For Long-lived charge transfer state from B-N frustrated Lewis pairs enchained in supramolecular copolymers
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1. Materials and methods

All solvents were obtained from Biosolve, Acros or Aldrich. All other chemicals were obtained from Aldrich. Dry DCM, THF, and DMF were tapped off a distillation setup which contained molecular sieves. CHCl₃ was dried over molecular sieves and triethylamine was stored on KOH pellets. (S)-(−)-Citronellol was purchased from Aldrich and converted into the corresponding (S)-3,7-dimethyloctan-1-amine according to a described procedure. All other chemicals were used as received. Septum-sealed anhydrous decalin was purchased from ACROS Organics and used as received for preparing stock solutions (unless otherwise mentioned).

Melting points (mp) were determined with a Yanaco MP-S3 instrument. ¹H NMR and ¹³C NMR measurements were carried out on a Varian Gemini 400 MHz (100 MHz for ¹³C), a JEOL AL-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C), a JEOL ECS-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C), or a JEOL ECA-600 II spectrometer equipped with an UltraCOOL probe (150 MHz for ¹³C). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) except for compounds 1 and 2. Proton chemical shifts for compound 1 and 2 are reported using the residual protons of the solvents. Carbon chemical shifts are reported using the resonance of CDCl₃ as internal standard. ¹¹B NMR spectra were recorded with a JEOL ECA600 (191 MHz for ¹¹B) in C₆D₆ and CDCl₃. The chemical shifts in ¹¹B NMR are reported using BF₃·OEt₂ (δ 0.00) as an external standard. Mass spectra were measured with a Bruker microTOF Focus spectrometry system with the ionization method of APCI. MALDI-TOF-MS were acquired using a PerSeptive Biosystem Voyager-DE PRO spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrices. IR spectra were recorded on a Perkin–Elmer spectrum two FTIR spectrometer. Polarization optical microscopy (POM) measurements were done using a Jena polarization microscope equipped with a Linkam THMS 600 heating device, with crossed polarizers. The thermal transitions were determined with DSC by using a DSC Q2000 under a nitrogen atmosphere with heating and cooling rates of 10 °C min⁻¹. Bulk small angle X-ray scattering (SAXS) was performed on an instrument from Ganesha Lab. The flight tube and sample holder are all under vacuum in a single housing, with a GeniX generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1 × 10⁸ ph s⁻¹. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.431 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver benenate.

UV-Vis, circular dichroism (CD) and photoluminescence measurements were performed on a Jasco J-815 spectropolarimeter, equipped with a Jasco MPTC-490S Peltier temperature controlled multi-cell holder and a Jasco FMO-427S/15 emission monochromator. In all experiments the linear dichroism was also measured, unless otherwise mentioned, no linear dichroism was observed. Separate UV-Vis spectra were obtained from a Jasco V-750 UV-Visible spectrophotometer equipped with a Jasco PAC-743 Peltier temperature controlled multi-cell holder (solution measurement) and from a Perkin-Elmer Lambda 1050 UV/Vis/NIR spectrophotometer (bulk measurement). CPL measurements were carried out using a custom-built setup equipped with a photo-elastic modulator and a 16-channel photomultiplier array possessing a photon counting detection method. The excitation wavelength was selected from a Hg lamp using appropriate interference and bandpass filters (λ = 365 nm). The excitation light was depolarized by passing it through a bundle of optical fibers. The direction of the excitation was normal to the surface of the film and in line with the direction of emission collection. Time resolved photoluminescence spectra were recorded on an Edinburgh Instruments LifeSpec-PS spectrophotometer. Photoluminescent measurement of bulk samples were carried out on an Edinburgh FLS900 photoluminescence spectrometer. Water concentration in decalin was determined by Karl Fischer titrations using a Mettler-Toledo C30 Coulometric KF Titrator loaded with CombiCoulomat Frit KF reagent (for cells with diaphragm, contains methanol).
For all spectroscopic measurements, Hellma Quartz Suprasil cuvettes with an optical pathlength of 1 cm and spectroscopic grade solvents were employed. Solutions were prepared by weighing the necessary amount of compound for the given concentration and dissolved with a weighted amount of solvent based on its density. The stock solutions were heated up, sonicated till complete dissolution and cooled down to room temperature before use. Unless otherwise mentioned, all the spectroscopic measurements were performed with freshly prepared solutions. For optical and photoluminescence measurements related to the oxygen effects, the samples were prepared in N₂ equilibrated glovebox by using degassed anhydrous decalin and cuvettes equipped with a screw cap and a Teflon-lined septum. Wet decalin was prepared by layering decalin (15 mL) over water (1.5 mL). After mixing and equilibrating overnight, the top organic layer was collected and used for the experiment.
2. Synthetic procedures

2.1 Core synthesis

![Scheme S1. Synthetic scheme for brominated oxygen-bridged triphenylborane.]

**2.4-Dibromo-1,3-bis(3-bromophenoxy)benzene (1)**

In a round-bottom flask, a mixture of 2,5-dibromo-1,3-difluorobenzene (4.20 g, 15.4 mmol), 3-bromophenol (7.00 g, 40.5 mmol) and K$_2$CO$_3$ (8.80 g, 63.7 mmol) in 30 mL of anhydrous NMP was stirred at 180 °C for 2 h then 190 °C for 2 h under a nitrogen atmosphere. After cooling to room temperature, 100 mL of water was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was dissolved into CHCl$_3$ and passed through a pad of silica gel using CHCl$_3$ as eluent. The resulting yellow oil was subjected to silica gel column chromatography using hexane as eluent, giving 1 as a colorless solid (yield = 3.45 g, 39%).

**Mp:** 113.8–114.8 °C.

**1H NMR (400 MHz, CD$_2$Cl$_2$):** δ (ppm) 7.36–7.33 (m, 2H), 7.29 (t, $J_{HH} = 8.0$, 2H), 7.19 (t, $J_{HH} = 2.0$ Hz), 7.01 (ddd, $J_{HH} = 8.0$, 2.4, 1.2 Hz, 2H), 6.90 (s, 2H).

**13C NMR (100 MHz, CDCl$_3$):** δ (ppm) 156.6, 155.7, 131.3, 127.7, 123.3, 122.1, 121.5, 118.4, 117.5, 106.9. HRMS(APCI) m/z calcd for C$_{18}$H$_{10}$Br$_4$O$_2$ [M]$^+$ 573.7409, found: 573.7433.

**3,7,11-Tribromo-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (2).**

In a round-bottom flask, a 20 mL of xylene solution of 2 (2.30 g, 3.98 mmol) was added dropwise a hexane solution of nBuLi (1.6 M, 2.80 mL, 4.48 mmol) at –78 °C under a nitrogen atmosphere. The reaction mixture was allowed to gradually warm up to 25 °C. After stirring for 1 h, boron tribromide (1.24 g, 4.96 mmol) was added dropwise at 0 °C and the reaction mixture was stirred for 1 h. Then, N,N-diisopropylethylamine (1.30 mL, 7.44 mmol) was added dropwise at 0 °C followed by stirring at 130 °C for 12 h. After cooling to room temperature, an aqueous solution of NaOAc was added. The pale-yellow precipitates were collected by filtration, and successively washed with water, hexane, methanol and ethanol to afford 2 as a pale yellow solid (yield = 1.23 g, 61%).

**Mp:** 286.0–286.8 °C.

**1H NMR (400 MHz, CDCl$_3$):** δ (ppm) 8.41 (d, $J_{HH} = 8.4$, 2H), 7.73 (d, $J_{HH} = 1.6$ Hz, 2H), 7.52 (dd, $J_{HH} = 8.4$ Hz, $J_{HH} = 1.6$ Hz, 2H), 7.41 (s, 2H).

