

## Supporting information

### Phosphorus(V) Tetrapyrazinocorrolazines Bearing Axial Aryloxy Groups as pH-sensitive Fluorophores and Photosensitizers

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Table S7. Calculated composition of the lowest excited states and corresponding oscillator strength for [TPyzCAP(OPhOH)<sub>2</sub>].

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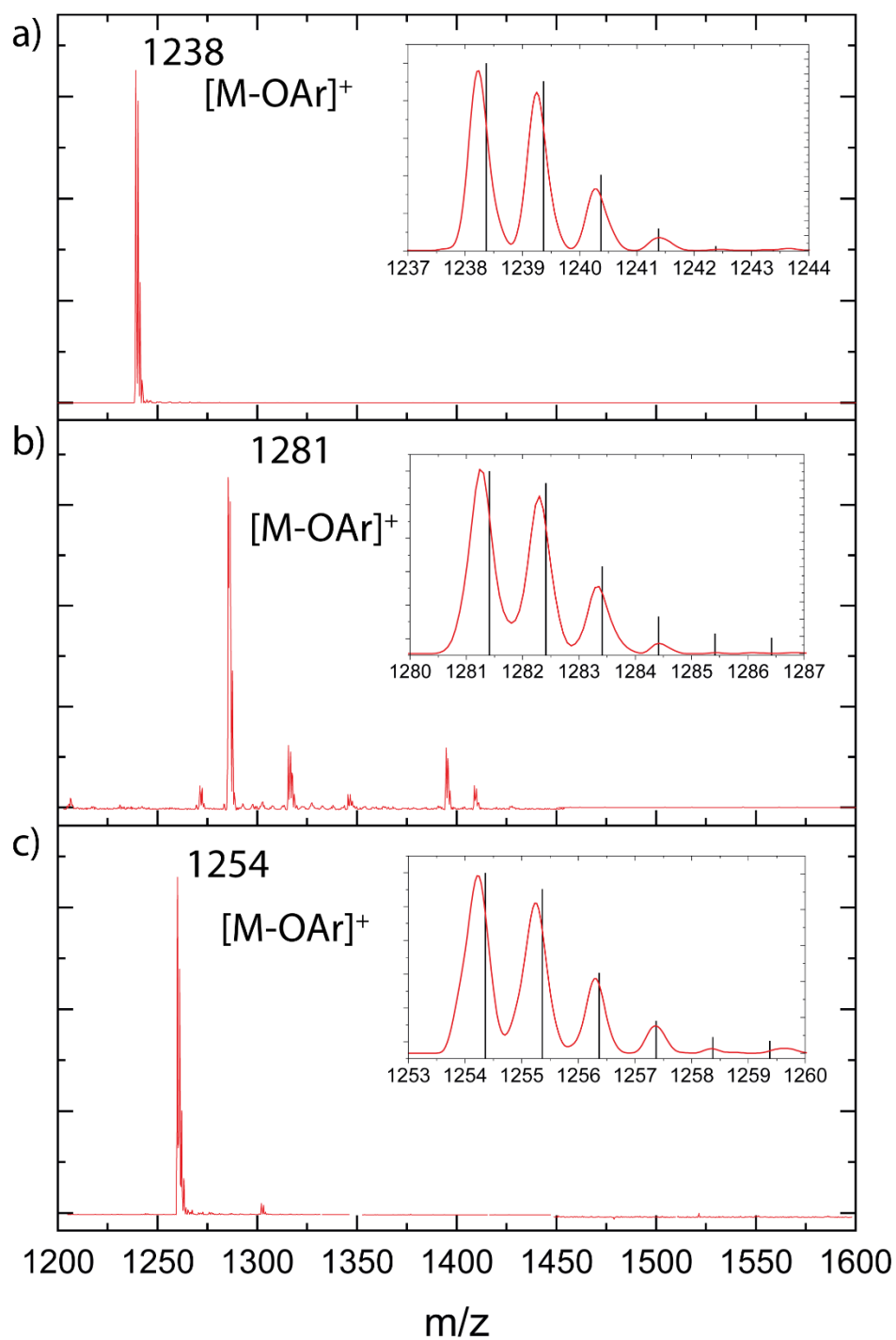
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## I. Spectral characterization



**Figure S1.** LDI-TOF mass spectra of  $[TPyzCAP(OAr)_2]$  (**2a-c**). Ar = phenyl (a), 4-dimethylaminophenyl (b), 4-hydroxyphenyl (c).

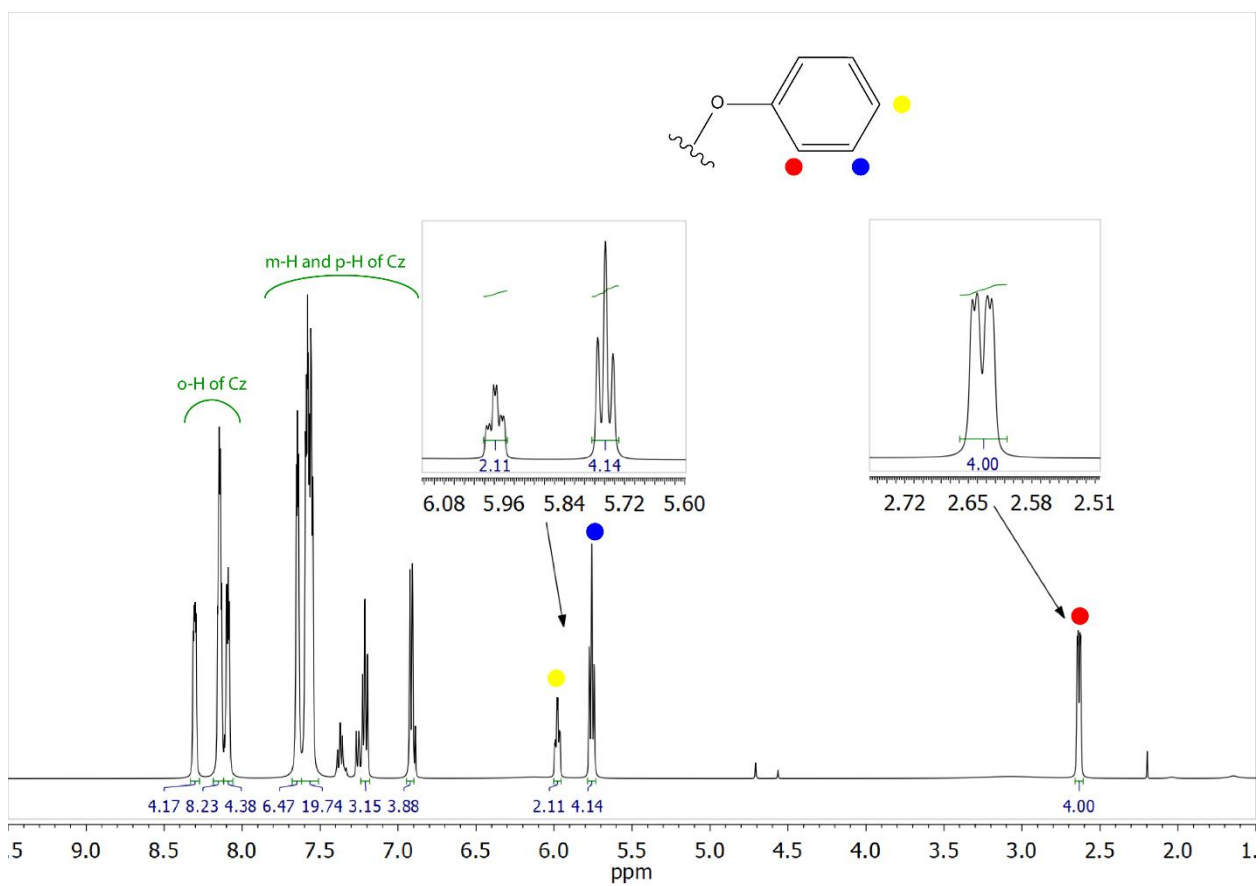


Figure S2.  $^1\text{H}$  NMR spectrum of  $[\text{TPyzCAP}(\text{OPh})_2]$  (**2a**) in  $\text{CDCl}_3$

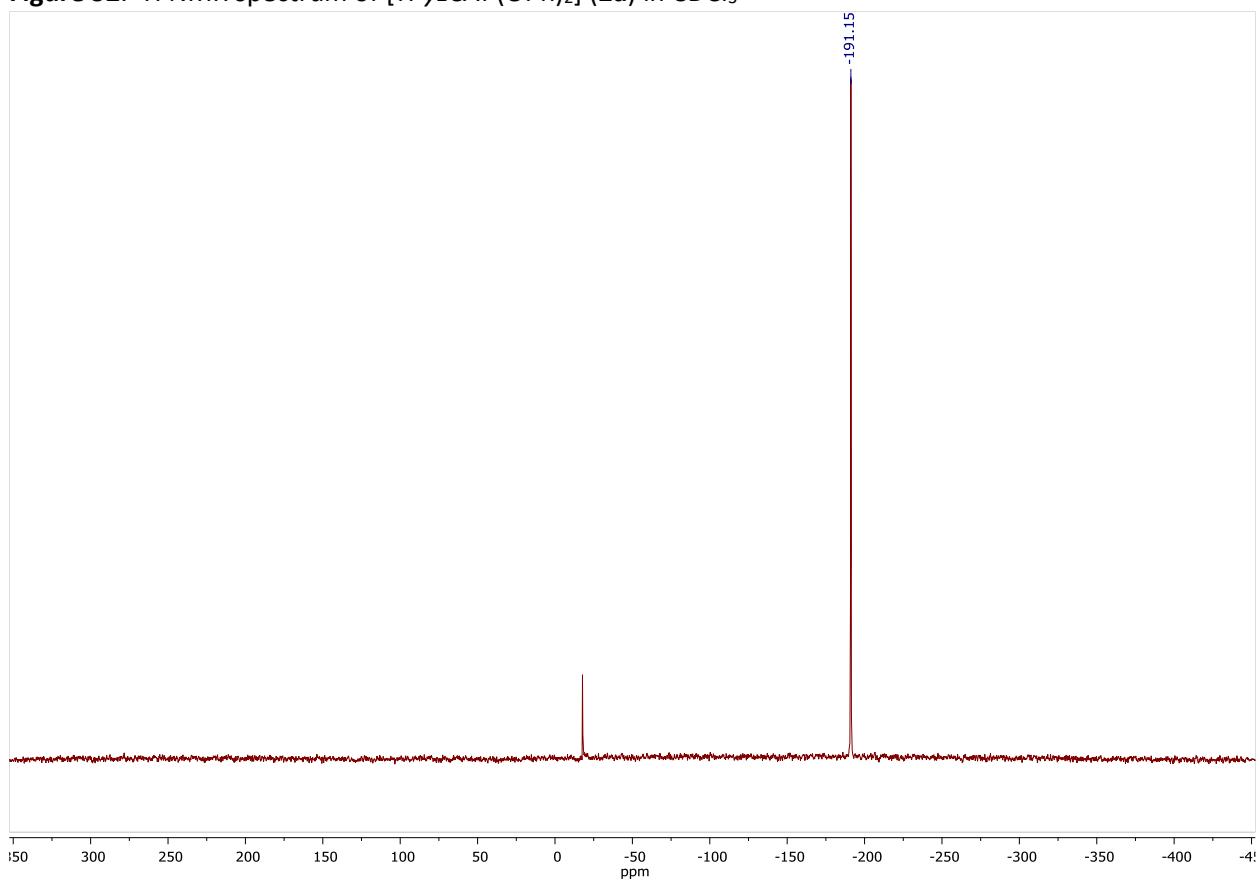


Figure S3.  $^{31}\text{P}$  NMR spectra of  $[\text{TPyzCAP}(\text{OPh})_2]$  (**2a**) in  $\text{CDCl}_3$ .

