Hetero Atom (Nitrogen) replaced by Phenyl Insertion in Molecular Eu-complex Facilitated Sun Light-like Emission for Sustainable White LEDs and Non-Contact Thermometer

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Contents:

SI (ia) Experimental section

General information for Measurements

For recording the ^{1}H and ^{13}C-NMR spectra, the AV 400 Advance-III 400MHz Fourier transform nuclear magnetic resonance (FT-NMR) Spectrometer, Bruker Ascend^{TM} 600, was used. All the ^{1}H and ^{13}C-NMR spectra were recorded in deuterated chloroform solution, and tetramethylsilane (TMS) was used as a standard reference for chemical shift measurement. The Fourier transform infrared spectroscopy (FTIR) was executed by JASCO, in the spectrum range of 400 – 4000 cm^{-1} by making KBr pellets. The CIE color coordinate for all emission spectra is calculated by MATLAB software. XPS was measured using the XPS AXIS SUPRA equipment (serial No. C332905/010). The absorption spectra of all the synthesized compounds in solution form were measured utilizing a UV-Visible spectrophotometer (JASCO V-730). The lifetimes of the Eu(III) complexes and the ligand were measured at 298 K with Edinburgh Instruments FLS 1000 based on the time-correlated single photon counting technology. A pulsed xenon lamp was used as the excitation source, and the signals were detected with a photomultiplier. All the measurements were carried out at room temperature (RT).

Synthesis of 5'-phenyl-[1,1':3',1''-terphenyl]-4-carbaldehyde (I):

[1,1':3',1''-terphenyl]-5'-ylboronic acid, [Pd(PPh)$_3$OAc], K_2CO_3, and 4-bromobenzaldehyde were taken in a round-bottomed flask, and ethanol, toluene, and water were added in 1:2:1 ratio. This mixture was heated at 90 °C for 12 hours. The mixture was filtered by using Celite, and the organic layer was extracted with ethyl acetate and dried over Na_2SO_4. The crude was purified using a 10:0.1 Hexane: ethyl acetate mixture. The product was obtained as a white solid (60% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.86 (dd, J = 6.6, 4.9 Hz, 1H), 7.82 (d, J = 1.6 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.51 (dd, J = 10.4, 4.7 Hz, 2H), 7.42 (dd, J = 8.3, 6.4 Hz, 1H).

Synthesis of 3-(5'-phenyl-[1,1':3',1''-terphenyl]-4-yl)-1-(pyridin-2-yl)imidazo[1,5-a]pyridine (L-DpPh):

The ligand (L-DpPh) was synthesised by following the procedure. 2'-Dipyridyl ketone (2 g, 10.85 mmol) was taken in a round-bottomed flask, and to this, glacial acetic acid (15 mL) was added at room temperature (RT). To this reaction mixture, the aldehyde (Intermediate I) (4.05 g, 11.94 mmol) and ammonium acetate (4.18, 54.28 mmol) were subsequently added. Then, the resultant mixture was stirred continuously for 12 hr at 110 °C. The progress of the reaction was monitored by TLC (ethyl acetate-pet ether, 1:9). As the reaction mixture was acidic, it was neutralized by mixing with a small amount of water and an ammonium hydroxide (NH4OH) solution. The obtained solid was filtered and dissolved in dichloromethane, and then dried with anhydrous sodium sulphate. The solvent was vaporised to get the crude compound (0.71 g). This was purified by using column chromatography by using silica gel and eluent as 5% methanol in chloroform. The obtained product was dissolved in a minimum amount of THF solution and an excess amount of hexane was added to the same, a pale yellowish green solid was formed 450 mg (50.00%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 9.2 Hz, 1H), 8.67 (d, J = 4.7 Hz, 1H), 8.36 (d, J = 7.2 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.91 – 7.82 (m, 5H), 7.74 (d, J = 7.1 Hz, 5H), 7.51 (t, J = 7.5 Hz, 4H), 7.43 (d, J = 7.4 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.01 – 6.94 (m, 1H), 6.71 (t, J = 7.3 Hz, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 154.68, 148.69, 142.60, 141.55, 141.50, 141.06, 137.86, 136.63, 130.53, 129.23, 128.94, 128.78, 127.94, 127.69, 127.41, 125.65, 125.08, 121.88, 121.77, 121.39, 120.57, 120.22, 114.19.

