Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Photoluminescence of LaI_3 Switched on and off by Association and Dissociation of Non-luminescent Tetrahydrofuran

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I. **Experimental Procedures**

General information

All reactions were carried out using a Vigor Ar-atmosphere glove box (<1 ppm O_2/H_2O). Solvents were dried and degassed through a Vigor solvent purification system and stored over 4Å sieves for 24h before use. Anhydrous LaI_3 was used as purchased. Powder X-ray diffraction measurements were conducted on a X'Pert Pro MPD diffractometer using Cu-Kα1 radiation. Single crystal X-ray Intensity data were collected on Bruker D8 Venture (Mo Kα) at 192 K. NMR spectra were recorded on Zhongke-Niujin Quantum-I Plus 400 spectrometer (Zhongke-Niujin, Wuhan, China). ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks. UV–visible absorption spectra were recorded on a Cary 6000i Agilent spectrophotometer, and diffuse reflectance spectrum was recorded on the same spectrophotometer equipped with an internal DRA 2500 integrating sphere using $BaSO_4$ as a reference. Luminescence spectra were collected on an Edinburgh FLS1000 spectrometer. Absolute emission quantum yield $<\eta_D>$ was measured using an integrating sphere, and calculated with the direct excitation method as follows : [1]

$$\langle \eta_D \rangle = \frac{E_B - E_A}{S_A - S_B} \qquad \text{S1}$$

in which E and S are respectively the integrals of the emission region and excitation scatter region, while subscripts A and B indicate the blank and sample. The absolute emission quantum yield $<\eta_D>$ was given by the FLUORACLE software. Lifetime of the solid samples sealed in a flat quartz cell (12mm diameter, 2 mm height) was measured by an Edinburgh FLS1000 spectrometer with an excitation laser wavelength of 250 nm at room temperature. Biexponential photoluminescence decay curve was analyzed in the lifetime measurement, and average lifetime $<\tau>$ was calculated from the decay time and pre-exponential factor using the following equation: [2]

$$\langle \tau \rangle = \frac{\alpha_1\tau_1 + \alpha_2\tau_2}{\alpha_1 + \alpha_2} \qquad \text{S2}$$

where α is a pre-exponential factor representing fractional contribution to the time-resolved decay of the component with a lifetime τ.

Synthesis of $LaI_3(THF)_4$

Anhydrous LaI_3 (0.24 g, 0.46 mmol) was added into THF (4 mL). After being stirred for ten minutes, the mixture was centrifuged with the insoluble solids (0.26 g, 70%) dried at room temperature. Colorless X-ray-quality crystals of $LaI_3(THF)_4$ were grown from the supernatant cooled overnight at -25 °C. ^1H NMR (C_6D_6): δ 3.70 (m, THF), 1.40 (m, THF) ppm. ^{13}C NMR (C_6D_6): δ 68.98 (THF), 25.70 (THF).

Detection of THF in n-hexane

Anhydrous LaI_3 (2 mg, 0.004 mmol) was added into 2 mL n-hexane containing 2 μL THF (0.1% v/v). After being stirred for ten minutes, the mixture was centrifuged with the solids separated and subjected to UV irradiation at 254 nm.

Detection of gaseous THF in argon atomsphere

2 μL THF was add into a capped 125mL glass bottle loaded with anhydrous 2 mg LaI_3 (0.004 mmol). THF was not in contact with LaI_3 before evaproation. After 30 minutes during which THF completely evaporated, the solids were taken out and irradiated with a UV lamp at 254 nm.

