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Supramolecular Glycopolymers in Water: A Reversible Route Toward Multivalent Carbohydrate−Lectin Conjugates Using Cucurbit[8]uril

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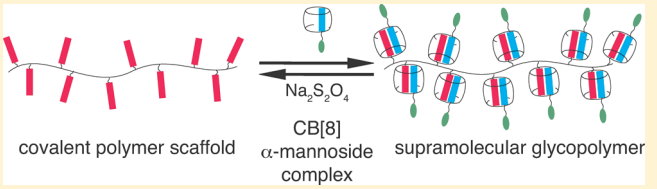
Supporting Information

ABSTRACT: Supramolecular self-assembly and *reversible* switching has been demonstrated for the first time between monovalent and multivalent carbohydrate ligands and the multivalency effect on lectin binding has been investigated. The self-assembly process is mediated through noncovalent interactions between pendant moieties on a polymer scaffold and a monosaccharide-functionalized viologen with cucurbit[8]uril (CB[8]) acting as a "supramolecular handcuff". The rate of binding of the tetrameric lectin Concanavalin A (Con A) to a mannose-containing supramolecular glycopolymer was investigated through a standard turbidimetric assay.

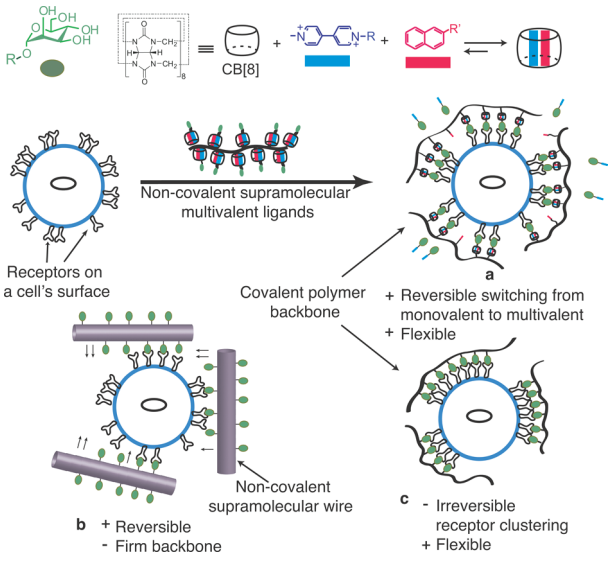


Interactions between carbohydrate-binding proteins (lectins) and cell-surface carbohydrate ligands have been shown to be critical for a wide variety of intercellular recognition processes, including cell proliferation, signaling, and recognition.[1−4] A number of multivalent systems have been reported in which either the loading of the saccharide binding epitopes or their overall geometry were varied to obtain information on ligand−receptor binding mechanisms.[3,5,6] Additionally, there are reports that describe the mimicking of the reversible tuning and switching of carbohydrate−lectin binding between "on" and "off" states, where binding intensity could be regulated by an external stimulus.[7,8] However, the need to further probe such binding mechanisms along with a spatial understanding of receptor location still remains.

In order to investigate the ligand−receptor binding mechanisms and to reveal the role of chemoreceptor arrays, synthetic multivalent ligands covalently bound onto polymeric backbones such as glycopolymers have been used in many recent studies.[9−12] The synthesis of pendant glycopolymers via various synthetic methods and the interactions with their respectively lectins have been recently reviewed.[13] A major limitation with these tailor-made glycopolymers, however, is that the static location and number of glycogen moieties along the polymer backbone can induce rearrangement of the polymer on a cell surface.

Previous studies have demonstrated that the distance between recognition motifs on a cell surface can be altered upon forming ligand−receptor complexes resulting in receptor clustering (Scheme 1c).[10,15] Therefore, a "dynamic" approach in which multivalent ligands evolve in response to the system's topological requirements is necessary, where particular multireceptor sites on a cell, along with their surface density may be controlled. Previously, a columnar supramolecular assembly formed by mannose-modified discotic components has been reported as a polyvalent scaffold for optimally mimicking and matching the

Scheme 1. Strategies Employed in Supramolecular Oligosaccharide−Lectin Binding[a]



[a] Key: (a) non-covalent multivalent ligands with flexible backbone; (b) non-covalent supramolecular wire;[14] (c) covalent multivalent ligands.[15]

arrangements of its multiple binding sites with lectin.[14] However, the cylindrical supramolecular glycopolymer formed through $\pi-\pi$ interactions between disk-shaped compounds, has limited flexibility and cannot adapt to the specific surface-topology of the receptor sites on a cell (Scheme 1b). Thus, a more flexible,

