Dynamic Interfacial Adhesion through Cucurbit[n]uril Molecular Recognition **

Ji Liu,[a] Cindy Soo Yun Tan [a,b] and Oren A. Scherman[a] **

Abstract *Supramolecular building block, such as cucurbit[n]uril (CB[n])-based host-guest complexes, have been extensively studied at the nano- and microscale as adhesion promoters. Herein, we exploit a new class of CB[n]-threaded highly-branched polyrotaxanes (HBP-CB[n]) as aqueous adhesives to macroscopically bond two wet surfaces, including biological tissue, through the formation of CB[8] heteroternary complexes. The dynamic nature of these complexes gives rise to adhesion with remarkable toughness, displaying recovery and reversible adhesion upon mechanical failure at the interface. Incorporation of functional guests, such as azobenzene moieties, allows for stimuli-activated adhesion/de-adhesion on demand. Macroscopic interfacial adhesion through dynamic host-guest molecular recognition represents an innovative strategy, for designing the next generation of functional interfaces, biomedical devices, tissue adhesives and wound dressings.*

Adhesion in nature is commonly driven by reversible interactions and can be controlled by a wide range of stimuli either from the environment or excreta from living organisms, at the molecular level, to fulfil specific (bio-)physical functions.[1–4] Non-covalent interactions, *e.g.* van der Waals forces in gecko footpads,[5] hydrogen bonding and/or metal-ligand complexes in secretions of mussels or tube worms,[6] are responsible for their micro/macroscopic adhesion. These examples have inspired a variety of adhesion promoters with sophisticated and adaptive adhesion performance in the past decades,[7–16] leading to tremendous advance in the adhesion science and industry.

Cucurbit[8]uril (CB[8]) host molecule has been utilized as supramolecular linking motif to dynamically bring together two separate entities, involving the formation of homo/heteroternary complexes under aqueous conditions,[17–20] similar to its macrocyclic analogues, such as pillararene and cyclodextrins.[21,22] Such dynamic host-guest conjugation has been used extensively for the construction of supramolecular polymers, transient hydrogel networks, microcapsules, colloidal clusters and bio-interfaces.[19] Although non-covalent interactions have been revealed to improve the interfacial adhesion,[2] use of directional and selective CB[n] molecular recognition has received limited attention in macroscopic applications.[13] In an effort to gain mesoscale CB[8]-mediated self-assembling, a new class of hydrophilic CB[n]-threaded highly-branched polyrotaxanes (HBP-CB[n]) were synthesized through a semi-batch reversible addition-fragmentation chain-transfer polymerisation (RAFT).[23,24] Such HBP-CB[n] polyrotaxanes are further exploited here as polymer adhesives, which are capable of dynamically bonding two soft materials through the interfacial CB[n] molecular recognition (**Figure 1**).

A bisfunctional viologen monomer, styrene-viologen-styrene (St-Vi^{2+}-St), was used as both a crosslinker and as a first guest for CB[n], in a copolymerization with *N*-hydroxylethyl acrylamide (HEAm, **Figure 1a**). Due to the high instantaneous CTA/St-Vi^{2+}-St ratio, a substantial suppression of the crosslinking was achieved to avoid the gelation, leading to the highly-branched polyrotaxanes (HBP-CB[n]), with CB[n] mechanically locked onto the HBP-CB[n] backbones.[23] In a specific synthesis, HBP-CB[8], with a CB[8] loading of 8.2 *mol%* (weight fraction of 48.9 *wt%*, **ESI Figure S1**) and M_w of $(5.6 \pm 2.8)\times10^6$ g mol^{-1} was obtained (monomer conversion $> 92\%$). On account of the hydrophilic polyHEAm backbones, the HBP-CB[8] polyrotaxanes could readily dissolve in water with a substantially improved CB[8] solubility over 20 mM, which is 2000$\times$ the solubility of pristine CB[8] ($< 10\ \mu$M[19]), overcoming the inherent challenges plagued by limited CB[8] solubility in water. HBP-CB[7] was also obtained following the same protocol and further used as a control, since no second guest can complex with a CB[7]·Vi^{2+} binary complex due to its small cavity.

