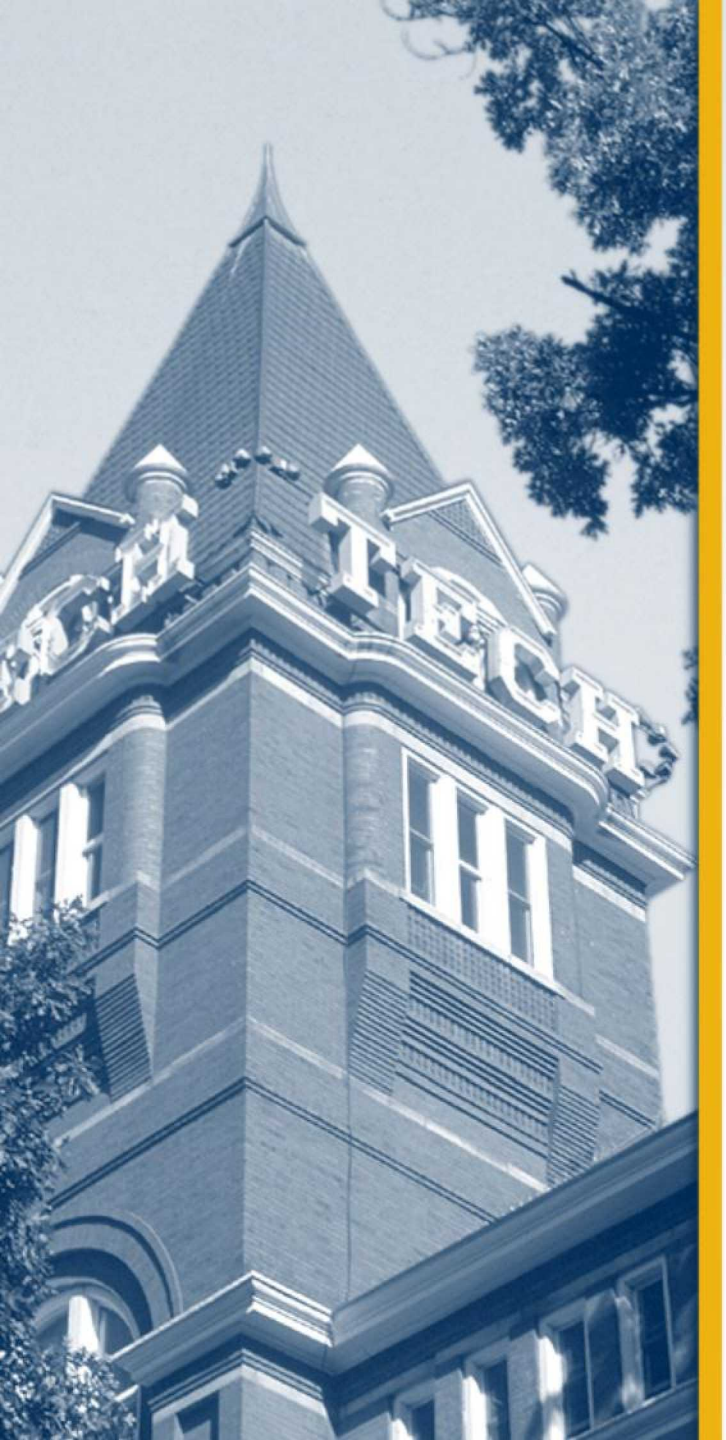


SAND2018-8753PE

# Using Computer Simulations to Select Simulants for Capture of Chemical Warfare Agents in Nanoporous Materials by Adsorption

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Presentation by

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In collaboration with

Sandia National Laboratories

Georgia Institute of Technology

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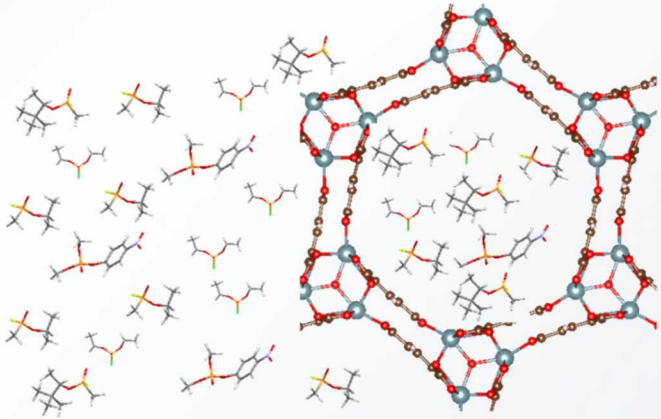
Sandia National Laboratories

# Introduction

- Nerve agents: extremely toxic synthetic chemicals which can be dispersed as a gas, liquid or aerosol
  - Tokyo subway station gas attack, 1995
  - Syria gas attacks in 2013 and 2018
- Use of simulant molecules instead of real agents in experiments to study and compare the activity of any adsorbent material due to toxicity of CWAs
- However, no detailed comparison between CWAs and simulants for adsorption processes

