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Ligand-to-ligand charge transfer state in lanthanide complexes containing π-bonded antenna ligands

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Experimental section, general remarks.

All synthetic manipulations were carried out in prepurified argon atmosphere in anhydrous solvent media, using a glovebox. Tetrahydrofuran was predried over NaOH and distilled from potassium/benzophenone ketyl. Hexane was distilled from Na/K alloy/benzophenone ketyl. Toluene was distilled from sodium/benzophenone ketyl. $LnCl_3(THF)_n$ (Ln = Nd, Gd, Tb) were prepared according to literature[S1], $[\{Cp^{Ph3}NdCl_2(THF)\}_2KCl]$, $[\{Cp^{Ph3}GdCl_2(THF)\}_2KCl(THF)]$, $[\{Cp^{Ph3}TbCl_2(THF)\}_2KCl(THF)]$ were prepared as described earlier[S2, S3]. Benzyl potassium was prepared according to a slightly modified literature procedure[S4]. Bipyridine was sublimed in high vacuum prior to use. THF solutions of potassium arylcyclopentadienides were prepared as described earlier[S2]. 1,2,4-triphenycyclopentadiene[S5] and 1,2,3,4-tetraphenylcyclopentadiene[S6] were recrystallized from absolute ethanol and dried in high vacuum prior to use. Elemental analyses were performed with a Thermo Scientific FLASH 2000 elemental CHNS/O analyzer. The analyses of the complexes **1Nd**, **1Gd**, **2Nd**, **2Gd**, **2Tb** for the C, H, N content were carried out with the addition of cobalt oxide (Co_3O_4) to ensure complete combustion.

Optical measurements

Luminescent measurements in the visible and NIR regions were performed with a Horiba-Jobin-Yvon-Spex Fluorolog FL 3-22 spectrometer, which has a 450 W xenon arc lamp as the excitation source for steady state measurements and 150W xenon pulse lamp for kinetic experiments. An R-928 PMT tube and InGaAs liquid N_2 cooled detector were used in spectral range 200-800 and 900-1500 nm respectively. The technique involved the use of a specially designed, cylindrical sealed quartz cuvettes for manipulation with air-sensitive compounds. Luminescence lanthanide lifetimes (τ) were measured at least three times by monitoring the decay at the maxima of the emission spectra. For phosphorescence spectrum initial delay = 0.1 ms. All complexes studied were powdered.

X-ray structure determination

Single crystal X-ray studies were carried out on a Bruker D8 QUEST diffractometer equipped with a CCD detector (MoK_{α}, $\lambda = 0.71073$ Å, graphite monochromator). The intensity data were integrated by the SAINT program[S7] and were corrected for absorption and decay using SADABS. [S8] All structures were solved by direct methods using SHELXS, [S9] and were refined on F^2 using SHELXL-2014/2017. [S10, S11] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.95 Å for aromatic, 0.99 Å for methylene, 1.00 Å for cyclopentadienyl hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.2U_{eq}(C)$. SHELXTL[S7] was used for molecular graphics. Crystal data, data collection and structure refinement details are summarized in Table S1.

Table S1. The crystallographic parameters and the structure refinement statistics for **1Ln** and **2Ln**

	1Gd	**1Nd**	**1Tb**	**2Gd**	**2Tb**
Formula	$C_{37}H_{33}Cl_2N_2OGd$	$C_{37}H_{33}Cl_2N_2ONd$	$C_{37}H_{33}Cl_2N_2OTb$	$C_{47}H_{45}Cl_2N_2O_2Gd$	$C_{47}H_{45}Cl_2N_2O_2Tb$
M	749.80	736.79	751.47	898.00	899.67
T, K	100	100	100	220	220
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	Pbca	Pbca	C2/c	C2/c
Z	8	8	8	8	8
a, Å	16.6120(6)	16.669(6)	16.5828(6)	35.8480(8)	35.8039(15)
b, Å	16.5336(6)	16.586(6)	16.5328(6)	11.3038(2)	11.2908(4)
c, Å	23.4439(8)	23.670(8)	23.5481(9)	21.2399(5)	21.2173(11)
α, °	90	90	90	90	90
β, °	90	90	90	109.3858(12)	109.434(2)
γ, °	90	90	90	90	90
V, Å^3	6439.0(4)	6544(4)	6455.9(4)	8118.8(3)	8088.5(6)
d_{calc}, g□cm^{-3}	1.547	1.496	1.546	1.469	1.478
μ, cm^{-1}	22.58	17.82	23.88	18.06	19.22
F(000)	3000	2968	3008	3640	3648
$2\Theta_{max}$, °	58	50	55	58	58
Complentess to Θ_{max}	0.999	1.0	0.997	0.998	0.998
Reflections collected	97528	69464	31077	59511	58885
Unique reflections	8558	8702	7400	10793	10747

