Electronic Supplementary Information (ESI)

Colorless and Transparent Polyimide Derived from a Sterically Hindered Bromine-Substituted Dianhydride Exhibiting Dual Fluorescent and Phosphorescent Emission

Kenta Kanosue,[a] Shuzo Hirata,[b] Martin Vacha,[c] Ramūnas Augulis,[d]

Vidmantas Gulbinas,*[d] Ryophei Ishige,[a] and Shinji Ando*[a]

[a]*Department of Chemical Science & Engineering, School of Materials & Chemical Technology,*

Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan

[b]*Department of Engineering Science, The University of Electro-Communications,*

Chofugaoka 1-5-1, Chofu, Tokyo, 182-8585 Japan

[c]*Department of Materials Science and Engineering, School of Materials & Chemical Technology,*

Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japand

[d]*Center for Physical Sciences and Technology, Saulėtekio Ave. 3, LT-10257 Vilnius, Lithuania*

*Corresponding authors: E-mail: sando@polymer.titech.ac.jp, vidmantas.gulbinas@ftmc.lt

tel.: +81-3-5734-2137; fax: +81-3-5734-2889

Synthesis

Synthesis of 2,2'-Dibromo-4,4'5,5'-biphenyltetracarboxylic Acid (3)

BPDA (**1**) of 30.00 g (0.10 mol) was dissolved in a solution of 18.13 g (0.45 mol) of NaOH in 300 mL of water in a two-neck round-bottom flask fitted with a condenser and an additional funnel, resulting in the corresponding sodium salt of biphenyltetracarboxylic acid (**2**). Bromination was carried out in five steps. In the first step, 1.50 mL of Br_2 was slowly added to the solution at 50 °C. After the addition was completed, the solution was heated at 90 °C until most of the Br_2 had reacted. The mixture was then cooled to room temperature and neutralized with an NaOH aqueous solution to pH 7.0. For the second, third, and fourth steps, 3.00 mL of Br_2 was used, and the solution treated as in the first step. In the fifth step, 4.00 mL of Br_2 was added at 50 °C. The solution was then heated at 90 °C overnight. After the mixture was cooled to room temperature, the precipitate that formed was collected by filtration, suspended in water, and acidified with 12M HCl to pH 2.0. The white powder was collected by filtration and dried at 90 °C under reduced pressure, and compound **3** was obtained (5.4 g, 0.01 mol, 11% yield). Mp: 190-200 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 7.68 (s, 2H), 8.04 (s, 2H). Elemental Analysis (%) Calcd for $C_{16}H_8Br_2O_8$: C 39.38, H 1.65, Br 32.74, O 26.23. Found: C 38.51, H 1.87, Br 34.54, O 24.87. HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_8Br_2O_4$ 486.8664; found 486.8655.
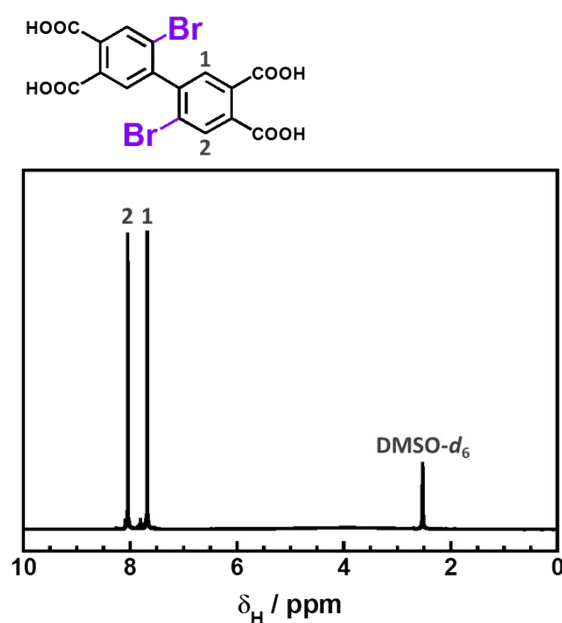

Figure S1. ^{1}H NMR spectrum of compound **3**.