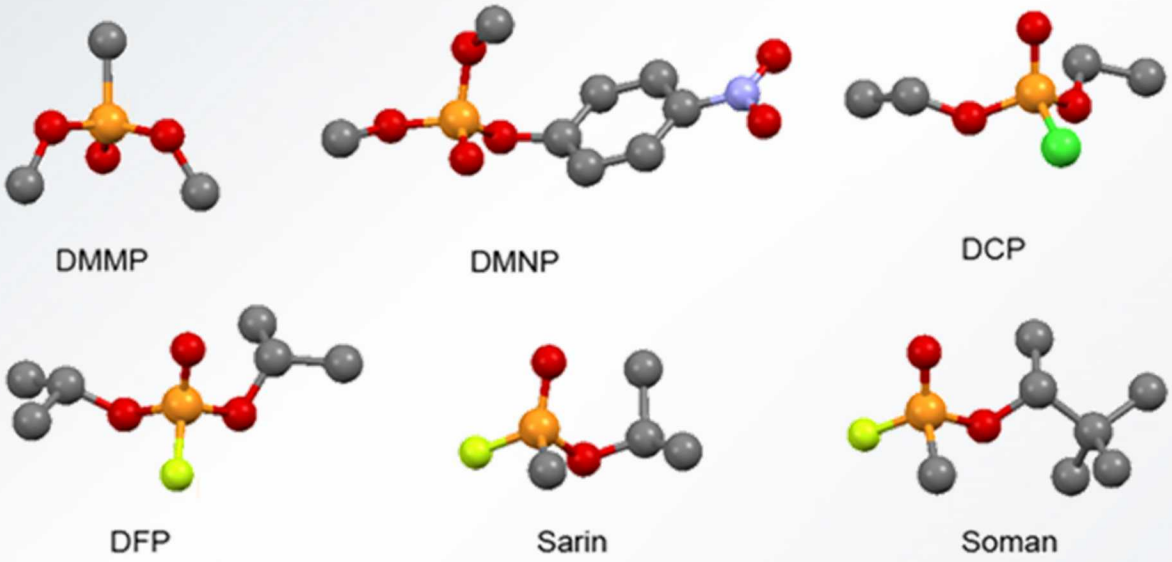


# Objectives

- Prediction of adsorption properties of CWAs and simulants in a library of thousands of MOFs using molecular simulations
- To address the question of whether simulants for CWAs are truly similar to CWAs in terms of their adsorption properties
- Probing the sensitivity of our results to newly DFT derived FF to draw robust conclusions

# Materials

- Adsorbents: CoRE MOFs database[1], a collection of >2900 experimental reported MOFs with high quality charges assigned to the frameworks
- Adsorbates:
  - CWAs: Sarin and Soman
  - Simulants: DMMP, DMNP, DCP and DFP




[1]Chung, Y. G. *et al. Chem. Mater.* 26, 6185–6192 (2014)

# Simulation Methods

- Force-field derivation
  - VASP package, PBE-D3 functional, $10^{-6}$ eV energy cutoff
  - DFT interaction energies of configurations are obtained using

$$E_{ads} = E_{adsorbate-MOF} - (E_{adsorbate} + E_{MOF})$$

  - Energies obtained above are fitted to Lennard-Jones potential of a force-field

$$V = -\sum 4\varepsilon_{ij}^{*}\left[\left(\frac{\sigma_{ij}^{*}}{r}\right)^{12} - \left(\frac{\sigma_{ij}^{*}}{r}\right)^{6}\right] + k\frac{q_i q_j}{R_{ij}}$$

where, $\varepsilon_{ij}^{*} = \sqrt{\varepsilon_i(\boldsymbol{C_{1j}}\varepsilon_j)}$, $\sigma_{ij}^{*} = \frac{\sigma_i + \boldsymbol{C_{2j}}\sigma_j}{2}$ (Lorentz-Berthelot mixing rule),

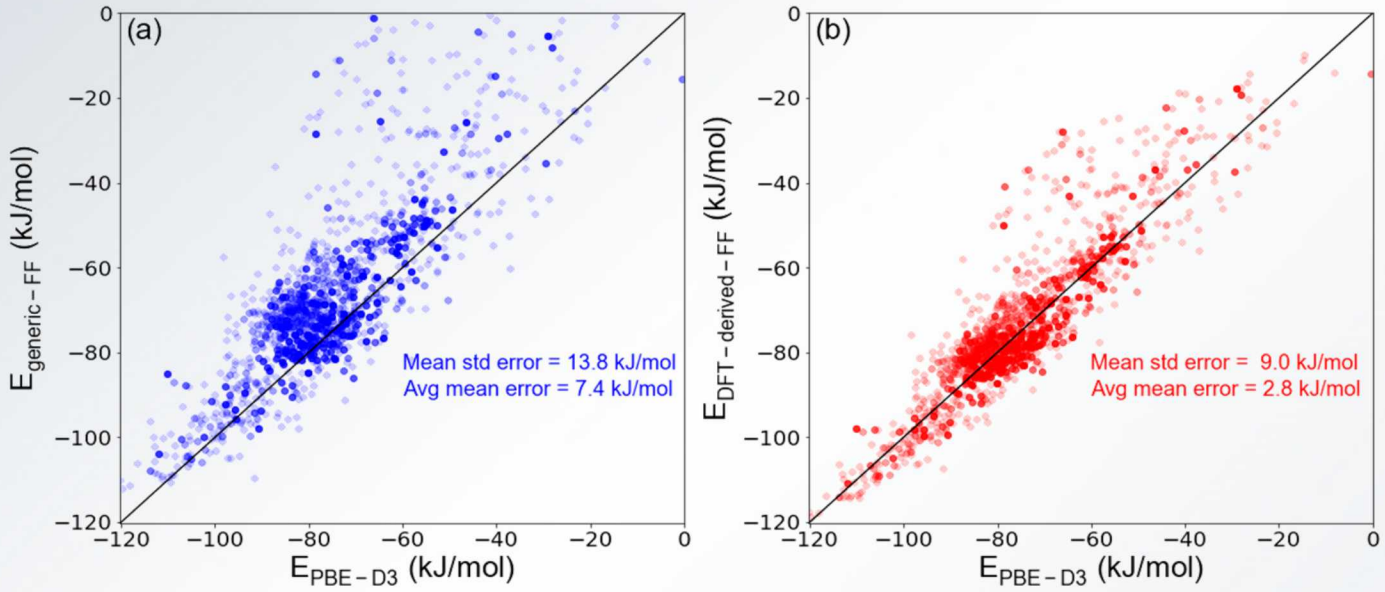
i and j are subscripts for MOF and adsorbate atoms respectively