Quantum chemical calculations

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations using Gaussian09 program were performed to investigate the luminescent properties of $LaI_3(THF)_4$.[3] The initial structural parameters were obtained from the X-ray crystallographic data. The ground state and singlet excited state geometries were then optimized using the DFT/TDDFT methods with the CAM-B3LYP hybrid functional and ECP46MWB/6-31G(d) basis sets.[4] The MWB large-core ECP basis set was used for La and I, and 6-31G(d) was used for all the other atoms. All of the structures have been verified to be the local minima through frequency analyses. The vertical excitation or emission energy was calculated based on the optimized ground or excited state structures using TDDFT at the CAM-B3LYP/ECP46MWB/6-31G(d) level. Visualization of the optimized structures and frontier molecular orbitals was performed with the Multiwfn 3.7 program.[5]

II. Characterization

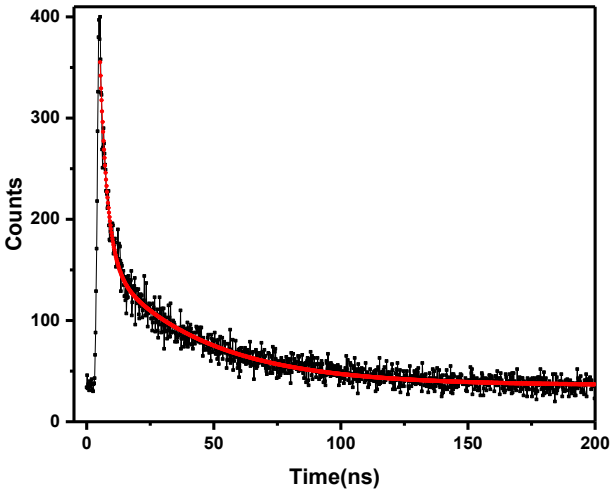

Fig. S1. Time-resolved emission intensity decay of $LaI_3(THF)_4$ (black) collected at 460 nm upon 250 nm excitation. Biexponential fit is given in red, affording τ_1=2.9 ns (89.7%), τ_2=39.7ns (10.3%), R^2=0.9623.

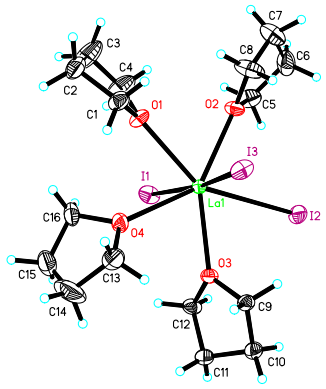

Fig. S2. Thermal ellipsoid plot of $LaI_3(THF)_4$, drawn at the 50% probability level.

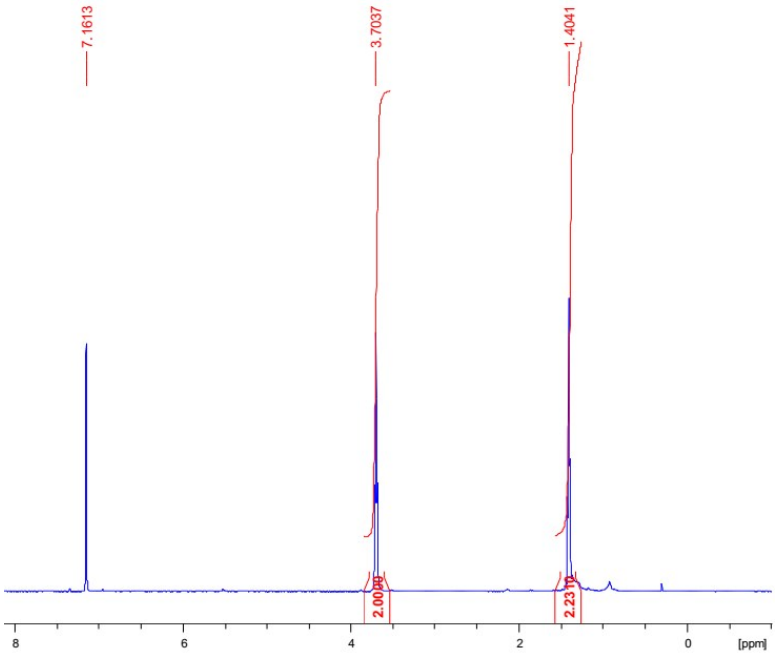

Fig. S3. ^{1}H NMR spectrum of $LaI_3(THF)_4$ at 294.1 K in C_6D_6.

