Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic supplementary information

Photoreduction and light-induced triplet-state formation in a single-site fluoroalkylated zinc phthalocyanine

Hans Moons,[a] Andrei Loas,[b,c] Sergiu M. Gorun*[b] and Sabine Van Doorslaer*[a]

[a] *University of Antwerp, Department of Physics, Universiteitsplein 1, 2610 Antwerp, Belgium. E-mail: sabine.vandoorslaer@ua.ac.be*
[b] *Center for Functional Materials and Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079, USA. Email: sergiu.gorun@shu.edu* [c] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

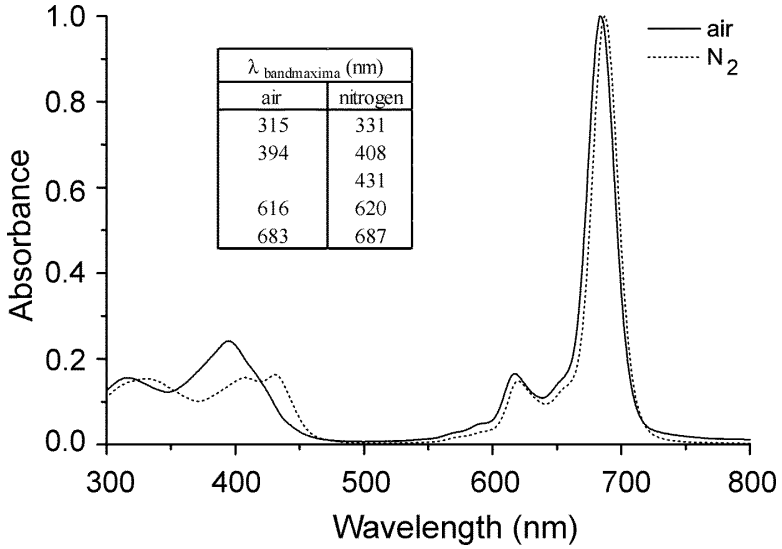


Figure S1. Normalized optical absorption spectra of $F_{64}PcZn$ in ethanol under N_2 atmosphere (dashed line) and in air (solid line) in the absence of UV irradiation. The wavelengths of the absorption maxima are listed in the table inset.

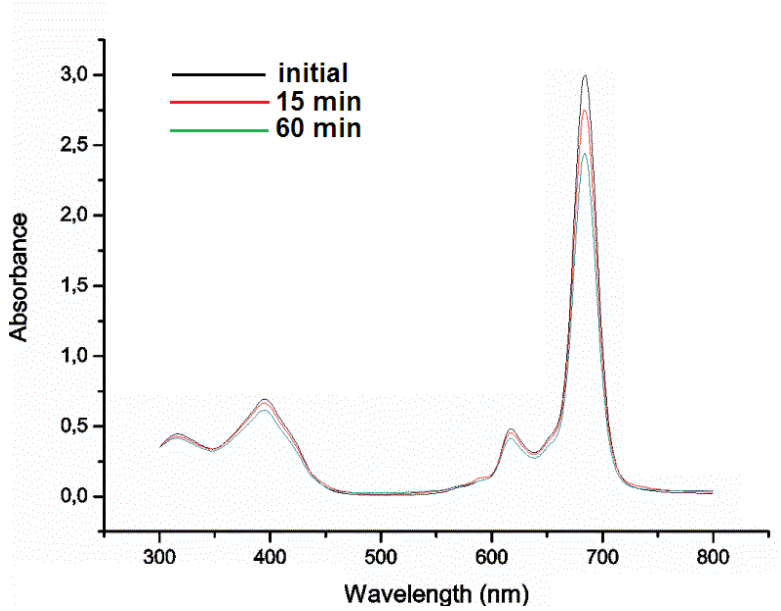


Figure S2. Optical absorption spectra of 0.05 mM F_{64}PcZn in ethanol recorded in air before (black), after 15 min (red) and after 60 min (green) of irradiation with a 450 W Xe lamp. A reduction to ca. 80% of the original intensity was observed after 60 min.

