

Supporting Information

Theoretical prediction of spin crossover temperatures in ligand-driven light-induced spin change systems

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S.I.1 Optimized structures for the $[\text{Fe}(\text{stpy})_4(\text{NCX})_2]$ ($\text{X} = \text{S}, \text{Se}, \text{BH}_3$) family with TPSSh functional.

i) $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$ S=2 ($E = -4473.83565915\text{au}$, $\langle S^2 \rangle = 6.0792$, $\nu_1 = 4.3913\text{cm}^{-1}$)

Fe	3.6114766325	1.8131401399	2.234176705
N	5.4747118136	2.1137585148	3.0699006129
N	1.7476915182	1.5145561405	1.4000455961
N	3.6196834936	3.9211450939	1.4555540786
N	3.6024349075	-0.2905655479	3.0025250694
N	2.648525491	2.5369478463	4.1243669073
N	4.5775286532	1.1299269813	0.3300603641
S	8.0391642881	2.5703606071	4.1218373984
S	-0.8259118542	1.0875347782	0.3581290717
C	6.5588651026	2.3061469716	3.5161803841
C	0.6596458278	1.3345829797	0.9580921849
C	2.4661152659	4.5912292216	1.243065273
C	2.4216872322	5.8792977724	0.7443610776
C	3.6144456236	6.5552842356	0.4331601756
C	4.8060409663	5.8495367693	0.665754574
C	4.7707446352	4.5589634928	1.1662369647
C	3.6771236794	7.9087190403	-0.1034371257
C	2.6252111265	8.6808577026	-0.4390831284
C	2.662371973	10.0347996529	-0.9831369908
C	1.4479793838	10.6556629261	-1.3203348492
C	1.4166321801	11.9405332087	-1.8490096444
C	2.6034177094	12.6388654972	-2.0516956573
C	3.8193397723	12.0397345885	-1.7192605773
C	3.8506592582	10.7573171125	-1.1920751116
C	4.2974365796	-0.6348605889	4.1087507777
C	4.3149268124	-1.9186044314	4.6202265687
C	3.5850814778	-2.9392062094	3.985909095
C	2.8660445536	-2.5664871367	2.8387496633
C	2.8988821439	-1.2590738334	2.3841057513
C	3.5346729675	-4.3220020431	4.4426896496
C	4.1903230376	-4.8369904914	5.5011453257

C	4.1508690244	-6.2170216726	5.9753866542
C	4.9212899921	-6.5640211958	7.0977937609
C	4.9251333843	-7.8609390805	7.5975299261
C	4.1556882618	-8.8455856022	6.9847016544
C	3.383619001	-8.5194798621	5.8687414087
C	3.3797519667	-7.225343128	5.3701348411
C	1.4278652331	2.117247158	4.5095221644
C	0.7988310936	2.5904285785	5.6492703094
C	1.4264509814	3.5482079641	6.4621468186
C	2.7043492317	3.9684940164	6.0529872626
C	3.2673839715	3.4513691976	4.902245556
C	0.7408267132	4.04442183	7.6488233841
C	1.1832249223	5.0172843622	8.469092512
C	0.5200278346	5.5443971214	9.6574944063
C	-0.6838846747	5.0311244655	10.1718766901
C	-1.2654517163	5.5832799967	11.3037100182
C	-0.6637002905	6.661229675	11.9546433321
C	0.5300028422	7.1804657043	11.4620259941
C	1.113337142	6.6263152083	10.3290395539
C	3.9713810077	1.3037439853	-0.8604176661
C	4.5557803686	0.9306494725	-2.0590618621
C	5.8327358336	0.3465669218	-2.0762827299
C	6.4494039414	0.1641883011	-0.8260644934
C	5.8023363229	0.56058006	0.3288544431
C	6.4338386971	-0.0240877559	-3.3510517018
C	7.6623047435	-0.5482302559	-3.5287560953
C	8.2891560182	-0.9183422629	-4.7939729885
C	7.6598038318	-0.7789953597	-6.0438450664
C	8.3111114025	-1.1447121262	-7.212396676
C	9.6073339738	-1.660207845	-7.168364532
C	10.245981714	-1.8066843448	-5.9404208343
C	9.5933804032	-1.4400433186	-4.7693879645
H	1.5616340962	4.0484855451	1.4839663839
H	1.4549603033	6.3477236319	0.6057359263
H	5.7650049835	6.309284892	0.4525636036
H	5.677715897	3.9998001824	1.3557828814
H	4.6842983393	8.2934338837	-0.2403805237
H	1.6229082289	8.2785898059	-0.3121169895
H	0.518906969	10.1155775684	-1.1654193386
H	0.4657026641	12.3962920435	-2.1024933515
H	2.5845882085	13.641967338	-2.4631867671
H	4.7478820129	12.5791998595	-1.8720673176
H	4.8074431836	10.3152842825	-0.9381141971
H	4.8551343429	0.1665547496	4.5753022122
H	4.8969555546	-2.1127015898	5.5128603857
H	2.2787037685	-3.3009845073	2.2984144589
H	2.3480015042	-0.9497697681	1.5055743737
H	2.8988378416	-4.9702490816	3.8454736638
H	4.8293381556	-4.181317619	6.0879713031
H	5.5238365012	-5.8004502191	7.5803039856
H	5.5290928025	-8.1023838557	8.4654280853
H	4.1551517969	-9.8588849829	7.3708383417
H	2.7809022161	-9.2814337991	5.3863138275
H	2.770181333	-6.9969925119	4.5031832562
H	0.9566274275	1.3881112238	3.8633042772
H	-0.1871260415	2.2172255613	5.9042507038

