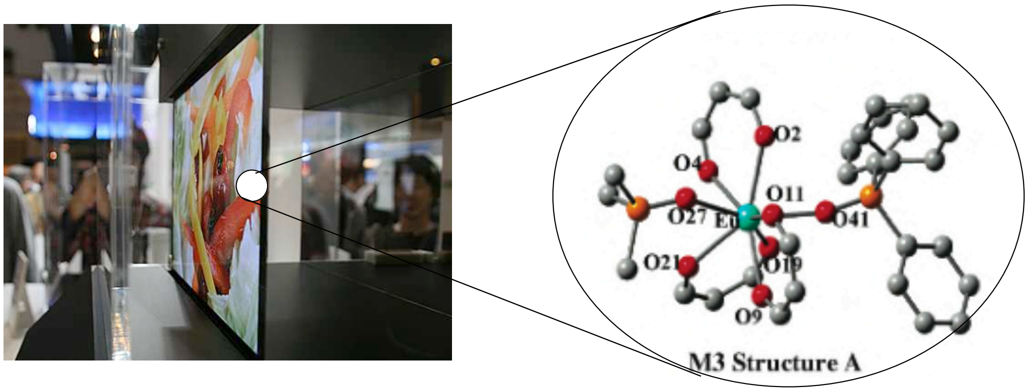
M2 Noriko Takahashi
28th May 2008

Materials for Organic Electroluminescence
– What's inside the black box? –



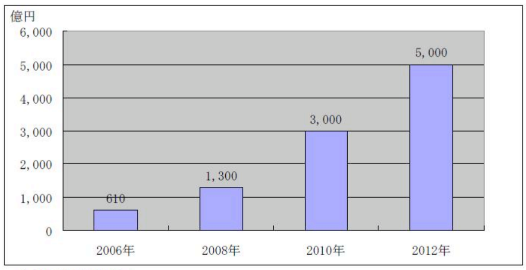
Message
You may have heard the word "Organic Electroluminescence(OEL)" in somewhere such as TV commercials or other advertisements.
And also you may have some ideas of what it is or what it's like.
HOWEVER, do you know exactly what it is?
In modern society, technology is developing too fast for us to catch up with.It's called "black box of technology".
I've been wondering what's inside the black box.How about you?
Don't be afraid. It's not hard to understand;just organic compounds that we're familiar!!
So let's open the black box.

Contents

1. Introduction

Organic Electroluminescence(OEL)
= Organic light-emitting diode(OLED)
= Light emitting Polymer(LEP)

- Next generation of full-color flat panel display
  ••• thin, light, beautiful
- In 2004, more than 5000 patents
- Commercial use now ••• small screens for mobile phone and portable audio players, digital cameras



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Estimated market scale

Comparsion of display technique

name	the present state	present & future
CRT (cathode-ray tube)	majority for TV mass productivity	low cost,lasting thick(can't be thin)
LCD (liquid crystal display)	majority for note PC, mobile phone mass productivity	thin,flat,everlasting backlight is necessary.
PDP (plasma display)	used in thin,large-scale TV	be used in large-scale display,but can't be small big consumption of electric power
OEL (organic electroluminescence)	partially used in mobile phone	high-quality durability is task to solve.
FED (field emission display)	trial manufacture	

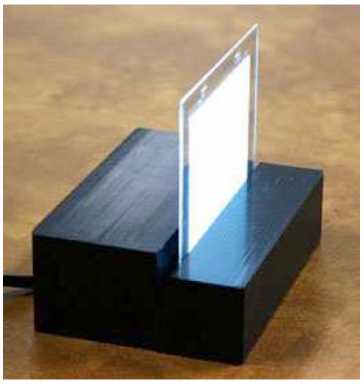
	consumption	speed	large-scale	quality	durability	cost	viewing angle	brightness	flexibility	heat-resistant
LCD	○	△	△	△	○	△	△	passive	×	△
OEL	◎	○	○	○	○	○	◎	active	◎	○

A significant benefit of OLED displays over liquid crystal displays is that OLEDs don't require a backlight to function.
Thus they draw far less power and can operate longer on the same charge.
Because there's no need to distribute the backlight, an OLED display can also be much thinner than an LCD panel.
However, degradation of OLED materials has limited their use.

Applycation of OEL –Not only display!!–

- General space illumination,large-area light-emitting elements
- Electronic paper
- Full color printing

紫色 LED
ON



History

Generally organic compounds are classfied as nonconductor.
But in order to make it flash, it's necessary to carry electricity.
Some organic compounds could be (semi)conductor:Usually they require over 100 V.
So it is highly challenging to make it behave as a conductor at low voltage.

1960s Study on electroluminescence of organic materials started;
  not worked well.(power-conversion efficiency remained less than 0.1 %.)
1977 Prof. Shirakawa succeeded to achieve high conductivity by chemical doping in π-conjugated high polymer.
  (Nobel prize for Chemistry in 2000)
1987 C.W.Tang and S.A. VanSlkye succeededed to fabricate multi layers cell.
1990 R.H. Friend succeeded to fabricate polymer materials.
1993 J. Kido succeeded to device white-color Organic Electroluminescence

Very severe competitions!!!!!

