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Phenyl substitution as an effective way to control the luminescent properties of polyphenylcyclopentadienyl lanthanide complexes

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S1. Experimental section, general remarks.

All synthetic manipulations were carried out in prepurified argon atmosphere using anhydrous solvents in 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. CpNa,[S1] $LnCl_3(THF)_3$ (Ln = Gd, Tb)[S2] and benzyl potassium (BnK)[S3] were prepared according to literature procedures. Diphenylcyclopentadiene ($Cp^{Ph2}H$, as a mixture of 1,3- and 1,4-tautomers)[S4] and tetraphenylcyclopentadiene ($Cp^{Ph4}H$)[S5] were recrystallized from absolute ethanol and heptane, respectively, and dried in high vacuum. 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3tach) was purchased from TCI, distilled from sodium and transferred in high vacuum into a Schlenk flask. $[CpLnCl_2(THF)_3]$ (Ln = Gd, Tb) were prepared from CpNa and $LnCl_3(THF)_3$ in THF using known method[S6] and recrystallized from THF/hexane solvent mixtures. Elemental analyses were performed with a PerkinElmer 2400 Series II elemental CHNS/O analyzer.

S2. X-ray structure determination.

X-ray diffraction data were collected on a Bruker D8 Quest diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite-monochromatized Mo K_α-radiation. The intensity data were integrated by the SAINT program[S7] and corrected for absorption and decay using SADABS.[S8] The structures were solved by direct methods using SHELXT[S9] and refined on F^2 using SHELXL-2018.[S10] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.950 Å for aromatic, 0.980 Å for methyl, 0.990 Å for methylene and 1.000 Å for cyclopentadienyl hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. The SHELXTL program suite[S11] 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 **1Gd**, **2Ln** and **3Ln**.

	1Gd	**2Gd**	**2Tb**	**3Gd**	**3Tb**
Formula	$C_{22}H_{40}N_6Cl_4Gd_2$	$C_{23}H_{28}N_3Cl_2Gd$	$C_{23}H_{28}N_3Cl_2Tb$	$C_{35}H_{36}N_3Cl_2Gd$, 1.5 C_4H_8O	$C_{35}H_{36}N_3Cl_2Tb$, 1.5 C_4H_8O
M	844.90	574.63	576.30	834.97	836.64
T, K	100(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pbca$	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1$
Z	4	4	4	4	4
a, Å	13.503(4)	18.0801(10)	18.0670(19)	10.4547(6)	10.4328(9)
b, Å	14.213(4)	9.4751(5)	9.4724(14)	14.2173(7)	14.2211(10)
c, Å	15.534(3)	14.5494(8)	14.5515(16)	25.8479(12)	25.8297(18)
β, °	90	110.846(2)	110.898(3)	98.039(2)	97.969(3)
V, Å^3	2981.3(13)	2329.3(2)	2326.5(5)	3804.2(3)	3795.2(5)
d_{calc}, g/cm^{-3}	1.882	1.639	1.645	1.458	1.464
μ, mm^{-1}	4.791	3.090	3.283	1.921	2.041
F(000)	1640	1140	1144	1700	1704
2Θ_{max}, °	50	58	55	54	54
Complentess to Θ_{max}	0.998	0.999	0.997	0.999	0.998
Reflections collected	9930	33291	17113	32350	32322
Unique reflections	2619	6191	5333	14825	16327
Reflections with $I > 2\sigma(I)$	1628	4706	4155	13599	14200
Number of parameters	157	265	265	881	881
R1	0.0514	0.0394	0.0443	0.0475	0.0521
wR2	0.1604	0.0824	0.1031	0.0994	0.1093
GOF	0.873	1.039	0.953	1.023	0.975
Largest difference in peak / hole (e/Å^3)	0.888/-0.788	1.141/-0.900	1.153/-1.222	1.484/-0.723	1.318/-0.784
CCDC number	2311251	2311254	2311253	2311252	2311250

Table S2 Selected structural parameters for **1Gd**, **2Ln** and **3Ln**.

