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1. Experimental Procedures

1.1. General details

All manipulations were performed under an atmosphere of purified argon using standard high-vacuum Schlenk-line technique. Argon was supplied by Air Liquide Europe. All the glassware were flame-dried under vacuum, cooled under vacuum and purged with Argon before use. Solvents were freshly collected from *Pure Solve MD7* solvent purification system under Argon. NMR spectra were recorded on a Jeol Eclipse+ 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{31}P, 162 MHz) spectrometer, at 298 K unless otherwise noted. Chemical shift values are quoted in δ (ppm) and coupling constants in *J* (Hz). ^{1}H chemical shift values were reported relative to tetramethylsilane (TMS) and were referenced to the residual proton resonances of the corresponding deuterated solvent signal. ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances of the deuterated solvents. ^{31}P NMR spectra are referenced externally to H_3PO_4 (85%, aq.). The following abbreviations (or combinations thereof) were used to describe multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet, brs, broad singlet. High-resolution mass spectra (HR-MS) were recorded on a Thermo Scientific Orbitrap LTQ XL spectrometer. Elemental analyses were performed on a Vario MICRO CUBE (elementar).

Electrochemistry. Cyclic voltammograms (CV) were obtained at room temperature (~24 °C) using an AUTOLAB PGSTAT 100 potentiostat. All electrochemical experiments were performed under an argon atmosphere. 1 mM solution of **2** was prepared in a 5:1 dry acetonitrile/DCM mixture. 100 mM $^{n}Bu_4NPF_6$ ($TBAPF_6$) as a supporting electrolyte was added to the solution. The resulting solution was purged for 15 minutes with argon (with stirring) to remove dissolved oxygen. The electrochemical setup consists of a freshly polished 3 mm glassy carbon (GC) working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ as a reference electrode. The potential of the reference electrode was calibrated with an Fc/Fc^+ redox couple before and after the electrochemical experiment. Here, all potentials were reported against the Fc/Fc^+ redox couple.

Spectroelectrochemistry: All the spectroelectrochemical experiments were performed in an argon-filled glovebox (MBraun) using a commercially available UV-spectroelectrochemical setup (ALS Japan). Here, a platinum mesh and a platinum wire were used as working and counter electrodes, respectively. An Ag-wire was used as a reference electrode (calibration was done by the $Fc^{+/0}$ redox couple before and after the experiment). Time-resolved spectra (0.5 s time interval) were collected using an Agilent 8453 UV-Vis spectrometer. Constant potential

electrolysis (CPE) experiments were performed using AUTOLAB potentiostat, PGSTAT302N, (Nova 2.1.4 software). The sample was dissolved in a 5:1 acetonitrile/DCM mixture. The sample concentration in the cuvette was 170 μM. 100 equivalent $^{n}Bu_4PF_6$ was used as the supporting electrolyte. Before CPE, the sample was allowed to pre-equilibrate at -0.39 V (*vs.* Fc/Fc^+) for 10 s. Controlled potential electrolysis experiments were done at 0.06 V (*vs.* Fc/Fc^+) for 600 s.

1.2. Computational details

All structures are optimized at the unrestricted B3LYP-D3/G-311G**/LANLDZ level of theory and identified as true minima by inspection of their vibrational frequencies. This functional and basis set combination is known to reproduce geometries of main group species very well. UV/vis spectra of the neutral different cationic species are calculated based on these optimized structures using a TD-DFT approach (B3LYP-D3/G-311G**/LANLDZ) using a continuum solvation model (IEFPCM) for acetonitrile. Selected species are examined with single point calculations using an active space. All these calculations are carried out using the Gaussian 09 suit of programs (G09, revision D.01).[1]

1.3. X-ray crystallographic details

Single crystals were mounted on a fiber loop and fixated using Fomblin oil. The data were collected on a Bruker D8 APEX-II equipped with an APEX-II CCD camera and a Rigaku SynergyS using MoKα radiation (λ = 0.71073 Å) and CuKα radiation (λ = 1.5406 Å), respectively. Data reduction was performed with SAINT,[2] absorption corrections for the area detector were performed using SADABS. Structures were solved by direct methods and refined by least squares methods on F^2 using the SHELX and the OLEX2 software suites, respectively.[3] All the non-hydrogen atoms were refined using an anisotropic model and all the hydrogen atoms were constrained in geometrical positions to their parent atom. Crystallographic data are presented in Table S2. Deposition Numbers 2412505 (**2**$_{cis}$) and 2412506 (**2**$_{trans}$) contain(s) the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax:+441223336033.

1.4. Reagent information

^{t}BuLi (1.7 M in hexane), benzoylferrocene, trimethylsilyl chloride, and 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) were purchased from Sigma-Aldrich and used as received. For column chromatography, silica gel (40-63 μm) from VWR was used. Column chromatography was carried out using pentane as eluent, based on Merck aluminium TLC sheets (silica gel 60F254). All solvents were purchased from VWR. Starting material **1** was synthesised following literature procedure.[4]

2. Synthetic Procedure

A THF solution (20 mL) of compound **1** (0.50 g, 0.94 mmol) was treated with 1.7 M ^{t}BuLi (1.16 ml, 1.97 mmol) at -78 °C in a Schlenk flask and the reaction mixture was stirred for 1h. To it, benzoylferrocene (0.27 g, 0.94 mmol) was added at -78 °C and allowed to stir at room temperature for 14h. The reaction mixture was treated with DBN (0.23 mL, 1.87 mmol) and TMSCl (0.24 mL, 1.87 mmol), respectively and the reaction mixture was stirred at r.t. for additional 12h. The solvent was removed in vacuo to get a red solid which was purified by column chromatography using pentane as eluent to obtain the desired compound **2** as 1:1 mixture of *cis* and *trans* isomers.

Red solid; Yield 0.59 g (87%); ^{1}H NMR (400 MHz, methylene chloride-d_2) δ 7.92 (td, J = 7.4, 3.4 Hz, 2H), 7.51 (s, 3H), 7.41 (d, J = 12.2 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.12 (m, 3H), 7.12 – 7.03 (m, 3H), 7.00 – 6.95 (m, 2H), 6.86 – 6.74 (m, 2H), 6.72 – 6.62 (m, 2H), 6.53 (tt, J = 8.0, 1.2 Hz, 1H), 6.50 – 6.45 (m, 1H), 6.45 – 6.37 (m, 2H), 5.93 (d, J = 8.0 Hz, 1H), 5.82 (d, J = 7.8 Hz, 1H), 4.40 (s, 1H), 4.28 (s, 3H), 3.98 (d, J = 15.7 Hz, 2H), 3.76 – 3.70 (m, 1H), 3.68 (d, J = 0.9 Hz, 5H), 3.62 (d, J = 0.7 Hz, 5H), 3.56 (s, 1H), 1.71 (s, 18H), 1.48 – 1.40 (m, 18H), 1.39 (d, J = 0.9 Hz, 9H), 1.37 (d, J = 0.9 Hz, 9H) (*Note*: Due to the overlapping chemical shifts of the two isomers in the aromatic region no clear assignment of the NMR resonances was possible); ^{13}C NMR (101 MHz, methylene chloride-d_2) δ 172.4 (d, J = 38.0 Hz), 171.9 (d, J = 38.5 Hz), 154.7 (d, J = 65.1 Hz), 151.2, 143.4 (d, J = 126.0 Hz), 141.5 (dd, J = 56.7, 27.1 Hz), 138.8 (d, J = 18.1 Hz), 138.1 (d, J = 19.0 Hz), 136.7 (d, J = 18.3 Hz), 135.8 (d, J = 21.7 Hz), 135.2 (d, J = 22.2 Hz), 134.1, 133.9, 133.6, 133.2 (d, J = 28.4 Hz), 133.1, 130.7, 129.7, 129.0, 128.2, 127.9, 127.8, 126.6, 126.4, 125.7 (d, J = 25.5 Hz), 125.4, 125.3, 125.2, 124.7 (d, J = 12.5 Hz), 123.3 (d, J = 40.9 Hz), 121.4, 88.3 (d, J = 87.2 Hz), 70.6 (d, J = 44.3 Hz), 69.0 (d, J = 5.3 Hz), 67.3, 38.3, 35.1, 33.2 (d, J = 22.2 Hz), 32.7, 31.2, 29.7; ^{31}P NMR (162 MHz) δ 233.5 and 233.3 ppm; HR-MS (APCI, Toluene) *m/z*: calcd for $[M]^{+}$ ($C_{49}H_{51}PFe$) 726.30733; found: 726.30752; Anal. calc. for $C_{49}H_{51}FeP$: C, 80.98; H, 7.07; found C, 81.08; H, 7.39.

3. Spectral data

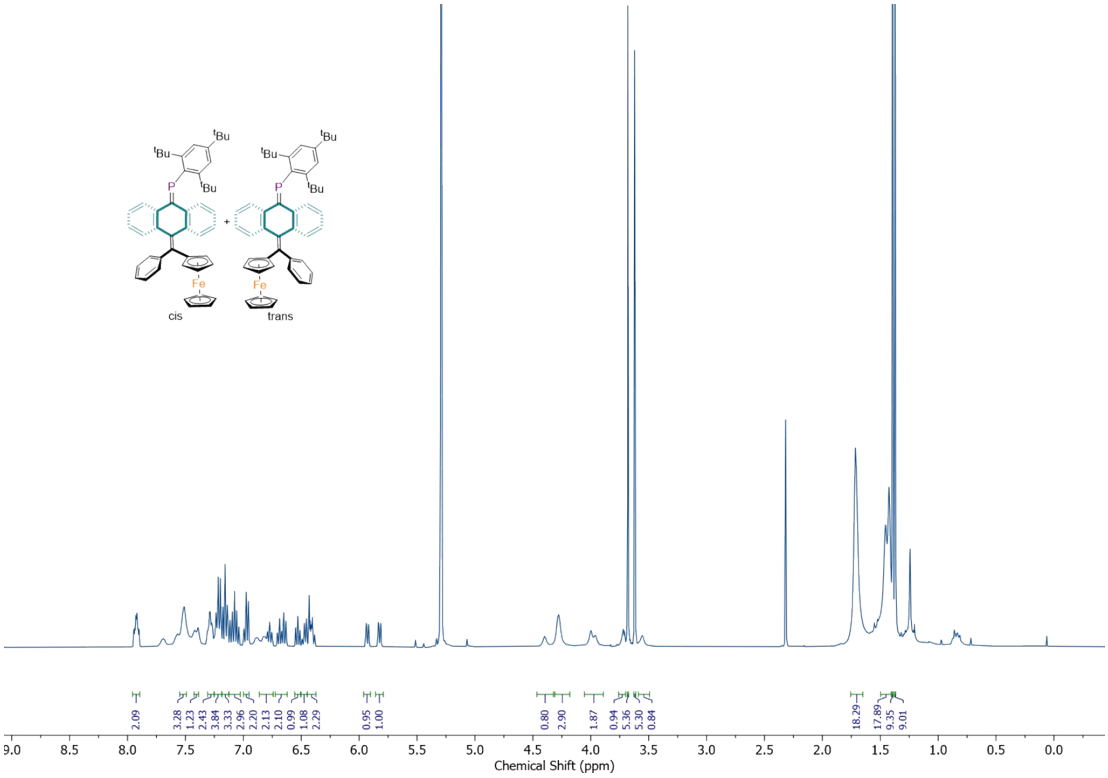

Figure S1. ^{1}H NMR spectrum of *cis*-/*trans*-**2** in methylene chloride-d_2.

