Poly[$n$]catenanes: Synthesis of molecular interlocked chains

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As the macromolecular version of mechanically interlocked molecules, mechanically interlocked polymers (MIPs) are intriguing candidates for creation of sophisticated molecular machines and smart soft materials. Poly[$n$]catenanes, where the molecular chains consist solely of interlocked macrocycles, contain one of the highest concentrations of topological bonds. We report, herein, a synthetic approach toward this unique polymer architecture in high yield (~75%) via efficient ring-closing of rationally-designed metallosupramolecular polymers (MSPs). Light-scattering, mass spectrometric, and nuclear magnetic resonance characterization of fractionated samples support assignment of the high molecular weight product (average Mn = 21.4 kDa) to a mixture of linear poly[7–26]catenanes, branched poly[13–130]catenanes and cyclic poly[4–7]catenanes. Increased hydrodynamic radius (R_h, in solution) and glass transition temperature (T_g, in bulk materials) were observed upon metallation with Zn^{2+}.

Mechanically interlocked molecules (MIMs) such as catenanes, rotaxanes and knots are attracting increasing attention on account of their aesthetic topological structures (1–3) and their potential in applications that range from molecular machines (4) to catalysis (5), drug delivery (6) and switchable surfaces (7). An impressive array of small molecule MIMs have been successfully synthesized, primarily through properly orienting the precursor components via a non-covalent templating event, that employs, e.g. metal-ligand (1, 2, 8–10), donor/acceptor (11), or hydrogen bonding (12) interactions or the hydrophobic effect (3), followed by a covalent fixing step. Compared to low molecular weight MIMs, mechanically interlocked polymers (MIPs), such as polyrotaxanes and polycatenanes, offer access to intriguing properties for functional soft materials platforms (13). Perhaps the most striking example to date is provided by the slide-ring gels (a subset of polyrotaxanes), where the mechanically interlocked rings act as mobile crosslinking sites. These materials exhibit anti-scratch and healing characteristics, and have been successfully applied as anti-scratch coatings for cell phones and automobiles (14). As highlighted by this example, the unusual mobility elements in MIPs (e.g., low energy barrier for the sliding of the ring along a thread or free rotation of rings) make them a unique class of polymers, with the potential to display a very unusual matrix of properties.

[n]Catenanes consist of n consecutively interlocking rings. Poly[n]catenanes are polymer chains composed entirely of interlocked rings and can be thought of as [n]catenanes where n is large and generally dispersity Đ ≥ 1. These interlocked polymers contain a very high concentration of topological bonds and can be considered the molecular equivalent of a macroscopic chain (Fig. 1A). Such structures retain their flexibility no matter the stiffness of their ring components on account of the conformational mobility of their topological structures allowing access to both high strength and excellent flexibility. Figure 1B shows the main conformational mobilities (rotational, elongational and rocking motions) in the backbone repeat unit of such a chain for appropriate ring sizes (13). Theoretical studies have suggested that poly[n]catenanes with such mobility elements could exhibit a large loss modulus and a low activation energy for flow, and could potentially act as outstanding energy damping materials and/or elastomers with excellent toughness and stimuli-responsive mechanical properties (13, 15, 16).

The synthesis of poly[n]catenanes, however, represents a major challenge. The confirmed synthesis of these polymeric topologies of high molecular weight has yet to be reported. Most of the prior work on polycatenanes has focused on poly[2]catenanes (generally accessed by polymerizing a bis-functionalized [2]catenane) (15, 17–23), poly/oligocatenanes with unclearly-defined architectures (24, 25), and polymeric [2]catenanes (i.e. two interlocked cyclic polymers) (26). These materials have afforded insights into the potentially interesting properties of MIPs. For example, poly[2]catenane)s have shown conformational flexibility along the polymer chain in
solution (indicated by a shorter Kuhn segment length than the length of its [2]catenane moiety) (15) and temperature-dependent motion of the rings in solution (18) or in bulk materials (22). It is worthwhile pointing out that on account of the covalent linking units present in the poly(2)catenane backbone, the degree of rotation of the ring components in the catenane moieties is limited (Fig. 1C). Poly[n]catenanes, on the other hand, have rings linked solely by topological bonds allowing full rotational mobility of every ring (with sufficient ring size) and as such should exhibit more conformational flexibility. One of the most successful attempts to access oligo[n]catenanes with at least 7 interlocked rings was recently achieved via the ring-opening polymerization of metallo-[2]catenanes by Meijer, Di Stefano and their co-workers (25). However, the specific architecture of the product could not be clearly defined. To date, the longest interlocked molecular chain with clearly defined structure is a linear [5]catenane (olympiadane) reported by Stoddart and co-workers (27) and, more recently, by Iwamoto et al. (28), both via stepwise approaches. Stoddart and co-workers have also used a similar strategy to access a branched [7]catenane (29). These step-wise strategies, however, are not efficient methodologies for the synthesis of long chain poly[n]catenanes. One key challenge in the synthesis of poly[n]catenanes is the conflicting reaction conditions for accessing macrocycles (requiring low concentration) and polymers (requiring high concentration). Takata, Kihara and co-workers proposed an elegant solution to this conflict by converting a bridged poly(2)catenane into poly[n]catenane (20), but to date there is no report of a poly[n]catenane synthesized via this route.

