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Interlocked Photo-Degradable Macrocycles Allow One-Off Photo-Triggerable Gelation of Organo- and Hydrogelators

Shun-Te Tung,[a],‡ Hung-Te Cheng,[a],‡ Alex Inthasot,[a] Fang-Che Hsueh,[a] Ting-Jia Gu,[a] Pei-Cong Yan,[a] Chien-Chen Lai,[b] and Sheng-Hsien Chiu*[a]

[a] Dr. S.-T. Tung, H.-T. Cheng, Dr. A. Inthasot, F.-C. Hsueh, T.-J. Gu, P.-C. Yan, and Prof. S.-H. Chiu
Department of Chemistry and Center for Emerging Material and Advanced Devices, National Taiwan University
No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan, 10617, R.O.C.
E-mail: shchiu@ntu.edu.tw

[b] Prof. C.-C. Lai
Institute of Molecular Biology, National Chung Hsing University and Department of Medical Genetics, China Medical University Hospital, Taichung, Taiwan, R.O.C.

‡ These authors contributed equally to this study.

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Abstract

[2]Rotaxanes displaying one-off photo-triggerable gelation properties have been synthesized through the "clipping" of photo-degradable macrocycles around the amide or urea functionalities of organo- and hydrogelators. Irradiation with UV light cleaved the photo-labile macrocyclic components from the [2]rotaxanes, resulting in the free gelators being released into solution and, thereafter, forming gels. When the rate of gelation was sufficiently rapid, selective gelation of specific regions of the solution—and, indeed, photo-patterning of the solution—was possible.

Main Text

Gels formed from low-molecular-weight gelators are useful materials in various fields, including foodstuffs, pharmaceuticals, biomedicine, and energy.[1] Although tremendous numbers of gelators have been developed, our continued inability to fully control noncovalent interactions means that many continue to be discovered through trial-and-error. Therefore, many unique structures exist for gelators—and small alterations may change their aggregation behavior significantly. Photo-controllable gelators, which undergo sol–gel transformations upon irradiation, would appear to have greater practical value than classic heat-and-cool gelators, because creating and/or transferring a hot solution may not be convenient in a device setting.[2] Nevertheless, covalently introducing a photo-responsive motif into the structure of a known gelator might not always be a practical approach toward preparing photo-responsive gelators—the valuable properties of the original gelator might not be retained after such structural alteration. Because one-off photo-triggerable materials,

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such as those used with UV curing in dentistry and semiconductors, have proven to be valuable in our daily lives, the question arises: Can we develop a general strategy to introduce one-off photo-triggerable behavior into known gelators without changing their original structures or synthetic pathways, thereby extending their practical use? In contrast to previous examples of gels formed from solutions of rotaxanes[3] or polyrotaxanes,[4] we suspected that interlocking a photo-cleavable macrocyclic component around a known gelator molecule would introduce steric bulk and/or functional group shielding[5] and, thereby, inhibit aggregation of the gelator as a direct consequence of forming its corresponding rotaxane;[6] subsequent photo-cleavage of the macrocyclic component would release the free gelator and lead to gelation of the solution (Figure 1). To make this approach more general, the photo-labile macrocycle would ideally recognize functionalities present in the structures of many gelators. Herein, we report an approach for introducing one-off photo-triggerable gelation properties into known organo- and hydrogelators: using Na^+ ions to template the "clipping" syntheses of corresponding [2]rotaxanes featuring an *o*-nitrobenzyl[7]–containing macrocycle encircling their amide and urea functionalities, respectively. UV light cleaved the interlocked *o*-nitrobenzyl–containing macrocycle and released the free gelators; solutiond of the [2]rotaxanes could, therefore, form gel after irradiation with a suitable amount of light. We also demonstrate the possibility of selective gelation of particular regions of these solutions, as well as photo-patterning of thin layers of such solutions.

Figure 1.

Scheme 1.

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The macrocycles **1** and **2**, which feature a photo-degradable *o*-nitrobenzyl unit and a normal benzyl unit, respectively, were obtained from an equimolar mixture (5 mM) of the diamine **3**[8] (or **4**), the dialdehyde **5**,[9] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB)[10] in $CHCl_3$ after reducing the equilibrium solution with $NaBH_4$, in yields of 72 and 88%, respectively (Scheme 1). The ^{1}H NMR spectrum of macrocycle **2** in $CDCl_2CDCl_2$ did not change after irradiation at 350 nm at room temperature for 15 min (Figures 2e and 2f).[11] In contrast, the signals of macrocycle **1** decreased rapidly upon UV irradiation and became negligible after 6 min (Figures 2a–d), consistent with its photo-degradation.

Figure 2.

Scheme 2.

As the guest for the first clipping reaction, we chose the dumbbell-shaped gelator **6**,[12] which forms organogels in toluene, hexanes, and dioxane; it features amide functionalities between its perylene bisimide core and two sizable terminal groups (Scheme 2). Thus, we heated an equimolar mixture of the gelator **6**, the diamine **4**, the dialdehyde **5**, and NaTFPB in $CDCl_3$ (5 mM) at 333 K for 4 h (i.e., until equilibrium had been reached).[8] Reduction of the resulting solution led to isolation of the [2]rotaxane **7** in 16% yield, together with a 58% yield of the recycled free gelator **6**. After considering the reaction efficiency and solubility of the free gelator **6**, we selected $CDCl_2CDCl_2$ as the solvent for examining (^{1}H NMR spectra) the photo-induced dissociation of the [2]rotaxane **7**. The signals of the [2]rotaxane **7** in $CDCl_2CDCl_2$ were slightly broad, suggesting that even when one of the amide functionalities was encircled by the macrocycle **1**, some degree of aggregation remained unavoidable under these conditions, presumably because of intramolecular

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hydrogen bonding and π-stacking of the free amide and perylene diimide units, respectively. Upon irradiation of a $CDCl_2CDCl_2$ solution of the [2]rotaxane **7** at 350 nm, the spectrum recorded after 3 min revealed the appearance of intense characteristic signals belonging to the free gelator **6** and the consumption of those representing the [2]rotaxane **7** (Figure 3). The free gelator **6** became the predominant product in the irradiated solution after 9 min (Figures 3f and 3g). These spectral features were consistent with the free gelator **6** having been released from the [2]rotaxane **7** through photo-cleaving of the interlocked macrocyclic component **1**.

