

## Supporting Information

# Large-Stokes-shifted Yellow Photoluminescence Emission from an Imide and Polyimides Forming Multiple Intramolecular Hydrogen Bonds

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### Materials

4,4'-Oxydiphthalic anhydride (ODPA) provided by Japan Synthetic Rubber (JSR) Co. Ltd. was used after sublimation under reduced pressure. 4,4'-Diaminodicyclohexylmethane (DCHM) purchased from Tokyo Chemical Industry (TCI) Co. Ltd. was purified by recrystallization from *n*-Hexane following by sublimation under reduced pressure. 2,3-Dimethylphenol (DMP), potassium carbonate and paraformaldehyde purchased from TCI Co. Ltd., xylene, acetone, potassium permanganate, pyridine, hydrobromic acid (47%-49% aq.), acetic acid and acetonitrile purchased from Kanto Chemical Co. Inc. were used as received. Iodomethane purchased from Wako Chemical Co. Inc., dimethylacetamide (DMAc, anhydrous), trifluoroacetic acid (TFA) and N,O-bis(trimethylsilyl)trifluoro-acetamide (BSTFA) purchased from Aldrich Co., Ltd. were used as received.

### Synthesis of DHBA

The synthetic route of DHBA is almost identical to that reported by Shin et al.<sup>1</sup> with some modifications on the synthetic procedure as shown in **Scheme S1**.

### ***Bis(2-hydroxy-3,4-dimethylphenyl) methane (BHDM)***

2,3-Dimethylphenol (DMP, 40 mmol, 5g) and paraformaldehyde (20 mmol, 0.6g) were dissolved in xylene (4.4 mL), then the solution was refluxed (under nitrogen flow) with a Dean-Stark apparatus for 10 h. After the reaction, the mixture was poured into *n*-hexane (50 mL) to obtain white precipitates. These precipitates were filtered, followed by recrystallization from *n*-hexane. Finally, BHDM was obtained (1.8 g, 7 mmol, 35 % yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, ppm):  $\delta$  = 2.1 (s, 6H), 2.2 (s, 6H), 3.9 (s, 2H), 5.5-6.4 (br, 2H), 6.7 (d, 2H, *J* = 8.1 Hz), 7.0 (d, 2H, *J* = 7.7 Hz).

### ***Bis(2-methoxy-3,4-dimethylphenyl) methane (BMDM)***

BHDM (1.8 g, 7 mmol), potassium carbonate (3.88 g, 28 mmol), and CH<sub>3</sub>I (4 g, 28 mmol) were added into 18 mL anhydrous acetone, then the mixture was refluxed under nitrogen flow for 32 h. During the reaction, 4 g (28 mmol) of CH<sub>3</sub>I was added every 8 h. After the reaction, potassium carbonate was removed by filtration, and acetone and CH<sub>3</sub>I were removed by rotary evaporation. After vacuum drying at 80 °C for 4h, BMDM was obtained (1.8 g, 6.3 mmol, 90% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*, ppm): δ = 2.2 (d, 12H), 3.7 (s, 1H), 4.0 (s, 1H), 6.75 (d, 2H, *J* = 8.3 Hz), 6.85 (d, 2H, *J* = 7.4 Hz).

### ***2,2'-Dimethoxybenzophenone-3,3',4,4'-tetracarboxylic Acid (DMBPTA)***

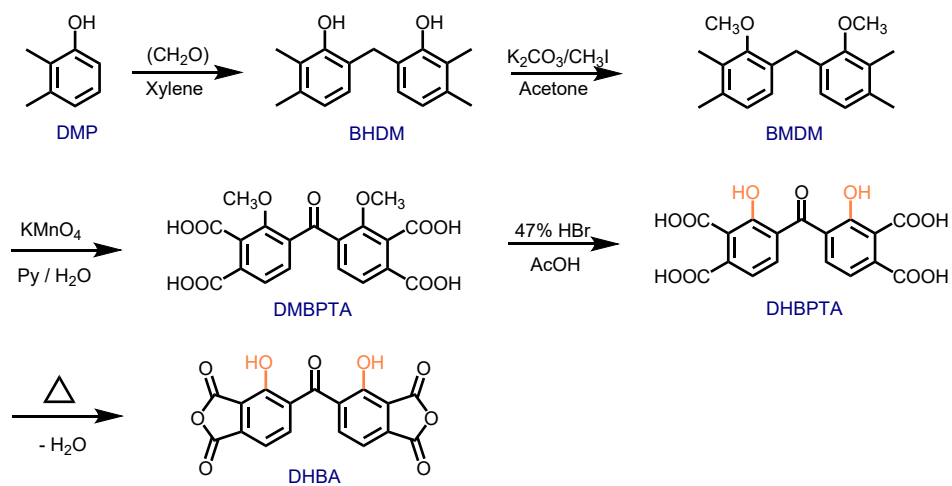
BMDM (1.8g, 6.3 mmol) was dissolved in a mixture of water (20 mL) and pyridine (20 mL) and refluxed at 100 °C. Then, 6 g (37.97 mmol) of potassium permanganate was added every 2 h, and this operation was repeated ten times. After the reaction, the solution was cooled to room temperature and filtered to remove deposited manganese dioxide. The filtrated solution was further concentrated by rotary evaporation and then acidified with concentrated HCl to pH 1 to generate white precipitate. The precipitate was filtered, followed by recrystallization from dilute HCl aq. solution. Finally, DMBPTA was obtained (1.2 g, 2.8 mmol, 44% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ = 3.4 (s, 1H), 7.5 (d, 2H, *J* = 8.5 Hz), 7.7 (d, 2H, *J* = 8.5 Hz), 13.4 (br, 4H).

