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Supporting Information

Design and mesomorphism of a triskelion shape-persistent HBC-TP hybrid : 2,8,14-tris(triphenylen-2-

yl)hexabenzocoronene

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1. Materials and Equipment

All commercially available starting materials were used directly without further purification. The solvents of air- and moisture-sensitive reactions were carefully distilled from appropriate drying agents before use.

¹H/¹³C NMR spectra were recorded using a Varian UNITY INOVA 400/100 MHz or Bruker 600 MHz spectrometer in CDCl₃, and TMS as the internal standard. High-resolution mass spectra (HRMS) spectra were recorded at the Bruker Fourier Transform High Resolution Mass Spectrometry (solariX XR) with MALDI as the ion source. Elemental analyses (EA) were performed on a Vario Micro Select (Elementar company, German).

The thermal gravimetrical analysis (TGA) was measured on a TA-TGA Q500 instrument with heating rate of 20°C/min in N₂ atmosphere. The phase transition temperatures and enthalpy changes were investigated using a TA-DSC Q100 differential scanning calorimeter (DSC) under N₂ atmosphere with heating or cooling rate of 10 °C/min. Liquid crystalline optical textures were observed and recorded on an Olympus BH2 Polarized Optical Microscope (POM) equipped with a Mettler FP82HT hot-stages of which temperatures were controlled by a XPR-201 and Mettler FP90. Temperature-variation SAXS (small-angle X-ray scattering) and WAXS (wide-angle X-ray scattering) experiments on Rigaku Smartlab X-Ray Diffractometer with TCU 110 temperature controller, while the sample temperature was controlled within ±1 K and the X-ray sources (Cu K α , λ =0.154 nm) were provided by 40 kW ceramic tubes.

UV/Vis. Absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer at room temperature. Fluorescence was measured on a HORIBA Fluoromax-4p, and the quantum yields were measured by a HORIB-F-3029 Integrating Sphere, Horiba, Kyoto, Japan. A suitable crystal was selected on a XtaLab Synergy R, DW system, HyPix diffractometer. The crystal was kept at 300.2(7) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

For DFT computation, the B3LYP-D3 method was used, with selected basis set of 6-311g(d,p). The energetically favorable molecular conformation in gas phase obtained via optimizing geometrical molecular structures and frequency calculation.

Cyclic voltammetry (CV) experiments were recorded on an Autolab PGSTAT302 voltammetric analyser and performed at room temperature in dry THF solutions containing 0.1 M tetran-butylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte at a scan rate of 50 mV s⁻¹. A three-electrode configuration consisting of a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/Ag+ (with a saturated AgNO₃ solution) couple reference electrode was used. The ferrocene/ferrocenium (Fc/Fc⁺) couple was used as the internal reference and showed a peak at +0.48 V vs. Ag/AgCl. Prior to experiments, the system was purged with purified nitrogen gas to exclude dissolved oxygen from the solution.

2. Synthesis

2.1 Synthesis of TP8/2-Bpin

This compound was prepared in 6 steps according to literature methods (Scheme S1)¹



Scheme S1. Synthesis of TP8/2-Bpin.

Compound **a.** In a 250 mL round-bottomed flask, 4-bromo-1,2-dimethoxybenzene (10 g, 4.6 mmol) in CH_3NO_2 (5 mL) and CH_2Cl_2 (20 mL) were weighed, and FeCl₃ (14.95 g, 9.2 mol) added, and the mixture reacted for 1 h at room temperature. Methanol was slowly added dropwise to the reaction system while stirring at -10 °C, until the solution showed earthy yellow color. Then, 20 mL of water was added, and the extraction was carried out by using a dispensing funnel and DCM. The solution was concentrated under reduced pressure, and the residue dried in a vacuum drying oven. Recrystallization was carried out in ethanol and ethyl acetate to yield 2,2'-dibromo-4,4',5,5'-tetramethoxy-1,1'-biphenyl as a pink flocculent compound (7.5 g, yield 75.5%). ¹H NMR (400 MHz, CDCl₃) δ 7.10 (s, 2H, ArH), 6.75 (s, 2H, ArH), 3.90 (s, 6H, OCH₃), 3.85 (s, 6H, OCH₃).

