All Day Carbon Capture and Sequestration through Molecular and Phase-Change Hybrid Module

Abstract: As the world slowly transitions from conventional fossil fuels to renewable forms of energy, environmentally friendly CO_2 capture is urgently needed. Currently, liquid amine and ionic liquid-based systems are utilized for this purpose which both require large industrial point source for efficient performance. Liquid amin scrubbing leads to the formation of stable carbamate salts with high enthalpy of formation, and it is therefore difficult to recover the initial liquid for cyclic operation while ionic liquid-based systems suffer from high operational cost. Solid-state chemisorbent materials provide a viable solution for direct air capture of CO_2 (DAC) with stable and long-cyclic performance. However, they require high temperature for the CO_2 desorption. Here, we propose a new transformative paradigm to conduct all-day DAC with a hybrid solar-driven module. On the energy aspect, the module harvest and store full spectrum of solar energy and generate temperature of >100 ^{o}C in 24/7 manner for continous ooperatiuon of the system. On the process aspect, the module harvests CO_2 and humidity from air and provides valuable products of $CaCO_3$ and drinking water. We envision this stand-alone paradigm open a new path to address global emissions and consequent environmental challenges.

Introduction. Global CO_2 emissions have increased at an alarming rate of approximately 40% in the last 10 years,[1] with the rate expected to double by 2050.[2] Consequently, the reduction of environmental CO_2 has major implications on the global society[3], and its capture is being viewed as one of the most prominent means of decarbonization. Demands for efficient CO_2 capture technologies are driving the exploration of different mechanisms.[4] Current commercial technologies employed for CO_2 capture include the use of amine-based solvents, mainly monoethanolamine (MEA), diethanolamine, and methyldienthanolamine.[5–7] However, these forms of capture lead to the formation of stable carbamate/carbonate salts[8], making it difficult to recover the amine-based solvent for cyclic operation. Furthermore, the large enthalpy of CO_2 capture reaction corresponds to highly energy intensive and costly cyclic systems.[9,10] Amine-based systems suffer from low CO_2 capture capacity,[10] toxicity,[11] loss of reagent due to evaporation, and equipment corrosion.[12] While over the half the CO_2 emissions are from large, industrial point sources, the remainder of this emission are from small mobile source which is dispersed in the air. Thus, an economical pathway to reduce atmospheric level of CO_2 is becoming a critical issue.

Direct air capture of CO_2 (DAC) is a promising approach to address this global challenge. The materials for DAC are divided in two categories of chemisorbent and physisorbent materials. While the desorption process in the latter category require less energy, these materials do not high CO_2 absorption capacity and absorption selectivity. They absorb a large portion of water from humid air along with CO_2 leading to their inefficient performance. On the other side, the chemisorbent material have high capacity and selectivity, but need a source of thermal energy with temperature of ~100 ^oC for desired cyclic performance.

Objectives. Here, we aim to develop a disruptive paradigm for efficient and economical DAC process through a solar-driven hybrid module. This hybrid system operates stand-alone in 24/7 manner with no external energy input, harvests atmospheric CO_2 and produces drinking water and $CaCO_3$ as byproducts.

Approach. Recently, we combined the physics of molecular energy and latent heat storage to introduce an *integrated* harvesting and storage hybrid paradigm for 24/7 energy delivery with temperature of > 100 ^oC. The hybrid paradigm utilizes heat localization during the day to provide a harvesting efficiency of 73% at small-scale and ~90% at large-scale. Remarkably, at night, the stored energy by the hybrid system is recovered with an efficiency of 80% and higher temperature than that of