### ***2,2'-Dihydroxybenzophenone-3,3',4,4'-tetracarboxylic Acid (DHBPTA)***

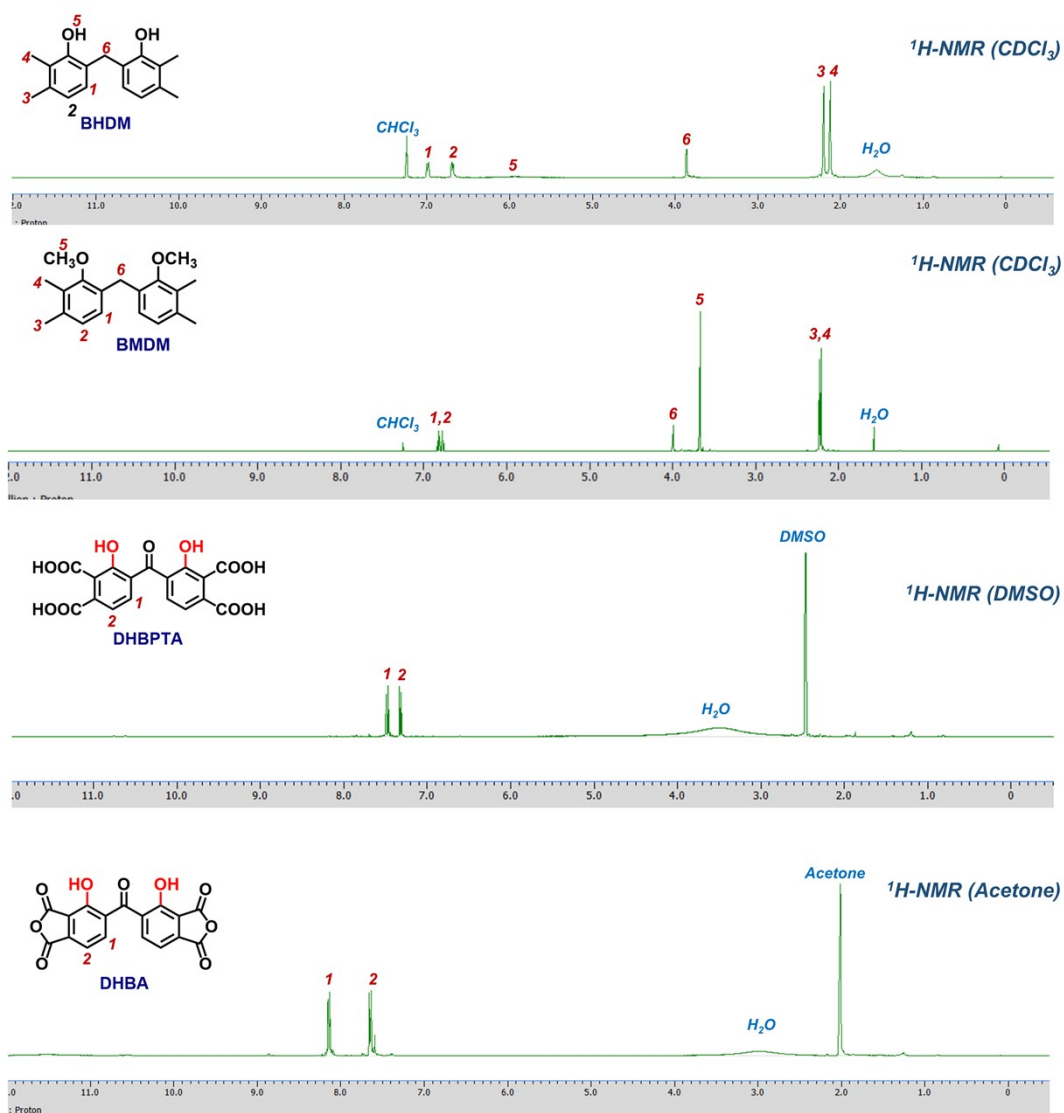
DMBPTA (1.2 g, 2.8 mmol) was dissolved in a mixture of 48% HBr aq. (2 mL) and acetic acid (4 mL), then the solution was refluxed at 100 °C under nitrogen flow for 4 h. During the reaction, yellow precipitates were gradually generated. After the reaction, the precipitates were collected by filtration and recrystallized from dilute HCl solution. Finally, DHBPTA was obtained (0.64 g, 1.8 mmol, 64% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ = 7,4 (d, 2H, *J* = 7.8 Hz), 7.6 (d, 2H, *J* = 8.3 Hz), 11.0 (br, 6H).

### ***2,2'-Dihydroxybenzophenone-3,3',4,4'-tetracarboxylic Acid (DHBA)***

DHBPTA (0.64 g, 1.8 mmol) was heated at 140 °C under vacuum for dehydration for 24 h. The crude product was recrystallized from anhydrous acetonitrile. Finally, DHBA was obtained (0.42 g, 1.2 mmol, 66% yield). <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>, ppm): δ = 7.6 (d, 2H, *J* = 7.8 Hz), 8.1 (d, 2H, *J* = 7.6 Hz), 11.0-12.0 (br, 2H).



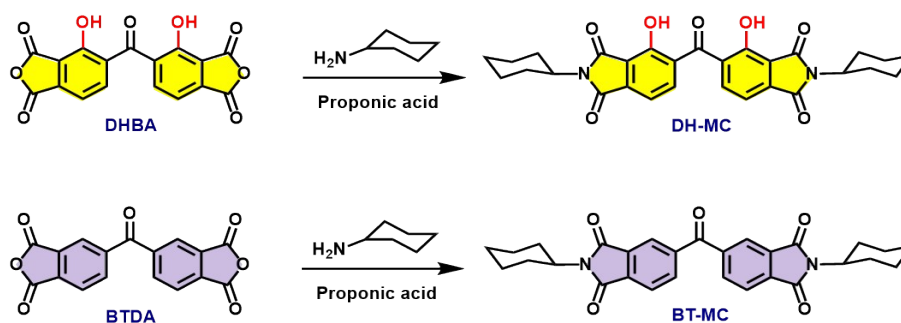
**Scheme S1.** Synthesis scheme of DHBA.



