

Metal-Organic Frameworks, Hydrogen Bonded Organic-Frameworks



Jesse Rowsell
1977-2015

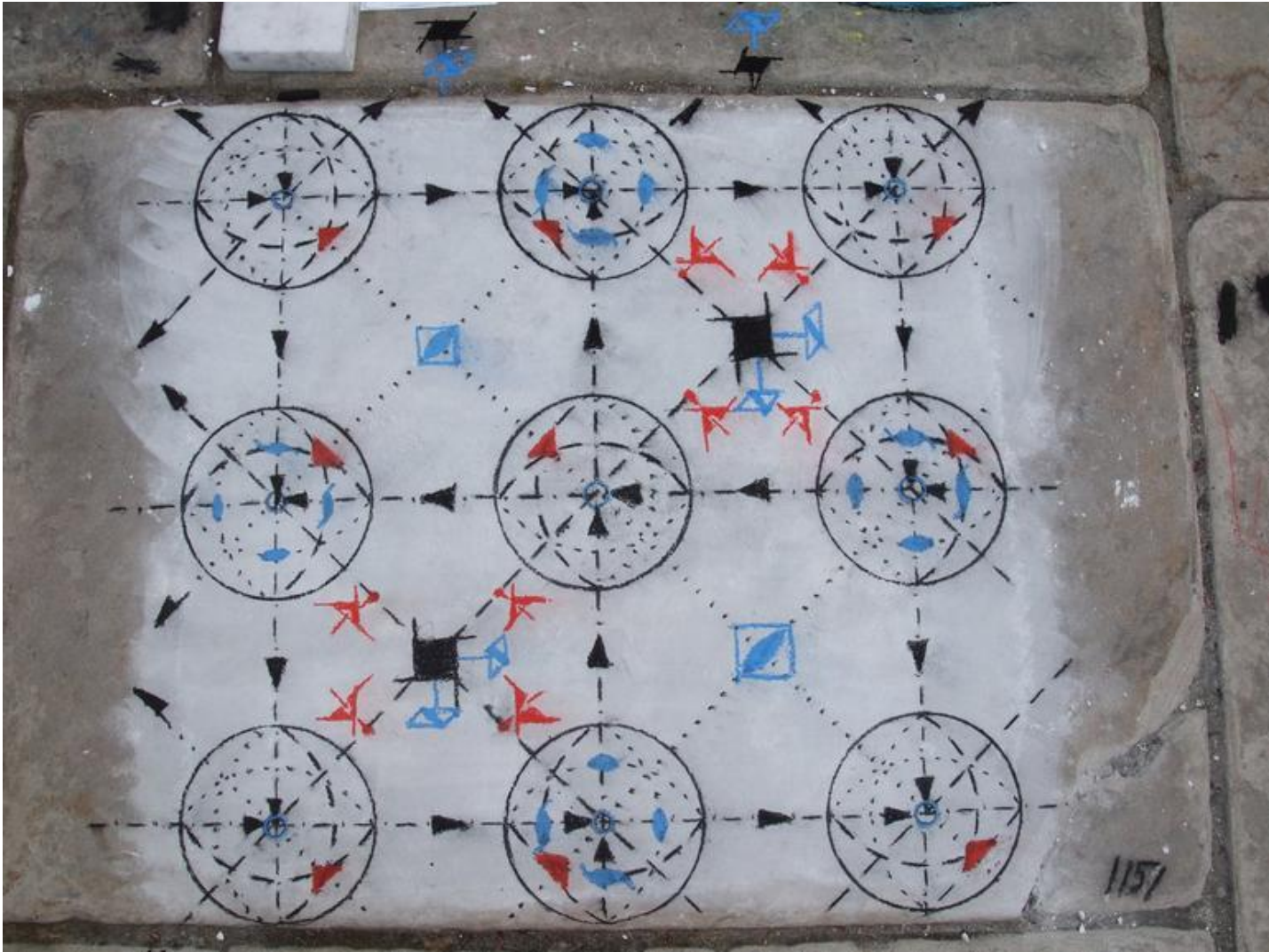
Outline

1. Who am I?
2. Who was Jesse Rowsell?
3. What is the crystalline structure of tcpb?
4. Who are our students?



NSF-MRI Grants
NSF-Grant # 1111896

Oberlin Chalk Walk



Publications as an undergraduate student

“Crystallographic investigation of the Co-B-O system”

J.L.C. Rowsell, N.J. Taylor and L.F. Nazar
J. Solid State Chem., 174, 189 (2003)

“Synthesis, structure, and solid-state electrochemical properties of Cr_3BO_6 :... ”

J.L.C. Rowsell and L.F. Nazar
J. Mater. Chem., 11, 3228 (2001)

“Structure and ion exchange properties of a new cobalt borate with a tunnel structure “templated” by Na^+ ”

J.L.C. Rowsell, N.J. Taylor and L.F. Nazar
J. Am. Chem. Soc., 124, 6522 (2002)

“Speciation and thermal transformation in alumina sols:”

J. Rowsell and L.F. Nazar
J. Am. Chem. Soc., 122, 3777 (2000)

“Layered lithium iron nitride: a promising anode material for Li-ion batteries”

J.L.C. Rowsell, V. Pralong and L.F. Nazar
J. Am. Chem. Soc., 123, 8598 (2001)

“A new class of materials for lithium-ion batteries: iron(III) borates”

J.L.C. Rowsell, J. Gaubicher and L.F. Nazar
J. Am. Chem. Soc., 123, 8598 (2001)

Early days of MOFs

J|A|C|S
COMMUNICATIONS

Published on Web 04/17/2004

Hydrogen Sorption in Functionalized Metal–Organic Frameworks

Jesse L. C. Rowsell, Andrew R. Millward, Kyo Sung Park, and Omar M. Yaghi*

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O. M. Yaghi and J. L. C. Rowsell

Minireviews

Microporous Materials

Strategies for Hydrogen Storage in Metal–Organic Frameworks

Jesse L. C. Rowsell and Omar M. Yaghi*

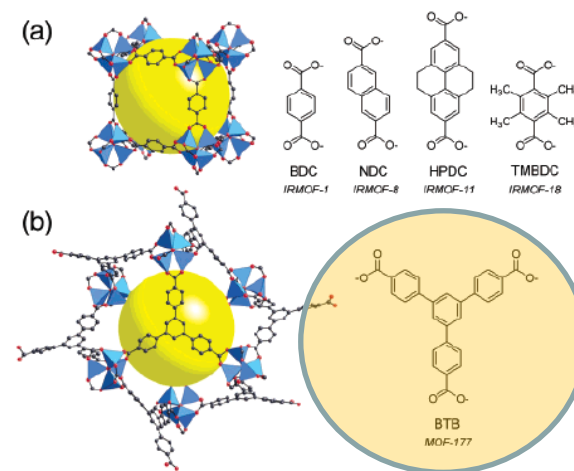
Keywords:

adsorption · hydrogen · metal–organic frameworks · microporous materials · organic–inorganic hybrid composites

Gas Adsorption Sites in a Large-Pore Metal–Organic Framework

Jesse L. C. Rowsell,¹ Elinor C. Spencer,² Juergen Eckert,^{3,4} Judith A. K. Howard,² Omar M. Yaghi^{1*}

The primary adsorption sites for Ar and N₂ within metal-organic framework-5, a cubic structure composed of Zn₄O(CO₂)₆ units and phenylene links defining large pores 12 and 15 angstroms in diameter, have been identified by single-crystal x-ray diffraction. Refinement of data collected between 293 and 30 kelvin revealed a total of eight symmetry-independent adsorption sites. Five of these are sites on the zinc oxide unit and the organic link; the remaining three sites form a second layer in the pores. The structural integrity and high symmetry of the framework are retained throughout, with negligible changes resulting from gas adsorption.

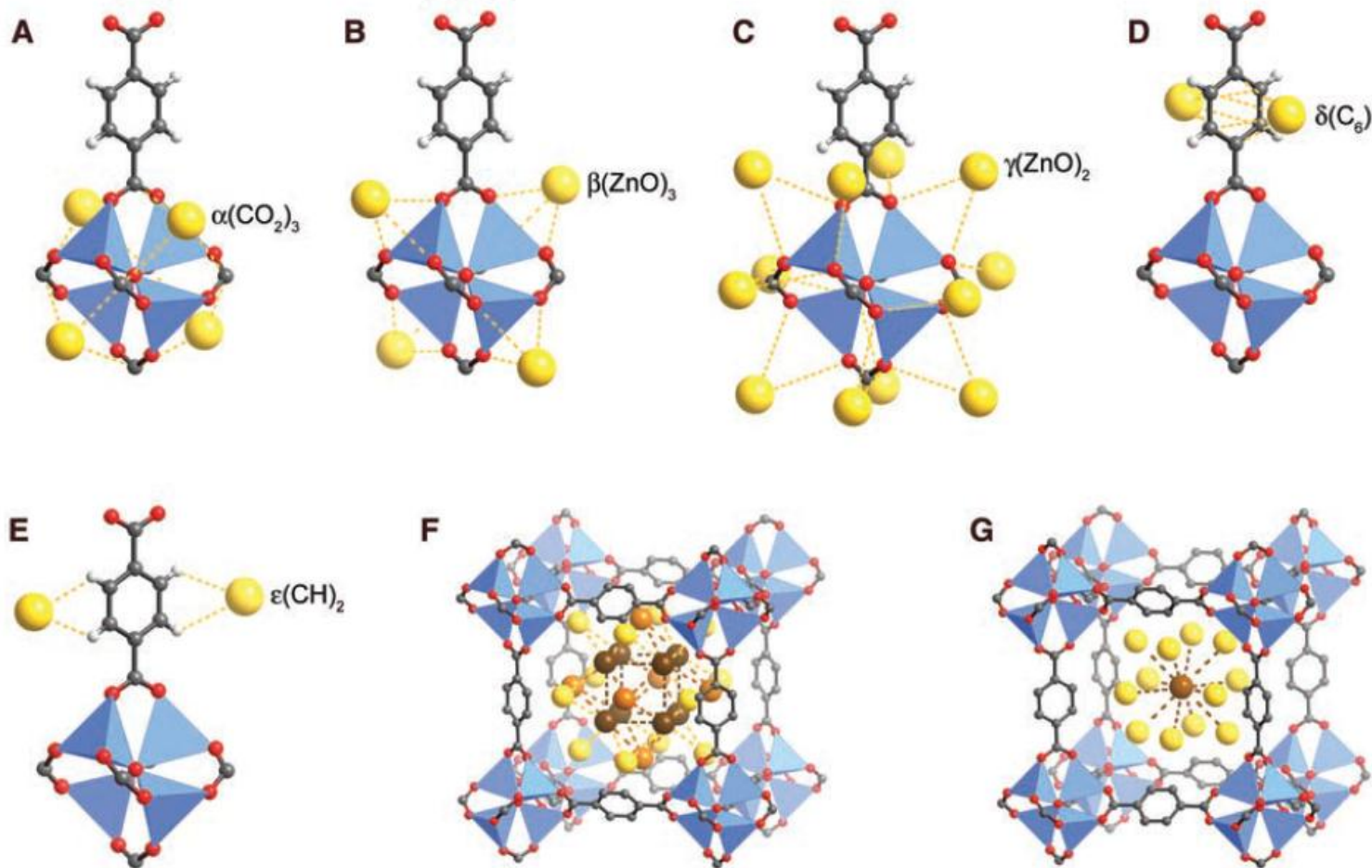


J.L.C. Rowsell et al., Science, 2005.

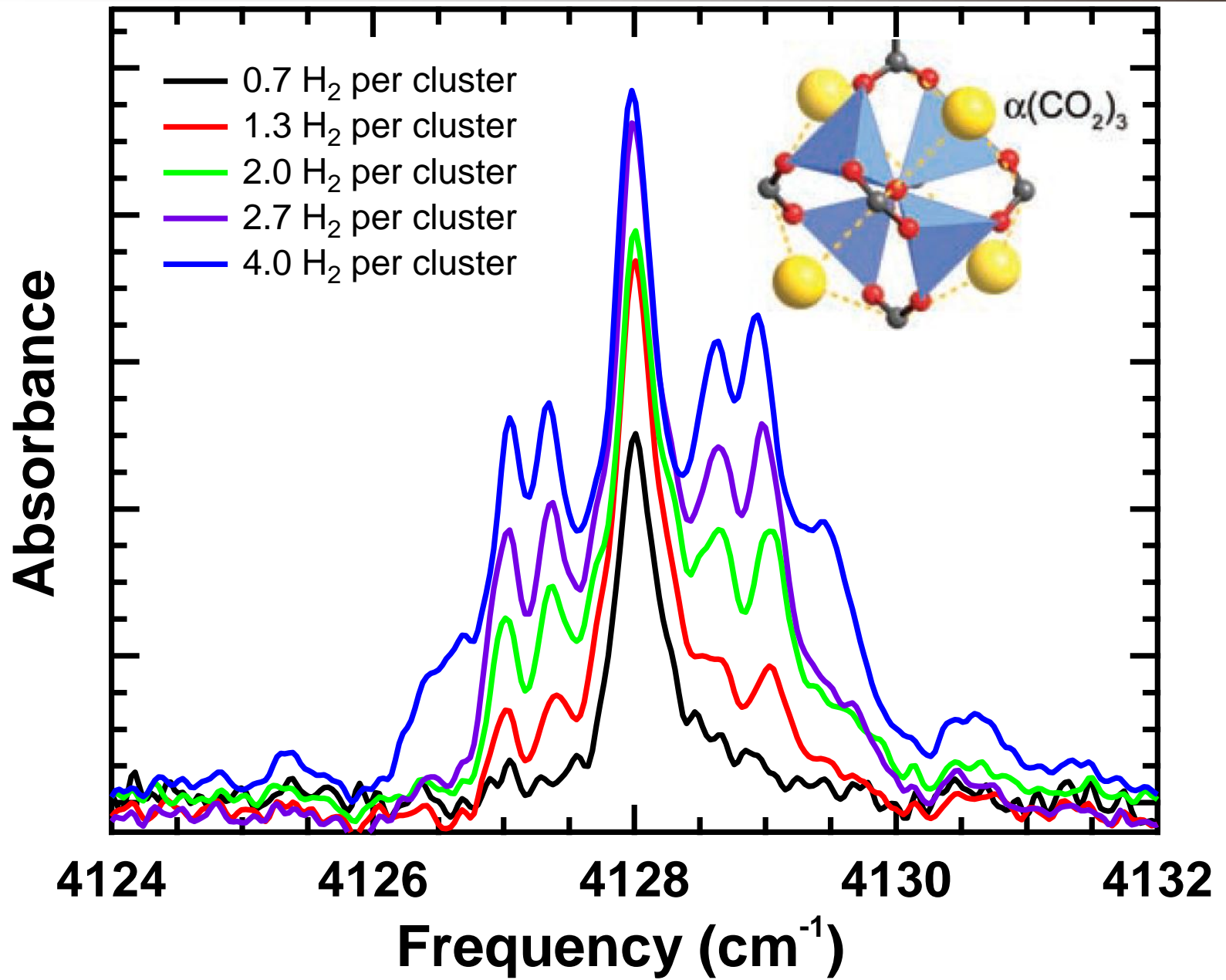
Binding sites in MOF-5

REPORTS

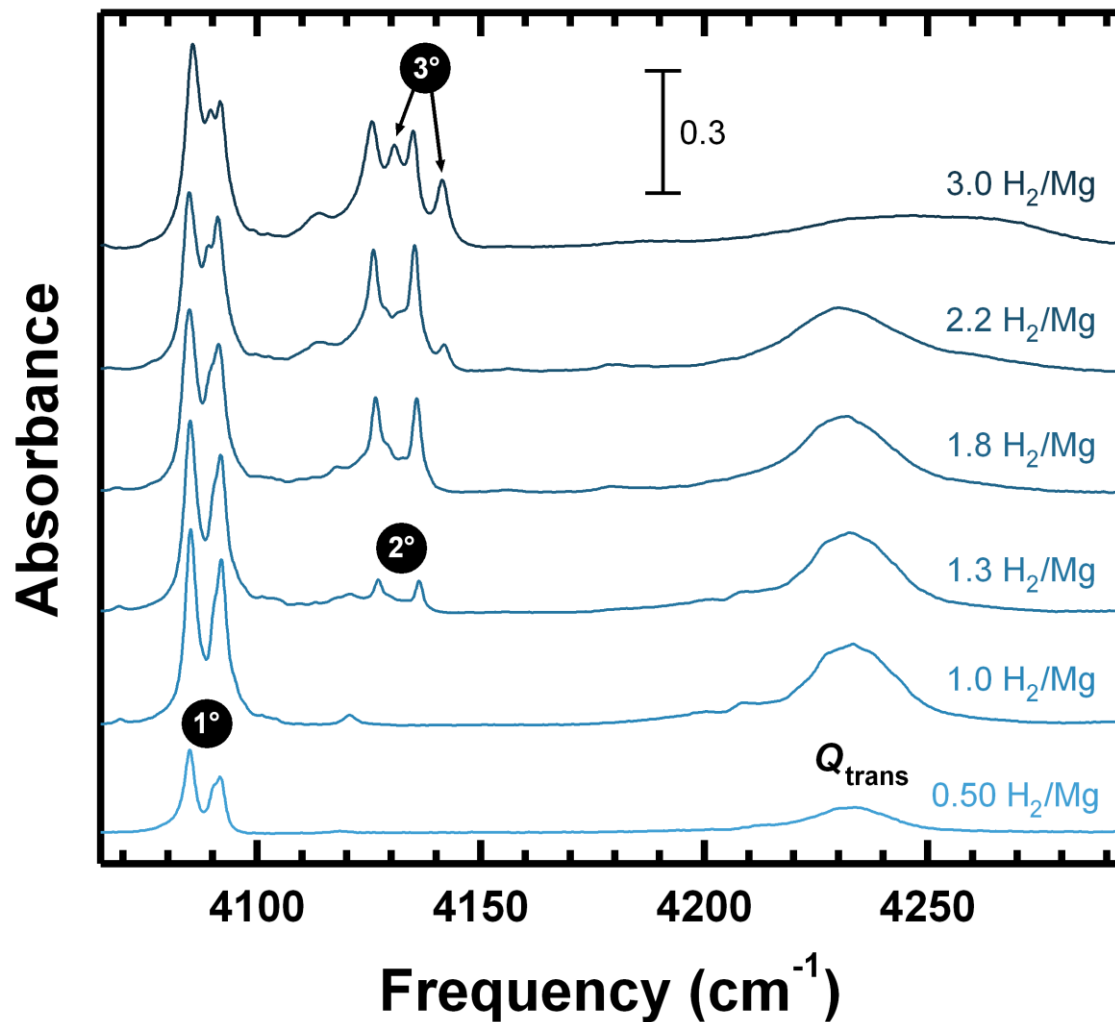
Fig. 3. At 30 K, eight symmetry-independent sites are crystallographically identified as partially occupied by Ar atoms (shown as yellow spheres) in the pores of MOF-5. These include (A to C) three sites primarily associated with the secondary building unit and those above the (D) face and (E) edges of the linker. Sites are labeled according to the description in the text. (F) Sites ϕ (orange spheres) and η (brown spheres) from a second layer in the large pore above site $\delta(C_6)$ (yellow spheres); (G) site θ (brown sphere) is located at the center of the small pore surrounded by site $\epsilon(CH_2)$ (yellow spheres).



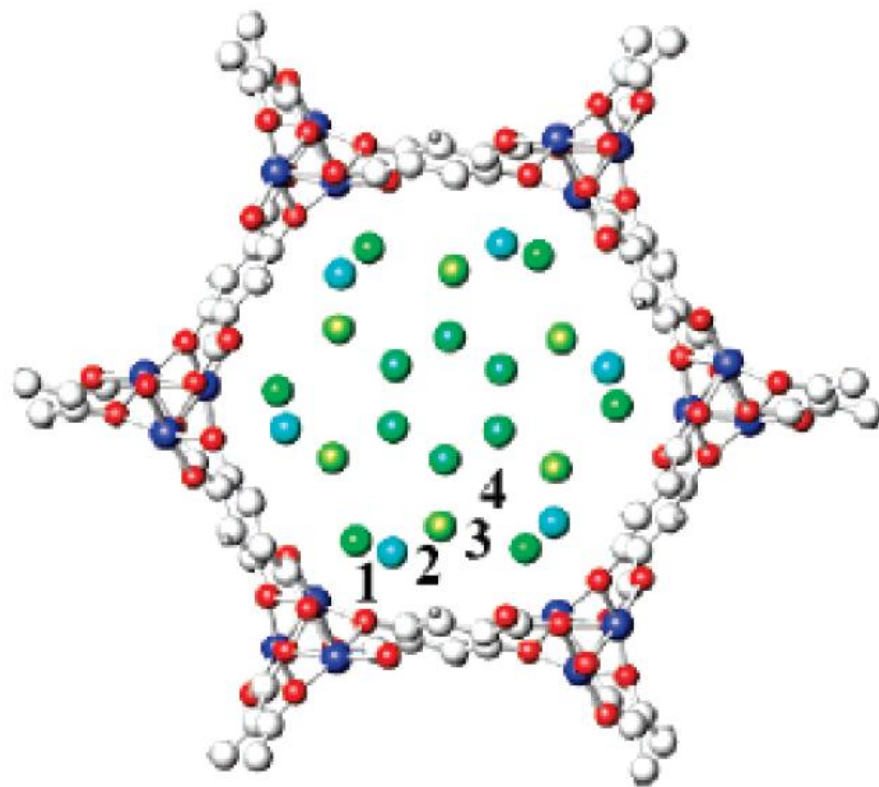
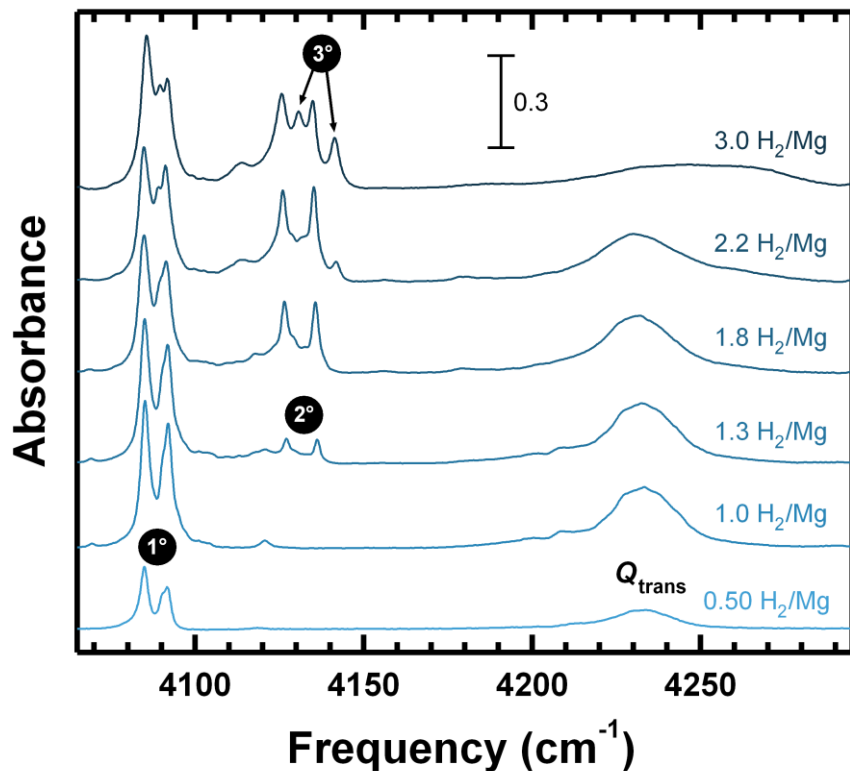
H₂···H₂ Interactions in MOF-5



Infrared Spectrum of H₂ in Mg-MOF-74



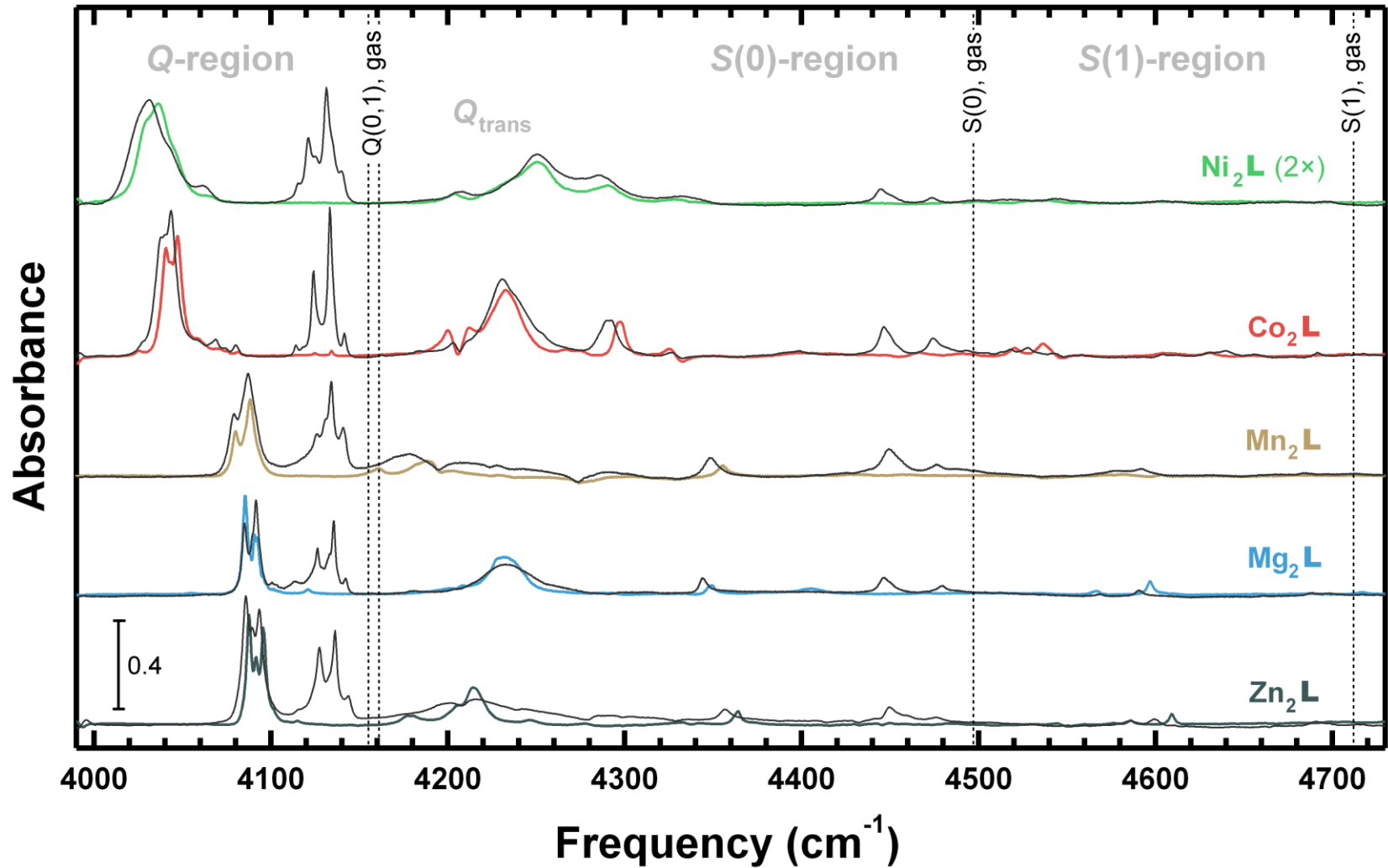
Band intensities plateau as sites fill



Liu *et al.*, Langmuir, 2008

FitzGerald *et al.*, JACS, 2011

Metal-specific band redshifts



1,3,5-Tris(4-carboxyphenyl)benzene tcpb

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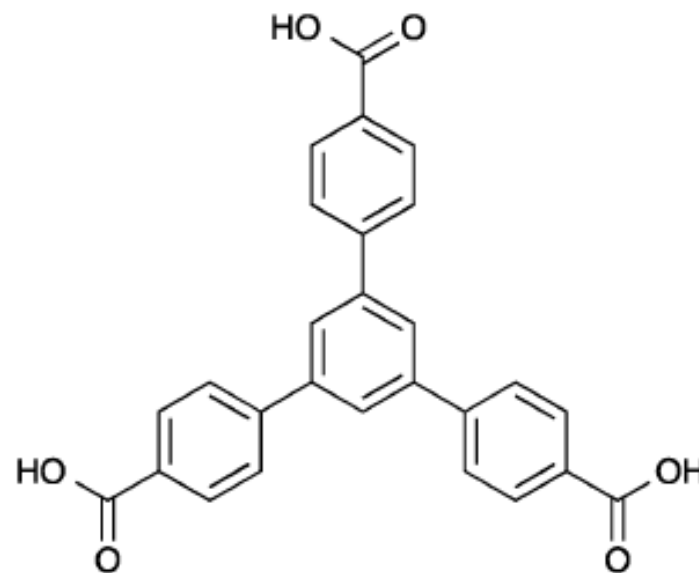
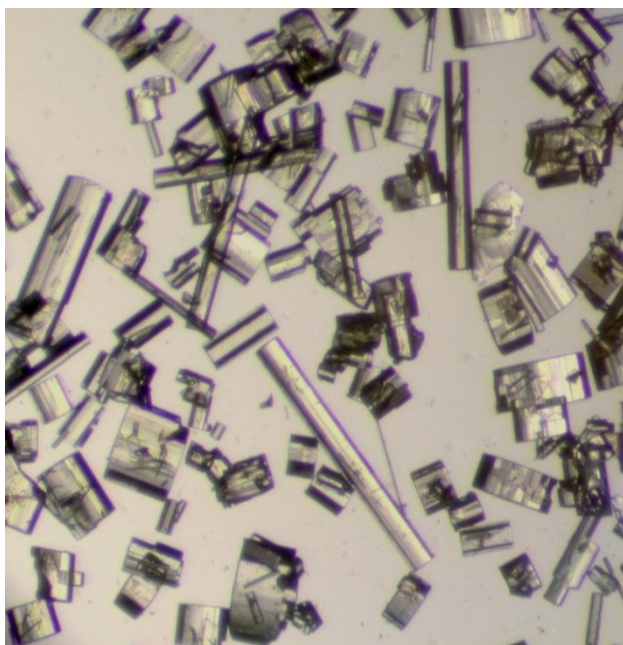


High surface area and Z' in a thermally stable 8-fold polycatenated hydrogen-bonded framework†‡

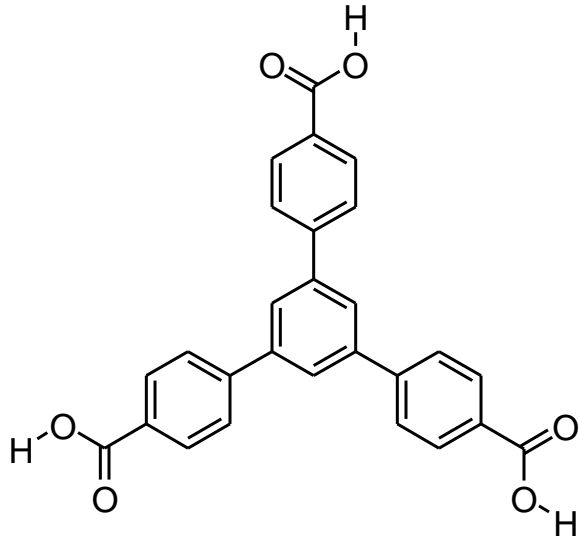
Cite this: DOI: 10.1039/c5cc04219d

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Accepted 15th June 2015

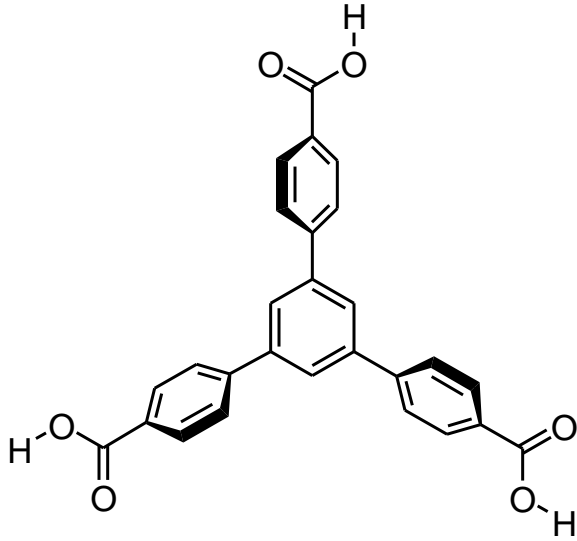
Cassandra A. Zentner,^{*a} Holden W. H. Lai,^a Joshua T. Greenfield,^a Ren A. Wiscons,^a Matthias Zeller,^b Charles F. Campana,^c Orhan Talu,^d Stephen A. FitzGerald^e and Jesse L. C. Rowsell^a



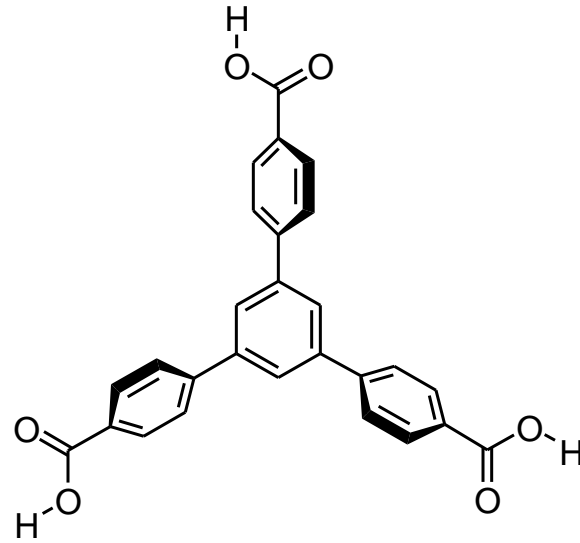
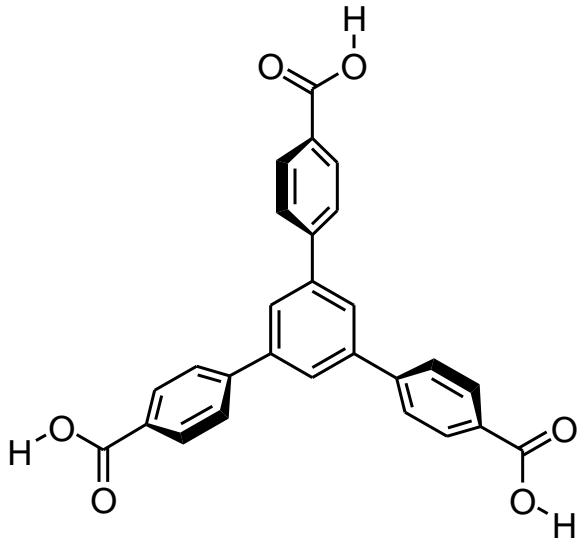
Predict the crystal packing of this molecule...



