Membrane Databases – New Schema and Dissemination

(Supplement to: Development of Design Rules for High Hydroxide Transport in Polymer Architectures)

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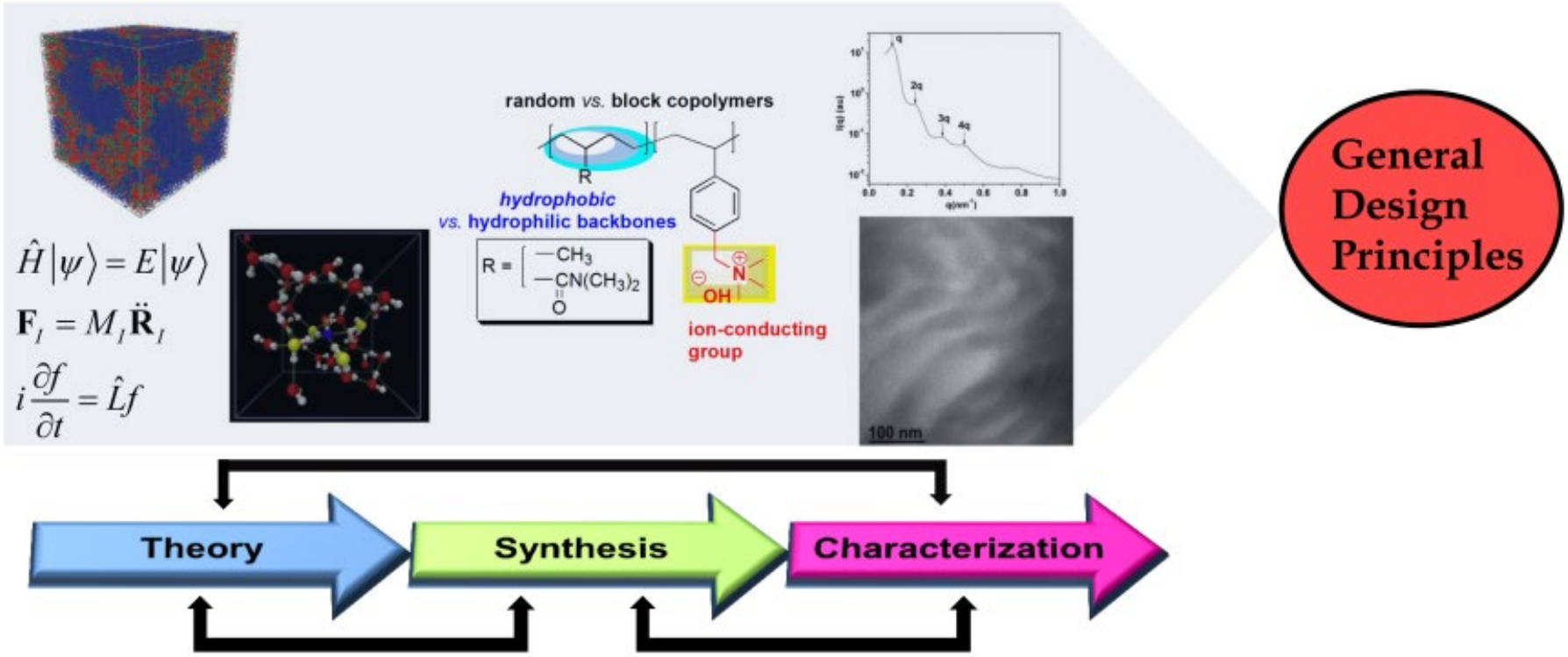
Hydroxide Transport in Polymer Architectures

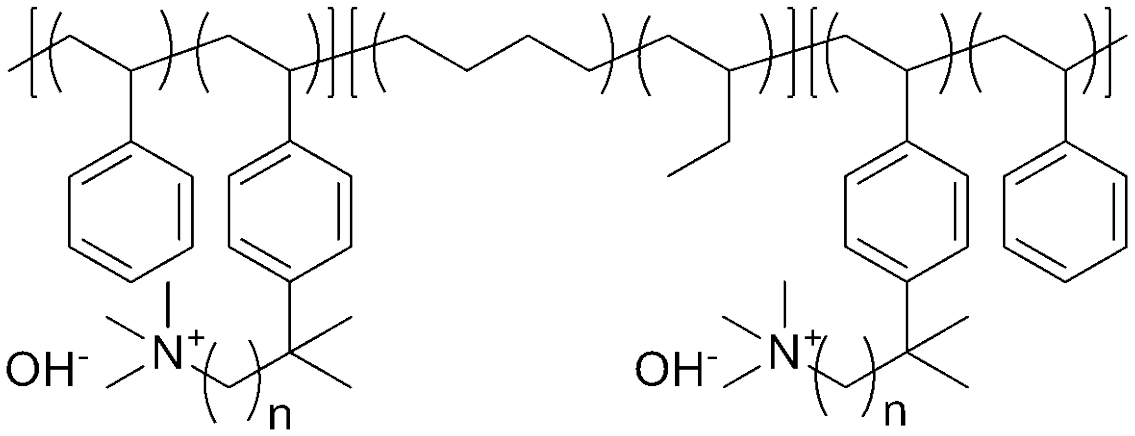
- How do we accelerate the design and development of new anion exchange membranes for electrochemical technology?
- How do we construct a thought paradigm, workflow, and set of analyses to attack the Materials Genome of membranes?
- How will large-scale simulation, data, and data analytics contribute to the rapid design and testing of new membranes?