To demonstrate the macroscopic adhesion of synthetic soft materials with HPB-CB[8], two hydrogels was tailored with either identical or non-identical second guest moieties, in order to facilitate the interfacial host-guest complexation. Benzylamine (Benz) and azobenzene (Azo) were chosen as second guest moieties, on account of their high affinity to the CB[8]·Vi^{2+} binary complex, resulting in CB[8]·Vi^{2+}·Benz (K_a = 2.0$\times10^6$ M^{-1}, **ESI Figure S2**)

** J.L. is financially supported by the Marie Curie FP7 SASSYPOL ITN (607602) programme. C.S.Y.T. thanks Ministry of Education of Malaysia and Universiti Teknologi MARA, Malaysia, for their financial supports. O.A.S thanks the EPRSC (EP/F0355351 and EP/G060649/1) and the ERC (ASPiRe, 240629) for their funding. The authors thank Dr. Raphael Michel, Dr. Marie Gracia, Dr. Laurent Corte and Prof. Ludwik Leibler in ESPCI-Paris for their kind help with the pealing tests and fruitful discussion.

* [a] Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom.
E-mail: oas23@cam.ac.uk.
[b] Faculty of Applied Sciences, Universiti Teknologi MARA, 94300 Kota Samarahan, Sarawak, Malaysia.

Supporting information for this article is available on the WWW under or from the author.

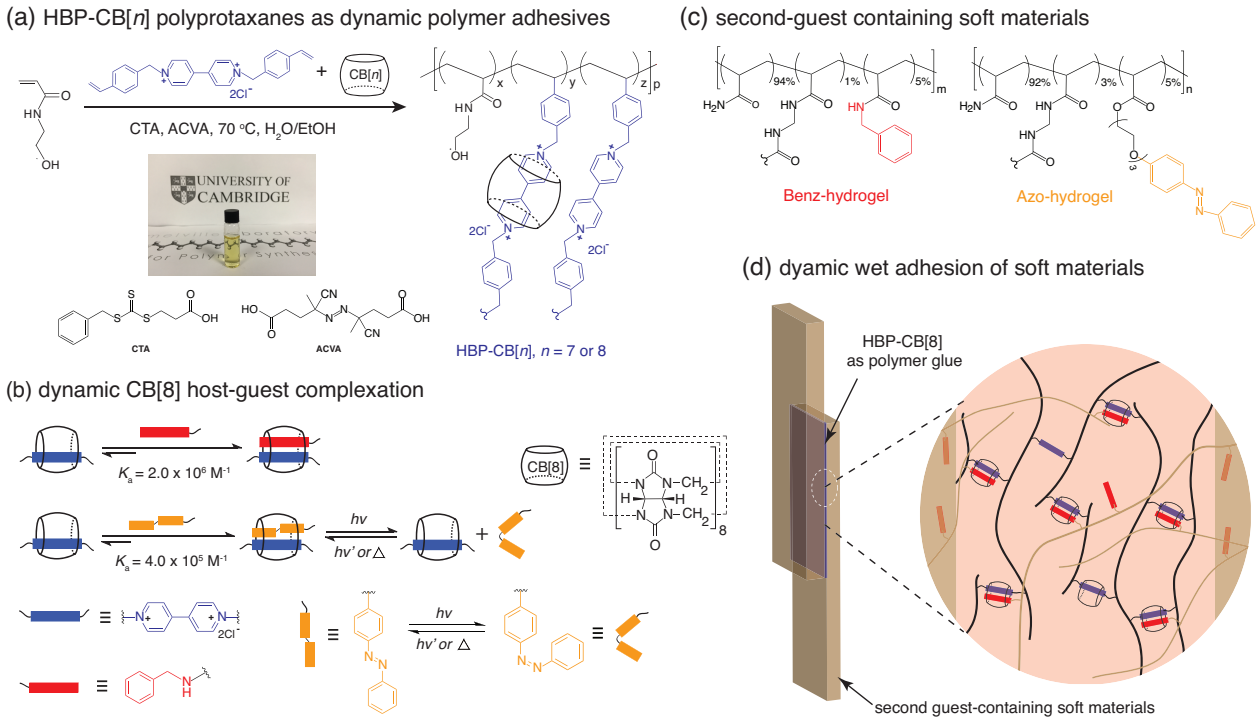


Figure 1. **(a)** Synthesis of the HBP-CB[*n*] polyrotaxanes *via* a semi-batch RAFT polymerization in the presence of CB[*n*], inset: image of the polymer solution with a CB[8] concentration of 20 mM (*ca.* 2000× the solubility of pristine CB[8]). CTA: benzyltrithiocarbonyl propionic acid; ACVA: 4,4'-azobis(4-cyanovaleric acid). **(b)** Stepwise formation of the heteroternary complexes among CB[8], viologen (Vi^{2+}) and a second guest such as benzyl amide or an azobenzene moiety; photo-induced dissociation/association in the case of the CB[8]·Vi^{2+}·Azo hetrotenary complex. **(c)** Chemical compositions of the hydrogel networks containing either benzyl amide or azobenzene moieties as second guests. **(d)** Schematic illustration of the dynamic interfacial gluing of two hydrogels with HBP-CB[8] polyrotaxane as adhesive.

