

SUPPORTING INFORMATION

Bacteriochlorin-Diketopyrrolopyrrole Triad as Donor for Solution Processed Bulk Heterojunction Organic Solar Cells

Flavien Ponsot, Léo Bucher, Nicolas Desbois, Yoann Rousselin, Pritam Mondal, Charles H. Devillers, Anthony Romieu, Claude P. Gros, Rahul Singhal and Ganesh D. Sharma

Table of Contents

Synthesis of **diBr-BC**, **DPP-1** and **BC-DPP-1**

Figure S1. ^1H NMR spectrum of compound **DPP-1** in CDCl_3 (500 MHz)

Figure S2. ^1H NMR spectrum of triad **BC-DPP-1** in CDCl_3 (500 MHz)

Figure S3. MALDI-TOF mass spectrum (low resolution, positive mode) of triad **BC-DPP-1**

Figure S4. MALDI-TOF mass spectrum (high resolution, positive mode) of triad **BC-DPP-1**

Figure S5. ESI^+ mass spectrum (low resolution) of triad **BC-DPP-1**

Figure S6. Differential Pulse Voltammetry of **diBr-BC**, **TMS-DPP-1** and **BC-DPP-1**

X-Ray data analysis

Device fabrication

Synthesis of diBr-BC, DPP-1 and BC-DPP-1

Chemicals and instruments

Unless otherwise noted, all commercially available reagents and solvents were used without further purification. Tetraethylammonium tetrafluoroborate (TEABF₄) was purchased from Alfa Aesar and recrystallized in MeOH. TLC were carried out on Merck DC Kieselgel 60 F-254 aluminum sheets. The spots were directly visualized or through illumination with UV lamp ($\lambda = 254/365$ nm). Column chromatography purifications were performed on silica gel (40-63 μm and 63-200 μm) from Sigma-Aldrich (technical grade). Size-exclusion chromatography purifications were performed with Bio-Beads[®] S-X3 support (ca. 125 g for up to 200 mg of dye, 40 \times 450 mm bed) from Bio-Rad (#152-2750). CH₂Cl₂ (HPLC-grade, Biosolve) and THF (HPLC-grade, Biosolve) were dried over alumina cartridges using a solvent purification system PureSolv PS-MD-5 model from Innovative Technology and kept under argon. Dry TEA was obtained by distillation over CaH₂ and stored under argon on 3Å molecular sieves. The following compounds were prepared according to literature procedure: 3,13-dibromo-5-methoxy-8,8,18,18-tetramethyl-bacteriochlorin (**diBr-BC**) [CAS: 1006370-88-2],¹ TMS-ethynyl thienyl-DPP dye **TMS-DPP-1** [CAS: 1637582-58-1]² and **BC-DPP-1**.³

¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance 500 spectrometer. Chemical shifts are expressed in parts per million (ppm) from the residual non-deuterated CHCl₃ signal.⁴ *J* values are expressed in Hz. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer equipped with a universal ATR sampling accessory. The bond vibration frequencies are expressed in reciprocal centimeters (cm⁻¹). Low- and high-resolution mass spectra (LRMS and HRMS) were recorded either with a Bruker Daltonics Ultraflex II LRF 2000 mass spectrometer (MALDI-TOF, matrix: dithranol) or a Bruker Amazon SL instrument equipped with an electrospray (ESI) source or a Thermo Scientific MSQ Plus single quadrupole equipped with an ESI source (parameters for the ESI-MS analysis of **BC-DPP-1** triad: probe temperature: 350 °C, needle: 3.0 kV, detector: 1153 V and cone voltage: 200 V). UV-visible spectra were obtained on a Varian Cary 50 scan (single-beam) spectrophotometer by using a rectangular quartz cell (Hellma, 100-QS, 45 \times 12.5 \times 12.5 mm, pathlength: 10 mm, chamber volume: 3.5 mL).

Electrochemical measurements were performed in CH₂Cl₂ under an Ar atmosphere in a three-electrode glass cell. Working electrode (WE) was a platinum (Pt) disk ($\text{\O} = 1$ mm, surface area of about 0.785 mm²). A Pt wire was used as counter electrode (CE). Saturated aqueous calomel (SCE) was used as reference electrodes (RE). The RE was separated from the WE compartment by a double frit comprising an intermediate background solution (0.1 M TEABF₄ + CH₂Cl₂). All the potentials reported in this manuscript are indicated vs. SCE. In these conditions, when operating

in CH₂Cl₂ (0.1 M TEABF₄), the formal potential for the Fc⁺/Fc couple was found to be +0.53 V vs. SCE. All the electrochemical studies were performed using Autolab PGSTAT 302N potentiostat. Cyclic voltammetry experiments were performed at the scan rate of 100 mV/s.