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Table 1. Polymer Scaffolds Prepared in This Study

polymer scaffold	DP	M_n (kDa)[a]	PDI (SEC)[b]
4a	21	6.9	1.05
4b	35	12.0	1.06
4′	41	14.1	1.11
9a	20	4.2	1.04
9b	38	7.0	1.09

[a] Determined by ^{1}H NMR. [b] Determined by SEC (DMF with 0.1 M LiBr at 65 °C)

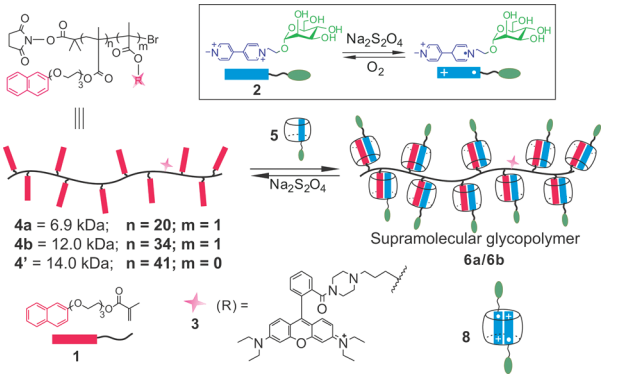
supramolecular arrangement was expected to give rise to further advantages as depicted in Scheme 1a.

In this work, we have developed an aqueous supramolecular system based on cucurbit[8]uril (CB[8])[16−23] to produce the desired flexibility and hence topological adaptability by virtue of reversible supramolecular interactions. Our molecular design is based on a supramolecular self-assembly process that is widely applicable to a variety of functional polymers.[24−31] We have employed a similar polymeric scaffold, which was previously used to form covalent multivalent ligands,[32,33] in order to allow for a direct comparison with our self-assembled system. A robust methodology was used to dynamically assemble multivalent ligands onto a static copolymer backbone, providing a reversible strategy toward the tuning of ligand valency and location.[34] To illustrate this concept we have focused on Concanavalin A (Con A) (which normally forms dimers or tetramers depending on pH), a mannose-specific lectin commonly used to probe protein-carbohydrate interactions,[35] and α-mannoside as the protein receptor and sugar ligand, respectively.

The copolymer scaffolds used in this study were prepared by ATRP (see Supporting Information); the linear 2-naphthol-appended methacrylate copolymers **4a**/**b** (6.9 kDa and 12.0 kDa, respectively) were prepared by copolymerizing 2-naphthoxy-triethylene glycol methacrylate monomer **1** and fluorescent rhodamine B methacrylate monomer **3** in the presence of *N*-hydroxysuccinimide initiator **7** using a catalytic bipyridine/Cu^{I}Br redox couple. The molecular weight and polydispersity index (PDI) of copolymers **4a** and **4b** are shown in Table 1. Measurements of the polymerization kinetics showed a linear increase of M_n with conversion and the narrow molecular weight distribution suggested that the polymerization occurred in a controlled fashion (see Supporting Information). This ensured that the 2-naphthol moieties were randomly distributed along the methacrylate polymer backbone (Scheme 2).

The addition of 1 equiv of CB[8] to a D_2O solution containing the small molecule α-mannoside viologen **2** led to the formation of **2**⊂CB[8] (complex **5**). The aromatic protons of the viologen moiety experienced an upfield shift in the ^{1}H NMR spectrum (Figure 1b), indicative of cavity binding with CB[8].[36] One equivalent of the neat, water insoluble copolymer **4a** was then added to the aqueous solution of complex **5** in order to produce the multivalent ternary complex glycopolymer **6a**. Extreme broadening of the aromatic viologen protons was observed in the ^{1}H NMR along with an upfield shift of the aromatic protons (6.5 ppm) from the naphthol units of copolymer **4a** (Figure 1c). These observations are in agreement with a set of control experiments carried out on the ternary complex formation of α-mannoside **2** with monomer **1** as well as with 2-naphthol itself (see Figure S11 in the Supporting Information). Integration of the ^{1}H NMR of glycopolymer **6a** (Figure 1c and Figure S16 in