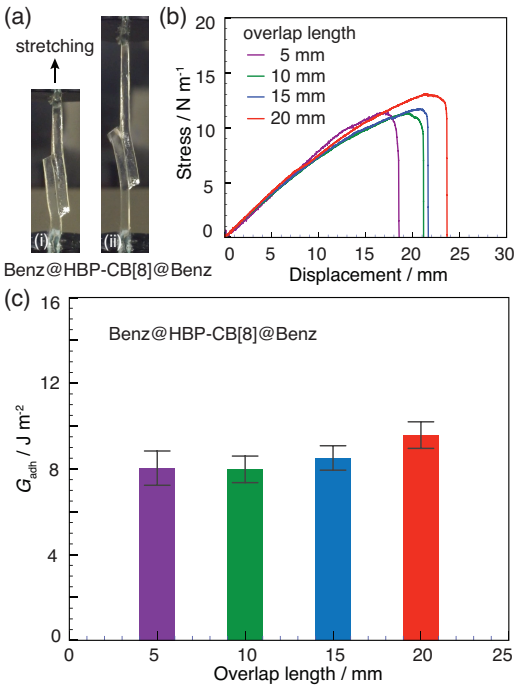


Figure 2. **(a)** Snapshot images of the the lap joint between two Benz-hydrogel ribbons bonded with HBP-CB[8] (Benz@HBP-CB[8]@Benz) before (i) and after (ii) stretching. **(b)** Stress-displacement curves of the lap-shear tests of Benz@HBP-CB[8]@Benz with different overlap lengths. **(c)** Adhesion energy (G_{adh}) measured from the lap-shear test for different overlap lengths (errors bars show s.d.).

and CB[8]·Vi^{2+}·Azo (K_a = 4.0×10^5 M^{-1}, **ESI Figure S3**) heteroternary complexes, respectively (**Figure 1b**). Moreover, photo-induced isomerization of azobenzene moieties promotes the reversible association/dissociation of the host-guest complexes,[25,26] imparting *on-demand* control over macroscopic adhesion through photo irradiation. In order to incorporate these guest moieties into a hydrogel material/interface, both Benz and Azo moieties were functionalized into monomers, and further copolymerised with acrylamide (AAm) and *N*, *N*'-methylenebisacrylamide (MBA), yielding Benz- and Azo-hydrogel, respectively (**Figure 1c**, see **ESI Experimental Details**). Elastic moduli of the equilibrium swollen Benz-hydrogel (Benz/AAm/MBA, 5/94/1 *mol%*) and Azo-hydrogel (Azo/AAm/MBA, 5/92/3 *mol%*) were 2.1 ± 0.3 kPa and 7.5 ± 1.5 kPa, respectively.

An aqueous solution containing HBP-CB[8] (20 g L^{-1}, CB[8] of *ca.* 20 mM) was spread over the interface between two Benz-hydrogel ribbon samples (2 μmol cm^{-2} of CB[8], **Figure 1d**). Macroscopic adhesion was observed within 5 min for the bonded lap joints of Benz-hydrogels (Benz@HBP-CB[8]@Benz), and the joint could hold a stress up to 11∼13 N m^{-1}, with a substantial elongation of the hydrogel ribbons (**Figure 2a-ii**). Interfacial peeling occurred at the moment adhesion failed (see **Supplementary Movie S1**). Increasing the overlap length slightly affects the stress at failure (**Figure 2b**) and adhesive energy

(G_{ad}, **Figure 2c**), in agreement with the fact that G_{ad} is independent on the overlap length, but width and thickness of the ribbons.[27] G_{adh} value for Benz@HBP-CB[8]@Benz was estimated to be 8.0∼9.5 J m^{-2}, on par with nanoparticles adhesives[10,11] and polymer adhesive based on dynamic adamantine/cyclodextrin host-guest interaction.[15]