Bond lengths (Å) and angles (°)	**1Gd**	**2Gd**	**2Tb**	**3Gd**[b]	**3Tb**[b]
Ln–C$_{Cp}$	2.66(1) – 2.72(1)	2.674(3) – 2.710(4)	2.659(6) – 2.696(6)	2.677(9) – 2.792(9); 2.677(8) – 2.769(8)	2.65(1) – 2.77(1); 2.652(9) – 2.758(9)
Ln–Cp$_{cent}$	2.414	2.412	2.395	2.458; 2.448	2.438; 2.428
Ln–Cl	2.678(4) (term.); 2.790(3), 2.823(4) (br.)	2.609(1), 2.627(1)	2.598(1), 2.612(2)	2.592(3), 2.597(2); 2.587(2), 2.597(3)	2.578(3), 2.582(3); 2.572(3), 2.585(3)
Ln–N	2.620(9) – 2.63(1)	2.556(4) – 2.569(4)	2.547(4) – 2.557(5)	2.564(8) – 2.596(8); 2.553(8) – 2.598(8)	2.546(9) – 2.572(9); 2.545(8) – 2.576(9)
Ln–Me$_3$tach$_{cent}$[a]	2.245	2.181	2.167	2.202; 2.203	2.182; 2.187
∠Cp$_{cent}$–Ln–Me$_3$tach$_{cent}$[a]	121.5	127.9	128.2	128.2; 127.0	128.3; 127.3
Rotation angles between Cp and Ph planes	–	26.7, 37.6	26.5, 37.4	26.8, 33.9, 53.4, 77.3; 29.5, 37.7, 52.2, 53.8	26.7, 33.7, 53.2, 77.3; 29.8, 37.8, 52.8, 54.0

[a] Me$_3$tach$_{cent}$ – centroid of the plane formed by the three nitrogen atoms of the ligand. [b] The parameters for the two crystallographically unique molecules are separated by a semicolon.

S3. Optical measurements.

Luminescent measurements in the visible region 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. The technique involved the use of specially designed, cylindrical sealed quartz cuvettes for manipulation with air-sensitive compounds. Time-resolved experiments, namely, luminescence lanthanide lifetimes (τ), were measured with initial delay = 0.05 ms, step size = 0.02 ms, and final window = 10 ms at least three times by monitoring the decay at the maxima of the emission spectra. For phosphorescence spectrum initial delay = 0.1 ms. The quantum yield measurements were carried out on solid samples with a Spectralone-covered G8 integration sphere (GMP SA, Switzerland) under ligand excitation, according to the absolute method of Wrighton.[S12–S14] Each sample was measured several times under slightly different experimental conditions. The estimated error for quantum yields was ± 10%. All complexes studied were powdered.

S4. Computational details.

The optimizations for ground singlet and first triplet states of [Cp^{Ph2}TbCl$_2$(Me$_3$tach)] (**2Tb**) and [Cp^{Ph4}TbCl$_2$(Me$_3$tach)] (**3Tb**) 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.[S15,S16] Large-core energy-adjusted RECPs for lanthanides put 5*s*, 5*p*, 6*d*, and 6*s* shells in the valence space, whereas 4*f* electrons belonged to the core pseudopotentials. For other atoms, a 6-311+g* basis set was employed. Tight SCF convergence and standard optimization convergence criteria along with ultrafine grids were always used during the calculations. All calculations were performed by the G09 program package.[S17]

S5. Synthesis of complexes 1Ln – 3Ln.

[CpGdCl$_2$(Me$_3$tach)]$_2$ (**1Gd**). A solution of Me$_3$tach (0.023 g, 0.18 mmol, 20% excess) in 2 mL of THF was added dropwise to a solution of [CpGdCl$_2$(THF)$_3$] (0.076 g, 0.15 mmol) in 10 mL of THF. The reaction mixture was stirred for 4 h, centrifuged (4000 rpm, 5 min) and layered with 20 mL of hexane to initiate crystallization. Colorless crystals were obtained after 2 days. The crystals were separated by decantation and dried under dynamic vacuum for 2 h. Yielded 0.038 g (0.045 mmol, 60%) of **1Gd**. Calcd for $C_{22}H_{40}N_6Cl_4Gd_2$: C, 31.27%; H, 4.78%; N, 9.95%. Found: C, 30.40%; H, 4.18%; N, 9.24%.