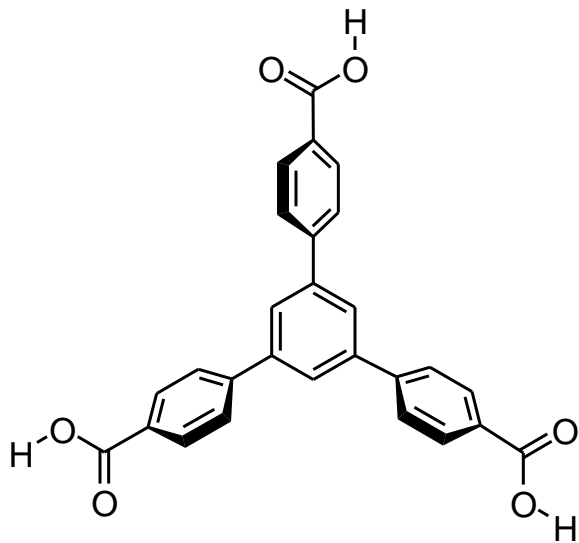
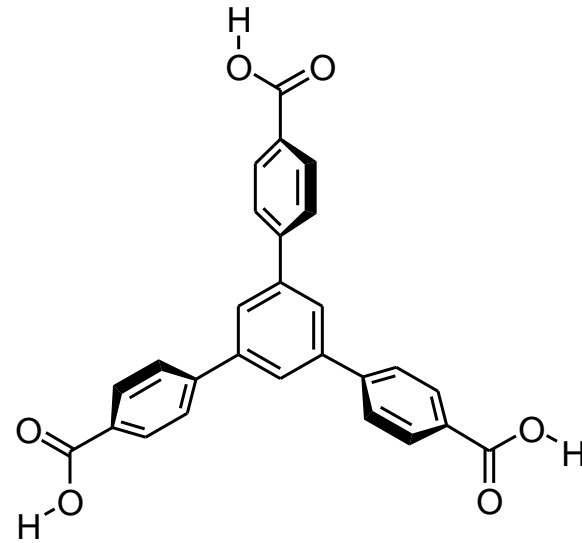
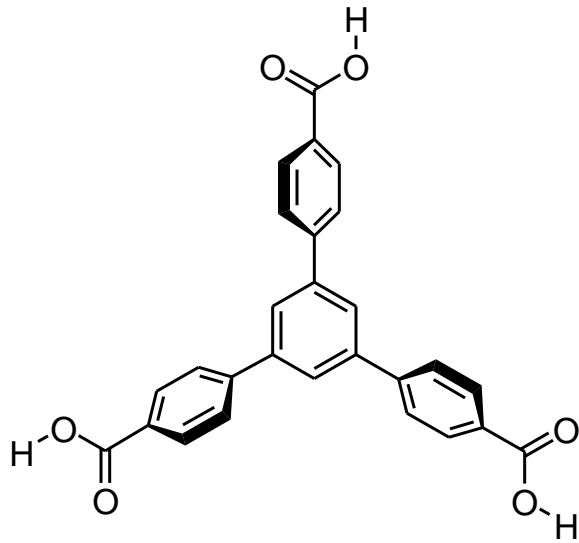
Predict the crystal packing of this molecule...



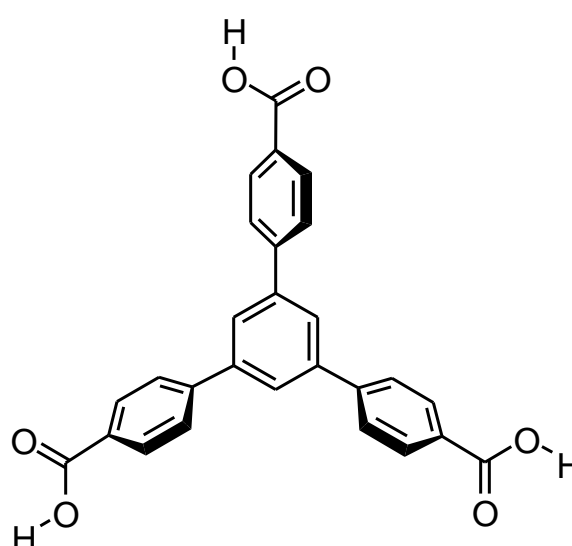
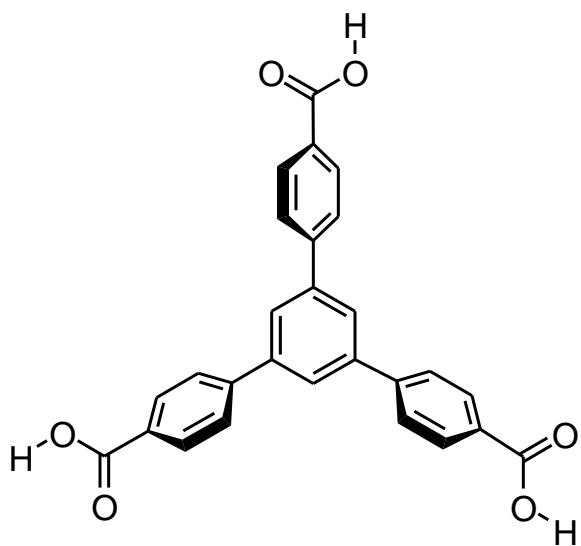
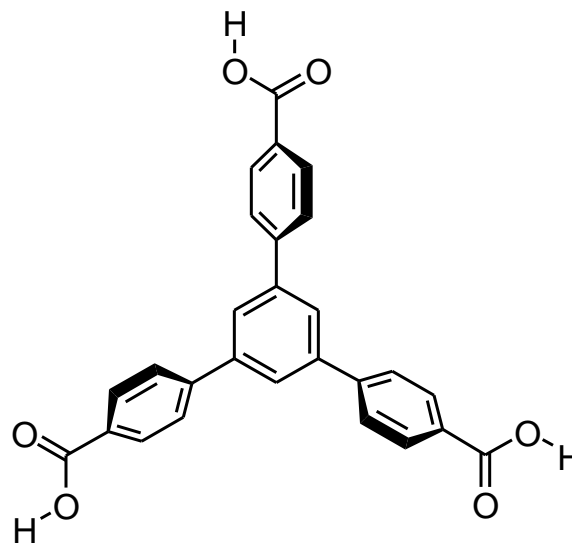
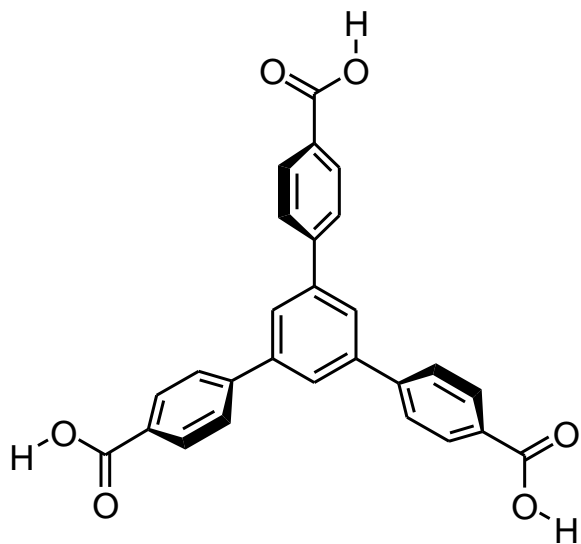
Predict the crystal packing of this molecule...



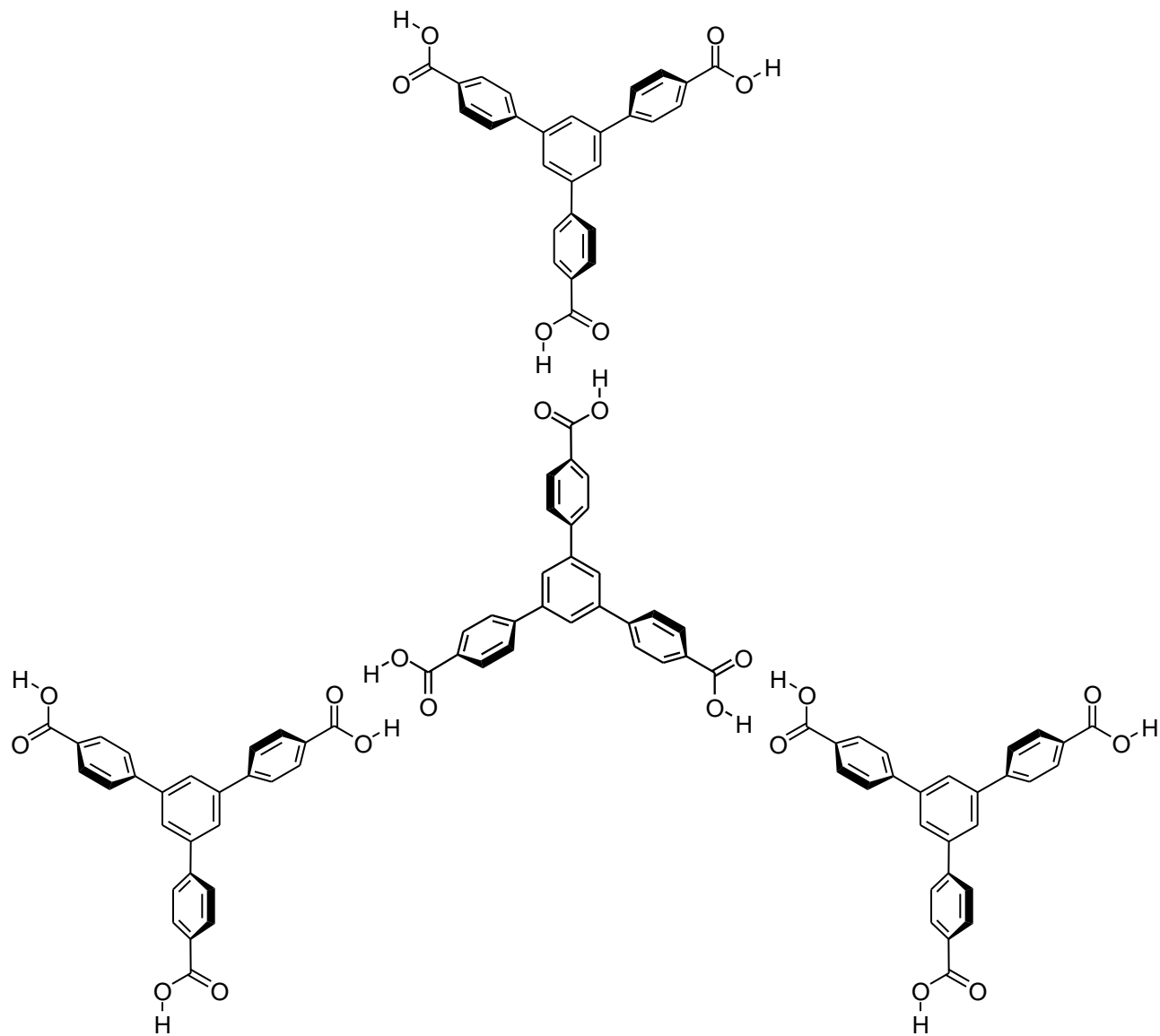
Predict the crystal packing of this molecule...



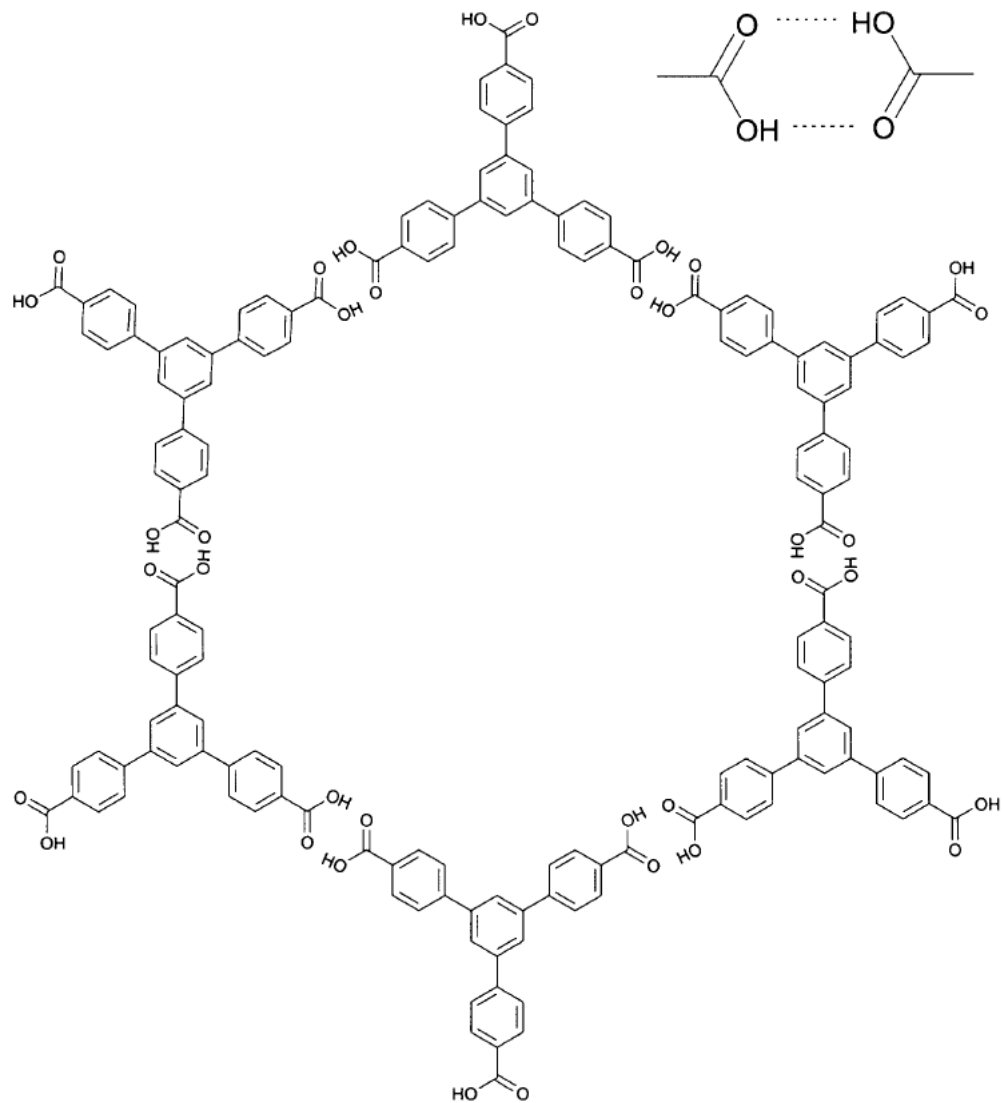
Predict the crystal packing of this molecule...



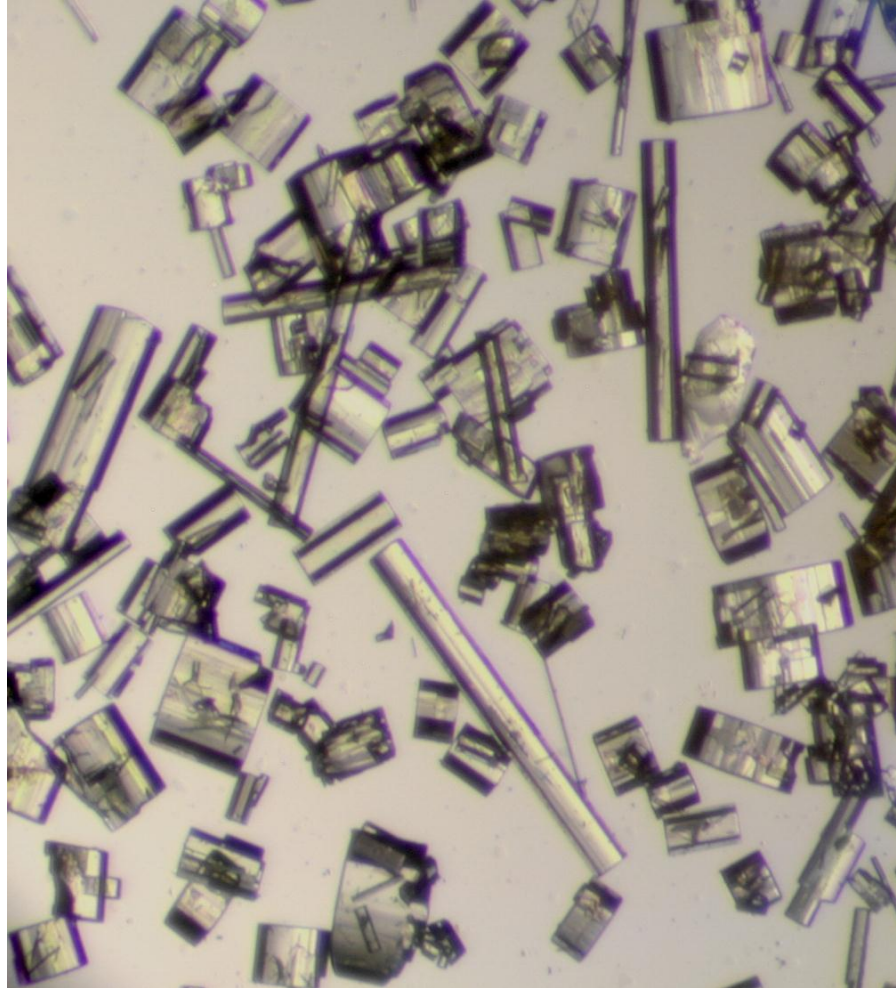
A starting model?



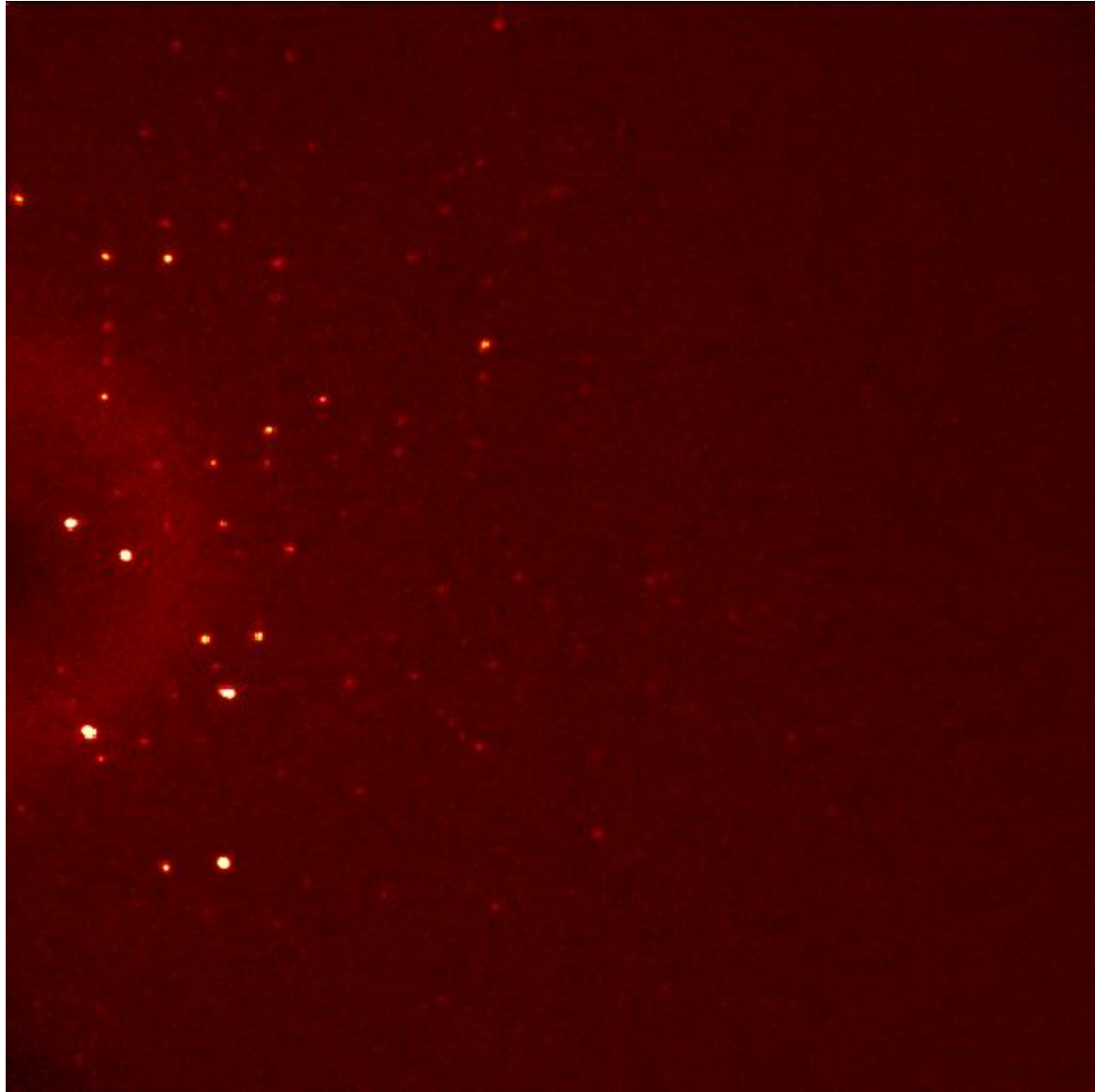
You might have guessed hexagonal



Single crystals after evaporation of ethanol



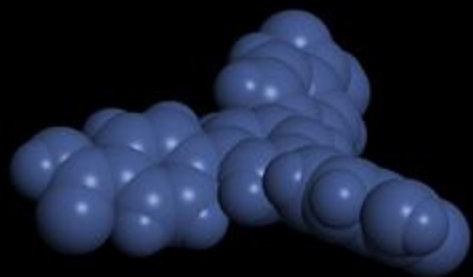
Large unit cells, twinning, poor resolution

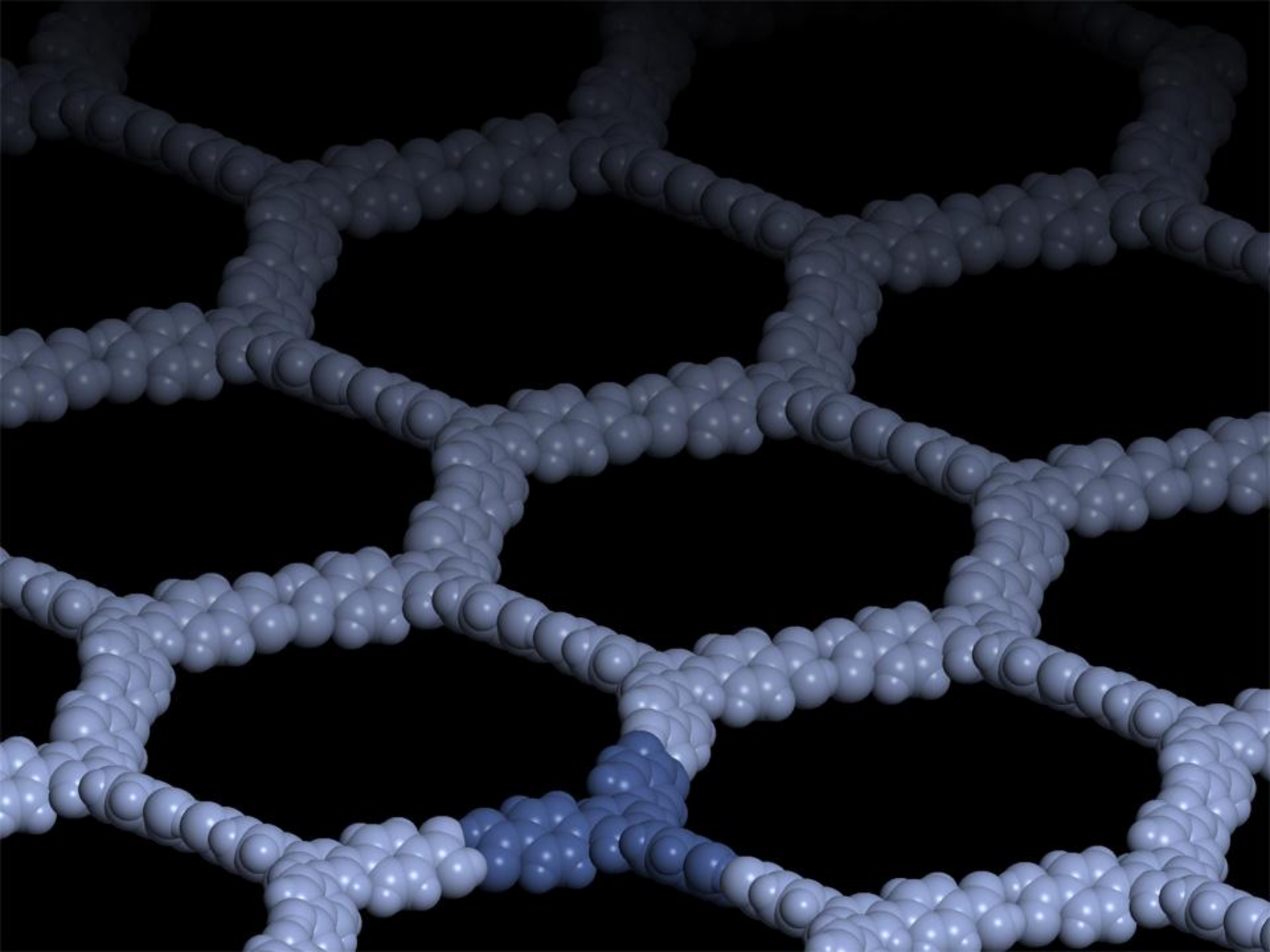


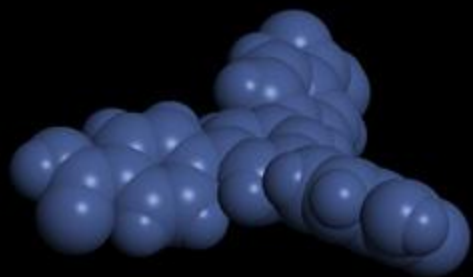
Crystal data

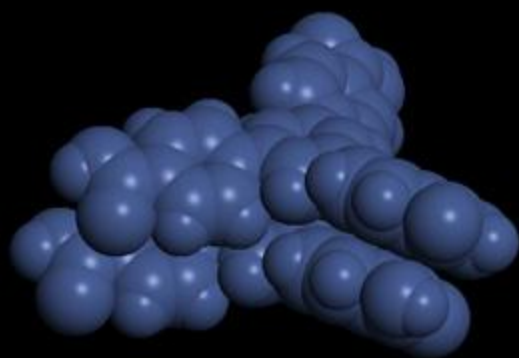
Space Group	I 2	
Cell Parameters	a = 31.419(6) Å	$\alpha = 90^\circ$
	b = 30.116(6) Å	$\beta = 90.412(2)^\circ$
	c = 45.320(9) Å	$\gamma = 90^\circ$
Cell Volume	42 880(14) Å ³	
Z, Z'	56, 14	[462 independent non-H atoms]
Radiation	Mo K α , Incoatec I μ S microfocus source	
Temperature	100 K	
Structure Solution	SHELXD	
Reflections	246 105 total, 49 674 unique, 27 787 ($I > 2\sigma[I]$)	
Completeness	98.7% to $\theta = 27.53^\circ$	
Parameters, Restraints	4201, 1	
R1(obs,all) / wR2(obs,all)	0.0875, 0.158 / 0.268, 0.330	