- Adsorption properties calculations
  - RASPA package, Monte-Carlo simulations
  - Widom insertion method
  - $10^{6}$ MC cycles

Fang, H. *et al. J. Phys. Chem. C* 116, 10692–10701 (2012)
Kulkarni, A. R. & Sholl. D.S. *J. Phys. Chem. C* 117, 7519–7525 (2013)

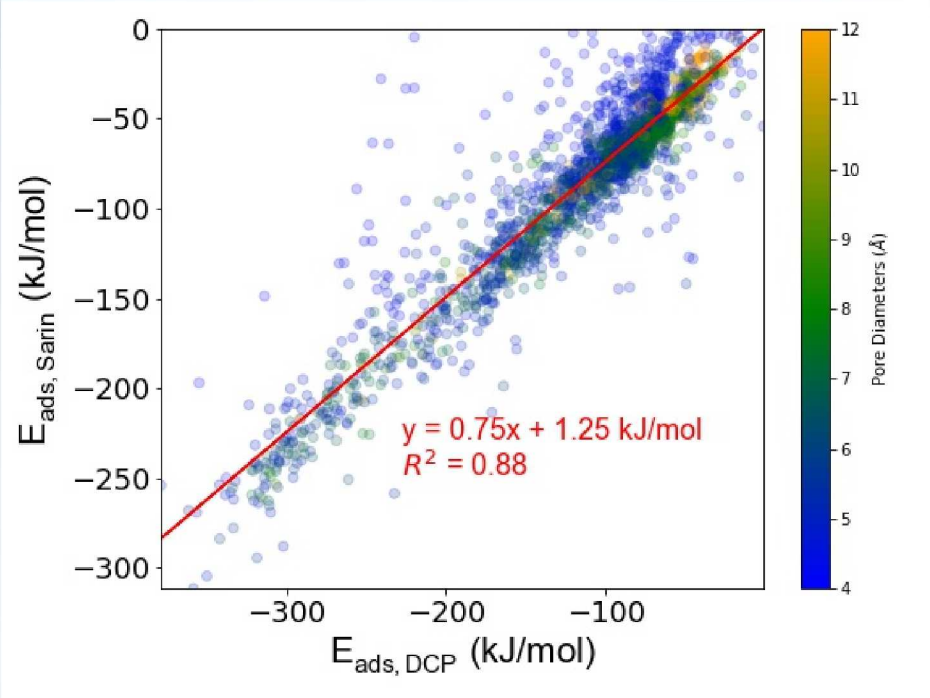
# DFT-derived FF vs generic FF

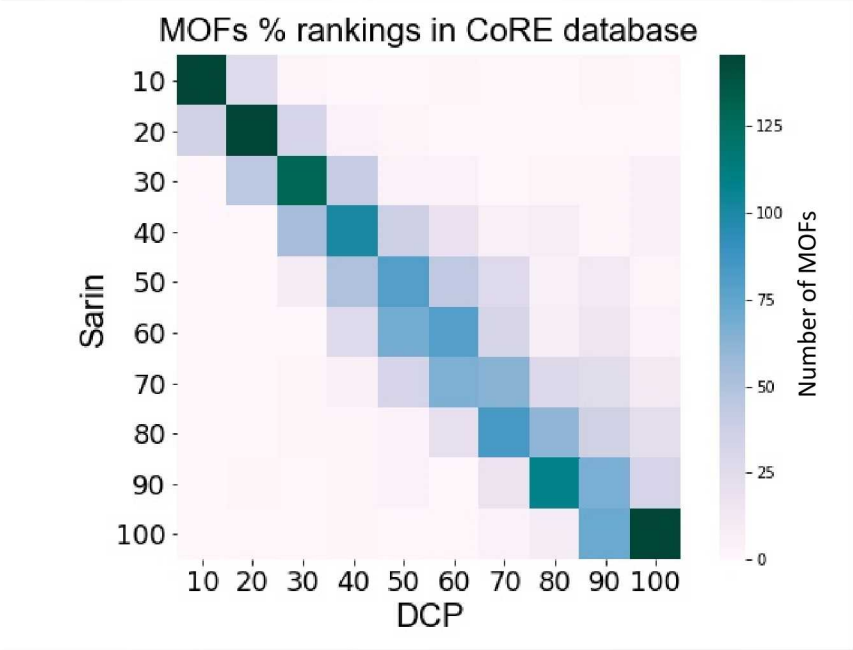
Interaction energies of 3000 configurations of 6 molecules in UiO-66