Scheme 2. Formation of Side-Chain Multivalent CB[8]-Glycopolymer Conjugate 6a/b



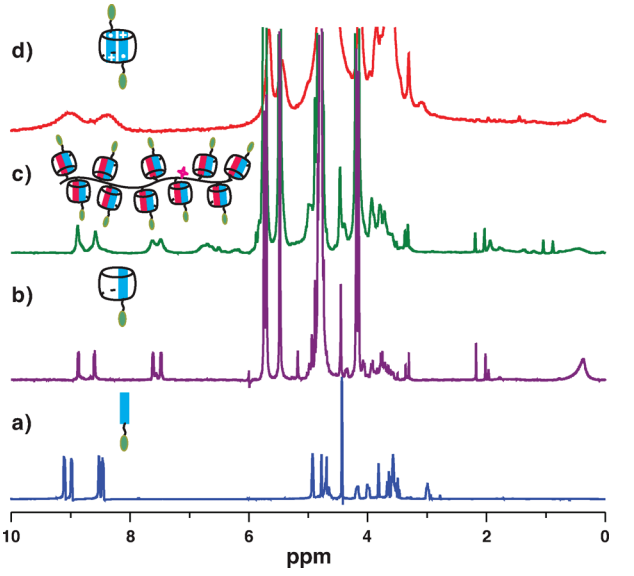


Figure 1. ^{1}H NMR spectra in D_2O of (a) 2, (b) **5**, (c) **6a**, and (d) the disassembly of **6a** upon addition of $Na_2S_2O_4$, each at 0.5 mM.

the Supporting Information) clearly indicated quantitative formation of the 1:1:1 ternary complexes with all naphthol groups indeed bound by **5**.

It is important to mention that the copolymer scaffolds **4a**/**b** could be solubilized in water in the presence of many fewer equivalents of **5**, as low as 30% at 0.01 mM, (see Figure S19 in the Supporting Information), suggesting that a water-soluble system using less than 1 equiv of complex **5** can evolve as the receptor binds reversibly to the polymer backbone. Thus, the α-mannoside can eventually bind to positions that are favorable for lectin binding without leading to receptor clustering. Additionally, it is worth noting that the 2-naphthol-appended polymethacrylate scaffolds **9a** and **9b**, which do not contain any triethylene glycol linkers, could also form ternary complexes with complex **5** in water (see Figure S18 in the Supporting Information).

Copolymer **4a** is a water insoluble, tacky material and sticks to the walls of a glass vial (Figure S17, Supporting Information); it exhibits a visibly intense pink color on account of the incorporation of the rhodamine-containing monomer (roughly one equivalent of the dye residue per chain). Sonicating

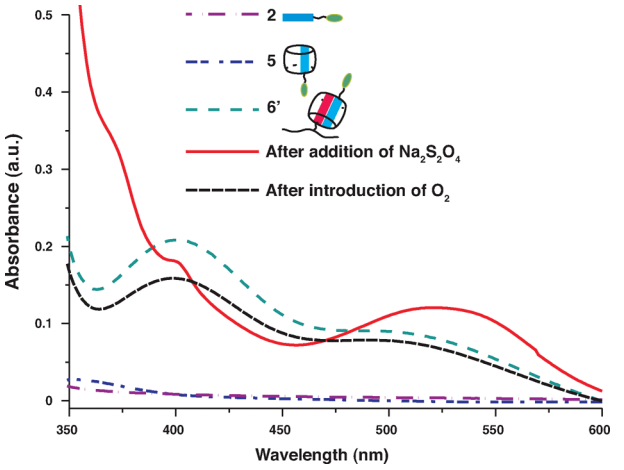


Figure 2. UV/vis spectra in water of **2**, **5**, **6′**, and **6′** after addition of $Na_2S_2O_4$, and regenerated **6** after introduction of O_2, respectively (each at 0.1 mM). A CT band appears upon forming the CB[8] complex **6′** (cyan line). The complex is disassembled upon addition of the reductant $Na_2S_2O_4$ (red line) and regenerated upon introduction of oxygen (black line).