The synthesis of Eu(III) chloride ($EuCl_3$. $6H_2O$, Sigma Aldrich, 99.9%) from Eu(III) oxide is done by the well-known process. The resultant product ($EuCl_3.6H_2O$) was then treated with an alcoholic solution of TTA (3 eq. BLD Pharma, 99 %) in the presence of 1 N sodium hydroxide solution (3.1 eq.) to get $Eu(TTA)_3(H_2O)_2$. The same procedure was used to synthesize $Eu(DBM)_3(H_2O)_2$ but used DBM (BLD Pharma, 99 %) (3eq) instead of TTA.

Synthesis of [Eu(TTA)$_3$L-DpPh]:

The precursor Eu(TTA)$_3$(H$_2$O)$_2$ (0.20 g, 0.23 mmol) in dry THF (20 mL) was taken in a 2-neck round bottom flask and stirred continuously until a solution was clear. After 20 minutes, the synthesized ligand L-DpPh (0.07 g, 0.23) pre-dissolved in dry THF was added drop by drop slowly. The reaction mixture was allowed to stir for 6 hours at 60 ^{o}C in inert condition. To this solution, excess hexane was added along the sides of the round-bottom flask resulted in the formation of a precipitate. The resulting mixture was filtered and subjected to several washings with hexane to obtain final complex in powder form (pale yellow color solid with 110 mg (~73.4%)). Elemental Analysis: Anal. Calc. for. C60H37EuF9O6S3; C, 54.80; H, 2.84; N, 3.20; Found: C, 54.81; H, 2.85; N, 3.21;

Synthesis of [Eu(DBM)$_3$L-DpPh]:

The precursor Eu(DBM)$_3$(H$_2$O)$_2$ (0.20 g, 0.23 mmol) in dry THF (20 mL) was taken in a 2-neck round-bottom flask and stirred continuously until a solution was clear. After 20 minutes, the synthesized ligand L-DpPh (0.07 g, 0.23), pre-dissolved in dry THF, was added drop by drop slowly. The reaction mixture was allowed to stir for 6 hours at 60 ^{o}C in an inert condition. To this solution, excess hexane was added along the sides of the round-bottom flask, resulting in the formation of a precipitate. The resulting mixture was filtered and subjected to several washings with hexane to obtain final complex in powder form (pale yellow color solid with 110 mg (~73.4%)). Elemental Analysis: Anal. Calc. for. C81H58EuN3O6; C, 73.63; H, 4.42; N, 3.18; Found: C, 73.64; H, 4.43; N, 3.17;

