Supporting Information

Precise Detection of Local Relaxation of Amorphous Polymers at Low Temperatures via O_2 Diffusion Probed by a Dual-Luminescent Imide Compound

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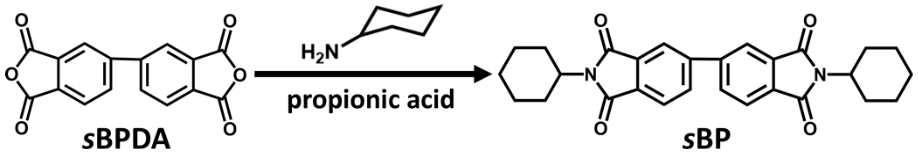
1. Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride (*s*BPDA), provided by Ube Industries Ltd., Japan, was purified by drying at 150 °C for 3 h, followed by sublimation at 280 °C for 4.5 h under vacuum. Polystyrene (PS, M_w~35,000) was purchased from Sigma-Aldrich Japan. Poly(methyl methacrylate) (PMMA, Sumipex-LG, M_w~100,000) and Polysulfone (PSF, Ultrason S, M_w~52,000) were provided from Sumitomo Chemical Co. Ltd., Japan, and BASF Japan Ltd., respectively. Cycloolefin copolymer (COC) was provided by Polyplastics Co., Ltd., Japan. Cycloolefin polymers (COP) including COP-A, COP-B, and COP-C were provided by Zeon Corp., Japan. Propionic acid, toluene, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Kanto Chemical Co., Inc., Japan. All chemicals and polymers were used as received without further purification.

2. Sample Preparation

The phosphorescence (PH) probe of *N*,*N*'-dicyclohexyl-biphenyl-3,3',4,4'-tetracarboxylicdiimide (*s*BP) was synthesized by the following the procedures reported by Doi et al.[1] A white powder of *s*BP was obtained (1.42 g, 3.1 mmol. 92% yield) by recrystallization from a toluene solution.



*s*BP-dispersed polymer films for optical measurements, which are designated as *s*BP-IC/matrix, were prepared by the following procedure. For the preparation of *s*BP/PS, PS (0.5 g) was dissolved in toluene (2.5 mL) and stirred at 25 °C for 24 h, followed by the addition of *s*BP (1 mg, 2.2 × 10^{-3} mmol). The solution was stirred for another 24 h at 25 °C and drop-cast onto a fused silica substrate (dimensions: 13 mm × 9 mm) under a nitrogen atmosphere and dried sequentially at 50 °C, 60 °C, and 70 °C for 3 h at each stage. Then, it was left at 25 °C overnight under ambient atmosphere and finally dried under vacuum at 80 °C for 9 h. *s*BP/COC and *s*BP/COP-A were prepared in the same manner. *s*BP/PMMA was prepared following a similar procedure, but chloroform was used as the solvent instead of toluene. For *s*BP/COP-B, a mixed solvent of cyclohexane and chloroform was used, with an additional drying step under a cyclohexane atmosphere for 6 h before drying under a nitrogen atmosphere. As a result, colorless, transparent, and flat dispersed films of PS, PMMA, COC, COP-A, and COP-B were successfully obtained. For the *s*BP/PSF, NMP was used as the solvent. After preparing the *s*BP and PSF solution in NMP, the solution was drop-cast onto a fused silica substrate and immediately dried under vacuum at 25 °C for 24 h. The temperature was subsequently raised to 80 °C, 100 °C, and 160 °C, for 6 h at each stage, resulting in a colorless and transparent film. The weight fraction of *s*BP in each polymer-dispersed film was set to 0.2 wt% except for 0.1 wt% for *s*BP/COP-B, with a final thickness of 200 μm.

3. Optical Measurement of Phosphorescent Imide Compound

UV-vis absorption and photoluminescence (PL) excitation/emission spectra were measured under ambient conditions using a JASCOV-760 spectrophotometer (JASCO Co., Japan) and a Hitachi F-7100 fluorescence (FL) spectrometer (Hitachi High-Technologies Co., Japan). The front-face method was adopted for film samples to reduce the self-absorption of emitted luminescence. FL quantum yields (Φ_{FL}) were measured using a calibrated integrating sphere (C9920-02, Hamamatsu Photonics K.K., Japan) connected to a multichannel analyzer (C7473-36, Hamamatsu Photonics, Japan) via an optical fiber.

FL and PH lifetime measurements were conducted using a PL lifetime measurement system (Quantaurus-Tau, C11367-24, Hamamatsu Photonics K.K., Japan) at 25 °C in air for FL and under vacuum for PH. The decay profiles were recorded using a flashing light-emitting diode at an excitation wavelength of 340 nm. FL decay curves were accumulated until the peak intensity reached 1000 counts. Emission decay curves were fitted using one- or two-exponential functions, ensuring a goodness-of-fit indicator (χ^2) in the range of 0.8–1.3. The average lifetime ($<\tau>$) was calculated as the intensity-weighted mean lifetime using the formula: $<\tau>=\Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, where A_i is the pre-exponential factor for a lifetime component τ_i.

Variable-temperature PL (VT-PL) spectra were measured with a custom-built spectroscopic system, as shown in **Fig. S2**. The excitation light source was a 340 nm LED (M340L4, Thorlabs, Inc., USA) equipped with a 334–346 nm band-pass filter (TS OD 4.0-340/25, Edmund Optics, Inc., USA) and a shutter with a shutter controller (F77-7, Suruga Seiki, Japan). The band-pass filter was set next to the light source to block wavelengths shorter than 340 nm, while the shutter was used to set the measurement duration. The film sample was placed vertically inside a silica cell designed for use with a cryostat. The shutter and cryostat were controlled remotely by the software to manage the shutter opening/closing and temperature adjustments. To remove unabsorbed excitation light, a 355 nm long-pass filter (BLP01-355R-25, Semrock, Inc., USA) was positioned in front of the detector (multichannel spectrometer PMA-12, Hamamatsu Photonics K.K., Japan).

VT-PL spectra were measured under various atmospheric conditions, including N_2, O_2, Ar, CO_2, and vacuum. The atmospheric condition inside the silica cell was adjusted as follows: the film was vertically put in the cell equipped with a T-shape stopcock, which was connected to both a vacuum pump and a gas-filled balloon. The cell was evacuated to 0.50 Torr for 15 min, followed by filling with the gas for another 15 min. This procedure was repeated 4 times to ensure complete replacement of the gas molecules both inside the cell and within the film. To maintain the selected atmosphere and prevent external contamination, the balloon remained connected throughout the measurement. For vacuum measurements, the same procedure was followed, but Ar was used as a purge gas, and the pump remained connected to sustain the vacuum throughout the measurement.

The VT-PL spectra were recorded as follows: the film was excited with a 340 nm LED, and the spectra were continuously recorded every 100 ms. Spectra, where the PH intensity of sBP reached equilibrium, was chosen for further analysis. VT-PL spectra were measured at every 10 K from 300 K to 100 K, with the film left to equilibrate for 10 min before each measurement.

4. Dynamic Mechanical Analysis

The polymer films used for the Dynamic Mechanical Analysis (DMA) were prepared in the following procedures. Pellets of COC, COP-A, and COP-B were placed between two stainless plates with a spacer frame with a 0.3 mm thickness. They were then heated in a hot pressing machine under vacuum stepwise at 130 °C, 200 °C, and 230 °C for COC, COP-A, and COP-B, respectively. The pellets were pressed with 40 kN for 15 min, annealed for 45 min, and gradually cooled to 300 K over a few hours. As a result, colorless, transparent films with smooth surfaces and uniform thickness were successfully obtained. For COP-C, the colorless, transparent film with 0.1 mm thickness was preduced by Zeon Corp., Japan.

DMA spectra were measured from -150 °C to the glass transition temperature (T_g) of each film under an N_2 atmosphere using a DMA 7100 (Hitachi High-Technologies Co., Japan). The films prepared with a hot-press were cut into 0.5 cm × 4 cm rectangular specimens and set in the measurement furnace. The specimens were first cooled to –150 °C, then gradually heated at a rate of 2 °C/min up to their respective T_gs. The storage modulus, loss modulus, and *tan* δ were successfully obtained at 1, 5, 10, 20, 33, 50, and 100 Hz. After a measurement, the peak temperature for γ-relaxation of COC was determined by using the first derivative curve of the *tan* δ spectrum. Spectrum decomposition (**Fig. S2a-b**) was conducted by the following procedure for COP-A, COP-B and COP-C to separate the overlapped β- and γ-relaxation components. As the high-temperature side of the *tan* δ spectrum for β-relaxation was distinguishable, hypothetical β-relaxation spectrum was generated by mirroring the high-temperature side, assuming a symmetrical spectral shape. Then, the γ-relaxation spectrum was generated by subtracting the β-relaxation spectrum from the measured *tan* δ spectrum. Finally, the β- and γ-relaxation temperature was determined by extrapolating the fitted Arrhenius plots (1) to 1 Hz as shown in **Fig. S2c-d**.

$$f \propto exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

Here, f represents the measurement frequency of DMA, E_a the activation energies for β- and γ-relaxations, R the gas constant, and T the absolute temperature.