[CpTbCl$_2$(Me$_3$tach)]$_2$ (**1Tb**). Following the procedure described above for **1Gd**, [CpTbCl$_2$(THF)$_3$] (0.128 g, 0.25 mmol) and Me$_3$tach (0.039 g, 0.30 mmol, 20% excess) yielded 0.042 g (0.050 mmol, 40%) of **1Tb**. Calcd for $C_{22}H_{40}N_6Cl_4Tb_2$: C, 31.14%; H, 4.76%; N, 9.91%. Found: C, 31.06%; H, 4.35%; N, 9.61%.

[Cp^{Ph2}GdCl$_2$(Me$_3$tach)] (**2Gd**). A solution of BnK (0.033 g, 0.25 mmol) in 2 mL of THF was slowly added to a stirred solution of Cp^{Ph2}H (0.055 g, 0.25 mmol) in 3 mL of THF. The reaction mixture was stirred for 15 min and then added to a suspension of GdCl$_3$(THF)$_3$ (0.119 g, 0.25 mmol) in 5 mL of THF. The resultant mixture was stirred for 12 h, then a solution of Me$_3$tach (0.032 g, 0.25 mmol) in 1.5 mL of THF was added dropwise. The reaction mixture was stirred for 24 h, the KCl precipitate was separated by centrifugation (4000 rpm, 10 min) and washed with 3 mL of THF. The combined solution was evaporated to dryness, the obtained powder was washed with 2×6 mL of toluene and redissolved in 20 mL of THF. The solution was layered with 20 mL of hexane to initiate crystallization. Off-white crystals were obtained after several days. The crystals were separated by decantation and dried under dynamic vacuum for 2 hours. Yielded 0.090 g (0.158 mmol, 63%) of **2Gd**. Calcd for $C_{23}H_{28}N_3Cl_2Gd$: C, 48.07%; H, 4.92%; N, 7.32%. Found: C, 48.40%; H, 5.17%; N, 7.49%.

[Cp^{Ph2}TbCl$_2$(Me$_3$tach)] (**2Tb**). Following the procedure described above for **2Gd**, TbCl$_3$(THF)$_3$ (0.120 g, 0.25 mmol), BnK (0.032 g, 0.25 mmol), Cp^{Ph2}H (0.055 g, 0.25 mmol), and Me$_3$tach (0.032 g, 0.25 mmol) yielded 0.064 g (0.111 mmol, 44%) of **2Tb**. Calcd for $C_{23}H_{28}N_3Cl_2Tb$: C, 47.93%; H, 4.90%; N, 7.29%. Found: C, 47.56%; H, 4.90%; N, 7.30%.

[Cp^{Ph4}GdCl$_2$(Me$_3$tach)] (**3Gd**). **3Gd** was obtained from GdCl$_3$(THF)$_3$ (0.119 g, 0.25 mmol), BnK (0.033 g, 0.25 mmol), Cp^{Ph4}H (0.093 g, 0.25 mmol), and Me$_3$tach (0.045 g, 0.35 mmol, 40% excess) following the procedure described above for **2Gd**. The powder obtained after evaporation of the THF supernatant was washed with 2.5 mL of toluene, dissolved in 8 mL of THF and centrifuged (4000 rpm, 5 min). The solution was layered with 12 mL of hexane to initiate crystallization. Off-white crystals were obtained after several days. The crystals were separated by decantation and dried under dynamic vacuum for 2 h. Yielded 0.100 g (0.138 mmol, 55%) of **3Gd**. Calcd for $C_{35}H_{36}N_3Cl_2Gd$: C, 57.84%; H, 5.00%; N, 5.78%. Found: C, 58.18%; H, 4.79%; N, 5.49%. Single crystal X-ray analysis revealed that the unit cell of **3Gd** contains 3 non-coordinated THF molecules; these solvent molecules were lost after the compound was dried in vacuo.