Compound **b**. In a 500 mL round-bottomed flask, compound **a** (16 g, 0.038 mol) in cold THF (100 mL) was reacted with *n*-BuLi (50 mL) at -78 °C for 24 h. The reaction was quenched by slow addition of MeOH at -40 °C while stirring, until the solution appeared milky white. Then, 50 mL of water was added, the compound was extracted in DCM, concentrated under reduced pressure, and dried in a vacuum drying oven. Recrystallization was carried out with methanol to yield 3,3',4,4'-tetramethoxy-1,1'-biphenyl as a pale-yellow powder (8.43 g, yield 84.3%). ¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.03 (m, 4H, ArH), 6.91 (d, *J* = 8.2 Hz, 2H, ArH), 3.92 (d, *J* = 14.5 Hz, 12H, OCH₃).

Compound **c**. In a 250 mL round-bottomed flask, compound **b** (2 g, 0.0073 mol), 2-methoxybromobenzene (2.34 g, 0.01 mol), DCM (25 mL), FeCl₃ (7 g, 0.022 mol), and CH₃NO₂ (5 mL) were mixed and reacted at room temperature for 4 h. Methanol was slowly added dropwise to the reaction system at -40 °C while stirring until a purple-black solid appeared. Then, water (50 mL) was added, and the solid filtrated using a Brinell's funnel, and dried in a vacuum drying oven, to yield a purple-black granular solid, 2-bromo-3,6,7,10,11-pentamethoxytriphenylene (2.67 g, 80.0%). ¹H NMR (400 MHz, DMSO) δ 10.46 (s, 1H, ArH), 8.82 (s, 1H, ArH), 7.93 (dd, *J* = 57.4, 50.1 Hz, 3H, ArH), 7.07 (d, *J* = 73.6 Hz, 1H, ArH), 3.91 (dd, *J* = 82.3, 15.9 Hz, 12H, OCH₃), 3.34 (s, 7H, CH₃). Compound **d**. In a 100 mL reaction tube, compound **c** (3.10 g, 6.99 mmol) was weighed and dissolved in DCM (25 mL), filled with argon. BBr₃ (8.76 g, 34.97 mmol) was slowly injected at -78 °C, then the reaction was warmed to room temperature (~12 h). The reaction mixture was slowly poured into a beaker with ice, stirred (30 min) until a purple-black solid precipitated. The solid was filtered using a funnel, rinsed with distilled water and dried. Finally, 2.4 g of the purple-black granular solid 2-bromo-3,6,7,10,11-penta(hydroxy)triphenylene was isolated (89%). ¹H NMR (400 MHz, DMSO) δ 8.40 (d, *J* = 3.9 Hz, 1H, ArH), 7.82 (d, *J* = 4.0 Hz, 1H, ArH), 7.76 (d, *J* = 4.4 Hz, 1H, ArH), 7.68 (d, *J* = 4.3 Hz, 1H, ArH), 7.64 (t, *J* = 5.2 Hz, 2H, ArH), 3.53 (s, 5H, OH).

