

Design and Synthesis of Multi-Color Luminescent Polyimides with Very Large Stokes Shifts and Their Performance for Solar Spectral Conversion

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Polymeric optical materials exhibiting high quantum-yield photoluminescence (fluorescence and phosphorescence) are expected to be used for wavelength down-conversion in a wide range of applications such as flat panel displays, photovoltaic devices, and crop cultivators^[1,2]. However, conventional photoluminescent polymers consisting of π -conjugated sequences, such as poly(*p*-phenylene) and polyalkylthiophene, do not have sufficient thermal resistance and environmental stability, and they do not comply with the high temperatures required by device fabrication processes in modern electronics and photonics applications. Polyimides (PIs) are a class of high-performance polymers that have been widely known for their high thermal, mechanical, and radiation stabilities originating from their rigid molecular structures and strong intermolecular interactions^[3]. Recently, fluorescence emission properties of PI films have attracted much interest owing to their applicability to new types of optical materials with high durability (**Figure 1**)^[4-14]. Owing to their high thermal and chemical stabilities, the physical properties of PIs are tolerable even though they pass through tough device manufacturing processes at elevated temperatures over 350 °C.

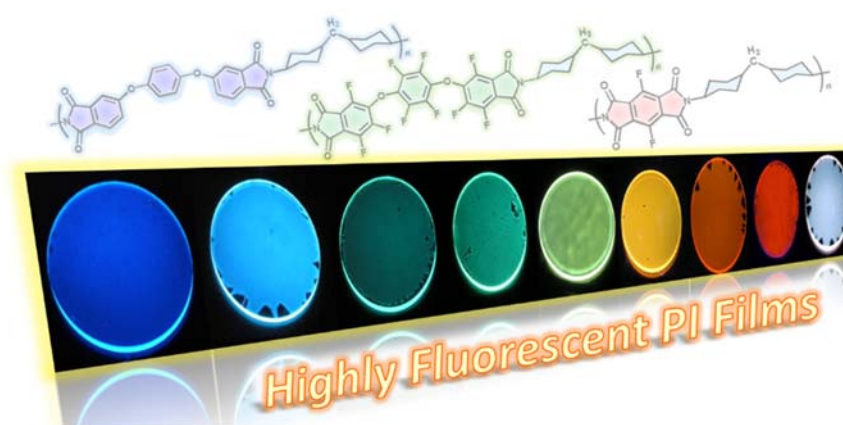


Figure 1. Highly fluorescent polyimide (PI) films.

It is well-known that wholly aromatic PIs (Ar-PIs) undergo two types of electronic transitions after irradiation by UV or short wavelength visible light. The first one is called “locally excited (LE) transition” that involves the dianhydride moieties; the second one is called “charge transfer (CT) transition” that originates from CT complex formation between the electron-donating diamine and the electron-accepting dianhydride moieties (**Figure 2**). Furthermore, LE transitions can be classified into “ π - π^* ” and “ n - π^* ” transitions. LE(π - π^*) transitions in PIs are generated at π -conjugated components of dianhydride moieties, whereas LE(n - π^*) transitions are generated from lone-pair electrons at carbonyl oxygen and nitrogen atoms in imide rings (n -orbital). Hasegawa et al.^[6] first demonstrated that PMDA/ODA and *s*-BPDA/PDA PIs exhibit weak fluorescent emission at 400–700 nm in response to optical excitation at CT absorption bands in the UV/short-visible region. However, their quantum efficiency (Φ) of CT fluorescence is very low due to the very small oscillator strengths of the CT transitions; for example, a Φ value of 9.7×10^{-7} was reported for the PMDA/ODA PI film. On the other hand, Horie et al.^[5] have further investigated absorption and fluorescence properties of semi-alicyclic PIs (Al-PIs) based on 4,4'-diaminocyclohexylmethane (DCHM) and 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (DMDHM) with PMDA. These PIs showed high optical transparency in the visible region due to effective suppression of intramolecular CT interactions due to the weak electron-donating property of the alicyclic diamine. However, these PIs exhibited CT emission peaks at around 500 nm in addition to LE emission peaks at around 400 nm,

although they had no apparent CT absorption peaks in the absorption spectra. The authors concluded that the CT emission was originated from interchain CT complexes formed between alicyclic diamine moieties of one molecular chain and dianhydride moieties of the other. This conclusion was supported by the enhancement of CT fluorescence with increasing thermal imidization temperature. Meanwhile, Ishii et al.^[8] have reported that an Ar-PI prepared from *s*-BPDA and *trans*-1,4-diaminocyclohexane (*t*-CHDA) showed an LE absorption peak at 320 nm and an intense emission peak at 385 nm, whereas no CT absorption and fluorescence were observed. The Φ value of *s*-BPDA/*t*-CHDA was reported as 0.05, which was much higher than those of Ar-PIs, such as PMDA/ODA. This large Φ value could be explained by the extended π -conjugation in the aromatic dianhydride moiety in addition to the suppression of intra/intermolecular CT interactions by introducing alicyclic diamine with weak electron-donating properties.

