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Building Shape-Persistent Arylene Ethynylene Macrocycles as Scaffolds for 1,4-Diiodobutadiyne

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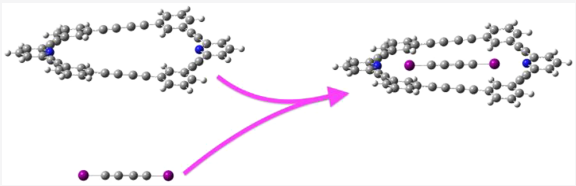
ABSTRACT: Two shape-persistent arylene ethynylene macrocycles have been designed and synthesized as scaffolds to bind the nonpolar molecule 1,4-diiodobutadiyne. Binding via halogen bonding interactions between the pyridine moieties of the macrocycle and 1,4-diiodobutadiyne is predicted by density functional theory calculations and has been demonstrated in solution by ^{13}C NMR titrations. The binding constant for the macrocycle-monomer complex (K = 10.5 L mol^{-1}) is much larger than for other comparable halogen bonds, strongly supporting cooperative binding of both ends of the diyne. These results demonstrate a fully inserted geometry of 1,4-diiodobutadiyne in the complex.



INTRODUCTION

Halogen bonding, as a highly directional interaction between a Lewis base and the "sigma hole" of an electron-deficient halogen atom, has attracted increasing attention for both crystal engineering and solution-phase molecular recognition.[1−6] Halogen bonding has been used to create self-assembling materials[7−9] and to drive solid-state reactions with high regiospecificity, such as [2 + 2] additions[10] and topochemical polymerizations.[11,12] We have used halogen bonding in the solid state to prepare polymers such as polydiiododiacetylene (PIDA) from monomers such as 1,4-diiodobutadiyne, preorganized with the help of a self-assembling scaffold host (Figure 1).[13,14] The pyridyl or nitrile groups of the host align the diyne monomers by halogen bonding with the iodine atoms.

In solution, halogen bonding has garnered attention as a molecular recognition tool that is often orthogonal in selectivity to hydrogen bonding of host and guest. For example, researchers have examined halogen bonding for anion recognition and transport[15−17] and for catalysis.[18] Utilizing the high directionality of halogen bonding, anion receptors incorporating multidentate binding sites give high anion binding constants.[19,20] Halogen bonding organocatalysts, suited to coordinate "soft" substrates, have been designed for Michael addition,[21] halide abstraction,[22] and reduction reactions.[23] Neutral−neutral halogen bonding has been exploited for molecular recognition, and it can be increased by multipoint interactions. The binding gets stronger as more binding sites are involved, with binding constants varying from 0.9 to 100 L mol^{-1}.[3]

In our studies of the polymer PIDA, which contains only a carbon backbone and iodine atom substituents, we discovered that the iodine atoms of the polymer are extremely labile, opening up the possibility of using PIDA as a precursor to the linear carbon allotrope carbyne.[24,25] We have attempted to prepare carbyne via the deiodination of PIDA, by suspending the polymer in solvent in the presence of soft Lewis bases.[26] However, aggregation of the PIDA polymer strands occurs before full deiodination takes place.

Anderson and co-workers have demonstrated that a rotaxane can be used to stabilize polyyne strands.[27] We have therefore developed a new strategy to make carbyne, by first synthesizing PIDA as a polyrotaxane structure, using macrocyclic hosts to prepare and surround each chain. The shape-persistent macrocycles will serve as scaffolds to bind 1,4-diiodobutadiyne and align the monomers in the appropriate geometry for polymerization, and then will protect the chain from aggregation during the formation of carbyne. As progress toward this goal, here we describe the synthesis, structure, and halogen-bonding properties of two shape-persistent arylene ethynylene macrocycles, $\mathbf{M_a}$ and $\mathbf{M_b}$ (Figure 2), that can bind 1,4-diiodobutadiyne in solution by halogen bonding.