Compound **TP**8/2. In a 250 mL round-bottomed flask, compound **d** (1.00 g, 0.0026 mol), 1-bromo-3,7dimethyloctane (3.43 g, 0.015 mol), K_2CO_3 (5.35 g, 0.039 mol), and zinc powder (1.45 g, 0.0221 mol) were weighed, and N,N-dimethylformamide (ca. 50 mL) was added, and the reaction was refluxed at 100 °C for 24 h. The reaction mixture was poured in a 250 mL beaker with an appropriate amount of ice, and dilute hydrochloric acid was slowly added until acid pH. The product was extracted by filtration using a Büchner funnel and then dried using a vacuum drying oven. Separation and purification was carried out using silica gel column chromatography (eluent: V_{DCM} : $V_{PE} = 1 : 3$), and crystallization was carried out in ethanol and ethyl acetate to yield a light yellow solid powder (1.27 g, yield 45%). ¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 1H), 7.86 (s, 1H), 7.81 (s, 4H), 4.28 (s, 10H), 2.00 (s, 5H), 1.85 – 1.70 (m, 10H), 1.58 – 1.51 (m, 5H), 1.42 – 1.15 (m, 30H), 1.04 (t, *J* = 5.3 Hz, 15H), 0.88 (dd, *J* = 6.6, 2.4 Hz, 30H).

TP8/2-Bpin. In a 50 mL reaction tube, **TP**8/2 (2.08 g, 0.0019 mol), B_2pin_2 (1.03 g, 0.0041 mmol), PdCl₂(dppf) (152.6 mg, 0.1869 mmol) in CH₂Cl₂ and CH₃COOK (0.59 g, 0.0060 mmol) were weighed, and 15 mL of dry 1,4-dioxane added at -78 °C under argon protection to remove oxygen, and then the reaction placed at 90 °C for 24 h. Extraction, concentration and drying were carried out, and pure target compound was finally obtained as a yellow solid by silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 1:2), and crystallization from ethanol and ethyl acetate (1.50 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.07 (s, 1H), 7.92 (s, 1H), 7.84 (d, *J* = 4.1 Hz, 2H), 7.81 (s, 1H), 4.39 – 4.25 (m, 11H), 2.01 (s, 6H), 1.77 (s, 12H), 1.55 (s, 7H), 1.45 – 1.12 (m, 36H), 1.07 – 1.00 (m, 16H), 0.88 (d, *J* = 6.6 Hz, 30H).

2.2 Synthesis of 2,8,14-triiodohexabenzo[bc,ef,hi,kl,no,qr]coronene, HBC-3I

This compound was prepared according to literature methods (Scheme S2).²

Synthesis of 1,3,5-tris(2'-bromophenylbenzene), **e**. 2-Bromoacetophenone (5 g, 25 mmol) and trifluoromethanesulfonic acid 10 mol% were stirred at 130 °C until complete conversion of the starting material (7 h). The resulting black solution was cooled to room temperature and quenched by addition of water. The mixture was then extracted with CH_2Cl_2 , the organic layer was washed with water and saturated saline, and dried over MgSO₄. The solvent was removed in vacuum and purified by column chromatography (silica gel, V_{PE} : V_{DCM} = 6:1) to give yellow powder **e** (3.3 g, yield: 73%). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 3H), 7.51 (s, 3H), 7.46 (d, J = 7.6 Hz, 3H), 7.38 (t, J = 8.0 Hz, 3H), 7.22 (t, J = 7.7 Hz, 3H).

Synthesis of 1,3,5-tris[3"-(trimethylsilyl)-2'-biphenyl]benzene, **f. e** (400 mg, 0.737 mmol), 3-(trimethylsilyl)phenylboronic acid (515 mg, 2.652 mmol), Pd(PPh₃)₄ (26 mg, 3 mol%), K₂CO₃ (1.02 g), in toluene (25 mL), ethanol (6 mL), and water (6 mL) were added to a 50 mL reaction tube. The mixture was degassed by two "freeze-pump-thaw" cycles and then heated to reflux under argon overnight. After purification by column chromatography (silica gel, V_{PE} : V_{DCM} = 10:1), a white solid, **f**, was obtained (514 mg, 93% yield). 1H NMR (400 MHz, CDCl3) δ 7.44 (d, J = 7.3 Hz, 1H), 7.37 (s, 2H), 7.35 (s, 1H), 7.33 (s, 1H), 7.32 (s, 1H), 7.25 - 7.20 (s, 1H), 7.30 - 7.31 (s, 1H). 7.25 - 7.20 (m, 2H), 6.89 (d, J = 7.7 Hz, 1H), 6.70 (s, 1H), 6.63 (d, J = 8.1 Hz, 1H), 0.18 (s, 9H).



