Rhenium tricarbonyl complexes with arenethiolate axial ligands
Supporting information

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Contents

Time-dependent ^{1}H NMR experiments

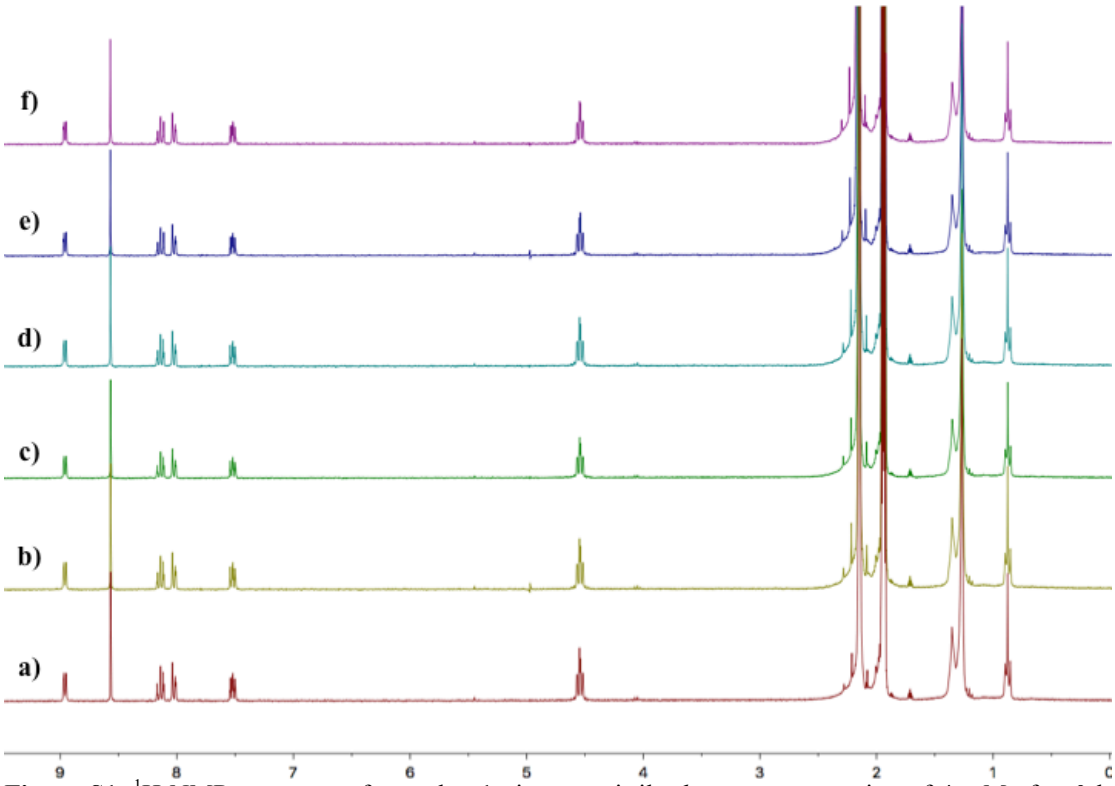

Figure S1. ^{1}H NMR spectrum of complex **1a** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

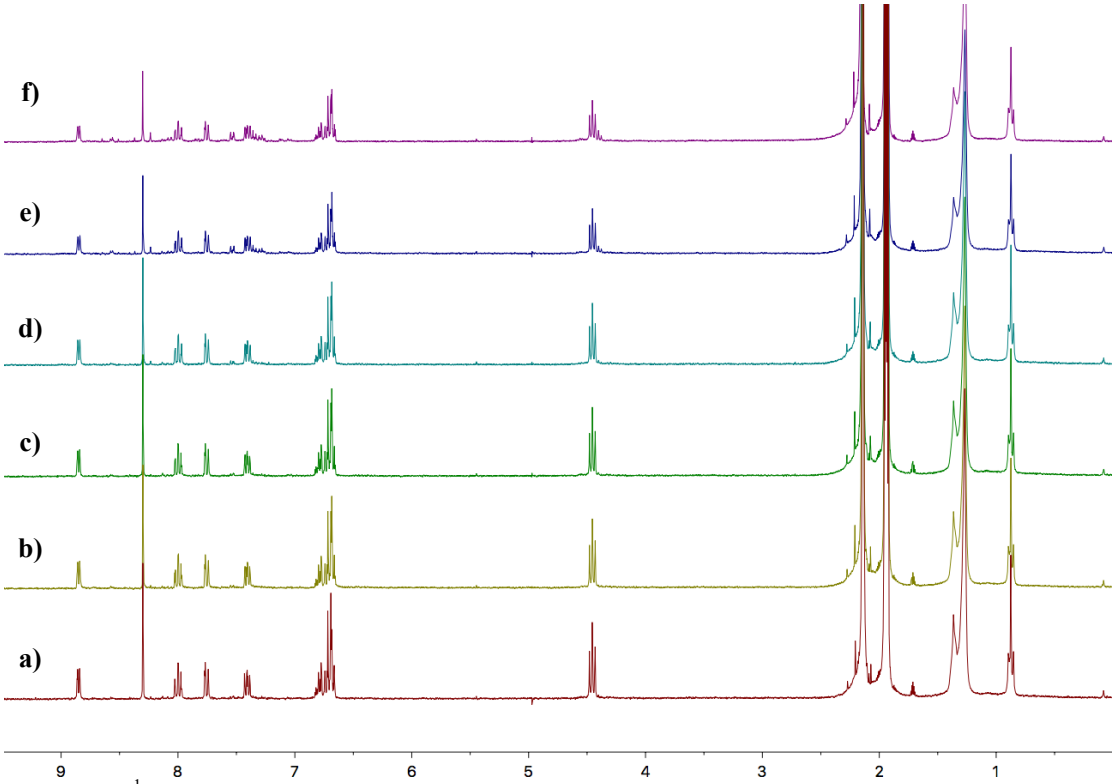

Figure S2. ^{1}H NMR spectrum of complex **1b** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

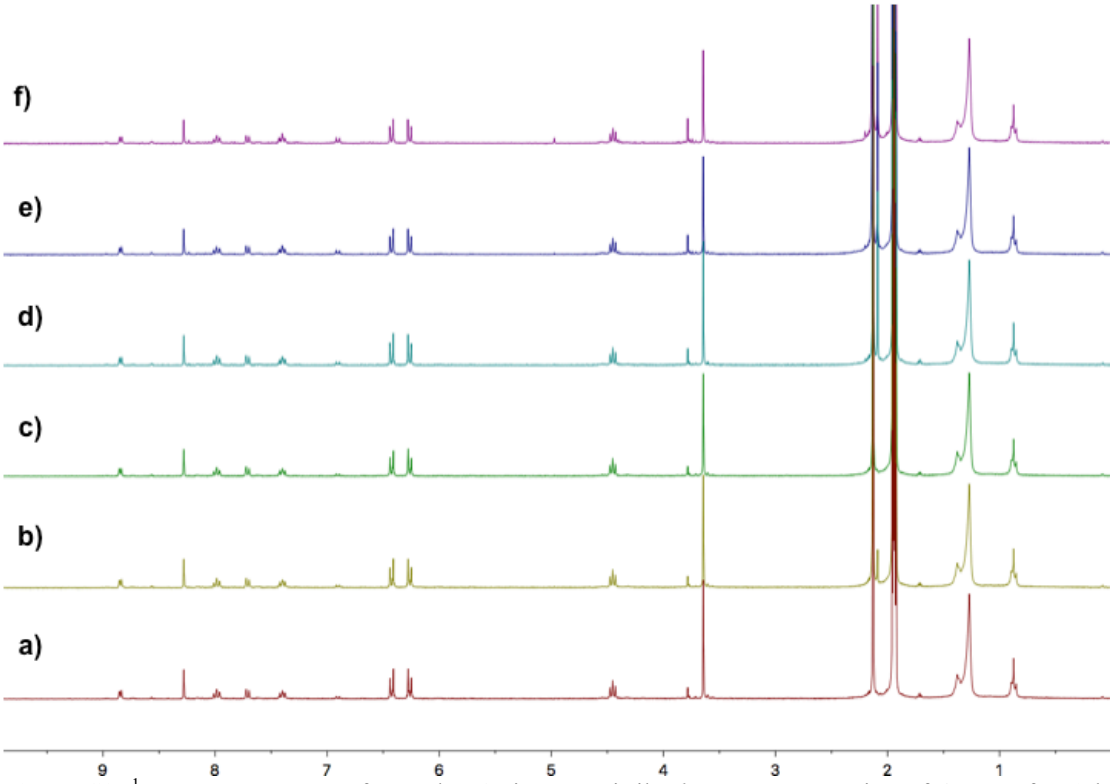

Figure S3. ^{1}H NMR spectrum of complex **1c** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

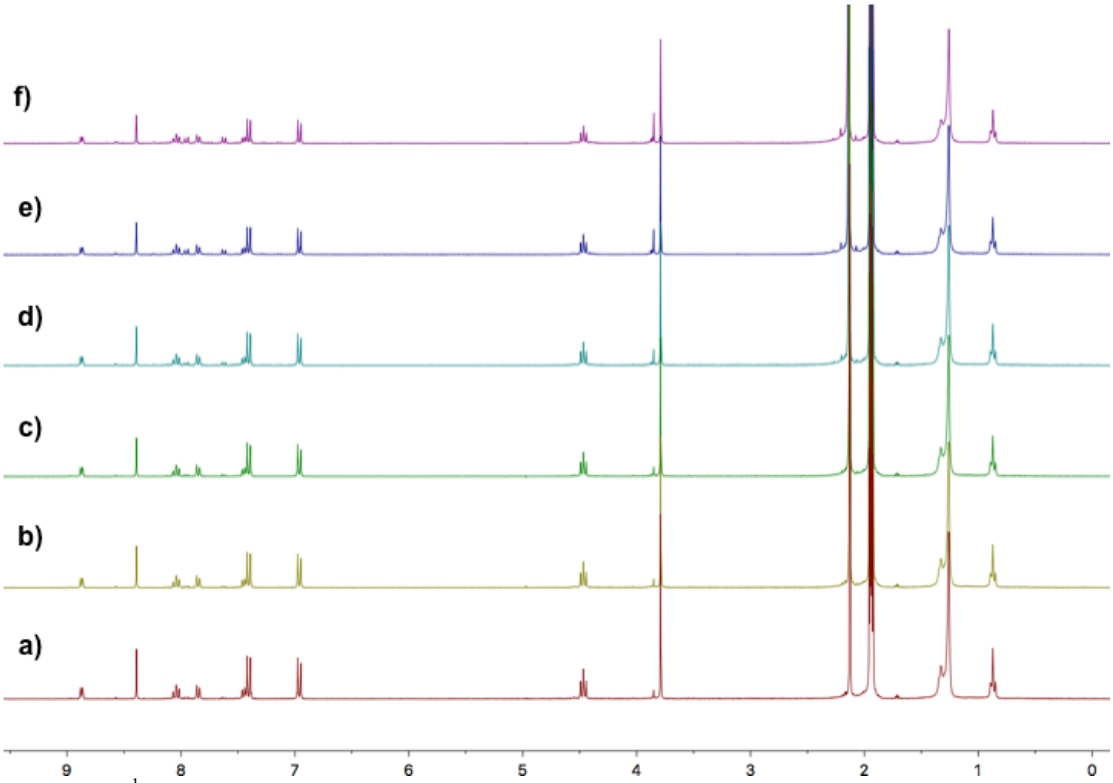

Figure S4. ^{1}H NMR spectrum of complex **1d** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

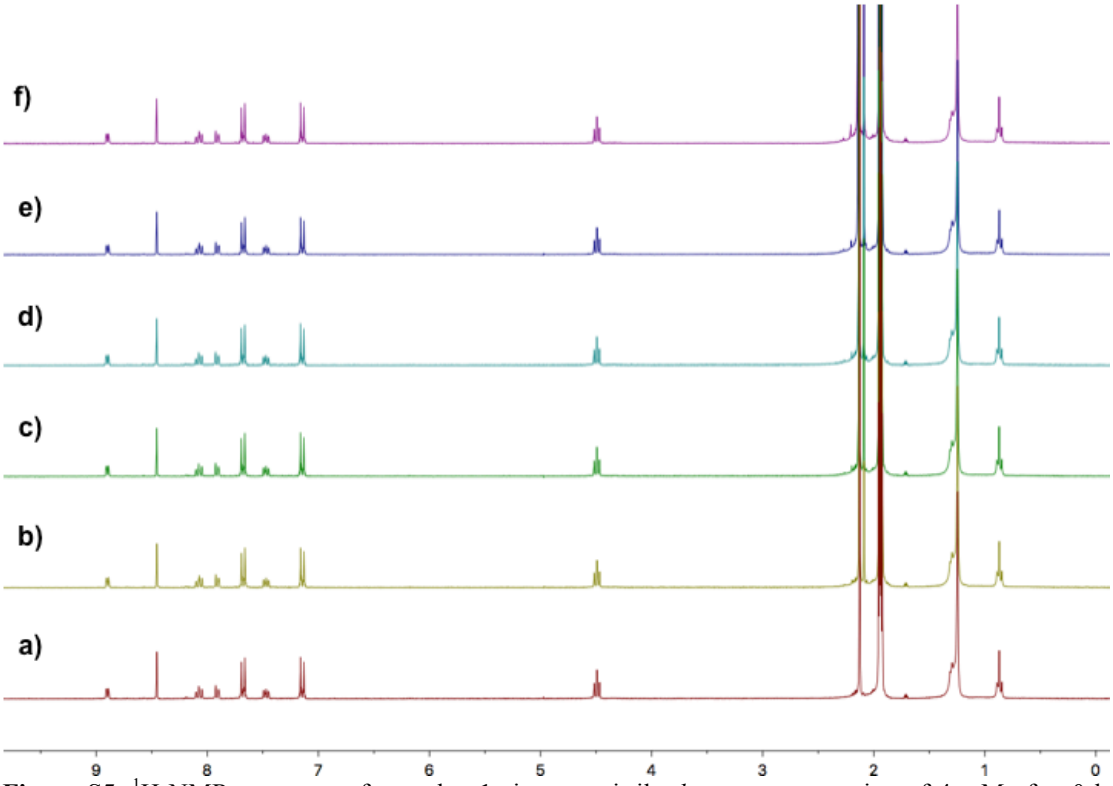

Figure S5. ^{1}H NMR spectrum of complex **1e** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e), and 72 hours (f).