- Generic FF is reasonable, but DFT-derived FF is more accurate

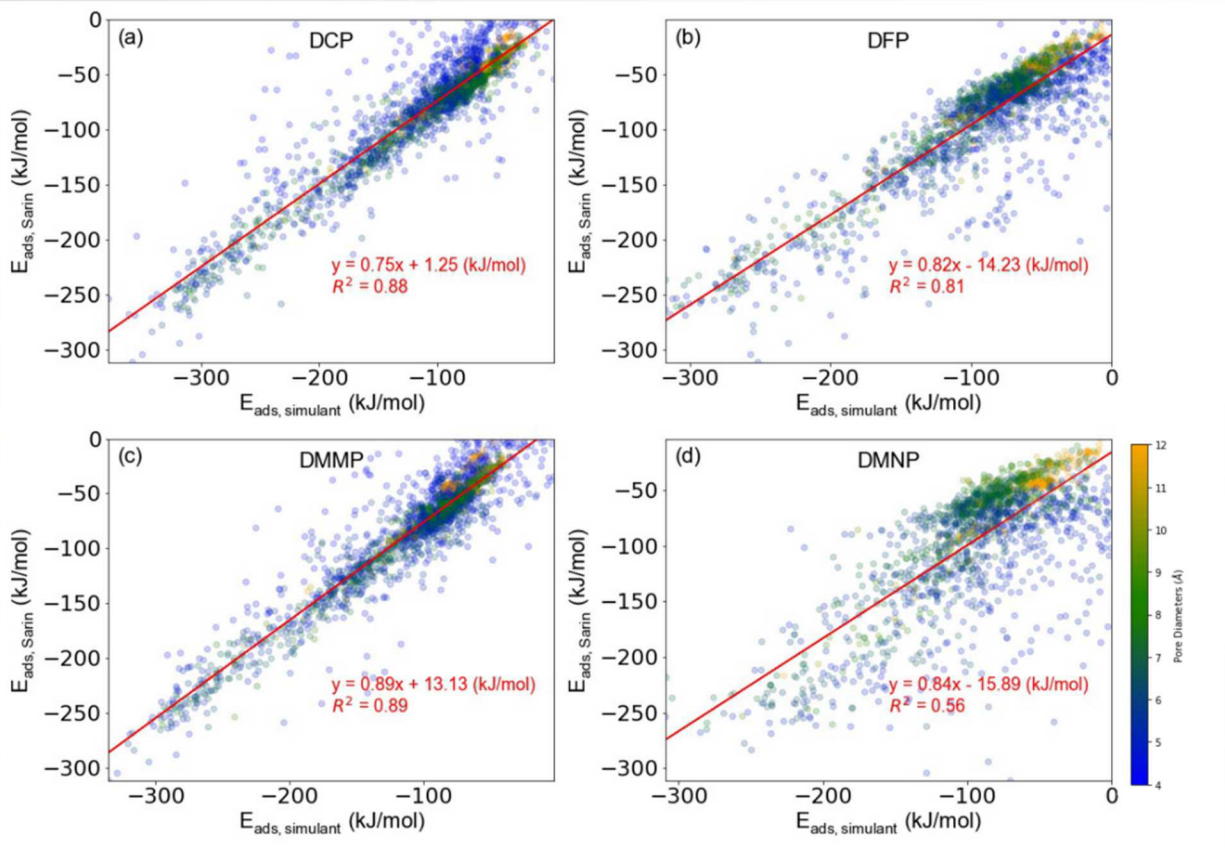
# Heats of Adsorption: Sarin vs DCP



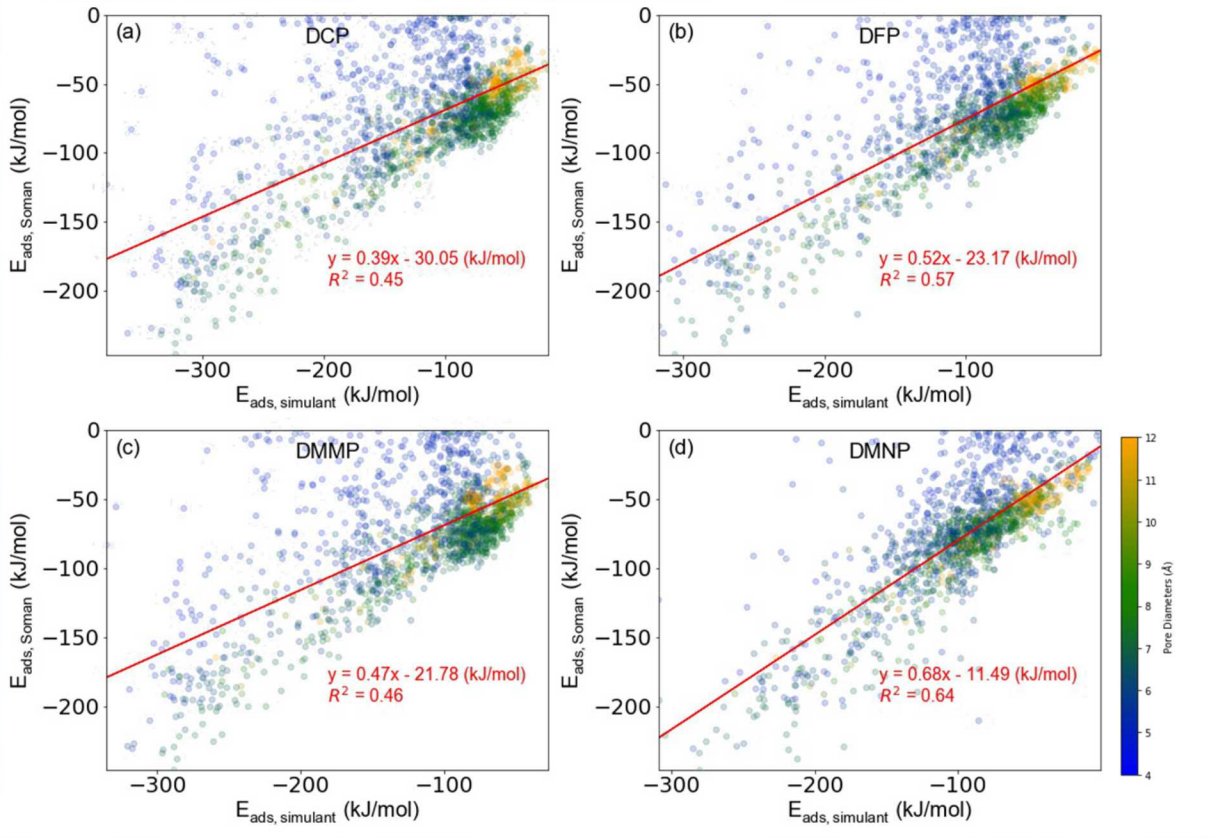

- Figures compares adsorption properties of Sarin and DCP in ~3000 MOFs using DFT-derived FF
- DCP is able to predict Sarin's MOFs rankings in CoRE database within 10% error for most MOFs