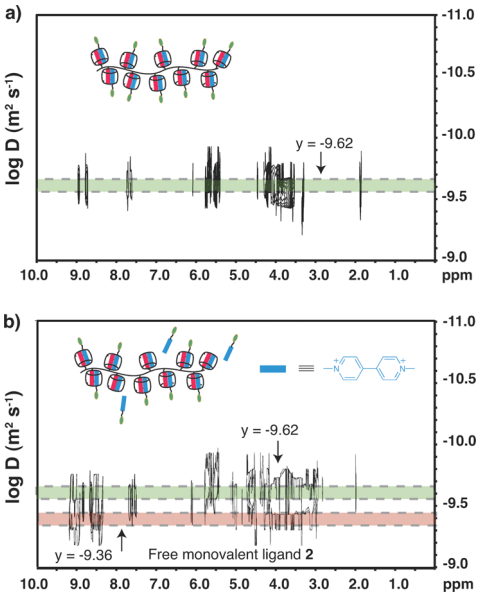


Figure 3. DOSY NMR spectra for (a) equimolar mixtures of **2**, **4′**, and CB[8] at 0.5 mM concentration in D_2O. (b) After addition of excessive methylviologen, some α-mannoside viologen was released from the polymer backbone.

4a (1 equiv) in water for 30 min in the presence of complex **5** resulted in a transparent orange solution of **6a**. α-Mannoside viologen **2** and polymer scaffold **4a** fluoresce green and pink respectively under UV radiation. When mixed to form the supramolecular glycopolymer **6a**, the orange solution fluoresces yellow-green. Two emission bands at 586 and 690 nm were observed in the fluorescence spectrum of **6a** arising from the rhodamine B tag on the polymer backbone.

Since the absorbances of both the CB[8] ternary complexes and the rhodamine B-tagged polymer scaffolds overlap around 400 nm, it was not possible to distinguish between them by UV/vis. Thus, a rhodamine B free polymer **4′** was also prepared to study the changes in the absorption spectrum upon ternary complex formation. In the presence of **5**, polymer **4′** readily formed supramolecular polymer **6′** clearly seen in the UV/vis spectrum shown in Figure 2, where a strong absorbance band between 400 and 500 nm appeared, typical for CB[8] viologen-naphthol ternary complexes.[36,37] Similar results were obtained from both ^{1}H NMR and UV/vis for the higher molecular weight multivalent polymer complex **6b** (Figure S18 in the Supporting Information).

NMR diffusion experiments (DOSY) were performed on an equimolar mixture of **2** and polymeric scaffold **4′** in the presence of the host CB[8] to provide further evidence for the formation of the ternary complex. The results are depicted in Figure 3a and show all three components CB[8], **2** and **4′** moved through solution at the same rate, which further supports that a supramolecular glycopolymer complex has been formed. Moreover, α-mannoside viologen **2** could be displaced by addition of a competitive first guest methylviologen (2 equiv) yielding the free monovalent ligand **2**. in Figure 3b, the diffusion coefficient of **2** is clearly separated as the glycopolymer and unbound α-mannoside viologen **2** move through solution as independent molecular species (log D = 9.62 and 9.36 m^2 s^{-1}, respectively).

In an effort to illustrate full reversibility of the supramolecular glycopolymer system, an aqueous solution of **6′** was treated with sodium dithionite ($Na_2S_2O_4$, 10 equiv), resulting in a purple solution. This was a direct consequence of the chemical reduction of dication **2** to its radical cation species and subsequent 2:1 complexation with CB[8] to form **8**,[38] which itself is a small molecule bivalent α-mannoside ligand. Furthermore, copolymer **4′** was released from the multivalent ternary complex and precipitated from the purple solution. A loss of the CT absorbance bands at λ = 400 and 500 nm and the appearance of new absorptions at λ = 360 and 540 nm in the UV/vis spectrum (Figure 2) were also observed. Additionally, ^{1}H NMR (Figure 1d) showed a downfield shift of the aromatic viologen protons and the complete absence of copolymer **4′** in solution. After filtration to remove copolymer **4′**, and subsequent oxidation of the viologen radical cation **8** with air, the purple solution again became transparent with an identical ^{1}H NMR spectrum to that previously observed for complex **5** alone (Figure 1b). If the filtration step was skipped and oxygen was introduced directly into the vessel containing divalent complex **8** and precipitated copolymer **4′**, an orange solution was observed after brief sonication, and both ^{1}H NMR and UV/vis confirmed the reformation of **6′**. This process could be repeated over at least 10 cycles.

