Polyimides and Imide Compounds Exhibiting High Optical Transparency and Enhanced Phosphorescence Emission under Atmospheric and Very High Pressure

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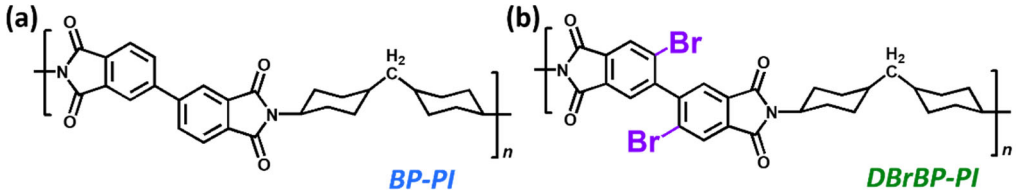
Photoluminescent organic polymers, such as polyphenylene and polyfluorene derivatives, have been widely studied because of their potential applications for spectral converters in the fields of luminescent solar concentrators, displays, LEDs, photovoltaic devices, and crop cultivation.[1-7] Down-converters are expected to convert short-wavelength light (ultraviolet (UV) or violet-blue light) to longer-wavelength light (green, yellow, red, or near-infrared (IR) light) with high quantum efficiency. Colorless, transparent, and environmentally stable polymer films with large luminescence Stokes shifts have been in demand for down-conversion of solar UV radiation. We have synthesized highly fluorescent polyimides (HFPI) with strong blue emission using a conventional dianhydride and an alicyclic diamine (BP-PI, **Scheme 1a**), of which the quantum yield (Φ) was as high as 0.11.[1] Moreover, we have reported a series of HFPIs derived from perfluorinated aromatic dianhydrides, such as 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA) and 1,4-difluoropyromellitic dianhydride (P2FDA), which exhibit strong bluish green and red fluorescence. Their much higher Φ values compared with those of conventional PIs are attributable, not only to effective suppression of the CT interaction, but also to the enhancement of the oscillator strengths of the local π-π* transitions at the π-conjugated dianhydride moieties. Although the photoluminescence properties of PI films have been improved dramatically on the basis of the above-mentioned molecular design concept, the energy gaps between the excitation and emission wavelengths, Stokes shifts (ν), are not satisfactory for spectral conversion applications. To develop thermally stable polymer films which exhibit enhanced phosphorescence at room temperature or lower temperatures with a very large Stokes shift and excellent thermal stability, we have synthesized a novel semi-aromatic polyimide (DBrBP-PI, **Scheme 1b**) using a biphenyl-tetracarboxylic dianhydride substituted with two bromine (Br) atoms.[8]



Scheme 1. Photoluminescent polyimides (PI), (a) fluorescent BP-PI and (b) phosphorescent DBrBP-PI.

Figure 1a shows the UV-vis absorption spectra of the BP-PI and DBrBP-PI films. The absorption band of DBrBP-PI was in a shorter-wavelength region than that of BP-PI. Similar hypochromic shift was also observed comparing absorption spectra of solutions of low-molecular-weight model compounds BP-PI (BP-MC) and DBrBP-PI (DBrBP-MC), which have the same chemical structure as the repeating unit of the corresponding PIs. The geometries of the model compounds in the ground state calculated by the DFT method revealed that DBrBP-MC has a much larger biphenyl dihedral angle of 88.5° than that of BP-MC (40.0°) because of the steric hindrances effect of the attached Br atoms (**Figure 1b**). This implies that DBrBP-MC has much lower degree of π-conjugation in the

biphenyl dianhydride moiety than BP-MC, which is in accordance with the hypochromic shift of the absorption band. Based on these facts, identical hypochromic absorption shift observed for DBrBP-PI should be also attributed to the steric hindrances effect of the attached Br atoms. No absorption band attributable to the aggregates of the PI chains was observed; this should be because of the intermolecular steric effect of the twisted biphenyl dianhydride structure, which can suppress the formation of aggregates even in the solid film. Both of the PI films exhibited absorption bands only in the UV region (< 400 nm), thus, they are perfectly colorless and transparent.[8]