5. Supporting Figures

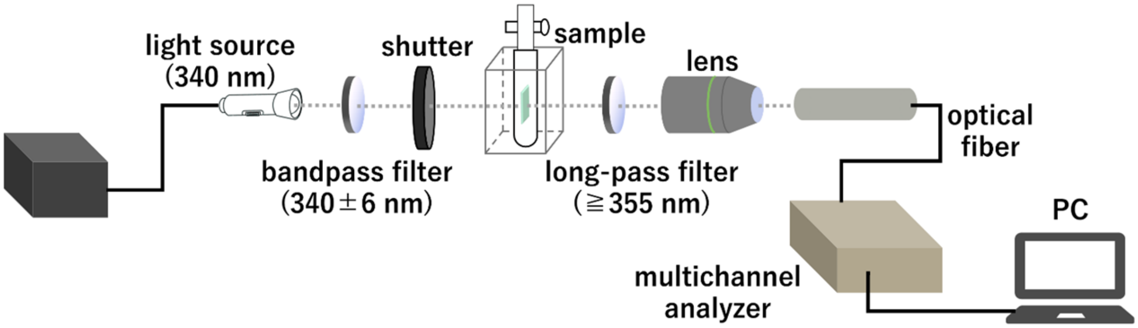


Fig. S1 Schematic figure of the optical system for variable temperature VT-PL spectra.

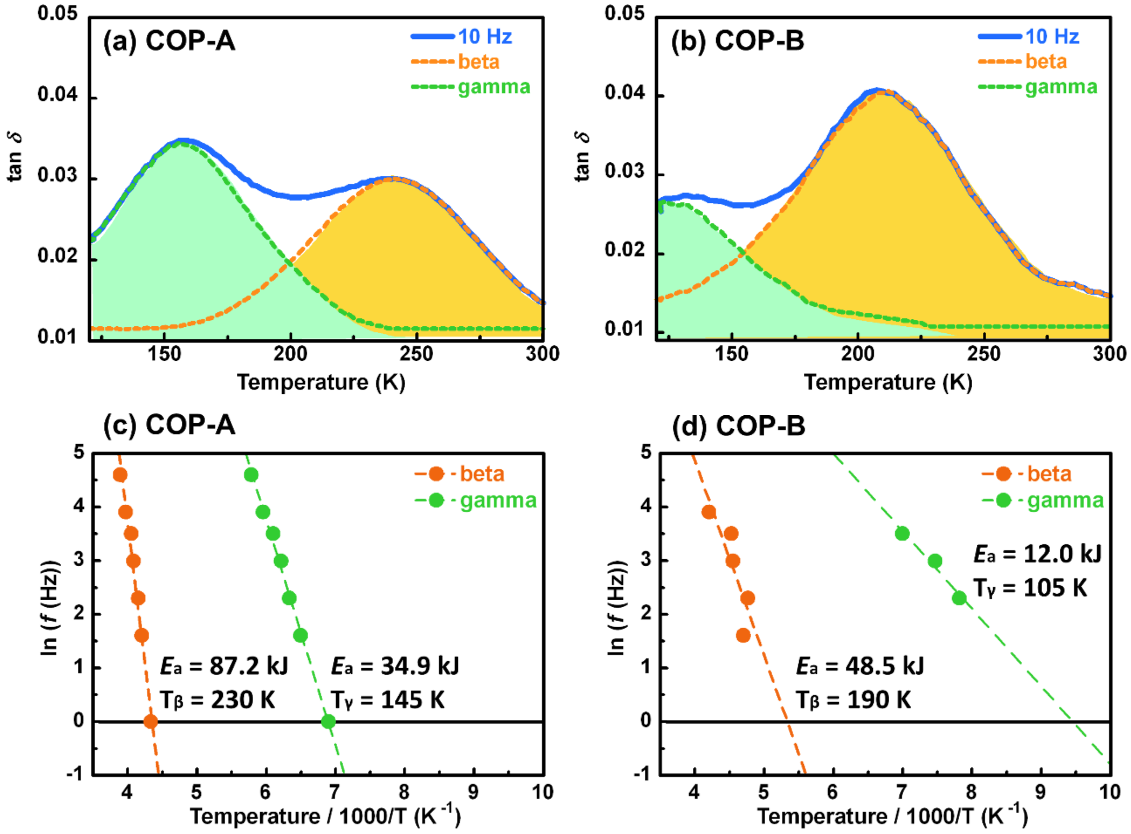


Fig. S2 Spectrum decomposition of (a) COP-A and (b) COP-B at 10 Hz. The Arrhenius plot of β- and γ-relaxations for (c) COP-A and (d) COP-B.

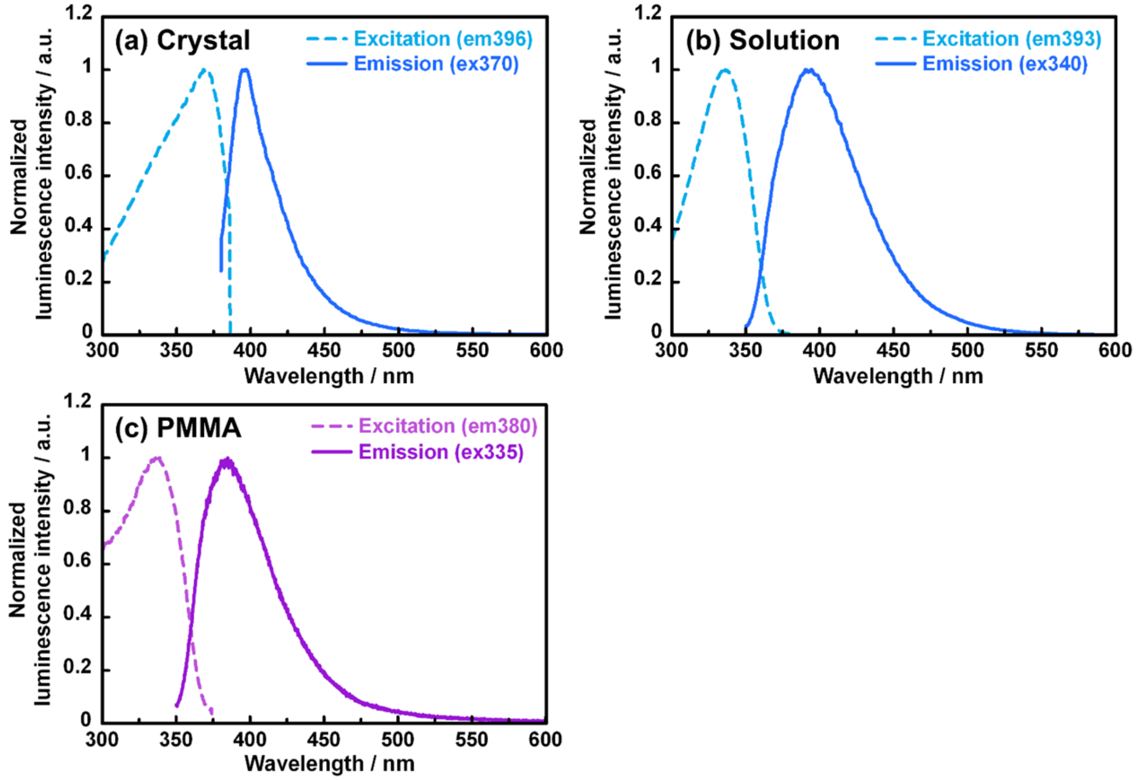


Fig. S3 Excitation and Emission spectra of *s*BP in (a) crystalline state, (b) chloroform solution (10^{-5} M), and (c) PMMA-dispersed film (*s*BP/PMMA).

