

Electronic Supplementary Information (ESI)

## Visible-to-UV photon upconversion in metal-free molecular aggregates based on glassy diphenylnaphthalene derivatives

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## 1. General methods

Nuclear magnetic resonance (NMR) spectra were recorded on an Avance III 400 spectrometer (Bruker). Chemical shifts were referenced to tetramethylsilane ( $\delta = 0.00$ ) for  $^1\text{H}$  NMR, and  $\text{CDCl}_3$  ( $\delta = 77.0$ ) for  $^{13}\text{C}$  NMR as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex Max spectrometer (Bruker Daltonics) using dithranol as the matrix. Elemental analysis was carried out with an MT-5 CHN corder (Yanaco). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TG/DTA7300 and DSC7000X systems (Hitachi High-Tech Science), respectively, at a scanning rate of  $10\text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$ . Density functional theory (DFT) computations were performed with the Gaussian 16 program package, using the B3LYP functional with the 6-31G(d) basis set.

## 2. Photophysical measurements

For basic photophysical measurements of emitters and sensitizer: UV-vis absorption and PL spectra were measured using a V-670Y spectrometer (Jasco) and an FP-8600Y spectrophotometer (Jasco), respectively. Photoluminescence quantum yields ( $\Phi_{\text{PL}}$ ) were determined using a C13534-01 Quantaaurus-QY plus system (Hamamatsu Photonics) under a  $\text{N}_2$  atmosphere. Transient PL decay measurements were carried out using a C11367 Quantaaurus-Tau fluorescence lifetime spectrometer (Hamamatsu Photonics) with an LED excitation source.

For TTA-UC measurements: The solution samples were prepared in an Ar-filled glove box ( $[\text{O}_2] < 0.1\text{ ppm}$ ) using deoxygenated toluene as the solvent. UC emission spectra were measured using a PD300-UV photodiode sensor (OPHIR Photonics) with a 445 nm diode laser (75 mW, RGB Photonics) as the excitation source, whose power was controlled by combining a software (Ltune) and a variable neutral density filter. The diameters of the laser beam ( $1/e^2$ ) were measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). A typical area of the laser beam spot was  $6.0 \times 10^{-4}\text{ cm}^2$ . The emitted light was focused by an achromatic lens to an optical fiber connected to a multichannel detector MCPD-9800 (Otsuka Electronics). A 425 nm short-pass filter was inserted between the sample and the detector. The detector was calibrated by using a standard lamp HL-3 plus-CAL (Ocean Optics).

The relative TTA-UC efficiencies were determined using coumarin 6 as a standard,<sup>[S1]</sup> according to the following formula,<sup>[S2][S3]</sup>

$$\eta_{\text{UC}} = 2\Phi_{\text{std}}(1 - 10^{-A_{\text{std}}}/1 - 10^{-A_{\text{UC}}})(E_{\text{UC}}/E_{\text{std}})(I_{\text{UC}}/I_{\text{std}})(n_{\text{UC}}/n_{\text{std}})^2$$

where  $\Phi$ ,  $A$ ,  $E$ ,  $I$ , and  $n$  represent the quantum yield, absorbance at 445 nm, integrated

photoluminescence spectral profile, excitation intensity, and the refractive index of the solvent, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems.

The absolute TTA-UC efficiencies were measured using a C13534-02 Quantaaurus-QY Plus system (Hamamatsu Photonics).<sup>[S2]</sup> The sample was held in an integrating sphere and excited by the 445 nm laser (75 mW, RGB Photonics). The UC emission decay measurements were performed using a C11567-01 Quantaaurus-Tau system (Hamamatsu Photonics).

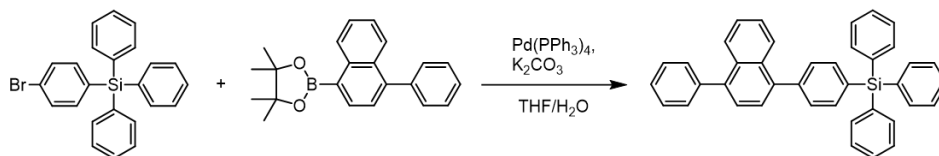
### 3. Film sample fabrication

Quartz glass substrates (size: 1.5 cm × 1.5 cm) were cleaned with detergent, deionized water, acetone, and isopropanol in this order. In an N<sub>2</sub>-filled glove box, chloroform solutions (300 μL) containing the photosensitizer and DPN-based emitter (**DPN:BBCz-SB-Br** = 99.9:0.1 mol%; **SiDPN-1:BBCz-SB-Br** = 99.9:0.1 mol%; **SiDPN-2:BBCz-SB-Br** = 99.8:0.2 mol%) were drop-cast onto the substrate together with silica spacers (particle size = 0.1 μm) and heated to 80 °C to volatilize the solvent. They were sandwiched with another quartz glass substrate and then heated to the melting point (*T<sub>m</sub>*) of the emitters. The peripheries of the sandwiched glass samples were sealed with a sealant (ThreeBond 2086M).