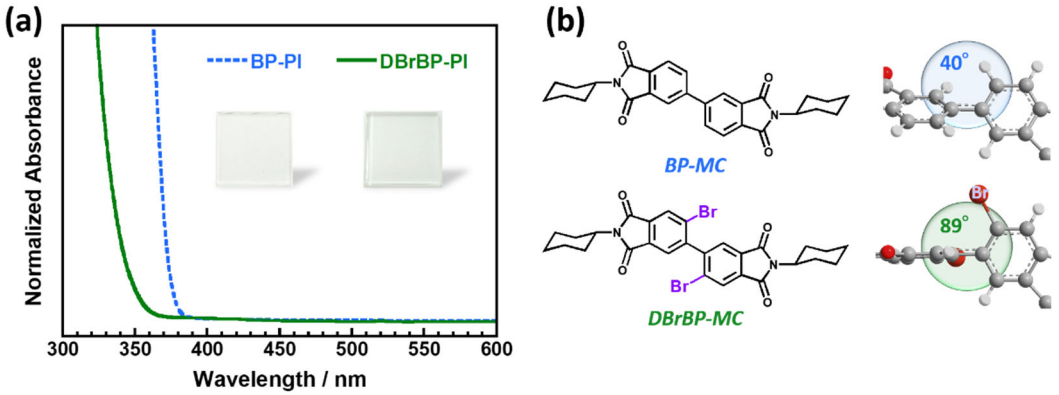


Figure 1. (a) UV-vis absorption spectra of BP-PI and DBrBP-PI films, and (b) biphenyl dihedral angles of the optimized structures of the model compounds (BP-MC and DBrBP-MC) obtained from DFT calculation. The spectra were normalized by their film thicknesses.

Figure 2a shows the photoluminescence excitation and emission spectra, and **Figure 2b** shows the photoluminescence decay curves of the BP-PI film measured at 298 K in ambient air and under vacuum conditions. The BP-PI film showed excitation and emission peaks at 367 and 406 nm, respectively, with a relatively small ν of 2617 cm^{-1}. This small Stokes shift clearly indicates that the emission of BP-PI is attributable to fluorescence from an excited singlet state with limited conformational or electronic changes in the excited state. The photoluminescence measured at 420 nm decayed non-exponentially with the longest delay component of 6.3 ns under atmospheric conditions. This decay behaviour did not change even under vacuum conditions, which proves the typical fluorescent nature of the BP-PI film.

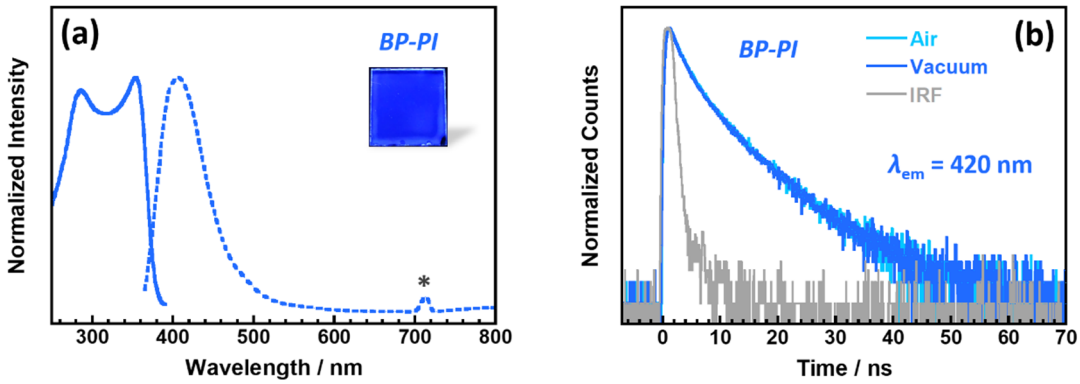


Figure 2. Photoluminescence properties of BP-PI film. a) Emission spectrum measured under excitation at 367 nm and excitation spectrum measured by monitoring emission intensity at 406 nm. b) photoluminescence decay curves at 420 nm under atmospheric and vacuum conditions.

