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A Systems Approach to Controlling Supramolecular Architecture and Emergent Solution Properties via Host−Guest Complexation in Water

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Abstract: The assembly behavior of aryl/alkyl imidazolium ionic liquid salts in aqueous solution has been investigated. These salts undergo self-assembly into one-dimensional stacks via hydrophobic and $\pi-\pi$ interactions upon increasing concentration, which led to a substantial increase in the solution viscosity in water. Addition of the macrocyclic host molecules cucurbit[*n*]urils (CB[*n*]) were found to effectively alter the supramolecular assemblies, as evidenced from the dramatic increase (by CB[7]) and decrease (by CB[8]) in solution viscosity and aggregation size in water, on account of the different binding stoichiometries, 1:1 complexation with CB[7] and 2:1 complexation with CB[8]. Furthermore, the aggregate architectures were controllably modified by competitive guests for the CB[*n*] hosts. This complex supramolecular *systems approach* has tremendous implications in the fields of molecular sensor design, nonlinear viscosity modification, and controlled release of target molecules from a defined supramolecular scaffold in water.

Introduction

Ionic liquids are a class of materials with great potential as green solvents for applications ranging from new chemical technologies to use in industrial processes.[1,2] The first report that employed cationic imidazolium ionic liquids in organometallic catalysis appeared in the mid-1990s;[3] a wide variety of imidazolium-based ionic liquids have since been prepared and well-studied as media in chemical synthesis,[4] catalysis,[5] in the preparation of conducting polymers, and fabrication and operation of polymeric electrochemical devices,[6,7] as well as in separation technology.[8−10] Most of the recent studies on imidazolium salts in aqueous systems focus on alkylimidazolium derivatives with a wide variety of both the anionic counterion species[11] and alkyl chain length;[12] both of these factors control the hydrophilicity of imidazolium ionic liquids and can lead to a self-assembled structure.[13,14] Mixed aryl/alkyl ionic liquids, a new member in ionic liquid family, have been referred to as the next generation of ionic liquids, which leads to a wider range of physical and chemical properties than current ionic liquids by introducing inductive interactions.[15] These mixed aryl/alkyl molecules contain aromatic substituents as well as an imidazolium core, and these materials can lead to unique self-assembly behavior in water, forming π stacked aggregates.[16]

Cucurbit[*n*]urils (CB[*n*]s) are a family of macrocyclic hosts that has been extensively studied in recent years within the fields of molecular recognition and aqueous self-assembly.[17−20] In 2008, we first reported on *N*-methyl-*N*′-alkylimidazolium ionic liquids as novel guests for CB[6];[21] this report was followed by a series of publications from several groups focusing on the physical chemical properties and applications of these imidazolium salts with both CB[6] and CB[7].[10,22−24] The location of the imidazolium guest(s) inside the CB[*n*] cavity and the

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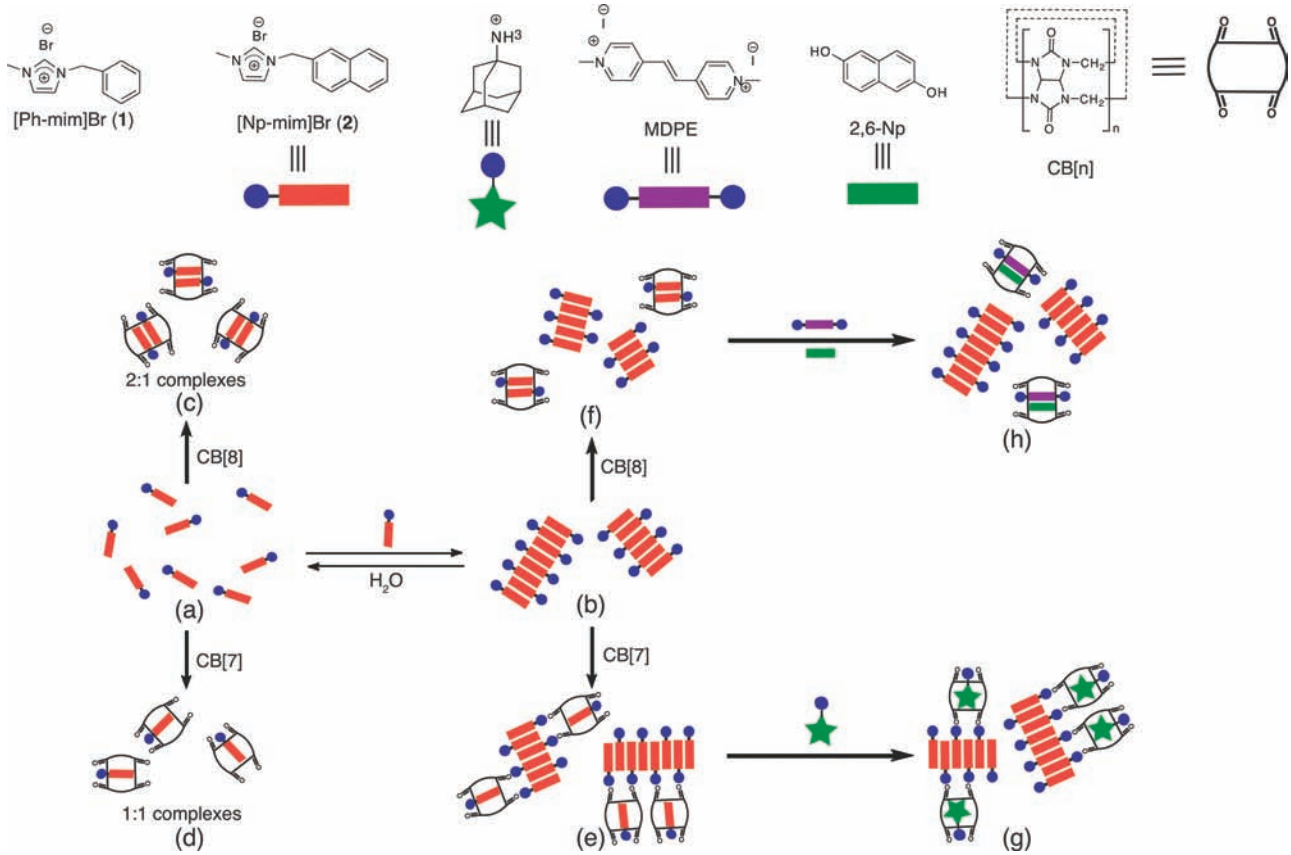
Scheme 1. A Systems Approach To Control a Wide Variety of Self-Assembled Structures and Aggregated Motifs Based on Aryl/Alkylimidazolium Salts in Water[a]



