Electronic Supplementary Information

Near-Infrared Thermally Activated Delayed Fluorescence of D-π-A-π-D Difluoroboron Complex for Efficient Singlet Oxygen Generation in Aqueous Media

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A. Experimental Section

1. Materials and Characterization.

All manipulations were performed under an inert nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. Toluene was distilled under nitrogen from sodium- benzophenone. All other starting materials were obtained commercially as analytical-grade and used without further purification. 4-(9H-carbazol-9-yl)benzaldehyde (**1**)[1] and intermediate **2**[2] were synthesized according to the modified reported procedures.

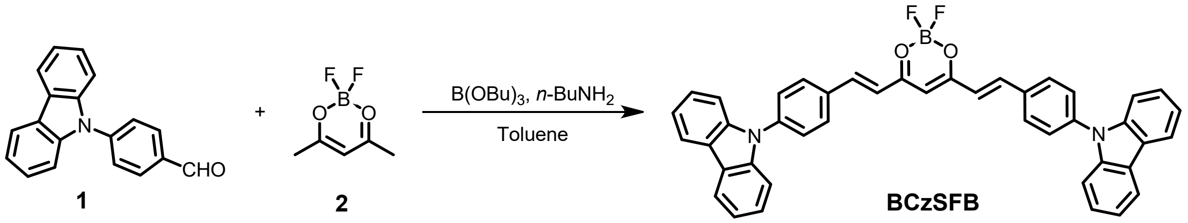
^{1}H and ^{13}C NMR spectra were collected on German BRUKER AVANCE III 400 MHz (all the chemical shifts are relative to TMS). High resolution mass spectrometry was obtained on SCIEX X-500R QTOF (ESI mode).

Single-crystal X-ray diffraction data were collected at room temperature (293 K) on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å). CrysAlisPro[3] was used for the data collection, data reduction and empirical absorption correction. The crystal structure was solved by direct methods, using SHELXS-2014 and least-squares refined with SHELXL-2014[4] using anisotropic thermal displacement parameters for all non-hydrogen atoms. CCDC No. 2108516 contains supplementary crystallographic data for **BCzSFB**. This material can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Powder X-ray diffraction analyses (PXRD) patterns were collected on a Rigaku Ultima-IV automated diffraction system with Cu Kα radiation (λ = 1.5406 Å). Measurements were made in a 2θ range of 5−50° at room temperature with a step of 0.02° (2θ) and a counting time of 0.2 s/ step. The operating power was 40 KV, 30 mA. UV-vis absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer at room temperature. Elemental analysis for C, H, N were carried out using a Perkin–Elmer

Elementarvario elemental analysis instrument. The IR spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet 6700 (Thermo) FT-IR spectrometer with KBr pellets. Thermo gravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. Room temperature time-resolved photoluminescence (PL) experiments were conducted on an Edinburgh FLS1000 fluorescence spectrometer equipped with a xenon arc lamp (Xe900) and a microsecond flash-lamp (uF900), respectively. Delayed PL spectra and time-resolved lifetime were measured by a microsecond flash lamp at frequency of 100 Hz. The PL lifetimes (τ) of solid state samples were obtained by fitting the decay curve with a multi-exponential decay function of $I(t) = A_1exp(-t/\tau_1) + A_2exp(-t/\tau_2) + \cdots + A_iexp(-t/\tau_i)$, where A_i and τ_i represent the amplitudes and lifetimes, respectively, of the individual components for multi-exponential decay profiles. The morphology of **BCzSFB** nanoparticles and bacteria were investigated by using a field emission scanning electron microscope (SEM Sigma 500).

2. Synthesis and characterization of BCzSFB.



Scheme S1. Synthetic route of difluoroboron *β*-diketonate modified by carbazole fragment (**BCzSFB**).

To a solution of pentane-2, 4-dione (100 mg, 1.0 mmol) in toluene (3 mL) was slowly added $BF_3 \cdot OEt_2$ (0.13 mL, 1.0 mmol, 47%) and stirred at 65 °C for 2 h. Then, the solution of 4-(9H-carbazol-9-yl)benzaldehyde **1** (271 mg, 2.0 mmol) in toluene (2 mL) was added into the above reaction mixture of **2**, followed by $B(OBu)_3$ (0.81 mL, 3.0 mmol). The resulting solution was stirred for 30 min and *n*-$BuNH_2$ (50 µL, 0.5 mmol) was added and stirred at 65 °C for 24 h. The reaction mixture was cooled and concentrated under reduced pressure and purified by column chromatography (silica gel: 200-300, PE : DCM = 2 : 1) to obtain BF_2-curcumin analogue **BCzSFB** as a red solid (Yield: 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 15.6 Hz, 2H), 8.16 (d, J = 7.6 Hz, 4H), 7.89 (d, J = 8.4 Hz, 4H), 7.72 (d, J =

8.4 Hz, 4H), 7.52 (d, *J* = 8.1 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 6.85 (d, *J* = 15.6 Hz, 2H), 6.21 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 180.19, 146.58, 141.33, 140.38, 132.75, 130.91, 129.43, 127.36, 126.43, 124.11, 121.09, 120.91, 120.70, 110.03. HRMS (ESI-TOF) m/z: [M]$^+$ Calcd for $C_{43}H_{29}BF_2N_2O_2$ 654.2290; Found 654.2304.

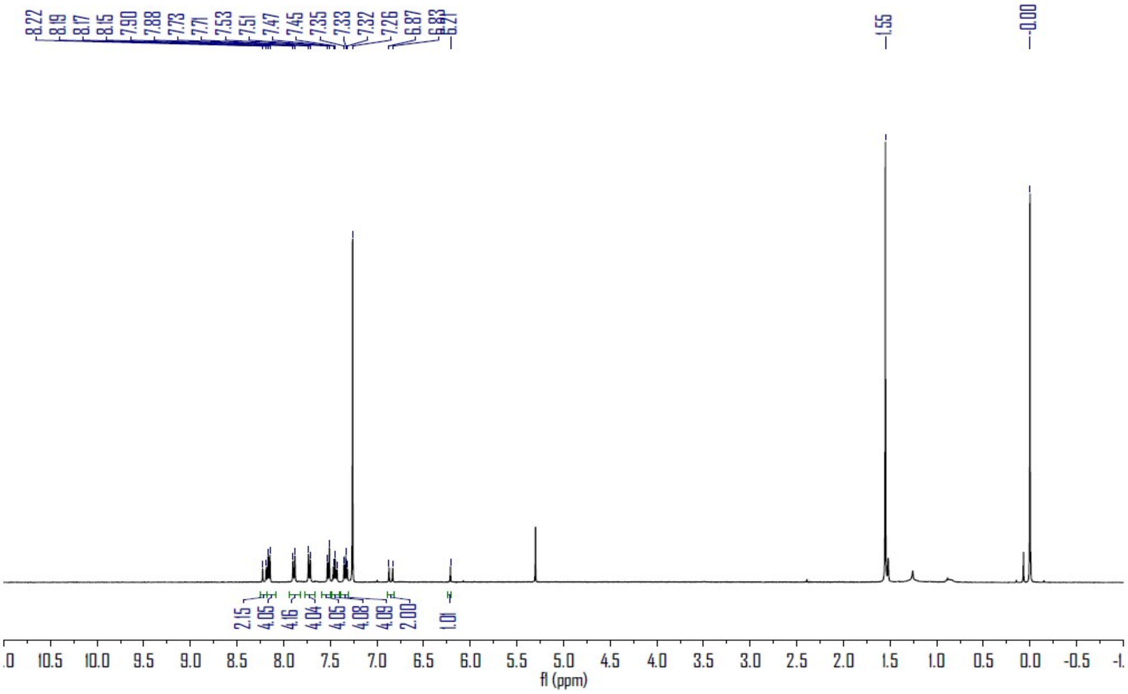


Figure S1. 400 MHz ^{1}H NMR spectrometry of **BCzSFB** in CDCl$_3$ at room temperature.

