDDFT calculations were carried out with a pruned (99,590) grid for numerical integration.

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