Theoretical Studies on the Polymer-Ion Interaction and the Solvent Effects in the PBI-based Systems

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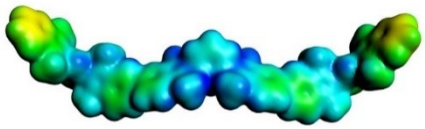
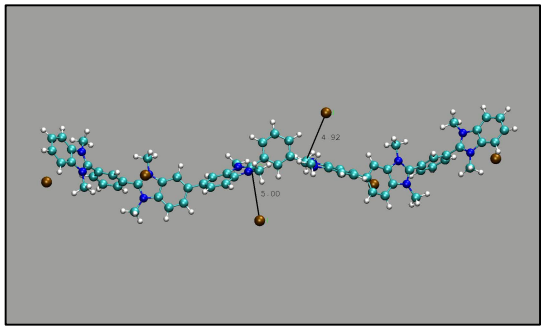
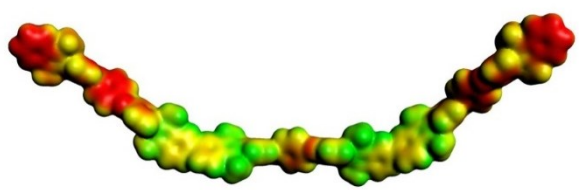
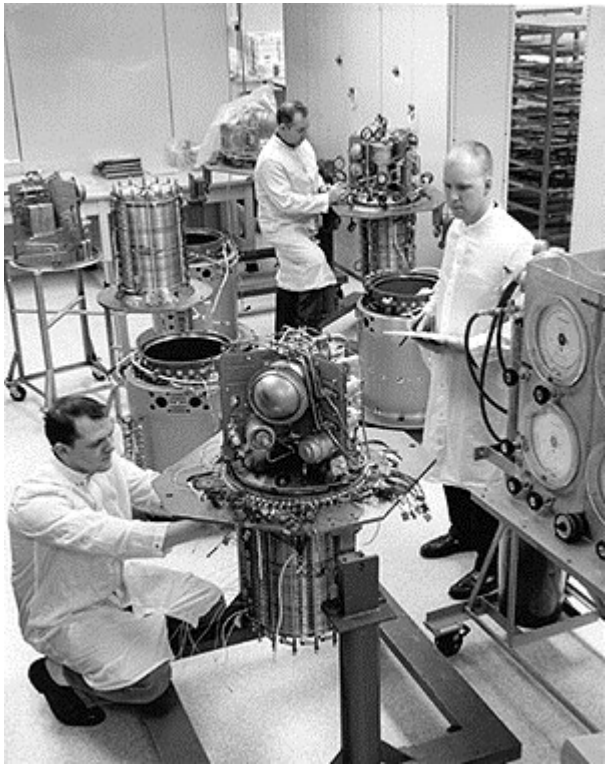
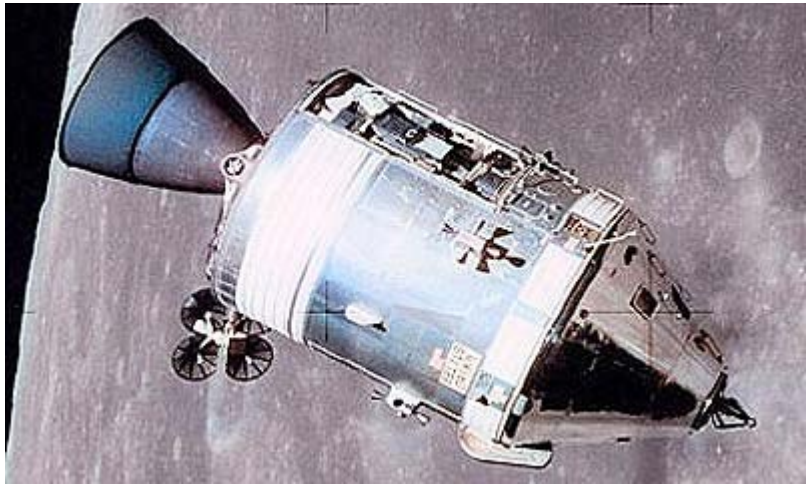




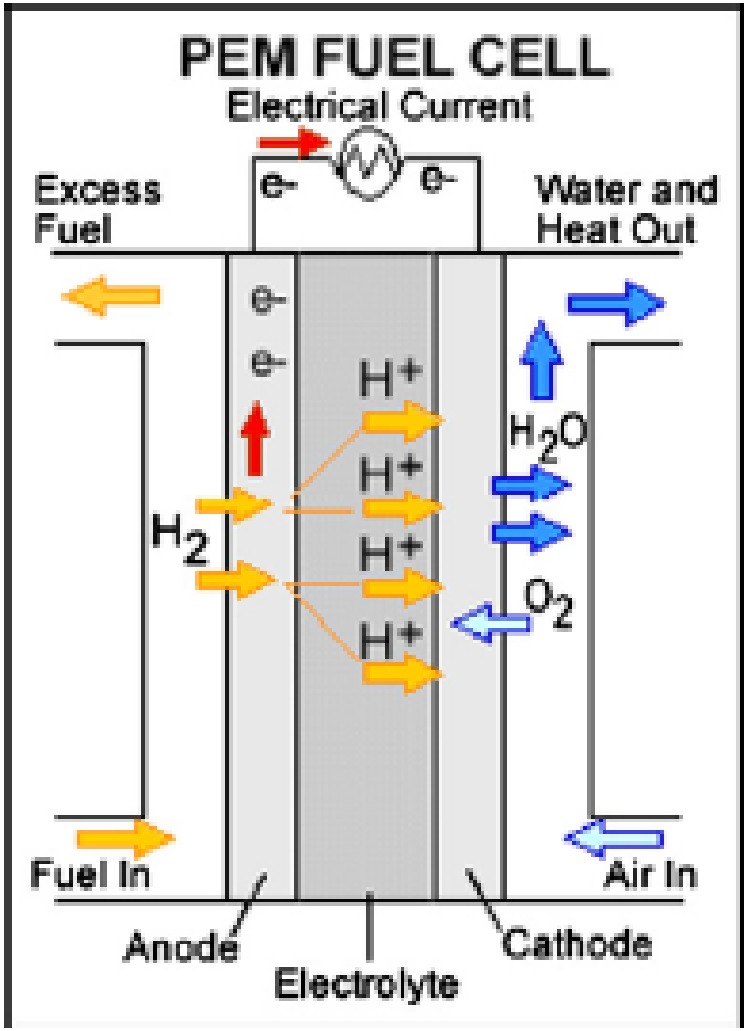


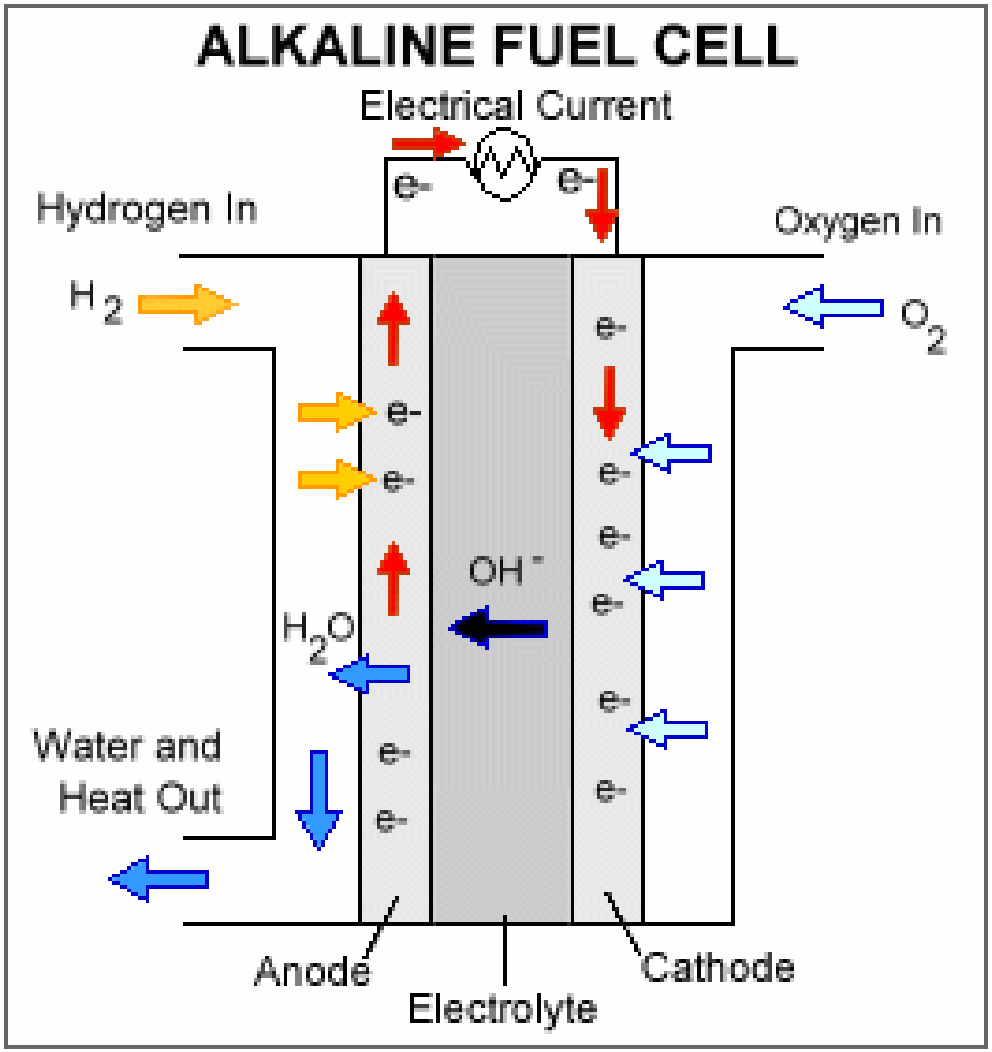
Alkaline Fuel Cells





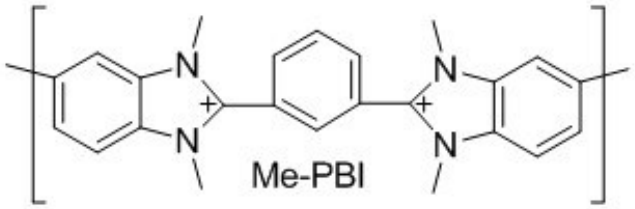
A Pratt & Whitney alkali fuel cell being assembled for an Apollo spacecraft, 1964

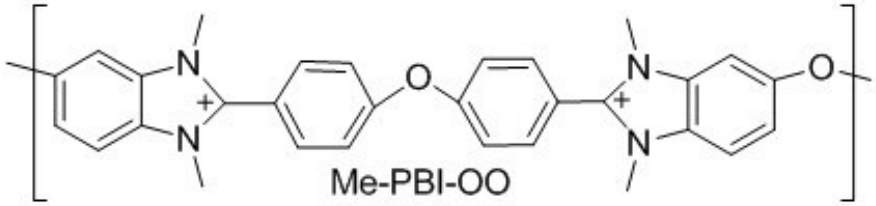


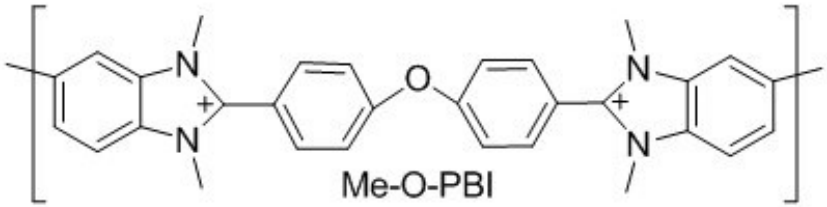


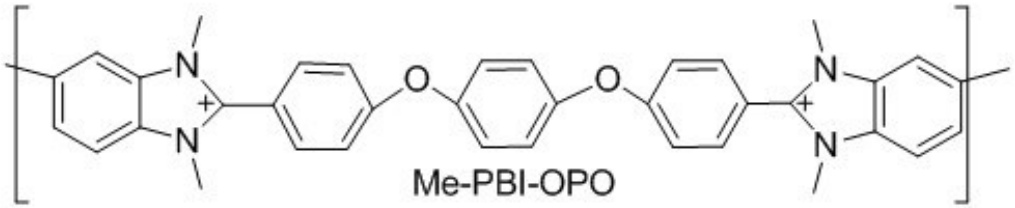
Schematic of a PEM and Alkaline fuel cell

