

SUPPORTING INFORMATION

Synthesis and Electronic Properties of Nitrogen-Rich Nanographenes

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General considerations. Unless otherwise specified, all operations involving air- or water-sensitive reagents were carried out in an MBraun drybox under a nitrogen atmosphere or using standard Schlenk and vacuum line techniques. Glassware was oven-dried at 140 °C for 2 h prior to use on the Schlenk line or in the MBraun drybox. Tetrahydrofuran (THF), diethyl ether, toluene, pentane, and hexanes for air- and moisture-sensitive reactions were dried by the method of Grubbs.¹ Dry *N,N*-dimethylformamide (DMF) was purchased from Millipore Sigma and cannula transferred to freshly-activated 3 Å molecular sieves and stored in a Teflon-sealed Schlenk tube under N₂ atmosphere for 12 h prior to use. *Meta*-xylene was vacuum transferred from sodium benzophenone ketyl. Deuterated solvents were purchased from Cambridge Isotope Laboratories and CDCl₃ was used as received. All solvents, once dried and degassed, were stored under a nitrogen atmosphere over 3 Å molecular sieves. Iodo[bis(diphenylphosphino)-9,9-dimethylxanthene]copper(I) was prepared following a previously reported procedure.² All other reagents were used as received. ¹H, and ¹³C{¹H} spectra were recorded on Varian Mercury 300 MHz or Varian 400 MHz spectrometers at ambient temperatures, unless otherwise denoted. ¹H and ¹³C{¹H} NMR spectra are reported referenced internally to residual solvent peaks reported relative to tetramethylsilane. Gas chromatography-mass spectrometry (GC-MS) were performed on an Agilent 6890A instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 μm film) and an Agilent 5973N mass-selective EI detector. Absorption spectra were recorded on a Varian Cary Bio 50 spectrophotometer.

Electrochemical measurements: CVs were recorded with a Pine Instrument Company AFCBP1 biopotentiostat with the AfterMath software package. All measurements were performed in a three electrode cell, which consisted of glassy carbon (working; ø = 3.0 mm), silver wire (counter) and bare platinum wire (reference), in an N₂-filled MBraun glovebox at RT. Dry tetrahydrofuran that contained ~100 mM [ⁿBu₄N][PF₆] was used as the electrolyte solution. The ferrocene/ferrocenium (FcH/FcH⁺) redox wave was used as an internal standard for all measurements.

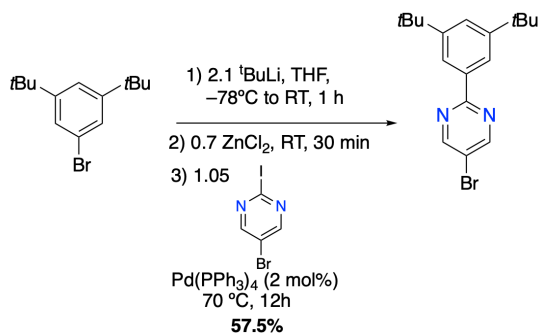
Preparation of pre-reduced magnetic stir bars: Sodium mirror (10-20 mg) is prepared in a 20-mL scintillation vial along with 200-300 mg of benzophenone dissolved in THF to form a purple solution, which is then added to a 20-mL vial containing 10-20 Teflon-coated magnetic stir bars and stirred for 12 h. The solution is decanted, and the stir bars are rinsed with THF until the mother liquor is colorless, resulting in black, pre-reduced magnetic stir bars that are dried under vacuum for 1 h and are to be used for reactions involving Na and NaK.

Absorption spectroscopy: UV-vis spectra were recorded on a Varian Cary Bio 50 spectrophotometer in a 1 mm cuvette. Single equivalents of ZnCl₂ (103 mM in CHCl₃) were added to 0.060 mM HPC-N₁₂(Ar^{tBu})₆. After addition of an equivalent, a spectrum was recorded.

Emission spectroscopy: Corrected room temperature emission spectra were collected in the Beckman Institute Laser Resource Center using a modified Jobin Yvon Spec Fluorolog-3 instrument. Samples were excited with a xenon arc lamp, employing a monochromator for wavelength selection, and emission was detected at 90° using two Ocean Optics EQDPro CCD spectrometers spanning 300–930 nm. Single equivalents of metal salt or trifluoromethane sulfonic acid (103 mM) were added to 0.060 mM HPC-N₁₂(Ar^{tBu})₆. After addition of an equivalent, a spectrum was recorded. The entrance and exit slits were 5 nm, and voltage was set to 400 V.

MALDI-TOF: Mass spectra were recorded on a Bruker Autoflex MALDI TOF/TOF. Dithranol (0.091 mM in CHCl₃) was employed as the matrix. 3 μL of the dithranol solution were combined with 1 μL of 0.060 mM HPC-N₁₂(Ar^{tBu})₆ + metal salt mixture. This mixture was drop casted onto a MALDI plate and allowed to dry under ambient conditions.

Synthetic Procedures



5-Bromo-2-(3,5-di-*tert*-butylphenyl)pyrimidine (1). Adapted from a previously-reported procedure:³ In an N_2 -purged glove box, a Schlenk flask fitted with a screw-in Teflon stopper was charged with a solution of 3,5-di-*tert*-butylbromobenzene (20 g, 75 mmol) in THF (250 mL). The flask was sealed, brought outside of the box and cooled to -78°C with a dry ice/acetone bath. A pentane solution of *tert*-butyllithium (80 mL, 2.0 M, 160 mmol) was added dropwise via cannula. The reaction was allowed to warm to room temperature and stirred for 1 h forming a yellow solution. The reaction was then brought back into an N_2 -purged glovebox and ZnCl_2 (7.2 g, 53 mmol) was added slowly to the reaction resulting in the loss of the yellow coloration and formation of a white precipitate. The mixture was allowed to stir at room temperature for 30 min. 5-bromo-2-iodopyrimidine (22.3 g, 78 mmol) was added to the mixture. The flask was then placed in a cold well previously cooled with liquid nitrogen. $\text{Pd}(\text{PPh}_3)_4$ (1.3 g, 1.0 mmol) was added slowly, the flask sealed, and brought outside of the box. The vessel was fitted with an oven-dried reflux condenser and warmed to 70°C for 12 h. After cooling to room temperature, water (100 mL) was added to quench the reaction, and the mixture concentrated in vacuo to about 100 mL. The resulting suspension was taken up in CH_2Cl_2 (200 mL) and washed with 5 x 100 mL of water. The organic layer was washed with brine (2 x 100 mL), dried over MgSO_4 , and filtered. Removal of the volatiles under a reduced pressure afforded an orange solid, which was charged with 200 mL of hexanes and heated to reflux. The mixture was filtered, and the filtrate was concentrated under a reduced pressure, allowing a white solid to crash out, which was filtered and washed with cold hexanes. The off-white solid (15.2 g, 57.5% yield) is analytically pure **1a**. ^1H NMR (400 MHz, CDCl_3): δ = 8.84 (s, 2H, ArH), 8.31 (app d, 2H, ArH), 7.62 (t, 1H, ArH), 1.43 (s, 18H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 163.75 (aryl-C), 157.84 (aryl-C), 151.40 (aryl-C), 135.93 (aryl-C), 125.6 (aryl-C), 122.65 (aryl-C), 118.05 (aryl-C), 35.18 ($\text{C}(\text{CH}_3)_3$), 31.64 ($\text{C}(\text{CH}_3)_3$). HRMS (FAB+) m/z Calcd. for $[\text{M} + \text{H}^+]$ $\text{C}_{18}\text{H}_{13}\text{BrN}_2$ 347.1123, found 347.1122.

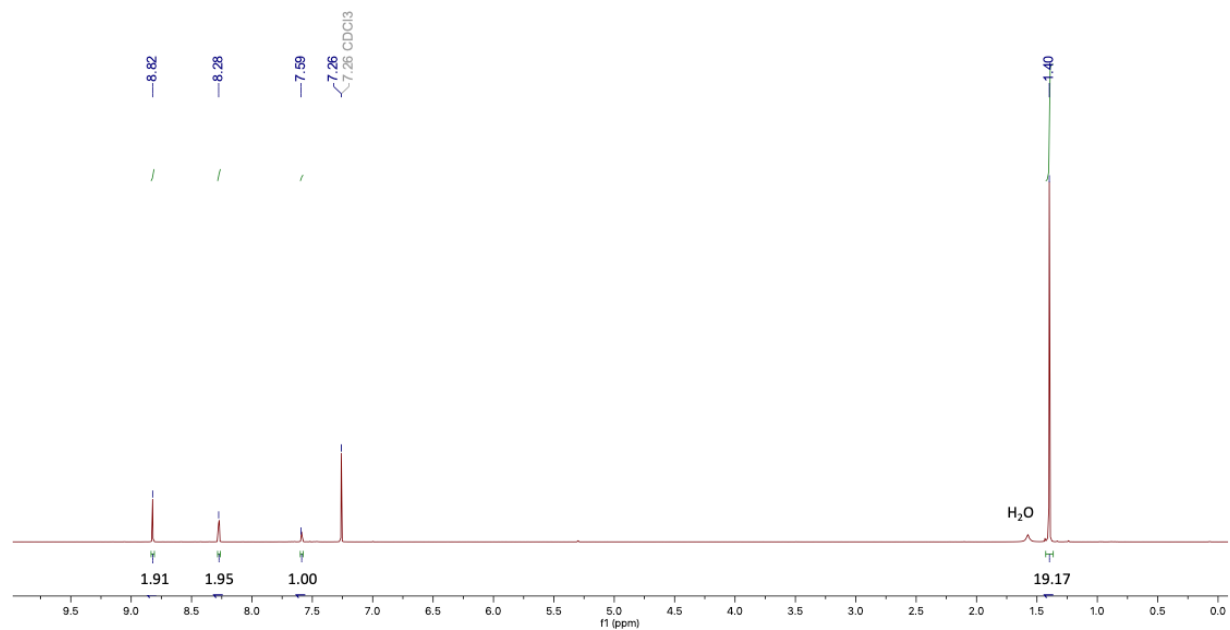


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of 5-bromo-2-(3,5-di-*tert*-butylphenyl)pyrimidine (**1**).

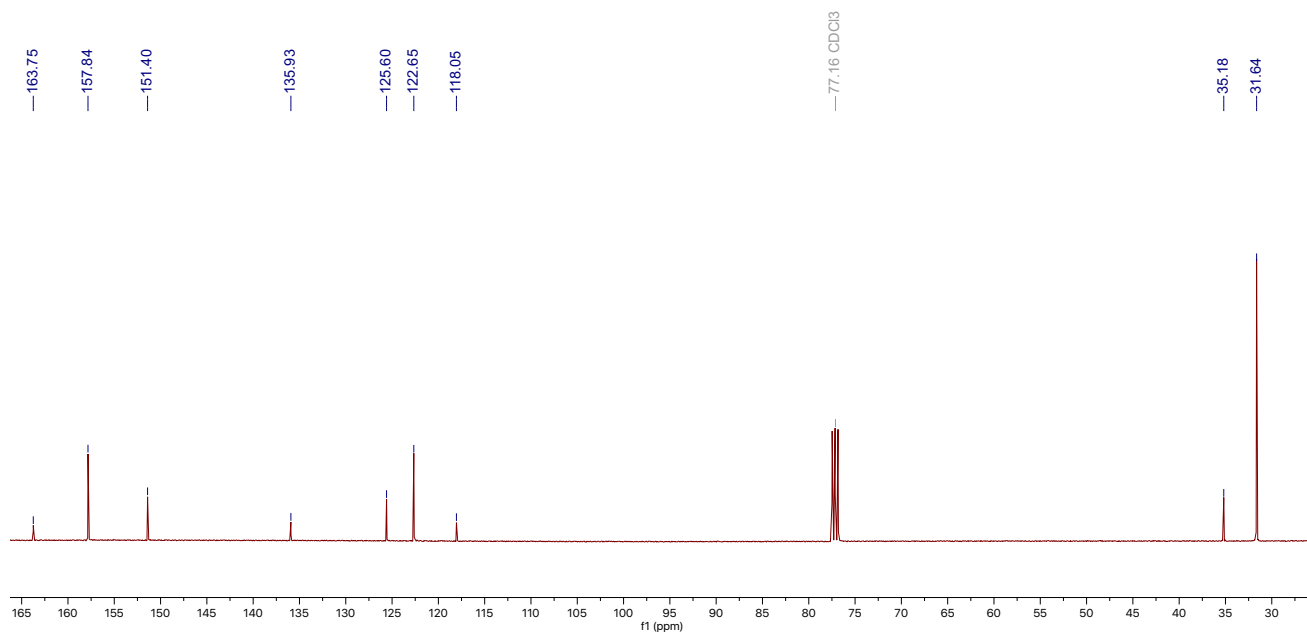
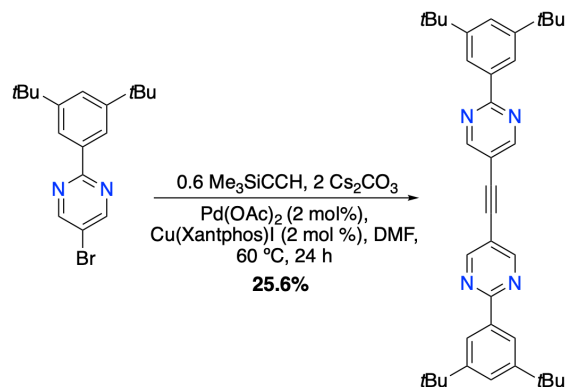


Figure S2. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 5-bromo-2-(3,5-di-*tert*-butylphenyl)pyrimidine (**1**).



