

Development of High-Efficient Photon Upconversion in Rigid Matrix

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Development of High-Efficient Photon Upconversion in Rigid Matrix

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Chapter 1 General Introduction

1-1 Basics of the Triplet–Triplet Annihilation-Based Photon Upconversion

The efficient use of renewable energy is fundamentally significant for the sustainable survival of humanity. Especially, solar energy has attracted more attention than hydro-power, wind-power, and geothermal energies because it is ubiquitous and often does not require the construction of large-scale facilities.

The elimination of mismatch between the solar spectrum and the wavelength range used by current applications is necessary for the efficient utilization of solar energy. The sunlight spectrum has a wide range from ultraviolet to near-infrared. However, for example, solar cell materials do not utilize near-infrared low-energy light at all, and photocatalytic reactions are further limited to the wavelength that uses the high-energy wavelength region. Photon upconversion (PUC) is a technology that converts low energy (long wavelength) light to high energy (short wavelength) light and is attracting attention to resolve the above mismatch. There are several PUC mechanisms such as a two-photon absorption¹ or energy transfer upconversion of lanthanide particles,² but these require strong excitation light intensity and do not work at all with solar level excitation intensity.

Among them, triplet–triplet annihilation-based photon upconversion (TTA-UC) is an especially prominent methodology that can convert long-wavelength light to shorter-wavelength light at a relatively weak excitation intensity such as solar irradiance.^{3–19} In the typical TTA-UC mechanism, a photo-excited triplet sensitizer undergoes intersystem crossing (ISC) to its excited triplet state which is followed by triplet energy transfer (TET) to an emitter. The sensitized emitter triplets annihilate (TTA), resulting in the emissive upconverted excited singlet (Figure 1-1-1). Overall, two low photons have been converted into one photon of higher energy, which occurs in combinations of two or more chromophores.

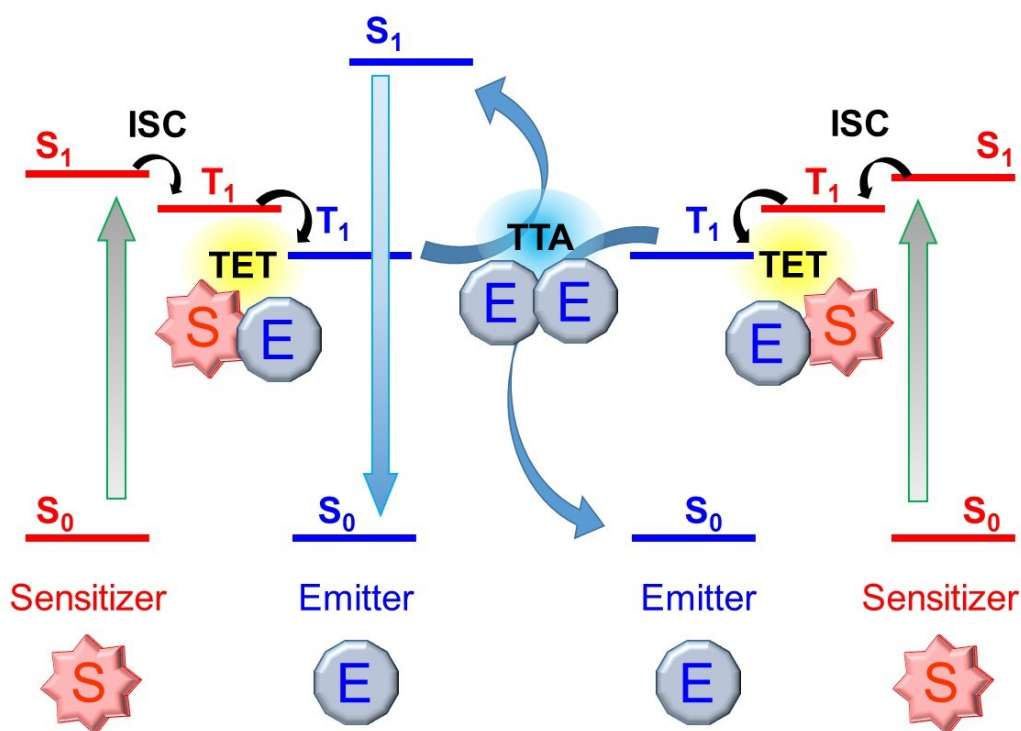


Figure 1-1-1. Schematic illustration for the TTA-UC process consisting of sensitizer/emitter pair. A photo-absorbed (green arrows) sensitizer undergoes intersystem crossing (ISC) and occurs triplet–triplet energy transfer (TET) to the emitter. The triplet-excited emitter pairs occur triplet–triplet annihilation (TTA) and then generates an excited singlet emitter. The upconverted shorter wavelength emission (blue arrows) is observed from the longer sensitizer absorption.

The optimal excitation and emission wavelengths vary depending on the applications using TTA-UC. To meet this demand, various combinations of chromophores with different conversion wavelengths have been reported so far (Figure 1-1-2).¹² In particular, the upconversion from the near-infrared to visible regions with a large anti-Stokes shift is one of the important challenges. This has been achieved through breakthroughs in sensitizers that can reduce energy loss during the TTA-UC process as much as possible. For example, thermally activated delayed fluorescence molecules (TADF) with an infinitesimally small difference between the S_1 and T_1 energy levels,^{20,21} inorganic particles such as quantum dots and perovskites that can omit the ISC process,^{22–24} and osmium complexes with strong S_0 - T_1 absorption have been reported.²⁵ These studies will contribute to the practical applications of the TTA-UC.

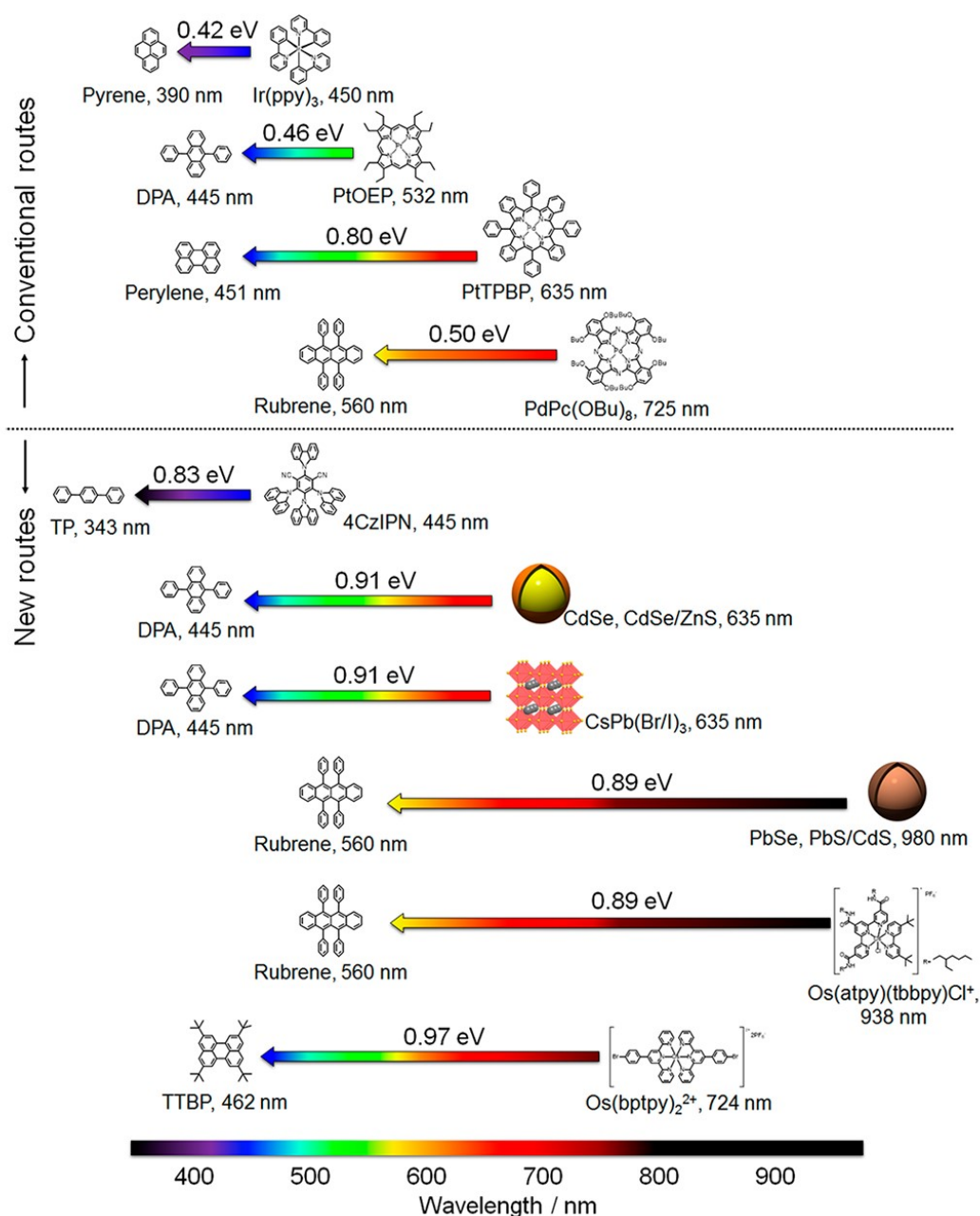


Figure 1-1-2. Typical pairs of sensitizer and emitter and their excitation and emission wavelengths, respectively. There are also shown the widths of the anti-Stokes shift.¹²

The applications using TTA-UC have been demonstrated in the past decade. The TTA-UC system works at low power intensity ($<100 \text{ mW cm}^{-2}$) and with coherent and non-coherent light, meaning sunlight can activate the process. It has been developed such as photovoltaics,^{9,13,26–28} photocatalysis,^{18,29–31} and photochemical synthesis.^{32–34}

The variety of TTA-UC applications has also been demonstrated using acceptable intensity light other than sunlight. The upconverted emission has been studied for its applications in lighting and

imaging materials using its visual response directly such as sensing,^{35,36} night vision,³⁷ and anticounterfeiting (Figure 1-1-3a).^{38,39} Among them, bio-imaging⁴⁰⁻⁴³ is considered a particularly compatible application. In conventional luminescence imaging using fluorescent probes, the S/N ratio is a problem due to the autofluorescence of the tissue. However, by its nature of being an anti-Stokes process, TTA-UC removes this complication. Another advantage in bio-imaging is that the long wavelengths used in excitation have greater penetration into tissue (Figure 1-1-3b).

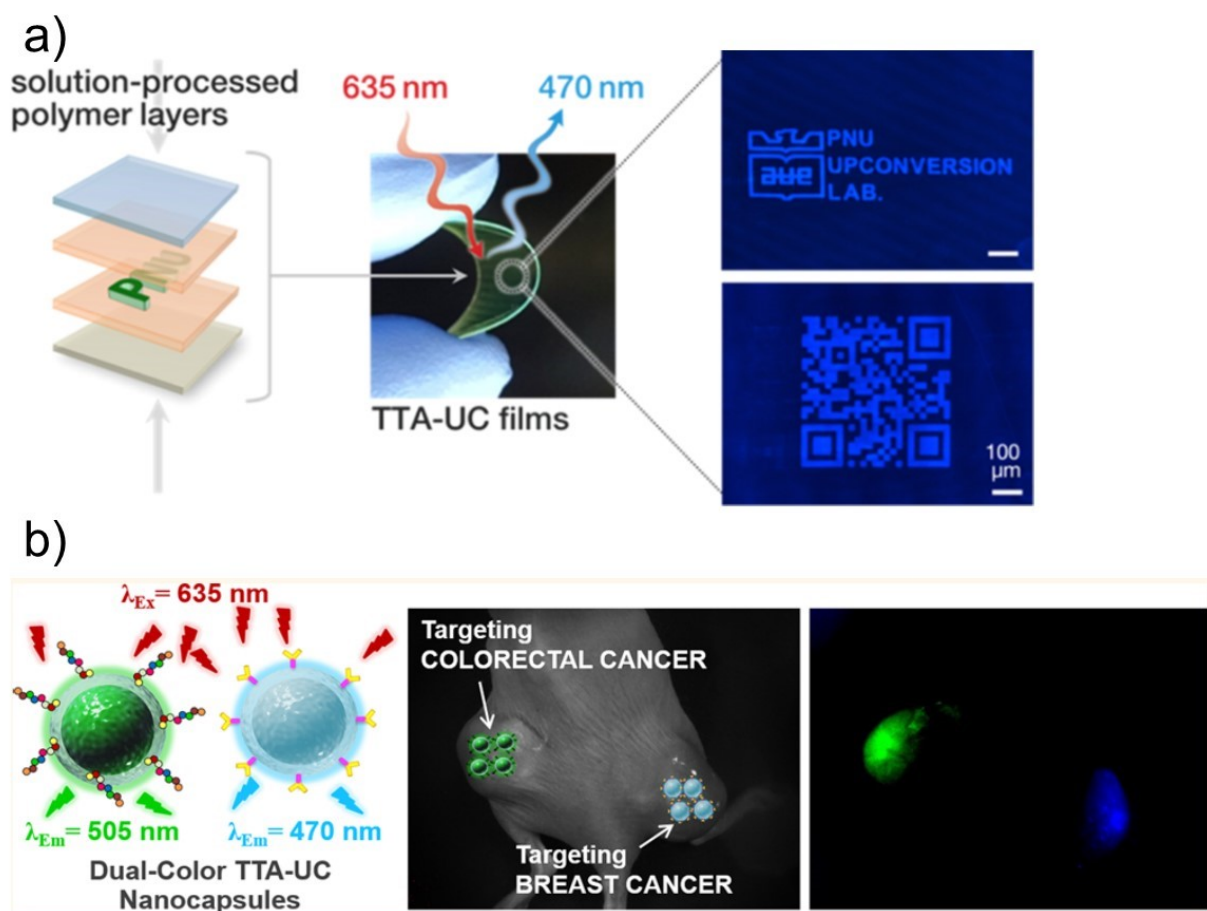


Figure 1-1-3. Examples of the demonstrations for TTA-UC applications. a) The demonstration film for the photonic device and anticounterfeiting.³⁸ The micro-patterned UC film is fabricated by soft lithography. Fluorescence micrographs of the film containing PdTPBP and perylene under laser excitation at 635 nm, taken through a 500 nm short-pass filter. b) The demonstration of the bioimaging using the nano-capsules encapsulated two distinct triplet-triplet annihilation UC chromophore pairs.⁴² The capsules were conjugated with either antibodies or peptides to selectively target breast or colon cancer cells, respectively.

1-2 Evaluation of TTA-UC Properties

For all TTA-UC applications, the TTA-UC quantum yield and emission at low excitation intensity are intrinsically important properties. It is necessary to mention the quantum yield (Φ_{UC}) and the upconversion threshold (I_{th}) when discussing and comparing the TTA-UC.^{7-9, 44-48}

1-2-1 TTA-UC Quantum Yield (Φ_{UC})

Φ_{UC} corresponds to the number of upconverted photons per number of excited state photosensitizers produced under steady-state conditions and can be expressed as:⁷

$$\begin{aligned}\Phi_{uc} &= \frac{\text{number of upconverted photons}}{\text{number of excited-state photosensitizer}} \quad (1-1) \\ &= 0.5f \Phi_{ISC} \Phi_{ET} \Phi_{TTA} \Phi_A\end{aligned}$$

where Φ_{ISC} , Φ_{ET} , Φ_{TTA} , and Φ_A represent the quantum yield of ISC of the sensitizer, the quantum yield of sensitizer-to-emitter TET, the quantum yield of TTA, and the fluorescence quantum yield of the annihilator. The parameter f represents the probability to obtain a singlet excited state as a result of the annihilation of two triplet states. To maximize the Φ_{UC} , each TTA-UC processes are necessary to be more efficient, which can be improved by the chromophore structure and the measurement conditions.

The Φ_{ISC} almost reaches 1 by using heavy metal porphyrins as a sensitizer which promotes the fast ISC thanks to the spin-orbital coupling by heavy atom effect.³ The Φ_{ET} and Φ_{TTA} can also be adjusted to 1 by optimally adjusting the sensitizer and emitter concentrations.⁸ As discussed later, TTET and TTA are more dominant than non-radiative decay in the low-viscosity organic solvents due to the large diffusion coefficient of the chromophores. The use of rigid polyacens brings Φ_A closer to 1. The emitters have been commonly used for the process due to a large fluorescence yield and long-living metastable triplets suitable for TTA. However, the emitter concentration is necessary to carefully optimize because the Φ_A decreases due to the effects of reabsorption, concentration quenching, and aggregations. The parameter f of 1 can be taken by using an appropriate emitter by considering the

relationship between its T_2 and twice T_1 levels.⁴⁶ TTA is a two-particle collision process, which results in the generation of excitons with different spin-character according to the statistical combination of the spin for the colliding triplets. The excited triplet pairs transition to three different energy levels, S_1 (multiplicity of 1), T_2 (multiplicity of 3), and Q (multiplicity of 5). Quintet (Q) states require the simultaneous excitation of two electrons and its formation probability is energetically zero. Therefore, only S_1 and T_2 are taken into consideration in practice. The intermediate collision complexes generate either a singlet excited state S_1 or one of the three degenerate high-energy T_2 triplet states with a statistical ratio of 1:3. The resulting T_2 states quickly decay back to T_1 , becoming again available for further annihilations. Therefore, upon collision of four triplet exciton pairs, five triplets are destroyed, but only two of them give a singlet, which sets $f = 2/5$ (Figure 1-2-1a). However, if the energy of T_2 is larger than the $2T_1$ plus thermal energy, not only the formation of a quintet state but also that of high-energy triplets is prevented. In this case, only singlet excitons can be formed upon TTA, resulting in the $f = 1$ (Figure 1-2-1b).

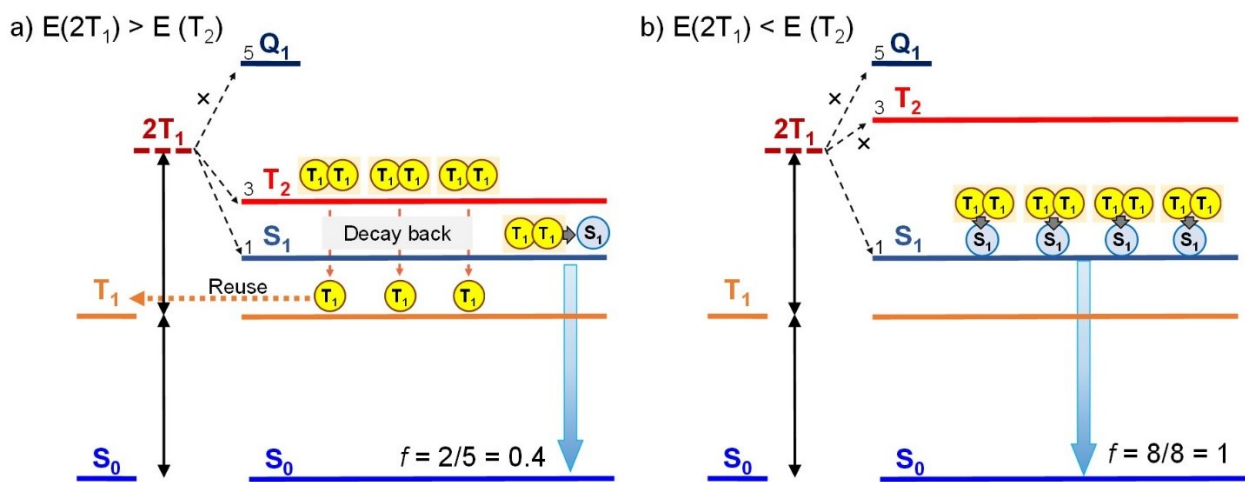


Figure 1-2-1. Schematic illustration for the TTA involving four triplet pairs. a) In the case of where T_2 levels are energetically accessible, three of the four generate on T_2 triplet states and one of four on a singlet excited S_1 statistically. However, three triplet pairs on T_2 decay back to T_1 , only one triplet pairs produce a singlet excited state. Therefore, $f = 2/5 = 0.4$. b) In the case where the T_2 level is not energetically accessible, all triplet pairs produce four singlet excited states. Thus, $f = 8/8 = 1$.⁴⁶

Sensitizer and emitter pairs that properly meet the above condition are often employed as benchmark chromophores in TTA-UC. A pair of a sensitizer Pt(II) octaethylporphyrin (PtOEP) and an emitter 9,10-diphenylanthracene (DPA) is most generally employed chromophores in TTA-UC studies.^{3,7-9} Since the f value of DPA is known to be 0.4, the theoretical maximum TTA-UC quantum yield is 20%. Yanai and colleagues had reported the TTA-UC quantum yield of this combination was exactly measured to be 18%, which is significantly close to the theoretical value (Figure 1-2-2a).⁴⁹ In addition, perylene or its derivatives are well studied as emitters because the f value can be 1, which makes it possible to approach the maximum TTA-UC quantum yield of 50%. Monguzzi and colleagues reported the TTA-UC quantum yield of the palladium(II) mesotetraphenyl-tetrabenzoporphyrin (PdPh₄TBP) and perylene in tetrahydrofuran reached up to 38% under appropriate concentration conditions, indicating the f of 1 (Figure 1-2-2b).⁴⁶

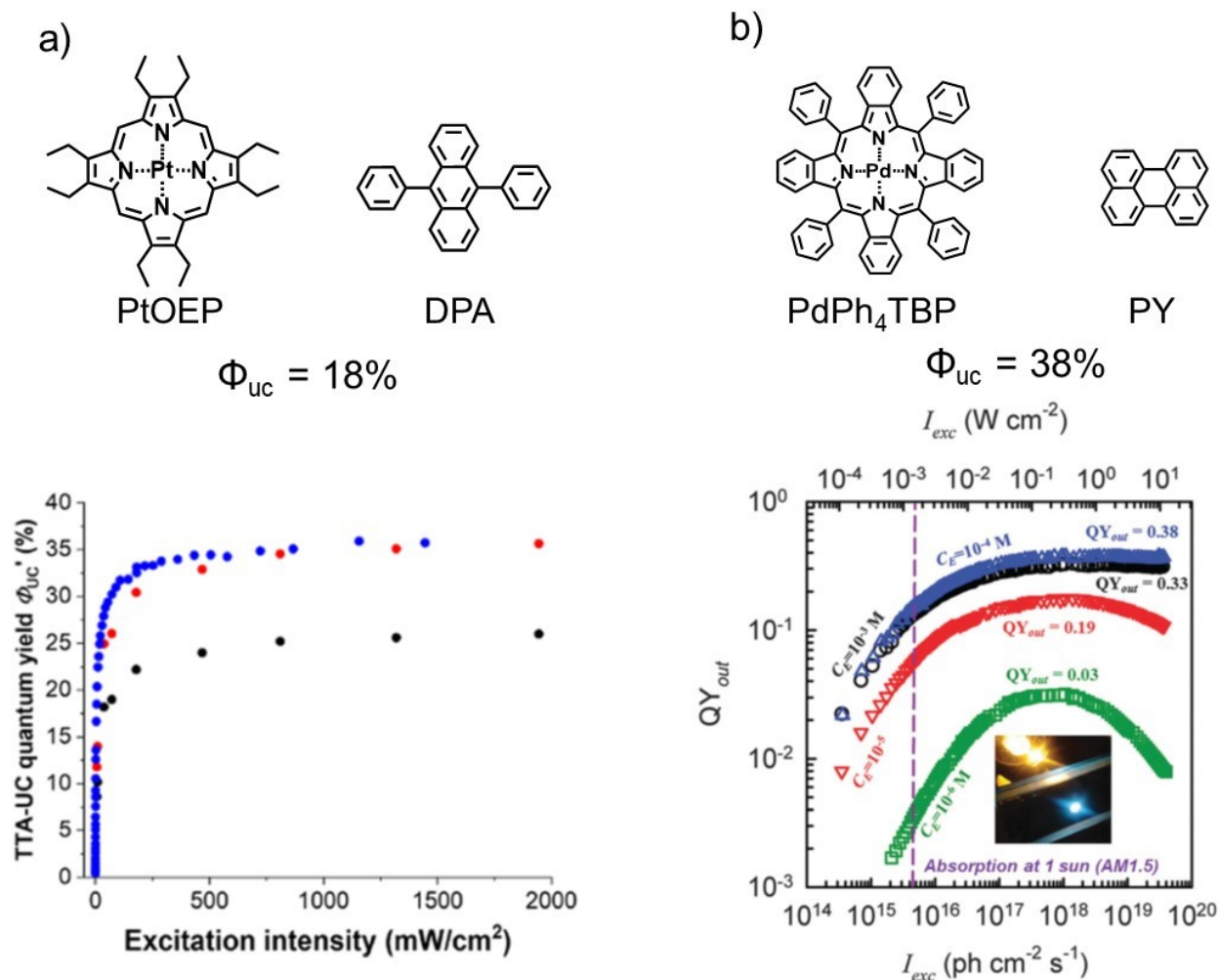


Figure 1-2-2. TTA-UC quantum yield of the benchmark chromophores pairs. a) The combination of PtOEP and DPA ($\Phi_{UC} = 18\%$, Φ_{UC}' in the graph is just multiplied Φ_{UC} by 2). Absolute TTA-UC quantum yield Φ_{UC}' of PtOEP (100 μM) and DPA (10 mM) in deaerated THF without (black) and with (red) the reabsorption correction and relative TTA-UC quantum yield Φ_{UC}' of PtOEP (100 μM) and DPA (10 mM) in deaerated THF (blue).⁴⁹ b) The pairs of PdPh₄TBP and PY ($\Phi_{UC} = 38\%$). The optimal chromophore concentrations are [PdPh₄TBP] = 10 μM and [PY] = 100 μM in tetrahydrofuran (blue cycle in the graph).⁴⁶

There are two methods to experimentally measure the TTA-UC quantum yield: an absolute method using an integrating sphere and a relative method using the quantum yield of reference samples. The absolute method is technically difficult to obtain the exact TTA-UC quantum yields due to the severe reabsorption of the upconverted emission by the triplet sensitizer molecules in the integrating sphere. The relative method is determined relative to the reference sample according to the following equation (1-2),^{9,49}

$$\Phi_{UC} = \Phi_{std} \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{UC}}} \right) \left(\frac{E_{UC}}{E_{std}} \right) \left(\frac{I_{std}}{I_{UC}} \right) \left(\frac{n_{UC}}{n_{std}} \right)^2 \quad (1-2)$$

where Φ , A , E , I , and n represent the quantum yield, absorbance at excitation intensity, integrated photoluminescence spectral profile, excitation intensity, and the refractive index of the samples, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. In general, the theoretical maximum of TTA-UC quantum yield Φ_{UC} , which is defined as the ratio of emitted photons to absorbed photons, is 50%. On the other hand, in the TTA-UC community, it is more popular to define the TTA-UC efficiency η_{UC} with the maximum of 100% by just multiplying the TTA-UC quantum yield by 2 for the sake of understanding the efficiency of the TTA-UC process. This has been recently discussed by the tutorial review.⁵⁰

The absolute method using an integrating sphere has been employed as the only way to measure TTA-UC quantum yields of samples with strong light scattering such as solids, gels, and particle dispersions. On the other hand, the relative method is an effective measurement method for samples with small light scattering, such as transparent solutions in a quartz cell. Recently, the absolute method that can be measured the precise values of the TTA-UC quantum yield had reported.⁴⁹ The method was carried out a correction of the reabsorption effect by comparing photoluminescence spectra of TTA-UC solutions with and without the integrating sphere normalized at a peak position of sensitizer phosphorescence. The obtained values can be used as certified values when one wants to check measurement setups and deaerated conditions of solutions for relative TTA-UC quantum yield measurements.

1-2-2 Upconversion Threshold Intensity (I_{th})

An upconversion threshold intensity I_{th} is defined as the excitation intensity that leads to $\Phi_{TTA} = 0.5$ and a half of the maximum Φ_{UC} value.^{44-48,51} The I_{th} value is experimentally calculable by plotting the UC emission intensity as a function of excitation intensity, as shown in Figure 1-2-3. In the low excitation intensity region, the sensitized emitter triplets occur predominantly in non-radiative decay rather than TTA. In this weak TTA region, the UC emission intensity depends quadratically on the excitation intensity variation, as expected for a two-photon process. On the other hand, in the high excitation intensity region, the TTA process dominates due to the well-sensitized emitter triplet, and the UC emission intensity becomes linear with excitation intensity. Additionally, the competing quenching and decay processes are negligible, so the UC quantum yield is constant (Figure 1-2-3a). This allows for a fair comparison of UC efficiencies among different systems.

The change from a quadratic to linear excitation intensity dependence is often reported in a log–log plot. In such a plot, the slope is 2 in the weak annihilation region and 1 in the strong annihilation region. The I_{th} value is obtained from the intersection of these two lines with slopes 2 and 1 (Figure 1-2-3b).

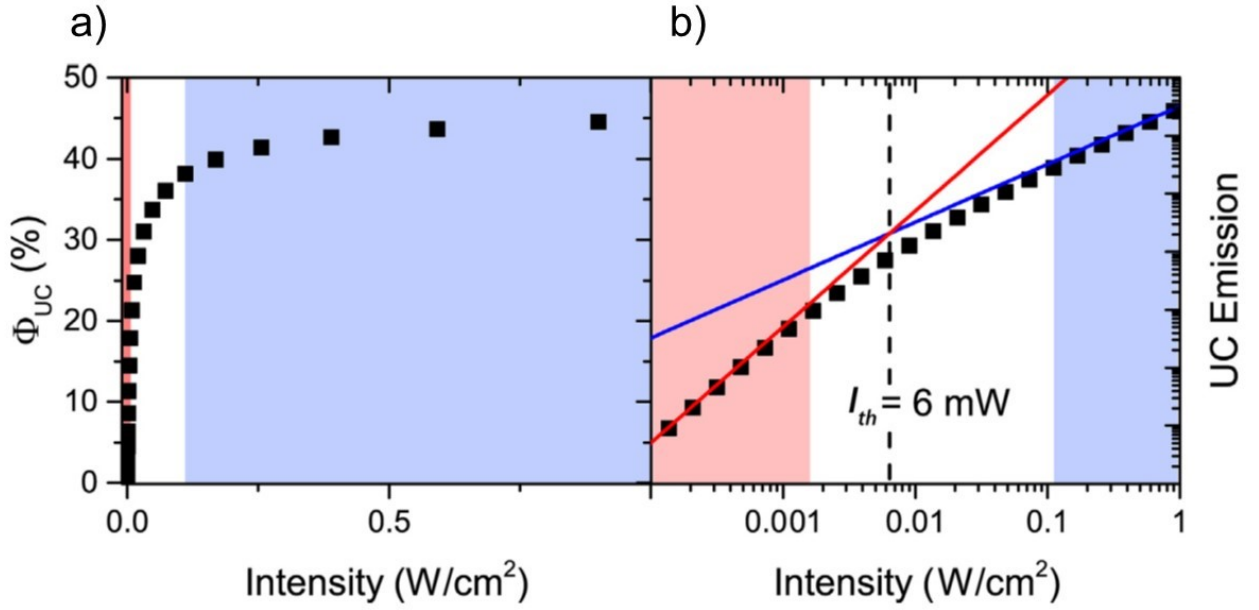


Figure 1-2-3. Typical plots of TTA-UC quantum yield Φ_{UC} (a) and UC emission intensity plotted in log–log scale (b) as a function of excitation intensity.⁵¹ The red shaded areas in these graphs correspond to the weak annihilation regions. Similarly, the blue shaded areas are the quantitative TTA process regions. The Φ_{UC} is determined by the constant value in the blue area. The I_{th} value is obtained from the intersection of these two lines with slopes 2 (red line) and 1 (blue line).

