Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.

CHAPTER 1

Introduction: Cucurbituril-containing Functional Materials in the Context of Smart Materials

DÖNÜS TUNCEL[a,b]

[a] Department of Chemistry, Bilkent University, Ankara 06800, Turkey;
[b] UNAM – National Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey
Email: dtuncel@fen.bilkent.edu.tr

1.1 Smart Materials in General

Smart materials can sense and react to external stimuli by adapting their existing properties to new ones.[1–3] They have ability to gather together many important and interesting features so that these features may act in accord in order to achieve important tasks. Applied external stimuli can be generalized as chemical, physical and biological. The most frequently used chemical stimuli are pH, ionic strengths, moisture, redox and competitive guests. Stress, temperature, electric and magnetic fields, and light can be given as examples of physical stimuli, while biochemical stimuli include antigens, enzymes, ligands or other biochemical agents.

The responses against external stimuli can be physical (changes in the color, shape, size *etc.*), chemical (changes in the functional groups, reactivity, hydrophilicity *etc.*) or changes in mechanical properties. Because the

Smart Materials No. 36
Cucurbituril-based Functional Materials
Edited by Dönüs Tuncel
© The Royal Society of Chemistry 2020
Published by the Royal Society of Chemistry, www.rsc.org

View Online

responses give rise to large macroscopic changes that are reversible and can be repeated many times, these materials can be used in a wide range of applications such as sensors, actuators, artificial muscles, catalysis, smart interfaces, tissue engineering, biosensors, diagnostics, drug delivery, robotics and biomimetics.

Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.

1.2 Supramolecular Smart Materials

Supramolecular smart materials constructed through noncovalent interactions, such as hydrogen bonding, π–π stacking and hydrophobic interactions, have a dynamic nature and can undergo spontaneous and continuous assembly/disassembly processes under certain triggers.[4–8] Owing to the dynamic and reversible nature of noncovalent interactions, these materials have the ability to adapt to their environment and possess a wide range of interesting features, including degradability, shape-memory and self-healing. The selection of the noncovalent interactions and building blocks used in the construction of the supramolecular materials are crucial as the nature of noncovalent interactions and the structure of the building blocks determine the degree of stimuli-responsiveness and the smartness of the resulting materials. Therefore, the supramolecular approach allows the design of materials by incorporating the desired functionalities and features for targeted applications.

1.2.1 Cucurbituril Containing Smart Materials

In the context of the supramolecular approach, host–guest inclusion complexes stabilized by hydrophobic effect are quite attractive inasmuch as the high selectivity between the host and guest molecules provides dynamic but strong interactions.[9–13] Using this approach, small building blocks can be brought together to construct more complicated structures with desirable topological diversity and programmable functions for specific applications. Their assembly and the disassembly processes in general can be controlled by applying appropriate triggers.

The most common macrocycles used as host molecules are cyclodextrins,[14–16] pillarenes,[17] calixarenes[18] and cucurbiturils,[19–23] which can accommodate guest molecules in their cavities on the basis of complementary shape and size. Among them, cucurbit[*n*]urils (CB[*n*]) are a relatively new class of macrocycles with versatile recognition properties and an ability to accommodate different organic guest molecules in aqueous solution with exceptionally high binding constants.[19–23]

In recent years, CB[*n*]-containing functional materials have been receiving increasing attention due to their versatile applications in areas including but not limited to theranostics, photonics, self-healing, sensing and catalysis.[24–28] The abundant host–guest cucurbituril (CB) homologues allow one to prepare a variety of functional and smart materials including molecular switches, reversible, stimuli-responsive hydrogels, porous organic frameworks,

View Online

Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.

nanoparticles, micelles, vesicles, colloidosomes. Because its cavity is larger than other homologues, CB[8] is highly appealing for complexation-induced nanostructure formation. In this regard, the ability of CB[8] to form ternary complexes with suitably sized and functionalized guests has been extensively utilized in the preparation of nanoparticles, stimuli-responsive reversible micelles, vesicles and capsules for the encapsulation, delivery and controlled release of drugs.

In this regard, this book aims to provide a comprehensive overview of cucurbituril-based functional materials. It starts with Chapter 2, on CB chemistry, which provides a detailed account of the synthesis, isolation, formation mechanisms, and structural and physical properties of CB homologues, derivatives and functional CBs. The discussion also contains some elements of the historical background of CBs.

Chapter 3 summarizes the key roles of the carbonyl groups containing portals of CBs on the host–guest inclusion complex formation. Due to the presence of carbonyl groups, the portals of CBs are partially negatively charged, and, accordingly, this chapter presents research work showing that electrostatic interactions may have considerable effects on the stability of complexes formed by CB hosts.

In Chapter 4, the preparation of cucurbituril-based pseudorotaxanes, rotaxanes and polyrotaxanes is discussed with selected examples. This includes notions of self-sorting, which enables the setup of homo- and hetero(pseudo)rotaxanes. The implications of thermodynamic and kinetic control are briefly showcased as well. In the main part, these assemblies are discussed in the context of stimuli-responsive systems, whose supramolecular chemistry and functionality can be controlled by using chemical inputs (pH, ions), redox signals or light. Finally, some applications are highlighted, such as drug delivery and molecular information processing.

