Supporting Information

Tetrathiafulvalene Derivatives as Cation Sensor: Density Functional Theory Investigation of the Hyper-Rayleigh Scattering First Hyperpolarizability

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Table S1. Comparison of basis set effects on the dynamic HRS first hyperpolarizability of the ligand **5**

Ligand	Basis set	β_{HRS}
5	6-31G(d)	2.01
	6-31+G(d)	1.99
	6-31++G(d)	2.16
	6-311++G(d,p)	2.06
	aug-cc-pVDZ	2.14

Table S2 Average bond length of the key bond and dihedral angles of experimental and the calculated parameters

Bond(Å)							
Bond	Ni-S1	Ni-S2	Ni-Cl1	Ni-Cl2	Ni-N1	Ni-N2	R
Experimental	2.403	2.418	2.345	2.368	2.094	2.097	2.288
Theoretical	2.544	2.542	2.413	2.415	2.161	2.161	2.373

Dihedral Angles(°)		
	∠C1-C6-C7-C8	∠C10-C11-C12-C14
Experimental	172.17°	177.30°
Theoretical	163.78°	167.33°

Table S3. The static HRS first hyperpolarizability ($\beta_{HRS}(0)$) and TDDFT result for the ligand **1** and corresponding metal complexes

Compounds	$\beta_{HRS}(0)$	Excited	E/(eV)	λ/nm	f_{os}	Major Contributions
1	34.44	1	3.20	388.0	0.7360	HOMO→LUMO (+89%)
Cu^{2+}	15.10	1	0.91	1369.	0.0030	*β*HOMO-2→LUMO(+41%)
Ni^{2+}	14.44	13	3.25	381.6	0.6245	*β*HOMO- *a*HOMO→LUMO (+37%) *β*HOMO→LUMO (+35%)
Cd^{2+}	33.36	1	3.25	381.9	0.8180	HOMO→LUMO+1(+80%
Zn^{2+}	33.30	1	3.24	383.2	0.8021	HOMO→LUMO (+83%)
Mg^{2+}	15.21	1	3.24	382.9	0.8120	HOMO→LUMO (+86%)

Table S4. The static HRS first hyperpolarizability ($\beta_{HRS}(0)$) and TDDFT result for the ligand **2** and corresponding metal complexes

Compounds	$\beta_{HRS}(0)$	Excited state	E/(eV)	λ/nm	f_{os}	Major Contributions
2	17.62	1	2.99	414.6	0.5667	HOMO→LUMO(+89%)
Cu^{2+}	19.30	1	0.92	1348.7	0.0030	*β*HOMO-3→LUMO(+45%) *β*HOMO-36→LUMO(+28%)
Ni^{2+}	19.22	2	0.82	1506.2	0.0683	HOMO→LUMO (+75%)
Cd^{2+}	19.58	1	2.96	419.2	0.5143	HOMO→LUMO(+90%)
Zn^{2+}	19.49	1	2.96	418.6	0.5209	HOMO→LUMO(+90%)
Mg^{2+}	20.27	1	2.96	419.5	0.5080	HOMO→LUMO(+90%)

Table S5. The static HRS first hyperpolarizability ($\beta_{HRS}(0)$) and TDDFT result for the ligand **3** and corresponding metal complexes

Compounds	$\beta_{HRS}(0)$	Excited state	*E(*ev)	*λ/nm*	f_{os}	Major Contributions
3	31.52	1	2.86	432.8	1.4279	HOMO→LUMO(+84%)
Ni^{2+}	13.89	13	2.96	419.4	0.6673	*a*HOMO-1→LUMO *β*HOMO→LUMO (+30%)

Cu^{2+}	14.95	17	2.97	417.8	0.7249	*β*HOMO→LUMO+1(+28) *a*HOMO→LUMO(+28%)
Cd^{2+}	13.88	1	2.97	418.0	0.6987	HOMO→LUMO(+59%) HOMO-1→LUMO+3(+16%)
Zn^{2+}	15.32	1	2.96	418.9	0.6842	HOMO→LUMO (+57%)
Mg^{2+}	14.42	1	2.96	419.0	0.6691	HOMO→LUMO (+58%)

Table S6. The static HRS first hyperpolarizability ($\beta_{HRS}(0)$) and TDDFT result for the ligand **4** and corresponding metal complexes

