Supporting Information

Coordination-driven self-assembly of a sandwich shaped Eu(III) complex for induced circularly polarized luminescence

Sen Yin,[a] Xiaomeng Li,[a] Hongjing Wang,[a] Jingya Li,*[b] Wenru Huang,[a] Ting Gao,[a] Pengfei Yan,[a] Yanyan Zhou[a]* and Hongfeng Li*[a]

Table of Contents

1. Experimental Section

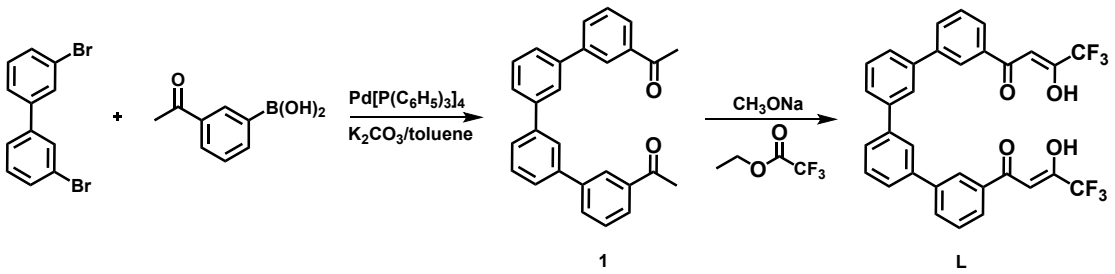
1.1 Methods

CD and CPL experiments were performed on an Olis DM245 spectrometer at room temperature. All samples were dissolved in $CHCl_3$ (1×10^{-4} M), and quartz cuvettes with optical pathway of 1 mm were employed. CD spectra were recorded in the range of 250−450 nm with increments of 1 nm, and a slit width of 2 mm for the excitation was utilized. CPL spectra were recorded with a 375 nm laser as light source. The emission of left- and right-handed polarized light were collected using a 10 spectral average sequence in the range of 550−720 nm, with 1 s integration time. The slit width of emission was 0.6 mm. Emission was collected at 90° to excitation light direction.

X-ray crystallography

Single-crystal X-ray diffraction study of $(HNEt_3)[EuL_2]$ was collected on a Xcalibur, Eos, Gemini diffractometer with Mo Kα radiation (λ = 0.71073 Å) under 298 K. A suitable crystal was selected for analysis. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-2018 program.[1]

1.2 Synthetic route of ligand



Scheme S1. Synthesis of ligand, **L**.

1.3 Characterization of ligand, intermediate and complexes

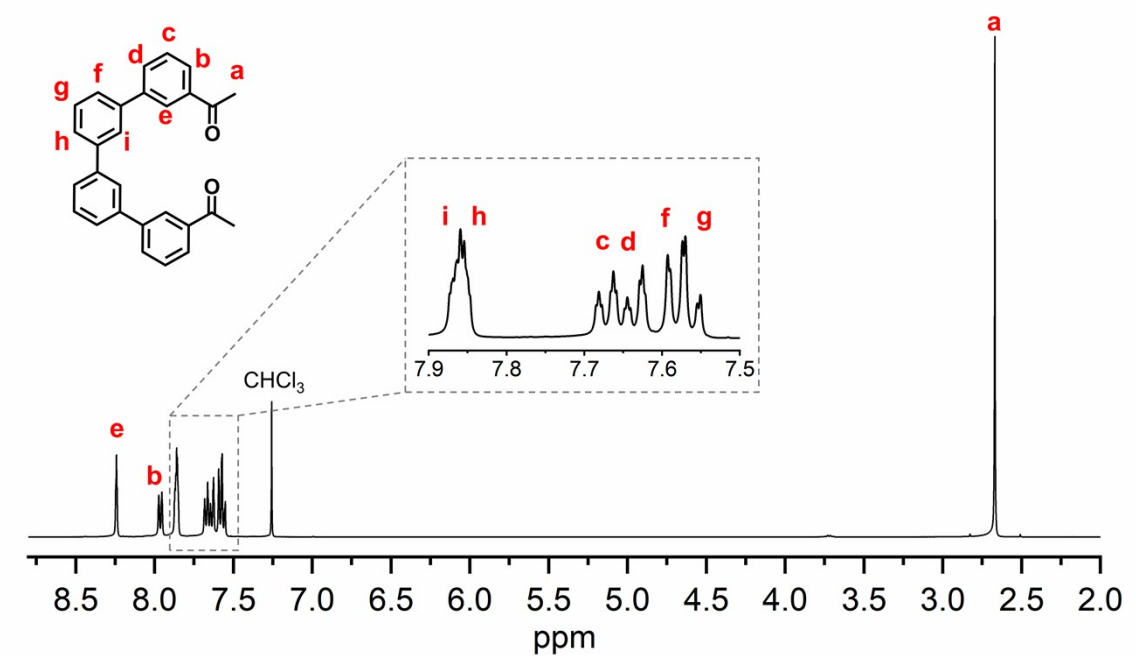


Figure S1. 400 MHz ^{1}H NMR spectrum of intermediate in $CDCl_3$.