Chapter 5 deals with hybrid nanomaterials of CBs with metals (Au, Ag, Pd, Pt), lanthanides and silica. These nanomaterials are either prepared in the presence of CBs (CB-assisted synthesis) or have been first prepared before CBs are used as capping agents to stabilize the resulting nanostructures. The plasmonic and SERS applications of CB-Au and CB-Ag hybrid nanoparticles and electrocatalytic applications of CB-Pt and CB-Pd are also presented.

Chapters 6, 7 and 8 give an overview on the stimuli-responsive supramolecular assemblies constructed mainly through host–guest complexation of CB homologues. Particularly, the ternary complex formation ability of CB[8], with suitably sized electron donor and acceptor guests, has been utilized in those assemblies. Chapter 6 focuses on the preparation and properties of stimuli-responsive reversible hydrogels and their applications in various areas, including drug delivery, wound dressing and healing, tissue engineering, diagnostic devices, wood conservation, adhesives, stretchable and wearable electronics, injection and printing substances. In the follow-up chapter (Chapter 7), the ability of CB[8] to form ternary complexes with suitably sized and functionalized guests has been demonstrated in the preparation of single-chain nanoparticles, stimuli-responsive reversible micelles and pH-responsive

View Online

prodrug micelles for the encapsulation, delivery and controlled release of drugs and bioactive nanostructures based on peptide amphiphile vesicles, as well as reversible and stimuli-responsive microcapsules prepared to make use of the advantages of microfluidics. Nanostructures prepared from functionalized CB derivatives are also discussed.

Chapter 8 continues the discussion on supramolecular frameworks formed through the ternary complexes of CBs. The authors demonstrate how self-assembly provides a straightforward strategy for the construction of water-soluble porous supramolecular organic frameworks (SOFs) from rationally designed rigid multitopic molecular components and CB[8]. Using this strategy, a variety of two-dimensional honeycomb, square, and rhombic SOFs have been constructed, some of which exhibit interesting absorption and sensing functions.

The discussion on CB-containing nanomaterials continues in Chapter 10, but the nanomaterials covered in this chapter are prepared through the cross-linking of functionalized CBs, not through ternary complex formation. This chapter presents how functionalized CB[6]-based nanocapsules are constructed by a direct, one-pot method without using any preorganized structure, emulsifier or template, and the cavity of CBs in these nanocapsules is further available for molecular recognition. Their applications in various areas include heterogeneous catalysis, drug delivery and *in vivo* imaging.

Chapters 9, 11 and 12 demonstrate the applications of CB homologues and derivatives. Chapter 9 presents the research works on the interactions of CB homologues and derivatives with biomolecules and drugs because many promising discoveries of supramolecular interactions between CBs and biomolecules and small organic drug molecules have emerged with potential implications in the field of pharmaceutical sciences, which has become one of the most significant areas of potential applications for CBs. This chapter covers the noncovalent interactions of peptides, proteins and drug molecules with CB homologues and derivatives, in addition to discussing the ability of CBs to modulate the functions and bioactivities of these species through host–guest chemistry and the potential impact of CBs on protein enrichment, together with other relevant topics.

Chapter 11 covers some of the recent works on the molecular properties of cucurbituril-based supramolecular functional assemblies of a few organic dyes and of polyoxometalates that have technological and biological importance, especially in the domains of aqueous dye laser, light-emitting devices, photofunctional devices, energy storage devices, molecular architectures, supramolecular catalysts, radiotracer separation, antibacterial agents and drug delivery vehicles.

Chapter 12 deals with the supramolecular assemblies of CBs with conjugated polymers and porphyrins. The effect of CBs on the photophysical properties of conjugated polymers is discussed, and the optoelectronic application of CB-containing π-conjugated materials is demonstrated. Moreover, the application of CB-based photosensitizers in photodynamic therapy is summarized.

Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.

View Online

Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.

Acknowledgements

We gratefully acknowledge the financial support of the Scientific and Technological Research Council of Turkey (TUBITAK) grant number 215Z035.