H	3.2695340667	4.694262984	6.6247613316
H	4.2513426699	3.7547935219	4.5696186694
H	-0.2176562334	3.5728502637	7.8496560406
H	2.1340021616	5.4938280571	8.2422952358
H	-1.1676135526	4.1905870296	9.6870349643
H	-2.1938769925	5.1712511754	11.684327919
H	-1.1227093127	7.0887372288	12.8392050904
H	1.0078255414	8.0166809692	11.9607170999
H	2.0445861921	7.0355935308	9.949450298
H	2.9871446531	1.7525353762	-0.8237966127
H	4.0180721965	1.097900802	-2.9860813132
H	7.4317735595	-0.2840786832	-0.7416133624
H	6.2600732166	0.4389808326	1.3017508098
H	5.8047020838	0.1616816048	-4.2175219876
H	8.2852041127	-0.7226785533	-2.6546913421
H	6.6529066796	-0.3817325361	-6.103903479
H	7.8071979014	-1.0285743117	-8.1658951113
H	10.1122793081	-1.9445738453	-8.0849246761
H	11.2532459329	-2.2060903395	-5.8939850656
H	10.097188301	-1.555318941	-3.8145019563

ii) [Fe(stpy)₄(NCS)₂] S=0 (E = -4473.84610296au , <S²> = 0.00, v₁ = 5.5755cm⁻¹)

Fe	3.5811061289	1.8361337056	2.1682941763
N	5.3355602122	2.1183557094	2.9470198005
N	1.8270558787	1.5502752957	1.3955637541
N	3.5930397643	3.7041612366	1.456456888
N	3.5717371456	-0.0308485411	2.8727599111
N	2.7342501061	2.4914469265	3.853651301
N	4.436599253	1.1996768584	0.4790735162
S	7.8850888152	2.5403216652	4.0603393766
S	-0.7281669116	1.1055498796	0.3043846954
C	6.4081765168	2.2952773034	3.4166235101
C	0.7517825921	1.3630897289	0.9360830552
C	2.4569923502	4.4423377466	1.3987010204
C	2.423869923	5.732747402	0.9103412782
C	3.5984441453	6.3458332304	0.4409190878
C	4.766960616	5.5707051467	0.5121372434
C	4.7322290601	4.2821565406	1.0123092578
C	3.6643771204	7.6975354377	-0.0962680979
C	2.6195524811	8.523744111	-0.3014514876
C	2.661401329	9.8798751772	-0.8390052321
C	1.4475112493	10.5487981314	-1.0695077287
C	1.4214492721	11.8383838539	-1.5868276998
C	2.613080241	12.4938305087	-1.8829269683
C	3.8288322956	11.8472965111	-1.6551885207
C	3.8549228051	10.55989485	-1.1401308515
C	4.1172792603	-0.3317346729	4.0771049953
C	4.1399903083	-1.6119360112	4.591859493
C	3.583772575	-2.6800952366	3.866796749
C	3.0202723133	-2.3516536282	2.6235247648
C	3.0298349958	-1.0474016478	2.1643988638
C	3.5623148059	-4.0631730583	4.3212777108
C	4.0715597914	-4.5291168073	5.4787360623
C	4.0625992016	-5.9090808613	5.9535753497

C	4.6682631785	-6.1979390661	7.1879479559
C	4.6935202574	-7.4920832114	7.6939584391
C	4.1111303853	-8.5320980864	6.9754234286
C	3.5042041088	-8.2642104532	5.7475014372
C	3.4791276332	-6.9728295245	5.2424028422
C	1.5886800811	1.9566401256	4.3335510911
C	0.9861268686	2.4081752251	5.4939738745
C	1.5499238582	3.4592091733	6.2349658777
C	2.7412351206	4.0023747467	5.7231643331
C	3.2909744389	3.5067168722	4.5591417092
C	0.8934499484	3.9168249359	7.4516488561
C	1.3227931181	4.9075551555	8.2579500191
C	0.6901534785	5.3938490319	9.4795385996
C	-0.4979157419	4.8599967912	10.0098489395
C	-1.0483670034	5.3721382911	11.1754627096
C	-0.4311353199	6.4300004201	11.8447217419
C	0.7458529726	6.9707286139	11.3353390213
C	1.2976717118	6.4572169277	10.1680022163
C	3.8987791126	1.4764235859	-0.730565973
C	4.4931025707	1.0851716479	-1.9163448145
C	5.7048648682	0.3759249221	-1.9126852595
C	6.2399844337	0.0784706488	-0.6474134689
C	5.5954251438	0.4959763946	0.4991310635
C	6.326283437	0.0038857108	-3.1760257375
C	7.5430501597	-0.5561890632	-3.3250323138
C	8.1989518153	-0.923204388	-4.5759480179
C	7.5810594837	-0.8274400333	-5.8355052125
C	8.2630725026	-1.1814440571	-6.9901561399
C	9.5787284878	-1.6422623028	-6.9215352461
C	10.2049570428	-1.7487649774	-5.6831119195
C	9.5213281324	-1.3952635373	-4.5259911458
H	1.5639222412	3.949503721	1.7531925678
H	1.4739949029	6.2527036727	0.9035050682
H	5.7146445727	5.9753960257	0.1744598
H	5.6236401195	3.6764435257	1.0830315094
H	4.6655435254	8.0323331163	-0.3545588007
H	1.6199235286	8.1685852798	-0.0622908031
H	0.514648666	10.0424060288	-0.8409869837
H	0.4707896597	12.3316353287	-1.7576550571
H	2.5982684075	13.5008484492	-2.2848626109
H	4.7613526345	12.3539435523	-1.8793486769
H	4.8119736383	10.0818196652	-0.9645407135
H	4.5521988002	0.5001572837	4.6109672503
H	4.5985595565	-1.765039274	5.56091972
H	2.567531214	-3.120161598	2.0068799707
H	2.5913489172	-0.7753450444	1.21566847
H	3.0843411196	-4.7563815766	3.6342406101
H	4.5516175675	-3.8269189666	6.1562149885
H	5.1249972852	-5.391042735	7.752919789
H	5.1679853959	-7.688231542	8.6492894177
H	4.1281067987	-9.5435497801	7.3659662673
H	3.0477020961	-9.0696397095	5.1823218904
H	2.9999869253	-6.7904134436	4.2870943708
H	1.1615618635	1.1579329199	3.7449233006
H	0.0657110284	1.9381414	5.822254196
H	3.2538857514	4.8138191209	6.2244598375

