Controlled Polymerization of Norbornene Cycloparaphenylenes Expands Carbon Nanomaterials Design Space

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General Experimental

Commercially available materials were used without purification. Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware and under an inert atmosphere of purified nitrogen using syringe/septa technique. Tetrahydrofuran (THF), 1,4-dioxane, and dimethylformamide (DMF) were dried by filtration through alumina according to the methods described by Grubbs. Thin layer chromatography (TLC) was performed using Sorbent Technologies Silica Gel XHT TLC plates. Developed plates were visualized using UV light at wavelengths of 254 and 365 nm. Silica column chromatography was conducted with Zeochem Zeoprep 60 Eco 40-63 µm silica gel. Automated flash chromatography was performed using a Biotage Isolera One. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance III HD 500 MHz (\(^1\)H: 500 MHz, \(^{13}\)C: 126 MHz) or 600 MHz (\(^1\)H: 600 MHz, \(^{13}\)C: 151 MHz) NMR spectrometer. All spectra were taken in CDCl\(_3\), and the chemical shifts (δ) were reported in parts per million (ppm) referenced to TMS (δ 0.00 ppm) for \(^1\)H NMR and residual CHCl\(_3\) (δ 77.16 ppm) for \(^{13}\)C NMR. Gel permeation chromatography (GPC) for polymer molecular weight determination was performed either on a TOSOH EcoSEC HLC-8320GPC with an Agilent PolyPore column (in THF referenced to polystyrene standards using a refractive index detector) or on an Agilent 1260 HPLC equipped with a Wyatt 8-angle DAWN NEON light-scattering detector, ViscoStar NEON viscometer, and Optilab NEON refractive index detector (flow rate of 1 mL/min in chloroform stabilized with 0.5%-1.0% ethanol through two Agilent PLgel MIXED-C columns at 35 °C). dn/dc values were determined by 100% mass recovery using Astra 7.3. UV-Vis absorption spectra in solution were collected on an Agilent Cary 100 spectrophotometer. Solid-state absorption spectra of drop-casted thin films were collected using Shimadzu UV-1800 UV-Vis spectrophotometer. Fluorescence spectra were collected on a Horiba Jobin Yvon Fluoromax-4 fluorometer (2 nm excitation slit width; 1 nm emission slit width) or a Photon Technology International QuantaMaster 4 spectrofluorometer. All fluorescence measurements were performed with excitation at 340 nm. Quantum yields of THF solutions (~1 x 10\(^{-5}\) M.) and solid powders were measured using a Horiba model 914D photomultiplier detector system with a calibrated integrating sphere. The concentration of polymeric samples in THF was estimated by the absorbance of the CPP fragments by comparing the absorption intensities of them with those of the monomers. Quantum yields were calculated based on three consecutive measurements. All absorption and fluorescence measurements were carried out under ambient conditions.
Polymer Synthesis & Structural Characterization

General synthetic procedure for poly(nbCPP)s

NbCPP monomer was added to a small flame-dried flask with a stir bar, placed under N₂, then dissolved in degassed chloroform. A solution of bromopyridyl Grubbs G3 in degassed chloroform was quickly added to the vial via syringe, and the reaction was stirred at room temperature for 20-30 minutes. The reaction was quenched with ethyl vinyl ether, stirred for an additional 5 minutes, and the material was precipitated from cold methanol. The polymer was collected by centrifugation or filtration and dried under vacuum.

| Identity | [M]:[I] | Init. | Solvent | Conc. (M) | Time (min) | Conv. | $M_n$ – GPCRI (g/mol) | $Đ$ – GPCRI |
|----------|---------|-------|---------|----------|-----------|------|---------------------|------------|
| 1†‡      | p[8]    | 50    | G3      | 0.010    | 20        | full | 8,500               | 1.18       |
| 2        | p[8]    | 60    | G3      | 0.010    | 20        | full | 9,500               | 1.08       |
| 3        | p[8]    | 100   | G3      | 0.010    | 20        | full | 15,400              | 1.12       |
| 4†*      | p[8]    | 100   | G3      | 0.010    | 20        | full | 13,300              | 1.23       |
| 5        | p[8]    | 150   | G3      | 0.010    | 20        | full | 15,900              | 1.30       |
| 6†       | p[8]    | 200   | G3      | 0.010    | 20        | full | insoluble           | insoluble  |
| 7        | p[8]    | 200   | G3      | 0.010    | 20        | full | insoluble           | insoluble  |
| 8        | p[8]    | 200   | G3      | 0.010    | 20        | full | insoluble           | insoluble  |
| 9††      | p[9]    | 50    | G3      | 0.010    | 20        | full | 10,900              | 1.22       |
| 10       | p[9]    | 200   | G3      | 0.010    | 20        | >95% | 43,600              | 1.32       |
| 11       | p[10]   | 15    | G3      | 0.010    | 30        | >98% | 2,950               | 1.27       |
| 12†‡     | p[10]   | 50    | G3      | 0.010    | 30        | full | 13,600              | 1.19       |
| 13       | p[10]   | 50    | G3      | 0.010    | 30        | full | 15,800              | 1.12       |
| 14       | p[10]   | 50    | G3      | 0.010    | 30        | full | 11,300              | 1.10       |
| 15       | p[10]   | 60    | G3      | 0.010    | 20        | >95% | 16,800              | 1.10       |
| 16†*     | p[10]   | 100   | G3      | 0.010    | 30        | full | 25,000              | 1.22       |
| 17†‡     | p[10]   | 200   | G3      | 0.010    | 30        | full | 48,200              | 1.56       |
| 18       | p[10]   | 250   | G3      | 0.010    | 30        | >95% | 41,700              | 1.26       |
| 19       | p[10]   | 500   | G3      | 0.010    | 30        | full | 89,600              | 1.45       |