Figure 3.

Figure 4.

Having confirmed its photo-degradation ability, we found that the [2]rotaxane **7** could be dissolved in dioxane at a concentration of 20 mg/mL (containing 15 mg/mL of **6**) without forming a gel. The critical gel concentration (CGC) of the gelator **6** in dioxane is reported to be less than 4.8 mg/mL (2 mM) at 298 K;[11] thus, the encircling of the macrocycle **1** around one of the amide units of the gelator **6** inhibited the gelation aggregation of the [2]rotaxane **7** and increased the amount of the gelator **6** (in interlocked form) that could be dissolved in dioxane. Irradiation of a dioxane solution of the [2]rotaxane **7** (3 mM; containing 10 mg of **7**) at 350 nm for 9 min, then leaving the sample at room temperature for 30 min, led to gelation of the solution; subsequent column chromatography resulted in isolation of **7** (2.9 mg, 29% recovery yield) and the free gelator **6** (5.1 mg; 96% yield). Thus, gelation of this solution occurred before all the molecules of the [2]rotaxane had dissociated—namely, at the point where the free gelator had accumulated in the solution at a concentration higher than its CGC. In theory, if the gelation process were sufficiently rapid to minimize diffusion of the

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free gelator, selective gelation should be possible only in the particular regions of the solution exposed to light. Accordingly, we covered (aluminum foil) the top half of a dioxane solution of the [2]rotaxane **7** (3 mM) in an NMR tube and then irradiated (UV light, 350 nm) the whole tube for 9 min. As displayed in Figure 4a, only the bottom part of the solution that had been irradiated formed a gel—the top half, protected from the light by the aluminum foil, remained a liquid. Thus, encircling the photo-labile macrocycle **1** around the gelator **6** endowed one-off photo-triggerable gelation properties to the [2]rotaxane **7**, with the capability of photo-patterning[13] a solution through gelation (*vide infra*).

Scheme 3.

Because hydrogels are more biologically compatible materials than organogels, we examined whether the same concept could also be applied to construct photo-triggered hydrogelators. We heated a solution of **8** (an acetylated synthetic precursor to the urea-containing C_3-symmetry hydrogelator **9**)[14] with equimolar amounts (5 mM) of the diamine **4**, the dialdehyde **5**, and NaTFPB in $CDCl_3$ at 333 K for 4 h (i.e., until equilibrium had been reached). Subsequent $NaBH_4$-mediated reduction and saponification led to isolation of the [2]rotaxane **10** in an overall yield (three steps from **8**) of 30% (Scheme 3).[15]

Figure 5.

To prove that the macrocyclic component **1** of the [2]rotaxane **10** could also be photo-cleaved to release the free gelator **9**, we irradiated a solution of the

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[2]rotaxane **10** (5 mM) in CD_3SOCD_3 under UV light (350 nm) and used ^1H NMR spectroscopy to monitor the progress of the reaction (Figure 5). Photo-cleavage of the [2]rotaxane **10** was relatively rapid, with the characteristic signals of the free gelator **9** appearing already after 1 min of irradiation; the reaction was complete after 9 min.

Figure 6.

The gradual decrease in the intensity of the signals representing the *o*-nitrobenzyl unit of the interlocked macrocyclic component **1** and the corresponding increase in the intensity of the signals (H_a, H_b) representing the free gelator **9** confirmed that the presence of the gelator in solution was due to the removal of the photo-labile macrocycle from the [2]rotaxane **10**. Because **9** is a hydrogelator, we examined the photo-triggerable gelation of the [2]rotaxane **10** in water. Although encircling the somewhat hydrophobic organic macrocycle **1** around the gelator **9** might not have been expected to enhance the water-solubility of the resulting [2]rotaxane **10**, we found that the presence of the macrocyclic component inhibited the aqueous solution from gelation, allowing the solubility of the [2]rotaxane **10** to reach 50 mg/mL (containing 40 mg/mL of **9**)—significantly higher than the CGC of the gelator **9** (15 mg/mL). Thus, when using 350-nm light to irradiate a tube containing a degassed aqueous solution of the [2]rotaxane **10** [6.3 mg, 2.5% w/v (25 mg/mL)] for 9 min, the solution, similar to the reported heat-and-cool process of the gelator **9**, formed a gel after sitting at room temperature for 12 h (Figure 6). After dialysis, the amount of the [2]rotaxane **10** and the free gelator **9** present in the gel were approximately 1.5 (24% recovery yield) and 3.6 mg (94% yield), respectively, based on the integration ratio of signals in the ^1H NMR spectrum,[16] again confirming that the gelation did not require

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decomposition of all the molecules of the [2]rotaxane. Unlike the situation with the [2]rotaxane **7**, the gelator **9** released after cleaving the macrocyclic component **1** from the [2]rotaxane **10** required a significantly longer time to form a gel than did the gelator **6**; accordingly, the free gelator **9** had time to diffuse evenly in the solution. Indeed, even when we used aluminum foil to keep dark the top half of a solution of the [2]rotaxane **10** in an NMR tube, the whole solution formed a gel after sitting at room temperature for 12 h (Figure 6).[17] Thus, the aqueous solution of the [2]rotaxane **10** was not suitable for demonstrating selective gelation and photo-patterning functions. Nevertheless, such a gelation system might be useful in some particular conditions; for example, to form a gel from an entire solution when irradiation of the whole solution is not possible.