In a properly designed upconversion system, where TET is efficient and annihilator decay is governed only by first order decay (non-radiative decay) and second order decay (TTA), I_{th} can be defined by the following equation (1-3),

$$I_{th} = k_{E,T}^2 (\alpha(E) \Phi_{ET} \gamma_{TTA})^{-1} \quad (1-3)$$

Where $k_{E,T}$ is the decay rate constant of the triplet excited emitter, the $\alpha(E)$ and Φ_{ET} show the absorption coefficient of the sensitizer and the quantum yield of the sensitizer-to-emitter TET, and γ_{TTA} is the rate constant of the TTA. Incidentally, γ_{TTA} is related to the triplet diffusion coefficient (D_T) and the effective triplet diffusion distance (a_0), that is generally around 1 nm,⁴⁵ through the equation, $\gamma_{TTA} = 8\pi a_0$. This means that the I_{th} equation above can be replaced by the following equation including D_T ,

$$I_{th} = (\alpha(E)\Phi_{ET}8\pi D_T a_0 \tau_T^2)^{-1} \quad (4)$$

where τ_T is the triplet lifetime of the emitter, which is the reciprocal of $k_{E,T}$.

The I_{th} value is a significantly important factor, and a lower value is preferable for the practical applications of the TTA-UC. The typical solar intensity is a few to 10 mWcm⁻², depending on the spectral width of the sensitizer absorption. This means that TTA-UC systems with high I_{th} may be difficult to utilize for solar energy devices even if the UC quantum yield is high. Furthermore, biological applications can also be applied if the I_{th} is lower than the current clinical demands for therapeutic light intensity (typically 1 W cm⁻²).⁵²

To lower the I_{th} value, as can be seen from the I_{th} equation, the following four conditions should be satisfied: 1) high absorption of the sensitizer, 2) efficient energy transfer from the sensitizer to the emitter, 3) the large diffusion coefficient, and 4) the long lifetime of the triplet excited emitter.

These conditions are also close to ideal for the combination of the benchmark chromophores, PtOEP and DPA, as was the case for the UC quantum yield. The I_{th} in low viscosity solvent (THF) is observed to be a significantly low value of 1.0 mW cm⁻².^{8,49}

As described above, the evaluations of both the quantum yield and the I_{th} are crucial for the TTA-UC properties. Another important factor, which had been discussed in the previous section, is the degree of the anti-Stokes shift. In order to improve these properties, researches have been studied all over the world.

1-3 Matrices for Solid-State Photon Upconversion

As mentioned in the previous sections, TTA-UC proceeds most efficiently under conditions of a high diffusion coefficient and a completely deaerated atmosphere. Experimentally, the TTA-UC evaluation sample is prepared under the following conditions: 1) in a completely inert atmosphere such as in a glovebox, 2) dissolving the chromophores in a deoxygenated low-viscosity organic solvent, 3) putting in an airtight container such as a quartz cell, and 4) sealing it hermetically. However, the liquid host systems are not usually suitable for real-world use in many other of the aforementioned applications. A liquid layer in a device causes mechanical problems such as the evaporation of the solvent, spilling, and leakage over time. The use of a solid-state system would offer a solution to these device-construction problems.^{51,53,54}

In the following sections, several approaches for the solid-state TTA-UC system will be discussed. To develop the solid-state TTA-UC system, significant problems must be overcome: the difficulty of achieving both mechanical integrity for the applications and sufficient contact among the embedded chromophores to enable the efficient TTA-UC process. The solid-state TTA-UC systems were initially evaluated by simple methods of dispersing the benchmark UC chromophores in a host polymer. The host polymers used in the method can be classified into two types: the low T_g polymer that allows the diffusion of the UC chromophores and the high T_g polymer that suppresses the diffusion. While each of them had significant progress and problems, triplet energy migration-based TTA-UC (TEM-UC) was proposed, which greatly advanced the possibility of the practical application of the solid-state TTA-UC. At present, many materials and matrices that incorporate the basic concept of TEM-UC while achieving both mechanical properties and close interaction between chromophores have been developed (Figure 1-3-1).

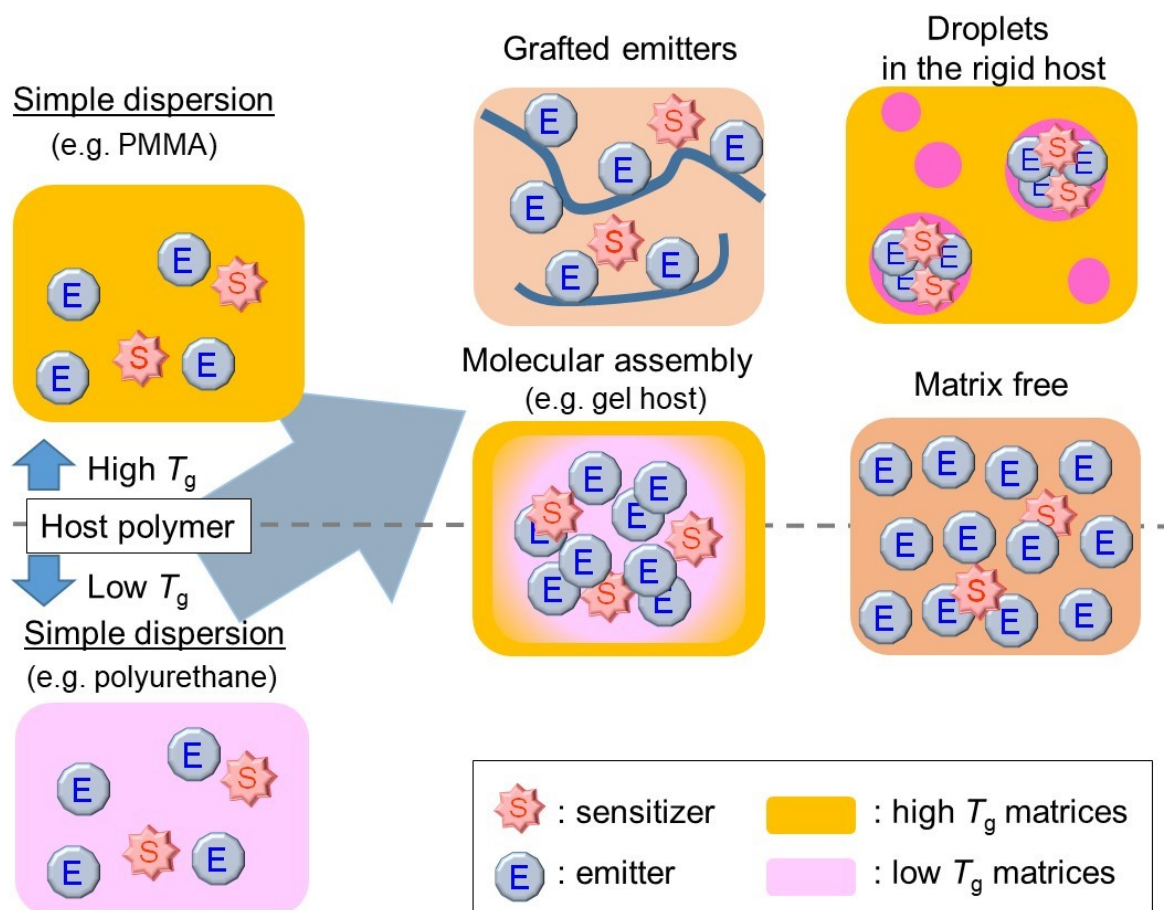


Figure 1-3-1. Schematic illustration of several approaches for solid-state TTA-UC. Initially, the study had started with simple dispersion of chromophores into the host polymer, which showed an immediate dichotomy between efficient energy transfer and prevention of oxygen diffusion in the matrices. A solution to this issue has been proposed in triplet energy migration-based TTA-UC (TEM-UC). In TEM-UC, it is important to assemble the chromophores without aggregation or precipitation. There are several approaches to achieve the effective TTA-UC in the solid-state such as emitter-grafted polymers, molecular assemblies where the chromophores are assembled in like a gel host, droplet types where the assembled chromophores are dispersed in a rigid host, and a matrix-free approach.

1-3-1 TTA-UC in Low T_g Matrices.

The studies of the solid-state TTA-UC were first examined from low T_g polymer hosts. The term "low T_g " here refers to polymers with T_g sufficiently lower than room temperature. These materials are typically flexible elastomers at room temperature, allowing the incorporated UC chromophores

(a pair of the sensitizer and the emitter) to diffuse within the polymer host as in the solution system. Castellano and colleagues have reported the first example of solid-state TTA-UC using a solvent-free and low T_g matrix.⁵⁵ Their group prepared the UC films consisting of polyethylene oxide/polyepichloridone copolymer with a T_g of -43°C as a host polymer and benchmark chromophores of PdOTP and DPA. The films were obtained by casting the chromophores and polymer uniformly dispersed in DMF onto glass and subsequently dried. The obtained films were displayed a blue emission under 544 nm laser irradiation. In addition, the same group established the diffusion-related dependence in polymeric hosts by evaluating the temperature dependence of the UC emission intensity using polyurethane resins with different T_g .⁵⁶ Since this report, research results on TTA-UC using polyurethane have been reported due to its high transparency, processability, and low T_g .^{5,57,58} Similarly, poly(alkyl acrylate)s are also useful host polymers due to their high transmittance and the ability to adjust the T_g with the side alkyl chain length. Monguzzi's group had prepared polyacrylate polymers with the different side alkyl chain lengths and evaluated the T_g dependence of upconversion properties and diffusion rates in these polymer hosts.^{59,60} The TTA-UC quantum yields Φ_{UC} of 21% in the lowest T_g polymer was reported to be comparable to the solution systems.⁴⁹ This is a similar result when polyurethane is used,^{56,57} indicating that the relationship between the T_g , diffusion rate, and quantum yield is not specific to the host polymer, but in general to similar polymer hosts.

The study of low T_g host polymers in which TTA-UC occurs based on molecular diffusion brings significant progress for the practical application of TTA-UC. It is important to lower the T_g and increase the molecular diffusion for the efficient TTA-UC. However, the fact that the molecules can diffuse means that oxygen can also penetrate and diffuse from outside the system, which is an essential problem just like in the solution system. In recent years, methodologies for TTA-UC based on molecular diffusion while eliminating the effects of oxygen have been reported. These will be discussed in later sections.

1-3-2 TTA-UC in High T_g Matrices.

In this section, the solid-state TTA-UC in which the chromophores are dispersed in a high T_g (above room temperature) host polymer will be mentioned. In this instance, unlike the solution system and the low T_g matrix described in the previous section, the molecular diffusion is suppressed in the rigid matrix. This means that the penetration and diffusion of oxygen molecules from outside the system are also suppressed, and thus suppressing the quenching of triplet excitons. Moreover, the high T_g matrices have the advantage of providing mechanical structure and stability, making it easy to adapt to the applications using TTA-UC. Poly (methyl methacrylate) (PMMA)^{61–65} and polystyrene (PS)^{66–68} are commonly used in TTA-UC studies with high T_g host polymers. These polymers are suitable for TTA-UC evaluation due to their solid mechanical strength, high T_g , and transparency.

Despite the above advantages, TTA-UC materials in which chromophores are simply dispersed in a high T_g matrix have an unsolved issue. TTA-UC efficiency in the rigid matrix is significantly lower than that of TTA-UC in the molecular diffusion system. This is because the excited triplets are mainly decayed before efficient energy transfer due to the suppression of molecular diffusion. Generally, the energy transfer via the Dexter mechanism requires molecules to be close to each other within 1 nm.⁴⁵ The energy transfer easily occurs in the molecular diffusion system such as in a solution. On the other hand, when the molecular diffusion is suppressed, energy migration is the only way for the excited-triplet energy transfer. It is required that the chromophore concentration in the rigid host is sufficiently high to achieve efficient migration. However, polymer films embedded with high concentrations of chromophores tend to undergo severe precipitation or phase separation. It is the key to achieving efficient TTA-UC how high concentrations of chromophores can be uniformly dispersed in the high T_g host polymers.

In 2009, the first rigid film for TTA-UC with PtOEP and DPA dispersing in PMMA as a host polymer had been reported.⁶¹ Afterward, kinds of research for the TTA-UC in the rigid matrices, for example, the study on the exciton dynamics in PMMA,⁶³ the production methods of the TTA-UC chromophore/PMMA blend film samples,⁶² and development of increase for the TTA-UC efficiency,^{63–65,68} have been reported. However, despite these efforts, the TTA-UC efficiency is only 1-2% at

best. There are two common features for these rigid films: the phosphorescence of the excited sensitizer and the aggregation of the emitter was observed from the films. The phosphorescence observation indicated insufficient TTET, i.e., low concentration of emitters. When the emitter concentration was increased to improve TTET, it saturated in the film and then the aggregation occurred. This is also indicated that the highest efficiency was not achieved in the condition of the highest emitter concentration.^{64,65,68}

The high T_g host polymers provide the mechanical structure and suppression of oxygen quenching. On the other hand, it is significantly difficult to achieve the efficient energy transfer process between chromophores as in solutions. However, these efforts have led to the development of methodologies for the intentional assembly of chromophore molecules.

1-3-3 Molecular Assembly

The molecular assembly system is a methodology to improve TTA-UC efficiency by consciously assembling UC chromophore molecules, as opposed to the simple dispersion systems. The assembled molecules proceed the efficient excited-triplet energy transfer by molecular diffusion, energy migration, or both. The TEM-based TTA-UC with molecular assembly systems has been pioneered by the Kimizuka group.^{53,69} The remarkable efficient TTA-UC under air was observed at the assembly site incorporating the UC chromophore pair such as in nanofibers self-assembled by surfactants,⁷⁰ inside gels with a strong hydrogen-bonding network of gelatin layers as an effective oxygen barrier layer,⁷¹ and inside capsules made of polyvinyl alcohol.^{28,72} The effects of TEM-UC with molecular assembly systems have also been displayed. For example, in supramolecular gels,⁷⁰ the same degree of I_{th} values and outstanding higher diffusion coefficients compared to solution systems have been reported. The solid film coated by PVA also contributes to the improvement of the TTA-UC quantum yield due to increasing the excited triplet lifetime of the sensitizer.^{28,72}

TTA-UC properties have been improved by molecular assembly systems not only for the self-assembled materials but also for the rigid embedded particles. Monguzzi and co-workers have prepared cross-linked polystyrene nanoparticles with a T_g of 197 °C densely embedded with PtOEP

and DPA.^{66,67} The TTA-UC quantum yield of the particles was recorded to be 3.7%, which was exceptionally high for a solid-state system. The molecular diffusion of the embedded chromophores was strongly suppressed, indicating the TTA-UC in the particles clearly occurred via TEM.

The molecular assembly system is a very promising methodology for TTA-UC in solid-state systems, where molecular diffusion tends to be limited because TTA-UC properties can be enhanced thanks to the triplet energy migration.

1-3-4 Grafted Emitters

Polymers with emitters covalently grafted to the side chains have been developed to create localized highly-concentrated chromophore sites in the rigid film. These have been expected to improve the TTA-UC properties compared to a simple chromophore dispersion system. Typically, polymers with DPA covalently reacted to an acrylic monomer and copolymerized with methyl methacrylate have been reported.^{73–76} Unfortunately, the problems such as insufficient TTET and not achieving maximum TTA-UC quantum yield at maximum emitter concentration^{73,74,76} have not been solved as with the systems with emitter monomers simply dispersed in PMMA.^{64,65,68} However, this system is simpler than the molecular assembly system, which is advantageous in terms of practical application. Future research will be expected to develop the system.

1-3-5 Droplets in the Rigid Matrix

Recently, the approaches used embedded liquid nanodroplets in the high T_g host to achieve the high molecular diffusion rate of solution-based TTA-UC systems have been reported.^{77–80}

The nanodroplet is a solution of UC chromophores dissolved in a hydrophobic solvent, and it is dispersed in a hydrophilic host polymer. Some host polymers with high T_g have been reported to be polymerized from the beginning, such as cellulose,⁷⁷ or polymerized after the droplets are dispersed, such as acryl monomers.^{78–80} Weder and co-workers have evaluated the TTA-UC quantum yield and the storage stability for the nanodroplets in a rigid acryl host polymer by using three commonly used TTA-UC chromophore pairs.^{79,80} Among them, the DPA: PdOEP pairs gave a remarkable maximum

Φ_{UC} of $23 \pm 3\%$ in ambient conditions. Furthermore, all tested TTA-UC systems showed remarkable storage stability for 3 months in the air.

This system is advanced research, but it may require severe molecular control and careful engineering. The achievement of its easy applicability to real devices and intrinsic stability of droplets will be important in the future.

1-3-6 Matrix-Free

Finally, research on a matrix-free system in which the emitter is chemically modified to also serve as a matrix is briefly discussed. Kimizuka group has reported the first sample of DPA and PtOEP modified with alkyl chains making them liquid at room temperature.⁸¹ They showed the triplet migration even when the liquid was frozen, proving that triplet migration can occur. This approach was further studied by preparing ionic liquid DPA-derivatives.⁸² In recent years, there has been a shift from liquid to solid form in terms of long-term oxygen tolerance. Ogawa *et al.* has found that certain ionized sensitizers and emitters crystallized without aggregation or phase separation with relatively high TTA-UC quantum yields.⁸³ Raišys *et al.* has synthesized anthracene derivatives modified with fluorene. The compound has a T_g of 65 °C, higher than room temperature, while the steric hindrance inhibits aggregation and precipitation. The compound has been evaluated to discuss the excited-triplet diffusion and quenching in TEM-UC.

1-4 Challenging Issues for TTA-UC Matrices

For providing the TTA-UC materials for practical applications, it is necessary to simultaneously satisfy the following conditions: (1) the high TTA-UC performance in air, (2) the high moldability and simple processability, and (3) the stable TTA-UC properties over time.

To achieve these conditions, several approaches were described in the previous section. Despite these efforts, it remains challenging to achieve air-stable triplet-energy-migration (TEM)-based TTA-UC in transparent films of technological versatility, which is indispensable for the innovation of TTA-UC and their implementation in society.

Especially, the solid-state TTA-UC in the rigid host polymer is a very attractive system because it satisfies the above requirements of (2) and (3). On the other hand, the requirement of (1), which is the efficient TTA-UC in the rigid polymer, has not been achieved so far because of inefficient TEM in the matrix (Figure 1-4-1).

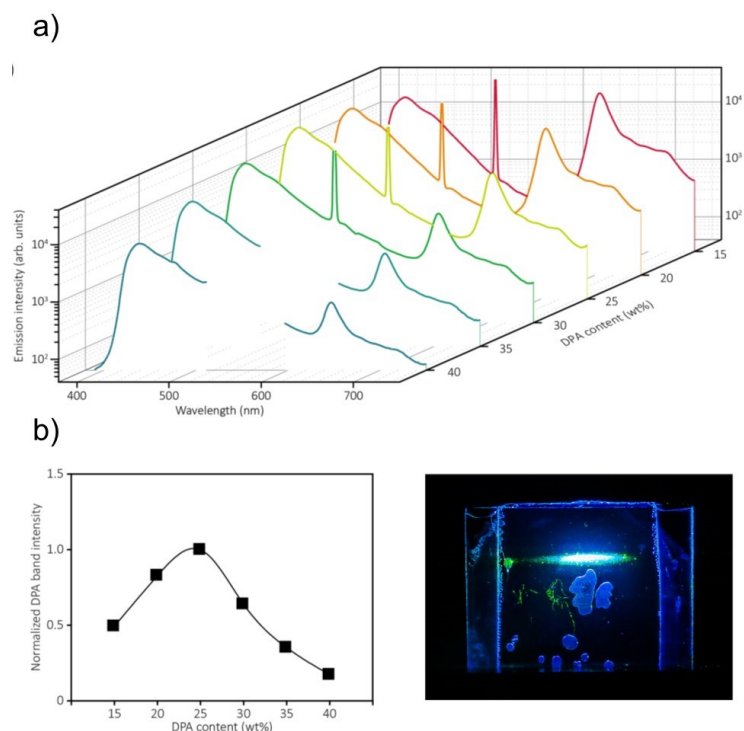


Figure 1-4-1. Typical solid-state TTA-UC properties in the rigid host polymer.⁶⁴ The sample was used PtOEP and DPA as UC chromophores and PMMA as a host polymer. a) photoluminescence spectra of the films excited at 532 nm as a function of DPA concentration. Both the UC emission from DPA and Phosphorescence from PtOEP were observed. b) Dependence of the UC emission intensity on the DPA concentration. The nonmonotonous behavior of UC was clearly observed. The UC intensity increases with DPA concentration up to 25 wt% DPA and then decreases as the DPA concentration further increases. The evaluated samples displayed the visible DPA precipitation.

1-5 Survey of This Thesis

The main purpose of this thesis is to design and establish guidelines for rigid resins with high photon upconversion efficiency. Especially, thermoset epoxy resins will be proposed to solve the issues described in the previous section.

In chapter 2, the first example of transparent and rigid epoxy films showing air-stable TTA-UC is described. A sensitizer platinum (II) octaethylporphyrin (PtOEP) and an emitter 9,10-diphenylanthracene (DPA) were dissolved in a mixture of an epoxy monomer, an acid anhydride monomer, and a phosphorus-based reaction promoter. The resulting liquid precursor was only thermally cured to form a rigid and transparent film which shows air-stable TTA-UC. While the common emitter DPA tends to aggregate in the epoxy resins at high concentration, the ionic liquid emitter composed of 9,10-diphenylanthracene-2-sulfonate anion (DPAS) and trihexyl(tetradecyl)phosphonium cation (P_{66614}) showed much-enhanced dispersibility in the epoxy resin, resulting in high TTA-UC efficiency and low threshold excitation intensity.

In chapter 3 describes the guidelines for rigid epoxy resins with high photon upconversion efficiency. The highest TTA-UC efficiency to date in a rigid solid where chromophore molecules do not diffuse has been achieved by covalently and non-covalently introducing the emitter moiety in epoxy resin without aggregation at ultra-high concentrations exceeding 30 wt%. The high emitter concentration speeds up the triplet diffusion and suppresses the back energy transfer from emitter to sensitizer so that the sensitized emitter triplet can be effectively utilized for TTA. The important result is now possible to understand it in detail for the first time in a rigid solid by systematically changing the emitter concentration. Furthermore, the solid-state TTA-UC exhibits high air stability, reflecting the high oxygen barrier performance of epoxy resins. The high moldability of epoxy resins allows the construction of upconversion materials with complex geometries at nano- to macroscopic scales.

In chapter 4 summarizes the whole thesis work.

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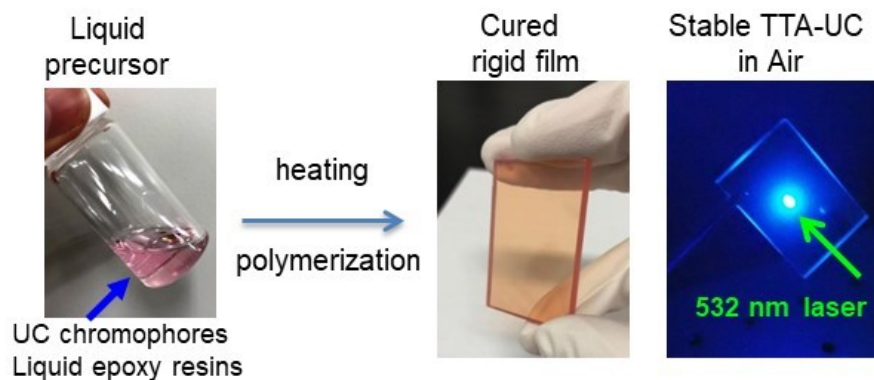
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Chapter 2 Bulk Transparent Photon Upconverting Films by Dispersing High Concentration Ionic Emitters in Epoxy Resins



Abstract

It remains challenging to achieve efficient and air-stable photon upconversion (UC) in rigid, technologically valuable transparent films. Here we report the first example of epoxy resins that show an air-stable and efficient triplet-triplet annihilation (TTA)-based UC. Epoxy resins are thermally cross-linked polymers widely used as coating and sealing materials in actual devices. To achieve efficient TTA-UC in rigid epoxy films, it is essential to execute both the triplet sensitization and triplet exciton diffusion processes without relying on molecular diffusion. This requires homogeneously dispersing emitter molecules without aggregation in three-dimensionally cross-linked rigid polymer networks at a high concentration (ca. 1000 mM) such that the inter-emitter distance is less than 1 nm, where Dexter energy transfer can occur. This difficult requirement is solved by employing an ionic liquid emitter that consists of 9,10-diphenylanthracene sulfonate and lipophilic phosphonium ions bearing long alkyl chains. The obtained epoxy resins show a high TTA-UC efficiency ($\eta_{\text{UC}} = 3.8\%$) and low threshold excitation intensity ($I_{\text{th}} = 40 \text{ mW cm}^{-2}$) in air. These UC parameters are achieved by virtue of a very high sensitizer-to-emitter triplet energy-transfer efficiency (92.8%) and a significantly long emitter triplet lifetime (17.8 ms) that reflect the high emitter concentration and the rigid chromophore environment, respectively. The bulk transparent upconverting resins can be prepared in air and function in air, which opens a new avenue toward a wide range of real-world applications.

2-1 Introduction

Photon upconversion based on triplet–triplet annihilation (TTA-UC) is a prominent methodology that can convert long-wavelength light to shorter-wavelength light at a relatively weak excitation intensity such as solar irradiance.^{1–20} In the typical TTA-UC mechanism, a photo-excited triplet sensitizer undergoes intersystem crossing (ISC) to its excited triplet state which is followed by triplet energy transfer (TET) to an emitter. The sensitized emitter triplets annihilate (TTA) and emit an upconverted delayed fluorescence. In recent years, the application of TTA-UC has been expanding to various fields such as photovoltaics,^{11,19, 21–24} photocatalysts,^{25,26} bioimaging^{27–29} and optogenetics.³⁰

However, to achieve the practical use of TTA-UC, there are three outstanding problems to be resolved. First, it is crucial to develop useful technologies that prevent oxygen quenching of the photo-excited triplet states in air. Second, transparent solid films capable of TTA-UC in air are required because the use of volatile organic solvents is not suitable for most applications. To achieve TTA-UC in films and to impart oxygen tolerance, soft polymer matrices with glass transition temperatures (T_g) lower than room temperature have been employed.^{26,31–33} For example, Castellano and Kim *et al.* have demonstrated the highly efficient TTA-UC by dispersing the chromophores in soft polyurethane films.^{33,34} Balushev and Landfester *et al.* have reported the oxygen protection of TTA-UC by embedding the non-volatile hexadecane chromophore solution into cellulose films.³⁵ Simon and Weder *et al.* have shown the highly efficient TTA-UC by confining non-volatile upconverting droplets in glassy polymers.^{36–38} However, the fact that the soft media permit molecular diffusion of the chromophore suggests oxygen can also diffuse, and aggregation and phase separation of the chromophores over time are also possible concerns. Third, although triplet lifetimes of sensitizer and emitter chromophores are one of the most critical parameters that influence the performance of TTA-UC, they are considered as inherent properties of the employed chromophores, and their active control by means of environmental design has been rarely established.

Besides the molecular diffusion-based TTA-UC in soft polymer matrices, another methodology to achieve air-stable TTA-UC is to confine densely self-assembled chromophores within oxygen-blocking media.^{39–42} The Yanai and Kimizuka group have demonstrated this strategy in various

molecular assembly systems. For example, the sensitizer-doped emitter nanoparticles were embedded within oxygen-blocking poly(vinyl alcohol), showing the air-stable TTA-UC.^{24,43} Monguzzi and Meinardi *et al.* have reported the air-stable TTA-UC with the long triplet lifetime in nanoparticles dispersed in water.^{44,45} Despite these efforts, it remains challenging to achieve air-stable triplet-energy-migration (TEM)-based TTA-UC in transparent films of technological versatility, which is indispensable for the innovation of TTA-UC and their implementation in society.

Here, we show the first example of transparent and rigid epoxy resins showing air-stable TTA-UC. Epoxy resins are thermoset resins formed by step-growth reactions without generating volatiles, which allows the formation of void-free composite materials. The combination of good processing characteristics, and extremely low permeability to moisture and oxygen led to many applications, including adhesives, encapsulation, and sealing materials for LEDs.⁴⁶ To achieve the TEM-based TTA-UC in cross-linked epoxy resins, it is pivotal to homogeneously disperse the UC chromophores without phase segregation. While the common UC emitter 9,10-diphenylanthracene (DPA) tends to aggregate in the epoxy resins at high concentration, the ionic liquid (IL) emitter composed of 9,10-diphenylanthracene-2-sulfonate (DPAS) anion and trihexyl(tetradecyl)phosphonium cation (P₆₆₆₁₄) showed much-enhanced dispersibility in the epoxy resin up to 1000 mM. A sensitizer platinum (II) octaethylporphyrin (PtOEP) and the emitter P₆₆₆₁₄DPAS are dissolved in a mixture of an epoxy monomer, an acid anhydride monomer, and a phosphorus-based reaction promoter. The resulting mixture is thermally cured to form rigid and transparent films, which show air-stable TTA-UC with high TTA-UC efficiency ($\eta_{UC} = 3.8\%$) and low threshold excitation intensity ($I_{th} = 40 \text{ mW cm}^{-2}$) thanks to a significantly high sensitizer-to-emitter TET efficiency of 92.8% and a long emitter triplet lifetime of 17.8 ms.

