ELECTRONIC SUPPORTING INFORMATION

TUNING ON AND OFF CHEMICAL- AND PHOTO-ACTIVITY OF EXFOLIATED $MOSE_2$ NANOSHEETS THROUGH MORPHOLOGICALLY SELECTIVE "SOFT" COVALENT FUNCTIONALIZATION WITH PORPHYRINS

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Summary

EXTENDED PHYSICOCHEMICAL CHARACTERIZATION

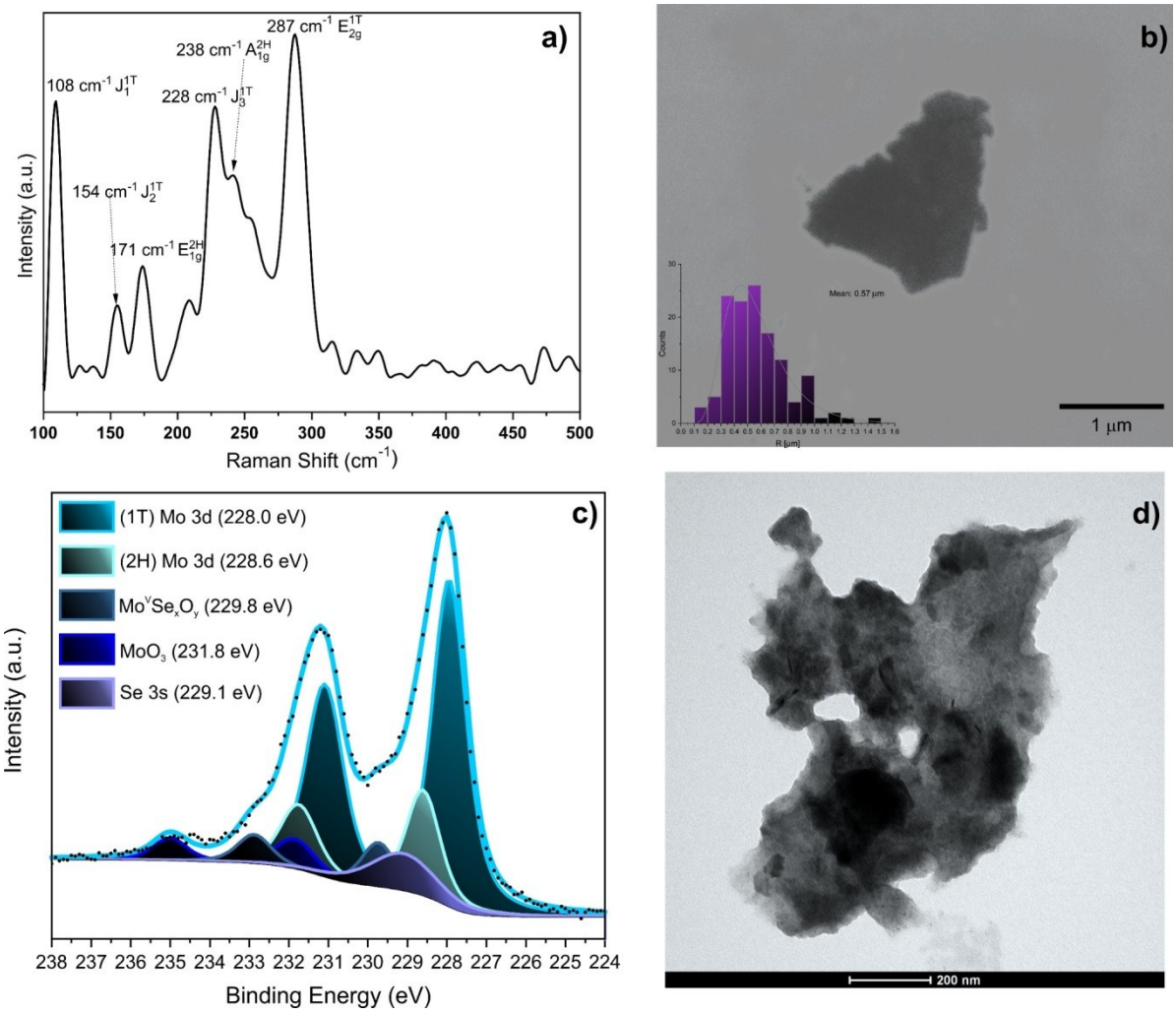


Figure S1. Characterization of the pristine ce-$MoSe_2$. a) Raman spectrum, b) Mo 3d XPS core level region, c) SEM (inset: size distribution) and d) TEM images.

Table S1. Elemental analysis of pristine ce-$MoSe_2$ as a result of the XPS data.

Element	% at.
Mo	30.7 ±1.0
Se	59.3 ±1.0
O	11.0 ±1.0

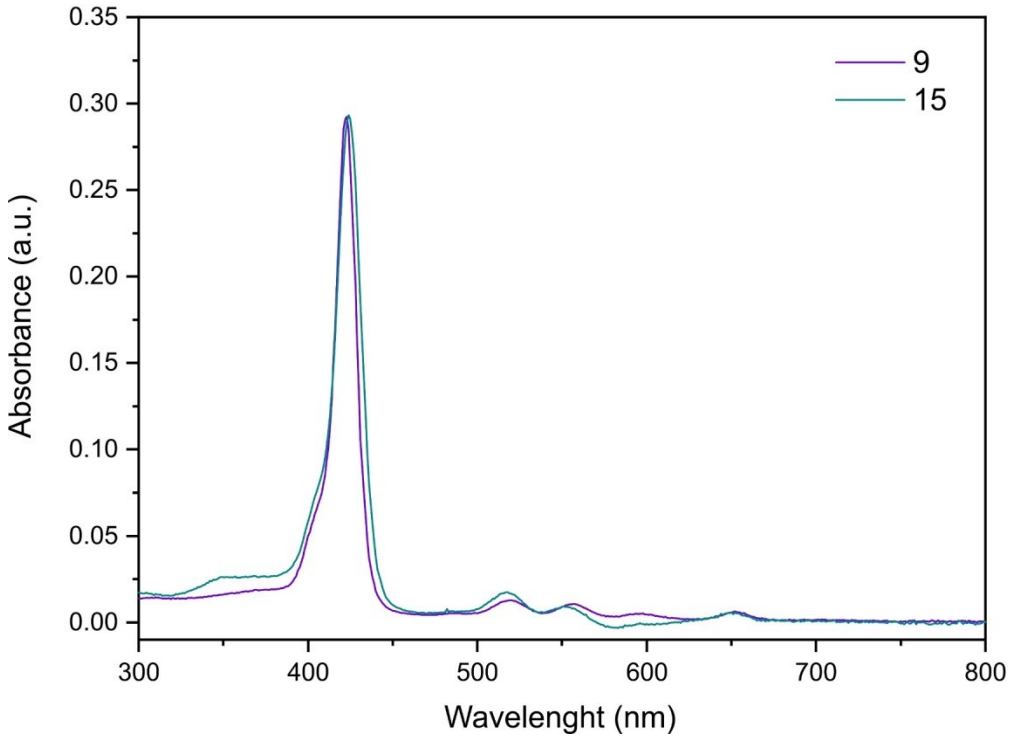


Figure S2. Experimental UV-Vis spectra of porphyrins **9** and **15** in DMF

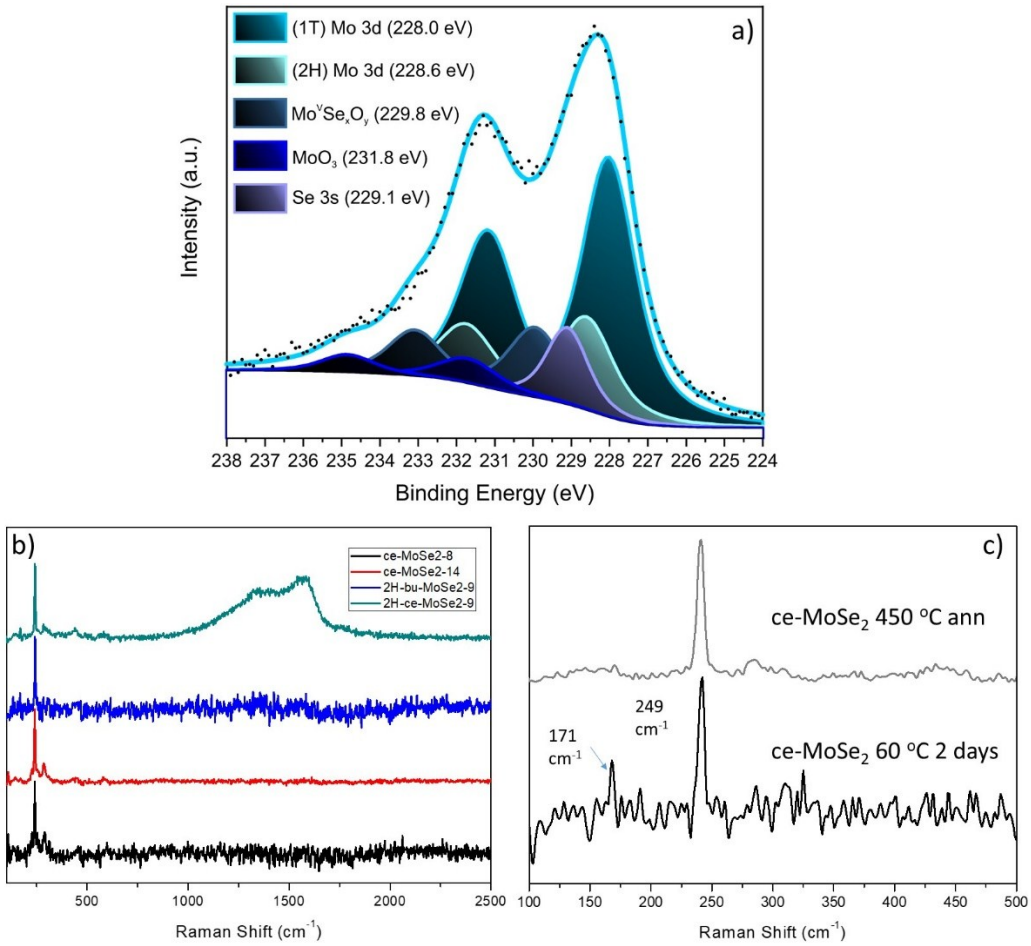


Figure S3. a) Mo 3d core level region of chemically exfoliated ce-$MoSe_2$ after 2 days at 60 °C (reaction blank). b) Raman spectra of control samples with protected thioacetate porphyrins, bulk $MoSe_2$ and chemically exfoliated $MoSe_2$ thermally annealed at 450 °C. c) Raman spectra of control samples chemically exfoliated $MoSe_2$ after 2 days at 60 °C (reaction blank) and the thermally annealed $MoSe_2$ to induce 1T → 2H phase transition.

Table S2. Elemental analysis determined by means of XPS of functionalized samples **ce-$MoSe_2$-9** and **ce-$MoSe_2$-15** (values reported in atomic percentage, C and O values were omitted).

Sample	Mo	Se	N	S	Mo/Se	Se/S
ce-$MoSe_2$-9	24.7	46.8	14.5	13.9	1.92	9
ce-$MoSe_2$-15 (0.2 mM)	15.5	23.1	30.4	30.9	1.49	4
ce-$MoSe_2$-15 (0.02 mM)	24.7	46.8	14.0	14.3	1.89	9
ce-$MoSe_2$-15 (0.002 mM)	30.4	59.6	-	-	1.92	-

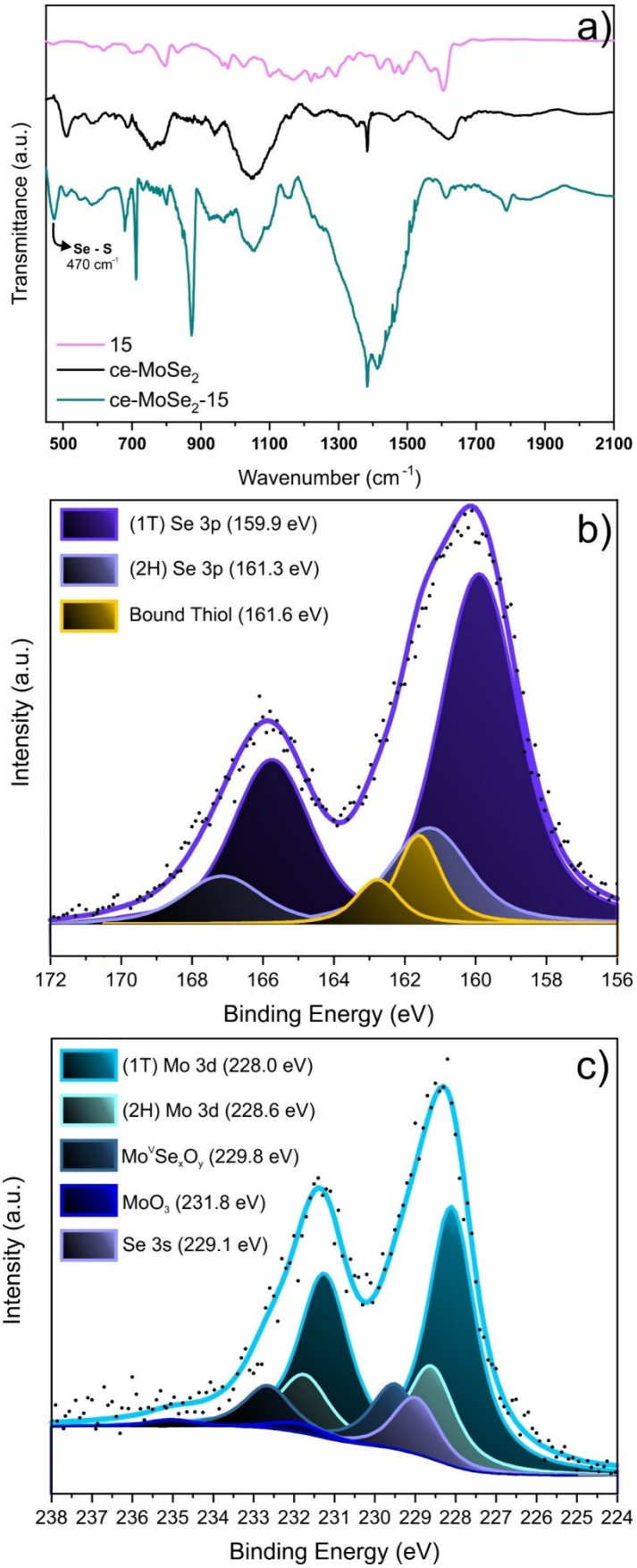


Figure S4. a) FTIR spectra of pristine ce-$MoSe_2$, **ce-$MoSe_2$-15** and molecule **15**; b) Se 3p – S 2p core level region of sample **ce-$MoSe_2$-9**; c) Mo 3d core level region of **ce-$MoSe_2$-15**.

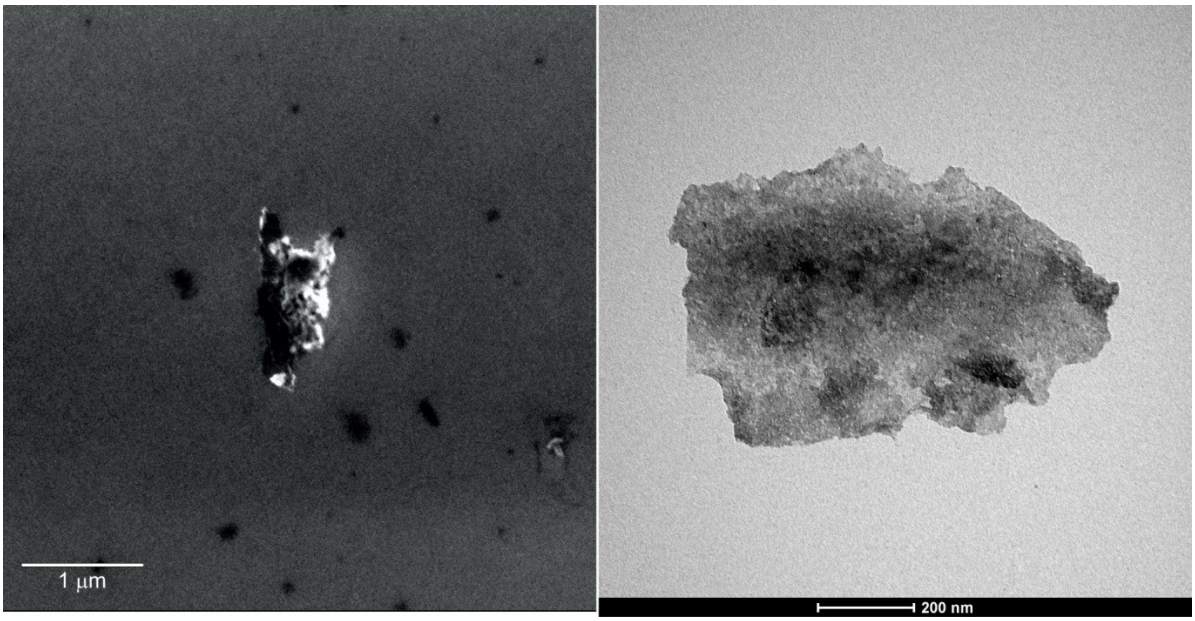


Figure S5. SEM and TEM images of **ce-$MoSe_2$-15.**

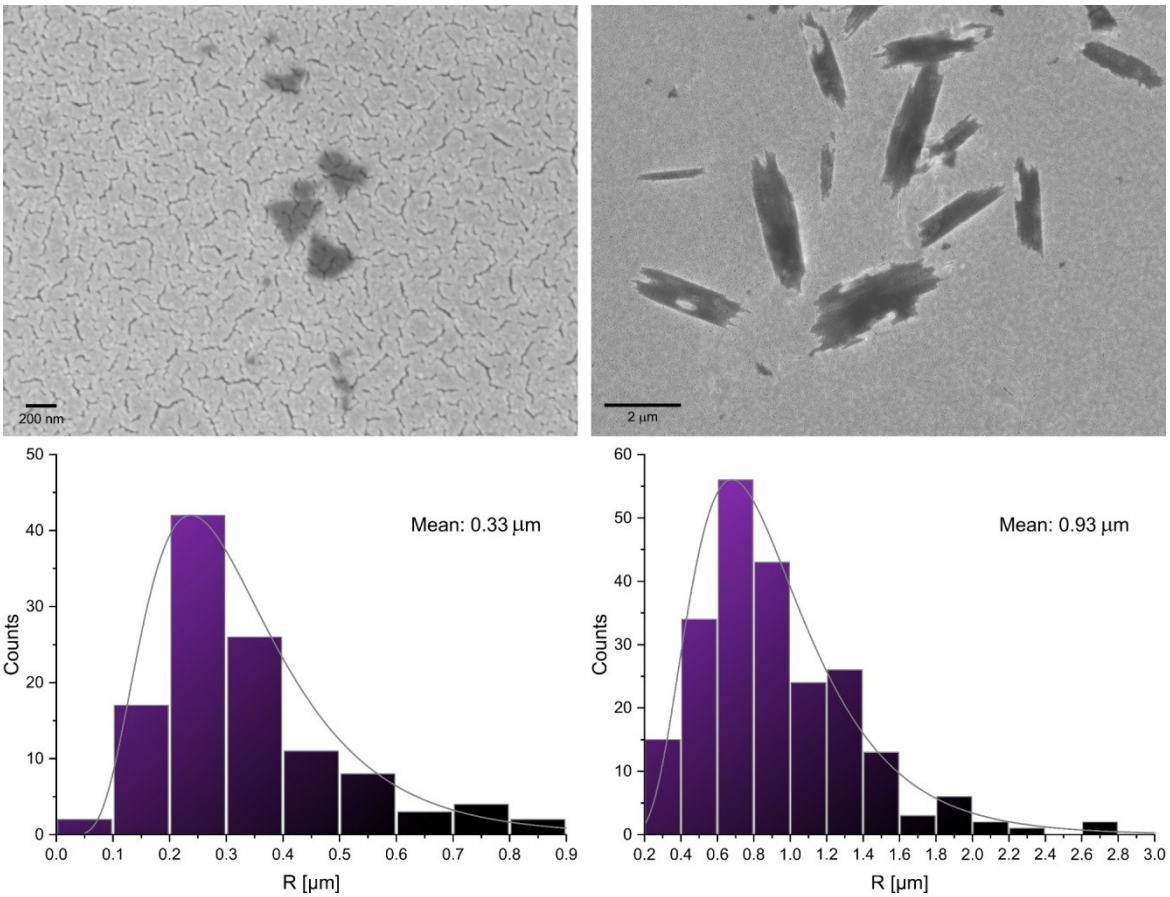


Figure S6. SEM images of a) thin and b) thick fraction of ce-$MoSe_2$ with their corresponding lateral-size distributions.