AEM Synthesis & Characterization

Systematic variations in sidechain structures of AEMs

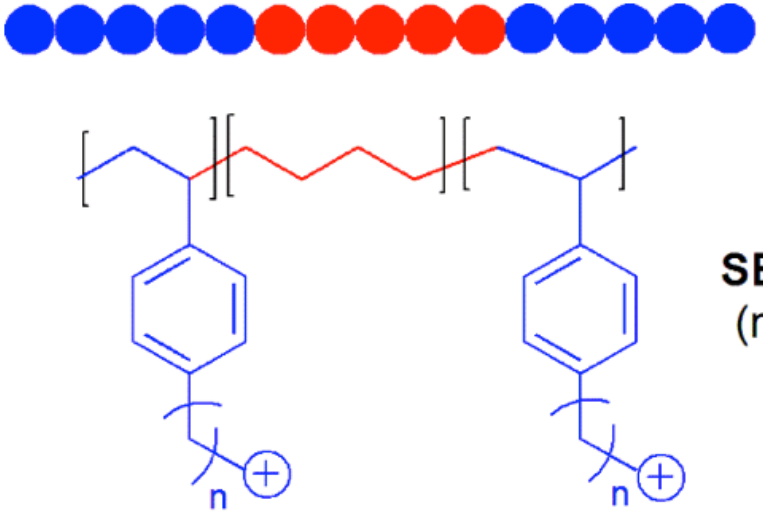
Investigate the effects of tether chain length and cation structure on hydroxide ion diffusion



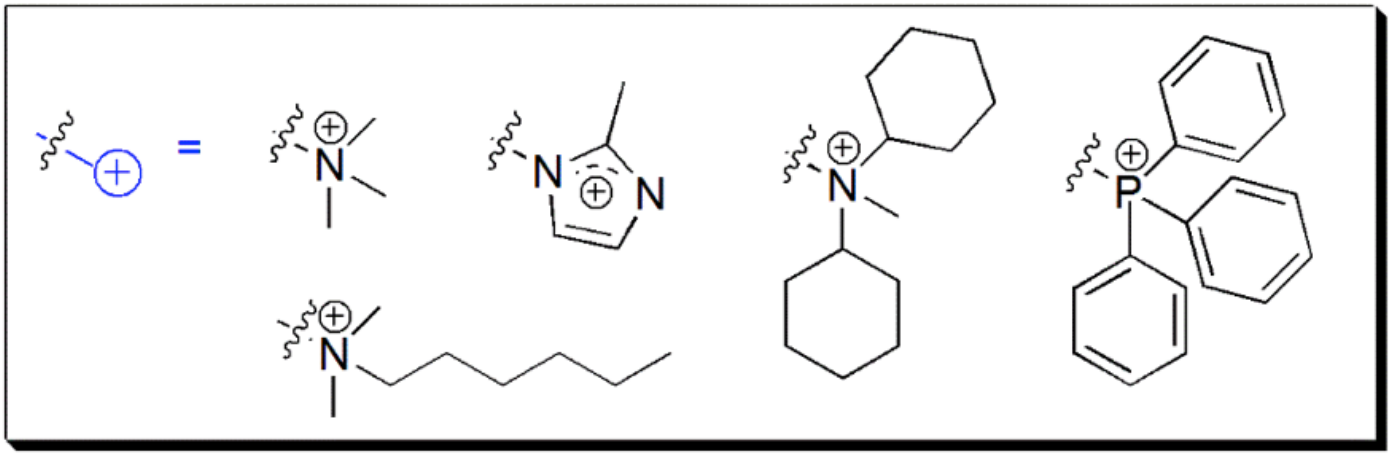
SEBS triblock copolymer
Styrene: 45 wt% (30 mol%)
M_w = 120 kg/mol, M_w/M_n = 1.1

(n = 1, 3, 5)