[a] The $\pi-\pi$ stacking can be easily tuned through the addition of the macrocyclic hosts CB[7] and CB[8] as well as select small molecule competitive guests.

binding stoichiometry are of particular interest, as one can employ the complexes as a hierarchical assembly motif and thus control structure. A larger homologue in the cucurbituril family, CB[8], is capable of simultaneously binding two guest molecules in its cavity, thus forming a ternary complex. Kim et al. have demonstrated that CB[8] can serve to stabilize a charge-transfer (CT) complex in its cavity between viologen derivatives and hydroxynaphthalenes;[25] variations of the ternary complexes based on this CT couple have led to a wide variety of self-assembled architectures.[26−30]

As hydrophobic moieties prefer the interior of a cucurbit-[*n*]uril host over their aqueous surroundings, these mixed aryl/alkylimidazolium aggregates in water can be altered upon the addition of both CB[7] and CB[8] host molecules. However, as the stoichiometries for binding are 1:1 and 2:1 in the case of CB[7] and CB[8], respectively, they each affect the self-assembly behavior differently, forming aggregates and three-dimensional structures in a readily controlled manner and leading to new emergent properties of the aqueous systems. In the past decade, a variety of supramolecular systems have been explored, such as the self-sorting behavior of small molecules and the self-organization of nanostructures leading to supramolecular materials.[31−37] However, contrary to self-sorting, the approach we take represents a dynamic interplay between all of the components in the system. Specifically, we present a *systems approach* for designing supramolecular architectures under thermodynamic control based on the self-assembly of

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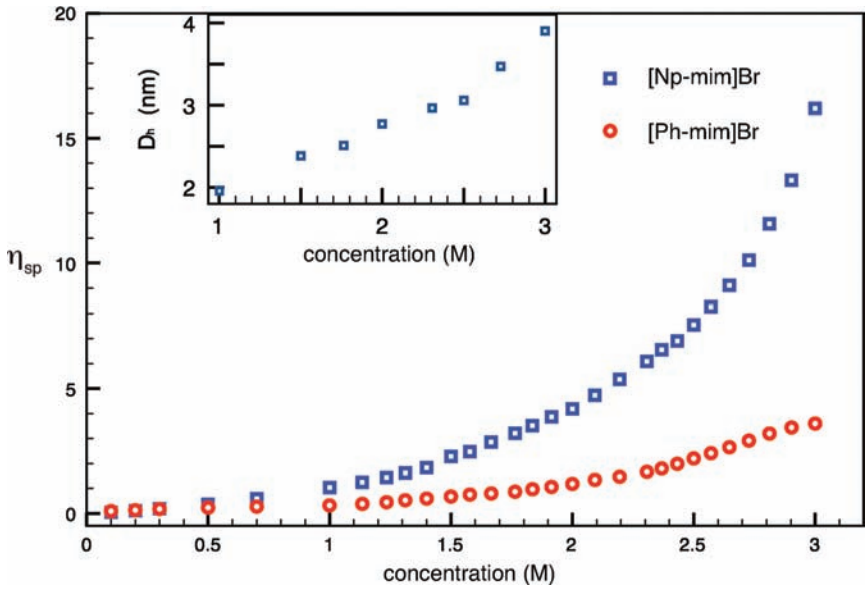

Figure 1. A plot of specific viscosity of [Ph-mim]Br (**1**) and [Np-mim]Br (**2**) as a function of concentration (the standard deviation for all η_{sp} measurements is lower than 0.01%). The inset depicts the hydrodynamic diameters (D_h) of [Np-mim]Br aggregates as a function of concentration (over the same range).

mixed aryl/alkylimidazolium ionic liquids with CB[7] and CB[8] in aqueous media, as shown in Scheme 1.

Results and Discussion

Formation of Supramolecular Aggregates. To examine the supramolecular self-assembly of the aryl/alkylimidazolium salts 1-phenyl-3-methylimidazolium bromide and 1-naphthyl-3-methylimidazolium bromide {[Ph-mim]Br (**1**) and [Np-mim]Br (**2**)} in water, a number of different characterization techniques were carried out. These included solution viscosity (kinematic viscosity), dynamic light scattering (DLS), fluorescence spectroscopy, and multidimensional NMR spectrometry. In order to discern whether **1** and/or **2** were able to undergo self-assembly and form aggregates in water, Ubbelohde solution viscosity studies were first performed in pure water at 25 °C. As depicted in Figure 1, the specific viscosity (η_{sp}) for both **2** and **1** increased as a function of concentration; however, the increase was much more noticeable for **2**, which exhibited a remarkable increase in η_{sp} from 0.05 up to 16.2 as its concentration increased from 0.1 to 3 M.

The most reasonable explanation for this marked increase in solution viscosity for **2** is the formation of an extended structure (Scheme 1b); however, in order to ascertain the specific architecture of such aggregates, both DLS and fluorescence studies were necessary. Dynamic light scattering measurements were performed on **2** over the same concentration range of the viscosity studies above and also in pure water at 25 °C. The size of the [Np-mim]Br aggregates ranged from 2 nm to over 4 nm as the concentration increased from 1 to 3 M. On the other hand, the η_{sp} of [Ph-mim]Br only showed a moderate increase upon increasing concentration, and indeed, DLS measurements did not show any formation of aggregates. The major difference between [Ph-mim]Br (**1**) and [Np-mim]Br (**2**) is the larger aromatic ring system of **2** that leads to stronger hydrophobic and $\pi-\pi$ stacking interactions in concentrated aqueous solution. On the basis of previous studies of $\pi-\pi$ interactions on porphyrin-containing systems, the π systems of two neighboring molecules have an interplanar separation of between 3.4 and 3.6 Å, depending on the strength of the $\pi-\pi$ interaction.[38] Choosing an intermediate value of 3.5 Å and taking into account the DLS data, we can estimate the average number of molecule **2** in one aggregate to be approximately 5−8 at a concentration of 1 M and 15−20 at 3 M.

In order to gain a further insight into the types of interactions between each of the aryl/alkylimidazolium molecules in the aqueous supramolecular aggregates, fluorescence spectroscopy was carried out. Figure 2 shows fluorescence spectra of a solution of **2** as a function of concentration from 0.5 to 50 mM. As the concentration of molecules in solution increased, the emission peak (λ = 335 nm) was significantly quenched, and simultaneously, a new emission band emerged at 405 nm. A single isosbestic point was found at 370 nm, which suggests that there is an equilibrium that exists between two species, "free" molecules in solution and $\pi-\pi$ stacks.[39,40] The inset of Figure 2 shows the corresponding titration plot upon increasing concentration of [Np-mim]Br; the change of intensity of the emission measured at both 335 and 405 nm provides an insight in the reduction of free molecules in solution (335 nm) and the consequent formation of $\pi-\pi$ stacks (405 nm).