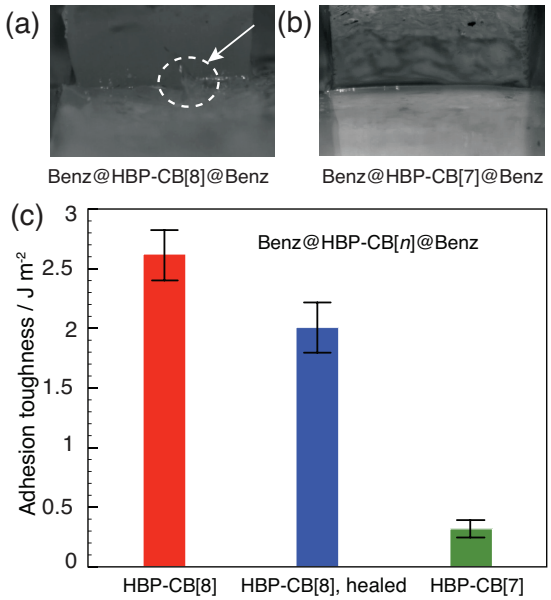


Figure 3. Snapshot images of the 90-degree peeling for **(a)** Benz@HBP-CB[8]@Benz and **(b)** Benz@HBP-CB[7]@Benz control. The arrow shows the appearance of fingers during peeling, which are not observed in the HBP-CB[7] control. **(c)** Interfacial adhesion toughness measured by peeling tests. After an interfacial failure, the Benz@HBP-CB[8]@Benz was re-bonded for 30 min without any additional materials before being subjected to a second peeling measurement (HBP-CB[8], healed).

Direct comparison of the HBP-CB[8] adhesives with other artificial adhesives is difficult, on account of several experimental and theoretical variables involved, including interfacial wetting, surface roughness, binding motifs, binding density/strength, chain dynamics, nature of the substrates and surface energy.[28] However, in our case, the adhesion performance could be compared with its homologue HBP-CB[7]. As CB[7] can not accommodate two guest molecules simultaneously to form heterotenary complexes,[17,19] very weak interfacial adhesion/cohesion is detected for Benz@HBP-CB[7]@Benz (see **ESI Figure S4**). Unlike the peeling features detected for HBP-CB[8], sliding in the lap-shear test was observed (see **Supplementary Movie S2**), with G_{adh} below 0.6 J m^{-2}. This sharp contrast corroborates the critical role of CB[8] host-guest complexation in interfacial adhesion.

In addition to HBP-CB[7], another control was also attempted using free CB[8], rather than CB[8]-threaded polymer (HBP-CB[8]), to achieve macroscopic adhesion. In this case, hydrogel sample containing viologen as a first guest is required. Copolymerization of a monofunctional viologen monomer (St-MV^{2+})[26] with AAm and MBA crosslinker readily generates the MV^{2+}-functionalized hydrogels. Unfortunately, it is impossible to achieve the same CB[8] density at the interface, due to limited CB[8] solubility. Applying the same volume of saturated CB[8] solution (*ca.* 5 μM) at the interface between MV^{2+}- and Benz-hydrogel could not achieve macroscopic adhesion, since the interfacial strength was too weak to hold the sample for further lap-shear tests.

In order to exclude the interference of interfacial friction in the lap-shear tests, we then carried out a standard 90-degree peeling test, where the interfacial toughness is equal to the normalised steady-state peeling force (see **ESI Experimental Details**). **Supplementary Movie 3** records the peeling process of Benz@HBP-CB[8]@Benz. The Benz-hydrogel sample deformed around the interfacial crack and generated fingers (**Figure 3a**), subsequently, the fingers detached and interfacial crack propagated along the interface. An interfacial toughness for the Benz@HBP-CB[8]@Benz sample was estimated to be 2.6 $\pm$ 0.2 J m^{-2}. As for the Benz@HBP-CB[7]@Benz control, interfacial crack readily propagated along the interface without kinking or generating fingers (**Figure 3b** and **Supplementary Movie 4**), yielding low interfacial toughness (0.3 $\pm$ 0.1 J m^{-2}). On account of its dynamic nature, CB[8] molecular recognition imparts a variety of supramolecular self-assemblies with astounding reversible and self-healable characteristics.[17,19,29–31] Benz@HBP-CB[8]@Benz lap-joints were subjected to peeling until failure, they were then re-bonded and subjected to another peeling measurement. The as-measured interfacial toughness reaches as high as 2.0 $\pm$ 0.2 J m^{-2}, and the slight decrease may be attributed to factors such as contamination and interfacial damage upon failure.[12]