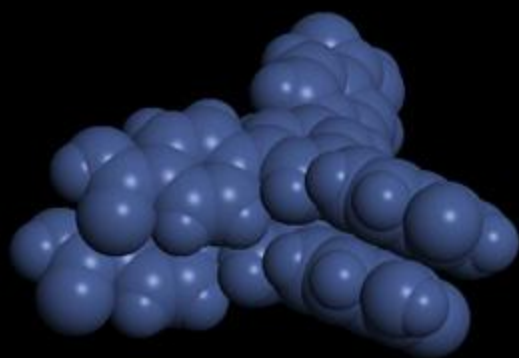
Matthias Zeller, Youngstown State University
Charles Campana, Bruker Madison, WI

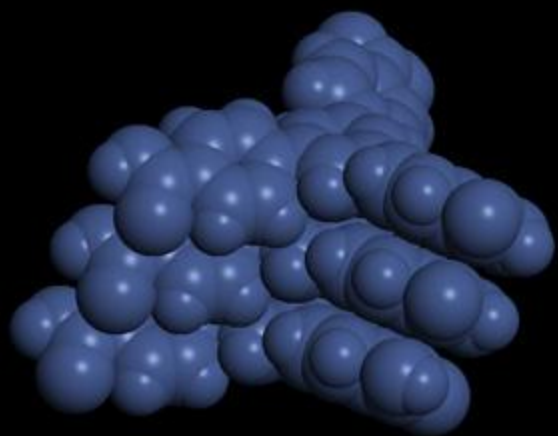


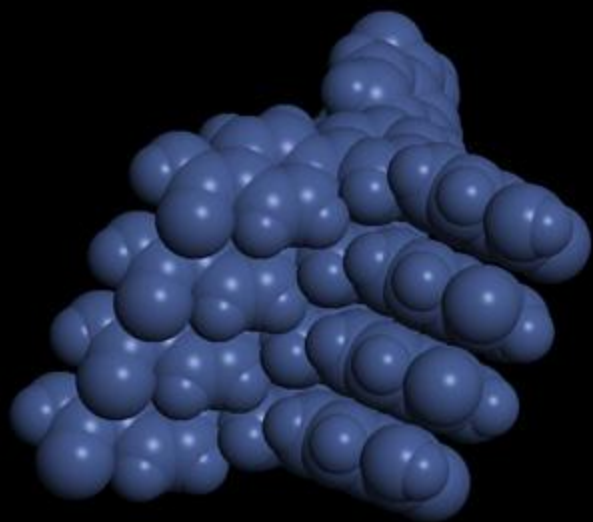


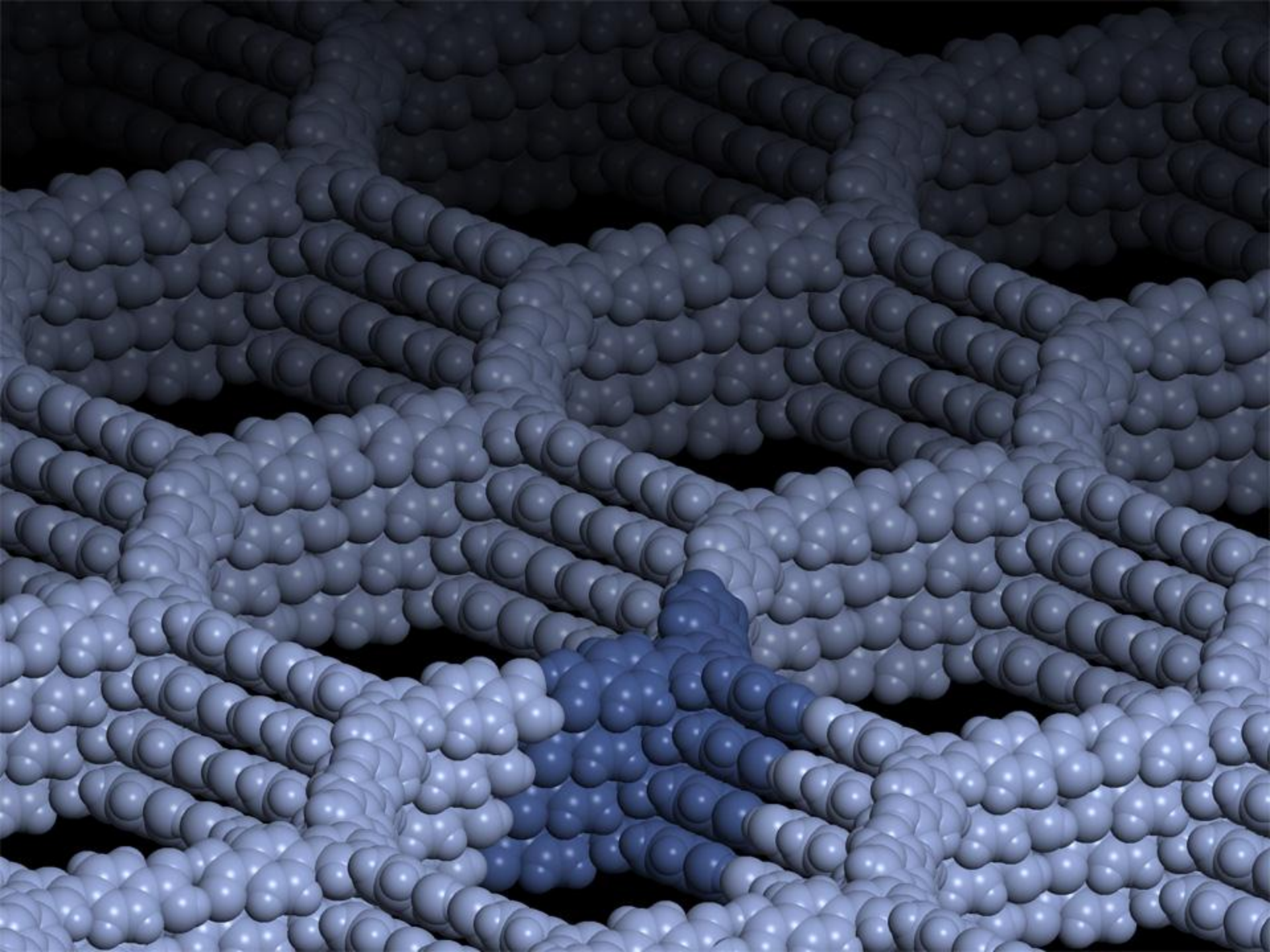


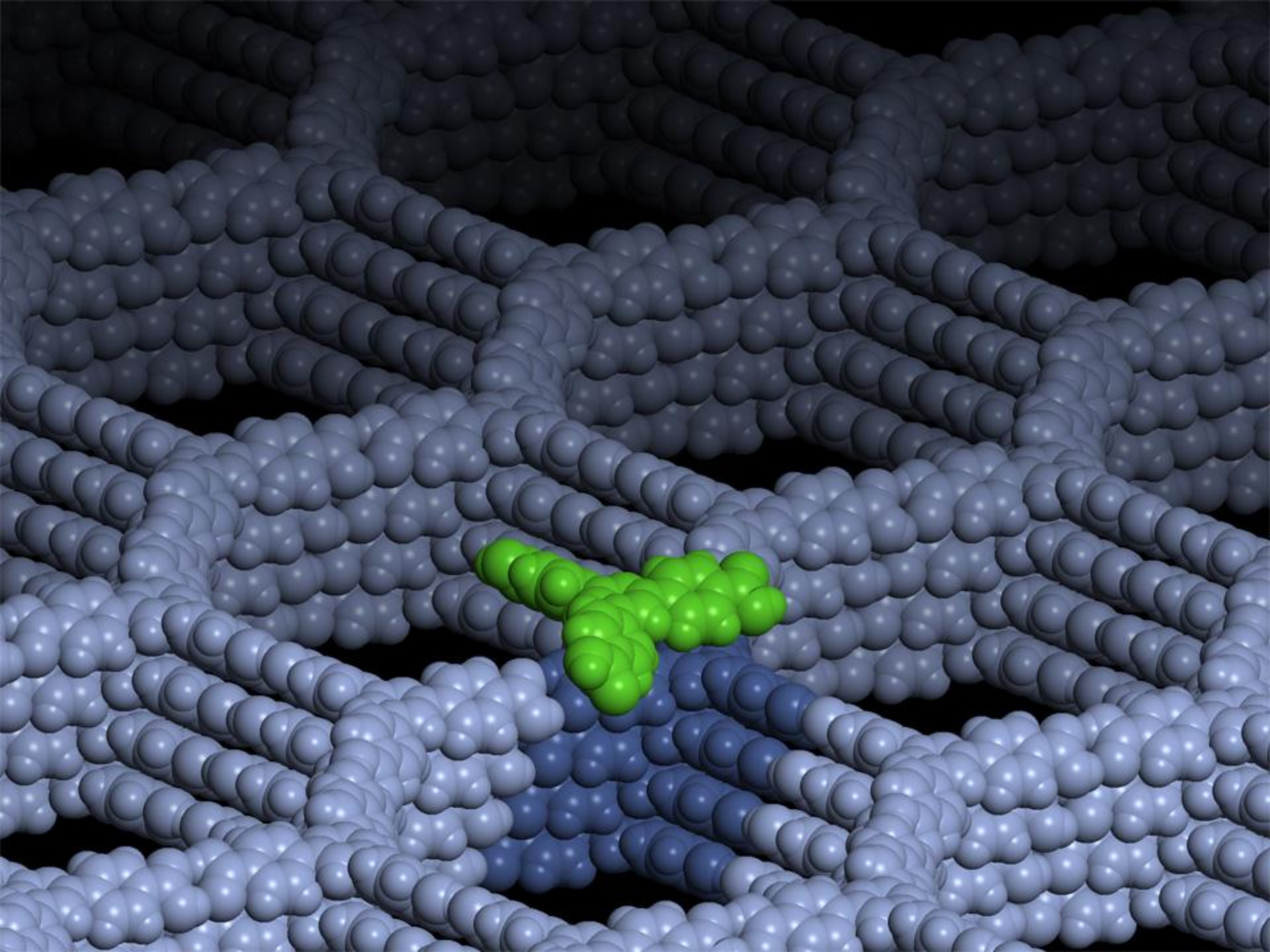


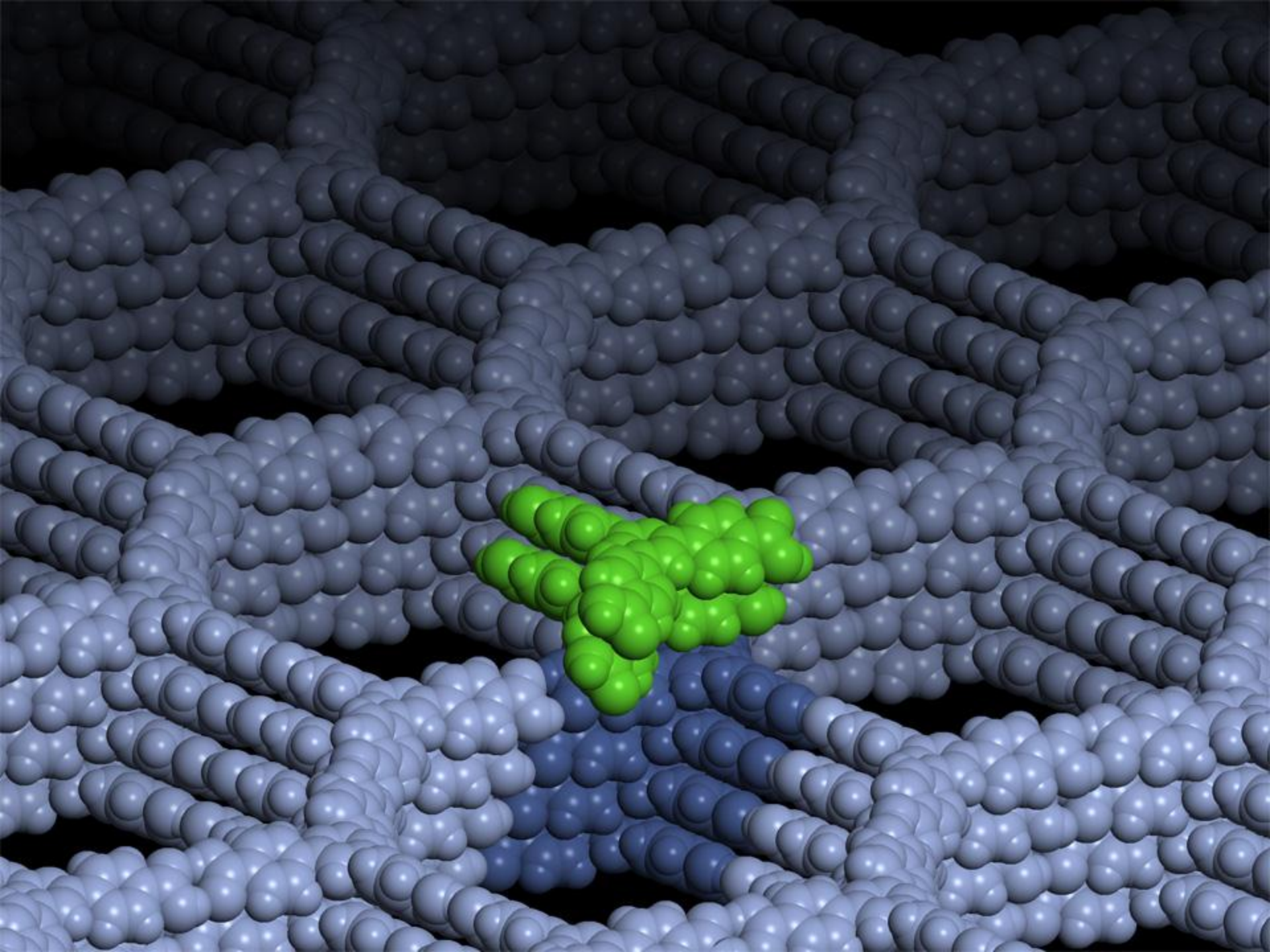


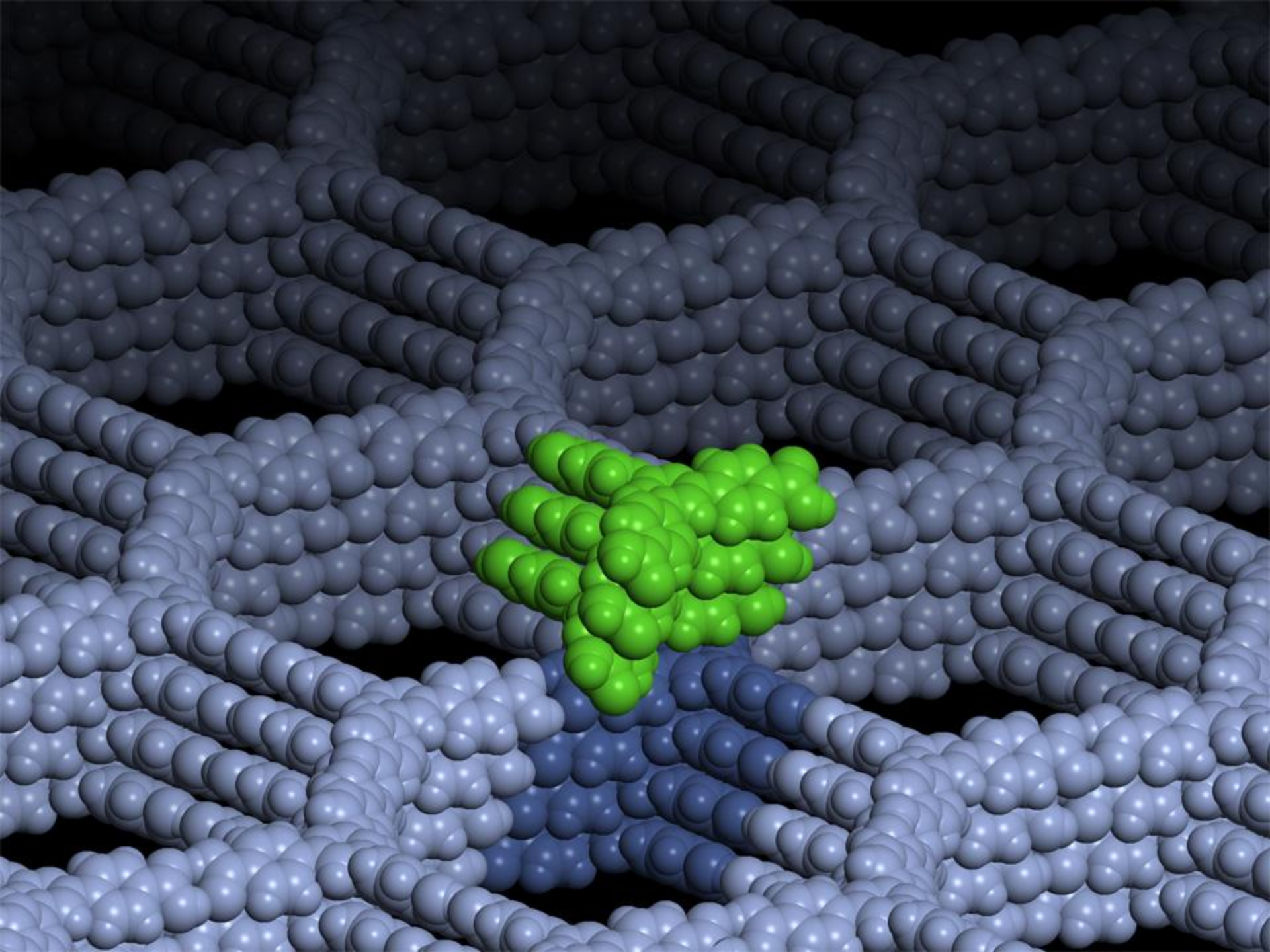


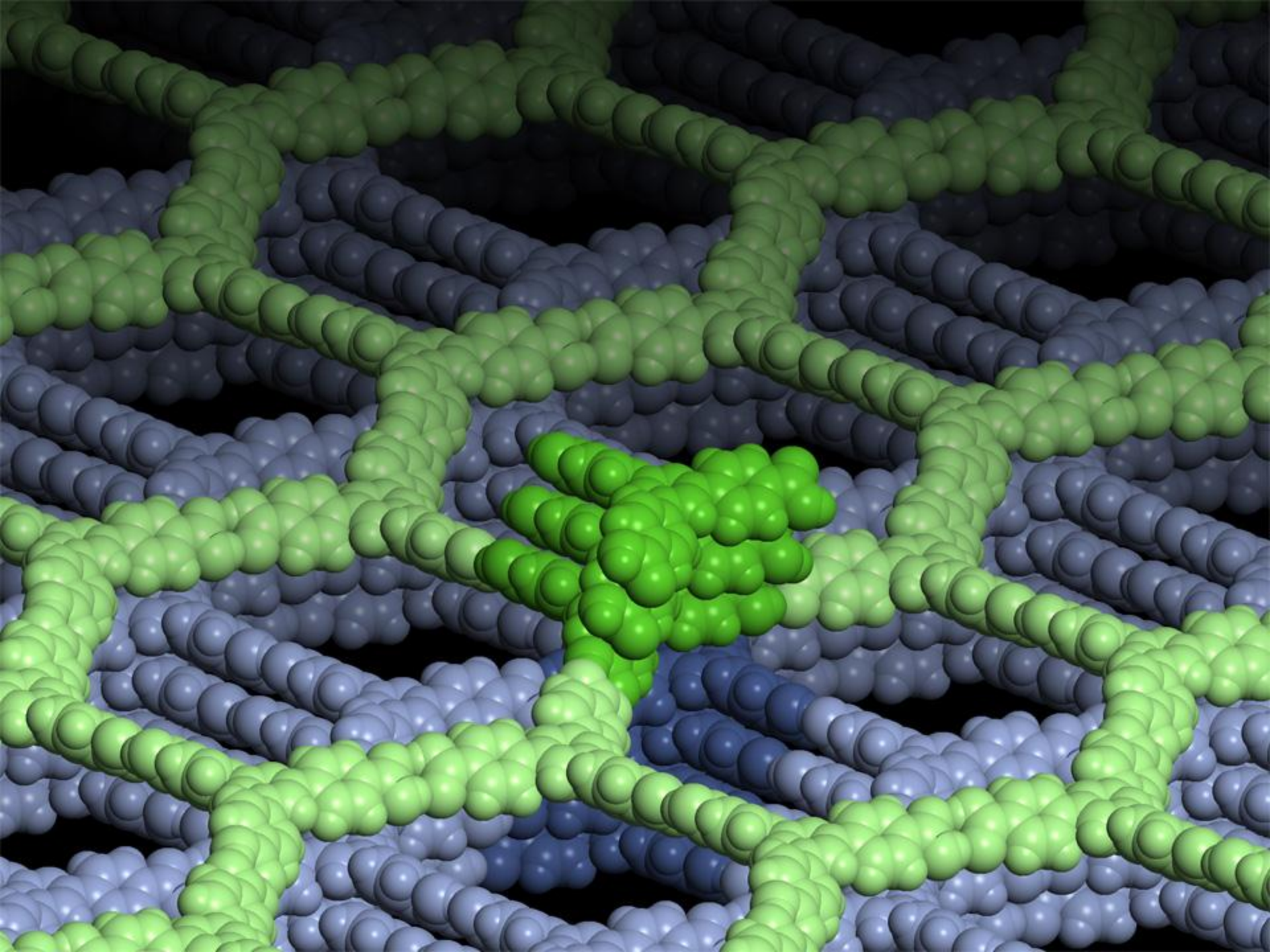


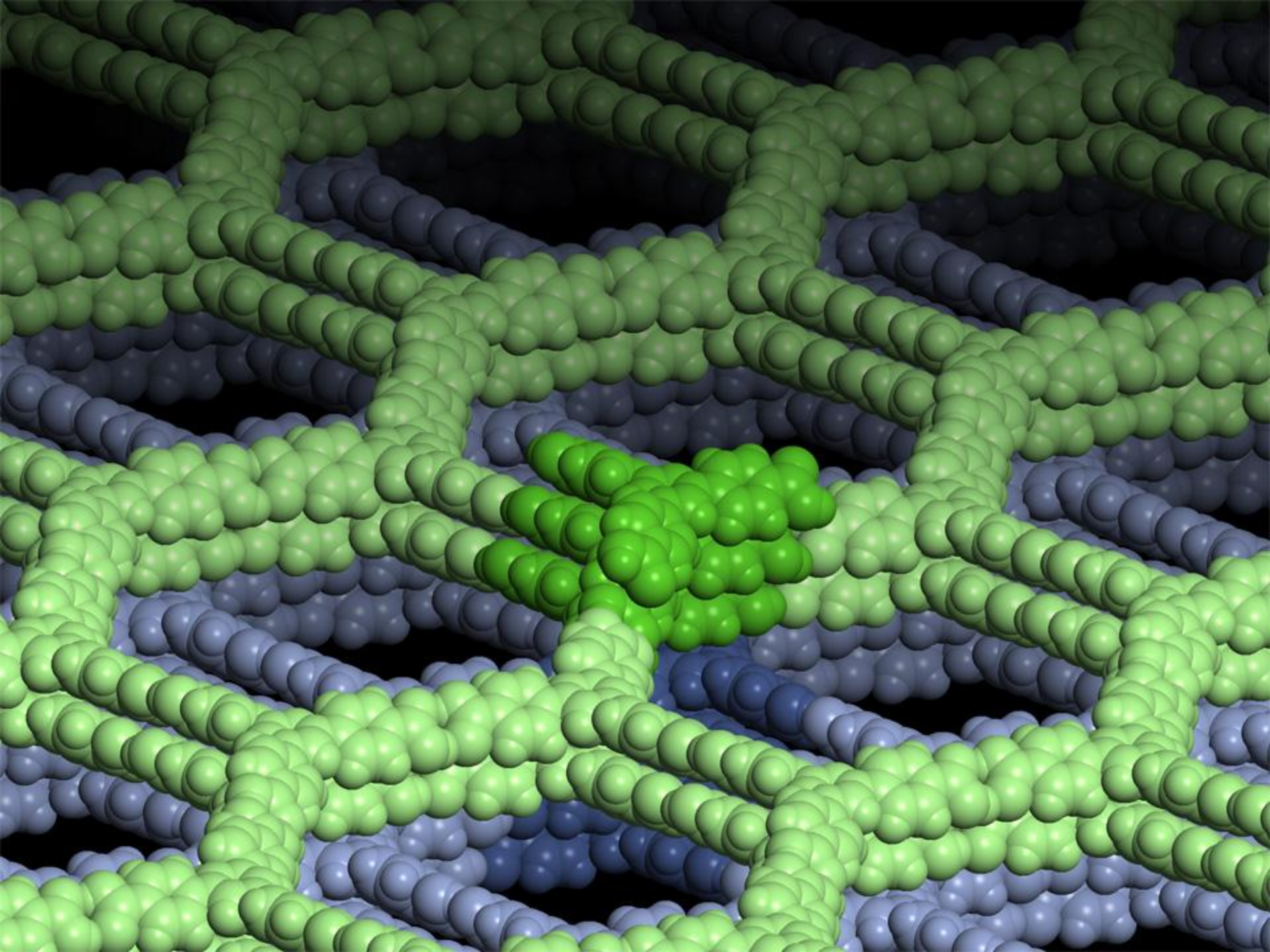


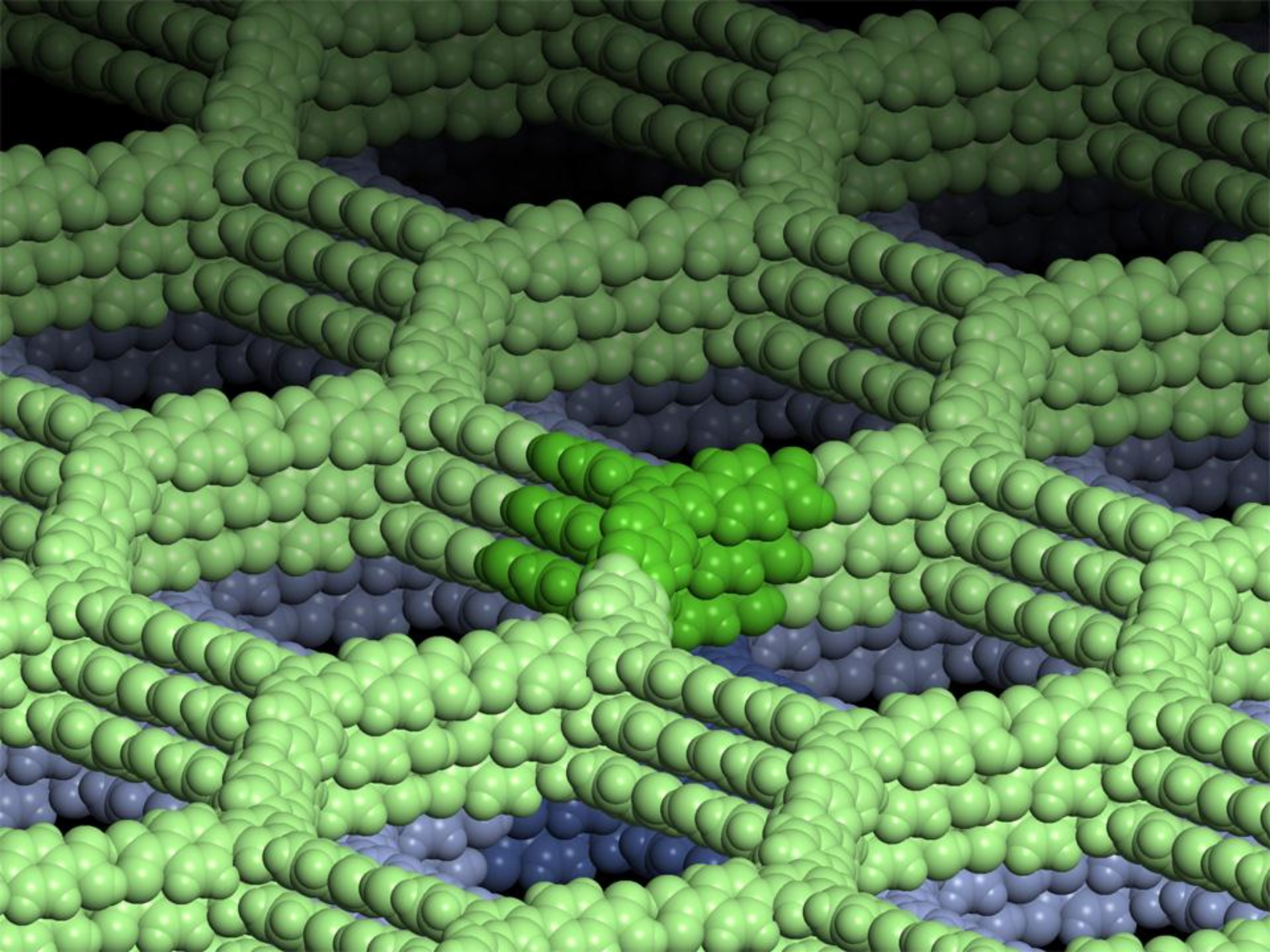