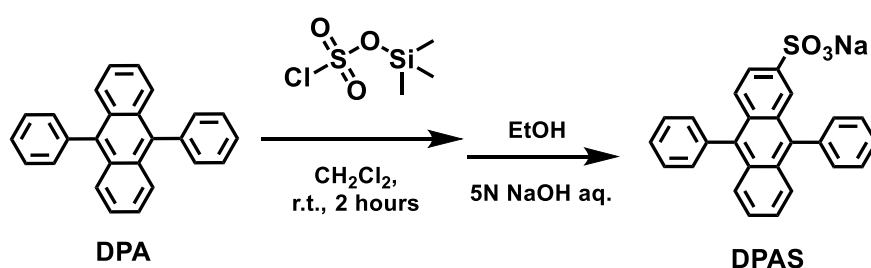
2-2 Experimental Section

2-2-1 Characterization

The ^1H NMR (500 MHz) spectra were measured on a Bruker AscendTM 500 spectrometer using TMS as the internal standard. The infusion ES-MS measurements were performed by an AB SCIEX Triple TOF 5600+ instrument. Elemental analysis was conducted with a J-Science JM10 instrument, and FT-IR spectra were recorded on a SHIMADZU IRAffinity-1S Fourier transform infrared spectrophotometer. X-ray diffraction (XRD) analysis was conducted on a Rigaku NANO-Viewer by the transmission method on the films with a copper Cu K α source. Differential scanning calorimetry (DSC) was performed in a NETSCH Japan K. K. DSC 204 F1 Phoenix[®]. Dynamic mechanical analysis (DMA) was done with a T A Instruments Japan Co. Q-800 instrument. The test dimensions of the cured film were 4 mm width, 20 mm length, and 0.2 mm thickness. UV-vis-NIR absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence spectra were measured by using a Hitachi High-Tech Science Co. F-7000 spectrometer. The absolute quantum yields were measured by using a Hamamatsu C10027 instrument. The density of the cured film was measured by using SHIMADZU AccuPyc II 1340 instrument. Time-resolved fluorescence lifetime measurements were done using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11567-01 (for phosphorescence and delayed fluorescence lifetime). The quality of the fit was evaluated by fitting parameters χ^2 (<1.2) and visual inspection of the residuals. The upconversion luminescence emission spectra were recorded on a multichannel detector Otsuka Electronics MCPD-9800 instrument with the excitation source using an external, adjustable 532 nm semiconductor laser. The detector was calibrated by using a standard lamp Ocean Optics HL-3 plus-CAL. The diameter of the laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics), with a typical laser size of $9.8 \times 10^{-4} \text{ cm}^2$. The temperature control was conducted with a Linkam 10033L as a temperature control stage, a Linkam LNP94/2 as a liquid nitrogen controller and a Linkam TMS94 as a temperature controller.

2-2-2 Materials

PtOEP (>98%) and DPA (>95%) were purchased from Aldrich and Tokyo Chem., Ind., Co., Ltd., respectively. Dichloromethane was obtained from Kanto Chem. Co., Inc.. P₆₆₆₁₄DPAS was synthesized by modifying our previous procedure⁴⁷ to improve the yield. Hydrogenated bisphenol-A-glycidyl ether was obtained from Mitsubishi Chem. Co.. 4-Methyl(hexahydro)phthalicanhydride/-(hexahydro)phthalicanhydride mixture was purchased from New Japan Chem. Co., Ltd.. Tetrabutylphosphonium *O,O*-diethylphosphorodithioate was acquired from Nippon Chem. Ind., Co..



Scheme 2-2-1. Synthetic scheme of DPAS.

Synthesis of sodium 9,10-diphenylanthracene-2-sulfonate (DPAS): In the round-bottomed flask, 9,10-diphenyl anthracene (DPA, >95%, purchased from Tokyo Chem. Ind., Co., Ltd., 20.0 g, 60.5 mmol) and 300 mL of dry CH_2Cl_2 (purchased from Kanto Chem. Co.) were added and DPA was dissolved. Trimethylsilyl sulfonyl chloride (>99%, purchased from Aldrich, 12.6 g, 66.6 mmol) was added slowly to the solvent, and the mixture was stirred for 2 hours at room temperature (20 °C). After confirming the complete dissolution of the starting materials (monitored by GC and TLC), 20 mL of ethanol (>99.5%, purchased from Junsei chem. Co.) was added to the mixture and stirred for an hour at room temperature to quench unreacted trimethylsilyl sulfonyl chloride. The reaction solvent was evaporated, and 200 mL of ethanol was added to the residue and dispersed. About 60 mL of 5N NaOH aq. was slowly added to the solvent while stirring, the precipitate was filtered, and the slurry-washed by distilled water to remove NaCl. The precipitate was recrystallized by methanol to produce DPAS (20.4 g, 47.2 mmol, 78%). The ^1H NMR (500 MHz, Methanol- d_4) parameters involved: δ (ppm) = 7.35–7.37 (m, 2H), 7.43–7.46 (t, 4H), 7.55–7.71 (m, 10H), and 8.26 (s, 1H).

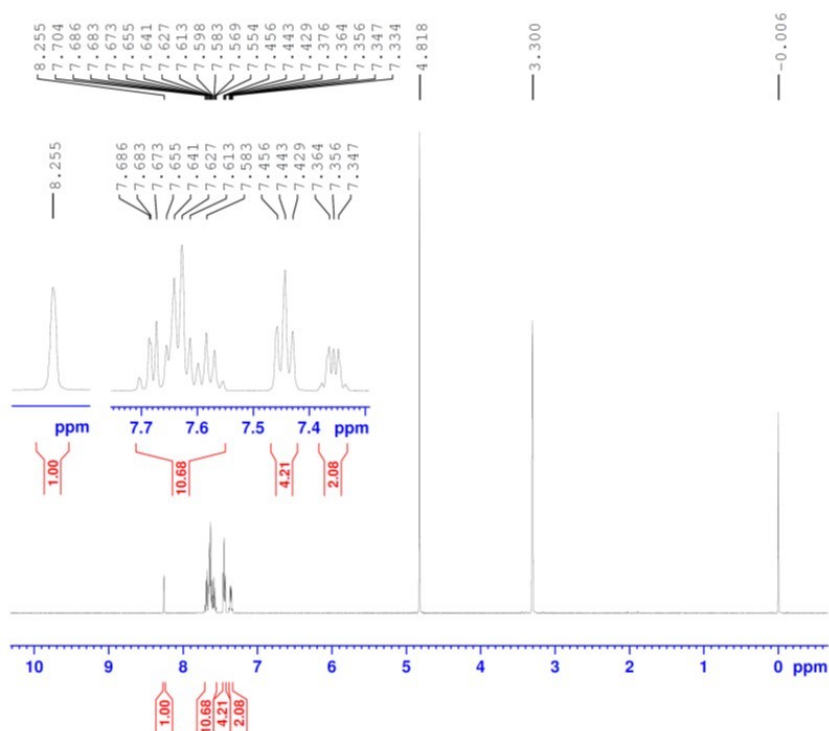
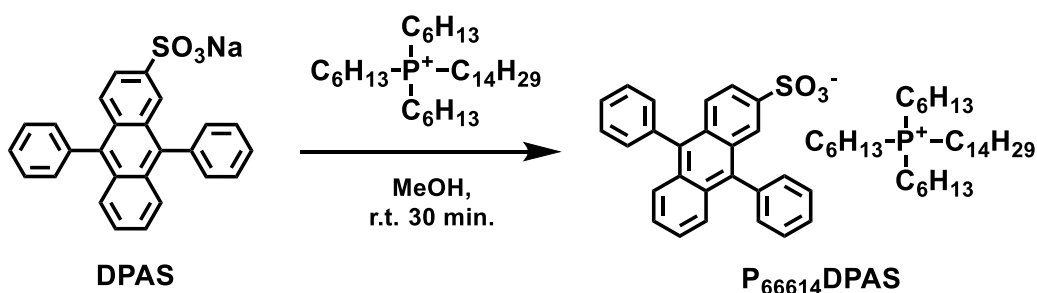


Figure 2-2-1. ^1H NMR spectrum (500 MHz, Methanol- d_4) of DPAS.



Scheme 2-2-2. Synthetic scheme of $\text{P}_{66614}\text{DPAS}$.

Synthesis of trihexyl(tetradecyl)phosphonium 9,10-diphenylanthracene-2-sulfonate ($\text{P}_{66614}\text{DPAS}$): DPAS (10.0 g, 23.1 mmol) and trihexyl(tetradecyl) phosphonium chloride (>95%, purchased from Kanto Chem. Co., 11.9 g, 22.9 mmol) were dissolved in 200 mL of methanol (special grade, purchased from Junsei chem. Co.). After stirring for 30 minutes at room temperature (20 °C), methanol was removed under reduced pressure, and dichloromethane was added to the residue and washed with distilled water twice. The organic layer was dried with MgSO_4 and removed under reduced pressure to yield the $\text{P}_{66614}\text{DPAS}$ (19.2 g, 21.5 mmol, 94%). The ^1H NMR (500 MHz, Methanol- d_4) parameters are: δ (ppm) = 0.87–0.93 (m, 12H), 1.27–1.55 (m, 48H), 2.14–2.20 (m,

8H), 7.35–7.43 (m, 2H), 7.43–7.46 (t, 4H), 7.57–7.69 (m, 10H), 8.25 (s, 1H). Elemental analysis, calculated for $C_{58}H_{85}O_3PS+0.2 H_2O$ are: C, 77.67; H, 9.60; N, 0.00; and found include: C, 77.37; H, 9.83; N, 0.03. The infusion ESI-MS involved, Negative: 409.09 ($DPA-SO_3^-$) and Positive: 483.502 ($((C_6H_{13})_3(C_{14}H_{29}) P^+)$).

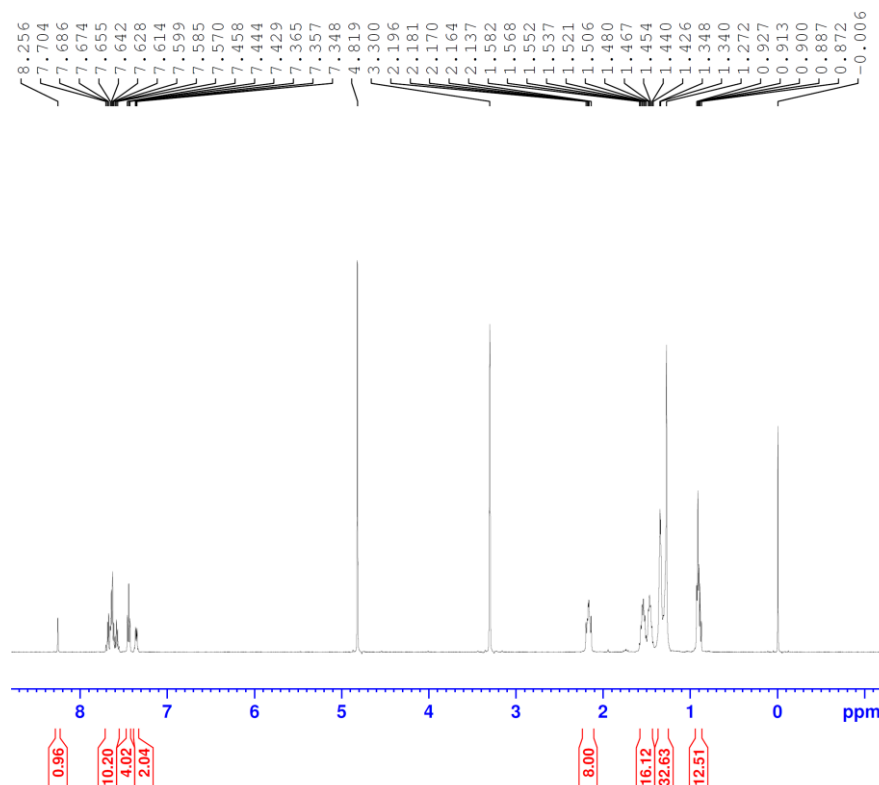


Figure 2-2-2. 1H NMR spectrum (500 MHz, Methanol- d_4) of $P_{66614}DPAS$.

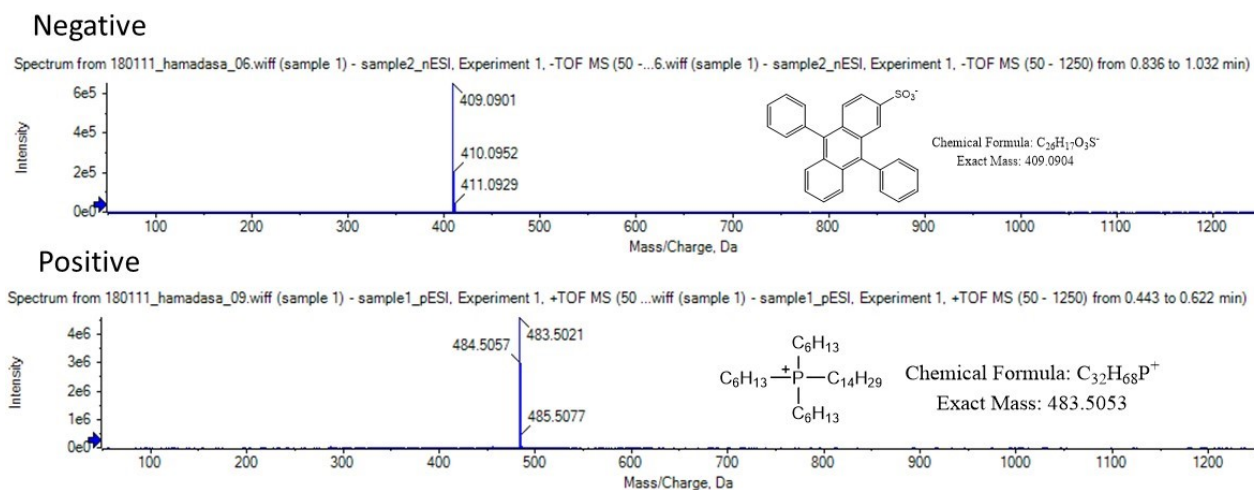


Figure 2-2-3. The infusion ESI-MS spectra of $P_{66614}DPAS$.

2-2-3 Film Preparation

10.0 g of hydrogenated bisphenol-A-glycidyl (epoxy resin, equivalent: 198) and 8.33 g of 4-methyl(hexahydro)phthalic anhydride/(hexahydro)phthalic anhydride (acid anhydride resin, equivalent: 165) were mixed to yield a mixture with a density of 1.103 g mL^{-1} . 1.0 mL of the monomer mixture was placed in a round bottom flask, to which P₆₆₆₁₄DPAS (0.893 g (1000 mM) and 0.0893 g (100 mM) for films **2-1** and **2-2**, respectively, Figure 2-3-1b) or DPA (0.033 g (100 mM) and 0.330 g (1000 mM) for films **2-3** and **2-4**, respectively, Figure 2-3-1b), 1.0 mL of a dichloromethane solution of PtOEP (0.1 mM), and a catalytic amount of tetrabutylphosphonium *O,O*-diethylphosphorodithioate were added and uniformly dispersed. Dichloromethane was removed under reduced pressure to produce the liquid precursor.

Thermal curing of the film was conducted according to the following procedure in air. A thickness-controlled silicone resin spacer (Tigers Polymer Co., product number; SR-50, thickness; 1 mm, 0.2 mm, or 0.05 mm) was placed on a release-molded quartz glass (40 mm² square). About 1.0 g of the liquid was dropped on the glass and sandwiched using another mold glass, and heated in an incubator. The thermal curing process consists of heating at 100 °C for 2 h, then the temperature is raised to 150 °C (50 °C/hour) and held at this temperature for 5 h, followed by cooling to room temperature over 8 h (−15 °C/hour). The glasses and spacer were peeled off, and the cured epoxy resins are obtained as free-standing solid films.

Sample preparation in the deaerated condition was performed by applying freeze-pump-thaw cycling of the precursor liquid 3 times and by preparing the sandwiched specimens as mentioned above, followed by thermal curing conducted on a hot plate in an N₂-filled glovebox (oxygen concentration <0.02 ppm). Thereafter, the periphery of the sandwiched glass samples was sealed by a sealant.

2-3 Results and Discussion

2-3-1 Preparation and Physical Properties of the Films.

Among many polymer resins, the combination of the bis-epoxide and acid anhydride monomers shown in Figure 2-3-1a was chosen due to the following advantages. First, the combination of hydrogenated bisphenol A-glycidyl ether and 4-methyl(hexahydro)phthalic anhydride/-(hexahydro)phthalic anhydride is widely used in the sealing of LEDs in the industry because of its high oxygen and moisture blocking ability.⁴⁶ Second, they are thermally cross-linkable without using initiators such as radicals, acids, or bases that may damage the dispersed UC chromophores. Third, chromophores are uniformly dispersed in the liquid resins before curing, which can be processed through spin coating, imprinting, injection molding, and other available methods to any shapes suitable for applications. Moreover, the mixtures are thermally cross-linked above 100 °C without segregation. The resulting cured resin exhibits a T_g above room temperature.

The sensitizer (PtOEP) and emitter (P_{66614} DPAS or DPA) were added to the resin precursor, followed by the thermal curing at 150 °C. We employed the phosphonium-based reaction promoter and emitter because of their chemical resistance to oxidation that causes the yellowing of the resins. Thin films with a thickness of 0.05 mm were mostly used to avoid the inner filter effect. The concentration of PtOEP was fixed at 0.1 mM. Two emitter concentrations of 100 and 1000 mM were tested for both P_{66614} DPAS and DPA. The obtained four films are referred to as films **2-1–4**, and their compositions and pictures are shown in Figure 2-3-1b. While DPA can be uniformly dispersed in the film at the concentration of 100 mM (Figure 2-3-1b, film **2-3**), DPA reached saturation solubility at 1000 mM, causing segregation of the precipitates in the film (Figure 2-3-1b, film **2-4**). In stark contrast, P_{66614} DPAS dispersed uniformly even at the high concentration of 1000 mM, forming a transparent film (Figure 2-3-1b, film **2-1**). When the neutral DPA covalently connected with long alkyl chains was used,⁴⁸ the liquid DPA and the epoxy film were completely phase-separated during the thermal curing. Therefore, both long alkyl chains and ionic structure are important for the good dispersibility of emitters in the epoxy resins. The condensation reaction between the bis-epoxy and phthalic dianhydride monomers entirely occurred in film **2-1**, as confirmed by FT-IR spectra (Figure 2-3-2).

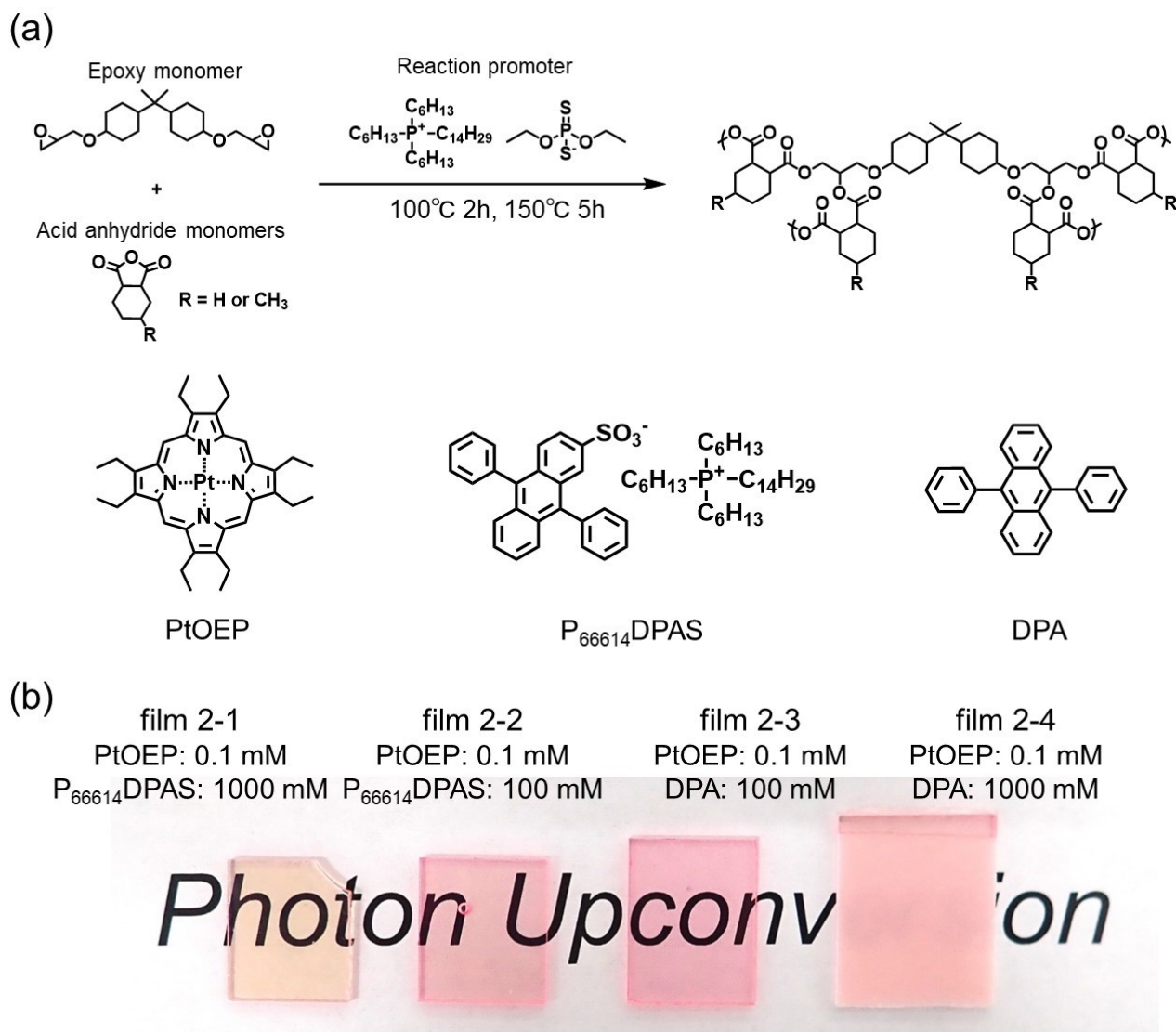


Figure 2-3-1. (a) Chemical structures of the epoxy monomer, acid anhydride monomer, and thermal cure promoters, PtOEP, DPA, and P_{66614} DPAS. Chemical reaction scheme for the epoxy monomer and acid anhydride monomers is also shown. (b) A photograph of the thermally cured films with different chromophore compositions. Film thickness, 1.0 mm.

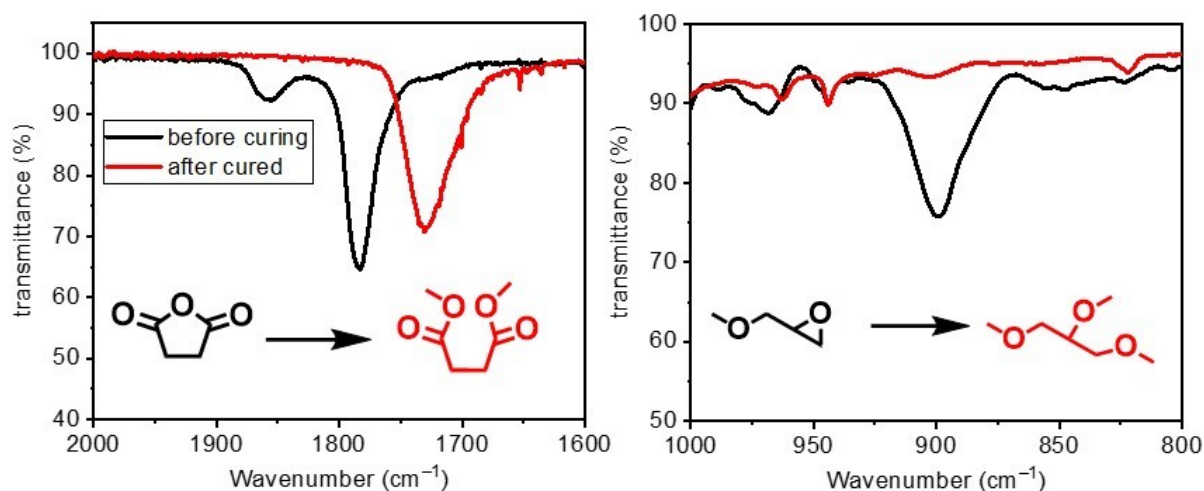


Figure 2-3-2. FT-IR spectra of the liquid precursor before curing (dark line) and cured film **2-1** (red line). The graph on the left displays the shift of the C=O stretching peak from acid anhydride (1786 cm^{-1}) to the ester (1730 cm^{-1}), whereas that on the right shows disappearance of the epoxy C—C asymmetric absorption (900 cm^{-1}).

The glass transition temperatures T_g of the transparent films **2-1–3** were determined by differential scanning calorimetry (DSC, Figure 2-3-3). A cured pristine epoxy film without TTA chromophores showed a T_g at $125\text{ }^{\circ}\text{C}$. Meanwhile, the UC chromophores-doped films exhibited a decrease in T_g values, which implies reduced cross-linking density. The T_g value of film **2-3** containing 100 mM of DPA decreased to $115\text{ }^{\circ}\text{C}$. Lower T_g values of $102\text{ }^{\circ}\text{C}$ and $31\text{ }^{\circ}\text{C}$ were observed for films **2-2** and **2-1**, which contain 100 and 1000 mM $\text{P}_{66614}\text{DPAS}$, respectively. The observed decreases in T_g for $\text{P}_{66614}\text{DPAS}$ -containing resins reflects the interactions between $\text{P}_{66614}\text{DPAS}$ and the polymer networks in the films. Importantly, film **2-1** showed no sign of glass transition at $-24\text{ }^{\circ}\text{C}$ in the DSC curve, which is characteristic of neat $\text{P}_{66614}\text{DPAS}$. These observations support that the ionic liquid $\text{P}_{66614}\text{DPAS}$ is well dispersed in film **2-1** without phase separation of the bulk domains. The absence of phase-separated bulk $\text{P}_{66614}\text{DPAS}$ in the cured film **2-1** was also supported by X-ray diffraction (XRD) analysis (Figure 2-3-4). The neat $\text{P}_{66614}\text{DPAS}$ exhibited a peak at 0.38° ($17.0\text{ \AA}$), which has been assigned to the separation between the strands of the continuous ionic networks as reported in our previous studies.^{47, 49} The epoxy resin without the UC chromophores showed a weak halo at 0.48°

(13.2 Å). Meanwhile, film **2-1** shows a new peak at 0.42° (15.3 Å), and the peaks of neat P₆₆₆₁₄DPAS and pristine epoxy resin (without UC chromophores) were not observed for film **2-1** containing 1000 mM of P₆₆₆₁₄DPAS. These results indicate that the emitter P₆₆₆₁₄DPAS and epoxy polymer networks are uniformly mixed without phase separation.

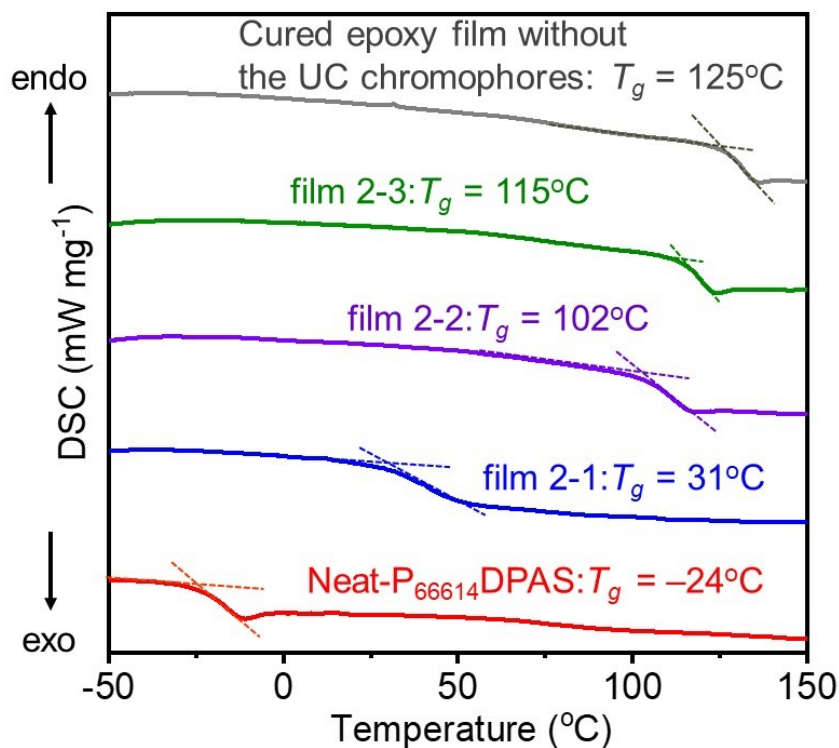


Figure 2-3-3. DSC thermograms of the cured films (film **2-1**, **2-2**, **2-3** and the epoxy resin without the UC chromophores) and the neat P₆₆₆₁₄DPAS (2nd cycle, scan rate: 10 °C min⁻¹, N₂ atmosphere).

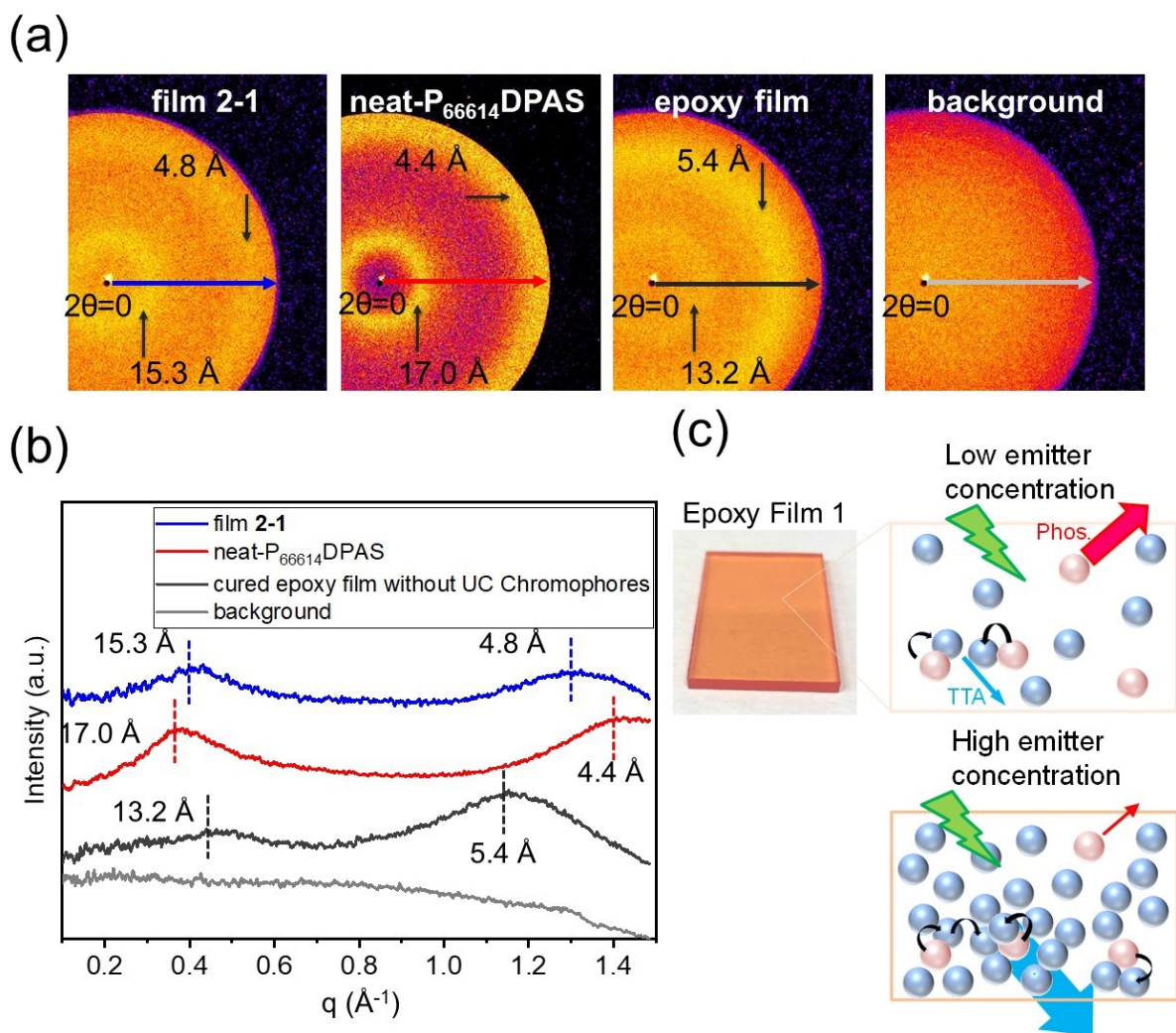


Figure 2-3-4. X-ray profile of the films: (a) two-dimensional pictures of the films (film **2-1**, neat-P₆₆₆₁₄DPAS, cured resin without chromophores and background). These indicate that the film is in a bulk state since the diffraction patterns are isotropic from the center. (b) One-dimensional XRD patterns of the films, with the blue line from film **2-1** containing 1000 mM of P₆₆₆₁₄DPAS exhibits peaks at 15.3 Å and 4.8 Å. The red line representing the neat-P₆₆₆₁₄DPAS showing peaks at 17.0 Å and 4.4 Å, whereas the dark line representing the film without chromophores displays peaks at 13.2 Å and 5.4 Å, while the gray line represents the background. The dimensions were calculated from $d = (2\pi/q)$. (c) Schematic representation of the TTA-UC in the film with low and high emitter concentration. These demonstrate that the TTA-UC occurred in uniformly mono-dispersed chromophores.