On account of the versatility of CB[8] to form heteroternatry complexes with a variety of second-guest aromatic molecules, use of HBP-CB[8] as a supramolecular adhesive could also be extended to other guest systems, such as photo-responsive azobenzene moieties.[25,26] A G_{adh} of *ca.* 15 J m^{-2} was estimated for the Azo@HBP-CB[8]@Azo joint (**Figure 4a** and **4c**), which is slightly higher than the Benz@HBP-CB[8]@Benz (9 J m^{-2}), likely due to the higher modulus of the Azo-hydrogel and hydrophobicity of the Azo-moieties. Moreover, dynamic and reversible bonding was also demonstrated between two different surfaces, such as Azo@HBP-CB[8]@Benz (**Figure 4b** and **Figure 4d**). This highlights the promise of dynamic adhesion at bio-interfaces and in actuation, when two surfaces with diverse chemical nature, roughness and strength are involved.[2]

Adhesion with tuneable interfacial bonding, similar to the naturally-observed adhesion phenomenon,[1,2] imparts the system with "on-demand" bonding/de-bonding capabilities. Having established effective adhesion with HBP-CB[8] and substrates containing photo-isomerizable Azo-moieties, we speculate that interfacial adhesion could be tuned through light irradiation. Upon 10 min irradiation (360 nm, 4.8 mW cm^{-2}), the shear stress substantially decreased from 13 to 3 N m^{-1} for Azo@HBP-CB[8]@Azo, and 10 to 2 N m^{-1} for Azo@HBP-CB[8]@Ben (**Figure 4a** and **Figure 4b**), since the *cis*-Azo moieties could not complex with the CB[8]·Vi^{2+} binary complexes.[26] However, upon 60-min irradiation at

