

Electronic Supplementary Information

The mixed alloyed chemical composition of chloro-
(chloro)_n-boron subnaphthalocyanines dictates their
physical properties and performance in organic
photovoltaic devices

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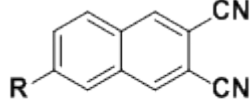
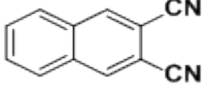
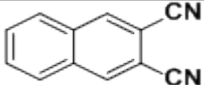
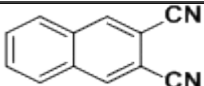
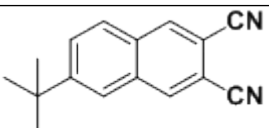
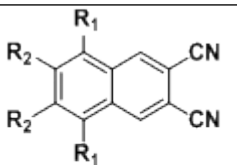
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Table S1. Summary of reported BsubNc synthesis.

Entry	Starting Material	Boron Source	Solvent	Temperature (°C)	Yield (%)	Reference
1	 R = H, C(CH ₃) ₃	PhBCl ₂	NAP	218	Anal.	1,2
2		BBr ₃	2,3-DM-6- ^t BuNAP	180	34.6	3
3		BCl ₃	1,2-DCB	180	53	4
4		BCl ₃	CIBZH: TOL (1:1)	130	35	5
5		BCl ₃	1-CINAP	microwave	82	6
6	 Cl-F ₆ BsubNc: R ₁ = H, R ₂ = F Cl-F ₁₂ BsubNc: R ₁ = R ₂ = F	BCl ₃	<i>p</i> -XYL: 1,2-DCB (1:1)	150-180	Cl-F ₆ BsubNc: 26 Cl-F ₁₂ BsubNc: 44	7

*NAP = naphthalene; 2,3-DM-6-^tBuNAP = 2,3-dimethyl-6-*tert*-butylnaphthalene; 1,2-DCB = 1,2-dichlorobenzene; CIBZH = chlorobenzene; TOL = toluene; 1-CINAP = 1-chloronaphthalene; *p*-XYL = *para*-xylene.

General Experimental Methods

Materials. Acetone, bromobenzene, dichloromethane, chlorobenzene, toluene, *para*-xylene, *N,N*-dimethylformamide (distilled), acetonitrile (HPLC-grade), ethylene glycol and sodium iodide were purchased from Caledon Labs (Caledon, Ontario, Canada) and used without further purification unless otherwise stated. Fumaronitrile was purchased from TCI America (Portland, Oregon, USA) and used as received. Boron tribromide, boron trichloride (1.0 M solution in heptane), boron trifluoride diethyl etherate, 1-methylnaphthalene, 1,2,4-trichlorobenzene, chloronaphthalene, anisole, dibutyl ether, diethylene glycol dimethyl ether, dipentene, (-)- β -pinene, 1-octadecene, *para*-cymene, oxazine 170, bathocuprione (BCP, purity: 99.6%), decamethylferrocene, tetrabutylammonium perchlorate, and neutral aluminum oxide (Al_2O_3) were purchased from Sigma-Aldrich Chemical Company (Mississauga, Ontario, Canada) and used as received. α -Sexithiophene (α -6T) was also purchased from Sigma-Aldrich Chemical Company (Mississauga, Ontario, Canada) and was purified once by train sublimation before use. $\alpha,\alpha,\alpha',\alpha'$ -Tetrabromo-*o*-xylene was purchased from Leap Labchem Company Limited (Hangzhou, China) and used as received. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was purchased from Heraeus Precious Metals GmbH & Co. (Leverkusen, Germany) and used as received. Commercial chloro boron subnaphthalocyanine (Cl-BsubNc) was purchased from Luminescence Technology Corp (Hsin-Chu, Taiwan) and used as received. Silver (purity: 99.999%) was purchased from R.D. Mathis Company (Long Beach, California, USA) and used as received. Silver paint (Conductive Silver 187) was purchased from Ted Pella Inc. (Redding, California, USA) and used as received. Aluminum plates coated with silica (pore size of 60Å) and fluorescent indicator were purchased from Whatman International Ltd. (Kent, England). Silica Gel P60 (mesh size 40-63 μm) was purchased from SiliCycle Inc. (Quebec City, Quebec, Canada). Glass substrates coated with indium-tin oxide (ITO) were purchased from Thin Film Devices Inc. (Anaheim, California, USA).

Methods. All reactions were performed under an atmosphere of argon gas using oven-dried glasswares. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica (pore size of 60Å) and fluorescent indicator and visualized under UV (254 nm) light. Column chromatography was performed using Silica Gel P60 (mesh size 40-63 μm) or neutral

aluminum oxide (Al_2O_3). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III spectrometer at 23 °C in CDCl_3 , operating at 400 MHz for ^1H NMR. Chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (0 ppm) for ^1H NMR. Coupling constants (J) are reported in hertz (Hz). Spin multiplicities are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Low resolution mass spectroscopy (LRMS) was carried out on a GCT Premier TOF mass spectrometer (Waters Corporation, Milford, Massachusetts, USA) with EI/CI sources. Ultraviolet-visible (UV-vis) absorption spectra were acquired on a PerkinElmer Lambda 1050 UV/VIS/NIR spectrometer using a PerkinElmer quartz cuvette with a 10 mm path length. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS55 fluorescence spectrometer using a PerkinElmer quartz cuvette with a 10mm path length. High pressure liquid chromatography (HPLC) analysis was carried out on a Waters 2695 separation module with a Waters 2998 photodiode array and a SunFire™ C18 3.5 μm 3.0 x 150 mm column. The mobile phase used was HPLC grade acetonitrile (80% by volume) and *N,N*-dimethylformamide (20% by volume). Cyclic and differential pulse voltammetry was carried out using a Bioanalytical Systems C3 electrochemical workstation. The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was Ag/AgCl_2 saturated salt solution. Spec-grade solvents were purged with nitrogen gas at room temperature prior to their use. Four cycles at a scan rate of 100 mV/s were measured for each sample. Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. Decamethylferrocene was used as an internal reference. All half-wave potentials were corrected to the half-wave reduction potential ($E_{1/2,\text{red}}$) of decamethylferrocene, which was previously reported to be -0.012 V vs. Ag/AgCl .⁸ Photoelectron measurements were performed using a PHI 5500 Multi-Technique system attached to a Kurt J. Lesker multiaccess chamber ultra high vacuum cluster tool (base pressure of $\sim 10^{-10}$ Torr). Monochromated Al $K\alpha$ photon source ($h\nu = 1486.7$ eV) was used for X-ray photoelectron spectroscopy (XPS) while a non-monochromated He I α photon source ($h\nu = 21.22$ eV) was used for ultraviolet photoelectron spectroscopy (UPS). Work function and valence-band measurements were carried out using UPS with the sample tilted to a take-off angle of 89° and under an applied bias of -15 V. The various organic molecules were deposited in a dedicated organic chamber from alumina crucibles transfer-arm evaporator (TAE) cell onto freshly cleaved highly ordered pyrolytic graphite (HOPG) substrates.

HOMO energy levels for each molecule were determined from 12 nm thick films as measured by a calibrated quartz crystal microbalance (QCM).

Device Fabrication. Organic photovoltaic (OPV) devices were fabricated on 25 mm by 25 mm glass substrates coated with ITO having a sheet resistance of 15 Ω per square. The ITO was pre-patterned, leaving 8 mm from one side as uncoated glass. Substrates were cleaned by successive sonications in detergent and solvents, followed by 5 minutes of atmospheric plasma treatment. PEDOT:PSS was spin-coated onto the substrates, 500 rpm, 10 s; 4000 rpm, 30 s. Substrates were baked on a hot plate at 110 °C for 10 minutes, and then transferred into a nitrogen atmosphere glove box ($O_2 < 10$ ppm, $H_2O < 10$ ppm). All subsequent device layers were thermally evaporated at ~ 1.0 A/s and a working pressure of $\sim 1 \times 10^{-7}$ Torr for organic layers and $\sim 1 \times 10^{-6}$ Torr for silver. The α -6T layer thickness for all devices was 55 nm. All Cl-BsubNc layer thicknesses were 25 nm, followed by a 10 nm layer of BCP. Silver electrodes were evaporated to a thickness of 80 nm through a shadow mask, defining 0.2 cm² as the active area for each device. A transfer back to the glove box was required between BCP and silver layers to change the shadow masks.

Device Characterization. Layer thickness and deposition rates of evaporated films were monitored using a quartz crystal microbalance calibrated against films deposited on glass and measured with a KLA-Tencor P16+ surface profilometer. To enhance the electrical contact during testing, silver paint was applied to the ITO and metal electrode contact points and left to dry for 20 minutes. Devices were kept in the nitrogen-filled glove box throughout testing. Voltage sweeps of the devices were performed under full illumination by a 300W Xe arc lamp (Oriel) with an AM 1.5G filter, and the corresponding currents were measured with a Keithley 2401 Low Voltage SourceMeter. Light intensity was calibrated to 100 mW/cm² with reference to a calibrated silicon photodetector. Wavelengths scans at 10 nm intervals were performed using an in-line CornerstoneTM 260 1/4 m Monochromator and the corresponding currents were measured using a Newport Optical Power Meter 2936-R and converted to external quantum efficiencies using a reference wavelength scan of a calibrated silicon photodetector.

Synthesis of Starting Material

2,3-Dicyanonaphthalene (DCNAP). DCNAP was prepared according to literature procedure.⁹

Synthesis of Cl-BsubNc (Torres Method):

Method 1.1 to 1.3 (Table S2): For **1.1**, to a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (0.250 g, 1.40 mmol, 1 equiv), chlorobenzene (2.5 mL), and toluene (2.5 ml) under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 1.40 mL, 1 equiv) was added. The reaction mixture was heated to 130 °C for two hours before it was cooled to room temperature. The solvent mixture was removed via rotary evaporation and the resulting solid was extracted with hexane in a Soxhlet extraction apparatus for 24 hours. Column chromatography (Si gel) was then performed on the washed product using toluene as the eluent and blue fractions were collected, concentrated, and dried in a vacuum oven (60 °C). In **1.2**, 2.5 molar equivalence of BCl₃ was used. In **1.3**, the reaction of **1.2** was repeated but *para*-xylene was substituted for toluene.

Table S2. Attempted syntheses adapted from Torres *et al.*⁵

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
1.1	BCl ₃ (1.0 M heptane, 1.0 eq)	CIBZH:TOL (1:1, 0.28 M)	130	35	5
1.2	BCl ₃ (1.0 M heptane, 2.5 eq)	CIBZH:TOL (1:1, 0.28 M)	130	24	5
1.3	BCl ₃ (1.0 M heptane, 2.5 eq)	CIBZH:XYL (1:1, 0.28 M)	130	46	5

*CIBZH = chlorobenzene; TOL = toluene; XYL = *para*-xylene.

HPLC-UV/Vis Chromatogram of Cl-BsubNc (Torres Method)

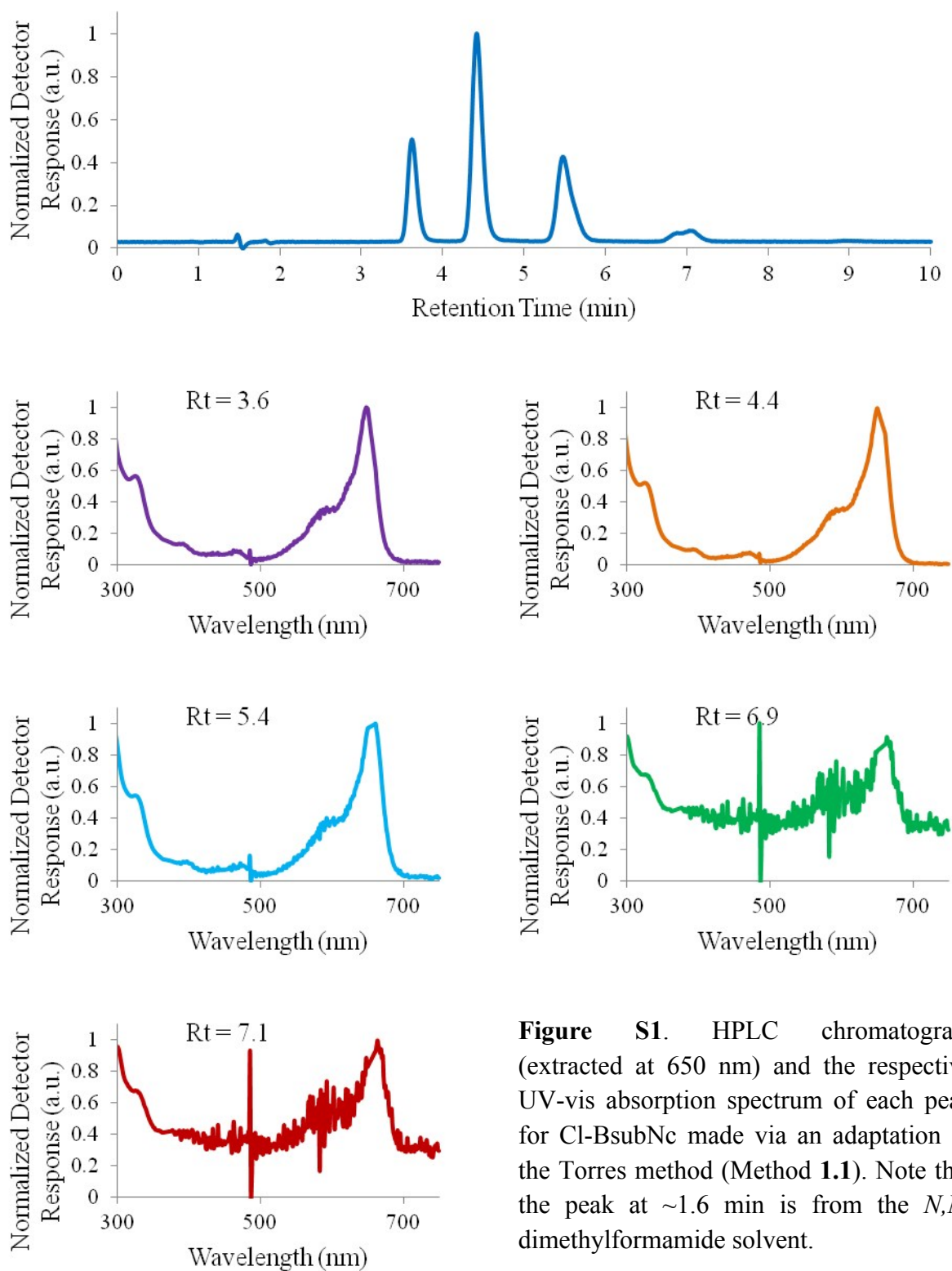


Figure S1. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for Cl-BsubNc made via an adaptation of the Torres method (Method 1.1). Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

Synthesis of Cl-BsubNc (Kennedy Method):

Method 2.1 to 2.5 (Table S3): For **2.1**, to a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (0.250 g, 1.40 mmol, 1 equiv) and dried 1,2-dichlorobenzene (10 mL) under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 0.93 mL, 0.66 equiv) was added. The reaction mixture was heated to 150 °C for one hour to distill off the heptane before it was heated to 180 °C for two hours. The reaction was cooled to room temperature and concentrated via rotary evaporation. Attempts to purify the crude product via column chromatography (neutral Al₂O₃) were performed using toluene as the eluent. In **2.2**, ACS grade 1,2-dichlorobenzene was used. In **2.3** and **2.4**, 1.1 and 3.3 molar equivalence of BCl₃ was used, respectively. In **2.5**, a solvent mixture of 1,2-dichlorobenzene and 1-methylnaphthalene (4:1 v/v) was used. For **2.3**, the reaction was scaled up by a factor of 7.6. The crude product (0.730 g) was purified by train sublimation. The apparatus was operated under a vacuum with a controlled flow of carbon dioxide gas generating an internal pressure of 100 mTorr. The temperature was increased from room temperature to ~580 °C (external temperature) and was held constant at that temperature overnight. A metallic purple band was collected (0.150 g, 21% yield relative to mass placed in the train sublimation apparatus). The sublimed product was subsequently purified a second time by train sublimation under the same condition (0.115 g, 76% yield relative to mass placed in the train sublimation apparatus), producing single crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 6H), 8.37-8.33 (m, 6H), 7.77-7.73 (m, 6H); MS (EI): *m/z* 580.1, 614.1, 648.1, 684.0; UV-vis_{toluene} λ_{max} (ε): 656 nm (78400 M⁻¹cm⁻¹).

Table S3. Attempted syntheses adapted from Zyskowski and Kennedy.⁴

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
2.1	BCl ₃ (1.0 M heptane, 0.66 eq)	1,2-DCB (dried, 0.14 M)	180	88	5
2.2	BCl ₃ (1.0 M heptane, 0.66 eq)	1,2-DCB (0.14 M)	180	84	5
2.3	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2-DCB (0.14 M)	180	81	5
2.4	BCl ₃ (1.0 M heptane, 3.3 eq)	1,2-DCB (0.14 M)	180	87	5
2.5	BCl ₃ (1.0 M heptane, 3.3 eq)	1,2-DCB:1-MNAP (4:1, 0.14 M)	180	49	2

*1,2-DCB = 1,2-dichlorobenzene; 1-MNAP = 1-methylnaphthalene.

HPLC-UV/Vis Chromatogram of Cl-BsubNc (Kennedy Method)

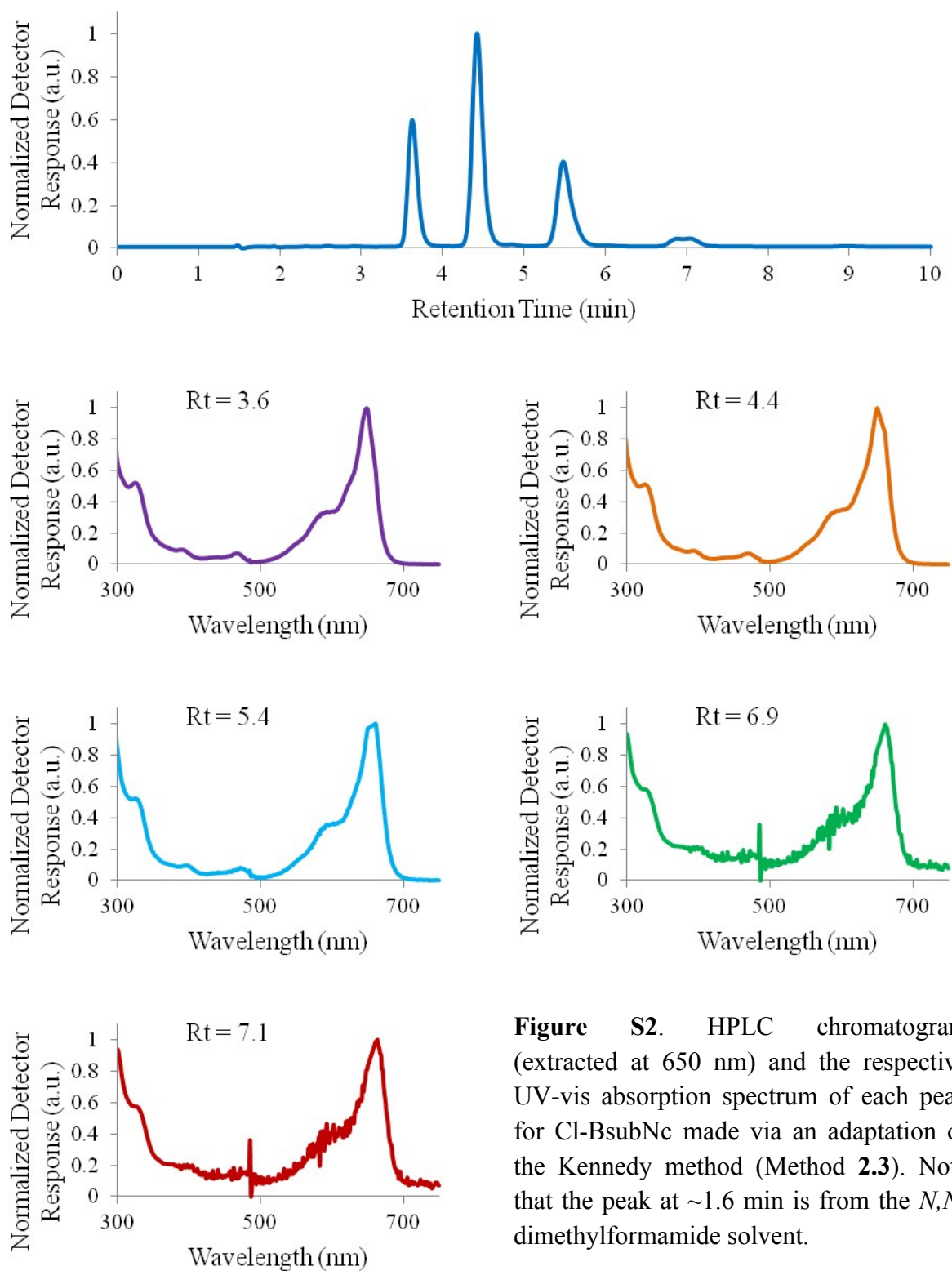


Figure S2. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for Cl-BsubNc made via an adaptation of the Kennedy method (Method 2.3). Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

Crystal Structure Details of Literature-Cl-Cl_nBsubNc

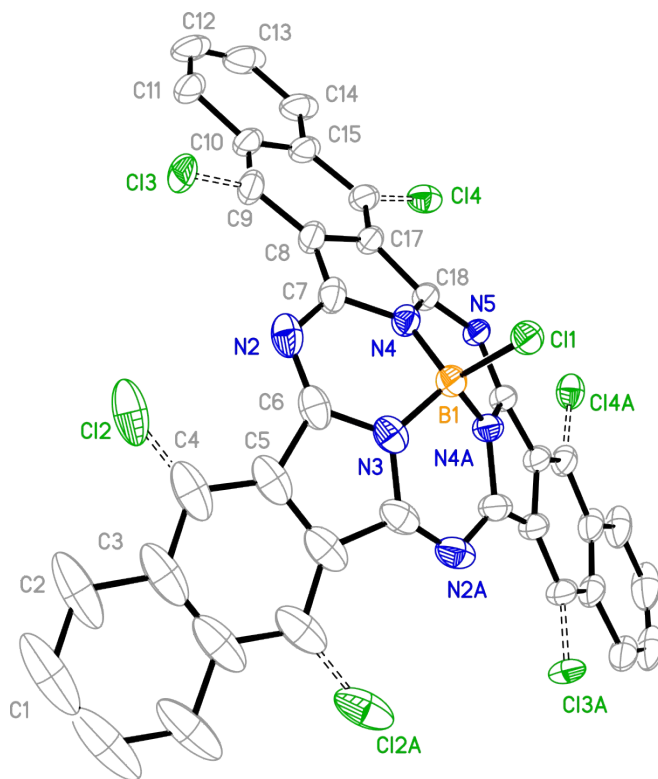


Figure S3. Ellipsoid plot (50% probability) showing the structure and atom numbering scheme of literature-Cl-Cl_nBsubNc (CCDC deposition number: 1452383). Hydrogen atoms have been omitted for clarity. Colors: boron - orange; nitrogen - blue; carbon - white; chlorine - green.

