

Supporting Information

Prolonged irradiation-induced delayed luminescence of PMMA-dispersed imide compounds containing ether- and thioether-bridged cores

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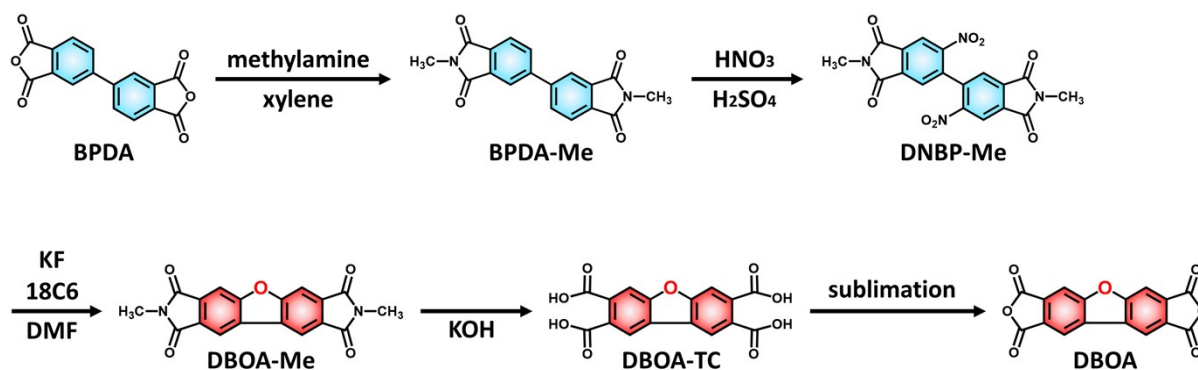
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1. Experimental section

1.1. Synthesis of DBOA

The synthetic procedure of DBOA is shown in **Scheme S1**.



Scheme S1 Synthesis scheme of DBOA.

4,4'-Bis(*N*-methyl phthalimide) (BPDA-Me)

BPDA (14.9 g, 50.6 mmol), 40% methylamine solution (33.0 mL, 382 mmol) were added in xylene (60 mL), and then dissolved by stirring at room temperature for 1h using mechanical stirrer. The solution was reflux in a Dean-Stark apparatus at 150 °C for 5 h. After the reaction, the solution was cooled to room temperature, the precipitate was filtered and washed by ethanol. The white powder was dispersed in $\text{NaHCO}_3/\text{H}_2\text{O}$ solution and stirred for 1 day, and

the precipitate was filtered. Finally, BPDA-Me was obtained (12.0 g, 37.4 mmol, 74% yield). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 8.28\text{--}8.25$ (m, 4H), 7.97 (d, 2H), 3.07 (s, 6H).

4,4'-Bis(5-nitro-N-methylphthalimide) (DNBP-Me)

BPDA-Me (5.0 g, 15.6 mmol) was dissolved in H_2SO_4 (7.5 mL) at 80 °C using mechanical stirrer. Then, HNO_3 (2.1 mL, 46.6 mmol) was added in small drops slowly so that the temperature does not rise too high at 80–90 °C. After the reaction, the solution was added to iced water and the yellowish precipitate was filtered. Finally, DNBP-Me was obtained (5.4 g, 13.2 mmol, 84% yield). ^1H NMR (400 MHz, Sulfuric acid- d_2 , ppm): $\delta = 8.40$ (s, 2H), 7.49 (s, 2H), 5.24–5.51 (t, 6H).

N,N'-Dimethyl dibenzofuran tetracarboxylic diimide (DBOA-Me)

DNBP-Me (1.0 g, 2.4 mmol), KF (0.85 g, 14.6 mmol), and 18C6 (0.01 g, 0.034 mmol) were added to DMF (25 mL), and the solution was reflux at 130 °C for 2 days. After the reaction, the solution was added to water, and the precipitate was filtered. Finally, DBOA-Me was obtained (0.56 g, 1.7 mmol, 69% yield). ^1H NMR (400 MHz, Sulfuric acid- d_2 , ppm): $\delta = 8.37$ (s, 2H), 7.92 (s, 2H), 5.24–5.52 (t, 6H).

Dibenzofuran-4,4',5,5'-tetracarboxylic acid (DBOA-TC)

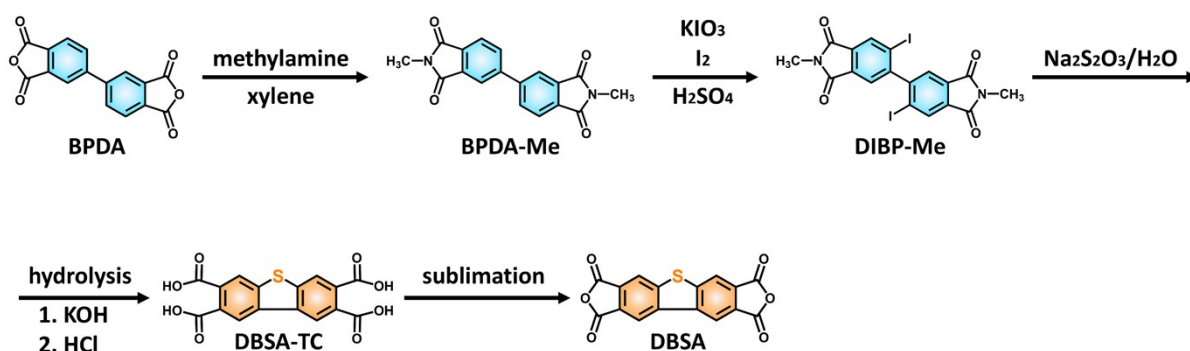
DBOA-Me (0.56 g, 1.7 mmol) and KOH (1.4 g, 25 mmol) was added to H_2O (25 mL). The bubbling of argon gas in the solution was performed for 5 min, and then DBOA-Me was hydrolyzed in autoclave at 200 °C for 3 h under high pressure. After the reaction, the solution was cooled to room temperature and filtered to remove the sediment. The solution was added to water and then acidified with concentrated HCl to pH 1 to generate white precipitate for 1 night with stirring. Finally, DBOA-TC was obtained (0.49 g, 1.4 mmol, 85% yield). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 8.86$ (s, 2H), 8.22 (s, 2H).