Table S1. Details for polymerizations carried out according to the general procedure with Grubbs G3 in chloroform. Unshaded rows correspond to data points in Figure 3. Poly(nb[n]CPP) names are abbreviated here as p[n]. †Sample used for collection of data in Table 1. ‡Sample used for collection of data in Table 2. *Sample used for spectra shown in Figures 5 and 6.
|   | Identity | [M]:[I] | Init. | Solvent | Conc. (M) | Time (min) | Conv. | $M_n$ – GPC<sub>Ri</sub> (g/mol) | $D$ – GPC<sub>Ri</sub> |
|---|----------|---------|-------|---------|-----------|------------|------|---------------------------------|------------------|
| 1 | p[8]     | 15      | G3    | THF     | 0.035     | 30         | full | 1,060                           | 1.24             |
| 2<sup>b</sup> | p[8] | 25      | G3    | THF     | 0.027     | 30         | n.d. | 5,980                           | 1.30             |
| 3 | p[8]     | 35      | G3    | THF     | 0.040     | 30         | full | 6,000                           | 1.49             |
| 4<sup>b</sup> | p[8] | 40      | G3    | THF     | 0.045     | 30         | full | 5,890                           | 1.20             |
| 5 | p[8]     | 50      | G3    | THF     | 0.028     | 30         | n.d. | 11,900                          | 1.63             |
| 6<sup>a</sup> | p[8] | 66      | G3    | THF     | 0.149     | 30         | full | 8,660                           | 1.56             |
| 7<sup>a</sup> | p[8] | 100     | G3    | THF     | 0.032     | 15         | n.d. | 17,000                          | 1.26             |
| 8<sup>a</sup> | p[8] | 100     | G3    | THF     | 0.032     | 15         | n.d. | 15,000                          | 1.24             |
| 9<sup>a</sup> | p[8] | 100     | G3    | THF     | 0.032     | 15         | n.d. | 15,900                          | 1.27             |
| 10 | p[8]    | 100     | G3    | DCM     | 0.025     | 15         | full | 10,700                          | 1.14             |
| 11<sup>b</sup> | p[10] | 40      | G3    | THF     | 0.036     | 30         | full | 8,460                           | 1.19             |
| 12<sup>b</sup> | p[10] | 64      | G3    | THF     | 0.031     | 30         | >98% | 13,300                          | 1.27             |
| 13<sup>a</sup> | p[10] | 100     | G3    | THF     | 0.024     | 60         | full | 6,870                           | 1.86             |
| 14<sup>a</sup> | p[10] | 200     | G3    | THF     | 0.035     | 60         | full | 38,300                          | 1.39             |
| 15<sup>a</sup> | p[10] | 100     | G1    | THF     | 0.024     | 60         | no rxn | 3,100                           | 1.40             |
| 16<sup>a</sup> | p[10] | 100     | G2    | THF     | 0.024     | 60         | full | 8,150                           | 1.99             |
| 17 | pM       | 15      | G3    | CHCl<sub>3</sub> | 0.010 | 30         | full | 1,540                           | 1.11             |
| 18 | pM       | 50      | G3    | CHCl<sub>3</sub> | 0.010 | 20         | full | 5,630                           | 1.05             |
| 19 | pM       | 60      | G3    | CHCl<sub>3</sub> | 0.010 | 20         | full | 7,020                           | 1.04             |
| 20 | pM       | 100     | G3    | CHCl<sub>3</sub> | 0.010 | 20         | full | 10,700                          | 1.03             |
| 21 | pM       | 200     | G3    | CHCl<sub>3</sub> | 0.010 | 20         | full | 17,000                          | 1.05             |
| 22 | pM       | 200     | G3    | CHCl<sub>3</sub> | 0.010 | 20         | full | 19,000                          | 1.04             |
| 23 | pM       | 250     | G3    | CHCl<sub>3</sub> | 0.010 | 30         | full | 21,100                          | 1.04             |
| 24 | pM       | 100     | G3    | DCM     | 0.025     | 15         | full | 10,000                          | 1.04             |
| 25<sup>a</sup> | pM       | 100     | G3    | THF     | 0.471     | 60         | full | 9,520                           | 1.03             |
| 26<sup>a</sup> | pM       | 100     | G3    | THF     | 0.471     | 20         | full | 8,650                           | 1.03             |
| 27 | pM       | 100     | G3    | THF     | 0.471     | 60         | full | 11,200                          | 1.04             |
| 28 | pM       | 150     | G3    | THF     | 0.989     | 30         | full | 14,000                          | 1.10             |
| 29 | pM       | 100     | G1    | THF     | 0.471     | 60         | ~95% | 7,790                           | 1.05             |
| 30 | pM       | 100     | G2    | THF     | 0.471     | 60         | full | 30,700                          | 1.94             |

Table S2. Selection of additional polymer samples prepared under different conditions. Poly(nb<sub>n</sub>CPP) names are abbreviated here as p[n]. Poly(diMeObnb) is abbreviated here as pM. <sup>a</sup>Carried out in oven-dried glassware in a glovebox. <sup>b</sup>Solution of monomer was added to initiator.
| Identity | [M]:[I]     | Init. | Solvent | Conc. (M) | Time (min) | Conv. | $M_n$ – GPC <sub>Ri</sub> (g/mol) | $D$ – GPC <sub>Ri</sub> |
|----------|--------------|-------|---------|-----------|------------|-------|----------------------------------|------------------------|
| 1*       | p[10]b[8]  | G3    | CHCl₃   | 0.010     | 50         | full  | 16,400                           | 1.21                   |
| 2<sup>a</sup> | p[10]b[8]  | G3    | THF     | 0.042     | 30         | full  | 10,300                           | 1.30                   |
| 3<sup>b</sup> | p[10]b[8]  | G3    | THF     | 0.149     | 60         | full  | 9,270                            | 1.70                   |
| 4        | p[10]b[8]  | G3    | THF     | 0.067     | 60         | full  | 17,600                           | 1.50                   |
| 5*       | p[8]s[10]  | G3    | CHCl₃   | 0.010     | 30         | full  | 27,300                           | 1.24                   |
| 6<sup>b</sup> | p[8]s[10]  | G3    | THF     | 0.149     | 60         | full  | 9,650                            | 1.12                   |
| 7<sup>b</sup> | p[8]s[10]  | G3    | THF     | 0.067     | 60         | full  | 20,100                           | 1.46                   |
| 8        | p[8]s[10]  | G3    | THF     | 0.100     | 40         | full  | 13,100                           | 1.34                   |
| 9        | p[8]s[10]  | G3    | THF     | 0.199     | 40         | full  | 10,300                           | 1.32                   |
| 10       | p[8]s[10]  | G3    | THF     | 0.067     | 40         | full  | 13,100                           | 1.33                   |

Table S3. Details for polymerization reactions to prepare copolymers. Values for monomer-to-initiator ratio are listed here with equivalents of nb[8]CPP followed by equivalents of nb[10]CPP for each equivalent of initiator. Poly(nb[10]-block-[8]CPP) is abbreviated here as p[10]b[8], and poly(nb[8]-stat-[10]CPP) is abbreviated as p[8]s[10]. For block copolymer samples, the time listed is total time, half of which was used for polymerizing each block. *Sample used for spectra shown in Figures 5 and 6. <sup>a</sup>Carried out in oven-dried glassware in a glovebox. <sup>b</sup>Solution of monomer was added to initiator.
Figure S1. a) Stacked $^1$H NMR of nb[8]CPP, nb[9]CPP, and nb[10]CPP in CDCl$_3$. b) Stacked $^1$H NMR spectra of poly(nb[8]CPP), poly(nb[9]CPP), and poly(nb[10]CPP) in CDCl$_3$. Polymer NMR spectra from samples 4, 9, and 16, Table S1. Chloroform and its satellite peaks are marked with circles, and other residual solvent, alkyl grease, and the reference TMS peak (and satellites) are marked with squares.
Figure S2. a) Baseline spectrum of the MALDI matrix, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB). b) MALDI spectra of poly(nb[8]CPP) from samples 2 and 4, Table S2. Vertical lines at values corresponding to DP 4-8 ($\Delta m/z = 672.87$) have been added to guide the eye. c) MALDI spectrum of poly(nb[10]CPP) from sample 14, Table S2. Vertical lines at values corresponding to DP 2-6 ($\Delta m/z = 825.07$) have been added to guide the eye. d) MALDI spectra of poly(nb[10]CPP-block-[8]CPP) showing characteristic “fingerprint” for this polymer structure (samples 2-3, Table S3). e) MALDI spectra of poly(nb[8]CPP-stat-[10]CPP) showing characteristic “fingerprint” for this polymer structure (samples 8-10, Table S3).
Figure S3. GPC calibration curve and calibration data based on refractive index measurements with PS.

