Electronic Supplementary Material (ESI) for Dalton Transactions.

Rational Design of a Room Temperature Molecular Spin Switch. The Light-Driven Coordination Induced Spin State Switch (LD-CISSS) Approach.

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I. Association Constants and Thermodynamic Parameters

I.1 Association of pyridine to Ni-TPP

The association constant (K) of pyridine to Ni-TPP was determined by temperature dependent ^{1}H NMR spectroscopy. Calculation of K can be simplified to a pseudo first order kinetic because of the excess of pyridine as the solvent (eq S1 and S2). The paramagnetic shift (δ_{para}) of the pyrrole protons of Ni-TPP in pure pyridine is not the maximum shift (δ_{max}). Because of a very low association constant there is always an equilibrium between the square bipyramidal paramagnetic complex and the square planar diamagnetic complex. To determine the association constant, the pyrrole shift (δ_{py}) has to be compared with the maximum shift which was obtained by NMR measurement of Ni-TPP in (the much stronger ligand) pure piperidine (δ_{pip}) (equation 3). From temperature dependence of the association constant the thermodynamic parameters ΔH and ΔS are calculated by Gibbs free enthalpy relation (equation S4).

$$Ni\text{-}TPP + 2\ Pyridine \leftrightharpoons Ni\text{-}TPP(Py)_2 \qquad \text{(eq S1)}$$

$$Ni\text{-}TPP_{dia} \leftrightharpoons Ni\text{-}TPP_{para} \qquad \text{(eq S2)}$$

$$K = \frac{[Ni\text{-}TPP_{para}]}{[Ni\text{-}TPP_{dia}]} = \frac{\delta_{py}-\delta_{dia}}{\delta_{max}-\delta_{py}} \qquad \text{(eq S3)}$$

$$\Delta G = \Delta H - T\Delta S = -RT\ln(K) \qquad \text{(eq S4)}$$

K:	association constant
δ_{py}:	shift of pyrrole protons in pure pyridine [ppm]
δ_{dia}:	diamagnetic shift of pyrrole protons [ppm] (9 ppm)
δ_{max}:	maximum paramagnetic shift of pyrrole protons [ppm]

Table S1. Determination of association constant of pyridine to Ni-TPP.

T / K	T^{-1} / K^{-1}	δ_{py} / ppm	δ_{max} / ppm	Ni-TPP$_{para}$ / %	Ni-TPP$_{dia}$ / %	K	ln(K)
300	0,00333	22,11	51,22	0,31052	0,68948	0,45036	-0,79771
310	0,00323	18,96	48,70	0,25088	0,74912	0,33490	-1,09392
320	0,00313	16,74	45,37	0,21281	0,78719	0,27035	-1,30805
330	0,00303	15,18	43,14	0,18102	0,81898	0,22103	-1,50946

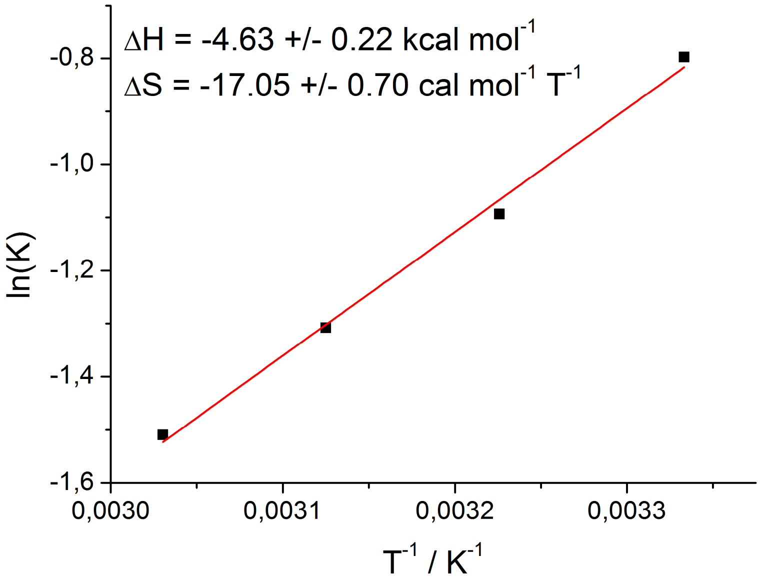


Figure S1. Gibbs free enthalpy plot for determination of thermodynamic parameters ΔH and ΔS for the association of pyridine to Ni-TPP.

I.2 Intramolecular association of record player 1 and 2

To determine the thermodynamic parameters ΔH and ΔS for the intramolecular coordination, the association constant (K_1) was measured as a function of temperature in DMSO. K_1 (Figure 14, equation S5) can be calculated from the pyrrole protons shifts of the *cis* isomer of the record player molecule. The maximum shift δ_{max} which is crucial to calculate the cis_{para}/cis_{dia} ratio (see eq. 1 and eq. S5), was measured differently for the record players **1** and **2**. For *cis*-**2** the value was obtained by an analogous experiment in pure pyridine. For *cis*-**1** this is not possible because association is too weak. Therefore we supposed the shifts obtained for Ni-TPP in piperidine to be the maximum shift δ_{max}. ΔH and ΔS were obtained by Gibbs free enthalpy plots (eq. S4, Figure S2 and S3).

$$cis_{dia} \leftrightharpoons cis_{para} \tag{S5}$$

$$K_1 = \frac{cis_{para}}{cis_{dia}} = \frac{\delta - \delta_{dia}}{\delta_{max} - \delta} \tag{S6}$$

K_1:	association constant
δ_{para}:	paramagnetic shift of pyrrole protons [ppm]
δ_{dia}:	diamagnetic shift of pyrrole protons [ppm] (9 ppm)
δ_{max}:	maximum paramagnetic shift of pyrrole protons [ppm]
δ:	absolute chemical shift of pyrrole protons [ppm]

Table S2 Determination of intramolecular association constant of record player **2**. The maximum shift (σ_{max}) was found by measurement in pure pyridine.

T / K	T^{-1} / K^{-1}	δ / ppm	δ_{max} / ppm	*cis*-**2**$_{para}$ / %	*cis*-**2**$_{dia}$ / %	K	ln(K)
300	0,00333	48,42	53,69	0,8819	0,1181	7,4674	2,0106
310	0,00323	45,94	51,95	0,8600	0,1400	6,1429	1,8153
320	0,00313	43,46	50,45	0,8300	0,1700	4,8824	1,5856
330	0,00303	41,16	49,03	0,8000	0,2000	4,0000	1,3863
340	0,00294	38,93	47,49	0,7775	0,2225	3,4952	1,2514

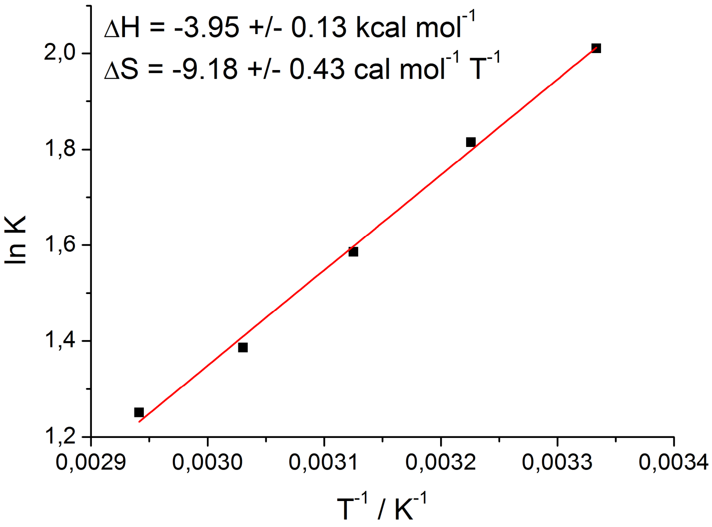


Figure S2. Gibbs free enthalpy plot for determination of thermodynamic parameters ΔH and ΔS for the intramolecular association of *cis*-**2**.

Table S3. Determination of intramolecular association constant of record player **1**. The maximum shift (δ_{max}) was found by measurement of Ni-TPP in pure piperidine (see Table S1).

T / K	T^{-1} / K^{-1}	δ / ppm	δ_{max} / ppm	*cis*-**1**$_{para}$ / %	*cis*-**1**$_{dia}$ / %	K	ln(K)
300	0,00333	11,45	51,22	0,0580	0,9420	0,0616	-2,7870
310	0,00323	11,13	48,70	0,0537	0,9464	0,0567	-2,8701
320	0,00313	10,87	45,37	0,0514	0,9486	0,0542	-2,9150
330	0,00303	10,66	43,14	0,0486	0,9514	0,0511	-2,9738

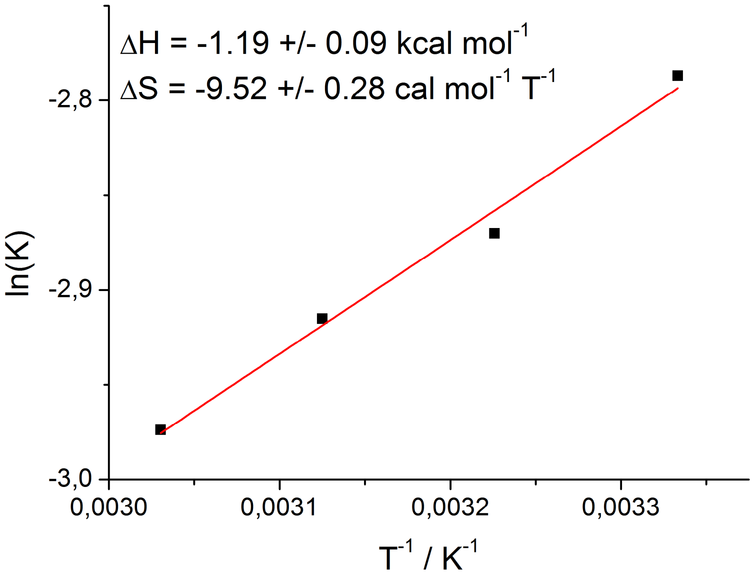


Figure S3. Gibbs free enthalpy plot for determination of thermodynamic parameters ΔH and ΔS for the intramolecular association of *cis*-**1**.