Table S4. Crystal data and structure refinement for literature-Cl-Cl_nBsubNc.

Identification code	d1491a_a	
Empirical formula	C ₃₆ H _{16.87} B Cl _{2.13} N ₆	
Formula weight	619.83	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 14.6230(5) Å	□ a = 14
	b = 18.4530(6) Å	□ b = 18
	c = 10.3923(3) Å	□ c = 10.
Volume	2804.24(16) Å ³	
Z	4	
Density (calculated)	1.468 Mg/m ³	
Absorption coefficient	2.515 mm ⁻¹	
F(000)	1264	
Crystal size	0.19 x 0.17 x 0.13 mm ³	
Theta range for data collection	4.793 to 67.293°.	
Index ranges	-17<=h<=17, -22<=k<=21, -12<=l<=12	
Reflections collected	32890	
Independent reflections	2588 [R(int) = 0.0536]	
Completeness to theta = 67.679°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7529 and 0.6630	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2588 / 0 / 235	
Goodness-of-fit on F ²	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1263	
R indices (all data)	R1 = 0.0600, wR2 = 0.1366	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.262 and -0.357 e.Å ⁻³	

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for literature-Cl-Cl_nBsubNc. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	7208(1)	2500	7632(1)	52(1)
Cl(2)	7565(2)	-463(2)	4188(3)	79(1)
Cl(3)	4149(3)	1260(2)	3617(3)	60(2)
Cl(4)	10450(4)	4151(4)	4398(4)	100(3)
N(1)	6863(1)	1865(1)	5226(2)	47(1)
N(2)	5540(2)	2500	4539(2)	43(1)
N(3)	8254(2)	2500	5367(3)	57(1)
N(4)	8263(2)	3758(1)	4874(2)	65(1)
C(1)	7345(2)	1250(1)	4913(2)	55(1)
C(2)	6674(2)	755(1)	4386(2)	56(1)
C(3)	6706(2)	40(1)	3997(3)	70(1)
C(3A)	6706(2)	40(1)	3997(3)	70(1)
C(4)	5926(3)	-296(1)	3475(3)	76(1)
C(5)	5919(3)	-1044(2)	3130(3)	101(1)
C(6)	5142(4)	-1350(2)	2631(4)	121(2)
C(7)	4363(4)	-943(2)	2428(3)	115(2)
C(8)	4330(3)	-231(2)	2751(3)	86(1)
C(9)	5108(2)	113(1)	3306(2)	67(1)
C(10)	5076(2)	842(1)	3705(2)	55(1)
C(10A)	5076(2)	842(1)	3705(2)	55(1)
C(11)	5830(2)	1152(1)	4250(2)	49(1)
C(12)	6002(2)	1882(1)	4726(2)	43(1)
C(13)	8695(2)	3125(2)	5023(2)	63(1)
C(14)	9600(2)	2889(2)	4619(2)	75(1)
C(15)	10365(2)	3277(3)	4232(3)	92(1)
C(15A)	10365(2)	3277(3)	4232(3)	92(1)
C(16)	11154(2)	2884(2)	3851(2)	105(2)
C(17)	11956(2)	3265(3)	3440(3)	139(2)
C(18)	12704(2)	2882(4)	3052(4)	169(5)
B(1)	7296(3)	2500	5827(4)	48(1)

Table S6. Bond lengths [\AA] and angles [$^\circ$] for literature-Cl-Cl_nBsubNc.

Cl(1)-B(1)	1.880(4)
Cl(2)-C(3)	1.574(4)
Cl(3)-C(10)	1.564(5)
Cl(4)-C(15)	1.627(8)
N(1)-C(12)	1.363(3)
N(1)-C(1)	1.375(3)
N(1)-B(1)	1.471(3)
N(2)-C(12)#1	1.339(2)
N(2)-C(12)	1.339(2)
N(3)-C(13)	1.369(3)
N(3)-C(13)#1	1.369(3)
N(3)-B(1)	1.481(5)
N(4)-C(13)	1.336(4)
N(4)-C(1)#1	1.343(3)
C(1)-N(4)#1	1.343(3)
C(1)-C(2)	1.449(4)
C(2)-C(3)	1.380(3)
C(2)-C(11)	1.442(3)
C(3)-C(4)	1.407(5)
C(4)-C(9)	1.425(5)
C(4)-C(5)	1.427(4)
C(5)-C(6)	1.371(6)
C(5)-H(5)	0.9300
C(6)-C(7)	1.381(7)
C(6)-H(6)	0.9300
C(7)-C(8)	1.357(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.425(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.409(3)
C(10)-C(11)	1.365(3)
C(11)-C(12)	1.457(3)
C(13)-C(14)	1.455(4)
C(14)-C(15)	1.388(4)
C(14)-C(14)#1	1.435(7)

C(15)-C(16)	1.419(5)
C(16)-C(16)#1	1.416(9)
C(16)-C(17)	1.433(5)
C(17)-C(18)	1.363(6)
C(17)-H(17)	0.9300
C(18)-C(18)#1	1.409(14)
C(18)-H(18)	0.9300
B(1)-N(1)#1	1.472(3)

C(12)-N(1)-C(1)	113.8(2)
C(12)-N(1)-B(1)	122.7(2)
C(1)-N(1)-B(1)	122.5(2)
C(12)#1-N(2)-C(12)	116.7(3)
C(13)-N(3)-C(13)#1	114.8(3)
C(13)-N(3)-B(1)	122.01(17)
C(13)#1-N(3)-B(1)	122.01(17)
C(13)-N(4)-C(1)#1	117.4(2)
N(4)#1-C(1)-N(1)	121.9(2)
N(4)#1-C(1)-C(2)	131.3(2)
N(1)-C(1)-C(2)	105.2(2)
C(3)-C(2)-C(11)	119.1(3)
C(3)-C(2)-C(1)	133.6(3)
C(11)-C(2)-C(1)	107.2(2)
C(2)-C(3)-C(4)	120.4(3)
C(2)-C(3)-Cl(2)	123.6(3)
C(4)-C(3)-Cl(2)	115.8(3)
C(3)-C(4)-C(9)	119.7(2)
C(3)-C(4)-C(5)	122.0(4)
C(9)-C(4)-C(5)	118.3(4)
C(6)-C(5)-C(4)	120.0(4)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	121.1(3)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	121.2(5)
C(8)-C(7)-H(7)	119.4

C(6)-C(7)-H(7)	119.4
C(7)-C(8)-C(9)	120.2(4)
C(7)-C(8)-H(8)	119.9
C(9)-C(8)-H(8)	119.9
C(10)-C(9)-C(4)	119.8(3)
C(10)-C(9)-C(8)	121.2(3)
C(4)-C(9)-C(8)	119.0(3)
C(11)-C(10)-C(9)	119.7(3)
C(11)-C(10)-Cl(3)	121.2(2)
C(9)-C(10)-Cl(3)	118.9(3)
C(10)-C(11)-C(2)	121.2(2)
C(10)-C(11)-C(12)	131.9(2)
C(2)-C(11)-C(12)	106.8(2)
N(2)-C(12)-N(1)	122.8(2)
N(2)-C(12)-C(11)	130.6(2)
N(1)-C(12)-C(11)	105.47(19)
N(4)-C(13)-N(3)	122.9(2)
N(4)-C(13)-C(14)	131.1(3)
N(3)-C(13)-C(14)	104.6(3)
C(15)-C(14)-C(14)#1	121.1(2)
C(15)-C(14)-C(13)	131.4(3)
C(14)#1-C(14)-C(13)	107.42(18)
C(14)-C(15)-C(16)	118.1(4)
C(14)-C(15)-Cl(4)	122.9(4)
C(16)-C(15)-Cl(4)	118.4(3)
C(16)#1-C(16)-C(15)	120.8(2)
C(16)#1-C(16)-C(17)	119.4(3)
C(15)-C(16)-C(17)	119.8(4)
C(18)-C(17)-C(16)	119.4(6)
C(18)-C(17)-H(17)	120.3
C(16)-C(17)-H(17)	120.3
C(17)-C(18)-C(18)#1	121.2(3)
C(17)-C(18)-H(18)	119.4
C(18)#1-C(18)-H(18)	119.4
N(1)-B(1)-N(1)#1	105.7(3)
N(1)-B(1)-N(3)	105.6(2)
N(1)#1-B(1)-N(3)	105.6(2)

N(1)-B(1)-Cl(1)	113.21(18)
N(1)#1-B(1)-Cl(1)	113.21(18)
N(3)-B(1)-Cl(1)	112.8(2)

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+1/2, z$

Table S7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for literature-Cl-Cl_nBsubNc. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cl(1)	60(1)	52(1)	44(1)	0	0(1)	0
Cl(2)	95(2)	48(2)	93(2)	11(1)	25(2)	37(2)
Cl(3)	63(2)	61(2)	55(2)	4(2)	-4(2)	-16(2)
Cl(4)	83(4)	174(7)	44(2)	29(3)	-8(2)	-49(4)
N(1)	52(1)	43(1)	45(1)	0(1)	2(1)	8(1)
N(2)	51(2)	33(1)	44(1)	0	2(1)	0
N(3)	50(2)	77(2)	45(2)	0	-1(1)	0
N(4)	65(1)	79(2)	51(1)	0(1)	2(1)	-26(1)
C(1)	69(2)	50(1)	46(1)	1(1)	5(1)	19(1)
C(2)	80(2)	40(1)	48(1)	0(1)	13(1)	12(1)
C(3)	111(2)	42(1)	59(2)	3(1)	30(2)	23(2)
C(3A)	111(2)	42(1)	59(2)	3(1)	30(2)	23(2)
C(4)	138(3)	35(1)	54(2)	-6(1)	38(2)	-8(2)
C(5)	192(4)	39(2)	73(2)	-9(1)	67(2)	-5(2)
C(6)	247(6)	41(2)	75(2)	-22(2)	72(3)	-48(3)
C(7)	212(5)	67(2)	66(2)	-28(2)	47(3)	-71(3)
C(8)	143(3)	62(2)	55(2)	-13(1)	22(2)	-48(2)
C(9)	114(2)	41(1)	47(1)	-7(1)	21(1)	-19(2)
C(10)	79(2)	41(1)	45(1)	-2(1)	9(1)	-11(1)
C(10A)	79(2)	41(1)	45(1)	-2(1)	9(1)	-11(1)
C(11)	68(2)	35(1)	44(1)	-2(1)	7(1)	2(1)
C(12)	51(1)	36(1)	43(1)	0(1)	3(1)	2(1)
C(13)	56(2)	91(2)	42(1)	2(1)	0(1)	-18(2)
C(14)	52(1)	135(3)	38(1)	1(1)	-3(1)	-10(2)
C(15)	60(2)	179(4)	38(1)	6(2)	-3(1)	-26(2)
C(15A)	60(2)	179(4)	38(1)	6(2)	-3(1)	-26(2)
C(16)	53(2)	226(5)	36(1)	5(2)	-1(1)	-13(2)
C(17)	58(2)	309(7)	49(2)	16(3)	3(2)	-37(3)
C(18)	57(2)	383(14)	66(2)	14(3)	12(2)	-24(3)
B(1)	51(2)	49(2)	45(2)	0	2(2)	0

Table S8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for literature-Cl-Cl_nBsubNc.

	x	y	z	U(eq)
H(3A)	7247	-221	4081	85
H(5)	6441	-1324	3244	122
H(6)	5139	-1841	2426	145
H(7)	3851	-1161	2064	138
H(8)	3798	34	2609	104
H(10A)	4544	1111	3598	66
H(15A)	10361	3781	4222	110
H(17)	11966	3769	3437	166
H(18)	13224	3129	2783	203

Table S9. Torsion angles [°] for literature-Cl-Cl_nBsubNc.

C(12)-N(1)-C(1)-N(4)#1	154.2(2)
B(1)-N(1)-C(1)-N(4)#1	-14.8(4)
C(12)-N(1)-C(1)-C(2)	-12.7(3)
B(1)-N(1)-C(1)-C(2)	178.4(2)
N(4)#1-C(1)-C(2)-C(3)	21.0(5)
N(1)-C(1)-C(2)-C(3)	-173.9(3)
N(4)#1-C(1)-C(2)-C(11)	-157.2(3)
N(1)-C(1)-C(2)-C(11)	7.9(3)
C(11)-C(2)-C(3)-C(4)	0.0(4)
C(1)-C(2)-C(3)-C(4)	-178.0(3)
C(11)-C(2)-C(3)-Cl(2)	-175.5(2)
C(1)-C(2)-C(3)-Cl(2)	6.5(4)
C(2)-C(3)-C(4)-C(9)	2.2(4)
Cl(2)-C(3)-C(4)-C(9)	178.1(2)
C(2)-C(3)-C(4)-C(5)	-176.4(2)
Cl(2)-C(3)-C(4)-C(5)	-0.5(4)
C(3)-C(4)-C(5)-C(6)	179.6(3)
C(9)-C(4)-C(5)-C(6)	1.0(4)
C(4)-C(5)-C(6)-C(7)	1.3(5)
C(5)-C(6)-C(7)-C(8)	-2.0(5)
C(6)-C(7)-C(8)-C(9)	0.2(5)
C(3)-C(4)-C(9)-C(10)	-2.3(4)
C(5)-C(4)-C(9)-C(10)	176.3(2)
C(3)-C(4)-C(9)-C(8)	178.7(2)
C(5)-C(4)-C(9)-C(8)	-2.7(4)
C(7)-C(8)-C(9)-C(10)	-176.9(3)
C(7)-C(8)-C(9)-C(4)	2.1(4)
C(4)-C(9)-C(10)-C(11)	0.1(3)
C(8)-C(9)-C(10)-C(11)	179.1(2)
C(4)-C(9)-C(10)-Cl(3)	-175.0(2)
C(8)-C(9)-C(10)-Cl(3)	4.1(4)
C(9)-C(10)-C(11)-C(2)	2.2(3)
Cl(3)-C(10)-C(11)-C(2)	177.1(2)
C(9)-C(10)-C(11)-C(12)	178.8(2)
Cl(3)-C(10)-C(11)-C(12)	-6.3(4)

C(3)-C(2)-C(11)-C(10)	-2.3(3)
C(1)-C(2)-C(11)-C(10)	176.2(2)
C(3)-C(2)-C(11)-C(12)	-179.6(2)
C(1)-C(2)-C(11)-C(12)	-1.2(3)
C(12)#1-N(2)-C(12)-N(1)	7.5(4)
C(12)#1-N(2)-C(12)-C(11)	-158.51(17)
C(1)-N(1)-C(12)-N(2)	-157.0(2)
B(1)-N(1)-C(12)-N(2)	11.8(4)
C(1)-N(1)-C(12)-C(11)	12.0(2)
B(1)-N(1)-C(12)-C(11)	-179.1(2)
C(10)-C(11)-C(12)-N(2)	-15.2(4)
C(2)-C(11)-C(12)-N(2)	161.7(2)
C(10)-C(11)-C(12)-N(1)	176.9(2)
C(2)-C(11)-C(12)-N(1)	-6.1(2)
C(1)#1-N(4)-C(13)-N(3)	-8.2(4)
C(1)#1-N(4)-C(13)-C(14)	156.2(3)
C(13)#1-N(3)-C(13)-N(4)	156.79(19)
B(1)-N(3)-C(13)-N(4)	-11.2(4)
C(13)#1-N(3)-C(13)-C(14)	-11.2(4)
B(1)-N(3)-C(13)-C(14)	-179.2(3)
N(4)-C(13)-C(14)-C(15)	17.3(5)
N(3)-C(13)-C(14)-C(15)	-176.2(3)
N(4)-C(13)-C(14)-C(14)#1	-160.3(2)
N(3)-C(13)-C(14)-C(14)#1	6.3(2)
C(14)#1-C(14)-C(15)-C(16)	-0.8(3)
C(13)-C(14)-C(15)-C(16)	-178.1(2)
C(14)#1-C(14)-C(15)-Cl(4)	-171.4(2)
C(13)-C(14)-C(15)-Cl(4)	11.3(5)
C(14)-C(15)-C(16)-C(16)#1	0.8(3)
Cl(4)-C(15)-C(16)-C(16)#1	171.8(2)
C(14)-C(15)-C(16)-C(17)	179.7(2)
Cl(4)-C(15)-C(16)-C(17)	-9.2(4)
C(16)#1-C(16)-C(17)-C(18)	0.2(4)
C(15)-C(16)-C(17)-C(18)	-178.8(3)
C(16)-C(17)-C(18)-C(18)#1	-0.2(4)
C(12)-N(1)-B(1)-N(1)#1	-26.7(4)
C(1)-N(1)-B(1)-N(1)#1	141.20(19)

C(12)-N(1)-B(1)-N(3)	-138.4(2)
C(1)-N(1)-B(1)-N(3)	29.5(3)
C(12)-N(1)-B(1)-Cl(1)	97.7(2)
C(1)-N(1)-B(1)-Cl(1)	-94.3(3)
C(13)-N(3)-B(1)-N(1)	139.4(2)
C(13)#1-N(3)-B(1)-N(1)	-27.7(4)
C(13)-N(3)-B(1)-N(1)#1	27.7(4)
C(13)#1-N(3)-B(1)-N(1)#1	-139.4(2)
C(13)-N(3)-B(1)-Cl(1)	-96.4(3)
C(13)#1-N(3)-B(1)-Cl(1)	96.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+1/2, z$

Synthesis of Cl-BsubNc (1-MNAP Method):

Method 3.1 to 3.6 (Table S10): For **3.1**, to a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (0.500 g, 2.81 mmol, 1 equiv), 1,2,4-trichlorobenzene (16 mL) and 1-methylnaphthalene (4 mL) under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 1.90 mL, 0.66 equiv) was added. The reaction mixture was heated to 130 °C for two hours before it was hot filtered under vacuum. The solid black mass was washed with hot toluene (~100 °C) until the filtrate was no longer blue in colour. The filtrate solution was concentrated to remove the toluene via rotary evaporation before it was precipitated into ice cold stirring hexane (200 mL), gravity filtered, washed with hexane (3 x 50 mL), and dried in a vacuum oven (60 °C). Attempts to purify the crude product via Soxhlet extraction and column chromatography on both Si gel and neutral Al₂O₃ were made. For **3.2 to 3.5**, the molar equivalence of BCl₃ was increased to 1.1, 2.5, 4.2, and 4.9, respectively. For **3.6**, the reaction was scaled up by a factor of 2.2. The crude product (0.376 g) was purified by train sublimation. The apparatus was operated under a vacuum with a controlled flow of carbon dioxide gas generating an internal pressure of 100 mTorr. The temperature was increased from room temperature to ~550 °C (external temperature) and was held constant at that temperature overnight. A metallic purple band was collected (14 mg, 3.7% yield relative to mass placed in the train sublimation apparatus). ¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 6H), 8.37-8.33 (m, 6H), 7.77-7.73 (m, 6H); MS (EI): *m/z* 580.1, 614.1.

