Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Insulation of Coumarin Derivative with [1]Rotaxane to Control Solvation-induced Effects in Excited-state Dynamics for Enhanced Luminescence

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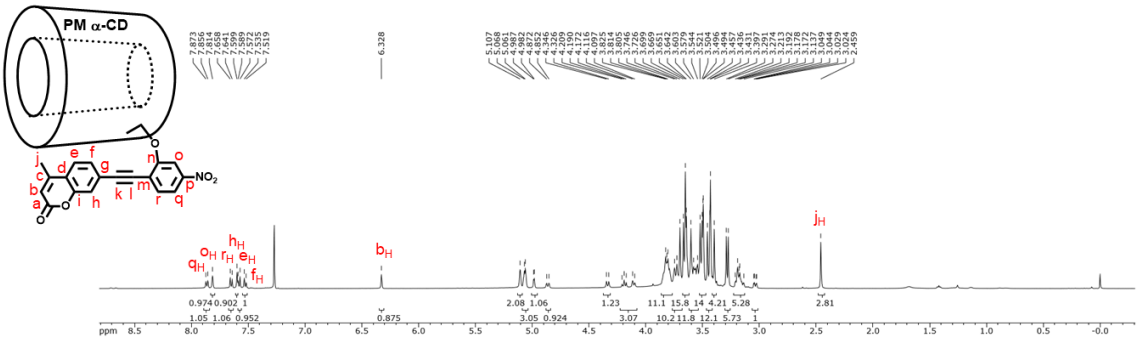
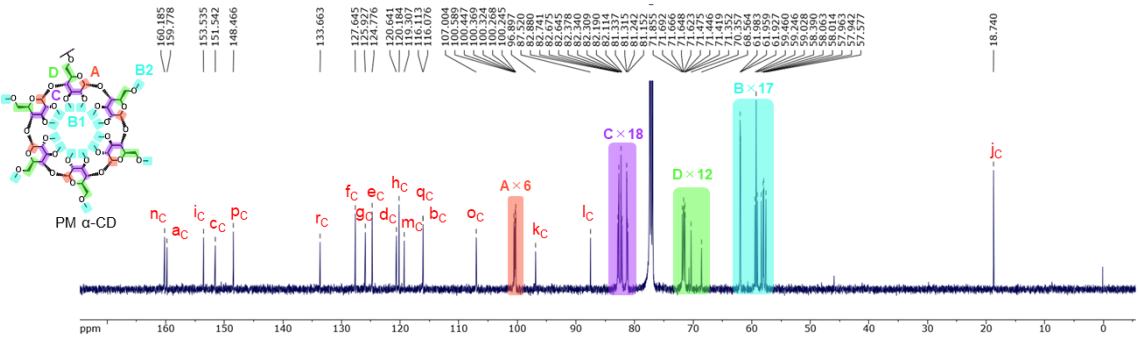
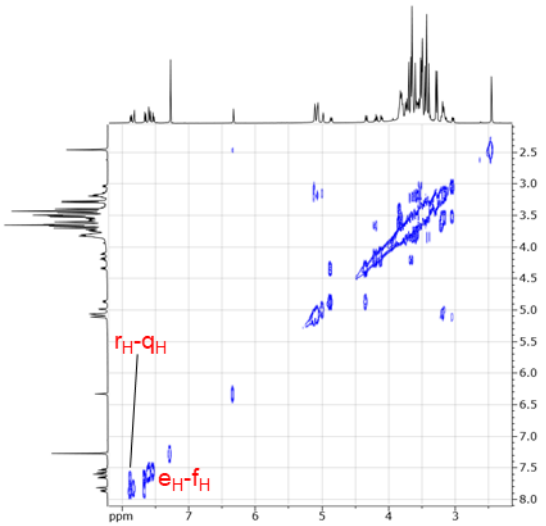
^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$, r.t.)



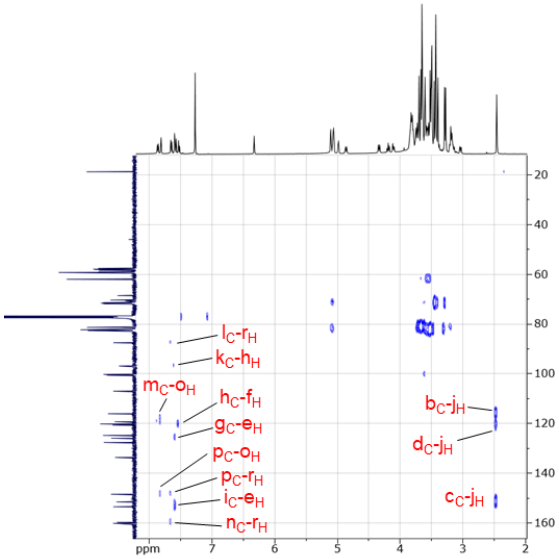
^{13}C NMR spectrum of **2** (126 MHz, $CDCl_3$, r.t.)



^{1}H-^{1}H COSY NMR spectrum of **2**



^{1}H-^{13}C HMBC NMR spectrum of **2**



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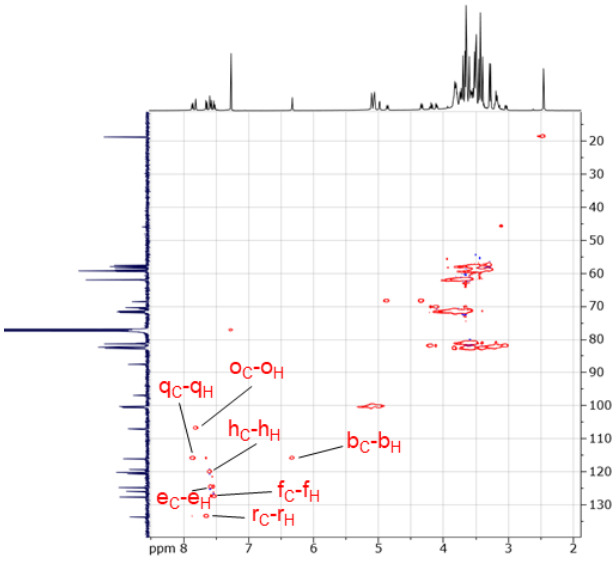
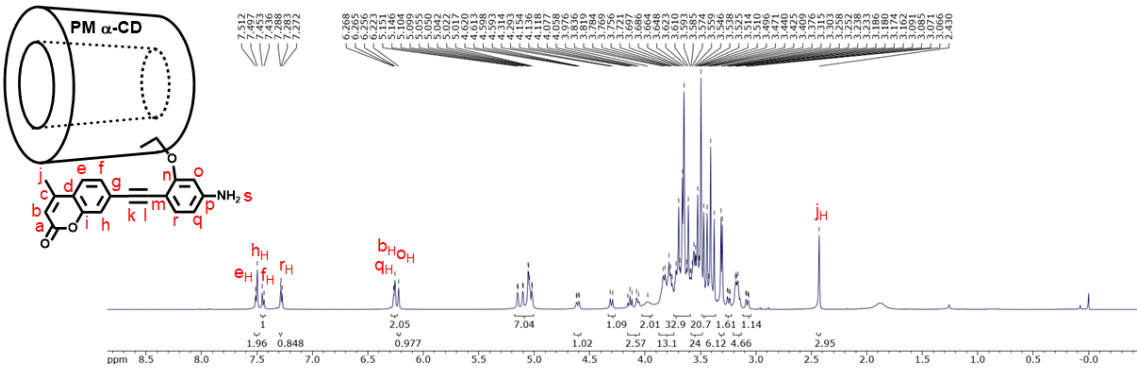
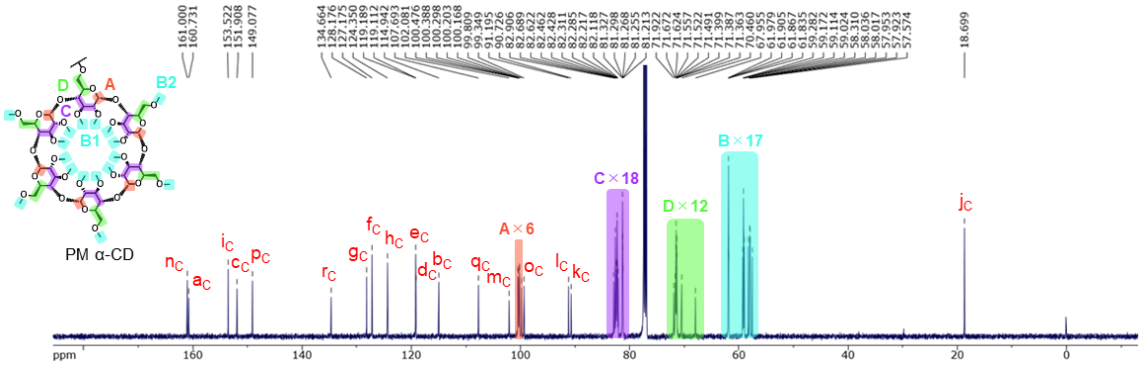


^{1}H NMR spectrum of ***uns*-CM** (500 MHz, $CDCl_3$, r.t.)



