Supplementary Material (ESI) for *Physical Chemistry Chemical Physics*

Supporting Information for:

Conformational flexibility of metalloporphyrins studied by density-functional calculations

by Thorsten Wölfle [a], Andreas Görling [a] and Wolfgang Hieringer*[a]

Computational details: Constraint definition

In order to calculate the relaxed potential energy surface scans, the following constraints have been used (cf. Figures 1,2 of the main paper). As a preliminary remark, note that the choice of suitable constraints to enforce both fixed twist and out-of-plane tilt angles in tetra phenyl phorphyrines is a non-trivial task. The twist angle Θ is defined by fixing the rotation of two dihedral angles between the phenyl groups and the porphyrin ring. These angles are the acute dihedral angles defined by the bond connecting the peripheral phenyl ring to the porphyrin core and the adjacent carbon atoms. Thus, two dihedral angles per phenyl ring (hence a total of eight dihedral angles in each M-TPP structure) are fixed. To describe the tilt angle Φ, in total four additional angles are fixed, set up by the central metal atom and the atoms of the bond between phenyl group and porphyrin ring. Thus, a total of twelve constraints is introduced per molecule.

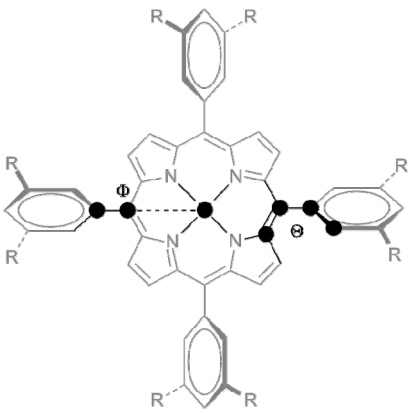

Figure S1: Illustration of the applied constraints (see text).

However, when choosing the C-C-M angle for tilting the phenyl rings, the subsequent constrained geometry optimization will lift the metal atom from the TPP plane in an unphysical way. To circumvent this error we reoptimized the cartesian coordinates of the central atom in cartesian coordinates while the remaining atoms were fixed, resulting in a gain in energy of 50 kJ/mol in worst case. The numbers quoted in the paper all have been corrected in this manner.

However, note that the angles that can be measured in the structures depend on the order in which the tilting and twisting operations are applied. When the tilt angle is applied first it is possible to measure the twist angle in the final structure. When twisting the phenyl ring first and then tilting it, one loses the reference point of measuring the twist angle, because the atoms fixing the tilt angle are not lying in the rotational axis of the phenyl ring.

Further note that the above procedure still leads to small artificial distortions of the peripheral phenyl groups at extreme out of-plane angles (such as Φ = 140°). We have checked (and corrected) the error in energy due to these distortions by additional geometry optimizations with cartesian constrains. For the "worst" case (tilt angle 140° and twist angle 90°) we found that the ensuing error is expected below 35 kJ/mol for each M-TPP, i. e. the error of the initial procedure is less that 10 kJ/mol for each phenyl group considered. (However, tilt angles as low as 140° may be considered rather unphysical anyway.)

Figures S2a,b,c contain illustrations of the computed potential energy surfaces (BP/SVP level of theory) for ZnTTBPP, CoTPP, and CoTTBPP, in analogy to Figure 2 of the main paper.

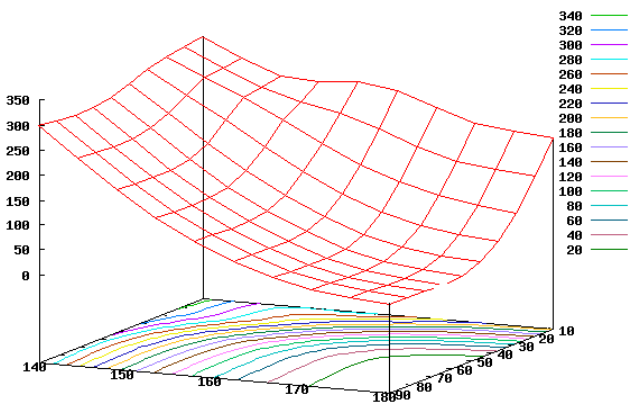

Figure S2a: Relaxed potential energy surface plot of CoTPP; kJ/mol.