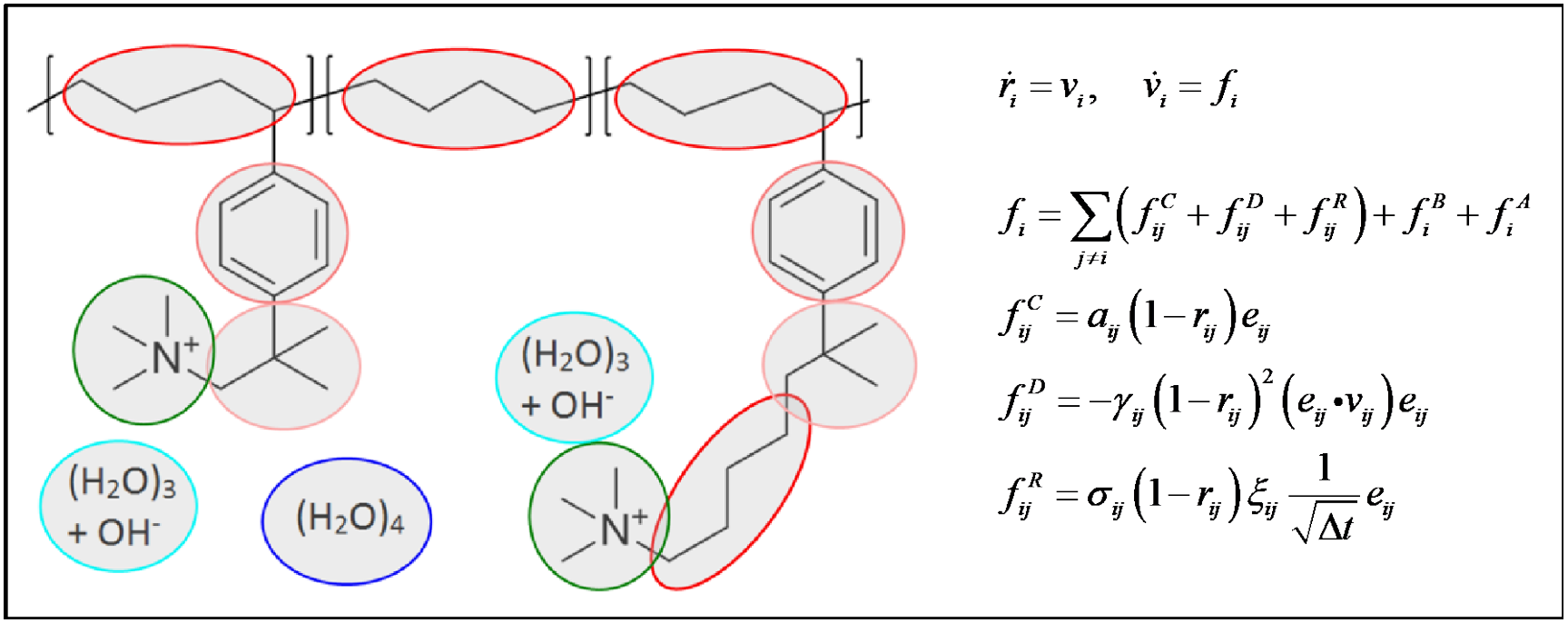
How Does Tether and Cation Influence Morphology and Properties?



SEBS AEMs
(n = 1, 3, 5)



Mesoscopic Modeling of Anion Exchange Membranes



$$\dot{r}_i = v_i, \quad \dot{v}_i = f_i$$

$$f_i = \sum_{j \neq i} \left(f_{ij}^C + f_{ij}^D + f_{ij}^R \right) + f_i^B + f_i^A$$