Dibenzofuran tetracarboxylic dianhydride (DBOA)

DBOA-TC (0.5 g, 1.5 mmol) was heated under vacuum at 150 °C for 8 h, then sublimated under reduced pressure at 280 °C to give DBOA as a white powder (0.2 g, 0.65 mmol, 45% yield).

1.2. Synthesis of DBSA

The synthetic procedure of DBSA is shown in **Scheme S2**.



Scheme S2 Synthesis scheme of DBSA.

4,4'-Bis(*N*-methyl phthalimide) (BPDA-Me)

BPDA-Me was synthesized as described in section “**1.1. Synthesis of DBOA.**”

4,4'-Bis(5-iodo-*N*-methylphthalimide) (DIBP-Me)

BPDA-Me (3.8 g, 11.7 mmol), KIO₃ (6.0 g, 28.0 mmol), and I₂ (4.5 g, 17.7 mmol) were dissolved in H₂SO₄ (50 mL), and the solution was stirred using mechanical stirrer at room temperature for 24 h. After cooling in refrigerator, the solution was added to Na₂S₂O₃/H₂O (80 g / 600 mL) and stirred for 1 night. The precipitate was filtered and added to water (450 mL), followed by addition of NaHCO₃ to pH 7. Finally, DIBP-Me of yellowish powder was obtained (6.6 g, 11.6 mmol, 99% yield). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ = 9.26 (s, 2H), 8.90 (s, 2H), 3.12 (s, 6H).

Dibenzothiophene-4,4',5,5'-tetracarboxylic acid (DBSA-TC)

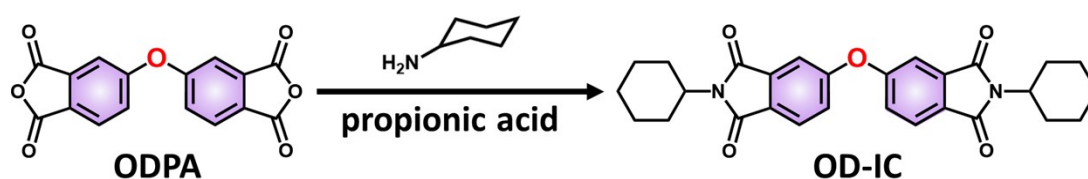
DIBP-Me (2.5 g, 4.37 mmol) and KOH (1.4 g, 25.0 mmol) was added to H₂O (25 mL). The bubbling of argon gas in the solution was performed for 5 min, and then DIBP-Me was hydrolyzed in autoclave at 220 °C for 3 h under high pressure. After the reaction, the solution was cooled to room temperature and filtered to remove the sediment. The solution was added to water and then acidified with concentrated HCl to pH 1 to generate white precipitate for 1 night with stirring. Finally, DBSA-TC was obtained (0.77 g, 2.1 mmol, 49% yield). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ = 8.94 (s, 2H), 8.64 (s, 2H).

Dibenzothiophene tetracarboxylic dianhydride (DBSA)

DBSA-TC (0.4 g, 1.1 mmol) was heated under vacuum at 150 °C for 8 h, then sublimated under reduced pressure at 280 °C to give DBSA as a white powder (0.15 g, 0.46 mmol, 42% yield).

1.3. Synthesis of ICs

OD-IC was synthesized as shown in **Scheme S3**. SD-IC, BO-IC, and BS-IC were synthesized in a similar manner.



Scheme S3 Synthesis route of OD-IC.

OD-IC^{S1}

¹H NMR (400 MHz, Chloroform-*d*, ppm): $\delta_{\text{H}} = 7.83\text{-}7.85$ (d, 2H, $J = 8.4$ Hz), $7.32\text{-}7.38$ (t, 4H, $J = 24$ Hz), $4.07\text{-}4.11$ (m, 2H), $2.17\text{-}2.21$ (br m, 4H), $1.86\text{-}1.89$ (br m, 4H), $1.68\text{-}1.75$ (br m, 6H), $1.26\text{-}1.39$ (br m, 6H) (**Fig. S1**). ¹³C NMR (MHz, Chloroform-*d*, ppm): $\delta_{\text{C}} = 167.6, 167.4$ (C=O), 161.0 (C–O), 135.0 (C=C), 127.6 (CH), 125.5 (C=C), 124.2 (CH), 113.5 (CH), 51.2 (NCH), 29.9 (CH₂), 26.1 (CH₂), 25.2 (CH₂) (**Fig. S2**).

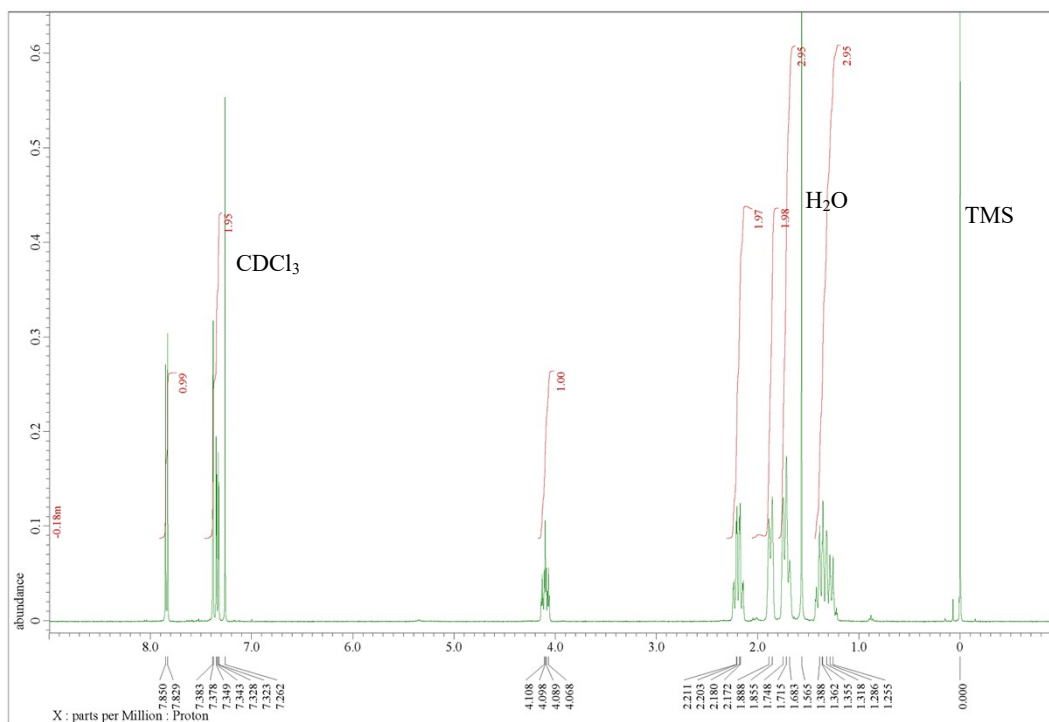


Fig. S1 ^1H NMR spectrum of OD-IC.

