Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Employing a Chiroptical Sensor for the Absolute Stereochemical Determination of α-Amino and α-Hydroxyphosphonates

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A. Materials and General Instrumentation

Anhydrous solvents used for CD measurements were purchased from Sigma-Aldrich and were spectra grade. Unless otherwise mentioned, solvents were purified as follows. CH_2Cl_2 was dried over CaH_2. CD spectra were recorded on a JASCO J-810 spectropolarimeter, equipped with a temperature controller (Neslab 111) for low temperature studies, and are reported as Mol. CD / λ [nm]. The synthesis of the porphyrin tweezer C_3-Zn-TPFPtz **1**[1] was reported previously, as were the synthesis of guest compounds *R*-**2a** – *S*-**2l**,[2] *R*-**2m**[3-4] and *S*-**2n** – *S*-**2p**[5] used in this study. Note that the aminophosphonate guest compounds reported previously were synthesized as their amine protected variants. The protecting group was removed, as described in the references prior to complexation with the porphyrin tweezer **1**. The deprotection was carried out in general as follows: To a small amount of the protected aminophosphonate (typically 2-3 mg), excess NIS (3-5 equiv) and 1 M sulfuric acid (1 equiv) was added in 1:1 acetonitrile:water solution (0.2 mL). The reaction was stirred at room temperature for 3 h, quenched with 5 M KOH, the organics were extracted with diethyl ether and the residue upon removal of the solvent under reduced pressure was subject to a quick purification with a pipet silica column (10% MeOH in $CHCl_3$). The eluted product was used immediately after purification as described below for complexation with the porphyrin tweezer.

B. General Procedure for CD Measurements

C_3-Zn-TPFPtz **1** (1.0 μL of a 0.001 M solution in anhydrous dichloromethane) was added to hexane (1.0 mL) in a 1.0 cm CD cell (cooled to 0 °C) to obtain a 1.0 μM solution. The background spectrum was recorded from 350 nm to 480 nm with a scan rate of 100 nm/min at 0 °C. Chiral α-aminophosphonate and α-hydroxyphosphonate from a stock solution in anhydrous dichloromethane (0.001 M for 1-10 equiv and 0.01 M for 10-20 equiv) was added to the prepared host C_3-Zn-TPFPtz **1** solution to afford the host-guest complex. The CD spectra were measured immediately (10 scans). The resultant ECCD spectra recorded in millidegrees were converted the molecular CD (Mol. CD) considering the host concentration of 1.0 μM.

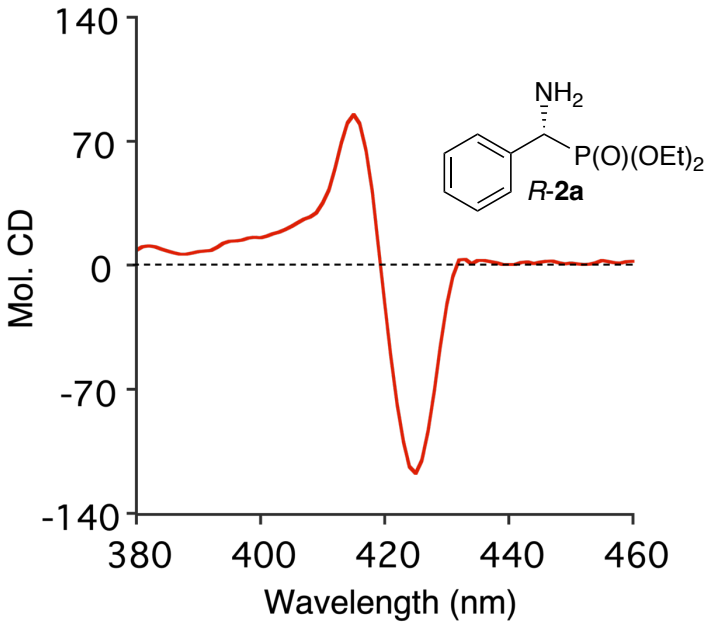


Figure S1. Negative ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *R*-**2a** at 0 °C in hexane.

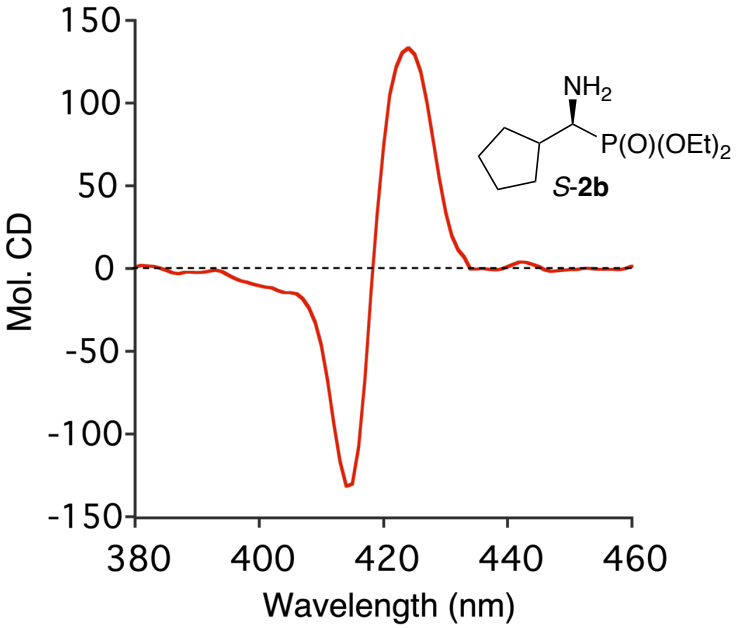


Figure S2. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *S*-**2b** at 0 °C in hexane.

