JOC The Journal of Organic Chemistry

Article

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[2]Rotaxane with Multiple Functional Groups

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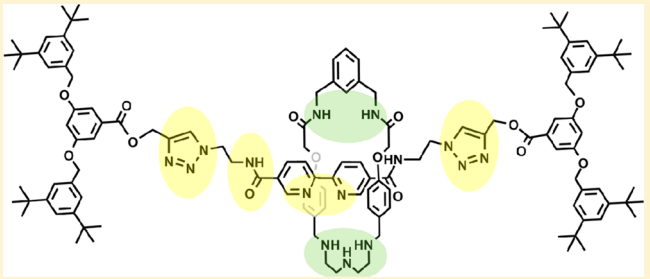
Supporting Information

ABSTRACT: High-yield syntheses of Cu(II)- and Ni(II)-templated [2]pseudorotaxane precursors (CuPRT and NiPRT, respectively) were achieved by threading bis(azide)bis(amide)-2,2′-bipyridine axle into a bis(amide)tris(amine) macrocycle. Single-crystal X-ray structural analysis of CuPRT revealed complete threading of the axle fragment into the wheel cavity, where strong aromatic $\pi-\pi$ stacking interactions between two parallel arene moieties of the wheel and the pyridyl unit of axle are operative in addition to metal ion templation. Attachment of a newly developed bulky stopper molecule with a terminal alkyne to CuPRT via a Cu(I)-catalyzed azide−alkyne cycloaddition reaction failed as a result of dethreading of the azide-terminated axle under the reaction conditions. However, the synthesis of a metal-free [2]rotaxane containing triazole with other functionalities in the axle was achieved in ∼45% yield upon coupling between azide-terminated NiPRT and the alkyne-terminated stopper. The [2]rotaxane was characterized by mass spectrometry, 1D and 2D NMR (COSY, DOSY, and ROESY) experiments. Comparative solution-state NMR studies of the [2]rotaxane in its unprotonated and protonated states were carried out to locate the position of the wheel on the axle of the metal-free [2]rotaxane. Furthermore, a variable-temperature ^{1}H NMR study in DMSO-d_6 of [2]rotaxane supported the kinetic inertness of the interlocked structure, where the newly developed stopper prevents dethreading of the 30-membered wheel from the axle.



INTRODUCTION

In general, rotaxanes have attracted more attention than other interlocked systems in studies of various non-covalent interactions and their potential applications in molecular devices and nanotechnology.[1−15] To obtain desirable properties in rotaxanes, various functional groups such as metal-chelating bipyridine units, amine/imine coordinating sites, paraquat, polyether, squaraine, amide, triazole/triazolium, and porphyrin have been introduced in the wheel, axle, or stopper component(s).[16−30] Judicial incorporation of different functional groups in such interlocked molecules has resulted in various highly complicated and well-defined mechanically interlocked systems, such as molecular shuttles,[31−44] molecular elevators,[45] molecular information ratchets,[46,47] and so on. Thus, interlocked molecules with multiple functional groups are in demand for the development of various new molecular machineries. The integration of porphyrin and 1,10-phenanthroline into the wheel component results in an adaptable [3]rotaxane receptor,[48] while an axle containing both amide and triazolium functionalities in rotaxanes exhibits anion recognition properties.[25] Furthermore, cation-induced motion of a molecular shuttle has been observed in a multistation rotaxane with an amide/amine axle and a polyether/amine-containing wheel.[49] Rotaxanes with amide functionalities in the wheel/axle components are promising for hydrogen-bonding and anion coordination properties.[50,51] Herein we report a new [2]rotaxane whose backbone contains various functionalities such as amide, tris(amine), bipyridyl, triazole, and ester, which are potential sites for metal coordination, hydrogen bonding, anion binding and $\pi-\pi$ stacking interactions. Furthermore, a new stopper unit has also been obtained that can resist dethreading of the 30-membered macrocycle wheel even at elevated temperature.

RESULTS AND DISCUSSION

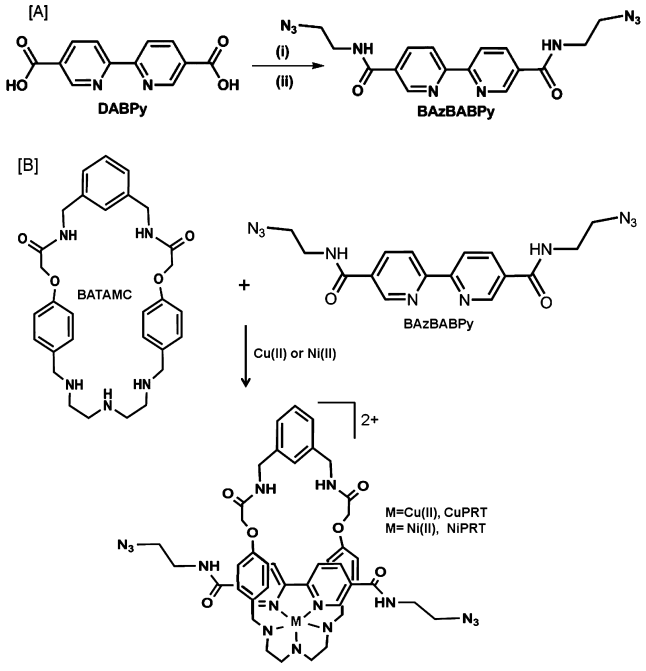
Strategy and Design Aspects. Different types of template strategies have been developed for effective syntheses of rotaxanes.[10,25,52−63] Transition metal ion-templated threading is one of the popular strategies for interlocked molecular systems.[28,64−67] In this direction, copper(I)-templated threaded molecules have been mostly explored by Sauvage and co-workers.[68−70] Our recent studies have shown that Cu(II) can act as an excellent template for high-yielding syntheses of threaded heteroleptic complexes (pseudorotaxanes) with "3 + 2" donor sets of a bis(amide)tris(amine) wheel and bidentate chelating axle.[71−73] In the present study, our obvious choice of wheel was a bis(amide)tris(amine) macrocycle (BATAMC). On the other hand, a 2,2′-bipyridine unit was chosen as the primary functionality in the axle design, which can be functionalized with bis(amide) and bis(azide) groups to introduce multiple functionalities in the axle component

Received: September 29, 2014
Published: October 29, 2014

   dx.doi.org/10.1021/jo502235z | J. Org. Chem. 2014, 79, 11170−11178

(BAzBABPy) (Scheme 1). Thus, "3 + 2" threading between BATAMC and BAzBABPy templated by Cu(II) or Ni(II)