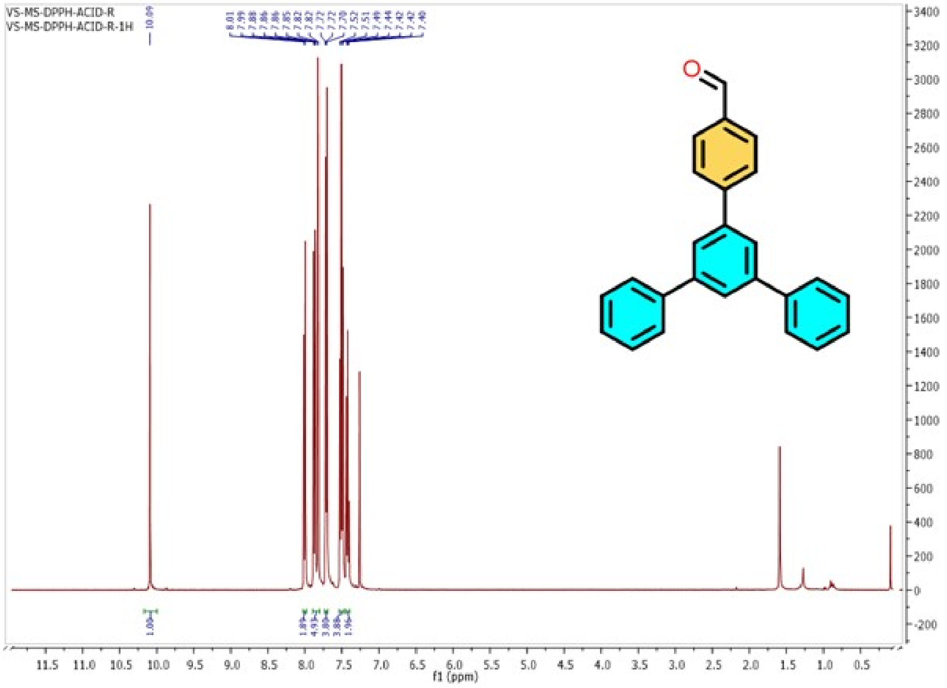


Fig. SI 1 ^{1}H NMR spectrum of aldehyde Intermediate – I

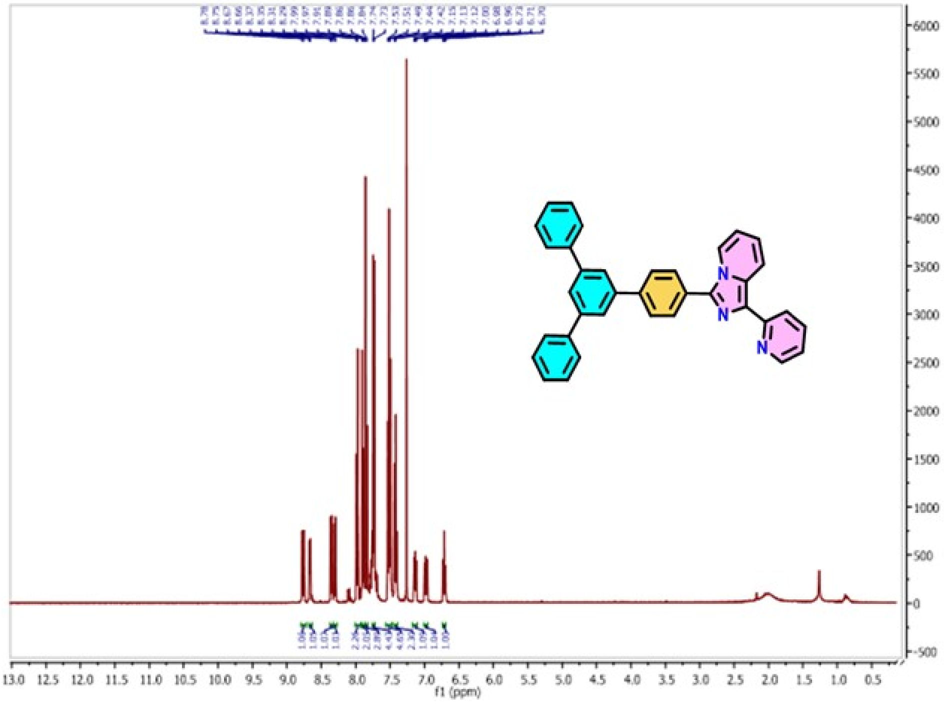


Fig. SI 2 ^{1}H NMR spectrum of L-DpPh

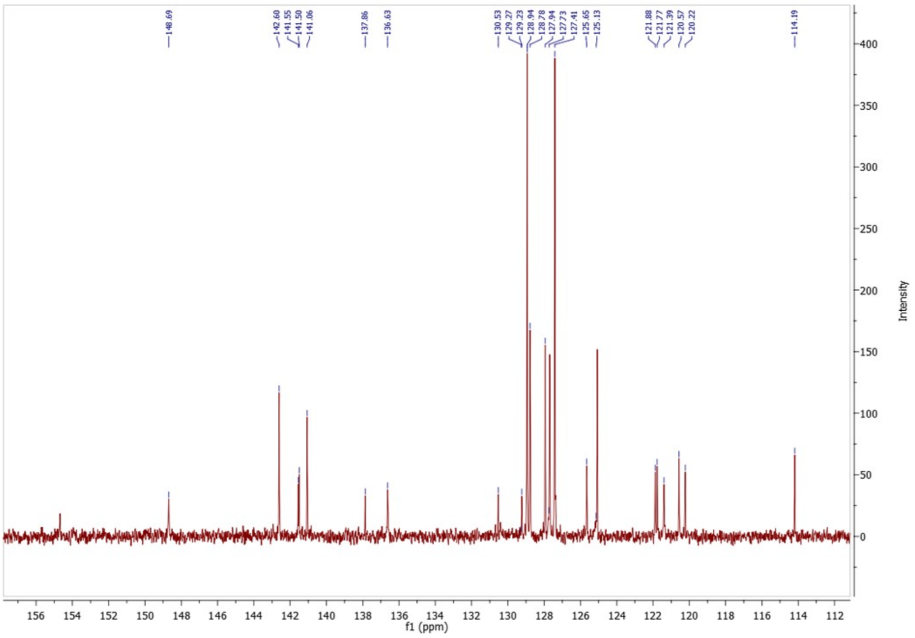


Fig. SI 3 ^{13}C NMR spectrum of L-DpPh

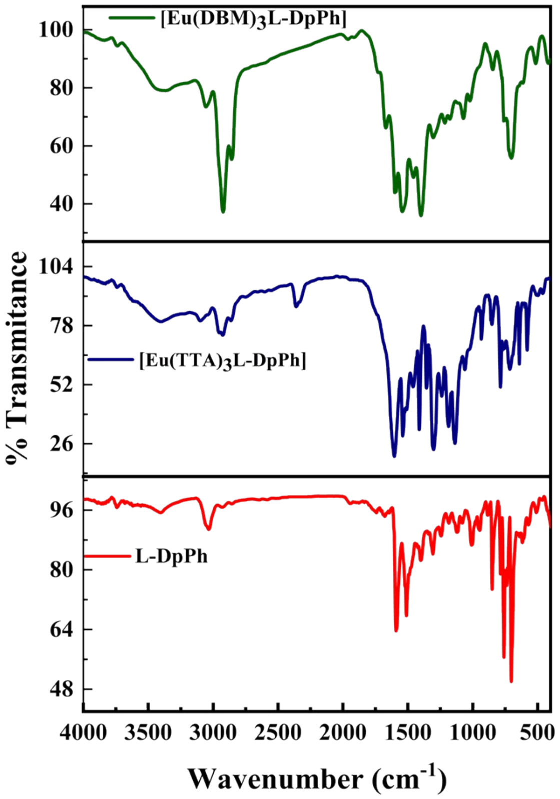


Fig. S14. FT-IR spectrum of L-DpPh

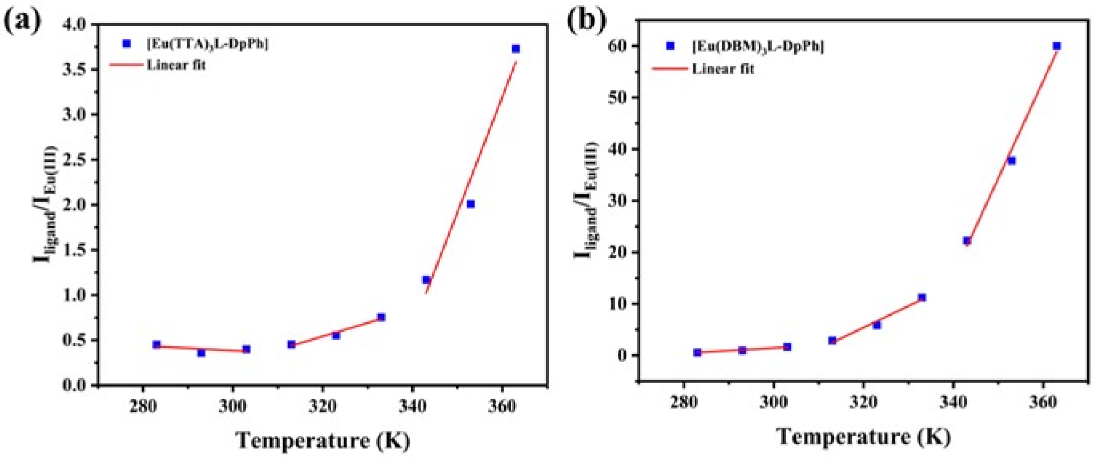


Fig. SI 5 Linear fitting plot of I_{lig}/I_{Eu} vs Temperature for the complexes **(a)** [Eu(TTA)$_3$L-DpPh], **(b)** [Eu(DBM)$_3$L-DpPh]

77K Phosphorescence spectra:

To determine the triplet level energies, a common practice can be used, i.e., the analogue of non-emitting lanthanide ion[1] (La^{3+}, Gd^{3+}, and Lu^{3+}). We have used Gd(III), as the emitting level $^6P_{7/2}$ of Gd(III), which has an energy higher energy and is hard to accept energy from the ligand[2]. Therefore, the triplet level emission of the ligand can be estimated by 77 K phosphorescence spectra.