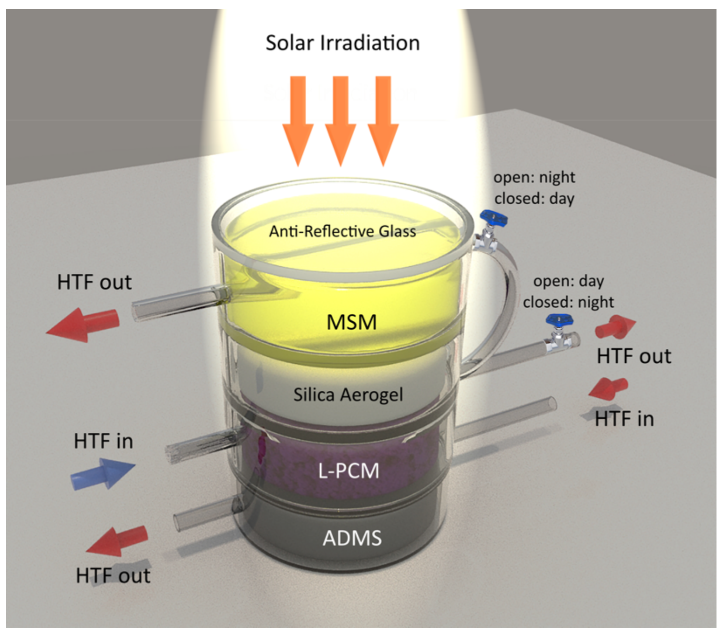

Figure 1: Concept of all-day carbon capture and sequestration. The hybrid consists of a molecular storage material (MSM), a silica aerogel, a localized phase-change material (L-PCM) and an ADMS compartment to capture and convert CO_2.

the day, in contrast to all the state-of-the-art systems. This new concept is recently disclosed by PI and Co-PI in Joule (Cover article)[13]. This concept provides required energy for CO_2 desorption of chemisorbent materials. In this program, we choose aqueous solution of $Ca(OH)_2$ as the heat transfer fluid (HTF). This fluid is an effective medium to absorb CO_2 and convert it to drinking water and $CaCO_3$. This concept is demonstrated in another collaborative work by PI and Co-PI[14]. We will initially synthesize amine-decorated mesoporous silica (ADMS) particles with high CO_2 absorption capacity. These ADMS particles have high active surface area for CO_2 capture and high selectivity of CO_2 adsorption compared to H_2O (i.e. > 94% CO_2 even in high humid air) making them a suitable choice for humid hot environments[15]. Once developed, we will characterize chemical composition, microstructure and CO_2 absorption of ADMS particles to optimize their performance and rationally design dimensions of each component in the hybrid module. The ADMS will be included underneath of the PCM material as shown in **Fig. 1** to avoid any interruption in the solar irradiation path through the hybrid module. The ADMS is in direct contact with air to absorb CO_2. Once saturated with CO_2, the air flow to the ADMS compartment will be stopped and the hot fluid will be circulated over the ADMS particles to absorb the CO_2 and re-activate the ADMS particles. The flow rate of HTF is adjusted to maximize CO_2 dissolutions with minimal heat losses. The hot solution of $Ca(OH)_2$ will lose some of it thermal energy in the desorption process and the outlet HTF from the ADMS compartment has lower temperate than the inlet stream. The outlet $Ca(OH)_2$ solution saturated with CO_2 is taken to a reservoir where the solution converts to drinking water and $CaCO_3$ as demonstrated by PIs[14]. The drinking water may be re-combined in the initial $Ca(OH)_2$ solution to re-circulate through the cycle or could be used as a byproduct of the system. We should add that this approach of carbon capture has value proposition as the byproduct $CaCO_3$ is more valuable than the initial solution of $Ca(OH)_2$. Note that during the day, the thermal energy for ADMS desorption will be provided by PCM, but at night the majority of thermal energy is provided by MSM. That is, the system runs continuously 24/7 to capture CO_2 and convert it to byproducts. Furthermore, the system has the potential to be implemented in point-source CO_2 emission settings with similar performance.

Outcomes and Time Frame. This project provides a transformative paradigm to capture atmospheric CO_2 and to convert it to valuable byproducts of water and $CaCO_3$. The project will start in August 2020 once funded and will run for 18 months. **Milestone 1 (6 mo):** Synthesis of high capacity ADMS, **Milestone 2 (12 mo):** Demonstration of efficient CO_2 capture and sequestration**, Milestone 3 (18 mo):** Demonstration of 24/7 performance of the system with no power input

Progress and Management Reporting. The PI and Co-PI are committed to provide required progress report and presentations based on the guidelines of the program.

Equipment and Facilities. The NanoTherm lab is equipped with a solar simulator with an optical concentrator up to 50x concentration and all metrology resources to examine performance of the hybrid module. Dr. Lee's group is equipped with 15 fume hoods in the SERC building for experiments ranging from organic and inorganic synthesis to surface science.

Internal and External Funding. We received funding from Petroleum Research Fund to study nano-scale physics of CO_2 hydrate structures, \$110 k. We received Advanced Manufacturing Fund to develop large-scale module for solar energy harvesting and storage, \$50 k.