References

1. (a) M. Wun-Fogle, *Materials for Smart Systems*, Cambridge University Press, 2014; (b) M. R. Aguilar and J. S. Roman, *Smart Polymers and Their Applications*, Woodhead Publishing, 2014; (c) Q. Li, *Intelligent Stimuli-responsive Material*, Wiley, 2013; (d) *Handbook of Stimuli-responsive Materials*, ed. M. H. Urban, Wiley-VCH, Weinheim, 2011; (e) *Intelligent Materials*, ed. M. Shahinpoor and H.-J. Schneider, Royal Society of Chemistry, Cambridge, UK, 2007.
2. (a) A. Grinthala and J. Aizenberg, *Chem. Soc. Rev.*, 2013, **42**, 7072–7085; (b) L. Zhai, *Chem. Soc. Rev.*, 2013, **42**, 7148–7160; (c) D. Habault, H. Zhang and Y. Zhao, *Chem. Soc. Rev.*, 2013, **42**, 7244–7256; (d) A. DoÅNring, W. Birnbaum and D. Kuckling, *Chem. Soc. Rev.*, 2013, **42**, 7391–7420; (e) J. Zhuang, M. R. Gordon, J. Ventura, L. Li and S. Thayumanavan, *Chem. Soc. Rev.*, 2013, **42**, 7421–7435.
3. (a) R. B. Grubbs and Z. Sun, *Chem. Soc. Rev.*, 2013, **42**, 7436–7445; (b) F. D. Jochumab and P. Theato, *Chem. Soc. Rev.*, 2013, **42**, 7468–7483; (c) M. Molina, M. Asadian-Birjand, J. Balach, J. Bergueiro, E. Miceliac and M. Calderoaln, *Chem. Soc. Rev.*, 2015, **44**, 6161–6186.
4. (a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (b) J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, 1996; (c) J. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, 2000.
5. (a) J.-M. Lehn, *Angew. Chem., Int. Ed.*, 1990, **29**, 1304; (b) J.-M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151.
6. (a) X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042–6065; (b) C. Heinzmann, C. Weder and L. Montero de Espinosa, *Chem. Soc. Rev.*, 2016, **45**, 342–358; (c) O. J. G. M. Goor, S. I. S. Hendrikse, P. Y. W. Dankers and E. W. Meijer, *Chem. Soc. Rev.*, 2017, **46**, 6621–6637.
7. L. Voorhaar and R. Hoogenboom, *Chem. Soc. Rev.*, 2016, **45**, 4013–4031.
8. R. Dong, Y. Pang, Y. Su and X. Zhu, *Biomater. Sci.*, 2015, **3**, 937–954.
9. X. Ma and H. Tian, *Acc. Chem. Res.*, 2014, **47**, 1971.
10. P. Wei, X. Yan and F. Huang, *Chem. Soc. Rev.*, 2015, **44**, 815.
11. J. Boekhoven and S. I. Stupp, *Adv. Mater.*, 2014, **26**, 1642.
12. X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042.
13. G. Yu, K. Jie and F. Huang, *Chem. Rev.*, 2015, **115**, 7240.
14. Q.-D. Hu, G.-P. Tang and P. K. Chu, *Acc. Chem. Res.*, 2014, **47**, 2017.
15. A. Harada, Y. Takashima and M. Nakahata, *Acc. Chem. Res.*, 2014, **47**, 2128.

View Online

16. Y. Kang, K. Guo, B. J. Li and S. Zhang, *Chem. Commun.*, 2014, **50**, 11083.
17. J. Murray, K. Kim, T. Ogoshi, W. Yao and B. C. Gibb, *Chem. Soc. Rev.*, 2017, **46**, 2479.
18. D.-S. Guo and Y. Liu, *Acc. Chem. Res.*, 2014, **47**, 1925.
19. (a) R. Behrend, E. Meyer and F. Rusche, *Justus Liebigs Ann. Chem.*, 1905, **339**, 1; (b) W. L. Mock, in *Comprehensive Supramolecular Chemistry*, ed. F. Vogtle, Pergamon Press, Oxford, 1996, vol. 2, p. 477; (c) W. A. Freeman, W. L. Mock and N.-Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367; (d) Y. M. Jeon, H. Kim, D. Whang and K. Kim, *J. Am. Chem. Soc.*, 1996, **118**, 9790; (e) D. Whang, Y. M. Jeon, J. Heo and K. Kim, *J. Am. Chem. Soc.*, 1996, **118**, 11333; (f) I.-S. Kim, J. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540.
20. D. Shetty, J. K. Khedkar, K. M. Park and K. Kim, *Chem. Soc. Rev.*, 2015, **44**, 8747.
21. S. J. Barrow, S. Kasera, M. J. Rowland, J. del Barrio and O. A. Scherman, *Chem. Rev.*, 2015, **115**, 12320.
22. L. Isaacs, *Acc. Chem. Res.*, 2014, **47**, 2052.
23. K. I. Assaf and W. M. Nau, *Chem. Soc. Rev.*, 2015, **44**, 394.
24. K. Kim, N. Selvapalam, Y. H. Ko, K. M. Park, D. Kim and J. Kim, *Chem. Soc. Rev.*, 2007, **36**, 267.
25. S. Gürbüz, M. Idris and D. Tuncel, *Org. Biomol. Chem.*, 2015, **13**, 330.
26. H. Zou, J. Liu, Y. Li, X. Li and X. Wang, *Small*, 2018, **14**, 1802234.
27. C. Stoffelen and J. Huskens, *Small*, 2016, **12**, 96.
28. A. Koc and D. Tuncel, *Isr. J. Chem.*, 2018, **58**, 334.

Published on 28 August 2019 on https://pubs.rsc.org | doi:10.1039/9781788015950-00001
Downloaded on 2/3/2020 1:09:47 PM.