Therefore, we selected the [2]rotaxane **7** to examine the feasibility of photo-patterning gel formation in a solution. To demonstrate that such a patterning could be achieved under simple conditions, we used a common laboratory hand-held UV lamp (365 nm, 4 W), rather than a photo-reactor, to irradiate a dioxane solution of the [2]rotaxane **7** (5 mM; 12 mg/mL) in a quartz cell (250 mm × 200 mm × 1 mm) through a mask patterned with the letters "NTU" (representing "National Taiwan University," Figure 4) for 1 h. Before removing the mask, the solution was left at room temperature for 30 min, at which point it had formed a gel, patterned in the form of the letters NTU, within the solution, revealing the potential applicability of this strategy to pattern particular gels on desired surfaces. Thus, [2]rotaxanes comprising photo-degradable macrocyclic components encircling known gelators can not only introduce photo-triggerable properties to the gelators but also, depending on the

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gelation rate, form photo-patternable solutions, thereby increasing the potential applications and practical value of such gelators.

Using Na^+ ions to template the "clipping" of photo-degradable macrocycles around the amide or urea functionalities of organo- and hydrogelators has allowed the construction of [2]rotaxanes displaying one-off photo-triggerable gelation properties. Using UV light to cleave the photo-labile *o*-nitrobenzene–containing macrocyclic components from the [2]rotaxanes released the free gelators into solution, thereafter forming gels. When the gelation rate was sufficiently rapid, selective gelation of specific regions of the solution—and, indeed, photo-patterning of the solution—was possible. This interlocking approach avoids the need for thermal gelation processing, and can introduce one-off photo-triggering behavior to known gelators without the need to covalently modify their structures. We believe that this approach will extend the practical applications of organo- and hydrogels.

Acknowledgment

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[16] The estimation was based on a rough assumption that the total amount of the free and interlocked gelators stayed the same before and after the reaction.

[17] After dialysis, the presence of 1.8 mg of the free gelator **9** in the gel was estimated based on the integration ratio of signals in the ^{1}H NMR spectrum (ref. [12]), corresponding to a concentration (7.2 mg/mL) lower than the reported CGC (15 mg/mL, ref. [11]). We suspect that the observed lower gelation concentration of the free gelator **9** arose mainly from the smaller diameter of the tube containing its solution (6.2 vs. 4.2 mm) and/or participation of the two free urea functionalities in the rotaxane **10**. After purifying the gelator **9** through both dialysis and reversed-phase HPLC, we determined the CGC to be no higher than 6 mg/mL in a normal NMR tube (4.2 mm in diameter).

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Scheme and Figure legends

Figure 1. Cartoon representation of the concept of endowing one-off photo-triggerable properties to known gelators.

Figure 2. ^{1}H NMR spectra (400 MHz, $CDCl_2CDCl_2$, 298 K) recorded after irradiation (at 350 nm) of a–d) macrocycle **1** (5 mM) for a) 0, b) 1, c) 2, and d) 6 min and e, f) macrocycle **2** (5 mM) for e) 0 and f) 15 min.

Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_2CDCl_2$, 298 K) of a–f) the [2]rotaxane **7** after irradiation (350 nm) for a) 0, b) 1, c) 3, d) 5, e) 7, and f) 9 min and g) the free gelator **6**.

Figure 4. Photographs demonstrating a) the selective photo-triggerable gelation of a dioxane solution of the [2]rotaxane **7** [3 mM (7.2 mg/mL); 9 min in a photo-reactor (350 nm)] and b) the photo-patterned gelation of a thin layer of a solution of **7** [5 mM (12 mg/mL); 1 h under a laboratory hand-held UV lamp (4 W, 365 nm)] through a mask displaying the letters "NTU." Samples were left at room temperature for 30 min after irradiation.

Figure 5. ^{1}H NMR spectra (400 MHz, CD_3SOCD_3, 298 K) of a–e) the [2]rotaxane **10** after irradiation with light (350 nm) for a) 0, b) 1, c) 2, d) 5, and e) 9 min and f) the free gelator **9**.

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Figure 6. Photographs demonstrating a) the photo-triggerable gelation of an aqueous solution of the [2]rotaxane **10** [2.5% (25 mg/mL); 9 min in a photo-reactor (350 nm)] and b) the gelation of the whole sample after irradiating the bottom portion of an aqueous solution of the [2]rotaxane **10** [2.5% (25 mg/mL); 9 min in a photo-reactor (350 nm)] in a NMR tube. Samples were left at room temperature for 12 h after irradiation.

Scheme 1. Synthesis of the macrocycles **1** and **2**.

Scheme 2. "Clipping" synthesis of the [2]rotaxane **7** from the organogelator **6**.

Scheme 3. "Clipping" synthesis of the [2]rotaxane **10** from the hydrogelator **8**.

Text for Table of Contents

"Clipping" a photo-degradable macrocycle around the amide or urea functionalities of organo- and hydrogelators has provided [2]rotaxanes displaying one-off photo-triggerable gelation properties—in one case allowing photo-patterning of a solution with specific "letters" of gel.