2007 SONY released OEL television in Japan.

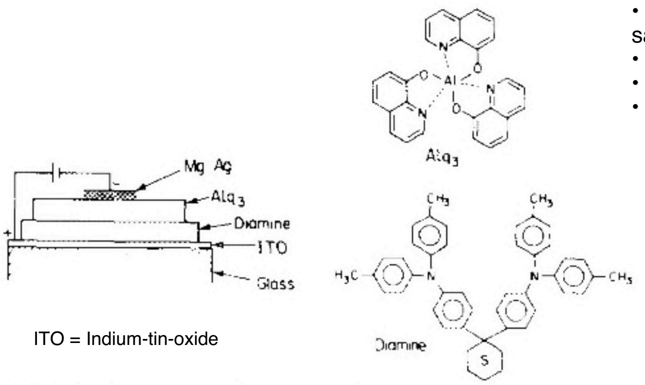


FIG. 1. Configuration of EL cell and molecular structures.

- First example of thin-film organic device (organic material is sandwiched between two injecting electrodes.)
- High brightness at a low voltage
- Fast degradation
- Broad spectrum

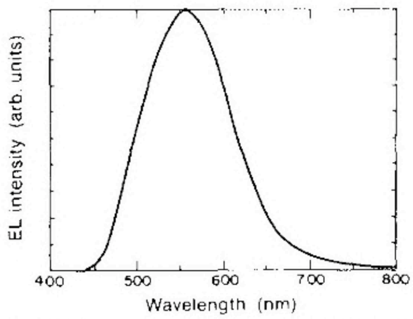
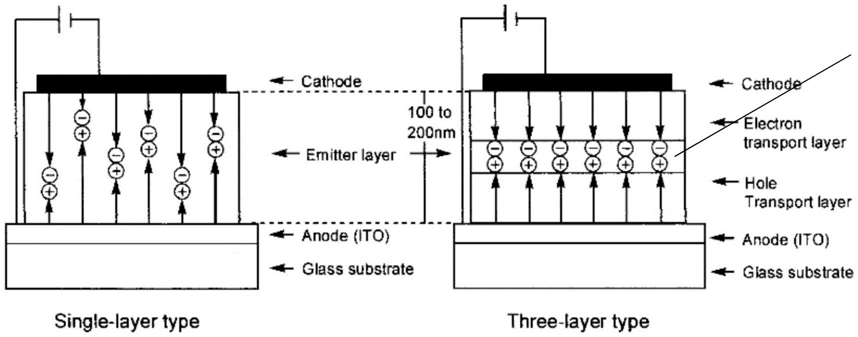


FIG. 3 Electroluminescence spectrum of ITO/diamine/Alq_3/Mg:Ag.

2. Materials – the Essential of Electroluminescence–

Structure



Recombination occurs here!!

Cathode and anode are inorganic compounds.To have good affinity between inorganic layer and organic layer, some buffers are necessary to be sandwiched;injection and transport layers.(Merit of multi-layers.)
In polymer system, single layer is used, that's why many elements are necessary to be included.
Four layers structure is the most common one.

The role of layers are following:

	Small molecules	Polymers *1	Required features
Electron injection layer	Alkali metals Li complex	Barium Calcium	Matching work function of cathode and HOMO,LUMO of transport layer
Electron transport layer *2	Al complex phenantrolines 1		High mobility of electron Hole-brocking
Hole injection layer	Aryl amines 5 Cu complex		
Hole transport layer *2	Aryl amines 2		
Emitting Layer	Al complex 3 Anthorathene **Organo lanthanide complex** Ir complex	π-conjugated 6 •••polyphenylenevilylene polyfluorene coloring matter	high luminescence efficiency
Cathode	ITO(Indium tin oxide)	ITO	high work function, transparent to visible light
Anode	Aluminium Al:Li Mg:Ag	Aluminium	low work function
Dopament	Polycyclic aromatics 4		high luminescene not cohered

*1 Single-layer
*2 Some emitting materials also can work as it.

Example of used materials

1 Electron transport layer

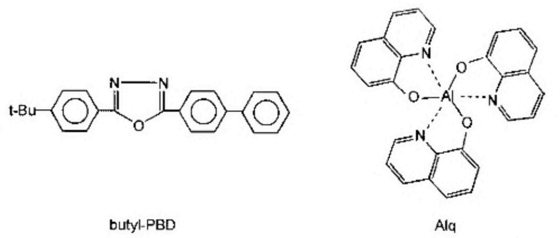
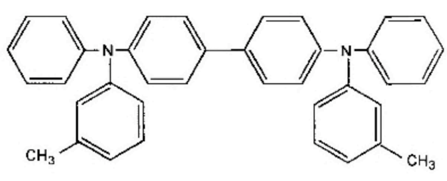


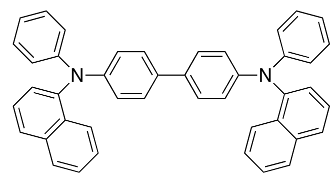
Figure 4. Chemical structure of electron-transporting material 1,3,4-oxadiazole derivative, PBD 8-hydroxyquinoline aluminum, Alq_3.