Compounds	$\beta_{HRS}(0)$	Excited	*E(*ev)	*λ/nm*	f_{os}	Major Contributions
4	5.48	1	3.06	405.4	0.6358	HOMO→LUMO(+96%)
Ni^{2+}	4.79	9	3.02	410.1	0.6868	*β*HOMO→LUMO(+48%)
Cu^{2+}	11.52	1	0.89	1396.	0.0028	*β*HOMO-2→LUMO(+47%) *β*HOMO-
Cd^{2+}	11.42	1	3.06	405.2	0.6826	HOMO→LUMO(+97%)
Zn^{2+}	11.47	1	3.07	404.4	0.6898	HOMO→LUMO(+97%)
Mg^{2+}	10.66	1	3.06	405.8	0.6880	HOMO→LUMO(+97%)

Table S7. The static HRS first hyperpolarizability ($\beta_{HRS}(0)$) and TDDFT result for the ligand **6** and corresponding metal complexe

Compounds	$\beta_{HRS}(0)$	Excited	*E(*ev)	*λ/nm*	f_{os}	Major Contributions
6	5.48	7	4.83	256.8	0.3591	HOMO→LUMO+7(+33%
Ni^{2+}	4.79	27	4.28	290.0	0.1293	*β*HOMO→LUMO+8 *β*HOMO→LUMO+10 *a*HOMO→LUMO+9 *a*HOMO→LUMO+7(+13
Cu^{2+}	2.93	1	0.43	2878.	0.0008	*β*HOMO- *β*HOMO-
Cd^{2+}	1.78	9	4.88	254.3	0.5798	HOMO→LUMO+7(+48% HOMO-1→LUMO+3
Zn^{2+}	1.81	9	4.88	254.3	0.5774	HOMO→LUMO+7 HOMO-1→LUMO+3
Mg^{2+}	2.25	8	4.86	255.0	0.2871	HOMO→LUMO+7 HOMO-7→LUMO

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C	1.73003700	1.18921800	-0.32114300
C	3.84831600	0.17084500	0.78491600
C	6.50116700	0.15035300	1.20377800
H	6.40008300	1.22701300	1.04568400
H	7.30624100	-0.02126400	1.92585500
C	6.82799400	-0.58178600	-0.08996800
H	7.08056800	-1.62388600	0.11802300
H	7.68363100	-0.10211400	-0.57792700
C	4.10303200	0.14260100	-0.54014000
C	0.42438300	1.41627000	-0.57698500
C	-1.93598700	1.25494700	-1.71220700
C	-2.18863600	1.29450500	-0.38006100
C	-2.55586300	-0.53884200	-3.78087700
H	-1.59722400	-0.35293000	-4.27106900
H	-2.43412200	-1.28062200	-2.99102000
C	-3.60190300	-0.99861600	-4.76264900
C	-3.64379600	-0.48564300	-6.06572000
H	-2.90611800	0.24440500	-6.38609100
C	-4.63996800	-0.92649300	-6.93408000
H	-4.69291400	-0.54585100	-7.95040500
C	-5.56249400	-1.86458500	-6.47408100
H	-6.35590400	-2.23964100	-7.11326800
C	-5.44153100	-2.31721800	-5.15968200
H	-6.14149400	-3.05111500	-4.76392700
C	-3.62863400	-0.29576900	1.45266100
H	-2.85196700	-0.13801500	2.20360300
H	-4.59376700	-0.31107500	1.97522100
C	-3.37396500	-1.62046700	0.75992200
C	-3.92498200	-1.95173400	-0.48361300
H	-4.53023000	-1.23508700	-1.02860700
C	-3.65839000	-3.20876700	-1.02310800
H	-4.05757400	-3.46651100	-1.99987500
C	-2.85988100	-4.09541500	-0.30035400
H	-2.62101100	-5.08383100	-0.68185700
C	-2.35896200	-3.67382100	0.93092700

H	-1.72579300	-4.33137200	1.52483700
N	-4.49199100	-1.90092500	-4.31440200
N	-2.59839400	-2.46607000	1.45604800
S	2.41502600	1.08611400	1.31966900
S	4.95541600	-0.45407000	2.00611600
S	5.46402300	-0.62446700	-1.35880000
S	2.96532300	1.02276900	-1.59616900
S	-0.25190400	1.57525900	-2.21542000
S	-0.80480600	1.65766600	0.68635600
S	-3.14069700	1.04824800	-2.98734800
S	-3.78787400	1.19003700	0.36503300