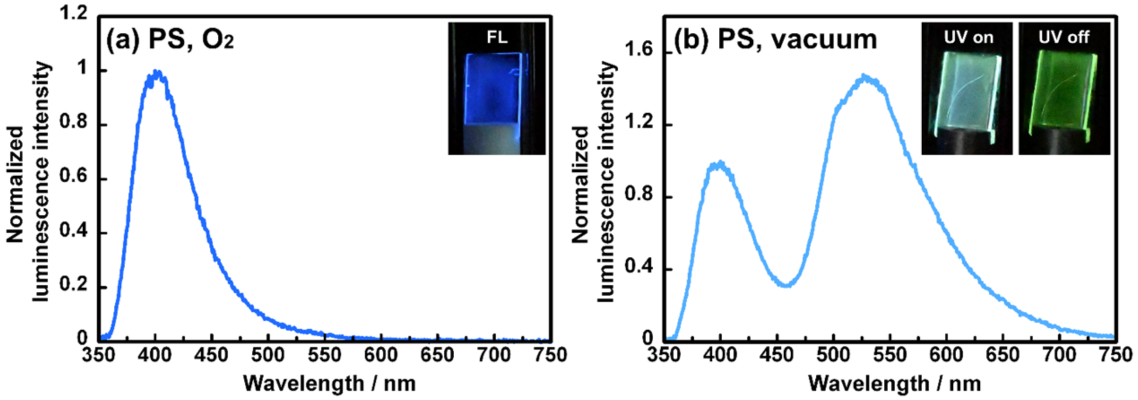


Fig. S4 Normalized luminescence spectrum of *s*BP/PS (a) in air at 300 K with photographs of FL and (b) in vacuum at 300 K with photographs of luminescence taken under 340 nm irradiation light and PH taken after turning off the 340 nm irradiation light.

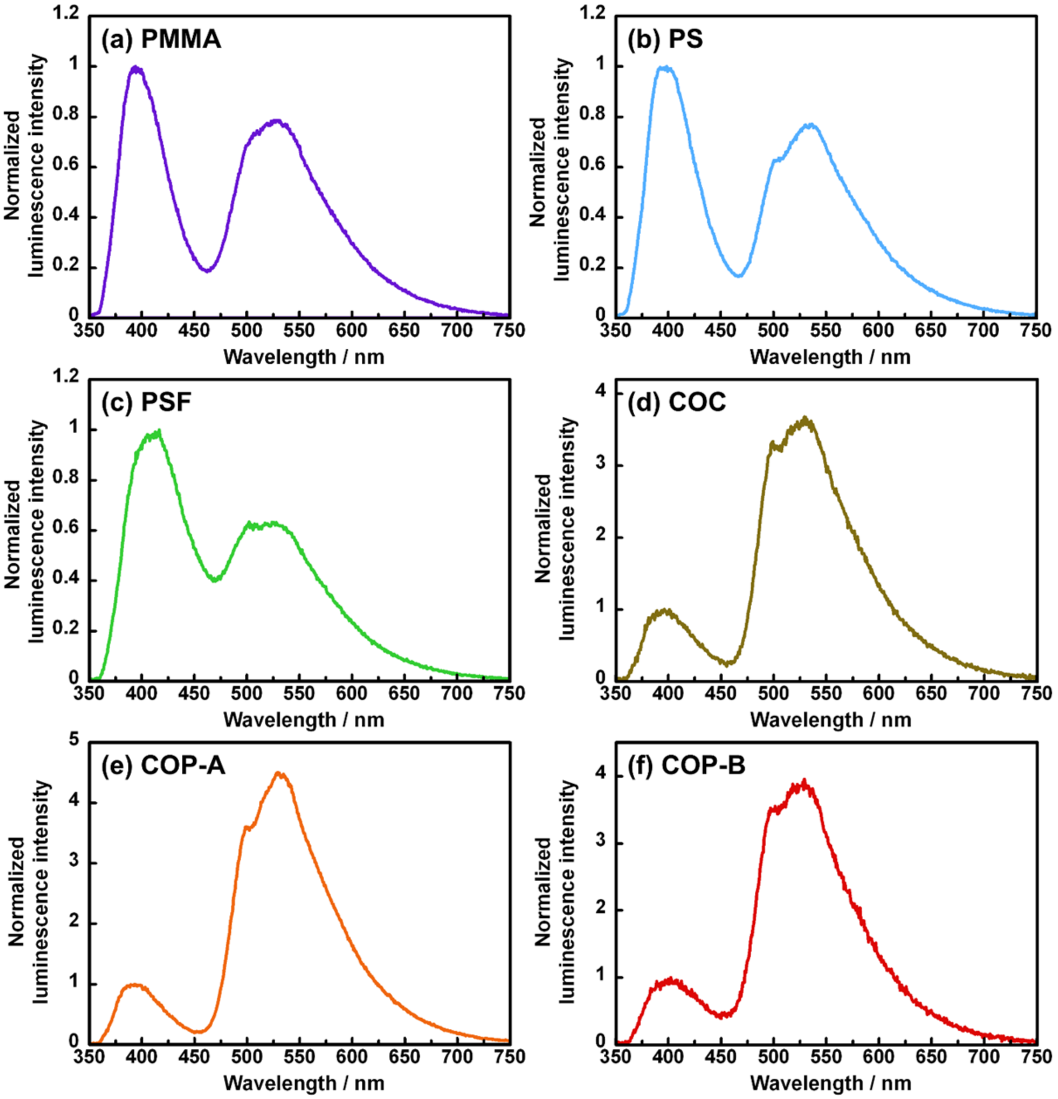


Fig. S5 Luminescence spectra of (a) *s*BP/PMMA, (b) *s*BP/PS, (c) *s*BP/PSF, (d) *s*BP/COC, (e) *s*BP/COP-A, and (f) *s*BP/COP-B at 100 K under O_2 atmosphere.

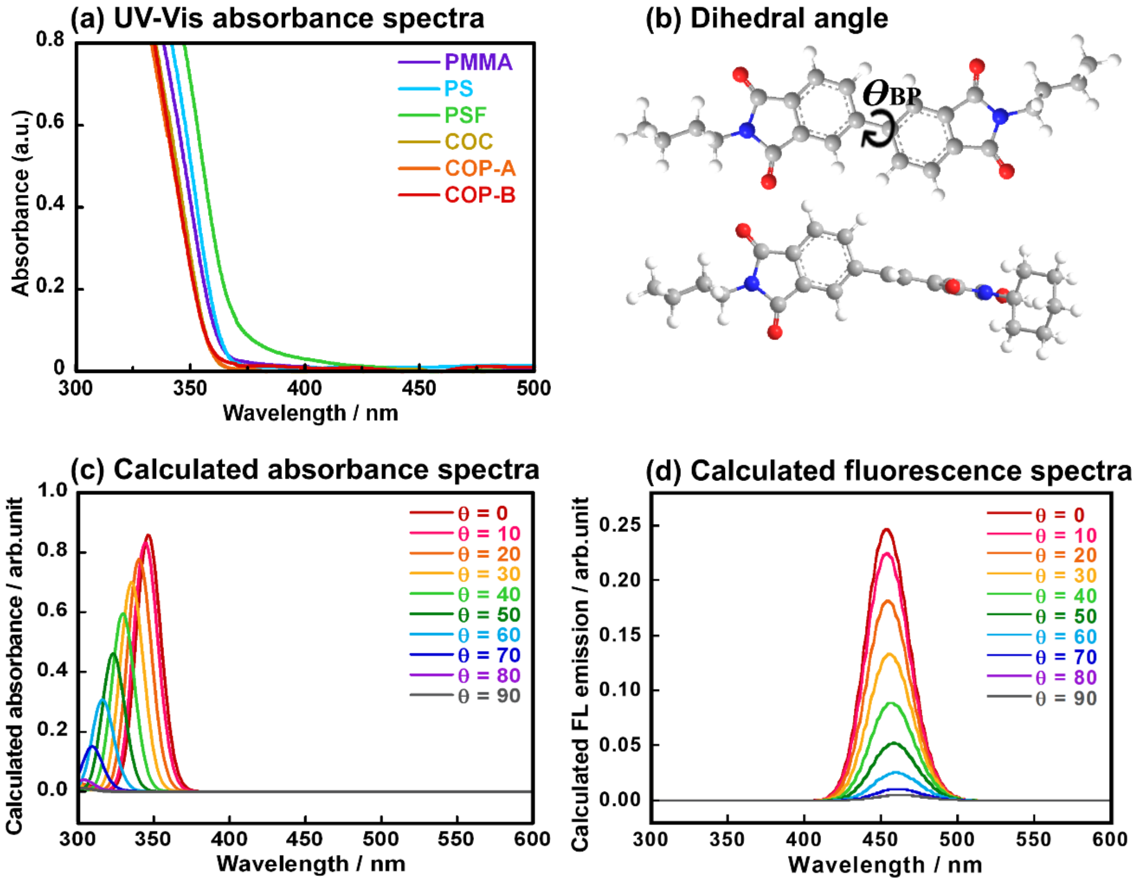


Fig. S6 (a) UV-vis absorption spectra of *s*BP/PMMA, *s*BP/PS, *s*BP/PSF, *s*BP/COC, *s*BP/COP-A, and *s*BP/COP-B. (b) The schematic picture of *s*BP and its dihedral angle θ_{BP}, $\theta_{BP} = 0$ on the top and $\theta_{BP} = 90$ on the bottom. Calculated (c) absorption spectra and (d) fluorescence spectra of *s*BP with different θ_{BP}.[2]

