

Supporting information

Precise Molecular Engineering for the Preparation of Pyridinium Photosensitizers with Efficient ROS Generation and Photothermal Conversion

Weidong Yin,^a Jianqing Li,^b Yucheng Ma,^a Weiqiang Li,^a Yanping Huo,^a Zujin Zhao,^{*b} and Shaomin Ji^{*a}

Light Industry and Chemical Engineering College, Guangdong University of Technology,
Guangzhou, Guangdong 510006, China.
E-mail: smji@gdut.edu.cn

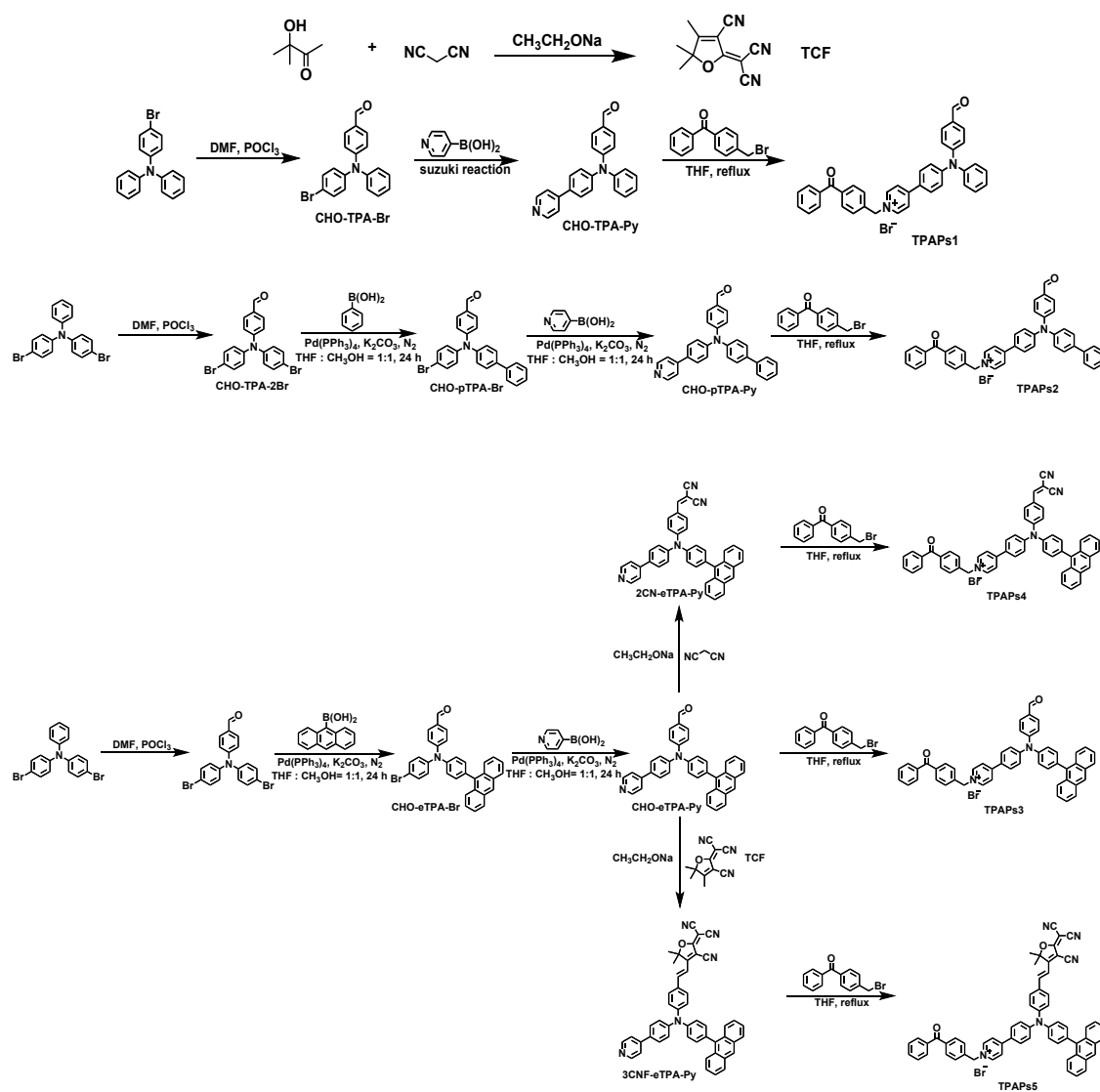
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1. General Information

Unless otherwise described, all reagents and solvents were purchased from commercial sources and used without further purification. All the samples were prepared according to the standard methods. For UV and fluorescence spectral data, each data was measured three times and the average value is taken.

2. Experimental Details



Scheme S1. Synthetic routes of TCF, TPAPs1, TPAPs2, TPAPs3, TPAPs4 and TPAPs5.

3. ^1H and ^{13}C NMR Spectra

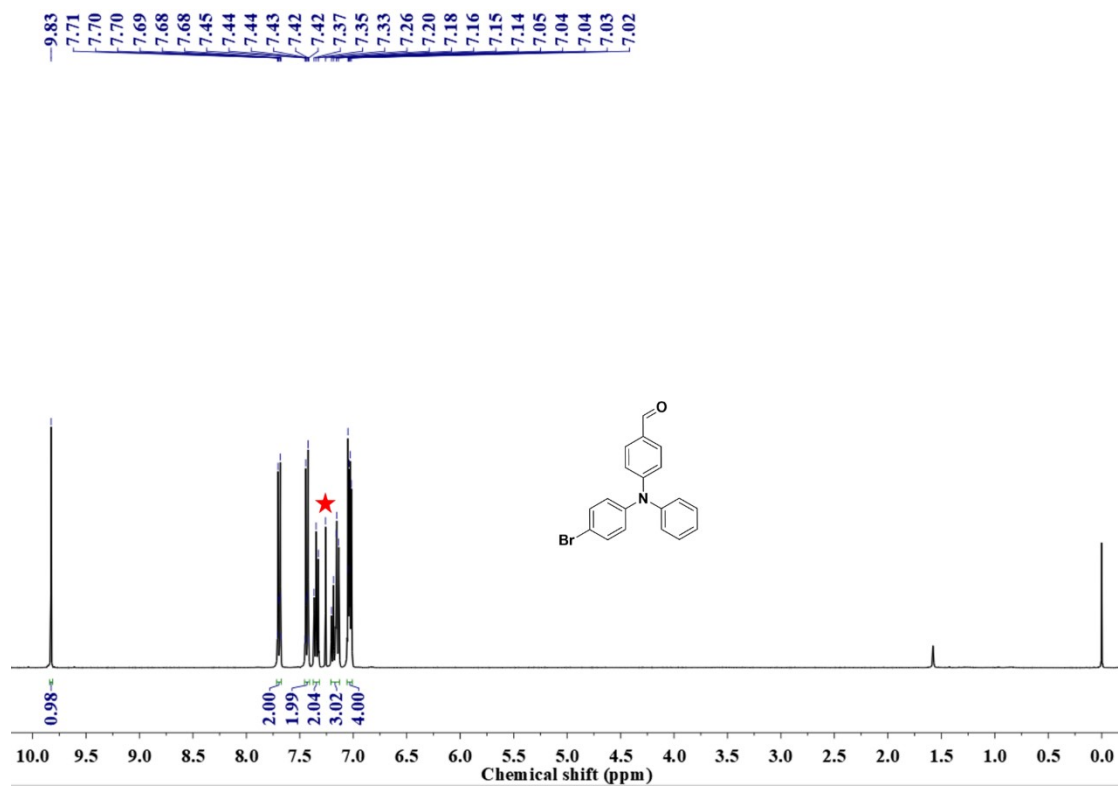


Figure S1. ^1H NMR spectrum of CHO-TPA-Br in CDCl_3 .

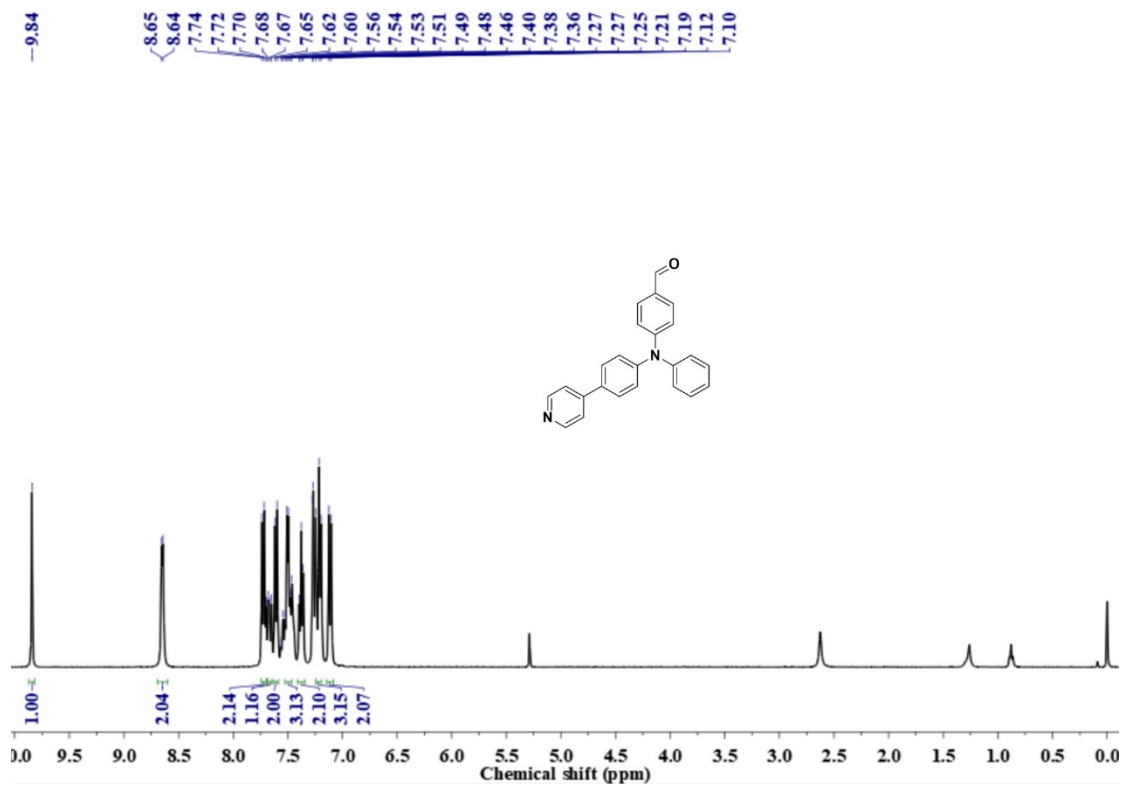


Figure S2. ^1H NMR spectrum of CHO-TPA-Py in CDCl_3 .

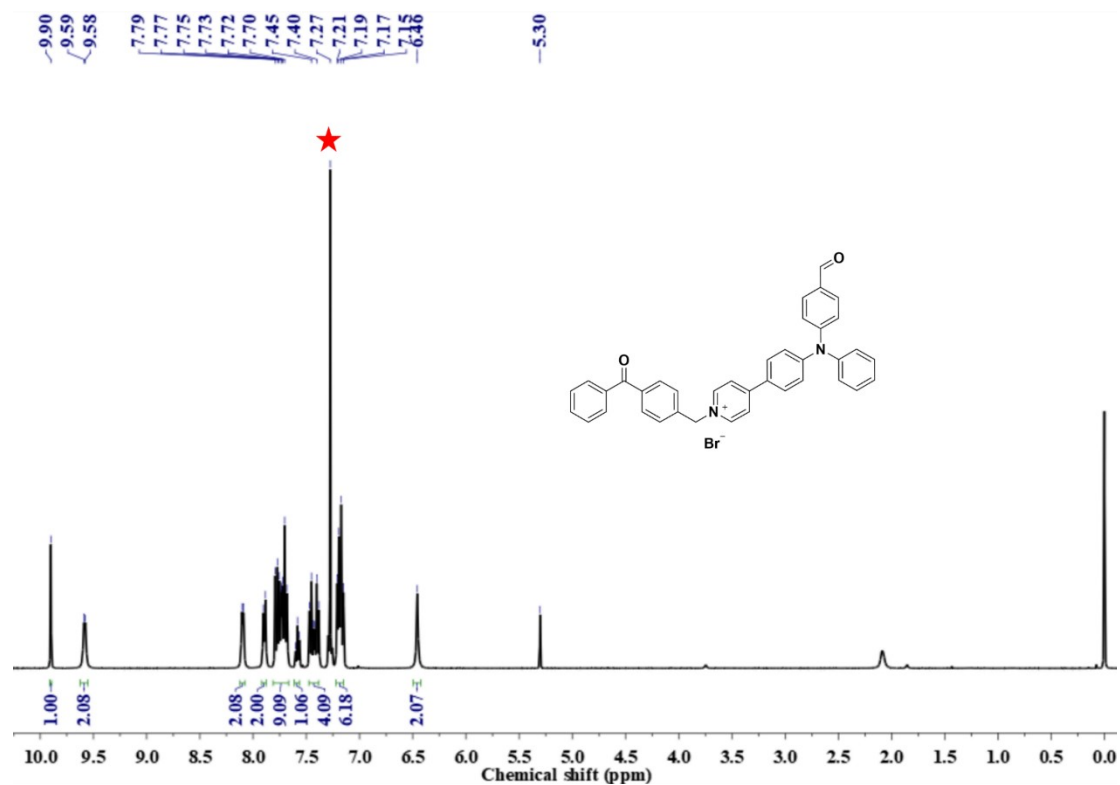


Figure S3. ^1H NMR spectrum of TPAPs1 in CDCl_3 .

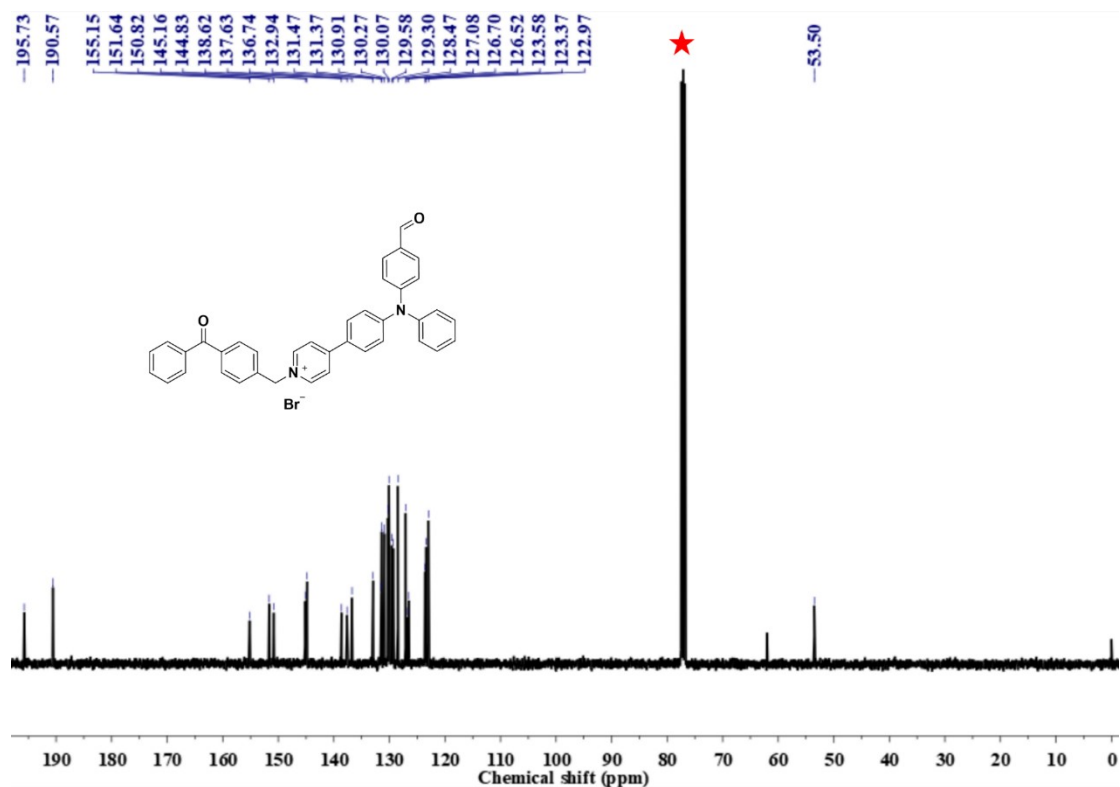


Figure S4. ^{13}C NMR spectrum of TPAPs1 in CDCl_3 .

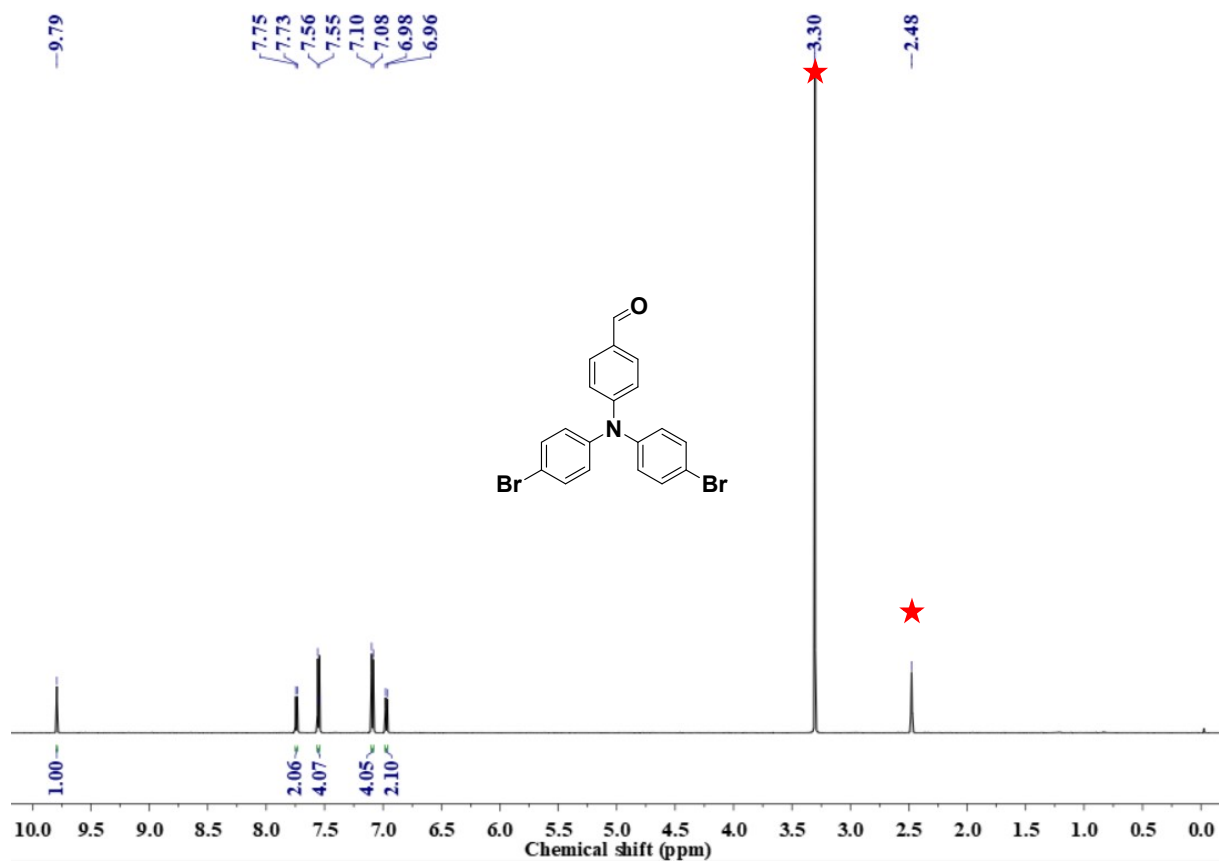


Figure S5. ^1H NMR spectrum of CHO-TPA-2Br in $\text{DMSO-}d_6$.