Future Proposal Submissions. We submitted a proposal to the DOE solicitation (DE-FOA-0002243) on the solar energy harvesting and storage on 6/15/2020. We are working on a proposal of atmospheric harvesting of CO_2 to DOE solicitation (DE-FOA-0001953) which is due 7/22/2020.

BIOGRAPHICAL SKETCH (Hadi Ghasemi, PhD)

(a) Professional Preparation

Univ. of Science and Tech.	Iran	Materials Science	Bachelor of Science, 2003
Sharif University of Technology	Iran	Materials Science	Master of Science, 2007
University of Toronto	Canada	Mech. Engineering	PhD, 2011
MIT	USA	Mech. Engineering	2011-2014

(b) Appointments

Sept. 2019 - Present	Cullen Associate Prof. of Mechanical Eng., University of Houston
Sept. 2014 - 2019	Bill D. Cook Assistant Prof. of Mechanical Eng., University of Houston
Dec. 2011- 2014	Postdoctoral Associate, Department of Mechanical Engineering, MIT

(c) Publications

Most Closely Related to the Proposed Project

1) Varun Kashyap, Siwakorn Sakunkaewkasem, Parham Jafari, Masoumeh Nazari, Bahareh Eslami, Sina Nazifi, Peyman Irajizad, Maria D. Marquez, T. Randall Lee, and Hadi Ghasemi, "Full spectrum solar thermal energy harvesting and storage by a molecular and phase-change hybrid material", **Joule**, 3(12), 3100-3111 (2019). https://www.sciencedirect.com/science/article/abs/pii/S2542435119305318

2) Varun Kashyap, Riddhiman Medhi, Peyman Irajizad, Parham Jafari, Masoumeh Nazari, Ali Masoudi, Maria D. Marquez, T. Randall Lee and Hadi Ghasemi, "Capture and conversion of carbon dioxide by solar heat localization", **Sustainable Energy and Fuels**, 3, 272-279, 2019. https://pubs.rsc.org/en/content/articlelanding/2019/se/c8se00546j/unauth#!divAbstract

3) Varun Kahshyap, Abdullah Al-Bayati, Seyed Mohammad Sajadi, Peyman Irajizad, Sing Hi Wang and Hadi Ghasemi, "Flexible anti-clogging graphite film for scalable solar desalination by heat localization**", Journal of Materials Chemistry A**, 5, 15227-15234, 2017. https://pubs.rsc.org/en/Content/ArticleLanding/2017/TA/C7TA03977H#!divAbstract

4) Seyed Mohammad Sajadi*,Nazanin Farokhnia*, Peyman Irajizad, Munib Hasnain and Hadi Ghasemi, "Flexible artificially networked structure for ambient/high pressure solar steam generation", **Journal of Materials Chemistry A**, 4, 4700-4705, 2016.(* Equal Contributor). http://pubs.rsc.org/en/content/articlelanding/2016/ta/c6ta01205a#!divAbstract

5) H. Ghasemi, G. Ni, A.M. Marconnet, J. Loomis, S. Yerci, N. Miljkovic, and G. Chen, "Solar steam generation by heat localization", **Nature Communications**, 5:4449, (2014). http://www.nature.com/ncomms/2014/140721/ncomms5449/full/ncomms5449.html

Other Significant Products

1) Navid Namdari, Behrouz Mohammadian, Parham Jafari, Reza Mohammadi, Hossein Sojoudi, Hadi Ghasemi and Reza Rizvi, "Advanced functional surfaces through controlled damage and instabilities", **Materials Horizons**, (2019).

https://pubs.rsc.org/en/content/articlelanding/2019/mh/c9mh01516g#!divAbstract

2) Yanfei Xu, Daniel Kraemer, Bai Song, Zhang Jiang, Jiawei Zhou, James Loomis, Jianjian Wang, Mingda Li, Hadi Ghasemi, Xiaopeng Huang, Xiaobo Li, Gang Chen, "Nanostructured Polymer Films with Metal-like Thermal Conductivity", **Nature Communications**, 10, 1771, (2019).

https://www.nature.com/articles/s41467-019-09697-7

3) Peyman Irajizad, Abdullah Al-Bayati, Bahareh Eslamiz, Taha Shafquat, Masoumeh Nazari, Parham Jafari, Varun Kashyap, Ali Masoudi, Daniel Araya and Hadi Ghasemi, "Stress-Localized Durable Icephobic Surfaces", **Materials Horizons**, 6, 758-766, (2019).