^{13}C NMR spectrum of ***uns*-CM** (126 MHz, $CDCl_3$, r.t.)



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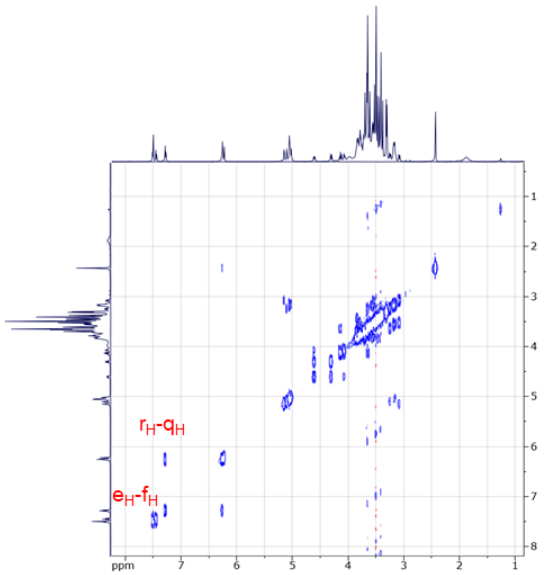

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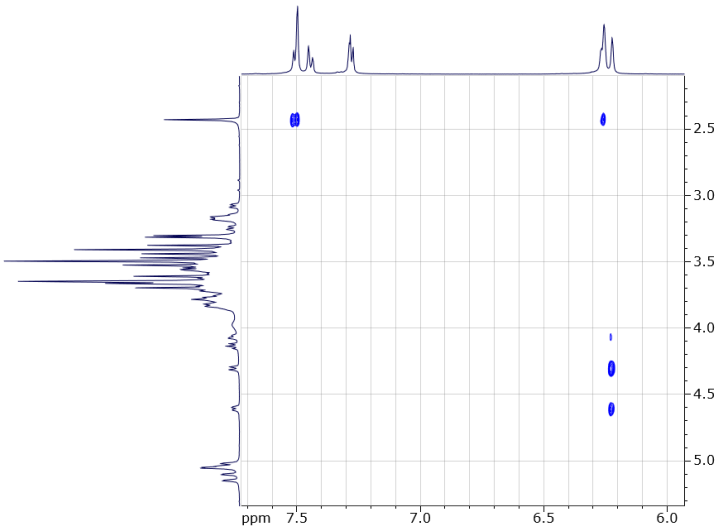

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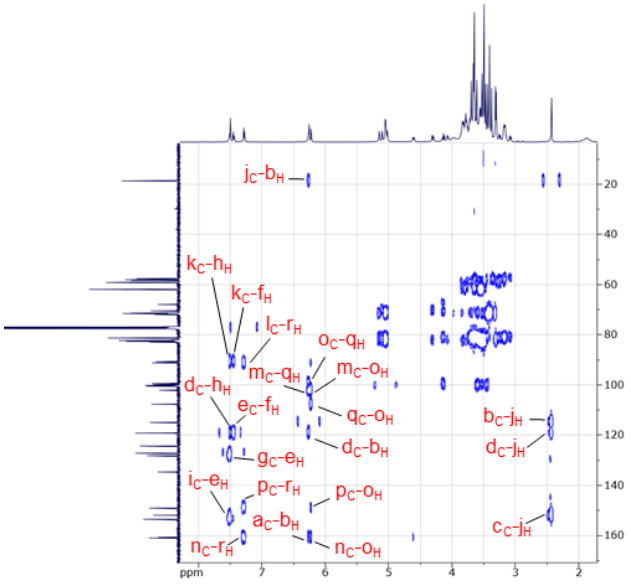

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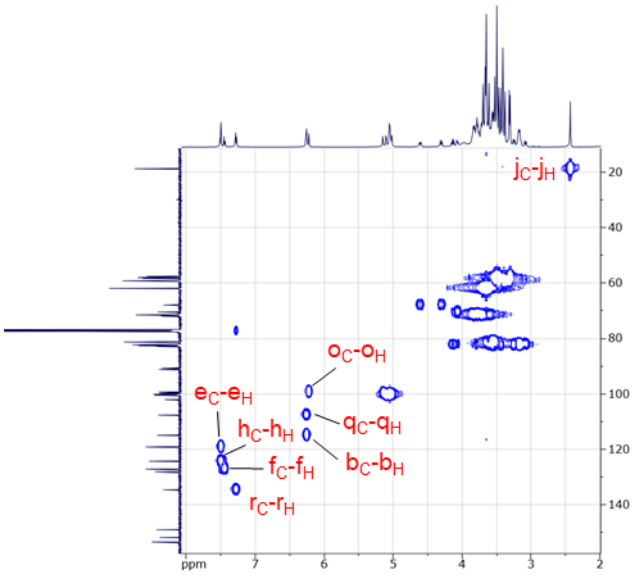