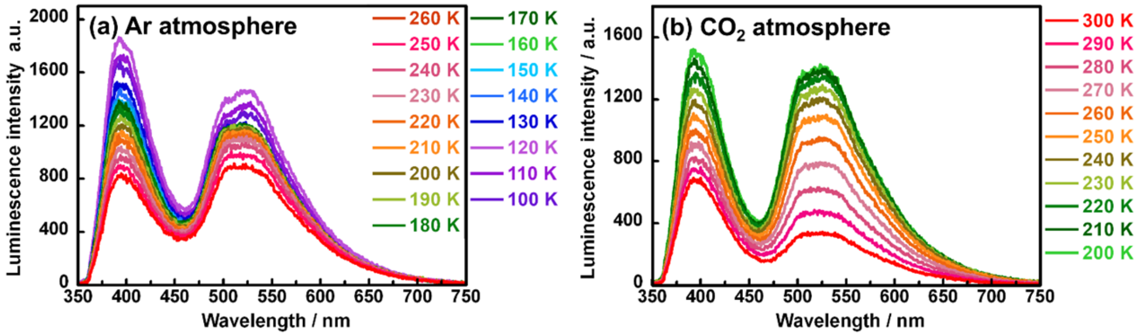


Fig. S7 VT-PL spectra of *s*BP/PMMA (a) under Ar from 260 K to 100 K and (b) under CO_2 from 300 K to 200 K.

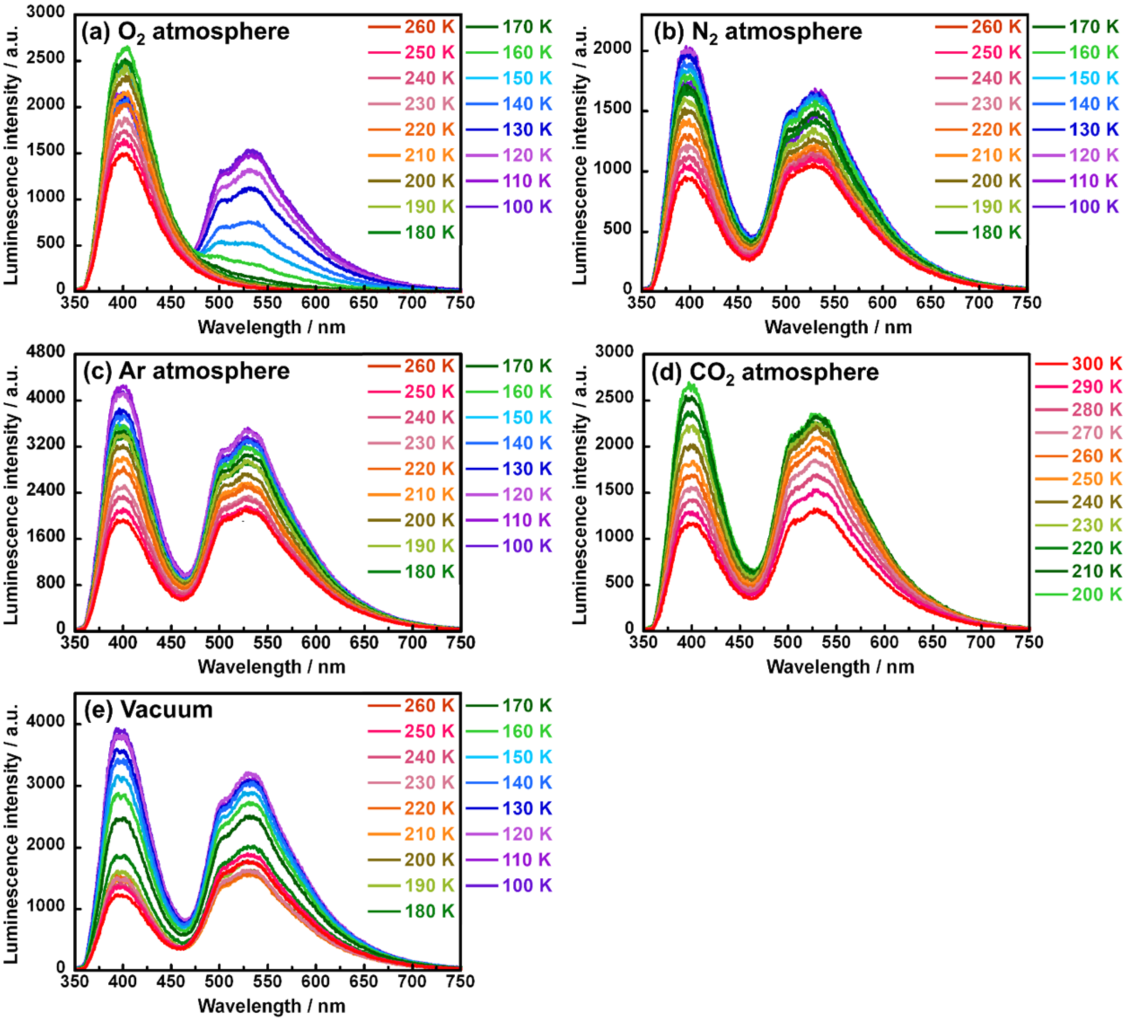


Fig. S8 VT-PL spectra of *s*BP/PS under (a) O_2, (b) N_2, (c) Ar, and (e) vacuum from 260 K to 100 K, and (d) under CO_2 from 300 K to 200 K.

