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Title	Luminescent lanthanide coordination polymers with transformative energy transfer processes for physical and chemical sensing applications
Author(s)	Hasegawa, Yasuchika; Kitagawa, Yuichi
Citation	Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 51, 100485 https://doi.org/10.1016/j.jphotochemrev.2022.100485
Issue Date	2022-06
Doc URL	https://hdl.handle.net/2115/91032
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Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	210903-JPPC-text-rev.pdf

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Luminescent Lanthanide Coordination Polymers with Transformative Energy Transfer Processes for Physical and Chemical Sensing Applications

Yasuchika Hasegawa, Yuichi Kitagawa

Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Kita-21, Nishi-10, Sapporo, Hokkaido 001-0021, Japan

Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Sapporo, Hokkaido, 060-8628, Japan

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Abstract

The photophysical process of lanthanide(III) ion is based on the 4f-4f transition, which is the Laporte forbidden with narrow emission band and long emission lifetime. The 4f-4f emission process is affected by introducing aromatic organic ligands. In this review, recent progress of one-, two-, and three-dimensional polymer-typed lanthanide complexes, luminescent lanthanide coordination polymers, are focused for physical and chemical sensing applications. Their changeable luminescence depended on the physical and chemical environments come from the energy transfer between lanthanide(III) ions and aromatic organic ligands. The characteristic physical (temperature, pressure, pH and mechanical force) and chemical (adsorption of metal ions and molecules) sensitive luminescence of lanthanide coordination polymers are useful for future sensing applications.

1. Introduction

One-, two-, and three-dimensional coordination polymers composed of metal ions and organic ligands have been recently investigated. In 1960, Kubo reported the first Cu coordination polymer linked with α, ω-dicarboxylic acids for studying on magnetic moments [1]. Yaghi described Zn-MOFs (MOFs: metal-organic frameworks) with porous cavities for molecular adsorption properties in 2000 [2]. At the present stage, many reviews about coordination polymers and MOF have been reported [3-12]. The typical structures of coordination polymers and MOFs are illustrated in Fig. 1. The organic joint ligands in coordination polymers and MOFs promote formation of one-, two-, and three-

dimensional backbone structures. The support ligands are generally categorized to be 1) small anionic type (Cl^-, β-diketonate etc.) and 2) small neutral type (H_2O, pyridine etc.). The characteristic structures are also depended on the coordination geometry and molecular structure on metal-coordination sites. Their coordination network structures provide specific magnetic, luminescence, adsorption, sensing, and catalytic properties, which are different from those of mono-nuclear metal complexes.

At the present stage, various types of coordination polymers and MOFs have been reported. Their paper-trends researched using information retrieval system "Web of Science" are shown in Fig. 2 (research date: March 24, 2021). The scientific paper number including keywords "coordination polymer" and "MOF" is rapidly increased from 2000 (Fig. 2a). Recent scientific-paper trends of coordination polymers with physical and chemical properties are summarized in Fig. 2b. The trend research with keywords "coordination polymer" and "magnetic*" (magnetics, magnetic properties, magnetic moments etc.)" gives large number of scientific papers in web of science (1920-2020: 12,153 papers), however, the number of papers is decreased from 2014. On the other hand, the trend research with keyword "coordination polymer" and "sens*" (sensor, sensing, sensitive, sensitized, sensitizer etc.)" shows rapid increase of scientific papers from 2012 (1960-2020: total 53,172 papers). This static trend data suggests that sensing-studies and sensing-applications using coordination polymers are recently focused on the field of science. The percentages of coordination polymer papers classified by element are described in Fig. 2c. The large number of Cu (9,996 papers: 18.8%), Co (9,592 papers: 18.0%) and Zn (7,948 papers: 14.9%) coordination polymers have been reported (gray bars). The paper number of "Eu" coordination polymers is smaller than those of other coordination polymers (2,210 papers: 4.2%). When the additional keyword "sens*" is

added in the research statics with keywords “coordination polymer” and “Eu”, the paper percentage on Eu coordination polymer is drastically increased (13.3%, red bar in Fig. 2c). The element “Eu” is well-known as red-luminescent lanthanide(III) ion (emission wavelength λ = 615 nm). The photophysical process of lanthanide(III) ion is based on the 4f-4f transition, which is the Laporte forbidden with narrow emission bands (FWHM < 10 nm) and long emission lifetimes (τ_{obs} > 1 μs) [13, 14]. The green-luminescent Tb(III) (λ = 545 nm), deep-red luminescent Sm(III) (λ = 650 nm), near-infrared luminescent Yb(III) (λ = 970 nm) and Nd(III) (λ = 1064 nm) ions are also used as an effective lanthanide luminophore.

We here focus on recent progress of luminescent lanthanide coordination polymer with sensing properties. In this review, scientific chemical manuscripts from 2016 to 2021 are selected as recent studies on lanthanide coordination polymers. Their physical sensing (temperature, pressure, pH, and mechanical stress) and chemical sensing (metal ion and molecule adsorption) properties are based on the changeable energy transfer under physical and chemical (adsorptions of metal ion and molecule) conditions in luminescent lanthanide coordination polymers [13-17]. Their conceptual design for changeable and transformative structures in solid have been recently reported as a softcrystal [18]. The characteristic sensing properties in luminescent lanthanide coordination polymers are based on the transformative energy transfer processes depended on the physical and chemical environments, which can regard as “lanthanide softcrystals”.

In case of lanthanide-based sensors, one-, two-, and three-dimensional coordination polymers given in Fig 1a-c are mostly rely on energy transfer events along with their coordination frame works. Conversely, guest molecule uptake plays an important role in MOFs/lanthanide-based sensors. According to the chemical (metal ions and molecules)-

sensing properties, various types of mono-nuclear lanthanide complex have been reported in liquid media [19-21]. Lanthanide coordination polymers and MOFs shows analytical advantages and priorities for ratiometric luminescence (comparison of emission band intensities) from several lanthanide ions such as Eu(III)/Tb(III), Tb(III)/Dy(III), Nd(III)/Yb(III) mixed-structures, resulting in precise chemical-sensing analysis [13].

In this review, transformative luminescent lanthanide coordination polymers with sensing properties are introduced.

2. Photophysical background for sensing applications

Lanthanides are defined as lanthanum (La) and 14 other elements (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) [5]. A general lanthanide is represented by the symbol "Ln". Alternating joint-sequences of lanthanide complexes with aromatic organic ligands provides lanthanide coordination polymers. Their structural conformations are categorized to be, 1) lanthanide(III) complexes with aromatic joint and support ligands (Fig. 1a and b) and 2) lanthanide(III) ions with aromatic joint ligands (Fig. 1c). The structures and energy levels of aromatic joint and support ligands are key points for effective physical- and chemical-sensing properties in luminescent lanthanide coordination polymers.

The organic joint or support ligands with aromatic π orbitals promote the photosensitized energy transfer from excited triplet state of the ligand (T_1) to 4f level of lanthanide ions (4f). The photo-irradiation of aromatic ligand with large absorption coefficient (π-π* transition: $\varepsilon > 10{,}000\ cm^{-1}M^{-1}$) promotes effective photosensitized luminescence of 4f-4f transitions ($\varepsilon < 10\ cm^{-1}M^{-1}$) in lanthanide(III) center. The photosensitized energy transfer

efficiency is depended on the energy matching between T_1 and accepting lanthanide excited states.

On the other hand, the energy back transfer from the lanthanide ion to the ligands is enhanced when the energy gap is less than 1850 cm^{-1}[22, 23]. The small energy gap promotes temperature-dependent luminescence. In 2004, we described the temperature-sensing ability of a green luminescent Tb(III) complex arising from a back energy transfer (BEnT) from the excited state of Tb(III) ($^5D_4$) to the excited triplet state of the ligands (T1) [24]. The energy gap between the emitting level of the Tb(III) ion and the exited triplet state of the haxafluoroacetylacetonate (hfa) ligand in $Tb(hfa)_3$ is estimated to be 1700 cm^{-1} [25]. The T_1 state is affected by molecule, steric and electronic structures of the aromatic ligands. The changeable T_1 level and lifetime under physical and chemical environments leads to effective physical- and chemical-sensing properties of luminescent lanthanide coordination polymers (Fig. 3a).

The luminescence of lanthanide coordination polymer is also influenced by the non-radiative process from emitting level of lanthanide ions.

For example, the temperature sensing mechanism is based on the thermal quenching process from excited Eu(III) to vibrational relaxation. Generally, harmonic energy matching of the vibrational overtone of typical C–H or O–H vibrational frequency in lanthanide complexes promotes effective vibrational relaxation. The Franck–Condon factor is related to vibrational quanta ν, which is the harmonic number matched with the energy gap of the lanthanide ion [26, 27]. The energy gap of Eu(III) ions ($^5D_0$–$^7F_6$: 12,297 cm^{-1}) is well-matched with the overtone of C–H vibrational frequencies ($5\nu \leq 13{,}000$ cm^{-1}) [13]. Their effective overtone matching frequencies promote a decrease of the emission quantum yield, resulting in temperature-dependent luminescence. The thermal quenching

process for achieving temperature-sensing properties is dependent on the energy gap between the emitting level and the highest energy accepting level in 4f-4f transition. The energy gap of a Tb(III) ion ($^5D_4$–$^7F_0$: 14,800 cm^{-1}) is larger than that of a Eu(III) ion. The larger energy gap promotes a larger matching overtone of the C–H or O–H vibrational frequency ($\nu = 6$) and a decrease of the Franck–Condon factor.

The changeable non-radiative pathway is given by additional quencher system such as metal ion, solvent, gas, and molecule (Fig. 3b). The MOF-typed lanthanide coordination polymers possess nano and micro-cavities for adsorption of metal ions or small molecules. The chemicals in their cavities lead to effective increase of non-radiative rate constant from emitting level of lanthanide(III) ion, resulting in decrease of emission quantum yield and lifetimes of lanthanide(III) coordination polymer.

The organic joint ligands in lanthanide(III) coordination polymers also promote control of the energy transfer efficiency between lanthanide(III) ions (Fig. 3c). We have reported that the energy transfer between Tb(III) and Eu(III) in Tb(III)/Eu(III) mixed coordination polymer is strongly affected by the energy level of the aromatic joint ligand [28, 29].

As mentioned above, direct excited energy transfer from Tb(III) to Eu(III) is negligible [30]. In the case of $[Tb/Eu(hfa)_3(dpbp)]_n$ (4,4'-bis(diphenylphosphoryl)biphenyl), Hatanaka has calculated the stepwise excitation energy transfer from Tb(III) to Eu(III) via the linker-centered T_1 state can occur with a reasonable reaction barrier, which is lower than the barrier (at 14.3 kcal mol^{-1}) for the quenching via an the ISC between the linker-centered T_1 state to the ground state (28.3 kcal mol^{-1}) [29].

The effective combination between aromatic ligand with changeable π orbital and lanthanide(III) ion with un-changeable 4f orbital offers characteristic luminescence with physical and chemical sensing properties.

3. Physical sensing properties

The physical phenomena such as temperature, pressure (presence of oxygen molecule), pH, and mechanical stress influence on the excited state in lanthanide coordination polymers, resulting in physical-sensitive luminescence. The key point for the physical-sensing application is control of the excited T_1 state of aromatic joint and support ligands in lanthanide coordination polymer. The energy level and stability of T_1 state are fine-tuned by characteristic molecular design of the lanthanide coordination polymers.

3.1. Temperature-sensing properties

Luminescent lanthanide(III) complexes with back energy transfer (BEnT) are the most useful component in the molecular design of a high-speed thermosensor. The temperature-sensing ability of a green luminescent Tb(III) complex is based on the back energy transfer (BEnT). The small energy gap between the $^5D_4$ (the excited state of Tb(III)) and T_1 states (<1850 cm^{-1}) leads to an effective BEnT in Tb(III) complexes [19, 20]. The β-diketonate ligand with trifluoromethyl groups, hexafluoroacetylacetonate (hfa), is one of the most promising candidates for the development of temperature-sensitive luminescent Tb(III) complexes (energy gap = 1700 cm^{-1}) [25]. The hfa ligand also forms hydrogen bond networks in solid Tb(III) coordination polymers which promotes thermal stability in the high-temperature range [31, 32]. On the basis of the BEnT process, the luminescent units composed of $Tb(hfa)_3$ parts are suitable for temperature-sensitive unit.

The temperature-sensing ability of $Tb(hfa)_3$ unit is affected by introducing phosphine oxide joint ligand in Tb(III) coordination polymer. We observed that Zn-linked Tb(III)

coordination polymer, $[Tb(hfa)_3ZnCl_2(dppy)_2]_n$ (Fig.4a-1), showed a wider sensing range and larger ligand-excited emission quantum yields than the previously color-changeable luminophore structure $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ (Fig. 4a-2 and 5a) [33].

The long-range LMCT (ligand-to-metal charge transfer) coupling in Eu(III) coordination polymers linked with chrysene joint ligands, $[Eu(hfa)_3(bdcp)]_n$ (bdcp: 6,12-bis(diphenylphosphoryl)chrysene) was also reported for effective temperature-sensing luminescence properties (Fig. 4a-3) [34]. The emission quantum yield of $[Eu(hfa)_3(bdcp)]_n$ is increased by addition of Gd(III) ion for cutting the long-range LMCT coupling. The control of LMCT coupling in Eu(III) coordination polymer is key point for effective temperature sensor. Temperature-sensitive luminescent Dy(III)-MOF, Dy-cpia (cpia: 5-(4-carboxyphenoxy)isophthalic acid), using thermal equilibrium between $^4F_{9/2}$ and $^4I_{15/2}$ states have been reported (Fig. 4b) [35]. The Dy-MOF is the first temperature-sensitive yellow Dy(III) luminophore, although various types of green Tb(III) and red Eu(III) coordination compounds have been used for temperature sensitive luminophore.