After successful preparation of the supramolecular glycopolymers, their specificity and recognition potential toward lectin binding was investigated. The native recognition elements for carbohydrates responsible for cell signaling processes are lectins, thus lectin binding assays are often employed in quantifying glycoprotein receptor−ligand interactions.[39,40] Con A was mixed with multivalent ligand **6′**, and binding resulted in rapid turbidity of the solution and eventual precipitation of the **6′** ·ConA network whereas in the presence of monovalent ligand **5** (dashed trace, Figure 4) no increase in turbidity was observed. The rate of **6′** · Con A network formation (k = 0.62 AU/min) was obtained by measuring the absorbance changes at 420 nm of appropriate solutions of the lectin and functional copolymers in HEPES buffer at pH = 7.4. A plateau was reached after the initial rapid increase in absorbance as shown in Figure 4 (solid trace). The marked absorbance profile in the presence of the multivalent ligand **6′** demonstrated the propensity of this noncovalent

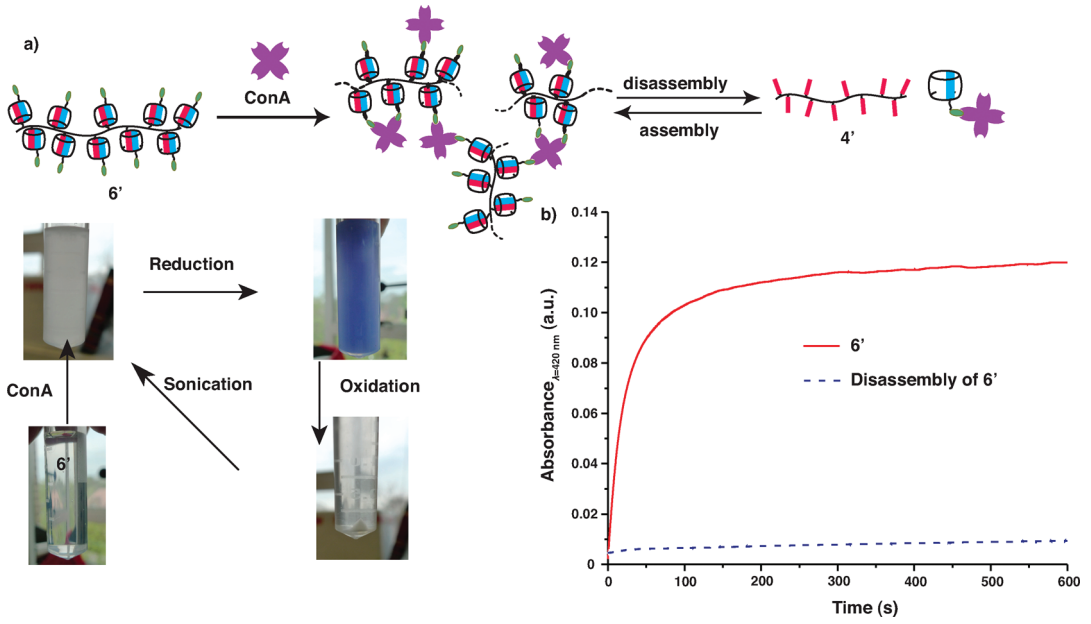


Figure 4. (a) Reversible multivalent ligand−lectin binding process. (b) Turbidimetric assay for the supramolecular glycopolymer **6′** (solid line) and complex **5** (dashed line) in the presence of Con A. The initial rate was determined by a linear fit applied to the steepest part of the curve.

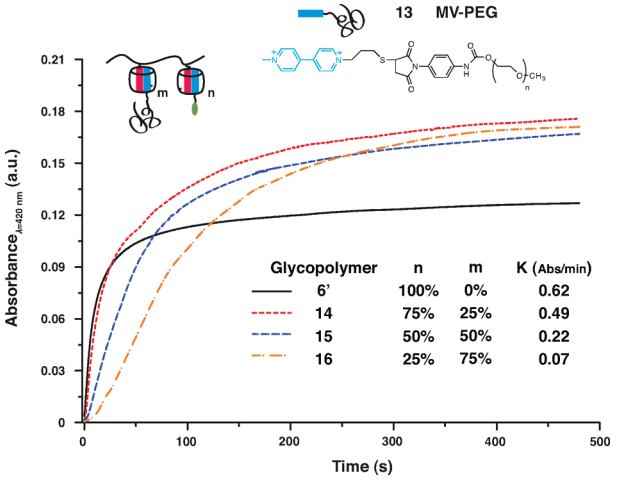


Figure 5. Turbidimetry assay results of glycopolymers with different density of α-mannoside on the polymeric backbone. Mixing of the glycopolymer with ConA occurs at $t = 0$.