II. Single Crystal X-ray Analysis

Data collection was performed using an Imaging Plate Diffraction System (IPDS-1) from STOE with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved with direct methods using SHELXS-97 and structure refinement was performed against F^2 using SHELXL-97. All non-hydrogen atoms except the disordered C atoms of lower occupancy) were refined anisotropic. The C-H H atoms were positioned with idealized geometry and refined isotropic with $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$ (1.5 for methyl H atoms) using a riding model. One of the phenyl rings is disordered and was refined using a split model with restraints (SAME and FLAT). The site with lower occupancy was refined only isotropic. There are three additional solvate DMSO molecules in the asymmetric unit of which two are disordered and therefore, were also refined using split model. Selected crystal data and details on the structure refinement are given in Table S4 and an ORTEP plot is presented in Figure S4.

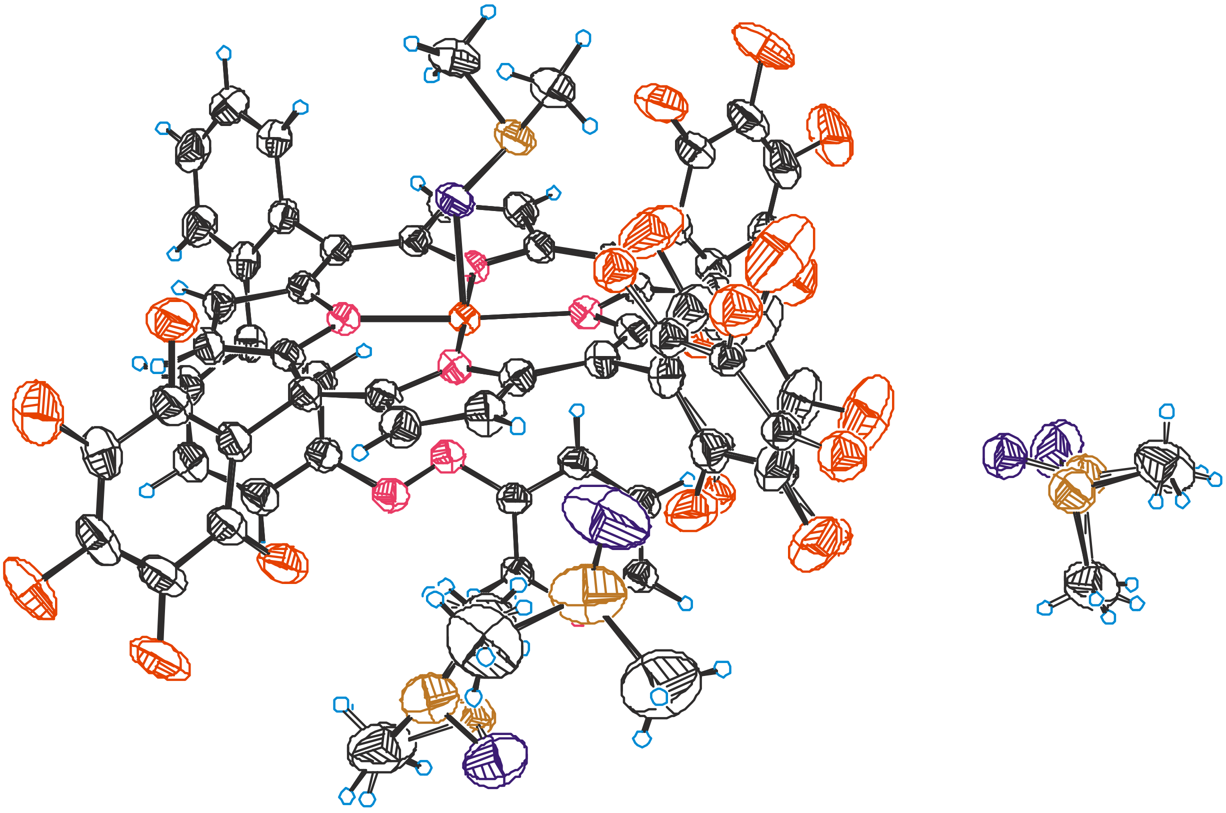


Figure S4. View of the asymmetric unit with displacement ellipsoids drawn at the 50% probability level.

Table S4. Crystal data and structure refinement for herges93.

Identification code	herges93	
Empirical formula	C126 H88 F30 N14 Ni2 O8 S8	
Formula weight	2870.00	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.3795(4) Å	α = 99.054(3)°.
	b = 14.9693(5) Å	β = 97.777(3)°.
	c = 16.9457(6) Å	γ = 117.019(2)°.
Volume	3119.06(17) Å^3	
Z	1	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.544 mm^{-1}	
F(000)	1460	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.63 to 25.00°.	
Index ranges	-17<=h<=17, -17<=k<=17, -19<=l<=20	
Reflections collected	27602	
Independent reflections	10894 [R(int) = 0.0463]	
Completeness to theta = 25.00°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10894 / 40 / 899	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1015	
R indices (all data)	R1 = 0.0676, wR2 = 0.1092	
Largest diff. peak and hole	0.395 and -0.386 e.Å^{-3}	

III. Thermal half-life

The thermal half-life was determined in DMSO, dichloromethane and chloroform by integration in ^{1}HNMR (Figure S5). The NMR samples were stored at 20 °C and kept in the dark.

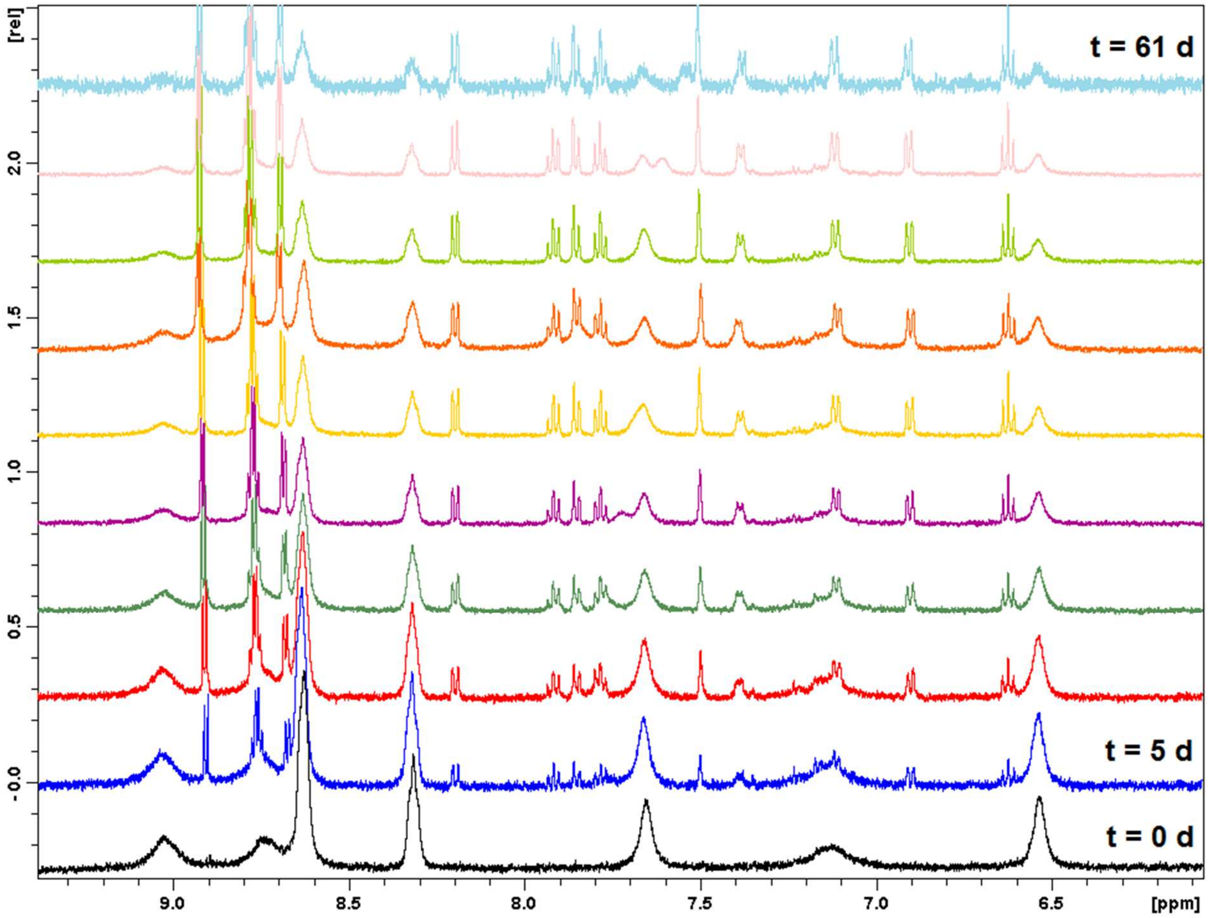


Figure S5. ^{1}H NMR spectra for determination of thermal half-life of *cis*-**2** in dichloromethane. The time between each measurement are 7 d beginning with the second spectrum (blue).