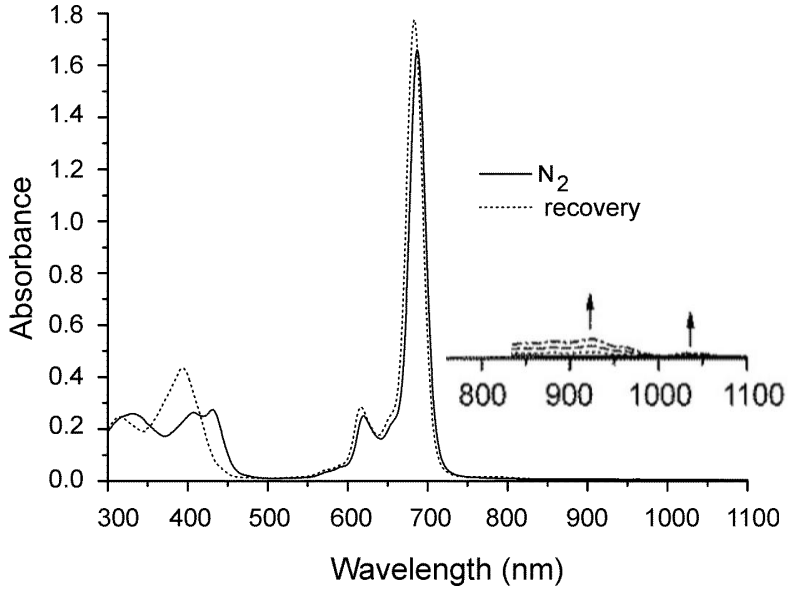


Figure S3. Reduction of F_{64}PcZn to $[F_{64}PcZn]^{\bullet-}$. Absorption spectra of F_{64}PcZn in ethanol under N_2 (solid line) and after red-light irradiation for 1 h followed by stiring in air for several hours (dashed lines, recovery). Inset: portion of Figure 2, main text, showing the time dependent growth of the $[F_{64}PcZn]^{\bullet-}$ near-IR absorbances at 924 and 1037 nm. The spectrum after recovery is identical to the spectrum obtained when dissolving F_{64}PcZn in ethanol in air (Figure S1).

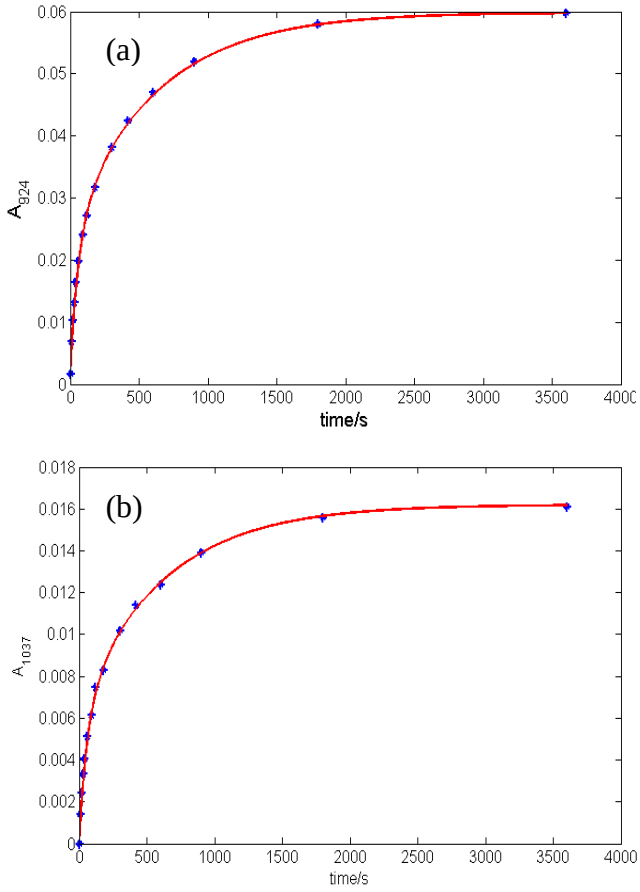


Figure S4. Anaerobic reduction of a 0.01 mM ethanolic solution of $F_{64}PcZn$ to $[F_{64}PcZn]^{\bullet-}$ under illumination with a 450 W Xe lamp equipped with a 570 nm cut-off filter. Time dependency of the near-IR absorbances of $[F_{64}PcZn]^{\bullet-}$ at (a) 924 nm, and (b) 1037 nm. The curves are simulated in both cases using three exponentials: $A_{max}[1-a\bullet\exp(-t/t_a)-b\bullet\exp(-t/t_b)-c\bullet\exp(-t/t_c)]$, with t_a = 55 s (a = 0.3), t_b = 102 s (b = 0.1) and t_c = 624 s (c = 0.6).

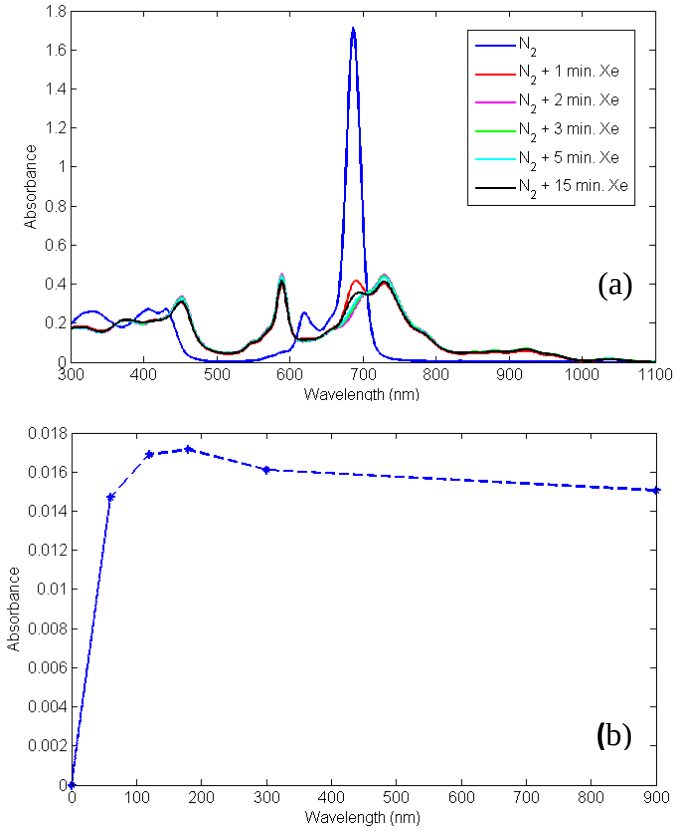


Figure S5. (a) Time-dependent, anaerobic degradation of a solution of F_{64}PcZn in ethanol illuminated with the full UV-visible spectrum of a 450 W Xe lamp (no filter). (b) Variation of $[F_{64}PcZn]^{\bullet-}$ measured by its absorbance at 1037 nm vs. the UV wavelength. A fast build-up of $[F_{64}PcZn]^{\bullet-}$ apparently ending with the complete reduction of F_{64}PcZn within 3 min is noticed, but F_{64}PcZn also photo degrades slowly.