2 Hole transport layer



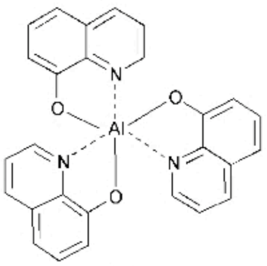
TPD

TPD has been used as material for copy machine.
TPD has relatively sharp emission peaks at 410-420 nm, purple,blue

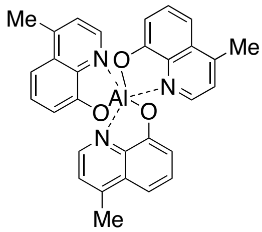


α-NPD

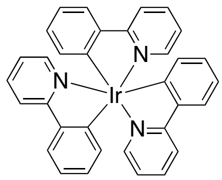
3 Emitting Layer(small molecules)



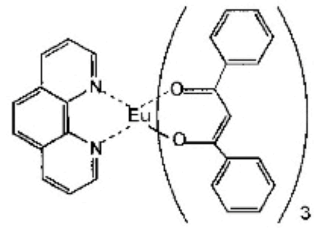
AlQ



Almq$_3$



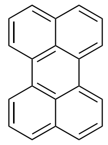
Ir(ppy)$_3$



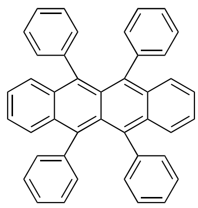
Eu(DBM)$_3$(Phen)

described in Chapter 3

4 Dopament



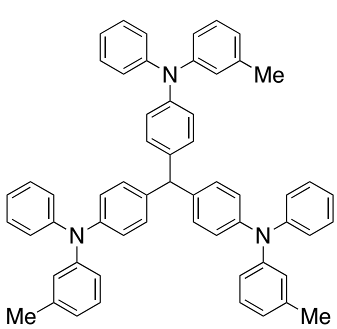
Perylene



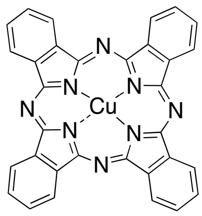
Rubrene

1-2 % doping of them makes luminescence effictive
color change,color mixing

5 Hole injection layer



m-MTDATA

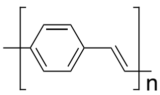


CuPc

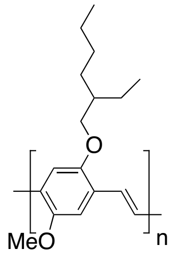
pigment
heat-resistance, durability

6 Emitting Layer(Polymer)

$\boxed{\pi\text{–conjugated}}$

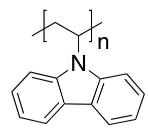


PPV

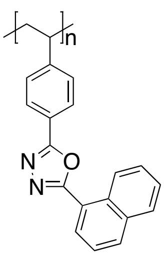


MEH-PPV

$\boxed{\text{coloring matter}}$



PVK



PVOXD

Conjugated chain provides gap between HOMO and LUMO small,
which causes wave length long.
Only yellow and red light.blue light is difficult to obtain.
Side chain makes polymer soluble in organic solvent.

Small pigments are polymerized:
same featues as small molecules.
PVK has hole-transportability.

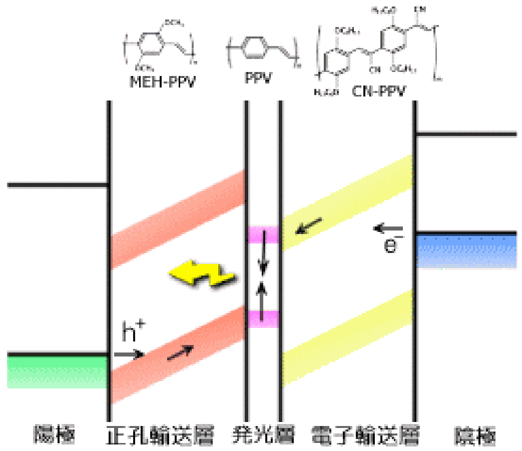
Which is better??
-small molecules or polymers??-

At present, researches on small molecules are much more popular than ones on polymers.
Small molecules are popular in Japan, on the other hand,so are polymers in Europe.
The manufacture of polymer is much better than that of small molecules.
(low cost, excellent printing technique)
So it's reasonable that research on polymer will be advanced.

Small molecules•••high efficiency, long lifetime, sppedy research
Polymer•••low efficiency, still not succeeded in blue-light, hard research(many function with one material)

3. Organo Lanthanide Metal Complex

Mechanism of luminescence



Recombination of hole and electron at emission layer makes molecules excited.Then emission of light from excited state occurs.

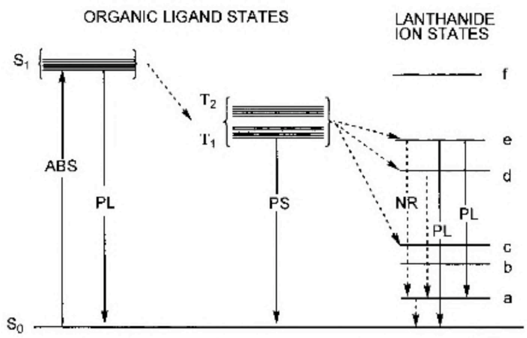
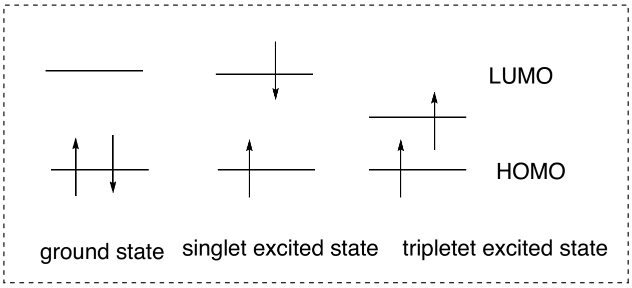


Figure 5. Energy transfer in lanthanide complexes: ABS = absorption; PS = phosphorescence; PL = photoluminescence; NR = nonradiative decay; a, b, c, d, e, and f = lanthanide ion energy levels.