Keywords

gel • photo-cleavage • photo-patterning • rotaxane • template

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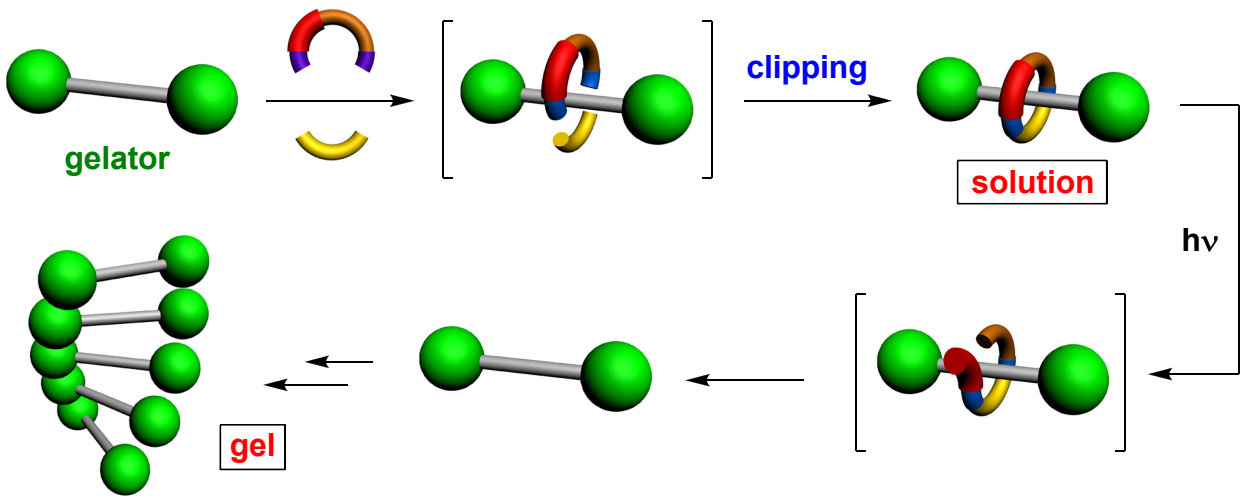

Figure 1.

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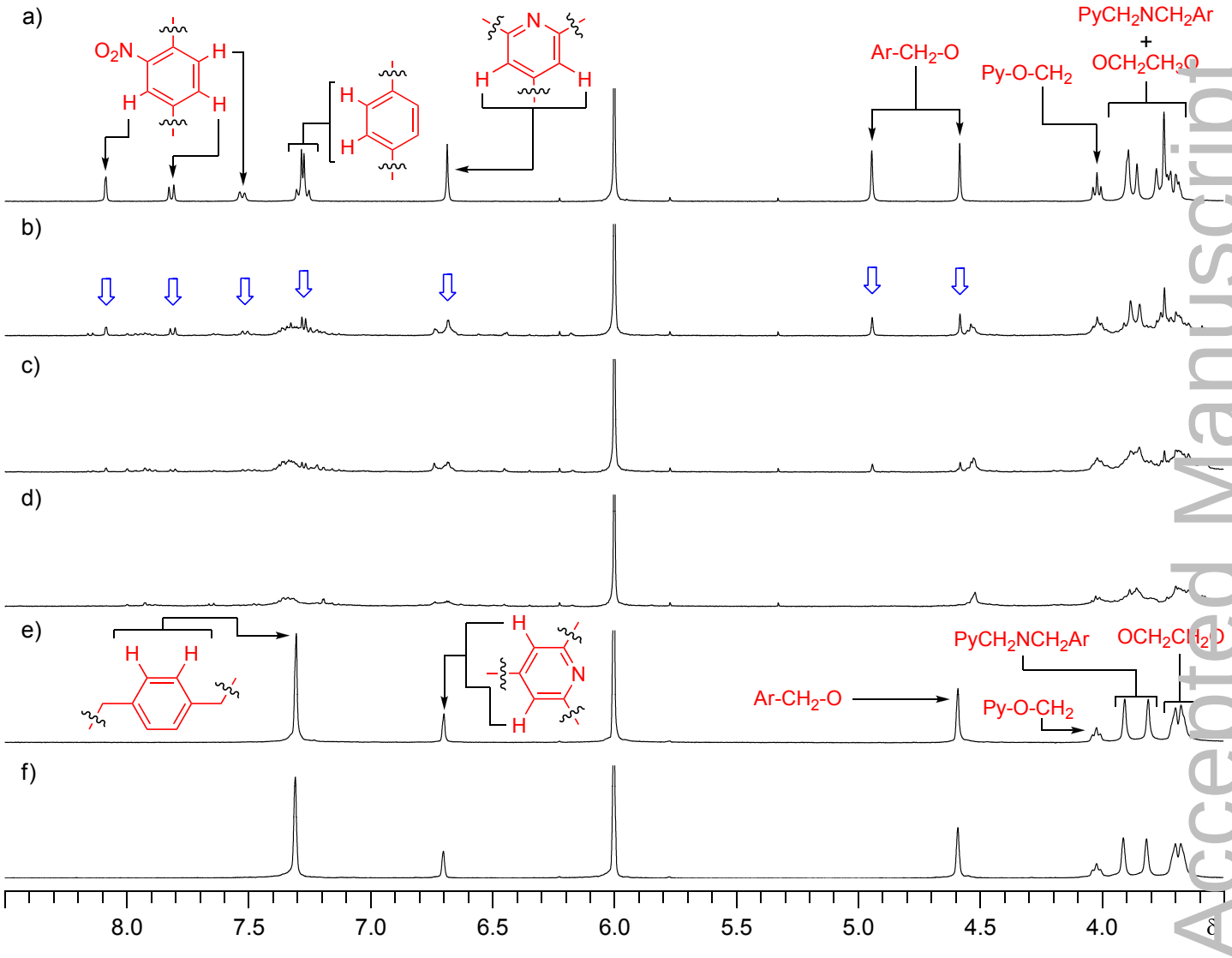

Figure 2.