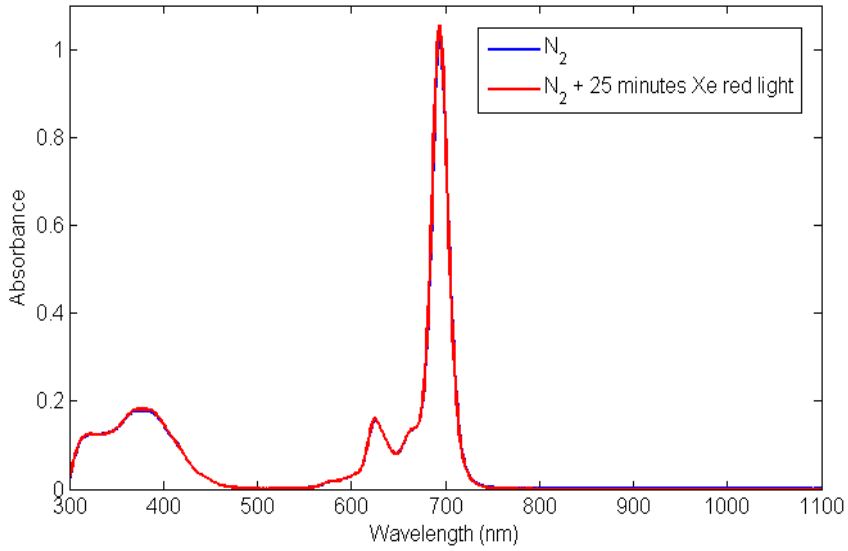


Figure S6. Anaerobic absence of photoreduction of a toluene solution of F_{64}PcZn, monitored by absorption spectra taken before (blue) and after (red) 25 minutes of illumination with a 450 W Xe lamp equipped with a cut-off filter at 570 nm.