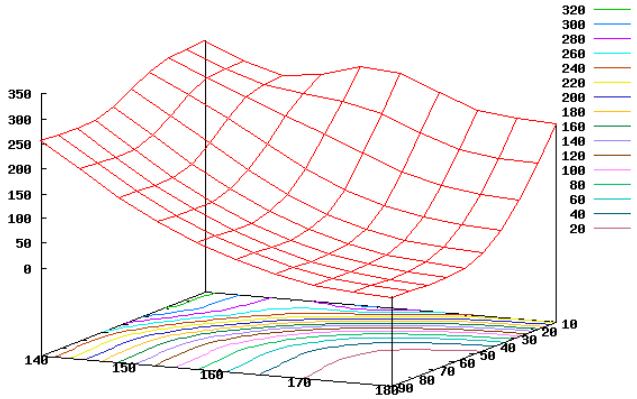

Figure S2b: Relaxed potential energy surface plot of ZnTTBPP; kJ/mol.

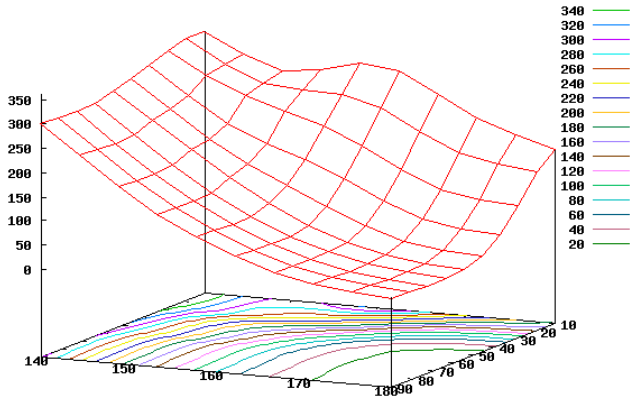

Figure S2c: Relaxed potential energy surface plot of CoTTBPP; kJ/mol.

Figure S3 shows an geometries corresponding the depression in the high-energy region of the potential energy surface plots shown in Figure 2 and S2.

Figure S3: Relaxed structures with angles fixed at Θ = 10°, Φ = 150° (top image) and Θ = 10°, Φ = 180° (bottom) to illustrate the depression in the high-energy region of the potential energy surface plots shown in Figures 2 and S2.