Synthesis of functionalized DPP and BC-DPP triad

Ethynyl-functionalized thienyl-DPP [CAS: 1637582-59-2] **DPP-1**

DPP-1 was prepared as recently described in the literature³ (29.5 mg, 54 μmol, yield 90%). R_f = 0.38 (CH₂Cl₂/heptane 7 : 3, v/v); ¹H NMR (300 MHz, CDCl₃): δ 8.92 (dd, ³J = 4.1 Hz, ⁴J = 1.2 Hz, 1H), 8.79 (d, ³J = 4.1 Hz, 1H), 7.65 (dd, ³J = 5.0 Hz, ⁴J = 1.2 Hz, 1H), 7.38 (d, ³J = 4.1 Hz, 1H), 7.30-7.27 (m, 1H), 4.01 (m, 4H), 3.58 (s, 1H), 1.85 (m, 2H), 1.46-1.10 (m, 16H), 0.87 (m, 12H). Other spectroscopic data are identical to those reported by Yu *et al.*²

Synthesis of BC-DPP-1

Bacteriochlorin-DPP hybrid **BC-DPP-1** was prepared as recently described in the literature³ (10.6 mg, 7.1 μmol, yield 39%). ¹H NMR (500 MHz, CDCl₃): δ 9.10 (d, ³J = 4.0 Hz, 1H), 9.03 (d, ³J = 4.0 Hz, 1H), 8.95 (dd, ³J = 4.0 Hz, ⁴J = 1.2 Hz, 2H), 8.85 (s, 1H), 8.81 (d, ⁴J = 2.2 Hz, 1H), 8.78 (d, ⁴J = 2.2 Hz, 1H), 8.55 (s, 1H), 8.53 (s, 1H), 7.70 (d, ³J = 4.0 Hz, 1H), 7.66 (m, 3H), 7.30 (m, 2H), 4.49 (s, 3H), 4.43 (s, 4H), 4.11 (m, 8H), 2.11-2.00 (m, 4H), 1.96 (2s, 12H), 1.50-1.34 (m, 32H), 0.96-0.87 (m, 24H), -1.35 (s, 1H), -1.55 (s, 1H); LRMS (MALDI-TOF, positive mode): *m/z* = 1492.5 [M]⁺, calcd for C₈₉H₁₀₄N₈O₅S₄ 1492.7; HRMS (MALDI-TOF, positive mode): *m/z* = 1492.7085 [M]⁺, calcd for C₈₉H₁₀₄N₈O₅S₄ 1492.7007; LRMS (ESI, positive mode, cone voltage 200 V): *m/z* = 1492.9 (55), 1493.9 (100), 1496.0 (50) and 1497.0 (30) [M]⁺, calcd for C₈₉H₁₀₄N₈O₅S₄ 1492.7.

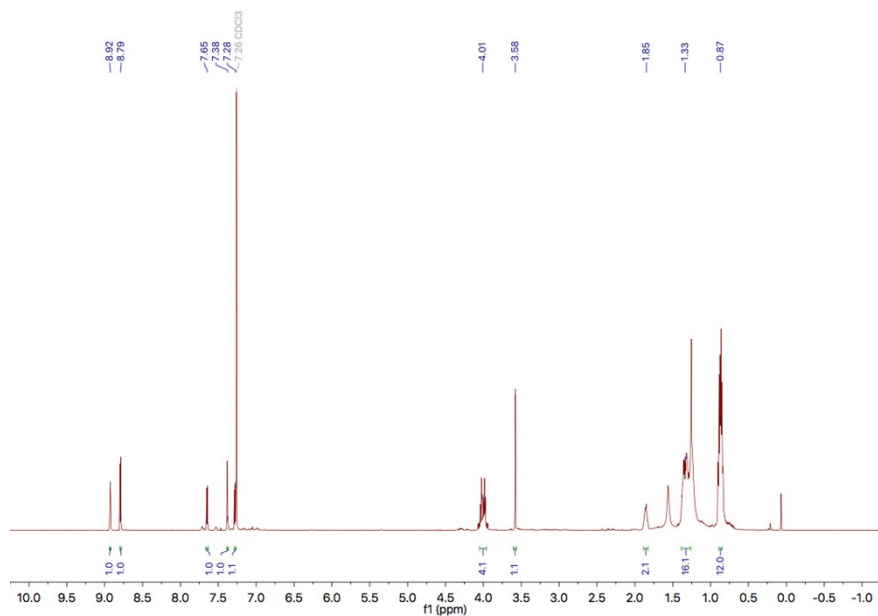


Fig. S1. ¹H NMR spectrum of compound **DPP-1** in CDCl₃ (500 MHz)