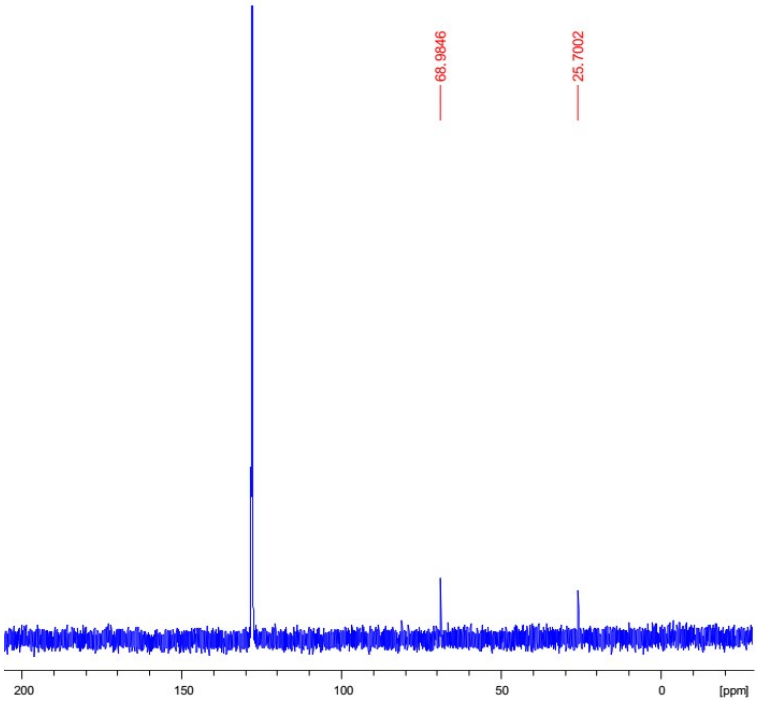

Fig. S4. ^{13}C NMR spectrum of $LaI_3(THF)_4$ at 293.7 K in C_6D_6.

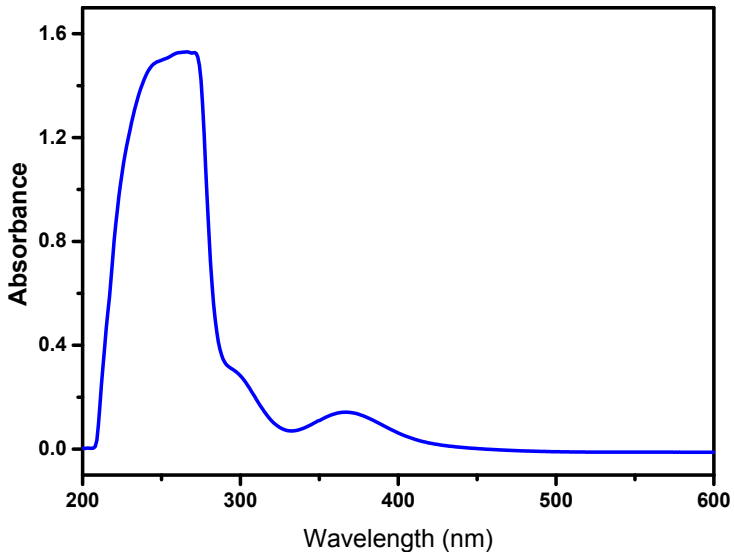

Fig. S5. UV–visible absorption spectrum of LaI_3 in THF.