PL(photoluminescence)••• emission from singlet excited state,fast(10 nsec.)
PS(phosphotescence)••• emission from triplet excited state,
slow(>msec.).degradation as heat,hardly to be observe.

Internal quantum efficiency was limited to 25%.
photoluminescence : phosphorescence = 1: 3

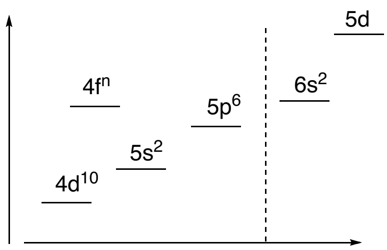
It was hard to obtain pure and sharp emission from organic materials;generally spectra show broad peaks.
Also fine tuning without affecting the EL material's physical properties was hard to realize.
Some metal complexes(ex. Ir) show highly efficient phosphorescence up to100%.

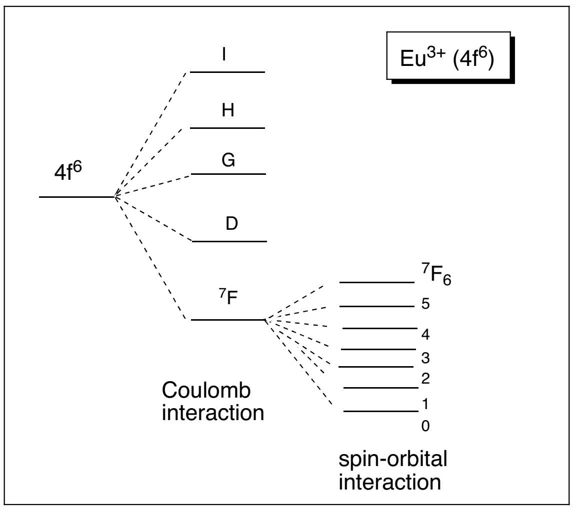
⇩

Lanthanides

It's Lanthanides that make it true!!
They exhibit extremely sharp emission bands due to their 4f electrons.
No limitation of the internal quantum efficiency up to 100%.

Ln = Xe($5s^2 5p^6$)$4f^n 6s^2$





4f electrons; 4f orbitals are effectively shielded from the influence of the external forces by the overlying $5s^2$ and $5P^6$ orbitals.
Emission bands as well as absorption bands(f-f transitions) are extremely sharp.

Each ion's complex

Eu^{3+},Tb^{3+} ・・・ mainly researched ions, because of their emission peaks in visible light range.

Tb the strongest emission at 545 nm (green color)
$^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ion

Eu the strongest emission at 615 nm (red color)
$^5D_4 \rightarrow {}^7F_5$ transition of Eu^{3+} ion

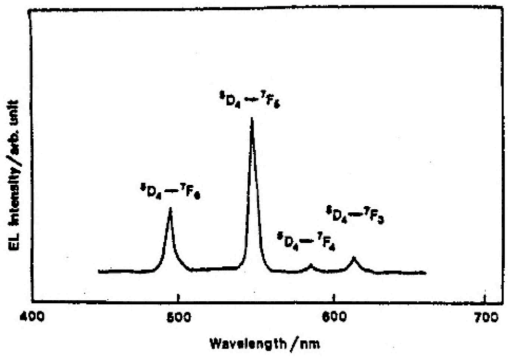
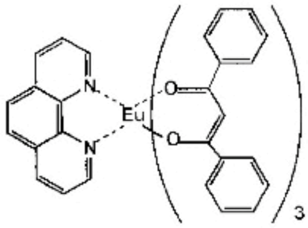


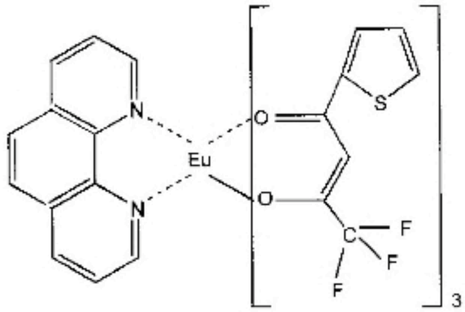
Figure 7. Electroluminescence spectrum of a Tb(acac)₃ cell.

