Supporting Information For

Synthesis of aza-BODIPYs with barrier-free rotor of the –*t*Bu group at 3-site and enhancement of photothermal therapy by triggering cancer cells apoptosis

Junzhu Zhao,[a†] Huan Wang,[b†] Dongxiang Zhang,[a†] Yue Shen,[a] Shan Zhang,[b] Junyi Ren,[b] Zhan Wang,[b] Ya-nan Sun,[a] Jianjun Du,*[c] Xin-Dong Jiang,*[a] and Guiling Wang*[b]

a. Liaoning & Shenyang Key Laboratory of Functional Dye and Pigment, Shenyang University of Chemical Technology, Shenyang, China. E-mail: xdjiang@syuct.edu.cn
b. Department of Cell Biology, China Medical University, Shenyang, 110122, China. E-mail: glingwang@cmu.edu.cn
c. State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China. E-mail: dujj@dlut.edu.cn

1. Experimental section

1.1 General

All solvents and chemical reagents were analytical grade in this article, purchased from Energy Chemical & Technology (Shanghai) Co. Ltd and used without further purification unless specifically stated. ^{1}H NMR spectra were measured on a VARIAN Mercury 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a VARIAN Mercury 125 MHz spectrometer. $CDCl_3$ was used as a solvent. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual $CDCl_3$ (δ = 7.26 ppm). For ^{13}C NMR chemical shifts (δ), all signals are reported with the internal chloroform signal at (δ= 77.0 ppm) as standard in ppm. UV/Vis spectra were recorded on a UV-2550 spectrophotometer at room temperature. Fluorescence spectra were recorded on F-98 spectrophotometer. A 690 nm laser were applied as the light source for light irradiation, controlling by a fiber coupled laser system for the laser output power and purchased from Changchun New Industries Optoelectronics Technology. Optical power density was measured by a CEL-NP 2000 power meter, purchased from Beijing Zhong Jiao Jin Yuan Technology Co., Ltd. Laser particle size analyzer purchased from Malvern. Confocal laser fluorescence microscope FV1200 (Olympus, Japan) was applied to estimate fluorescence imaging.

1.2 Synthesis of azaBDP 1

Under air, sodium nitrite (6.9 mg, 0.1 mmol) was added to 2-(*tert*-butyl)-4-phenyl-1*H*-pyrrole[1] (19.9 mg, 0.1 mmol) in acetic acid (0.5 mL) at 0 ℃, stirring vigorously for 10 min. Then, 7-methoxy-3-phenyl-4,5-dihydro-*1H*-benzo[*g*]indole[2] (27.5 mg, 0.1 mmol) was added, followed by acetic anhydride (0.2 mL). After stirring for 15 min at room temperature, the mixture was allowed to be heated to 80 ℃ for 2 h. Crushed ice was added to the mixture, and the organic dye was washed with brine for 3 times. The organic dye was dissolved in CH_2Cl_2, filtered through a pad of alumina (activity III). Using a rotary evaporator to remove the organic solvent, this residue was dissolved into dry 1,2-dichloroethane. Then, triethylamine (0.3 mL) was added, followed by $BF_3{\cdot}Et_2O$ (0.5 mL) with stirring for 0.5 h at room temperature, then heated to 80 ℃

with stirring for 4 h. The reaction was quenched with crushed ice, extracted with CH_2Cl_2 (3 × 80 mL) and dried over anhydrous Na_2SO_4. After solvent removal by evaporation, the resulting crude product was purified by column chromatography (CH_2Cl_2/*n*-hexane = 1:1) to afford dye **1** as green solids (22.4 mg, 0.042 mmol, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.72 (d, ^3J = 8.8 Hz, 1H), 8.01 (d, ^3J = 8.0 Hz, 2H), 7.71 (d, ^3J = 8.0 Hz, 2H), 7.48 (t, ^3J = 8.0 Hz, 2H), 7.42 (t, ^3J = 8.0 Hz, 1H), 7.36 (t, ^3J = 8.0 Hz, 2H), 7.33 (t, ^3J = 8.0 Hz, 1H), 7.02 (dd, ^3J = 8.8 Hz, ^4J = 2.8 Hz, 1H), 6.85 (d, ^4J = 2.8 Hz, 1H), 6.74 (s, 1H), 3.91 (s, 3H), 2.95 (s, 4H), 1.57(s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 168.0, 162.9, 155.7, 146.3, 145.2, 144.1, 140.4, 138.5, 133.3, 132.7, 132.3, 131.9, 130.5, 129.1, 128.7, 128.5, 128.4, 128.3, 119.9, 114.9, 114.6, 113.3. HRMS-MALDI (m/z): $[M+Na]^+$ calcd for $C_{33}H_{30}BF_2N_3ONa^+$: 556.23422, found 556.23401.

1.3 Synthesis of azaBDP 2

2-(*Tert*-butyl)-4-phenyl-*1H*-pyrrole (19.9 mg, 0.1 mmol) was employed as the first pyrrole moiety, and 2-(4-methoxyphenyl)-4-phenyl-*1H*-pyrrole[2] as the second pyrrole moiety (24.9 mg, 0.1 mmol) was used. Dye **2** as blue solids was obtained (21.8 mg, 0.043 mmol, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, ^3J = 8.8 Hz, 2H), 8.04 (d, ^3J = 7.2 Hz, 2H), 7.99 (d, ^3J = 7.2 Hz, 2H), 7.38-7.46 (m, 6H), 7.04 (d, ^3J = 8.8 Hz, 2H), 7.03 (s, 1H), 6.80 (s, 1H), 3.91 (s, 3H), 1.54(s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 162.2, 147.2, 143.8, 132.9, 132.4, 131.9, 131.8, 129.6, 129.5, 129.4, 129.2, 128.7, 128.6, 124.6, 124.5, 124.1, 119.3, 119.1, 116.6, 114.3, 55.6, 35.4, 30.3. HRMS (ESI) m/z calcd for $C_{31}H_{28}BF_2N_3ONa^+$ $(M+Na)^+$ 530.21857,found 530.21783.

1.4 Absorption and fluorescence spectra

After accurately weighing a certain mass of dyes, the stock solutions of **azaBDP**s **1-3** were dissolved in DMSO for concentrations of 10 mM and reserved in are frigerator for use. The testing concentrations were 10 μM in dichloromethane solution at room temperature. Absorption and fluorescence spectra were recorded in a

3 mL cuvette. Absorbance and fluorescence data were normalized. Three excitation wavelengths were maxima absorbance of **azaBDP**s **1-3**, respectively (slit: 5 nm/5 nm).

1.5 Evaluation of singlet oxygen generation capacity

1,3-diphenylisobenzofuran (DPBF) was employed as an indicator of singlet oxygen production. These mixed solutions were excited at the maximum absorption wavelength of the dyes, and the excitation intensity was regulated to 0.5 $mW \cdot cm^{-2}$ controlled by the optical power densitometer. Absorption spectra were investigated within 0-12 min at intervals of 2 min. The linear slope of the absorbance of log value of DPBF in 416 nm with light radiation time can be applied to evaluate the singlet oxygen production effect. Afterwards, with the reference of 2,6-diiodobodipy ($^1O_2$ production efficiency is 85% in toluene solution), the $^1O_2$ production efficiency can be calculated by the reported formula.[3-5]

$$\Phi_{sam} = \Phi_{std}\left(\frac{m_{sam}}{m_{std}}\right)\left(\frac{F_{std}}{F_{sam}}\right)$$

Where "*sam*" represents the unknown dye molecule and "*std*" represents the reference 2,6-diiodobodipy. "*m*" is the slope of DPBF absorption peak decline, "*F*" is the absorption correction factor, $F = 1\text{-}10^{-O.D.}$. O.D. represents the absorption value of the sample at the wavelength of light radiation.

1.6 Preparation and characterization of dye nanoparticles

The dyes and amphiphilic polymer DSPE-PEG_{2000} were self-assembled in ultrapure water by nano-deposition method.[6-7] The accurately weighing 1mg dye was fully dissolved in 1ml THF solution. Then, the above solution was dropwise added to 10 mL aqueous solution containing 5 mg DSPE-PEG_{2000}. THF was completely volatilized after 24 h vigorous agitation. The dye nanoparticles were obtained by high-speed centrifugation for 1 h. The aqueous solution of nanoparticles used in subsequent testing was prepared by precisely weighing a certain nanoparticles and

dissolved in ultrapure water. The average hydrodynamic diameter and polymer dispersity index (PDI) were obtained by dynamic light scattering (DLS) analysis.

1.7 Photothermal effect and photothermal conversion efficiency

The temperatures elevated of dye nanoparticles (20, 40, 80 μM) with different concentrations were investigated under the power density radiation (690 nm, 0.6 W·cm^2). And, the temperatures elevated of dye nanoparticles (80 μM) were investigated under 690 nm light radiation (0.2, 0.4, 0.6 W·cm^2). The temperatures were recorded in a temperature monitoring camera. The heating stage was light radiation for 5 min, in which the temperature change was recorded every 0.5 min, and the natural cooling was performed after the light source was removed. The 5 cycles of heating-cooling were used to evaluate the photothermal stability.

The calculation of photothermal conversion efficiency was based on the previously reported studies, and the calculation method was described by the following formula [8-10].

$$\eta = \frac{hs(T_{Max} - T_{Surr}) - Q_{Dis}}{I(1 - 10^{-A})}$$

Among them, η represents photothermal conversion efficiency, h is the heat transfer coefficient, s is the surface area of the container, Q_{Dis} represents heat dissipated from the laser mediated by the solvent and container. I is the laser power and A is the absorbance at 690 nm.

$$hs = \frac{mC}{\tau_s}$$

m is the mass of the solution containing the PTAs, C is the specific heat capacity of the solution, and τ_s is the associated time constant.

$$t = -\tau_s ln(\theta)$$

q is a dimensionless parameter, known as the driving force temperature.

$$\theta = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}}$$

T is the current temperature. T_{Max} and T_{Surr} represent the maximum steady state

temperature and the environmental temperature, respectively.