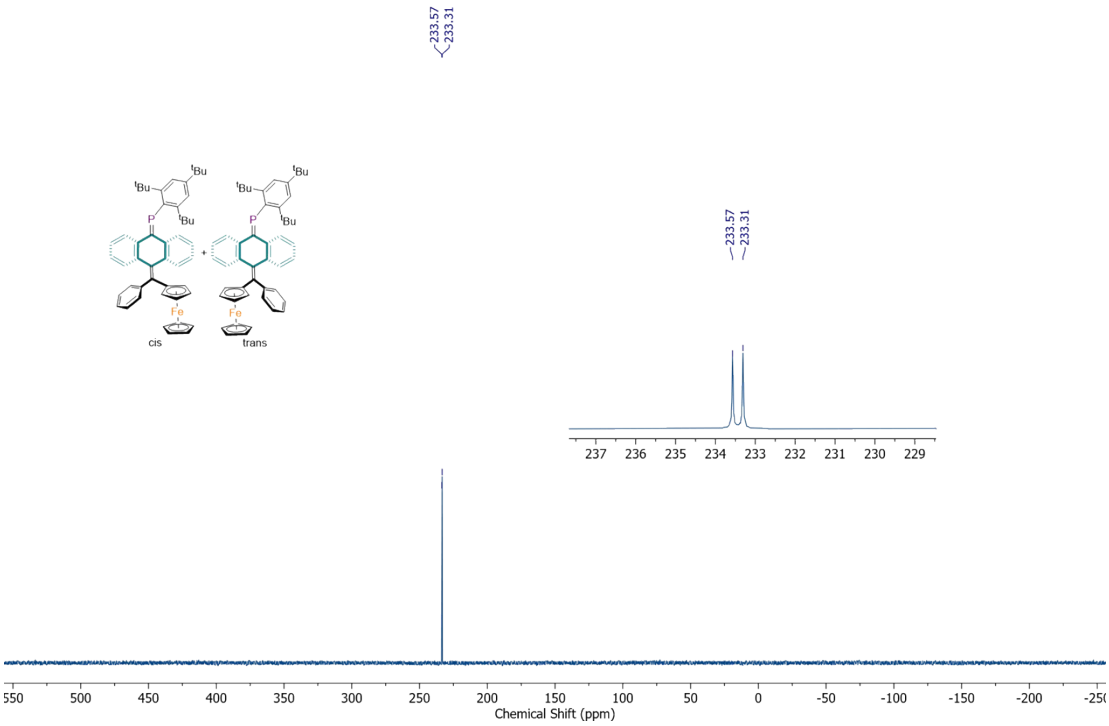

Figure S2. ^{31}P NMR spectrum of *cis*-/*trans*-**2**.

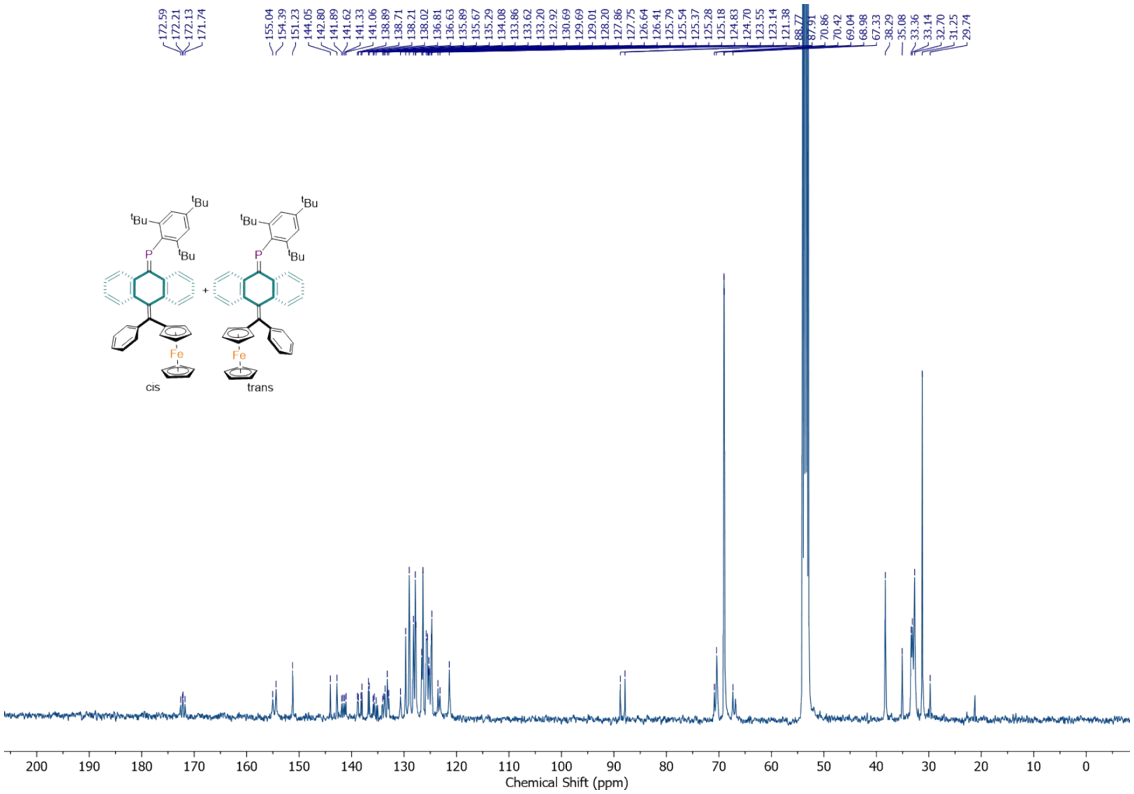

Figure S3. ^{13}C NMR spectrum of *cis*-/*trans*-**2**.

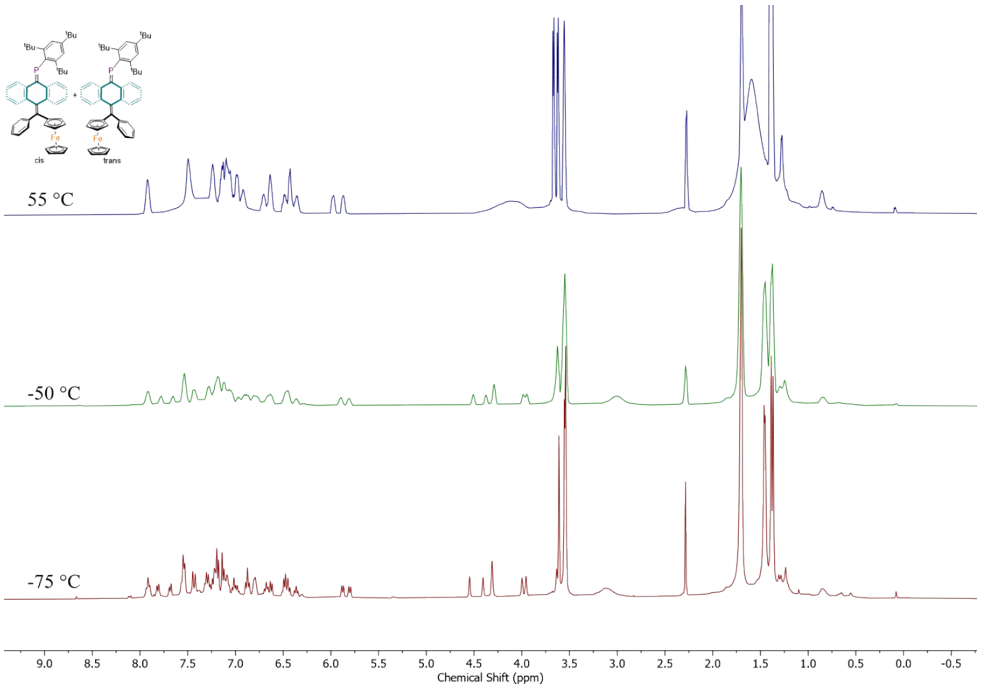

Figure S4. Variable Temperature (VT)-^{1}H NMR spectrum of *cis*-/*trans*-**2** in tetrahydrofuran-d_8.

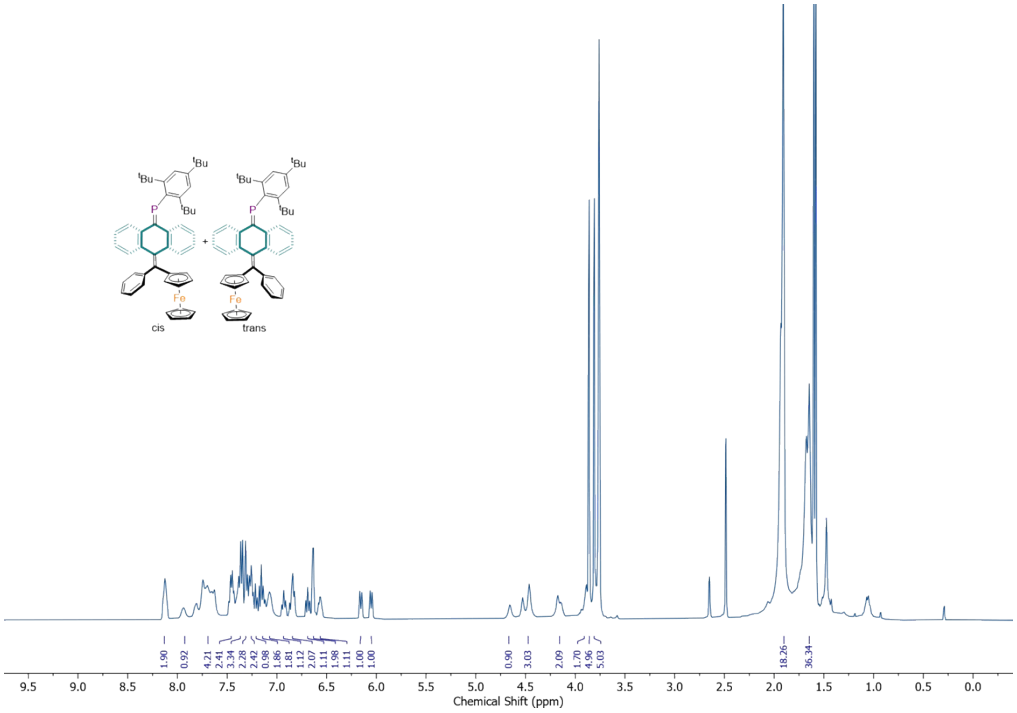

Figure S5. ^{1}H NMR spectrum of *cis*-/*trans*-**2** in tetrahydrofuran-d_8.