Eu^{3+}

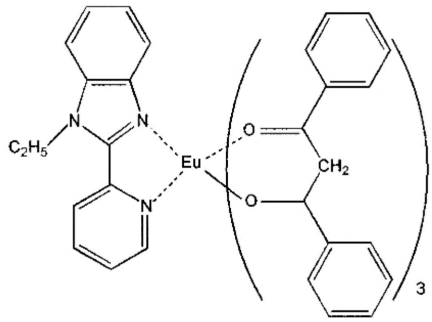
1991 Kido	$Eu(TTA)_3$	0.3 cd/m^2 at 18 V, not volatile
1994 Kido	$Eu(DBM)_3$(Phen)	460 cd/m^2, 614 nm,at 16 V, PBD as host
1994 Takada	$Eu(TTA)_3$(Phen)	microcavity,angular dependence
1994 Sano	$Eu(TTA)_3$(Phen)	137 cd/m^2
2001 Huang	$Eu(DBM)_3$EPBM	180 cd/m^2 at 18 V



$Eu(DBM)_3$(Phen)



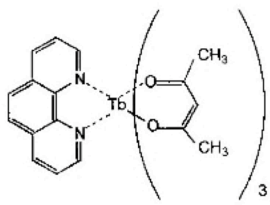
$Eu(TTA)_3$phen



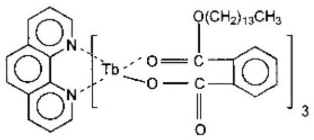
$Eu(DBM)_3$EPBM

Tb^{3+}

1990 Kido	$Tb(acac)_3$	7 cd/m^2
1999 H.J. Zhang	$Tb(MTP)_3$Phen	thermally stable,152 cd/m^2 at 24 V
2001 Jabbour	oxadiazole functionalized ligand, 100 cd/m^2 at 15 V	

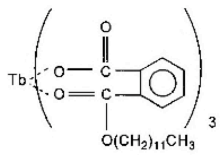


$Tb(acea)_3$Phen



$Tb(MTP)_3$Phen

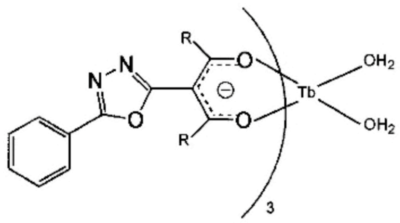
(A)



$Tb(MDP)_3$

(B)

Figure 15. (A) Chemical structure of Tb−tris(tetradecylphethalate)phenanthroline complex $Tb(MTP)_3$(Phen). (B) Chemical structure of alkyl chain-substituted phthalate−Tb complex $Tb(MDP)_3$.



R=CH_3

2001 Jabbour

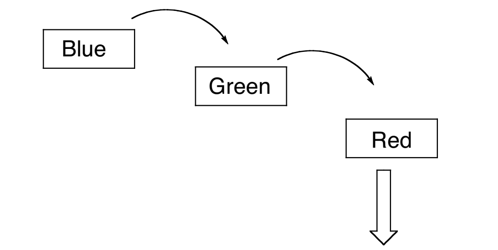
oxadiazole ligand plays an important role in high efficiency;
good electron-transporting and hole-blocking materials

two water molecules are coordinated and H-O vibration tends to quench the fluorescence intensity
If replaced with another ligand, EL efficiency will increase.

Secret of white color -exciting work of Prof. Kido-

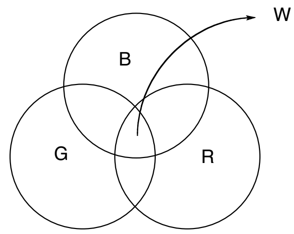
1990 Tb(acac)3 green light(545 nm)
1991 Eu(TTA)3 red light(615 nm)
1995 TPD blue light(410-420 nm)
•••polymer, emitting layer as well as hole-transporting material

At that time it's usually said that R+G+B ≠ W because•••

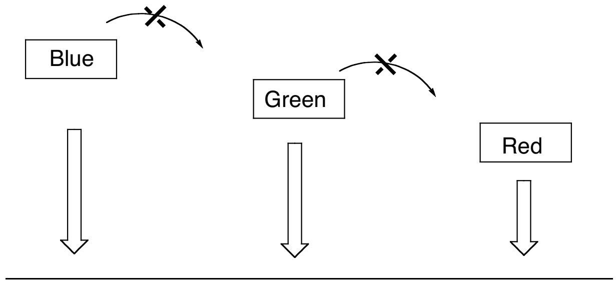


Energy transfer will occur to the lowest energy level.
Only red light is observed by just mixing with three colors.

*R and G and B are called "Light's three promary colors ".
Mixing them makes white-light.



One day a student obtained red-blue-white light while preparing red light by accident.
He was disappointed, but Prof. Kido took cue to realize white-light!!



Energy transfer is in inverse proportion to (distance)^6

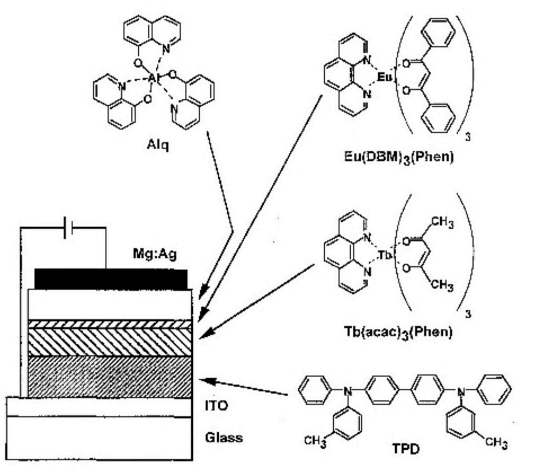


Fig. 1. Configuration of the EL cell and chemical structures of materials used.

