Supporting information for

Coordination Geometrical Effect On LMCT-depended Energy Transfer Processes Of Luminescent Eu(III) Complexes

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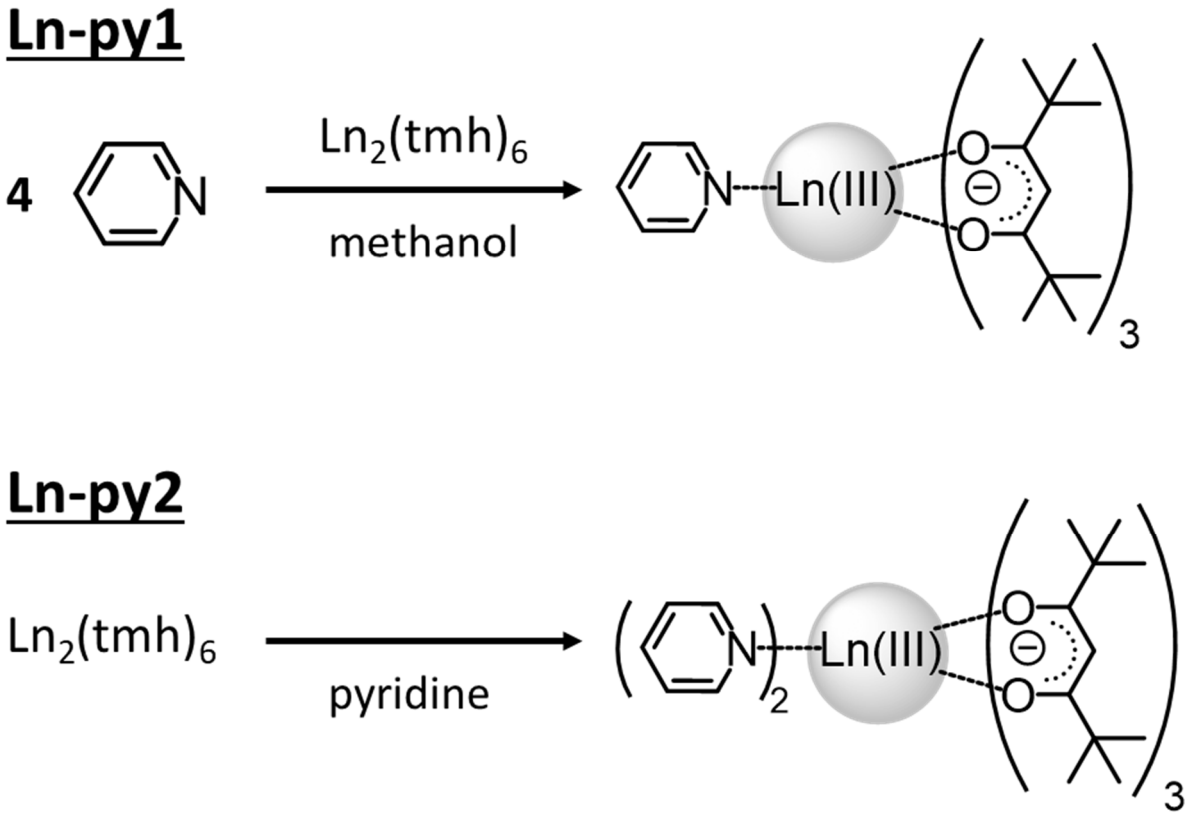
Scheme S1. Synthetic scheme of pyridine-based $Ln(tmh)_3$ complexes



Ln(III): Eu(III) or Gd(III).

Conditions: All reactions were performed under reflux.

Table S1. Crystallographic Data

	[Eu(tmh)$_3$(py)$_1$]	[Gd(tmh)$_3$(py)$_1$]	[Eu(tmh)$_3$(py)$_2$]	[Gd(tmh)$_3$(py)$_2$]
Chemical formula	$C_{38}H_{62}NO_6Eu$	$C_{38}H_{62}NO_6Gd$	$C_{43}H_{67}N_2O_6Eu$	$C_{43}H_{67}N_2O_6Gd$
F000	1632	1636	900	902
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*n* (no. 14)	*P*2$_1$/*n* (no. 14)	*P -1* (no. 2)	*P -1* (no. 2)
a/Å	19.79	19.79	10.36	10.36
b/Å	10.17	10.16	13.54	13.52
c/Å	21.48	21.50	17.06	17.03
α/deg	90	90	95.13	95.11
β/deg	109.0	109.1	98.87	98.75
γ/deg	90	90	105.5	105.5
Volume/ Å^3	4084	4084	2257	2251
Z	4	4	2	2
T/°C	-150	-150	-150	-150
R_1[a]/%	3.10	1.97	4.90	2.41
wR_2[b]/%	9.12	4.63	13.73	6.30

[a] $R_1 = \Sigma||F_0| - |F_c|| \,/\, \Sigma|F_0|$.

[b] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 \,/\, \Sigma w(F_0^2)^2]^{1/2}$.

Table S2. Calculated S_{CShM}[1,2] values for Eu(III) ions in Eu-py1

Complex	$S_{7\text{-MCO}}$	$S_{7\text{-MCTP}}$	$S_{7\text{-PBP}}$
Single-crystal	0.54562	1.20654	6.87932
DFT calculation	0.90311	1.75133	6.14860

$S_{7\text{-MCO}}$, $S_{7\text{-MCTP}}$, $S_{7\text{-PBP}}$ are *S* values calculated for monocapped-octahedron (Point group: C_{3v}), monocapped-trigonal prism (Point group: C_{2v}) and pentagonal-bipyramid (Point group: D_{5h}), respectively.