Reflections with $I > 2\sigma(I)$	7067	6492	6005	9176	9330
Number of parameters	389	389	388	495	495
R1	0.0231	0.0535	0.0438	0.0382	0.0316
wR2	0.0568	0.0996	0.1070	0.0857	0.0774
GOF	0.925	1.244	0.959	1.084	1.046
Largest difference in peak / hole (e/Å^3)	0.489/-0.497	1.023/-1.565	1.284/-2.271	1.044/-1.374	0.904/-0.743
CCDC number	2105265	2105264	2105268	2105267	2105266

Table S2. Selected structural parameters for complexes **1Ln**, **2Ln**

Bond lengths (Å), and rotation angles (°)	**1Nd**	**1Gd**	**1Tb**	**2Gd**	**2Tb**
Ln-C_{Cp}	2.755(4) - 2.813(4)	2.705(2) - 2.770(2)	2.695(4) - 2.760(4)	2.687(3) - 2.849(3)	2.670(2) - 2.842(2)
Ln-Ccent	2.509	2.455	2.446	2.501	2.487
Ln-N	2.561(4) 2.576(4)	2.505(2) 2.509(2)	2.484(3) 2.497(3)	2.511(3) 2.525(3)	2.491(2) 2.509(2)
Ln-Cl	2.671(1) 2.676(2)	2.624(1) 2.626(1)	2.613(1) 2.613(1)	2.6087(8) 2.6216(8)	2.5920(7) 2.6051(7)
Ln-O_{THF}	2.536(3)	2.490(1)	2.483(3)	2.539(2)	2.526(2)
Rotation angles between the Cp and Ph planes	8.63 21.76 50.38	7.75 20.38 51.78	8.21 20.57 53.99	24.8 67.4 45.8 29.5	24.6 67.5 46.1 28.9
Rotation angles between Ar planes in bipy ligand	3.7	4.57	4.1	2.1	2.2

TD-DFT -calculations

The electronic excitation energies for **1Tb** were calculated with the hybrid PBE functional and large-core energy-adjusted RECPs for Tb, developed by the Stuttgart and Dresden groups, along with the accompanying basis set ECP54MWB to describe the valence electron density. [S12,13] Large core energy-adjusted RECPs for lanthanides put 5s, 5p, 6d, and 6s shells in the valence space, whereas 4f electrons belonged to the core pseudopotentials. For other atoms, a 6-311+g* basis set was employed. For **1Tb** for TD-DFT calculation, we have used the experimental geometry but with normalization of C−H bonds to the ideal 1.08 Å value. All calculations were performed by the G09 program package. [S14]

Synthesis of complexes 1Ln and 2Ln

*[Cp^{Ph3}NdCl$_2$(bipy)(THF)] (**1Nd**).* *Method A*. A solution of bipy (0.039 g, 0.25 mmol) in 2 mL of THF was dropwise added to the 30 mL solution of [{Cp^{Ph3}NdCl$_2$(THF)}$_2$KCl] (0.155 g, 0.125 mmol) in THF. The reaction mixture was stirred for 12 h. Then, the reaction mixture was centrifuged (4000 rpm, 10 min); the precipitate was extracted with 2 × 5 mL of THF to dissolve the remaining complex and centrifuged again. The combined solution was layered with hexane (40 mL) to initiate crystallization. Crystals were obtained after several days. The crystals were dried under dynamic vacuum for 2 h, yielded 0.120 g (65%) of **1Nd**. Calcd for $C_{37}H_{33}N_2OCl_2Nd$: C, 60.31%; N, 3.80%; H, 4.52%. Found: C, 59.34%; N, 3.51%; H, 4.53%.

Method B. A solution of $PhCH_2K$ (0.034 g, 0.26 mmol) in 5 mL of THF was added slowly to the 10 mL THF solution of Cp^{Ph3}H (0.074 g, 0.25 mmol). The reaction mixture was stirred for 15 min. The obtained solution of KCp^{Ph3} was slowly added in small portions to a stirred suspension of NdCl$_3$(THF)$_{2.2}$ (0.102 g, 0.25 mmol) in THF (15 mL). The reaction mixture was stirred for 12 h. A solution of bipy (0.039 g, 0.25 mmol) in 2 mL of THF was dropwise added to the reaction mixture. The reaction mixture was stirred for 12 h. Then, the reaction mixture was centrifuged (4000 rpm, 10 min); the precipitate was extracted with 2 × 5 mL of THF to dissolve the remaining complex and centrifuged again. The combined solution was layered with hexane (40 mL) to initiate crystallization. Crystals were obtained after several days. The crystals were dried under dynamic vacuum for 2 h, yielded 0.103 g (56%) of **1Nd**.