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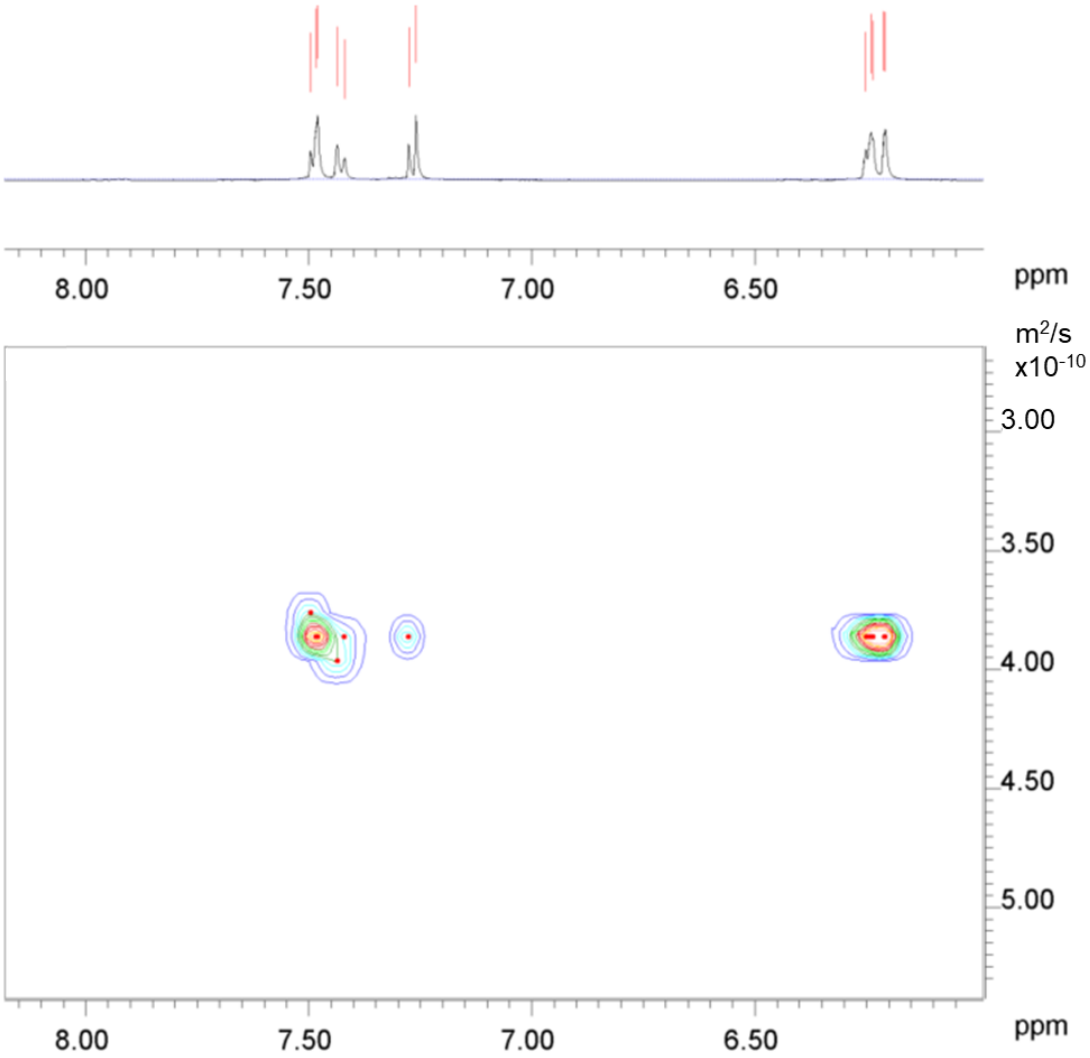
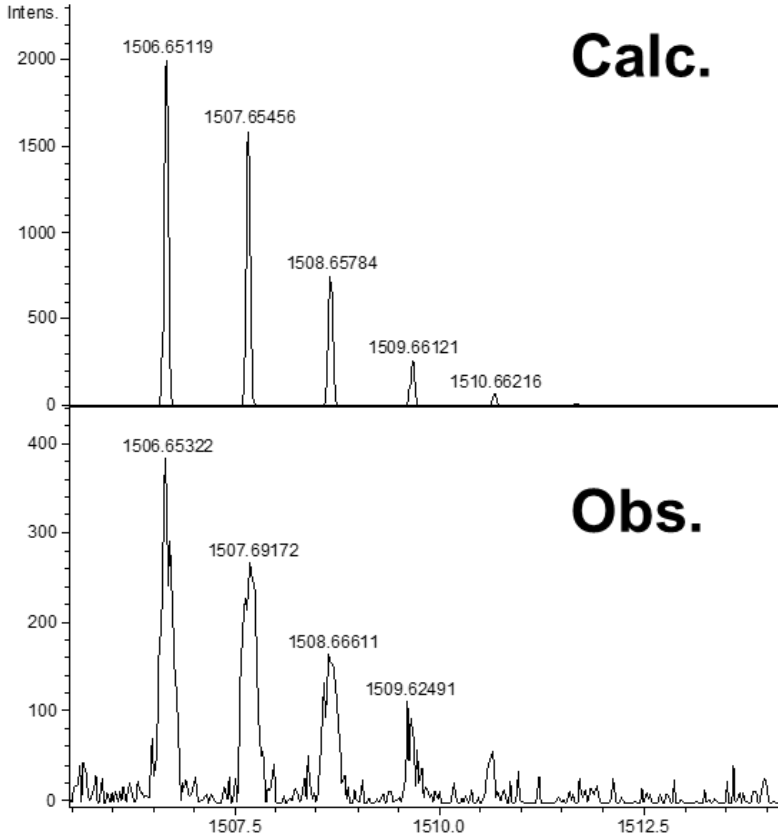
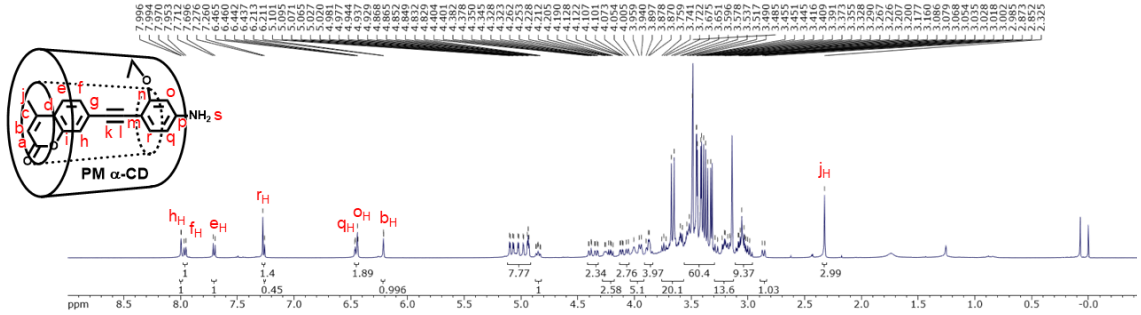


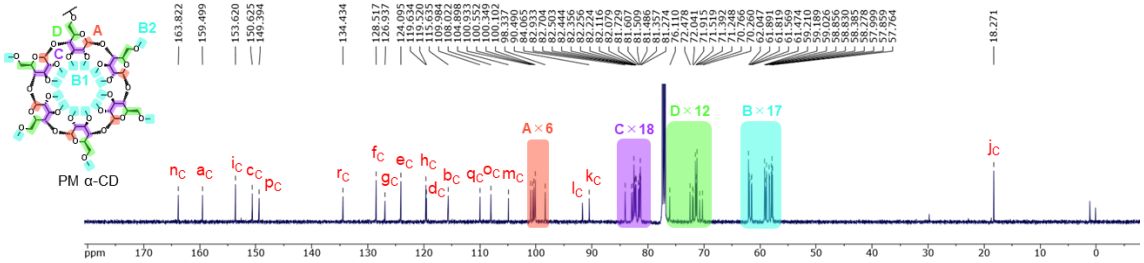
HR-MS spectrum of ***uns*-CM**



^{1}H NMR spectrum of ***ins*-CM** (500 MHz, $CDCl_3$, r.t.)



^{13}C NMR spectrum of ***ins*-CM** (126 MHz, $CDCl_3$, r.t.)



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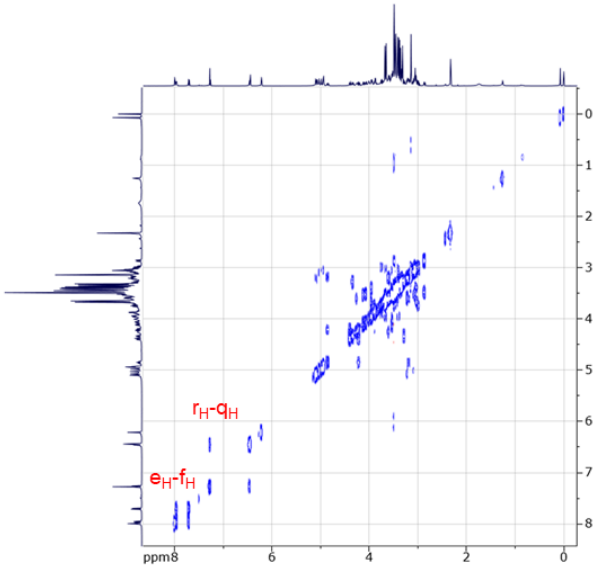

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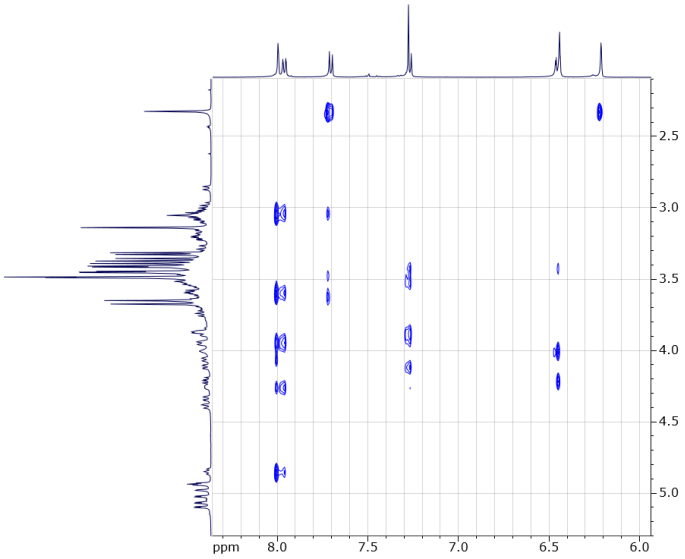
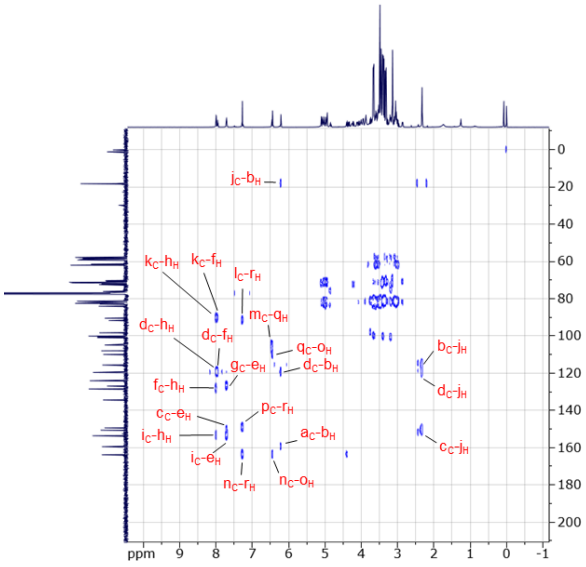
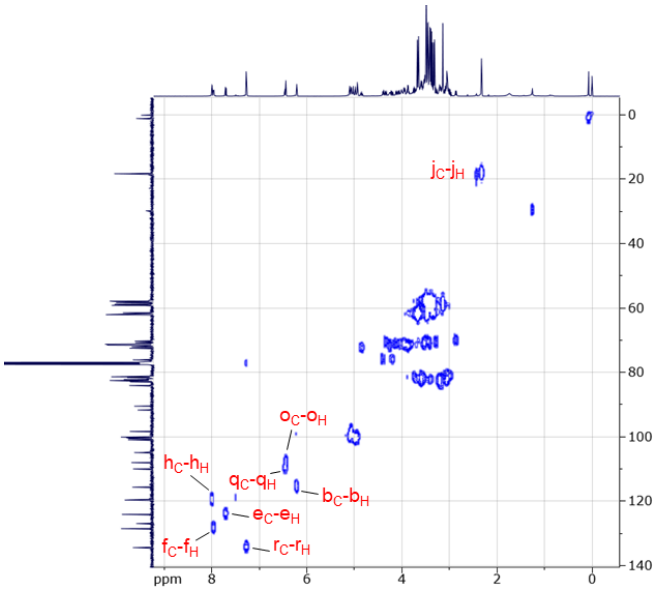