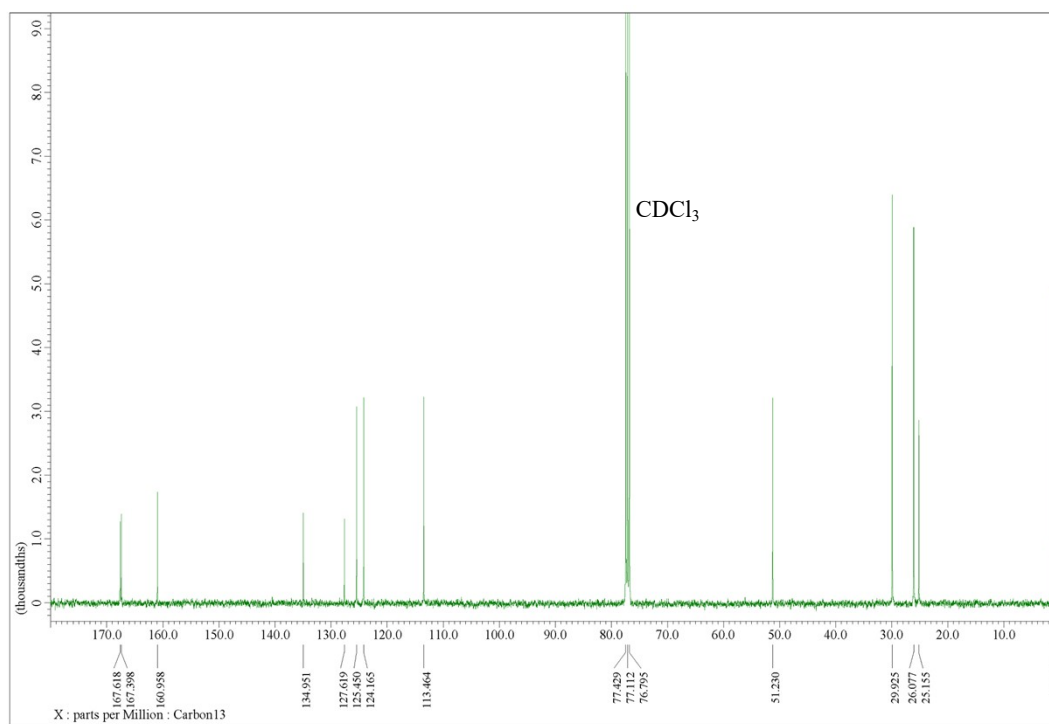


Fig. S2 ^{13}C NMR spectrum of OD-IC.

SD-IC

^1H NMR (400 MHz, Chloroform-*d*, ppm): $\delta_{\text{H}} = 7.70\text{--}7.71$ (d, 2H, $J = 7.6$ Hz), $7.58\text{--}7.63$ (t, 4H, $J = 17$ Hz), 4.03 (m, 2H), $2.09\text{--}2.13$ (br m, 4H), $1.78\text{--}1.82$ (br m, 4H), $1.64\text{--}1.67$ (br m, 6H), $1.21\text{--}1.31$ (br m, 6H) (**Fig. S3**). ^{13}C NMR (MHz, Chloroform-*d*, ppm): $\delta_{\text{C}} = 167.6$ (C=O), 142.0 (C-S), 135.8 (C=C), 133.5 (C=C), 131.1 (CH), 125.0 (CH), 124.0 (CH), 51.2 (NCH), 29.8 (CH_2), 26.0 (CH_2), 25.1 (CH_2) (**Fig. S4**).

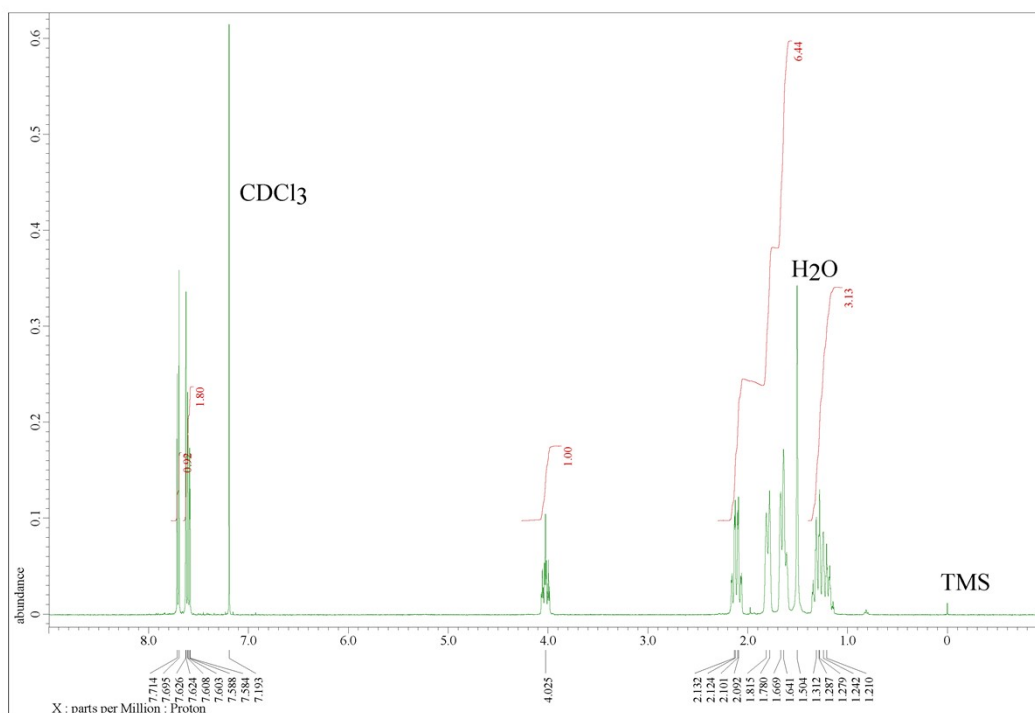


Fig. S3 ^1H NMR spectrum of SD-IC.