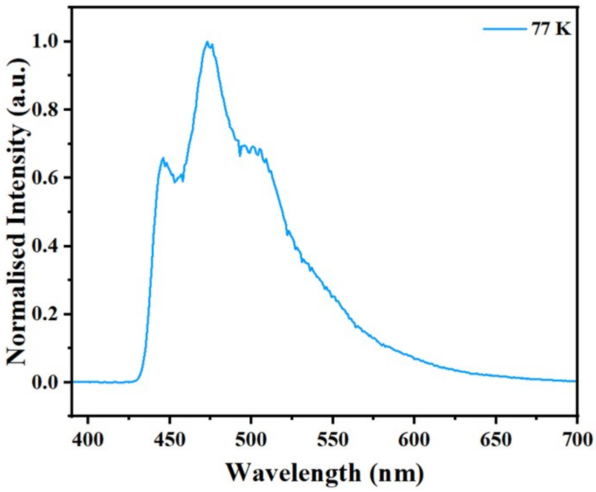


Fig. SI 6 77 K Phosphorescence spectra

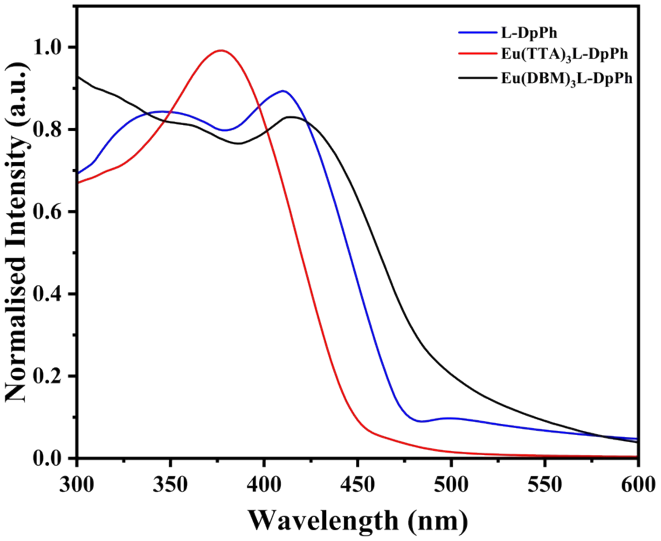


Fig. SI 7 UV-DRS absorption spectra of L-DpPh, [Eu(TTA)$_3$L-DpPh] and [Eu(DBM)$_3$L-DpPh]

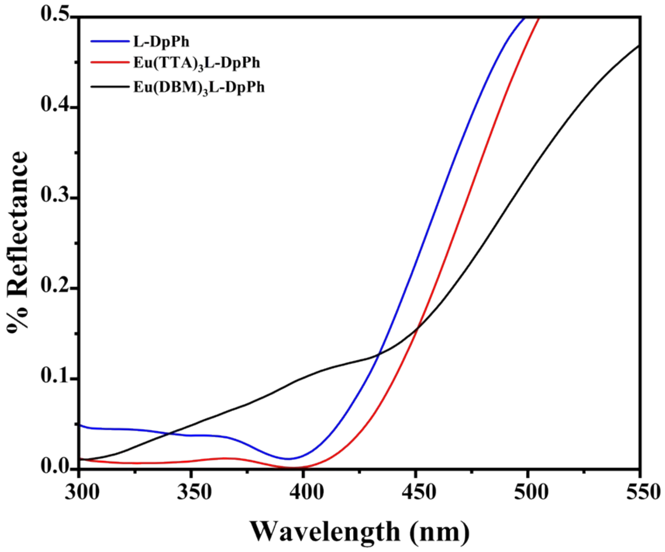


Fig. SI 8 UV-DRS reflectance spectra of L-DpPh, [Eu(TTA)$_3$L-DpPh] and [Eu(DBM)$_3$L-DpPh]