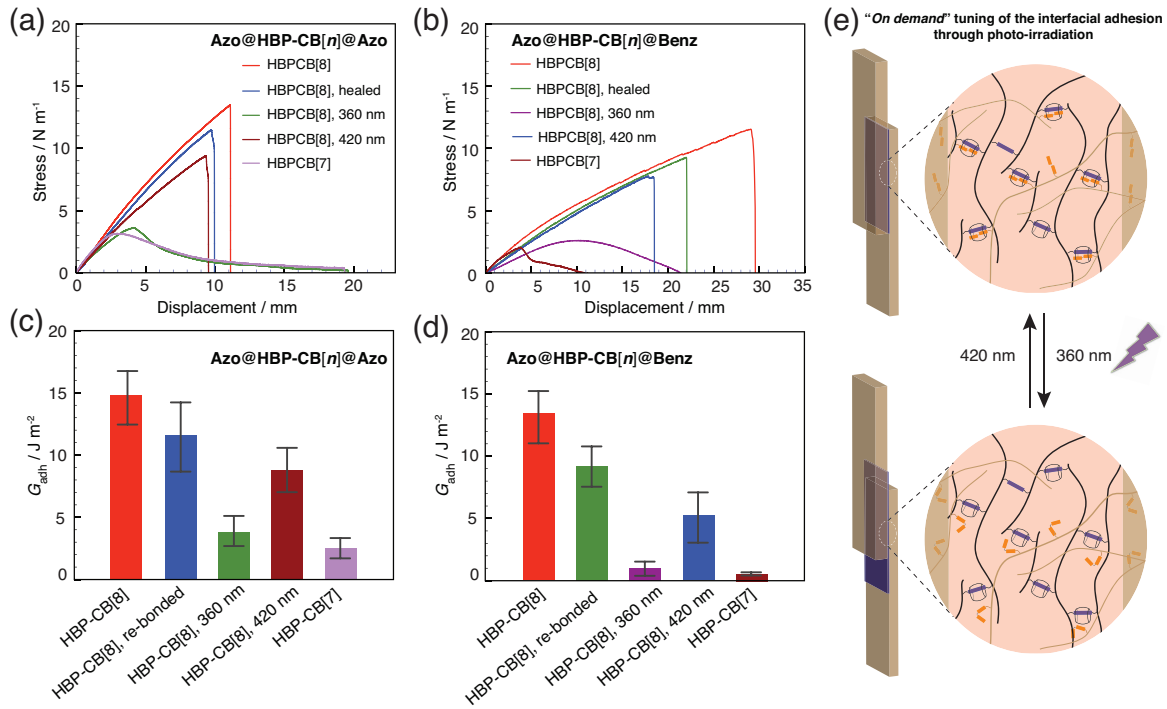


Figure 4. Stress-displacement curves from lap-shear tests: **(a)** identical Azo-hydrogel ribbons were bonded with HBP-CB[8] (Azo@HBP-CB[8]@Azo), with HBP-CB[7] as a control (Azo@HBP-CB[7]@Azo), as well as the self-healing test of Azo@HBP-CB[8]@Azo subjected to peeling failure and re-bonding without any extra material (Azo@HBP-CB[8]@Azo, re-bonded). Samples were exposed to irradiation at 360 nm (10 min) (Azo@HBP-CB[8]@Azo, 360 nm), and then 420 nm (60 min) (Azo@HBP-CB[8]@Azo, 420 nm). **(b)** Non-identical Azo- and Benz-hydrogel ribbons were bonded with HBP-CB[8] (Azo@HBP-CB[8]@Benz) as well as corresponding samples under different conditions. Summary of the G_{adh} values for **(c)** Azo@HBP-CB[8]@Azo and **(d)** Azo@HBP-CB[8]@Benz. **(e)** A schematic illustrating the tuneable interfacial adhesion with photo-irradiation.

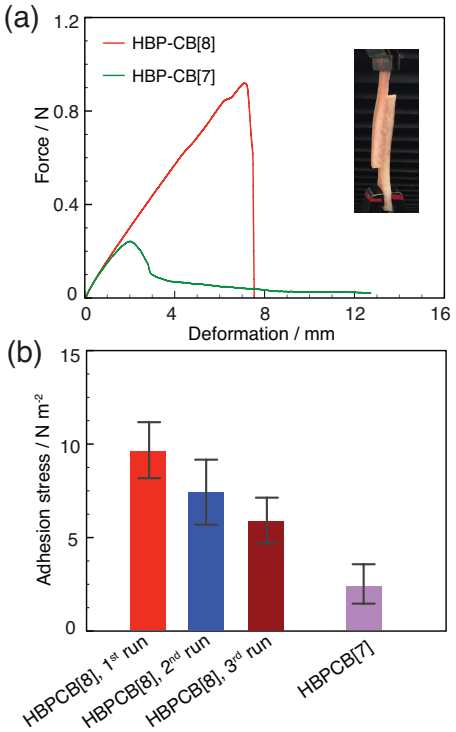


Figure 5. **(a)** Stress-displacement curves from lap-shear tests of two porcine skins bonded with the HBP-CB[8] polymer and with HBP-CB[7] as a control; insert: image of the bonded porcine skin sample. **(b)** Adhesion stress for consecutive bonding/de-bonding/re-bonding cycles of the lap joints with HBP-CB[8] as adhesive and HBP-CB[7] as a control.

420 nm, the recovered *trans*-Azo moieties further complex with CB[8]·Vi^{2+} complexes, promoting recovery of interfacial adhesion (**Figure 4e**). Nevertheless, less than 70% of the G_{adh} was recovered. This might be ascribed to the partial recovery of *trans*-Azo moieties in aqueous and complex systems,[26] dissimilar to the complete *trans*/*cis* reversibility in small molecular switches at solid state. This photo-tuneable interfacial adhesion represents a strategy to "on-demand" control over the dynamic interfacial affinity, mimicking those naturally-observed adaptive adhesion.[1,2]

Dynamic adhesion of wet and soft materials, such as biological tissues, is an important yet extremely challenging topic.[7,9,14,32–34] Covalent bond-based adhesives, such as super glue (cyanoacrylate), fibrin glue (TISSEEL, Baxter) and PEG-based adhesives (DURASEAL, Confluent Surgical), have been clinically used for tissue repairing and wound dressings.[4] However, due to the limited tolerance of local tissue shrinkage, motion or body-fluid flow, tough tissue interfacial adhesion is highly desirable.[10,11] In addition to the Benzyl and Azo moieties, the CB[8]·Vi^{2+} binary complex also exhibits strong binding affinity to phenylalanine or tryptophan ($K_a \sim 10^4$ M^{-1}),[17,19,20] indispensable amino acids found in proteins. Therefore, we envision that the HBP-CB[8] might also bond biological tissues. Porcine skins, commonly-used biological substrates as an alternative to human dermis, were obtained from a local butcher's shop, and

used to test the adhesion affinity of the HBP-CB[8] adhesive (**Figure 5a**). In addition to phenylalanine or tryptophan moieties (second guests for CB[8]·Vi^{2+} binary complexes), subcutaneous tissue is also rich in other functional groups, such as amine and carboxylic acid moieties, thus a much higher shear stress was detected for porcine skin joints bonded with HBP-CB[8] (**Figure 5**). The HBP-CB[8]-bonded skin joints could withhold a stress more than four times the HBP-CB[7] control (see **Supplementary Movie S5** and **S6**). Despite of slightly lower shear stress compared to DOPA-inspired adhesives (*ca.* 35 kPa),[35] the dynamic nature of the CB[8] host-guest interactions allows for consecutive bonding/debonding/re-bonding cycles (**Figure 5b**), which can effectively dissociate energy, yielding a tough biological interface. Such a combination of strong adhesion and large deformability is vital for tissue engineering and flexible devices, whereas existing adhesives are not tolerant to large deformation.[4]