While the fluorescence data was certainly suggestive of $\pi-\pi$ interactions, ^{1}H NMR spectroscopy as well as 2D NOESY spectroscopy was employed to confirm this kind of assembly was taking place in solution. Figure 3a shows a stack plot of ^{1}H NMR spectra with increasing concentration of [Np-mim]Br from 0.01 to 3 M. Upon increasing the concentration of **2** 100-fold, from 0.01 to 1 M, all peaks in the spectrum shifted upfield by approximately 0.5 ppm but remained relatively sharp. This indicated that the small molecules indeed undergo some form of assembly in solution; however, this could not be detected in the DLS measurements (Figure 1), as the size of the assemblies was below the detection limit of the apparatus. Upon increasing the concentration from 1 to 3 M, the peaks in the ^{1}H NMR

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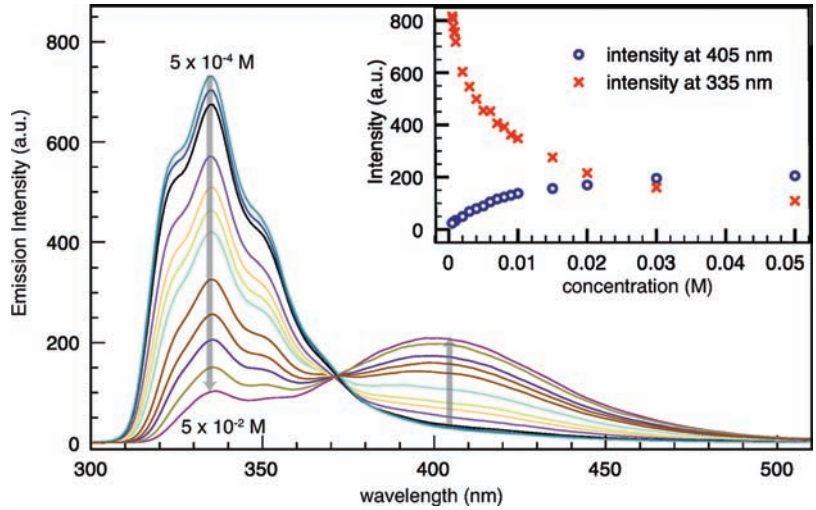

Figure 2. Fluorescence spectra of [Np-mim]Br (**2**) in water. As the concentration of **2** increases, the peak centered at $\lambda = 335$ nm decreases while the peak at $\lambda = 405$ nm increases. A direct comparison of this increase and decrease in intensity is shown in the inset. (See Supporting Information Figure S8 for the fluorescence spectra of all the control experiments.)

spectra did not shift much further but appeared to be slightly broader. It is worth pointing out that between 2.5 and 3 M, the peaks in the ^{1}H NMR spectra shift slightly back downfield and this is likely on account of the tremendous increase in solution viscosity as the exponential increase in viscosity is observed at this concentration in Figure 1. Additionally, overlapping signals between 7 and 8 ppm, corresponding to the aromatic protons on the naphthalene moiety as well as H_c and H_d on the imidazolium ring (see labeled structure of **2** in Figure 3a), became separated from one another, indicating the presence of a different environment, an aggregated state, in the high concentration regime. The NOESY spectrum (Figure 3b) also clearly indicated that molecular interactions occur in the [Np-mim]Br solution (2 M). The cross-peaks labeled in blue represent aromatic protons on *different* molecules interacting with each other, proving molecular interactions took place between the naphthalene rings.[41] Both the ^{1}H NMR and NOESY spectrum for **2** are in agreement with the observations and data obtained from the solution viscosity, DLS, and fluorescence measurements, indicating formation of the $\pi-\pi$ stacked aggregates in a concentrated **2** aqueous solution, as shown in Scheme 1b. In contrast, [Ph-mim]Br **1** formed little aggregation, as evidenced from its ^{1}H NMR and NOESY spectra in high concentration (see Supporting Information Figure S2 and S4).

Host−Guest Complexes. ^{1}H NMR titration experiments were performed in neutral D_2O to investigate the binding behavior of CB[*n*] and imidazolium guests. Titrations were carried out by gradually increasing the molar ratio of the host molecules (CB[*n*]) while the amount of guest molecules ([Ph-mim]Br and [Np-mim]Br) was kept constant. When CB[7] was titrated into an aqueous solution of [Ph-mim]Br (see Figure 4a), all of the peaks except H_a from [Ph-mim]Br in the spectrum became broad and shifted upfield, indicating formation of fast exchange CB[7]−[Ph-mim]Br complexes. Once the ratio of CB[7] to [Ph-mim]Br was beyond 1 equiv, all of the peaks from [Ph-mim]Br no longer shifted and became sharp again, which indicated a strong 1:1 CB[7]−[Ph-mim]Br binding interaction. In particular, the benzyl proton peaks (indicated by the red dots in Figure 4a) as well as H_e and H_c are clearly separated from each other and shifted upfield. This phenomenon suggests that the benzyl ring, the methylene linker, and a part of the imidazolium ring all reside inside the CB[7] cavity, and a calculated structure that fits the NMR data is shown in Figure 5a.[21,42,43] As the methyl group on the opposite nitrogen atom was placed in close proximity to the carbonyl groups of CB[7], a deshielding effect is observed and H_a experienced a downfield shift.[44] In a similar manner, [Np-mim]Br was also encapsulated in the CB[7] cavity in a 1:1 stoichiometry (^{1}H NMR titration spectra shown in Supporting Information Figure S1); however, as guest **2** is substantially larger, the entire imidazolium ring is located in the deshielding region of CB[7] (Figure 5b).

The larger guest **2** was envisioned to preferentially bind to the larger macrocyclic host CB[8]. Figure 4b shows a series of ^{1}H NMR spectra of a titration of CB[8] into an [Np-mim]Br solution from 0 to 0.5 equiv, yielding a 1:2 complex. Upon addition of CB[8], the aromatic proton peaks from the naphthyl moiety (indicated by the red dots in Figure 4b) broadened and experienced an upfield shift from 7.5 to 6.5 ppm. On the alkyl portion of the molecule, H_a and H_b experienced a slight downfield shift while the chemical shifts of both H_e and H_c remained unchanged. These observations can be rationalized with a 2:1 binding model of [Np-mim]Br with CB[8], in which only the aromatic naphthalene rings reside inside the hydrophobic CB[8] cavity (see Figure 5c). In contrast, with such a high selectivity for CB[7], the smaller [Ph-mim]Br guest does not bind to CB[8] strongly enough to be followed by ^{1}H NMR.