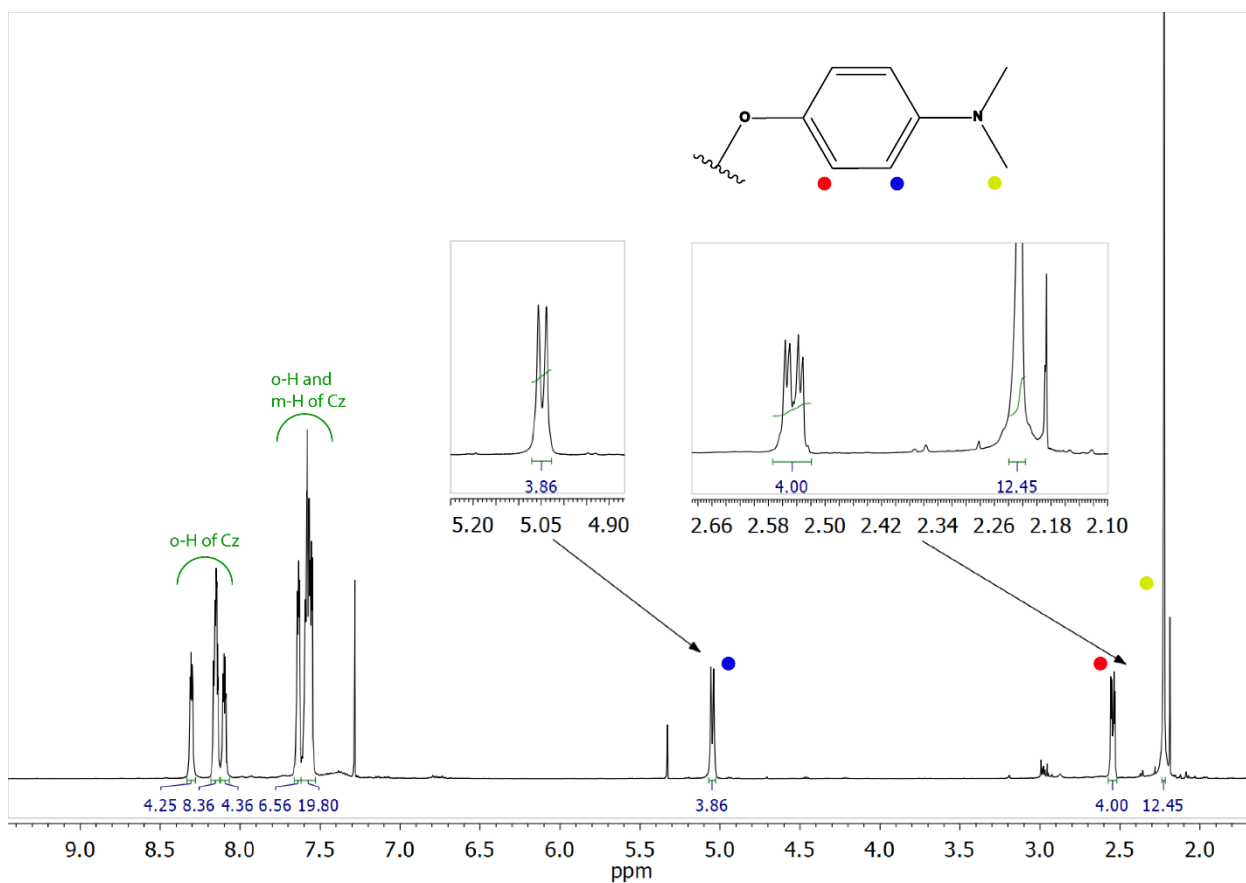


Figure S4.  $^1\text{H}$  NMR spectrum of  $[\text{TPyzCAP}(\text{OPhNMe}_2)_2]$  (**2b**) in  $\text{CDCl}_3$

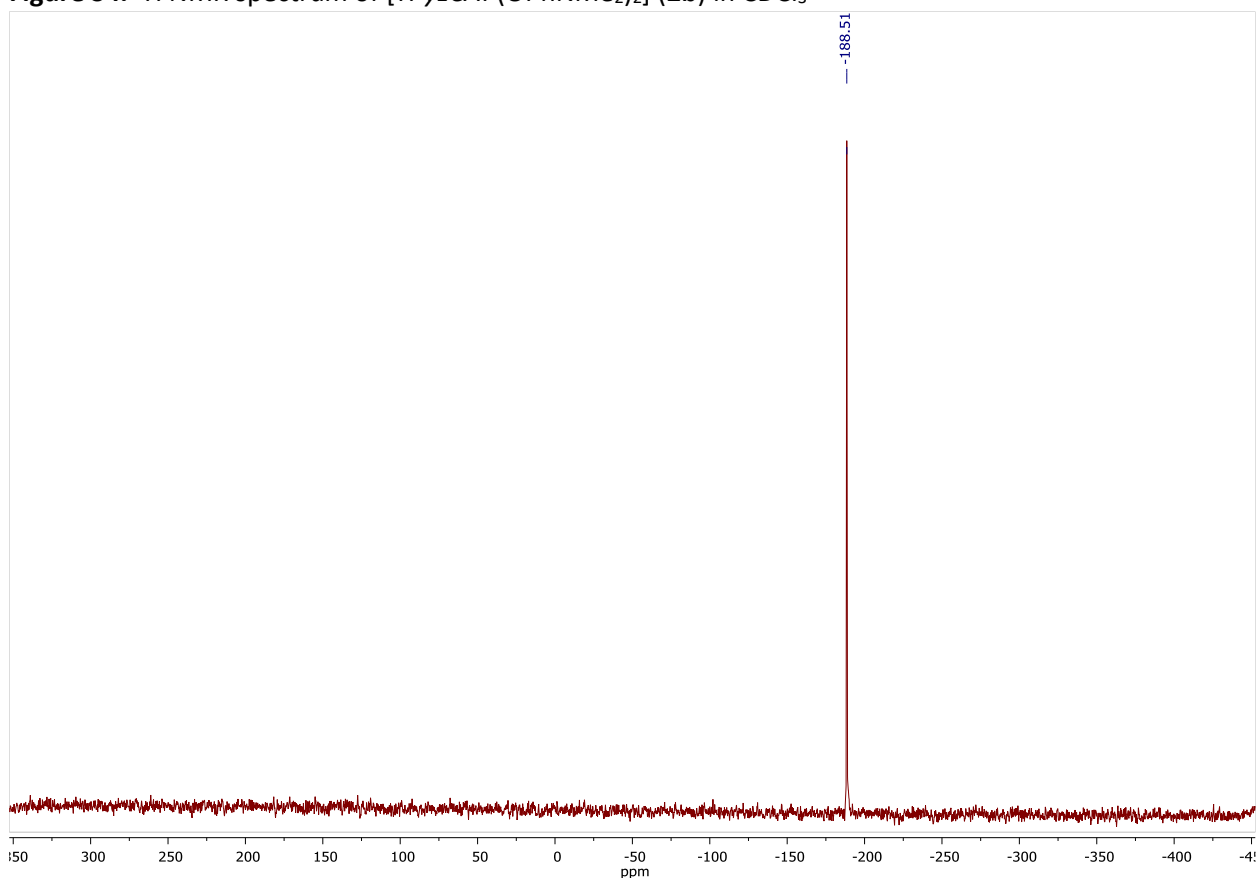


Figure S5.  $^{31}\text{P}$  NMR spectra of  $[\text{TPyzCAP}(\text{OPhNMe}_2)_2]$  (**2b**) in  $\text{CDCl}_3$ .

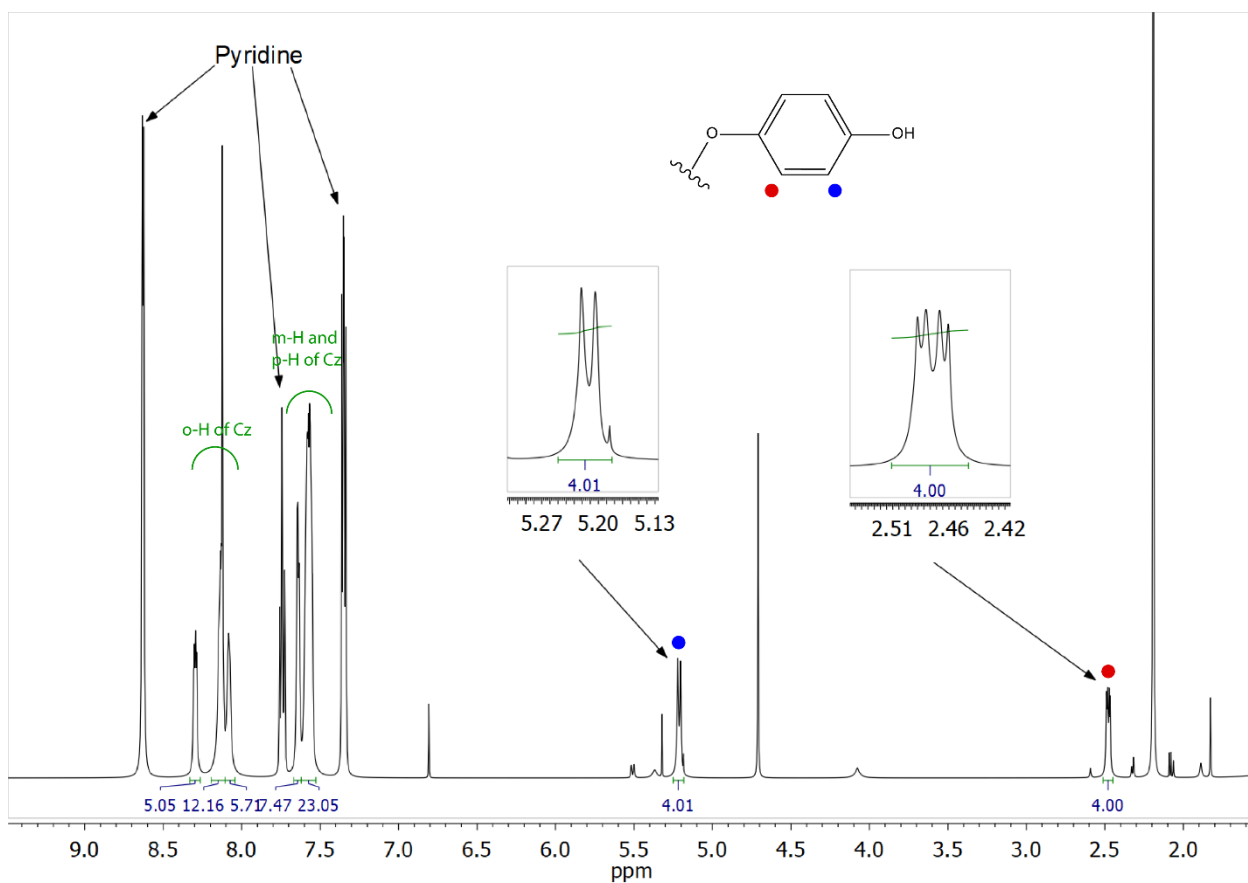


Figure S6.  $^1\text{H}$  NMR spectrum of  $[\text{TPyzCAP}(\text{OPhOH})_2]$  (**2c**) in  $\text{CDCl}_3$