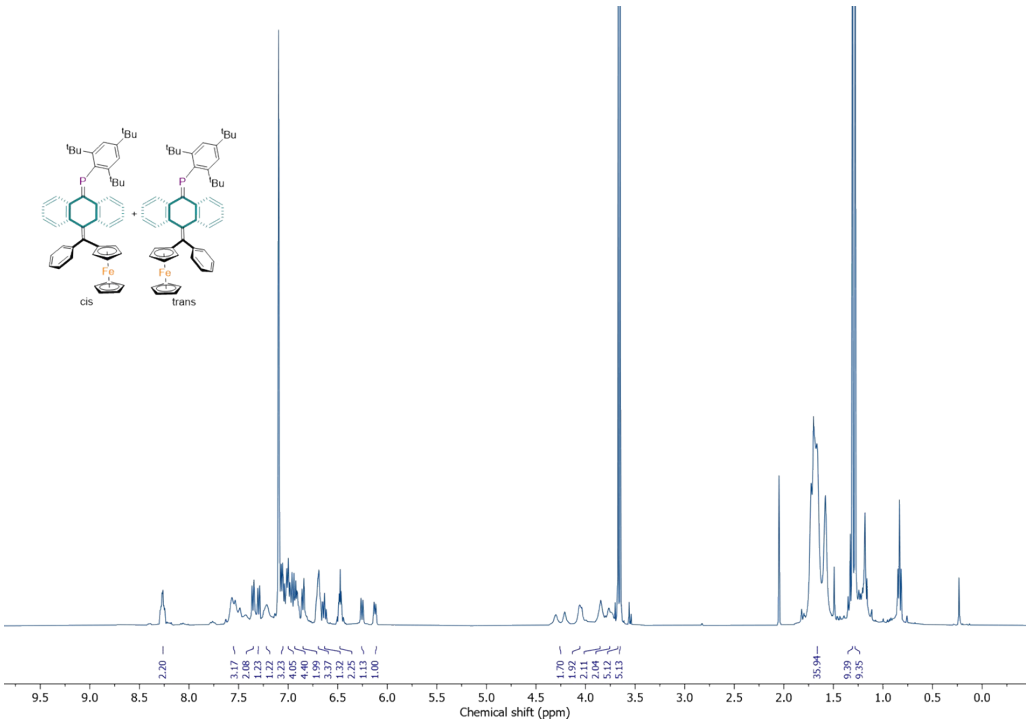

Figure S6. ^{1}H NMR spectrum of *cis*-/*trans*-**2** in benzene-d_6.

4. Solid-state structure of 2_{trans}

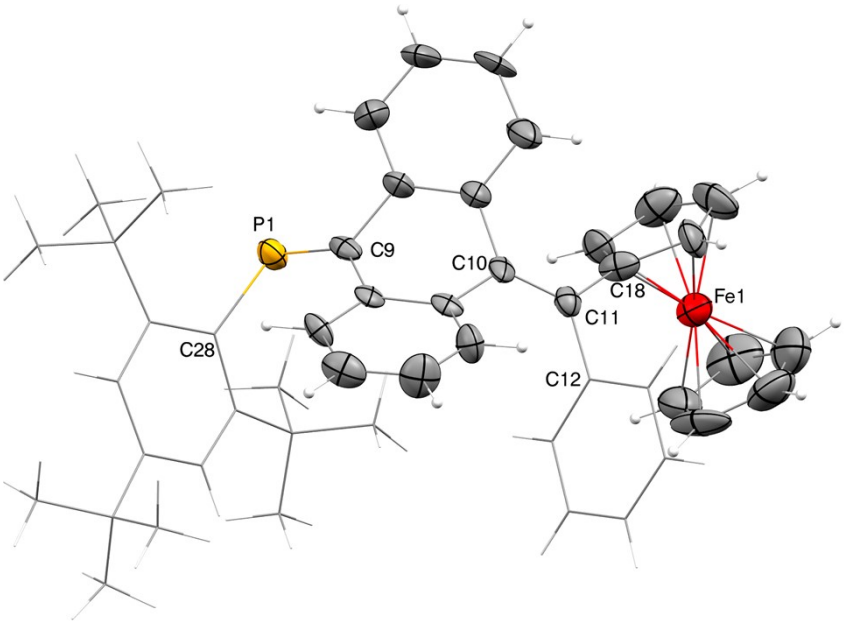

Figure S7: Solid-state structure of $\mathbf{2}_{trans}$. Thermal displacement ellipsoids are set at 50%-probability levels, and Mes* and Ph units are shown as capped-stick for clarity.

5. Table S1: Selected bond lengths (Å), and angles (°) in the solid-state structure of $\mathbf{2}_{cis}$ and $\mathbf{2}_{trans}$.

	$\mathbf{2}_{cis}$	$\mathbf{2}_{trans}$
P1=C9	1.701(2)	1.687(9)
C10-C11	1.352(3)	1.370(20)
P1-C28	1.846(2)	1.847(9)
C11-C12	1.501(3)	1.520(10)
C11-C18	1.488(3)	1.480(20
C9-P1-C28	106.6(1)	106.8(4)

6. Table S2: Refinement details for the X-ray structures of $\mathbf{2}_{cis}$ and $\mathbf{2}_{trans}$

Compound	$\mathbf{2}_{cis}$	$\mathbf{2}_{trans}$
CCDC	2412505	2412506
Empirical formula	$C_{49}H_{51}FeP$, C_6H_6	$C_{49}H_{51}FeP$
Formula weight	804.82	726.71
Temperature/K	150.00(10)	180.15
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\text{-}1$
a (Å)	9.43921(10)	10.741(1)
b (Å)	15.8638(2)	11.706 (4)
c (Å)	28.9421(4)	17.303 (6)
α (°)	90	104.924(7)
β (°)	91.3570(10)	100.810(6)
γ (°)	90	97.855(7)
V (Å^3)	4332.63(9)	2025.3(12)
Z	4	2
ρ_{calcd} (g/cm^3)	1.234	1.192
Range of 2θ	6.11 to 159.194	3.672 to 50.054
Absorption coefficient (mm^{-1})	3.403	0.444
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0 0.0547, wR_2 = 0.1517	R_1 = 0.1588, wR_2 = 0.2154
Final R indexes [*all data*]	R_1 = 0.0580, wR_2 = 0.1543	R_1 = 0.3005, wR_2 = 0.2608
Data / restraints / parameters	9064/0/524	6590/24/469
Goodness-of-fit on F^2	1.045	1.142
Independent reflections	9064 [R_{int}= 0.0278, R_{sigma}= 0.0237]	6590 [R_{int}=0.1965, R_{sigma}=0.3073]
Radiation	CuKα (λ= 1.54184)	MoKα (λ=0.71073)
Reflection collected	35457	19945

7. Packing diagrams

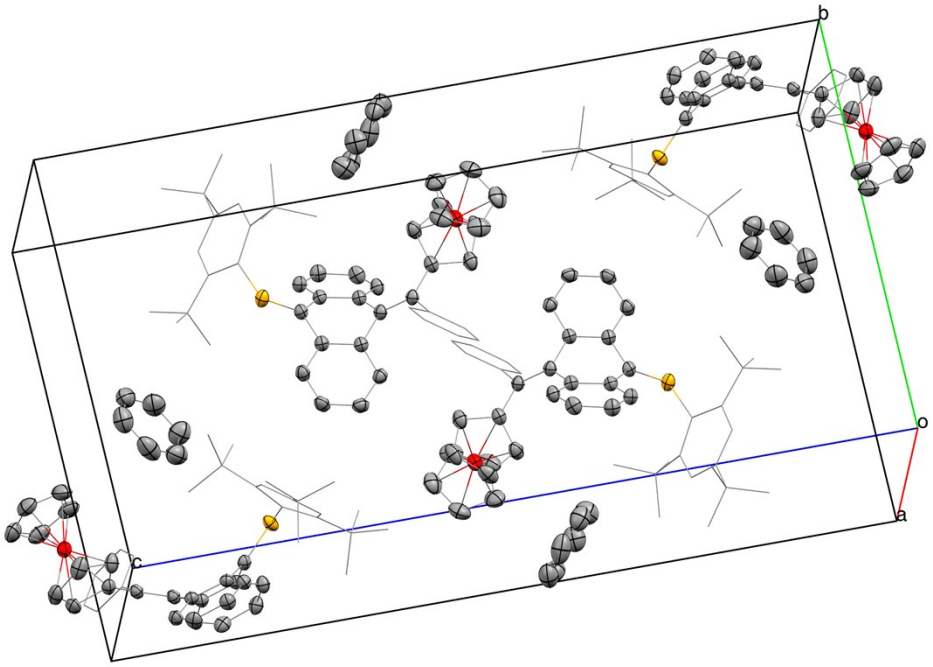

Figure S8. Packing diagram of $\mathbf{2}_{cis}$.