Isothermal titration calorimetry (ITC) has been widely used to measure equilibrium binding constants (K_a) in CB[*n*] host−guest chemistry[45−47] and was therefore applied to examine the binding strength of the CB[*n*]−imidazolium

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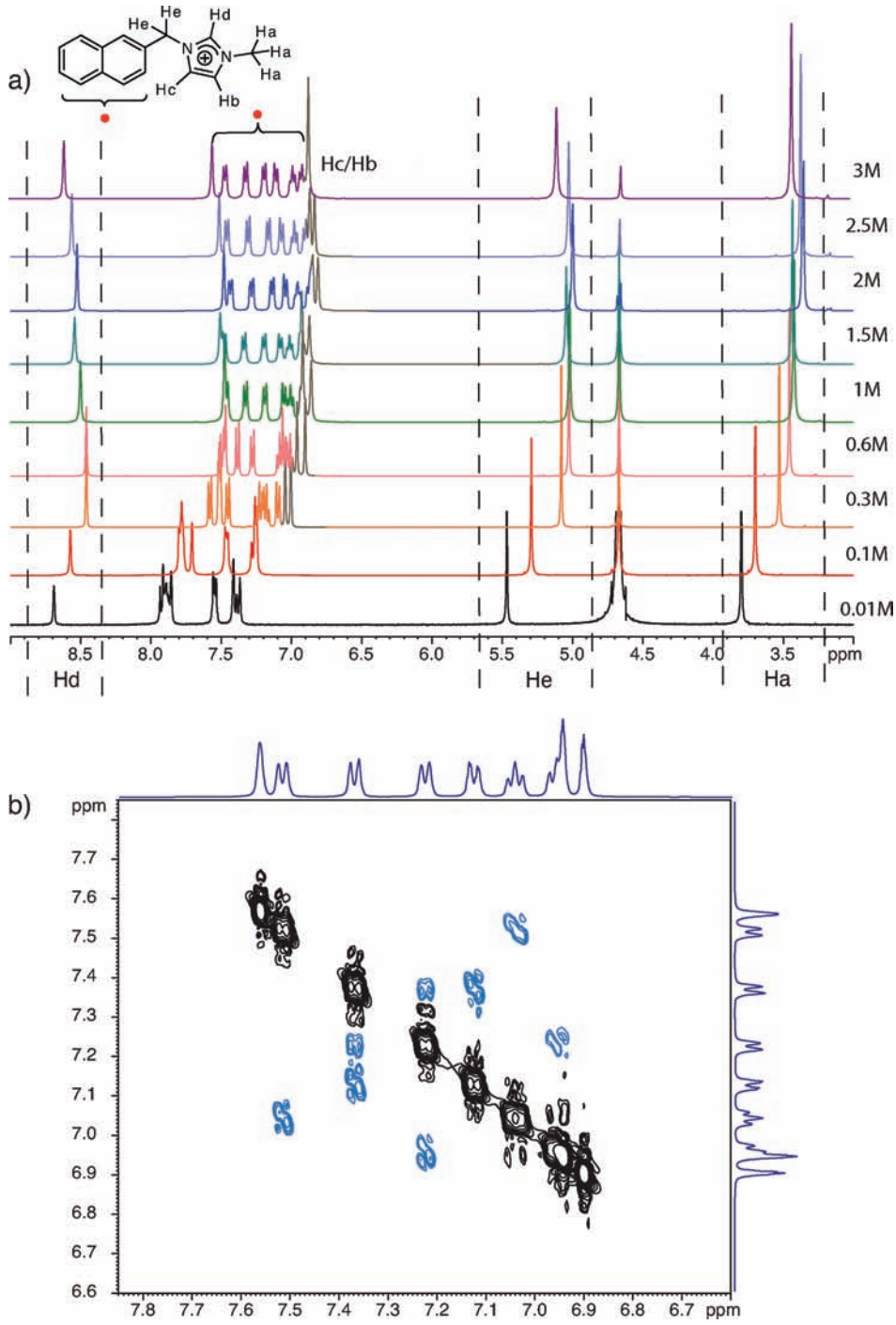

Figure 3. (a) A stack plot of the ^{1}H NMR spectra of [Np-mim]Br (**2**) in D_2O with increasing concentration. (b) A NOESY spectrum of [Np-mim]Br (**2**) in D_2O at a concentration of 2 M, the blue cross peaks show intermolecular interactions between two neighboring [Np-mim]Br molecules.

complexes in this study. Figure 6a depicts a typical isotherm for a strong binding interaction between CB[7] and [Ph-mim]Br [$K_a = (8.0 \pm 0.3) \times 10^5$ M^{-1}]. [Np-mim]Br also formed a reasonably strong complex with CB[7], resulting in a binding constant of $(3.0 \pm 0.3) \times 10^5$ M^{-1}; this slightly weaker K_a value is presumably due to the reduced steric fit of the larger naphthyl group inside the cavity. CB[8] was able to form 1:2 complexes with [Np-mim]Br with two successive binding constants $K_{a1} = (8.0 \pm 0.3) \times 10^5$ M^{-1} (for the first equivalent of [Np-mim]Br) and $K_{a2} = (4.0 \pm 0.3) \times 10^4$ M^{-1} (for the second equivalent of [Np-mim]Br inside the CB[8] cavity), as shown in Figure 6b. The ITC binding interaction between [Ph-mim]Br and CB[8] was very weak and was in agreement with the ^{1}H NMR data.