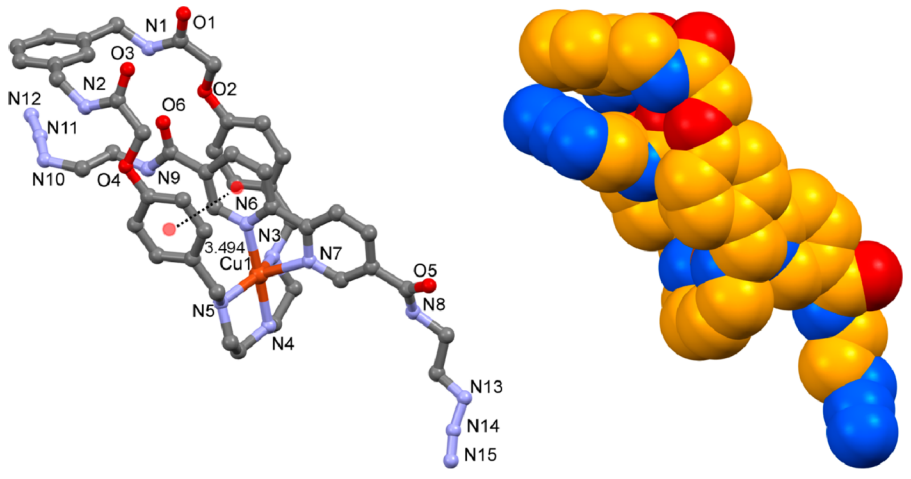
Scheme 1. (A) Synthetic Scheme for the Axle Fragment BAzBABPy [(i) $SOCl_2$, 80 °C; (ii) 2-Aminoethyl Azide, 0 °C]; (B) Synthetic Route for the [2]Pseudorotaxanes CuPRT and NiPRT



might result in heteroleptic complexes with pseudorotaxane architecture. In that case, the terminal azide functionalities in the axle fragment of the [2]pseudorotaxane could be utilized as a precursor for the synthesis of a [2]rotaxane via a copper(I)-catalyzed azide−alkyne cycloaddition reaction ("click" chemistry) with an alkyne-terminated stopper.

Synthesis of [2]Pseudorotaxane Precursors. The axle fragment, bis(azide)bis(amide)-2,2′-bipyridine (BAzBABPy) was synthesized in good yield in three steps starting from 5,5′-dimethyl-2,2′-bipyridine (Scheme 1A). First, 5,5′-dimethyl-2,2′-bipyridine was oxidized with potassium dichromate in sulfuric acid to give 2,2′-bipyridyl-5,5′-dicarboxylic acid (DABPy), which was reacted with thionyl chloride to synthesize the corresponding diacid chloride. Finally, the reaction of 2,2′-bipyridyl-5,5′-dicarbonyl chloride with 2-aminoethyl azide afforded the axle precursor BAzBABPy via amide bond formation. This bis(azide)-terminated linear-type molecule BAzBABPy can act as an axle fragment toward the synthesis of M(II) (M = Cu, Ni)-templated [2]-pseudorotaxanes by "3 + 2" heteroleptic threaded complex formation (Scheme 1B). These two [2]pseudorotaxanes (CuPRT and NiPRT) were synthesized upon reaction of BATAMC (1 equiv) with BAzBABPy (1 equiv) in the presence of $Cu(ClO_4)_2$ or $Ni(ClO_4)_2$ (1 equiv), respectively, in CH_3OH/CH_2Cl_2 solution at room temperature. The ESI-MS spectra of CuPRT and NiPRT showed prominent peaks at m/z 1072.97 and 1068.08 corresponding to $[CuPRT-ClO_4]^+$ and $[NiPRT-ClO_4]^+$, respectively. Thus, ESI-MS of both CuPRT and NiPRT clearly indicated 1:1:1 complexation of the wheel, axle, and M(II) template ion in the [2]pseudorotaxanes. Furthermore, the formation of the heteroleptic threaded complex between BATAMC and BAzBABPy was confirmed by a single-crystal X-ray diffraction study of CuPRT (Figure 1). In the complex, the Cu(II) center is pentacoordinated, with three coordination sites attached to the NH sites of BATAMC and the other two coordinated to the nitrogen atoms of the bidentate chelate of BAzBABPy. The Cu−N bond lengths around the Cu(II) center in CuPRT are in the range of 1.987−2.184 Å. Two parallel arene moieties of BATAMC and the pyridyl unit of BAzBABPy are within the $\pi-\pi$ stacking interaction distance. The interaction distances between the centroids of the arene units of BATAMC and the centroid of the pyridyl ring of BAzBABPy are 3.474 and 3.494 Å (Figure 1a). The space-filling model of CuPRT clearly shows complete threading of the BAzBABPy into the macrocyclic cavity of BATAMC with the azide terminals exposed outside the wheel in the [2]pseudorotaxane structure. Thus, the two azide terminals are accessible for further functionalization.

Synthesis of the [2]Rotaxane. Attempts were made to synthesize the metal-free [2]rotaxane using azide-terminated