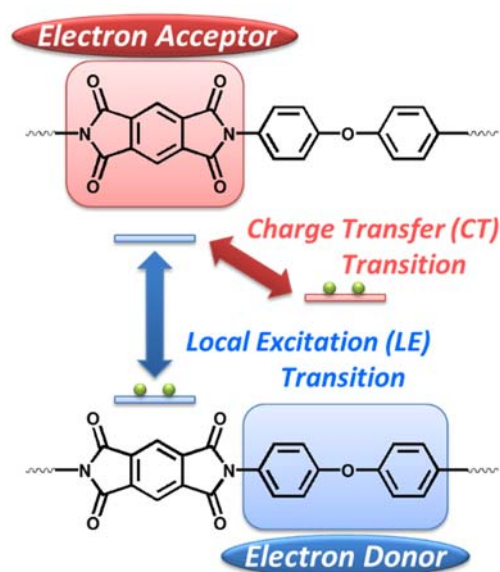


Figure 2. LE and CT transitions of Ar-PI.

Optical measurements of low-molecular-weight (low-Mw) imide model compounds, that have the same skeletal structures to the repeating units of PIs, dissolved in solution are straightforward and useful to understand and predict the fluorescence properties of PIs because PIs are generally insoluble in common organic solvents due to their rigid and linear molecular chains and strong intermolecular interactions. Recently, we have proposed and confirmed a novel molecular design concept for “highly fluorescent PIs (HFPIs)” based on the density functional theory (DFT) calculations and optical measurements of low-Mw imide model compounds^[9]. The principles for designing highly fluorescent PIs can be summarized as follows: (1) use alicyclic diamines, and (2) use aromatic dianhydrides that have flexible linkages with extended π -conjugation. According to this concept, we have successfully synthesized a strongly blue fluorescent PI derived from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDEA) and 4,4'-diaminocyclohexylmethane (DCHM), which exhibited a Φ value of 0.11. We have also reported a series of PIs synthesized from perfluorinated aromatic dianhydrides, such as 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA) and difluoropyromellitic dianhydride (P2FDA), which exhibited strong bluish green and red fluorescence, respectively.

Although their fluorescence intensity was significantly enhanced, these HFPIs are not fully suitable to wavelength down-converters because the energy differences between the absorption and fluorescence peaks, called 'Stokes shifts', are not large enough (**Figure 3**). For example, the spectral sensitivity of crystalline silicon (c-Si) solar cells begins in the near-UV region (~ 380 nm) and has its maximum in the near-infrared region (~ 800 nm). Owing to the spectral mismatch between solar power and c-Si solar cells, the contribution of UV light to electric power generation is very limited. In this case, it is highly preferable to convert UV light into visible light at longer wavelengths or near-infrared light. Therefore, in addition to the enhancement of their fluorescence quantum yields, enlargement of Stokes shifts is strongly desirable for fluorescent PIs specialized for spectral converters.