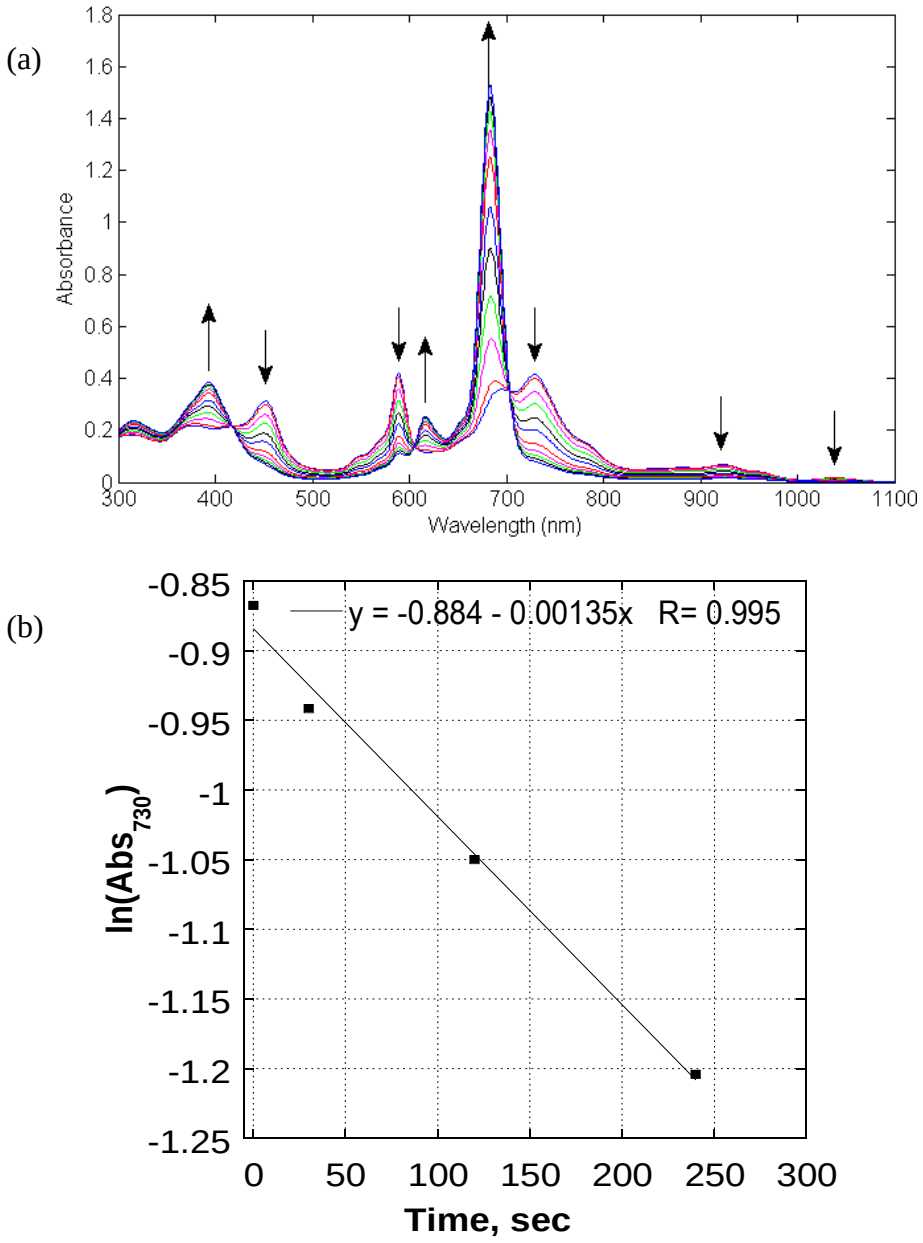


Figure S7. (a) Aerobic reoxidation of $[F_{64}PcZn]^{\bullet-}$ obtained anaerobically in ethanol after 15 minutes illumination with a 450 W Xe lamp (no filter). The arrows mark the slow reoxidation spectroscopic changes after stirring in air for 0.5, 2, 4, 10, 20, 50, 80, 110, 140 and 180 min. A similar, slow reoxidation is observed after red-light illumination of $F_{64}PcZn$. (b) Pseudo-first order fit of the disappearance of $[F_{64}PcZn]^{\bullet-}$ during the initial 5 minutes of the reoxidation reaction.

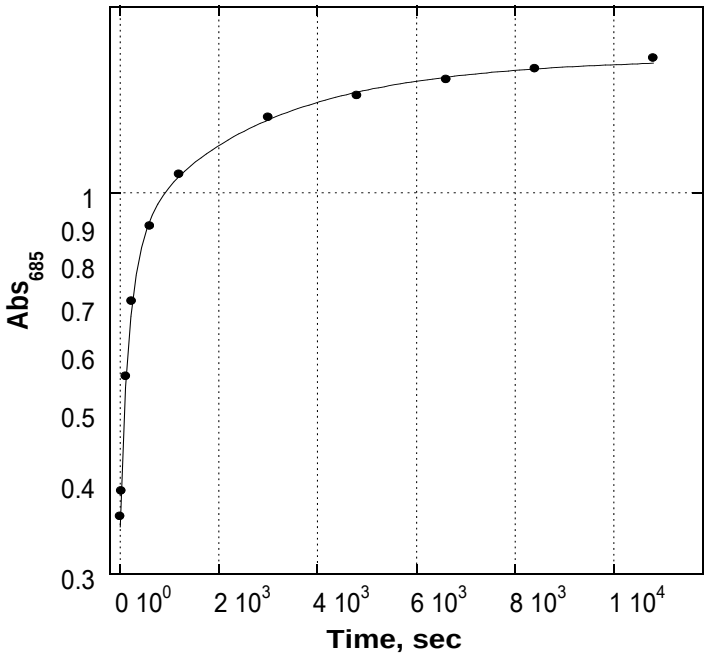


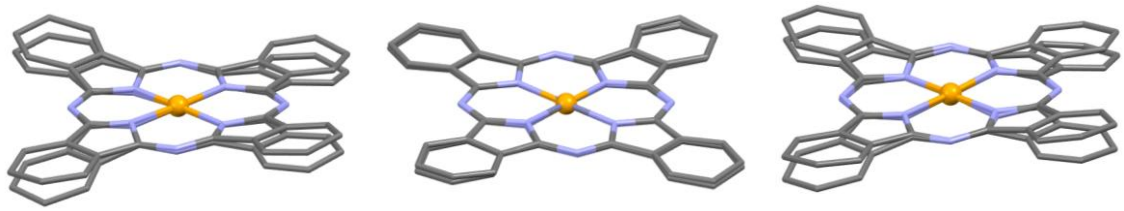
Figure S8. The aerobic reoxidation of $[F_{64}PcZn]^{\bullet-}$ to $F_{64}PcZn$. Time dependency of the 685 nm Q-band absorbance, modeled using two exponentials (R^2 = 1.0, estimated standard deviations in paranthesis): $A_{max}[1 - a \bullet \exp(-t/t_a) - b \bullet \exp(-t/t_b)]$ with $t_a = 2.6(3) \bullet 10^2$ s, a = 0.33(2) and $t_b = 3.2(2) \bullet 10^3$ s, b = 0.44(2). The preexponential factors are similar to those of the reduction, Figure S4, but the time constants are one order of magnitude larger.

Table S1. The goodness-of-fit between DFT models and the X-ray structure of $F_{64}PcZn(acetone)_2$. The distances between pairs of equivalent atoms of the ZnN_4 chromophores were minimized using the least-squares facility of Mercury (Cambridge Crystallographic Data Centre, UK)

	$F_{64}PcZn(acetone)_2$	**Model A** RMSD; D	**Model B** RMSD; D
$F_{64}PcZn(acetone)_2$	**X**	0.11; 0.25	0.45; 0.85
Model A		**X**	0.36; 0.73
Model B			**X**

RMSD: the square root of the mean squared deviation for the overlay

D: the maximum distance, in Å between two equivalent atoms in the overlay

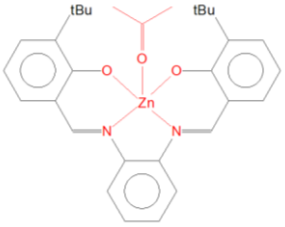


(a) (b) (c)