Table S10. Attempted syntheses adapted from Noll *et al.*¹⁰

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
3.1	BCl ₃ (1.0 M heptane, 0.66 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	70	2
3.2	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	68	2
3.3	BCl ₃ (1.0 M heptane, 2.5 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	68	2
3.4	BCl ₃ (1.0 M heptane, 4.2 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	26	2
3.5	BCl ₃ (1.0 M heptane, 4.9 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	22	2
3.6	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:1-MNAP (4:1, 0.14 M)	130	58	2

*1,2,4-TCB = 1,2,4-trichlorobenzene; 1-MNAP = 1-methylnaphthalene.

HPLC-UV/Vis Chromatogram and Mass Spectrum of Cl-BsubNc (1-MNAP Method)

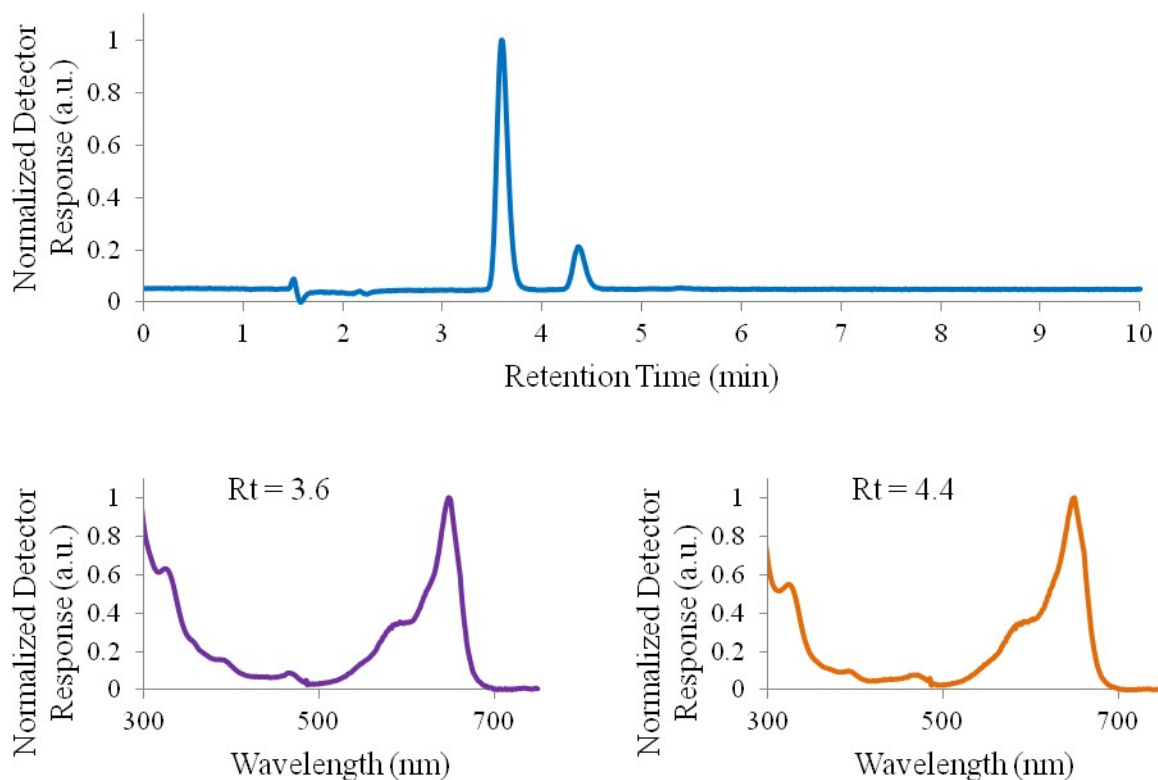


Figure S4a. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for Cl-BsubNc made via the 1-MNAP method (Method 3.6). Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

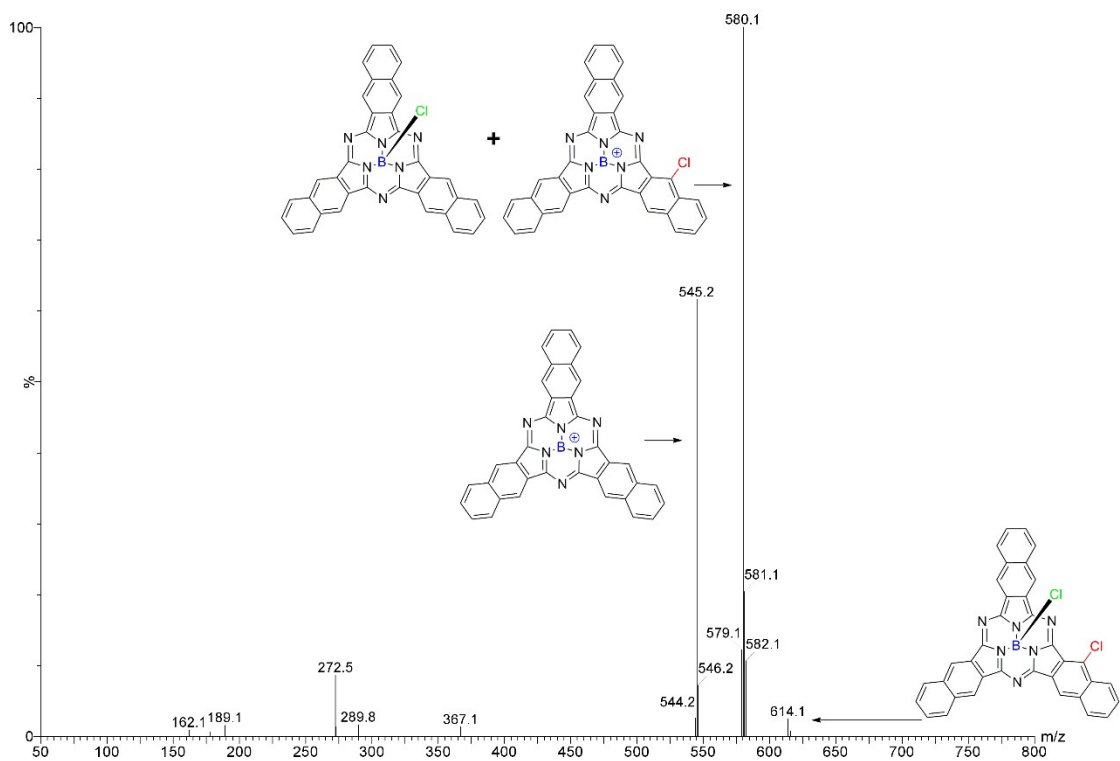


Figure S4b. Mass spectrum of sublimed Cl-BsubNc sample made via the 1-MNAP method (Method 3.6) indicating the additional presence of Cl-Cl₁BsubPc and absence of Cl-Cl₂BsubNc and Cl-Cl₃BsubNc.

Synthesis of Cl-BsubNc (Scope of Reactions Method):

Method 4.1 to 4.15 (Table S11): All reactions were performed in a similar manner as those in Method 1-3.

Table S11. Scope of reactions varying molar equivalence of BCl₃, solvent mixture composition, and concentration of 2,3-dicyanonaphthalene.

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
4.1	BCl ₃ (1.0 M heptane, 1.0 eq)	CINAP (0.47 M)	130	31	5
4.2	BCl ₃ (1.0 M heptane, 1.0 eq)	1-MNAP (0.47 M)	130	8	2
4.3	BCl ₃ (1.0 M heptane, 1.0 eq)	CIBZH:1-MNAP (1:1, 0.47 M)	130	4	2
4.4	BCl ₃ (1.0 M heptane, 1.0 eq)	1,2-DCB:TOL (1:1, 0.47 M)	130	40	5
4.5	BCl ₃ (1.0 M heptane, 1.0 eq)	1,2-DCB:1-MNAP (1:1, 0.47 M)	130	12	2
4.6	BCl ₃ (1.0 M heptane, 2.0 eq)	1,2-DCB:1-MNAP (1:1, 0.47 M)	130	22	2
4.7	BCl ₃ (1.0 M heptane, 4.0 eq)	1,2-DCB:1-MNAP (1:1, 0.47 M)	130	23	2
4.8	BCl ₃ (1.0 M heptane, 2.5 eq)	1,2-DCB (0.17 M)	180	70	5
4.9	BCl ₃ (1.0 M heptane, 2.5 eq)	1,2-DCB:1-MNAP (3:1, 0.17 M)	180	7	2
4.10	BCl ₃ (1.0 M heptane, 2.5 eq)	1,2-DCB:1-MNAP (6:1, 0.17 M)	180	0	0
4.11	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2-DCB (0.28 M)	180	88	5
4.12	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2-DCB:1-MNAP (4:1, 0.28 M)	180	38	2
4.13	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:1-MNAP (4:1, 0.28 M)	180	55	2
4.14	BCl ₃ (1.0 M heptane, 2.2 eq)	1,2-DCB:1-MNAP (4:1, 0.28 M)	180	1	2
4.15	BCl ₃ (1.0 M heptane, 2.2 eq)	1,2,4-TCB:1-MNAP (4:1, 0.28 M)	180	20	2

*CINAP = 1-chloronaphthalene; 1,2,4-TCB = 1,2,4-trichlorobenzene; 1-MNAP = 1-methylnaphthalene; 1,2-DCB = 1,2-dichlorobenzene; CIBZH = chlorobenzene; TOL = toluene.

Synthesis of Cl-BsubNc (Ethylene Glycol Method):

Method 5.1 to 5.10 (Table S12): Method 5.1 was carried out in a similar manner as those in Method 2. For 5.2 to 5.10, to a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (0.150 g, 0.84 mmol, 1 equiv), 1,2-dichlorobenzene, and ethylene glycol under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 2.0 mL, 2.4 equiv) was added. The reaction mixture was heated to 150 °C for one hour to distill off the heptane before it was heated to 180 °C for two hours. The crude product was precipitated into ice cold stirring hexane (50 mL), gravity filtered, washed with hexane (3 x 10 mL), and dried in a vacuum oven (60 °C).

Table S12. Attempted syntheses using ethylene glycol as an additive.

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
5.1	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (5 mL, 0.17 M)	180	85	5
5.2	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.94 mL):EG (0.056 mL) - 0.5 eq wrt BCl ₃ (0.17 M)	180	34	5
5.3	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.92 mL):EG (0.084 mL) - 0.75 eq wrt BCl ₃ (0.17 M)	180	72	5
5.4	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.91 mL):EG (0.095 mL) - 0.85 eq wrt BCl ₃ (0.17 M)	180	84	5
5.5	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.90 mL):EG (0.100 mL) - 0.9 eq wrt BCl ₃ (0.17 M)	180	75	5
5.6	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.89 mL):EG (0.106 mL) - 0.95 eq wrt BCl ₃ (0.17 M)	180	81	5
5.7	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.89 mL):EG (0.108 mL) - 0.97 eq wrt BCl ₃ (0.17 M)	180	54	5
5.8	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.89 mL):EG (0.109 mL) - 0.98 eq wrt BCl ₃ (0.17 M)	180	87	5
5.9	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.89 mL):EG (0.112 mL) - 1 eq wrt BCl ₃ (0.17 M)	180	0	0
5.10	BCl ₃ (1.0 M heptane, 2.4 eq)	1,2-DCB (4.78 mL):EG (0.223 mL) - 2 eq wrt BCl ₃ (0.17 M)	180	0	0

*1,2-DCB = 1,2-dichlorobenzene; EG = ethylene glycol.

Synthesis of Cl-BsubNc (Chlorinating Species Scavenging Method):

Method 6.1 to 6.4 (Table S13): All reactions were set-up in a similar manner as those in Method 2. To a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (1.10 g, 6.18 mmol, 1 equiv), 1,2,4-trichlorobenzene (16 mL), and the scavenger cosolvent (4 mL) under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 6.5 mL, 1.1 equiv) was added. The reaction mixture was heated to 150 °C for one hour to distill off the heptane before it was heated to 180 °C for two hours. The reaction mixture was hot filtered under vacuum and the solid black mass was washed with hot toluene (~100 °C) until the filtrate was no longer blue in colour. The filtrate solution was concentrated to remove the toluene via rotary evaporation before it was precipitated into ice cold stirring hexane (200 mL), gravity filtered, washed with hexane (3 x 50 mL), and dried in a vacuum oven (60 °C). For **6.4**, the crude product (0.295 g) was purified by train sublimation. The apparatus was operated under a vacuum with a controlled flow of carbon dioxide gas generating an internal pressure of 100 mTorr. The temperature was increased from room temperature to ~550 °C (external temperature) and was held constant at that temperature overnight. A metallic purple band was collected (18 mg, 6.1% yield relative to mass placed in the train sublimation apparatus). The sublimed product was subsequently purified a second time by train sublimation under the same condition (13 mg, 73% yield relative to mass placed in the train sublimation apparatus). ¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 6H), 8.38-8.33 (m, 6H), 7.78-7.73 (m, 6H); MS (EI): *m/z* 580.1; UV-vis_{toluene} λ_{max} (ε): 651 nm (79200 M⁻¹cm⁻¹).

Table S13. Attempted syntheses using potential chlorinating species scavenger as an additive.

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
6.1	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:DP (4:1, 0.28 M)	180	0	0
6.2	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:βP (4:1, 0.28 M)	180	17	2
6.3	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB:1-OD (4:1, 0.28 M)	180	0	0
6.4	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB: <i>p</i> -CYM (4:1, 0.28 M)	180	77	2

*1,2,4-TCB = 1,2,4-trichlorobenzene; DP = dipentene; βP = (-)-β-pinene, 1-OD = 1-octadecene; *p*-CYM = *para*-cymene.

HPLC-UV/Vis Chromatogram and Mass Spectrum of Cl-BsubNc (*p*-Cymene Method)

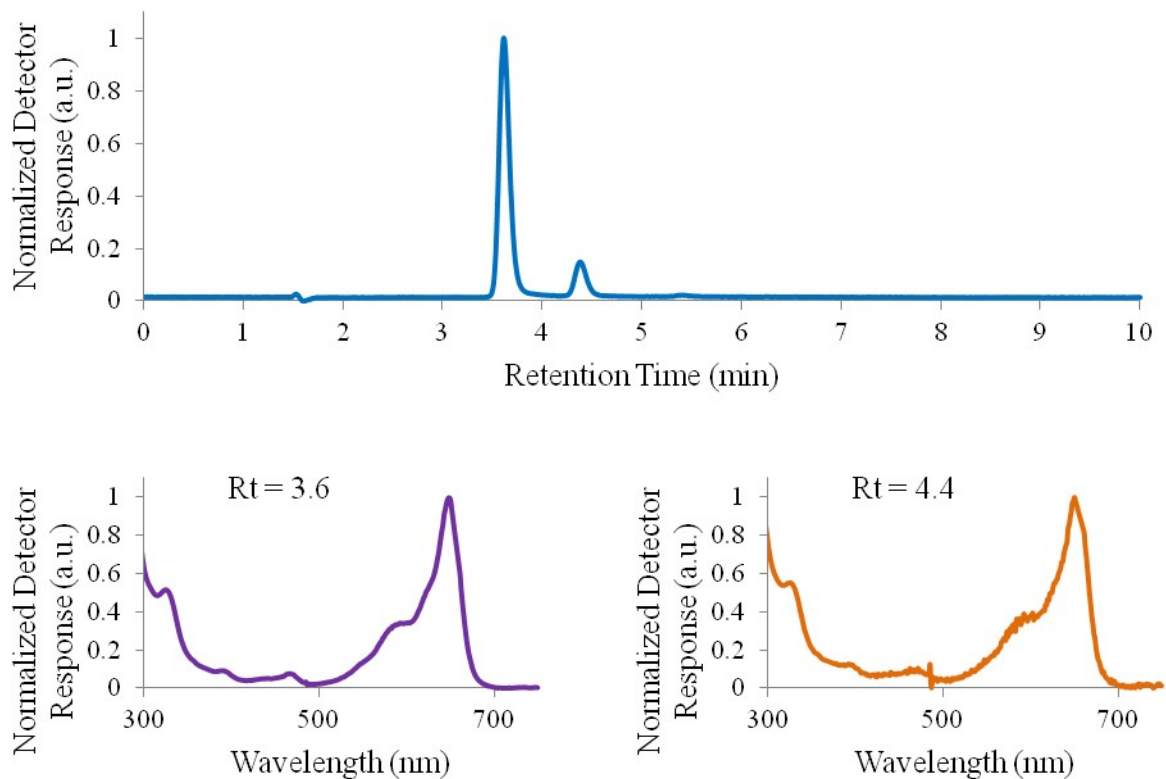


Figure S5a. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for Cl-BsubNc made via the *p*-cymene method (Method 6.4). Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

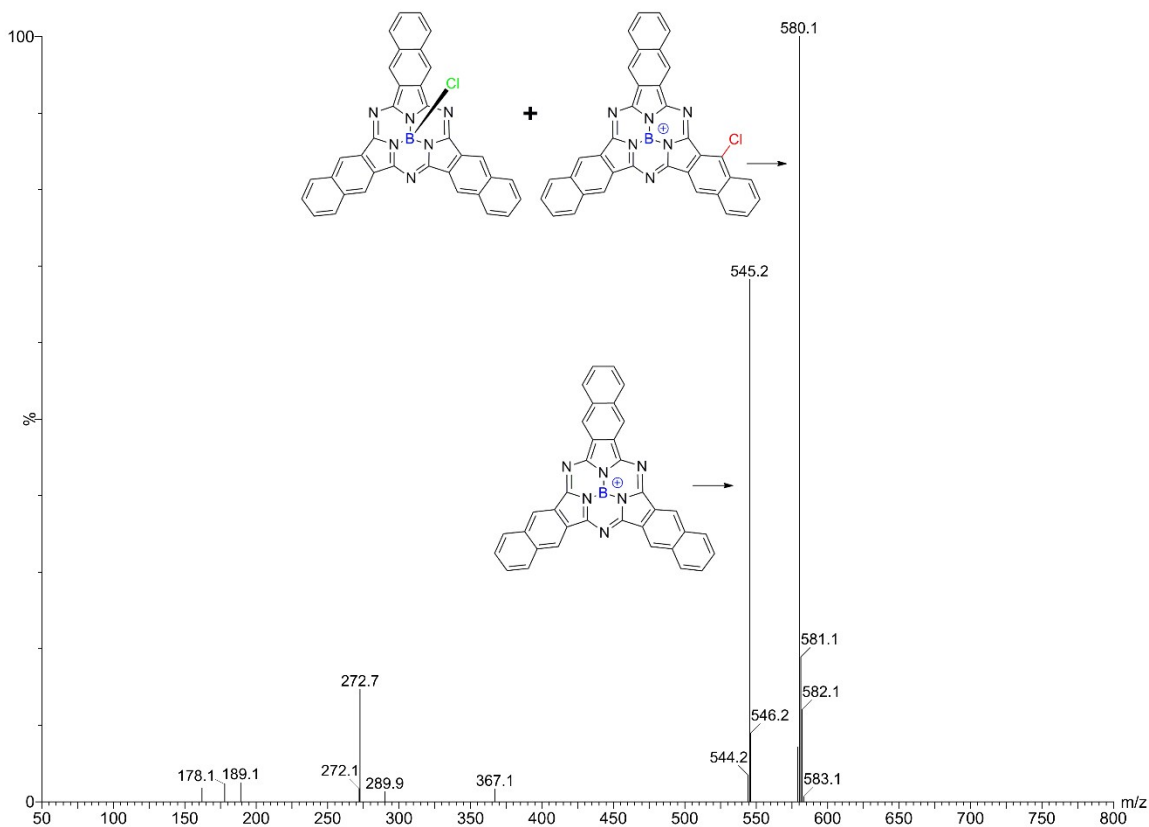


Figure S5b. Mass spectrum of sublimed Cl-BsubNc made via the *p*-cymene method (Method 6.4) indicating the additional presence of Cl-Cl₁BsubPc and absence of Cl-Cl₂BsubNc and Cl-Cl₃BsubNc.