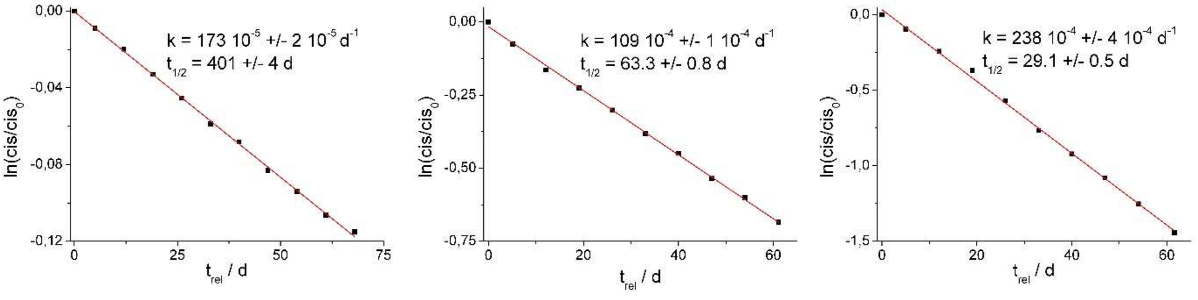


Figure S6. Linear plots for determination of the thermal half-life in DMSO (left), dichloromethane (middle) and chloroform (right).

IV. Computational Details

IV.1 Formation Enthalpies of Ni-TPP and Ni-TPPF20 complexes with pyridine

The geometry optimizations of the Ni-TPP and Ni-TPPF$_{20}$ complexes were performed at the PBE/DZP level of density functional theory. Single point energies were calculated at the optimized geometries using several functionals and basis sets. The calculated relative energies are compared with the corresponding experimentally determined ∆H values.

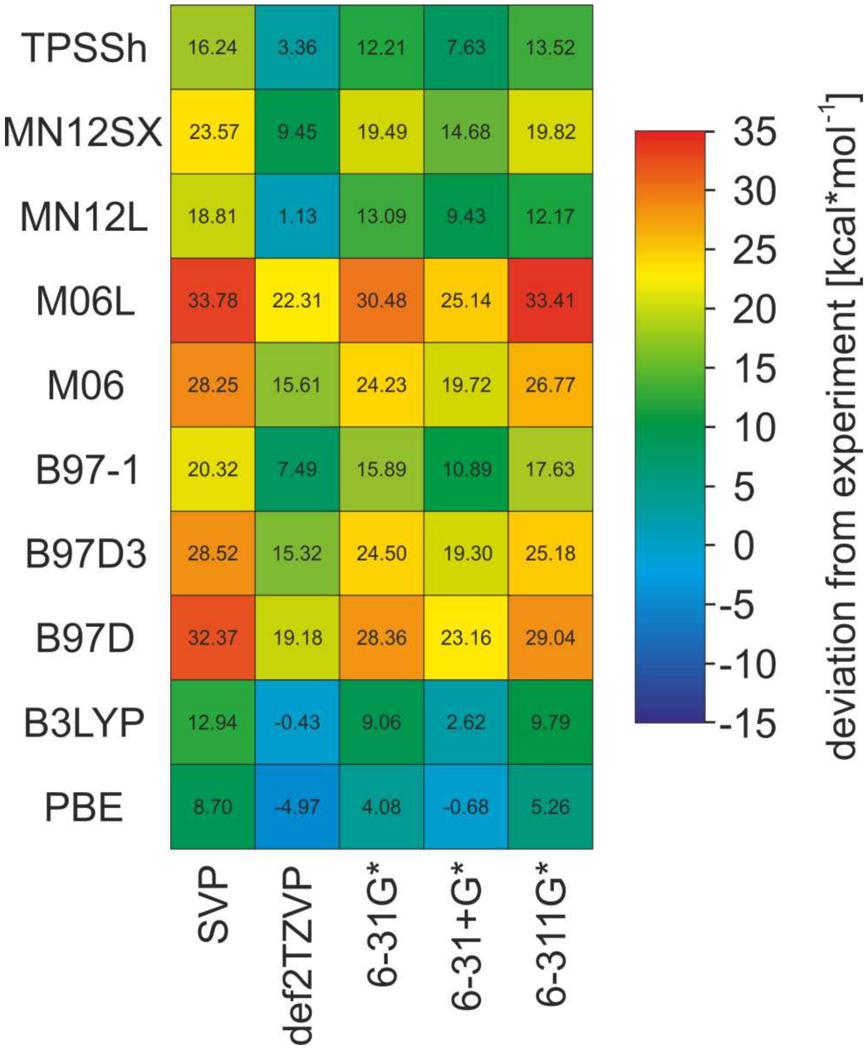
Table S5. Calculated enthalpies for the formation of the five coordinate (∆H 1 Py) and six coordinate (∆H 2 Py) complexes of Ni-TPP with pyridine.

Functional	Basis set	E_{abs} Pyridine (s) [Hartree]	E_{abs} Ni-TPP (s) [Hartree]	E_{abs} Ni-TPP · 1 Py (t) [Hartree]	E_{abs} Ni-TPP · 2 Py (t) [Hartree]	∆H 1 Py [kcal/mol]	∆H 2 Py [kcal/mol]
PBE	**SVP**	-247.7907293	-3416.8668675	-3664.6603572	-3912.4695187	**-1.73**	**-13.30**
PBE	**def2TZVP**	-248.0572139	-3419.0707883	-3667.1175150	-3915.1846324	**6.58**	**0.37**
PBE	**6-31G***	-247.9678670	-3418.2081610	-3666.1732030	-3914.1577327	**1.77**	**-8.68**
PBE	**6-31+G***	-247.9785310	-3418.2997021	-3666.2707783	-3914.2630143	**4.68**	**-3.92**
PBE	**6-311G***	-248.0184093	-3418.7028732	-3666.7192797	-3914.7554118	**1.26**	**-9.86**
B3LYP	**SVP**	-247.7907293	-3419.4665420	-3667.5878432	-3915.7044097	**-10.25**	**-17.54**
B3LYP	**def2TZVP**	-248.3773050	-3421.7070133	-3670.0874379	-3918.4682745	**-1.96**	**-4.17**
B3LYP	**6-31G***	-248.2842171	-3420.8212213	-3669.1173750	-3917.4114208	**-7.49**	**-13.66**
B3LYP	**6-31+G***	-248.2951273	-3420.9105850	-3669.2105602	-3917.5123502	**-3.04**	**-7.22**
B3LYP	**6-311G***	-248.3373511	-3421.3312805	-3669.6809926	-3918.0289152	**-7.76**	**-14.39**
B97D	**SVP**	-247.9229869	-3418.7190885	-3666.6649946	-3914.6239832	**-14.38**	**-36.97**
B97D	**def2TZVP**	-248.1885201	-3420.9173742	-3669.1158535	-3917.3323060	**-6.25**	**-23.78**
B97D	**6-31G***	-248.0970082	-3420.0365205	-3668.1516344	-3916.2830653	**-11.36**	**-32.96**
B97D	**6-31+G***	-248.1069197	-3420.1217110	-3668.2412745	-3916.3797896	**-7.93**	**-27.76**
B97D	**6-311G***	-248.1499864	-3420.5531952	-3668.7215460	-3916.9067779	**-11.52**	**-33.64**
B97D3	**SVP**	-247.9440954	-3418.8973575	-3666.8599549	-3914.8383211	**-11.61**	**33.12**
B97D3	**def2TZVP**	-248.2096286	-3421.0956432	-3669.3108138	-3917.5466439	**-3.48**	**-19.92**
B97D3	**6-31G***	-248.1181167	-3420.2147895	-3668.3465948	-3916.4974032	**-8.59**	**-29.10**
B97D3	**6-31+G***	-248.1280282	-3420.2999800	-3668.4362348	-3916.5941275	**-5.16**	**-23.90**
B97D3	**6-311G***	-248.1710949	-3420.7314642	-3668.9165063	-3917.1211159	**-8.75**	**-29.78**
B97-1	**SVP**	-248.0317295	-3418.8220858	-3666.8766852	-3914.9252599	**-14.35**	**-24.92**
B97-1	**def2TZVP**	-248.2991793	-3421.0304714	-3669.3397158	-3917.6480896	**-6.32**	**-12.09**
B97-1	**6-31G***	-248.2095684	-3420.1665399	-3668.3939938	-3916.6183326	**-11.22**	**-20.49**
B97-1	**6-31+G***	-248.2189648	-3420.2487233	-3668.4795083	-3916.7113422	**-7.42**	**-15.49**
B97-1	**6-311G***	-248.2599643	-3420,6570655	-3668.9363520	-3917.2124179	**-12.12**	**-22.23**
M06	**SVP**	-247.9089681	-3417.9229487	-3665.8559487	-3913.7932292	**-15.08**	**-32.85**
M06	**def2TZVP**	-248.1790803	-3420.1538082	-3668.3439753	-3916.5441810	**-6.96**	**-20.21**
M06	**6-31G***	-248.0926932	-3419.3195391	-3667.4318013	-3915.5508647	**-12.28**	**-28.83**
M06	**6-31+G***	-248.1014735	-3419.4028278	-3667.5189665	-3915.6445340	**-9.20**	**-24.32**
M06	**6-311G***	-248.1393864	-3419.7744237	-3667.9343651	-3916.1031842	**-12.90**	**-31.37**
Experiment[1]						**-**	**-4.63 (± 0.22)**