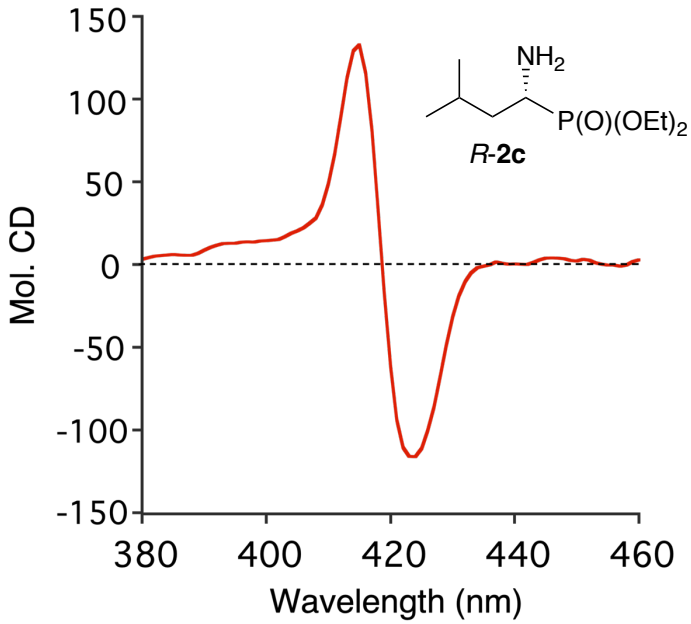


Figure S3. Negative ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *R*-**2c** at 0 °C in hexane.

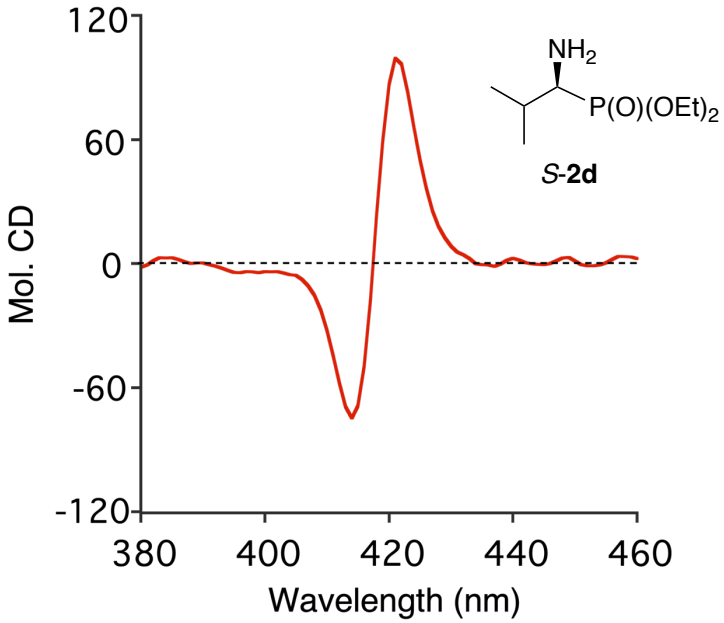


Figure S4. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *S*-**2d** at 0 °C in hexane.

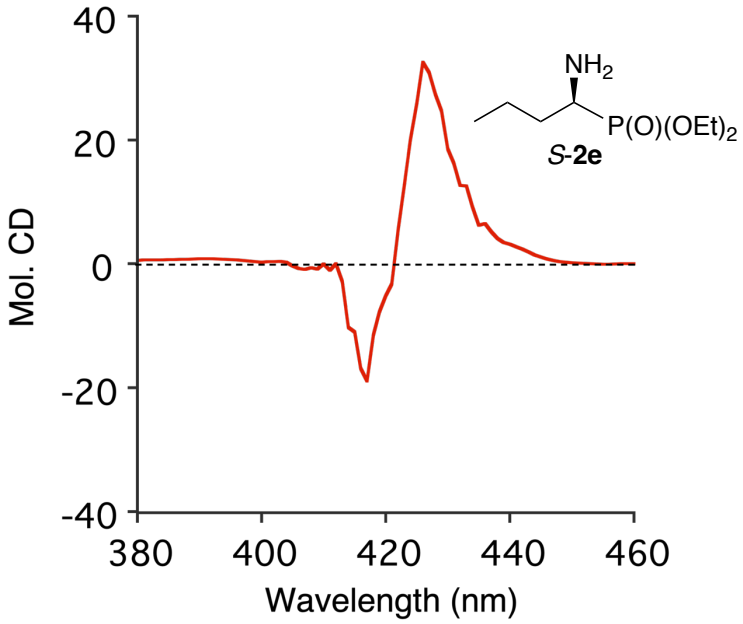


Figure S5. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *S*-**2e** at 0 °C in hexane.