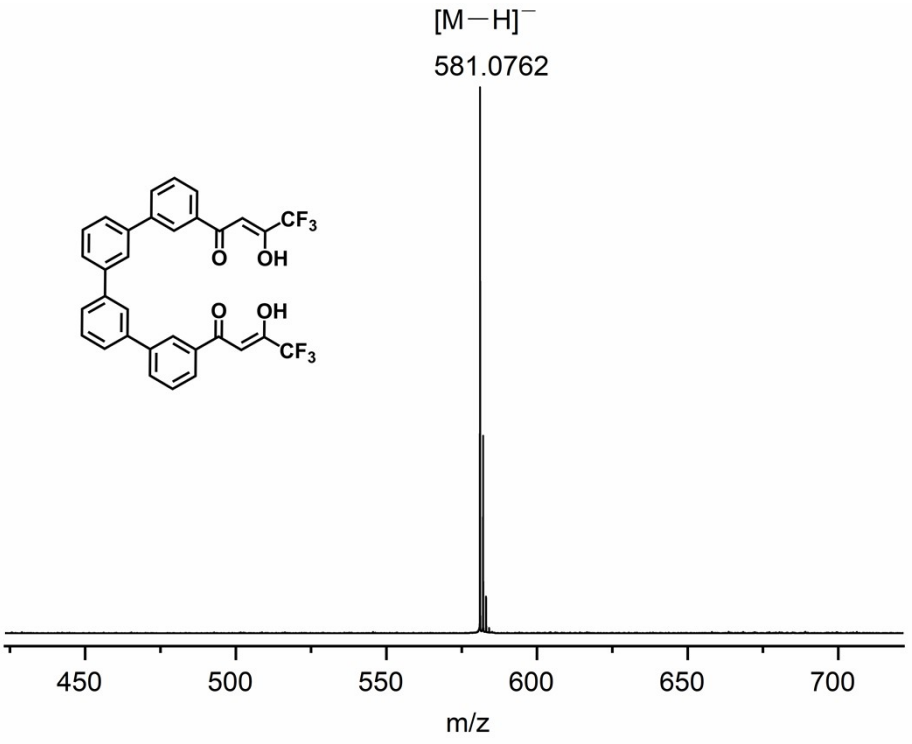


Figure S2. ESI-TOF mass spectrum of **L.**

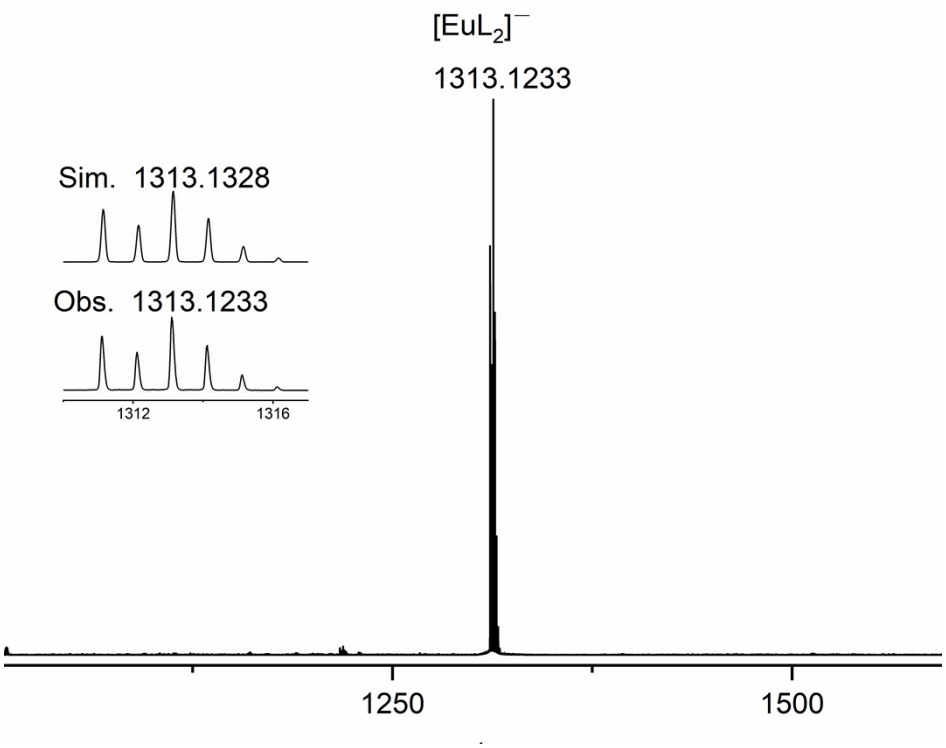


Figure S3. ESI-TOF mass spectrum of $(HNEt_3)[Eu\mathbf{L}_2]$**.**

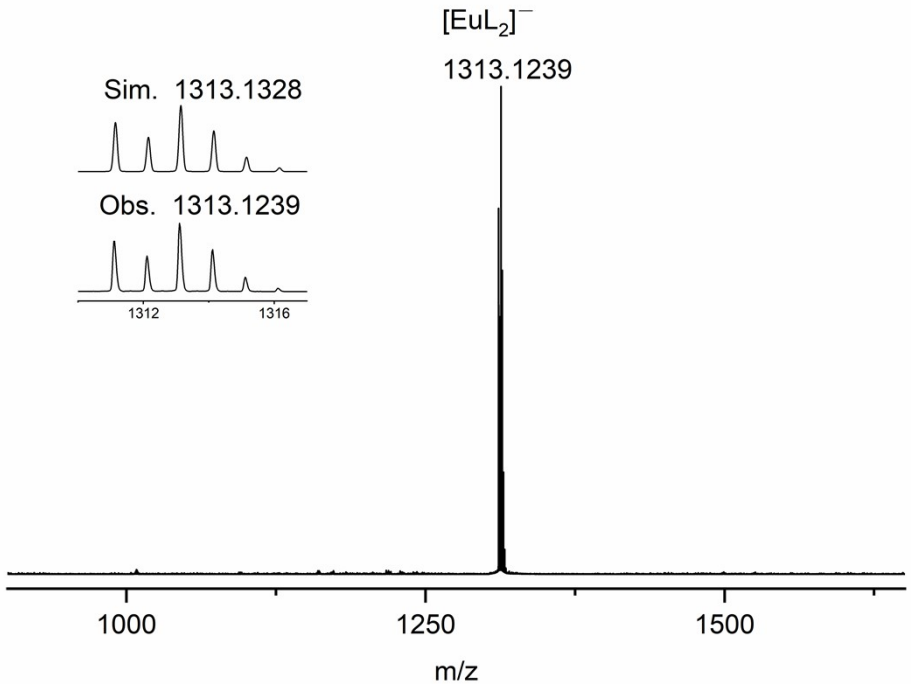


Figure S4. ESI-TOF mass spectrum of ((S)-HG)$[Eu\mathbf{L}_2]$.

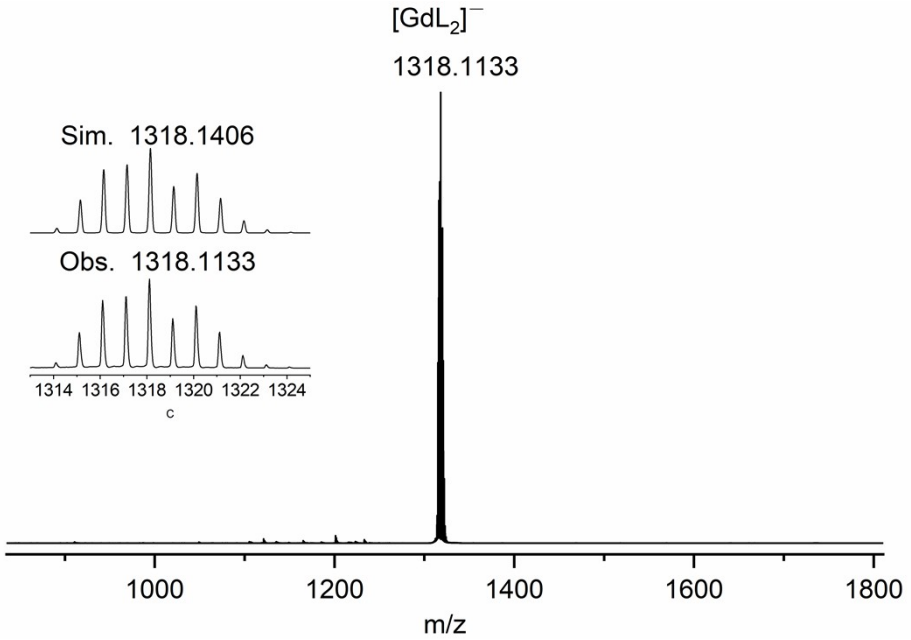


Figure S5. ESI-TOF mass spectrum of $(HNEt_3)[GdL_2]$.