Functional	Basis set	E_{abs} Pyridine (s) [Hartree]	E_{abs} Ni-TPP (s) [Hartree]	E_{abs} Ni-TPP · 1 Py (t) [Hartree]	E_{abs} Ni-TPP · 2 Py (t) [Hartree]	ΔH 1 Py [kcal/mol]	ΔH 2 Py [kcal/mol]
M06L	**SVP**	-248.0687614	-3419.1855020	-3667.2846714	-3915.3841936	**-19.08**	**-38.38**
M06L	**def2TZVP**	-248.3337423	-3421.3753539	-3669.7278725	-3918.0857184	**-11.78**	**-26.91**
M06L	**6-31G***	-248.2464260	-3420.5291092	-3668.8025191	-3917.0778657	**-16.93**	**-35.08**
M06L	**6-31+G***	-248.2520476	-3420.5927651	-3668.8656084	-3917.1442481	**-13.05**	**-29.74**
M06L	**6-311G***	-248.2948281	-3421.0047018	-3669.3281490	-3917.6549322	**-17.96**	**-38.01**
MN12L	**SVP**	-247.8521535	-3417.2579922	-3665.1132325	-3912.9996023	**-1.94**	**-23.41**
MN12L	**def2TZVP**	-248.1287599	-3419.6102290	-3667.7244417	-3915.8768738	**9.13**	**-5.73**
MN12L	**6-31G***	-248.0452923	-3418.7643711	-3666.8061492	-3914.8831520	**2.21**	**-17.69**
MN12L	**6-31+G***	-248.0525888	-3418.8478387	-3666.8926905	-3914.9753716	**4.86**	**-14.03**
MN12L	**6-311G***	-248.0837359	-3419.2500896	-3667.3272279	-3915.4442915	**4.14**	**-16.77**
MN12SX	**SVP**	-247.8661294	-3417.5000714	-3665.3818463	-3913.2772225	**-9.82**	**-28.17**
MN12SX	**def2TZVP**	-248.1687256	-3420.0148446	-3668.1852527	-3916.3746919	**-1.06**	**-14.05**
MN12SX	**6-31G***	-248.0796822	-3419.1437864	-3667.2350185	-3915.3415381	**-7.25**	**-24.09**
MN12SX	**6-31+G***	-248.0884745	-3419.2245312	-3667.3192706	-3915.4322110	**-3.93**	**-19.28**
MN12SX	**6-311G***	-248.1235963	-3419.6362946	-3667.7695159	-3915.9223955	**-6.04**	**-24.42**
TPSSh	**SVP**	-248.1262254	-3419.6494978	-3667.7920901	-3915.9351659	**-10.27**	**-20.84**
TPSSh	**def2TZVP**	-248.3895921	-3421.8318714	-3670.2251587	-3918.6237402	**-2.32**	**-7.96**
TPSSh	**6-31G***	-248.3013587	-3420.9770688	-3669.2903030	-3917.6065766	**-7.45**	**-16.81**
TPSSh	**6-31+G***	-248.3100135	-3421.0560251	-3669.3725370	-3917.6955463	**-4.08**	**-12.23**
TPSSh	**6-311G***	-248.3510699	-3421.4627812	-3669.8264166	-3918.1938041	**-7.88**	**-18.12**
Experiment[1]						**-**	**-4.6 (± 0.2)**

Table S6. Deviation from the experimental value of the calculated enthalpies for the formation of the six coordinate complexes of Ni-TPP with pyridine in kcal*mol^{-1}.

	SVP	**def2TZVP**	**6-31G***	**6-31+G***	**6-311G***
TPSSh	16.24	3.36	12.21	7.63	13.52
MN12SX	23.57	9.45	19.49	14.68	19.82
MN12L	18.81	1.13	13.09	9.43	12.17
M06L	33.78	22.31	30.48	25.14	33.41
M06	28.25	15.61	24.23	19.72	26.77
B97-1	20.32	7.49	15.89	10.89	17.63
B97D3	28.52	15.32	24.50	19.30	25.18
B97D	32.37	19.18	28.36	23.16	29.04
B3LYP	12.94	-0.43	9.06	2.62	9.79
PBE	8.70	-4.97	4.08	-0.68	5.26



	SVP	def2TZVP	6-31G*	6-31+G*	6-311G*
TPSSh	16.24	3.36	12.21	7.63	13.52
MN12SX	23.57	9.45	19.49	14.68	19.82
MN12L	18.81	1.13	13.09	9.43	12.17
M06L	33.78	22.31	30.48	25.14	33.41
M06	28.25	15.61	24.23	19.72	26.77
B97-1	20.32	7.49	15.89	10.89	17.63
B97D3	28.52	15.32	24.50	19.30	25.18
B97D	32.37	19.18	28.36	23.16	29.04
B3LYP	12.94	-0.43	9.06	2.62	9.79
PBE	8.70	-4.97	4.08	-0.68	5.26

Figure S7. Colour coded representation of the deviation of theoretically calculated and experimentally determined values for the formation of the six coordinate complex of Ni-TPP with two pyridine molecules at different levels of theory. The exact values are given in kcal*mol^{-1}.

The smallest deviation from the experimental value is observed at the MN12L/def2TZVP (overestimated by 1.13 kcal*mol$^{-1,}$), at the PBE/6-31+G* (underestimated by 0.68 kcal*mol^{-1}) and at the B3LYP/def2TZVP (underestimated by 0.43 kcal*mol^{-1}) level of density functional theory. Although there is no experimentally derived value for the complex formation enthalpy of the five coordinate complex of pyridine with Ni-TPP the calculated values at the MN12L/def2TZVP and the PBE/6-31+G* level of theory seem to be largely underestimated.

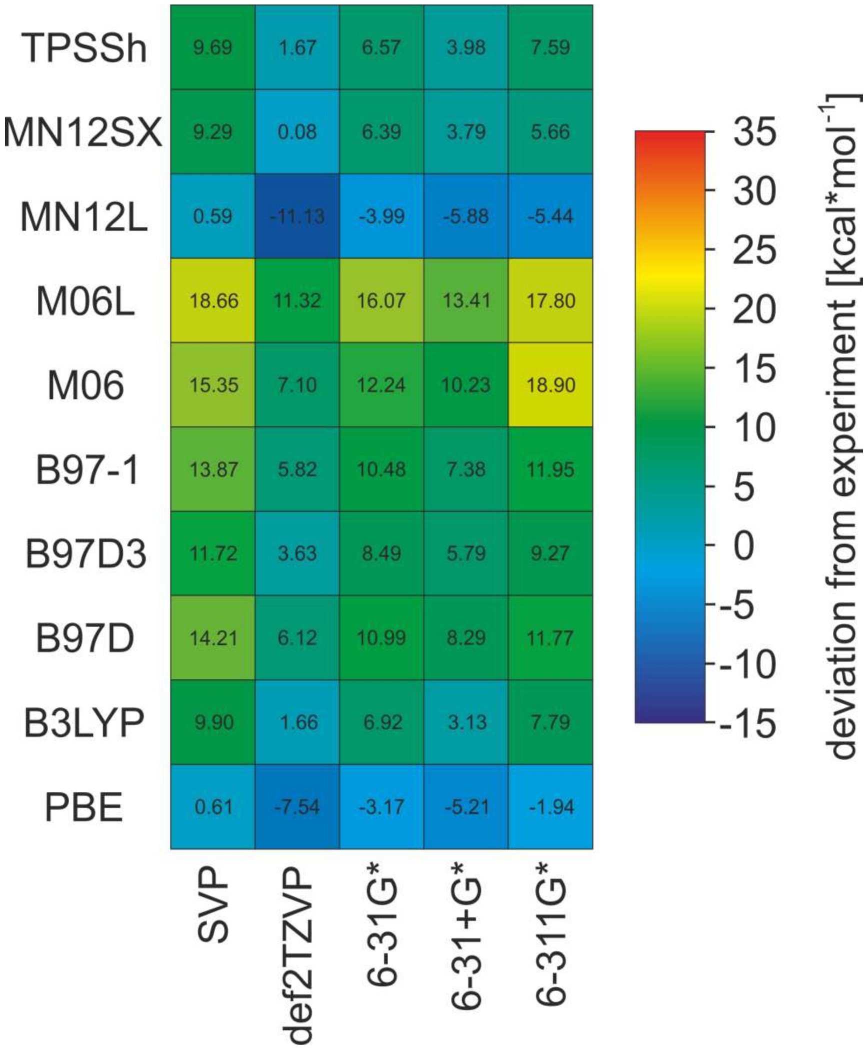
Table S7. Calculated enthalpies for the formation of the five coordinate (ΔH 1 Py) and six coordinate (ΔH 2 Py) complexes of Ni-TPPF$_{20}$ with pyridine.