Synthesis of 2,2'-Dibromo-4,4'5,5'-biphenyltetracarboxylic Dianhydride (4)

Compound **3** of 2.00 g (4.10 mmol) was heated at 180 °C for 8 h under reduced pressure and resulted in white powder of compound **4** (1.40 g, 3.10 mmol, 76% yield). Mp: 200 °C (sublimated). ^{1}H NMR (400 MHz, Acetone-d_6, ppm): δ = 8.17 (s, 2H), 8.55 (s, 2H). Elemental Analysis (%) Calcd for $C_{16}H_4Br_2O_6$: C 42.52, H 0.89, Br 35.36, O 21.24. Found: C 38.60, H 1.57, Br 34.31, O 23.10. HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_8Br_2O_4$ 449.8375; found 449.8378.
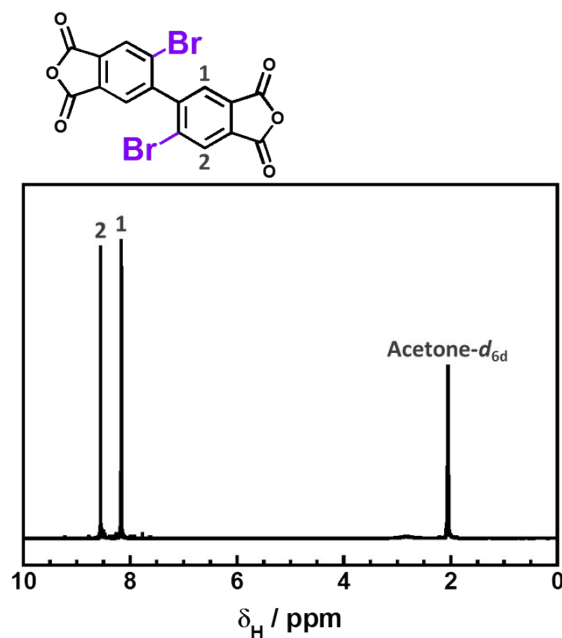
Figure S2. ^{1}H NMR spectrum of compound **4**.

Preparation of PI Films.

The precursor of PI, poly(amic acid) silyl ester, was prepared using *in situ* silylation method. DCHM (0.30 g, 1.43 mmol) and BSTFA (0.39 g, 1.52 mmol) were stirred in 5 mL of DMAc for 30 min. Compound **4** (0.65 g, 1.43 mmol) was added to the solution and then stirred overnight. The resulting viscous transparent solution was spin-coated onto a fused silica (amorphous SiO$_2$) substrate, followed by soft-baking at 70 °C for 1 h and subsequent thermal imidization via a one-step imidization procedure; the final curing conditions were 220 °C for 1.5 h under a N$_2$ flow. The heating rate from 70 °C to 220 °C was 4.6 °C/min.