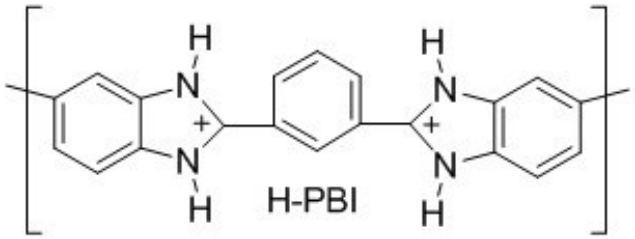
PBI-based systems











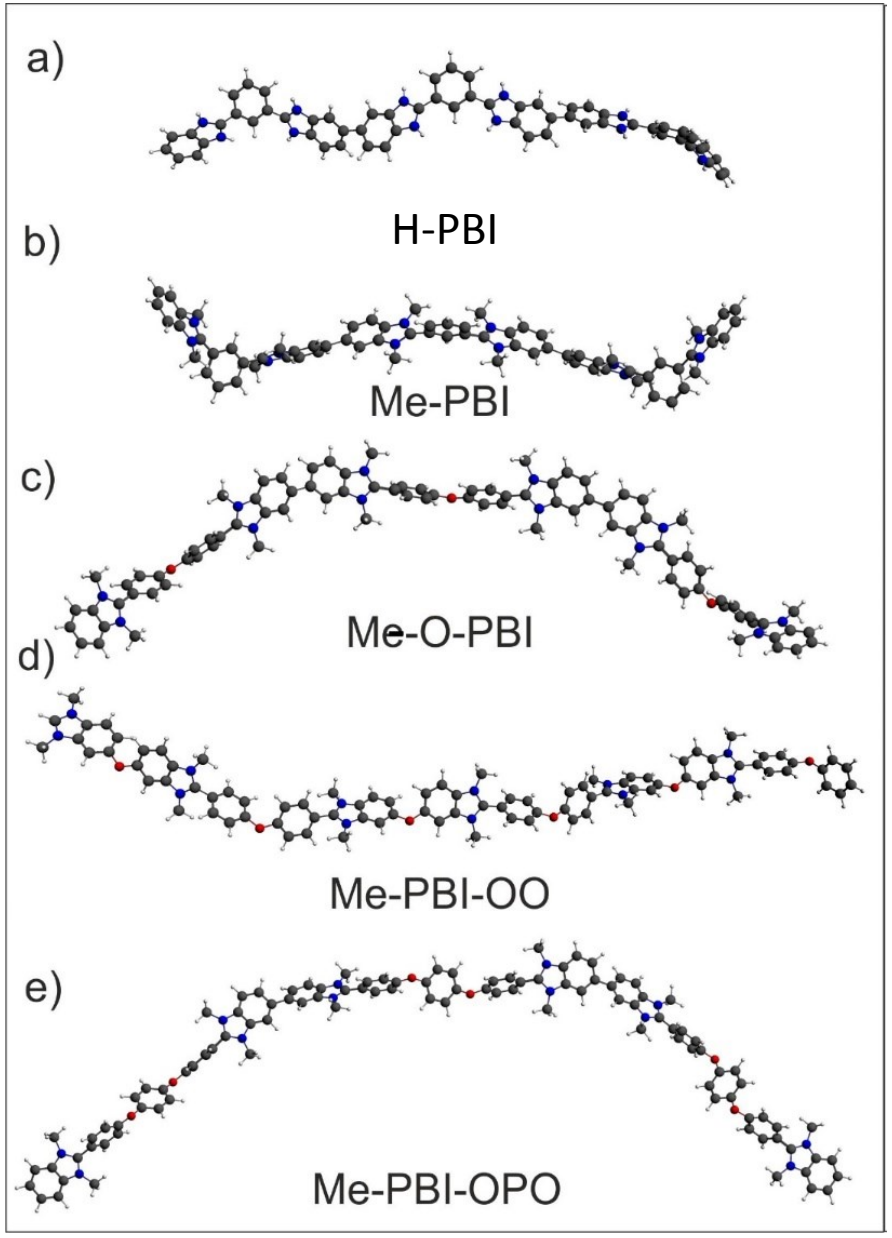
Computational details

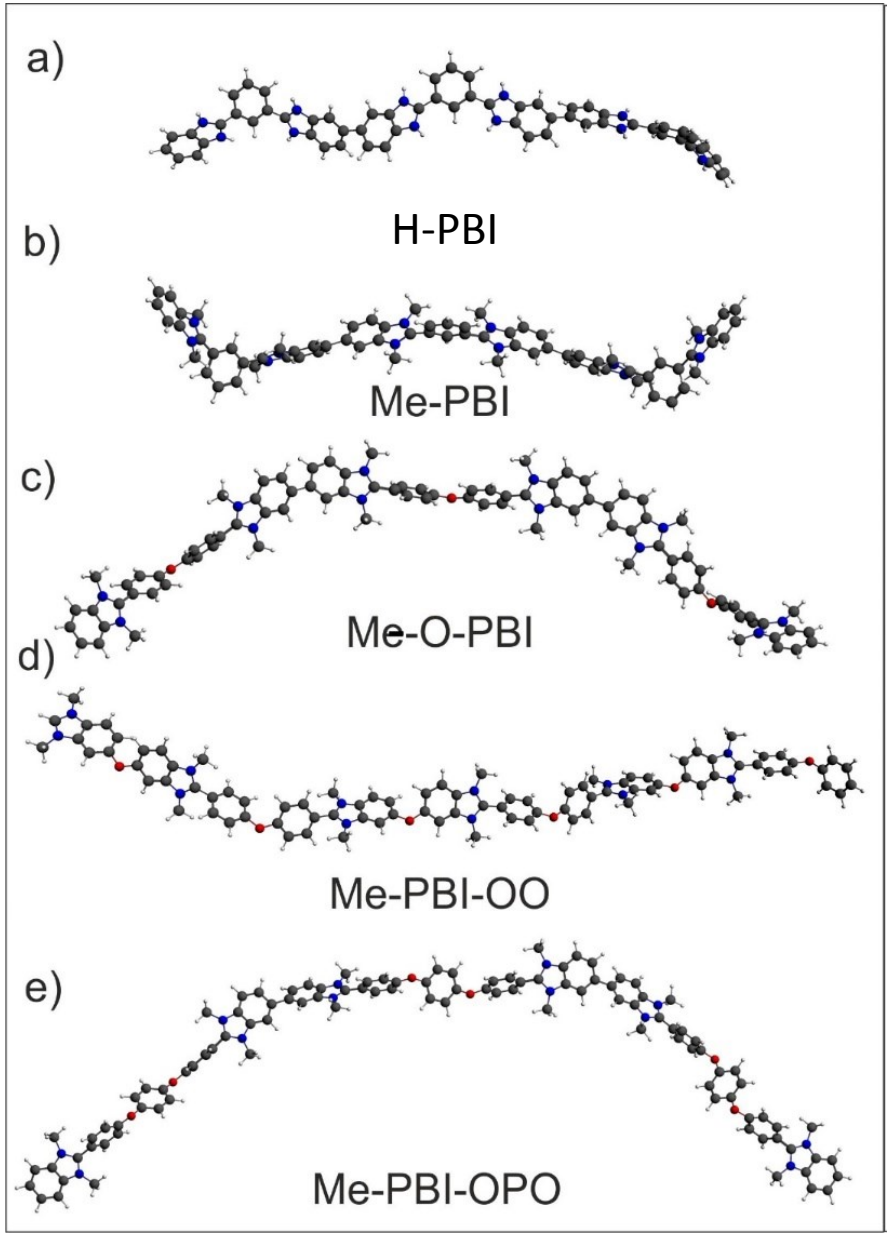
A*b initio* Density Functional Theory (DFT);
ADF 2013 program;
Becke-Perdew exchange correlation functional,
TZP basis set;

Ab initio Molecular Dynamics (DFT-based; CP2K program)

Analysis of the electronic structure
with Natural Orbitals for Chemical Valence (ETS-NOCV)