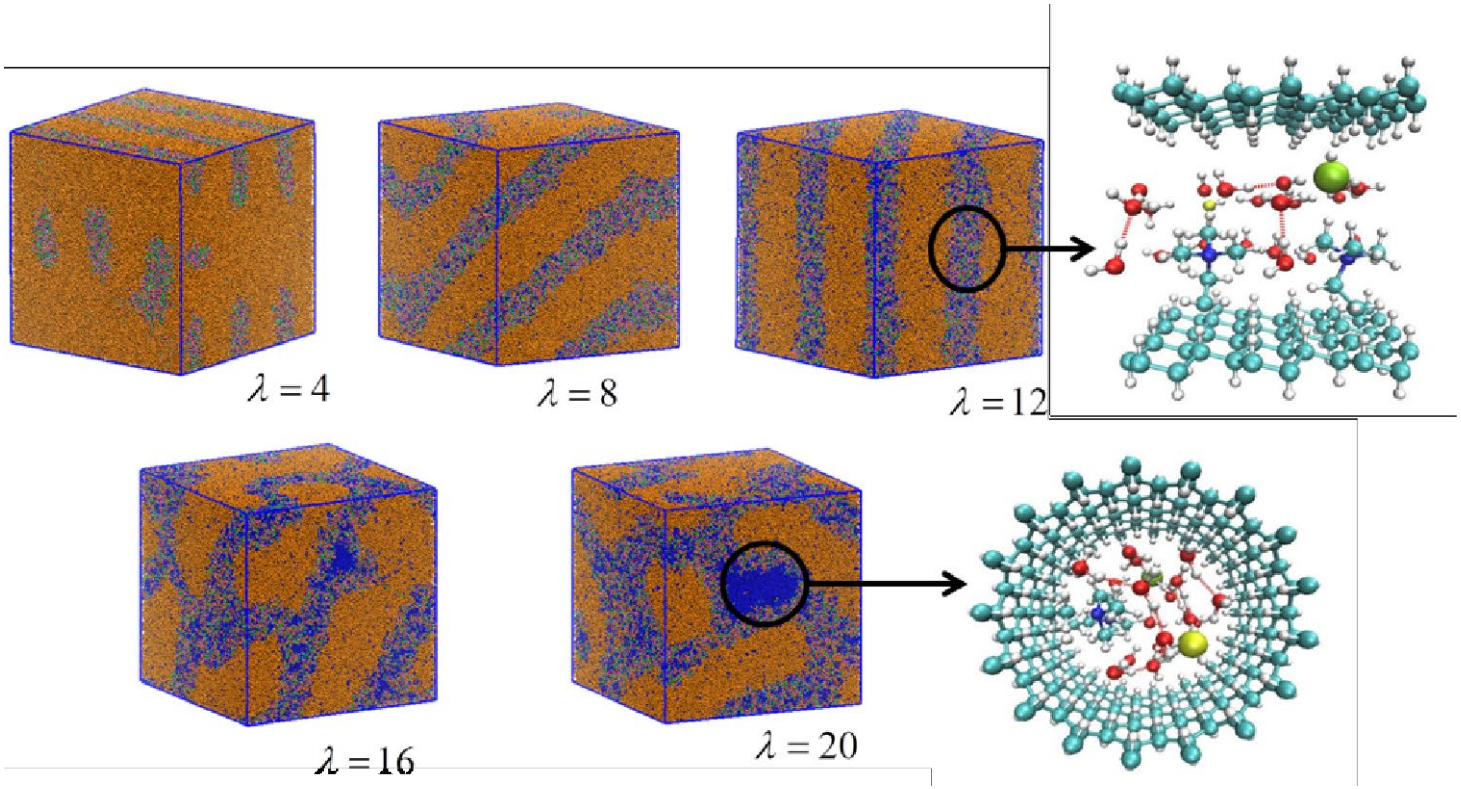
$$f_{ij}^C = a_{ij} \left(1 - r_{ij}\right) e_{ij}$$

$$f_{ij}^D = -\gamma_{ij} \left(1 - r_{ij}\right)^2 \left(e_{ij} \bullet v_{ij}\right) e_{ij}$$

$$f_{ij}^R = \sigma_{ij} \left(1 - r_{ij}\right) \xi_{ij} \frac{1}{\sqrt{\Delta t}} e_{ij}$$

Sepehr, F., H. Liu, X. Luo, C. Bae, M. E. Tuckerman, M. A. Hickner, S. J. Paddison, "Mesoscale