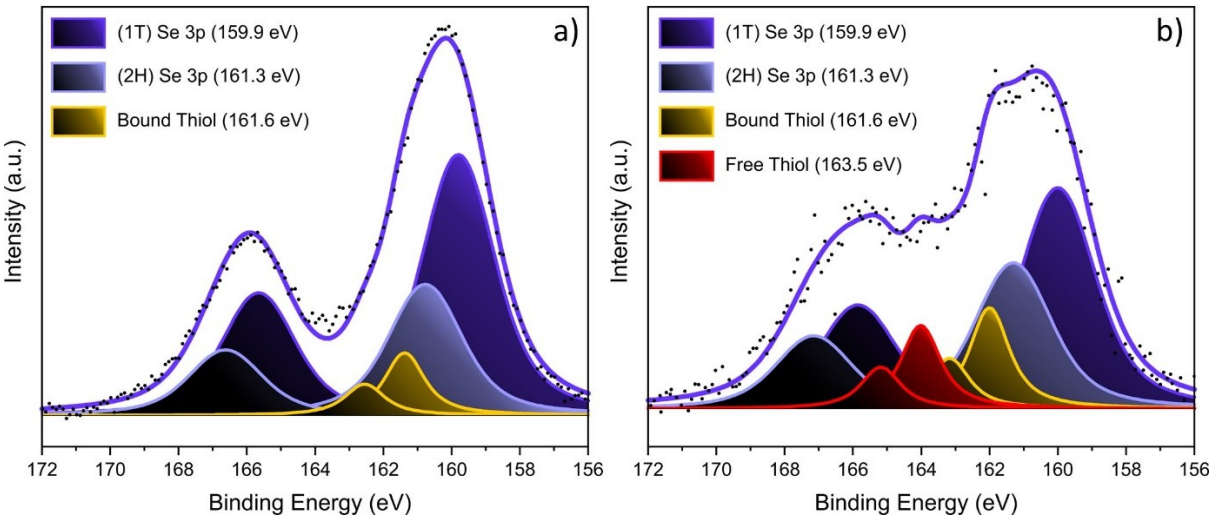


Figure S7. S 2p core region of the different size-selection samples. a) thicker fraction of ce-$MoSe_2$ conjugated with molecule **15**; b) thinner fraction of ce-$MoSe_2$ conjugated with molecule **15.**

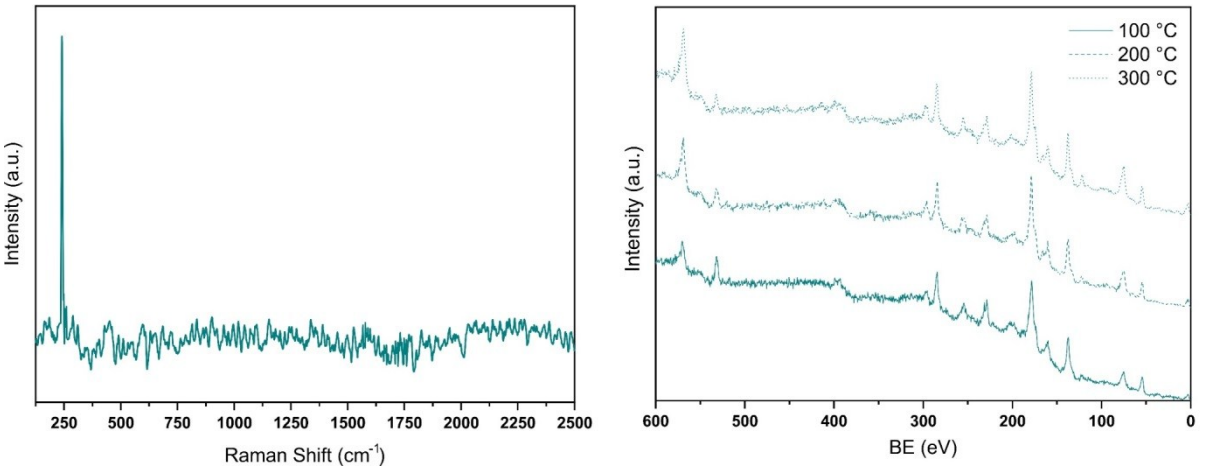


Figure S8. Right: Raman spectrum of sample **ce-$MoSe_2$-15** after vacuum annealing experiment; left XPS survey spectra during the step vacuum annealing at different temperatures of sample **ce-$MoSe_2$-15.**

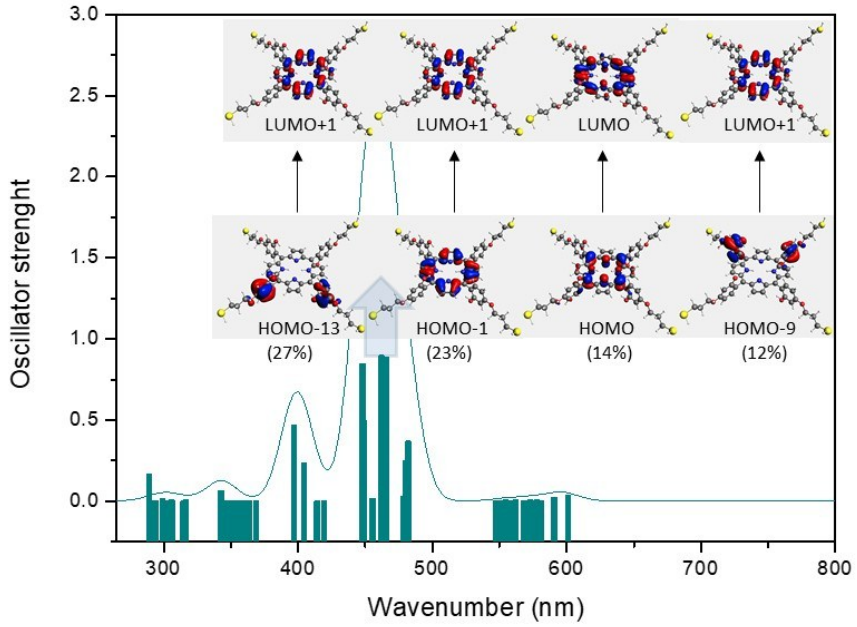


Figure S9. Simulated absorption spectrum of **15** in DMF, with the transitions corresponding to the Soret Band.

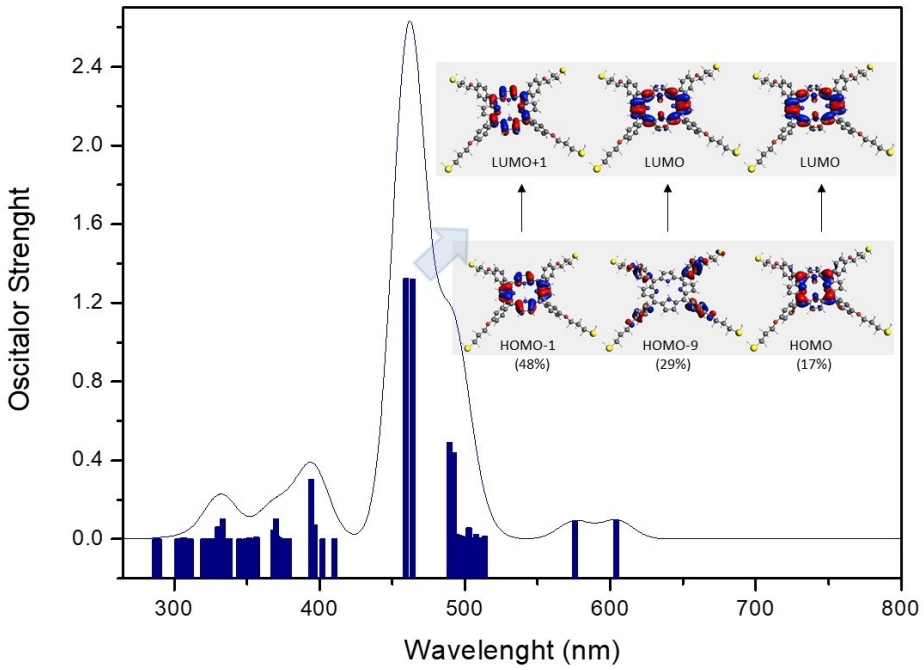


Figure S10. Simulated absorption spectrum of **9** in DMF, with the transitions corresponding to the Soret band.

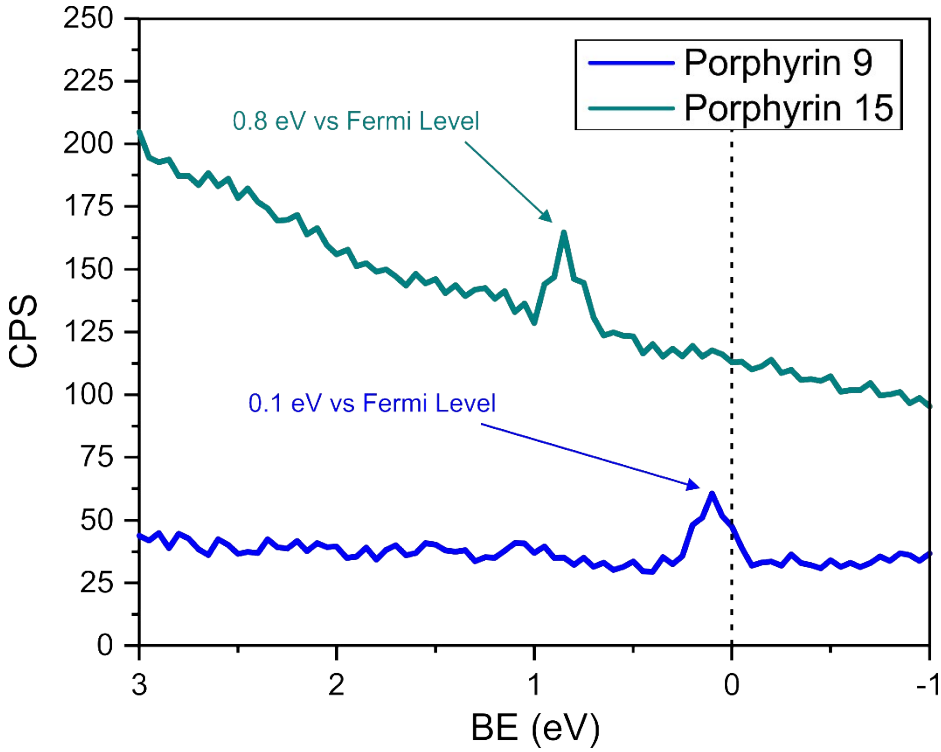


Figure S11. UPS spectra of porphyrins **9** and **15** dropcasted over glassy carbon

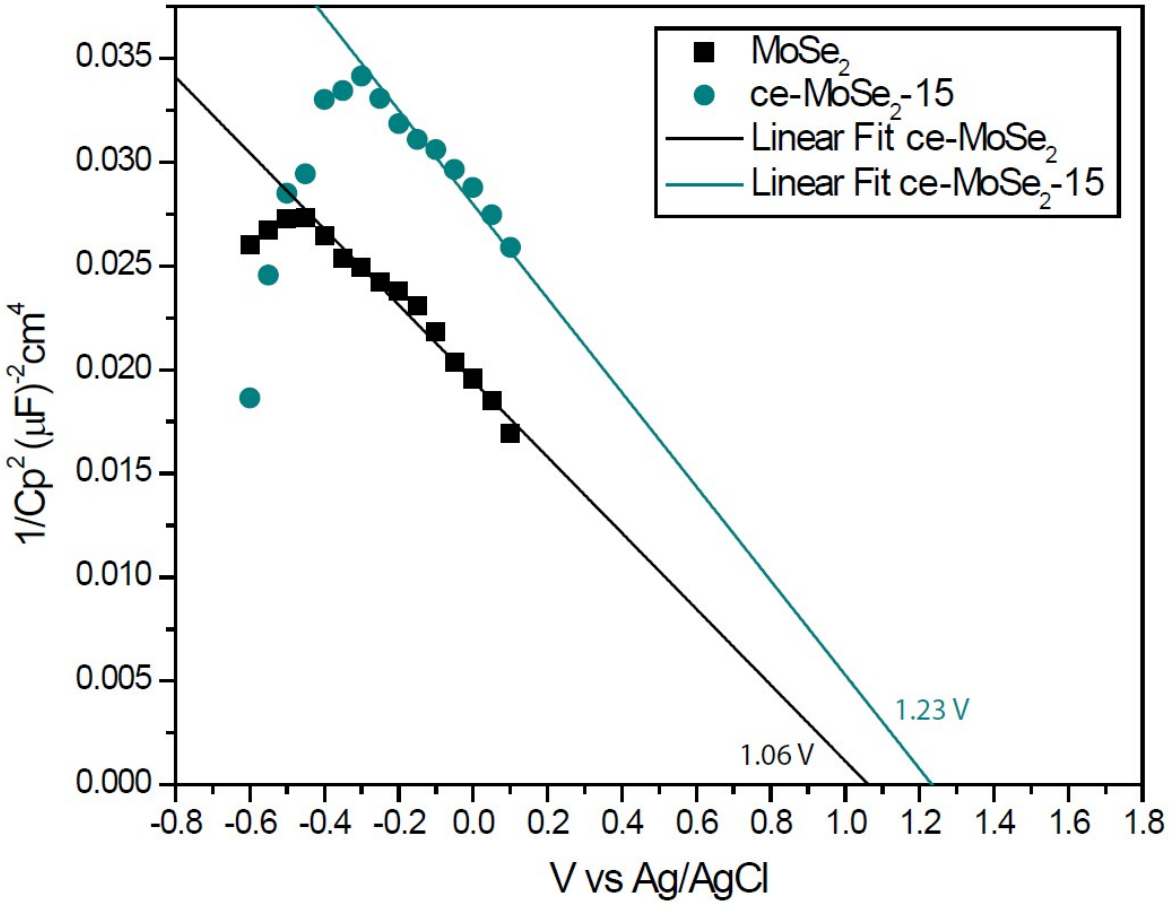


Figure S12. Mott-Schottky plots for pristine and functionalized materials

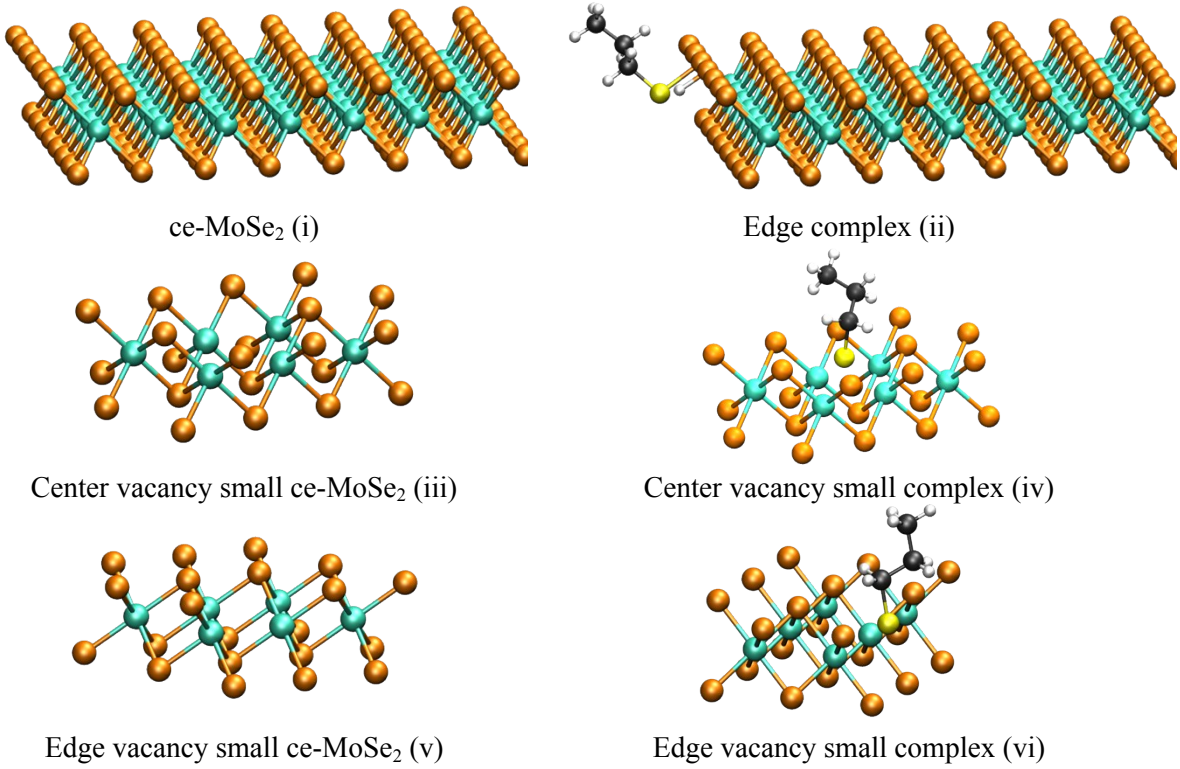


Figure S13. Optimized structures on bond-type formation

Table S3. Calculated energies of the Ce-$MoSe_2$ and the hybrids i – vi

Structure	Energy (Ha)	Energy (kcal/mol)	ΔE (kcal/mol)
C_3H_7SH	-2.1385594	-1341.96741	
i	-33.711116	-21154.0624	
i + C_3H_7SH	-35.849675	-22496.0298	0
ii	-35.895612	-22524.8555	-28.8
$C_3H_7S^-$	-2.0213191	-1268.39792	
iii	-4.1977518	-2634.1312	
iii + $C_3H_7S^-$	-6.2190708	-3902.52912	0
iv	-6.4143569	-4025.07307	-122.5
$C_3H_7S^-$	-2.0213191	-1268.39792	
v	-4.2016192	-2636.55804	
v + $C_3H_7S^-$	-6.2229382	-3904.95596	
vi	-6.4269413	-4032.96992	-128.0

Table S4. XPS results on sample **ce-$MoSe_2$-15** before and after the chronopotentiometry experiments

Mo 3d component	BE (eV)	%at. (Before HER)	%at. (After HER)
1T-$MoSe_2$	228.0	60.4	58.9
2H-$MoSe_2$	228.6	21.8	25.5
$Mo^{V}Se_xO_y$	229.8	15.2	14.6
MoO_3	231.8	2.6	1.0
S 2p component	**BE (eV)**	**% vs total signal (Before HER)**	**% vs total signal (After HER)**
Bound Thiol	161.6	9.0	8.4

EXTENDED ELECTROCHEMICAL DATA

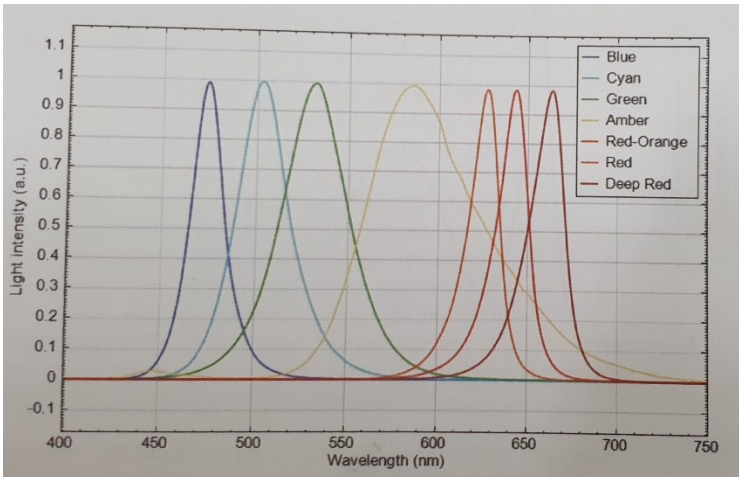


Figure S14. Emission spectra of the lights employed as excitation source for the photoelectrochemical reactions (blue and red).