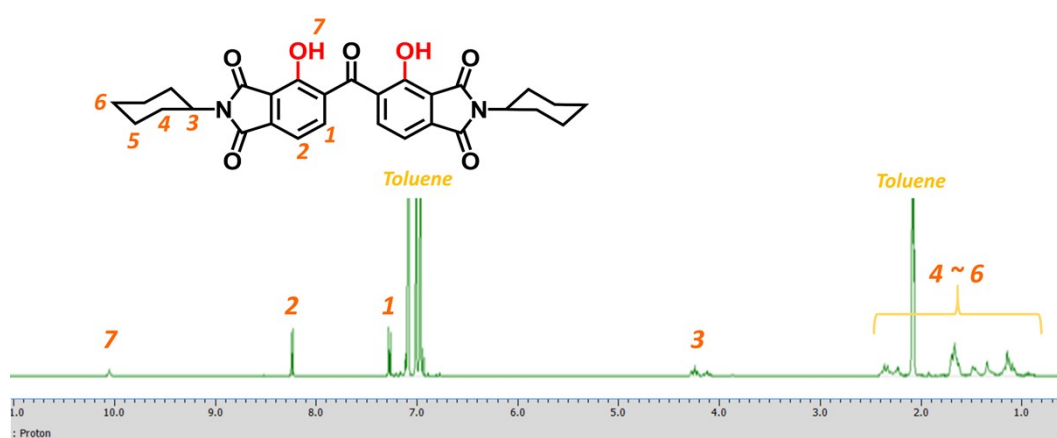
**Figure S1.** <sup>1</sup>H-NMR spectra of the synthesized BHDM, BMDM, DHBPTA, and DHBA.

## Synthesis of DH-MC and BT-MC

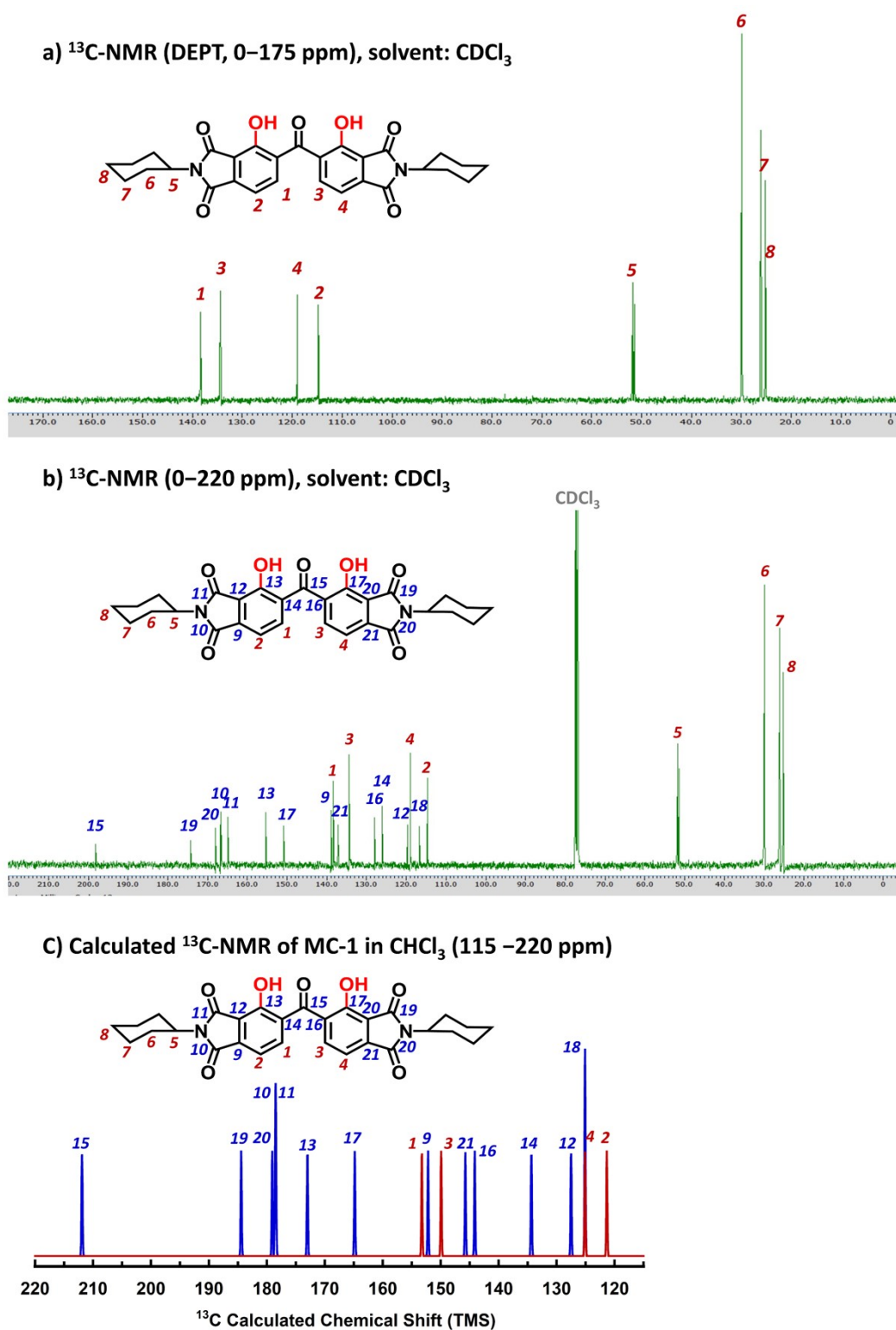
The synthesis schemes of DH-MC and BT-MC are listed in **Scheme S2**. Firstly, 0.5 g of DHBA (1.41 mmol) and 0.42 g of cyclohexylamine (CHA, 4.23 mmol) were added into 8.5 mL propionic acid and stirred for 30 min to give a homogenous solution. Then, the solution was refluxed at 140 °C for 4 h under nitrogen flow. During the reaction, yellow precipitates were gradually generated. After the reaction, the precipitates were collected by filtration and recrystallized from chloroform/ethyl acetate mixture. Finally, DH-MC was obtained (0.15 g, 0.3 mmol, 21% yield).  $^1\text{H}$  NMR (400 MHz, Toluene- $d_8$ , ppm):  $\delta$  = 10.1 (s, 2H), 8.2 (d, 2H,  $J$  = 8.2 Hz), 7.2 (d, 2H,  $J$  = 7.7 Hz), 4.2 (m, 2H), 1.0-2.4 (m, 20H). (**Figure S2**).  $^{13}\text{C}$  NMR (400 MHz, Chloroform- $d$ , ppm):  $\delta$  = 25.2, 26.2, 29.7, 51.7, 114.7, 116.7, 118.8, 119.7, 126.1, 128.0, 134.2, 137.4, 138.2, 138.9, 150.7, 155.6, 164.8, 166.8, 168.0, 174.3, 197.8 (**Figure S3**). HRMS (EI)  $m/z$  [M]<sup>-</sup> calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub> 515.54, found 515.18. Elemental analysis (%) calcd for C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>: C 67.43, H 5.46, N 5.42, O 21.68; found: C 68.40, H 5.50, N 5.42, O 20.23. Single crystals of DH-MC were prepared by slow recrystallization from its *o*-xylene solution. BT-MC was synthesized according to the reference.<sup>2</sup>