1,2-bis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)ethyne (2**).** Adapted from a previously-reported procedure:⁴ A 1-L, oven-dried Schlenk flask was allowed to cool under vacuum on the Schlenk line. Under a positive pressure of N₂, the Schlenk flask was charged with 5-bromo-2-(3,5-di-*tert*-butylphenyl)pyrimidine (**1a**) (12.8 g, 37 mmol), cesium carbonate (24.1 g, 74 mmol), and palladium (II) acetate (165 mg, 0.73 mmol). DMF (250 mL) was added to the Schlenk flask via cannula. To this mixture was added trimethylsilylacetylene (3.14 mL, 22 mmol) under positive N₂ pressure. The reaction mixture was degassed via one cycle of freeze-pump-thaw. Iodo[bis(diphenylphosphino)-9,9-dimethylxanthene]copper(I) (566 mg, 0.73 mmol) was added under positive N₂ pressure. The reaction mixture was subjected to two more cycles of freeze-pump-thaw, and the mixture was heated to 60 °C for 12 h. Volatiles were removed under a reduced pressure, and the crude solid was charged with CH₂Cl₂ (300 mL) and filtered to remove excess cesium carbonate. The filtrate was concentrated under a reduced pressure and purified via column chromatography with CH₂Cl₂ as the eluent. The white solid (5.3 g, 25.6%) was dried under vacuum for 12 h at room temperature prior to the next step. ¹H NMR (400 MHz, CDCl₃) δ = 8.95 (s, 4H, ArH), 8.36 (app d, 4H, ArH), 7.61 (t, 2H, ArH), 1.42 (s, 36H, C(CH₃)₃). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ = 164.02 (aryl-C), 159.13 (aryl-C), 151.45 (aryl-C), 136.22 (aryl-C), 125.93 (aryl-C), 123.02 (aryl-C), 115.89 (aryl-C), 90.03 (alkyne-CC), 35.22 (C(CH₃)₃) 31.65 (C(CH₃)₃). HRMS (FAB⁺) m/z Calcd. for [M + H⁺] C₃₈H₄₇N₄ 559.3801, found 559.3813.

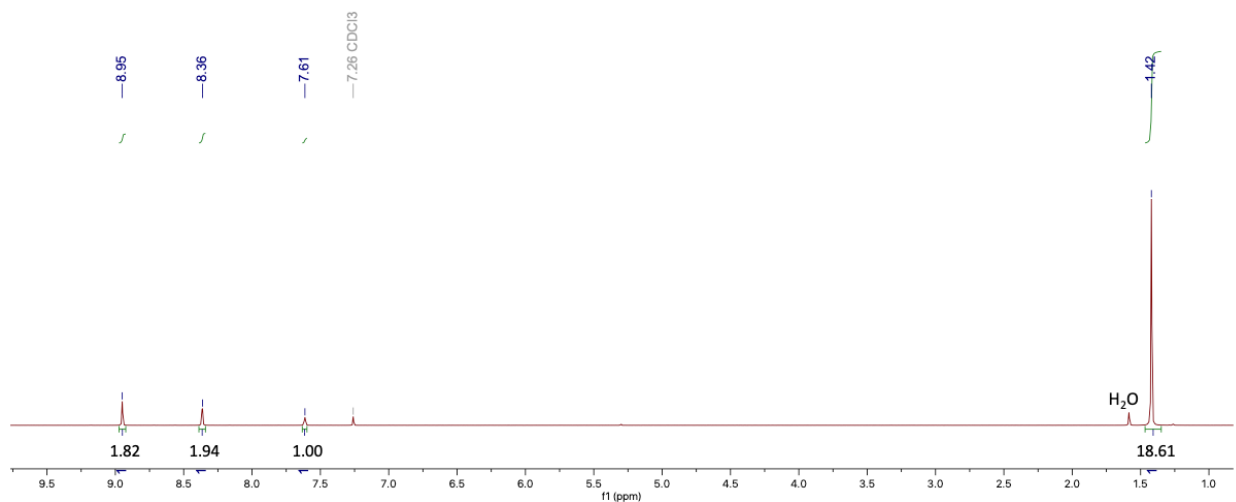


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,2-bis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)ethyne (**2**).

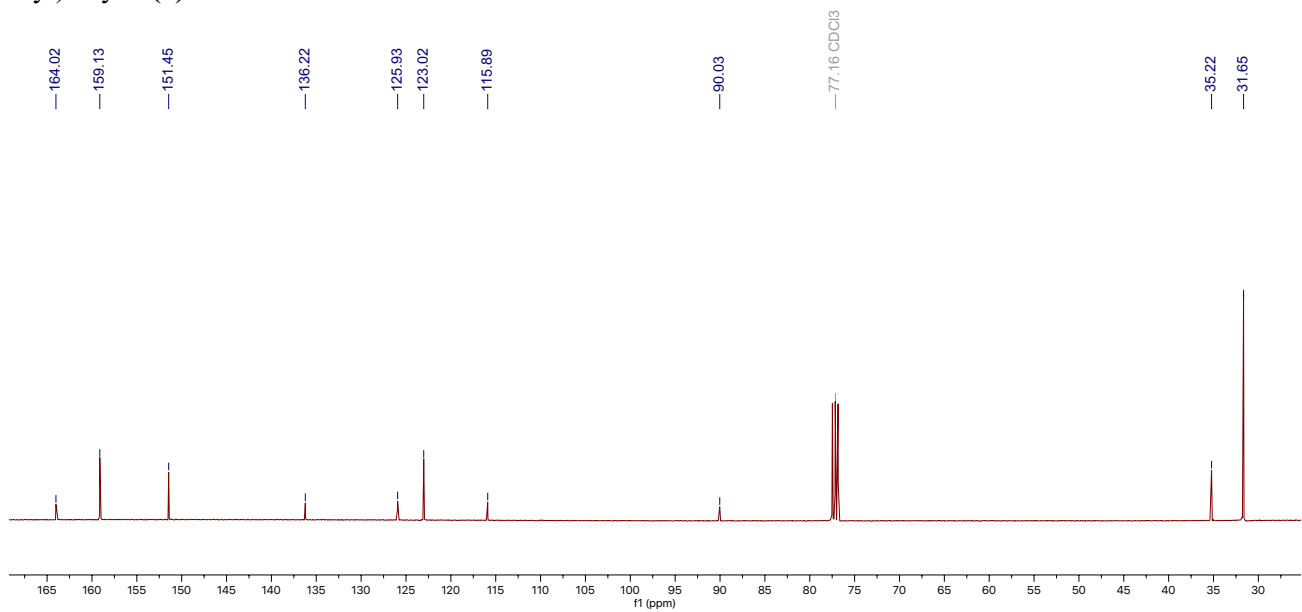
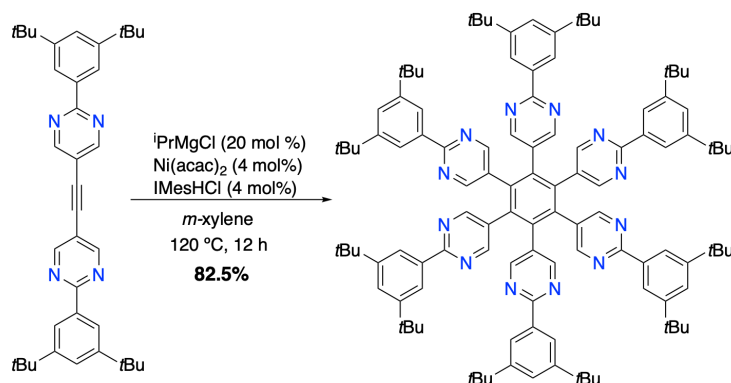


Figure S4. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 1,2-bis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)ethyne (**2**).



1,2,3,4,5,6-hexakis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)benzene (3). Adapted from a previously-reported procedure:⁵ An oven-dried Schlenk tube fitted with a screw-in Teflon stopper was charged with 1,2-bis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)ethyne (**2**) (2.00 g, 4 mmol), IMesHCl (54 mg, 0.16 mmol), and acetylacetonatonickel (II) (41 mg, 0.16 mmol). The flask was then charged with 10 mL of *m*-xylene via syringe. The solution was subjected to three cycles of freeze-pump-thaw and left under nitrogen. Isopropylmagnesium chloride (0.5 mL, 1.39 M in THF, 0.7 mmol) was added via syringe, and the solution was warmed to 120 °C for 16 h. Volatiles were removed under a reduced pressure. The crude solid was purified via column chromatography (10% EtOAc/Hexanes), and the fractions containing the desired product precipitated a white solid, which was filtered and washed with ethyl acetate and hexanes to yield the desired cyclotrimer **3a** (1.65 g, 82.5%). ¹H NMR (400 MHz, CDCl₃) δ = 8.49 (s, 2H, *ArH*), 8.09 (s, 2H, *ArH*), 7.47 (s, 1H, *ArH*), 1.28 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 164.15 (aryl-C), 157.82 (aryl-C), 151.25 (aryl-C), 138.07 (aryl-C), 135.64 (aryl-C), 128.94 (aryl-C), 125.91 (aryl-C), 122.81 (aryl-C), 34.82 (C(CH₃)₃), 31.53 (C(CH₃)₃). Anal. calcd. (%) for C₁₁₄H₁₃₈N₁₂: C, 81.68; H, 8.30; N, 10.03. Found: C, 80.99; H, 8.14; N, 9.89.

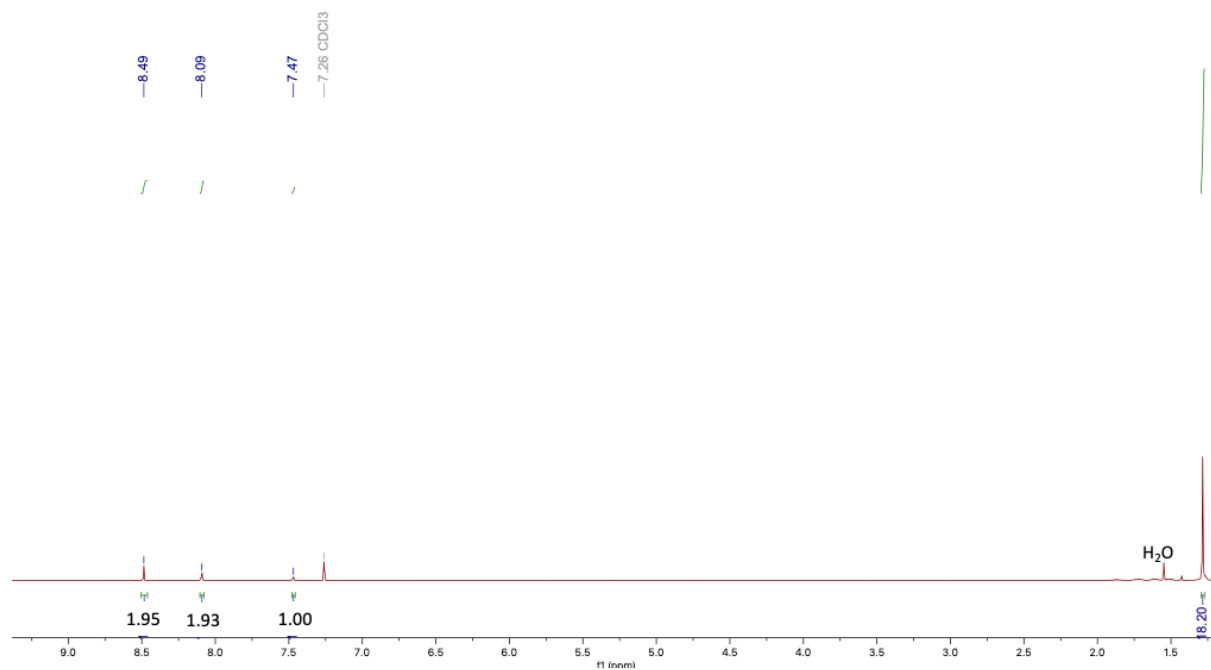


Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,2,3,4,5,6-hexakis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)benzene (**3**).