### 4. Synthesis and characterization

All reagents and solvents were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Fujifilm Wako Pure Chemical Corp., and were used without further purification unless otherwise noted. All reactions were performed under N<sub>2</sub>, using standard Schlenk techniques. **BBCz-SB-Br** and **BBCz-SB** were prepared according to the literature procedures.<sup>[S4] [S5]</sup>

#### Synthesis of SiDPN-1

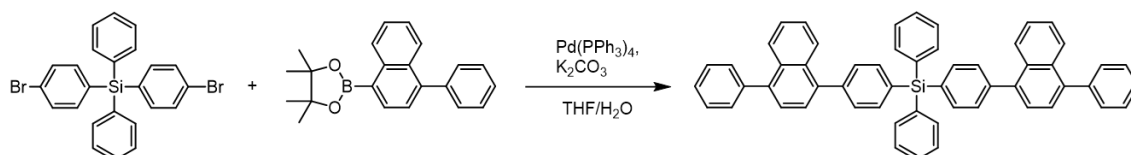


**Scheme S1** Synthesis of **SiDPN-1**.

A mixture of (4-bromophenyl)triphenylsilane (1.24 g, 2.99 mmol), 4,4,5,5-tetramethyl-2-(4-phenylnaphthalen-1-yl)-1,3,2-dioxaborolane (1.18 g, 3.57 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.17 g,