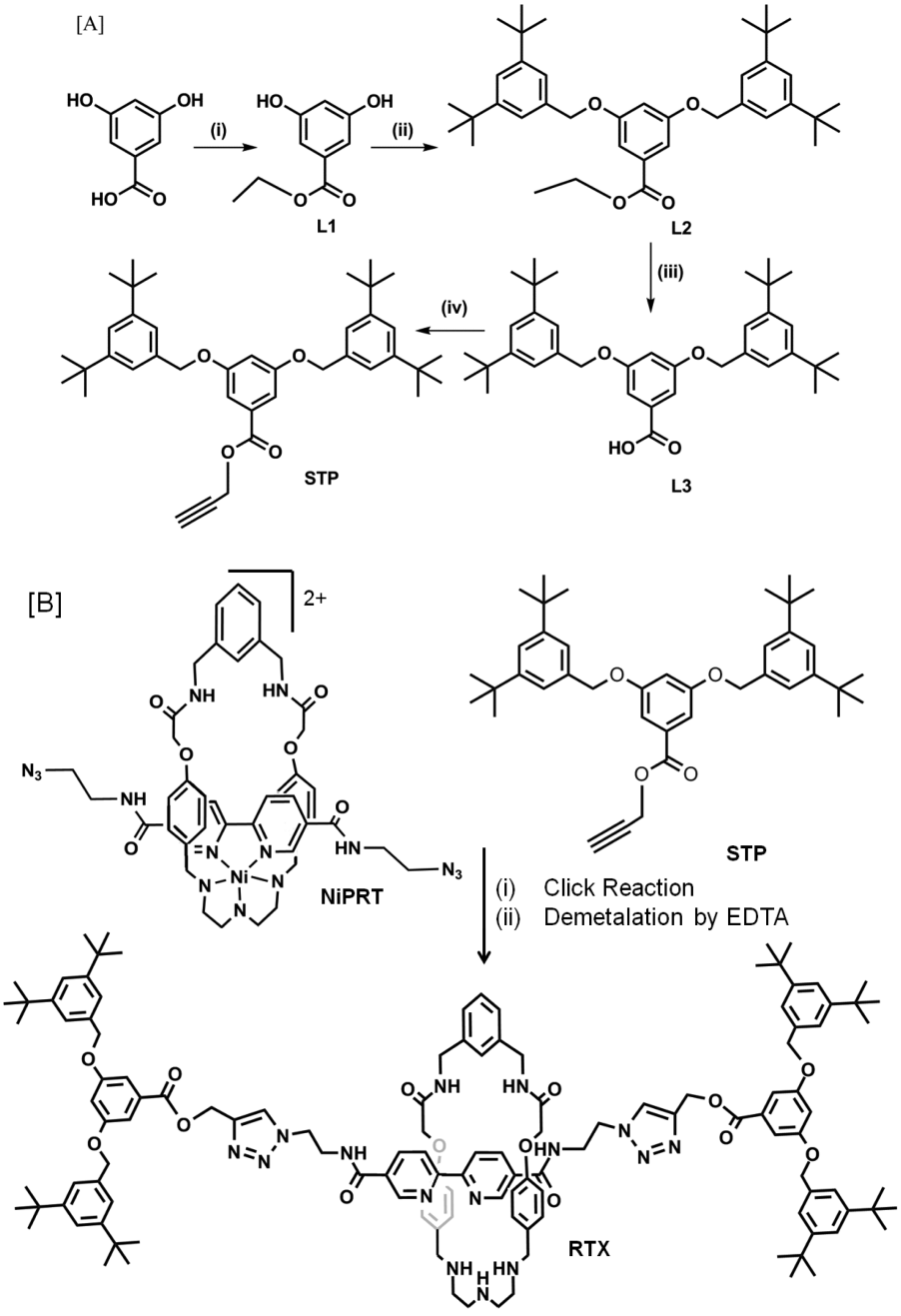


(a) (b)

Figure 1. Single-crystal X-ray structure of azide-terminated [2]pseudorotaxane CuPRT using (a) ball-and-stick and (b) space-filling models. H atoms, counteranions, and solvent molecules have been omitted for clarity.

dx.doi.org/10.1021/jo502235z | J. Org. Chem. 2014, 79, 11170−11178

Scheme 2. (A) Synthesis of STP [(i) Ethanol, H_2SO_4, Reflux, 12 h; (ii) 3,5-Di-*tert*-butylbenzyl Bromide, CH_3CN, Reflux, 24 h; (iii) LiOH, HCl, THF/H_2O, RT, 24 h; (iv) Propargyl Bromide, TBAF, THF, RT, 8 h]; (B) Synthetic Route for the Metal-Free [2]Rotaxane RTX



[2]pseudorotaxane precursors CuPRT and NiPRT by attaching stoppers at both the ends of the axle fragment. Traditional bulky stoppers, such as triphenylmethyl (trityl) units are the most popular stoppers and have been used extensively in the last few decades.[74−76] To achieve potential functional diversity in the interlocked molecules, we synthesized a new bulky molecule having ester functionality and a di-*tert*-butylbenzyl-substituted aromatic platform as a new stopper unit (Scheme 2A). The stopper was synthesized in good yield in four steps starting from 3,5-dihydroxybenzoic acid. Esterification of 3,5-dihydroxybenzoic acid generated 3,5-dihydroxybenzoic acid ethyl ester (L1), which upon reaction with 3,5-di-*tert*-butylbenzyl bromide in the presence of K_2CO_3 in dry CH_3CN afforded ethyl 3,5-bis(3,5-di-*tert*-butylbenzyloxy)-benzoate (L2). Then L2 was hydrolyzed to give 3,5-bis(3,5-di-*tert*-butylbenzyloxy)benzoic acid (L3) in LiOH in 1:1:1 THF/CH_3OH/H_2O. Finally, alkyne terminal stopper prop-2-ynyl 3,5-bis(3,5-di-*tert*-butylbenzyloxy)benzoate (STP) was obtained by the ester formation reaction between propargyl bromide and L3 in the presence of tetrabutylammonium fluoride in dry THF.

To synthesize the [2]rotaxane, the azide-terminated [2]-pseudorotaxane precursors CuPRT and NiPRT were separately reacted with alkyne-functionalized stopper STP by the Cu(I)-catalyzed click reaction. Our attempts to synthesize the [2]rotaxane from CuPRT either under click reaction conditions

dx.doi.org/10.1021/jo502235z | J. Org. Chem. 2014, 79, 11170−11178

of sodium ascorbate and Cu(II) or by the direct use of Cu(I) with Na_2CO_3 in an inert atmosphere were unsuccessful. ESI-MS studies of the above reaction mixtures indicated the formation of the axle terminated with the stopper without any interlocked product (Figure 25S in the Supporting Information), which indicates complete dethreading of the axle fragment from CuPRT under the reaction conditions followed by azide−alkyne cycloaddition reaction between the dethreaded axle fragment and the alkyne stoppers. In fact, no trace of Cu(II)-templated rotaxane could be observed by ESI-MS. In the presence of sodium ascorbate, the Cu(II) center in CuPRT could easily be reduced to Cu(I), and the overall coordination environment of the threaded adduct (3+2 format) might disfavor Cu(I) templation, which would result in dethreading of the azide axle from the reduced CuPRT. To avoid such a reduction process during stoppering, we further attempted the click reaction in an inert atmosphere using $[Cu(CH_3CN)_4](PF_6)$ catalyst in the presence of Na_2CO_3. Unfortunately, the reaction also failed under these reaction conditions. However, such difficulties were overcome when the Ni(II)-templated pseudorotaxane NiPRT was used as the precursor. The reaction of azide-terminated NiPRT with the alkyne-terminated ester-functionalized stopper STP in the presence of a catalytic amount of $Cu(CH_3CN)_4PF_6$ followed by in situ demetalation afforded the metal-free [2]rotaxane (RTX) (Scheme 2B). RTX was purified by column chromatography (SiO_2, eluting with 3% CH_3OH/DCM) in 45% yield. The free axle with stopper (AXL) was also isolated in 30% yield during the purification process by column chromatography. Eventually, the click reaction in the final step of the [2]rotaxane synthesis produces a 1,2,3-triazole unit in the axle backbone, a versatile functionality for anion recognition via polarized C−H hydrogen-bonding interactions. Furthermore, the N-donor sites of the triazole unit in RTX could potentially be used for metal ion coordination.