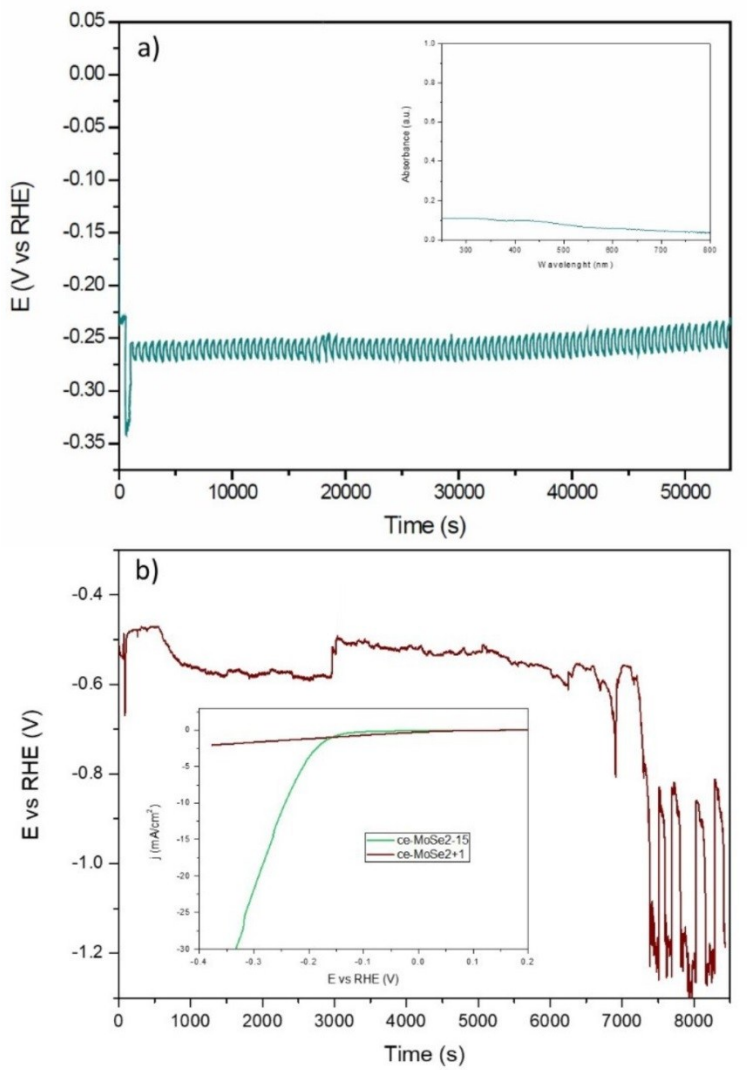


Figure S15. Chopped-light chronopotentiometry (10 mA cm^{-2}) curve of a) **ce-$MoSe_2$-15.** Inset: UV-Vis spectra (DMF) of the electrolyte after stability test; b) **ce-$MoSe_2$-1** Inset: HER performance in 0.5 M H_2SO_4

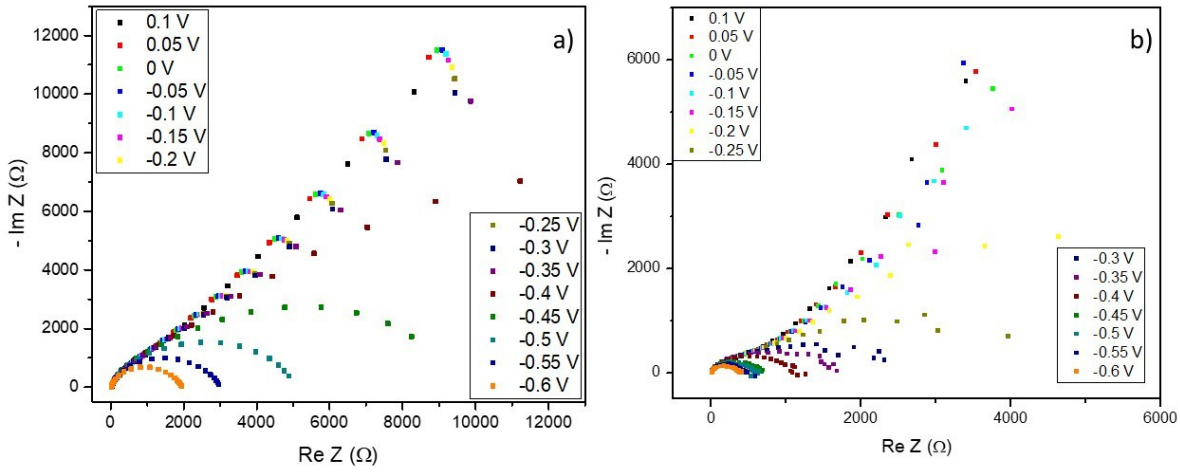


Figure S16. EIS measurements of a) ce-$MoSe_2$ and b) **ce-$MoSe_2$-15**

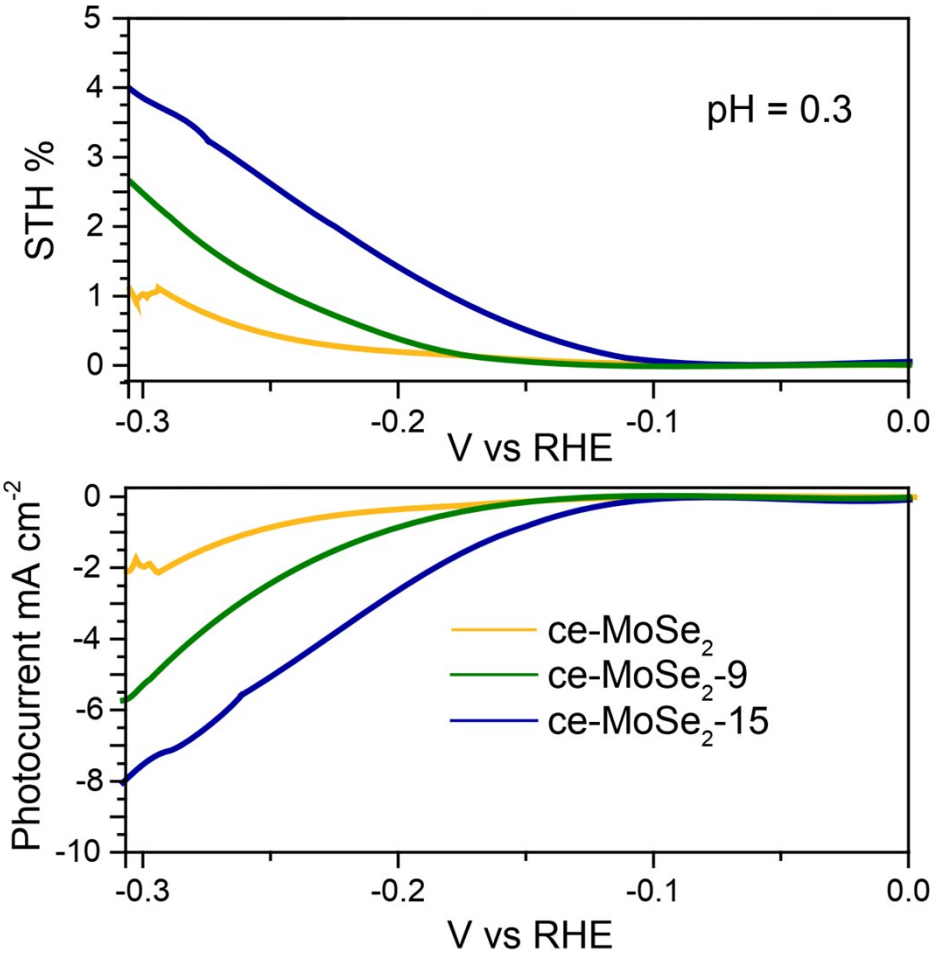
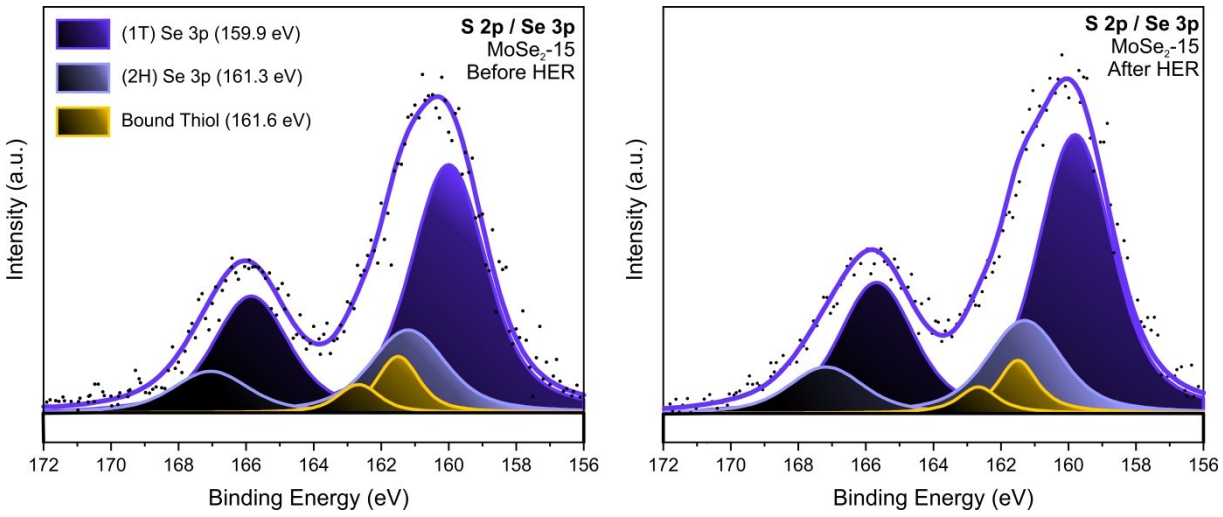


Figure S17. Efficiency on the H_2 production and developed photocurrent for samples ce-$MoSe_2$, **ce-$MoSe_2$-9** and **ce-$MoSe_2$-15** during PEC-HER experiments performed at 0.5 M H_2SO_4 conditions.



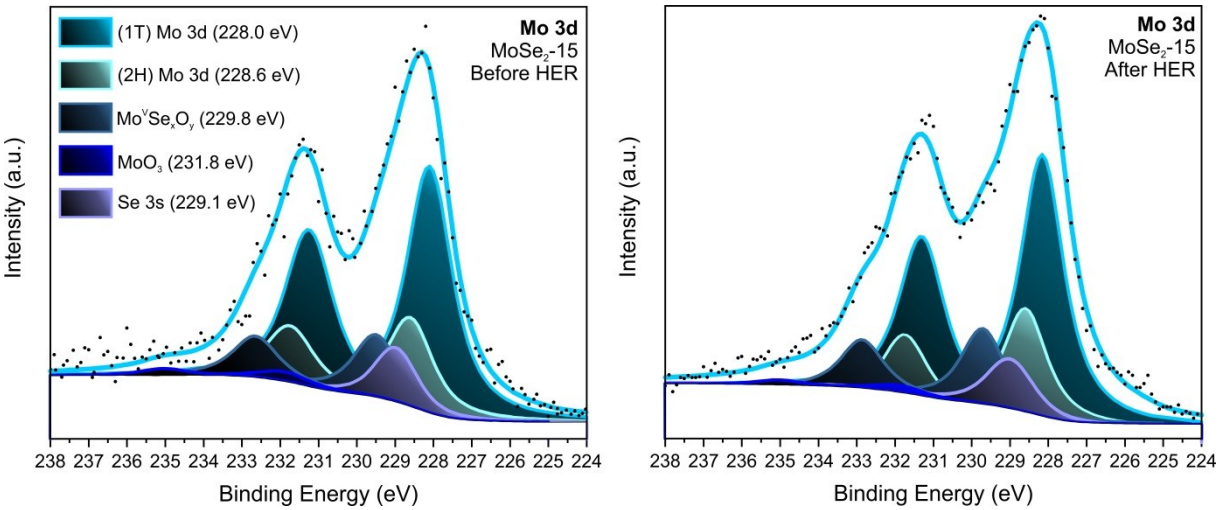


Figure S18. XPS S 2p – Se 3p core level region of sample **ce-MoSe$_2$-15** after chronopotentiometry.

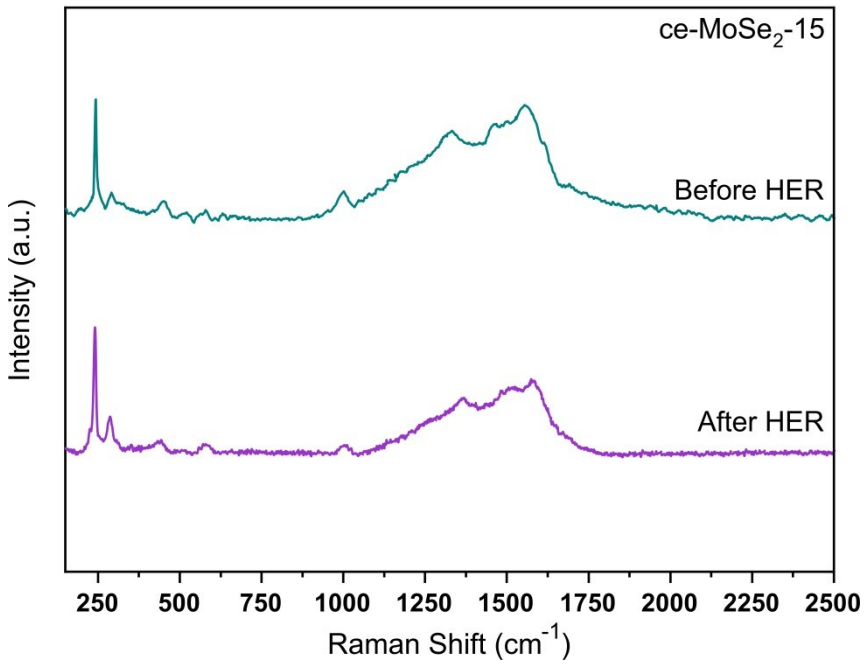


Figure S19. Raman spectrum of sample **ce-MoSe$_2$-15** after chronopotentiometry.

EXTENDED COMPUTATIONAL DETAILS

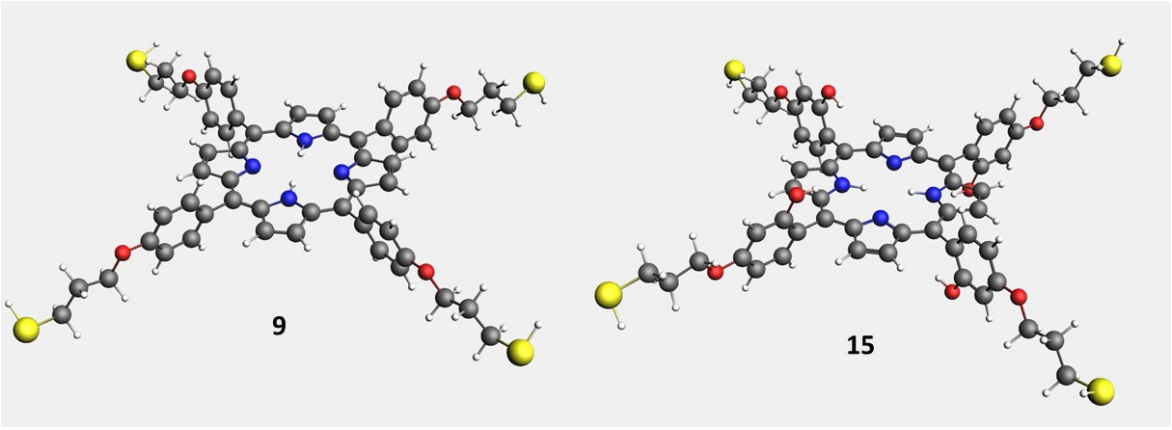


Figure S20. Optimized calculated structures of porphyrins **9** and **15**.

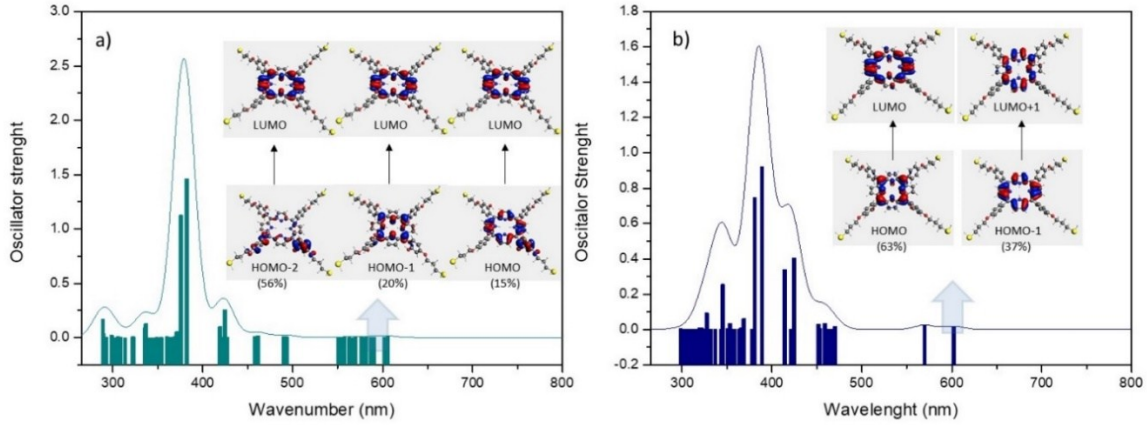


Figure S21. Simulated spectra in vacuum of a) **15** and b) **9** with the main components of the Q band at 600 nm.

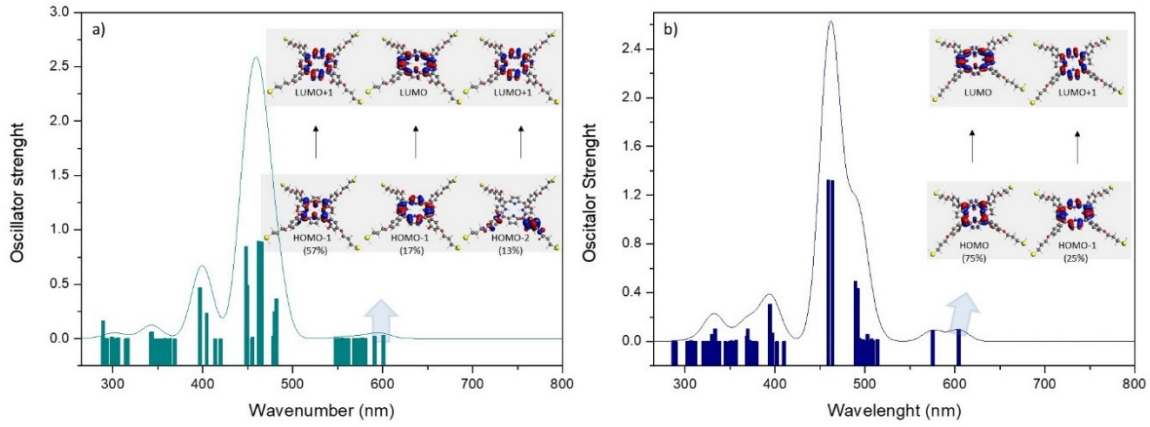


Figure S22. Simulated absorption spectra in DMF of a) **15** and b) **9** with the main components of the Q band at 600 nm.

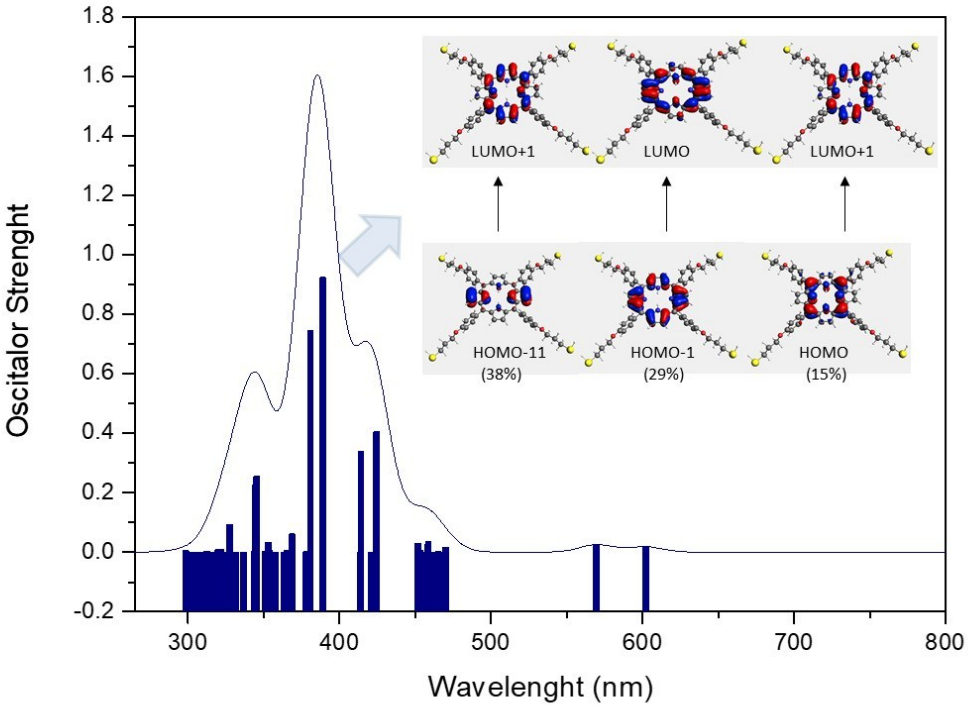


Figure S23. Simulated absorption spectrum of **9** in vacuum, with the transitions corresponding to the Soret Band.

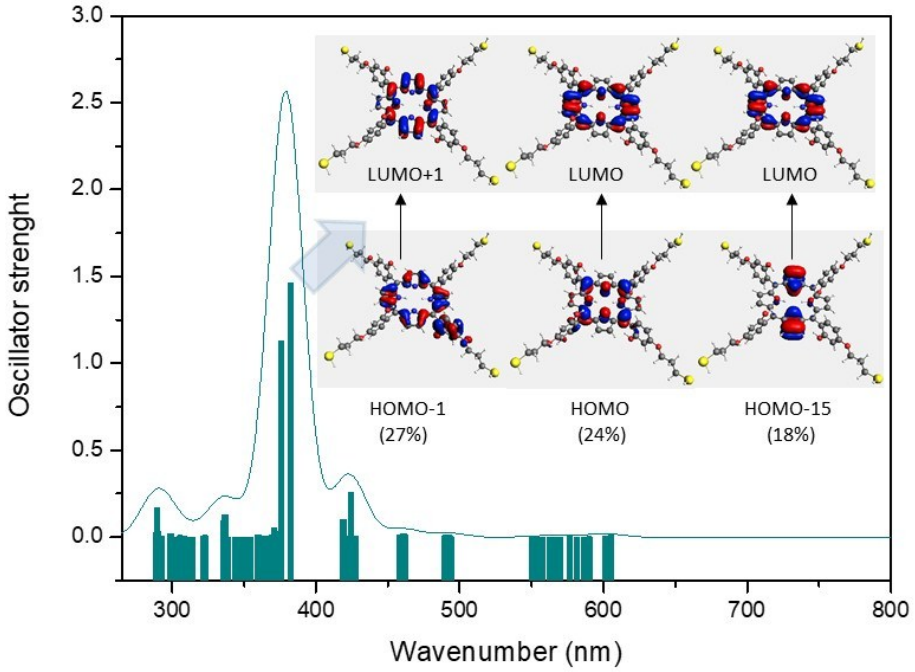


Figure S24. Simulated absorption spectrum of **15** in vacuum, with the transitions corresponding to the Soret Band.