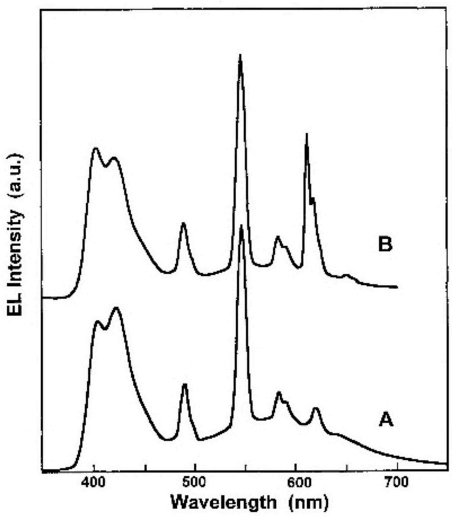


Fig. 3. EL spectra of (A) ITO/TPD(400 Å)/Tb(acac)$_3$(Phen)-(600 Å)/Mg : Ag, and (B) ITO/TPD(400 Å)/Tb(acac)$_3$-(Phen)(300 Å)/Eu(DBM)$_3$(Phen)(60 Å)/Alq(300 Å)/Mg : Ag. Spectra are offset for clarity.

A;blue-green-white light
a broad band ranging from 500-700 nm was observed.
B;white-light
three sharp strong peaks at around 410-420, 545, 615 nm, corresponding to the emission from TPD,Tb(acac)$_3$(Phen),and Eu(DBM)$_3$(Phen), respectively, are clearly seen.

Nd^{3+},Er^{3+}

intra-4f transition at near-infraed emission peak
useful for fiber optical telecommunication devices
Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (1530 nm)
Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1350 nm)

Nd^{3+} 1999 Yanagida, $Nd(DBM)_3$
Hasegawa sharp emission peak,degraded during the measurment
1999 Klink Nd-lissamine compex
triphenylene(excited at 350 nm), high intersystem crossing yield
2001 Slooff Nd-lissamine compex,
890 nm emitter, blended with polymer

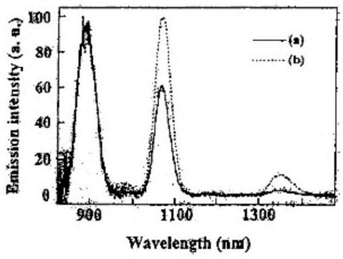


Figure 23. Emission spectra in the near-infrared region; (a) EL spectrum of ITO/TPD/Nd(DBM)$_3$bath/Alq$_3$/Mg:Ag device at the applied voltage of 19 V, (b) PL spectrum of deposited film of Nd(DBM)$_3$bath. Thickness of deposited film for PL was 2000 Å and excited by 390 nm light. (Reprinted with pern
American Institute o

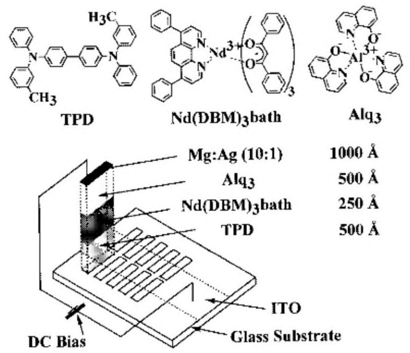


FIG. 1. Materials and configuration of the EL device.

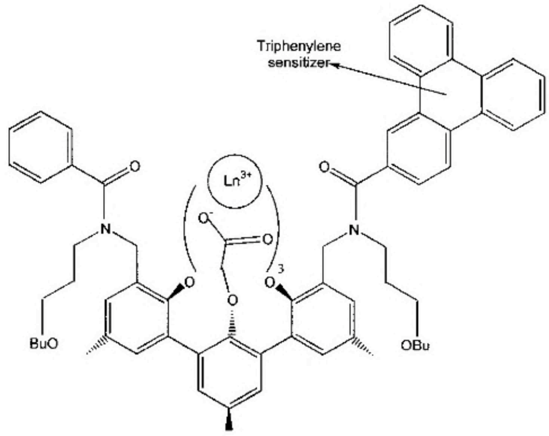


Figure 24. Chemical structure of Nd^{3+} lissamine complex, triphenylene-functionalized derivative. (Reprinted with permission from ref 45. Copyright 2002 American Institute of Physics).

Er^{3+} 1999 Gillin and Curry ErQ complex
rt(300 K), if excitation density was high, it got burning.
2000 Sun $Er(acac)_3(Phen)$
blend with PVK polymer, excited by 600-350 nm

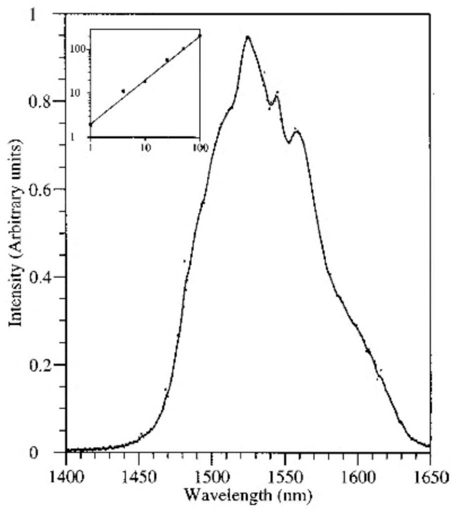
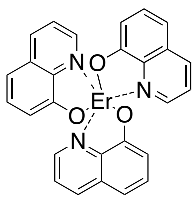
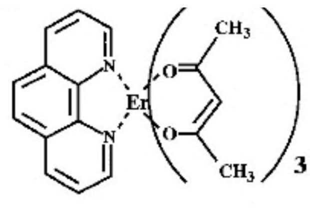