Synthesis of Cl-BsubNc (Electron-Poor Solvent Method):

Method 7.1 to 7.3 (Table S14): All reactions were set-up in a similar manner as those in Method 2. To a three-neck round bottom flask equipped with a gas inlet and a short-path condenser was added DCNAP (0.100 mg, 0.56 mmol, 1 equiv) and the solvent (2 mL) under an atmosphere of argon gas. The mixture was stirred for 10 minutes at room temperature before BCl₃ (1.0 M in heptane, 0.62 mL, 1.1 equiv) was added. The reaction mixture was heated to 150 °C for one hour to distill off the heptane before it was heated to 180 °C for two hours. The reaction mixture was hot filtered under vacuum and the solid black mass was washed with hot toluene (~100 °C) until the filtrate was no longer blue in colour. The filtrate solution was concentrated to remove the toluene via rotary evaporation before it was precipitated into ice cold stirring hexane (20 mL), gravity filtered, washed with hexane (3 x 10 mL), and dried in a vacuum oven (60 °C). For 7.4, the reaction was scaled up by a factor of 45. The crude product (0.75 g) was purified by train sublimation. The apparatus was operated under a vacuum with a controlled flow of carbon dioxide gas generating an internal pressure of 100 mTorr. The temperature was increased from room temperature to ~580 °C (external temperature) and was held constant at that temperature overnight. A metallic purple band was collected (79 mg, 10% yield relative to mass placed in the train sublimation apparatus). The sublimed product was subsequently purified a second time by train sublimation under the same condition (61 mg, 77% yield relative to mass placed in the train sublimation apparatus), producing single crystals suitable for X-ray diffraction. ¹H NMR (400 MHz, CDCl₃) δ 9.49-9.37 (m, 3H), 8.92-8.82 (m, 3H), 8.42-8.34 (m, 3H), 7.97-7.86 (m, 3H), 7.87-7.75 (m, 3H); MS (EI) 580.1, 614.1, 648.1, 684.0, 716.0, 749.9: *m/z*; UV-vis_{toluene} λ_{max} (ε): 664 nm (M⁻¹cm⁻¹).

Table S14. Attempted syntheses using electron-poor solvents.

Method	Boron Template/Source	Solvent System	Temperature (°C)	% Relative Conversion via HPLC	Number of BsubNc Products
7.1	BCl ₃ (1.0 M heptane, 1.1 eq)	NB (0.28 M)	180	-	5
7.2	BCl ₃ (1.0 M heptane, 1.1 eq)	1,2,4-TCB (0.28 M)	180	42	5
7.3	BCl ₃ (1.0 M heptane, 1.1 eq)	2,4-DNFB (0.28 M)	180	0	0
7.4	BCl ₃ (1.0 M heptane, 1.1 eq)	NB (0.28 M)	180	-	5

*NB = nitrobenzene; 1,2,4-TCB = 1,2,4-trichlorobenzene; 2,4-DNFB = 2,4-dinitro-1-fluorobenzene.

HPLC-UV/Vis Chromatogram and Mass Spectrum of Cl-BsubNc (Nitrobenzene Method)

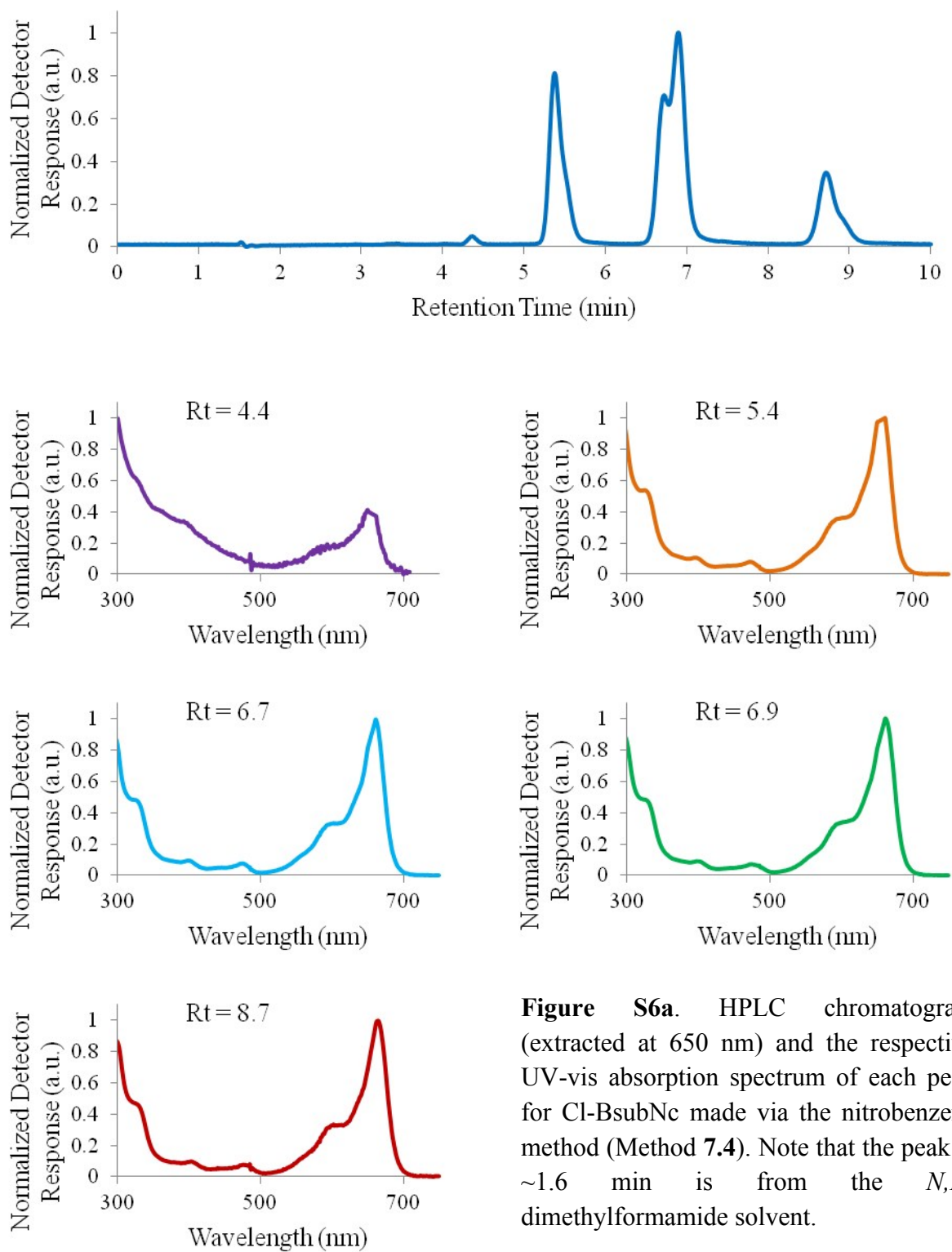


Figure S6a. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for Cl-BsubNc made via the nitrobenzene method (Method 7.4). Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

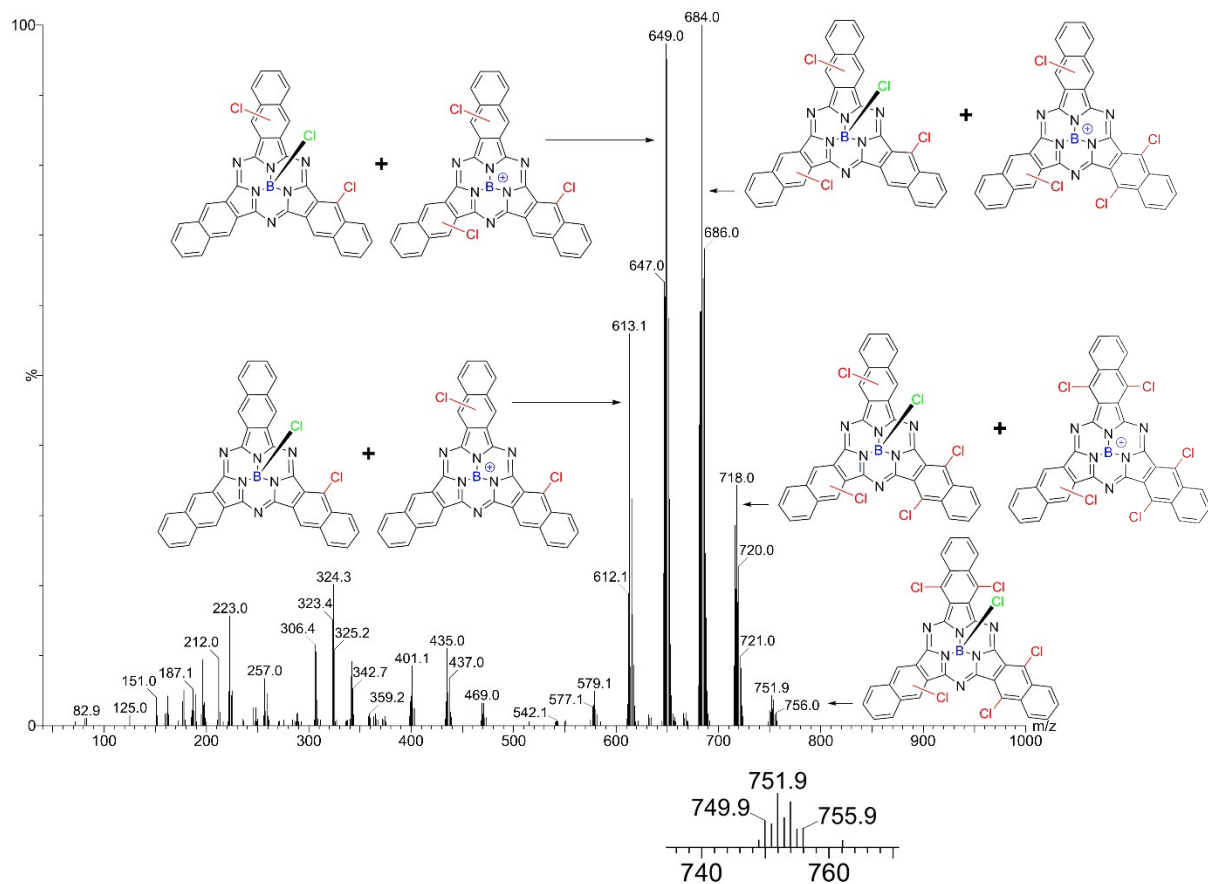


Figure S6b. Mass spectrum of sublimed Cl-BsubNc made via the nitrobenzene method (Method 7.4) indicating the additional presence of Cl-Cl₁BsubPc, Cl-Cl₂BsubPc, Cl-Cl₃BsubPc, Cl-Cl₄BsubPc and Cl-Cl₅BsubPc.

Crystal Structure Details of Nitrobenzene-Cl-Cl_nBsubNc

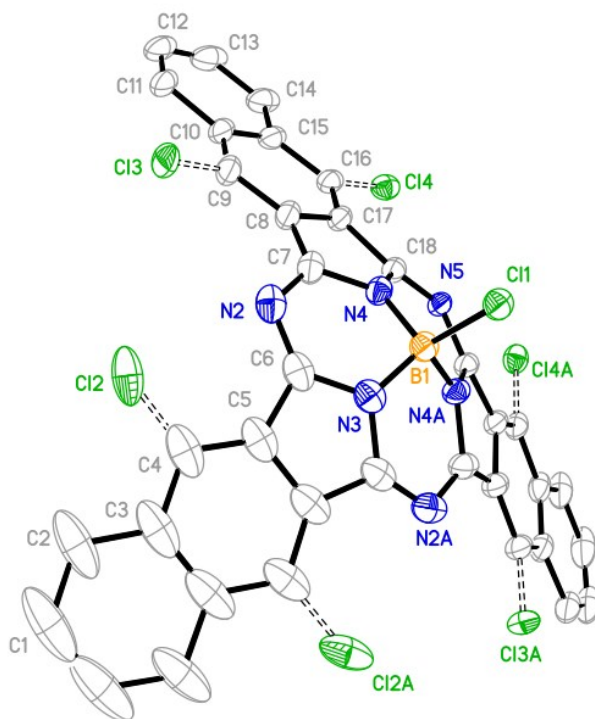


Figure S7. Ellipsoid plot (50% probability) showing the structure and atom numbering scheme of nitrobenzene-Cl-Cl_nBsubNc (CCDC deposition number: 1452384). Hydrogen atoms have been omitted for clarity. Colors: boron - yellow; nitrogen - blue; carbon - white; chlorine - green.

Table S15. Crystal data and structure refinement for nitrobenzene-Cl-Cl_nBsubNc.

Identification code	d1589b_a
Empirical formula	C36 H15.04 B Cl3.96 N6
Formula weight	682.51
Temperature	147(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 14.9062(5) Å □ a = 14 b = 18.3548(6) Å □ b = 18 c = 10.7766(3) Å □ c = 10.
Volume	2948.48(16) Å ³
Z	4
Density (calculated)	1.538 Mg/m ³
Absorption coefficient	3.933 mm ⁻¹
F(000)	1381.3
Crystal size	0.140 x 0.100 x 0.100 mm ³
Theta range for data collection	4.758 to 67.376°.
Index ranges	-17<=h<=17, -21<=k<=20, -12<=l<=12
Reflections collected	53684
Independent reflections	2705 [R(int) = 0.0595]
Completeness to theta = 67.376°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.6278
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2705 / 0 / 235
Goodness-of-fit on F ²	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1005
R indices (all data)	R1 = 0.0486, wR2 = 0.1084
Extinction coefficient	n/a
Largest diff. peak and hole	0.223 and -0.239 e.Å ⁻³

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for nitrobenzene-Cl-Cl_nBsubNc. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	2161(1)	7500	7635(1)	51(1)
Cl(2)	5269(1)	5846(1)	4377(1)	89(1)
Cl(3)	2598(1)	4556(1)	4278(1)	74(1)
Cl(4)	-863(1)	6307(1)	3646(1)	50(1)
N(2)	3182(1)	6233(1)	4967(2)	59(1)
N(3)	3176(2)	7500	5453(2)	52(1)
N(4)	1812(1)	6860(1)	5316(2)	44(1)
N(5)	517(2)	7500	4644(2)	40(1)
C(1)	7432(2)	7125(3)	2832(3)	161(4)
C(2)	6725(2)	6729(3)	3315(3)	127(2)
C(3)	5970(2)	7112(2)	3807(2)	97(1)
C(4)	5222(2)	6728(2)	4265(2)	83(1)
C(4A)	5222(2)	6728(2)	4265(2)	83(1)
C(5)	4487(2)	7109(2)	4688(2)	69(1)
C(6)	3608(2)	6872(2)	5107(2)	59(1)
C(7)	2285(2)	6245(1)	5008(2)	51(1)
C(8)	1630(2)	5750(1)	4478(2)	51(1)
C(9)	1677(2)	5040(1)	4072(2)	61(1)
C(9A)	1677(2)	5040(1)	4072(2)	61(1)
C(10)	922(2)	4707(1)	3533(2)	63(1)
C(11)	933(3)	3961(1)	3149(2)	83(1)
C(12)	201(3)	3654(2)	2643(3)	99(1)
C(13)	-582(3)	4052(2)	2458(3)	95(1)
C(14)	-635(2)	4767(1)	2815(2)	74(1)
C(15)	115(2)	5108(1)	3378(2)	58(1)
C(16)	73(2)	5839(1)	3796(2)	49(1)
C(16A)	73(2)	5839(1)	3796(2)	49(1)
C(17)	802(2)	6148(1)	4348(2)	44(1)
C(18)	968(1)	6878(1)	4826(2)	41(1)
B(1)	2240(2)	7500	5895(3)	47(1)

Table S17. Bond lengths [\AA] and angles [$^\circ$] for nitrobenzene-Cl-Cl_nBsubNc.

Cl(1)-B(1)	1.879(3)
Cl(2)-C(4)	1.625(4)
Cl(3)-C(9)	1.651(3)
Cl(4)-C(16)	1.646(3)
N(2)-C(7)	1.337(3)
N(2)-C(6)	1.343(3)
N(3)-C(6)	1.372(3)
N(3)-C(6)#1	1.372(3)
N(3)-B(1)	1.474(5)
N(4)-C(18)	1.364(3)
N(4)-C(7)	1.373(3)
N(4)-B(1)	1.475(3)
N(5)-C(18)#1	1.339(2)
N(5)-C(18)	1.339(2)
C(1)-C(1)#1	1.377(12)
C(1)-C(2)	1.382(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.429(4)
C(2)-H(2)	0.9500
C(3)-C(4A)	1.408(4)
C(3)-C(4)	1.408(4)
C(3)-C(3)#1	1.426(8)
C(4)-C(5)	1.378(4)
C(4A)-C(5)	1.378(4)
C(4A)-H(4A)	0.9500
C(5)-C(5)#1	1.437(6)
C(5)-C(6)	1.452(4)
C(7)-C(8)	1.451(3)
C(8)-C(9A)	1.376(3)
C(8)-C(9)	1.376(3)
C(8)-C(17)	1.441(3)
C(9)-C(10)	1.406(4)
C(9A)-C(10)	1.406(4)
C(9A)-H(9A)	0.9500
C(10)-C(15)	1.420(4)

C(10)-C(11)	1.430(3)
C(11)-C(12)	1.345(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.391(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.370(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.418(4)
C(14)-H(14)	0.9500
C(15)-C(16A)	1.418(3)
C(15)-C(16)	1.418(3)
C(16)-C(17)	1.362(3)
C(16A)-C(17)	1.362(3)
C(16A)-H(16A)	0.9500
C(17)-C(18)	1.457(3)
B(1)-N(4)#1	1.475(3)
C(7)-N(2)-C(6)	117.1(2)
C(6)-N(3)-C(6)#1	114.3(3)
C(6)-N(3)-B(1)	122.14(15)
C(6)#1-N(3)-B(1)	122.15(15)
C(18)-N(4)-C(7)	113.60(18)
C(18)-N(4)-B(1)	122.92(19)
C(7)-N(4)-B(1)	122.3(2)
C(18)#1-N(5)-C(18)	116.9(2)
C(1)#1-C(1)-C(2)	121.7(3)
C(1)#1-C(1)-H(1)	119.1
C(2)-C(1)-H(1)	119.1
C(1)-C(2)-C(3)	118.8(5)
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-H(2)	120.6
C(4A)-C(3)-C(3)#1	120.0(2)
C(4)-C(3)-C(3)#1	120.0(2)
C(4A)-C(3)-C(2)	120.5(4)
C(4)-C(3)-C(2)	120.5(4)
C(3)#1-C(3)-C(2)	119.4(3)
C(5)-C(4)-C(3)	119.5(4)

C(5)-C(4)-Cl(2)	121.0(3)
C(3)-C(4)-Cl(2)	119.4(3)
C(5)-C(4A)-C(3)	119.5(4)
C(5)-C(4A)-H(4A)	120.3
C(3)-C(4A)-H(4A)	120.3
C(4A)-C(5)-C(5)#1	120.5(2)
C(4)-C(5)-C(5)#1	120.5(2)
C(4A)-C(5)-C(6)	132.0(3)
C(4)-C(5)-C(6)	132.0(3)
C(5)#1-C(5)-C(6)	107.39(16)
N(2)-C(6)-N(3)	122.8(2)
N(2)-C(6)-C(5)	130.8(2)
N(3)-C(6)-C(5)	104.9(2)
N(2)-C(7)-N(4)	122.3(2)
N(2)-C(7)-C(8)	130.5(2)
N(4)-C(7)-C(8)	105.32(19)
C(9A)-C(8)-C(17)	119.5(2)
C(9)-C(8)-C(17)	119.5(2)
C(9A)-C(8)-C(7)	133.1(2)
C(9)-C(8)-C(7)	133.1(2)
C(17)-C(8)-C(7)	107.33(18)
C(8)-C(9)-C(10)	120.2(2)
C(8)-C(9)-Cl(3)	120.6(2)
C(10)-C(9)-Cl(3)	119.14(19)
C(8)-C(9A)-C(10)	120.2(2)
C(8)-C(9A)-H(9A)	119.9
C(10)-C(9A)-H(9A)	119.9
C(9A)-C(10)-C(15)	120.1(2)
C(9)-C(10)-C(15)	120.1(2)
C(9A)-C(10)-C(11)	121.8(3)
C(9)-C(10)-C(11)	121.8(3)
C(15)-C(10)-C(11)	118.1(3)
C(12)-C(11)-C(10)	120.7(3)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(11)-C(12)-C(13)	121.2(3)
C(11)-C(12)-H(12)	119.4