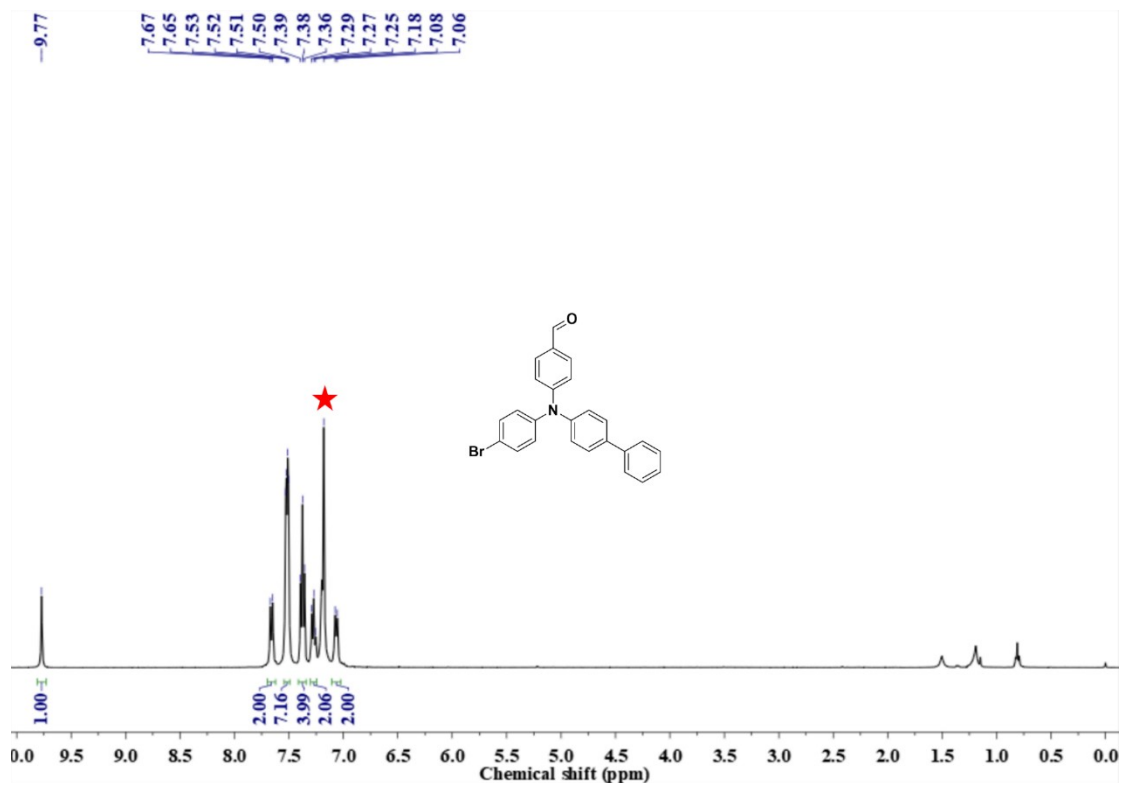


Figure S6. ^1H NMR spectrum of CHO-pTPA-Br in CDCl_3 .

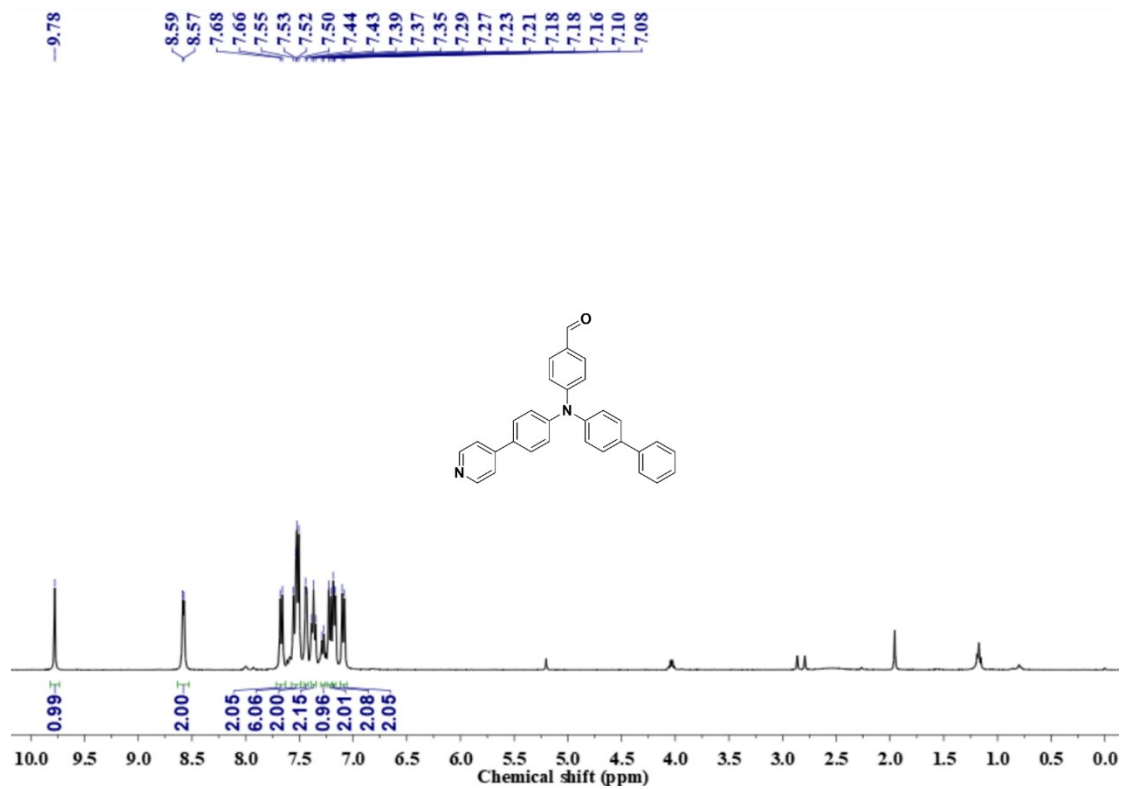


Figure S7. ^1H NMR spectrum of CHO-pTPA-Py in CDCl_3 .

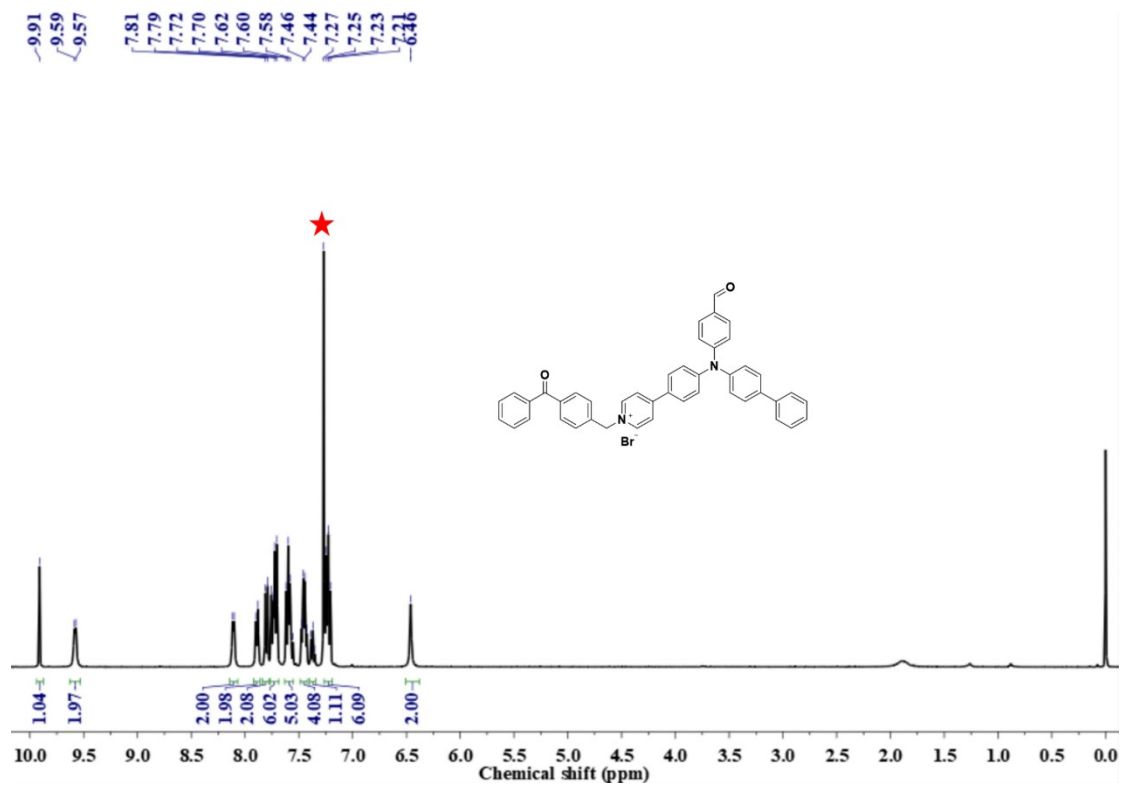


Figure S8. ^1H NMR spectrum of TPAPs2 in CDCl_3 .

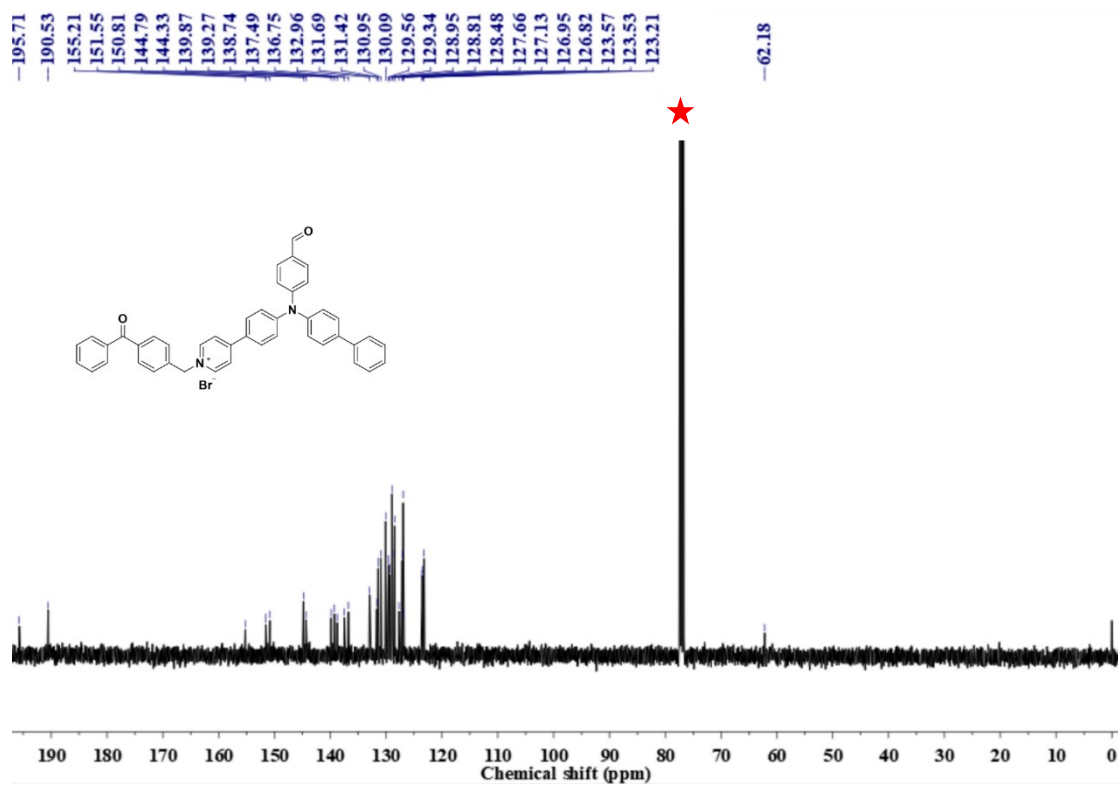


Figure S9. ¹³C NMR spectrum of TPAPs2 in CDCl₃.

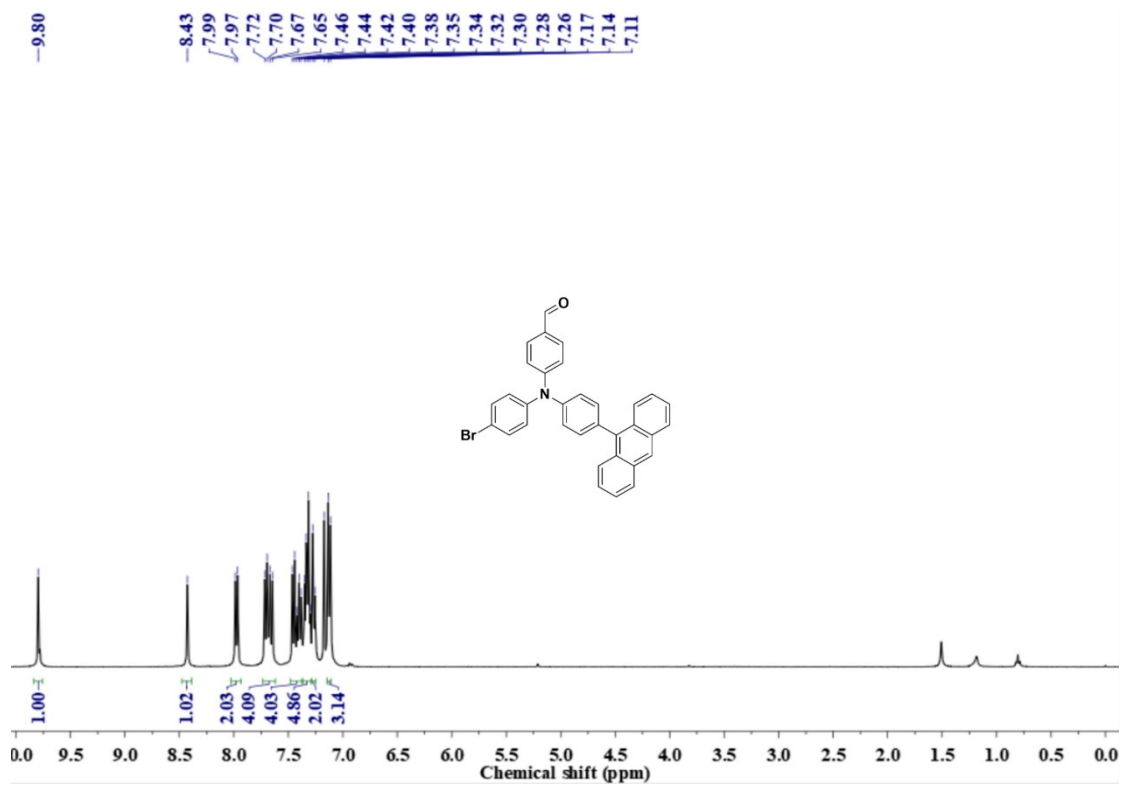


Figure S10. ¹H NMR spectrum of CHO-eTPA-Br in CDCl₃.

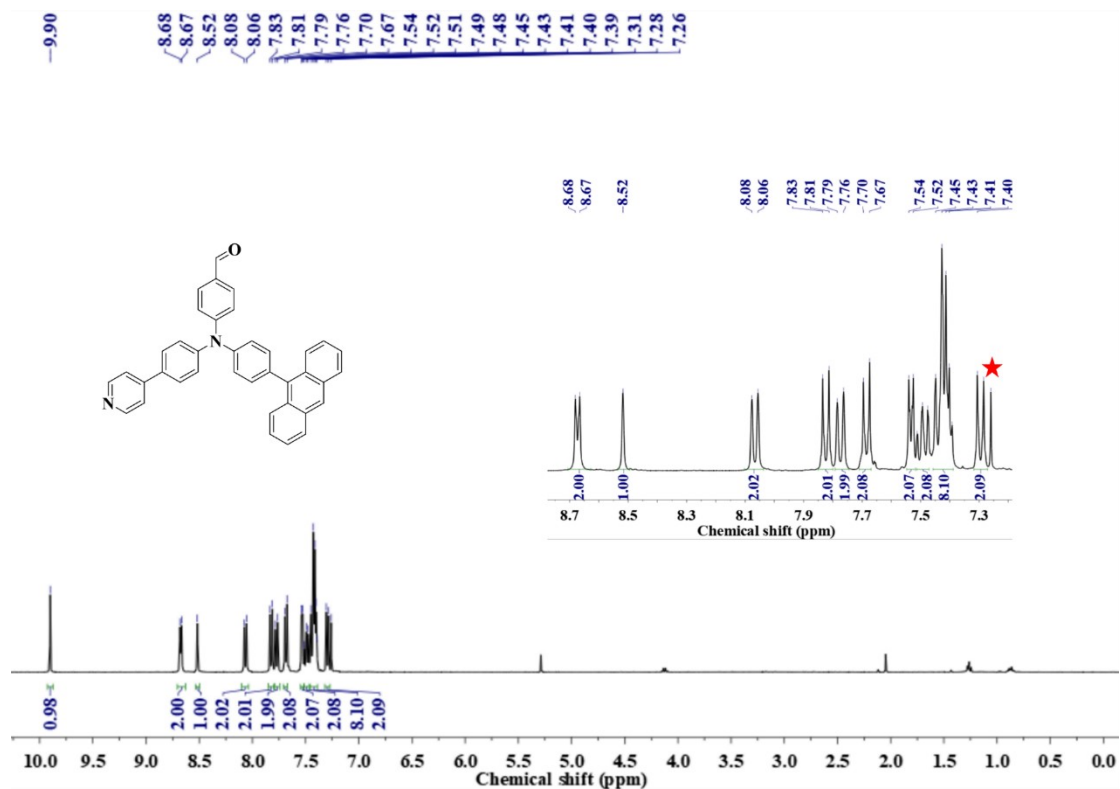


Figure S11. ¹H NMR spectrum of CHO-eTPA-Py in CDCl₃.

