

Hindered rotation in a Novel 1,2,4-triazinyl phenanthroline (t-phen) Ligand Leading to Improved Separation of Am³⁺ and Eu³⁺ vis-a-vis 1,2,4-triazinyl bipyridine (t-bipy): A Computational Validation of the Experimental Results

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Optimized geometries of the free ligands and their complexes with Am³⁺, Eu³⁺ and H⁺ (Values are in Ang)

Me₂(t-bipy) (optimized at HF-level)

ATOM	X	Y	Z
H	-5.8568092865	2.4848256417	-0.0500925876
C	-4.9970182658	1.8408811492	-0.0262780702
C	-5.1492929494	0.4669391965	0.0151541630
N	-4.1349221668	-0.3756038706	0.0457463069
C	-2.9031257871	0.1090992400	0.0366905922
C	-2.6398129940	1.4748050351	-0.0039891475
C	-3.7087931722	2.3483994317	-0.0358574740
H	-6.1322546618	0.0274596394	0.0240549694
C	-1.7867710865	-0.8823411616	0.0723688750
H	-1.6247173445	1.8181179141	-0.0097180938
H	-3.5396319641	3.4104836371	-0.0677104587
C	-2.0395660322	-2.2494794968	0.1116512164
C	-0.9604465873	-3.1101182509	0.1431473071
C	0.3234868846	-2.5967924323	0.1349743671
C	0.4705135678	-1.2162928169	0.0948191266
N	-0.5600611644	-0.3944581912	0.0646522224
H	-3.0500366643	-2.6050947429	0.1167380603
H	-1.1163433866	-4.1739737639	0.1739409497
H	1.1866529146	-3.2306619465	0.1585914262
C	1.8315959113	-0.5974677307	0.0842992912
N	2.8509923403	-1.4109018810	0.1126980186
N	4.0669807751	-0.9150965324	0.1053181283
C	4.2495077534	0.3726102535	0.0701223722
C	3.1253260785	1.2369055524	0.0395338736
N	1.9278315989	0.7352093034	0.0470735880
C	5.6660897173	0.8749169945	0.0640300128
C	3.2732478578	2.7315174664	-0.0014334929
H	2.2935802535	3.1862752699	-0.0235998987
H	3.8129956900	3.0911296040	0.8693566802
H	3.8300018265	3.0419054593	-0.8803549899
H	5.8644500733	1.5081626985	0.9236694487
H	6.3399476922	0.0303874332	0.0914176577
H	5.8743768679	1.4592229077	-0.8273282435

Me₂(t-phen) (optimized at HF-level)

ATOM	X	Y	Z
N	2.3669572429	-0.7872559748	-0.1262806781
C	2.1482513818	0.5303400044	-0.0897665245
N	3.0861917003	1.4357621939	-0.0740209411
N	4.3445097826	1.0556018180	-0.0953097593
C	4.6444028505	-0.2092106937	-0.1315304965
C	3.6043499743	-1.1756538833	-0.1475262792
C	0.7346480602	1.0204324939	-0.0644456359
C	0.4764820208	2.4067319318	-0.0126695800
C	-0.8216796262	2.8158517748	0.0093586320
C	-1.8560414673	1.8633412822	-0.0202516500
C	-1.4872251333	0.5136924238	-0.0716016499
N	-0.2084480507	0.1255778768	-0.0921083390
C	-3.2442127521	2.2392013843	0.0005782630
C	-4.2055668639	1.3056725731	-0.0289035797
C	-3.8733744430	-0.0937305635	-0.0822208494
C	-2.5334731736	-0.5033402735	-0.1039694159
C	-4.8632530101	-1.0923550680	-0.1142218841
C	-4.4901900467	-2.4028153067	-0.1646031790
C	-3.1170867897	-2.6973368086	-0.1824221007
N	-2.1818832935	-1.7946905430	-0.1535867260
C	6.1010458814	-0.5788260778	-0.1538009357
C	3.8873041285	-2.6505855741	-0.1886624435
H	-5.2146219044	-3.1959736401	-0.1903051792
H	-2.7913738451	-3.7236288642	-0.2222094112
H	-5.9023410070	-0.8118135694	-0.0987939266
H	-1.0646329930	3.8635100005	0.0493619832
H	1.2913543250	3.1014082345	0.0080820147
H	2.9516780995	-3.1904984303	-0.1907699698
H	4.4521002352	-2.9116692207	-1.0785561239
H	4.4749817562	-2.9568138708	0.6715345918
H	6.3501887332	-1.1487117222	-1.0438607598
H	6.6950470766	0.3239434476	-0.1406750384
H	6.3672668085	-1.1849482869	0.7069511641
H	-3.4931750238	3.2850887408	0.0403563186
H	-5.2442500010	1.5861449430	-0.0130215406

