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14. ABSTRACT Infinite coordination polymer (ICP) particles and metal-organic frameworks (MOFs) are attractive materials for a diverse array of applications, namely, catalysis, gas storage, chemical separations, photonics, and detection systems. Although promising, these micro- and nano-materials possess certain shortcomings that require further examination through fundamental studies. Towards overcoming these shortcomings, we proposed to investigate and drastically improve upon a series of key properties, specifically size and shape control, surface functionalization, volumetric surface area, and chemically specific gas adsorption. Through these efforts, we have made significant					
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Report Title

Final Report: Infinite Coordination Polymer Nano- and Micro- Particles

ABSTRACT

Infinite coordination polymer (ICP) particles and metal-organic frameworks (MOFs) are attractive materials for a diverse array of applications, namely, catalysis, gas storage, chemical separations, photonics, and detection systems. Although promising, these micro- and nano-materials possess certain shortcomings that require further examination through fundamental studies. Towards overcoming these shortcomings, we proposed to investigate and drastically improve upon a series of key properties, specifically size and shape control, surface functionalization, volumetric surface area, and chemically specific gas sorption. Through these efforts, we have made significant discoveries, leading to the realization of biomolecule-functionalized nano-ICPs, unprecedentedly robust MOF topologies, and unique MOF structures with significant hydrogen and methane adsorption properties. Specifically, the novel DNA-ICP conjugates realized herein have demonstrated their utility as an *in vitro* gene regulatory tool, lending this construct to potential applications in therapeutics and diagnostics. Additionally, the carborane-MOF and MOP constructs described herein possess unique structural properties, making them key candidates for applications in selective gas sorption and boron neutron capture therapy (BNCT).

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<u>Received</u>	<u>Paper</u>
02/12/2013 8.00	Tina C. Li, Francisco Fabregat-Santiago, Omar K. Farha, Alexander M. Spokoyny, Sonia R. Raga, Juan Bisquert, Chad A. Mirkin, Tobin J. Marks, Joseph T. Hupp. SiO ₂ Aerogel-templated, Porous TiO ₂ Photoanodes for Enhanced Performances in Dye-Sensitized Solar Cells Containing a Ni(III)/(IV) Bis (discarbollide) Shuttle, <i>The Journal of Physical Chemistry C</i> , (06 2011): 0. doi: 10.1021/jp112139h
02/12/2013 10.00	Hyojong Yoo, Mari S. Rosen, Aaron M. Brown, Michael J. Wiester, Charlotte L. Stern, Chad A. Mirkin. Elucidating the Mechanism of the Halide-Induced Ligand Rearrangement Reaction, <i>Inorganic Chemistry</i> , (11 2012): 0. doi: 10.1021/ic3018776
02/12/2013 9.00	Charles W. Machan, Mario Adelhardt, Amy A. Sarjeant, Charlotte L. Stern, Jörg Sutter, Karsten Meyer, Chad A. Mirkin. One-Pot Synthesis of an Fe(II) Bis-Terpyridine Complex with Allosterically Regulated Electronic Properties, <i>Journal of the American Chemical Society</i> , (10 2012): 0. doi: 10.1021/ja3045019
06/12/2015 24.00	C. Michael McGuirk, Jose Mendez-Arroyo, Alejo M. Lifschitz, Chad A. Mirkin. Allosteric Regulation of Supramolecular Oligomerization and Catalytic Activity via Coordination-Based Control of Competitive Hydrogen-Bonding Events, <i>Journal of the American Chemical Society</i> , (11 2014): 0. doi: 10.1021/ja508804n
06/12/2015 30.00	Alejo M. Lifschitz, Mari S. Rosen, C. Michael McGuirk, Chad A. Mirkin. Allosteric Supramolecular Coordination Constructs, <i>Journal of the American Chemical Society</i> , (06 2015): 0. doi: 10.1021/jacs.5b01054
06/12/2015 29.00	Daniel J. Clingerman, William Morris, Joseph E. Mondloch, Robert D. Kennedy, Amy A. Sarjeant, Charlotte Stern, Joseph T. Hupp, Omar K. Farha, Chad A. Mirkin. Stabilization of a highly porous metal-organic framework utilizing a carborane-based linker, <i>Chem. Commun.</i> , (06 2015): 0. doi: 10.1039/C4CC09212K
06/12/2015 28.00	C. Michael McGuirk, Michael J. Katz, Charlotte L. Stern, Amy A. Sarjeant, Joseph T. Hupp, Omar K. Farha, Chad A. Mirkin. Turning On Catalysis: Incorporation of a Hydrogen-Bond-Donating Squaramide Moiety into a Zr Metal-Organic Framework, <i>Journal of the American Chemical Society</i> , (01 2015): 0. doi: 10.1021/ja511403t
06/12/2015 27.00	Evelyn Auyeung, William Morris, Joseph E. Mondloch, Joseph T. Hupp, Omar K. Farha, Chad A. Mirkin. Controlling Structure and Porosity in Catalytic Nanoparticle Superlattices with DNA, <i>Journal of the American Chemical Society</i> , (02 2015): 0. doi: 10.1021/ja512116p
06/12/2015 26.00	Alejo M. Lifschitz, Ryan M. Young, Jose Mendez-Arroyo, Charlotte L. Stern, C. Michael McGuirk, Michael R. Wasielewski, Chad A. Mirkin. An allosteric photoredox catalyst inspired by photosynthetic machinery, <i>Nature Communications</i> , (03 2015): 0. doi: 10.1038/ncomms7541
06/12/2015 25.00	Colin M. Calabrese, Timothy J. Merkel, William E. Briley, Pratik S. Randeria, Suguna P. Narayan, Jessica L. Rouge, David A. Walker, Alexander W. Scott, Chad A. Mirkin. Biocompatible Infinite-Coordination-Polymer Nanoparticle-Nucleic-Acid Conjugates for Antisense Gene Regulation, <i>Angewandte Chemie International Edition</i> , (11 2014): 0. doi: 10.1002/anie.201407946