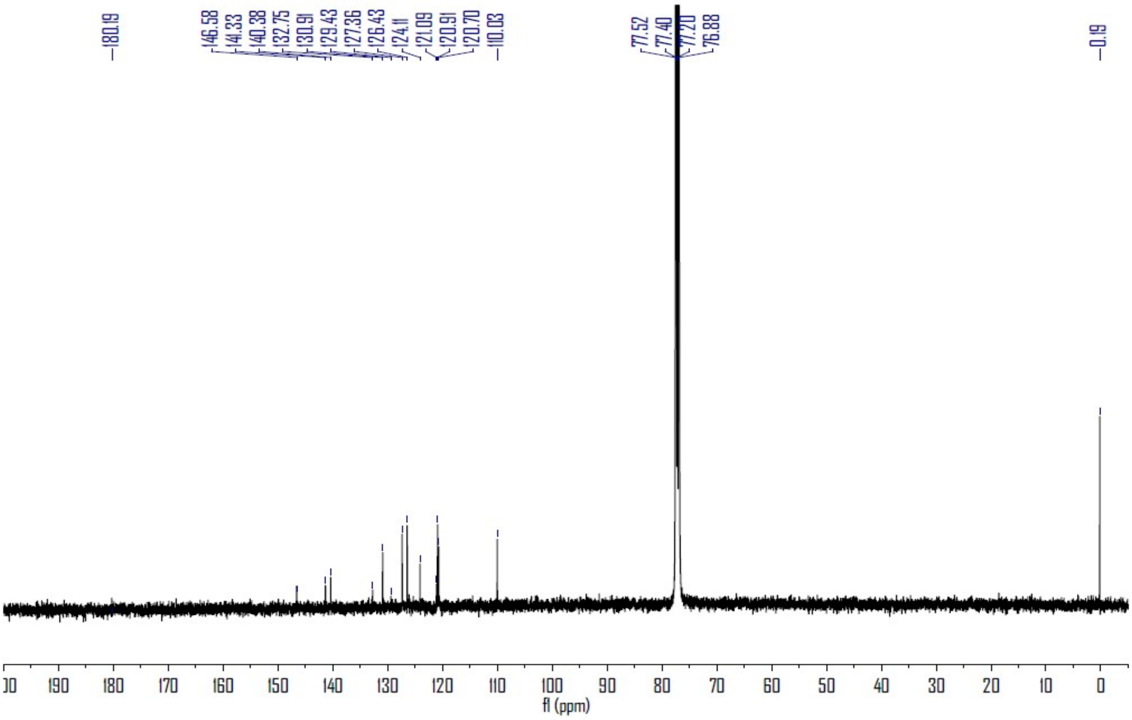


Figure S2. 100 MHz ^{13}C NMR spectrometry of **BCzSFB** in $CDCl_3$ at room temperature.

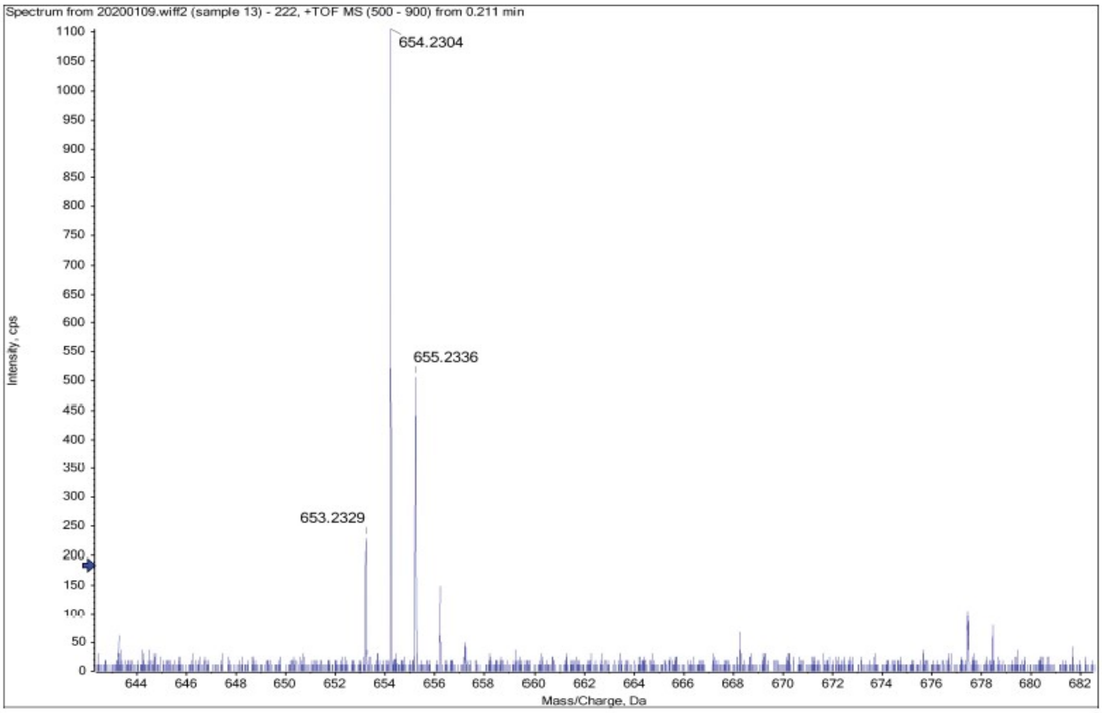


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Figure S3. High-resolution mass spectrometry of **BCzSFB** at room temperature.

3. Synthesis of BCzSFB single crystals.

Red rod-like crystals were obtained by the slow volatilization of **BCzSFB** chloroform solution in a teat tube for one week. Elemental analysis: Calc. (%) for $C_{45}H_{31}BCl_6F_2N_2O_2$ (**[BCzSFB]·2CHCl$_3$**): C, 60.51; H, 3.49; N, 3.13; found (%): C, 60.22; H, 3.15; N, 2.85. IR (KBr pellet, cm^{-1}): 3058(w), 1604(s), 1534(s), 1452(s), 1404(w), 1360(m), 1334(m), 1303(w), 1294(w), 1229(m), 1160(s), 1055(s), 998(s), 841(m), 755(s), 623(m), 580(w), 532(w). m.p.:323.6–324.5 ◦C.

4. Electronic structure calculations

The structure mode was directly used from the "cif" file of **BCzSFB** and calculated by density functional theory (DFT) method using Dmol^3 module in Material Studio software package.[5] The initial configuration was fully optimized by Perdew-Wang (PW91) generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP).

5. Nanoparticle preparation

BCzSFB-loaded nanoparticles (**BCzSFB NPs**) were facilely prepared according to a modified literature method.[6] A mixture of **BCzSFB** photosensitizer (1.0 mg), Pluronic F127 (10.0 mg) and THF (1.0 mL) was added dropwise to distilled-deionized water (10.0 mL) under continuous sonication with a microtip-equipped probe sonicator for 3 min. After sonication, the mixture solution was stirred overnight at room temperature to ensure evaporation of the THF. The final **BCzSFB** NPs were obtained by filtration through a 0.22 μm syringe filter for further use.

6. Singlet oxygen ($^1O_2$) detection in solution

A commonly used $^1O_2$ indicator 9,10-Anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used to evaluate the singlet oxygen generation ability of **BCzSFB** NPs aqueous suspension under white light irradiation (60 mW cm^{-2}), in which the absorbance of ABDA decreases upon reaction with the increasing singlet oxygen. Briefly, the solution of ABDA (50 μM) in DMSO was mixed with TBD-anchor (5 μM) or Rhodamine B (RhB) (5 μM) in phosphate buffered saline (PBS) solution and exposed to white light irradiation (60 mW cm^{-2}). The absorbance decrease of ABDA at 378 nm was recorded at various irradiation time.