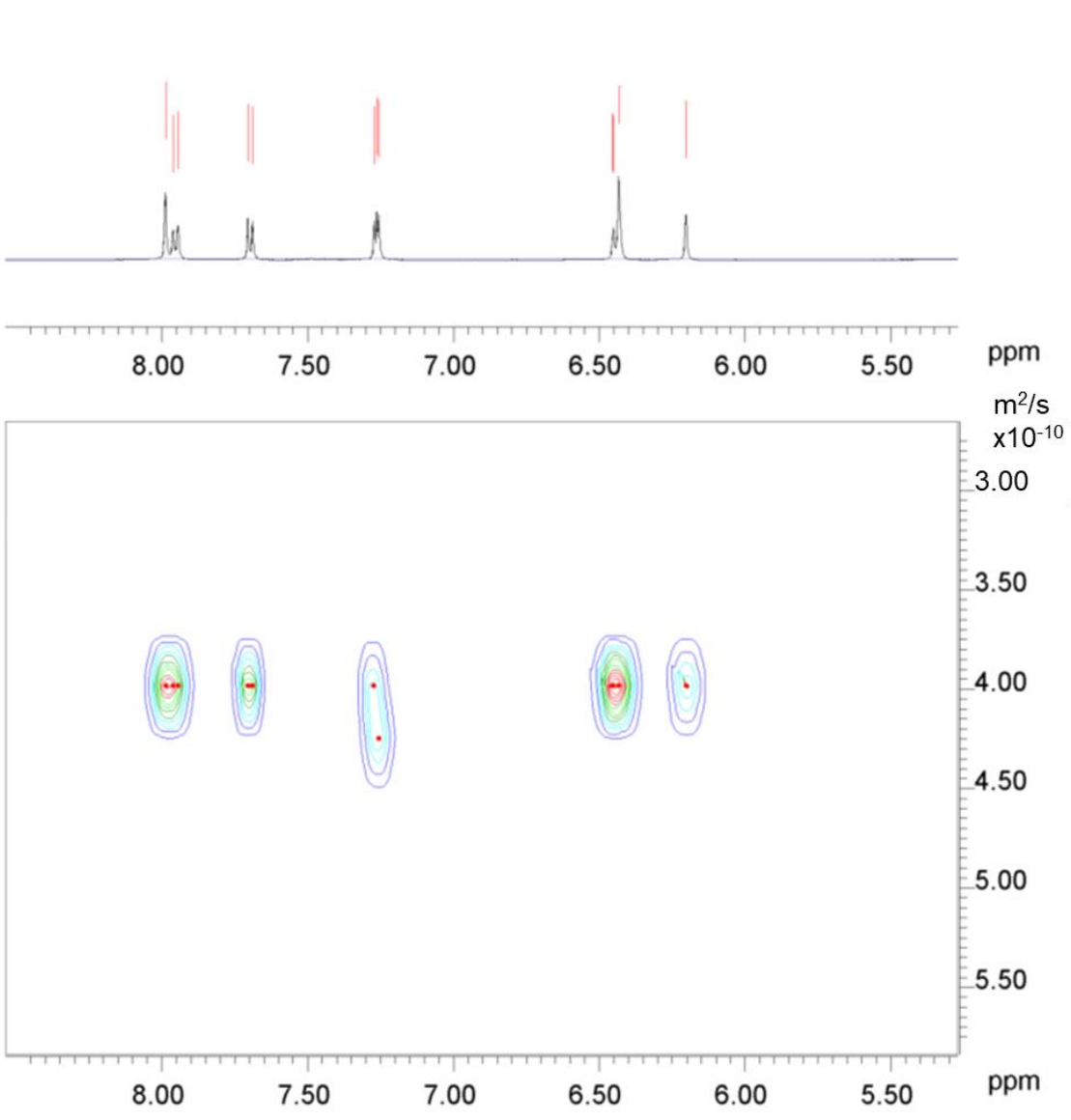
^{1}H-^{13}C HMBC NMR spectrum of ***ins*-CM**



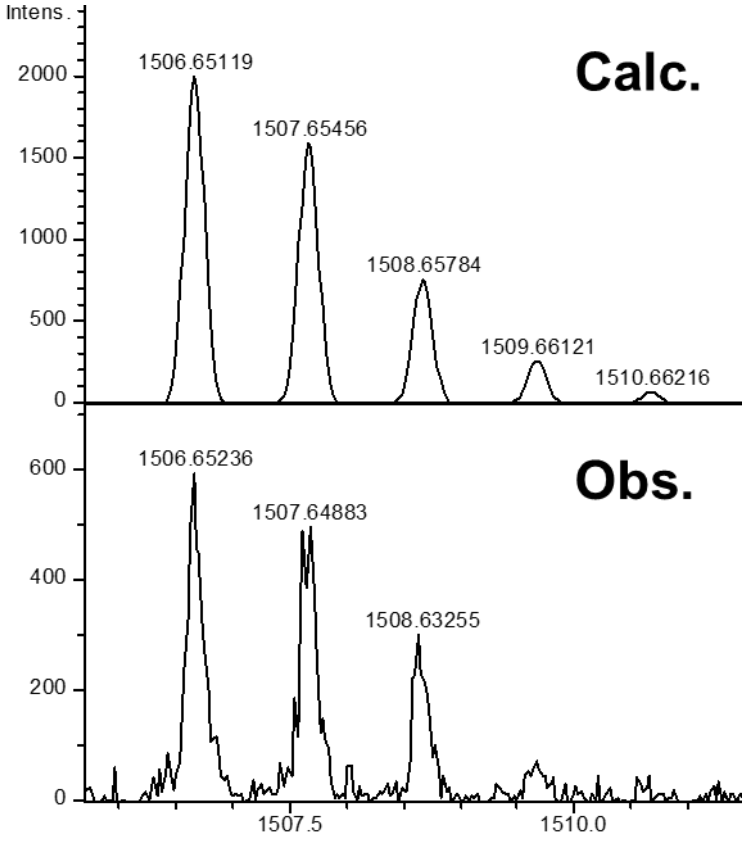
^{1}H-^{13}C HMQC NMR spectrum of ***ins*-CM**.