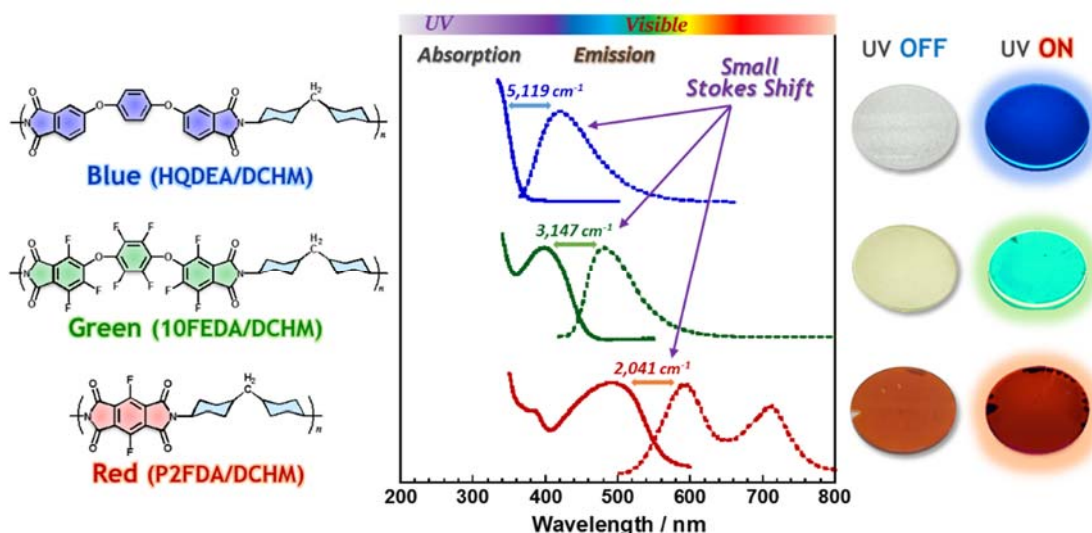


Figure 3. Optical absorption and fluorescence spectra of HFPI films.

We have recently reported that a series of PIs and low-Mw imide compounds containing hydroxy (-OH) groups, which form ideal intramolecular hydrogen bonding (*intra*-HB) between the -OH and imide C=O groups, exhibit strong various colored fluorescence with very large Stokes shifts ($\nu = 7,655 \sim 11,394 \text{ cm}^{-1}$) via excited-state intramolecular proton transfer (ESIPT) (**Figure 4**)^[10,12,14]. In our previous study, we reported that 3-hydroxy-*N*-cyclohexylphthalimide (3HNHPI), an imide compound containing an -OH group and forming a six-membered intramolecular hydrogen bonding (*intra*-HB) between the -OH and C=O groups, exhibits strong green fluorescence with a large Stokes shift ($\nu = 11,394 \text{ cm}^{-1}$, $\Phi = 0.35$). It has been reported that molecules with *intra*-HB structures similar to 3HNHPI undergo ESIPT as a result of the increased proton-donating and accepting properties of -OH and C=O groups, respectively, upon UV excitation. ESIPT compounds could be widely applied in laser dyes, high-energy radiation detectors, UV-photo-stabilizers, and fluorescent probes^[15]. In case of 3HNHPI, ESIPT phenomenon was strongly suggested to take place in the excited state. Excitation of an enol form by UV irradiation readily generates the Franck-Condon excited state, which rapidly undergoes an ESIPT process to generate an excited-state keto tautomer. During the subsequent relaxation to the ground state by radiative or non-radiative processes, a reverse proton transfer occurs to yield the original ground-state enol. Because of the large energy difference between the enol and keto tautomer, the excited-state keto tautomer exhibits an unusual green emission with a large Stokes shift. Additionally, we prepared another series of HFPIs using 4,4'-oxydiphthalic dianhydride (ODPA) and DCHM end-capped with 3HNHPI structure, and these PIs exhibit multicolor fluorescence (blue, light blue, white, and light-green) depending on the amount of fluorescent 3HNHPI termini while maintaining colorlessness and transparency ($\Phi = 0.08 \sim 0.14$)^[10]. Later on, we investigated that CHCl_3 solution of a pyromellitic diimide compound 3H-MC exhibited an intense fluorescence band at 592 nm with a very large Stokes shift of $10,356 \text{ cm}^{-1}$ when excited at 367 nm ($\Phi = 0.19$)^[14]. The corresponding PI, 3H-PI, in a solid film state, also exhibited an intense ESIPT fluorescence at similar emission wavelength of 590 nm with a very large Stokes shift of $10,448 \text{ cm}^{-1}$ when excited at 360 nm ($\Phi = 0.07$). This indicates that ESIPT takes place not only in solution but also in solid film state. Although the 3H-PI film exhibits a large Stokes shifted ESIPT fluorescence, the film showed strong yellow coloration due to dense aggregation of PI chains in the solid state. Thus, we introduced bulky trifluoromethyl groups in the diamine moiety of 3H-PI (3H-6F) to suppress the aggregation formation, and the 3H-6F solid film showed highly colorlessness and transparency in the visible region as well as a largely Stokes shifted ESIPT fluorescence ($\nu = 10,316 \text{ cm}^{-1}$, $\Phi = 0.08$). In a similar fashion, CHCl_3 solution of an imide compound P2H-Ch ($\Phi = 0.16$), and the corresponding PI P2H-DC film ($\Phi = 0.01$) exhibited an intense large Stokes shifted red ESIPT fluorescence at around 640 nm ($\nu > 7,500 \text{ cm}^{-1}$)^[12]. To the best of our knowledge, thermally stable polymers such as PIs with ESIPT moieties incorporated in their main chain have never been reported.