In a similar manner to that preparing DBrBP-PI, reaction of BPDA (0.24 g, 0.82 mmol), DCHM (0.17 g, 0.82 mmol), and BSTFA (0.23 g, 0.89 mmol) in DMAc (4 mL) yielded a BP-PI film.
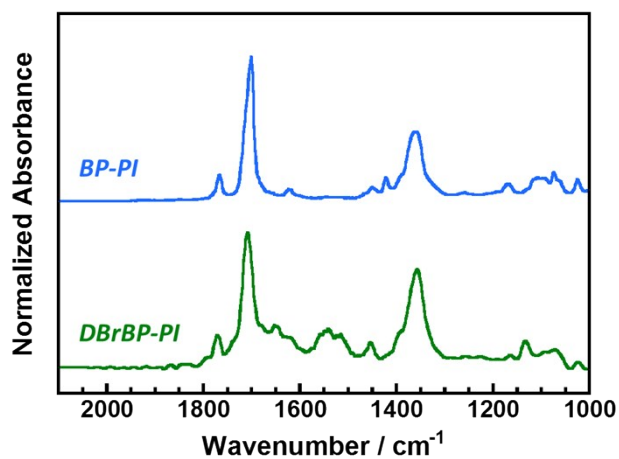
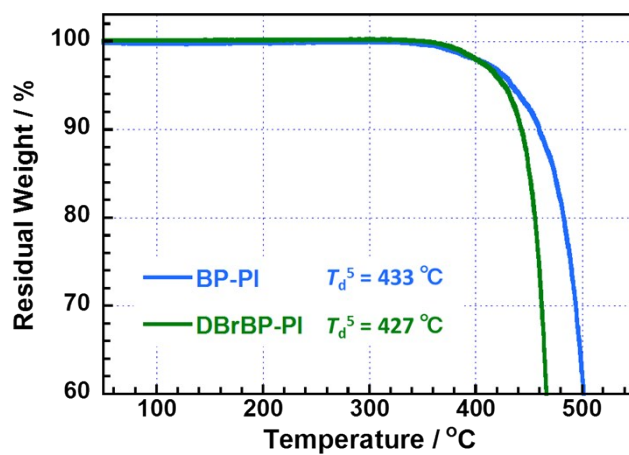**Figure S3**. ATR FT-IR spectra of BP-PI and DBrBP-PI films.

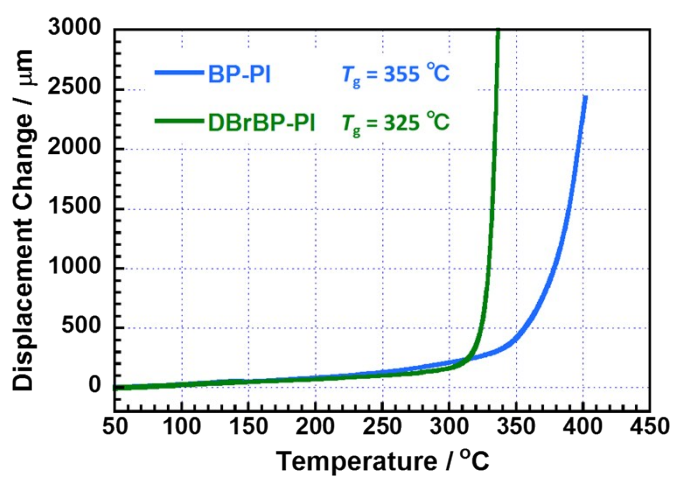**Figure S4**. TGA curves of BP-PI and DBrBP-PI films.

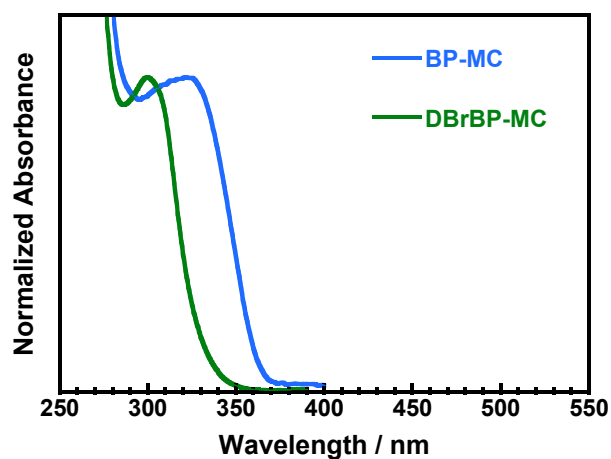**Figure S5**. TMA curves of BP-PI and DBrBP-PI films.