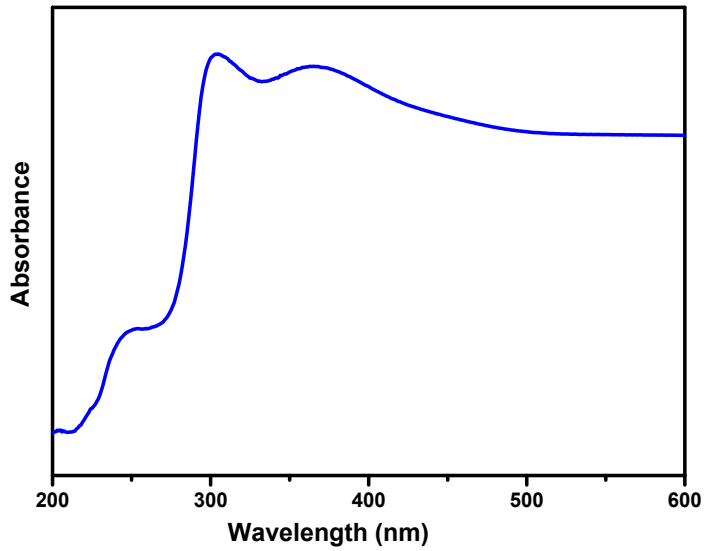

Fig. S6. Diffuse reflectance spectrum of $LaI_3(THF)_4$.

Table S1. Crystal data and structure refinements of $LaI_3(THF)_4$

	$LaI_3(THF)_4$
CCDC No.	2044769
Empirical formula	$C_{16}H_{32}I_3LaO_4$
Formula weight	808.02
Temperature/K	192(2)
Crystal system	Monoclinic
Space group	P21/c
a /Å	8.7172(4)
b/Å	17.4748(8)
c/Å	16.6830(8)
α/°	90
β/°	93.060(2)
γ/°	90
Volume/Å^3	2537.7(2)
Z	4
ρ_{calc}g/cm^3	2.115
μ/mm^{-1}	5.347
F(000)	1504
θ range/deg	2.614 to 26.000
Index ranges	$-10 \le h \le 10$ $-21 \le k \le 21$ $-19 \le l \le 20$
Reflections collected	31983
Independent reflections	4991 $R_{int} = 0.0478$
Completeness	99.8%
Data/restraints/parameters	4991 / 0 / 217
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	$R_1 = 0.0317$ $wR_2 = 0.0772$
Final R indexes [all data]	$R_1 = 0.0386$ $wR_2 = 0.0818$
Largest diff. peak/hole / e Å^{-3}	1.611/-1.020

Cartesian coordinates of $LaI_3(THF)_4$ obtained at the CAM-B3LYP level of theory.

ground state

Atom	X	Y	Z
La	0.01141000	0.00322000	-0.00588600
I	-0.44357500	0.43787500	3.15707100
I	3.26261700	-0.06042500	-0.13868800
I	-0.38448400	-0.49875400	-3.16295800
O	-2.07611800	1.56649400	-0.35247800
O	0.76073900	2.48169200	-0.01696400
O	0.66387300	-2.46857300	0.33686300
O	-2.19044200	-1.43688500	0.21972300
C	-3.06465200	1.46871900	-1.41149600
H	-2.58852900	1.76078400	-2.35038400
H	-3.36749100	0.42435100	-1.49280400
C	-4.17906100	2.42123100	-1.00613200
H	-4.88364900	1.92996500	-0.32627800
H	-4.73860400	2.78674000	-1.87016700
C	-2.36073400	2.71616600	0.48771400
H	-1.42231800	3.24448100	0.65023000
H	-2.73343900	2.35030100	1.44871500
C	1.07833100	3.08453800	-1.30000600
H	1.24012400	2.28555300	-2.02700100
H	0.21592300	3.68429900	-1.61269900
C	1.27722600	-3.28129800	-0.70528600
H	0.48617700	-3.88632700	-1.16005100
H	1.69793500	-2.61303600	-1.45650100
C	2.31560900	-4.12885700	0.01092200
H	2.50541000	-5.06983000	-0.51072100
H	3.25496100	-3.57441400	0.08865000
C	1.68940200	-4.31634000	1.39361300
H	2.41639400	-4.58170900	2.16435500
H	0.91749500	-5.09329500	1.36854400
C	1.07126600	-2.95086800	1.64899400
H	1.79963400	-2.24538300	2.05748100
H	0.18688100	-2.96494100	2.28798600
C	-2.36889400	-2.72345800	-0.42694900
H	-2.07968800	-2.61065000	-1.47311000
H	-1.70181700	-3.44058300	0.05892500
C	-3.83273800	-3.07669900	-0.21482900
H	-4.45469400	-2.61849800	-0.99098100
H	-4.00243200	-4.15563400	-0.23655900
C	-4.11667700	-2.44165300	1.14704000
H	-3.72374400	-3.06972900	1.95305200
H	-5.17910200	-2.27103100	1.33569800
C	-3.33390500	-1.13993400	1.05996400
H	-2.95878900	-0.77267500	2.01517400
H	-3.91851800	-0.35123000	0.57533400
C	-3.40815400	3.51785400	-0.27099800
H	-2.93172700	4.19409900	-0.98850500
H	-4.03190200	4.11492800	0.39806000
C	2.08949800	4.39529700	0.39800100
H	1.38067900	5.22973300	0.43497400
H	3.01092100	4.70845700	0.89372400
C	1.49811500	3.15273200	1.04743400
H	0.79725300	3.35459600	1.85858200
H	2.27104400	2.46615500	1.39896600
C	2.31000700	3.93704100	-1.04470500
H	2.39236700	4.76259700	-1.75552300