- 08/29/2014 17.00 Jung Su Park, Alejo M. Lifschitz, Ryan M. Young, Jose Mendez-Arroyo, Michael R. Wasielewski, Charlotte L. Stern, Chad A. Mirkin. Modulation of Electronics and Thermal Stabilities of Photochromic Phosphino–Aminoazobenzene Derivatives in Weak-Link Approach Coordination Complexes, *Journal of the American Chemical Society*, (11 2013): 0. doi: 10.1021/ja407148n
- 08/29/2014 23.00 Charlotte L. Stern, Michael O’Keeffe, Randall Q. Snurr, Joseph T. Hupp, Omar K. Farha, Chad A. Mirkin, Daniel J. Clingerman, William Morris, Christopher E. Wilmer, Amy A. Sarjeant, Robert D. Kennedy. Metallocarborane-Based Metal–Organic Framework with a Complex Topology, *Crystal Growth & Design*, (03 2014): 0. doi: 10.1021/cg401817g
- 08/29/2014 22.00 Jose Mendez-Arroyo, Joaquín Barroso-Flores, Alejo M. Lifschitz, Amy A. Sarjeant, Charlotte L. Stern, Chad A. Mirkin. A Multi-State, Allosterically-Regulated Molecular Receptor With Switchable Selectivity, *Journal of the American Chemical Society*, (07 2014): 0. doi: 10.1021/ja503506a
- 08/29/2014 21.00 V. V. Roznyatovskiy, C. M. McGuirk, M. R. Wasielewski, C. A. Mirkin, A. M. Lifschitz, R. M. Young, J. Mendez-Arroyo. Chemically regulating Rh(i)-Bodipy photoredox switches, *Chemical Communications*, (02 2014): 0. doi: 10.1039/c4cc01345j
- 08/29/2014 20.00 C. Michael McGuirk, Charlotte L. Stern, Chad A. Mirkin. Small Molecule Regulation of Self-Association and Catalytic Activity in a Supramolecular Coordination Complex, *Journal of the American Chemical Society*, (03 2014): 0. doi: 10.1021/ja500214r
- 08/29/2014 19.00 Kaylie L. Young, Michelle L. Personick, Michael Engel, Pablo F. Damasceno, Stacey N. Barnaby, Reiner Bleher, Tao Li, Sharon C. Glotzer, Byeongdu Lee, Chad A. Mirkin. A Directional Entropic Force Approach to Assemble Anisotropic Nanoparticles into Superlattices, *Angewandte Chemie International Edition*, (12 2013): 0. doi: 10.1002/anie.201306009
- 08/29/2014 18.00 Chad A. Mirkin, Charlotte L. Stern, Robert D. Kennedy. Zwitterionic Weak-Link Approach Complexes Based on Anionic Icosahedral Monocarbaboranes, *Inorganic Chemistry*, (12 2013): 0. doi: 10.1021/ic401851z
- 08/30/2013 11.00 Chad A. Mirkin, J. Fraser Stoddart, Abrin L. Schmucker, Gokhan Barin, Keith A. Brown, Matthew Rycenga, Ali Coskun, Onur Buyukcakir, Kyle D. Osberg. Electronic and Optical Vibrational Spectroscopy of Molecular Transport Junctions Created by On-Wire Lithography, *Small*, (06 2013): 1900. doi: 10.1002/smll.201201993
- 08/30/2013 12.00 Robert D. Kennedy, Charles W. Machan, C. Michael McGuirk, Mari S. Rosen, Charlotte L. Stern, Amy A. Sarjeant, Chad A. Mirkin. General Strategy for the Synthesis of Rigid Weak-Link Approach Platinum(II) Complexes: Tweezers, Triple-Layer Complexes, and Macrocycles, *Inorganic Chemistry*, (05 2013): 5876. doi: 10.1021/ic302855f
- 08/30/2013 13.00 Alejo M. Lifschitz, Chad M. Shade, Alexander M. Spokoyny, Jose Mendez-Arroyo, Charlotte L. Stern, Amy A. Sarjeant, Chad A. Mirkin. Boron-Dipyromethene-Functionalized Hemilabile Ligands as “Turn-On” Fluorescent Probes for Coordination Changes in Weak-Link Approach Complexes, *Inorganic Chemistry*, (05 2013): 5484. doi: 10.1021/ic400383t
- 08/30/2013 14.00 Chad A. Mirkin, Charlotte L. Stern, Mari S. Rosen. Heteroligated PtII Weak-Link Approach complexes using hemilabile N-heterocyclic carbene–thioether and phosphino–thioether ligands, *Chemical Science*, (08 2013): 0. doi: 10.1039/c3sc51557e
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- 08/30/2013 16.00 Vaiva Krungleviciute, Daniel J. Clingerman, Joseph E. Mondloch, Yang Peng, Christopher E. Wilmer, Amy A. Sarjeant, Randall Q. Snurr, Joseph T. Hupp, Taner Yildirim, Omar K. Farha, Robert D. Kennedy, Chad A. Mirkin. Carborane-Based Metal–Organic Framework with High Methane and Hydrogen Storage Capacities, *Chemistry of Materials*, (08 2013): 0. doi: 10.1021/cm4020942

- 08/31/2012 2.00 Chad A. Mirkin, Alejo M. Lifschitz, Charlotte L. Stern, Amy A. Sarjeant, Charles W. Machan. Crystallographic Snapshots of the Bond-Breaking Isomerization Reactions Involving Nickel(II) Complexes with Hemilabile Ligands, *Angewandte Chemie International Edition*, (02 2012): 0. doi: 10.1002/anie.201107620
- 08/31/2012 1.00 Michael J. Wiester, Pirmin A. Ulmann, Chad A. Mirkin. Enzyme Mimics Based Upon Supramolecular Coordination Chemistry, *Angewandte Chemie International Edition*, (01 2011): 0. doi: 10.1002/anie.201000380
- 08/31/2012 3.00 Mari S. Rosen, Alexander M. Spokoyny, Charles W. Machan, Amy Sarjeant, Chad A. Mirkin, Charlotte Stern. Chelating Effect as a Driving Force for the Selective Formation of Heteroligated Pt(II) Complexes with Bidentate Phosphino-Chalcoether Ligands, *Inorganic Chemistry*, (02 2011): 0. doi: 10.1021/ic101973s
- 08/31/2012 4.00 Charles W. Machan, Alexander M. Spokoyny, Matthew R. Jones, Amy A. Sarjeant, Charlotte L. Stern, Chad A. Mirkin. Plasticity of the Nickel(II) Coordination Environment in Complexes with Hemilabile Phosphino Thioether Ligands, *Journal of the American Chemical Society*, (03 2011): 0. doi: 10.1021/ja109624m
- 08/31/2012 5.00 Alexander M. Spokoyny, Daniel J. Clingerman, Mari S. Rosen, Charles W. Machan, Michael J. Wiester, Robert D. Kennedy, Charlotte L. Stern, Amy A. Sarjeant, Chad A. Mirkin. A coordination chemistry dichotomy for icosahedral carborane-based ligands, *Nature Chemistry*, (07 2011): 0. doi: 10.1038/nchem.1088
- 08/31/2012 6.00 D. Zheng, D. A. Giljohann, D. L. Chen, M. D. Massich, X.-Q. Wang, H. Iordanov, C. A. Mirkin, A. S. Paller. Topical delivery of siRNA-based spherical nucleic acid nanoparticle conjugates for gene regulation, *Proceedings of the National Academy of Sciences*, (07 2012): 0. doi: 10.1073/pnas.1118425109

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TOTAL:

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Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

1. "Biocompatible Infinite Coordination Polymer Nanoparticle-Nucleic Acid Conjugates for Antisense Gene Regulation"
~~Chad A. Mirkin, William E. Briley, Colin M. Calabrese, Timothy J. Merkel, IP 62/039,696.~~
2. "The Role of Modulators on the Colloidal Stability and Polydispersity of a Nanoscale Metal-Organic Framework" Chad A. Mirkin and William Morris, IP 62/116,619.

Patents Awarded

Awards

- 2015 Royal Society of Chemistry (RSC) Centenary Prize
 - 2014 Friends of the National Library of Medicine Distinguished Medical Science Award
 - 2014 Honorary Degree, Universidade Federal do Rio Grande do Sul
-

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Alejo Lifschitz	0.45	
Colin Calabrese	0.45	
FTE Equivalent:	0.90	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Natalija Chernyak	0.12
FTE Equivalent:	0.12
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Chad Mirkin	0.40	Yes
FTE Equivalent:	0.40	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>	
Alejo Lifschitz	
Total Number:	1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

5 Biocompatible Infinite Coordination Polymer Nanoparticle-Nucleic Acid Conjugates for Antisense Gene Regulation

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Chad A. Mirkin

5f-1a: Northwestern University

5f-c: 2145 Sheridan Road

Evanston IL 60208

5a: William E. Briley

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5f-c: 2145 Sheridan Road

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5a: Colin M. Calabrese

5f-1a: Northwestern University

5f-c: 2145 Sheridan Road

Evanston IL 60208

5a: Timothy J. Merkel

5f-1a: Northwestern University

5f-c: 2145 Sheridan Road

Evanston IL 60208

5 The Role of Modulators on the Colloidal Stability and Polydispersity of a Nanoscale Metal-Organic Framework

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Chad A. Mirkin

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5f-c: 2145 Sheridan Road

Evanston IL 60208

5a: William Morris

5f-1a: Northwestern University

5f-c: 2145 Sheridan Road

Evanston IL 60208

Scientific Progress

Technology Transfer

See patent activity.