approach toward forming dynamic, macromolecular cross-links. Such rapid lectin binding is comparable to covalent glycopolymer approaches used to build multivalent networks with the same covalent polymeric backbone.[32,33]

As the formation of the CB[8] ternary complexes is a thermodynamically controlled process, we were able to adjust the density of the mannoside groups on the polymer backbone by simply mixing α-mannoside viologen **2** with viologen terminated poly(ethylene glycol) monomethyl ether (**MV-PEG**, M_n 5000 g mol $^{-1}$, **13**). When these polymers featuring a lower α-mannoside density were used, the observed rate of network formation decreased as well (Figure 5) indicating that indeed less α-mannoside was available on the multivalent scaffold for binding to the Con A. This is consistent with a previously described system by Kiessling et al. for macromolecular ligands prepared by ROMP.[39]

As our system is fully reversible, addition of sodium dithionite to the turbid mixture that contained Con A and the multivalent ligand **6′** network, resulted in the immediate precipitation of polymer **4′** and a bluish-purple solution on account of the formation of the viologen radical cation species and subsequent 2:1 complexation with CB[8] to form **8** (Scheme 2). While complex **8** is itself a bivalent ligand, it did not promote any network formation with Con A because of the limited distance between two mannoside residues. The isolated precipitate was confirmed to be polymer scaffold **4′** by ^{1}H NMR (see Figure S20 in the Supporting Information). The supernatant was then reoxidized with air and subjected to a second turbidimetric assay with the addition of more Con A. No absorbance changes at 420 nm were observed, which confirmed that no multivalent ligand **6′** was formed in solution as **4′** had been completely removed by the previous filtration.

In conclusion, a water-soluble supramolecular glycopolymer has been obtained through a straightforward and efficient protocol combining both supramolecular self-assembly and a facile controlled radical polymerization route. Moreover, a controlled reversible route toward building a multivalent carbohydrate ligand has been demonstrated. This work has included the first example of reversible switching between monovalent (α-mannoside viologen) and multivalent ligands (supramolecular glycopolymer) and their effects on lectin binding, and our results indicate that reversible tuning and switching of supramolecular-mediated ligand valencies in a model carbohydrate−lectin system is possible through a rational design approach. This dynamic interlink exhibits redox-responsive behavior, and provides a reversible, self-evolving route toward multivalent ligands, which adapt to the system's topological requirements through multiple, dynamic, noncovalent interactions. Through this strategy, the properties of a polymer backbone can be conjugated to various substrates in a facile manner. Such a concept will be of interest as a versatile

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tool to further probe cellular signaling and ligand−receptor binding mechanisms. The utility of this approach applied to carbohydrate−protein recognition, offers exciting possibilities toward mimicking biological processes for the further study of ligand−receptor binding mechanisms. We are currently investigating additional stimuli to control the responsivity of the system such as changes in pH, applied current and the application of specific wavelengths of light.

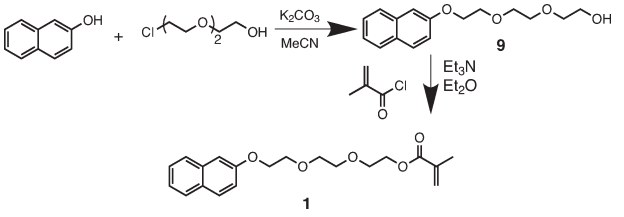
EXPERIMENTAL SECTION

Materials. All starting materials were purchased from Alfa Aesar and Sigma-Aldrich and used as received unless stated otherwise. CB[8] was prepared according to literature procedure.[20]

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Avance 500 BB-ATM (500 MHz) spectrometers, UV/visible spectra on a Varian Cary 4000 UV−vis spectrophotometer. ATR FT-IR spectra were measured on a 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. High-resolution mass spectra were recorded on a Bruker Bio ASpex II 4.7e FT-ICR mass spectrometer liquid chromatography - mass spectrometry Waters ZQ. Gel permeation chromatography was carried out in dimethylformamide (DMF) on two Jordi 5 μm DVB columns connected in series with a SPD-M20A prominence diode array detector and Shimadzu RI detector (Viscotak) calibrated in relation to polystyrene standards. Samples were filtered over 0.45 μm PTFE filters before injection using a 0.75 mL/min flow rate.