Ni^{2+}

Ni	-5.78744300	-0.48470500	-1.04018400
Cl	-7.03040500	-1.13516400	-2.93971200
Cl	-7.17263800	-0.46746300	0.87470400
S	-3.93039600	0.26915800	0.61856100
S	-0.94501000	0.77435800	0.42405300
S	2.36156000	0.63504900	0.49349100
S	5.01283500	-0.69276700	0.93080200
S	5.20527600	-0.84813600	-2.47897400
S	2.42652400	0.40145600	-2.46296100
S	-0.89179400	0.56566600	-2.54361600
S	-3.80780100	-0.31308500	-2.73376000
N	-5.95960200	1.60573300	-1.54682900
N	-4.97811500	-2.41625100	-0.52463600
C	-6.72814100	2.40674800	-0.79011800
H	-7.26175500	1.90656300	0.01261100
C	-6.82430700	3.77852300	-1.01412400
H	-7.46107100	4.38427600	-0.37804000
C	-6.08251500	4.34002200	-2.05018500
H	-6.11892200	5.40785900	-2.24677300
C	-5.28818800	3.50695800	-2.83662900
H	-4.70137500	3.90780400	-3.65745300
C	-5.26198200	2.13624200	-2.56918300
C	-4.51396600	1.20867400	-3.49773800
H	-3.73926700	1.74050400	-4.05504500
H	-5.22474400	0.76931300	-4.20844200
C	-2.44531500	0.25242900	-1.73726400
C	0.06234700	0.61170200	-1.03831400
C	1.41032000	0.54462000	-1.00959900

C	3.78343300	-0.17279600	-0.22061600
C	6.59646300	-0.61767100	-0.04657500
H	7.29304000	-0.02299200	0.55458600
H	6.96854100	-1.64285300	-0.10505000
C	6.48096800	-0.01713900	-1.44044600
H	7.43206700	-0.14822400	-1.96692500
H	6.24696700	1.04982600	-1.40486700
C	3.81014400	-0.27821300	-1.56620500
C	-2.46393700	0.33778300	-0.38406800
C	-3.86809300	-1.39004200	1.41727100
H	-2.92948800	-1.50244900	1.96485300
H	-4.69512600	-1.31250500	2.13338900
C	-4.11875000	-2.56564500	0.50130700
C	-3.52343100	-3.79786600	0.78029700
H	-2.82091700	-3.88342300	1.60362800
C	-3.85250500	-4.90613600	0.00107800
H	-3.40263300	-5.87335400	0.20671600
C	-4.76357400	-4.74865900	-1.04006100
H	-5.05427900	-5.58138000	-1.67179100
C	-5.29750300	-3.48353500	-1.27540000
H	-5.99569400	-3.28481700	-2.08311000

Cu^{2+}

Cl	-6.68800600	-1.72461100	-2.27806600
Cl	-6.81785800	-0.86868500	1.92967400
S	-3.50797900	-0.17792000	1.39372300
S	-0.51432200	0.25740500	1.19858900
S	2.79517300	0.18159200	1.28225500
S	5.45829000	-1.09833800	1.78928100
S	5.66706300	-1.40525800	-1.60862400
S	2.87431700	-0.18609100	-1.65988900
S	-0.44963300	-0.10497700	-1.75452700
S	-3.37147100	-0.94548300	-1.91631800
N	-5.80790200	0.93753200	-0.73057800
N	-4.93692400	-2.91559200	0.34242600
C	-6.59644000	1.76216900	-0.01968600
H	-7.22872400	1.28020800	0.71762800
C	-6.58299600	3.14462000	-0.18519300
H	-7.24362500	3.76227500	0.41370200
C	-5.69833800	3.69522600	-1.10639400
H	-5.63910400	4.77012300	-1.25187100
C	-4.88553200	2.83889200	-1.84618300

H	-4.19100800	3.23289800	-2.58112000
C	-4.97242200	1.45590900	-1.65943000
C	-4.19711000	0.55727500	-2.59559600
H	-3.47216200	1.14576900	-3.16212700
H	-4.90358900	0.10028000	-3.29864400
C	-2.01326700	-0.34752900	-0.94301100
C	0.49967100	0.03988300	-0.25200300
C	1.84859100	0.00290700	-0.21718300
C	4.22792500	-0.64369900	0.61098200
C	7.04521300	-1.05060800	0.81602200
H	7.73348700	-0.42252700	1.39237500
H	7.42823400	-2.07338800	0.80426600
C	6.92910500	-0.51433000	-0.60383200
H	7.88395400	-0.65758800	-1.12034100
H	6.68276400	0.55040200	-0.61671300
C	4.26121600	-0.81025700	-0.72834100
C	-2.03731300	-0.19389900	0.40449100
C	-3.58678700	-1.85644500	2.14902100
H	-2.65503700	-2.06099900	2.68099900
H	-4.39121900	-1.72367300	2.88165300
C	-3.94116500	-3.02055200	1.25172900
C	-3.28142900	-4.23710300	1.44916100
H	-2.46998400	-4.29046900	2.16786900
C	-3.67754900	-5.36792000	0.73802800
H	-3.17186400	-6.31715400	0.89052900
C	-4.72923600	-5.25359200	-0.16515600
H	-5.08249700	-6.10145400	-0.74217100
C	-5.32315500	-4.00663300	-0.34117000
H	-6.11521800	-3.84633000	-1.06420700
Cu	-5.80545100	-1.08589800	-0.19134700