7. Bacteri culture and preparation of bacteria solution for staining

Staphylococcus aureus (*S. aureus*, ATCC6538) and Escherichia coli (*E.coli*, ATCC 25922) were purchased from China Center of Industrial Culture Collection. A single colony of bacteria on solid culture medium [Nutrient agar medium (NA) for *S. aureus and E. coli*] was transferred to 50 mL corresponding liquid culture medium and grown at 37 ℃ for 12-14 h. The concentrations of bacteria were determined by measuring the optical density at 600 nm and then 10^{8} colony forming unit (CFU) of bacteria was transferred to a 1.5 mL EP tube. Bacteria were harvested by centrifuging at 7000 rpm for 2 min, after removal of the supernatant, the residues washed by sterile PBS two times, and then the bacteria were resuspended and diluted with PBS to an optical density of 1.0 at 600 nm (OD_{600}=1.0 with about 10^{8} CFU mL^{-1}).

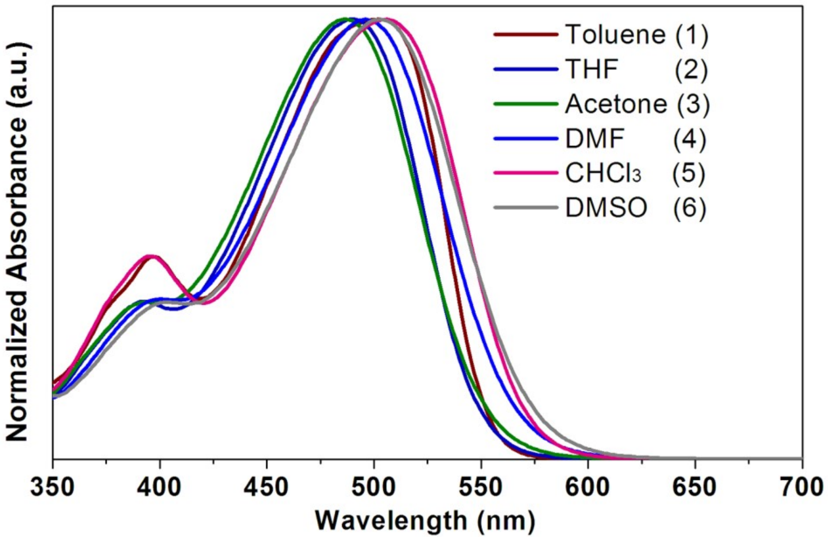
8. Assessment of antibacterial activity

The antibacterial activity of **BCzSFB** was evaluated by traditional surface plating method.

The antibacterial activity of **BCzSFB** in dark was conducted as follows: *S. aureus* (ATCC6538) and *E. coli* (ATCC 25922) suspensions were serially diluted by 10^{4} fold with PBS respectively. 200 μL bacteria suspension was mixed completely with 200 μL **BCzSFB** (2×10^{-6} M), after keep warm at 37 ℃ for 20 min in dark. 100 μL mixture was spread on the Nutrient agar plate, and then incubation at 37 ℃ for 12-14 h.

The antibacterial activity of **BCzSFB** under white light was conducted as follows: the bacteria were treated under the same conditions as the experiment in the dark except for that the samples were incubated for 5 min in the dark and then irradiated under white light (60 mW cm^{-2}) for 15 min.

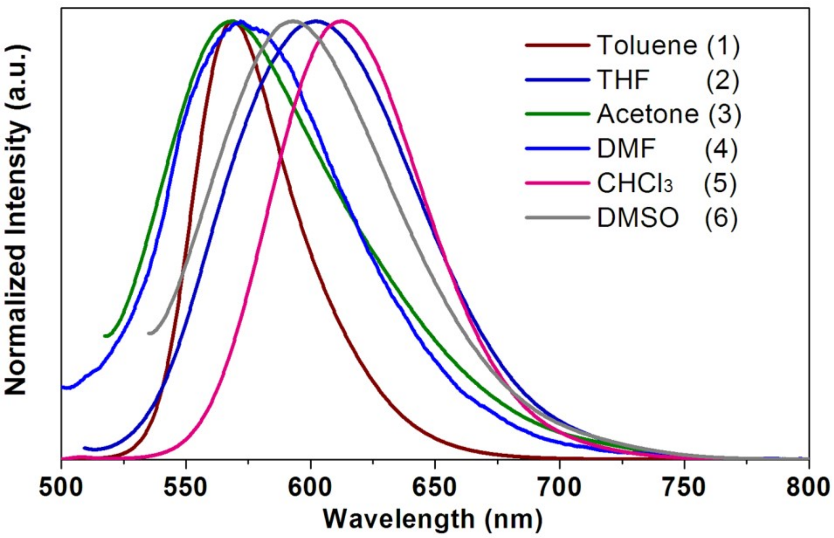
B. Supporting Figures and Tables



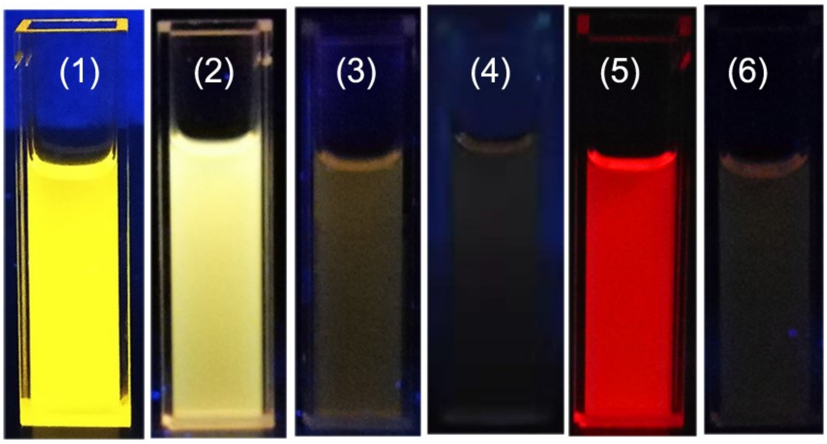
(a)

(b)

Figure S4. (a) Normalized UV-Vis absorption spectra of 2.0×10^{-5} M **BCzSFB** in different solvents. (b) The corresponding solution under daylight.

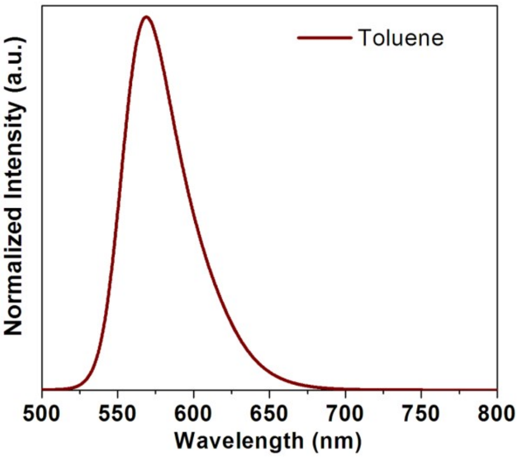


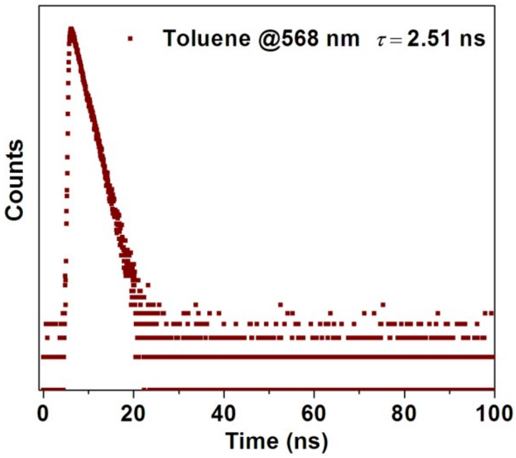
(a)