The combination of lanthanide(III) ions in coordination polymer bodies also promotes effective temperature-sensing properties. We reported the first thermometric observation of Tb(III)/Eu(III) coordination polymers as a Chameleon luminophore in 2013 [28, 29]. The $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ exhibits brilliant green, yellow, orange, and red photoluminescence under UV irradiation (365 nm) at 250, 300, 350, and 400 K, respectively (Fig. 4a-2 and 5b). $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ has a higher temperature sensitivity (0.83% K^{-1}) than $[Tb(hfa)_3(dpbp)]_n$ (0.64% K^{-1}). This result indicates that energy is transferred to both the excited triplet state of the hfa ligands (BEnT) and to the Eu(III) ion from the emitting level of the Tb(III) ion (Fig. 3: model c). The energy transfer efficiency from the Tb(III) ion to Eu(III) ion ($\eta_{Tb\text{-}Eu}$) is also shown in Fig. 5c.

Recently, effective addition of Gd(III) ion in Tb(III)/Eu(III) mixed MOFs (Fig. 4c) have been reported for high sensitivity (6.11% K^{-1}) [36]. Ratiometric Tb(III)/Eu(III) mixed MOFs for cryogenic luminescent thermometer (35.5K: 3.26% K^{-1}) have been also presented (Fig. 4d) [37]. Chorazy and Ohkoshi described Tb(III)/Dy(III)-Co layered cyanide-bridged frameworks for ratiometric thermometer [38]. The cyanide-bridged Tb(III)/Dy(III)-Co frameworks promote red luminescent $[Co(CN)_6]^{3-}$, green luminescent Tb(III) and yellow luminescent Dy(III). Their emission properties, including the energy transfer from organic ligands and cyanide complexes towards lanthanide ions, are strongly modulated by the change of temperature in the broad 120–300 K range.

Near-Infrared thermometer was demonstrated using the energy transfer between Nd(III) and Yb(III) ions in Nd(III)/Yb(III) mixed MOFs (Fig. 4e) [39]. Near-IR luminophore is expected to be useful for temperature sensing application in biomedical system. The combination of organic dye and Tb(III)/Eu(III) double-layer MOFs also effective for wide-range thermometer (Fig. 4f) [40].

Flexible and amorphous lanthanide coordination polymers provide useful thermometer for practical applications. Chen reported flexible Tb(III)/Eu(III) poly-MOF membranes using co-polymerization of BABDC and butylmethacrylate for ratiometric temperature-sensing materials (Fig. 4g) [41]. The flexible structure provides advanced and precise temperature sensing analysis on the rough surface of solid materials. We showed the first transparent amorphous Eu(III) coordination polymer with triphenylamine $[Eu(hfa)_3(tppa)_n]_m$, for thermometric energy transfer between excited Eu(III) ion ($^5D_0$) and LLCT (ligand-to-ligand charge transfer) band (Fig. 4a-4) [42]. The glass transition and thermo-sensing ability were achieved by introduction of triphenylamine unit of tridentate tppa joint ligand.

The temperature-sensing properties of lanthanide coordination polymers are summarized in Table 1. Temperature-sensitive paints (TSPs) using luminescent lanthanide coordination polymers are promising molecules to accurately measure the physical parameters on the material surfaces.

3.2. Pressure-sensing (oxygen-sensing) properties

In the fields of aerodynamic science and engineering, pressure sensitive paints (PSPs) are promising molecules to accurately measure the physical parameters of a material surfaces [43-45]. The luminescent PSPs provide multi-dimensional pressure data for the mapping of surfaces, whereas optoelectronic sensors analyze only single points on a surface [46]. There are high expectations that the luminescent PSPs for surface measurements will overcome this intrinsic limitation of optoelectronic devices. Recent high-speed aircraft and automobiles have been designed using luminescent PSP techniques in wind-tunnel experiments [47]. The pressure-sensing ability of luminescent PSPs is based on the excited quenching process of phosphorescent materials in an oxygenated environment. The electronic configuration of oxygen molecules (O_2) is normally a spin-active triplet state, which promotes effective luminescence quenching of the excited triplet state (T_1) of phosphorescent materials [48].

In 2000, Amao described the first oxygen sensor based on this process, using a luminescent Eu(III) complex with thenoyltrifluoroacetylacetonate ligands for pressure-sensing application on the material surface [49]. Effective oxygen-sensing property on the material surface is achieved by presence of porous structure in the crystals for adsorption of oxygen molecules. According to the recent Eu(III) coordination polymer for oxygen sensitive luminescence, Zhang presented red-luminescent Eu(III)/Tb(III)

porous coordination polymers linked with dibenzoic acid with pyridyl-imidazol (pidpa: 2-(2-pyridyl)-1H-imidazol-4,5-di(4-benzoic acid, Fig. 6a) [50]. The combination between luminescent organic dye and Eu(III) complex leads to producing wide-range emission color change under pressure. We reported the red-luminescent Eu(III) porous coordination polymers with six-coordinated triphenylene units (hcpt: 2,3,6,7,10,11-hexakis(4-carboxyphenyl)triphenylene, Fig. 6b and 7a) [51]. The oxygen-sensing red-luminescence is based on the equilibrium state between T_1 of hcpt and $^5D_0$ of Eu(III). The excited equilibrium state between T_1 and $^5D_0$ provides changeable emission lifetime for oxygen-concentration measurements, which is independent on the emission intensity and photo-detection sensitivity (Fig. 7b and c). The emission lifetime-based pressure-sensitive systems have shown significant potential for unsteady flow diagnostics of aircrafts, high-speed vehicles and turbomachinery. Environment-visualized analysis using time-resolved phosphorescence (> μs) can also remove some short-lifetime luminescent noises on the luminescent surfaces such as organic light-emitting devices (OLEDs) and biomedical applications. Yan described oxygen-sensitive Eu(III) MOF nano-fibers covered with polydimethylsiloxane [52]. The nano-rod shaped Eu-MOF connected with the polypropylene surface has been covered with water-resisted polydimethylsiloxane for the first time. The near-infrared luminescence of Yb(III) porous coordination polymer with tiapy (1,3,6,8-tetrakis(3,5-isophthalic acid)pyrene) for oxygen-sensing has been also reported (Fig. 6c) [53]. The tiapy units composed of pyrene moieties bearing four benzene rings and eight carboxyl groups form a new type of Yb(III) coordination polymer showing high thermal stability (decomposition temperature 400 °C) in conjunction with significant NIR luminescence (4f-4f emission quantum yield under argon of 6.6 %). Solid-state lanthanide luminophores prepared from thermally stable

pyrene dyes are expected to open-up new frontiers in the fields of physical chemistry, coordination chemistry, and materials science.

3.3. pH-sensing properties

Rocha reported luminescent Eu(III) coordination polymer with pH-sensing properties in 2009 (Fig. 8a) [54]. Various types of pH-sensitive lanthanide coordination polymers have been reported. Recently, Cui and Qian described color-changeable Tb(III)/Eu(III) mixed MOFs with dpda ligands (dpda: 4-(3,5-dicarboxyphenyl)pyridine-2,6-dicarboxylic acid) for pH-sensing properties (Fig. 8b) [55, 56]. The pH-sensing ability is depended on the energy transfer between Tb(III) and Eu(III) ions. The key point for pH-sensing ability is un-coordinated carboxyl units in dpda joint ligands. The energy level of dpda linker with un-coordinated carboxyl units is changeable depended on pH. We have already reported that the energy transfer between Tb(III) and Eu(III) ions is directly linked with energy level of linker ligands [28, 29]. The changeable energy level promotes effective pH-sensing property in Tb(III)/Eu(III) mixed MOFs.

Generally, lanthanide coordination polymer is composed of Lewis acid (lanthanide(III) ion) and Lewis base (ligand). The Lewis acid-base product is easily decomposed under low-pH condition, The protection of the coordination site might be key point for produce a stable pH-sensitive lanthanide coordination polymer. On other hand, various types of luminescent lanthanide complexes with pH sensing ability have been reported [19-21]. The environment-visualized analysis using time-resolved phosphorescence using lanthanide complexes for biomedical application have also been described [57]. Water-solved lanthanide coordination polymer may be a promising candidate for novel pH-

sensing materials. Fan and Liu recently reported water-solved lanthanide coordination polymers (Fig. 8c) [58, 59].

3.4. Mechano-sensing properties

Luminescence upon mechanical grinding solid materials is called triboluminescence. In the 17th century, it was first noted by Francis Bacon that: “It is well known that all sugar, whether candied or plain, if it be hard, will sparkle when broken or scraped in the dark.” Triboluminescence materials, unlike well-known photoluminescence materials, have the advantage of emission without a light source. The fracture-induced luminescence properties of triboluminescence materials make them attractive for applications as structural damage sensors, pressure sensors, and advanced security marking techniques [60-63].

Lanthanide (III) coordination polymers based on β-diketonate and aromatic bridging ligands have been well-known as a strong mechano-sensitive luminescence [64, 65]. Triboluminescence and photoluminescence occur from distinct stimuli, namely grinding and photoirradiation; however, their spectra usually exhibit similar profiles. Relationships between TL and PL are still being discussed from a scientific point of view. Recently, we found a large spectral difference between these two physical phenomena using lanthanide(III) coordination polymers $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu=1) (dpf: 2,5-bis(diphenylphosphoryl)furan) with efficient TL and PL properties (Fig. 8d-1 and Fig. 9) [66]. The emission color upon grinding (yellow triboluminescence) is clearly different from that upon UV irradiation (reddish orange photoluminescence) in Tb(III)/Eu(III)-mixed coordination polymers $[Tb,Eu(hfa)_3(dpf)]_n$. The contribution of Tb(III)-centered emission is larger than that of Eu(III)-centered emission in triboluminescence, in contrast

to photoluminescence. According to the results, we consider the triboluminescence of Ln(III) coordination compounds to be responsible for both. the ligand-excitation and direct Ln(III)-excitation, unlike the selective excitation with a specific wavelength (for example, λ_{ex}=380 nm) in photoluminescence. Their triboluminescence lifetimes measured using laser and aerodynamic shock waves is smaller than photoluminescence lifetimes due to the shock compression that accompanied oxygen quenching [67].

Characteristic triboluminescence phenomena of Eu(III) coordination polymer with triangular spacer ligands ($[Eu(hfa)_9(tppb)_2]_n$ (tppb: tris(4-diphenylphosphoryl)benzene) (Fig. 8d-2) and large hydrogen-bonding network linkers ($[Eu(hfa)_3(tol)]_n$, tol: 2,5-bis(di-*p*-tolylphosphoryl)furan) have been also reported (Fig. 8d-3) [68, 69]. We also present the first tribo-excited chemical reaction of stacked Eu(III) coordination polymer (($[Eu(hfa)_3(bpa)]_n$, bpa: 2,6-bis(diphenylphsphory)anthracene) under mechanical grinding (Fig. 8d-4) [70]. The product obtained by the tribo-excited chemical reaction was different from that obtained by the photo-chemical reaction. The tribo-luminescence and tribo-reaction are useful for mechano-sensing application.

4. Chemical sensing properties

Luminescent lanthanide coordination polymers with porous cavities and three-dimensional frameworks, luminescent lanthanide MOFs, are useful for adsorption of chemical species. Their adsorption phenomena in these cavities promote increase of non-radiative process and changeable luminescence from lanthanide ions (Fig. 3 model b). In this section, recent progress of chemical-sensitive luminescent lanthanide coordination polymers is introduced.

4.1. Metal ion sensing Properties

Metal ion sensing application using luminescent molecular system is directly linked to frontier field of analytical chemistry and environmental science. Since metal ion sensing application is performed in water solution, water-stable structures of luminescent lanthanide coordination polymers are the required. Metal ion plays a role in effective quencher for luminescence of lanthanide coordination polymer. Among them, Fe and Cu ions with d-d transition bands in visible region perform as a characteristic quencher for luminescence of visible luminescent Eu(III) coordination polymers. At the present stage, various types of luminescent lanthanide MOFs with metal ion sensing properties in water media have been reported.

The recent effective metal ion sensing studies have been achieved using asymmetric linker ligands in luminescent lanthanide MOFs. Li, Hou, and Bai reported red-luminescent Eu(III) MOFs with asymmetric linker ligands for Fe(III) sensing property [71-73]. Liu described green-luminescent Tb(III) MOFs for efficient Fe(III), Ce(III), and acetone sensing abilities [74]. Luminescent Tb(III) and Eu(III) MOFs with asymmetric linker ligands or Fe(III) and Cr(VI) sensing application have been presented [75]. Cu(II)-sensitive Eu(III) asymmetric MOFs have been also reported [76, 77].

Combination of mixed lanthanide MOFs is effective for colorless metal ion sensing. Li presented white luminescent Tb(III)/Eu(III)/Sm(III) mixed asymmetric coordination polymer for Mn(II) and Ag(I) sensing applications [78]. The Tb(III)/Eu(III)/Sm(III) coordination polymer shows metal-depended luminescence color transformation of (Mn(II): white to blue, Ag(I): white to red). Wang described Eu(III)/Zn(II) mixed asymmetric MOF for Mg(II) sensing property [79]. The characteristic polyrotaxane structure by two interpenetrating ribbon chains produce effective Mn(II) sensing in solod

state. Luminescent lanthanide coordination polymers with symmetric joint ligands have been also reported for metal ion sensing [80-84].