Optical spectroscopic techniques including UV/vis and fluorescence were also utilized in an effort to study these CB[*n*]−imidazolium complexes. Upon addition of CB[7] to either [Ph-mim]Br or [Np-mim]Br (see Figure 7a, blue trace), UV/vis absorbance was reduced and slightly red-shifted, presumably due to binding (see Supporting Information Figure S5 for the UV/vis spectra of [Ph-mim]Br with CB[7]). In the presence of CB[8], a significant reduction in the UV/vis absorbance for [Np-mim]Br is observed and the absorption peak also broadened (see Figure 7a, red trace), and again the binding

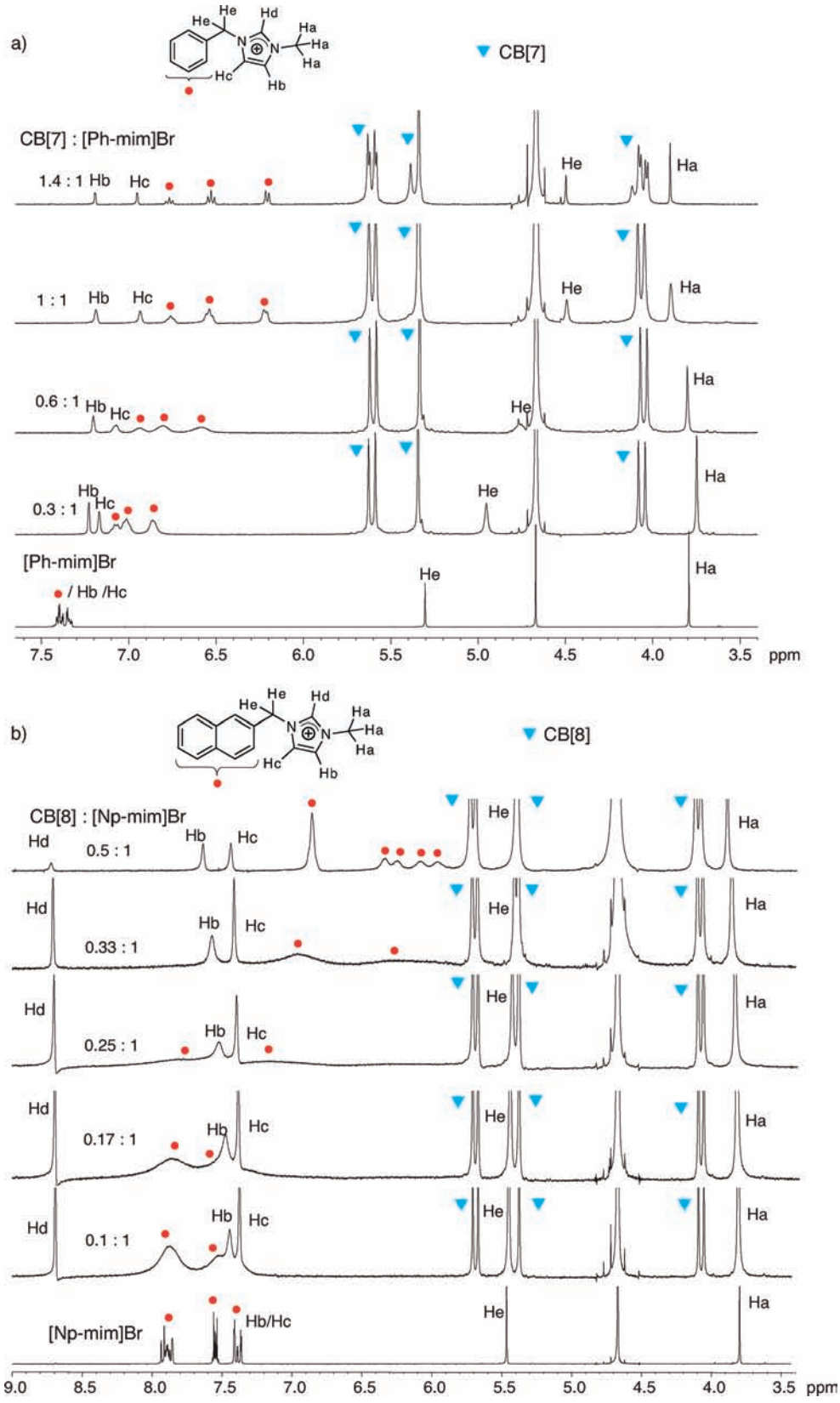

Figure 4. ^{1}H NMR spectra in D_2O at 25 °C of (a) [Ph-mim]Br (**1**) with increasing amounts of CB[7] and (b) [Np-mim]Br (**2**) with increasing amounts of CB[8]. The red dots indicate aromatic chemical shifts and the blue triangles highlight the chemical shifts of CB[7] and CB[8], respectively.

of CB[8] with [Ph-mim]Br was too weak to observe any noticeable changes in the UV/vis spectrum. The interaction with CB[8] was further probed by a series of titration experiments (Supporting Information Figure S10) and is clearly caused by two [Np-mim]Br guest molecules binding inside one CB[8] host molecule.

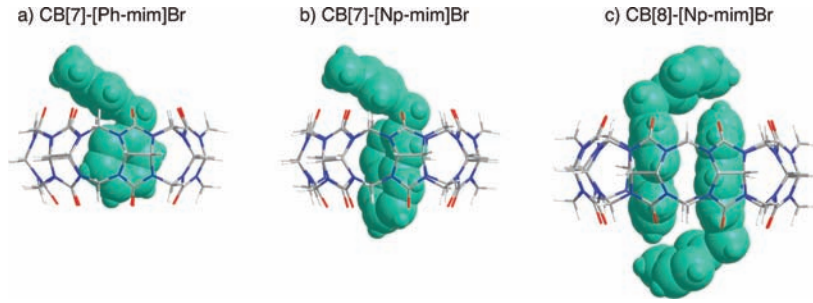

Figure 5. Complexation models calculated at the HF/3-21G level of theory for several CB[*n*]−arylimidazolium complexes: (a) CB[7]−[Ph-mim]Br (1:1), (b) CB[7]−[Np-mim]Br (1:1), (c) CB[8]−[Ph-mim]Br (1:2), and (d) CB[8]−[Np-mim]Br (1:2).