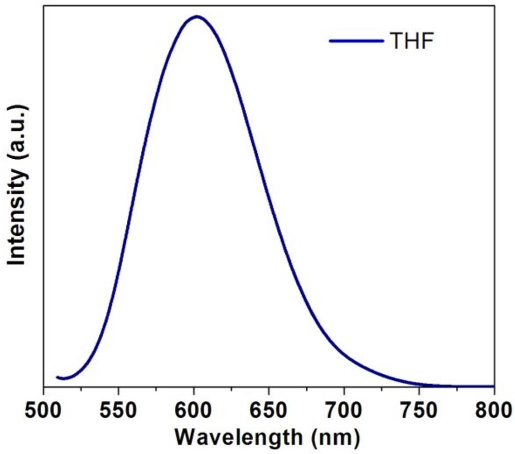


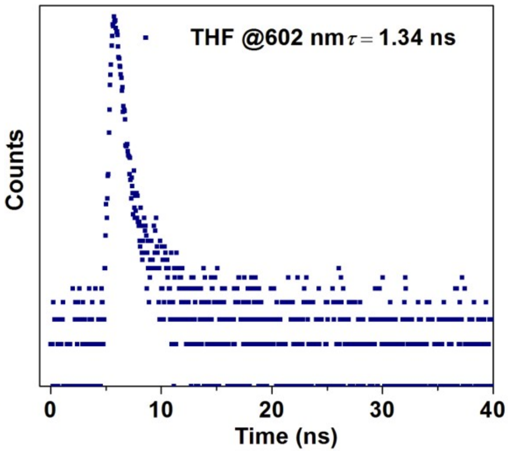
(b)

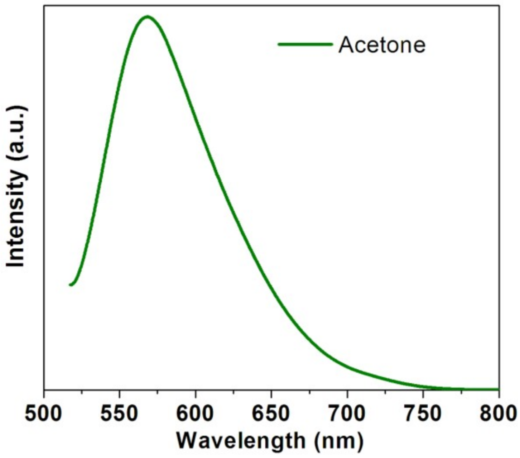
Figure S5. (a) Normalized steady state photoluminescence spectra of 2.0×10^{-5} M **BCzSFB** in different solvents. (b) The corresponding solution under UV (365nm).

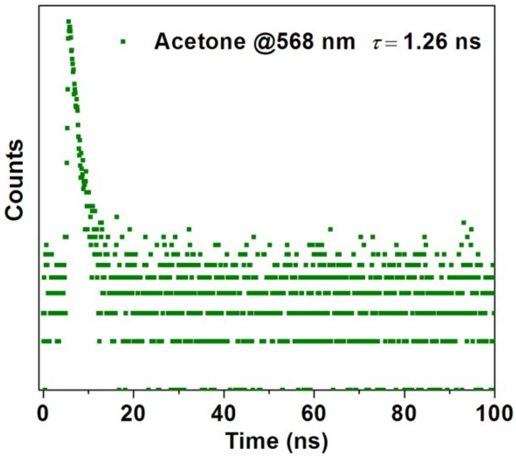

Toluene
Normalized Intensity (a.u.)
500
550
600
650
700
750
800
Wavelength (nm)


Toluene @568 nm $\tau = 2.51$ ns
Counts
0
20
40
60
80
100
Time (ns)


THF
Intensity (a.u.)
500
550
600
650
700
750
800
Wavelength (nm)


THF @602 nm $\tau = 1.34$ ns
Counts
0
10
20
30
40
Time (ns)


Acetone
Intensity (a.u.)
500
550
600
650
700
750
800
Wavelength (nm)


Acetone @568 nm $\tau = 1.26$ ns
Counts
0
20
40
60
80
100
Time (ns)

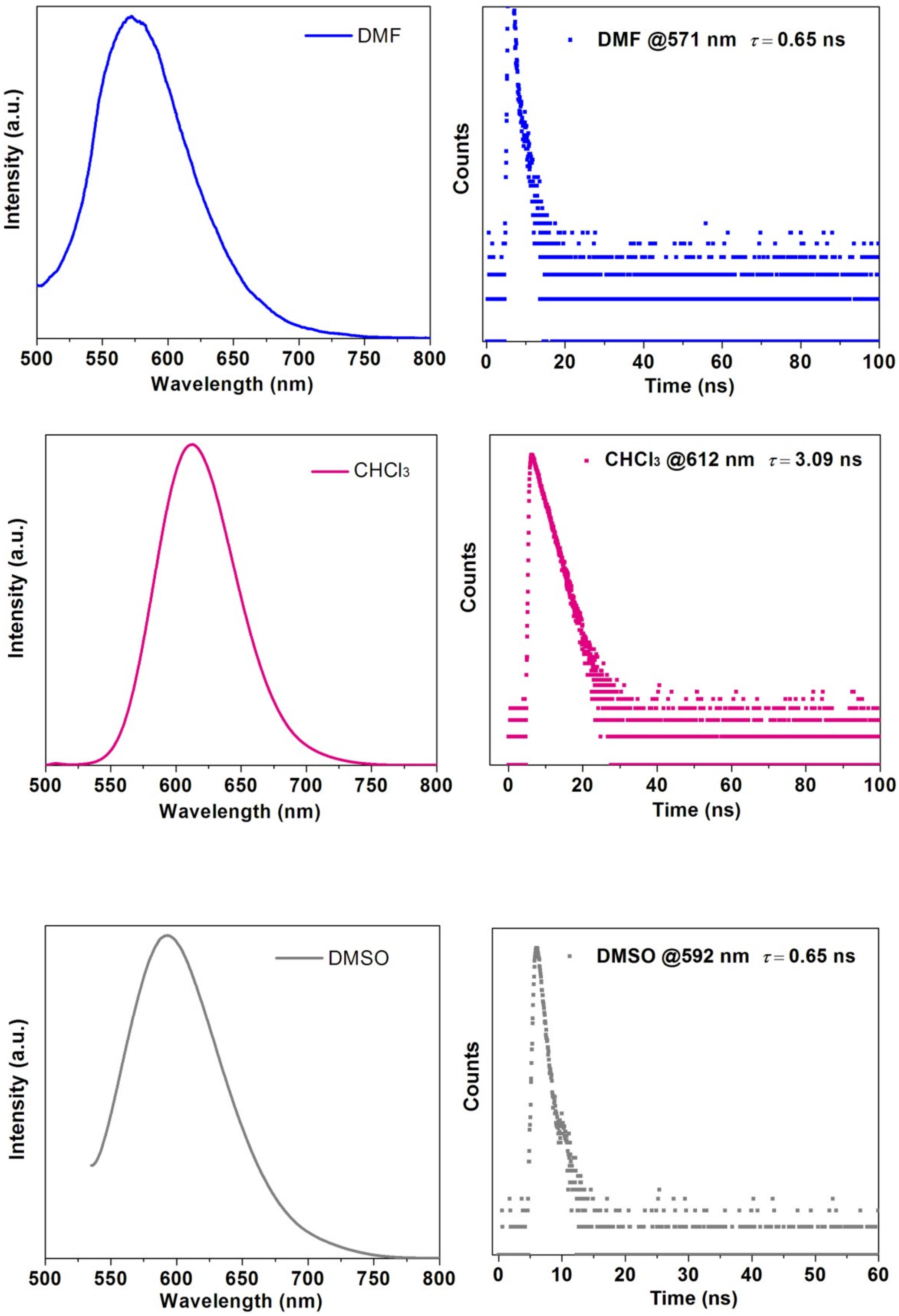


Figure S6. Steady state photoluminescence spectra (left) and decay curve (right) of 2.0×10^{-5} M **BCzSFB** in different solvents.