Table S3. Calculated S_{CShM}[1,2] values for Eu(III) ions in Eu-py2

Complex	$S_{8\text{-SAP}}$	$S_{8\text{-TDD}}$	$S_{8\text{-CU}}$
Single-crystal	0.54030	2.51783	10.41749
DFT calculation	0.97356	1.95962	8.14986

$S_{8\text{-SAP}}$, $S_{8\text{-TDD}}$, $S_{8\text{-CU}}$ are *S* values calculated for square antiprism (Point group: D_{4d}), triangular dodecahedron (Point group: D_{2d}) and cube (Point group: O_h), respectively.

Table S4. Atomic orbital (AO) contributions for the MOs responsible for ^{7}LMCT states of Eu-py1

No. (α MO)	Character	Orbital energy / eV	AO contribution			
			Eu (4*f*)	Eu (others)	tmh	py
188 (HOMO-5)	σ(tmh)	-9.68045	0.0214	0.0127	0.9645	0.0014
189 (HOMO-4)	σ(tmh)	-9.61473	0.0110	0.0197	0.9621	0.0072
190 (HOMO-3)	σ(tmh)	-9.51522	0.0131	0.0168	0.9618	0.0083
191 (HOMO-2)	π(tmh)	-8.77275	0.0026	0.0140	0.9803	0.0031
192 (HOMO-1)	π(tmh)	-8.60681	0.0028	0.0147	0.9818	0.0007
193 (HOMO)	π(tmh)	-8.52218	0.0059	0.0115	0.9815	0.0011
194 (LUMO)	4f(Eu)	-0.79164	0.9526	0.0025	0.0424	0.0025

Table S5. Atomic orbital (AO) contributions for the MOs responsible for ^{7}LMCT states of Eu-py2

No. (α MO)	Character	Orbital energy / eV	AO contribution			
			Eu (4*f*)	Eu (others)	tmh	py
209 (HOMO-5)	σ(tmh)	-9.44145	0.0214	0.0111	0.9632	0.0043
210 (HOMO-4)	σ(tmh)	-9.37940	0.0079	0.0190	0.9617	0.0114
211 (HOMO-3)	σ(tmh)	-9.29238	0.0093	0.0145	0.9629	0.0133
212 (HOMO-2)	π(tmh)	-8.51399	0.0055	0.0051	0.9667	0.0226
213 (HOMO-1)	π(tmh)	-8.41832	0.0019	0.0157	0.9770	0.0055
214 (HOMO)	π(tmh)	-8.28201	0.0031	0.0068	0.9827	0.0074
215 (LUMO)	4f(Eu)	-0.47539	0.9565	0.0026	0.0366	0.0043

Table S6. Cartesian coordinates (in Å) of Eu-py1 for optimized structure obtained from DFT calculations

Atom	X	Y	Z	Atom	X	Y	Z
Eu	10.29936	14.19516	9.538657	H	9.628102	7.645113	8.044382
O	11.48106	15.33867	11.22989	H	8.591609	8.321317	9.323349
O	12.1525	12.91025	10.05594	C	8.651128	10.01241	7.107069
C	12.66037	15.27079	11.69437	H	7.642356	9.949095	7.547863
C	13.56221	14.20727	11.44607	H	8.734879	9.234262	6.330815
C	13.2598	13.07723	10.66244	H	8.756711	10.99868	6.635036
H	14.53736	14.26088	11.9192	C	11.13466	9.904797	7.531226
C	13.11441	16.4372	12.60448	H	11.2408	9.141242	6.742964
C	11.96774	17.44811	12.76251	H	11.2828	10.89899	7.085201
H	11.64415	17.83847	11.78688	H	11.93049	9.743199	8.275803
H	12.29562	18.29226	13.39065	C	9.442763	11.49119	13.04749
H	11.08949	16.98302	13.23417	C	9.580741	10.00277	13.39824
C	14.32585	17.14142	11.95607	H	8.726512	9.414616	13.02707
H	15.18433	16.46235	11.84352	H	9.618344	9.881556	14.49301
H	14.64584	17.99397	12.57857	H	10.50507	9.571308	12.98363
H	14.06702	17.52686	10.95652	C	8.155064	12.05347	13.68365
C	13.50321	15.88994	13.99469	H	8.030688	13.11654	13.43306
H	12.66225	15.342	14.45055	H	8.193882	11.95007	14.7805
H	13.77379	16.72188	14.66641	H	7.266594	11.51127	13.31988
H	14.3628	15.20499	13.94425	C	10.6711	12.25932	13.59122
C	14.25681	11.91029	10.49078	H	11.6032	11.87497	13.14849
C	15.5998	12.12168	11.20355	H	10.73573	12.14959	14.68633
H	16.12329	13.01504	10.82765	H	10.60684	13.32799	13.34072
H	15.47363	12.22658	12.29278	O	9.157068	14.95548	7.63635
H	16.2548	11.25304	11.02706	O	11.81779	15.32269	8.197644
C	13.57047	10.64301	11.04767	C	9.498149	15.2845	6.451314
H	14.18643	9.752477	10.83974	C	10.79933	15.69236	6.088802
H	13.43709	10.71556	12.14007	C	11.88429	15.72622	6.991816
H	12.57859	10.50936	10.59221	H	10.97279	16.00605	5.066986
C	14.50242	11.7364	8.97624	C	8.364291	15.17985	5.408875
H	13.54969	11.60605	8.444896	C	7.144602	15.95944	5.941781
H	15.13761	10.85432	8.791861	H	6.832146	15.56775	6.919865
H	15.01161	12.61874	8.555832	H	6.29798	15.86813	5.242146
O	9.680509	12.13491	8.646636	H	7.379426	17.03168	6.053386
O	9.256542	13.0159	11.24212	C	8.740443	15.71122	4.018124
C	9.633164	10.98133	9.183023	H	9.015237	16.77772	4.049026
C	9.533783	10.75496	10.57555	H	7.881513	15.60648	3.335627
C	9.397071	11.7794	11.53216	H	9.580219	15.15066	3.579119
H	9.572909	9.732057	10.92843	C	8.009303	13.67807	5.310048
C	9.737346	9.808261	8.184085	H	8.859715	13.09846	4.915112
C	9.567954	8.422328	8.823475	H	7.150622	13.5325	4.633945
H	10.35764	8.210483	9.561375	H	7.757336	13.27594	6.301731