In summary, we report the use of CB[*n*]-threaded highly-branched polyrotaxanes (HBP-CB[*n*]) to form dynamically-bonded soft materials, including synthetic hydrogels and biological tissues, through CB[*n*]-mediated molecular recognition. Elaborate design/choice of the second guest moiety can effectively impart more flexibility and versatility on the systems, with *on-demand* control over interfacial adhesion, *e.g.*, the photo-tuning with Azo-tailored materials and interfaces. Additional benefit of these supramolecular polymer adhesives arise from manipulation at room temperature and mild aqueous condition, under which the adhesion could be set and self-healed without additional curing materials. We envision that HBP-CB[*n*] polymers have promising potential in tissue repair, wound dressings, elastic tissue sealing without the need for suturing, *etc*. Future work will focus on *in vitro* and *in vivo* evaluation regarding the biocompatibility, efficiency on tissue repairing and biological inflammatory responses.

References

[1] E. A. Dubiel, Y. Martin, P. Vermette, *Chem. Rev.* **2011**, *111*, 2900–2936.

[2] C. Heinzmann, C. Weder, L. M. de Espinosa, *Chem. Soc. Rev.* **2016**, *45*, 342–358.

[3] B. P. Lee, P. B. Messersmith, J. N. Israelachvili, J. H. Waite, *Ann. Rev. Mater. Res.* **2011**, *41*, 99.

[4] J. Li, A. D. Celiz, J. Yang, Q. Yang, I. Wamala, W. Whyte, B. R. Seo, N. V. Vasilyev, J. J. Vlassak, Z. G. Suo, D. J. Mooney, *Science* **2017**, *357*, 378–381.

[5] K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full, *Nature* **2000**, *405*, 681–685.

[6] P. B. Messersmith, *Science* **2008**, *319*, 1767–1768.

[7] G. P. Maier, M. V. Rapp, J. H. Waite, J. N. Israelachvili, A. Butler, *Science* **2015**, *349*, 628–632.

[8] H. Shao, R. J. Stewart, *Adv. Mater.* **2010**, *22*, 729–733.

[9] H. Yuk, T. Zhang, G. A. Parada, X. Liu, X. Zhao, *Nat. Commun.* **2016**, *7*, 12028.

[10] S. Rose, A. Prevoteau, P. Elzière, D. Hourdet, A. Marcellan, L. Leibler, *Nature* **2014**, *505*, 382–385.

[11] A. Meddahi-Pellé, A. Legrand, A. Marcellan, L. Louedec, D. Letourneur, L. Leibler, *Angew. Chem. Int. Ed.* **2014**, *53*, 6369–6373.

[12] C. A. Anderson, A. R. Jones, E. M. Briggs, E. J. Novitsky, D. W. Kuykendall, N. R. Sottos, S. C. Zimmerman, *J. Am. Chem. Soc.* **2013**, *135*, 7288–7295.

[13] Y. Ahn, Y. Jang, N. Selvapalam, G. Yun, K. Kim, *Angew. Chem.* **2013**, *125*, 3222–3226.

[14] L. Rossetti, L. A. Kuntz, E. Kunold, J. Schock, K. W. Müller, H. Grabmayr, J. Stolberg-Stolberg, F. Pfeiffer, S. A. Sieber, R. Burgkart, A. R. Bausch, *Nat. Mater.* **2017**, *16*, 664–670.

[15] Y. Zhao, Y. Wu, L. Wang, M. Zhang, X. Chen, M. Liu, J. Fan, J. Liu, F. Zhou, Z. Wang, *Nat. Commun.* **2017**, *8*, 2218.

[16] S. Lamping, T. Otremba, B. J. Ravoo, *Angew. Chem. Int. Ed.* **2018**, *57*, 2474–2478.

[17] K. I. Assaf, W. M. Nau, *Chem. Soc. Rev.* **2015**, *44*, 394–418.

[18] L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* **2015**, *115*, 7196–7239.