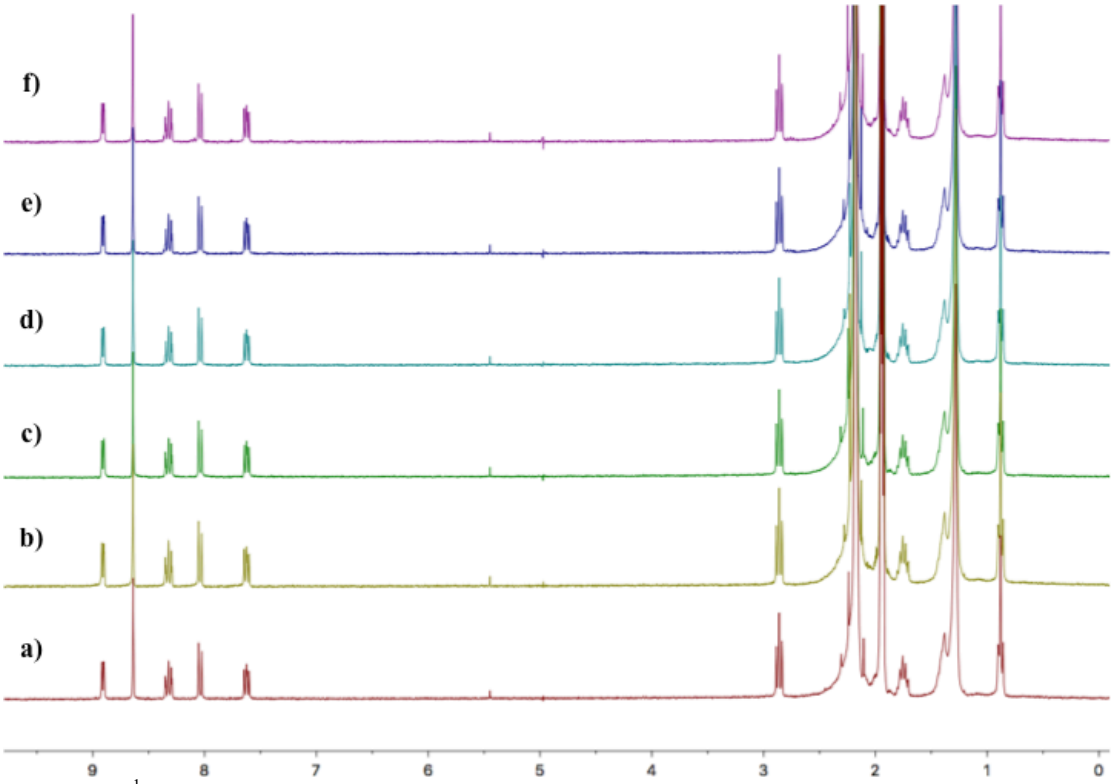

Figure S6. ^{1}H NMR spectrum of complex **2a** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

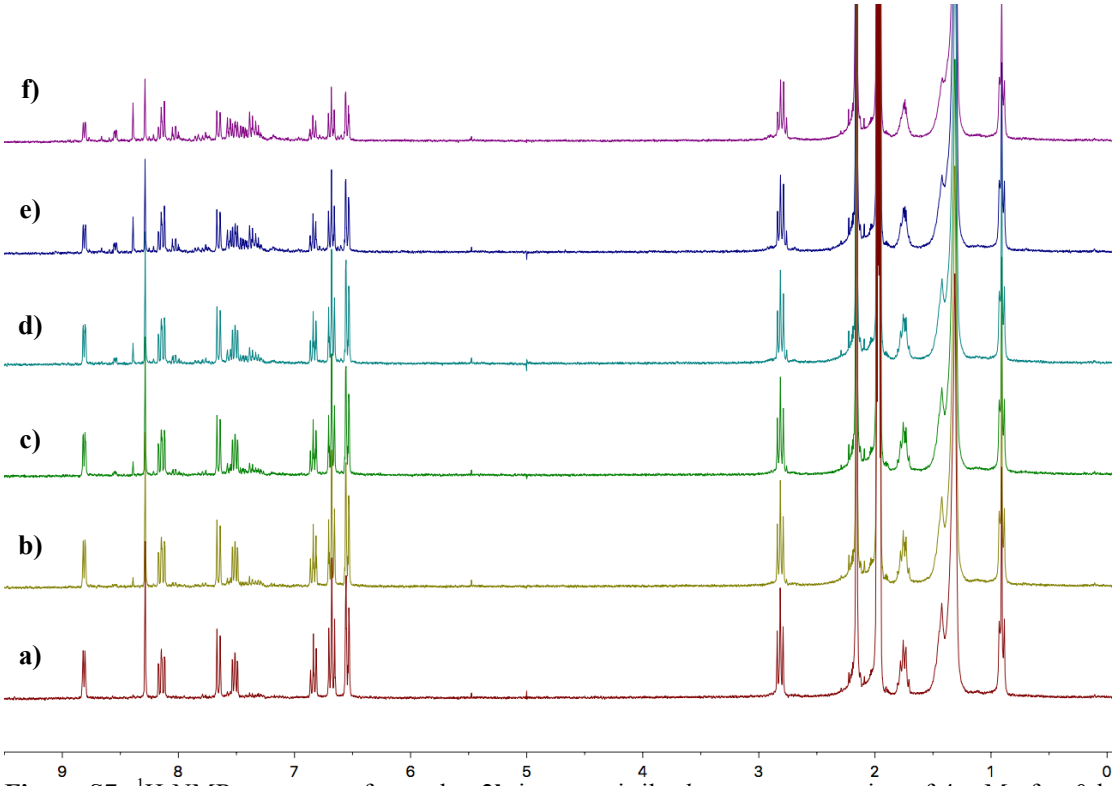

Figure S7. ^{1}H NMR spectrum of complex **2b** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e) and 72 hours (f).

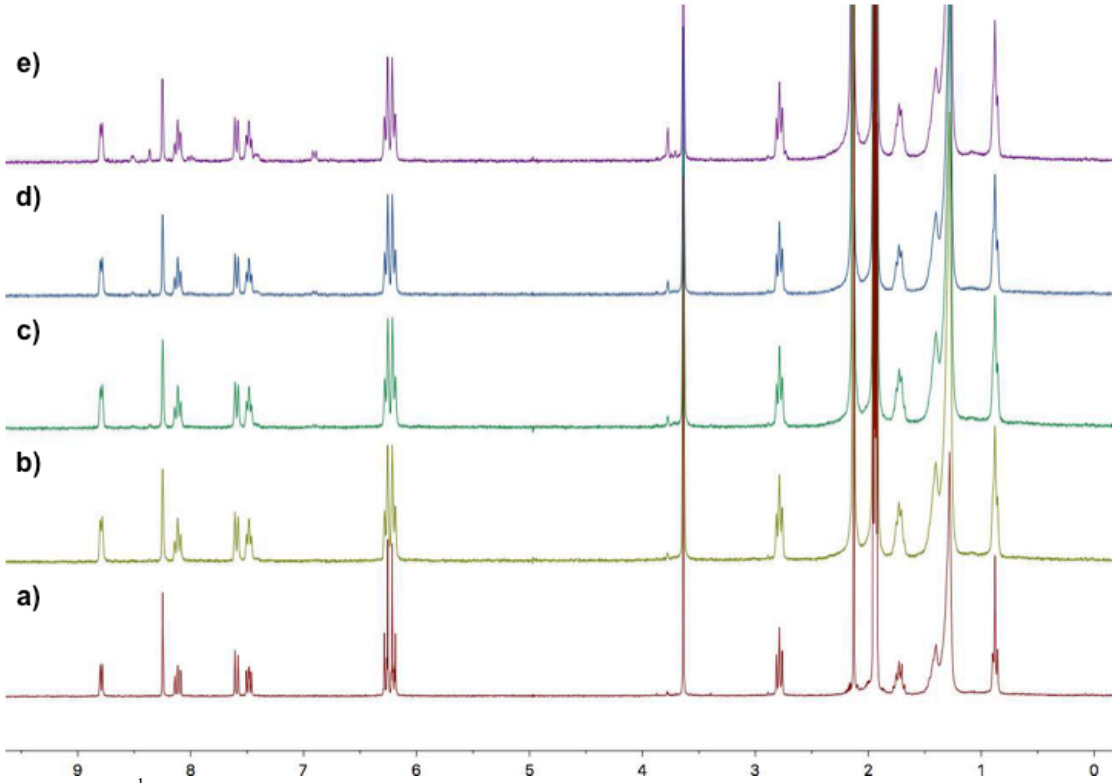

Figure S8. ^{1}H NMR spectrum of complex **2c** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e).

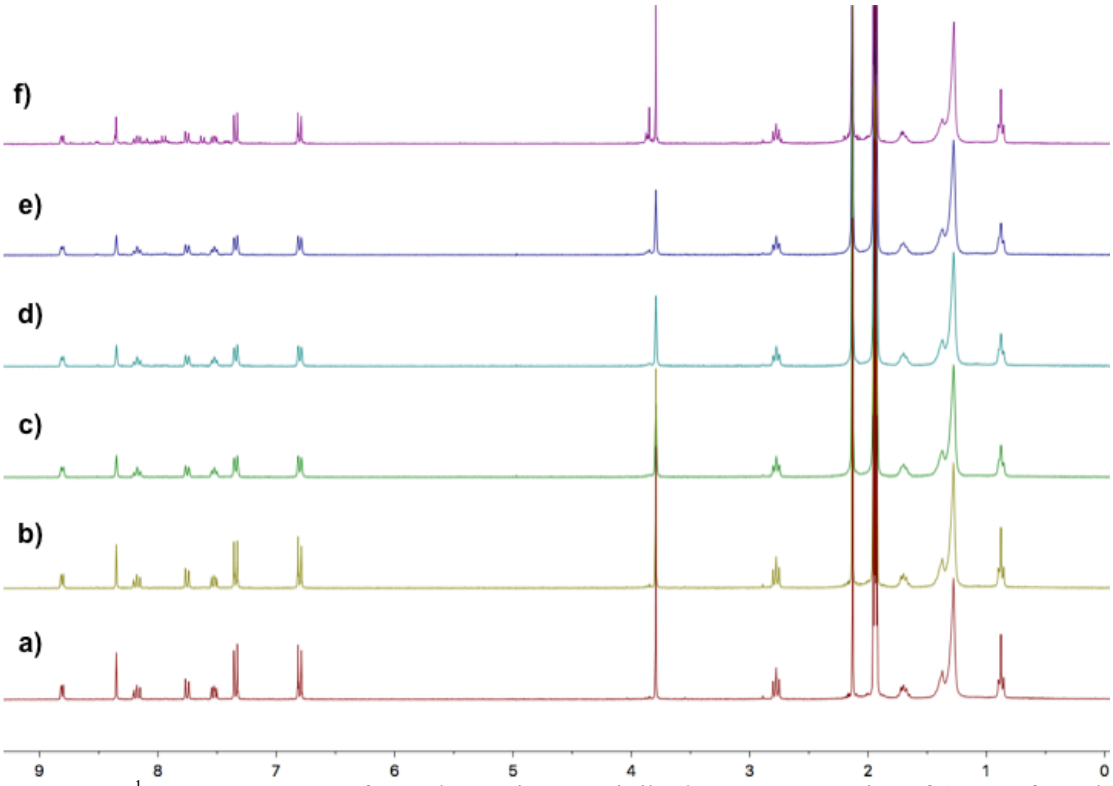

Figure S9. ^{1}H NMR spectrum of complex **2d** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e), and 72 hours (f).