^{1}H DOSY NMR spectrum of ***ins*-CM**



HR-MS spectrum of ***ins*-CM**



S2. Kinetic stabilities of *ins*-CM and *uns*-CM

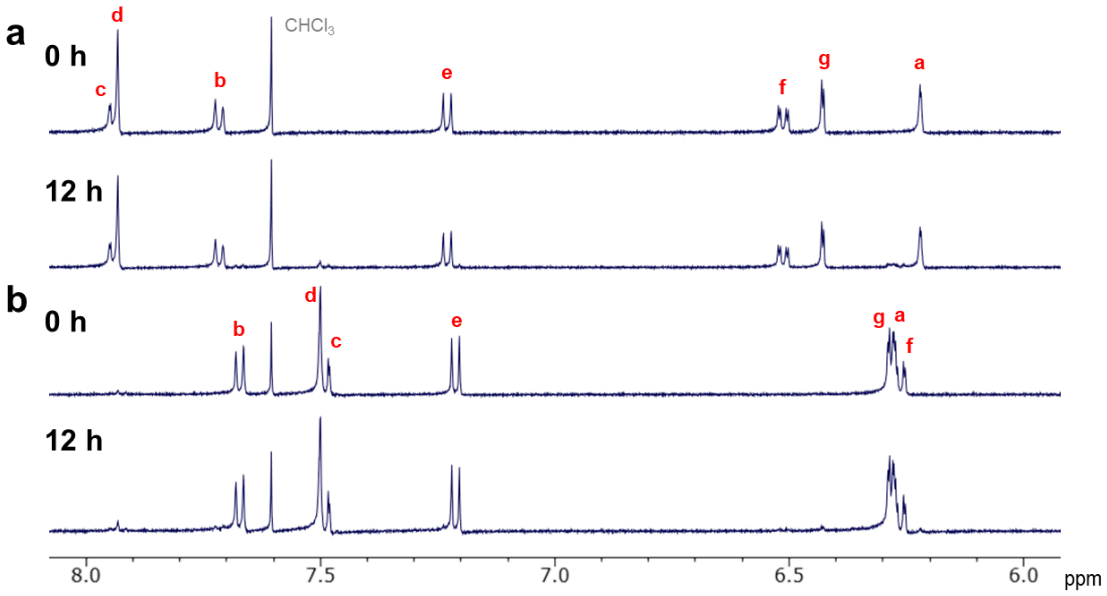


Fig. S1 ^{1}H NMR spectra (500 MHz) of (a) ***ins*-CM** and (b) ***uns*-CM** before and after 12 h in acetonitrile-d_3 at room temperature.

S3. Optical Measurements

S3.1 Absorption and emission spectra

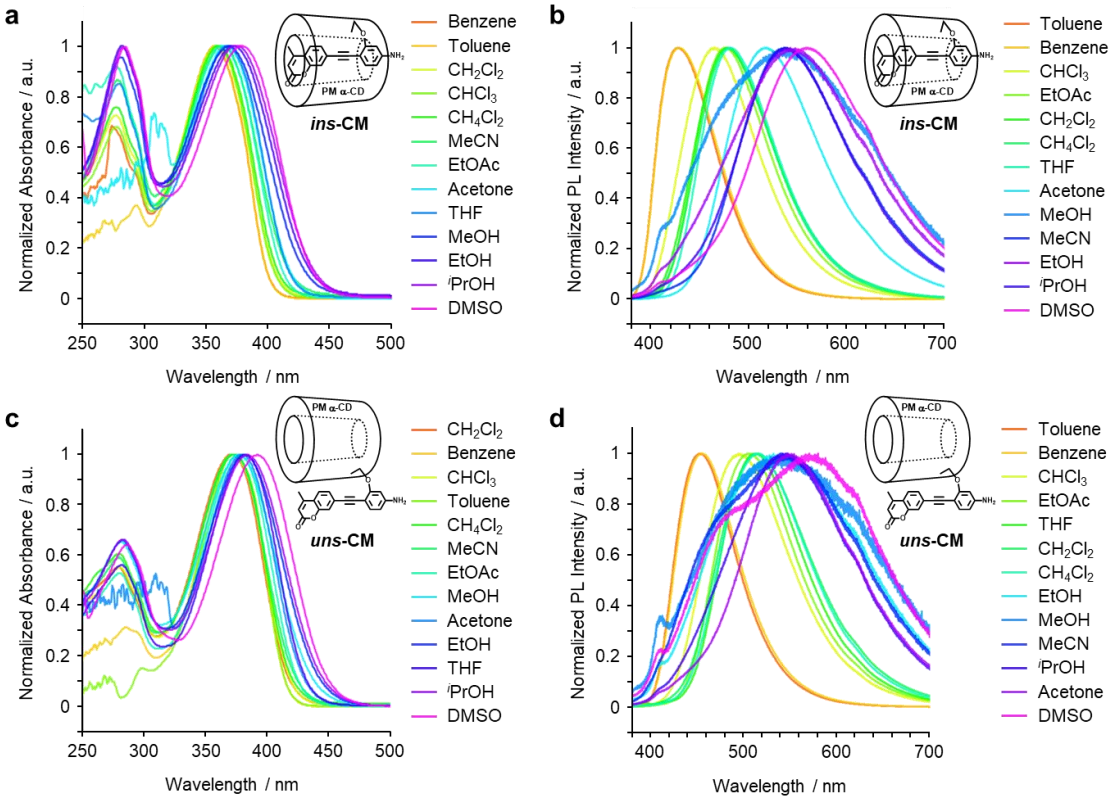


Fig. S2 (a) Normalized absorption spectra and (b) photoluminescence spectra of ***ins*-CM** (excitation at 365 nm) in various solvents. (c) Normalized absorption spectra and (d) photoluminescence spectra of ***uns*-CM** (excitation at 365 nm) in various solvents.

Table S1. Summary of optical properties of ***ins*-** and ***uns*-CM**.

	***ins*-CM**						***uns*-CM**					
	λ_{abs} [a]	λ_{fl} [b]	Φ_f [c]	τ [d]	k_f [e]	k_{nr} [f]	λ_{abs} [a]	λ_{fl} [b]	Φ_f [c]	τ [d]	k_f [e]	k_{nr} [f]
Solvent	(nm)	(nm)	(%)	(ns)	(ns^{-1})	(ns^{-1})	(nm)	(nm)	(%)	(ns)	(ns^{-1})	(ns^{-1})
Benzene	358	428	81.7	1.37	0.60	0.13	372	455	93.2	1.76	0.53	0.039
Toluene	358	428	77.2	1.37	0.56	0.17	372	454	93.6	1.75	0.53	0.037
CH_2Cl_2	359	478	86.0	2.54	0.34	0.055	371	515	41.4	1.42	0.29	0.41
$CHCl_3$	360	465	88.7	2.12	0.42	0.053	372	495	68.3	1.91	0.36	0.17
CH_4Cl_2	360	481	92.8	2.53	0.37	0.028	372	516	60.2	2.21	0.27	0.18
MeCN	364	537	12.7	1.14	0.11	0.77	373	547	2.0	0.815	0.025	1.20
EtOAc	364	477	77.7	2.68	0.29	0.083	377	507	58.2	2.34	0.25	0.18
Acetone	367	517	33.8	2.12	0.16	0.31	380	549	5.3	0.529	0.10	1.8
THF	368	482	80.4	2.65	0.30	0.074	382	512	53.5	2.15	0.25	0.22
MeOH	369	536	1.5	0.48	0.031	2.1	377	543	0.9	0.419	0.021	2.4
EtOH	372	543	4.9	0.462	0.11	2.1	382	532	2.3	0.771	0.030	1.3
^{i}PrOH	375	538	16.3	0.778	0.21	1.1	384	548	6.2	0.514	0.12	1.8
DMSO	379	559	7.6	0.562	0.14	1.6	392	571	2.7	0.824	0.033	1.2

[a] Maximum absorption wavelength. [b] Maximum emission wavelength excited at 365 nm. [c] Fluorescent quantum yield excited at 365 nm. [d] Fluorescent lifetime excited at 365 nm. [e] Radiative rate constant ($k_f = \Phi/\tau$). [f] Non-radiative deactivation rate constant ($k_{nr} = (1-\Phi)/\tau$).

S3.2 Lippert-Mataga plots

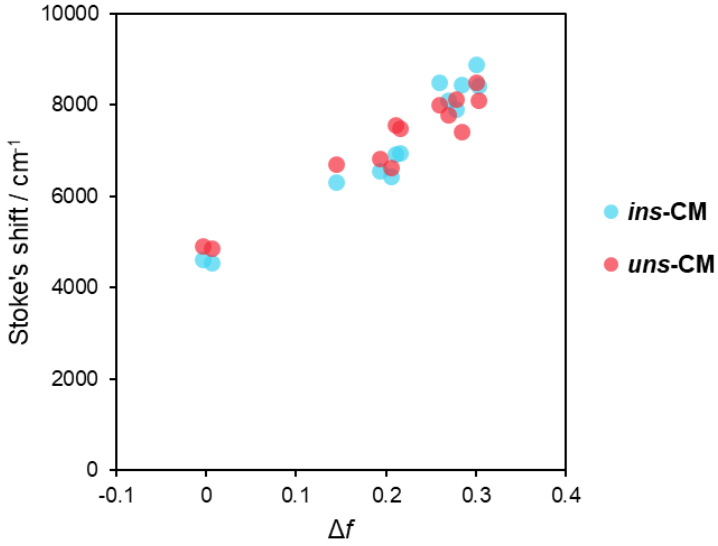


Fig. S3 Plot to the Lippert-Mataga expression of ***ins*-CM** and ***uns*-CM**.