[Cp^{Ph4}TbCl$_2$(Me$_3$tach)] (**3Tb**). **3Tb** was obtained from TbCl$_3$(THF)$_3$ (0.120 g, 0.25 mmol), BnK (0.033 g, 0.25 mmol), Cp^{Ph4}H (0.093 g, 0.25 mmol) and Me$_3$tach (0.045 g, 0.35 mmol, 40% excess) following the procedure described above for **3Gd**. Yielded 0.103 g (0.141 mmol, 57%) of **3Tb**. Analytically pure sample was obtained after second recrystallization from THF/hexane mixture. Calcd for $C_{35}H_{36}N_3Cl_2Tb$: C, 57.71%; H, 4.99%; N, 5.77%. Found: C, 57.96%; H, 5.23%; N, 5.59%. Single crystal X-ray analysis revealed that the unit cell of **3Tb** contains 3 non-coordinated THF molecules; these solvent molecules were lost after drying the compound in vacuo.

S6. Luminescence excitation and phosphorescence spectra of complexes 1Ln – 3Ln.

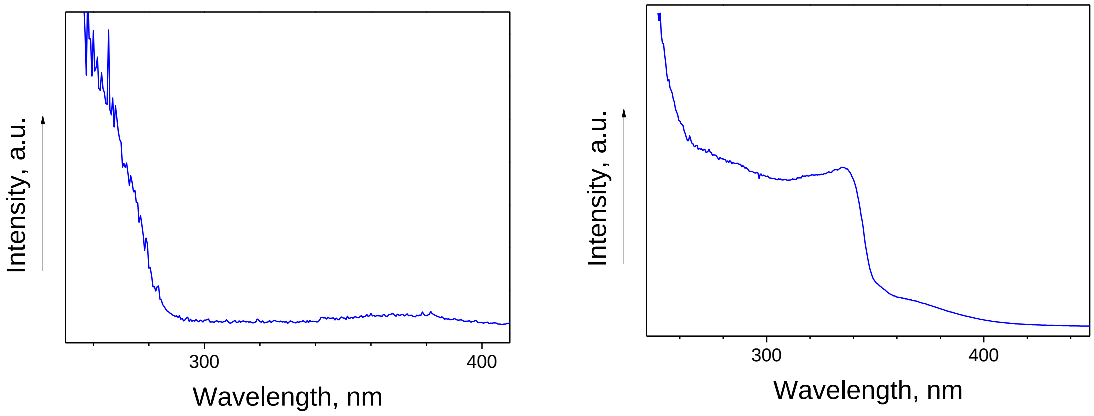

Figure S1 Excitation spectra of **1Gd** (left) and **3Gd** (right) at 77 K.

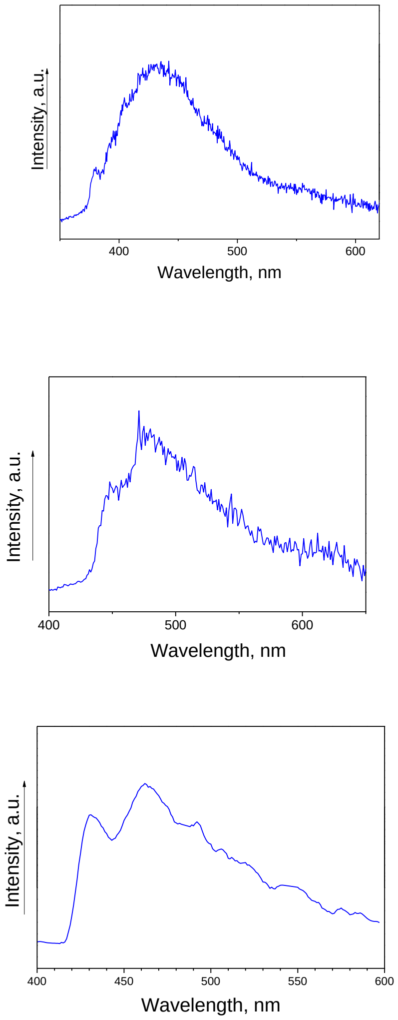

Figure S2 Phosphorescence spectra of **1Gd–3Gd** at 77 K.

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