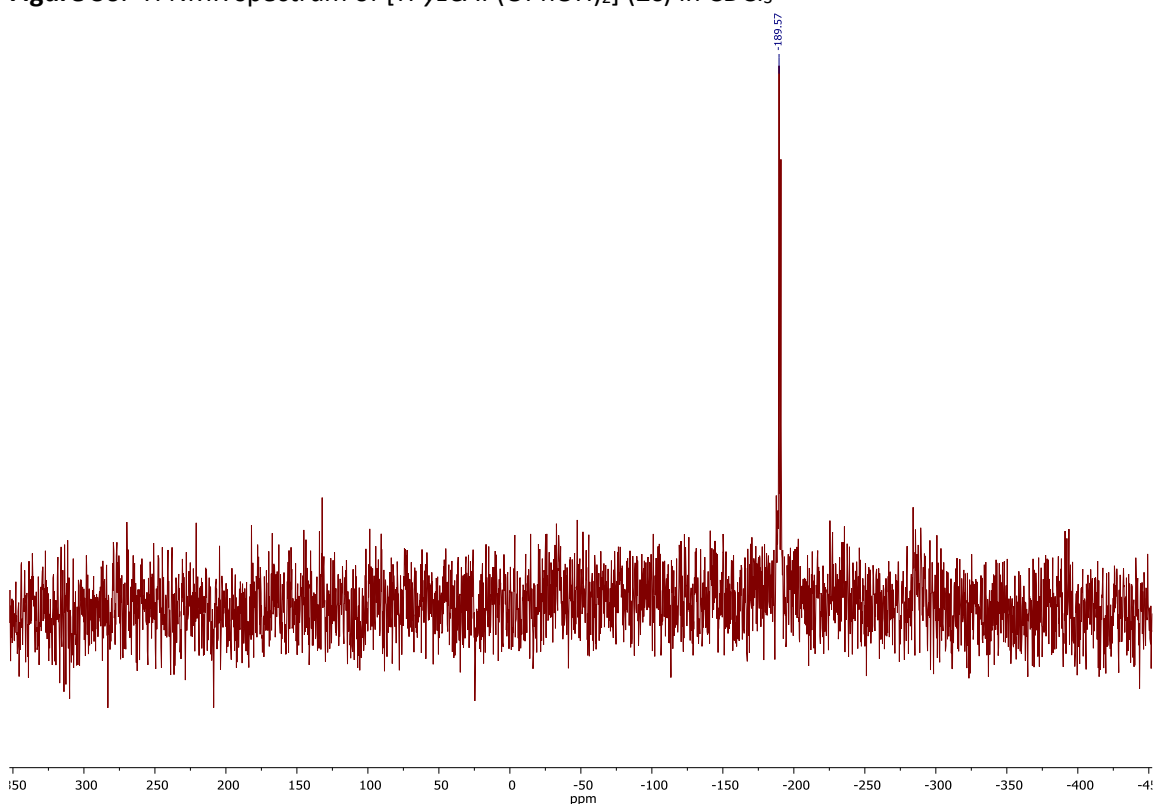


Figure S7.  $^{31}\text{P}$  NMR spectra of  $[\text{TPyzCAP}(\text{OPhOH})_2]$  (**2c**) in  $\text{CDCl}_3$ .

## II. DFT Calculations

Table S1. Cartesian coordinates of TPyzCAP(OH)<sub>2</sub> at B3LYP/cc-pVDZ level of theory:

C	-2.35090794196888	2.65989752311006	0.22687104099568
C	-1.10463815539405	3.34346813449046	0.21759221819201
C	-0.09264179734503	2.38512161953451	0.57307902804273
C	1.28570990378913	2.27169612558713	0.74977647624637
C	3.00337198501601	0.87443182605268	1.34175347627922
N	3.60056896661618	-0.22468612126339	1.78202963370732
C	2.87521290607832	-1.30475267714308	2.03372076464481
C	3.38381349077329	-2.54269582996315	2.58987931129150
C	2.31580116908487	-3.45393916559232	2.68717486314830
C	1.12029471470368	-2.79385488738096	2.21093367445765
N	1.49913924707663	-1.50409695316857	1.82533689835738
N	1.65410941991308	0.99920401284882	1.13873871002494
N	-0.74627712900605	1.18416378337332	0.79101942458644
C	-2.09719146714351	1.26317006797125	0.54848261713899
N	-2.93529688991941	0.23977061554314	0.60672567443468
C	-2.48253932240738	-0.95398444082630	0.96174638015763
N	-0.07958197520026	-3.33792437694923	2.12457639613520
C	-1.13533833005280	-2.66407656921065	1.70447796076035
C	-2.45403118731050	-3.21440425037598	1.45629565824863
C	-3.26836272441577	-2.17165466539258	0.97658229798145
N	-1.19527593767460	-1.30688807273604	1.38605201950191
C	2.49761645779699	3.04362962130642	0.66027181573153
C	3.57101780281690	2.17174822728059	0.99135218061706
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C	-2.15479157072349	5.28728797696735	-0.31571477282733
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C	5.06130169426149	3.81166347895720	0.47684206398989
N	4.61938527377222	-2.83284101649797	3.01350162973134
C	4.79488134236733	-4.06689216962883	3.50083577893492
C	3.72230286032424	-5.04648403221515	3.47592402218475
N	2.48053486410657	-4.71439617335477	3.10781145126767
N	-2.90950424137449	-4.46208279036056	1.62081182263932
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C	-4.94351128283036	-3.64080473587350	0.56808612245982
N	-4.50630061054036	-2.37702138033582	0.51350833713540
C	-4.73888433924092	5.34046998708516	-0.03351303300045

N	4.84557114568296	2.54760028857158	0.87079870005752
C	-5.89632493616414	4.72759810691004	-0.54626025169542
C	-7.14893832127258	5.31836469168470	-0.37322595910843
C	-7.26966867837979	6.51786799450931	0.33693769217108
C	-6.12626026581431	7.12839853521593	0.86175435315843
C	-4.86945231144382	6.55089083785294	0.67127565291374
H	-3.98783062571724	7.03162651503753	1.09750752909190
H	-8.25116314497571	6.97297374409864	0.49206946718306
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H	-5.79911758949179	3.77361840151920	-1.06600646487168
H	-8.03586855825777	4.83232293192431	-0.78700155447075
C	-1.98426855954655	6.69049228394417	-0.78778514366531
C	4.13270267019267	6.21635558835098	0.15024992603424
C	6.48042636224772	4.13102980071710	0.15017507798923
C	6.14665321919219	-4.32431446991389	4.07580885054663
C	3.90793075752711	-6.48693360100813	3.81315468883985
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C	-6.21763920671595	-3.88569678473377	-0.16754231888392
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H	-1.27011897951613	10.28557134756906	-2.14416618108791
H	-3.21442439120377	8.98066319273451	-3.00946478761251
H	-3.66807031603957	6.70362611964270	-2.15610374058882
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C	5.09627234562044	6.94426405859432	0.87161259608850
C	5.21658151564485	8.32418350279930	0.70069992269252
C	4.38055473654235	8.99823968246794	-0.19597379226394
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C	7.51204336575086	3.48359422124600	0.85616920264874
C	8.85017763318372	3.72559129818542	0.53990701416984
C	9.18339356022778	4.60454849883821	-0.49715647161474
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H	2.49104759549381	6.35328569220188	-1.24380780812208
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C	6.33785062061262	-5.08393276309152	5.24461385347561
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C	8.55060245589733	-3.94285868806487	3.97444676622847
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H	9.40982200788990	-3.48772684541608	3.47575727001775
C	5.01007219420325	-7.22066910746436	3.33931469927424
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C	3.06645854817068	-8.50108111484562	4.88849304762987
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C	5.13940353985132	-8.57711357478338	3.64224046294202
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H	5.99621129068165	-9.13663571619926	3.25977680300779
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H	-7.52408979735491	-7.64691015508259	2.60548747579541
H	-6.02455481259628	-9.62160263563035	2.35435082088478
H	-2.82085408138768	-6.99461878566810	1.12053257910928
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O	0.14844856484520	0.16871753941302	2.95638858120318
H	-0.72230752293134	0.55376086445622	3.13921135470783
O	0.44243700209446	-0.65378287934735	-0.34068631831982
H	1.28708035132009	-1.10188364359241	-0.49741095462741

**Table S2.** Cartesian coordinates of TPyzCAP(OPh)<sub>2</sub> at B3LYP/cc-pVDZ level of theory:

C	-2.54511007480660	2.15379568571405	0.18353276053760
C	-1.61858957196274	3.22544941279462	0.07922878101292
C	-0.30205222396535	2.72174167188643	0.43622519584132
N	0.85771687793744	3.35493208820809	0.47640839806553
C	1.94732861482879	2.68368763006513	0.80984295784035
C	3.40617481164348	1.00820128751665	1.40792792418353
N	3.90114377875239	-0.17164745607079	1.73120303295016
C	3.14357873530105	-1.24781197489429	1.82876261487056
C	3.59860440449425	-2.56341619184179	2.22010415680054
C	2.48737921230334	-3.42343359960563	2.21138373885915
C	1.32069978416526	-2.65161321048571	1.83563721465034
N	1.77020991911936	-1.34353318346980	1.59418164082208
N	2.07075038721815	1.32798991538607	1.15386867817161
N	-0.48277787089220	1.39393604098605	0.73275279514141
C	-1.79682462618872	0.98868401660610	0.57539833793230
C	-1.95168830267370	-0.37552952390881	0.80738765137215
N	0.09093924671150	-3.13087380618337	1.75152776857308
C	-0.89425628549363	-2.32013075435714	1.40541261479498
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C	-2.96492356288786	-1.39469660219609	0.88232481273019
N	-0.74703150803293	-0.98953610972558	1.10312491071722
C	3.27887098224141	3.24884020724450	0.88491552591730
C	4.17207686140698	2.22281645713306	1.23704647608587
N	-3.85641277114919	2.32013301258400	-0.01762208459304
C	-4.24559366695210	3.55013445794594	-0.37667430879005
C	-3.28132563817335	4.60428508860956	-0.62292046837903
N	-1.98195048387420	4.43845918151023	-0.34222284665215
N	3.66851896483384	4.51770668405108	0.72199420931459
C	4.97908027664050	4.74788758614347	0.86528536444015
C	5.91721421766690	3.66079091391139	1.08077015323956

N	4.81713404538608	-2.96377551150992	2.60158119007572
C	4.92820830699091	-4.25575515555048	2.93138583519959
C	3.81286279538980	-5.17272150250184	2.77819712379868
N	2.58860712510401	-4.73272545929562	2.46415639851004
N	-2.99099666156104	-3.72348301096944	1.50617417369974
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C	-4.95411700164865	-2.48461198047930	0.78106966626038
N	-4.27354018956972	-1.34364340786380	0.61302654009375
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N	5.49440066710283	2.41283372806386	1.31354931375510
C	-6.51630150944387	2.68952843549932	-0.96354185621636
C	-7.90649844943813	2.81025452219727	-1.00626870308159
C	-8.52868146266845	3.96231569915171	-0.51313135783961
C	-7.75011963906871	4.99222274966475	0.02492459770469
C	-6.35841380465243	4.88277959639331	0.05104452617838
H	-5.76318096510183	5.69162197294403	0.47749479621582
H	-9.61710166113047	4.05527372555087	-0.54247671865164
H	-8.22824864486306	5.88772414380435	0.42887272020237
H	-6.02777627440930	1.78189227687886	-1.32098631315269
H	-8.50541293440147	1.99707876223426	-1.42330288795068
C	-3.61790967431549	5.91997590357807	-1.23719611092666
C	5.36153367291197	6.18841552527850	0.83258950855140
C	7.39924763234450	3.81033194534086	1.01680055384338
C	6.25239864463889	-4.63775512221252	3.50020960998851
C	3.92480197291660	-6.65409985506230	2.90260889034565
C	-5.05003774673568	-4.89739099086077	1.74021512747840
C	-6.37585154055593	-2.42665424087366	0.33609324775700
C	-2.95327178529984	7.07508007795914	-0.78617215979522
C	-3.20471784330949	8.31475462487409	-1.37580884034048
C	-4.10477287081233	8.41718111708303	-2.44188173029880
C	-4.74979148077111	7.27002415129382	-2.91539291927730
C	-4.51355926066651	6.03139868657864	-2.31607240577855
H	-2.23223114527842	6.98328150213935	0.02736131400275
H	-2.68923298933263	9.20431747566502	-1.00581321334474
H	-4.29716133455872	9.38673382552724	-2.90773526271436
H	-5.43958567200836	7.33763945580982	-3.75998459670373
H	-5.01680495162242	5.14315565245753	-2.70090532059049
C	4.69579411736696	7.05280885927024	-0.05563762733148
C	6.30447972862053	6.72968561998657	1.72499383851254
C	6.58494226457970	8.09740212312210	1.71590641829737
C	5.93740637437478	8.94421273532153	0.81048415977260
C	4.99090984143184	8.41672477576332	-0.07442614992907