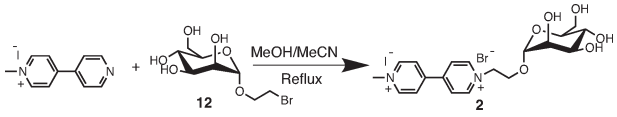
Typical Procedure for Preparation of Polymers. 2,2′-Bipyridine ligand (0.011 g, 0.072 mmol), the initiator **7** (0.010 g, 0.038 mmol), 2-naphthoxy-triethylene glycol methacrylate monomer **1** (0.52 g, 1.45 mmol), and rhodamine B monomer **3** (0.024 g, 0.038 mmol) were added to a Schlenk tube fitted with a rubber septum along with dry toluene (2 mL) as the solvent. The tube was then subjected to five freeze−pump−thaw cycles. This solution was then cannulated under nitrogen into another Schlenk tube containing Cu^{I}Br (5.0 mg, 0.03 mmol), which had been previously evacuated and refilled with nitrogen, and a magnetic follower. The solution was stirred at ambient temperature under a nitrogen atmosphere with constant stirring (t = 0 for kinetic studies). Samples were removed periodically using a degassed syringe for molecular weight and conversion analysis. At the end of the polymerization, the mixture was diluted with 10 mL of toluene, and air was bubbled through the mixture for at least 12 h. The catalyst was then removed by passing the reaction mixture through a column packed with neutral alumina. The solvents were removed under vacuum, then the residue was dissolved in a minimal volume of THF and precipitated in a methanol/water mixture (2:1, v/v). The product was then isolated by centrifugation as a pink solid (0.28 g, 56%).

Synthesis of Monomers.



2-Naphthol (8.6 g, 0.06 mol) was added to a solution of triethylene glycol monochlorohydrin (5.0 g, 0.03 mol) and potassium carbonate (8.20 g, 0.06 mol) in 150 mL of acetonitrile. The resulting solution was heated at reflux under N_2 for 36 h. The solvent was removed under reduced pressure and the reaction mixture was loaded onto a column previously filled with SiO_2 and pre-eluted with hexane. The column was the washed with a 2:3 (v/v) hexane:ethyl acetate mixture. After removal of the solvent, 2-(2-(2-(naphthalen-2-yloxy)ethoxy)ethoxy)ethanol (**9**) was obtained as a light red oil (5.1 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.70−7.75 (m, 3H); 7.42 (t, J = 6.9 Hz, 1H); 7.32 (t, J = 8.0 Hz, 1H); 7.17 (dd, J = 2.3, 2.5 Hz, 1H); 7.13 (d, J = 2.4 Hz, 1H); 4.23 (t, J = 4.6 Hz, 2H); 3.91 (t, J = 3.4 Hz, 2H); 3.68−3.75 (m, 6H); 3.60 (m, 2H); 2.78 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 156.6 (1C, CO); 134.5 (1C, CH); 129.8 (1C, CH); 129.5 (1C, CH); 128.1 (1C, CH); 127.2 (1C, CH); 126.8 (1C, CH); 123.7 (1C, CH); 118.9 (1C, C); 106.7 (1C, C); 72.5 (1C, CH_2); 70.6 (1C, CH_2); 69.8 (1C, CH_2); 69.1 (1C, CH_2); 67.3 (1C, CH_2); 61.7 (1C, CH_2). Anal. Calcd for $C_{16}H_{20}O_4$ C, 69.54; H, 7.30. Found: C, 69.34; H, 7.26.