The synthetic strategy toward poly[n]catenanes outlined herein, and illustrated in Fig. 1D, aims at decoupling the above-mentioned conflicting synthetic requirements through the pre-assembly of a metallosupramolecular polymer (MSP) as a template, followed by an efficient ring-closing reaction and demetallation of the resulting metallated poly[n]catenane. Pioneered by Sauvage, metal-ligand coordination has been one of the most successful synthetic routes toward supramolecular polymers (30). For example, the pre-assembly of a pseudo[3]rotaxane assembled from a monomorphic polyol and a macrocycle, [3]rotaxane, and a ditopic thread (1 with R = hexyl) in a ratio of 2:2:1 (9).

Building on these studies, we targeted the MSP assembly of the rationally designed 68-membered ditopic Bip-macrocycle 2 with the threading molecule 1 and the subsequent ring closing of the 1 (Fig. 1E). Upon the addition of 2 equivalents of Zn2+ to the 1:1 mixture of 1 and 2, the components self-assembled into the alternating supramolecular copolymer (Fig. 1D; monitored by 1H NMR, fig. S1). The alternation is a consequence of the principle of maximal site occupancy (34)—two Bip moieties in the same (or different) macrocycle 2 cannot bind the same Zn2+ ion; therefore, each Bip unit in 2 must form a 2:1 Bip:Zn2+ ion complex with a Bip unit in 1 in order to maximize enthalpic gain (see fig. S2). The formation of an MSP was confirmed by Diffusion-Ordered Spectroscopy (DOSY) (fig. S3). The large binding constant (>10^6 M^-1 in acetonitrile) between Bip and Zn2+ (35) maintains the MSP under the relatively dilute conditions required to favor the ring closing reaction (although cyclic MSPs should be favored under very dilute conditions). The ring-closing metathesis (RCM) reaction showed excellent olefin conversion at 2.5 mM (with respect to 1, fig. S4), and the resulting reaction mixture could be readily demetallated with tetrabutylammonium hydroxide. Figure 2A compares the partial 1H NMR spectrum of the demetallated crude product (focusing on the pyridyl protons H_{A/a}) with all the possible non-interlocked by-products 4 (macrocycle obtained from 1), 2 and 5 (acyclic diene metathesis [ADMET] polymerized 1, see fig. S5 for structure). The majority of the H_{A/a} peaks of the crude product show an up-field chemical shift (in the region 8.11–8.27 ppm, highlighted in yellow) that does not correspond to any of the possible non-interlocked species, but are in good agreement with the chemical shifts observed in the previous studies on Bip-containing [3]catenanes (9), consistent with the formation of interlocked structures. The crude product also contains a small percentage (~20%) of non-interlocked molecules that were assigned to unreacted 2 and polymer/oligomer 5 based on their 1H NMR chemical shift.
step also removes some oligomeric interlocked products primarily on account of the smaller number of interlocked metal-ion binding sites making them statistically less likely to attract enough metal ions to alter their solubility.