H	6.81155194305130	6.08158407252506	2.44134983493000
H	7.31212156539692	8.50346429554485	2.42311690798894
H	6.16457573954854	10.01305586479337	0.79971149149576
C	8.20101299757086	3.06685012669626	1.90197071594694
C	9.59294737001342	3.14170794840173	1.83298202669525
C	10.20730032606700	3.94068227773834	0.86275702120097
H	7.71518303557545	2.42477407593166	2.63809966665940
H	10.20120494890437	2.56733836032741	2.53596574516414
C	9.41890477295463	4.66248138978004	-0.03925235320961
H	11.29716937192140	3.99507058452026	0.80478737610474
C	8.02614071068571	4.60316413747332	0.03869890367690
H	9.89016013703904	5.27446484674086	-0.81202773609606
H	7.42293202782541	5.16525661157113	-0.67580780144320
H	4.47366380574990	9.07243103862753	-0.77909413869572
H	3.93930830982388	6.63885541688500	-0.72383737884141
C	7.41882104208261	-4.05888090464977	2.96780581230890
C	6.36681112759028	-5.49077961462308	4.61265430000612
C	7.61803284072552	-5.76951962369150	5.16594386590917
C	8.66989185152270	-4.35304738922091	3.51199342652217
C	8.77446104390523	-5.21041492457381	4.61249967485035
H	5.47201091585328	-5.92752494903174	5.05866364914392
H	7.68845904585464	-6.42544637723907	6.03690953434274
H	9.75334909848609	-5.43649549944109	5.04238095153264
H	7.32704296787061	-3.36984454143455	2.12698271230718
H	9.56733067949215	-3.90465525304223	3.07884875847505
C	5.01879828834986	-7.36581205140303	2.37811832548472
C	2.86370336455638	-7.37369813191784	3.48196712344843
C	2.91191162466136	-8.76595632122245	3.56570047763726
C	4.00884741368670	-9.46438905193388	3.04987477629480
C	5.05621762285917	-8.75978032486459	2.44759168619512
H	1.99938740128872	-6.82410300561811	3.85748309802330
H	2.08505278535791	-9.30892112855331	4.02996528904057
H	4.04427284977855	-10.55490626820766	3.11041023130222
H	5.83917564412540	-6.82912809590603	1.89924891630212
H	5.90830125724026	-9.29803741500262	2.02563197603538
C	-6.26986535075832	-4.83193694387864	2.43758627924887
C	-4.46347672989040	-6.15668494183053	1.51759555070147
C	-6.89346959346908	-5.99829517576952	2.88468281256002
C	-5.09795214128794	-7.32194626553308	1.95030348946785
C	-6.31589777525605	-7.24732220028362	2.63450999469724
H	-6.72715471526921	-3.86372024846654	2.64672966732194
H	-7.83478518082426	-5.92947152376040	3.43506211602644

H	-6.80980870303609	-8.15922424050665	2.97882592906840
H	-3.50025553529345	-6.20565446949214	1.00771560051698
H	-4.63497913834932	-8.29300522711392	1.75887831356455
C	-7.11894651973400	-1.25549975746426	0.57187063962276
C	-6.97389642837221	-3.47483470060850	-0.38636282403238
C	-8.43882990906162	-1.15139616084215	0.12894031641849
C	-8.28765465965958	-3.35991501130713	-0.84496930448102
C	-9.02855116924704	-2.20343749849446	-0.58024100015236
H	-6.64534498070956	-0.42737124170537	1.10113086502109
H	-9.00654367449188	-0.24109126906161	0.33613300413191
H	-10.06025924104314	-2.12058090798405	-0.93076689495920
H	-6.40558614868824	-4.38058164158956	-0.60325986186988
H	-8.73397270754266	-4.17915228185126	-1.41361516984136
P	0.71720656960240	0.09171561137100	1.15743192804552
O	0.46021634418059	0.26174224953671	2.87244822693747
C	0.36111549549461	1.41423527639119	3.62279813551062
O	1.04440624951389	-0.08426106145729	-0.54489598479802
C	1.03575223224200	-1.22868511189183	-1.31388688889312
C	-0.13739563240064	-1.63374926496355	-1.96588306941943
C	2.23316032578305	-1.92460319964571	-1.53518425289087
C	-0.11344065478705	-2.74286651100566	-2.81579900760785
C	2.24693784836151	-3.03228084455746	-2.38652814382894
C	1.07463307622250	-3.44998127898295	-3.02465300596477
C	1.49916837698177	1.92251220069376	4.26575970076150
C	-0.88799186892255	2.01317517626596	3.83839875088652
C	1.38713896562756	3.03730898138430	5.10042593238304
C	-0.98994799802773	3.12771469574957	4.67532582642376
C	0.14558057807262	3.64813748879821	5.30378188344153
H	-1.05568755421861	-1.06309490424768	-1.81859817924031
H	3.14872296529234	-1.57768893023959	-1.05327284703379
H	-1.03137172281555	-3.05161798690332	-3.32208650464655
H	3.18382631851382	-3.56894391823187	-2.55476836347558
H	1.08937536803979	-4.31631678378557	-3.68969399640609
H	2.45977589185466	1.42512667016561	4.12183688800705
H	-1.77430668463013	1.58770546862797	3.36515172067198
H	2.27812885658840	3.42713745380290	5.59864985391315
H	-1.96726327152684	3.58806258135175	4.84024710017821
H	0.06188319485118	4.51934760700147	5.95725156156560

**Table S3.** Cartesian coordinates of TPyzCAP(OPhOH)<sub>2</sub> at B3LYP/cc-pVDZ level of theory:

C	-2.57189201082916	2.17798293003830	0.31014683602189
C	-1.66512868756006	3.27232610094736	0.30451429534804

C	-0.34563905922234	2.76752663212057	0.65592553388300
N	0.81166096056611	3.40580241904853	0.71030116965552
C	1.91163528269960	2.72651795617655	0.99298737276727
C	3.37923756791477	1.03309977957742	1.51448856284308
N	3.87823984340384	-0.14946139340649	1.82488839592886
C	3.12140985353966	-1.22563216946514	1.93160456983400
C	3.57061139509215	-2.53255561943981	2.35925049207658
C	2.46117042569228	-3.39578439313936	2.34138677642595
C	1.30354339708905	-2.63569707177621	1.91265611323912
N	1.75564674140705	-1.32799425354468	1.66773570867560
N	2.03723823983713	1.36940002691579	1.33327414036197
N	-0.51348637537307	1.42389341612264	0.88036906399459
C	-1.81296506511284	1.00582310944497	0.65536017643178
C	-1.95130866853980	-0.37122877929724	0.80786829524842
N	0.08048523357457	-3.12280837632561	1.78491738045618
C	-0.89926421049252	-2.31931992000607	1.40404438322713
C	-2.31084890852156	-2.60828614349601	1.19860429366234
C	-2.95176493172667	-1.40423897459229	0.80030286659935
N	-0.75365505249992	-0.98196792568316	1.13149494945888
C	3.25525650178686	3.26979409144924	0.96903540769392
C	4.15181516400703	2.23139540578374	1.27489658650821
N	-3.87968864464490	2.32885462606315	0.06998136283718
C	-4.28279804091435	3.57425929203358	-0.21053420768871
C	-3.34050930199335	4.66873244963977	-0.33075112322988
N	-2.04420016753345	4.50731537810407	-0.03213893737411
N	3.66529347999071	4.51666953938271	0.70716813443252
C	4.99065934020289	4.70527968164066	0.69952274084114
C	5.91569963303894	3.60170351207275	0.88260507371599
N	4.77954898393405	-2.91818981738573	2.78399240164532
C	4.88451005725642	-4.19952733546156	3.15589226098975
C	3.77217245407094	-5.12096236196448	3.01021079538451
N	2.55713135950971	-4.69631601947810	2.64283970794307
N	-2.99426897948311	-3.74061686098610	1.38447988289010
C	-4.30774089249023	-3.69041265698031	1.12377398666403
C	-4.92217231256569	-2.50687484402483	0.55465754236342
N	-4.23827094039232	-1.36059417814848	0.44619793493249
C	-5.75973096995931	3.73620217401058	-0.34376023351561
N	5.47908087268585	2.38164928111287	1.21848073147546
C	-6.49434628410629	2.79244206997721	-1.08289189429757
C	-7.87925712550896	2.91856863412909	-1.21386073158927
C	-8.55284537780497	3.97004939861081	-0.58222848202474
C	-7.83465477778498	4.88889196672926	0.19044525214038

C	-6.44776047786125	4.77858725564485	0.30306479092388
H	-5.89420998841422	5.50514310288633	0.89985017407685
H	-9.63541611279832	4.07344084735181	-0.69113402124493
H	-8.35742151799974	5.69900461029126	0.70415102815972
H	-5.96565555995484	1.96445485448366	-1.55748473618392
H	-8.43421300135095	2.19324175984749	-1.81314418340288
C	-3.70944638920291	6.03316709259343	-0.80523063793536
C	5.41839851656876	6.11781774276727	0.49218702667189
C	7.38893952958137	3.67752815808383	0.65781533930130
C	6.20389605619896	-4.57011965359917	3.74525569195808
C	3.88578716444297	-6.59443597854177	3.21123687670255
C	-5.06307941350673	-4.91284421627422	1.51791956609888
C	-6.30451011949576	-2.44469188374900	-0.00025014177192
C	-3.07376197887929	7.14871456865621	-0.22903284375108
C	-3.38199468296770	8.44192507998007	-0.65509549997144
C	-4.31357089006685	8.64169198122272	-1.68028750438440
C	-4.92250806932829	7.53730981539050	-2.28536971448907
C	-4.62685529272522	6.24401251070171	-1.85084632886120
H	-2.33217256246465	6.98203019237177	0.55340023763070
H	-2.88813816564133	9.29562416322784	-0.18453257179565
H	-4.56240952909052	9.65154226628671	-2.01689033737050
H	-5.63343685169372	7.68348404953824	-3.10193211197932
H	-5.10786865685525	5.39440692180431	-2.33645149669164
C	4.73249858331854	6.90398383567138	-0.45095333879704
C	6.45165454419575	6.70570932707562	1.24336775076863
C	6.81296643005348	8.03709635116779	1.02878269535486
C	6.15546181174343	8.79765662763251	0.05567898585746
C	5.10877591835825	8.22860566432823	-0.67786432513160
H	6.97607602760103	6.11920421245935	1.99962265447772
H	7.61343043282090	8.48191170019399	1.62463805342418
H	6.45920701949759	9.83082396060196	-0.13168139352608
C	8.23289810629293	2.87682440147584	1.45089942299234
C	9.60752679331534	2.84212095838827	1.21527954994852
C	10.16163214710686	3.59051945835670	0.17077093752946
H	7.78744638638841	2.26942082728285	2.23962508041324
H	10.24894486320669	2.21920103314416	1.84320631705734
C	9.33146751776699	4.38061215344740	-0.63068885946479
H	11.23589815298517	3.54934455648878	-0.02685846777865
C	7.95676580274401	4.42713465855498	-0.38912015675616
H	9.75503574262329	4.95954255357976	-1.45491817521485
H	7.32123172936840	5.03589136958253	-1.03271729098808
H	4.57849798832158	8.82089035885550	-1.42732082325482