1.8 Live-dead cell imaging experiment

Gastric cancer cells SGC-7901 were incubated in confocal imaging dish for different treated groups. Control Group: no processing; Light Group: sole NIR laser radiation (0.2 W·cm^2, 20 min) treated; **1**-NPs Group: sole 30 μM **1**-NPs incubation; "**1**-NPs+ light" Group: NIR laser radiation (0.2 W·cm^2, 20 min) was conducted after 30 μM **1**-NPs incubation. Meanwhile, calcein AM and propidium iodide PI double-staining kits were applied to image living cells (green fluorescence emission) and dead cells (red fluorescence emission), respectively. Calcein AM was excited with a 488 nm laser, detected in the range from 500 to 529 nm; propidium iodide PI was excited with a 559 nm laser, detected in the range from 570 to 619 nm by a confocal laser scanning microscopy.

2. Table and Figure

Table S1 Photophysical properties of dyes **1-3** in CH_2Cl_2 at 298 K.

Dye	$\lambda_{abs}/\lambda_{em}$ (nm)	Stokes-shift (nm)	ε [M^{-1} cm^{-1}]	Φ_f
1	662/677	15	95000	0.13
2	636/665	29	75000	0.15
3	690/716	26	108000	0.44

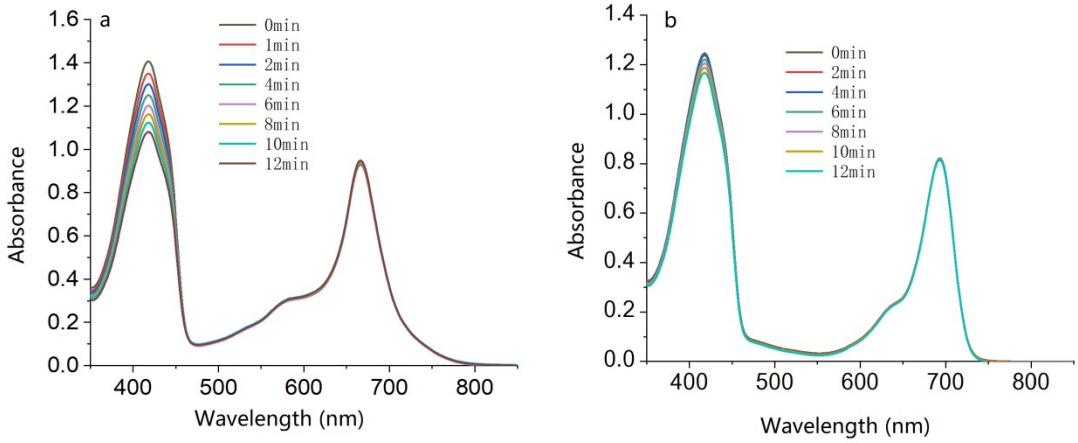


Fig. S1 Time-dependent photo-degradation of DPBF with a) ***t*Bu-azaBDP 2** and b) **Ph-azaBDP 3**.

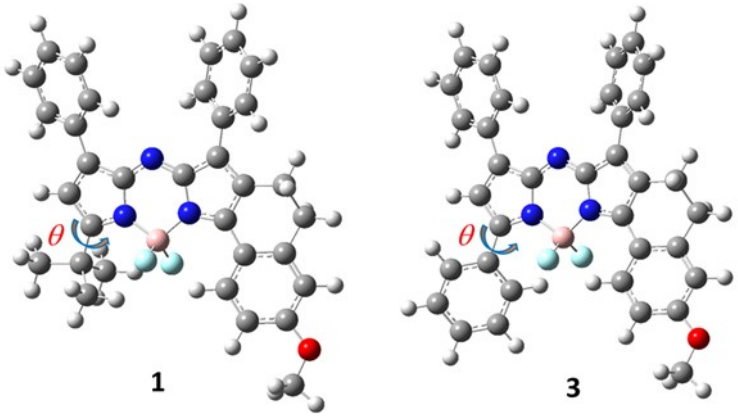


Fig. S2 Dihedral angles θ for the chemical bond of ***t*Bu-azaBDP 1** and **Ph-azaBDP 3**.

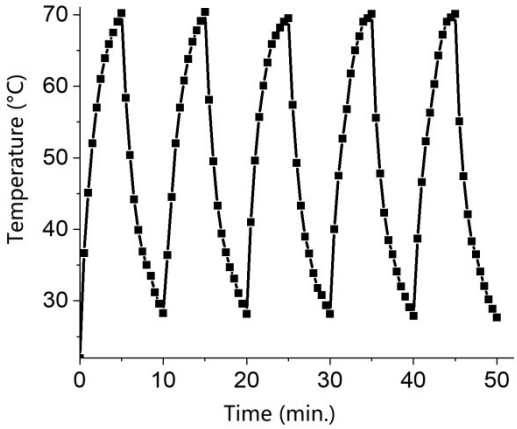


Fig. S3 Photothermal stability of ***t*Bu-azaBDP 1**-NPs during five circles of heating-cooling processes.

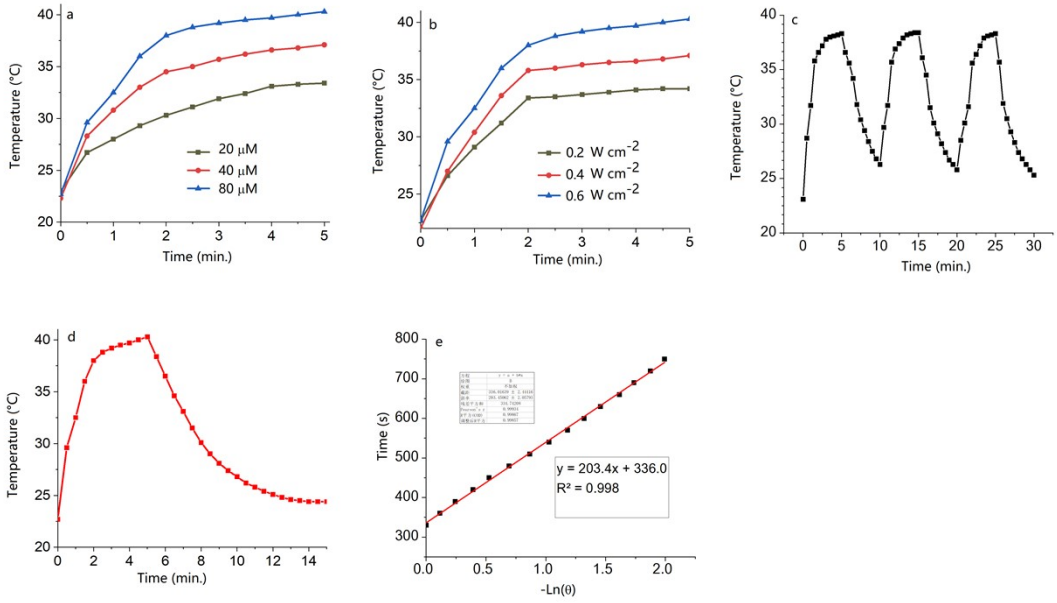


Fig. S4 a) Temperature changes (22.7-40.3 °C) of ***t*Bu-azaBDP 2**-NPs at different concentrations (20, 40, 80 μM) under 690 nm laser irradiation (0.6 W·cm^{-2}); b) Temperature changes of ***t*Bu-azaBDP 2**-NPs (80 μM) under 690 nm laser irradiation with different power density (0.2, 0.4, 0.6 W·cm^{-2}); c) Photothermal stability during three circles of heating-cooling processes; d) Temperature response curves of ***t*Bu-azaBDP 2**-NPs in aqueous solutions under irradiation and naturally cooling; e) Linear fitting of –Lnθ and time.