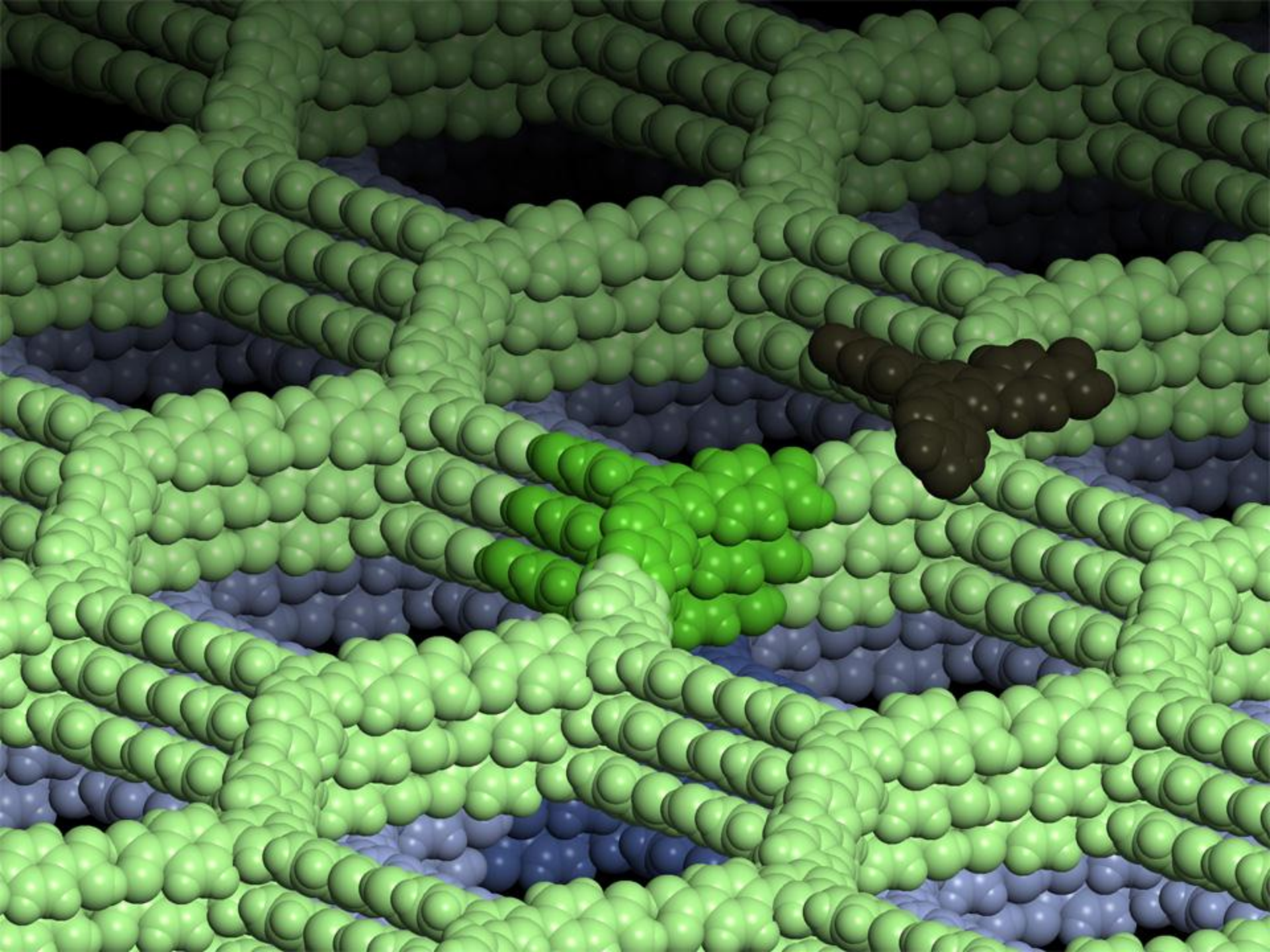


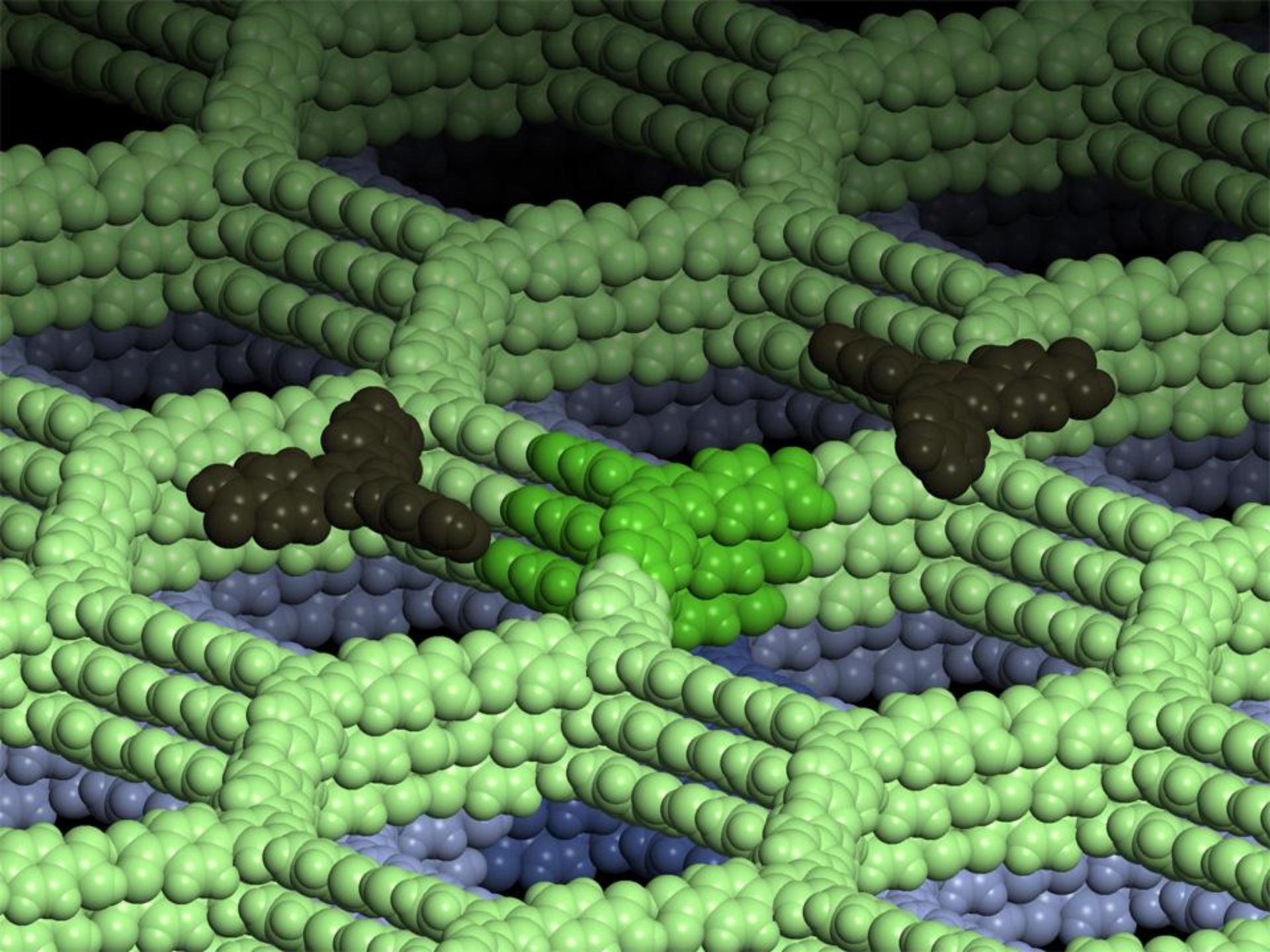


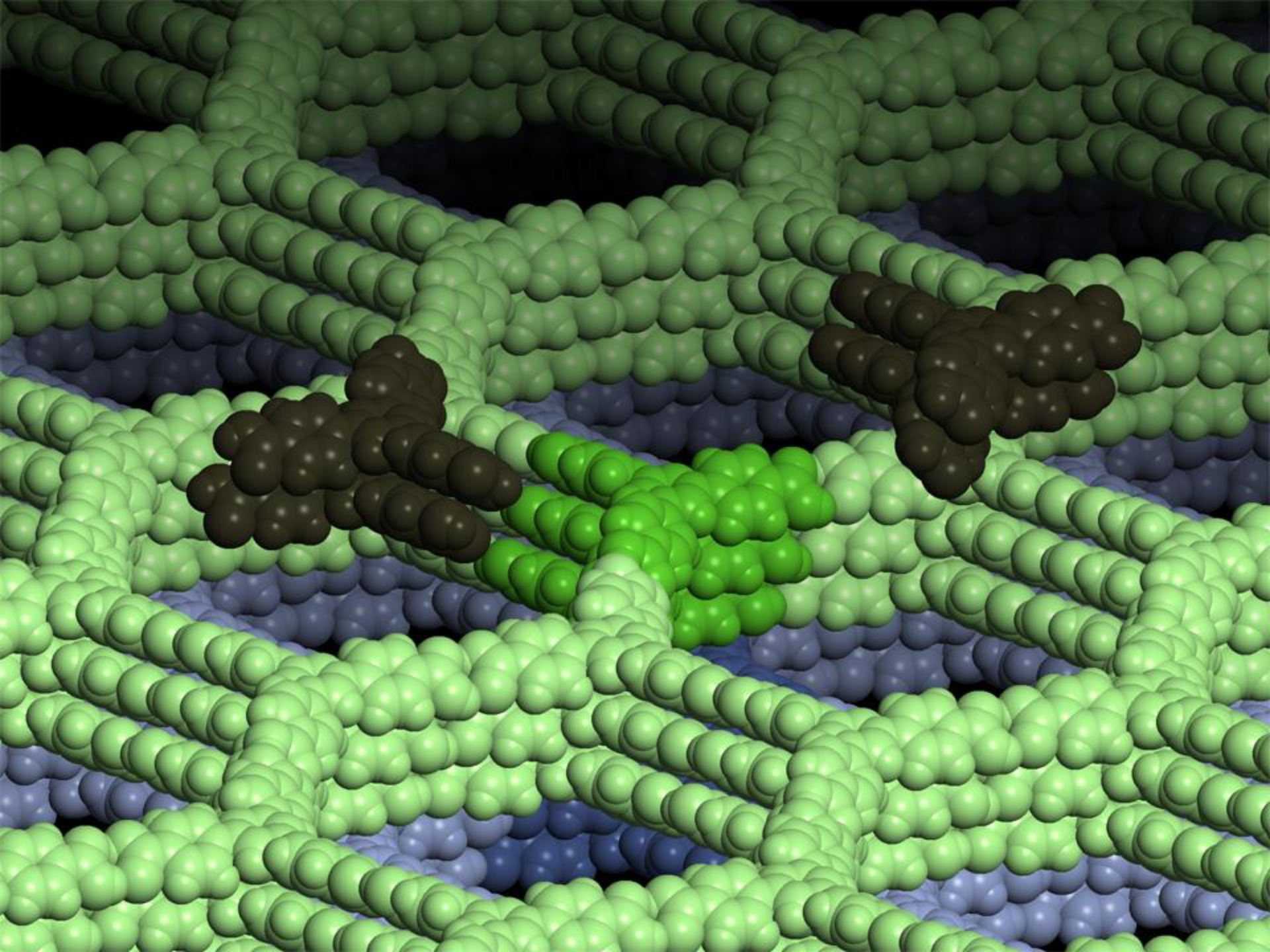


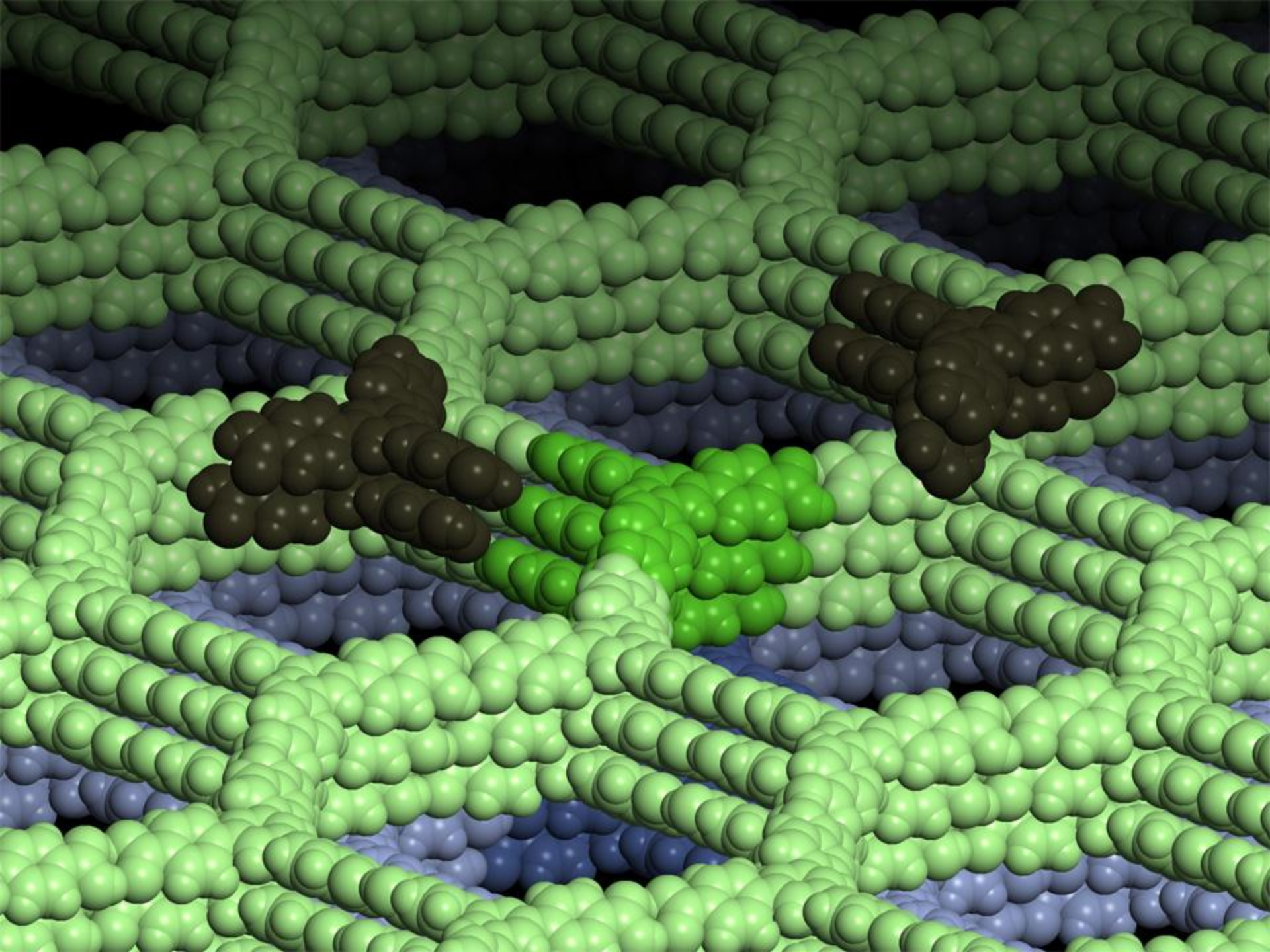


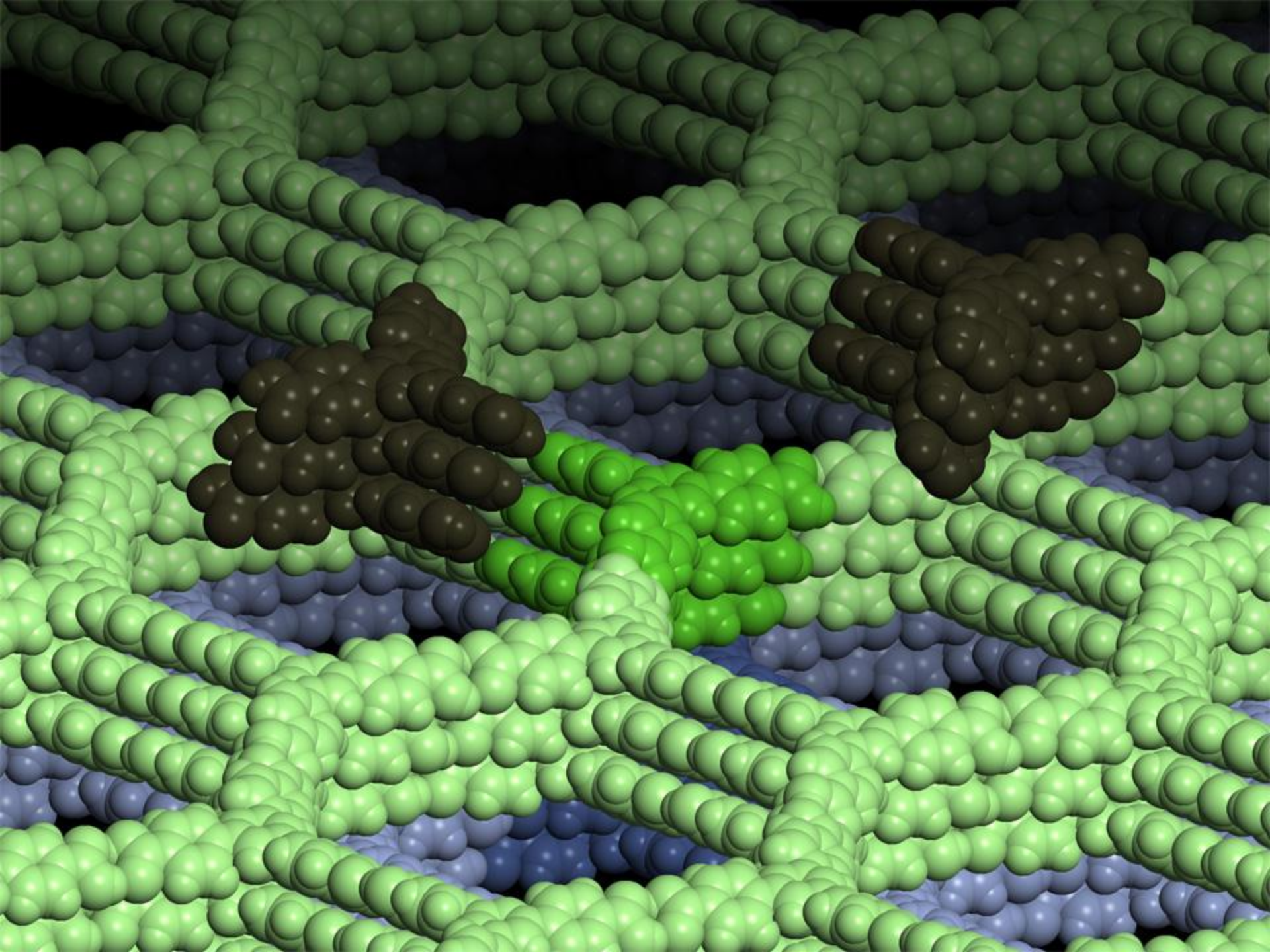


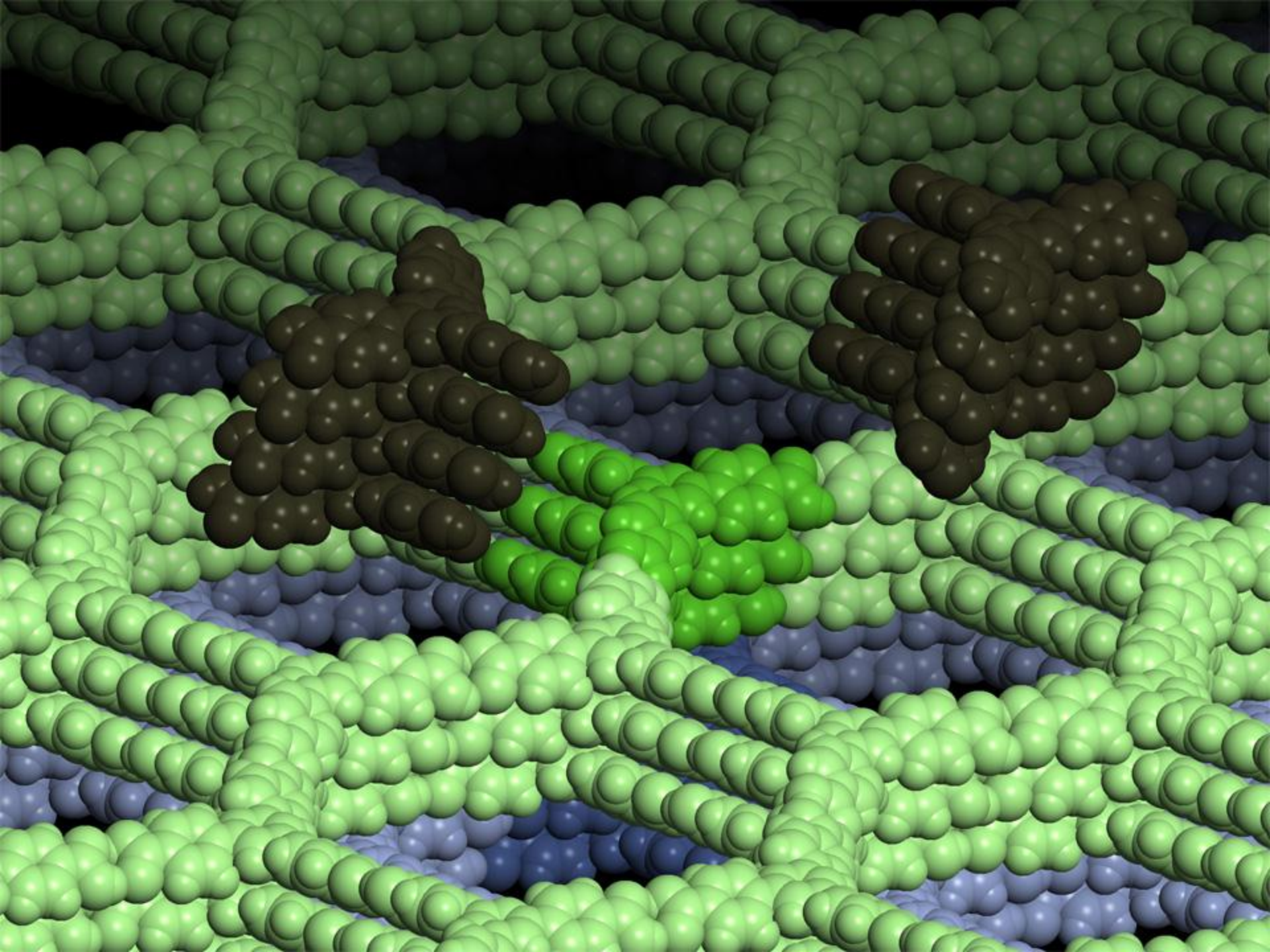


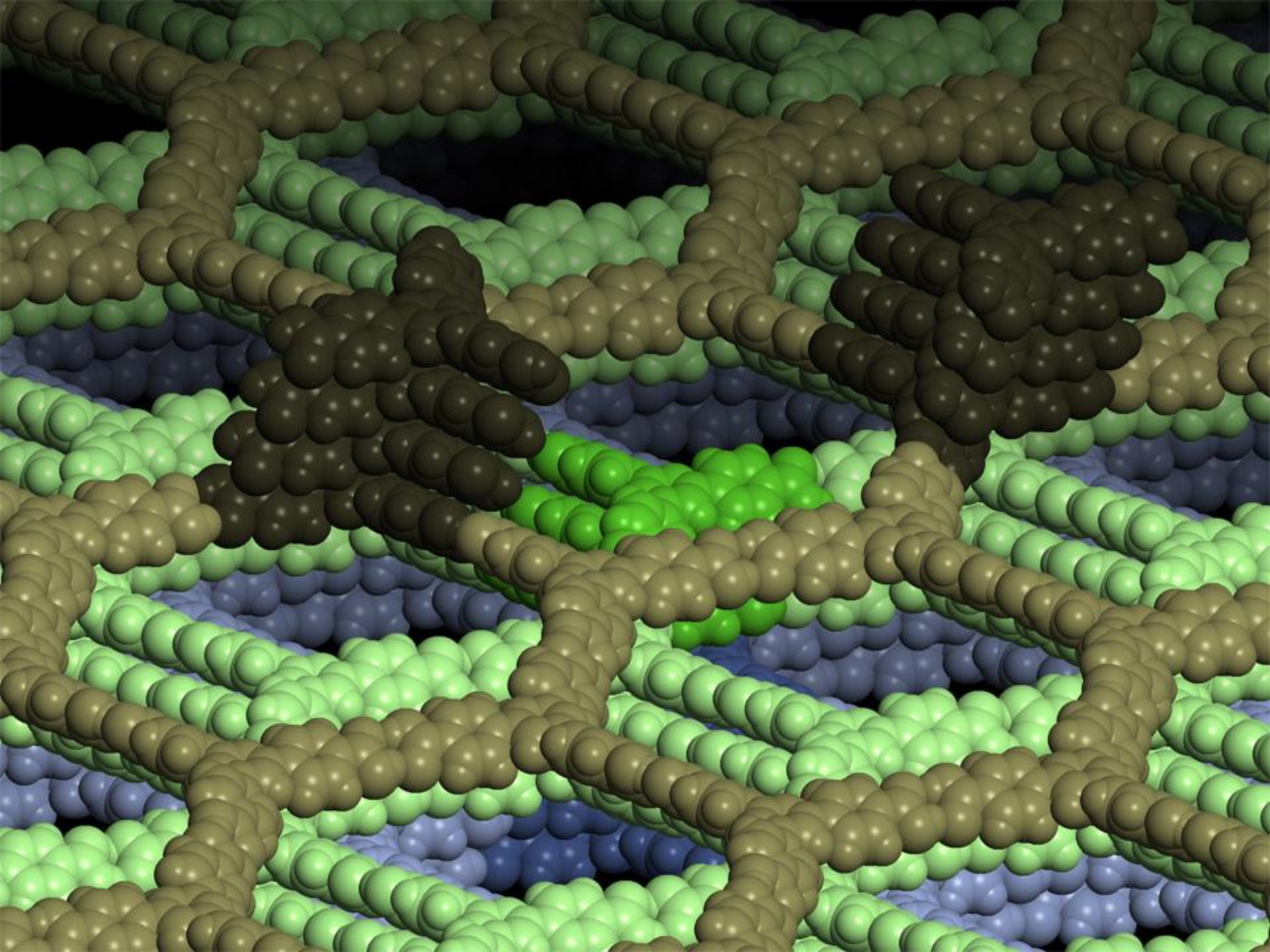


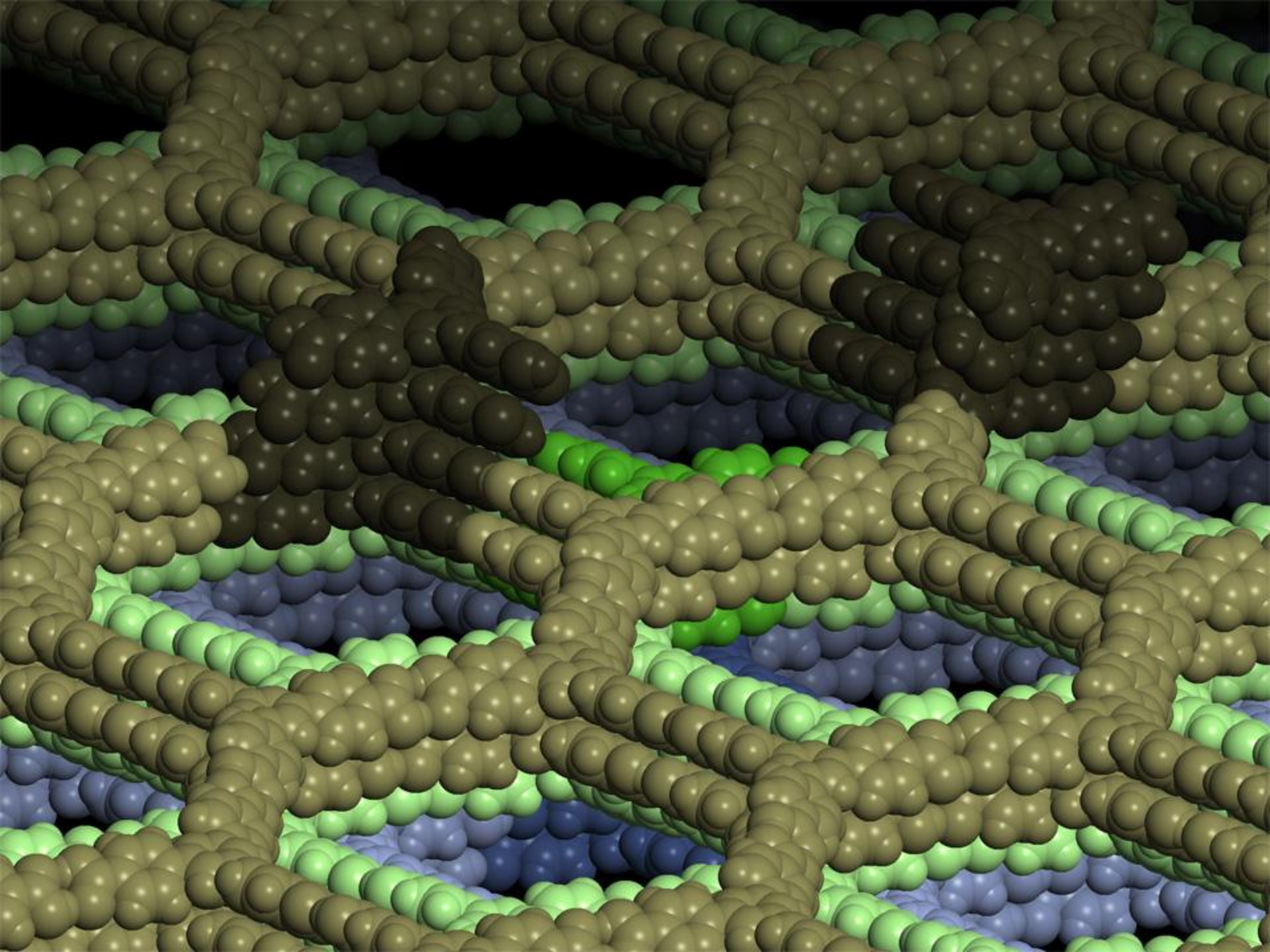


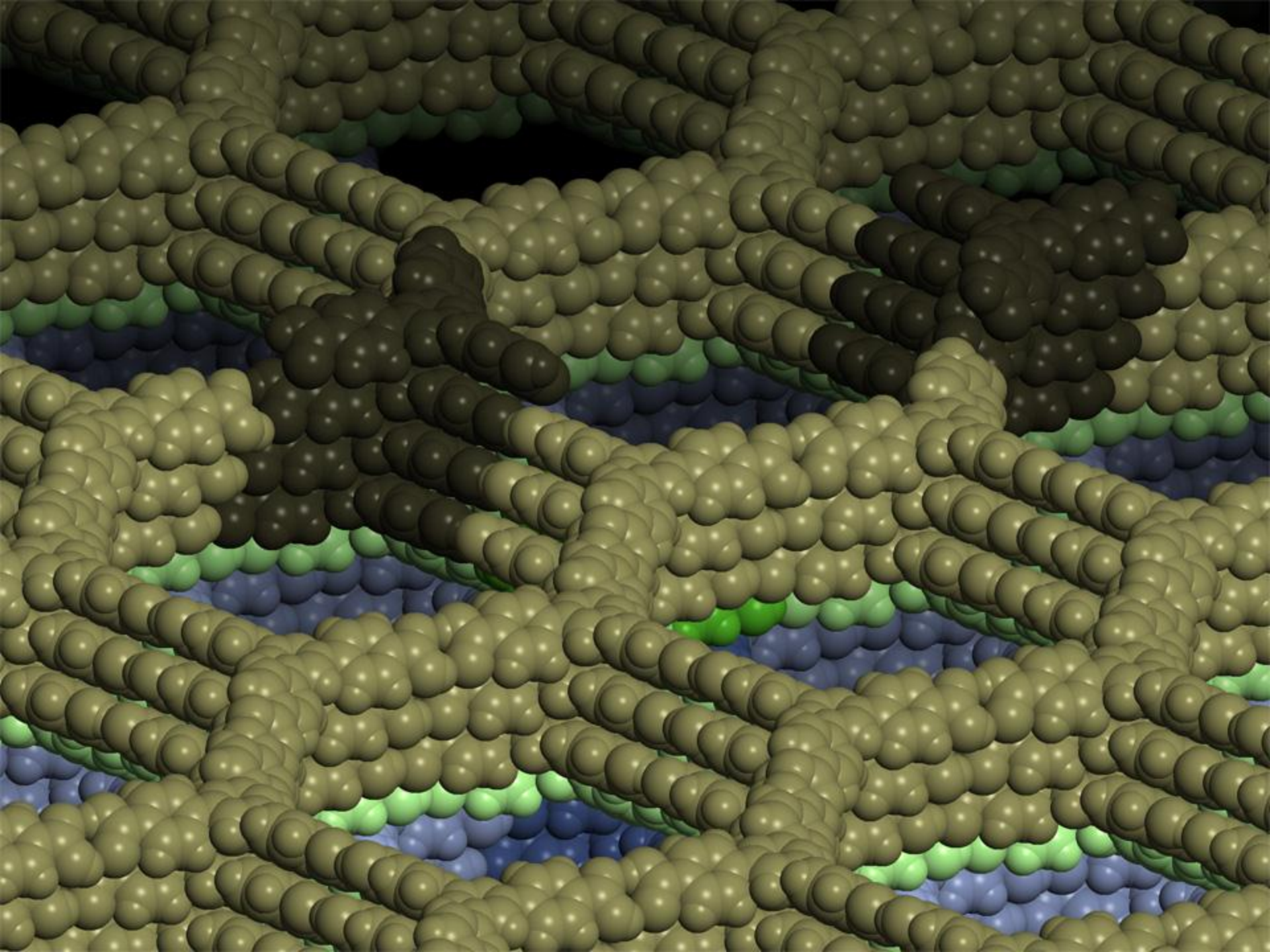


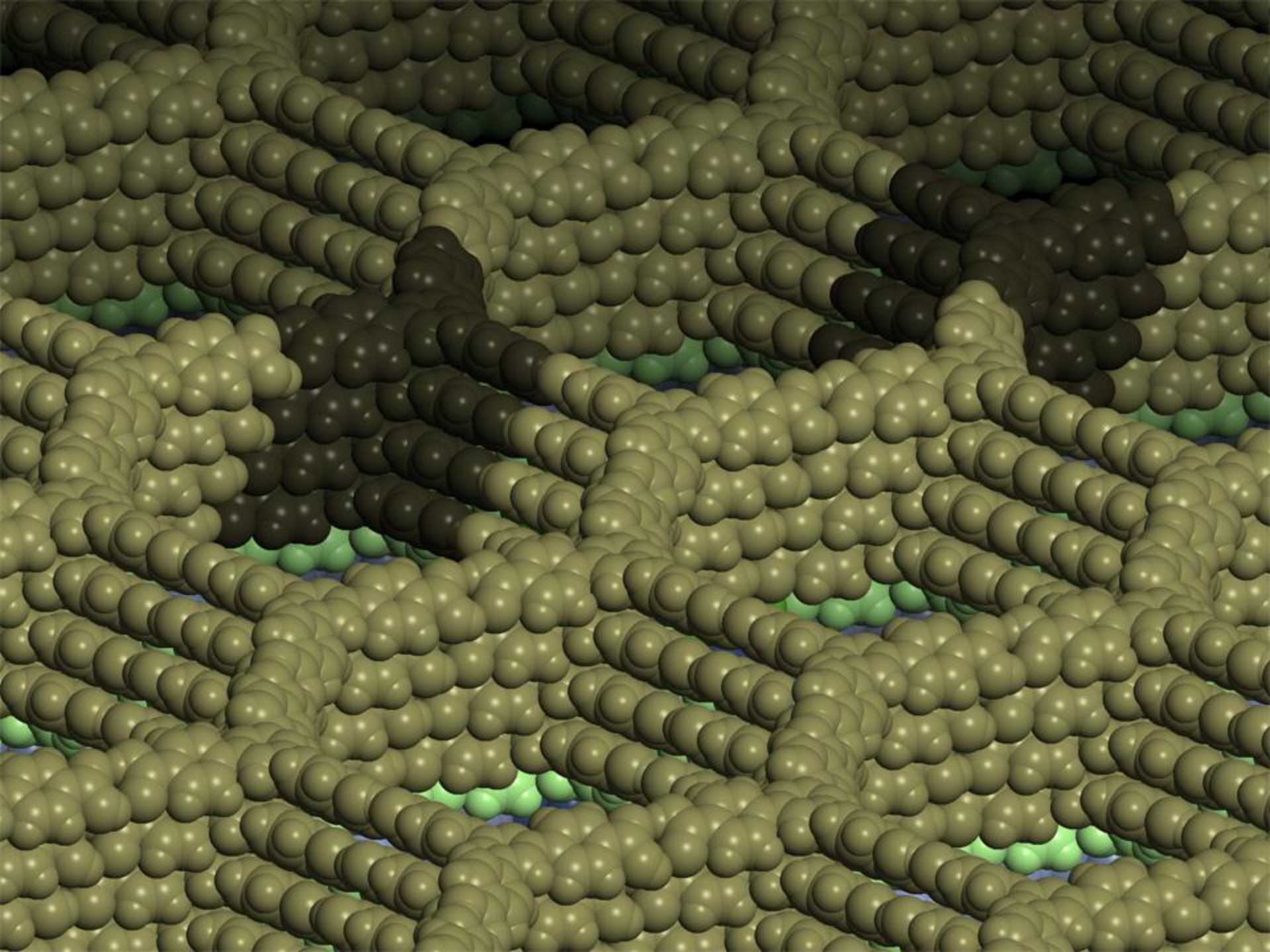


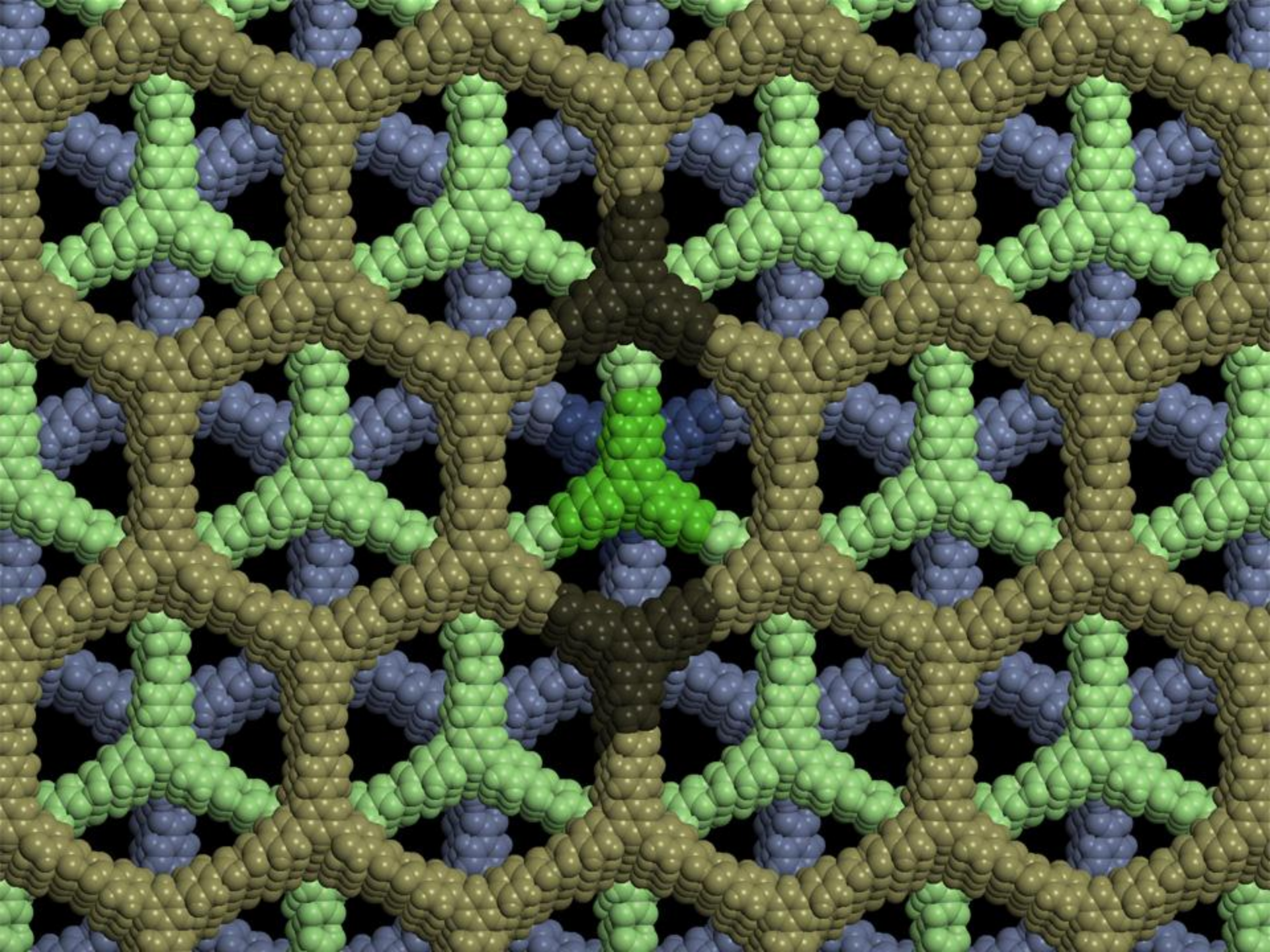


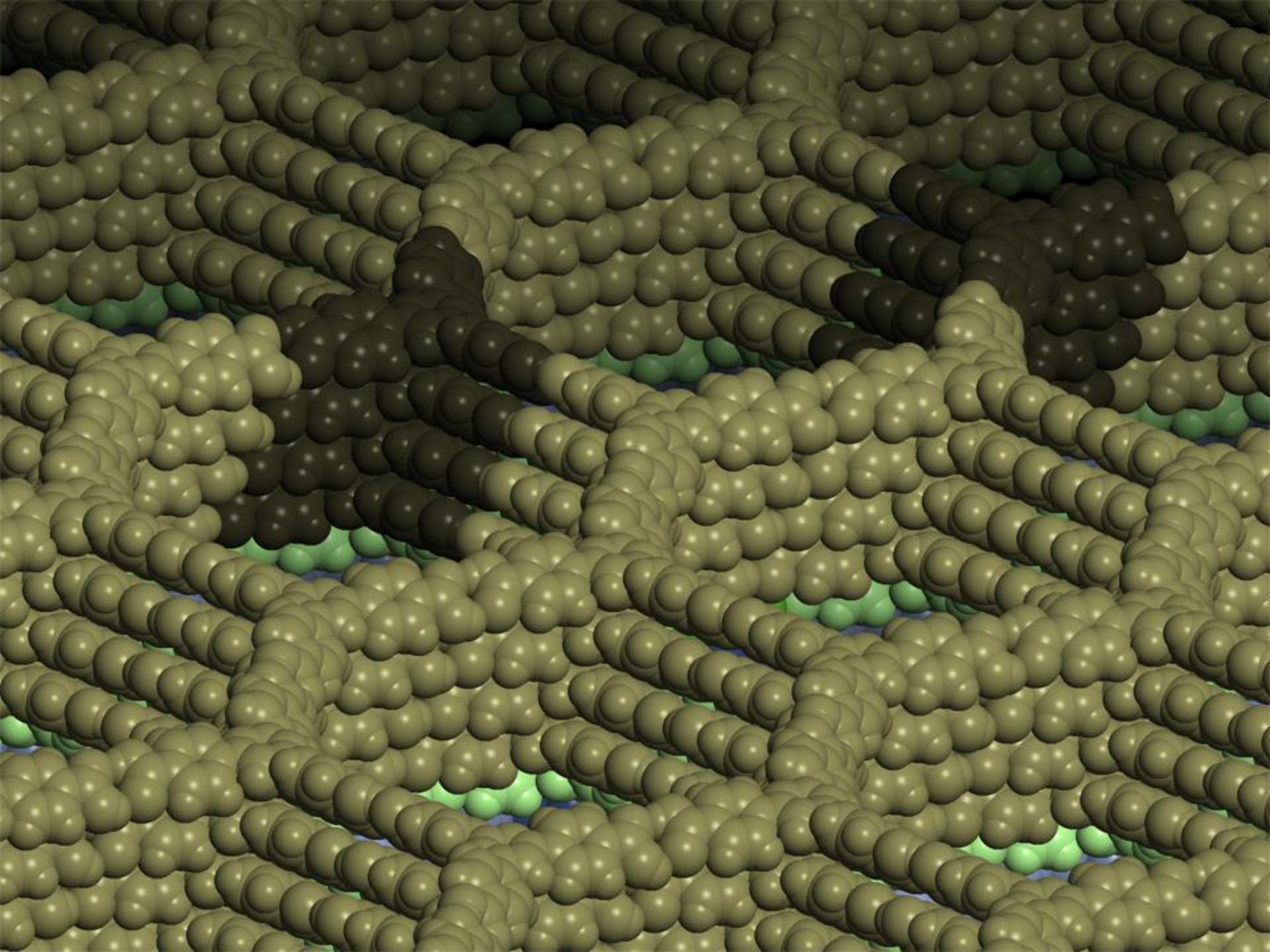