H	3.90496076230611	6.45782399047974	-1.00456942580817
C	7.37251292099911	-4.00615072265258	3.20136742275502
C	6.31780241529502	-5.40874596888157	4.86900219716942
C	7.57068606434404	-5.69815281633716	5.41329872742028
C	8.62525376429397	-4.30945500828454	3.73748606758185
C	8.72939284111621	-5.16192065868947	4.84230176168567
H	5.42421608745877	-5.83457831105660	5.32749738658457
H	7.64186787403330	-6.34681098033618	6.28953403571513
H	9.70756919334488	-5.40756795789143	5.26403051364426
H	7.27994044986740	-3.32411047794516	2.35519784387116
H	9.52195361194128	-3.87239689073220	3.29094605542779
C	4.98229310265241	-7.32673518051154	2.72068891634848
C	2.83824974013020	-7.28494813307930	3.84709746371605
C	2.90668322761818	-8.66781538031048	4.02830219446938
C	4.01074846934106	-9.38442659820648	3.55379627340540
C	5.03984230922164	-8.71170246609831	2.88659901704053
H	1.97228584524840	-6.72098912643029	4.19637007754100
H	2.09306696762760	-9.18899147244558	4.53832296409204
H	4.06729598289044	-10.46608849116841	3.70008647709501
H	5.79072888779422	-6.81161667732062	2.20014564438420
H	5.89370001595230	-9.26844138987155	2.49339534359770
C	-6.27673023856520	-4.82942365004935	2.22236427587686
C	-4.51022010255567	-6.18069953633455	1.26507494033612
C	-6.92580065394325	-5.98822210801414	2.65222822725147
C	-5.17395947451775	-7.33880938102314	1.67306832807510
C	-6.38353767802035	-7.24641381906621	2.37002729642174
H	-6.70650019802835	-3.85278762677238	2.45283730919140
H	-7.85989349586722	-5.90618257688154	3.21267353565849
H	-6.89885582692183	-8.15072149027519	2.70298028930836
H	-3.55092596864770	-6.24474593789341	0.74966288026464
H	-4.73809520146053	-8.31583902948370	1.44955881088113
C	-7.00834197281975	-1.22741293667399	0.08129665965618
C	-6.89256240362676	-3.51970215506241	-0.69229335379065
C	-8.27373438800289	-1.09676242256289	-0.49123537568150
C	-8.15390288000797	-3.38085054956970	-1.27586298332550
C	-8.85258248910503	-2.17385844296599	-1.17127398529078
H	-6.53695852082910	-0.38207433288407	0.58361290400246
H	-8.80646347948061	-0.14645832316241	-0.40914429766361
H	-9.83968943358680	-2.06944424340222	-1.62835549233612
H	-6.35550735740605	-4.46283606392899	-0.79805051494406
H	-8.59106162538684	-4.22125427978833	-1.82013092659628
P	0.69459642896870	0.11586561053323	1.26827764080529



O	0.40686043110744	0.19718154656408	2.97968595569391
C	0.24164122457532	1.29854448740335	3.79563590562904
O	1.03611704641607	0.02453981974602	-0.43585990941493
C	1.18031795821755	-1.09051064154161	-1.23807324225059
C	0.07054004389204	-1.66400442587891	-1.87664523577502
C	2.46337534830700	-1.56811614014670	-1.53301579912627
C	0.23913242565703	-2.70294590749281	-2.79078943592939
C	2.63518696846303	-2.60524850198145	-2.45409420700150
C	1.52383223961008	-3.17763584205255	-3.08813233839813
C	1.34900874285605	1.87386339041818	4.43807433831863
C	-1.04487767926728	1.75390156434168	4.10714963876069
C	1.17302025500320	2.89010083492145	5.37532273903529
C	-1.22401103819922	2.76998637901141	5.05088483218119
C	-0.11615529791184	3.34142186615172	5.69136952705712
H	-0.92606070353888	-1.26861057833522	-1.67414180753335
H	3.32706775092997	-1.10015699929132	-1.05606001024421
H	-0.61542568010306	-3.15431880744286	-3.29884940078106
H	3.64169980455516	-2.96424355302701	-2.69281844351927
O	1.62498861877788	-4.18257866875165	-4.01047756143642
H	2.34851432761806	1.49495863880900	4.21811777180820
H	-1.90603135569856	1.28343573071447	3.62825114822378
H	2.02490188180845	3.34073982722280	5.88846110168865
H	-2.23326182806932	3.11233884291694	5.30245415361178
O	-0.22369667719709	4.32377430394462	6.63730000478701
H	2.55768142375814	-4.42458510109154	-4.10910748346065
H	-1.15969781167582	4.54115192211570	6.75882184475832

**Table S4** Cartesian coordinates of TPyzCAP(OPhNMe<sub>2</sub>)<sub>2</sub> at B3LYP/cc-pVDZ level of theory:

C	-2.55979593943177	2.24510023672540	0.30701895280517
C	-1.63204848292078	3.32166850148458	0.27157123631487
C	-0.31051882686447	2.78879420882344	0.57180590496087
N	0.85959532335321	3.40527368036364	0.60087280004493
C	1.95248149218215	2.71071810147162	0.87832405525823
C	3.38451803110030	1.00219568669652	1.44275260433992
N	3.86174937133899	-0.18504378079569	1.77257381194364
C	3.08763227800640	-1.24800005544892	1.87536473471210
C	3.51623816081055	-2.56258832975798	2.30115546214278
C	2.39702075851493	-3.41214935249041	2.26696632866527
C	1.25306138388830	-2.63576420339492	1.82947432007941
N	1.72565149161056	-1.33431683918364	1.58922126231956
N	2.05220322037504	1.36127406257121	1.25332433099673
N	-0.49884337215591	1.44530023026677	0.78753258428437

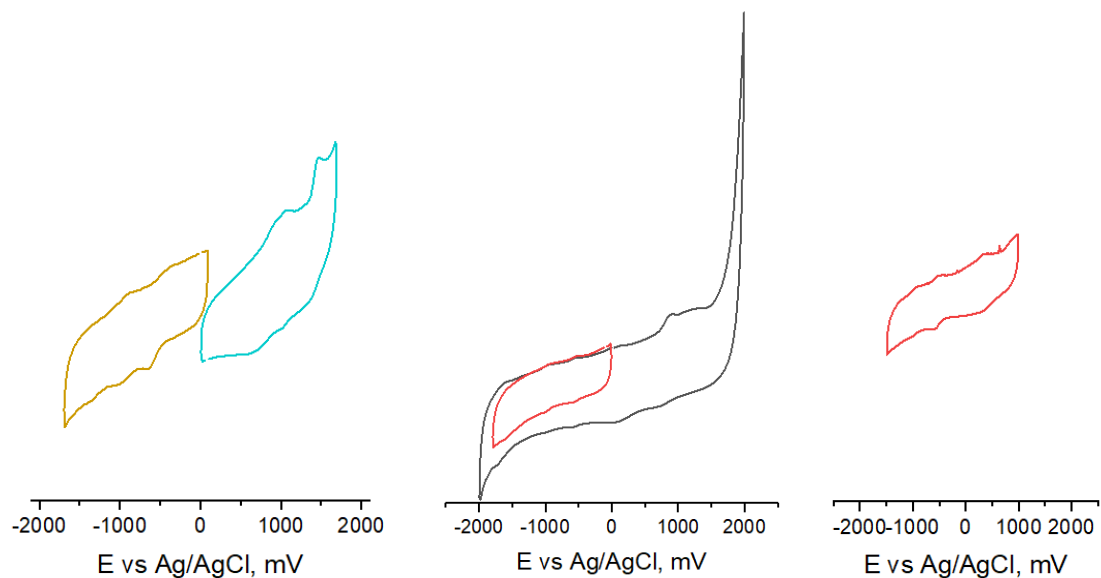
C	-1.81142325791789	1.05382129723387	0.60387391249918
C	-1.97681345628890	-0.32111716493487	0.75805666230619
N	0.02304706437547	-3.10449640837625	1.70799466845733
C	-0.94860208959291	-2.28613939734065	1.33369231106354
C	-2.37383314366516	-2.54418145938960	1.19138721201842
C	-3.00492435454293	-1.32547114006923	0.81959262199770
N	-0.78230320745151	-0.95855247523429	1.03653379133237
C	3.30921434786085	3.22171661664624	0.82000755101399
C	4.18326786537415	2.17178116689637	1.15441495955785
N	-3.87480398276491	2.42523407898303	0.14360643609709
C	-4.26795770306697	3.68176730330978	-0.09880103627863
C	-3.30967099987625	4.75439766232537	-0.27007501622749
N	-2.00340716835123	4.56613933296957	-0.03907476413979
N	3.75279284888227	4.44265947165754	0.49626005918784
C	5.08341960437178	4.58726917141197	0.44771937438995
C	5.97872149515967	3.46456526027233	0.65480619258719
N	4.71710662802111	-2.96630419865533	2.73028682707830
C	4.80411622237706	-4.25201549644375	3.09263937720696
C	3.68023489957806	-5.15663450004480	2.93923836489855
N	2.47332468377514	-4.71455505178977	2.56479378746139
N	-3.07223896378431	-3.65773367644464	1.42557257932680
C	-4.39925244678988	-3.57256419667861	1.25796277646079
C	-5.02003909448641	-2.36997690383464	0.74302578953500
N	-4.31416911315279	-1.24531071301131	0.56781665561622
C	-5.74716215654298	3.87476780995762	-0.12316173464123
N	5.51170502552070	2.27743576827266	1.05982667487875
C	-6.55451082496961	2.92546025844979	-0.77455873682931
C	-7.94412038908226	3.06517424654806	-0.78496684246594
C	-8.54893792842621	4.13701182337715	-0.11871068547816
C	-7.75571854382972	5.06524753000658	0.56388810602785
C	-6.36521755470741	4.94112693418533	0.55527476762650
H	-5.75468681352682	5.67254579346116	1.08674837527260
H	-9.63613739773424	4.24880571968852	-0.12783485009202
H	-8.22300321436632	5.89285096303415	1.10283388948066
H	-6.07802313589629	2.07881060499579	-1.27087688254104
H	-8.55683986877177	2.33279475898271	-1.31532855127995
C	-3.67643153538503	6.12318828780401	-0.73245973440895
C	5.55102728712500	5.97436480571185	0.16769069824113
C	7.44496312083032	3.47235197636752	0.37374327234817
C	6.11962381179359	-4.64389165883770	3.67747398412788
C	3.76996600483985	-6.63215635447687	3.13989917222929
C	-5.15561136705424	-4.77946718982450	1.69760998038812