COORDINATES

Molecule 9

C	-7.065001	21.547233	-9.202666
C	-7.524355	20.406712	-8.476512
N	-8.613603	19.932601	-9.151370
C	-8.880754	20.697859	-10.251218
C	-7.889260	21.724935	-10.278705
H	-6.207676	22.146176	-8.928242
H	-7.822238	22.494312	-11.035544
C	-6.971927	19.875105	-7.300533
H	-9.138602	19.109297	-8.887354
C	-10.450276	15.644988	-7.009796
C	-11.356990	14.543033	-7.060479
C	-12.173036	14.715121	-8.143761
C	-11.794425	15.927884	-8.795821
N	-10.754675	16.444549	-8.075259
H	-11.368888	13.723799	-6.354817
H	-12.967683	14.061363	-8.475904
H	-10.254454	17.290289	-8.315390
C	-12.371313	16.481501	-9.949888
C	-11.952324	17.664939	-10.593672
C	-12.627541	18.212746	-11.756669
C	-11.948482	19.333105	-12.094793
C	-10.865494	19.455305	-11.135723
N	-10.893946	18.438967	-10.232098
H	-13.505318	17.800977	-12.237963
H	-12.161665	20.016282	-12.906925
C	-9.924227	20.505454	-11.170190
C	-7.432719	18.728038	-6.620269
N	-8.449485	17.916708	-7.018498
C	-6.857186	18.269402	-5.369042
H	-6.049474	18.743683	-4.826495
C	-9.439229	15.867099	-6.061311
C	-7.544023	17.156108	-5.023112
H	-7.408077	16.543155	-4.141496
C	-8.530080	16.946923	-6.068228
C	-5.797173	20.601093	-6.737850
C	-3.569229	21.971383	-5.680440
C	-5.957793	21.764892	-5.975618
C	-4.497921	20.145378	-6.954838
C	-3.389842	20.813511	-6.440006
C	-4.868171	22.439682	-5.452063
H	-6.959436	22.144387	-5.783060
H	-2.399237	20.418210	-6.641669
H	-5.004154	23.339808	-4.856547
C	-10.025428	21.507340	-12.270382
C	-10.202775	23.405423	-14.349563
C	-10.653474	22.742801	-12.071067
C	-9.493491	21.249108	-13.532370
C	-9.573376	22.178216	-14.566669
C	-10.745866	23.676780	-13.088664
H	-11.083476	22.973533	-11.098313
H	-8.998122	20.297898	-13.717989
H	-9.140336	21.928383	-15.530148
H	-11.239621	24.632137	-12.924897
C	-13.522040	15.734467	-10.535173
C	-15.691492	14.318690	-11.652493
C	-14.817737	15.873006	-10.022811
C	-13.343269	14.871839	-11.615113
C	-14.405448	14.166390	-12.174668
C	-15.886526	15.182441	-10.568797
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H	-12.347449	14.741480	-12.034516
H	-14.211156	13.505700	-13.013625
H	-16.890179	15.301109	-10.166454
C	-9.325751	14.867314	-4.961302
C	-9.064508	13.007699	-2.854826
C	-8.331024	13.890605	-4.977018
C	-10.201212	14.883071	-3.868429
C	-10.076374	13.974389	-2.831278
C	-8.193616	12.965612	-3.945405
H	-7.640432	13.846747	-5.816996
H	-10.987430	15.634306	-3.823571
H	-10.753952	14.003626	-1.980801
H	-7.404017	12.223416	-4.009096
O	-10.340169	24.390002	-15.275489
O	-16.802740	13.687119	-12.113207
O	-9.018224	12.174479	-1.782610
O	-2.570153	22.707004	-5.127073
C	-1.234203	22.280328	-5.326453
H	-1.097974	21.265301	-4.921404
H	-1.005194	22.249326	-6.403267
C	-0.320293	23.262145	-4.617936
H	-0.580664	23.290103	-3.552988
H	-0.497308	24.267854	-5.017774
C	1.144350	22.888144	-4.784855
H	1.419003	22.877118	-5.845870
H	1.337368	21.894125	-4.365446
S	2.177943	24.103780	-3.921279
H	3.361003	23.543241	-4.229618
C	-9.794600	24.178355	-16.565641
H	-8.712463	23.987583	-16.489694
H	-10.260889	23.296383	-17.032581
C	-10.060367	25.421327	-17.395727
H	-9.622792	26.288433	-16.886113
H	-11.140139	25.598836	-17.452325
C	-9.485613	25.302845	-18.798921
H	-9.923576	24.446130	-19.326671
H	-8.402032	25.138191	-18.777657
S	-9.845861	26.700108	-19.888170
H	-9.148445	27.624500	-19.202610
H	-4.340333	19.244862	-7.545519
C	-7.966683	11.227165	-1.713279
H	-8.046132	10.512101	-2.547527
H	-6.995199	11.738498	-1.798521
C	-8.069951	10.505967	-0.381311
H	-8.039151	11.248815	0.425047
H	-9.039586	10.000666	-0.309732
C	-6.947691	9.496264	-0.195407
H	-6.982760	8.727708	-0.978008
H	-5.963234	9.973093	-0.267471
S	-7.025724	8.543330	1.339330
H	-6.837072	9.576376	2.180761
C	-16.662960	12.801556	-13.210252
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H	-15.952483	11.998467	-12.958414
C	-18.029339	12.218496	-13.522150
H	-18.728697	13.038386	-13.726335
H	-18.409911	11.688981	-12.641572
C	-17.982895	11.270307	-14.710444
H	-17.630175	11.777115	-15.616189

H	-17.285193	10.444828	-14.520376
S	-19.541123	10.429720	-15.076340
H	-20.241621	11.526708	-15.418284

Molecule 15

C	4.16775032	0.30639965	-0.15770738
C	2.81891586	0.76302217	-0.04254488
N	2.03015391	-0.35260572	-0.04099118
C	2.78669824	-1.48536352	-0.14603812
C	4.14829079	-1.05810626	-0.21931547
H	5.03313704	0.95407460	-0.18856697
H	4.99537029	-1.72402327	-0.30946194
C	2.38407101	2.09646708	0.04919008
H	1.02135618	-0.34050500	0.03469530
C	-2.94800815	0.82265410	0.33735875
C	-4.30772173	0.39403664	0.43017505
C	-4.32894019	-0.96883655	0.33683975
C	-2.98292960	-1.42293547	0.18496874
N	-2.19414168	-0.30745276	0.19222904
H	-5.15225367	1.05768719	0.55486612
H	-5.19377953	-1.61689874	0.37202803
H	-1.18608653	-0.31789665	0.10732710
C	-2.55008794	-2.75495524	0.06255788
C	-1.20359367	-3.17129111	-0.04349289
C	-0.81974637	-4.56705095	-0.16634552
C	0.53101734	-4.58296353	-0.22144428
C	0.95587234	-3.19582230	-0.14531230
N	-0.11171106	-2.35914977	-0.03761229
H	-1.49571129	-5.41153654	-0.20631325
H	1.18176313	-5.44375565	-0.30674198
C	2.31454891	-2.80898087	-0.18785308
C	1.03821322	2.51235040	0.15948786
N	-0.05094462	1.69756303	0.19250961
C	0.65344133	3.90965614	0.25832773
H	1.32747836	4.75654181	0.25727451
C	-2.47442264	2.14544696	0.38775155
C	-0.69502963	3.92325281	0.35189116
H	-1.34566145	4.78406897	0.43696222
C	-1.11785391	2.53379155	0.31116871
C	3.44770546	3.14294543	0.04627811
C	5.44983400	5.12386796	0.04550014
C	3.86610900	3.74851123	-1.15503029
C	4.06082516	3.55929431	1.22491798
C	5.05040976	4.53560068	1.24932119
C	4.85569401	4.72418374	-1.15180417
H	2.64477922	2.75177591	-2.19015215
H	5.48963094	4.82082006	2.19884074
H	5.16403660	5.18155887	-2.08785226
C	3.35402552	-3.87639997	-0.26389010
C	5.34170274	-5.86891455	-0.39453010
C	3.76851466	-4.40455268	-1.49487494
C	3.96143980	-4.37945015	0.89151366
C	4.93686506	-5.35754080	0.84542994
C	4.75484505	-5.39262942	-1.56343919
H	2.56588836	-3.33126377	-2.47514068
H	3.65118684	-3.98426542	1.85692715
H	5.39757206	-5.73684269	1.75350370
H	5.03304271	-5.75958547	-2.54524078
C	-3.61720217	-3.79630819	0.03218702
C	-5.64055668	-5.75648370	-0.03041600
C	-4.30536675	-4.09922046	-1.14762137
C	-3.97334089	-4.50508490	1.18876061
C	-4.97702092	-5.47727315	1.16095056
C	-5.29931743	-5.05865699	-1.19640695
H	-4.04137158	-3.56210068	-2.05660806
H	-2.69069492	-3.61862500	2.25107177
H	-5.20751734	-5.98903188	2.08877397
H	-5.81991186	-5.28376609	-2.12326167
C	-3.50643721	3.21529284	0.51541550
C	-5.44207246	5.24781547	0.74923864
C	-3.86629729	3.73053911	1.77645493
C	-4.14611179	3.74410268	-0.60246826
C	-5.10334528	4.74812038	-0.51184208
C	-4.82313608	4.73215695	1.88803422
H	-2.64476483	2.61615254	2.68383267
H	-3.88001162	3.35897759	-1.58507141
H	-5.56465519	5.12327243	-1.41860598
H	-5.08574225	5.11903985	2.86873080
O	6.30785365	-6.82052427	-0.34939831
O	-6.62568543	-6.68021342	-0.16417409
O	-6.35228987	6.22935740	0.97761145
O	6.39894597	6.08796996	-0.07210540
C	7.02355335	6.56303747	1.10783884
H	6.26659985	6.96614250	1.79832725
H	7.54400967	5.73754530	1.61809547
C	8.00773830	7.64659743	0.70908126
H	7.46921001	8.43972018	0.17652309
H	8.73805966	7.22742375	0.00649995
C	8.72476744	8.22838850	1.91770175
H	9.28777221	7.44838359	2.44290490
H	8.00396326	8.66753597	2.61691825
S	9.87625206	9.51950463	1.37057930
H	10.34396181	9.83247884	2.59215389
C	6.77680702	-7.36983463	-1.56875998
H	5.94754114	-7.85586869	-2.10635430
H	7.17509972	-6.57059289	-2.21315264
C	7.86437218	-8.37520520	-1.23611879
H	7.45086241	-9.13635816	-0.56323369
H	8.66907667	-7.87217932	-0.68828769
C	8.43068374	-9.03933165	-2.48131942
H	8.85294742	-8.28985015	-3.16271491
H	7.65474911	-9.57256506	-3.04269403
S	9.81469329	-10.16252477	-2.17816990
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H	3.74867377	3.10391984	2.16294880
C	-6.99167414	6.82350194	-0.13863345
H	-6.23944421	7.24855198	-0.82102086
H	-7.56434293	6.06446067	-0.69414180
C	-7.91313530	7.91227114	0.37793589
H	-7.32239260	8.63887135	0.94867710
H	-8.63703931	7.47065809	1.07335725
C	-8.64406053	8.61475357	-0.75576931
H	-7.92842509	9.06963073	-1.45022753
H	-9.26431985	7.90295761	-1.31241671
S	-9.70776727	9.91528725	-0.07093097
H	-10.20512261	10.33897986	-1.24653636
C	-7.00551529	-7.43165383	0.97602995
H	-6.13686550	-7.98407441	1.36712189
H	-7.36228725	-6.75697448	1.76990192
C	-8.10677517	-8.39017498	0.56030629
H	-7.74045025	-9.01816674	-0.26095909
H	-8.95789260	-7.82164404	0.16916336
C	-8.56286099	-9.26634772	1.71682935

H	-7.73678894	-9.86460372	2.11837581
H	-8.93705753	-8.65130833	2.54505880
S	-9.95240006	-10.36028442	1.34138710
H	-9.31723733	-11.12447487	0.43389697
O	-3.30414494	3.28061621	2.92522439
O	3.33011959	3.41347829	-2.35457634
O	3.24530057	-3.98929819	-2.67569802
O	-3.37610116	-4.28697194	2.38686784

C_3H_7SH

C	9.848183	0.070705	13.485273
H	10.771576	0.470741	13.047639
H	9.322441	0.899425	13.976204
C	8.965243	-0.587779	12.411087
H	9.501605	-1.429810	11.953253
H	8.061352	-1.004064	12.875797
H	10.129497	-0.653481	14.258577
C	8.558525	0.406784	11.317209
H	7.986822	1.236476	11.745968
H	9.444702	0.808947	10.815183
S	7.500627	-0.458834	10.057647
H	7.298400	0.613689	9.257203

ce-$MoSe_2$ (i)

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Mo	7.369559	-4.489806	15.829191
Mo	-7.188656	-15.067038	12.464715
Mo	3.432723	-4.215803	-0.130114
Mo	-6.401326	-15.121808	15.656612
Mo	4.220115	-4.270624	3.061723
Mo	-5.613934	-15.176629	18.848449
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Mo	5.794836	-4.380216	9.445457
Mo	-4.039212	-15.286220	25.232184
Mo	6.582166	-4.434985	12.637355
Mo	-6.205838	-13.203661	7.173760
Mo	-1.481612	-13.532485	26.324903
Mo	-5.418445	-13.258482	10.365596
Mo	-4.631055	-13.313304	13.557433
Mo	-3.843725	-13.368073	16.749331
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Mo	-2.269003	-13.477664	23.133066
Mo	-4.435567	-11.395156	5.074581
Mo	0.288597	-11.723928	24.225784
Mo	-3.648237	-11.449926	8.266478
Mo	-2.860846	-11.504747	11.458316
Mo	-2.073453	-11.559568	14.650153
Mo	-1.286124	-11.614337	17.842050
Mo	-0.498733	-11.669159	21.033887
Mo	-2.665357	-9.586600	2.975463
Mo	2.058868	-9.915424	22.126607
Mo	-1.877966	-9.641421	6.167301
Mo	-1.090636	-9.696190	9.359198
Mo	-0.303245	-9.751013	12.551035
Mo	0.484147	-9.805833	15.742872
Mo	1.271477	-9.860603	18.934769
Mo	-0.895087	-7.778095	0.876285
Mo	3.829079	-8.106868	20.027489
Mo	-0.107757	-7.832865	4.068183
Mo	0.679635	-7.887686	7.260020
Mo	1.466965	-7.942456	10.451917
Mo	2.254356	-7.997276	13.643754
Mo	3.041747	-8.052097	16.835592
Mo	0.875123	-5.969538	-1.222833
Mo	5.599348	-6.298362	17.928309
Mo	1.662514	-6.024360	1.969004
Mo	2.449844	-6.079130	5.160901
Mo	3.237235	-6.133950	8.352739
Mo	4.024567	-6.188720	11.544636
Mo	4.811957	-6.243541	14.736473
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Se	-4.253878	-15.888265	16.807244
Se	-3.466486	-15.943086	19.999081
Se	-2.679156	-15.997856	23.190978
Se	-1.891764	-16.052676	26.382816
Se	-4.058329	-13.970169	8.324332
Se	-3.270998	-14.024938	11.516229
Se	-2.483607	-14.079760	14.708066
Se	-1.696276	-14.134530	17.899964
Se	-0.908886	-14.189350	21.091801
Se	-0.121555	-14.244120	24.283698
Se	-2.288119	-12.161613	6.225213
Se	-1.500727	-12.216434	9.417050
Se	-0.713398	-12.271203	12.608949
Se	0.073994	-12.326024	15.800786
Se	0.861324	-12.380793	18.992683
Se	1.648716	-12.435615	22.184520
Se	-0.517910	-10.353055	4.126095
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Se	1.056873	-10.462698	10.509770
Se	1.844204	-10.517468	13.701667
Se	2.631594	-10.572289	16.893504
Se	3.418925	-10.627058	20.085401
Se	1.252361	-8.544551	2.026918
Se	2.039692	-8.599321	5.218815
Se	2.827082	-8.654142	8.410652
Se	3.614475	-8.708962	11.602488
Se	4.401805	-8.763733	14.794387
Se	5.189196	-8.818554	17.986223
Se	3.022570	-6.735995	-0.072200
Se	3.809963	-6.790816	3.119636
Se	4.597293	-6.845586	6.311534
Se	5.384684	-6.900406	9.503371
Se	6.172074	-6.955228	12.695208
Se	6.959405	-7.009998	15.887105
Se	-7.565895	-12.492026	9.214964
Se	-6.778564	-12.546796	12.406861
Se	-5.991173	-12.601617	15.598698
Se	-5.203781	-12.656438	18.790536
Se	-4.416451	-12.711207	21.982433
Se	-3.629060	-12.766028	25.174270
Se	-5.795685	-10.683469	7.115846
Se	-5.008293	-10.738291	10.307683
Se	-4.220963	-10.793061	13.499581
Se	-3.433572	-10.847881	16.691418
Se	-2.646180	-10.902703	19.883255
Se	-1.858850	-10.957472	23.075152

Se	-4.025415	-8.874965	5.016667
Se	-3.238084	-8.929734	8.208566
Se	-2.450692	-8.984556	11.400403
Se	-1.663363	-9.039326	14.592300
Se	-0.875971	-9.094147	17.784137
Se	-0.088580	-9.148968	20.975975
Se	-2.255204	-7.066409	2.917550
Se	-1.467813	-7.121230	6.109387
Se	-0.680483	-7.176	9.301284
Se	0.106908	-7.230820	12.493121
Se	0.894239	-7.285590	15.685019
Se	1.681629	-7.340411	18.876856
Se	-0.484934	-5.257904	0.818372
Se	0.302395	-5.312674	4.010269
Se	1.089788	-5.367494	7.202106
Se	1.877117	-5.422264	10.394004
Se	2.664509	-5.477085	13.585841
Se	3.451839	-5.531855	16.777738
Se	1.285276	-3.449347	-1.280746
Se	2.072667	-3.504168	1.911090
Se	2.859997	-3.558937	5.102989
Se	3.647387	-3.613759	8.294825
Se	4.434719	-3.668529	11.486723
Se	5.222109	-3.723350	14.678559
Se	-10.123495	-14.245761	8.122244
Se	-8.386200	-17.532408	9.330790
Se	-9.336166	-14.300531	11.314143
Se	-6.615930	-15.723903	7.231612
Se	-5.399330	-14.574534	27.273449
Se	-3.662035	-17.861182	28.481994
Se	-4.611939	-14.629355	30.465286
Se	-2.841730	-12.820799	28.366167
Se	-1.104434	-16.107445	29.574713
Se	0.497945	-3.394578	-4.472645
Se	2.235241	-6.681225	-3.264098
Se	4.005451	-4.872668	-5.363216
Se	3.055546	-1.640842	-3.379925
Se	4.792841	-4.927490	-2.171380
Se	6.009440	-3.778120	17.870458
Se	8.729676	-5.201493	13.787926
Se	7.779711	-1.969616	15.771278
Se	9.517006	-5.256262	16.979824
Se	-7.598808	-17.587229	12.522627
Se	-8.548773	-14.355352	14.505979
Se	3.842875	-1.695613	-0.188028
Se	5.580171	-4.982260	1.020518
Se	-6.811478	-17.642	15.714526
Se	-7.761383	-14.410173	17.697816
Se	4.630268	-1.750433	3.003809
Se	6.367562	-5.037081	4.212355
Se	-6.024087	-17.696821	18.906362
Se	-6.974052	-14.464943	20.889714
Se	5.417597	-1.805203	6.195706
Se	7.154893	-5.091850	7.404252
Se	-5.236756	-17.751590	22.098260
Se	-6.186662	-14.519763	24.081550
Se	6.204989	-1.860024	9.387543
Se	7.942285	-5.146671	10.596089
Se	-4.449366	-17.806412	25.290097
Se	6.992319	-1.914794	12.579441
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Se	-4.845719	-13.915347	5.132495
Se	-1.071459	-11.012294	26.266989
Se	0.665836	-14.298941	27.475535
Se	-6.583015	-10.628700	3.923949
Se	-3.075510	-12.106791	3.033377
Se	0.698751	-9.203737	24.167872
Se	2.436046	-12.490385	25.376417
Se	-4.812805	-8.820144	1.824830
Se	-1.305239	-10.298286	0.934198
Se	2.469021	-7.395232	22.068693
Se	4.206317	-10.681880	23.277239
Se	-3.042535	-7.011638	-0.274347
Se	0.464971	-8.489730	-1.164919
Se	4.239231	-5.586676	19.969575
Se	5.976526	-8.873324	21.178121
Se	-1.272325	-5.203082	-2.373465
Se	7.746797	-7.064819	19.078942

