Supporting Information for

Light Harvesting Fullerene Dyads as Organic Triplet Photosensitizers for Triplet-triplet Annihilation Upconversions

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1.0 NMR and HR-MS spectra

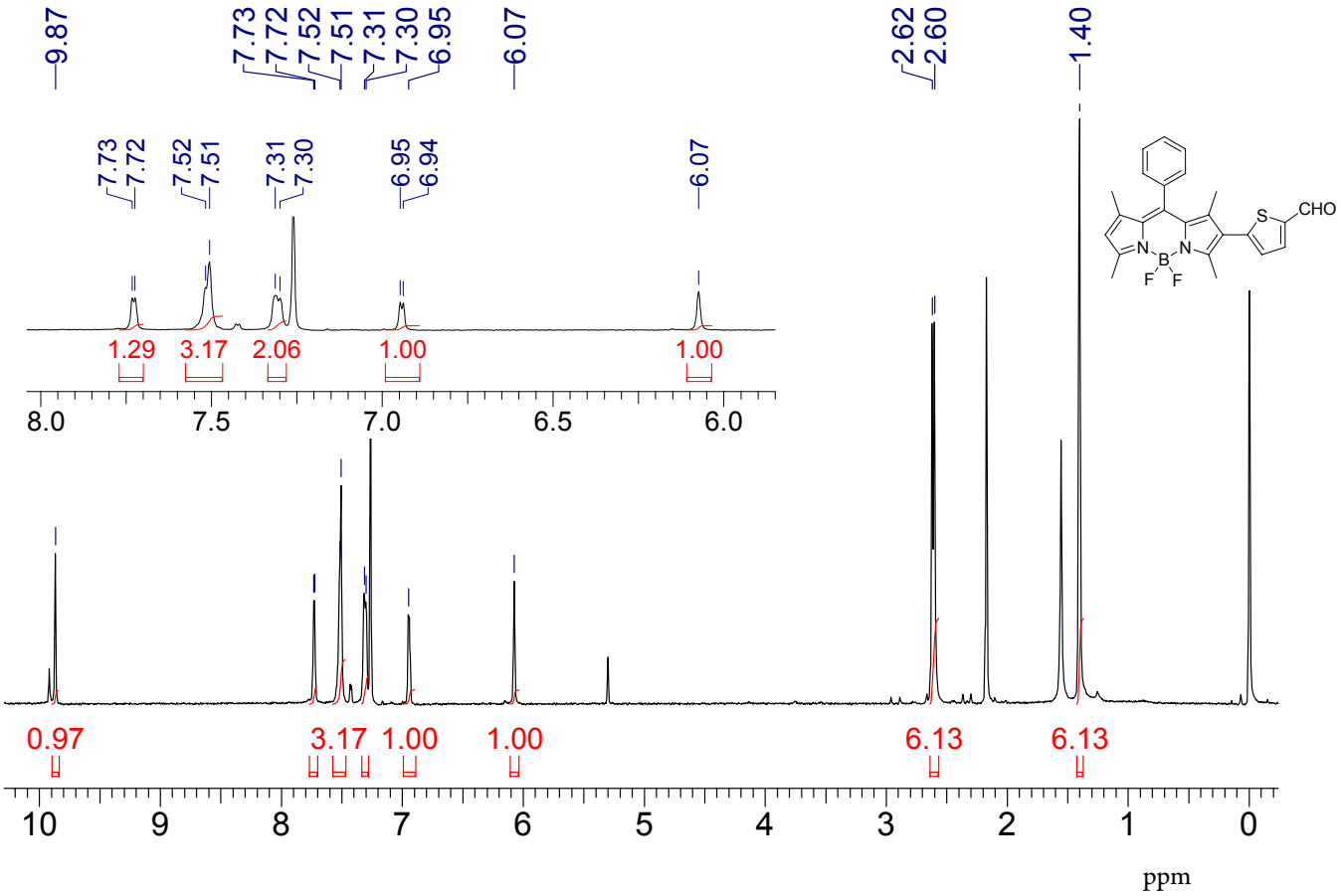


Figure S1. ^{1}H NMR of **2** (400 MHz, $CDCl_3$).

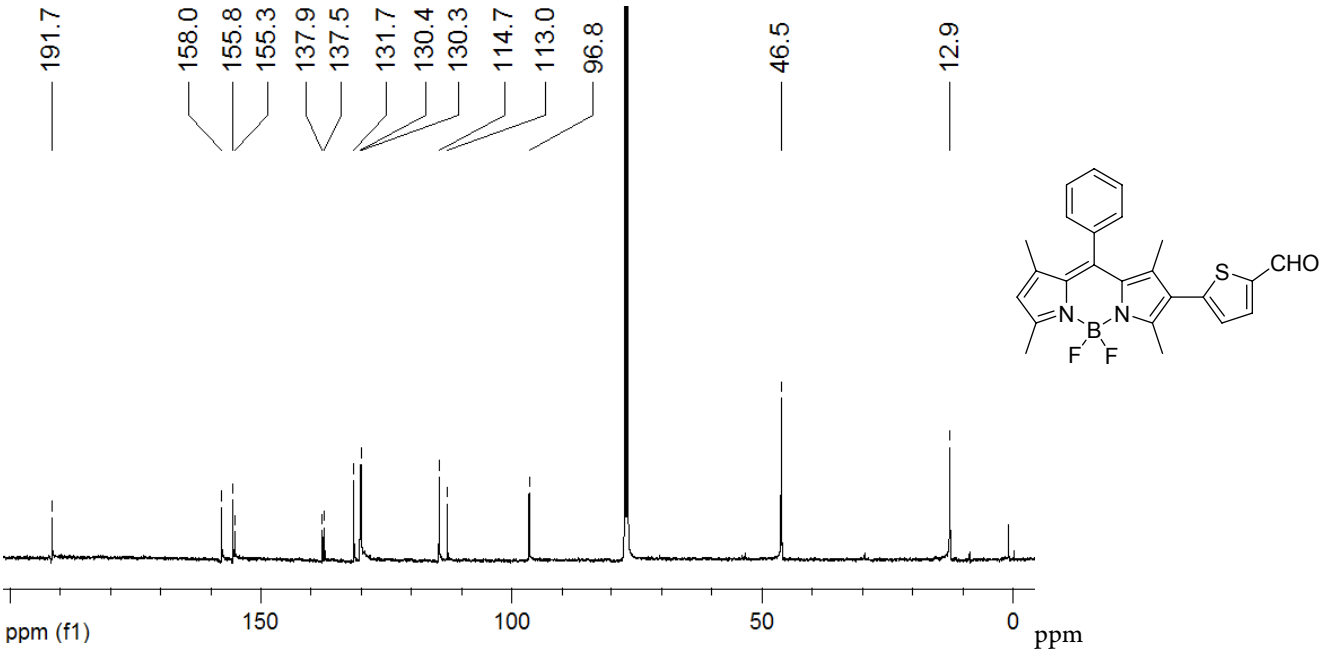


Figure S2. ^{13}C NMR of compound **2** (100 MHz, $CDCl_3$).

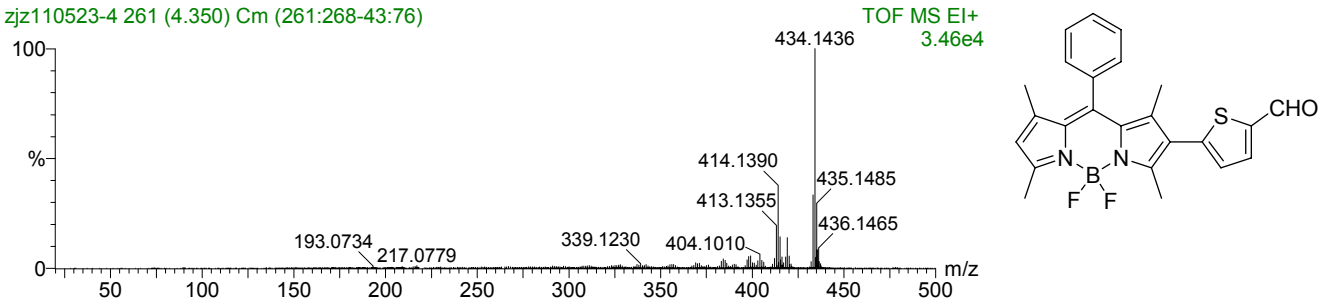


Figure S3. MALDI-HRMS of compound **2.**

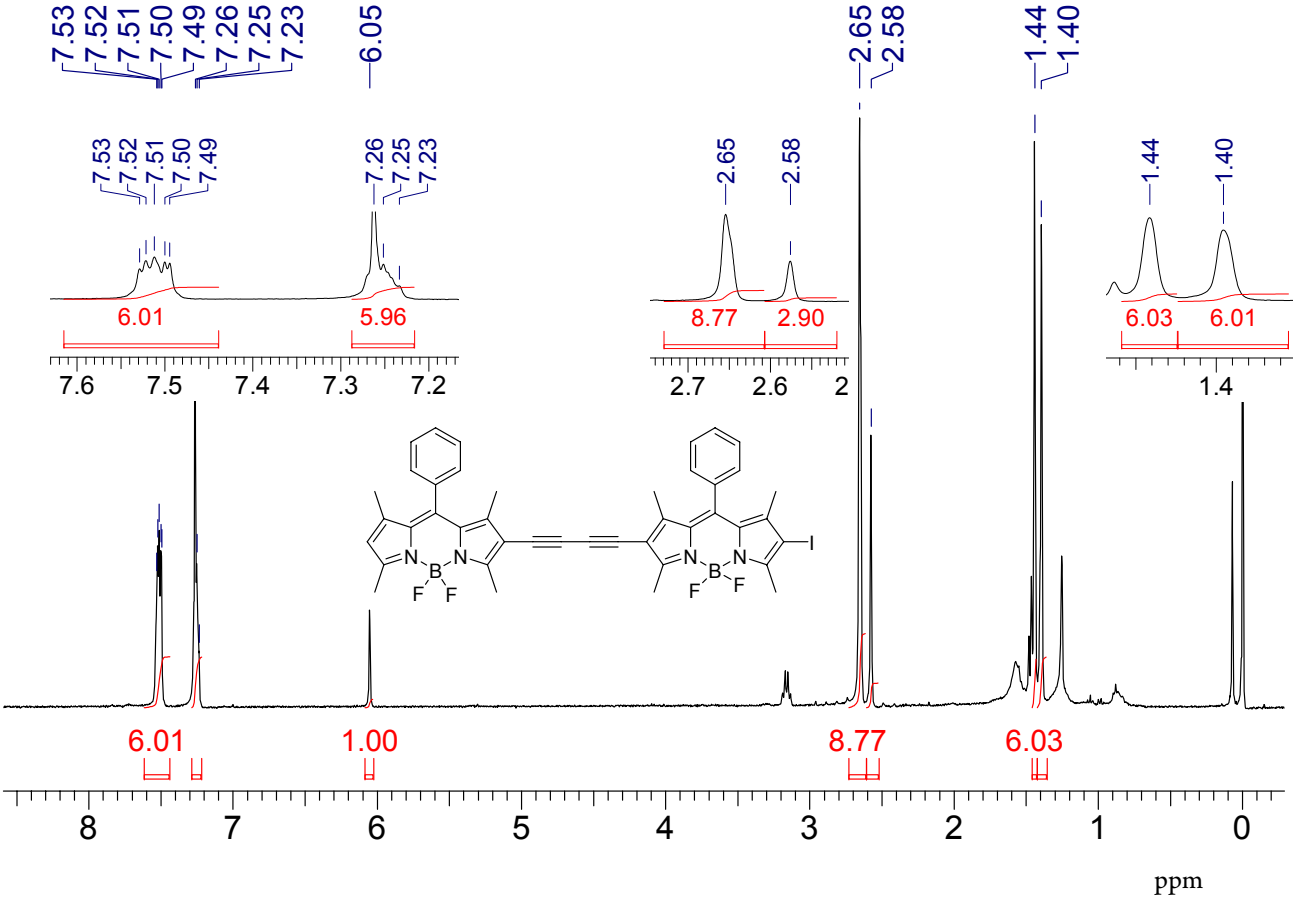


Figure S4. ^{1}H NMR of compound **4** (400 MHz, $CDCl_3$).