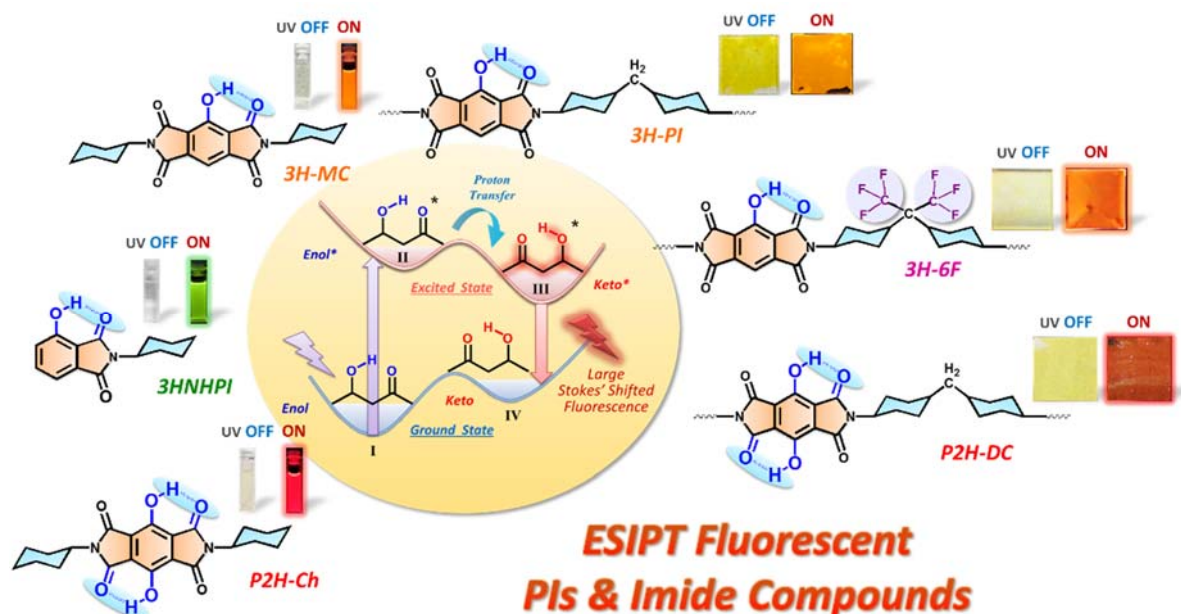


Figure 4. Fluorescence properties of -OH containing PIs and low-Mw imide compounds.

Interestingly, an -OH containing imide compound P2H-Ch and an -OH containing PI P2H-DC show significant changes in their appearance in response to basicity^[12]. The pKa values of phenolic -OH groups are generally smaller than those of alkyl alcohol -OH groups. This originates from the resonance effect with the neighboring aromatic rings, which effectively stabilizes the conjugation of phenolic compounds. Therefore, deprotonation of -OH groups easily occurs in the presence of basic reagents (e.g., NaOH and DBU). P2H-Ch shows obvious variations in absorption spectra depending on the DBU concentration [DBU] in CHCl₃ (**Figure 5a**). When [DBU] reached to 10⁻³ M, the color of the solution immediately changed from pale yellow to bright pink. In addition, a new strong absorption peak was observed at 540 nm while the original absorption band at 421 nm disappeared. This spectral change clearly indicates that deprotonation was promoted by DBU, and the new absorption band is attributed to the mono-anion form. Furthermore, when [DBU] is increased up to 1 M, the color of the solution gradually changed from bright pink to light blue. In addition, another new absorption peak was observed at a much longer wavelength (638 nm), and the band at 540 nm significantly weakened. This indicates that the second deprotonation step took place, and the new absorption band is attributable to the di-anion form. As seen in the photos in **Figure 5a**, the pH-dependent color change, i.e., halochromism, from pale yellow (enol, neutral) to light blue (di-anion) through bright pink (mono-anion) is very vivid and prominent. Similar to P2H-Ch solution, P2H-DC PI film also shows highly visible halochromism after soaking the PI film in NaOH aqueous solutions (pH 11 and 14) (**Figure 5b**). At pH 11, the intensity of the absorption band at 407 nm for P2H-DC gradually decreased and the intensity of the new band at 529 nm increased. The wavelength of the new band agrees well with the absorption band of P2H-Ch dissolved in CHCl₃/DBU ([DBU] = 10⁻³ M), indicating that the band is attributable to the mono-anion form of P2H-DC. After soaking in a basic solution, the film color gradually changed from pale yellow to deep red due to the first deprotonation of the -OH group in the dianhydride moiety. Furthermore, at pH 14, another new absorption band was observed at a much longer wavelength around 630 nm. This also coincides well with the absorption band of P2H-Ch dissolved in CHCl₃/DBU ([DBU] = 1 M), indicating that the new band is attributable to the di-anion form of P2H-DC. The film color then changed to deep blue due to the second deprotonation of the residual -OH groups. These facts indicate that imide compounds and PIs with -OH groups at the pyromellitic moiety are highly sensitive to the basic conditions, exhibiting significant halochromism. Therefore, they can be used not only in electronics and photonics applications, but also as pH sensors with color changes from yellow through deep red (at pH 11) to deep blue (pH 14).