# Heats of Adsorption: Sarin vs Simulants



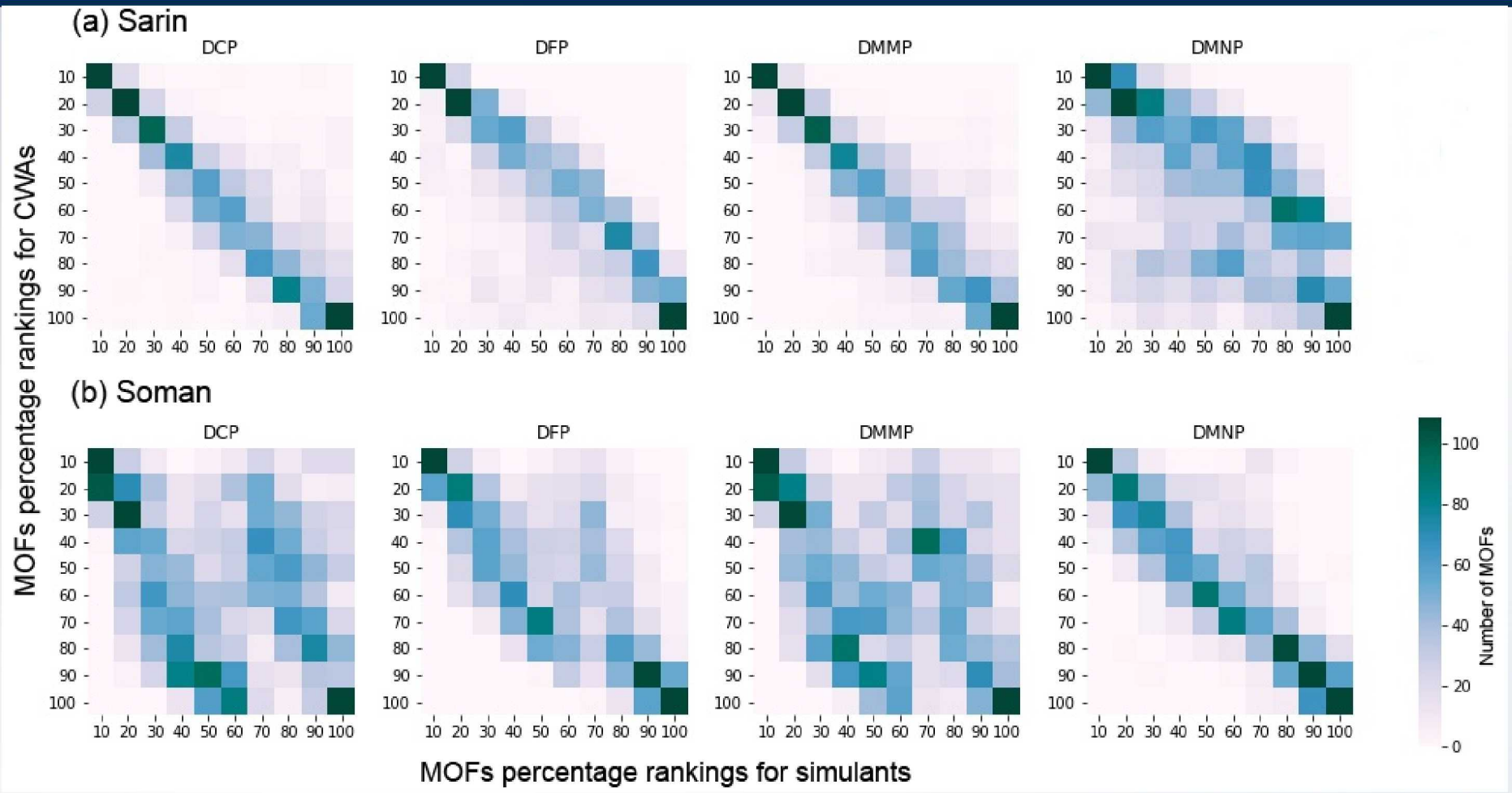

- High performing MOFs pore diameters are in the range of 6-10 Å
- DCP and DMMP are the closest to Sarin

# Heats of Adsorption: Soman vs Simulants




- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

# Correlation Between MOFs Rankings: CWAs vs Simulants




- DCP and DMMP are able to best predict MOFs ranking of Sarin based on adsorption properties
- DMNP is the only simulant that is able to closely predict MOFs ranking of Soman based on adsorption properties

# Conclusions

- DCP and DMMP are the best suited simulants to predict adsorption behavior of Sarin in nanoporous materials
- DMNP is the only simulant that is suited to predict Soman's adsorption behavior in nanoporous materials
- Our DFT-derived FF is performing better than generic FF in predicting interaction energies of CWAs and simulants in MOFs, however, generic FFs are also well suited to predict qualitative adsorption behavior of CWAs and simulants
- Our qualitative predictions are independent of the force-field used in the simulations