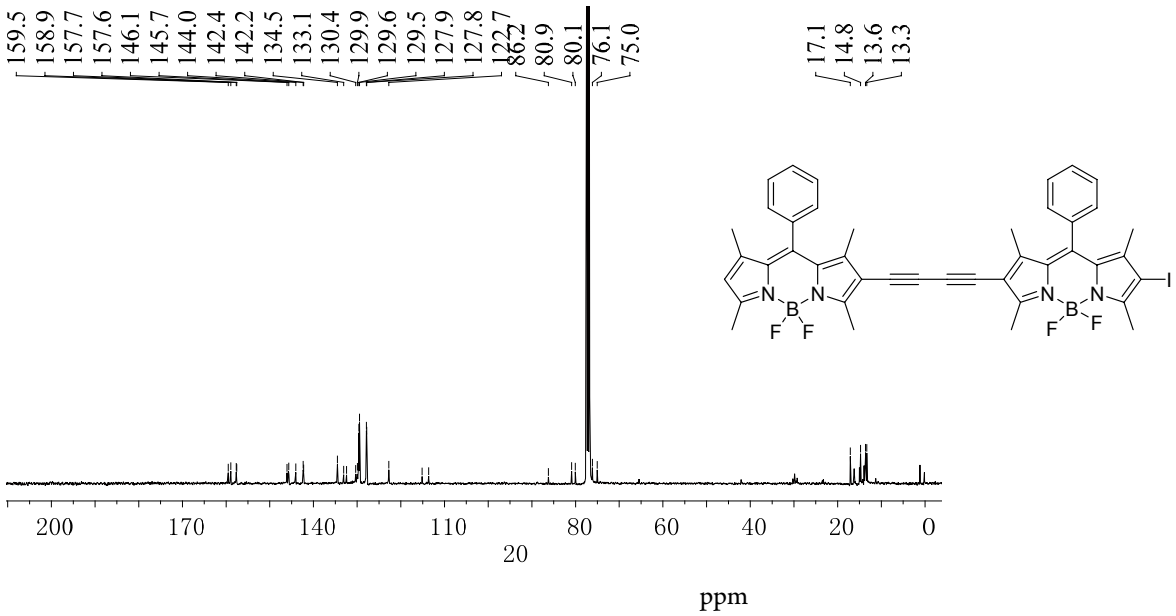


Figure S5. ^{13}C NMR of compound **4** (100 MHz, $CDCl_3$).

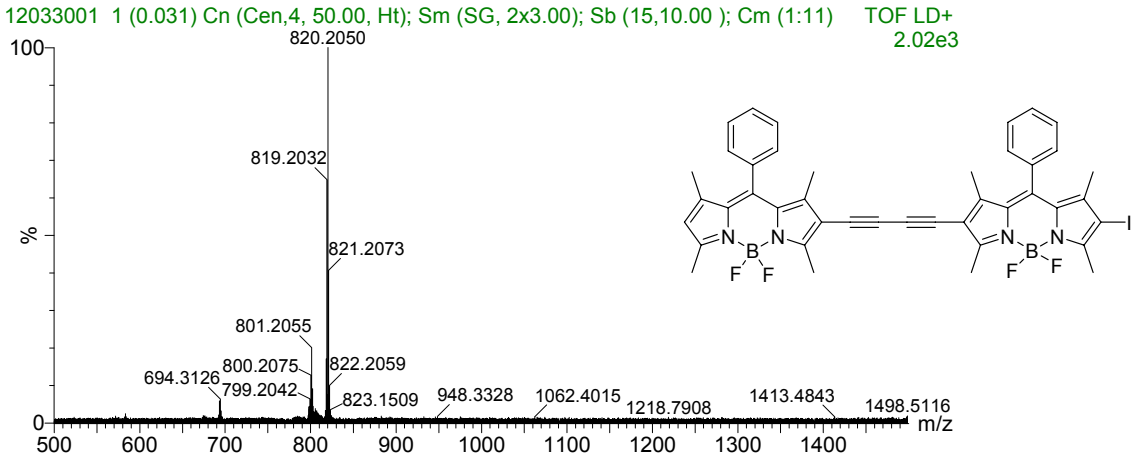


Figure S6. MALDI-HRMS of **4.**

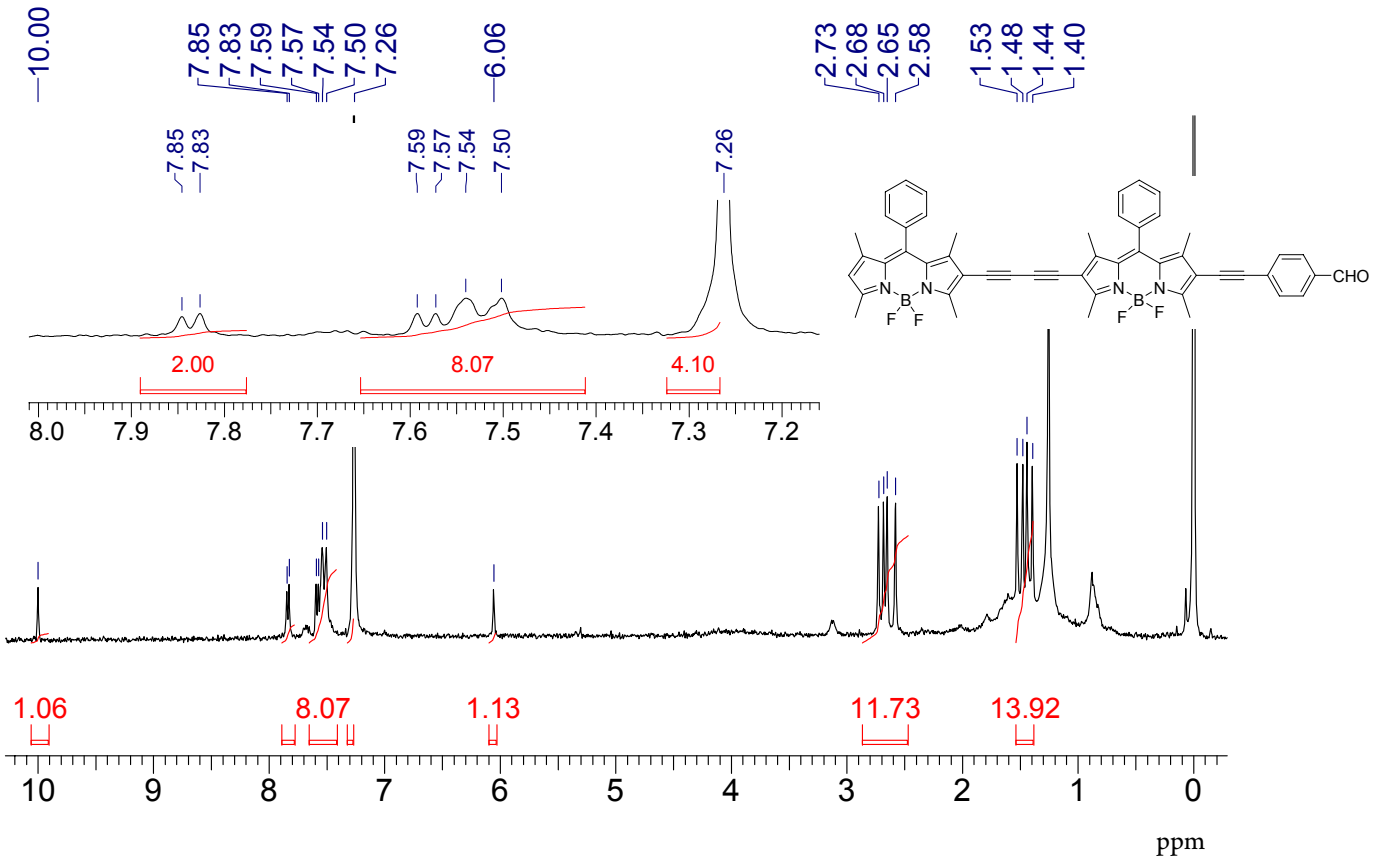


Figure S7. ^{1}H NMR of **5** (400 MHz, $CDCl_3$).

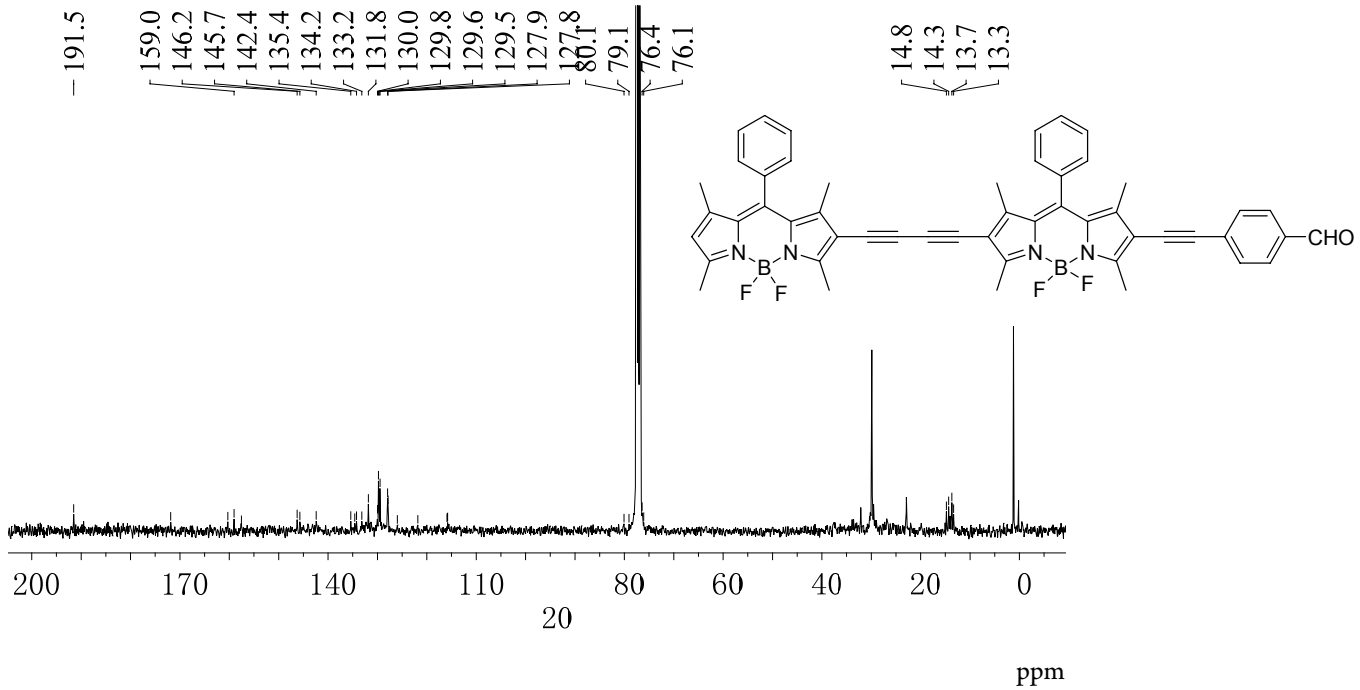


Figure S8. ^{13}C NMR of **5** (100 MHz, $CDCl_3$).