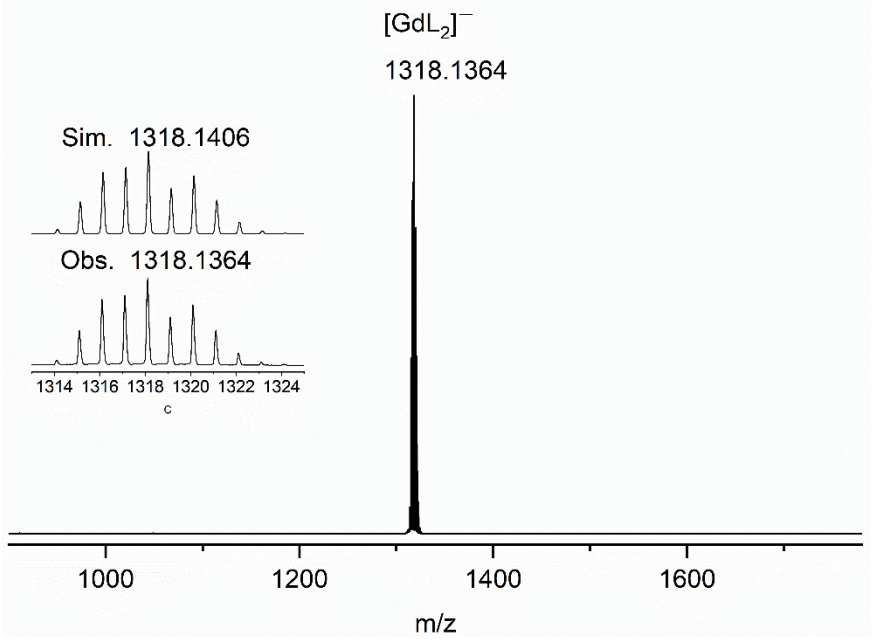


Figure S6. ESI-TOF mass spectrum of $((R)\text{-}HG)[GdL_2]$.

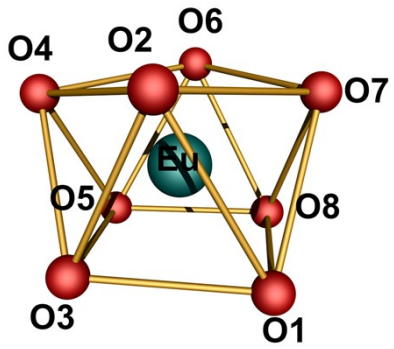


Figure S7. Coordination polyhedra of $(HNEt_3)[Eu\mathbf{L}_2]$

Table S1. Shape analysis of europium complexes using SHAPE 2.1 software

Complexes	Square antiprism	Triangular dodecahedron	Biaugmented trigonal prism
$(HNEt_3)[EuL_2]$	1.047	1.909	3.137

2. Photophysical properties

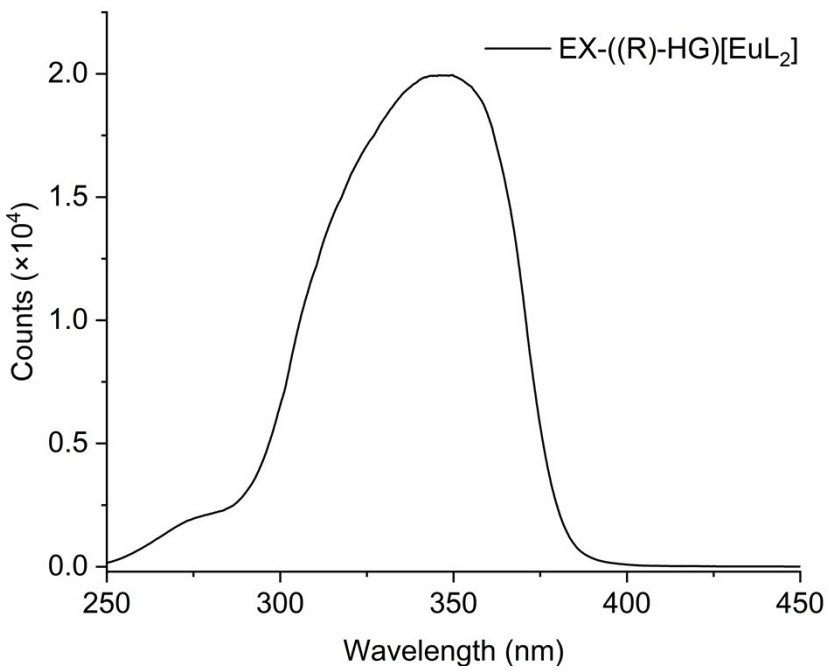


Figure S8. Excitation spectra of ((R)-HG)[Eu**L**$_2$] in $CDCl_3$ (5.0×10^{-5} M).