H	4.2108478996	3.9021659184	4.1552151319
H	-0.0240037588	3.3887776438	7.6981658871
H	2.2421790206	5.4264738964	7.9970924299
H	-0.996286527	4.0379549794	9.5083916134
H	-1.9654141505	4.9455291057	11.5673905551
H	-0.8662980172	6.8263919551	12.7554332227
H	1.2347837253	7.7924059205	11.8471971269
H	2.2160887988	6.8829828933	9.7755485709
H	2.9648980573	2.0188949818	-0.7140126631
H	4.010873532	1.3419149234	-2.8530466449
H	7.161257575	-0.4806968628	-0.541272056
H	5.9977815098	0.2906597387	1.479860828
H	5.7344531695	0.2349317339	-4.057788701
H	8.1367345933	-0.7526677405	-2.4353614159
H	6.5572645054	-0.4793541224	-5.9130161868
H	7.7675154255	-1.1008343535	-7.9516419879
H	10.1074727516	-1.9179802118	-7.8272471445
H	11.2263346851	-2.1075645716	-5.6177505938
H	10.0155490622	-1.4784582604	-3.5628275307

iii) [Fe(stpy)₄(NCSe)₂] S=2 (E = -8480.35324030au , <S²> = 6.0711, ν₁ = 4.2353cm⁻¹)

Fe	-0.1061548475	-0.2388387151	-0.2150588067
Se	-4.6579420586	-1.0044206278	-2.2010074092
Se	4.4655362595	0.5164241133	1.730057688
N	-1.9743174094	-0.5462818736	-1.0545228911
N	1.7630753408	0.0685263166	0.6243247036
N	-0.1046707469	1.8672180765	-0.9912956868
N	0.8632323016	-0.9179091811	-2.11640261
N	-0.1064576865	-2.341318113	0.5504329451
N	-1.070784197	0.4786469741	1.6723198869
C	-3.049512626	-0.7293836604	-1.5149938499
C	2.845580237	0.2478349063	1.0688994379
C	-1.2608396501	2.53282282	-1.2051616611
C	-1.3098679817	3.8206862173	-1.7036120823
C	-0.1195511978	4.5019326311	-2.0125554873
C	1.0746676708	3.8013476167	-1.7778544426
C	1.0442274075	2.5103544666	-1.2784941689
C	-0.061948856	5.8556552916	-2.5488746297
C	-1.1170328834	6.6209395357	-2.8901721625
C	-1.0858398707	7.974838765	-3.4345799563
C	-2.3020950559	8.5851153906	-3.7840741916
C	-2.3389879035	9.8691969988	-4.3142717569
C	-1.1560883503	10.5771903384	-4.5058512016
C	0.061519562	9.9887308711	-4.1607450447
C	0.0984194245	8.7070542819	-3.6321568367
C	0.262425057	-0.7397448696	-3.3092161105
C	0.8514399573	-1.1098128679	-4.5064018039
C	2.1282701641	-1.6942382542	-4.5201696964
C	2.7392622969	-1.881388378	-3.267923065
C	2.087519461	-1.4888527308	-2.1145004466
C	2.7352165666	-2.060634297	-5.7934210624
C	3.9680160346	-2.5760161262	-5.9663891136
C	4.6030824163	-2.9421463719	-7.2285583209
C	3.9731675126	-2.8220341137	-8.480089759