**13C NMR (150 MHz, CDCl$_3$):** δ (ppm) 160.5, 157.3, 135.5, 129.2, 128.5, 127.0, 121.9, 120.5, 113.3, 112.9. **11B NMR spectrum was not obtained due to its poor solubility.**

**HRMS(APCI) m/z calcd for C$_{18}$H$_{10}^{11}$B$_3$Br$_3$O$_2$ [M]$^+$ 503.8162, found: 503.8179.**
Brominated oxygen-bridged triphenylamine was synthesized as described in literature with slight modifications.²

![Scheme S2. Synthetic scheme for brominated oxygen-bridged triphenylamine.](image)

### 4-Bromo-2,6-difluoro-N,N-bis(2-methoxyphenyl)aniline (3)
In a round-bottom flask, iodoanisole (19.98 g, 85.4 mmol), 4-bromo-2,6-difluoroaniline (7.75 g, 37.2 mmol), K₂CO₃ (21.8 g, 158 mmol), and copper powder (7.96 g, 125 mmol) were dissolved in 100 mL of dichlorobenzene. The mixture was heated at 180 °C for 5 days. After cooling to room temperature, the mixture was filtered, washed with water, dried over MgSO₄, filtered, and concentrated under reduced pressure. After washing the resulting solid with 400 mL of hexane, the solid was dissolved in 150 mL of dichloromethane and the mixture was poured to 400 mL of hexane. The precipitates were collected by filtration and dried at 50 °C under reduced pressure, giving 3 as a colorless solid (yield = 7.1615 g, 46%).

³H NMR (400 MHz, CDCl₃) δ 7.08-6.96 (m, 4H), 6.91-6.82 (m, 6H), 3.60 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 153.38, 136.29, 124.72, 124.66, 121.20, 115.48, 115.40, 115.29, 115.21, 114.76, 113.21, 56.14, 53.41; m/z (MALDI-TOF-MS): calculated for C₂₀H₁₆BrF₂NO₂ 419.03, found 419.07 [M]⁺.

### 4-Bromo-N,N-bis(4-bromo-2-methoxyphenyl)-2,6-difluoroaniline (4)
In a round-bottom flask, 1 (2.63 g, 6.26 mmol) was dissolved in 50 mL of chloroform. Acetic acid (50 mL) and N-bromosuccinimide (2.45 g, 13.8 mmol) were added and the mixture was stirred at room temperature for 23 h. The mixture was then neutralized with 300 mL of an aqueous NaHCO₃ solution. The organic layer was collected, dried over Na₂SO₄, and concentrated under reduced pressure. The brown oil thus obtained was dissolved in 300 mL of hot acetonitrile, cooled down to room temperature and concentrated under reduced pressure, leading to precipitation. Colorless precipitates were collected by filtration, washed with acetonitrile and dried at 50 °C under reduced pressure to give 2 as a colorless solid (yield = 1.79 g, 50%).

³H NMR (400 MHz, CDCl₃) δ 7.03-6.92 (m, 6H), 6.74-6.72 (d, 2H), 3.59 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 153.77, 134.92, 125.58, 124.09, 117.21, 116.27, 115.67, 115.40, 56.25; m/z (MALDI-TOF-MS): calculated for C₂₀H₁₄Br₂F₂NO₂ 574.85, found 574.86 [M]⁺.
3,7,11-Tribromobenzo[5,6][1,4]oxazino[2,3-kl]phenoxazine (5)

In a round-bottom flask, 2 (901 mg, 1.56 mmol) in 30 mL of dry dichloromethane were cooled to −78 °C under an argon atmosphere. Then, BBr₃ in dichloromethane (1 M, 4 mL, 4 mmol) was added slowly to the reaction flask. The reaction mixture was stirred at −78 °C for 30 min, the cooling bath was removed, and the stirring was continued for 4 h. During the reaction, the colour changed from light brown to light blue/green. The reaction mixture was poured into 100 mL of water. The aqueous layer was re-extracted with 3x50 mL dichloromethane. Organic layers were combined, dried over Na₂SO₄ and evaporated under reduced pressure, giving a greyish foam-like solid. To this crude mixture, dry DMF (20 mL) and K₂CO₃ (670 mg, 4.83 mmol) were added. The mixture was stirred under an argon atmosphere at 100 °C. After 17 h, the mixture was concentrated under reduced pressure. The crude mixture was dissolved in 200 mL of dichloromethane and washed with 200 mL of water. The aqueous layer was re-extracted with 3x50 mL of dichloromethane. Organic layers were combined, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography using chloroform as eluent to give 3 as a colorless solid (yield = 703 mg, 88%).

1H NMR (400 MHz, CDCl₃) δ 7.12–7.04 (m, 6H), 6.68 (s, 2H); 13C NMR (100 MHz, CDCl₃) δ 147.22, 145.26, 127.61, 126.90, 120.91, 119.54, 115.87, 115.49, 115.32, 114.98; m/z (MALDI-TOF-MS): calculated for C₁₈H₈Br₃NO₂ 506.81, found 506.82 [M]+.

2.2 Synthesis of side chains

Chiral (S)-3,7-dimethyloctanol was previously synthesized in the group as described in literature.¹

![Scheme S3. Synthetic scheme for side chains.](image)

Methyl-3,4,5-trioctyloxybenzoate (7a)

In a round-bottom flask, 1-bromooctane (15.5 mL, 89.6 mmol) and 125 mL DMF were combined. After purging with N₂, K₂CO₃ (24.9 g, 179.2 mmol) and methyl gallate (5 g, 27.2 mmol) were added. The mixture was stirred and heated to 70 °C for 21 h. After cooling down to room temperature, the mixture was filtered and diluted with 200 mL diethyl ether. The liquid was washed with 3x250 mL water, 200 mL HCl (0.5 M) and 50 mL brine. The organic layer was dried over MgSO₄ and evaporated under reduced pressure. The obtained yellow/brown liquid was diluted with dichloromethane and passed through a short pad of basic Al₂O₃ to collect yellow filtrates. Solvent removal under reduced pressure yielded yellow liquid (13.7g, 97% yield).

1H NMR (400 MHz, CDCl₃) δ 7.25 (s, overlapping with CHCl₃ peak), 4.03-3.99 (t, 6H), 3.89 (s, 3H), 1.85–1.71 (m, 6H), 1.49-1.28 (m, 6H), 0.89-0.87 (t, 9H); 13C NMR (100 MHz, CDCl₃) δ 205.63, 166.94, 152.82, 142.36, 124.65, 107.98, 73.49, 69.17, 52.10, 31.91, 31.84, 30.33, 29.52, 29.37, 29.35, 29.31, 29.29, 26.08, 26.05, 22.70, 22.68, 14.10; m/z (MALDI-TOF-MS): calculated for C₃₂H₆₅O₅ 520.41, found 520.44 [M]+.
3,4,5-Tri(octyloxy)benzoic acid (8a)

In a round-bottom flask, 7a (7 g, 13.4 mmol), KOH (4.98 g, 87.4 mmol) and 50 mL absolute ethanol were combined. The mixture was stirred and heated to 78 °C for 4 h. After cooling to room temperature, the mixture was acidified with 1 M HCl and precipitated in 100 mL H2O. Yellow precipitates were collected by vacuum filtration and re-crystallized from ethanol. Creamy solids were collected by filtration and dried at 80 °C under reduced pressure (2.5 g, 37% yield).

\[ \text{3,4,5-Tris(octyloxy)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide (9a)} \]

In a round-bottom flask, 8a (2.4 g, 4.7 mmol), DMAP (771 mg, 6.3 mmol) were dissolved in 20 mL dry dichloromethane and 1.3 mL DMSO. The mixture was cooled in an ice bath, EDC-HCl (1.2 g, 6.1 mmol) and 21 mL dry DCM were added, and the mixture was stirred under Ar. After 30 mins, boronic ester (1.6 g, 7.3 mmol) was added in several portions and the mixture was stirred for 24 h. The mixture was washed with 3 x 100 mL 1 M HCl and 2 x 100 mL water, dried over MgSO4, filtered and evaporated under reduced pressure. The brown oil was purified by SiO2 column chromatography with 5-10% ethyl acetate/heptane as eluents. The product was obtained as yellow/brown solids (yield = 1.5987 g, 48%) (S)-3,7-Dimethyloctyl 4-methylbenzenesulfonate (6)