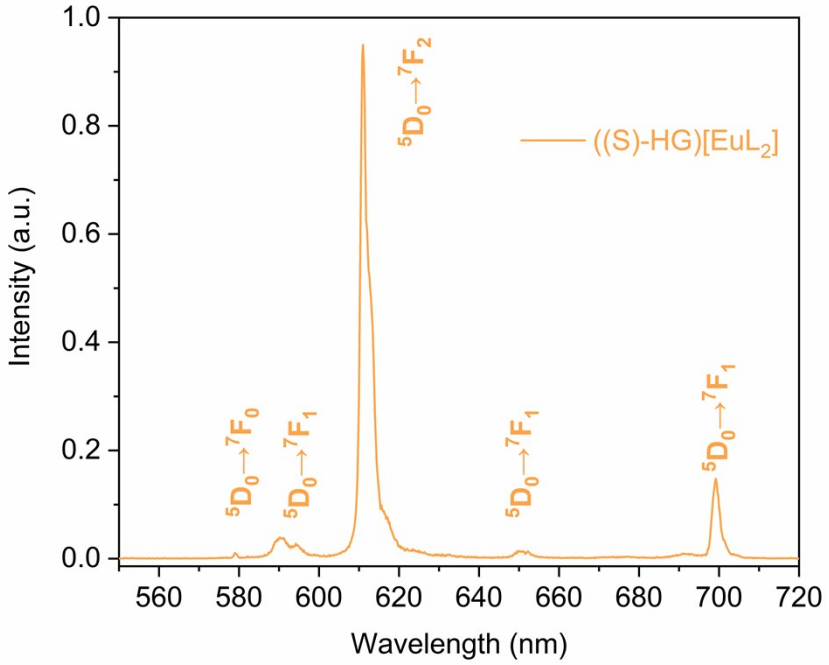


Figure S9. emission spectra of ((S)-HG)[Eu**L**$_2$] in $CDCl_3$ (5.0×10^{-5} M).

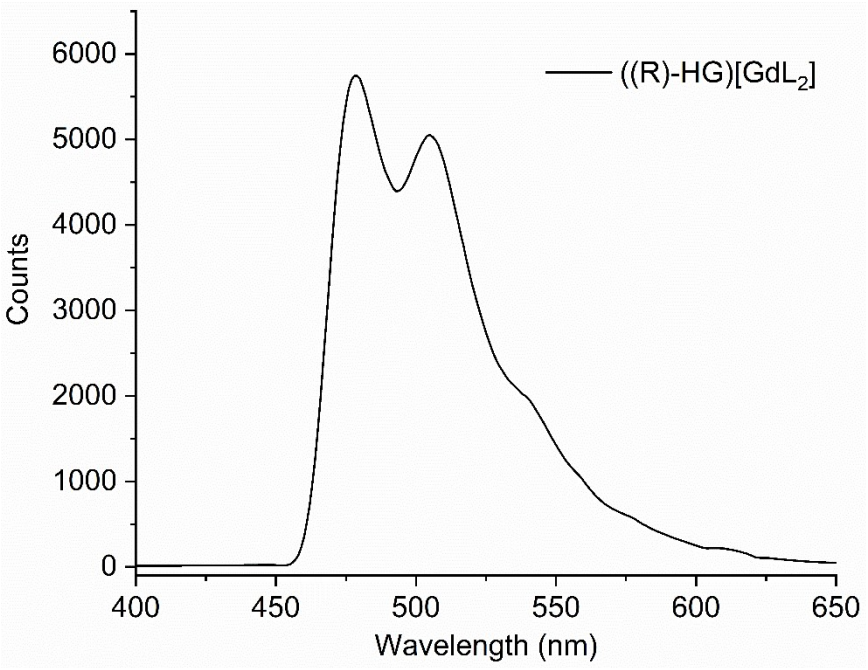


Figure S10. Phosphorescence spectrum of ((R)-HG)[Gd**L**$_2$] at 77 K in THF.

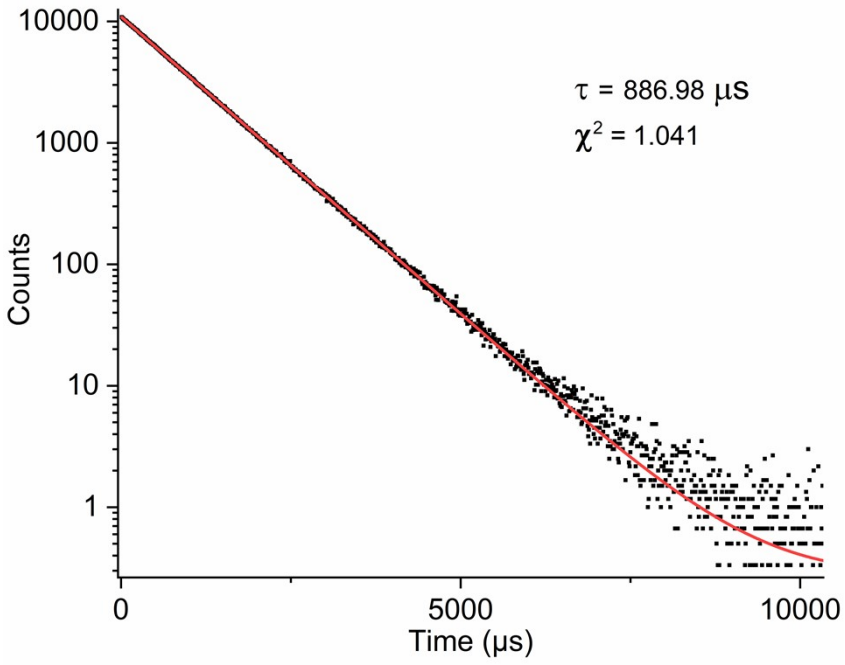


Figure S11. Luminescence decay curve of of (R-HG)[Eu**L**$_2$] in $CDCl_3$ (1.0×10^{-4} M) monitored at 612 nm.

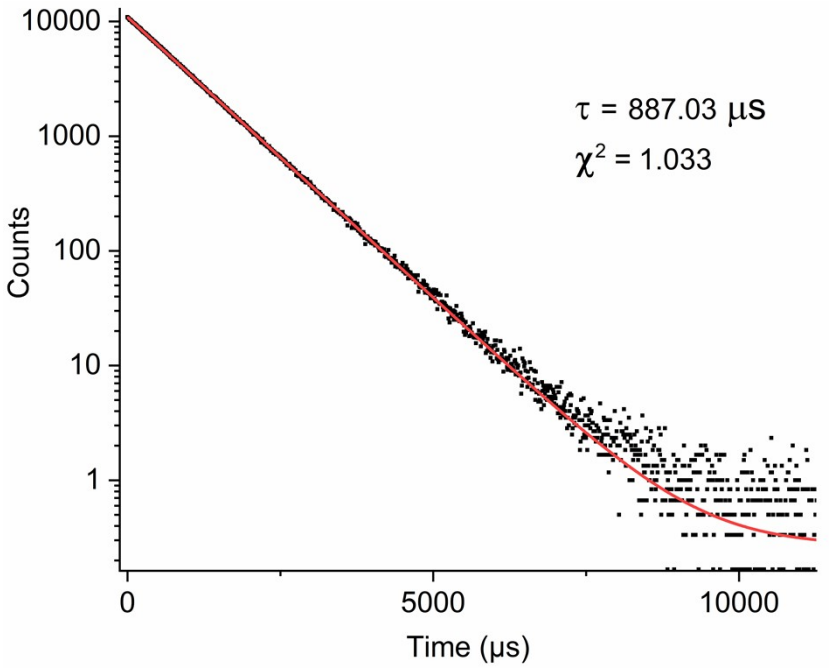


Figure S12. Luminescence decay curve of (S-HG)[Eu$\mathbf{L_2}$] in $CDCl_3$ (1.0×10^{-4} M) monitored at 612 nm.