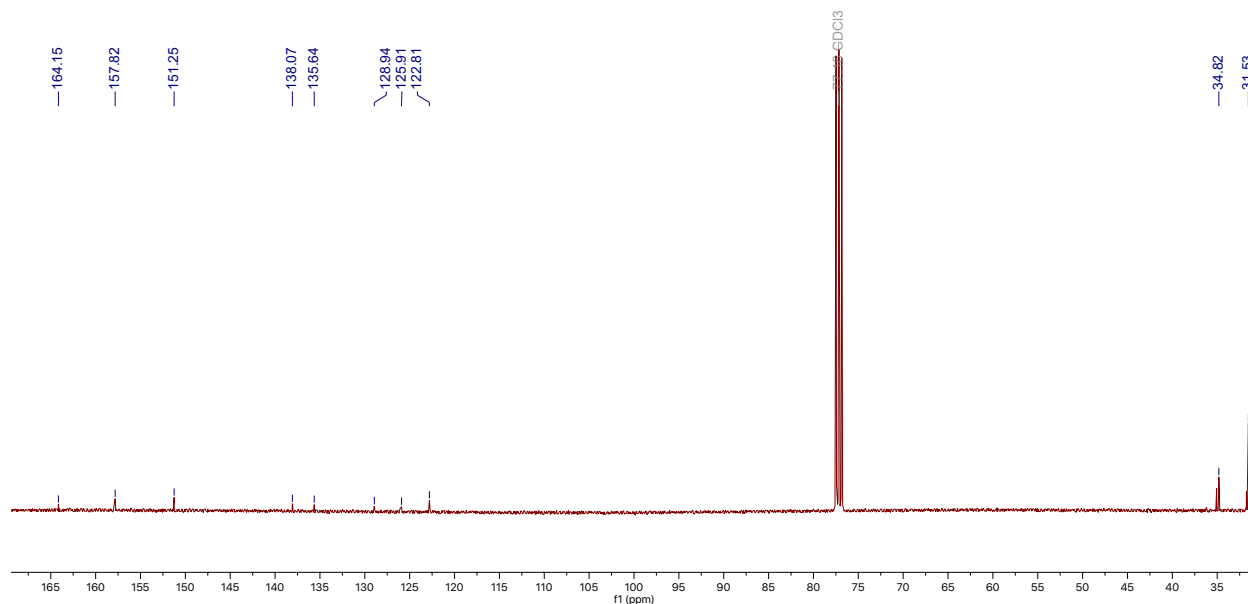
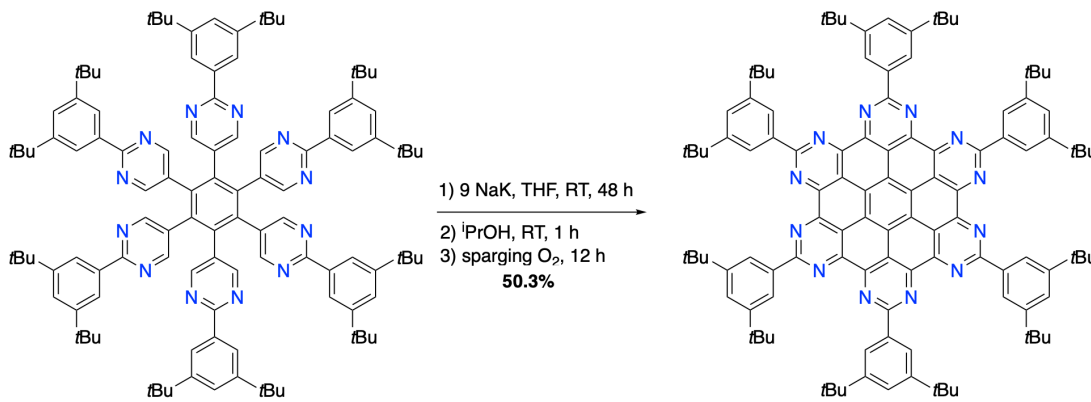


Figure S6. ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of 1,2,3,4,5,6-hexakis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)benzene (**3**).

Monitoring the ring closure of 3a and 3b. In an N₂-purged glovebox, a 1-2 mL aliquot was removed from the reduction of **3** and quenched slowly with isopropanol on the benchtop. This mixture was then charged with a minimal amount of DDQ to oxidize the putative anionic intermediate,⁶ resulting in a red-yellow solution. The volatiles were removed on the rotary evaporator, and the crude solid was taken up in CDCl₃ and filtered to record the ¹H NMR spectrum.



HPC-N₁₂(Ar^{tBu})₆. In an N₂-purged glovebox, a 20-mL scintillation vial is charged with 1,2,3,4,5,6-hexakis(2-(3,5-di-*tert*-butylphenyl)pyrimidin-5-yl)benzene (200 mg, 0.12 mmol). In a separate vial, sodium (24.7 mg, 1.07 mmol) and potassium (42 mg, 1.07 mmol) are weighed out and carefully mixed with a spatula. The alloy is suspended in THF and charged with a magnetic pre-reduced stir bar. Compound **3** is suspended in THF and added to the sodium and potassium alloy to immediately form a purple suspension. This mixture is stirred at room temperature for 48 h. The dark brown solution is transferred to a Teflon-sealed Schlenk tube and quenched with isopropanol, followed by MeOH over 1 h to form a dark yellow mixture. This solution is then sparged with dioxygen for 12 h, concentrated under a reduced pressure, and extracted with chloroform and filtered. The filtrate is allowed to sit at -20 °C for 7 h to form deep-red crystals. The mother liquor is decanted, and the crystals are rinsed with cold chloroform. **HPC-N₁₂(Ar^{tBu})₆** is then dried in vacuo at room temperature for 12 h before further use (100.4 mg, 50.3%). Single crystals suitable for X-ray diffraction were grown from slow evaporation at room temperature of a saturated chloroform solution. ¹H NMR (400 MHz, CDCl₃) δ = 9.25 (br s, 2H, ArH), 7.83 (s, 1H, ArH), 1.65 (s, 18H, C(CH₃)₃). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ = 153.82 (aryl-C), 150.40 (aryl-C), 136.74 (aryl-C), 124.85 (aryl-C), 123.48 (aryl-C), 119.67 (aryl-C), 116.22 (aryl-C), 115.35 (aryl-C), 34.27 (C(CH₃)₃), 31.04 (C(CH₃)₃). Anal. calcd. (%) for C₁₁₄H₁₂₆N₁₂: C, 82.27; H, 7.63; N, 10.10. Found: C, 82.00; H, 7.43; N, 9.90.

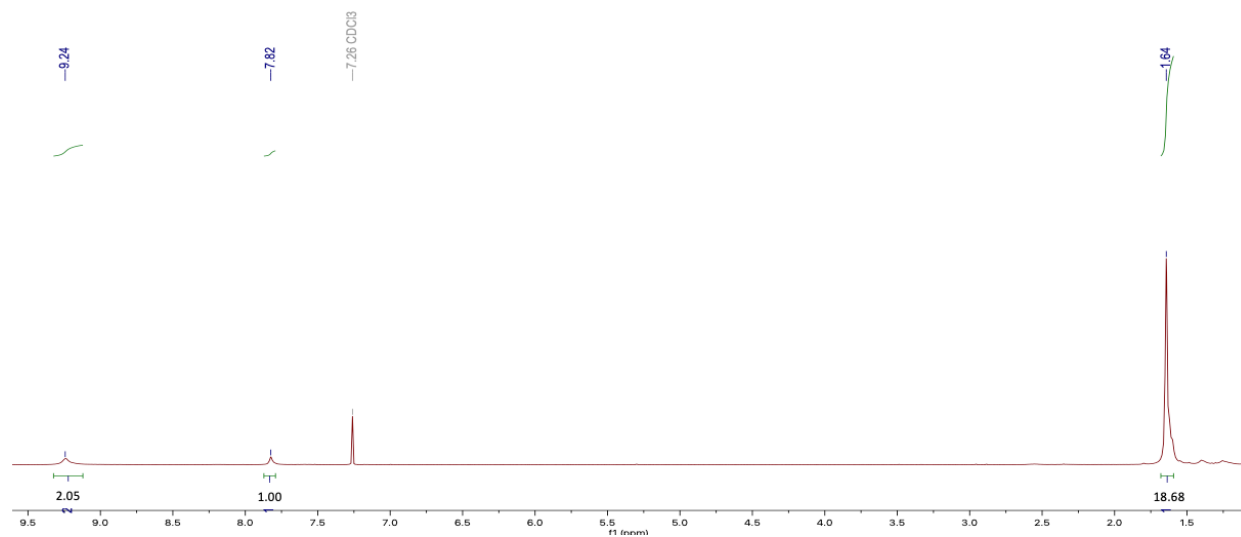


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3) of $\text{HPC-N}_{12}(\text{Ar}^{\text{tBu}})_6$.

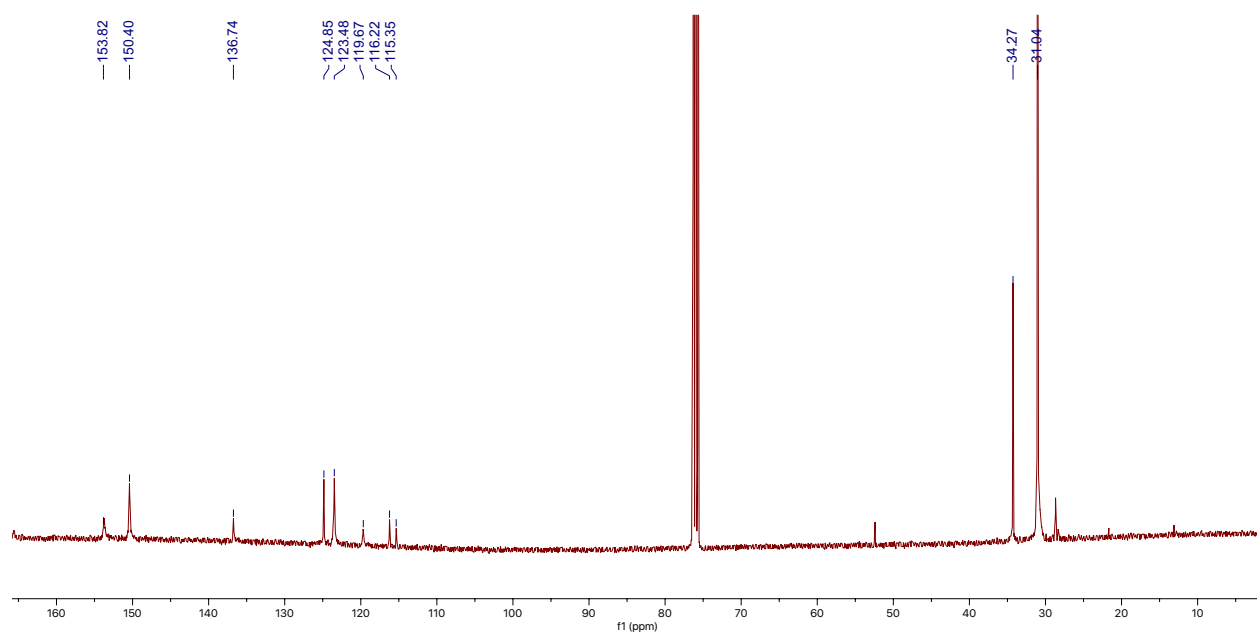


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of $\text{HPC-N}_{12}(\text{Ar}^{\text{tBu}})_6$.

Additional Spectroscopy and Electrochemistry Data

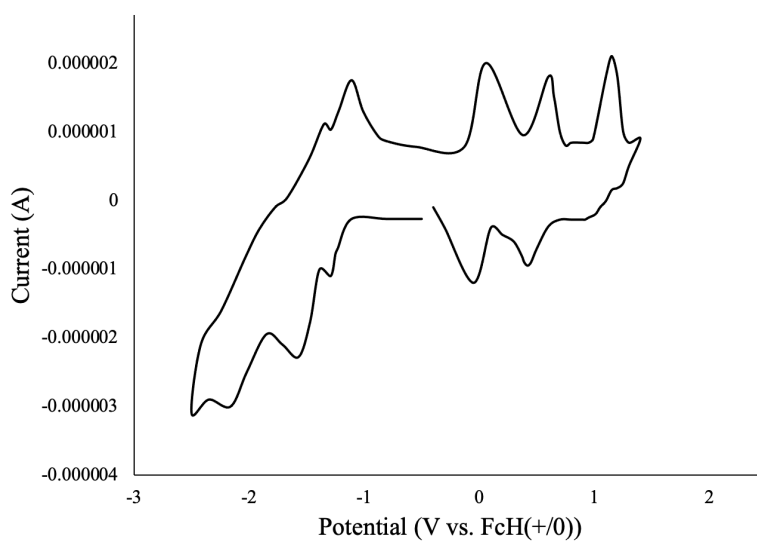


Figure S9. CV of $\text{HPC-N}_{12}(\text{Ar}^{\text{tBu}})_6$ (1 mM) collected at 200 mV/s. 0.1 M $(^{\text{t}}\text{Bu})_4\text{NPF}_6$ in THF. Working electrode: glassy carbon. Reference electrode: Ag/AgCl. Counter electrode: Pt wire.