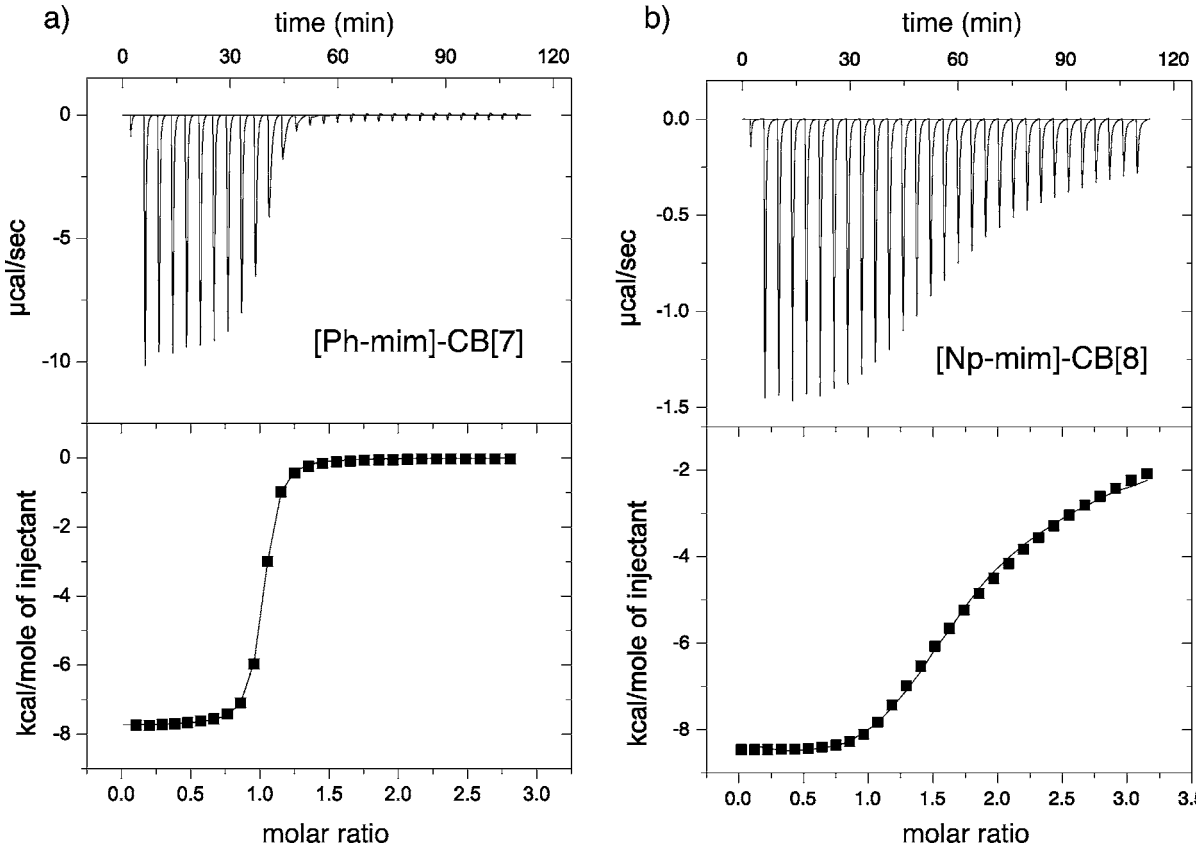

Figure 6. Calorimetric titration plots of (a) CB[7] with [Ph-mim]Br (**1**) and (b) CB[8] with [Np-mim]Br (**2**) in 10 mM sodium phosphate buffer (pH 7) at 25 °C.

Emission spectra (Figure 7b) were obtained to probe the binding of CB[8] with [Np-mim]Br. The λ_{max} of [Np-mim]Br emission centered at 335 nm, and its intensity was reduced upon addition of CB[8] into a dilute aqueous solution of [Np-mim]Br (10^{-5} M). Simultaneously, a new emission band emerged at 405 nm (Figure 7b), which was similar to the behavior observed upon increasing the concentration of [Np-mim]Br in the absence of CB[8] (Figure 2), suggestive of $\pi-\pi$ stacking inside the CB[8] cavity, which would be direct evidence of a 2:1 complex.[48] In contrast, CB[7] binding with [Np-mim]Br (**2**) in a dilute aqueous solution (10^{-5} M) had no noticeable effect on the emission spectrum and confirmed the formation of 1:1 binding complexes.

Using CB[*n*] To Control Supramolecular Aggregates. As the larger CB[*n*] homologues were found to be selective host molecules for both [Ph-mim]Br (**1**) and [Np-mim]Br (**2**), it was envisioned that addition of CB[*n*] host molecules to concentrated aqueous solutions of the imidazolium salts could alter the structure of the $\pi-\pi$ stacked aggregates. Figure 8 illustrates that the solution specific viscosity (η_{sp}) for both [Ph-mim]Br and [Np-mim]Br (2 M) increased upon addition of CB[7]. It is worth noting that the addition of only 0.1 equiv of CB[7] into a [Np-mim]Br solution increased the solution viscosity by 3 times. DLS studies (inset of Figure 8) have also confirmed the viscosity results, as the aggregate size has been increased from 3.2 to 9.6 nm.

^{1}H NMR and UV/vis clearly indicated that CB[7] formed 1:1 complexes with both **1** and **2** in dilute aqueous solutions; however, the interactions of CB[7] with the $\pi-\pi$ stacked aggregates in the concentrated regime were unclear from the solution viscosity and DLS studies. Therefore, 2D NOESY NMR experiments were conducted to examine the proton

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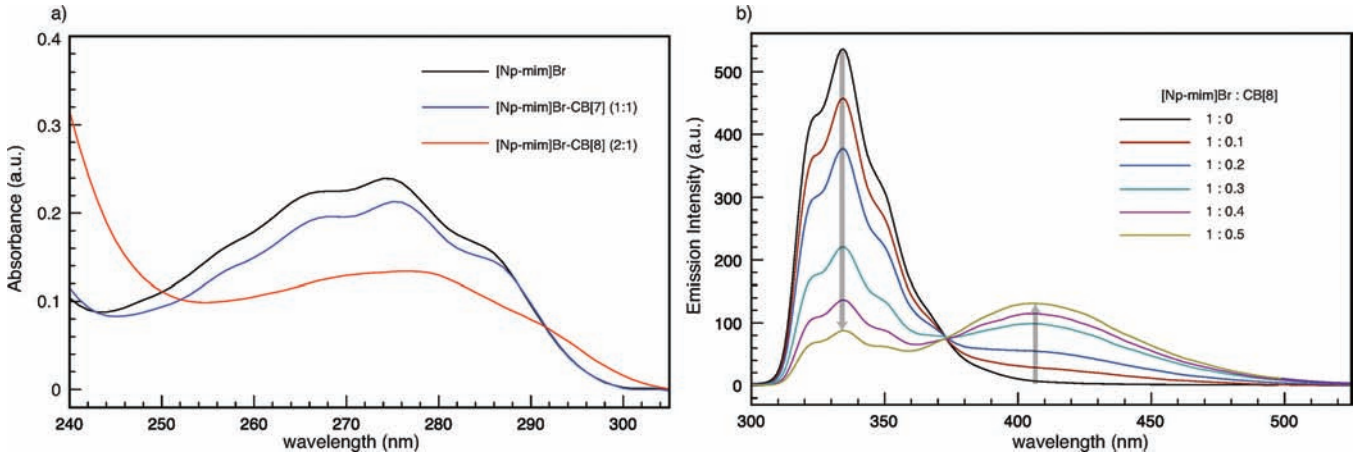

Figure 7. (a) Aqueous UV/vis spectra of [Np-mim]Br (**2**) (black trace), **2** with CB[7] in 1:1 ratio, and **2** with CB[8] in 2:1 ratio (10^{-5} M). (b) Emission spectra of a titration of CB[8] into an aqueous solution of [Np-mim]Br (10^{-5} M).