Edge complex ii

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Mo	-3.251182	-15.340910	28.424055
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Mo	7.369148	-4.489105	15.828765
Mo	-7.188394	-15.067422	12.464789
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Mo	-6.400976	-15.122099	15.656666
Mo	4.219353	-4.270292	3.061376
Mo	-5.613497	-15.176828	18.848484
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Mo	-4.826079	-15.231506	22.040361
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Mo	6.581668	-4.434376	12.636949
Mo	-6.205848	-13.204033	7.173788
Mo	-1.481096	-13.532302	26.324810
Mo	-5.418368	-13.258762	10.365604
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Mo	-2.268575	-13.477574	23.132993
Mo	-4.435763	-11.395424	5.074542
Mo	0.288928	-11.723641	24.225625
Mo	-3.648345	-11.450102	8.266419
Mo	-2.860866	-11.504831	11.458236
Mo	-2.073386	-11.559559	14.650053
Mo	-1.285969	-11.614236	17.841931
Mo	-0.498490	-11.668965	21.033748
Mo	-2.665739	-9.586764	2.975358
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Mo	-1.878260	-9.641493	6.167175
Mo	-1.090842	-9.696170	9.359052
Mo	-0.303363	-9.750900	12.550869
Mo	0.484116	-9.805628	15.742686
Mo	1.271534	-9.860305	18.934563
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Mo	3.829038	-8.106374	20.027196
Mo	-0.108236	-7.832833	4.067990
Mo	0.679243	-7.887562	7.259807
Mo	1.466661	-7.942239	10.451684
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Mo	0.874371	-5.969496	-1.223073
Mo	5.599123	-6.297765	17.927949
Mo	1.661850	-6.024225	1.968745
Mo	2.449268	-6.078902	5.160622
Mo	3.236747	-6.133630	8.352439
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Se	-5.828340	-15.778982	10.423556
Se	-5.040860	-15.833710	13.615374
Se	-4.253443	-15.888388	16.807251
Se	-3.465963	-15.943117	19.999068
Se	-2.678546	-15.997794	23.190945
Se	-1.891066	-16.052522	26.382762
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Se	-3.270835	-14.025051	11.516189
Se	-2.483357	-14.079779	14.708006
Se	-1.695938	-14.134457	17.899883
Se	-0.908460	-14.189185	21.091700
Se	-0.121041	-14.243862	24.283578
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Se	-0.518206	-10.353053	4.125942
Se	0.269274	-10.407782	7.317759
Se	1.056752	-10.462510	10.509576
Se	1.844171	-10.517187	13.701453
Se	2.631649	-10.571916	16.893270
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Se	1.251880	-8.544445	2.026697
Se	2.039299	-8.599122	5.218574
Se	2.826777	-8.653851	8.410392
Se	3.614257	-8.708578	11.602208
Se	4.401675	-8.763256	14.794086
Se	5.189154	-8.817985	17.985902
Se	3.021904	-6.735785	-0.072487
Se	3.809384	-6.790514	3.119329
Se	4.596802	-6.845191	6.311207
Se	5.384281	-6.899919	9.503023
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Se	6.959177	-7.009325	15.886717
Se	-7.565904	-12.492474	9.215019
Se	-6.778485	-12.547151	12.406897
Se	-5.991006	-12.601879	15.598714
Se	-5.203526	-12.656607	18.790531
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Se	-5.795878	-10.683813	7.115835
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Se	-4.220981	-10.793219	13.499529
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Se	-1.858605	-10.957353	23.075041
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Se	1.089214	-5.367342	7.201855
Se	1.876631	-5.422019	10.393732
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Se	3.451529	-5.531424	16.777426
Se	1.284341	-3.449276	-1.281024
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Se	2.859238	-3.558681	5.102670
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Se	8.729263	-5.200716	13.787472
Se	7.779117	-1.968885	15.770812
Se	9.516681	-5.255393	16.979349
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Se	-6.186134	-14.519944	24.081593
Se	6.204220	-1.859478	9.387118
Se	7.941784	-5.145987	10.595655
Se	-4.448570	-17.806454	25.290131
Se	6.991638	-1.914156	12.578995
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Se	-1.071126	-11.012082	26.266858
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Se	-6.583296	-10.629136	3.923958
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Se	0.698898	-9.203422	24.167673

Se	2.436462	-12.489931	25.376210
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Se	4.239008	-5.586153	19.969243
Se	5.976572	-8.872662	21.177780
Se	-1.273162	-5.203207	-2.373657
Se	7.746657	-7.064054	19.078535
C	9.163263	2.077071	10.245730
H	10.202706	2.181874	9.909441
H	8.527983	2.654959	9.562572
C	8.737155	0.602	10.287944
H	9.363213	0.040340	10.993594
H	7.706284	0.521256	10.654640
H	9.084851	2.529558	11.240726
C	8.828161	-0.056673	8.906518
H	8.189719	0.449570	8.173181
H	9.858295	-0.034888	8.523924
S	8.422373	-1.857171	8.880089
H	6.900166	-1.757551	5.947820

Center vacancy small ce-$MoSe_2$ (iii)

Mo	9.870569	-0.051187	0.192843
Mo	8.215039	2.785176	0.033902
Mo	6.559510	5.621538	-0.125038
Mo	3.272104	5.605140	-0.185337
Mo	6.583163	-0.067585	0.132544
Mo	4.927633	2.768778	-0.026397
Se	3.234472	7.573894	1.330892
Se	1.602595	4.721133	1.429533
Se	3.258125	1.884771	1.588473
Se	6.545531	1.901169	1.648773
Se	4.891	4.737532	1.489833
Se	8.201061	-0.935193	1.807713
Se	9.908200	-2.019940	-1.323387
Se	8.252671	0.816422	-1.482327
Se	11.488467	-0.918796	1.868012
Se	9.832937	1.917566	1.709072
Se	11.540077	0.832819	-1.422028
Se	4.941612	6.489047	-1.800204
Se	6.521878	7.590291	1.391192
Se	8.177407	4.753929	1.550132
Se	9.884548	3.669182	-1.580968
Se	8.229018	6.505445	-1.739904
Se	3.309735	3.636386	-1.701566
Se	1.654206	6.472650	-1.860503
Se	4.913655	-0.951591	1.747413
Se	4.965265	0.824	-1.542626
Se	6.620795	-2.036338	-1.383687

Center vacancy small complex (iv)

Mo	9.870569	-0.051187	0.192843
Mo	8.215039	2.785176	0.033902
Mo	6.559510	5.621538	-0.125038
Mo	3.272104	5.605140	-0.185337
Mo	6.583163	-0.067585	0.132544
Mo	4.927633	2.768778	-0.026397
Se	3.234472	7.573894	1.330892
Se	1.602595	4.721133	1.429533
Se	3.258125	1.884771	1.588473
Se	6.545531	1.901169	1.648773
Se	4.891	4.737532	1.489833
Se	8.201061	-0.935193	1.807713
Se	9.908200	-2.019940	-1.323387
Se	8.252671	0.816422	-1.482327
Se	11.488467	-0.918796	1.868012
Se	9.832937	1.917566	1.709072
Se	11.540077	0.832819	-1.422028
Se	4.941612	6.489047	-1.800204
Se	6.521878	7.590291	1.391192
Se	8.177407	4.753929	1.550132
Se	9.884548	3.669182	-1.580968
Se	8.229018	6.505445	-1.739904
Se	3.309735	3.636386	-1.701566
Se	1.654206	6.472650	-1.860503
Se	4.913655	-0.951591	1.747413
Se	4.965265	0.824	-1.542626
Se	6.620795	-2.036338	-1.383687
S	6.603361	3.650371	-1.657512
C	6.853133	3.837235	-3.482453
H	6.207262	4.679905	-3.751558
H	7.897737	4.160960	-3.526033
C	6.592797	2.590992	-4.333032
H	7.253459	2.673952	-5.208588
C	5.139731	2.442279	-4.799421
H	4.827680	3.313154	-5.389575
H	5.023546	1.545915	-5.419358
H	4.454853	2.353542	-3.951574
H	6.920061	1.693383	-3.798196

Edge vacancy small ce-$MoSe_2$ (v)

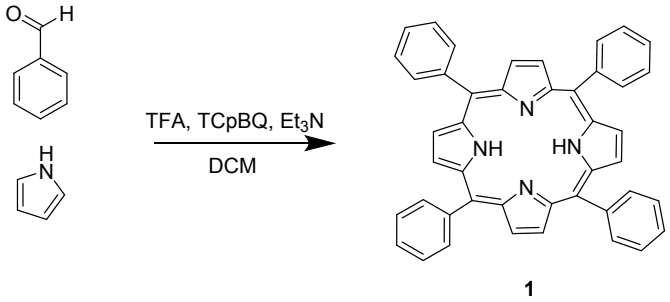
Mo	9.882300	-0.042400	0.059800
Mo	8.170600	2.762100	-0.065300
Mo	6.458900	5.566600	-0.190300
Mo	3.172500	5.491300	-0.119900
Mo	6.596	-0.117700	0.130100
Mo	4.884200	2.686800	0.005100
Se	3.159	7.477100	1.374400
Se	1.584300	4.597300	1.569700
Se	3.296100	1.792700	1.694700
Se	6.582400	1.868	1.624400
Se	4.870700	4.672600	1.499400
Se	8.294200	-0.936500	1.749400
Se	9.895900	-2.028200	-1.434500
Se	8.184100	0.776300	-1.559600
Se	11.580600	-0.861200	1.679100
Se	9.868800	1.943300	1.554100
Se	11.470500	0.851600	-1.629900
Se	4.760600	6.385300	-1.809600
Se	6.445300	7.552400	1.304
Se	6.472400	3.580800	-1.684600
Se	8.157100	4.747900	1.429
Se	9.758800	3.656100	-1.754900
Se	8.047	6.460600	-1.879900
Se	3.186	3.505500	-1.614200
Se	1.474200	6.310	-1.739300
Se	5.007800	-1.011800	1.819800
Se	6.609500	-2.103500	-1.364200

Edge vacancy small complex (vi)

Mo	9.882349	-0.042416	0.059766
Mo	8.170604	2.762097	-0.065260
Mo	6.458860	5.566609	-0.190286
Mo	3.172475	5.491307	-0.119943
Mo	6.595964	-0.117718	0.130109
Mo	4.884220	2.686795	0.005083
Se	3.158959	7.477071	1.374352
Se	1.584319	4.597257	1.569722
Se	3.296064	1.792744	1.694748
Se	6.582449	1.868046	1.624404
Se	4.870704	4.672559	1.499378
Se	8.294193	-0.936466	1.749430
Se	9.895865	-2.028179	-1.434530
Se	8.184120	0.776333	-1.559556
Se	11.580578	-0.861164	1.679087
Se	9.868833	1.943348	1.554061
Se	11.470505	0.851635	-1.629899
Se	4.760633	6.385258	-1.809602
Se	6.445344	7.552373	1.304009
Se	6.472376	3.580846	-1.684582
Se	8.157089	4.747861	1.429035
Se	9.758760	3.656148	-1.754925
Se	8.047018	6.460560	-1.879945
Se	3.185991	3.505544	-1.614238
Se	1.474248	6.309956	-1.739259
Se	5.007808	-1.011768	1.819774
Se	6.609480	-2.103481	-1.364186
S	4.487738	0.463029	-1.214937
C	4.946637	0.607155	-3.010440
H	5.545656	1.510385	-3.150320
H	5.579559	-0.262526	-3.219440
C	3.706209	0.615778	-3.906472
H	3.035253	1.427588	-3.602486
H	3.154448	-0.323074	-3.767903
C	4.097355	0.794113	-5.384759
H	4.767584	-0.008931	-5.717620
H	3.209177	0.784008	-6.027991
H	4.615063	1.749153	-5.538726

SYNTHESIS OF PORPHYRINS

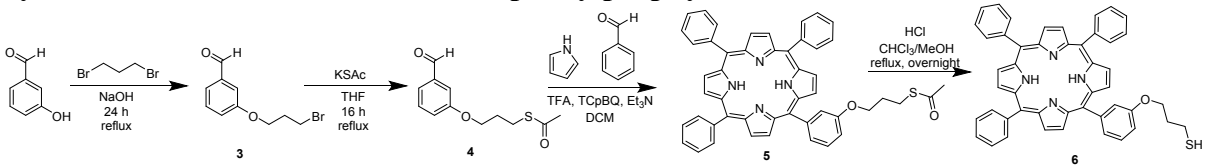
Synthesis of tetraphenylporphyrin 1:



Scheme S1. Synthetic route of porphyrin **1.**

Synthesis of 5,10,15,20-tetraphenylporphyrin **1**: 0.204 mL (2.0 mmol) of benzaldehyde and 0.139 mL (2 mmol) of pyrrole were dissolved under darkness in 50 mL of DCM. 0.137 mL (2 mmol) of trifluoroacetic acid was added, and the reaction was vigorously stirred for 1.5 h. Then, 0.369 g (1.5 mmol) of tetrachloro-1,4-benzoquinone was added, and the reaction was gently refluxed for 1 additional hour. After cooling down, 0.277 mL (2 mmol) of Et_3N was added to neutralize the acids, and the solvent was concentrated. Purification was performed by column chromatography with DCM. A purple solid was obtained in a 65% yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 8.86 (s, 8H), 8.28 – 8.17 (m, 8H), 7.83 – 7.69 (m, 12H), -2.75 (s, 2H).

Synthesis of 1x thiol-terminated tetraphenylporphyrin 6:



Scheme S2: Synthetic route of porphyrin **6.**

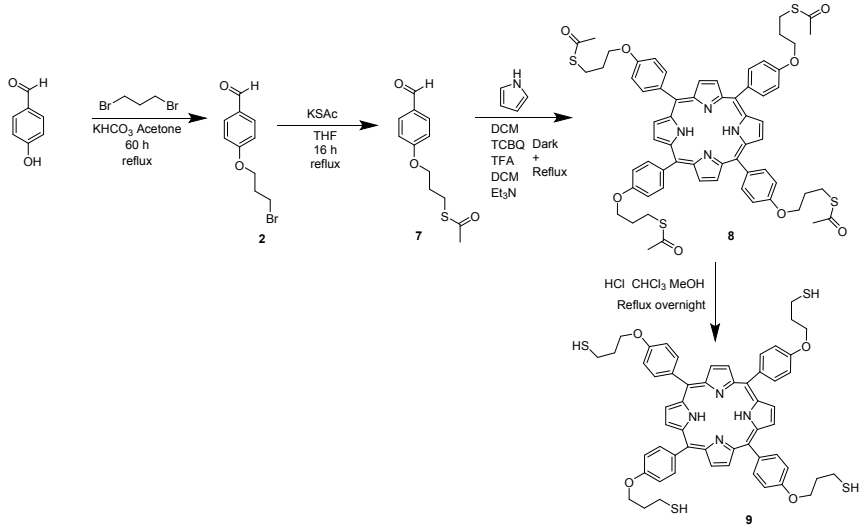
Synthesis of 3-(3-bromopropoxy)benzaldehyde **3:** 1.221 g (10 mmol) of 3-hydroxybenzaldehyde was dissolved in 6 mL (12 mmol) of NaOH 2M aqueous solution. Then, 1.22 mL (12 mmol) of 1,3-dibromopropane was added. The reaction was magnetically stirred at 100 °C 24 h. Then, the layers were separated, and the aqueous phase was extracted twice with chloroform. Organic fractions were mixed, and then washed twice with NaOH 2M, once with HCl 2M and finally twice with water. The obtained fractions were dried with $MgSO_4$ and the solvent concentrated. Purification was performed with column chromatography employing a 4:1 mixture of petroleum ether/ethyl acetate to obtain a yellow oil in a 54% yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 9.98 (s, 1H), 7.59 – 7.34 (m, 3H), 7.25 – 7.14 (m, 1H), 4.18 (t, J = 5.8 Hz, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.36 (q, J = 6.1 Hz, 2H).

Synthesis of S-(3-(3-formylphenoxy)propyl) ethanethioate **4:** 0.984 g (4.05 mmol) of **3** and 0.925 g (8.1 mmol) of potassium thioacetate were suspended in 30 mL of THF. The reaction was magnetically stirred at reflux conditions 16 h. After cooling down, reaction crude was filtrated to remove precipitates, washed with additional THF and finally concentrated. The residue was dissolved in ethyl acetate, washed twice with brine, dried with with $MgSO_4$ and the solvent concentrated. Purification was performed with column chromatography employing a 4:1 mixture of petroleum ether/ethyl acetate to obtain a brownish oil in an 80% yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 9.99 (s, 1H), 7.61 – 7.42 (m, 2H), 7.39 (d, J = 2.1 Hz, 1H), 7.24 – 7.10 (m, 1H), 4.09 (t, J = 6.0 Hz, 2H), 3.09 (t, J = 7.1 Hz, 2H), 2.36 (s, 3H), 2.12 (p, J = 6.5 Hz, 2H).

Synthesis of S-(3-(3-(5,15,20-triphenylporphyrin-10-yl)phenoxy)propyl) ethanethioate **5:** 0.120 g (0.5 mmol) of **4**, 0.153 mL (1.5 mmol) of benzaldehyde and 0.138 mL (2 mmol) of pyrrole were dissolved under darkness in 50 mL of DCM. 0.137 mL (2 mmol) of trifluoroacetic acid was added, and the reaction was vigorously stirred for 1.5 h. Then, 0.369 g (1.5 mmol) of tetrachloro-1,4-benzoquinone was added, and the reaction was gently refluxed for 1 additional hour. After cooling down, 0.277 mL (2 mmol) of Et_3N was added to neutralize the acids, and the solvent was concentrated. Purification was performed by column chromatography with DCM to separate the target porphyrin of the resulting statistical mixture. A purple solid was obtained in a 20% yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 9.05 – 8.87 (m, 8H), 8.42 – 8.22 (m, 6H), 8.01 – 7.75 (m, 10H), 7.70 (t, J = 7.9 Hz, 1H), 7.42 – 7.32 (m, 1H), 4.33 (t, J = 5.8 Hz, 2H), 3.72 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), -2.65 (s, 2H).

Synthesis of 3-(3-(5,15,20-triphenylporphyrin-10-yl)phenoxy)propane-1-thiol **6**: 0.04 g (0.05 mmol) of **5** was dissolved in 9 mL of $CHCl_3$. To this mixture, 9 mL of an HCl 2 M solution in methanol was added, and the reaction was held under reflux conditions overnight. After cooling down, solvent was removed, the residue was dissolved in DCM, and it was washed once with 2M NaOH and three times with water. Solvent was dried and concentrated to give a red-wine solid. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 9.05 – 8.80 (m, 8H), 8.27 (dd, J = 7.2, 1.9 Hz, 6H), 7.94 – 7.60 (m, 12H), 7.35 (dd, J = 8.3, 1.9 Hz, 1H), 4.29 (t, J = 5.9 Hz, 2H), 2.84 (c, J = 7.1 Hz, 2H), 2.19 (p, J = 7.0 Hz 2H), 1.46 (t, J = 8.2 Hz, 1H), -2.73 (s, 2H).

Synthesis of 4x thiol-terminated tetraphenylporphyrin 9:



Scheme S3: Synthetic route of porphyrin **9**

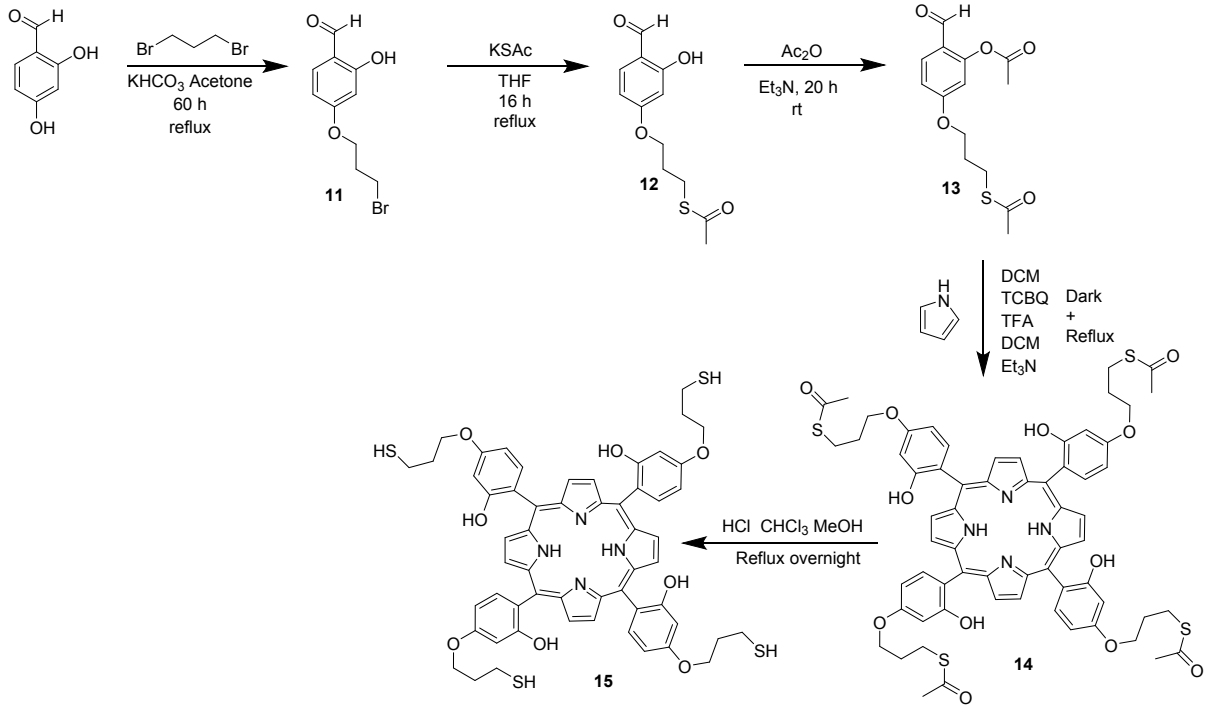
Synthesis of 4-(3-bromopropoxy) benzaldehyde **2:** 2.0 g (16.37 mmol) of 4-hydroxybenzaldehyde was dissolved in 125 mL of acetone. Then, 2.03 g (20.27 mmol) of potassium bicarbonate were suspended with strong stirring. To this suspension, 3.744 mL (32.74 mmol) of 1,3-dibromopropane were added, reaction was set under reflux conditions and maintained for 60 h. After cooling down, solvent was removed by rotary evaporation, water was added, and reaction crude was extracted 3 times with 20 mL of $CHCl_3$. The organic fractions were collected, dried over $MgSO_4$ and concentrated. Purification by column chromatography (1:4 ethyl acetate – hexane as eluent) afforded a white-yellow solid in 52.4 % yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: 9.91 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 4.22 (t, J = 6.0 Hz, 2H), 3.66 (t, J = 7.1 Hz, 2H), 2.38 (m, 2H).