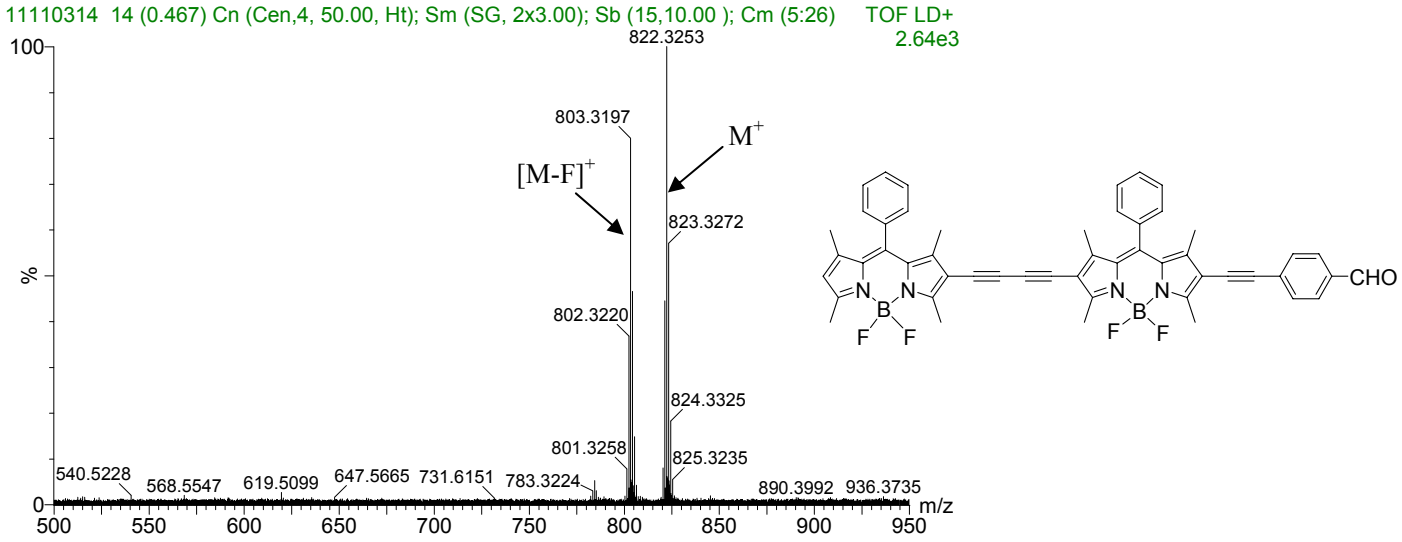


Figure S9. MALDI-HRMS of **5.**

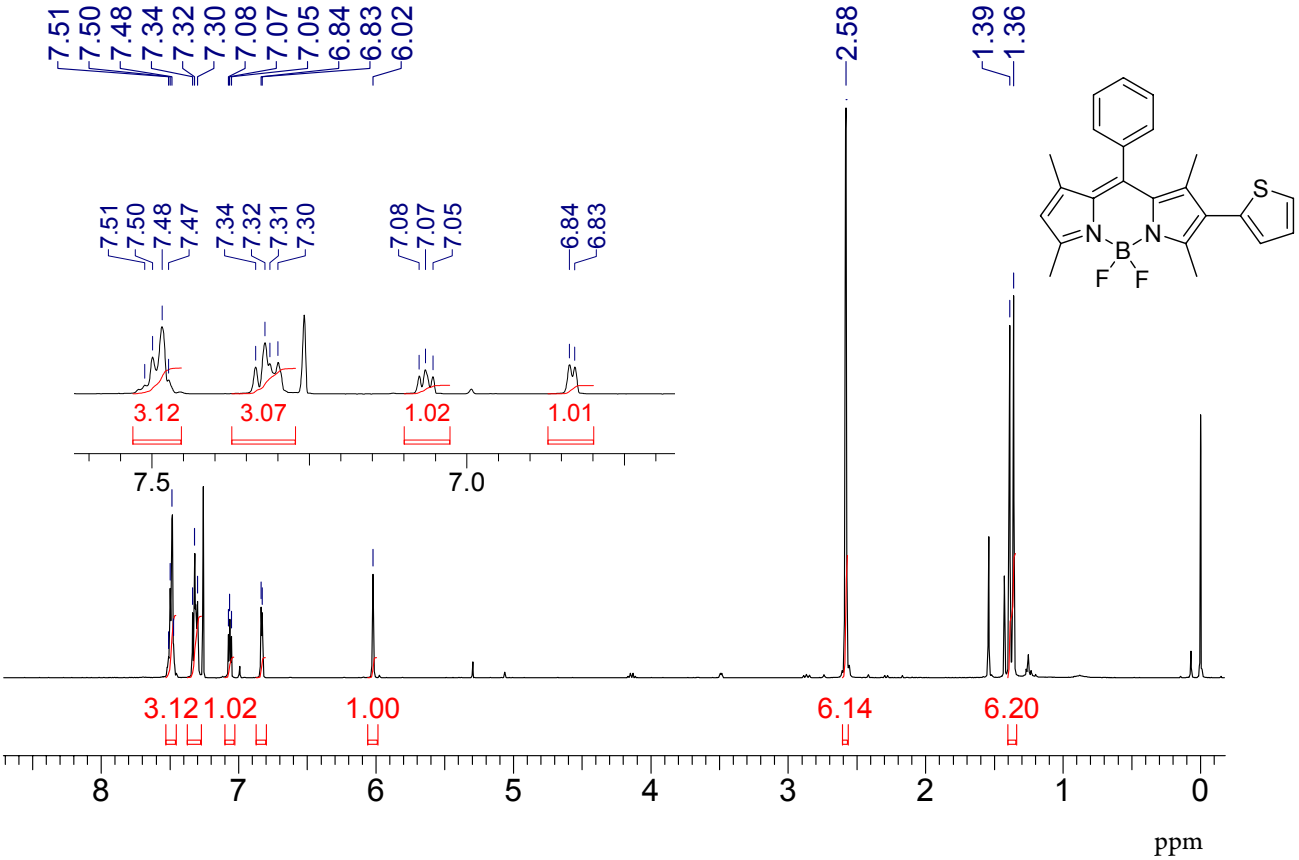


Figure S10. ^{1}H NMR of **C-1-L** (400 MHz, $CDCl_3$).

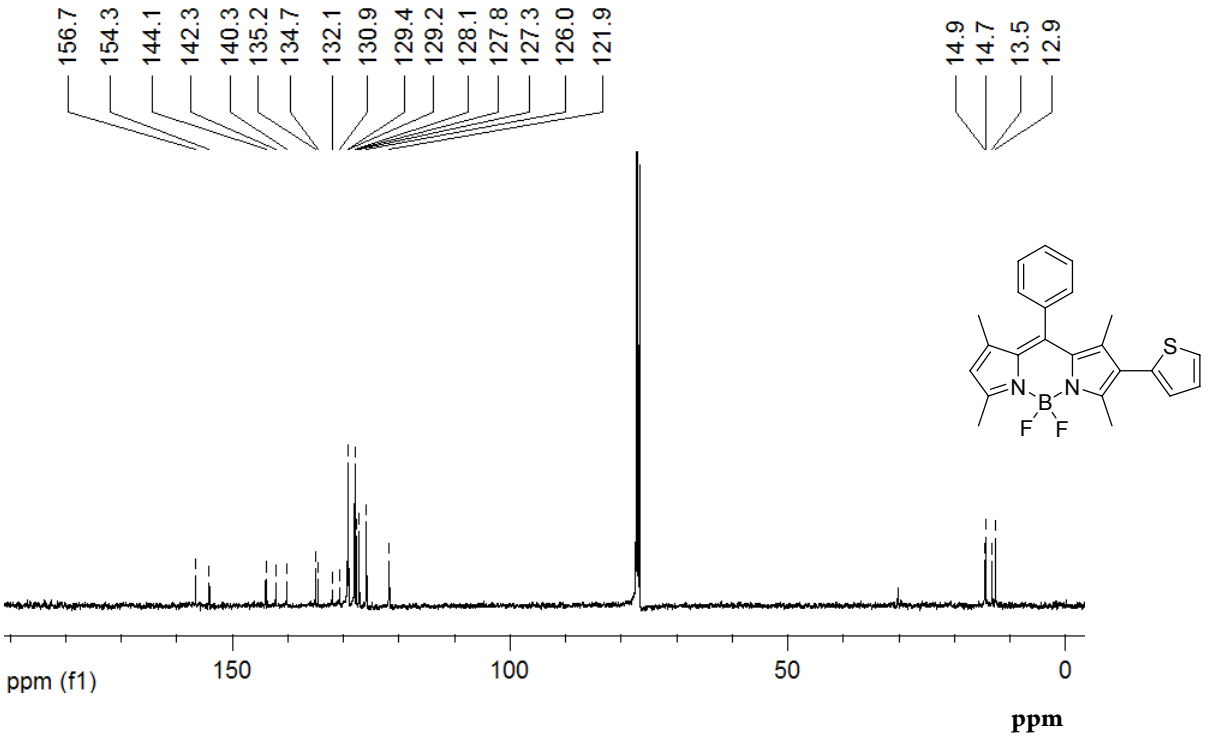


Figure S11. ^{13}C NMR of **C-1-L** (100 MHz, $CDCl_3$).