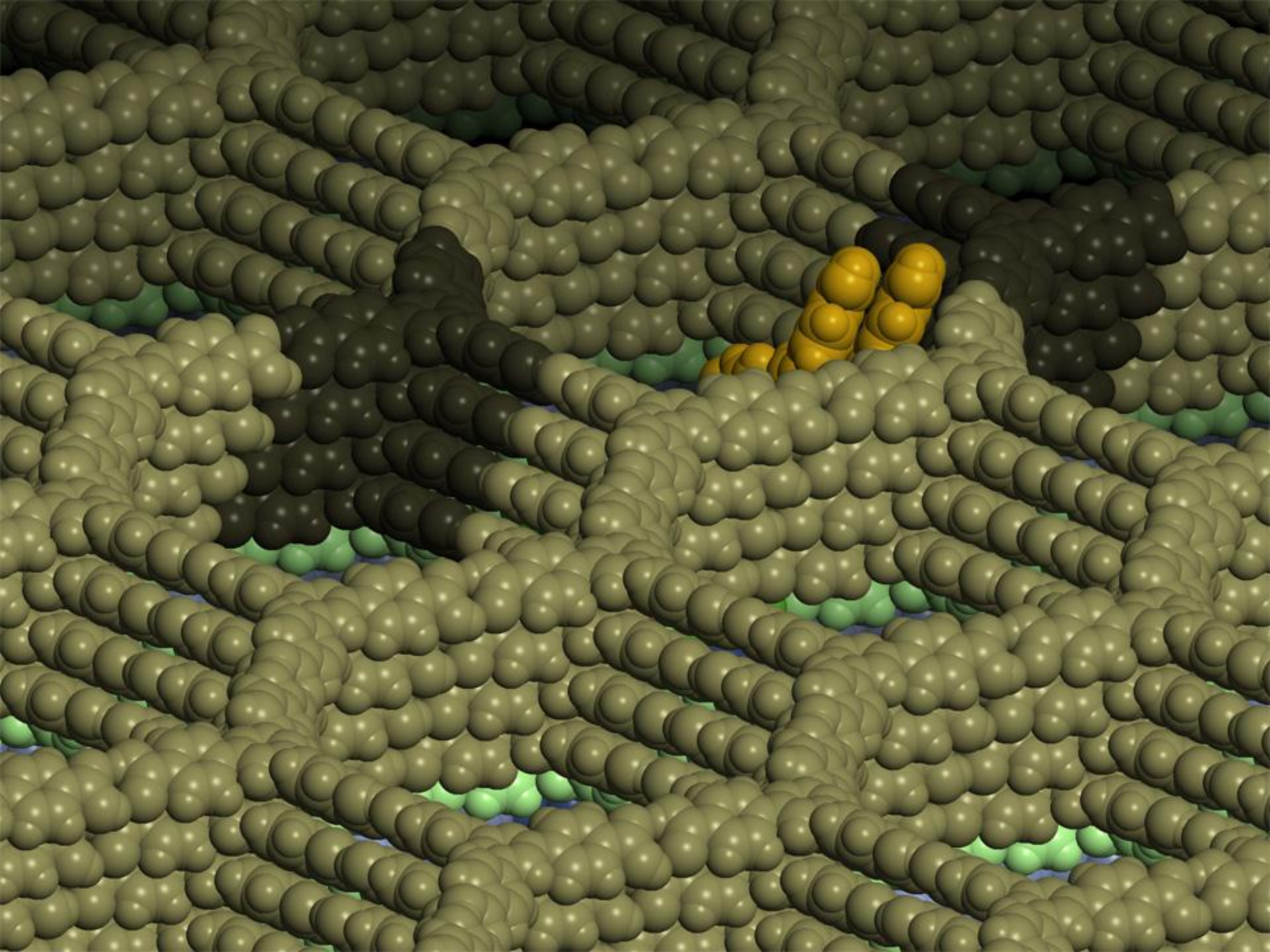


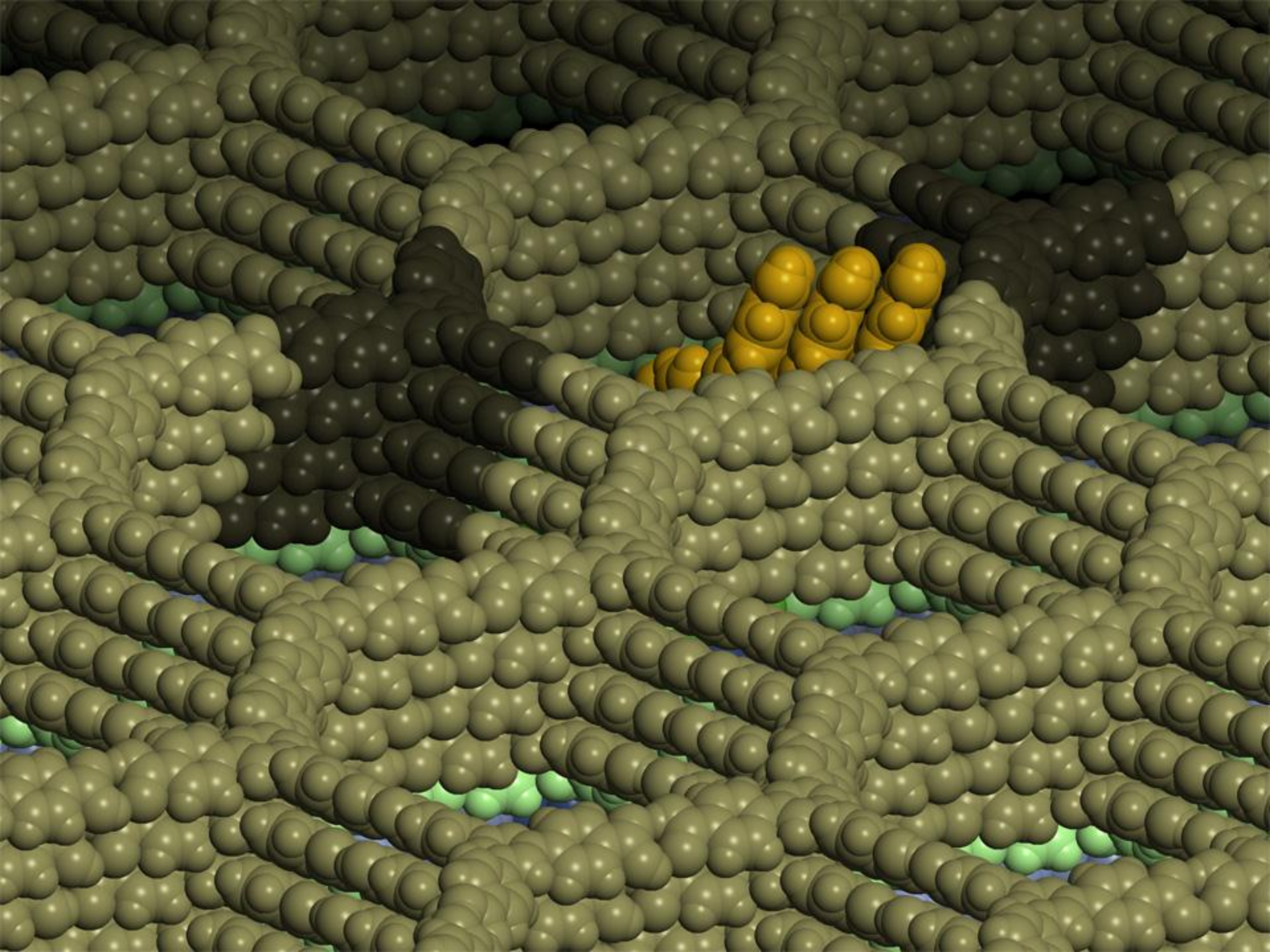


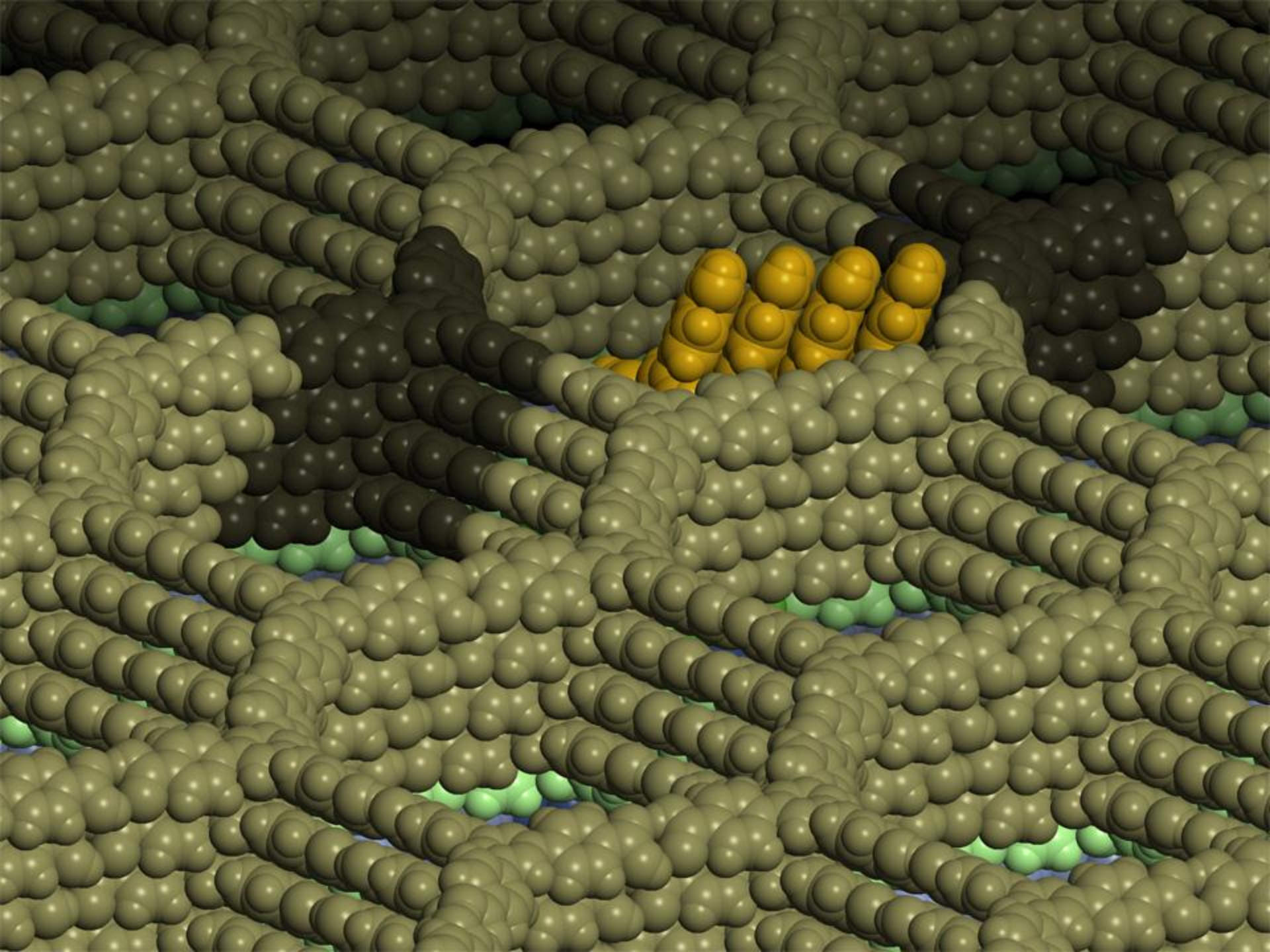




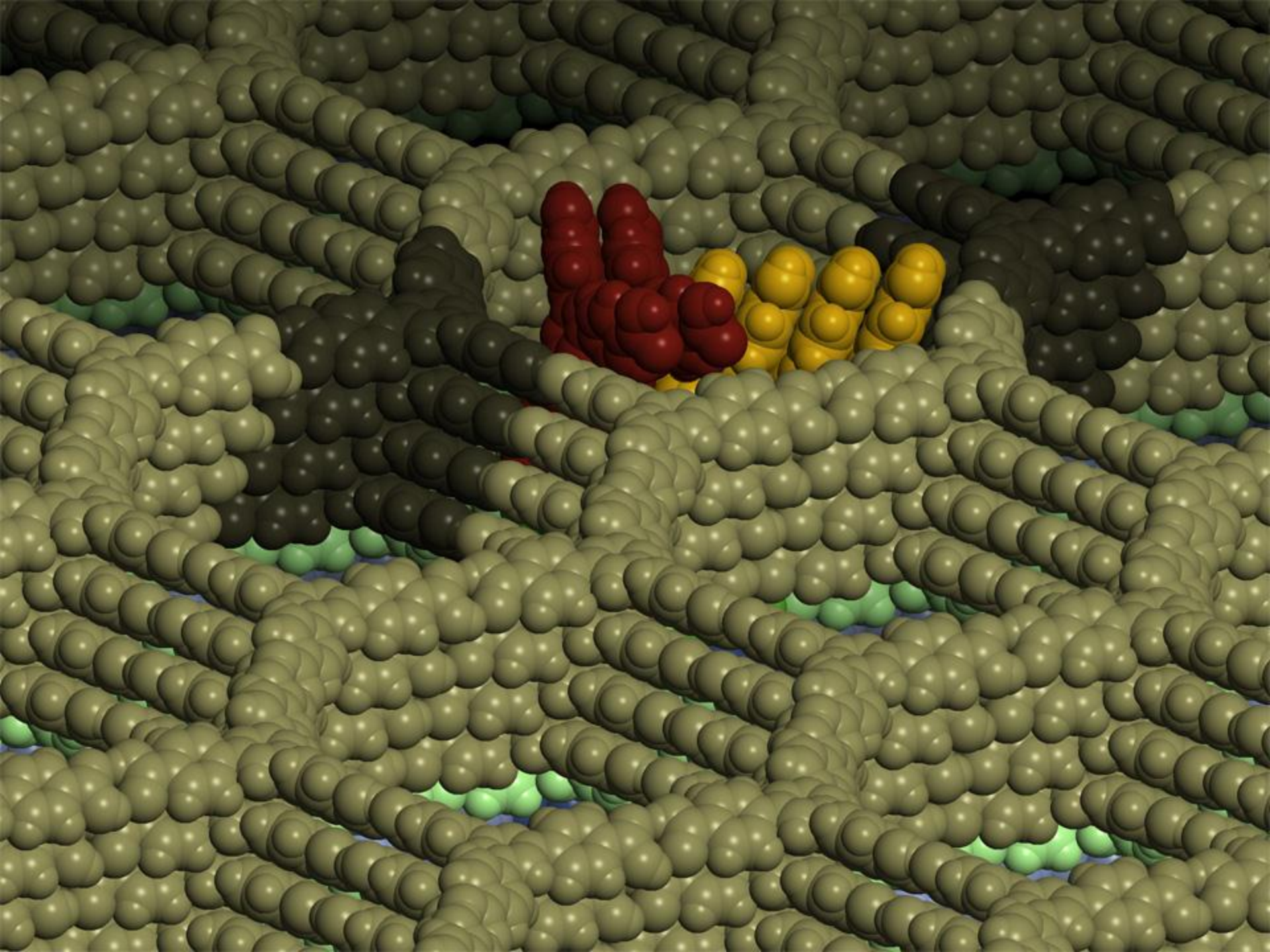


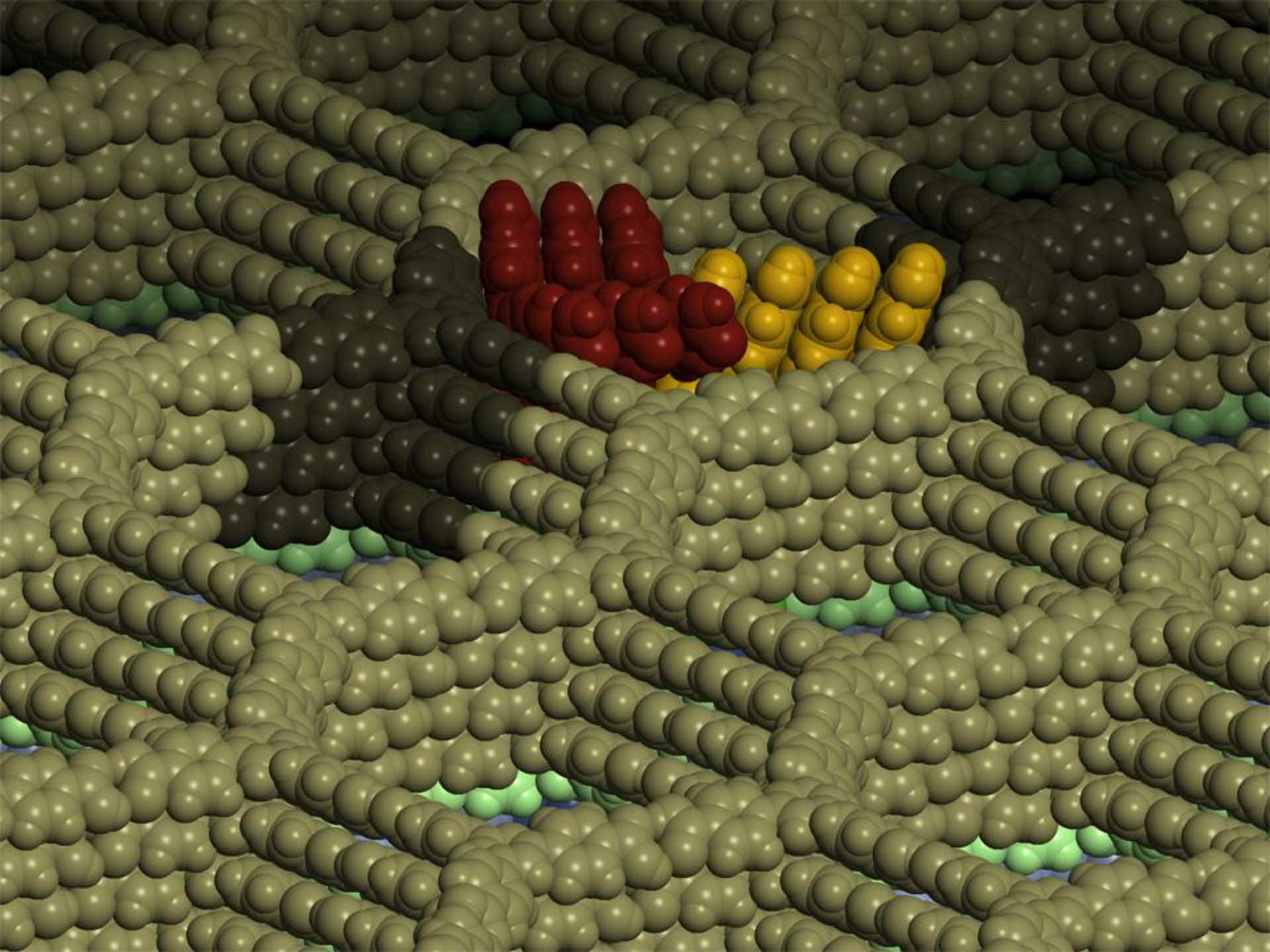


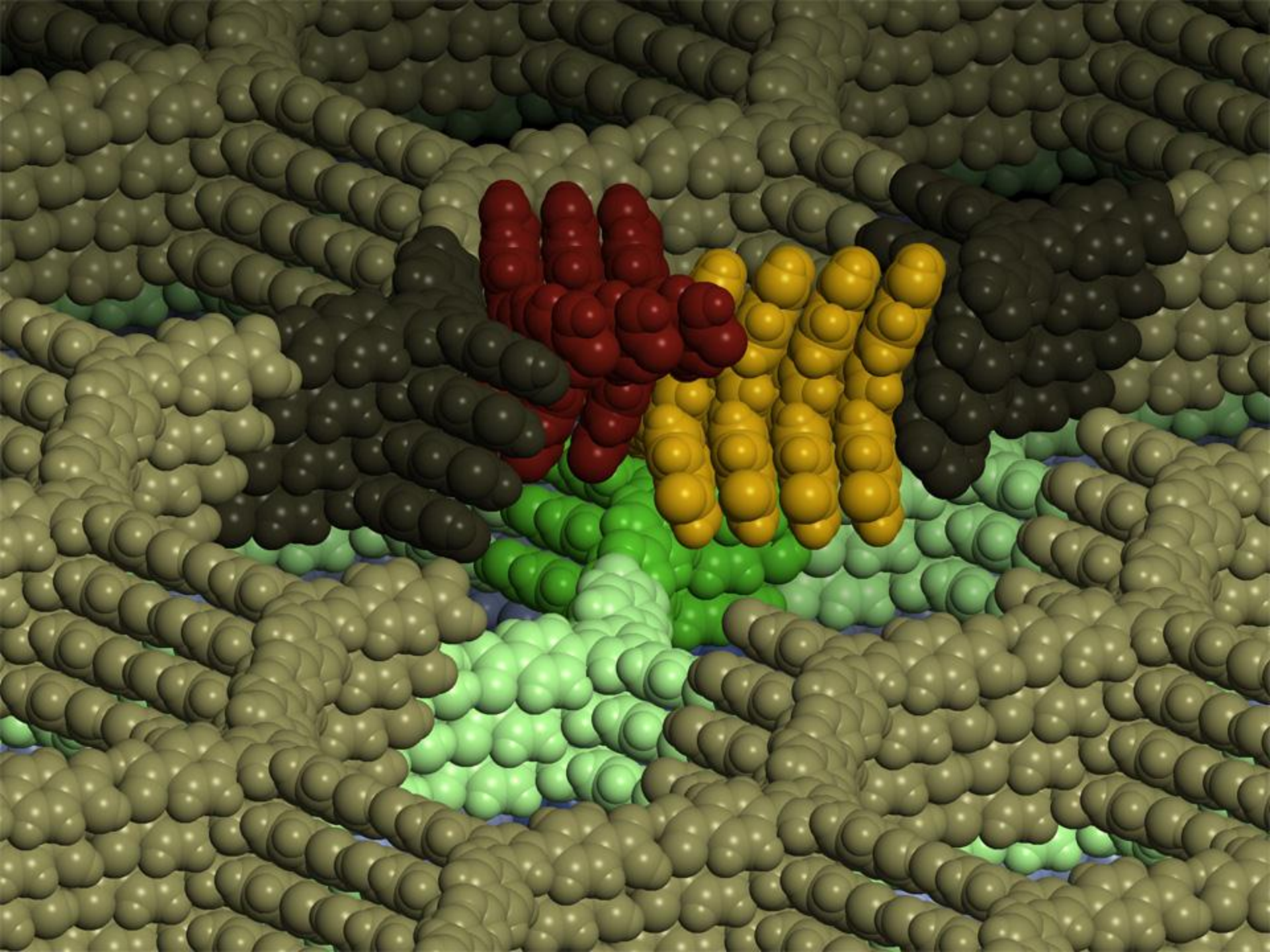


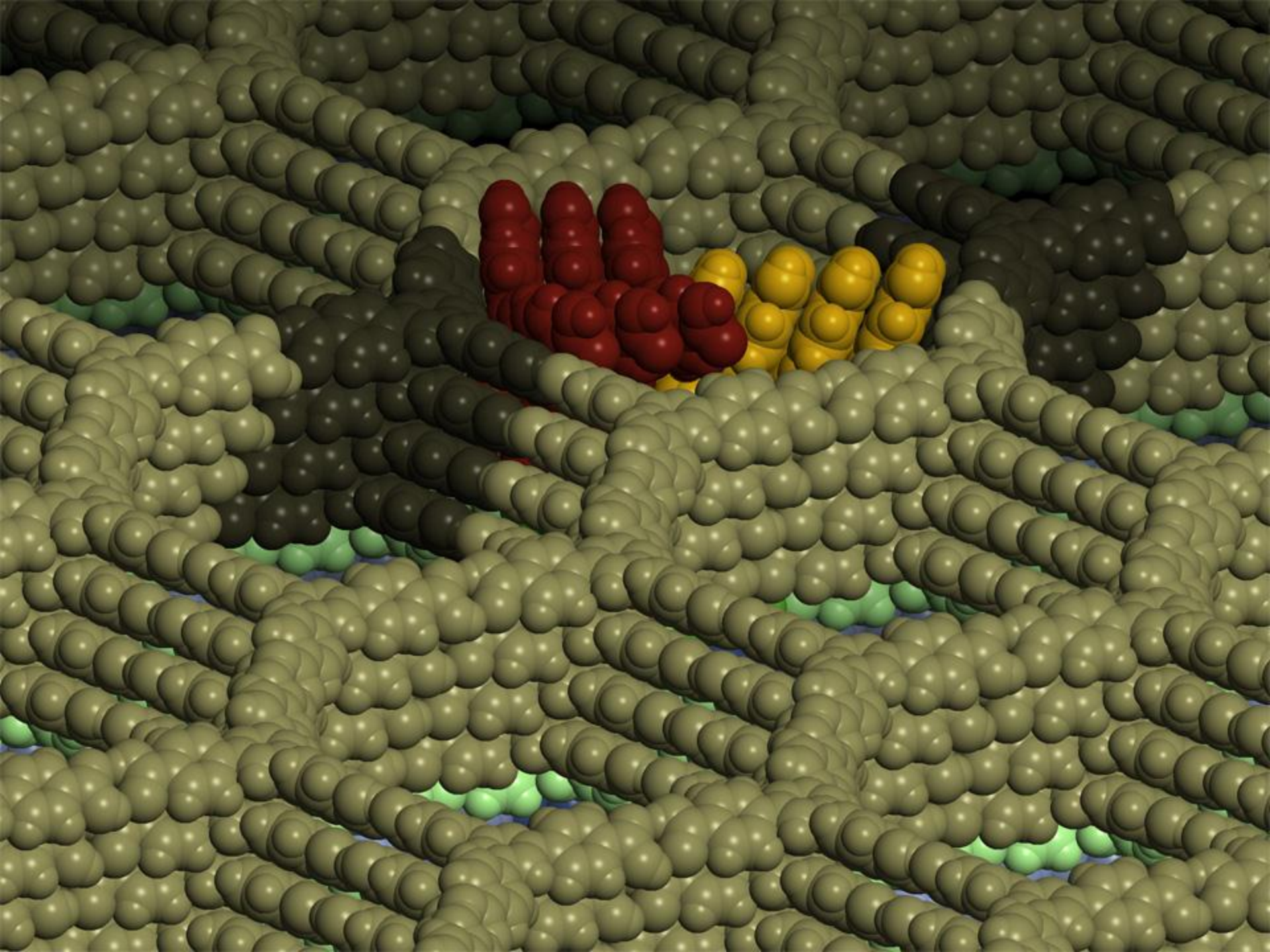


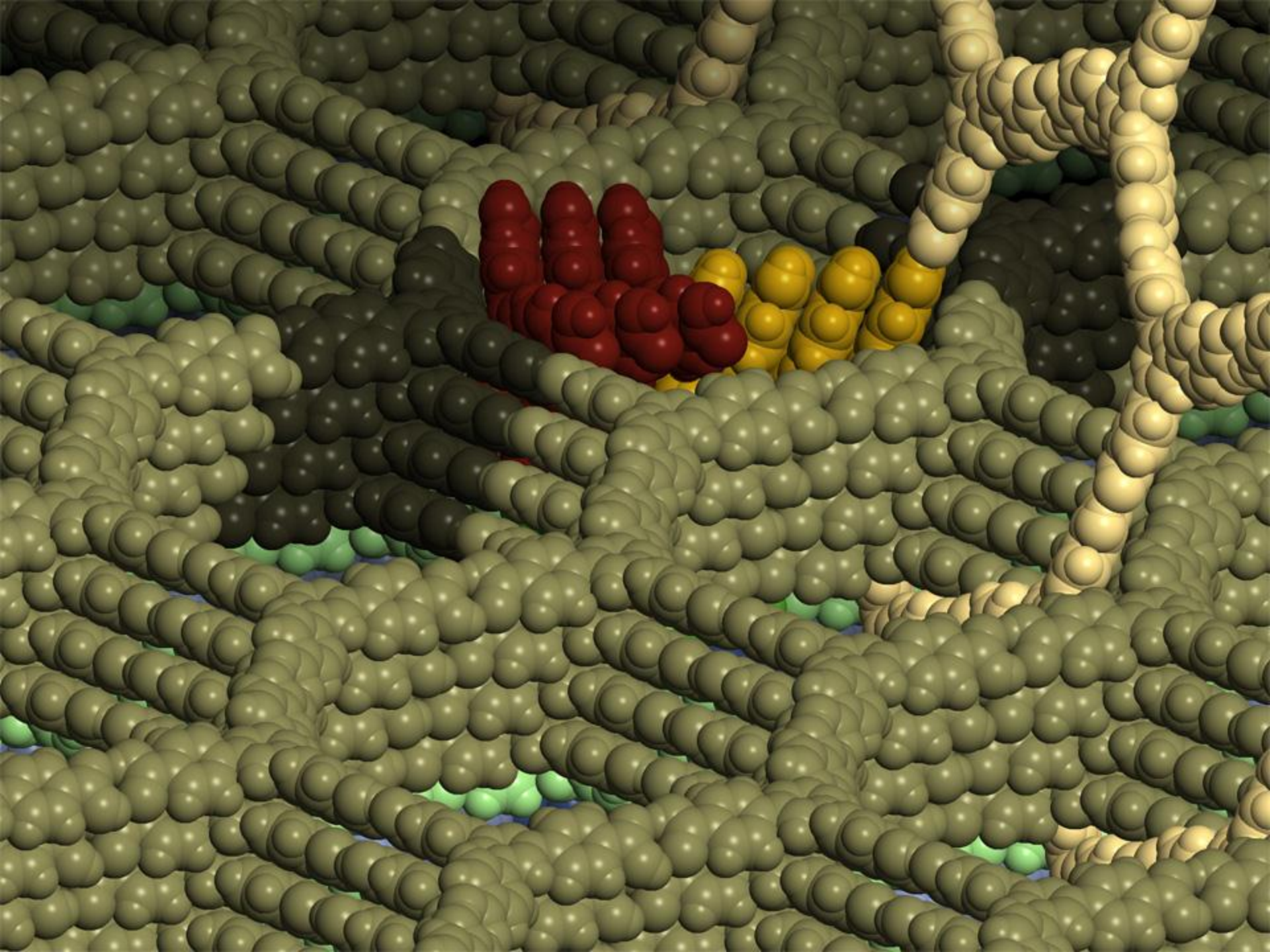


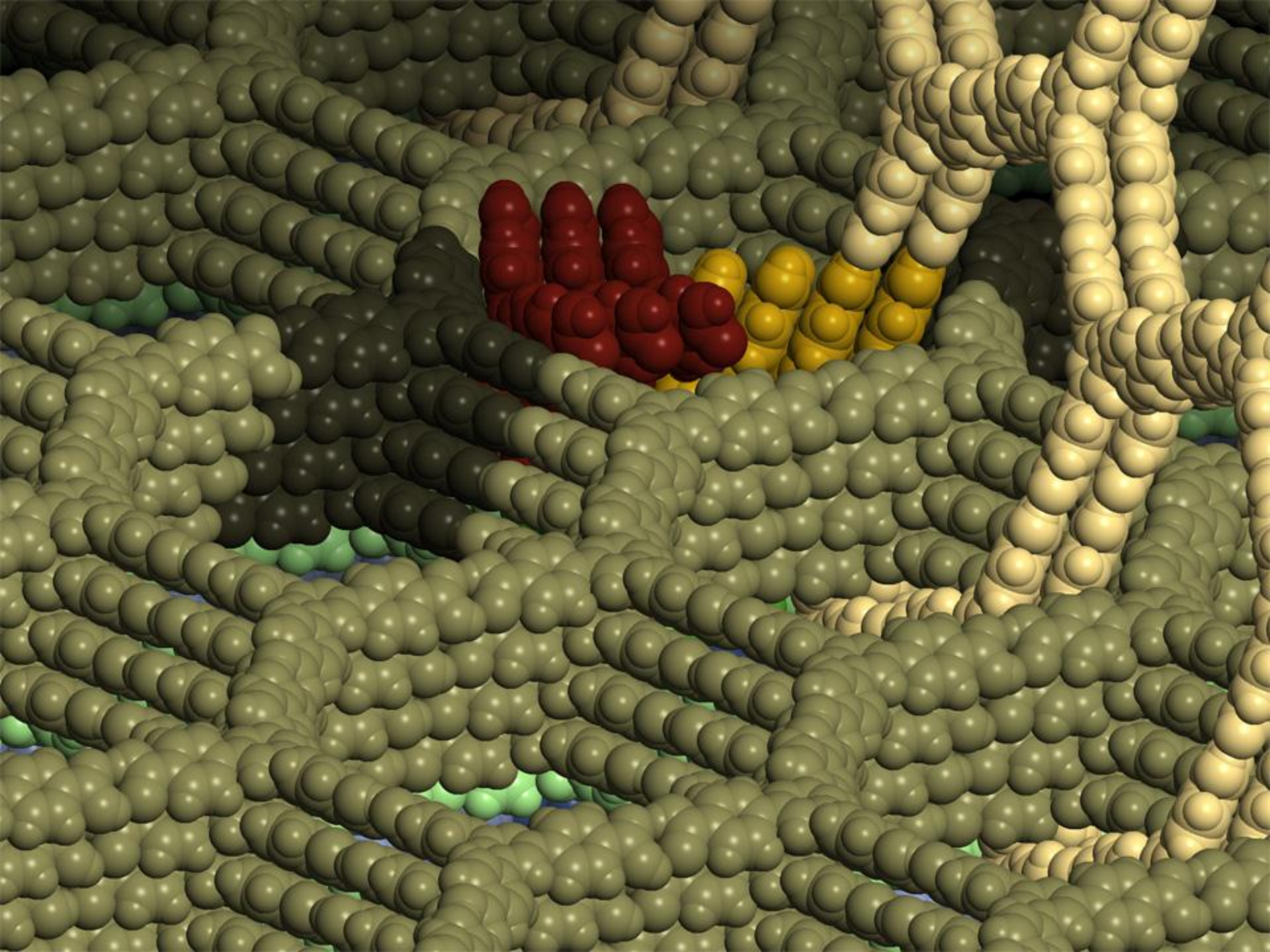


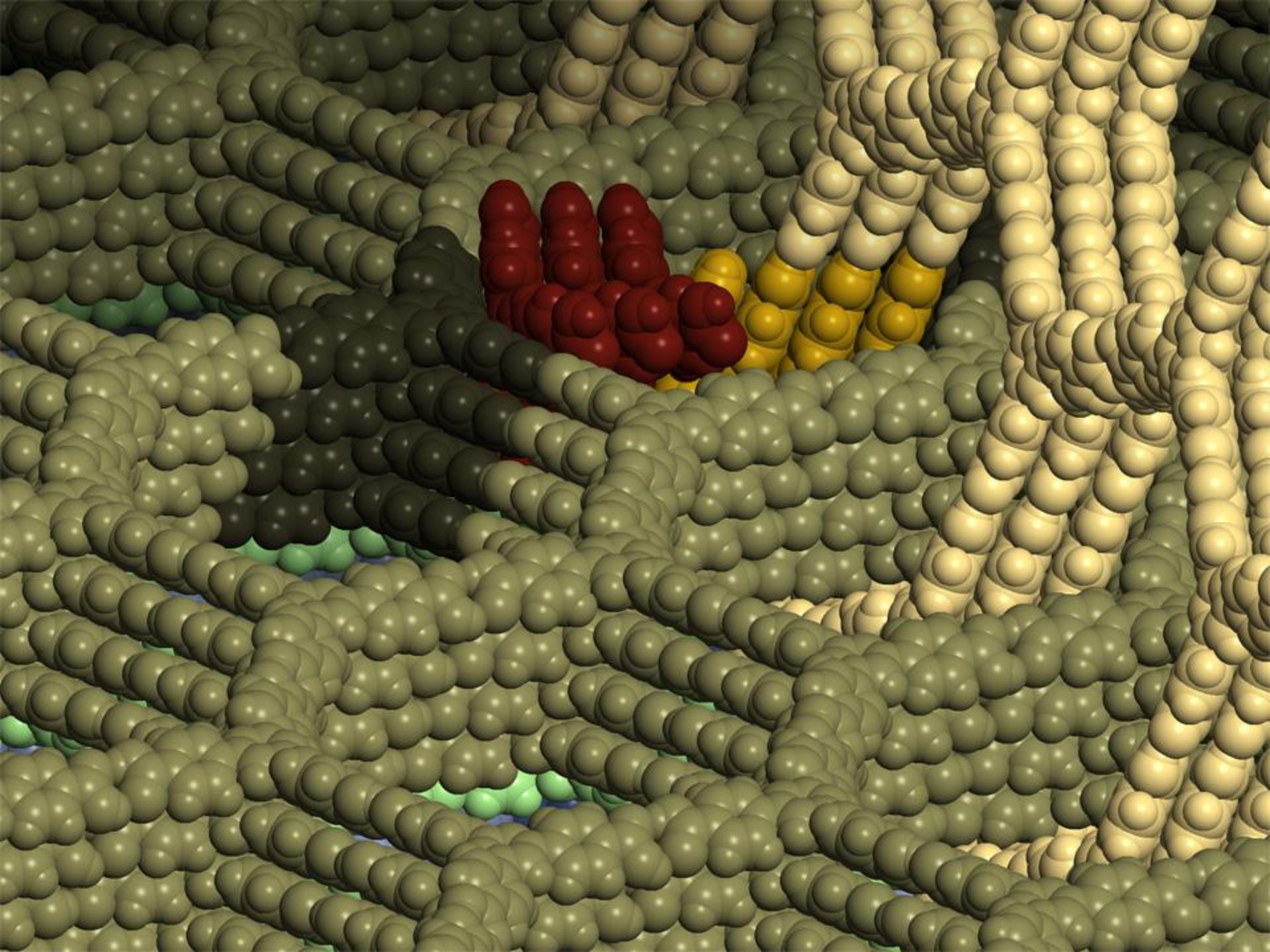


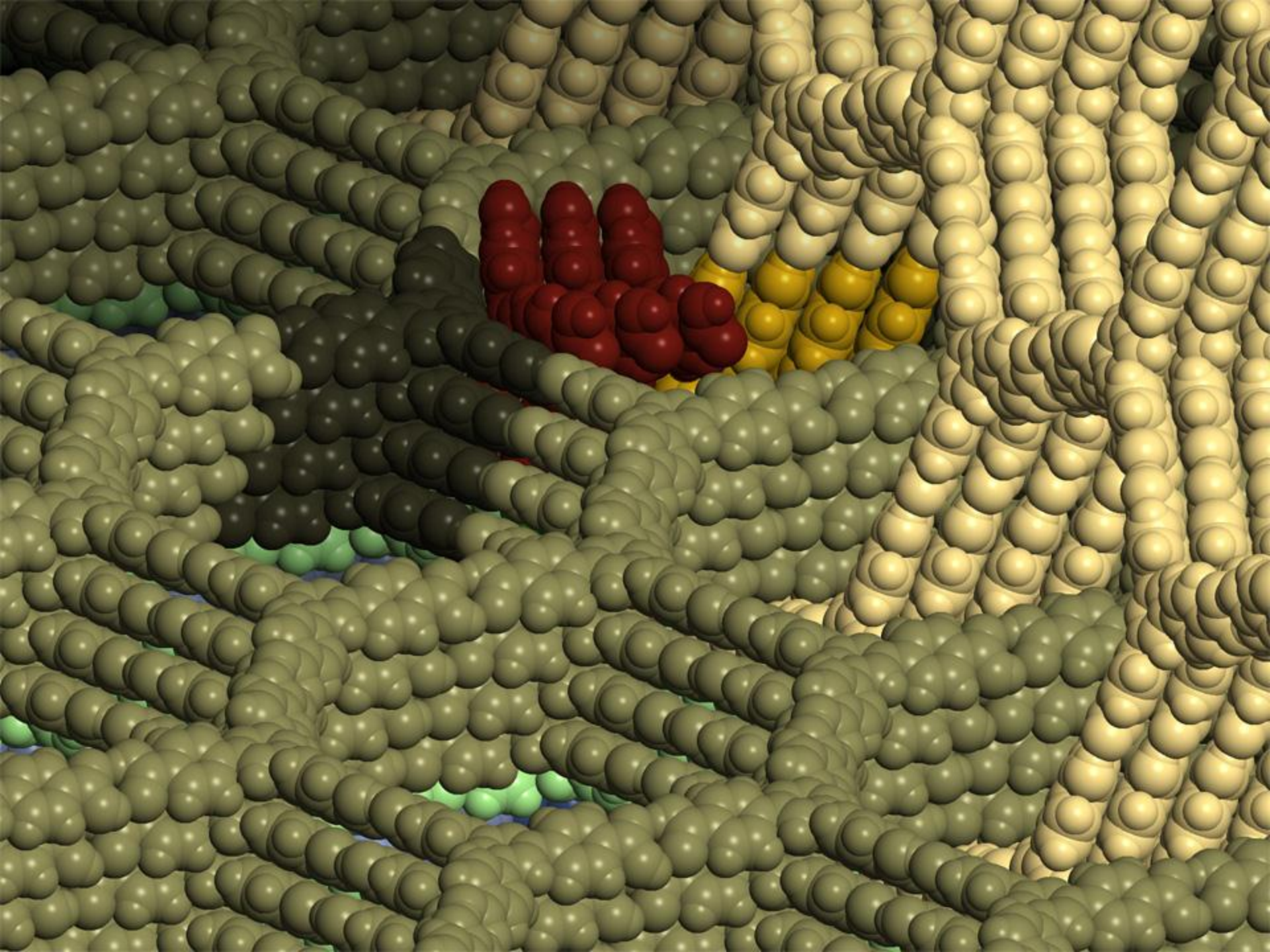


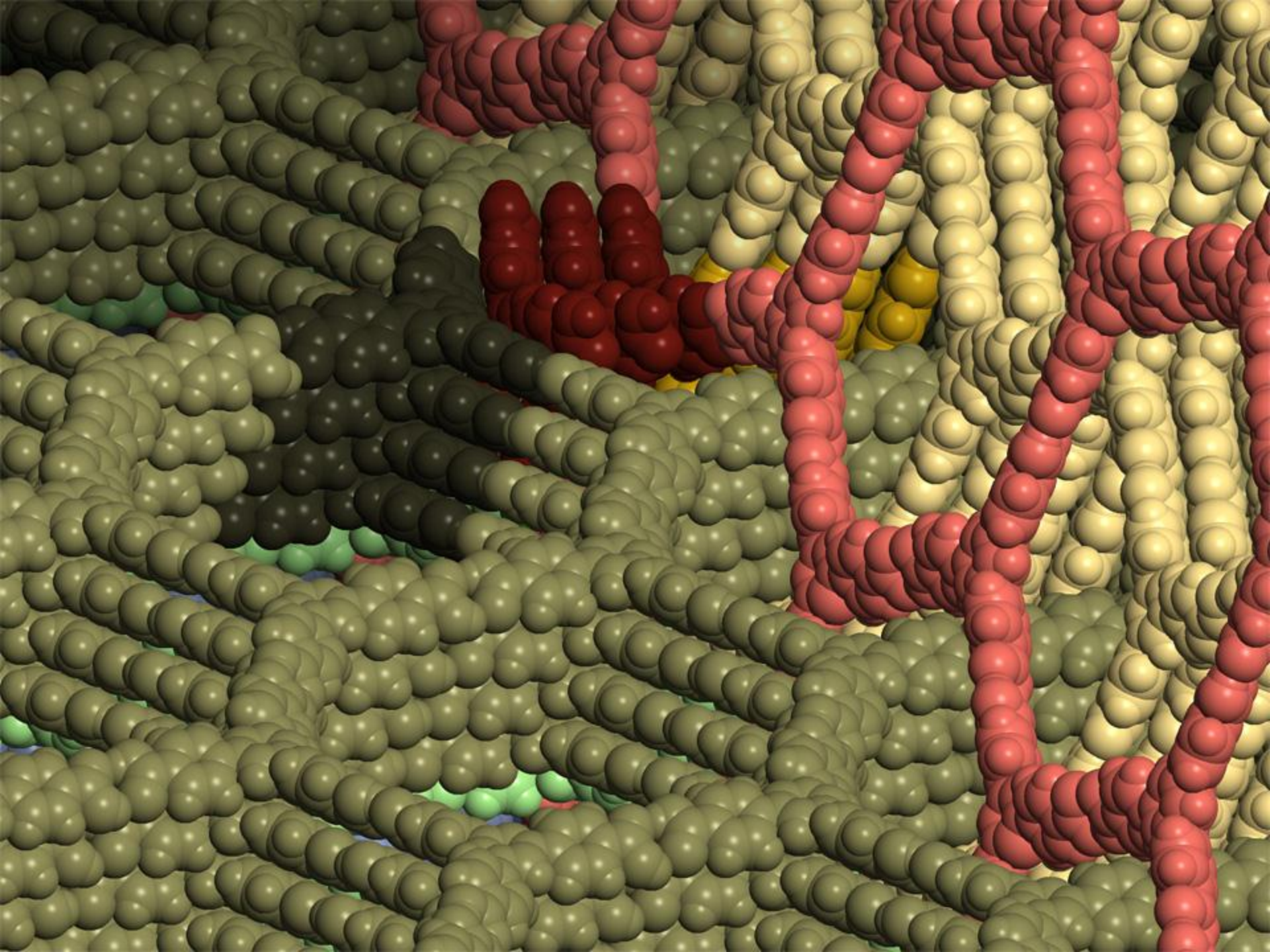