Cd^{2+}

Cl	-7.03783600	-2.07867100	-2.35883000
Cl	-7.29084400	-0.75001300	1.99545600
S	-3.76247600	-0.30323800	1.45986400
S	-0.78972200	0.17230900	1.23609800
S	2.52145500	0.10749200	1.30745900
S	5.19775900	-1.16288900	1.76755400
S	5.39249400	-1.37791300	-1.63737500
S	2.58967700	-0.18169500	-1.64402500
S	-0.73292400	-0.10339900	-1.72281100
S	-3.63710200	-0.96535900	-1.92227100

N	-5.78431100	1.17987800	-0.81880600
N	-4.79053600	-3.15907200	0.42037400
C	-6.35876300	2.09465300	-0.02167400
H	-7.02781500	1.70128300	0.73947700
C	-6.10184800	3.46057900	-0.13436400
H	-6.59277100	4.16059200	0.53346900
C	-5.19806500	3.88701800	-1.10359600
H	-4.95917200	4.94071400	-1.21686200
C	-4.59596900	2.93678700	-1.92834100
H	-3.88571500	3.23400900	-2.69366800
C	-4.92021400	1.58692500	-1.76849200
C	-4.34267600	0.55416500	-2.70635500
H	-3.60313500	1.00536200	-3.37130500
H	-5.14234300	0.11578200	-3.31656400
C	-2.29209600	-0.39168000	-0.91465100
C	0.22104400	-0.00034700	-0.22133800
C	1.57016500	-0.03463900	-0.19251600
C	3.95760600	-0.68789400	0.60793700
C	6.77970300	-1.07132500	0.78882100
H	7.46321200	-0.45019500	1.37816700
H	7.17427900	-2.08900000	0.74949100
C	6.65083100	-0.50023200	-0.61619800
H	7.60437300	-0.62055600	-1.14085200
H	6.39363100	0.56187700	-0.60062000
C	3.98587300	-0.81865900	-0.73547400
C	-2.31325500	-0.27302800	0.43765300
C	-3.72339300	-1.95876300	2.28095100
H	-2.83891500	-2.03347900	2.91730200
H	-4.61357600	-1.89831300	2.91941900
C	-3.82669500	-3.15326400	1.36143000
C	-2.96430500	-4.24013500	1.52718800
H	-2.18673600	-4.20187800	2.28372900
C	-3.11946000	-5.36563000	0.71787100
H	-2.45864800	-6.21980000	0.83553800
C	-4.12700200	-5.37024500	-0.24287700
H	-4.28365900	-6.21967100	-0.89933800
C	-4.93490200	-4.24012700	-0.36232600
H	-5.71459300	-4.17314800	-1.11695400
Cd	-6.20194000	-1.19880600	-0.19208200