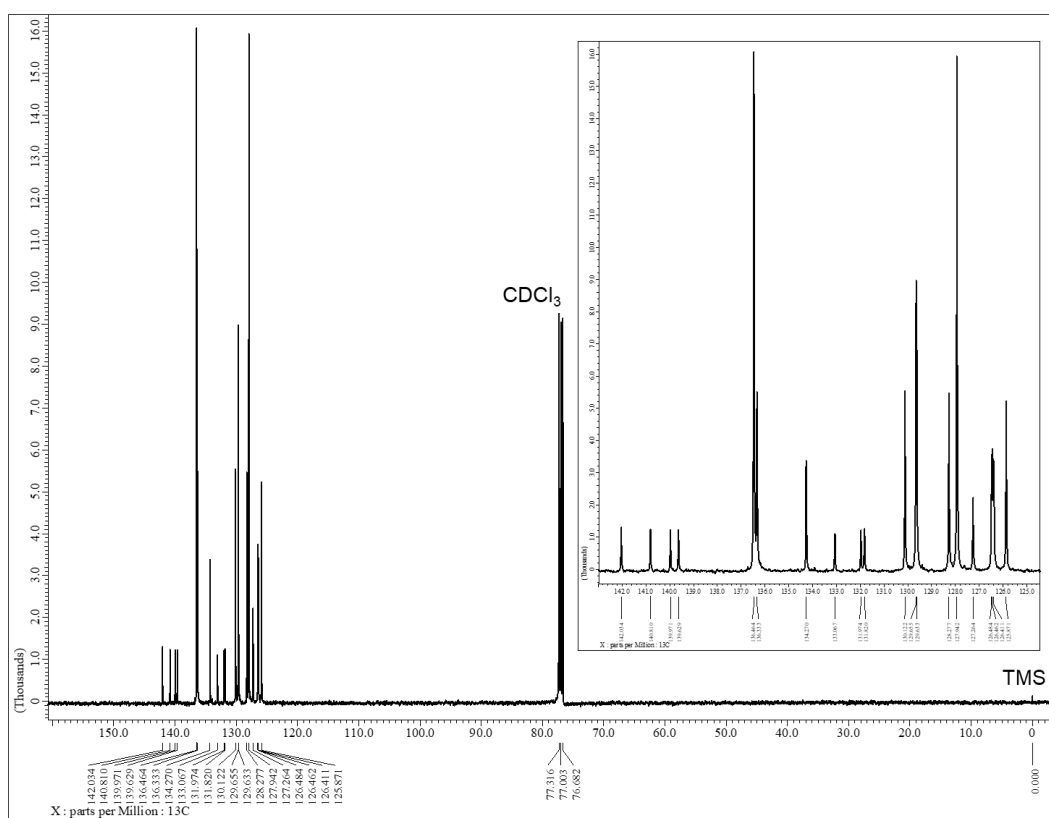
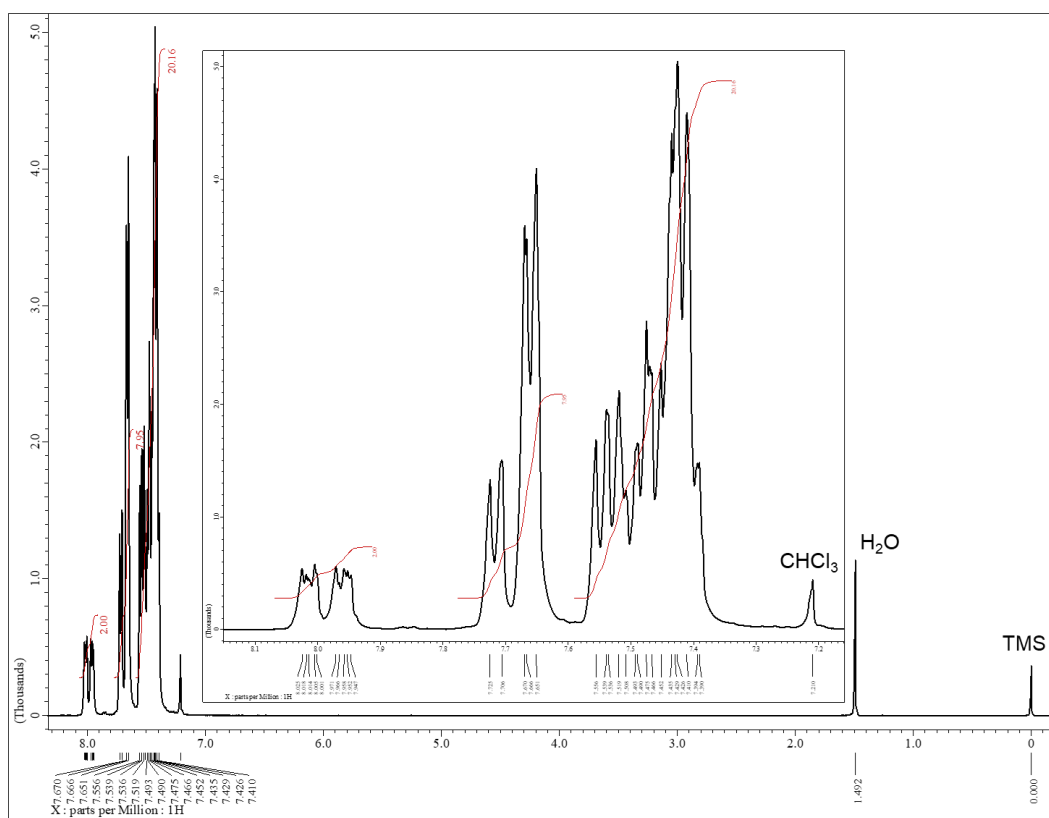
0.15 mmol), K<sub>2</sub>CO<sub>3</sub> (2.10 g, 15.2 mmol) in THF (45 mL) and water (15 mL) was stirred for 24 h at 75 °C. After cooling to room temperature, the reaction was quenched with water, and the product was extracted with ethyl acetate. The combined organic layers were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4:1, v/v) to afford **SiDPN-1** as a white solid (yield = 1.23 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03–7.95 (m, 2H), 7.72–7.65 (m, 8H), 7.56–7.39 (m, 20H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.03, 140.81, 139.97, 139.63, 136.46, 136.33, 134.27, 133.07, 131.97, 131.82, 130.12, 129.66, 129.63, 128.27, 127.94, 127.26, 126.48, 126.46, 126.41, 125.87. MS (MALDI-TOF): *m/z* calcd 538.21 [*M*]<sup>+</sup>; found 538.28. Anal calcd (%) for C<sub>40</sub>H<sub>30</sub>Si: C 89.17, H 5.61; found C 89.31, H 5.67.