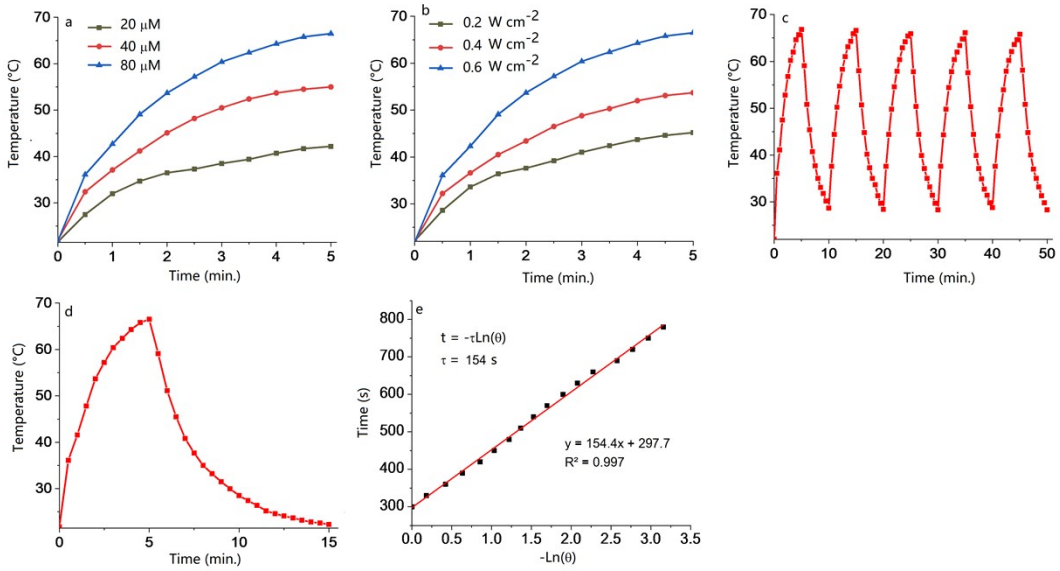
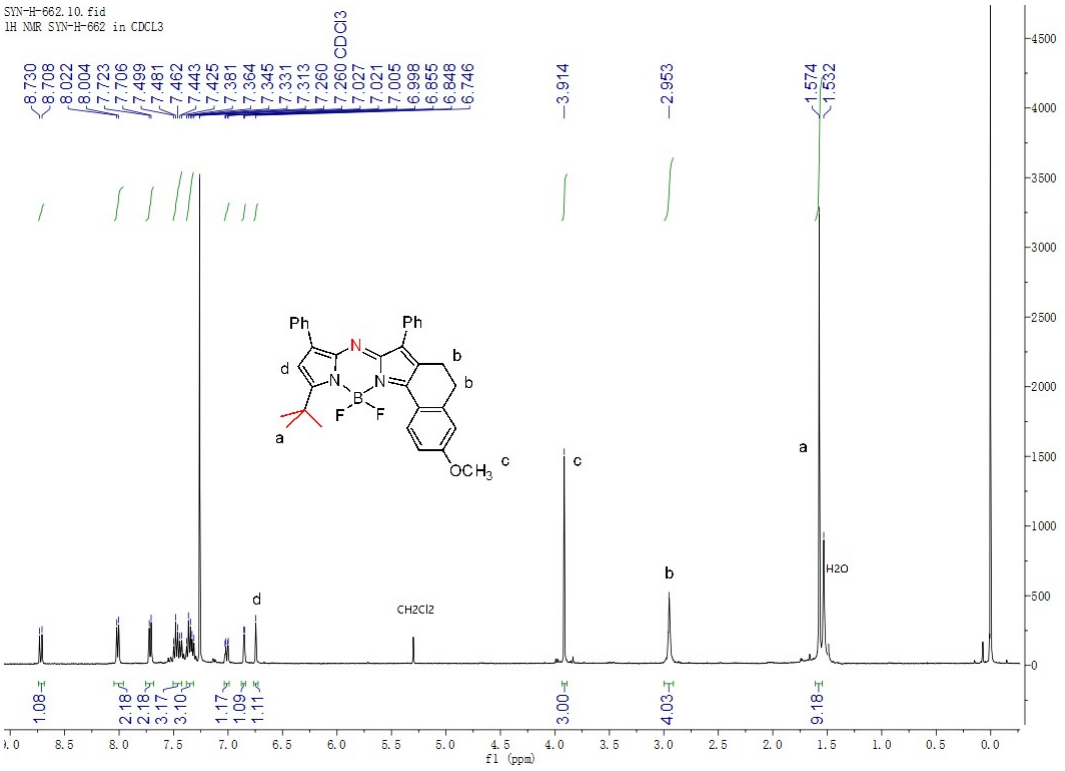
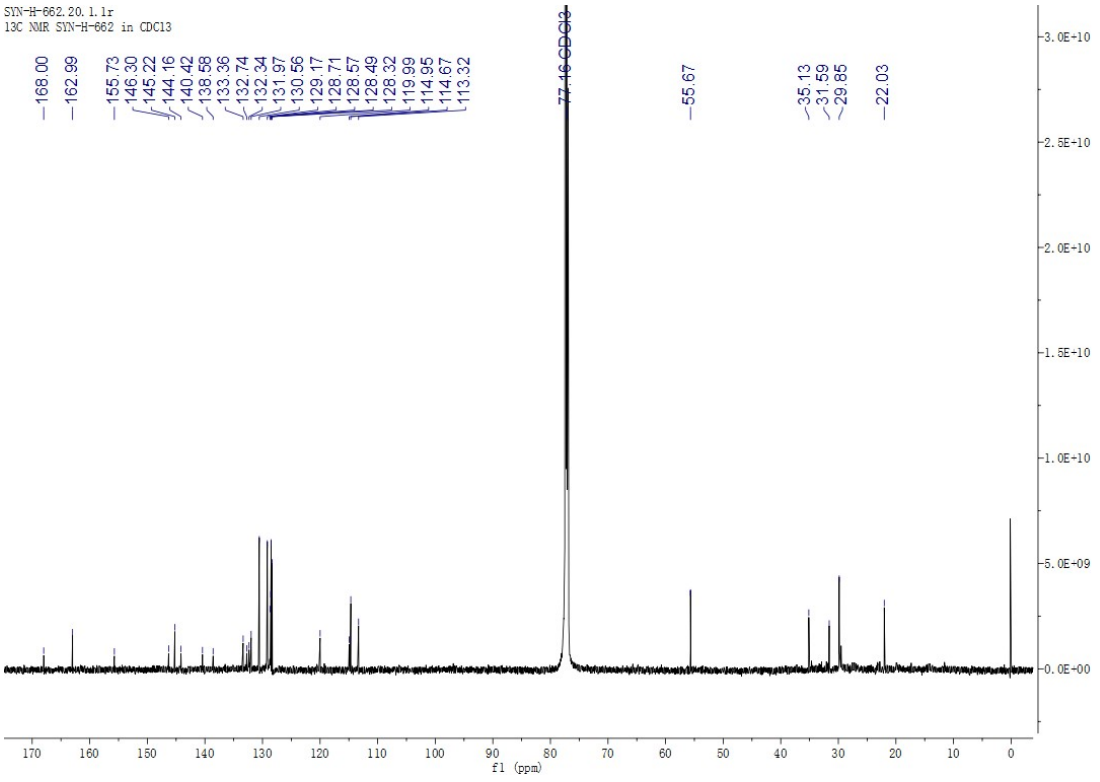


Fig. S5 a) Temperature changes (21.8-66.5 °C) of **Ph-azaBDP 3**-NPs at different concentrations (20, 40, 80 μM) under 690 nm laser irradiation (0.6 W·cm^{-2}); b) Temperature changes of **Ph-azaBDP 3**-NPs (80 μM) under 690 nm laser irradiation with different power density (0.2, 0.4, 0.6 W·cm^{-2}); c) Photothermal stability during five circles of heating-cooling processes; d) Temperature response curves of **Ph-azaBDP 3**-NPs in aqueous solutions under irradiation and naturally cooling; e) Linear fitting of -Lnθ and time.