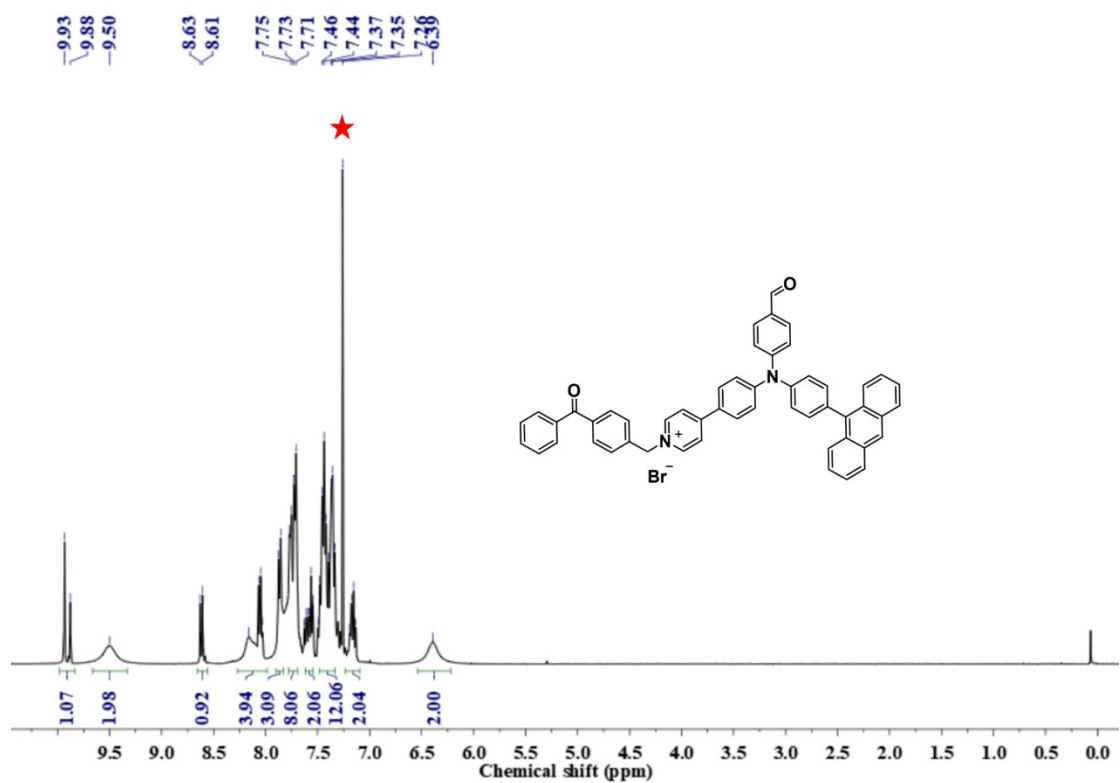


Figure S12. ¹H NMR spectrum of TPAPs3 in CDCl₃.

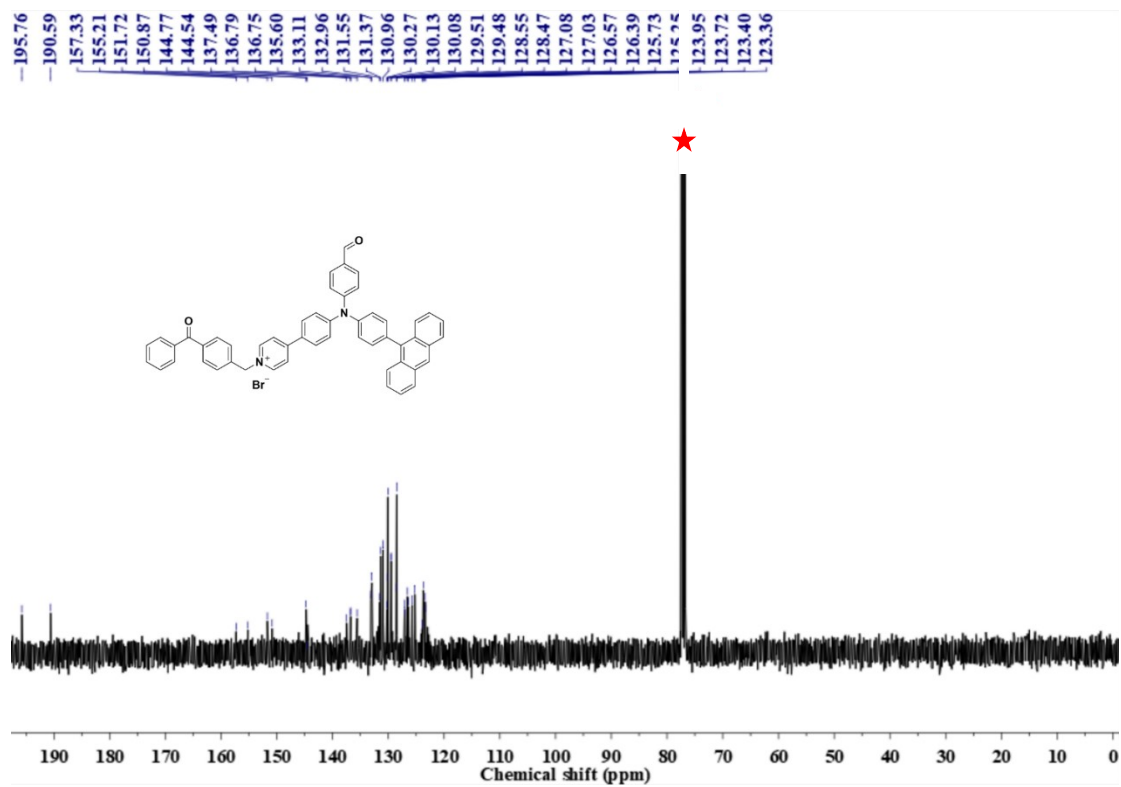


Figure S13. ^{13}C NMR spectrum of TPAPs3 in CDCl_3 .

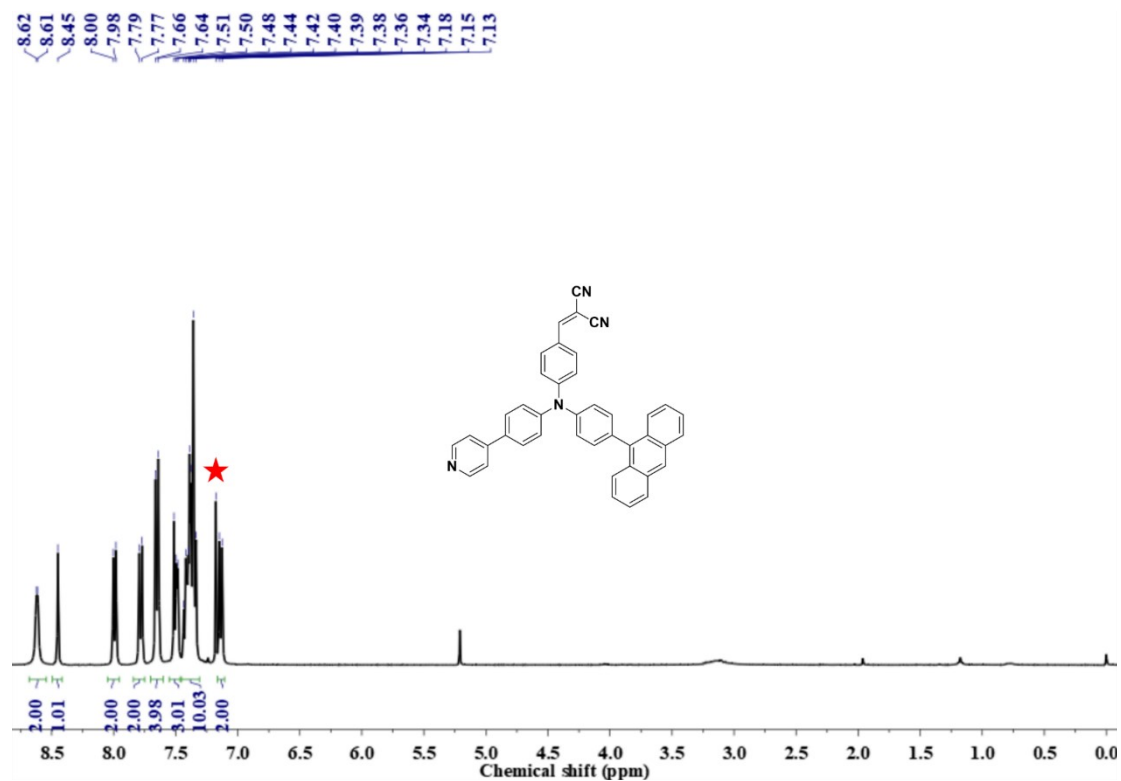


Figure S14. ^{13}C NMR spectrum of 2CN-eTPA-Py in CDCl_3 .

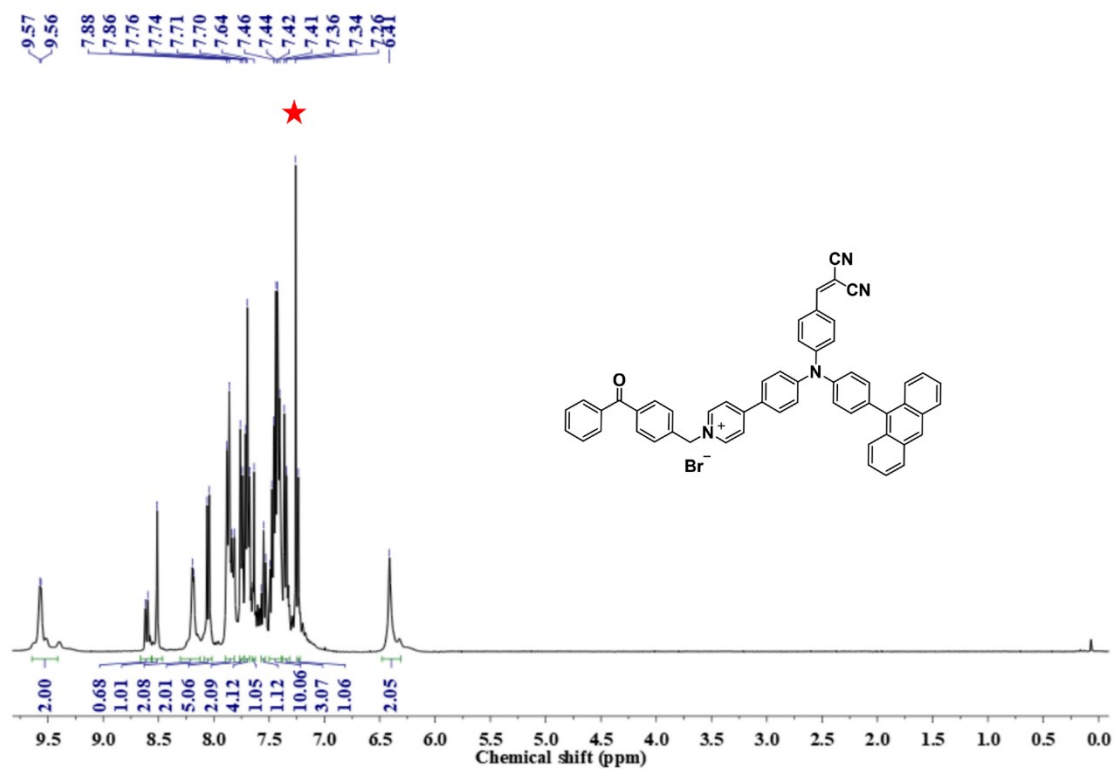


Figure S15. ¹H NMR spectrum of TPAPs4 in CDCl₃.

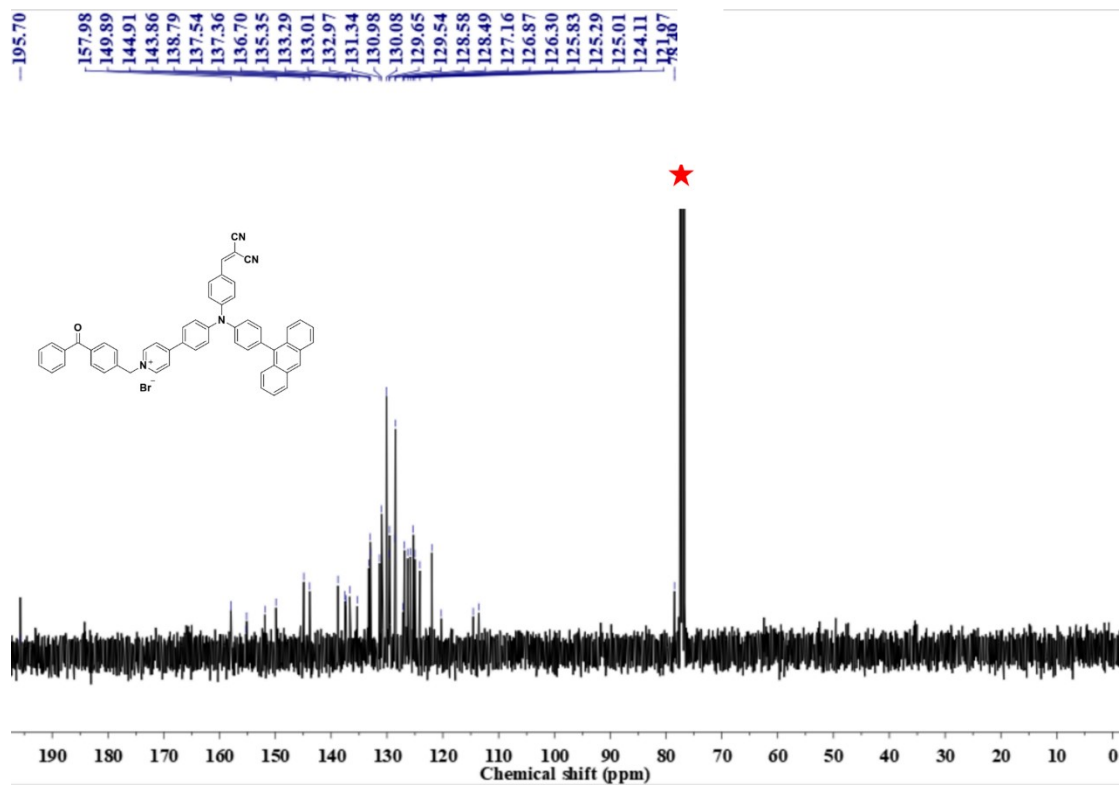


Figure S16. ¹³C NMR spectrum of TPAPs4 in CDCl₃.

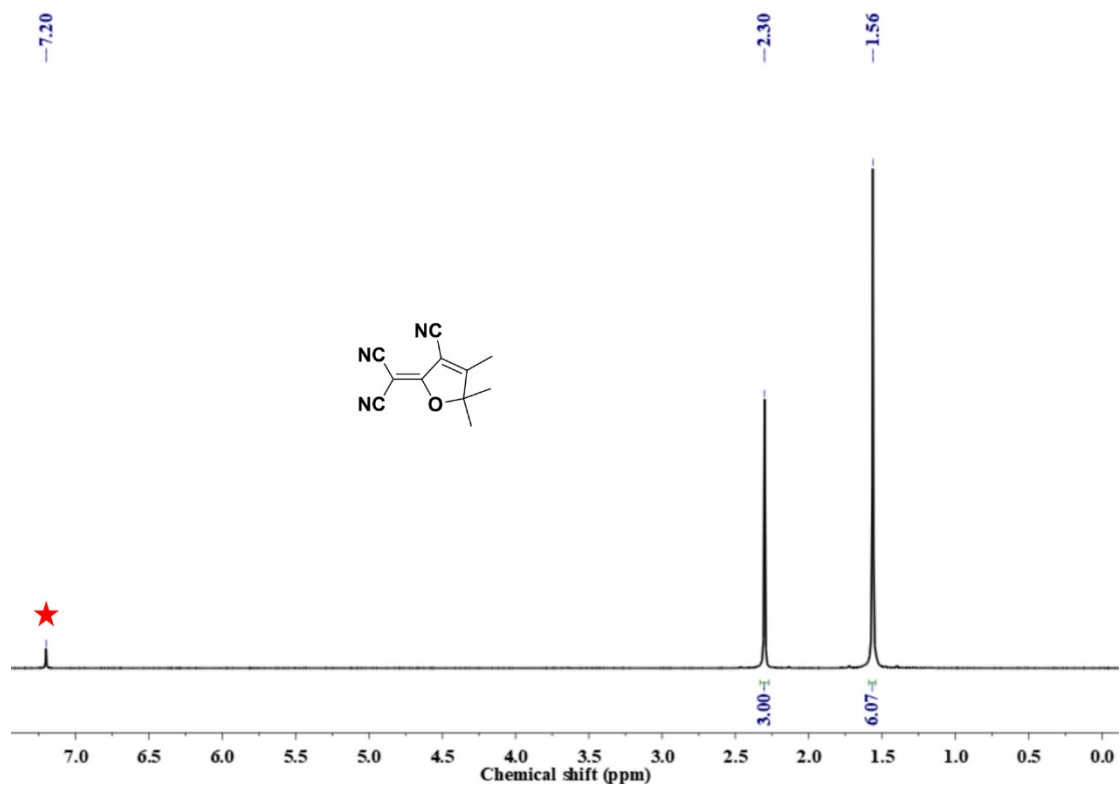


Figure S17. ^1H NMR spectrum of the TCF in CDCl_3 .