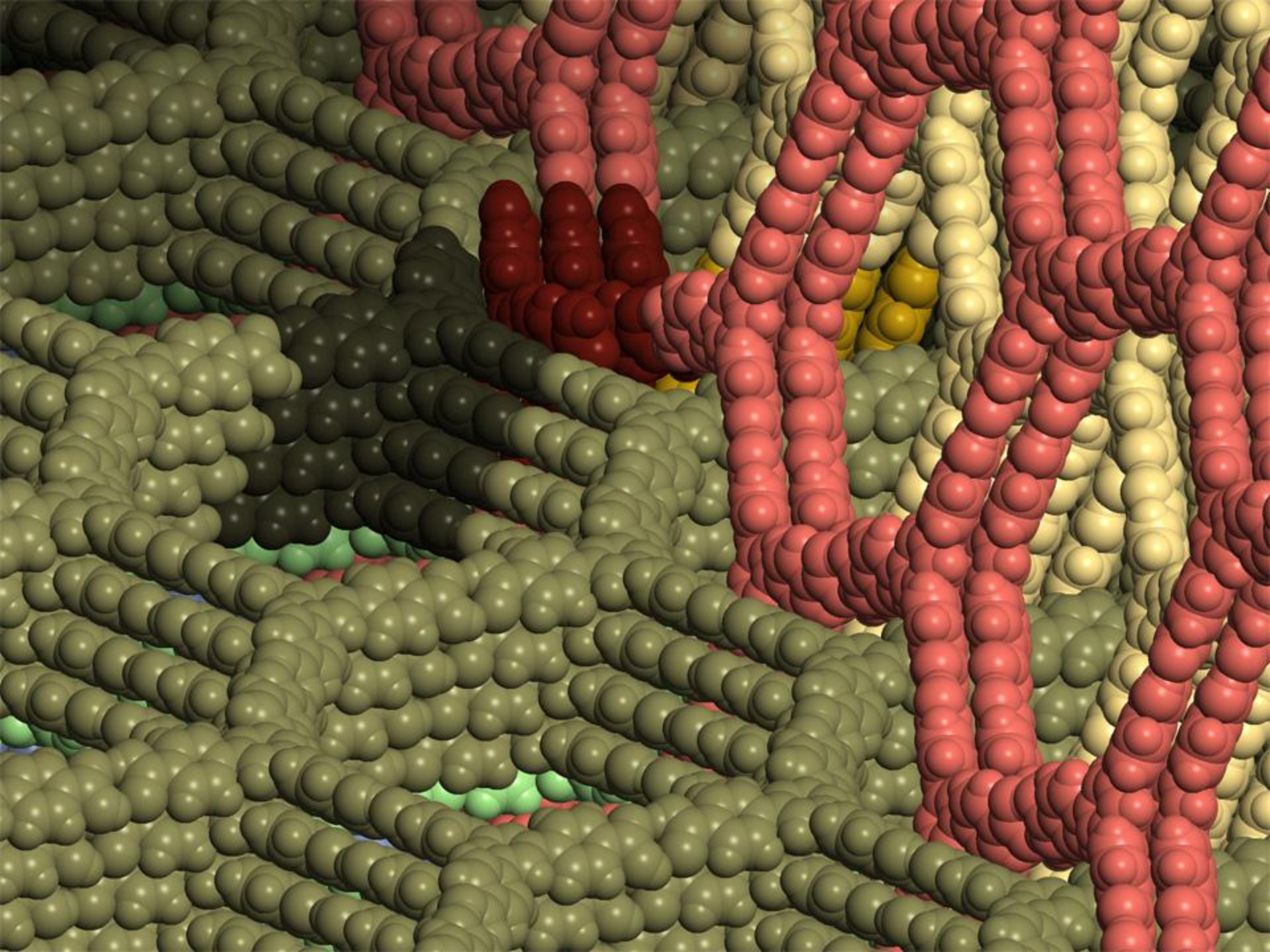


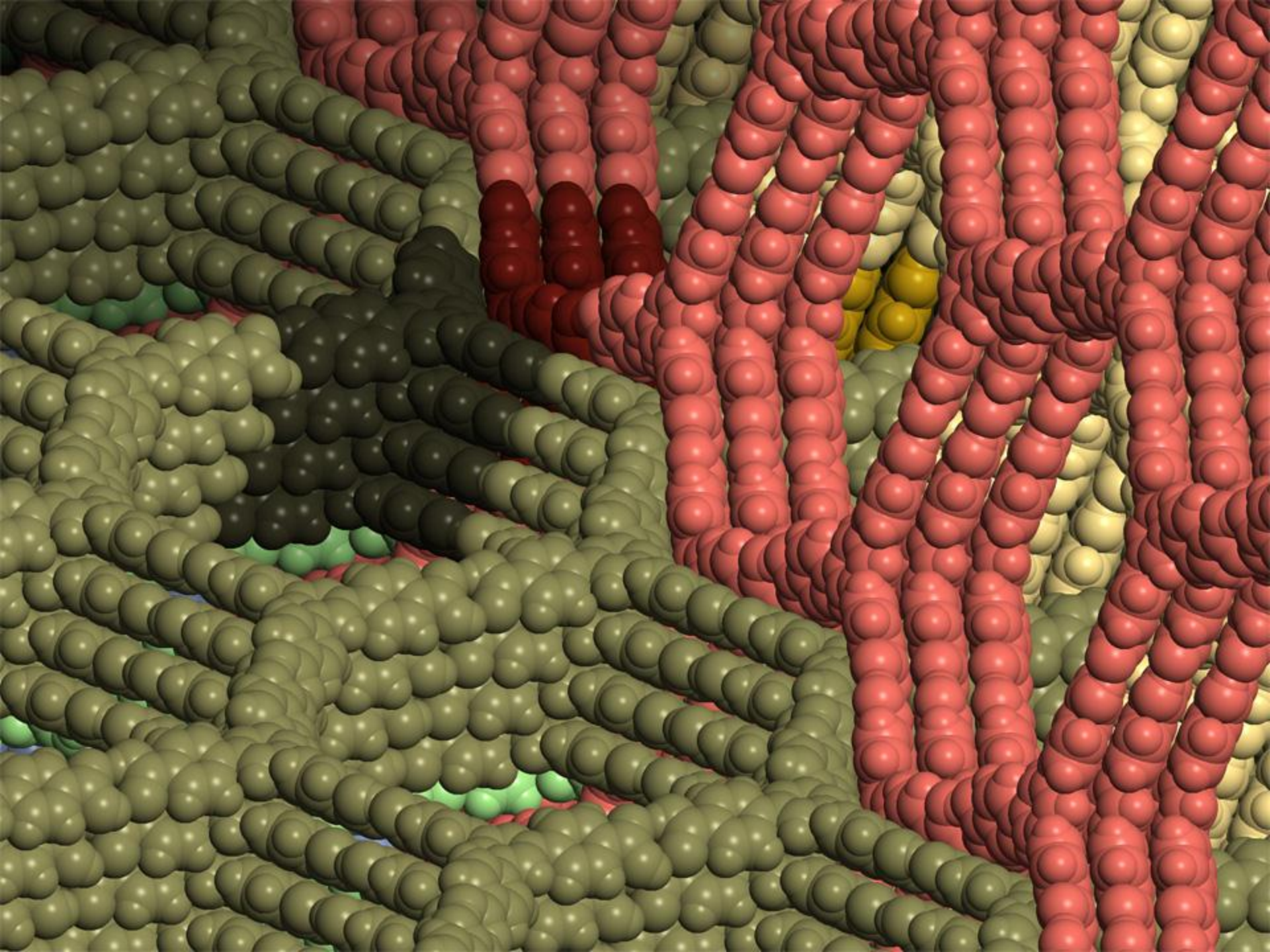




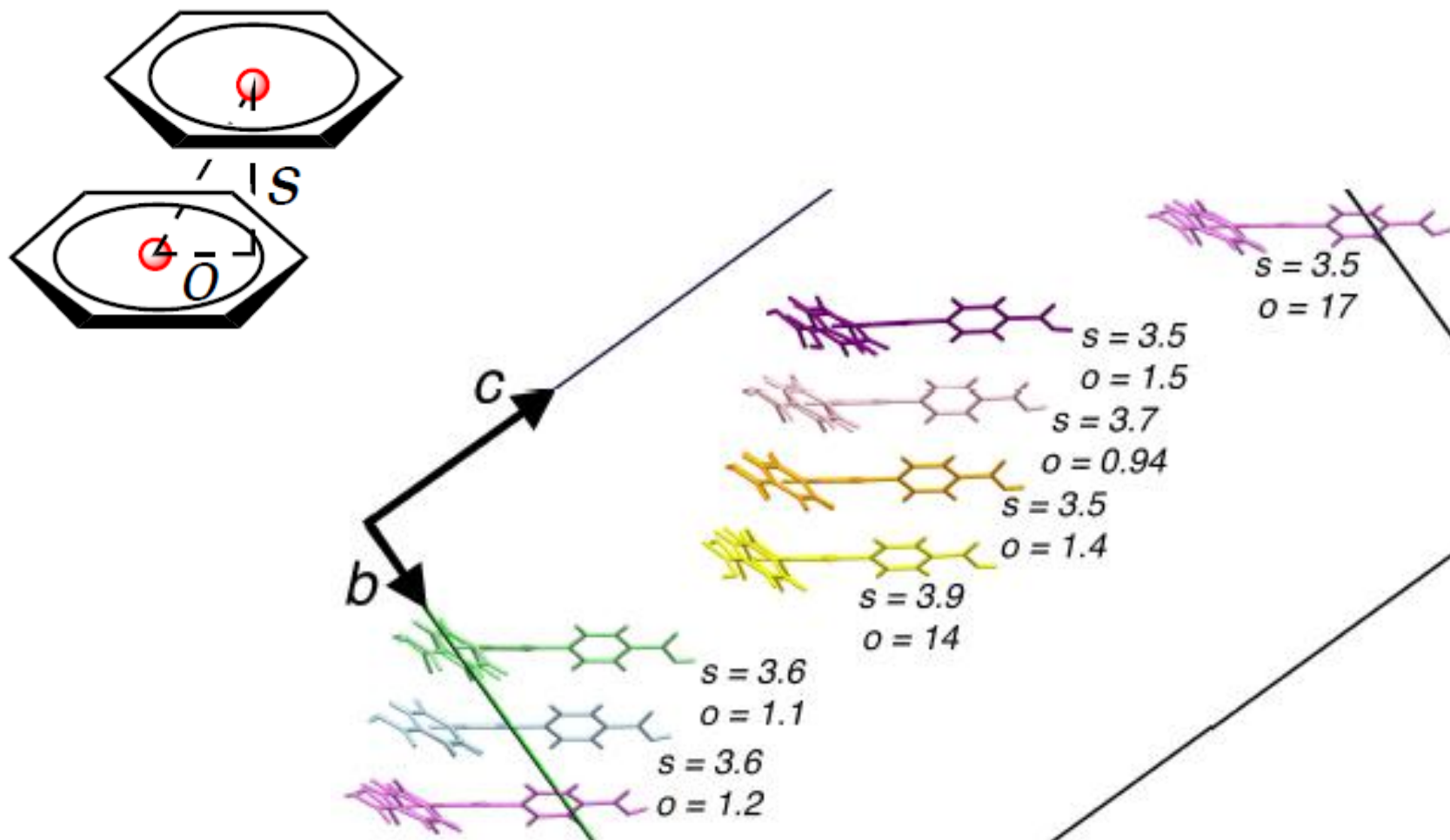




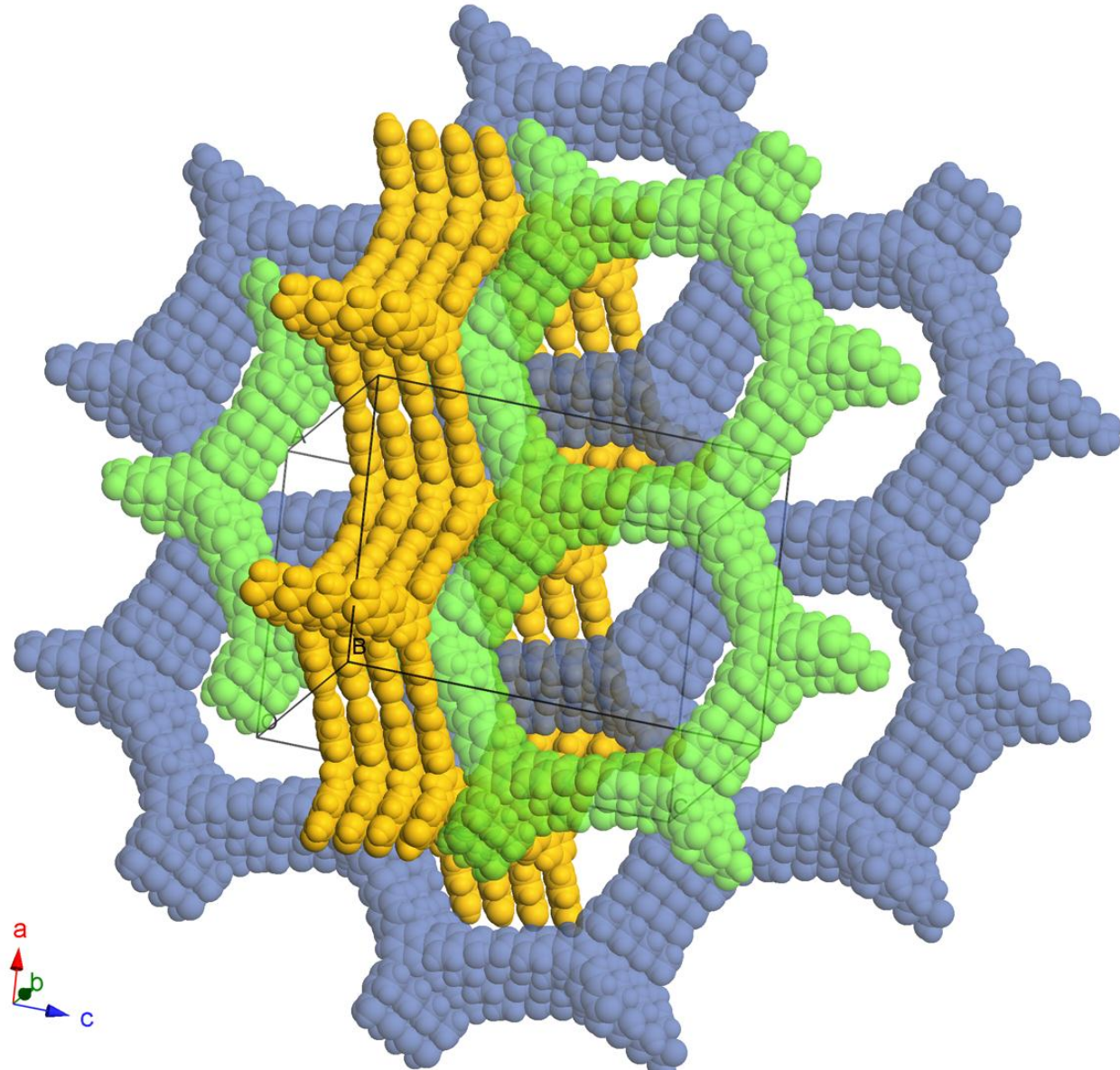




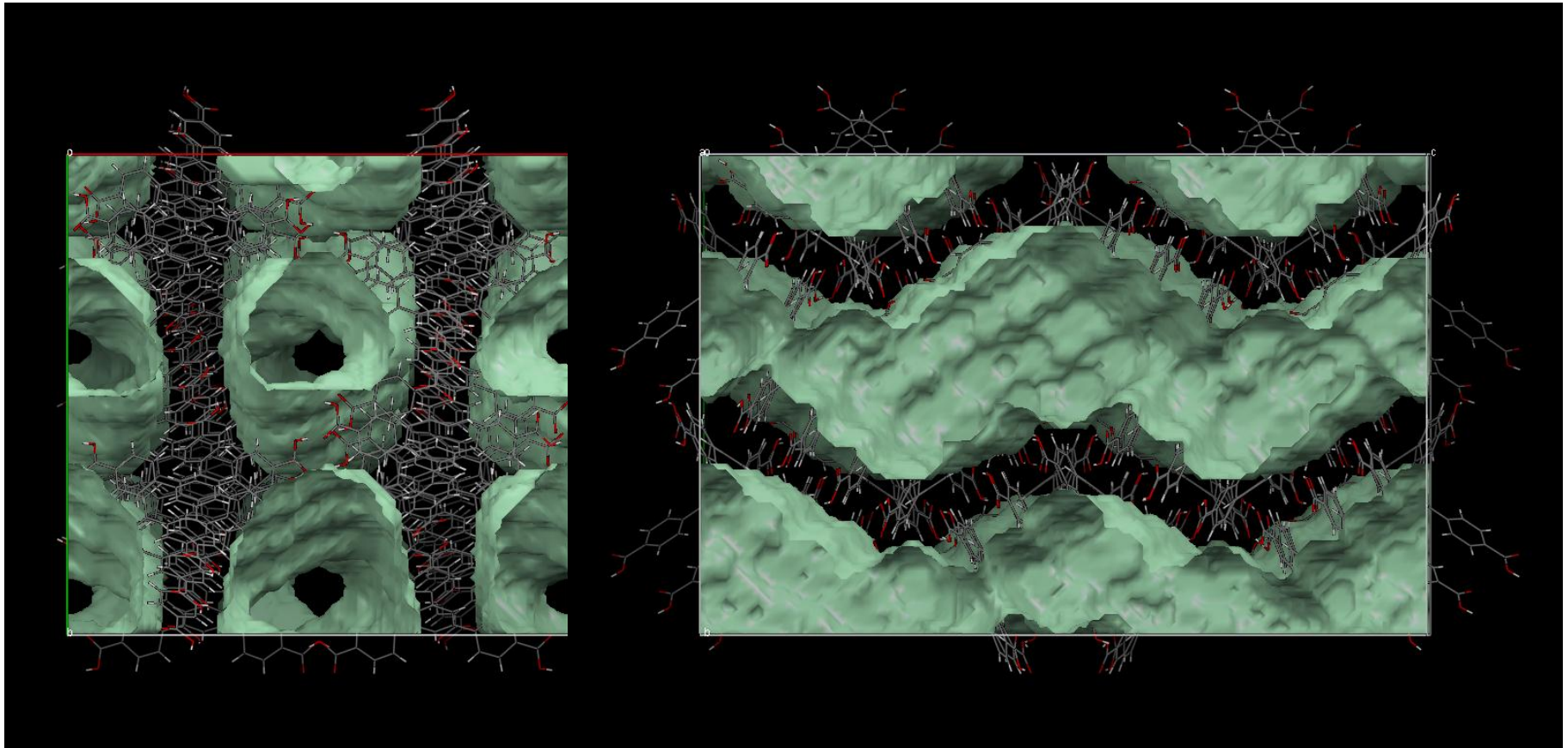
Stacking of hexagonal sheets



Catenation of non-parallel layers

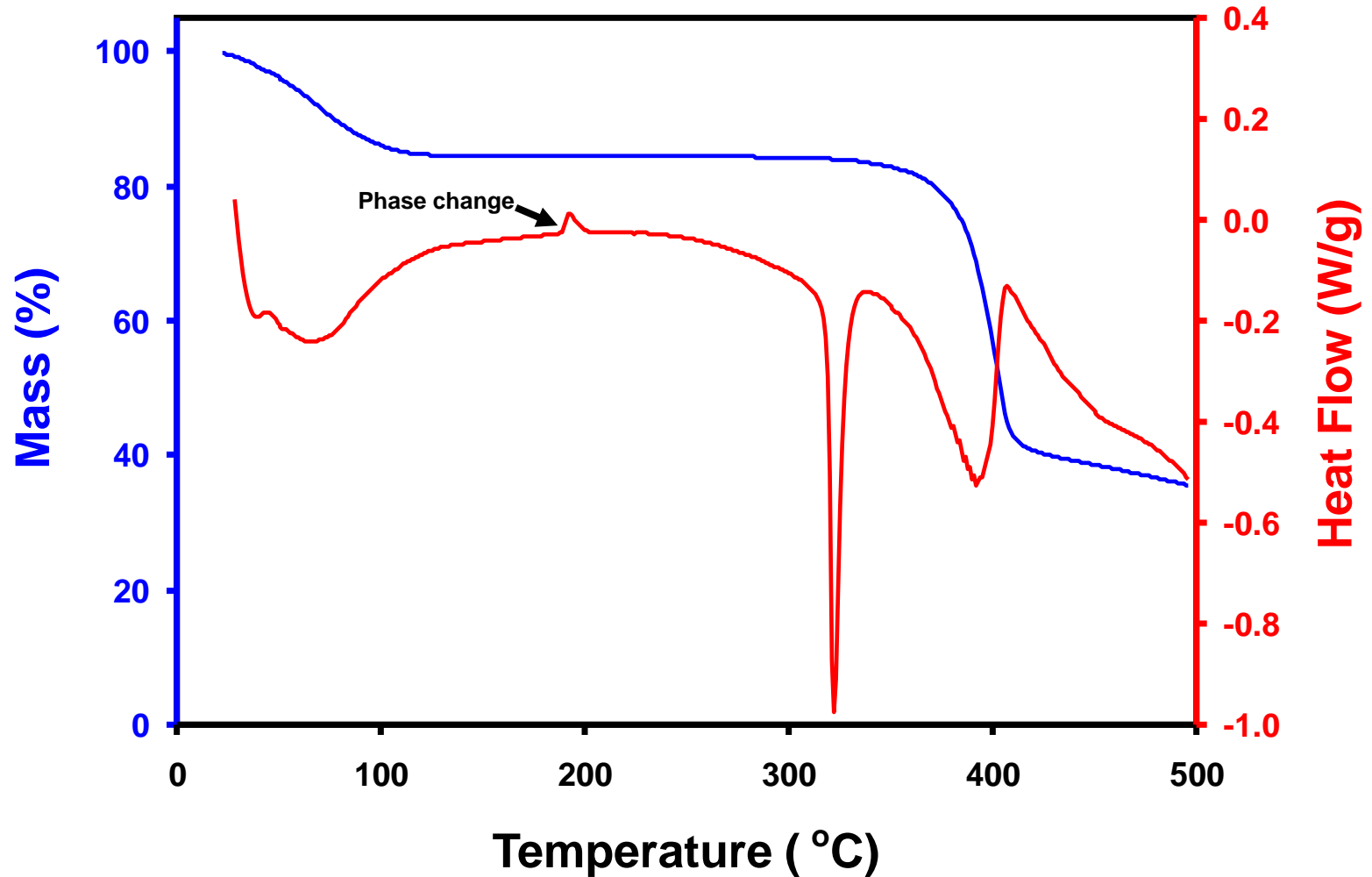


Remaining void volume is substantial

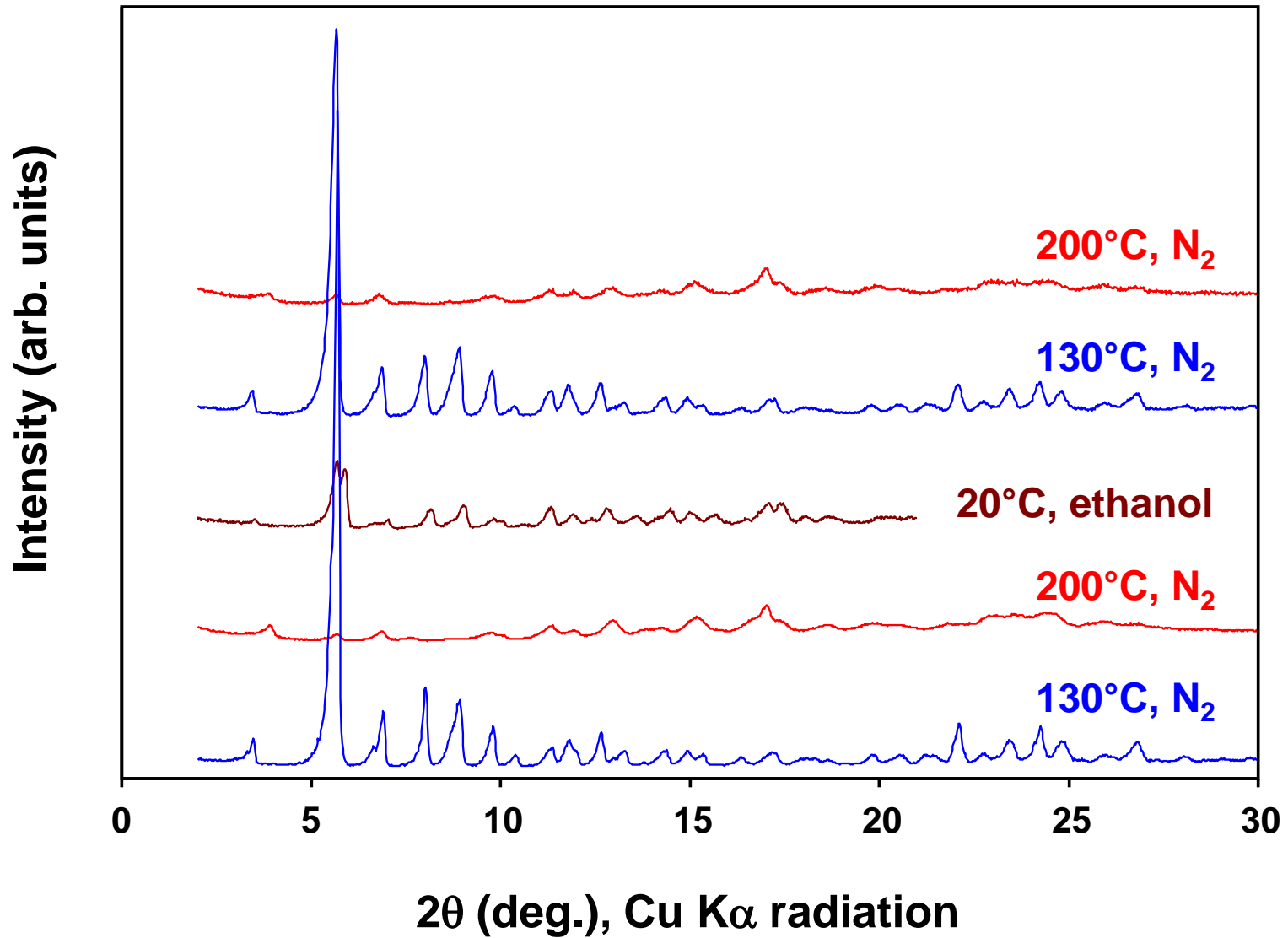


38% void volume, could be occupied by 167 ethanol molecules,
SQUEEZE identifies 1540 e⁻ (45 ethanol)