Dilute sample solutions (typically 2.0 × 10^{-5} M) were prepared from stock solutions (0.2 mM) at ambient conditions. The absorption and fluorescence spectra were obtained from organic solutions (2.0 × 10^{-5} M) using a 1 cm quartz cuvette. The fluorescence quantum yields (Φ_f) of **BCzSFB** in various solvents were determined according to the following equation:

$$\emptyset_s = \emptyset_{ref} \times \frac{F_s}{F_{ref}} \times \frac{A_{ref}}{A_s} \times \frac{n_s^2}{n_{ref}^2}$$

in which Φ_{ref} is the fluorescence quantum yield of reference, F is the area under the emission spectra, A is the absorbance at the excitation wavelength, and n is the refractive index of the used solvent. s and ref stand for sample (**BCzSFB**) and reference, respectively. We chose rhodamine 6G in water (Φ_{ref} = 0.75, λ_{ex} = 488 nm) as the reference.[7]

Table S1. The photophysical data of **BCzSFB** in different solvents at 298 K (2.0 × 10^{-5} mol/L).

Compound	Solvents	$\lambda_{abs}{}^a$ (nm)	ε × $10^{4\,b}$ (cm^{-1} M^{-1})	$\lambda_{em}{}^c$ (nm)	τ^d (ns)	$\Phi_f{}^e$
BCzSFB	Toluene	500	5.25	568	2.51	0.57
	THF	492	7.45	602	1.34	0.43
	Acetone	487	7.85	568	1.26	0.09
	DMF	497	7.30	574	0.65	0.03
	$CHCl_3$	508	6.25	612	3.09	0.59
	DMSO	503	6.45	592	0.65	0.07

[a] Absorption maximum; [b] Extinction coefficients calculated at the absorption maxima; [c] Fluorescence emission maxima; [d] Fluorescence lifetime; [e] Fluorescence quantum yield determined by a standard method with rhodamine 6G in water (Φ_f = 0.75, λ_{ex} = 488 nm) as reference.

Figure S7. Digital photograph of **BCzSFB** crystal under daylight.

Table S2. Crystallographic data for **BCzSFB**.

Sample	**BCzSFB**
Chemical formula	$C_{45}H_{31}BCl_6F_2N_2O_2$
Formula weight	893.3
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	12.8298(15)
b (Å)	9.8983(11)
c (Å)	16.8160(16)
β (°)	90.790(9)
V (Å^3)	2135.3(4)
Z	2
D (g cm^{-3})	1.3892
μ (mm^{-1})	0.451
T (K)	293(2)
R_{int}	0.1347
Goof	1.059
R_1 ($I>2\sigma(I)$)	0.0990
wR_2 ($I>2\sigma(I)$)	0.2328

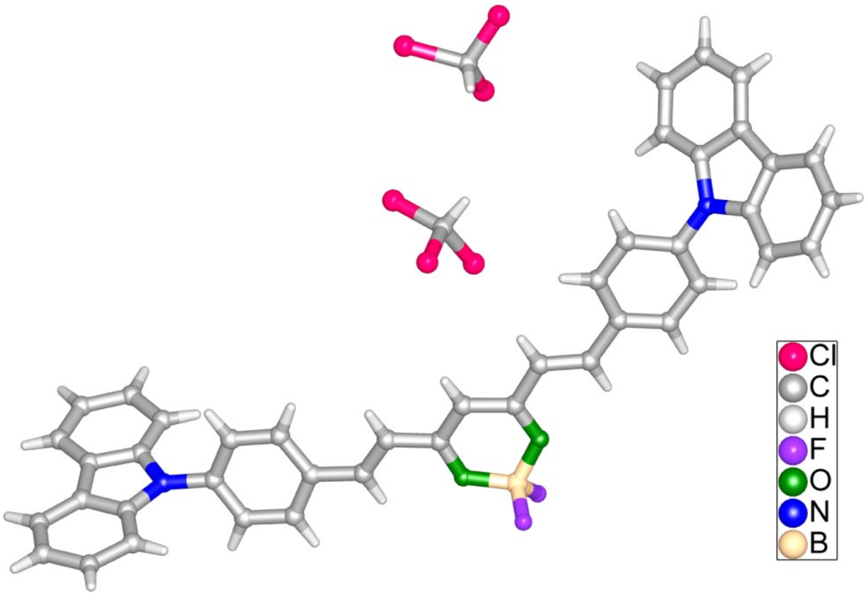


Figure S8. View of the asymmetry unit of **BCzSFB** crystal structure.