The rigid nature of film **2-1** ($[P_{66614}DPAS] = 1000 \text{ mM}$) at room temperature was further characterized by dynamic mechanical analysis (DMA) measurements (Figure 2-3-5). A transition in DMA $\tan\delta$ value was observed for film **2-1** at around 62°C , indicating that the storage modulus is larger than the loss modulus at room temperature. The DSC and DMA results confirm that the cured films doped with UC chromophores are mechanically rigid at room temperature.

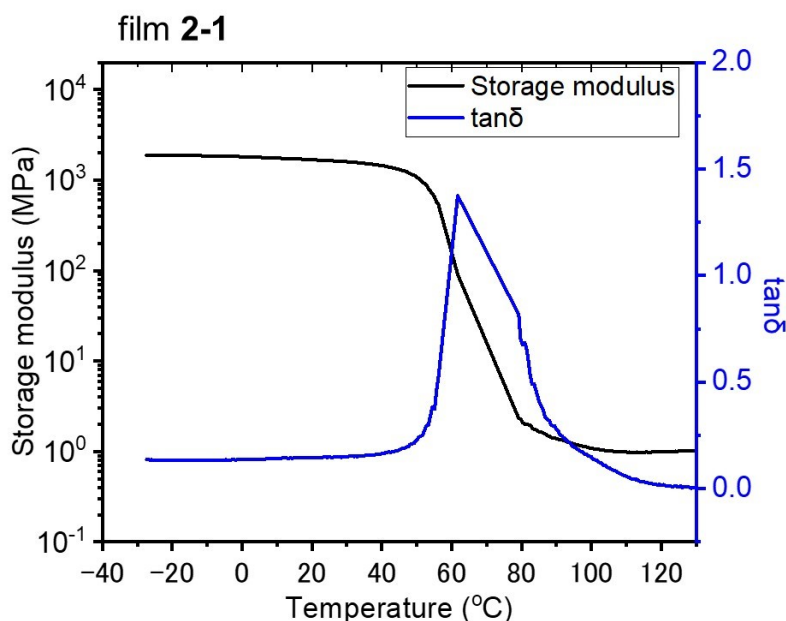


Figure 2-3-5. Temperature dependence of the storage modulus and loss tangent for film **2-1**. The thermal gradient was $10^\circ\text{C min}^{-1}$, whereas the measurement frequency was 1.0 Hz .

2-3-2 Photoluminescence Properties of the Films

Figure 2-3-6 shows UV-vis absorption spectra and fluorescence spectra obtained for film **2-1**, neat $P_{66614}DPAS$, and a dichloromethane solution of $P_{66614}DPAS$ (concentration, 0.1 mM). The dichloromethane solution of $P_{66614}DPAS$ exhibited $\pi-\pi^*$ vibronic absorption peaks at 357, 375, and 395 nm and fluorescence peaks at 422 and 434 nm, respectively. Meanwhile, neat- $P_{66614}DPAS$ showed a broadened absorption spectrum with slightly red-shifted peaks at 357.5, 376, and 396 nm as compared with the dichloromethane solution, indicating the presence of weak interchromophore interactions. The absorption spectrum of film **2-1** showed similar peak positions (358.5, 376.5, and 396 nm) to those of neat $P_{66614}DPAS$, but with a little peak narrowing. This comparison implies that

the interchromophore interactions are slightly weakened in film **2-1** as compared with those in the neat ionic liquid. These spectral observations agree well with the picture of homogeneous mixing of P₆₆₆₁₄DPAS in the film. In fluorescence spectra, the 0–0 fluorescence peak at 422 nm is observed in dichloromethane solution, while it is weakened and disappeared for neat P₆₆₆₁₄DPAS and film **2-1**, respectively. These changes are ascribable to the inner filter effect that depends on the sample's concentration and thickness. Meanwhile, the neat P₆₆₆₁₄DPAS and film **2-1** showed a peak around 440 nm close to that observed for the dichloromethane solution, and red-shifted broad emission due to excimer formation was not observed in these condensed samples.

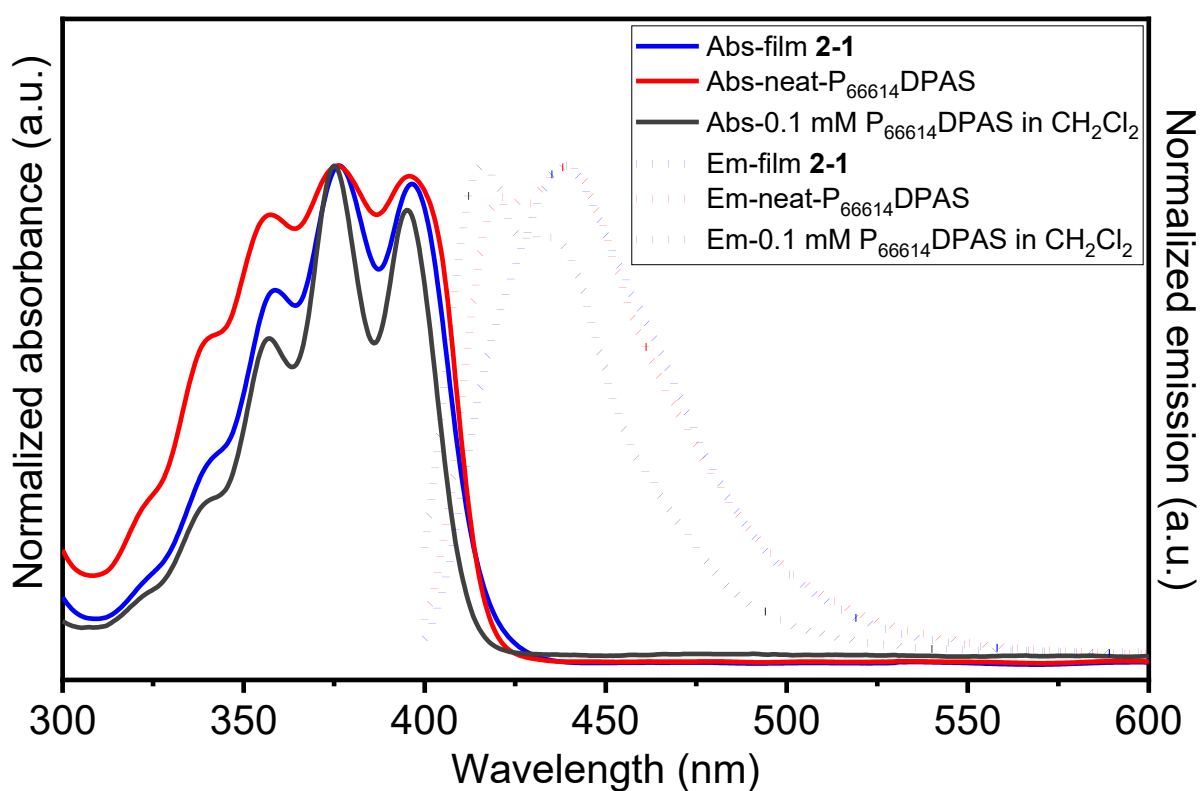


Figure 2-3-6. UV–vis spectra (solid line) and emission spectra (dashed line) of film **2-1**, neat-P₆₆₆₁₄DPAS, and 0.1 mM P₆₆₆₁₄DPAS in dichloromethane solution. The excitation wavelength was $\lambda_{\text{ex}} = 365$ nm.

Photoluminescence spectra were obtained for films **2-1**, **2**, and **3** under excitation at 532 nm in ambient conditions. The scattered laser light was removed by a 520–540 nm notch filter. Upconverted emission peaks of the emitter at around 440 nm were observed for all three films in air

(Figure 2-3-7). Since films **2-2** and **2-3** showed a strong phosphorescence of PtOEP at 650 nm, it was necessary to additionally use a 510 nm short-pass filter for removing the phosphorescence signals. The signals above 700 nm in films **2-2** and **2-3** are due to the remaining PtOEP phosphorescence that could not be removed by the 510 nm short-pass filter. The phosphorescence of films **2-2** and **2-3** was also observed by eyes under irradiation at 532 nm even with the 510 nm short-pass filter (Figure 2-3-7b). On the other hand, under an identical condition, film **2-1** showed a blight blue upconverted emission (Figure 2-3-7b).

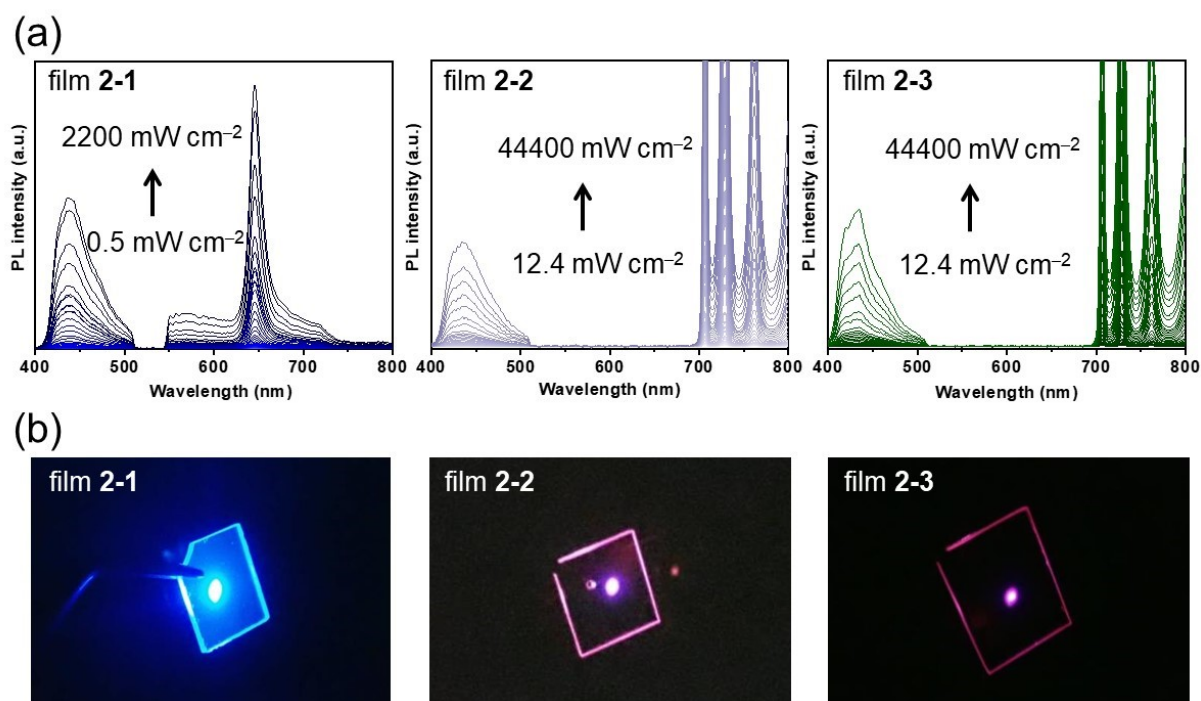


Figure 2-3-7. (a) Photoluminescence (PL) spectra of films **2-1**, **2**, and **3** at different excitation intensities of a 532 nm laser. A 520–540 nm notch filter was used to remove the scattered excitation light. In addition, a 510 nm short-pass filter was used to remove the strong PtOEP phosphorescence only for films **2-2** and **2-3**. The thickness of each film was 0.05 mm. (b) Photographs of films **2-1**, **2**, and **3** under the 532 nm laser irradiation taken through the 510 nm short-pass filter.

Importantly, there is no decrease in the UC emission intensity below T_g , indicating that TTA-UC occurs by energy migration rather than molecular diffusion in the resins (Figure 2-3-8). Using the density of film **2-1** (1.09 g mL^{-1}), the average distance between the DPAS emitters in film **2-1** is estimated as 0.87 nm, which is shorter than the Dexter radius of 0.91 nm for DPA.⁵⁰ The distance

between the emitters is close enough that the triplet energy can effectively migrate between emitters and cause TTA.

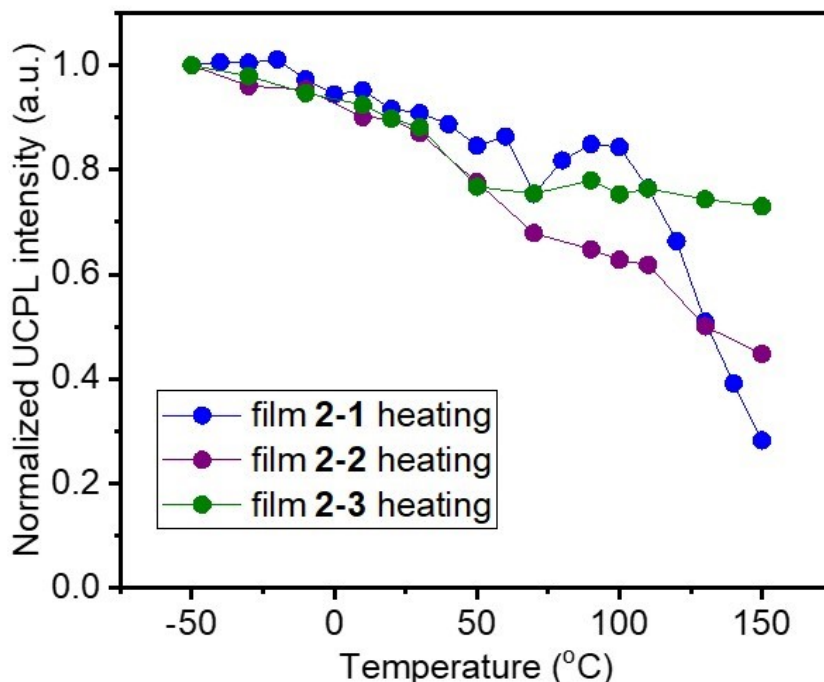


Figure 2-3-8. Temperature dependence of the TTA-UC emission intensity for film **2-1** (blue), film **2-2** (purple), and film **2-3** (green). The laser intensity at 532 nm was kept at 1000 mW cm⁻². The UC emission intensity is normalized to the value at -50 °C.

The sensitizer-to-emitter TET efficiency was quantified by measuring phosphorescence quantum yields of films **2-1–3** and a cured film containing only PtOEP without an emitter (film **2-5**). The TET efficiency Φ_{TET} was estimated by the following equation,

$$\Phi_{\text{TET}} = 1 - \frac{\Phi_{\text{P}}}{\Phi_{\text{P},0}} \quad (2-1)$$

where Φ_{P} and $\Phi_{\text{P},0}$ represent phosphorescence quantum yields of the film with and without the emitter, respectively. As expected from the strong phosphorescence intensity, low Φ_{TET} values of 6.6 and 4.9% were observed for films **2-2** and **2-3** (Table 2-3-1). In contrast, film **2-1** showed a high Φ_{TET} value of 92.8%. In the rigid epoxy films where the UC chromophores cannot diffuse, the close (<0.87 nm) sensitizer-emitter distance is satisfied only at the high emitter concentration of 1000 mM in film **2-1**, which allowed the efficient TET through the Dexter mechanism. Note that the molecular dispersion

of PtOEP in the cured films was confirmed by the absence of phosphorescence of PtOEP aggregates at 780 nm (Figure 2-3-9).

Table 2-3-1. The Absolute fluorescence ($\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{em}} = 400\text{--}600 \text{ nm}$) and phosphorescence ($\lambda_{\text{ex}} = 532 \text{ nm}$, $\lambda_{\text{em}} = 570\text{--}830 \text{ nm}$) quantum yields of the films.

films	contents in the film			quantum yields		Φ_{TET} (%)
	PtOEP (mM)	P ₆₆₆₁₄ DPAS (mM)	DPA (mM)	fluorescence	phosphorescence	
film 2-1	0.1	1000			2.8	92.8
film 2-2	0.1	100			37.2	4.9
film 2-3	0.1		100		36.5	6.6
film 2-5	0.1				39.1	
film 2-6		1000		59.4		
film 2-7		100		80.7		
film 2-8			100	79.5		

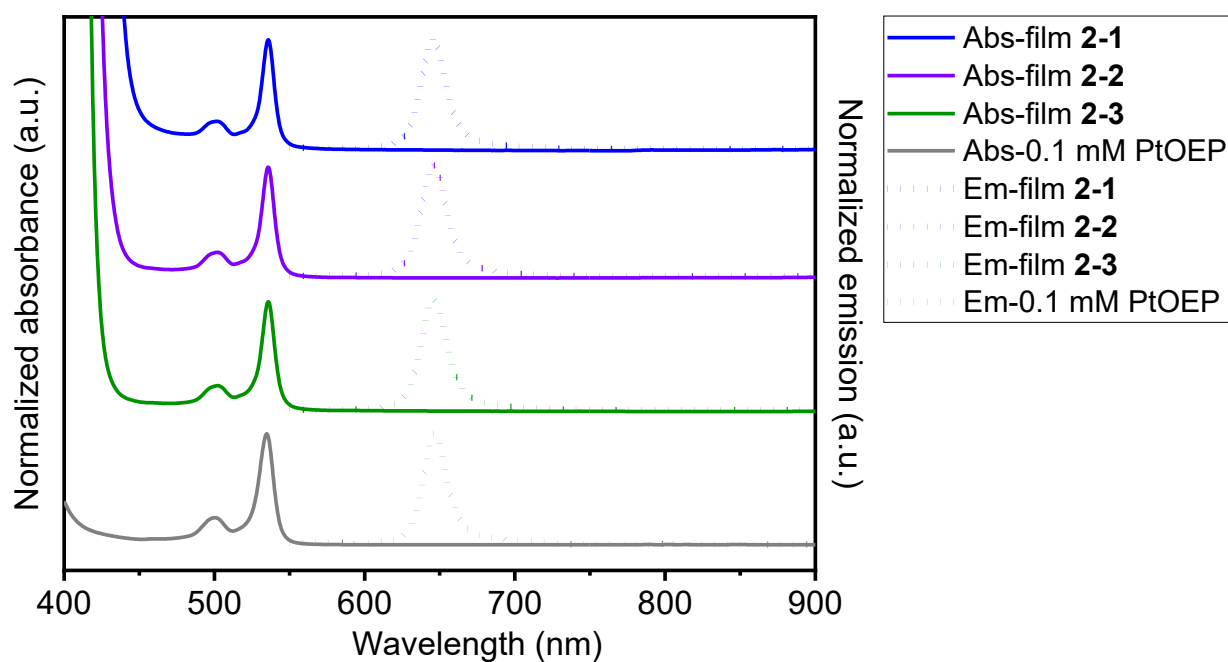


Figure 2-3-9. UV-vis absorption spectra (solid line) and phosphorescence spectra (dashed line) of films 2-1–3, and 0.1 mM PtOEP in dichloromethane solution. The excitation wavelength was $\lambda_{\text{ex}} = 532 \text{ nm}$.

We then determined the TTA-UC efficiencies η_{UC} for films **2-1**, **2**, and **3** by the relative method. The maximum η_{UC} is normalized to 100% by multiplying the TTA-UC quantum yield (50% maximum) by 2. The η_{UC} of each film was determined relative to Nile red in a cured epoxy film according to the following equation,

$$\eta_{UC} = 2\Phi_{std} \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{UC}}} \right) \left(\frac{E_{UC}}{E_{std}} \right) \left(\frac{I_{std}}{I_{UC}} \right) \left(\frac{n_{UC}}{n_{std}} \right)^2 \quad (2-2)$$

where Φ , A , E , I and n represent the quantum yield, absorbance at 532 nm, integrated photoluminescence spectral profile, excitation intensity, and the refractive index of the films, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. Since the standard and the UC films are based on identical epoxy resin, the refractive index ratio is approximated as 1. The absolute fluorescence quantum yield of Nile red in the cured film was 0.82.

As can be seen in Figure 2-3-10, films **2-2** and **2-3** containing 100 mM of the emitter showed low η_{UC} values of about 0.09%. This should be partly due to the poor TET efficiency. Films **2-2** and **2-3** showed almost the same behavior, suggesting that the UC characteristics are independent of the emitter structure and are rather influenced by the low emitter concentration. Meanwhile, film **2-1** that contains a 1000 mM emitter showed a much higher η_{UC} of 3.8% (Figure 2-3-10). This is a significantly high value as a rigid TTA-UC system, and comparable to the previously reported high η_{UC} of 5.0% in the hyper cross-linked polymer nanoparticles.^{44,45} These results indicate that the high emitter concentration (1000 mM) is necessary for the simultaneous pursuit of efficient sensitizer-to-emitter TET and the subsequent TEM and TTA among emitters in molecular-diffusion-free rigid films. It should also be noted that a high fluorescence quantum yield of 59.4% was maintained in a cured film containing the high-concentration (1000 mM) P₆₆₆₁₄DPAS (Table 1), indicating the absence of severe fluorescence quenching by chromophore aggregation or decomposition.

Importantly, almost no difference was observed between the η_{UC} values of the films prepared in air and those prepared and sealed in the glovebox (Figure 2-3-10). These results indicate that the diffusion of molecular oxygen in the films is significantly suppressed by the tightly cross-linked

polymer networks. It is notable that the high oxygen blocking ability of the epoxy resin is well maintained even at the high emitter concentration of 1000 mM (film **2-1**).

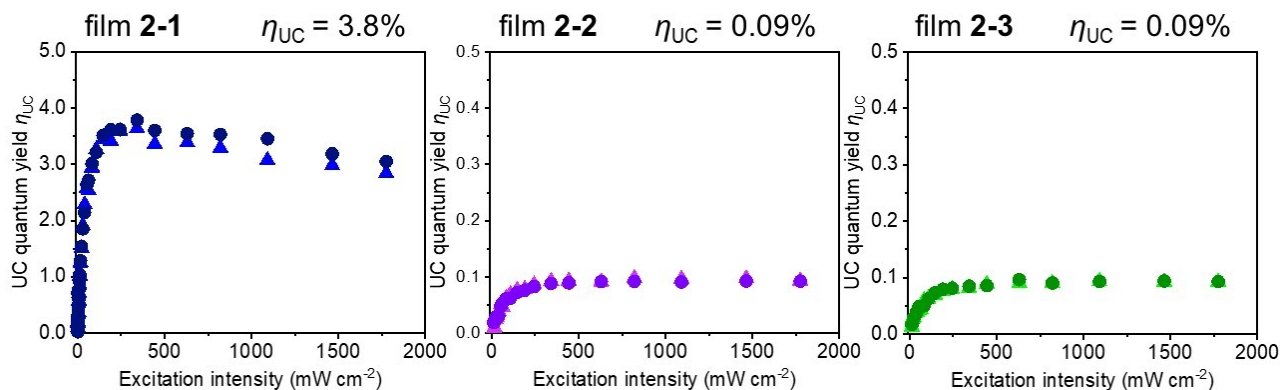


Figure 2-3-10. TTA-UC efficiency η_{UC} of the films (left: film **2-1**; middle: film **2-2**; and right: film **2-3**, respectively) prepared in air (circles) and prepared and sealed in the glovebox (triangles) measured as a function of excitation intensity at an excitation wavelength of 532 nm. The η_{UC} of each film was determined by the relative method. The thickness of the films, 0.05 mm.

The threshold excitation intensity I_{th} was estimated from the excitation intensity dependence of the UC emission intensity at 440 nm. In a general TTA-UC system, the dependence of the UC photoluminescence intensity on the excitation intensity changes from second-order to linear.⁵⁰⁻⁵³ This typical dependence was also observed for these films. For films **2-2** and **2-3** containing 100 mM of the emitters, the intersections of the tangent lines with slopes 2 and 1 in the logarithmic plots (I_{th}) were both 87 mW cm⁻² (Figure 2-3-11). Meanwhile, a lower I_{th} of 40 mW cm⁻² was observed for film **2-1** containing 1000 mM of P₆₆₆₁₄DPAS. The higher TET efficiency in film **2-1** than those in films **2-2** and **2-3** should contribute to this difference.

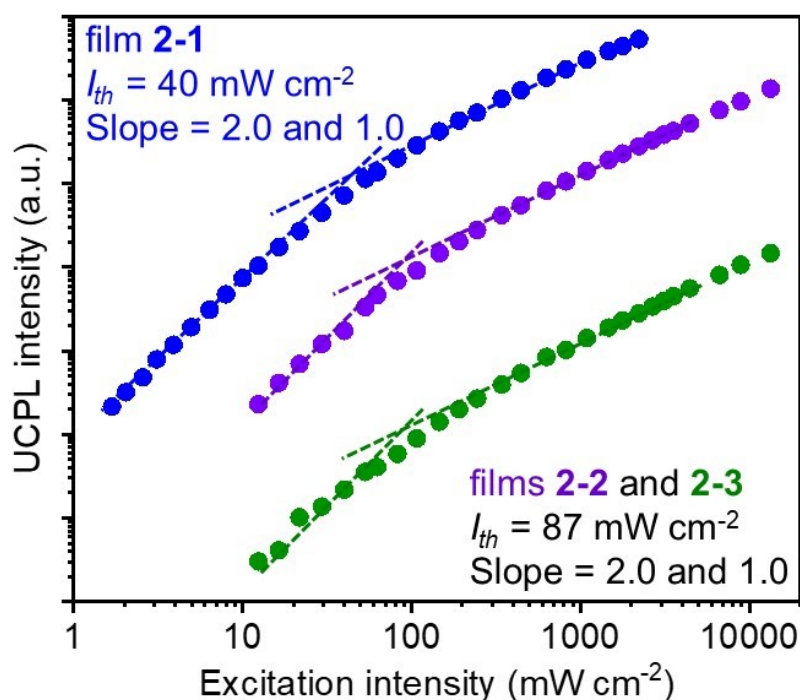


Figure 2-3-11. Dependence of UCPL intensity at $\lambda = 440 \text{ nm}$ on the excitation intensity of films **2-1** (blue), **2-2** (purple), and **2-3** (green). The values in the graph represent the slope and I_{th} values.

Notably, a significantly long emitter triplet lifetime τ_A of 17.8 ms was obtained by fitting a UC emission decay of Film **1** with the known relationship of $I_{UC}(t) \propto e^{(-2t/\tau_A)}$ (Figure 2-3-12).⁵⁴ The UC decays of films **2-2** and **2-3** were not obtainable due to the very weak UC fluorescence intensity. The observed very long lifetime in film **2-1** should reflect the suppressed molecular motion in the rigid polymer networks, which showed T_g higher than room temperature. The long triplet lifetime should be beneficial for triplet exciton diffusion among the emitter molecules, contributing to achieving the relatively high η_{UC} and low I_{th} values.

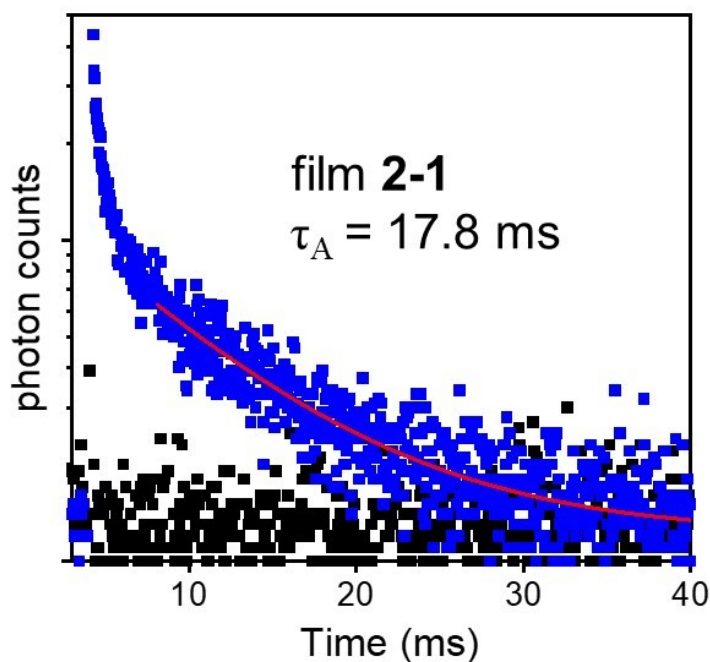


Figure 2-3-11. Photoluminescence decay of film **2-1** (blue, film thickness of 0.05 mm) at 440 nm under pulsed excitation at 532 nm. Single exponential fitting of the tail part (red line) provides the triplet lifetime of 17.8 ms. The instrumental response function (IRF) is shown as black squares.

In order to confirm the stability of the cured films, we measured the UC efficiency of the films stored at room temperature under air for 1.5 years. Significantly, there was almost no change in the UC efficiency compared to the values measured immediately after film formation (Figure 2-3-12a). Additionally, the absorption spectra of PtOEP in the films were consistent before and after the storage (Figure 2-3-12b), indicating that no sensitizer aggregation nor degradation have occurred in the film over time. These results confirm that excellent long-term stability can be achieved by the rigid epoxy matrices. Under continuous laser irradiation, the UC intensity of films **2-2** and **2-3** with high T_g was well maintained, but a gradual decrease was observed for film **2-1** (Figure 2-3-12c). It is suggested that high T_g of films **2-2** and **2-3** contributes to the stability of the UC emission under continuous laser irradiation. It is important to develop resins with high T_g as well as high emitter concentration in the future for better stability.