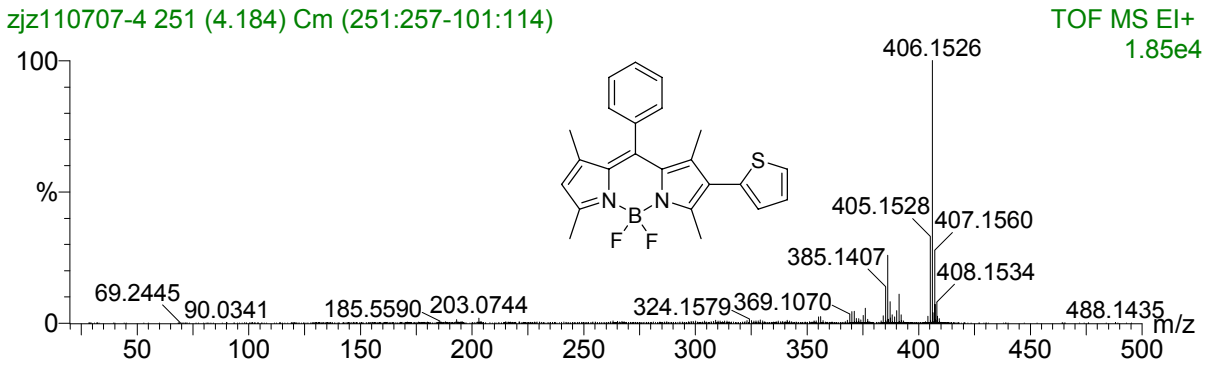


Figure S12. MALDI-HRMS of **C-1-L.**

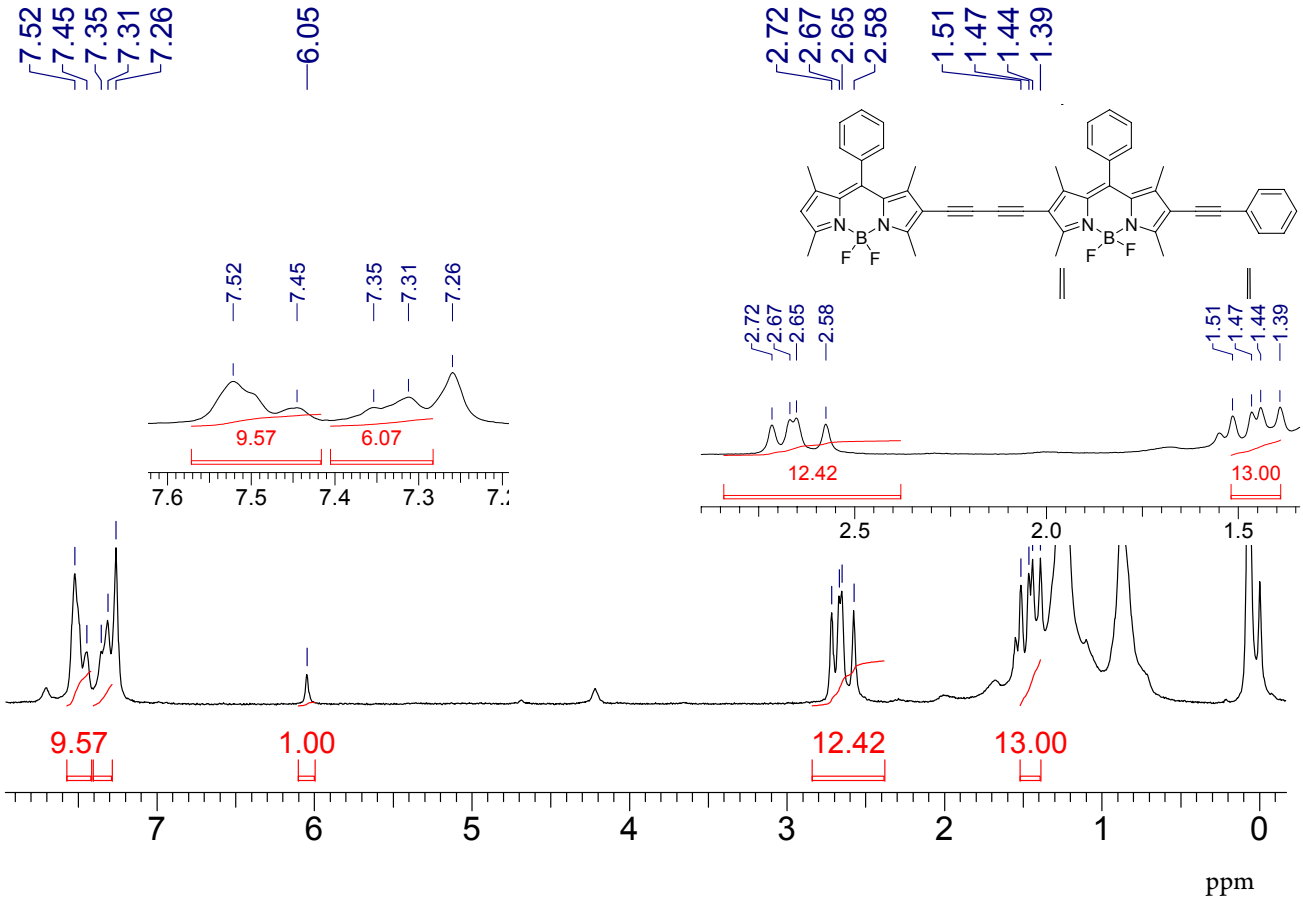


Figure S13. ^{1}H NMR of **C-2-L** (400 MHz, $CDCl_3$).

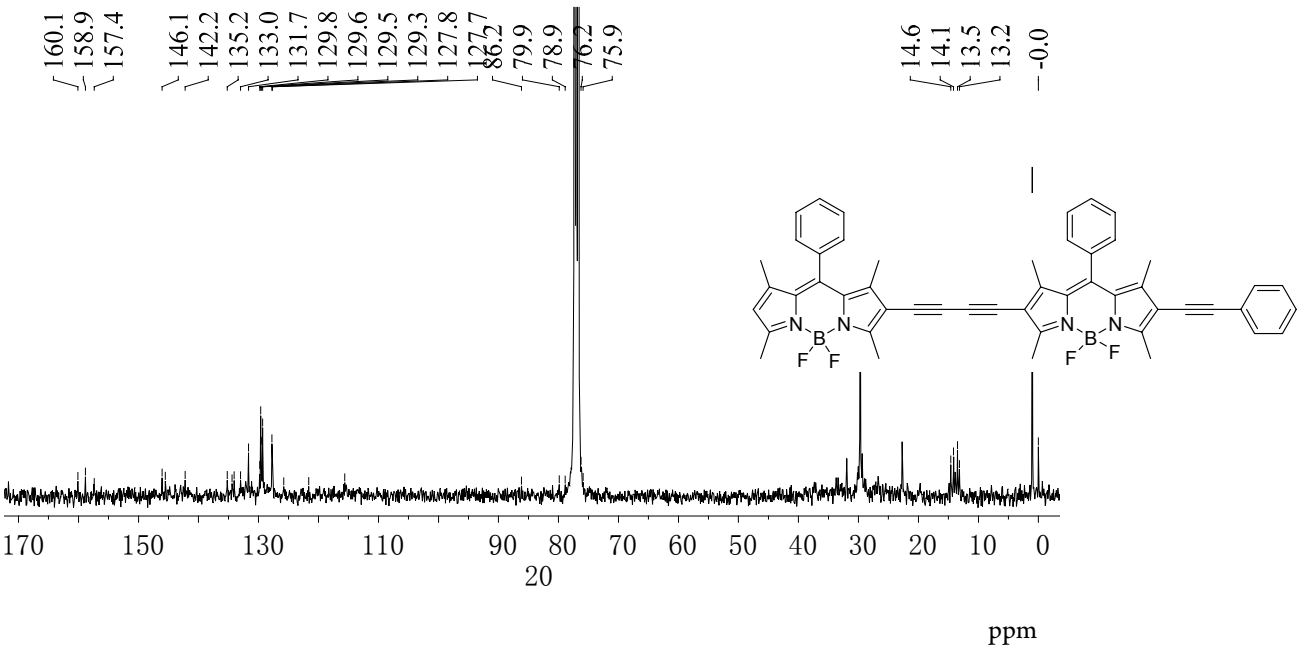


Figure S14. ^{13}C NMR of **C-2-L** (100 MHz, $CDCl_3$).

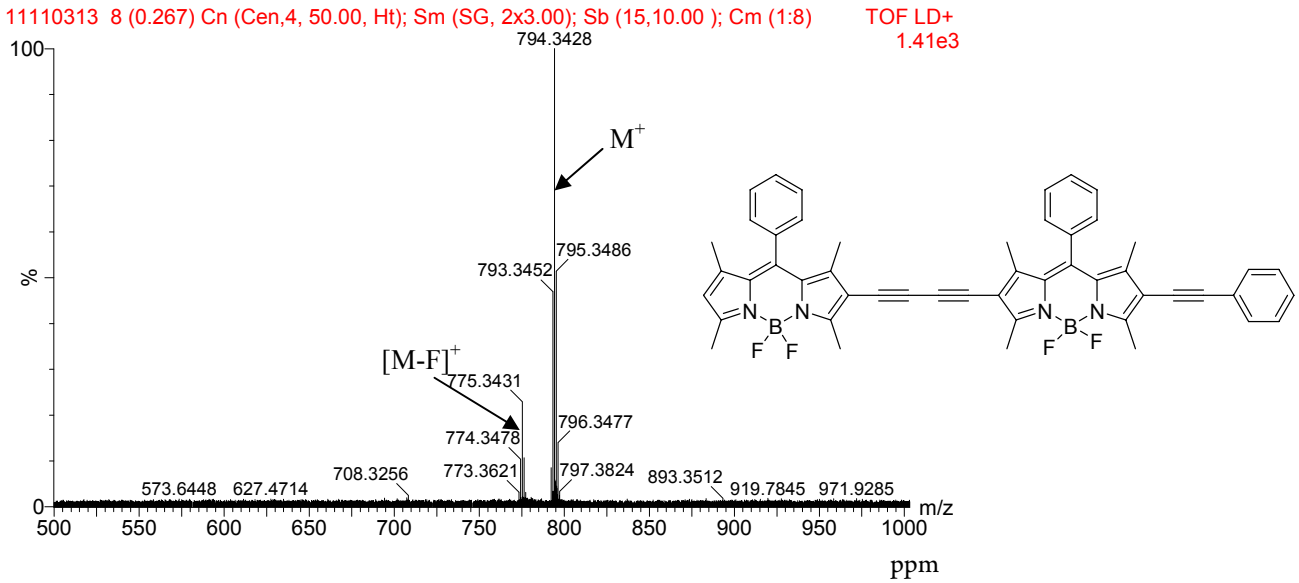


Figure S15. MALDI-HRMS of **C-2-L.**

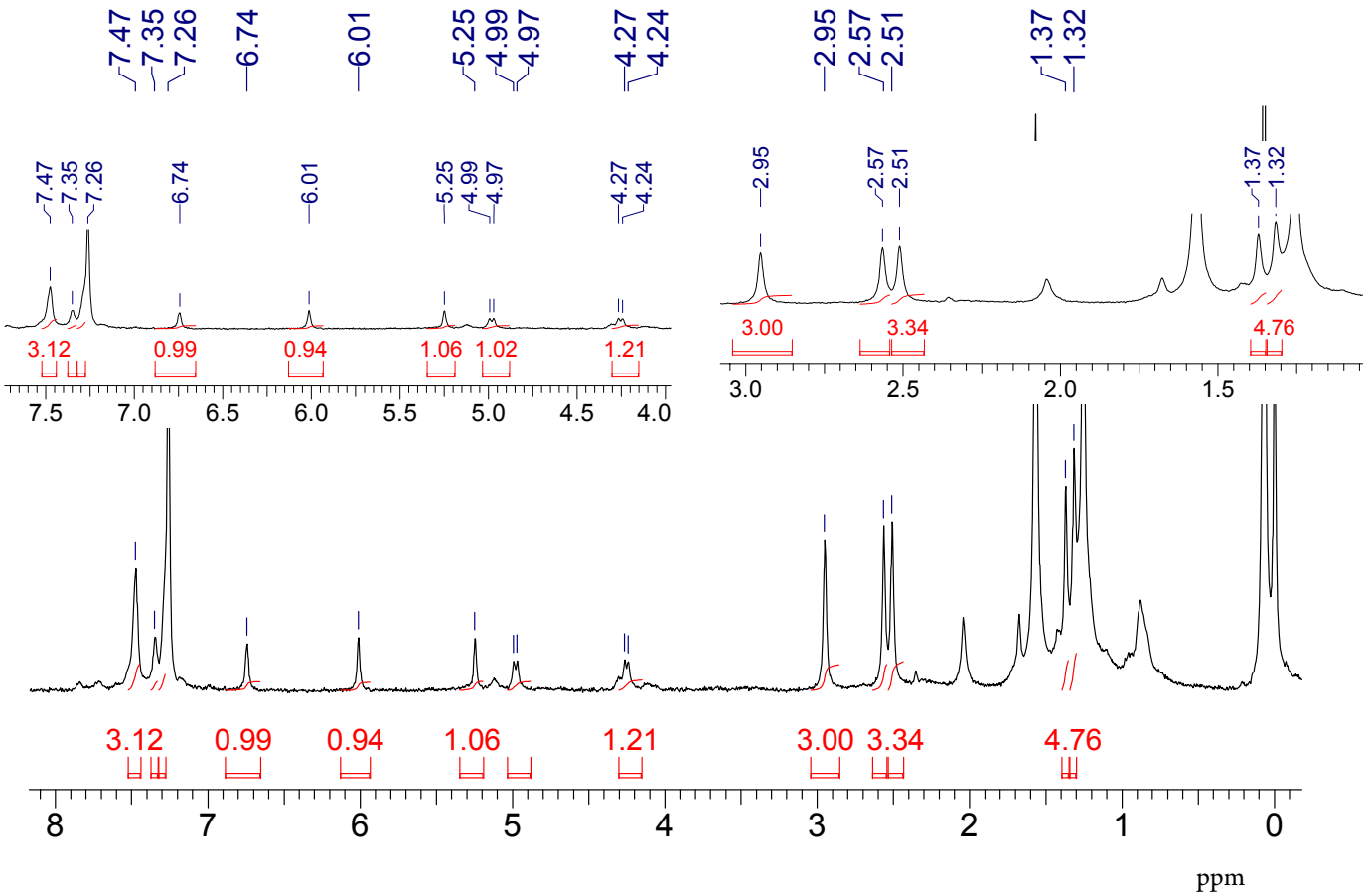


Figure S16. ^{1}HNMR of **C-1** (400 MHz, $CDCl_3$).