All NMR peaks of the interlocked product 3 have been assigned based on two-dimensional NMR studies (figs. S6 to S8). The spectroscopy confirms that 3 contains ~50% macrocycles 2 and ~50% of a component(s) derived from 1 (based on 1H NMR integration, fig. S10) which is consistent with the formation of the targeted alternating poly[n]catenane structure. The interlocked structure is further confirmed by Nuclear Overhauser Effect Spectroscopy (NOESY, Fig. 2C). Lowering the temperature (−17°C) to diminish the ring motions in the polycatenane gives rise to numerous NOE cross peaks in dilute (1% w/v) solutions of 3. Of particular interest are inter-component NOE cross peaks between protons in the different macrocycles (2 and 4). At least four inter-component NOE cross peaks, including, for example, one between Hα of 4 and Hα/a of 2, were observed in 3 (Fig. 2C) but not in the simple mixtures of 2+4 or 2+5 (figs. S11 and S12). Given that NOE signals normally require the protons to be <0.5 nm apart, these data strongly suggest that macrocycles 2 and 4 have to be interlocked and that 3 is indeed a poly[n]catenane.

Having confirmed the interlocked structure, we next measured the absolute molecular weight of the polymers using gel-permeation chromatography coupled to a multi-angle light scattering detector (GPC-MALS) (37). The GPC chromatogram of 3 (Fig. 3A, black line) shows a broad peak consistent with a number average molecular weight Mn = 21.4 kDa and dispersity D = 1.44 (Table 1). At each elution volume the absolute molecular weight is shown as the red dotted line, indicating that the product distribution 3 contains species with molecular weight up to ~200 kDa, which corresponds to a poly[130]catenane. Deconvolution of the broad peak in the chromatogram yields three sub-peaks (I)–(III) implying that the poly[n]catenane product may contain three different architectures. The measured absolute molecular weights (from MALS) of these three peaks are ca. 20–200 kDa, 10–40 kDa and 6–10 kDa which would correspond to poly[13–130]catenanes, poly[7–27]catenanes and poly[4–7]catenanes, respectively. The relative percentage of the three peaks is estimated (based on peak areas) to be 28%, 61% and 11%, respectively.

One possible explanation for peaks (I)–(III) is the formation of branched, linear and cyclic architectures, respectively, as illustrated in Fig. 3B. In addition to the targeted linear poly[n]catenanes, it is certainly possible that interchain reactions (dimerization/oligomerization of 4) can occur, leading to higher molecular weight branched poly[n]catenanes. Furthermore, it is also possible that there is a percentage of the MSPs that are lower molecular weight cyclic structures, which in turn would lead to cyclic polycatenanes. One piece of evidence suggestive of cyclic polycatenanes is the observed transition peak between (II) and (III) in the absolute molecular weight measurement (Fig. 3A, at ~9.2 mL). If (III) does correspond to a cyclic geometry, we would expect these more compact structures to co-elute with lower-molecular-weight linear polymers (38).

In order to more fully characterize the poly[n]catenane mixture, we performed preparative GPC on 3, obtaining four fractions 3a–3d. 1H NMR studies confirmed that all four fractions contain ~50% macrocycles 2, consistent with them all being poly[n]catenanes (fig. S14). GPC-MALS of each fraction confirmed successful size-based separation (Fig. 3C and fig. S15), and the four fractions showed decreasing molecular weight (Table 1) with relatively narrow D (1.11 to 1.18, Table 1). Based on the elution times, fractions 3a and 3b mostly correspond to peak (I), 3c predominantly corresponds to peak (II), and 3d contains a mixture of peaks (II) and (III). Matrix-Assisted Laser Desorption Ionization-Time of Flight mass spectrometry (MALDI-TOF MS) confirmed the presence of high molecular weight polymers with molecular ion peaks corresponding up to a poly[53]catenane in 3b (Fig. 3D) and up to a poly[27]catenane for 3c (fig. S16).

