Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Electronic strain effect on Eu(III) complexes for enhanced circularly polarized luminescence

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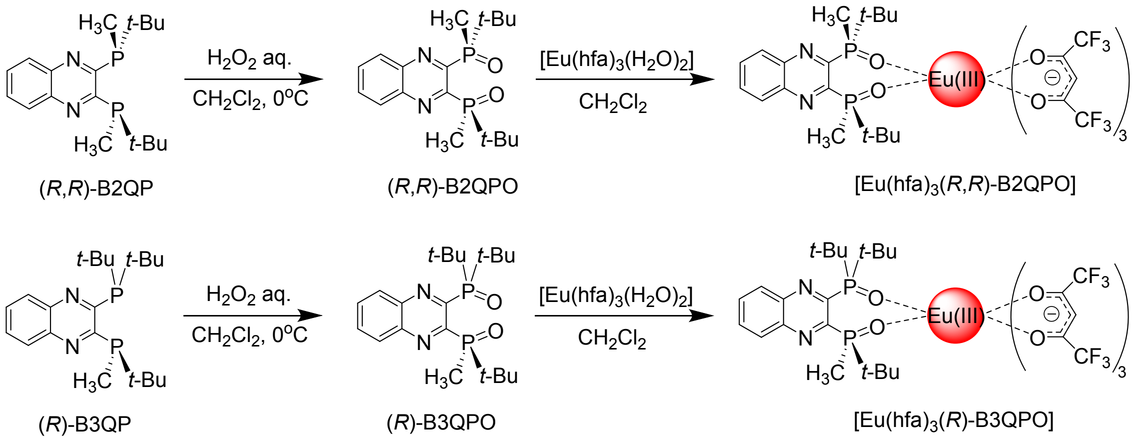
Scheme S1 Synthetic scheme of Eu(III) complexes.



Preparation of (*S*,*S*)-2,3-Bis(*tert*-butylmethylphosphineoxide)quinoxaline ((*S*,*S*)-B2QPO): (*S*,*S*)-B2QPO was synthesized by the same procedure as described for the (*R*,*R*)-B2QPO. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25°C): δ = 8.14 (dd, J = 6.4, 3.7 Hz, 2H), 7.92 (dd, J = 6.4, 3.7 Hz, 2H), 2.11 (d, J = 12.3 Hz, 6H), 1.43 (d, J = 14.6 Hz, 18H) ppm. IR (ATR): ν = 2822-2999 (m, C-H), 1151 (s, P=O) cm^{-1}. APCI-MS (*m*/*z*): calcd for $C_{18}H_{29}N_2O_2P_2$ [*m* + H]$^+$: 367.2, found 367.2.

Preparation of (*S*)-2-*tert*-butylmethylphophineoxide-3-(di-*tert*-butylphosphineoxide)quinoxaline) ((*S*)-B3QPO): (*S*)-B3QPO was synthesized by the same procedure as described for the (*R*)-B3QPO. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25°C): δ = 8.23-8.09 (m, 2H), 7.98-7.85 (m, 2H), 2.24 (d, J = 12.8 Hz, 3H), 1.55-1.25 (m, 27H) ppm. IR (ATR): ν = 2861-2967 (m, C-H), 1161 (s, P=O) cm^{-1}. APCI-MS (*m*/*z*): calcd for $C_{21}H_{35}N_2O_2P_2$ [*m* + H]$^+$: 409.2, found 409.2.

Preparation of [Eu(hfa)$_3$(H$_2$O)$_2$] (hfa: hexafluoroacetylacetonato): [Eu(hfa)$_3$(H$_2$O)$_2$] was prepared with the procedure described in previous report[1].

Preparation of [Eu(hfa)$_3$((*S*,*S*)-B2QPO)]: [Eu(hfa)$_3$((*S*,*S*)-B2QPO)] was synthesized by the same procedure as described for the [Eu(hfa)$_3$((*R*,*R*)-B2QPO)]. Yield: 45%. ESI-Mass (*m*/*z*): [M−hfa]$^+$ calcd. for $C_{28}H_{30}EuF_{12}N_2O_6P_2$, 933.06; found, 933.10. Anal. calcd. for $C_{33}H_{31}EuF_{18}N_2O_8P_2$, C 34.78, H 2.74, N 2.46; found, C 34.36, H 2.53, N 2.29%. FT-IR (ATR) : 1652 (st, C=O), 1252 (st, C-F), 1141 (st, P=O) cm^{-1}.