### Synthesis of SiDPN-2

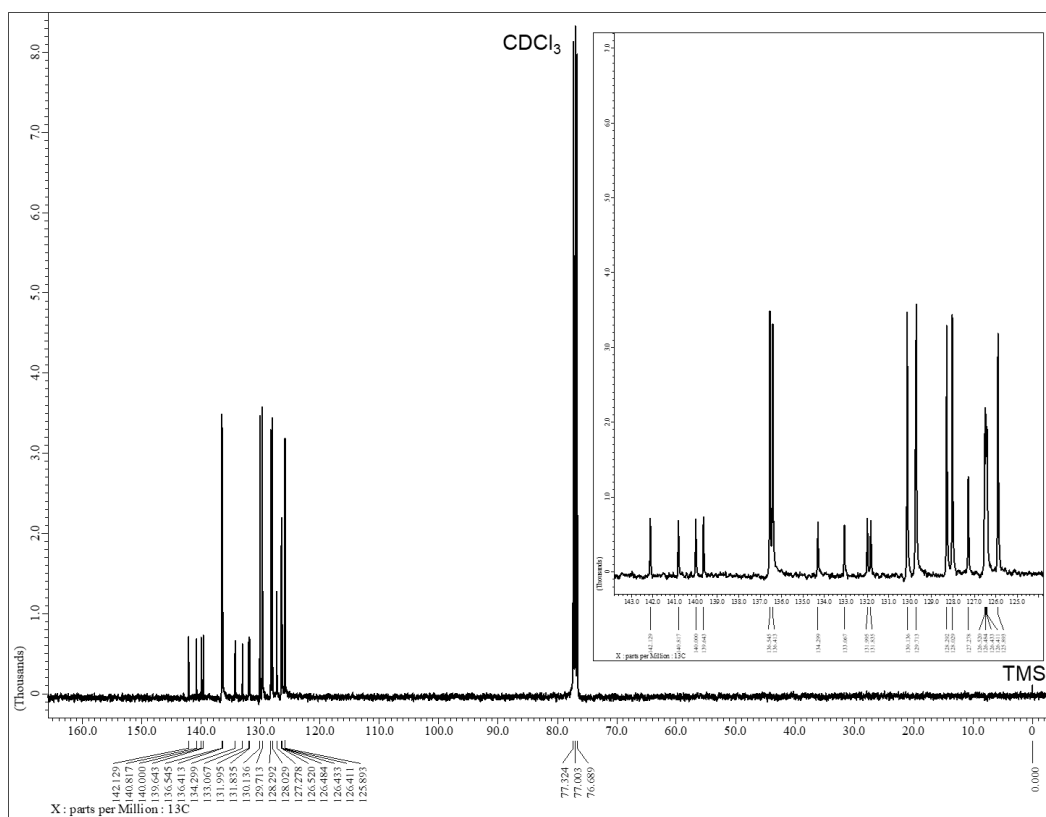
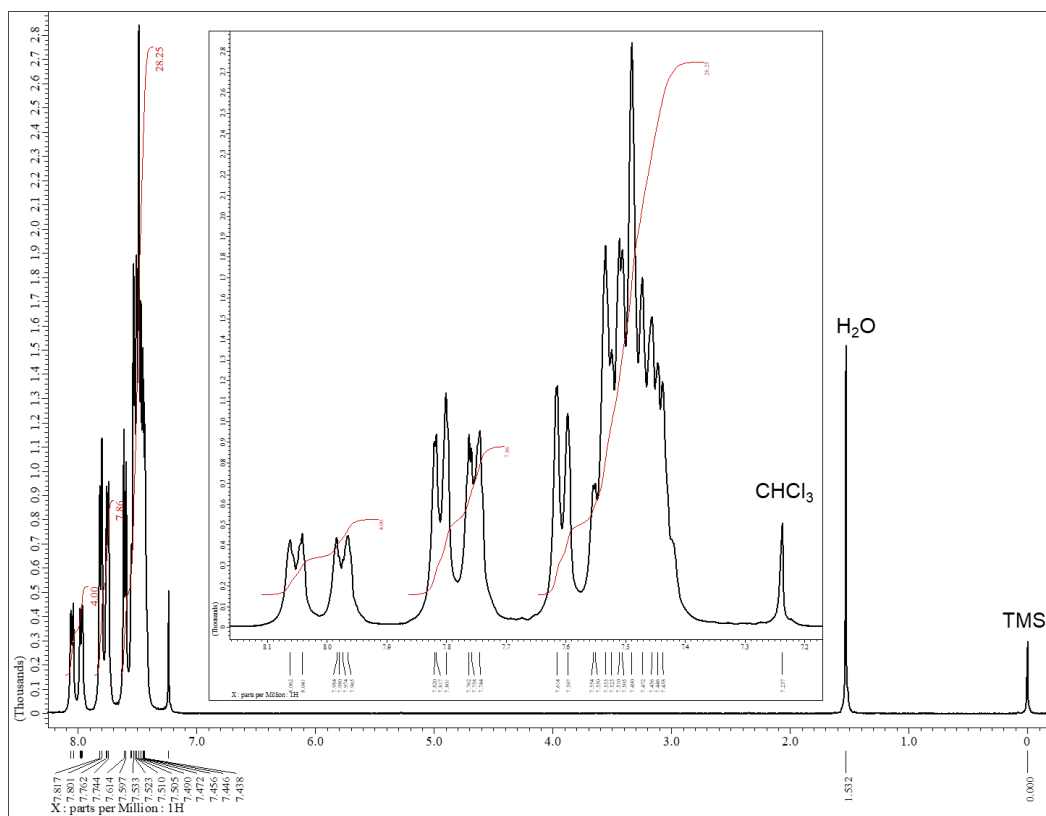