In a round-bottom flask, (S)-3,7-dimethyloctanol (8.9 g, 56.5 mmol) and p-toluenesulfonyl chloride (10.8 g, 56.6 mmol) were dissolved in 40 mL dry dichloromethane under Ar atmosphere. The reaction mixture was cooled in an ice bath. 10 mL pyridine was added dropwise, and the reaction mixture was stirred in an ice bath for 30 min then at room temperature for 1 day. The mixture was diluted with 30 mL dichloromethane, washed with 30 mL 2 M HCl, 30 mL 2 M NaOH, 100 mL water and 100 mL brine. The organic layer was collected, dried over MgSO4, filtered and evaporated under reduced pressure. The crude was dissolved in dichloromethane and pass through silica plug. Solvent removal gave the product as light-yellow liquid (yield = 14.9 g, 84%)
**Methyl-3,4,5-tri(S-3,7-dimethyloctyloxy)benzoate (7b)**

In a round-bottom flask, 6 (16.4 g, 52.3 mmol), methyl gallate (3.2 g, 17.2 mmol), tetrabutylammonium bromide (1.9 g, 5.8 mmol) were dissolved in 50 mL acetone. K$_2$CO$_3$ (23.2 g, 167.5 mmol) was added. The reaction mixture was heated to 55°C overnight. After cooling down to room temperature, the mixture was filtered, diluted with 200 mL water and extracted with 3x200 mL diethyl ether. The organic layers were combined, washed with 150 mL water and 150 mL brine, dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography using 25-75% ethyl acetate in heptane as eluents. The product was obtained as yellow oil (yield = 8.8198 g, 85%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (s, overlapping with CHCl$_3$ peak), 4.08-4.01 (m, 6H), 3.89 (s, 3H), 1.89-1.12 (m, 30H), 0.95-0.91 (m, 9H), 0.88-0.85 (d, 18H).

**3,4,5-Tri(S-3,7-dimethyloctyloxy)benzoic acid (8b)**

In a round-bottom flask, 7b (8.8 g, 14.6 mmol), NaOH (15 g, 375 mmol) and 60 mL absolute ethanol were combined. The mixture was refluxed overnight. After cooling to room temperature, the solvent was removed under reduced pressure. The crude was dissolved in 200 mL dichloromethane and 150 mL water. The organic layer was collected, washed with 150 mL 1M HCl and 150 mL water and 150 mL brine. The organic layer was dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The yellow/brown oil was purified by column chromatography using 50-75% ethyl acetate in dichloromethane as eluents. The product was obtained as yellow oil (yield = 8.2383 g, 96%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (s, 2H), 4.13-4.02 (m, 6H), 1.92-1.11 (m, 30H), 0.96-0.92 (m, 9H), 0.88-0.85 (d, 18H).

**3,4,5-Tris((S)-3,7-dimethyloctyloxy)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzamide (9b)**

In a round-bottom flask, 8b (2.8 g, 4.8 mmol), DMAP (770 mg, 6.3 mmol) were dissolved in 40 mL dry dichloromethane and 1.2 mL DMSO. The mixture was cooled in an ice bath, EDC-HCl (1.1 g, 5.9 mmol) was added, and the mixture was stirred under Ar. After 30 mins, boronic ester (1.6 g, 7.3 mmol) was added and the mixture was stirred for 21 h. The mixture was diluted with 50 mL dichloromethane, washed with 3x100 mL 1M HCl and 2x100 mL water, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The brown oil was purified by SiO$_2$ column chromatography using 5-10% ethyl acetate in heptane as eluents. The product was obtained as yellow/orange solids (yield = 1.9245 g, 50%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.83-7.81 (d, 2H), 7.72 (s, 1H), 7.66-7.74 (d, 2H), 7.06 (s, 2H), 4.10-4.01 (m, 6H), 1.91-1.15 (m, 30H), 0.96-0.92 (t, 9H), 0.88-0.86 (d, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.49, 153.31, 141.70, 140.65, 135.89, 129.85, 118.86, 105.87, 83.78, 71.82, 67.87, 39.38, 39.29, 37.52, 37.36, 36.40, 29.88, 29.69, 28.00, 24.90, 24.75, 24.73, 22.71, 22.63, 22.60, 19.61, 19.59; m/z (MALDI-TOF-MS): calculated for C$_{49}$H$_{82}$BNO$_6$ 791.62, found 792.61 [M+H]$^+$ and 814.60 [M+Na]$^+$. 

S8
2.3 Synthesis of B and N monomers

Scheme S4. Synthetic scheme for B and N monomers.
In a Schlenk flask, Pd(OAc)$_2$ (0.03 mmol) were dissolved in dry toluene (7.9 mL). The mixture was stirred at 110 °C for 48 h. The mixture was then diluted with CHCl$_3$ (80 mL) and washed with water (3×100 mL). The organic fraction was collected, dried over MgSO$_4$, and concentrated under reduced pressure. The mixture was first purified with silica gel column chromatography using 3/6 hexane/CH$_2$Cl$_2$ as eluent, then with HPLC (CHCl$_3$) and finally with preparative GPC (hexane) affording 3 as a yellow solid (yield = 200 mg, 45%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.82-8.80 (d, 2H), 7.88-7.84 (m, 9H), 7.75-7.69 (m, 9H), 7.53 (s, 2H), 7.10 (s, 6H), 4.26-4.12 (m, 18H), 1.88-1.18 (m, 90H), 0.97-0.93 (m, 27H), 0.89-0.87 (m, 54H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.76, 161.10, 157.83, 153.33, 145.38, 141.68, 138.18, 136.31, 135.94, 129.75, 128.18, 127.90, 120.66, 106.84, 105.85, 71.81, 67.81, 39.38, 39.29, 37.53, 37.38, 36.40, 29.87, 29.68, 28.01, 24.77, 24.74, 22.73, 22.64, 22.62, 19.60, 19.58; $^{11}$B NMR (191 MHz, CDCl$_3$) δ 34.5; m/z (MALDI-TOF-MS): calculated for C$_{147}$H$_{218}$BN$_3$O$_{14}$ 2260.65, found 2261.44 [M+H]$^+$; IR (cm$^{-1}$) ν 3301, 2953, 2925, 2869, 1647, 1633, 1610, 1583, 1521, 1493, 1468, 1423.

In a Schlenk tube under an argon atmosphere, tribromide 2 (100 mg, 0.20 mmol), XPhos (61 mg, 0.13 mmol), K$_2$PO$_4$ (439 mg, 2.07 mmol) and Pd$_2$(dba)$_3$-CHCl$_3$ (32.68 mg, 0.03 mmol) were dissolved in dry toluene (7.9 mL). The mixture was stirred at 110 °C for 48 h. The mixture was then diluted with CHCl$_3$ (80 mL) and washed with water (3×100 mL). The organic fraction was collected, dried over MgSO$_4$, and concentrated under reduced pressure. The mixture was first purified with silica gel column chromatography using 3/6 hexane/CH$_2$Cl$_2$ as eluent, then with HPLC (CHCl$_3$) and finally with preparative GPC (hexane) affording 3 as a yellow solid (yield = 200 mg, 45%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.82-8.80 (d, 2H), 7.88-7.84 (m, 9H), 7.75-7.69 (m, 9H), 7.53 (s, 2H), 7.10 (s, 6H), 4.26-4.12 (m, 18H), 1.88-1.18 (m, 90H), 0.97-0.93 (m, 27H), 0.89-0.87 (m, 54H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.76, 161.10, 157.83, 153.33, 145.38, 141.68, 138.18, 136.31, 135.94, 129.75, 128.18, 127.90, 120.66, 106.84, 105.85, 71.81, 67.81, 39.38, 39.29, 37.53, 37.38, 36.40, 29.87, 29.68, 28.01, 24.77, 24.74, 22.73, 22.64, 22.62, 19.60, 19.58; $^{11}$B NMR (191 MHz, CDCl$_3$) δ 34.5; m/z (MALDI-TOF-MS): calculated for C$_{147}$H$_{218}$BN$_3$O$_{14}$ 2260.65, found 2261.44 [M+H]$^+$; IR (cm$^{-1}$) ν 3301, 2953, 2925, 2869, 1647, 1633, 1610, 1583, 1521, 1493, 1468, 1423.
**N,N′,N″-(Nitrilotris([1,1′'-biphenyl]-4,4'-diyl))tris(3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzamide) (S-N2)**