Final Progress Report
June 15, 2011 - March 14, 2015

Infinite Coordination Polymer Nano- and Micro-Particles

Agreement Number: W911NF-11-1-0229

Prof. Chad Mirkin
Northwestern University
Department of Chemistry
2145 Sheridan Road
Evanston, IL, 60208

Abstract

Infinite coordination polymer (ICP) particles and metal-organic frameworks (MOFs) are attractive materials for a diverse array of applications, namely, catalysis, gas storage, chemical separations, photonics, and detection systems. Although promising, these micro- and nano-materials possess certain shortcomings that require further examination through fundamental studies. Towards overcoming these shortcomings, we proposed to investigate and drastically improve upon a series of key properties, specifically size and shape control, surface functionalization, volumetric surface area, and chemically specific gas sorption. Through these efforts, we have made significant discoveries, leading to the realization of biomolecule-functionalized nano-ICPs, unprecedentedly robust MOF topologies, and unique MOF structures with significant hydrogen and methane adsorption properties. Specifically, the novel DNA-ICP conjugates realized herein have demonstrated their utility as an *in vitro* gene regulatory tool, lending this construct to potential applications in therapeutics and diagnostics. Additionally, the carborane-MOF and MOP constructs described herein possess unique structural properties, making them key candidates for applications in selective gas sorption and boron neutron capture therapy (BNCT).

Subject Terms

Nanoparticles, infinite coordination polymer (ICP), microparticles, metal-organic frameworks (MOF)

Number of Pages: 15

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Statement of Problem Studied

We have recently described a new class of inorganic nanoparticles made by judiciously halting the polymerization of metal ions and polydentate ligands at early stages in the chemical process. These materials, known as infinite coordination polymer (ICP) particles, can be synthesized with a wide array of metal ions and ligand building blocks, spanning the micro- and nanoscale dimensions.¹ The community's interest in ICP particles is growing rapidly, as an ever growing list of potential applications is being realized. This vast array of potential applications is in part due to the fact that these structures, consisting of repeating ligands interconnected by metallic nodes, can be made from readily available and highly tailorable metal and ligand precursors.² This modularity allows ICP particles to have chemically adjustable porosities and relatively high internal surface areas, giving researchers access to a network structure that can be logically modified for many applications, such as catalysis,³ gas storage,⁴ separations,⁵ photonics,⁶ and detection systems.⁷

Considering that much of the groundwork for ICPs has only been laid in the past decade, significant advances have already been made. Yet, for ICPs to fulfill their technological potential, considerable further fundamental insights and discoveries are required. One such critical and fundamental parameter is the shape and size of ICP particles. The realization of a logical pathway towards accurate and precise particle design is desirable. With the ever-emerging field of nanomaterials and nanomedicine, the ready and repeatable realization of ICP particles on the nano-scale may have huge implications in future applications, such as therapeutics and diagnostics. Another significant current shortcoming in ICP technology is the limited ability to functionalize and characterize their surfaces. The functionality of micro- and nano-materials is directly dependent on the chemistry of their surfaces.⁸ Whereas there are a wide variety of techniques for attaching ligands to the surfaces of inorganic nanoparticles, similar approaches for ICPs are limited. Thus, for the advancement and application of ICP particles on these dimensions, developing a thorough understanding of the possible routes to surface functionalization is crucial. Therefore, a major goal of the proposed research was to develop an unprecedented tailorable and modular understanding of both particle size/shape and particle surface functionalization. In particular, we aimed to utilize this fundamental understanding for the realization of nano-scale ICP-biomolecule hybrids for *in vitro* gene regulation.

In addition to elucidating novel physical and chemical parameters for ICPs, we have made significant advances in expanding the chemical catalogue of a closely related material, metal-organic frameworks (MOFs), and in the process realized a series of novel and technologically relevant architectures. Previously, our group has shown that MOFs and ICPs containing inorganic carborane units can be effectively employed for the separation of gas mixtures.⁹⁻¹² In order to expand upon these promising early efforts, we proposed to examine the ability of these unique inorganic moieties to significantly affect key parameters and functionalities of known MOF structures. Namely, we planned to study how the inclusion of carborane, and the related bis(dicarbollide), moieties into the linkers of these structures

manipulates volumetric surface area, selective gas sorption, and structural robustness. In addition, these studies have led to realization of novel polyhedron-type structures with record-setting levels of boron. Such structures lend themselves to applications such as boron neutron capture therapy (BNCT). Through our concerted efforts, we have made significant advancements in: 1) the control of ICP particle size on the nano-scale, 2) the controlled functionalization of ICP particles with biomolecules, and 3) the improvement of the structural integrity and selective gas sorption properties of carborane-functionalized MOFs.

Summary of Results

DNA-ICP Particles for *in vitro* Gene Regulation¹³

In the Mirkin lab, we have previously developed a gold nanoparticle-based construct for the delivery of genetic material to cells, termed spherical nucleic acids (SNAs).¹⁴ These constructs are composed of gold nanoparticle cores (typically, 10-30 nm) with oligonucleotides (e.g., DNA) densely decorated on the surface of the particle in a highly oriented fashion.¹⁵ Importantly, SNAs have the ability to enter cells via endocytotic pathways and effect designed changes in the biochemical processes of the cell. Unfortunately, concerns have been raised about the potential long-term toxicity of gold nanoparticles and their metabolic fate. Thus, our lab is extremely interested in new forms of SNAs with alternative cores that are biocompatible and readily synthesized. In particular, we have targeted ICP-based constructs, as these materials can be synthesized from the combination of chemical building blocks approved by the FDA and well-understood and biologically abundant metals. In order to realize ICP particles for the delivery of oligonucleotides to cells, some fundamental hurdles had to be overcome, namely the repeatable synthesis of relatively mono-disperse particles (i.e., size control) and the high-yielding covalent attachment of oligonucleotides to the surface (i.e., surface functionalization). Towards these goals, we have developed a novel ligand motif for the realization of post-synthetic surface functionalization as well as a promising methodology for the generalizable synthesis of monodisperse nano-scale ICPs.

It is known that synthetically modular ditopic 3-hydroxy-4-pyridinone (HOPO) ligands can form coordination polymers with Fe(III), the most abundant transition metal in the body.¹⁶ Derivatives of this ligand motif also have been approved by the FDA for the treatment of iron-overload in humans. Therefore, using this HOPO-Fe(III) tandem, we saw an opportunity to design biocompatible ICP particles that could be post-synthetically modified on their surface with DNA. Thus, we synthesized the HOPO derivative DABA-bis-HP-N₃, which contains two potentially coordinating moieties as well as an azide group for oligonucleotide attachment (Figure 1). Particles were synthesized by combining DABA-bis-HP-N₃ and ferric nitrate in dilute NaOH. The crude particles were purified by centrifugal filtration using a 100 kDa molecular-weight cutoff filter. The desired particles were collected and their size was measured using dynamic light scattering (DLS), which gave a mean diameter of 10-20 nm. The particles also were characterized by TEM and AFM imaging, which corroborated the DLS results. After synthesis and characterization of the mono-disperse particles, which contained pendant azide