t-bipy (optimized at DFT (BP86) level)

ATOM	X	Y	Z
C	-1.1647569655	0.7804466853	0.0000000000
N	-0.0270871335	0.1125202888	0.0000000000
C	1.1165444359	0.7694043481	0.0000000000
C	1.1828769029	2.1557082363	0.0000000000
C	-0.0089314937	2.8587565169	0.0000000000
C	-1.2055950530	2.1718448266	0.0000000000
C	-2.4196179233	-0.0292249112	0.0000000000
N	-3.5620676707	0.6393833731	0.0000000000
C	-4.6939149207	-0.0377439917	0.0000000000
C	-4.7542606469	-1.4195349325	0.0000000000
C	-3.5595025065	-2.1190946090	0.0000000000
C	-2.3687364507	-1.4194752945	0.0000000000
H	2.1319672808	2.6522369615	0.0000000000
H	-0.0009766667	3.9342948901	0.0000000000
H	-2.1502767787	2.6769159331	0.0000000000
H	-5.5977054812	0.5474791053	0.0000000000
H	-5.7028004575	-1.9242098535	0.0000000000
H	-3.5554600322	-3.1949697699	0.0000000000
H	-1.4187316277	-1.9153249071	0.0000000000
C	2.3642808346	-0.0533425581	0.0000000000
N	3.5031232955	0.6027913525	0.0000000000
N	4.6298111732	-0.0571022358	0.0000000000
C	4.5996096923	-1.3617862542	0.0000000000
C	3.3787817438	-2.0372626896	0.0000000000
N	2.2556510992	-1.3817181874	0.0000000000
H	5.5425419174	-1.8750977448	0.0000000000
H	3.3356645211	-3.1128829717	0.0000000000

t-phen (optimized at DFT (BP86) level)

ATOM	X	Y	Z
C	-4.2711857200	2.0926963552	0.0000000000
C	-4.4731209349	0.7442124439	0.0000000000
C	-3.3631178320	-0.1194313497	0.0000000000
C	-2.0873508394	0.4595921012	0.0000000000
N	-1.9040030011	1.7858779959	0.0000000000
C	-2.9473648761	2.5617026322	0.0000000000
C	-3.5123527051	-1.5511552083	0.0000000000
C	-0.9190805264	-0.4152965038	0.0000000000
C	-1.1109023834	-1.8027823738	0.0000000000
C	-2.4394375547	-2.3543830255	0.0000000000
C	0.0367268063	-2.6146409495	0.0000000000
H	-0.0691928409	-3.6855468373	0.0000000000
C	1.2722161581	-2.0415652401	0.0000000000
C	1.3487250836	-0.6334662186	0.0000000000
N	0.2986752445	0.1337214427	0.0000000000
H	-4.5063945189	-1.9630358712	0.0000000000
H	-5.0913917519	2.7867606637	0.0000000000
H	-5.4675895263	0.3323739833	0.0000000000
H	-2.7560920923	3.6219784917	0.0000000000
H	-2.5520862681	-3.4242497528	0.0000000000
H	2.1687737686	-2.6272670724	0.0000000000
C	2.6851348968	0.0390745350	0.0000000000
N	2.7322866123	1.3709619924	0.0000000000
C	3.9231195323	1.8899593628	0.0000000000
C	5.0574465215	1.0748042273	0.0000000000
N	4.9357408931	-0.2234080429	0.0000000000
N	3.7375093182	-0.7464670340	0.0000000000
H	4.0059571907	2.9632209376	0.0000000000
H	6.0539345532	1.4746914436	0.0000000000