https://pubs.rsc.org/en/content/articlelanding/2019/mh/c8mh01291a#!divAbstract

4) Peyman Irajizaad, Munib Hasnain, Nazanin Farokhnia, Seyed Sajadi, and Hadi Ghasemi, "Magnetic slippery extreme icephobic surfaces", **Nature Communications**, 7, 13395, (2016).

http://www.nature.com/articles/ncomms13395

5) Seok Woo Lee, Yuan Yang, Hyun-Wook Lee, Hadi Ghasemi, Daniel Kraemer, Gang Chen and Yi Cui, "An electrochemical system for efficiently harvesting low-grade heat energy", **Nature Communications**, 5:3942, (2014).
http://www.nature.com/ncomms/2014/140521/ncomms4942/full/ncomms4942.html

(d) Synergistic Activities

1. **Reviewer for more than 40 international journals including** Science, Nature Energy, Nature Sustainability, Nature Communications, Science Advances, Nano Letters, Advanced Materials, Advanced Functional Materials, ACS Nano, Nano Energy, PNAS, Joule, Journal of Materials Chemistry A, Nature Scientific Reports, Langmuir, Applied Physics Letter, Advances in Colloid and Interface Science, International Journal of Heat and Mass Transfer, International Journal of Thermal Sciences, International Journal of Multiphase Flow, Current Opinion in Colloid and Interface Science, Colloids and Surfaces A, Applied Energy, Energy, Journal of Materials Science & Engineering C, Applied Surface Science and others; **Panelist for National Science Foundation**- CBET program and AFOSR.

2. **Co-Chair of ASME NEES (Nanoengineering for Energy and Sustainability) committee. Organized micro/nano poster forum (Topic organizer) in IMECE conferences (2015 and 2016)**. The forum allows graduate students and post-doctoral associates to network with leaders and advocators in micro- and nanotechnology and to be recognized for their hard and creative work; **Track chair of "micro and nano technology in energy systems"** in ASME 2014, 8th International Conference on Energy Sustainability; **Topic organizer of "Solar thermochemistry and solar fuels" and "micro and nano technology in energy systems"** in IMECE 2014.

3. **Established a quarterly platform for K-12 students to visit PI's research group**. The PI teaches the students about research in micro/nano engineering. The involved students in these tours conduct hands-on experiments. (Oct. 2014-now); **Created summer internship opportunity for undergraduate students through SURF, PURS, and Honor programs at the University of Houston**.

4. Received **second place winner of Texas New Venture Competition (2019), TEEX Product Development Center Prize (2019), Early Innovator Award (2019), University Research Excellence Award (2019), College Research Excellence Award (2018), NASA iTech Top Three Innovator Award (2017), University Teaching Excellence Award (2016), AFOSR Young Investigator Award (YIP) (2016),** and **Departmental Citizenship Award (2015).** PI research has been highlighted in **Nature, Science, Economist, Discovery News, Scientific American, Popular Science, Yahoo News, NPR, and Business Standard, MIT news, among others.**

T. Randall Lee
Cullen Distinguished University Chair, Department of Chemistry, University of Houston
4800 Calhoun Road, Houston, TX 77204-5003, 713-743-2724, trlee@uh.edu

PROFESSIONAL PREPARATION

Rice University	Houston, TX	Chemistry	B.A. 1985
Harvard University	Cambridge, MA	Chemistry	Ph.D. 1991
California Institute of Technology	Pasadena, CA	Chemistry	Postdoc 1991–93

APPOINTMENTS

2012–present	Assoc. Dean Research, College of Natural Sciences & Mathematics, UH, Houston, TX
2006–present	Cullen Distinguished University Chair, Department of Chemistry, UH, Houston, TX
2004–2012	Associate Chair, Department of Chemistry, UH, Houston, TX
2003–present	Professor of Chemistry, Department of Chemistry, UH, Houston, TX
1999–2003	Associate Professor of Chemistry, Department of Chemistry, UH, Houston, TX
1993–1999	Assistant Professor of Chemistry, Department of Chemistry, UH, Houston, TX

CLOSELY RELATED PRODUCTS (five products most closely related to the proposed project)

"Full Spectrum Solar Thermal Energy Harvesting and Storage by a Molecular and Phase-Change Hybrid Material" V. Kashyap; S. Sakunkaewkasem; P. Jafari; M. Nazari; B. Eslami; S. Nazifi; Peyman Irajizad; M. D. Marquez; T. R. Lee; H. Ghasemi, *Joule* **2020**, 3(12), 3100-311.