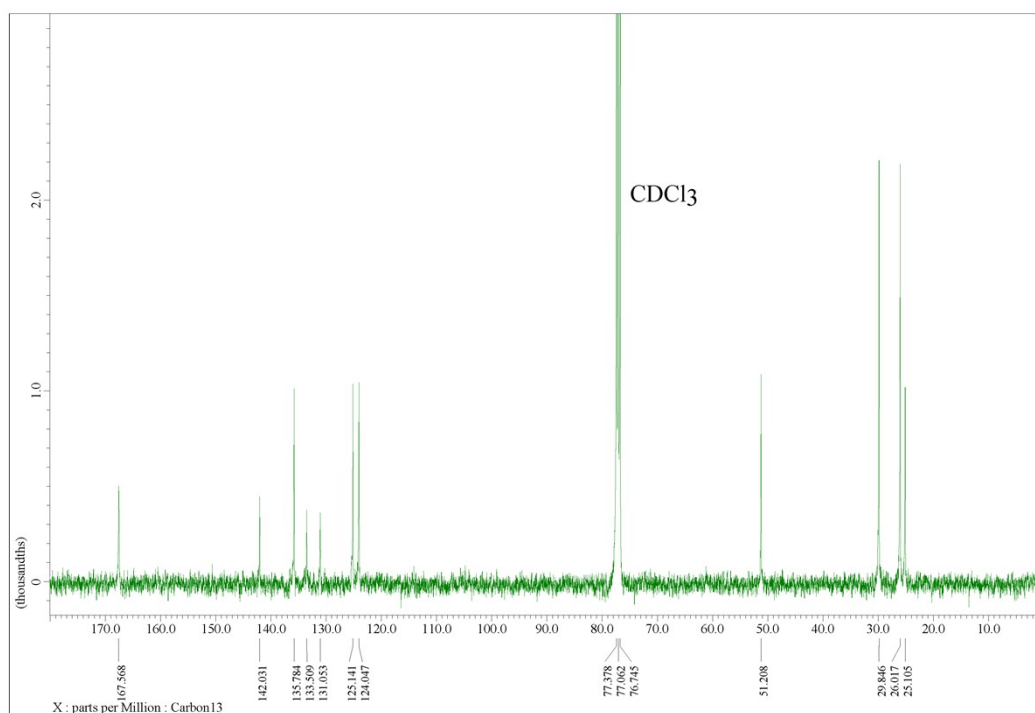


Fig. S4 ^{13}C NMR spectrum of SD-IC.

BO-IC

^1H NMR (400 MHz, Chloroform-*d*, ppm): δ_{H} = 8.48 (s, 2H, J = 0.8 Hz), 8.06 (s, 2H, J = 1.2 Hz), 4.18 (m, 2H), 2.23-2.27 (br m, 4H), 1.88-1.92 (br m, 4H), 1.77-1.80 (br m, 6H), 1.35-1.42 (br m, 6H) (**Fig. S5**). ^{13}C NMR (MHz, Chloroform-*d*, ppm): δ_{C} = 167.6, 167.4 (C=O), 160.2 (C–O), 132.9 (C=C), 128.0 (C-C), 127.8 (C=C), 117.0 (CH), 108.1 (CH), 51.4 (NCH), 29.9 (CH₂), 26.0 (CH₂), 25.1 (CH₂) (**Fig. S6**).

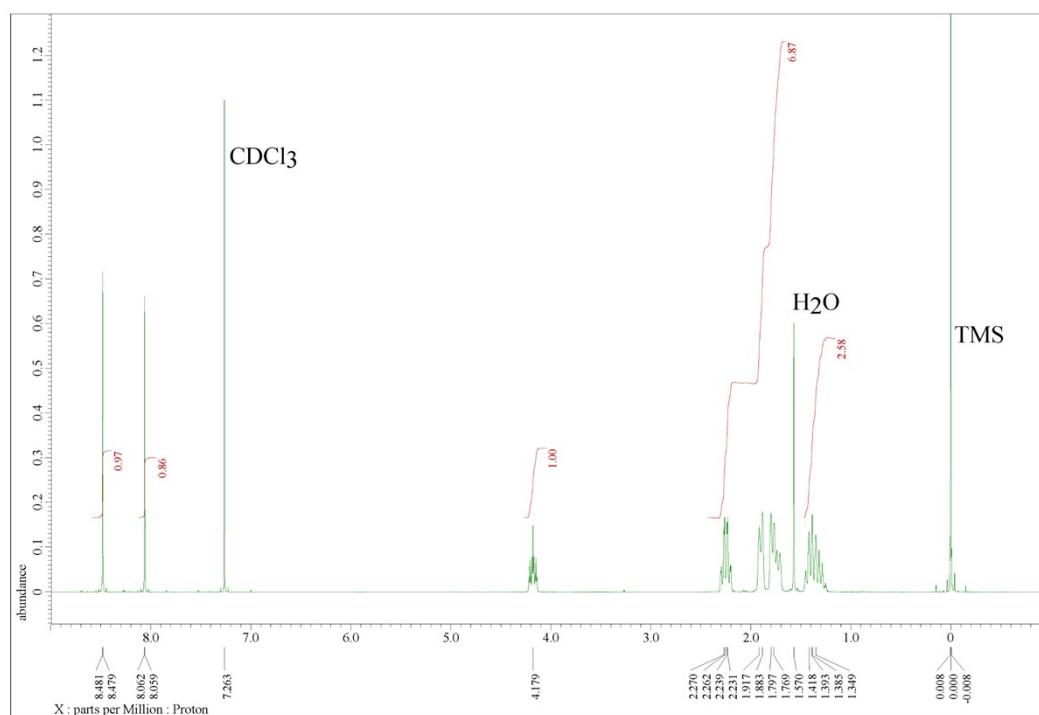


Fig. S5 ^1H NMR spectrum of BO-IC.