In a three neck round bottom flask under argon, tris(4-bromophenyl)amine (150 mg, 0.31 mmol), 9b (1.15 g, 0.1.46 mmol), K$_2$CO$_3$ (149 mg, 2.49 mmol), and Pd$_2$(PPh$_3$)$_4$ (18 mg, 0.015 mmol) were introduced and dissolved in dioxane (5 mL) and water was then added (0.2 mL). The reaction was stirred and heated to 100 °C under argon for 36 h. The reaction mixture was then diluted with CHCl$_3$ (80 mL) and washed with water (3 x 80 mL). The organic fraction was collected, dried over MgSO$_4$ and evaporated under reduced pressure. The product was first purified with SiO$_2$ plug in CHCl$_3$ (50mL) and precipitation from CHCl$_3$ into CH$_3$CN, affording beige solids (yield = 365 mg, 60%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.73-7.69 (m, 9H), 7.63-7.61 (d, 6H), 7.55-7.53 (d, 6H), 7.23 (d partially covered by CHCl$_3$ signal), 7.08 (s, 6H), 4.12-4.02 (m, 18H), 1.92-1.15 (m, 90H), 0.97-0.93 (m, 27H), 0.88-0.86 (d, 54H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 165.61, 153.30, 146.71, 141.59, 136.95, 136.72, 134.91, 129.93, 127.61, 127.21, 124.46, 120.44, 105.81, 71.81, 67.83, 39.37, 39.28, 37.51, 37.35, 36.38, 29.86, 29.67, 28.00, 24.75, 24.73, 22.72, 22.63, 22.61, 19.60, 19.57; m/z (MALDI-TOF-MS): calculated for C$_{147}$H$_{222}$N$_4$O$_{12}$ 2235.69, found 2235.68 [M]$^+$; IR (cm$^{-1}$) ν 3300, 2955, 2926, 2870, 2845, 1675, 1644, 1582, 1522, 1494, 1469, 1426.

**N,N′,N″-(Nitrilotris([1,1′'-biphenyl]-4,4'-diyl))tris(3,4,5-tris(octyloxy)benzamide) (a-N2)**

In a round-bottom flask, 9a (1.1 g, 1.6 mmol), tris(4-bromophenyl)amine (153 mg, 0.3 mmol), K$_2$CO$_3$ (347 mg, 2.5 mmol) Pd(PPh$_3$)$_4$ (21 mg, 0.02 mmol), 5 mL dioxane and 0.2 mL water were combined under Ar atmosphere. The mixture was heated to 100 °C. After 14.5 h, the mixture was cooled down to room temperature and diluted with 80 mL CHCl$_3$, washed with 2x80 mL water and 80 mL brine. The organic layer was dried over MgSO$_4$, filtered and evaporated to dryness. The crude was dissolved in CHCl$_3$, passed through a short silica column, concentrated under reduced pressure and precipitated in acetonitrile. Purple precipitates were collected by filtrations and re-dispersed in hot acetonitrile. Filtering the mixture in hot acetonitrile gave a product as purple solids (yield = 269 mg, 43%)  

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (s, 3H), 7.71-7.69 (d, 6H), 7.62-7.60 (d, 6H), 7.54-7.52 (d, 6H), 7.25-7.23 (d, 6H), 7.07 (s, 6H), 4.07-4.01 (m, 18H), 1.87-1.73 (m, 18H), 1.53-1.29 (m, 90H), 0.91-0.87 (t, 27H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.93, 165.59, 153.29, 146.71, 141.63, 136.96, 136.71, 134.92, 129.91, 127.61, 127.21, 124.46, 120.44, 105.89, 73.59, 69.53, 31.91, 31.84, 30.94, 30.33, 29.53, 29.38, 29.30, 26.09, 22.71, 22.68, 14.11.; m/z (MALDI-TOF-MS): calculated for C$_{129}$H$_{186}$N$_4$O$_{12}$ 1983.41, found 1983.40 [M]$^+$; IR (cm$^{-1}$) ν 3279, 2923, 2854, 1646, 1583, 1517, 1496, 1468, 1426.
3. Supramolecular homopolymers

3.1. Homopolymers UV-Vis spectra and cooling curves

Figure S1 shows the variable-temperature (VT) UV-Vis measurements of all homopolymers, following the protocol described in the main text. Their UV-Vis cooling curves verify the formation of supramolecular homopolymers in a cooperative fashion, further supporting the CD cooling curves (main text, Figure 1).

Poly(S-N1) shows a more complex assembly process when compared to other homopolymers. In 70-55 °C regime, S-N1 monomers start to aggregate as indicated by the significant increase in UV-Vis intensity (Figure S1d). However, there is a negligible change in CD signal (main text, Figure 1d), implying that S-N1 forms small or non-ordered aggregates in this temperature regime. Below 55°C, a rapid decrease in CD signal is observed, indicating a cooperatively increased structural order of poly(S-N1). Such a large temperature range for the elongation step is not observed in the non-bridged poly(S-N2).
Figure S1. UV-Vis measurements of supramolecular homopolymers. VT-UV-Vis spectra of a) poly(S-B1), c) poly(S-N1), e) poly(S-N2) and g) poly(a-N2) obtained via slow cooling from 100 or 90 °C (red lines) to 20°C (blue lines) with 5 °C interval (grey lines). UV-Vis cooling curves of b) poly(S-B1), d) poly(S-N1), f) poly(S-N2) and h) poly(a-N2). Measurements were performed at c = 30 µM in decalin, cooling rate = 0.3 °C min⁻¹.
3.2. Infrared spectroscopy

IR measurement of poly(a-N2) in decalin at room temperature (Figure S2a, light blue line) shows the NH stretching bands at 3312 cm⁻¹. The amide I and amide II bands are observed at 1645 cm⁻¹ and 1583 cm⁻¹. These values are in the same range to those of S-B1 and S-N1 in their solid state (Figure S2b), which display a mesophase (see below), but are different from those of a-N2 in chloroform (Figure S2a, olive line), where a-N2 is molecularly dissolved.

This result indicates that the systems are held by a H-bonding network both in decalin solution and in bulk.

![Figure S2. Infrared measurements. a) Spectra of a-N2 at a concentration of 2 mM in chloroform (olive line) and decalin (light blue line). b) Spectra of S-B1 and S-N1 in bulk. Measurements were performed at room temperature.](image)

3.3. Van’t Hoff analysis

Van’t Hoff analysis of the supramolecular homopolymers was performed as previously described.\(^3\) Each elongation temperature was calculated as the crossing points between the baseline (CD = 0 mdeg for molecularly dissolved state) and the tangent to the CD curve in its pseudo-linear regime. The equilibrium constant of elongation is defined as \( K_\varepsilon = \frac{1}{[M]} \) where [M] is the total monomer concentration.\(^4\) [M] has been normalized over a reference concentration [M]₉₀₉ = 1 μM to render it unitless and allow the calculation of \( \ln(K_\varepsilon) \). It is of note that van’t Hoff analysis using this normalization does not allow to retrieve the entropic value.