| Time [min] | Molecular weight | Error [%] |
|------------|------------------|-----------|
| 5.370      | 1,815,000        | -1.21500  |
| 5.730      | 891,000          | -7.11192  |
| 5.983      | 550,000          | -9.51625  |
| 6.443      | 275,300          | 5.23950   |
| 6.857      | 132,900          | 7.56389   |
| 7.202      | 72,450           | 9.47418   |
| 7.538      | 38,640           | 7.88548   |
| 7.885      | 19,640           | 3.59758   |
| 8.200      | 10,210           | -4.55587  |
| 8.547      | 5,120            | -10.90941 |
| 8.940      | 2,590            | -7.26598  |
| 9.423      | 1,200            | 3.83824   |

Figure S4. $^1$H NMR of poly(diMeObnb) in CDCl$_3$. Spectrum from sample 27, Table S2.
Figure S5. Comparison between GPC$_{RI}$ (a) and GPC$_{MALS}$ (b) chromatographs for samples in Table 1.
Table S4. dn/dc values for samples in Table 1.

| Identity       | [M]:[I] | dn/dc (mL/g) |
|---------------|---------|-------------|
| poly(nb[8]CPP)| 50      | 0.2392      |
| poly(nb[8]CPP)| 100     | 0.2718      |
| poly(nb[9]CPP)| 50      | 0.2967      |
| poly(nb[10]CPP)| 50    | 0.2802      |
| poly(nb[10]CPP)| 100   | 0.3192      |
| poly(nb[10]CPP)| 200   | 0.3121      |

Figure S6. Mark-Houwink-Sakurada plots for a) poly(nb[8]CPP), b) poly(nb[9]CPP), and c) poly(nb[10]CPP) samples from Table 1, and d) K and a parameters from lines of best fit using the equation $\eta = KM^a$. 
**Figure S7.** Log(rg) vs. log(M) plot for a DP 200 sample of poly(nb[10]CPP) (sample 17 from Table S1).

**Figure S8.** IR spectra of poly(nb[8]CPP) and poly(nb[10]CPP). Spectra from samples 4 and 16, Table S1.
Figure S9. $^1$H NMR (left) and GPC (right) evidence for formation of poly(nb[10]CPP-block-[8]CPP) (data from sample 2, Table S3). Chloroform and its satellite peaks are marked with circles.

Figure S10. $^1$H NMR spectra of block and statistical copolymers with varying ratios of nb[8]CPP and nb[10]CPP units. Ratios are denoted with nb[8]CPP first. a) Spectra from samples 3 and 6, Table S3. b) Spectra from samples 8-10, Table S3. c) Spectra from samples 4 and 7, Table S3. Chloroform and its satellite peaks are marked with circles, and other residual solvent peaks are marked with squares.
**Photophysical Characterization Data**

![Absorbance and fluorescence spectra of nbCPPs and poly(nbCPP)s in THF. Polymer data from samples 1, 9, and 12, Table S1.](image)

**Figure S11.** Absorbance and fluorescence spectra of nbCPPs and poly(nbCPP)s in THF. Polymer data from samples 1, 9, and 12, Table S1.

![Solid-state a) absorbance and b) fluorescence emission spectra of nbCPP and poly(nbCPP) powders. Polymer data from samples 1, 6, 9, 12, and 17, Table S1.](image)

**Figure S12.** Solid-state a) absorbance and b) fluorescence emission spectra of nbCPP and poly(nbCPP) powders. Polymer data from samples 1, 6, 9, 12, and 17, Table S1.
The Förster distance between nb[10]CPP as a donor and nb[8]CPP as an acceptor was calculated with the equation

\[ R_0 = 0.211 \left( \kappa^2 n^{-4} Q D J(\lambda) \right)^{1/6} \]

in which
- \( \kappa^2 \) was estimated as 2/3,
- \( n \), the solvent refractive index, was 1.404 for THF,
- \( Q_D \) was 0.788,
- and \( J(\lambda) \) was calculated to be \( 1.764 \times 10^{13} \) using a|e - UV-Vis-IR Spectral Software (see above).
Figure S14. Absorbance and fluorescence spectra of poly(nbCPP)s synthesized in THF, from samples 6 and 12, Table S2 and samples 2 and 6, Table S3.

Figure S15. Image of fluorescence emission under 365 nm UV light of (left to right) poly(nb[10]CPP), poly(nb[8]CPP), and poly(nb[10]CPP-block-[8]CPP) from samples 6 and 12, Table S2 and sample 3, Table S3.
Figure S16. a) Fluorescence emission spectra of statistical copolymers with varying ratios of nb[8]CPP and nb[10]CPP units. Spectra from samples 8-10, Table S3. b) Fluorescence emission spectra of block copolymers with varying ratios of nb[8]CPP and nb[10]CPP units. Spectra from samples 2 and 4, Table S3. Copolymers are shown with nb[8]CPP:nb[10]CPP ratios. c) Fluorescence emission spectra of poly(nb[8]CPP) and poly(nb[10]CPP) blended in different ratios (samples 4 and 16, Table S1).
Fluorescence Quenching Experiments