C	4.6333614849	-3.1822037792	-9.6453896706
C	5.9390752126	-3.6727484802	-9.5960454744
C	6.5781766706	-3.8004113797	-8.3662573799
C	5.9166161643	-3.4396396817	-7.1984959647
C	-0.7988226568	-3.3142083058	-0.0741543657
C	-0.8234383866	-4.6228100351	0.3771732431
C	-0.1068191328	-4.9927416284	1.5267536717
C	0.6106206783	-3.967696304	2.1679212221
C	0.5849541772	-2.6828163162	1.6599842151
C	0.4877348068	-8.2730972114	3.5030276336
C	-0.2824114308	-9.283476268	2.9000312349
C	-0.266732011	-10.5795009702	3.3934095411
C	0.5163527047	-10.9052670302	4.5017698988
C	1.2847486275	-9.9184683237	5.112455967
C	1.2690671393	-8.6196425639	4.6179832052
C	-2.2917543583	0.0570921741	2.055360134
C	-2.921655411	0.5260071315	3.196253249
C	-2.2947797998	1.4805821758	4.0134770936
C	-1.0169324821	1.9030678024	3.6064423717
C	-0.4530543131	1.3909039748	2.4541035523
C	-3.19814882	3.4594215388	7.220225359
C	-4.4063081788	2.9498550505	7.7282385588
C	-4.986400321	3.4969857576	8.8632390635
C	-4.3788898908	4.5660119001	9.5234930882
C	-3.1810148827	5.0815016796	9.0371310102
C	-2.5991314626	4.532380688	7.9009762284
C	-0.1468610923	-6.3773931113	1.978800758
C	0.5155654448	-6.8911868163	3.0335872079
C	-2.9808076008	1.9713687655	5.2021324991
C	-2.5358570777	2.9373188069	6.0291907501
H	-2.1642476714	1.9876115964	-0.9659996042
H	-2.2784682165	4.2846538121	-1.8437148606
H	2.0321152511	4.2652431472	-1.9885912974
H	1.954055135	1.9561747393	-1.0882186141
H	0.9435459456	6.246228963	-2.6811912374
H	-2.1173516499	6.2120052871	-2.7689867631
H	-3.2280487259	8.037316234	-3.637899432
H	-3.2911153125	10.3167794574	-4.5775593646
H	-1.1792500918	11.5797577302	-4.9184025201
H	0.9868888546	10.5360128379	-4.304629161
H	1.0562578804	8.2734555084	-3.3678472872
H	-0.721578901	-0.2902155322	-3.2773566293
H	0.3172311345	-0.9396550462	-5.4348429911
H	3.7207257255	-2.3308587996	-3.1802508708
H	2.5421136503	-1.6156188947	-1.1408779111
H	2.1080900271	-1.8778690549	-6.6619542048
H	4.5892460365	-2.7440431066	-5.0898952447
H	2.9586529812	-2.4452378753	-8.5438466193
H	4.1289705183	-3.0815606629	-10.600370768
H	6.4508942628	-3.9529113824	-10.5100757933
H	7.5926094172	-4.1806998238	-8.3158958556
H	6.4206826677	-3.5399722214	-6.2420800726
H	-1.3479179639	-3.0088137958	-0.9551219971
H	-1.4022197129	-5.3603733512	-0.1680860308
H	1.1893683641	-4.1589250788	3.0632270728
H	1.1334568772	-1.8790985764	2.1333212672

H	-0.9007531718	-9.055262821	2.0392902509
H	-0.8688628999	-11.3431486044	2.9129709844
H	0.5249865281	-11.9200569761	4.8838464526
H	1.8970544016	-10.1596968251	5.9745258836
H	1.8709175928	-7.8543552581	5.0986277216
H	-2.7632064199	-0.6699327653	1.4069592753
H	-3.9077499724	0.151597169	3.448706729
H	-0.4520729804	2.6267642802	4.1810394446
H	0.5308560054	1.6973084936	2.1242700095
H	-4.8946001583	2.1164139663	7.2357962667
H	-5.9181856676	3.0881233344	9.238983255
H	-4.8368214838	4.9896106086	10.4104816287
H	-2.698863932	5.9107803999	9.5431420533
H	-1.6645594106	4.9385451848	7.5262749325
H	-0.7789634349	-7.0281547126	1.3804235403
H	1.1523558697	-6.2331728825	3.6202150723
H	-3.9408877071	1.5013819662	5.3987816907
H	-1.5827998167	3.4114045896	5.8069232947

iv) [Fe(stpy)₄(NCSe)₂] S=0 (E = -8480.36594887au , <S²> = 0.0000, ν₁ = 5.7643cm⁻¹)

Fe	-0.1270381983	-0.217773976	-0.2834030117
Se	-4.5624599261	-0.9896037325	-2.2008073327
Se	4.3070154169	0.5301179137	1.6522310512
N	-1.875437281	-0.5131893193	-1.0535652804
N	1.6220208989	0.0733779117	0.4925924826
N	-0.1268085593	1.6527679931	-0.9944319026
N	0.7327000026	-0.8486170008	-1.9748892339
N	-0.1253425662	-2.0869916643	0.4204045607
N	-0.9778044982	0.4318929418	1.4044927861
C	-2.9465639581	-0.7030926735	-1.5117899061
C	2.69200327	0.2546322681	0.9569181154
C	-1.2676703319	2.383568495	-1.0527712907
C	-1.309161325	3.6738287477	-1.540666987
C	-0.1383974932	4.2951908968	-2.008613107
C	1.0353618545	3.5281878438	-1.9360703489
C	1.0088058904	2.2390653713	-1.4371638872
C	-0.0813262001	5.6474695984	-2.5452612454
C	-1.1330144091	6.4630034926	-2.7579486821
C	-1.1011797009	7.819511546	-3.2950473158
C	-2.3202865341	8.4746197299	-3.5372597035
C	-2.355791387	9.7639166354	-4.0547091114
C	-1.1686966826	10.4326962279	-4.3389573964
C	0.0520344092	9.7999672976	-4.0993602719
C	0.0876019359	8.5128381136	-3.5842298034
C	0.1927916427	-0.5756078759	-3.1845922685
C	0.7890864855	-0.9630741013	-4.3705166926
C	2.0057225342	-1.6638983823	-4.3673891827
C	2.5432834852	-1.9575388199	-3.1023192033
C	1.8962461985	-1.5446798537	-1.9556250085
C	2.6294307972	-2.0318993211	-5.6307594414
C	3.8512122359	-2.5811942667	-5.7787063384
C	4.5110049501	-2.9444866646	-7.0285540473
C	3.8913690346	-2.8613942278	-8.2881258181
C	4.5775242037	-3.2111179064	-9.441616287