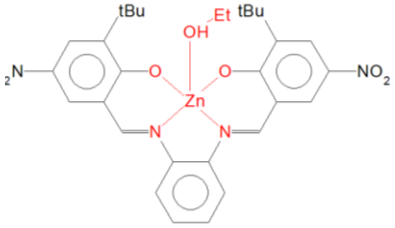
Figure S9. Graphical representation of the overlays of DFT models and the experimental X-ray structure of $F_{64}PcZn(acetone)_2$. The overlay atoms used for the fitting were those of the ZnN_4 chromophores. (a) Model A vs. Model B. (b) $F_{64}PcZn(acetone)_2$ vs. Model A. (c) $F_{64}PcZn(acetone)_2$ vs. Model B. Note that the best structural fit to the experimental data is Model A.

Table S2. Structural parameters of five-coordinated ZnN_2O_2 chromophores, plus axial O atoms

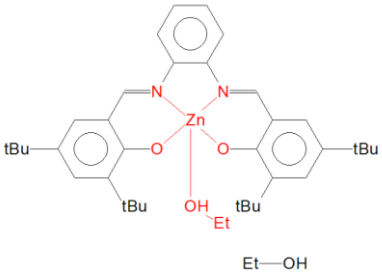
Reference code	Zn-O, Å	Zn-O-C, °
LOBQID	2.183	134.08
ADEKEB	2.071	121.99
REYPIV	2.162	120.1



LOBQID



ADEKEB



REYPIV

LOBQID. N. E. Eltayeb, S. G. Teoh, S. Chantrapromma, H.-K. Fun and R. Adnan, *Acta Crystallogr*., *Sect. E: Struct. Rep. Online*, 2008, **64**, 738.

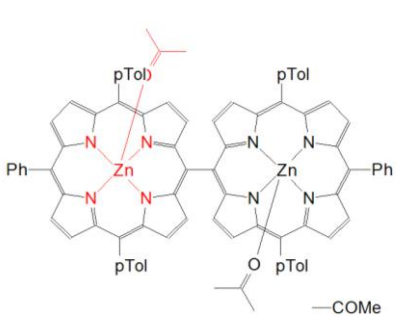
ADEKEB. D. Anselmo, E. C. Escudero-Adan, M. M. Belmonte and A. W. Kleij, *Eur. J. Inorg. Chem.*, 2012, 4694.

REYPIV. O. Rotthaus, O. Jarjayes, F. Thomas, C. Philouze, E. Saint-Aman and J.-L. Pierre, *Dalton Trans.*, 2007, 889.

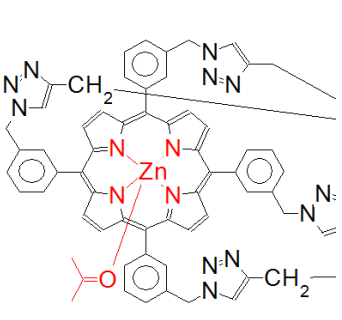
Table S3. Structural parameters of five-coordinated ZnN_4 chromophores, plus axial O atoms

Refcode	**Zn-O, Å**	**Zn-O-C, °**
FAPCEG	2.212, 2.182	134.436, 139.015
KEHVAW	2.253	141.618
OCIREZ	2.167	138.869
ODIQOH[a]	2.445	145.069
CAFBAN	2.131	121.185
HEZFAU	2.133, 2.149	123.773, 123.498
HEZFEY	2.162	126.859
HUPDUR	2.11	127.085
KADXEU	2.151	117.642
TIMQEM	2.177	127.652
UHUVID	2.114	124.289

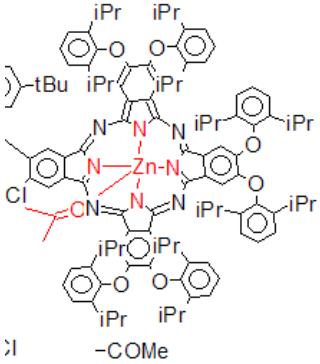
[a]Six-coordinated bis acetone complex, $F_{64}PcZn(acetone)_2$, modeled in the main text.