**Scheme S2.** Synthesis scheme of DH-MC and BT-MC.



**Figure S2.**  $^1\text{H}$ -NMR spectra of BH-MC in Toluene- $d_8$ .

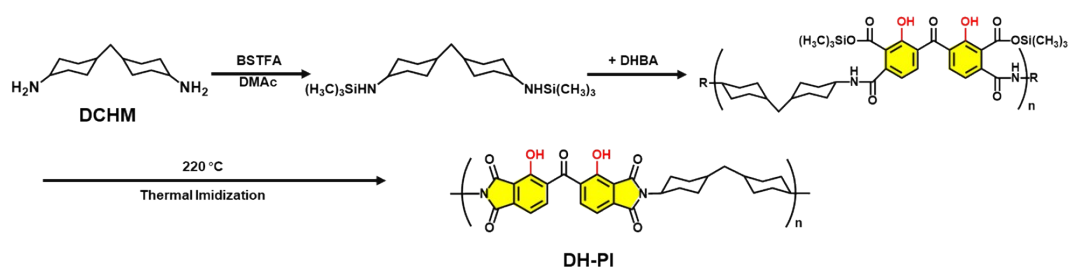


**Figure S3.** (a)  $^{13}\text{C}$ -DEPT and (b)  $^{13}\text{C}$ -NMR spectra of BH-MC in  $\text{CDCl}_3$ , and (c) calculated  $^{13}\text{C}$ -NMR spectra of BH-MC (MC-1) in  $\text{CHCl}_3$ . The solvent effect of  $\text{CHCl}_3$  in the calculation was incorporated based on the PCM.

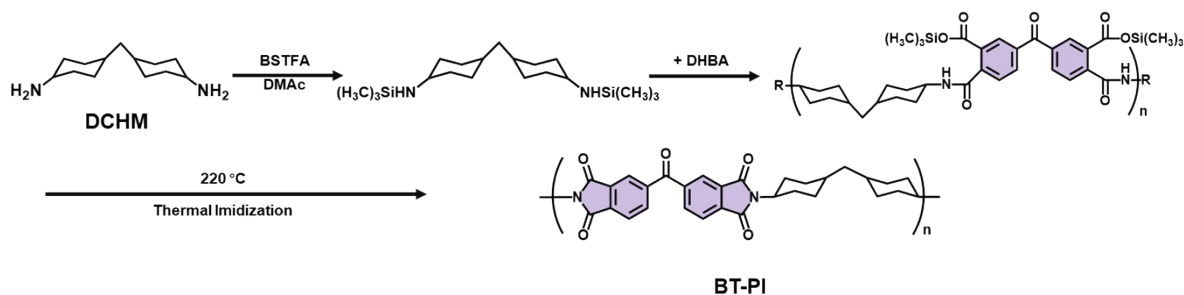
## Synthesis of PIs and film preparation

### DH-PI and BT-PI

Firstly, DCHM and 1.05 molar equivalent of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) were dissolved in DMAc and stirred for 30 min. Then, an equimolar amount (to DCHM) of DHBA or BTDA was added and stirred for 48 h to prepare a homogeneous PASE solution. Trimethylsilylation of amino groups by BSTFA can avoid salt formation between unreacted amino and carboxyl groups, which results in insoluble precipitation. PI films were formed by spin coating of PASE solution onto fused silica (amorphous SiO<sub>2</sub>) substrates, followed by drying at 70 °C for 50 min and subsequent thermal imidization at 220 °C for 1.5 h. All the heating procedures were conducted under nitrogen flow, and the heating rate was set to 3.0 °C/min. The synthesis scheme is shown in **Scheme S3** and **Scheme S4**.