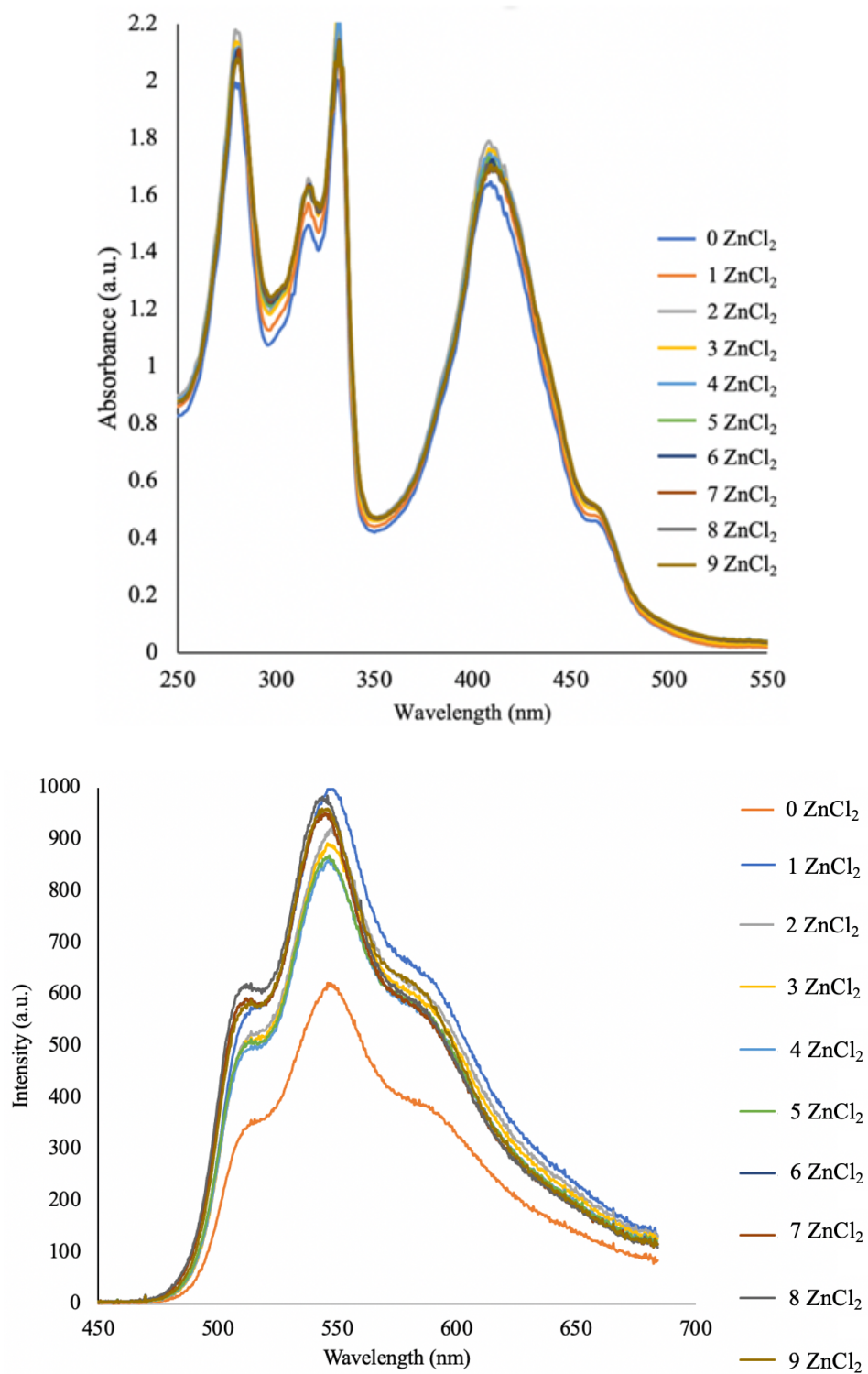


Figure S10. A. Absorption spectra of HPC-N₁₂(Ar^{tBu})₆ (0.060 mM in CHCl₃). B. Emission spectra (excitation wavelength: 410 nm) of HPC-N₁₂(Ar^{tBu})₆ recorded after adding successive equivalents of ZnCl₂.

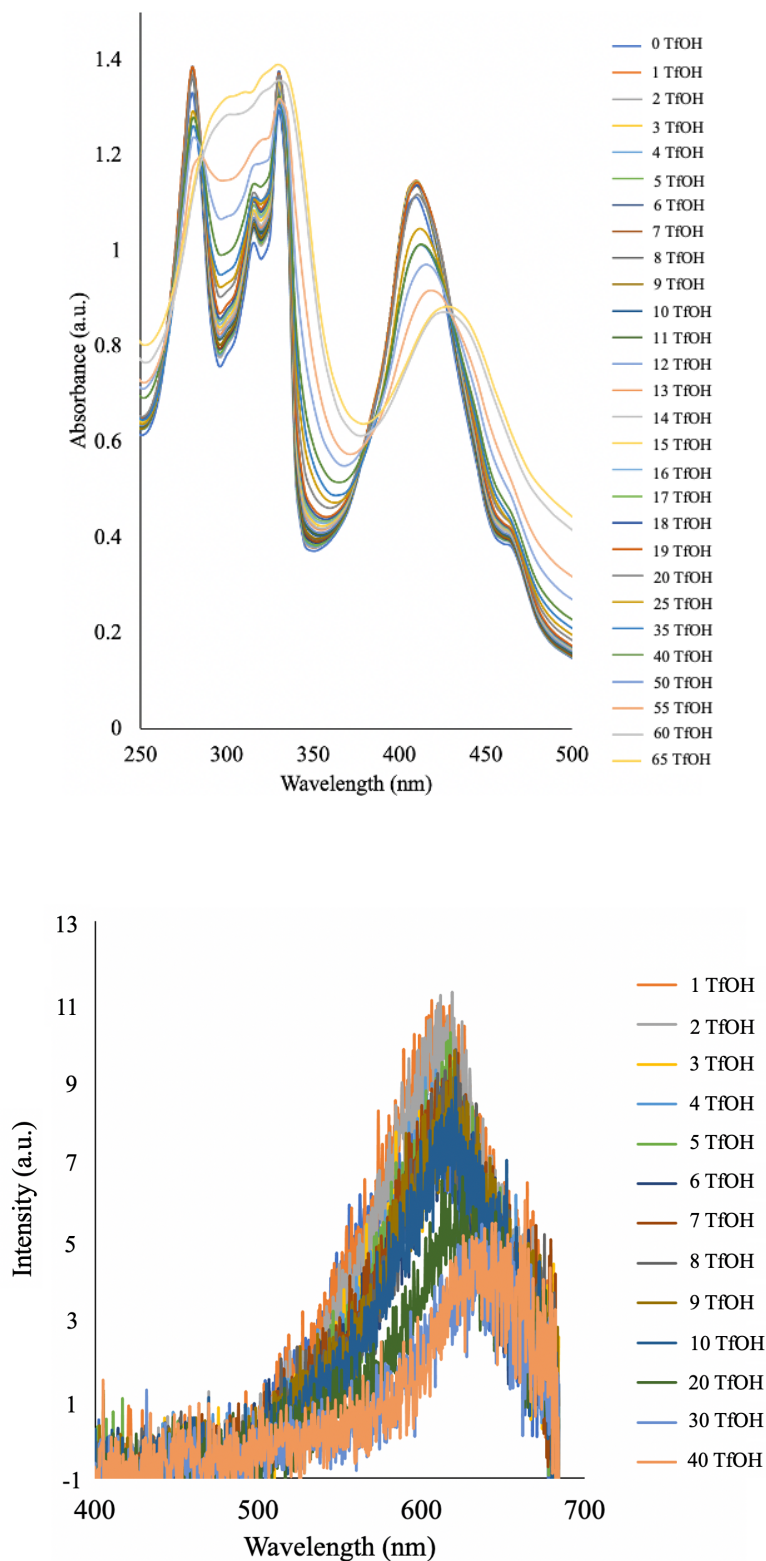


Figure S11. A. Absorption spectra of HPC-N₁₂(Ar^{tBu})₆ (0.060 mM in CHCl₃). B. Emission spectra (excitation wavelength: 410 nm) of HPC-N₁₂(Ar^{tBu})₆ recorded after adding successive equivalents of TfOH (100 mM in CHCl₃).

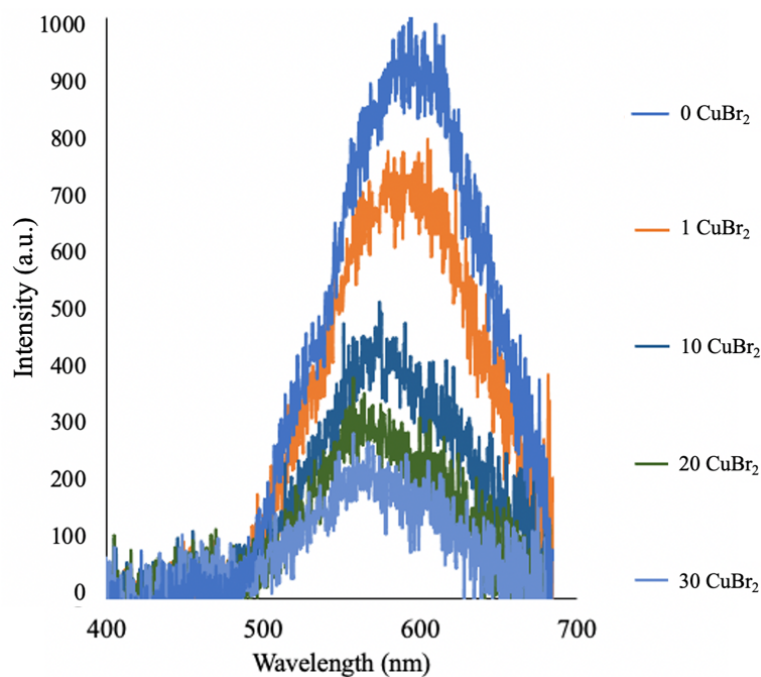


Figure S12. Emission spectra (excitation wavelength: 410 nm) of $\text{HPC-N}_{12}(\text{Ar}^{\text{tBu}})_6$ (0.060 mM in THF) recorded after adding successive equivalents of CuBr_2 .

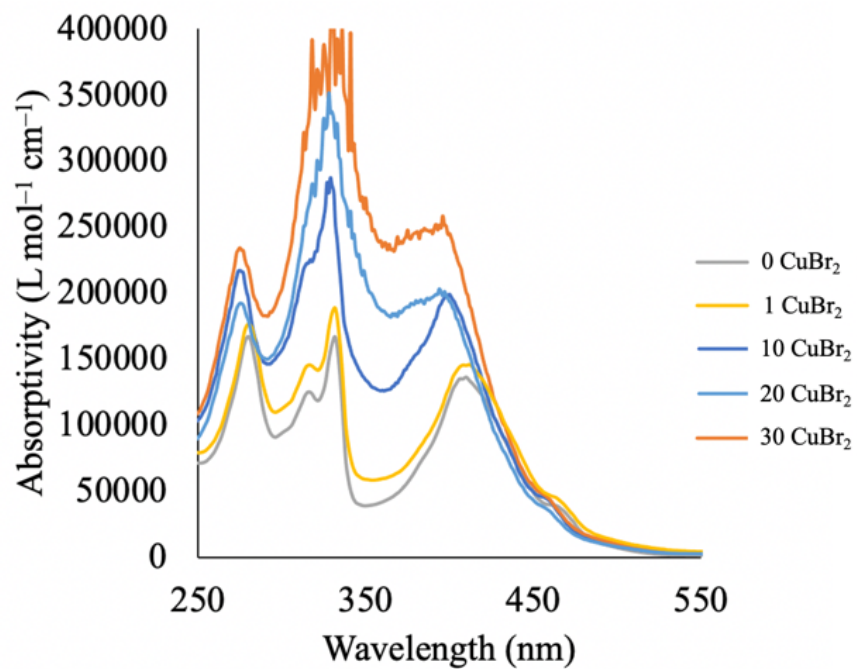


Figure S13. Absorption spectra of $\text{HPC-N}_{12}(\text{Ar}^{\text{tBu}})_6$ (0.060 mM in THF) recorded after adding successive equivalents of CuBr_2 .