Synthesis of S-(3-(4-formylphenoxy) propyl) ethanethioate 7: 1.458 g (6 mmol) of **2** and 1.37 g (12 mmol) of potassium thioacetate were suspended in 40 mL of THF, and the mixture was gently magnetically stirred under reflux conditions for 16 h. After cooling down, reaction crude was filtrated to remove precipitates, washed with additional THF and finally concentrated. The residue was dissolved in ethyl acetate, washed twice with brine and twice with water too. The organic fraction was dried over $MgSO_4$ and concentrated. Purification by column chromatography (1:4 ethyl acetate – petroleum ether as eluent) afforded an orange oil in 92 % yield. 9.75 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 3.97 (t, J = 6.3 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.22 (s, 3H), 1.98 (q, J = 6.3 Hz, 2H).

Synthesis of S,S',S",S"' - (((porphyrin - 5,10,15,20 – tetrayltetrakis (benzene -4,1- diyl)) tetrakis (oxy)) tetrakis(propane-3,1-diyl)) tetraethanethioate **8**: 0.238 g (1 mmol) of **7** and 0.068 mL (1 mmol) of pyrrole were dissolved under darkness in 30 mL of dichloromethane (DCM). 0.076 mL (1 mmol) of trifluoroacetic acid was added, and the reaction was vigorously stirred for 1.5 h. Then, 0.184 g (0.75 mmol) of tetrachloro-1,4-benzoquinone was added, and the reaction was gently refluxed for 1 additional hour. After cooling down, 0.138 mL (1 mmol) of Et_3N was added to neutralize the acids, and the solvent was concentrated. Purification was performed with column chromatography employing a 10:1 mixture of DCM/Methanol (MeOH) to obtain a red wine solid in a 64% yield. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 8.89 (s, 8H), 8.14 (d, J = 8.5 Hz, 8H), 7.26 (d, J = 8.4 Hz, 8H), 4.32 (t, J = 6.0 Hz, 8H), 3.26 (t, J = 7.1 Hz, 8H), 2.44 (s, 12H), 2.35 – 2.24 (m, 8H). -2.05 (s, 2H).

Synthesis of 3,3',3",3"' - ((porphyrin - 5,10,15,20 – tetrayltetrakis (benzene - 4,1 - diyl)) tetrakis (oxy)) tetrakis (propane-1-thiol) **9**: 0.10 g (0.087 mmol) of **8** was dissolved in 9 mL of $CHCl_3$. To this mixture, 9 mL of a HCl 2 M solution in MeOH was added, and the reaction was held under reflux conditions overnight. After cooling down, solvent was removed, the residue was dissolved in DCM, and it was washed once with 2M NaOH and three times with water. Solvent was dried and concentrated to give a red-wine solid. ^{1}H-NMR ($CDCl_3$) 300 MHz: δ 8.92 (s, 8H), 7.89 – 7.80 (m, 8 H), 7.66 (t, J = 7.9 Hz, 4H), 7.35 (dd, J = 8.2, 2.0 Hz, 6H), 4.29 (t, J = 5.9 Hz, 8H), 2.83 (c, J = 7.2 Hz, 8H), 2.32 – 2.07 (m, 8H), 1.43 (t, J = 8.0 Hz, 4H), -2.61 (s, 2H).

Synthesis of OH-containing 4x thiol-terminated tetraphenylporphyrin 15:



Scheme S4. Synthetic route of porphyrin **15.**

Synthesis of 4-(3-bromopropoxy)-2-hydroxybenzaldehyde **11**: 2.0 g (14.48 mmol) of 2,4-dihydroxybenzaldehyde was dissolved in 125 mL of acetone. Then, 2.03 g (20.27 mmol) of potassium bicarbonate were suspended with strong stirring. To this suspension, 2.939 mL (28.96 mmol) of 1,3-dibromopropane were added, reaction was set under reflux conditions and maintained for 60 h. After cooling down, solvent was removed by rotary evaporation, water was added, and reaction crude was extracted 3 times with 20 mL of $CHCl_3$. The organic fractions were collected, dried over $MgSO_4$ and concentrated. Purification by column chromatography (1:4 ethyl acetate – hexane as eluent) afforded a white solid in 72.4 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.39 (s, 1H), 9.62 (s, 1H), 7.35 (d, J = 8.6 Hz, 1H), 6.46 (dd, J = 8.6, 2.3 Hz, 1H), 6.35 (d, J = 2.1 Hz, 1H), 4.08 (t, J = 5.8 Hz, 2H), 3.52 (t, J = 6.0 Hz 2H), 2.21 (q, J = 5.9 Hz, 2H).

Synthesis of S-(3-(4-formyl-3-hydroxyphenoxy)propyl) ethanethioate **12**: 1.533 g (6 mmol) of **11** and 1.37 g (12 mmol) of potassium thioacetate were suspended in 40 mL of THF, and the mixture was gently magnetically stirred under reflux conditions for 16 h. After cooling down, reaction crude was filtrated to remove precipitates, washed with additional THF and finally concentrated. The residue was dissolved in ethyl acetate, washed twice with brine and twice with water too. The organic fraction was dried over $MgSO_4$ and concentrated. Purification by column chromatography (1:4 ethyl acetate – petroleum ether as eluent) afforded a brown solid

in 81 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.48 (s, 1H), 9.71 (s, 1H), 7.43 (d, J = 8.7 Hz, 1H), 6.53 (dd, J = 8.7, 2.3 Hz, 1H), 6.41 (d, J = 2.2 Hz, 1H), 4.06 (t, J = 6.1 Hz, 2H), 3.05 (t, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.1 (q, J = 6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.61, 194.41, 165.96, 164.44, 135.29, 115.20, 108.65, 101.12, 66.67, 30.66, 28.97, 25.65.

Synthesis of 5-(3-(acetylthio)propoxy)-2-formylphenyl acetate **13**. 1.971 g (7.76 mmol) of **12** were mixed in solvent-free conditions with 2.217 g (21.72 mmol) of acetic anhydride and 0.471 g (4.65 mmol) of triethylamine. With magnetic stirring, the reaction was conducted at room temperature for 20 h. Then, reaction crude was poured in water and extracted 3 times with 25 mL of $CHCl_3$. The collected organic fractions were then washed once with 50 mL of a 0.1 M HCl solution and finally twice with water. Drying over $MgSO_4$ and concentrating in vacuum yielded quantitatively a brown-red pure oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.82 (d, J = 8.7 Hz, 1H), 6.89 (dd, J = 8.6, 2.4 Hz, 1H), 6.67 (d, J = 2.4 Hz, 1H), 4.07 (t, J = 7.0 Hz, 2H), 3.06 (t, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 2.11 (q, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.63, 187.51, 169.15, 164.35, 153.17, 133.38, 121.70, 112.60, 109.32, 66.88, 30.67, 29.06, 25.63, 20.91.

Synthesis of S,S',S'',S''' - (((porphyrin -5,10,15,20- tetrayltetrakis (3- hydroxybenzene -4,1-diyl)) tetrakis(oxy)) tetrakis(propane-3,1-diyl)) tetraethanethioate **14:** 0.297 g (1 mmol) of **13** was dissolved in 25 mL of dichloromethane, and then 0.067 g (1 mmol) of pyrrole and 0.114 g (1 mmol) of trifluoroacetic acid were added. Reaction was kept under dark with vigorous stirring for 1.5 h. Then, 0.186 g (0.75 mmol) of tetrachlorobenzoquinone were added, and reaction was gently refluxed additionally for 1 h. Then, acid was neutralized employing 0.101 g (1 mmol) of trimethylamine and the solvent evaporated. Purification by column chromatography ($CHCl_3$ as eluent) afforded a violet solid in 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (t, J = 6.0 Hz, 8H), 7.99 (ddd, J = 6.5, 5.9, 4.4 Hz, 4H), 7.24 – 7.05 (m, 8H), 4.33 (t, J = 5.9 Hz, 8H), 3.26 (t, J = 7.1 Hz, 8H), 2.45 (s, 12H), 2.40 – 2.18 (m, 8H), -2.88 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.87, 168.87, 159.48, 150.71, 136.49, 127.03, 114.21, 111.20, 108.57, 66.81, 30.78, 29.40, 25.97, 19.48.

Synthesis of 6,6',6'',6'''-(porphyrin-5,10,15,20-tetrayl)tetrakis(3-(3-mercaptopropoxy)phenol) **15:** 0.197 g (0.163 mmol) of **14** was dissolved in 12 mL of $CHCl_3$. To this, 12 mL of a 2M HCl solution in MeOH was added, and the mixture was refluxed overnight. After cooling down, solvent was concentrated in vacuum, the crude was dissolved in MeOH and then precisely neutralized with a 2M NaOH solution in water. Following this, solvent was removed under reduced pressure, water was added and the solid was filtered off, washed with additional water and dried in vacuum to yield a dark violet solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.56 (s, 4H), 8.70 (m, 8H), 7.82 (m, 4H), 6.93 (m, 8H), 4.30 (t, J = 7.1 Hz, 8H), 2.77 (q, J = 6.9 Hz, 8H), 2.17 (m, 8H), 0.84 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.67, 159.31, 150.83, 136.71, 126.97, 114.51, 111.47, 108.73, 66.17, 29.47, 25.71, 19.37.

NMR SPECTRA

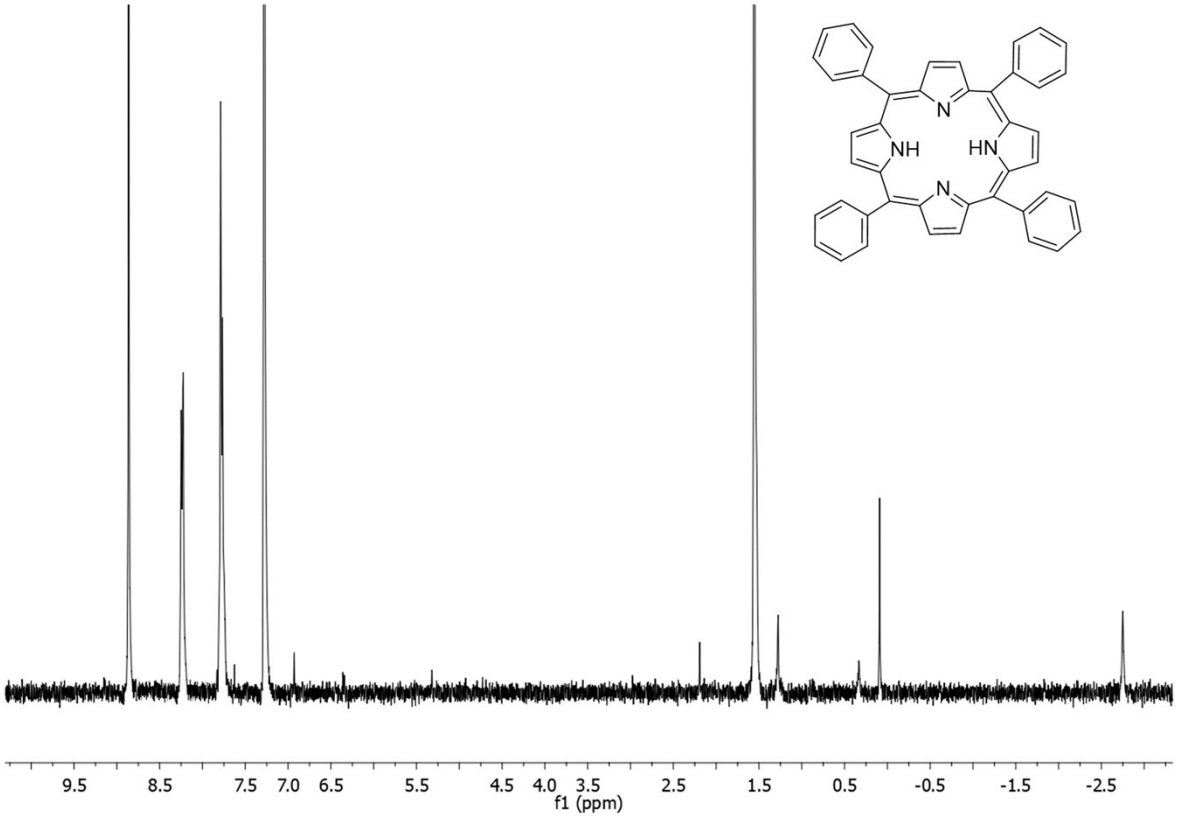


Figure S25. 5,10,15,20-tetraphenylporphyrin **1** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

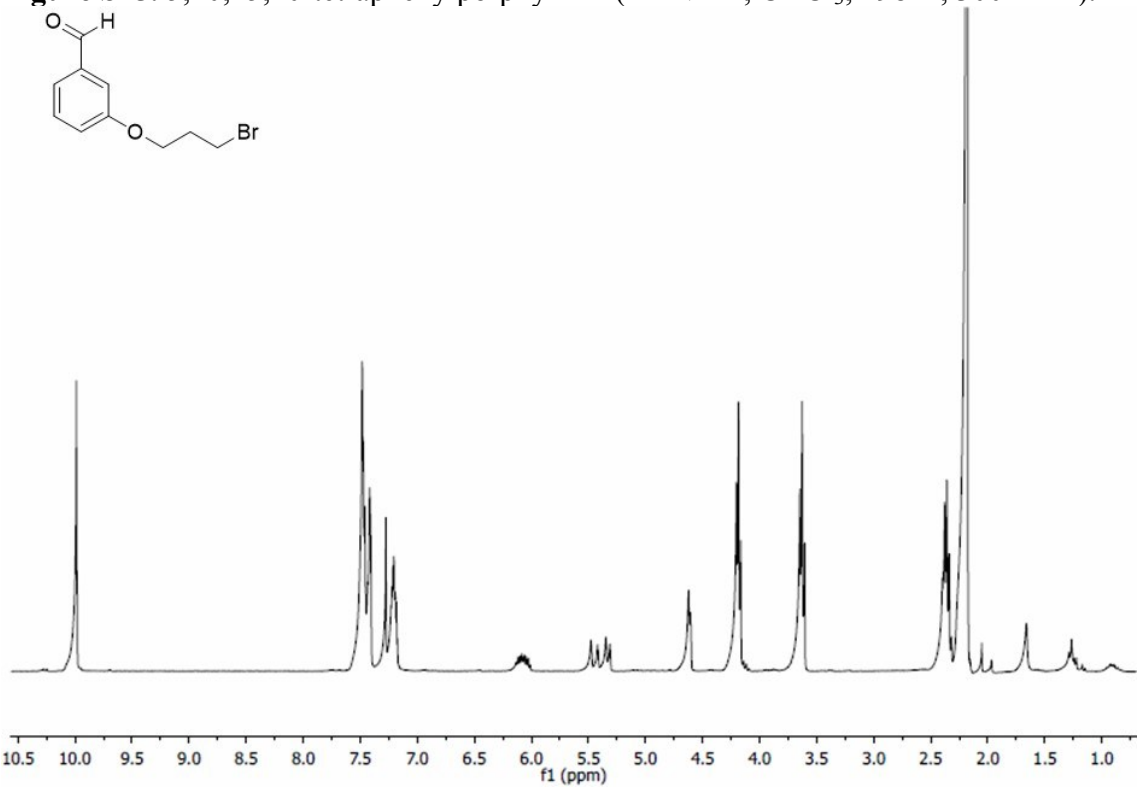


Figure S26. 3-(3-bromopropoxy)benzaldehyde **3** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

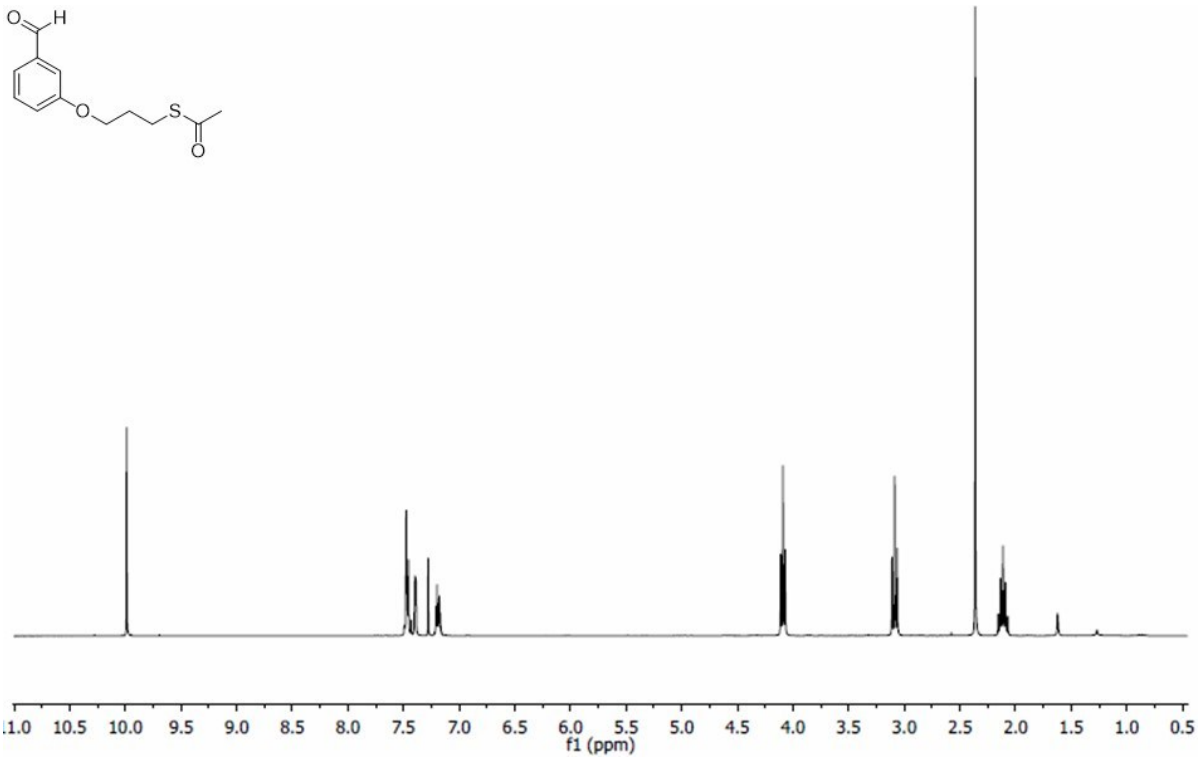


Figure S27. S-(3-(3-formylphenoxy)propyl) ethanethioate **4** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