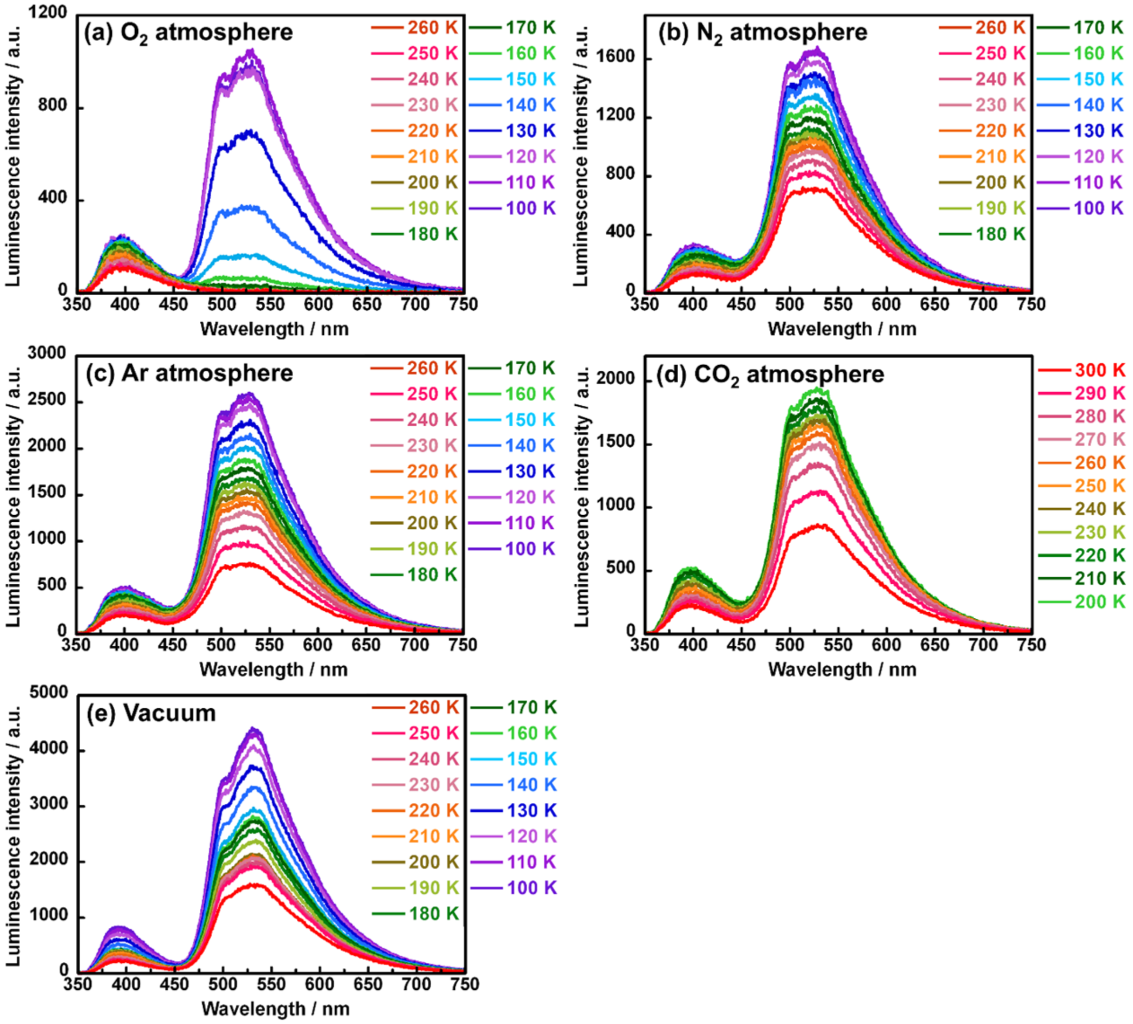


Fig. S9 VT-PL spectra of *s*BP/COP-A under (a) O_2, (b) N_2, (c) Ar, and (e) vacuum from 260 K to 100 K, and (d) under CO_2 from 300 K to 200 K.

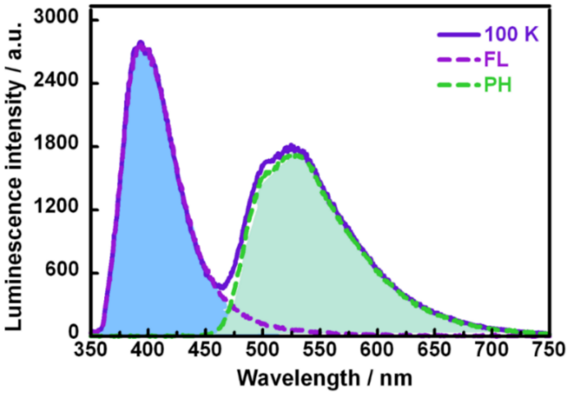


Fig. S10 An example of spectrum decomposition into FL and PH (*s*BP/PMMA at 100 K).

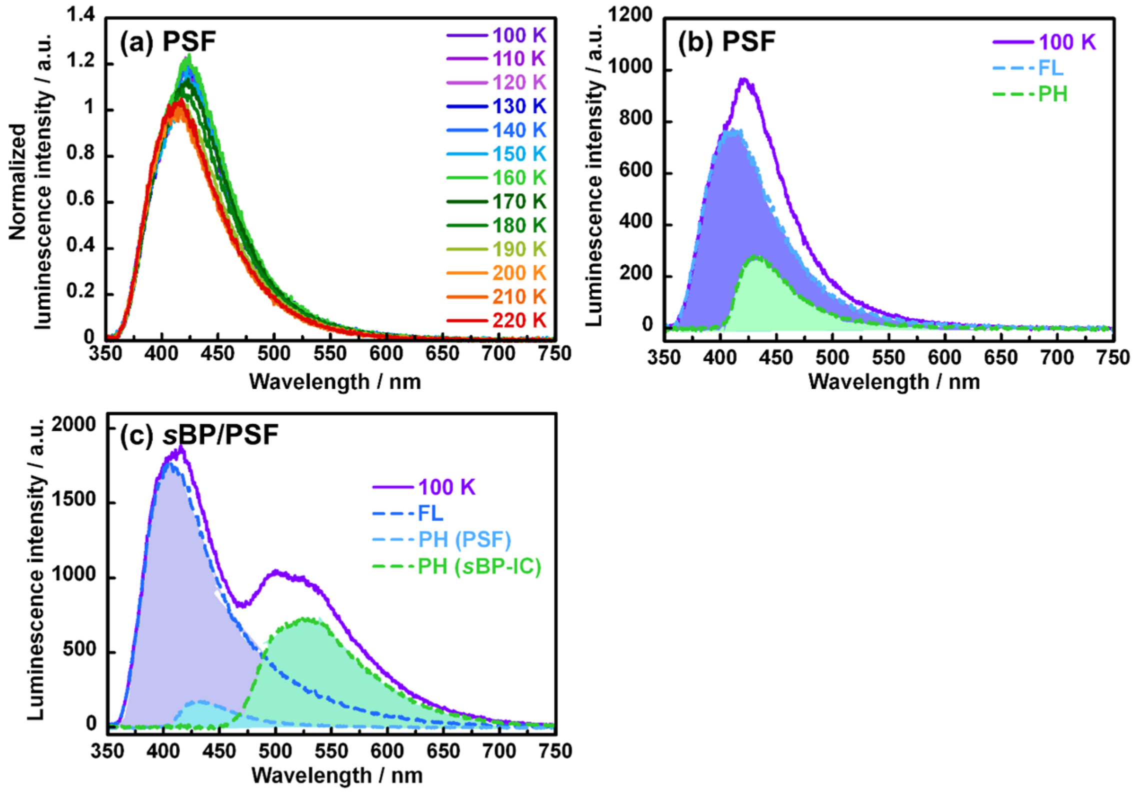


Fig. S11 (a) VT-PL spectra of pure PSF film under O_2. Spectrum decomposition of (b) pure PSF and (c) *s*BP/PSF at 100 K.