Crystal structure retained after desolvation

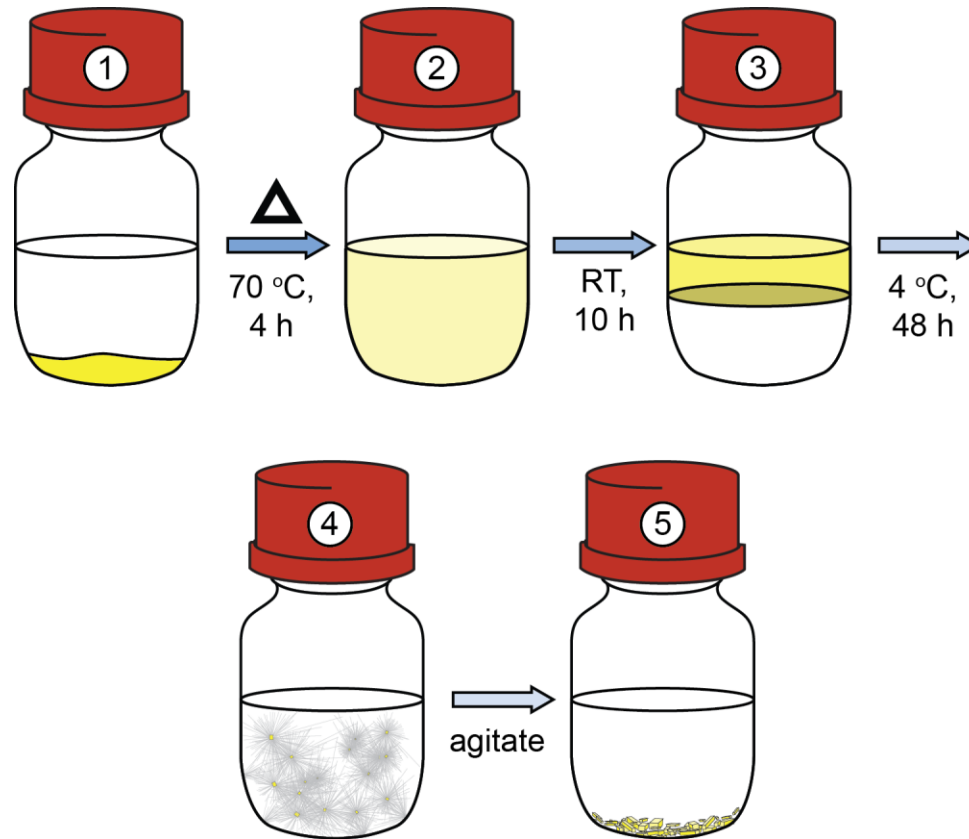


Reversible (de)solvation

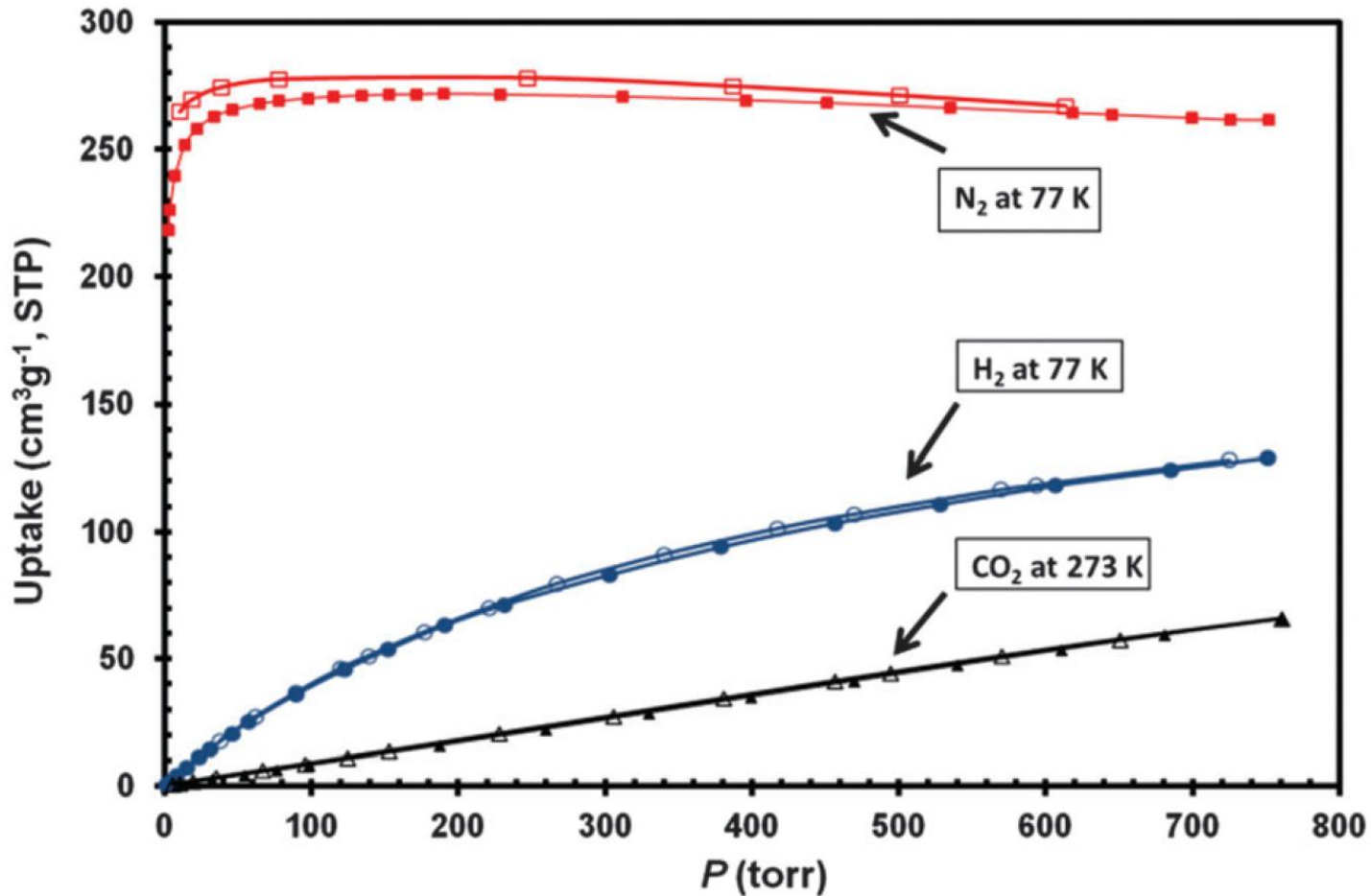


Bulk crystallization from THF/H₂O

50/50 Mixture of water and tetrahydrofuran



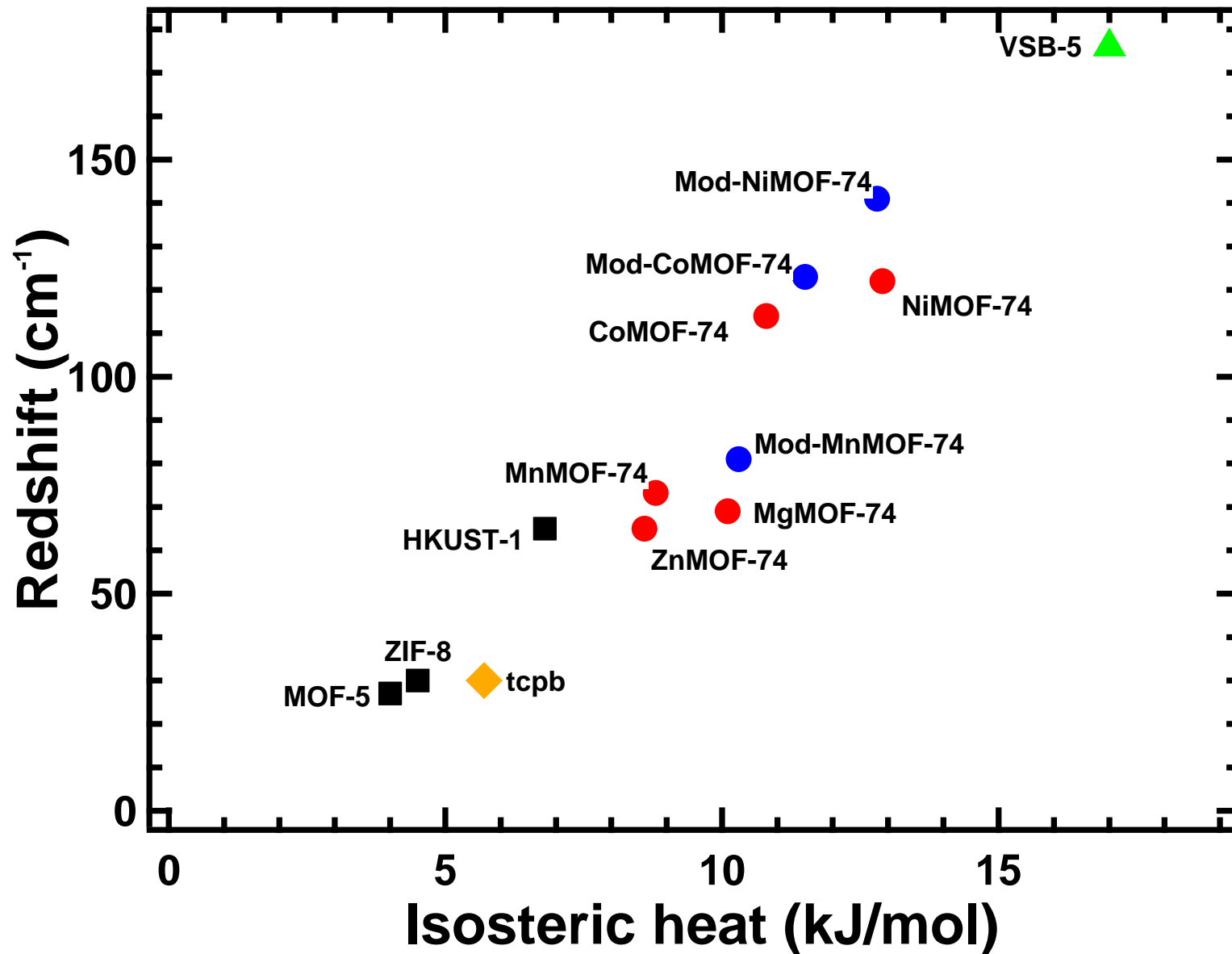
Gas adsorption confirms microporosity



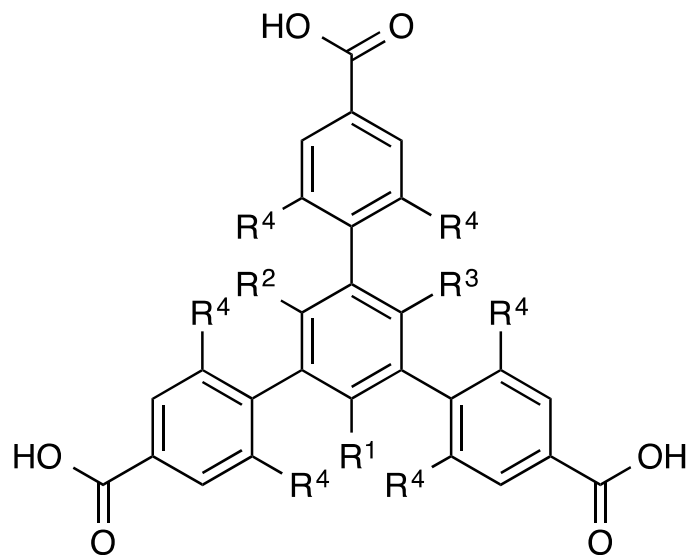
Orhan Talu,
Cleveland State University

Initial Isosteric Heat H₂ = -5.7 kJ/mol
Initial Isosteric Heat CO₂ = -22 kJ/mol
BET surface area 1100 m²/g