S3.3 Luminescence decay curve

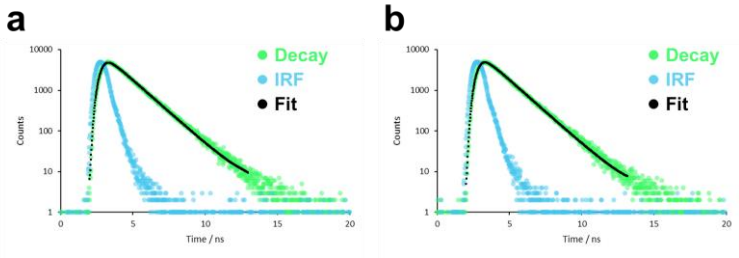


Fig. S4 Emission decay curve of ***ins*-CM** and instrument response function (IRF) in (a) benzene and (b) toluene.

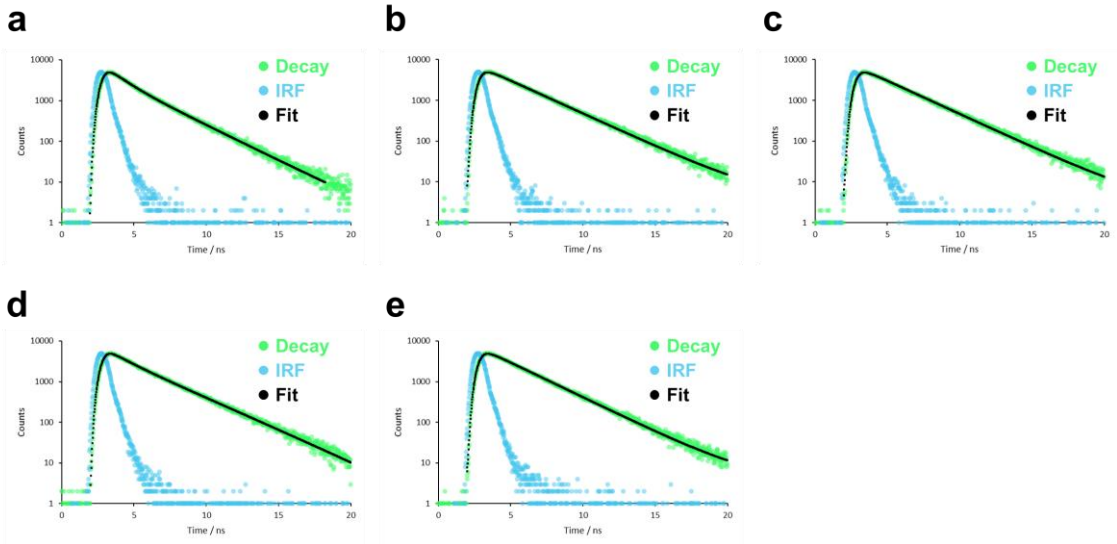


Fig. S5 Emission decay curve of ***ins*-CM** and instrument response function (IRF) in (a) $CHCl_3$, (b) EtOAc, (c) THF, (d) CH_2Cl_2, and (e) CH_4Cl_2.

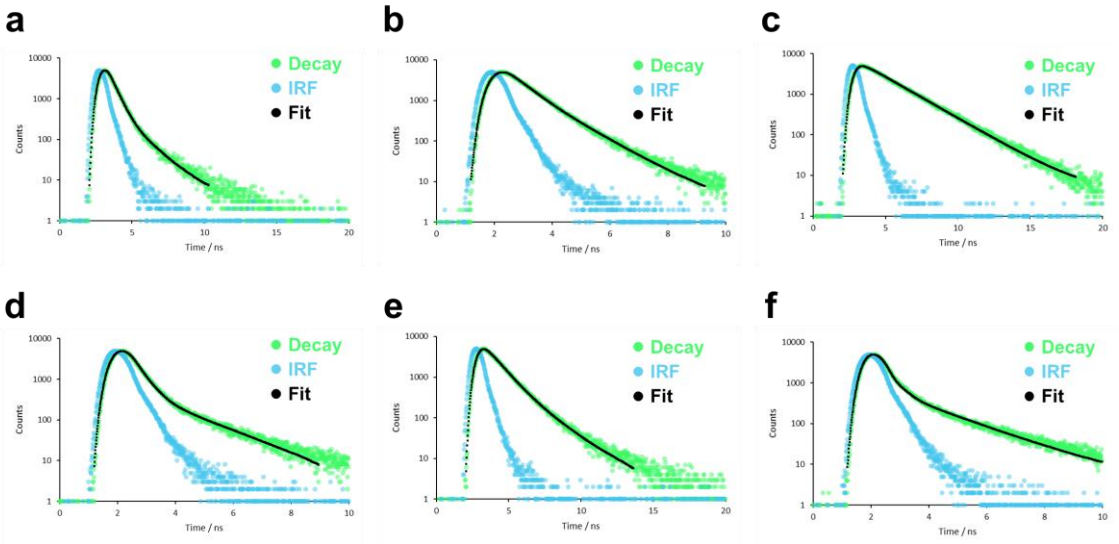


Fig. S6 Emission decay curve of ***ins*-CM** and instrument response function (IRF) in (a) DMSO, (b) ^{i}PrOH, (c) acetone, (d) EtOH, (e) MeCN, and (f) MeOH.

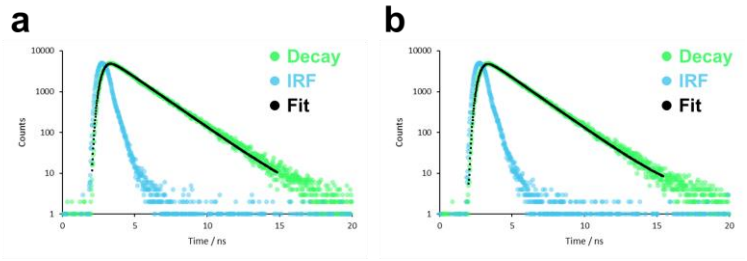


Fig. S7 Emission decay curve of ***uns*-CM** and instrument response function (IRF) in a) benzene and b) toluene.

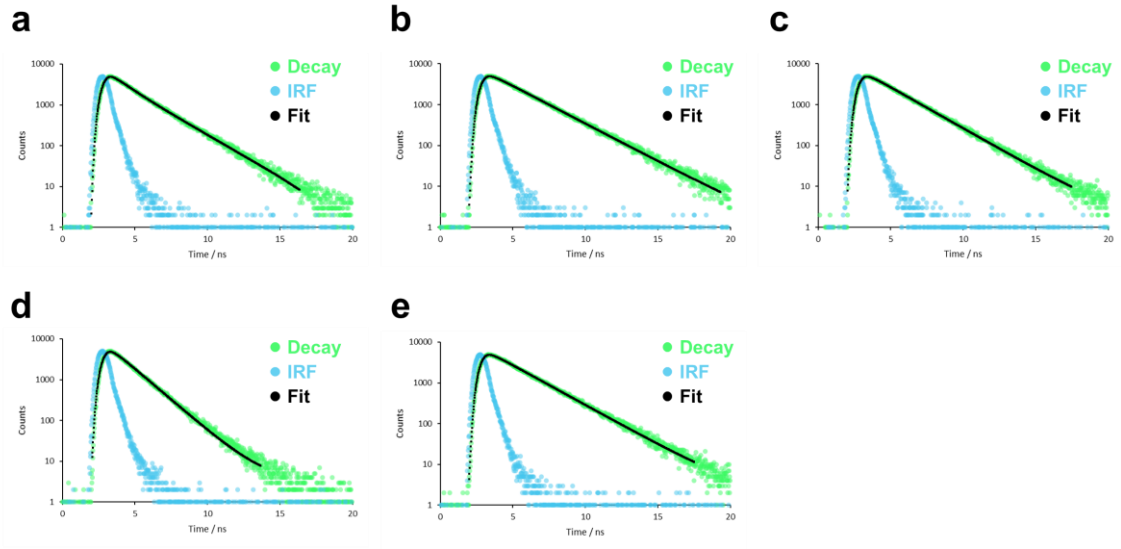


Fig. S8 Emission decay curve of ***uns*-CM** and instrument response function (IRF) in (a) $CHCl_3$, (b) EtOAc, (c) THF, (d) CH_2Cl_2, and (e) CH_4Cl_2.