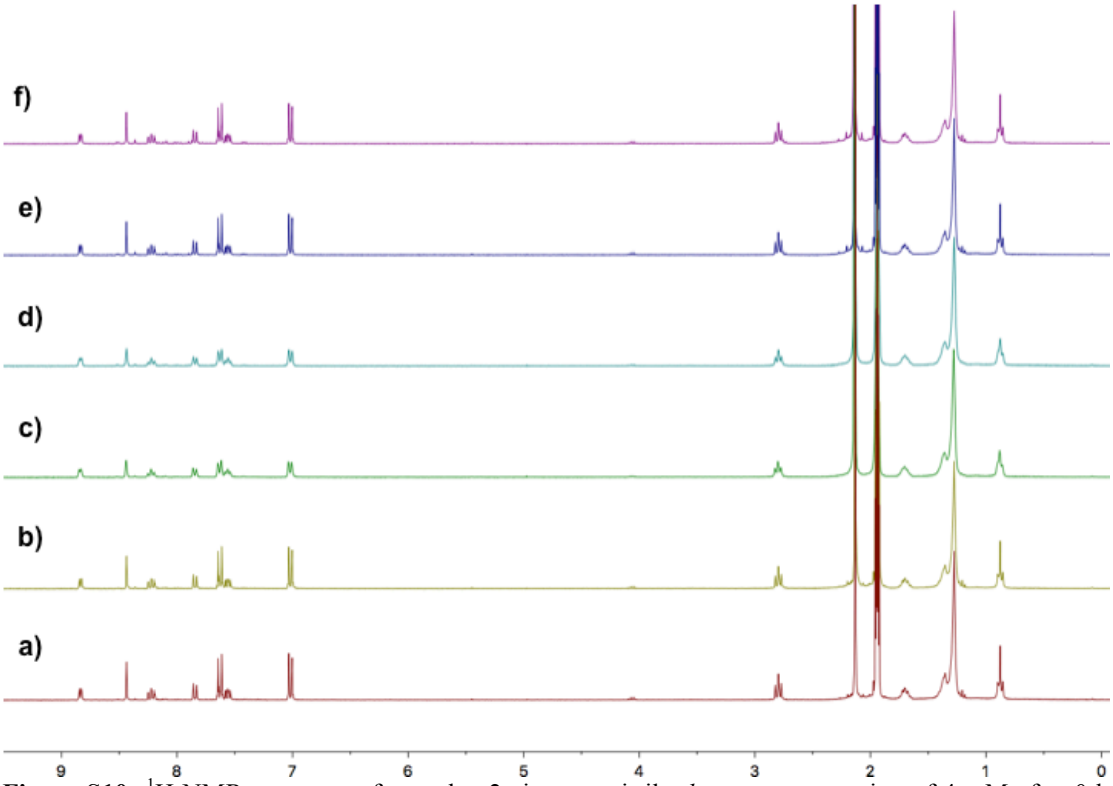

Figure S10. ^{1}H NMR spectrum of complex **2e** in acetonitrile-d_3 at a concentration of 4 mM after 0 hour (a), 8 hours (b), 16 hours (c), 24 hours (d), 48 hours (e), and 72 hours (f).

Cyclic voltammetry

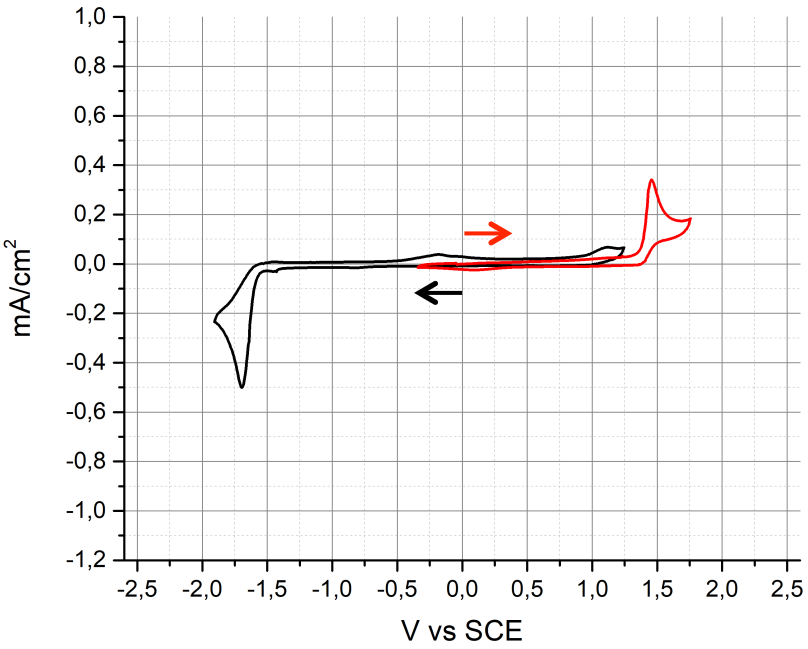

Figure S11. Cyclic voltammograms of **1a** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

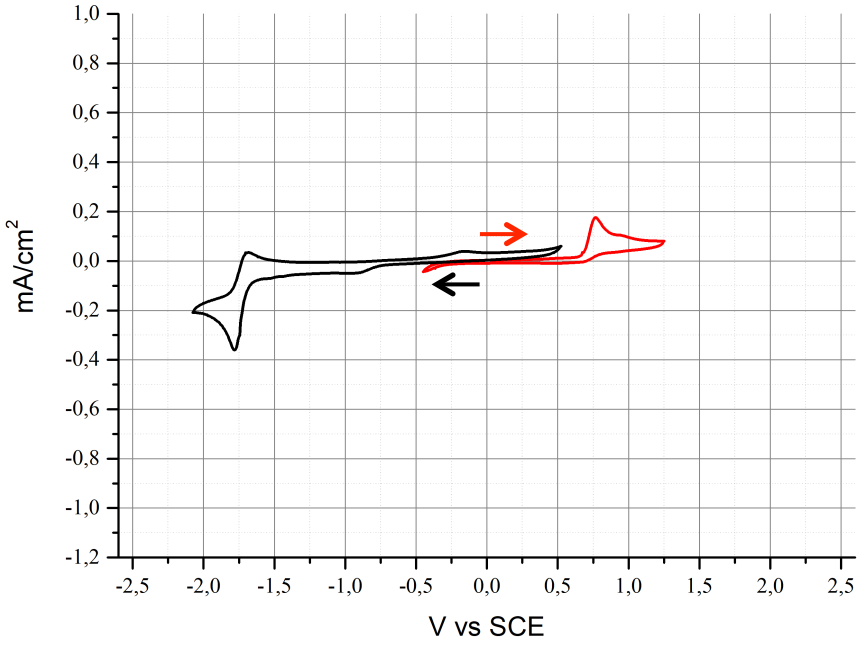

Figure S12. Cyclic voltammograms of **1b** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

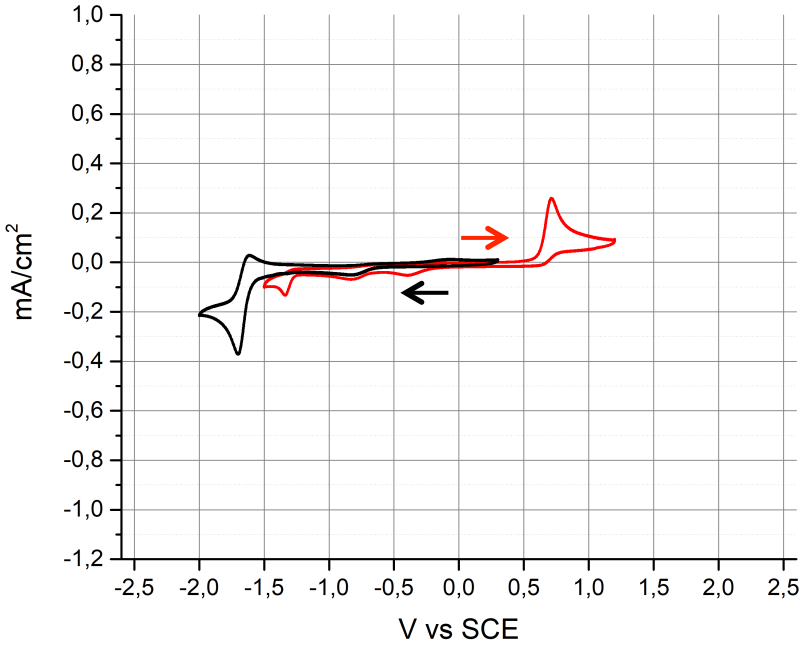

Figure S13. Cyclic voltammograms of **1c** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

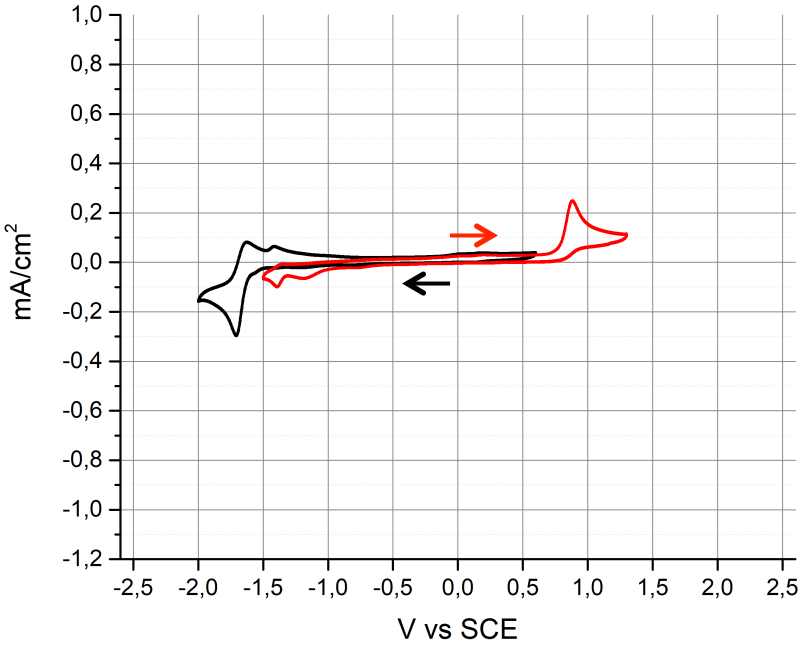

Figure S14. Cyclic voltammograms of **1d** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

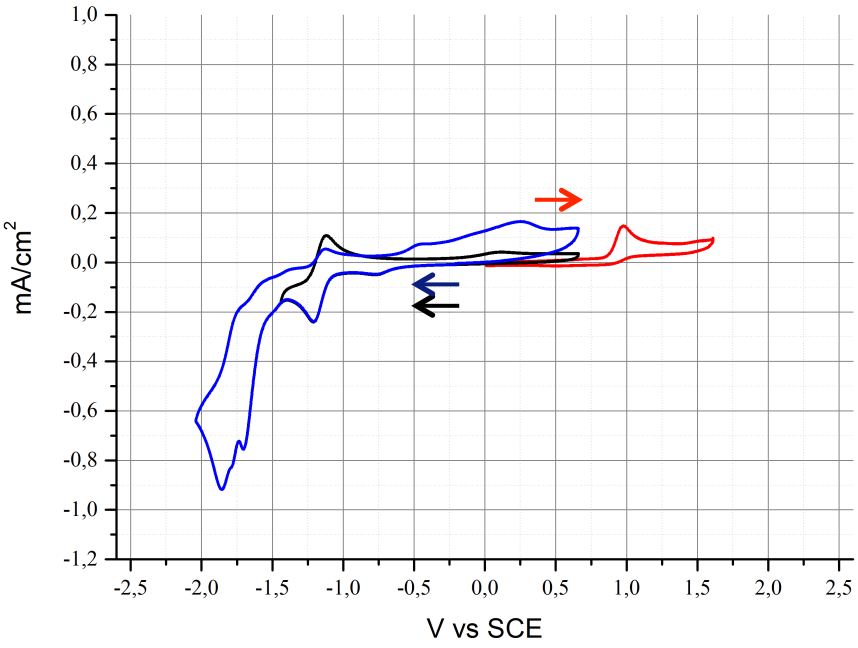

Figure S15. Cyclic voltammograms of **1e** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