**Scheme S2** Synthesis of **SiDPN-2**.

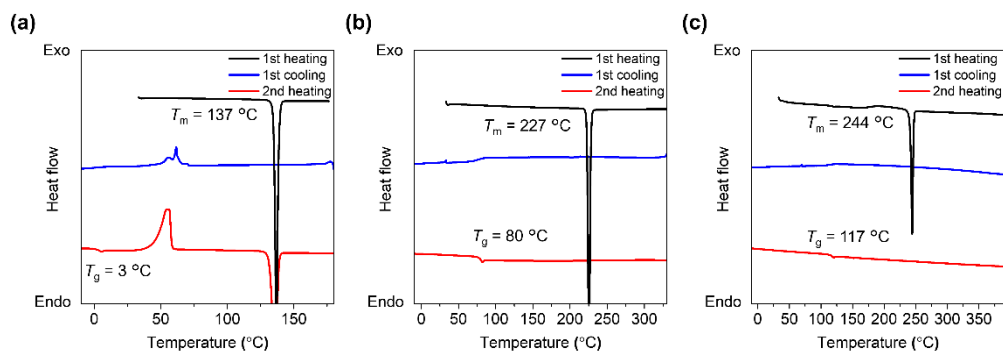
A mixture of bis(4-bromophenyl)diphenylsilane (1.48 g, 2.99 mmol), 4,4,5,5-tetramethyl-2-(4-phenylnaphthalen-1-yl)-1,3,2-dioxaborolane (2.37 g, 7.17 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.35 g, 0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (4.15 g, 30.0 mmol) in THF (45 mL) and water (15 mL) was stirred for 24 h at 75 °C. After cooling to room temperature, the reaction was quenched with water, and the product was extracted with ethyl acetate. The combined organic layers were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/CH<sub>2</sub>Cl<sub>2</sub> = 9:1, v/v) to afford **SiDPN-2** as a white solid (yield = 1.95 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06–7.96 (m, 4H), 7.82–7.74 (m, 8H), 7.61–7.44 (m, 28H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.13, 140.82, 140.00, 139.64, 136.55, 136.41, 134.30, 133.07, 132.00, 131.84, 130.14, 129.71, 128.29, 128.03, 127.28, 126.52, 126.52, 126.48, 126.43, 125.89. MS (MALDI-TOF): *m/z* calcd 740.29 [*M*]<sup>+</sup>; found 740.39. Anal calcd (%) for C<sub>56</sub>H<sub>40</sub>Si: C 90.77, H 5.44; found C 90.83, H 5.51.



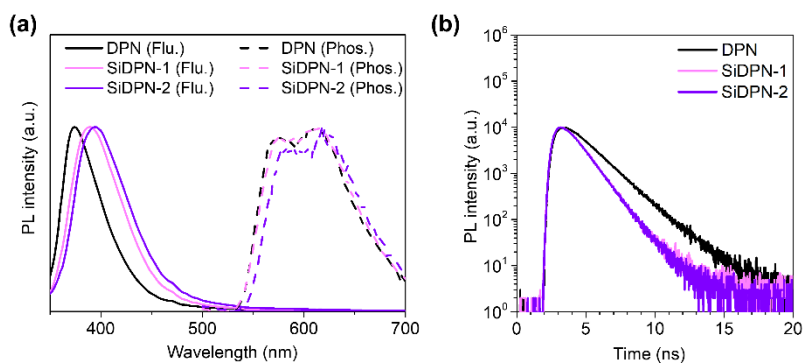
**Fig. S1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of SiDPN-1 in CDCl<sub>3</sub>.