The result shows comparable enthalpies of elongation (\( \Delta H_\varepsilon \)) for the three supramolecular homopolymers, highlighting that the difference in the \( T_c \) observed for the three systems (at equal concentration of monomers) does not depend on the enthalpic contribution on the elongation and therefore it is due to the entropic contribution (\( \Delta S_\varepsilon \)).
Figure S3. Van’t Hoff analysis of the homopolymers. a) CD cooling curve of poly(S-B1) (top, purple lines) poly(S-N1) (middle, blue lines), and poly(S-N2) (bottom, cyan lines) as a function of monomer concentration. b) Van’t Hoff’ plot and calculated thermodynamic values of elongation, $\Delta H$ and $\Delta S$.

As visible in Figure S3a, poly(S-B1) displays a secondary transition when the assembly is performed at concentrations higher than 100 μM. We performed the rest of the experiments at low concentration (15-30 μM) to avoid this issue.
3.4. Homopolymers’ photoluminescence spectra and cooling curves

![poly(S-B1) spectra and cooling curve](image_a)

Figure S4. Photoluminescent measurements of supramolecular homopolymers. VT-PL spectra of a) poly(S-B1), c) poly(S-N1), e) poly(S-N2) and g) poly(a-N2) obtained via slow cooling from 100 or 80 °C (red lines) to 20 °C (blue lines) with 5 °C interval (grey lines). PL cooling curves of b) poly(S-B1), d) poly(S-N1), f) poly(S-N2) and h) poly(a-N2). Measurements were performed at c = 30 µM in decalin using λ_{ex} = 387 nm.
VT-photoluminescence (PL) measurements further support the formation of supramolecular homopolymers (Figure S4). All monomers show high fluorescent intensity at high temperature ($\lambda_{em} = 400$ nm for both $S$-$N_2$ and $a$-$N_2$, $\lambda_{em} = 408$ nm for $S$-$B_1$ and $\lambda_{em} = 440$ nm for $S$-$N_1$). Upon slow cooling to 20 °C, the emission of the monomeric species is quenched and subjected to a red shift. In addition, the increased emission intensity of poly($S$-$N_2$) between 80 °C and 50 °C and poly($a$-$N_2$) between 100 °C and 70 °C is probably due to a decrease in the non-radiative relaxation decays of the monomers.

The emissions of all chiral homopolymers are circularly polarized (Figure S5). $g_{LUM}$ values at the main emission bands are in the order of $10^{-3}$, typical for supramolecular assemblies.$^5$

Figure S5. Circularly polarized luminescence measurements of supramolecular homopolymers. CPL spectra of a) poly($S$-$B_1$), b) poly($S$-$N_1$) and c) poly($S$-$N_2$) ($\lambda_{ex} = 365$ nm, 20 °C). Measurements were performed in decalin at $c = 30 \mu$M.
4. Supramolecular copolymers: experimental results and simulations

4.1 Photoluminescence studies

The effect of $S$-$B1/S$-$N1$ mixing ratios on the photophysical properties of the copolymers was evaluated (Figure S6). The comparison of the intensities of the exciplex band (550 nm) to that of the homopolymers (~470 nm) shows that the exciplex band is the predominant emission at various $S$-$B1/S$-$N1$ mixing ratios. It is of note that small batch-to-batch variations in the photoluminescence intensities were observed preventing a comparison by using the absolute band’s intensities.

The photoluminescence decay was fitted with a one-component exponential equation ($y = A + Be^{-x/\tau}$, where $\tau$ is the lifetime). Figure S7 shows an example of $\text{poly}[(S-B1)-co-(S-N1)]$. Two components were fitted, yielding the lifetimes of ~96 ns and ~6 µs. It is of note that an accurate fitting is not possible due to the large number of components.

Figure S6. Effect of B-N ratio on photoluminescence properties. PL spectra of $\text{poly}[(S-B1)-co-(S-N1)]$ obtained after slow cooling from 100 to 20 °C. Measurements were performed at $c = 30 \mu M$ in degassed decalin using $\lambda_{exc} = 387 \text{ nm}$.

Figure S7. Lifetime measurements of $\text{poly}[(S-B1)-co-(S-N1)]$. Exponential decay fitting of the emission at 550 nm measured at a) 5 µs and b) 50 µs timescales. ($\lambda_{exc} = 400 \text{ nm}$, $c = 30 \mu M$ in degassed decalin, 20 °C).
UV-Vis spectrum of $\text{poly}[(S-B1)-co-(S-N1)]$ at 4 mM in decalin (Figure S8a) shows a weak shoulder peak at ~500 nm, which is not present in $\text{poly}(S-B1)$ and $\text{poly}(S-N1)$. In line with previously reported B-N FLP pairs, this weak band is attributed to the ground state charge-transfer between $S-B1$ and $S-N1$, demonstrating the presence of FLP interactions in the ground state. In addition, the CT band of $\text{poly}[(S-B1)-co-(S-N1)]$ is CD active (Figure S8b), suggesting that the molecules involved in such transition are subjected to a helical environment. It is hence likely to conclude that the B-N FLPs are enchain in the copolymer structure.

![UV-Vis spectrum](image)

**Figure S8.** Optical measurements of $S$-B1/$S$-N1 supramolecular copolymer. a) UV-Vis spectra of concentrated $\text{poly}[(S-B1)-co-(S-N1)]$ (orange line; $c_{S-B1} = 2$ mM, $c_{S-N1} = 2$ mM), $\text{poly}(S-B1) c_{S-B1} = 4$ mM (purple line), $\text{poly}(S-N1) c_{S-N1} = 4$ mM (blue line). b) CD spectrum of concentrated $\text{poly}[(S-B1)-co-(S-N1)]$ ($c_{S-B1} = 2$ mM, $c_{S-N1} = 2$ mM). Measurements were performed in decalin at $c = 4$ mM, optical pathlength = 0.2 cm.
Figures S9a–d show that, as expected, the presence of O₂ and H₂O does not have a significant impact on the photoluminescence of poly(S-B1) and poly(S-N1) homopolymers. Conversely, the exciplex emission band of poly[(S-B1)-co-(S-N1)] is significantly affected by the presence of O₂. Figure S9e shows quenched exciplex emission for the benchtop-prepared solution when compared to the degassed solution. Such O₂ sensitivity confirms that the exciplex emission’s process involves a triplet state as also supported by the long emission lifetime (Figure 3b, main text).

The effect of H₂O on the photophysical properties of poly[(S-B1)-co-(S-N1)] is minimal as indicated by the comparable profiles of the exciplex emission when using dry (12.7 ± 3.9 ppm H₂O) and wet (33.8 ± 1.7 ppm H₂O) decalin. This confirms that neither the excited state nor the helical arrangement of the supramolecular copolymer (Figure S9f) are sensitive to variation in H₂O concentration.³

**Figure S9.** Effect of O₂ and H₂O content on photoluminescence properties of supramolecular polymers. PL spectra of a) poly(S-B1), c) poly(S-N1) and e) poly[(S-B1)-co-(S-N2)] (λₐₓ = 385 nm, 20 °C). CD spectra of b) poly(S-B1), d) poly(S-N1) and f) poly[(S-B1)-co-(S-N2)] (20 °C). Measurements were performed at c = 30 µM in degassed dry decalin (10.8 ± 0.9 ppm H₂O), dry decalin (12.7 ± 3.9 ppm H₂O) and wet decalin (33.8 ± 1.7 ppm H₂O). Water contents in decalin were measured by Karl-Fischer titration and reported as mean ± sd (n = 3).
Similar to poly[(S-B1)-co-(S-N1)], O₂ dramatically lowers the exciplex emission of poly[(S-B1)-co-(S-N2)] (Figure S10a). The O₂ quenching is also observed as a decrease in the lifetime of the excited state at \( \lambda = 520 \text{ nm} \) of poly[(S-B1)-co-(S-N2)] (Figure S10b). Poly[(S-B1)-co-(S-N2)] exhibits circularly polarized emission both in the band at \( \lambda_{\text{em}} = 460 \text{ nm} \), attributable to the homopolymers emission, and in the exciplex band at \( \lambda_{\text{em}} = 530 \text{ nm} \) (Figure S10c). The \( g_{\text{LUM}} \) values of poly[(S-B1)-co-(S-N1)] at 550 nm and (poly[(S-B1)-co-(S-N2)]) at 530 nm are \( \sim 7 \cdot 10^{-3} \) and \( \sim 1 \cdot 10^{-3} \), respectively.