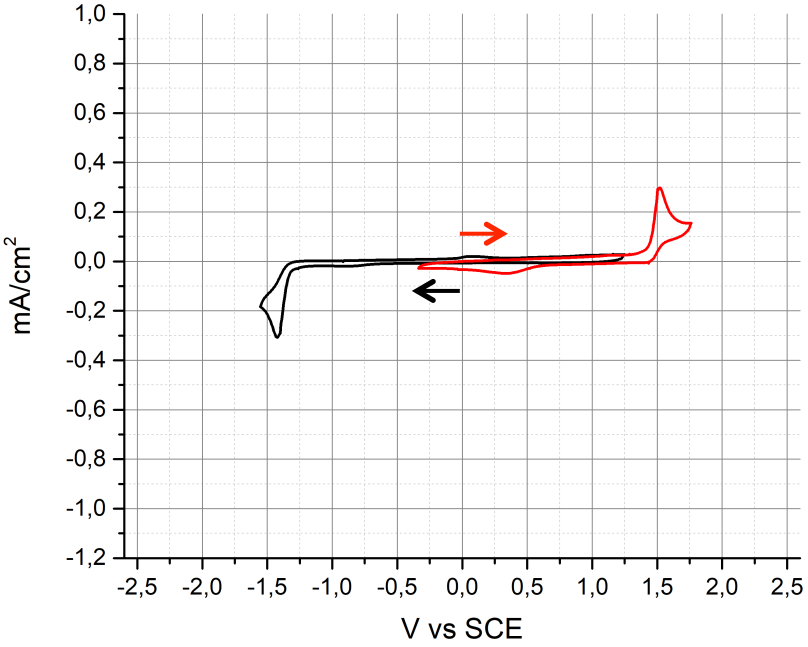

Figure S16. Cyclic voltammograms of **2a** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

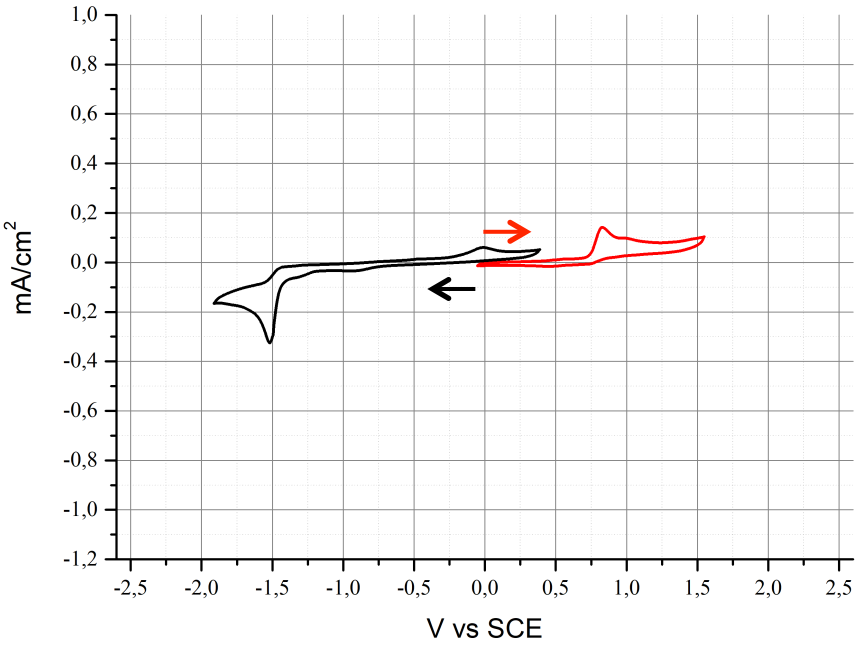

Figure S17. Cyclic voltammograms of **2b** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

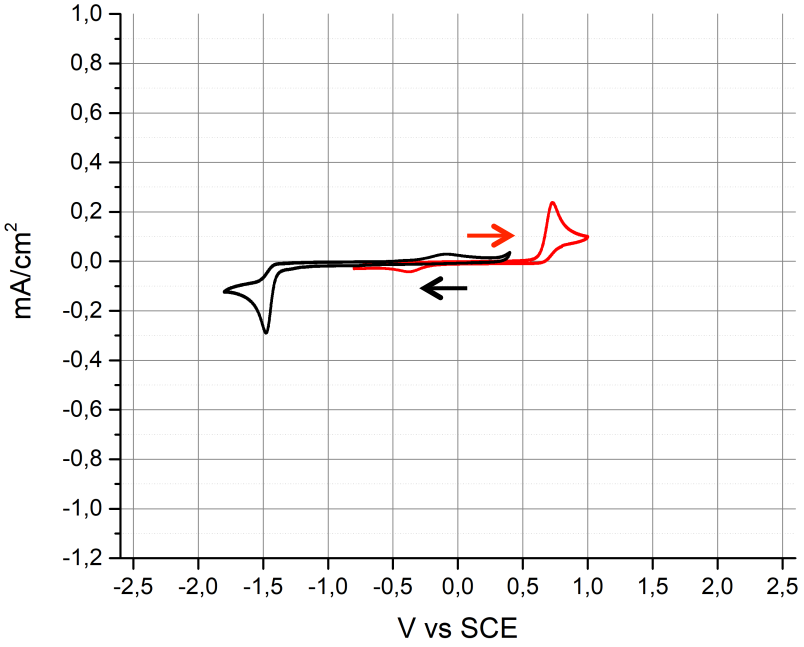

Figure S18. Cyclic voltammograms of **2c** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

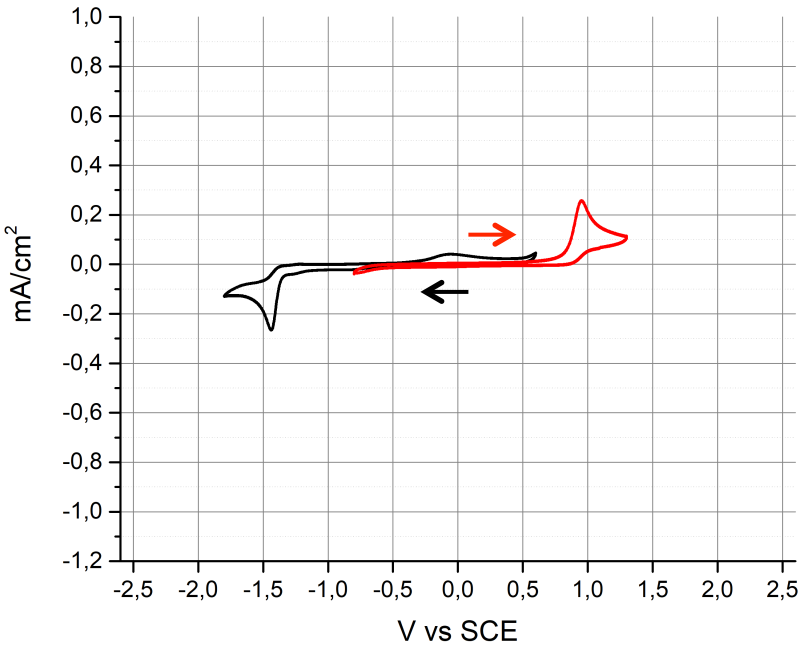

Figure S19. Cyclic voltammograms of **2d** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

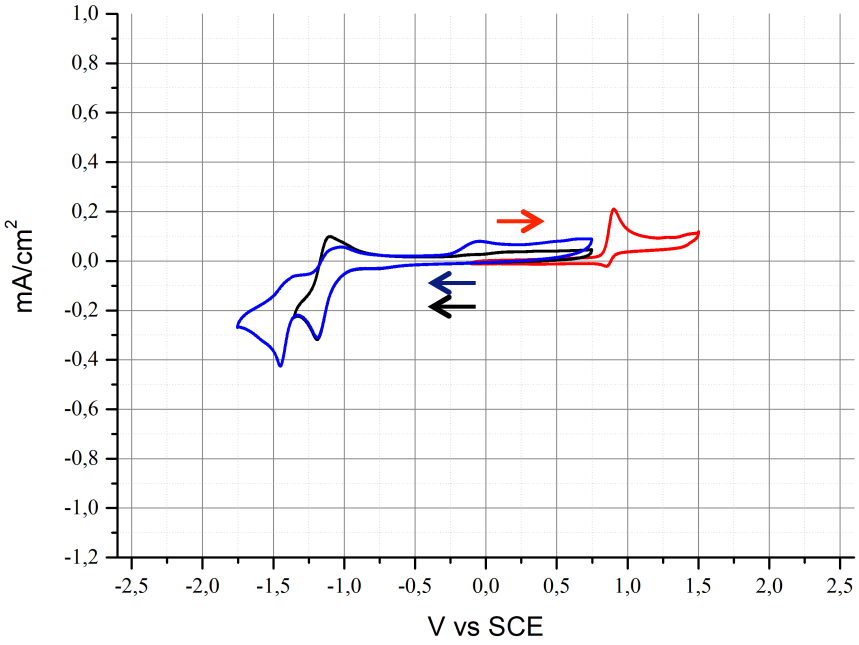

Figure S20. Cyclic voltammograms of **2e** (1 mM) in acetonitrile (0.1 M nBu$_4$NPF$_6$), under argon at RT.

DFT calculations.

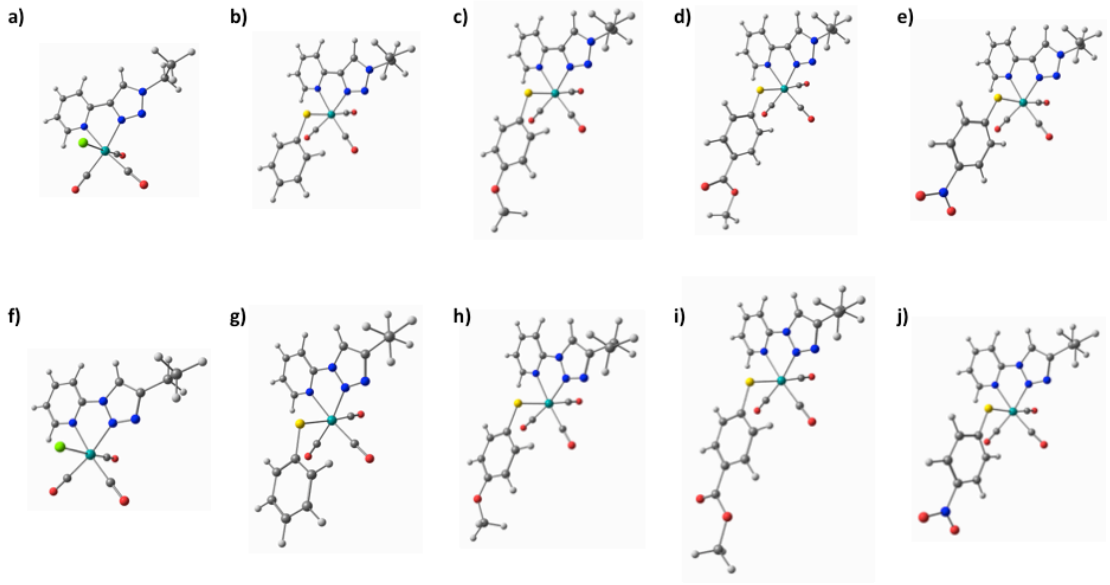

Figure S21. Optimized geometries of complex **1a'** (a), **1b'** (b), **1c'** (c), **1d'** (d), **1e'** (e), **2a'** (f), **2b'** (g), **2c'** (h), **2d'** (i), **2e'** (j). H atoms are in light gray, C atoms in gray, O atoms in red, N atoms in blue, S atoms in yellow, Cl atoms in light green.

Table S1. Cartesian coordinates of the optimized geometry of complex **1a'** at the B3LYP level of theory.

Atom	X	Y	Z
C	1.72175691	2.47390486	-0.07821989
C	-0.56871010	2.14488385	0.10811800
C	-0.80132711	3.51768485	0.07193497
C	0.27858189	4.38266385	-0.04392900
C	1.56271990	3.85138986	-0.11968692
H	2.70427291	2.02672086	-0.13512384
H	-1.81252811	3.89706384	0.13321491
H	0.11980989	5.45324085	-0.07425902
H	2.43348590	4.48656086	-0.21024889
N	0.68515291	1.62612685	0.03313807
N	-1.26315910	-0.16609115	0.26476700
N	-2.31398110	-0.92880716	0.38895396
C	-4.72571411	-0.66937217	0.53099484
H	-4.65637913	-1.53522716	1.18824086
H	-5.34121713	0.08381684	1.02165680
C	-5.28224504	-1.04812319	-0.83805718
H	-6.28295104	-1.46615320	-0.71217222
H	-5.35318901	-0.17561820	-1.49025720
H	-4.65269001	-1.79845020	-1.31928114
C	-1.62273410	1.14994084	0.23214696
C	-2.99633811	1.18761584	0.34661190
H	-3.70615911	1.99588484	0.36936285
N	-3.36640711	-0.10933416	0.44189690
Re	0.85657192	-0.61017314	0.05570111
C	1.15679682	-0.67613211	1.94015313
C	2.75149093	-0.73470414	-0.28178179
C	0.71047993	-2.52855915	-0.01864786
O	1.34132177	-0.71516309	3.08161714
O	0.59235894	-3.67397915	-0.07425285
O	3.88268694	-0.79045014	-0.50016174
Cl	0.38081904	-0.41344319	-2.47090891

Table S2. Cartesian coordinates of the optimized geometry of complex **1b'** at the B3LYP level of theory.