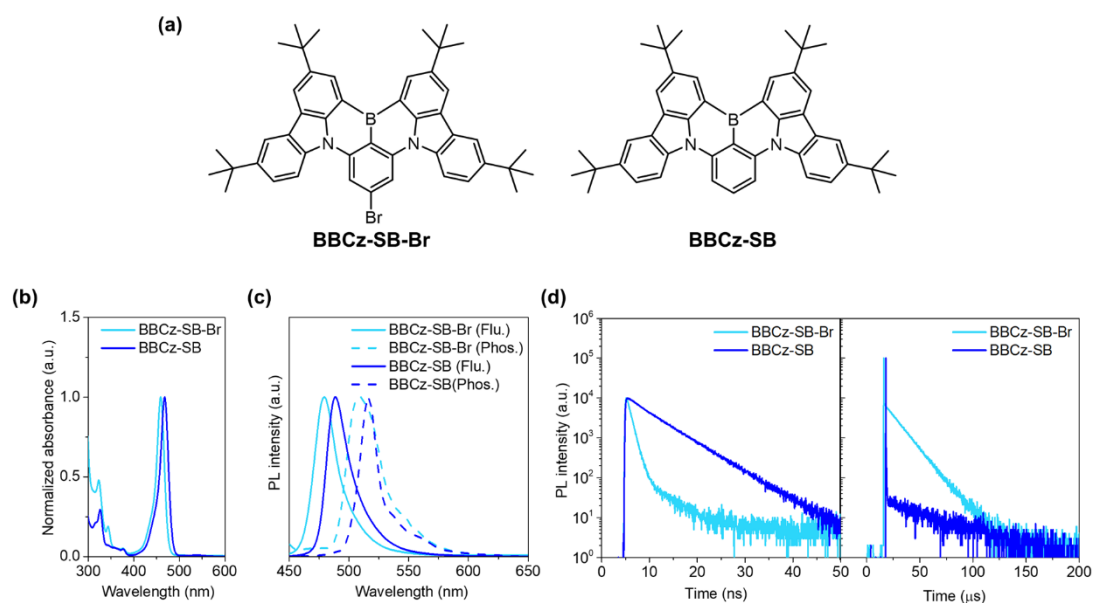
**Fig. S2** <sup>1</sup>H and <sup>13</sup>C NMR spectra of SiDPN-2 in CDCl<sub>3</sub>.



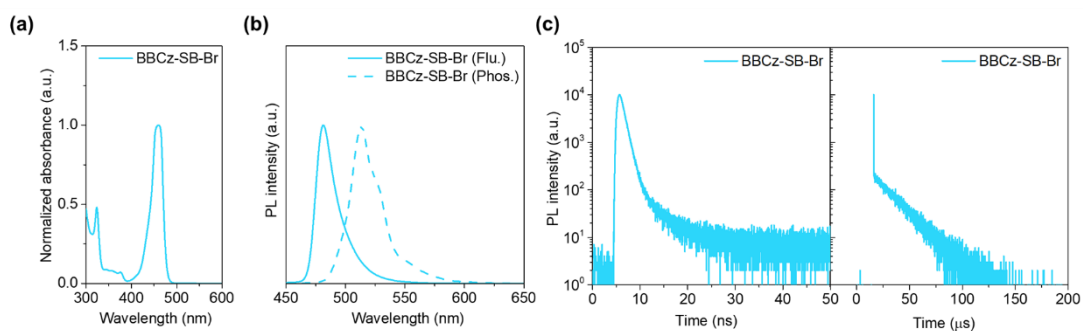
**Fig. S3** DSC thermograms of (a) DPN, (b) SiDPN-1, and (c) SiDPN-2 at a scanning rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$ .



**Fig. S4** (a) Fluorescence (300 K) and phosphorescence (77 K) spectra and (b) fluorescence decays of the emitters in neat films with  $1\text{ }\mu\text{m}$  thickness.



**Fig. S5** (a) Molecular structures of **BBCz-SB-Br** and **BBCz-SB**. (b) Normalized absorption spectra, (c) fluorescence (300 K) and phosphorescence (77 K) spectra, and (d) fluorescence decays of **BBCz-SB-Br** and **BBCz-SB** in deoxygenated toluene solution ( $10^{-5}$  M).



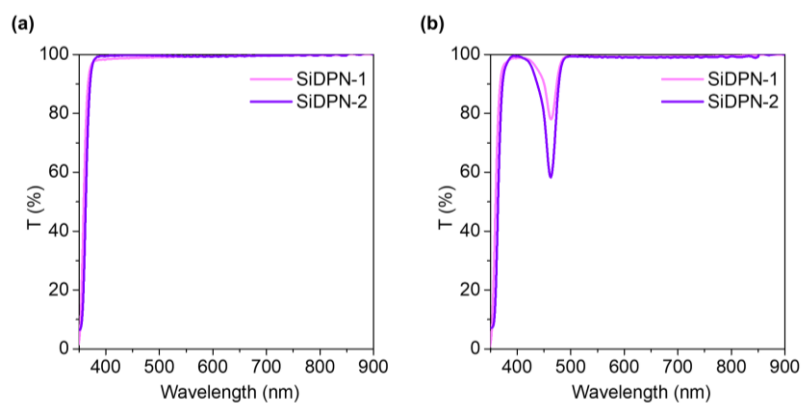
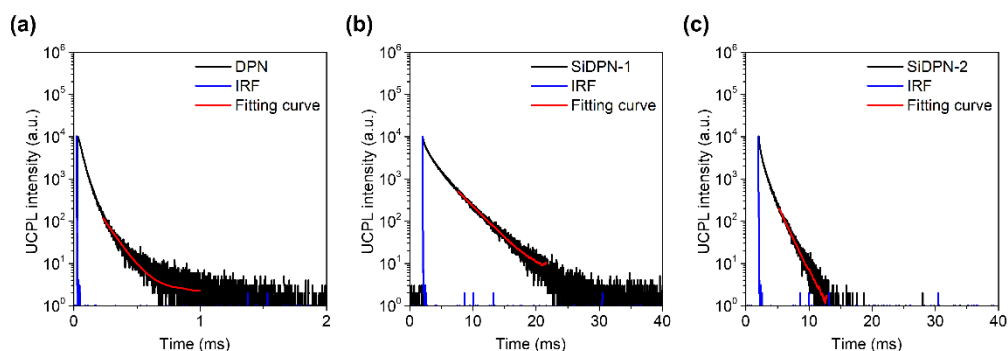
**Fig. S6** (b) Normalized absorption spectra, (c) fluorescence (300 K) and phosphorescence (77 K) spectra, and (d) fluorescence decays of **BBCz-SB-Br** in deoxygenated toluene solution (100  $\mu$ M).