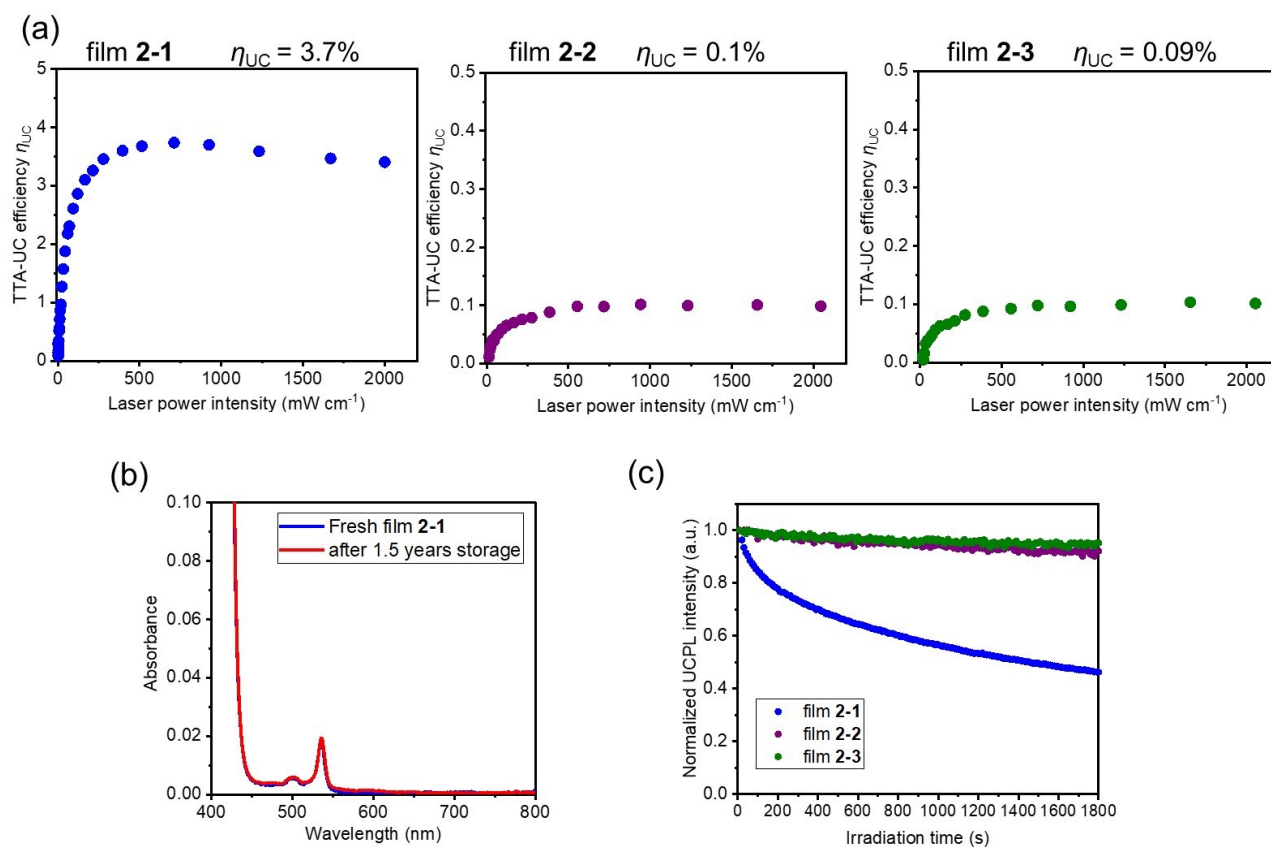


Figure 2-3-12. (a) TTA-UC efficiency η_{UC} of the films (left: film **2-1**; middle: film **2-2**; and right: film **2-3**) measured as a function of excitation intensity at an excitation wavelength of 532 nm and (b) UV-vis absorption spectra of the film **2-1** before (blue line) and after (red line) after long-term storage at room temperature under air for 1.5 years. (c) UC luminescence intensity of the film **2-1** (blue), film **2-2** (purple), and film **2-3** (green) under continuous laser irradiation at 532 nm (1000 mW cm^{-2} , 1800 sec).

2-4 Conclusion

In this chapter, the first example of rigid epoxy resins was developed and showed the efficient TTA-UC in air. The rigid and transparent epoxy films containing UC chromophores were obtained by simply heating the liquid mixture of the monomers and UC chromophores. The significance of the present study is three-fold: first, in contrast to DPA, the common emitter that aggregates at the high concentration in the film, the ionic liquid emitter P₆₆₆₁₄DPAS having phosphonium ions with long alkyl chains are homogeneously dispersed without phase separation up to the very high concentration (1000 mM) in the cross-linked rigid epoxy film. This high concentration of the emitter is found to be necessary for efficient sensitizer-to-emitter TET and triplet energy migration among emitters in the rigid system. Second, thanks to the high oxygen blocking ability of the employed epoxy resin that is widely used as sealing materials for LEDs, the cured bulk films show the highly air-stable TTA-UC. Third, the adaptive dispersion nature of ionic liquid emitters – that exhibit efficient triplet energy migration characteristics and miscibility with sensitizer molecules – in the rigid, cross-linked epoxy resins is advantageous to avoid bulk phase separation. It renders the UC chromophores dispersed in the rigid chromophore environment, leading to a surprisingly long emitter triplet lifetime of 17.8 ms. The high TET efficiency and the long emitter triplet lifetime allows effective triplet exciton diffusion and annihilation; they result in the significantly high TTA-UC efficiency ($\eta_{UC} = 3.8\%$), low threshold excitation intensity ($I_{th} = 40 \text{ mW cm}^{-2}$), and excellent performance as a rigid TTA-UC system. This work overcomes the critical challenge of achieving efficient and air-stable TTA-UC in technologically promising rigid, thermally stable, and transparent films that can be manipulated in a large area. As the present air-stable, transparent TTA-UC epoxy resins are prepared from the liquid mixtures, they can be processed into any shape by available techniques such as spin-coating, injection molding and imprinting. It highlights the potential for a wide range of applications in many disciplines.

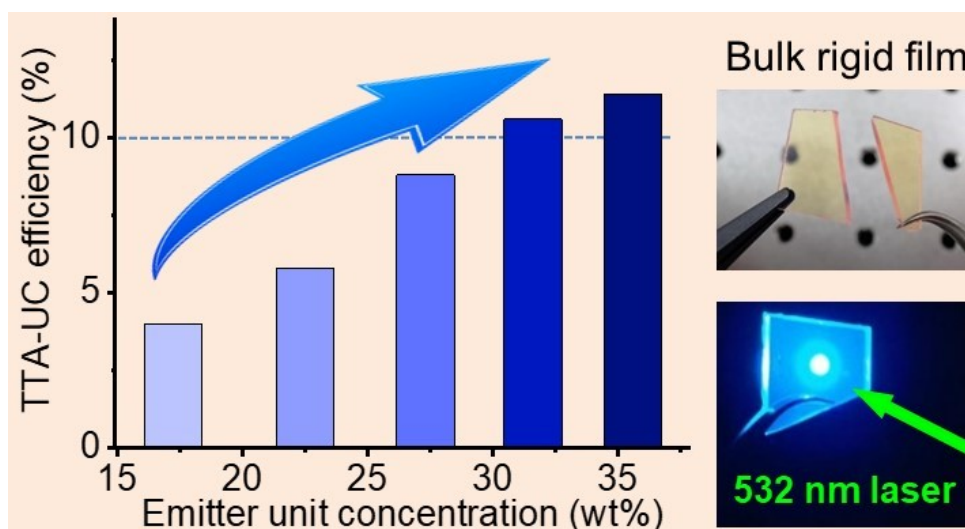
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Chapter 3 Design Guidelines for Rigid Epoxy Resins with High Photon Upconversion Efficiency: Critical Role of Emitter Concentration



Abstract

The development of rigid, transparent, air-stable, and moldable materials with a high TTA-UC efficiency remains a challenging issue for the practical application of TTA-UC. In addition to the noncovalent introduction of ionic liquid emitters into the epoxy network, we covalently introduce emitters with polymerization sites to increase the emitter concentration to 35.6 wt% and achieve a TTA-UC quantum yield Φ_{UC} of 5.7% (theoretical maximum: 50%), which corresponds to a TTA-UC efficiency η_{UC} of 11.4% (theoretical maximum: 100%) and is the highest ever achieved for a rigid polymer material. More importantly, the high emitter concentration speeds up the triplet diffusion and suppresses the back energy transfer from the emitter to sensitizer so that the sensitized emitter triplet can be effectively utilized for TTA. The generality of our finding is also confirmed for epoxy resins of similar emitter unit concentrations without the ionic liquid. This work provides important design guidelines for achieving highly efficient TTA-UC in rigid solid materials, which has been very difficult to achieve in the past. Furthermore, the solid-state TTA-UC exhibits high air stability, reflecting the high oxygen barrier performance of epoxy resins. The high moldability of epoxy resins allows the construction of upconversion materials with complex geometries at nano- to macroscopic scales.

3-1 Introduction

Photon upconversion (UC) is a technology that converts low-energy photons to higher-energy photons.^{1–17} In particular, TTA-UC can convert a low-intensity light such as sunlight, which is promising for various applications such as photocatalysis^{18,19} photovoltaics,^{11,20–24} bioimaging,^{25–27} and optogenetics.²⁸ While efficient TTA-UC can be achieved in solution due to the fast molecular diffusion, it is strongly desired to develop solvent-free solid upconverters for practical applications. There have been pioneering studies on TTA-UC in soft polymer matrices with glass transition temperatures (T_g) lower than room temperature.^{18,29–33} However, these systems may suffer from the intrusion of oxygen quenchers and the aggregation of emitters over time.

On the other hand, triplet energy migration (TEM)-based TTA-UC in rigid polymers with T_g higher than room temperature has the potential to offer more stable performances.^{34–37} The difficulty of this method lies in how to disperse the chromophores in the rigid polymer matrices at high concentrations without aggregation. In order for the triplet to diffuse effectively by Dexter energy transfer between emitters, the average distance between emitters should be less than 1 nm.³⁸ Monguzzi and Meinardi et al. reported the TTA-UC with high efficiency ($\eta_{UC} = 7.4\%$) in air-saturated water by introducing high-concentration chromophores into highly cross-linked polystyrene microparticles.^{39,40} Although it had been difficult to develop such a rigid TTA-UC system in bulk, in chapter 2, we have introduced that the ionic liquid emitters composed of 9,10-diphenylanthracene-2-sulfonate anion (DPAS) and trihexyl(tetradecyl)phosphonium cation (P_{66614})⁴¹ could be dispersed up to the high concentration of 1000 mM without aggregation in the rigid epoxy resin and reported that the transparent bulk film showed the relatively high TTA-UC efficiency of $\eta_{UC} = 3.8\%$ in air.⁴² This was also the first example of TTA-UC in epoxy resin, which is used industrially as an encapsulant for LEDs and other devices due to its high oxygen barrier performance. However, further increasing the emitter concentration was difficult because it would soften the resin, and thus a new strategy was needed to improve the TTA-UC efficiency.

In this chapter, we present design guidelines on how to obtain a rigid resin with high TTA-UC efficiency. In addition to the noncovalent introduction of ionic liquid emitter P_{66614} DPAS into the

resin, the emitter unit is also covalently introduced into the epoxy polymer networks. The covalent introduction of the DPA emitter in the resin networks allows us to further increase the total concentration of the DPA unit from the previous 17.2 wt% (1000 mM) to 35.6 wt% (2500 mM) in the rigid epoxy films. The introduction of such ultrahigh concentration of emitters enables not only nearly quantitative triplet energy transfer from the sensitizer to the emitter but also effective triplet exciton diffusion between emitters, resulting in the highest TTA-UC quantum yield Φ_{UC} of 5.7% (theoretical maximum: 50%) and TTA-UC efficiency $\eta_{UC} = 11.4\%$ (theoretical maximum: 100%) for a rigid polymer material. Importantly, the systematic study varying the emitter concentration reveals that the higher emitter concentration allows the triplet to diffuse away from the sensitizer, suppressing the back energy transfer. As a result, the triplet of sensitized emitters can be used for TTA efficiently, leading to the realization of the high TTA-UC efficiency. The generality of our design guidelines is confirmed by the fact that epoxy resins with a similar emitter unit concentration (34.8 wt%) without the ionic liquid P₆₆₆₁₄DPAS also showed similar TTA-UC efficiency η_{UC} of 10.1%. Furthermore, the TTA-UC in epoxy resin is stable in air and can be molded into nano-to-macroscopic structures, indicating its suitability for practical use.

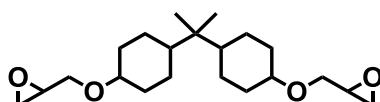
3-2 Experimental Section

3-2-1 Characterization

The density of the cured film was measured by using SHIMADZU AccuPyc II 1340 instrument. The upconversion luminescence emission spectra were recorded on a multichannel detector Otsuka Electronics MCP-9800 instrument with the excitation source using an external, adjustable 532 nm semiconductor laser. The detector was calibrated by using a standard lamp Ocean Optics HL-3 plus-CAL. The diameter of the laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics), with a typical laser size of $1.2 \times 10^{-3} \text{ cm}^2$. The temperature control was conducted with a Linkam 10033L as a temperature control stage, a Linkam LNP94/2 as a liquid nitrogen controller, and a Linkam TMS94 as a temperature controller. Time-resolved fluorescence lifetime measurements were done using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11567-01 (for the phosphorescence and delayed fluorescence lifetime). The quality of the fit was evaluated by fitting parameters χ^2 (<1.2) and visual inspection of the residuals. The ^1H NMR (500 MHz) spectra were measured on a Bruker AscendTM 500 spectrometer using TMS as the internal standard. The LC-MS measurements were performed by an AB SCIEX Triple TOF 5600+ instrument. Elemental analysis was conducted with a J-Science JM10 instrument, and FT-IR spectra were recorded on a SHIMADZU IRAffinity-1S Fourier transform infrared spectrophotometer. Differential scanning calorimetry (DSC) was performed in a NETSCH Japan K.K. DSC 204 F1 Phoenix[®]. Dynamic mechanical analysis (DMA) was done with a T A Instruments Japan Co. Q-800 instrument. The test dimensions of the cured film were 4 mm width, 20 mm length, and 0.2 mm thickness. UV-vis-NIR absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer while fluorescence spectra were measured by using a Hitachi High-Tech Science Co. F-7000 spectrometer. The thickness of spin-coated film was measured with a RYOKOSHA surf coder ET4000A instrument. A 375 nm diode laser (75 mW, RGB Photonics) was used as a 375 nm light source for the temperature dependence of the fluorescence intensity.

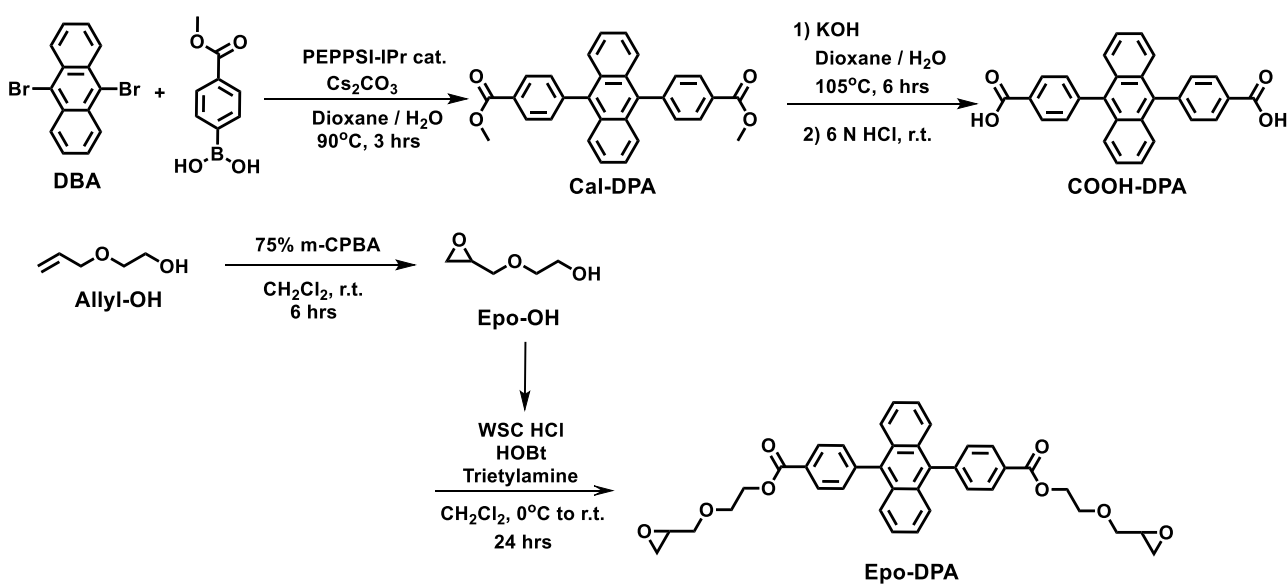
3-2-2 Materials

PtOEP (>98%) was purchased from Aldrich Co. P₆₆₆₁₄DPAS was used as described in the chapter 2. Hydrogenated bisphenol A-glycidyl ether (Epoxy A, the chemical structure is shown in Scheme 3-2-1) was obtained from Mitsubishi Chem. Co. A 4-methyl(hexahydro)phthalic anhydride/(hexahydro)phthalic anhydride mixture was purchased from New Japan Chem. Co., Ltd. Dichloromethane was obtained from Kanto Chem. Co.



Scheme 3-2-1. Chemical structure of the Epoxy A.

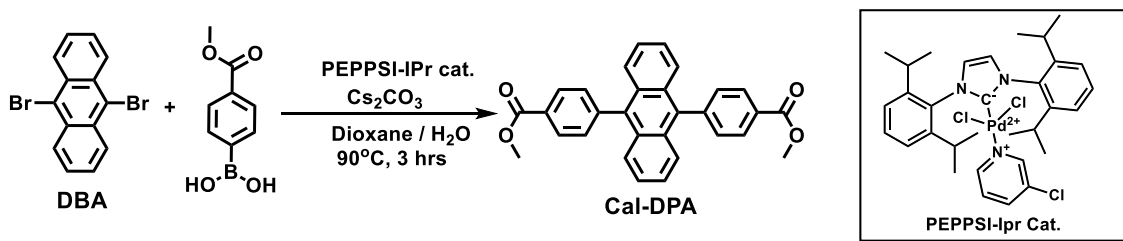
Synthesis of Epo-DPA



Scheme 3-2-2. Total synthetic routes of the Epo-DPA.

All reaction solvents for synthesis and cesium carbonate (Cs_2CO_3) were purchased from Junsei Chem.. 9,10-dibromoanthracene (DBA), [1,3-Bis(2,6-Diisopropylphenyl)imidazole-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSITM-IPr) were purchased from Aldrich Co.. 4-methoxycarbonylphenylboronic acid, ethylene glycol monoallyl ether (Allyl-OH) and triethylamine were purchased from Tokyo Chem. Ind. Co., Ltd.. 6 mol L⁻¹ hydrochloric acid (6 N HCl aq.), potassium hydroxide (KOH), *m*-chloroperoxybenzoic acid (*m*-CPBA), 1-(3-dimethylaminopropyl)-

3-ethylcarbodiimide hydrochloride (WSC HCl) and 1-hydroxybenzotriazole (HOBt) were purchased from FUJIFILM Wako Pure Chem. Co..



Scheme 3-2-3. Synthetic scheme of Cal-DPA.

Synthesis of 9,10-(4-methoxycarbonylphenyl) anthracene (Cal-DPA): In a 2000 mL of 4-neck flask, DBA (24.9 g, 74.0 mmol), 4-methoxycarbonylphenylboronic acid (31.6 g, 162.8 mmol) and 900 mL of 1,4-dioxane were added and stirred under nitrogen atmosphere at 90°C . PEPPSITM-IPr (0.5 g, 0.74 mmol) in 100 mL of 1,4-dioxane and Cs_2CO_3 (53.0 g, 162.8 mmol) in 100 mL of distilled water were added to the mixture respectively and reacted for 3 hours at 90°C until complete disappearance of the DBA (monitored by TLC). After the mixture was cooled to room temperature, 500 mL of distilled water was added with stirring. The precipitate was filtered and washed with distilled water. The precipitate was extracted with CHCl_3 three times. The solvent was removed under reduced pressure and the residue was reprecipitated by acetonitrile to give the Cal-DPA (27.8 g, 62.3 mmol, 84 %).

^1H NMR (500 MHz, CDCl_3) δ : (ppm) = 4.02 (s, 6H), 7.35 (dd, 4H), 7.57 (d, 4H), 7.62 (dd, 4H), 8.29 (d, 4H).

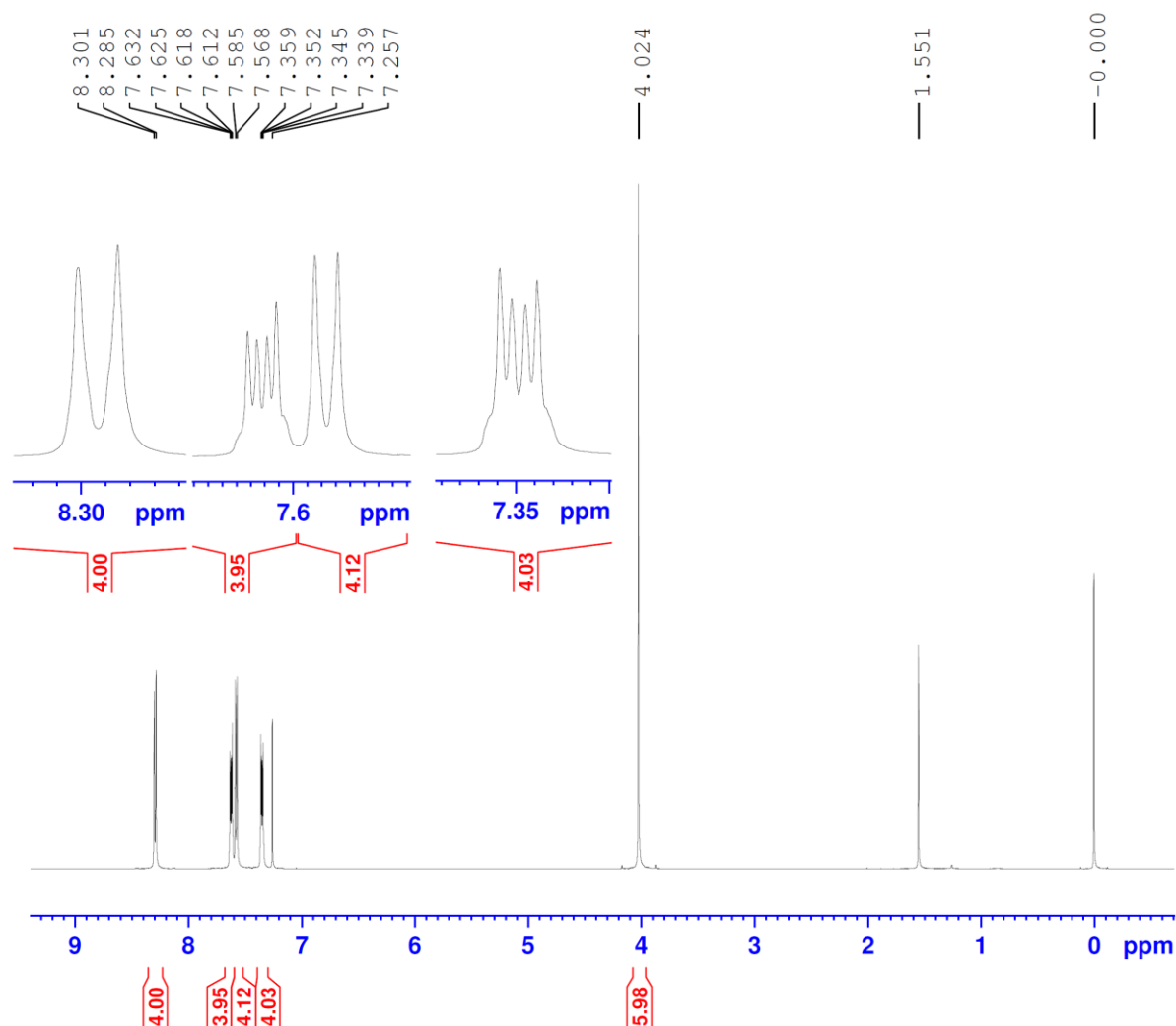
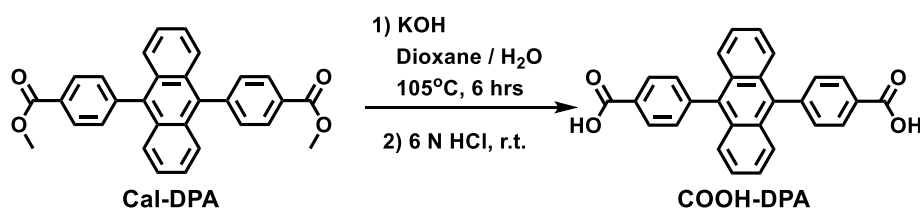


Figure 3-2-1. ¹H NMR spectrum (500 MHz, CDCl₃) of Cal-DPA.



Scheme 3-2-4. Synthetic scheme of COOH-DPA.

Synthesis of 9,10-(4-carboxyphenyl) anthracene (COOH-DPA): KOH (31.4 g, 560 mmol) was dissolved in 100 mL of pure water. It was added to a mixture of Cal-DPA (25.0 g, 56.0 mmol) in 400 mL of 1,4-dioxane. The mixture was stirred under reflux for 6 h until complete disappearance of the Cal-DPA (monitored by TLC). After that, 200 mL of distilled water was added to the residue and cooled to room temperature. 6 N HCl aq. was added to the suspension until the pH value was adjusted

to 2. The precipitate was filtered and washed with water to give the COOH-DPA (23.0 g, 54.9 mmol, 98%). ^1H NMR (500 MHz, dimethylsulfoxide- d_6) 7.45 (dd, 4H), 7.56 (dd, 4H), 7.62 (d, 4H), 8.22 (d, 4H), 13.1 (s, 2H).

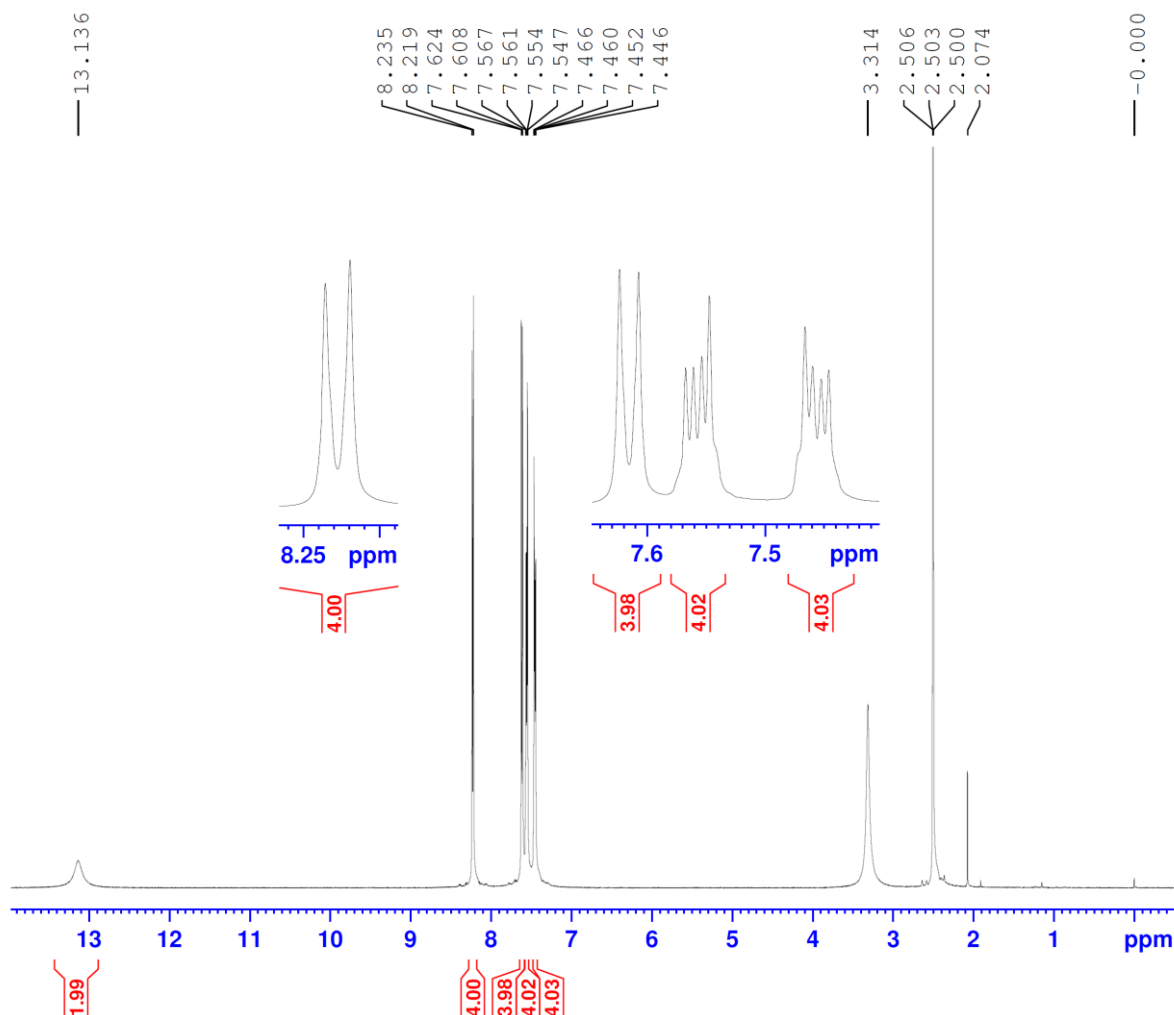
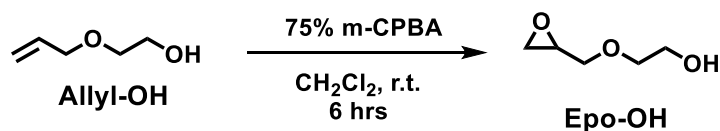


Figure 3-2-2. ^1H NMR spectrum (500 MHz, dimethylsulfoxide- d_6) of COOH-DPA.



Scheme 3-2-5. Synthetic scheme of COOH-DPA.