Procedure for fluorescence quenching experiments
Monomer quenching: A 0.0003 M stock solution of the monomer and a 0.001 M stock solution of C\textsubscript{60} were prepared in toluene. These stock solutions were used to prepare a [H] solution and a [H+G] solution, with monomer at 5.13 × 10\textsuperscript{-7} M in both and C\textsubscript{60} at 5.00 × 10\textsuperscript{-5} M in the latter. Fluorescence measurements were obtained of a toluene blank followed by the [H] solution. [H+G] solution was added to [H] solution in 15 uL increments and the fluorescence was measured. This procedure was performed in triplicate for each monomer (≥15 data points per trial). Fluorescence spectra were integrated (400-625 nm for nb[10]CPP and 425-675 nm for nb[8]CPP), and the fluorescence intensity of each data point was compared to the initial fluorescence intensity.
Polymer quenching: A stock solution of the polymer was prepared using the same polymer mass and solvent volume as was used for the respective monomer stock solution. Due to solubility, polymer stock solutions were prepared in THF. Along with the C\textsubscript{60} stock solution prepared as described above, the polymer stock solution was used to prepare a [H] solution and a [H+G] solution in toluene. Fluorescence measurements were obtained of a toluene blank followed by the [H] solution. [H+G] solution was added to [H] solution in 2.5 uL increments and the fluorescence was measured. This procedure was performed in triplicate for each monomer (≥15 data points per trial). Fluorescence spectra were integrated from 400 to 675 nm, and the fluorescence intensity of each data point was compared to the initial fluorescence intensity.
Regression: Regression was performed with python using scipy.optimize.least_squares. Although it was outside the scope of this study to assess the equivalence of binding sites in the polymers and the possible contribution of cooperativity,\textsuperscript{4} we estimated K\textsubscript{a} and K\textsubscript{SV} values for the monomers and polymers using magnitude of quenching (F/F\textsubscript{0} or F\textsubscript{0}/F) versus total concentration of C\textsubscript{60}. These values are most suitable for comparative purposes.
| Sample                                      | $K_a$                          | $K_{SV}$                      |
|--------------------------------------------|--------------------------------|--------------------------------|
| nb[8]CPP                                   | $(5.85 \pm 3.13) \times 10^4$ | $(9.13 \pm 0.27) \times 10^4$ |
| nb[10]CPP                                  | $(2.55 \pm 0.09) \times 10^6$ | $(4.71 \pm 0.15) \times 10^6$ |
| poly(nb[8]CPP)                             | $(2.22 \pm 0.26) \times 10^7$ | $(4.81 \pm 0.24) \times 10^6$ |
| poly(nb[10]CPP)                            | $(2.15 \pm 0.49) \times 10^6$ | $(1.65 \pm 0.08) \times 10^8$ |
| poly(nb[10]CPP-block-[8]CPP)               | $(8.78 \pm 1.34) \times 10^7$ | $(9.95 \pm 1.22) \times 10^7$ |
| poly(nb[8]CPP-stat-[10]CPP)                | $(8.44 \pm 1.98) \times 10^7$ | $(8.52 \pm 0.41) \times 10^7$ |
| poly(nb[8]CPP)/poly(nb[10]CPP blend)       | $(1.13 \pm 0.28) \times 10^8$ | $(3.19 \pm 0.41) \times 10^7$ |

Table S5. $K_a$ and $K_{SV}$ values for nbCPP monomers and poly(nbCPP)s. Polymer data collected with samples 4 and 16, Table S1, and samples 1 and 5, Table S3.

Figure S17. Plots of $C_{60}$ concentration versus a) $F/F_0$ for nbCPP monomers, b) $F_0/F$ for nbCPP monomers, c) $F/F_0$ for poly(nbCPP)s, and d) $F_0/F$ for poly(nbCPP)s.
Figure S18. Fluorescence response of a) nb[10]CPP, b) nb[8]CPP, c) poly(nb[10]CPP), and d) poly(nb[8]CPP) to C\textsubscript{60} addition. Polymer data from samples 4 and 16, Table S1.

Figure S19. Fluorescence response of a) poly(nb[10]CPP), b) a poly(nb[8]CPP)/poly(nb[10]CPP) blend, c) poly(nb[10]CPP-\textit{block}-[8]CPP), and d) poly(nb[8]CPP-\textit{stat}-[10]CPP) to C\textsubscript{60} addition. Data shown from one trial each with samples 6 and 12, Table S2 and samples 2 and 6, Table S3. Concentrations of polymer and C\textsubscript{60} for this set of trials differed from the general procedure above, but the outcomes were the same.
Monomer Synthesis & Structural Characterization

Safety Summary

No unexpected or unusually high safety hazards were encountered. Care should be taken when using \( n \)-butyllithium: for example, using a luer lock syringe for \( n \)-BuLi transfers, using a syringe with double the capacity of the volume to be transferred, and not using \( n \)-BuLi while working alone.

The following procedure was used for safely handling sodium metal when preparing the sodium naphthalenide reagent: Tweezers, a small beaker, a squirt bottle of hexanes, and a jar containing sodium in oil were gathered. A piece of weigh paper was folded diagonally for later ease of transferring sodium. Using tweezers, a small chunk of sodium was removed from the jar and rinsed with hexanes over the beaker. The piece of sodium was set on a second piece of weigh paper to blot it and/or to turn it to rinse another side. Once the sodium was mostly clean/dry, it was weighed on the folded paper. Additional chunks were cut off the sodium block in the jar using a spatula with a squared end or the broad end of a scoopula, and the rinsing/weighing steps were repeated. Once the desired amount of sodium was obtained, it was folded inside the weigh paper and pounded flat with a mallet. The weigh paper was opened, and the sodium was cut into small pieces with a blade, then carefully poured into a dry reaction flask. Weigh papers, spatulas, tweezers, the blade, and anything else which could have residual sodium on it were placed under running water. (This method should NOT be used to quench larger amounts of sodium!)

Detailed Synthetic Procedures

Compounds 1,5,6 3,7 4,8 9,9 10,10 12,11 SPhos-Pd-G2,12 and Grubbs G313 were prepared according to the literature.

Three-ring norbornene-fused dibromide 2.

A flame-dried flask was charged with 1,4-dibromobenzene (8.2 g, 34.8 mmol, 3.00 equiv.), which was dissolved in THF (80 mL) and then cooled to -78 °C for 20 minutes. \( n \)-BuLi (15.8 mL, 24.8 mmol, 3.00 equiv.) was added dropwise. The reaction was stirred at -78 °C for 20 minutes, after which a solution of norbornene-benzoquinone 1 (2.00 g, 11.6 mmol, 1.00 equiv.) in THF (8 mL) was added dropwise. The reaction was stirred for 1 hour at -78 °C. Methyl iodide (7.2 mL, 116.2 mmol, 10.00 equiv.) and a few mL of DMF were added to the reaction, which was stirred overnight at room temperature then quenched with water. The THF was removed under reduced pressure, and the resulting solution was extracted with ethyl acetate (3x). The combined organic layers were washed with 5% aqueous LiCl (3x), water (2x), and brine (1x), then dried over sodium sulfate.
Concentration under reduced pressure yielded solid product, which was filtered and washed with hexanes. Additional product was obtained by purifying the filtrate via silica gel column chromatography (0 to 8% ethyl acetate in hexanes) followed by a final wash of product-containing fractions with hexanes. Combined yield was 1.69 g (29%). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.49-7.44 (m, 4H), 7.34-7.30 (m, 4H), 6.87 (t, \( J = 1.9 \) Hz, 2H), 5.92 (s, 2H), 3.50 (p, \( J = 1.6 \) Hz, 2H), 1.99 (dt, \( J = 6.3, 1.6 \) Hz, 1H), 1.89 (dt, \( J = 6.3, 1.7 \) Hz, 1H). \( ^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 153.8, 142.3, 142.2, 134.5, 131.5, 127.8, 121.5, 75.9, 74.1, 52.8, 49.8. IR (neat): 2983.3, 2931.2, 2873.7, 1481.0, 1392.1, 1299.1, 1070.9, 1007.4, 938.4, 823.3, 726.6, 681.9 cm\(^{-1}\). HRMS (TOF MS EI+) (m/z): [M]\(^+\) calculated for C\(_{25}\)H\(_{22}\)Br\(_2\)O\(_2\): 511.9987; found: 511.9997.