Scheme S2. Synthesis of HBC-3I.

Synthesis of 1,3,5-tris(3"-iodo-2'-biphenyl)benzene, **g**. **f** (500 mg, 0.665 mmol) was dissolved in CHCl₃ (130 mL) and the solution degassed by argon bubbling for 20 min. Then, iodine monochloride (2.4 mL, 1.0 M CH₂Cl₂) was slowly added. After stirring for 1 h, sodium sulfite solution was added. The organic layer was washed three times with water and dried with MgSO₄. The solution was concentrated to 10 mL and 100 mL of methanol was added to precipitate the product. The white solid was collected and dried under vacuum to give the white solid **g** (564 mg, 93% yield). 1H NMR (400 MHz, CDCl3) δ 7.62 (s, 1H), 7.35 (s, 2H), 7.03 (t, J = 7.9 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.82 (d, J = 6.4 Hz, 1H), 6.77 (d, J = 6.4 Hz, 1H), 6.81 (d, J = 6.4 Hz, 1H), 6.82 (d, J = 6.4 Hz, 1H).

Synthesis of **HBC-3I**. **g** (100 mg, 0.184 mmol) was dissolved in dichloromethane (80 mL), the solution degassed by argon bubbling for 20 min, and then $FeCI_3$ (1.08 g) in CH_3NO_2 (4 mL) added dropwise. After stirring for 1 h, the reaction was quenched by the addition of methanol (100 mL), and dried under vacuum to obtain yellow powder **HBC-3I** (76 mg, 76% yield). This compound is insoluble and NMR could not be recorded. This compound was used as it is in the next reaction.

2.3 Synthesis of HBC-3TP

In a 50 mL reaction tube, **TP**8/2-Bpin (757 mg, 0.67 mmol), Pd(PPh₃)₄ (20 mg, 0.015 mmol), K₂CO₃ (306 mg, 2.3 mmol) and 2,8,14-triiodohexabenzocoronene (**HBC-3I**, 100 mg, 0.11 mmol) were mixed in toluene (20 mL), ethanol (5 mL) and water (5 mL). Under the protection of argon, the reaction mixture was stirred at 90 °C for 72 h. After the reaction was complete, the solid residue was purified by flash chromatography column (silica gel, V_{PE} : V_{DCM} = 1:1), and crystallized from EtOH and AcOEt (1:1), yielding yellow solid **HBC-3TP** (121 mg, yield 31%). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 11.3 Hz, 4H), 7.97 – 7.83 (m, 17H), 7.72 (d, *J* = 7.5 Hz, 3H), 7.50 (t, *J* = 7.6 Hz, 3H), 7.43 – 7.38 (m, 2H), 7.22 (d, *J* = 10.7 Hz, 3H), 5.29 (s, 1H), 4.34 – 4.19 (m, 30H), 2.01 (d, *J* = 7.3 Hz, 15H), 1.78 (s, 28H), 1.56 (dt, *J* = 13.3, 6.7 Hz, 19H), 1.40 – 1.15 (m, 93H), 1.03 (p, *J* = 5.9 Hz, 40H), 0.95 (d, *J* = 6.3 Hz, 6H), 0.89 (d, *J* = 6.4 Hz, 84H). HRMS (ESI) calcd for C₂₄₆H₃₄₈O₁₅ [M]⁺ m/z = 3544.6535 (100.0%), 3543.6502 (75.5%), 3545.6569 (73.1%), found 3544.6538, 3543.6512, 3545.6578. Elemental Analysis (C₂₄₆H₃₄₈O₁₅, MW 3545.47, %): calc. C

3. NMR



Figure S2. ¹H NMR (CDCl₃, 400 MHz) spectrum of **b**.