"Capture and Conversion of Carbon Dioxide to Water by Solar Heat Localization" V. Kashyap; R. Medhi; P. Irajizad; P.; Jafari; M. Nazari; A. Masoudi; T. R. Lee; H. Ghasemi, *Sustain. Energy Fuels* **2019**, *3*, 272-279.

"Temperature-Responsive Hydrogel-Coated Gold Nanoshells" H. H. Park; L.-o. Srisombat; A. C. Jamison; T. Liu; M. D. Marquez; H. Park; S. Lee; T.-C. Lee; T. R. Lee, *Gels* **2018**, *4*, 28.

"Broadening the Photoresponsive Activity of Anatase TiO2 Nanospheres via Decoration with Partial Gold Shells" O. Khantamat; C.-H. Li; S.-P. Liu; T. Liu; H. J. Lee; O. Zenasni; T.-C. Lee; C. Cai; T. R. Lee, *J. Coll. Interface Sci.* **2018**, *513*, 715-725.

"Plasmonically Enhanced Photocatalytic Hydrogen Production from Water: The Critical Role of Tunable Surface Plasmon Resonance from Gold-Silver Nanoshells" C.-H. Li; M.-C. Li; S.-P. Liu; A. C. Jamison; D. Lee; T. R. Lee; T.-C. Lee, *ACS Appl. Mater. Interfaces* **2016**, *8*, 9152-9161.

OTHER SIGNIFICANT PRODUCTS (out of 262 total peer-reviewed publications)

"Uniformly Spherical and Monodisperse Antimony- and Zinc-Doped Tin Oxide Nanoparticles for Optical and Electronic Applications" R. Medhi; C.-H. Li; S. H. Lee; M. D. Marquez; A. J. Jacobson; T.-C. Lee; T. Randall Lee, *ACS Appl. Nano Mater*. **2019**, 2, 6554-6564.

"Mimicking Polymer Surfaces Using Cyclohexyl- and Perflurocyclohexyl-Terminated Self-Assembled Monolayers" T. Yu; M. D. Marquez; O. Zenasni; T. R. Lee, *ACS Appl. Nano Mater*. **2019**, *2*, 5809-5816.

"Quaternary-Ammonium-Terminated Films Formed from Mixed Bidentate Adsorbates Provide a High-Capacity Platform for Oligonucleotide Delivery" J. Hoang; C. S. Park; H. J. Lee; S. Patil; O. Zenasni; P. H. Gunaratne; T. R. Lee, *ACS Appl. Mater. Interfaces* **2018**, *10*, 40890-40900.

"Specific Detection of Proteins Using Exceptionally Responsive Magnetic Particles" Y.-T. Chen; R. Medhi; I. Nekrashevich; D. Litvinov; S. Xu; T. R. Lee, *Anal. Chem*. **2018**, *90*, 6749-6756.

"Broadening the Photoresponsive Activity of Anatase TiO2 Nanospheres via Decoration with Partial Gold Shells" O. Khantamat; C.-H. Li; S.-P. Liu; T. Liu; H. J. Lee; O. Zenasni; T.-C. Lee; C. Cai; T. R. Lee, *J. Coll. Interface Sci.* **2018**, *513*, 715-725.

SYNERGISTIC ACTIVITIES

2013–present Co-coordinated the efforts of the UH College of Natural Sciences and Mathematics in conjunction with the UH College of Engineering to prepare a successfully-funded $4M proposal (with an additional $4M in state matching funds) to the Robert A. Welch Foundation to provide resources for establishing the Center of Polymer Excellence at the University of Houston (http://www.uh.edu/nsm/chemistry/people/faculty/Harth/Polymer-Center.php). Subsequent efforts have centered on growth and outreach of the center, with an emphasis on building industrial collaborations.

2013–present Coordinated the efforts of the UH College of Natural Sciences and Mathematics in conjunction with the UH College of Engineering to write and submit a successfully-funded $1.5M proposal to the Howard Hughes Medical Institute to provide resources to establish the University of Houston STEM Center. The STEM Center is beginning its sixth year of service to advance local, state, and national teaching and learning for STEM students (http://stem.uh.edu).