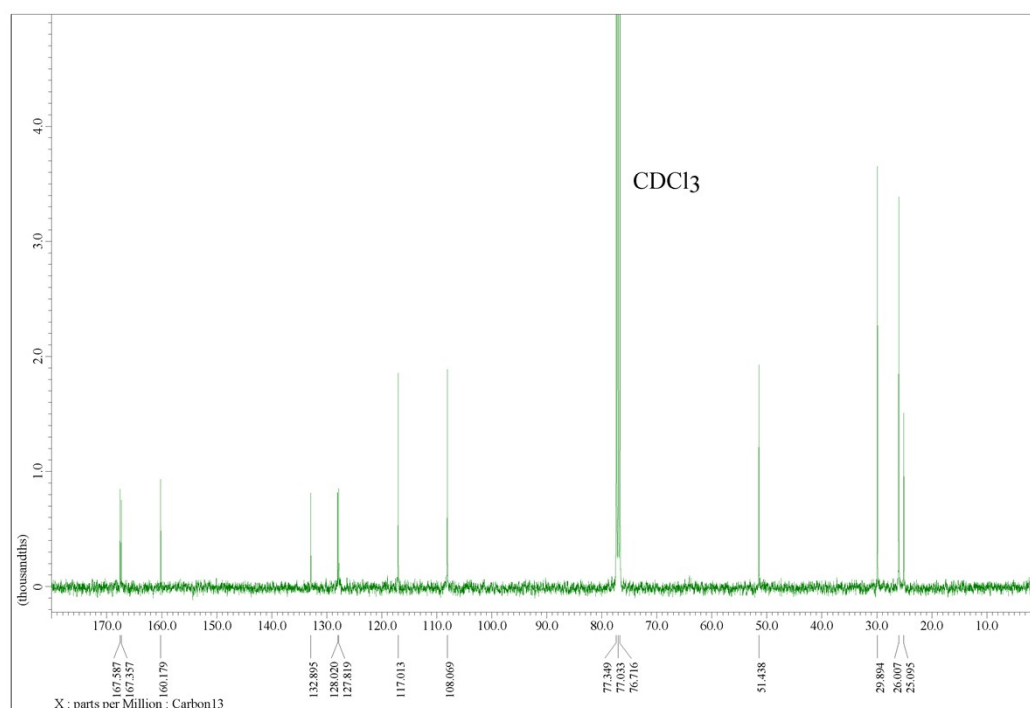


Fig. S6 ^{13}C NMR spectrum of BO-IC.

BS-IC

^1H NMR (400 MHz, DMSO-*d*, ppm): δ_{H} = 9.23 (s, 2H), 8.72 (s, 2H), 4.06 (t, 2H), 2.12-2.15 (br m, 4H), 1.67-1.86 (br m, 8H), 1.22-1.38 (br m, 8H) (**Fig. S7**). ^{13}C NMR (MHz, Chloroform-*d*, ppm): δ_{C} = 167.8, 167.6 (C=O), 145.9 (C–O), 138.6 (C=C), 131.3 (C–C), 129.2 (C=C), 118.6 (CH), 117.5 (CH), 51.5 (NCH), 29.9 (CH₂), 26.1 (CH₂), 25.1 (CH₂) (**Fig. S8**).

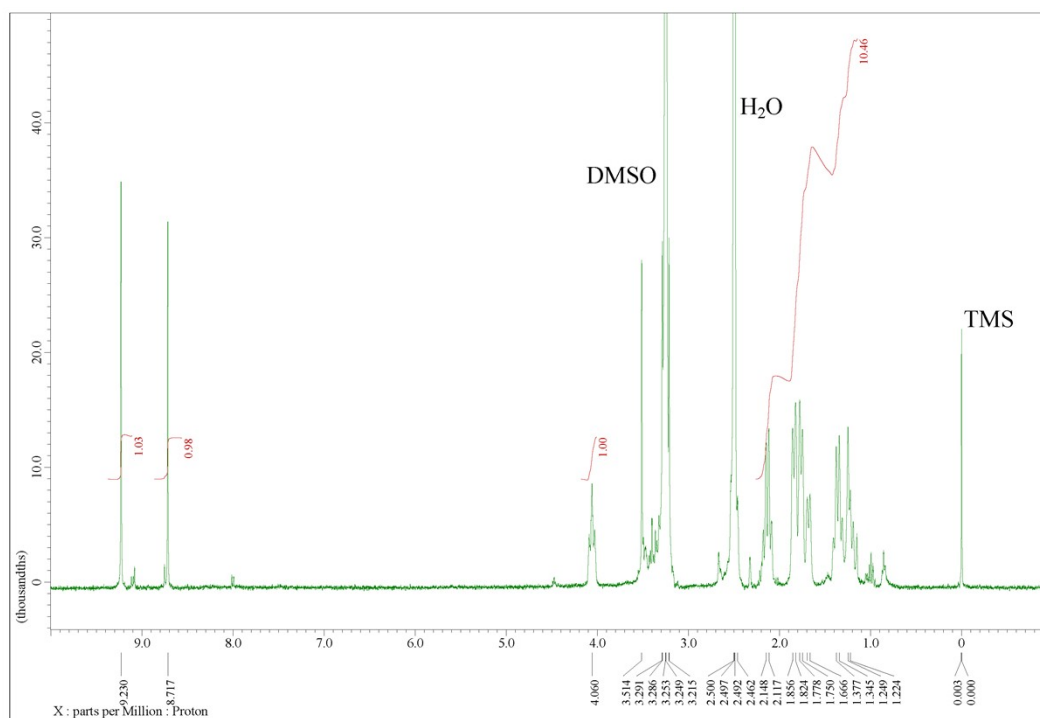


Fig. S7 ^1H NMR spectrum of BS-IC.