Am(t-bipy)³⁺ (optimized at DFT (BP86) level)

ATOM	X	Y	Z
C	0.0084332	-0.0056225	-0.0800238
C	-0.0130901	-0.0049219	1.4007407
C	1.1284895	0.0035580	2.2198398
C	0.9810840	0.0151436	3.6218478
C	-0.3071471	0.0155018	4.1830389
C	-1.4054956	0.0002346	3.3103620
N	-1.2685068	-0.0077078	1.9590643
H	2.1395210	0.0066293	1.7858981
H	1.8737960	0.0240622	4.2702808
H	-0.4668054	0.0192167	5.2739271
H	-2.4355056	-0.0166942	3.7235037
N	-1.2093462	0.0057616	-0.6955025
C	-1.2571323	0.0086667	-2.0659403
C	-0.1137233	0.0031882	-2.8762952
C	1.1458282	-0.0110250	-2.2426701
C	1.2046160	-0.0155799	-0.8438797
C	-2.6176075	0.0120027	-2.6190061
H	-0.2139241	0.0033375	-3.9745420
H	2.0725512	-0.0188253	-2.8410109
H	2.1850468	-0.0244033	-0.3439952
N	-2.9380057	0.0144961	-3.9163490
C	-4.2166852	0.0155505	-4.2634627
C	-5.2470753	-0.0005551	-3.2541348
N	-4.8673010	0.0056287	-1.9790239
N	-3.5974642	0.0176772	-1.6706637
H	-4.4775558	0.0251540	-5.3419415
H	-6.3268177	-0.0172657	-3.4875070
Am	-3.2903493	0.0326267	0.6977650

Eu(t-bipy)³⁺ (optimized at DFT (BP86) level)

ATOM	X	Y	Z
C	-0.0579460	-0.0013787	-0.0307271
C	-0.0465415	0.0033157	1.4519290
C	1.1464728	0.0054120	2.2124256
C	1.0854048	0.0111118	3.6180589
C	-0.1708270	0.0119218	4.2423387
C	-1.3220725	0.0052567	3.4256568
N	-1.2743518	0.0037897	2.0730869
H	2.1318591	0.0029504	1.7241656
H	2.0134847	0.0133094	4.2143030
H	-0.2747174	0.0092927	5.3402202
H	-2.3211130	-0.0105974	3.9023676
N	-1.2785928	0.0068524	-0.6429756
C	-1.3343550	0.0040063	-2.0053611
C	-0.1892218	-0.0066578	-2.8259560
C	1.0717060	-0.0175990	-2.2028813
C	1.1375450	-0.0124527	-0.8039131
C	-2.6869615	0.0113313	-2.5950538
H	-0.2956716	-0.0233816	-3.9231643
H	1.9952403	-0.0311878	-2.8058164
H	2.1228180	-0.0109036	-0.3152608
N	-2.9095659	0.0257960	-3.9130611
C	-4.1463817	0.0407326	-4.3771854
C	-5.2491591	-0.0244771	-3.4536438
N	-4.9682765	-0.0053047	-2.1557811
N	-3.7397413	0.0362040	-1.7189906
H	-4.3146693	0.0850088	-5.4733696
H	-6.3062028	-0.0894712	-3.7701158
Eu	-3.3483343	0.0629554	0.7590245

Am(t-phen)³⁺ (optimized at DFT (BP86) level)