\( nb[8]\)CPP macrocycle 6.

A flame-dried flask was charged with dibromide 2 (300 mg, 0.583 mmol, 1.00 equiv.), bisboronate 3 (487 mg, 0.642 mmol, 1.10 equiv.), and SPhos-Pd-G2 (42 mg, 0.058 mmol, 0.10 equiv.). The flask was evacuated and backfilled with nitrogen for 5 cycles. Dry dioxane (195 mL) was sparged with nitrogen for 1 hr. A 2.00 M. aqueous solution of K\(_3\)PO\(_4\) was sparged with nitrogen for 1 hr. Dioxane was added to the reaction flask, which was then heated to 80 °C. 19.5 mL of K\(_3\)PO\(_4\) solution was added. The reaction was stirred overnight at 80 °C. After the reaction was cooled to room temperature, the dioxane was removed under reduced pressure, then the resulting material was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate, filtered through celite, and concentrated under reduced pressure. Silica gel column chromatography (6 to 16% ethyl acetate in 50/50 DCM/hexanes) yielded 160 mg (29%). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.55 (d, \( J = 8.6 \) Hz, 4H), 7.51 (s, 4H), 7.50 (d, \( J = 7.9 \) Hz, 4H), 7.43 (d, \( J = 8.7 \) Hz, 4H), 7.21 (d, \( J = 8.6 \) Hz, 4H), 6.98 (t, \( J = 1.8 \) Hz, 2H), 6.14-6.06 (overlapping, 10H), 3.79 (t, \( J = 1.8 \) Hz, 2H), 3.48 (s, 6H), 3.40 (s, 6H), 3.23 (s, 6H), 2.05 (dt, \( J = 6.3, 1.6 \) Hz, 1H), 1.97 (dt, \( J = 6.2, 1.6 \) Hz, 1H). \( ^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 154.11, 143.35, 143.19, 142.79, 140.82, 139.61, 139.54, 134.87, 133.60, 133.44, 132.83, 132.70, 127.13, 126.82, 126.38, 126.28, 126.26, 77.61, 74.60, 74.00, 73.79, 53.03, 52.15, 51.78, 49.68. IR (neat): 2934.9, 2897.5, 2821.1, 1712.9, 1491.7, 1448.9, 1397.2, 1175.2, 1073.9, 946.7, 818.3 cm\(^{-1}\). HRMS (TOF MS EI+) (m/z): [M]\(^+\) calculated for C\(_{59}\)H\(_{54}\)O\(_6\): 858.3920; found: 858.3954.
A 0.5 M sodium naphthalenide solution was prepared by sonicating sodium and naphthalene in THF in a flame-dried flask, then stirring the solution overnight. Macrocycle 6 (83 mg, 0.097 mmol, 1.00 equiv.) was dispersed in THF in a flame-dried flask and stirred at -78 °C for 30 min. Sodium naphthalenide (>2.90 mL, 1.45 mmol, 15.00 equiv.) was added dropwise to the reaction flask until the mixture was brown. The reaction was stirred for 30 minutes and then quenched with dropwise addition of 1 M. iodine solution in THF until orange. Sodium thiosulfate was added until the orange color dissipated, and the reaction was warmed to room temperature. THF was removed under reduced pressure, and the resulting solution was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. Automated silica gel column chromatography (5 to 40% DCM in hexanes) yielded 55 mg (85%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.47 (overlapping, 24H), 7.28 (d, \(J = 7.9\) Hz, 4H), 7.01 (t, \(J = 1.9\) Hz, 2H), 6.53 (s, 2H), 4.38 (t, \(J = 1.9\) Hz, 2H), 2.45 (dt, \(J = 7.2, 1.6\) Hz, 1H), 2.28 (d, \(J = 7.4\) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 148.59, 143.15, 139.08, 138.25, 138.05, 137.91, 137.89, 137.86, 137.80, 132.84, 129.05, 69.44, 49.98. IR (neat): 3021.8, 1889.6, 1582.9, 1480.7, 1388.8, 1256.9, 998.7, 942.1, 809.7, 723.2 cm\(^{-1}\). HRMS (TOF MS EI\(^+\)) (m/z): \([M]\)^{+} calculated for C\(_{53}\)H\(_{36}\): 672.2817; found: 672.2833.

**nb[9]CPP macrocycle 7.**

A flame-dried flask was charged with dibromide 2 (475 mg, 0.9 mmol, 1.00 equiv.), bisboronate 4 (810 mg, 0.1 mmol, 1.05 equiv.), and SPhos-Pd-G2 (67 mg, 0.1 mmol, 0.10
equiv.). The flask was evacuated and backfilled with nitrogen for 5 cycles. A 2.00 M. aqueous solution of K$_3$PO$_4$ was sparged with nitrogen for 1 hr. Dioxane (308 mL) was added to the reaction flask, sparged for 20 min., then heated to 80 °C for 10 min. 31 mL of K$_3$PO$_4$ solution was added, and the reaction was stirred for 30 min. at 80 °C. After the reaction was cooled to room temperature, the dioxane was removed under reduced pressure, then the resulting material was filtered through a celite pad with DCM and water. The filtrate was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. Silica gel column chromatography (0 to 10% ethyl acetate in DCM) yielded 30.6 mg (35%).

$^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 7.64 (d, $J = 8.3$ Hz, 4H), 7.63 (d, $J = 8.1$ Hz, 4H), 7.59 (d, $J = 8.2$ Hz, 4H), 7.55 (d, $J = 8.2$ Hz, 4H), 7.50 (d, $J = 8.4$ Hz, 4H), 7.48 (d, $J = 8.4$ Hz, 4H), 6.91 (t, $J = 1.9$ Hz, 2H), 6.18 (overlapping, 8H), 5.99 (s, 2H), 3.61 (t, $J = 2.0$ Hz, 2H), 3.48 (s, 6H), 3.47 (s, 6H), 3.20 (s, 6H), 1.98 (d, $J = 6.0$ Hz, 1H), 1.93 (d, $J = 6.0$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 153.99, 142.72, 139.74, 134.70, 133.63, 128.52, 75.06, 74.25, 67.21, 52.86, 52.19, 49.94. IR (neat): 2932.6, 2870.8, 1149.2, 1147.9, 1074.4, 1074.4, 1027.6, 950.6, 906.0, 847.7, 753.7 cm$^{-1}$. HRMS (TOF MS EI+) (m/z): [M+H]$^+$ calculated for C$_{65}$H$_{59}$O$_6$: 935.4312; Found: 935.5661.