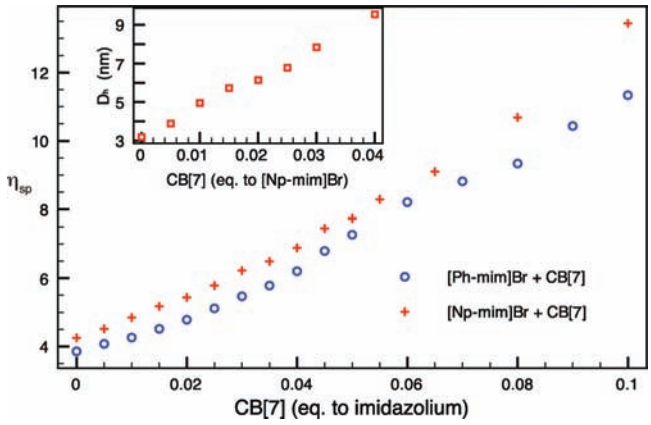

Figure 8. A plot of solution specific viscosity depicting both [Ph-mim]Br (**1**) and [Np-mim]Br (**2**) (at a concentration of 2 M in water) as a function of CB[7] equivalents. Inset shows the D_h of the [Np-mim]Br aggregates formed (in a static 2 M solution) corresponding to Scheme 1e upon addition of CB[7].

interactions between the 1:1 CB[7]−[Np-mim]Br complexes and the [Np-mim]Br $\pi-\pi$ stacked aggregates which remained at high concentration (2 M). As shown in Figure 9, the signals labeled in blue represent the interactions between the naphthalene ring protons on neighboring [Np-mim]Br molecules, indicating that stacks still remained in solution. Additionally, interactions between the CB[7] host and the naphthalene guests (labeled in green) could also be observed.

Interestingly, interactions between proton H_a (imidazolium methyl group) and the naphthalene ring (Figure 9, labeled in red) were also observed in this spectrum, which can be rationalized in the following manner on account of *both* portal and cavity binding with CB[7]. As the symmetric CB[7] is added into the concentrated solution of imidazolium **2**, it can strongly bind to one guest molecule, incorporating the naphthyl moiety into its cavity to form the CB[7]−imidazolium complex, where the positive charge on the imidazolium ring only occupies one of the two CB[7] portals. As a consequence, the other CB[7] portal is now free to bind another positively charged species through ion−dipole interactions,[21,49] such as the alkylimidazolium portion of the stacks (see Scheme 1e). Thus, for high solution concentrations of **2**, CB[7]−**2** complexes can be adapted and display both portal and cavity binding motifs which form branched architectures from the $\pi-\pi$ stacked aggregates (Scheme 1e).

As a result of all the different noncovalent interactions being used to assemble this system, modification of the supramolecular structures becomes possible. The removal of the portal-bound CB[7] branches from the $\pi-\pi$ stacked aggregates can be achieved by simple addition of a competitive portal guest for CB[7] such as NaCl or KCl salt.[30,50,51] Furthermore, the system can be perturbed by addition of a competitive cavity guest for CB[7], such as 1-adamantylamine;[52] the binding interaction for 1-adamantylamine with CB[7] ($K_a = 4 \times 10^{12}$ M^{-1})[53] is substantially stronger than for [Np-mim]Br [$K_a = (3.0 \pm 0.3) \times 10^5$ M^{-1}] and induced the release of **2** upon addition (see Figure S13 in Supporting Information). Therefore, this system allows for a great amount of external control over the aggregation state as well as for the triggered release of complexed guests (Scheme 1g).

While CB[7] retains an "open" portal in a 1:1 complex, CB[8], on the other hand, complexes two [Np-mim]Br guests inside its cavity, as depicted in Figure 5c; thus, both portals are each fully occupied with a positively charged imidazolium moiety. These 2:1 complexes of **2** with CB[8] dissolved easily in an aqueous environment and did not append themselves onto any $\pi-\pi$ stacked aggregates of [Np-mim]Br present in solution. Therefore, addition of CB[8] to a concentrated solution of [Np-mim]Br results in a reduction of the aggregate size up to the solubility limit of CB[8] (see Scheme 1f), which can easily be seen in the DLS (as shown in Figure 10).

In a similar experiment described above for CB[7], a competitive guest pair could be added to the system containing CB[8] to perturb complexation. Here the double charged *N*,*N*′-dimethyldipyridyliumylethylene diiodide (MDPE)[54] was used together with 2,6-dihydroxynaphthalene (2,6-Np) in a 1:1 ratio

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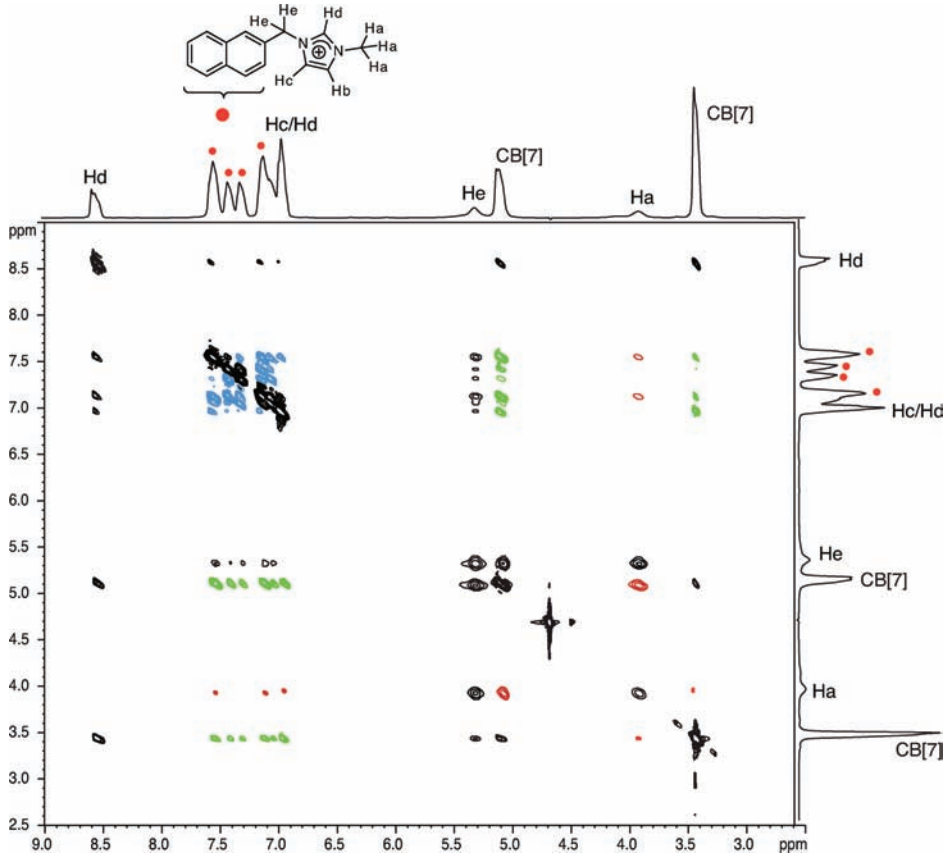