Atom	X	Y	Z	Atom	X	Y	Z
C	13.27132	16.26726	6.585805	H	12.66182	17.51641	4.884106
C	13.56692	17.47291	7.505664	N	8.605504	15.91192	10.54807
H	12.84828	18.29041	7.329155	C	7.878392	16.77986	9.823327
H	14.58096	17.85995	7.312752	C	7.047551	17.73859	10.40489
H	13.49641	17.17278	8.561366	C	6.965605	17.79838	11.79745
C	14.29947	15.14945	6.864605	C	7.717914	16.8963	12.5536
H	14.24291	14.83129	7.914974	C	8.523499	15.97273	11.8889
H	15.32003	15.50897	6.653692	H	7.97653	16.68225	8.740874
H	14.10794	14.26872	6.229545	H	6.477781	18.42092	9.771932
C	13.36722	16.70327	5.117194	H	6.325181	18.53614	12.28639
H	13.1687	15.86563	4.429975	H	7.686035	16.90409	13.64429
H	14.38347	17.07332	4.905767	H	9.131227	15.24592	12.42833

Table S7. Cartesian coordinates (in Å) of Eu-py2 for optimized structure obtained from DFT calculations

Atom	X	Y	Z	Atom	X	Y	Z
Eu	8.108327	19.80851	20.69336	H	2.87984	15.5405	20.13641
O	7.531718	20.2304	18.44889	H	4.465307	14.87595	20.59564
O	8.673759	22.05971	20.18863	C	3.831908	16.93308	22.35846
C	7.619527	21.18305	17.6132	H	4.3393	16.09981	22.86773
C	8.09608	22.47497	17.92467	H	2.744272	16.75944	22.42159
C	8.57583	22.84914	19.20022	H	4.064154	17.85696	22.91216
H	8.092	23.22206	17.14099	C	3.478024	18.20073	20.22259
C	7.146228	20.81909	16.18746	H	3.649451	19.15063	20.74807
C	8.04595	19.66357	15.69741	H	2.399018	17.9765	20.24419
H	9.098237	19.98526	15.62763	H	3.785344	18.3438	19.17556
H	7.722129	19.32255	14.70014	C	9.040423	15.45679	21.83815
H	7.995614	18.816	16.39549	C	8.326229	14.26785	22.49682
C	5.688675	20.32224	16.3026	H	7.704507	14.58963	23.34713
H	5.324093	19.96805	15.32442	H	9.071124	13.55063	22.87827
H	5.621193	19.49808	17.02766	H	7.682946	13.72979	21.78263
H	5.023212	21.13518	16.63943	C	9.887457	14.95661	20.64836
C	7.214918	21.97972	15.18508	H	9.252343	14.47555	19.88572
H	6.582074	22.82596	15.49624	H	10.63094	14.21745	20.99025
H	6.857641	21.64155	14.19879	H	10.41973	15.79589	20.17718
H	8.24494	22.34822	15.0572	C	9.963696	16.13984	22.87159
C	9.030572	24.29743	19.49718	H	10.48293	16.99552	22.41744
C	10.47811	24.227	20.02894	H	10.71167	15.42348	23.24985
H	10.53511	23.54876	20.8928	H	9.384359	16.51951	23.72767
H	10.82469	25.2269	20.33733	O	9.998207	20.30414	22.07186
H	11.16507	23.85379	19.25066	O	7.484219	19.5686	22.92423
C	8.974866	25.23705	18.28428	C	10.27971	20.25395	23.30342
H	9.622432	24.88555	17.4654	C	9.35535	19.91553	24.32754
H	9.321565	26.24197	18.5755	C	8.014488	19.57889	24.08466
H	7.950245	25.33935	17.89367	H	9.718803	19.89937	25.34992
C	8.102702	24.83665	20.60758	C	11.74623	20.55888	23.69838
H	7.055642	24.87323	20.26441	C	11.79382	21.69583	24.74018
H	8.406401	25.85561	20.89953	H	11.31581	22.60871	24.34881
H	8.146729	24.18642	21.49268	H	12.8416	21.93881	24.98493
O	6.116463	18.49896	20.38564	H	11.28599	21.42296	25.67727
O	8.679054	17.56844	20.82331	C	12.54351	20.98239	22.45511
C	5.779316	17.36964	20.83947	H	12.53415	20.19434	21.68916
C	6.68989	16.39352	21.33227	H	13.58924	21.1915	22.73379
C	8.083126	16.5409	21.29936	H	12.11701	21.88914	21.99997
H	6.274222	15.47536	21.73437	C	12.37128	19.27558	24.28895
C	4.263178	17.05535	20.87978	H	11.85534	18.95519	25.20653
C	3.964849	15.73941	20.13256	H	13.43217	19.44971	24.53631
H	4.296188	15.79944	19.08305	H	12.319	18.44589	23.56555