ATOM	X	Y	Z
N	-2.8082126	0.0116666	-1.3706617
C	-1.8222658	0.0229983	-2.3101139
N	-2.0978338	0.0387896	-3.6179173
C	-3.3777637	0.0382442	-3.9816650
C	-4.4171938	-0.0330155	-2.9938180
N	-4.0814214	-0.0404565	-1.7027746
C	-0.4579184	0.0175938	-1.7483811
N	-0.4204633	0.0000678	-0.3854739
C	0.7864212	-0.0172181	0.2409646
C	2.0257409	-0.0285590	-0.4906153
C	1.9522464	-0.0063739	-1.9117600
C	0.7044062	0.0308872	-2.5458990
C	0.8010460	-0.0057081	1.6896904
C	2.0484113	-0.0211485	2.3851474
C	2.0124929	-0.0113490	3.8116896
C	0.7792831	0.0264049	4.4677138
C	-0.4024735	0.0581077	3.6996868
N	-0.4039666	0.0269378	2.3430421
H	2.9532142	-0.0259084	4.3885270
H	0.7143175	0.0409562	5.5679148
H	-1.3826379	0.1112564	4.2101373
H	0.6134241	0.0597544	-3.6440098
H	2.8776007	-0.0183740	-2.5124255
H	-3.6170944	0.0767095	-5.0629416
H	-5.4903962	-0.0879759	-3.2485733
C	3.2633318	-0.0364937	0.2373272
C	3.2733092	-0.0422714	1.6299378
H	4.2149624	-0.0248617	-0.3198668
H	4.2346788	-0.0549291	2.1708062
Am	-2.4752451	-0.1057319	1.0043118

Eu(t-phen)³⁺ (optimized at DFT (BP86) level)

ATOM	X	Y	Z
N	-2.8839422	-0.0035110	-1.3919673
C	-1.8581745	0.0133348	-2.2913742
N	-2.0808511	0.0432558	-3.6096952
C	-3.3365420	0.0505202	-4.0403486
C	-4.4157755	-0.0404977	-3.1004731
N	-4.1335766	-0.0562292	-1.7980571
C	-0.4951759	0.0118972	-1.7141985
N	-0.4452249	-0.0024747	-0.3529281
C	0.7618478	-0.0172575	0.2640718
C	1.9949139	-0.0281786	-0.4811041
C	1.9115234	-0.0039729	-1.9024125
C	0.6592016	0.0320574	-2.5248532
C	0.7957865	-0.0069548	1.7232011
C	2.0596285	-0.0225574	2.3962003
C	2.0599073	-0.0058225	3.8237242
C	0.8421715	0.0337504	4.5064033
C	-0.3530341	0.0533667	3.7597721
N	-0.3895692	0.0246713	2.4031161
H	3.0149969	-0.0183384	4.3764263
H	0.8003288	0.0535777	5.6076828
H	-1.3218820	0.0941933	4.2910582
H	0.5587836	0.0623676	-3.6218157
H	2.8324243	-0.0166662	-2.5098118
H	-3.5246727	0.1042877	-5.1313306
H	-5.4765155	-0.1075617	-3.4015295
C	3.2405927	-0.0414543	0.2264214
C	3.2700492	-0.0460181	1.6256093
H	4.1860949	-0.0350748	-0.3416052
H	4.2404865	-0.0573900	2.1506243
Eu	-2.5138013	-0.0673204	1.0591936

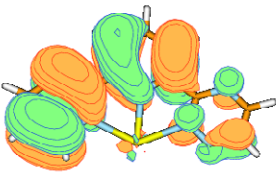
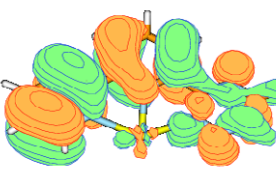
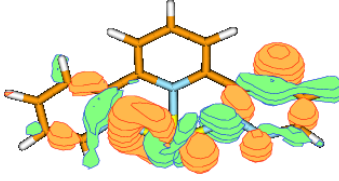
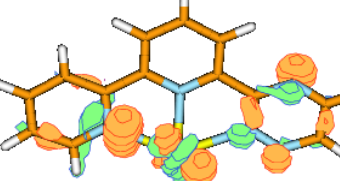
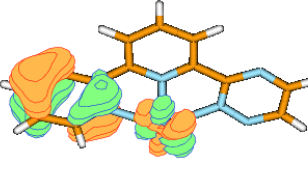
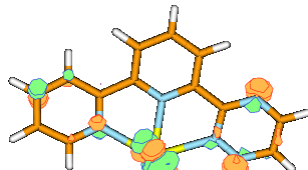
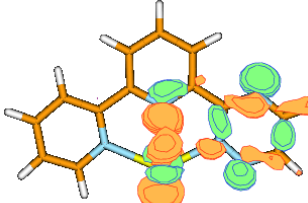
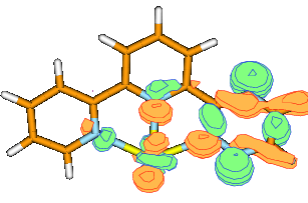
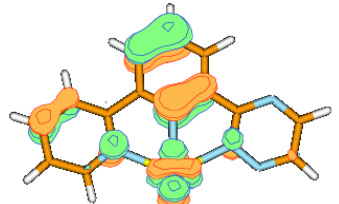
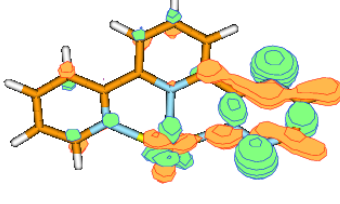
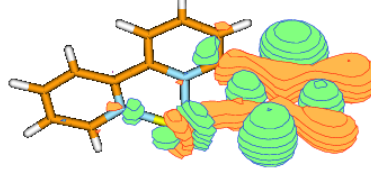
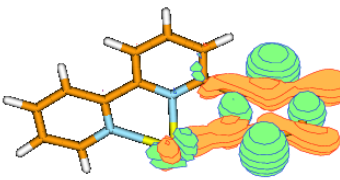
H(t-bipy)⁺ (optimized at HF-level)