**Scheme S3.** Synthesis scheme of DH-PI.

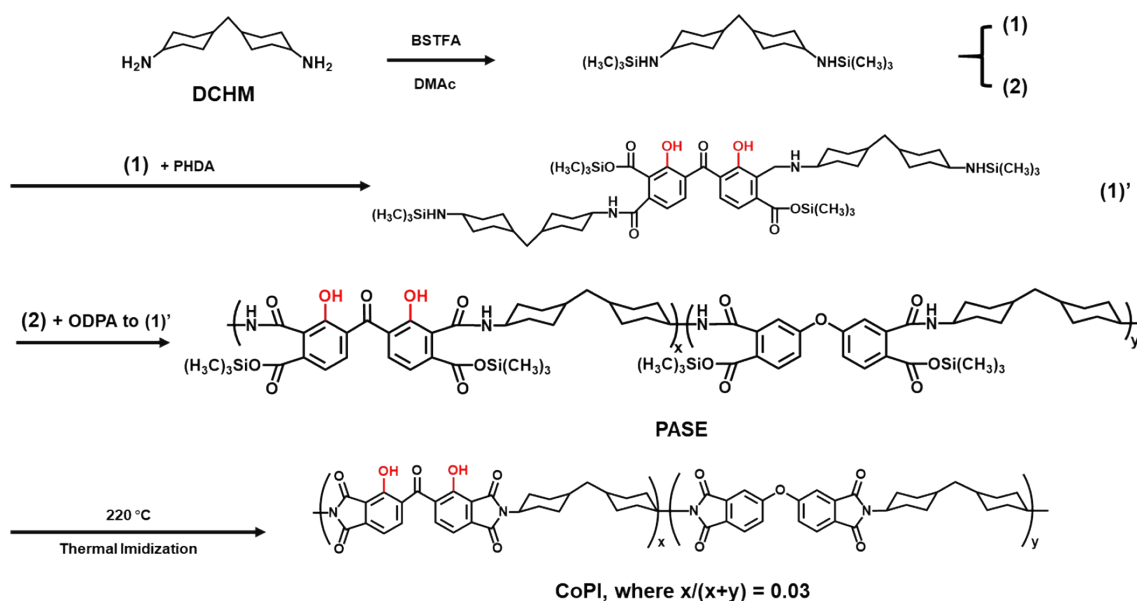


**Scheme S4.** Synthesis scheme of BT-PI.

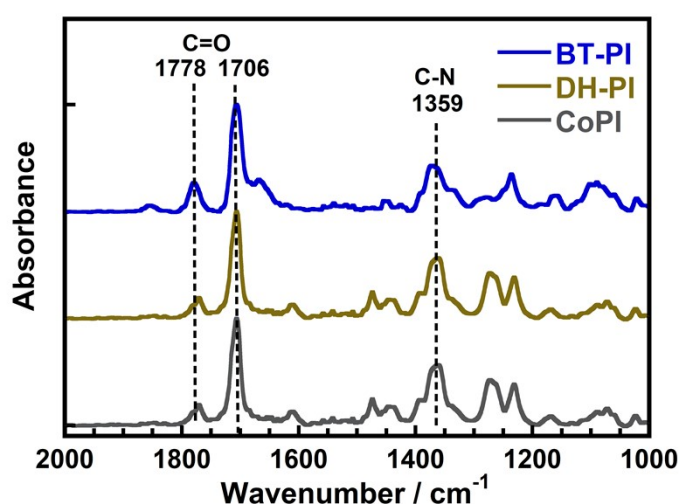
### Copolyimide (CoPI)

Firstly, DCHM (24.35 mg, 0.12 mmol) and BSTFA (31.28 mg, 0.12 mmol) were mixed in DMAc (0.3 mL), followed by stirring for 30 min to give a homogeneous silylester solution (**1**). Meanwhile, the other DCHM (381.45 mg, 1.81 mmol), BSTFA (490.16 mg, 1.90 mmol) were mixed in DMAc (3.4 mL) and then stirring for 30 min to prepare a homogeneous silylester solution (**2**). Then, DHBA (20.5 mg, 0.06 mmol) was added to **1** and stirred for another 30 min. Finally, ODPa (580.5 mg, 1.87 mmol) and **2** were added to **1** and stirred for 48 h to give

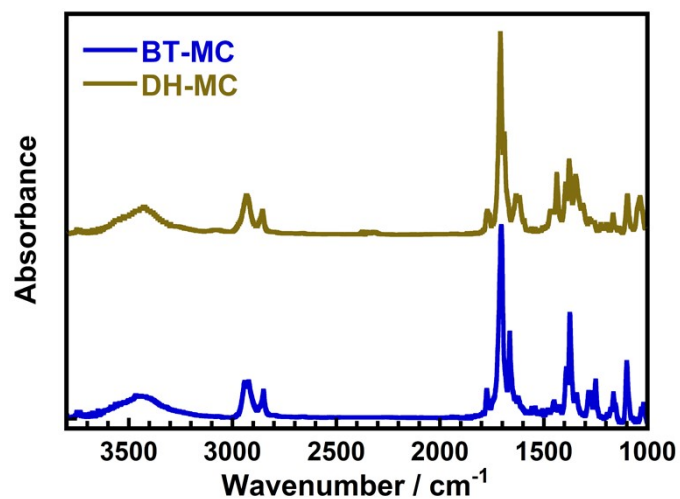
a homogeneous PASE solution. The prepared PASE solution was spin-coated onto fused silica substrates and then dried at 70 °C for 1 h, followed by thermal imidization at 220 °C for 1.5 h. All the heating procedures were conducted under nitrogen flow, and the heating rate was set to 3.0 °C/min. The synthesis scheme of the CoPI is displayed in **Scheme S5**. The symmetric and anti-symmetric C=O stretching vibrations in the imide ring (1778 and 1706  $\text{cm}^{-1}$ , respectively), and C–N stretching (1359  $\text{cm}^{-1}$ ) at the imide-cyclohexane moiety are clearly observed, which confirm the imide structures in the PIs.



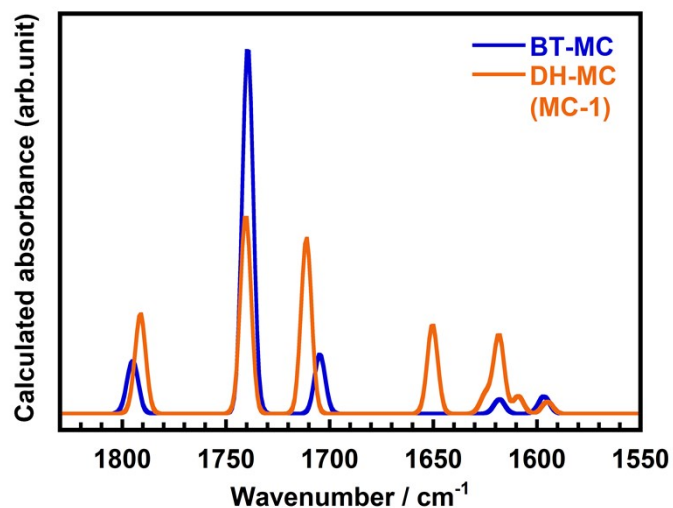
**Scheme S5.** Synthesis scheme of copolyimide (CoPI).



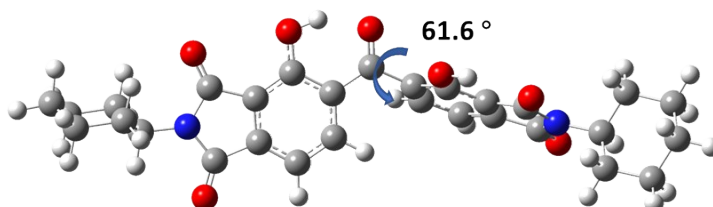
**Figure S4.** FT-IR spectra of BT-PI, DH-PI, and CoPI films.