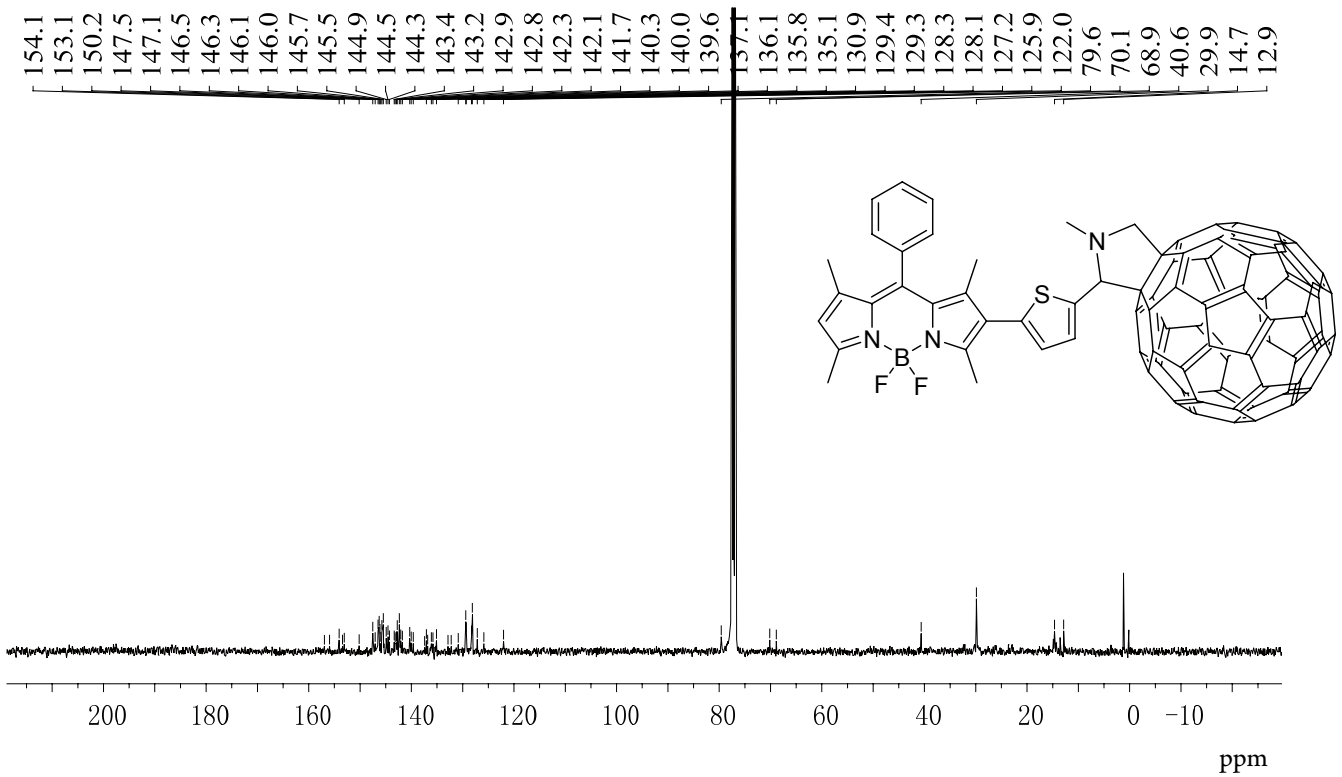


Figure S17. ^{13}C NMR of **C-1** (100 MHz, $CDCl_3$).

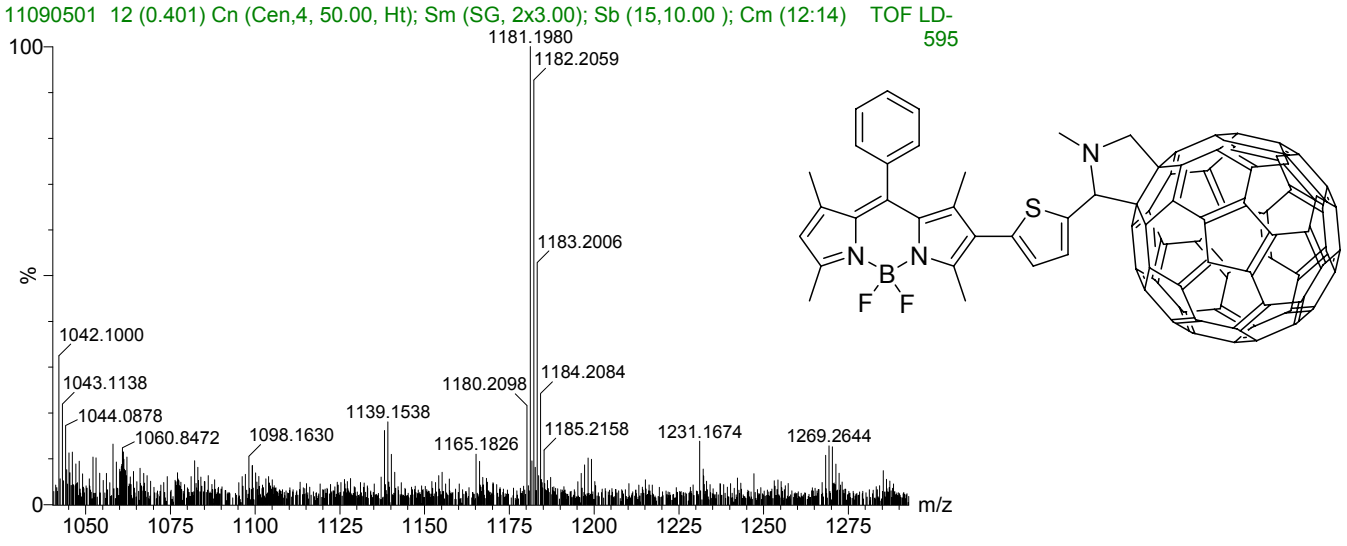


Figure S18. MALDI-HRMS of **C-1.**

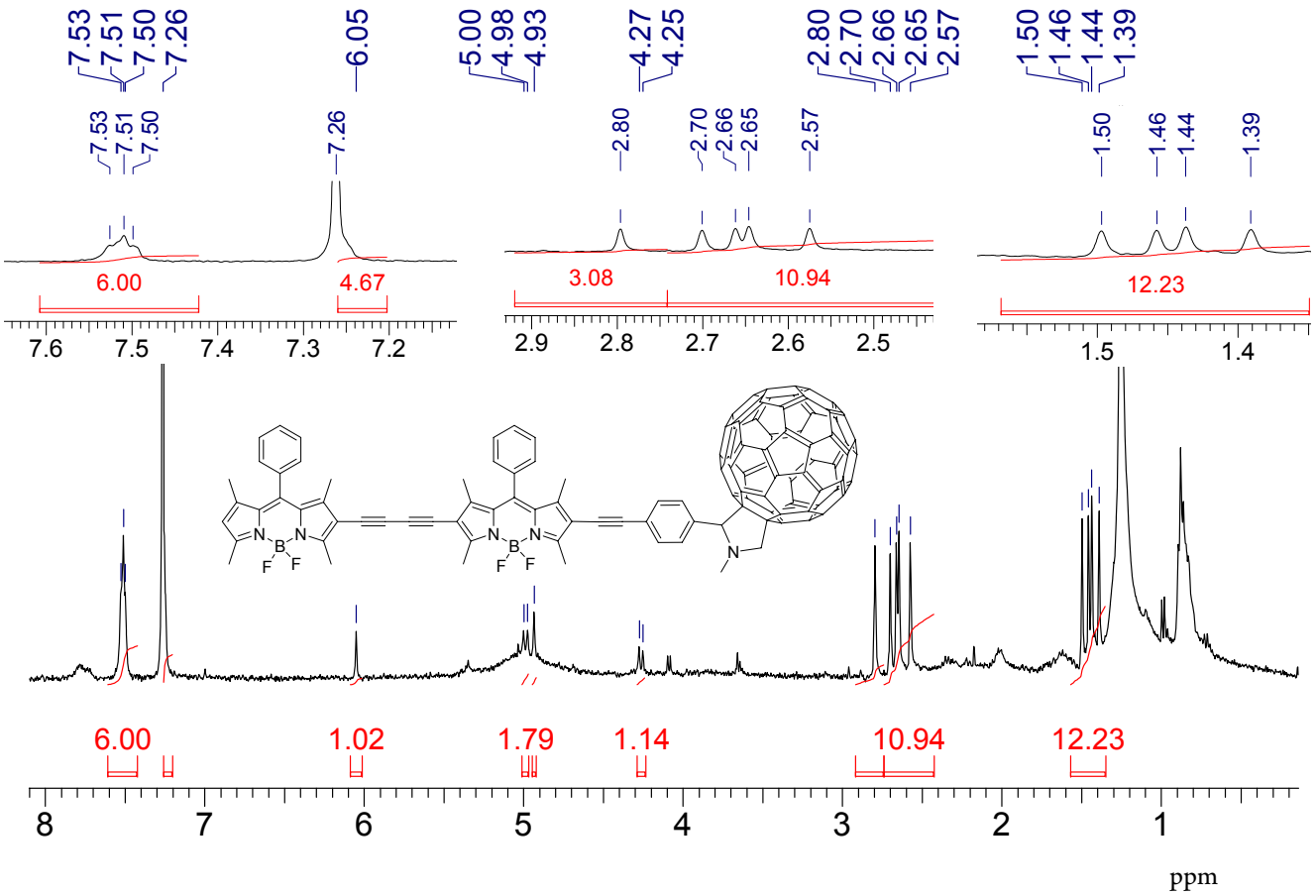


Figure S19. ^{1}HNMR of **C-2** (400 MHz, $CDCl_3$).