Analysis of the charge distribution
with Molecular Electrostatic Potenial


a)
H-PBI
b)
Me-PBI
c)
Me-O-PBI
d)
Me-PBI-OO
e)
Me-PBI-OPO



116 atoms

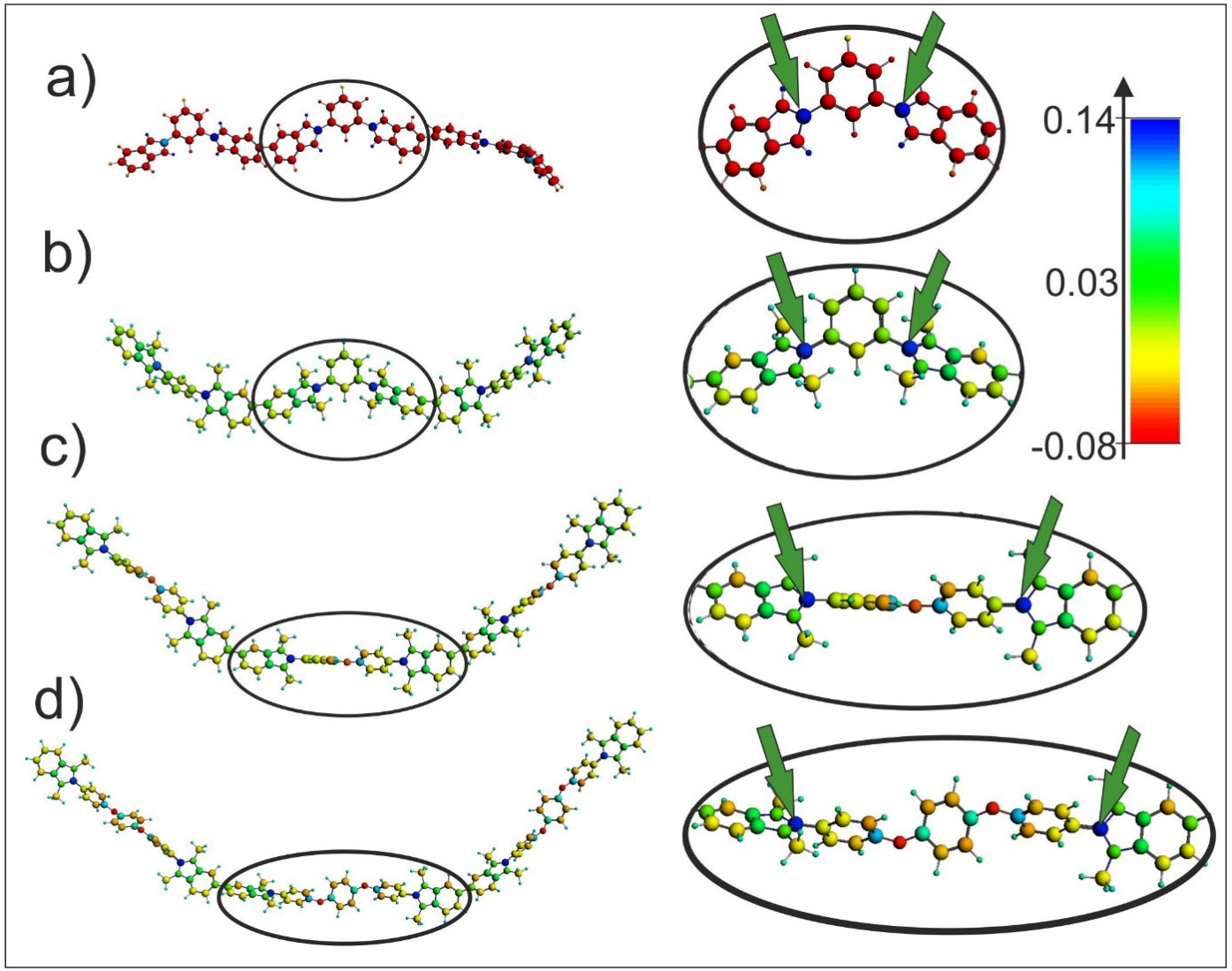
218 atoms

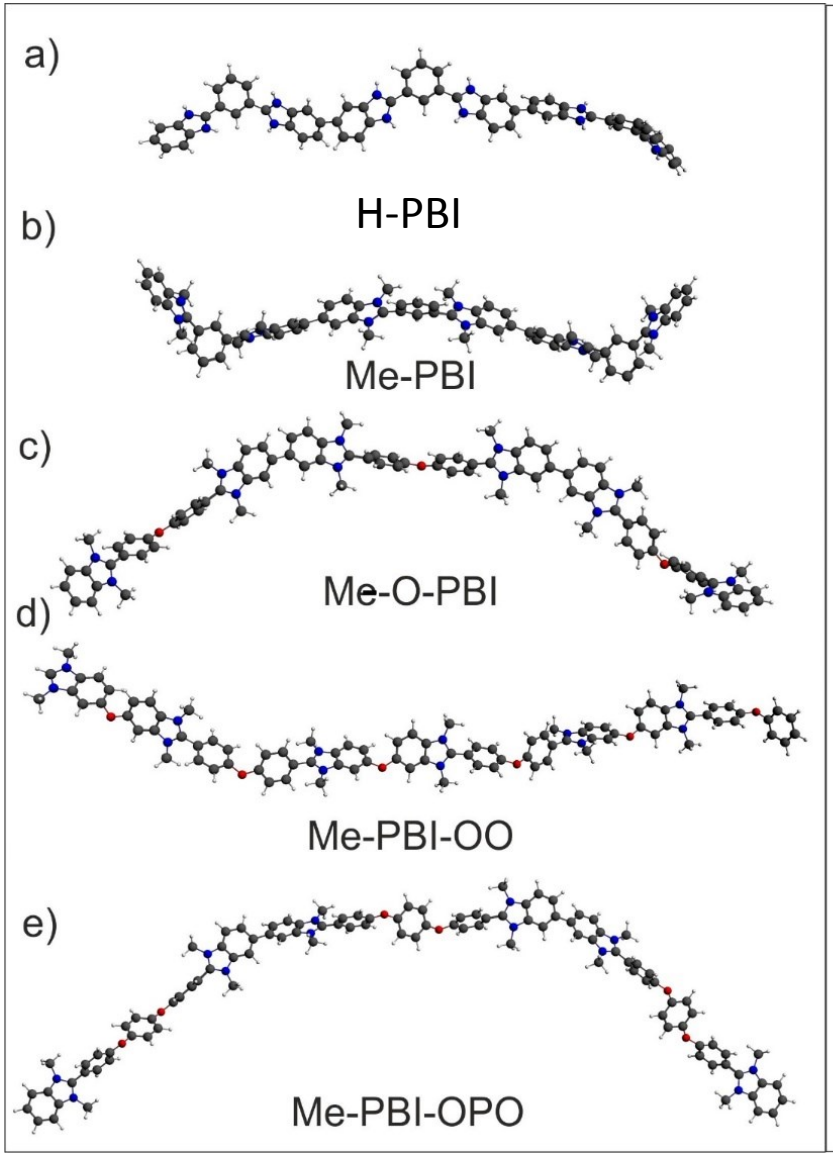
H-PBI

Me-PBI

Me-O-PBI

Me-PBI-OPO




a)
H-PBI
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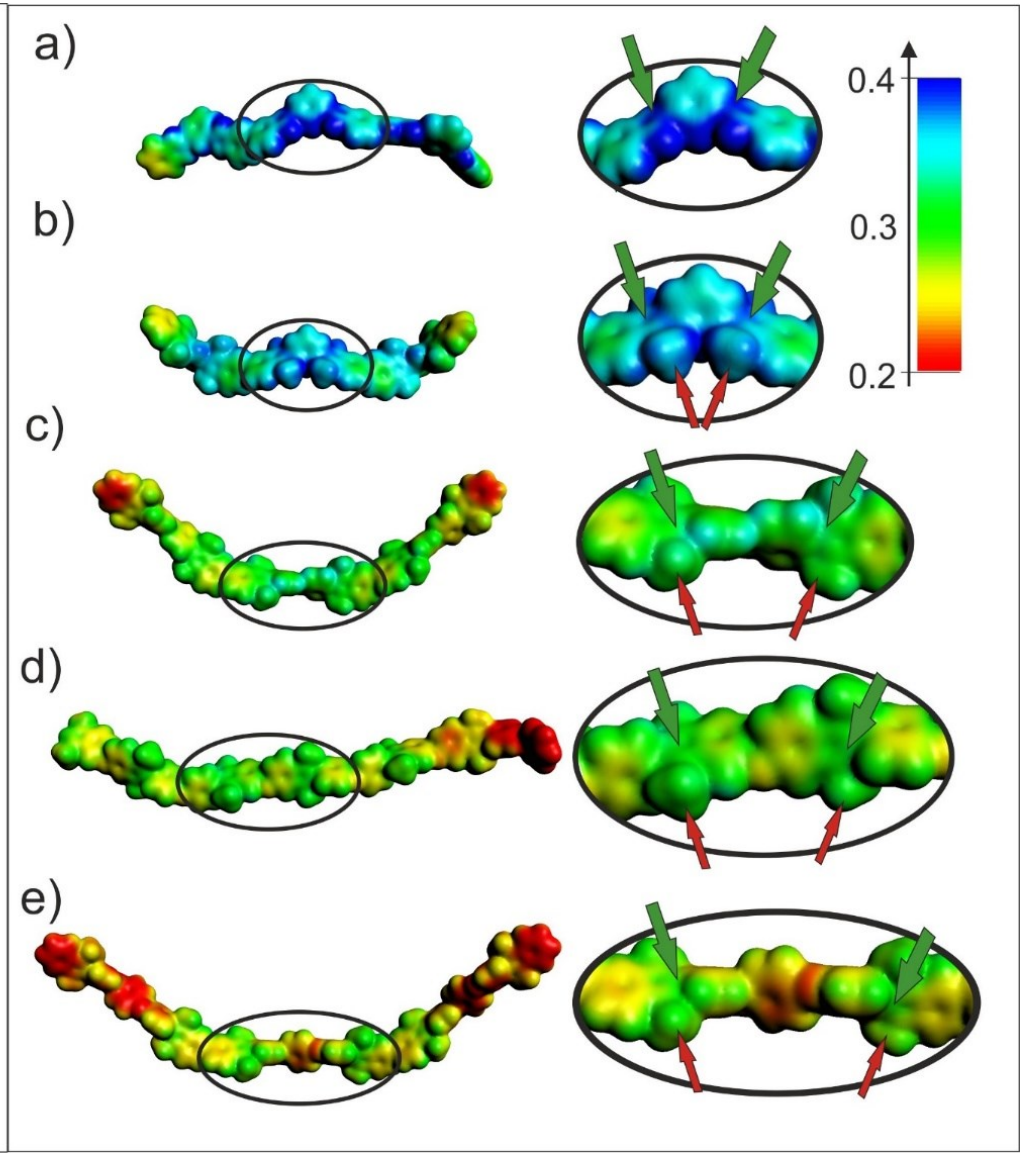
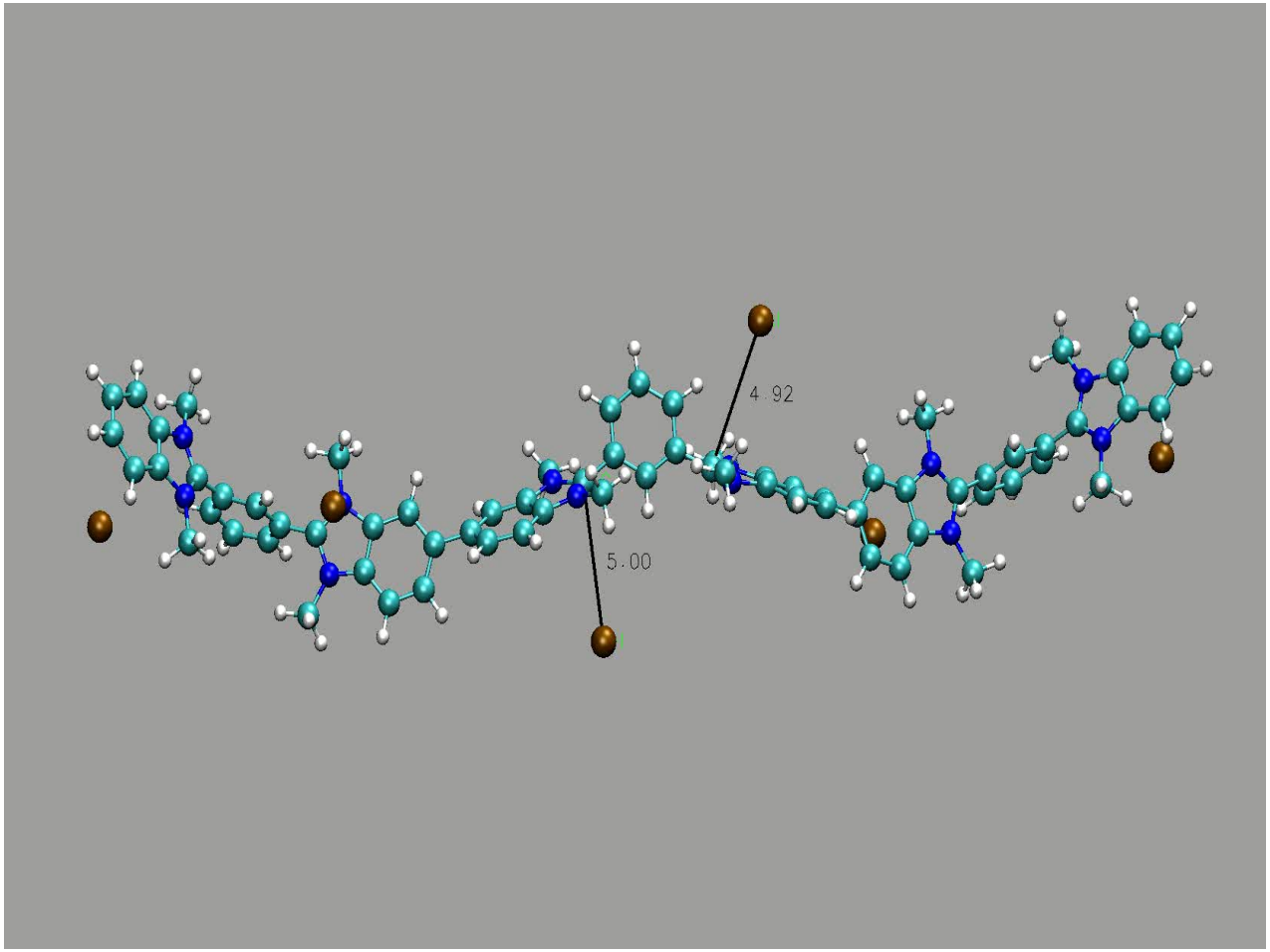
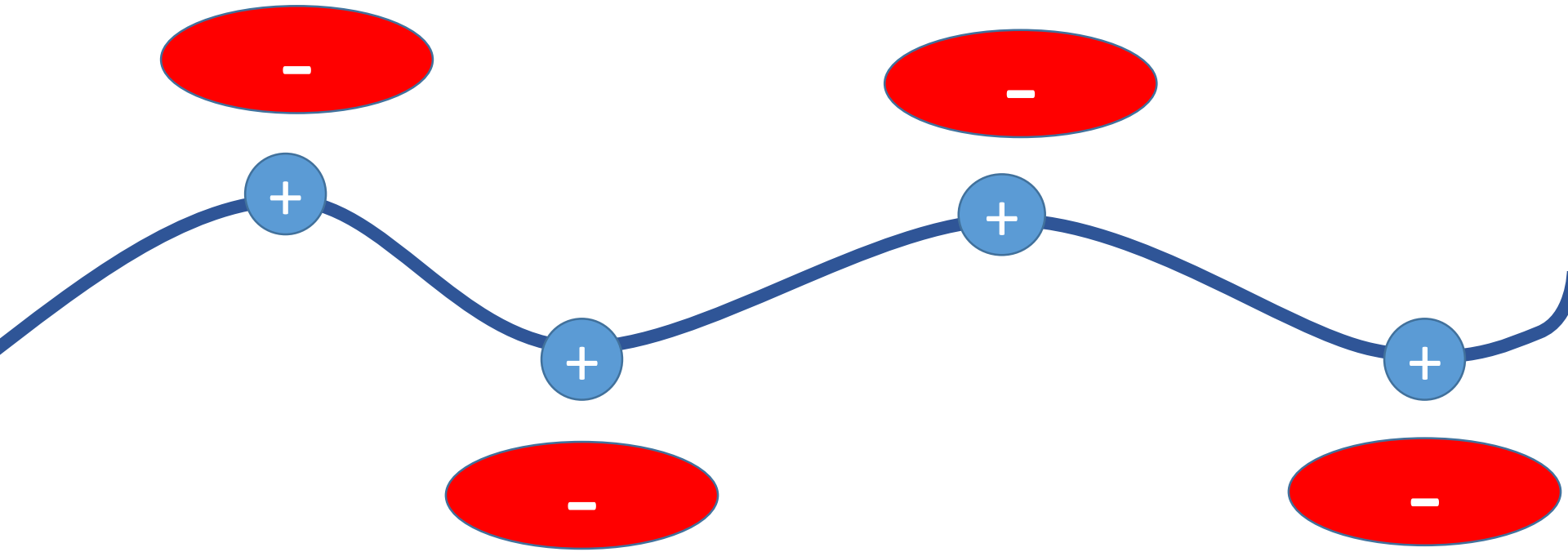