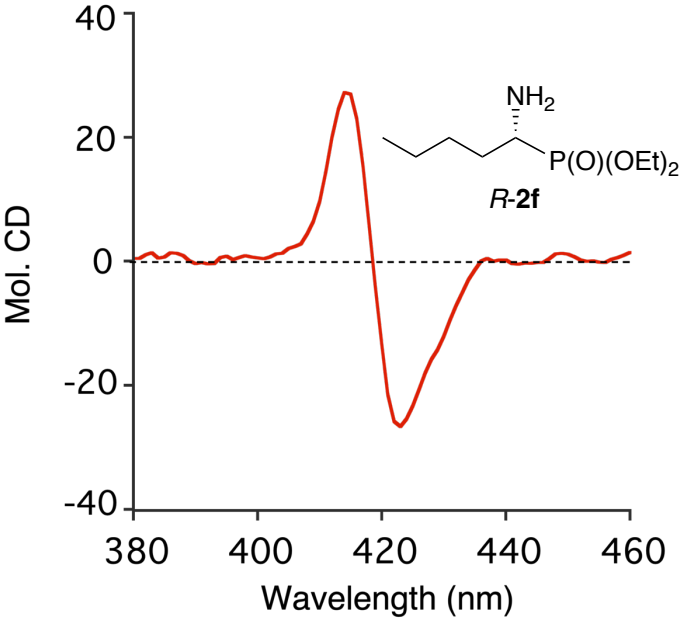


Figure S6. Negative ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *R*-**2f** at 0 °C in hexane.

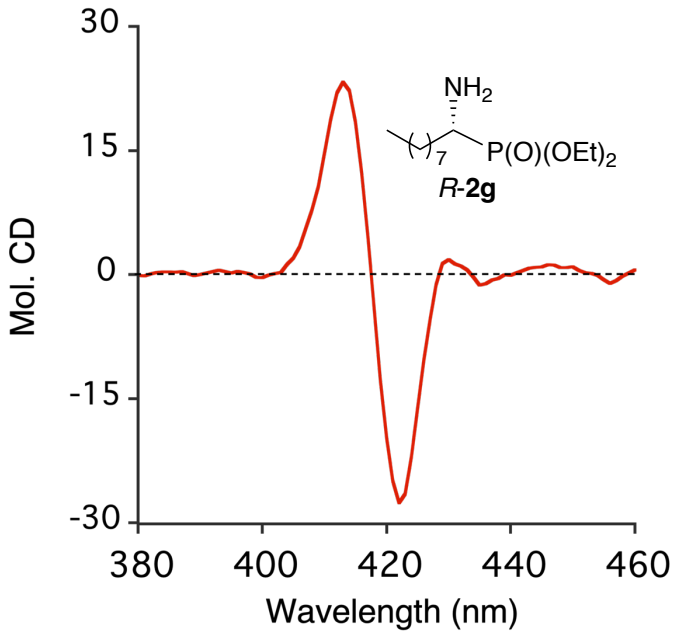


Figure S7. Negative ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 10 equiv of *R*-**2g** at 0 °C in hexane.

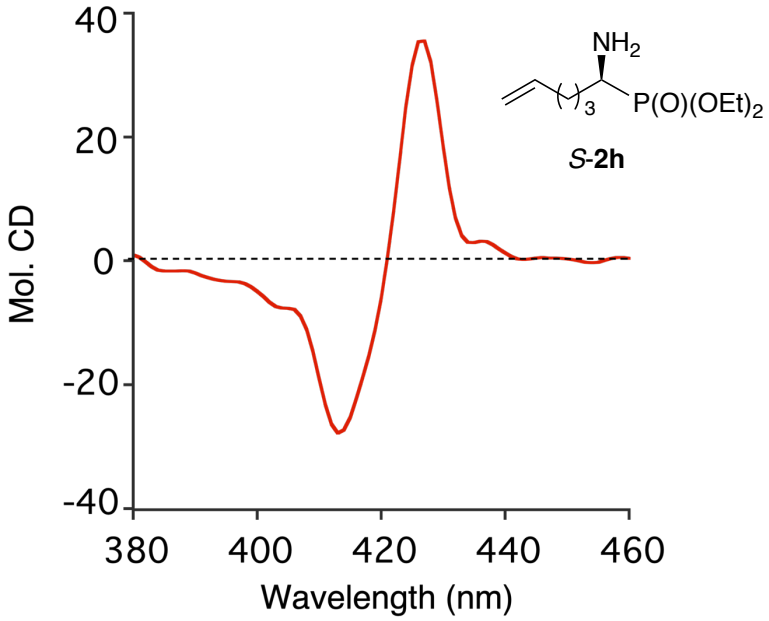


Figure S8. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *S*-**2h** at 0 °C in hexane.

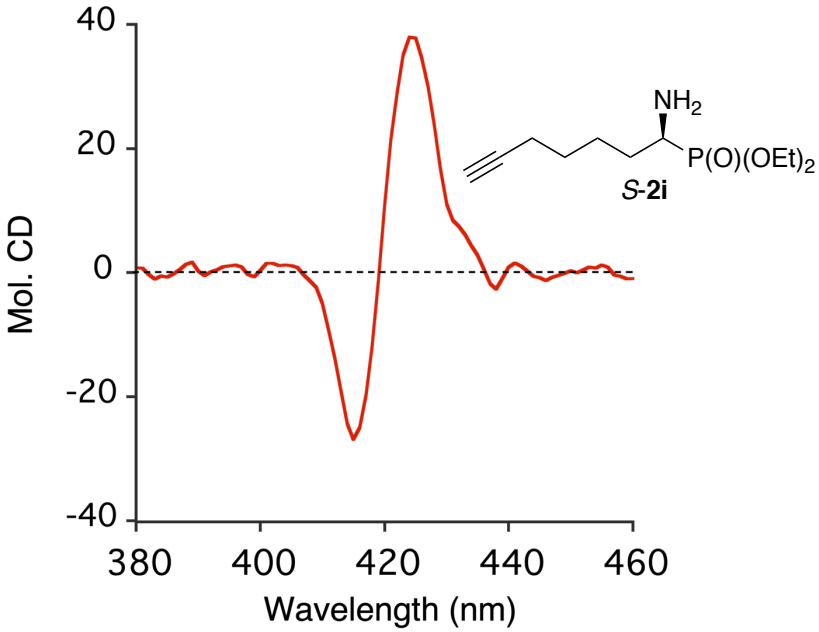


Figure S9. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 10 equiv of *S*-**2i** at 0 °C in hexane.