**Table S1.** Photophysical data of **BBCz-SB-Br** and **BBCz-SB**

|                   | State                                 | $\Phi_{\text{PL}}$<br>(%) | $\tau_{\text{p}}^a$ (ns)<br>/ $\tau_{\text{d}}^a$ ( $\mu\text{s}$ ) | $k_{\text{r}}^b$<br>( $10^7 \text{ s}^{-1}$ ) | $k_{\text{ISC}}^c$<br>( $10^7 \text{ s}^{-1}$ ) | $k_{\text{RISC}}^d$<br>( $10^6 \text{ s}^{-1}$ ) | $\Phi_{\text{p}}^e / \Phi_{\text{d}}^e$<br>(%) | $\Phi_{\text{ISC}}^f$<br>(%) | $E_{\text{S}}^g$<br>(eV) | $E_{\text{T}}^g$<br>(eV) |
|-------------------|---------------------------------------|---------------------------|---|---|---|--|--|------------------------------|--------------------------|--------------------------|
| <b>BBCz-SB</b>    | In toluene<br>( $10^{-5} \text{ M}$ ) | 98                        | 5.6 / 42  | 10  | 7.5   | 0.041  | 57 / 41  | 42                           | 2.63                     | 2.49                     |
| <b>BBCz-SB-Br</b> | In toluene<br>( $10^{-5} \text{ M}$ ) | 89                        | 0.9 / 13  | 0.18  | 100   | 40   | 0.2 / 88                                       | $\approx 100$                | 2.70                     | 2.53                     |
| <b>BBCz-SB-Br</b> | In toluene<br>( $100 \mu\text{M}$ )   | 85                        | 1.0 / 19  | 0.46  | 90  | 9.0  | 0.5 / 85                                       | $\approx 100$                | 2.66                     | 2.53                     |

<sup>a</sup>Emission lifetimes for prompt fluorescence ( $\tau_{\text{p}}$ ) and delayed fluorescence ( $\tau_{\text{d}}$ ). <sup>b</sup>Rate constant of radiative decay ( $\text{S}_1 \rightarrow \text{S}_0$ ).<sup>[S6]</sup> <sup>c</sup>Rate constant of ISC ( $\text{S}_1 \rightarrow \text{T}_1$ ).<sup>[S6]</sup> <sup>d</sup>Rate constant of RISC ( $\text{T}_1 \rightarrow \text{S}_1$ ).<sup>[S6]</sup> <sup>e</sup>Fractional quantum yields for prompt fluorescence ( $\Phi_{\text{p}}$ ) and delayed fluorescence ( $\Phi_{\text{d}}$ );  $\Phi_{\text{p}} + \Phi_{\text{d}} = \Phi_{\text{PL}}$ . <sup>f</sup>Quantum yield of ISC;  $\Phi_{\text{ISC}} = 1 - \Phi_{\text{p}}$ . <sup>g</sup>Lowest excited singlet ( $E_{\text{S}}$ ) and triplet ( $E_{\text{T}}$ ) energies estimated from onset wavelengths of the fluorescence and phosphorescence spectra recorded at 300 and 77 K, respectively.