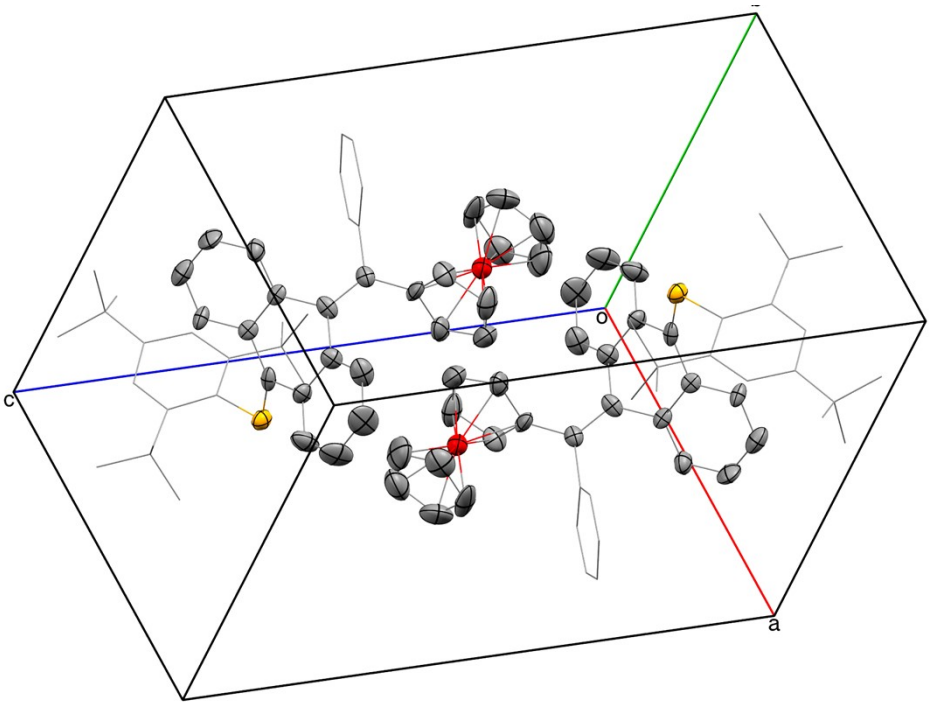

Figure S9. Packing diagram for of $\mathbf{2}_{trans}$.

8. Electrochemistry

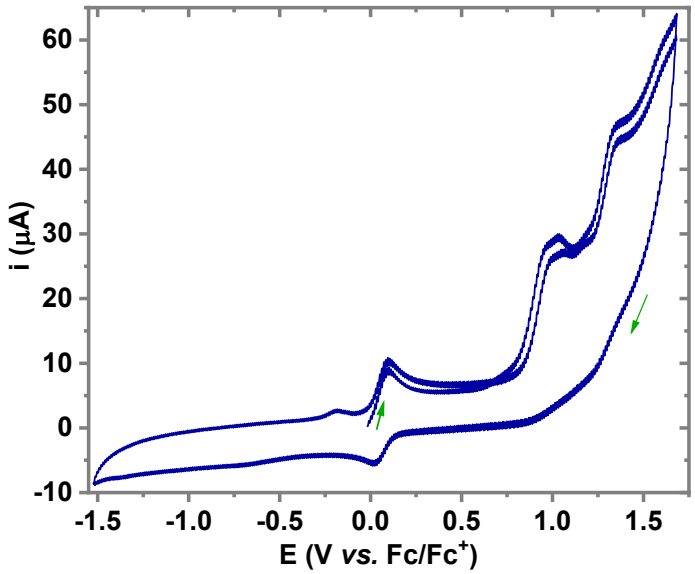

Figure S10. Cyclic voltammograms of *cis*-/*trans*-**2** (1 mM) in 5:1 acetonitrile-DCM mixture at a scan rate of 100 mV/s. The working electrode is glassy carbon, the counter electrode is platinum, and the reference electrode is non-aqueous $Ag/AgNO_3$ (calibrated with Fc/Fc^+ redox couple). 100 mM $^nBu_4NPF_6$ was used as the supporting electrolyte.

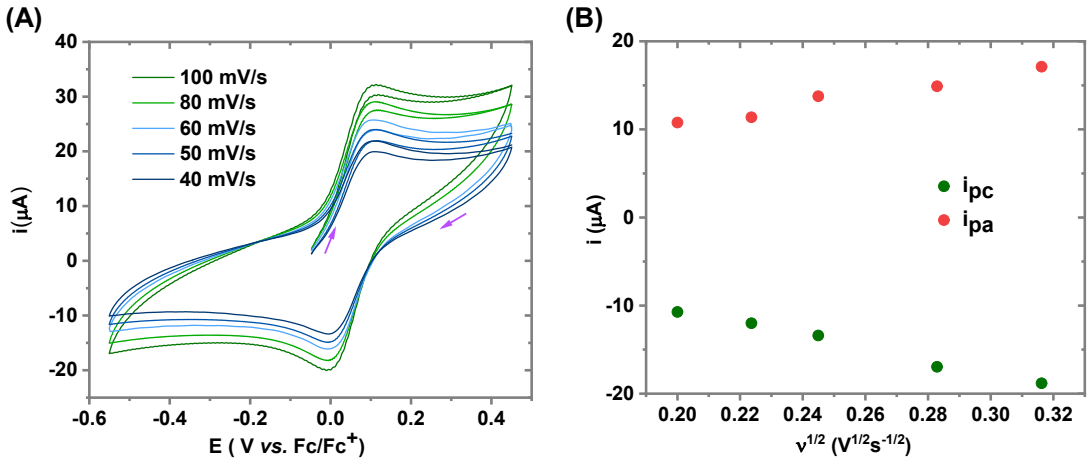

Figure S11. (**A**) Scan rate-dependent cyclic voltammograms of *cis*-/*trans*-**2** in the region showing Fc/Fc^+ electrochemical response; (**B**) The Randles-Sevcik plot showing diffusion-limited electrochemical behavior. The working electrode is glassy carbon, the counter electrode is platinum, and the reference electrode is non-aqueous $Ag/AgNO_3$ (calibrated with Fc/Fc^+ redox couple). 100 mM $^nBu_4NPF_6$ was used as the supporting electrolyte.

9. Spectroelectrochemistry

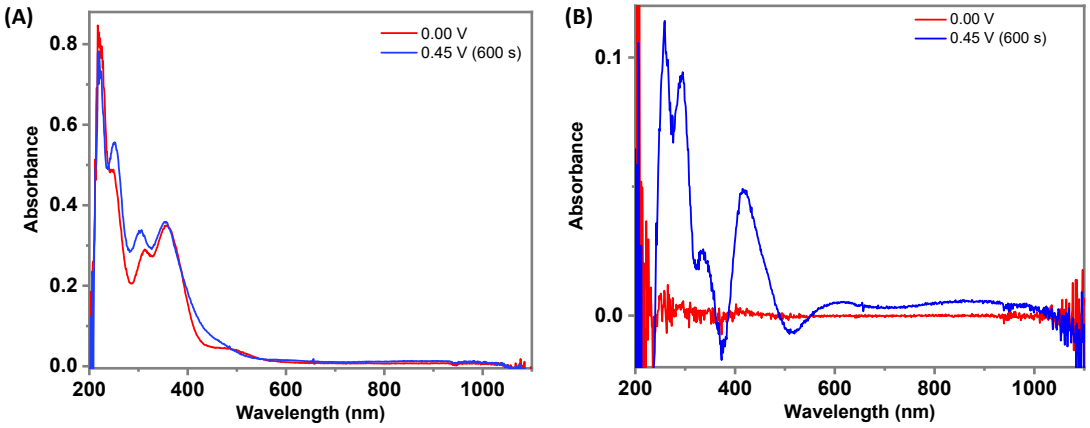

Figure S12: Electronic absorption spectra of *cis*-/*trans*-**2** before (red) and after oxidation (blue) at 0.45 V (*vs*. Fc/Fc^{+}) for 600 s. (**A**) absolute spectra, (**B**) difference spectra. All potentials reported here are against Fc/Fc^{+} redox couple.

10. Frontier Molecular orbitals and TD DFT calculations

Neutral (cis isomer)

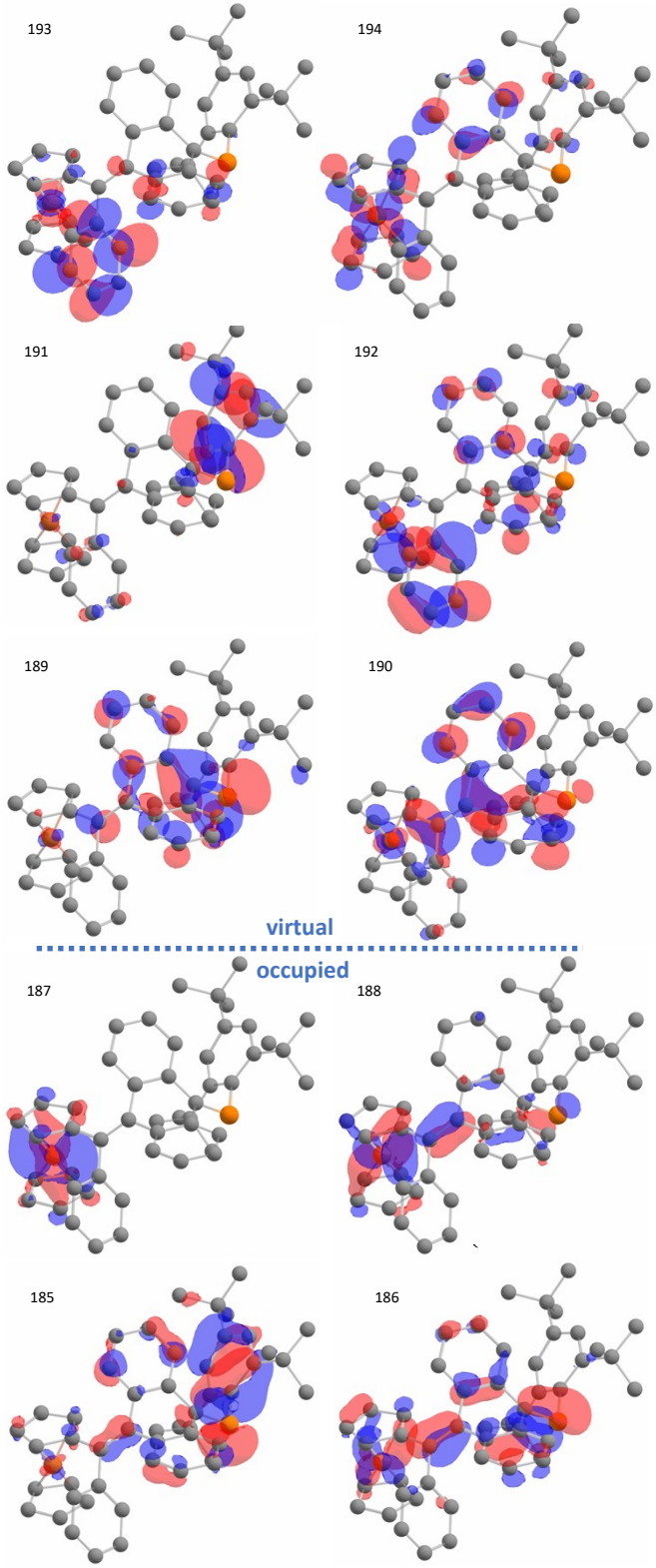

Figure S13: Selected molecular orbitals of *Z*-**2**, at the B3LYP-D3/6-311G**/LANLDZ(MeCN) level of theory