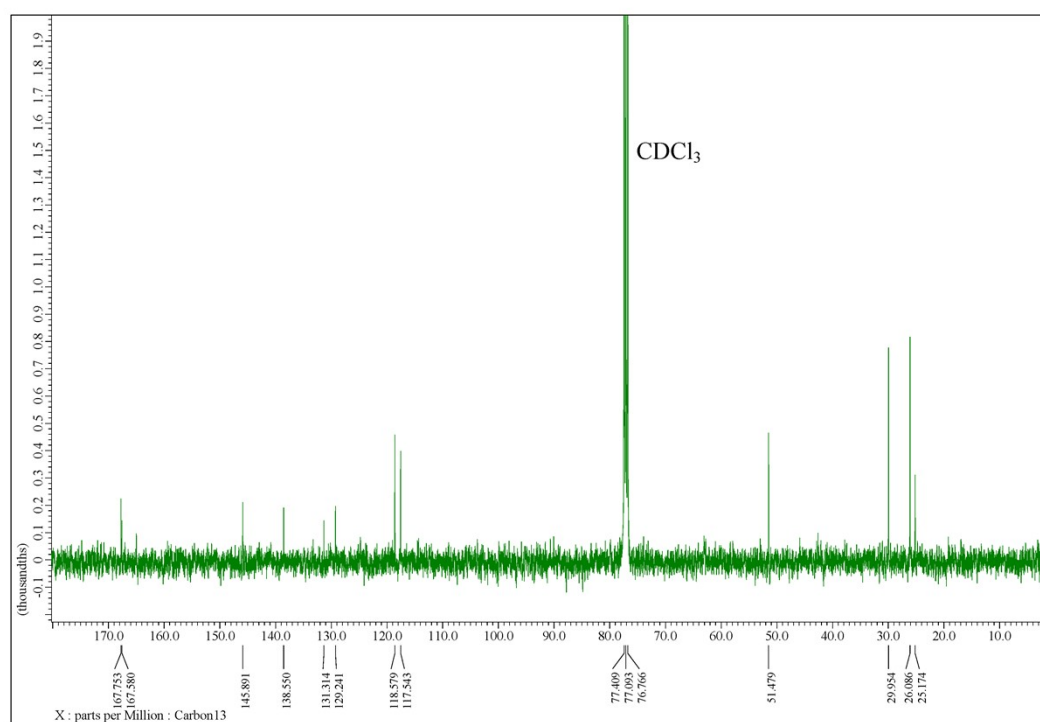


Fig. S8 ^{13}C NMR spectrum of BS-IC.

1.4. Measurement methods^{S1}

Emission spectra during/after UV irradiation

Emission spectra during/after UV irradiation in air at room temperature were measured using an optical system showed **Fig. S9**. Measurement of emission spectra was started just before the opening of the shutter and performed at every 100 ms during UV irradiation for 15 min. The measurements were performed with a multichannel analyzer (PMA-12, C10027-02, Hamamatsu Photonics, Japan) in the range of 350–1100 nm, using UV-LED L10561 (365 nm, Hamamatsu Photonics, Japan) and UV-LED M340L4 (340 nm, Hamamatsu Photonics, Japan) as a light source, two bandpass filters (TS OD 4.0-340/25, Edmund Optics Co., Ltd., USA) (FF01-360/12-25, Semrock Inc., USA) whose transmission ranges were 334–346 nm and 354–366 nm, respectively, to transmit the UV light at 365/340 nm irradiated to the films, electromagnetic shutter F77-4 (SURUGA SEIKI Co., Ltd., Japan) between the films and bandpass filter to control the UV irradiation duration, long-pass filter (BLP01-355R-25 and FF01-380/LP-25, Semrock Inc., USA) next to the films to remove the light from a light source, objective lens (10X, N.A. 0.25) to focus the light from the films on the multichannel analyzer.

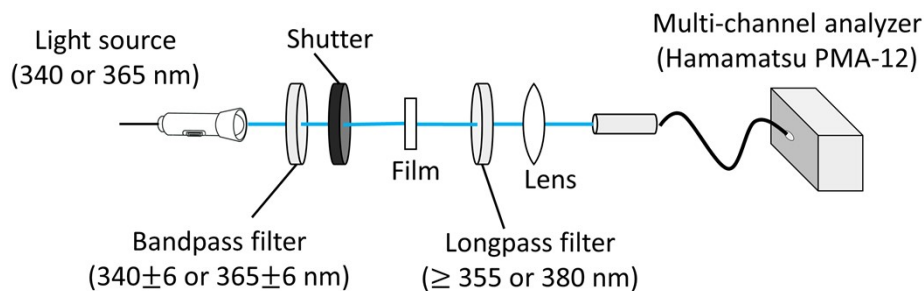


Fig. S8 Schematic diagram for an optical system for measurements of emission spectra with a long time UV irradiation.

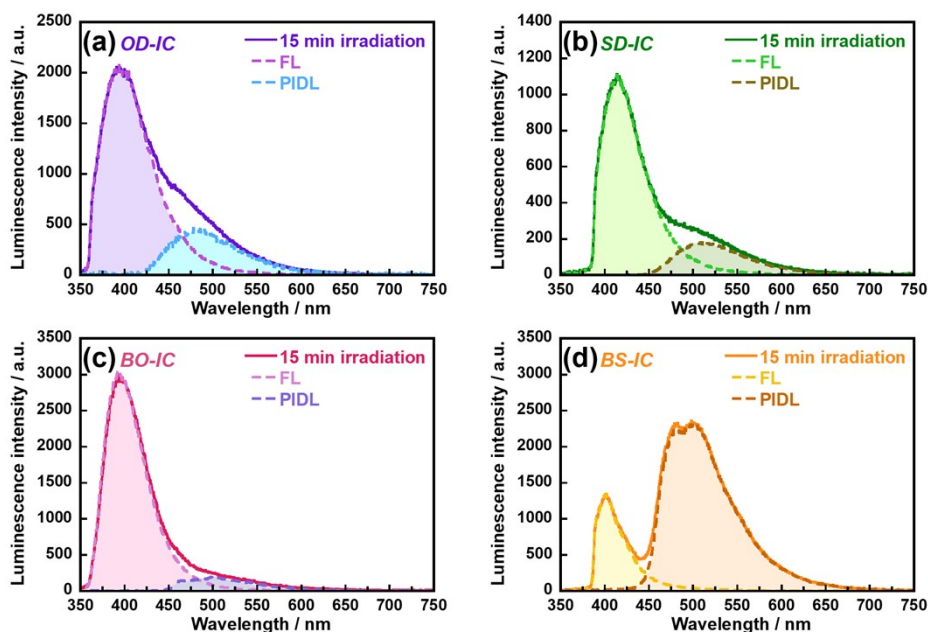


Fig. S9 Decomposed spectra into FL and PIDL (PH) components of (a) OD-IC, (b) SD-IC, (c) BO-IC, and (d) BS-IC dispersed in PMMA films. The emission spectra just after UV irradiation in air at room temperature were chosen as FL spectra and just after the end of UV irradiation for 15 min were chosen as the PIDL spectra.