Atom	X	Y	Z
C	0.77280200	-3.01098200	-0.81260500
C	2.28220800	-1.25878800	-1.00652300
C	3.10796700	-2.01870100	-1.83276900
C	2.73657100	-3.31883700	-2.14618900
C	1.54782400	-3.82384800	-1.62633400
H	-0.15688700	-3.36974900	-0.39349100
H	4.02357000	-1.59353300	-2.22185300
H	3.36360200	-3.92711800	-2.78582900
H	1.21822400	-4.83085200	-1.84402500
N	1.12195500	-1.75152900	-0.49920400
N	1.67796800	0.74802100	0.19950300
N	2.08049700	1.96009100	0.46579200
C	3.94215700	3.41214800	-0.11156800
H	3.75895600	3.81012000	0.88557300
H	5.00670500	3.19976800	-0.20499500
C	3.46255600	4.37318600	-1.19534800
H	3.99886700	5.31891800	-1.09540600
H	3.65581700	3.97243500	-2.19234400
H	2.39386400	4.57010700	-1.09477700
C	2.57163800	0.11121900	-0.61287800
C	3.59449500	1.00455000	-0.85430200
H	4.50140400	0.93842800	-1.42944200
N	3.24526000	2.11633700	-0.16984600
Re	-0.10372700	-0.36999400	0.79221700
C	0.71620100	-1.01872500	2.40767400
C	-1.62156700	-1.52470600	1.05046600
C	-0.98833400	1.03683200	1.75571500
O	1.19207000	-1.41031300	3.38723300
O	-1.49948000	1.90581600	2.31874000
O	-2.52594800	-2.23161300	1.18043000
S	-1.03684600	0.46853400	-1.46456000
C	-2.80178300	0.74861100	-1.28392200
C	-3.72404400	-0.25633600	-1.61103700
C	-3.29455000	1.99430500	-0.86748400
C	-5.09568100	-0.02388200	-1.51971800
H	-3.36040800	-1.22328100	-1.93842200
C	-4.66636200	2.22444300	-0.77549100
H	-2.59646000	2.78393200	-0.61594500
C	-5.57447700	1.21705400	-1.10071900
H	-5.79066800	-0.81587700	-1.77783000
H	-5.02500300	3.19538700	-0.45060800
H	-6.64115900	1.39753400	-1.03066700

Table S3. Cartesian coordinates of the optimized geometry of complex **1c'** at the B3LYP level of theory.

Atom	X	Y	Z
C	1.68717100	-2.87019400	-0.92194900
C	2.85367700	-0.87354200	-1.11807600
C	3.76412600	-1.45441600	-1.99876100
C	3.61479100	-2.79167700	-2.33905600
C	2.55710600	-3.51217900	-1.79061400
H	0.85445000	-3.39833100	-0.47895200
H	4.57319900	-0.86389600	-2.40739000
H	4.31128300	-3.26306800	-3.02096900
H	2.40101600	-4.55598000	-2.02764300
N	1.82208600	-1.57687000	-0.58179300
N	1.96128400	0.96270600	0.17698700
N	2.15506500	2.22010800	0.46577600
C	3.70051200	3.99482700	-0.14112900

H	3.56374600	4.30845400	0.89310800
H	4.76839300	3.98353000	-0.35651800
C	2.94142300	4.90043500	-1.10621100
H	3.31325600	5.92181700	-1.00347000
H	3.08669400	4.58334800	-2.14067600
H	1.87329300	4.89779600	-0.88270200
C	2.91397300	0.51596300	-0.69293900
C	3.74941500	1.58340700	-0.94872700
H	4.62469700	1.69542100	-1.56438400
N	3.24173600	2.59754500	-0.21387500
Re	0.43317000	-0.46878000	0.80353400
C	1.42685500	-1.00294800	2.36318400
C	-0.84602700	-1.87877000	1.08317200
C	-0.64189400	0.73472100	1.84492000
O	2.00690200	-1.32954800	3.31008500
O	-1.27390800	1.48550500	2.45376500
O	-1.60705200	-2.73635800	1.22569500
S	-0.73804000	0.24401800	-1.38360000
C	-2.51502200	0.24813100	-1.11876600
C	-3.29459500	-0.88048900	-1.42260200
C	-3.17902600	1.38890400	-0.65783200
C	-4.67394500	-0.86691000	-1.26691800
H	-2.81049100	-1.77950100	-1.78550300
C	-4.56628400	1.41634600	-0.49504500
H	-2.60680300	2.27747000	-0.41865800
C	-5.32394500	0.28266100	-0.80020200
H	-5.26955000	-1.74127100	-1.50358600
H	-5.03570300	2.32204100	-0.13474600
O	-6.68240600	0.19741200	-0.68237900
C	-7.39357100	1.33956400	-0.20845100
H	-8.44290300	1.05099100	-0.19292300
H	-7.07827500	1.61488500	0.80300300
H	-7.26337100	2.19699700	-0.87641700

Table S4. Cartesian coordinates of the optimized geometry of complex **1d'** at the B3LYP level of theory.

Atom	X	Y	Z
C	-1.95916100	-2.60120200	1.55118700
C	-3.08778400	-0.57419900	1.47049700
C	-3.87955000	-0.93482200	2.55875000
C	-3.69045200	-2.17698000	3.14866500
C	-2.71318000	-3.02509400	2.63538700
H	-1.19093300	-3.23351600	1.12863500
H	-4.62873900	-0.25056200	2.93388400
H	-4.29525100	-2.47735400	3.99498200
H	-2.53062500	-4.00153200	3.06336800
N	-2.13366900	-1.40223500	0.96935200
N	-2.36111800	0.93105600	-0.27668200
N	-2.59030400	2.10479700	-0.79839500
C	-4.05662900	4.00175600	-0.39896300
H	-4.01010400	4.10050800	-1.48265900
H	-5.10209400	4.04624800	-0.09559000
C	-3.22164600	5.07160500	0.29814300
H	-3.60484900	6.05657800	0.02421800
H	-3.27748500	4.97036900	1.38365500
H	-2.17631000	5.01018200	-0.00913200
C	-3.19996400	0.69842500	0.77499600
C	-3.99988300	1.81532500	0.89759800
H	-4.79539400	2.07377400	1.57426400
N	-3.58676600	2.64091600	-0.08923800
Re	-0.93481300	-0.64368500	-0.78131200

C	-2.14460300	-1.44981500	-2.04609600
C	0.25846600	-2.14795600	-0.93786900
C	-0.03802800	0.28898900	-2.20342600
O	-2.85518800	-1.94040000	-2.81378400
O	0.47181900	0.88136500	-3.05302900
O	0.95419500	-3.06722000	-1.00592400
S	0.44748400	0.46959700	1.08039200
C	2.20591700	0.45876100	0.87015500
C	2.98862800	0.95783300	1.93452700
C	2.87986700	0.00165800	-0.27659400
C	4.36908600	0.99373100	1.85228600
H	2.49535300	1.31646600	2.83073500
C	4.26554600	0.03785400	-0.35660300
H	2.31620300	-0.38362100	-1.11375900
C	5.03335600	0.53324600	0.70509700
H	4.95502700	1.37828900	2.67834900
H	4.75791000	-0.32043600	-1.25151800
C	6.51102000	0.59099100	0.66901000
O	7.21032800	1.01260700	1.57053600
O	7.02340000	0.11979700	-0.48746500
C	8.45888000	0.14093700	-0.60223800
H	8.67784000	-0.27080100	-1.58437700
H	8.83395200	1.16227900	-0.52531600
H	8.91395500	-0.47128400	0.17738100

Table S5. Cartesian coordinates of the optimized geometry of complex **1e'** at the B3LYP level of theory.

Atom	X	Y	Z
C	-1.73688500	-2.57100700	1.59834700
C	-2.81637400	-0.51676300	1.51822300
C	-3.59642400	-0.84736900	2.62417300
C	-3.42726400	-2.08831400	3.22274800
C	-2.48097400	-2.96541600	2.70031500
H	-0.99277800	-3.22645300	1.16804300
H	-4.32156800	-0.14118600	3.00582500
H	-4.02367900	-2.36558900	4.08277900
H	-2.31472700	-3.94202500	3.13446900
N	-1.89251200	-1.37349500	1.00786600
N	-2.08805400	0.95041900	-0.25976500
N	-2.29512800	2.12524100	-0.78830900
C	-3.69725200	4.06687800	-0.37731300
H	-3.73854900	4.13437200	-1.46380200
H	-4.71062100	4.16374400	0.01037500
C	-2.76404200	5.11850500	0.21479900
H	-3.13085400	6.11122900	-0.05338400
H	-2.72939100	5.04635100	1.30348700
H	-1.75253800	5.00637800	-0.17894600
C	-2.90961000	0.75165500	0.81221100
C	-3.67393100	1.89266500	0.94139400
H	-4.44552200	2.18081300	1.63363900
N	-3.25918800	2.69642600	-0.06259900
Re	-0.71258700	-0.66416500	-0.77420700
C	-1.96589000	-1.45484200	-2.00615900
C	0.44136600	-2.19898200	-0.94018100
C	0.17390500	0.23281800	-2.22682700
O	-2.70326700	-1.93603400	-2.75315000
O	0.67698200	0.80408100	-3.09415500
O	1.11468100	-3.13391400	-1.01379800
S	0.72862400	0.43226500	1.05451100
C	2.46793900	0.43442200	0.79389500
C	3.27685600	0.98144000	1.81916700

C	3.11411100	-0.06204500	-0.35728800
C	4.65185300	1.02950000	1.70363400
H	2.80478000	1.36925900	2.71374600
C	4.49212200	-0.01854400	-0.48157900
H	2.53072400	-0.48404700	-1.16177500
C	5.25996800	0.52659100	0.54861500
H	5.26255600	1.44774600	2.49140300
H	4.98039700	-0.40069700	-1.36716300
N	6.70339900	0.57242000	0.42011300
O	7.35987200	1.06477900	1.34072500
O	7.21815300	0.11758700	-0.60406300

Table S6. Cartesian coordinates of the optimized geometry of complex **2a'** at the B3LYP level of theory.

Atom	X	Y	Z
C	1.63675900	2.51448200	-0.06851400
C	-0.62298900	2.09913900	0.09627700
C	-0.93582300	3.45081700	0.05647100
C	0.11110900	4.35597500	-0.05335300
C	1.41838700	3.88120000	-0.11609600
H	2.63484300	2.10350400	-0.11389600
H	-1.96095400	3.78694900	0.11009100
H	-0.09582900	5.41775300	-0.08780400
H	2.26031000	4.55426400	-0.20077900
N	0.63261100	1.62238800	0.03617100
N	-1.24808600	-0.19454300	0.26785600
N	-2.30512800	-0.93293800	0.38861900
C	-4.79031100	-0.66910300	0.53079600
H	-4.81213400	-1.38475000	1.35763500
H	-5.46659500	0.14611200	0.79766200
C	-5.27221900	-1.35453800	-0.75841000
H	-6.27819700	-1.75644500	-0.61898900
H	-5.29864100	-0.64821500	-1.59174500
H	-4.61047800	-2.17931600	-1.03211900
C	-2.97616200	1.18282700	0.30536400
H	-3.51589900	2.11258700	0.28814400
Re	0.87368600	-0.59525800	0.05829500
C	1.18913400	-0.66154100	1.94315800
C	2.76920800	-0.69411400	-0.28908400
C	0.75898500	-2.51692800	-0.01702400
O	1.38578600	-0.70218900	3.08134600
O	0.65551400	-3.66233700	-0.07394200
O	3.89839200	-0.72845600	-0.51548300
C	-3.40263200	-0.12193300	0.41734900
N	-1.62138200	1.10759000	0.21339200
Cl	0.38781300	-0.39879000	-2.46115000

Table S7. Cartesian coordinates of the optimized geometry of complex **2b'** at the B3LYP level of theory.