Binding energy trend for H₂

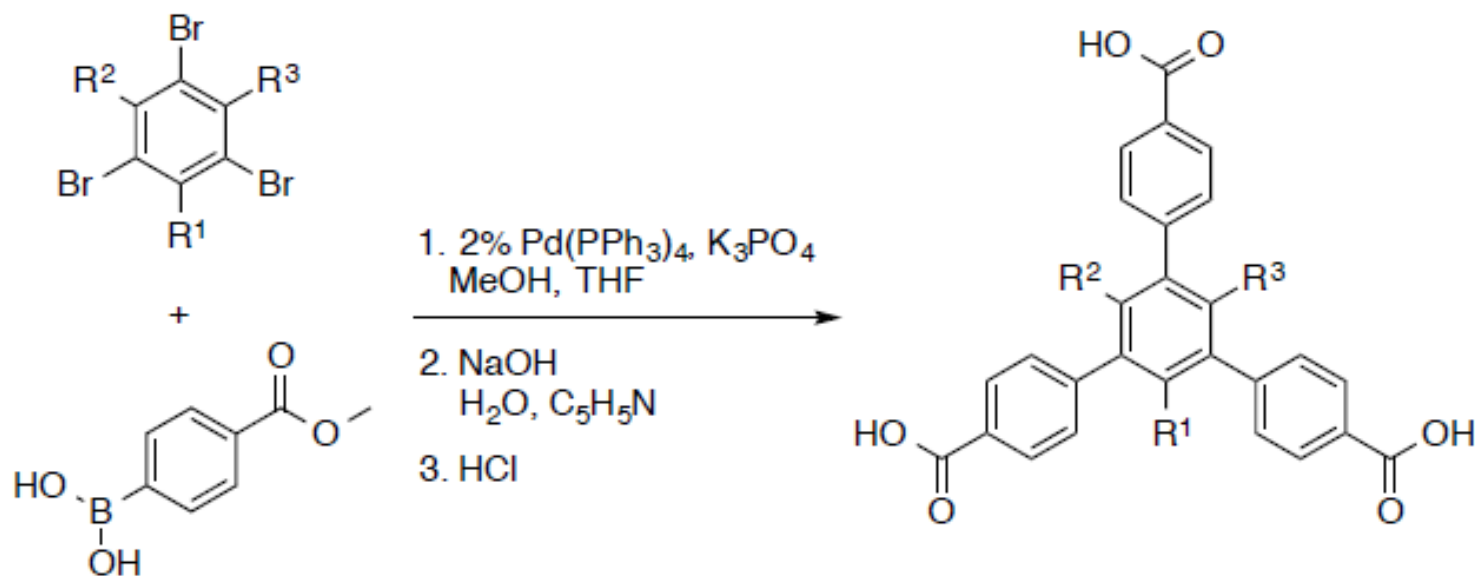


tcpb derivatives



R ¹	R ²	R ³	R ⁴
H	H	H	H
H	H	CH ₃	H
H	H	OCH ₃	H
H	CH ₃	OCH ₃	H
H	H	NH ₂	H
H	CH ₃	NH ₂	H
H	NH ₂	NH ₂	H
H	H	NO ₂	H
CH ₃	CH ₃	CH ₃	H
H	H	H	CH ₃

Derivative synthesis

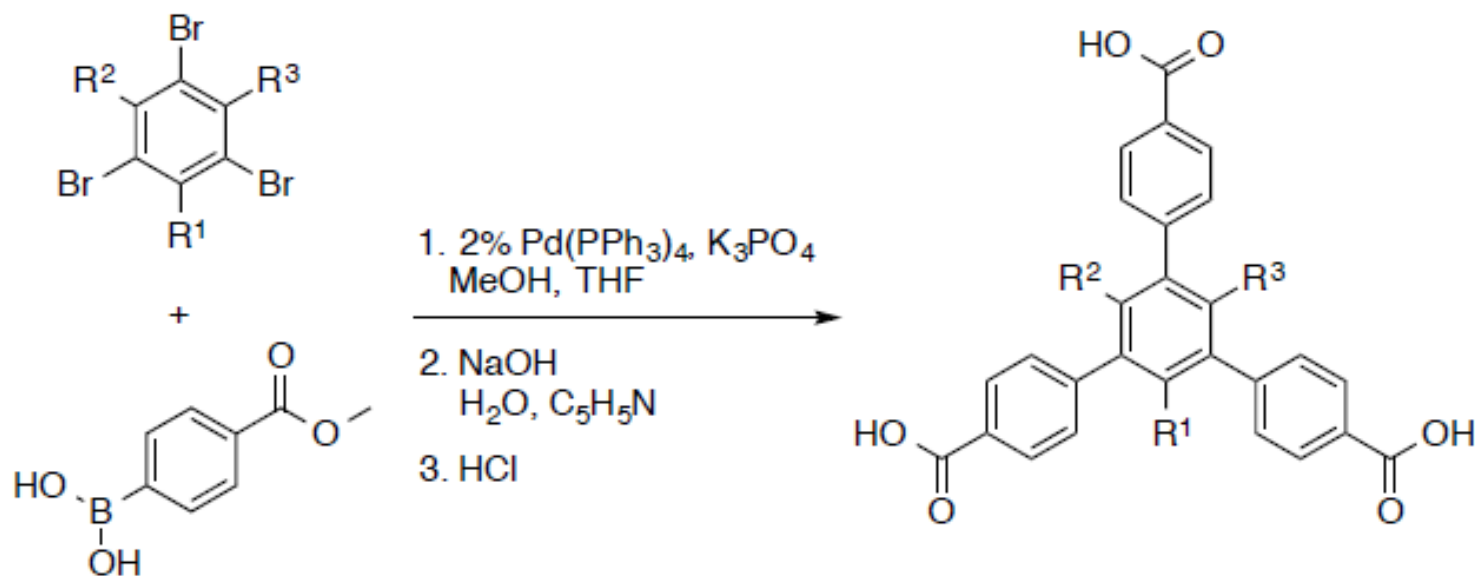


Code	R ¹	R ²	R ³	Overall Yield
2	H	H	CH ₃	93 %
3	H	H	OCH ₃	62 %
4	H	CH ₃	OCH ₃	75 %
5 ^a	H	H	NH ₂	94 %
6 ^a	H	CH ₃	NH ₂	98 %
7 ^a	H	NH ₂	NH ₂	78 %

The first step was performed under nitrogen atmosphere for all of the compounds.

^a The second step, hydrolysis of the methyl esters, was performed under nitrogen atmosphere.

Derivative synthesis

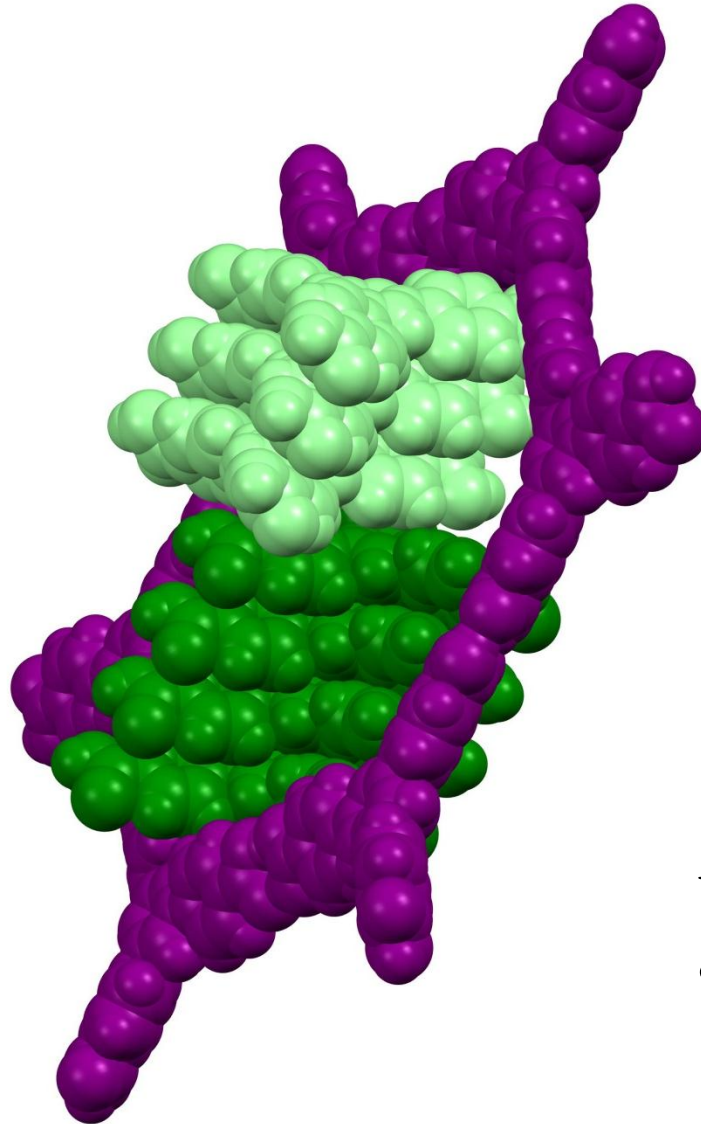


Code	R ¹	R ²	R ³	Overall Yield
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The first step was performed under nitrogen atmosphere for all of the compounds.

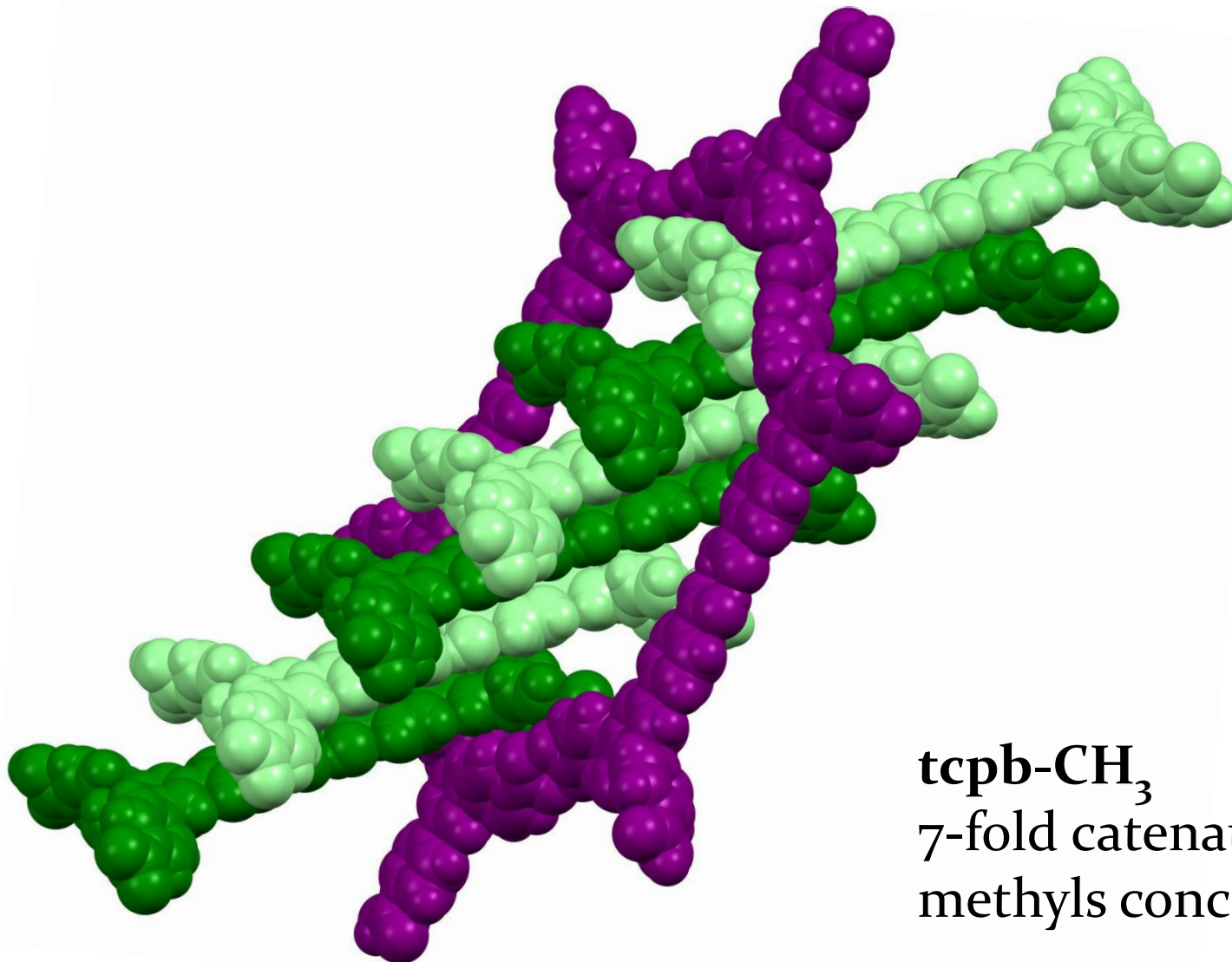
^a The second step, hydrolysis of the methyl esters, was performed under nitrogen atmosphere.

Comparison of local structure

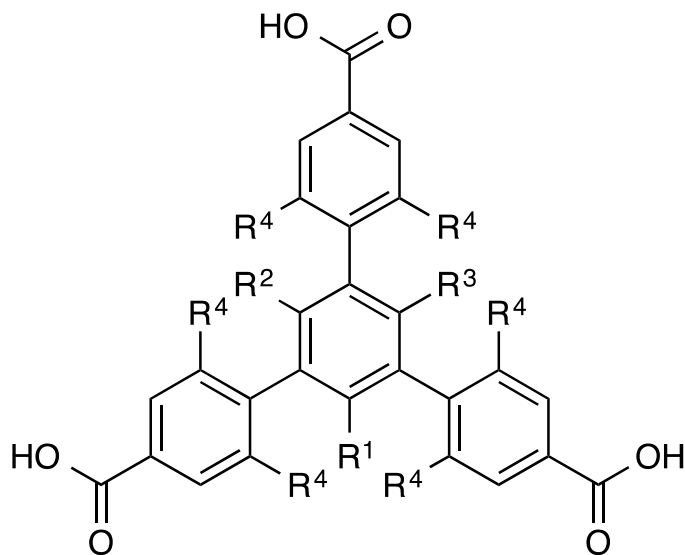


tcpb
8-fold catenation

Comparison of local structure

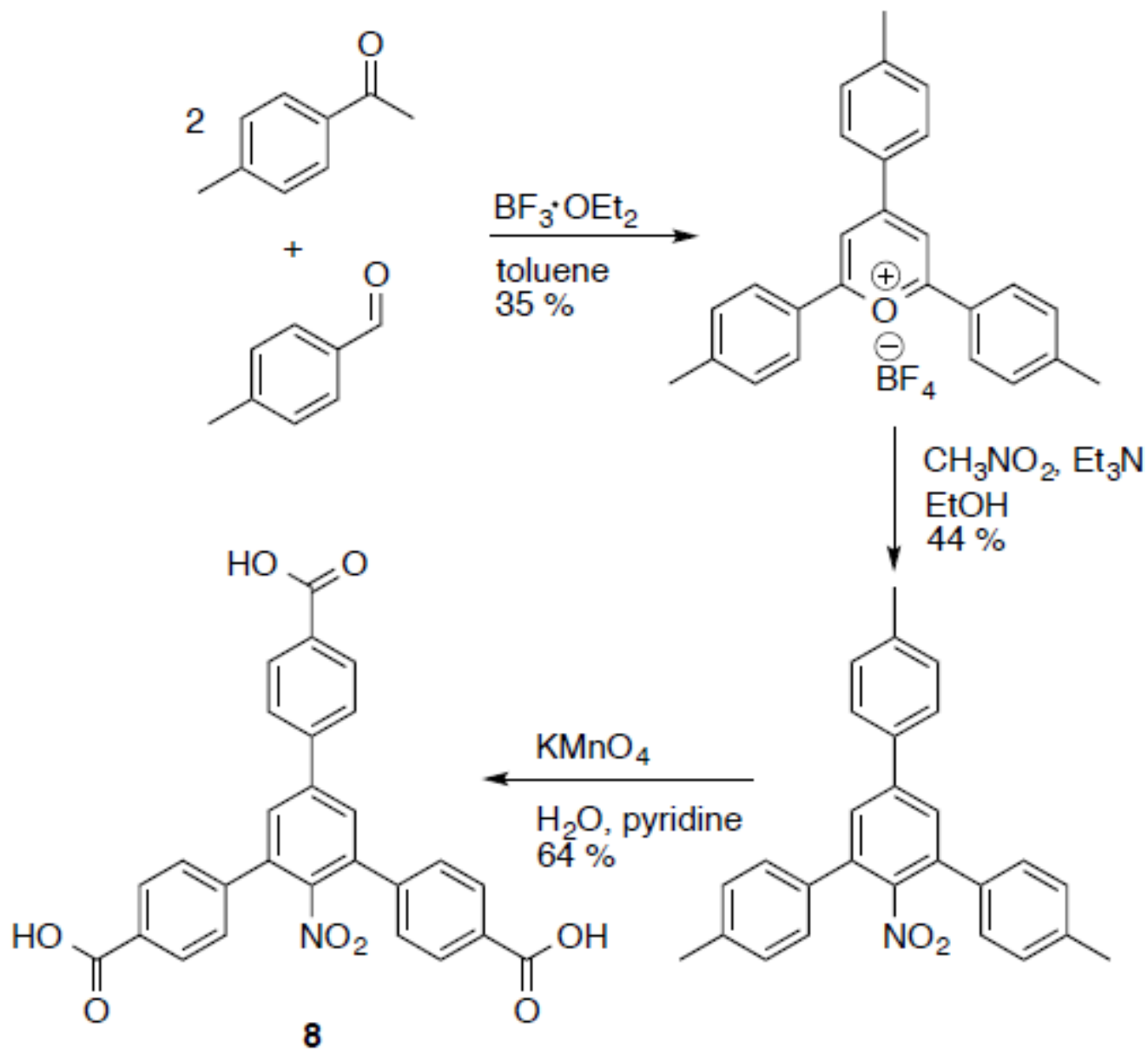


tcpb derivatives

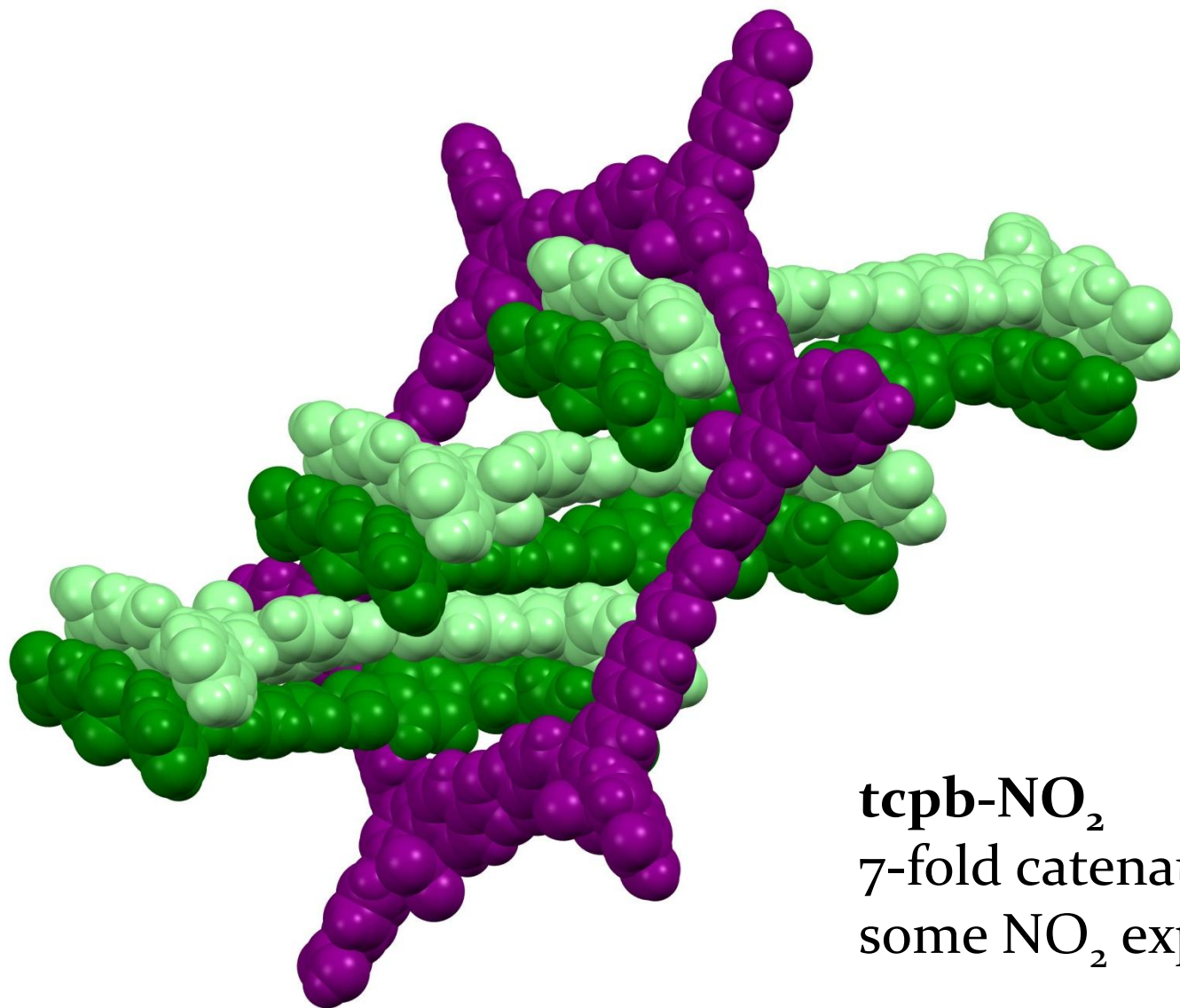


R ¹	R ²	R ³	R ⁴
H	H	H	H
H	H	CH ₃	H
H	H	OCH ₃	H
H	CH ₃	OCH ₃	H
H	H	NH ₂	H
H	CH ₃	NH ₂	H
H	NH ₂	NH ₂	H
H	H	NO ₂	H
CH ₃	CH ₃	CH ₃	H
H	H	H	CH ₃

tcpb-NO₂ synthesis



Comparison of local structure



tcpb-NO₂
7-fold catenation,
some NO₂ exposed

Oberlin student coauthors on our papers

Kelty
Allen
UC Berkeley



Ross
Myers
Columbia



Jenny
Schloss
M.I.T.



Jesse
Hopkins
Cornell



Brian
Burkholder
U. Washington



Chris
Pierce
Ohio State



Patrick
Landreman
Stanford



Michael
Friedman
Boston U.



Elizabeth
Gilmour
U. Memphis



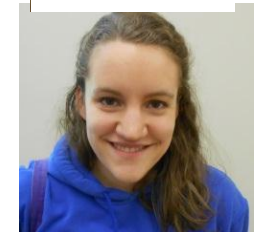
John
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Jocienne
Nelson
Cornell



Student leaders on tcpb paper



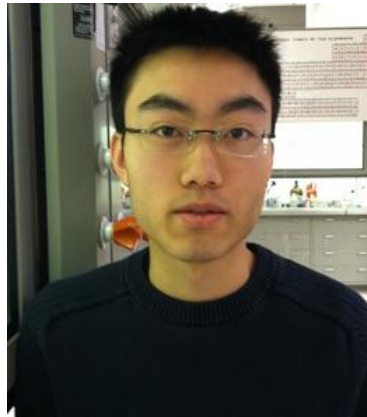
Cassandra Zentner

Oberlin → ?



Ren Wiscons

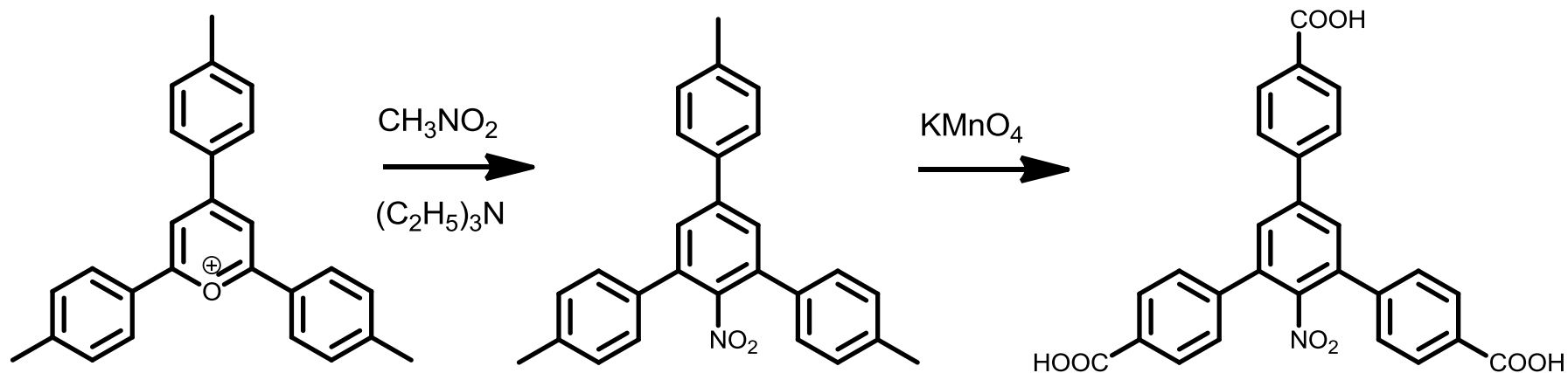
U. Michigan



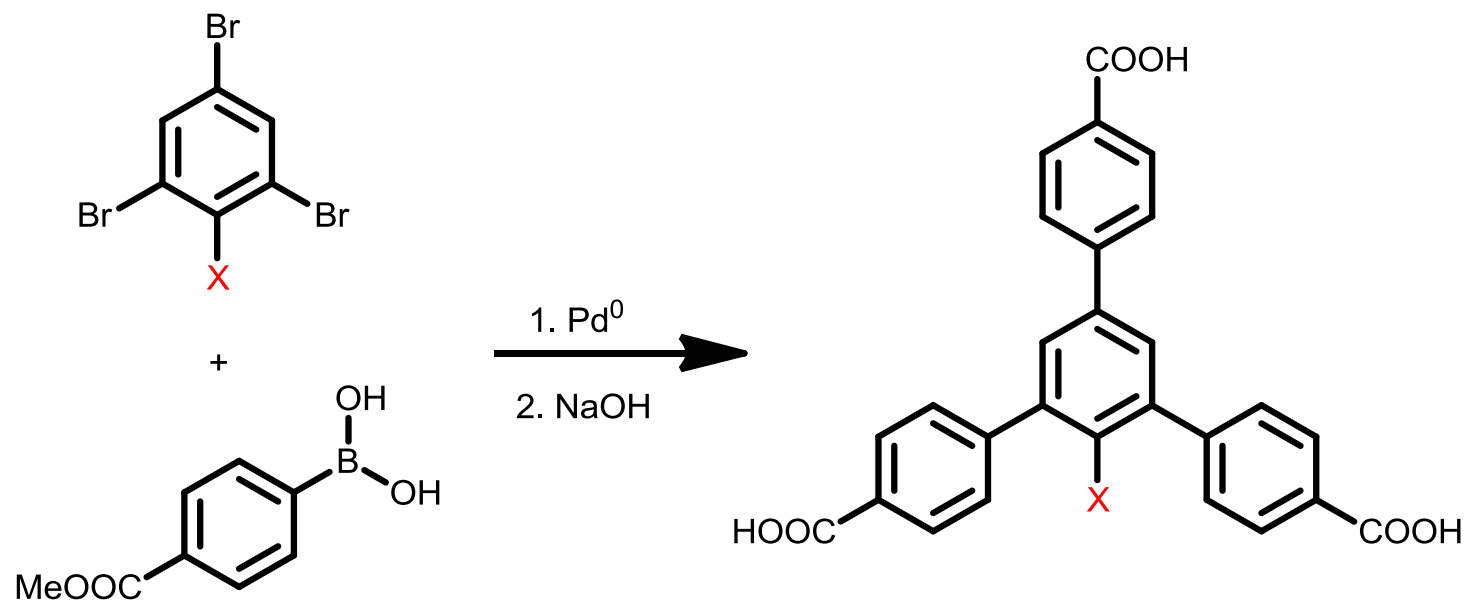
Holden Lai

U.C. Berkeley

Core functionalization: pyrylium intermediate



Core functionalization: Suzuki coupling



Smaller IR band redshifts for adsorbed H₂