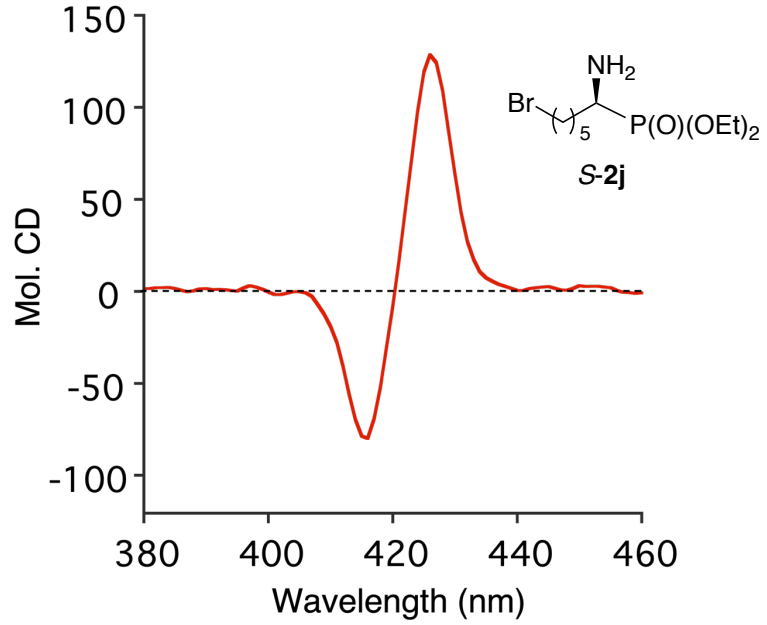


Figure S10. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *S*-**2j** at 0 °C in hexane.

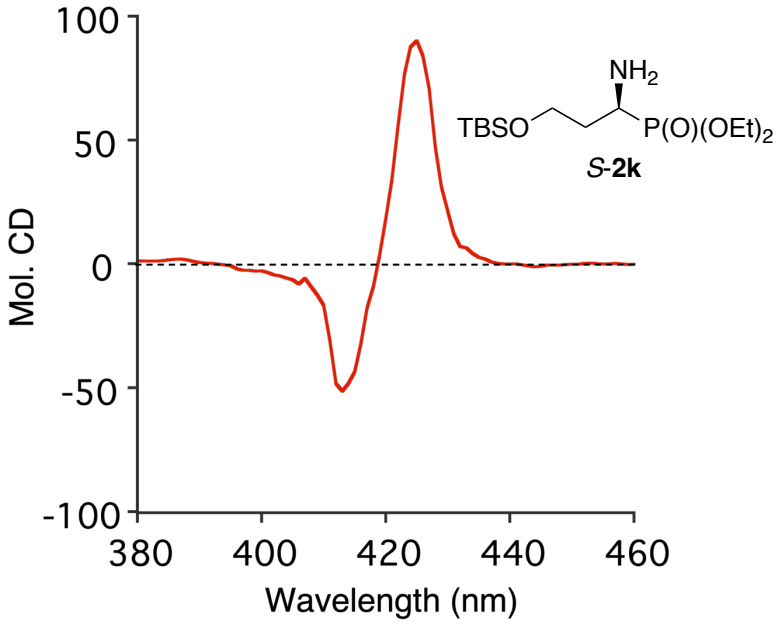


Figure S11. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 5 equiv of *S*-**2k** at 0 °C in hexane.

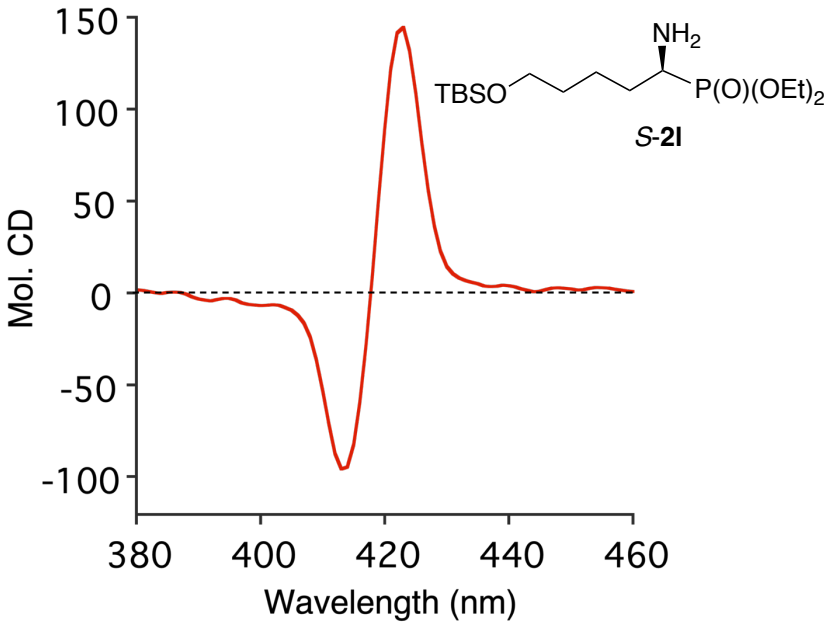


Figure S12. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *S*-**2l** at 0 °C in hexane.