Functional	Basis set	E_{abs} Pyridine (s) [Hartree]	E_{abs} Ni-TPPF$_{20}$ (s) [Hartree]	E_{abs} Ni-TPPF$_{20}$ · 1 Py (t) [Hartree]	E_{abs} Ni-TPPF$_{20}$ · 2 Py (t) [Hartree]	ΔH 1 Py [kcal/mol]	ΔH 2 Py [kcal/mol]
PBE	**SVP**	-247.7907293	-5398.2561063	-5646.0562612	-5893.8700228	**-5.91**	**-20.37**
PBE	**def2TZVP**	-248.0572139	-5402.8912268	-5650.9448704	-5899.0159446	**2.24**	**-6.46**
PBE	**6-31G***	-247.9678670	-5401.0661947	-5649.0374536	-5897.0259916	**-2.13**	**-15.10**
PBE	**6-31+G***	-247.9785310	-5401.3249080	-5649.3035868	-5897.2999247	**-0.09**	**-11.27**
PBE	**6-311G***	-248.0184093	-5402.2065906	-5650.2303544	-5898.2710974	**-3.36**	**-17.37**
B3LYP	**SVP**	-247.7907293	-5402.5030745	-5650.6322531	-5898.7535772	**-15.20**	**-25.47**
B3LYP	**def2TZVP**	-248.3773050	-5407.1878216	-5655.5762203	-5903.9610289	**-6.96**	**-11.67**
B3LYP	**6-31G***	-248.2842171	-5405.3401985	-5653.6438962	-5901.9421489	**-12.22**	**-21.03**
B3LYP	**6-31+G***	-248.2951273	-5405.5853926	-5653.8939606	-5902.1998376	**-8.43**	**-15.18**
B3LYP	**6-311G***	-248.3373511	-5406.4969677	-5654.8551831	-5903.2078326	**-13.09**	**-22.69**
B97D	**SVP**	-247.9229869	-5400.8449421	-5648.7990261	-5896.7633224	**-19.51**	**-45.44**
B97D	**def2TZVP**	-248.1885201	-5405.4729934	-5653.6797152	-5901.9006561	**-11.42**	**-31.77**
B97D	**6-31G***	-248.0970082	-5403.6333071	-5651.7562737	-5899.8924453	**-16.29**	**-40.86**
B97D	**6-31+G***	-248.1069197	-5403.8638296	-5651.9924009	-5900.1356356	**-13.59**	**-36.37**
B97D	**6-311G***	-248.1499864	-5404.7973107	-5652.9744939	-5901.1649089	**-17.07**	**-42.44**
B97D3	**SVP**	-247.9440954	-5401.0140187	-5648.9852364	-5896.9683011	**-17.02**	**-41.47**
B97D3	**def2TZVP**	-248.2096286	-5405.6420700	-5653.8659255	-5902.1056348	**-8.93**	**-27.80**
B97D3	**6-31G***	-248.1181167	-5403.8023837	-5651.9424840	-5900.0974239	**-13.79**	**-36.90**
B97D3	**6-31+G***	-248.1280282	-5404.0329062	-5652.1786112	-5900.3406142	**-11.09**	**-32.41**
B97D3	**6-311G***	-248.1710949	-5404.9663873	-5653.1607042	-5901.3698875	**-14.57**	**-38.47**
B97-1	**SVP**	-248.0317295	-5401.3914598	-5649.4537321	-5897.5068438	**-19.17**	**-32.58**
B97-1	**def2TZVP**	-248.2991793	-5406.0335369	-5654.3504409	-5902.6626377	**-11.12**	**-19.29**
B97-1	**6-31G***	-248.2095684	-5404.2325759	-5652.4672857	-5900.6955988	**-15.78**	**-27.54**
B97-1	**6-31+G***	-248.2189648	-5404.4537805	-5652.6929486	-5900.9287006	**-12.68**	**-23.21**
B97-1	**6-311G***	-248.2599643	-5405.3452003	-5653.6326550	-5901.9131734	**-17.25**	**-30.15**
M06	**SVP**	-247.9089681	-5400.5139687	-5648.4558475	-5896.3985664	**-20.65**	**-41.83**
M06	**def2TZVP**	-248.1790803	-5405.1162430	-5653.3150886	-5901.5199375	**-12.40**	**-28.57**
M06	**6-31G***	-248.0926932	-5403.4156060	-5651.5362555	-5899.6606404	**-17.54**	**-37.43**
M06	**6-31+G***	-248.1014735	-5403.6300767	-5651.7562956	-5899.8868309	**-15.53**	**-33.76**
M06	**6-311G***	-248.1393864	-5404.4115854	-5652.5811008	-5900.7553256	**-18.91**	**-40.77**
M06L	**SVP**	-248.0687614	-5402.0397616	-5650.1467109	-5898.2508189	**-23.96**	**-46.14**
M06L	**def2TZVP**	-248.3337423	-5406.6038731	-5654.9640963	-5903.3259196	**-16.62**	**-34.24**
M06L	**6-31G***	-248.2464260	-5404.9308296	-5653.2113125	-5901.4910196	**-21.37**	**-42.26**
M06L	**6-31+G***	-248.2520476	-5405.1035487	-5653.3854141	-5901.6681649	**-18.71**	**-37.98**
M06L	**6-311G***	-248.2948281	-5405.9736862	-5654.3053239	-5902.6366285	**-23.10**	**-45.99**
MN12L	**SVP**	-247.8521535	-5399.3201561	-5647.1816918	-5895.0733352	**-5.89**	**-30.67**
MN12L	**def2TZVP**	-248.1287599	-5404.1015468	-5652.2210231	-5900.3776348	**5.83**	**-11.65**
MN12L	**6-31G***	-248.0452923	-5402.3872746	-5650.4346608	-5898.5164173	**-1.31**	**-24.20**
MN12L	**6-31+G***	-248.0525888	-5402.5903480	-5650.6421335	-5898.7295185	**0.50**	**-21.33**
MN12L	**6-311G***	-248.0837359	-5403.4250803	-5651.5086005	-5899.6307526	**0.14**	**-23.97**
Experiment						**-5.3 (± 0.1)[1]**	**-11.2 (± 0.5) [1]**

Functional	Basis set	E_{abs} Pyridine (s) [Hartree]	E_{abs} Ni-TPPF$_{20}$ (s) [Hartree]	E_{abs} Ni-TPPF$_{20}$ · 1 Py (t) [Hartree]	E_{abs} Ni-TPPF$_{20}$ · 2 Py (t) [Hartree]	ΔH 1 Py [kcal/mol]	ΔH 2 Py [kcal/mol]
MN12SX	**SVP**	-247.8661294	-5399.4128008	-5647.3021828	-5895.2024524	**-14.59**	**-36.01**
MN12SX	**def2TZVP**	-248.1687256	-5404.5409211	-5652.7182271	-5900.9113245	**-5.38**	**-20.68**
MN12SX	**6-31G***	-248.0796822	-5402.7480843	-5650.8463954	-5898.9573695	**-11.69**	**-31.33**
MN12SX	**6-31+G***	-248.0884745	-5402.9530764	-5651.0560362	-5899.1731650	**-9.09**	**-27.07**
MN12SX	**6-311G***	-248.1235963	-5403.8161618	-5651.9572273	-5900.1147793	**-10.96**	**-32.27**
TPSSh	**SVP**	-248.1262254	-5402.6133303	-5650.7634505	-5898.9111366	**-14.99**	**-28.46**
TPSSh	**def2TZVP**	-248.3895921	-5407.2502970	-5655.6509960	-5904.0534318	**-6.97**	**-15.03**
TPSSh	**6-31G***	-248.3013587	-5405.4493352	-5653.7696028	-5902.0898919	**-11.87**	**-23.74**
TPSSh	**6-31+G***	-248.3100135	-5405.6662364	-5653.9910398	-5902.3180590	**-9.28**	**-19.95**
TPSSh	**6-311G***	-248.3510699	-5406.5633806	-5654.9349936	-5903.3068560	**-12.89**	**-25.94**
Experiment						**-5.3 (± 0.1)[1]**	**-11.2 (± 0.5) [1]**

Table S8. Deviation from the experimental value of the calculated enthalpies for the formation of the five coordinate complexes of Ni-TPPF$_{20}$ with pyridine in kcal*mol^{-1}.