2010–present Editor Positions: Deputy Editor, *ACS Applied Nano Materials* (2017–present); Associate Editor, *ACS Applied Materials & Interfaces* (2010–2018).

2012–present Associate Dean for Research for the College of Natural Sciences and Mathematics at the University of Houston.

2004–present Notable continuous committee service to the University of Houston community: University of Houston Undergraduate Health Professions Advisory Committee (2004–present), University of Houston Faculty Senate & Executive Committee of the Faculty Senate (2004–present), and Phi Beta Kappa, Mu of Texas Chapter, Organizing Committee and Advisory Committee (2013–present).

References

(1) IEA. CO2 Emissions from Fule Combustion: Highlights. *Outlook* **2010**, *38* (1), 1–134. https://doi.org/10.1670/96-03N.

(2) International Energy Agency. *Energy Technology Perspectives: Scenarios & Strategies To 2050*; 2010. https://doi.org/10.1049/et:20060114.

(3) IPCC. *Climate Change 2007 Synthesis Report*; 2007. https://doi.org/10.1256/004316502320517344.

(4) Ritter, J.A., Ebner, A. D. *State-of-the-Art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries*; 2009; Vol. 44. https://doi.org/10.1017/CBO9781107415324.004.

(5) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Advances in CO2 Capture Technology-The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenh. Gas Control* **2008**, *2* (1), 9–20. https://doi.org/10.1016/S1750-5836(07)00094-1.

(6) Rochelle, G. T. Amine Scrubbing for $C0_2$ Capture. *Science (80-.).* **2009**, *325* (5948), 1652–1654. https://doi.org/10.2307/40301873.

(7) Dutcher, B.; Fan, M.; Russell, A. G. Amine-Based CO2capture Technology Development from the Beginning of 2013-A Review. *ACS Appl. Mater. Interfaces* **2015**, *7* (4), 2137–2148. https://doi.org/10.1021/am507465f.

(8) Vaidya, P. D.; Kenig, E. Y. CO2-Alkanolamine Reaction Kinetics: A Review of Recent Studies. *Chem. Eng. Technol.* **2007**, *30* (11), 1467–1474. https://doi.org/10.1002/ceat.200700268.

(9) Dawodu, O. F.; Meisen, A. Degradation of Alkanolamine Blends by Carbon Dioxide. *Can. J. Chem. Eng.* **1996**, *74* (6), 960–966. https://doi.org/10.1002/cjce.5450740620.

(10) Ramdin, M.; De Loos, T. W.; Vlugt, T. J. H. State-of-the-Art of CO \n 2 Capture with Ionic Liquids. *Ind. Eng. Chem. Res.* **2012**, *51*, 8149–8177. https://doi.org/10.1021/ie3003705.

(11) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chemie - Int. Ed.* **2010**, *49* (35), 6058–6082. https://doi.org/10.1002/anie.201000431.

(12) Davidson, R. Post-Combustion Carbon Capture from Coal Fired Plants: Solvent Scrubbing. *Clean Coal Cent.* **2007**, *125* (July).

(13) Kashyap, V.; Lee, R.; Ghasemi, H.; Kashyap, V.; Sakunkaewkasem, S.; Jafari, P.; Nazari, M.; Eslami, B. Full Spectrum Solar Thermal Energy Harvesting and Storage by a Molecular and Phase-Change Hybrid Material. *Joule* **2019**, *3* (12), 3100–3111.

(14) Kashyap, V.; Medhi, R.; Irajizad, P.; Jafari, P.; Nazari, M.; Masoudi, A.; Marquez, M. D.; Lee, T. R.; Ghasemi, H. Capture and Conversion of Carbon Dioxide by Solar Heat Localization. *Sustain. Energy Fuels* **2019**, *3* (1), 272–279. https://doi.org/10.1039/c8se00546j.

(15) Kumar, A.; Madden, D. G.; Lusi, M.; Chen, K.-J.; Daniels, E. A.; Curtin, T.; Perry, J. J.; Zaworotko, M. J. Direct Air Capture of CO2 by Physisorbent Materials. *Angew. Chemie Int. Ed.* **2015**, *54* (48), 14372–14377. https://doi.org/10.1002/anie.201506952.