XYZ coordinates of the fully optimized structure of ZnTPP at the BP/TZVP level of theory:

```
77
Energy = -3693.001401785
N      2.0554132   -0.0232713   -0.0317365
C      2.8655733   -1.1407960    0.0229544
C      4.2484944   -0.7312538    0.1330441
C      4.2639361    0.6350013    0.1328223
C      2.8906284    1.0756712    0.0226400
C      2.4252024   -2.4807073    0.0002007
C      3.4715428   -3.5509541    0.0004219
C      4.3205943   -3.7257711   -1.1064707
C      5.2961811   -4.7265251   -1.1071713
C      5.4426252   -5.5668032    0.0009400
C      4.6055481   -5.4012485    1.1087818
C      3.6269474   -4.4034408    1.1075676
C      2.4807011    2.4252028   -0.0003486
C      1.1407906    2.8655733   -0.0231062
N      0.0232662    2.0554136    0.0315971
C     -1.0756767    2.8906288   -0.0227788
C     -0.6350073    4.2639359   -0.1329685
C      0.7312476    4.2484935   -0.1331956
Zn    -0.0000039   -0.0000031   -0.0000519
N     -0.0232722   -2.0554188    0.0316149
C     -1.1407977   -2.8655794   -0.0230632
C     -0.7312567   -4.2485005   -0.1331534
C      0.6349984   -4.2639424   -0.1329501
C      1.0756698   -2.8906345   -0.0227765
C     -2.4252090    2.4807023    0.0002309
C     -3.4715486    3.5509499    0.0005185
C     -3.6268978    4.4034187    1.1076856
C     -4.6054686    5.4012552    1.1089471
C     -5.4425831    5.5668459    0.0011390
C     -5.2962051    4.7265755   -1.1069870
C     -4.3206489    3.7257913   -1.1063331
C     -2.4807087   -2.4252086   -0.0002865
C     -3.5509553   -3.4715492   -0.0004523
C     -3.7257429   -4.3205713    1.1064676
```

```
C    -4.7265213   -5.2961332    1.1072362
C    -5.5668601   -5.4425747   -0.0008294
C    -5.4013162   -4.6055458   -1.1087094
C    -4.4034777   -3.6269764   -1.1075671
C     3.5509475    3.4715435   -0.0005347
C     4.4034716    3.6269481   -1.1076514
C     5.4013116    4.6055158   -1.1088113
C     5.5668577    5.4425636   -0.0009460
C     4.7265196    5.2961423    1.1071227
C     3.7257349    4.3205871    1.1063686
N    -2.0554209    0.0232664   -0.0317016
C    -2.8655801    1.1407915    0.0229968
C    -4.2484990    0.7312500    0.1331174
C    -4.2639415   -0.6350052    0.1329043
C    -2.8906355   -1.0756758    0.0226994
H    -5.0956584    1.4040566    0.2194981
H    -5.1260967   -1.2885190    0.2190808
H    -1.4040636   -5.0956625   -0.2195031
H     1.2885115   -5.1260992   -0.2191135
H     5.0956558   -1.4040597    0.2194102
H     5.1260923    1.2885155    0.2189815
H     1.4040527    5.0956550   -0.2195608
H    -1.2885218    5.1260920   -0.2191271
H     3.0751649    4.2029562    1.9748770
H     4.2710148    2.9790435   -1.9760151
H     4.8523533    5.9412481    1.9787064
H     6.0488770    4.7166494   -1.9805700
H     6.3472352    6.2055519   -0.0011025
H     2.9790080   -4.2709876    1.9759064
H     4.2029379   -3.0752555   -1.9750168
H     4.7166816   -6.0487840    1.9805627
H     5.9412903   -4.8523855   -1.9787487
H     6.2056646   -6.3471308    0.0011541
H    -3.0751807   -4.2029153    1.9749790
H    -4.2710199   -2.9790887   -1.9759438
H    -4.8523460   -5.9412317    1.9788267
H    -6.0488830   -4.7166946   -1.9804653
H    -6.3472377   -6.2055629   -0.0009714
H    -2.9789481    4.2709193    1.9760093
H    -4.2030654    3.0752608   -1.9748781
H    -4.7165475    6.0487872    1.9807374
H    -5.9413394    4.8524683   -1.9785414
H    -6.2056000    6.3471954    0.0013905
```