a)
b)
c)
d)
e)
0.4
0.3
0.2

Interactions with anions



Trimer Me-PBI^{6+} + 6I^{-}

ETS-NOCV method for bond analysis

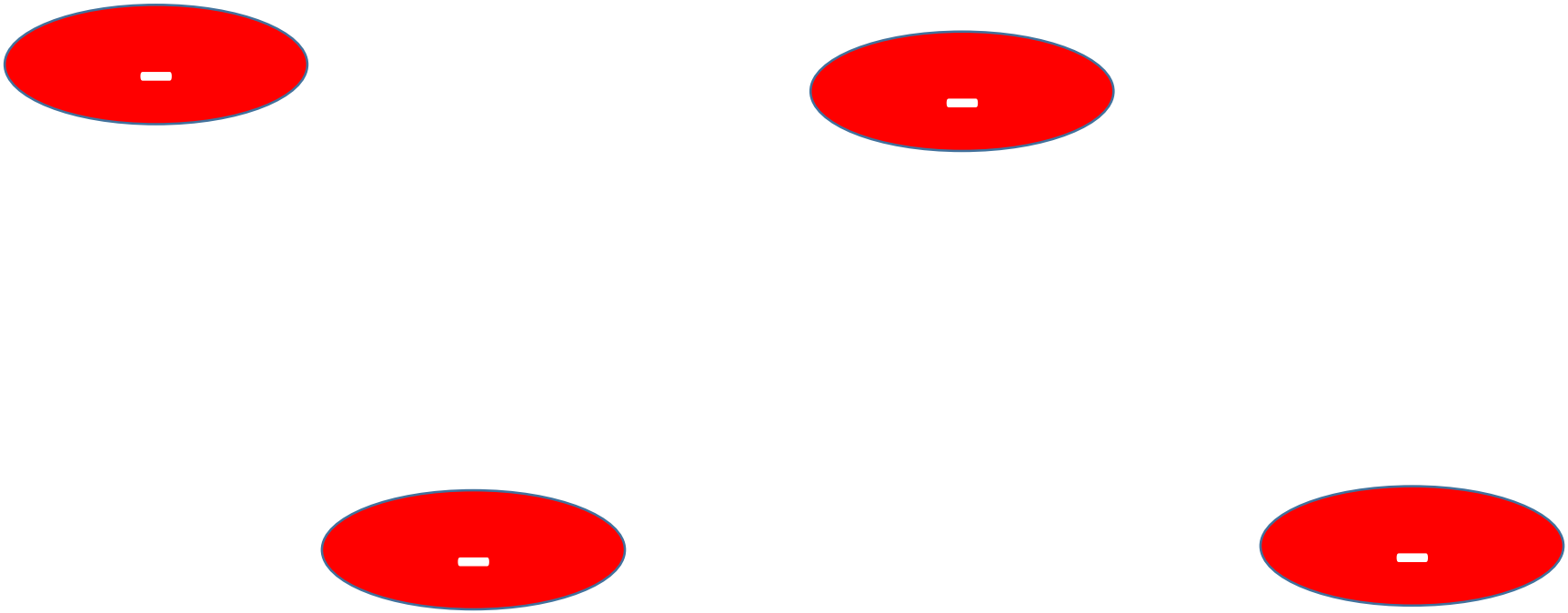


ETS-NOCV method for bond analysis

$$E^{(+)}$$

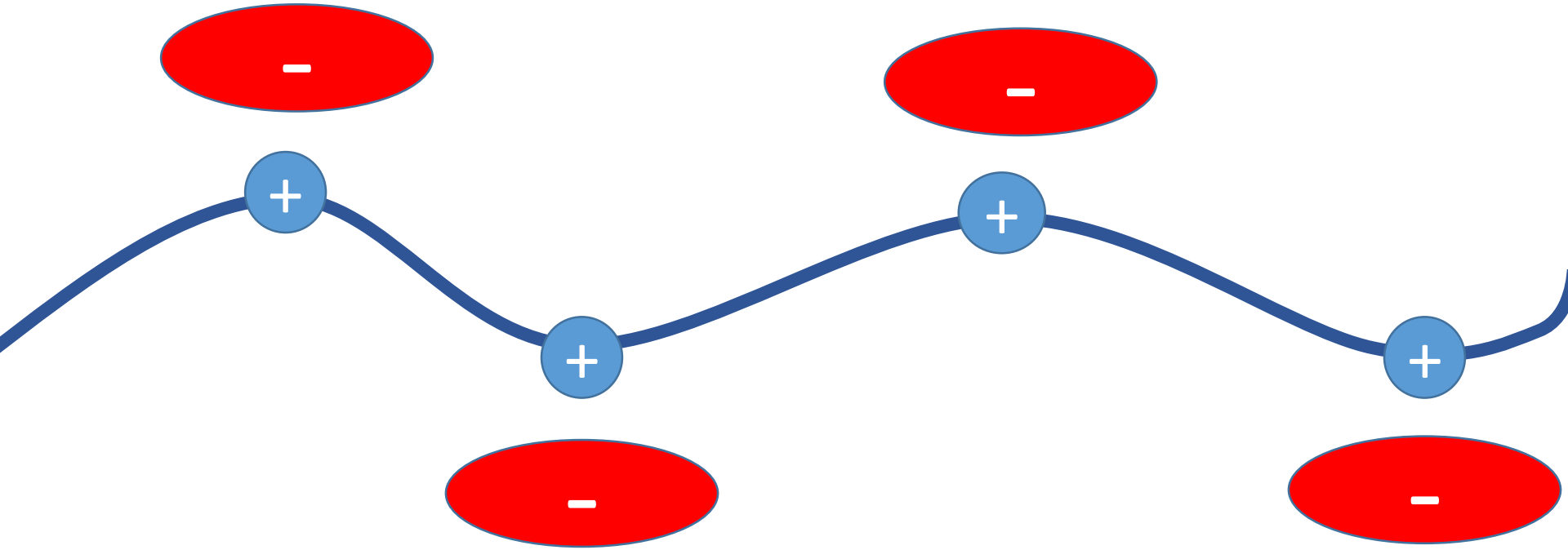
ETS-NOCV method for bond analysis

$E^{(-)}$

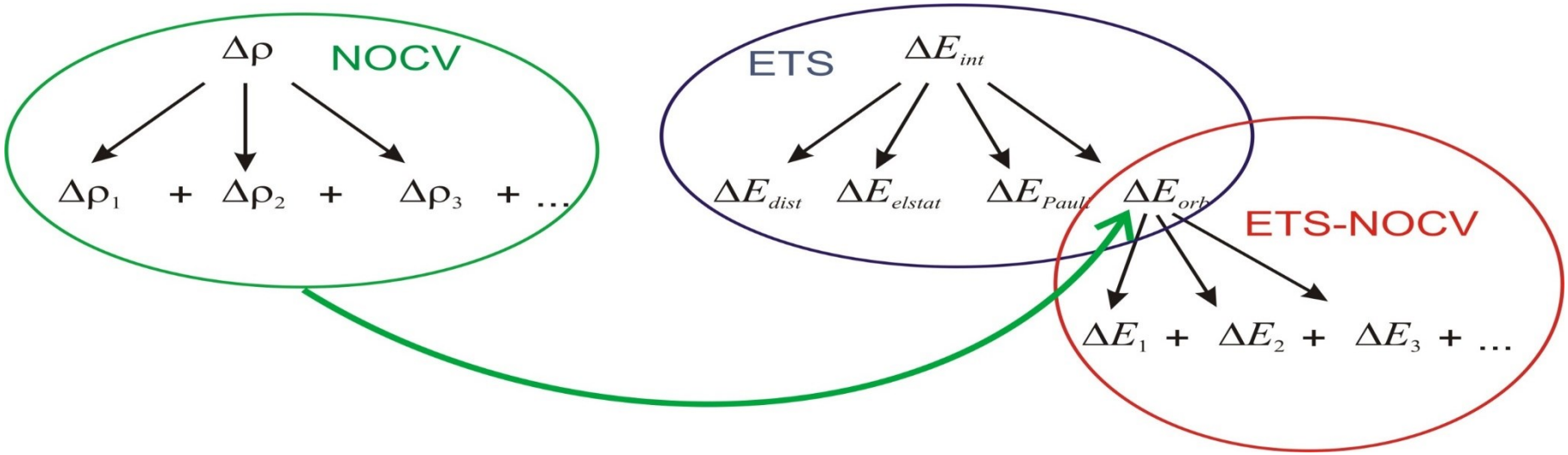


ETS-NOCV method for bond analysis

$$\Delta E^{(+/-)} = E^{(+/-)} - [\, E^{(+)} - E^{(-)} \,]$$



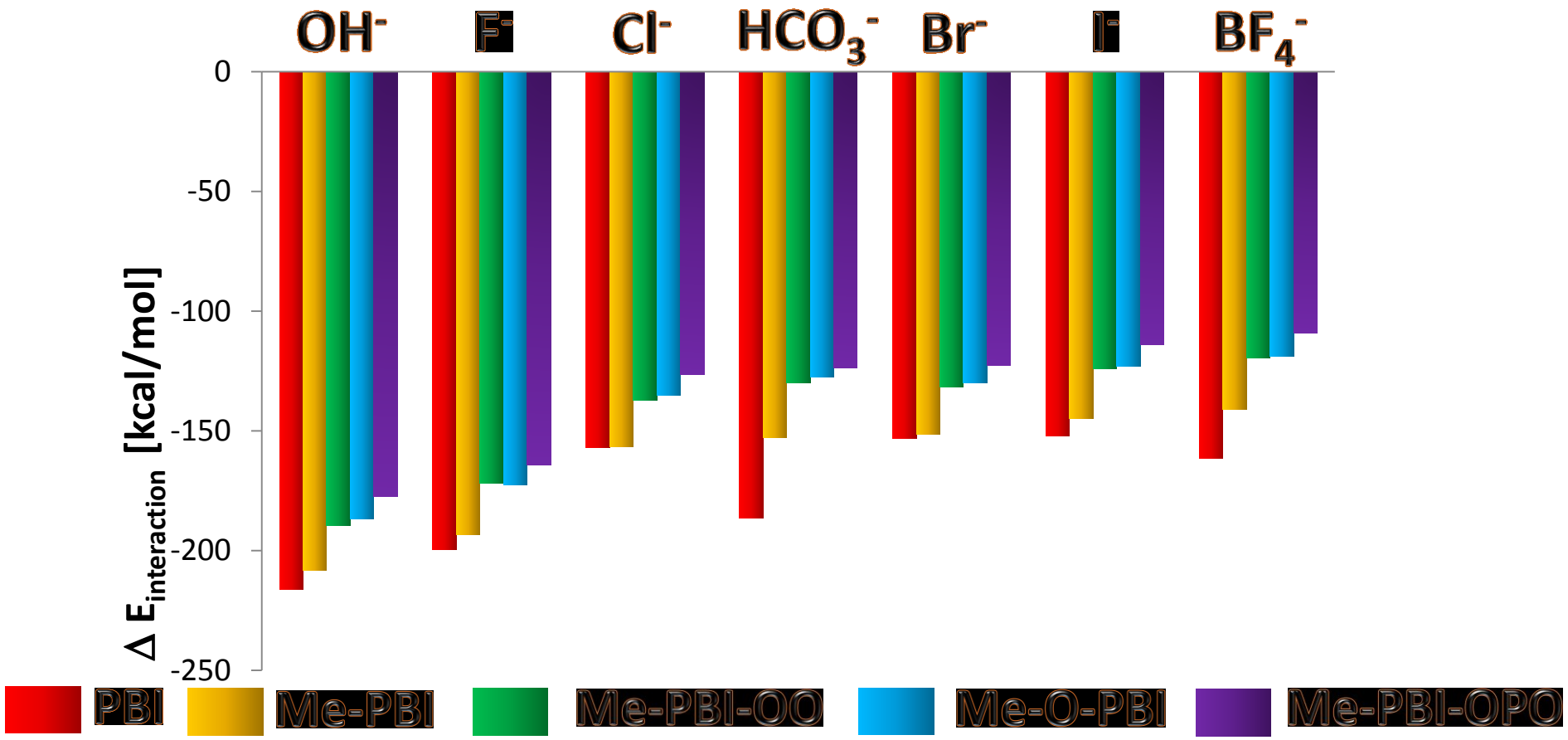