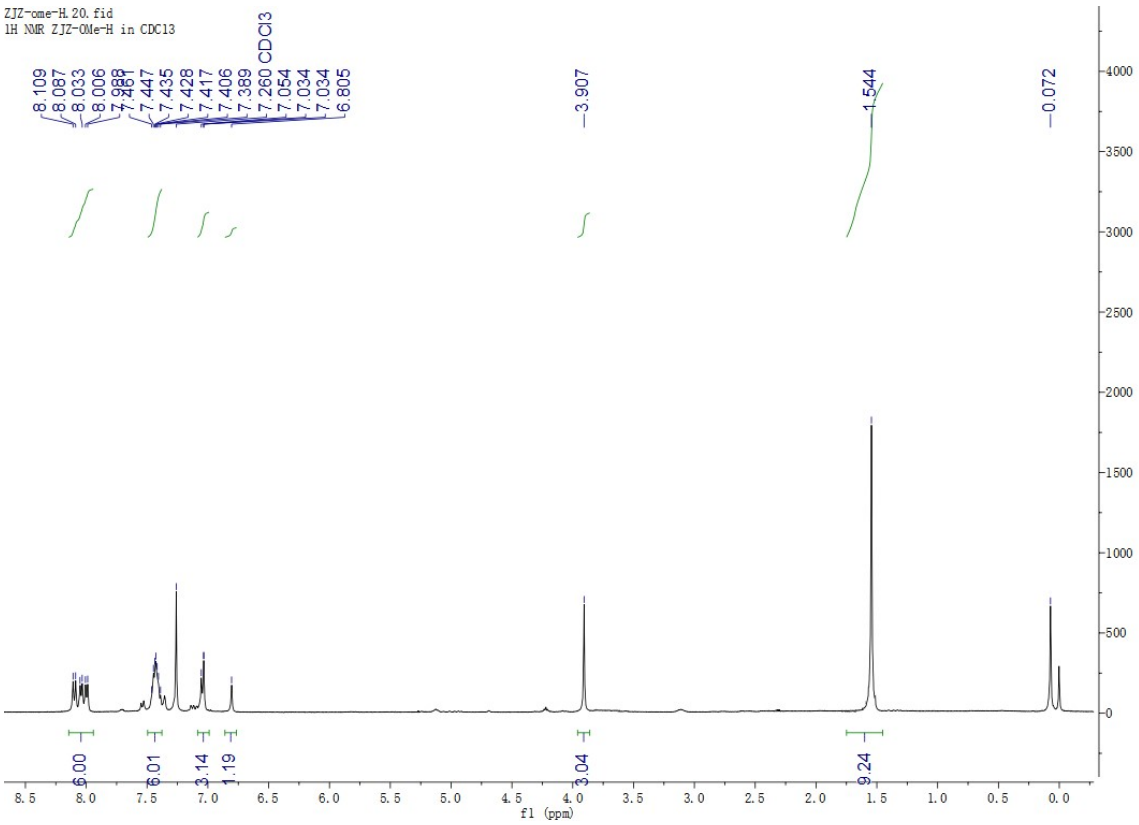
3. NMR



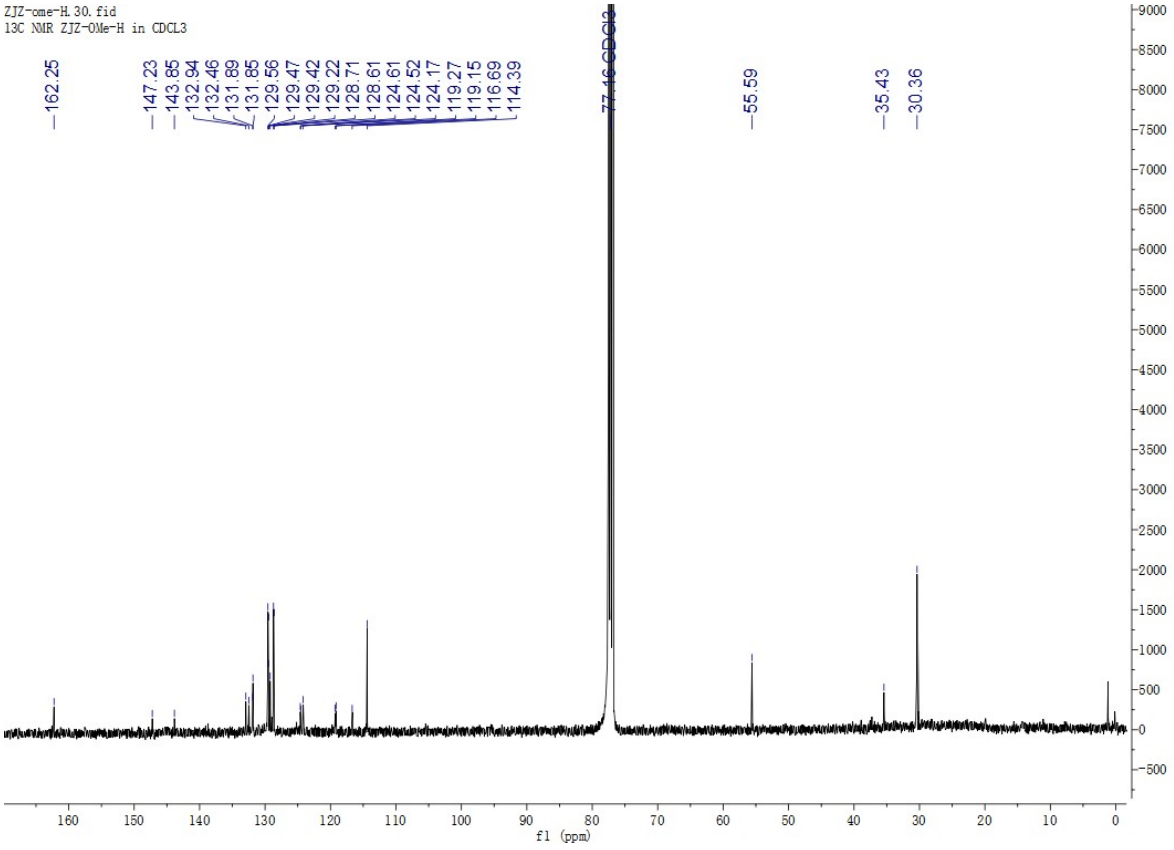
^{1}H NMR for dye **1**



^{13}C NMR for dye **1**

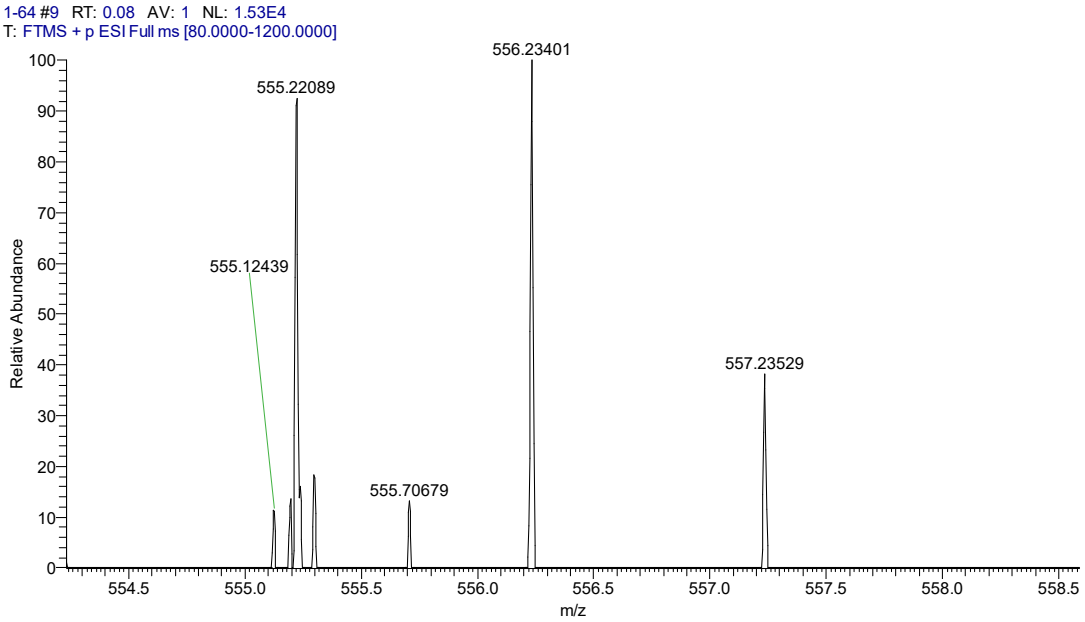


^{1}H NMR for dye **2**

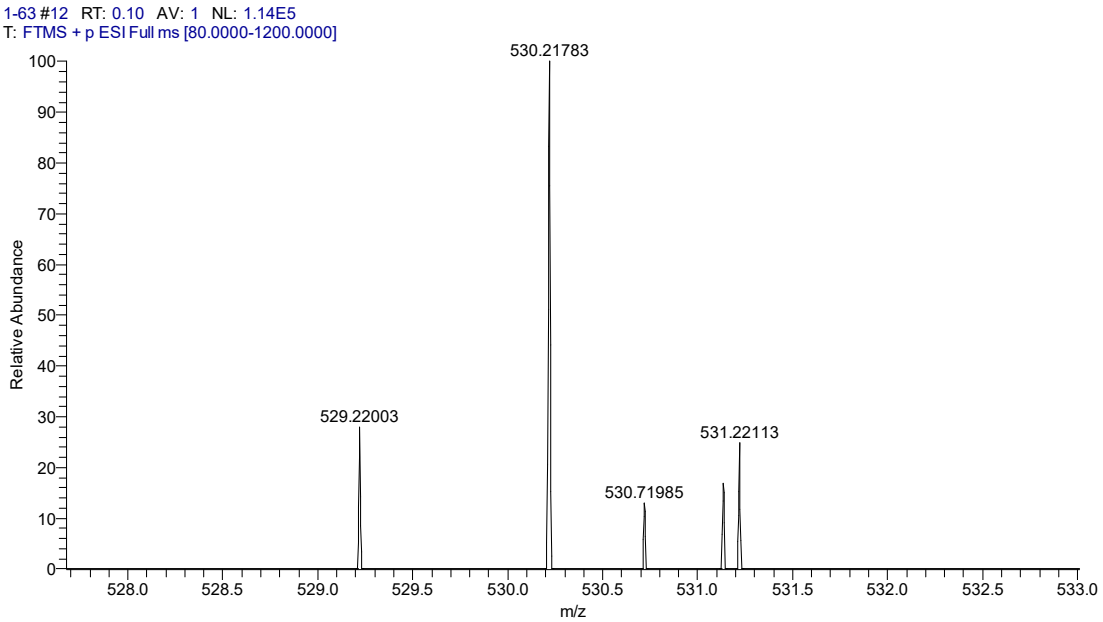


^{13}C NMR for dye **2**

4. HRMS



1. HRMS (ESI) m/z calcd for $C_{33}H_{30}BF_2N_3ONa^+$ $(M+Na)^+$ 556.23422,found 556.23401.



2. HRMS (ESI) m/z calcd for $C_{31}H_{28}BF_2N_3ONa^+$ $(M+Na)^+$ 530.21857, found 530.21783.

5. X-ray data for *t*Bu-azaBDP 1

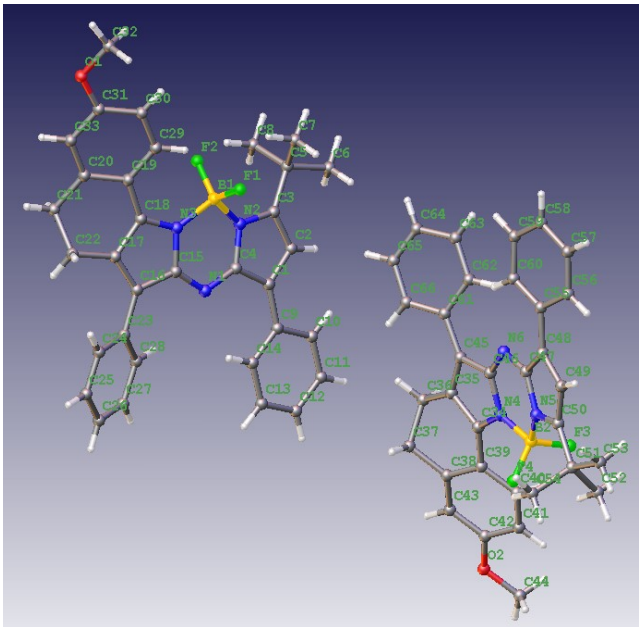


Table 1 Crystal data and structure refinement for syn.