RESULTS AND DISCUSSIONS

The preorganized bond angles of shape-persistent macrocycles make the synthesis of these compounds more straightforward than other large rings,[28−31] as shown in Scheme 1. To prepare macrocycles $\mathbf{M_a}$ and $\mathbf{M_b}$, we first synthesized "half-ring" precursors **6a** and **6b**. Dibromopyridyl amine **1**[32] is coupled to carboxylic acid **2a** or **2b** to yield amides **3a** and **3b**.[33] Double Sonogashira coupling of dibromopyridine **3a** or **3b** with

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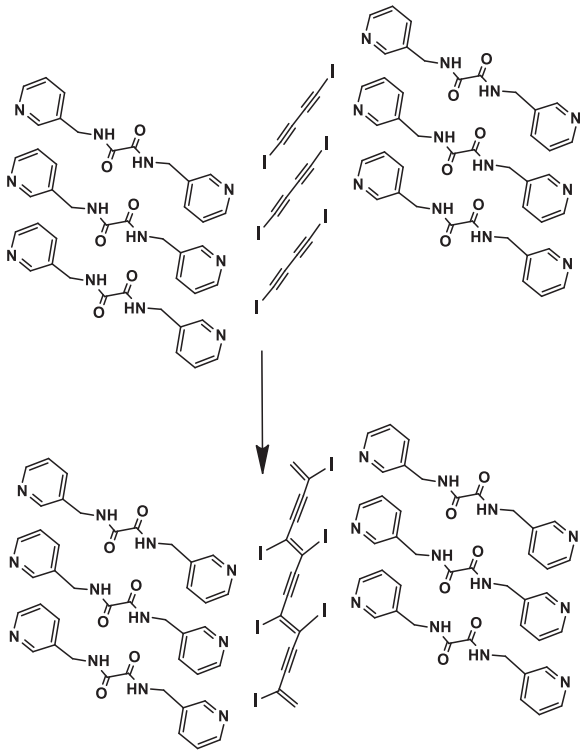

Figure 1. Polydiiododiacetylene prepared from 1,4-diiodobutadiyne.

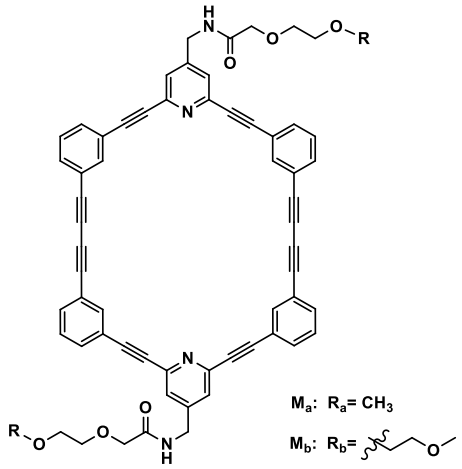

Figure 2. Arylene ethynylene macrocyclic hosts for diiodobutadiyne.

monoprotected dialkynyl benzene **4**[34] gives the TIPS-protected half-rings **5a** and **5b**, which are then treated with tetrabutylammonium fluoride to give the deprotected half-rings **6a** and **6b**, respectively.

Several different homocoupling reactions, including Hay[35] and Eglinton[30] coupling, have been explored for the ring-closure reaction. The Hay coupling reaction gave a very low yield of the desired product, while the Eglinton coupling suffered from the challenge of removing pyridine. Reaction under Rossi's conditions, using bis(triphenylphosphine) palladium(II) chloride and copper iodide as cocatalysts,[36] gave the best results, as shown in Scheme 2. A syringe pump has been used to control the addition rate, and the concentration of macrocycle half-ring **6a**/**6b** was kept as low as 0.5 mmol/L to minimize oligomerization side reactions. Monitoring the reaction by TLC, an intermediate species with lower R_f value can be seen forming and then disappearing during the course of the reaction, while the desired product first appears after 8 h, as the spot with the lowest R_f value. The reaction was continued until neither the starting material or the intermediate were visible by TLC.