C	-6.44865306550345	-2.26367011436646	0.32909252750067
C	-3.00489792252107	7.23290276269597	-0.18731659899164
C	-3.31302751900997	8.52772764212186	-0.60900273005873
C	-4.27908653439341	8.73390131529005	-1.60058365088572
C	-4.92533528982823	7.63431287848322	-2.17507195546334
C	-4.63111451909301	6.33997119300695	-1.74269119695829
H	-2.23630799999625	7.06050206866670	0.56746326766293
H	-2.79168236699400	9.37776742087061	-0.16193605999917
H	-4.52606644525783	9.74496240694806	-1.93498981900126
H	-5.66429622999173	7.78542602853482	-2.96546703058971
H	-5.14165529543112	5.49279430836311	-2.20219431495015
C	4.87899307115755	6.73705781167773	-0.80388167453749
C	6.61339608950025	6.56212769046907	0.87683279408078
C	7.01395229086060	7.86984218513093	0.59593465590449
C	6.36762449372992	8.60567523446010	-0.40339332088706
C	5.29420448085277	8.03685014116742	-1.09740592261491
H	7.12984422777852	5.99321699285363	1.65203070344050
H	7.83691138698354	8.31515970130635	1.16005630263857
H	6.70138233670493	9.61867238037279	-0.64270835039378
C	8.28230888798122	2.64684468248013	1.14869737149233
C	9.64157240643567	2.53603697158378	0.85608551973657
C	10.18853747380270	3.23402396383917	-0.22642264255553
H	7.84114368243448	2.07721038117278	1.96724538266470
H	10.27624388990590	1.89236040381450	1.46987438521600
C	9.36554922872833	4.05145843465168	-1.00753196358778
H	11.24903640215276	3.12956795756441	-0.47014716943098
C	8.00635764182769	4.17268876481328	-0.71030846144199
H	9.78120287496450	4.59258283581336	-1.86105187785776
H	7.37609568920690	4.79856280056146	-1.34226227215004
H	4.77334513476102	8.60994103176519	-1.86819226668293
H	4.03132482969250	6.29218056155330	-1.32732276334212
C	7.29403847893336	-4.09411309122723	3.13142313935370
C	6.22608264554163	-5.48787953968831	4.79775738143823
C	7.47679123977472	-5.79572831855794	5.33718056772701
C	8.54433236606909	-4.41578496600214	3.66246886020157
C	8.64072135376331	-5.27277640483411	4.76449874441249
H	5.32827092380832	-5.90335563227114	5.25751344843865
H	7.54207919501380	-6.44817788314399	6.21109285349551
H	9.61689545087901	-5.53234470993597	5.18261814454705
H	7.20766032581422	-3.40805999982570	2.28783385291898
H	9.44528406534775	-3.98914705693381	3.21429411279406
C	4.85400286815290	-7.38237948251991	2.64914071429026

C	2.71113202504953	-7.30553933310609	3.77550781001210
C	2.75630128430630	-8.68958454453108	3.95574607499641
C	3.84808020432820	-9.42430726932831	3.48064574500149
C	4.88853600966801	-8.76831689264846	2.81434130795451
H	1.85468139816205	-6.72726868337024	4.12494228237888
H	1.93412991350574	-9.19760330404645	4.46544100755207
H	3.88588813326536	-10.50694870687282	3.62593072037576
H	5.67067236080544	-6.88018496798367	2.12874520975171
H	5.73315250323118	-9.33887843296674	2.42094550508247
C	-6.32425494425534	-4.67601320803457	2.47258354151078
C	-4.64128481966279	-6.05721553220354	1.41426706231248
C	-6.96653567223169	-5.82337404848289	2.94236951923859
C	-5.29840827689026	-7.20364191031913	1.86392228412687
C	-6.46331020037138	-7.09082093283889	2.63098191291481
H	-6.72378356121949	-3.69296627655182	2.72810734286485
H	-7.86438607763747	-5.72426146828656	3.55680096221460
H	-6.97309139438105	-7.98598617657141	2.99579644771317
H	-3.71410948630580	-6.13767370145474	0.84530931426734
H	-4.89166077440245	-8.18777205892689	1.61737644475045
C	-7.12859728565551	-1.05249057237152	0.55747578167383
C	-7.11213403429594	-3.29230773238034	-0.36373406178779
C	-8.44684830392855	-0.88550129241483	0.13089578426356
C	-8.42501094611921	-3.11508821684208	-0.80676952517187
C	-9.09932157013073	-1.91520577066906	-0.55588918293539
H	-6.60129938597289	-0.24189160103119	1.06144837853238
H	-8.96224941843095	0.05654559669021	0.33257782860331
H	-10.12644685678253	-1.77982510594882	-0.90406100632339
H	-6.59509106531839	-4.22876228072611	-0.57763125944470
H	-8.92172352269639	-3.91930559930648	-1.35446736232186
P	0.68704547671671	0.12271898406712	1.17867588976574
O	0.42588871945460	0.20564988869975	2.89379443430538
C	0.03409639172506	1.28221526365245	3.66918609265925
O	0.99653091702444	0.03334013432849	-0.52789056640891
C	1.38429450127824	-1.05917944508262	-1.28196553238915
C	0.43280264246026	-1.81175455174569	-1.97765110696511
C	2.74016981498586	-1.35088272580182	-1.47322958770056
C	0.82132013109298	-2.83675675842232	-2.84148866899744
C	3.13740106056551	-2.37274604082479	-2.33255517110736
C	2.18868931373056	-3.14040818255815	-3.05131050794161
C	0.99086986972177	2.04177009196367	4.35103327216722
C	-1.32014743964114	1.53707254737922	3.91295375832277
C	0.60730516370645	3.03658789739012	5.25080413615192

C	-1.71290045286165	2.53240242711040	4.80612369415708
C	-0.75879807451942	3.31566242227449	5.49980886696468
H	-0.62526022384405	-1.57109231272864	-1.85532339689625
H	3.49702714779152	-0.76224695510641	-0.95214861911522
H	0.04429417859069	-3.39712203788996	-3.35980984449825
H	4.20344901453481	-2.56175418171921	-2.45094150894018
N	2.58985954649865	-4.13550740103320	-3.93622660141174
H	2.04934573404834	1.82266834298105	4.19694453614454
H	-2.07842224048999	0.92867667918404	3.41736928489630
H	1.38837567697440	3.59139204376496	5.76888763885655
H	-2.77845224086208	2.68707920594652	4.97018617947056
N	-1.15100309082211	4.30744113122342	6.39413976259574
C	1.59579381412950	-5.00509249914674	-4.53312782228419
C	3.98384152175093	-4.53510764323930	-3.97765293896733
H	4.63556025780532	-3.69892441747882	-4.28704556883703
H	4.10766071178065	-5.33767051626217	-4.71642405701744
H	4.35735599149922	-4.90577343700633	-3.00156432472195
H	1.01840071776776	-5.58563129335986	-3.78491832541184
H	2.09875916331160	-5.71591289161115	-5.20222814625820
H	0.87324932876993	-4.43103703020696	-5.14025762677260
C	-2.54869973689445	4.41584823152131	6.76812695041519
C	-0.15590429178090	4.93806820884730	7.24001431405430
H	-2.94879935317220	3.48863264640880	7.22753668715388
H	-3.18230931989849	4.65493888493618	5.89610359267739
H	-2.66665083252118	5.23200539302021	7.49290009654060
H	0.59115668763776	5.48907895731545	6.64184838782277
H	0.39255646705500	4.21577226274545	7.87880654062266
H	-0.65421723294156	5.66344414276880	7.89676686401594

## III. Electrochemical measurements



**Figure S8.** Cyclic voltammogram of  $[TPyzCAP(OPh)_2]$  in acetonitrile solution with 0.1M tbaClO<sub>4</sub> as supporting electrolyte. Scan rate – 50mV/s

**Figure S9.** Cyclic voltammogram of  $[TPyzCAP(OPhOH)_2]$  in acetonitrile solution with 0.1M tbaClO<sub>4</sub> as supporting electrolyte. Scan rate – 50mV/s

**Figure S10.** Cyclic voltammogram of  $[TPyzCAP(OPhNMe_2)_2]$  in acetonitrile solution with 0.1M tbaClO<sub>4</sub> as supporting electrolyte. Scan rate – 50mV/s.

## IV. TD DFT calculations

**Table S5.** Calculated composition of the lowest excited states and corresponding oscillator strength for [TPyzCAP(OH)<sub>2</sub>].

Excited state	Composition	F	$\lambda_{\text{calc}}$	Type	$\lambda_{\text{exp}}$
[Ph <sub>8</sub> Pyz <sub>4</sub> CzP(OH) <sub>2</sub> ]					
1	HOMO -> LUMO (74%) (1a -> 1a*) HOMO-1 -> LUMO+1 (19%) (1b -> 1b*)	0.35	580.0	Q	-
2	HOMO -> LUMO+1 (69%) (1a -> 1b*) HOMO-1 -> LUMO (25%) (1b -> 1a*)	0.08	568.1	Q	-
3	HOMO-2 -> LUMO (62%) HOMO-1 -> LUMO (9%)	0.12	449.4	CT Ph->Cz	
4	HOMO -> LUMO+2 (69%) HOMO-4 -> LUMO (14%)	0.08	445.9	CT Ph->Cz	
5	HOMO-3 -> LUMO (56%) HOMO-4 -> LUMO (13%) HOMO -> LUMO+4 (9%)	0.17	441.1	CT Ph->Cz	
6	HOMO-1 -> LUMO (29%) HOMO-5 -> LUMO (18%) HOMO-2 ->LUMO (16%)	0.51	433.7	CT Ph->Cz	
7	HOMO-4 -> LUMO (42%) HOMO-3 -> LUMO (17%) HOMO-5 -> LUMO (16%)	0.13	428.4	CT Ph->Cz	
8	HOMO-2 -> LUMO+1 (21%) HOMO-1 ->LUMO+1 (18%) HOMO -> LUMO+4 (13%) HOMO-4 -> LUMO (13%) HOMO-3 -> LUMO+1 (12%) HOMO -> LUMO+5 (9%)	0.21	424.0	CT Ph->Cz	
9	HOMO -> LUMO+5 (21%) HOMO-1 -> LUMO+1 (14%) HOMO -> LUMO+4 (11%) HOMO-2 -> LUMO+1 (11%)	0.13	419.2	CT Cz -> Pyz CT Ph -> Cz	
11	HOMO-3 -> LUMO+1 (21%) HOMO -> LUMO+3 (20%) HOMO-2 -> LUMO+1 (17%) HOMO-1 -> LUMO+1 (10%)	0.30	415.3	CT Ph -> Cz CT Cz -> Pyz	
12	HOMO-4 -> LUMO+1 (38%) HOMO-2 -> LUMO+1 (18%) HOMO -> LUMO+5 (14%)	0.32	406.5	CT Ph -> Cz CT Cz -> Pyz	
13	HOMO-3 -> LUMO+1 (48%) HOMO -> LUMO+5 (21%) HOMO-4 -> LUMO+1 (10%)	0.20	405.4	CT Ph -> Cz CT Cz -> Pyz	
14	HOMO-4 -> LUMO+1 (42%) HOMO -> LUMO+5 (16%)	0.74	400.9	CT Ph -> Cz CT Cz -> Pyz B	-
17	HOMO-5 -> LUMO (19%) HOMO-1 -> LUMO (15%) (1b -> 1a*) HOMO -> LUMO+3 (14%)	1.19	386.5	CT Ph -> Cz CT Cz -> Pyz B	-
19	HOMO-13 -> LUMO (45%) HOMO-5 -> LUMO+1 (13%)	0.21	377.6	CT Pyz -> Cz (impure, make sure (sigma orbs + pi orbs)) CT Ph -> Cz	
20	HOMO-13 -> LUMO (22%)	0.17	377.3	CT Pyz -> Cz	

	HOMO-5 -> LUMO+1 (19%) HOMO-14 -> LUMO (14%)			(impure, make sure (sigma orbs + pi orbs)) CT Ph -> Cz	
21	HOMO-5 -> LUMO+1 (33%) HOMO-14 -> LUMO (13%) HOMO-15 -> LUMO (10%)	0.32	375.0	CT Pyz -> Cz (impure, make sure (sigma orbs + pi orbs)) CT Ph -> Cz	
29	HOMO -> LUMO+6 (90%)	0.24	351.6	CT Cz -> Ph???	
32	HOMO-1 -> LUMO+3 (38%) HOMO-5 -> LUMO (20%) HOMO-7 -> LUMO (11%)	0.17	345.3	CT Cz -> Pyz CT Ph -> Cz	
34	HOMO-1 -> LUMO+4 (27%) HOMO-5 -> LUMO (19%) HOMO-6 -> LUMO (19%)	0.13	342.9	CT Cz -> Pyz CT Ph + Pyz -> Cz	
39	HOMO-7 -> LUMO (45%) HOMO-1 -> LUMO+3 (13%)	0.09	336.0	CT Ph -> Cz CT Cz -> Pyz	



**Table S6.** Calculated composition of the lowest excited states and corresponding oscillator strength for [TPyzCAP(OPh)<sub>2</sub>].