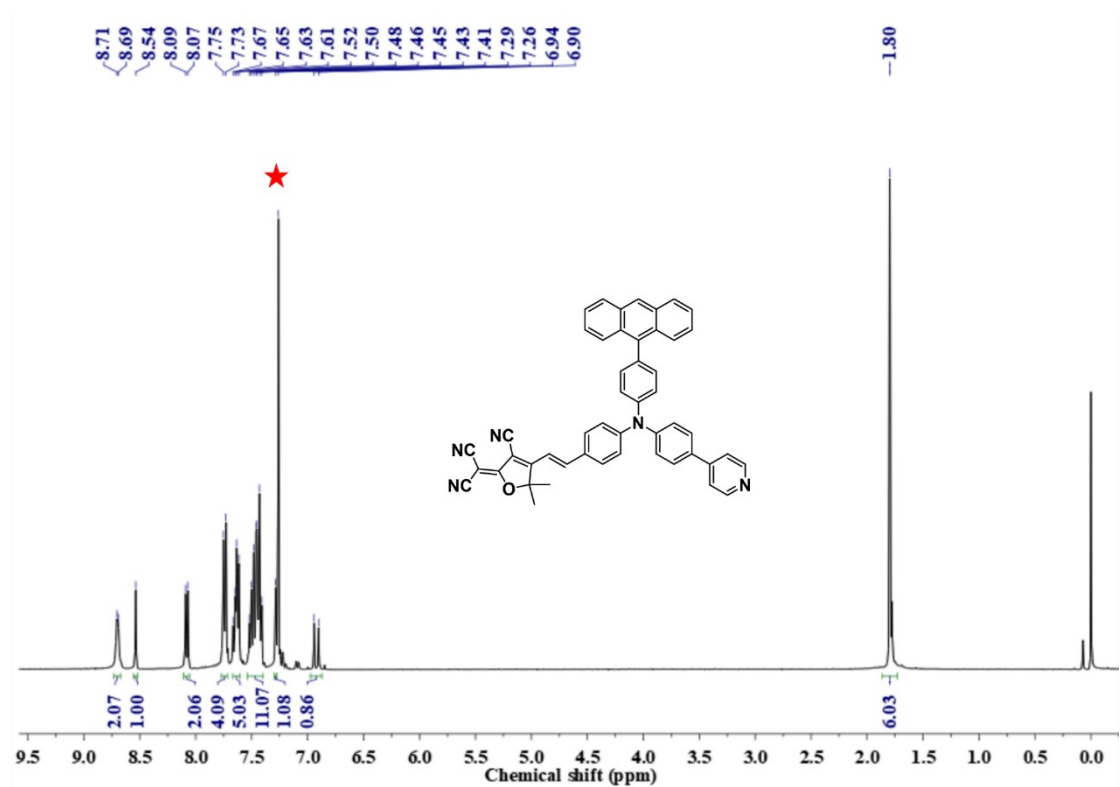


Figure S18. ^1H NMR spectrum of 3CNF-eTPA-Py in CDCl_3 .

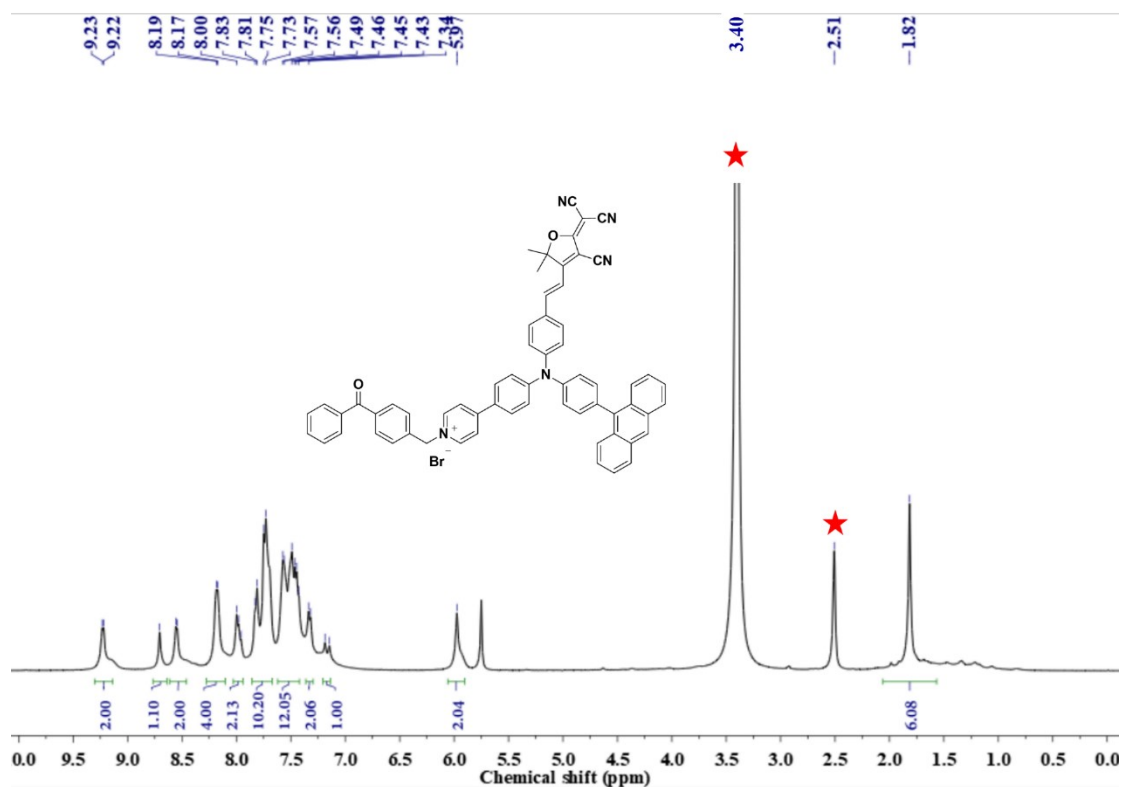


Figure S19. ¹H NMR spectrum of TPAPs5 in DMSO-*d*₆.

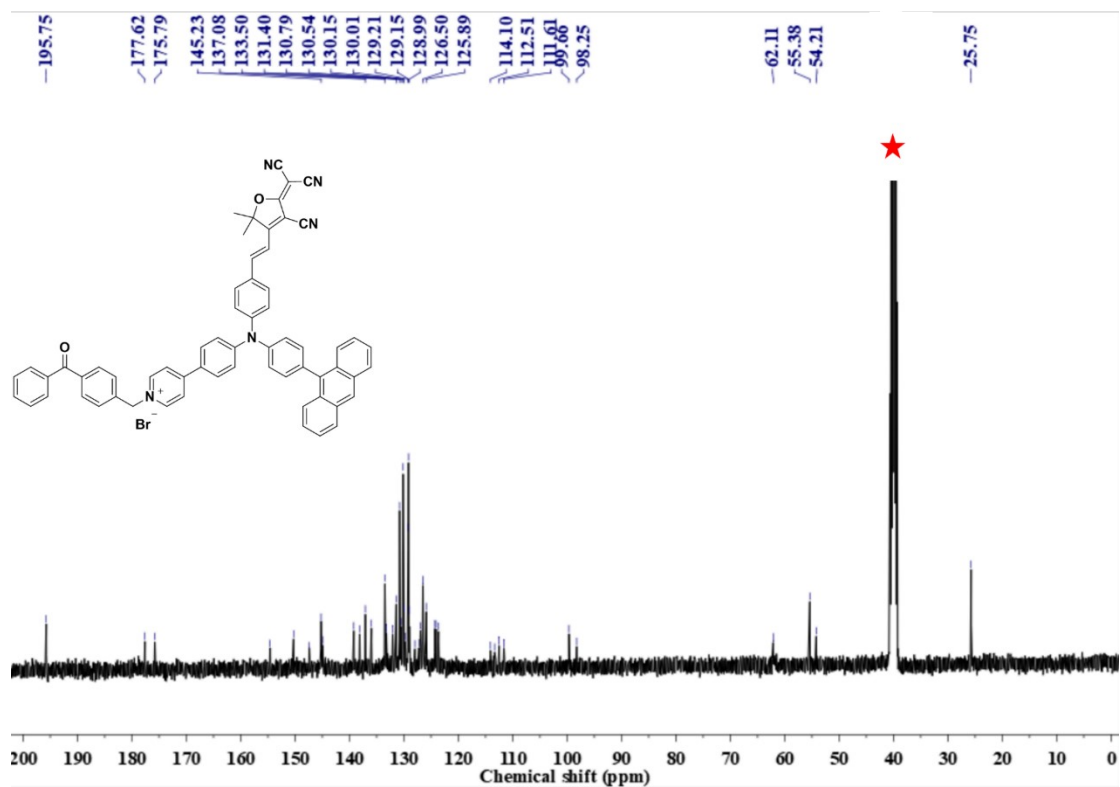
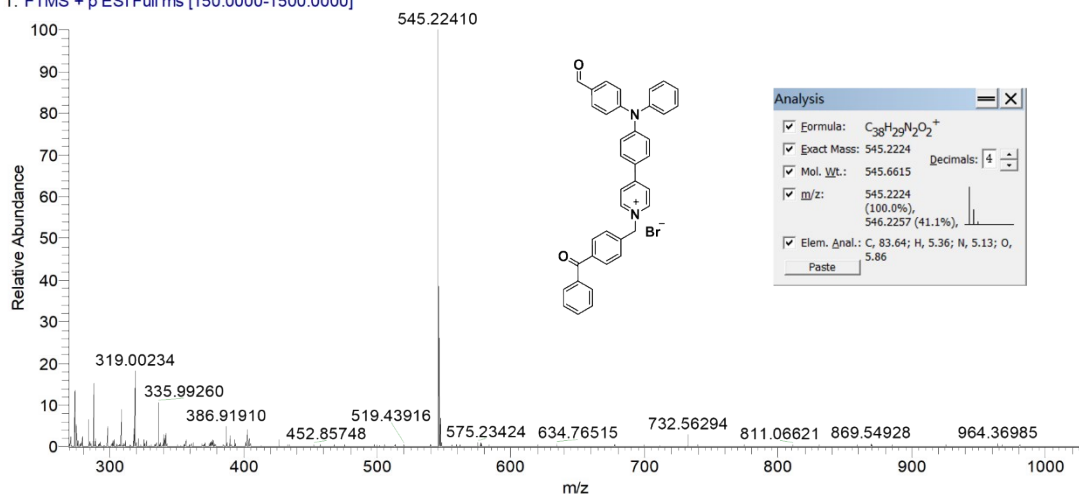
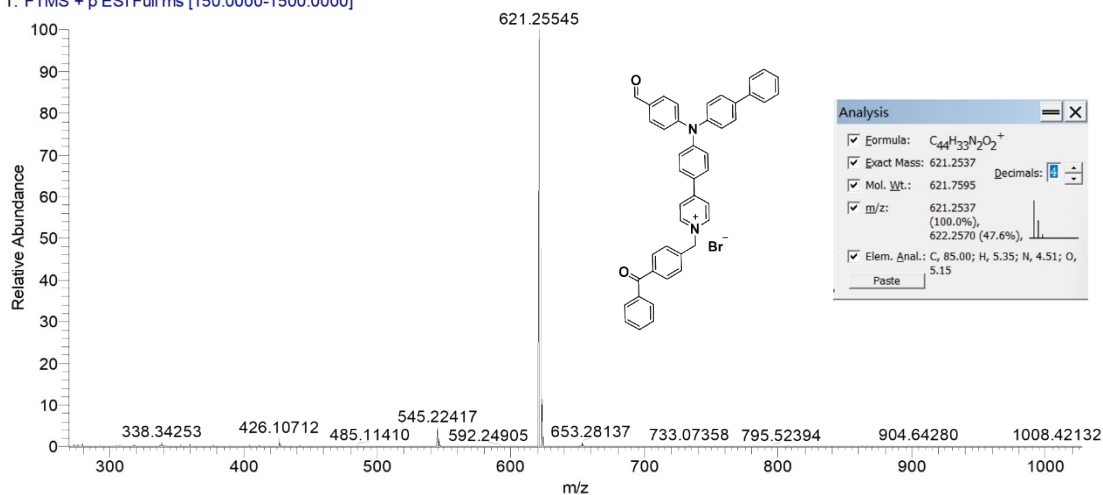


Figure S20. ¹³C NMR spectrum of TPAPs5 in DMSO-*d*₆.

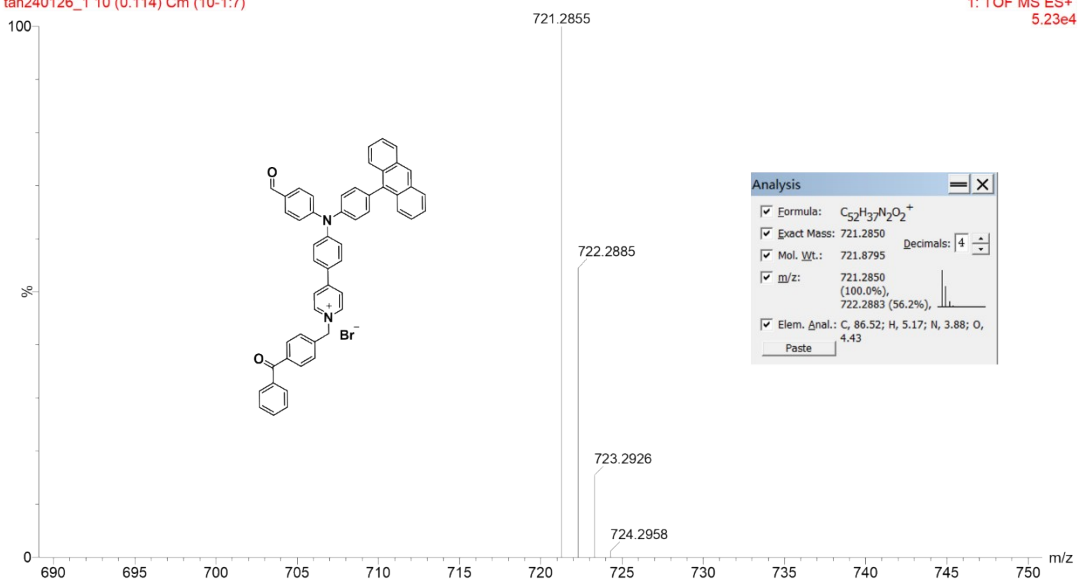
12 #17 RT: 0.16 AV: 1 SB: 1 0.02 NL: 6.12E6
T: FTMS + p ESI Full ms [150.0000-1500.0000]



13 #5 RT: 0.04 AV: 1 SB: 1 0.02 NL: 1.09E7
T: FTMS + p ESI Full ms [150.0000-1500.0000]



ywd-14; MW=721
tan240126_1 10 (0.114) Cm (10-1:7)



ywd-15; MW=769
tan240126_2_53 (0.506) Cm (53-1:7)

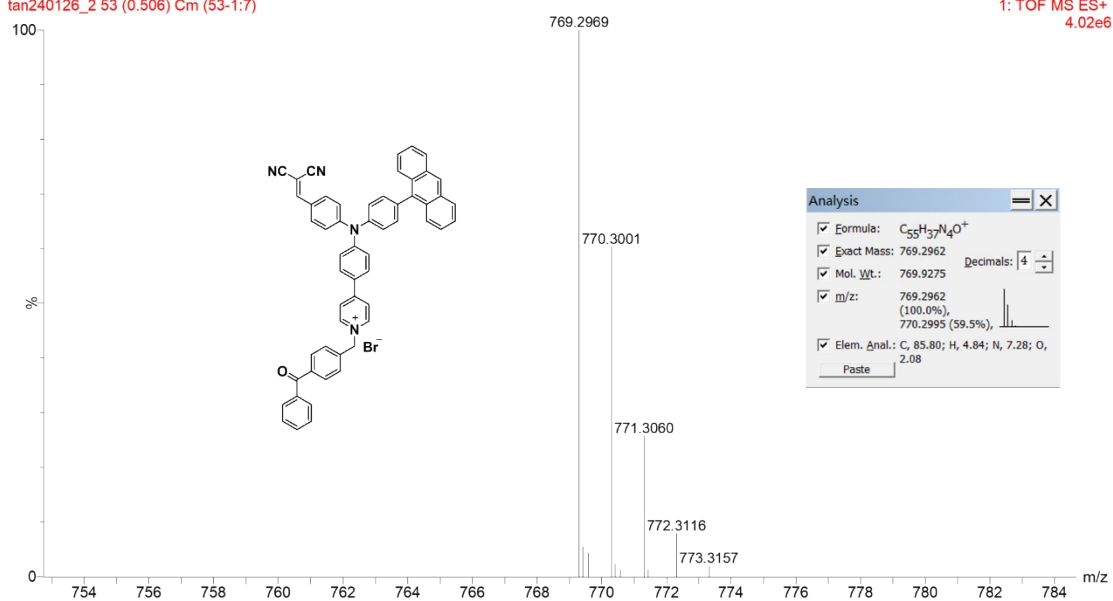


Figure S24. HRMS spectrum of TPAPs4.

ywd-16; MW=902
tan240126_3_67 (0.637) Cm (67-1:7)

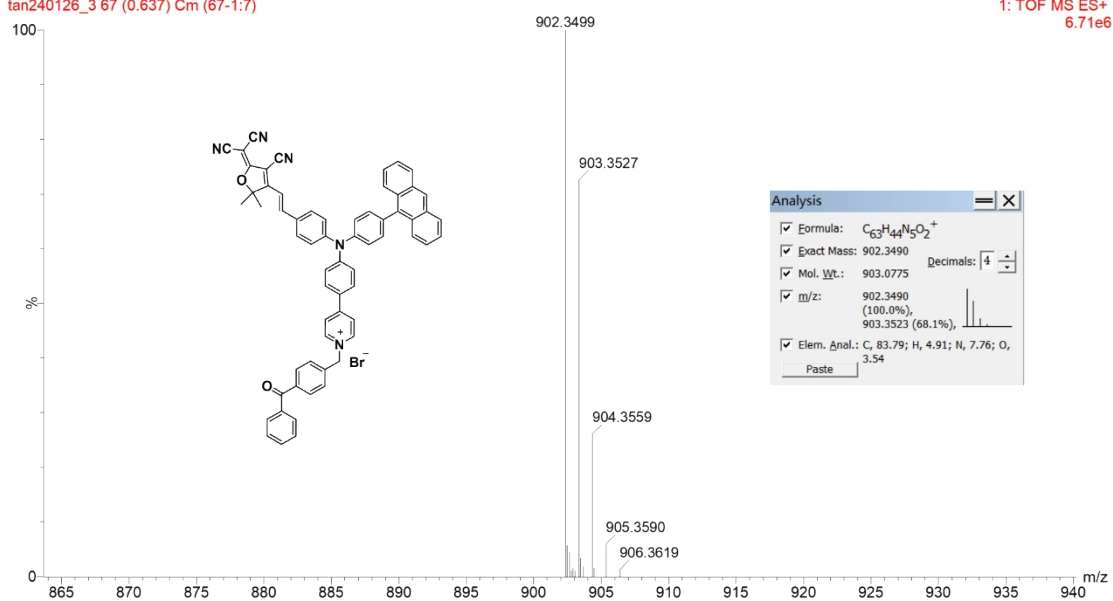


Figure S25. HRMS spectrum of TPAPs5.