To test the appropriateness of this macrocyclic scaffold, density functional theory (DFT) studies have been conducted, investigating the binding of the macrocyclewith 1,4-diiodobutadiyne in solution. Geometries of four potential complexes between the parent macrocycle and 1,4-diiodobutadiyne were explored at the MN15/def2-SVP level of theory, using the SMD implicit chloroform solvent model.[37−40] The calculations indicate that the most stable geometry for the host−guest complex has the guest fully inserted into the host cavity, as designed, with two halogen bonds, one between each iodine atom of the guest and a pyridine of the host (Figure 3). The geometry was further optimized at the MN15/def2-TZVP level, again in the presence of SMD chloroform. The calculated N···I distance is 2.96 Å, close to the N···I distance of 2.98 Å in the X-ray crystal structure of a similar diiodobutadiyne-pyridine complex.[41] The computed Gibbs free energy of binding is −2 kcal mol^{-1}, a modest but favorable interaction.

A modification to the SMD solvation model, SMD18,[42] has recently been introduced, employing a more appropriate atomic radius for iodine. To ascertain the effect of SMD18 on this complex, the system was reoptimized at the MN15/def2-TZVP + SMD18 level of theory. The free energy of binding becomes more favorable, calculated at −4 kcal mol^{-1}. It is interesting to note that the N···I distance is essentially the same with both solvation models (2.93 Å with SMD18).

NMR titration has been widely used to quantify and determine the energetics of noncovalent interactions in solution, in a variety of supramolecular chemistry systems.[43−47] Iodoalkynes exhibit a significant change in ^{13}C NMR chemical shifts in the presence of Lewis base,[48,49] providing an effective tool for measuring the interactions between 1,4-diiodobutadiyne and our macrocyclic hosts. We therefore conducted ^{13}C NMR titration experiments to investigate the binding activity between 1,4-diiodobutadiyne and macrocycle $\mathbf{M_b}$, the more soluble of the two macrocycles in $CDCl_3$. The concentration of 1,4-diiodobutadiyne in $CDCl_3$ was held constant, while a solution of $\mathbf{M_b}$ was added. As the concentration of macrocycle $\mathbf{M_b}$ increases, the chemical shift of the α-carbon on 1,4-diiodobutadiyne shifts to higher frequency. Other pyridyl compounds (compounds **7**, **8**, **3a**, **5a**, and **6a**) were tested for comparison, as shown in Figure 4. As can be seen, the chemical shift change observed with the macrocycle is significantly larger than for any of the other pyridyl compounds, consistent with cooperative binding to both pyridine moieties of the host. Note that half-ring **6b** has significantly weaker binding than less sterically blocked pyridyl compounds **7** and **8**. Thus, the steric hindrance of the macrocycle may negatively affect the strength of binding, although the greater rigidity of the $\mathbf{M_b}$ structure likely reduces this effect. As shown in Table 1, the resulting binding constant for $\mathbf{M_b}$ and 1,4-diiodobutadiyne at room temperature (10.5 L mol^{-1}) is much greater than for any of the other pyridyl compounds tested. It is also much larger than the previously reported binding constant of pyridine and 1-(2-iodoethynyl)-4-nitrobenzene (K = 0.8 L mol^{-1}),[45] and for a two-point binding