One way to characterize the architectures (branched, linear or cyclic) of the poly[n]catenanes in fractions 3a–d is to elucidate the average number of chain ends (NC) of the polymers in each fraction. By definition, NC equals 0 for cyclic poly[n]catenanes, 2 for linear poly[n]catenanes and ±4 for branched poly[n]catenanes (Fig. 3B). With absolute molecular weight of each fraction available from MALS, their degrees of polymerization (DP which we define here as equivalent to n) can be readily calculated by M_MALS/1544 (results listed in Table 1), where M_MALS is the number average molecular weight from GPC-MALS and 1544 Da is the mean molecular weight of 2 and 4 (assuming a 1:1 ratio in the polymer); it is then possible to calculate NC by combining these data with NMR chain-end analysis (eq. S1). The key for such calculations is to find diagnostic chain-end peaks of poly[n]catenanes in the 1H NMR spectra. To do this, a (predominantly) [3]catenane 6 was targeted and synthesized by reacting 1 in the presence of two equivalents of 2 and Zn2+ ions (fig. S17), and its NMR spectrum was compared with 3a–d in Fig. 3E. The three groups of peaks for Hα/a of 6 with ca. 1:1:1 peak areas (fig. S17) were observed and defined as regions α (8.235–8.270 ppm), β (8.195–8.235 ppm) and γ (8.150–8.195 ppm), respectively. The lower intensity of region α in 3a–d compared to 6, along with longer NMR relaxation time of the protons in region α (fig. S18) confirm that this region corresponds to the chain-end (for details see supplementary materials). With this assignment, the average number of chain ends, NC, can be calculated by Eq. 1

\[ N_C = \frac{D_P \times \frac{2I_\alpha}{I_{A/a}}}{I_{A/a}} \]  

where Iα/a is the total peak integration of HA/a and Iα is the
chain-end peak integration of H_A/a (i.e. region $\delta$, see eqs. S1 to S3 for derivation details). The results of the N_c calculations for 3 and 3a-d are summarized in Table 1. Fractions 3a (N_c = 8.7) and 3b (N_c = 4.7) are predominantly branched, whereas 3c (N_c = 1.7) and 3d (N_c = 1.2) appear to contain different amounts of cyclic poly[n]catenanes that result in N_c < 2. In order to identify the proportion of cyclic poly[n]catenanes in these latter fractions, additional studies were undertaken to specifically target a cyclic poly[n]catenane 7. This was achieved by carrying out the MSP formation (using Fe^{2+} as the metal ion) and ring closing reaction at much lower concentrations (for details see supplementary materials and fig. S19). Comparison of the H_A/a region in the 'H-NMR (Fig. 3E) of the cyclic poly[n]catenanes containing fractions 3c, 3d and 7, all show an additional upfield shift to 8.06–8.15 ppm (Fig. 3E, green region), which is defined as region $\delta$, whereas the non-cyclic containing samples, 3a, 3b or 6, do not have any peaks in this region. Therefore, it is reasonable to conclude that region $\delta$ is unique for cyclic poly[n]catenanes. Compared to the acyclic poly[n]catenane (3a, 3b) or [3]catenane 7, it appears that ca. 50% of the A/a peaks of the cyclic poly[n]catenane 7 are shifted more upfield. One possible explanation is the cyclic architecture restricts the conformational mobility resulting in a more compact molecule (for example see fig. S19E) allowing additional shielding effects from neighboring aromatic moieties. Given that the integral of the H_A/a in 7 shows that ~50% of its H_A/a protons are present in the $\delta$ region (fig. S20) it is possible to determine the average number of chain ends for the acyclic poly[n]catenanes (N_c) present in each fraction by Eq. 2 (for derivation see eqs. S3 to S5)

$$N_c = DP \times \frac{2l_p}{l_{A/a} - 2l_p}$$

The results of these calculations show that both 3c and 3d have N_c ≤ 2 (with N_c < 2) consistent with the fact that they both contain a mixture of linear and cyclic poly[n]catenanes with the percentage of cyclic poly[n]catenanes in 3c and 3d being ~15% and ~34%, respectively (calculated via eq. S6). Table 1 summarizes the molecular weight and architectural data of 3 and the four fractions 3a-d. The highest molecular weight fraction 3a is assigned to highly branched poly[32–130]catenanes (based on MALS, fig. S15A) with an average DP = 55. Fraction 3b consists of lower degree of branching poly[n]catenanes with an average DP = 25. Fractions 3c and 3d contain mainly linear (with some cyclic) poly[n]catenanes with up to 27 (average DP = 11, fig. S15C) and 20 (average DP = 8, fig. S15D) interlocked rings, respectively. Based on the data from the four fractions, we can estimate that the overall percentage of branched, linear and cyclic poly[n]catenanes is ~24%, ~60% and ~16%, respectively, which matches well with the GPC peak deconvolution result (28%, 61%, 11%, respectively, Fig. 3A). Taken together these data are consistent with the poly[n]catenane 3 being a mixture of branched poly[13–130]catenanes, linear poly[7–27]catenanes and cyclic poly[4–7]catenanes, in approximately the aforementioned ratios.