Figure 9. NOESY spectrum of a concentrated solution of [Np-mim]Br (**2**) in D_2O (2 M) with 0.1 equiv of CB[7].

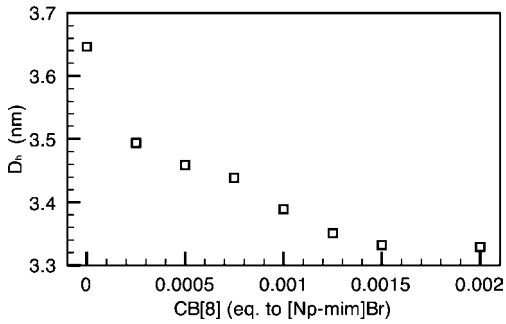

Figure 10. The D_h of [Np-mim]Br aggregates in 2 M aqueous solution as a function of added CB[8].

as the competitive guest pair and successfully decomplexed CB[8]−[Np-mim]Br, as observed in ^{1}H NMR (see Supporting Information Figure S12). Displacement of **2** then resulted in the reformation of the $\pi-\pi$ stacked [Np-mim]Br aggregates (Scheme 1h). Thus, full control over the system is gained through competitive guest binding with the ability to either reduce or increase the $\pi-\pi$ stacked aggregates and hence the viscosity and overall structure of the system.

Conclusion

We have explored a novel *supramolecular system* based on aryl/alkylimidazolium where a wide variety of self-assembled structures and aggregated motifs can be obtained in an aqueous environment. Control and amplification of the solution architectures were accomplished through the addition of discrete macrocyclic host molecules CB[7] and CB[8] and a number of competitive guests. Two-dimensional aggregates could be formed through hydrophobic and $\pi-\pi$ interactions in aqueous solutions as a function of concentration and highly selective guests with CB[7] based on both portal and cavity binding. Arylimidazolium salts containing a larger aromatic moiety displayed stronger self-assembly behavior in water, resulting in extremely large increases in both solution viscosity and aggregate size. Through the addition of CB[8] host molecules, the size of these large one-dimensional stacks could be controlled in a reversible manner by assembling and disassembling host−guest complexes based on a 2:1 stoichiometry. On the other hand, CB[7] could be used to control the [Np-mim]Br aggregates and also yield a new supramolecular architecture based on both portal and cavity binding motifs. Thus, a multicomponent supramolecular aqueous *systems approach*, which is degradable, controllable, and environment-friendly, makes way for potential applications in the fields of controlled release and nonlinear viscosity modification, both heavily reliant on the binding and subsequent release of small molecules from a defined supramolecular scaffold or superstructure in an aqueous environment.

Experimental Section

Materials and Methods. Materials were obtained from commercial suppliers and were used without further purification. Solution viscosities were measured using Schott-Geräte Ubbelohde microviscometers with a suspended level bulb using a PVS1 measuring device, and the microviscometers were thermostated in a PV15 water bath at 25.00 (0.01) °C using a DLK10 thermostat unit (all manufactured by Lauda). ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance QNP 400, and NOESY spectra were recorded on a Bruker Avance 500. DLS measurements were carried out on a Malvern Zetasizer NanoZS at 25 °C. Optical spectra were

performed on a Varian Cary 4000 UV−vis spectrophotometer and an Eclipse fluorescence spectrophotometer at 25 °C. ITC experiments were carried out on a VP-ITC from Microcal Inc. at 25 °C in 10 mM sodium phosphate buffer (pH 7).

Synthesis of CB[*n*]. CB[*n*] was synthesized from glycoluril with formaldehyde by basic procedures published by Day and Kim,[55,56] and further isolation and purification were carried out by our previously reported method.[10]

Synthesis of Arylmethylimidazolium. A solution of 1-methylimidazole (1.47 g, 18 mmol) and 2-(bromomethyl)naphthalene (4.42 g, 20 mmol) or benzyl bromide (3.42 g, 20 mmol) in 100 mL of toluene was refluxed until a large amount of insoluble product occurred. The insoluble compound was isolated and washed with toluene.

[Ph-mim]Br. Compound **1** ($C_{11}H_{13}N_2Br$) was obtained as a yellowish oil (91%). UV/vis: see Supporting Information Figure S5. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 9.27 (1H, s), 7.93 (1H, t), 7.10 (1H, t), 7.40 (5H, m), 5.43 (2H, s), 3.84 (3H, s). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 137.53 (NCN), 135.81 (C, aromatic ring), 129.82, 129.58, and 129.21 (5CH, aromatic ring), 124.84 and 123.19 (2CH, imidazolium ring), 52.62 (CH_2), 36.78 (CH_3). HRMS (ESI+): *m*/*z* calcd for $[C_{11}H_{13}N_2]^+$ 173.1075, found 173.1079.

[Np-mim]Br. Compound **2** ($C_{15}H_{15}N_2Br$) was obtained as a white crystal (87%). UV/vis: see Figure 7. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 9.23 (1H, s), 7.90 (4H, m, aromatic ring), 7.82 (1H, t), 7.71 (1H, t), 7.53 (3H, m), 5.56 (2H, s), 3.83 (3H, s). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 137.68 (NCN), 133.61, 133.59, 133.15, 129.65, 128.74, 128.56, 128.43, 127.63, 127.62, and 126.61 (10C, aromatic ring), 124.88 and 123.33 (2CH, imidazolium ring), 52.91 (CH_2), 36.78 (CH_3). HRMS (ESI+): *m*/*z* calcd for $[C_{15}H_{15}N_2]^+$ 223.1241, found 223.1235.

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Supporting Information Available: ^{1}H NMR titration, 2D-NOESY spectra, UV/vis absorption spectra, emission spectra, and ITC measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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