Atom	X	Y	Z
C	0.96053200	-2.96055300	-0.87844000
C	2.34104000	-1.12104000	-0.99754500
C	3.24591600	-1.77768400	-1.82152200
C	2.96764100	-3.09106700	-2.17317500
C	1.80622700	-3.69253400	-1.69424600
H	0.04945700	-3.38851400	-0.48614200
H	4.13732500	-1.28137000	-2.17662500
H	3.65058500	-3.63443200	-2.81326400
H	1.55420800	-4.71345600	-1.94607200
N	1.21663100	-1.68574100	-0.52409000
N	1.61984700	0.79417800	0.22337900
N	1.99245600	2.00675700	0.48526100

C	3.86637200	3.57201200	-0.06680900
H	3.90037200	3.87637000	0.98312600
H	4.90054600	3.45023500	-0.39672900
C	3.17290300	4.66341000	-0.89889200
H	3.69829900	5.61453300	-0.78765100
H	3.16277200	4.40052800	-1.95950800
H	2.13982900	4.80442700	-0.57332500
C	3.53462400	1.10956400	-0.83867100
H	4.38433300	0.88430200	-1.45768900
Re	-0.10212600	-0.42229500	0.77280000
C	0.72608600	-1.05611300	2.39342600
C	-1.56979100	-1.64742800	1.00167000
C	-1.06176300	0.92717400	1.74883200
O	1.20147700	-1.44156300	3.37426800
O	-1.61380800	1.76414600	2.31894500
O	-2.44081500	-2.39650200	1.11054900
S	-1.06260300	0.37243200	-1.48526200
C	-2.81789500	0.69454000	-1.28051300
C	-3.76620200	-0.29686000	-1.57169200
C	-3.27550800	1.95982600	-0.88421800
C	-5.13073200	-0.03185800	-1.46375400
H	-3.42919600	-1.27824400	-1.88406900
C	-4.64026300	2.22222300	-0.77598900
H	-2.55615400	2.73906100	-0.66192800
C	-5.57509100	1.22821900	-1.06453400
H	-5.84706000	-0.81337000	-1.69374400
H	-4.97235600	3.20771800	-0.46728400
H	-6.63626800	1.43387800	-0.98175000
C	3.17660900	2.24719000	-0.15143500
N	2.54040000	0.21463200	-0.58714800

Table S8. Cartesian coordinates of the optimized geometry of complex **2c'** at the B3LYP level of theory.

Atom	X	Y	Z
C	1.76569300	-2.82366900	-0.95214000
C	2.86329100	-0.80382300	-1.09277400
C	3.81521200	-1.31327900	-1.96652700
C	3.71137200	-2.64789900	-2.33231000
C	2.66949500	-3.41583000	-1.81764800
H	0.94306700	-3.38290100	-0.53053600
H	4.61051700	-0.69014200	-2.34860800
H	4.43580600	-3.07896800	-3.01108000
H	2.55409300	-4.45853500	-2.07958300
N	1.85334500	-1.53031900	-0.58320900
N	1.92950500	0.97186800	0.19302600
N	2.13435800	2.22246800	0.46097500
C	3.73665600	4.04931100	-0.14145400
H	3.78650800	4.33839900	0.91222300
H	4.75706300	4.08424100	-0.52973600
C	2.84685600	5.04196200	-0.90775800
H	3.23517100	6.05734600	-0.80162100
H	2.81432000	4.79800000	-1.97244500
H	1.82444300	5.02615100	-0.52362900
C	3.72937600	1.57455400	-0.94341900
H	4.57480400	1.48374300	-1.60141100
Re	0.42807200	-0.48744600	0.79390700
C	1.41111000	-1.01597200	2.36578400
C	-0.83591300	-1.91476000	1.06019800
C	-0.67376100	0.69662100	1.83185000
O	1.97944600	-1.34123200	3.31880500
O	-1.31814500	1.43829000	2.43630400

O	-1.58436300	-2.78354200	1.19076900
S	-0.74377600	0.19924200	-1.39799900
C	-2.51946700	0.22080900	-1.12542300
C	-3.30775400	-0.90752000	-1.40628200
C	-3.17223000	1.37497900	-0.68265900
C	-4.68614000	-0.88085400	-1.24472500
H	-2.83179400	-1.81618800	-1.75551100
C	-4.55839400	1.41540600	-0.51456000
H	-2.59228500	2.26345900	-0.46262200
C	-5.32549500	0.28174200	-0.79563000
H	-5.28923500	-1.75477700	-1.46316200
H	-5.01966900	2.33086100	-0.16884300
N	2.88727500	0.54144500	-0.66616800
C	3.24167900	2.63975200	-0.22106800
O	-6.68350800	0.20846300	-0.66980500
C	-7.38446600	1.36363600	-0.21194900
H	-8.43555000	1.08240500	-0.18586800
H	-7.06173400	1.65410400	0.79286700
H	-7.25208600	2.20833000	-0.89546800

Table S9. Cartesian coordinates of the optimized geometry of complex **2d'** at the B3LYP level of theory.

Atom	X	Y	Z
C	2.15006000	-2.84174300	-0.86517700
C	3.24693100	-0.82859400	-1.08596000
C	4.18775400	-1.36714400	-1.95387900
C	4.07944200	-2.71345600	-2.27314000
C	3.04416300	-3.46324300	-1.72027500
H	1.33216600	-3.38605400	-0.41584600
H	4.97770800	-0.75706000	-2.36689600
H	4.79548700	-3.16743500	-2.94583900
H	2.92586600	-4.51421400	-1.94518800
N	2.24214100	-1.53676200	-0.54156100
N	2.32511500	0.99129400	0.14597100
N	2.53520200	2.24920100	0.37229600
C	4.13934700	4.05040400	-0.29697400
H	4.18410900	4.37697700	0.74585000
H	5.16195400	4.06807700	-0.68051600
C	3.25679200	5.01714100	-1.10378700
H	3.64759100	6.03457700	-1.03223300
H	3.22949200	4.73488300	-2.15910500
H	2.23222400	5.01806400	-0.72506400
C	4.12077100	1.55058300	-1.01825300
H	4.96308700	1.43538500	-1.67642700
Re	0.83091100	-0.44548300	0.81366900
C	1.83351800	-0.91855800	2.38872300
C	-0.42666200	-1.86505300	1.15092200
C	-0.25350400	0.77380500	1.83054000
O	2.41609100	-1.21008100	3.34328600
O	-0.88512000	1.53515800	2.42310900
O	-1.17027200	-2.72965100	1.32509100
S	-0.36534500	0.15942900	-1.39628100
C	-2.12882500	0.14030500	-1.09538300
C	-2.89147900	-1.00421900	-1.38107400
C	-2.79476600	1.28400100	-0.62522700
C	-4.26739900	-1.00565000	-1.19703400
H	-2.39575900	-1.89423900	-1.74892600
C	-4.17145200	1.28361200	-0.43955100
H	-2.22413800	2.17808000	-0.40651100
C	-4.92408400	0.13650700	-0.72338300
H	-4.84959000	-1.89177100	-1.41853100

H	-4.66746900	2.17406100	-0.07607700
C	-6.39739400	0.08192400	-0.54449700
O	-7.08375500	-0.89318300	-0.77664900
O	-6.90800300	1.24263600	-0.09084600
C	-8.33483900	1.27572700	0.11047400
H	-8.55267200	2.27534600	0.47784600
H	-8.85659400	1.09249300	-0.82954300
H	-8.63371500	0.52582800	0.84366100
N	3.27686600	0.53012000	-0.70383500
C	3.64006300	2.64054300	-0.32829400

Table S10. Cartesian coordinates of the optimized geometry of complex **2e'** at the B3LYP level of theory.

Atom	X	Y	Z
C	-1.76232500	-2.53124600	1.62379300
C	-2.81258500	-0.48568300	1.48583400
C	-3.61915600	-0.75732500	2.58255300
C	-3.46825500	-1.98637300	3.20960200
C	-2.52535100	-2.88805900	2.72261200
H	-1.01894800	-3.20065200	1.21601000
H	-4.33938900	-0.03424300	2.93628200
H	-4.07995200	-2.23294200	4.06771800
H	-2.37756200	-3.85462100	3.18407400
N	-1.89744300	-1.34352900	1.00119900
N	-2.07692700	0.94010100	-0.27707700
N	-2.31801500	2.10935900	-0.77916600
C	-3.81236100	4.07429800	-0.36609600
H	-4.01702300	4.13004200	-1.43901400
H	-4.76412900	4.22591000	0.14799900
C	-2.81780700	5.17864500	0.02833800
H	-3.21643300	6.15931300	-0.24057300
H	-2.62867100	5.16990800	1.10453500
H	-1.86351900	5.04579800	-0.48622200
C	-3.68778600	1.83137600	0.94768900
H	-4.42756100	1.91116900	1.72394200
Re	-0.70004400	-0.67318600	-0.76883700
C	-1.93955200	-1.47666200	-2.01120200
C	0.46057900	-2.20454400	-0.92637700
C	0.19234700	0.22153500	-2.22069300
O	-2.66248800	-1.96724100	-2.76446100
O	0.69519100	0.79444100	-3.08530600
O	1.13442100	-3.13834700	-0.99017100
S	0.73512300	0.42341300	1.06056400
C	2.47521500	0.43534300	0.79729900
C	3.27914800	0.99297800	1.82011400
C	3.12420100	-0.06303400	-0.35072000
C	4.65409100	1.04889300	1.70504400
H	2.80412200	1.38298800	2.71212200
C	4.50223800	-0.01180900	-0.47446700
H	2.54483600	-0.49311000	-1.15371400
C	5.26549400	0.54342600	0.55324200
H	5.26167100	1.47540900	2.49075800
H	4.99332200	-0.39586600	-1.35763800
N	6.70959800	0.59722200	0.42528300
O	7.36191300	1.09873500	1.34342100
O	7.22715100	0.13955800	-0.59579000
N	-2.89672600	0.73668800	0.78443400
C	-3.31185400	2.69977200	-0.05269500

Table S11. Selected predicted bond lengths in complexes **1-2 a-e**.

	C(1)−O(1)	C(2)−O(2)	C(3)−O(3)	Re(1)−C(1)	Re(1)−C(2)	Re(1)−C(3)	Re(1)–N(1)	Re(1)–(N2)
1a	1.153	1.153	1.157	1.925	1.929	1.909	2.243	2.176
1b	1.155	1.155	1.157	1.921	1.925	1.924	2.254	2.185
1c	1.155	1.155	1.157	1.921	1.924	1.925	2.253	2.186
1d	1.154	1.155	1.155	1.923	1.926	1.927	2.253	2.184
1e	1.154	1.155	1.155	1.924	1.927	1.927	2.252	2.183
2a	1.151	1.152	1.156	1.927	1.930	1.912	2.231	2.169
2b	1.153	1.154	1.156	1.922	1.925	1.927	2.240	2.179
2c	1.154	1.154	1.156	1.922	1.925	1.928	2.240	2.178
2d	1.153	1.154	1.156	1.923	1.926	1.926	2.240	2.178
2e	1.153	1.153	1.154	1.925	1.928	1.930	2.240	2.177

(1) refers to the CO trans to pyridine, (2) to the CO trans to triazole and (3) to the CO trans to axial ligand, N(1) refers to pyridine and N(2) to triazole ring.

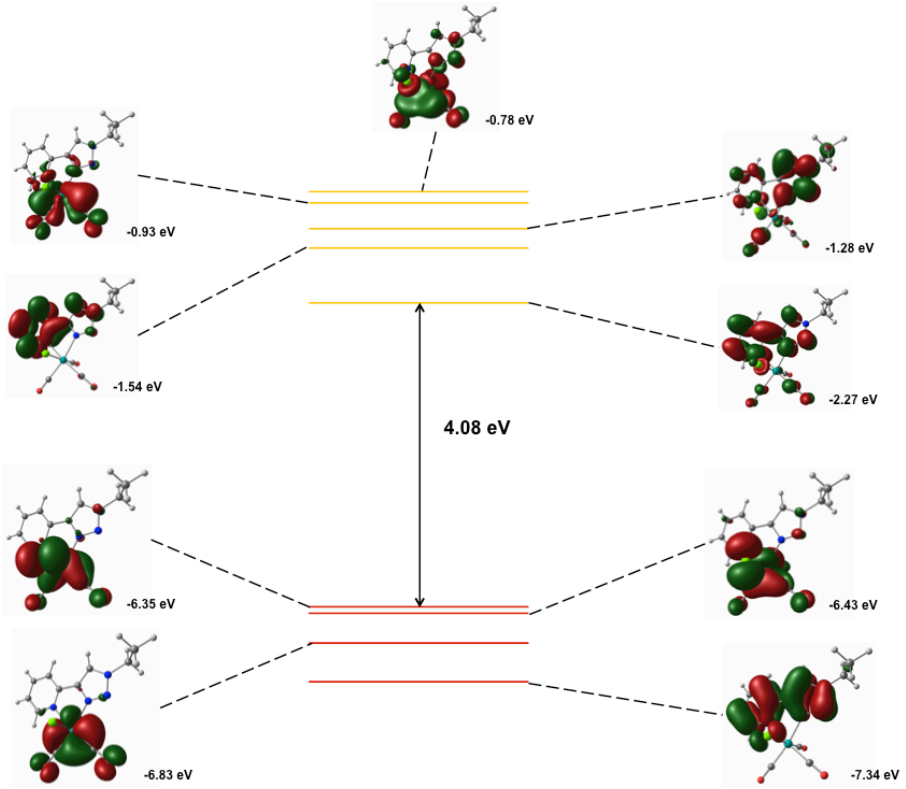

Figure S22. Molecular orbitals diagram for complex **1a'**.