ETS-NOCV method for bond analysis



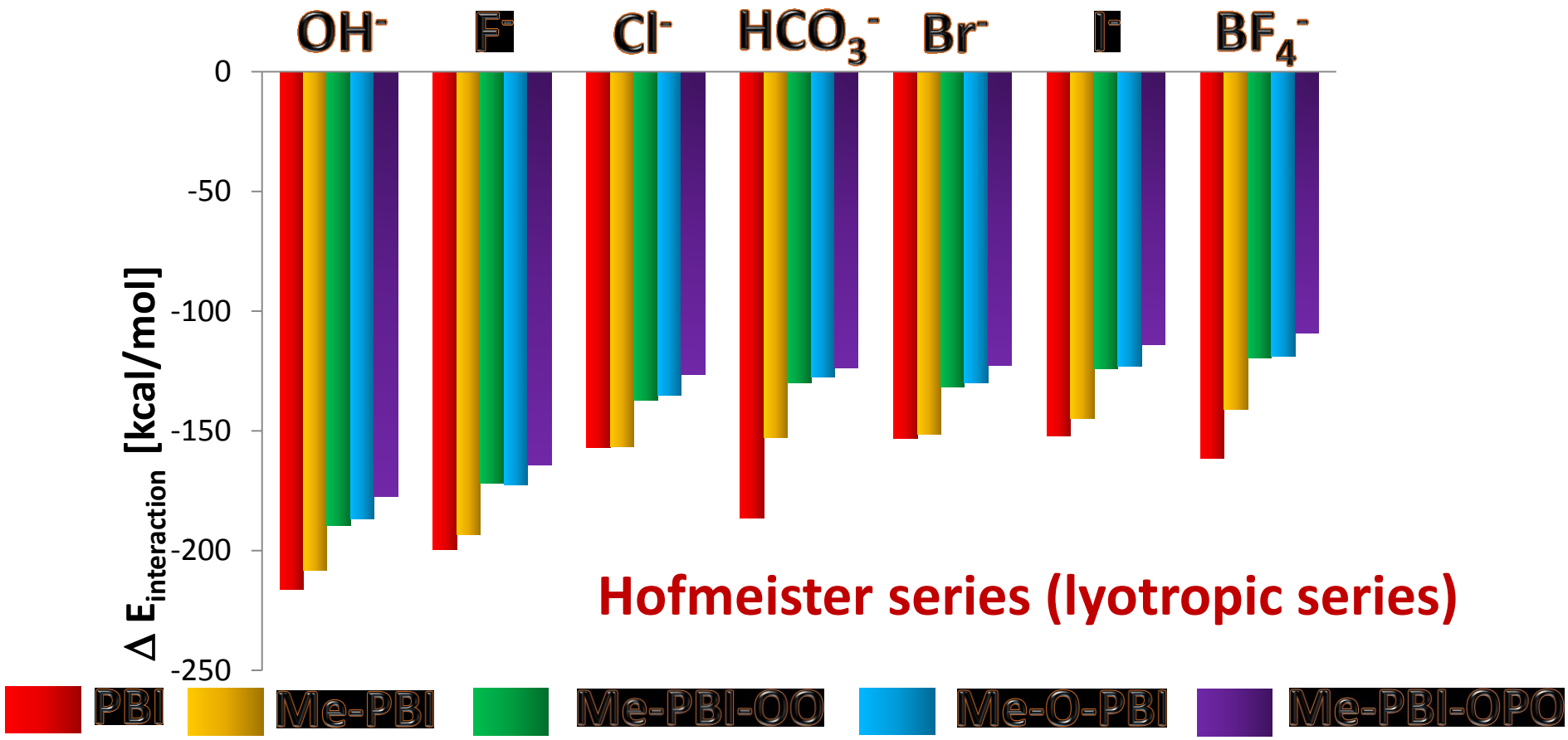
In ADF program, since version 2009.01

M.Mitoraj, A.Michalak, J.Mol.Model. 2007, 13, 347-355.
A.Michalak, M.Mitoraj, T. Ziegler, J. Phys. Chem. A, 2008, 1933-1939.
M.Mitoraj, A. Michalak, T. Ziegler *J. Chem. Theory Comput.*, 2009, *5* , 962–975.

Interactions with anions

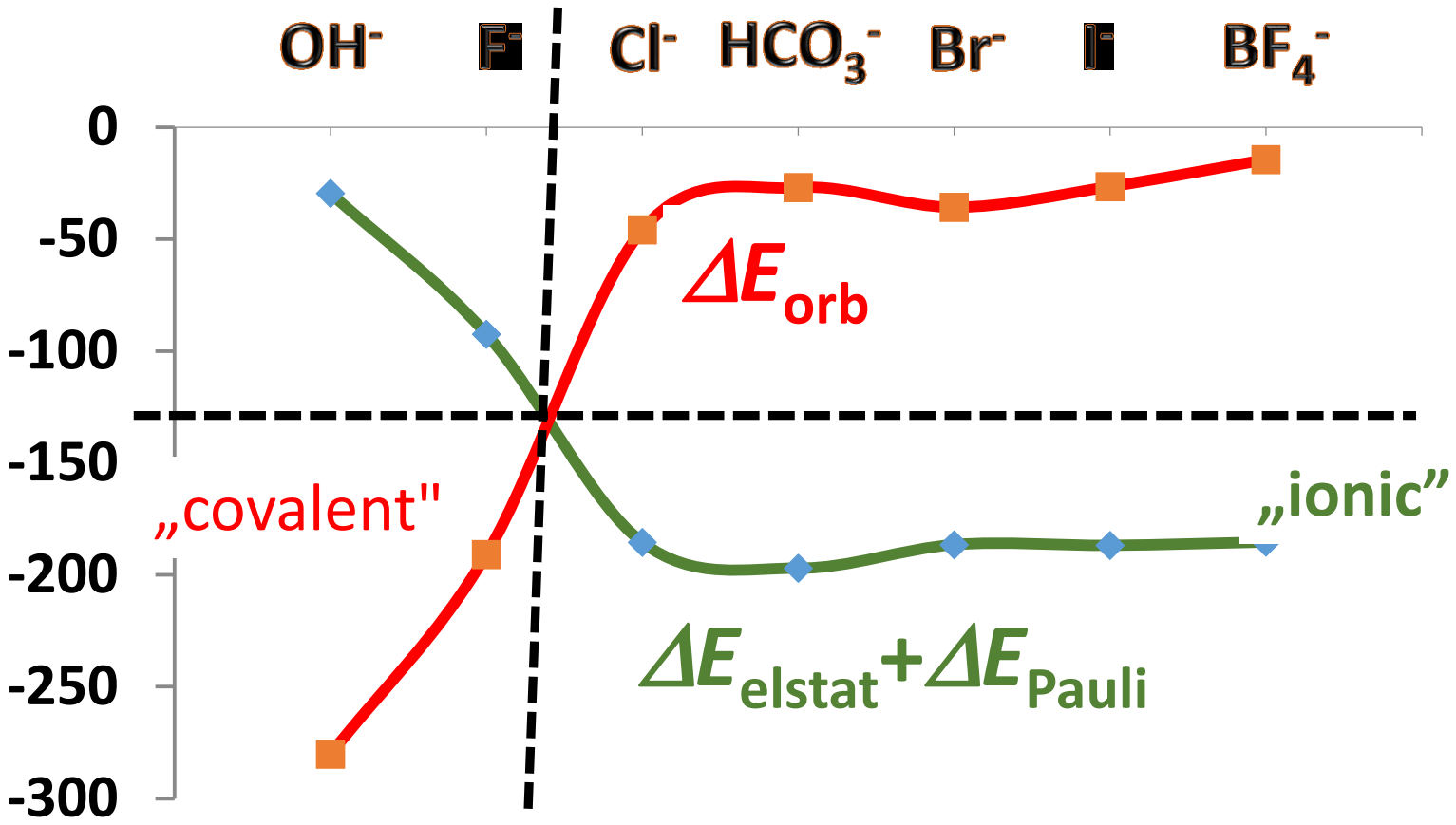


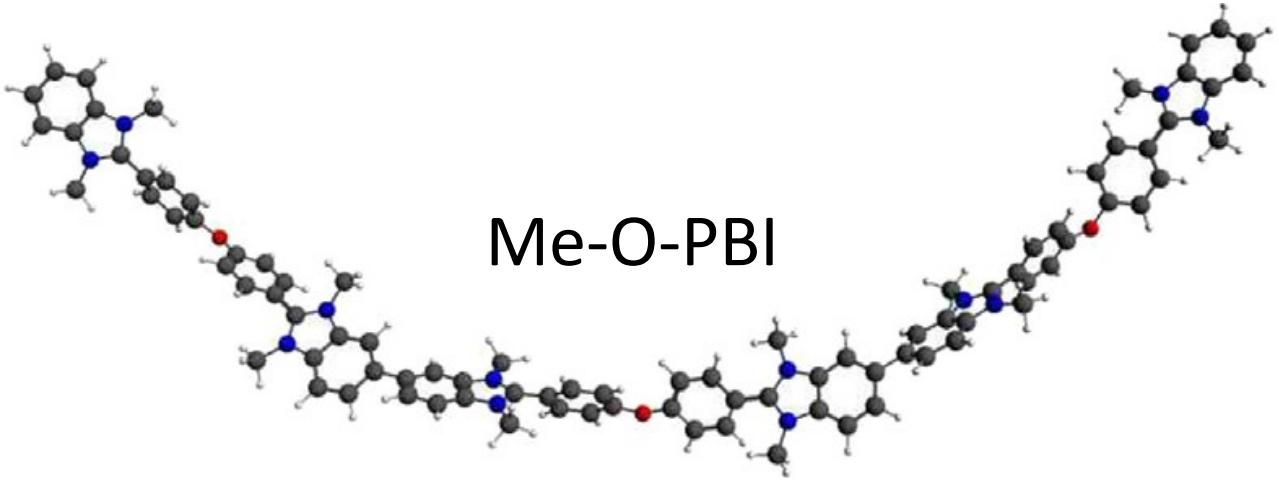
Interactions with anions



Hofmeister series (lyotropic series)