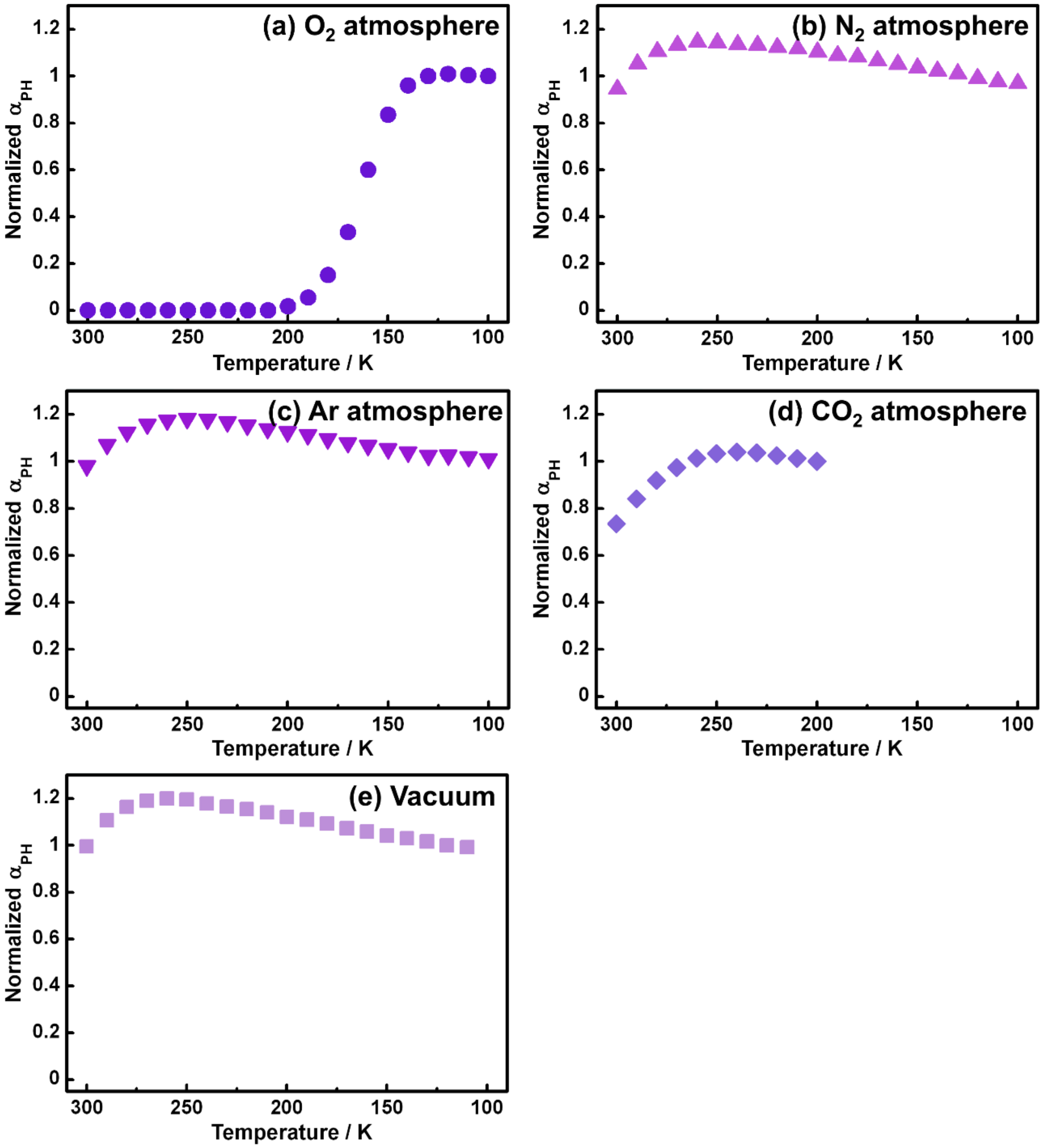


Fig. S12 Temperature variations of normalized PH area ratio under (a) O_2, (b) N_2, (c) Ar, (d) CO_2, and (e) vacuum of *s*BP/PMMA.

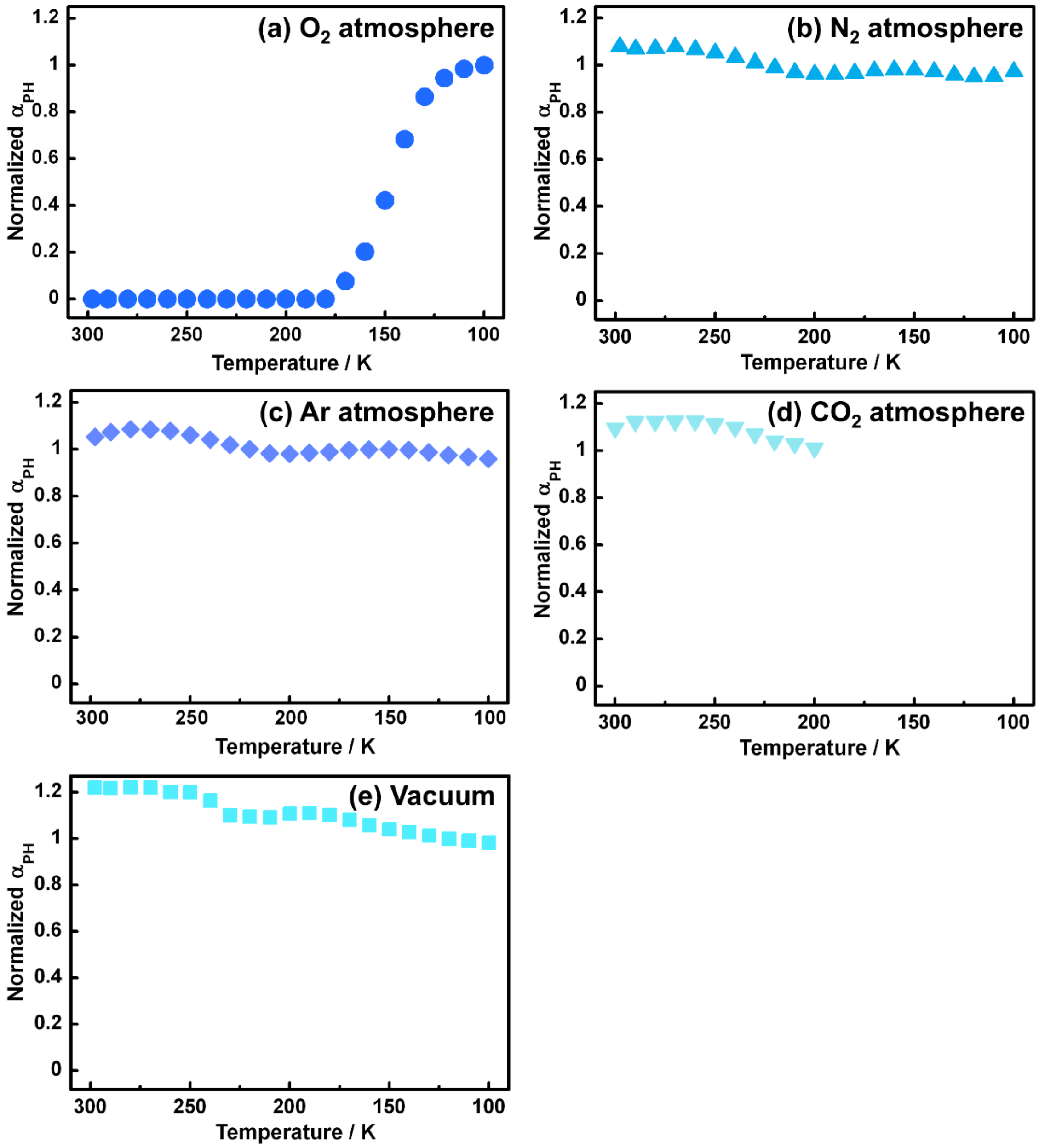


Fig. S13 Temperature variations of normalized PH area ratio under (a) O_2, (b) N_2, (c) Ar, (d) CO_2, and (e) vacuum of *s*BP/PS.

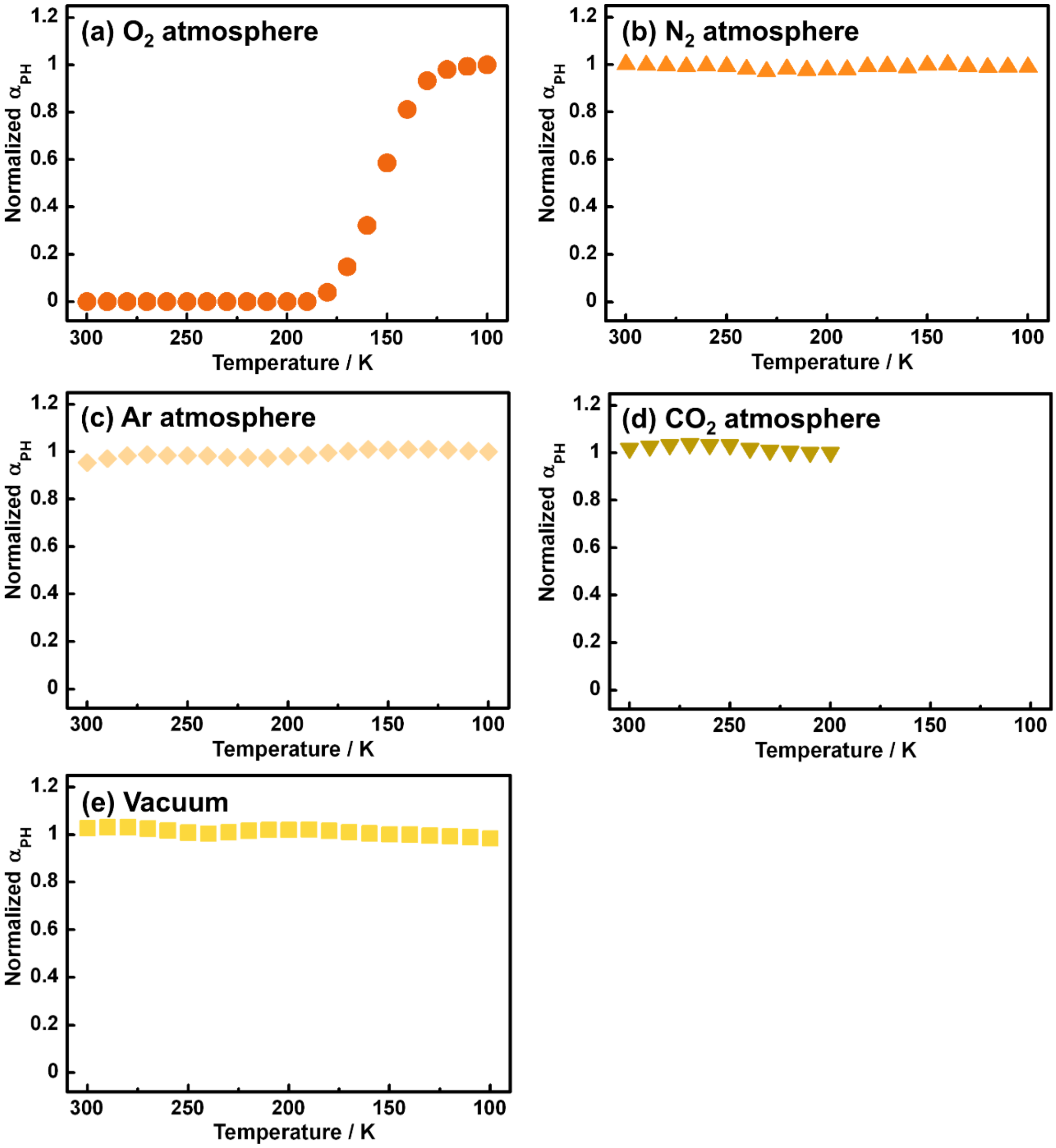


Fig. S14 Temperature variations of normalized PH area ratio under (a) O_2, (b) N_2, (c) Ar, (d) CO_2, and vacuum of *s*BP/COP-A.