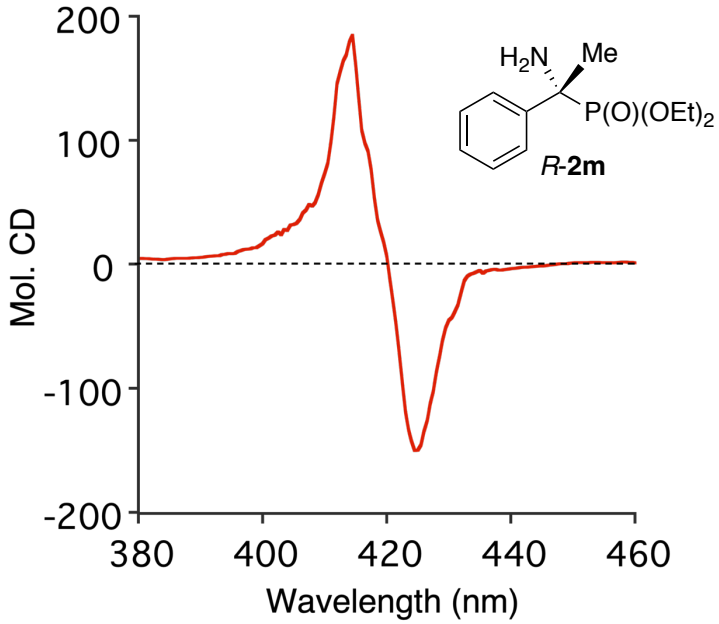


Figure S13. Negative ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *R*-**2m** at 0 °C in hexane.

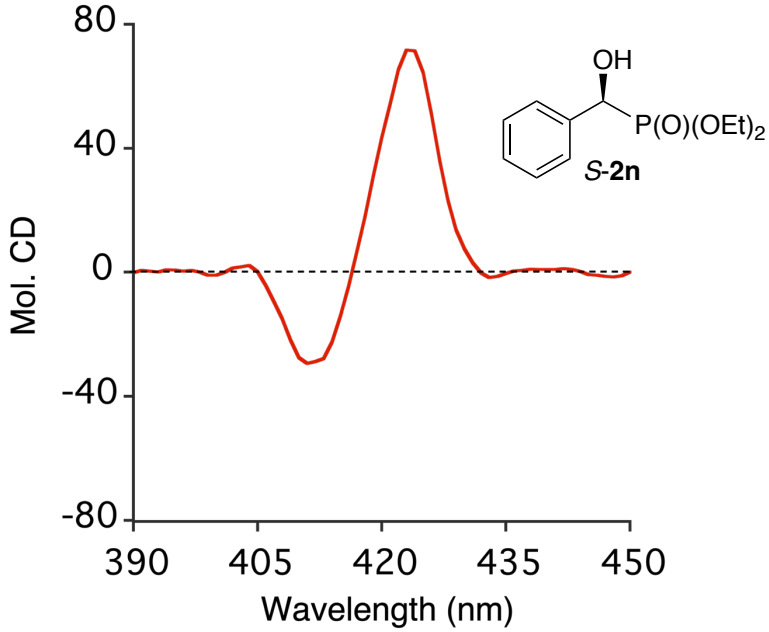


Figure S14. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *S*-**2n** at 0 °C in hexane.

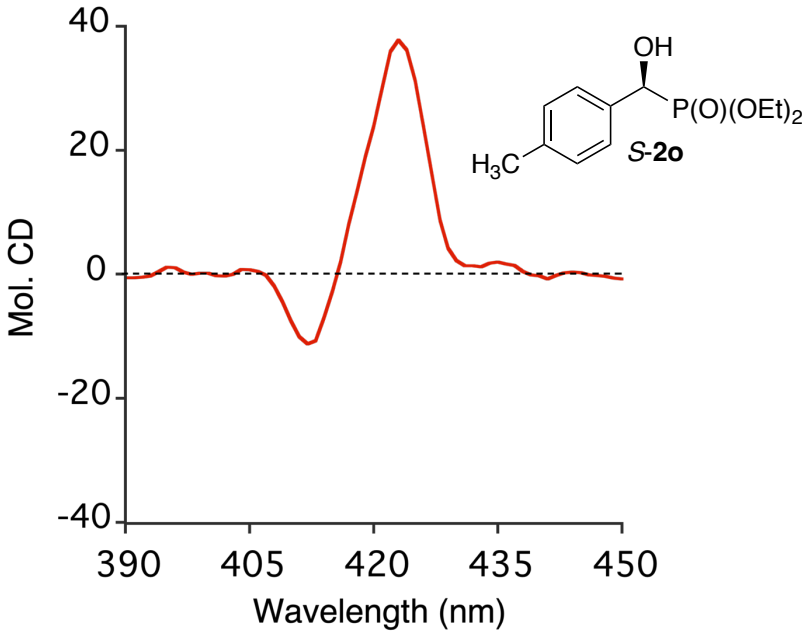


Figure S14. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *S*-**2o** at 0 °C in hexane.