Formation of the [2]rotaxane was confirmed by ESI-MS and 1D and 2D NMR spectroscopy (COSY, DOSY, and ROESY) experiments. The ESI-MS spectrum of RTX shows prominent peaks at m/z 2106.22 and 1053.12 that correspond to $[RTX + H]^+$ and $[RTX + 2H]^{2+}$, respectively, and the similarity between the calculated and experimental isotope distribution patterns is quite obvious (Figure 2).

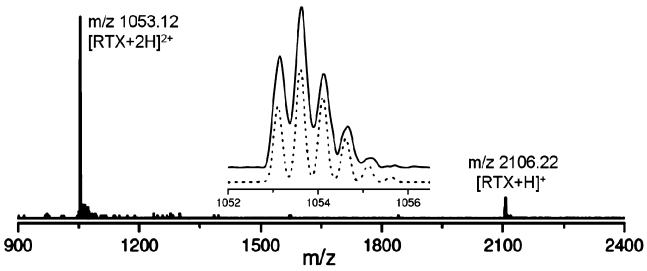


Figure 2. ESI-MS (positive-ion mode) spectrum of RTX. The inset shows the similarity of the calculated (dotted) and experimental (bold) isotope distribution patterns of $[RTX + 2H]^{2+}$.

Comparative ^{1}H NMR spectra of the wheel BATAMC, the axle with stopper AXL, and the [2]rotaxane RTX in $CDCl_3$ are shown in Figure 3. In the spectrum of RTX, the triazole C−H proton H^7 is shifted downfield relative to that of AXL ($\Delta\delta$ = 0.2 ppm), indicating its hydrogen-bonding interaction. The bipyridine protons H^1, H^2, and H^3 of the axle and protons H^g and H^i of the wheel in RTX show upfield shifts with respect to their non-interlocked counterparts. Such chemical shifts indicate that these protons in RTX are located in the shielded region composed of aromatic moieties of the wheel and axle. This indicates that the aromatic units of the axle and wheel components are positioned face-on in case of the interlocked RTX system. Downfield perturbations of proton H^c and the amide protons H^e of the macrocycle and the amide proton H^4 of the axle indicate hydrogen-bonding interactions between the macrocycle and the axle in RTX. Additionally, splitting of the resonances corresponding to the methylene protons H^k and H^l of the macrocycle indicate the reduced symmetry of these protons in the interlocked structure of RTX.

The DOSY NMR spectrum of RTX provides further evidence for the formation of the interlocked structure. Figure 4 depicts the DOSY spectrum of RTX in $CDCl_3$ at 298 K. It is evident from the spectrum that all of the peaks correlated to the signals in the chemical shift dimensions are in a horizontal line. Thus, all of proton signals due to the wheel BATAMC and the axle AXL of the [2]rotaxane display the same diffusion coefficient ($D = 3.3 \times 10^{-10}$ m^2 s^{-1}), indicating that they are parts of the same species.

Two-dimensional ^{1}H−^{1}H rotating-frame Overhauser effect spectroscopy (ROESY) provides further evidence of the interlocked nature of RTX (Figure 20S in the Supporting Information). The ^{1}H−^{1}H ROESY spectrum displays several through-space cross-coupling interactions between the two components of the [2]rotaxane. Important interactions include those between H^g and H^1 and those between H^c and H^3, which indicate that the bipyridine moiety of the axle is spatially close to the wheel cavity, further confirming the interlocked architecture of RTX in solution (Figure 5).

The stability of the interlocked structure and the location of the wheel on the axle component were also investigated in the protonated state of RTX by 1D and 2D NMR studies. Since RTX contains three amine groups in the wheel and bipyridine/triazole groups in the axle, a strong acid such as TFA can easily protonate the system. Figure 6 shows the ^{1}H NMR spectrum of RTX in the presence of TFA (10 equiv) in $CDCl_3$. Comparison of the ^{1}H NMR spectra of protonated and unprotonated RTX reveals protonation of RTX in which the three amine sites of the wheel and the bipyridine and triazole units of the axle are protonated (Figure 6). The resonances of protons H^i, H^k, and H^l of the macrocycle, H^1, H^2, and H^3 of the bipyridine unit, and H^7 of the triazole moiety are observed to be shifted downfield in the case of protonated RTX. Furthermore, comparison of the ^{1}H NMR spectra of protonated RTX, protonated BATAMC, and protonated AXL and an ^{1}H−^{1}H NOESY study of protonated RTX indicate that the wheel resides on the bipyridinium unit of the axle (Figure 24S in the Supporting Information and Figure 7). The analysis of the ^{1}H−^{1}H NOESY spectrum of protonated RTX, which shows several clear cross-peaks between protons related to the protonated axle and protonated wheel (H^g and H^2; H^g and H^3; H^h and H^3; and H^c and H^2), firmly proves the host−guest interaction (Figure 7). The important interactions between H^g and H^2, between H^g and H^3, and between H^h and H^3 confirm that the electron-rich phenylene units of the protonated wheel and the electron-poor bipyridinium moiety of the protonated axle are in close proximity and that strong aromatic π−π interactions are present. These interactions might favor the wheel to reside on the bipyridium moiety of the axle in protonated and unprotonated RTX.

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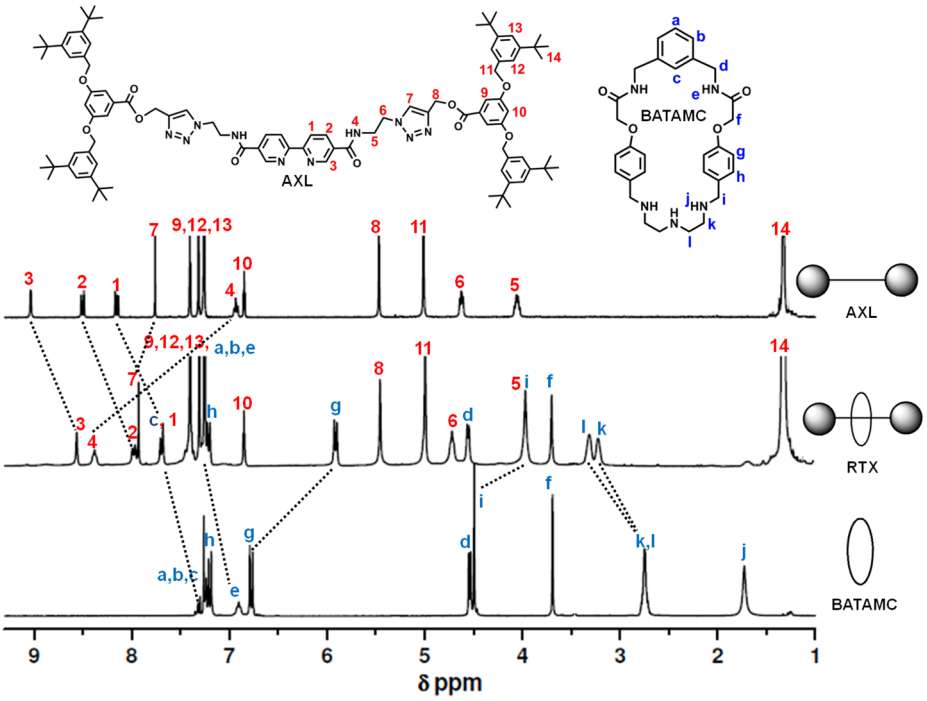