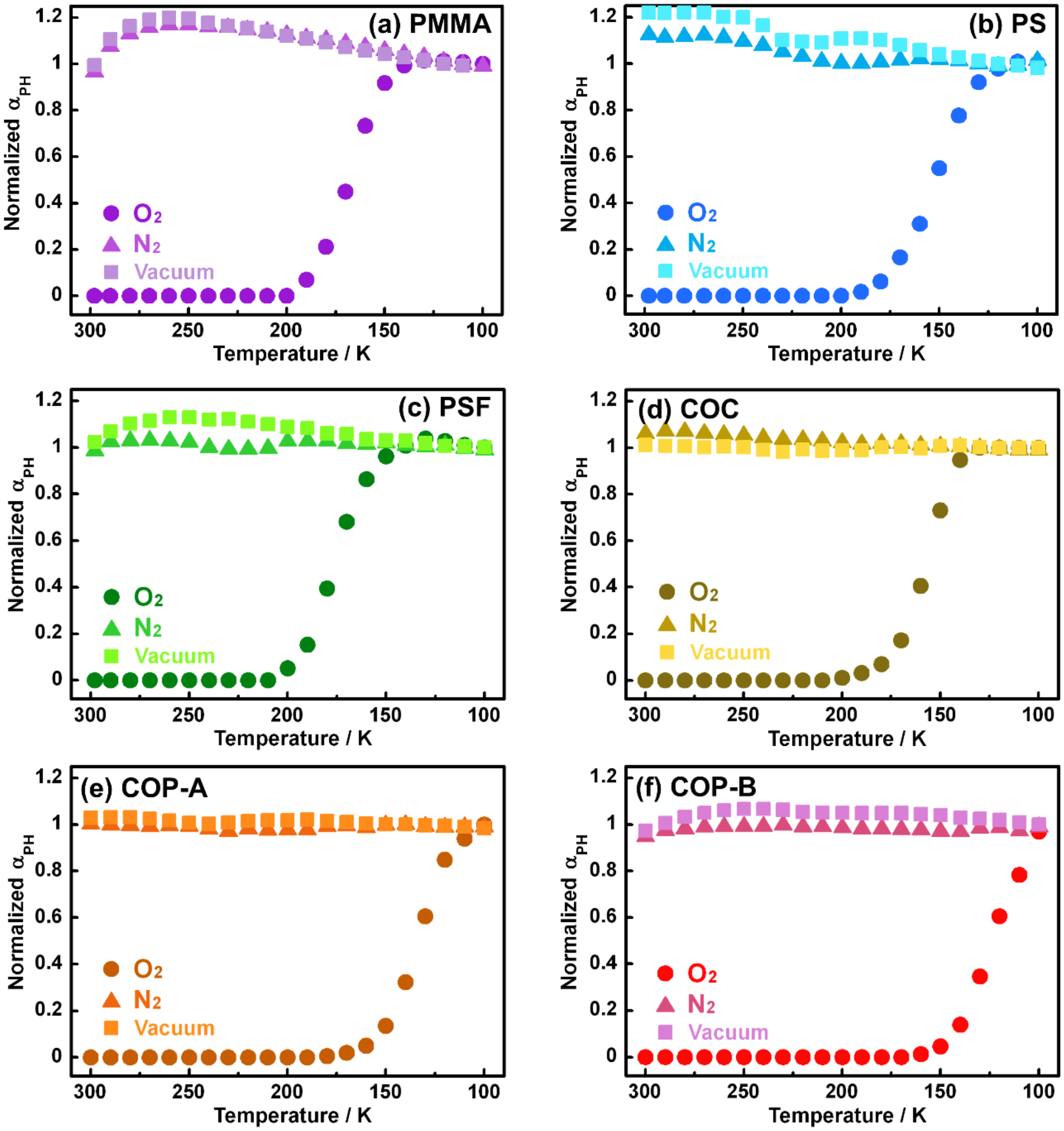


Fig. S15 Temperature variations of the normalized PH area of (a) *s*BP/PMMA, (b) *s*BP/PS, (c) *s*BP/PSF, (d) *s*BP/COC, (e) *s*BP/COP-A, and (f) *s*BP/COP-B from 300 K to 100 K.

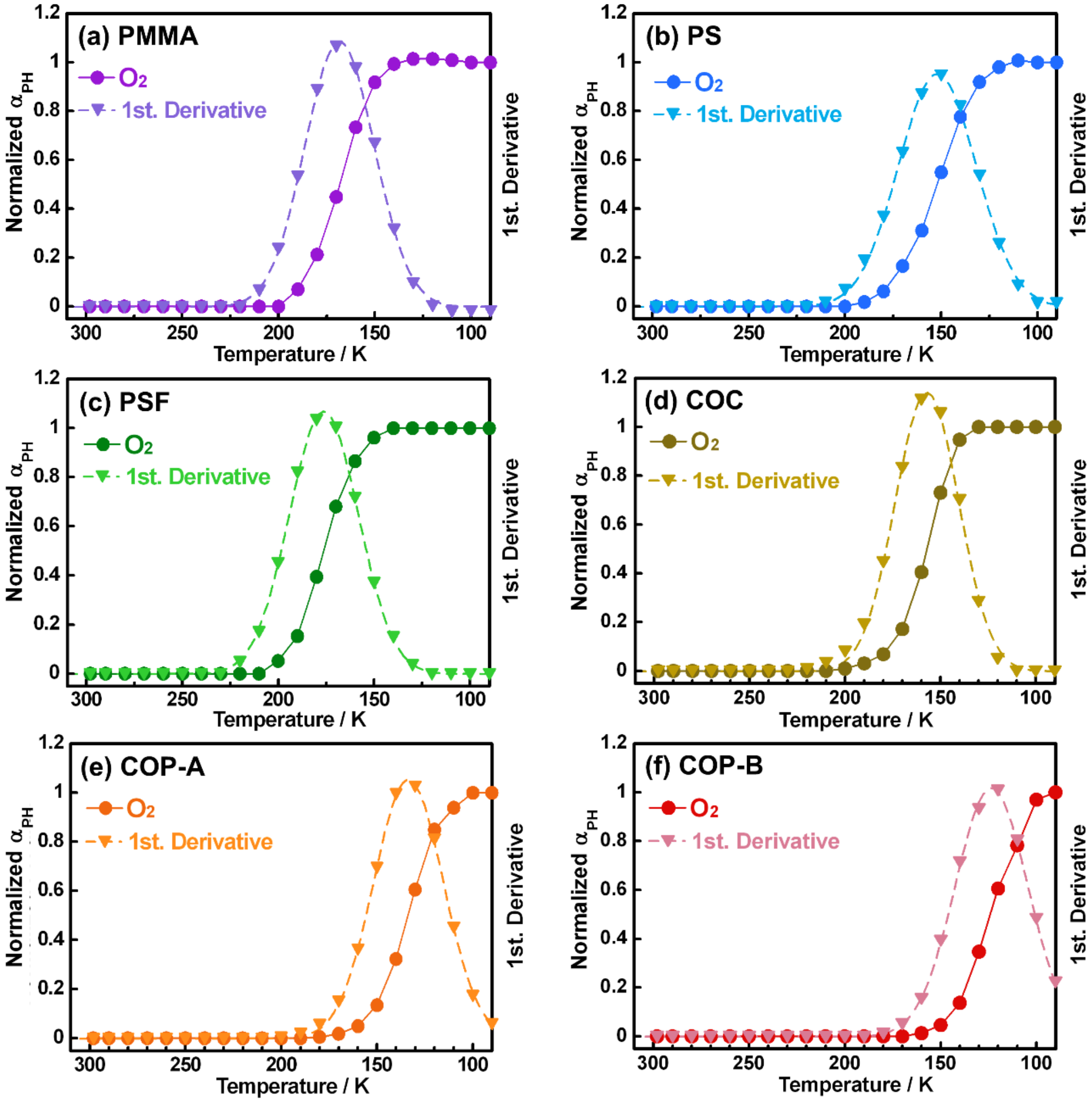


Fig. S16 Temperature dependence of the normalized PH area under O_2 atmosphere and its first derivative of (a) *s*BP/PMMA, (b) *s*BP/PS, (c) *s*BP/PSF, (d) *s*BP/COC, (e) *s*BP/COP-A, and (f) *s*BP/COP-B from 300 K to 100 K.