1.5. Estimation of rate constants^{S1}

The rate constants of each photophysical process (k_x) relating to the T_1 state are listed in **Table 2**. They were estimated using the experimental values by the following methods.

k_{ISC} : rate constant of intersystem crossing

The deactivation processes from S_1 state are FL, internal conversion (IC), and ISC, and the sum of these Φ s becomes unity (Equation S1). It is reported that Φ of IC (Φ_{IC}) of rigid aromatic molecules is negligibly small at 77 K in dried air. Based on this report, Φ of ISC (Φ_{ISC}) at 77 K is calculated using Equation S1 with $\Phi_{IC} = 0$ and Φ_f measured at 77 K. In general, Φ_{ISC} does not show temperature dependence, and Φ_{ISC} at 77 K can be used as Φ_{ISC} at room temperature. Thus, k_{ISC} is calculated using Equation S2.

$$\Phi_f + \Phi_{IC} + \Phi_{ISC} = 1 \quad (S1)$$

$$k_{ISC} = \frac{1 - \Phi_f}{\tau_f} = \frac{\Phi_{ISC}}{\tau_f} \quad (S2)$$

k_p : rate constant of PH

k_p is calculated using Φ of PH and ISC and τ of PH (Φ_p , Φ_{ISC} , and τ_p) measured under vacuum at room temperature with the following equation.

$$k_p = \frac{\Phi_p}{\Phi_{ISC}\tau_p} \quad (S3)$$

k_{TS} : rate constant of non-radiative deactivation from T_1 to S_0

The rate constant of non-radiative deactivation from T_1 (k_{nr}) is represented as:

$$k_{nr} = \frac{1}{\tau_p} - k_p \quad (S4)$$

The non-radiative deactivation processes from T_1 state are that caused by molecular motion and that of OQ, and k_{nr} in atmospheric air is the sum of these rate constants (k_{TS} and k_Q). Under vacuum, k_Q is 0 due to no existence of oxygen, and k_{nr} under vacuum is used as k_{TS} .

k_Q : rate constant of OQ

k_{nr} in atmospheric air is the sum of the rate constants, k_{TS} and k_Q . Based on the hypothesis that k_{TS} is the same value between under vacuum and in atmospheric air, the difference between k_{nr} in atmospheric air and under vacuum represents k_Q . k_Q is the product of $[^3O_2]$ and k_q (the rate constant of the energy transfer from the IC in the T_1 state to 3O_2 molecules).

2. Results and discussion

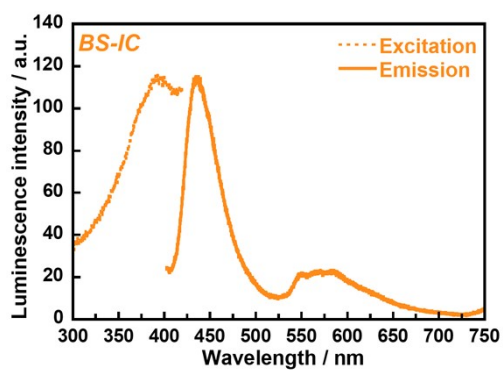


Fig. S10 Excitation/emission spectra for BS-IC in solid state ($\lambda_{\text{ex}} = 390$ nm, $\lambda_{\text{em}} = 435$ nm).

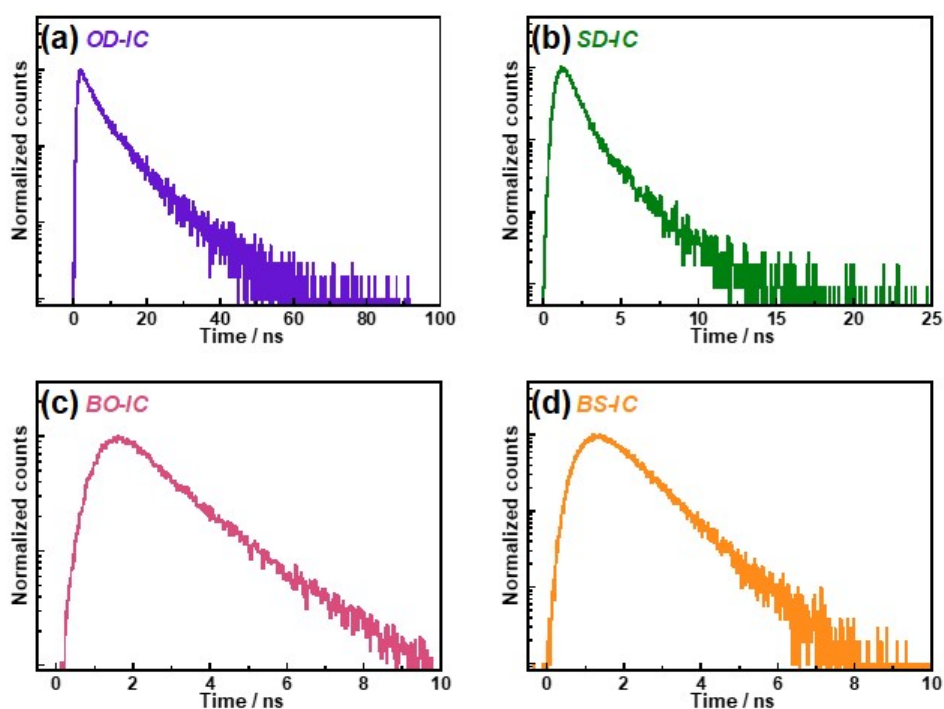


Fig. S11 FL decay curves of ICs in air dispersed in PMMA films, (a) OD-IC ($\lambda_{\text{ir}}, \lambda_{\text{em}} = 340, 390$ nm), (b) SD-IC (365, 415 nm), (c) BO-IC (340, 385 nm), and (d) BS-IC (365, 400 nm).