$nb[9]CPP$. A 0.5 M. sodium naphthalenide solution was prepared by sonicating sodium and naphthalene in THF in a flame-dried flask, then stirring the solution overnight. Macrocycle 7 (220 mg, 0.24 mmol, 1.00 equiv.) was dispersed in THF in a flame-dried flask and stirred at -78 °C for 30 min. Sodium naphthalenide (7.1 mL, 3.54 mmol, 15.00 equiv.) was added dropwise to the reaction flask until the mixture was brown. The reaction was stirred for 20 minutes and then quenched with dropwise addition of 1 M. iodine solution in THF until orange. Sodium thiosulfate was added until the orange color dissipated and the reaction was warmed to room temperature. THF was removed under reduced pressure, and the resulting solution was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. The material was adsorbed on silica and purified by silica gel column chromatography (19% then 40% DCM in hexanes), yielding 60 mg (34%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 7.56 (overlapping, 28H), 7.33 (d, $J = 8.2$ Hz, 4H), 7.04 (t, $J = 1.9$ Hz, 2H), 6.60 (s, 2H), 4.38 (p, $J = 1.7$ Hz, 2H), 2.45 (dt, $J = 7.5$, 1.6 Hz, 1H), 2.30 (dt, $J = 7.4$, 1.7 Hz, 1H). $^{13}$C NMR (151 MHz,
CDCl$_3$ $\delta$ 148.80, 143.21, 139.28, 138.18, 133.02, 128.55, 127.52, 69.44, 53.58, 49.95. IR (neat): 3020.4, 1586.4, 1480.2, 1386.7, 1261.0, 999.3, 805.2, 729.5 cm$^{-1}$. HRMS (TOF MS EI+) (m/z): [M+H]$^+$ calculated for C$_{59}$H$_{41}$: 749.3208; found: 749.3198.

Seven-ring dichloride 11.

To a slurry of sodium hydride (220 mg, 5.4 mmol, 1.30 equiv.) in 10 mL THF was added a solution of ketone 9 (1.80 g, 4.1 mmol, 1.00 equiv.) in 10 mL THF at -78 °C. The reaction mixture was stirred for 2 hr at -78 °C. In a separate flask, bromochloride 10 (2.52 g, 6.2 mmol, 1.50 equiv.) was dissolved in 20 mL THF. This solution was cooled to -78 °C, then $n$-BuLi (2.4 mL, 5.8 mmol, 1.40 equiv.) was added dropwise and the reaction was stirred for 30 min. This mixture was then transferred to the slurry containing the deprotonated ketone. The resulting mixture was stirred for 2 hr, at which time Mel (2.6 mL, 4.1 mmol, 10.00 equiv.) and dry DMF (5 mL) were added. The reaction was allowed to warm to room temperature overnight. The reaction was quenched with water and extracted with diethyl ether (3x). The combined organic layers were washed with 5% aqueous LiCl (3x), water (2x), and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. The material was sonicated with hexanes until solid formed, then it was filtered and washed with hexanes. The product was purified further by automated silica gel chromatography in 5 to 12% ethyl acetate in hexanes. 1.50 g were collected (46%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.37-7.24 (overlapping, 16H), 6.11 (d, $J = 10.2$ Hz, 4H), 6.07 (s, 4H), 6.04 (d, $J = 10.4$ Hz, 4H), 3.43-3.40 (overlapping, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.09, 142.69, 142.20, 133.84, 133.48, 133.46, 133.12, 128.61, 127.60, 126.21, 126.13, 77.36, 74.70, 74.58, 52.14, 52.13, 52.12. IR (neat): 2939.8, 2819.0, 1489.0, 1452.1, 1403.3, 1228.2, 1179.3, 1070.6, 1013.2, 947.7, 820.3, 729.2, 664.0 cm$^{-1}$. HRMS (TOF MS EI+) (m/z): [M]$^+$ calculated for C$_{48}$H$_{46}$Cl$_2$O$_6$: 788.2671; found: 788.2695.
Seven-ring bisboronate 5.

Potassium acetate (373 mg, 3.8 mmol, 6.00 equiv.) was flame-dried in a flask and cooled under nitrogen. Ground B$_2$Pin$_2$ (482 mg, 1.9 mmol, 3.00 equiv.), dichloride 11 (500 mg, 0.6 mmol, 1.00 equiv.), Pd(OAc)$_2$ (14 mg, 0.1 mmol, 0.10 equiv.), and SPhos (68 mg, 0.2 mmol, 0.26 equiv.) were added to the flask, which was then evacuated and backfilled with nitrogen for 5 cycles. The flask was sealed with a septum and purged with nitrogen for 1 hr. Dry dioxane (5 mL) was sparged with nitrogen for 1 hr then added to reaction flask. The reaction was heated to 80 °C, then stirred overnight. After the reaction was cooled to room temperature, the mixture was filtered through a plug of celite, and the filtrate was concentrated under reduced pressure. The material was sonicated with methanol and filtered. The product was then run through a very short silica plug using ethyl acetate and concentrated again to yield 430 mg (70%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J = 8.0$ Hz, 4H), 7.40 (d, $J = 8.3$ Hz, 4H), 7.34 (s, 8H), 6.10-6.06 (m, 12H), 3.42 (m, 18H), 1.33 (s, 24H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.63, 142.94, 142.80, 135.09, 133.54, 133.48, 133.44, 133.27, 126.20, 126.13, 125.45, 83.90, 75.04, 74.79, 74.74, 52.10, 52.08, 25.01, 24.97. IR (neat): 2979.9, 2938.2, 2896.7, 2821.6, 1501.1, 1489.4, 1450.9, 1403.2, 1358.1, 1179.3, 1079.3, 1013.8, 948.7, 826.4, 757.3, 657.2 cm$^{-1}$. HRMS (FTMS ESI) (m/z): [M+Na]$^+$ calculated for C$_{60}$H$_{70}$B$_2$O$_{10}$Na: 995.5047; found: 995.5031.

nb[10]CPP macrocycle 8.