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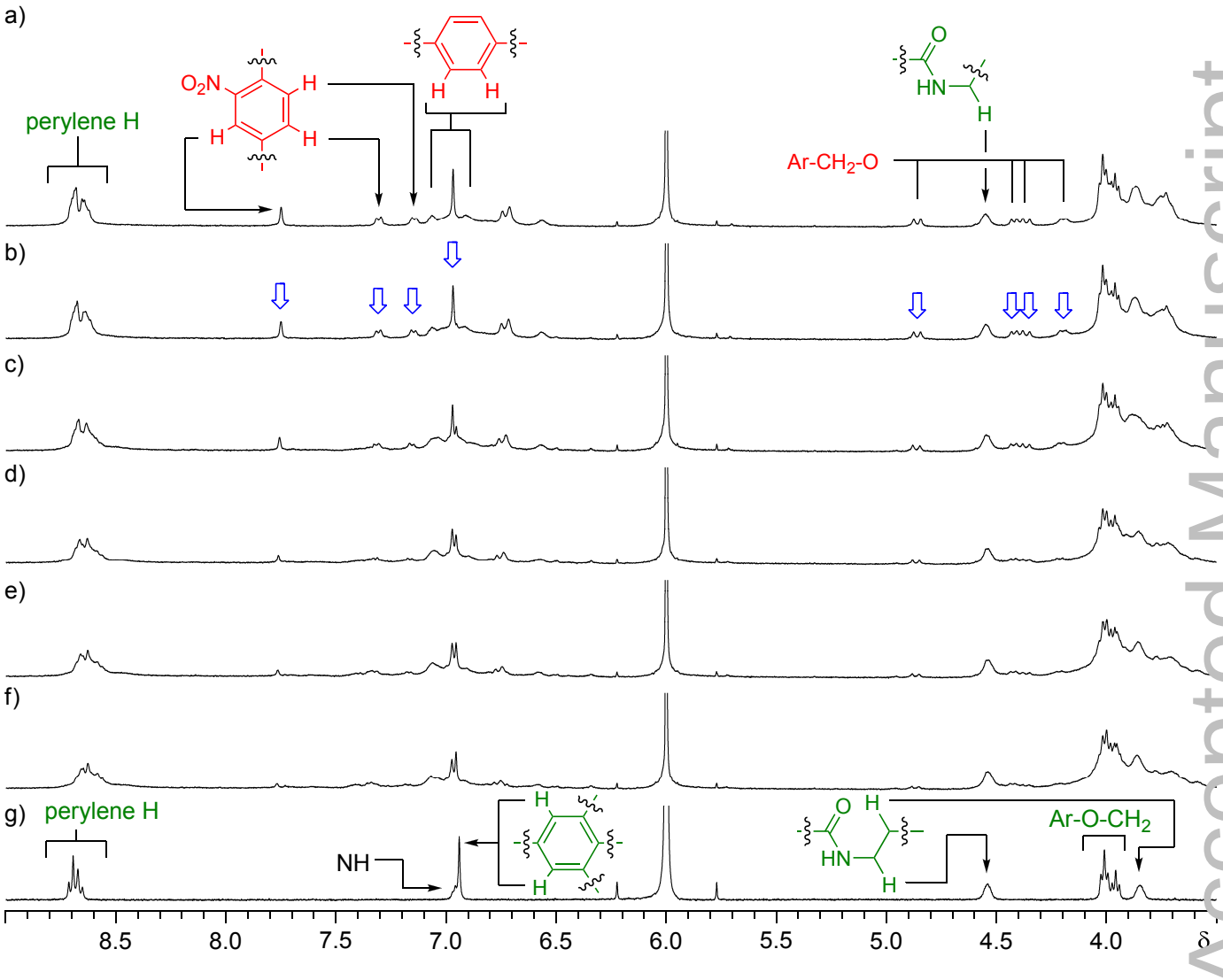

Figure 3.

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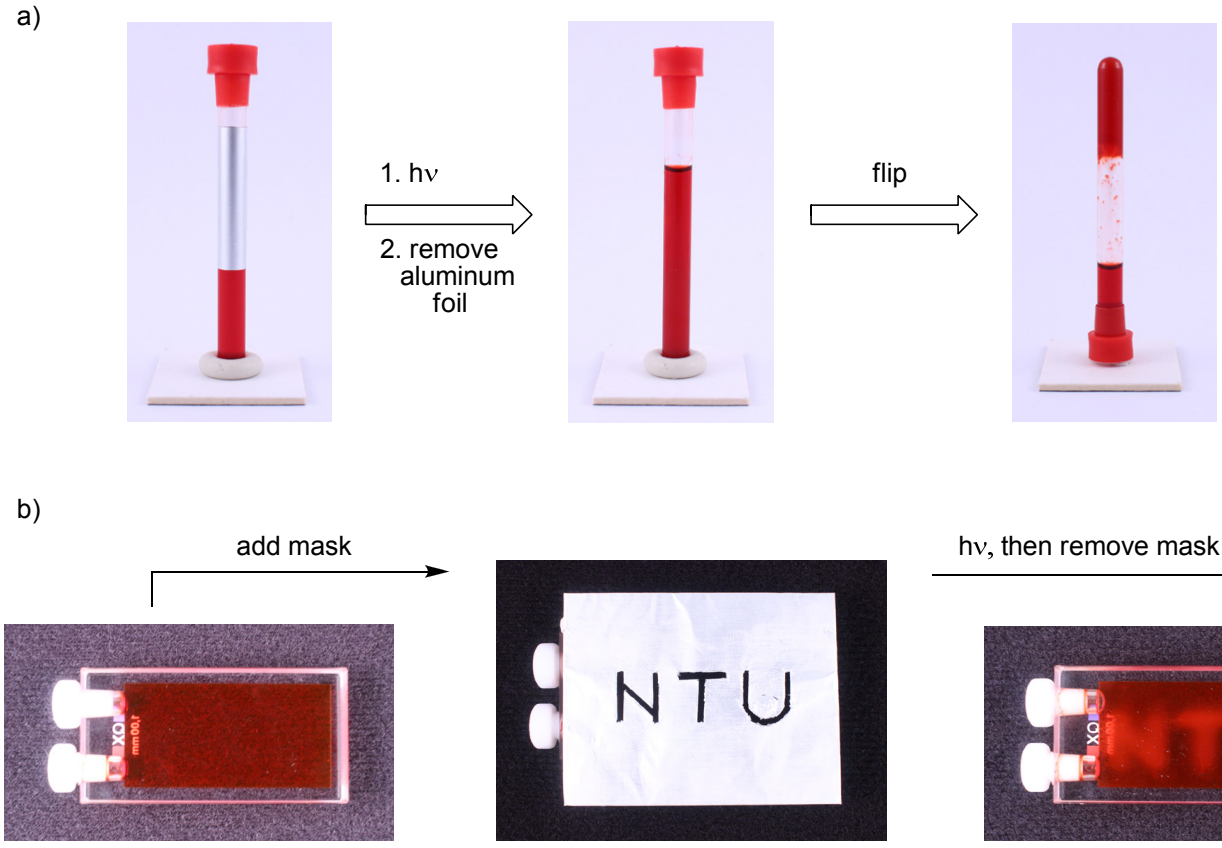

Figure 4.