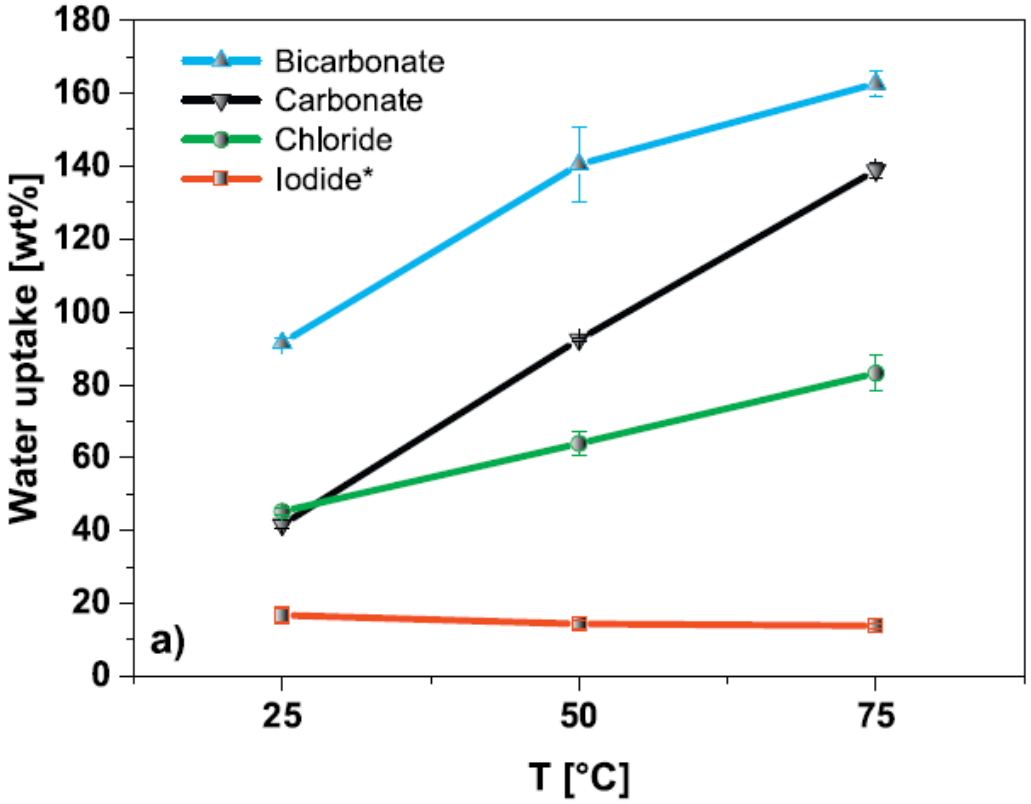
Me-PBI: Interactions with anions (ETS-NOCV)

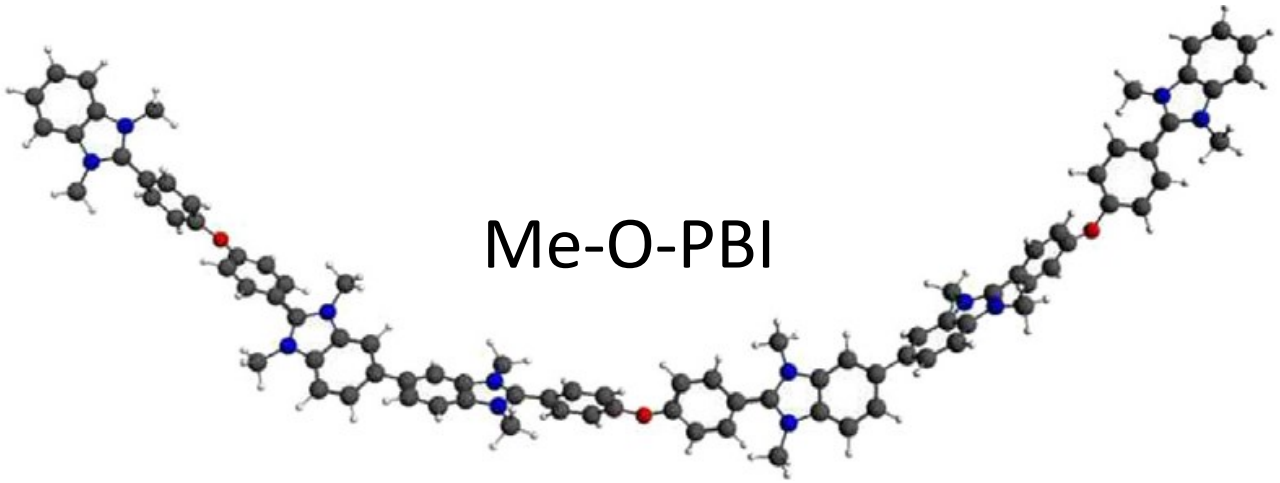




Me-O-PBI

Water uptake, solvation





Me-O-PBI

Water uptake, solvation

Experimental data for water uptake:

HCO_3^- > CO_3^{2-} > Cl^- > I^-

11:14

Solvation of free ions

$Cl^- > HCO_3^- > I^-$

does not explain the water-uptake data

our results:

	COSMO	Cluster cycle* $\Delta G_{solv}(A)$
Cl^-	-77.22	-83,29
HCO_3^-	-76.63	-80,21
I^-	-60.89	-67,39

literature results:

	Smith:		Warshel:	
	Exp	calc	exp	calc
Cl^-	-87.06	-89.21	-78.1	-77.9
HCO_3^-	-85.42	-81.64		-76.0
I^-	-71.70	-75.28	-60.3	-62.9

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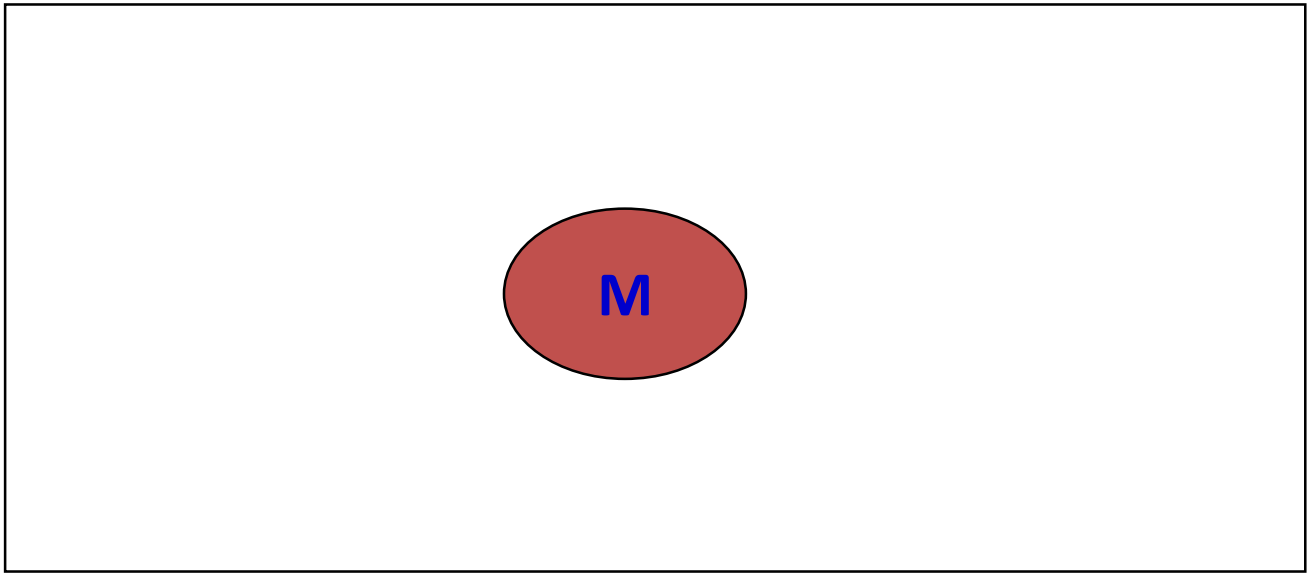
Modeling solvent effects in theoretical calculations

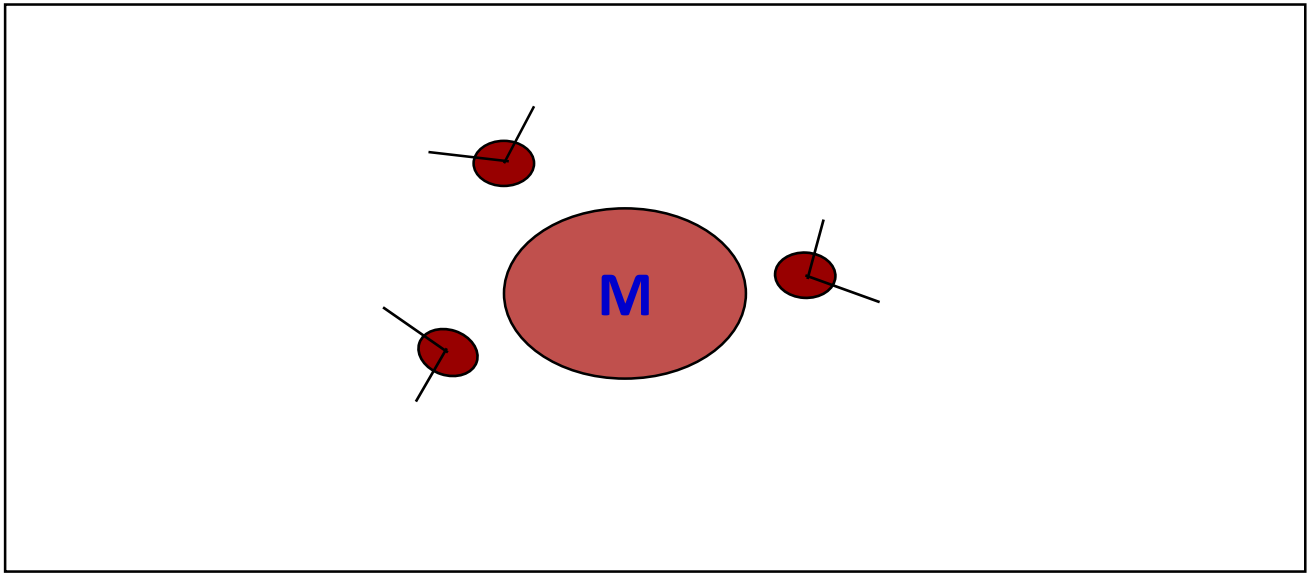
Explicit solvation



$(P^{6+})(X^{-})_{6(g)}$

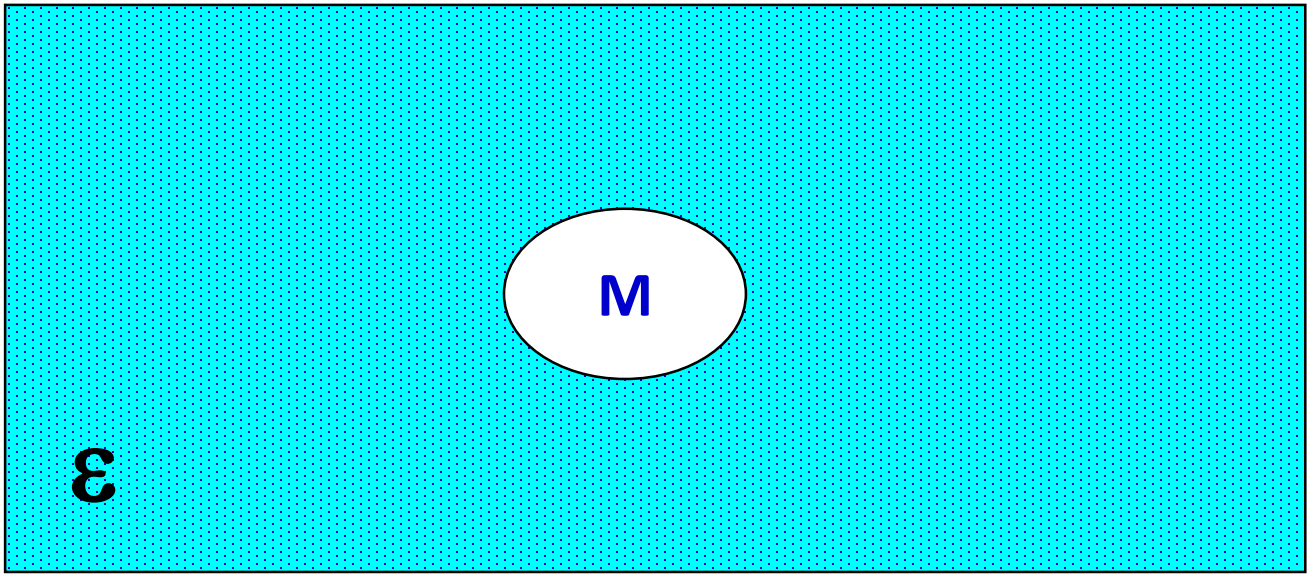
Modeling solvent effects in theoretical calculations