Preparation of [Eu(hfa)$_3$((*S*)-B3QPO)]: [Eu(hfa)$_3$((*S*)-B3QPO)] was synthesized by the same procedure as described for the [Eu(hfa)$_3$((*R*)-B3QPO)]. Yield: 42%. ESI-Mass (*m*/*z*): [M−hfa]$^+$ calcd. for $C_{31}H_{36}EuF_{12}N_2O_6P_2$, 975.11; found, 975.11. Anal. calcd. for $C_{36}H_{37}EuF_{18}N_2O_8P_2$, C 36.59, H 3.16, N 2.37; found, C 36.55, H 2.99, N 2.28%. FT-IR (ATR) : 1650 (st, C=O), 1251 (st, C-F), 1140 (st, P=O) cm^{-1}.

Preparation of [Gd(hfa)$_3$(H$_2$O)$_2$]: [Gd(hfa)$_3$(H$_2$O)$_2$] was synthesized by the same procedure as described for the [Eu(hfa)$_3$(H$_2$O)$_2$].

Preparation of [Gd(hfa)$_3$((*R*,*R*)-B2QPO)]: [Gd(hfa)$_3$((*R*,*R*)-B2QPO)] was synthesized by the same procedure as described for the [Eu(hfa)$_3$((*R*,*R*)-B2QPO)]. Yield 45%. ESI-Mass (*m*/*z*): [M−hfa]$^+$ calcd. for $C_{28}H_{30}GdF_{12}N_2O_6P_2$, 938.06; found, 938.06. Anal. calcd. for $C_{33}H_{31}GdF_{18}N_2O_8P_2$, C 34.62, H 2.73, N 2.45; found, C 34.34, H 2.56, N 2.34%. FT-IR (ATR) : 1653 (st, C=O), 1253 (st, C-F), 1139 (st, P=O) cm^{-1}.

Preparation of [Gd(hfa)$_3$((*R*)-B3QPO)]: [Gd(hfa)$_3$((*R*)-B3QPO)] was synthesized by the same procedure as described for the [Eu(hfa)$_3$((*R*)-B3QPO)]. Yield 43%. ESI-Mass (*m*/*z*): [M−hfa]$^+$ calcd. for $C_{31}H_{36}GdF_{12}N_2O_6P_2$, 980.11; found, 980.11. Anal. calcd. for

$C_{36}H_{37}GdF_{18}N_2O_8P_2$, C 36.43, H 3.14, N 2.36; found, C 36.34, H 3.00, N 2.29%. FT-IR (ATR)：1650 (st, C=O), 1250 (st, C-F), 1137 (st, P=O) cm^{-1}.

Table S1. X-ray crystal data of Eu(III) complexes

	[Eu(hfa)((*R*,*R*)-B2QPO)]	[Eu(hfa)((*S*,*S*)-B2QPO)]	[Eu(hfa)$_3$((*R*)-B3QPO)]	[Eu(hfa)$_3$((S)-B3QPO)]
Chemical formula	$C_{33}H_{31}EuF_{18}N_2O_8P_2$	$C_{33}H_{31}EuF_{18}N_2O_8P_2$	$C_{36}H_{37}EuF_{18}N_2O_8P_2$	$C_{36}H_{37}EuN_2O_8F_{18}P_2$
Formula weight	1139.50	1139.50	1181.57	1181.57
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$(#4)	$P2_1$(#4)	$P2_1$(#4)	$P2_1$(#4)
a / Å	11.6631(2)	11.6679(3)	11.19040(10)	11.2020(2)
b / Å	19.2898(2)	19.2967(4)	20.5895(2)	20.6003(3)
c / Å	20.1981(2)	20.2075(4)	20.3663(2)	20.3840(4)
α / deg.	90	90	90	90
β / deg.	93.5450(10)	93.568(2)	99.7900(10)	99.687(2)
γ / deg.	90	90	90	90
Volume / Å^3	4535.45(10)	4540.94(18)	4624.16(8)	4636.83(14)
Z	4	4	4	4
Temperature / K	123.15	123.15	123.15	123.15
d_{calc} / g cm^{-3}	1.669	1.667	1.697	1.693
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	85714	108043	137245	108302
Goodness-of-fit on F^2	1.053	1.042	1.031	1.033
R_1	0.0439	0.0418	0.0240	0.0303
WR_2	0.1177	0.1141	0.0572	0.0711
Flack parameter	0.000(4)	-0.005(4)	-0.012(3)	0.000(4)