Figure S3. ¹H NMR (CDCl₃, 400 MHz) spectrum of **d**.



Figure S4. ¹H NMR (CDCl₃, 400 MHz) spectrum of TP8/2.



Figure S6. ¹H NMR (CDCl₃, 400 MHz) spectrum of e.



Figure S7. ¹H NMR (CDCl₃, 400 MHz) spectrum of f.



Figure S8. ¹H NMR (CDCl₃, 400 MHz) of g.



Figure S9. ¹H NMR (CDCl₃, 40 MHz) of HBC-3TP at 55 °C.



4. HRMS



Figure S11. HRMS m/z (ESI) spectrum of HBC-3TP.

5. TGA and DSC

Table S1. Decomposition temperatures at various percentage losses of HBC-3TP

Compound	T _{dec1%} /°C	T _{dec2%} /°C	T _{dec5%} /°C
HBC-3TP	242	289	336

 T_{dec} . (Temperature with 1%, 2% and 5% weight-loss) were obtained by TGA measurements with heating rate of 10 °C/min in nitrogen.

Table S2. HBC-3TP thermal data (transition temperatures and enthalpy of phase transition)

Compound	2nd heating [1st cooling] /°C (∆H, kJ·mol ⁻¹)
HBC-3TP	Col _{rec} 288 (7.08) I [I 261 (-17.37) Col _{rec}]

I: isotropic phase; Col_{rec}: columnar rectangular mesophase.

6. S/WAXS



Figure S12. S/WAXS patterns of HBC-3TP recorded at various temperatures, on both heating (top) and on cooling (bottom).

Table S3. S/WAXS patterns indexation of the mesophase of HBC-3TP recorded on cooling at 200°C.

$2\theta_{meas.}$ ^[a]	d _{meas.} [a]	d _{calc.} ^[a]	$2\theta_{calc.}^{[a]}$	Intensity ^[b]	Indexation ^{[c}]	Mesophases
2 123	36.43	36.43	2 123	S (ch)	11	Col
2.425	30.43	30.43	2.423		11	
2.896	30.48	30.32	2.911	VS (br)	21	a = 94.92 A
3.720	23.73	23.73	3.720	S (sh)	40	b = 39.45 Å
4.850	18.20	18.21	4.848	S (sh)	22	S = 3744.59 Ų
5.635	15.67	15.82	5.581	M (sh)	60	
5.845	15.11	15.17	5.821	VW (sh)	42	
6.078	14.53	14.68	6.015	M (sh)	61	
6.457	13.68	13.68	6.455	M (sh)	52	
7.296	12.10	12.14	7.275	VW (sh)	33	
7.440	11.87	11.86	7.447	W (sh)	80	
7.791	11.34	11.36	7.776	W (sh)	81	
8.30	10.64	10.80	8.179	W (sh)	53	
8.58	10.29	10.19/10.16	8.670/8.696	W (sh)	91/82	
8.87	9.96	9.86	8.961	W (sh)	04	
10.13	8.72	8.75	10.100	VW (sh)	54	
12.93	6.84	6.82/6.84	12.970/12.931	VW (sh)	75/104	
17.75	4.99	-		S (br)	h _{ch}	
22.57	3.94	-		S (sh)	h _π	

[a] $2\theta_{meas.}$ and $2\theta_{calc.}$: Experimentally measured and theoretically calculated diffraction angle for each reflection (°); $d_{meas.}$ and $d_{calc.}$: experimentally measured and theoretically calculated d-spacing (Å); [b] Intensity and shape of the reflection: VS, S, M, W, VW stand for very strong, strong, medium, weak, very weak; sh and br stand for sharp and broad peak, respectively; [c] *hk*: Miller indexation; h_{ch} and h_{π} : average distance between molten chains and average π - π stacking; [d] a,b, S: lattice parameters and area.