Figure S10. Photoluminescent measurements of S-B1/S-N2 supramolecular copolymers. a) PL spectra poly[(S-B1)-co-(S-N2)] obtained after slow cooling from 100 to 20 °C in degassed and air-equilibrated decalin (\( \lambda_{\text{exc}} = 387 \text{ nm}, 20 °C \)). b) Lifetime measurement of poly[(S-B1)-co-(S-N2)] in degassed (dark-green line) and air-equilibrated (light-green line) decalin (\( \lambda_{\text{em}} = 520 \text{ nm}, \lambda_{\text{exc}} = 400 \text{ nm}, 20 °C \)). c) CPL spectrum of poly[(S-B1)-co-(S-N2)] (\( \lambda_{\text{exc}} = 365 \text{ nm}, 20 °C \)). Measurements were performed at \( c = 30 \mu\text{M} \).
Figures S11 shows VT-PL measurements of B-N supramolecular copolymers. The corresponding cooling curves are shown in Figure 3d in the main text.

**Figure S11. Photoluminescent measurements of supramolecular copolymers.** VT-PL spectra of a) poly[(S-B1)-co-(S-N1)] and b) poly[(S-B1)-co-(S-N2)] obtained via slow cooling from 100 °C (red lines) to 20°C (blue lines) with 5°C interval (grey lines). Measurements were performed at \(c = 30 \mu\text{M}\) in degassed decalin using \(\lambda_{\text{exc}} = 387\) nm.

**4.2 CD and UV-Vis spectroscopy: additional data for poly[(S-B1)-co-(S-N2)]**

Figure S12 shows the VT-CD and UV-Vis spectra of poly[(S-B1)-co-(S-N2)]. At high temperature, the system is molecularly dissolved and CD silent (red lines). Upon slow cooling to 20 °C, the supramolecular polymerization occurs as indicated by the rise of CD bands (blue lines at 20 °C). VT-UV-Vis spectra displays a decreased absorption intensity and a spectral shift upon cooling to 20 °C, further confirming the aggregation.

**Figure S12. Optical measurements of S-B1/S-N2 supramolecular copolymer.** a) VT-CD spectra of poly[(S-B1)-co-(S-N2)]. b) VT-UV-Vis spectra of poly[(S-B1)-co-(S-N2)]. Measurements were performed at \(c = 30 \mu\text{M}\) in decalin via slow cooling from 100 (red lines) to 20 °C (blue lines) with 5 °C interval (grey lines).
4.3 Copolymers simulation details and results

Simulations of supramolecular copolymerization of a hypothetical supramolecular copolymer poly(A-co-B) between monomers A and B were done with the Matlab® script “EXAMPLE-JACS2018.m” published by from Ten Eikelder et al.8

The simulation is based on a mass balance model and the result of the simulation defined by the following parameters:

- Enthalpies and entropies of homopolymerizations $\Delta H_{A-A}$; $\Delta S_{A-A}$; $\Delta H_{B-B}$; $\Delta S_{B-B}$;
- Nucleation penalties of homopolymerization $NP_A$; $NP_B$;
- Enthalpy and entropy of copolymerization $\Delta H_{A-B}$; $\Delta S_{A-B}$.

The thermodynamic parameter of homopolymerization ($\Delta H_{A-A}$; $\Delta S_{A-A}$; $NP_A$; $\Delta H_{B-B}$; $\Delta S_{B-B}$; $NP_B$) are based on the multi-curve fitting result of the homopolymerization CD cooling curve of poly(S-B1) and poly(S-N2) (Table S1). (Homopolymerization fitting performed with the Matlab® script published by ten Eikelder et al.).4 The multicurve fitting gives results in line with the van’t Hoff analysis (Figure S3).

$\Delta H_{A-B}$; $\Delta S_{A-B}$ values were selected as the averages of the homopolymerization values found by fitting (Table S2).

Table S1. Multi-curves fitting of poly(S-B1) and poly(S-N2) homopolymers used for the copolymerization simulation

|        | poly(S-B1) | poly(S-N2) |
|--------|------------|------------|
| $\chi^2$ | 0.27       | 0.25       |
| $\Delta H_e$ / kJ mol$^{-1}$ | -91 ± 1    | -118 ± 2   |
| $\Delta S_e$ / J mol$^{-1}$ K$^{-1}$ | -177 ± 4   | -280 ± 4   |
| $NP / kJ mol^{-1}$ | -12.7 ± 0.2 | -17.2 ± 0.6 |

*Fitting of homopolymerization was performed by using one-component homopolymerization script reported by ten Eikelder et al. Poly(S-B1) fitting performed up between 100 - 40 °C for 15 and 30 µM and between 100 - 60 °C for 100 µM.

Table S2. Thermodynamic parameters used for simulating the copolymer poly(A-co-B) as shown in Figures 4c,d in the main text and Figure S13.

|        | A-A values | B-B values | A-B values |
|--------|------------|------------|------------|
| $\Delta H$ / kJ mol$^{-1}$ | Fixed by fitting poly(S-B1) at $c=15$ µM | Fixed by fitting poly(S-N2) at $c=15$ µM | Guess based on averaged values |
|        | -91        | -118       | -104       |
| $\Delta S$ / kJ mol$^{-1}$ K$^{-1}$ | -180       | -280       | -240       |
| $NP / kJ mol^{-1}$ | -12.7      | -17.2      | ---        |
As reported in the main text, the simulated copolymers cooling curve based on the initial parameters reported in Table S2 displays two transitions attributable to the two homopolymers $T_c$. Despite this feature, the simulation shows a non-zero level of copolymerization between A and B. This is verified by: i) the incorporation of B monomers at approximately 5 °C higher temperatures compared to poly(B) homopolymer (blue lines in Figure S13 and Figures 4c in the main text); ii) the average block length displaying $AB \neq 0$ (Figure 4c in the main text); and iii) the equivalent bond concentration in copolymer in the order of 2 µM (Figure S13). In addition, in the temperature regime between 70 and 50 °C, the number of A-B contacts is higher than B-B contacts (Figure 4c in the main text). This supports the hypothesis of nucleation of the second monomer (B in the simulation case and S-N2 in the experimental case) on top of the first growing polymer (A and S-B1 in the simulation and experimental results, respectively).

We noticed that the simulation of the copolymerization curves is highly sensitive to small variations in the selected parameters ($\Delta H_{A-B}$; $\Delta S_{A-B}$) By changing $\Delta S_{A-B}$ on the order of few J mol$^{-1}$ (which falls within the range of the uncertainty of the homopolymerization fitting), the copolymerization curve displays pronounced differences in the simulated co-assembly behavior passing from a two-transition cooling curve to a single-transition one with a higher concentrations of A-B bonds.