[Cp^{Ph3}GdCl$_2$(bipy)(THF)] **1Gd**. *Method A*. Following the procedure described above, [{Cp^{Ph3}GdCl$_2$(THF)}$_2$KCl(THF)] (0.167 g, 0.125 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.118 g (63%) of **1Gd**. Calcd for $C_{37}H_{33}N_2OCl_2Gd$: C, 59.27%; N, 3.74%; H, 4.44%. Found: C, 58.40%; N, 3.51%; H, 4.43%. *Method B*. Following the procedure described above, GdCl$_3$(THF)$_{2.1}$ (0.104 g, 0.25 mmol), Cp^{Ph3}H (0.074 g, 0.25 mmol), $PhCH_2K$ (0.034 g, 0.26 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.101 g (54%) of **1Gd**.

[Cp^{Ph3}TbCl$_2$(bipy)(THF)] **(1Tb)**. *Method A*. Following the procedure described above, [{Cp^{Ph3}TbCl$_2$(THF)}$_2$KCl(THF)] (0.167 g, 0.125 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.131 g (70%) of **1Tb**. Calcd for $C_{37}H_{33}N_2OCl_2Tb$: C, 59.13%; N, 3.73%; H, 4.43%. Found: C, 59.14%; N, 3.75%; H, 4.43%. *Method B*. Following the procedure described above, TbCl$_3$(THF)$_3$ (0.120 g, 0.25 mmol), Cp^{Ph3}H (0.074 g, 0.25 mmol), $PhCH_2K$ (0.034 g, 0.26 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.113 g (60%) of **1Tb**.

Complexes **2Ln** were prepared in a similar way to the *Method B* synthesis of **1Nd**.

[Cp^{Ph4}NdCl$_2$(bipy)(THF)] (**2Nd**). Following the procedure described above, NdCl$_3$(THF)$_{2.2}$ (0.102 g, 0.25 mmol), Cp^{Ph4}H (0.093 g, 0.25 mmol), $PhCH_2K$ (0.034 g, 0.26 mmol) and bipy

(0.039 g, 0.25 mmol) yielded 0.099 g (49%) of 2Nd. Calcd for $C_{43}H_{37}N_2OCl_2Nd$: C, 63.54%; N, 3.45%; H, 4.59%. Found: C, 62.86%; N, 3.38%; H, 4.73.

[Cp^{Ph4}GdCl$_2$(bipy)(THF)] (**2Gd**). Following the procedure described above, $GdCl_3(THF)_{2.1}$ (0.104 g, 0.25 mmol), Cp^{Ph4}H (0.093 g, 0.25 mmol), $PhCH_2K$ (0.034 g, 0.26 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.111 g (54%) of **2Gd**. Calcd for $C_{43}H_{37}N_2OCl_2Gd$: C, 62.53%; N, 3.39%; H, 4.52%. Found: C, 62.25%; N, 2.93%; H, 4.61%.

[Cp^{Ph4}TbCl$_2$(bipy)(THF)] (**2Tb**). Following the procedure described above, $TbCl_3(THF)_3$ (0.120 g, 0.25 mmol), Cp^{Ph4}H (0.093 g, 0.25 mmol), $PhCH_2K$ (0.034 g, 0.26 mmol) and bipy (0.039 g, 0.25 mmol) yielded 0.118 g (57%) of **2Tb**. Calcd for $C_{43}H_{37}N_2OCl_2Tb$: C, 62.41%; N, 3.39%; H, 4.51%. Found: C, 62.21%; N, 3.00%; H, 4.69%.

The differences between molecular formulae of **2Gd** and **2Tb** listed for microanalysis and in Table S1 are due to the loss of noncoordinated solvent molecules.

Excitation spectra of [{(1,2,4-$Ph_3C_5H_2$)$TbCl_2$(THF)}$_2$KCl(THF)]$_2$ and $TbCl_3(bipy)_2(H_2O)_3$