Figure 3a shows the photoluminescence excitation and emission spectra, and **Figure 3b** shows the photoluminescence decay curves of the DBrBP-PI film measured at 298 K in ambient air and under vacuum conditions. In contrast to BP-PI, the emission spectrum of the DBrBP-PI film consists

of two broad components, which can be quantified by fitting using two Gaussian broadening functions. The spectrum is dominated by the prominent emission at 512 nm with a very large Stokes shift (ν=12,215 cm^{-1}) when excited at 315 nm at 298 K. This emission can be attributed to phosphorescence from an excited triplet state induced by enhanced intersystem crossing (ISC) originating from the heavy atom effect due to Br atoms in the dianhydride moiety. Interestingly, the photoluminescence at 520 nm lasted for more than 1 ms even under atmospheric condition (Figure 3b). This long lifetime is attributable not only to the ISC enhanced by Br atoms, but also to the rigid skeletal structure of the PI with restricted internal rotation at the biphenyl moiety, which effectively suppresses the local molecular motions inducing non-radiative decay of triplet excitons. In addition, the photoluminescence lifetime was significantly increased under vacuum conditions (Figure 3b), which indicates that the emission at 512 nm observed in the steady-state spectrum is highly sensitive to atmospheric oxygen, and this fact confirms the attribution of the large-Stokes-shifted emission to the excited triplet state. These facts indicate that the introduction of Br atoms to the BPDA moiety endows the PI with colorlessness with high transparency and large-Stokes-shifted phosphorescence properties, which is unusual not only for PIs but also for the main-chain-type polymers. Thus, DBrBP-PI is a promising candidate for spectral down-converting materials.

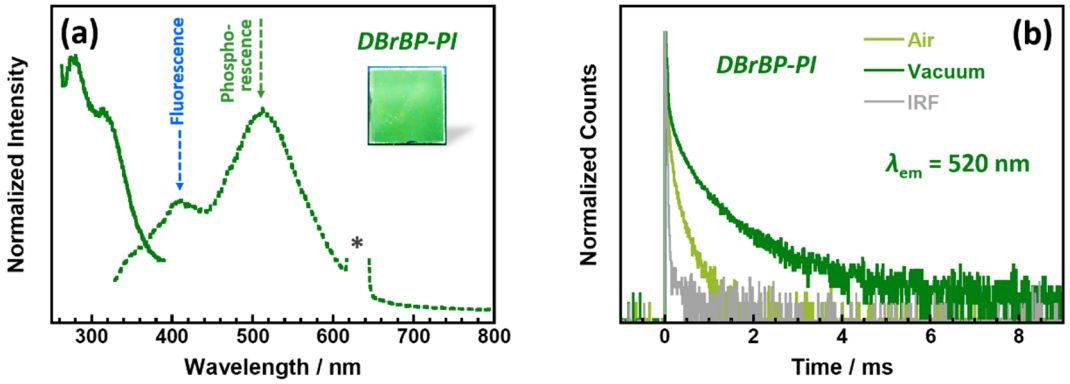


Figure 3. Photoluminescence properties of DBrBP-PI film. a) Emission spectrum measured under excitation at 315 nm and excitation spectrum measured by monitoring emission intensity at 512 nm. b) Photoluminescence decay curves at 520 nm under atmospheric and vacuum conditions.

We also measured steady-state emission spectra under vacuum conditions. The emission intensity and spectral shape of BP-PI did not show significant changes under vacuum (**Figure 4a**), which indicates the insensitivity of the excited singlet state to oxygen. In contrast, the emission intensity at around 510 nm of DBrBP-PI was significantly enhanced under vacuum (**Figure 4b**). This result indicates that this emission was effectively quenched by the triplet-triplet energy transfer to oxygen under atmospheric conditions, which is typical phosphorescence behaviour.[8]

The phosphorescence properties could be significantly affected by this molecular motion. To verify this view, we conducted photoluminescence measurements at lower temperatures (**Figure 5**). The luminescence intensity of BP-PI increased by 5-6 times at low temperatures, and the Φ value at liquid nitrogen temperature (77 K) was estimated to be 0.51, which is 2.3 times larger than the value at 298 K (Φ= 0.22). Because of the nature of the fluorescence of BP-PI, which has a short photoluminescence lifetime, the fluorescence intensity did not increase significantly at low temperatures because of the low sensitivity to the molecular motions. In contrast, the luminescence intensity of DBrBP-PI at low temperatures was significantly higher than that at 298 K by ca. 45 times. The Φ value at 77 K was estimated to be 0.76, which was 38 times as large as the value at 298 K (Φ = 0.02) and exceeded that of BP-PI at 77 K (Φ= 0.51). This Φ value is close to that of benzophenone dissolved in an organic solvent at 77 K (Φ= ~0.9), in which the probability of ISC is almost 100 %. Since the DBrBP-PI film exhibits intense phosphorescence at low

temperatures as well as under deoxygenated conditions, it could be promising for use in space, for example, as spectral down-converters for space solar cells, since the lowest temperature in the mesosphere (altitude of ca. 80 km from the ground) is around −90 °C.