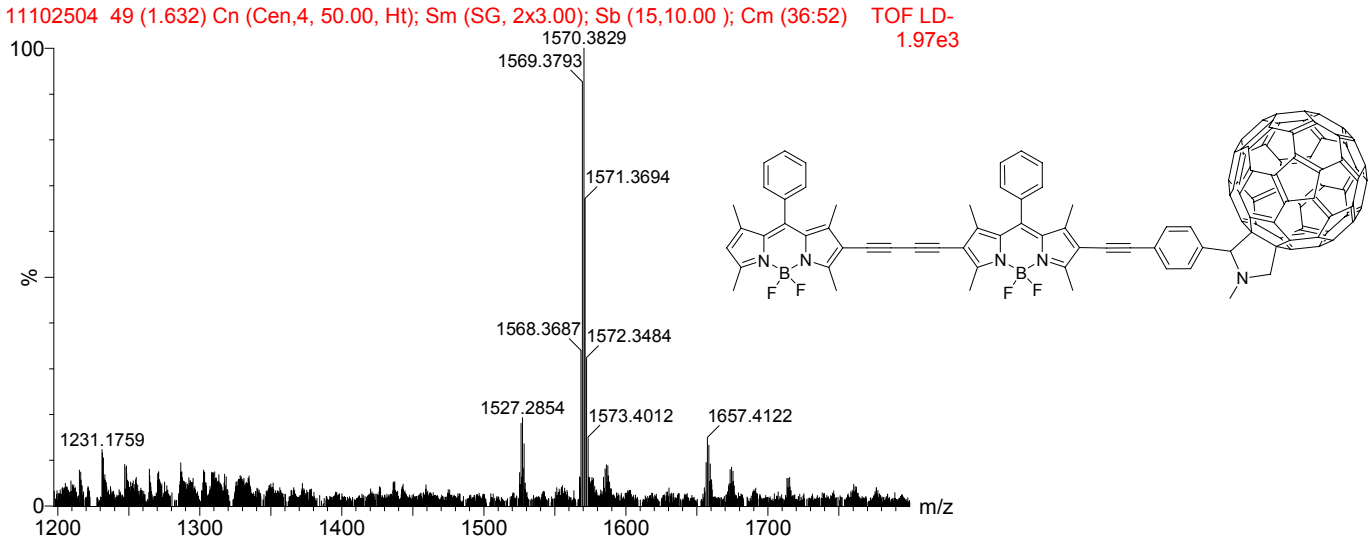


Figure S20. MALDI-HRMS of **C-3**.

2.0 Transient absorption details

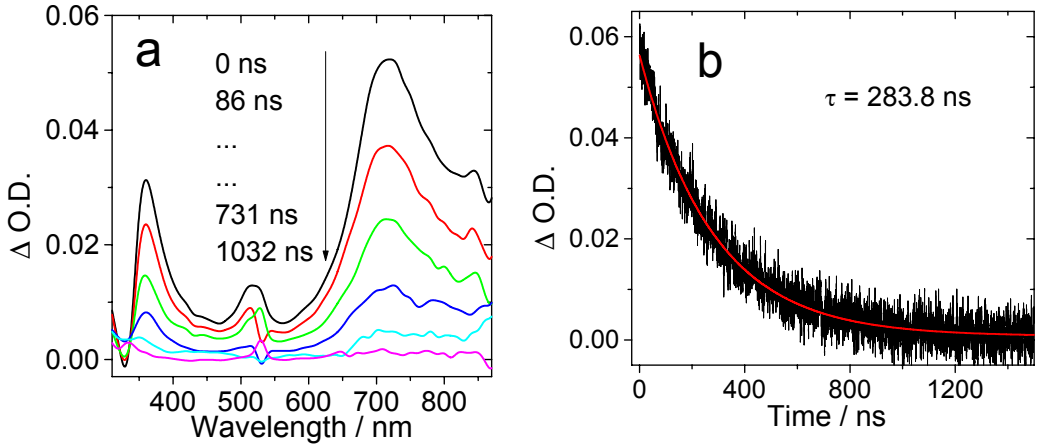


Figure S21. (a) Transient absorption difference spectra of **C-1** in air-saturated toluene after pulsed excitation (λ_{ex} = 532 nm). (b) Decay traces of **C-1** at 700 nm. 25 °C.

The lifetime is much shorter than that in deaerated solution, thus the transient is due to triplet excited states.

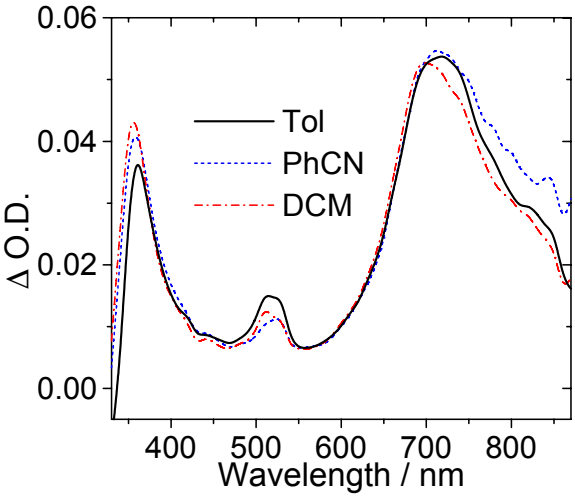


Figure S22. Transient absorption difference spectra of **C-1** in solvents with different polarities in Ar atmosphere after pulsed excitation (λ_{ex} = 532 nm). 25 °C.

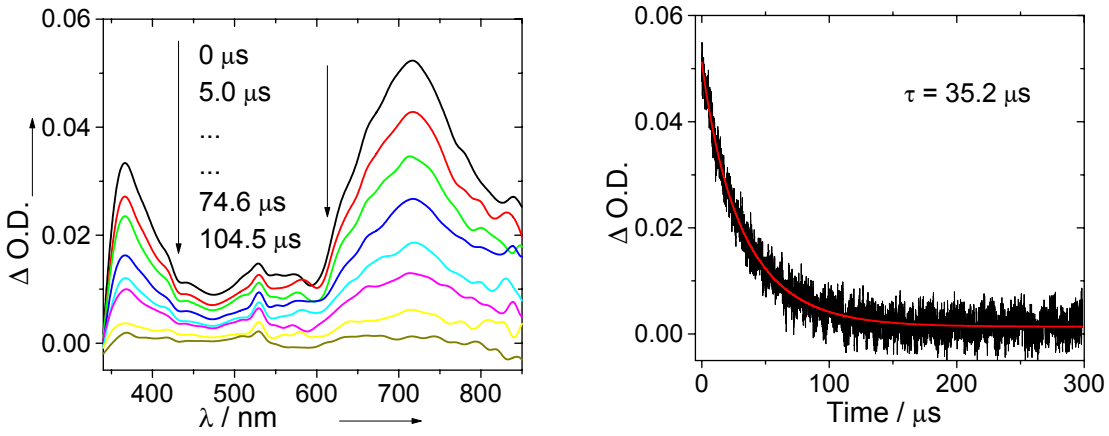


Figure S23. (a) Transient absorption difference spectra of **C-2** in deaerated toluene after pulsed excitation (λ_{ex} = 532 nm). (b) Decay traces of **C-2** at 700 nm. 25 °C.

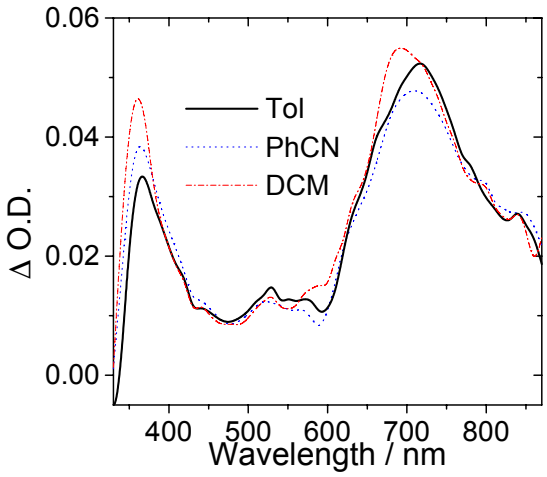


Figure S24. Transient absorption difference spectra of **C-2** in solvents with different polarities in Ar atmosphere after pulsed excitation (λ_{ex} = 532 nm). 25 °C.

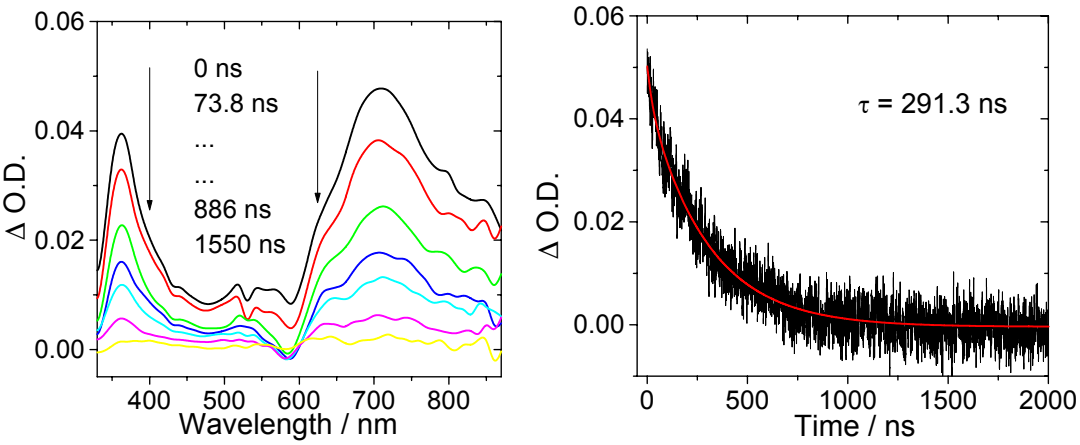


Figure S25. (a) Transient absorption difference spectra of **C-2** in air-saturated toluene after pulsed excitation (λ_{ex} = 532 nm). (b) Decay traces of **C-2** at 700 nm. 25 °C.

The lifetime is much shorter than that in deaerated solution, thus the transient is due to triplet excited states.

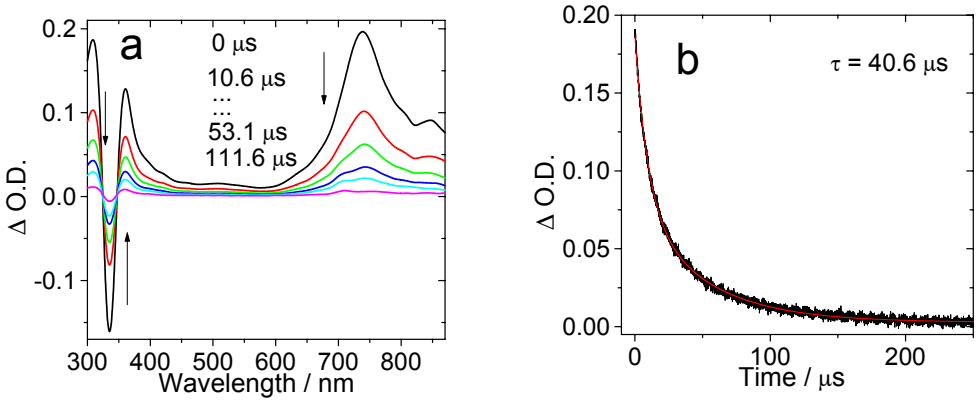


Figure S26. (a) Transient absorption difference spectra of C_{60} in deaerated toluene after pulsed excitation (λ_{ex} = 355 nm). (b) Decay traces of C_{60} at 700 nm. 25 °C.