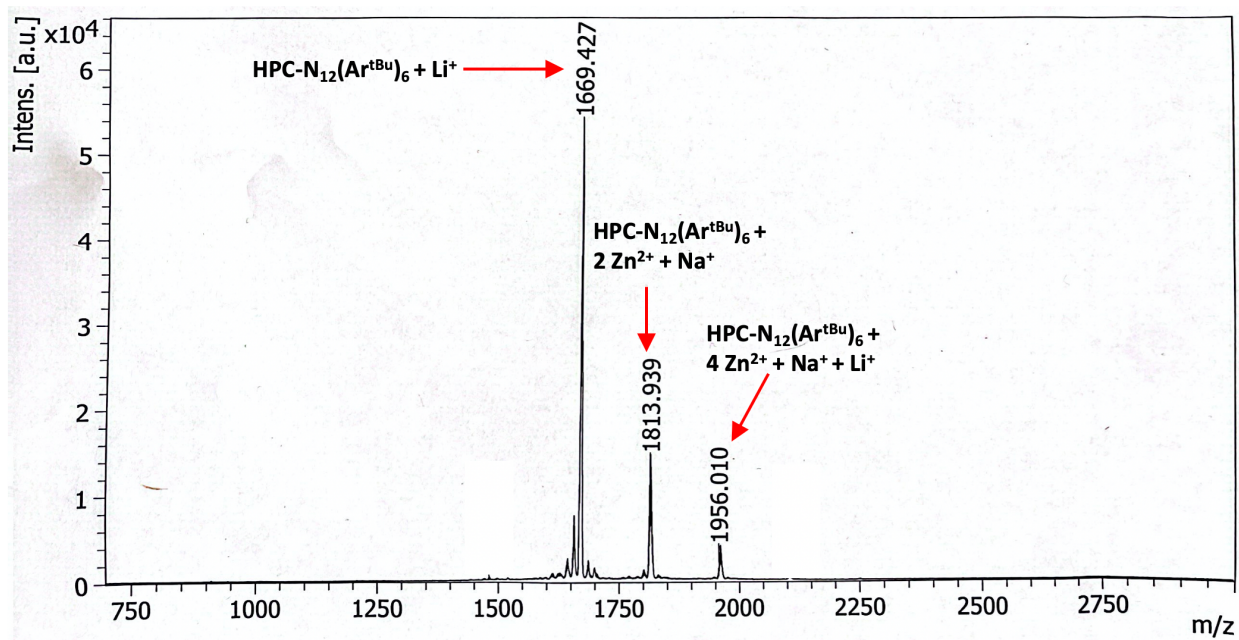


Figure S14. MALDI-TOF of 20 ZnCl₂ added to HPC-N₁₂(Ar^{tBu})₆ in CHCl₃. Matrix: dithranol

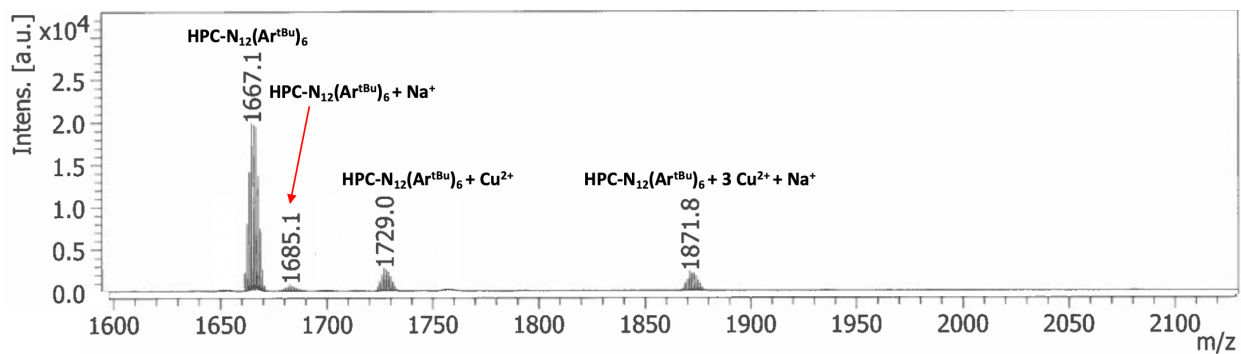
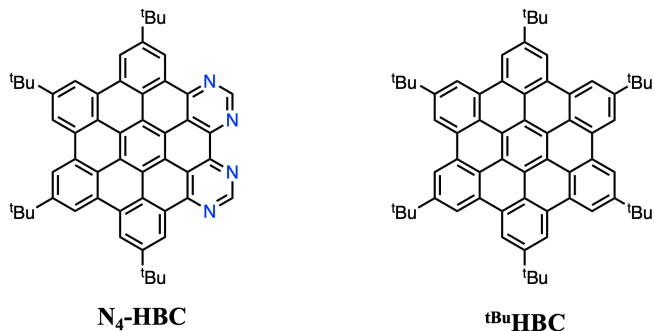


Figure S15. MALDI-TOF of 20 CuBr₂ added to HPC-N₁₂(Ar^{tBu})₆ in THF Matrix: dithranol

Table S1. Comparing most positive reduction determined by cyclic voltammetry between hexabenzocoronene variants.



Compound	$E_{1/2}$ (V vs. FcH ^{0/+})	Electrolyte	Reference
HPC-N₁₂(Ar^{tBu})₆	-1.31	0.1 M ⁿ (Bu) ₄ PF ₆ /THF	<i>This work</i>
N₄-HBC	-1.6	0.1 M ⁿ (Bu) ₄ PF ₆ /CH ₃ CN	Draper and co-workers ⁷
t^{Bu}HBC	-2.1	0.1 M ⁿ (Bu) ₄ PF ₆ /THF	Müllen and co-workers ⁸
t^{Bu}HBC	-1.7	0.1 M ⁿ (Bu) ₄ PF ₆ /CH ₂ Cl ₂	Guldi, Jux, and co-workers ⁹

Density Functional Theory (DFT) Calculations

All computations were performed using ORCA software¹⁰ version 4.1.2 on the Resnick High-Performance Computing Cluster at Caltech. Geometry optimizations and orbital energies were performed using the restricted Kohn-Sham formalism with the B3LYP functional¹¹ and the 6-311G(d,p) basis set.¹²

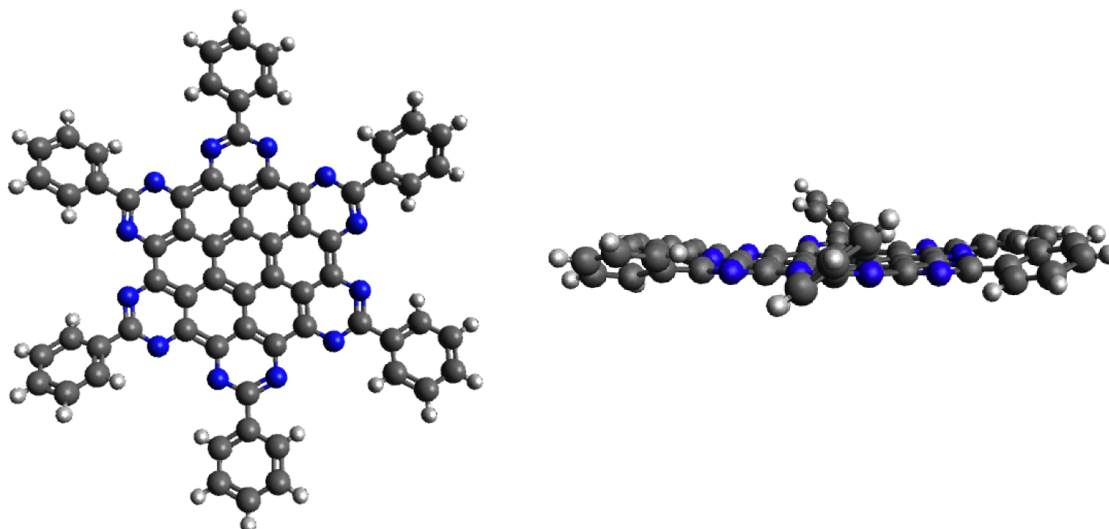


Figure S16. Geometry-optimized structure of **HPC-N₁₂Ph₆**. Right: rotated by 90° into the page.

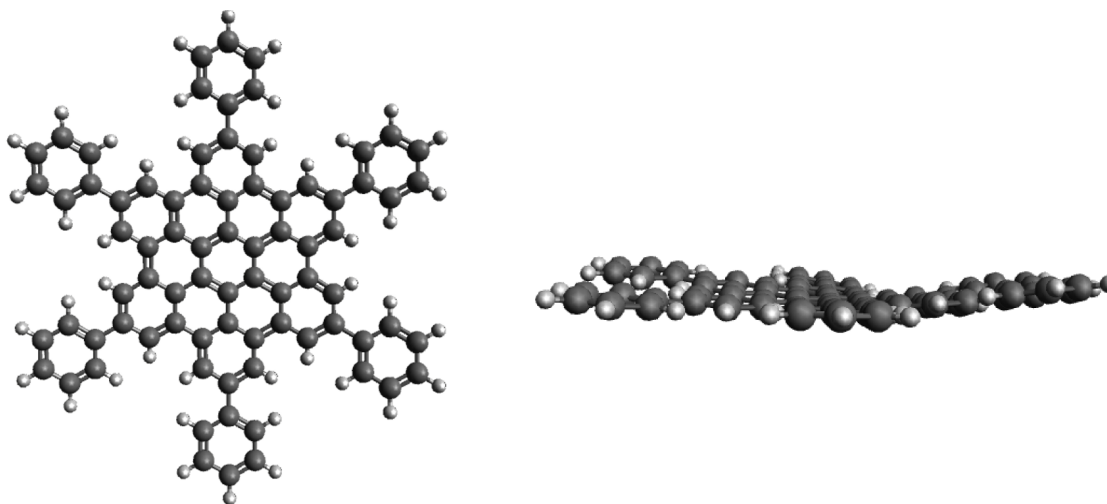


Figure S17. Geometry-optimized structure of **HBC-Ph₆**. Right: rotated by 90° into the page.

HPC-N₁₂Ph₆ was modeled using Avogadro software starting from the crystal structure of **HPC-N₁₂(Ar^{tBu})₆** and submitted for geometry optimization. The structure of **HBC-Ph₆** was generated by replacing each nitrogen atom with C—H. In the optimized structure, the phenyl rings are essentially coplanar with the HBC (Figure S17). When **HBC-Ph₆** is modified such that each Ph rings are rotated relative to the HBC plane for a dihedral angle of 45°, the rings show little rotation upon geometry optimization. The HOMO-LUMO gap changes (increases from 3.347 eV to 3.576 eV), but remains greater than that of **HPC-N₁₂Ph₆**. At this level of theory, these results indicate that the HOMO-LUMO gap is influenced by a combination of nitrogen incorporation and aryl substituent presence / orientation in the periphery of the polyaromatic system.

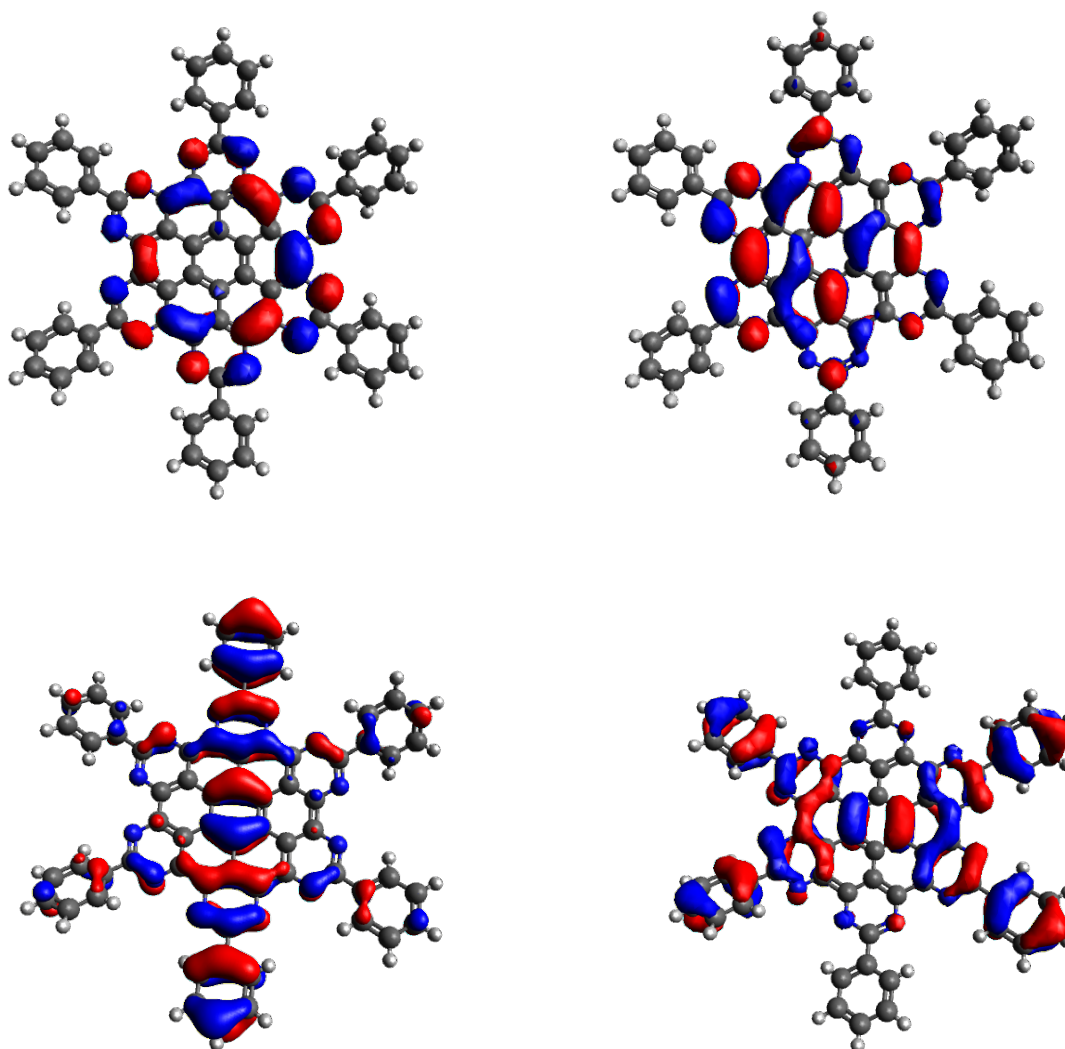


Figure S18. Clockwise from top left: LUMO (-3.250 eV), LUMO+1 (-3.190 eV), HOMO-1 (-6.296 eV), and HOMO (-6.269 eV) of $\text{HPC-N}_{12}\text{Ph}_6$. Isosurfaces are shown at 0.02 value.