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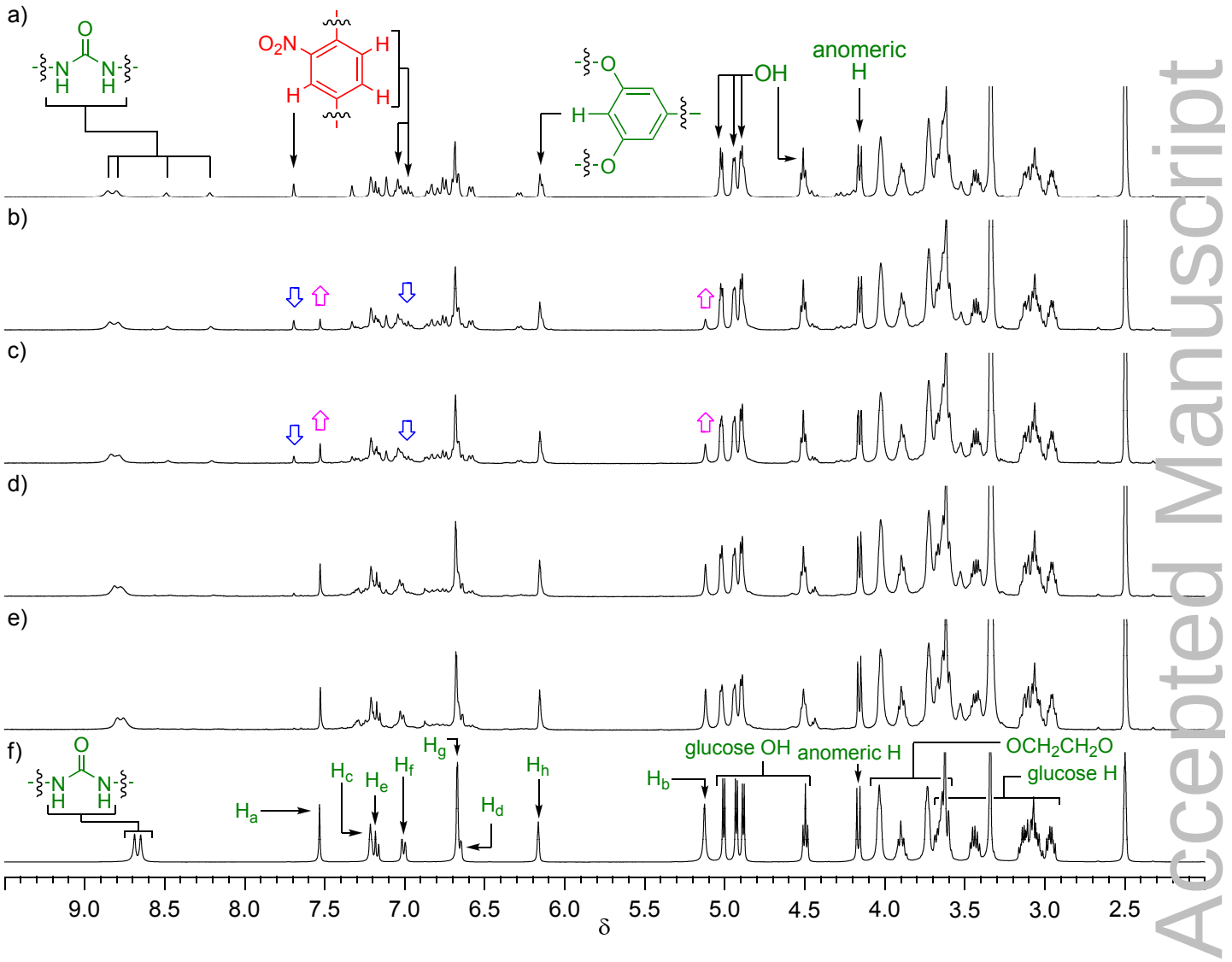


Figure 5.