	SVP	**def2TZVP**	**6-31G***	**6-31+G***	**6-311G***
TPSSh	9.69	1.67	6.57	3.98	7.59
MN12SX	9.29	0.08	6.39	3.79	5.66
MN12L	0.59	-11.13	-3.99	-5.80	-5.44
M06L	18.66	11.32	16.07	13.41	17.80
M06	15.35	7.10	12.24	10.23	18.90
B97-1	13.87	5.82	10.48	7.38	11.95
B97D3	11.72	3.63	8.49	5.79	9.27
B97D	14.21	6.12	10.99	8.29	11.77
B3LYP	9.90	1.66	6.92	3.13	7.79
PBE	0.61	-7.54	-3.17	-5.21	-1.94



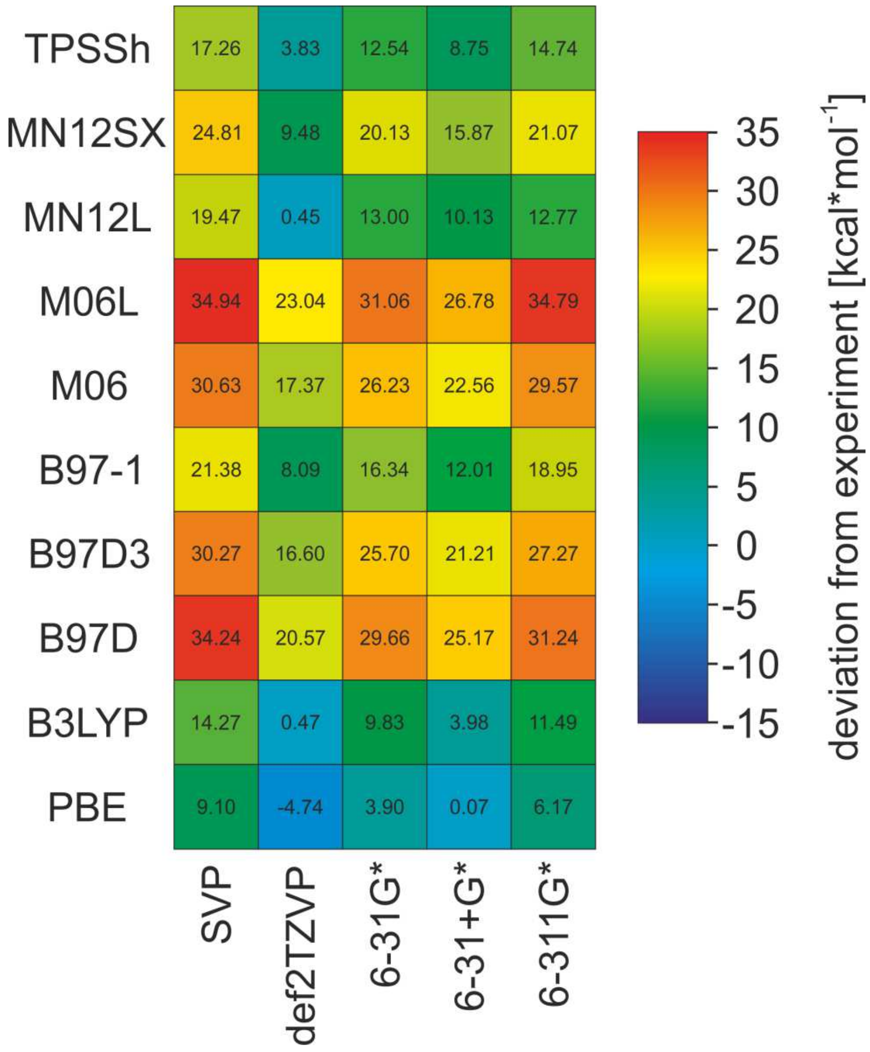
	SVP	def2TZVP	6-31G*	6-31+G*	6-311G*
TPSSh	9.69	1.67	6.57	3.98	7.59
MN12SX	9.29	0.08	6.39	3.79	5.66
MN12L	0.59	-11.13	-3.99	-5.88	-5.44
M06L	18.66	11.32	16.07	13.41	17.80
M06	15.35	7.10	12.24	10.23	18.90
B97-1	13.87	5.82	10.48	7.38	11.95
B97D3	11.72	3.63	8.49	5.79	9.27
B97D	14.21	6.12	10.99	8.29	11.77
B3LYP	9.90	1.66	6.92	3.13	7.79
PBE	0.61	-7.54	-3.17	-5.21	-1.94

Figure S8. Colour coded representation of the deviation of theoretically calculated and experimentally determined values for the formation of the five coordinate complex of Ni-TPPF$_{20}$ with one pyridine molecule at different levels of theory. The exact values are given in kcal*mol^{-1}.

The smallest deviation from the experimental value is obtained at the MN12SX/def2TZVP (overestimated by 0.08 kcal*mol^{-1}), the B3LYP/def2TZVP (overestimated by 1.66 kcal*mol^{-1}) and at the TPPSh/def2TZVP (overestimated by 1.67 kcal*mol^{-1}) level of density functional theory. It should be noted that the values calculated at the MN12L/SVP (overestimated by 0.59 kcal*mol^{-1}) and the PBE/SVP (overestimated by 0.61 kcal*mol^{-1}) level of theory are also in very good agreement with the experimentally derived value, however fail largely in case of the six coordinated complex. Therefore both are not a reliable method to calculate complex formation enthalpies of Ni(II) porphyrins in general.

Table S9. Deviation from the experimental value of the calculated enthalpies for the formation of the six coordinate complexes of Ni-TPPF$_{20}$ with pyridine in kcal*mol^{-1}.

	SVP	**def2TZVP**	**6-31G***	**6-31+G***	**6-311G***
TPSSh	17.26	3.83	12.54	8.75	14.74
MN12SX	24.81	9.48	20.13	15.87	21.07
MN12L	19.47	0.45	13.00	10.13	12.77
M06L	34.94	23.04	31.06	26.78	34.79
M06	30.63	17.37	26.23	22.56	29.57
B97-1	21.38	8.09	16.34	12.01	18.95
B97D3	30.27	16.60	25.70	21.21	27.27
B97D	34.24	20.57	29.66	25.17	31.24
B3LYP	14.27	0.47	9.83	3.98	11.49
PBE	9.17	-4.74	3.90	0.07	6.17



	SVP	def2TZVP	6-31G*	6-31+G*	6-311G*
TPSSh	17.26	3.83	12.54	8.75	14.74
MN12SX	24.81	9.48	20.13	15.87	21.07
MN12L	19.47	0.45	13.00	10.13	12.77
M06L	34.94	23.04	31.06	26.78	34.79
M06	30.63	17.37	26.23	22.56	29.57
B97-1	21.38	8.09	16.34	12.01	18.95
B97D3	30.27	16.60	25.70	21.21	27.27
B97D	34.24	20.57	29.66	25.17	31.24
B3LYP	14.27	0.47	9.83	3.98	11.49
PBE	9.10	-4.74	3.90	0.07	6.17

Figure S9. Colour coded representation of the deviation of theoretically calculated and experimentally determined values for the formation of the six coordinate complex of Ni-TPPF$_{20}$ with two pyridine molecules at different levels of theory. The exact values are given in kcal*mol^{-1}.

The smallest deviation from the experimental value is observed at the PBE/6-31+G* (overestimated by 0.07 kcal*mol^{-1}), MN12L/def2TZVP (overestimated by 0.45 kcal*mol^{-1}) and at the B3LYP/def2TZVP (overestimated by 0.45 kcal*mol^{-1}) level of density functional theory. However, PBE/6-31+G* as well as the MN12L/def2TZVP level of theory fail largely in the prediction of the complex formation enthalpies of the five coordinated complex and therefore cannot be applied as a general method to calculate complex formations enthalpies of Ni(II) porphyrins.

In summary B3LYP/def2TZVP//PBE/DZP obviously is the level of choice since the complex formation energy of the 5- and 6-coordinate complexes are both in good agreement with experiment.

IV.2 Record player design

Density functional theory calculations (B3LYP/6-31G*) were performed on 36 different structures that looked promising based on geometry and synthesizability. The structures are presented in figure S10. For obvious reasons the structures were coined “record players” because the porphyrin resembles a disk, the azopyridine works like a tone arm by placing the pyridine nitrogen lone pair (needle) onto the nickel ion.