Figure 3. Partial stacked ^{1}H NMR spectra (300 MHz) in $CDCl_3$ at 298 K of (bottom) the macrocycle BATAMC, (middle) the [2]rotaxane RTX, and (top) the stopper-terminated free axle AXL (top). The labels correspond to those shown in the inset pictures of BATAMC and AXL.

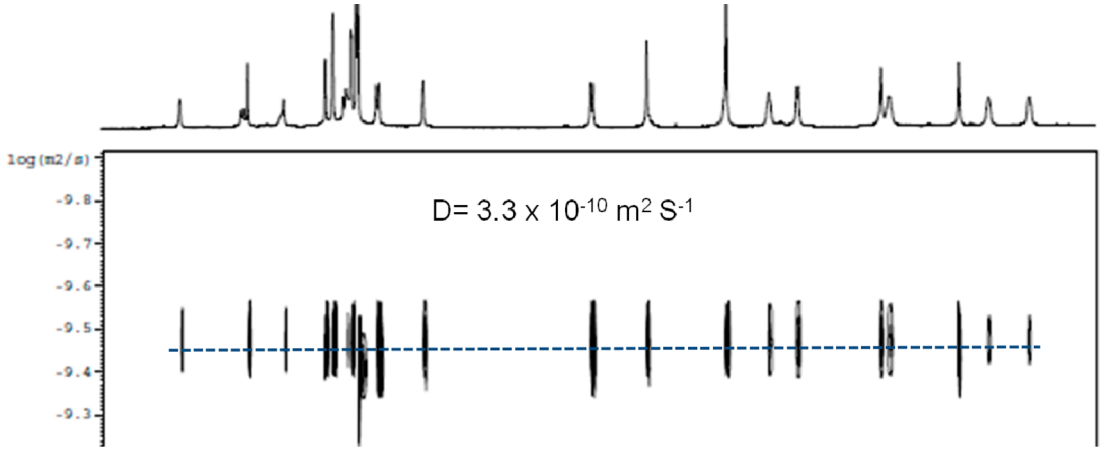

Figure 4. Partial DOSY spectrum in $CDCl_3$ of RTX with a diffusion coefficient value (D) showing a single supramolecular aggregate.

The kinetically inert nature of the interlocked compound RTX was verified via slippage experiments. No evidence of dethreading was observed, as judged by variable-temperature (VT) ^{1}H NMR spectroscopy, even when RTX (4 mM) was heated for several hours at 353 K in DMSO-d_6. The temperature of RTX solution was raised from 298 to 353 K, and the spectra are shown in Figure 8. The VT-NMR analysis reveals that there was no significant change in the protons of the [2]rotaxane. However, the amide protons (−NH) corresponding to the wheel (yellow) and axle (green) were slightly shifted upfield by 0.16 and 0.23 ppm, respectively, at 353 K. These upfield shifts at elevated temperature could be due to breakage of hydrogen bonds between amide −NH protons and solvent molecules. Thus, the VT-NMR study indicates that the stopper is sufficiently bulky to prevent dethreading of the 30-membered wheel in the [2]rotaxane architecture even at an elevated temperature.

CONCLUSION

An azide-terminated 2,2′-bipyridine-based bis(amide)bis(azide) axle has been established as a versatile thread for the tris-chelating macrocycle wheel templated by Cu(II) and Ni(II). The azide axle fragment allows easy coordination with the template metal center in the cavity of the tris-chelating wheel in an orthogonal orientation, forming metallopseudorotaxanes with azide groups exposed outside the cavity of the wheel. This indeed makes these pseudorotaxanes suitable precursors for synthesis of other interlocked molecules. A metal-free [2]-rotaxane enriched with a number of functional groups such as 2,2′-bipyridine, amide, ester, and triazole functionalities was synthesized from the Ni(II)-templated [2]pseudorotaxane upon coupling with a newly developed alkyne-terminated stopper unit via the click reaction. The mechanically interlocked bis(amide)tris(amine) wheel was found be located at the center of the axle in both the free and protonated states

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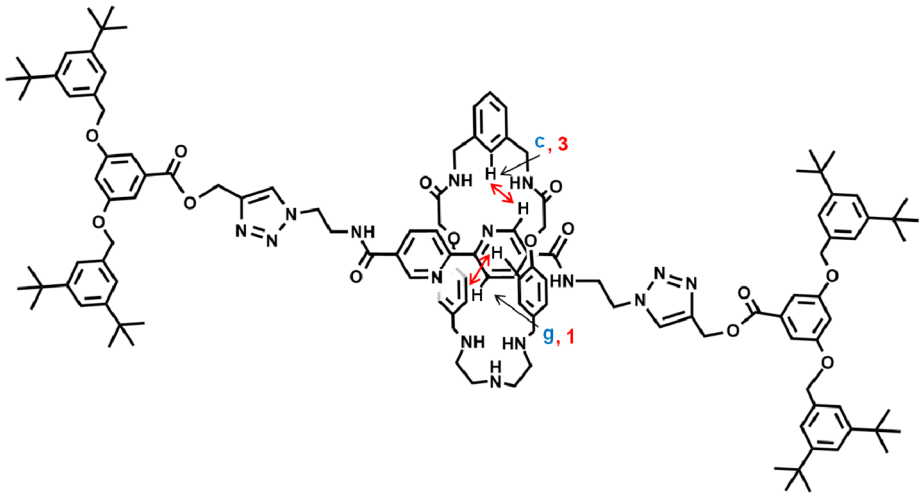

Figure 5. Chemical structure of RTX with intercomponent through-space $^{1}H-^{1}H$ interactions.