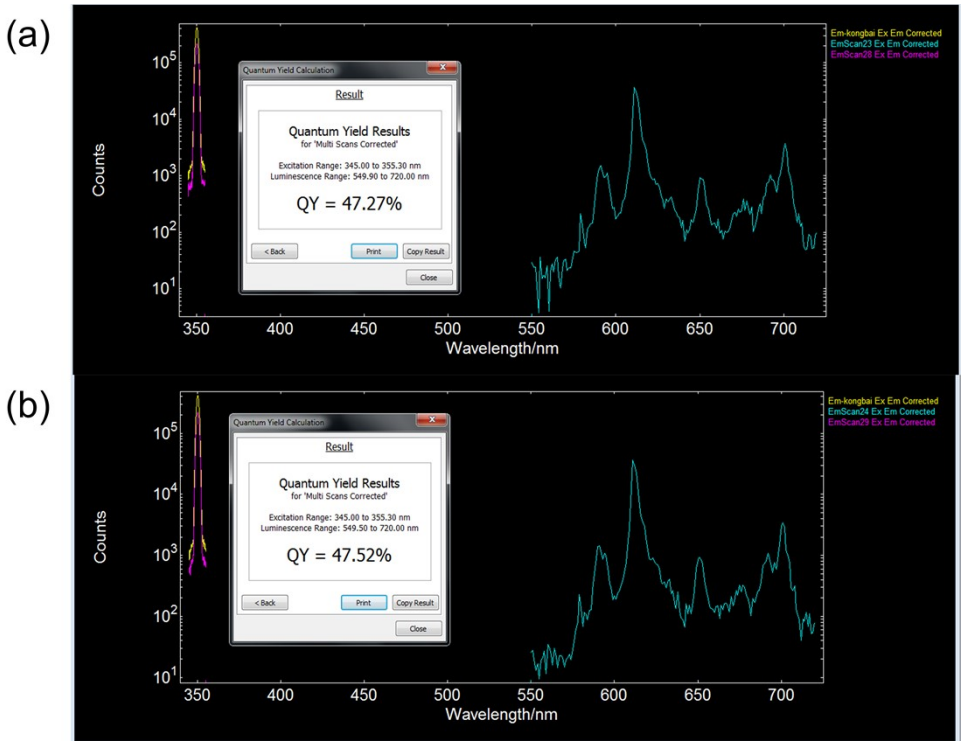


Figure S13. The screenshot of the luminescence quantum yields measurement of (a) (R-HG)[Eu$\mathbf{L_2}$]; (b) (S-HG)[Eu$\mathbf{L_2}$]

3. Exchange constants determination

NMR titrations were conducted on a Bruker Avance III 400 MHz spectrometer and the chemical shifts are referenced internally to tetramethylsilane (TMS) or solvents in parts per million (ppm). In all cases, NMR titrations were performed maintaining the concentration (usually around 4.0×10^{-3} M) of the host constant in $CDCl_3$.

In an NMR tube, chiral (S)-HG) (50 eq.) was dissolved in CD_3Cl solution and then by addition of various equivalents of (S)-HG into achiral $(HNEt_3)[EuL_2]$ in $CDCl_3$, delivered accurately using 10 µL pipette. The formation of the host-guest species could be easily followed looking at the chemical shift for proton (He) of the b-diketone moiety.

The data were analysed with the Bindfit web-based app at Supramolecular.org - Binding Constant Calculators | Supramolecular.[1-3]

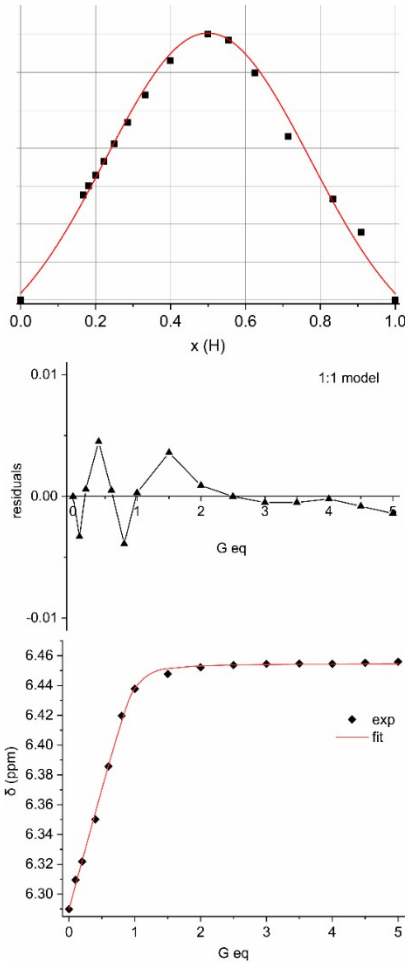


Figure S14. The job plots and residuals of $(HNEt_3)[EuL_2]$ with (S)-HG in $CDCl_3$ (4 mM)

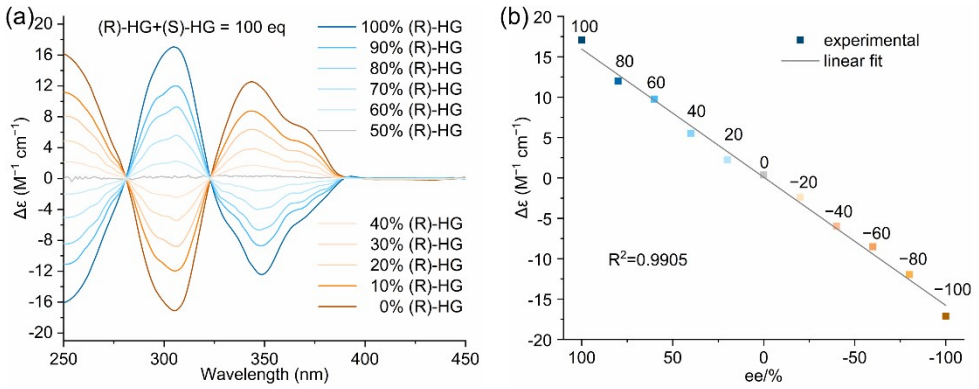


Figure S15 (a) CD spectra of $(HNEt_3)[Eu\mathbf{L}_2]$ by the addition of (R/S)-HG with various enantiomeric excess. (b) The corresponding calibration plots of ee% vs Δε at 305 nm.