C(13)-C(12)-H(12)	119.4
C(14)-C(13)-C(12)	120.7(3)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(13)-C(14)-C(15)	119.9(3)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(16A)-C(15)-C(14)	121.3(3)
C(16)-C(15)-C(14)	121.3(3)
C(16A)-C(15)-C(10)	119.4(2)
C(16)-C(15)-C(10)	119.4(2)
C(14)-C(15)-C(10)	119.3(2)
C(17)-C(16)-C(15)	119.8(2)
C(17)-C(16)-Cl(4)	120.16(16)
C(15)-C(16)-Cl(4)	120.0(2)
C(17)-C(16A)-C(15)	119.8(2)
C(17)-C(16A)-H(16A)	120.1
C(15)-C(16A)-H(16A)	120.1
C(16A)-C(17)-C(8)	121.02(19)
C(16)-C(17)-C(8)	121.02(19)
C(16A)-C(17)-C(18)	132.2(2)
C(16)-C(17)-C(18)	132.2(2)
C(8)-C(17)-C(18)	106.63(19)
N(5)-C(18)-N(4)	122.67(18)
N(5)-C(18)-C(17)	130.31(19)
N(4)-C(18)-C(17)	105.74(17)
N(3)-B(1)-N(4)#1	105.83(19)
N(3)-B(1)-N(4)	105.83(19)
N(4)#1-B(1)-N(4)	105.5(2)
N(3)-B(1)-Cl(1)	112.4(2)
N(4)#1-B(1)-Cl(1)	113.28(16)
N(4)-B(1)-Cl(1)	113.28(16)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z

Table S18. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for nitrobenzene-Cl-Cl_nBsubNc.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cl(1)	68(1)	48(1)	36(1)	0	-4(1)	0
Cl(2)	82(1)	141(2)	43(1)	-31(1)	-14(1)	46(1)
Cl(3)	92(1)	48(1)	83(1)	11(1)	26(1)	32(1)
Cl(4)	57(1)	49(1)	44(1)	3(1)	-4(1)	-8(1)
N(2)	66(1)	67(1)	43(1)	0(1)	-4(1)	19(1)
N(3)	53(2)	65(2)	39(1)	0	-5(1)	0
N(4)	56(1)	38(1)	37(1)	0(1)	-1(1)	6(1)
N(5)	51(1)	30(1)	38(1)	0	3(1)	0
C(1)	76(2)	352(12)	54(2)	-14(3)	13(2)	25(3)
C(2)	70(2)	270(6)	42(1)	-17(2)	2(1)	33(3)
C(3)	59(1)	201(4)	31(1)	-6(2)	-6(1)	17(2)
C(4)	62(2)	153(3)	34(1)	-9(2)	-7(1)	22(2)
C(4A)	62(2)	153(3)	34(1)	-9(2)	-7(1)	22(2)
C(5)	55(1)	117(2)	34(1)	-2(1)	-8(1)	11(1)
C(6)	56(1)	85(2)	36(1)	2(1)	-4(1)	13(1)
C(7)	67(1)	47(1)	38(1)	2(1)	0(1)	15(1)
C(8)	76(2)	37(1)	39(1)	1(1)	7(1)	9(1)
C(9)	98(2)	39(1)	46(1)	4(1)	20(1)	16(1)
C(9A)	98(2)	39(1)	46(1)	4(1)	20(1)	16(1)
C(10)	116(2)	34(1)	40(1)	-3(1)	26(1)	-5(1)
C(11)	161(3)	36(1)	54(1)	-6(1)	45(2)	-4(2)
C(12)	200(4)	40(1)	56(2)	-15(1)	51(2)	-32(2)
C(13)	175(4)	62(2)	48(1)	-16(1)	27(2)	-57(2)
C(14)	121(2)	57(2)	43(1)	-7(1)	13(1)	-37(2)
C(15)	98(2)	39(1)	36(1)	-4(1)	15(1)	-17(1)
C(16)	74(1)	37(1)	35(1)	0(1)	6(1)	-9(1)
C(16A)	74(1)	37(1)	35(1)	0(1)	6(1)	-9(1)
C(17)	64(1)	32(1)	36(1)	0(1)	5(1)	2(1)
C(18)	54(1)	34(1)	34(1)	1(1)	2(1)	2(1)
B(1)	56(2)	48(2)	36(2)	0	-2(2)	0

Table S19. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for nitrobenzene-Cl-Cl_nBsubNc.

	x	y	z	U(eq)
H(1)	7932	6873	2492	193
H(2)	6741	6212	3319	153
H(4A)	5225	6210	4282	100
H(9A)	2220	4774	4158	73
H(11)	1463	3681	3252	100
H(12)	218	3155	2407	118
H(13)	-1086	3825	2079	114
H(14)	-1173	5033	2687	88
H(16A)	-462	6114	3692	58

Table S20. Torsion angles [$^{\circ}$] for nitrobenzene-Cl-Cl_nBsubNc.

C(1)#1-C(1)-C(2)-C(3)	1.0(3)
C(1)-C(2)-C(3)-C(4A)	177.6(3)
C(1)-C(2)-C(3)-C(4)	177.6(3)
C(1)-C(2)-C(3)-C(3)#1	-1.0(3)
C(3)#1-C(3)-C(4)-C(5)	1.3(3)
C(2)-C(3)-C(4)-C(5)	-177.3(2)
C(3)#1-C(3)-C(4)-Cl(2)	-174.35(11)
C(2)-C(3)-C(4)-Cl(2)	7.0(3)
C(3)#1-C(3)-C(4A)-C(5)	1.3(3)
C(2)-C(3)-C(4A)-C(5)	-177.3(2)
C(3)-C(4A)-C(5)-C(5)#1	-1.3(3)
C(3)-C(4A)-C(5)-C(6)	174.2(2)
C(3)-C(4)-C(5)-C(5)#1	-1.3(3)
Cl(2)-C(4)-C(5)-C(5)#1	174.27(12)
C(3)-C(4)-C(5)-C(6)	174.2(2)
Cl(2)-C(4)-C(5)-C(6)	-10.3(4)
C(7)-N(2)-C(6)-N(3)	9.2(3)
C(7)-N(2)-C(6)-C(5)	-154.7(2)
C(6)#1-N(3)-C(6)-N(2)	-156.55(16)
B(1)-N(3)-C(6)-N(2)	10.2(4)
C(6)#1-N(3)-C(6)-C(5)	10.9(3)
B(1)-N(3)-C(6)-C(5)	177.6(2)
C(4A)-C(5)-C(6)-N(2)	-16.0(4)
C(4)-C(5)-C(6)-N(2)	-16.0(4)
C(5)#1-C(5)-C(6)-N(2)	159.9(2)
C(4A)-C(5)-C(6)-N(3)	178.0(2)
C(4)-C(5)-C(6)-N(3)	178.0(2)
C(5)#1-C(5)-C(6)-N(3)	-6.17(18)
C(6)-N(2)-C(7)-N(4)	-7.2(3)
C(6)-N(2)-C(7)-C(8)	155.1(2)
C(18)-N(4)-C(7)-N(2)	153.9(2)
B(1)-N(4)-C(7)-N(2)	-14.3(3)
C(18)-N(4)-C(7)-C(8)	-12.2(2)
B(1)-N(4)-C(7)-C(8)	179.6(2)
N(2)-C(7)-C(8)-C(9A)	20.3(4)

N(4)-C(7)-C(8)-C(9A)	-175.2(2)
N(2)-C(7)-C(8)-C(9)	20.3(4)
N(4)-C(7)-C(8)-C(9)	-175.2(2)
N(2)-C(7)-C(8)-C(17)	-157.0(2)
N(4)-C(7)-C(8)-C(17)	7.6(2)
C(17)-C(8)-C(9)-C(10)	0.2(3)
C(7)-C(8)-C(9)-C(10)	-176.8(2)
C(17)-C(8)-C(9)-Cl(3)	-176.56(16)
C(7)-C(8)-C(9)-Cl(3)	6.4(4)
C(17)-C(8)-C(9A)-C(10)	0.2(3)
C(7)-C(8)-C(9A)-C(10)	-176.8(2)
C(8)-C(9A)-C(10)-C(15)	1.4(3)
C(8)-C(9A)-C(10)-C(11)	-177.3(2)
C(8)-C(9)-C(10)-C(15)	1.4(3)
Cl(3)-C(9)-C(10)-C(15)	178.29(17)
C(8)-C(9)-C(10)-C(11)	-177.3(2)
Cl(3)-C(9)-C(10)-C(11)	-0.5(3)
C(9A)-C(10)-C(11)-C(12)	179.5(2)
C(9)-C(10)-C(11)-C(12)	179.5(2)
C(15)-C(10)-C(11)-C(12)	0.7(3)
C(10)-C(11)-C(12)-C(13)	1.1(4)
C(11)-C(12)-C(13)-C(14)	-1.6(4)
C(12)-C(13)-C(14)-C(15)	0.2(4)
C(13)-C(14)-C(15)-C(16A)	-177.9(2)
C(13)-C(14)-C(15)-C(16)	-177.9(2)
C(13)-C(14)-C(15)-C(10)	1.7(3)
C(9A)-C(10)-C(15)-C(16A)	-1.4(3)
C(11)-C(10)-C(15)-C(16A)	177.46(19)
C(9)-C(10)-C(15)-C(16)	-1.4(3)
C(11)-C(10)-C(15)-C(16)	177.46(19)
C(9A)-C(10)-C(15)-C(14)	179.1(2)
C(9)-C(10)-C(15)-C(14)	179.1(2)
C(11)-C(10)-C(15)-C(14)	-2.1(3)
C(14)-C(15)-C(16)-C(17)	179.1(2)
C(10)-C(15)-C(16)-C(17)	-0.5(3)
C(14)-C(15)-C(16)-Cl(4)	0.6(3)
C(10)-C(15)-C(16)-Cl(4)	-178.95(16)

C(14)-C(15)-C(16A)-C(17)	179.1(2)
C(10)-C(15)-C(16A)-C(17)	-0.5(3)
C(15)-C(16A)-C(17)-C(8)	2.2(3)
C(15)-C(16A)-C(17)-C(18)	177.7(2)
C(15)-C(16)-C(17)-C(8)	2.2(3)
Cl(4)-C(16)-C(17)-C(8)	-179.34(16)
C(15)-C(16)-C(17)-C(18)	177.7(2)
Cl(4)-C(16)-C(17)-C(18)	-3.8(3)
C(9A)-C(8)-C(17)-C(16A)	-2.1(3)
C(7)-C(8)-C(17)-C(16A)	175.62(18)
C(9)-C(8)-C(17)-C(16)	-2.1(3)
C(7)-C(8)-C(17)-C(16)	175.62(18)
C(9A)-C(8)-C(17)-C(18)	-178.66(19)
C(9)-C(8)-C(17)-C(18)	-178.66(19)
C(7)-C(8)-C(17)-C(18)	-0.9(2)
C(18)#1-N(5)-C(18)-N(4)	7.6(4)
C(18)#1-N(5)-C(18)-C(17)	-157.52(15)
C(7)-N(4)-C(18)-N(5)	-156.6(2)
B(1)-N(4)-C(18)-N(5)	11.4(3)
C(7)-N(4)-C(18)-C(17)	11.7(2)
B(1)-N(4)-C(18)-C(17)	179.7(2)
C(16A)-C(17)-C(18)-N(5)	-15.0(4)
C(16)-C(17)-C(18)-N(5)	-15.0(4)
C(8)-C(17)-C(18)-N(5)	161.0(2)
C(16A)-C(17)-C(18)-N(4)	177.9(2)
C(16)-C(17)-C(18)-N(4)	177.9(2)
C(8)-C(17)-C(18)-N(4)	-6.1(2)
C(6)-N(3)-B(1)-N(4)#1	-138.7(2)
C(6)#1-N(3)-B(1)-N(4)#1	27.0(3)
C(6)-N(3)-B(1)-N(4)	-27.0(3)
C(6)#1-N(3)-B(1)-N(4)	138.7(2)
C(6)-N(3)-B(1)-Cl(1)	97.2(2)
C(6)#1-N(3)-B(1)-Cl(1)	-97.2(2)
C(18)-N(4)-B(1)-N(3)	-137.9(2)
C(7)-N(4)-B(1)-N(3)	29.1(3)
C(18)-N(4)-B(1)-N(4)#1	-26.1(3)
C(7)-N(4)-B(1)-N(4)#1	140.96(18)

C(18)-N(4)-B(1)-Cl(1)	98.4(2)
C(7)-N(4)-B(1)-Cl(1)	-94.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+3/2, z$

Table S21. Comparison of selected crystallographic parameters for the single crystals obtained for literature-Cl-Cl_nBsubNc and nitrobenzene-Cl-Cl_nBsubNc.

Literature-Cl-Cl _n BsubNc	Number	Object1	Object2	Length		Unit cell dimensions	a =	14.623	Å
	1	centroid: C3 C2 C11 C10 C9 C4	centroid: C6 C7 C5 C4 C9 C8	3.654	Å		b =	18.453	Å
	2	centroid: C4 C5 C9 C8 C7 C6	centroid: C4 C9 C10 C3 C2 C11	3.654	Å		c =	10.3923	Å
	3	centroid: C17 C18 C18 C17 C16 C16	centroid: N1 C12 N2 C12 N1 B1	3.705	Å	Density (calculated)		1.468	Mg/m3

Nitrobenzene-Cl-Cl _n BsubNc	Number	Object1	Object2	Length		Unit cell dimensions	a =	14.9062	Å
	1	centroid: C12 C13 C14 C15 C10 C11	centroid: C8 C9 C10 C15 C16 C17	3.664	Å		b =	18.3548	Å
	2	centroid: C16 C15 C10 C9 C8 C17	centroid: C10 C11 C12 C13 C14 C15	3.664	Å		c =	10.7766	Å
	4	centroid: C1 C1 C2 C2 C3 C3	centroid: N4 B1 N4 C18 N5 C18	3.754	Å	Density (calculated)		1.538	Mg/m3

Differences									
Benzoisindoline/Benzoisindoline	-0.010	Å	Unit cell dimensions	a =	-0.2832	Å			
Benzoisindoline/Benzoisindoline	-0.010	Å		b =	0.0982	Å			
Benzoisindoline/B N N N C C	-0.049	Å		c =	-0.3843	Å			
			Density (calculated)		-0.07	Mg/m3			

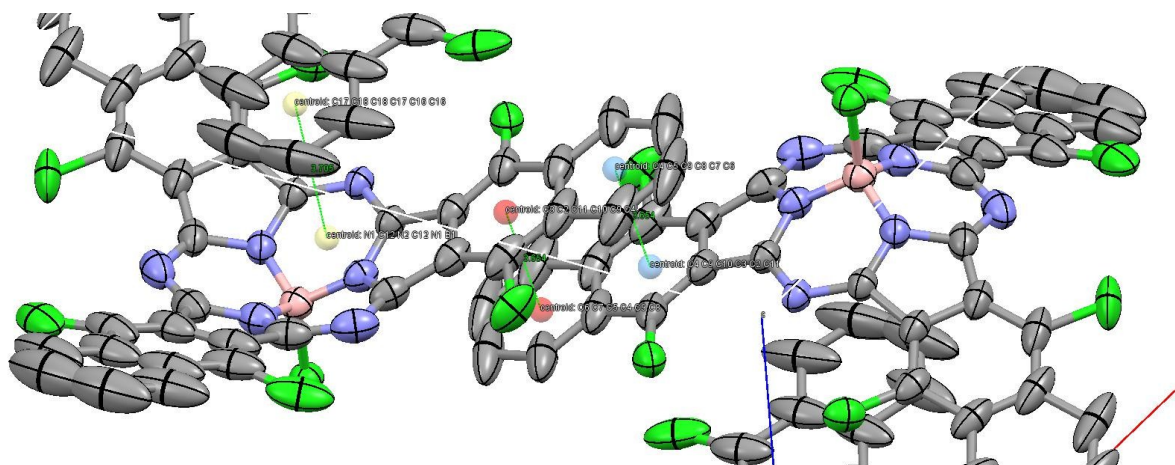


Figure S8. Solid-state arrangement of Cl-Cl_nBsubNc within crystals obtained from the literature method and train sublimed.

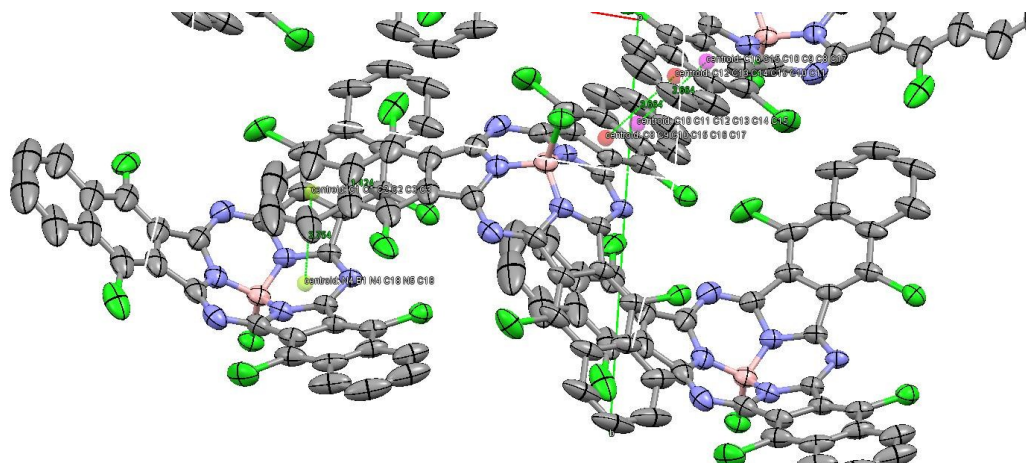


Figure S9. Solid-state arrangement of Cl-Cl_nBsubNc within crystals obtained from the nitrobenzene method and train sublimed.