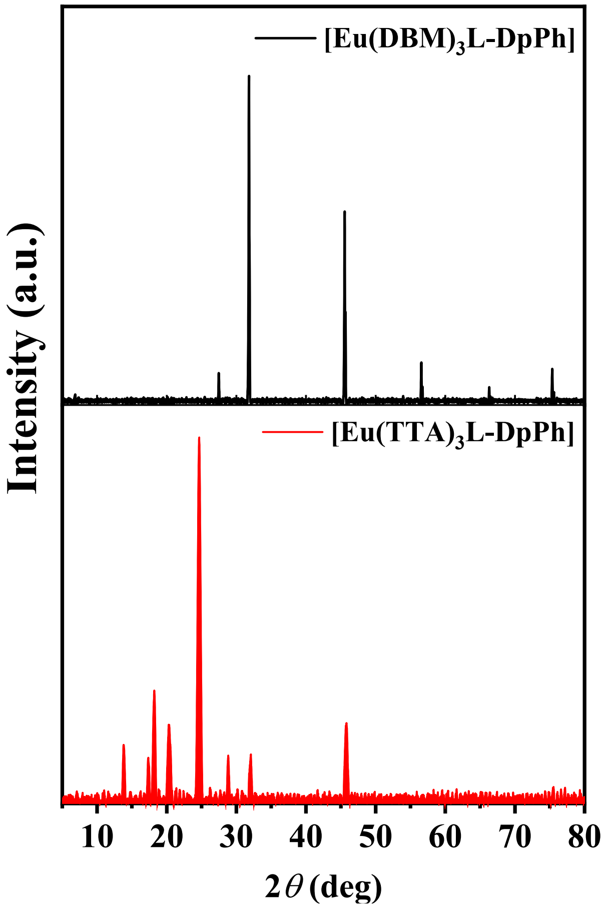


Fig. SI 9. PXRD pattern of the complexes

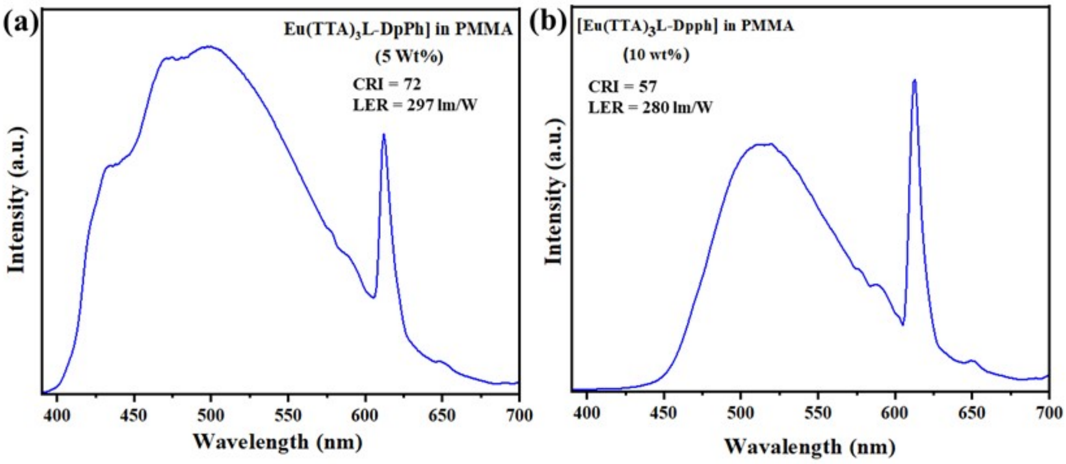


Fig. SI 10 EL spectrum of fabricated WLEDs by using n-UV LED (390 nm, 20A forward bias current) for [Eu(TTA)$_3$L-DpPh] with (a) 5 wt% and (b)10 wt% in PMMA

SI (ib) DFT Analysis

Density Functional Theory calculation

The ligand sub-atomic structures were optimized within the density functional theory (DFT) framework utilizing B3LYP/6-31G (d, p) level of theory. A UV-visible spectrum of the molecule is obtained by exciting the molecule vertically after conformation of the ground state geometry for the ligand. Further, to depict PL emission and excitation mechanism of the Eu(III) complex, the triplet energized condition of the ligand is additionally accessed by utilizing the same procedure specified previously. The optimization study of the ligand is effectively accomplished by the G16W program.

Table ST.1 Comparison of the values of HOMO, LUMO, Eg, S1, T1, λ_{em} (in solid) L-DpPh with the previously reported ligand L-TPA[3]

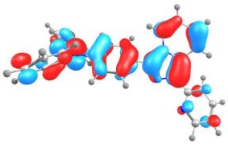
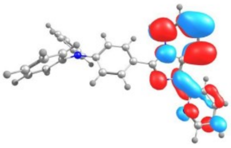
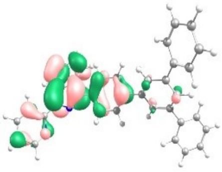
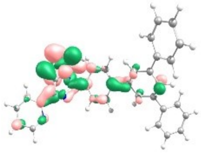
Ligand	HOMO (eV)	LUMO (eV)	Eg (eV)	S_1 (eV)	T_1 (eV)	λ_{em} (Solid) (nm)
L-TPA	 -4.74	 -1.14	3.60	3.17	2.30	553
L-DpPh	 -5.02	 -1.27	3.75	3.23	2.23	460

Table ST.2 The computed vertical transitions and their oscillator strengths (*f*) and configuration of the ligand L-DpPh.