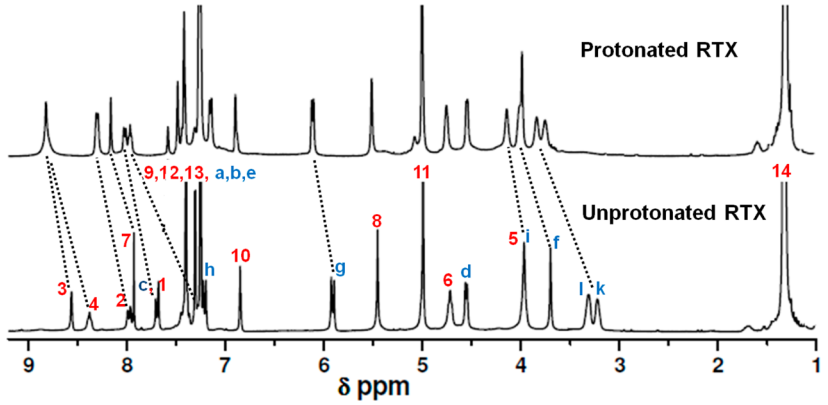

Figure 6. Comparison of the ^{1}H NMR spectra of (top) protonated and (bottom) unprotonated RTX in $CDCl_3$ at 298 K.

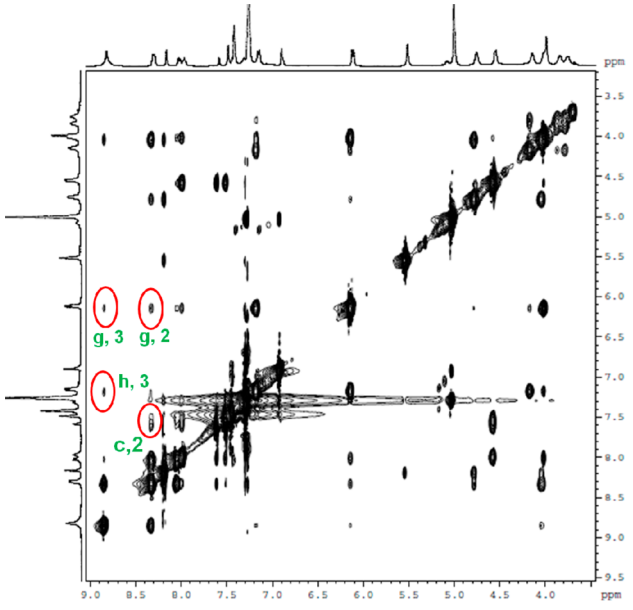

Figure 7. $^{1}H-^{1}H$ NOESY NMR spectrum of protonated [2]rotaxane RTX in $CDCl_3$ at 298 K. Assignable intercomponent through-space interactions are highlighted.

of the [2]rotaxane. Moreover, the newly developed stopper is able to prevent dethreading of the 30-membered wheel from the axle of the [2]rotaxane even at an elevated temperature. We are presently exploring various embedded functionalities in such rotaxane molecules.

EXPERIMENTAL SECTION

General Details. The reagents were obtained from commercial suppliers and used as received without further purification, unless otherwise indicated. 2,2′-Bipyridine-5,5′-diacid chloride,[77] 2-azido-1-ethylamine,[78] the macrocycle BATAMC,[71] and L1[79] were synthesized using previously reported procedures. Peak assignments in the ^{1}H NMR spectra were confirmed using COSY spectra of selected compounds. DEPT-135 spectra were used to interpret the ^{13}C NMR spectra. The special interactions between the protons of the wheel and those of the axle were interpreted by COSY and ROESY NMR spectroscopy in $CDCl_3$.

X-ray Crystallography. Crystals of CuPRT suitable for single-crystal X-ray diffraction studies were obtained upon slow evaporation of a methanol solution at room temperature. A single crystal was selected from the mother liquor, immersed in Paratone oil, mounted on the tip of a glass fiber, and cemented using epoxy resin. Intensity data for the CuPRT crystal were collected using Mo Kα radiation (λ = 0.7107 Å) at 298 K. The data integration and reduction were done using the SAINT[80] software provided with the software package for the SMART APEX II system. An empirical absorption correction was applied to the collected reflections using SADABS,[81] and the structure was solved by direct methods using SHELXTL[82] and refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[83] program package. Graphics were generated using MERCURY 2.3[84]

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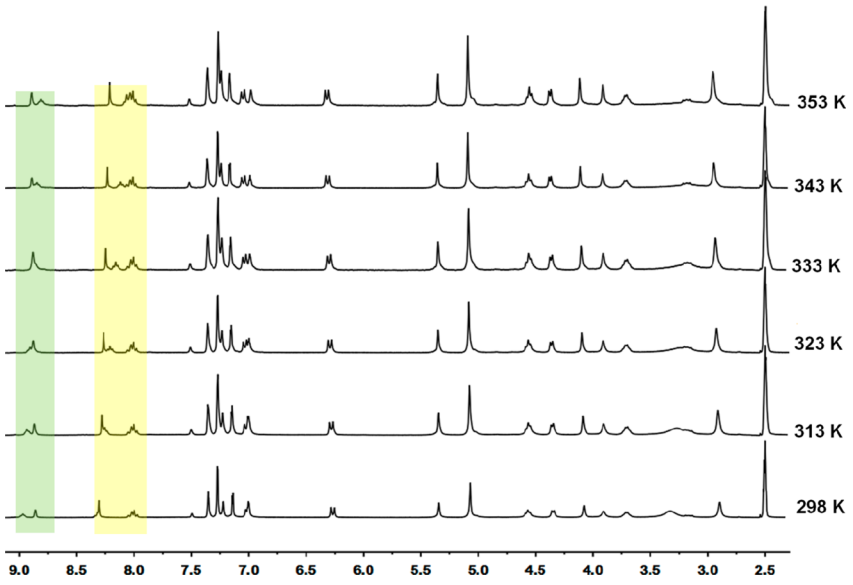

Figure 8. Variable-temperature ^{1}H NMR spectra of RTX in DMSO-d_6 (300 MHz).

and PLATON,[85] and the non-hydrogen atoms were refined anisotropically until convergence.

Synthesis of BAzBABPy. To a solution of 2-azido-1-ethylamine (0.172 g, 2.0 mmol) and NEt_3 (0.348 mL, 2.5 mmol) in dry THF (25 mL) was added 2,2′-bipyridine-5,5′-diacid chloride (281 mg, 1 mmol) dissolved in dry THF (10 mL) dropwise using a pressure-equalizing funnel. The mixture was allowed to stir in a nitrogen atmosphere for 0.5 h at 0 °C and then for 3 h at room temperature. An off-white precipitate then developed and was filtered. The precipitate was washed with $NaHCO_3$ solution (50 mL) and water (100 mL) and dried in vacuum to obtain BAzBABPy as an off-white solid in 84% yield (0.320 g). ESI-MS$^+$ *m*/*z*: calcd for $C_{16}H_{17}N_{10}O_2$ $[M + H]^+$ 381.37, found 381.16. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.35 (s, 4H, $-CH_2$), 8.39 (d, 2H, J = 9 Hz, Ar-*H*), 8.54 (d, 2H, J = 6 Hz, Ar-*H*), 9.03 (b, 2H, $-NH$), 9.13 (s, 2H, Ar-*H*). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 39.1, 49.7, 120.6, 130.0, 136.3, 148.4, 156.4, 165.1. Anal. Calcd for $C_{16}H_{16}N_{10}O_2$: C, 50.52; H, 4.24; N, 36.82. Found: C, 50.34; H, 4.19; N, 36.93.