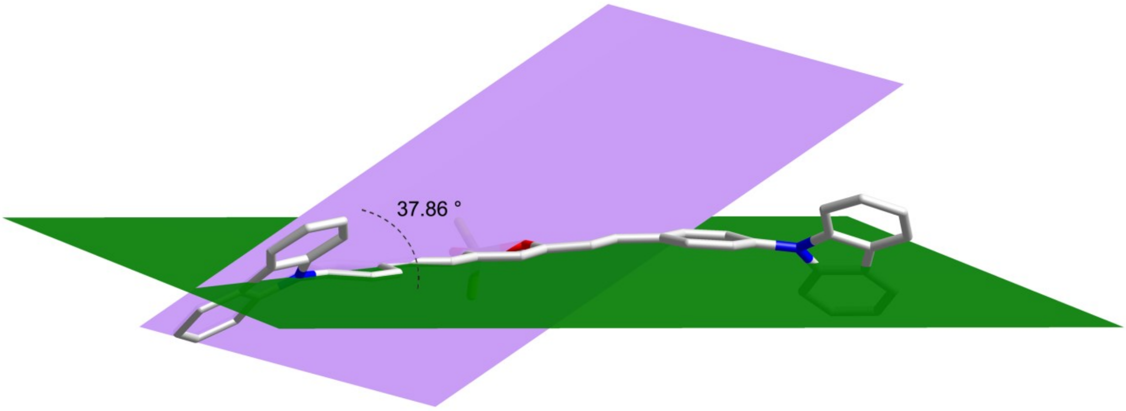
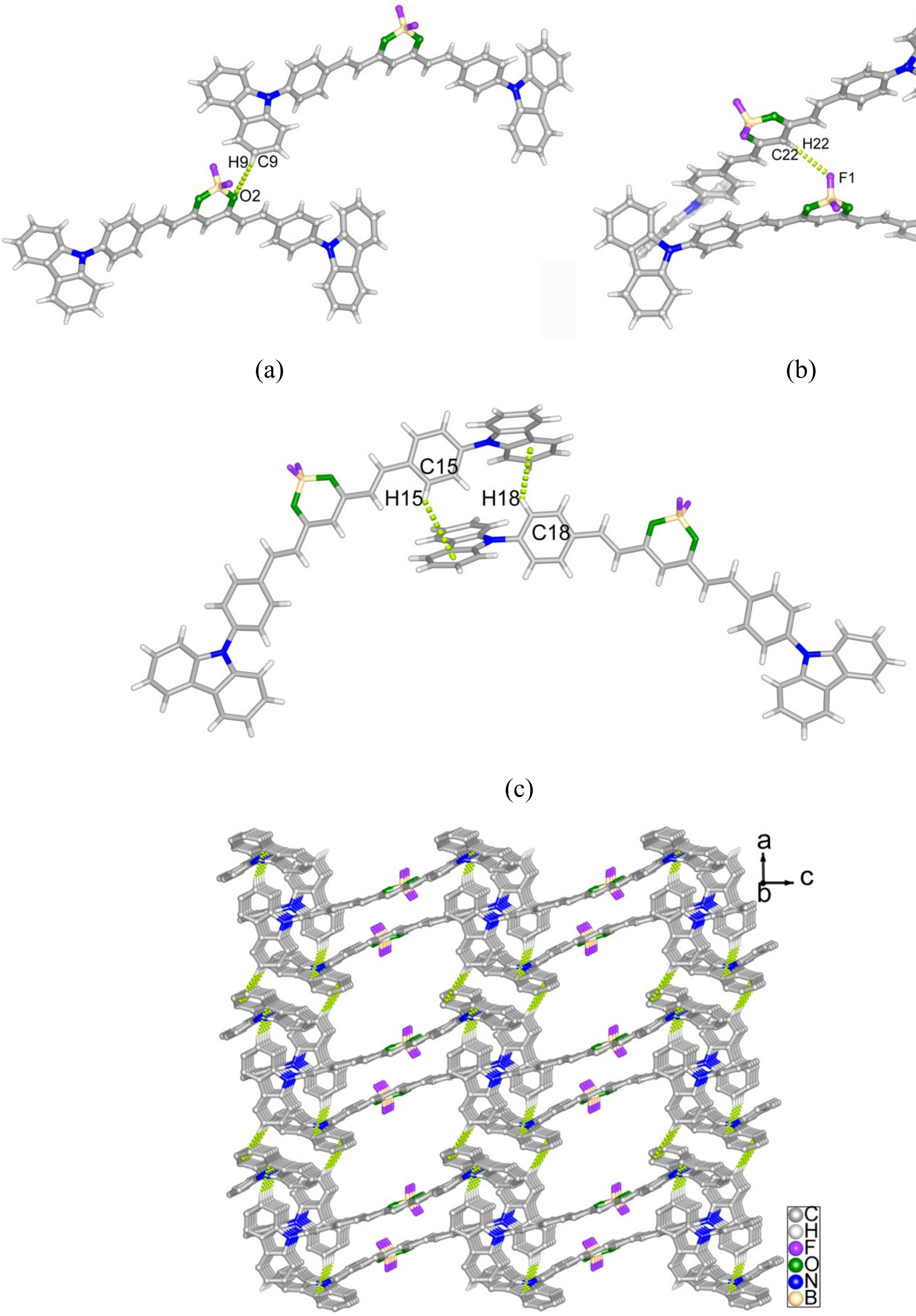
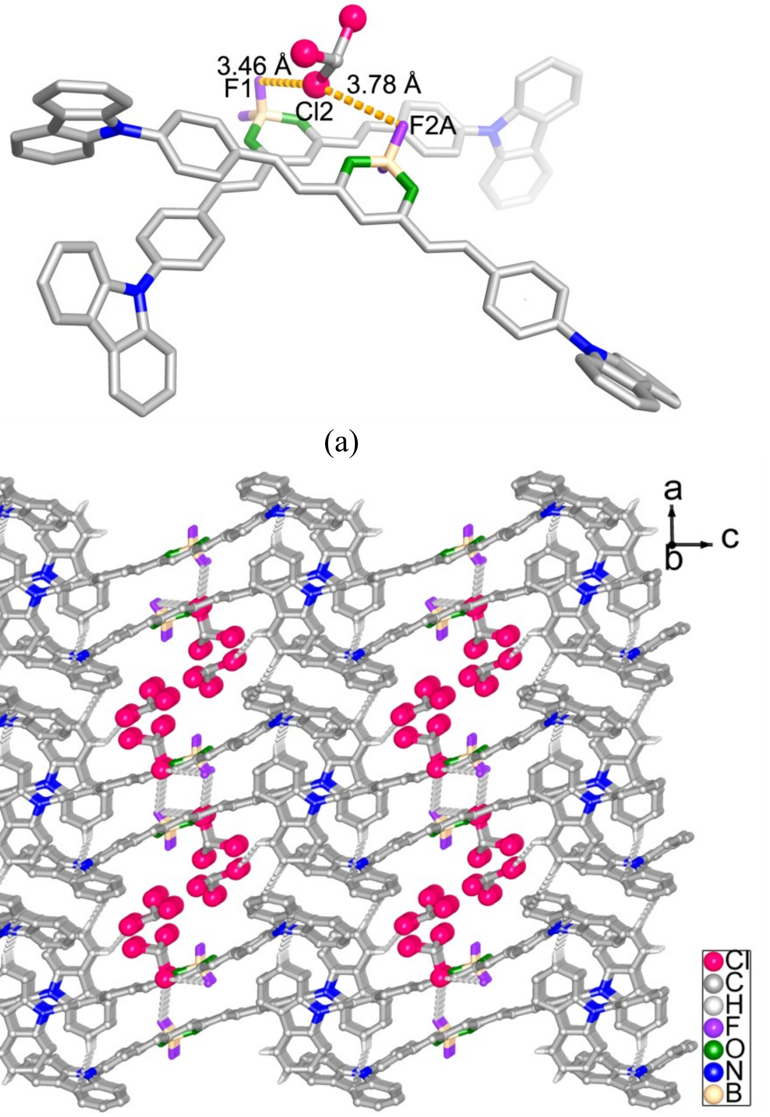


Figure S9. View of the torsion angle between carbazole unit and styrene group of the isolated single **BCzSFB** molecule from theory calculations.



(a) (b) (c) (d)

Figure S10. View of C−H···O (a), C−H···π (b), and C−H···π (c) interactions between the **BCzSFB** molecules. (d) View of the 3D hydrogen-bonded organic framework (HOF) with 1D channels running along b direction.



(a)

(b)

Figure S11. (a) View of the B−F···Cl halogen bonds interactions between $CHCl_3$ and **BCzSFB** molecules. (b) View of the 3D HOF structure with the encapsulation of $CHCl_3$ guests in the 1D channels.

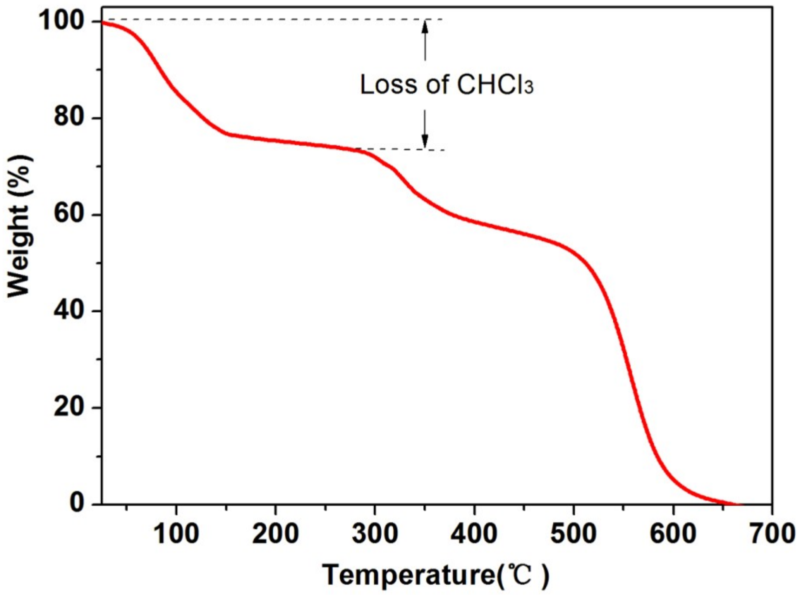


Figure S12. Thermo gravimetric curve of **BCzSFB** crystalline sample. The first weight loss up to 280 °C can be assigned to the complete loss of $CHCl_3$ molecules (calculated: 26.7 %).

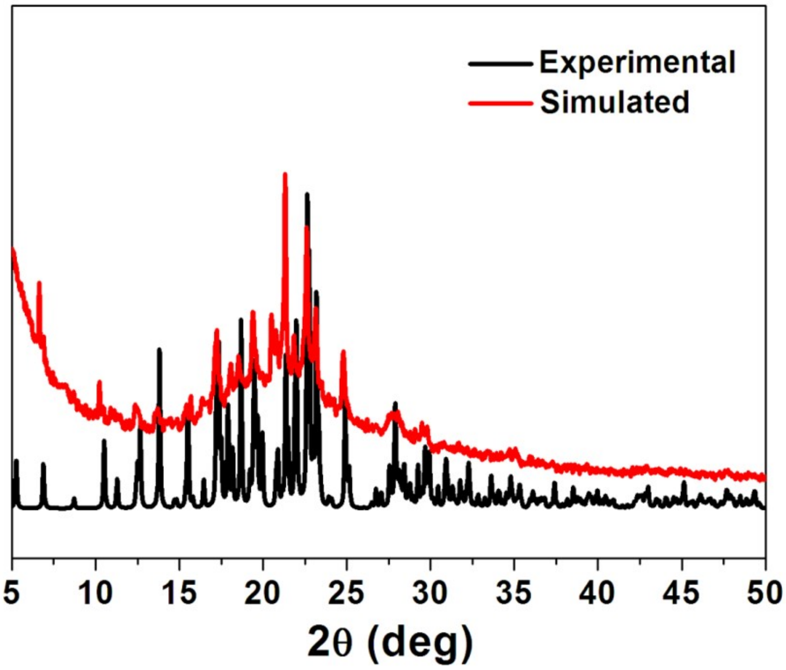


Figure S13. PXRD patterns of simulated (black) and as synthesized **BCzSFB** crystalline sample (red).