THANK YOU

# Extra Slide 1

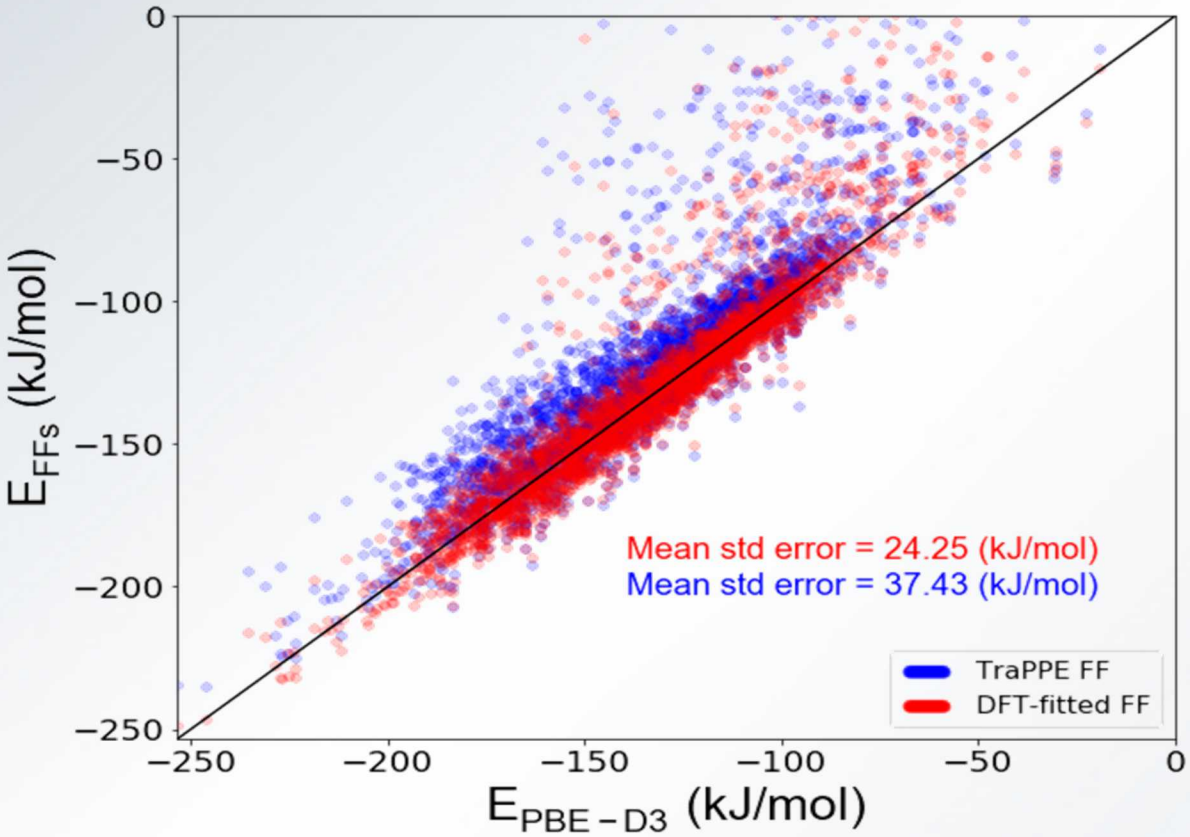



Figure E1: A parity plot between interaction energies calculated using classical force fields and quantum chemistry calculations using (a) a generic FF and (b) a DFT-derived FF for all CWAs and simulants adsorbed in 5 randomly selected MOFs from the database

# Extra Slide 2

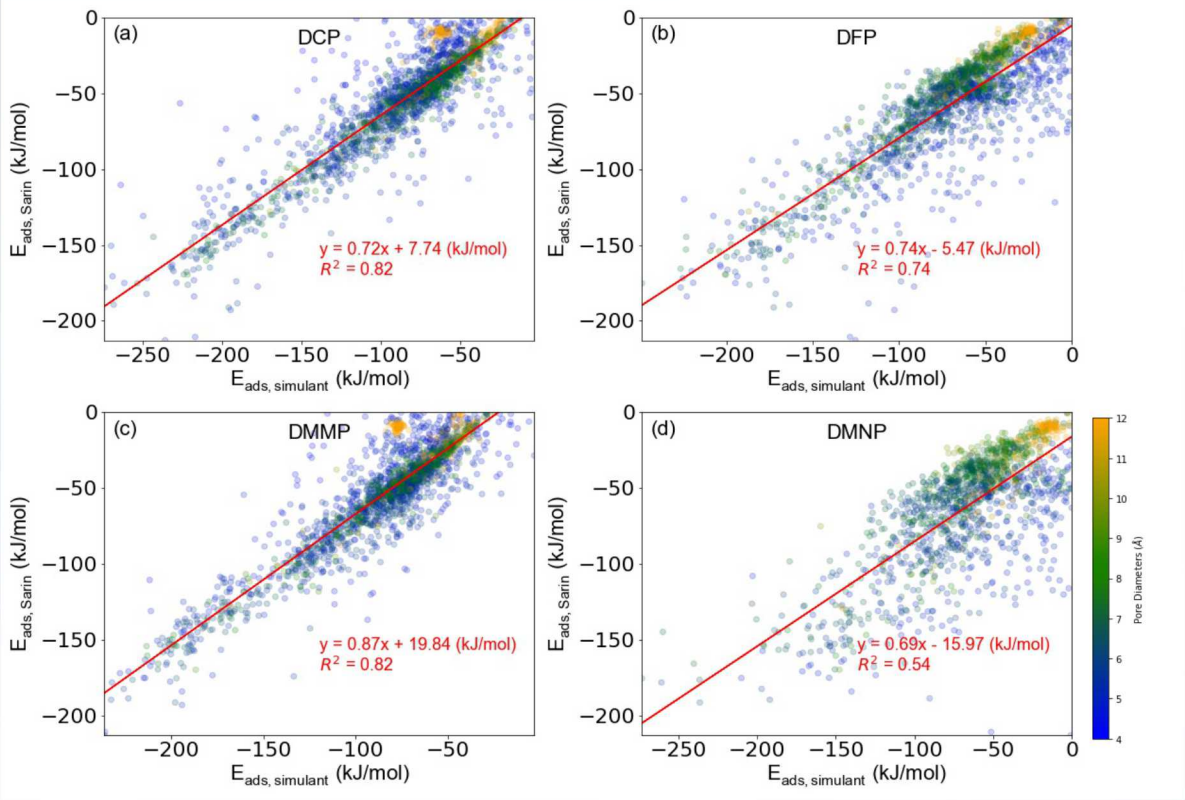



Figure E2: Heat of adsorption of Sarin compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