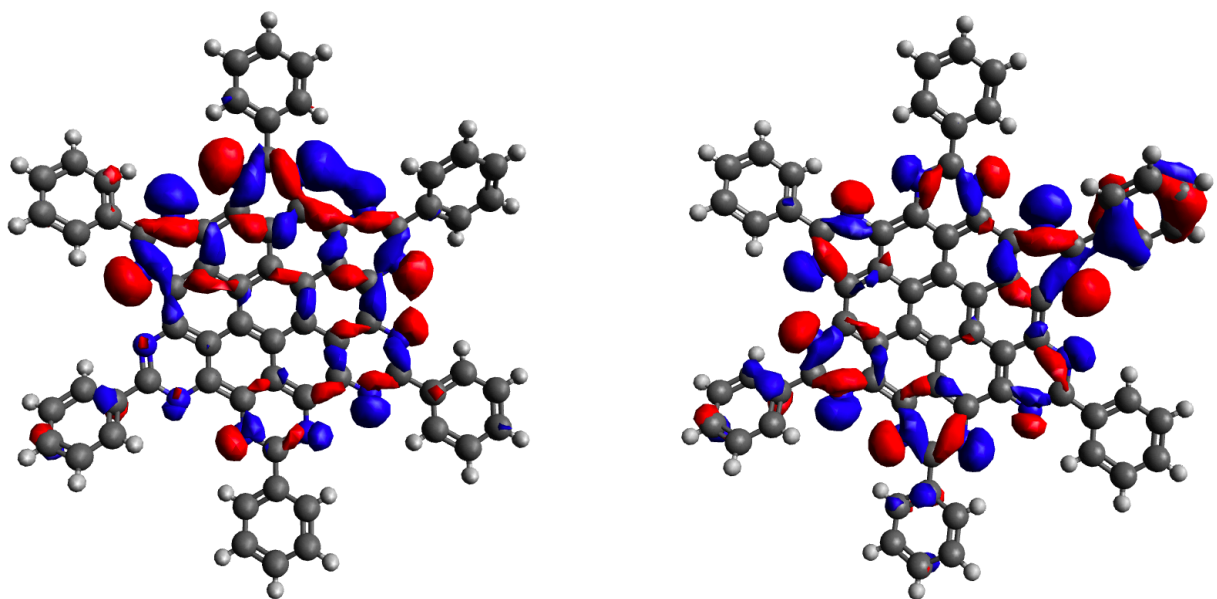


Figure S19. (left) HOMO-6 and (right) HOMO-2 for **HPC-N₁₂Ph₆**. Isovalues set to 0.02.

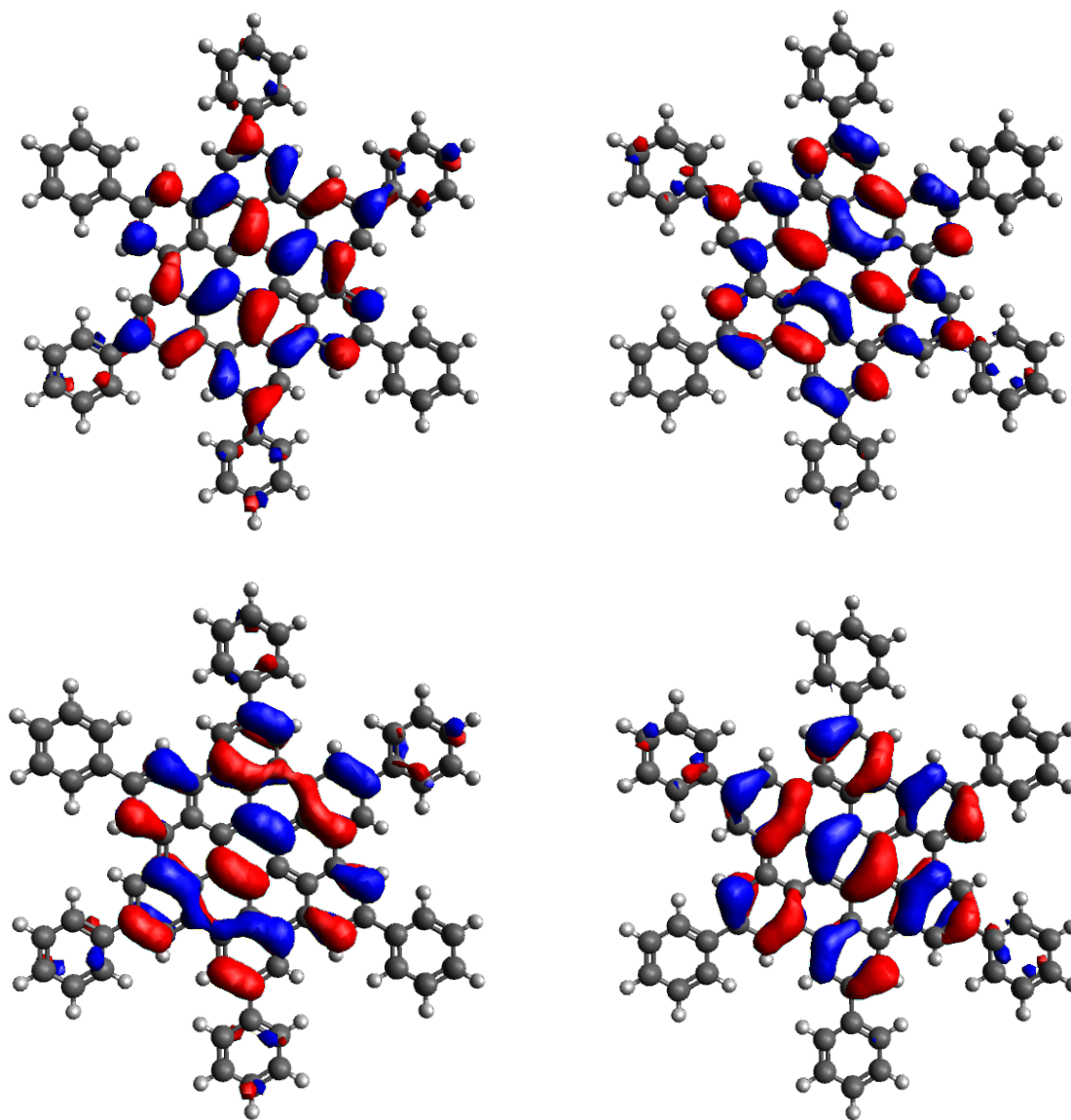


Figure S20. Clockwise from top left: LUMO (−1.983 eV), LUMO+1 (−1.953 eV), HOMO-1 (−5.350 eV), and HOMO (−5.330 eV) of **HBC-Ph₆**. Isosurfaces are shown at 0.02 value.

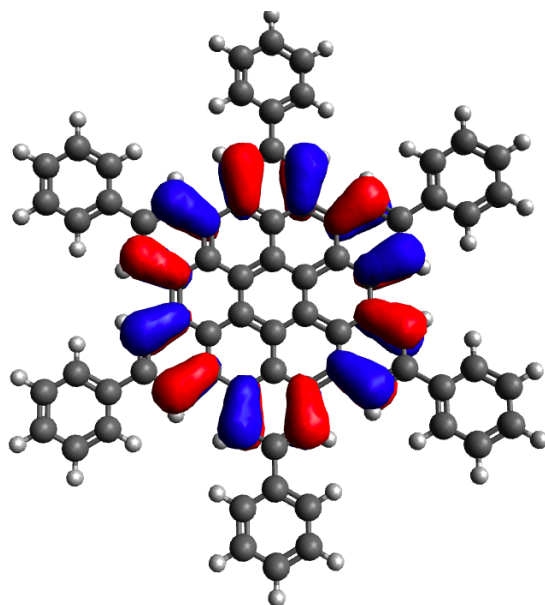


Figure S21. HOMO-2 for **HBC-Ph₆**. Isovalue set to 0.02.

Table S2. HOMO-LUMO energy differences (eV) (computed from B3LYP/6-311G(d,p)).

HBC	3.568
HBC-Ph₆	3.347
HPC-N₁₂	3.635
HPC-N₁₂Ph₆	3.019

Table S3. Cartesian coordinates obtained for the optimized geometry of **HPC-N₁₂**.

N	10.210694	1.114678	9.574955
N	4.182042	8.128486	13.773238
N	8.907951	3.602846	16.345539
N	10.726567	1.035419	12.359151
N	3.665661	8.207244	10.989105
N	5.484301	5.639819	7.002708
N	4.095899	7.384091	8.750411
N	5.377297	7.188247	15.660537
N	9.015201	2.054679	7.687723
N	7.282290	5.365938	16.696740
N	10.296512	1.858772	14.597805
N	7.110462	3.877184	6.651460
C	9.554088	1.939529	10.408885
C	5.282938	6.454228	10.632569
C	9.823511	1.898285	11.862209
C	9.109130	2.788294	12.715713
C	8.146520	3.710214	12.191837
C	4.568675	7.344359	11.486059
C	6.677092	4.700446	8.876330
C	4.838244	7.303238	12.939371
C	6.938026	4.660570	10.283795
C	7.453865	4.581809	13.064524
C	8.590254	2.867646	9.917997
C	5.801847	6.374925	13.430302
C	6.503278	5.492904	12.546907
C	7.714957	4.542111	14.471962
C	7.888627	3.749469	10.801424
C	6.191116	4.774809	6.253476
C	9.391221	2.725330	14.111279
C	6.039302	6.358789	14.835419
C	8.352990	2.883939	8.512857
C	7.033321	5.407073	15.376327
C	10.904036	1.071718	13.691949
C	3.488260	8.171009	9.656268
C	6.245377	5.532156	11.156467
C	5.725453	5.606683	8.324809
C	8.201579	4.468408	17.094717
C	8.666700	3.635924	15.023524
C	5.000981	6.517318	9.236968
C	4.493438	8.017452	15.077064
C	7.358978	3.835693	7.971888
C	9.899255	1.225653	8.271144
H	8.401195	4.437979	18.171098

H	3.956183	8.691225	15.752899
H	2.751358	8.875174	9.255691
H	5.991070	4.804538	5.177153
H	10.436929	0.552341	7.595187
H	11.640963	0.367628	14.092615

Table S4. Cartesian coordinates obtained for the optimized geometry of HPC-N₁₂Ph₆.

N	10.27700	1.23800	9.58400
N	4.27400	8.17000	13.74800
N	8.88900	3.59600	16.32200
N	10.74900	1.11200	12.34700
N	3.71900	8.21300	10.97900
N	5.47200	5.61200	7.03500
N	4.13900	7.38400	8.76200
N	5.49400	7.24600	15.61000
N	9.07500	2.16000	7.70900
N	7.24200	5.31800	16.66100
N	10.28800	1.87600	14.57600
C	9.52400	1.96000	10.42500
C	5.26000	6.40900	10.64000
C	9.78300	1.90300	11.87300
C	9.02700	2.72900	12.73200
C	13.04900	-0.16400	13.34700
H	12.98600	0.01900	12.41700
C	8.02800	3.61300	12.20600
C	4.58100	7.32100	11.47900
C	6.61100	4.63800	8.90800
C	4.84700	7.28300	12.93300
C	6.84800	4.57200	10.31100
C	7.34500	4.47500	13.07100
C	8.51800	2.82100	9.93800
C	5.76500	6.31800	13.42900
C	6.41700	5.40000	12.55400
C	2.59900	9.21000	9.07800
C	7.63000	4.45700	14.46900
C	7.78200	3.65800	10.83100
C	8.47900	4.48700	18.54100
C	2.51400	9.39800	7.70700
H	3.03000	8.85200	7.12500
C	9.33700	2.69000	14.09900
C	11.29200	1.31500	6.13900
H	10.91800	2.16200	5.92400
C	6.03100	6.33100	14.81000
C	8.31400	2.87300	8.55100
C	6.98300	5.33900	15.35600
C	5.99600	4.85300	4.79400
C	10.94700	1.12000	13.67200
C	1.85300	10.00800	9.94200
H	1.91400	9.87300	10.88000

C	10.94900	0.69800	7.33600
C	3.53900	8.20500	9.64400
C	6.17500	5.45100	11.17700
C	5.70100	5.55700	8.34600
C	12.09600	-0.05300	15.54800
H	11.39700	0.23100	16.12400
C	12.17100	0.71300	5.25600
C	8.18500	4.45400	17.08700
C	8.60500	3.59100	15.02000
C	12.04400	0.26500	14.20000
C	14.15800	-0.86300	13.84200
C	4.99800	6.48900	9.26100
C	4.64900	8.13500	15.04300
C	7.28500	3.78400	8.00300
C	3.35900	11.34700	17.48300
H	3.08400	12.07900	18.02300
C	4.15700	9.23300	15.92000
C	1.67500	10.38500	7.16800
C	5.45600	6.01500	4.23900
H	5.10500	6.68800	4.81100
C	10.03600	1.39600	8.27100
C	2.87500	9.75800	15.76400
H	2.29100	9.39300	15.11000
C	12.29400	-1.23200	6.75400
C	11.46900	-0.55500	7.65500
H	11.26100	-0.95200	8.49200
C	9.04800	4.64600	21.23900
H	9.23900	4.69200	22.16800
C	8.01100	5.42800	20.72000
C	12.63500	-0.57600	5.58900
H	13.21400	-1.01600	4.97900
C	6.47500	3.84400	3.96400
H	6.82600	3.04800	4.34500
C	2.44700	10.81500	16.56500
C	1.01900	11.00000	9.43900
C	13.16900	-0.78900	16.07000
C	14.17500	-1.15400	15.19300
H	14.92000	-1.63200	15.53900
C	4.65000	10.85300	17.64100
C	5.42300	6.20100	2.86100
C	5.03000	9.77100	16.86500
H	5.89400	9.39200	16.97700
C	9.51100	3.72100	19.08300
H	10.01200	3.14000	18.52200
C	7.74300	5.32700	19.36600
H	7.03900	5.84400	18.99300
C	6.44400	3.99200	2.57900
C	0.94100	11.15400	8.05800
H	0.35700	11.81700	7.70900
C	9.81100	3.80200	20.43400
C	5.91600	5.17300	2.06100

H	5.89000	5.28200	1.11700
C	6.16300	4.74600	6.25800
H	1.60700	10.53300	6.14900
H	0.47300	11.60500	10.07200
H	14.93200	-1.14900	13.22200
H	13.20700	-1.04800	17.06800
H	10.58400	3.24800	20.83600
H	7.46400	6.05900	21.32600
H	5.30400	11.28000	18.31600
H	1.49000	11.19200	16.48400
H	5.04700	7.06800	2.44700
H	6.80100	3.25000	1.95600
H	12.47400	1.18700	4.39100
H	12.63500	-2.18600	6.95200
N	7.05400	3.82700	6.70200

Table S5. Cartesian coordinates obtained for the optimized geometry of **HBC-Ph₆**.