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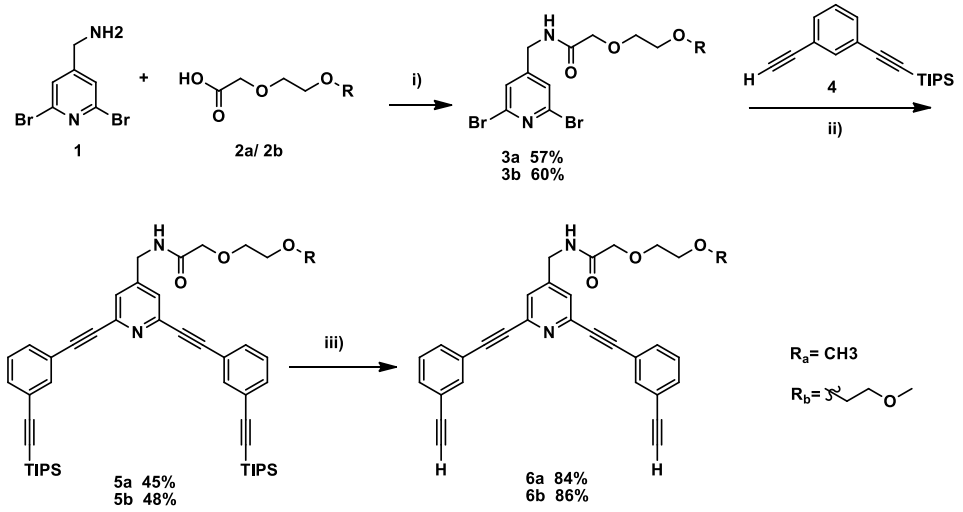
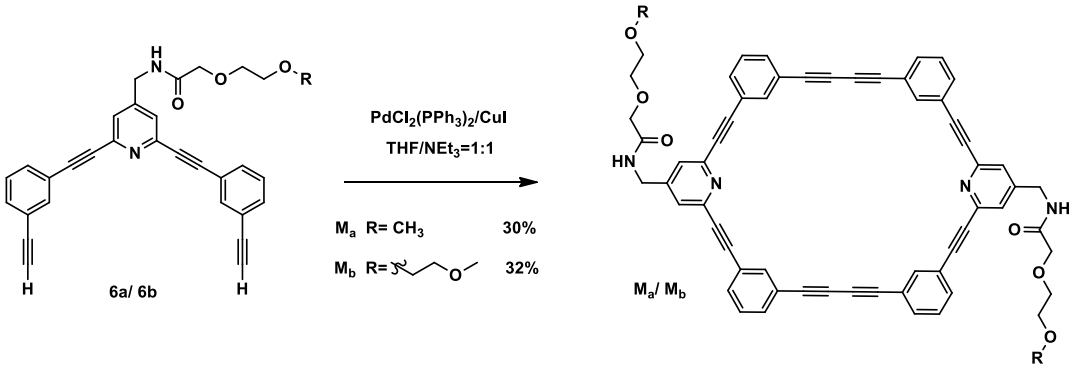
Scheme 1. Synthesis of Macrocycle Precursors[a]



[a]Reagents and conditions: (i) EDC·HCl, benzotriazol-1-ol, DMAP; (ii) $PdCl_2(PPh_3)_2$, CuI, THF/triethylamine; (iii) TBAF, THF.

Scheme 2. Synthesis of Macrocycles M_a and M_b by Palladium-Catalyzed Homo-Coupling



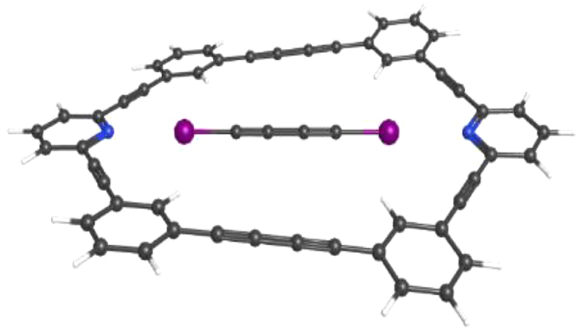


Figure 3. Calculated geometry of the macrocycle skeleton and 1,4-diiodobutadiyne.

complex between a perfluoroiodobenzene donor and an oxadiazole acceptor (K = 2 L mol^{-1}).[50] The relative strength of the binding constant in our system strongly supports a cooperative binding model, in which both ends of the monomer are simultaneously halogen-bonded to the host.

To investigate the thermodynamics of the binding between the macrocycle and 1,4-diiodobutadiyne, NMR titrations were conducted at temperatures ranging from 295 to 310 K. The change in chemical shift ($\Delta\delta$) was fitted against pyridyl host concentration, using a 1:1 binding isotherm model (Figure S2). The maximum $\Delta\delta$ has been estimated to be 9.8 ppm, using the chemical shift of (iodoethynyl)benzene in concentrated pyridine solution.[51] This fitting provides the binding constant K, and additional thermodynamic parameters of the binding interaction were obtained from the Van't Hoff and Gibbs free energy equations (Table 2), in excellent agreement with the calculation results. The plot of ln K versus $1/T$ (Figure S4) yields ΔH = −4.0 kcal mol^{-1} and $T\Delta S$ = −2.6 kcal mol^{-1} at 295 K. In comparison, Dumele and co-workers prepared and studied halogen-bonding molecular capsules with four-point binding, and measured a greater enthalpy (ΔH = −12.6 kcal mol^{-1}), but it was compensated by higher entropy cost ($T\Delta S$ = −7.8 kcal mol^{-1} at 283 K).[52]