Atom	X	Y	Z	Atom	X	Y	Z
C	7.058499	19.15261	25.22275	C	5.956231	22.1988	22.13922
C	7.626044	19.38115	26.63088	H	5.202431	20.80904	19.27924
H	8.530536	18.77945	26.81075	H	3.288105	22.43972	19.40841
H	6.879399	19.08632	27.38626	H	3.134571	23.95265	21.4206
H	7.877281	20.44047	26.80019	H	4.910502	23.76064	23.20131
C	6.767537	17.64908	25.01891	H	6.745889	22.07459	22.88293
H	7.674668	17.04669	25.1898	N	10.24003	19.46132	19.18318
H	6.419401	17.45737	23.99397	C	11.16359	20.43005	19.09066
H	5.995234	17.3087	25.72901	C	12.24435	20.3609	18.20975
C	5.745968	19.94789	25.06384	C	12.37013	19.23736	17.39004
H	5.005711	19.61662	25.81034	C	11.41125	18.22556	17.48657
H	5.327576	19.8044	24.05788	C	10.36596	18.38067	18.39742
H	5.917197	21.0277	25.21137	H	11.01757	21.27887	19.75897
N	6.037609	21.39578	21.06842	H	12.97015	21.17519	18.1741
C	5.093321	21.49447	20.12078	H	13.20253	19.15017	16.68776
C	4.033289	22.39893	20.20471	H	11.46802	17.32784	16.86863
C	3.951273	23.23381	21.3213	H	9.594411	17.61841	18.52262
C	4.933171	23.13134	22.31007				

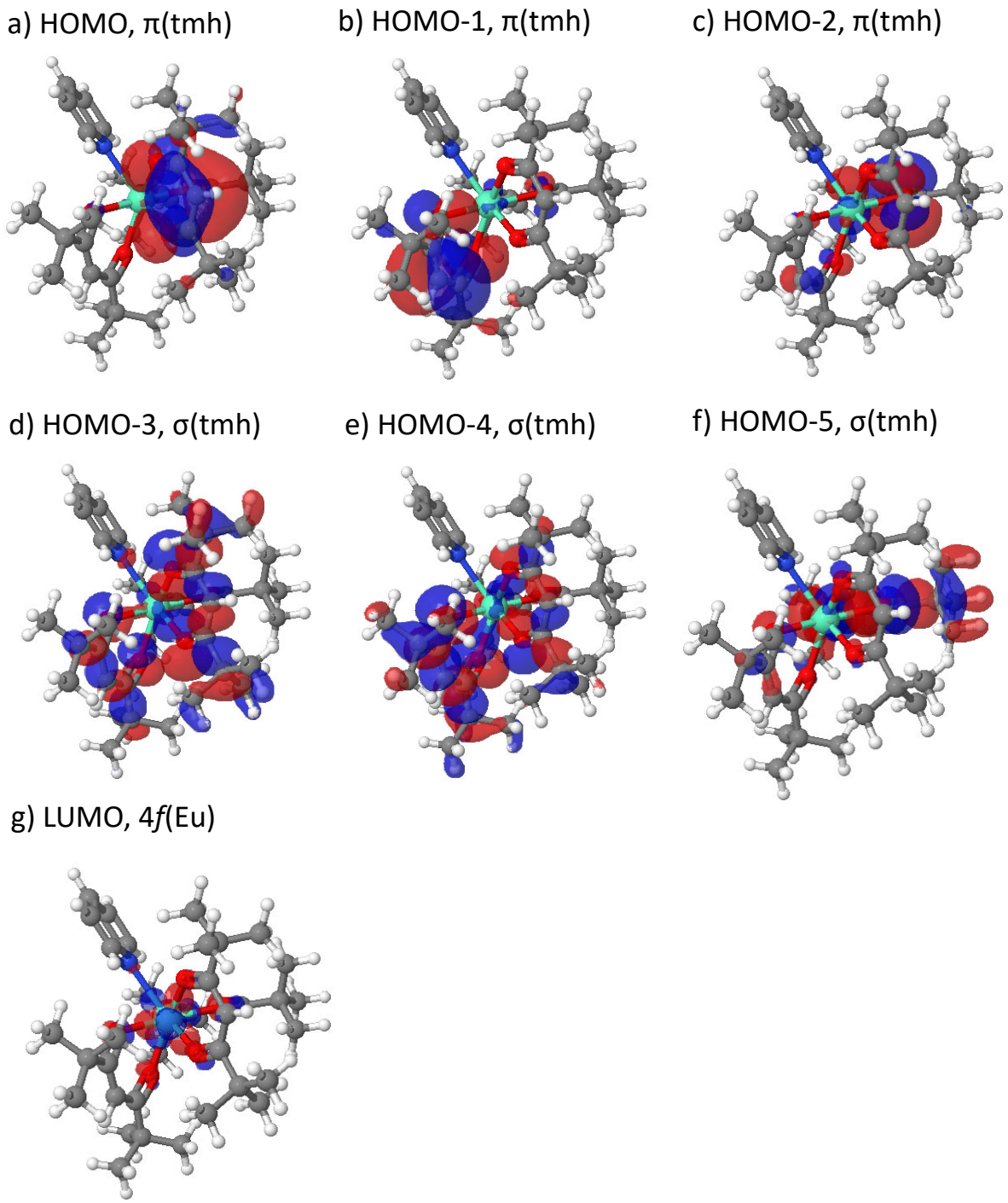
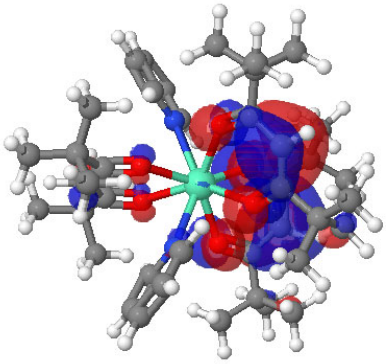
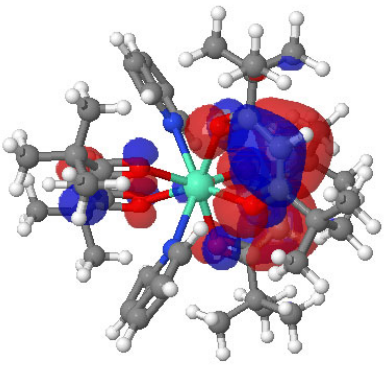