3.0 up-conversion details

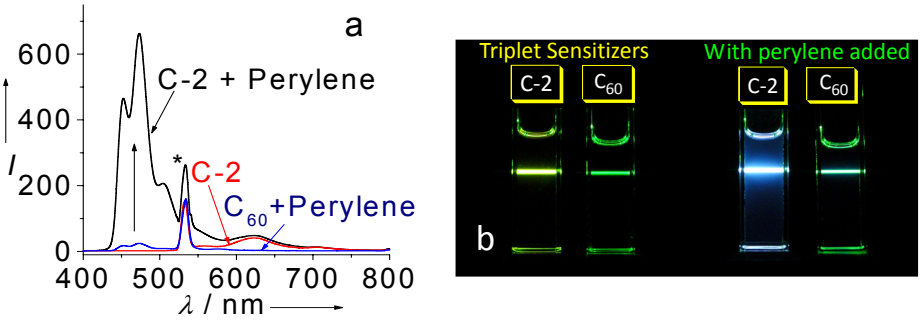


Figure S27. (a) TTA upconversion with **C-2** as the triplet sensitizers and perylene as the acceptor (4.1×10^{-4} M). *c* [sensitizers] = 1.0×10^{-5} M. The asterisks indicates the scattered laser. (b) The photographs of the emissions of triplet sensitizers alone and the upconversion. In toluene. Excited with CW laser (λ_{ex} = 532 nm), 12 mW, 20 °C.

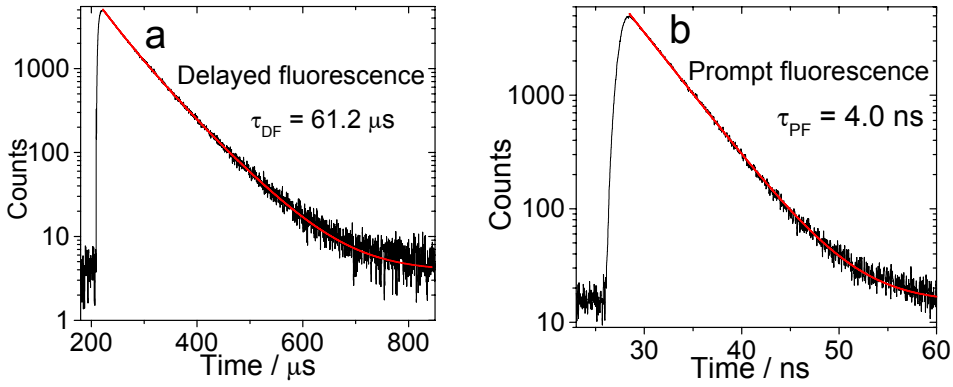


Figure S28. (a) Delayed fluorescence observed in the TTA upconversion with compound **C-2** as triplet photosensitizer and perylene as the triplet acceptor. Excited at 589 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 470 nm. Under this circumstance the compound **C-2** is selectively excited and the emission is due to the upconverted emission of perylene. In deaerated toluene. *c*[Sensitizers] = 1.0×10^{-5}M; *c* [perylene] = 4.1×10^{-4} M; 20 °C. (b) The prompt fluorescence decay of perylene determined in a different experiment (excited with picosecond 405 nm laser, the decay of the emission was monitored at 470 nm), *c* [perylene] = 1.0×10^{-5} M; 20 °C.

4.0 Stability of the compounds C-1 and C-2

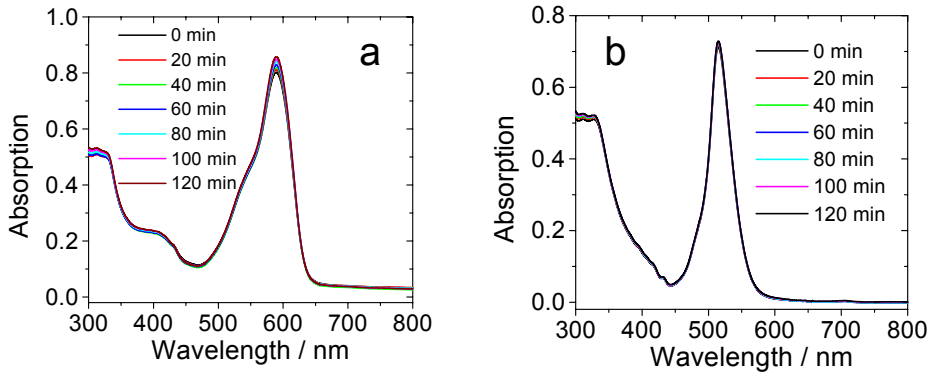


Figure S29. Photostability of (a) **C-1** and (b) **C-2**, monitored by the UV-vis absorption spectra of the sensitizers **C-1** and **C-2** (in toluene) before and after the irradiation by xenon lamp (35 W). The photo-irradiation power density is 40 mW cm^{-2}. c [sensitizer] = 1.0×10^{-5} M. 20 °C.

5.0 Excitation spectrum of C-1.

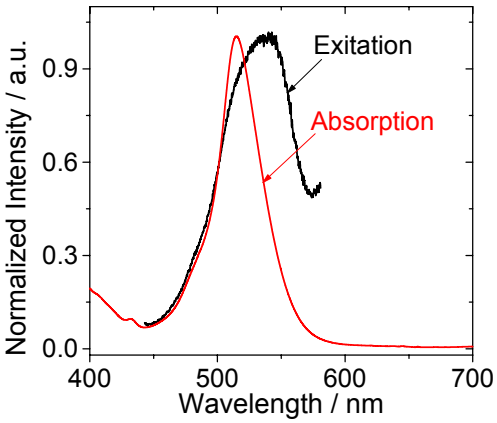


Figure S30. Comparison of the normalized UV-vis absorption and the excitation spectra of **C-1**. The excitation spectra of **C-1** were recorded with λ_{em} = 710 nm. $c = 1.0 \times 10^{-5}$ mol dm^{-3}, in toluene, 20 °C.

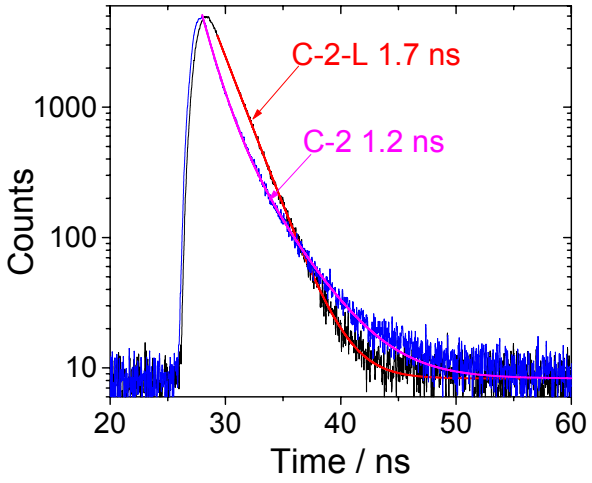
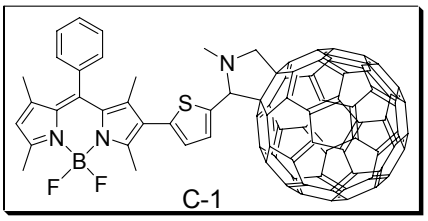


Figure S31. Comparison of the lifetime decay at 630 nm of **C-2-L** and **C-2**. In 1.0×10^{-5} mol dm^{-3} toluene solution. 20 °C.

5.0 Optimized triplet state geometries of C-1 (at DFT//B3LYP/ rb3lyp/6-31g(d))

Symbolic Z-matrix:
Charge = 0 Multiplicity = 3

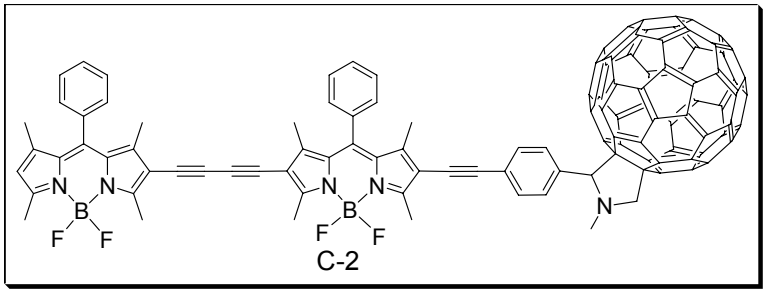


C	-5.78155763	-1.89263758	-0.11129410
C	-5.63652210	0.16484170	-1.08329751
C	-6.83367365	0.06763971	-0.30798705
C	-7.86834123	0.98998030	-0.05673748
C	-8.94794542	0.66064579	0.77597783
C	-10.11584135	1.40019329	1.17199023
C	-10.14109168	-0.66672292	2.11810522
N	-6.87317499	-1.20732419	0.26656240
N	-9.01567148	-0.59942873	1.38321435
B	-7.99211404	-1.75807718	1.20505475
F	-8.61848527	-2.85390378	0.61302422
F	-7.44518548	-2.11164719	2.43489889
C	-5.11305986	1.33521040	-1.86181780
H	-5.71149461	1.53501715	-2.75859100
H	-5.11910013	2.25518751	-1.27070159
H	-4.08698045	1.13820009	-2.18287266
C	-10.52317083	-1.88217201	2.89736437
H	-11.45622240	-1.71279300	3.44049866
H	-10.64529266	-2.74217098	2.23005579
H	-9.73272697	-2.14600349	3.60759992
C	-10.54091938	2.79068180	0.80135986
H	-10.61595502	2.92517479	-0.28273261
H	-11.52120637	3.00417671	1.23868416
H	-9.83814622	3.54909186	1.16281333
C	-5.54200522	-3.30224890	0.32372664
H	-6.44731812	-3.89814440	0.17712050
H	-4.71667567	-3.74604397	-0.23591708
H	-5.30706349	-3.34154641	1.39359097
C	-7.81966274	2.34547643	-0.68572070
C	-7.27213791	3.43071852	0.01196113
C	-8.32209505	2.54701622	-1.97799475
C	-7.22432383	4.69578951	-0.57563813
C	-8.27847047	3.81417576	-2.56203743
H	-8.74862943	1.70860091	-2.52204699
H	-6.79390085	5.52876897	-0.02645557
H	-8.67350113	3.95918461	-3.56392708
C	-7.72846862	4.89042832	-1.86317022
H	-7.69266486	5.87573615	-2.31959473
H	-6.88047086	3.27849537	1.01413187
C	-10.83715138	0.55544267	2.00528181
H	-11.77742442	0.78409787	2.49081260
C	0.70809294	1.65581654	0.29037170

C	1.12273182	1.82708364	1.66644341
C	2.10680933	2.77265595	1.98971299
C	2.72107560	3.56429450	0.94165218
C	2.32152788	3.40721308	-0.38292438
C	1.28915313	2.44014743	-0.71640627
C	0.45298676	0.24969854	0.06081211
C	0.71605202	-0.46141171	1.33021703
C	1.12924532	0.52749040	2.30397664
C	2.12165017	0.21843002	3.24563033
C	3.14307707	2.43959479	2.94819799
C	4.13663366	3.72801880	1.26345470
C	5.09664666	3.72230620	0.22900207
C	4.68604296	3.55434809	-1.13340943
C	3.31542885	3.39855823	-1.44908964
C	2.91015689	2.42179720	-2.41225241
C	1.65241314	1.82890502	-1.96589569
C	1.42092308	0.46421885	-2.15385460
C	0.77711607	-0.33105530	-1.14830317
C	1.29650817	-1.71382714	1.32034731
C	1.46914863	-2.57004026	0.06167168
C	1.17560773	-1.80110152	-1.31546088
C	2.40946829	-1.63938765	-2.21733645
C	2.42110495	-0.36329143	-2.81532123
C	3.63081245	0.22861642	-3.27769131
C	3.87437252	1.61605555	-3.06122662
C	5.29401440	1.78882180	-2.75308100
C	5.68432427	2.73154341	-1.80607934
C	4.39517712	3.03872785	2.49275874
C	7.58842048	0.44369268	0.37843843
C	7.23810509	1.03543333	1.59445727
C	6.61942571	0.23814662	2.63964940
C	6.38406799	-1.11730237	2.42899965
C	6.75174347	-1.73525858	1.17115622
C	6.92393266	-1.14193874	-1.21919114
C	6.91850934	0.16066371	-1.85558195
C	7.32635037	1.14371195	-0.86999882
C	6.72509236	2.40477527	-0.84663604
C	6.35550809	3.01305087	0.41893514
C	6.60653739	2.34262287	1.61389149
C	5.62042659	1.06206578	3.30998749
C	4.40989447	0.47995181	3.75438954
C	4.15992907	-0.91024892	3.52883872
C	5.12232569	-1.71079582	2.87071520
C	4.72118248	-2.67718296	1.90318735
C	5.71278734	-2.69314802	0.84120579
C	5.30110871	-2.85223809	-0.47847810