HPLC-UV/Vis Chromatogram and Mass Spectrum of Cl-BsubNc (Commercial)

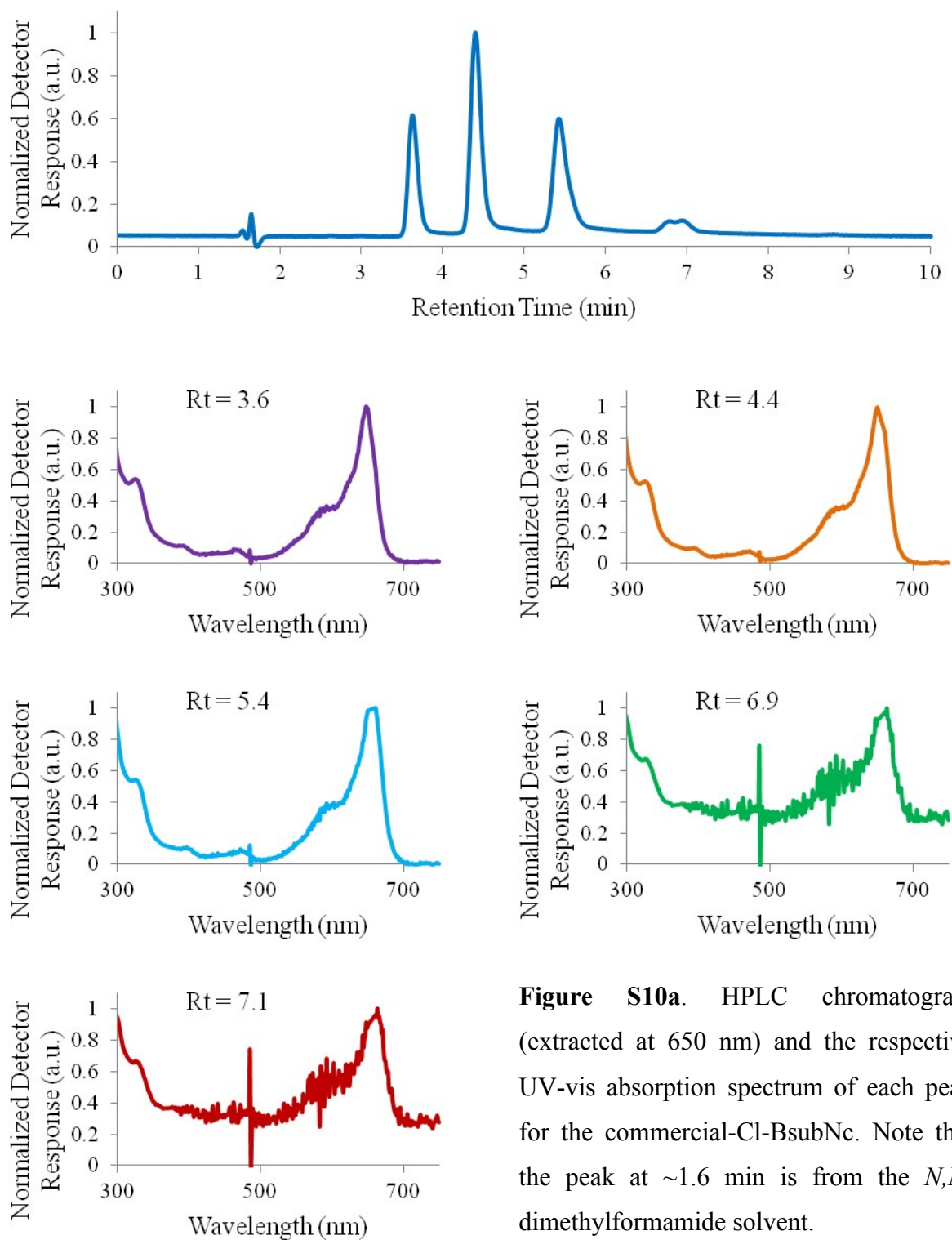


Figure S10a. HPLC chromatogram (extracted at 650 nm) and the respective UV-vis absorption spectrum of each peak for the commercial-Cl-BsubNc. Note that the peak at ~1.6 min is from the *N,N*-dimethylformamide solvent.

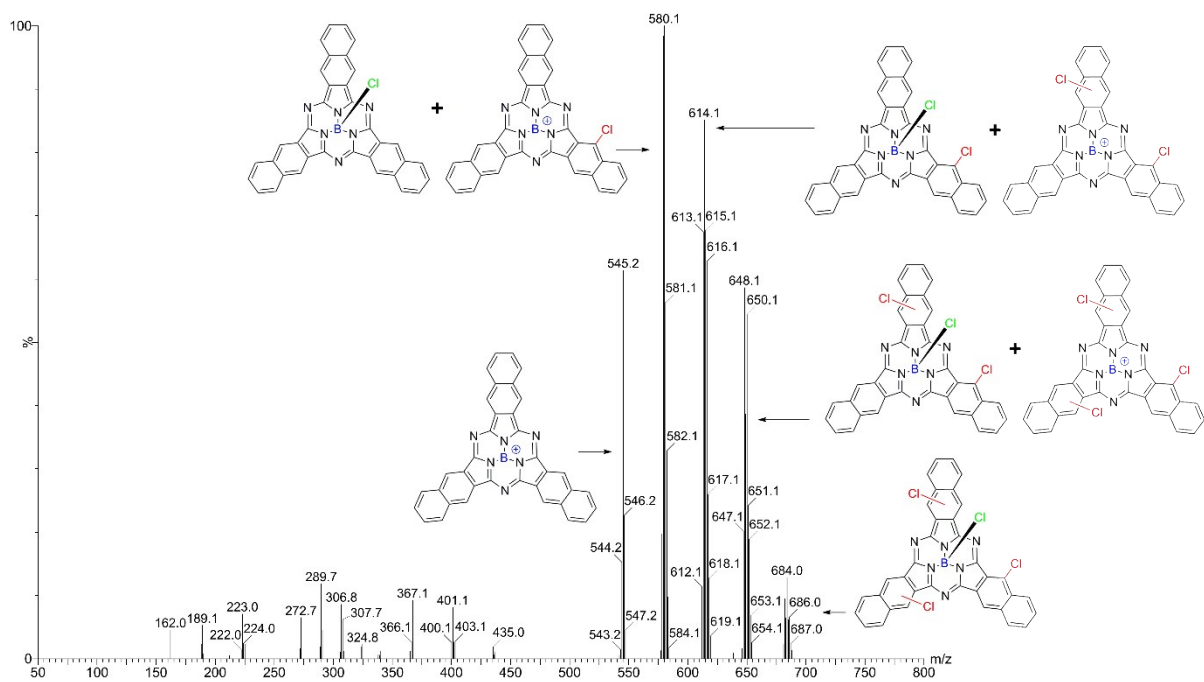


Figure S10b. Mass spectrum of commercial Cl-BsubNc indicating the additional presence of Cl-Cl₁BsubPc, Cl-Cl₂BsubNc and Cl-Cl₃BsubNc.

X-ray Photoelectron Spectroscopy

B 1s and N 1s core level XPS spectra are shown in Figure S12. Binding energies of various chlorine, boron, and nitrogen bonds for each Cl-Cl_nBsubNc are summarized in Table S22. Deconvolution (*i.e.* peak fitting) was performed for each spectrum (Cl 2p, B 1s, N 1s) to determine the number of distinct chemical states for chlorine (Figure S11), boron (Figure S13), and nitrogen (Figure S14). Each deconvoluted curve represents a distinct chemical state for B 1s and N 1s. For Cl 2p, due to a spin orbital splitting effect, each distinct chemical state is represented by two deconvoluted curves (2p_{1/2} and 2p_{3/2}); there are four deconvoluted curves in each Cl 2p XPS plot to indicate two distinct chemical states for chlorine. Integrated peak intensity ratios are summarized in Table S23.

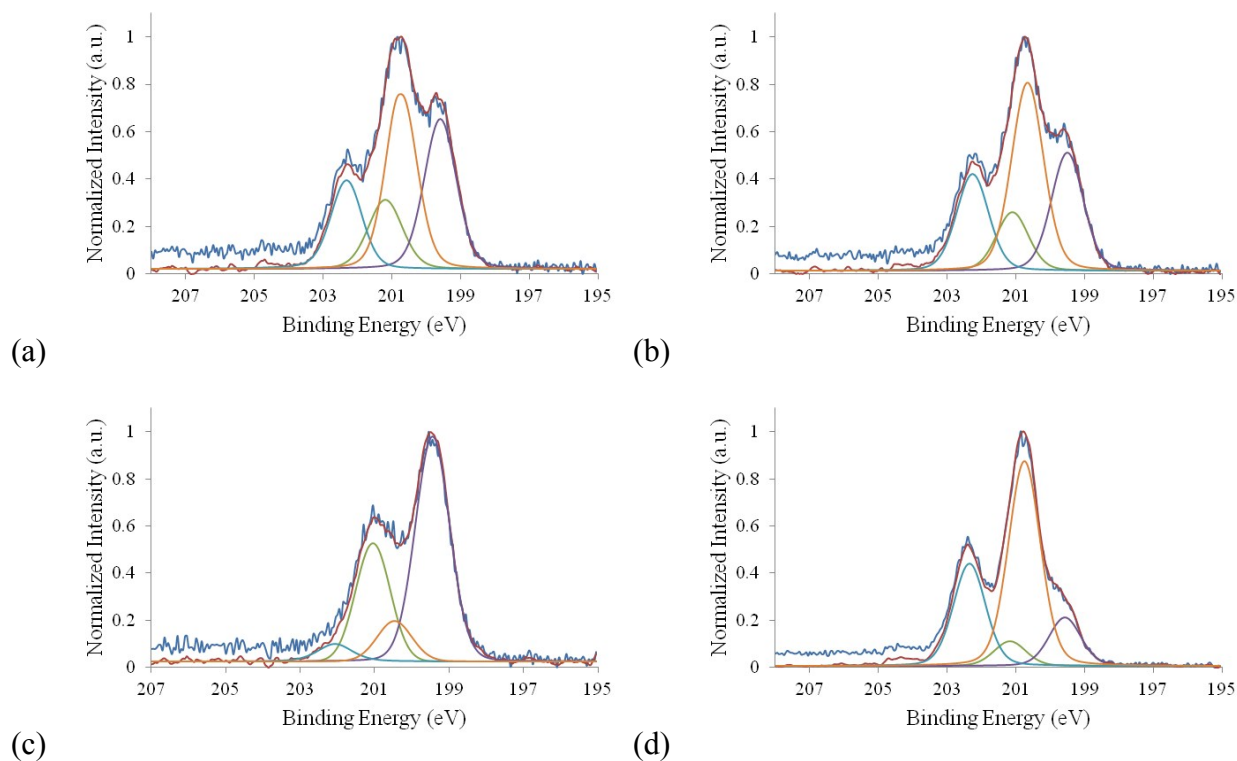


Figure S11. Deconvolution of Cl 2p XPS data of (a) literature-Cl-Cl_nBsubNc, (b) commercial-Cl-Cl_nBsubNc, (c) *p*-cymene-Cl-Cl_nBsubNc, and (d) nitrobenzene-Cl-Cl_nBsubNc. Colors: blue – experimental XPS curve; red – summed of the fitted curves; light blue – Cl-C, Cl 2p_{1/2} curve; green – Cl-B, Cl 2p_{1/2} curve; orange – Cl-C, Cl 2p_{3/2} curve; purple – Cl-B, Cl 2p_{3/2} curve.

Table S22. Core level binding energies of Cl-Cl_nBsubNcs.

	Compound	Cl 2p		B 1s	N1s	
		Cl(-B)	Cl(-C)	B(-Cl and -N)	N(-B)	N(-C)
Binding Energy (eV)	Literature-Cl-Cl _n BsubNc	199.59	200.72	191.98	399.33	400.1
	Commercial-Cl-Cl _n BsubNc	199.50	200.66	191.96	399.30	400.07
	<i>p</i> -Cymene-Cl-Cl _n BsubNc	199.45	200.47	191.84	399.20	399.93
	Nitrobenzene-Cl-Cl _n BsubNc	199.57	200.75	192.06	399.44	400.21
	Average	199.53	200.65	191.96	399.32	400.08
	Kahn <i>et al.</i> ¹¹	199.3	200.5	-	-	-

*Cl(-B) = chlorine bonded to boron; Cl(-C) = chlorine bonded to carbon; N(-B) = isoindoline nitrogen; N(-C) = bridging nitrogen.

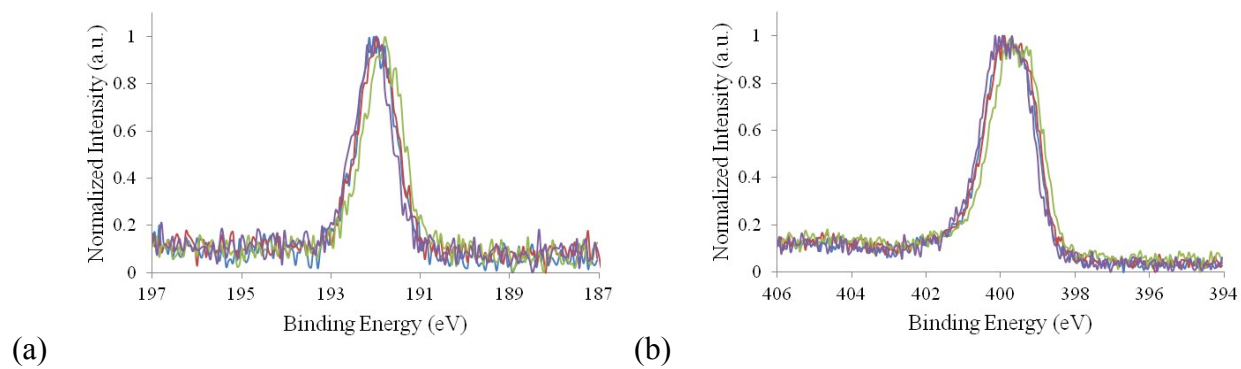


Figure S12. Overlay of the literature-Cl-Cl_nBsubNc (blue), commercial-Cl-Cl_nBsubNc (red), *p*-cymene-Cl-Cl_nBsubNc (green) and nitrobenzene-Cl-Cl_nBsubNc (purple) (a) normalized B 1s core-level XPS spectra and (b) normalized N 1s core-level XPS spectra.

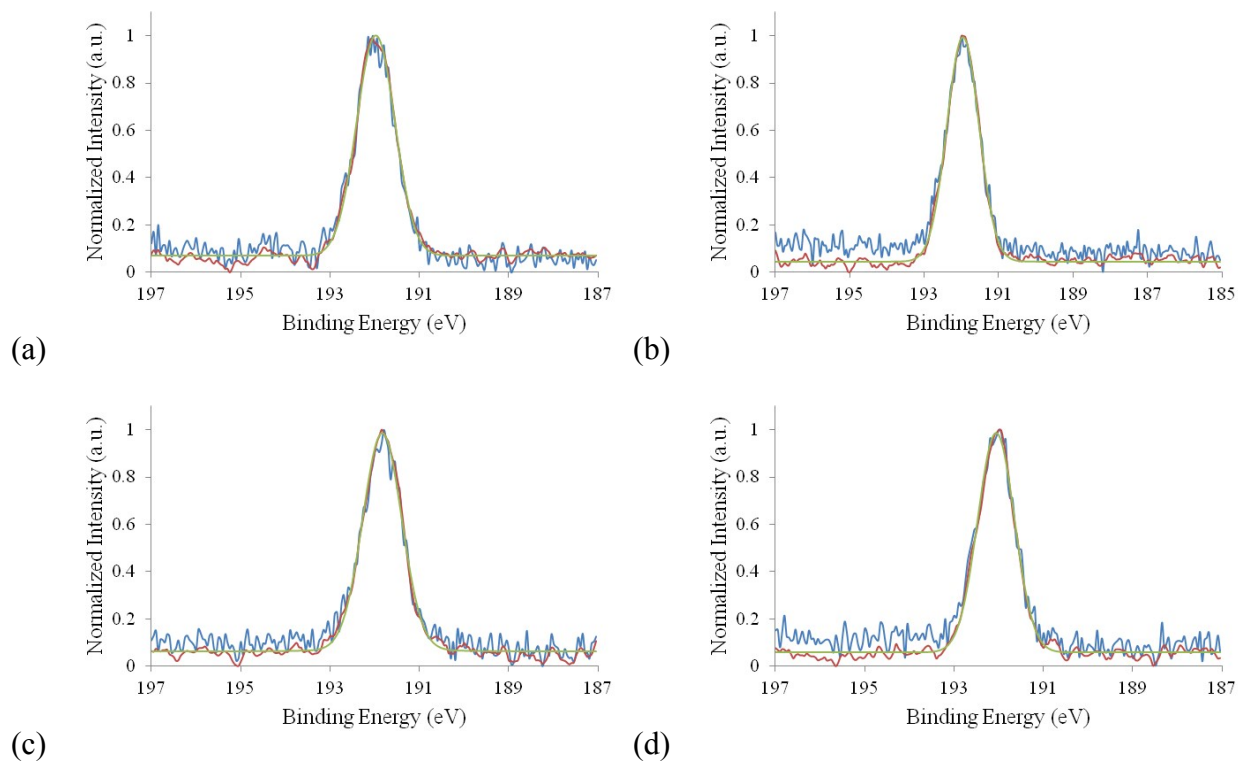


Figure S13. Deconvolution of B 1s XPS data of (a) literature-Cl-Cl_nBsubNc, (b) commercial-Cl-Cl_nBsubNc, (c) *p*-cymene-Cl-Cl_nBsubNc, and (d) nitrobenzene-Cl-Cl_nBsubNc. Colors: blue – experimental XPS curve; red – summed of the fitted curves; green – fitted curve 1.

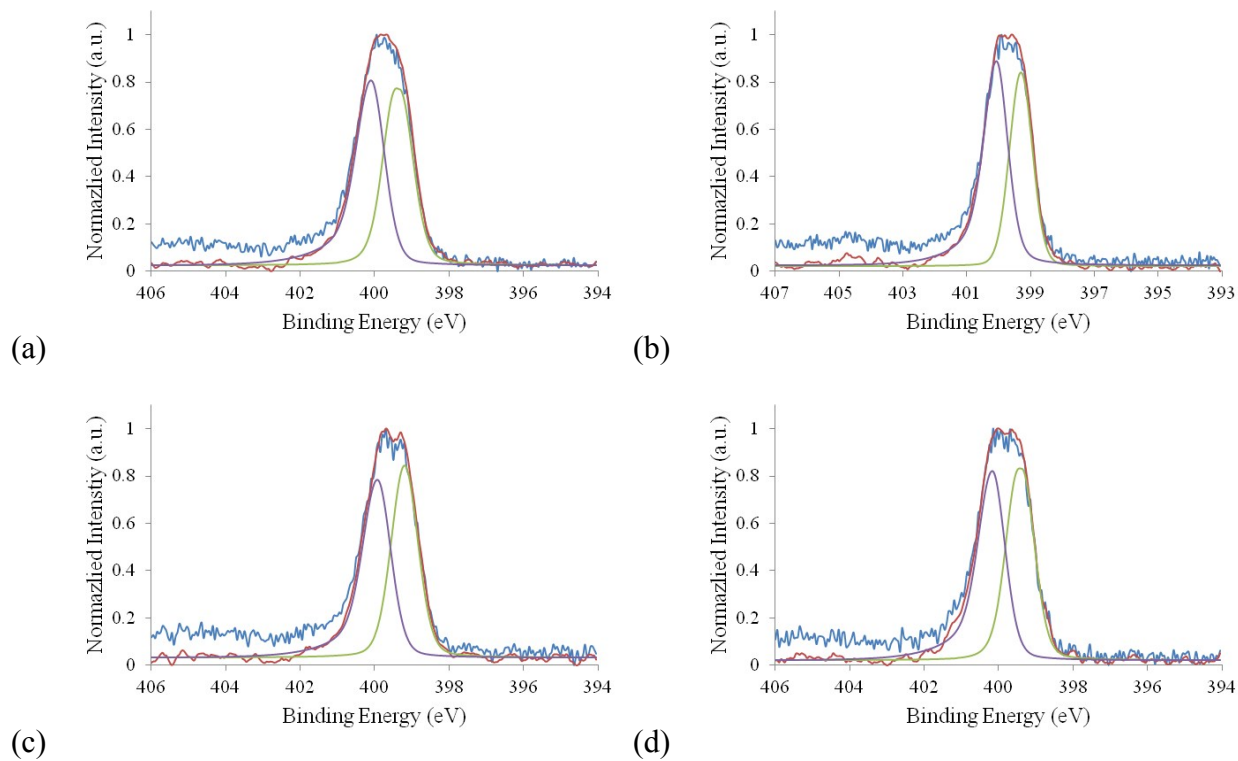


Figure S14. Deconvolution of N 1s XPS data of (a) literature-Cl-Cl_nBsubNc, (b) commercial-Cl-Cl_nBsubNc, (c) *p*-cymene-Cl-Cl_nBsubNc, and (d) nitrobenzene-Cl-Cl_nBsubNc. Colors: blue – experimental XPS curve; red – summed of the fitted curves; green – fitted curve 1; purple – fitted curve 2.

Table S23. Integrated peak intensity ratios of Cl-Cl_nBsubNcs.