Figure S6. UV-vis absorption spectra of model compounds BP-MC and DBrBP-MC dissolved in CHCl$_3$. Spectra were normalized with absorbance of their absorption peaks.
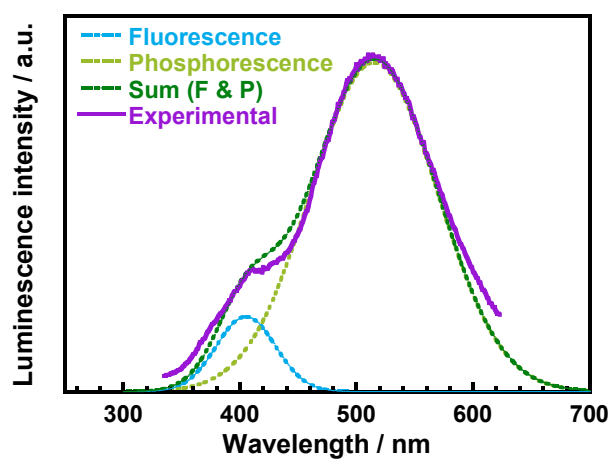

Figure S7. Fitting of the photoluminescent emission spectrum of DBrBP-PI measured at 298 K by using two Gaussian broadening functions. The area ratio of the fluorescent (light blue) and phosphorescent (light green) components was estimated as 1 : 10.
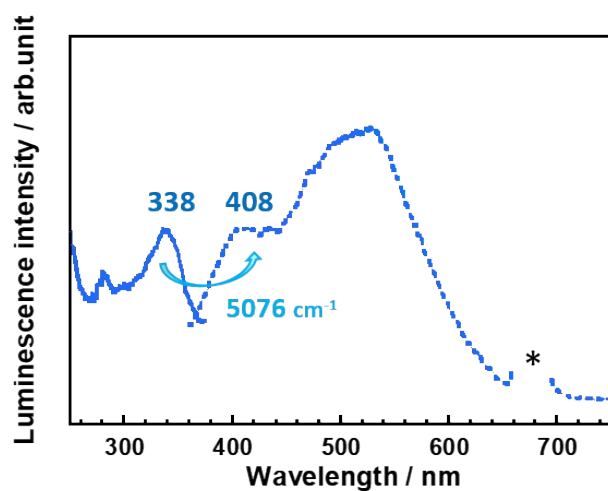
Figure S8. Photoluminescence excitation/emission spectra of DBrBP-PI films measured at 298 K. The emission spectra were measured using excitation wavelengths of 338 nm, and excitation spectra were measured by monitoring emission intensity at 408 nm. Asterisks indicate second order diffraction of excitation light.
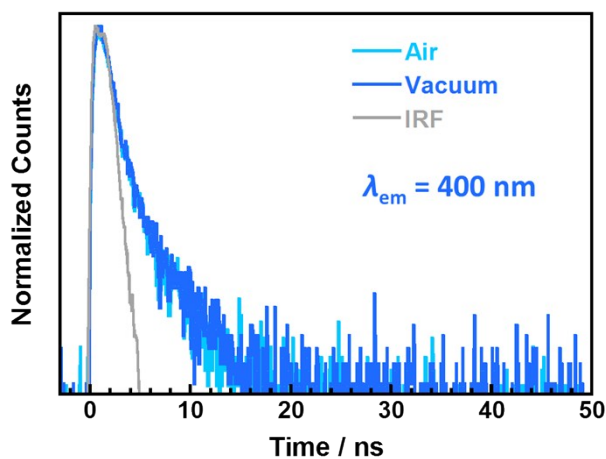