A flame-dried flask was charged with dibromide 2 (720 mg, 1.40 mmol, 1.00 equiv.), bisboronate 5 (1.43 g, 1.47 mmol, 1.05 equiv.), and SPhos-Pd-G2 (101 mg, 0.14 mmol, 0.10 equiv.). The flask was evacuated and backfilled with nitrogen for 5 cycles. The flask was then purged with nitrogen. A 2.00 M. aqueous solution of K$_3$PO$_4$ was sparged with
nitrogen for 1 hr. Dioxane (470 mL) was added to the reaction flask via cannulation, and the solution was sparged for 20 min. before being heated to 80 °C for 10 min. 47 mL of K₃PO₄ solution was added, and the reaction was stirred for 30 min. at 80 °C. After the reaction was cooled to room temperature, the dioxane was removed under reduced pressure, then the resulting material was filtered through a celite pad with DCM and water. The filtrate was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. The material was purified by automated silica gel column chromatography (0 to 14% ethyl acetate in DCM), then washed with acetone and filtered, yielding 415 mg (28%). ¹H NMR (500 MHz, CDCl₃): δ 7.43-7.35 (overlapping, 24H), 6.96 (s, 2H), 6.17-6.14 (overlapping, 8H), 6.07 (m, 4H), 6.00 (s, 2H), 3.73 (s, 2H), 3.44 (s, 6H), 3.38 (s, 6H), 3.37 (s, 6H), 3.20 (s, 6H), 2.17 (d, J = 6.0 Hz, 1H), 2.10 (d, J = 6.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 154.21, 143.26, 143.05, 142.97, 142.47, 141.92, 140.42, 140.37, 134.78, 134.01, 133.85, 133.23, 133.02, 132.86, 127.35, 127.25, 126.77, 126.48, 126.29, 126.27, 77.02, 75.00, 74.52, 74.19, 73.96, 52.98, 52.18, 52.06, 50.03. IR (neat): 2978.9, 2936.2, 2896.6, 2821.4, 1608.8, 1490.1, 1450.6, 1403.0, 1358.2, 1173.4, 1072.8, 1013.7, 948.0, 822.2, 656.7 cm⁻¹. HRMS (TOF MS EI+) (m/z): [M+Na]⁺ calculated for C₇₃H₆₈O₈Na: 1095.4812; found: 1095.4840.

nb[10]CPP.

A 0.5 M sodium naphthalenide solution was prepared by sonicating sodium and naphthalene in THF in a flame-dried flask, then stirring the solution overnight. Macrocycle 8 (395 mg, 0.368 mmol, 1.00 equiv.) was dispersed in THF in a flame-dried flask and stirred at -78 °C for 30 min. Sodium naphthalenide (>11.0 mL, 5.52 mmol, 15.00 equiv.) was added dropwise to the reaction flask until the mixture was brown. The reaction was stirred for 20 minutes and then quenched with dropwise addition of 1 M iodine solution in THF until orange. Sodium thiosulfate was added until the orange color dissipated, and the reaction was warmed to room temperature. The resulting solution was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. The material was adsorbed on silica and purified by automated silica gel column chromatography (15-35% DCM in hexanes), yielding 229 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.56 (overlapping, 32H), 7.36 (d, J = 8.2 Hz, 4H), 7.05 (t, J = 1.7 Hz, 2H), 6.65 (s, 2H), 4.37 (s,
2H), 2.45 (d, J = 7.6 Hz, 1H), 2.31 (d, J = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 148.72, 143.11, 139.27, 138.26, 138.19, 138.17, 138.15, 133.07, 128.40, 128.01, 127.40, 127.37, 127.35, 127.24, 127.20, 69.27, 49.76. IR (neat): 3021.3, 1895.4, 1589.7, 1479.3, 1386.6, 1000.2, 905.4, 805.7, 730.6 cm$^{-1}$. HRMS (TOF MS EI+) (m/z): [M]$^+$ calculated for C$_{65}$H$_{44}$: 824.3443; found: 824.3467.

diMeObnb.

A slurry of sodium hydride (3.44 g, 86.1 mmol, 3.00 equiv.) in 20 mL THF was cooled to 0 °C. A solution of diketone 12 (5.00 g, 28.7 mmol, 1.00 equiv.) in 20 mL THF was added in stream. After 10 min., methyl iodide (8.9 mL, 143.5 mmol, 5.00 equiv.) was added, and the reaction was allowed to warm to room temperature. Water was added to quench the reaction, and the resulting mixture was extracted with DCM (3x). The combined organic layers were washed with water (2x) and brine (1x), then dried over sodium sulfate and concentrated under reduced pressure. The crude material was dissolved in 50/50 DCM/hexanes and passed through a plug of silica. Concentration of the filtrate yielded a colorless oil which solidified on standing (1.16 g, 20%). $^1$H NMR (600 MHz, CDCl$_3$): δ 6.83 (t, J = 1.9 Hz, 2H), 6.50 (s, 2H), 4.16 (p, J = 1.7 Hz, 2H), 3.79 (s, 6H), 2.22 (dt, J = 6.9, 1.6 Hz, 1H), 2.18 (dt, J = 6.9, 1.7 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.86, 143.12, 140.65, 109.67, 70.27, 56.44, 47.13. IR (neat): 2999.2, 2952.8, 2922.5, 2828.5, 1492.7, 1451.1, 1436.6, 1293.9, 1252.8, 1195.6, 1090.0, 1056.0, 1007.1, 965.5, 792.3, 734.2, 709.3, 619.3 cm$^{-1}$. HRMS (TOF MS EI+) (m/z): [M]$^+$ calculated for C$_{13}$H$_{14}$O$_2$: 202.0994; found: 202.0995.
Nuclear Magnetic Resonance Spectra
X-Ray Crystallography Data

Single crystals suitable for crystallographic analysis were grown from slow evaporation of a solution of 2 in DCM/hexanes and slow diffusion of pentane into solutions of nb[8]CPP, nb[9]CPP, and nb[10]CPP in THF. Crystal data has been deposited to the Cambridge Crystallographic Database with CCDC numbers 1949617, 1949616, 2051663, and 1949615.