10.1002/chem.201705753

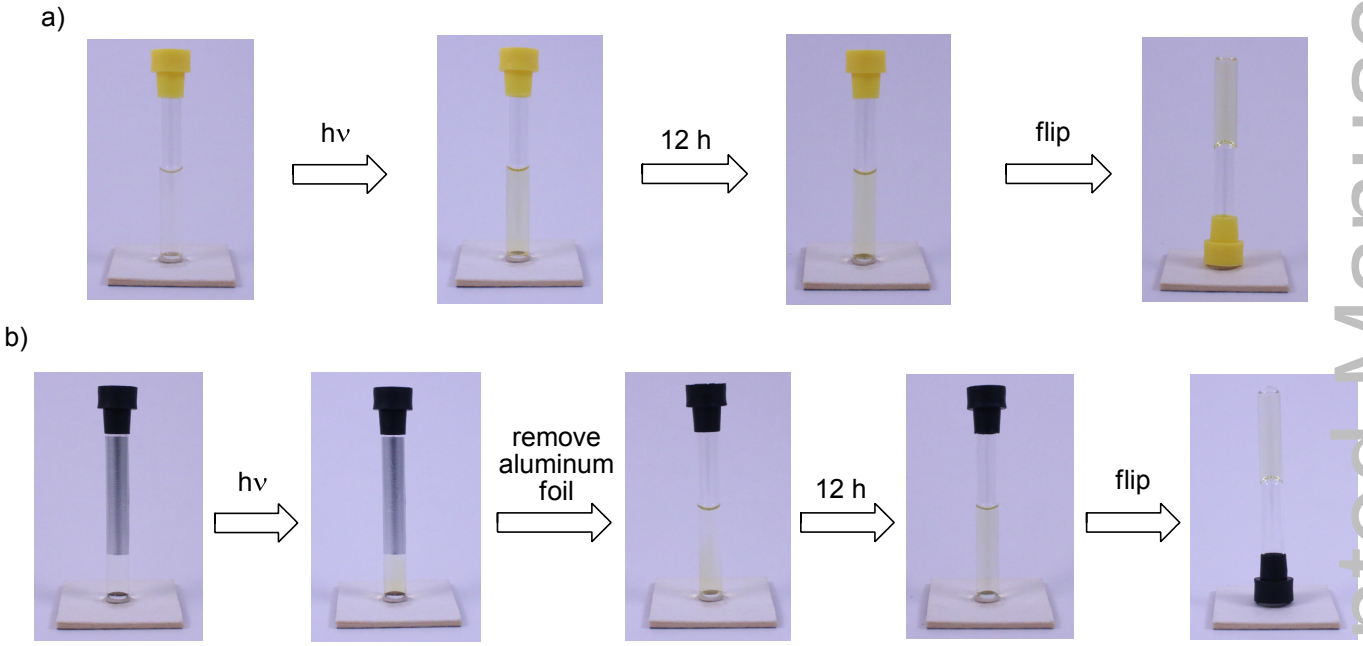
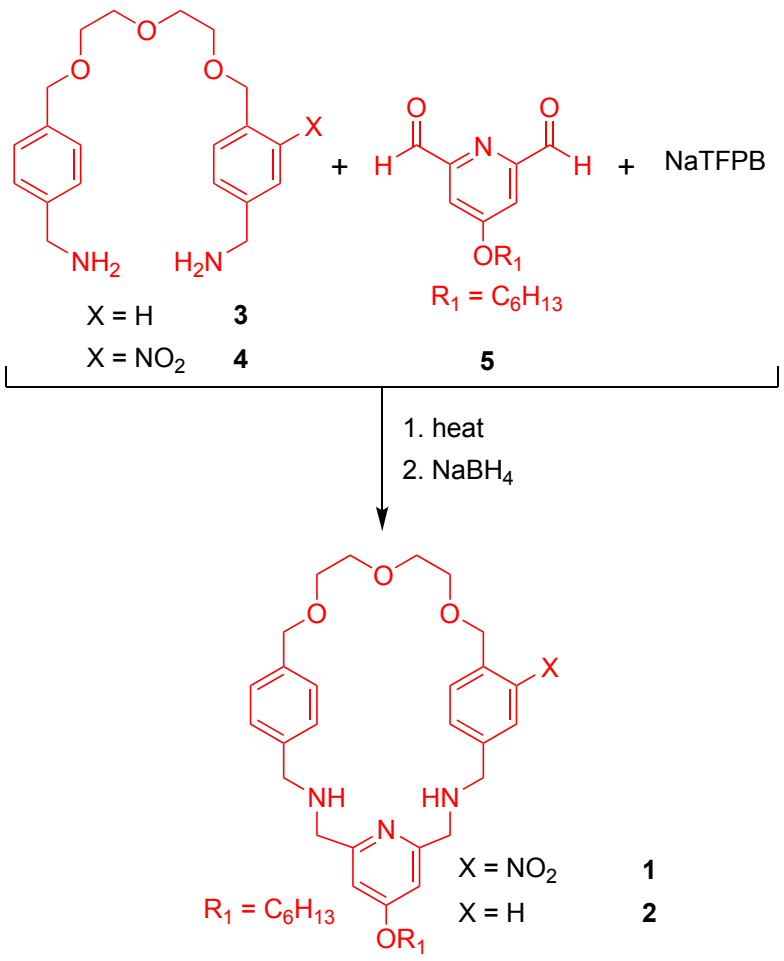


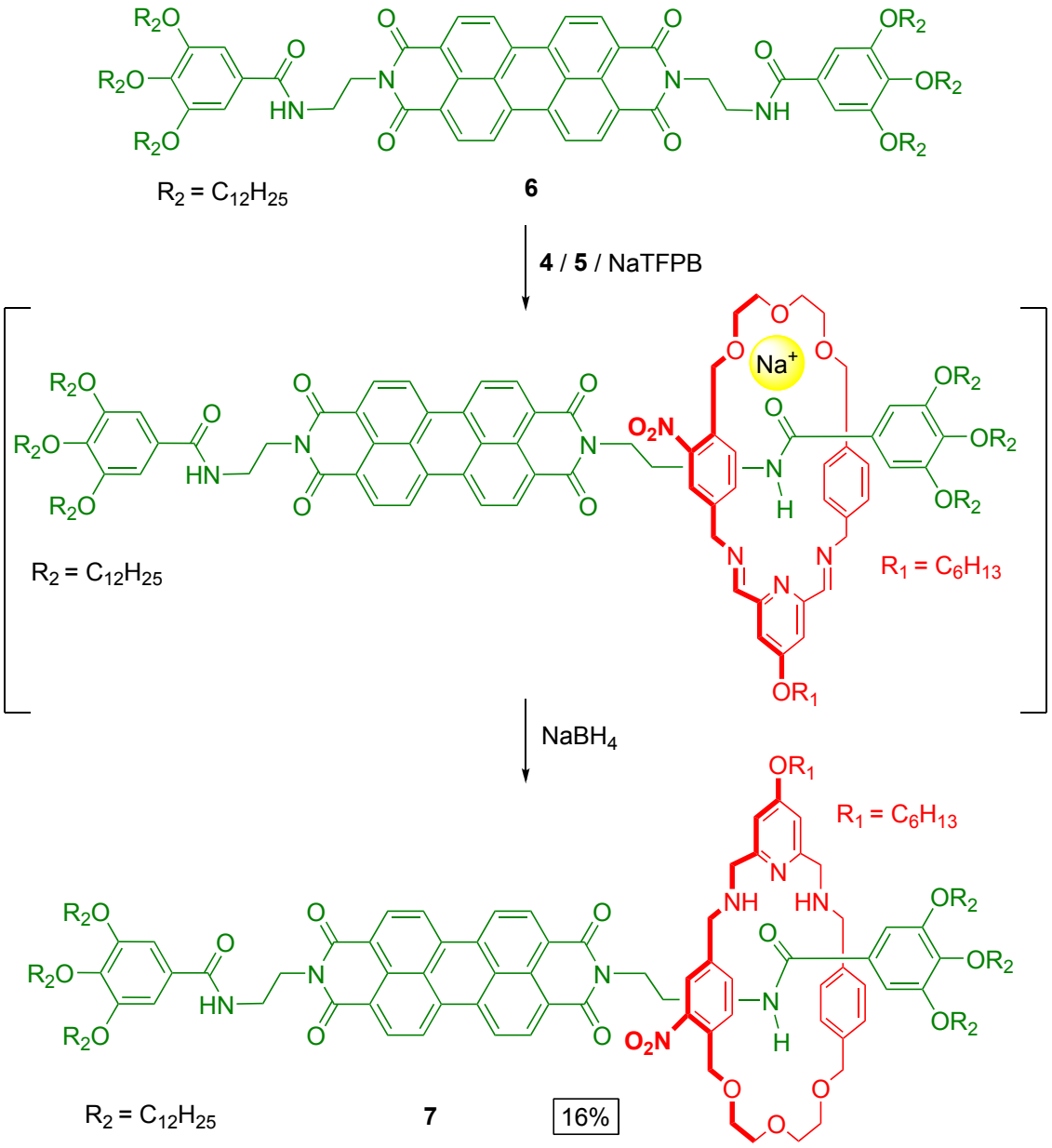
Figure 6.