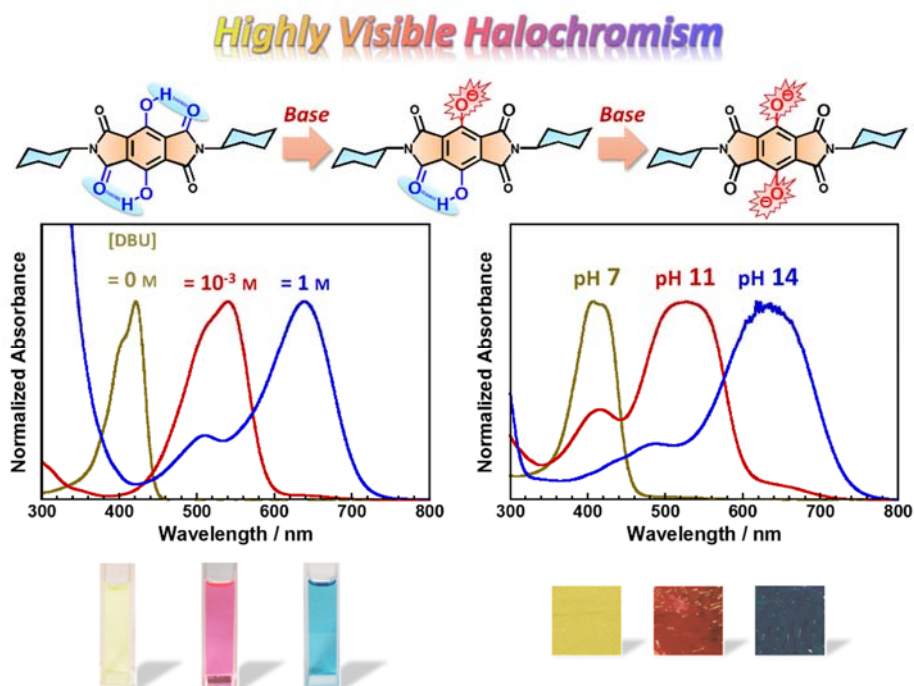


Figure 5. Highly visible halochromism of (a) P2H-Ch solution, and (b) P2H-DC film.

Recently, we have investigated the transmission light-conversion properties in the UV/visible region of an HFPI copolymer derived from HQDEA (99.7 %) and P2HDA (0.3 %) as the dianhydride components (**Figure 6**). As mentioned above, HQDEA and P2H-DC afford blue- and red-emitting HFPIs, and efficient energy transfer from HQDEA moiety to P2H-DC moiety occurs in the excited state. The film thus obtained looks pale pink in color and has a strong absorption band below 380 nm. In turn, the converted light intensities in the red (~ 600 nm) regions are obviously enhanced by 10 ~ 16 % due to its fluorescent emission, whose Φ value was as high as 0.13. This spectrum demonstrates that judiciously designed HFPI films are promising for tough/flexible wavelength converters, in which the UV and violet components of solar and LED light are efficiently converted to long-wavelength-visible light without consuming external energy.