Simulations of Anion Exchange Membranes Based on Quaternary Ammonium Tethered Triblock Copolymers," *Macromolecules* **2017**, 50(11), 4397-4405.

DPD Simulations of Morphology Provide Characteristic "Pores" for Detailed AIMD Models

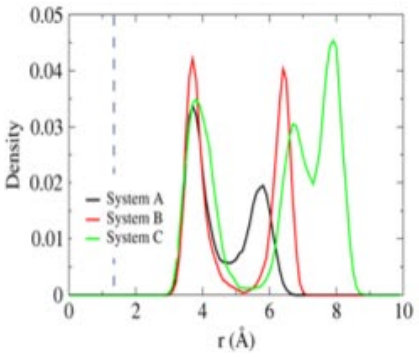


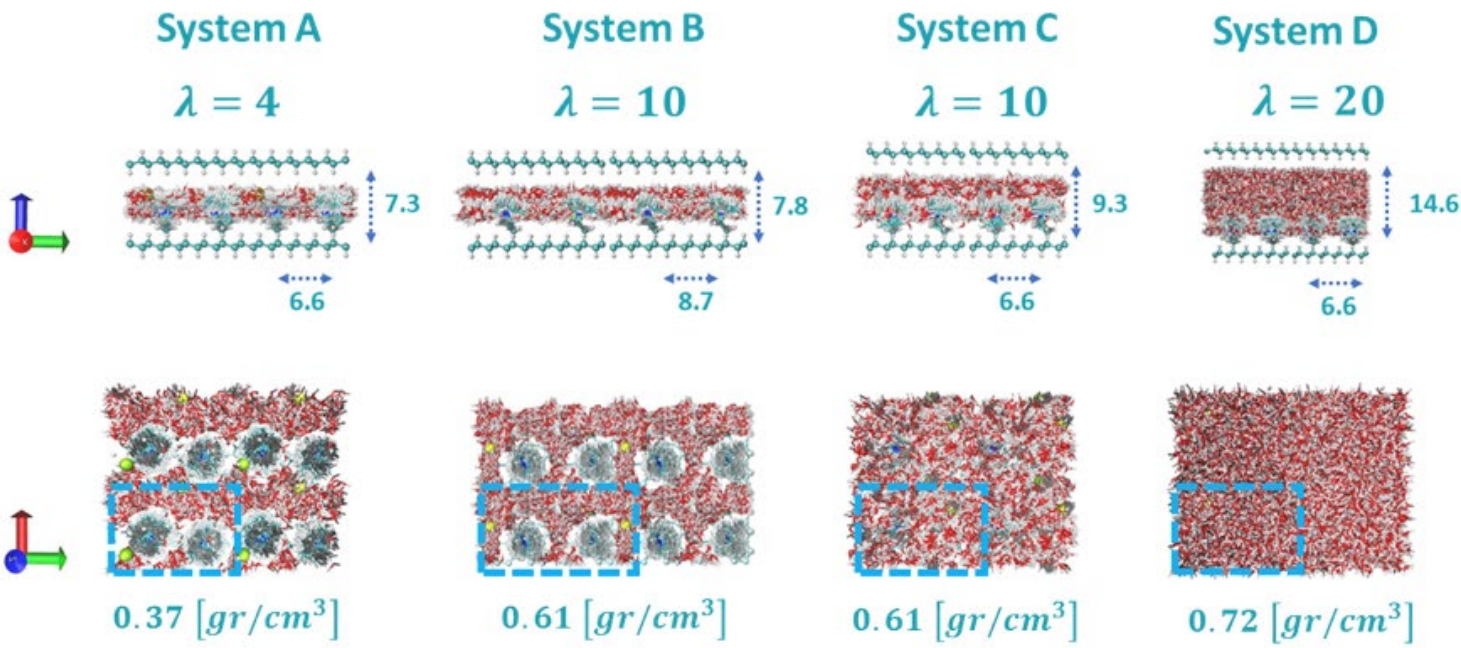
$$\lambda = \frac{n_{H_2O}}{n_{cation}}$$