Figure S1. α-orbital representations for MOs responsible for ^{7}LMCT states of Eu-py1

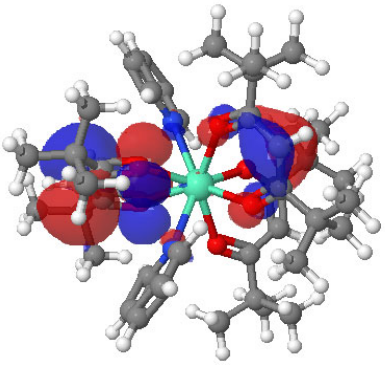
a) HOMO, π(tmh)



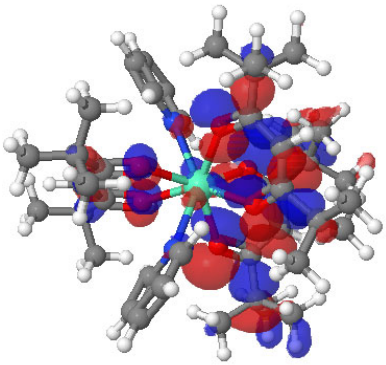
b) HOMO-1, π(tmh)



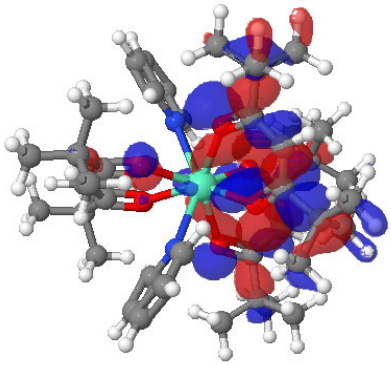
c) HOMO-2, π(tmh)



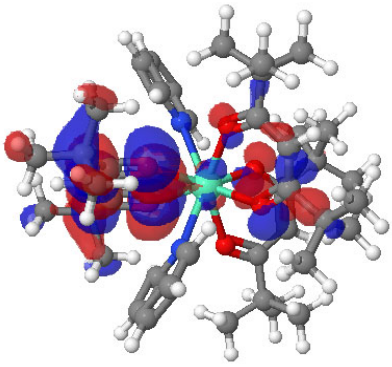
d) HOMO-3, σ(tmh)



e) HOMO-4, σ(tmh)



f) HOMO-5, σ(tmh)



g) LUMO, 4*f*(Eu)

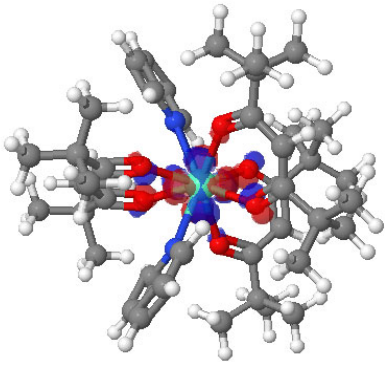


Figure S2. α-orbital representations for MOs responsible for ^{7}LMCT states of Eu-py2

Eu-py1's absorption edge is red-shifted compared to Eu-py2, indicating LMCT states at lower energy reaching the VIS region. Gd-py1 and Gd-py2 showed almost exactly similar profiles, indicating that both structures show similar excited states for tmh and py ligands.