Figure S9. Photoluminescence decay curve measured at 400 nm of DBrBP-PI film at 298 K.
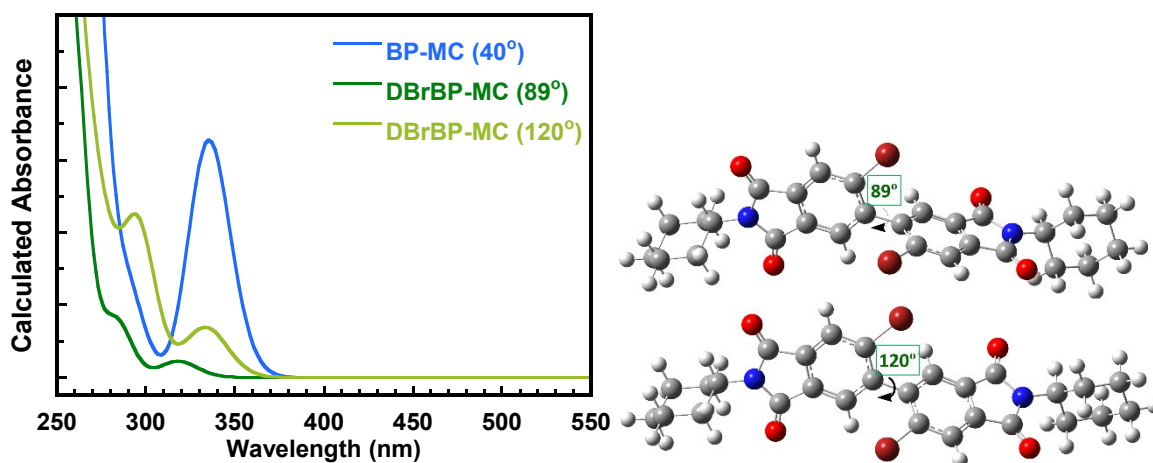
Figure S10. Calculated absorption spectra of model compounds based on TD-DFT, and two schematic views of DBrBP-MC with biphenyl dihedral angles of 89° and 120°.
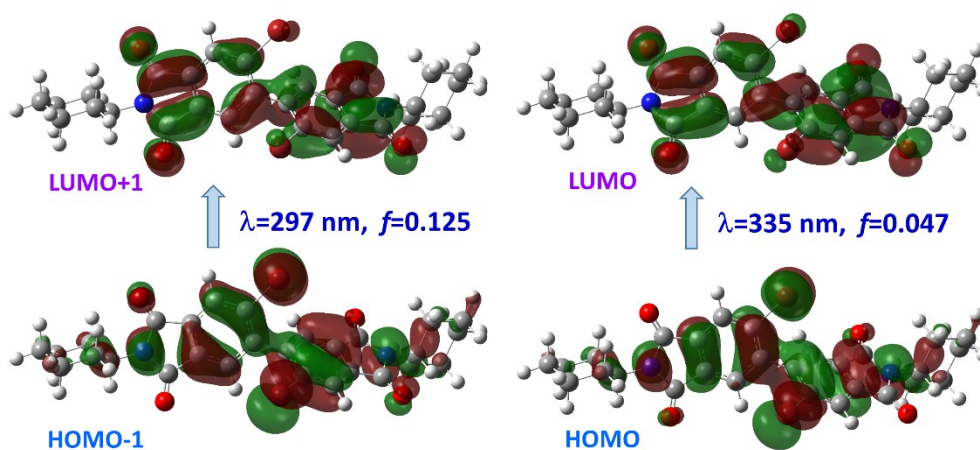

Figure S11. Calculated one-electron transitions corresponding to the excitation of DBrBP-PI at 315 nm and 336 nm, respectively. λ and f denote the absorption wavelength and the oscillation strength of each transition, respectively.

Table S1. Fluorescence decay time constants (τ) of the DBrBP-PI film monitored at 408 nm with different excitation wavelengths. The decay curves were fitted by two exponential functions, and τ_{av} is weighted average. The measurement was performed by a fluorescence lifetime spectrometer (Hamamatsu, Quantaurus-Tau)

Excitation wavelength	τ_{av} [ns]	τ_1 [ns]	A_1	τ_2 [ns]	A_2
280 nm	0.938	0.290	38.7	1.93	3.79
340 nm	1.140	0.392	29.3	2.17	3.82
365 nm	1.500	0.482	25.3	2.69	3.89