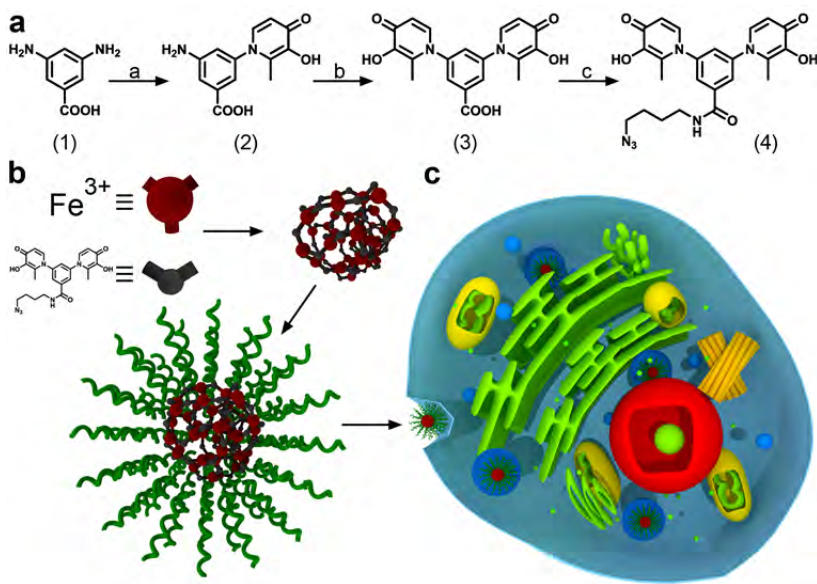


Figure 1: Synthesis and assembly of ICP particles and their cellular uptake. (a) Synthetic route to DABA-bis-HP-N₃ **4**: a) maltol, *n*-propanol, reflux, 16 h; b) maltol, ethoxyethanol, 64 h, reflux; c) 4-azidobutan-1-amine, HATU, diisopropylethylamine, DMSO, RT, 4h. (b) Assembly of ICP particles from Fe(NO₃)₃ and **4**, followed by DNA conjugation.

DLS, zeta potential, UV/Vis, and inductively couple plasma mass spectrometry (ICPMS). All of these techniques corroborated the nano-scale ICP-DNA hybrid architecture. Importantly, the layer of DNA on the surface of the particles imparts properties similar to their gold-nanoparticle predecessors, namely, increases in size, surface charge, and colloidal stability. Significantly, we have shown that through judicious organic ligand design and reaction conditions one can simply and repeatedly synthesize size-controlled ICP nanoparticles. Additionally, by appending desired

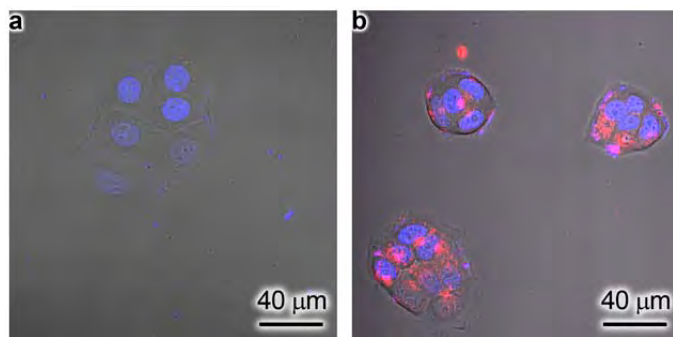


Figure 2: Cellular uptake. (a, b) Confocal microscopy images of HeLa cells treated with Cy5-ssDNA (a) and ICP-DNA particles (b; 100 nm DNA in each case). Hoechst stain denotes the nucleus in blue, whereas the Cy5 dye attached to DNA is red.

moieties, oligonucleotides were covalently appended via azide-strained alkyne “click-chemistry”. DNA functionalized with the strained alkyne

dibenzocyclooctyne (DBCO) were conjugated to the azide-functionalized ICP particles by simply mixing the two reactants in aqueous NaCl, followed by repeated filtration to removed unreacted DNA. The resulting colloid proved to be stable in Tris:HCl buffer over a wide range of temperatures. The resulting structures were characterized by AFM,

functional moieties to the organic ligand, the ICP particle surface can be functionalized post-synthetically using chemistry that is orthogonal to the coordination events within the particle itself.

Having demonstrated that we can overcome the synthetic hurdles for the realization of nano-scale ICPs and their selective surface functionalization, we examined if indeed these ICP-DNA hybrid structures could enter cells and deliver genetic information for the regulation of endogenous biochemical

processes. To test our hypothesis, cellular uptake was examined in HeLa cervical cancer cells using dye-labeled DNA (Figure 2). The ICP-DNA particles were found to cross cell membranes with efficiency very similar to the analogous gold nanoparticle-based SNA. Knowing that the particles were able to readily enter cells, we tested whether or not they could efficiently deliver their genetic cargo to the cell and effect expression of a known cancer-related mRNA transcript *in vitro*. SKOV-3 ovarian cancer cells were chosen for this purpose since they over express the HER2 gene, which is known to contribute to malignant cell growth and differentiation. Cells were treated with non-targeting ICP-DNA particles, HER2-targeting ICP-DNA particles, or HER2-targeting free DNA complexed with the commercial transfection agent Lipofectamine™ (Figure 3). Treatment with anti-HER2 ICP-DNA particles reduced HER2 expression by up to 81 % in a dose-dependent fashion. Importantly, in contrast to Lipofectamine™, no toxic effects or

cell death resulted from treatment with the ICP-DNA particles.

In summary, we have elucidated a facile method for the synthesis of biocompatible, DNA-functionalized ICP nanoparticles that are able to readily traverse the cellular membrane and deliver genetic material for the regulation of protein translation. The core of the ICP particle is composed of benign building blocks that are not expected to pose significant health hazards. This study represents a major step towards clinically viable gene regulation and demonstrates the utility and modularity of ICP technology.

Our ongoing efforts are focused on the systematic synthetic modification of HOPO derivatives to include various orthogonal organic functionalities that promote DNA conjugation. By creating a library of HOPO derivatives with different organic moieties capable of

orthogonal “click-type” reactions, we can deliver ICP-DNA nanoparticles with multiple different DNA sequences on a single particle. The construction of these architectures will allow for the simultaneous regulation of multiple intracellular processes using a single chemical entity.

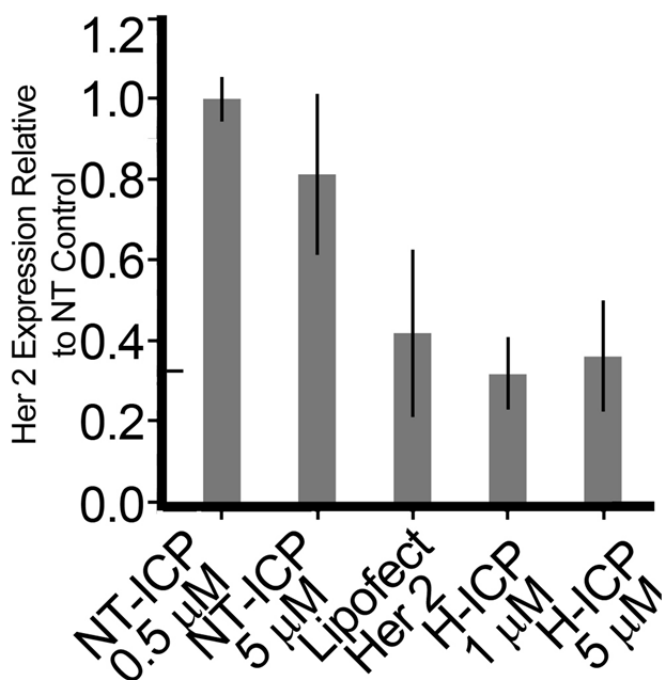


Figure 3: Expression of HER2 protein in SKOV-3 cells treated with nontargeting (NT) ICP-DNA particles, HER2-targeting ssDNA + Lipofectamine™ (25 nm DNA basis), and HER2-targeting ICP-DNA in increasing doses.