Table S2. X-ray crystal data of Gd(III) complexes

	Gd(hfa)(R,R-B2QPO)	Gd(hfa)(R-B3QPO)
Chemical formula	$C_{33}H_{31}F_{18}GdN_2O_8P_2$	$C_{36}H_{37}F_{18}GdN_2O_8P_2$
Formula weight	1144.79	1186.86
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$(#4)
a / Å	11.6565(2)	11.16540(10)
b / Å	19.2883(3)	20.5710(2)
c / Å	20.1991(3)	20.3672(2)
α / deg.	90	90
β / deg.	93.4630(10)	99.6950(10)
γ / deg.	90	90
Volume / Å^3	4533.15(12)	4611.20(8)
Z	4	4
Temperature / K	123.15	123.15
d_{calc} / g cm^{-3}	1.677	1.710
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	127032	119067
Goodness-of-fit on F^2	1.031	1.026
R_1	0.0395	0.0212
WR_2	0.1070	0.0512
Flack parameter	-0.006(3)	-0.007(2)

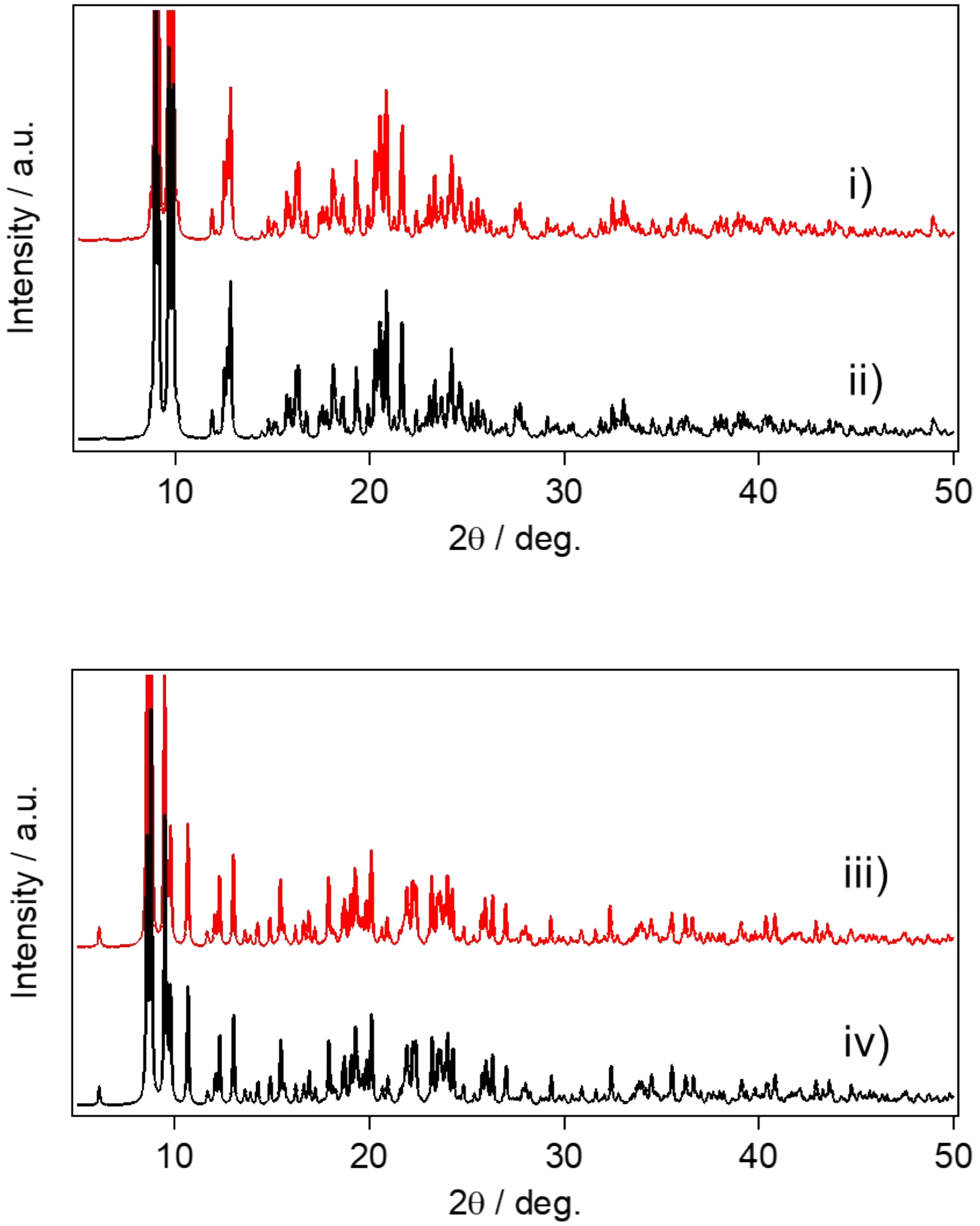


Figure S1. Simulated XRD patterns of i) [Eu(hfa)$_3$((*R*,*R*)-B2QPO)], ii) [Gd(hfa)$_3$((*R*,*R*)-B2QPO)], iii) [Eu(hfa)$_3$((*R*)-B3QPO)], and iv) [Gd(hfa)$_3$((*R*)-B3QPO)] from CIF files.

The absorption spectra of chiral phosphine oxide ligands, precursor complex ([Eu(hfa)$_3$(H$_2$O)$_2$]), and chiral Eu(III) complexes are shown in Figure S1. The absorption bands at 300-350 nm are attributed to π-π* transitions of hfa and phosphine oxide ligands. The bands at around 250 nm are attributed to the existing of phosphine oxide ligands.