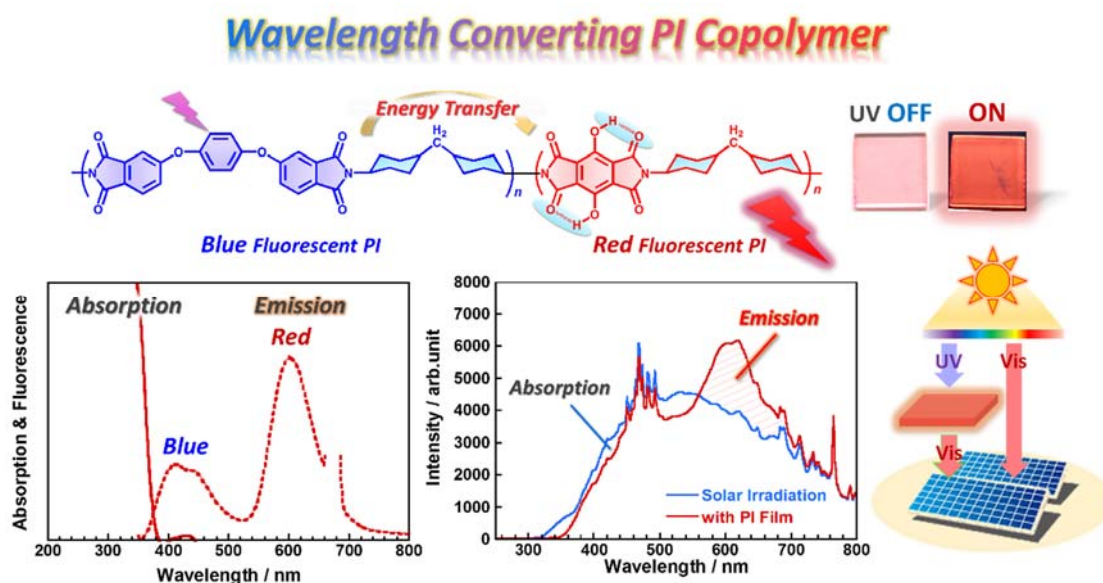


Figure 6. Highly fluorescent PI copolymer and its spectral conversion property.

Room-temperature phosphorescence (RTP), which is emitted from organic compounds without heavy metals, has attracted increasing attention owing to its various functional applications, such as cellular imaging and temperature and oxygen sensors^[16,17]. In general, the lowest triplet excited state (T_1) lies at a lower energy level than the lowest singlet excited state (S_1), resulting in a larger Stokes shift of phosphorescence compared

to that of fluorescence. RTP has been investigated mainly for heavy-metal-containing organo-complexes in which strong spin–orbital couplings facilitate intersystem crossing (ISC)^[18]. On the other hand, phosphorescence from purely organic molecules has been observed only under cryogenic conditions or in rigid matrices where local molecular motions are suppressed. However, it was recently reported that organic carbonyl compounds substituted with heavy halogens (Br, I) enhance the possibilities of ISC, which results in large-Stokes-shifted RTP emission.^[16] Owing to the many advantages of purely organic RTP compounds, such as facile synthetic procedures, nontoxicity, and low environmental load in addition to large Stokes shifts, relevant studies are currently increasing. Most recently, we have developed novel highly phosphorescent PIs and low-Mw imide compounds based on heavy atom effects of bromine (Br) and iodine (I) atoms in the dianhydride moieties. (Figure 7)^[19].