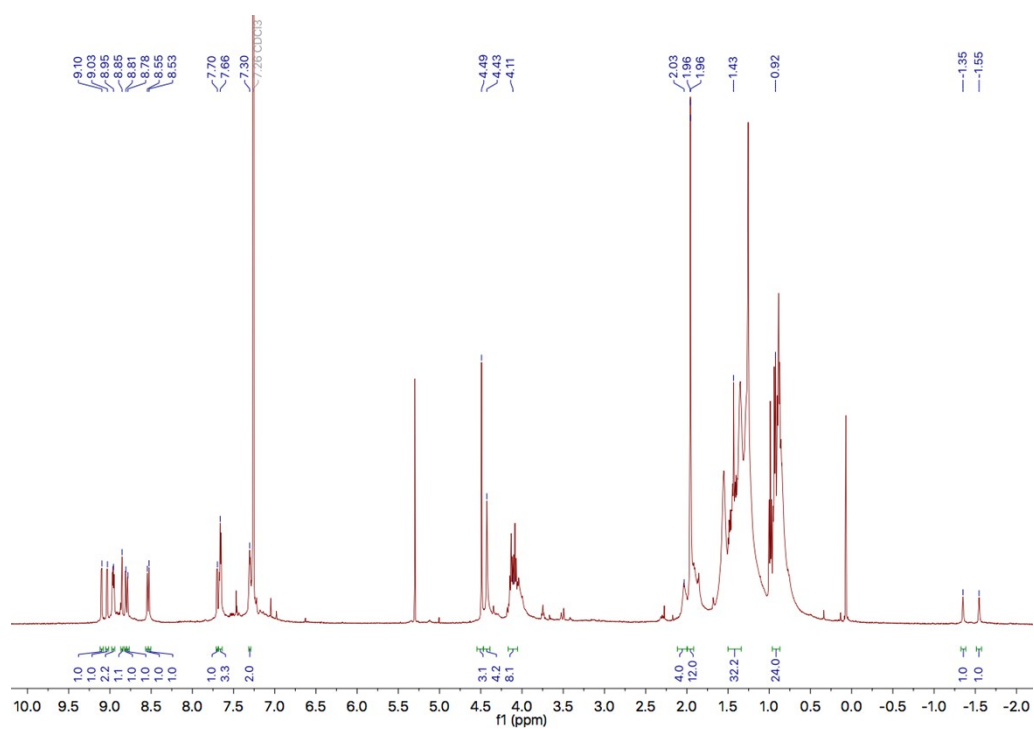


Fig. S2. ¹H NMR spectrum of triad **BC-DPP-1** in CDCl₃ (500 MHz)

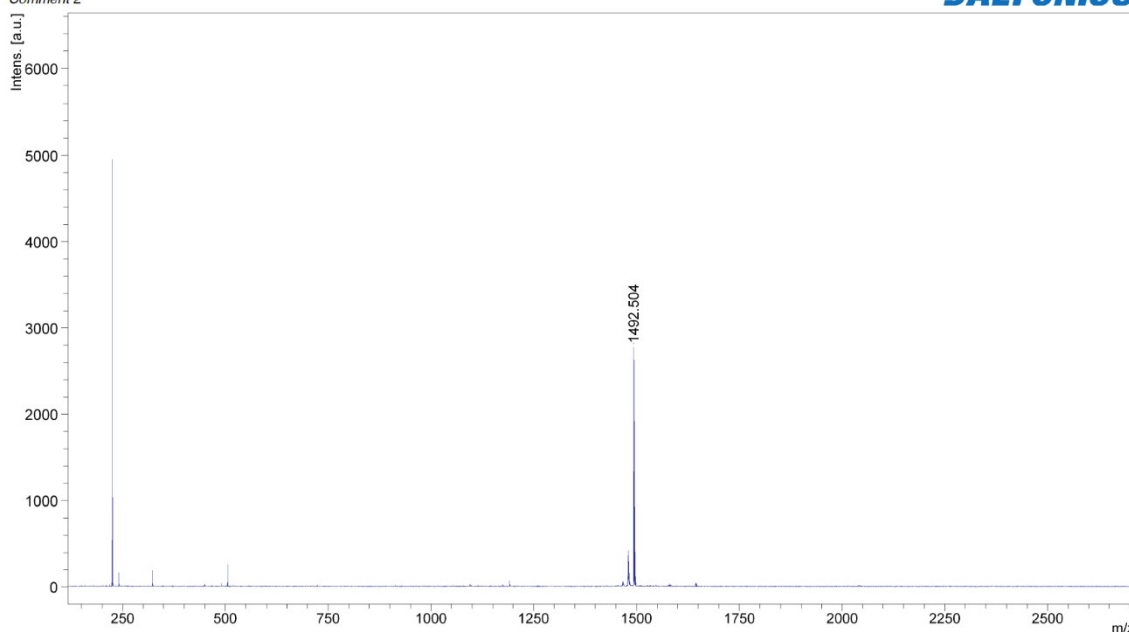


Fig. S3. MALDI-TOF mass spectrum (low resolution, positive mode) of triad **BC-DPP-1**