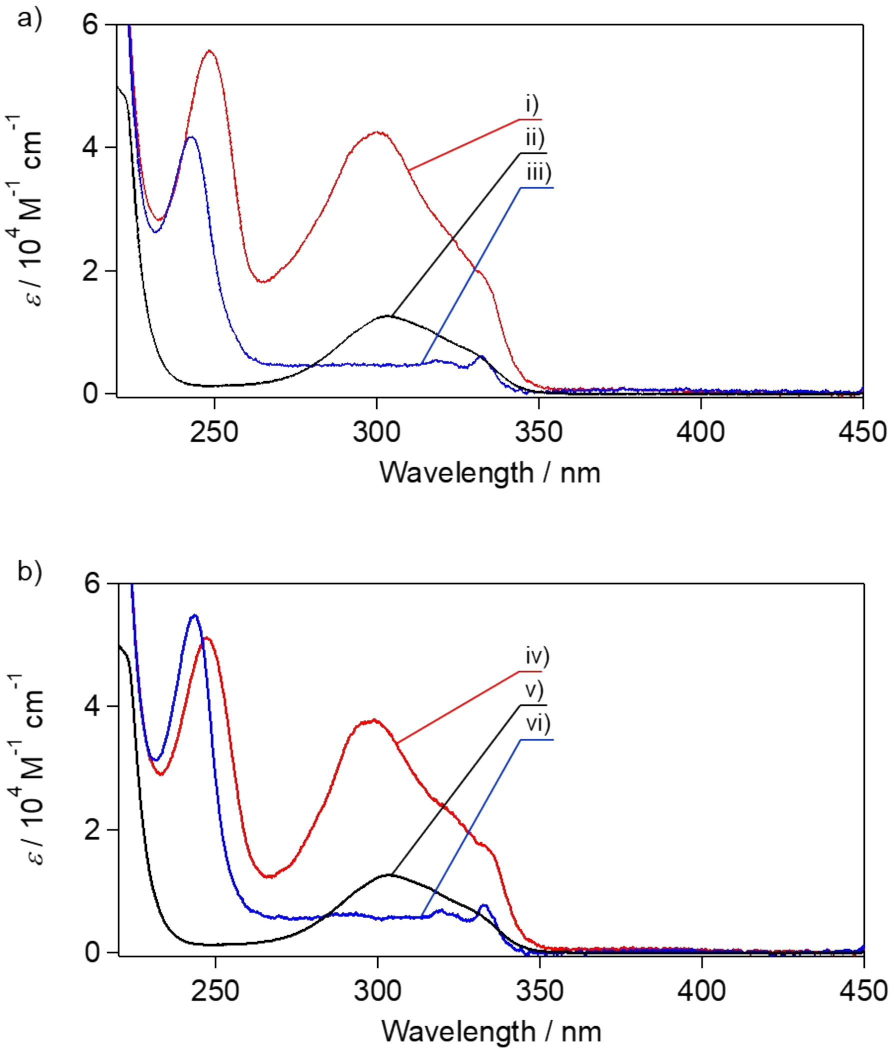


Figure S2. UV-vis absorption spectra of (a) [Eu(hfa)$_3$((*R*,*R*)-B2QPO)] ((i), red line), [Eu(hfa)$_3$(H$_2$O)$_2$] ((ii), black line) and (*R*,*R*)-B2QPO ((iii), blue line), (b) [Eu(hfa)$_3$((*R*)-B3QPO)] ((iv), red line), [Eu(hfa)$_3$(H$_2$O)$_2$] ((v), black line) and (*R*)-B3QPO ((vi), blue line) in dichloromethane (1.0×10^{-4} M) at room temperature.