Zn^{2+}

Cl	-6.96220300	-1.86204900	-2.18430000

Cl	-7.11597000	-0.91629900	1.84186400
S	-3.67315400	-0.22906900	1.43193700
S	-0.69772600	0.24512100	1.20526200
S	2.61222600	0.16166400	1.28701600
S	5.27148600	-1.12687600	1.78985500
S	5.47585700	-1.42931800	-1.61012100
S	2.68737700	-0.20098500	-1.65577600
S	-0.63614100	-0.10592600	-1.74597100
S	-3.54361100	-0.96649100	-1.92526100
N	-5.73361000	1.04827800	-0.74529200
N	-4.77923700	-2.99918600	0.35228600
C	-6.38091700	1.92494200	0.04155100
H	-6.99218600	1.48612800	0.82491100
C	-6.26670400	3.30513000	-0.11177900
H	-6.81252400	3.96858100	0.55065300
C	-5.43323400	3.79561600	-1.11278000
H	-5.30380800	4.86449800	-1.25735600
C	-4.76099300	2.88809000	-1.92997000
H	-4.10435200	3.23335400	-2.72242000
C	-4.94341800	1.51686200	-1.73192500
C	-4.29962800	0.53563700	-2.68135400
H	-3.57325000	1.03871500	-3.32338900
H	-5.07236300	0.08061900	-3.31370800
C	-2.19710500	-0.36943100	-0.93339500
C	0.31539600	0.03081500	-0.24531200
C	1.66420500	-0.01066500	-0.21187100
C	4.04201100	-0.66668700	0.61290400
C	6.85730800	-1.08785200	0.81447300
H	7.55027600	-0.46569700	1.39159300
H	7.23354000	-2.11309100	0.79988100
C	6.74305400	-0.54737700	-0.60393600
H	7.69672200	-0.69463200	-1.12147500
H	6.50254400	0.51870700	-0.61413300
C	4.07354100	-0.83081200	-0.72672500
C	-2.21994500	-0.21862600	0.41526200
C	-3.66086100	-1.88327500	2.24254200
H	-2.75789600	-1.99761200	2.84635700
H	-4.52674400	-1.80177900	2.91114900
C	-3.84446100	-3.06616200	1.32123200
C	-3.08752000	-4.22292700	1.52409400
H	-2.32975800	-4.23958900	2.30119400
C	-3.32148300	-5.34449700	0.72974300
H	-2.74260400	-6.25173600	0.87783600
C	-4.30344700	-5.27564500	-0.25438100

H	-4.52310300	-6.11954500	-0.89972300
C	-5.00228300	-4.08084000	-0.41363000
H	-5.75756300	-3.95833100	-1.18467400
Zn	-6.01705400	-1.15338700	-0.18825700

Mg^{2+}

Cl	-6.87119900	-1.82891300	-2.20634500
Cl	-7.03770400	-0.91911200	1.84111500
S	-3.67827600	-0.27149600	1.44541600
S	-0.69914700	0.22039600	1.23402300
S	2.61055800	0.12438100	1.30610200
S	5.27332200	-1.17196000	1.77001600
S	5.46739100	-1.39487900	-1.63552100
S	2.67751500	-0.16939600	-1.64481000
S	-0.64290000	-0.05669500	-1.72690100
S	-3.55396000	-0.92647400	-1.90981000
N	-5.69714800	1.07368300	-0.74115800
N	-4.73469300	-3.01091900	0.34686800
C	-6.37213300	1.94023500	0.03709100
H	-6.95785800	1.49037000	0.83395300
C	-6.31725500	3.32049500	-0.14352400
H	-6.88293100	3.97309200	0.51290600
C	-5.51665500	3.82648100	-1.16359000
H	-5.43432700	4.89695800	-1.32943200
C	-4.81558800	2.93297600	-1.97195100
H	-4.18300900	3.29056100	-2.77836100
C	-4.93869200	1.56014200	-1.74542000
C	-4.26799600	0.58655400	-2.68497400
H	-3.51329800	1.08695600	-3.29579300
H	-5.02128200	0.14301500	-3.34827700
C	-2.19935200	-0.34689800	-0.91644700
C	0.31041100	0.03810800	-0.22377800
C	1.65915200	-0.00959000	-0.19416800
C	4.03923300	-0.68611300	0.60853000
C	6.85637900	-1.10236000	0.79137400
H	7.54762500	-0.48939800	1.38023100
H	7.23776100	-2.12509500	0.75342600
C	6.73540500	-0.53129200	-0.61438600
H	7.68772300	-0.66401800	-1.13826500
H	6.49136200	0.53392900	-0.60029400
C	4.06689000	-0.81899100	-0.73464500
C	-2.21973700	-0.23009600	0.43501000

C	-3.62878300	-1.92411700	2.25913800
H	-2.70940600	-2.02626900	2.83998500
H	-4.47889200	-1.85114500	2.94869200
C	-3.82551700	-3.10637500	1.33907200
C	-3.11333500	-4.28567500	1.56894000
H	-2.37581000	-4.32249500	2.36459400
C	-3.36682300	-5.40442000	0.77663300
H	-2.82356400	-6.32998600	0.94502300
C	-4.32179500	-5.30940000	-0.23167400
H	-4.55476500	-6.15031000	-0.87614800
C	-4.97504900	-4.09302900	-0.41679000
H	-5.70823100	-3.95073900	-1.20591100
Mg	-5.87493400	-1.12431900	-0.19508300