Compound	Cl-B / B	Cl-C / B	Cl-C / Cl-B	Cl _{total} / N _{total}	6 (Cl _{total} / N _{total}) - 1
Literature-Cl-Cl _n BsubNc	0.93	1.06	1.21	0.40	1.40
Commercial-Cl-Cl _n BsubNc	0.90	1.36	1.61	0.46	1.76
<i>p</i> -Cymene-Cl-Cl _n BsubNc	0.93	0.10	0.18	0.22	0.32
Nitrobenzene-Cl-Cl _n BsubNc	0.80	3.12	4.17	0.90	4.40
Kahn <i>et al.</i> ¹¹	-	-	~1.5	-	-

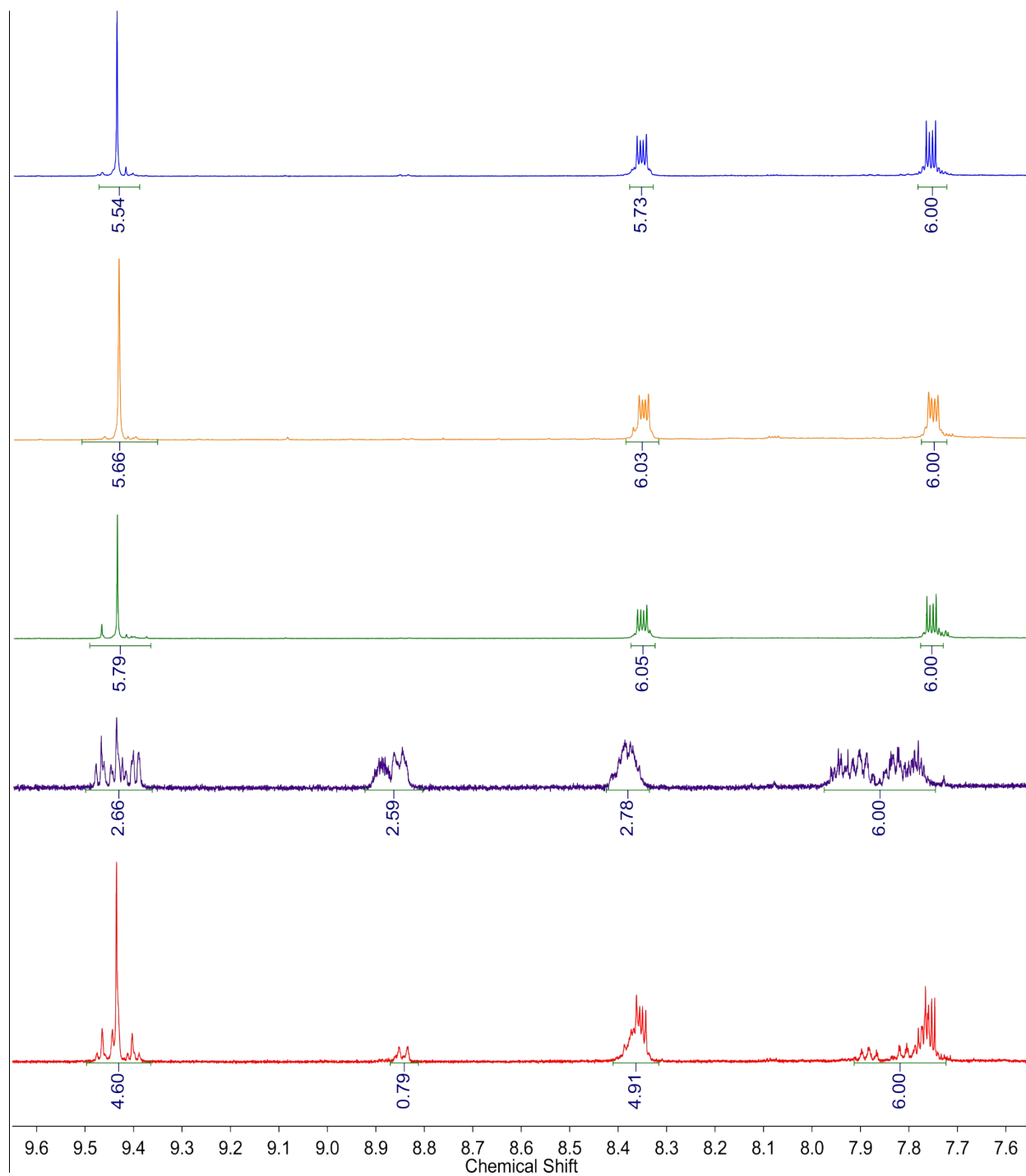
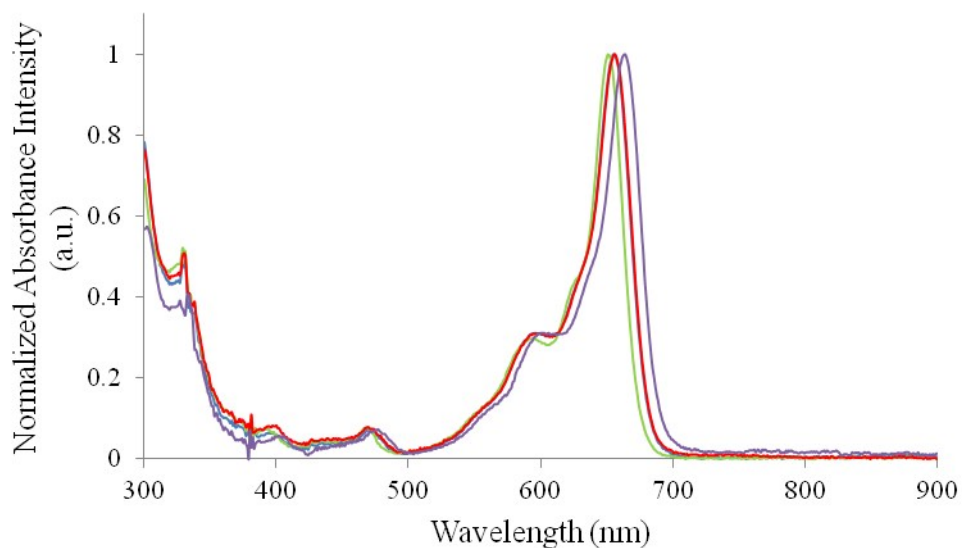
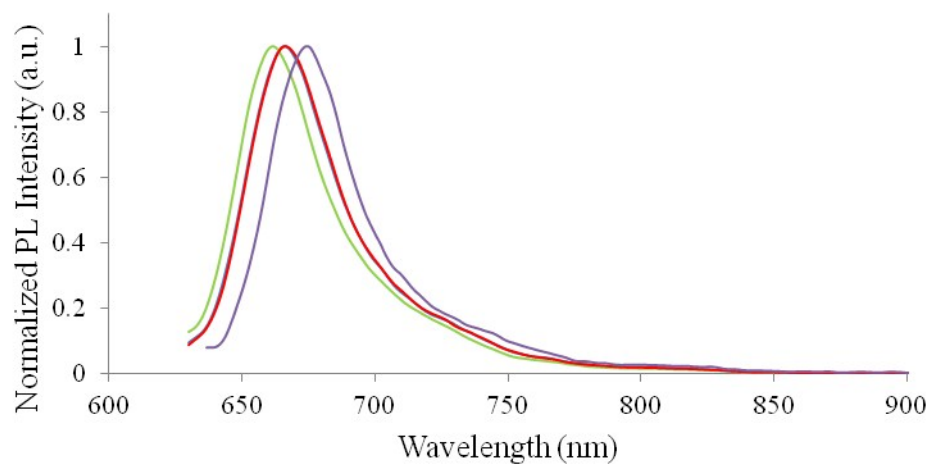


Figure S15. ¹H NMR (400 MHz, CDCl₃, 296 K) spectrum of the aromatic region for literature-Cl-Cl_nBsubNc (blue), 1-MNAP-Cl-Cl_nBsubNc (orange), *p*-cymene-Cl-Cl_nBsubNc (green), nitrobenzene-Cl-Cl_nBsubNc (purple), and commercial-Cl-Cl_nBsubNc (red). Integration values are shown below the peaks.

UV-Vis Absorption and Photoluminescence Plots of Cl-Cl_nBsubNc



(a)



(b)

Figure S16. Overlay of the literature-Cl-Cl_nBsubNc (blue), commercial-Cl-Cl_nBsubNc (red), *p*-cymene-Cl-Cl_nBsubNc (green) and nitrobenzene-Cl-Cl_nBsubNc (purple) (a) normalized absorption spectra and (b) normalized photoluminescence (PL) spectra.

Wavelength of Maximum Absorption of of Cl-Cl_nBsubPcs

Table S24. λ_{max} of Absorption Values of Peripherally Chlorinated Cl-BsubPc.

BsubPc Compound	λ_{max} (nm)
Cl-BsubPc	565
Cl-Cl ₆ BsubPc	574
Cl-Cl ₁₂ BsubPc	593

All measurements were done in toluene solutions at room temperature.

Determination of Fluorescence Quantum Yields

The fluorescence quantum yields (Φ) were calculated using the formula below:

$$\Phi = \Phi_{\text{R}} (I / I_{\text{R}})(OD_{\text{R}} / OD)(n^2 / n_{\text{R}}^2) \quad (\text{Eq S1})$$

where I is the integrated fluorescence intensity, OD is the optical density (*i.e.* absorbance), and n is the refractive index of the solvent. The subscript _R is oxazine 170, a reference fluorophore, which has previously been reported to have a $\Phi = 0.579^{12}$ in ethanol at room temperature. Integrated fluorescence intensity values were acquired from PerkinElmer FL WinLab (version 4.00.03) while the optical density values were acquired from PerkinElmer UV WinLab (version 6.02.0723). Analyses of all BsubNc compounds were acquired in toluene at room temperature.

Solid State UV-vis Absorption and Photoluminescence Plots of Cl-Cl_nBsubNc

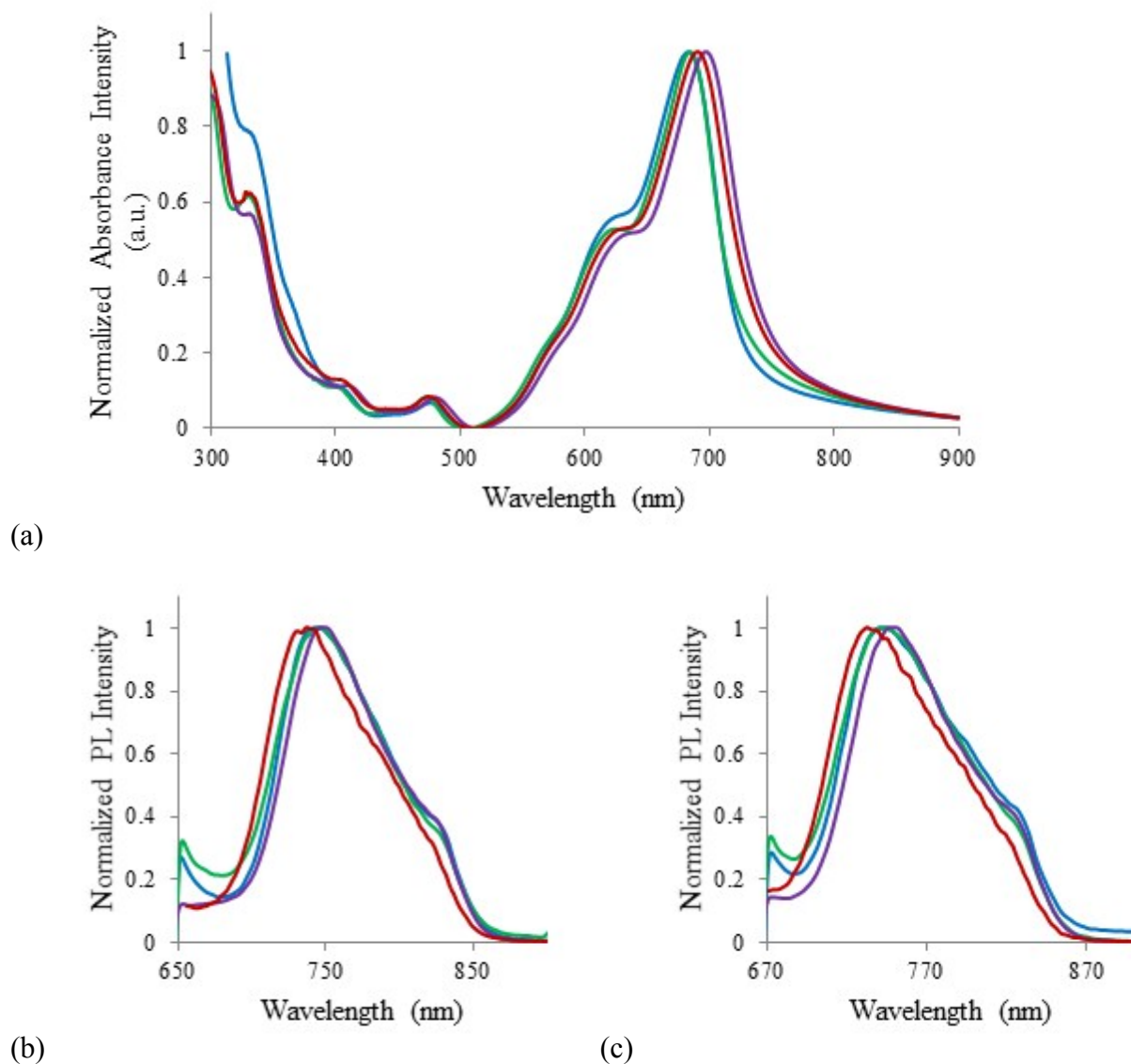


Figure S17. Overlay of literature-Cl-Cl_nBsubNc (blue), *p*-cymene-Cl-Cl_nBsubNc (green), nitrobenzene-Cl-Cl_nBsubNc (purple), and commercial-Cl-Cl_nBsubNc (red) (a) normalized solid-state absorption spectra and (b,c) normalized solid-state photoluminescence (PL) spectra excited at 630 nm and 650 nm, respectively.

Cyclic and Differential Pulse Voltammograms

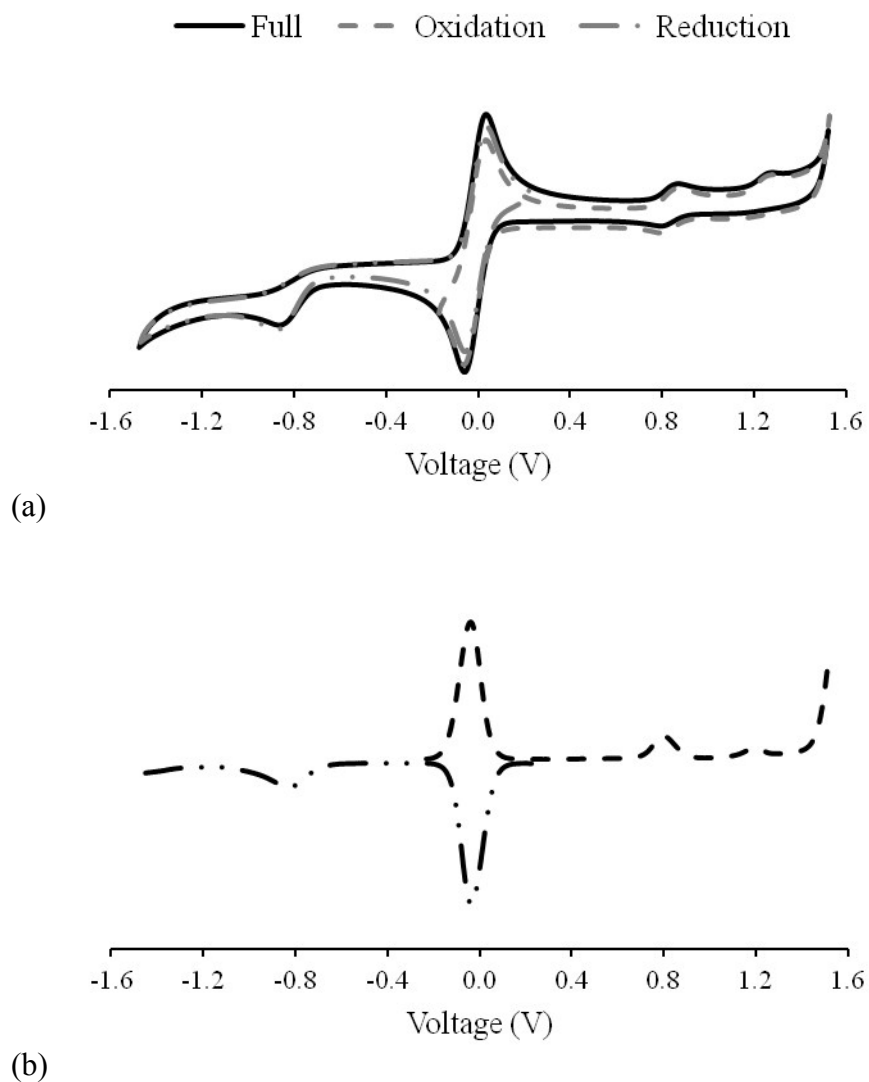


Figure S18. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of literature- $\text{Cl-Cl}_n\text{BsubNc}$ in DCM with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

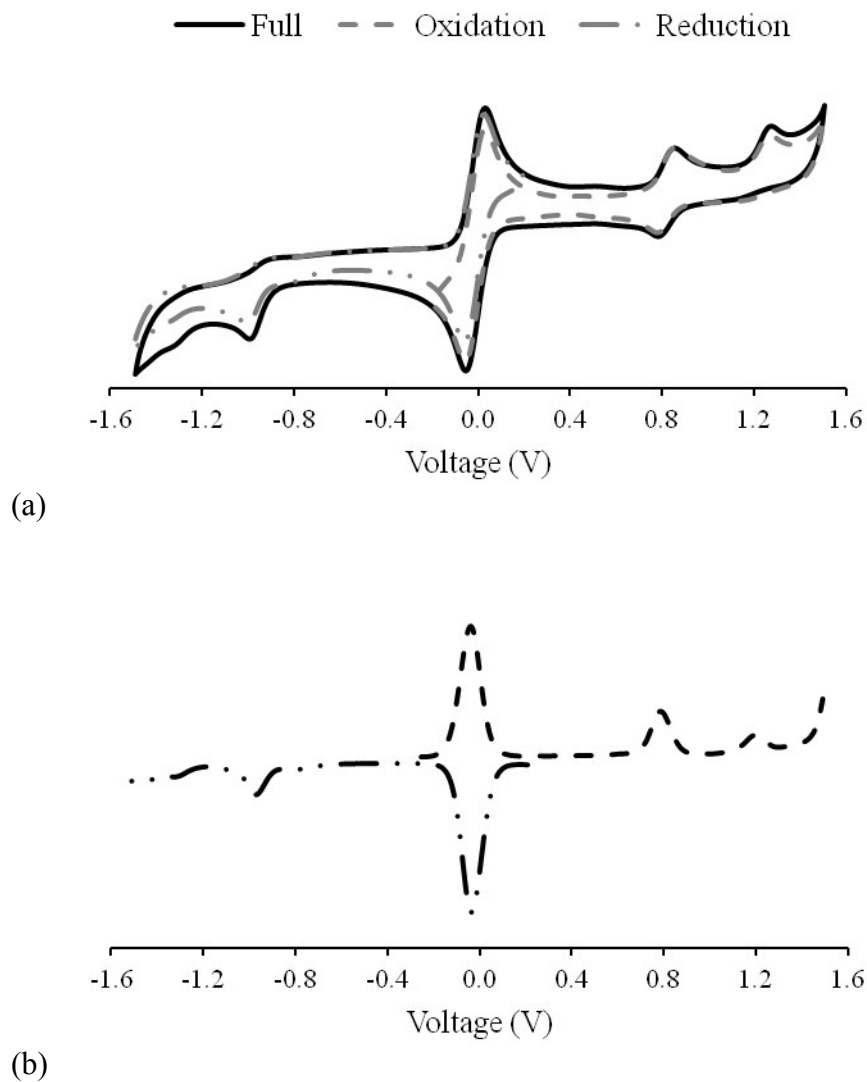


Figure S19. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of *p*-cymene-Cl-Cl_nBsubNc in DCM with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