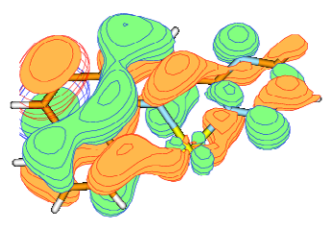
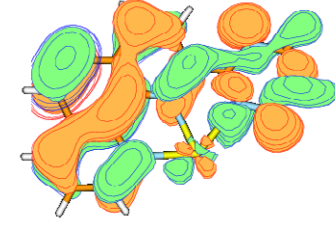
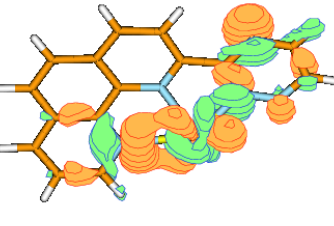
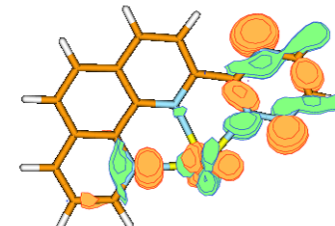
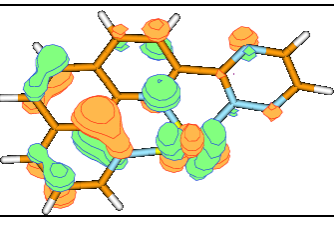
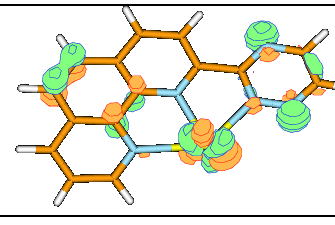
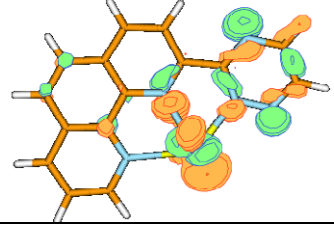
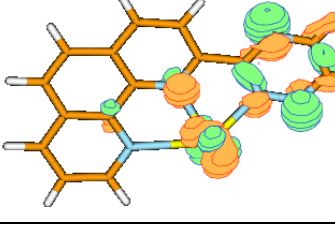
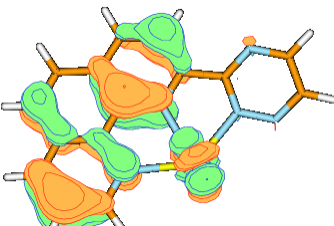
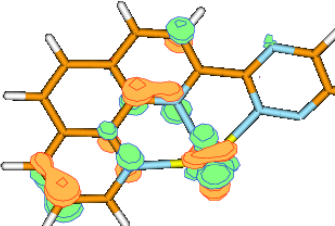
ATOM	X	Y	Z
C	-1.2168679435	0.9731358562	0.0000000000
N	-0.0520333098	0.3235365754	0.0000000000
C	1.1495176152	0.9141750017	0.0000000000
C	1.2249540324	2.2830506577	0.0000000000
C	0.0335795119	3.0034942551	0.0000000000
C	-1.1882005002	2.3584828230	0.0000000000
C	-2.4300548877	0.1139192211	0.0000000000
N	-2.1673537540	-1.1853438316	0.0000000000
C	-3.1669544491	-2.0368155759	0.0000000000
C	-4.4968920492	-1.6286787075	0.0000000000
C	-4.7691261150	-0.2775021591	0.0000000000
C	-3.7131434945	0.6252971409	0.0000000000
H	2.1818946585	2.7638427935	0.0000000000
H	0.0648045511	4.0777138594	0.0000000000
H	-2.0980482626	2.9225515298	0.0000000000
H	-2.9105941039	-3.0804986564	0.0000000000
H	-5.2852692154	-2.3573301672	0.0000000000
H	-5.7827912256	0.0786498977	0.0000000000
H	-3.9068817842	1.6800315531	0.0000000000
C	2.3335258380	0.0159372130	0.0000000000
N	2.0784990703	-1.2611384047	0.0000000000
N	3.0746941781	-2.1098961137	0.0000000000
C	4.2916027942	-1.6410618472	0.0000000000
C	4.5313261815	-0.2587024871	0.0000000000
N	3.5348299320	0.5794522126	0.0000000000
H	5.0904205020	-2.3575123358	0.0000000000
H	5.5304488744	0.1377769847	0.0000000000
H	-0.0959874058	-0.6862907789	0.0000000000