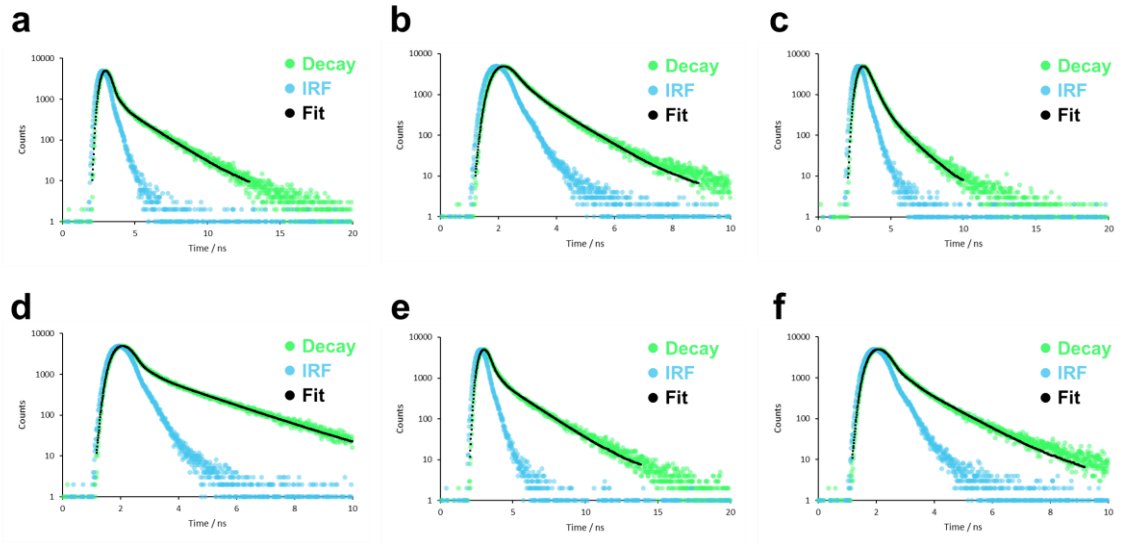


Fig. S9 Emission decay curve of ***uns*-CM** and instrument response function (IRF) in (a) DMSO, (b) ^{i}PrOH, (c) acetone, (d) EtOH, (e) MeCN, and (f) MeOH.

S4. DFT Calculation of Coumarin Derivatives

DFT calculations were conducted for ***ins*-CM** and coumarin derivative (**S1**) bearing methoxy group instead of PM α-CD in ***ins*-CM** under B3LYP/ 6-31G(d,p) level with Gaussian09.[1] Details of their DFT-optimized geometries are presented in the following Tables S1 and S2.

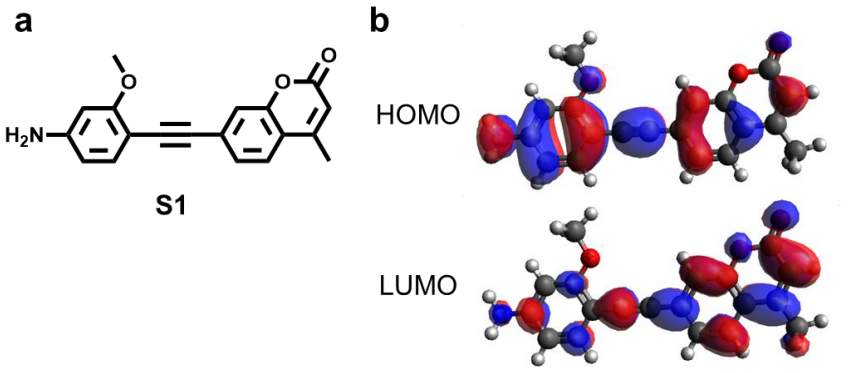


Fig. S10 (a) Chemical structure of **S1** as a coumarin derivative bearing methoxy group instead of PM α-CD in ***ins*-CM**. (b) DFT-optimized structure and the corresponding HOMO/LUMO orbitals of **S1**. (B3LYP/6-31G(d, p)).

Table S2. Optimum structural coordinates of **S1** by B3LYP/ 6-31G(d,p), Stoichiometry $C_{19}H_{15}NO_3$.

Center	Atomic	Coordinates (Angstroms)			Center	Atomic	Coordinates (Angstroms)		
Number	Symbol	X	Y	Z	Number	Symbol	X	Y	Z
1	C	5.248047	0.732101	0.000482	16	O	3.064044	1.792665	0.004682
2	C	6.000942	-0.457250	-0.001200	17	O	-3.691780	1.583160	-0.005350
3	C	5.332533	-1.694070	-0.000450	18	C	-5.084780	1.659449	-0.006530
4	C	3.946710	-1.729210	0.002437	19	C	-5.794030	0.389413	-0.003510
5	C	3.170302	-0.556240	0.003519	20	C	-5.165350	-0.814710	-0.000130
6	C	3.855595	0.689631	0.004016	21	O	-5.589340	2.758437	-0.009750
7	N	7.387116	-0.401780	0.050450	22	C	-5.947440	-2.100350	0.002768
8	C	1.754726	-0.610740	0.003190	23	H	5.770004	1.681985	0.007165
9	C	0.538404	-0.672310	0.002505	24	H	5.903727	-2.617750	0.002592
10	C	-0.879360	-0.727010	0.001852	25	H	3.432014	-2.684460	0.000759
11	C	-1.636790	0.455996	-0.001380	26	H	7.874150	-1.230020	-0.260370
12	C	-3.026530	0.390571	-0.001980	27	H	7.813530	0.450927	-0.282520
13	C	-3.714000	-0.841490	0.000655	28	H	-1.152770	1.425188	-0.003390
14	C	-2.938040	-2.018890	0.003947	29	H	-3.436180	-2.982570	0.006166
15	C	-1.556300	-1.972110	0.004530	30	H	-0.975610	-2.887750	0.007281
					31	H	-6.875080	0.468711	-0.004240
					32	H	-5.710240	-2.704100	0.886032

33	H	-7.021430	-1.904290	0.001508	36	H	2.855754	3.794295	0.021946
34	H	-5.709010	-2.708850	-0.876890	37	H	4.290358	3.219668	0.912862
35	C	3.674658	3.074173	0.016544	38	H	4.291715	3.235727	-0.876270

Table S2. Optimum structural coordinates of ***ins*-CM** by B3LYP/ 6-31G(d,p), Stoichiometry $C_{71}H_{105}NO_{32}$.

Center	Atomic	Coordinates (Angstroms)			Center	Atomic	Coordinates (Angstroms)		
Number	Symbol	X	Y	Z	Number	Symbol	X	Y	Z
1	C	0.30306	-1.72406	5.51502	28	H	-1.97937	0.88661	-3.22618
2	C	-0.84804	-1.23412	6.15350	29	H	-2.09942	0.51663	-0.80791
3	C	-1.80706	-0.55266	5.37928	30	H	1.60717	0.34797	-6.48454
4	C	-1.60123	-0.36544	4.02322	31	H	-1.28100	1.94123	-5.32257
5	C	-0.44653	-0.84002	3.36553	32	H	-0.65651	1.05228	-6.72424
6	C	0.50174	-1.54061	4.15172	33	H	-1.77560	0.27080	-5.59259
7	N	-1.01259	-1.37513	7.52290	34	O	1.67824	-1.99262	3.61485
8	C	-0.25769	-0.59216	1.97912	35	O	3.82607	-2.70231	1.99938
9	C	-0.13606	-0.36333	0.78623	36	O	5.73355	-3.22226	-1.09468
10	C	-0.03766	-0.12611	-0.61512	37	O	3.59578	-5.16240	-1.21381
11	C	1.16266	-0.35034	-1.30870	38	O	1.14358	-3.98962	-0.15016
12	C	1.21197	-0.14072	-2.68446	39	O	-0.56010	-5.27823	0.81795
13	C	0.09183	0.30184	-3.41642	40	O	0.59187	-5.20104	-2.63994
14	C	-1.09877	0.53607	-2.69891	41	O	-2.15401	-4.48125	-2.87996
15	C	-1.17131	0.32958	-1.33368	42	O	-1.70191	-4.31783	3.27955
16	O	2.41209	-0.38449	-3.29315	43	O	-3.16271	-3.02993	-0.58969
17	C	2.59896	-0.22213	-4.66405	44	O	-4.84082	-2.48325	0.95766
18	C	1.44131	0.22731	-5.42019	45	O	-5.12945	-3.02485	-2.62120
19	C	0.23646	0.48790	-4.84869	46	O	-5.88448	-0.26472	-2.34509
20	O	3.69685	-0.45935	-5.11682	47	O	-6.33824	-0.47954	2.57163
21	C	-0.93009	0.96352	-5.67105	48	O	-4.37128	1.01875	-0.16770
22	H	1.06807	-2.25162	6.07649	49	O	-4.12136	2.48340	1.66187
23	H	-2.70502	-0.16349	5.85097	50	O	-5.64965	3.11645	-1.61798
24	H	-2.34238	0.16926	3.44117	51	O	-3.54149	5.05426	-1.49410
25	H	-1.95979	-1.31223	7.86711	52	O	-2.83690	4.47729	3.19357
26	H	-0.47956	-2.10997	7.96487	53	O	-1.22515	3.94013	-0.07540
27	H	2.05989	-0.68007	-0.79878	54	O	0.33311	5.13734	1.20831
					55	O	-0.36055	5.31375	-2.36425
					56	O	2.37989	4.57284	-2.32900