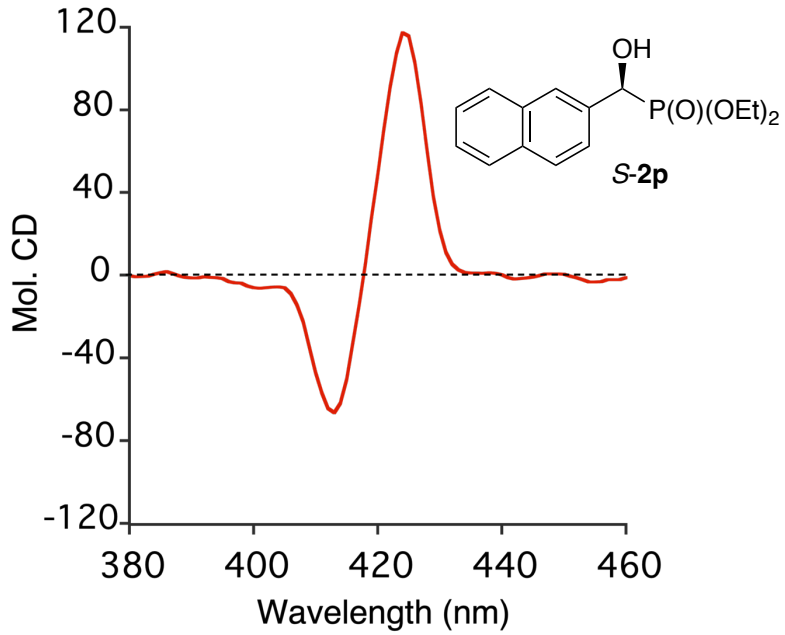


Figure S15. Positive ECCD spectrum of C_3-Zn-TPFPtz **1** complexed with 1 equiv of *S*-**2p** at 0 °C in hexane.

C. Conformational Modeling Studies

All calculations were performed using the Spartan 18 software package running on a Linux platform. In the bis-Zn-porphyrin tweezer framework with the pendant phenyl groups omitted, the substrate aminoalkyl phosphonate was inserted with distance constraints of 2.2 Å applied to the Zn-NH_2 and Zn-O(phosphonate) distances. Candidate conformations were then generated using the Monte Carlo procedure, varying linker and substrate single bond torsions (within the above distance constraints) followed by molecular mechanics (MMFF) relaxation. The resulting collection of 24 structures were all subjected to optimization using the semi empirical PM6 method, retaining the above distance constraints. With each porphyrin's axis defined as the C-Zn-C line across the ring starting from the linker-connected C atom, (+) and (-) helicity was assigned as the dihedral angle between these porphyrin axes, i.e. the Zn-C...C-Zn torsion angle between porphyrins. After restoration of the six omitted phenyl groups (*vide supra*) and release of the above distance constraints, the lowest energy (+) and (-) conformations were then subjected to reoptimization using the B3LYP/6-31G* DFT method; their coordinates are listed below. It is important to note that the variation in geometry was only found in the rotation of the phenyl groups and with little change in the orientation of the porphyrin rings relative to each other. Thus, the lowest energy conformer was a good representative of the orientation of the two coupling porphyrin rings and their interaction with the bound guest molecule. As recommended by an astute reviewer, these structures were then subjected to single-point energy evaluation at the B3LYP-D3(BJ)/6-31G*/SM8 hexane level of theory, which includes dispersion and solvation effects. The energy difference computed between the resulting structures was 0.67 kcal for "gas phase" B3LYP/6-31G* and 1.1 kcal for the more complete representation. The structures' relative energies are very close, but they do appear consistent with the observed ECCD. However, the main

function of this computational modeling effort was to provide realistic pictorial representations of the complexes formed between the tweezer and the substrate.

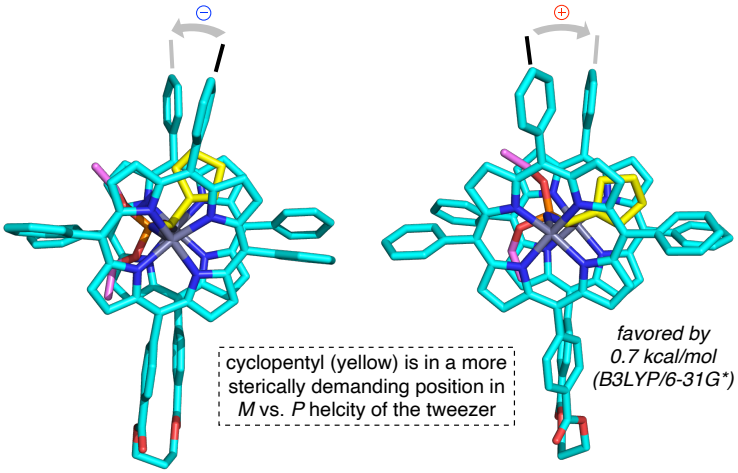
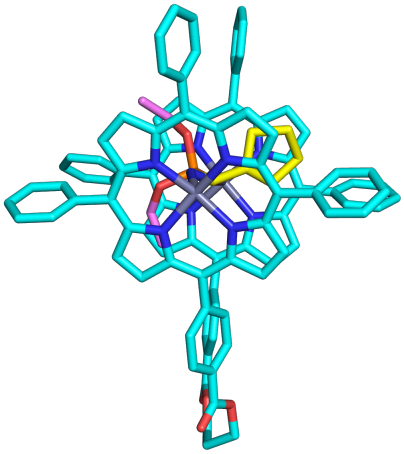


Figure S16. Energy optimized (DFT-B3LYP/6-31G*) structures of P and M helical conformers of C_3-Zn-TPFPtz **1** complexed with S-**2b.** In the P conformer, favored by 0.7 kcal/mol, the porphyrin bound to the amino group moves away from the cyclopentyl group to minimize steric interaction.