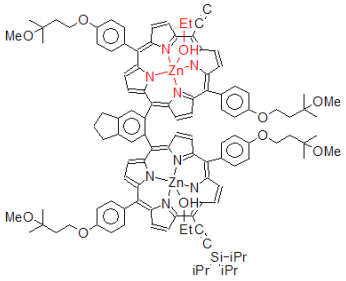
FAPCEG



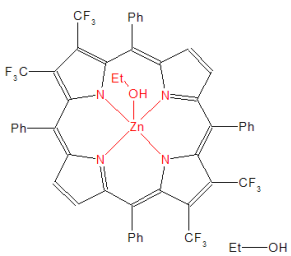
KEHVAW



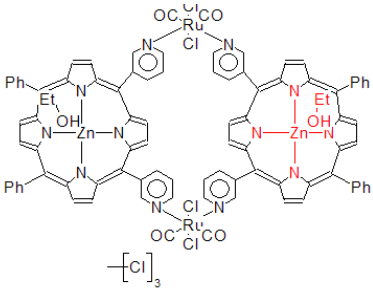
OCIREZ



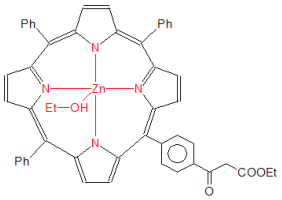
CAFBAN



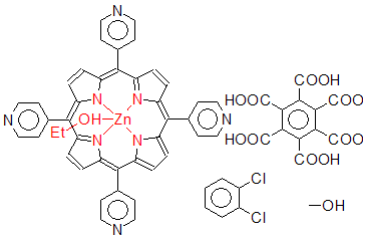
HUBDUR



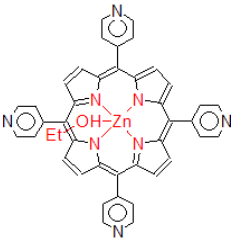
HEZFAU / HEZFEY



QARCUJ

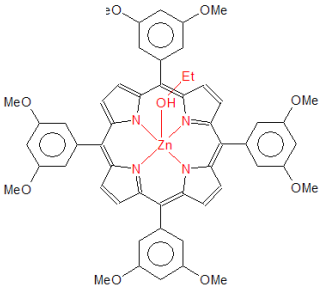


KADXEU



UHUVID

TIMQEM



CAFBAN. J. T. Fletcher and M. J. Therien, *Inorg. Chem.*, 2002, **41**, 331.

FAPCEG. A. K. D. Dime, C. H. Devillers, H. Cattey, B. Habermeyer and D. Lucas, *Dalton Trans*., 2012, **41**, 929.

HEZFAU, HEZFEY. E. Iengo, E. Zangrando, M. Bellini, E. Alessio, A. Prodi, C. Chiorboli and F. Scandola, *Inorg. Chem.*, 2005, **44**, 9752.

HUPDUR. Y. Terazono, B. O. Patrick and D. H. Dolphin, *Inorg. Chem.*, 2012, **41**, 6703.

KADXEU. S. Lipstman and I. Goldberg, *Beilstein J. Org. Chem.*, 2009, **5**, 77.

KEHVAW. L. C. Gilday, N. G. White and P. D. Beer, *Dalton Trans.*, 2012, **41**, 7092.

OCIREZ. C. G. Bezzu, M. Helliwell, B. M. Kariuki and N. B. McKeown, *J. Porphyrins Phthalocyanines*, 2011, **15**, 686.

ODIQOH. B. A. Bench, A. Beveridge, W. M. Sharman, G. J. Diebold, J. E. van Lier and S. M. Gorun, *Angew. Chem. Int. Ed*., 2002, **41**, 747.

QARCUJ. L.-C. Song, X.-F. Liu, Z.-J. Xie, F.-X. Luo and H.-B. Song, *Inorg. Chem.*, 2011, **50**, 11162.

TIMQEM. M. Sankar, P. Bhyrappa, B. Varghese, K. K. Praneeth and G. Vaijayanthimala, *J. Porphyrins Phthalocyanines* 2005, **9**, 413.

UHUVID. R. Koner and I. Goldberg, *Cryst. Eng. Comm.*, 2009, **11**, 1217.

DFT computations – coordinates of optimized structures in Å

MODEL A

F	-3.541729	8.263566	-1.435284
F	-2.555124	6.378983	-1.870430
F	3.739737	6.850637	-1.813905
F	5.268103	8.267680	-1.147813
F	5.829626	6.500445	-2.292453
F	3.290397	7.530656	0.788821
F	4.029874	5.958947	2.124345
F	5.193301	7.761322	1.786979
F	7.926224	4.515719	1.529023
F	8.040524	2.371556	1.199642
F	7.643333	-3.793838	-1.812813
F	7.287892	-5.911719	-2.139711
F	9.063903	-5.273047	-1.050554
F	7.173941	-6.387175	0.561848
F	8.584904	-4.980829	1.871110
F	6.783578	-3.799211	2.143200
F	8.337903	-3.155648	0.740392
F	3.203813	-7.900282	1.535760
F	4.534380	-9.439781	0.730850
F	5.350093	-7.747057	1.833585
F	2.469676	-8.500793	-1.018381
F	5.794846	-7.629515	-0.872316
C	8.234177	3.571758	0.624984
C	4.550615	-7.322870	-0.387440
F	6.867672	2.451446	-2.674526
F	8.467970	1.666145	-1.400723
F	8.788751	3.458029	-2.565345
F	7.633145	4.992081	-1.156044
C	5.192730	6.166587	-0.006176
F	-2.382268	-8.247240	-1.084354
F	-3.035155	-6.633338	-2.414918
F	-4.216639	-8.443621	-2.209635
F	-2.995151	-7.645076	1.503804
F	-7.704478	-2.448480	0.931006
F	-8.107222	-4.274167	2.014720
F	-6.200175	-3.274087	2.293657
F	-7.091417	-3.076910	-1.651105
F	-6.947367	-5.210283	-2.035478
F	-8.642234	-4.431139	-0.909584
F	-6.847918	-5.766125	0.649217
F	-5.609174	-7.091813	-0.829103
F	-3.580244	8.626175	1.516461
F	-4.299448	6.864222	2.577614
F	-2.187063	7.044715	2.104637
F	-1.186064	5.440395	0.253525
F	2.581131	5.269479	-0.038702