C	5.91839186	-2.07115130	-1.52899010
C	5.91973057	0.48260716	-2.78354467
C	4.88385994	-0.48437193	-3.09662982
C	4.87958579	-1.73077307	-2.47823960
C	3.62230825	-2.32519862	-2.02488671
C	3.88234079	-3.01599317	-0.79358175
C	2.92784864	-3.01604458	0.23834692
C	3.34429030	-2.82233146	1.57028379
C	2.34790184	-2.00625055	2.25173349
C	2.74252840	-1.07795195	3.21830458
C	5.61202458	2.34836813	2.67891518
C	3.15204261	1.19222392	3.56664295
C	7.34212075	-0.96880881	0.15817612
C	0.50895202	-3.79699816	-0.00248282
C	0.09420802	-2.71207203	-2.04400920
H	0.94964412	-4.68198264	0.46863023
H	-0.43100376	-3.57460827	0.53430520
H	0.36104206	-2.78240123	-3.10529622
N	0.33313749	-4.01472081	-1.42525898
C	-0.54814751	-5.10588900	-1.80576805
H	-0.55798369	-5.20102619	-2.89663087
H	-0.15686080	-6.03993196	-1.38801144
H	-1.58841593	-4.98041290	-1.46215627
C	-4.98330450	-1.07296963	-0.95668609
C	-3.71707426	-1.45512578	-1.58565138
C	-3.37212208	-1.42673473	-2.91585077
S	-2.34281573	-1.99167277	-0.62889704
C	-2.03549299	-1.84508399	-3.17031218
H	-4.07158146	-1.13703566	-3.69253473
C	-1.33024042	-2.19080732	-2.04417041
H	-1.60522499	-1.90019101	-4.16594858

8.0 Optimized triplet state geometry of C-2 (DFT//B3LYP/ rb3lyp/6-31g(d))



Symbolic Z-matrix:

Charge = 0 Multiplicity = 3

C	3.30935322	0.71924040	-2.26329465
C	3.20553399	3.00326045	-1.47876106

C	4.68443334	0.84212812	-2.43203741
H	2.81632141	-0.21873854	-2.49879163
C	4.57962167	3.11337355	-1.65472066
H	2.63326895	3.84686420	-1.10580334
C	5.34998315	2.04291832	-2.13477626
H	5.24240348	-0.01469403	-2.79222147
H	5.06788735	4.05516425	-1.41671926
C	8.06630712	-2.56115739	-1.42562186
C	9.32572188	-3.17659970	-1.78742596
C	10.00217868	-3.98610979	-0.86346249
C	9.44693046	-4.19104222	0.46073380
C	8.23297769	-3.60633802	0.81091883
C	7.52251421	-2.78227307	-0.15271069
C	8.01241042	-1.24290847	-2.02146192
C	9.26999449	-1.04459476	-2.76903086
C	10.06543844	-2.24382326	-2.61092623
C	11.45884093	-2.15374607	-2.48343595
C	11.44109026	-3.87217586	-0.71956338
C	10.54933986	-4.21578634	1.41886708
C	10.38042812	-3.64332500	2.69784664
C	9.13281280	-3.03670950	3.05591532
C	8.06250398	-3.01262783	2.13085729
C	7.27772549	-1.82701358	1.97607084
C	6.93692047	-1.68144367	0.56324395
C	6.91877419	-0.41288941	-0.02081573
C	7.42559614	-0.18779885	-1.34753183
C	9.87211618	0.19725434	-2.78820550
C	9.20965426	1.48885885	-2.29944205
C	7.84582135	1.27811543	-1.49590202
C	7.90759284	1.68517256	-0.02448512
C	7.21281767	0.76437520	0.78305134
C	7.51400578	0.61869181	2.16737032
C	7.55803618	-0.67898103	2.75305545
C	8.65030777	-0.70660233	3.72566013
C	9.42061394	-1.85755266	3.86452387
C	11.77077086	-4.01969394	0.69592064
C	12.71257851	-0.29518920	3.27274951
C	13.28746551	-1.36165326	2.57703633
C	13.83862478	-1.15069055	1.24969354
C	13.80045454	0.11776533	0.67744621
C	13.21080106	1.22721131	1.39934535
C	11.40861783	1.64149015	3.03475406
C	10.67034042	0.70587902	3.86013164
C	11.47269082	-0.49376258	4.00726181
C	10.86139817	-1.74997166	4.01275998
C	11.45739336	-2.85383716	3.28160301

C	12.64491939	-2.66385259	2.57900248
C	13.54839112	-2.33059014	0.44318599
C	13.23255078	-2.18600847	-0.92867101
C	13.17929173	-0.88326933	-1.51637798
C	13.45271762	0.26412439	-0.73567456
C	12.66577268	1.44302828	-0.88136957
C	12.49680173	2.04057662	0.43205105
C	11.27864464	2.62259549	0.77016720
C	10.72544465	2.42783549	2.09373842
C	9.28059904	0.59800733	3.72529331
C	8.58243417	1.41385559	2.74864390
C	9.29030585	2.30431910	1.94691800
C	8.95447081	2.44733969	0.53037623
C	10.17861352	2.64421867	-0.19397012
C	10.35282873	2.07768292	-1.47111819
C	11.57710580	1.46259168	-1.79876094
C	11.29440296	0.28607312	-2.60940298
C	12.08470209	-0.85900519	-2.48373311
C	12.81462341	-3.25366292	1.25730730
C	12.15713809	-2.97872772	-1.51155314
C	12.67131745	1.02621840	2.67609891
C	8.78043822	2.46238667	-3.48624231
C	6.83937295	2.25578663	-2.30520715
H	9.01920718	3.48859095	-3.18097280
H	9.32790384	2.24592837	-4.40629936
H	7.05739387	3.23803539	-1.86673767
N	7.34862286	2.34322505	-3.67345591
C	6.93106232	1.33685141	-4.64917861
H	5.84907048	1.39291368	-4.78680414
H	7.40129044	1.57929834	-5.60718520
H	7.19646731	0.29913895	-4.39331285
C	-2.26818505	0.37217056	-1.63164441
C	-2.31320939	2.44939578	-0.67478569
C	-3.62555116	1.88979471	-0.70859753
C	-4.86494759	2.38499433	-0.26515248
C	-6.04281910	1.63172648	-0.40470197
C	-7.39396758	1.90579449	-0.03357792
C	-8.14060895	0.77876213	-0.42302965
C	-7.23894236	-0.15420548	-1.01967884
N	-3.54249269	0.62158890	-1.30435899
N	-6.00412439	0.36110168	-1.00212498
B	-4.73391831	-0.35255999	-1.56300112
F	-4.87754423	-0.57301386	-2.92838693
F	-4.52469338	-1.54766613	-0.88548863
C	-1.84436275	3.77144407	-0.14913430
H	-2.34809716	4.61148965	-0.63833352

H	-2.03028285	3.87576198	0.92520445
H	-0.76869187	3.86936562	-0.31970496
C	-7.56111404	-1.49621844	-1.58389027
H	-8.63659975	-1.67830808	-1.53308629
H	-7.22494207	-1.56228848	-2.62369764
H	-7.03311759	-2.28030387	-1.03033901
C	-7.98383808	3.10970317	0.63452143
H	-7.83339658	4.02113663	0.04641093
H	-9.05909815	2.96228966	0.76756613
H	-7.53882959	3.29299093	1.61817570
C	-1.82326475	-0.89247831	-2.28434671
H	-2.35189047	-1.03885494	-3.23215789
H	-0.74702719	-0.86384623	-2.46682726
H	-2.06425812	-1.75352115	-1.65200934
C	-4.92933317	3.73713362	0.36972602
C	-4.75462093	3.87935562	1.75260078
C	-5.16224172	4.87654060	-0.41194912
C	-4.81250016	5.14241051	2.34407844
C	-5.21904817	6.13875465	0.18147347
H	-5.29810849	4.77051463	-1.48489148
H	-4.67638857	5.24076152	3.41760218
H	-5.40035781	7.01539561	-0.43439533
C	-5.04446618	6.27420900	1.56008920
H	-5.08945015	7.25687474	2.02126115
H	-4.57364785	2.99834852	2.36249299
C	-20.51814381	0.27766453	1.60752369
C	-20.50013639	-1.77376032	0.62800798
C	-19.17103158	-1.22453531	0.65084085
C	-17.94528921	-1.72335501	0.18910547
C	-16.75698577	-0.97848680	0.32440867
C	-15.41379934	-1.25845084	-0.05975462
C	-14.65523307	-0.13841582	0.33514672
C	-15.54444728	0.79372812	0.94724800
N	-19.24049043	0.03383322	1.26291930
N	-16.78316015	0.28542376	0.93424546
B	-18.04560032	0.99930454	1.51459289
F	-18.25513160	2.20311124	0.84947763
F	-17.88264648	1.21245279	2.88052067
C	-20.98213108	-3.08821198	0.08863258
H	-20.79006302	-3.18998659	-0.98477327
H	-20.49436132	-3.93921830	0.57560408
H	-22.06091161	-3.17890048	0.24912240
C	-15.21068873	2.12845916	1.52297485
H	-14.13512015	2.30745503	1.46175272
H	-15.74209821	2.92096702	0.98498759
H	-15.53400497	2.18389632	2.56743795

C	-14.83653099	-2.46018501	-0.74349355
H	-15.28330857	-2.62649293	-1.72946648
H	-13.75977833	-2.32253305	-0.87568636
H	-14.99580890	-3.37761168	-0.16716043
C	-20.94481197	1.53983281	2.28231188
H	-20.71210744	2.40746513	1.65561681
H	-22.01801306	1.52154451	2.48766516
H	-20.39892203	1.67568372	3.22189770
C	-17.89598715	-3.06957725	-0.45965333
C	-17.67407926	-4.21915359	0.31030750
C	-18.07338853	-3.19687033	-1.84369397
C	-17.63029307	-5.47610096	-0.29534602
C	-18.02927568	-4.45465448	-2.44753238
H	-18.24532954	-2.30792437	-2.44463275
H	-17.45694217	-6.36049632	0.31171575
H	-18.16756869	-4.54124803	-3.52183583
C	-17.80777235	-5.59639946	-1.67498020
H	-17.77307419	-6.57491302	-2.14583850
H	-17.53575709	-4.12463635	1.38400810
C	-13.26976490	0.05307603	0.17017724
C	-9.52599182	0.57837812	-0.26574286
C	-10.72983682	0.40796933	-0.12691847
C	-12.06568806	0.22016116	0.02841038
C	2.54158900	1.79857533	-1.78224582
C	-0.06894853	1.58776430	-1.44405887
C	1.13540703	1.67834157	-1.60306978
C	-1.46512437	1.48890969	-1.25571714
C	-21.31548253	-0.82293631	1.22647038
H	-22.38418504	-0.90044840	1.38099588