CONCLUSIONS

In conclusion, two shape-persistent arylene ethynylene macrocycles have been synthesized in good yield by Pd-catalyzed homocoupling. Computational study supports binding of 1,4-diiodobutadiyne to these macrocycles in a fully inserted geometry. NMR titration experiments have further demon-

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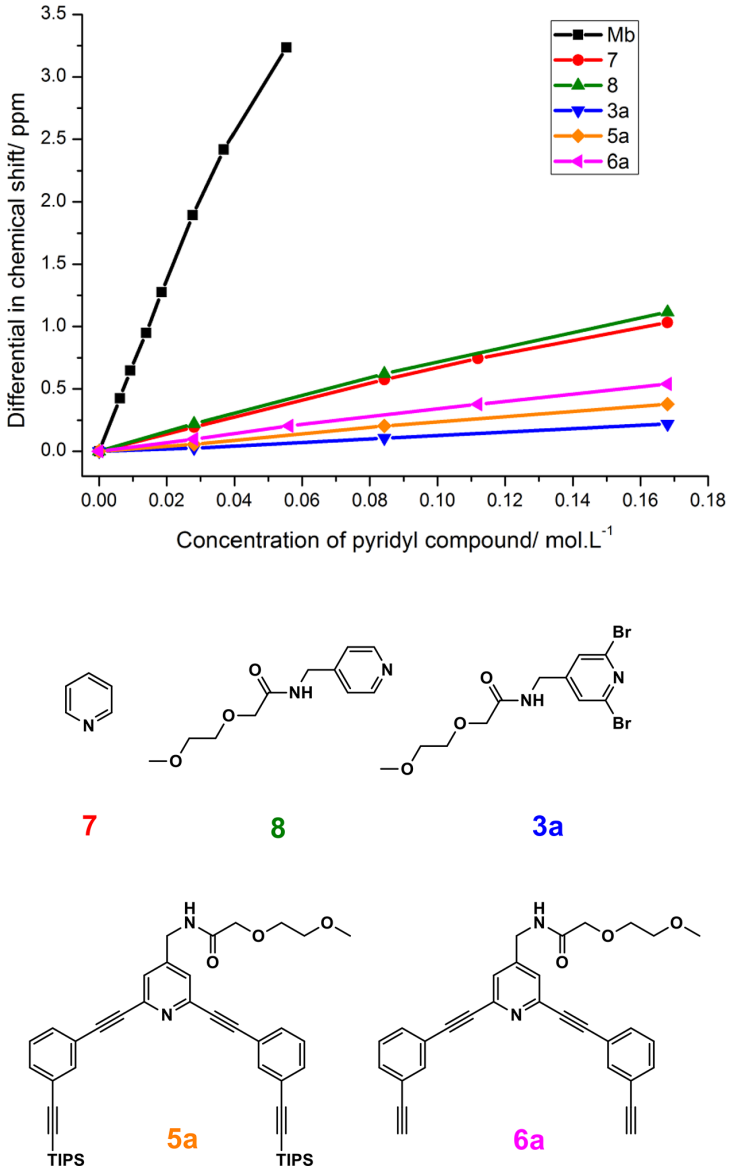

Figure 4. NMR titration of pyridyl hosts and 1,4-diiodobutadiyne at 298 K in $CDCl_3$. See the SI for full details.

Table 1. Thermodynamic Parameters for Binding of 1,4-Diiodobutadiyne with Pyridyl Hosts in $CDCl_3$ at 298 K

compound	7	8	3a	5a	6a	M_b
K^a/ L mol^{-1}	0.54	0.80	0.15	0.26	0.46	10.5
ΔG^b/ kcal mol^{-1}	0.36	0.14	1.12	0.81	0.46	−1.39

[a]Determined at 298 K in $CDCl_3$ by nonlinear curve fitting of ^{13}C NMR binding titration data to 1:1 binding isotherm; errors of 20% are generally assumed. [b]Calculated from averaged K at 298 K.