C	5.8990239347	-3.6547397729	-9.3715646391
C	6.5270258137	-3.7485751584	-8.1330306851
C	5.8392508412	-3.3995413512	-6.9770467415
C	-0.6623449923	-3.1061925717	-0.2880619033
C	-0.6658423978	-4.4104597088	0.1707290904
C	-0.1001164419	-4.7367330577	1.4135303394
C	0.4515198654	-3.6662094142	2.1385578682
C	0.4220940759	-2.3859755793	1.6244593416
C	0.3963704246	-7.9637177577	3.4986713273
C	-0.1880744772	-9.0289573628	2.7905672057
C	-0.1569662226	-10.3201650914	3.2956764767
C	0.4570779433	-10.5861719183	4.5204802681
C	1.0404480383	-9.5446127355	5.2359682362
C	1.0091376745	-8.2506057462	4.7299823648
C	-2.1209586225	-0.1084885913	1.8841488692
C	-2.724532076	0.3378572736	3.0459423463
C	-2.163985419	1.3887468657	3.78961071
C	-0.975564058	1.9382323279	3.2779023368
C	-0.4251054096	1.4480314013	2.112040389
C	-3.0204611175	3.3042113614	7.0460374428
C	-4.2139866924	2.7749800002	7.5686712941
C	-4.7626516731	3.2805655054	8.7379451819
C	-4.1381763718	4.3270546847	9.418312472
C	-2.9559062211	4.8632368903	8.9164185786
C	-2.4058800597	4.3563555071	7.7453699351
C	-0.1152474443	-6.1199668828	1.8676053056
C	0.3991002422	-6.5838673219	3.0236285377
C	-2.8205428851	1.839778807	5.0086465853
C	-2.3889531533	2.8241754505	5.8214915286
H	-2.1586435957	1.8863134496	-0.6992636696
H	-2.2626495585	4.1870040964	-1.5480154927
H	1.9808750025	3.9394145251	-2.2717441763
H	1.9052320086	1.6408126307	-1.3668689723
H	0.9182567807	5.9917741415	-2.7969020613
H	-2.1307136148	6.0973854756	-2.5266268676
H	-3.2495507397	7.9576538103	-3.3179777704
H	-3.3101785083	10.2464974187	-4.2348509904
H	-1.1908761803	11.4395826486	-4.7408698377
H	0.9808865585	10.3172562176	-4.3141781596
H	1.0481756742	8.0456231993	-3.3989691343
H	-0.744657748	-0.039371184	-3.1698263154
H	0.3041625164	-0.7100171511	-5.3067653301
H	3.4684577182	-2.5100883438	-2.9960538942
H	2.3016899868	-1.7485953031	-0.9759190761
H	2.0354394303	-1.8069981138	-6.5126127067
H	4.4466023047	-2.7702908122	-4.8885835133
H	2.8630712678	-2.527025633	-8.3664929837
H	4.0807256729	-3.1406982004	-10.4032401452
H	6.4309462524	-3.9271648088	-10.2764037352
H	7.5528950577	-4.0940771393	-8.066698541
H	6.3347312075	-3.4727761154	-6.0137372689
H	-1.1026617553	-2.8378010329	-1.2369433313
H	-1.1158760368	-5.1804796346	-0.4459091793
H	0.9116278069	-3.8171438271	3.1071707227
H	0.853034458	-1.553235991	2.1601697792
H	-0.6729547357	-8.8478608766	1.8379189175

H	-0.6143596926	-11.1268825543	2.7330941297
H	0.478697512	-11.5975129462	4.9110627531
H	1.5203533093	-9.73943503	6.1888275724
H	1.4666531138	-7.4424219257	5.292458682
H	-2.5464986976	-0.9077285376	1.2951549273
H	-3.6430425995	-0.1365045848	3.3731485879
H	-0.4656552978	2.7505999669	3.78036488
H	0.4923098377	1.8501677365	1.7092770375
H	-4.7182026139	1.9622043006	7.0580599584
H	-5.684020623	2.8579363002	9.1239586668
H	-4.572060804	4.7183655779	10.3318206956
H	-2.4615535431	5.6761622878	9.436930577
H	-1.4832827055	4.7783789	7.3587513943
H	-0.5924067879	-6.8148114103	1.1817334023
H	0.8789574461	-5.8799557656	3.6994628361
H	-3.7387808537	1.3115481143	5.251621509
H	-1.4675735569	3.3416767185	5.5648970871

v) [Fe(stpy)₄(NCBH₃)₂] S=2 (E = -3730.69267885au , $\langle S^2 \rangle = 6.0496$, $\nu_1 = 4.8529\text{cm}^{-1}$)