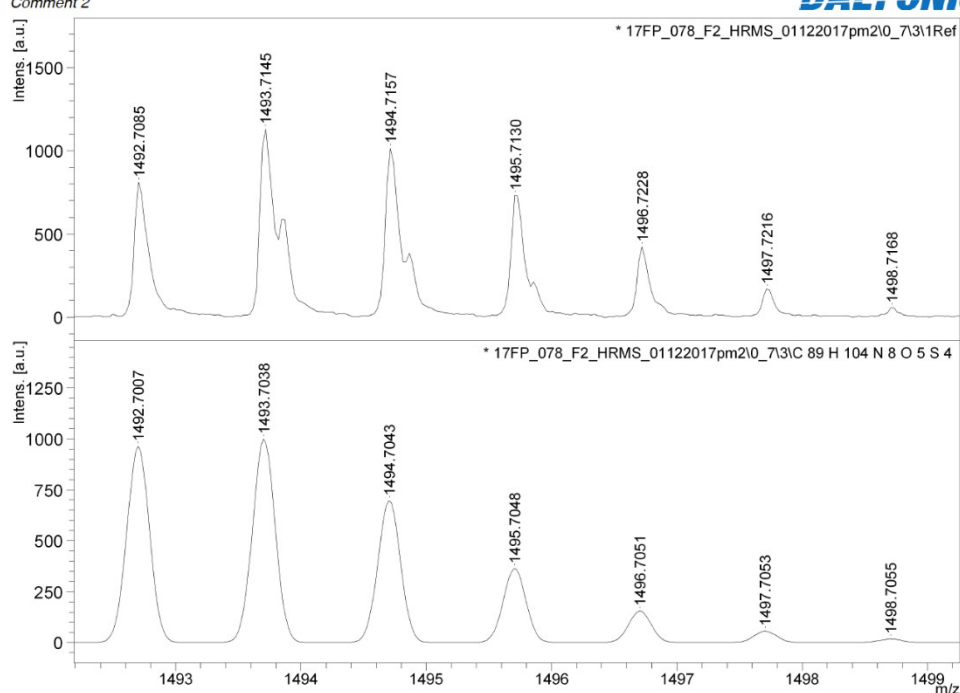


Fig. S4. MALDI-TOF mass spectrum (high resolution, positive mode) of triad **BC-DPP-1**