**Figure S5.** Experimental FT-IR spectra of BT-MC and DH-MC powders (1000–3800  $\text{cm}^{-1}$ ).

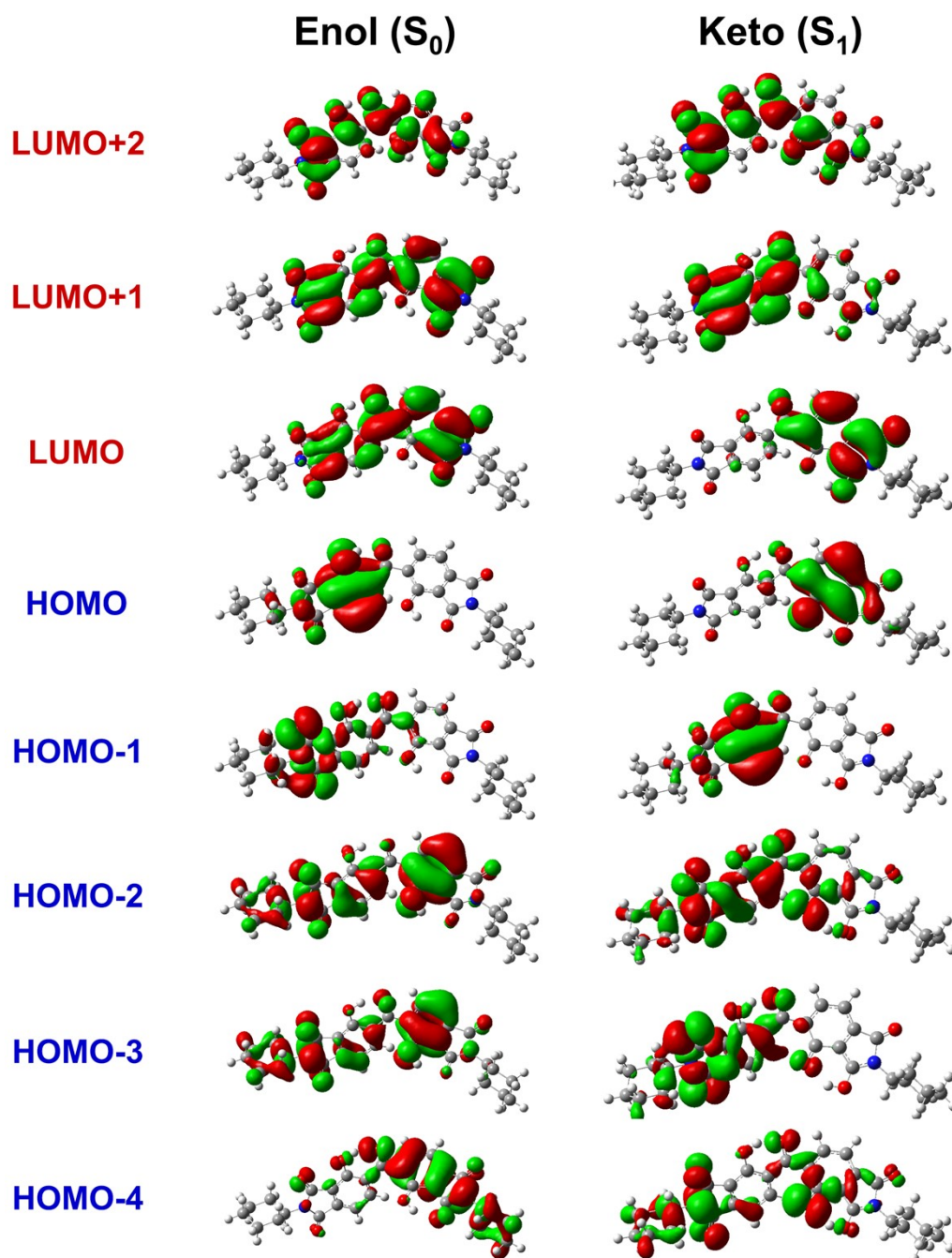


**Figure S6.** Calculated FT-IR spectra of BT-MC and DH-MC (MC-1).

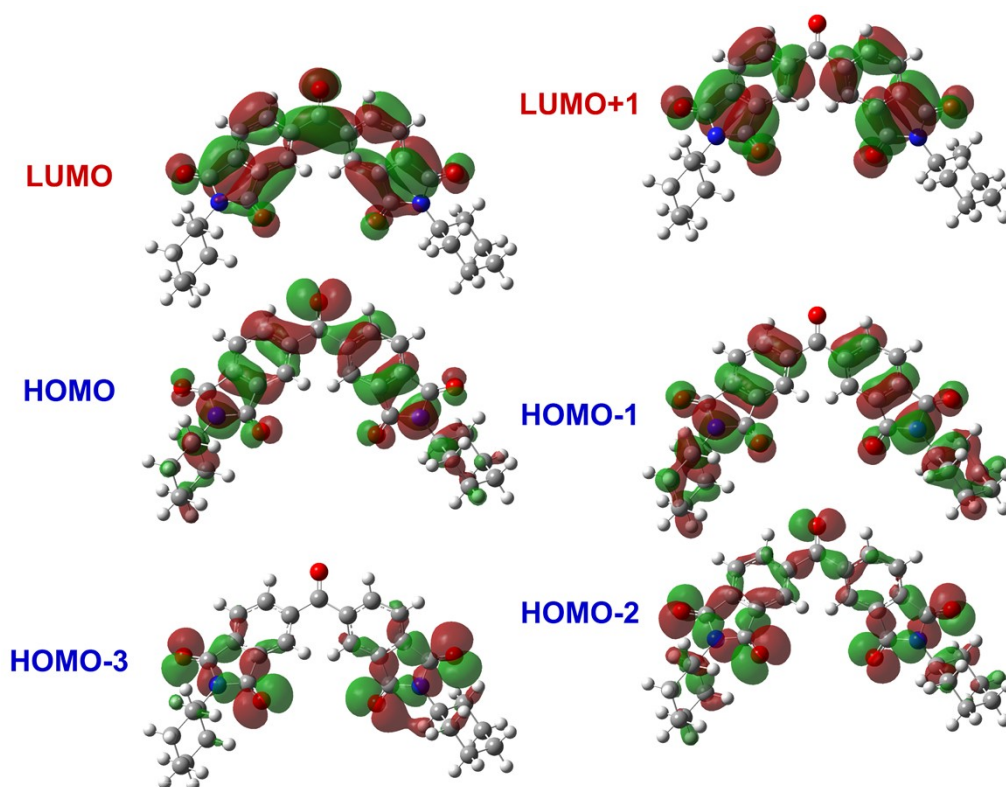


**Figure S7.** Optimized geometry of MC-1 in the ground state ( $S_0$ ).





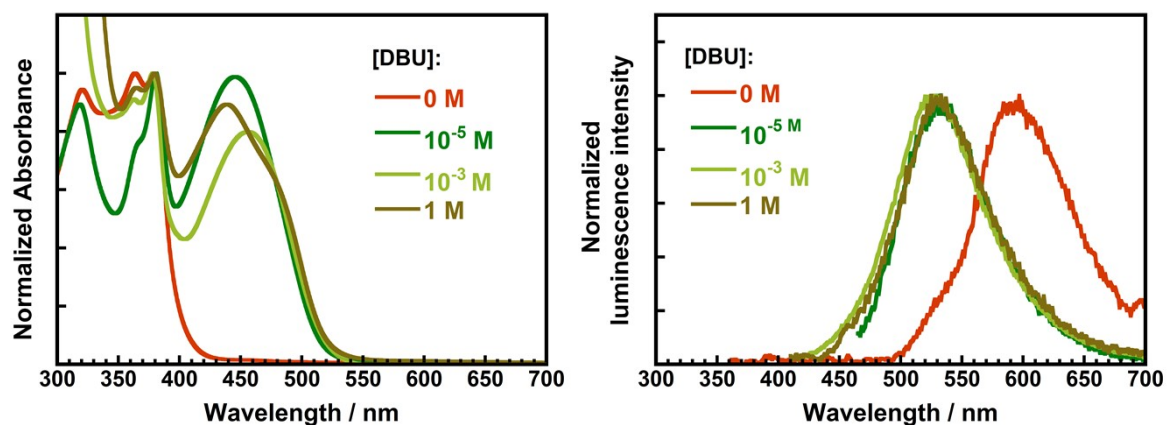
**Figure S8.** Calculated molecular orbitals of the enol and keto forms of **MC-1** (DH-MC). HOMO- $m$  and LUMO+ $m$  denote the ( $m+1$ )th highest occupied orbital and the ( $m+1$ )th lowest unoccupied orbital, respectively.



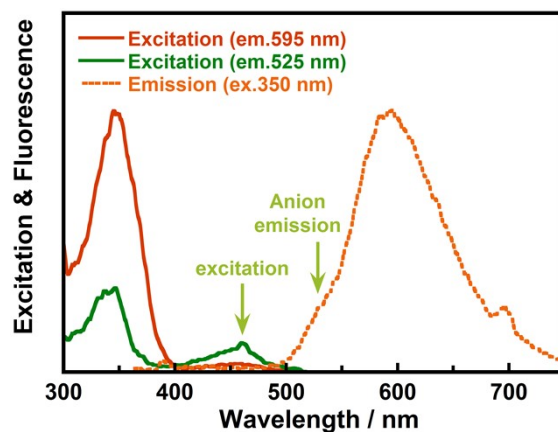
**Figure S9.** Calculated molecular orbitals of BT-MC. HOMO  $-m$  and LUMO  $+m$  denote the  $(m + 1)$ th highest occupied orbital and the  $(m + 1)$ th lowest unoccupied orbital, respectively.

**Table S1.