Explicit solvation



$$(P^{6+})(X^{-})_{6(g)} + (H_2O)_{n(g)} \xrightarrow{\Delta G_{bind}} [P^{6+})(X^{-})_6(H_2O)_n]_{(g)}$$

Continuum models (implicit solvation)



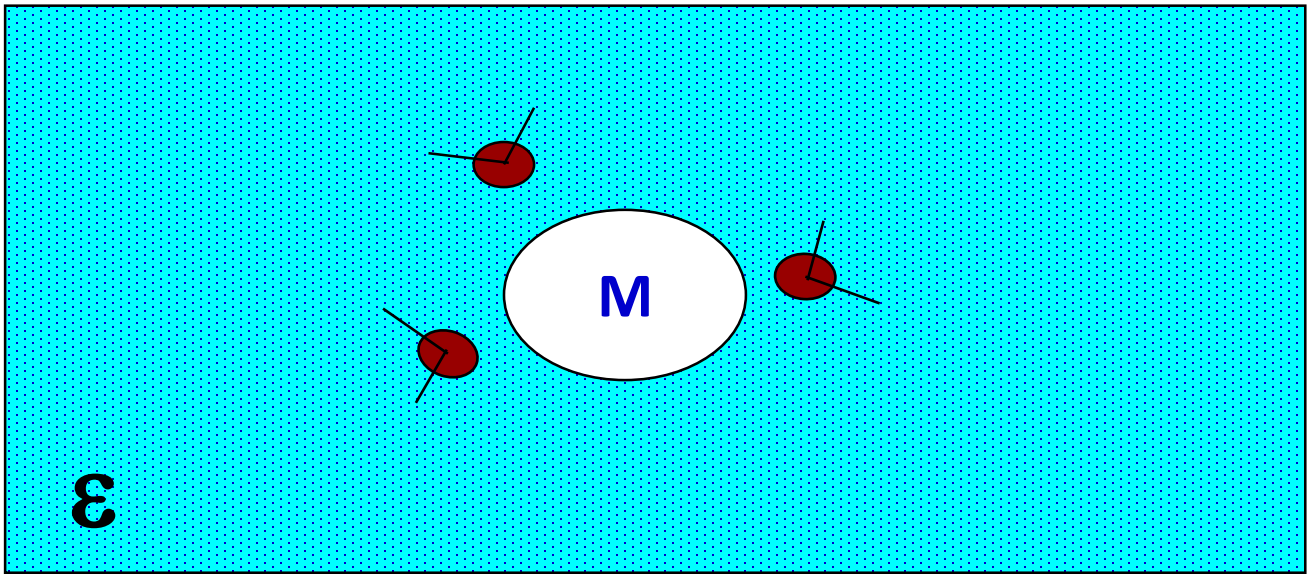
$(P^{6+})(X^{-})_{6(g)}$

$\Delta G_{sol}[(P^{6+})(X^{-})_6]$

$(P^{6+})(X^{-})_{6(aq)}$

11:14

Continuum models + explicit solvation

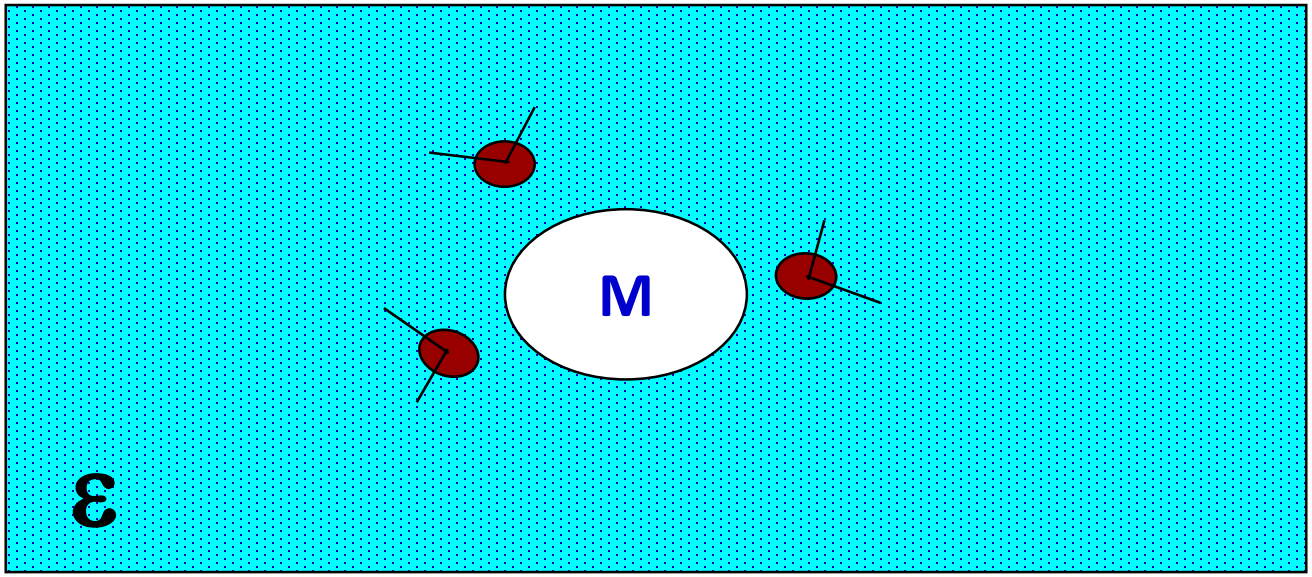


$$(P^{6+})(X^{-})_{6(g)} + (H_2O)_{n(g)} \xrightarrow{\Delta G_{bind}} [P^{6+})(X^{-})_6(H_2O)_n]_{(g)}$$

$$\downarrow \Delta G_{sol}[(P^{6+})(X^{-})_6]$$

$$(P^{6+})(X^{-})_{6(aq)}$$

Continuum models + explicit solvation



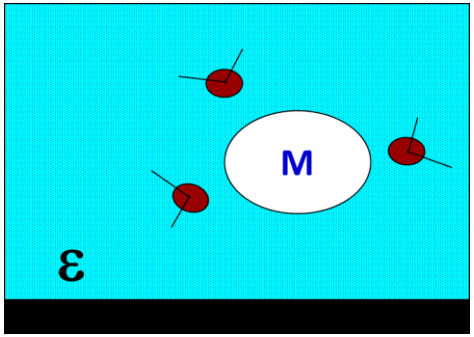
$$(P^{6+})(X^{-})_{6(g)} + (H_2O)_{n(g)} \xrightarrow{\Delta G_{bind}} [P^{6+})(X^{-})_6(H_2O)_n]_{(g)}$$

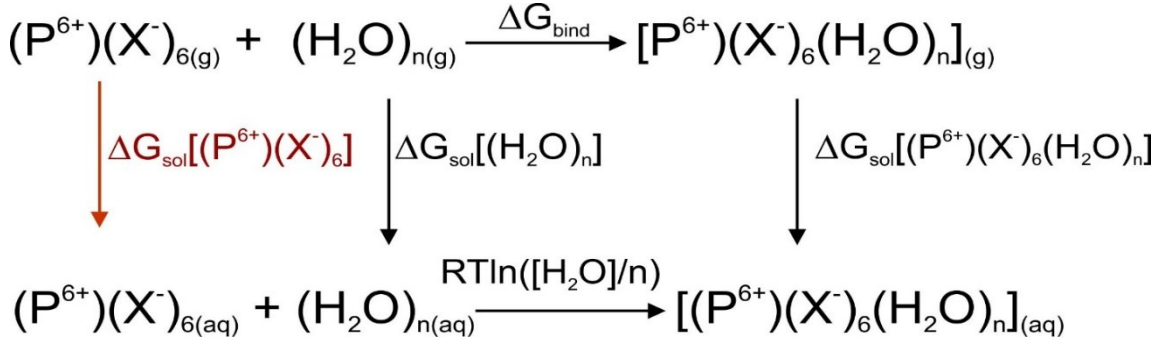
$$\Delta G_{sol}[(P^{6+})(X^{-})_6] \quad \Delta G_{sol}[(H_2O)_n] \quad \Delta G_{sol}[(P^{6+})(X^{-})_6(H_2O)_n]$$

$$(P^{6+})(X^{-})_{6(aq)} + (H_2O)_{n(aq)} \xrightarrow{RTln([H_2O]/n)} [(P^{6+})(X^{-})_6(H_2O)_n]_{(aq)}$$

Continuum models + explicit solvation

Thermodynamic cycles



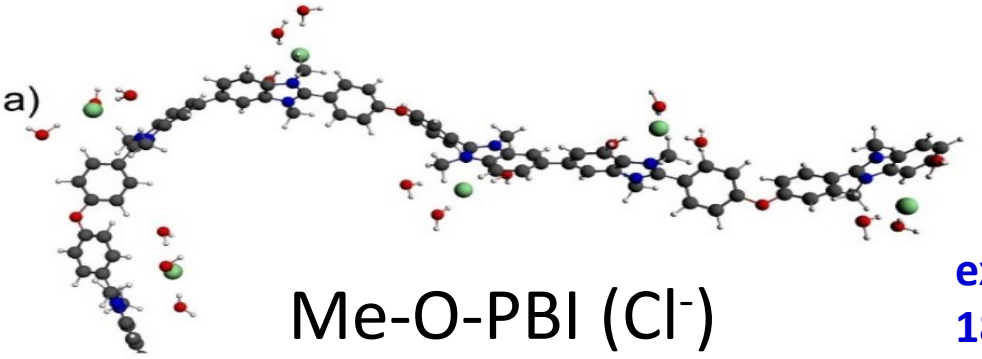


$$\Delta G_{sol}\left[\left(\mathrm{P}^{6+}\right)(\mathrm{X}^{-})_6\right] + \Delta G_{sol}\left[(\mathrm{H_2O})_n\right] = \Delta G_{bind} + \Delta G_{sol}\left[\left(P^{6+}\right)(\mathrm{X}^{-})_6(\mathrm{H_2O})_n\right] - RTln([H_2O]/n)$$

$$\Delta G_{sol}\left[\left(\mathrm{P}^{6+}\right)(\mathrm{X}^{-})_6\right] = \Delta G_{bind} + \Delta G_{sol}\left[\left(\mathrm{P}^{6+}\right)(\mathrm{X}^{-})_6(\mathrm{H_2O})_n\right] - RTln([\mathrm{H_2O}]/n) - \Delta G_{sol}\left[(\mathrm{H_2O})_n\right]$$

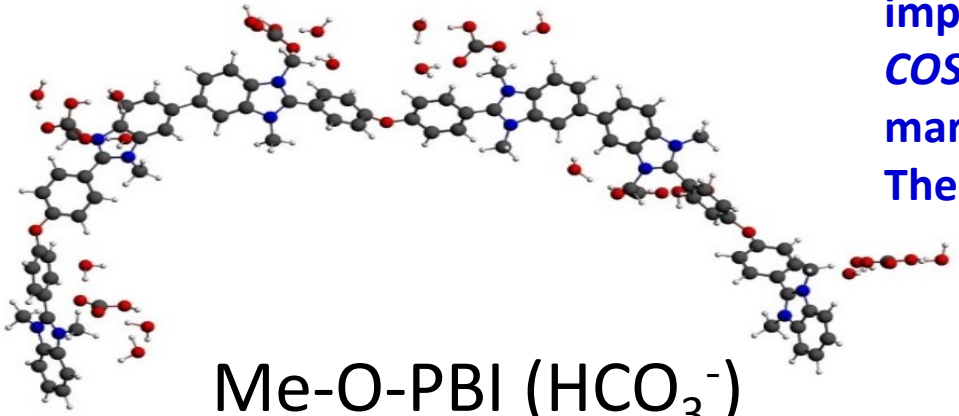
Bryantsev, V. S.; Diallo, M. S.; Goddard III, W. A. J. Phys. Chem. B 2008, 112, 9709.