C	4.25600	0.22000	6.32600
H	4.08400	0.62700	5.48500
C	5.05200	0.89000	7.26000
C	5.33700	0.25500	8.46800
H	5.88400	0.70100	9.10300
C	5.94100	-1.02000	11.02600
H	6.32200	-0.17400	10.82300
C	6.19300	-1.57700	12.26500
C	5.64000	-2.82000	12.53300
H	5.77700	-3.20600	13.39100
C	4.67100	-5.53100	13.07300
H	5.12300	-5.05000	13.75600
C	4.30200	-6.85100	13.31100
C	3.61300	-7.51900	12.30500
H	3.40400	-8.43900	12.42400
C	1.68000	-8.74000	10.52700
H	1.92100	-9.16800	11.34000
C	0.72200	-9.33100	9.71100
C	0.43800	-8.72300	8.48800
H	-0.15700	-9.15400	7.88500
C	-0.40500	-7.30700	6.05100
H	-0.75600	-8.17300	6.23200
C	-0.90000	-6.60800	4.96100
C	-0.29900	-5.38300	4.65900
H	-0.59800	-4.90000	3.89700
C	0.98000	-2.89000	3.92400
H	0.38700	-3.31500	3.31600
C	1.46300	-1.61800	3.61000
C	2.37800	-1.04100	4.48300
H	2.73700	-0.18700	4.27700
C	2.79200	-1.68300	5.65900
C	3.70900	-1.03800	6.60700
C	4.00900	-1.67700	7.83600

C	4.84300	-1.01000	8.77800
C	5.14800	-1.64700	10.06100
C	4.61500	-2.92900	10.33900
C	4.88500	-3.53000	11.59000
C	4.40300	-4.88500	11.86200
C	3.65400	-5.56100	10.87300
C	3.21800	-6.87900	11.12300
C	2.29800	-7.53100	10.18500
C	1.92900	-6.86800	9.00000
C	1.00200	-7.49600	8.11900
C	0.58500	-6.79600	6.89800
C	1.15100	-5.52800	6.59800
C	0.73000	-4.84700	5.44300
C	1.33500	-3.55900	5.09500
C	2.25200	-2.95300	5.98800
C	2.61400	-3.61800	7.21400
C	3.47000	-2.97900	8.13900
C	3.79400	-3.61100	9.36500
C	3.29400	-4.90300	9.63800
C	2.45400	-5.55600	8.70700
C	2.09000	-4.90000	7.50600
C	-2.06500	-7.15900	4.11700
C	-2.54000	-6.43100	3.02600
C	-2.64400	-8.38500	4.44300
C	-3.59500	-6.93000	2.26200
H	-2.08400	-5.46400	2.76900
C	-3.69800	-8.88400	3.67800
H	-2.26900	-8.95900	5.30400
C	-4.17400	-8.15700	2.58800
H	-3.97000	-6.35700	1.40100
H	-4.15400	-9.85100	3.93500
H	-5.00500	-8.55000	1.98500
C	-0.00400	-10.61800	10.14400
C	-0.96200	-11.19400	9.30900
C	0.29600	-11.21000	11.37100
C	-1.62000	-12.35900	9.70100
H	-1.19800	-10.72700	8.34100
C	-0.36100	-12.37600	11.76300
H	1.05100	-10.75600	12.03000
C	-1.31900	-12.95100	10.92800
H	-2.37400	-12.81300	9.04200
H	-0.12400	-12.84200	12.73000
H	-1.83700	-13.87000	11.23700
C	4.64400	-7.54700	14.64100
C	4.26200	-8.87300	14.85300
C	5.33700	-6.85400	15.63400
C	4.57200	-9.50400	16.05800
H	3.71600	-9.41900	14.07000
C	5.64800	-7.48600	16.83800
H	5.63900	-5.81000	15.46700
C	5.26500	-8.81000	17.05000

H	4.27100	-10.54800	16.22500
H	6.19400	-6.93900	17.62100
H	5.51000	-9.30800	18.00000
C	7.05600	-0.84500	13.30900
C	7.29400	-1.43200	14.55300
C	7.60000	0.40500	13.01300
C	8.07500	-0.76900	15.49900
H	6.86500	-2.41700	14.78700
C	8.38300	1.06700	13.95900
H	7.41300	0.86800	12.03300
C	8.62000	0.48100	15.20200
H	8.26300	-1.23100	16.47900
H	8.81200	2.05200	13.72500
H	9.23600	1.00300	15.94800
C	5.60100	2.29700	6.96100
C	6.39400	2.95100	7.90500
C	5.30700	2.91800	5.74700
C	6.89200	4.22600	7.63500
H	6.62600	2.46200	8.86200
C	5.80600	4.19300	5.47700
H	4.68200	2.40300	5.00300
C	6.59800	4.84700	6.42000
H	7.51700	4.74100	8.37800
H	5.57400	4.68200	4.52000
H	6.99100	5.85100	6.20700
C	0.99800	-0.88000	2.34100
C	1.49700	0.39100	2.05100
C	0.07900	-1.48200	1.48100
C	1.07600	1.05900	0.90100
H	2.22100	0.86500	2.72900
C	-0.34100	-0.81300	0.33000
H	-0.31400	-2.48300	1.70900
C	0.15700	0.45700	0.04100
H	1.46900	2.06000	0.67200
H	-1.06500	-1.28800	-0.34800
H	-0.17400	0.98400	-0.86600

Table S6. Cartesian coordinates obtained for the optimized geometry of **HBC-Ph₆** (90° dihedral).

C	4.25600	0.22000	6.32600
H	4.08400	0.62700	5.48500
C	5.05200	0.89000	7.26000
C	5.33700	0.25500	8.46800
H	5.88400	0.70100	9.10300
C	5.94100	-1.02000	11.02600
H	6.32200	-0.17400	10.82300
C	6.19300	-1.57700	12.26500
C	5.64000	-2.82000	12.53300
H	5.77700	-3.20600	13.39100
C	4.30200	-6.85100	13.31100

C	0.72200	-9.33100	9.71100
C	-0.40500	-7.30700	6.05100
C	-0.90000	-6.60800	4.96100
C	-0.29900	-5.38300	4.65900
C	0.98000	-2.89000	3.92400
H	0.38700	-3.31500	3.31600
C	1.46300	-1.61800	3.61000
C	2.37800	-1.04100	4.48300
H	2.73700	-0.18700	4.27700
C	2.79200	-1.68300	5.65900
C	3.70900	-1.03800	6.60700
C	4.00900	-1.67700	7.83600
C	4.84300	-1.01000	8.77800
C	5.14800	-1.64700	10.06100
C	4.61500	-2.92900	10.33900
C	4.88500	-3.53000	11.59000
C	4.40300	-4.88500	11.86200
C	3.65400	-5.56100	10.87300
C	3.21800	-6.87900	11.12300
C	2.29800	-7.53100	10.18500
C	1.92900	-6.86800	9.00000
C	1.00200	-7.49600	8.11900
C	0.58500	-6.79600	6.89800
C	1.15100	-5.52800	6.59800
C	0.73000	-4.84700	5.44300
C	1.33500	-3.55900	5.09500
C	2.25200	-2.95300	5.98800
C	2.61400	-3.61800	7.21400
C	3.47000	-2.97900	8.13900
C	3.79400	-3.61100	9.36500
C	3.29400	-4.90300	9.63800
C	2.45400	-5.55600	8.70700
C	2.09000	-4.90000	7.50600
C	0.43800	-8.72300	8.48800
C	1.68000	-8.74000	10.52700
C	3.61300	-7.51900	12.30500
C	4.67100	-5.53100	13.07300
H	-0.79800	-8.28100	6.25400
H	-0.63600	-4.83800	3.80200
C	4.64500	-7.54800	14.64100
C	5.79700	-8.32700	14.74300
C	3.80300	-7.39900	15.74400
C	6.10800	-8.95800	15.94800
H	6.46100	-8.44400	13.87400
C	4.11400	-8.03000	16.94900
H	2.89500	-6.78500	15.66300
C	5.26700	-8.80900	17.05000
H	7.01700	-9.57200	16.02800
H	3.45100	-7.91300	17.81800
H	5.51200	-9.30700	18.00000
C	-0.00400	-10.61800	10.14400

C	-1.20200	-10.53800	10.85400
C	0.53600	-11.86500	9.82700
C	-1.86000	-11.70300	11.24700
H	-1.62800	-9.55500	11.10400
C	-0.12200	-13.03000	10.21900
H	1.48100	-11.92800	9.26700
C	-1.32000	-12.95000	10.92900
H	-2.80400	-11.64000	11.80600
H	0.30400	-14.01300	9.96900
H	-1.83900	-13.86900	11.23900
C	-2.06500	-7.15900	4.11700
C	-1.80326	-7.96826	3.01200
C	-3.38141	-6.84911	4.45990
C	-2.85827	-8.46694	2.24780
H	-0.76549	-8.21194	2.74234
C	-4.43647	-7.34875	3.69540
H	-3.58734	-6.21135	5.33134
C	-4.17531	-8.15773	2.58963
H	-2.65239	-9.10566	1.37606
H	-5.47367	-7.10534	3.96582
H	-5.00633	-8.55168	1.98728
C	0.99800	-0.88000	2.34100
C	1.72923	-0.99844	1.15786
C	-0.15361	-0.09378	2.37298
C	1.30874	-0.33004	0.00832
H	2.63732	-1.61869	1.13240
C	-0.57467	0.57373	1.22251
H	-0.72979	-0.00047	3.30451
C	0.15587	0.45502	0.04005
H	1.88421	-0.42328	-0.92390
H	-1.48332	1.19274	1.24840
H	-0.17604	0.98195	-0.86602
C	5.60200	2.29700	6.96100
C	6.76476	2.44537	6.20483
C	4.93761	3.42376	7.44563
C	7.26392	3.71960	5.93519
H	7.28963	1.55707	5.82256
C	5.43542	4.69808	7.17394
H	4.02023	3.30680	8.04158
C	6.59816	4.84628	6.41876
H	8.17993	3.83647	5.33818
H	4.91055	5.58638	7.55622
H	6.99149	5.85099	6.20500
C	7.05600	-0.84500	13.30900
C	8.44668	-0.95975	13.26905
C	6.44984	-0.06659	14.29454
C	9.22853	-0.29747	14.21484
H	8.92542	-1.57297	12.49201
C	7.23194	0.59666	15.24028
H	5.35419	0.02437	14.32650
C	8.62148	0.48115	15.19997

H	10.32443	-0.38746	14.18282
H	6.75256	1.21105	16.01685
H	9.23736	1.00473	15.94549
H	-0.20827	-9.19256	7.83464
H	2.06081	-9.25086	11.52480
H	3.38544	-8.51743	12.43295
H	5.23160	-4.94530	13.74046

Table S7. Cartesian coordinates obtained for the optimized geometry of **HBC-Ph₆** (45° dihedral).