Identification code	syn
Empirical formula	$C_{33}H_{30}BF_2N_3O$
Formula weight	533.41
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.3136(7)
b/Å	14.8807(9)
c/Å	17.5862(12)
α/°	88.651(5)
β/°	88.668(5)
γ/°	78.809(5)
Volume/Å^3	2646.5(3)
Z	4
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	0.091
F(000)	1120.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.432 to 50
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	18848
Independent reflections	9325 [R_{int} = 0.0642, R_{sigma} = 0.0956]
Data/restraints/parameters	9325/0/729
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.1175, wR_2 = 0.2991
Final R indexes [all data]	R_1 = 0.1442, wR_2 = 0.3154
Largest diff. peak/hole / e Å^{-3}	0.70/-0.51

Crystal structure determination of [syn]

Crystal Data for $C_{33}H_{30}BF_2N_3O$ (*M* =533.41 g/mol): triclinic, space group P-1 (no. 2), *a* = 10.3136(7) Å, *b* = 14.8807(9) Å, *c* = 17.5862(12) Å, *α* = 88.651(5)°, *β* = 88.668(5)°, *γ* = 78.809(5)°, *V* = 2646.5(3) Å^3, *Z* = 4, *T* = 179.99(10) K, μ(Mo Kα) = 0.091 mm^{-1}, *Dcalc* = 1.339 g/cm^3, 18848 reflections measured (4.432° ≤ 2Θ ≤ 50°), 9325 unique (R_{int} = 0.0642, R_{sigma} = 0.0956) which were used in all calculations. The final R_1 was 0.1175 (I > 2σ(I)) and wR_2 was 0.3154 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	-1528(3)	7890(2)	5262.7(17)	32.6(8)
F2	-516(3)	8626(2)	4348.6(17)	31.5(8)
O1	-6035(5)	10451(4)	2980(3)	64.2(16)
N1	554(4)	5841(3)	4329(2)	23.8(10)
N2	735(4)	7239(3)	4949(2)	24.3(10)
N3	-1054(4)	7190(3)	4033(2)	22.8(10)
C1	2244(5)	5940(4)	5270(3)	25.7(12)
C2	2515(6)	6684(4)	5647(3)	28.4(12)
C3	1611(5)	7471(4)	5455(3)	27.3(12)
C4	1119(5)	6297(4)	4818(3)	23.9(12)
C5	1651(6)	8439(4)	5703(3)	31.3(13)
C6	2686(7)	8375(4)	6330(4)	40.6(16)
C7	331(6)	8945(4)	6032(4)	37.6(15)
C8	2110(7)	8987(4)	5028(4)	40.6(15)
C9	3008(5)	5000(4)	5317(3)	26.0(12)
C10	4082(6)	4806(4)	5803(4)	40.8(16)
C11	4838(7)	3936(4)	5860(4)	45.7(17)
C12	4558(6)	3236(4)	5434(4)	37.6(15)
C13	3506(6)	3411(4)	4949(4)	35.3(14)
C14	2731(6)	4284(4)	4891(3)	31.5(13)
C15	-453(5)	6271(4)	3927(3)	23.6(11)
C16	-1072(5)	5920(4)	3300(3)	24.8(12)
C17	-1997(6)	6643(4)	3031(3)	28.6(13)
C18	-2003(5)	7410(4)	3508(3)	25.6(12)
C19	-2969(6)	8243(4)	3414(3)	29.5(13)
C20	-3586(6)	8392(4)	2695(3)	35.6(14)
C21	-3108(7)	7728(4)	2067(3)	42.0(16)
C22	-2908(6)	6742(4)	2371(3)	36.5(15)
C23	-764(5)	4976(4)	3018(3)	25.2(12)
C24	-1755(6)	4606(4)	2689(4)	38.2(15)
C25	-1499(7)	3731(5)	2414(4)	46.7(17)
C26	-240(7)	3190(5)	2475(4)	47.1(17)
C27	747(7)	3548(4)	2786(4)	45.1(16)
C28	494(6)	4438(4)	3067(4)	38.6(15)
C29	-3423(6)	8869(4)	3985(3)	30.6(13)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C30	-4440(6)	9612(4)	3868(3)	34.5(14)
C31	-5032(6)	9745(5)	3167(3)	41.0(16)
C32	-6624(7)	11032(5)	3573(4)	54(2)
C33	-4583(7)	9135(5)	2584(3)	45.4(18)
B1	-612(6)	7774(4)	4667(3)	26.1(14)
F3	6419(3)	2059(2)	10197.6(17)	32.2(8)
F4	5471(3)	1362(2)	9280.6(17)	31.4(8)
O2	11214(5)	-260(3)	7955(3)	54.0(14)
N4	5993(4)	2834(3)	8984(2)	24.9(10)
N5	4139(4)	2699(3)	9893(2)	24.6(10)
N6	4323(4)	4133(3)	9277(2)	24.9(10)
C34	6964(5)	2656(4)	8446(3)	24.6(12)
C35	6951(5)	3443(4)	7963(3)	27.2(12)
C36	7920(6)	3386(4)	7313(3)	33.8(14)
C37	8184(7)	2414(4)	7016(3)	38.5(15)
C38	8654(6)	1731(4)	7639(3)	32.5(13)
C39	7991(5)	1835(4)	8360(3)	26.3(12)
C40	8449(6)	1220(4)	8943(3)	30.1(13)
C41	9516(6)	508(4)	8835(3)	33.4(14)
C42	10153(6)	408(4)	8125(4)	37.5(15)
C43	9713(6)	1022(4)	7544(4)	39.3(15)
C44	11756(8)	-882(5)	8539(4)	58(2)
C45	6006(5)	4157(4)	8259(3)	25.5(12)
C46	5378(5)	3747(4)	8887(3)	23.1(11)
C47	3739(5)	3642(4)	9765(3)	23.7(11)
C48	2578(6)	3965(4)	10225(3)	27.4(12)
C49	2305(6)	3200(4)	10605(3)	28.6(13)
C50	3248(6)	2435(4)	10410(3)	27.1(12)
C51	3200(6)	1457(4)	10662(3)	30.8(13)
C52	4525(6)	928(4)	10950(4)	39.0(15)
C53	2186(7)	1473(4)	11311(4)	42.5(16)
C54	2768(7)	950(4)	9986(4)	40.1(15)
C55	1852(5)	4927(4)	10296(3)	27.6(12)
C56	1000(6)	5135(4)	10915(4)	38.1(15)
C57	303(7)	6025(5)	11008(4)	47.2(17)
C58	467(7)	6707(4)	10503(4)	45.8(17)
C59	1302(7)	6497(5)	9901(5)	52.4(19)
C60	1986(7)	5612(4)	9785(4)	43.6(16)
C61	5670(5)	5127(4)	8023(3)	24.7(12)
C62	5096(6)	5794(4)	8552(3)	34.1(14)
C63	4808(6)	6716(4)	8351(4)	38.3(15)
C64	5086(6)	6992(4)	7605(3)	36.9(15)
C65	5619(7)	6367(5)	7101(4)	42.3(16)
C66	5902(6)	5448(4)	7294(3)	36.2(14)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
B2	5523(6)	2189(4)	9600(3)	25.8(14)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for syn. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	28.1(18)	41.6(19)	25.3(17)	-8.2(14)	0.8(13)	1.3(15)
F2	34.2(19)	28.9(17)	28.2(17)	-0.7(13)	-6.1(14)	2.3(15)
O1	67(4)	67(3)	35(3)	0(2)	-7(2)	45(3)
N1	23(2)	29(2)	18(2)	3.7(18)	-0.4(18)	-4(2)
N2	23(2)	26(2)	21(2)	-0.5(18)	-2.8(18)	0(2)
N3	20(2)	28(2)	19(2)	-0.6(18)	-1.4(17)	0.8(19)
C1	26(3)	28(3)	23(3)	3(2)	-1(2)	-4(2)
C2	24(3)	32(3)	29(3)	1(2)	-9(2)	-5(2)
C3	24(3)	32(3)	26(3)	-1(2)	-2(2)	-5(2)
C4	25(3)	22(3)	24(3)	1(2)	-5(2)	-3(2)
C5	32(3)	28(3)	33(3)	-3(2)	-11(3)	-4(3)
C6	44(4)	35(3)	43(4)	-4(3)	-18(3)	-4(3)
C7	40(4)	34(3)	36(3)	-13(3)	-4(3)	3(3)
C8	43(4)	33(3)	45(4)	-1(3)	-6(3)	-5(3)
C9	24(3)	28(3)	24(3)	5(2)	-1(2)	-1(2)
C10	35(4)	36(3)	48(4)	2(3)	-14(3)	1(3)
C11	34(4)	37(4)	62(4)	8(3)	-22(3)	5(3)
C12	32(3)	28(3)	50(4)	4(3)	5(3)	2(3)
C13	38(4)	26(3)	42(4)	-4(3)	3(3)	-5(3)
C14	32(3)	31(3)	30(3)	2(2)	-3(2)	-1(3)
C15	22(3)	25(3)	22(3)	1(2)	1(2)	0(2)
C16	25(3)	32(3)	18(3)	-2(2)	-2(2)	-6(2)
C17	24(3)	38(3)	23(3)	0(2)	-3(2)	-3(3)
C18	23(3)	32(3)	20(3)	1(2)	-1(2)	-3(2)
C19	29(3)	34(3)	23(3)	3(2)	-3(2)	-1(3)
C20	36(3)	40(3)	26(3)	-1(3)	-3(3)	6(3)
C21	48(4)	47(4)	23(3)	0(3)	-9(3)	12(3)
C22	35(3)	43(4)	28(3)	-8(3)	-10(3)	5(3)
C23	29(3)	29(3)	18(3)	0(2)	-1(2)	-6(2)
C24	34(4)	39(3)	43(4)	-4(3)	-3(3)	-11(3)
C25	52(5)	53(4)	41(4)	-6(3)	-8(3)	-23(4)
C26	56(5)	37(4)	51(4)	-23(3)	10(3)	-16(3)
C27	42(4)	35(3)	56(4)	-5(3)	-6(3)	-1(3)
C28	38(4)	32(3)	48(4)	-2(3)	-10(3)	-10(3)
C29	28(3)	37(3)	23(3)	1(2)	-5(2)	2(3)
C30	33(3)	35(3)	30(3)	-1(3)	0(3)	8(3)
C31	37(4)	45(4)	31(3)	4(3)	-2(3)	17(3)
C32	51(4)	53(4)	44(4)	0(3)	3(3)	30(4)
C33	50(4)	52(4)	24(3)	3(3)	-12(3)	18(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*		*z*	U(eq)
B1	26(3)	26(3)	24(3)	-5(3)	-2(3)	2(3)
F3	30.5(18)	39.3(19)	22.7(16)	3.0(14)	-1.9(13)	3.4(15)
F4	36.7(19)	25.7(17)	28.5(17)	-2.0(13)	4.2(14)	2.0(15)
O2	52(3)	59(3)	34(2)	0(2)	5(2)	30(2)
N4	26(3)	26(2)	22(2)	-0.4(19)	1.4(19)	-3(2)
N5	28(3)	26(2)	18(2)	3.3(18)	2.8(18)	-3(2)
N6	23(2)	31(2)	20(2)	-0.5(19)	1.6(18)	-4(2)
C34	24(3)	28(3)	21(3)	-3(2)	0(2)	-4(2)
C35	27(3)	26(3)	26(3)	1(2)	0(2)	-1(2)
C36	32(3)	35(3)	30(3)	3(3)	6(2)	2(3)
C37	43(4)	40(3)	28(3)	-3(3)	10(3)	2(3)
C38	32(3)	35(3)	28(3)	-7(2)	3(2)	1(3)
C39	23(3)	31(3)	23(3)	-2(2)	1(2)	-2(2)
C40	28(3)	32(3)	29(3)	-2(2)	3(2)	-2(3)
C41	29(3)	34(3)	33(3)	-1(3)	-3(2)	5(3)
C42	35(4)	36(3)	37(3)	-9(3)	-3(3)	4(3)
C43	39(4)	43(4)	30(3)	-4(3)	8(3)	4(3)
C44	46(4)	56(5)	57(5)	-4(4)	-5(3)	28(4)
C45	24(3)	34(3)	17(3)	0(2)	1(2)	-3(2)
C46	23(3)	24(3)	22(3)	1(2)	-4(2)	-3(2)
C47	25(3)	23(3)	24(3)	0(2)	-1(2)	-6(2)
C48	27(3)	30(3)	25(3)	-2(2)	-2(2)	-5(2)
C49	25(3)	29(3)	30(3)	-2(2)	7(2)	-1(2)
C50	27(3)	32(3)	22(3)	2(2)	-2(2)	-4(2)
C51	35(3)	30(3)	26(3)	3(2)	4(2)	-3(3)
C52	46(4)	29(3)	40(4)	9(3)	3(3)	-5(3)
C53	48(4)	33(3)	44(4)	3(3)	16(3)	-5(3)
C54	46(4)	33(3)	42(4)	-2(3)	5(3)	-9(3)
C55	23(3)	28(3)	31(3)	-3(2)	-2(2)	-3(2)
C56	34(3)	37(3)	40(4)	-4(3)	1(3)	0(3)
C57	45(4)	45(4)	49(4)	-17(3)	2(3)	0(3)
C58	35(4)	30(3)	67(5)	-14(3)	-6(3)	8(3)
C59	47(4)	32(4)	73(5)	12(3)	4(4)	1(3)
C60	37(4)	34(3)	53(4)	5(3)	13(3)	7(3)
C61	24(3)	26(3)	25(3)	1(2)	-8(2)	-5(2)
C62	41(4)	36(3)	29(3)	1(3)	1(3)	-16(3)
C63	41(4)	35(3)	42(4)	-6(3)	-3(3)	-12(3)
C64	41(4)	33(3)	36(3)	6(3)	-13(3)	-3(3)
C65	55(4)	44(4)	30(3)	7(3)	-1(3)	-18(3)
C66	47(4)	32(3)	29(3)	1(3)	2(3)	-7(3)
B2	27(3)	29(3)	21(3)	3(3)	0(2)	-5(3)