F	6.226402	1.242455	-0.354847
F	6.063468	-2.517126	-0.112956
F	2.045299	-6.193349	-0.124143
F	-1.731277	-6.011803	-0.140607
F	-5.393455	-1.994028	0.077714
N	1.780761	-1.866482	-0.087990
N	0.594969	3.029214	0.047865
C	1.724682	2.351208	-0.022484
C	3.060323	2.981960	-0.106169
C	4.003922	1.942729	-0.167781
C	3.496271	4.304969	-0.116099
C	4.878573	4.655510	-0.174153
C	5.834505	3.591824	-0.362853
C	5.357662	2.249323	-0.283812
C	-0.878577	-3.097879	-0.022395
C	4.389322	-5.793631	-0.185930
C	5.458516	-4.817165	-0.078850
C	5.103510	-3.441994	-0.117382
C	-2.650979	-5.049819	-0.092094
N	-2.978659	-0.227637	0.092828
C	-2.409605	-1.416915	0.042823
N	-1.057576	-1.724139	0.022169
C	-3.162620	-2.689467	0.008785
C	-2.216819	-3.727725	-0.032053
C	-4.520746	-2.998784	0.028083
C	-5.000585	-4.342825	0.027269
C	-4.033514	-5.400850	-0.134951
C	1.478485	-3.212722	-0.074262
C	2.730763	-3.957574	-0.096183
C	3.776184	-3.002239	-0.121137
C	3.148821	-1.688034	-0.118756
C	3.051221	-5.318673	-0.123066
C	-3.528699	5.044872	0.367438
C	-4.245552	2.692573	0.362112
C	-2.924890	2.253124	0.225464
C	-1.877524	3.206790	0.214833
C	-2.192647	4.567172	0.289568
C	-2.302663	0.940567	0.114124
N	-0.935881	1.119388	0.043337
C	-0.629901	2.463676	0.099184
N	3.823163	-0.519327	-0.145421
C	3.253393	0.670026	-0.113550
N	0.252313	-3.777071	-0.056634
N	1.904004	0.976777	-0.029428
Zn	0.422726	-0.373567	-0.015930
C	-3.697311	6.583542	0.273121
C	-3.428396	7.296213	1.651227
C	-6.533130	-4.505419	0.217913
C	-7.322672	-4.294143	-1.128112
C	-7.149556	-3.581790	1.384504

C	-4.332762	-6.906097	-0.370349
C	-4.219630	-7.745555	0.957138
C	-3.449048	-7.574391	-1.539581
C	6.970219	-5.114032	0.098909
C	7.685877	-4.220453	1.231619
C	7.760241	-5.014230	-1.259436
C	7.349701	3.745412	-0.666267
C	7.880377	2.785996	-1.846460
C	3.583341	-7.942019	-1.515991
C	4.400028	-8.121038	0.961369
F	9.534615	3.698254	0.307353
F	-5.111326	-7.306404	1.860378
F	3.235582	-6.995041	-2.412945
F	4.252077	-8.898737	-2.173834
F	-4.477903	-9.040065	0.701905
C	4.385304	6.872010	1.195449
C	4.995932	6.966328	-1.348258
F	6.495918	6.362682	0.365057
F	-4.975979	6.920592	-0.085082
F	-5.207051	1.769665	0.392825
C	-2.824399	7.270150	-0.893007
F	-1.671466	7.799805	-0.456576
C	-4.589517	4.063611	0.508263
F	-8.263175	4.574807	-0.122679
F	-6.920057	3.143719	-1.089575
F	-5.723568	2.919692	2.773197
F	-7.535770	4.114604	2.725747
F	-7.395635	2.357615	1.474772
C	-6.079176	4.349931	0.831282
C	-6.698885	3.392570	1.968416
F	-6.236676	5.594497	1.381833
C	-6.983382	4.329276	-0.457532
F	-6.584179	5.277607	-1.320666

MODEL B

C	-0.144726	0.717108	3.363652
O	0.026077	-0.268306	2.327262
C	-0.579831	0.091508	4.682199
H	-0.920336	1.411741	2.984351
H	0.791826	1.304838	3.496951
H	0.735912	-0.884566	2.598879
H	0.196235	-0.599039	5.074480
H	-1.523345	-0.477485	4.558247
H	-0.744534	0.879735	5.445252
C	-0.733114	-0.171860	-3.325312
O	0.241502	0.060813	-2.292469
C	-0.091170	-0.623255	-4.630987
H	-1.402637	-0.958538	-2.924203
H	-1.351880	0.740210	-3.485927