A Carborane-Based MOF with High Methane and Hydrogen Storage Capacity¹⁷

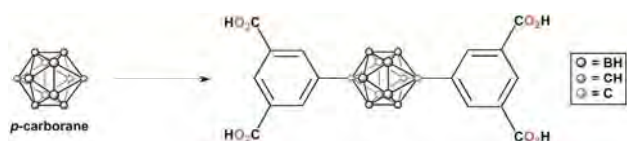


Figure 4: Synthesis of carborane-bis(isophthalic acid) ligand (**LH₄**) used to construct **NU-135**. Reaction conditions: i) *n*-BuLi, THF; CuCl, THF -40 to 70 °C; diethyl 5-iodoisophthalate, Pd(PPh₃)₄, NMP, 100 °C, 16 h (42 %). ii) LiOH (1 M), THF/H₂O 2:1, RT, 36 h; H₃O⁺ (84 %).

ability of MOFs to adsorb gases, especially in a chemically specific manner, is a function of the pore geometry, volume, surface area, and density. These properties in turn are highly dependent on the structure and chemical make-up of the linker struts used to build the MOF. Previously, we have shown that the inclusion of carborane moieties into the linker struts of MOFs can impart exciting properties on the construct, such as high thermal stability and selective adsorption.¹⁹ However, these previously reported structures had low surface area and small pore volumes, making them relatively poor performers overall. Thus, using this concept of carborane-functionalization, we continued to explore if we could realize novel architectures with appreciably larger surface area and volume parameters. We hoped to elucidate any properties of the MOF that were a direct consequence of the inclusion of the chemically unique carborane

Nanoporous materials such as MOFs form an important class of materials that can potentially be used for the separation and storage of energy and environmentally relevant gases, such as methane and hydrogen.¹⁸ In particular, MOFs have been pegged as potential sorption materials for onboard storage of methane and/or hydrogen in the next generation of vehicles, which could be useful to the ARO. Importantly, the

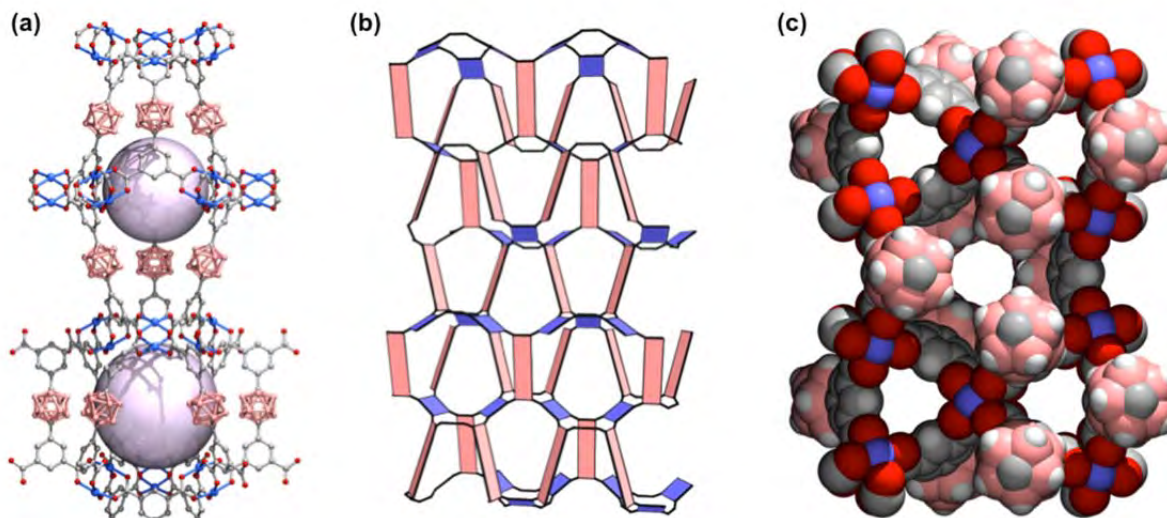


Figure 5: Representations of the crystal structure of **NU-135**. (a) Detail of pores, viewed along the *ab* plane. Lilac spheres indicate the largest sphere-shaped voids that can be found within the evacuated MOF as defined by the internal van der Waals surface of the material. Hydrogen atoms removed for clarity. (b) Simplified **nbo** network viewed along the *ab* plane. Blue squares = Cu₂ paddlewheels; pink rectangles = carborane bis(isophthalic acid) ligands. (c) Space-filling representation, viewed along the *c* axis, illustrating the carborane-lined pores. Atom code; C = grey; H = white; O = red; B = pink; Cu = blue.

moiety by directly comparing our new MOF to a reported isorecticular predecessor containing purely organic (phenylene-based) linker struts.

To realize a new carborane-based MOF with a large pore volume and surface area, the long *para*-carborane-containing strut **LH₄** was synthesized (Figure 4). By combing this strut with copper nitrate under common solvothermal conditions, blue crystals were realized, which upon single-crystal X-ray diffraction analysis proved to be a new MOF architecture (**NU-135**, Figure 5). Importantly, this structure is isorecticular with the MOF built from the purely organic (terphenylene) analog strut (NOTT-101).²⁰ Therefore, we could directly compare these structures to determine how the presence of the carborane affects structural and functional parameters. Upon activation of the structure by supercritical CO₂, the volumetric surface area of **NU-135** was determined to be ca. 30 % greater than that of the NOTT-101 analog. This significant change in surface area is a direct function of the globular nature of the carborane, thus acting as an effective sphere with a diameter approximately that of a single benzene ring. This is highly interesting as increasing volumetric surface area is a well-known method for increasing gas adsorption. Therefore, in collaboration with the National Institute of Standards and Technology (NIST), the gas uptake properties of **NU-135** were measured (Figure 6). **NU-135** shows significantly high overall uptake compared to previous carborane-functionalized ICPs and MOFs, owing to the increased surface area and pore volume. Importantly, we observed very high

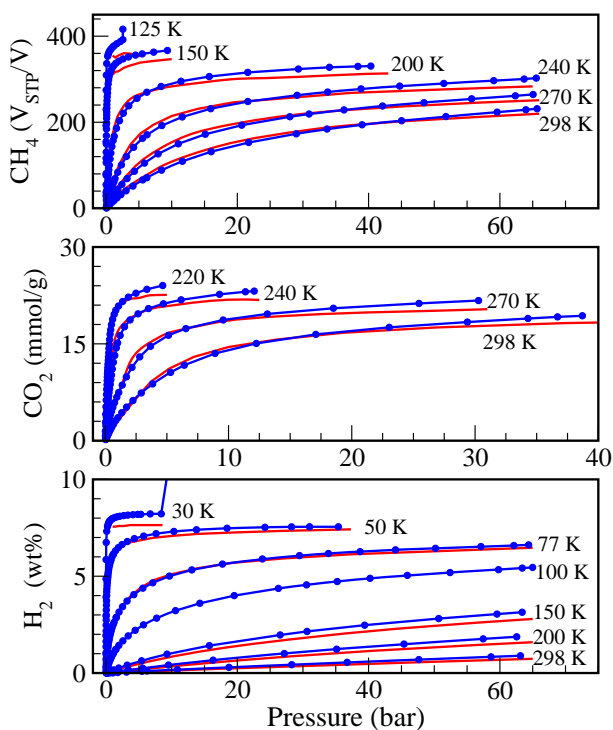


Figure 6: Experimental (blue) and simulated (red) high-pressure absolute gas adsorption isotherms for **NU-135** at several temperatures.

capacity of methane uptake, specifically an absolute methane storage capacity of 10.3 mmol/cm³ at 65 bar. This represents is an important advance as it demonstrates the ability of a material to absorb natural gas to the extent where it may become commercially attractive. Sample degradation was not observed over multiple cycles. The ability of **NU-135** to adsorb hydrogen, another potential fuel of the future, was also examined. **NU-135** was measured to have a maximum absolute volumetric hydrogen uptake value of ca. 49 g/L above ca. 55 bar at 77 K. This value places **NU-135** amongst the highest for all MOFs for volumetric hydrogen storage.