Table 4 Bond Lengths for syn.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom		*x*			*y*	*z*	U(eq)
F1	B1	1.385(7)		F3	B2	1.401(7)	
F2	B1	1.393(7)		F4	B2	1.375(7)	
O1	C31	1.363(7)		O2	C42	1.360(7)	
O1	C32	1.419(8)		O2	C44	1.416(8)	
N1	C4	1.320(7)		N4	C34	1.353(7)	
N1	C15	1.321(7)		N4	C46	1.392(7)	
N2	C3	1.379(7)		N4	B2	1.562(7)	
N2	C4	1.404(7)		N5	C47	1.399(7)	
N2	B1	1.548(7)		N5	C50	1.382(7)	
N3	C15	1.403(7)		N5	B2	1.563(8)	
N3	C18	1.349(7)		N6	C46	1.313(7)	
N3	B1	1.560(7)		N6	C47	1.323(7)	
C1	C2	1.381(8)		C34	C35	1.428(8)	
C1	C4	1.429(7)		C34	C39	1.462(8)	
C1	C9	1.468(8)		C35	C36	1.494(8)	
C2	C3	1.388(8)		C35	C45	1.396(8)	
C3	C5	1.524(8)		C36	C37	1.521(8)	
C5	C6	1.541(8)		C37	C38	1.500(9)	
C5	C7	1.530(8)		C38	C39	1.424(8)	
C5	C8	1.542(9)		C38	C43	1.374(8)	
C9	C10	1.396(8)		C39	C40	1.385(8)	
C9	C14	1.393(8)		C40	C41	1.384(8)	
C10	C11	1.379(9)		C41	C42	1.396(9)	
C11	C12	1.376(9)		C42	C43	1.378(9)	
C12	C13	1.377(9)		C45	C46	1.450(7)	
C13	C14	1.390(8)		C45	C61	1.469(8)	
C15	C16	1.443(7)		C47	C48	1.438(8)	
C16	C17	1.375(8)		C48	C49	1.379(8)	
C16	C23	1.473(8)		C48	C55	1.487(8)	
C17	C18	1.431(8)		C49	C50	1.390(8)	
C17	C22	1.497(8)		C50	C51	1.520(8)	
C18	C19	1.441(8)		C51	C52	1.530(8)	
C19	C20	1.422(8)		C51	C53	1.527(8)	
C19	C29	1.395(8)		C51	C54	1.543(8)	
C20	C21	1.508(8)		C55	C56	1.384(8)	
C20	C33	1.370(8)		C55	C60	1.368(9)	
C21	C22	1.527(9)		C56	C57	1.390(9)	
C23	C24	1.395(8)		C57	C58	1.365(10)	
C23	C28	1.390(8)		C58	C59	1.352(10)	
C24	C25	1.374(9)		C59	C60	1.385(9)	
C25	C26	1.393(10)		C61	C62	1.411(8)	
C26	C27	1.367(9)		C61	C66	1.390(8)	
C27	C28	1.399(9)		C62	C63	1.387(9)	
C29	C30	1.383(8)		C63	C64	1.405(9)	

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom		*x*		*y*		*z*	U(eq)
C30	C31	1.380(8)	C64	C65	1.330(9)		
C31	C33	1.396(9)	C65	C66	1.377(9)		