Su and Guan demonstrated on the ratiometric metal ion mapping and sensing array using luminescent Tb(III)/Eu(III) coordination polymer. (Fig. 10) [85, 86]. The ratiometric metal mapping figure is composed of Tb(III) transition ratio (emission intensities at 547 (the electric dipole transition: ED) and 491 (the magnetic dipole transition: MD) nm: x-axis) and Eu(III) transition ratio (emission intensities at 616 (ED) and 592 MD) nm: Y-axis). This ratiometric mapping figure is based on the coordination geometrical change of Tb(III) and Eu(III) cites. They also reported that the film fabricated using bimetallic $Eu_{0.47}Tb_{0.53}$-MOF and polyvinyl alcohol could serve as an easy and convenient luminescent platform for distinguishing different metal ions.

4.2 Molecular sensing Properties

Large number of luminescent lanthanide coordination polymers for molecule sensing have been also extensively studied since 2017. Bernini and Yan reported solvent-sensitive Eu(III) and Tb(III) coordination polymers [87, 88]. Vapor (small gas molecule) -sensitive Tb(III) coordination polymers have been also reported [89, 90]. According to the ionic molecule sensing in water media, luminescent lanthanide MOFs for picric acid, uric acid, ascorbic acid, amino acid and phosphate anion have been presented [91-101]. According to the molecular sensing system, two types of coordination polymer and MOF structures have been categorized: 1) adsorption in the cavities of MOF structure such as a crownether-typed molecule, and 2) presence of free-carboxylic acid for attachment or reaction with bio-molecules. The conceptual designs of the lanthanide coordination

polymer are similar to those of the supramolecular chemistry, zeolite-typed catalysis and bio-proved molecular science.

Luminescent lanthanide coordination polymers with porous network structures are also effective for antibiotic applications [102-105]. The antibiotics are commonly used in medicine, agriculture, and livestock farming. They have been regarded as an important species of organic contaminants in water. The biomolecule-detection using lanthanide coordination polymers in serum have been also reported [106-107]. Recently, luminescent lanthanide coordination polymer for detection of high explosive material "FOX-7" have been performed [108]. The FOX-7 (1,1-Diamino-2,2-dinitroethene) has been reckoned to be a high-energy-density material. The detection of such high energy content materials are expected to become an emergent field for addressing the crucial issue of national security and safety. Feng reported that lanthanide coordination polymers $[Tb(\mu_m\text{-ddpp})_nH_2O]$ (ddpp: 2,5-di(2′,4′-dicarboxylpheny)pyridine, m = 3, 6; n = 1, 2, 4) showed inorganic molecule (CrO_4^{2-}) sensing properties in $NH_3 \cdot H_2O$–NH_4Cl buffered aqueous solution (pH = 7.4). [109]. The luminescence is effectively quenched by introduction of CrO_4^{2-} anion. These lanthanide coordination polymers are can be used as a potential luminescent probe for a toxic anion. The ratiometric small molecule mapping figure using luminescent Tb(III)/Eu(III) coordination polymer is also reported [85, 86].

The molecule-sensitive lanthanide coordination polymers are useful in application in the field of analytical chemistry, medical science, biotechnology and environmental science. The physical-sensing property in lanthanide coordination polymer is depended on the energy transfer processes in excited state, which is related to the emitting levels lanthanide(III) ions and excited triplet levels of ligands. In a configurational coordinate diagram, these levels appear as parallel parabolas (a small offset case) because the 4f

electrons are well shielded from their surroundings [14]. The energy level of 4f orbital in lanthanide(III) coordination compounds is not influenced by the ligand field and coordination structure. The 4f-4f transitions in lanthanide coordination compounds are Laporte forbidden. From the photophysical view-points, physical-sensing properties of lanthanide coordination polymers is different form the resonant energy transfer (FRET etc.) and electron transfer process (PET etc.) in organic dyes and transition metal complex with π–π*, MLCT, and LMCT transitions (Laporte allowed).

On the other hand, molecular-sensing properties might be depended on the energy level of quenchers (energy transfer process) and structure in the crystals (adsorption phenomena, cavity size etc.). Typical nano-structural images of reported lanthanide coordination polymers are shown in Fig. 11. According to the cavity size (nano- and micro pores), the adsorption capacity and kinetics data of lanthanide coordination polymers is estimated using nitrogen adsorption isotherm and Langmuir model analysis, respectively. [53, 107].

All chemical structures for metal ion and molecular-sensing properties are listed in supporting information.

3 Conclusion remarks

In this review, we introduced luminescent lanthanide coordination polymers for physical and chemical sensing properties. Their characteristic 4f-4f luminescence with narrow emission bands and long emission lifetimes is useful in for physical and chemical sensing applications. On the other hand, lanthanide coordination materials with chiral organic ligands show effective circularly polarized luminescence (CPL), which is approximately a thousand times larger than those of chiral organic molecules [110-112]. We recently

found that their dissymmetry factors of CPL, g_{CPL} values, were larger than those of lanthanide complexes [113, 114]. The enhanced g_{CPL} value in Eu(III) coordination compound might be related to be the perturbation of electric dipole transition and the LMCT bands between Eu(III) and aromatic chiral ligands [115, 116]. The strong circularly polarized luminescence from lanthanide coordination compounds attracts considerable attention because of its applications in sophisticated photo-information technologies, such as security tags, lasers, data storage, and organic electroluminescent (EL) devices for three-dimensional displays [113-114]. The transformative lanthanide coordination polymers with CPL and sensing properties are expected to be new three-dimensional physical sensors and chiral-molecular sensing systems in future.

The luminescent lanthanide coordination polymers are generally insoluble powers in water and organic solvents, although they show characteristic luminescence properties depended on the physical and chemical environments. Generally, coordination site in lanthanide coordination polymer shows eight coordination structure with asymmetric square-antiprism or trigonal dodecahedron symmetry, which is much different from coordination structure in transition-metal coordination polymer. Their specific geometrical structure promotes three-dimensional networks with asymmetric coordination bonds, tight-packed molecular interactions. The three-dimensional structure with specific bonds and interaction normally offer insoluble characteristics in water and organic solvent. Recently, water-soluble lanthanide coordination polymers with cation sites have been reported [58, 59]. In order to fabricate the physical and chemical sensors on the material bodies, homogeneous lanthanide coordination polymers on polymer matrix should be developed for practical

use. We here introduce two strategies for development of homogeneous lanthanide coordination polymers in polymer inks and binders.

1) Glass formation

The amorphous structures of lanthanide coordination polymers provide homogeneous paints containing adhesive polymers for fixation on the material bodies. The amorphous lanthanide coordination polymers are also easy-blended in various types of polymer matrices. Recently, glass-transformative lanthanide coordination compounds under heat-treatment have been reported [117-120]. We reported glass-transformative lanthanide coordination materials with aromatic chiral ligands [121]. The glass-structural transformation of lanthanide coordination polymers should be a key point for novel application for advanced material chemistry.

2) Nano-size formation

Nano-sized luminescent materials are well-dispersed in liquid and polymer media. Luminescent lanthanide coordination nanoparticles have been recently reported [122-124]. The decomposition temperatures of lanthanide coordination nanoparticles are much higher than those of lanthanide complexes. The nanoparticles in organic polymer provide high-transparent optical materials. We also described polymer thin films including inorganic nano-materials for photonic applications [125-126]. Luminescent lanthanide coordination nanoparticles with physical and chemical sensing properties may be useful for industrial sensing applications.

The two strategies “formation of amorphous and/or nanoparticle structures” for improvement of solubility lead to development of polymer-hybrid materials such as plastics, inks, aerosols, gels for sensing devices.

Finally, transformative luminescent lanthanide coordination polymers for sensing application are expected to open-up a frontier field between photophysical chemistry and material science.

4 Acknowledgments

The authors greatly appreciate the financial supports by Grant-in-Aid for Scientific Research (JP20H04653, JP20H05197, JP20K21201, and JP20H02748). This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI) of MEXT, Japan.

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Figure captions

Fig. 1. Illustrated figures of a) one-, 2) two-, and 3) three-dimensional coordination polymers and metal-organic frameworks (MOFs).

Fig. 2. Scientific paper trends between 1920-2020. The researched static data using Web of Science: May 24, 2021. a) Published paper population including research keyword “coordination polymer” (blue bars: 53,172 papers) and “MOF (metal organic frameworks)” with “framework” (orange bars: 21,629 papers). Published paper number including research keyword “MOF” (with other meaning phrase such as “metal oxide fluoride”) is 24,913 papers, which is similar to that including “MOF” with “framework.” b) Published paper number including research keyword “coordination polymers” with additional key words “magnetic*” (blue line), “adsorp*” (gray line), “cataly*” (green line), “emission” (skyblue line), and “sens*” (red line). c) Published paper percentages including research keyword “coordination polymers” with additional key words “Cu”, “Co”, Zn”, “Cd”, “Ni”, “Mn”, “Ag”, “Fe”, and “Eu” (total 52,965 papers: 99.6%).

Published paper percentages including research keyword “coordination polymers” with “Al”, “Ru”, “Pd”, “Ca”, “Au”, “Ti”, “W”, “Pt”, “Mo” and “Tb” are less than 4.0 %.

Fig. 3. Transformative energy transfer pathways in lanthanide coordination polymers for physical and chemical sensing properties. a) changeable photosensitized energy transfer by tunable excite triplet state of organic ligands in lanthanide coordination polymers. b) Energy transfer quenching by adsorption of metal ions or molecules in material cavities. c) Changeable energy transfer between lanthanide ions in lanthanide coordination polymers.

Fig. 4. Chemical structures of temperature-sensitive one-dimension lanthanide coordination polymers.

Fig. 5. a) Temperature-dependent emission spectra of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ in the solid state in the temperature range of 200–450 K (λ_{ex}=380 nm). b) Color pictures of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ under UV (365 nm) irradiation, which show brilliant green, yellow, orange, and red emission. c) Temperature-dependence of the energy transfer efficiency. Reprinted with permission from Hasegawa. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

Fig. 6. Chemical structures of oxygen-sensitive three-dimension lanthanide coordination polymers.

Fig. 7. a) Emission decay profiles and b) histograms of the emission lifetime of Eu(III)-hcpt in solid state under vacuum, Ar, air, Ar-O_2 (1 : 1) and O_2 atmosphere. Excitation source: Nd: YAG (wavelength: 355 nm (3ω), plus width 10 ns). c) The schematic diagram of the back energy transfer (BEnT) from $^5D_0$ emitting level of Eu(III) to T_1 state of hcpt ligand in Eu(III)-hcpt. c) Schematic representation of Eu(III) coordination polymers with photosensitized energy transfer (EnT), back energy transfer (BEnT), and O_2 quenching

process (O_2-Q). Reprinted with permission from Hasegawa. Copyright 2020 Wiley-VCH Verlag GmbH & Co.

Fig. 8. Chemical structures of pH- and mechano-sensitive lanthanide coordination polymers.

Fig. 9. Normalized TL and PL spectra and images of a) $[Tb/Eu(hfa)_3(dpf)]_n$ (Tb/Eu=1) and b) $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu=10). c) A simplified diagram of the excitation processes of TL (orange line) and PL (blue line) in Tb(III)/Eu(III) mixed coordination polymers (Abs=absorption, ET=energy transfer, GS, ground state, ^{1}S=singlet excited state, ^{3}T=triplet excited state, ISC=intersystem crossing, NR=non-radiative relaxation). Reprinted with permission from Hasegawa. Copyright 2017 Wiley-VCH Verlag GmbH & Co.

Fig. 10. Decoded map for different metal ions based on the ratios of I_{547}/I_{491} and I_{616}/I_{592} in emission spectra of $Eu_{0.47}Tb_{0.53}$-CTP-COOH PVA film. Reference 65 (Springer nature: open access article).

Fig. 11. Structural pictures of lanthanide coordination polymers with molecular-sensing properties. a) Ref. 87: $[Y_{1-x}Ln1_{x1},Ln2_{x2})x(Salicylate)(Succinate)0.5(H_2O)]$ Copyright 2017 The Royal Society of Chemistry. b) Ref. 103: $Eu_{1-x}Tb_x$-MOF using a flexible ligand H_4L (L: 5,5′-(propane-1,3-diylbis(oxy))di-isophthalic acid). Copyright 2020 American Chemical Society. c) Ref.104: Zn-PDC/Tb^{3+} Coordination Polymer Nanostructure (PDC: pyridinedicarboxylic acid). Copyright 2018 American Chemical Society. d) Ref 106: Tb-GMP-Eu coordination polymer nanoparticles (GMP: guanine monophosphate). Copyright 2018 The Royal Society of Chemistry.