Fe	3.602987285572	1.927319872768	2.157275379250
N	5.487345398651	2.248534819970	3.018110550914
N	1.720320163555	1.604522775673	1.294464217556
N	3.612777857697	4.016201807196	1.361203602594
N	3.594225127018	-0.164053188769	2.953446747057
N	2.620801080015	2.646470180503	4.033152078159
N	4.585095813206	1.208632589799	0.280000335388
B	7.929018093812	2.702660185051	4.174278691884
B	-0.722899168418	1.157173974549	0.139038481517
C	6.529805343358	2.440683303118	3.509988878585
C	0.677125440418	1.415085754207	0.803038405191
C	2.462681697106	4.706614717985	1.198442854014
C	2.419890914572	5.996653273083	0.705707677315
C	3.610347944748	6.654280205565	0.349529579184
C	4.798305649800	5.927321163144	0.529639815306
C	4.761764973986	4.635118146260	1.024809858052
C	3.674588046997	8.010257855134	-0.179896733756
C	2.622658465559	8.802688924346	-0.464295564702
C	2.660093789529	10.161567100031	-0.995436236640
C	1.443446927325	10.803658818447	-1.280333148754
C	1.412360766755	12.095690694130	-1.791363076951
C	2.601470913932	12.779062785740	-2.028257827047
C	3.819754150818	12.158298496362	-1.748277495086
C	3.850900791051	10.868757351964	-1.238848772454
C	4.234902397089	-0.476980605980	4.101243426298
C	4.260175048596	-1.754157193634	4.627660240188
C	3.595636209795	-2.801649153211	3.966154322349
C	2.928340664660	-2.460891585861	2.778458681726
C	2.951541672064	-1.158501219781	2.309722464035
C	3.562852745079	-4.180960511953	4.434921073564
C	4.208166941025	-4.669155977923	5.512212229448
C	4.192627080783	-6.044072683992	6.001597481579
C	4.985152438790	-6.368248335341	7.115353048258
C	5.016376386521	-7.660220202329	7.626569400293
C	4.251300625098	-8.661214561820	7.035169365891

C	3.455349940062	-8.357017202215	5.929788134373
C	3.424586821011	-7.067923053805	5.419197693140
C	1.415719761421	2.181209540509	4.417697800079
C	0.783036834941	2.606910781552	5.573049986835
C	1.392010944984	3.556662017335	6.409260151102
C	2.647876543020	4.033938647162	5.995185811766
C	3.215318756651	3.565387011774	4.825854980412
C	0.708868167026	3.984010745781	7.623283421499
C	1.194642520264	4.830996185706	8.551728061951
C	0.531982064758	5.274124920303	9.774273096279
C	-0.777630210234	4.902963037216	10.127174126960
C	-1.351159020117	5.356042510003	11.305822377222
C	-0.636090626616	6.192020894653	12.164748478605
C	0.660533702888	6.572064535635	11.830934393578
C	1.235119242615	6.118637774429	10.649517858585
C	4.002688695663	1.375519809334	-0.923863643317
C	4.582391130283	0.938160773219	-2.102434289742
C	5.831223481666	0.296129590559	-2.085702489588
C	6.426285581105	0.127943446827	-0.823144752528
C	5.784351398744	0.586918718379	0.310986689962
C	6.423804269174	-0.148564261305	-3.340427763657
C	7.639144185383	-0.710629861455	-3.489832232954
C	8.254539495721	-1.163067526956	-4.733512668495
C	7.604766505533	-1.127849386697	-5.980059598765
C	8.245536339282	-1.569864568402	-7.127862056621
C	9.550791295054	-2.060070870722	-7.065115662878
C	10.208950473972	-2.105321999186	-5.839605648650
C	9.566648354698	-1.663122039383	-4.689211238492
H	1.557780785676	4.181233043507	1.474107306621
H	1.456228382574	6.480854017348	0.607191777704
H	5.755571514160	6.371771120937	0.280278417482
H	5.667771648818	4.062012201884	1.172577037190
H	4.681575068495	8.378706641381	-0.356251994024
H	1.619737281892	8.416176938673	-0.299026605055
H	0.512642905309	10.275172450703	-1.098265845978
H	0.459907647926	12.568642030542	-2.004167659055
H	2.582679005739	13.787648086452	-2.426071302194
H	4.750016102224	12.686304212448	-1.927917853598
H	4.809464182051	10.409822914372	-1.024738969473
H	4.743266870270	0.342180148619	4.592467659188
H	4.795436694397	-1.921092314290	5.554172912862
H	2.390128697169	-3.216195264612	2.216409159567
H	2.440467165979	-0.878300744810	1.397949498622
H	2.958225227834	-4.849724661428	3.828258256107
H	4.824233396232	-3.993365461098	6.100707927659
H	5.584615736824	-5.591584471484	7.580413717476
H	5.637616062245	-7.884966578330	8.486619791573
H	4.271380910457	-9.670644217686	7.430771980995
H	2.854438373969	-9.131769836748	5.465996326265
H	2.794424799501	-6.855210961293	4.563075124983
H	0.959352140213	1.452545780170	3.760558753108
H	-0.188487784447	2.196939142531	5.826330285853
H	3.189615598317	4.772694409548	6.572716217367
H	4.182667695837	3.917147591485	4.492309643322
H	-0.278319907233	3.551438122810	7.761927109301
H	2.191008219629	5.243040289055	8.410219937918