XYZ coordinates of the fully optimized structure of CoTPP at the BP/TZVP level of theory:

```
77
Energy = -3296.388689982 S2=0.76210495
N     1.9589618   -0.1752732    0.0319008
C     2.7041041   -1.3405070   -0.0796750
C     4.1002640   -1.0715105    0.1540124
C     4.2112555    0.2617182    0.4122574
C     2.8892891    0.8236719    0.2946251
C     2.1931795   -2.6183483   -0.3235567
C     3.1567505   -3.7378162   -0.5552058
C     3.9211972   -3.7816792   -1.7340400
C     4.8276810   -4.8215695   -1.9586003
C     4.9891502   -5.8315226   -1.0051322
C     4.2386442   -5.7950492    0.1743002
C     3.3287347   -4.7577789    0.3968004
C     2.6183772    2.1931790    0.3231989
C     1.3405156    2.7041006    0.0794168
N     0.1752675    1.9589545   -0.0320015
C    -0.8237072    2.8892749   -0.2946348
C    -0.2617689    4.2112398   -0.4123540
C     1.0714935    4.1002519   -0.1542797
Co    0.0000011   -0.0000081   -0.0000076
N    -0.1752635   -1.9589719   -0.0320524
C    -1.3404943   -2.7041295    0.0794927
C    -1.0714962   -4.1002678   -0.1543045
C     0.2617229   -4.2112308   -0.4126142
C     0.8236719   -2.8892691   -0.2949063
C    -2.1932166    2.6183596   -0.3230799
C    -3.1568127    3.7378631   -0.5544796
C    -3.3286599    4.7576973    0.3976898
C    -4.2386105    5.7949909    0.1754655
C    -4.9892784    5.8316256   -1.0038593
C    -4.8279234    4.8218168   -1.9574989
C    -3.9214086    3.7818944   -1.7332076
C    -2.6183332   -2.1932187    0.3234137
C    -3.7378029   -3.1568102    0.5549825
C    -3.7816790   -3.9213660    1.7337434
C    -4.8215871   -4.8278515    1.9582179
C    -5.8315442   -4.9892109    1.0047362
C    -5.7950490   -4.2386066   -0.1746335
C    -4.7577624   -3.3286949   -0.3970470
C     3.7378750    3.1567558    0.5546977
C     4.7577285    3.3286935   -0.3974342
C     5.7950270    4.2386103   -0.1750950
C     5.8316355    4.9891713    1.0042985
C     4.8217942    4.8277442    1.9578918
C     3.7818804    3.9212458    1.7334966
N    -1.9589624    0.1752533    0.0321299
C    -2.7041187    1.3404989   -0.0792597
C    -4.1002517    1.0714805    0.1545501
C    -4.2112146   -0.2617706    0.4126902
C    -2.8892574   -0.8237111    0.2948927
H    -4.8833846    1.8225517    0.1459840
H    -5.1053644   -0.8274966    0.6524346
H    -1.8225642   -4.8834027   -0.1456307
H     0.8274239   -5.1053840   -0.6524042
H     4.8833924   -1.8225848    0.1453053
H     5.1054340    0.8274229    0.6519456
H     1.8225661    4.8833832   -0.1456773
H    -0.8275032    5.1054123   -0.6519948
H     2.9954068    3.7937046    2.4795466
H     4.7256734    2.7504146   -1.3225446
H     4.8440161    5.4076051    2.8824741
H     6.5748528    4.3644810   -0.9285297
H     6.6426309    5.6984880    1.1783982
H     2.7505001   -4.7258318    1.3219423
H     3.7936384   -2.9951073   -2.4799831
H     4.3645549   -6.5749589    0.9276414
H     5.4074956   -4.8436862   -2.8832141
H     5.6984569   -6.6424993   -1.1793598
H    -2.9951035   -3.7938939    2.4796976
H    -4.7257958   -2.7503822   -1.3221391
H    -4.8437136   -5.4077560    2.8827752
H    -6.5749501   -4.3644464   -0.9279955
H    -6.6425463   -5.6985024    1.1789073
H    -2.7502732    4.7256380    1.3227326
H    -3.7939424    2.9954326   -2.4792828
H    -4.3644275    6.5747886    0.9289382
H    -5.4078459    4.8440772   -2.8820417
H    -5.6986266    6.6426132   -1.1778669
```

Constraint example: XYZ coordinates of an optimized structure of ZnTPP with twist and tilt angles constrained to $\Theta = 40°$ and $\Phi = 160°$; BP/SVP level of theory:

```
77
Energy = -3690.722285772
N     2.0951670    0.2521789   -0.6015728
C     3.0170687   -0.7524225   -0.3678476
C     4.2535435   -0.1720887    0.1266846
C     4.0813627    1.1892979    0.1378701
C     2.7386197    1.4511923   -0.3502864
C     2.7290881   -2.1399279   -0.4870402
C     3.7352126   -3.1674992   -0.0936141
C     5.1213217   -3.0289537   -0.3722167
C     6.0632680   -3.9496590    0.1094736
C     5.6558674   -5.0314088    0.9087673
C     4.2923793   -5.1805503    1.2141104
C     3.3508702   -4.2604700    0.7296595
```