 Table S4. HBC-3TP mesophase and molecular parameters at various temperatures.

T	V _{mol}	ρ	χar	N _{mol}	S	h _{mol}	h_{π}	ξ
250	6980±400	0.85±0.05	20.9	2	3745	3.73±0.20	4.03	31
200	6550±250	0.90±0.03	22.3	2	3745	3.50±0.15	3.94	77
150	6185±140	0.93±0.02	23.6	2	3688	3.35±0.08	3.86	78
100	5880±70	1.00 ± 0.01	24.8	2	3643	3.23±0.04	3.79	81
50	5640±20	1.04±0.00	25.9	2	3611	3.12±0.01	3.77	80

 V_{mol} : molecular volume (Å³); ρ: molecular density (g. cm⁻³); χ_{ar} : aromatic volume fraction ($\chi_{ar} = V_{ar}/V_{mol}$); N_{mol}: number of molecules (motifs)/per lattice unit (N_{mol} = N_{Col}, number of columns per lattice = 2); h_{mol}: molecular thickness, h_{mol} = N_{mol}×V_{mol}/S; h_π: stacking $\pi-\pi$ interactions; ξ : stacking correlation length (Å), calculated from the Scherrer equation with shape factor K = 0.9.



Figure S13. Representation of the columns with a triskelion cross-section.

7. DFT







Figure S15. DFT calculated optimized molecular structures (top and side-views) of **HBC-3TP** methoxy homolog.

Table S5. List of selected molecular orbital energies for **HBC-3TP** and their HOMO-LUMO energy gaps ($\triangle E$).

	HOMO-2	HOMO-1	НОМО	ΔE	LUMO	LUMO+1	LUMO+2
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
HBC-3TP	-5.41	-5.29	-5.28	3.39	-1.89	-1.88	-1.68



HBC-TP3

Figure S16. Comparison of electronic properties (energy levels, frontier orbitals (HOMO and LUMO)) of **HBC-3TP**



Figure S17. Partial molecular orbital diagram for **HBC-3TP** with some selected isodensity frontier molecular orbital mainly involved in the electronic transitions. All the DFT energy values are given in electronvolts. The arrows are intended to highlight the HOMO-LUMO energy gaps.