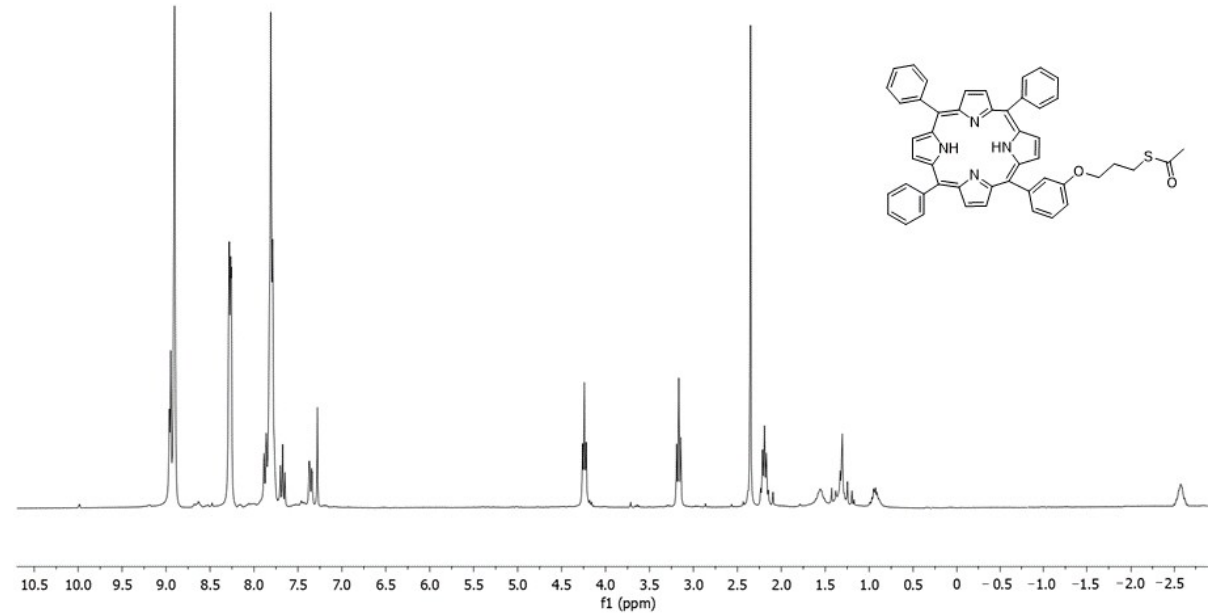


Figure S28. S-(3-(3-(5,15,20-triphenylporphyrin-10-yl)phenoxy)propyl) ethanethioate **5** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

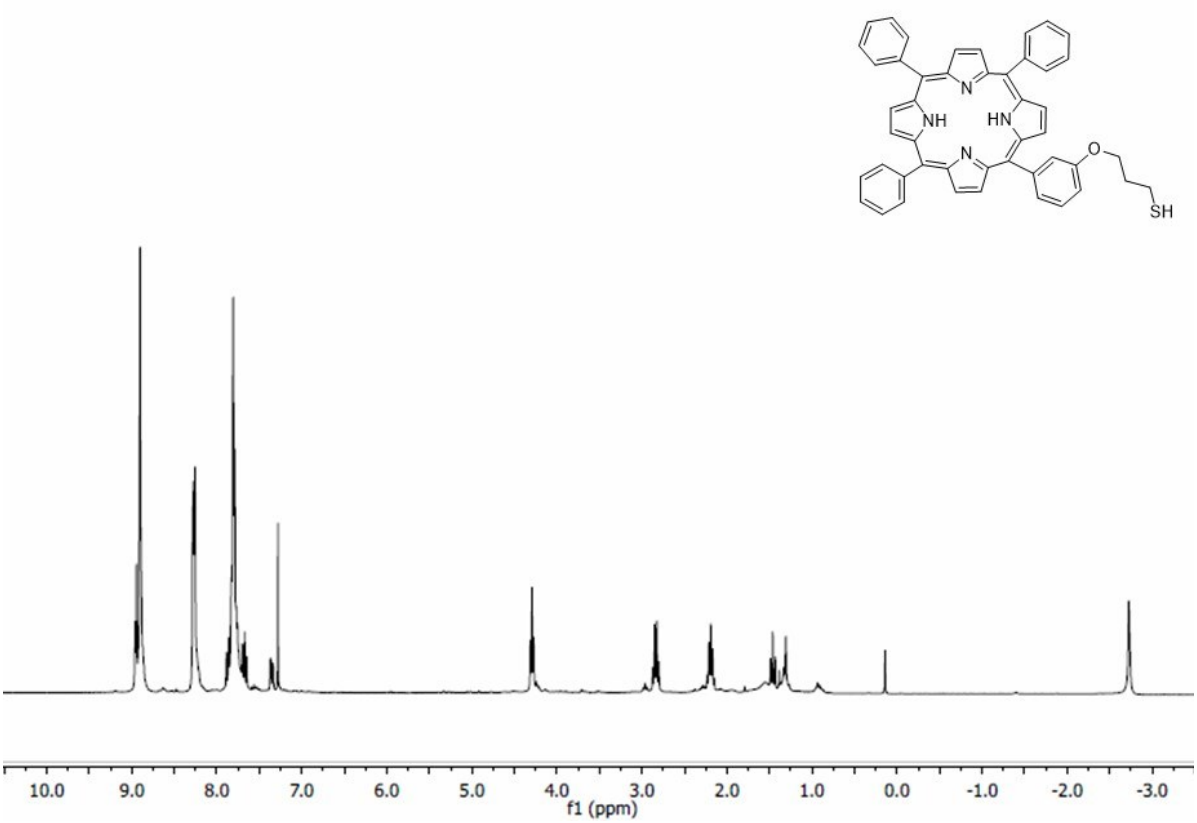


Figure S29. 3-(3-(5,15,20-triphenylporphyrin-10-yl)phenoxy)propane-1-thiol **6** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

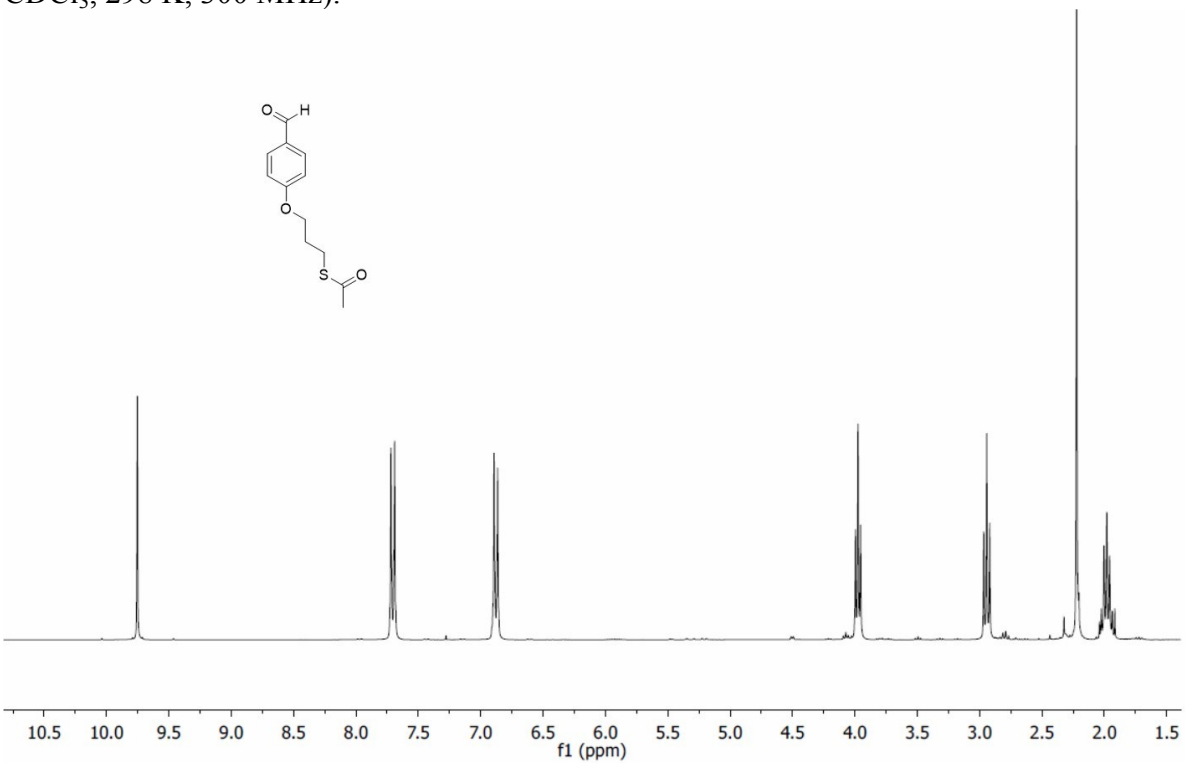


Figure S30. S-(3-(4-formylphenoxy)propyl) ethanethioate **7** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

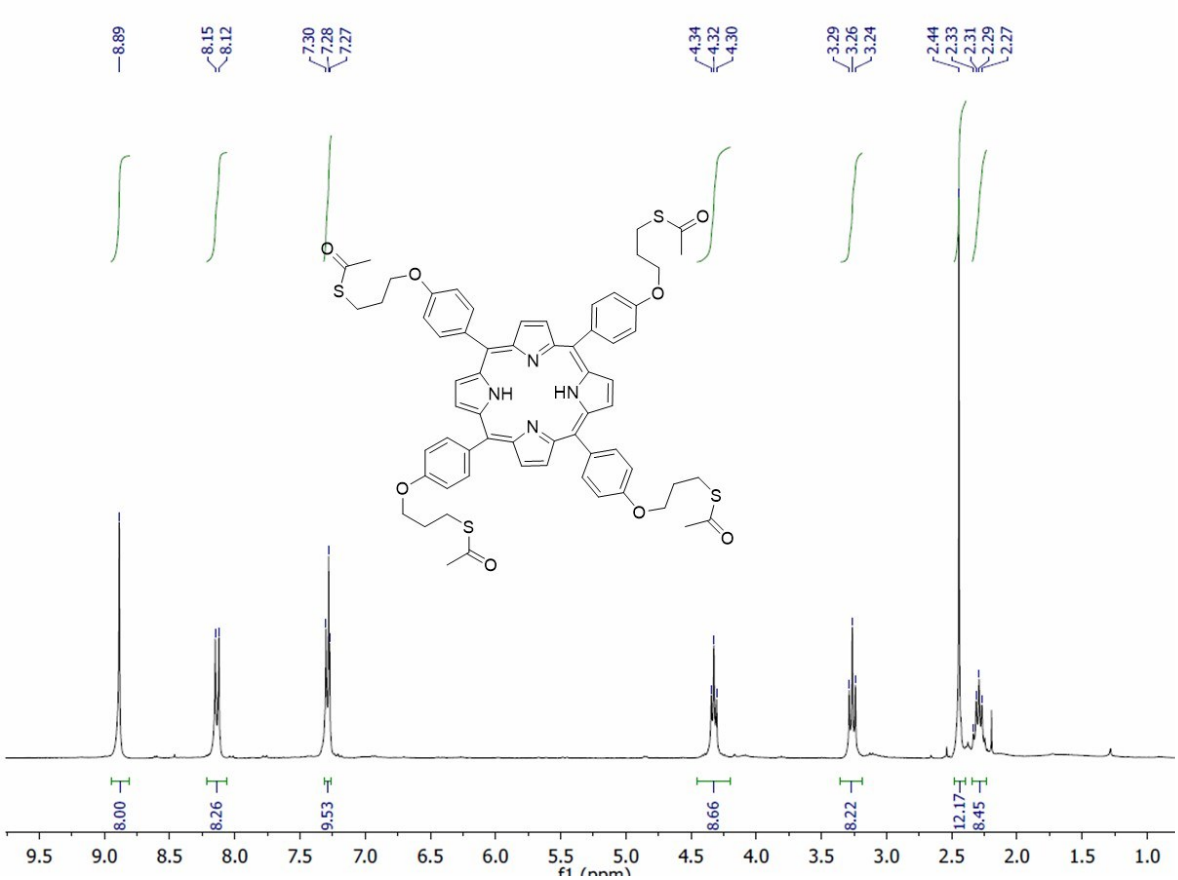


Figure S31. S,S',S'',S''' - (((porphyrin - 5,10,15,20 – tetrayltetrakis (benzene – 1,4 -diyl)) tetrakis (oxy)) tetrakis (propane-3,1-diyl)) tetraethanethioate **8** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

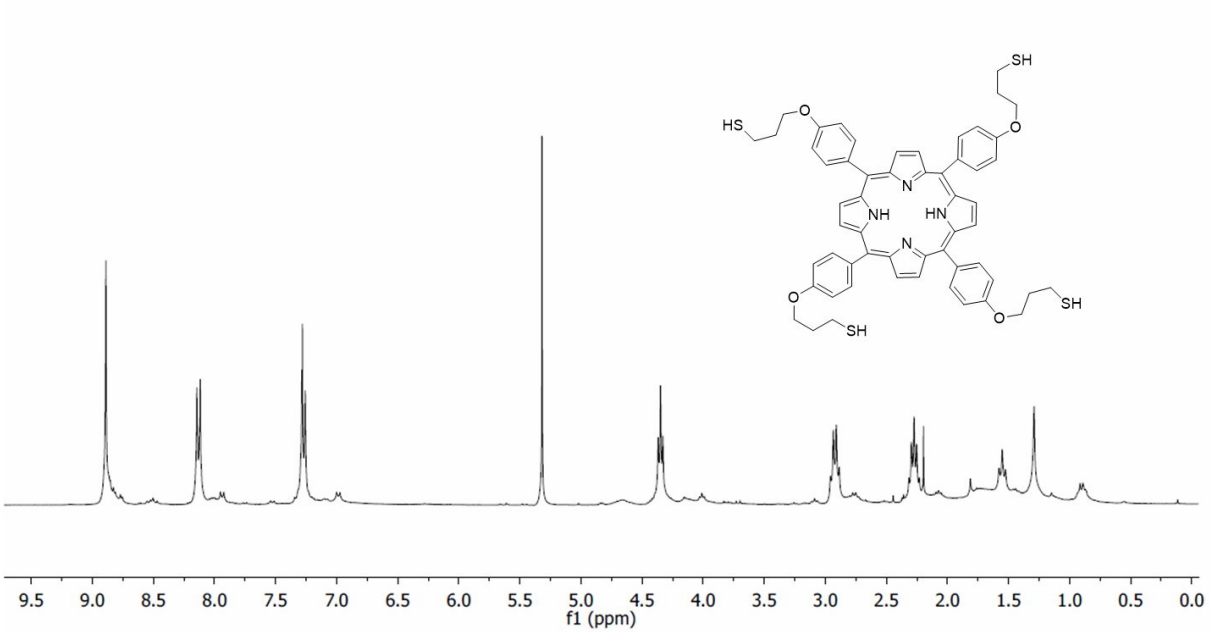


Figure S32. 3,3',3'',3''' - ((porphyrin - 5,10,15,20 – tetrayltetrakis (benzene – 1,4 - diyl)) tetrakis (oxy)) tetrakis (propane-1-thiol) **9** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

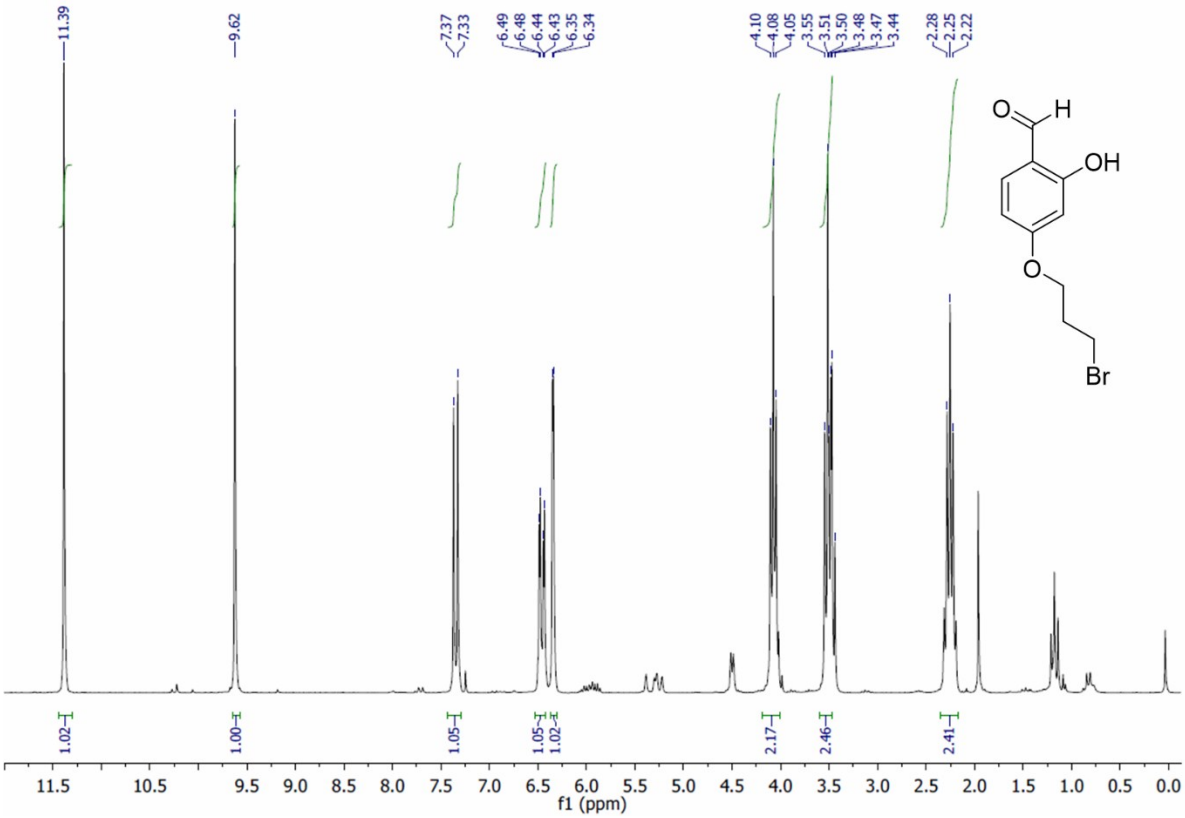


Figure S33. 4-(3-bromopropoxy)-2-hydroxybenzaldehyde **11** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

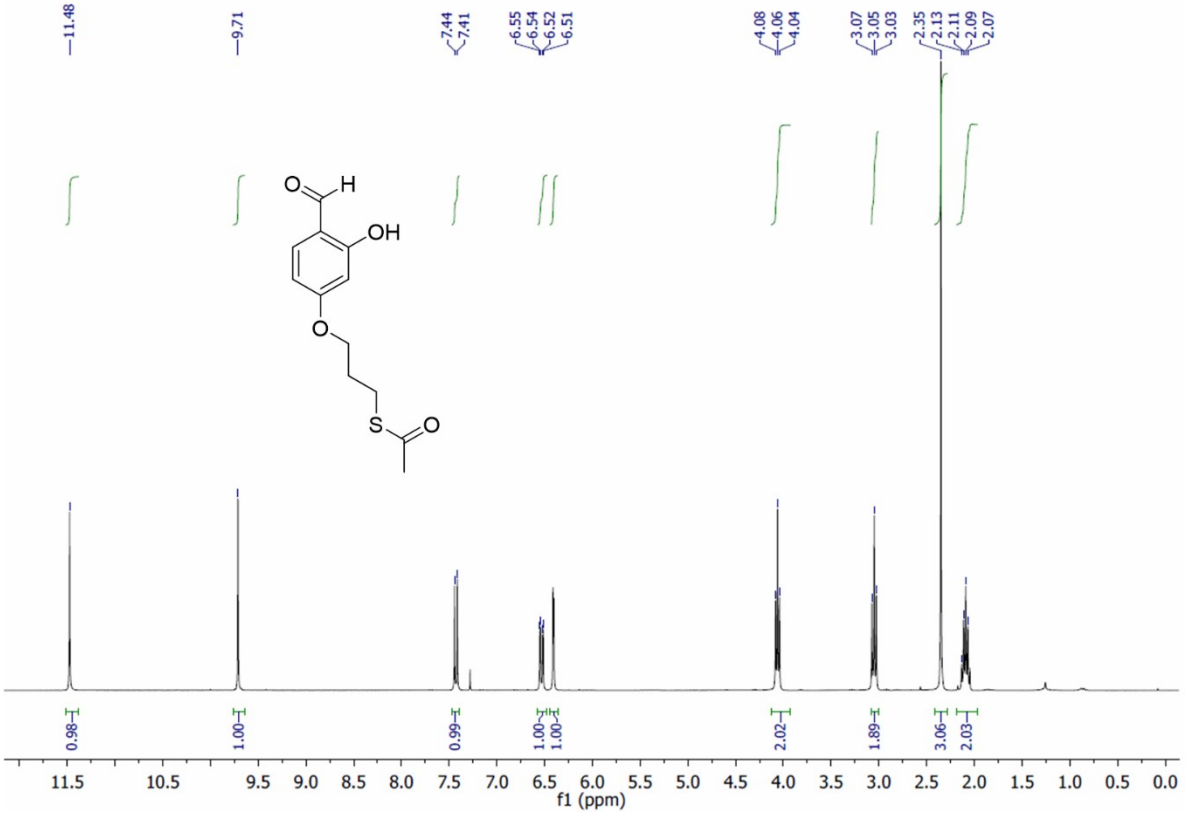


Figure S34. S-(3-(4-formyl-3-hydroxyphenoxy)propyl) ethanethioate **12** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

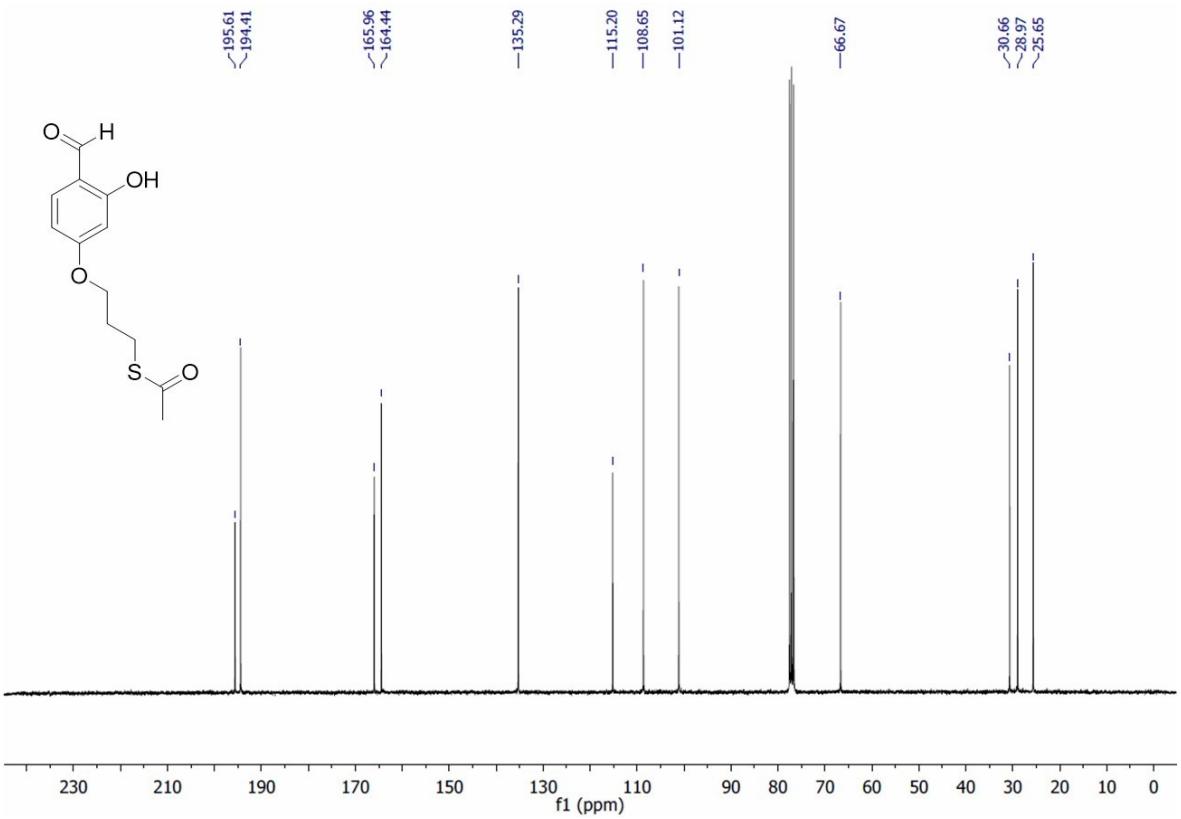


Figure S35. S-(3-(4-formyl-3-hydroxyphenoxy)propyl) ethanethioate **12** (^{13}C-NMR, $CDCl_3$, 298 K, 75 MHz).