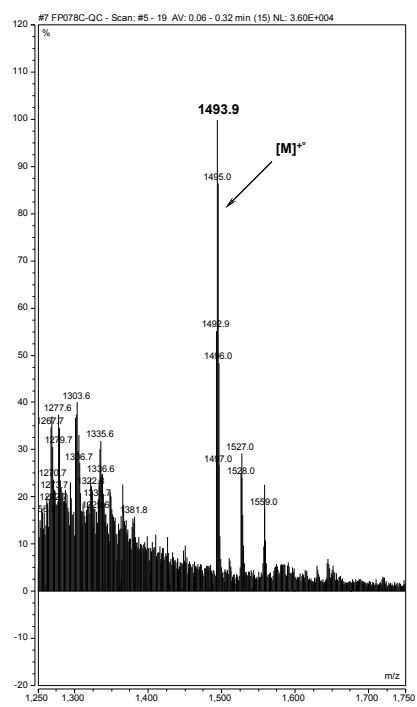


Fig. S5. ESI+ mass spectrum (low resolution) of triad **BC-DPP-1**

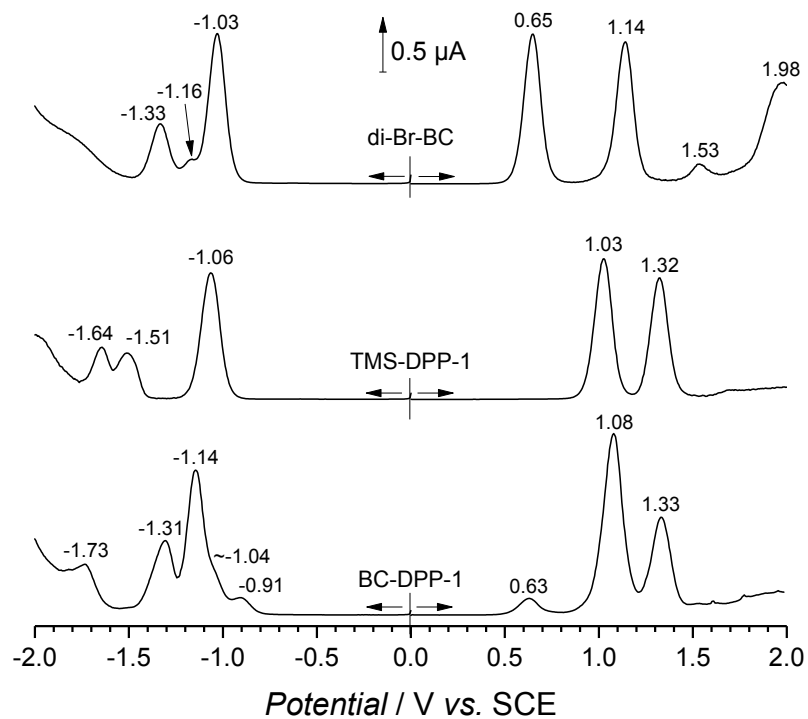
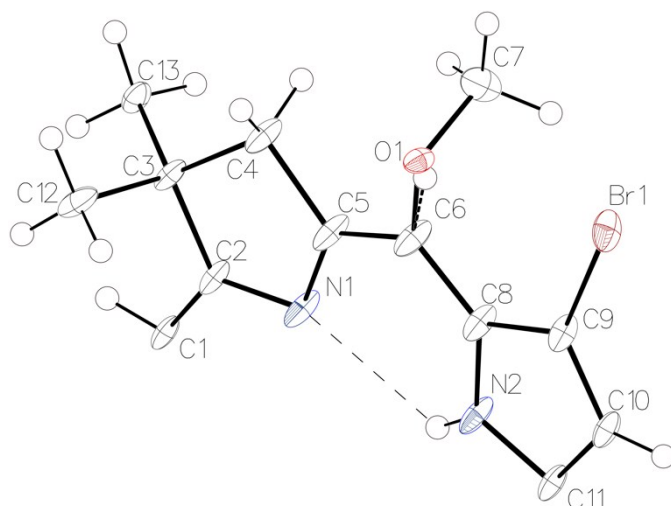


Figure S6. Differential Pulse Voltammetry (DPV) of **diBr-BC** ($C = 1.05 \times 10^{-3} \text{ M}$), **TMS-DPP-1** ($C = 1.10 \times 10^{-3} \text{ M}$) and **BC-DPP-1** ($C = 0.55 \times 10^{-3} \text{ M}$) in CH_2Cl_2 (+ 0.1 M TEABF_4) ($\nu = 10 \text{ mV}\cdot\text{s}^{-1}$, WE: Pt, $\varnothing = 1 \text{ mm}$).

Submitted by: **Flavien Ponsot**
 Solved by: **Yoann Rousselin**
 Sample ID: **20181113FP157C**

Crystal Data and Experimental



Experimental. Single clear dark violet prism-shaped crystals of **diBr-BC** were recrystallized from chloroform by slow evaporation. A suitable crystal 0.42x0.20x0.14 mm³ was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture (Mo) diffractometer. The crystal was kept at a steady $T = 100.0(1)$ K during data collection. The structure was solved with the **ShelXT**⁵ structure solution program using the Intrinsic Phasing solution method and by using **Olex2**⁶ as the graphical interface. The model was refined with version 2018/3 of **ShelXL**⁷ using Least Squares minimization.

Crystal Data. C₂₅H₂₆Br₂N₄O, $M_r = 558.32$, monoclinic, $I2/a$ (No. 15), $a = 18.3753(10)$ Å, $b = 5.8406(3)$ Å, $c = 21.3396(19)$ Å, $\beta = 92.947(2)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 2287.2(3)$ Å³, $T = 100.0(1)$ K, $Z = 4$, $Z' = 0.5$, $\mu(\text{MoK}\alpha) = 3.570$, 15003 reflections measured, 2629 unique ($R_{int} = 0.0372$) which were used in all calculations. The final wR_2 was 0.0729 (all data) and R_1 was 0.0302 ($I > 2(I)$).