C	2.1141036	2.7247051	-0.4502438
C	0.7318561	2.8934315	-0.7764653
N	-0.2727306	1.9638910	-0.5801510
C	-1.4729512	2.6150881	-0.8003372
C	-1.2114854	3.9588818	-1.2672218
C	0.1545617	4.1314297	-1.2522407
Zn	-0.0229393	-0.0158008	-0.5908285
N	0.2269808	-1.9949170	-0.6058406
C	-0.7739981	-2.9212000	-0.8331849
C	-0.1884211	-4.1522536	-1.3169637
C	1.1776651	-3.9796910	-1.3059715
C	1.4308900	-2.6430500	-0.8146938
C	-2.7766739	2.1072929	-0.5032709
C	-3.7891257	3.1292335	-0.1113981
C	-3.4185292	4.2089165	0.7354041
C	-4.3677593	5.1224701	1.2175379
C	-5.7256192	4.9795398	0.8860663
C	-6.1199060	3.9102046	0.0630052
C	-5.1702947	2.9961941	-0.4161578
C	-2.1618486	-2.7572444	-0.5287231
C	-2.8843132	-4.0036187	-0.1459696
C	-2.2514467	-4.9641718	0.6885787
C	-2.9388919	-6.0920946	1.1607541
C	-4.2902983	-6.2915776	0.8323054
C	-4.9438761	-5.3463973	0.0227493
C	-4.2561681	-4.2178961	-0.4465763
C	2.8305195	3.9652222	-0.0381406
C	4.2073323	4.1828158	-0.3126105
C	4.8872269	5.3047084	0.1831501
C	4.2203432	6.2393461	0.9940797
C	2.8634392	6.0361459	1.2970979
C	2.1838800	4.9148664	0.7983170
N	-2.1409913	-0.2828902	-0.6438484
C	-3.0668442	0.7181732	-0.4110130
C	-4.3119459	0.1306915	0.0528402
C	-4.1398997	-1.2307111	0.0463921
C	-2.7885150	-1.4853353	-0.4217592
H	-5.1987491	0.6688820	0.4023546
H	-4.8641880	-1.9762683	0.3894018
H	-0.7515616	-5.0321046	-1.6517357
H	1.9474311	-4.6906781	-1.6300262
H	5.1342834	-0.7155580	0.4833081
H	4.7992283	1.9296204	0.5048735
H	0.7232519	5.0160562	-1.5642613
H	-1.9756356	4.6747274	-1.5938715
H	1.1358029	4.7463030	1.0892688
H	4.7339738	3.4988486	-0.9961371
H	2.3286098	6.7496837	1.9454044
H	5.9487893	5.4551854	-0.0757682
H	4.7549676	7.1196218	1.3877798
H	2.2951829	-4.3645144	1.0247696
H	5.4560004	-2.2258796	-1.0473001
H	3.9573809	-6.0136469	1.8540204
H	7.1276428	-3.8246274	-0.1509387
H	6.3971011	-5.7534693	1.2922285
H	-1.2084737	-4.7991426	0.9999311
H	-4.7715729	-3.5248022	-1.1299063
H	-2.4140966	-6.8142552	1.8087308
H	-6.0006059	-5.4936804	-0.2561744
H	-4.8311534	-7.1771267	1.2051846
H	-2.3681958	4.3072756	1.0497041
H	-5.4936431	2.2039402	-1.1090928
H	-4.0425136	5.9451252	1.8761960
H	-7.1795331	3.7902125	-0.2180806
H	-6.4726304	5.6956479	1.2672510

Further data can be obtained from the authors upon request.

[a] *Lehrstuhl für Theoretische Chemie, Department Chemie und Pharmazie and Interdisciplinary Center for Interface-Controlled Processes, Friedriche-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany. Fax: ++49 9131 8527736; Tel: ++49 9131 8528646; E-mail: hieringer@chemie.uni-erlangen.de*