Synthesis of L2. In a 100 mL round-bottom flask, L1 (0.910 g, 5 mmol) was dissolved in 50 mL of dry acetonitrile. K_2CO_3 (2 g, 15 mmol) and 3,5-di-*tert*-butylbenzyl bromide (2.8 g, 10 mmol) were added to that solution at room temperature. The reaction mixture was allowed to stir at 80 °C in a nitrogen atmosphere for 24 h. Then the solvent was evaporated under reduced pressure, and the solid was dissolved in dichloromethane. This solution was extracted with a solution of brine. After evaporation of the solvent, a liquid compound was obtained that was became solid upon the addition of a small portion of methanol (5 mL). The resulting off-white solid was purified by silica gel column chromatography, eluting with 2% ethyl acetate/petroleum ether, to afford the targeted disubstituted product L2 in 60% yield (1.75 g). ESI-MS$^+$: *m*/*z* 609.38 $[M + 23]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.367 (s, 36H, $-C(CH_3)_3$), 1.43 (t, 4H, J = 4 Hz, $-CH_3$), 4.41 (q, 2H, J = 6.9 Hz, $-CH_2$), 5.07 (s, 1H, Ar$-CH_2$), 6.892 (t, 1H, J = 2.4 Hz, Ar-*H*), 7.31 (br, 4H, Ar-*H*), 7.36 (d, 2H, J = 2.4 Hz, Ar-*H*), 7.442 (t, 2H, J = 2.8 Hz, Ar-*H*). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 14.5, 31.6, 30.0, 61.3, 71.4, 107.3, 108.5, 122.4, 122.5, 132.5, 135.6, 151.3, 160.1, 166.6. Anal. Calcd for $C_{39}H_{54}O_4$: C, 79.82; H, 9.27. Found: C, 80.02; H, 9.41.

Synthesis of L3. The reaction mixture of L2 (587 mg, 1 mmol) and LiOH monohydrate (126 mg, 3 mmol) in 1:2 water/THF (3 mL) was stirred at 30 °C for 24 h. The THF layer was evaporated, and dilute HCl was added to the aqueous part. A white precipitate of L3 was formed. The solution was filtered, and the white precipitate was isolated by repeated washing with water. This white solid L3 was dried and used in the next step without further purification. Yield: 0.48 g (86%). ESI-MS$^+$ *m*/*z*: calcd for $C_{37}H_{50}O_4K$ $[M + K]^+$ 597.89, found 597.27. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 36H, $-C(CH_3)_3$), 5.07 (s, 4H, Ar$-CH_2$), 6.93 (t, 1H, J = 3 Hz, Ar-*H*), 7.31 (br, 4H, Ar-*H*), 7.42−7.44 (m, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 32.5, 36.0, 72.3, 109.4, 110.0, 123.4, 123.5, 132.3, 136.4, 152.2, 161.2, 172.8. Anal. Calcd for $C_{37}H_{50}O_4$: C, 79.53; H, 9.02. Found: C, 79.71; H, 9.16.

Synthesis of the Stopper STP. To a solution of L3 (1.1 g, 2 mmol) in dry THF (5 mL) was added 1.2 equiv of TBAF (627.5 mg, 2.4 mmol) (1 M in THF), and the mixture was stirred at 30 °C in a nitrogen atmosphere. To this solution was added propargyl bromide (0.196 mL, 2.2 mmol). After the addition, the reaction mixture was allowed to stir at room temperature in a nitrogen atmosphere for another 6 h. The solution was evaporated, and the residue was dissolved in CH_2Cl_2. The resulting solution was washed three times with saturated $NaHCO_3$ solution followed by saturated NaCl solution. The off-white solid was isolated and dried over vacuum to yield the desired product STP. Yield: 950 mg (80%). ESI-MS$^+$ *m*/*z*: calcd for $C_{40}H_{52}O_4Na$ $[M + Na]^+$ 619.38, found 619.48. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 36 H, $-C(CH_3)_3$), 2.51 (t, 1H, J = 3 Hz, $-CH$), 4.92 (d, 2H, J = 3 Hz, $-CH_2$), 5.04 (s, 4H, Ar$-CH_2$), 6.88 (t, 1H, J = 3 Hz, Ar-*H*), 7.28 (d, 4H, J = 2 Hz, Ar-*H*), 7.36 (d, 2H, J = 2 Hz, Ar-*H*), 7.41 (t, 2H, J = 2 Hz, Ar-*H*). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 31.6, 35.0, 52.7, 71.4, 75.2, 77.8, 107.9, 108.7, 122.4, 122.5, 131.3, 135.5, 151.3, 160.2, 166.8. Anal. Calcd for $C_{40}H_{52}O_4$: C, 80.50; H, 8.78. Found: C, 80.24; H, 8.70.

Synthesis of [2]Pseudorotaxanes CuPRT and NiPRT. A solution of $M(ClO_4)_2{\cdot}6H_2O$ (M = Cu, Ni) (0.1 mmol) in CH_3OH (5 mL) was added to a solution of BATAMC (53.1 mg, 0.1 mmol) in 1:1 CH_3OH/CH_2Cl_2 (5 mL) at room temperature. To this solution was added the diazide axle BAzBABPy (38 mg, 0.1 mmol). The resultant mixture was stirred for 4 h, and the solvent was evaporated. The solid was washed repeatedly with CH_2Cl_2 and dried in vacuo to give the pure products CuPRT and NiPRT in yields of 87 and 85 mg, respectively (70−75%). The complexes were characterized by ESI-MS and elemental analysis. Data for CuPRT: ESI-MS$^+$ *m*/*z*: calcd for $C_{46}H_{53}ClCuN_{15}O_{10}$ $[CuPRT + ClO_4^-]^+$ 1073.32, found 1072.97. Anal. Calcd for $C_{46}H_{53}Cl_2CuN_{15}O_{14}$: C, 47.04; H, 4.55; N, 17.89. Found: C, 47.10; H, 4.62; N, 17.95. Data for NiPRT: ESI-MS$^+$ *m*/*z*: calcd for $C_{46}H_{53}ClNiN_{15}O_{10}$ $[NiPRT + ClO_4^-]^+$ 1068.31, found 1068.08. Anal. Calcd for $C_{46}H_{53}Cl_2N_{15}NiO_{14}$: C, 47.24; H, 4.57; N, 17.96. Found: C, 47.18; H, 4.62; N, 17.88. Single crystals of CuPRT suitable for X-ray analysis were obtained by slow evaporation of a methanol solution at room temperature.