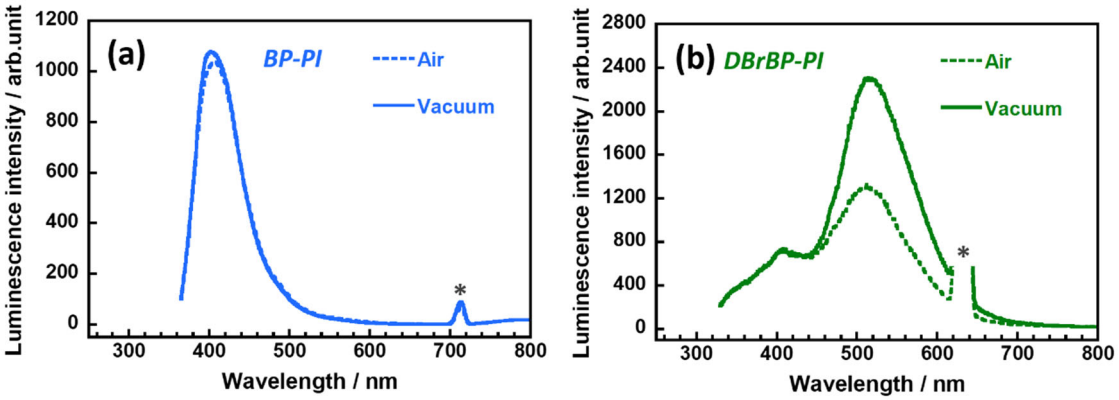


Figure 4. Photoluminescence emission spectra of (a) BP-PI and (b) DBrBP-PI films under atmospheric and vacuum conditions. Excitation wavelengths were 367 nm for BP-PI and 315 nm for DBrBP-PI. Asterisks indicate second order diffraction of excitation light.

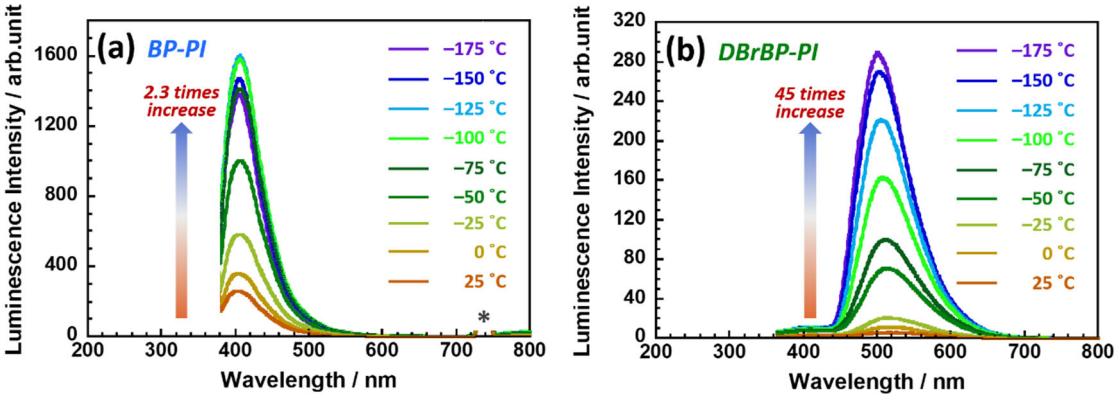


Figure 5. Photoluminescence emission spectra of (a) BP-PI and (b) DBrBP-PI films at low temperatures. Spectra were measured using excitation wavelengths of 367 nm for BP-PI and 315 nm for DBrBP-PI. Asterisk indicates second order diffraction of excitation light.