T Zelovich, Z Long, MA Hickner, SJ Paddison, C Bae, ME Tuckerman
"Ab initio Molecular Dynamics Study of Hydroxide Diffusion Mechanisms in Nano-Confined Structural mimics of Anion Exchange Membranes"
The Journal of Physical Chemistry C **2019**.

DPD Simulations of Morphology Provide Characteristic "Pores" for Detailed AIMD Models

Connecting hydroxide diffusion to cation and tethering group chemistries from first principles

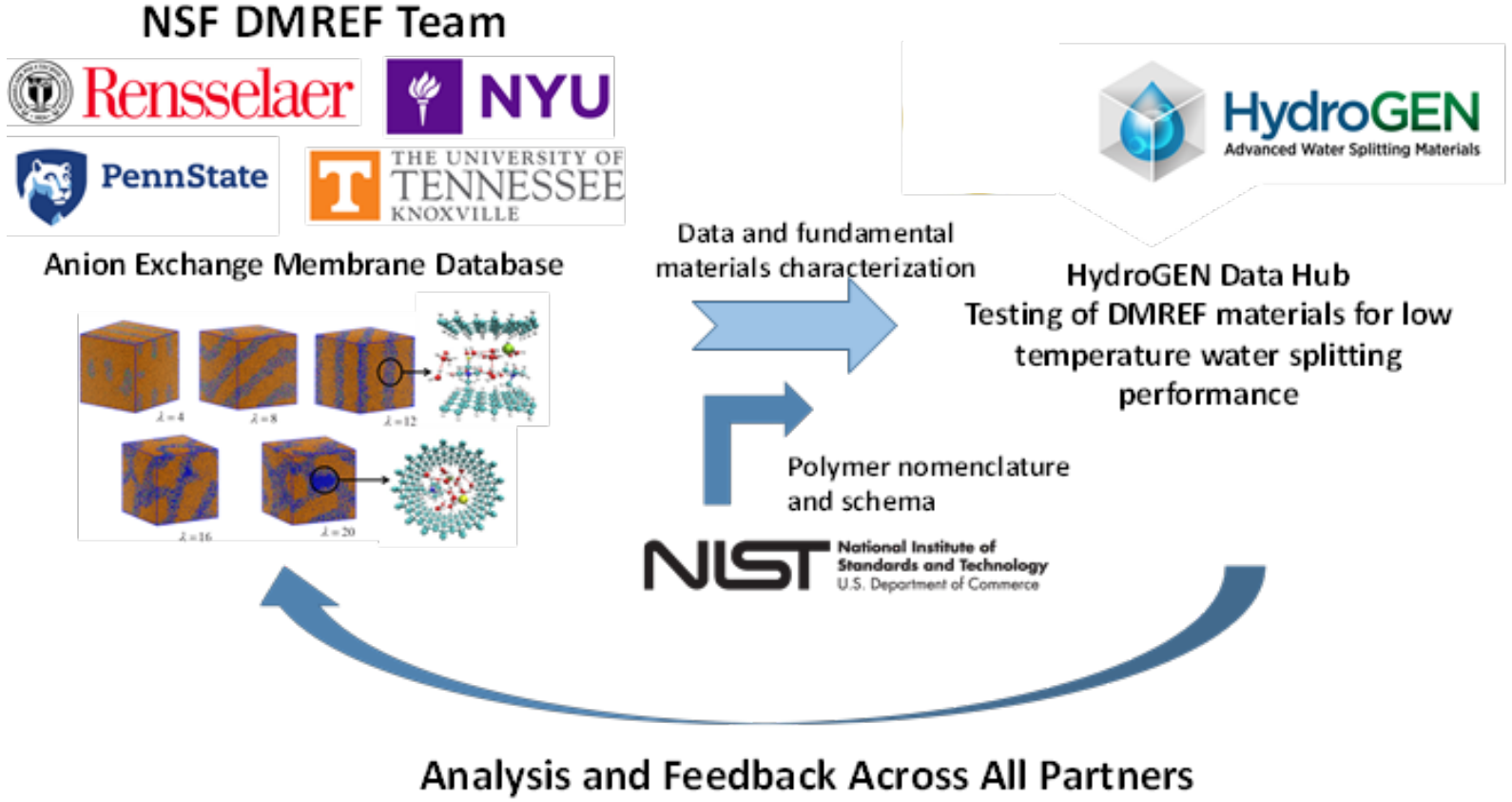




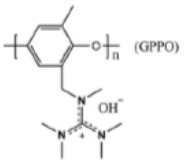
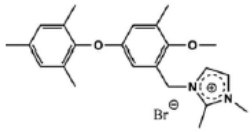
- Aqueous hydroxide transport is governed by both vehicular and structural diffusion (see figure below) mechanisms.[4,5]
- *Ab initio* molecular dynamics simulations used to study effect of cation spacing, water content, size of pore, and temperature on hydroxide diffusion.
- Results of local-scale interactions guide further synthesis.

Membrane Databases
New Schema and Dissemination

- Take DMREF knowledge and literature observations and construct new membrane database.
- Make large database available to HydroGEN and EMN users for device work.



Membrane Database

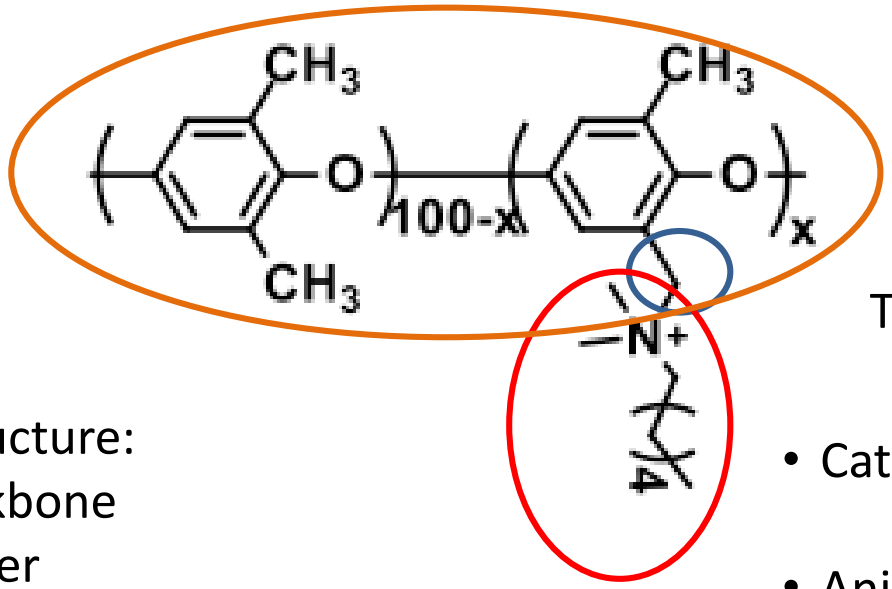
	Cation Structure	Backbone Structure	IEC (mmol/g)	Anion conductivity (mS/cm)	Swelling ratio (%)	Water uptake (%)	Alkaline stability	Ref
1.	 (GPPO)	PPO	2.69	71 (25°C)	12.5 (25°C) 18.9 (80°C)	49.9 (25°C) 72.9 (80°C)		1
2.			2.23	64 (25°C)	25.0 (25°C) 45.0 (80°C)	77.1 (25°C) 98.7 (80°C)	1M KOH @ 25°C, 8 days, no degradation	
3.	BTMA		2.65	44 (25°C)	37.5 (25°C) 75.6 (80°C)	100.6 (25°C) 430.1 (80°C)	20-40% loss of QA (come from other refs)	
4.	 (DMI)		2.8	40 (25°C) 75 (60°C)	37.5 (20°C)	136.7 (20°C)		2
5.			2.5	35 (25°C) 65 (60°C)	30.3 (20°C)	102.2 (20°C)	2M KOH @ 25°C, 9days, No degradation 2M KOH @ 60°C, 9days, Loss of IEC=50%	

Will also scope automated machine reading of the literature - see Olivetti, et al.