10.1002/chem.201705753



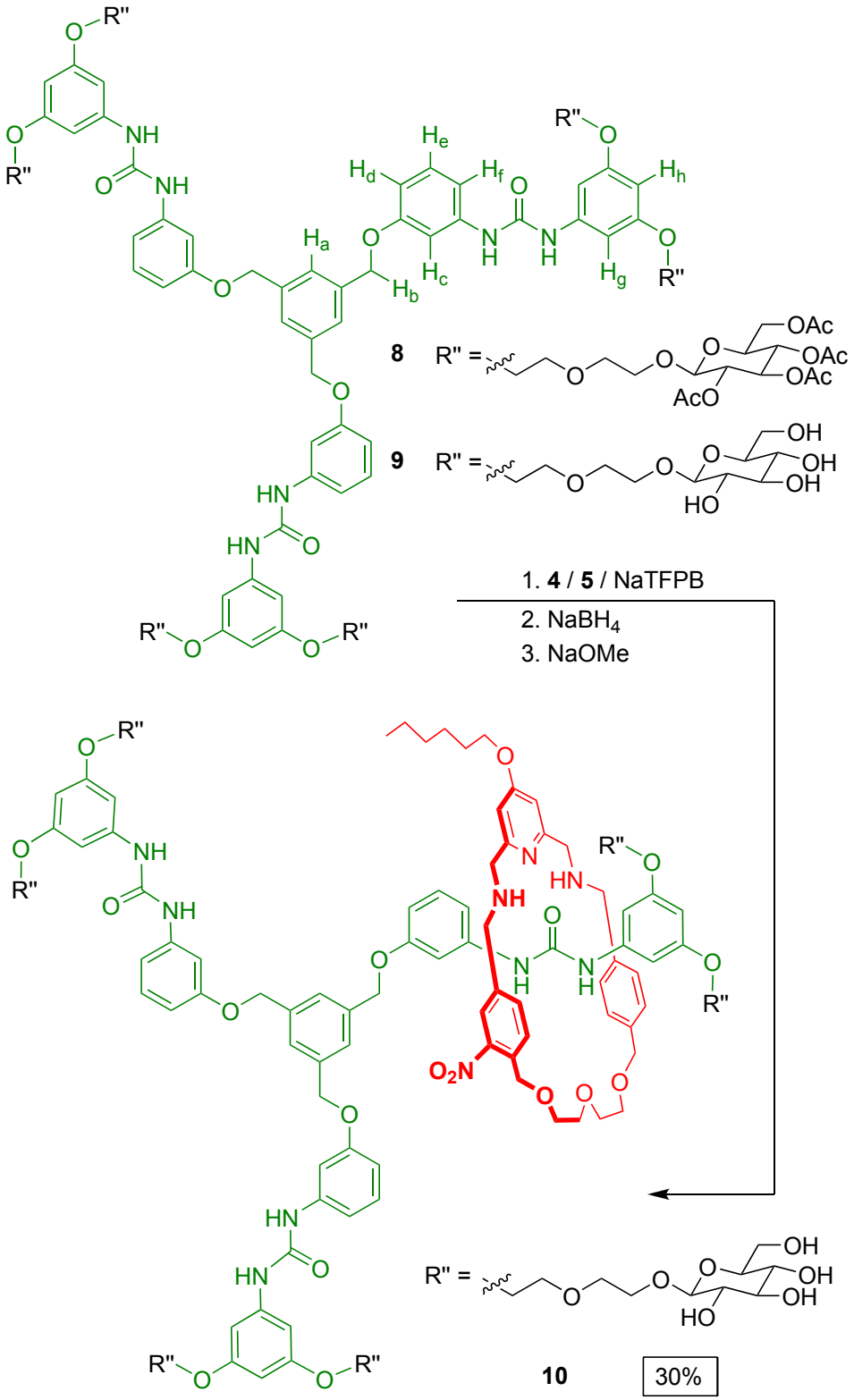
Scheme 1.

10.1002/chem.201705753



Scheme 2.

10.1002/chem.201705753



Scheme 3.