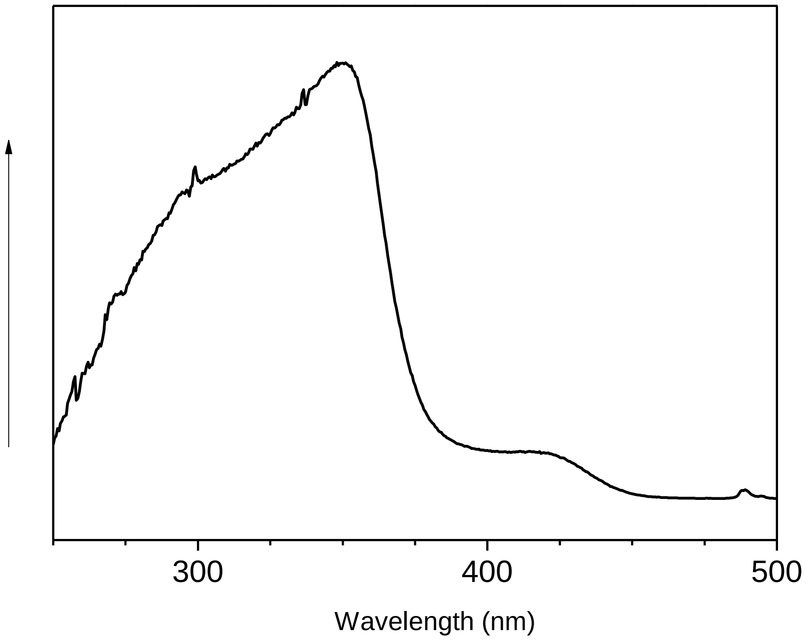

Figure S1. Excitation luminescence Spectrum of [{(1,2,4-$Ph_3C_5H_2$)$TbCl_2$(THF)}$_2$KCl(THF)]$_2$ [S3]

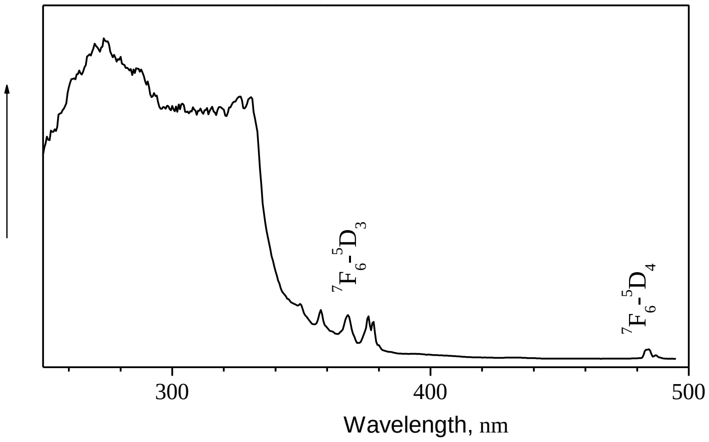

Figure S2. Excitation luminescence Spectrum of $TbCl_3(bipy)_2(H_2O)_3$[S16]

References

S1 F. T. Edelmann and P. Poremba, in *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrman/Brauer)*, eds. F. T. Edelmann and W. A. Herrmann, Verlag, Stuttgart, Germany, 1997, pp. 34–35.

S2 M. E. Minyaev, A. A. Vinogradov, D. M. Roitershtein, R. S. Borisov, I. V. Ananyev, A. V. Churakov and I. E. Nifant’ev, *J. Organomet. Chem.*, 2016, **818**, 128.

S3 D. M. Roitershtein, L. N. Puntus, A. A. Vinogradov, K. A. Lyssenko, M. E. Minyaev, M. D. Dobrokhodov, I. V. Taidakov, E. A. Varaksina, A. V. Churakov and I. E. Nifant’ev, *Inorg. Chem.*, 2018, **57**, 10199.

S4 L. Lochmann and J. Trekoval, *J. Organomet. Chem.*, 1987, **326**, 1.

S5 S. S. Hirsch and W. J. Bailey, *J. Org. Chem.*, 1978, 43, 4090.

S6 M. P. Castellani, J. M. Wright, S. J. Geib, A. L. Rheingold and W. C. Trogler, *Organometallics*, 1986, **5**, 1116.

S7 2008 Bruker. APEXII, Bruker AXS Inc.: Madison, Wisconsin, USA, .

S8 G. M. Sheldrick., SADABS. University of Göttingen, Germany 1997.

S9 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

S10 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3.

S11 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 50.

S12 M. Dolg, H. Stoll, A. Savin and H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 17394.

S13 M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1993, **85**, 441.

S14 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, Ortiz, J.; Izmaylov, A.; Sonnenberg, J.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota,K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J.; Peralta, J.; Ogliaro, F.; Bearpark, M.; Heyd, J.; Brothers, E.; Kudin, K.; Staroverov, V.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.; Iyengar, S.; Tomasi, J.; Cossi, M.; Millam, J.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J.; Martin, R.; Morokuma, K.; Farkas, O.; Foresman, J.; Fox, D. *Gaussian 09*; Gaussian, Inc., Wallingford CT, 2016.

S15 L. N. Puntus, K. A. Lyssenko, I. S. Pekareva and J.-C. G. Bünzli, *J. Phys. Chem. B*, 2009, **113**, 9265.