FIG. 2. The 300 K erbium related photoluminescence excited using the 457 nm line from an argon ion laser. The inset shows the integrated intensity of the erbium photoluminescence as a function of excitation power (1–100 mW).





Er(acac)$_3$(phen)

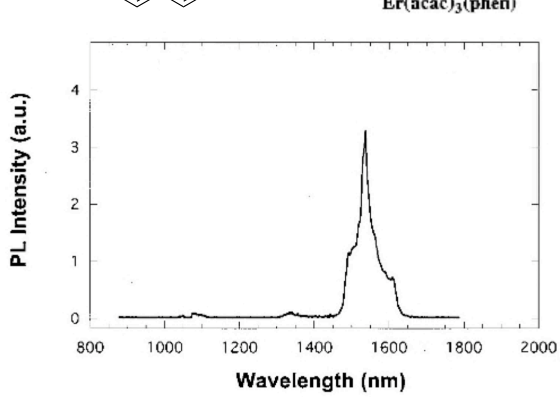
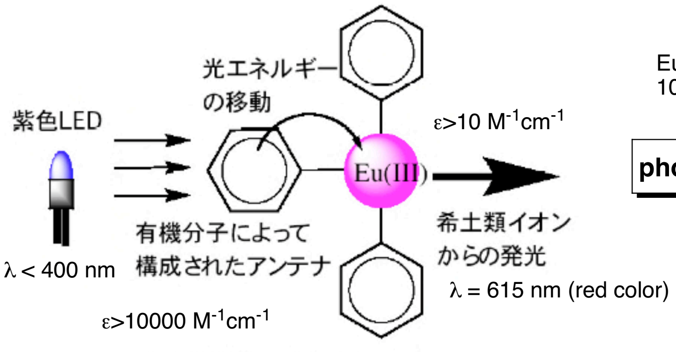


FIG. 3. Photoluminescence spectrum of Er(acac)$_3$(phen) at room temperature (excited by a 350 nm line).

Development of Lanthanide complex as secret ink –Work of Prof. Hasegawa–

Eu ion has been known as a useful red-light emitter.
Because of •••

Role of ligand
OEL:multi-layer, stability and volitability rather than efficiency
Ink: single-layer, high absorption , energy transfer



希土類錯体の発光メカニズム

Eu ion is excited by ligand excitation
100-1000 times bigger than Eu ion itself.

photosensitization energy transfer

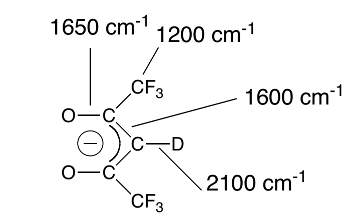
• Vibrating deactivation
Emission intensity of Ln is weak.
Because energy transfer via vibration is considered as the dominant quenching process.

:Energy gap of the radiative transition in Nd^{3+} ion(5400 cm^{-1}) = C-H and O-H bond vibration(5900 cm^{-1} and 6900 cm^{-1})
,solvent molecules with C-H and O-H bond lead to effective quenching of the Nd^{3+} ion excited state.

⇩

replacement of C-H bond with C-F bond and C-D bond.
••• C-F bond (1200 cm^{-1}) and C-D(2100 cm^{-1}), O-D bond (2500 cm^{-1})
deuterated solvent and deuterated HFA as ligand

1996 proposal of low vibration ligand
(without aromatic rings)
2000 (hfa) ligand good durability



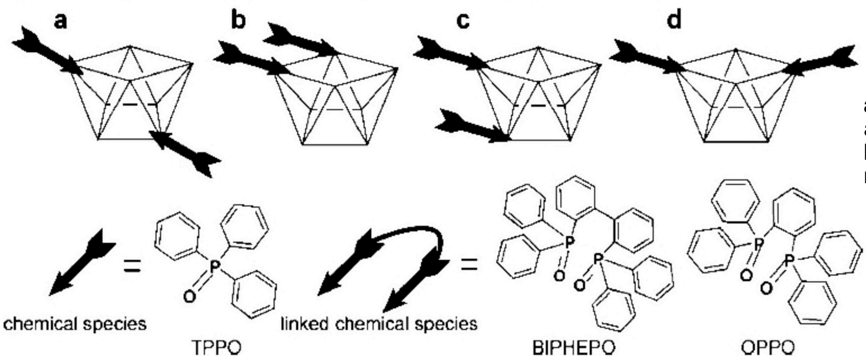
HFA(hexafluoroacetylacetone)

• Synergism
Ln ions are square-antiprism,coordination number = 8
two water molecules were coordinated, which made high vibration
Other organophosphine ligand are developed(TPPO).(P=O 1100 cm^{-1})

• Dissymmetric
Reducing the symmetry enhances its photophysical properties; toleration of forbidden transition.