4 Photophysical Properties

Table S1. Calculated energy of the singlet (S) and triplet (T) excited states

Compounds	TPAPs1	TPAPs2	TPAPs3	TPAPs4	TPAPs5
S ₁	3.0048	2.9442	2.7562	2.6565	2.7395
S ₂	3.7954	3.7964	2.9902	2.9407	2.8841
S ₃	3.8293	3.8281	3.5815	3.5707	3.4187
T ₁	2.0282	1.9969	1.6778	1.6787	1.6303
T ₂	3.0460	3.0460	2.0184	2.0271	1.6770
T ₃	3.0665	3.0470	2.7674	2.2566	2.0479
T ₄	3.2326	3.1622	3.0461	2.6643	2.6587
T ₅	3.3865	3.2328	3.0662	3.0434	2.7617
T ₆	3.4620	3.3880	3.2564	3.2842	3.0440

Table S2. Photophysical properties of the compounds

Compounds	λ_{abs} (nm)	λ_{em} (nm)	Φ	ϵ (M ⁻¹ cm ⁻¹)	τ (ns)		$\Delta E_{\text{L-H}}$ (eV)
					τ_1	τ_2	
TPAPs1	425	522	40.53	31962	0.55	2.97	4.792
TPAPs2	428	545	26.47	30162	0.39	2.21	4.602
TPAPs3	427	613	30.57	32787	0.68	3.54	3.623
TPAPs4	456	630	10.23	35314	0.45	2.87	3.517
TPAPs5	530	715	0.45	30628	0.40	1.97	3.614

Table S3. Simulated recombination energy of the compounds

	TPAPs1	TPAPs2	TPAPs3	TPAPs4	TPAPs5
E1	-1724.720357	-1955.696028	-2262.796848	-2411.292794	-2850.185607
E2	-1724.609930	-1955.587828	-2262.756707	-2411.256563	-2850.155863
E3	-1724.582138	-1955.559025	-2262.723872	-2411.220435	-2850.112022
E4	-1724.698083	-1955.659195	-2262.766675	-2411.265228	-2850.153745
ΔE_{x}	0.027792	0.028803	0.032835	0.036128	0.043841
	0.75622032 eV	0.78372963 eV	0.89344035 eV	0.98304288 eV	1.19291361 eV
ΔE_{y}	0.022274	0.036833	0.030173	0.027566	0.031862
	0.60607554 eV	1.00222593 eV	0.82100733 eV	0.75007086 eV	0.86696502 eV
Er	1.3623 eV	1.7859 eV	1.7144 eV	1.7331 eV	2.0598 eV

5 AIE Properties

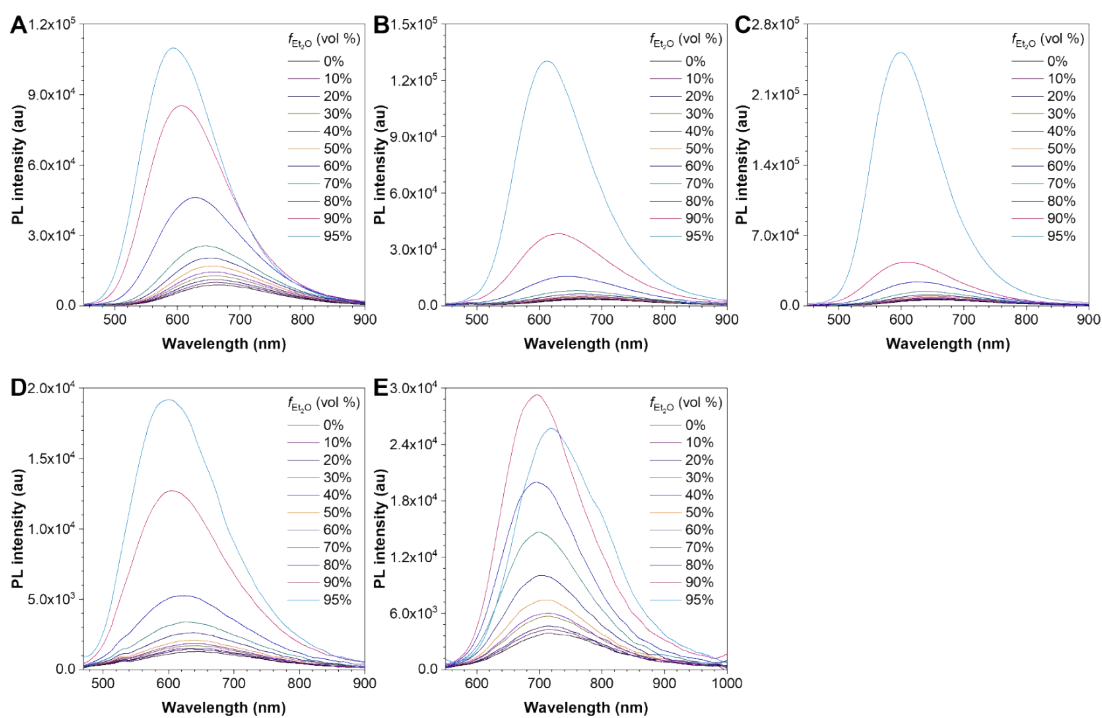


Figure S26. PL spectra of (A) TPAPs1, (B) TPAPs2, (C) TPAPs3, (D) TPAPs4 and (E) TPAPs5 in acetonitrile/diethyl ether mixture with different diethyl ether fractions (0-95%).

6 Solvation Effect

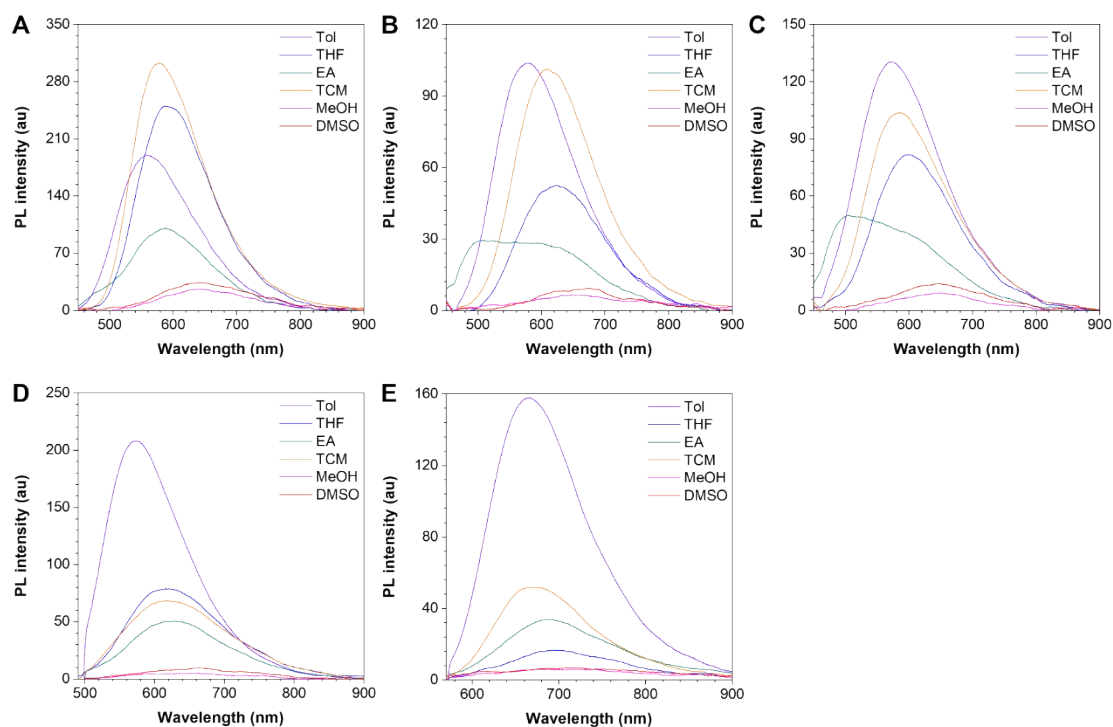


Figure S27. PL spectra of (A) TPAPs1, (B) TPAPs2, (C) TPAPs3, (D) TPAPs4 and (E) TPAPs5 in different solvents.

7 ROS Generation

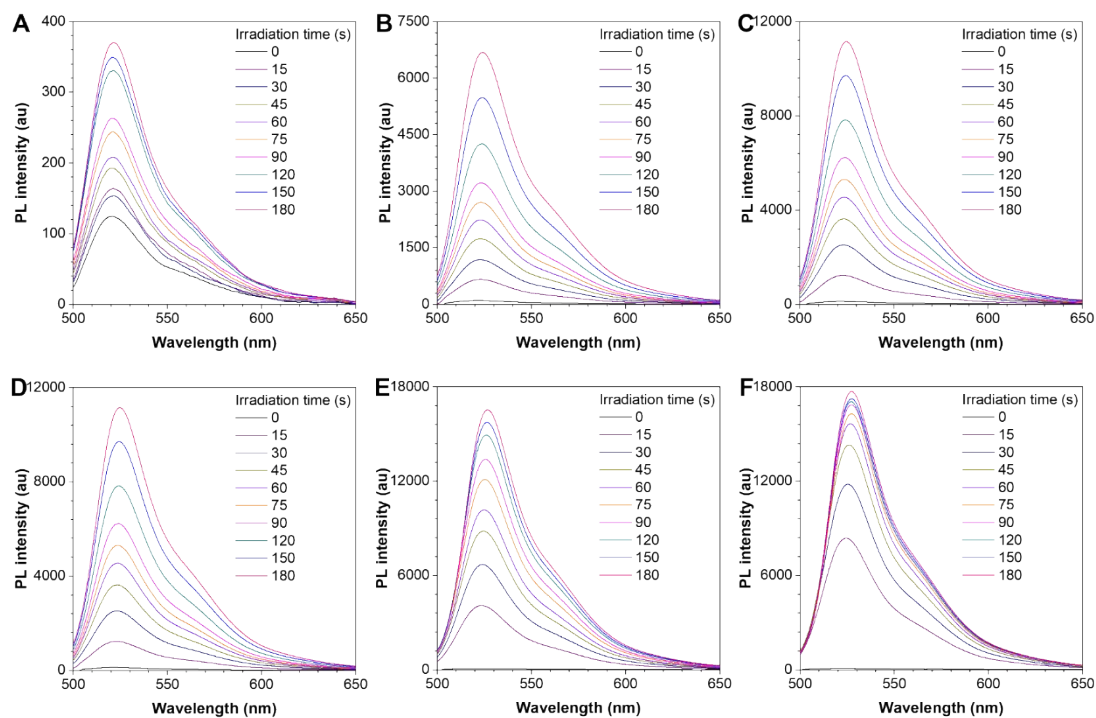


Figure S28. ROS generation of (A) DCFH, (B) TPAPs1, (C) TPAPs2, (D) TPAPs3, (E) TPAPs4 and (F) TPAPs5 upon exposure to white light using DCFH (10 μ M) as an indicator.

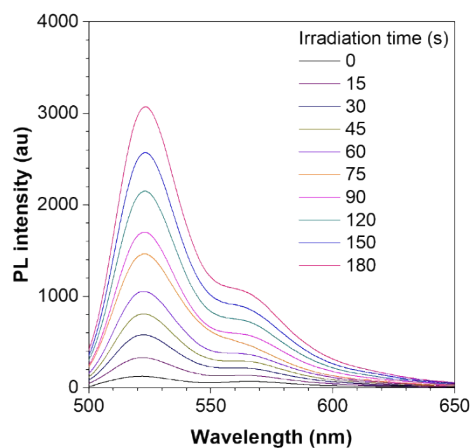


Figure S29. (A) ROS generation of RB (1 μ M) upon exposure to white light using DCFH (10 μ M) as an indicator.

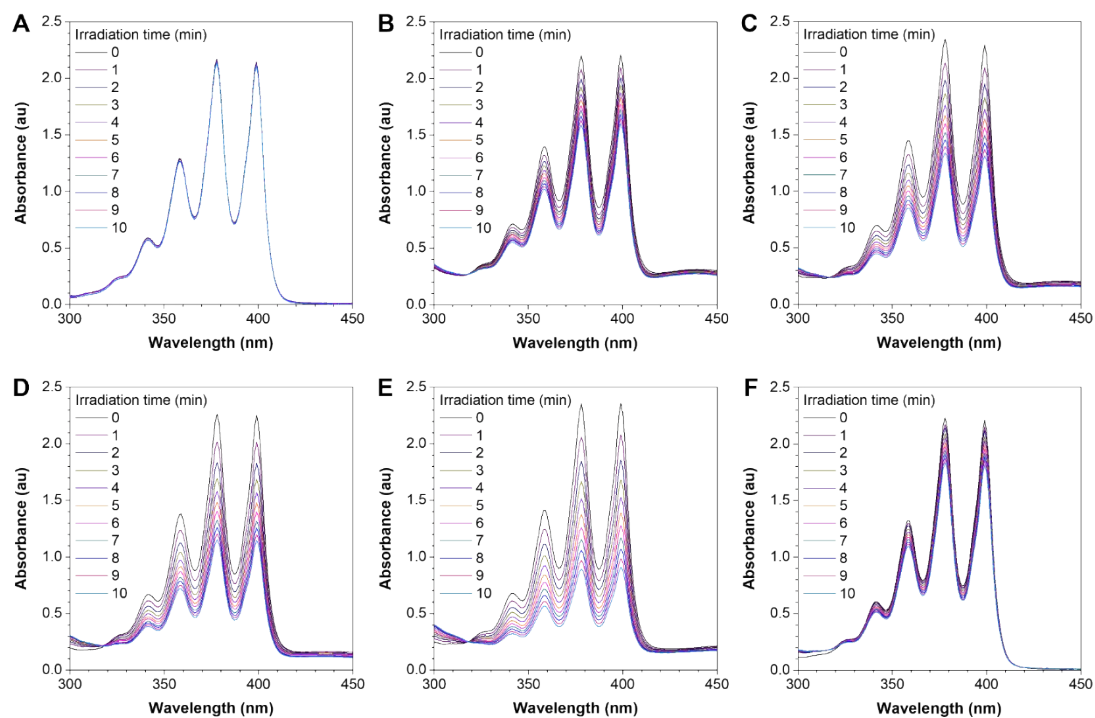


Figure S30. Absorption of ABDA (200 μM , $^1\text{O}_2$ probe) in water in the absence (black, A) and presence of (B) TPAPs1, (C) TPAPs2, (D) TPAPs3, (E) TPAPs4 and (F) RB (10 μM) under white light irradiation for different time.

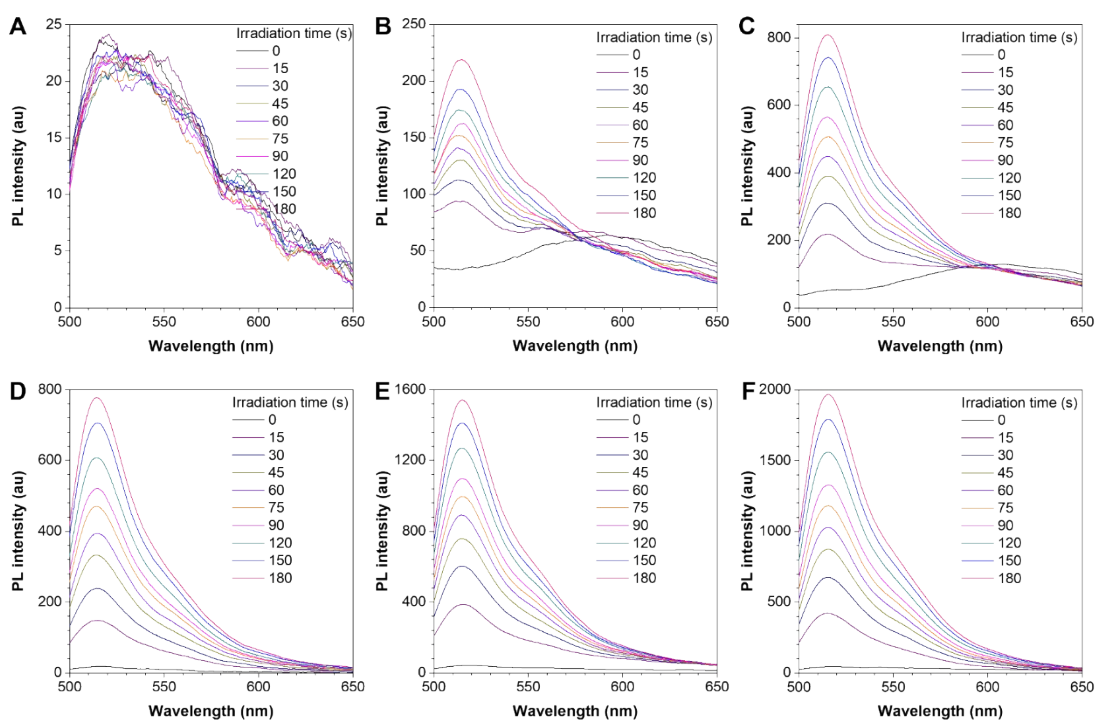


Figure S31. PL spectra of HPF (5 μM , $\text{OH}\cdot$ probe) in the absence (black, A) and presence of (B) TPAPs1, (C) TPAPs2, (D) TPAPs3, (E) TPAPs4 and (F) TPAPs5 (1 μM) in PBS upon white light irradiation with 10 mW/cm^2 for different time.