Synthesis of ethylene glycol monoglycidyl ether (Epo-OH): Allyl-OH (20.4 g, 200 mmol) and *m*-CPBA (70% in water, 59.2 g, 240 mmol) were dissolved in 300 mL of CH_2Cl_2 . The reaction mixture was stirred at room temperature for 6 hours until complete disappearance of the Allyl-OH (monitored by GC). After that, the solvent was removed under reduced pressure. The reacted *m*-CPBA precipitate

was filtered, and the filtrate was purified by flash column chromatography (eluent : ethyl acetate) to give Epo-OH (17.7 g, 150 mmol, 60%). ^1H NMR (500 MHz, CDCl_3) δ : (ppm) = 2.1 (t, 1H), 2.65 (dd, 1H), 2.82 (t, 1H), 3.12 (m, 1H), 3.46 (dd, 1H), 3.61 (m, 1H), 3.66 (m, 1H), 3.75 (q, 2H), 3.83 (dd, 1H).

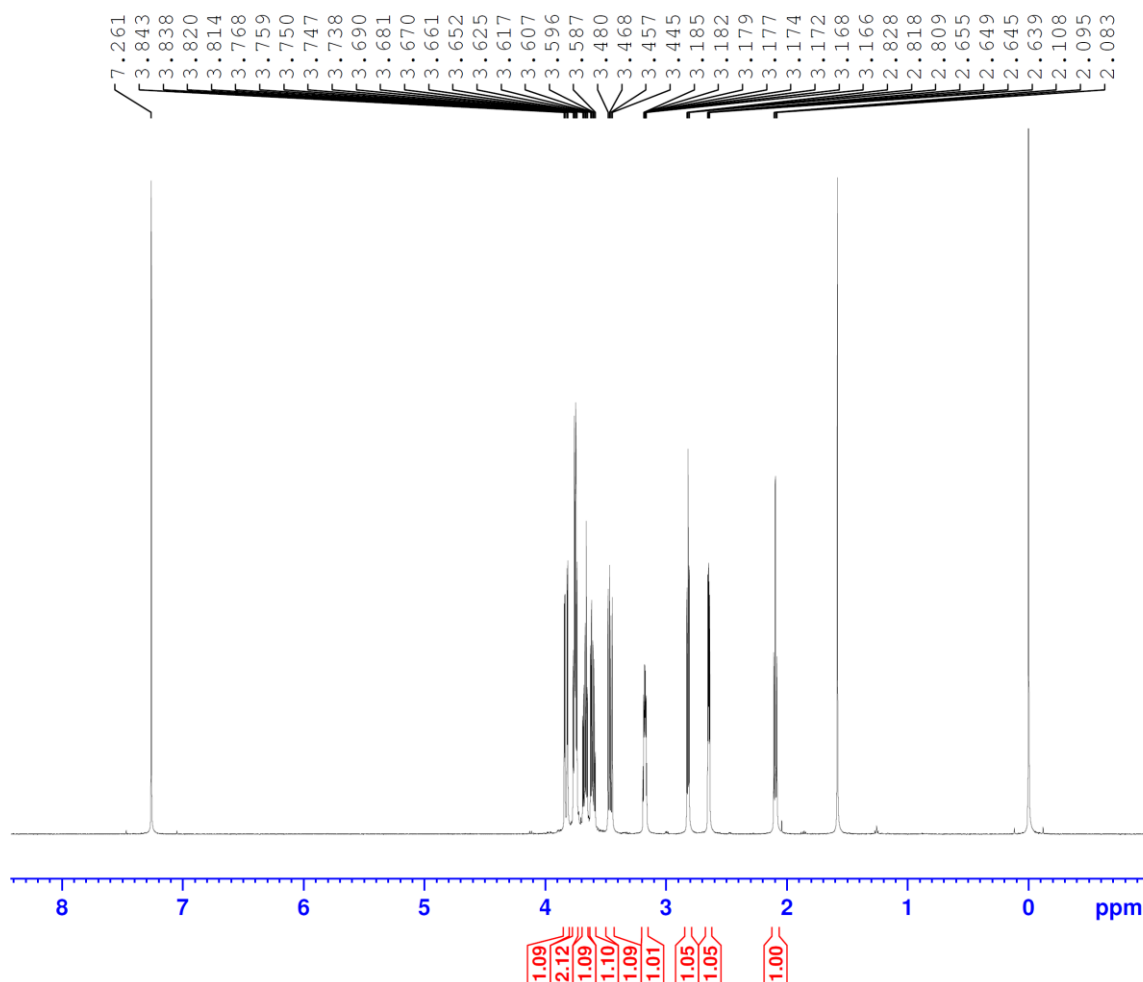
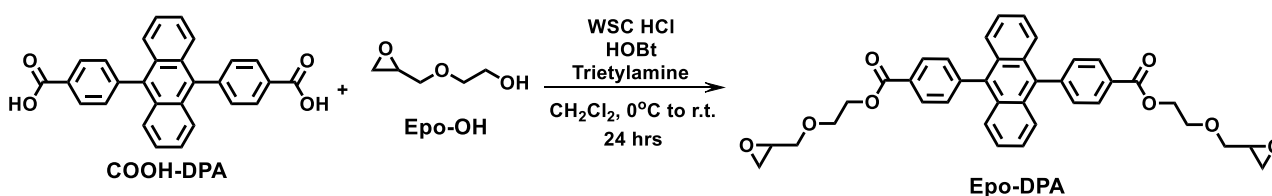


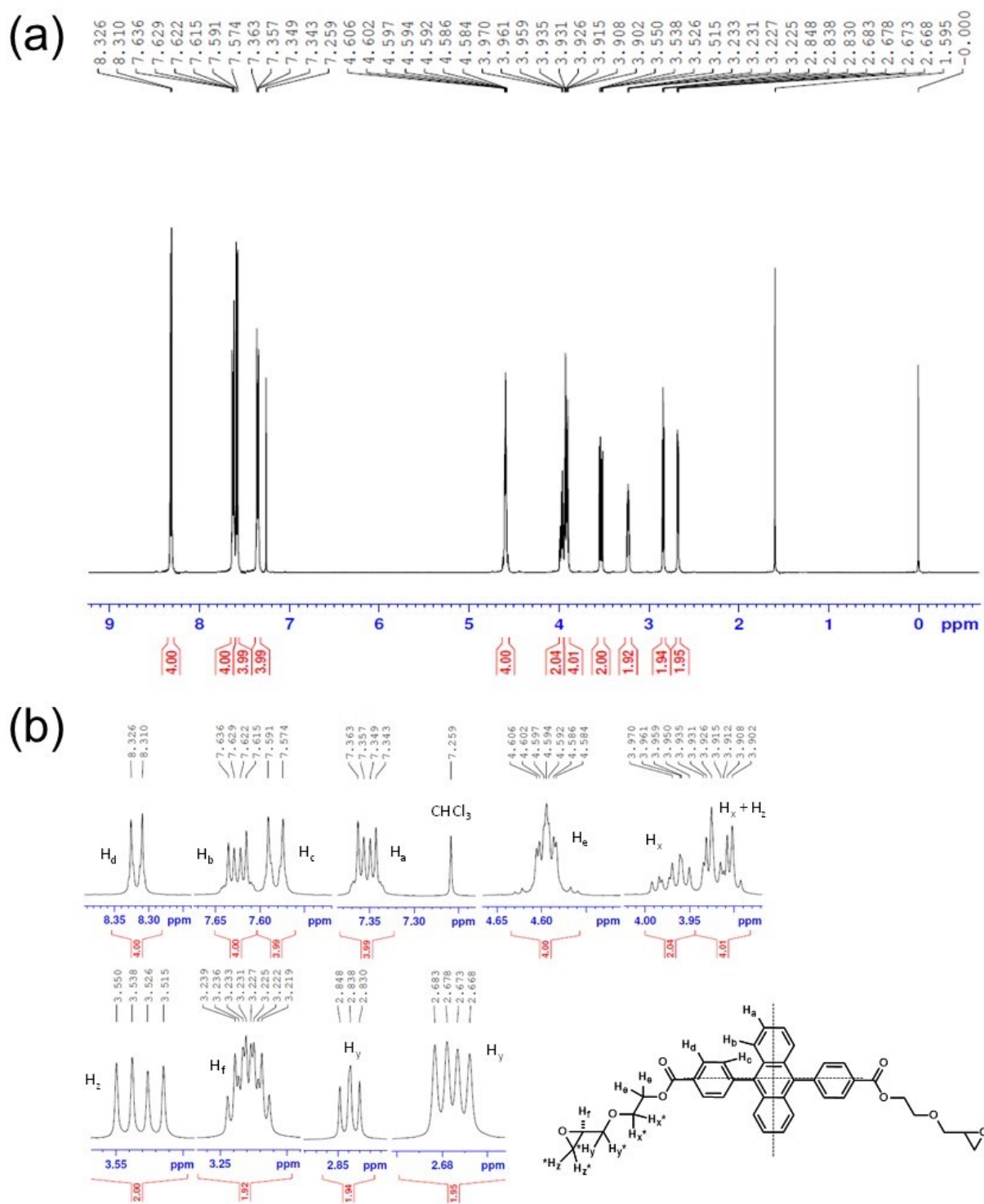
Figure 3-2-3. ^1H NMR spectrum (500 MHz, CDCl_3) of Epo-OH.



Scheme 3-2-6. Synthetic scheme of Epo-DPA.

Synthesis of 9,10-(4-ethylene glycol monoglycidyl ether) anthracene (Epo-DPA): In a round-bottomed flask, COOH-DPA (10.5 g, 25 mmol), Epo-OH (7.1 g, 60 mmol) and triethylamine (15.2 g,

150 mmol) were dissolved in 200 mL of dichloromethane. A mixture of WSC HCl (11.5 g, 60 mmol), HOBt (8.1 g, 60 mmol) and 100 mL of dichloromethane was added slowly to the reaction mixture with stirring in an ice bath. After that, the mixture was stirred at room temperature for a day. It was washed with 5 wt% NaHCO₃ aq., 10 wt% NH₄Cl aq. and brine. The Organic layer was dried with MgSO₄ and removed under reduced pressure. The residue was purified by flash column chromatography (eluent: dichloromethane : ethyl acetate, 90:10 (v/v)) to give pure Epo-DPA (8.8 g, 13.1 mmol, 52.5%). ¹H NMR (500 MHz, CDCl₃) : δ : (ppm) = 2.67 (dd, 2H), 2.84 (t, 2H), 3.23 (m, 2H), 3.53 (dd, 2H), 3.91 (m, 4H), 3.95 (m, 2H), 4.59 (m, 4H), 7.35 (dd, 4H), 7.58 (d, 4H), 7.63 (dd, 4H), 8.32 (d, 4H). Elemental analysis, calculated for C₃₈H₃₄O₈: C, 73.77; H, 5.54; O, 20.69; N, 0.00; found: C, 73.49; H, 5.54; O, 20.82; N, 0.01. LC–MS, calculated for C₃₈H₃₄O₈, 618.22, found 619.23 (M + H⁺).



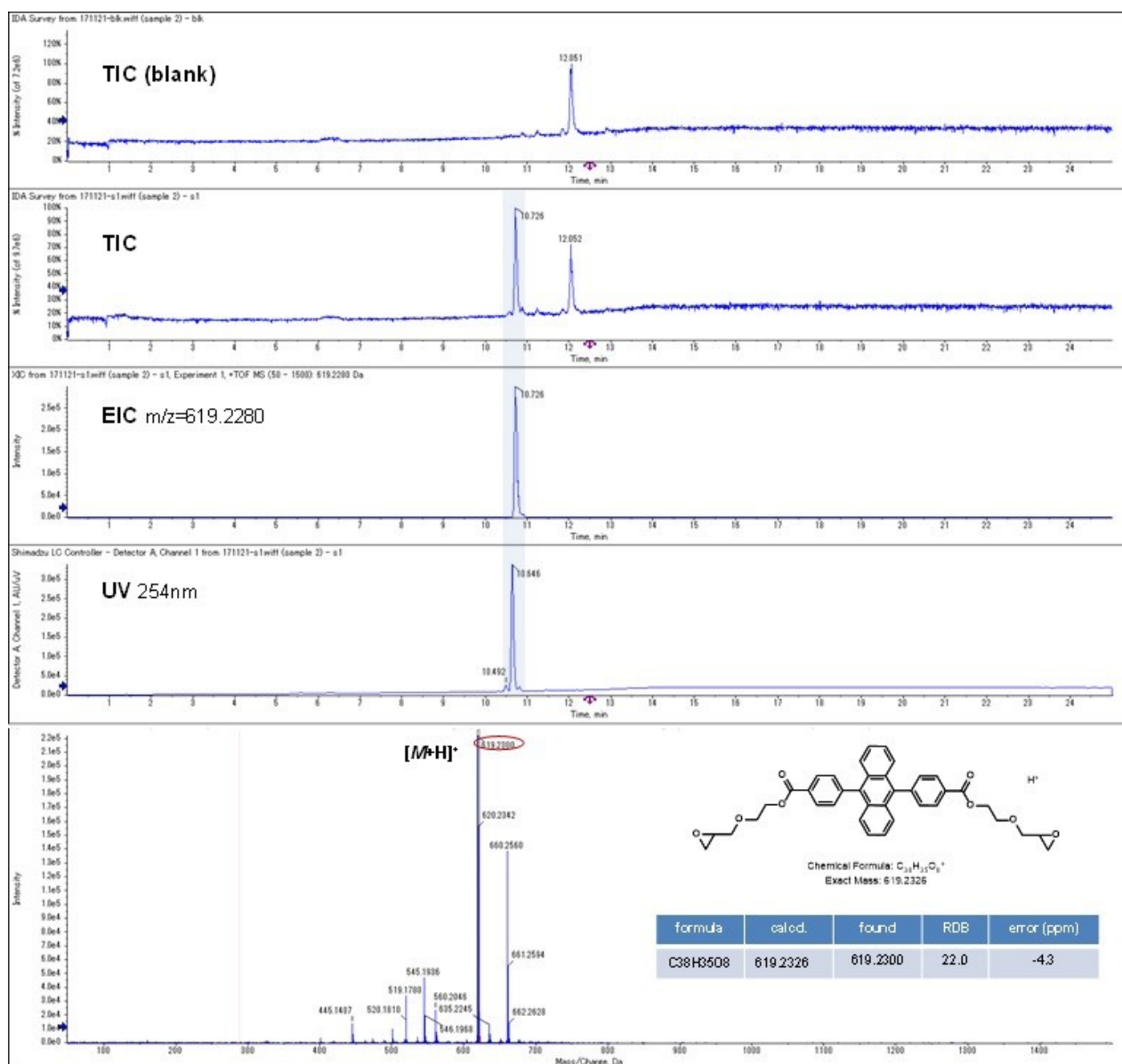


Figure 3-2-5. LC-MS analysis of Epo-DPA. TIC means total ion chromatography and EIC is extracted ion chromatography, respectively.

3-2-3 Preparation of the Cured Films

The liquid precursors for the films **3-1–14** were produced by the following Table 3-2-1.

Table 3-2-1. The contents of the liquid precursors for the films **3-1–14**. The DPA unit concentration (wt%) was calculated by (the total weight of DPA unit/the total amount of precursor) × 100. A catalytic amount of reaction promoter (tetrabutylphosphonium O,O-diethylphosphoro dithioate) was added to the precursors **3-11–14**.

films	materials / weight, mol%					DPA unit concentration (wt%)
	PtOEP	P ₆₆₆₁₄ DPAS	Epo-DPA	Epoxy A	Acid anhydride	
	(mg) (mol%)	(mg) (mol%)	(mg) (mol%)	(mg) (mol%)	(mg) (mol%)	
film 3-1	0.00723 0.01	89.3 100	92.8 150	0	49.5 300	35.6
film 3-2	0.00723 0.01	89.3 100	69.5 112.5	13.2 37.5	49.5 300	31.6
film 3-3	0.00723 0.01	89.3 100	46.4 75	26.5 75	49.5 300	27.3
film 3-4	0.00723 0.01	89.3 100	23.2 37.5	39.7 112.5	49.5 300	22.5
film 3-5	0.00723 0.01	89.3 100	0	52.9 150	49.5 300	17.2
film 3-6	0	89.3 100	92.8 150	0	49.5 300	35.6
film 3-7	0	89.3 100	69.5 112.5	13.2 37.5	49.5 300	31.6
film 3-8	0	89.3 100	46.4 75	26.5 75	49.5 300	27.3
film 3-9	0	89.3 100	23.2 37.5	39.7 112.5	49.5 300	22.5
film 3-10	0	89.3 100	0	52.9 150	49.5 300	17.2
film 3-11	0.00723	0	0	52.9	49.5	-
film 3-12	0.00723 0.01	0	154.7 250	0	82.5 500	34.8
film 3-13	0.00723 0.01	0	108.3 175	26.5 75	82.5 500	26.6
film 3-14	0.00723 0.01	0	61.9 100	52.9 150	82.5 500	16.7

The precursor materials and 1 mL of CH_2Cl_2 were added to the round-bottomed flask and stirred until dispersed uniformly. After that, CH_2Cl_2 was removed under reduced pressure at 90 °C while the neat-precursor was obtained.

The thermal curing of the films was conducted according to the following procedure in air (Figure 3-2-6). A 0.05 mm thick polyimide sheets (DU PONT–TORAY CO. Ltd., Kapton 200 EN) were placed on release-molded quartz glass (40 mm² square) as spacers. About 100 mg of the precursor was dropped on the glass and sandwiched using another mold glass and heated in an incubator. The thermal curing process occurred at 100 °C for 2 h, then raised to 150 °C (50 °C/hour), held at 150 °C for 5 h, and cooled to room temperature over 8 h (–15 °C/hour). The glasses and spacers were peeled off, and the cured films were recovered.

For the films **3-12–14**, the liquid precursor could not be obtained due to the reprecipitation of the Epo-DPA when the temperature was cooled even slightly after CH_2Cl_2 was removed by heating at 90 °C. Therefore, after the removal of CH_2Cl_2 at 120 °C, the hot precursor was directly dropped onto a quartz glass placed on a hot plate heated at 120 °C and then sandwiched with another quartz glass. The film was further heated to 150 °C at 1 °C min^{–1} and kept at 150 °C for 5 h to obtain a transparent cured film with no precipitation.

The sample preparation in the deaerated condition was performed by applying freeze–pump–thaw cycling of the precursor liquid 3 times, preparing the sandwiched geometry as mentioned above, and thermally curing on a hot plate in a N_2 -filled glovebox (oxygen concentration <0.02 ppm). Thereafter, a sealant was applied to the sides of the glasses.

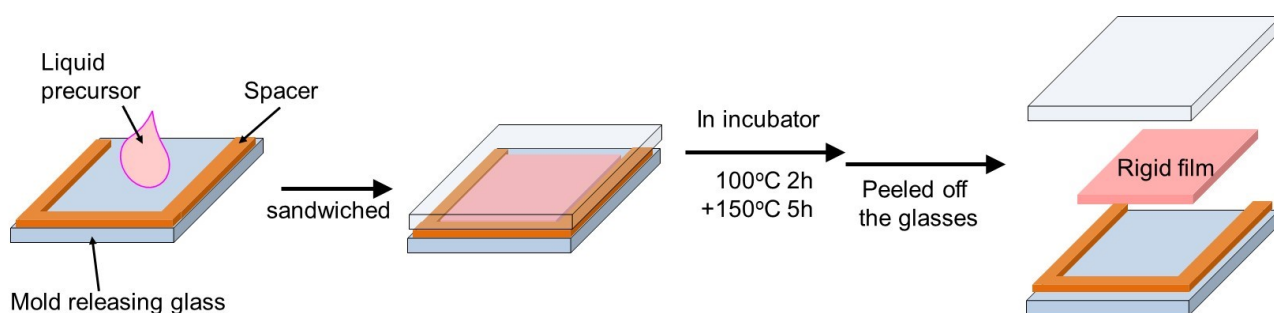


Figure 3-2-6. Schematic illustration of the preparation for the cured film.

3-2-4 Determination

The TTA-UC efficiencies η_{UC} of films were determined relative to Nile red in a cured epoxy film according to the following equation,

$$\eta_{UC} = 2\Phi_{std} \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{UC}}} \right) \left(\frac{E_{UC}}{E_{std}} \right) \left(\frac{I_{std}}{I_{UC}} \right) \left(\frac{n_{UC}}{n_{std}} \right)^2 \quad (3-1)$$

where Φ , A , E , I and n represent the quantum yield, absorbance at 532 nm, integrated photoluminescence spectral profile, excitation intensity, and the refractive index of the films, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. Since the standard and the UC films are based on identical epoxy resin, the refractive index ratio is approximated as 1. The absolute fluorescence quantum yield of Nile red in the cured film was 0.82. Note the maximum η_{UC} is normalized to 100% by multiplying the TTA-UC quantum yield (50% maximum) by 2.

The sensitizer-to-emitter TET efficiency was quantified by measuring phosphorescence quantum yields of the films and a cured film containing only PtOEP without emitter (film **3-11**). The TET efficiency Φ_{TET} was estimated by the following equation,

$$\Phi_{TET} = 1 - \frac{\Phi_P}{\Phi_{P,0}} \quad (3-2)$$

where Φ_P and $\Phi_{P,0}$ represent phosphorescence quantum yields of the film with and without the emitter, respectively.

3-3 Results and Discussion

3-3-1 Physical Properties of the Films

For the covalent introduction of DPA units into the epoxy networks, a novel DPA derivative containing two epoxy functionalities (Epo-DPA, Figure 3-3-1a) was synthesized. Into the epoxy resin consisting of Epo-DPA and acid anhydrides, the triplet sensitizer platinum(II) octaethylporphyrin (PtOEP) and the ionic liquid emitter P₆₆₆₁₄DPAS were introduced (Figure 3-3-1a). While pristine DPA tends to aggregate in the polymer matrices at high concentrations, P₆₆₆₁₄DPAS can be homogeneously dispersed without phase separation up to 1000 mM.⁴² A liquid precursor that consisted of P₆₆₆₁₄DPAS, PtOEP (0.01 mol% versus P₆₆₆₁₄DPAS), Epo-DPA (150 mol%), and a 4-methyl(hexahydro)phthalic anhydride/(hexahydro)phthalic anhydride mixture (300 mol%) was thermally cured at 150 °C to form an epoxy resin named as film **3-1** (Table 3-2-1). The completion of the condensation reaction was monitored by the shift of the C=O stretching peak from that of acid anhydride (1782 cm⁻¹) to ester (1730 cm⁻¹) and by the disappearance of the epoxy C—C asymmetric absorption (901 cm⁻¹) in FT-IR spectra (Figure 3-3-2). The obtained film **3-1** was rigid and transparent, and it displayed a strong upconverted blue emission under 532 nm green laser irradiation in air (Figure 3-3-1b). This clearly shows that the epoxy resin containing emitters in ultrahigh density still maintains the high oxygen barrier ability (Figure 3-3-1c).

The rigid nature of the film **3-1** at room temperature was characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The glass transition temperature T_g of the film **3-1** was determined as 35 °C by DSC measurements (Figure 3-3-3a). There was no glass transition at around -24 °C due to neat P₆₆₆₁₄DPAS in the DSC curve, indicating the homogeneous distribution of P₆₆₆₁₄DPAS in the film **3-1** without phase separation. In the DMA of the film **3-1**, a relaxation process was observed as a peak of $\tan \delta$ at around 80 °C, confirming that it is a rigid film with an elastic mechanical response at room temperature (Figure 3-3-3b).

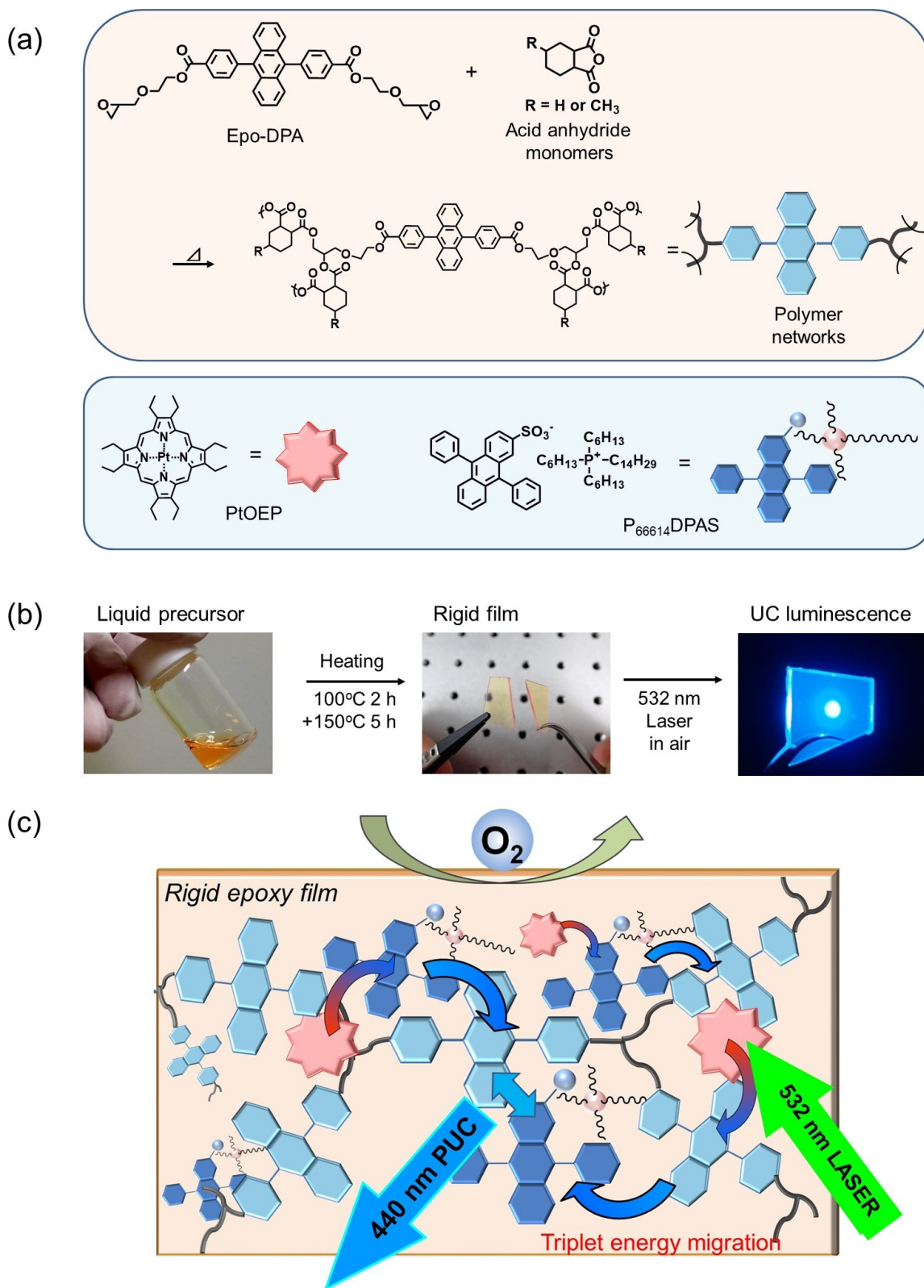


Figure 3-3-1. (a) Condensation reaction scheme of Epo-DPA and acid anhydride monomers, and chemical structures of the sensitizer PtOEP and the ionic liquid emitter P₆₆₆₁₄DPAS. (b) Photographs of the liquid precursor, the cured film **3-1**, and the film **3-1** under 532 nm laser irradiation in air (film thickness: 1 mm). (c) Schematic illustration of air-stable TTA-UC in the cured bulk film.

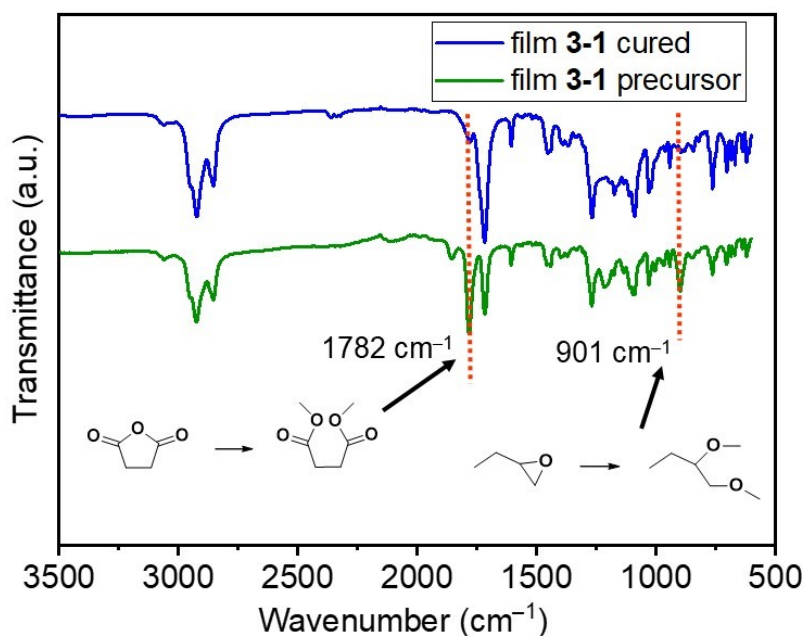


Figure 3-3-2. FT-IR spectra of the liquid precursor (green line) and cured film **3-1** (blue line). The disappearance of the C=O stretching peak from acid anhydride (1782 cm^{-1}) and the epoxy C—C asymmetric absorption (901 cm^{-1}) were observed after curing the liquid precursor.

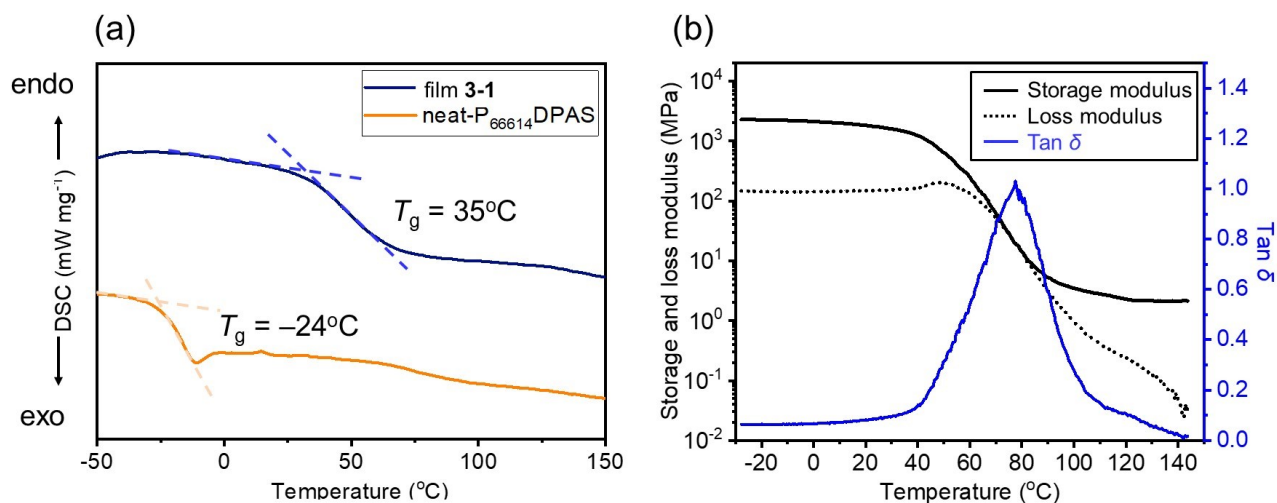


Figure 3-3-3. (a) DSC thermograms of the cured film **3-1** and the neat $\text{P}_{66614}\text{DPAS}$ (2nd cycle, scan rate: $10^{\circ}\text{C min}^{-1}$, N_2 atmosphere). The T_g of the film **3-1** and the neat $\text{P}_{66614}\text{DPAS}$ were estimated as 35°C , and -24°C , respectively. (b) Temperature dependence of the storage/loss modulus and loss tangent for film **3-1**. The thermal gradient was $10^{\circ}\text{C min}^{-1}$ and then obtained $\text{tan } \delta = 80^{\circ}\text{C}$. The measurement frequency was 1.0 Hz .