- High performing MOFs pore diameters are in the range of 6-10 Å
- DCP and DMMP are the closest to Sarin

# Extra Slide 3

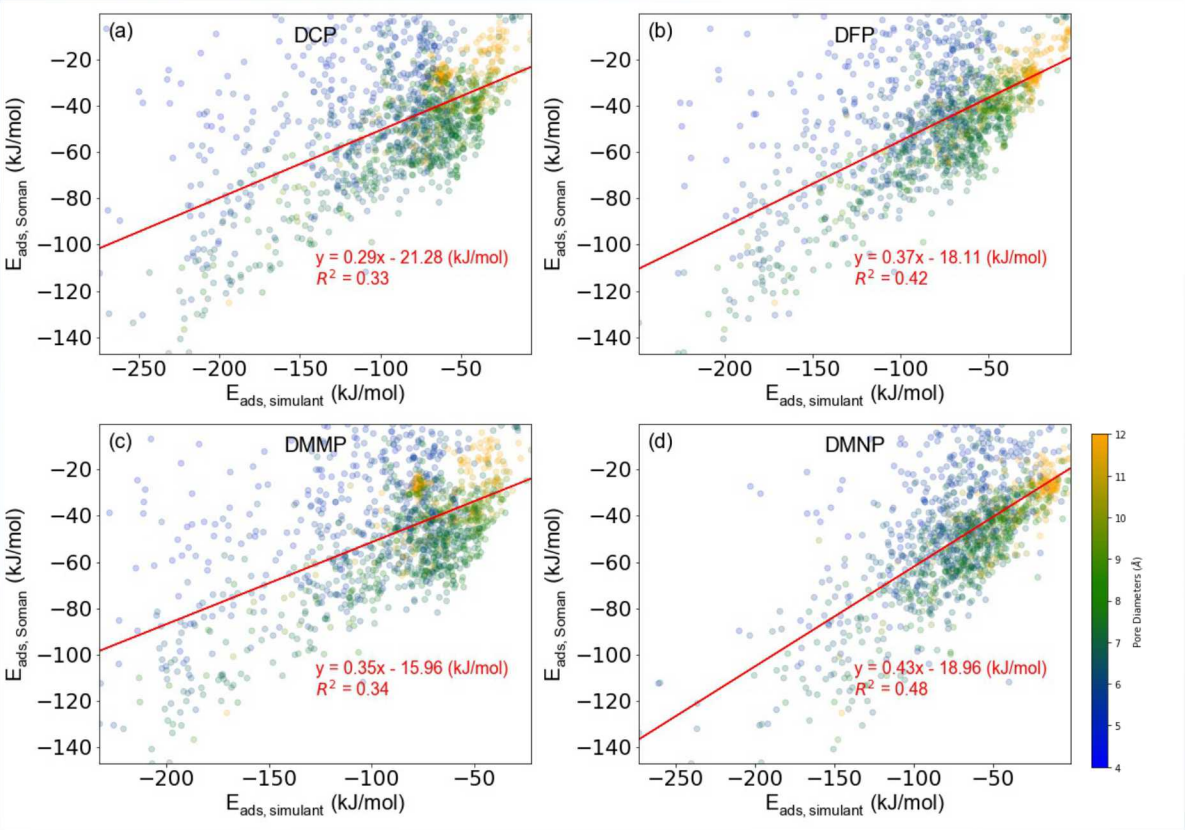
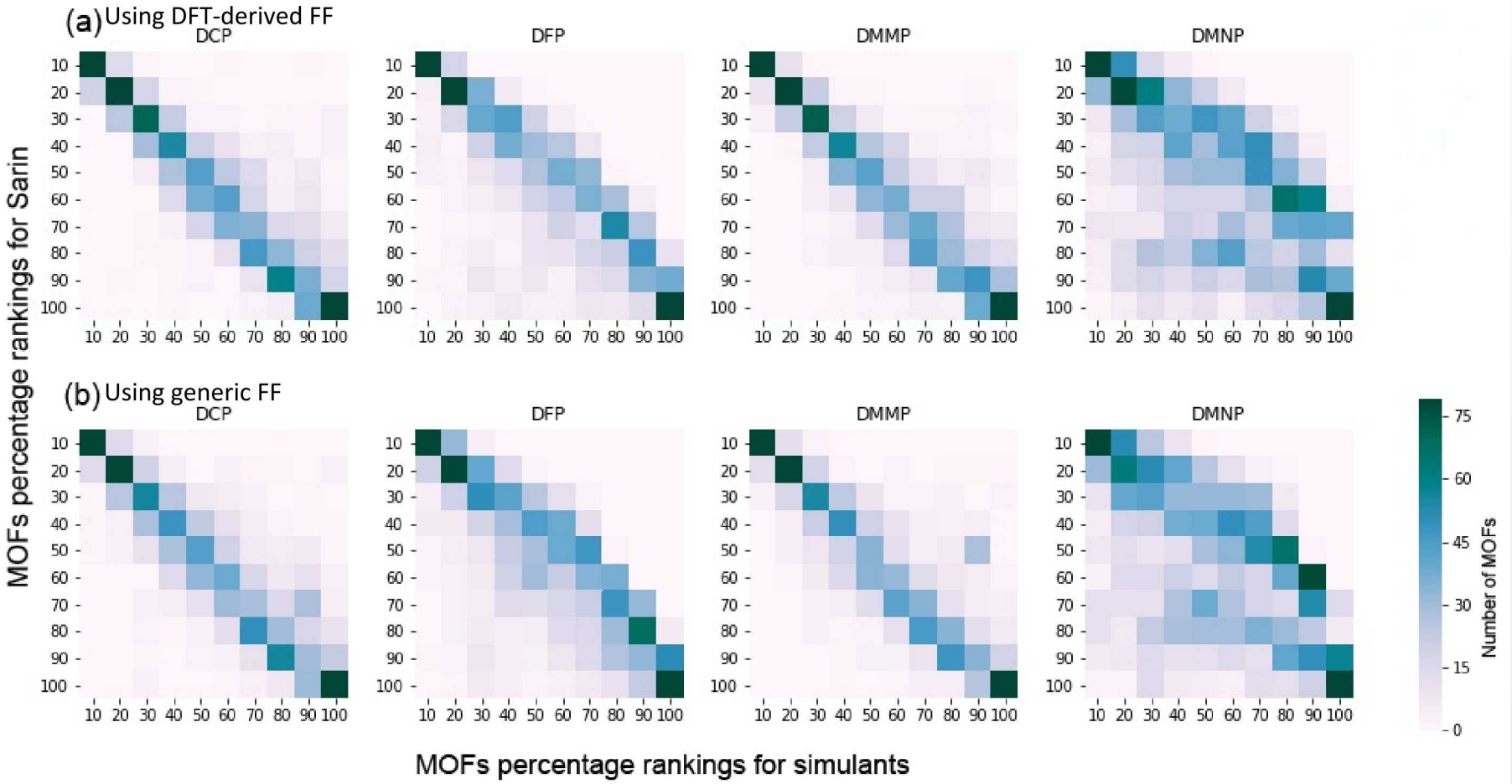