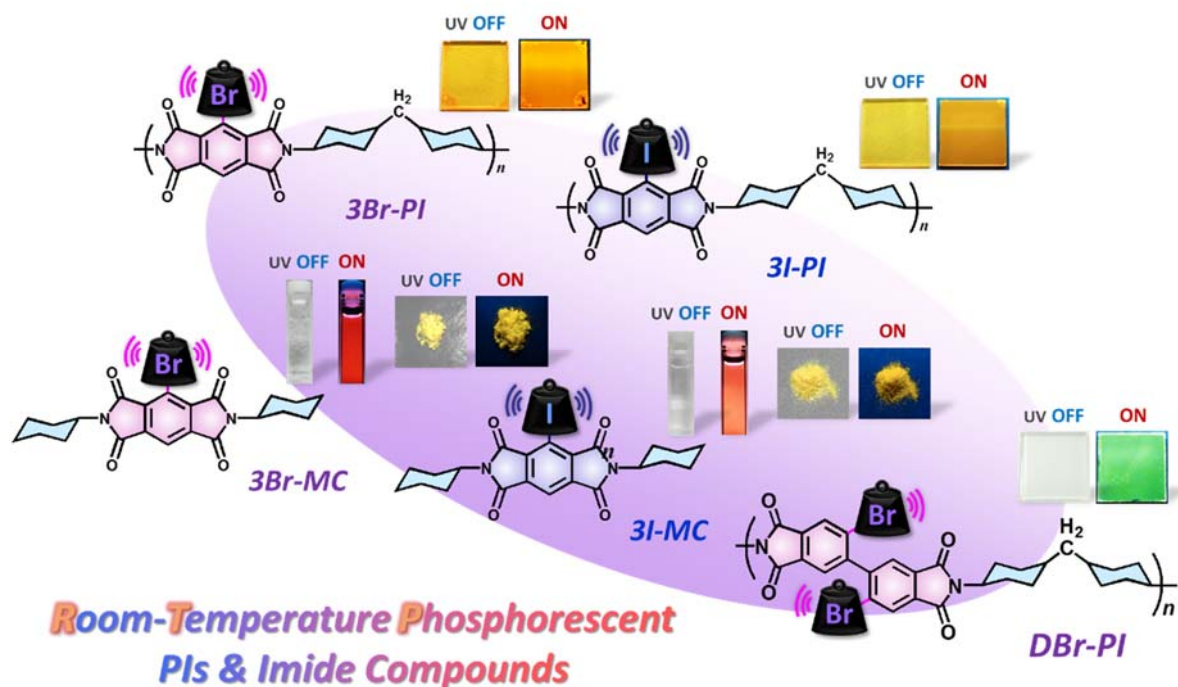


Figure 7. Room-temperature phosphorescent PIs and imide compounds.

For example, CHCl_3 solutions of low-Mw imide compounds containing Br or I atom (3Br-MC, 3I-MC) exhibit bright red color RTP at around 590 nm with very large Stokes shifts of more than $10,000\text{ cm}^{-1}$ ($\Phi = 0.01 \sim 0.02$). In general, the phosphorescence lifetimes are much longer (orders of micro- or milliseconds) than the fluorescence lifetimes (orders of pico- or nanoseconds) due to additional spin inversion process during relaxation from the excited triplet states to the singlet ground states. However, both of emission lifetimes of 3Br-MC and 3I-MC solutions monitored at the RTP peak wavelengths were nanosecond-order; the longest relaxation components were estimated as 7.1 ns for 3Br-MC and 13.0 ns for 3I-MC. In the case of dilute solutions, photoluminescence lifetimes are mainly dominated by quenching effects from molecular motion and dissolved oxygen. Since the emission spectra and lifetimes of 3Br-MC and 3I-MC solutions did not change after bubbling with nitrogen, such short lifetimes should be caused by vigorous motions in solutions, which induces nonradiative decay. Similar to the low-Mw imide compounds, PIs containing Br or I atom (3Br-PI, 3I-PI), in the solid film state, also exhibit bright red color RTP at around 590 nm with very large Stokes shifts of ca $10,000\text{ cm}^{-1}$ ($\Phi = 0.01 \sim 0.03$). The RTP lifetimes of 3Br-PI and 3I-PI films were estimated to be on the order of milliseconds even under the atmospheric condition; 2.3 ms for 3Br-PI and 1.0 ms for 3I-PI, which should be due to significantly restricted molecular motions in solid films compared with in solution. The RTP lifetimes measured under vacuum were significantly elongated to 9.9 ms for 3Br-PI and 3.3 ms for 3I-PI, and this fact can also be evidence that the large-Stokes-shifted emission at around 590 nm originates from the excited triplet state. Note that the RTP lifetime of 3I-PI is shorter than that of 3Br-PI both under atmospheric and vacuum conditions, which is attributable to the efficient ISC from the excited triplet to the ground states because the heavy atom effect is more significant in the iodine-containing PI. These indicate that the introduction of heavy halogens into the dianhydride moieties of PIs and imide compounds makes them highly phosphorescent at room temperature via ISC. In addition, the thermal decomposition temperatures at a 5% weight loss (T_d^5) were 406 and 379 °C for 3Br-PI and 3I-PI films, respectively, which indicates that the incorporation of heavy halogens does not deteriorate

the thermal stabilities of PIs. Furthermore, both of 3Br-PI and 3I-PI films show high average refractive indices ($n_{av} = 1.5942$ and 1.6111) and small in-plane/out-of-plane birefringence ($\Delta n = 0.0206$ and 0.0172) at 633 nm . The high refractive indices originate from the high polarizabilities per unit volume of Br and I atoms. The low birefringence could be due to the large atomic radii and spherical electron distributions of Br and I atoms, which reduce the polarizability anisotropy of PI chain units and loosen the interchain packing arrangement in the solid films. In contrast to the colorless low-Mw imide model compound solutions (3Br-MC, 3I-MC), 3Br-PI and 3I-PI films showed yellowish color due to the strong visible absorption caused by aggregated PI chains. Since PI chains form densely packed aggregate structures with the aid of intermolecular π - π interactions in solid films, these absorption bands are attributable to PI aggregates. In addition, it is well-known that, in halogenated aromatic compounds, strong intermolecular halogen- π interactions are induced with neighboring molecules, which also facilitate aggregation. To the best of our knowledge, amorphous polymers having RTP functions in their backbone structures have never been reported.