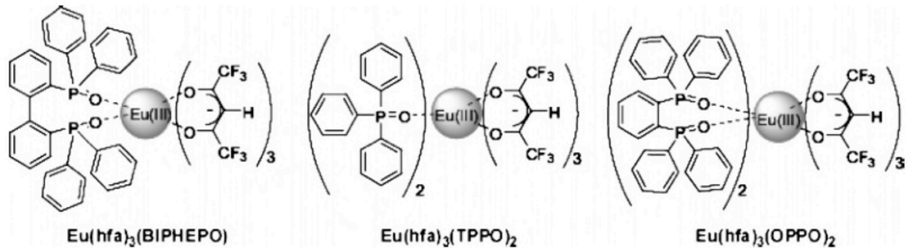
SAP = square-antiprism

CHART 1: Schematic Diagrams of Supposable SAP Structures and Chemical Species



a and **d** contain the symmetry axis, mirror plane.
b and **c** have no symmetry axis, mirror plane, inversion center

CHART 2: Chemical Structures of Eu(III) Complexes



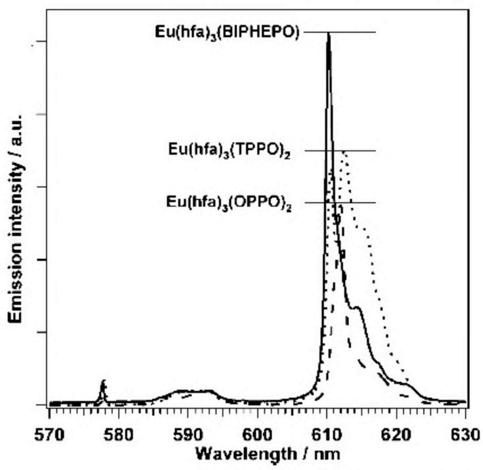
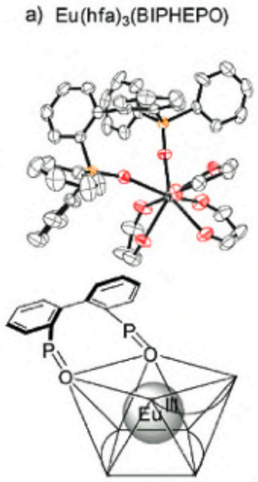


Figure 2. Emission spectra of Eu(hfa)$_3$(BIPHEPO) (solid line), Eu(hfa)$_3$(TPPO)$_2$ (dotted line), and Eu(hfa)$_3$(OPPO)$_2$ (dashed line) in acetone-d_6 excited at 465 nm.

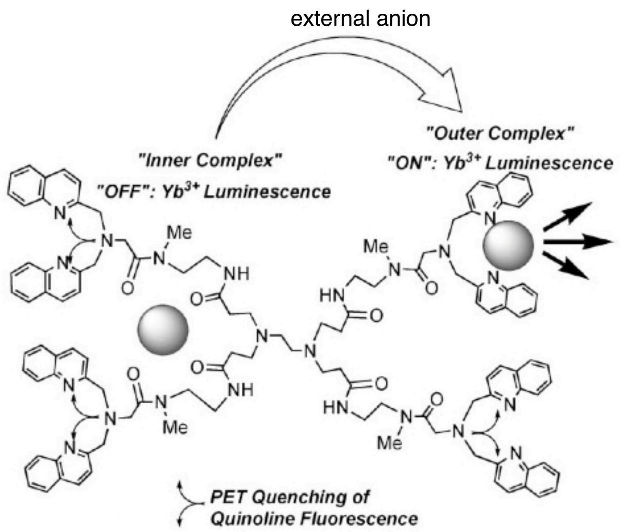
Eu compleax with BIPHEPO(structure **b**) showed the best lasing propety.



⟹ This work have succeeded in commercial application!!

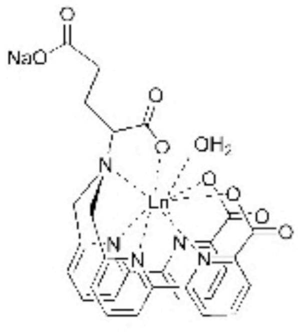
Development Lanthanide Complex in Biology

"on–off" switchable near-infrared luminescence
(2007 Tsukube)



Scheme 1 On–off switchable dendrimer container for luminescent Yb^{3+} cations. (Possible mechanism).

Highly luminescent lanthanide tags suitable for protein labeling and time–resolved luminescence imaging
(2004 Ziessel)



$[LnL(H_2O)]Na$

4. Futures

OEL will become popular without doubt!!

Necessary for practical application
• development of durability,cost(SONY 11 inch 200,000 yen),
energy-saving(crucial for 21 century),
• mass productivity with high-quality(up to mg-scale purity)
not only materials but also manufacturing methods
• matters around techiniques are important; patent,strategy(company,nation) etc.

Academic point of view
• Photophysics of Ln is still under development.
As application is developed, photophysics of Ln will be developed, also opposite is the case.
• Organic chemistry can make material endlessly,
New materials will be developed in the future, so keep eyes on it.
• No materials, No progress.

SONY XEL-1 "MIRAIKAN"

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