Compound	diBr-BC
CCDC	1910052
Formula	C ₂₅ H ₂₆ Br ₂ N ₄ O
$D_{calc.}/\text{g cm}^{-3}$	1.621
μ/mm^{-1}	3.570
Formula Weight	558.32
Colour	clear dark violet
Shape	prism
Size/mm ³	0.42x0.20x0.14
T/K	100.0(1)
Crystal System	monoclinic
Space Group	$I2/a$
$a/\text{Å}$	18.3753(10)
$b/\text{Å}$	5.8406(3)
$c/\text{Å}$	21.3396(19)
$\alpha/^\circ$	90
$\beta/^\circ$	92.947(2)
$\gamma/^\circ$	90
$V/\text{Å}^3$	2287.2(3)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK α
$\theta_{min}/^\circ$	2.854
$\theta_{max}/^\circ$	27.552
Measured Refl.	15003
Independent Refl.	2629
Reflections with $I > 2I(I)$	>2165
R_{int}	0.0372
Parameters	160
Restraints	0
Largest Peak	0.561
Deepest Hole	-0.558
GooF	1.015
wR_2 (all data)	0.0729
wR_2	0.0682
R_1 (all data)	0.0423
R_1	0.0302

Structure Quality Indicators

Reflections:	d min (Mo)	0.77	I/σ	34.5	R _{int}	3.72%	complete	100%
Refinement:	Shift	-0.001	Max Peak	0.6	Min Peak	-0.6	Goof	1.015

A clear dark violet prism-shaped crystal with dimensions 0.42x0.20x0.14 mm³ was mounted on a MITIGEN holder oil. Data were collected using an Bruker D8 Venture (Mo) diffractometer equipped with an Oxford Cryosystems low-temperature device operating at $T = 100.0(1)$ K. Data were measured using ϕ and ω scans using MoK $_{\alpha}$ radiation. The total number of runs and images was based on the strategy calculation from the program **APEX3** (Bruker, 2015) The maximum resolution that was achieved was $\theta = 27.552^{\circ}$ (0.77 Å). The diffraction pattern was indexed The total number of runs and images was based on the strategy calculation from the program **APEX3** (Bruker, 2015) and the unit cell was refined using **SAINT** (Bruker, V8.38A, after 2013) on 7598 reflections, 51% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.38A, after 2013). The final completeness is 99.90 % out to 27.552° in θ . A multi-scan absorption correction was performed using **SADABS-2016/2** (Bruker, 2016) was used for absorption correction. $wR_2(\text{int})$ was 0.0847 before and 0.0528 after correction. The Ratio of minimum to maximum transmission is 0.7707. The absorption coefficient μ of this material is 3.570 mm⁻¹ at this wavelength ($\lambda = 0.711\text{Å}$) and the minimum and maximum transmissions are 0.379 and 0.491. The structure was solved and the space group $I2/a$ (# 15) determined by the **ShelXT**⁵ structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL**.⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. H atom on N2 nitrogen atom was located in the Fourier difference maps. His positional parameters was either refined freely with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. Methoxy group and hydrogen atom on beta carbon C6 were found disordered and S.O.F. were fixed at 50%. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

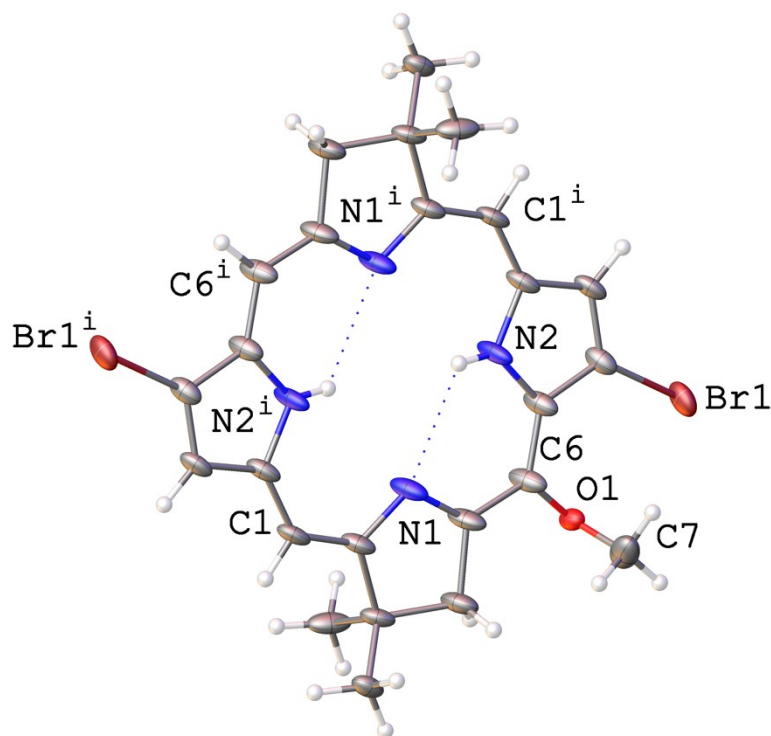


Figure 1: View of diBr-BC without disorder. Symmetry code used for generating equivalent atoms $i = 1-x, -y, 1-z$.