Selected transitions:

584 nm f= 0.1
187→194 (0.34964); 188→196 (0.28718); 187A→196A (-0.21048); 187→189 (0.18677); 187→190 (-0.1863); 188→194 (0.17729); 186→196 (0.15305); 188→193 (-0.14828); 187→192 (-0.13871); 187→193 (0.12337)

584 nm f= 0.0044
187→196 (0.32006); 188→194 (-0.31); 187→194 (0.20019); 188→196 (0.18336); 188→189 (-0.17706); 186→194 (-0.17048); 187→193 (-0.16573); 188→190 (0.15975); 188→192 (0.12427); 188→193 (-0.10735); 186→196 (0.10202)

483 nm f= 0.0108
187→194 (0.29561); 182→196 (-0.22263); 187→196 (0.21709); 182→194 (0.20939); 188→189 (0.20667); 188→196 (-0.165); 182→190 (-0.12884); 182→193 (0.12298); 187→198 (0.1109); 183→196 (-0.10865); 187→193 (-0.10741); 182→192 (-0.10607); 188→190 (-0.10199); 183→194 (0.10137)

437 nm f= 0.0958
188→189 (0.63465); 188→194 (-0.13472); 182→196 (0.12985)

Neutral (*trans* isomer)

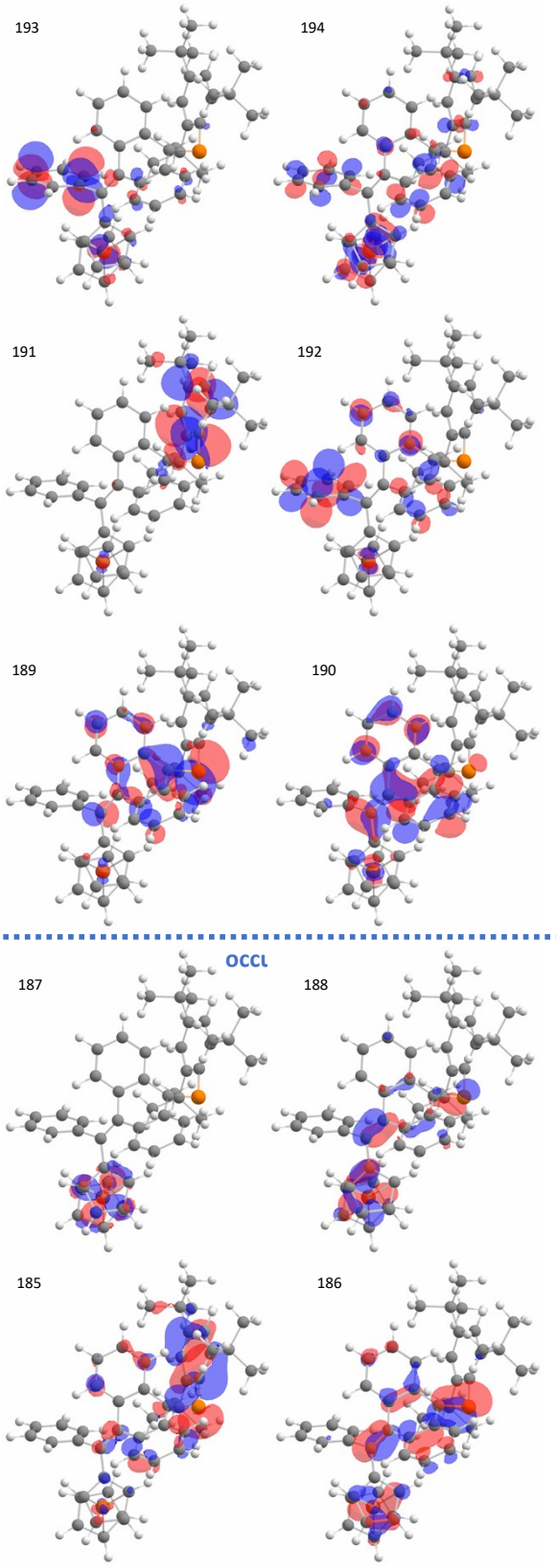

Figure S14: Selected molecular orbitals of *E*-**2**, at the B3LYP-D3/6-311G**/LANLDZ(MeCN) level of theory

Selected transitions:

588 nm f= 0.0034
187→194 (0.31147); 188→196 (-0.3024); 188A→193A (0.1909); 186A→196 (-0.17347); 187→198 (-0.16463); 187→196 (0.16427); 188→189 (0.1561); 188→190 (-0.15237); 187→195 (-0.14581); 187→189 (0.11718); 186→193 (0.11018); 188→192 (0.10687); 188→195 (-0.10527)

587 nm f= 0.0018
187→196 (0.34452); 188→194 (0.27347); 187→193 (-0.21868); 187→190 (0.17664); 187→189 (-0.16434); 186→194 (0.15809); 188→196 (0.14953); 188→198 (-0.14532); 188→195 (-0.12863); 187→195 (0.12052); 187→192 (-0.11995); 188→189 (0.11025); 187→194 (-0.10688)

485 nm f= 0.0111
187→196 (0.26673); 187→194 (0.24428); 188A→189A (-0.20467); 182→196 (0.18354); 188→196 (0.159); 182→194 (-0.15749); 182→193 (-0.1346); 187→198 (-0.12277); 182→195 (0.12153); 182→190 (0.12076); 187→193 (-0.10441); 187→189 (0.10105)

438 nm f= 0.1062
188→189 (0.62442); 182→196 (0.13466); 188→194 (-0.11815)

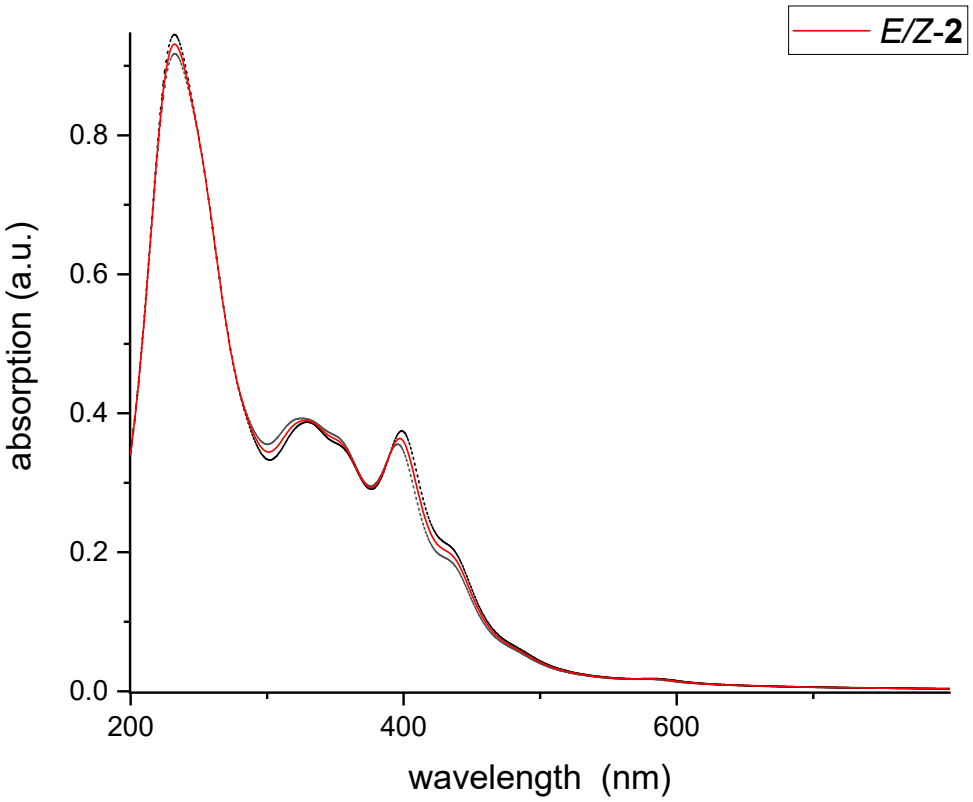

Figure S15: Calculated optical spectra of *E*-**2** and *Z*-**2** at the TD-DFT B3LYP-D3/6-311G**/LANLDZ (IEFPCM:MeCN) level of theory. The averaged spectra assumed a 1:1 ratio of isomers, based on the NMR analysis.