A solution of **9** (2.00 g, 7.20 mmol) and Et_3N (1.50 mL, 10.80 mmol) in Et_2O (50 mL) was cooled to −20 °C and a solution of methacryloyl chloride (0.80 mL, 8.70 mol) in Et_2O (5 mL) was added dropwise over ca. 1 h. The mixture was then stirred at ambient temperature overnight. The triethylammonium chloride salt was filtered off and the volatiles removed under reduced pressure. The crude product was therefore purified by flash chromatography (SiO_2, hexane/ethyl acetate (4:1, v/v). The relevant fractions were collected, combined and concentrated to dryness under reduced pressure. The product was obtained as a colorless oil (2.1 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.70−7.76 (m, 3H); 7.44 (t, J = 6.9 Hz, 1H); 7.32 (t, J = 8.0 Hz, 1H); 7.18 (dd, J = 2.3, 2.5 Hz 1H); 7.13 (d, J = 2.4 Hz, 1H); 6.13 (s, 1H); 5.55 (s, 1H); 4.31 (t, J = 4.6 Hz, 2H); 4.24 (t, J = 3.4 Hz, 2H); 3.92 (m, 2H); 3.68−3.76 (m, 6H); 1.95 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 167.8 (1C, CO); 157.2 (1C, C); 136.6 (1C, CCH3); 134.9 (1C, CH); 129.8 (1C, CH); 128.0 (1C, CH); 127.2 (1C, CH); 126.8 (1C, C); 126.1 (1C, CH); 124.1 (1C, CH_2); 119.4 (1C, CH); 107.2 (1C, CH); 71.3 (1C, CH_2); 71.1 (1C, CH_2); 70.2 (1C, CH_2); 69.6 (1C, CH_2); 69.4 (1C, CH_2); 67.8 (1C, CH_2); 64.3 (1C, CH_2); 18.7 (1C, CH_3). Anal. Calcd for $C_{20}H_{24}O_5$ C, 69.75; H, 7.02. Found: C, 69.78; H, 7.14. Mass spectrometry (ESI−MS), m/z: 344.10.



Methylpyridinium iodide (1.82 g, 6.30 mmol) and **12** (1.88 g, 6.30 mmol) were dissolved in acetonitrile/methanol mixture (50 mL, 4:1, v/v). The resulting solution was heated at reflux for 20 h and left to cool with stirring. The product was filtered off, washed with 20 mL acetonitrile and sonicated for approximately 30 min. Then poured the acetonitrile off and washed again with another 20 mL acetonitrile. Then the product was recrystallized in methanol. The product was obtained as red solid (1.83 g, yield 50%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.13 (d, J = 6.6 Hz, 2H); 9.11 (d, J = 6.72 Hz, 2H); 8.54 (d, J = 6.6 Hz, 2H); 8.47 (d, J = 6.6 Hz, 2H); 4.93 (t, J = 4.8 Hz, 2H); 4.78 (d, J = 1.4 Hz, 1H); 4.44 (s, 3H); 4.17 (m, 1H); 3.99 (m, 1H); 3.86 (m, 1H); 3.76 (m, 2H); 3.60 (m, 1H); 3.56 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 151.2 (1C, C); 151.1 (1C, C); 146.8 (1C, CH); 146.5 (1C, CH); 127.3 (1C, CH); 127.1 (1C, CH); 100.0 (1C, CH); 73.6 (1C, CH); 70.8 (1C, CH); 70.1 (1C, CH); 66.8 (1C, CH); 65.8 (1C, CH_2); 61.7 (1C, CH_2); 61.2 (1C, CH_2); 48.8 (3C, CH_3). Anal. Calcd for $C_{19}H_{26}BrIN_2O_6$ C, 38.99; H, 4.48; N, 4.79. Found: C, 38.89; H, 4.59; N, 4.85. Mass spectrometry (ESI−MS), m/z: 189.21.

Assembly and Disassembly of Multivalent Ligands. **2** (1.1 mg, 1.8 μmol) and cucurbit[8]uril (3.0 mg, 1.8 μmol) were dissolved in 3 mL of distilled water. This resulting solution was sonicated for 30 min, and then **4a** (0.6 mg, 1.8 μmol) was added into this solution. The resulting mixture was sonicated for 30 min.

Sodium dithionite (4.0 mg, 0.024 mol, 10 equiv) was added into the solution containing glycopolymer complex **6a** (5.4 mg, 1 equiv). This mixture was stirred in air for 10 min. The insoluble solid was filtered off, containing polymer scaffold **4a** and CB[8].

■ ASSOCIATED CONTENT

Supporting Information. Experimental details including the synthesis and structures of **3**, **12**, **4a/b**, **4′** and **9a/b**, pseudofirst order kinetic plots of the polymerizations (Figures S1−S10), NMR (Figure S11), UV/vis (Figure S12), and ITC (Figures S13 and S14) spectra of the complexes formed with 2-naphthol and **1**, **2**, and **5**, fluorescence (Figure S15) and NMR (Figure S16) spectra of **6a**, photographs (Figure S17) of solutions containing **4a**, **5**, and **6a** under sunlight and UV light, UV/vis spectra (Figure S18) of **6b**, **10a**, and **10b**, NMR titration studies (Figure S19). This material is available free of charge via the Internet at http://pubs.acs.org.

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