Cartesian coordinates for geometry minimized *P*-helical C_3-Zn-TPFPtz **1** complexed with *S*-**2b**



Atom	X	Y	Z
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C	-0.449319	0.805582	-7.721008
C	-2.095046	0.580977	-5.960275
C	0.274784	0.389182	-5.439897
C	0.569451	0.591264	-6.797679
C	-1.788519	0.807584	-7.308736
H	1.606709	0.599712	-7.119959
H	-0.226623	0.988711	-8.767086

C	-6.988486	2.404149	-2.828240
C	-4.244067	2.007488	-2.557770
C	-6.458984	2.023478	-1.600122
C	-6.150899	2.572013	-3.939125
C	-4.770331	2.381649	-3.793323
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H	-3.172637	1.863017	-2.447259
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N	-3.168596	2.034622	1.823368
C	-3.502696	3.639271	0.198422
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H	-6.211231	-0.643231	-1.364966
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C	-4.722335	-2.800304	2.449736
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C	-3.651036	-3.655220	4.573742
C	-2.858352	-3.097587	5.530368
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C	-1.097819	2.730062	5.718046
H	-0.744999	3.694135	6.054888
C	-1.715426	2.464415	4.435020
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H	1.062178	-2.116998	-6.109303
C	2.653009	-3.115871	-4.974617
H	2.763716	-4.080102	-5.449079
C	3.430989	-2.640545	-3.849736
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C	1.011059	2.612921	-3.729111
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H	1.402280	4.483558	-2.652140
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N	2.591561	1.361697	-2.605799

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H	7.158601	2.047190	1.424528
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C	6.220907	-1.567972	-0.688485
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H	6.494503	-4.718980	-1.678965
C	5.262177	-2.896588	-2.165698
N	5.237465	-1.624054	-1.646553
C	4.438374	-3.383572	-3.201194
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H	-1.305209	0.224053	-3.990559
H	-3.130243	0.570354	-5.638561
H	-8.053620	2.572204	-2.949631
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O	-4.087669	1.015928	-7.818673
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H	-6.000947	3.109875	-9.614669
C	-6.496835	3.221448	-7.561674
H	-7.440520	2.674971	-7.657520
H	-6.732332	4.291008	-7.600460
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O	-7.967444	3.208267	-5.360874
O	-5.919138	2.919698	-6.274398
Zn	3.708773	-0.235845	-1.882593
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P	-0.224809	-1.187688	0.794512
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O	0.196789	-2.664235	1.297649
C	-1.980918	-2.293747	-0.886301
H	-2.760134	-2.033351	-0.165480
H	-1.648776	-3.322433	-0.706365
C	-0.442640	-3.288748	2.456365
H	-0.491148	-2.561045	3.269685
H	-1.466466	-3.556109	2.180874
C	1.341173	-0.325461	0.336699
H	1.003809	0.542570	-0.243526
C	2.212208	0.192980	1.499853
C	1.580583	1.323159	2.353771
C	2.348848	1.243525	3.682114
C	2.450034	-0.271338	3.924019
C	2.735489	-0.869295	2.525121
H	3.083710	0.619555	0.994695

H	0.517152	1.140072	2.534660
H	1.673394	2.296829	1.859420
H	3.351574	1.676479	3.565048
H	1.845447	1.772439	4.497930
H	3.210547	-0.546075	4.663367
H	2.268954	-1.851251	2.401679
H	3.811958	-1.014416	2.381475
O	-1.118262	-0.470890	1.761656
N	2.151101	-1.156770	-0.583418
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C	-2.167389	-1.631383	8.277560
C	0.054081	-1.286022	7.405857
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H	-3.245407	-1.587679	8.150013
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H	1.676835	-1.741909	8.743637
H	-2.286424	-2.346574	10.303318
H	0.181721	-2.429682	10.610582
C	-1.417321	4.823252	3.707756
C	-0.480323	7.429727	4.220392
C	-2.314958	5.875944	3.946184
C	-0.041708	5.099725	3.732455
C	0.423642	6.391548	3.986148
C	-1.851488	7.167207	4.201165
H	-3.382056	5.672255	3.936199
H	0.665038	4.296134	3.545545
H	1.493075	6.585165	3.996439
H	-2.562931	7.967410	4.388069
H	-0.118654	8.435262	4.418504
C	3.278889	4.588335	-0.731629
C	2.912632	7.274518	0.030818
C	2.131876	4.985769	-0.025582
C	4.236921	5.563546	-1.052973
C	4.055576	6.894468	-0.675370
C	1.950399	6.316305	0.354969
H	1.377792	4.244331	0.225716
H	5.122685	5.271640	-1.610319
H	4.805886	7.635604	-0.938691
H	1.061909	6.599189	0.912602
H	2.771822	8.311256	0.325106
C	7.716755	-0.562209	1.024538
C	9.894361	-0.803592	2.796913
C	9.018529	-0.771761	0.541307
C	7.528244	-0.474339	2.413085
C	8.605918	-0.593586	3.291490
C	10.096837	-0.891734	1.418427
H	9.180490	-0.831273	-0.531251
H	6.526249	-0.315484	2.802842
H	8.437050	-0.526188	4.363168
H	11.097080	-1.048213	1.022823