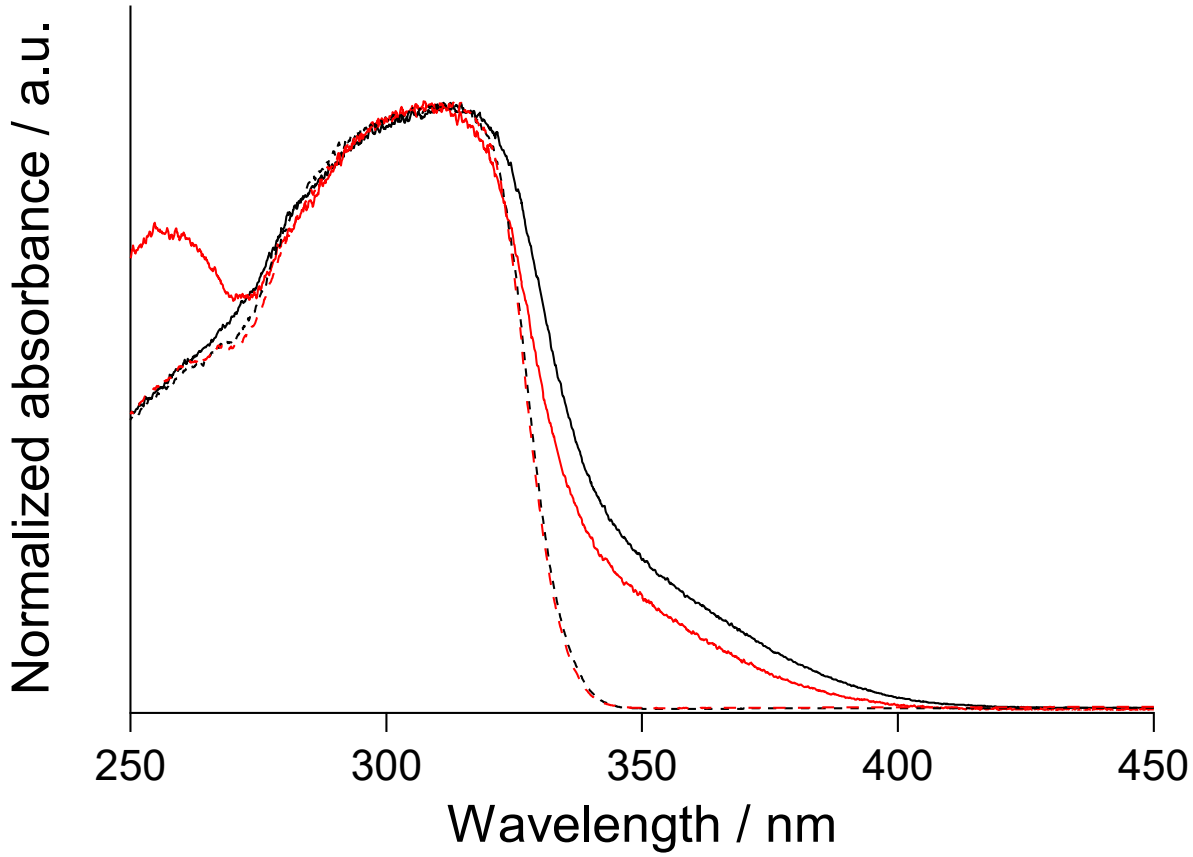


Figure S3. Reflectance spectra of Eu-py1 (back solid line) and Eu-py2 (red solid line). Gd-py1 (black dash line) and Gd-py2 (red dash line) were also included for comparison.

Table S8. Emission quantum yields for Eu-py1 and Eu-py2 under different conditions

	Φ_{464_air}	Φ_{464_Ar}	Φ_{530_air}	Φ_{530_Ar}
Eu-py1	42.2 ± 0.4 %	48.1 ± 0.3 %	60.0 ± 2.8 %	65.5 ± 1.5 %
Eu-py2	42.5 ± 0.4 %	47.9 ± 2.5 %	63.2 ± 7.3 %	62.4 ± 4.7 %

Φ_{464}: Corresponds to the $^5D_2 \leftarrow {}^7F_{1,0}$ transition in Eu(III) complexes.

Φ_{530}: Corresponds to the $^5D_1 \leftarrow {}^7F_1$ transition in Eu(III) complexes.

Table S9. Emission quantum yields for Eu-py2 under pyridine solution (10^{-4} M)

	Φ_{330_air}	Φ_{330_Ar}
Eu-py2	0.26 ± 0.04 %	0.17 ± 0.03 %

Excited at 330 nm (π-π* bands).

Φ_{330_air}: Corresponds to the quantum yields measured after air bubbling.

Φ_{330_Ar}: Corresponds to the quantum yields measured after argon bubbling.

Unfortunately, the quantum yields for Eu-py1 under pyridine or other solvents were not measured because of the instability of this compound.

Table S10. Excitation energies for ^{5}LMCT and ^{9}LMCT states of Eu-py1 and Eu-py2 obtained by TD-DFT calculation

	^{5}LMCT / cm^{-1}	^{9}LMCT / cm^{-1}
Eu-py1	49,035 (203.93 nm)	23,476 (425.96 nm)
Eu-py2	49,936 (200.26 nm)	24,239 (412.57 nm)

Calculated based on the optimized-geometry structure in the ground state.

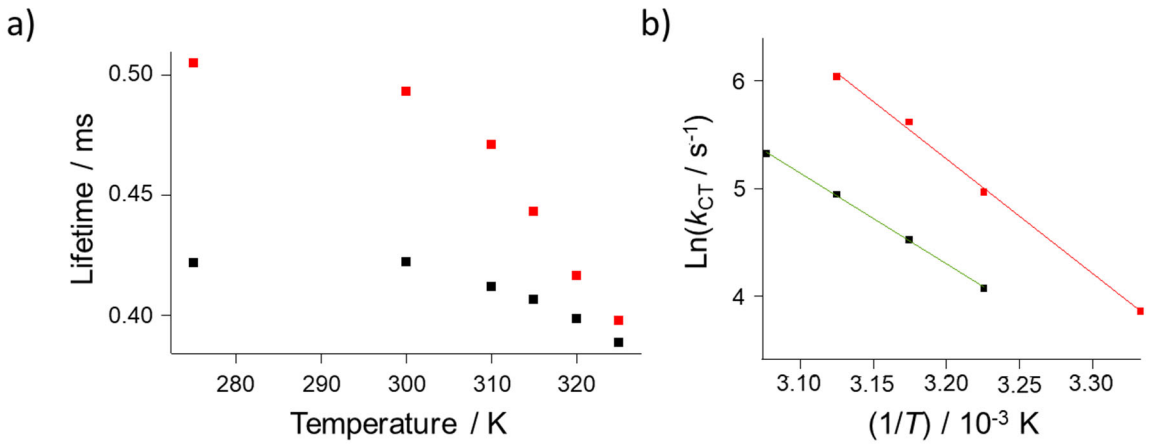


Figure S4. a) Emission lifetime temperature-dependent derived from $^5D_0 \rightarrow {}^7F_J$ for Eu-py1 (black dot) and Eu-py2 (red dot). Excitation wavelength was at 355 nm (Nd:YAG laser, 3ω). Measured in vacuum. The emission lifetimes were obtained from single-exponential analyses. b) Arrhenius analyses of emission lifetime temperature dependence for Eu-py1 (black dot and green fitting line) and Eu-py2 (red dot and pink fitting line).