H(t-phen)⁺ (optimized at HF-level)

ATOM	X	Y	Z
C	-4.1329130361	2.1531650550	0.0000000000
C	-4.4166379893	0.8202540764	0.0000000000
C	-3.3524913818	-0.1073139795	0.0000000000
C	-2.0661832752	0.4242702325	0.0000000000
N	-1.7873661887	1.7337671920	0.0000000000
C	-2.7842831652	2.5679464743	0.0000000000
C	-3.5425089194	-1.5355755659	0.0000000000
C	-0.9561009491	-0.4885944205	0.0000000000
C	-1.1507096133	-1.8684517749	0.0000000000
C	-2.4961676365	-2.3784498548	0.0000000000
C	-0.0043842039	-2.6791443868	0.0000000000
H	-0.1165906653	-3.7485854919	0.0000000000
C	1.2579440225	-2.1300968077	0.0000000000
C	1.3849433511	-0.7480543058	0.0000000000
N	0.2958573282	0.0054915797	0.0000000000
H	-4.5466954911	-1.9185388363	0.0000000000
H	-4.9142598216	2.8894661408	0.0000000000
H	-5.4334732251	0.4710534245	0.0000000000
H	-2.5424548784	3.6157675460	0.0000000000
H	-2.6439106942	-3.4424714799	0.0000000000
H	2.1409602120	-2.7358727694	0.0000000000
C	2.6934133978	-0.0432784573	0.0000000000
N	3.7940555320	-0.7831134081	0.0000000000
C	4.9073302476	-0.1065355787	0.0000000000
C	4.8808063355	1.2954593575	0.0000000000
N	3.7488723796	1.9449055084	0.0000000000
N	2.6359881679	1.2584843300	0.0000000000
H	5.8341867316	-0.6508351882	0.0000000000
H	5.7791647929	1.8822482668	0.0000000000
H	0.3978518889	1.0093712805	0.0000000000

**Valence level occupied molecular orbitals of the Am^{3+} and Eu^{3+}
complexes of t-bipy and t-phen**

Orbital	$\text{Am}(\text{t-bipy})^{3+}$	$\text{Eu}(\text{t-bipy})^{3+}$
HOMO		
HOMO-1		
HOMO-2		
HOMO-3		
HOMO-4		
HOMO-5		

Orbital	$\text{Am}(\text{t-phen})^{3+}$	$\text{Eu}(\text{t-phen})^{3+}$
HOMO		
HOMO-1		
HOMO-2		
HOMO-3		
HOMO-4		
HOMO-5	