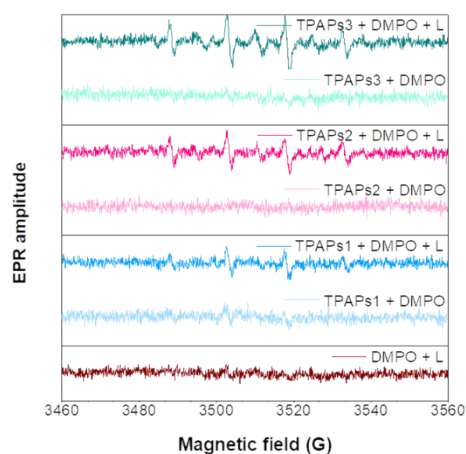


Figure S32. EPR signals of DMPO (10 μL) in the presence TPAPs1, TPAPs2 and TPAPs3 in H_2O with/without white light irradiation (10 mW/cm^2) for 5 min.

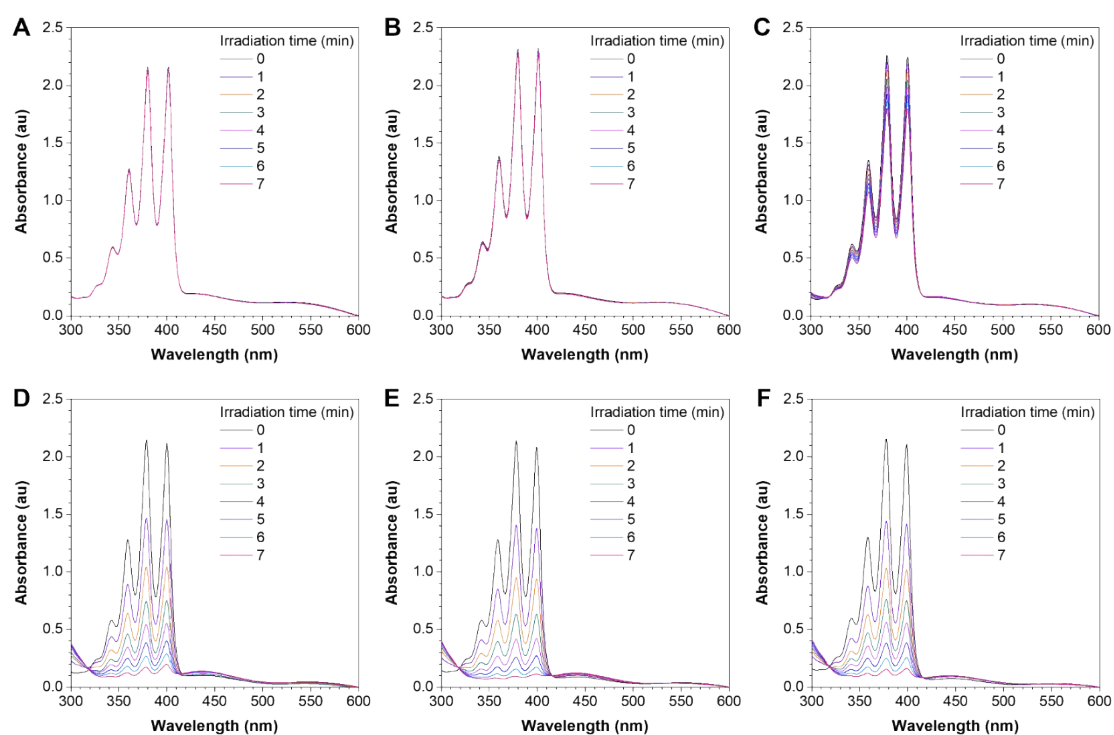


Figure S33. Absorption spectra of ABDA (200 μM , $^1\text{O}_2$ probe) in the presence of TPAPs5 (10 μM) in DMSO/ H_2O mixture with different H_2O fractions (0%, 20%, 40%, 60%, 80% and 95%) upon white-light irradiation (25 mW/cm^2).

8 Photothermal Conversion

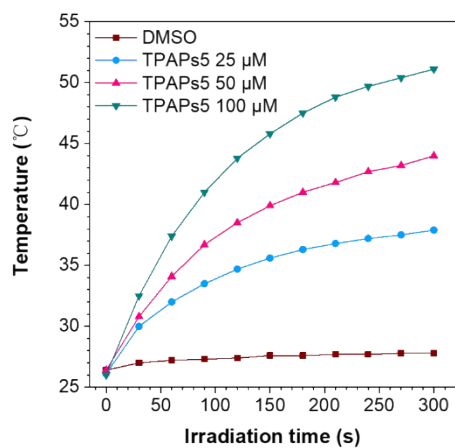


Figure S34. Corresponding heating curves of different concentration of TPAPs5 in DMSO solution (25, 50, 100 μM) under 532 nm (0.3 W/cm^2) laser irradiation.

9 Cell Imaging and Cell Viability

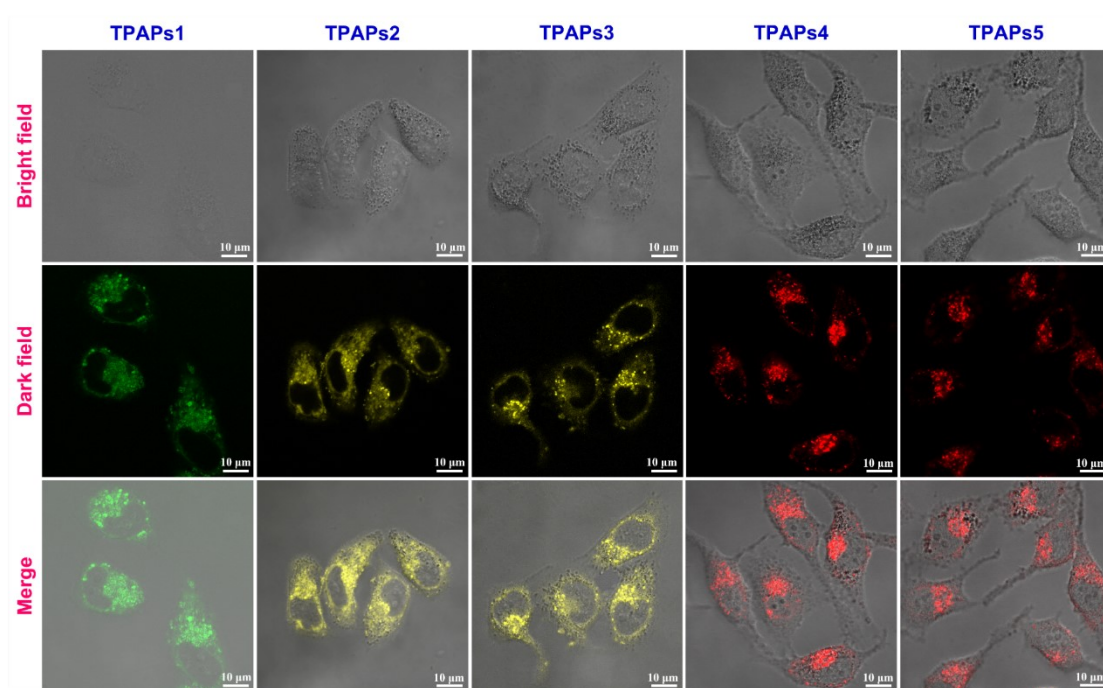


Figure S35. Fluorescence images of HeLa cells stained with 10 μM TPAPs1, TPAPs2, TPAPs3, TPAPs4 and TPAPs5 for 0.5 h, respectively.

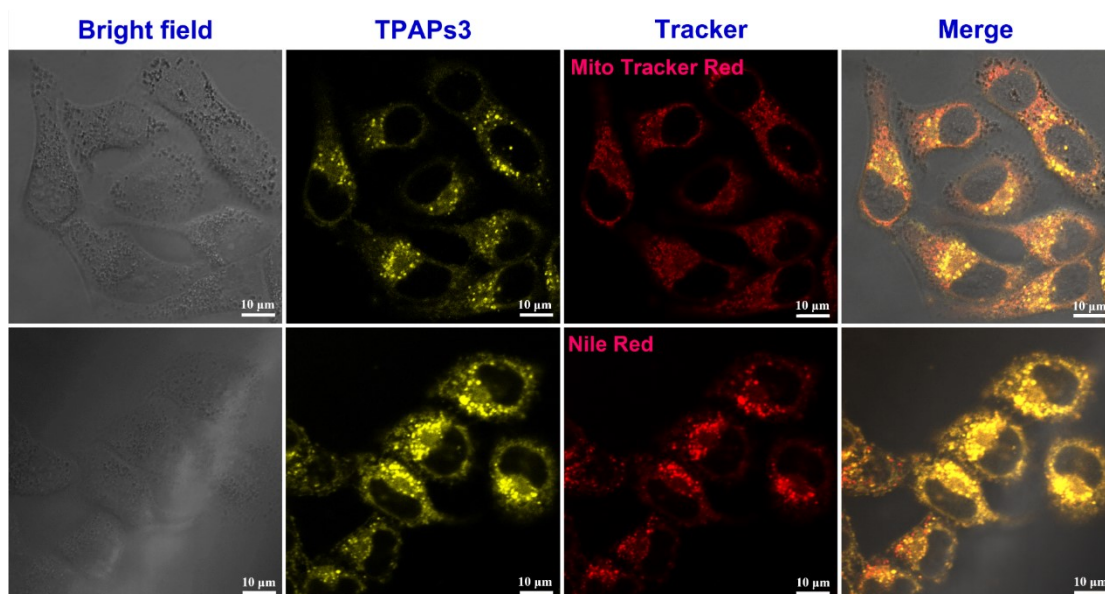


Figure S36. CLSM images of HeLa cells co-stained with TPAPs3 (conc.: 10 μ M; incubation time: 0.5 h) and Mito-Tracker Red and Nile red (conc.: 1 μ M; incubation time: 0.5 h).

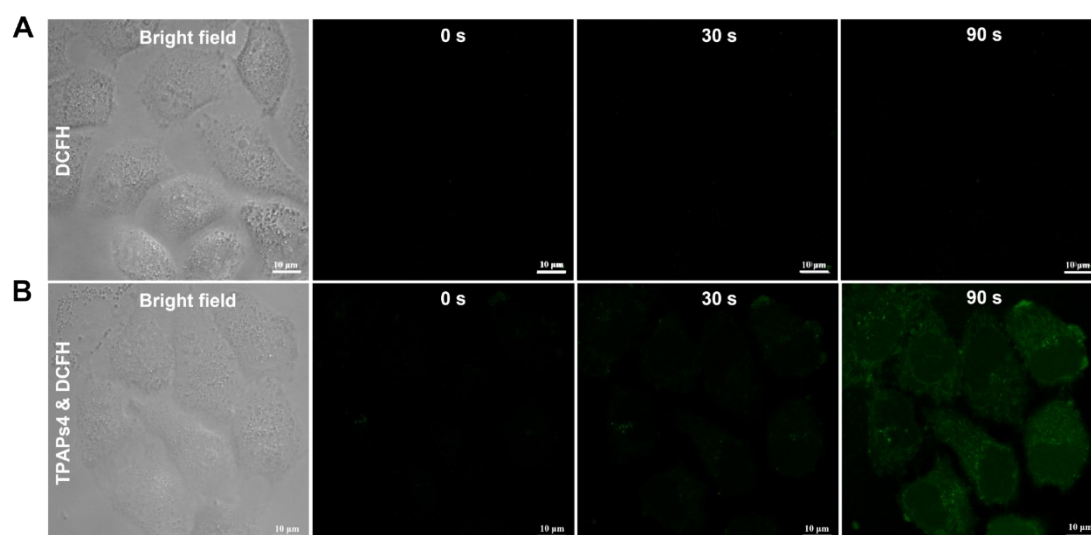


Figure S37. Intracellular ROS generation of (A) PBS and (B) TPAPs4 (conc.: 5 μ M, incubation time: 0.5 h) were evaluated by DCFH-DA upon white light irradiation (microscope) for different time.

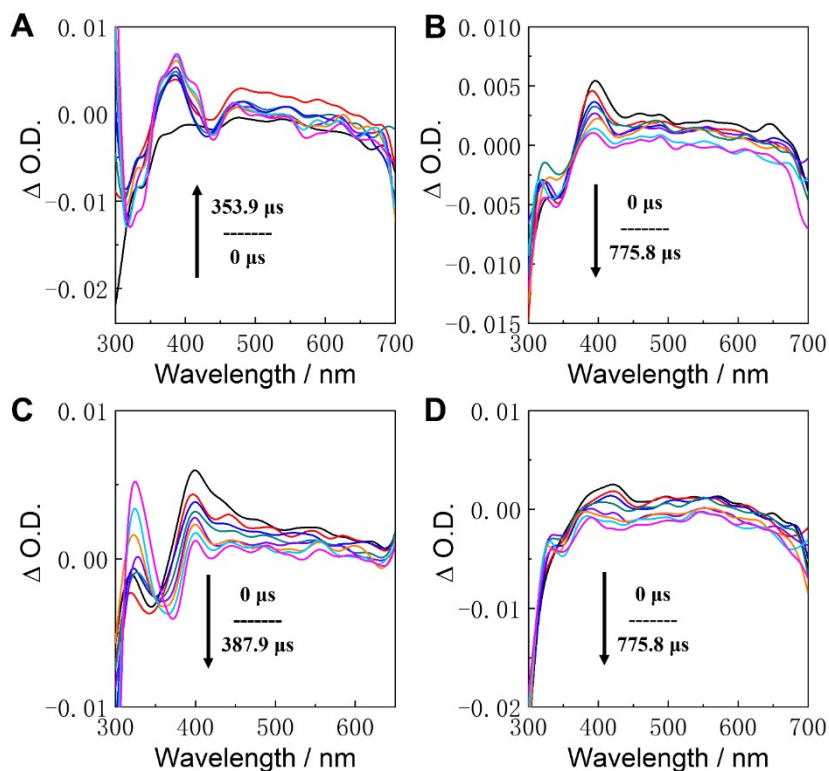


Figure S38. Nanosecond transient absorption spectra of (A) TPAPs1, (B) TPAPs2, (C) TPAPs3 and (D) TPAPs4 in different time, conditions: $c = 1 \times 10^{-5}$ M, in DMSO, N_2 , 298K.

Table S4. Cartesian coordinates of optimized TPAPs1 calculated by the DFT, CAM-B3LYP/6-311G(d), Gaussian 09 program

atom	x	y	z
C	8.20505512	-1.73199197	0.09897306
C	9.44819466	-2.31359233	0.34882596
C	9.52989677	-3.53790250	0.98748853
C	8.36951034	-4.20600205	1.35938945
C	-6.44100265	1.03558690	0.28139102
C	-7.27029436	0.81815414	1.37442412
C	-8.34789647	1.66185706	1.59840150
C	-8.59385482	2.72415517	0.73972515
C	-7.76275592	2.93853181	-0.35140740
C	-6.68983851	2.09228332	-0.58724588
H	-7.07237509	-0.01294827	2.04006911
H	-8.99529567	1.48978942	2.44918448
H	-9.43566660	3.38150017	0.91753223
H	-7.95754839	3.75987442	-1.02982963
H	-6.04491840	2.24487920	-1.44432548
C	-4.04637999	0.60581261	0.02224191
C	-3.00895200	-0.13453770	-0.58047084
C	-1.72230950	0.34189911	-0.59563708

C	-1.37714131	1.56821870	-0.00265761
C	-2.41682489	2.29850315	0.59771990
C	-3.71202883	1.84533804	0.60454496
H	-3.22916386	-1.08466430	-1.04492848
H	-0.96350107	-0.27355420	-1.06183131
H	-2.21823937	3.26159489	1.05058514
H	-4.48421344	2.44198738	1.06807829
C	-5.65761728	-1.23032961	-0.18528085
C	-6.62608424	-1.57246706	-1.12249861
C	-6.95469088	-2.90475559	-1.31357629
C	-6.31836635	-3.89868202	-0.58042960
C	-5.35390023	-3.55052581	0.36287331
C	-5.02953894	-2.22472562	0.56705230
H	-7.12000607	-0.79544138	-1.69145317
H	-7.70901252	-3.17434945	-2.04478918
N	-5.34190748	0.14486373	0.03506628
H	-4.88362754	-4.33988767	0.93616538
H	-4.29601558	-1.94774506	1.31404717
C	-0.01349594	2.05748157	-0.01147299
C	0.44162835	3.03636909	0.89608964
C	1.73239772	3.48059868	0.86452031
C	2.23131192	2.06043929	-0.91198730
C	0.95179533	1.58552080	-0.92593015
H	-0.21169693	3.43724994	1.65654311
H	2.09998422	4.22611258	1.55603545
H	2.98697348	1.71151205	-1.60172976
H	0.69430179	0.85413048	-1.67735373
C	4.01130169	3.54988461	-0.07686944
H	4.14705469	4.11599983	0.84372120
H	4.05588194	4.25086815	-0.91141794
C	5.06372233	2.48478141	-0.21446521
C	5.35452582	1.63927925	0.85248433
C	6.32911839	0.66291231	0.72659660
C	7.03882297	0.52827515	-0.46518394
C	6.76601527	1.39231293	-1.52097527
C	5.77777882	2.35489865	-1.40228430
H	4.82867142	1.74971155	1.79482676
H	6.55969055	0.02487436	1.56948665
H	5.57837843	3.02469839	-2.23188384
H	7.35511624	1.30637421	-2.42478007
C	7.12827615	-3.64695936	1.09128976
C	7.04439553	-2.41024351	0.46949925
H	10.33930380	-1.78904310	0.02909968
H	10.49822573	-3.97833490	1.18971649

H	8.43372362	-5.16848410	1.85221677
H	6.22425408	-4.17784507	1.36300887
H	6.07180357	-1.99001085	0.24641629
C	-6.66216450	-5.32584431	-0.78897056
O	-6.13815171	-6.23193229	-0.19860247
N	2.62476626	3.00102367	-0.02681277
C	8.18465507	-0.43707446	-0.63806743
O	9.08818718	-0.12817772	-1.38082298
H	-7.45196652	-5.51393983	-1.54350321