For clarifying relations between the luminescence properties and the aggregation state of the phosphorescent PI thin film, UV/vis absorption and photoluminescence spectra were measured under high pressures up to 8 GPa using a diamond anvil cell (**Figure 6**).[3,9] **Figure 7** shows the variations in (a) optical absorption and (b) photo-luminescence spectra of DBrBP-PI film at elevated pressures. The PI film exhibited visible fluorescence and phosphorescence at room temperature and atmospheric pressure. At higher pressures, intermolecular distances are shortened with compressing free volumes, and the dipolar-dipolar interactions, which induces intermolecular energy transfer and non-radiative deactivation, are significantly enhanced. As shown in Figures 7(b), both the fluorescence and phosphorescence intensities were significantly decreased at elevated pressures. However, in the low pressure range (< 2 GPa), in which free volume is effectively compressed, different attenuation behaviours of fluorescence and phosphorescence intensities were observed. Figure 7(c) clearly demonstrates that the attenuation rate of the fluorescence intensity was obviously larger than that of the phosphorescence intensity. The difference in attenuation behaviours is attributable to the difference in the energy transfer and deactivation mechanisms between singlet and triplet excitons, i.e. the Förster resonance energy transfer (FRET) for the fluorescence by singlet excitons, and the Dexter electron transfer (DET) for the phosphorescence by triplet excitons. (**Figure 8**)

In general, singlet excitons with fluorescence-emission ability can also undergo energy transfer between molecules several tens of nm away by the interaction of dipolar electric fields based on the Förster mechanism. On the other hand, the triplet excitons with phosphorescence-emitting ability can be transferred by overlap of molecular orbitals based on the Dexter mechanism. In this case, energy transfer is possible only between molecules adjacent to several nm.[10] Therefore, since singlet excitons can undergo energy transfer between spatially distant PI molecular chains, the energy transfer probability can be increased with the densification of the aggregation state at elevated pressures, which enhances non-radiative deactivation (Figure 8). On the other hand, triplet excitons are relatively less susceptible to elevation of pressure due to the Dexter-type energy transfer mechanism between the adjacent PI chains.

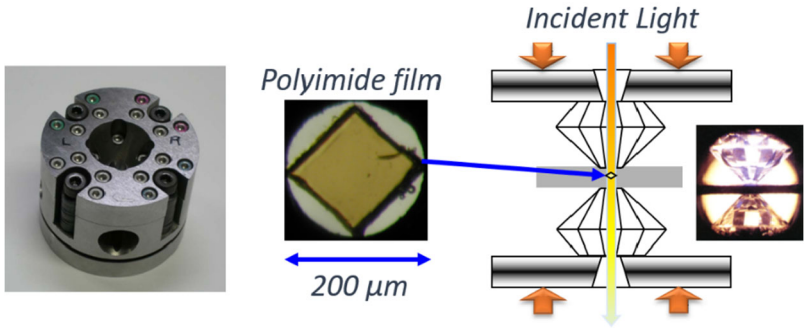


Figure 6. Photo of a diamond anvil cell (DAC) and schematic view of the experimental setup.