C	0.76000	1.20900	0.07100
C	-0.72400	1.25500	-0.07100
C	-1.42400	0.10000	-0.10900
C	-0.75900	-1.14700	-0.02200
C	0.65200	-1.22200	0.12200
C	1.41000	-0.03400	0.16400
C	1.50500	2.39700	0.06900
C	0.86100	3.63700	-0.06900
C	3.05900	4.70200	-0.25200
C	2.99700	2.36100	0.15900
C	-1.38900	2.50100	-0.12900
C	-2.81300	2.55900	-0.22200
C	-2.67200	4.95900	-0.01100
C	-0.63400	3.70200	-0.06100
C	-2.91100	0.14600	-0.26000
C	-3.64800	-1.06100	-0.32100
C	-5.66300	0.18400	-0.68700
C	-3.56000	1.34500	-0.34600
C	-1.55100	-2.40000	-0.01500
C	-0.88900	-3.63000	0.15700
C	-3.03000	-4.72100	0.36400
C	-2.95800	-2.36400	-0.09100
C	1.31000	-2.47700	0.18800
C	2.81300	-2.53500	0.26800
C	2.68300	-4.88000	0.03600
C	0.61000	-3.64800	0.13800
C	2.89000	-0.08500	0.33000
C	3.64400	1.11500	0.38200
C	5.64700	-0.17000	0.78700
C	3.55600	-1.33100	0.42200
C	1.66000	4.77400	-0.28200
C	3.67800	3.52400	-0.02400
C	-3.41200	3.78100	-0.16800
C	-1.27900	4.88400	0.04700
C	-5.02900	-0.99600	-0.59000
C	-4.97000	1.33200	-0.55900
C	-1.62700	-4.74500	0.38700
C	-3.67200	-3.56400	0.12100
C	3.40500	-3.75400	0.16700
C	1.28400	-4.81800	0.02000

C	5.02900	1.01700	0.65700
C	4.95300	-1.31800	0.66900
H	1.21700	5.72600	-0.53200
H	4.75400	3.54600	-0.02000
H	-4.47600	3.90600	-0.22200
H	-0.74100	5.80200	0.21900
H	-5.60700	-1.89100	-0.74900
H	-5.54200	2.23900	-0.64200
H	-1.16000	-5.68300	0.64400
H	-4.74900	-3.58000	0.11800
H	4.47400	-3.87000	0.17200
H	0.76300	-5.74800	-0.14400
H	5.63200	1.89500	0.82000
H	5.51200	-2.22900	0.79500
C	-3.35500	6.27900	0.08700
C	-2.83400	7.39600	-0.57900
C	-4.52100	6.42100	0.84900
C	-3.44500	8.66200	-0.48600
H	-1.94600	7.27200	-1.18400
C	-5.18900	7.65700	0.95000
H	-4.90300	5.55900	1.37800
C	-4.63000	8.77100	0.28000
H	-5.11700	9.72400	0.35500
C	3.85900	5.93900	-0.47400
C	4.98600	5.92200	-1.30600
C	3.48600	7.13900	0.14500
C	5.76600	7.07600	-1.51500
H	5.25000	4.99800	-1.80200
C	4.21000	8.33000	-0.05800
H	2.62400	7.13800	0.79800
C	5.35600	8.27600	-0.88600
H	5.92900	9.17000	-1.04300
C	7.11300	-0.21100	1.05200
C	7.62900	-1.02900	2.06700
C	7.98800	0.56900	0.28200
C	9.01500	-1.09000	2.32300
H	6.92800	-1.60200	2.65500
C	9.38000	0.55100	0.51100
H	7.56100	1.17500	-0.50200
C	9.86800	-0.29200	1.53200
H	10.93200	-0.32600	1.71400
C	3.35600	-6.20300	-0.08200
C	2.88600	-7.29700	0.65500
C	4.44900	-6.37600	-0.94100
C	3.47300	-8.57200	0.53900
H	2.05500	-7.14700	1.33000
C	5.08900	-7.62300	-1.07500
H	4.79000	-5.52800	-1.52000
C	4.58200	-8.71400	-0.32800
H	5.05000	-9.67500	-0.42300
C	-3.79700	-5.97500	0.60100

C	-4.92700	-5.97600	1.42800
C	-3.39200	-7.17200	-0.00500
C	-5.67700	-7.14800	1.64800
H	-5.21600	-5.05300	1.91100
C	-4.08700	-8.37700	0.20700
H	-2.52900	-7.15500	-0.65700
C	-5.23600	-8.34400	1.03300
H	-5.78700	-9.25000	1.19700
C	-7.13700	0.21400	-0.91500
C	-7.69200	1.08000	-1.86900
C	-7.98100	-0.62100	-0.16800
C	-9.08600	1.13700	-2.08200
H	-7.01600	1.69500	-2.44300
C	-9.37700	-0.61500	-0.36200
H	-7.52600	-1.26100	0.57200
C	-9.90600	0.27900	-1.31800
H	-10.97400	0.30600	-1.47000
H	-6.49100	7.74400	1.77900
H	-2.80400	9.86300	-1.21700
H	3.72800	9.62900	0.62700
H	7.01900	6.98600	-2.41600
H	2.88700	-9.74700	1.35400
H	6.30100	-7.75100	-2.02600
H	-3.57500	-9.67000	-0.46800
H	-6.93400	-7.08000	2.54500
H	9.62000	-1.98900	3.42400
H	10.37000	1.40500	-0.31200
H	-9.73400	2.09300	-3.10700
H	-10.33100	-1.53700	0.42900

Crystallographic Information

CCDC deposition number 2335088 contains the supplementary crystallographic data for this paper.¹³ These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

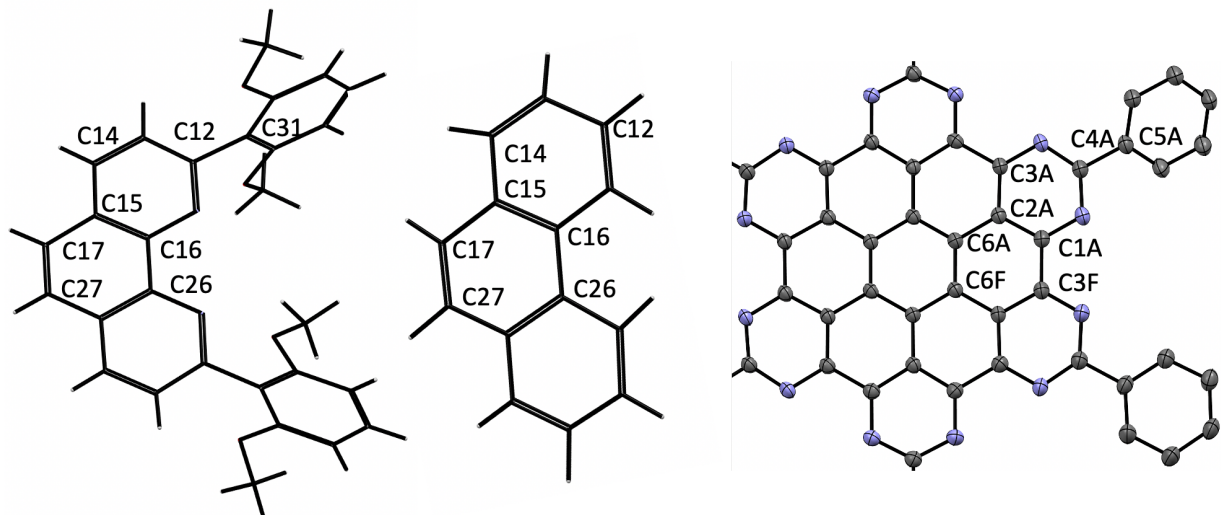
Refinement Details. In each case, crystals were mounted on a glass fiber or MiTeGen loop using Paratone oil, then placed on the diffractometer under a constant nitrogen stream. Low temperature (175 K) X-ray data were obtained on a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS based diffractometer (Mo I μ S HB micro-focus sealed X-ray tube, $K\alpha = 0.71073 \text{ \AA}$ or Cu I μ S HB micro-focused X-ray tube, $K\alpha = 1.54178$). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.¹⁴ Absorption corrections were applied using SADABS.¹⁵ Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved in the Olex 2 software interface¹⁶ by intrinsic phasing using XT (incorporated into SHELXTL)¹⁷ and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined using anisotropic displacement parameters, except in some cases with heavily distorted solvent. Hydrogen atoms were placed in the idealized positions and refined using a riding model. The structure was refined (weighted least squares refinement on F2) to convergence. Graphical representation of structures with 50% probability thermal ellipsoids was generated using Diamond 3 visualization software.¹⁸

Table S8. Crystal data and structure refinement for **HPC-N₁₂(Ar^{tBu})₆**.

CCDC Number ⁶	2335088
Empirical formula	C _{116.94} H _{128.94} Cl _{8.84} N ₁₂
Formula weight	2015.80
Temperature/K	175.0
Crystal system	Triclinic
Space group	P-1
a/Å	14.3540(6)
b/Å	18.2341(6)
c/Å	23.2636(10)
α/°	110.586(3)
β/°	101.322(3)
γ/°	93.081(3)
Volume/Å ³	5538.9(4)
Z	2
ρ _{calc} g/cm ³	1.209
μ/mm ⁻¹	2.448
Abs. Correction	Semi-empirical
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range/°	5.344 to 133.268
GOF	1.050
Diffractometer	PHOTON

$$^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}$$

Table S9. Comparison of select bond lengths between **2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline** (left) and **HPC-N₁₂(Ar^{tBu})₆** (right, truncated structure).



2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline bond lengths (Å) ¹⁹	Decamethylphenanthrene bond lengths (Å) ²⁰	HPC-N₁₂(Ar^{tBu})₆ bond lengths (Å)
C16-C26: 1.457	C16'-C26': 1.453	C3F-C1A: 1.480(2)
C12-C31: 1.508	<i>N/A</i>	C4A-C5A: 1.486(2)
C15-C14: 1.415	C15'-C14': 1.420	C3A-C2A: 1.412(4)
C17-C27: 1.356	C17'-C27': 1.332	C6A-C6F: 1.408(4)
C17-C15: 1.461	C17'-C15': 1.446	C6A-C2A: 1.427(3)
C15-C16: 1.425	C15'-C16': 1.393	C2A-C1A: 1.406(3)

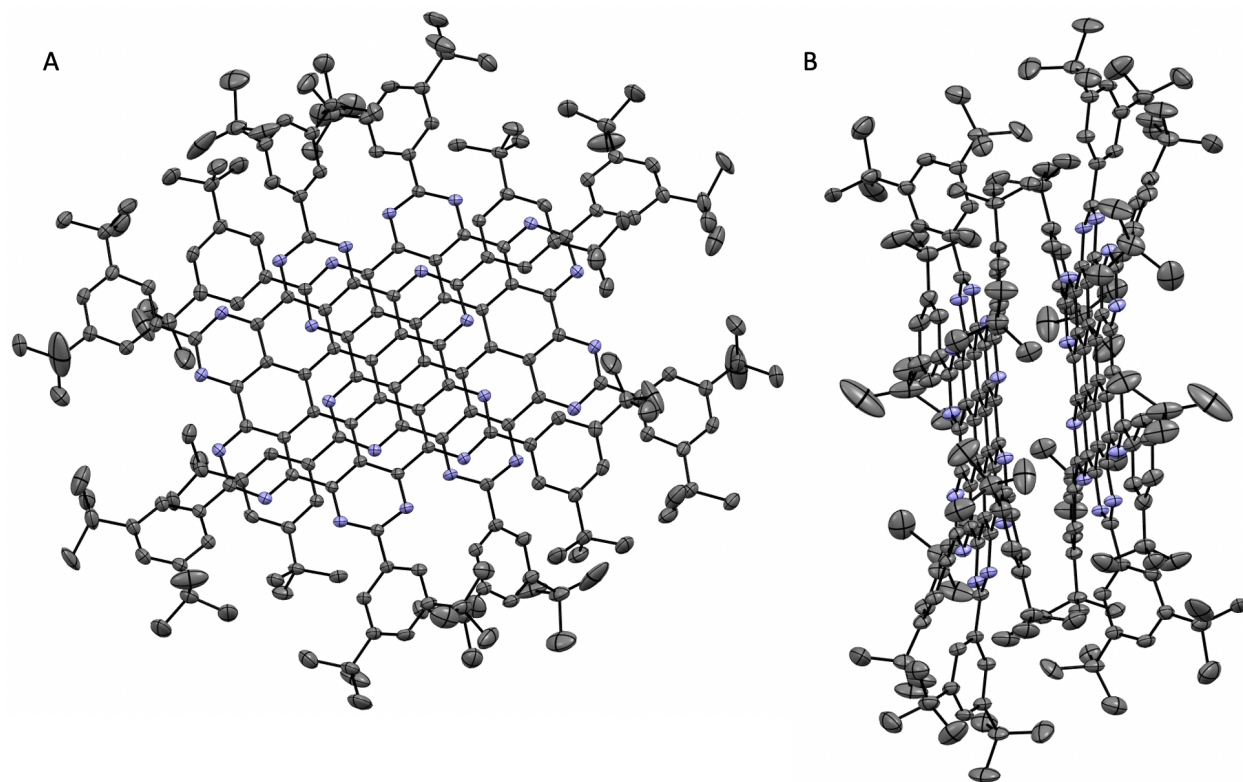


Figure S22. A. Top-down view of HPC-N₁₂(Ar^{tBu})₆ unit cell and B. side-on view, each highlighting optimal π stacking requires each unit to be offset.

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