Table 2. Thermodynamic Parameters for Binding of M_b and 1,4-Diiodobutadiyne in $CDCl_3$, from 295 to 310 K

T/K	295	298	301	304	307	310
K^a/ L mol^{-1}	11.4	10.5	9.88	9.23	8.70	8.13
ΔG / kcal mol^{-1}	−1.43	−1.39	−1.37	−1.34	−1.32	−1.29

[a]Determined in $CDCl_3$ by nonlinear curve fitting of ^{13}C-NMR binding titration data to 1:1 binding isotherm; errors of 20% are generally assumed.

strated cooperative halogen bonding between the macrocycle and 1,4-diiodobutadiyne, leading to much stronger binding than for comparable monodentate halogen-bond complexes. The shape-persistent arylene ethynylene structure of macrocycles $\mathbf{M_a}$ and $\mathbf{M_b}$ provides a promising template for aligning 1,4-diiodobutadiyne, but new derivatives that are more crystalline will be needed to prepare PIDA as a polyrotaxane.

EXPERIMENTAL SECTION

Reagents were purchased from Sigma-Aldrich, TCI, and Alfa Aesar and used as received. Dry THF was obtained by distillation from Na/

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benzophenone. All reactions were performed under Ar unless otherwise stated. CuI catalyst was freshly purified for use. ^{1}H NMR (500 MHz/700 MHz) and ^{13}C{^{1}H} NMR (125 MHz/175 MHz) spectra were measured on either a Bruker Ascend 700 spectrometer or a Bruker 500 Advance spectrometer and are provided with all chemical shifts quoted on the ∂ scale [ppm], and all coupling constants (J) expressed in Hz. HRMS (ESI) tests were performed on a Waters Q-TOF Ultima ESI at the School of Chemical Sciences, UIUC.

Compound 3a, *N*-((2,6-Dibromopyridin-4-yl)methyl)-2-(2-methoxyethoxy)acetamide. Compound **1**, (2,6-dibromopyridin-4-yl)methanamine (3.35 g, 12.6 mmol), prepared from 2,6-dibromopyridine-4-carboxylic acid by the reported method,[32,53] was dissolved in 100 mL DCM in an ice-bath. Compound **2a** (1.69 g, 12.6 mmol), EDC·HCl (2.41 g, 12.6 mmol), benzotriazol-1-ol•H_2O (1.93 g, 12.6 mmol) and DMAP (138 mg, 1.13 mmol) were added into the mixture sequentially. The mixture was stirred overnight, then diluted with 200 mL of DCM, washed with aq. $NaHCO_3$ and brine, concentrated under vacuum, and separated by column chromatography (Hex/EA = 1:1/SiO_2) to give compound **3a** as a white solid (2.73 g, 57.4%, mp 138−139 °C). HRMS (ESI): calcd for $C_{11}H_{15}N_2O_3Br_2$ $[M + H]^+$ 380.9449, found 380.9456. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.35 (s, 2H), 4.39 (d, J = 6.5 Hz, 2H), 4.05 (s, 2H), 3.68−3.69 (m, 2H), 3.53−3.54 (m, 2H), 3.33(s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.4, 152.6, 140.8, 125.5, 71.3, 71.1, 70.1, 58.9, 40.6.

Compound 3b, *N*-((2,6-Dibromopyridin-4-yl)methyl)-2-(2-(2-methoxyethoxy)ethoxy)acetamide. White solid (60.2%, mp 137−138 °C). HR-MS (ESI): calcd for $C_{13}H_{19}N_2O_4Br_2$ $[M + H]^+$ 424.9712, found 424.9722 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.39 (s, 2H), 4.40 (d, J = 6.5 Hz, 2H), 4.06 (s, 2H), 3.70−3.71 (m, 2H), 3.62−3.66 (m, 4H), 3.48−3.49 (m, 2H), 3.25 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.8, 153.2, 140.8, 125.6, 71.6, 71.2, 70.2, 69.9, 58.7, 40.6.