57	O	2.95593	5.43666	2.62958	93	C	-2.58767	3.95641	0.37617
58	O	3.10705	2.96477	0.01554	94	C	-2.74822	2.84691	1.43569
59	O	4.39613	2.24368	1.84389	95	C	-2.19127	3.28657	2.78296
60	O	5.48223	3.15817	-1.49214	96	C	-7.05699	3.06811	-1.45318
61	O	6.24316	0.36822	-1.31047	97	C	-3.51955	5.00034	-2.91252
62	O	5.49712	0.12658	3.49504	98	C	-2.24597	5.04789	4.34204
63	O	4.35729	-1.13986	0.31569	99	C	-0.47485	5.12455	0.04108
64	C	4.74654	-2.30844	0.99253	100	C	0.42892	5.30308	-1.18618
65	C	4.87601	-3.48268	-0.00125	101	C	1.51474	4.22265	-1.25633
66	C	3.51322	-3.89307	-0.58069	102	C	2.29340	4.14705	0.06452
67	C	2.42504	-4.02107	0.49693	103	C	1.34582	4.11162	1.28598
68	C	2.48467	-2.88135	1.52753	104	C	2.07471	4.32306	2.61551
69	C	1.63498	-3.14933	2.75681	105	C	-0.00772	6.32725	-3.29432
70	C	7.09629	-3.01569	-0.75542	106	C	2.72369	3.51319	-3.21029
71	C	3.84096	-5.12425	-2.61538	107	C	2.35342	6.68725	2.92241
72	C	0.40861	-5.18364	-0.21891	108	C	4.37691	2.98691	0.64073
73	C	-0.32539	-5.28836	-1.56290	109	C	5.43673	2.39646	-0.29636
74	C	-1.41088	-4.21522	-1.69708	110	C	5.14587	0.91955	-0.58765
75	C	-2.35410	-4.21315	-0.48611	111	C	4.93806	0.12178	0.70610
76	C	-1.55165	-4.23212	0.83554	112	C	4.03599	0.85568	1.72749
77	C	-2.41817	-4.49313	2.06393	113	C	4.13007	0.28589	3.13686
78	C	0.42516	-6.20353	-3.63201	114	C	6.79132	3.43906	-1.96499
79	C	-2.12452	-3.44406	-3.84743	115	C	5.90113	-0.17440	-2.58660
80	C	-1.19241	-5.51402	3.84634	116	C	5.64920	-0.40965	4.79149
81	C	-4.53385	-3.09630	-0.28545	117	H	0.60805	-3.38559	2.47709
82	C	-5.35200	-2.39077	-1.37359	118	H	2.05323	-3.99809	3.31374
83	C	-4.98628	-0.90532	-1.44166	119	H	7.66749	-3.10387	-1.68254
84	C	-5.06989	-0.23481	-0.06494	120	H	7.45543	-3.77656	-0.04626
85	C	-4.46557	-1.09493	1.07049	121	H	7.26491	-2.01469	-0.34052
86	C	-4.93088	-0.62949	2.45302	122	H	3.81239	-6.16187	-2.95946
87	C	-6.30551	-3.26720	-3.37867	123	H	4.82000	-4.69136	-2.84153
88	C	-5.26344	0.40541	-3.43230	124	H	3.05743	-4.55806	-3.13296
89	C	-7.04533	-1.65444	2.94015	125	H	-3.24625	-3.77973	2.07265
90	C	-4.87946	2.14886	0.51995	126	H	-2.83703	-5.50913	2.00027
91	C	-4.91526	3.36159	-0.43113	127	H	1.17918	-6.01398	-4.39972
92	C	-3.50351	3.79345	-0.84060	128	H	-0.57292	-6.16299	-4.08233

129	H	0.59028	-7.21129	-3.22180	165	H	3.33046	2.75227	-2.71380
130	H	-1.09841	-3.23322	-4.17806	166	H	3.16707	7.40977	3.02927
131	H	-2.58475	-2.52586	-3.46758	167	H	1.79315	6.64643	3.86941
132	H	-2.70824	-3.79819	-4.70118	168	H	1.67011	7.01828	2.13324
133	H	-2.00158	-6.22382	4.07877	169	H	3.60505	-0.67203	3.19120
134	H	-0.69967	-5.23112	4.78044	170	H	6.67481	4.01223	-2.88816
135	H	-0.46976	-6.00841	3.18797	171	H	7.35333	2.52197	-2.17159
136	H	-4.54404	-1.32716	3.20912	172	H	7.35804	4.04765	-1.24372
137	H	-4.50924	0.36177	2.63906	173	H	6.83902	-0.50355	-3.04210
138	H	-6.83675	-2.33735	-3.61041	174	H	5.43884	0.57730	-3.23519
139	H	-6.99334	-3.94661	-2.85259	175	H	5.23038	-1.03180	-2.49222
140	H	-5.98686	-3.74733	-4.30711	176	H	6.72109	-0.52297	4.97377
141	H	-6.06823	0.75333	-4.08584	177	H	5.16228	-1.39223	4.88683
142	H	-4.61777	-0.27514	-4.00503	178	H	5.22947	0.25803	5.56068
143	H	-4.69228	1.27519	-3.09215	179	H	5.68471	-2.13707	1.53001
144	H	-6.64497	-2.08356	3.87105	180	H	5.26406	-4.33226	0.58506
145	H	-7.00939	-2.42415	2.16209	181	H	3.19246	-3.12402	-1.29529
146	H	-8.08271	-1.35461	3.11082	182	H	2.56726	-4.98365	1.00704
147	H	-2.34575	2.48824	3.52434	183	H	2.13074	-1.96099	1.05707
148	H	-1.11030	3.44857	2.67552	184	H	1.06819	-6.04587	-0.08416
149	H	-7.38647	2.15984	-0.93211	185	H	-0.81772	-6.27113	-1.56280
150	H	-7.49253	3.06347	-2.45494	186	H	-0.92154	-3.23537	-1.75493
151	H	-7.42794	3.94867	-0.90877	187	H	-2.99568	-5.10366	-0.54949
152	H	-2.60201	4.51688	-3.27083	188	H	-1.06178	-3.25741	0.94454
153	H	-3.52540	6.03693	-3.26074	189	H	-4.85641	-4.13878	-0.18597
154	H	-4.39902	4.48245	-3.31122	190	H	-6.40756	-2.48042	-1.08093
155	H	-2.28227	4.36405	5.20458	191	H	-3.95580	-0.83254	-1.80642
156	H	-2.81454	5.94891	4.58470	192	H	-6.12707	-0.05279	0.16032
157	H	-1.19641	5.32539	4.16142	193	H	-3.37176	-1.01401	1.02236
158	H	1.32434	4.41115	3.41552	194	H	-5.87762	1.92303	0.90872
159	H	2.69901	3.44943	2.81184	195	H	-5.37486	4.18941	0.13132
160	H	-0.13929	7.33268	-2.86574	196	H	-3.07218	3.02790	-1.49783
161	H	-0.68650	6.22328	-4.14500	197	H	-2.82084	4.91805	0.84440
162	H	1.02706	6.21847	-3.63423	198	H	-2.18317	1.96720	1.10331
163	H	3.31579	3.95968	-4.01371	199	H	-1.14261	5.98544	0.14020
164	H	1.82679	3.05332	-3.64944	200	H	0.92822	6.27431	-1.05828

201	H	1.03057	3.25583	-1.44522
202	H	2.93506	5.03288	0.13434
203	H	0.86387	3.12361	1.30998
204	H	4.63959	4.00960	0.92709
205	H	6.39509	2.46506	0.23704
206	H	4.22881	0.86256	-1.18484
207	H	5.91749	-0.05237	1.16315
208	H	2.99345	0.77721	1.39279
209	H	3.63459	0.99128	3.82259

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