3-3-2 Photoluminescence Properties of the Films

The absence of strongly interacting dimer/excimer in the film **3-1** was confirmed by absorption and fluorescence measurements. The film **3-1** exhibited π - π^* vibronic absorption peaks at 359.5, 377.5, and 398 nm, which were only slightly red-shifted compared with those of 0.1 mM Epo-DPA (357, 375, and 395.5 nm) and 0.1 mM P₆₆₆₁₄DPAS (357, 375, and 395 nm) in CH₂Cl₂ solutions (Figure 3-3-4). The peak width of the film **3-1** was narrower than those of neat P₆₆₆₁₄DPAS, and close to those of the Epo-DPA and P₆₆₆₁₄DPAS solutions. These results indicate the homogeneous distribution of the DPA chromophoric moieties without significant aggregation in the film **3-1**. The fluorescence spectrum of the film **3-1** appears to be slightly red-shifted compared to those of the Epo-DPA and P₆₆₆₁₄DPAS solutions, which is mainly due to the inner filter effect as discussed in the chapter 2. No excimer formation was observed in film **3-1**. Despite the extremely high concentration of the DPA moiety (35.6 wt%), the chromophoric units were found to be homogeneously distributed in the film **3-1** without aggregation.

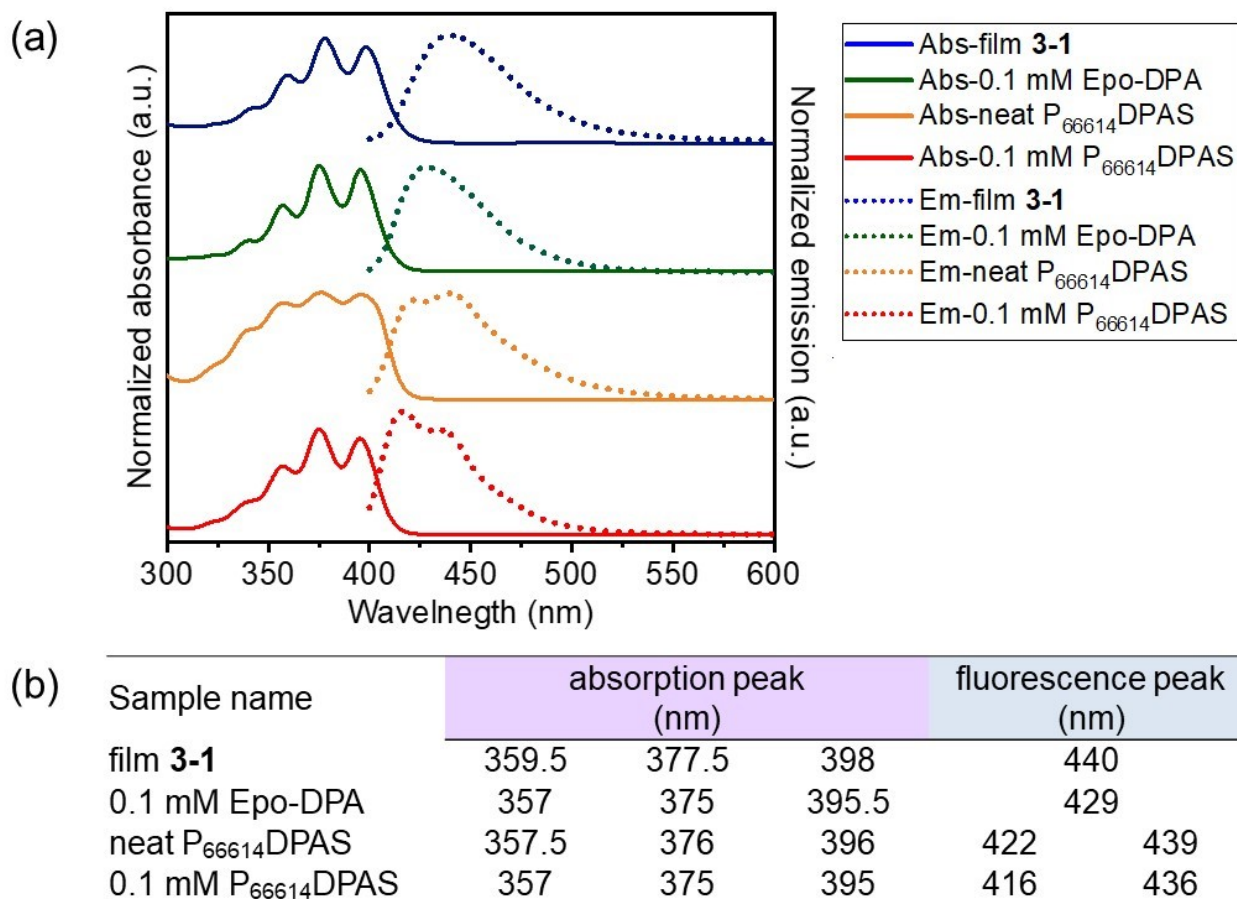


Figure 3-3-4. (a) UV-vis absorption spectra (solid line) and fluorescence spectra (dashed line) of film **3-1** (blue), 0.1 mM Epo-DPA in CH₂Cl₂ solution (green), neat P₆₆₆₁₄DPAS (orange), and 0.1 mM P₆₆₆₁₄DPAS in CH₂Cl₂ solution (red). The excitation wavelength was $\lambda_{\text{ex}} = 365$ nm. (b) A table of the exhibited π - π^* vibronic absorption peaks and fluorescence peaks for the film **3-1**, 0.1 mM Epo-DPA in CH₂Cl₂ solution, neat P₆₆₆₁₄DPAS and 0.1 mM P₆₆₆₁₄DPAS in CH₂Cl₂ solution, respectively.

Upconverted emission of the film **3-1** was observed at around 440 nm under excitation at 532 nm in air (Figure 3-3-5). The fact that no PtOEP phosphorescence was observed at around 650 nm regardless of the excitation intensity indicates the nearly 100% sensitizer-to-emitter TET. Note that the molecular dispersion of PtOEP in the film **3-1** was confirmed by the absence of phosphorescence of PtOEP aggregates at 780 nm.

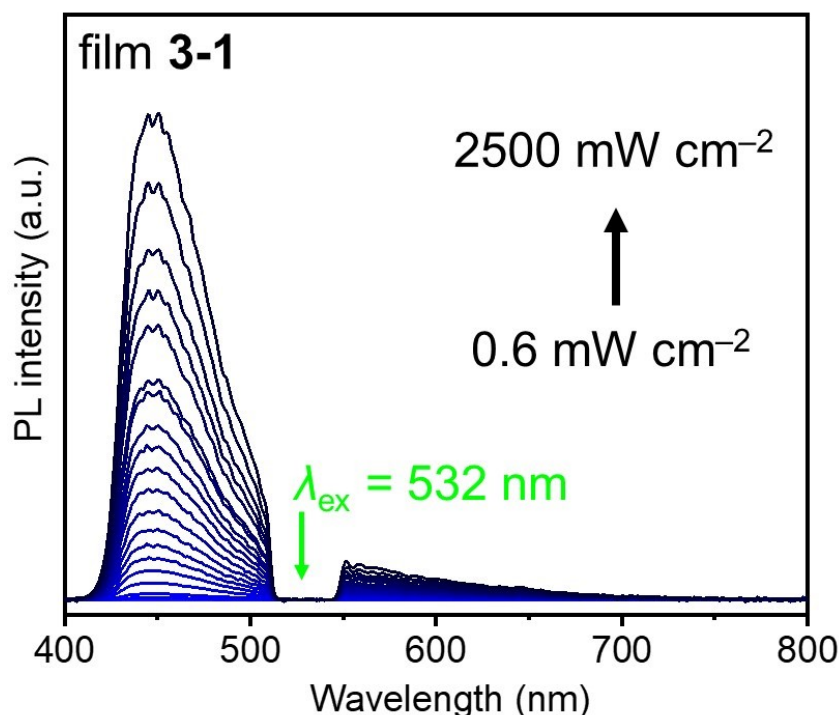


Figure 3-3-5. Photoluminescence (PL) spectra of the film **3-1** in air at different excitation intensities of a 532 nm laser. A 520–540 nm notch filter was used to remove the scattered excitation light.

The TTA-UC efficiency η_{UC} ($= 2\Phi_{UC}$, the theoretical maximum is set as 100%) was determined by a relative method using Nile red in the epoxy film as a standard. Since the transparency of the epoxy films was very high and there was almost no light scattering, the relative method can be used to estimate the TTA-UC efficiency with high reliability (Figure 3-3-6a).^{43,44} The η_{UC} value of the film **3-1** reached up to 11.4% (Figure 3-3-6b), which is the highest ever reported among the rigid polymeric TTA-UC systems.^{39,40,45–47} Importantly, the TTA-UC efficiency of the film **3-1** prepared and measured in air was almost identical with the film **3-1** prepared and sealed in a deaerated glovebox (Figure 3-3-6b). This result demonstrates that the excellent oxygen barrier property was maintained in the epoxy resin containing emitter DPA units as much as one-third by weight.

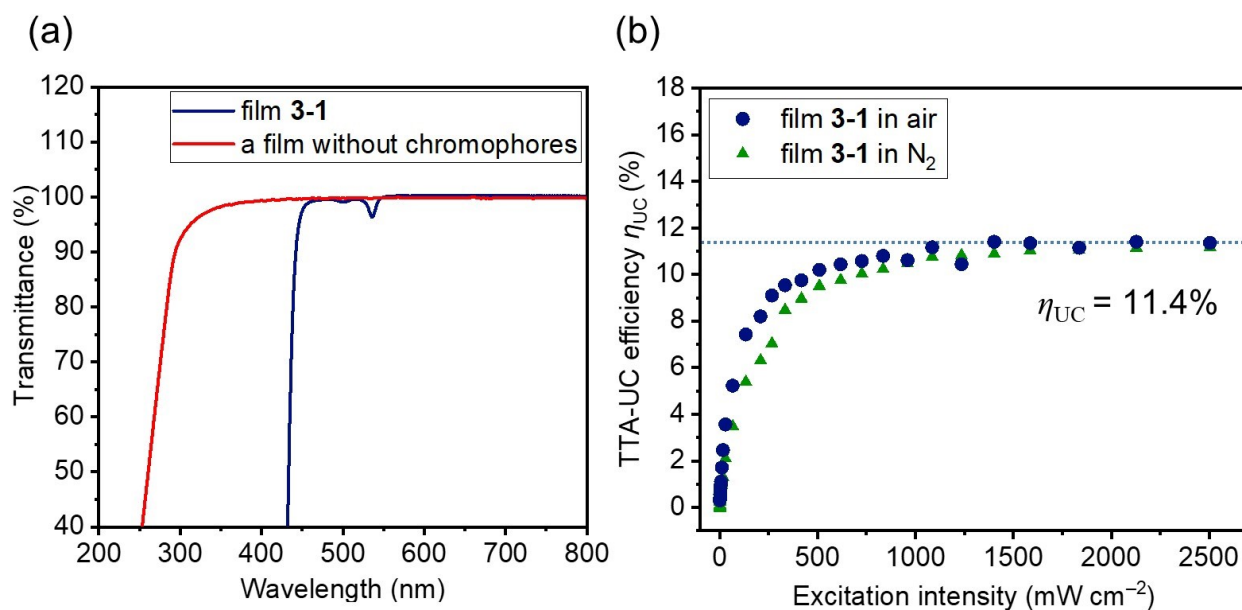


Figure 3-3-6. (a) Transmittance spectra of the film **3-1** (blue) and a cured film prepared with epoxy A and acid anhydride without any chromophores (red). The thickness of the films is 0.05 mm. (b) TTA-UC efficiency η_{UC} of the film **3-1** prepared and measured in air (blue circles) and prepared and sealed in the glovebox (green triangles) measured as a function of excitation intensity at an excitation wavelength of 532 nm.

Besides the superior TTA-UC efficiency, the film **3-1** shows a relatively low threshold excitation intensity I_{th} . In general, the dependence of TTA-UC photoluminescence intensity on the excitation intensity turns from quadratic to linear, and the intersection of the tangent lines with slopes 2 and 1 in the double-logarithmic plot is defined as I_{th} .^{38,48–50} The I_{th} value of the film **3-1** was as low as 39.1 mW cm^{-2} (Figure 3-3-7).

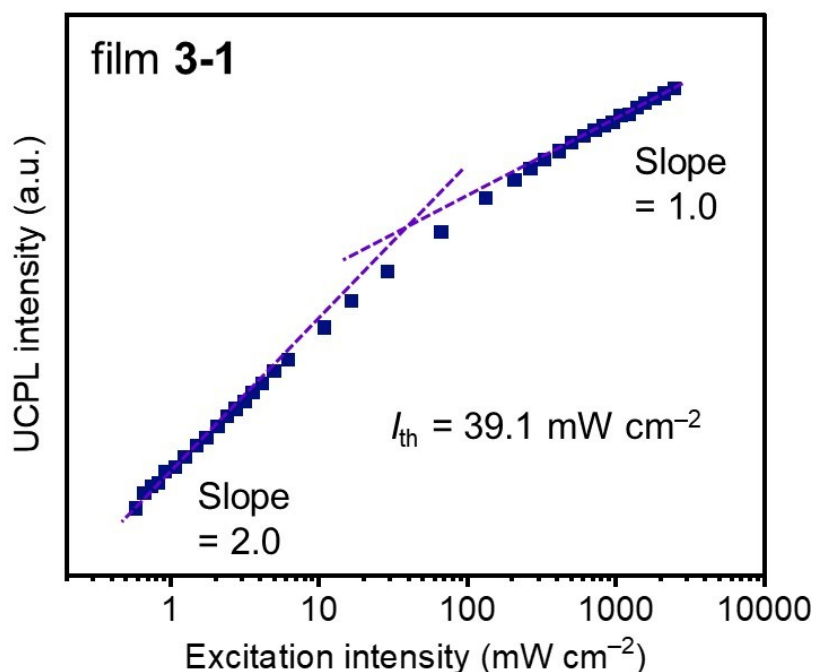


Figure 3-3-6. Dependence of UCPL intensity of the film **3-1** at 440 nm on the excitation intensity.

To unveil the important role of emitter density in upconversion performance, films **3-1-5** were prepared by changing Epo-DPA to emitter-free hydrogenated bisphenol A-glycidyl ether (Epoxy A) at different molar ratios (Figure 3-3-7b). Interestingly, upon decreasing the mixing ratio of Epo-DPA, the intensity of the upconversion emission at around 440 nm became relatively smaller, and the intensity of the PtOEP phosphorescence at around 650 nm became larger (Figure 3-3-7a). The TTA-UC efficiency η_{UC} decreased from 11.4% to 3.98% as the mixing ratio of Epo-DPA decreased (Figure 3-3-7c). Meanwhile, the sensitizer-to-emitter TET efficiency, calculated from the phosphorescence quantum yield, was as high as 88.3% even for the film **3-5** containing no Epo-DPA (Table 3-3-1), and thus, this alone cannot explain the large change in the TTA-UC efficiency. When the mixing ratio of Epo-DPA in the films was reduced, the fluorescence quantum yield became rather higher, which is also not a reason to explain the decrease in the TTA-UC efficiency (Table 3-3-1).

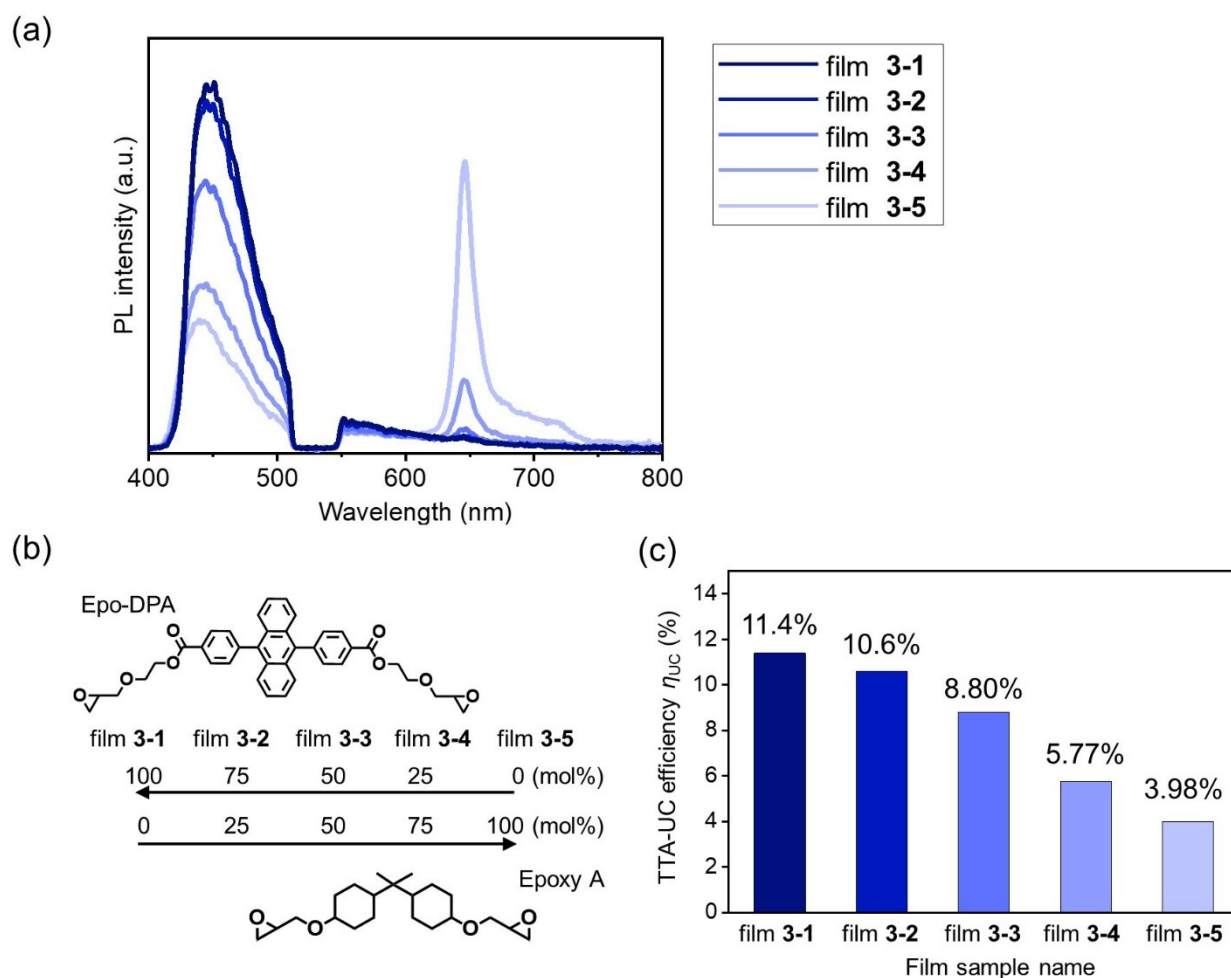


Figure 3-3-7. (a) PL spectra of the films **3-1–5** at an excitation intensity of 1040 mW cm^{-2} of the 532 nm laser. The 520–540 nm notch filter was used to remove the scattered excitation light. (b) The molar ratio between Epo-DPA and Epoxy A in the films **3-1–5**. (c) TTA-UC efficiency η_{UC} of the films **3-1–5** prepared and measured in air. The η_{UC} values were estimated in the linear region at high excitation intensity.

Table 3-3-1. Absolute fluorescence ($\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{em}} = 400\text{--}600 \text{ nm}$) and phosphorescence ($\lambda_{\text{ex}} = 532 \text{ nm}$, $\lambda_{\text{em}} = 600\text{--}800 \text{ nm}$) quantum yields of the films. The size of the film samples is 15 mm^2 square and thickness is 0.05 mm . The sensitizer-to-emitter TET efficiency was estimated by the equation (3-2): $\Phi_{\text{TET}} = 1 - \Phi_{\text{P}}/\Phi_{\text{P},0}$, where Φ_{P} and $\Phi_{\text{P},0}$ represent phosphorescence quantum yields of the film with (films **3-1–5**) and without (film **3-11**) the emitter, respectively.

films	quantum yields		Φ_{TET} (%)
	fluorescence (%)	phosphorescence (%)	
film 3-1	35.1	0	100
film 3-2	48	1.2	97.8
film 3-3	55.3	2.8	95
film 3-4	57.7	3.5	93.7
film 3-5	71.2	6.5	88.3
film 3-6	46.9		
film 3-7	60.7		
film 3-8	67.6		
film 3-9	76		
film 3-10	82.9		
film 3-11		55.7	

3-3-3 Triplet Energy Migration Efficiency in the Films

A clue to understanding the large changes in the TTA-UC efficiency was obtained from the decay behavior of the PtOEP phosphorescence (Figure 3-3-8). As the mixing ratio of Epo-DPA increased, the phosphorescence lifetime of PtOEP became shorter, which is consistent with the observed increase in TET efficiency (Table 3-3-1). In addition to the short-lifetime component, the films with smaller mixing ratios of Epo-DPA (films **3-3-5**) showed a delayed component with a lifetime longer than the one of original PtOEP phosphorescence. The lifetime of the delayed component of the PtOEP phosphorescence was compared with the triplet lifetime of the emitter $\tau_{A,T}$ in each film that was obtained by fitting a UC emission decay with the known relationship of $I_{UC}(t) \propto \exp(-2t/\tau_{A,T})$ (Figure 3-3-9).⁵¹ The lifetime of the delayed phosphorescence was 14.5 ms for film **3-5** (Figure 3-3-9b), which was in the same order as the emitter triplet lifetime of 19.3 ms (Figure 3-3-9a). A similar phenomenon was recently reported by Monguzzi et al. in a solution system, where they found that the delayed sensitizer phosphorescence lifetime coincided with the emitter triplet lifetime, indicating that back and forth energy transfer between the sensitizer and emitter occurs, and thermodynamic equilibrium is reached.⁵² In our films **3-3-5**, the delayed component of PtOEP phosphorescence should originate from the emitter-to-sensitizer triplet back energy transfer. On the other hand, such a delayed component was nearly absent in the phosphorescence decays of films **3-1** and **3-2**, giving an important insight that the triplet back energy transfer to the sensitizer can be suppressed by increasing the concentration of emitters in the rigid resin. Although it has been discussed that the triplet back energy transfer depends on the emitter concentration in solution,⁵² the effect of triplet back energy transfer in rigid solid materials has not been elucidated so far. In this study, the effect of triplet back energy transfer was clarified for the first time by systematic investigations in a system where emitters can be dispersed at high concentrations.

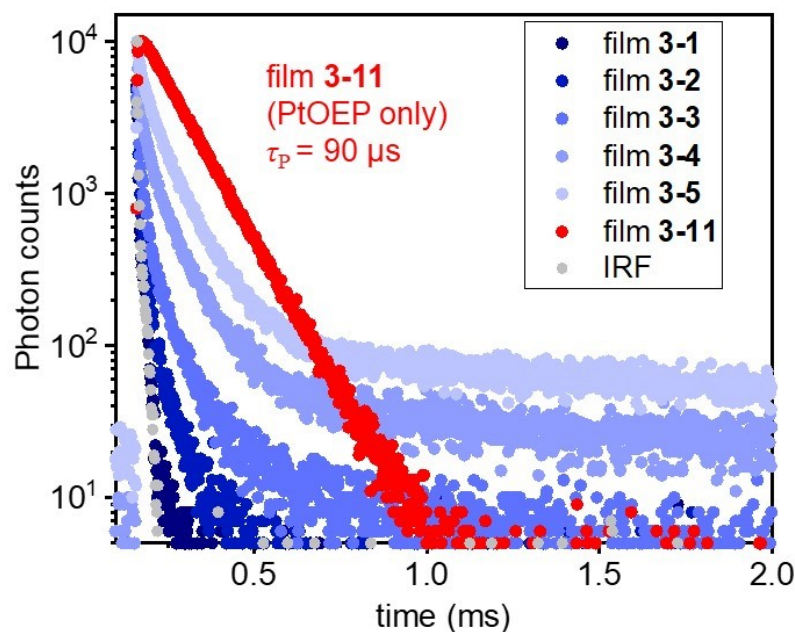


Figure 3-3-8. Phosphorescence decay of films **3-1–5** and **3-11** (PtOEP only film, Table 3-3-1) at 650 nm under pulsed excitation at 532 nm. Single exponential fitting of the decay of film **3-11** provides the phosphorescence lifetime of 90 μs .

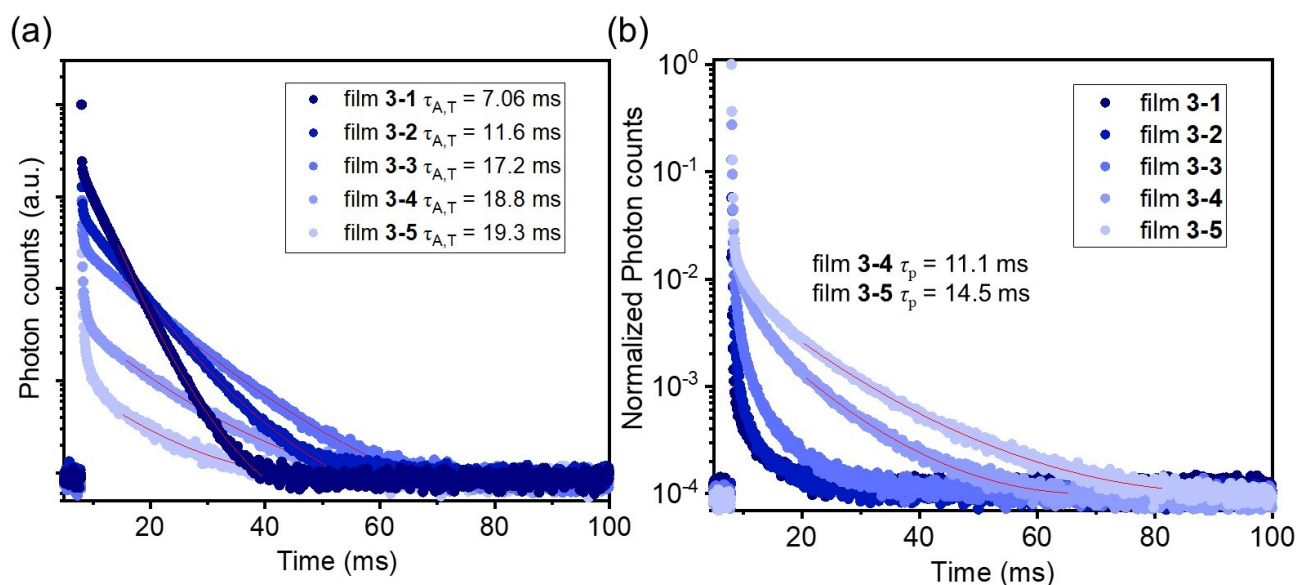


Figure 3-3-9. (a) UC emission decays of the films **3-1–5** under pulsed excitation at 532 nm ($\lambda_{em} = 440$ nm). (b) The long time-scale-range phosphorescence decays of the films **3-1–5** under pulsed excitation at 532 nm ($\lambda_{em} = 650$ nm). The tail fitting of the phosphorescence decays provides the delayed phosphorescence lifetime (τ_D) of 11.1 ms (film **3-4**) and 14.5 ms (film **3-5**), respectively.

In order to understand why increasing the emitter concentration prevented triplet back energy transfer, the effective triplet exciton diffusion coefficient D_T was estimated using the following equation,³⁸

$$D_T = (8\pi a_0 \alpha \Phi_{TET} I_{th})^{-1} \tau_{A,T}^{-2} \quad (3-3)$$

where a_0 is the effective triplet–triplet interaction distance (9.1 Å for DPA triplet)³⁸ and α is the absorption coefficient at an excitation wavelength of 532 nm. The relevant parameters are summarized in Table 3-3-2. The triplet diffusion coefficient D_T was $1.90 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for the film without Epo-DPA, but it increased to $15.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ with increasing the concentration of Epo-DPA. Therefore, the increase in the concentration of emitters in the resin caused faster triplet exciton diffusion after receiving the triplet energy from the sensitizer. It would allow triplet excitons to migrate longer distances by leaving behind the sensitizer, thus suppressing the triplet back energy transfer.