From the empirically determined volumetric surface area and the combined results of methane and hydrogen adsorption studies we can conclude that the unique quasi-spherical geometry of carboranes allows for the synthesis of MOFs that are

isorecticular to their organic analogs, yet exhibited enhanced structural and functional parameters. The incorporation of carborane polyhedrals into other high-performance MOFs is an exciting prospect, and it will hopefully lead to novel materials with record-breaking gas sorption properties. This novel strategy, in which a carborane moiety is employed to greatly increase volumetric surface area, will allow us and others to expand the current capability of porous materials for gas storage applications.

Stabilization of a Highly Porous MOF Using a Carborane-Based Linker Strut²¹

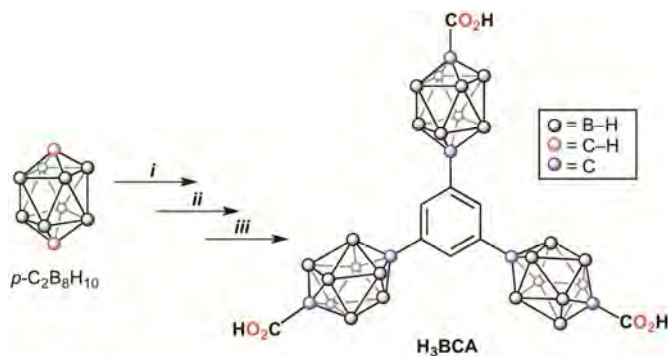


Figure 7: Reaction conditions: i) *n*-BuLi, THF; CuCl, THF - 40 to 70 °C; 1,3,5-tribromobenzene, PdCl₂(PPh₃)₂, 70 °C, 12 h (79 %). ii) *n*-BuLi, THF; ethyl chloroformate -78 °C to RT, 12 h (68 %); iii) LiOH, THF/EtOH/H₂O 3:2:1 rt, 12 h; H₃O⁺ (90 %).

Having demonstrated that the inclusion of carborane motifs into MOFs can impart structural parameters that are unachievable with their organic analogs, we sought to examine if we could use the steric bulk and rigidity of carboranes to stabilize highly porous MOF topologies that are known to be unstable with the analogous purely organic linker. As previously stated, structures with high surface areas and porosity are desirable for applications in gas storage of interest to the ARO.

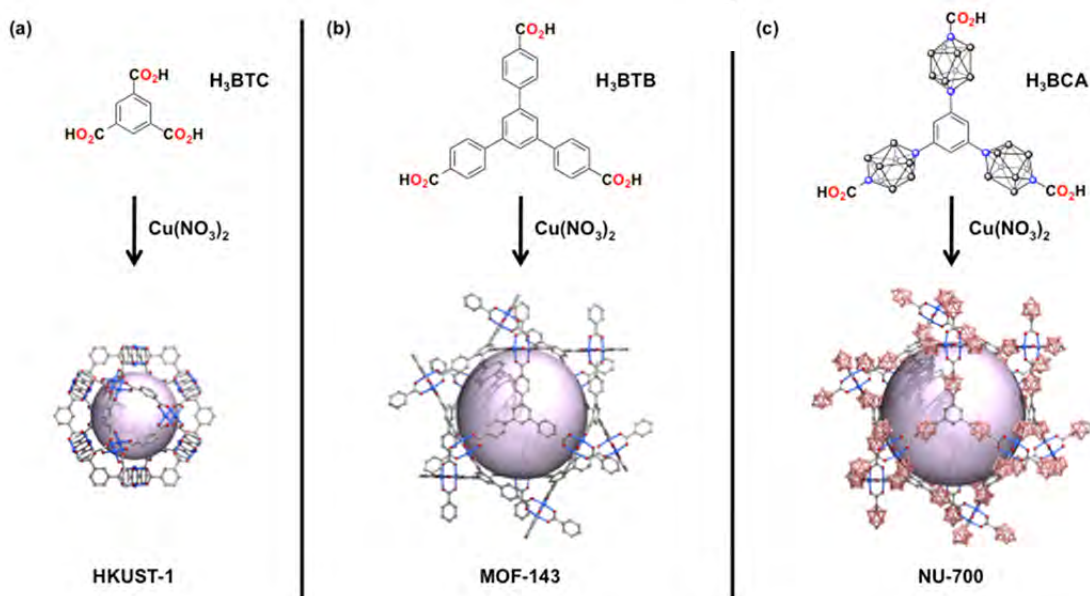


Figure 8: Detail of pores, viewed along the 111 plane of (a) HKUST-1; (b) MOF-143; (c) NU-700. Lilac spheres indicate the largest sphere-shaped voids that can be found within the evacuated MOF as defined by the internal van der Waals surface of the material. Hydrogen atoms removed for clarity.

One method for accessing such MOF architectures is through using linker struts that impart significant spacing between the metal nodes. This has been shown to occur with three-fold symmetric tritopic linker struts, but somewhat unexpectedly, when many of these structures are activated (e.g., vacuum, heat, supercritical CO₂) their crystallinity is destroyed and their porosity is lost. Thus, we hypothesized that by modifying these tritopic organic linkers to contain rigid and sterically bulky polyhedral carboranes we could rigidify and stabilize these highly porous structures and realize new and promising architectures for efficient gas storage.

Having synthesized the three-fold symmetric tritopic carborane-containing linker **H₃BCA** (Figure 7), the linker was added to copper nitrate under solvothermal conditions, which yielded single crystals suitable for an X-ray diffraction study. The crystallographically determined structure (**NU-700**) proved to be isorecticular with the unstable organic analog MOF-143 (Figure 8). Critically, we were able to demonstrate that, in contrast to MOF-143, **NU-700** could be activated via supercritical CO₂ and vacuum/heating. Upon activation, the porosity of the framework was measured using nitrogen adsorption at 77 K, which gave a Brunauer-Emmett-Teller surface area of 1,870 m²/g. The improved stability of **NU-700** over MOF-143 is attributed to the unique properties of the constituent carboranyl moieties. In addition to rigidity and steric bulk, we hypothesize that the radially oriented, hydridic B-H units of carborane exhibits a highly symmetric and uniform charge density that precludes strong interactions with the solvent molecules, which is known to destroy MOF crystals through capillary forces. Importantly, this work demonstrates a potentially general platform for the stabilization of difficult-to-activate MOFs, whereby simple replacement of phenyl spacers with carboranes does not affect the