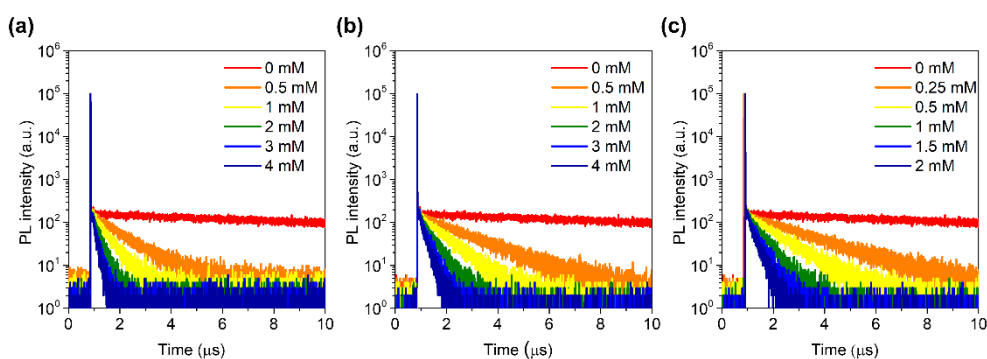
**Fig. S7** Transmission spectra of **SiDPN-1** and **SiDPN-2** in (a) neat films and (b) upconversion films including the **BBCz-SB-Br** sensitizer.**Fig. S8** UC emission decay curves of 1  $\mu\text{m}$ -thick (a) **DPN**, (b) **SiDPN-1**, and (c) **SiDPN-2** films containing **BBCz-SB-Br** sensitizer ( $[\text{BBCz-SB-Br}] = 0.1 \text{ mol}\%$  for **DPN** and **SiDPN-1**;  $0.2 \text{ mol}\%$  for **SiDPN-2**).

## 5. Stern-Volmer analysis

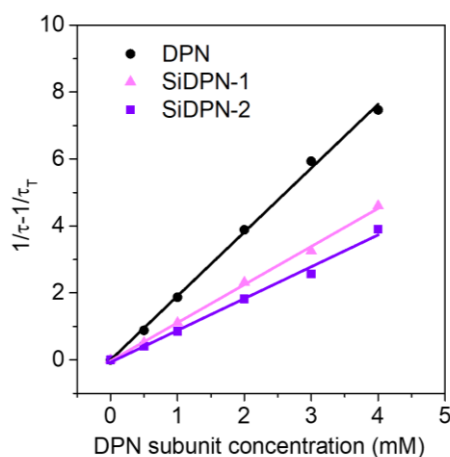
$\Phi_{\text{TET}}$  can be determined by the following equation:<sup>[S7][S8]</sup>

$$\Phi_{\text{TET}} = \frac{k_{\text{TET}} \cdot [\text{emitter}]}{k_{\text{TET}} \cdot [\text{emitter}] + k_r + k_{\text{nr}}} = \frac{1/\tau - 1/\tau_T}{1/\tau}$$

where  $k_r$  is the rate constant of the radiative process,  $k_{\text{nr}}$  is the rate constant of the non-radiative process, and  $k_{\text{TET}}$  is the rate constant of TET process. In fact, defining  $\tau_T$  and  $\tau$  as the delayed fluorescence lifetime of the triplet sensitizer in the absence and presence of acceptor, respectively,  $k_r + k_{\text{nr}} = 1/\tau_T$ , and  $k_{\text{TET}} \cdot [\text{acceptor}] = (1/\tau - 1/\tau_T)$ .



**Fig. S9** Variation of delayed fluorescence lifetime of **BBCz-SB-Br** with different concentrations of (a) **DPN**, (b) **SiDPN-1**, and (c) **SiDPN-2** in deoxygenated toluene solution.  $[\text{BBCz-SB-Br}] = 100 \mu\text{M}$ .



**Fig. S10** Stern–Volmer plots of **DPN**, **SiDPN-1**, and **SiDPN-2**.

**Table S2.** Delayed fluorescence lifetime and  $\Phi_{\text{TET}}$  of **BBCz-SB-Br** with different emitter concentrations

| DPN subunit concentration (mM) | DPN         |                     | SiDPN-1     |                     | SiDPN-2     |                     |
|--------------------------------|-------------|---------------------|-------------|---------------------|-------------|---------------------|
|                                | $\tau$ (ns) | $\Phi_{\text{TET}}$ | $\tau$ (ns) | $\Phi_{\text{TET}}$ | $\tau$ (ns) | $\Phi_{\text{TET}}$ |
| 0                              | 19457       | 0                   | 19457       | 0                   | 19457       | 0                   |
| 0.5                            | 1070        | 0.95                | 1761        | 0.91                | 2156        | 0.89                |
| 1                              | 520         | 0.97                | 863         | 0.96                | 1105        | 0.94                |
| 2                              | 255         | 0.99                | 422         | 0.98                | 535         | 0.97                |
| 3                              | 168         | 0.99                | 303         | 0.98                | 382         | 0.98                |
| 4                              | 134         | 0.99                | 211         | 0.99                | 253         | 0.99                |
| 10                             |             | $\approx 1$         |             | $\approx 1$         |             | 0.99                |
| 20                             |             | $\approx 1$         |             | $\approx 1$         |             | $\approx 1$         |

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