Table S2. Association constants for the host-guest systems

Complexes	K/ M^{-1}	Error (%)
$(S\text{-}HG)_2[Eu_2(\mathbf{L}^3)_4]$	2.1×10^4	±24

a. For noncooperative binding K_2 is calculated as $K_2 = 1/4\ K_1$ from the K_1 value obtained.[1]

Table S3. Crystal data of the $(HNEt_3)[Eu\mathbf{L}_2]$

	$(HNEt_3)[EuL_2]$
CCDC Number	2234661
formula	$C_{70}\ H_{54}\ Eu\ F_{12}\ N\ O_9$
Mr	1433.10
color	Colorless
cryst syst	Triclinic
space group	*P*–1
a (Å)	14.7676(3)
b (Å)	19.8952(5)
c (Å)	23.4556(5)
α (deg)	65.0780(10)
β (deg)	80.3730(10)
γ (deg)	86.0460(10)
V (Å^3)	6161.6(2)
Z	4
ρ (g cm^3)	1.545
μ (mm^{-1})	1.115
F (000)	2896.0
R_1,[$I>2\sigma(I)$]	0.0490
wR_2,[$I>2\sigma(I)$]	0.0944
R_1, (all data)	0.0846
wR_2, (all date)	0.1103
GOF on F^2	1.021

4. DFT calculation

xyz-data of the calculated (PBE0) M-((R)-HG)[EuL_2] complexes:

Eu	0.50016500	-0.20010100	0.28580900
O	2.36506000	0.86380700	1.54789100
O	1.66147900	1.31375000	-1.23467600
O	-0.21637300	1.98292300	1.06700400
O	-1.06917000	0.67008500	-1.31010000
O	-1.46084100	-0.74148800	1.57118600
O	-0.42841300	-2.19607600	-0.70291400
O	2.26245200	-1.41315200	-0.87659700
O	1.09487500	-1.86851900	1.91512400
F	1.92647400	4.13010700	-3.30710200
F	3.03016900	3.69552700	-1.49742100
F	3.22807300	2.40279900	-3.21750000
F	4.13042300	1.22618100	3.57943200
F	3.68067500	-3.99419200	-2.78975000
F	4.81364600	2.34816100	1.86053300
C	-3.62279100	1.32243000	-2.00957600
C	-6.03720000	0.67858400	-2.03753300
F	4.69037400	-2.73227200	-1.36056700
C	-2.57485300	2.21697000	-2.24304600
F	3.86463600	3.36767900	3.51110000
C	0.30122100	3.03590800	1.50912800
C	-0.51275000	4.28787200	1.45272600
C	-7.31967400	1.06543000	-1.62792000
C	1.22679800	2.25038600	-1.97002400
C	-4.17523900	-0.95974100	2.17563600
C	-1.88211500	4.16933300	1.20857100
C	-0.07629100	2.56264000	-2.30869400
C	-4.95430700	1.66141600	-2.27013500
C	-1.18807100	1.76501200	-1.91632900
C	1.60123400	3.08119600	2.08265300
F	0.46319800	-4.90541200	3.55406800
C	-3.26691400	-5.14075400	-1.53996300
F	1.96950400	-3.43658100	4.05374100
C	-0.77403900	6.68783800	1.53580400
C	-0.96353300	-4.43857700	-1.14971100
C	2.31228500	-2.54394800	-1.43460000
C	-2.87306800	3.49837900	-2.72184700
C	-5.56763500	-1.09095000	2.18277800
C	-6.74875300	2.49253300	1.83363900
C	-8.00574100	2.43225700	2.44481500
C	-5.78761200	-0.68329500	-2.21882100

C	-8.03705300	-1.24507800	-1.58595300
C	-6.43176000	0.10710000	2.27630600
C	1.34882600	-3.53895000	-1.48963200
C	-6.10963900	-2.37951000	2.08186600
C	-6.17578600	3.74899800	1.30500000
C	-4.80899600	3.98429500	1.47404400
C	-1.86031700	-1.84917600	2.02158100
C	-3.33531600	-2.07049900	2.08396300
C	-8.46768400	1.22678100	2.96544200
C	0.04158100	5.56417500	1.60774700
C	2.47894900	2.01632000	2.07558400
C	-8.30797000	0.10955800	-1.41471200
C	-3.89938300	-3.34822800	1.99465400
F	3.80590900	-1.86235500	-3.12923200
C	-2.72000600	5.28803300	1.15965700
C	0.01163500	-3.31216100	-1.07847300
C	-5.12534600	-3.49495000	-1.71881500
C	-6.39006500	-3.08105800	-2.14401300
C	-5.99459300	1.31967700	1.73943300
C	2.34677000	3.14200800	-2.51020300
C	-2.28429500	-4.14683300	-1.48542700
C	-5.28278700	-3.49370000	1.98756800
C	-2.14279300	6.55366300	1.32699600
C	-6.76030700	-1.65859900	-1.98016800
C	-4.65164200	-4.79191800	-1.93299100
C	-2.88831400	-6.45251900	-1.21956600
C	-0.60252900	-5.75625200	-0.85472900
C	-6.32764200	5.85702600	0.12948100
C	-0.99893300	-2.87635300	2.48430200
C	-7.23494400	-4.02251300	-2.74144100
C	-4.17678000	5.11853000	0.96183900
C	-5.51098200	-5.71083800	-2.54967100
C	-7.68760100	0.07634900	2.89620300
C	-6.93784200	4.71078900	0.63225000
C	-1.57265500	-6.75390200	-0.88030000
C	-4.19309400	3.85618900	-2.97050300
C	0.38221000	-2.77692800	2.43064100
C	-6.79405600	-5.32924900	-2.93122700
C	-5.22367500	2.94731400	-2.75728600
C	-4.95918900	6.06011800	0.28110900
F	2.02918000	-4.44055500	2.13796100
C	3.62430000	-2.80177400	-2.18566600
C	3.82517200	2.25352500	2.77132000
C	1.20599300	-3.90685000	3.05608000