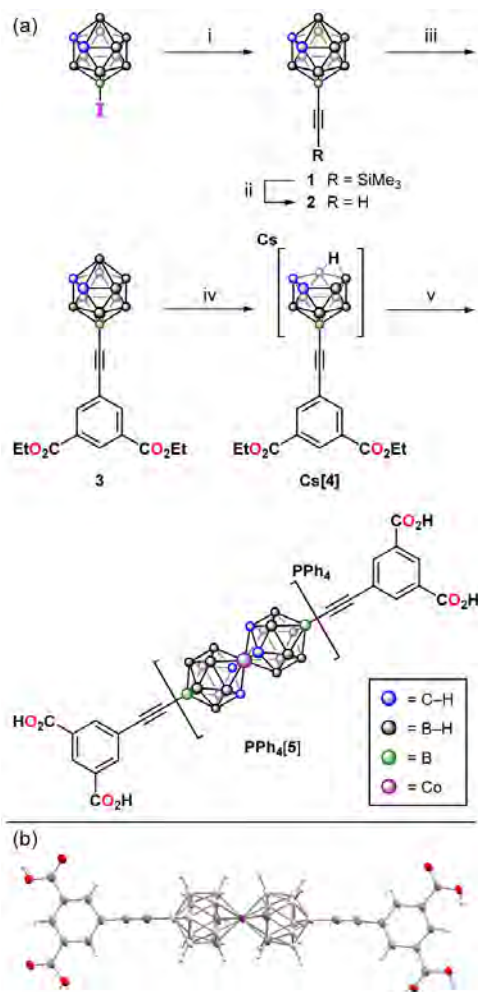


Figure 9: (a) Synthesis of linker [PPh₄][5].^a (b) ORTEP-type representation of the crystallographically determined molecular structure of the [5] anion in its cesium salt.^b a) Reagents and conditions: (i) (trimethylsilyl)ethynylmagnesium bromide (3 equiv), PdCl₂(PPh₃)₂ (5 mol%), THF/Et₂O, 65°C, 16 h, 92%. (ii) KOH (2 equiv), H₂O/MeOH (1:4), rt, 2 h, 96%. (iii) diethyl 5-iodoisophthalate, Pd(PPh₃)₄ (3 mol%), CuI (10 mol%), *i*-Pr₂NEt/THF (1:1), 65°C, 24 h, 85%. (iv) CsF, EtOH, reflux, 6h, 95%. (v) CoCl₂, NaOH (40% aq), 105°C, 1 h; Et₂O, HCl (aq); [PPh₄]Br, H₂O. b) Thermal ellipsoids are drawn at 50% probability. Atom color code: Co = purple; C = grey; H = white; B = pink; O = red. Cesium cations are omitted for clarity.

underlying structure.

Metallo-carborane-Based MOF with a Complex Topology²²

In our efforts to realize novel MOF structures with unique structural and functional properties through the inclusion of carborane-based linker struts, we examined the realization of MOFs based on axially functionalized bis(dicarbollide) metal complexes as linkers. We originally became interested in these chemical motifs as they present an intriguing combination of rich redox chemistry and a linear geometry,²³ making these complexes perfectly suited for the construction of redox-active MOF materials. In particular, we imagined the realization of metallocarborane-based constructs for stimuli responsive porous materials, selective gas separation and storage, sensing, and waste remediation. Towards these goals, we targeted an analog of the highly porous and phase-pure MOF NOTT-104, which is based on a linear terphenylene-derived linker.²⁴ Therefore, we synthesized the symmetric and linear cobalt bis(dicarbollide)-based linker **PPh₄[5]** (Figure 9). This linker design was chosen specifically because of the above-mentioned propensity of the organic analogs to form, reliably and in high purity, highly porous MOFs with a singular topology (**fof**). In stark contrast to the organic analogs, the solvothermal reaction between **PPh₄[5]** and copper nitrate yielded an array of topologies, included one never-before-seen architecture.

The mixing of **PPh₄[5]** and copper nitrate under solvothermal conditions resulted in the growth of small, green crystals, which upon closer inspection consisted of three different crystal habits: plates, prisms, and cubes. Through single-crystal X-ray diffraction studies it was determined that the plate-like crystals were the predicted archetypical **fof** topology (**NU-150**) (Figure 10). Of particular interest in this structure is the apparent bend at

each alkyne region in the struts, giving an overall linear structure and allowing for the **fof** topology. In contrast, studies of the prismatic crystals elucidated the alternative and rare, but

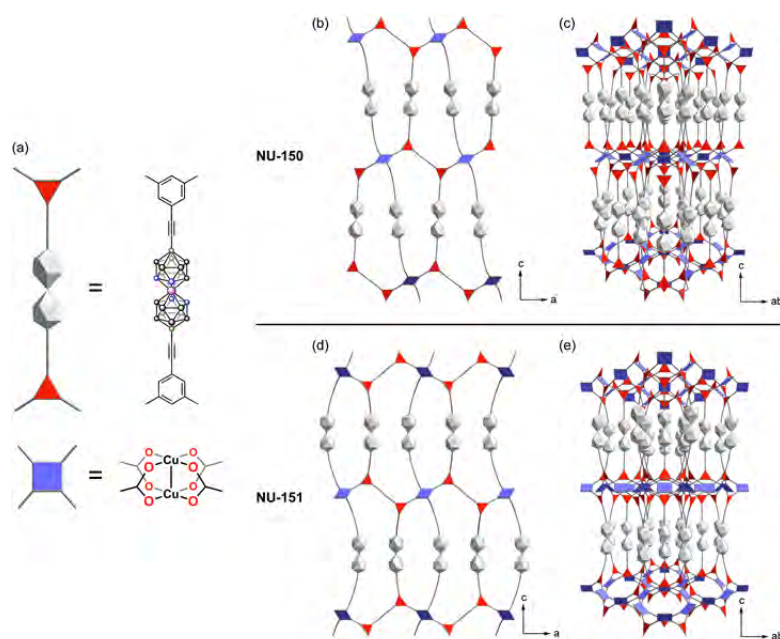


Figure 10: Representation of crystal structure of **NU-150** and **NU-151**. (a) Simplified representation of the linker (top) and biscopper(II) paddlewheel node (bottom). (b,c) Orthographic and perspective views, respectively, of **NU-150**. (d,e) Orthographic and perspective views, respectively, of **NU-151**. In all cases the anionic nature of the bis(dicarbollide) complex gives the framework an overall negative charge.

known, **sty** topology (**NU-151**, Figure 10). Although the overall topology is fairly similar between these two architectures, in **NU-151** the bending of the alkyne regions of the strut area aligned in concert, giving each strut a pronounced bend in the crystal structure. Finally, a single crystal X-ray diffraction study of the cubic crystal revealed a novel **hbk** topology (**NU-152**, Figure 11), which is uniquely composed of interconnected metal-organic polyhedral (MOPs). These coordination polyhedral, are composed of 12 biscopper paddlewheels, making up the vertices of a cuboctahedron. In this structure, the cobalt bis(dicarbollide)-based linkers exhibit not only bending in the alkyne regions, but also twisting at the cobalt metal center. These structural considerations behave in concert to allow this unprecedented topology. Importantly, this novel arrangement of linkers in three-dimensions produces a void space in **NU-152** (79 %) that is significantly greater than that observed in **NU-150** and **NU-151** (70 %). Importantly, this work illustrates that the expected topology is not always obtained, even when a particularly robust system is used. In this case, it seems that the length and flexibility of the linker play an important role in the formation of the unprecedented framework and deviation from the predicted one. This work exemplifies how new topologies may be accessed by using structural units that possess properties that are not usually associated with MOFs, such as flexibility and curvature.