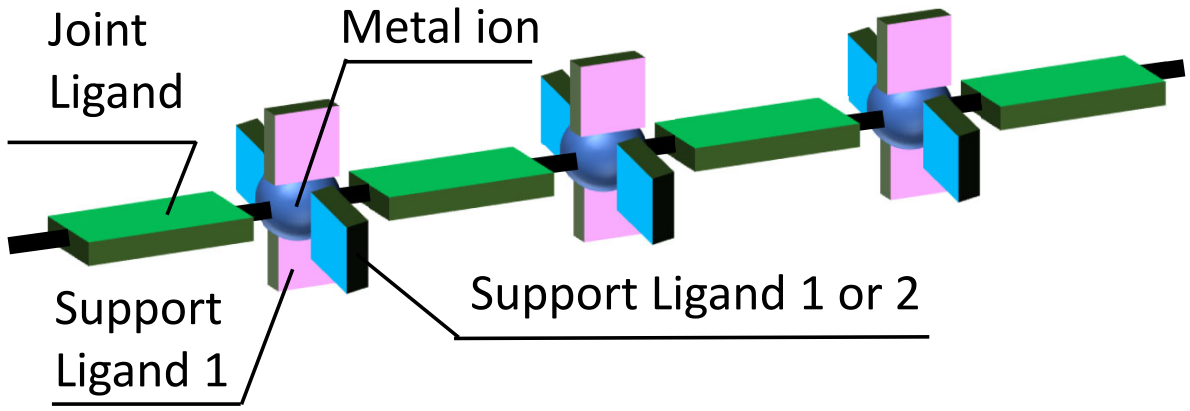
Table 1. Temperature-dependent emission parameters of lanthanide coordination polymers

Ln	Ligand	[a]Sr / $\%K^{-1}$	[h]Arrhenius parameters
Tb[28,33]	Hexafluoroacetylacetone 4,4'-Bis(diphenylphosphoryl)biphenyl	b	ΔE= 1900 cm^{-1} A= 3.68 × 10^7 s^{-1}
$Eu_{0.1}Tb_{0.99}$[28]	Hexafluoroacetylacetone 4,4'-Bis(diphenylphosphoryl)biphenyl	b	-
Tb[33]	Hexafluoroacetylacetone 1,4-Bis(diphenylphosphoryl)benzene	-	ΔE= 1700 cm^{-1} A= 4.06 × 10^7 s^{-1}
Tb[33]	Hexafluoroacetylacetone $ZnCl_2(dppy)_2$ (dppy: 4-(Diphenylphosphinyl)pyridine)	-	ΔE= 2500 cm^{-1} A= 7.92 × 10^7 s^{-1}
Eu[34]	Hexafluoroacetylacetone 6,12-Bis(diphenylphosphoryl)chrysene	[c]2.70 (475K)	ΔE= 4520 cm^{-1} A= 1.90 × 10^9 s^{-1}
$Eu_{0.5}Gd_{0.5}$[34]	Hexafluoroacetylacetone 6,12-Bis(diphenylphosphoryl)chrysene	[c]3.73 (450K)	ΔE= 5310 cm^{-1} A=1.02 × 10^{11} s^{-1}
Dy[35]	5-(4-Carboxyphenoxy)isophthalic acid	[d]0.42 (473K)	35
$Eu_{0.0066}/Tb_{0.9934}$[36]	2,6-Di(2',4'-dicarboxylphenyl)pyridine	[e]3.76 (450K)	36
$Eu_{0.013}/Tb_{0.06}$ $/Gd_{0.927}$[36]	2,6-Di(2',4'-dicarboxylphenyl)pyridine	[e]6.11 (430K)	36
$Eu_{0.1}Tb_{0.9}$[37]	1,3-Benzenedicarboxylic acid	[f]3.26 (35.5K)	37
$Tb_{0.5}Dy_{0.5}$[38]	4-Hydroxybyridine $[Co(CN)_6]^{3-}$	[f]2.23 (170K)	38
$Nd_{0.99}Yb_{0.01}$[39]	2,6-Naphtalenedicarboxylic acid	[g]0.25	39

		(300K)	
Eu_xTb_y[40] (x : y = 5 : 13)	Biphenyl-3,5-dicarboxylic acid 4,4'-Bis(imidazole-1-yl)diphenyl ether	-	40
$Eu_{0.0025}/Tb_{0.9975}$[41]	2,5-Bis(allyloxy)terephthalic acid	[e]3.61 (240 K)	41
Eu[42]	Hexafluoroacetylacetone Tridiphenylphosphoryl-4'4'4'-triphenylamine	-	ΔE= 5400 cm^{-1}

[a]Relative thermal sensitivity: $S_r = \frac{-\partial\Delta/\partial T}{\Delta}$, where Δ is the measured temperature-sensitive parameters, and T is the temperature. [b]Estimated temperature sensitivities for Tb(III) emission intensity are 0.64 $\%K^{-1}$ (Tb) and 0.83 $\%K^{-1}$ ($Eu_{0.1}Tb_{0.99}$). Temperature-sensitive parameter: [c]Emission lifetime, [d]emission intensity, [e]emission intensity ratio of Tb(III) to Eu(III), [f]Mott-Seitz model[37-38], and [g]emission intensity ratio of Yb(III) to Nd(III), [h]Arrhenius analysis is based on temperature-dependent back energy transfer process.[33,34,42]

a)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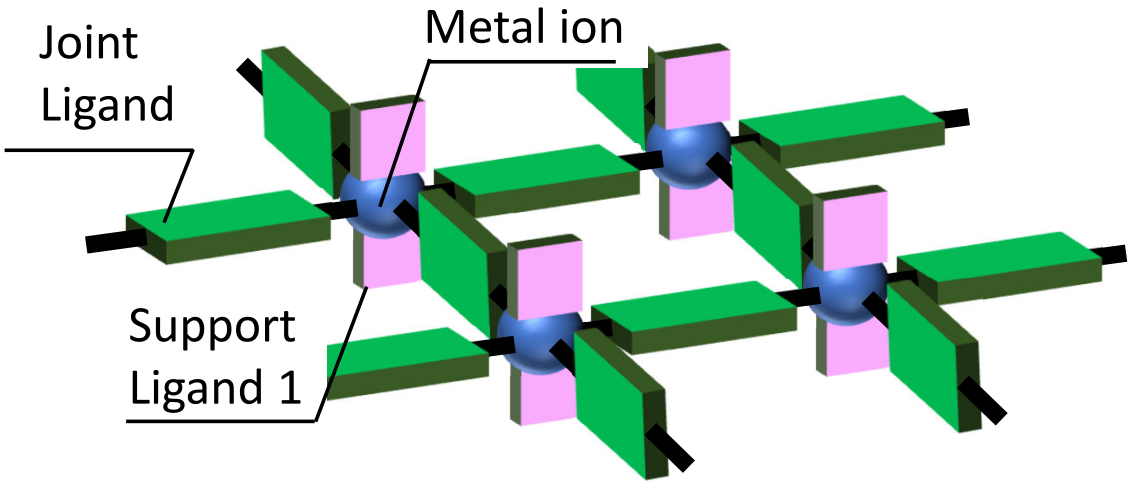
b)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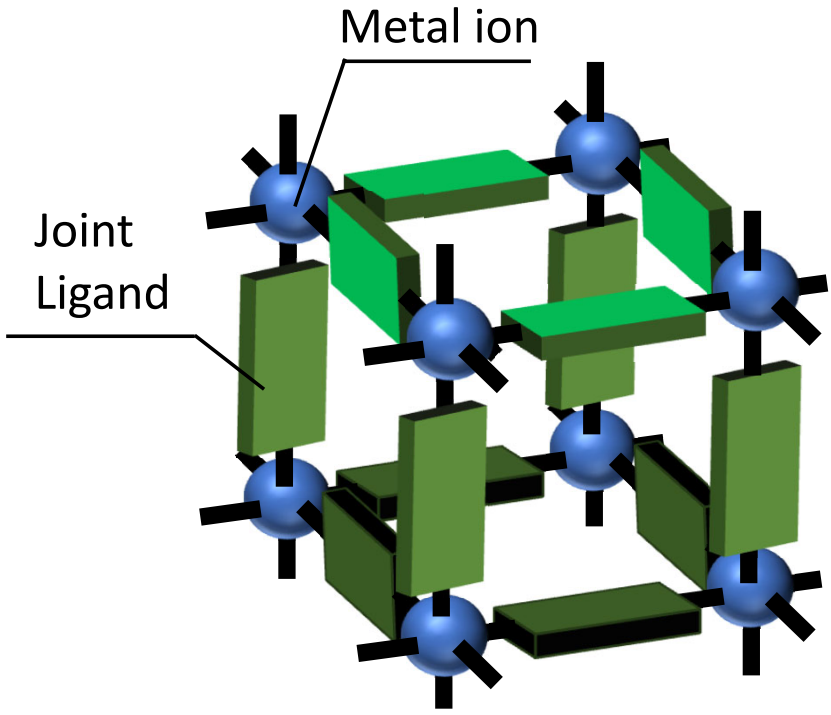
c)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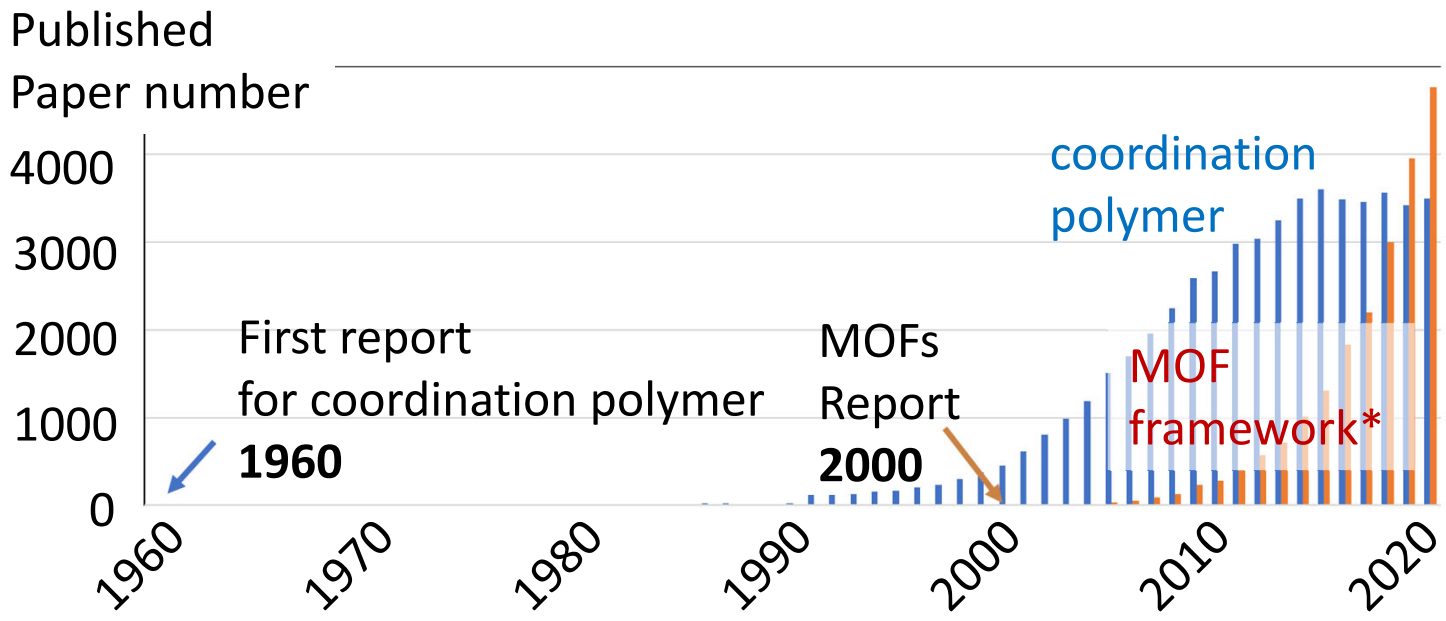
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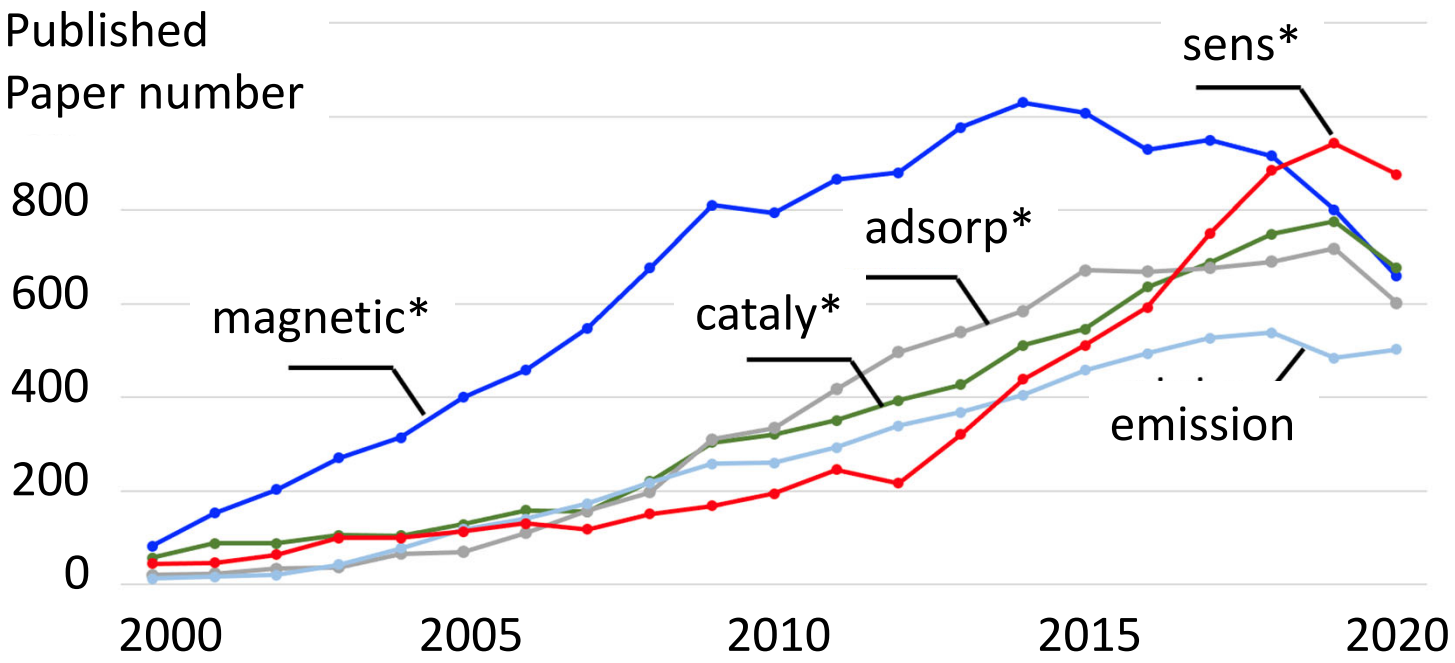
b)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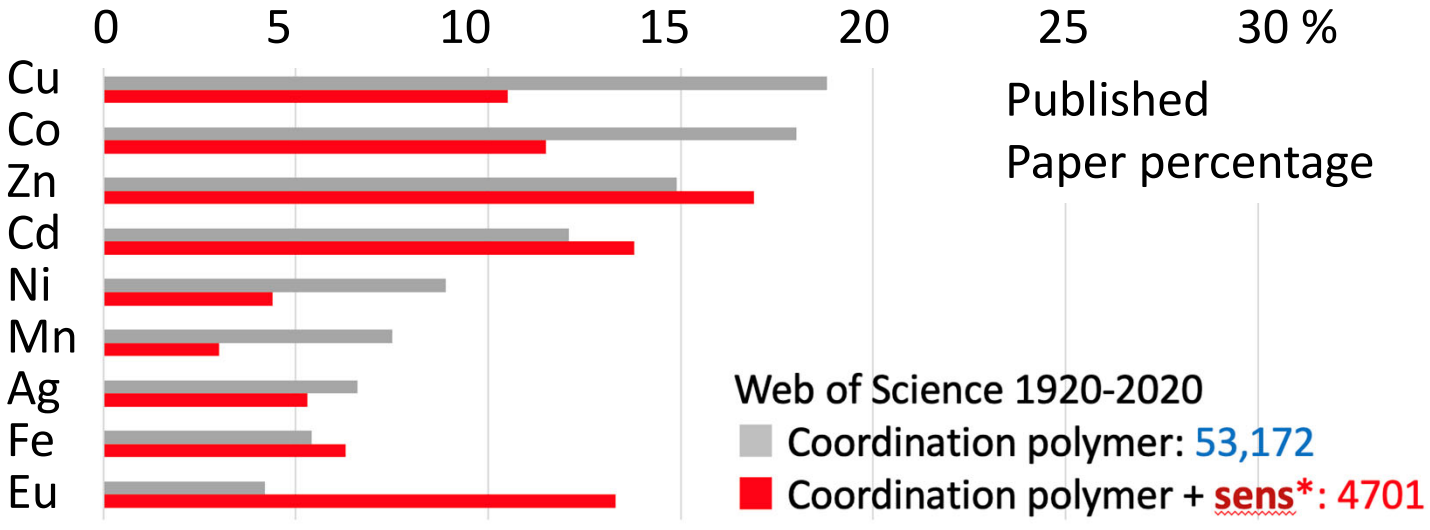
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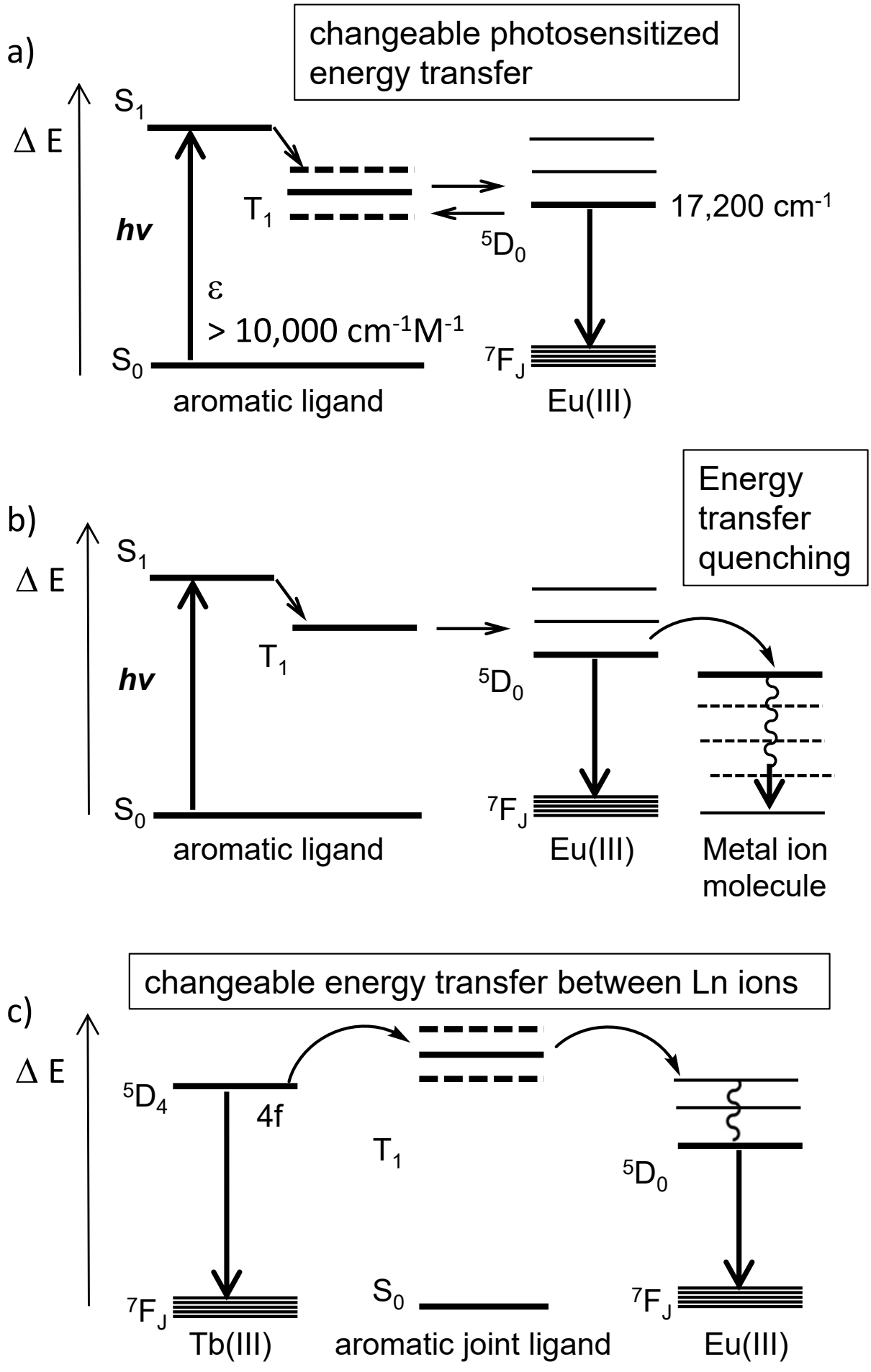
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S0
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17,200 cm-1
7FJ
aromatic ligand
Eu(III)
b)
Energy transfer quenching
ΔE
S1
T1
hv
S0
5D0
7FJ
aromatic ligand
Eu(III)
Metal ion molecule
c)
changeable energy transfer between Ln ions
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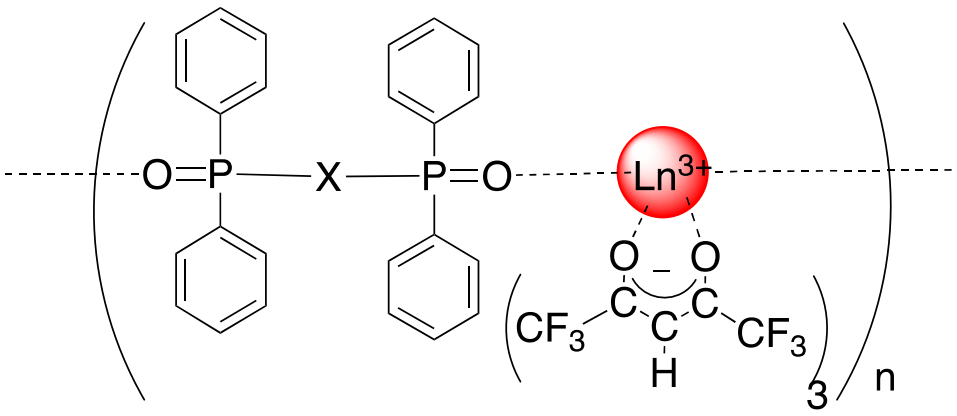
Eu(III)