Figure E3: Heat of adsorption of Soman compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

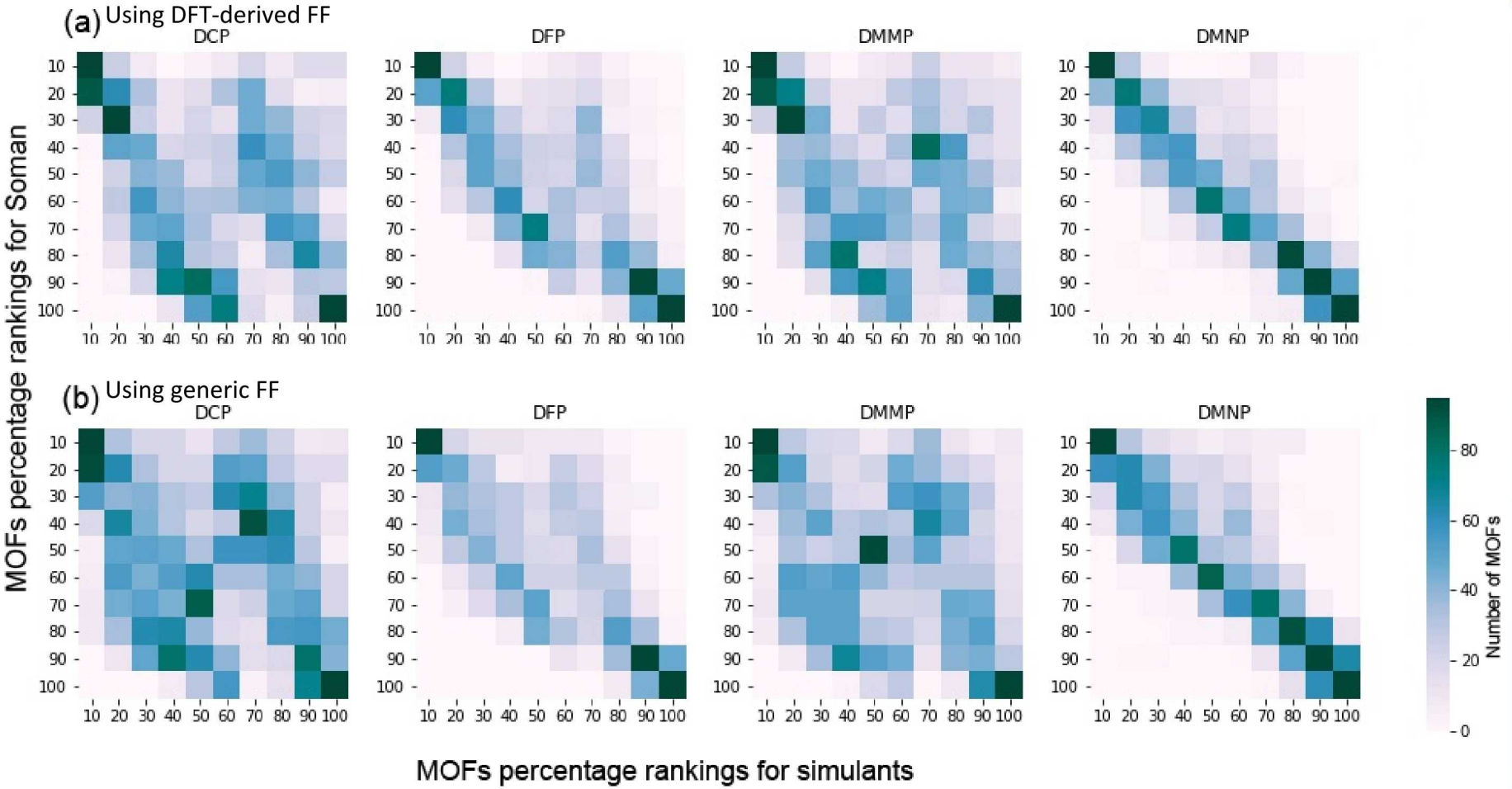
- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

# Correlation Between MOFs Rankings: CWAs vs Simulants




- DCP and DMMP are able to best predict MOFs ranking of Sarin based on adsorption properties
- DMNP is the only simulant that is able to closely predict MOFs ranking of Soman based on adsorption properties

# Correlation Between MOFs Rankings: Soman vs Simulants




- Both generic and DFT-derived FFs show similar behaviors