It is known that catenanes prepared via metal templating exhibit metallo-responsive behavior (36) and, as such, the metallo stimuli-responsive properties of these poly[n]catenanes were investigated in both solution and bulk, by measuring the hydrodynamic radius R_h (with dynamic light scattering, DLS, Fig. 4A and fig. S21) and the glass transition temperature (T_g, Fig. 4B) for these poly[n]catenanes should lock the conformational motions of the rings, thereby inducing a switch from a highly flexible polymer to a semi-rigid polymer, where the flexibility comes primarily from the tetaethylene glycol (TEG) moieties (Fig. 4A). For predominantly linear poly[n]catenane, the addition of Zn^{2+} shows a significant (~70%) R_h increase from 3.9 nm to 6.6 nm (Fig. 4A). This result agrees well with all-atom molecular dynamics simulations of metallated linear poly[n]catenanes (for details see supplementary materials). Molecules were simulated with the OPLS all-atom force field (39) with 1,1,2,2-tetrachloro-ethane as the solvent, and the properties of the polymer were probed using a force-extension experiment. To model a poly[n]catenane under tension, a [8]catenane was connected to itself through periodic boundary conditions (Fig. 4C); the extension is enforced through the system (box) length, which is systematically varied; the corresponding tension follows from the pressure tensor (see eq. S9). The force-extension behavior is well described by the extensible worm-like chain (EWLC) model (40), as shown in Fig. 4C. According to this interpretation, each macrocycle’s contribution to the contour length, $l = 2.40 \pm 0.03$ nm, is considerably smaller than the persistence length, $l_p = 7.46 \pm 2.88$ nm, which is characteristic of a semi-rigid polymer. Again, this flexibility can be primarily attributed to the TEG segments of macrocycle 2, as evidenced by larger fluctuations in the inter-metal distances for 2 versus 4 (figs. S28 and S29). Based on simulations of a non-periodic metallated [4]catenane, R_h is approximately 34% of the end-to-end distance (R_{ee}). For poly[n]catenane of arbitrary DP R_{ee} can be calculated using wormlike chain statistics (eq. S15) and the results of the force extension simulations. R_h for an average poly[n]catenane in fraction 3e is thereby estimated at 6.89 ± 1.38 nm, in good agreement with DLS results (6.6 nm), further supporting the conclusion that fraction 3c is primarily linear poly[n]catenane (see supplementary materials for further discussion). The simulated structure of a metallated linear poly[n]catenane under ~15 picoNewton tension is illustrated in Fig. 4D, showing a segment of 12 interlocked rings.

Similar to linear poly[n]catenane, metallation of branched poly[n]catenane with Zn^{2+} shows a ~50% increase
in $R_n$ upon metatllation (5.0 nm to 7.6 nm, fig. S21B), presumably as a consequence of an extension of its arms. Metallation of cyclic poly[n]catenane 7 shows only a relatively small change of $R_n$ (~10%, from 2.4 nm to 2.6 nm, fig. S21C), which is consistent with its cyclic architecture restricting chain extension. In the bulk, the $T_m$s of poly[n]catenate with predominantly linear (3c) and branched architectures (3b) were found to be 97°C and 104°C, respectively, compared to 137°C for 5 (the linear ADMET polymer of 1) (Fig. 4B and fig. S22, determined by differential scanning calorimetry, DSC). In general, polymers with higher freedom of segmental motion show lower $T_m$s, which is consistent with the more facile conformational molecular motions expected in the poly[n]catenanes backbones. Metallation with Zn$^{2+}$ locks these conformational motions and significantly reduces the flexibility of poly[n]catenate; as such, no $T_m$s are observed upon heating up to 160°C for both linear and branched samples (Fig. 4B and fig. S22).

In conclusion, the successful synthesis of main-chain poly[n]catenanes via a MSP templated strategy has been achieved in ~75% yield. The isolated product mixture encompasses linear poly[7–27]catenanes, branched poly[13–130]catenanes and cyclic poly[4–7]catenanes. This synthetic strategy opens the door to the design and synthesis of a variety of new interlocked polymers.