Table S5. Cartesian coordinates of optimized TPAPs2 calculated by the DFT, CAM-B3LYP/6-311G(d), Gaussian 09 program

atom	x	y	z
C	-9.18575074	1.72835785	1.15783437
C	-10.40880515	2.14437554	1.68422040
C	-10.46674323	2.72870598	2.93670703
C	-9.29997815	2.92742552	3.66493825
C	4.78407395	0.35864005	0.01985637
C	5.86323052	0.52770471	-0.83757874
C	6.43029612	1.78087410	-0.99660257
C	5.93086382	2.89212590	-0.31517076
C	4.84501071	2.70278724	0.54178987
C	4.28042299	1.45061336	0.71632476
H	6.26644195	-0.32642745	-1.36778504
H	7.28722539	1.89616729	-1.64840202
H	4.43143201	3.55082489	1.07328261
H	3.44192174	1.31793987	1.38963248
C	2.89556997	-1.18873985	-0.10072057
C	2.21354538	-2.30601778	0.42404033
C	0.89988850	-2.54014543	0.10657743
C	0.17392351	-1.67867970	-0.73433610
C	0.85699449	-0.55918249	-1.24059210
C	2.17427925	-0.31804637	-0.94309897
H	2.72461787	-2.97417660	1.10202916
H	0.41350756	-3.39082842	0.56719697
C	7.51243979	5.92324595	-1.91946065
H	0.36266494	0.11759337	-1.92611625
H	2.67295409	0.53726282	-1.37576306
C	5.07347245	-1.96724597	0.70831942
C	5.84032937	-1.72383713	1.84264220
C	6.69783608	-2.70447971	2.31384694
C	6.79106631	-3.92942833	1.66472558
C	6.02671232	-4.16592260	0.52412119
C	5.17855474	-3.18978052	0.04203434

H	5.76579047	-0.76817177	2.34513600
H	7.29599867	-2.51738681	3.19904075
N	4.21345416	-0.94532801	0.20442194
H	6.12870171	-5.12052546	0.02287077
H	4.59921253	-3.36118854	-0.85665745
C	7.68675410	6.76030005	-0.82668577
C	6.71814071	5.08376868	0.59854641
H	6.79405177	4.03201404	-2.61649752
H	6.43339340	4.75251012	1.59018937
C	7.28850944	6.33612676	0.43296362
H	7.81512351	6.24957289	-2.90699862
H	8.13267293	7.73873841	-0.95596624
H	7.43030872	6.97988146	1.29250342
C	6.94448326	4.66983272	-1.75350017
C	-1.21146035	-1.93417405	-1.06571056
C	-1.79080029	-3.21448427	-0.94501099
C	-3.09959833	-3.42855546	-1.26962143
C	-3.37787802	-1.18759125	-1.83955566
C	-2.07558426	-0.92016725	-1.53153041
H	-1.20492868	-4.06196836	-0.62172757
H	-3.55595768	-4.40618990	-1.19864426
H	-4.06309235	-0.42266221	-2.17713420
H	-1.73345686	0.09960221	-1.62650816
C	-5.29994061	-2.70736872	-2.11990422
H	-5.53552407	-3.70136742	-1.74207232
H	-5.32395747	-2.74831435	-3.20965120
C	6.53852885	4.23275392	-0.49231274
C	-6.27653547	-1.68861469	-1.60029835
C	-6.59328007	-1.64263417	-0.24557985
C	-7.49877495	-0.70861948	0.23047163
C	-8.11306840	0.18430320	-0.64560876
C	-7.81598162	0.11862330	-2.00321505
C	-6.89572794	-0.80151583	-2.47623106
H	-6.14285207	-2.34855829	0.44397573
H	-7.75161054	-0.69605719	1.28243332
H	-6.67671307	-0.84469537	-3.53773078
H	-8.33331377	0.78762663	-2.67855571
C	-8.07624936	2.54048690	3.13784892
C	-8.01803705	1.93588209	1.89115841
H	-11.30302522	2.00350598	1.09093960
H	-11.42072022	3.03811569	3.34504511
H	-9.34486074	3.39233557	4.64229867
H	-7.16535148	2.71435643	3.69729511
H	-7.05725512	1.65455890	1.47878249

C	7.70205410	-4.98334419	2.17196275
O	7.81683857	-6.06728879	1.66591324
N	-3.89193654	-2.43003130	-1.71274440
C	-9.18594479	1.15365903	-0.21714581
O	-10.04958249	1.44321431	-1.01325497
H	8.28687571	-4.70608308	3.07179626

Table S6. Cartesian coordinates of optimized TPAPs3 calculated by the DFT, CAM-B3LYP/6-311G(d), Gaussian 09 program

atom	x	y	z
C	-9.66832790	-2.68792167	-0.48409081
C	-10.75491464	-3.50187010	-0.80569743
C	-10.57807657	-4.62171023	-1.59862851
C	-9.30894040	-4.95502131	-2.05666827
C	3.72359944	0.92952683	0.02562605
C	4.61778792	0.62819025	1.04471866
C	5.22478826	-0.61765735	1.08543597
C	4.94637560	-1.58406261	0.12081725
C	4.04663047	-1.26640120	-0.89543557
C	3.44401680	-0.01931793	-0.95089674
H	4.84290881	1.37211017	1.80027401
H	5.92480617	-0.84791449	1.88034523
H	3.82742694	-2.00403631	-1.65898407
H	2.75604318	0.22147158	-1.75373704
C	1.75076929	2.37842135	0.01028904
C	1.12776652	3.56836368	-0.41906214
C	-0.23750970	3.70107239	-0.38283298
C	-1.07190558	2.67649166	0.09617073
C	-0.44265236	1.49524831	0.52532069
C	0.91988639	1.33910257	0.47628846
H	1.72977345	4.38502907	-0.79207142
H	-0.65909348	4.64329745	-0.71196326
C	7.31964702	-4.48362539	-0.61452561
H	-1.03161520	0.65876105	0.88207848
H	1.36186439	0.40987737	0.80736809
C	3.99456925	3.35169275	-0.12935832
C	4.98098033	3.37191221	-1.10921174
C	5.85231550	4.44662438	-1.18382236
C	5.74200999	5.50572716	-0.29094228
C	4.75621500	5.47800976	0.69343558
C	3.89174690	4.40529772	0.78074468
H	5.06358819	2.54533647	-1.80431185
H	6.62165085	4.46353328	-1.94924166
N	3.11695674	2.22924069	-0.03200369

H	4.69746846	6.30459727	1.39164583
H	3.13780014	4.36990996	1.55845740
C	6.82145971	-5.44986986	0.25121826
C	5.10496121	-3.90950315	1.03990054
C	5.73436967	-5.19587754	1.07891283
H	7.29428440	-6.42664507	0.28292587
C	6.70181607	-3.19177424	-0.65871681
C	-2.51098759	2.83211174	0.14649285
C	-3.19497816	3.78518879	-0.63681044
C	-4.55248904	3.91413697	-0.56462337
C	-4.68163249	2.20828210	1.01391998
C	-3.32722614	2.04087696	0.98251040
H	-2.66541931	4.41650113	-1.33565935
H	-5.09254612	4.63633180	-1.16173130
H	-5.32509568	1.61293125	1.64673001
H	-2.89645751	1.30122018	1.64189425
C	-6.76962849	3.34499744	0.35638580
H	-7.05091637	3.97078071	-0.48944421
H	-6.95244468	3.91796820	1.26628203
C	5.59916483	-2.92502052	0.16902321
C	8.92696857	-3.79693215	-2.29456221
C	8.32401771	-2.50997976	-2.33441559
C	7.25541898	-2.21780099	-1.54864034
H	8.89537425	-5.73188635	-1.41726025
C	-7.55081784	2.06065109	0.36020978
C	-7.67409841	1.30761013	-0.80415722
C	-8.39955835	0.12729564	-0.80176586
C	-9.02627450	-0.31052711	0.36360377
C	-8.92456690	0.45752611	1.51943468
C	-8.18263891	1.62684882	1.52238063
H	-7.21392365	1.64879736	-1.72633946
H	-8.50538443	-0.43705781	-1.71963543
C	8.43944762	-4.74837903	-1.45982273
H	-8.11673142	2.21753352	2.43073400
C	3.98069768	-3.69163508	1.89765820
H	-9.45232907	0.13152091	2.40694176
C	-8.21825936	-4.16601250	-1.71982221
C	-8.39672111	-3.03143146	-0.94239387
H	-11.73234640	-3.24050103	-0.41947513
H	-11.42855992	-5.24248642	-1.85488865
H	-9.16941403	-5.83711679	-2.67119211
H	-7.22569065	-4.43788171	-2.06013413
H	-7.53632013	-2.43283181	-0.66739527
C	6.66771531	6.66078531	-0.37298151

O	6.61641062	7.61369092	0.35708788
N	-5.29629452	3.13620663	0.24948508
C	-9.91800114	-1.52553523	0.41387453
O	-10.84405624	-1.52666029	1.19231898
H	7.43457220	6.59761065	-1.17118344
H	9.77860849	-4.00919158	-2.93055950
H	8.72866199	-1.75495239	-2.99923420
H	6.81418194	-1.22988012	-1.58683279
C	3.52995467	-4.66658818	2.72903410
C	4.16276567	-5.93909708	2.76929956
C	5.22776227	-6.19152394	1.96809805
H	3.48579313	-2.72877407	1.87944375
H	2.67772764	-4.47749218	3.37254325
H	3.78872711	-6.70274732	3.44151516
H	5.71704192	-7.15959958	1.98895459

Table S7. Cartesian coordinates of optimized TPAPs4 calculated by the DFT, CAM-B3LYP/6-311G(d), Gaussian 09 program

atom	x	y	z
C	-10.48325965	-1.71283063	-0.60486765
C	-11.65857354	-2.37901291	-0.95347819
C	-11.60860888	-3.52468828	-1.72740069
C	-10.38183320	-4.03186742	-2.13896908
C	3.22339576	0.06157291	0.28257300
C	4.00662967	-0.44169156	1.31293937
C	4.42070097	-1.76462288	1.28263414
C	4.05582286	-2.60699374	0.23424602
C	3.26686125	-2.08715481	-0.79086761
C	2.85762292	-0.76293884	-0.77478926
H	4.29734622	0.20478863	2.13311227
H	5.03603374	-2.15346040	2.08575671
H	2.98330876	-2.72774433	-1.61807847
H	2.25691477	-0.36503016	-1.58512889
C	1.48662367	1.78569582	0.29799457
C	1.05485012	3.05979069	-0.11960930
C	-0.28055973	3.37964160	-0.13712522
C	-1.26659234	2.46828723	0.27459807
C	-0.82720449	1.20255037	0.69596674
C	0.50293025	0.86128513	0.69947532
H	1.77920255	3.79239218	-0.44736901
H	-0.55532429	4.37763215	-0.45737410
C	6.03538749	-5.75931906	-0.61375473
H	-1.54195191	0.44763521	1.00128086
H	0.79910655	-0.12821446	1.01863739

C	3.85596446	2.41720015	0.29166704
C	4.91598128	2.29870682	-0.60455127
C	5.94223473	3.22267000	-0.60763404
C	5.94018226	4.29808296	0.29063281
C	4.87669518	4.39258140	1.19766294
C	3.84951480	3.46974435	1.20419067
H	4.93487498	1.47236010	-1.30418299
H	6.74404357	3.09671343	-1.32040950
N	2.82158466	1.44072246	0.29833231
H	4.86404966	5.20047770	1.92113859
H	3.04733793	3.55403781	1.92738091
C	5.34579085	-6.70546030	0.13505160
C	3.81650634	-4.99427379	0.95594478
C	4.25156167	-6.35870098	0.91855050
H	5.67112976	-7.74088275	0.10861507
C	5.61256508	-4.39084478	-0.58094848
C	-2.67472007	2.81699205	0.26065220
C	-3.18626721	3.84980307	-0.55065692
C	-4.51715894	4.15802900	-0.54249139
C	-4.94610505	2.48970463	1.02309185
C	-3.62510883	2.14401503	1.05529653
H	-2.54427878	4.40140581	-1.22239905
H	-4.92824060	4.94299524	-1.16265914
H	-5.69232538	1.98731527	1.62278314
H	-3.32655006	1.35607429	1.73184593
C	-6.83158663	3.89205222	0.26875906
H	-6.98976332	4.52928700	-0.60013199
H	-6.97396648	4.50533850	1.15936140
C	4.50498289	-4.02963854	0.20311329
C	7.83580810	-5.18927839	-2.13385397
C	7.42612055	-3.82832781	-2.09705826
C	6.35840872	-3.44342769	-1.35102899
H	7.46900941	-7.16046130	-1.43049368
C	-7.77646775	2.72337602	0.25972319
C	-7.96041378	1.97519824	-0.89978215
C	-8.83684344	0.90214505	-0.90955100
C	-9.55463576	0.57008421	0.23802218
C	-9.38959738	1.33583160	1.38813687
C	-8.49889359	2.39601911	1.40398400
H	-7.42900578	2.23787600	-1.80928635
H	-8.98691133	0.34278985	-1.82429768
C	8.37619845	4.83547517	-1.58992625
C	7.16164178	-6.12018201	-1.41365735
H	-8.38556759	2.98737168	2.30722756

C	6.96604163	5.32790842	0.36896028
H	6.84870710	6.01378643	1.20205562
C	2.67945467	-4.67934371	1.76526967
C	8.02878994	5.58366015	-0.42288089
N	8.65331090	4.23432870	-2.52809580
H	-9.98579604	1.09725785	2.25997480
C	8.88650656	6.68667134	-0.10916385
N	9.56477008	7.57517560	0.15175180
C	-9.20629605	-3.39071612	-1.77472800
C	-9.25537073	-2.23049499	-1.01649668
H	-12.60384661	-1.98323327	-0.60325114
H	-12.52616038	-4.03001945	-2.00500231
H	-10.34258528	-4.93414056	-2.73858274
H	-8.24898318	-3.79824813	-2.07865606
H	-8.33149679	-1.74831546	-0.71948399
N	-5.39443383	3.48783222	0.23295538
C	-10.60304791	-0.51376570	0.27090582
O	-11.54540406	-0.37771803	1.01716555
H	8.69039395	-5.47477352	-2.73629046
H	7.97841957	-3.09219699	-2.67038160
H	6.06588557	-2.40123786	-1.32992338
C	2.03809249	-5.63838454	2.48209802
C	2.47779597	-6.98996054	2.44673285
C	3.54800160	-7.33432587	1.68776794
H	2.33012558	-3.65509886	1.80333741
H	1.17999732	-5.37569053	3.09108819
H	1.95324489	-7.73972596	3.02777951
H	3.89111195	-8.36290229	1.65185645

Table S8. Cartesian coordinates of optimized TPAPs5 calculated by the DFT, CAM-B3LYP/6-311G(d), Gaussian 09 program

atom	x	y	z
C	-0.24247687	-0.07514419	-0.14392643
N	-1.31964993	0.78517649	-0.13940065
C	-1.12748020	2.20363926	-0.03485331
C	-2.66035301	0.31120362	-0.22139267
C	-1.70210143	2.90525040	1.01726615
C	-1.53567122	4.27881064	1.10471748
C	-0.78902944	4.97406926	0.15516656
C	-0.21826254	4.25552675	-0.89427533
C	-0.38985248	2.88380583	-0.99677843
C	-3.55730871	0.90155871	-1.10492286
C	-4.86695405	0.45842164	-1.16057325
C	-5.31492230	-0.59230461	-0.35642198

C	-4.40616510	-1.16097837	0.54368537
C	-3.10334597	-0.71259966	0.61659901
C	-0.35050630	-1.38486995	-0.65173745
C	0.73085890	-2.23094110	-0.65480528
C	1.97884734	-1.84095266	-0.14173138
C	2.07911730	-0.53293572	0.36031472
C	1.01187141	0.33120570	0.35174409
C	-0.60752408	6.45160032	0.25548540
C	3.10928352	-2.74967128	-0.12711212
C	-1.37376378	7.30369619	-0.55657058
C	-1.18955660	8.72128017	-0.46124017
C	-0.26051766	9.23056883	0.43805646
C	0.49966890	8.39788779	1.25045283
C	0.32897605	6.97832859	1.15997362
C	1.45177736	8.92703053	2.17355307
C	2.19618569	8.10892859	2.95861305
C	2.03730839	6.69917489	2.86621416
C	1.14212947	6.15508993	2.00160060
C	-2.35460037	6.81985112	-1.47909959
C	-3.07830808	7.67350933	-2.24872707
C	-2.88333096	9.07889419	-2.15864138
C	-1.97023332	9.58191273	-1.29095405
C	3.19097899	-3.86419322	-0.98636274
C	4.26347963	-4.70912677	-0.94407007
N	5.28769465	-4.51128468	-0.08837104
C	5.25118648	-3.45291525	0.74837781
C	4.20072397	-2.57998431	0.74914172
C	6.41114493	-5.49253572	-0.01811652
C	7.76013390	-4.84186529	0.10633132
C	8.32970833	-4.18751152	-0.98246587
C	9.57634488	-3.59360836	-0.86926731
C	10.27951418	-3.65837866	0.33230644
C	9.72034391	-4.33632798	1.41124866
C	8.46577408	-4.91274934	1.30443071
C	11.68262872	-3.13024004	0.49665596
C	12.14796184	-1.95351781	-0.28964741
O	12.42023407	-3.69261617	1.27323556
C	13.51710277	-1.83838756	-0.53221795
C	14.01532125	-0.74488147	-1.21783606
C	13.15375089	0.25845932	-1.64513611
C	11.79386283	0.16522924	-1.38508252
C	11.28983844	-0.94026285	-0.71625888
C	-6.69775527	-1.04940892	-0.48118771
C	-7.18078975	-2.20060629	0.00989972