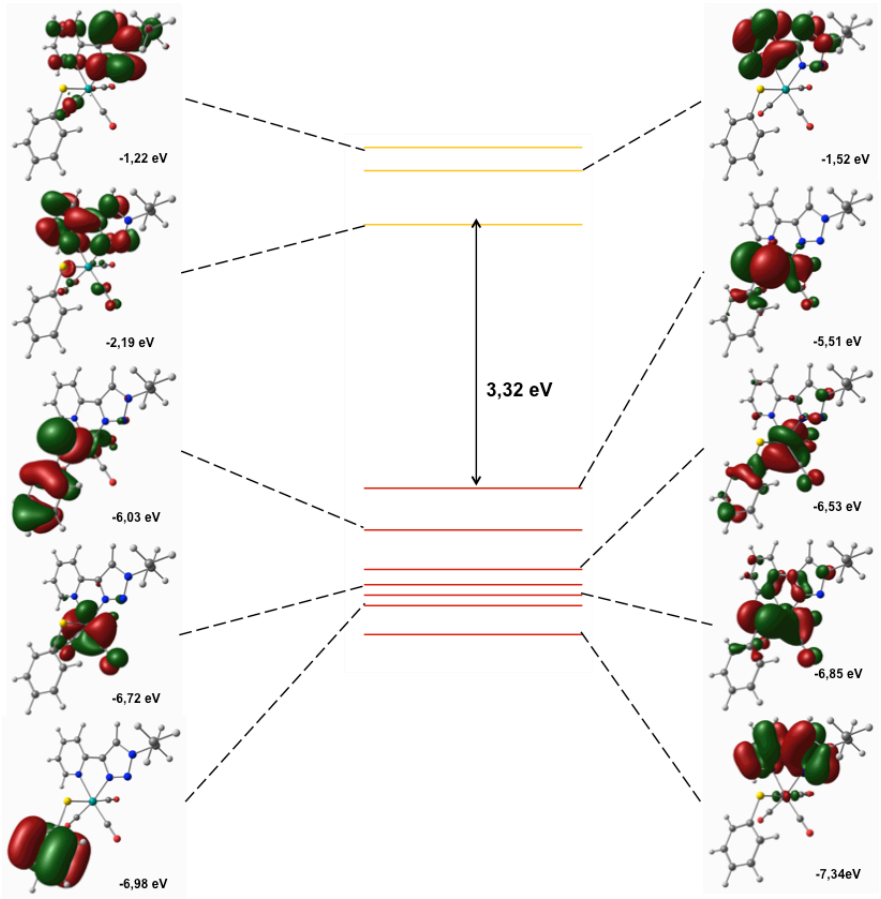

Figure S23. Molecular orbitals diagram for complex **1b'**.

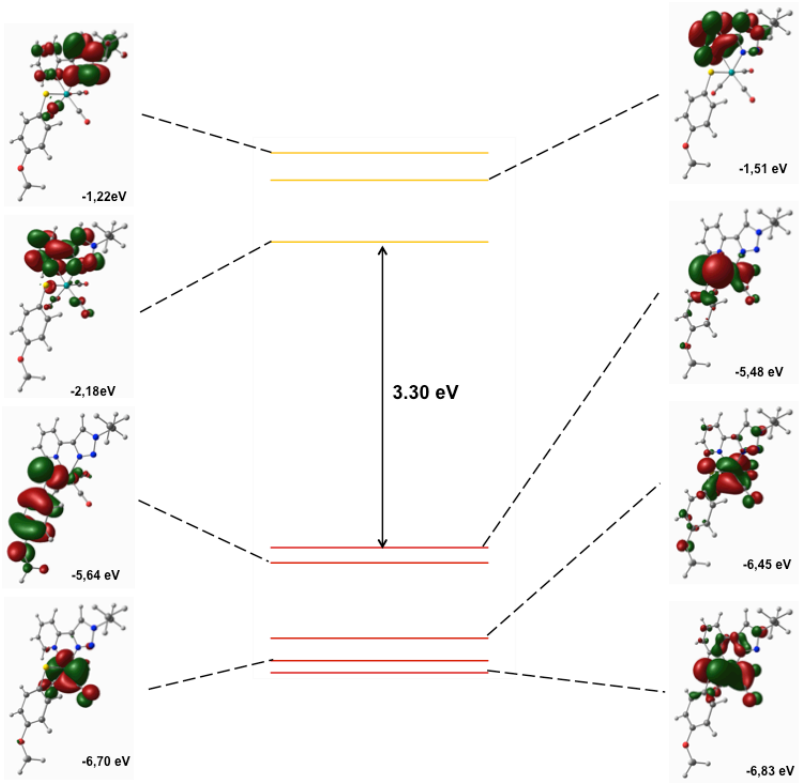

Figure S24. Molecular orbitals diagram for complex **1c'**.

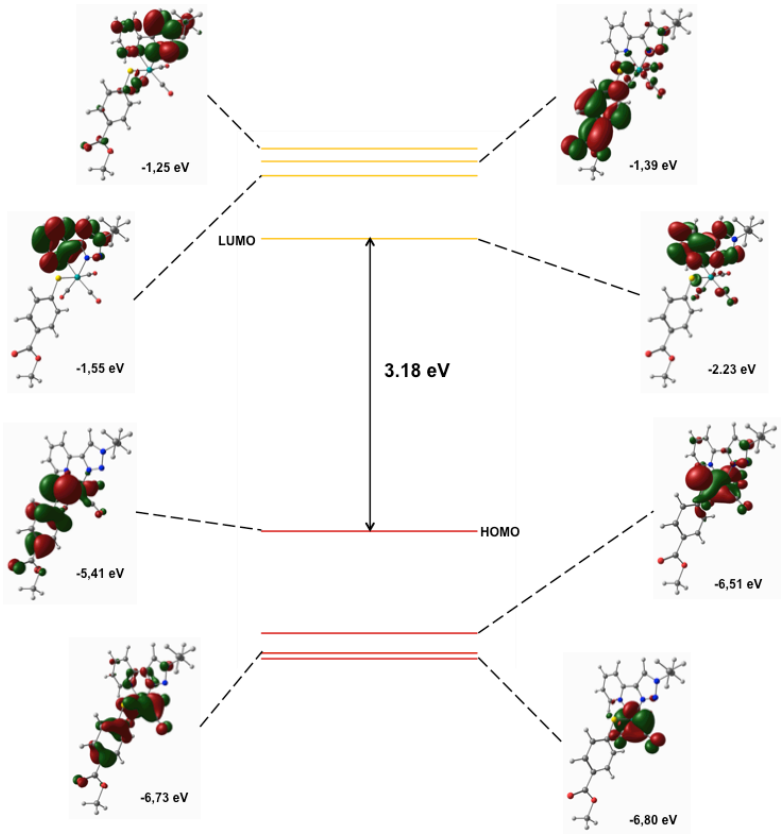

Figure S25. Molecular orbitals diagram for complex **1d'**.

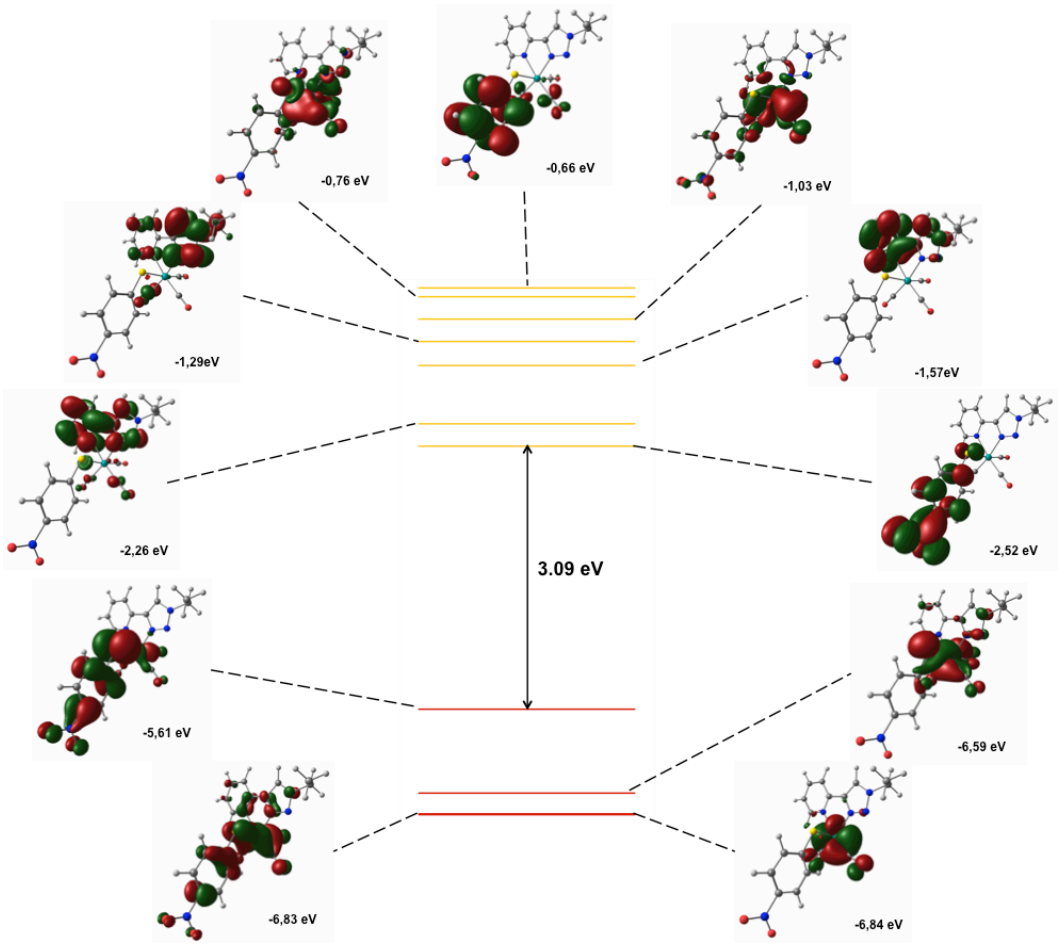

Figure S26. Molecular orbitals diagram for complex **1e'**.

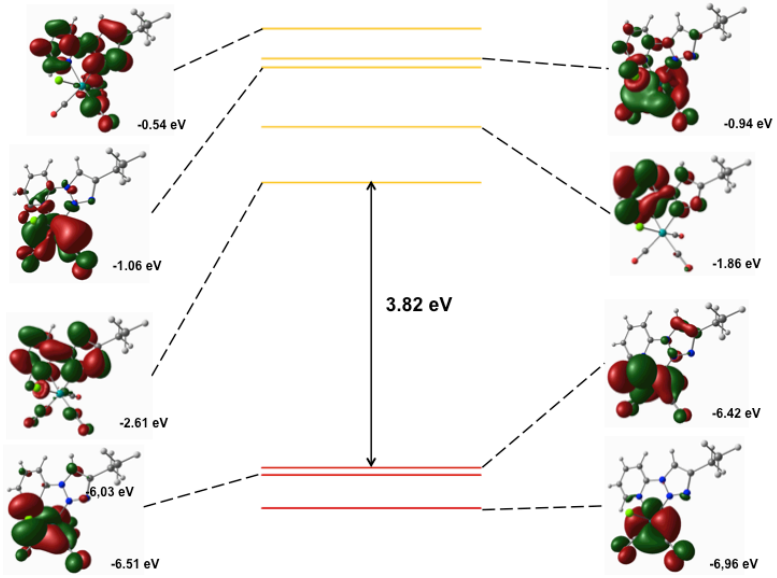

Figure S27. Molecular orbitals diagram for complex **2a'**.

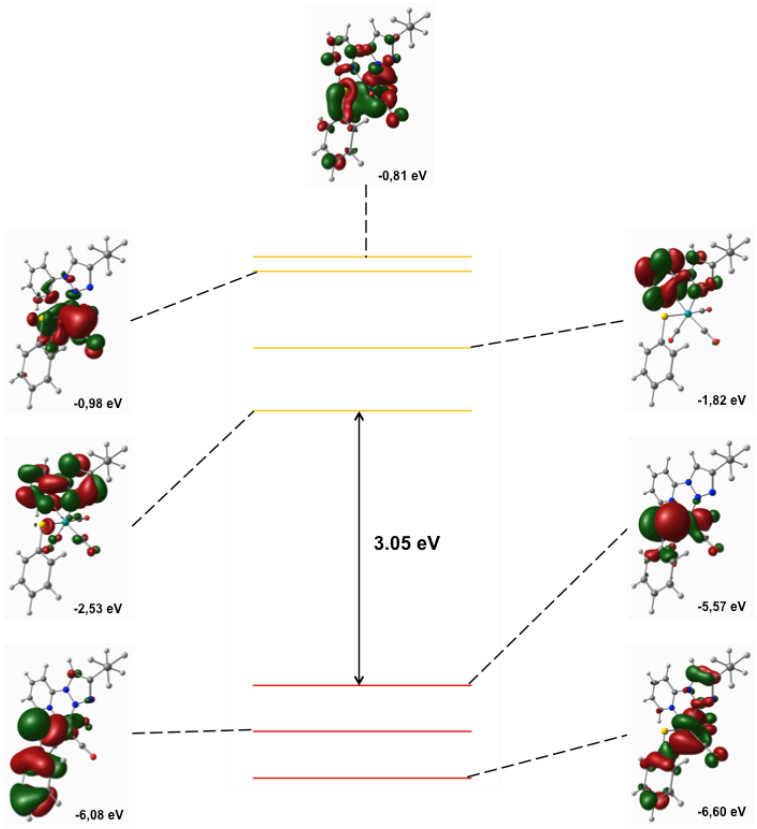

Figure S28. Molecular orbitals diagram for complex **2b'**.