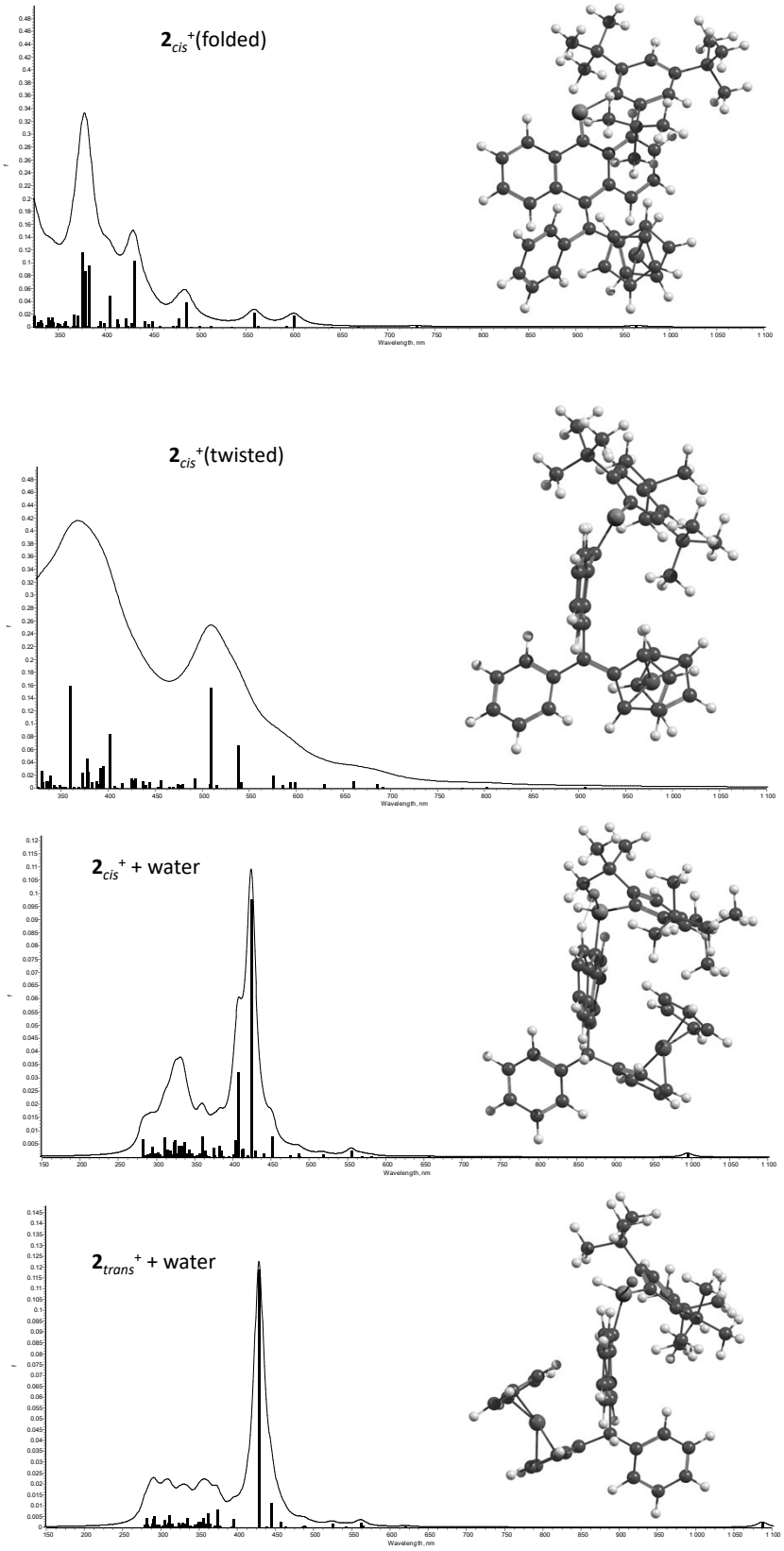

Figure S16: Calculated optical spectra of cationic derivatives of **2** at the TD-DFT B3LYP-D3/6-311G**/LANLDZ level of theory.

11. Cartesian coordinates

2$_{trans}$

6	5.850247	-0.858	-2.741242
6	6.093100	-1.619198	-1.599026
6	4.843180	-2.132546	-1.148656
6	3.825654	-1.628725	-2.012556
6	4.447569	-0.805875	-2.996719
26	4.819758	-0.062394	-1.102830
6	4.928680	2.007520	-1.071939
6	3.630799	1.576924	-0.688324
6	3.746104	0.768120	0.489421
6	5.145320	0.675991	0.796454
6	5.865923	1.450420	-0.155374
6	2.620929	0.148972	1.226618
6	2.819853	-1.284449	1.604921
6	3.684989	-1.634057	2.647248
6	3.899071	-2.971507	2.976259
6	3.245060	-3.980126	2.271365
6	2.371941	-3.639967	1.239066
6	2.164876	-2.304394	0.910108
6	1.466126	0.823025	1.480555
6	1.298579	2.271887	1.214596
6	0.074945	2.712632	0.669858
6	-0.985257	1.709273	0.409811
6	-1.014573	0.626848	1.417423
6	0.215694	0.200350	1.988248
6	-0.115734	4.084676	0.438590
6	0.880724	5.002931	0.741913
6	2.078557	4.566750	1.309336
6	2.279026	3.213604	1.548108
6	-2.205248	0.031502	1.858227
6	-2.199645	-0.943447	2.846334
6	-0.996255	-1.339872	3.424976
6	0.196246	-0.769136	2.997860
15	-1.869610	1.949320	-1.032708
6	-3.209107	0.648499	-1.039068
6	-2.931709	-0.686602	-1.456692
6	-3.835863	-1.685345	-1.095945
6	-5.024896	-1.431520	-0.416957
6	-5.359737	-0.099183	-0.207973
6	-4.499962	0.961706	-0.519456
6	-1.701638	-1.113234	-2.311690
6	-0.434008	-1.255410	-1.443411
6	-5.913236	-2.601513	0.031839
6	-7.173832	-2.128737	0.777207
6	-5.024126	2.405677	-0.248079
6	-4.772661	3.320944	-1.468894
6	-1.935206	-2.489488	-2.982988
6	-1.455515	-0.121024	-3.469385
6	-4.385931	3.008018	1.025550
6	-6.555206	2.426104	-0.023054
6	-5.099914	-3.505836	0.986039
6	-6.358186	-3.421572	-1.200404
1	-3.606852	-2.709425	-1.345108
1	-3.145716	0.348866	1.440047
1	-6.315440	0.123562	0.233489
1	-0.983557	-2.083885	4.213327
1	1.124160	-1.072445	3.460461
1	5.580654	0.100370	1.596532
1	3.205351	2.874939	1.994248
1	4.176142	-0.853667	3.217134
1	-3.137527	-1.376960	3.174300
1	2.705282	1.806464	-1.190644
1	2.848074	5.281184	1.578442
1	4.681443	-2.746898	-0.277792
1	1.487213	-2.039898	0.112435
1	-4.590279	2.375450	1.893646
1	-4.810635	3.997484	1.221638
1	-3.306315	3.117690	0.941400
1	6.938930	1.556599	-0.201851
1	5.165234	2.600980	-1.941820
1	-1.065896	4.426550	0.047034
1	2.767369	-1.806586	-1.915646
1	0.711879	6.059205	0.565862
1	7.050215	-1.786152	-1.129729
1	4.571189	-3.224169	3.788890
1	-7.095681	1.968829	-0.855845
1	-6.884470	3.464848	0.058366
1	-6.851104	1.925435	0.901775
1	-1.945560	-3.310586	-2.262459
1	-1.114170	-2.687480	-3.676450
1	-2.868410	-2.512434	-3.551384
1	3.409944	-5.020453	2.527739
1	1.853250	-4.415572	0.686537
1	-2.349250	-0.024916	-4.091675
1	-0.635799	-0.480740	-4.098332
1	-1.178062	0.875513	-3.122732
1	3.941458	-0.250819	-3.771324
1	6.591857	-0.235465	-3.285114
1	-3.713197	3.468582	-1.677880
1	-5.209316	4.307779	-1.288384
1	-5.237227	2.899907	-2.364638
1	-0.074319	-0.300430	-1.067016
1	0.368243	-1.705350	-2.037714
1	-0.633402	-1.900983	-0.584576
1	-5.709645	-4.349245	1.324383
1	-4.772521	-2.943616	1.864518
1	-4.208132	-3.908262	0.500819

1	-5.503840	-3.833880	-1.741566
1	-6.926050	-2.797396	-1.895344
1	-6.993814	-4.257299	-0.892174
1	-7.758603	-2.995246	1.097014
1	-7.815764	-1.514176	0.140461
1	-6.921361	-1.550667	1.670307

2$_{cis}$

6	4.834097	-1.592253	-1.557405
6	5.358077	-2.829156	-1.083885
6	4.318943	-3.804220	-1.148709
6	3.151823	-3.169080	-1.666673
6	3.470554	-1.803125	-1.918441
26	3.750646	-2.243670	0.086629
6	2.135895	-1.834924	1.305871
6	3.045261	-0.726964	1.338421
6	4.305609	-1.245926	1.799615
6	4.152112	-2.633360	2.074841
6	2.809399	-2.996714	1.768631
6	2.768670	0.678599	0.961944
6	3.838957	1.332031	0.141760
6	3.597705	1.581697	-1.213945
6	4.577731	2.149199	-2.021082
6	5.821275	2.480248	-1.484232
6	6.068410	2.249773	-0.132610
6	5.083764	1.681571	0.673639
6	1.605621	1.335025	1.222263
6	1.336539	2.724936	0.774170
6	0.059065	2.996932	0.235882
6	-0.938251	1.898904	0.175201
6	-0.856165	0.986639	1.335882
6	0.423580	0.743118	1.897743
6	2.257270	3.770355	0.904176
6	1.945939	5.055385	0.476430
6	0.695243	5.320444	-0.078992
6	-0.243205	4.301681	-0.183837
6	-1.978678	0.398970	1.937535
6	-1.852258	-0.374428	3.083998
6	-0.598584	-0.567434	3.663561
6	0.527258	-0.009681	3.071413
15	-1.886037	1.869184	-1.244160
6	-3.139408	0.503989	-1.012383
6	-4.428228	0.810395	-0.481155
6	-5.222928	-0.250092	-0.028764
6	-4.831959	-1.580999	-0.115244
6	-3.650696	-1.849455	-0.800874
6	-2.804310	-0.853969	-1.290348
6	-5.024716	2.247412	-0.365452
6	-4.360050	3.054147	0.774499
6	-1.564018	-1.318016	-2.110433
6	-1.737545	-2.767795	-2.627388
6	-5.656949	-2.737991	0.468696
6	-4.778143	-3.524054	1.469280
6	-1.357292	-0.451903	-3.372889
6	-0.296955	-1.312059	-1.233444
6	-6.108729	-3.680612	-0.669461
6	-6.910118	-2.247489	1.214974
6	-6.539217	2.217696	-0.049203
6	-4.897223	2.997659	-1.712278
1	-3.380226	-2.882183	-0.952772
1	-2.957713	0.567668	1.519865
1	-6.175757	-0.027252	0.418750
1	-0.498418	-1.146476	4.574555
1	1.503475	-0.161692	3.513301
1	1.114460	-1.788752	0.979162
1	3.223765	3.574857	1.346933
1	2.627729	1.332631	-1.627156
1	-2.737715	-0.806584	3.536454
1	5.222507	-0.690575	1.896897
1	2.673204	5.850975	0.591522
1	2.791419	-1.049286	-2.281610
1	5.274524	1.533168	1.729999
1	-4.484369	2.540617	1.731729
1	-4.832311	4.038102	0.856144
1	-3.294626	3.207223	0.615373
1	2.390118	-3.989457	1.823643
1	4.932052	-3.298860	2.411132
1	-1.233103	4.516413	-0.567200
1	5.354752	-0.648644	-1.590501
1	0.440478	6.323586	-0.401504
1	2.186519	-3.631601	-1.802057
1	4.370508	2.333629	-3.069183
1	-7.099633	1.634367	-0.784369
1	-6.922603	3.240627	-0.073814
1	-6.752220	1.821986	0.946736
1	-1.717115	-3.506082	-1.822453
1	-0.905571	-3.005278	-3.295019
1	-2.666230	-2.892014	-3.190465
1	6.587174	2.921680	-2.111673
1	7.026281	2.519280	0.298445
1	-2.256983	-0.450479	-3.994185
1	-0.531164	-0.855950	-3.965503
1	-1.106894	0.584741	-3.143178
1	6.353054	-2.988639	-0.697915
1	4.390196	-4.830174	-0.821997
1	-3.861962	3.169617	-2.006827
1	-5.381729	3.976192	-1.640555
1	-5.384501	2.432104	-2.511202
1	-0.238	-0.311138	-0.928374
1	0.541522	-1.760869	-1.770944
1	-0.473974	-1.901505	-0.331432
1	-5.346859	-4.349703	1.907843
1	-4.436117	-2.873161	2.278598
1	-3.893455	-3.945580	0.986900
1	-5.256617	-4.102076	-1.207198
1	-6.729013	-3.143790	-1.392233
1	-6.694454	-4.512070	-0.265133