Table S1: Bond Lengths in Å for diBr-BC.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.871(2)	C3	C12	1.528(3)
N1	C2	1.358(3)	C3	C4	1.534(4)
N1	C5	1.348(3)	C9	C8	1.423(3)
N2	C11	1.376(3)	C8	C6	1.400(3)
N2	C8	1.365(3)	C5	C6	1.387(3)
C2	C1	1.371(3)	C5	C4	1.513(3)
C2	C3	1.533(3)	C6	O1	1.285(4)
C1	C11 ¹	1.393(3)	O1	C7	1.406(7)
C13	C3	1.521(3)	----		
C11	C10	1.413(3)	¹ 1-x,-y,1-z		
C10	C9	1.364(3)			

Table S2: Bond Angles in ° for diBr-BC.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N1	C2	108.4(2)	C10	C9	Br1	125.06(18)
C8	N2	C11	111.4(2)	C10	C9	C8	109.2(2)
N1	C2	C1	125.1(2)	C8	C9	Br1	125.79(18)
N1	C2	C3	112.6(2)	N2	C8	C9	105.3(2)
C1	C2	C3	122.2(2)	N2	C8	C6	125.4(2)
C2	C1	C11 ¹	129.6(2)	C6	C8	C9	129.3(2)
N2	C11	C1 ¹	126.7(2)	N1	C5	C6	125.5(2)
N2	C11	C10	106.3(2)	N1	C5	C4	112.5(2)
C1 ¹	C11	C10	127.0(2)	C6	C5	C4	122.0(2)
C9	C10	C11	107.8(2)	C5	C6	C8	127.3(2)
C2	C3	C4	100.59(18)	O1	C6	C8	117.6(2)
C13	C3	C2	114.29(19)	O1	C6	C5	114.6(2)
C13	C3	C12	110.22(19)	C5	C4	C3	102.9(2)
C13	C3	C4	112.5(2)	C6	O1	C7	106.9(4)
C12	C3	C2	107.8(2)	----			
C12	C3	C4	111.0(2)	¹ 1-x,-y,1-z			

Table S3: Torsion Angles in ° for diBr-BC.

Atom	Atom	Atom	Atom	Angle/°
Br1	C9	C8	N2	179.69(19)
Br1	C9	C8	C6	-0.7(4)
N1	C2	C1	C11 ¹	3.7(4)
N1	C2	C3	C13	136.3(2)
N1	C2	C3	C12	-100.8(3)
N1	C2	C3	C4	15.5(3)
N1	C5	C6	C8	-1.0(5)
N1	C5	C6	O1	-172.6(3)
N1	C5	C4	C3	14.2(3)
N2	C11	C10	C9	-0.6(3)
N2	C8	C6	C5	1.2(5)
N2	C8	C6	O1	172.6(3)
C2	N1	C5	C6	175.9(3)
C2	N1	C5	C4	-4.6(3)
C2	C3	C4	C5	-16.2(2)
C1	C2	C3	C13	-47.7(3)
C1	C2	C3	C12	75.2(3)
C1	C2	C3	C4	-168.5(2)
C1 ¹	C11	C10	C9	176.6(2)
C13	C3	C4	C5	-138.3(2)
C11	N2	C8	C9	-0.4(3)

Atom	Atom	Atom	Atom	Angle/°
C11	N2	C8	C6	179.9(3)
C11	C10	C9	Br1	-179.33(18)
C11	C10	C9	C8	0.3(3)
C10	C9	C8	N2	0.1(3)
C10	C9	C8	C6	179.7(3)
C3	C2	C1	C11 ¹	-171.7(2)
C9	C8	C6	C5	-178.3(3)
C9	C8	C6	O1	-7.0(5)
C8	N2	C11	C1 ¹	-176.6(2)
C8	N2	C11	C10	0.6(3)
C8	C6	O1	C7	98.8(4)
C5	N1	C2	C1	176.8(2)
C5	N1	C2	C3	-7.4(3)
C5	C6	O1	C7	-88.7(4)
C6	C5	C4	C3	-166.3(3)
C12	C3	C4	C5	97.7(2)
C4	C5	C6	C8	179.5(3)
C4	C5	C6	O1	7.9(4)

¹1-x,y,1-z

Table S4: Hydrogen Bond information for **diBr-BC**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N2	H2	N1	0.77(3)	2.42(3)	2.926(3)	124(3)

Table S5: Atomic Occupancies for all atoms that are not fully occupied in **diBr-BC**.