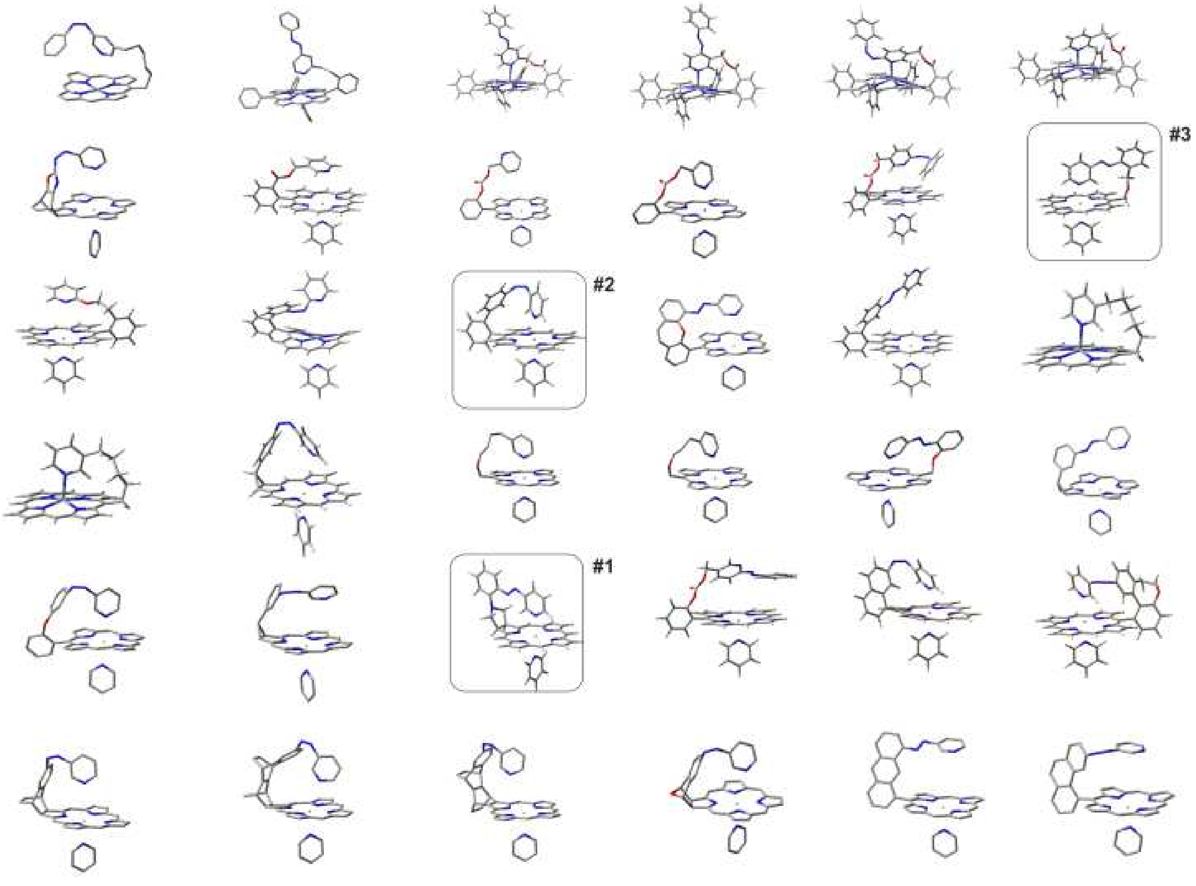


Figure S10. Potential candidates for a light-driven coordination-induced spin state switch (LD-CISSS). The structures were optimized at the B3LYP/6-31G* level of density functional theory and ranked according to an optimal N-Ni distance and a minimal deviation from orthogonal binding of the pyridine unit to the porphyrin plane. The three most promising candidates are highlighted.

IV.3 Energy difference of *cis*$_{\text{para}}$ and *cis*$_{\text{dia}}$

The energies of the coordinated and uncoordinated record players **1** and **2** were calculated at the B3LYP/def2TZVP//PBE/SVP level of theory. The calculated values for ΔH (*cis*-**1**: -0.25 and *cis*-**2**: -3.26 kcal mol^{-1} see Figure S11) are in good agreement with the experimental data. (*cis*-**1**: -1.19 and *cis*-**2**: -3.95 kcal mol^{-1} see Figure S2 and S3).

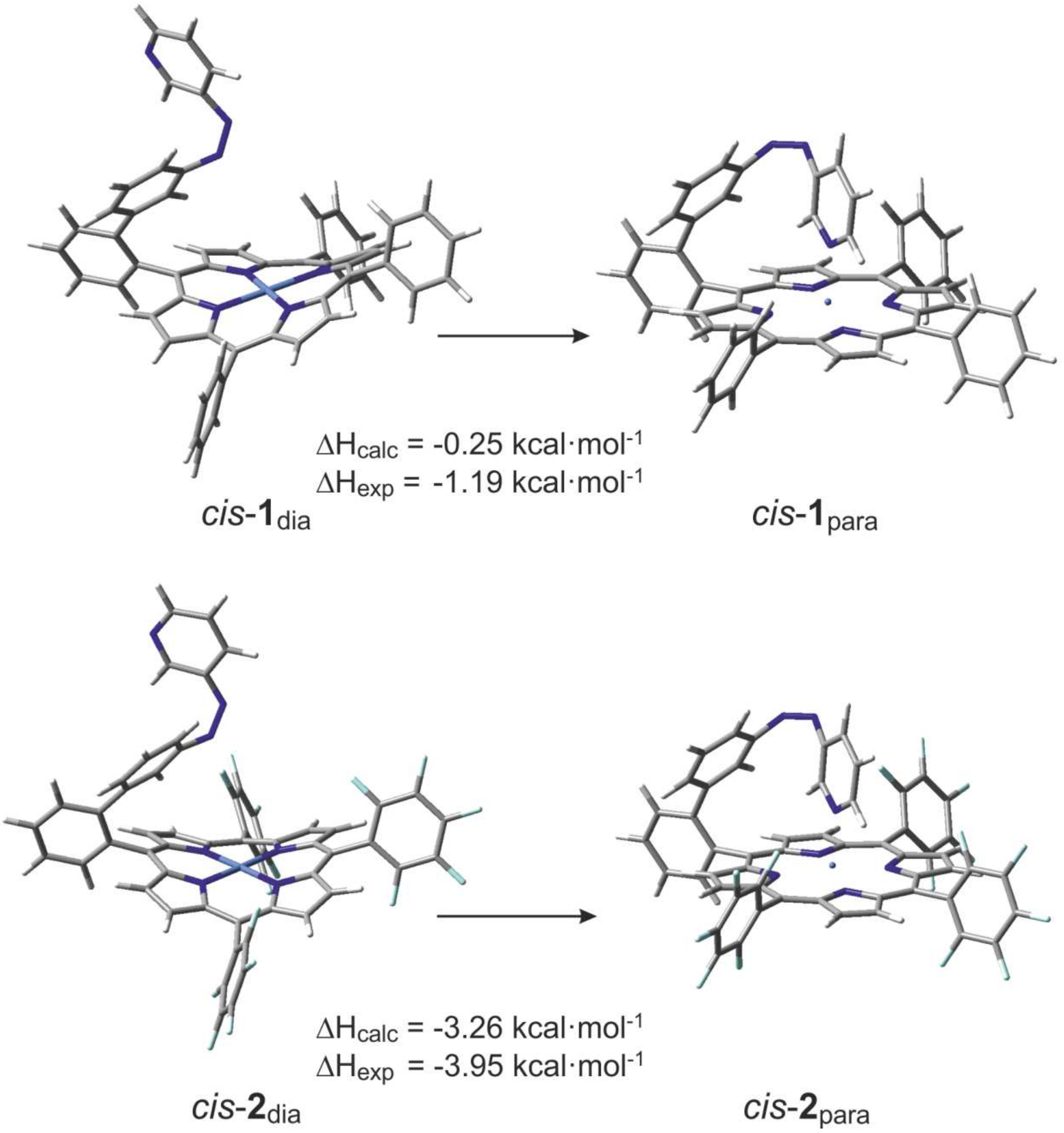


Figure S11. Calculated enthalpies (B3LYP/def2TZVP//PBE/SVP) of the intramolecular coordination of the magnetic conformers of *cis*-**1** and *cis*-**2**.

V. Ni-TPPF$_{20}$ maximum shift and titration with piperidine

The maximum chemical shift of octahedral, paramagnetic Ni-TPPF$_{20}$ pyrrole protons was observed with pyridine (green), *N*-methylimidazole (yellow) and piperdine (blue) as axial ligands (Figure S12). The Ligands were add to a 2 mM solution of Ni-TPPF$_{20}$ in acetone. Addition was discontinued as no further shift was observed. The spin density distribution in the porphyrin plane seems to be similar for all octahedral complexes independent of the nature of the axial ligand.