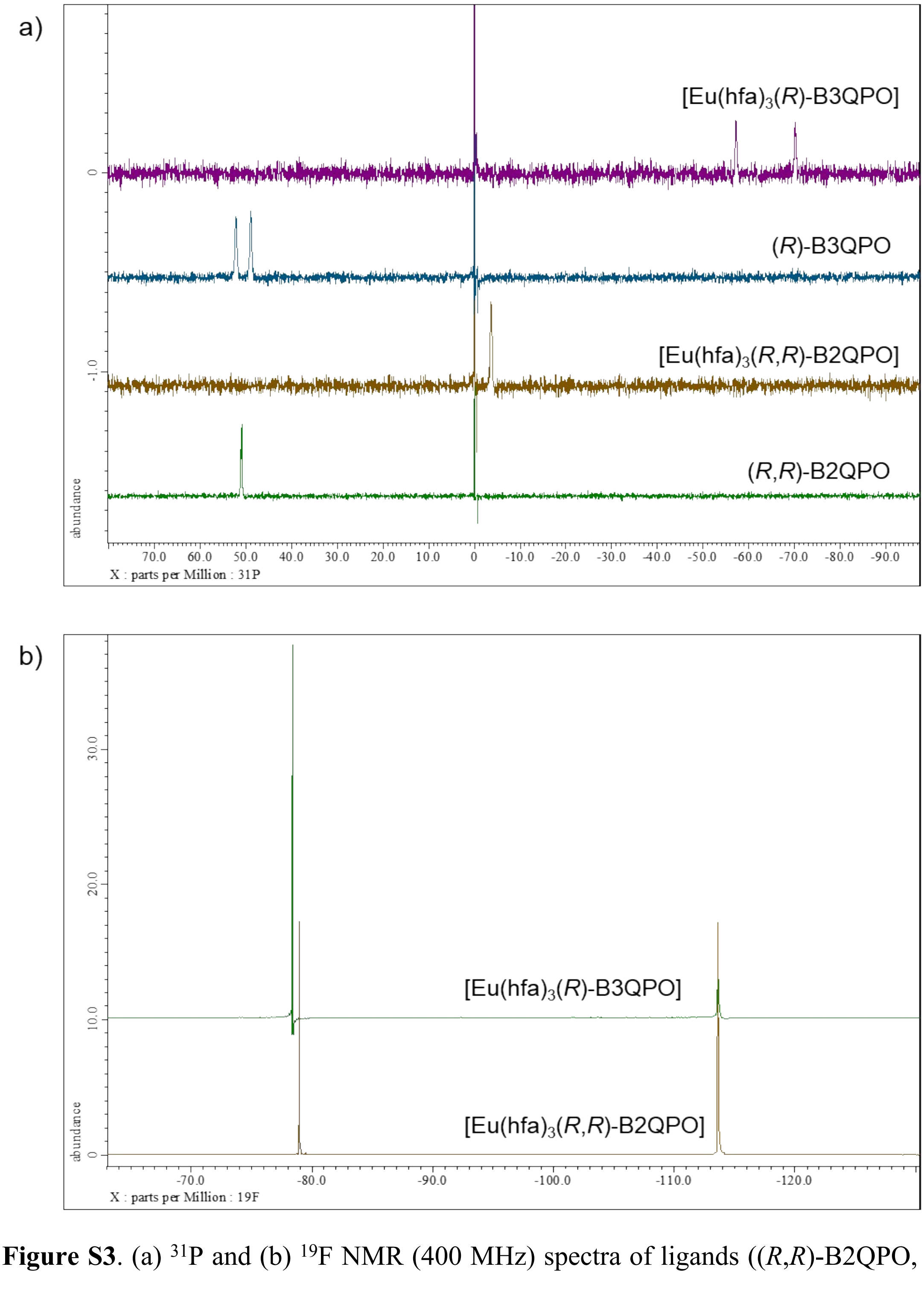


Figure S3. (a) ^{31}P and (b) ^{19}F NMR (400 MHz) spectra of ligands ((*R*,*R*)-B2QPO, (*R*)-B3QPO) and complexes ([Eu(hfa)$_3$((*R*,*R*)-B2QPO)], [Eu(hfa)$_3$((*R*)-B3QPO)]).

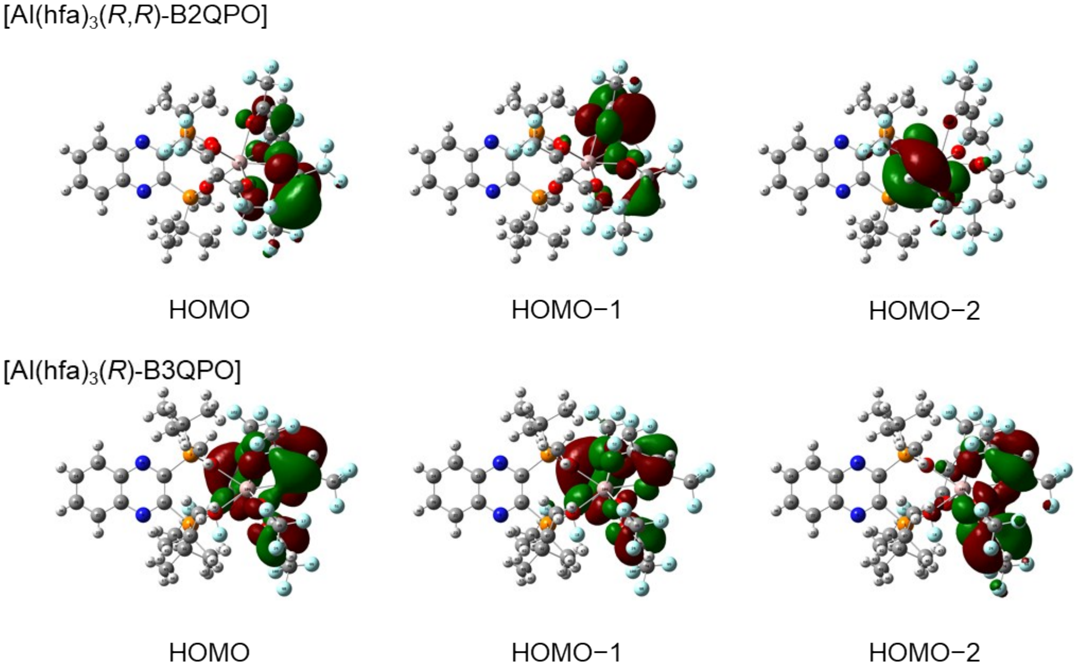


Figure S4. Molecular orbitals of [Al(hfa)$_3$((*R*,*R*)-B2QPO)] and [Al(hfa)$_3$((*R*)-B3QPO)]

Table S3. Calculated HOMO, HOMO−1, and HOMO−2 energy levels of [Al(hfa)$_3$((*R*,*R*)-B2QPO)] and [Al(hfa)$_3$((*R*)-B3QPO)] obtaind by DFT calculations.

Complex	Energy level / eV		
	HOMO	HOMO−1	HOMO−2
[Al(hfa)$_3$((*R*,*R*)-B2QPO)]	−6.050	−6.173	−6.437
[Al(hfa)$_3$((*R*)-B3QPO)]	−6.216	−6.259	−6.302

Reference

1 Y. Hasegawa, Y. Wada, S. Yanagida, H. Kawai, N. Yasuda and T. Nagamura, Polymer thin films containing Eu(III) complex as lanthanide lasing medium, *Appl. Phys. Lett.*, 2003, **83**, 3599–3601.