Table 5 Bond Angles for syn.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C31	O1	C32	117.6(5)	C42	O2	C44	118.7(5)
C4	N1	C15	120.0(5)	C34	N4	C46	107.2(4)
C3	N2	C4	107.4(4)	C34	N4	B2	130.4(5)
C3	N2	B1	131.0(5)	C46	N4	B2	122.4(4)
C4	N2	B1	120.4(4)	C47	N5	B2	120.3(4)
C15	N3	B1	121.9(4)	C50	N5	C47	107.1(4)
C18	N3	C15	107.4(4)	C50	N5	B2	131.3(4)
C18	N3	B1	130.7(5)	C46	N6	C47	120.4(5)
C2	C1	C4	105.3(5)	N4	C34	C35	110.2(5)
C2	C1	C9	125.9(5)	N4	C34	C39	128.6(5)
C4	C1	C9	128.9(5)	C35	C34	C39	121.0(5)
C1	C2	C3	110.4(5)	C34	C35	C36	119.0(5)
N2	C3	C2	108.3(5)	C45	C35	C34	107.6(5)
N2	C3	C5	125.6(5)	C45	C35	C36	133.2(5)
C2	C3	C5	125.9(5)	C35	C36	C37	108.7(5)
N1	C4	N2	124.6(5)	C38	C37	C36	111.0(5)
N1	C4	C1	126.7(5)	C39	C38	C37	118.6(5)
N2	C4	C1	108.7(4)	C43	C38	C37	122.5(5)
C3	C5	C6	108.2(5)	C43	C38	C39	118.9(5)
C3	C5	C7	113.2(5)	C38	C39	C34	116.0(5)
C3	C5	C8	109.6(5)	C40	C39	C34	125.0(5)
C6	C5	C8	107.5(5)	C40	C39	C38	118.6(5)
C7	C5	C6	107.5(5)	C41	C40	C39	121.6(5)
C7	C5	C8	110.6(5)	C40	C41	C42	119.3(6)
C10	C9	C1	118.9(5)	O2	C42	C41	124.5(6)
C14	C9	C1	123.4(5)	O2	C42	C43	116.0(6)
C14	C9	C10	117.7(5)	C43	C42	C41	119.4(6)
C11	C10	C9	121.0(6)	C38	C43	C42	122.1(6)
C12	C11	C10	120.7(6)	C35	C45	C46	105.1(5)
C11	C12	C13	119.3(6)	C35	C45	C61	130.2(5)
C12	C13	C14	120.5(6)	C46	C45	C61	124.7(5)
C13	C14	C9	120.8(5)	N4	C46	C45	109.6(5)
N1	C15	N3	123.4(5)	N6	C46	N4	123.6(5)
N1	C15	C16	127.6(5)	N6	C46	C45	126.6(5)
N3	C15	C16	108.9(4)	N5	C47	C48	108.7(5)
C15	C16	C23	126.3(5)	N6	C47	N5	124.5(5)
C17	C16	C15	105.9(5)	N6	C47	C48	126.7(5)
C17	C16	C23	127.8(5)	C47	C48	C55	127.2(5)
C16	C17	C18	108.1(5)	C49	C48	C47	105.5(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom			*x*	*y*			*z*	U(eq)
C16	C17	C22	132.3(5)	C49	C48	C55		127.2(5)
C18	C17	C22	119.5(5)	C48	C49	C50		109.8(5)
N3	C18	C17	109.7(5)	N5	C50	C49		108.9(5)
N3	C18	C19	129.3(5)	N5	C50	C51		126.1(5)
C17	C18	C19	121.0(5)	C49	C50	C51		124.7(5)
C20	C19	C18	116.5(5)	C50	C51	C52		113.1(5)
C29	C19	C18	125.5(5)	C50	C51	C53		109.3(5)
C29	C19	C20	117.7(5)	C50	C51	C54		108.8(5)
C19	C20	C21	118.8(5)	C52	C51	C54		109.2(5)
C33	C20	C19	119.7(5)	C53	C51	C52		107.5(5)
C33	C20	C21	121.5(5)	C53	C51	C54		108.8(5)
C20	C21	C22	110.6(5)	C56	C55	C48		117.9(5)
C17	C22	C21	108.6(5)	C60	C55	C48		123.4(5)
C24	C23	C16	119.6(5)	C60	C55	C56		118.6(6)
C28	C23	C16	121.9(5)	C55	C56	C57		120.1(6)
C28	C23	C24	118.5(5)	C58	C57	C56		120.8(6)
C25	C24	C23	121.1(6)	C59	C58	C57		118.7(6)
C24	C25	C26	120.1(6)	C58	C59	C60		121.7(7)
C27	C26	C25	119.5(6)	C55	C60	C59		120.1(6)
C26	C27	C28	120.7(6)	C62	C61	C45		120.1(5)
C23	C28	C27	120.1(6)	C66	C61	C45		123.7(5)
C30	C29	C19	122.0(5)	C66	C61	C62		116.2(5)
C31	C30	C29	119.6(6)	C63	C62	C61		121.2(6)
O1	C31	C30	125.1(6)	C62	C63	C64		119.4(6)
O1	C31	C33	115.3(5)	C65	C64	C63		119.7(6)
C30	C31	C33	119.5(5)	C64	C65	C66		121.4(6)
C20	C33	C31	121.4(6)	C65	C66	C61		122.0(6)
F1	B1	F2	109.6(5)	F3	B2	N4		108.8(5)
F1	B1	N2	110.0(5)	F3	B2	N5		109.8(4)
F1	B1	N3	110.5(5)	F4	B2	F3		110.1(5)
F2	B1	N2	112.2(5)	F4	B2	N4		109.3(4)
F2	B1	N3	108.0(4)	F4	B2	N5		112.4(5)
N2	B1	N3	106.5(4)	N4	B2	N5		106.3(4)

Table 6 Torsion Angles for syn.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C31	C33	C20	-179.5(7)	O2	C42	C43	C38	-179.9(6)
N1	C15	C16	C17	-175.2(5)	N4	C34	C35	C36	-178.2(5)
N1	C15	C16	C23	5.1(9)	N4	C34	C35	C45	5.2(6)
N2	C3	C5	C6	174.5(5)	N4	C34	C39	C38	163.8(5)
N2	C3	C5	C7	55.5(7)	N4	C34	C39	C40	-23.6(9)
N2	C3	C5	C8	-68.5(7)	N5	C47	C48	C49	-1.1(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom			x		y				z	U(eq)
N3	C15	C16	C17	1.8(6)	N5	C47	C48	C55	177.1(5)	
N3	C15	C16	C23	-177.9(5)	N5	C50	C51	C52	53.1(7)	
N3	C18	C19	C20	162.3(6)	N5	C50	C51	C53	172.9(5)	
N3	C18	C19	C29	-23.4(10)	N5	C50	C51	C54	-68.4(7)	
C1	C2	C3	N2	0.2(7)	N6	C47	C48	C49	176.7(5)	
C1	C2	C3	C5	-174.6(5)	N6	C47	C48	C55	-5.1(9)	
C1	C9	C10	C11	-179.2(6)	C34	N4	C46	N6	174.6(5)	
C1	C9	C14	C13	178.7(5)	C34	N4	C46	C45	-0.2(6)	
C2	C1	C4	N1	176.0(5)	C34	N4	B2	F3	77.5(7)	
C2	C1	C4	N2	-1.0(6)	C34	N4	B2	F4	-42.7(7)	
C2	C1	C9	C10	2.7(9)	C34	N4	B2	N5	-164.3(5)	
C2	C1	C9	C14	-176.4(6)	C34	C35	C36	C37	32.6(7)	
C2	C3	C5	C6	-11.5(8)	C34	C35	C45	C46	-5.0(6)	
C2	C3	C5	C7	-130.6(6)	C34	C35	C45	C61	174.3(5)	
C2	C3	C5	C8	105.5(6)	C34	C39	C40	C41	-173.4(5)	
C3	N2	C4	N1	-175.9(5)	C35	C34	C39	C38	-21.7(8)	
C3	N2	C4	C1	1.2(6)	C35	C34	C39	C40	151.0(6)	
C3	N2	B1	F1	-66.0(7)	C35	C36	C37	C38	-56.1(7)	
C3	N2	B1	F2	56.2(7)	C35	C45	C46	N4	3.4(6)	
C3	N2	B1	N3	174.2(5)	C35	C45	C46	N6	-171.3(5)	
C4	N1	C15	N3	-5.7(8)	C35	C45	C61	C62	-154.5(6)	
C4	N1	C15	C16	170.9(5)	C35	C45	C61	C66	24.6(9)	
C4	N2	C3	C2	-0.8(6)	C36	C35	C45	C46	179.0(6)	
C4	N2	C3	C5	174.0(5)	C36	C35	C45	C61	-1.6(10)	
C4	N2	B1	F1	99.8(5)	C36	C37	C38	C39	44.3(8)	
C4	N2	B1	F2	-137.9(5)	C36	C37	C38	C43	-134.3(6)	
C4	N2	B1	N3	-19.9(7)	C37	C38	C39	C34	-4.9(8)	
C4	C1	C2	C3	0.5(6)	C37	C38	C39	C40	-178.1(6)	
C4	C1	C9	C10	-179.9(6)	C37	C38	C43	C42	178.7(6)	
C4	C1	C9	C14	1.0(9)	C38	C39	C40	C41	-0.9(9)	
C9	C1	C2	C3	178.5(5)	C39	C34	C35	C36	6.3(8)	
C9	C1	C4	N1	-1.9(10)	C39	C34	C35	C45	-170.3(5)	
C9	C1	C4	N2	-178.9(5)	C39	C38	C43	C42	0.1(10)	
C9	C10	C11	C12	0.4(11)	C39	C40	C41	C42	0.4(9)	
C10	C9	C14	C13	-0.4(9)	C40	C41	C42	O2	179.5(6)	

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom			x		y				z	U(eq)
C10	C11	C12	C13	-0.2(11)	C40	C41	C42	C43	0.3(10)	
C11	C12	C13	C14	-0.2(10)	C41	C42	C43	C38	-0.6(10)	
C12	C13	C14	C9	0.5(9)	C43	C38	C39	C34	173.8(6)	
C14	C9	C10	C11	-0.1(10)	C43	C38	C39	C40	0.6(9)	
C15	N1	C4	N2	-0.7(8)	C44	O2	C42	C41	-2.6(10)	
C15	N1	C4	C1	-177.2(5)	C44	O2	C42	C43	176.7(7)	
C15	N3	C18	C17	-2.3(6)	C45	C35	C36	C37	-151.9(6)	
C15	N3	C18	C19	174.4(6)	C45	C61	C62	C63	177.9(6)	
C15	N3	B1	F1	-105.0(5)	C45	C61	C66	C65	-177.5(6)	
C15	N3	B1	F2	135.2(5)	C46	N4	C34	C35	-3.0(6)	
C15	N3	B1	N2	14.5(7)	C46	N4	C34	C39	172.0(5)	
C15	C16	C17	C18	-3.2(6)	C46	N4	B2	F3	-105.1(5)	
C15	C16	C17	C22	176.3(6)	C46	N4	B2	F4	134.6(5)	
C15	C16	C23	C24	149.7(6)	C46	N4	B2	N5	13.1(7)	
C15	C16	C23	C28	-30.6(8)	C46	N6	C47	N5	-2.0(8)	
C16	C17	C18	N3	3.5(6)	C46	N6	C47	C48	-179.5(5)	
C16	C17	C18	C19	-173.5(5)	C46	C45	C61	C62	24.8(8)	
C16	C17	C22	C21	-147.9(6)	C46	C45	C61	C66	-156.1(6)	
C16	C23	C24	C25	179.4(6)	C47	N5	C50	C49	-0.1(6)	
C16	C23	C28	C27	-179.4(6)	C47	N5	C50	C51	173.5(5)	
C17	C16	C23	C24	-30.0(9)	C47	N5	B2	F3	99.6(5)	
C17	C16	C23	C28	149.7(6)	C47	N5	B2	F4	-137.4(5)	
C17	C18	C19	C20	-21.3(8)	C47	N5	B2	N4	-17.9(6)	
C17	C18	C19	C29	153.0(6)	C47	N6	C46	N4	-3.8(8)	
C18	N3	C15	N1	177.5(5)	C47	N6	C46	C45	170.2(5)	
C18	N3	C15	C16	0.3(6)	C47	C48	C49	C50	1.0(6)	
C18	N3	B1	F1	74.8(7)	C47	C48	C55	C56	-162.3(6)	
C18	N3	B1	F2	-45.1(7)	C47	C48	C55	C60	17.5(9)	
C18	N3	B1	N2	-165.7(5)	C48	C49	C50	N5	-0.6(6)	
C18	C17	C22	C21	31.6(8)	C48	C49	C50	C51	-174.3(5)	
C18	C19	C20	C21	-5.6(9)	C48	C55	C56	C57	179.7(6)	
C18	C19	C20	C33	175.3(6)	C48	C55	C60	C59	-178.3(6)	
C18	C19	C29	C30	-174.0(6)	C49	C48	C55	C56	15.5(9)	
C19	C20	C21	C22	44.3(8)	C49	C48	C55	C60	-164.7(6)	
C19	C20	C33	C31	-1.4(11)	C49	C50	C51	C52	-134.2(6)	
C19	C29	C30	C31	-0.1(10)	C49	C50	C51	C53	-14.5(8)	
C20	C19	C29	C30	0.3(9)	C49	C50	C51	C54	104.2(6)	