4.4 Mixed sergeant and soldier copolymerization of poly[(S-B1)-co-(a-N2)]

Figure S14a shows that poly(a-N2) is CD silent, indicating the formation of racemic mixture of its helical structure. The mixed sergeant-and-soldier experiment was carried out as discussed in the main text (Figure 4a, in the main text). Similar to poly[(S-B1)-co-(S-N2)] in Figure 4b (main text), the cooling curves of poly[(S-B1)-co-(a-N2)] show two transition temperatures which could be assigned to the corresponding homopolymers’ $T_c$ (Figure S14d). Similar to other copolymers (Figure 3d in the main text), the emission of poly[(S-B1)-co-(a-N2)] also start to emerge at ~75 °C (Figure S14f). At 20 °C, poly[(S-B1)-co-(a-N2)] shows the maximum emission at 515 nm (Figure S14e), which is slightly blue-shifted compared to poly[(S-B1)-co-(S-N2)] (Figure 2b in the main text).
Figure S14. Optical measurements of S-B1/a-N2 supramolecular copolymer. VT-CD spectra of a) poly(a-N2) and b) poly[(S-B1)-co-(a-N2)]. c) VT-UV-Vis spectra of poly[(S-B1)-co-(a-N2)]. Measurements were performed at $c = 30 \, \mu$M in decalin via slow cooling from 100 °C (red lines) to 20 °C (blue lines) with 5 °C interval (grey lines). d) CD cooling curves of poly[(S-B1)-co-(a-N2)] (light green line; $c_{\text{tot}} = 30 \, \mu$M) and poly(S-B1) (purple line; $c_{S-B1} = 15 \, \mu$M). UV-Vis cooling curve of poly(a-N2) (light blue line; $c_{a-N2} = 15 \, \mu$M). Measurements were performed in decalin, cooling rate $= 0.3 \, ^\circ\text{C min}^{-1}$. e) VT-PL spectra of poly[(S-B1)-co-(a-N2)] obtained via slow cooling from 100 °C (red lines) to 20°C (blue lines) with 5°C interval (grey lines). f) VT-PL cooling curve of poly[(S-B1)-co-(a-N2)] monitored at 530 nm ($\lambda_{\text{ex}} = 387 \, \text{nm}$). Measurements were performed at $c = 30 \, \mu$M in degassed decalin.
4.5 CD and UV-Vis spectroscopy: additional data for poly[(S-B1)-co-(S-N1)]

VT-CD and VT-UV-Vis spectra and the cooling curves of poly[(S-B1)-co-(S-N1)] are shown in Figure S15. We would like to note that the CD signal at 412 nm includes the CD contributions of both S-B1 and S-N1 components in the copolymer (Figure S15c), while the CD signal at 441 nm (Figure 4f in the main text) and the UV-Vis signal at 432 nm (Figure S15d) belong to S-N1 component only since S-B1 does not absorb at that wavelength.

Figure S15. Optical measurements of S-B1/S-N1 supramolecular copolymer. a) VT-CD spectra of poly[(S-B1)-co-(S-N1)]. b) VT-UV-Vis spectra of poly[(S-B1)-co-(S-N1)]. Measurements were performed at c = 30 µM in decalin via slow cooling from 100 (red lines) to 20 °C (blue lines) with 5 °C interval (grey lines). c) CD cooling curves of poly[(S-B1)-co-(S-N1)] (orange line; cS-B1 = 30 µM), poly(S-B1) (purple line; cS-B1 = 15 µM), poly(S-N1) (blue line; cS-N2 = 15 µM), and the linear sum of [poly(S-B1) + poly(S-N1)] (black line, cS-B1 = cS-N1 = 15 µM). d) UV-Vis cooling curves of poly[(S-B1)-co-(S-N1)] (orange line; cS-B1 = 30 µM) and poly(S-N1) (blue line; cS-N2 = 15 µM). Measurements were performed in decalin, cooling rate = 0.3 °C min⁻¹.
4.6 $^{11}$B NMR data for poly(S-B1) and poly[(S-B1)-co-(S-N1)]

$^{11}$B NMR measurements were performed to evaluate the influence of S-N1 on the chemical environment of the boron center of S-B1 both in their molecularly dissolved state and enchained in the copolymer. As a reference, pure S-B1 (4 mM) and a 1:1 S-B1/S-N1 mixture (8 mM) were dissolved in CDCl$_3$. Both solution at 20 °C display blue emission under 365-nm light indicating, as expected, the absence of supramolecular aggregates (data not shown). The $^{11}$B NMR spectra display a weak board peak at 34.5 ppm for S-B1 and 34.9 ppm for S-B1/S-N1 mixture respectively (Figures S16e and S16g). The absence of a shift in such conditions suggests that no B-N interaction is observed in molecularly dissolved solutions in CDCl$_3$.

To perform $^{11}$B NMR of assembled systems, poly(S-B1) ($c = 4$ mM) and poly[(S-B1)-co-(S-N1)] (- $c_{tot} = 8$ mM; $c_{S-B1} = c_{S-N1} = 4$ mM) gels were prepared by dissolving monomers in hot C$_6$D$_6$ and letting the solutions to cool and assemble in an ice bath. In contrast to blue emission from poly(S-B1) gel, poly[(S-B1)-co-(S-N1)] gel shows yellow emission under 365-nm light (as expected for assembled polymers). Both gels are stable at 20 °C for several days (Figures S16a-d). However, due to strong aggregation, the B peak of both poly(S-B1) and poly[(S-B1)-co-(S-N1)] was not detected (Figures S16f and S16h). Although several conditions were tested, we did not find any conditions which permitted the detection of assembled B peaks in solvent comparable to decalin. The absence of B peaks in both gels indicates that the majority of monomers is incorporated in the supramolecular (co)polymers and, therefore, the B-N pairs (observed via other techniques, main text Figures 2, 3, 4 and Supporting Information section 4) are assembled within the polymeric chain.

Figure S16. $^{11}$B NMR measurements. Photographs of a,b) poly(S-B1) gel and c,d) poly[(S-B1)-co-(S-N1)] gel, obtained by fast cooling of a hot C$_6$D$_6$ solution in an ice bath, under a,c) ambient light and b,d) 365-nm light. $^{11}$B NMR spectra of e) S-B1 solution in CDCl$_3$, f) poly(S-B1) gel in C$_6$D$_6$, g) S-B1/S-N1 solution in CDCl$_3$, and h) poly[(S-B1)-co-(S-N1)] gel in C$_6$D$_6$. Measurements were performed at $c_{S-B1} = c_{S-N1} = 4$ mM.
5. Bulk properties

UV-vis spectroscopy on a dropcasted film of poly[(S-B1)-co-(S-N1)] shows a broad charge transfer band at 500 nm (Figure S17, orange line) which is absent in both homopolymers’ films (Figure S17, purple and blue lines). This absorption shoulder is in line with what observed for poly[(S-B1)-co-(S-N1)] in solution (Figure S8a) and with previously reported FLPs literature.6

![Figure S17](image)

**Figure S17.** Optical measurements of S-B1/S-N1 supramolecular copolymer. UV-Vis spectra of poly[(S-B1)-co-(S-N1)] (orange line), poly(S-B1) (purple line), poly(S-N1) (blue line). Samples were prepared by dropcasting the solutions in dichloromethane on a square borosilicate glass (3x3 cm, a thickness of 0.1 cm) and drying on a hot plate. No additional thermal annealing was performed.
Full DSC traces of supramolecular homopolymers and copolymers of S-B1 and S-N1 are shown in Figure S18. For sample preparation, an appropriate amount of compound was weighed in a vial and dissolved in a small volume of dichloromethane. The solution was then dropped on a DSC pan and dried on a hot plate. This process was repeated until there is enough quantity for DSC measurements (5.263 mg for poly(S-B1), 6.582 mg for poly(S-N1), 5.020 mg for poly[(S-B1)0.5-co-(S-N1)0.5] and 4.890 mg for poly[(S-B1)0.3-co-(S-N1)0.7]). It is of note that poly[(S-B1)0.3-co-(S-N1)0.7] (189 °C, Figure S18d) shows a slightly higher melting temperature than that of poly[(S-B1)0.5-co-(S-N1)0.5] (187 °C, Figure S18c), which could be attributed to higher content of S-N1 in poly[(S-B1)0.3-co-(S-N1)0.7].