…165 and counting

Need Robust Naming Conventions for Database

Backbone – poly(2,6-dimethyl-1,4-phenylene oxide)



Tether - Methylene (benzyl)

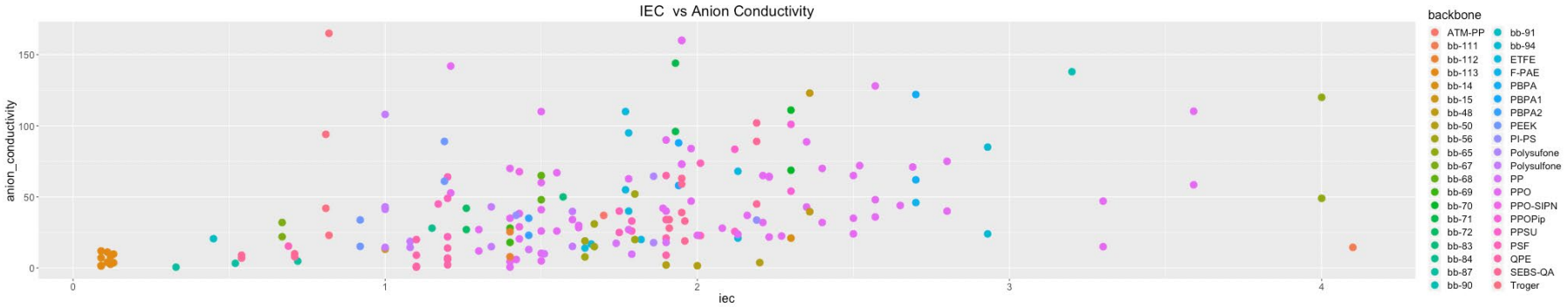
One structure:

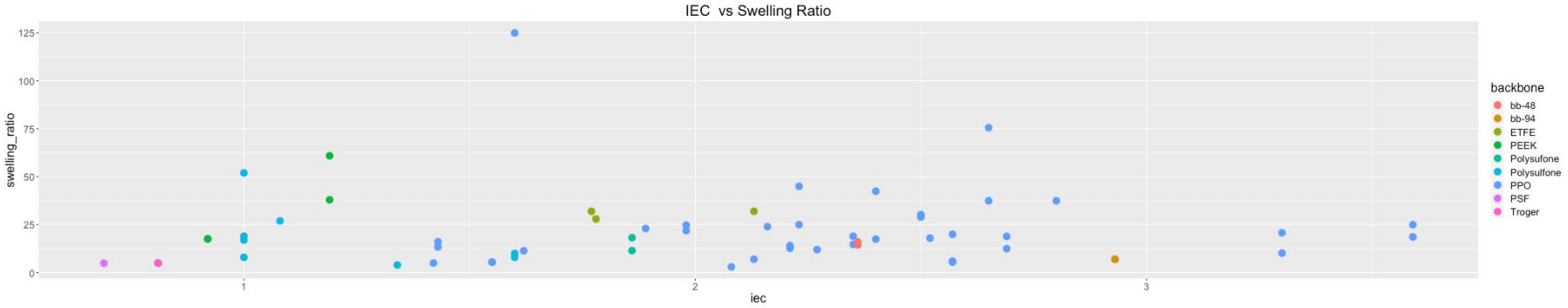
- 1 backbone
- 1 tether
- 1 or multiple cations
- 0,1 or multiple comonomers

- Cation – Hexyl, dimethyl, alkyl
- Anion – depends on how it is characterized
- We should leave this as a variable since results are reported with different anions.

Database Allows for Large-Scale, Customized Analysis – Potential for Machine Learning

Need database curation and structure coding for automated analysis of structure-function relationships of these materials.





Where We're Headed

OPV Database | Search | Email Updates | **OPV Data Management**

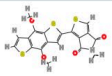
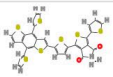
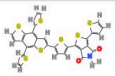
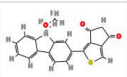
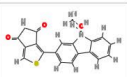
To search by selecting building blocks based on pictures of their structure, use Advanced Search, by clicking the "Search" tab at the top of this page.
Results for T-core-T small molecules are found in the "Oligomer" tab. To limit searches to these small molecules, search by "T." for tag name.

Energy Diagram: select up to 6 structures / oligomers by clicking the "plus buttons" to populate an energy level diagram for display and printing