Arrhenius equation: $\ln (1/\tau_{obs} - 1/\tau_{const}) = \ln (k_{CT}) = \ln (A) - (E_a/k_B T)$

where, τ_{obs} is the observed emission lifetime at each temperature; τ_{const} is the emission lifetime in which up to that temperature the lifetime obtained for such transition is constant (lowest T); k_B is the Boltzmann constant.

Table S11. Frequency factors A and activation energies E_a of temperature-dependent $^5D_0$ emission of Eu(III) complexes

	Frequency factor A / s^{-1}	Activation energy E_a / cm^{-1}
Eu-py1	3.7×10^{13} ($\times e^{\pm 0.424}$)	5850 (± 94)
Eu-py2	7.2×10^{15} ($\times e^{\pm 2.17}$)	6795 (± 472)

The temperature depended emission lifetimes from $^5D_0$ state (17,250 cm^{-1}) was observed in the range of milli-second scale. The E_a values of Eu-py1 and Eu-py2 are calculated to be 5,850 cm^{-1} and 6,795 cm^{-1}, respectively. These large activation energies correlate well to the energy gap between the $^5D_0$ state of Eu(III) and calculated ^{7}LMCT states. Qualitatively, higher E_a values for Eu-py2 also correspond to higher LMCT levels compared to Eu-py1. The frequency factors A for Eu-py2 were two orders of magnitude larger than for Eu-py1, which indicates dominant effect from geometry/vibration contribution between LMCT and $^5D_0$ states.

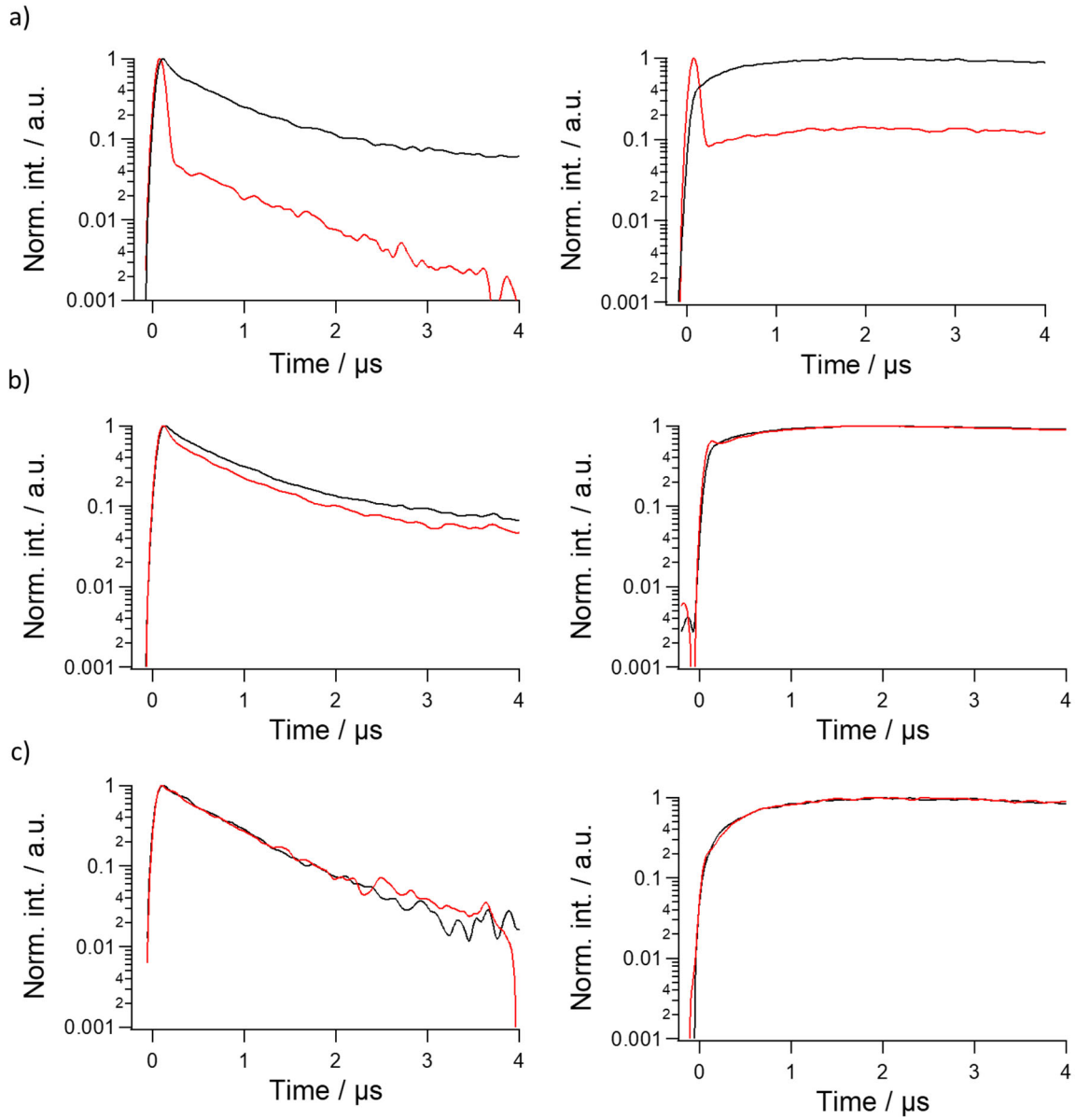


Figure S5. Time-resolved emission decay profiles derived from $^5D_0$ (right) and $^5D_1$ (left) states for Eu-py1 (black) and Eu-py2 (red) under a) 267 nm, b) 400 nm and c) 464 nm laser irradiation.