Figure S18. Differential scanning calorimetry. DSC traces of a) poly(S-B1), b) poly(S-N1) and poly[(S-B1)-co-(S-N1)] at c) 1:1 and d) 3:7 B-N ratios. The S-B mixture was prepared by dissolving both compounds in dichloromethane and drying on a DSC pan prior to the DSC measurement. Red and blue lines represent heating and cooling ramps, respectively (heat/cool rate = 10 °C min⁻¹).
Poly(S-B1), poly(S-N1) and poly[(S-B1)-co-(S-N1)] display birefringence under polarized light, indicative of order in bulk, and flow upon rubbing treatment (Figure S19). These observations indicate the presence of mesophases in these materials.

![POM images of poly(S-B1) at 180 °C, poly(S-N1) at 193 °C and poly[(S-B1)-co-(S-N1)] at 193 °C. Scale bar is 100 µm.]

**Figure S19.** Polarized optical microscopy. POM images of a) poly(S-B1) at 180 °C, b) poly(S-N1) at 193 °C and c) poly[(S-B1)-co-(S-N1)] at 193 °C. Scale bar is 100 µm.
Long-range order in bulk was examined by medium- and wide-angle x-ray scattering (MAXS/WAXS) at room temperature. The samples were heated in situ to 200 °C and cooled to room temperature by liquid nitrogen with a temperature gradient of 5 °C min⁻¹ (Figure 20a). Poly(S-B1), poly(S-N1) and poly[(S-B1)-co-(S-N1)] (1:1 mixture) display a hexagonally packed cylindrical phase, which is common for 1D discotic supramolecular polymers. The inter-disc π-π distance between S-B1 units in the column is 0.35 nm, no π-π distance for poly(S-N1) and poly[(S-B1)-co-(S-N1)] is observed. Furthermore, the scattering pattern of poly[(S-B1)-co-(S-N1)] follows the arrangement of poly(S-N1), commonly observed for mixed liquid-crystalline materials in which both components adapt to follows the long-range order of the most dominant component.⁹ The absence of a linear combination of both poly(S-B1) and poly(S-N1) scattering patterns in the 1:1 mixture is therefore a further prove of a copolymerized structure.

For comparison, the samples were subjected to fast cooling by heating to 200 °C instantaneously on a hot plate then cooling to room temperature under ambient condition with a temperature gradient of 20 °C min⁻¹ (Figure 20b). Both poly(S-N1) and poly(S-N1) show cylindrical phase analogous to what recorded by slow cooling with a domain spacing of 3.5 and 3.3 nm, respectively. The inter-disc π-π distance in both cases are 0.35 nm. To our surprise, a lamellar phase with a thickness of 3.4 nm is observed for poly[(S-B1)-co-(S-N1)] showing that the microstructure and the long-range order are subjected to dramatic changes when applying variations in the sample preparation. This effect is indicative of concurrent competitive processes such as H-bonding formation and B-N interactions.

![Figure S20. Medium/wide-angle X-ray scattering. 1D transmission scattering profiles of poly[(S-B1)-co-(S-N1)] (orange line), poly(S-N1) (blue line) and, poly(S-B1) (purple line), at 20 °C. The samples were heated to 200 °C then cooled with a temperature gradient of a) 5 °C min⁻¹ (in situ) and b) 20 °C min⁻¹ (under ambient condition).](image-url)
6. NMR Spectra

3,3’-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(bromobenzene) (1)
3,7,11-tribromo-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (2)
4-Bromo-2,6-difluoro-N,N-bis(2-methoxyphenyl)aniline (3)
4-Bromo-N,N-bis(4-bromo-2-methoxyphenyl)-2,6-difluoroaniline (4)
3,7,11-Tribromobenzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine (5)
Methyl-3,4,5-trioctyloxybenzoate (7a)
3,4,5-Tri(octyl)benzoic acid (8a)
3,4,5-Tris(octyloxy)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzamide (9a)
(S)-3,7-Dimethyloctyl 4-methylbenzenesulfonate (6)
Methyl-3,4,5-tri(S-3,7-dimethyloctyloxy)benzoate (7b)
3,4,5-Tri(S-3,7-dimethyloctyloxy)benzoic acid (8b)
3,4,5-Tris(((S)-3,7-dimethyloctyl)oxy)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) benzamide (9b)
$N,N',N''-(5,9\text{-Dioxa-13b-boranaphtho}[3,2,1\text{-de}]\text{anthracene-3,7,11-triyltris(benzene-4,1-diyl)}\text{tris}(3,4,5\text{-tris((S)-3,7-dimethyloctyl)oxy)benzamide})$ (S-B1)
$N,N',N''$-((Benzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine-3,7,11-triyltris(benzene-4,1-diyl))tris(3,4,5-tris((S)-3,7-dimethyloctyl)oxy)benzamide) (S-N1)
$N,N',N''$-(Nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(3,4,5-tris((S)-3,7-dimethyloctyl)oxy) benzamide) (S-N2)
$N,N',N''-(Nitrilotris[1''',1''''-biphenyl]-4',4'''-diyl)tris(3,4,5-tris(octyloxy)benzamide) \text{ (a-N2)}$
7. References

(1) Terashima, T.; Mes, T.; De Greef, T. F. A.; Gillissen, M. A. J.; Besenius, P.; Palmans, A. R. A.; Meijer, E. W. Single-Chain Folding of Polymers for Catalytic Systems in Water. J. Am. Chem. Soc. 2011, 133 (13), 4742–4745.

(2) Wakamiya, A.; Nishimura, H.; Fukushima, T.; Suzuki, F.; Saeki, A.; Seki, S.; Osaka, I.; Sasamori, T.; Murata, M.; Murata, Y.; Kaji, H. On-Top π-Stacking of Quasiplanar Molecules in Hole-Transporting Materials: Inducing Anisotropic Carrier Mobility in Amorphous Films. Angew. Chem. Int. Ed. 2014, 53 (23), 5800–5804.

(3) Van Zee, N. J.; Adelizzi, B.; Mabesoone, M. F. J.; Meng, X.; Aloi, A.; Zha, R. H.; Lutz, M.; Filot, I. A. W.; Palmans, A. R. A.; Meijer, E. W. Potential Enthalpic Energy of Water in Oils Exploited to Control Supramolecular Structure. Nature 2018, 558 (7708), 100–103.

(4) ten Eikelder, H. M. M.; Markvoort, A. J.; de Greef, T. F. A.; Hilbers, P. A. J. An Equilibrium Model for Chiral Amplification in Supramolecular Polymers. J. Phys. Chem. B 2012, 116 (17), 5291–5301.

(5) Sánchez-Carnerero, E. M.; Agarrabeitia, A. R.; Moreno, F.; Maroto, B. L.; Muller, G.; Ortiz, M. J.; de la Moya, S. Circularly Polarized Luminescence from Simple Organic Molecules. Chem. Eur. J. 2015, 21 (39), 13488–13500.

(6) Holtrop, F.; Jupp, A.; van Leest, K.; Paradiz Dominguez, M.; Williams, R.; Brouwer, F.; de Bruin, B.; Ehlers, A.; Slootweg, C. Photoinduced and Thermal Single-Electron Transfer to Generate Radicals from Frustrated Lewis Pairs. Chem. Eur. J. 2020, 26 (41), 9005–9011.

(7) Aramaki, Y.; Imaizumi, N.; Hotta, M.; Kumagai, J.; Ooi, T. Exploiting Single-Electron Transfer in Lewis Pairs for Catalytic Bond-Forming Reactions. Chem. Sci. 2020, 11 (17), 4305–4311.

(8) ten Eikelder, H. M. M.; Adelizzi, B.; Palmans, A. R. A.; Markvoort, A. J. Equilibrium Model for Supramolecular Copolymerizations. J. Phys. Chem. B 2019, 123 (30), 6627–6642.

(9) Yano, K.; Itoh, Y.; Araoka, F.; Watanabe, G.; Hikima, T.; Aida, T. Nematic-to-Columnar Mesophase Transition by in Situ Supramolecular Polymerization. Science. 2019, 363 (6423), 161–165.