H	10.734254	-0.896450	3.480283
C	4.665364	-4.790012	-3.664334
C	5.095949	-7.434764	-4.534556
C	3.689545	-5.780066	-3.467831
C	5.860243	-5.150045	-4.308187
C	6.073878	-6.459670	-4.739390
C	3.902437	-7.090550	-3.897311
H	2.761375	-5.516301	-2.968004
H	6.619703	-4.391322	-4.474938
H	7.003698	-6.716499	-5.240280
H	3.136414	-7.843512	-3.730396
H	5.262228	-8.455128	-4.869561
H	-4.013263	-4.672186	4.527325
C	-5.392362	-4.129221	2.274435
C	-6.665993	-6.623880	1.955061
C	-6.414836	-4.533455	3.148090
C	-5.021721	-5.000570	1.237952
C	-5.650885	-6.235970	1.078926
C	-7.046079	-5.767617	2.990016
H	-6.719406	-3.866300	3.949766
H	-4.229854	-4.706007	0.553758
H	-5.344501	-6.896953	0.272084
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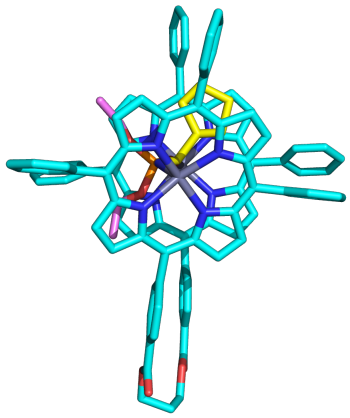
H	-7.157374	-7.585276	1.831618
C	0.365491	-4.512045	2.837157
H	1.386391	-4.239359	3.123670
H	0.415798	-5.227388	2.009854
H	-0.113936	-5.002127	3.691538
C	-2.472533	-2.107168	-2.307032
H	-1.682792	-2.328744	-3.031732
H	-2.820559	-1.081633	-2.461776
H	-3.316116	-2.780976	-2.491885
H	1.484079	-0.637138	4.296661
H	-4.602041	3.426470	-8.601270

Cartesian coordinates for geometry minimized *M*-helical C_3-Zn-TPFPtz **1** complexed with *S*-**2b**



Atom	X	Y	Z
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C	0.674578	-1.234576	7.381512
C	1.923755	0.249425	5.938464
C	-0.283553	-0.531075	5.257660
C	-0.367765	-1.252326	6.461914
C	1.832383	-0.487343	7.127222
H	-1.266612	-1.823229	6.675320
H	0.607131	-1.788762	8.311919
C	7.537043	-0.676664	2.917068
C	4.813207	-0.130677	2.713512
C	6.965357	-0.452129	1.668315
C	6.747429	-0.633836	4.073758
C	5.376688	-0.364737	3.964336
C	5.594376	-0.170398	1.546748
H	4.763984	-0.336631	4.858173
H	3.752161	0.086011	2.629777
C	4.965360	0.100023	0.215333
C	4.539891	1.418608	-0.035486
N	3.863090	1.847004	-1.148808
C	4.829878	2.545330	0.826618
H	5.376261	2.498969	1.757772
C	4.329492	3.650456	0.212937
H	4.388827	4.675416	0.548423
C	3.710581	3.205005	-1.018827
C	4.851379	-0.974141	-0.688468
C	5.325298	-2.317434	-0.430299
H	5.813558	-2.648153	0.475278
C	5.039920	-3.057521	-1.536785
H	5.250135	-4.104618	-1.700693
C	4.380331	-2.174438	-2.475951
N	4.274443	-0.915793	-1.933440
C	3.880789	-2.575691	-3.730506
C	3.187475	-1.738898	-4.628028
C	2.714889	-2.153118	-5.931743
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C	2.106095	-1.073037	-6.494559

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C	1.726749	1.317828	-5.765276
C	1.886492	2.400484	-4.879090
C	1.449877	3.752232	-5.157078
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C	1.831884	4.516222	-4.098287
H	1.677108	5.576207	-3.959882
C	2.512840	3.638464	-3.168286
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H	-1.408885	-5.074684	3.189381
C	-2.721961	-3.379795	2.499403
C	-2.056252	0.652343	3.977322
C	-1.777147	1.908293	4.640910
H	-1.034354	2.060528	5.410108
C	-2.641812	2.827509	4.133475
H	-2.723025	3.871485	4.398403
C	-3.469764	2.140136	3.166409
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C	-4.519209	2.744576	2.446266
C	-5.360754	2.081519	1.529763
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C	-7.092528	1.724465	0.127624
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H	6.451831	-1.034794	9.748283
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Zn	-3.782114	-0.571226	1.715019
Zn	3.057049	0.637120	-2.629853
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O	-1.033227	-0.779605	-2.722907
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H	-1.947656	-7.747001	-0.754658
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C	1.709945	1.607942	-8.273666
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H	1.611719	-1.147246	1.195132
H	2.446632	-2.677070	1.476274

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