Atom	Occupancy
H6	0.5
O1	0.5
C7	0.5
H7A	0.5
H7B	0.5
H7C	0.5

Device fabrication

The BHJ solar cells were prepared in an ITO/PEDOT:PSS/active layer/PFN/Al configuration. Firstly, ITO-coated glass substrates were ultrasonically cleaned for 10 min each with deionized water, acetone, ethanol and iso-propanol, successively and then dried. The PEDOT:PSS solution was spin-coated onto the pre-clean ITO substrates at 2000 rpm followed by baking at 120 °C for 15 min in air. The BC-DPP-1 and PC₇₁BM with different weight ratios (1:1, 1:1.5, 1:2 and 1:2.5) with same concentration of 14 mg/mL, were dissolved in chloroform (CF) to make the blend for a BHJ layer. In order to get the thin active layer the solution was deposited by spin-coating on top of the PEDOT:PSS layer at 2500 rpm for 60 s and then dried at 40 °C for 10 min. The ternary blend was prepared by keeping the weight of PC₇₁BM constant and varying the weight ratio between **BD-DPP-1** and SM1 in chloroform. For the solvent additive (SA) and solvent vapor annealing (SVA) treatment, the optimized ternary and binary active layer were prepared in 97 v% CF + 3 v% pyridine and subsequently SVA in THF environment 40s. The thickness of the active layer is about 90 ± 5 nm. The methanolic solution of polyelectrolyte interlayer poly[9,9-bis(3'-(N,N-dimethylamino)-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) (2 mg/mL) in the presence of a trace amount of acetic acid (~2 µl mL⁻¹) was spin-coated on top of the BHJ layer at 3000 rpm for 30 s. Finally, aluminium top electrode was deposited by thermal evaporation at 2.0x10⁻⁵ Pa. The active area of the devices was about 16 mm². All devices were prepared and tested in an ambient atmosphere without encapsulation. The current–voltage (*J–V*) characteristics of the BHJOSCs were measured with a computer controlled Keithley 2400 source meter in the dark and under a simulated AM 1.5G illumination of 100 mW /cm². A xenon light source attached with the optical filter was used to give the stimulated irradiance. The IPCE spectra of the OSCs was measured using Bentham PVE 300 EQE system. The hole-only (ITO/PEDOT:PSS/active layer/Au and electron-only (ITO/Al/active layer/Al) devices were prepared to measure the hole and electron mobility, respectively.

Table S6 Photovoltaic parameters of the OSCs based on BC-DPP-1:xSM1:PC₇₁BM (TSA) active layers

x	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
10 %	15.08	0.87	0.64	8.39
20 %	15.81	0.87	0.66	9.08
30 %	16.28	0.88	0.68	9.74
40 %	16.13	0.88	0.67	9.51
50 %	15.08	0.86	0.66	8.56
100 %	14.05	0.85	0.62	7.40

References :

- (1) Krayer, M.; Ptaszek, M.; Kim, H.-J.; Meneely, K. R.; Fan, D.; Secor, K.; Lindsey, J. S. Expanded Scope of Synthetic Bacteriochlorins via Improved Acid Catalysis Conditions and Diverse Dihydrodipyrin-Acetals. *J. Org. Chem.* **2010**, *75* (4), 1016-1039, DOI: 10.1021/jo9025572.
- (2) Yu, C.; Liu, Z.; Yang, Y.; Yao, J.; Cai, Z.; Luo, H.; Zhang, G.; Zhang, D. New dithienyl-diketopyrrolopyrrole-based conjugated molecules entailing electron withdrawing moieties for organic ambipolar semiconductors and photovoltaic materials. *J. Mater. Chem. C* **2014**, *2* (47), 10101-10109, DOI: 10.1039/c4tc01872a.
- (3) Ponsot, F.; Desbois, N.; Bucher, L.; Berthelot, M.; Mondal, P.; Gros, C. P.; Romieu, A. Near-infrared emissive bacteriochlorin-diketopyrrolopyrrole triads: Synthesis and photophysical properties. *Dyes Pigm.* **2019**, *160*, 747-756.
- (4) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176-2179, DOI: 10.1021/om100106e.
- (5) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *71* (1), 3-8, DOI: doi:10.1107/S2053229614024218.
- (6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42* (2), 339-341, DOI: doi:10.1107/S0021889808042726.
- (7) Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *71* (1), 3-8, DOI: doi:10.1107/S2053273314026370.