H	0.827706	0.790700	-2.575710
H	0.575137	0.163116	-5.044247
H	-0.871878	-0.834646	-5.390436
H	0.507807	-1.544126	-4.480437
F	2.236706	-7.189740	-2.957849
F	3.609583	-8.873663	-2.700965
F	2.950699	-7.097178	1.030149
F	1.903003	-8.279343	-0.486880
F	3.829855	-8.922424	0.250782
C	3.904088	-7.018371	-1.213236
C	3.106665	-7.840712	-0.082307
F	5.196281	-7.440820	-1.018891
C	3.499036	-7.530735	-2.644894
F	4.311541	-7.006244	-3.576586
F	7.668608	-2.771441	-2.127392
F	5.885937	-3.092111	-3.358221
F	7.362792	-3.894151	0.327194
F	6.958393	-6.028707	0.290056
F	8.562566	-5.214374	-0.939254
C	6.317445	-4.791175	-1.661710
C	7.322025	-4.979472	-0.465146
F	6.386105	-5.952172	-2.392112
C	6.890432	-3.704098	-2.701375
F	7.643596	-4.339750	-3.614065
F	-3.296705	8.445954	-2.704105
F	-2.335698	6.499534	-2.726846
F	3.897840	7.245902	-0.662708
F	5.321935	8.486081	0.442428
F	6.029515	6.848851	-0.808979
F	3.006851	7.625098	1.881798
F	3.446987	5.873329	3.121136
F	4.707328	7.638811	3.215163
F	7.341156	4.302166	3.028770
F	7.459018	2.211564	2.447819
C	7.780509	3.463031	2.077372
F	7.027711	2.830142	-1.532424
F	8.335397	1.812146	-0.099762
F	8.917723	3.717181	-0.937077
F	7.556815	5.120790	0.420713
C	4.978503	6.264516	1.265015
F	-3.047108	-7.907632	-0.055845
F	-3.862651	-6.490425	-1.514059
F	-5.028884	-8.202612	-0.864767
F	-3.269883	-6.914226	2.468712
F	-7.941743	-1.691782	1.832834
F	-8.217384	-3.341610	3.200561
F	-6.277031	-2.375215	3.082372
F	-7.713782	-2.683007	-0.692512
F	-7.652486	-4.853028	-0.794915
F	-9.157173	-3.874883	0.440651

F	-7.181196	-5.044305	1.899806
F	-6.185839	-6.610262	0.472485
F	-3.740464	9.230011	0.115024
F	-4.690635	7.665131	1.296168
F	-2.524843	7.721530	1.131501
F	-1.336375	5.837461	-0.314848
F	2.392305	5.512356	0.674925
F	5.926876	1.378298	0.443717
F	5.584409	-2.274898	-0.813600
F	1.451444	-5.829983	-0.810301
F	-2.237639	-5.581071	0.411538
F	-5.761876	-1.437537	0.625847
N	1.394512	-1.583993	0.045930
N	0.348570	3.366838	0.140399
C	1.462852	2.652422	0.173373
C	2.812387	3.227572	0.395767
C	3.723433	2.158466	0.354798
C	3.282491	4.516385	0.629072
C	4.659417	4.804571	0.852090
C	5.604578	3.725368	0.689871
C	5.082977	2.413000	0.505239
C	-1.329967	-2.699909	0.012721
C	3.789068	-5.480417	-1.081857
C	4.872602	-4.514751	-1.180625
C	4.590708	-3.171970	-0.820790
C	-3.126977	-4.584758	0.466837
N	-3.323517	0.236847	0.074345
C	-2.797533	-0.977877	0.080142
N	-1.486776	-1.339528	-0.126718
C	-3.576312	-2.216660	0.327500
C	-2.665414	-3.285119	0.285028
C	-4.919052	-2.474016	0.585048
C	-5.417359	-3.785004	0.834504
C	-4.501938	-4.890623	0.678579
C	1.027021	-2.884477	-0.188479
C	2.228463	-3.640220	-0.532465
C	3.307625	-2.720770	-0.505047
C	2.743284	-1.423536	-0.140408
C	2.487208	-4.981678	-0.820709
C	-3.686280	5.515889	-0.494247
C	-4.497470	3.205829	-0.288243
C	-3.194670	2.718017	-0.168371
C	-2.114572	3.636310	-0.148702
C	-2.379206	4.998090	-0.306644
C	-2.615687	1.386507	-0.000803
N	-1.256576	1.528209	0.117606
C	-0.897121	2.849672	0.037235
N	3.456138	-0.281519	-0.002457
C	2.932248	0.927514	0.112231
N	-0.216067	-3.406066	-0.082300

N	1.608987	1.293969	0.008812
Zn	0.058823	-0.027213	0.030449
C	-3.768141	7.025851	-0.823862
C	-3.671875	7.928361	0.461754
C	-6.906983	-3.863624	1.257374
C	-7.878517	-3.810398	0.020321
C	-7.341608	-2.771874	2.358070
C	-4.851686	-6.400771	0.712664
C	-4.561420	-7.043774	2.119682
C	-4.158235	-7.267305	-0.453922
C	7.150821	3.837117	0.684222
C	7.868062	3.007389	-0.494490
F	9.122685	3.564997	2.013985
F	-5.307382	-6.450075	3.065323
F	-4.875138	-8.353848	2.097278
C	3.990667	6.863508	2.386533
C	5.051367	7.233052	0.026624
F	6.200734	6.351425	1.881966
F	-4.967429	7.343266	-1.412662
F	-5.498171	2.316731	-0.273765
C	-2.707700	7.519990	-1.929702
F	-1.608593	8.085477	-1.403576
C	-4.800709	4.588357	-0.382175
F	-8.321748	5.097159	-1.613854
F	-6.918004	3.516394	-2.177461
F	-6.318536	3.796749	1.819966
F	-8.041233	5.022919	1.329722
F	-7.799783	3.105159	0.362821
C	-6.304422	4.951182	-0.329127
C	-7.131444	4.178835	0.816047
F	-6.487054	6.266527	0.021070
C	-7.015892	4.777543	-1.721915
F	-6.462218	5.590851	-2.635684