H	3.20900200	3.31883200	-1.11600700

excited state

Atom	X	Y	Z
La	0.24302600	-0.01795000	-0.05981700
I	2.67027100	0.01628800	-2.28578700
I	-3.27408400	0.52133500	-0.79147100
I	-2.19604000	-0.32006500	2.36245800
O	1.99919200	1.35171200	1.35807000
O	-0.16393700	2.47800200	-0.66161100
O	-0.66352500	-2.33712800	-0.97561100
O	1.72761800	-1.75580300	1.17649900
C	1.88723900	1.50462600	2.78756700
H	0.99077100	2.09288500	3.01127100
H	1.76301300	0.51138600	3.22339400
C	3.15909300	2.22427000	3.21380900
H	3.97919500	1.51037100	3.34663100
H	3.03131900	2.77418500	4.14899500
C	3.02817000	2.22937100	0.83857800
H	2.61328600	2.76488400	-0.01608400
H	3.85583200	1.61016000	0.48387700
C	-0.75507400	3.44142600	0.24192700
H	-1.45997100	2.91753500	0.89058500
H	0.04892200	3.86908600	0.85152400
C	-1.75128300	-3.15196700	-0.46933500
H	-1.35241200	-3.79114200	0.32590900
H	-2.50942200	-2.49311300	-0.04846500
C	-2.23968200	-3.97036800	-1.65700200
H	-2.67097000	-4.92565700	-1.34851500
H	-3.00208100	-3.41408600	-2.21106700
C	-0.96999500	-4.11447800	-2.49712500
H	-1.16556300	-4.35140500	-3.54546600
H	-0.32005900	-4.89496000	-2.08611000
C	-0.33361100	-2.74405300	-2.32913000
H	-0.76268700	-2.01391400	-3.02268200
H	0.75174300	-2.72323800	-2.43169300
C	1.27758400	-3.07914500	1.55336500
H	0.38944900	-2.96699400	2.17899700
H	1.00949700	-3.61705900	0.63993200
C	2.46373800	-3.71895300	2.26042400
H	2.47017700	-3.44862900	3.32135000
H	2.44746400	-4.80868200	2.18647100
C	3.64762400	-3.07657100	1.53510200
H	3.81267500	-3.55744900	0.56569600
H	4.58027400	-3.12196700	2.10204300
C	3.16485900	-1.64791600	1.33797900
H	3.56376900	-1.15964600	0.44794400
H	3.36225400	-1.02762600	2.21845800
C	3.42538600	3.12515800	2.00613100
H	2.78483600	4.01271800	2.04826300
H	4.46249900	3.46067100	1.93402000
C	-0.50882500	4.45951300	-1.89105700
H	0.40801500	5.03252800	-1.71656300
H	-0.99424800	4.85672700	-2.78523600
C	-0.19512400	2.97661200	-2.02375000
H	0.76926400	2.74935000	-2.48000700
H	-0.98542400	2.44522700	-2.56361000
C	-1.40768100	4.48641400	-0.65279200
H	-1.45653500	5.46642500	-0.17242500
H	-2.42439600	4.17616900	-0.91039900

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