The energy transfer and quenching processes of both Eu(III) complexes were investigated to confirm the relationship between coordination structure and LMCT energy level. According to the forward energy transfer process from tmh ligand to Eu(III) ion, time-resolved luminescence was measured using a streak camera excited at 267 nm, 400 nm and 464 nm in different time-delay orders. In these time-resolution profiles, the emission decay and uprising derived from $^5D_1$ and $^5D_0$ levels of Eu-py1 were observed with very similar profiles from that

of Eu-py2 (Figure S5). The temporal profiles of emission from $^5D_0$ level shows a rise time, which corresponds to the emission decay of $^5D_1$ level. These emission profiles show direct evidence of energy transfer from the $^5D_1$ to the $^5D_0$ level. From the components of the emission decay in $^5D_1$ level, we estimated the transition rate of $^5D_1 \rightarrow {}^5D_0$ for Eu-py1 and Eu-py2. The transition rate of Eu-py2 (0.5 µs) is similar to that of Eu-py1 (0.6 µs) under all excitation wavelengths. The decay profile of $^5D_1$ level does not show a rise time for Eu-py1 and Eu-py2. These results indicate that the energy transfer from LMCT to the $^5D_1$ level occurs at a faster rate than observed or occurs to higher Eu(III) excited states such as $^5D_2$ and $^5D_3$.

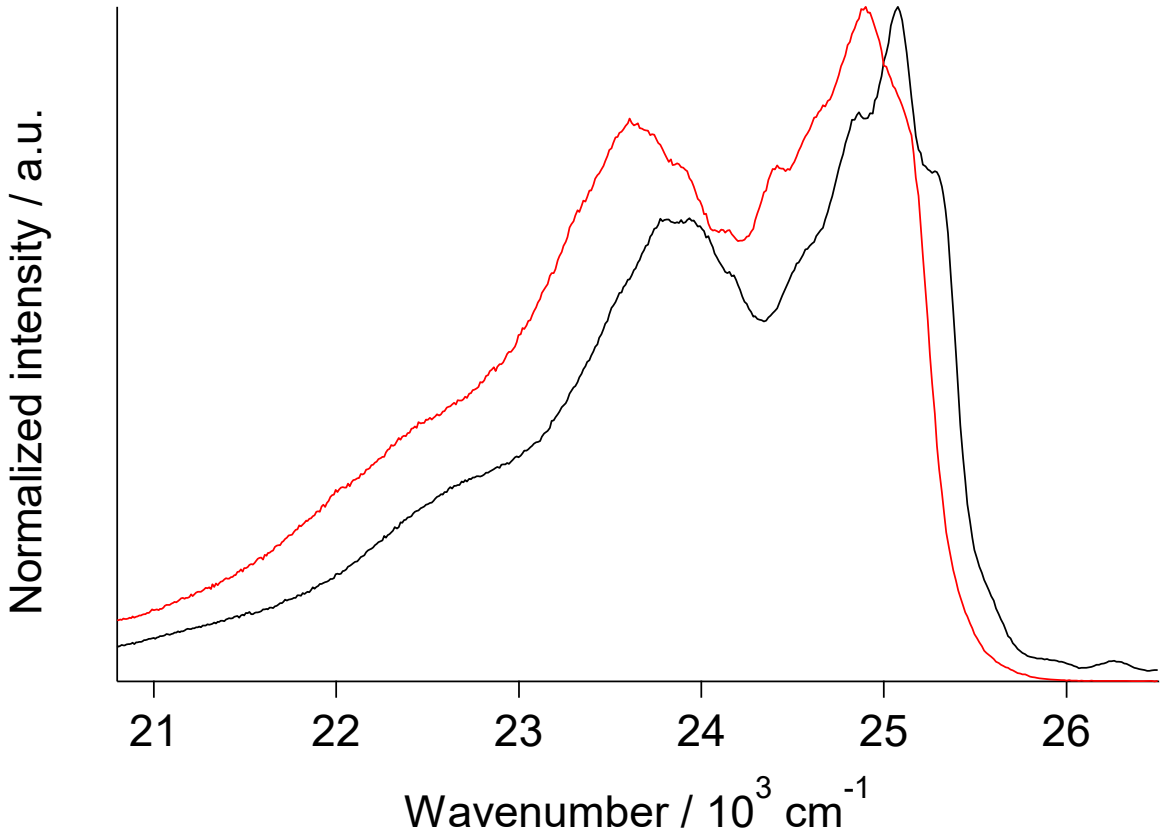


Figure S6. Phosphorescence spectra of Gd-py1 (black line) and Gd-py2 (red line) in crystals at 100 K. Excited at 330 nm. Measured in vacuum.

Phosphorescence of tmh ligand is observed with respective vibrational bands (0-0, 0-1 and 0-2). From the peak top of the 0-0 band, the triplet state of Gd-py1 was estimated at 25,075 cm^{-1}, and of Gd-py2 was estimated at 24,900 cm^{-1}. Both values are very similar and indicate that the triplet excited states of both Gd(III) complexes are unchanged.

References

[1] D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. Eur. J.* 2005, *11*, 1479–1494.

[2] M. Pinsky, D. Avnir, *Inorg. Chem.* 1998, *37*, 5575–5582.