C	-8.53282507	-2.68626352	-0.09164006
C	-8.94399130	-3.87853513	0.40694470
C	-10.36228729	-4.03926646	0.13044595
O	-10.79421690	-2.96031025	-0.51925960
C	-9.71959650	-2.00364554	-0.73639252
C	-9.59001766	-1.84430646	-2.24604867
C	-10.13813945	-0.71826250	-0.03478113
C	-11.21598371	-5.05528149	0.42323335
C	-8.08517637	-4.78718110	1.08105643
N	-7.30867802	-5.44885246	1.60811653
C	-12.58118047	-4.95792868	0.02829886
N	-13.68130245	-4.87839827	-0.29157328
C	-10.79416197	-6.22549945	1.11295740
N	-10.47283152	-7.17890831	1.66750371
H	-2.28374233	2.37547305	1.76297472
H	-1.98787834	4.82306510	1.92584227
H	0.35779077	4.78290984	-1.64604809
H	0.04812186	2.33733409	-1.82464096
H	-3.22758095	1.71096808	-1.74463770
H	-5.55291215	0.92765285	-1.85771138
H	-4.72515626	-1.94195903	1.22306504
H	-2.42246154	-1.14778705	1.33840049
H	-1.29306592	-1.72883875	-1.05418037
H	0.58539344	-3.23212966	-1.04260214
H	3.02269494	-0.16414456	0.74457227
H	1.13407263	1.33289249	0.73951704
H	-0.12627006	10.30556129	0.50861326
H	1.56669308	10.00414558	2.23329885
H	2.91451931	8.52285268	3.65685224
H	2.64094851	6.05509279	3.49621060
H	1.03661900	5.07909995	1.94344686
H	-2.52263633	5.75309657	-1.55605243
H	-3.81778754	7.28392512	-2.93957135
H	-3.47082526	9.74233027	-2.78274409
H	-1.81732541	10.65285773	-1.20960324
H	2.42205103	-4.06110302	-1.71953537
H	4.34468607	-5.56650042	-1.59836401
H	6.09760297	-3.34290955	1.41192957
H	4.21847232	-1.77112718	1.46545136
H	6.34862481	-6.09155834	-0.92550723
H	6.21359608	-6.15177823	0.82802561
H	7.80631885	-4.15185907	-1.93292746
H	10.01707719	-3.10737771	-1.73036572
H	10.29463484	-4.41966645	2.32542375

H	8.04539256	-5.44287614	2.15331224
H	14.17641333	-2.61760321	-0.17030847
H	15.07836330	-0.66806027	-1.41372585
H	13.54549012	1.11913391	-2.17519961
H	11.12521441	0.95794518	-1.70041188
H	10.22948047	-0.99454830	-0.49956404
H	-7.34995983	-0.38652273	-1.03955971
H	-6.50792965	-2.87170449	0.53373235
H	-8.84388239	-1.09445903	-2.50720174
H	-9.30992239	-2.78897993	-2.71264584
H	-10.55059724	-1.53082206	-2.65486559
H	-9.40613708	0.07477827	-0.18586689
H	-11.09559361	-0.38626966	-0.43633679
H	-10.25330483	-0.88243421	1.03679444

Table S9. Calculated SOCME between triplets and singlets of TPAPs1

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETs					
Root		Z	<T HSO S> (Re, Im) cm-1		
T	S		X	Y	
1	0	(0.00, -0.00)	(0.00, 0.48)	(-0.00, -0.36)	
1	1	(0.00, 0.03)	(0.00, 0.49)	(-0.00, -0.07)	
1	2	(0.00, 0.24)	(0.00, -0.20)	(-0.00, -0.02)	
1	3	(0.00, 3.18)	(0.00, 2.38)	(-0.00, 5.05)	
1	4	(0.00, 0.20)	(0.00, -0.02)	(-0.00, -0.13)	
1	5	(0.00, 0.07)	(0.00, -0.05)	(-0.00, -0.04)	
2	0	(0.00, 7.51)	(0.00, -8.25)	(-0.00, 3.45)	
2	1	(0.00, -0.19)	(0.00, -0.09)	(-0.00, 0.07)	
2	2	(0.00, 0.22)	(0.00, -0.07)	(-0.00, -0.14)	
2	3	(0.00, -0.52)	(0.00, -0.45)	(-0.00, -0.91)	
2	4	(0.00, -0.01)	(0.00, 0.11)	(-0.00, -0.02)	
2	5	(0.00, -0.06)	(0.00, 0.10)	(-0.00, -0.04)	
3	0	(0.00, -15.77)	(0.00, -19.00)	(-0.00, -28.19)	
3	1	(0.00, 3.39)	(0.00, 2.59)	(-0.00, 5.56)	
3	2	(0.00, 0.14)	(0.00, 0.03)	(-0.00, 0.06)	
3	3	(0.00, -0.02)	(0.00, 0.17)	(-0.00, 0.37)	
3	4	(0.00, -0.03)	(0.00, -0.02)	(-0.00, -0.06)	
3	5	(0.00, 0.01)	(0.00, 0.06)	(-0.00, 0.04)	
4	0	(0.00, 24.54)	(0.00, -28.56)	(-0.00, 12.53)	
4	1	(0.00, -0.28)	(0.00, -0.62)	(-0.00, -0.52)	
4	2	(0.00, 0.74)	(0.00, -0.16)	(-0.00, -0.46)	
4	3	(0.00, 0.10)	(0.00, 0.08)	(-0.00, 0.14)	
4	4	(0.00, 0.03)	(0.00, -0.07)	(-0.00, -0.00)	
4	5	(0.00, -0.20)	(0.00, 0.36)	(-0.00, -0.12)	
5	0	(0.00, 4.78)	(0.00, -6.50)	(-0.00, 1.68)	
5	1	(0.00, -0.16)	(0.00, -0.07)	(-0.00, -0.16)	
5	2	(0.00, 0.15)	(0.00, 0.14)	(-0.00, -0.12)	
5	3	(0.00, 2.36)	(0.00, 2.04)	(-0.00, 4.03)	
5	4	(0.00, 0.10)	(0.00, -0.05)	(-0.00, -0.01)	
5	5	(0.00, 1.19)	(0.00, -1.17)	(-0.00, 0.00)	

Table S10. Calculated SOCME between triplets and singlets of TPAPs2

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETs					
Root		Z	<T HSO S> (Re, Im) cm-1		
T	S		X	Y	
1	0	(0.00, 0.05)	(0.00, -0.27)	(-0.00, 0.05)	
1	1	(0.00, 0.02)	(0.00, -0.17)	(-0.00, 0.48)	
1	2	(0.00, -0.04)	(0.00, -0.15)	(-0.00, 0.99)	
1	3	(0.00, 0.07)	(0.00, -0.09)	(-0.00, -0.03)	
1	4	(0.00, -0.03)	(0.00, 0.01)	(-0.00, -0.15)	
1	5	(0.00, 0.18)	(0.00, 0.17)	(-0.00, 0.10)	
2	0	(0.00, -0.03)	(0.00, -0.03)	(-0.00, 1.24)	
2	1	(0.00, 0.10)	(0.00, 0.20)	(-0.00, -0.79)	
2	2	(0.00, -0.19)	(0.00, -0.16)	(-0.00, 0.57)	
2	3	(0.00, 0.23)	(0.00, 0.15)	(-0.00, 0.03)	
2	4	(0.00, -0.02)	(0.00, -0.00)	(-0.00, -0.04)	
2	5	(0.00, -0.09)	(0.00, -0.15)	(-0.00, -0.10)	
3	0	(0.00, -0.04)	(0.00, -0.21)	(-0.00, 0.71)	
3	1	(0.00, 0.01)	(0.00, -0.00)	(-0.00, 0.17)	
3	2	(0.00, 0.01)	(0.00, -0.03)	(-0.00, -0.11)	
3	3	(0.00, -0.00)	(0.00, 0.00)	(-0.00, -0.00)	
3	4	(0.00, 0.00)	(0.00, -0.05)	(-0.00, 0.07)	
3	5	(0.00, -0.01)	(0.00, -0.00)	(-0.00, -0.01)	
4	0	(0.00, 4.08)	(0.00, -1.44)	(-0.00, -9.62)	
4	1	(0.00, -0.70)	(0.00, 0.21)	(-0.00, 1.14)	
4	2	(0.00, 0.48)	(0.00, -0.42)	(-0.00, -1.45)	
4	3	(0.00, 0.00)	(0.00, -0.00)	(-0.00, 0.01)	
4	4	(0.00, 0.00)	(0.00, -0.00)	(-0.00, -0.00)	
4	5	(0.00, -0.02)	(0.00, 0.00)	(-0.00, 0.04)	
5	0	(0.00, 14.63)	(0.00, -4.28)	(-0.00, -33.44)	
5	1	(0.00, -1.69)	(0.00, 0.77)	(-0.00, 3.93)	
5	2	(0.00, 2.22)	(0.00, -0.84)	(-0.00, -4.92)	
5	3	(0.00, 0.00)	(0.00, 0.00)	(-0.00, 0.01)	
5	4	(0.00, 0.00)	(0.00, -0.00)	(-0.00, -0.01)	
5	5	(0.00, -0.08)	(0.00, 0.02)	(-0.00, 0.16)	

Table S11. Calculated SOCME between triplets and singlets of TPAPs3

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETs					
Root		<T HSO S> (Re, Im) cm-1			
T	S	Z	X	Y	
1	0	(0.00, -0.00)	(0.00, 0.09)	(-0.00, 0.15)	
1	1	(0.00, 0.00)	(0.00, 0.01)	(-0.00, 0.01)	
1	2	(0.00, -0.21)	(0.00, -0.01)	(-0.00, -0.20)	
1	3	(0.00, -0.01)	(0.00, 0.01)	(-0.00, 0.09)	
1	4	(0.00, -0.01)	(0.00, -0.04)	(-0.00, 0.03)	
1	5	(0.00, -1.46)	(0.00, -0.12)	(-0.00, -1.14)	
2	0	(0.00, -0.11)	(0.00, -0.56)	(-0.00, 0.00)	
2	1	(0.00, 0.01)	(0.00, -0.06)	(-0.00, -0.11)	
2	2	(0.00, -0.01)	(0.00, -0.00)	(-0.00, -0.00)	
2	3	(0.00, -0.02)	(0.00, 0.46)	(-0.00, 0.23)	
2	4	(0.00, -0.08)	(0.00, 0.03)	(-0.00, 0.01)	
2	5	(0.00, -0.07)	(0.00, -0.01)	(-0.00, -0.05)	
3	0	(0.00, 0.02)	(0.00, 0.04)	(-0.00, 0.11)	
3	1	(0.00, -0.01)	(0.00, 0.08)	(-0.00, 0.15)	
3	2	(0.00, 0.04)	(0.00, 0.02)	(-0.00, 0.02)	
3	3	(0.00, -0.01)	(0.00, -0.00)	(-0.00, -0.02)	
3	4	(0.00, -0.02)	(0.00, 0.01)	(-0.00, -0.01)	
3	5	(0.00, 0.02)	(0.00, 0.00)	(-0.00, 0.01)	
4	0	(0.00, -0.02)	(0.00, -0.04)	(-0.00, 0.04)	
4	1	(0.00, -0.21)	(0.00, -0.01)	(-0.00, -0.20)	
4	2	(0.00, 0.00)	(0.00, -0.00)	(-0.00, -0.00)	
4	3	(0.00, 0.00)	(0.00, -0.00)	(-0.00, 0.01)	
4	4	(0.00, 0.00)	(0.00, -0.00)	(-0.00, 0.00)	
4	5	(0.00, -0.17)	(0.00, -0.57)	(-0.00, -0.11)	
5	0	(0.00, -0.01)	(0.00, -0.05)	(-0.00, 0.01)	
5	1	(0.00, -0.01)	(0.00, -0.04)	(-0.00, 0.03)	
5	2	(0.00, -0.00)	(0.00, 0.00)	(-0.00, -0.00)	
5	3	(0.00, -0.12)	(0.00, 0.06)	(-0.00, -0.02)	
5	4	(0.00, -0.01)	(0.00, 0.00)	(-0.00, -0.00)	
5	5	(0.00, -0.00)	(0.00, -0.00)	(-0.00, -0.00)	

Table S12. Calculated SOCME between triplets and singlets of TPAPs4

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETs					
Root		<T HSO S> (Re, Im) cm-1			
T	S	Z	X	Y	
1	0	(0.00, -0.01)	(0.00, 0.06)	(-0.00, 0.12)	
1	1	(0.00, 0.00)	(0.00, 0.00)	(-0.00, 0.01)	
1	2	(0.00, 0.18)	(0.00, -0.31)	(-0.00, 0.32)	
1	3	(0.00, -0.12)	(0.00, -0.03)	(-0.00, -0.10)	
1	4	(0.00, -0.00)	(0.00, 0.00)	(-0.00, 0.08)	
1	5	(0.00, -0.01)	(0.00, -0.04)	(-0.00, 0.05)	
2	0	(0.00, -0.07)	(0.00, -0.64)	(-0.00, -0.08)	
2	1	(0.00, 0.00)	(0.00, -0.03)	(-0.00, -0.10)	
2	2	(0.00, 0.00)	(0.00, -0.00)	(-0.00, 0.00)	
2	3	(0.00, -0.00)	(0.00, -0.00)	(-0.00, -0.00)	
2	4	(0.00, 0.03)	(0.00, 0.40)	(-0.00, 0.16)	
2	5	(0.00, -0.07)	(0.00, 0.07)	(-0.00, 0.01)	
3	0	(0.00, -0.00)	(0.00, 0.03)	(-0.00, 0.11)	
3	1	(0.00, -0.01)	(0.00, 0.04)	(-0.00, 0.15)	
3	2	(0.00, -0.03)	(0.00, -0.06)	(-0.00, -0.22)	
3	3	(0.00, 0.03)	(0.00, 0.00)	(-0.00, -0.01)	
3	4	(0.00, -0.01)	(0.00, 0.00)	(-0.00, -0.01)	
3	5	(0.00, -0.02)	(0.00, 0.01)	(-0.00, -0.01)	
4	0	(0.00, 0.02)	(0.00, 0.06)	(-0.00, 0.24)	
4	1	(0.00, 0.18)	(0.00, -0.31)	(-0.00, 0.31)	
4	2	(0.00, 0.00)	(0.00, 0.00)	(-0.00, 0.01)	
4	3	(0.00, 0.05)	(0.00, 0.06)	(-0.00, 0.11)	
4	4	(0.00, -0.03)	(0.00, 0.02)	(-0.00, -0.01)	
4	5	(0.00, -0.00)	(0.00, 0.00)	(-0.00, -0.00)	
5	0	(0.00, 0.03)	(0.00, 0.03)	(-0.00, -0.08)	
5	1	(0.00, 0.12)	(0.00, 0.03)	(-0.00, 0.10)	
5	2	(0.00, 0.05)	(0.00, 0.06)	(-0.00, 0.11)	
5	3	(0.00, 0.00)	(0.00, 0.00)	(-0.00, 0.00)	
5	4	(0.00, 0.00)	(0.00, -0.00)	(-0.00, -0.00)	
5	5	(0.00, 0.00)	(0.00, 0.00)	(-0.00, 0.00)	

Table S13. Calculated SOCME between triplets and singlets of TPAPs5

CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETS					
Root		Z	<T HSO S> (Re, Im) cm ⁻¹		
T	S		X	Y	
1	0	(0.00, -0.01)	(0.13, 0.01)	(0.13, -0.01)	
1	1	(0.00, -0.00)	(0.01, -0.00)	(0.01, 0.00)	
1	2	(0.00, 0.13)	(-0.06, 0.17)	(-0.06, -0.17)	
1	3	(0.00, -0.01)	(-0.05, 0.03)	(-0.05, -0.03)	
1	4	(0.00, 0.16)	(-0.09, 0.03)	(-0.09, -0.03)	
1	5	(0.00, 0.00)	(0.05, -0.01)	(0.05, 0.01)	
2	0	(0.00, -0.07)	(0.19, 0.23)	(0.19, -0.23)	
2	1	(0.00, 0.00)	(0.08, -0.00)	(0.08, 0.00)	
2	2	(0.00, -0.01)	(-0.01, -0.00)	(-0.01, 0.00)	
2	3	(0.00, 0.05)	(0.05, 0.23)	(0.05, -0.23)	
2	4	(0.00, -0.00)	(0.00, 0.00)	(0.00, -0.00)	
2	5	(0.00, 0.03)	(-0.14, 0.07)	(-0.14, -0.07)	
3	0	(0.00, -0.03)	(-0.17, -0.24)	(-0.17, 0.24)	
3	1	(0.00, 0.01)	(-0.06, 0.01)	(-0.06, -0.01)	
3	2	(0.00, -0.01)	(-0.03, 0.01)	(-0.03, -0.01)	
3	3	(0.00, 0.08)	(-0.10, -0.06)	(-0.10, 0.06)	
3	4	(0.00, 0.01)	(-0.00, -0.00)	(-0.00, 0.00)	
3	5	(0.00, -0.04)	(0.13, 0.04)	(0.13, -0.04)	
4	0	(0.00, -0.01)	(0.10, -0.02)	(0.10, 0.02)	
4	1	(0.00, -0.01)	(0.12, -0.02)	(0.12, 0.02)	
4	2	(0.00, -0.02)	(0.12, -0.03)	(0.12, 0.03)	
4	3	(0.00, -0.01)	(0.00, -0.01)	(0.00, 0.01)	
4	4	(0.00, -0.04)	(0.02, 0.00)	(0.02, -0.00)	
4	5	(0.00, 0.01)	(-0.01, 0.01)	(-0.01, -0.01)	
5	0	(0.00, -0.01)	(-0.13, 0.03)	(-0.13, -0.03)	
5	1	(0.00, 0.13)	(-0.05, 0.16)	(-0.05, -0.16)	
5	2	(0.00, -0.00)	(0.02, -0.00)	(0.02, 0.00)	
5	3	(0.00, 0.00)	(0.01, 0.00)	(0.01, -0.00)	
5	4	(0.00, 0.04)	(-0.05, -0.00)	(-0.05, 0.00)	
5	5	(0.00, -0.01)	(0.01, -0.01)	(0.01, 0.01)	

Table S14. Cartesian components of the spin-orbit matrix elements (absolute values in cm⁻¹) between low-lying singlet and triplet states for *m*-THPC and TPAPs5

	<i>m</i> -THPC	TPAPs5
$S_1 \hat{H}_{\text{soc}} T_1\rangle$	2.4×10^{-1} (x)	1.0×10^{-2} (x)
	6.8×10^{-2} (y)	1.0×10^{-2} (y)
$S_1 \hat{H}_{\text{soc}} T_2\rangle$	8.8×10^{-3} (z)	8.0×10^{-2} (x)
		8.0×10^{-2} (y)
$S_1 \hat{H}_{\text{soc}} T_3\rangle$	1.4×10^{-1} (x)	1.0×10^{-2} (z)
	2.2×10^{-2} (y)	6.1×10^{-2} (x)
$S_1 \hat{H}_{\text{soc}} T_4\rangle$	2.2×10^{-3} (z)	6.1×10^{-2} (y)
		1.0×10^{-2} (z)
		1.2×10^{-1} (x)
		1.2×10^{-1} (y)