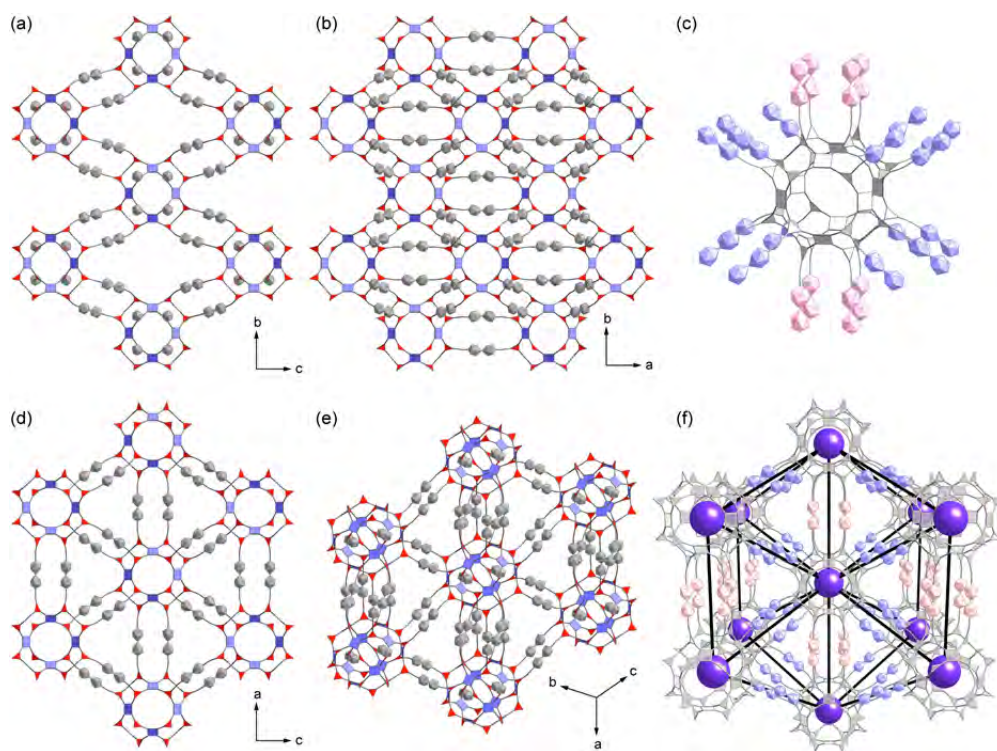


Figure 11: Representations of the crystal structure of **NU-152**. (a,b,d,e) The bis(dicarbollide) linkers are represented by two red triangles connected by grey conjoined icosahedra, and the biscopper(II) paddlewheels are represented by blue squares (as shown in Figure 5.1). (c) A single cuboctahedral supercluster (grey) with crystallographically independent linkers shown in blue and pink. (f) Purple spheres represent the centroids of the 10-coordinate cuboctahedra, and black lines represent the connectivities between the cuboctahedra via sets of four 'pink' linkers or sets of two 'blue' linkers.

Carborane-Based Metal-Organic Polyhedron²⁵

Inspired by the presence of the unique metal-organic polyhedra (MOPs) in the three-dimensional **hbk** topology of **NU-152**, we sought to realize an analogous free-standing polyhedron containing carborane moieties, as boron-rich nanomaterials have recently proven to be potentially applicable for the neutron capture therapy of tumors.²⁶ By synthesizing boron-rich nanomaterials in this way (i.e., through the combination of organic ligands and metals), we could realize well-defined constructs that could be structurally characterized through single-crystal X-ray diffraction studies, a uncommon feature in this field. Towards this goal, we synthesized the carborane-based ligand **LH₂** (**2**, Figure 12),

which unlike the previous carborane-containing motifs does not possess the necessary symmetry to form three-dimensional infinite networks. To realize the targeted MOP, **LH₂** was mixed with copper acetate under solvothermal conditions, yielding blue, block-like crystals. Upon isolation, visual inspection showed crystals of a single crystal habit that were shown to possess bulk purity

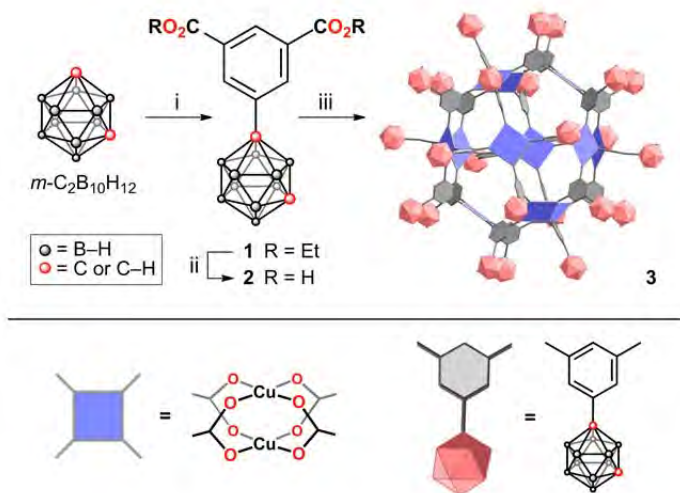


Figure 12: The synthesis of compound **3**. Reaction conditions: i) *n*-BuLi, THF; CuCl, THF, -40 to 70 °C; diethyl 5-iodoisophthalate, PdCl₂(PPh₃)₂, NMP, 100 °C, 48 h (48 %). ii) LiOH (1 M), THF/H₂O 2:1, rt, 36 h; H₃O⁺ (100 %). iii) Cu₂(OAc)₄·2H₂O, DMF, RT, 4 days (42 %). The representation of the compound **3** is simplified: pink icosahedra = carborane cages; blue squares = biscopper paddlewheel nodes; grey hexagons = benzene rings.

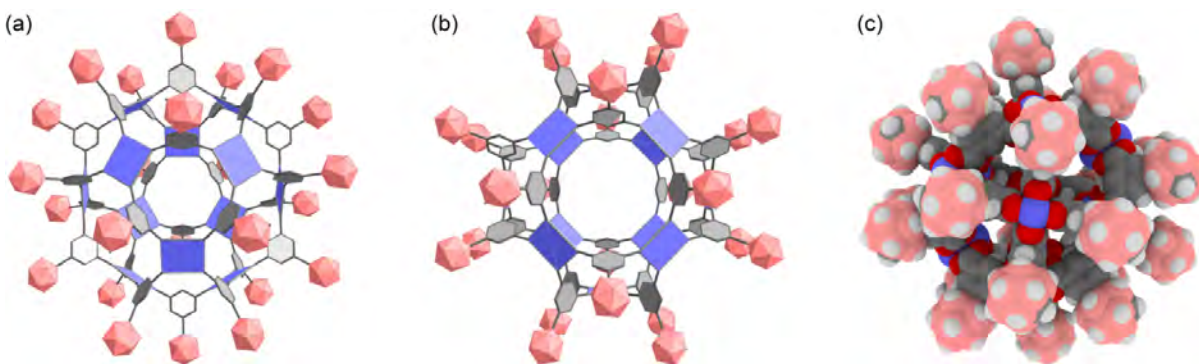


Figure 13: Representation of the crystallographically derived molecular structure of **3**. (a) View along the crystallographic *c* axis. This axis corresponds to a molecular *C*₃ symmetry axis. (b) View along the molecular *C*₄ symmetry axis. Color key for (a) and (b): pink icosahedra = carborane cages; blue squares = biscopper paddlewheel nodes; grey hexagons = benzene rings. (c) Space-filling representation of **3**. Color key: pink = B; red = O; blue = Cu; grey = carbon; white = hydrogen. (Coordinated solvent removed for clarity).

via powder X-ray diffraction (PXRD). Importantly, the crystallinity of the complex allows for a single crystal X-ray diffraction study, allowing for the elucidation of the structure of the realized supramolecular cage (**CB-MOP**, **3**) (Figure 13). The determined structure has a diameter of 3.6 nm and an internal cavity with a diameter of 1.6 nm. The structure could be activated, giving a surface area of 625 m²/g, is consistent with the porous nature of the material and demonstrative of its stability. Each molecular polyhedron contains 240 boron atoms, corresponding to a gravimetric boron content of 29 %, which is currently the largest amount of boron atoms reported in a molecular species. Owing to its high and dense boron content, a carborane-base MOP, such as **CB-MOP** (**3**), is a prime candidate for exploration of boron neutron capture therapy.

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