Compound 5a, *N*-((2,6-Bis((3-((triisopropylsilyl)ethynyl)-phenyl)ethynyl)pyridin-4-yl)methyl)-2-(2-methoxyethoxy)-acetamide. Benzene, 1-ethynyl-3-[2-[tris(1- methylethyl) silyl] ethynyl][34] (**4**,1.52 g, 5.40 mmol) was added to a mixture of compound **3a** (344 mg, 0.90 mmol), $PhCl_2(PPh_3)_2$ (63.0 mg, 0.09 mmol), and CuI (17 mg, 0.09 mmol) in 120 mL of NEt_3/THF (1:1). The mixture was heated to reflux overnight, filtered through Celite, concentrated under vacuum, and purified by column chromatography (ethyl acetate/SiO_2), to give compound **5a** as a yellow oil (318 mg, 45.8%). HR-MS (ESI): calcd for $C_{49}H_{65}N_2O_3Si_2$ $[M + H]^+$ 785.4534, found 785.4528. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 7.42 (s, 2H), 7.31 (t, J = 7.5 Hz, 2H), 4.51 (d, J = 6.0 Hz, 2H), 4.12 (s, 2H), 3.72−3.74 (m, 2H), 3.56−3.58 (m, 2H), 3.35 (s, 3H), 1.14 (s, 42H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.5, 148.1, 143.9, 135.7, 132.5, 131.7, 128.4, 125.1, 123.9, 122.2, 105.8, 91.7, 88.8, 88.6, 71.5, 71.2, 70.3, 59.0, 41.3, 18.6, 11.3.

Compound 5b, *N*-((2,6-Bis((3-((triisopropylsilyl)ethynyl)-phenyl)ethynyl)pyridin-4-yl)methyl)-2-(2-(2-methoxyethoxy)-ethoxy)acetamide. Yellow oil (48.3%). HR-MS (ESI): calcd for $C_{51}H_{69}N_2O_4Si_2$ $[M + H]^+$ 829.4796, found 829.4781. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (J = 6.5 Hz, 1H), 7.71 (s, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.42 (s, 2H), 7.30 (t, J = 8.0 Hz, 2H), 4.50 (d, J = 6.5 Hz, 2H), 4.11 (s, 2H), 3.73−3.74 (m, 2H), 3.66−3.68 (m, 2H), 3.62−3.64 (m, 2H), 3.46−3.48 (m, 2H), 3.26 (s, 3H), 1.13(s, 42H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.7, 148.7, 143.6 135.6, 132.4, 131.7, 128.4, 125.0, 123.9, 122.2, 105.8, 91.7, 88.8, 88.6, 71.7, 71.2, 70.3, 70.0, 60.1, 58.8, 41.1, 18.6, 11.2.

Compound 6a, *N*-((2,6-Bis((3-ethynylphenyl)ethynyl)-pyridin-4-yl)methyl)-2-(2-methoxyethoxy)acetamide. Macrocycle half ring **5a** (322 mg, 0.41 mmol) was dissolved in 50 mL of wet THF. Then, 3 equiv of TBAF (1.23 mmol) in THF solution was added into the solution dropwise. The mixture was stirred for 2 h, then concentrated in vacuo, and purified by column chromatography (Hex/EA = 1:1), to give compound **6a** a pale-yellow powder. (163 mg, 84.7%, mp 156−157 °C). HR-MS (ESI): calcd for $C_{31}H_{25}N_2O_3$ $[M + H]^+$ 473.1865, found 473.1860. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.61(s, 1H), 7.56 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.41 (s, 2H), 7.32 (t, J = 7.7 Hz, 2H), 4.50 (d, J = 6.3 Hz, 2H), 4.11 (s, 2H), 3.71−3.72 (m, 2H), 3.55−3.57 (m, 2H), 3.34 (s, 3H), 3.11 (s, 2H). ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 170.4, 148.2, 143.7, 135.5, 132.6, 132.3, 128.5, 125.1, 122.6, 122.3, 88.7, 88.6, 82.5, 78.0, 71.4, 71.2, 70.3, 59.0, 41.3.