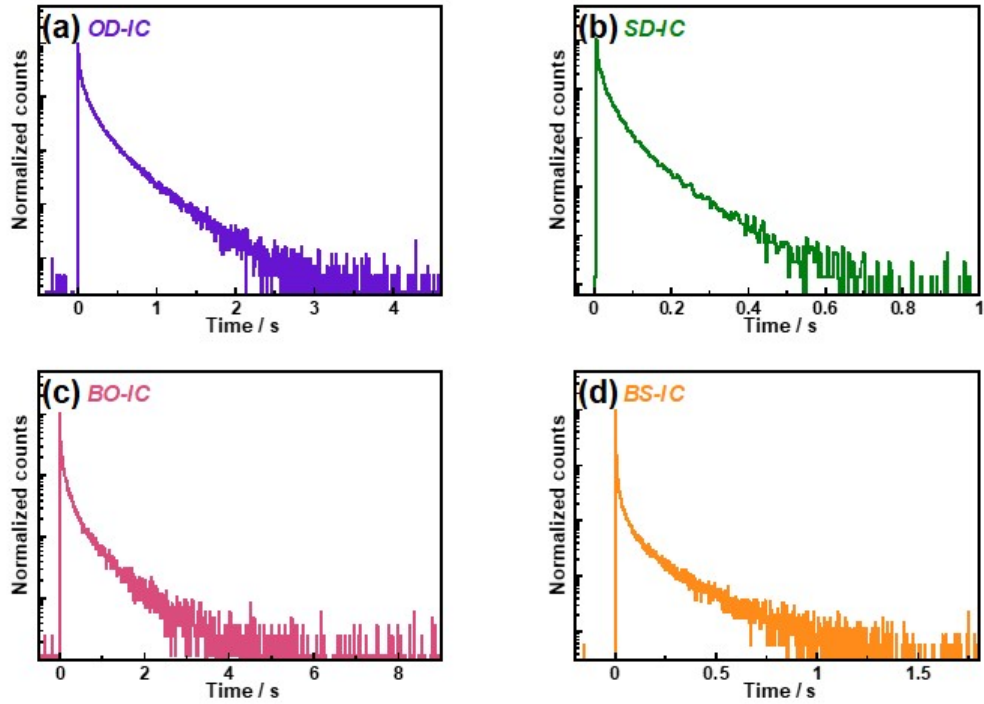


Fig. S12 PH decay curves under vacuum conditions of ICs dispersed in PMMA films, (a) OD-IC ($\lambda_{ir}, \lambda_{em} = 340, 480$ nm), (b) SD-IC (360, 500 nm), (c) BO-IC (340, 470 nm), and (d) BS-IC (360, 480 nm).

Table S1 Components of fitting for FL decay curves in air. Approximate accuracy (χ^2), average lifetime ($\langle\tau\rangle$), (τ_1, τ_2), (A_1, A_2) for OD-IC, SD-IC, BO-IC, and BS-IC dispersed in PMMA films. The average lifetime was calculated as $\langle\tau\rangle = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$.

Sample	χ^2	$\langle\tau\rangle$ [ns]	τ_1 [ns]	A_1	τ_2 [ns]	A_2
OD-IC	0.99	5.92	2.42	94	7.60	63
SD-IC	0.95	1.04	0.59	155	2.05	20
BO-IC	1.27	1.48	1.48	242	–	–
BS-IC	1.33	0.88	0.88	296	–	–

Table S2 Components of fitting for PH decay curves under vacuum. Approximate accuracy (χ^2), average lifetime ($\langle\tau\rangle$), (τ_1 , τ_2), (A_1 , A_2) for OD-IC, SD-IC, BO-IC, and BS-IC dispersed in PMMA films. The average lifetime was calculated as $\langle\tau\rangle = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i$.

Sample	χ^2	$\langle\tau\rangle$ [ms]	τ_1 [ms]	A_1	τ_2 [ms]	A_2
OD-IC	1.19	227	93	5206	342	1662
SD-IC	0.88	48	24	3580	74	1110
BO-IC	0.96	362	112	1087	572	253
BS-IC	0.89	135	39	513	200	152

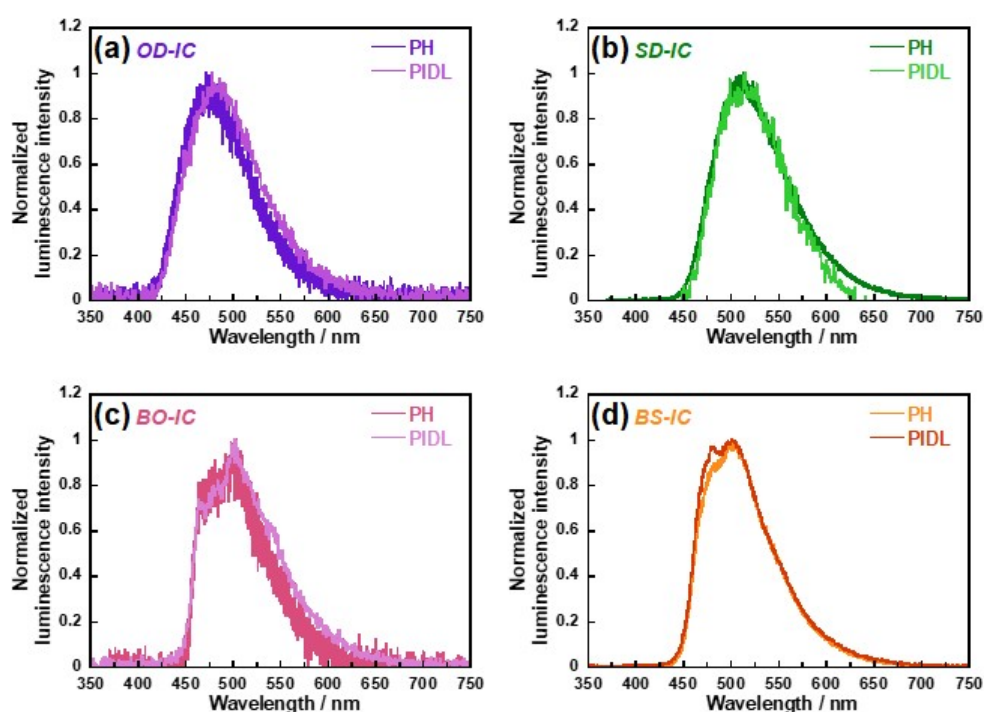


Fig. S13 Comparison of emission spectra of PIDL and PH observed under vacuum conditions for (a) OD-IC, (b) SD-IC, (c) BO-IC, and (d) BS-IC dispersed in PMMA films.

References

- (S1) 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**, e202200310.