a)



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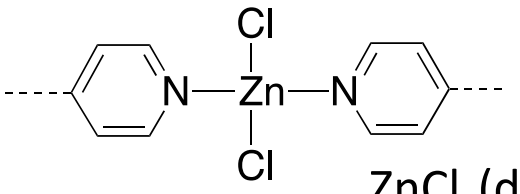

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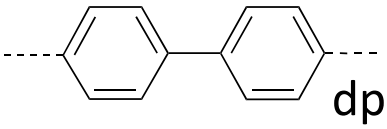

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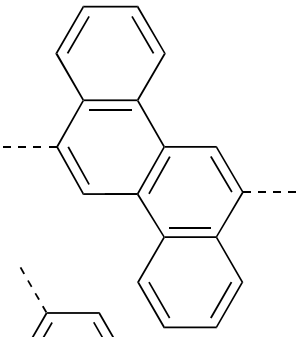

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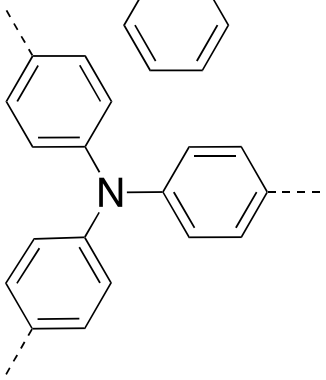

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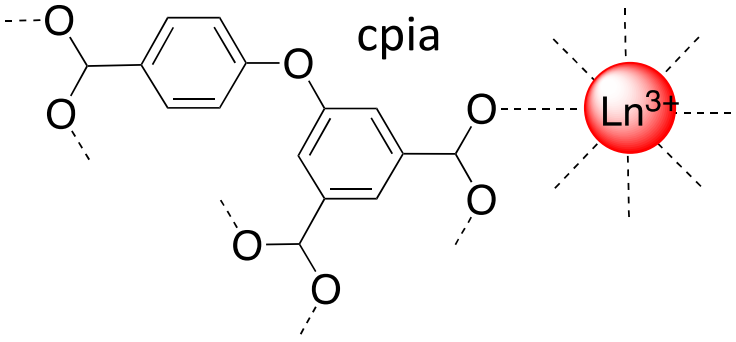

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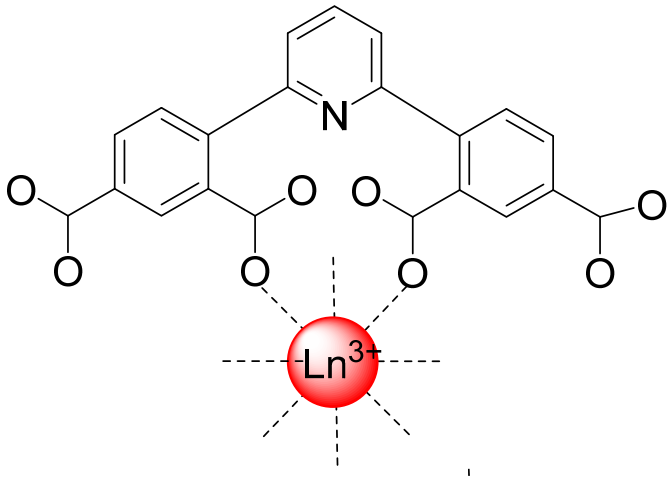

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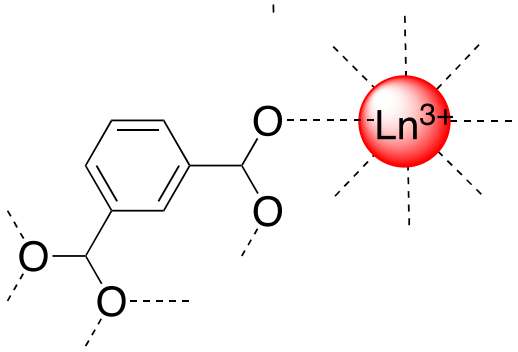

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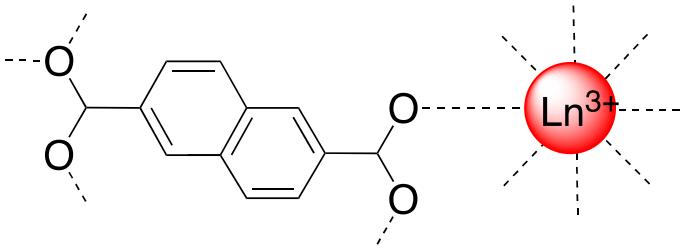