λ_{abs}/nm	ΔE/eV	f	Transitions (Percentage Contribution)
445.4	2.78	0.0010	H→L+1(+39%), H-1→L(+37%), H-1→L+1(+26%)
428.3	2.89	0.0031	H→L(+41%), H-1→L(+27%), H→L+1(+26%)
401.6	3.09	1.6345	H-1→L+1(+45%), H→L(+42%), H→L+1(+16%)
400.7	3.09	1.4662	H→L+1(+44%)
395.1	3.14	0.0038	H→L+2(+60%), H-7→L(+16%), H-2→L+1(+14%)
394.3	3.14	0.0219	H-1→L+2(+58%), H-2→L(+26%)
387.7	3.20	0.0002	H-2→L(+59%), H→L+2(+16%)
386.1	3.21	0.0028	H-2→L+1(+60%), H-3→L(+19%), H→L(+11%)
385.4	3.22	0.0157	H-4→L(+46%), H-1→L+1(+13%)
383.9	3.23	0.0443	H-3→L(+45%), H-4→L+1(+32%), H-4→L(+16%)
379.7	3.27	0.3693	H-3→L+1(+50%), H-4→L(+43%)
379.4	3.27	0.4186	H-4→L+1(+54%), H-4→L+2(+13%)
366.1	3.39	0.0492	H-5→L(+65%)
364.6	3.40	0.0008	H-5→L+1(+62%)
362.5	3.42	0.0046	H-2→L+2(+59%), H-3→L(+17%), H-7→L(+14%)
360.1	3.44	0.0049	H-3→L+2(+43%), H→L+2(+17%), H-8→L+1(+17%)
359.9	3.45	0.0390	H-6→L(+38%), H-2→L+2(+29%), H-8→L(+16%)
358.3	3.46	0.1079	H-6→L+1(+61%), H-6→L(+16%)
357.7	3.47	0.0432	H-6→L(+48%), H-7→L(+25%), H-5→L+1(+22%)
355.9	3.48	0.0522	H-3→L+2(+39%), H-7→L+1(+31%), H-7→L(+22%)
355.8	3.48	0.0436	H-4→L+2(+46%), H-7→L+1(+32%), H-3→L+2(+21%)
351.9	3.52	0.0821	H→L+3(+56%), H-1→L+3(+21%), H-2→L+3(+12%)
351.0	3.53	0.1010	H-1→L+3(+57%), H-8→L(+11%)
348.9	3.55	0.0051	H-8→L(+54%), H-7→L(+26%), H-6→L+1(+11%)
347.2	3.57	0.1065	H-8→L+1(+55%), H-7→L+1(+24%), H-5→L+2(+14%)
344.4	3.60	0.0014	H-2→L+3(+40%), H→L+4(+20%), H-1→L+4(+19%)
342.2	3.62	0.0007	H-5→L+2(+63%)
341.5	3.63	0.0194	H-4→L+3(+43%), H-1→L+5(+15%), H-8→L(+14%)
341.1	3.64	0.0010	H-3→L+3(+35%), H-8→L+1(+15%), H→L+5(+15%)
337.4	3.68	0.0366	H-6→L+2(+64%), H-6→L+1(+12%)
333.7	3.72	0.0095	H→L+4(+45%), H-1→L+4(+20%), H-7→L+2(+19%)
333.2	3.72	0.0058	H-7→L+2(+55%), H-1→L+4(+10%), H-3→L+4(+10%)
333.0	3.72	0.0034	H-1→L+4(+45%), H→L+5(+16%), H-3→L+4(+16%)
330.9	3.75	0.0084	H→L+5(+37%), H→L+8(+20%), H-5→L+3(+18%)
328.1	3.78	0.0001	H-1→L+5(+43%), H→L+5(+33%), H→L+4(+20%)
326.5	3.80	0.0489	H-8→L+2(+60%), H-7→L+2(+25%)
326.2	3.80	0.0100	H-4→L+6(+32%), H-2→L+3(+17%)
324.1	3.83	0.0019	H-3→L+3(+30%), H→L+8(+18%), H-6→L+3(+16%)
323.8	3.83	0.0083	H-2→L+3(+34%), H-4→L+3(+20%), H-1→L+7(+19%)
317.3	3.91	0.0204	H-3→L+3(+34%), H-2→L+5(+21%), H-6→L+4(+18%)
316.2	3.92	0.0166	H-2→L+4(+34%), H-4→L+3(+30%), H-6→L+5(+16%)

Table S6. Selected calculated excitation energies (ΔE), oscillator strengths (f), main orbital components, and assignment for the **HBC-3TP** in THF solution.

315.8	3.93	0.0179	H-5→L+3(+32%), H-2→L+12(+15%), H→L+11(+14%)
314.5	3.94	0.0220	H-3→L+4(+31%), H-3→L+3(+26%), H-6→L+3(+22%)
312.6	3.97	0.0043	H-7→L+3(+52%), H→L+4(+10%)
312.1	3.97	0.0020	H-4→L+4(+33%), H-2→L+3(+21%), H-7→L+3(+16%)
311.6	3.98	0.0028	H-8→L+3(+30%), H-2→L+4(+28%), H-5→L+3(+18%)
310.1	4.00	0.2771	H-4→L+4(+22%), H-5→L+3(+20%), H-6→L+7(+12%)
309.7	4.00	0.3128	H-6→L+3(+23%), H-5→L+8(+20%), H-3→L+7(+17%)
308.4	4.02	0.1003	H-4→L+6(+26%), H→L+6(+24%), H-8→L+3(+20%)
308.3	4.02	0.0250	H-3→L+4(+33%), H-3→L+5(+21%), H→L+4(+13%)