Unlike 3Br-PI and 3I-PI, a PI having biphenyl type dianhydride with Br atoms (DBr-PI) shows colorlessness and good transparency in the visible region. This is because the effective suppression of aggregate formation owing to the steric effects of the biphenyl dianhydride moiety. Interestingly, DBr-PI film exhibits a bright green RTP ($\Phi = 0.02$) with an emission peak at 515 nm with a very large Stokes shift of $12,215\text{ cm}^{-1}$. In addition, the RTP intensity of DBr-PI film is significantly enhanced under low temperature and vacuum conditions (**Figure 8**). The increase in RTP intensity under low temperature and vacuum is due to the restriction of molecular motions of DBr-PI polymer chains and the suppression of triplet-triplet quenching caused by oxygen existing inside/outside of the PI film. The Φ value of DBr-PI film at liquid nitrogen temperature (-196 C) was estimated to be 76% , which is 38 times larger than that at room temperature. Such PIs exhibiting strong RTP emission under low temperature and vacuum conditions are expected to be used as down-converters in cosmic space.

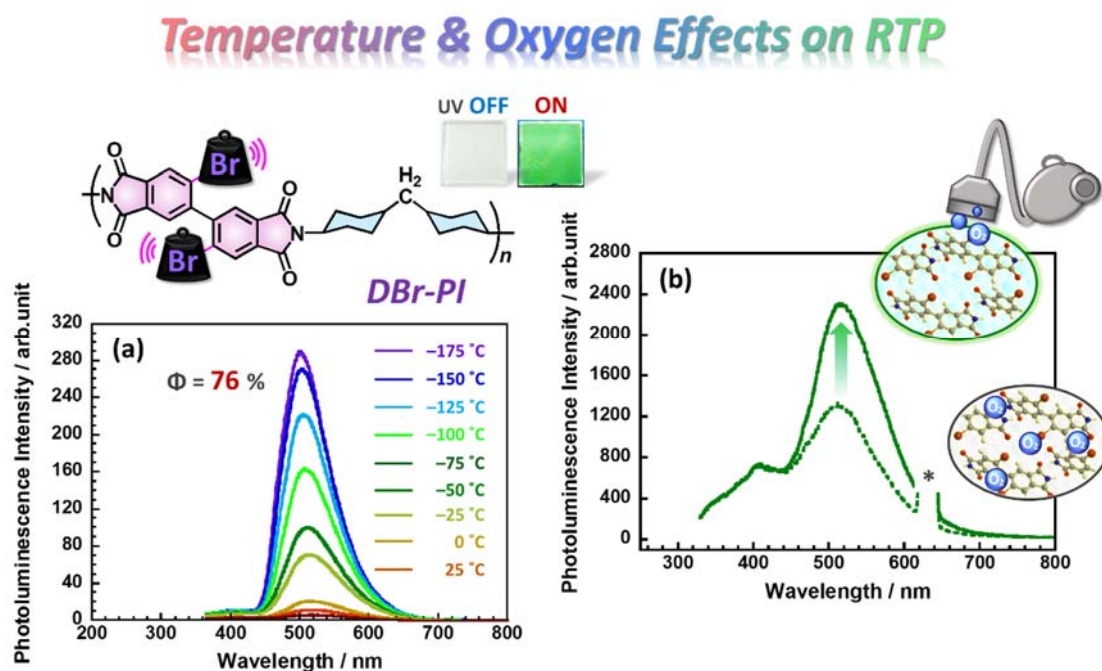


Figure 8. Photoluminescence spectra of DBr-PI film under (a) low temperature, and (b) vacuum conditions.

Novel highly fluorescent and phosphorescent PI films with very large Stokes shifts have been successfully developed by utilizing ESIPT and heavy-halogen-based RTP. In addition, highly colorless and transparent PI films were obtained by introducing steric effects in the dianhydride or diamine moieties. Such PIs showing high colorlessness and large-Stokes-shifted-emission can be used for wavelength down-converters applicable to solar cells, crop cultivation, and so on. Especially, fluorescent PI films having -OH groups in the dianhydride moiety show highly visible halochromism, implying that these kinds of PIs also can be used for pH sensing materials. In contrast, since the RTP intensities of heavy-halogen containing PIs show obvious changes depending on the surrounding temperature and oxygen concentrations, they can be applied for temperature and air/oxygen sensing materials. In conclusion, novel photo-luminescent PIs with very large Stokes shifts exhibiting high

thermal, environmental and radiation stabilities are valuable and promising materials for energy conservation in the future world.

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