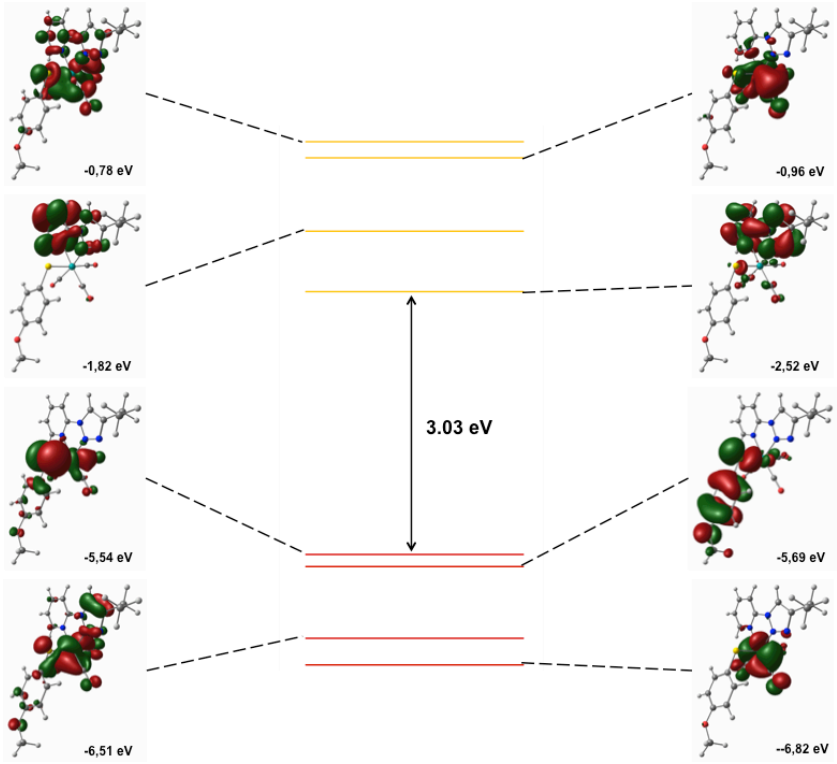

Figure S29. Molecular orbitals diagram for complex **2c'**.

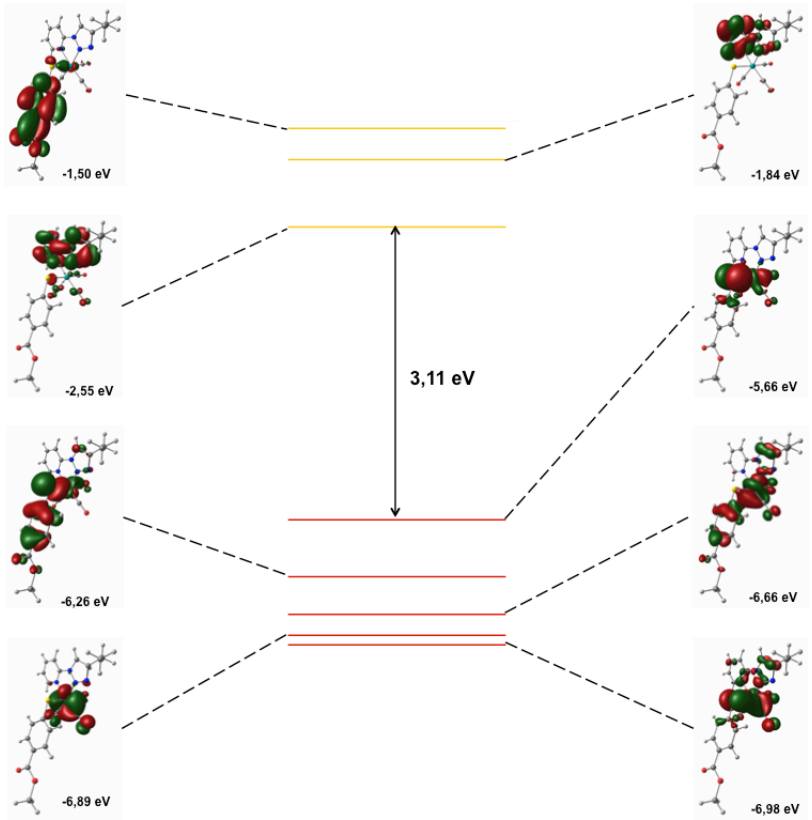

Figure S30. Molecular orbitals diagram for complex **2d'**.

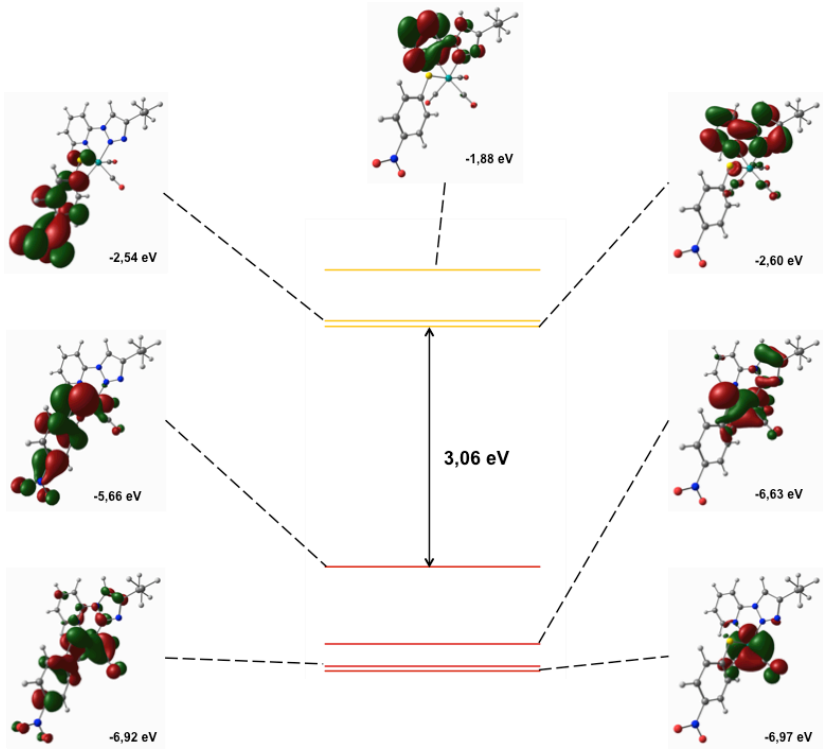

Figure S31. Molecular orbitals diagram for complex **2e'**.

TD-DFT

Table S12. Predicted transitions for complex **1b**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.9106	648.93	0.0006
S2	H → L+1	3.0253	409.82	0.0026
S3	H-1 → L H →L+2	3.1414	394.68	0.0698
S4	H-2 → L H-1 → L H → L+2	3.1695	391.18	0.0967
S5	H-2 → L	3.3199	373.46	0.0238
S6	H-3 → L	3.3441	370.75	0.0034
S7	H → L+3	3.4382	360.61	0.1588
S8	H-2, H → L+4	3.6802	336.89	0.0098
S9	H-5 → L	3.9100	317.10	0.0454
S10	H-6 → L	4.0514	306.01	0.0002

Table S13. Predicted transitions for complex **1c**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.6685	743.10	0.0004
S2	H → L+1	2.7766	446.53	0.0013
S3	H →L+2	2.9035	427.01	0.0046
S4	H-2 → L H-1 → L	3.1395	394.92	0.0345
S5	H-2, H-1 → L	3.1873	388.99	0.1318
S6	H → L+3	3.2042	386.94	0.1417
S7	H-3 → L	3.3764	367.21	0.0077
S8	H → L+4	3.4275	361.74	0.0047
S9	H-5, H-4 → L H-1 → L+5	3.8229	324.32	0.0178
S10	H-5, H-4 → L H-1 → L+5	3.8623	321.01	0.0793

Table S14. Predicted transitions for complex **1d**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	2.0581	602.41	0.0008
S2	H-1 → L H → L+1 H → L+2	3.1717	390.91	0.1667
S3	H-1 → L H → L+1	3.1829	389.53	0.0994
S4	H-2 → L H-1 → L H → L+2 H → L+3	3.3032	375.34	0.0432
S5	H-3, H-2 → L H → L+3	3.3425	370.93	0.0484
S6	H-1 → L H → L+2, L+3, L+4	3.3627	368.70	0.5198

S7	H-3, H-2 → L H → L+2	3.3978	364.89	0.0111
S8	H → L+2, L+3, L+4, L+5	3.7231	333.01	0.0776
S9	H-2 → L+5 H → L+4, L+5	3.8308	323.65	0.0195
S10	H-5 → L H → L+6	4.0210	308.34	0.0260

Table S15. Predicted transitions for complex **1e**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	2.1753	569.97	0.0015
S2	H → L+1	2.5934	478.07	0.5946
S3	H-2, H-1 →L	3.2120	386.00	0.1156
S4	H → L+2	3.3086	374.73	0.0085
S5	H-3, H-2, H-1 → L	3.3412	371.08	0.0211
S6	H-3 → L H → L+3	3.4326	361.19	0.0239
S7	H-3, H-2 → L H → L+3	3.4965	354.60	0.0160
S8	H-1 → L+1	3.5387	350.36	0.0027
S9	H → L+4, L+5	3.6881	336.17	0.0384
S10	H-3, H-2 → L+1	3.7975	326.49	0.0019

Table S16. Predicted transitions for complex **2b**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.6302	760.54	0.0005
S2	H → L+1	2.7504	450.79	0.0031
S3	H-1 →L	2.9234	424.11	0.2004
S4	H-2 → L	3.0686	404.05	0.0061
S5	H-3 → L	3.1545	393.04	0.0043
S6	H → L+2	3.3849	366.29	0.1582
S7	H → L+3, L+4	3.6057	343.85	0.0015
S8	H-5 → L	3.6483	339.84	0.0536
S9	H-4 → L	3.7278	332.59	0.0000
S10	H → L+3, L+4	3.8557	321.56	0.0253

Table S17. Predicted transitions for complex **2c**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.3671	906.90	0.0001
S2	H → L+1	2.4844	499.06	0.0024
S3	H-2, H-1 →L	2.8860	429.61	0.0565
S4	H-2, H-1 →L	2.9377	422.05	0.1502
S5	H-3 → L H → L+2	3.1286	396.29	0.1158
S6	H-3 → L H → L+2	3.1793	389.98	0.0160

S7	H → L+3, L+4	3.3249	372.90	0.0009
S8	H-5 → L H → L+4	3.5643	347.85	0.0399
S9	H-5 → L H → L+3, L+4	3.6161	342.87	0.0341
S10	H-6, H-4 → L	3.7404	331.48	0.0003

Table S18. Predicted transitions for complex **2d**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.7829	695.42	0.0009
S2	H-1 → L H → L+1	2.9024	427.17	0.0334
S3	H-1 → L H → L+1	2.9564	419.38	0.2228
S4	H-2 → L H → L+1	3.1356	395.41	0.0018
S5	H-3, H-2 → L	3.1613	392.19	0.0158
S6	H → L+2, L+3	3.3564	369.40	0.5854
S7	H-5 → L H → L+2, L+3	3.7084	334.33	0.0879
S8	H → L+3, L+4, L+5	3.7416	331.37	0.0019
S9	H-5 → L H → L+2, L+3, L+5	3.7835	327.69	0.0933
S10	H-4 → L	3.9119	316.94	0.0000

Table S19. Predicted transitions for complex **2e**

State	Excitations	Ecal /eV	λcal /nm	*f*
S1	H → L	1.9095	649.29	0.0015
S2	H-1 → L H → L+1	2.6446	468.82	0.6489
S3	H-1 → L H → L+2	2.9758	416.64	0.0965
S4	H-1 → L H → L+2	3.0565	405.64	0.0498
S5	H-3, H-2 → L	3.1527	393.26	0.0093
S6	H-3, H-2 → L	3.2461	381.95	0.0055
S7	H-1 → L+1	3.5967	344.72	0.0008
S8	H-4 → L H → L+3	3.6774	337.15	0.0376
S9	H-4 → L H-2 → L+1 H → L+4, L+5, L+6	3.8361	323.20	0.0074
S10	H-4 → L H-2 → L+1 H → L+4, L+6	3.8525	321.83	0.0348