REFERENCES AND NOTES


15. R. J. Wojcik, M. A. Meader, S. J. Rowan, Using the dynamic bond to access macroscopically responsive structurally dynamic polymers. Nat. Mater. 10, 14–27

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/cgi/content/full/science.aap7675/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S29
Tables S1 to S3
References (41–93)

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Fig. 1. Structure, conformational mobility of and synthetic approach to poly[n]catenanes. (A) Schematic representation of the poly[n]catenane architecture, which can be thought of as the molecular equivalent a robust and flexible metal chain; (B) the common conformational motions observed in catenanes; (C) comparison of the ring rotational mobilities in a poly[[2]catenane] versus a poly[n]catenane; (D) the targeted synthesis of poly[n]catenane 3 via assembling 1 and 2 into a metallo-supramolecular polymer (MSP) followed by ring-closing to yield poly[n]catenate (i.e. metallated poly[n]catenane) and demetallation; and (E) the structure of 1, 2 and 4 (ring-closed product of 1). A few key protons are labeled with blue capital letters in 4 and red lower-case letters in 2. The box highlights the structure of the Bip ligand moiety.
Fig. 2. NMR characterization and purification of the poly[\(n\)]catenanes. (A) Partial \(^1\)H NMR (600 MHz, CDCl\(_3\)) spectrum of the H\(_{A/B}\) region of the purified poly[\(n\)]catenane compared to individual rings 2, 4 and byproduct ADMET polymer 5 (for structure see fig. S5), with the protons corresponding to interlocked Bips moieties highlighted in yellow; (B) Chromatography-free purification of poly[\(n\)]catenanes via selective metallation and extraction; (C) partial \(^1\)H-\(^1\)H NOESY spectrum of the purified poly[\(n\)]catenane solution (1% w/v in CDCl\(_3\)) measured at \(-17^\circ\)C. Some NOE cross-peaks between 2 and 4 moieties are highlighted. For the full spectrum see fig. S13.
Fig. 3. Molecular weight and architecture characterization of the poly[n]catenanes. (A) GPC chromatogram, MALS absolute molecular weight measurement and peak deconvolution of 3. (B) Proposed architectures corresponding to the three deconvoluted peaks, the formation mechanism and corresponding $N_C$. (C) GPC chromatograms of fractionated polycatenane fractions (3a-d, intensity normalized by their relative mass % shown in figure) compared to the unfractionated poly[n]catenane 3. The elution volume ranges of the three deconvoluted peaks (I-III) are also shown in the figure. (D) MALDI-TOF of polycatenane fraction 3b; the lower peaks (marked with *) are from multiply charged molecular ions; (E) Partial $^1$H NMR (500 MHz, CDCl₃) spectra showing the $H_{\alpha/\beta}$ region of 3a-d compared to two controls: [3]catenane 6 and cyclic polycatenane 7. The four regions ($\alpha$, $\beta$, $\gamma$, $\delta$) are defined. The chain-end peaks and unique peaks for cyclic catenanes are highlighted in yellow and green, respectively.
Fig. 4. Experimental studies on and simulation of the metallated poly[n]catenanes. (A) Illustration of metallo-responsive conformational change of a linear poly[n]catenane between flexible and semi-rigid structures indicated by \( R_g \) change (details see fig. S21). The flexibility of metallated poly[n]catenane is primarily due to the TEG moiety of macrocycle 2. (B) The DSC of linear poly[n]catenane (demetallated and metallated) compared to the ADMET polymer 5 (\( T_g \) calculated by half-height midpoint). (C) Simulated force-extension curve produced by varying the box length of a metallated linear [8]catenane connected to itself through periodic boundary conditions in the \( z \)-direction. Data from simulations (green circles, size of data point includes error) are fit by the extensible worm-like chain (EWLC) model (black dashes). (D) Visualization of metallated linear poly[n]catenane (showing a segment of 12 interlocked rings) under \(~15\) pN tension from all-atom molecular dynamics simulations in 1,1,2,2-tetrachloroethane solvent (solvent and hydrogen atoms omitted for clarity).
Table 1. The molecular weight and architecture of 3 and 3a–d.

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