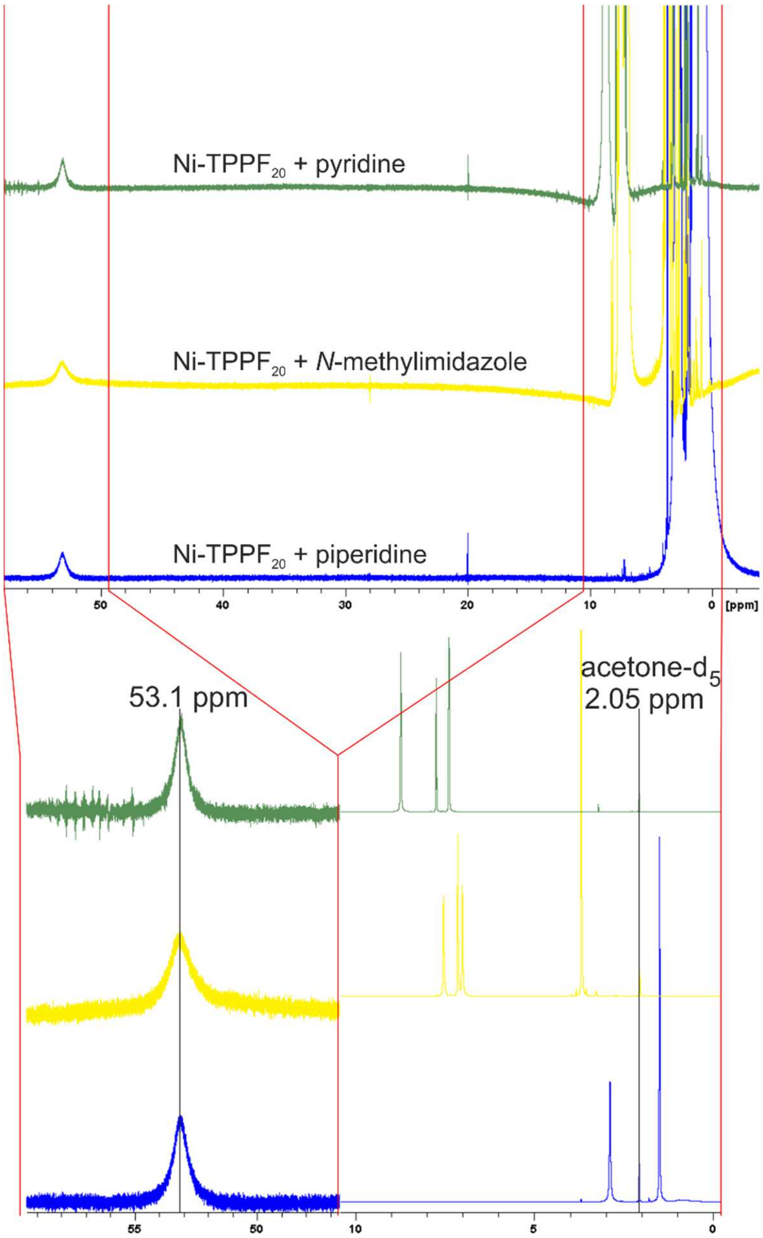


Figure S12. ^{1}H NMR spectra (acetone-d$_6$, 300 K) of Ni-TPPF$_{20}$ with an excess of pyridine-d$_5$ (green), methylimidazole (yellow) and piperidine (blue). All three axial ligands gives rise to the same chemical shift of the pyrrole protons signal at 53.1 ppm with respect to the acetone-d$_5$ signal at 2.05 ppm.

To figure out the maximum chemical shift (δ_{max}) of the square pyramidal complex, Ni-TPPF$_{20}$ was titrated with piperidine. The advantage over pyridine is the much higher association constant of the first ligand (K_1). The square pyramidal complex is formed with much less equivalents and can therefore be observed more accurate. The shift of the pyrrole protons in ^{1}H NMR was observed indicating the amount of paramagnetic nickel(II). The titration (Figure S13) was evaluated using nonlinear fitting. The following binding model was assumed:

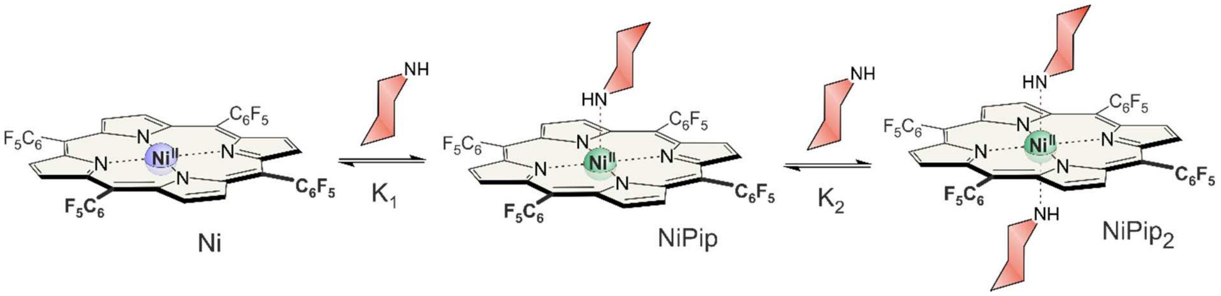


Figure S13. Binding model for the association of piperdine to Ni-TPPF$_{20}$.

$$K_1 = \frac{[NiPip]}{[Ni][Pip]} \qquad \text{(eq S7)}$$

$$K_2 = \frac{[NiPip_2]}{[NiPip][Pip]} \qquad \text{(eq S8)}$$

Table S10. Experimental ([Ni-TPPF$_{20}$], [Pip] and δ measured) and calculated values (δ calculated, [Ni], [NiPip] and [NiPip$_2$]) for the complex concentrations of Ni, NiPip and NiPip$_2$ in the titration series of Ni-TPPF$_{20}$ with piperidine.

[Ni-TPPF$_{20}$] mol L^{-1}	[Pip] mol L^{-1}	δ measured ppm	δ calculated ppm	[Ni] mol L^{-1}	[NiPip] mol L^{-1}	[NiPip$_2$] mol L^{-1}
9.230E-03	0.000E+00	8.58	8.58	9.230E-03	0.000E+00	0.000E+00
9.116E-03	6.691E-04	11.58	11.44	8.539E-03	5.769E-04	8.894E-08
9.005E-03	1.322E-03	14.30	14.23	7.878E-03	1.126E-03	3.675E-07
8.487E-03	4.361E-03	26.80	26.83	5.055E-03	3.427E-03	5.300E-06
8.297E-03	5.481E-03	31.28	31.03	4.170E-03	4.117E-03	9.276E-06
7.940E-03	7.576E-03	37.40	37.62	2.832E-03	5.087E-03	2.085E-05
7.612E-03	9.499E-03	41.89	41.95	1.985E-03	5.591E-03	3.592E-05
7.311E-03	1.127E-02	44.75	44.66	1.468E-03	5.791E-03	5.213E-05
7.239E-03	1.102E-01	53.16	53.19	8.167E-05	6.113E-03	1.044E-03
7.169E-03	2.072E-01	53.45	53.45	3.679E-05	5.354E-03	1.778E-03
7.100E-03	3.023E-01	53.55	53.54	2.209E-05	4.749E-03	2.329E-03
6.966E-03	4.871E-01	53.59	53.59	1.104E-05	3.866E-03	3.089E-03
6.837E-03	6.652E-01	53.60	53.61	6.778E-06	3.258E-03	3.573E-03
6.593E-03	1.002E+00	53.61	53.61	3.403E-06	2.477E-03	4.113E-03
6.153E-03	1.609E+00	53.62	53.61	1.427E-06	1.673E-03	4.479E-03

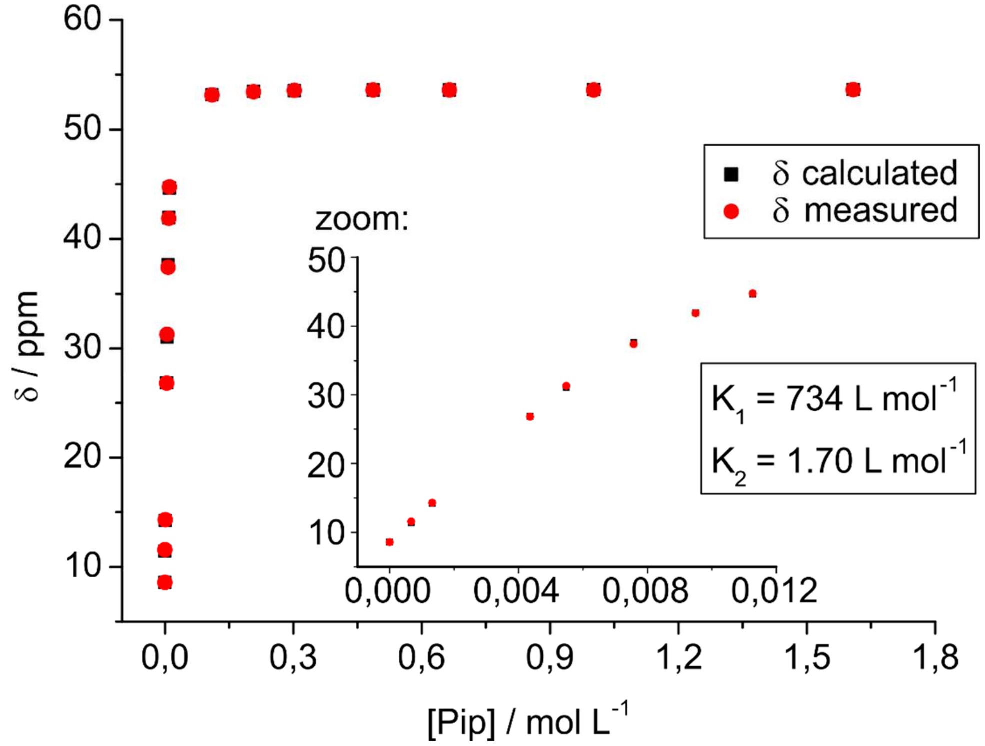


Figure S14. Measured (500 MHz, 298 K) and calculated values for the chemical shifts of the titration series.

The values of the maximum shifts are δ_{max}(NiPip) = 53.7 ppm and δ_{max}(NiPip$_2$) = 53.6 ppm. This small difference is within the accuracy of the method and can be neglected. Note that the chemical shifts in the titration series were observed at 298 K which gives rise to a slightly higher paramagnetic shifts than the experiments performed at 300 K.

Lit:

1. S. Thies, C. Bornholdt, F. Köhler, F.D. Sönnichsen, C. Näther, F. Tuczek and R. Herges, *Chem. Eur. J.* **2010** , *16*, 10074–10083.