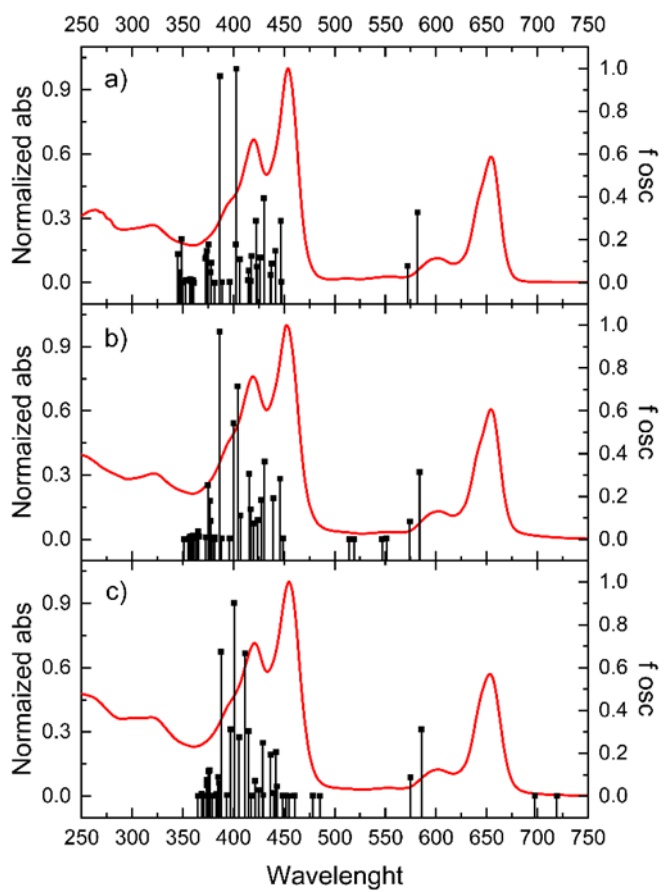
Excited state	Composition	F	$\lambda_{\text{calc}}$	Type	$\lambda_{\text{exp}}$
[Ph <sub>8</sub> Pyz <sub>4</sub> CzP(OPh) <sub>2</sub> ]					
1	HOMO -> LUMO (76%) (1a -> 1a*) HOMO-1 -> LUMO+1 (18%) (1b -> 1b*)	0.33	581.7	Q	655
2	HOMO -> LUMO+1 (72%) (1a -> 1b*) HOMO-1 -> LUMO (23%) (1b -> 1a*)	0.08	572.0	Q	601
4	HOMO-3 -> LUMO (58%) HOMO-1 -> LUMO (25%) HOMO -> LUMO+3 (10%)	0.29	446.8	CT Ph -> Cz CT Cz -> Pyz	
5	HOMO-2 -> LUMO (62%) HOMO-6 -> LUMO (15%)	0.15	441.5	CT Ph -> Cz CT L -> Cz	
6	HOMO-2 -> LUMO (56%) HOMO-4 -> LUMO (24%)	0.09	437.4	CT Ph -> Cz	
8	HOMO-1 -> LUMO (23%) HOMO-2 -> LUMO+1 (19%) HOMO-3 -> LUMO (19%) HOMO -> LUMO+5 (11%)	0.39	430.0	CT Ph -> Cz	
9	HOMO-6 -> LUMO (25%) HOMO-2 -> LUMO (23%) HOMO-1 -> LUMO+1 (16%) HOMO-4 -> LUMO (15%)	0.12	426.3	CT L -> Cz CT Ph -> Cz	
11	HOMO-4 -> LUMO (47%) HOMO-1 -> LUMO+1 (27%) HOMO -> LUMO+4 (10%)	0.29	422.3	CT Ph -> Cz CT Cz -> Pyz	
12	HOMO-3 -> LUMO (35%) HOMO-5 -> LUMO+1 (30%) HOMO -> LUMO+5 (19%)	0.12	417.6	CT Ph -> Cz CT L -> Cz CT Cz -> Pyz	
16	HOMO -> LUMO+5 (34%) HOMO-2 -> LUMO+1 (28%) HOMO-7 -> LUMO (11%)	0.11	406.2	CT Cz -> Pyz CT Ph -> Cz CT L -> Cz	
17	HOMO-3 -> LUMO+1 (36%) HOMO -> LUMO+5 (31%) HOMO-1 -> LUMO+1 (10%) (1b -> 1b*)	0.99	402.7	CT Ph -> Cz CT Cz -> Pyz B	455
18	HOMO-4 -> LUMO+1 (81%) HOMO-6 -> LUMO+1 (10%)	0.18	402.3	CT Ph -> Cz CT L -> Cz	
21	HOMO-7 -> LUMO (16%) HOMO -> LUMO+3 (12%) HOMO-1 -> LUMO (12%) (1b -> 1a*)	0.97	386.4	CT L -> Cz CT Cz -> Pyz B	420
23	HOMO-17 -> LUMO (52%) HOMO-12 -> LUMO (16%) HOMO-16 -> LUMO (13%)	0.09	377.9	CT Ph -> Cz CT L -> Cz	
25	HOMO-7 -> LUMO+1 (29%) HOMO-13 -> LUMO (28%) HOMO-19 -> LUMO (16%)	0.18	375.1	CT Ph -> Cz CT L -> Cz	
26	HOMO-12 -> LUMO (63%) HOMO-11 -> LUMO+1 (16%)	0.15	373.4	CT Ph -> Cz CT L -> Cz	
27	HOMO-13 -> LUMO (69%) HOMO-7 -> LUMO+1 (12%)	0.12	373.4	CT Ph -> Cz CT L -> Cz	
28	HOMO-11 -> LUMO+1 (61%) HOMO-12 -> LUMO (12%)	0.11	372.3	CT Ph -> Cz CT L -> Cz	
38	HOMO -> LUMO+6 (89%)	0.21	348.7	CT L -> Pyz	

**Table S7.** Calculated composition of the lowest excited states and corresponding oscillator strength for [TPyzCAP(OPhOH)<sub>2</sub>].

Excited state	Composition	F	$\lambda_{\text{calc}}$	Type	$\lambda_{\text{exp}}$
[Ph <sub>8</sub> Pyz <sub>4</sub> CzP(OHQ) <sub>2</sub> ]					
1	HOMO -> LUMO (75%) (1a -> 1a*) HOMO-3 -> LUMO+1 (17%) (1b -> 1b*)	0.31	583.7	Q	654
2	HOMO -> LUMO+1 (70%) (1a -> 1b*) HOMO-3 -> LUMO (22%) (1b -> 1a*)	0.08	574.2	Q	603
8	HOMO-5 -> LUMO (45%) HOMO-3 -> LUMO (25%) HOMO -> LUMO+3 (12%) HOMO-4 -> LUMO (10%)	0.28	445.9	CT Ph -> Cz	
9	HOMO-4 -> LUMO (40%) HOMO -> LUMO+4 (18%) HOMO-5 -> LUMO (13%) HOMO-6 -> LUMO (12%)	0.19	439.3	CT Ph -> Cz	
10	HOMO-3 -> LUMO (20%) HOMO-4 -> LUMO (16%) HOMO-4 -> LUMO+1 (11%) HOMO -> LUMO+5 (11%)	0.36	430.4	CT Ph -> Cz	
11	HOMO-3 -> LUMO+1 (20%) HOMO-4 -> LUMO (17%) HOMO-5 -> LUMO (12%) HOMO -> LUMO+4 (11%) HOMO-6 -> LUMO (10%)	0.18	427.4	CT Ph -> Cz	
12	HOMO-6 -> LUMO (28%) HOMO-4 -> LUMO+1 (22%) HOMO -> LUMO+5 (17%)	0.09	423.8	CT Ph -> Cz	
14	HOMO-4 -> LUMO+1 (23%) HOMO -> LUMO+3 (20%) HOMO-7 -> LUMO (17%) HOMO -> LUMO+3 (17%)	0.14	417.0	CT Ph -> Cz	
15	HOMO-5 -> LUMO+1 (39%) HOMO -> LUMO+4 (13%) HOMO -> LUMO+3 (12%) HOMO-3 -> LUMO+1 (10%)	0.31	415.6	CT Ph -> Cz	
16	HOMO -> LUMO+5 (34%) HOMO-4 -> LUMO+1 (32%) HOMO-7 -> LUMO (14%)	0.11	406.9	CT Ph -> Cz	
17	HOMO-5 -> LUMO+1 (32%) HOMO-6 -> LUMO+1 (30%) HOMO -> LUMO+4 (17%)	0.72	404.1	CT Ph -> Cz	452
18	HOMO-6 -> LUMO+1 (59%)	0.54	400.1	CT Ph -> Cz	
21	HOMO-7 -> LUMO (21%) HOMO-3 -> LUMO (13%) (1b -> 1a*) HOMO -> LUMO+3 (10%)	0.97	386.3	CT Ph -> Cz B	420
25	HOMO-16 -> LUMO (33%) HOMO-7 -> LUMO+1 (16%) HOMO-14 -> LUMO (11%)	0.09	377.3	CT Ph -> Cz CT L -> Cz	
26	HOMO-19 -> LUMO (29%) HOMO-16 -> LUMO (27%) HOMO-7 -> LUMO+1 (12%)	0.18	376.8	CT Ph -> Cz	
27	HOMO-7 -> LUMO+1 (42%) HOMO-19 -> LUMO (23%)	0.25	374.7	CT Ph -> Cz	

**Table S8.** Calculated composition of the lowest excited states and corresponding oscillator strength for [TPyzCAP(OPhNMe<sub>2</sub>)<sub>2</sub>].