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom			x		y				z	U(eq)
C20	C21	C22	C17	-54.8(7)	C50	N5	C47	N6	-177.1(5)	
C21	C20	C33	C31	179.5(7)	C50	N5	C47	C48	0.8(6)	
C22	C17	C18	N3	-176.0(5)	C50	N5	B2	F3	-65.7(7)	
C22	C17	C18	C19	6.9(8)	C50	N5	B2	F4	57.3(7)	
C23	C16	C17	C18	176.6(5)	C50	N5	B2	N4	176.8(5)	
C23	C16	C17	C22	-3.9(10)	C55	C48	C49	C50	-177.2(5)	
C23	C24	C25	C26	1.3(10)	C55	C56	C57	C58	-1.3(10)	
C24	C23	C28	C27	0.4(9)	C56	C55	C60	C59	1.6(10)	
C24	C25	C26	C27	-2.4(11)	C56	C57	C58	C59	1.3(11)	
C25	C26	C27	C28	2.4(11)	C57	C58	C59	C60	0.2(11)	
C26	C27	C28	C23	-1.4(10)	C58	C59	C60	C55	-1.7(12)	
C28	C23	C24	C25	-0.3(9)	C60	C55	C56	C57	-0.1(9)	
C29	C19	C20	C21	179.6(6)	C61	C45	C46	N4	-176.0(5)	
C29	C19	C20	C33	0.5(10)	C61	C45	C46	N6	9.3(9)	
C29	C30	C31	O1	-179.6(7)	C61	C62	C63	C64	0.4(9)	
C29	C30	C31	C33	-0.8(10)	C62	C61	C66	C65	1.6(9)	
C30	C31	C33	C20	1.6(12)	C62	C63	C64	C65	0.0(10)	
C32	O1	C31	C30	-7.9(11)	C63	C64	C65	C66	0.3(10)	
C32	O1	C31	C33	173.3(7)	C64	C65	C66	C61	-1.2(11)	
C33	C20	C21	C22	-136.5(7)	C66	C61	C62	C63	-1.2(9)	
B1	N2	C3	C2	166.4(5)	B2	N4	C34	C35	174.6(5)	
B1	N2	C3	C5	-18.7(9)	B2	N4	C34	C39	-10.3(9)	
B1	N2	C4	N1	15.2(8)	B2	N4	C46	N6	-3.2(8)	
B1	N2	C4	C1	-167.7(5)	B2	N4	C46	C45	-178.1(4)	
B1	N3	C15	N1	-2.7(8)	B2	N5	C47	N6	14.3(8)	
B1	N3	C15	C16	-179.8(5)	B2	N5	C47	C48	-167.8(4)	
B1	N3	C18	C17	177.9(5)	B2	N5	C50	C49	166.7(5)	
B1	N3	C18	C19	-5.4(10)	B2	N5	C50	C51	-19.7(9)	

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for syn.

Atom	x	y	z	U(eq)
H2	3206.31	6661.14	5981.64	34
H6A	2447.2	8012.98	6750.57	61
H6B	2716.8	8978.93	6499.76	61
H6C	3538.89	8093.1	6131.13	61
H7A	-318.62	9040.77	5640.92	56
H7B	437.39	9525.95	6220.34	56
H7C	46.6	8585.27	6440.17	56

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
H8A	2948.23	8667.91	4836.42	61
H8B	2196.4	9582.34	5194.57	61
H8C	1470.38	9053.53	4632.25	61
H10	4289.29	5270.82	6093.85	49
H11	5545.99	3820.73	6189.88	55
H12	5074.46	2650.75	5472.95	45
H13	3312.53	2941.76	4658.02	42
H14	2018.41	4392.45	4564.43	38
H21A	-2279.98	7846.98	1855.26	50
H21B	-3750.07	7814.65	1664.66	50
H22A	-3751.33	6596.57	2531.49	44
H22B	-2530.63	6322.41	1974.17	44
H24	-2603.28	4956.82	2654.32	46
H25	-2167.16	3499.6	2186.05	56
H26	-73.21	2590.39	2306.25	56
H27	1595.55	3196.69	2809.96	54
H28	1169.11	4669.72	3287.2	46
H29	-3029.18	8785.01	4458.04	37
H30	-4724.03	10018.1	4258.16	41
H32A	-7345.71	11476.11	3374.37	82
H32B	-5978.59	11341.99	3776.15	82
H32C	-6947.16	10672.89	3967.9	82
H33	-4969.65	9236.17	2108.8	55
H36A	8737.62	3540.71	7480.55	41
H36B	7565.93	3815.91	6911.6	41
H37A	7379.04	2284.53	6806.99	46
H37B	8847.36	2359.93	6611.03	46
H40	8029.98	1288.17	9417.41	36
H41	9804.7	100.33	9232.53	40
H43	10147.75	954.68	7073.67	47
H44A	12511.79	-1298.46	8341.85	87
H44B	11103.89	-1220.39	8720.06	87
H44C	12019.66	-548.86	8950.19	87
H49	1596.16	3196.5	10941.02	34
H52A	5160.75	845.43	10537.01	58
H52B	4415.95	339.58	11147.55	58
H52C	4831.17	1264.98	11344.26	58
H53A	2395.38	1841.87	11713.84	64
H53B	2204.91	859.95	11498.72	64
H53C	1319.85	1727.71	11127.38	64
H54A	1926.26	1272.99	9811.51	60
H54B	2695.94	340.03	10145.29	60
H54C	3412.18	921.92	9579.93	60
H56	892.98	4679.2	11268.1	46

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syn. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
H57	-281.79	6157.18	11418.68	57
H58	13.52	7304.34	10571.69	55
H59	1420.61	6958.7	9556.1	63
H60	2536.99	5483.33	9359.5	52
H62	4906.09	5610.82	9045.03	41
H63	4434.8	7148.86	8706.42	46
H64	4897.67	7609.35	7464.02	44
H65	5805.19	6554.46	6609.32	51
H66	6259.76	5029.69	6924.21	43

Experimental

Single crystals of $C_{33}H_{30}BF_2N_3O$ **[syn]** were **[]**. A suitable crystal was selected and **[]** on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 179.99(10) K during data collection.

6. References

[1] Y. Su, N. Xu, C. Wang, Q. Qiao, R. Li, D. Zhang, X. Liu, Z. Xu, X.-D. Jiang, *J. Am. Chem. Soc*. 2022, Submitted.

[2] J. Li, J. Wang, D. Zhang, T. Cui, Z. Xu and X.-D. Jiang, *Dyes Pigm.*, 2022, **199**, 110092.

[3] C. Murali Krishna, Yves Lion and Peter Riesz, *Photochem. Photobiol.,* 2010, **45**, 1-6.

[4] J. R. Kanofsky. Measurement of singlet-oxygen in vivo: progress and pitfalls. *Photochem. Photobiol.*, 2011, **87**, 14-17.

[5] B. R. Rabello, A. P. Gerola, D. S. Pellosi, A. L. Tessaro, J. L. Aparício, W. Caetano and N. Hioka, *J. Photochem. Photobiol. A Chem.*, 2012, **238**, 53-62.

[6] J. Zhu, J. Zou, Z. Zhang, J. Zhang, Y. Sun, X. Dong and Q. Zhang, *Mater. Chem. Front.*, 2019, **3**, 1523-1531.

[7] D. Xi, M. Xiao, J. Cao, L. Zhao, N. Xu, S. Long, J. Fan, K. Shao, W. Sun, X. Yan, and X. Peng, *Adv. Mater.*, 2020, **32**, 1907855.

[8] H. S. Jung, P. Verwilst, A. Sharma, J. L. Sessler and J. S. Kim, *Chem. Soc. Rev.*, 2018, **47**, 2280-2297.

[9] B.-D. Zheng, Q.-X. He, X. Li, J. Yoon and J.-D. Huang, *Coord. Chem. Rev.*, 2021, **426**, 213548.

[10] Q. Chen, X. Liu, J. Zeng, Z. Cheng and Z. Liu, *Biomaterials*, 2016, **98**, 23-30.