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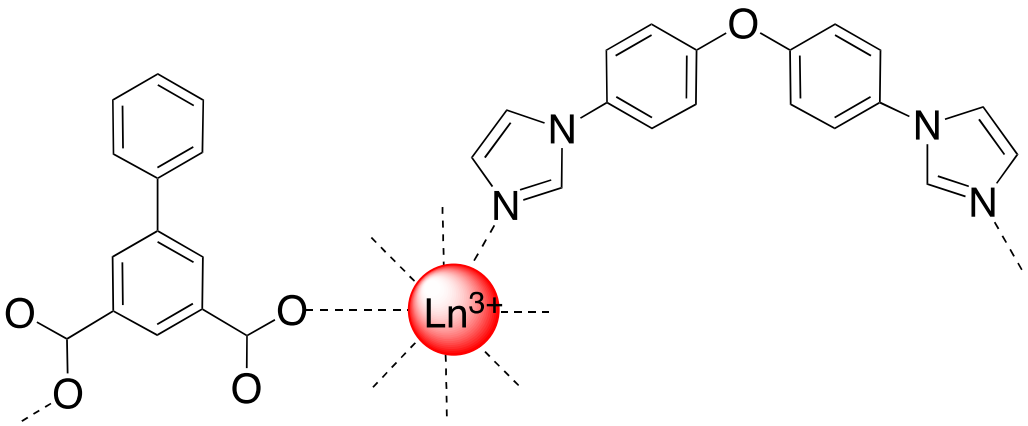
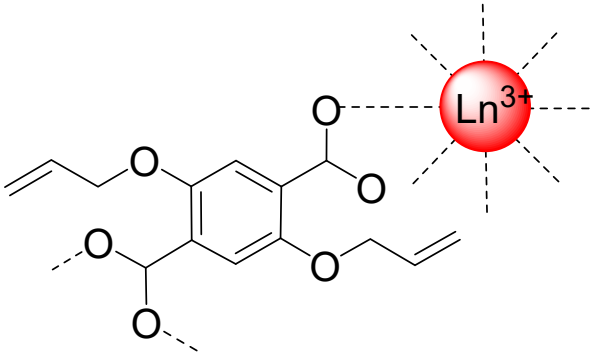
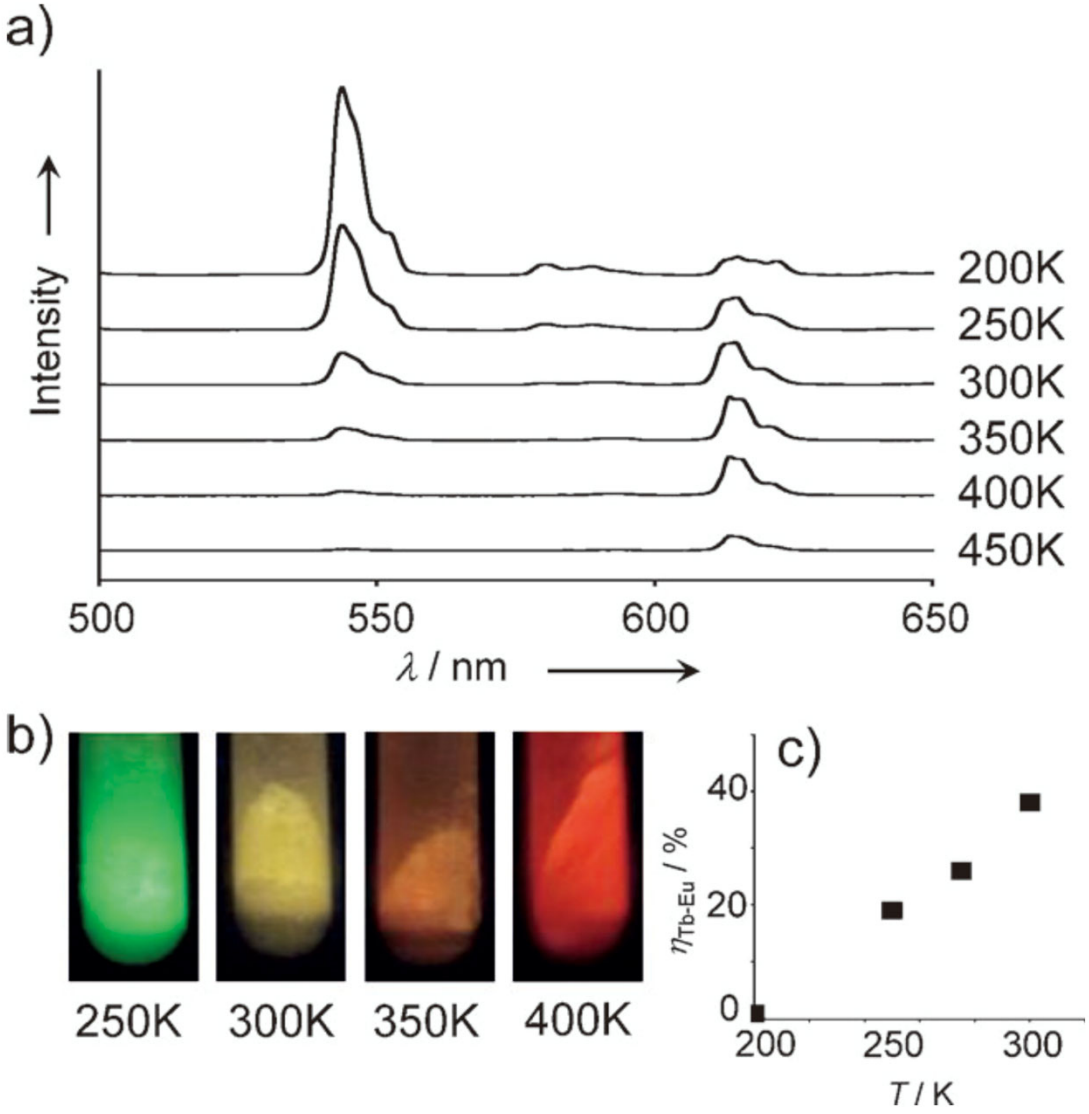
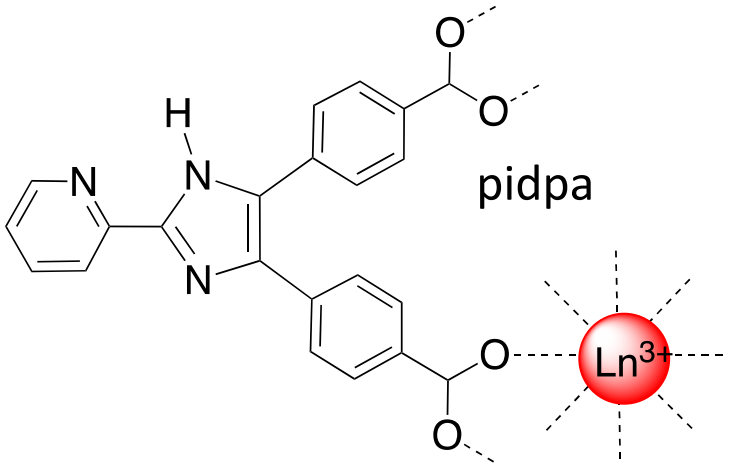


g)

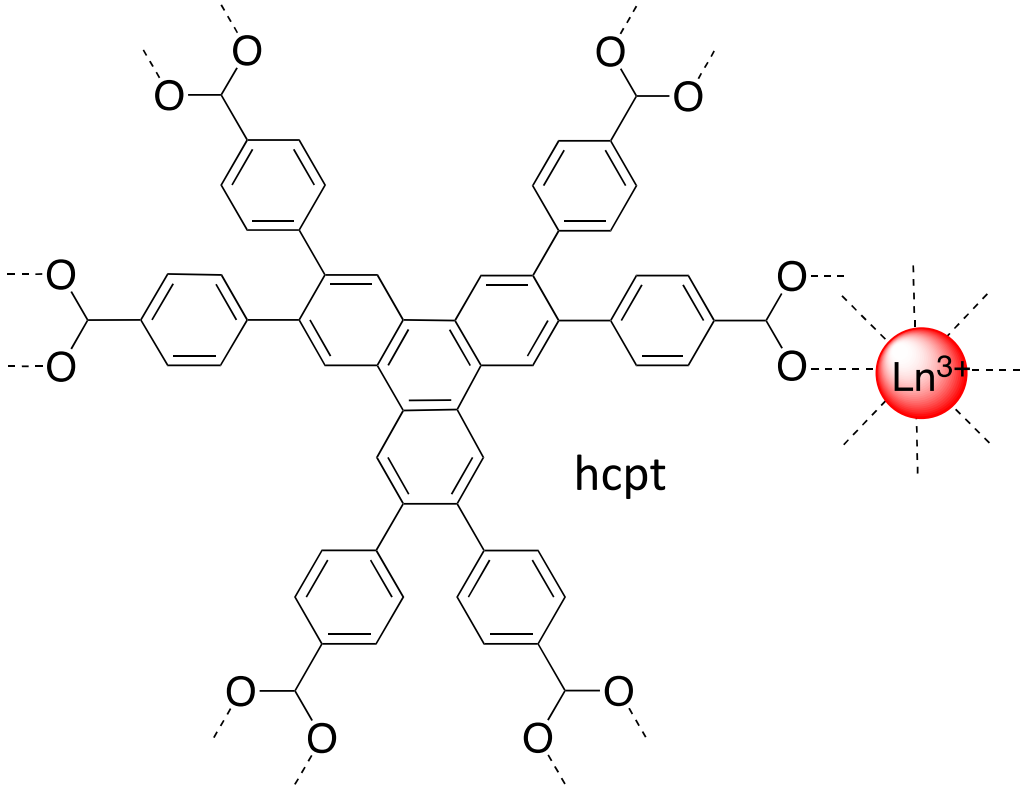



a)
Intensity
200K
250K
300K
350K
400K
450K
500
550
600
650
λ / nm
b)
250K
300K
350K
400K
c)
40
20
0
η Tb-Eu / %
200
250
300
T / K

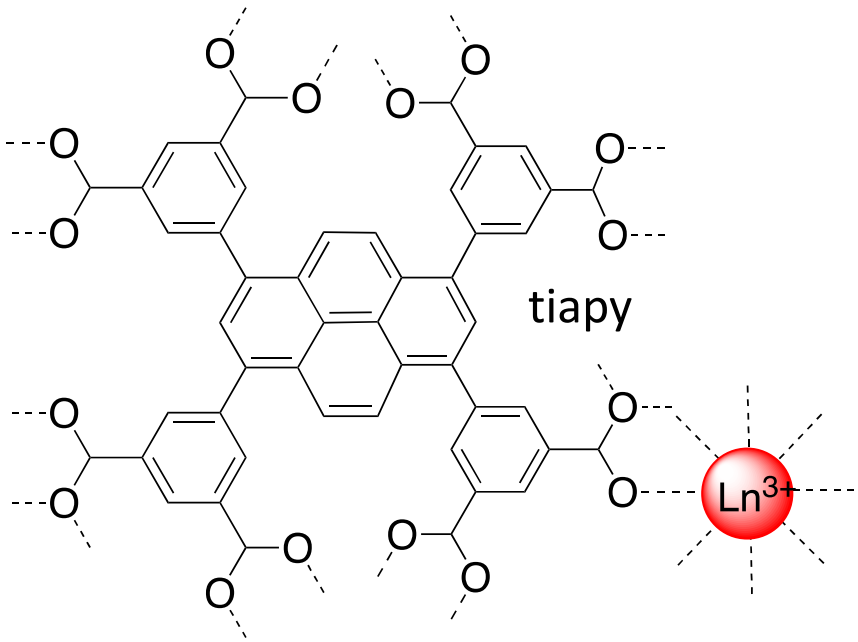
a)


H
N
N
N
O
O
O
O
O
Ln3+
pidpa

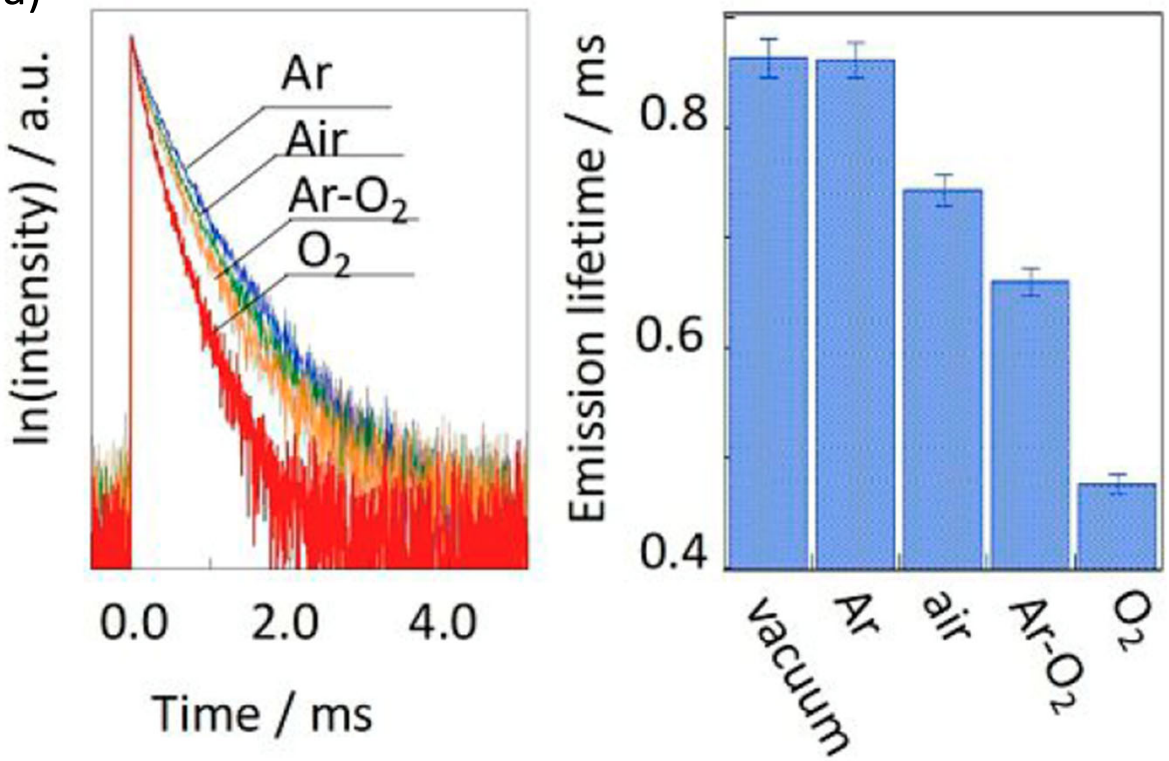
b)