** Calculated electronic transitions of BT-MC in the optimized  $S_0$  geometry ( $S_1$ – $S_3$ ) and that in the optimized  $S_1$  geometry ( $S_1^*$ ).

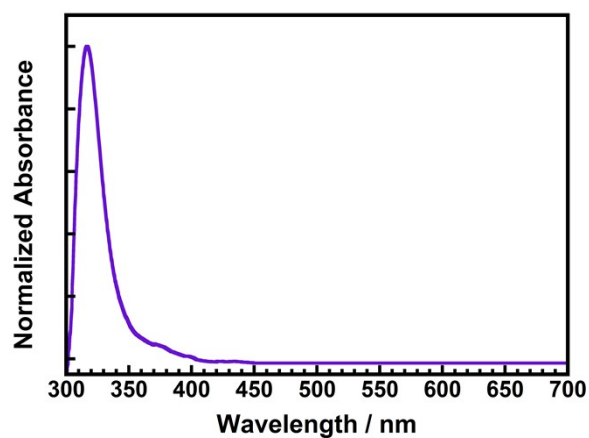
State	Transition wavelength/nm	Oscillator strength	Orbitals	Assignment of transition	Contribution
$S_1$	369.6	0.0021	HOMO – LUMO	LE ( $n-\pi^*$ )	0.24
			HOMO-2 – LUMO	LE ( $n-\pi^*$ )	0.11
$S_2$	340.5	0.0004	HOMO-3 – LUMO	LE ( $n-\pi^*$ )	0.29
			HOMO-2 – LUMO+1	LE ( $n-\pi^*$ )	0.07
$S_3$	338.3	0.0002	HOMO-4 – LUMO	CT ( $\pi-\pi^*$ )	0.14
			HOMO-2 – LUMO	LE ( $n-\pi^*$ )	0.14
$S_1^*$	443.0	0.0015	HOMO – LUMO	LE ( $n-\pi^*$ )	0.33



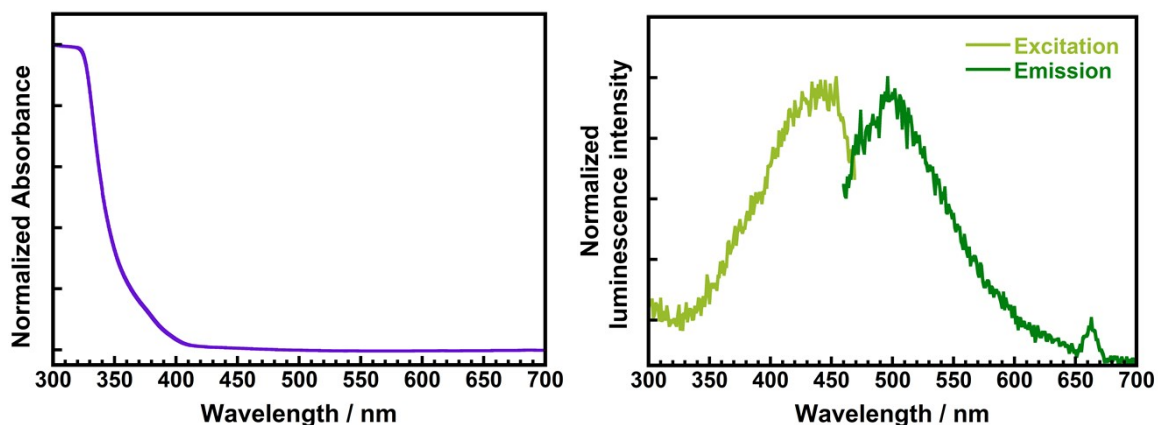
**Figure S10.** Steady-state UV-vis absorption spectra (left) and emission spectra (right) of DH-MC dissolved in toluene/DBU ([DH-MC]:  $10^{-5}$  M) with different DBU concentrations ([DBU]: 0 M,  $10^{-3}$  M,  $10^{-5}$  M, and 1 M).