8. Photophysical properties

Table S7. Photophy	sical parameters	of HBC-3TP	, TP6 and HBC.
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Compound	Solvent	λ _{abs} (nm)	ε×10⁴ (L·mol⁻¹·cm⁻¹)	λ_{em} (nm)	QY (%)
НВС-ЗТР	тыр	282	0.26	489ª 23.66	
		370	0.16	542 ^b	2.51 ^b
TP 6	THF	278	0.097	381	22.57
HBC	THF	352	0.11	480	0

Notice: the solubility of **HBC** is poor, and the specific concentration is unknown, **TP**6: 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene, **HBC**, hexabenzo[*bc,ef,hi,kl,no,qr*]coronene. ^a λ_{em} and QY in THF solution at concentration of 10⁻⁵ mol. L⁻¹; ^b λ_{em} and QY in thin film.



Figure S18. PL spectrum of HBC-3TP in thin film.

9. CV



Figure S19. Cyclic voltamogram of HBC-3TP (THF solution).

Table S8. Electrochemical properties of HBC-3TP

Compound	E _{ox} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c	$E_g^{opt}(eV)^d$
HBC-3TP	0.83	-5.33	-2.45	2.88

^aE_{ox} measured from CV; ^bCalculated from the empirical formula: $E_{HOMO} = -(E_{ox}+4.5)$; ^c $E_{LUMO} = E_{HOMO} + E_{g}^{opt}$, estimated from the onset of the absorption edge of thin solution; ^d $E_{g} = hc/\lambda_{abs} = 1240/\lambda_{abs}$, $\lambda_{abs} = 430$ nm, $E_{g} = 2.88$ eV.

10. SCLC

Experimental condition for SCLC measurement:

Carrier mobility was measured by space charge limited current (SCLC) method. The device structure: ITO/PEDOT:PSS/HBC-3TP (119 nm)/Au for hole transport and ITO/ZnO/HBC-3TP (113 nm)/PFN-Br/Ag for electron transport. Indium tin oxide (ITO) substrates were cleaned by ultrasonication with soap water, deionized water, acetone, and isopropanol alcohol in sequence. The clean substrates modified by a UV–ozone treatment for 30 min. Hole-only devices were fabricated as follows: poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) was first filtrated through a 0.45 µm nylon filter and then spin coated on the ITO substrates with a spin speed of 3000 rpm for 40 s. The substrates were baked on a hot plate at 150 °C for 15 min. The active-layer of HBC-3TP were prepared by spin-coating (1200 rpm, 60 s) on the top of the PEDOT:PSS from the solution of CHCl₃ (20 mg/mL), and spin coated HBC-3TP films were heated to 241 °C for 5 min and then cooled to room temperature at rate of 5 °C/min. Finally, a 100 nm Au was evaporated onto the surface of the active-layer of HBC-3TP were prepared according to the process mentioned above. PFN-Br solution spin coated on the active-layer. Finally, Ag electrode were prepared by the thermal evaporation on to top of the active layers.

Equation (1) was used to calculate the mobility:

$$\mu = \frac{8 * J * L^3}{9\varepsilon_r \varepsilon_0 V^2}$$

where, J stands for current density, ε_r is the dielectric constant (ε_r = 3), ε_0 is the permittivity of vacuum (ε_0 = 8.85×10⁻¹² F/m), μ the mobility, and L the thickness of samples.



Figure S20. Annealing temperature dependence of I—V curves for HBC-3TP.

¹ C. Zeng, P. Hu, B. Wang, W. Fang and K.-Q. Zhao, *Chin. J. Org. Chem.*, 2023, **43**, 3287-3296.

² J. Wu, M. Baumgarten, M. G. Debije, J. M. Warman and K. Mullen, *Angew. Chem. Int. Ed.*, 2004, **43**, 5331-5335.