O
O
O
O
O
O
O
O
O
O
O
O
Ln3+
hcpt

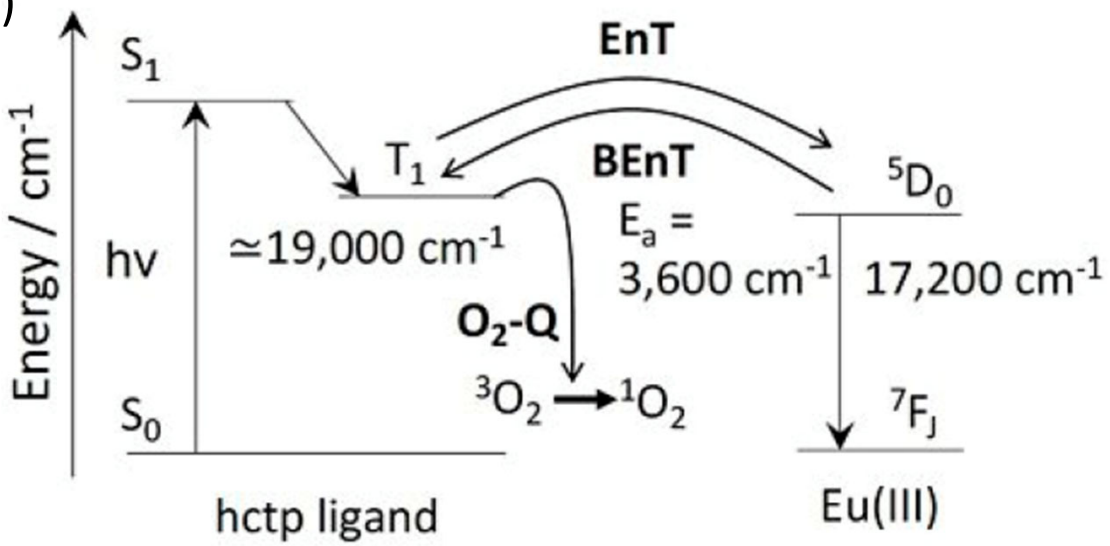
c)


O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
O
Ln3+
tiapy

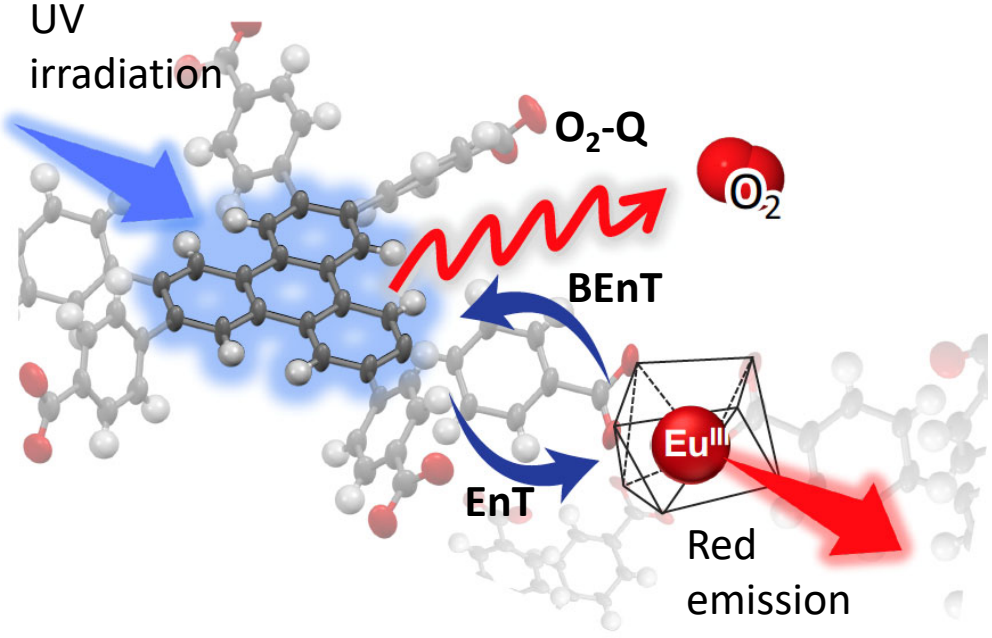
a)


ln(intensity) / a.u.
Ar
Air
Ar-O2
O2
0.0
2.0
4.0
Time / ms
Emission lifetime / ms
0.8
0.6
0.4
vacuum
Ar
air
Ar-O2
O2

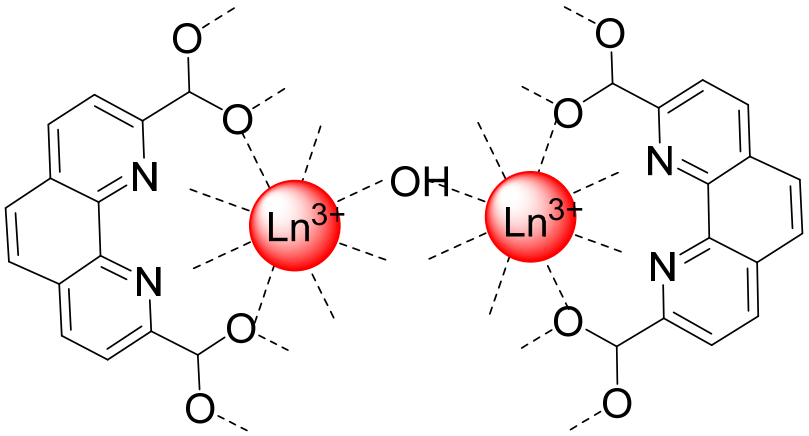
b)


Energy / cm-1
S1
T1
S0
hv
≃19,000 cm-1
EnT
BEnT
Ea =
3,600 cm-1
O2-Q
3O2 → 1O2
5D0
17,200 cm-1
7FJ
hctp ligand
Eu(III)

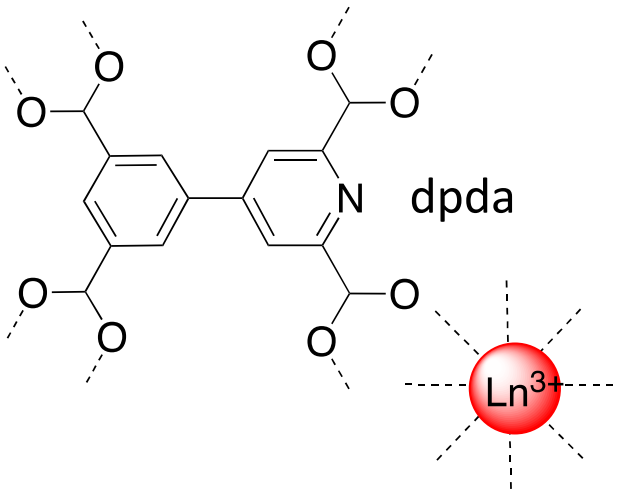
c)


UV
irradiation
O2-Q
O2
BEnT
EnT
EuIII
Red
emission

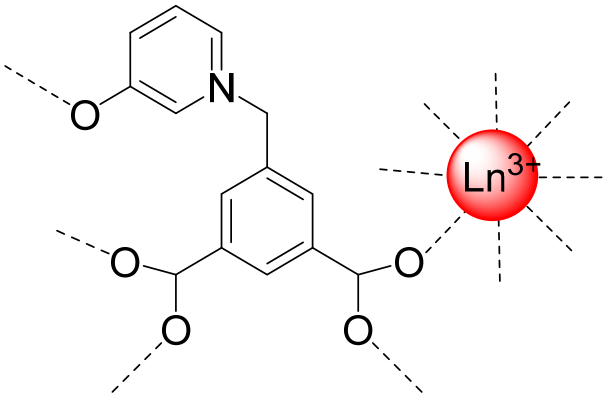
a)



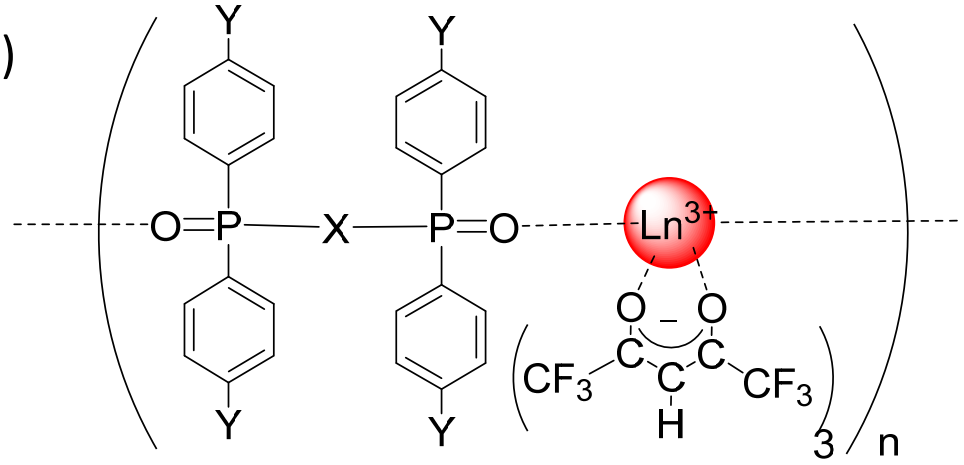
b)



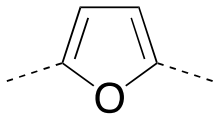
c)



d)