Table 3-3-2. Epo-DPA:Epoxy A molar ratio, TTA-UC efficiency η_{UC} , threshold excitation intensity I_{th} (Figure 3-3-10), emitter triplet lifetime $\tau_{A,T}$, triplet diffusion coefficient D_T , singlet formation probability $f \Phi_{TTA}$ of the films **3-1–5**.

films	Epo-DPA:Epoxy A (molar ratio)	η_{UC} (%)	I_{th} (mW cm ⁻²)	$\tau_{A,T}$ (ms)	D_T (10 ⁻⁹ cm ² s ⁻¹)	$f \Phi_{TTA}$ (%)
film 3-1	100 : 0	11.4	39.1	7.06	15.8	24.3
film 3-2	75 : 25	10.6	57.1	11.6	4.09	17.9
film 3-3	50 : 50	8.80	64.0	17.2	1.61	13.7
film 3-4	25 : 75	5.77	55.2	18.8	1.63	8.1
film 3-5	0 : 100	3.98	47.2	19.3	1.90	5.4

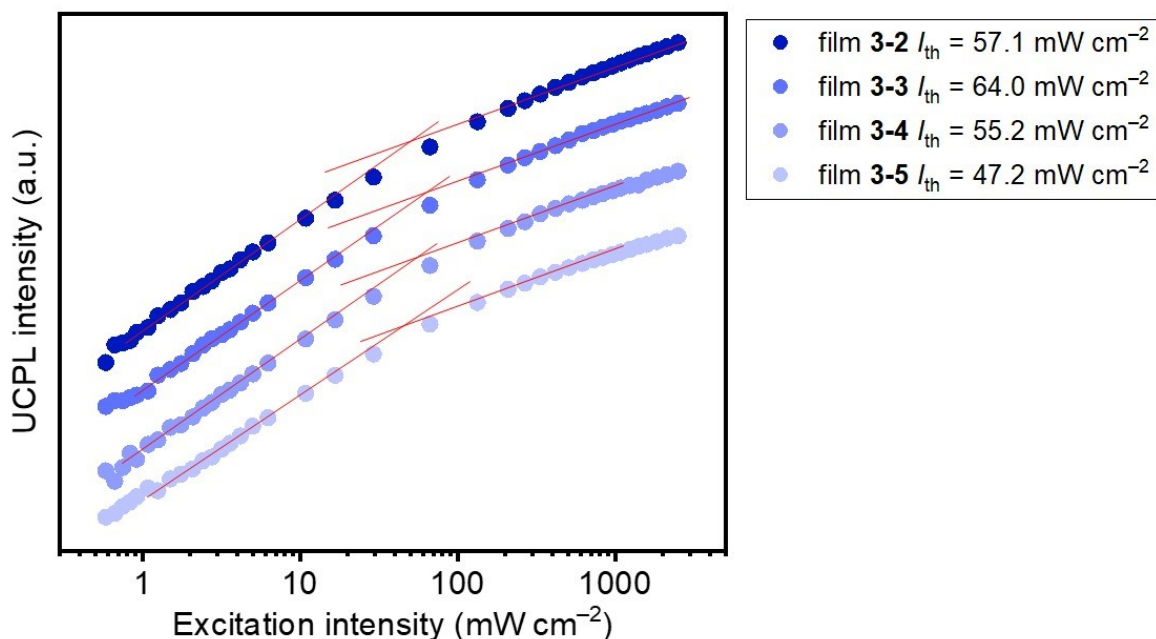


Figure 3-3-10. Dependence of UCPL intensity at 440 nm on the excitation intensity for films **3-2–5**. The dashed lines are fitting results with slopes of 2 and 1 in the low- and high-excitation intensity regimes, respectively.

We return the discussion to the TTA-UC efficiency and quantify the probability that the sensitized triplet of emitters produced a fluorescent S_1 using the following equation,⁶

$$\eta_{UC} = f \Phi_{ISC} \Phi_{TET} \Phi_{TTA} \Phi_A \quad (3-4)$$

where Φ_{ISC} , Φ_{TET} , Φ_{TTA} , and Φ_A are the quantum efficiency of the sensitizer ISC (≈ 1 in the case of PtOEP), TET from the sensitizer to emitter (Table 3-3-1), the sensitized emitter triplet performing TTA, and emitter fluorescence, respectively, and f is the probability of generating S_1 by TTA. Since the singlet back energy transfer from the emitter to sensitizer was almost absent (Figure 3-3-11), we used Φ_A values of the films without the sensitizer (films **3-6–10**, Table 3-3-1) to avoid the effect of reabsorption of emitter fluorescence by the sensitizer in the integrating sphere. The conversion efficiency from the emitter T_1 to S_1 ($f \Phi_{TTA}$, Table 3-3-2) was as low as 5.4% in film **3-5** without Epo-DPA, while it increased to 24.3% in film **3-1** with the high concentration of Epo-DPA. The obtained results indicate that the triplet of the sensitized emitter is used for TTA more efficiently by increasing the emitter concentration.

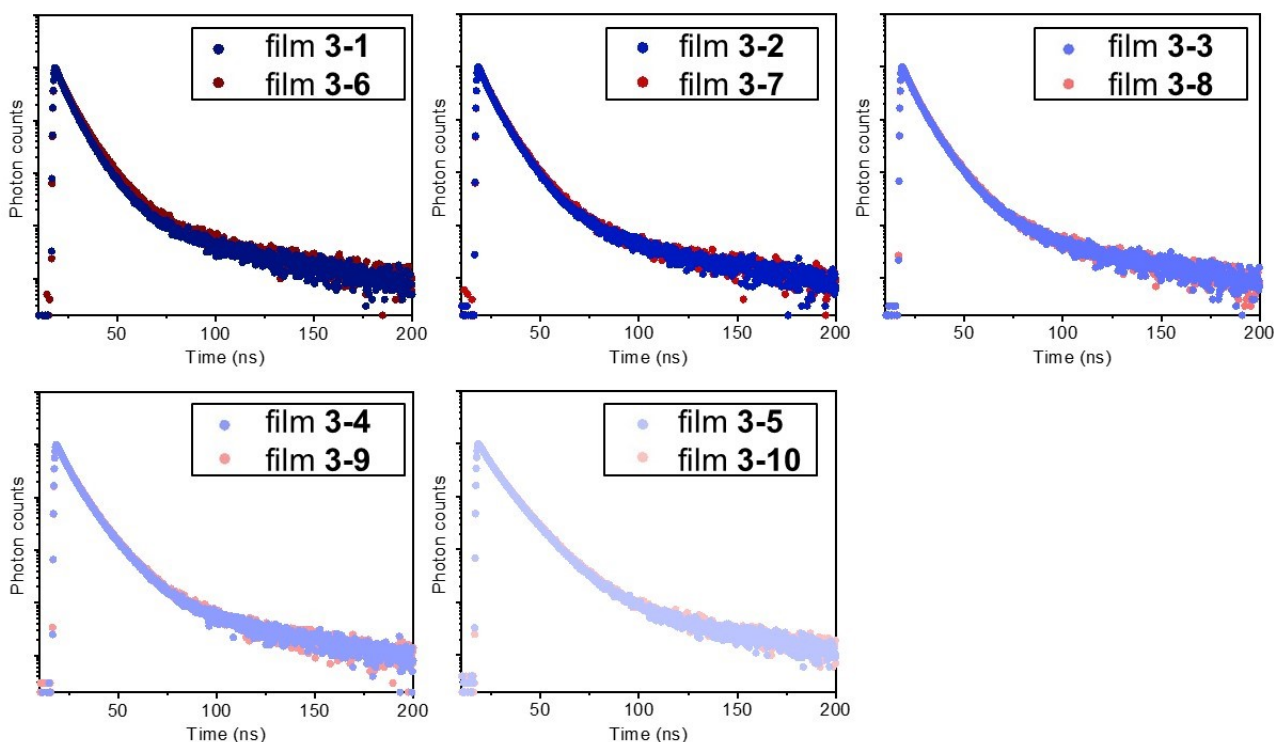


Figure 3-3-11. Comparison of fluorescence decays for the films with and without PtOEP. The excitation wavelength was 365 nm and the detection wavelength was 440 nm. Almost no difference was observed in the fluorescence decays with/without PtOEP, indicating the absence of singlet back energy transfer.

The TTA-UC efficiency in rigid solid materials has usually been much lower than expected due to the deactivation of the triplet.^{53–56} The present results are very encouraging, because we demonstrate that even in solid materials with an ultrahigh density of emitter, the triplet can be effectively used for TTA, and thus, efficient upconverting rigid films can be created. This is partly because the triplet can leave the sensitizer without deactivation by increasing the concentration of emitters to more than 30 wt%.

In the films **3-1–5**, increasing the concentration of Epo-DPA resulted in a shortening of the triplet lifetime $\tau_{A,T}$. There are several possible reasons for this phenomenon. It is known that the triplet lifetime $\tau_{A,T}$ depends on the rigidity of the surrounding environment.^{40,57} The fact that the triplet lifetime of film **5** without Epo-DPA was 19.3 ms, much longer than the lifetime of DPA in solution (a few μ s), suggests that the triplet lifetime was elongated in the rigid epoxy resin.⁴² Increasing the

concentration of Epo-DPA may have caused a change in the local molecular mobility. The slight red-shift in the absorption spectra of the film **1** compared to the solution suggests that there is an interaction between adjacent chromophores, which may induce nonradiative deactivation of the triplet and/or triplet quenching by defect sites.^{47,58,59} However, since the TTA-UC efficiency increased with increasing Epo-DPA concentration, it is clear that the positive effect of enhanced triplet diffusion among chromophores far outweighs the negative effect of increased interaction between chromophores.

To confirm the critical role of emitter concentration and the generality of our current design guidelines, we prepared additional films with DPA introduced only in the epoxy network without using the ionic liquid P₆₆₆₁₄DPAS and investigated their upconversion properties. The DPA concentrations in the P₆₆₆₁₄DPAS-free films are 34.8 wt% (film **3-12**), 26.6 wt% (film **3-13**), and 16.7 wt% (film **3-14**), which are close to the ones in the P₆₆₆₁₄DPAS-containing films, 35.6 wt% (film **3-1**), 27.3 wt% (film **3-3**), and 17.2 wt% (film **3-5**), respectively (Table 3-3-1).

The TTA-UC efficiencies η_{UC} of films **3-12**, **3-13**, and **3-14** were 10.1, 8.8, and 3.6%, respectively, which were close to the TTA-UC efficiencies of films **3-1** (11.4%), **3-3** (8.8%), and **3-5** (3.98%), respectively (Figure 3-3-12b). Very interestingly, the TTA-UC efficiency was found to depend only on the concentration of the DPA unit, regardless of whether the ionic liquid P₆₆₆₁₄DPAS was used or not. This result clearly shows the generality of our claim that emitter concentration is a critical parameter to obtain high TTA-UC efficiency in rigid films.

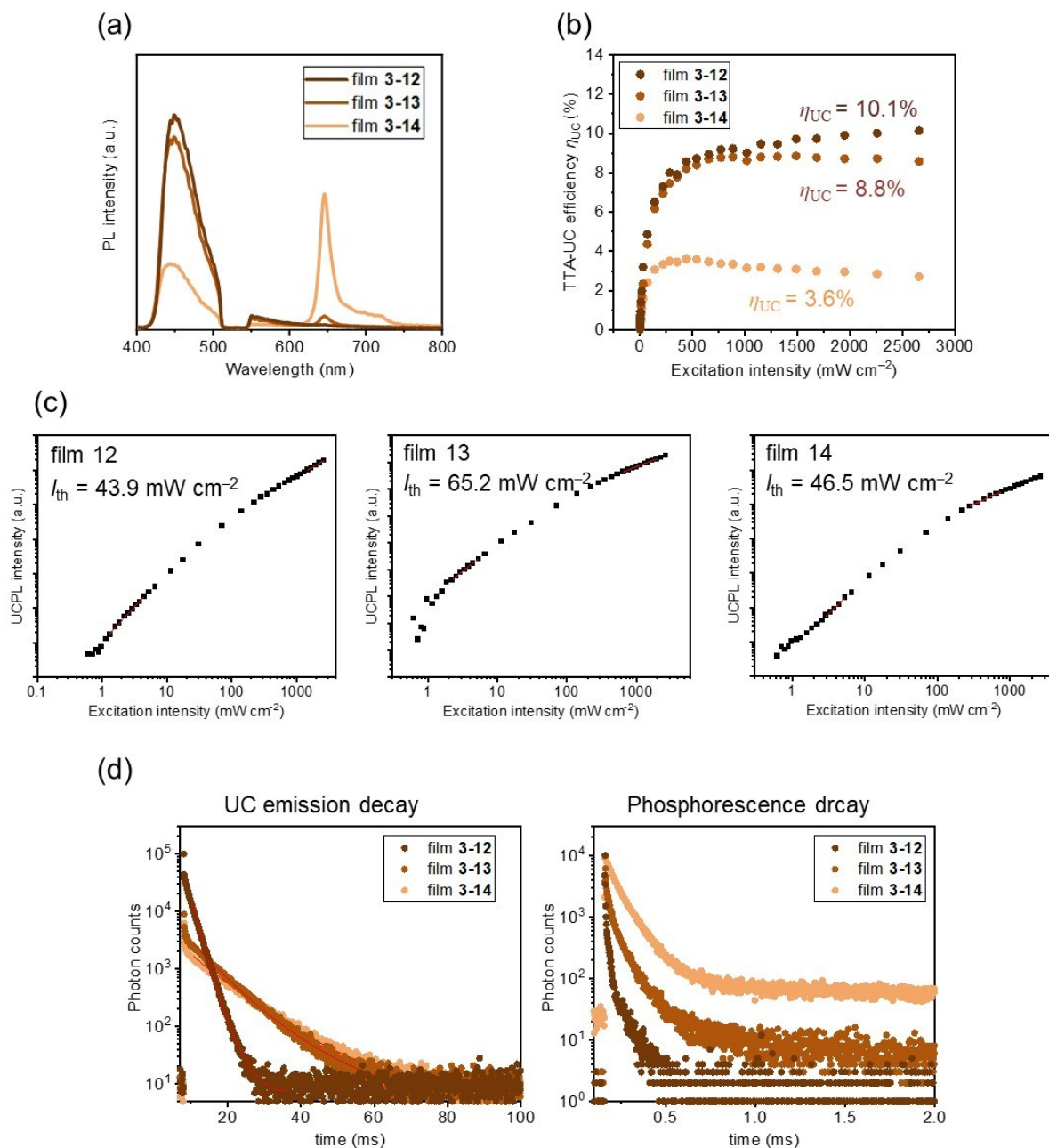


Figure 3-3-12. (a) PL spectra of the films **3-12–14** at an excitation intensity of 1680 mW cm^{-2} of the 532 nm laser. The 520–540 nm notch filter was used to remove the scattered excitation light. (b) TTA-UC efficiency η_{UC} of the films **12–14** measured as a function of excitation intensity at an excitation wavelength of 532 nm. The η_{UC} of each film was determined by the relative method. The thickness of the films, 0.05 mm. (c) Dependence of UCPL intensity at 440 nm on the excitation intensity for films **3-12–14**. (d) UC emission decays and phosphorescence decays of the films **3-12–14** under pulsed excitation at 532 nm ($\lambda_{em} = 440$ and 650 nm, respectively).

In terms of parameters other than the TTA-UC efficiency, the film **3-12** showed a slightly higher threshold excitation intensity I_{th} and a shorter triplet lifetime $\tau_{A,T}$ than the film **3-1** (Table 3-3-3). There was no such difference between films **3-13** and **3-3** and films **3-14** and **3-5**. These results suggest that the presence or absence of the ionic liquid P₆₆₆₁₄DPAS caused a slight difference in the DPA assembled structure when the DPA unit concentration was very high, around 35 wt%. In the comparison between films **3-1** and **3-12**, all the TTA-UC parameters were slightly better when the ionic liquid was included. It should also be noted that the films **3-12–14** without the ionic liquid P₆₆₆₁₄DPAS have some technical problems in preparation. After the precursor mixture was heated at 120°C to remove dichloromethane, Epo-DPA precipitated immediately when the temperature was lowered even slightly. No such precipitation was observed in the P₆₆₆₁₄DPAS-including film, indicating that the ionic liquid acted as a good solvent for Epo-DPA. The similar TTA-UC efficiency could be obtained without the ionic liquid P₆₆₆₁₄DPAS, but the composition including the ionic liquid is superior for processing into various shapes of samples.

Table 3-3-3. The comparison of UC properties for films with/without P₆₆₆₁₄DPAS.

films	η_{UC} (%)	I_{th} (mW cm ⁻²)	$\tau_{A,T}$ (ms)
film 3-12	10.1	43.9	4.34
(film 3-1)	11.4	39.1	7.06
film 3-13	8.8	65.2	15.7
(film 3-3)	8.8	64.0	17.2
film 3-14	3.6	46.5	19.4
(film 3-5)	3.98	47.2	19.3

The film **3-12** has the maximum DPA unit concentration with the current monomer structures. As for lowering the DPA unit concentration introduced in the chapter 2, the TET efficiency Φ_{TET} decreased to 4.9% and TTA-UC efficiency η_{UC} decreased to 0.09% when using a concentration 10 times lower than that of film **3-5**. Therefore, we investigated the possible range of DPA unit concentrations that could be experimentally tested and concluded that the higher the DPA unit

concentration, the better the TTA-UC performance. Even when the concentration of DPA unit was increased to a very high value of around 35 wt%, the TTA-UC efficiency did not decrease, and undesirable chromophore aggregation and self-quenching did not occur. This is different from the previous upconversion materials using vinyl polymers,^{45,53} suggesting that the homogeneous incorporation of the chromophores in epoxy resin without precipitation at high temperature is an effective methodology in preventing chromophore aggregation up to high concentrations. The use of the ionic liquid P₆₆₆₁₄DPAS was found to be not mandatory, but it plays an essential role in preventing the precipitation of the Epo-DPA monomer and in improving the processability of the film as shown below.

3-3-4 Storage Stability of the Films

Excellent in-air and long-term stability were observed as a characteristic of the rigid epoxy resin. The film **1** showed almost no change in TTA-UC efficiency after 1.5 years of storage in air at room temperature (Figure 3-3-13a). The absorption spectra of the film **3-1** before/after the 1.5 years of storage also showed no change, which indicates no aggregation or phase separation of the sensitizers occurred over time (Figure 3-3-13b). Additionally, the UC intensity was maintained at 84% even after 1800 s of continuous laser irradiation at an excitation intensity of 1040 mW cm⁻² (Figure 3-3-13c). Since there was no difference in stability between films made in air and nitrogen atmospheres, the chromophores were probably degraded by the laser-induced local heating, not by oxygen. Temperature dependence of the TTA-UC emission intensity for film **3-1** shows no decrease in the UC emission intensity below T_g , indicating that TTA-UC occurs by energy migration rather than molecular diffusion in the glassy resins (Figure 3-3-13d).⁴² A decrease in the TTA-UC emission intensity was observed upon heating above T_g . By lowering the temperature again, the TTA-UC emission intensity was reversibly recovered, indicating the high thermal stability of the resin material. The decrease of the TTA-UC emission intensity for the film under air was larger than that observed under N₂, probably due to the effect of oxygen quenching (Figure 3-3-13d). To understand the observed decrease of TTA-UC emission intensity by heating, we have additionally measured the

temperature dependence of the fluorescence intensity of the emitter in the film **3-1** with a 375 nm light source. The fluorescence intensity of the film also decreased with increasing temperature, which followed the curve of the TTA-UC emission intensity (Figure 3-3-13d). These results indicate that the TTA-UC intensity of the film decreased with increasing temperature partly due to thermal deactivation of the emitter fluorescence and the oxygen quenching above T_g .

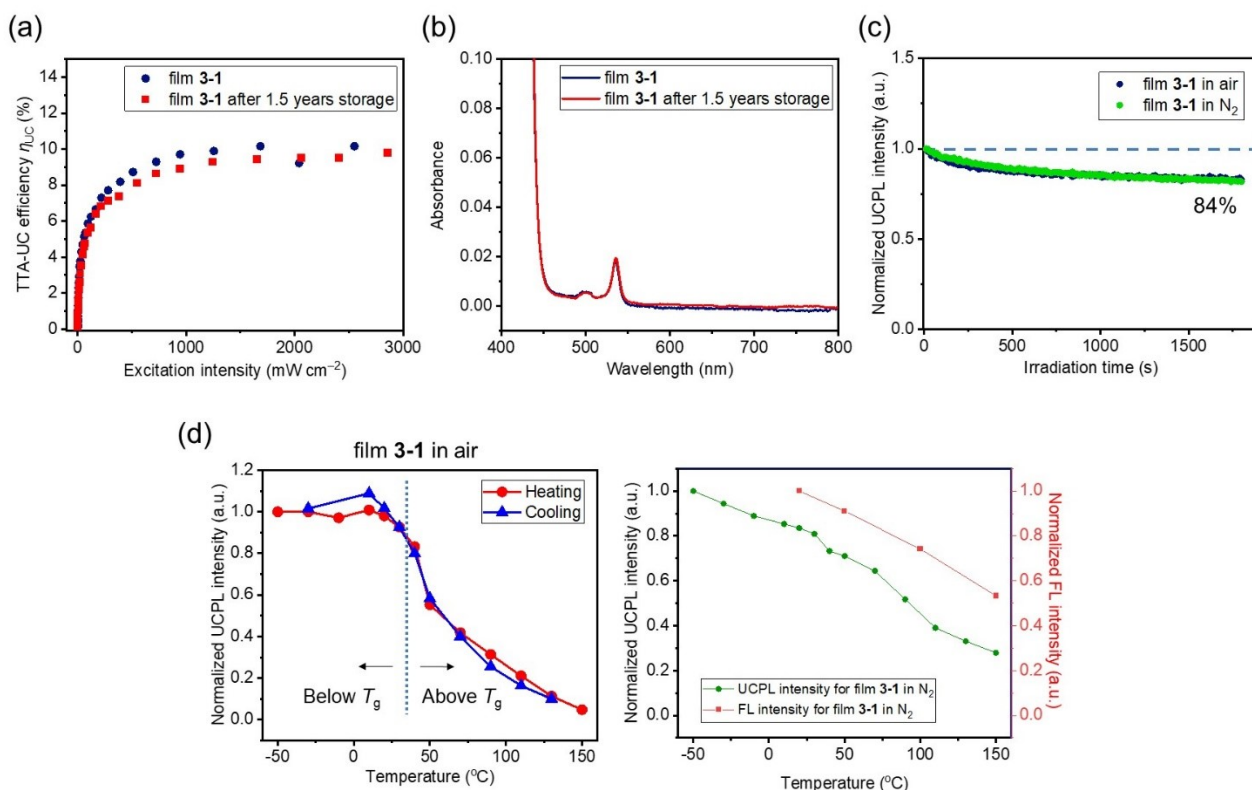


Figure 3-3-13. (a) TTA-UC efficiency η_{UC} of the film **3-1** measured as a function of excitation intensity at an excitation wavelength of 532 nm before (blue circles) and after (red square) long-term storage at room temperature in the air for 1.5 years. (b) UV-vis absorption spectra of the film **3-1** before (blue line) and after (red line) long-term storage for 1.5 years in air. (c) UCPL intensity of the film **3-1** prepared under air (blue) and under N_2 (green) under continuous laser irradiation at 532 nm (1040 mW cm^{-2} , 1800 sec). (d) Temperature dependence of the TTA-UC emission intensity for the film **3-1**. The 532 nm laser intensity was kept at 683 mW cm^{-2} . The UC emission intensity is normalized to the value at $-50 \text{ }^{\circ}\text{C}$.

3-3-5 Processability Demonstrations of the Films

The advantage of resin materials is that they can be molded in a wide size range from nano to millimeters. Nanothin films of the resin were obtained by spin-coating 10 wt% precursor solution using cyclopentanone as a solvent, followed by heating on a hot plate at 150 °C. The thickness of the obtained film was estimated as 300 nm by surf-coder measurements. Even though the thickness of the obtained nanofilm was in the nanoscale, it clearly showed blue TTA-UC emission in the air by green light irradiation (Figure 3-3-14a). Furthermore, it is possible to mold the resin into more complex shapes by using arbitrarily shaped molds. As a demonstration, we were able to mold the resin into a lens shape by using molds of millimeter and micrometer sizes, and the resulting small resin material showed blue TTA-UC emission when irradiated with green light (Figure 3-3-14b). The high moldability of the resin is expected to be very advantageous in the practical application of TTA-UC.

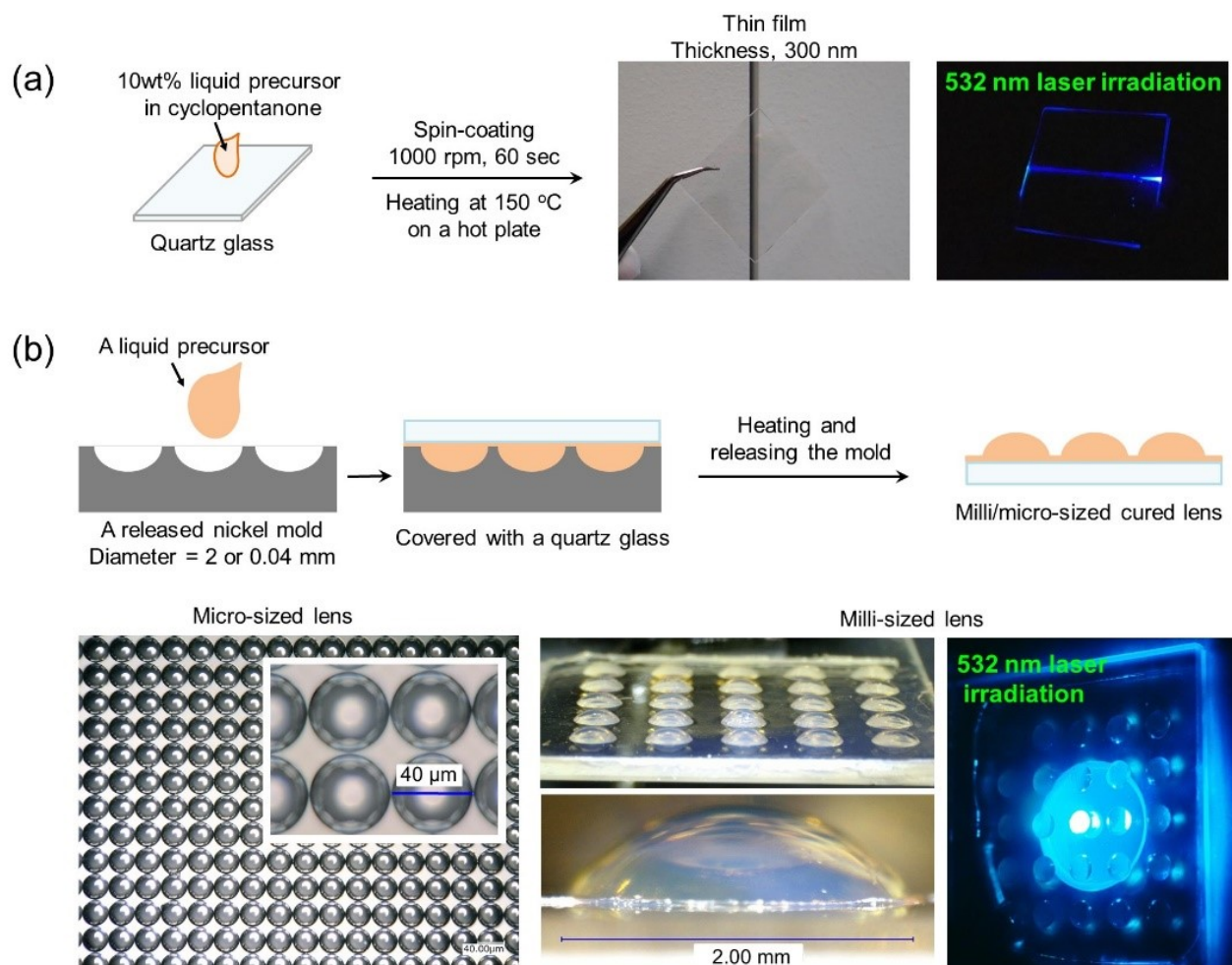


Figure 3-3-14. (a) Preparation of the thin resin film by spin-coating and subsequent heating. The photographs were taken under room light and 532 nm laser irradiation through a 510 nm short-pass filter. (b) The procedure of making the milli/microlens of resin by molding. Microscopic images of the obtained milli/microlens and photograph under 532 nm laser irradiation through a 510 nm short-pass filter.

3-4 Conclusions

In this chapter, the TTA-UC properties of the films by covalently and noncovalently introducing the emitter moiety in epoxy resin without aggregation at ultrahigh concentrations exceeding 30 wt% were developed and evaluated. The results showed the achievement of the highest TTA-UC efficiency to date in a rigid solid where chromophore molecules do not diffuse. The key finding is that the high concentration of emitters over 30 wt% is important not only for triplet energy transfer from sensitizer to emitter and triplet exciton diffusion between emitters but also for the suppression of triplet back energy transfer from emitter to sensitizer. The suppression of triplet back energy transfer has been mainly studied in solution,⁵² and it is now possible to understand it in detail for the first time in a rigid solid by systematically changing the emitter concentration. The generality of our design guidelines is confirmed by the similar TTA-UC efficiencies for the epoxy resins without the ionic liquid, but the inclusion of ionic liquids prevents monomer reprecipitation and improves processability. The results of this study provide important design guidelines for the development of rigid TTA-UC materials with excellent oxygen tolerance and long-term stability for future applications. The advantage of epoxy resins with highly condensed yet dispersed chromophores is that they can be molded into films and more complex shapes in a wide range of sizes from centimeters to nanometers. In the future, it will be possible to develop chromophore systems that exhibit TTA-UC at different wavelengths with designable shapes suitable for target applications in a wide range of fields, from energy to biology.

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Chapter 4 Conclusion

In this thesis, rational design guidelines for an efficient triplet energy migration-based photon upconversion system in a rigid matrix have been proposed. The issues that have been achieved for each study are summarized below.

In chapter 2, the first sample of rigid epoxy resins showing the efficient TTA-UC have been introduced. Generally, it was difficult to disperse the emitters in high concentrations in the rigid film, where the molecular diffusion was suppressed. In the proposed method, the rigid bulk film uniformly and highly containing UC chromophores can be obtained by simply heating the liquid mixture of monomer resins and UC chromophores. The TTA-UC efficiency of 3.8% is relatively high among the previous reports of rigid film systems, which is due to the significant increase in the energy efficiency of TEM-UC. A unique property of the triplet lifetime for the emitter in the bulk film was also found to be significantly enhanced by the suppressing of molecular motion. More additionally, thanks to the excellent oxygen blocking ability, there was no difference in the TTA-UC performance in air and deaerated atmosphere. This study overcomes the critical challenge of achieving efficient and air-stable TTA-UC in technologically promising thermal stable, transparent, and rigid films.

In chapter 3, to further progress the results of chapter 2, the rigid films with an ultra-high concentration of the chromophore molecules have been developed. It is widely accepted that high concentrations of chromophores are required, ideally without concomitant aggregation or self-quenching, to ensure efficient energy transfer processes in solid-state TTA-UC systems. Some reported literature aimed to optimize the TTA-UC efficiency by increasing the emitter content, however, the highest efficiency was not achieved in the condition of the highest emitter concentration. In consequence, it is desired to provide the design guidelines on how to increase the emitter concentration without aggregation or phase separation. We have achieved the highest TTA-UC efficiency to date by covalently and non-covalently introducing the emitter moiety in epoxy resin without aggregation at ultra-high concentrations exceeding 30wt%. The high concentration of

emitters over 30 wt% is important not only for triplet energy transfer from sensitizer to the emitter and triplet exciton diffusion between emitters but also for the suppression of triplet back energy transfer from emitter to sensitizer. The fact could be understood in detail for the first time in a rigid solid by systematically changing the emitter concentration. The film has also kept the mechanical properties such as transparency, rigidity, oxygen tolerance, and processability at the same time. More additionally, processability by fabricating thin films and microlenses can be demonstrated.

In the future, it will be expected to develop chromophore systems that exhibit TTA-UC at different wavelengths with designable shapes for target applications.

Finally, the author is convinced that the design guidelines for the development of TTA-UC in rigid matrices described in this thesis contribute not only the advancement of the TTA-UC systems toward practical use but also to the fundamental understanding of the TTA-UC mechanism in the solid-state TTA-UC system. The author also hopes that further development based on the design guidelines will lead to the establishment of a society in which light energy will be effectively utilized in the future.

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