Synthesis of the [2]Rotaxane RTX Using $Cu(CH_3CN)_4PF_6$ inside the Glovebox. NiPRT (0.23 g, 0.2 mmol) and STP (0.23 g, 0.4 mmol) were suspended in 4 mL of 1:1 CH_2Cl_2/CH_3CN solution. Sodium carbonate (0.10 mg, 0.10 mmol) was added as a solid, followed by the addition of $Cu(CH_3CN)_4PF_6$ (112 mg, 0.03 mmol) in the glovebox. The reaction mixture was stirred overnight at room temperature and then evaporated. A 10 mL saturated solution of Na_2EDTA in water was added to the crude residue, and the mixture was stirred for 6 h. The solution was poured into 25 mL of $CHCl_3$ and washed with water. The organic layer was evaporated under reduced pressure to obtain an off-white solid. The resulting solid was purified by silica column chromatography, eluting with 3% CH_3OH/CH_2Cl_2, to afford the targeted [2]rotaxane RTX in 45% yield (170 mg) along with the free axle AXL (95 mg, 30%).

Synthesis of RTX Using $CuSO_4{\cdot}5H_2O$ and Sodium Ascorbate. NiPRT (0.23 g, 0.2 mmol) and STP (0.23 g, 0.4 mmol) were suspended in 4 mL of 1:1 THF/H_2O solution. Then an aqueous solution of sodium ascorbate (50 mg) and $CuSO_4{\cdot}H_2O$ (50 mg) was added to the reaction mixture under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature and then evaporated. A 10 mL saturated solution of Na_2EDTA in water was added to the crude residue, and the mixture was stirred for 6 h. The solution was poured into 25 mL of $CHCl_3$ and washed with water. The organic layer was evaporated under reduced pressure to obtain an off-white solid. The resulting solid was purified by silica column chromatography, eluting with 3% CH_3OH/CH_2Cl_2, to afford RTX in 40% yield (150 mg) along with AXL.

Data for RTX. ESI-MS^+ m/z: calcd for $C_{126}H_{158}N_{15}O_{14}$ $[M + H]^+$ 2106.69, found 2106.22. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 36H, $-C(CH^{14}{}_3)_3$), 3.23 (s, 4H, $-CH^k{}_2$), 3.31 (s, 4H, $-CH^l{}_2$), 3.70 (s, 4H, $-CH^f{}_2$), 3.97 (s, 8H, $-CH^{i,s}{}_2$), 4.56 (d, 4H, J = 3 Hz, Ar$-CH^d{}_2$), 4.72 (m, 4H, $-CH^6{}_2$), 4.99 (s, 8H, Ar$-CH^{11}{}_2$), 5.46 (s, 4H, $-CH^8{}_2$), 5.93 (d, 4H, J = 9 Hz, Ar-H^g), 6.86 (t, 2H, J = 3 Hz, Ar-H^{10}), 7.20–7.41 (m, 25H, Ar-$H^{9,12,13,a,b,e,h}$), 7.68–7.71 (m, 3H, Ar-$H^{c,l}$), 7.93 (s, 2H, $-CH^7$), 7.98 (d, 2H, J = 6 Hz, Ar-H^2), 8.38 (b, 2H, $-NH^4$), 8.56 (s, 2H, Ar-H^3). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 31.5, 34.9, 40.2, 43.3, 45.0, 49.0, 49.6, 52.3, 58.0, 66.1, 71.3, 107.4, 108.6, 114.3, 121.6, 122.3,122.4, 123.7, 125.2, 129.0,129.3, 130.3, 131.2, 131.4, 135.3, 136.8,138.8, 143.2, 146.9, 151.2, 155.5, 156.4, 160.1, 165.6, 166.3. 166.9. Anal. Calcd for $C_{126}H_{157}N_{15}O_{14}$: C, 71.87; H, 7.52; N, 9.98. Found: C, 71.59; H, 7.48; N, 9.78.

Data for AXL. MALDI-TOF MS m/z: calcd for $C_{96}H_{120}N_{10}O_{10}Na$ $[M + Na]^+$ 1597.03, found 1597.49. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.32 (s, 36H, $-C(CH^{14}{}_3)_3$), 4.08–4.02 (m, 4H, $-CH^5{}_2$), 4.64–4.60 (m, 4H, $-CH^6{}_2$), 5.01 (s, 8H, Ar$-CH^{11}{}_2$), 5.47 (s, 4H, $-CH^8{}_2$), 6.85 (t, 2H, J = 3 Hz, Ar-H^{10}), 6.93 (t, 2H, J = 6 Hz, $-NH^4$), 7.25 (s, 4H, Ar-H^{13}), 7.32 (d, 8H, J = 3 Hz, Ar-H^{12}), 7.40 (t, 4H, J = 3 Hz, Ar-H^9), 7.76 (s, 2H, $-CH^7$), 8.14 (dd, 2H, J = 9 Hz, 3 Hz, Ar-H^1), 8.50 (d, 2H, J = 9 Hz, Ar-H^2), 9.04 (d, 2H, J = 3 Hz, Ar-H^3). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 31.6, 35.0, 40.0, 49.8, 58.2, 71.4, 107.5, 108.7, 121.4, 122.5,122.6, 125.3, 129.7, 131.5, 135.5, 136.0, 143.3, 148.1, 151.3, 157.6, 160.2, 166.2, 166.3. Anal. Calcd for $C_{96}H_{120}N_{10}O_{10}$: C, 73.25; H, 7.68; N, 8.90. Found: C, 73.12; H, 7.81; N, 9.08.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Compound characterization data and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

P.G. gratefully acknowledges the Science and Engineering Research Board (SERB), New Delhi (Project SR/S1/IC-39/2012) for financial support. S. Saha acknowledges the Indian Association for the Cultivation of Science (IACS), Kolkata for a research fellowship. S. Santra and B.A. acknowledge the Council of Scientific & Industrial Research (CSIR), New Delhi for senior research fellowships. X-ray crystallography of CuPRT was performed at the DST-funded National Single Crystal X-ray Facility at the Department of Inorganic Chemistry at IACS.

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