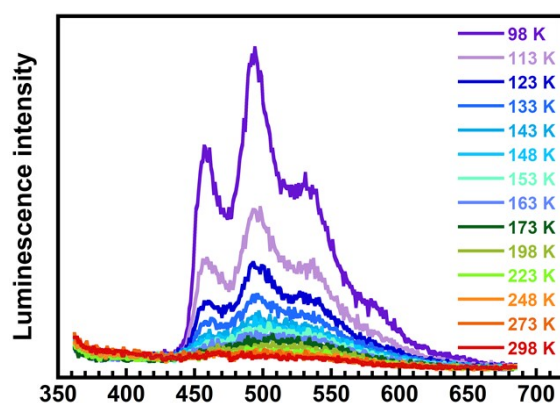
**Figure S11.** Steady-state excitation and fluorescence spectra of DH-MC dissolved in toluene ([DH-MC]:  $10^{-5}$  M). The monitoring wavelengths of fluorescence are 525 and 595 nm.



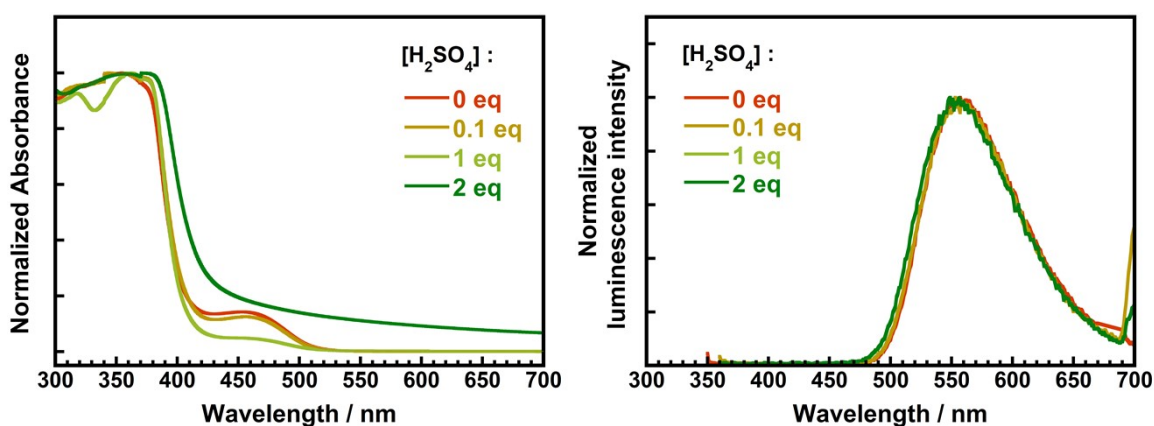
**Figure S12.** Steady-state UV-vis absorption spectrum of BT-MC dissolved in toluene ([BT-MC]:  $10^{-5}$  M).



**Figure S13.** Steady-state UV-vis absorption spectrum (left) and excitation/emission spectra (right,  $\lambda_{\text{ex}} = 440 \text{ nm}$ ,  $\lambda_{\text{em}} = 490 \text{ nm}$ ) of BT-PI film.



**Figure S14.** Temperature dependent emission spectra at lower temperatures of BT-PI film ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ).



**Figure S15.** Steady-state UV-vis absorption spectra (left) and emission spectra ( $\lambda_{\text{ex}} = 340 \text{ nm}$ , right) of DH-PI films with different doping  $\text{H}_2\text{SO}_4$  concentrations. in which 'eq' means an equivalent of  $[\text{H}^+]$  ions to  $-\text{OH}$  groups.

**Table S2.** Average photoluminescence lifetime ( $\langle\tau\rangle$ ), energy transfer efficiency ( $E_{\text{FRET}}$ ) and total quantum yield ( $\Phi_{\text{total}}$ ) of ODPA/DCHM PI<sup>3</sup>, DH-PI, and CoPI films.

PI	$\langle\tau\rangle_{405}^{\S} / \text{ns}$	$\langle\tau\rangle_{545}^{\S} / \text{ns}$	$E_{\text{FRET}}$	$\Phi_{\text{total}}^{\#}$	
ODPA/DCHM	7.66	–	–	0.09	ref.2
DH-PI	–	1.64	–	0.04	this study
CoPI	1.78	3.17	0.77	0.14	this study

–: not detected;  $\S$ :  $\lambda_{\text{ex}} = 340 \text{ nm}$ ;  $\S$ :  $\lambda_{\text{ex}} = 340 \text{ nm}$ ;  $\#$ :  $\lambda_{\text{ex}} = 340 \text{ nm}$ .

#### References:

- 1 G. J. Shin, J. C. Jung, J. H. Chi, T. H. Oh and J. B. Kim, Synthesis and micropatterning properties of a novel base-soluble, positive-working, photosensitive polyimide having ano-nitrobenzyl ether group, *J. Polym. Sci. Part A Polym. Chem.*, 2007, **45**, 776–788.
- 2 T. Yamashita, T. Kudo, Y. Yoshida and S. Tagawa, Transient Absorption Spectra of Electron Beam Sensitive Polyimides and their Model Compounds, *J. Photopolym. Sci. Technol.*, 2005, **18**, 699–705.
- 3 N. Liang, E. Fujiwara, M. Nara, R. Ishige and S. Ando, Colorless Copolyimide Films Exhibiting Large Stokes-Shifted Photoluminescence Applicable for Spectral Conversion, *ACS Appl. Polym. Mater.*, 2021, **3**, 3911–3921.