H	-1.355119795105	4.258822217646	9.473797810407
H	-2.363097595090	5.058469406571	11.558566725564
H	-1.089335467281	6.543888706834	13.084863181863
H	1.225031341692	7.222247320652	12.490282792437
H	2.247183687678	6.417931407595	10.394586897100
H	3.039857538102	1.869467325726	-0.918492314730
H	4.061627167255	1.098946833544	-3.039984180791
H	7.385346509808	-0.362628574096	-0.711975590847
H	6.227032370046	0.471562221897	1.291608544500
H	5.801045722567	0.013405251935	-4.216102297233
H	8.260647576569	-0.849703135315	-2.608369199231
H	6.588709593060	-0.756984969994	-6.053515957115
H	7.725718476310	-1.534985482563	-8.079183609895
H	10.047086066915	-2.404960888729	-7.965443795295
H	11.222793679429	-2.485537098875	-5.778839647692
H	10.085276786059	-1.700231263190	-3.736062875534
H	7.747100728106	3.428457514162	5.131951874524
H	8.381105719174	1.627225827324	4.513941640302
H	-0.928189666998	-0.040032330126	0.173769881405
H	-1.552821252209	1.767370568613	0.783299222168
H	8.635256355947	3.237065278162	3.342481913162
H	-0.664691728680	1.562781960098	-1.004936861989

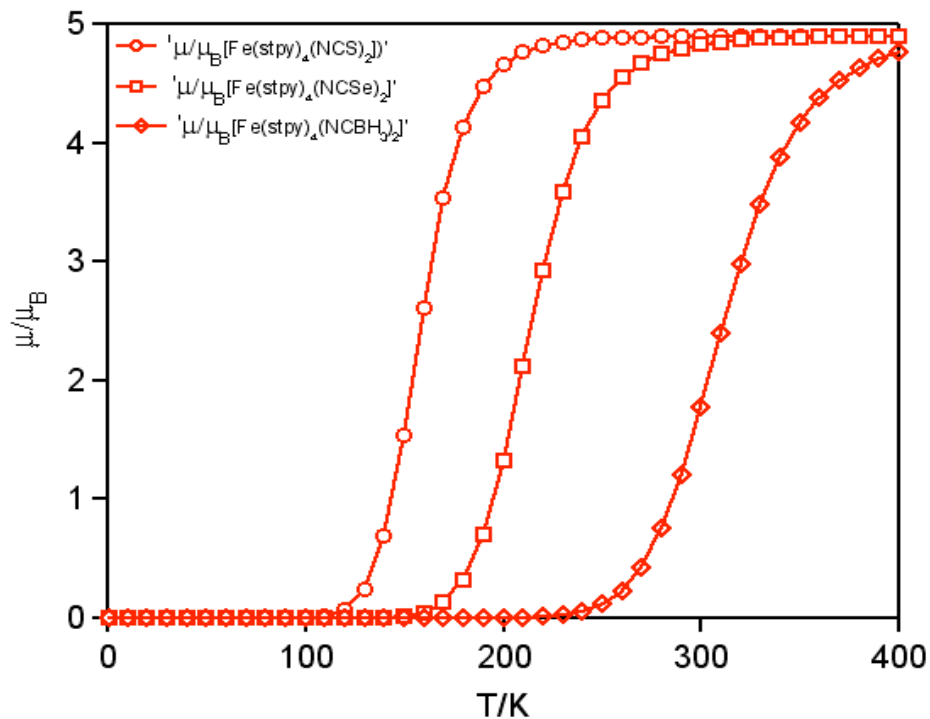
vi) [Fe(stpy)₄(NCBH₃)₂] S=0 (E = -3730.71066540au , <S²> = 0.0000, v₁ = 5.9032cm⁻¹)

Fe	3.6212567004	1.9166790848	2.1398651908
N	5.3580548669	2.2132887004	2.9320544761
N	1.8840535874	1.6187447756	1.3504723717
N	3.6226262622	3.7881332851	1.430389116
N	3.6204899347	0.0448628183	2.847971975
N	2.7445352619	2.5544830966	3.8224935984
N	4.498123583	1.2795951649	0.4572770586
B	-0.5973555175	1.2086566952	0.2524602483
B	7.8233126764	2.6082959559	4.0713049622
C	6.4069604844	2.383901844	3.4153629483
C	0.8295963602	1.4427858727	0.8812885536
C	2.4858286093	4.5269327686	1.3901685992
C	2.4452753958	5.8179369472	0.9051155456
C	3.6130629032	6.4339853179	0.4228013875
C	4.7826414948	5.6590036823	0.4757958174
C	4.7549094721	4.3686291112	0.971170096
C	3.6713644451	7.7876743565	-0.1095854366
C	2.6246352806	8.6192031854	-0.2810756878
C	2.6552939515	9.9779756221	-0.8120133618
C	1.4388572594	10.6622146992	-0.9732986621
C	1.4011372164	11.9567645639	-1.4773440274
C	2.5833873307	12.6005408997	-1.8309056579
C	3.8016539206	11.9377119239	-1.6744855192
C	3.8394383156	10.6455882421	-1.1721380851
C	4.1399042534	-0.2478197019	4.0662686869
C	4.1617989509	-1.5254905301	4.5866585305
C	3.6306629425	-2.6013173196	3.854316891
C	3.0912491104	-2.2819493284	2.5979741716
C	3.1030918931	-0.9801841964	2.1328203748
C	3.6102953927	-3.9821189252	4.3150426718