Excited state	Composition	F	$\lambda_{\text{calc}}$	Type	$\lambda_{\text{exp}}$
[Ph <sub>8</sub> Pyz <sub>4</sub> CzP(O-pDMAP) <sub>2</sub> ]					
5	HOMO-2 -> LUMO (75%) (1a -> 1a*) HOMO-3 -> LUMO+1 (18%) (1b -> 1b*)	0.31	585.5	Q	653
6	HOMO-2 -> LUMO+1 (75%) (1a -> 1b*) HOMO-3 -> LUMO (23%) (1b -> 1a*)	0.09	574.7	Q	603
14	HOMO-4 -> LUMO (30%) HOMO-2 -> LUMO+3 (17%) HOMO-3 -> LUMO (17%) (1b -> 1a*) HOMO-5 -> LUMO (16%) HOMO -> LUMO+5 (11%)	0.20	441.9	CT Ph -> Cz CT Cz -> Pyz	
16	HOMO-2 -> LUMO+4 (34%) HOMO-3 -> LUMO+1 (16%) (1b -> 1b*) HOMO-4 -> LUMO (13%) HOMO-5 -> LUMO (12%) HOMO-6 -> LUMO (10%)	0.19	436.6	CT Cz -> Pyz CT Ph -> Cz	
18	HOMO-2 -> LUMO+5 (29%) HOMO-4 -> LUMO (17%) HOMO-3 -> LUMO (16%) (1b -> 1a*) HOMO-4 -> LUMO+1 (12%)	0.25	428.9	CT Cz -> Pyz CT Ph -> Cz	
22	HOMO-7 -> LUMO (37%) HOMO-4 -> LUMO+1 (26%) HOMO-2 -> LUMO+3 (11%)	0.30	414.9	CT Ph -> Cz CT Cz -> Pyz	
23	HOMO-5 -> LUMO+1 (26%) HOMO-3 -> LUMO+1 (21%) (1b -> 1b*) HOMO-2 -> LUMO+4 (10%)	0.67	411.4	CT Ph -> Cz CT Cz -> Pyz	
24	HOMO-4 -> LUMO+1 (39%) HOMO-2 -> LUMO+5 (23%) HOMO-5 -> LUMO+1 (15%)	0.27	405.5	CT Ph -> Cz CT Cz -> Pyz	
25	HOMO-5 -> LUMO+1 (43%) HOMO-2 -> LUMO+4 (14%) HOMO-3 -> LUMO+1 (10%) (1b -> 1b*)	0.90	400.7	CT Ph -> Cz CT Cz -> Pyz B	455
26	HOMO-6 -> LUMO+1 (80%)	0.31	397.0	CT Ph -> Cz	
28	HOMO-7 -> LUMO (18%) HOMO-8 -> LUMO (17%) HOMO-3 -> LUMO (12%) (1b -> 1a*)	0.67	387.8	CT Ph -> Cz CT L -> Cz B	419
30	HOMO-8 -> LUMO (64%) HOMO-11 -> LUMO (15%)	0.09	384.7	CT L -> Cz CT Ph -> Cz	
33	HOMO-7 -> LUMO+1 (46%) HOMO-16 -> LUMO (15%)	0.12	376.5	CT Ph -> Cz	
34	HOMO-15 -> LUMO (57%) HOMO-14 -> LUMO (10%)	0.11	375.3	CT Ph -> Cz	



**Figure S11.** Predicted (black) and experimental (red) absorption spectra of [TPyzCAP(OAr)<sub>2</sub>].

## V. Fluorescence measurements

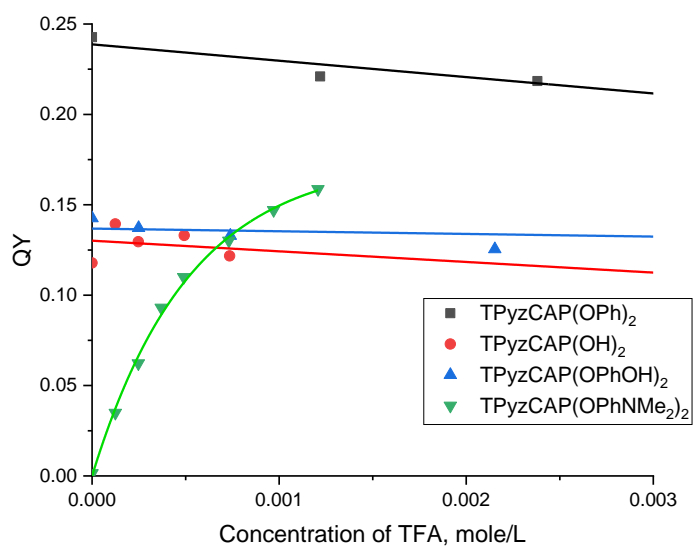


Figure S12. Dependence of fluorescence quantum yield from TFA concentration in  $\text{CH}_2\text{Cl}_2$ .

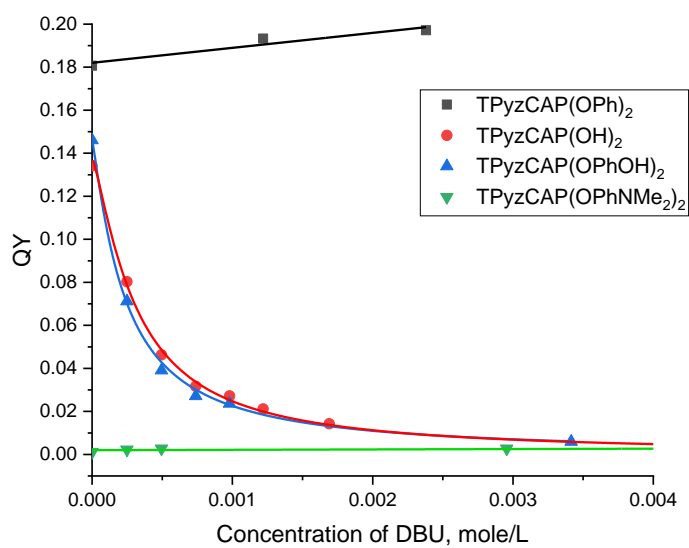
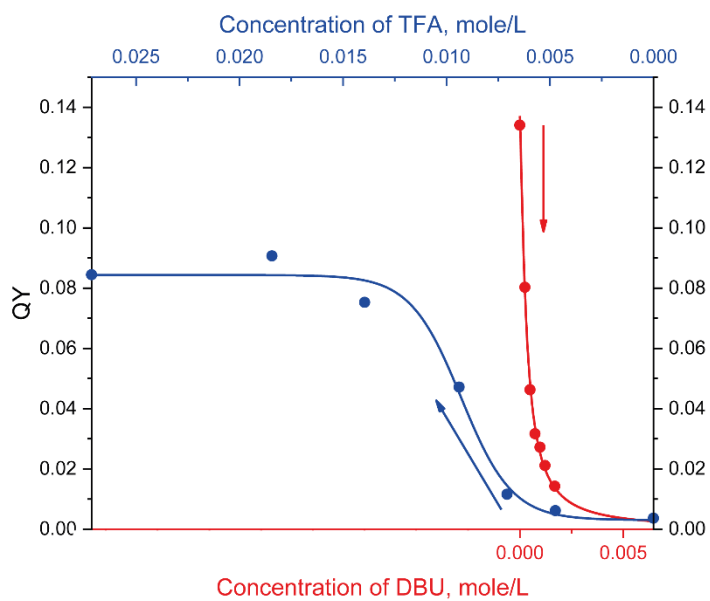
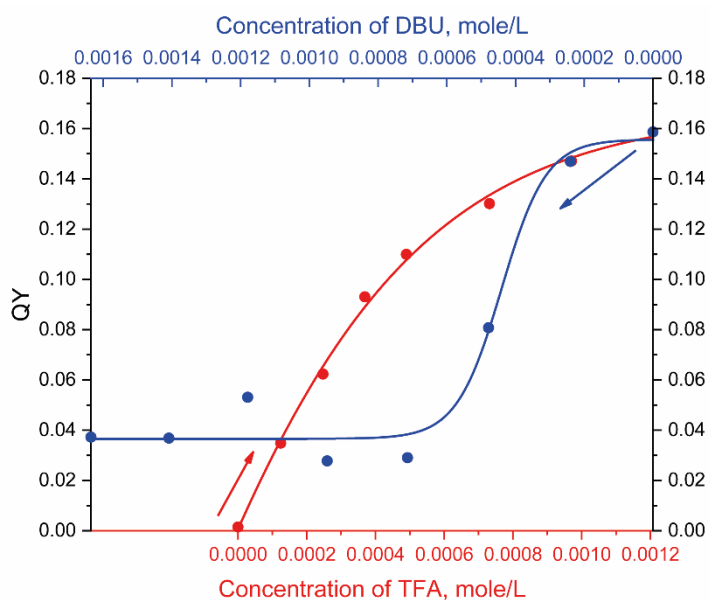


Figure S13. Dependence of fluorescence quantum yield from DBU concentration in  $\text{CH}_2\text{Cl}_2$ .

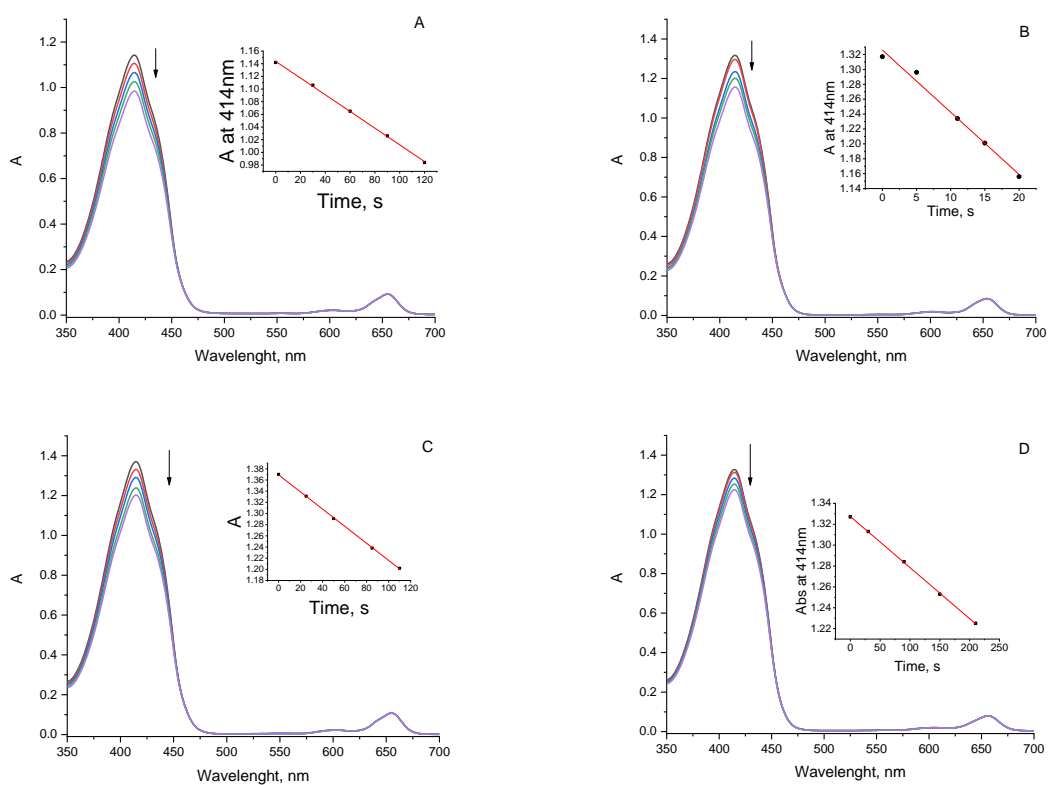


**Figure S14.** Reversible changes of [TPyzCAP(OH)<sub>2</sub>] fluorescence quantum yield during consecutive titration with DBU and TFA in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S15.** Reversible changes of [TPyzCAP(OPhNMe<sub>2</sub>)<sub>2</sub>] fluorescence quantum yield during consecutive titration with TFA and DBU in CH<sub>2</sub>Cl<sub>2</sub>.

## VI. Singlet oxygen measurements



**Figure S16.** Spectral changes of DPBF solutions with photosensitizers in THF during irradiation. Photosensitizer is: A – TPyzCAP(OH)<sub>2</sub>; B – TPyzCAP(OPh)<sub>2</sub>; C – TPyzCAP(OPhOH)<sub>2</sub>; D – TPyzCAP(OPhNMe<sub>2</sub>)<sub>2</sub>