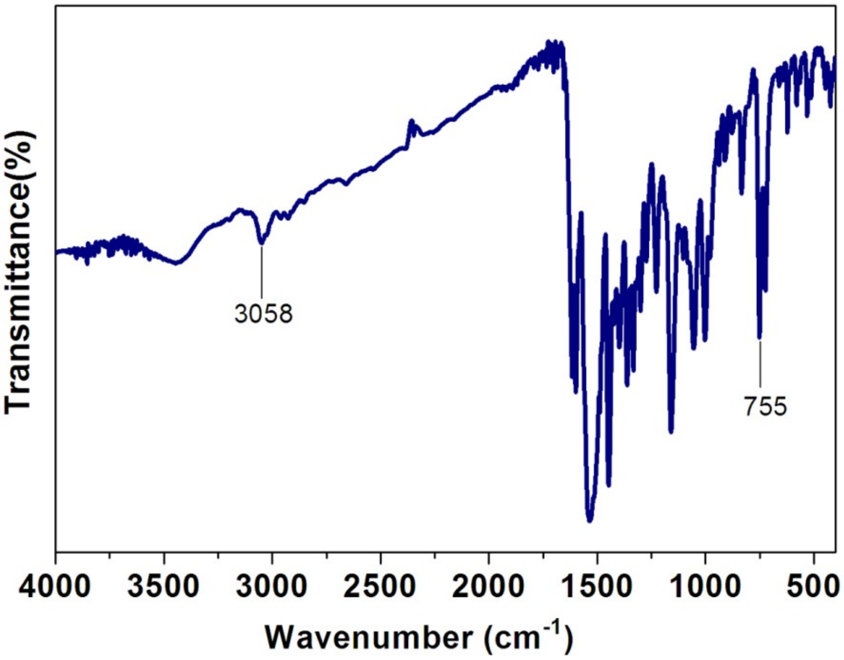
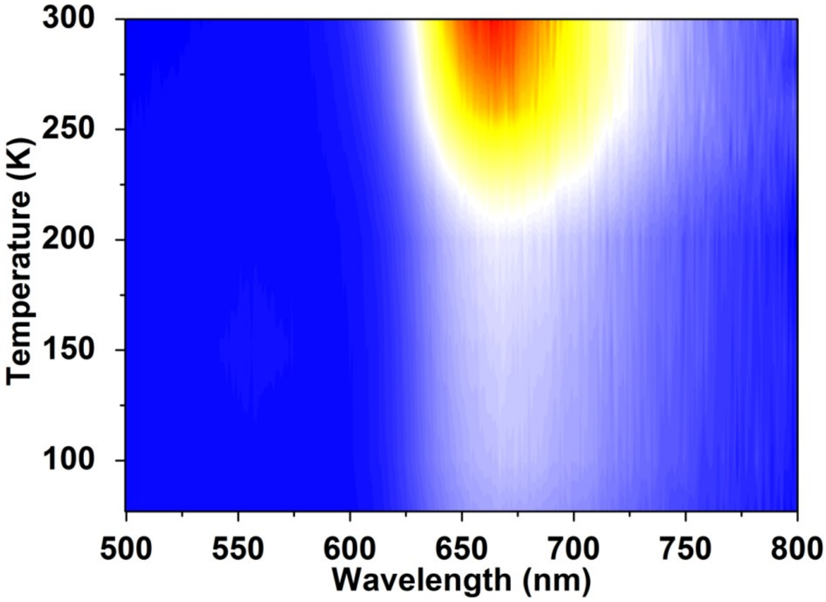
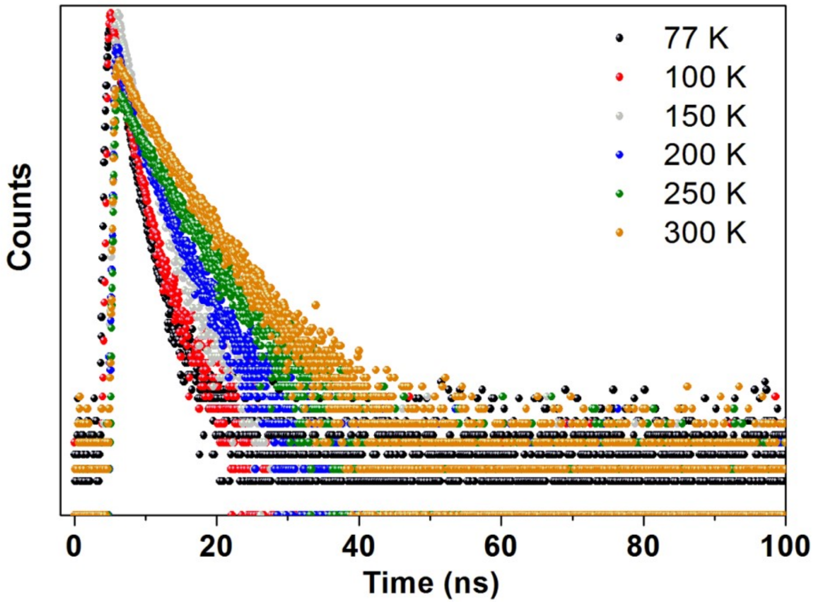


Figure S14. FT-IR spectra of **BCzSFB** crystalline sample.



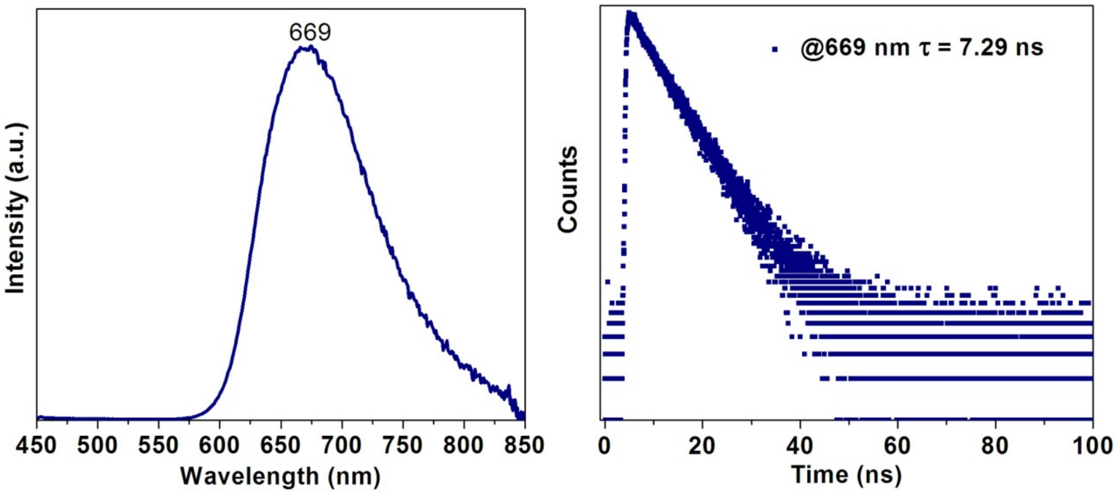
(a)



(b)

Figure S15. (a) Two dimensional plot show the prompt photoluminescence (PL) spectrums of **BCzSB** measured in the range of 77 and 300 K. (b) Temperature-dependent prompt photoluminescence decay curves of **BCzSB**.