Diffraction intensities were collected at 173 K on a Bruker Apex2 CCD diffractometer using CuKα radiation, λ = 1.54178 Å. Space groups were determined based on systematic absences. Absorption corrections were applied by SADABS. Structures were solved by direct methods and Fourier techniques and refined on $F^2$ using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in all structures were refined in calculated positions in a rigid group model. The structure of nb[8]CPP was determined in non-centrosymmetrical space group symmetry R3c, but not in possible centro-symmetrical space group R-3c. The refinement in non-centrosymmetrical space group symmetry R3c shown that the Flack parameter is close to zero, but not to 0.5 as could be expected if the centro-symmetrical space group R-3c is correct. Crystals of nb[8]CPP are formed as thin strips and give very weak X-ray diffraction at high angles. Even using a strong Incoatec IµS Cu source for nb[8]CPP it was possible to collect data only up to $2\theta_{\text{max}} = 98.44^\circ$. However, the collected data provide an appropriate number of measured reflections per a number of refined parameters, 4073/472. In both nb[8]CPP and nb[10]CPP, solvent pentane molecules fill out empty space in the packing and in the hoops and are highly disordered. These disordered solvent molecules were treated by SQUEEZE. The corrections of the X-ray data by SQUEEZE are 760 and 480 electron/cell; the required values are 756 and 336 electron/cell for eighteen and eight pentane molecules in the full unit cells, respectively in nb[8]CPP and nb[10]CPP. The five-member ring in nb[8]CPP is disordered over two positions with opposite orientations as well. Resolution for nb[8]CPP and nb[10]CPP structures is relatively low due to a lot of disordered fragments in the structures and weak X-ray diffraction at high angles, but the found X-ray structures clearly shown the structure of the hoops in these compounds. There are two symmetrically independent molecules in the structure of nb[9]CPP. Besides the main molecules the crystal structure includes five solvent pentane molecules. They fill out empty space in the packing and in the hoops. These THF molecules were refined with restrictions on its bond lengths: the standard O-C and C-C distances were used in the refinement as the targets for corresponding bonds. Thermal parameters for atoms in these pentane molecules are elongated indicating that they are highly disordered. Some short H...H contacts in the structure are related to the contacts between these disordered groups. All calculations were performed by the Bruker SHELXL-2014 package.

Crystallographic Data for 2: C_{25}H_{22}Br_{2}O_{2}, M = 514.24, 0.11 x 0.08 x 0.06 mm, T = 173(2) K, Monoclinic, space group $P2_1/c$, $a = 12.3702(5)$ Å, $b = 15.2429(6)$ Å, $c = 12.0344(4)$ Å, $\beta = 112.703(1)^\circ$, $V = 2093.36(14)$ Å$^3$, $Z = 4$, $D_c = 1.632$ Mg/m$^3$, $\mu$(Cu) = 5.058 mm$^{-1}$, $F(000) = 1032$, $2\theta_{\text{max}} = 133.31^\circ$, 16491 reflections, 3694 independent reflections [$R_{\text{int}} = 0.0496$, $R_1 = 0.0313$, $wR_2 = 0.0848$ and GOF = 1.044 for 3694 reflections (262
parameters) with I \geq 2\sigma(I), R_1 = 0.0344, wR_2 = 0.0870 and GOF = 1.044 for all reflections, max/min residual electron density +0.573/-0.507 eÅ⁻³.

Crystallographic Data for \textbf{nb[8]CPP}: C₅₈H₄₈, C₅₃H₃₆\cdot(C₅H₁₂), M = 744.96, 0.09 x 0.08 x 0.01 mm, T = 173(2) K, Trigonal, space group R3c, a = 16.343(5) Å, b = 16.343(5) Å, c = 80.413(4) Å, V = 18600.8(14) Å³, Z = 18, \(D_c = 1.197 \text{ Mg/m}³\), \(\mu(\text{Cu}) = 0.508 \text{ mm}⁻¹\), \(F(000) = 7128\), \(2\theta_{\text{max}} = 98.44°\), 25725 reflections, 4073 independent reflections \([R_{\text{int}} = 0.0604]\), R₁ = 0.0534, wR₂ = 0.1340 and GOF = 1.085 for 4073 reflections (472 parameters) with I \geq 2\sigma(I), R₁ = 0.0688, wR₂ = 0.1424 and GOF = 1.087 for all reflections, max/min residual electron density +0.140/-0.137 eÅ⁻³.

Crystallographic Data for \textbf{nb[9]CPP}: C₇₁H₆₄O₃, M = 965.22, 0.17 x 0.15 x 0.02 mm, T = 173(2) K, Triclinic, space group P-1, a = 9.9507(4) Å, b = 17.1984(7) Å, c = 32.2140(12) Å, \(\alpha = 82.982(2)°\), \(\beta = 85.750(2)°\), \(\gamma = 89.947(2)°\), V = 5456.4(4) Å³, Z = 4, \(D_c = 1.175 \text{ Mg/m}³\), \(\mu(\text{Cu}) = 0.538 \text{ mm}⁻¹\), \(F(000) = 2056\), \(2\theta_{\text{max}} = 133.65°\), 60692 reflections, 19175 independent reflections \([R_{\text{int}} = 0.0585]\), R₁ = 0.0978, wR₂ = 0.2717 and GOF = 1.058 for 19175 reflections (1333 parameters) with I \geq 2\sigma(I), R₁ = 0.1454, wR₂ = 0.3101 and GOF = 1.070 for all reflections, max/min residual electron density +0.140/-0.137 eÅ⁻³.

Crystallographic Data for \textbf{nb[10]CPP}: C₇₅H₆₈, C₆₅H₄₄\cdot2(C₅H₁₂), M = 969.29, 0.11 x 0.08 x 0.06 mm, T = 173(2) K, Monoclinic, space group P2₁/c, a = 6.5747(3) Å, b = 28.3155(16) Å, c = 32.6239(17) Å, \(\beta = 91.334(4)°\), V = 6071.8(5) Å³, Z = 4, \(D_c = 1.060 \text{ Mg/m}³\), \(\mu(\text{Cu}) = 0.447 \text{ mm}⁻¹\), \(F(000) = 2072\), \(2\theta_{\text{max}} = 133.40°\), 46166 reflections, 10685 independent reflections \([R_{\text{int}} = 0.0443]\), R₁ = 0.0507, wR₂ = 0.1396 and GOF = 1.051 for 10685 reflections (586 parameters) with I \geq 2\sigma(I), R₁ = 0.0617, wR₂ = 0.1461 and GOF = 1.051 for all reflections, max/min residual electron density +0.391/-0.198 eÅ⁻³.

**Figure S20.** ORTEP representation of the X-ray crystallographic structure of 2 (CCDC Registry # 1949617).
Figure S21. ORTEP representation of the X-ray crystallographic structure of nb[8]CPP (CCDC Registry # 1949616).

Figure S22. ORTEP representation of the X-ray crystallographic structure of nb[9]CPP (CCDC Registry # 2051663).
Figure S23. ORTEP representation of the X-ray crystallographic structure of nb[10]CPP (CCDC Registry # 1949615).

Figure S24. The unit cell for nb[8]CPP crystals (a, top) contains 18 nbCPP molecules, comprising six unique trimers. One trimer (green) is shown in two additional views. The unit cell for nb[9]CPP crystals (b, top) contains four nbCPP molecules. The unit cell for nb[10]CPP crystals (c, top) contains four nbCPP molecules. In all cases, solvent molecules have been omitted for clarity. Examination of the norbornene alkene in the crystal structures of nb[8]CPP, nb[9]CPP, and nb[10]CPP (a-c, bottom) shows that the norbornene moiety is largely unaffected by the number of phenyl rings in the hoop.
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