Luminophores	**State**	**Energy (eV)**	**λ_{max} (nm)**	***f***	**Configuration**
L-DpPh Singlet	Gas	3.2367	382.41	0.1023	HOMO→LUMO (58.90 %)
		3.4174	368.38	0.7705	HOMO→LUMO (33.95 %) HOMO→LUMO+1 (61.08 %)
		3.7372	314.43	0.0046	HOMO→LUMO+2 (69.04 %)
Triplet	Gas	2.2352	538.25	0	HOMO→LUMO (63.86 %)
		2.6462	491.03	0	HOMO→LUMO (17.13 %) HOMO→LUMO+1 (58.62 %) HOMO→LUMO+3 (11.75 %)
		3.0744	394.56	0	HOMO-2→LUMO (14.23 %) HOMO-2→LUMO+1 (22.75 %) HOMO-2→LUMO+4 (16.13 %) HOMO-1→LUMO+2 (41.82 %) HOMO→LUMO+3 (31.12 %)

Optimised Cartesian coordinates of L-DpPh:

L-DpPh:

Optimized Cartesian coordinates:

symmetry c1

	x	*y*	*z*
C	-4.421087000	1.296837000	-0.185161000
C	-3.021610000	1.194035000	-0.266356000
C	-2.360792000	-0.021466000	-0.015091000
C	-3.130581000	-1.148936000	0.322111000
C	-4.531765000	-1.079223000	0.407935000
C	-5.161760000	0.150903000	0.152047000
H	-2.444152000	2.057444000	-0.578318000
H	-2.630491000	-2.077948000	0.573479000
H	-6.242368000	0.217432000	0.217005000
C	-5.330416000	-2.278055000	0.781633000
C	-6.461879000	-2.164744000	1.613577000
C	-4.974987000	-3.557913000	0.311770000
C	-7.212091000	-3.291394000	1.961927000
H	-6.737772000	-1.192600000	2.009407000
C	-5.723873000	-4.684902000	0.661623000
H	-4.121728000	-3.664251000	-0.350598000
C	-6.846419000	-4.556688000	1.487944000
H	-8.075683000	-3.182471000	2.610720000
H	-5.436311000	-5.660747000	0.282532000
H	-7.428442000	-5.431621000	1.759442000
C	-5.105588000	2.587427000	-0.468871000
C	-6.334591000	2.620093000	-1.157123000

C	-4.541234000	3.810285000	-0.054976000
C	-6.977287000	3.832933000	-1.420694000
H	-6.773949000	1.692157000	-1.509063000
C	-5.182823000	5.023257000	-0.320276000
H	-3.607902000	3.806389000	0.498961000
C	-6.404222000	5.040082000	-1.003880000
H	-7.919950000	3.835824000	-1.959228000
H	-4.733804000	5.953356000	0.014164000
H	-6.902902000	5.981927000	-1.209358000
C	-0.880077000	-0.110315000	-0.104287000
C	-0.247365000	-1.265980000	-0.598560000
C	-0.058135000	0.957883000	0.312344000
C	1.142818000	-1.349496000	-0.689327000
H	-0.850073000	-2.106639000	-0.926501000
C	1.327990000	0.883217000	0.219646000
H	-0.513661000	1.847465000	0.734711000
C	1.957592000	-0.268094000	-0.298863000
H	1.587214000	-2.278472000	-1.028846000
H	1.951395000	1.702258000	0.558799000
C	3.418330000	-0.290477000	-0.343812000
C	5.512566000	0.108866000	0.214797000
C	5.572304000	-0.740206000	-0.905560000
C	3.890972000	-1.710325000	-2.401151000
H	2.842766000	-1.792651000	-2.642089000
C	4.886754000	-2.241450000	-3.171350000
H	4.621585000	-2.802554000	-4.059140000
C	6.260949000	-2.038717000	-2.830149000