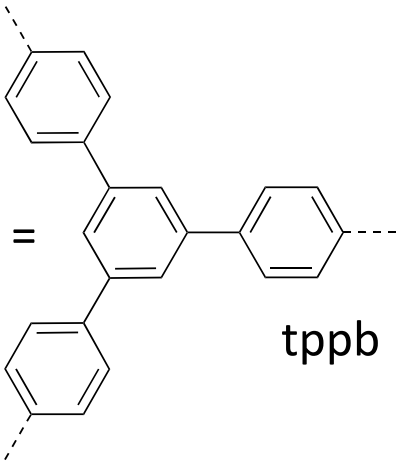
1) X =



dpf

Y = H

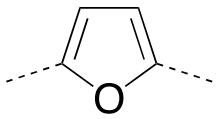
2) X =



tppb

Y = H

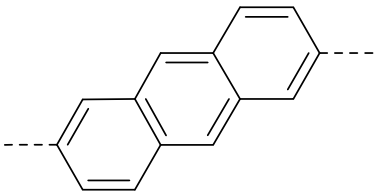
3) X =



dpf

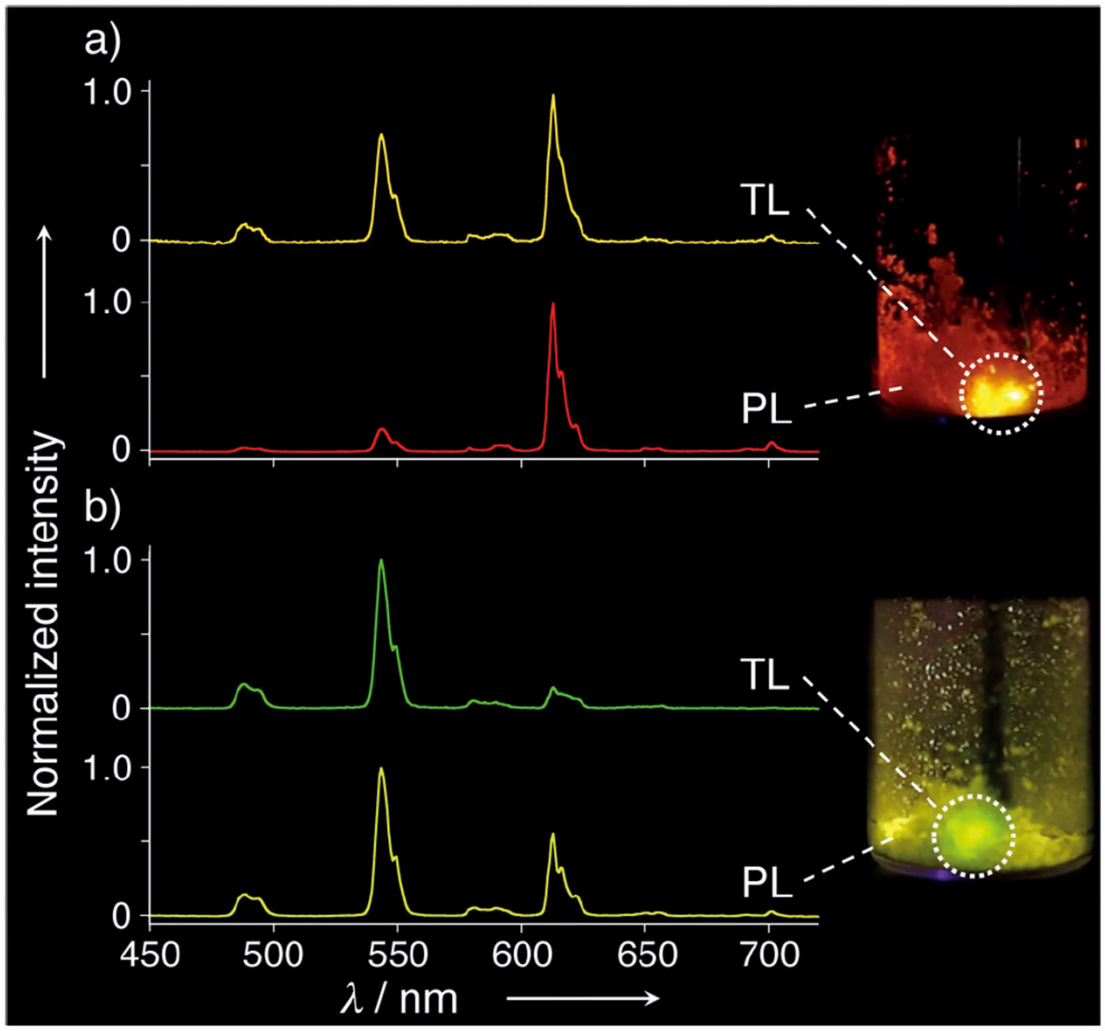
Y = CH_3

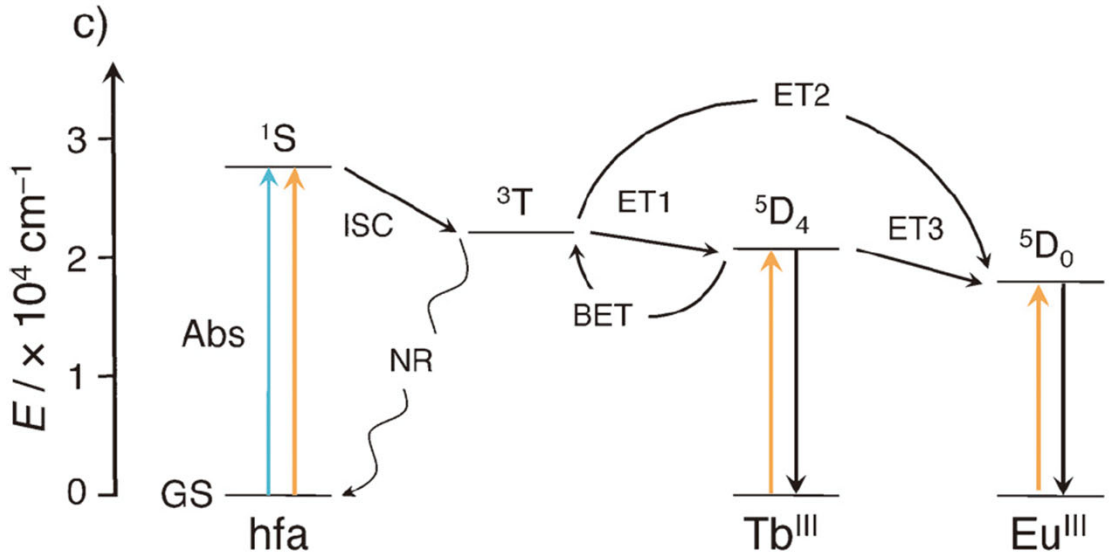
4) X =



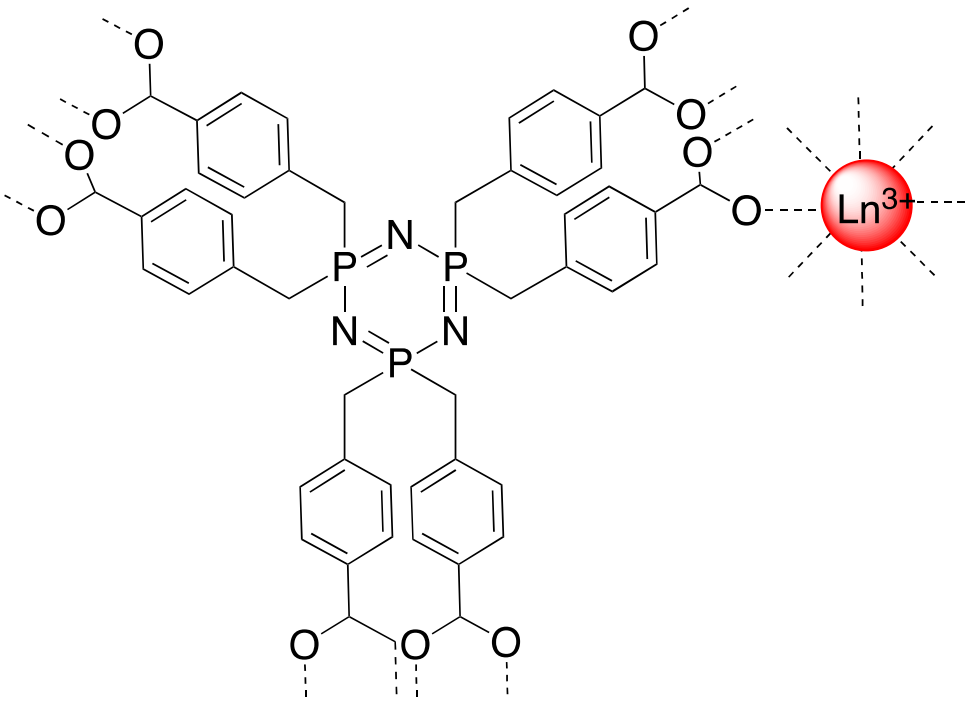
bpa

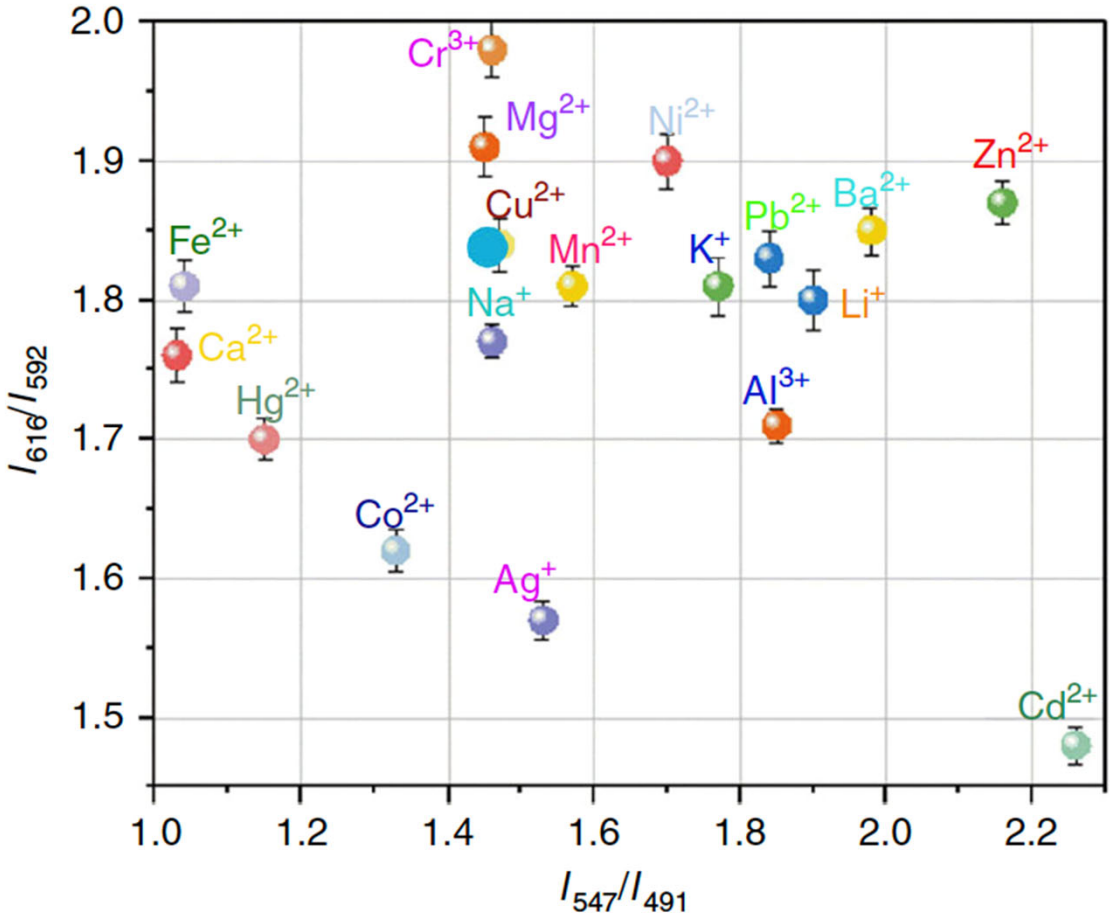
Y = H

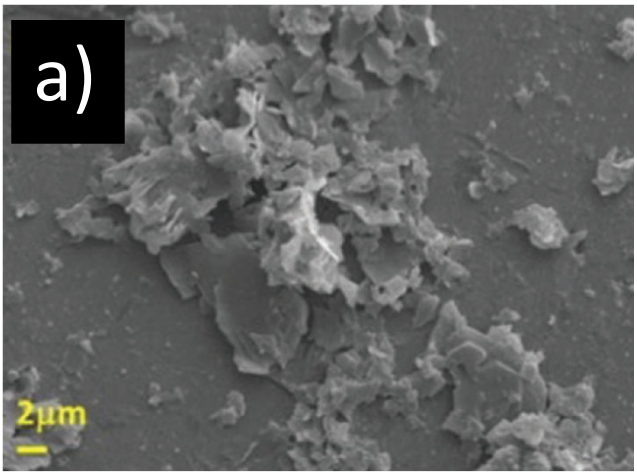

a)
1.0
0
TL
1.0
0
PL
b)
1.0
0
TL
1.0
0
PL
Normalized intensity
450
500
550
600
650
700
λ / nm

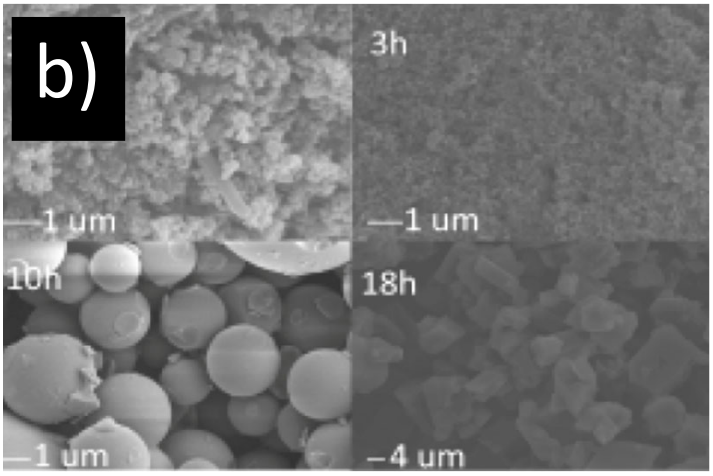

c)
E / × 10⁴ cm⁻¹
3
2
1
0
¹S
ISC
³T
ET1
ET2
⁵D₄
ET3
⁵D₀
Abs
NR
BET
GS
hfa
Tb^III
Eu^III

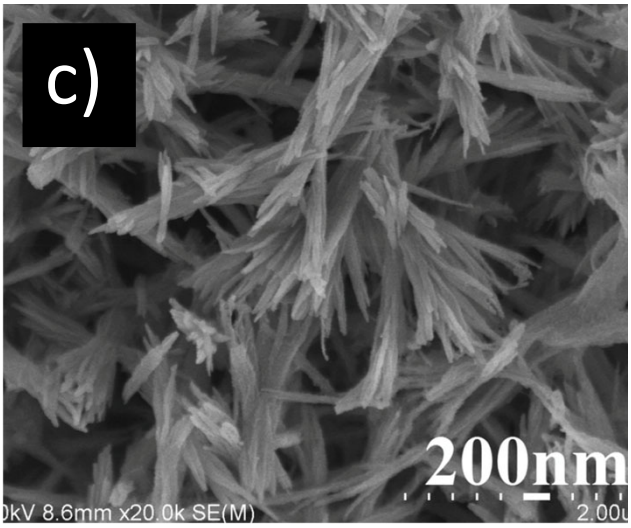
Y. Hasegawa, Figure 10

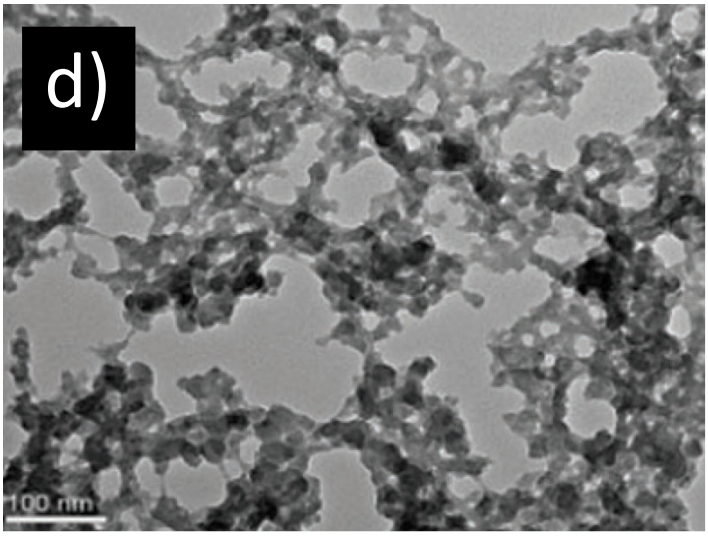





a)
2μm


b)
3h
1 um
1 um
10h
18h
1 um
4 um


c)
200nm
0kV 8.6mm x20.0k SE(M)


d)
100 nm