1	-7.447746	-3.103023	1.632507
1	-7.598380	-1.718743	0.550083
1	-6.651302	-1.580811	2.042123

2$_{cis}^{+}$(folded)

6	-4.424989	0.840399	-0.462810
6	-3.152594	0.511667	-1.019133
6	-2.838338	-0.851203	-1.295371
6	-3.684814	-1.833983	-0.783167
6	-4.849921	-1.546248	-0.075453
6	-5.221748	-0.209487	0.010136
15	-1.892083	1.857058	-1.269167
6	-0.923291	1.879128	0.138244
6	0.077353	2.974510	0.188445
6	1.351723	2.721359	0.745941
6	1.613713	1.343878	1.213113
6	0.436436	0.746405	1.880270
6	-0.839183	0.966729	1.297553
6	-0.212934	4.271105	-0.264577
6	0.726067	5.289708	-0.166009
6	1.969993	5.040586	0.413300
6	2.277303	3.764776	0.866198
6	0.544762	0.011150	3.066932
6	-0.574568	-0.569031	3.649102
6	-1.820172	-0.415668	3.040942
6	-1.950989	0.346609	1.886659
6	2.794955	0.692647	0.996037
6	3.908996	1.318457	0.214401
6	3.705567	1.599103	-1.142779
6	4.729322	2.127905	-1.922280
6	5.978553	2.383804	-1.356
6	6.186632	2.127197	-0.002251
6	5.157262	1.601644	0.778076
6	-1.629651	-1.327607	-2.155207
6	-1.438585	-0.447327	-3.409730
6	-5.684760	-2.688044	0.523360
6	-6.168489	-3.624158	-0.607336
6	-4.998625	2.285484	-0.343976
6	-6.509399	2.275271	-0.010903
6	3.015799	-0.710313	1.383339
6	4.246789	-1.300765	1.837498
6	4.039633	-2.692335	2.067912
6	2.689217	-2.995376	1.722275
6	2.074436	-1.792185	1.276979
26	3.706598	-2.255736	0.070390
6	5.346553	-2.845878	-1.095683
6	4.294451	-3.799277	-1.227747
6	3.150286	-3.118641	-1.745346
6	3.502317	-1.749563	-1.947628
6	4.857015	-1.578797	-1.541155
6	-0.337051	-1.352789	-1.314530
6	-1.844811	-2.766700	-2.684594
6	-6.917961	-2.174829	1.287327
6	-4.803279	-3.487044	1.511415
6	-4.873233	3.031762	-1.692669
6	-4.307585	3.083007	0.787034
1	-3.437739	-2.871584	-0.942239
1	-2.929535	0.485533	1.457824
1	-6.164880	0.027668	0.470323
1	-0.480035	-1.121190	4.576619
1	1.513025	-0.084754	3.543341
1	1.071101	-1.699940	0.902688
1	3.236077	3.579187	1.330035
1	2.727231	1.422654	-1.574534
1	-2.702199	-0.863144	3.483842
1	5.185071	-0.786259	1.957822
1	2.690844	5.841343	0.526521
1	2.844102	-0.969369	-2.292538
1	5.316212	1.449917	1.839802
1	-4.411547	2.565552	1.744569
1	-4.776352	4.066279	0.885154
1	-3.245524	3.240558	0.606037
1	2.231370	-3.972295	1.740457
1	4.784208	-3.394109	2.410476
1	-1.196292	4.484966	-0.663472
1	5.391986	-0.641825	-1.519628
1	0.475052	6.286001	-0.510353
1	2.178864	-3.554317	-1.919728
1	4.551180	2.348708	-2.968328
1	-7.084771	1.696289	-0.737450
1	-6.881158	3.301845	-0.036074
1	-6.716553	1.887649	0.989216
1	-1.821498	-3.516482	-1.890487
1	-1.039952	-3.013894	-3.381942
1	-2.790919	-2.862833	-3.221508
1	6.776436	2.798199	-1.960671
1	7.144740	2.351589	0.452047
1	-2.358155	-0.408466	-3.998084
1	-0.647527	-0.863841	-4.040565
1	-1.150288	0.578933	-3.174788
1	6.328489	-3.037740	-0.691951
1	4.338114	-4.837920	-0.939438
1	-3.838798	3.194805	-1.998693
1	-5.343865	4.015941	-1.617911
1	-5.373472	2.473303	-2.487988
1	-0.036139	-0.361104	-0.980107
1	0.483176	-1.777132	-1.902516
1	-0.489949	-1.982231	-0.433547
1	-5.378284	-4.303839	1.956445
1	-4.443667	-2.842880	2.318940
1	-3.931842	-3.923068	1.017016
1	-5.332831	-4.068914	-1.152494
1	-6.785491	-3.077709	-1.325158
1	-6.768017	-4.439662	-0.192761

1	-7.461121	-3.019890	1.717302
1	-7.610204	-1.641097	0.631048
1	-6.637963	-1.508419	2.107850

2$_{cis}^{+}$(twisted)

26	3.459714	-2.167588	-0.665235
6	1.854342	-2.988396	0.388788
6	3.835643	-0.062253	-0.672108
6	3.051780	-3.087228	1.163410
6	2.054478	-3.715722	-0.814477
6	3.029545	-0.508126	-1.806696
6	5.053196	-0.862750	-0.730125
6	3.982066	-3.876536	0.437204
6	3.368411	-4.265544	-0.788521
6	3.794341	-1.400615	-2.583253
6	5.034078	-1.627798	-1.917434
1	0.968542	-2.442576	0.663268
1	3.229601	-2.631907	2.124893
1	1.346459	-3.803814	-1.623409
1	2.040350	-0.158612	-2.045445
1	5.843100	-0.886260	-0.001313
1	4.992310	-4.104907	0.739174
1	3.831466	-4.841617	-1.574222
1	3.467233	-1.885016	-3.489936
1	5.803401	-2.316041	-2.231484
6	3.347945	0.782717	0.359038
6	4.144332	1.301773	1.462829
6	3.531900	1.924733	2.579378
6	5.559375	1.338526	1.405742
6	4.286226	2.458594	3.610095
6	6.309546	1.893047	2.432237
6	5.681220	2.435688	3.551779
1	2.455341	1.985544	2.642484
1	6.074187	0.997398	0.521677
1	3.785982	2.910472	4.458196
1	7.389581	1.918065	2.349480
1	6.268955	2.863261	4.355196
6	1.948143	1.242286	0.196475
6	1.678503	2.244548	-0.776526
6	0.892064	0.717991	0.991908
6	0.325531	2.622458	-1.056932
6	-0.473934	1.045461	0.685063
6	-0.774525	1.857006	-0.479772
6	0.113033	3.726803	-1.916584
6	2.740647	2.952469	-1.411074
6	1.161220	4.389577	-2.515061
6	2.490466	3.989508	-2.272635
1	-0.897209	4.071953	-2.092140
1	3.763459	2.687672	-1.178018
1	0.961671	5.239798	-3.156345
1	3.311338	4.524080	-2.734979
6	1.158486	-0.191126	2.053382
6	-1.475440	0.529908	1.538781
6	0.153597	-0.682993	2.848471
6	-1.176301	-0.297199	2.600114
1	2.181938	-0.481903	2.243405
1	-2.502772	0.800114	1.372287
1	0.383934	-1.359128	3.663296
1	-1.975730	-0.656013	3.236883
15	-2.221676	1.886218	-1.481715
6	-3.386793	0.623244	-0.809870
6	-3.153253	-0.765619	-1.051519
6	-4.476724	1.028695	0.014541
6	-3.854288	-1.678978	-0.265999
6	-5.142898	0.041285	0.748198
6	-4.808387	-1.307098	0.680760
1	-3.663892	-2.732140	-0.398956
1	-5.943783	0.336914	1.403032
6	-4.960885	2.500419	0.153853
6	-5.480953	-2.380307	1.549452
6	-2.222727	-1.339633	-2.164955
6	-6.283421	2.602137	0.946277
1	-6.614415	3.643070	0.949249
1	-7.078685	2.005526	0.493236
1	-6.169369	2.298937	1.989812
6	-3.928185	3.365958	0.910983
1	-3.722154	2.951486	1.901499
1	-2.977239	3.452413	0.380840
1	-4.315878	4.379741	1.042848
6	-5.249535	3.096094	-1.243890
1	-4.362128	3.147621	-1.877849
1	-6.116	2.498813	-1.767067
1	-5.631919	4.115381	-1.143181
6	-6.468739	-1.779631	2.565029
1	-6.895945	-2.578016	3.176132
1	-5.976585	-1.073111	3.239373
1	-7.298857	-1.266142	2.073058
6	-6.253463	-3.365051	0.641729
1	-7.026391	-2.842538	0.072305
1	-5.592963	-3.865642	-0.069563
1	-6.737759	-4.136120	1.247341
6	-4.391260	-3.148098	2.332952
1	-4.847888	-3.923112	2.954340
1	-3.675341	-3.634914	1.666795
1	-3.835336	-2.470905	2.987684
6	-2.390155	-0.558937	-3.486528
1	-2.051900	0.479163	-3.415823
1	-1.797084	-1.029087	-4.275820
1	-3.435797	-0.546333	-3.802619
6	-2.589244	-2.807553	-2.494177
1	-3.649037	-2.918570	-2.733597
1	-2.014694	-3.129266	-3.366032
1	-2.343230	-3.493859	-1.680613
6	-0.739345	-1.342709	-1.735805