C	4.1522148836	-4.4459324005	5.4585684703
C	4.1464106442	-5.8227763911	5.9417557037
C	4.8391035377	-6.1203597335	7.1272979382
C	4.8752822483	-7.4131495435	7.6359805512
C	4.2146806336	-8.4416074955	6.9703448415
C	3.5176547882	-8.1639826002	5.7934654835
C	3.4822080466	-6.8741140612	5.2851770036
C	1.6089564339	1.9846363766	4.2869794247
C	0.9836830272	2.406441887	5.4455814234
C	1.5141732768	3.4609336328	6.2057736833
C	2.692702006	4.0444179006	5.7091546911
C	3.265506497	3.5781609715	4.5437599362
C	0.8372060894	3.8795737747	7.4247113169
C	1.2652388268	4.8230774962	8.2867265735
C	0.6072661778	5.2603189155	9.513531027
C	-0.6486087795	4.7869426318	9.9333855252
C	-1.2199904958	5.2393798551	11.1133005957
C	-0.5565105214	6.1765795516	11.9066586801
C	0.6858685605	6.6590930307	11.5055545165
C	1.2581543784	6.206588513	10.3227434834
C	3.9797196388	1.5626972342	-0.7597146474
C	4.5655006701	1.1356447903	-1.936849433
C	5.7490661292	0.3805989822	-1.9181112836
C	6.273924508	0.091982035	-0.6464643782
C	5.6379949944	0.5452388338	0.4910227833
C	6.3475464052	-0.0489574119	-3.1737602112
C	7.5164809197	-0.70530784	-3.31258838
C	8.1378947391	-1.145330024	-4.5573469931
C	7.5337059474	-1.005476961	-5.8194575636
C	8.1784142583	-1.4405910736	-6.9676712022
C	9.4420902207	-2.0280191137	-6.8898821556
C	10.0543004628	-2.1780934519	-5.648972602
C	9.4079794103	-1.7430751233	-4.4981557775
H	1.59578231	4.0361502148	1.7546891497
H	1.4940465692	6.3351741249	0.9098735405
H	5.7258947691	6.065040073	0.1278600303
H	5.6489021985	3.7652187496	1.0254671612
H	4.6668947563	8.1199243132	-0.3913548909
H	1.6312200644	8.2678582611	-0.0122230567
H	0.5133357644	10.164656342	-0.7000315725
H	0.4489278642	12.4626232747	-1.593623842
H	2.5594869576	13.6109896327	-2.2236648415
H	4.726853601	12.4348802404	-1.9451652333
H	4.7984100684	10.153802583	-1.0544974589
H	4.5530966325	0.5874858544	4.6117604128
H	4.5955273685	-1.669401486	5.5682846827
H	2.656697849	-3.0556232047	1.9748908788
H	2.6839272134	-0.7199726082	1.1721645238
H	3.1114430183	-4.6753252499	3.6431273134
H	4.6671393497	-3.7458083489	6.1122521825
H	5.3570090528	-5.3222187485	7.6503420959
H	5.4186651889	-7.6171452673	8.5520820874
H	4.238775367	-9.4517792218	7.3638093412
H	2.9974582789	-8.9601567361	5.2719903409
H	2.9283264617	-6.6820905831	4.3732172463
H	1.2060983289	1.1806811609	3.6889744621

H	0.0730026294	1.908285723	5.7588280751
H	3.1751721208	4.8673079391	6.2214989762
H	4.1757825422	4.0089025025	4.1540558886
H	-0.0911276669	3.3531948575	7.6295930186
H	2.2063917814	5.3276501326	8.0811590769
H	-1.18654206	4.0640141347	9.3306202953
H	-2.1901956657	4.8622764985	11.4181429714
H	-1.0079490126	6.5274948515	12.828016012
H	1.209660633	7.3886337335	12.1134498186
H	2.2279187059	6.5858825828	10.0152805582
H	3.065090211	2.1368798586	-0.7600528723
H	4.0945685008	1.3941136398	-2.8786839602
H	7.1796852831	-0.4892761939	-0.527555746
H	6.0337150376	0.3405756003	1.4746383917
H	5.7746897756	0.2110953784	-4.0598007262
H	8.0913944562	-0.9393868306	-2.4196727743
H	6.5495187307	-0.5589088315	-5.9047312476
H	7.6940362738	-1.3244305562	-7.931164039
H	9.9415824444	-2.3670932423	-7.7906459193
H	11.0353476471	-2.6346299079	-5.5765888243
H	9.8907722552	-1.861927188	-3.5329549342
H	-0.4599892439	0.4970346137	-0.7236317232
H	-1.2870719593	0.6699403329	1.0967352065
H	8.0180046782	3.8068756592	4.1317830449
H	7.797272146	2.1098954647	5.1803117423
H	8.6479800369	2.0631330699	3.3632367378
H	-1.0468101348	2.2960609169	-0.0546840994

S.I.2 Magnetic moment (μ_B) vs. temperature (K) for the $[\text{Fe}(\text{stpy})_4(\text{NCX})_2]$ ($X = \text{S}, \text{Se}, \text{BH}_3$) systems.



The curves can be fitted using $f(x) = A + \frac{B}{1 + e^{((C-x)/D)}}$. Below are the fitting parameters for each molecule.

Ligand	A	B	C	D	$T_{1/2}(\text{calc.})/\text{K}$
NCS	-0.021	4.895	159.12	11.465	159.06
NCSe	-0.020	4.874	214.64	14.937	214.68
NCBH ₃	-0.012	4.743	310.31	18.691	309.26

S.I.3 Comparison of crystal data and calculated geometric parameters for [Fe(stpy)₄(NCS)₂] in high-spin (S=2) state

High-spin	d(Fe-N) _{ax} /Å	d(Fe-N) _{eq} /Å	angle/°
B3LYP(*)	2.07	2.28	90.0
OLYP	2.04	2.35	90.0
OPBE	2.03	2.30	90.0
TPSSh	2.06	2.24	90.0
Crystal	2.10	2.22	90.0