H	-3.36931600	0.35302400	-1.59241900
H	-7.53316800	2.11384200	-1.43856700
H	-3.71148600	0.01793100	2.25778700
H	-2.27969000	3.17319000	1.04251500
H	-0.23507300	3.43099500	-2.93126300
H	1.92027200	3.98253900	2.58491600
H	-0.34119300	7.67716000	1.65636600
H	-2.08749700	4.23016900	-2.87711700
H	-8.60372000	3.33468000	2.54454800
H	-4.81597100	-0.99650900	-2.58918100
H	-8.80600300	-1.98591800	-1.38158700
H	1.59362000	-4.47703900	-1.96866100
H	-7.18797900	-2.50602400	2.03791200
H	-4.22819900	3.27563000	2.05637600
H	-9.43544200	1.18976500	3.45896000
H	1.10902100	5.68914300	1.75842300
H	-9.29306800	0.42323500	-1.07988100
H	-3.26307800	-4.22048900	1.88067100
H	-4.50748100	-2.78436000	-1.17932800
H	-5.05641500	1.34673400	1.19353700
H	-2.52351000	-3.11758500	-1.73003800
H	-5.72044700	-4.48225900	1.88101800
H	-2.77444600	7.43813000	1.31737000
H	-3.63500700	-7.24220500	-1.21358500
H	0.41917200	-5.98890700	-0.56695400
H	-6.92290900	6.59214800	-0.40611500
H	-1.42990200	-3.74625400	2.95956400
H	-8.21931000	-3.72182500	-3.09106000
H	-5.16734900	-6.71980100	-2.76113300
H	-8.04562700	-0.84409400	3.34963500
H	-8.00254300	4.54913200	0.48212000
H	-1.30500100	-7.77467600	-0.62091700
H	-4.42172800	4.85276800	-3.33762300
H	-7.44594300	-6.05180000	-3.41532400
H	-6.24718000	3.23292700	-2.98433700
H	-4.49349500	6.94216100	-0.15074200
C	5.27989400	-0.01919600	-0.32348000
N	4.50863700	0.79312600	-1.03611100
N	4.87539300	-0.47662900	0.86216900
N	6.48919700	-0.36467200	-0.79889100
C	7.11641800	2.90976700	-4.29078600
C	6.77366500	1.62741300	-3.86770500
C	8.02473000	-1.22351100	-2.45471700
C	6.86153300	-0.26752900	-2.20393400

C	7.20285600	1.15083100	-2.62719300
C	4.54662200	-2.00833200	2.70662000
C	5.45509600	-1.63365400	1.54011200
C	8.31320700	3.26336000	-2.22953000
C	7.88956500	3.72863100	-3.47331700
C	7.97024800	1.98312600	-1.80805300
C	7.82433700	-2.42010000	1.89714800
C	9.12786800	-2.24353100	2.35686600
C	9.50571200	-1.03093800	2.92619500
C	8.57445400	0.00087900	3.03278300
C	7.27145500	-0.17671300	2.57749400
C	6.88188300	-1.39357300	2.00801200
H	4.89517000	1.29686600	-1.82028400
H	3.49835600	0.87204600	-0.89935800
H	3.98131300	-0.11291300	1.20525900
H	7.11161800	-0.84870900	-0.16560500
H	6.77029200	3.27031700	-5.25543300
H	6.16274700	0.99144000	-4.50591000
H	8.31846100	-1.18574000	-3.50691100
H	7.73546600	-2.25097000	-2.20839800
H	8.89722100	-0.94234800	-1.85331300
H	6.00143300	-0.60970900	-2.79336900
H	4.91171700	-2.92434000	3.17851900
H	3.52290500	-2.17354300	2.36144200
H	4.53838200	-1.21367500	3.45745600
H	5.46650500	-2.47100900	0.83090800
H	8.90709500	3.90335800	-1.58263600
H	8.15276700	4.73125200	-3.79863300
H	8.28407700	1.62955900	-0.82847700
H	7.53066100	-3.36931500	1.45207400
H	9.84717000	-3.05309500	2.26640700
H	10.52222900	-0.88815100	3.28246500
H	8.86386700	0.95059400	3.47490200
H	6.54994400	0.63094400	2.65608300

xyz-data of the calculated (PBE0) M-((S)-HG)[EuL_2] complexes:

Eu	-0.36880600	-0.22970500	-0.20631400
O	-2.14484300	-1.60181600	0.84166600
O	-1.00603300	-1.70088600	-1.96733000
O	0.60322000	-2.28764000	0.61147900
O	1.56145000	-0.69719700	-1.53539200
O	1.27020800	0.57259700	1.40129800
O	0.29053400	1.97324100	-0.94002600
O	-2.26348800	0.83052900	-1.29961100
O	-1.47927100	1.16362700	1.50640200
F	-0.52797100	-4.42794900	-4.11178000
F	-1.94148300	-4.25501600	-2.48290400
F	-2.07782400	-2.91994800	-4.17863600
F	-4.13069200	-2.16570600	2.53896200
F	-3.97646700	3.32644100	-3.06689400
F	-4.24043900	-3.68300900	0.99923600
C	4.25307300	-0.88434300	-1.90648600
C	6.49828200	0.16354500	-1.60491600
F	-4.81197300	2.11326000	-1.48769400
C	3.41323500	-1.92797800	-2.30142600
F	-3.35988500	-4.14631800	2.91739600
C	0.23331900	-3.39748300	1.06284800
C	1.24525100	-4.49415100	1.11771000
C	7.77202200	-0.00575700	-1.04715600
C	-0.33391600	-2.53714400	-2.63293100
C	3.80661200	1.24379600	2.34471800
C	2.59357800	-4.14511400	1.02748900
C	1.04288600	-2.65165000	-2.75362900
C	5.64530600	-0.98193700	-1.99511300
C	1.93828200	-1.72271400	-2.16553500
C	-1.08019700	-3.63871700	1.54836300
F	-2.94412500	2.47176900	3.44431900
C	2.67963100	5.38582100	-1.28536100
F	-2.81796800	3.61477800	1.61300700
C	1.89331500	-6.81540000	1.26827200
C	0.49577700	4.30385600	-1.17868200
C	-2.45868800	1.98952400	-1.75706500
C	3.98682800	-3.11825300	-2.76407000
C	5.14037100	1.62278000	2.52623900
C	6.97931500	-1.68050300	2.26528000
C	8.12555900	-1.42071000	3.02419100
C	6.02799300	1.46607100	-1.78486800
C	8.04334000	2.39165600	-0.85909600
C	6.19225500	0.59558800	2.69822200