H	7.036660000	-2.457532000	-3.460388000
C	6.590402000	-1.290614000	-1.723573000
H	7.624262000	-1.088725000	-1.474047000
C	6.620402000	0.665828000	0.992676000
C	7.825142000	-0.042724000	1.177618000
C	8.859761000	0.539140000	1.912587000
H	7.932353000	-1.047226000	0.784438000
C	7.438622000	2.439733000	2.258825000
C	8.670566000	1.809645000	2.465919000
H	9.790732000	0.002338000	2.064776000
H	7.239453000	3.421203000	2.678634000
H	9.447317000	2.294568000	3.046659000
N	6.437318000	1.897702000	1.539534000
N	4.197667000	0.373807000	0.520758000
N	4.214431000	-0.985737000	-1.261959000

Imaginary frequencies of the optimised geometries of L-DpPh:

Mode	Frequency
80	938.74
23	278.33
87	982.98
8	54.29
113	1187.87
112	1187.78
25	308.58
77	918.24
4	44.37
141	1480.75
90	999.21
13	122.75
6	48.66
134	1375.81
24	300.45
89	999.03

83	973.85
7	49.25
48	634.37
38	502.78
131	1362.76
16	151.46
37	461.48
17	192.92
20	239.47
15	143.63
1	10.83
26	326.82
96	1018.05
22	270.27
117	1211.46
27	351.77
14	126.34
10	77.96
3	24.4
21	241.22
52	658.29
73	862.1
2	17.07
86	978.34
18	203.93
97	1027.04
32	419.27
85	975.93
84	975.69
45	623.98
95	1015.73
34	423.45
19	218.93
28	371.32
72	861.57
88	988.62
42	597.31
76	906.96
79	937.17
50	637.9
93	1010.12
5	45.54
49	636.22
81	945.44
12	94.21
126	1325.53

183	3220.34
41	578.57
101	1068.3
105	1119.18
9	59.49
51	643.13
11	82.22
114	1199.88
33	420.15
161	1684.51
106	1119.81
29	391.58
107	1121.88
125	1325.31
119	1266.03
133	1369.47
166	3183.66
39	514.94
116	1211.11
120	1267.39
43	610.72
186	3268.24
160	1665.35
44	621.18
31	418.06
165	3183.34
30	415.65
135	1384.17
104	1110.29
78	924.76
118	1223.41
142	1494.18
103	1109.79
130	1349
143	1500.87
62	764.62
110	1169.25
150	1575.52
164	3177.2
58	725.52
139	1468.83
184	3221.42
100	1057.04
163	3176.98
68	837.49
63	768.13

111	1181.15
144	1509.96
174	3201.02
175	3201.99
71	860.56
92	1005.52
169	3192.37
35	435.34
122	1292.21
159	1660.03
70	842.76
128	1339.34
123	1303.46
94	1012.13
54	709.19
182	3212.11
99	1044.26
46	626.21
36	441.26
127	1327.57
185	3231.07
47	630.71
108	1146.24
91	1000.36
176	3202.41
102	1075.52
75	903.03
61	756.82
177	3204.75
167	3184.56
40	532.16
69	842.57
147	1541.46
137	1442.19
181	3207.98
154	1630.8
158	1659.23
178	3205.89
152	1620.22
121	1290.73
60	755.55
172	3197.22
129	1340.64
115	1210.86
151	1605.85
138	1451.19

56	716.04
57	717.66
53	662.55
168	3187.47
98	1037.93
65	780.82
66	782.55
136	1438.85
59	743.83
179	3206.54
170	3192.77
157	1644.02
146	1539.97
74	866.14
67	810.27
173	3198.64
124	1318.38
171	3193.48
109	1153.08
55	714.86
140	1473.14
180	3207.6
156	1642.48
82	964.39
64	779.61
153	1628.21
162	3154.95
132	1365.01
149	1567.51
145	1521.68
148	1556.31
155	1641.78

Reference:

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2. S. Hussan, M. Farid, Y. Wang, A series of lanthanide–quinoxaline-2,3(1H,4H)- dione complexes containing 1D chiral Ln2O3 (Ln ¼ Eu, Tb, Sm, Dy) chains: luminescent properties and response to small molecules, *RSC Adv.,* 2021, 11, 33309

3. K. Singh, R. Boddula and S. Vaidyanathan, Versatile luminescent europium (III)− β-Diketonate-imidazo-bipyridyl complexes intended for white LEDs: A detailed photophysical and theoretical study, *Inorg. Chem.*, 2017, **56**, 9376–9390.