Figure S16. Photograph of the Tyndall effect on **BCzSB** NPs aqueous suspension.



(a) (b)

Figure S17. Prompt PL spectrum (a) and time-resolved PL decay curve (b) of **BCzSB** NPs dispersion in water measured at room temperature.

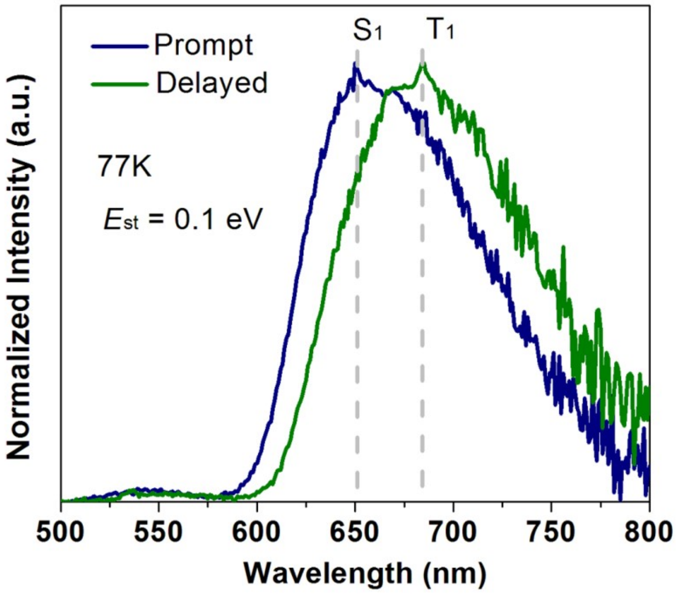


Figure S18. The prompt and delayed PL spectra of **BCzSB** NPs measured at 77 K. The energy gap (ΔE_{ST}) between the S_1 (650 mn, 1.91 eV) and T_1 (684 mn, 1.81 eV) excited state levels was calculated from the emission peaks of prompt and delayed spectra measured at 77 K. It gives a small ΔE_{ST} value of 0.1 eV.

Singlet oxygen quantum yield measurements

According to the reported method,[8] the $^1O_2$ quantum yield of **BCzSFB** NPs in water was determined by using water-soluble disodium 9,10-anthracendipropionic acid (Na_2-ADPA) as the trapping agent and a conventional photosensitizer Rose Bengal (RB) as the standard reference ($^1O_2$ quantum yield Φ_{RB} = 75% in water). In brief, a solution of Na_2-ADPA (100 μL) in milli-Q water (1 mg/mL) was added to 4 mL of **BCzSFB** NPs dispersions, and the sample was irradiated with white light with a power density of 60 mW cm^{-2}. The absorption of Na_2-ADPA at 378 nm was recorded at various irradiation times to obtain the decay rate of the photosensitizing process in a UV-Vis spectrophotometer.

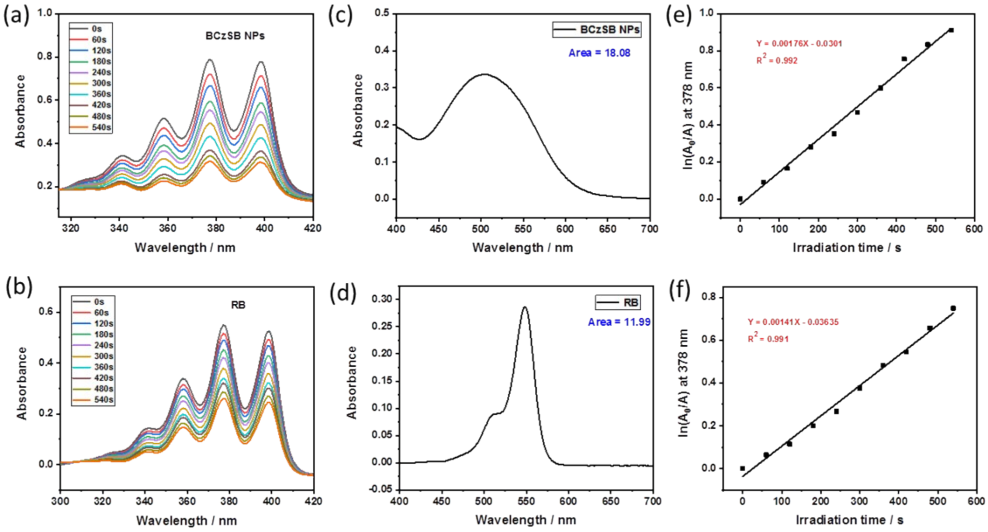
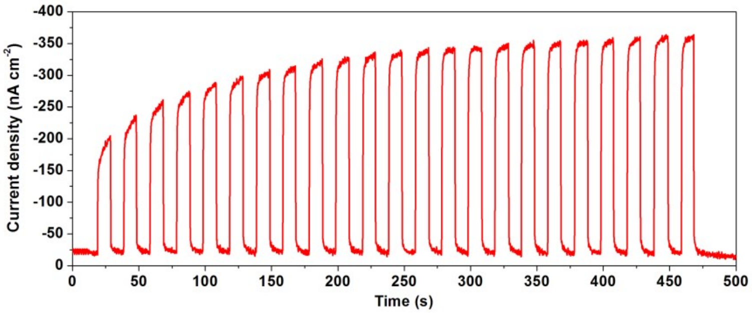


Figure S19. Chemical trapping measurements of the $^1O_2$ quantum yield. Photodegradation of Na_2-ADPA with **BCzSFB** NPs (a) and RB (b). The absorption peak area of **BCzSFB** NPs (c) and RB (d). The decomposition rate constants of Na_2-ADPA by **BCzSFB** NPs (e) and RB (f).

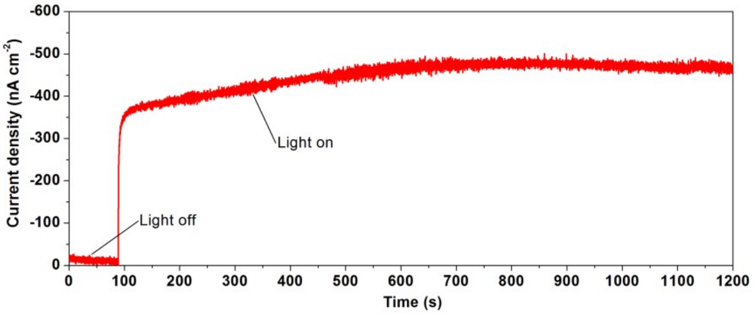
The $^1O_2$ quantum yield of **BCzSFB** NPs in water (Φ_{BCzSFB}) was calculated using the following formula:

$$\varnothing_{BCzSFB} = \varnothing_{RB} \times \frac{K_{BCzSFB}}{K_{RB}} \times \frac{A_{RB}}{A_{BCzSFB}}$$

Where K_{BCzSFB} and K_{RB} are the decomposition rate constants of Na_2-ADPA by **BCzSFB** NPs and **RB**, respectively. A_{BCzSFB} and A_{RB} represent the light absorbed by the **BCzSFB** NPs and **RB**, respectively, which are determined by integration of the optical absorption bands in the wavelength range 400-700 nm. Φ_{RB} is the $^1O_2$ quantum yield of **RB** (Φ_{RB} = 75% in water).



(a)



(b)

Figure S20. (a) Transient current density-time curve of **BCzSB** modified indium tin oxide (ITO) electrode recorded at a bias potential of 0 V vs Ag/AgCl by periodic on-off cycles of 300 W Xe lamp irradiation. (b) Photocurrent measurement of **BCzSB** under long-term light irradiation.

Photoelectron response performance was recorded by a CHI 660E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) in a standard three-electrode system. **BCzSB** NPs modified ITO as the working electrode, Ag/AgCl as a reference electrode, a platinum wire electrode as a counter electrode, and 0.5 M sodium sulfate aqueous solution as electrolyte. The system was irradiated by a 300 W Xe lamp.

C. Supporting References

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