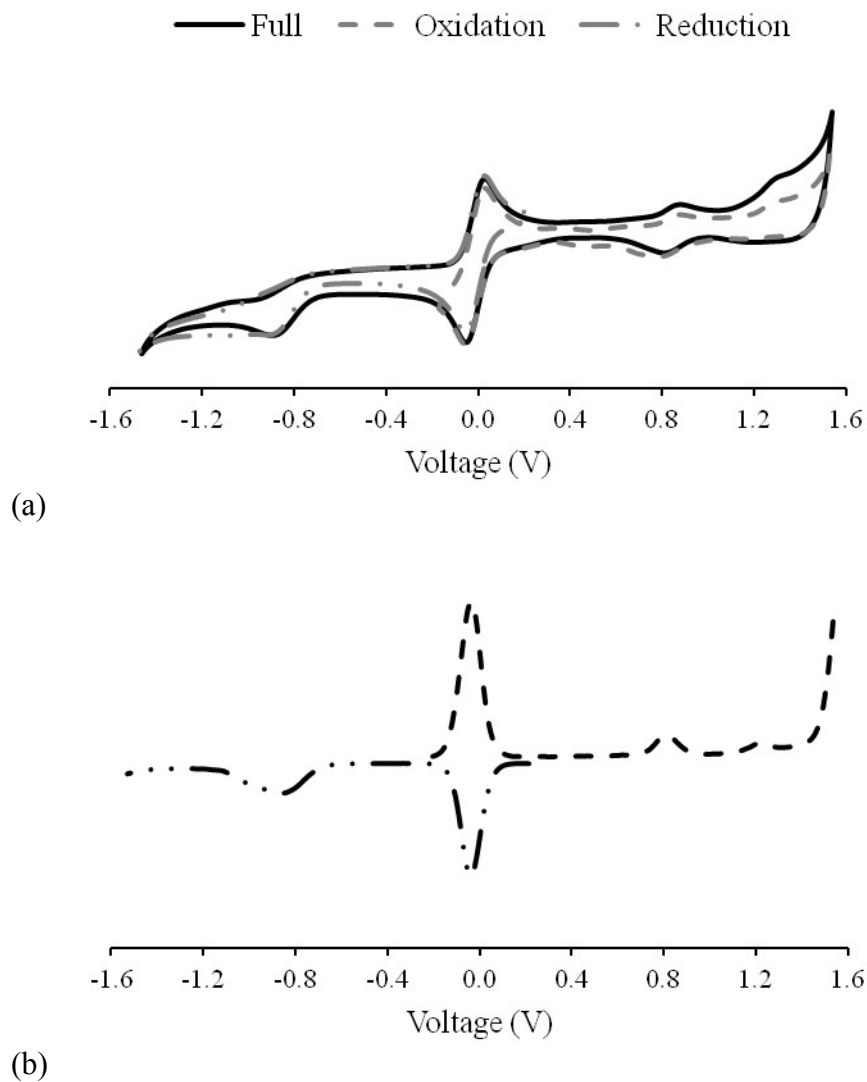
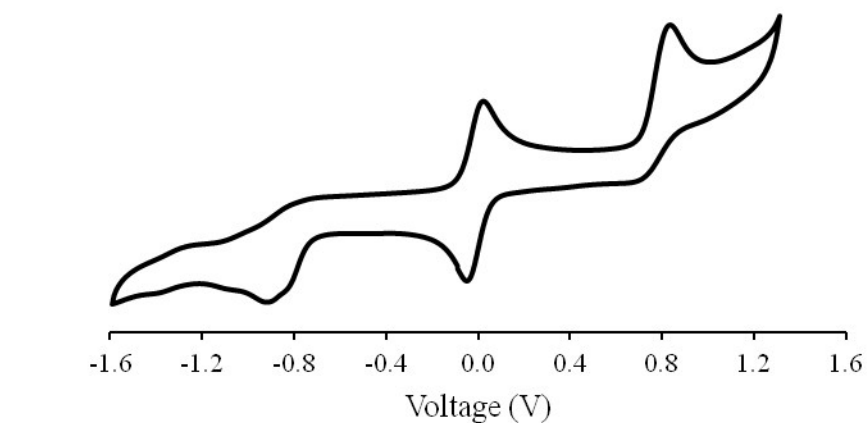
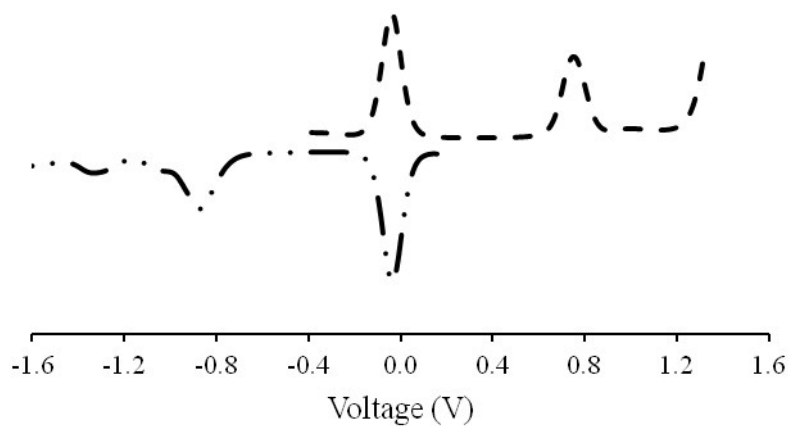


Figure S20. (a) Cyclic voltammety and (b) differential pulse voltammety traces of commercial-Cl-Cl_nBsubNc in DCM with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

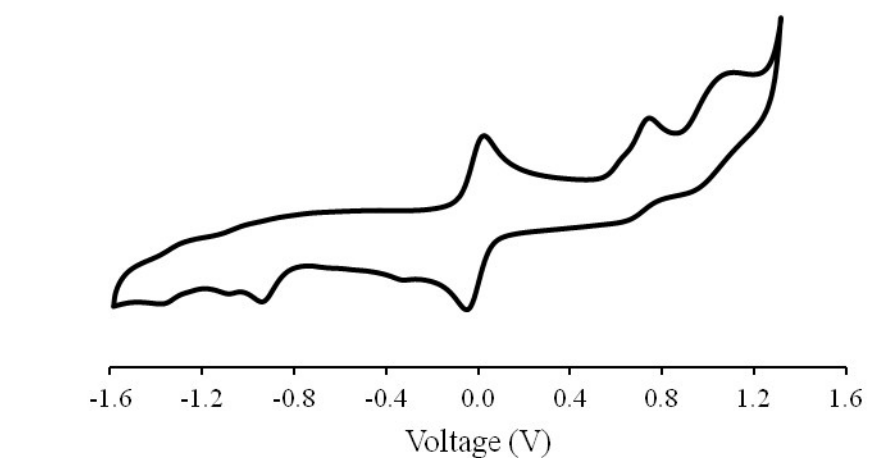


(a)

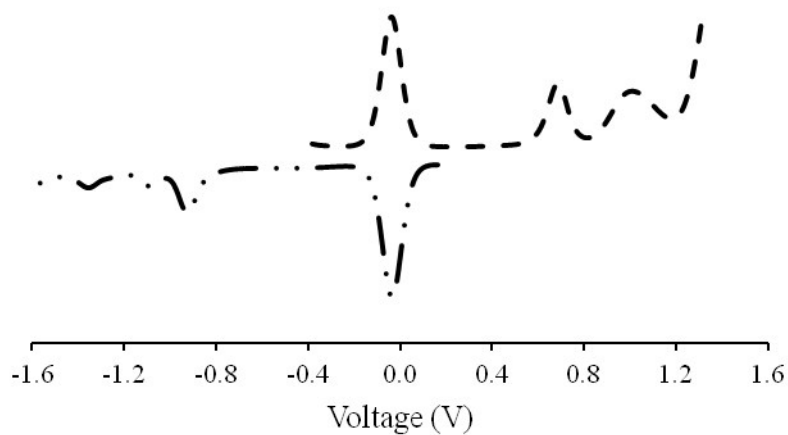


(b)

Figure S21. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of literature-Cl-Cl_nBsubNc in DMF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

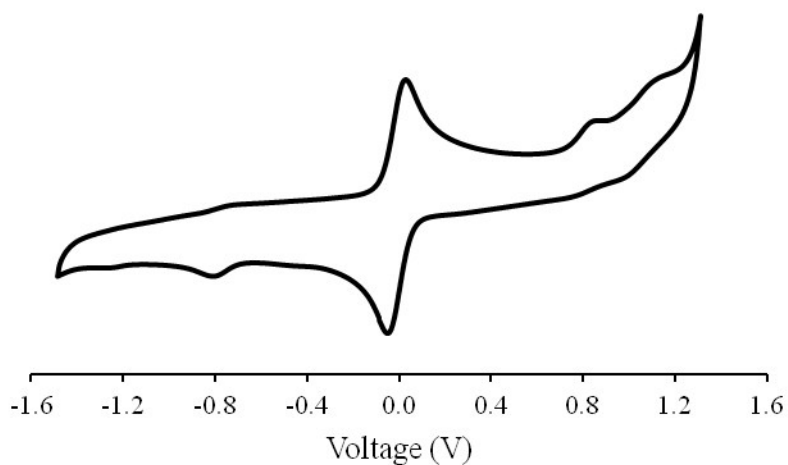


(a)

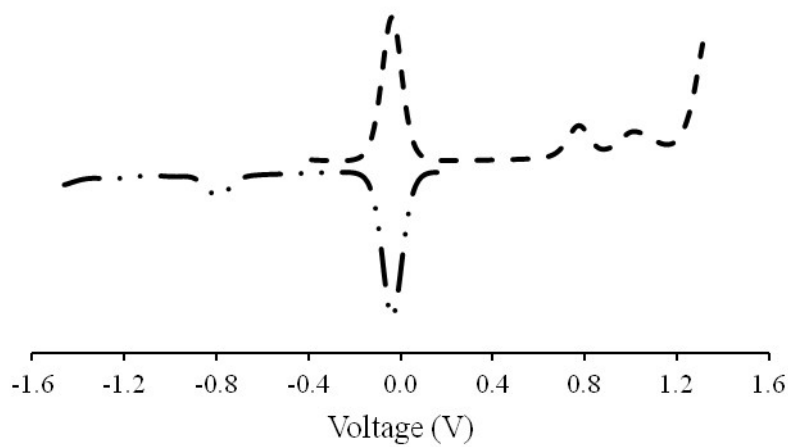


(b)

Figure S22. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of *p*-cymene-Cl-Cl_nBsubNc in DMF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

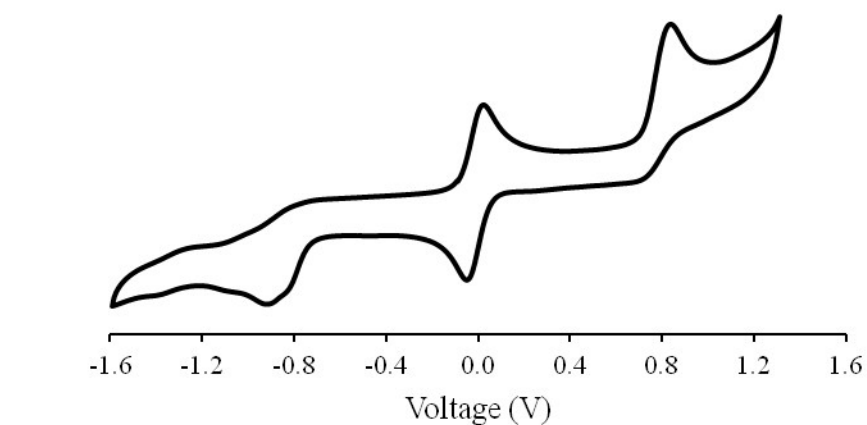


(a)

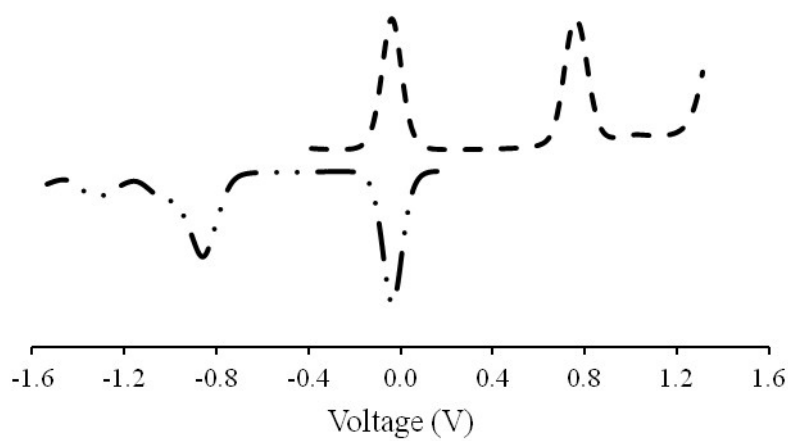


(b)

Figure S23. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of nitrobenzene-Cl-Cl_nBsubNc in DMF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.



(a)



(b)

Figure S24. (a) Cyclic voltammetry and (b) differential pulse voltammetry traces of commercial- $\text{Cl}-\text{Cl}_n\text{BsubNc}$ in DMF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference at room temperature.

Table S25. Electrochemical properties (DPV) of literature, commercial, and *p*-cymene Cl-Cl_nBsubNc.

Compound	E ^{1'} _{ox} E ^{2'} _{ox} ^a (V)		E ^{1'} _{red} E ^{2'} _{red} ^a (V)	
Literature-Cl-Cl _n BsubNc	+0.80 ^b	+1.20 ^b	-0.83 ^b	
Commercial-Cl-Cl _n BsubNc	+0.81 ^b	+1.22 ^b	-0.86 ^b	-0.97 ^b
<i>p</i> -Cymene-Cl-Cl _n BsubNc	+0.79 ^b	+1.20 ^b	-0.97 ^b	-1.29 ^b

E' = redox potential from DPV. ^a In degassed DCM solution relative to Ag/AgCl. ^b Peak potential.

Alternative Processing Methods for Analyzing DP Voltammograms

Three additional processing methods were employed to determine if the results from the apex peak method (used in all prior voltammetry experiments) are in line with these alternative methods. The first method derives the potential values from the onset of a peak, the second method derives the potential values from the first derivative zero point, and the third method derives the potential values from the maximum slope point. The results are summarized below:

Table S26. DPV potential values derived from three different processing methods for the four Cl-Cl_nBsubNc sources.

Compound	Method 1 ^a		Method 2 ^b		Method 3 ^c	
	E ^{1'} _{ox} E ^{2'} _{ox} (V)	E ^{1'} _{red} E ^{2'} _{red} E ^{3'} _{red} (V)	E ^{1'} _{ox} E ^{2'} _{ox} (V)	E ^{1'} _{red} E ^{2'} _{red} E ^{3'} _{red} (V)	E ^{1'} _{ox} E ^{2'} _{ox} (V)	E ^{1'} _{red} E ^{2'} _{red} E ^{3'} _{red} (V)
Literature	0.65, 0.92	-0.75, N/A, -1.21	0.52, 0.91	-0.60, N/A, -1.17	0.70, 0.95	-0.83, N/A, -1.25
Commercial	0.66, 0.94	-0.75, N/A, -1.18	0.50, 0.93	-0.60, N/A, -1.16	0.71, 0.97	-0.82, N/A, -1.24
<i>p</i> -Cymene	0.59, 0.86	-0.85, -1.03, -1.27	0.48, 0.82	0.68, -1.02, -1.19	0.65, 0.92	-0.89, -1.05, -1.32
Nitrobenzene	0.68, 0.91	-0.69, -0.94, -1.17	0.52, 0.88	-0.55, -0.95, -1.08	0.73, 0.96	-0.75, -0.96, -1.21

^a E' derived from peak onset. ^b E' derived from the first derivative zero point. ^c E' derived from the maximum slope point.

Ultraviolet Photoelectron Spectroscopy

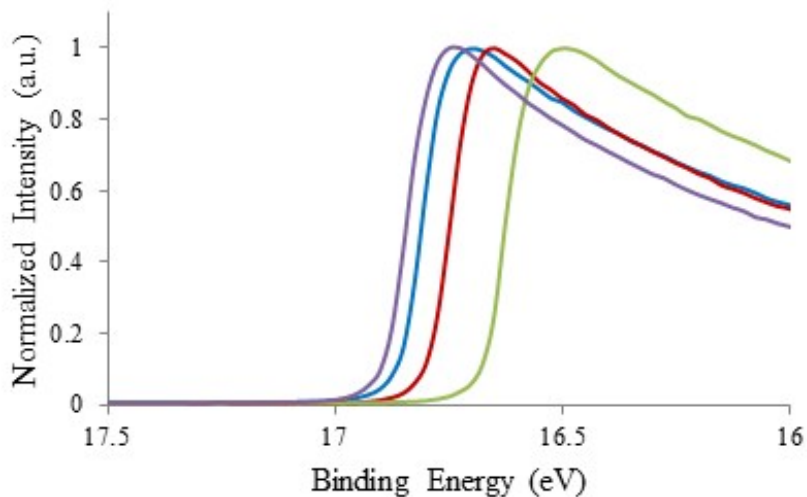
The ionization energy (*i.e.* HOMO energy level) is determined using the following equation:

$$\text{Ionization energy} = \phi + \Delta e, \quad (\text{Eq S2})$$

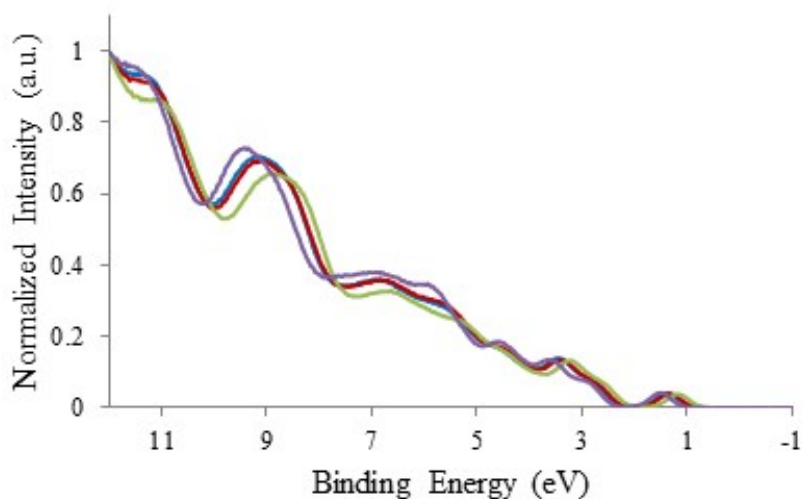
where ϕ is the work function and Δe is the HOMO-Fermi gap. The Δe is determined from the UPS HOMO-derived plot (Figure S25b) via the extrapolation of the linear portion of the tailing peak with the x-axis. The ϕ is calculated from the following equation.

$$\phi = E_{\text{UV}} - \text{SEC} + B, \quad (\text{Eq S3})$$

where E_{UV} is the energy of the incident UV light, SEC is the secondary electron cutoff, and B is the electrical bias applied during measurement. The SEC is determined from the UPS SEC plot (Figure S25a) via the extrapolation of the linear portion of the onset peak with the x-axis. The E_{UV} and B used in these measurements are 21.22 and -15 eV, respectively.



(a)



(b)

Figure S25. Ultraviolet photoelectron spectroscopy (UPS) He $I\alpha$ ($h\nu = 21.22$ eV) valence band spectra of literature-Cl-Cl_nBsubNc (blue), commercial-Cl-Cl_nBsubNc (red), *p*-cymene-Cl-Cl_nBsubNc (green) and nitrobenzene-Cl-Cl_nBsubNc (purple) showing (a) the secondary electron cutoff and (b) the HOMO-derived peak.

References

1. J. Rauschnabel and M. Hanack, *Tetrahedron Lett.*, 1995, **36**, 1629-1632.
2. M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. Del Rey, A. Sastre and T. Torres, *Synthesis*, 1996, 1139-1151.
3. N. Kobayashi, T. Ishizaki, K. Ishii and H. Konami, *J. Am. Chem. Soc.*, 1999, **121**, 9096-9110.
4. C. D. Zyskowski and V. O. Kennedy, *J. Porphyrins Phthalocyanines*, 2000, **4**, 707-712.
5. S. Nonell, N. Rubio, B. del Rey and T. Torres, *Perkin 2*, 2000, 1091-1094.
6. L. Giribabu, C. V. Kumar, A. Surendar, V. G. Reddy, M. Chandrasekharam and P. Y. Reddy, *Synth. Commun.*, 2007, **37**, 4141-4147.
7. Y. Takao, T. Masuoka, K. Yamamoto, T. Mizutani, F. Matsumoto, K. Moriwaki, K. Hida, T. Iwai, T. Ito, T. Mizuno and T. Ohno, *Tetrahedron Lett.*, 2014, **55**, 4564-4567.
8. I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, *J. Phys. Chem. B*, 1999, **103**, 6713-6722.
9. M. Bouvet, P. Bassoul and J. Simon, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 1994, **252**, 31-38.
10. J. R. Stork, R. J. Potucek, W. S. Durfee and B. C. Noll, *Tetrahedron Lett.*, 1999, **40**, 8055-8058.
11. J. Endres, I. Pelczer, B. P. Rand and A. Kahn, *Chemistry of Materials*, 2016, **28**, 794-801.
12. K. Rurack and M. Spieles, *Analytical Chemistry*, 2011, **83**, 1232-1242.