Compound 6b, *N*-((2,6-Bis((3-ethynylphenyl)ethynyl)-pyridin-4-yl)methyl)-2-(2-(2-methoxyethoxy)ethoxy)-acetamide. Pale yellow powder (86.2%, mp 155−156 °C). HR-MS (ESI): calcd for $C_{33}H_{29}N_2O_4$ $[M + H]^+$ 517.2127, found 517.2128. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (t, J = 6.1 Hz, 1H), 7.71 (s, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.41 (s, 2H), 7.32 (t, J = 7.8 Hz, 2H), 4.51 (d, J = 6.2 Hz, 2H), 4.11 (s, 2H), 3.71−3.72 (m, 2H), 3.54−3.56 (m, 2H), 3.50−3.52 (m, 2H), 3.45−3.47 (m, 2H), 3.34 (s, 3H), 3.11 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.4, 148.5, 143.1, 135.0, 132.2, 131.8, 128.2, 124.7, 122.2, 122.0, 88.4, 88.0, 82.1, 78.0, 71.2, 70.8, 69.9, 69.8, 69.6, 58.3, 40.7.

Macrocycle M_a. Compound **6a** (60.0 mg, 0.127 mmol) was dissolved in 30 mL of THF and added dropwise into a mixture of $PhCl_2(PPh_3)_2$ (8.4 mg, 0.012 mmol) and CuI (4.8 mg, 0.025 mmol) in a solution of 40 mL of NEt_3 and 130 mL of THF. The whole addition took approximately 3 h, controlled by syringe pump, and the mixture was stirred for 12 h in total. Then the solvent was removed in vacuo, and the solid mixture was washed with MeOH and purified by prep TLC in $CHCl_3$ with 4% MeOH to give macrocycle $\mathbf{M_a}$ as a white solid (35.8 mg, 30.3%, mp 161−162 °C). HR-MS (ESI): calcd for $C_{62}H_{45}N_4O_6$ $[M + H]^+$ 941.3339, found 941.3328. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.61 (s, 2H), 7.56 (d, J = 7.0 Hz, 4H), 7.20 (d, J = 7.0 Hz, 4H), 7.43 (s, 4H), 7.36 (t, J = 7.0 Hz, 4H), 4.51 (d, J = 6.3 Hz, 4H), 4.12 (s, 4H), 3.72−3.73 (m, 4H), 3.57−3.58 (m, 4H), 3.35 (s, 6H). ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 170.5, 148.0, 143.8, 136.7, 132.7, 132.4, 128.6, 125.0, 122.6, 122.3, 89.1, 88.3, 80.5, 74.5, 71.4, 71.2, 70.3, 59.0, 41.3.

Macrocycle M_b. White solid (32.1%, mp 160−161 °C). HR-MS (ESI): calcd for $C_{66}H_{53}N_4O_8$ $[M + H]^+$ 1029.3863, found 1029.3854. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.57 (d, J = 7.7 Hz, 4H), 7.52 (d, J = 7.7 Hz, 4H), 7.44 (s, 4H), 7.36 (t, J = 7.7 Hz, 4H), 4.52 (d, J = 6.3 Hz, 4H), 4.13 (s, 4H), 3.74−3.76 (m, 4H), 3.68−3.69 (m, 4H), 3.63−3.65 (m, 4H), 3.49−3.50 (m, 4H), 3.27 (s, 6H). ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 170.8, 148.9, 143.4, 136.5, 133.0, 132.4, 128.6, 124.9, 122.6, 122.4, 89.0, 88.9, 80.6, 79.5, 74.7, 71.7, 71.3, 70.3, 70.1, 58.9, 41.2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.9b02859.

Experimental details for NMR titrations; computational details for study of host−guest complexes, including structural coordinates and energies; NMR spectra for all new compounds (PDF)

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Author Contributions

All the authors have given approval to the final version of the manuscript

Notes

The authors declare no competing financial interest.

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