[19] J. Liu, C. S. Y Tan, Y. Lan, O. A. Scherman, *Macromol. Chem. Phys.* **2016**, *217*, 319–332.

[20] J. Liu, Y. Lan, Z. Y. Yu, C. S. Y. Tan, R. M. Parker, C. Abell, O. A. Scherman, *Acc. Chem. Res.* **2017**, *50*, 208–217.

[21] G. Yu, K. Jie, F. Huang, *Chem. Rev.* **2015**, *115*, 7240–7303.

[22] B. Shi, K. Jie, Y. Zhou, J. Zhou, D. Xia, F. Huang, *J. Am. Chem. Soc.* **2015**, *138*, 80–83.

[23] C. S. Tan, J. Liu, A. S. Groombridge, S. J. Barrow, C. A. Dreiss, O. A. Scherman, *Adv. Funct. Mater.* **2018**, *28*, 1702994.

[24] J. Zhang, J. Liu, Z. Yu, S. Chen, O. A. Scherman, C. Abell, *Adv. Funct. Mater.* **2018**, *in press*, DOI: 10.1002/adfm.201800550.

[25] H. Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, *Nat. Commun.* **2012**, *3*, 603.

[26] C. S. Tan, J. del Barrio, J. Liu, O. A. Scherman, *Polym. Chem.* **2015**, *6*, 7652–7657.

[27] K Kendall, *J. Adhes.* **1975**, *7*, 137–140.

[28] E. Petrie, *Handbook of adhesives and sealants. McGraw-Hill New York* **2007**, 39–58.

[29] J. Liu, C. S. Y. Tan, Z. Y. Yu, Y. Lan, C. Abell, O. A. Scherman, *Adv. Mater.* **2017**, *29*, 1604951.

[30] J. Liu, C. S. Y. Tan, Z. Y. Yu, N. Li, C. Abell, O. A. Scherman, *Adv. Mater.* **2017**, *29*, 1605325.

[31] Z. Yu, J. Liu, C. S. Y. Tan, O. A. Scherman, C. Abell, *Angew. Chem. Int. Ed.* **2018**, *57*, 3079–3083.

[32] H. Yuk, T. Zhang, S. Lin, G. A. Parada, X. Zhao, *Nat. Mater.* **2016**, *15*, 190–196.

[33] A. H. Hofman, I. A. van Hees, J. Yang, M. Kamperman, *Adv. Mater.* **2018**, *in press*, DOI:10.1002/adma.201704640.

[34] J. Liu, O. A. Scherman, *Adv. Funct. Mater.* **2018**, *in press*, DOI:10.1002/adfm.201800848.

[35] S. A. Burke, M. Ritter-Jones, B. P. Lee, P. B. Messersmith, *Biomed. Mater.* **2007**, *2*, 203–210.

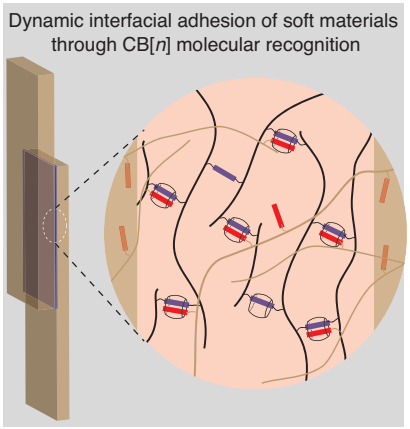
Entry for the Table of Contents (Please choose one layout only)

Layout 1:

Dynamic Interfacial Adhesion

Ji Liu,[a] *Cindy Soo Yun Tan* [a,b] *and Oren A. Scherman*[a]*

Dynamic Interfacial Adhesion through Cucurbit[*n*]uril Molecular Recognition



Dynamic interfacial adhesion of two wet soft materials was accomplished with cucurbit[8]uril-threaded highly-branched polyrotaxanes (HBP-CB[8]), through CB[8]-mediated molecular recognition. The dynamic nature of the host-guest complexation imparts interfacial adhesion with astounding toughness, energy dissipation and reversible bonding upon mechanical failure, as well as *on-demand* control over bonding and de-bonding.
Keywords: Supramolecular adhesive; Cucurbit[*n*]uril; Polyrotaxanes; Dynamic; Stimuli-responsive.

Layout 2:

Catch Phrase:

*Author(s), Corresponding Author(s)**

. . . . . *Page Page*

Title Text

((The TOC Graphic should not exceed the size of this area))

Text for Table of Contents, max. 450 characters.