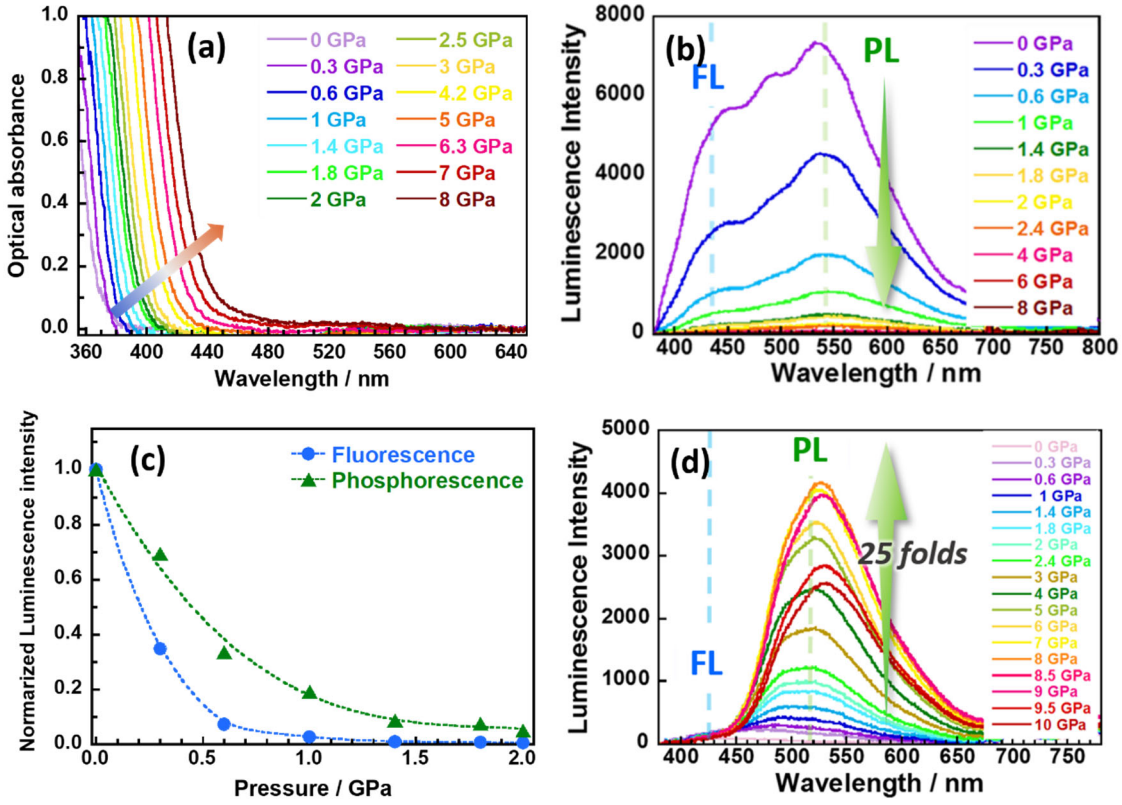


Figure 7. Pressure-induced variations in (a) optical absorption and (b) photo-luminescence spectra of DBrBP-PI film. (c) Pressure dependence of fluorescent and phosphorescent intensities of DBrBP-PI film. (d) (d) Pressure-induced variations in photo-luminescence spectra of DBrBP-MC dispersed in PMMA film (1 wt%).

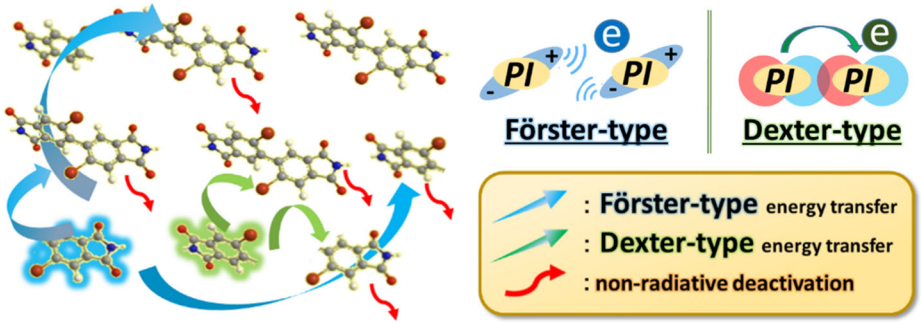


Figure 8. Schematic views of energy deactivation mechanisms for singlet and triplet excitons in PI films. Singlet excitons can undergo energy transfer between spatially distant PI chains via Förster-type mechanism, whereas triplet excitons undergo energy transfer between adjacent PI chains via Dexter-type mechanism.

Furthermore, to elucidate the influence of local molecular motion on the room temperature phosphorescence (RTF) of imide compound, DBrBP-MC was dispersed in polymethylmethacrylate (PMMA) at a low concentration (1 wt%), and emission spectra were measured under high pressures (**Figure 7d**). Contrary to DBrBP-PI, the phosphorescence intensity was significantly increased at elevated pressures; the emission intensity at 8 GPa was larger by ca. 25 times than the atmospheric pressure (0 GPa). This indicates that the nonradiative deactivation of excitation energy of the imide compound was greatly suppressed by the two factors; 1) Attenuation in intermolecular energy transfer by homogeneous dispersion in PMMA matrix, and 2) Suppression of local molecular motion by pressurization. These facts lead us to new design concepts toward colorless and thermally stable solar down-converters with high efficiency using RTF PIs.

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