1	-0.621624	-1.841456	-0.772263
1	-0.139619	-1.880820	-2.476136
1	-0.328873	-0.339726	-1.646303

$\mathbf{2}_{cis}^{+}$ + water

6	0.737566	3.632572	0.196033
6	0.889324	3.719776	1.613265
6	0.651252	2.426511	2.157001
6	0.352326	1.549289	1.087348
6	0.409779	2.282223	-0.125210
26	2.293872	2.403657	0.790935
6	3.877881	2.053690	-0.586859
6	3.899621	0.971449	0.337615
6	4.023294	1.545094	1.638647
6	4.139547	2.960789	1.514592
6	4.047078	3.275189	0.127399
6	3.859580	-0.528920	0.089774
6	4.736278	-1.013534	-1.072755
6	4.478490	-2.252307	-1.668276
6	5.317470	-2.749986	-2.660902
6	6.431119	-2.020432	-3.071971
6	6.706901	-0.795663	-2.471048
6	5.868904	-0.298373	-1.474277
6	2.426416	-1.082360	0.120447
6	1.998806	-1.864135	1.217053
6	0.635215	-2.375709	1.260872
6	-0.309055	-1.956431	0.288542
6	0.142769	-1.208489	-0.833163
6	1.533209	-0.821319	-0.941738
6	2.872941	-2.215554	2.336
6	2.489066	-3.056115	3.304024
6	1.192766	-3.623509	3.294137
6	0.303869	-3.295160	2.312797
6	-0.723998	-0.812142	-1.900893
6	-0.278606	-0.146480	-3.008137
6	1.094511	0.169332	-3.140649
6	1.960292	-0.155460	-2.134897
15	-2.120885	-2.487660	0.381759
8	-2.458012	-3.449940	1.480722
6	-3.151301	-0.977474	0.205013
6	-2.980126	0.153754	1.069704
6	-3.233318	1.408982	0.526247
6	-3.749239	1.597151	-0.762927
6	-4.178847	0.463451	-1.436596
6	-3.938670	-0.838103	-0.969687
6	-3.928885	3.016491	-1.319662
6	-4.913897	3.801564	-0.423159
6	-2.847341	0.028593	2.618508
6	-2.867177	1.409154	3.307481
6	-4.633923	-2.001852	-1.749019
6	-3.822546	-2.454196	-2.984981
6	-1.618390	-0.724979	3.155164
6	-4.111596	-0.748022	3.076305
6	-4.970280	-3.204556	-0.835913
6	-6.008011	-1.499402	-2.272991
6	-2.559123	3.731381	-1.324165
6	-4.474187	3.016845	-2.758533
1	0.165223	0.493255	1.168167
1	0.245666	1.874656	-1.109528
1	0.727920	2.148824	3.197227
1	4.038424	0.984548	2.561600
1	3.758089	1.968714	-1.653639
1	0.852280	4.443608	-0.506479
1	1.159149	4.603343	2.171737
1	4.266615	3.663397	2.324213
1	4.084201	4.261553	-0.309710
1	3.613725	-2.828187	-1.360989
1	6.118546	0.646319	-1.005240
1	5.098612	-3.709835	-3.113914
1	7.579129	-0.226332	-2.770768
1	7.081592	-2.406924	-3.847451
1	-0.680157	-3.738728	2.316183
1	3.886209	-1.842703	2.326386
1	0.904095	-4.326755	4.066106
1	3.187463	-3.309762	4.093038
1	3.010312	0.046703	-2.270479
1	-1.771450	-1.037237	-1.846688
1	1.459867	0.649987	-4.040680
1	-0.978455	0.116758	-3.792359
1	-3.064260	2.283099	1.135297
1	-4.719950	0.581740	-2.360443
1	-6.569875	-2.350857	-2.662793
1	-6.596238	-1.042845	-1.473812
1	-5.918865	-0.781998	-3.090217
1	-3.592676	-1.602058	-3.631033
1	-2.881920	-2.943670	-2.727240
1	-4.408487	-3.167895	-3.570045
1	-4.112085	-3.766645	-0.475699
1	-5.533701	-2.875114	0.039841
1	-5.590980	-3.911337	-1.391504
1	-4.541207	4.043515	-3.126360
1	-3.821468	2.461369	-3.437930
1	-5.476492	2.585280	-2.813748
1	-5.884798	3.301747	-0.384507
1	-4.544553	3.897259	0.600436
1	-5.064926	4.809631	-0.819507
1	-2.664525	4.749145	-1.710605
1	-2.134987	3.795885	-0.319936
1	-1.847720	3.196220	-1.960049
1	-4.095040	-1.772233	2.733
1	-4.150118	-0.784190	4.168940
1	-5.020035	-0.257607	2.717619
1	-3.782294	1.967211	3.099310
1	-2.817554	1.263567	4.388696

1	-2.011411	2.027113	3.018948
1	-0.675135	-0.282869	2.834590
1	-1.636198	-0.698292	4.247897
1	-1.631052	-1.772678	2.878249
1	-2.213395	-3.034158	-0.908623
1	4.365080	-0.929905	0.963429

$\mathbf{2}_{trans}^{+}$ + water			
6	2.488328	-1.700784	-2.329447
6	2.653067	-2.401277	-1.102324
6	3.910379	-3.072016	-1.139611
6	4.522788	-2.797768	-2.400451
6	3.643223	-1.943794	-3.134786
26	4.219313	-1.016211	-1.361227
6	4.388286	1.067498	-1.413767
6	4.216383	0.674819	-0.047571
6	5.290728	-0.219702	0.256690
6	6.126840	-0.355177	-0.891218
6	5.568557	0.451223	-1.927362
6	3.161893	1.108815	0.959044
6	2.893386	2.618138	1.005913
6	1.720360	3.087450	1.607416
6	1.487614	4.452563	1.737041
6	2.424635	5.373611	1.271511
6	3.603087	4.916133	0.689949
6	3.838301	3.547370	0.562588
6	1.915212	0.216593	0.885819
6	1.758176	-0.831929	1.820816
6	0.549363	-1.640038	1.807508
6	-0.447618	-1.397552	0.830905
6	-0.170042	-0.501634	-0.228554
6	0.972272	0.377742	-0.152082
6	2.752644	-1.146670	2.805351
6	2.591844	-2.160513	3.705774
6	1.409727	-2.939188	3.694482
6	0.422616	-2.680334	2.787743
6	-0.974426	-0.444182	-1.411853
6	-0.760463	0.479124	-2.393957
6	0.269301	1.442113	-2.243655
6	1.105137	1.382911	-1.165182
15	-2.175876	-2.124955	1.003685
8	-2.411999	-2.841583	2.298970
6	-3.345836	-0.808361	0.492838
6	-4.127481	-1.021993	-0.675487
6	-4.494302	0.106745	-1.422240
6	-4.189977	1.402096	-1.028530
6	-3.669779	1.565525	0.260170
6	-3.282627	0.503205	1.067940
6	-4.675812	-2.397782	-1.172100
6	-4.909832	-3.395085	-0.012478
6	-3.026032	0.774437	2.579826
6	-1.616539	0.411053	3.086988
6	-4.489831	2.634197	-1.892881
6	-3.198137	3.469534	-2.047972
6	-4.070443	-0.056428	3.368978
6	-3.251418	2.260560	2.933406
6	-4.987992	2.254296	-3.298304
6	-5.576887	3.491784	-1.204628
6	-6.078972	-2.185309	-1.805051
6	-3.781358	-3.017517	-2.270777
1	1.657204	-1.059815	-2.580896
1	1.969503	-2.387455	-0.270288
1	3.833512	-1.530235	-4.112951
1	3.728330	1.707037	-1.974218
1	5.422708	-0.737547	1.194248
1	4.337572	-3.656305	-0.339194
1	5.493242	-3.139484	-2.724888
1	5.948971	0.550911	-2.932057
1	7.008626	-0.971999	-0.967109
1	0.981579	2.382658	1.969305
1	4.773712	3.215943	0.127254
1	0.571609	4.796601	2.203149
1	4.346827	5.622194	0.339182
1	2.241035	6.436903	1.369288
1	-0.487102	-3.261042	2.807502
1	3.666919	-0.574008	2.857138
1	1.284048	-3.741676	4.411497
1	3.367932	-2.364250	4.434572
1	1.867916	2.137313	-1.059455
1	-1.768529	-1.157242	-1.548167
1	0.393779	2.223302	-2.984552
1	-1.392077	0.487151	-3.273906
1	-3.581400	2.568915	0.644024
1	-5.030259	-0.042510	-2.344756
1	-6.531687	-3.160232	-1.998783
1	-6.738374	-1.632827	-1.132195
1	-6.043120	-1.660568	-2.760896
1	-3.632601	-2.309071	-3.090828
1	-2.798601	-3.320240	-1.903642
1	-4.260577	-3.909954	-2.682568
1	-4.009626	-3.757188	0.478618
1	-5.537651	-2.942625	0.758282
1	-5.428331	-4.276571	-0.397455
1	-5.140276	3.159051	-3.891611
1	-4.264064	1.627560	-3.827354
1	-5.942503	1.723081	-3.263884
1	-6.496588	2.917025	-1.069396
1	-5.253473	3.844872	-0.222929
1	-5.808891	4.369166	-1.815079
1	-3.395442	4.358545	-2.653562
1	-2.808189	3.801911	-1.083582
1	-2.415264	2.886102	-2.539201
1	-3.921101	-1.126603	3.222475
1	-3.979436	0.156238	4.438240
1	-5.085452	0.202129	3.055823
1	-4.254088	2.604808	2.670551
1	-3.139586	2.383054	4.012746

1	-2.518420	2.915379	2.452045
1	-0.835819	0.826191	2.445229
1	-1.479812	0.821566	4.090939
1	-1.478105	-0.662777	3.176298
1	-2.182279	-2.957051	-0.130108
1	3.625639	0.915126	1.923420

12. Reference

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyoto, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
2. Bruker AXS Inc, Madison, Wisconsin, USA, 2007.
3. a) G. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. **2009**, *42*, 339-341.
4. R. Deka, M. A. Ansari, S. Chattopadhyay, R. Lomoth, A. Thapper, A. Orthaber, *Angew. Chem. Int. Ed*. **2024**, *63*, e202406076.