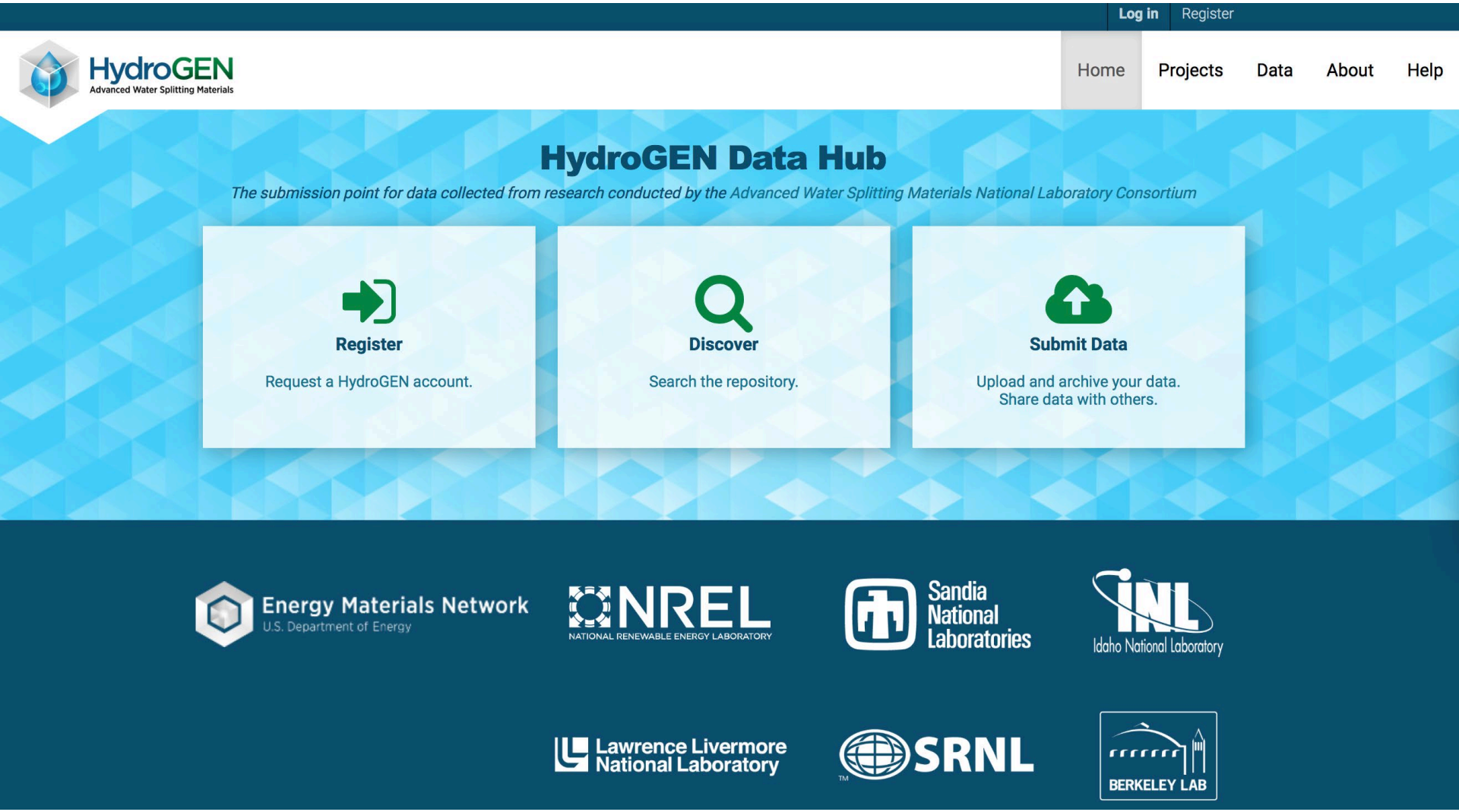
structure graph | Tag Name (Example: BDT_) | b3lyp/6-31g(d)

Polymer | Oligomer

603 records | Display 20 | 1 2 3 4 5 6 7 8 9 10 31

	Max O#	Thumb	Tag	HOMO	LUMO	Opt LUMO	Gap	Sum *f* Osc (n=2)	Spectral Overlap (n=2)	Basis
⊕	4		BDT_MeO-MeO-H-H_CTD_Me-Me	-5.115	-3.238	-3.433	1.682	2.094	4597.662	b3lyp/6-31g(d)
⊕	4		BDT_Th-Th-H-H_Th_H-H_CTD_Me-Me_Th_H-H	-4.824	-2.935	-3.272	1.552	3.824	9957.934	b3lyp/6-31g(d)
⊕	2		BDT_Th-Th-H-H_Th_H-H_TPD_Me_Th_H-H	-4.901	-2.924	-3.284	1.617	3.852	9137.942	b3lyp/6-31g(d)
⊕	3		BDT_Th-Th-H-H_CTD_Me-Me	-5.086	-3.201	-3.407	1.679	2.018	4566.334	b3lyp/6-31g(d)
⊕	4		BDT_Th-Th-H-H_TPD_Me	-5.103	-3.032	-3.278	1.825	2.214	4038.037	b3lyp/6-31g(d)
⊕	2		FLR_Me-MeO-H-H-H-H-H-H_CTD.HH	-5.312	-3.005	-3.329	1.983	2.013	3102.140	b3lyp/6-31g(d)
⊕	2		FLR_MeO-Me-H-H-H-H-H-H_CTD.HH	-5.330	-2.982	-3.313	2.017	1.958	3006.523	b3lyp/6-31g(d)

https://organicelectronics.nrel.gov/project/detail/project_id/19



https://datahub.h2awsm.org

Things to do

- Naming and structure coding
- Finalize schema and build in flexibility for expansion
- Leverage data tools from NREL OPV database
- Expand database entries through the end of the supplement and consider curated user submissions
- Chart pathway forward for use in EMN with DOE