C	-1.63044500	3.10182200	-1.72473700
C	5.44127100	2.99187300	2.52745000
C	6.70149400	-3.00206200	1.66241900
C	5.38627500	-3.47323500	1.66250700
C	1.40385600	1.70398900	1.92944700
C	2.79194300	2.18823300	2.18285800
C	8.30178000	-0.17101200	3.61146100
C	0.89767700	-5.84519900	1.23176000
C	-2.11659100	-2.73590700	1.41695400
C	8.53570100	1.10072600	-0.68829300
C	3.11411400	3.55004100	2.20195800
F	-4.06694400	1.17897400	-3.29089400
C	3.60707300	-5.10596300	1.09703500
C	-0.29327600	3.03998300	-1.26309300
C	4.80586500	4.08948100	-1.30250000
C	6.16606500	3.92606200	-1.57858500
C	6.04515600	-0.65502000	2.09474400
C	-1.21701600	-3.54995200	-3.36753800
C	1.87297500	4.24730900	-1.39018100
C	4.43869900	3.94218900	2.36614600
C	3.23522200	-6.45161600	1.21523900
C	6.76917700	2.58722700	-1.40217700
C	4.13684800	5.29410800	-1.53362600
C	2.06309800	6.59649600	-0.93799300
C	-0.09994800	5.52522000	-0.84855300
C	7.35665800	-5.02583300	0.51188500
C	0.31080500	2.53278500	2.31516100
C	6.89042000	5.02869400	-2.04390400
C	5.02637100	-4.68761400	1.07568500
C	4.88163500	6.37779600	-2.01775000
C	7.34168100	0.82571100	3.46489000
C	7.69389200	-3.80270300	1.08587500
C	0.69020100	6.66327900	-0.72153700
C	5.36991900	-3.23926700	-2.83791000
C	-1.00694700	2.17810800	2.10722200
C	6.24678100	6.24516100	-2.25334200
C	6.19338300	-2.18123900	-2.46834700
C	6.03618900	-5.46588100	0.49596700
F	-1.61388100	4.17188300	3.32015900
C	-3.83098300	2.16534300	-2.41704600
C	-3.46561000	-3.18839100	1.98899700
C	-2.08515600	3.12922900	2.63296100
H	3.78376800	0.00790700	-1.50459700
H	8.15092000	-1.00651700	-0.85868100

H	3.52525600	0.19578700	2.34191100
H	2.83532500	-3.09620300	0.88849800
H	1.42796800	-3.45355400	-3.36633200
H	-1.28539200	-4.56356100	2.06856000
H	1.62189200	-7.86415400	1.35222600
H	3.36466500	-3.96189700	-3.04383200
H	8.85852000	-2.20726200	3.18492000
H	5.06789900	1.61773600	-2.26891300
H	8.63326200	3.24800100	-0.54193600
H	-1.99671100	4.03207000	-2.13712000
H	6.47507700	3.31391300	2.61819200
H	4.62479700	-2.88966300	2.17065200
H	9.18358000	0.01873400	4.21799500
H	-0.14503200	-6.14552400	1.26321800
H	9.51460800	0.95298300	-0.24007000
H	2.34502900	4.29862200	2.03703500
H	4.26501800	3.25637600	-0.86460900
H	5.19759500	-0.82824700	1.43874400
H	2.30180500	3.28841200	-1.66193000
H	4.69567800	4.99739900	2.34209000
H	4.00371100	-7.21665900	1.29094700
H	2.66767400	7.49069000	-0.81137600
H	-1.16733100	5.57300100	-0.65157000
H	8.13048900	-5.63516800	0.05203000
H	0.51407500	3.44836200	2.85257600
H	7.94676400	4.92216600	-2.27717000
H	4.38869600	7.32025900	-2.24044900
H	7.47389200	1.77782700	3.97177300
H	8.72451400	-3.45676600	1.06561000
H	0.23569000	7.60863600	-0.43753700
H	5.81146100	-4.16644400	-3.19248000
H	6.80920700	7.09241200	-2.63702000
H	7.27126500	-2.28052900	-2.56373700
H	5.78570500	-6.40600800	0.01134700
C	-5.21090300	0.24490600	0.74453600
N	-4.33104500	0.75571400	1.59955900
N	-4.84101200	-0.74830700	-0.06651400
N	-6.47555000	0.69687100	0.71310600
C	-10.63714400	1.71775000	2.62655700
C	-9.24513300	1.73225700	2.65718700
C	-6.46779000	3.15950200	1.01952700
C	-6.99586200	1.80866400	1.51116100
C	-8.50865600	1.76079600	1.47283200
C	-4.62249700	-2.06635600	-2.08079500

C	-5.52609300	-1.10984800	-1.30696000
C	-10.58034600	1.74460400	0.21927800
C	-11.30771500	1.72176500	1.40697200
C	-9.18974000	1.77006200	0.25154700
C	-7.92658400	-1.41557900	-1.99231200
C	-9.19132400	-1.97959700	-1.84999100
C	-9.45552300	-2.83609500	-0.78429300
C	-8.44788400	-3.12455500	0.13273900
C	-7.18040600	-2.56654100	-0.01353200
C	-6.90570300	-1.70682300	-1.08159200
H	-4.61545100	1.43176500	2.28748500
H	-3.31918400	0.65180400	1.48051500
H	-3.88225100	-1.07976800	0.06092700
H	-7.15489700	0.08411700	0.27805600
H	-11.19677100	1.69624500	3.55759200
H	-8.72523600	1.71938400	3.61269500
H	-6.87971700	3.96003300	1.64187700
H	-5.37630500	3.21464900	1.05957700
H	-6.77477000	3.33078200	-0.01596800
H	-6.69586200	1.66350900	2.56004800
H	-5.09248600	-2.32568800	-3.03330600
H	-3.65105500	-1.60594100	-2.28312400
H	-4.46374200	-2.98961600	-1.51554500
H	-5.65119200	-0.19731600	-1.90168200
H	-11.09679400	1.74661200	-0.73661400
H	-12.39372300	1.70540800	1.38116400
H	-8.63135700	1.79638000	-0.68178000
H	-7.72295900	-0.74452600	-2.82511500
H	-9.97161600	-1.74510700	-2.56918600
H	-10.44345400	-3.27258700	-0.66604400
H	-8.64732700	-3.78998100	0.96849300
H	-6.39677300	-2.79787900	0.70113500

5. Supplementary References

1 G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1997

2 P. Thordarson, *Chem. Soc. Rev.,* 2011, **40**, 1305−1323.

3 E. N. W. Howe, M. Bhadbhade and P. Thordarson, *J. Am. Chem. Soc.,* 2014, **136**, 7505−7516.

4 D. B. Hibberta and P. Thordarson, *Chem. Commun.,* 2016, **52**, 12792−12805.