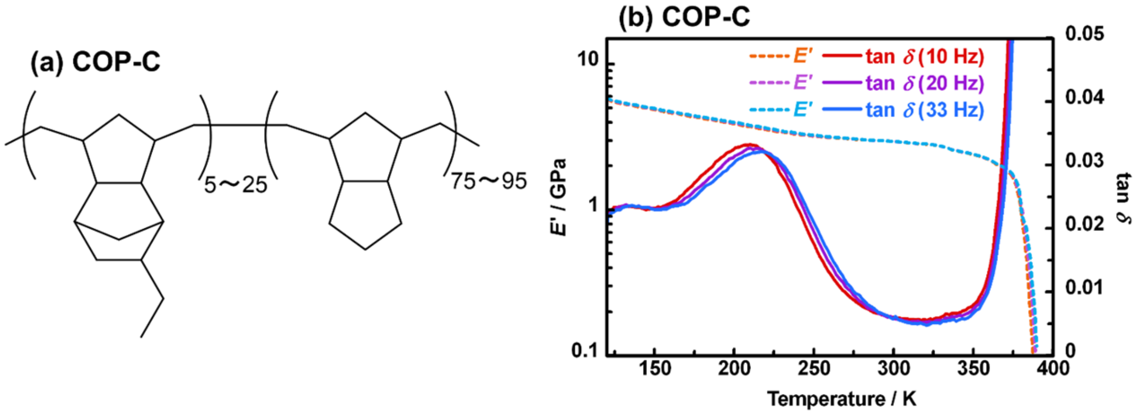


Fig. S17 (a) Chemical structure of COP-C. (b) Isochronal temperature dependence of storage modulus (*E*′) and *tan* δ of COP-C at 10 Hz, 20 Hz, and 33 Hz measured with DMA.

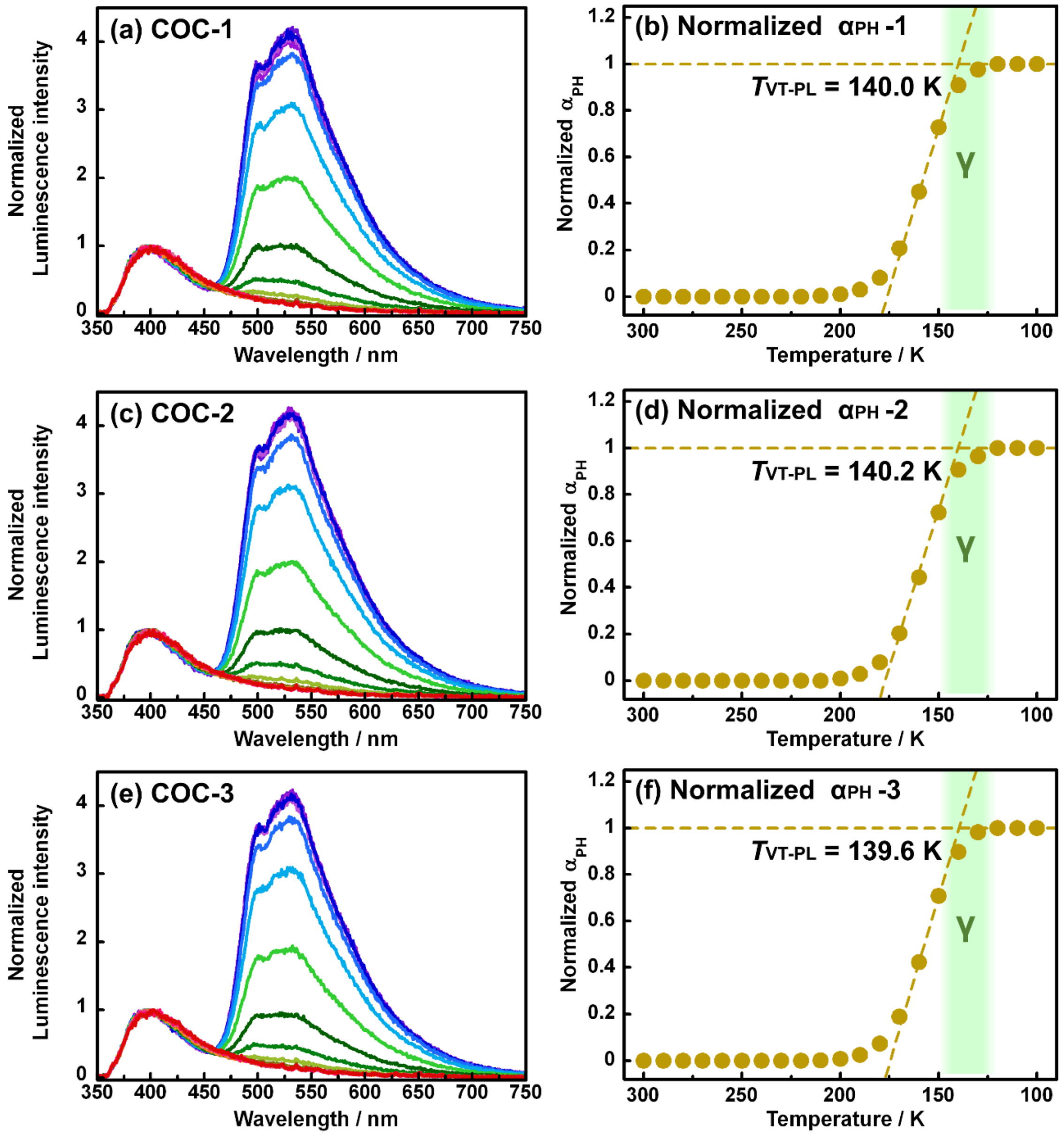


Fig. S18 Repeated VT-PL measurement of sBP/COC under O_2 atmosphere.

6. Supporting Table

Table S1. Basic optical properties of six dispersed films at 298 K. Excitation and emission wavelength (λ_{ex}, λ_{em}), FL quantum yields (Φ_{FL}), FL lifetime (τ_{FL}) in air, and PH lifetime (τ_{PH}) under vacuum.

	λ_{ex}	λ_{em}	Φ_{FL} [a]	τ_{FL} (ns) [a,b]	τ_{PH} (ms) [a,b]
*s*BP/PMMA	335	380	0.063	1.41	–
		528		–	900
*s*BP/PS	340	385	0.068	0.83	–
		533		–	877
*s*BP/PSF	340	– [c]	–	–	–
		529		–	751
*s*BP/COC	335	378	0.016	0.42	–
		527		–	668
*s*BP/COP-A	340	381	0.013	0.45	–
		530		–	775
*s*BP/COP-B	341	381	0.011	0.23	–
		528		–	812

[a] Under 340 nm excitation.

[b] Average lifetime calculated from the emission decay curves.

[c] Obscured by the intrinsic FL of PSF.

7. Supporting References

(1) Doi, M.; Ishige, R.; Ando, S. Long-Lived Luminescence Emitted from Imide Compounds Dispersed in Polymer Matrices after Continuous Ultraviolet Irradiation and Its Relation to Oxygen Quenching. *ChemPhotoChem* **2023**, *7* (5).

(2) Liu, H.; Isoda, R.; Doi, M.; Muto, K.; Ando, S. Pressure-Induced Enhancement of Room-Temperature Phosphorescence in Heavy Halogen-Containing Imide and Polyimide. *J. Phys. Chem. B* **2024**, *128* (31), 7690–7701.