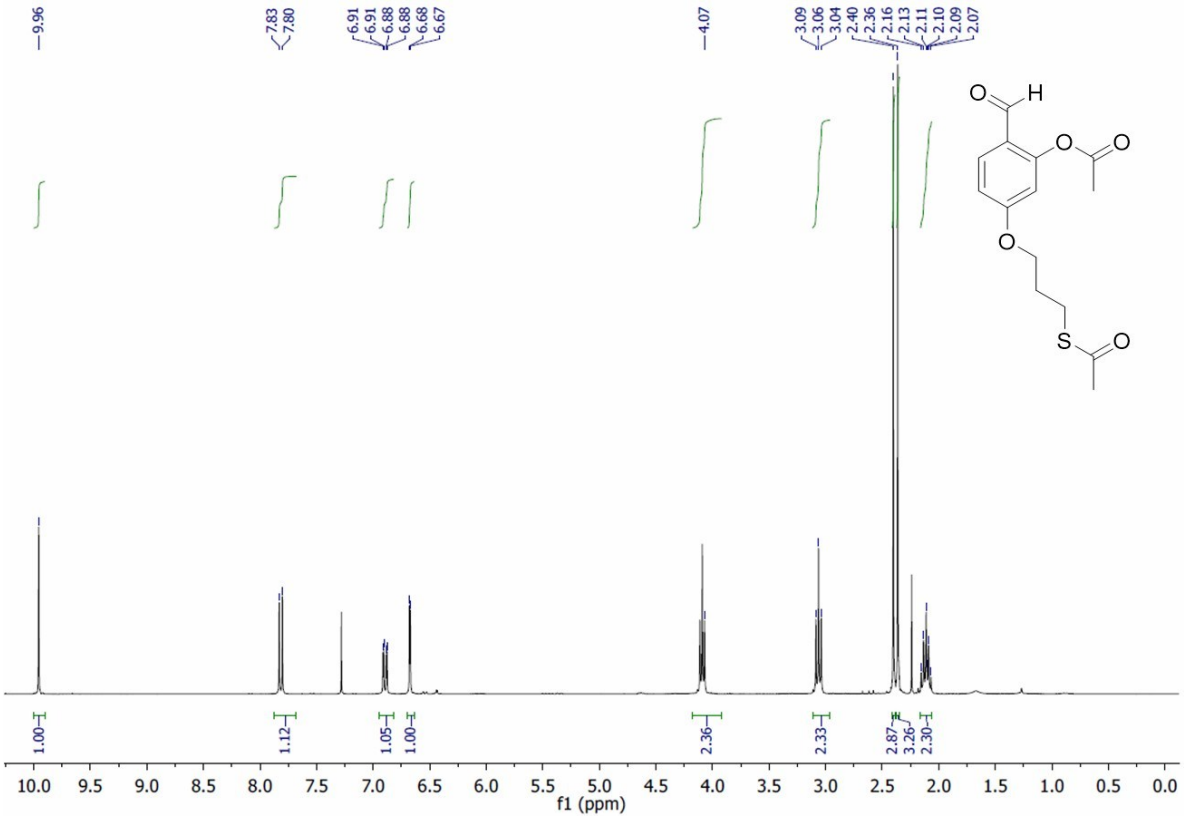


Figure S36. 5-(3-(acetylthio)propoxy)-2-formylphenyl acetate **13** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

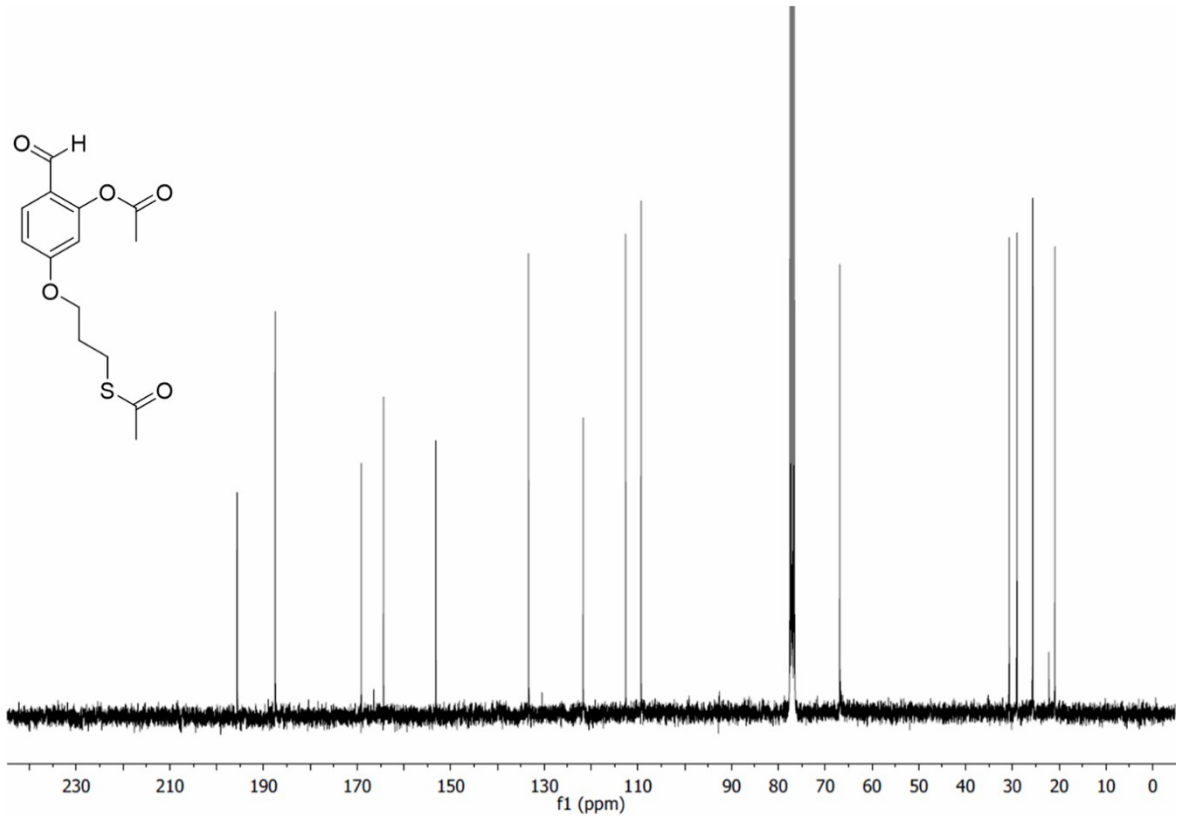


Figure S37. 5-(3-(acetylthio)propoxy)-2-formylphenyl acetate **13** (^{13}C-NMR, $CDCl_3$, 298 K, 75 MHz).

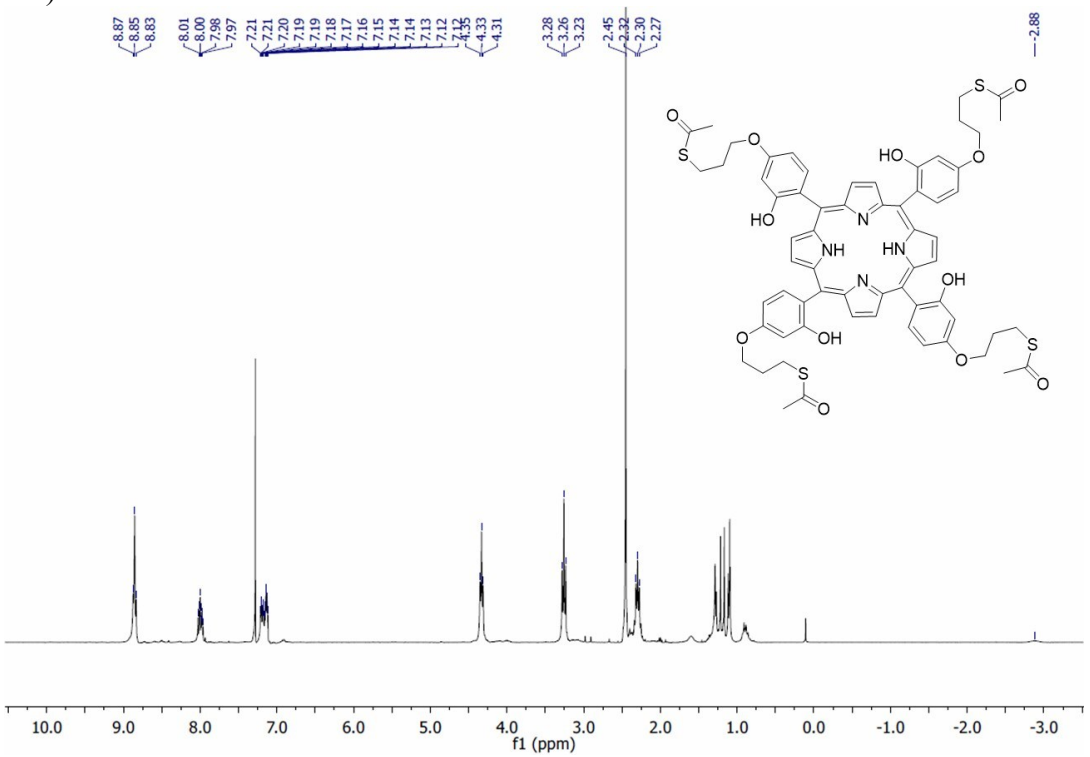


Figure S38. S,S',S'',S''' - (((porphyrin -5,10,15,20- tetrayltetrakis (3- hydroxybenzene -4,1-diyl)) tetrakis(oxy)) tetrakis(propane-3,1-diyl)) tetraethanethioate **14** (^{1}H-NMR, $CDCl_3$, 298 K, 300 MHz).

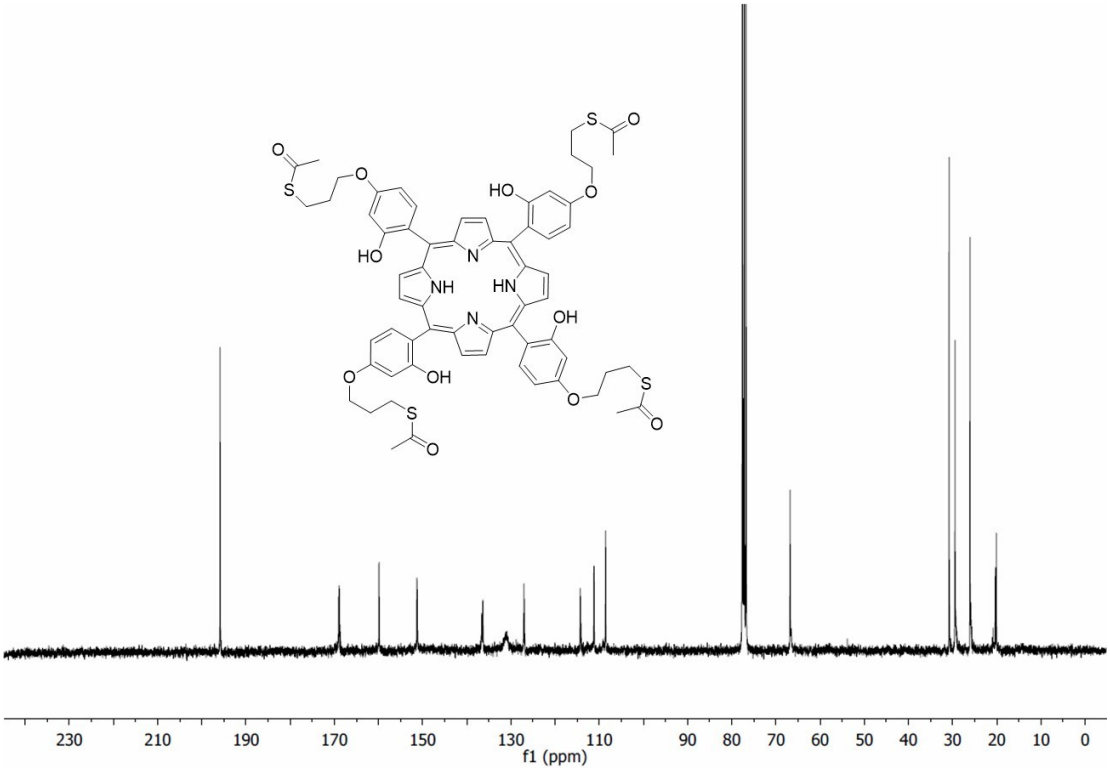


Figure S39. S,S',S'',S''' - (((porphyrin -5,10,15,20- tetrayltetrakis (3- hydroxybenzene -4,1-diyl)) tetrakis(oxy)) tetrakis(propane-3,1-diyl)) tetraethanethioate **14** (^{13}C-NMR, $CDCl_3$, 298 K, 75 MHz).

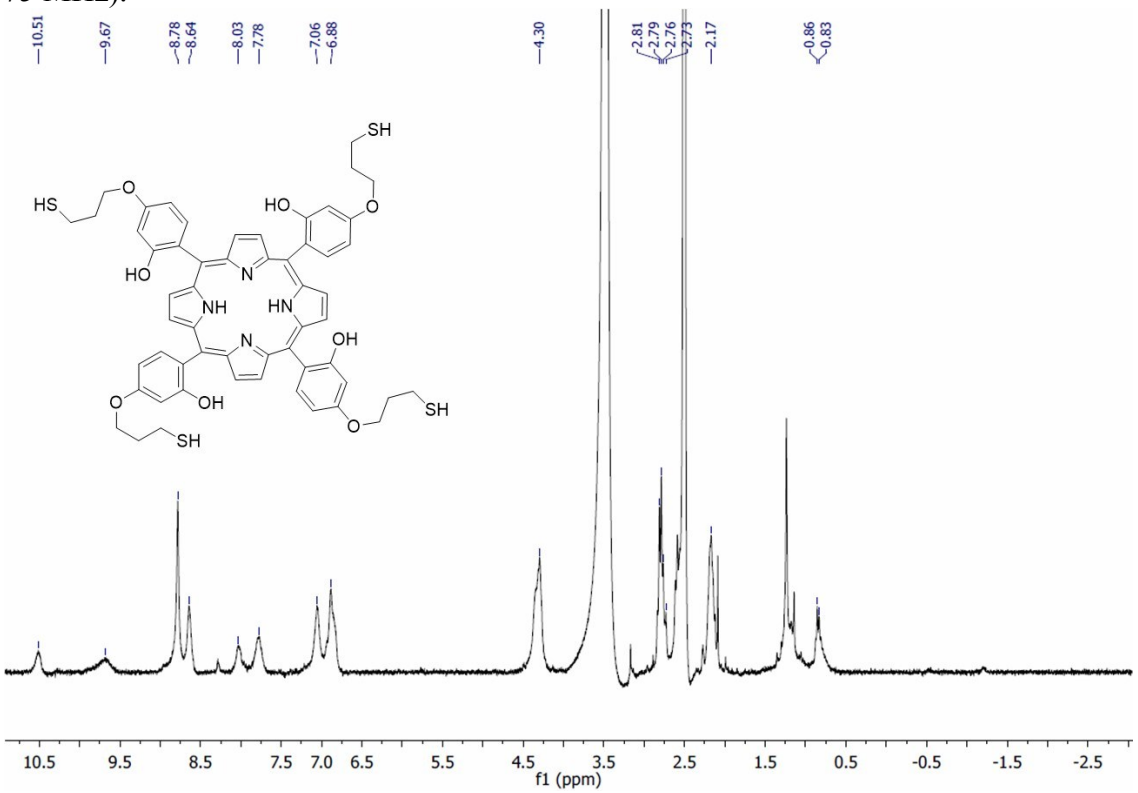


Figure S40. 6,6',6'',6'''-(porphyrin-5,10,15,20-tetrayl)tetrakis(3-(3-mercaptopropoxy)phenol) **15** (^{1}H-NMR, DMSO-d_6, 298 K, 300 MHz).

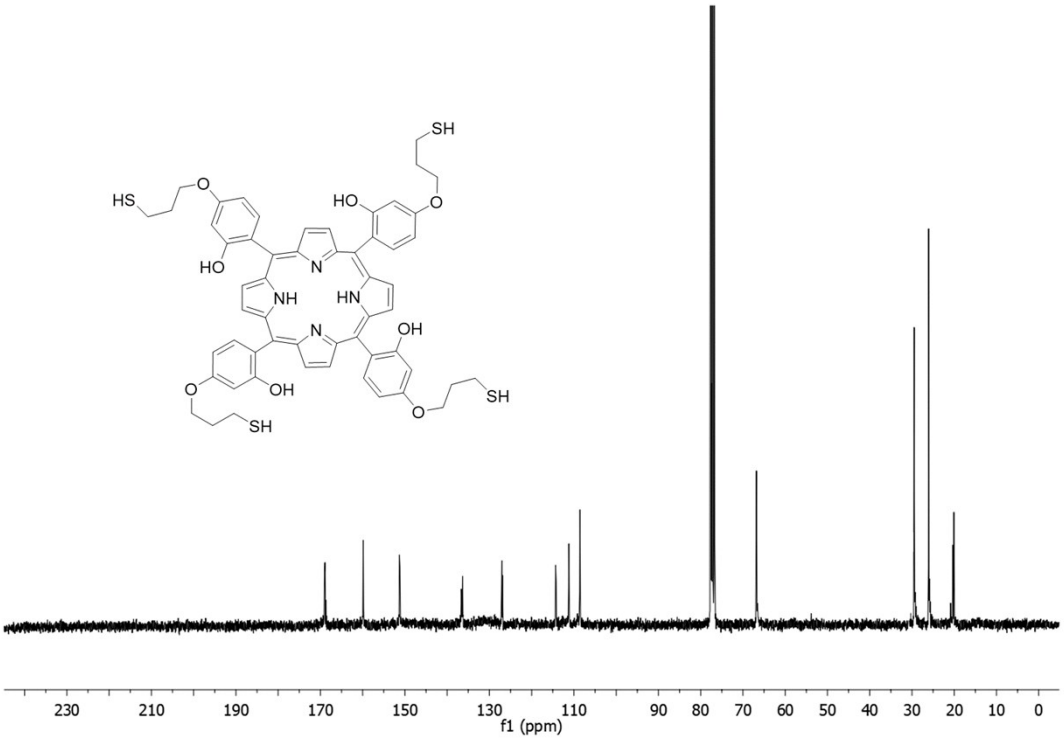


Figure S41. 6,6',6",6"'-(porphyrin-5,10,15,20-tetrayl)tetrakis(3-(3-mercaptopropoxy)phenol) **15** (^{13}C-NMR, $CDCl_3$, 298 K, 75 MHz).