a)



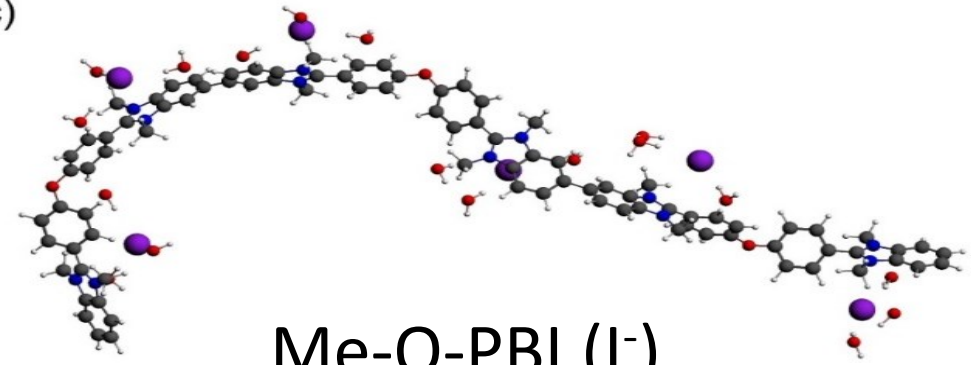
Me-O-PBI (Cl^-)

b)



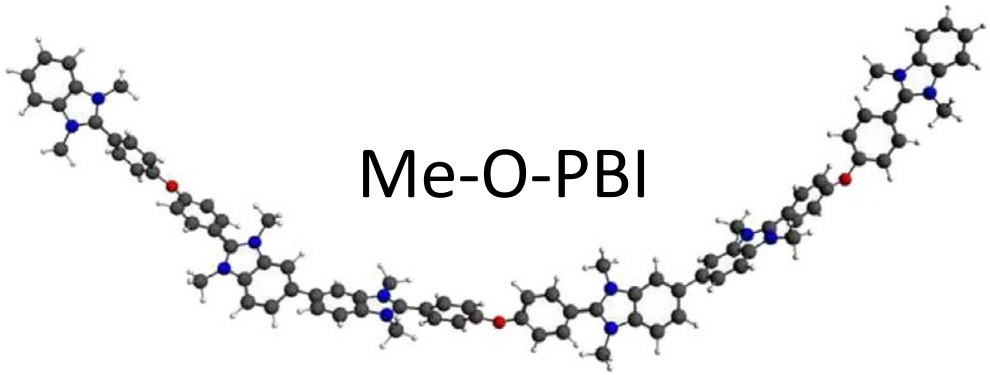
Me-O-PBI (HCO_3^-)

c)



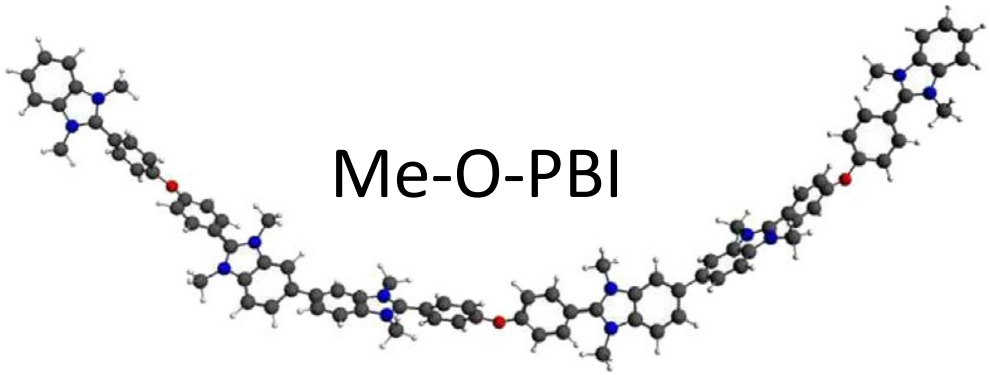
Me-O-PBI (I^-)

explicit solvation:
18 water molecules included in the model (or 21, 24)
implicit solvation:
***COSMO continuum* model**
marge:
Thermodynamic ‚cluster'



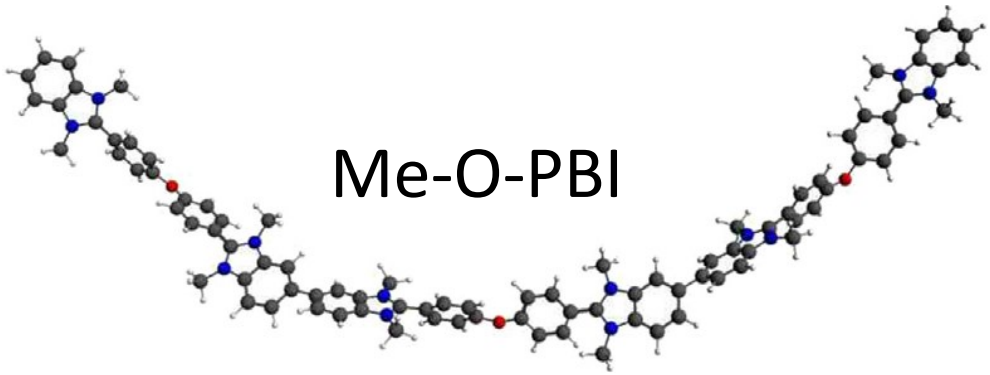
Me-O-PBI

P	Implicit (COSMO)
	$\Delta G_{solv}(P)$
Me-O-PBI^{6+} + 6 Cl^-	-22.96
Me-O-PBI^{6+} + 6 HCO_3^-	-34.83
Me-O-PBI^{6+} + 6 I^-	-24.25



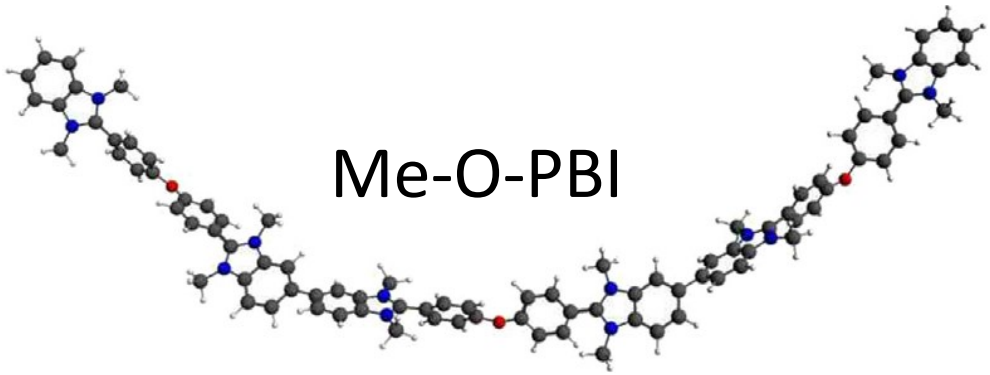
Me-O-PBI

P	Implicit (COSMO)	Explicit (ETS)
	$\Delta G_{solv}(P)$	$\Delta E_{P\text{-}18H2O}$
Me-O-PBI^{6+} + 6 Cl^-	-22.96	-38.10
Me-O-PBI^{6+} + 6 HCO_3^-	-34.83	-38.66
Me-O-PBI^{6+} + 6 I^-	-24.25	-31.25



Me-O-PBI

P	Implicit (COSMO)	Explicit (ETS)	Thermodynamic Cycle
	$\Delta G_{solv}(P)$	$\Delta E_{P\text{-}18H2O}$	$\Delta G_{solv}(P)$
$Me\text{-}O\text{-}PBI^{6+} + 6\ Cl^-$	-22.96	-38.10	-43.41
$Me\text{-}O\text{-}PBI^{6+} + 6\ HCO_3^-$	-34.83	-38.66	-49.76
$Me\text{-}O\text{-}PBI^{6+} + 6\ I^-$	-24.25	-31.25	-34.40

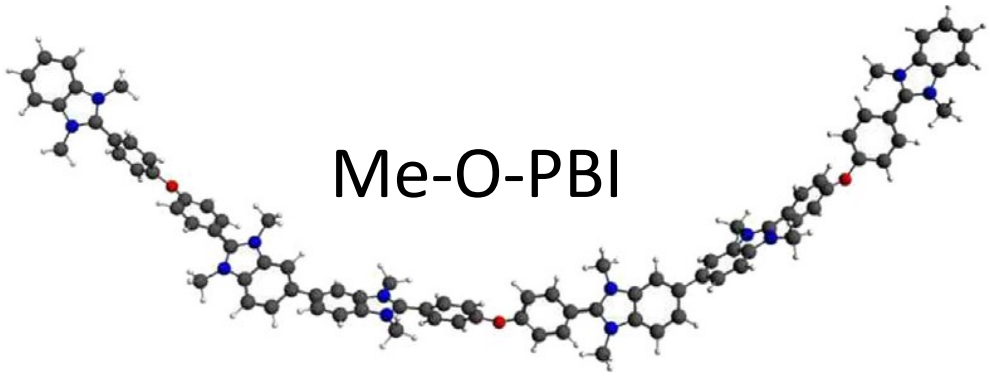


Me-O-PBI

P	Implicit (COSMO)	Explicit (ETS)	Thermodynamic Cycle
	$\Delta G_{solv}(P)$	$\Delta E_{P\text{-}18H2O}$	$\Delta G_{solv}(P)$
$Me\text{-}O\text{-}PBI^{6+} + 6\ Cl^-$	-22.96	-38.10	-43.41
$Me\text{-}O\text{-}PBI^{6+} + 6\ HCO_3^-$	-34.83	-38.66	-49.76
$Me\text{-}O\text{-}PBI^{6+} + 6\ I^-$	-24.25	-31.25	-34.40

$HCO_3^- > Cl^- > I^-$

11:14



Me-O-PBI

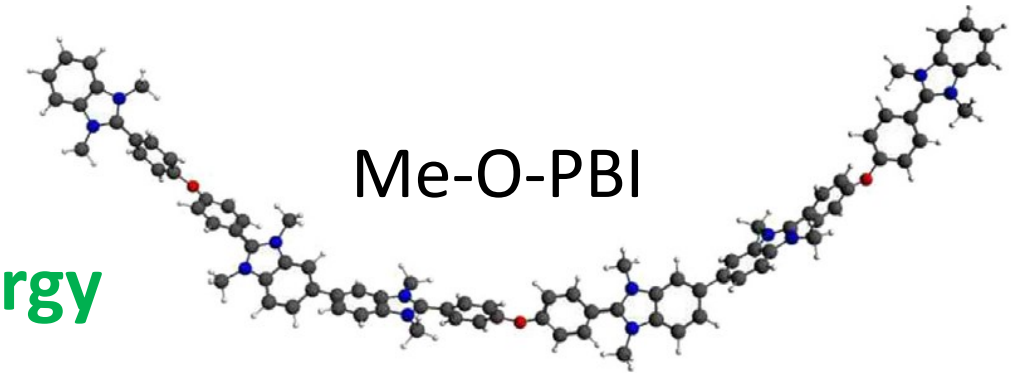
P	Implicit (COSMO)	Explicit (ETS)	Thermodynamic Cycle
	$\Delta G_{solv}(P)$	$\Delta E_{P\text{-}18H2O}$	$\Delta G_{solv}(P)$
Me-O-PBI^{6+} + 6 Cl^-	-22.96	-38.10	-43.41
Me-O-PBI^{6+} + 6 HCO_3^-	-34.83	-38.66	-49.76
Me-O-PBI^{6+} + 6 I^-	-24.25	-31.25	-34.40

HCO_3^- > Cl^- > I^-

Why?

11:14

Ion binding energy

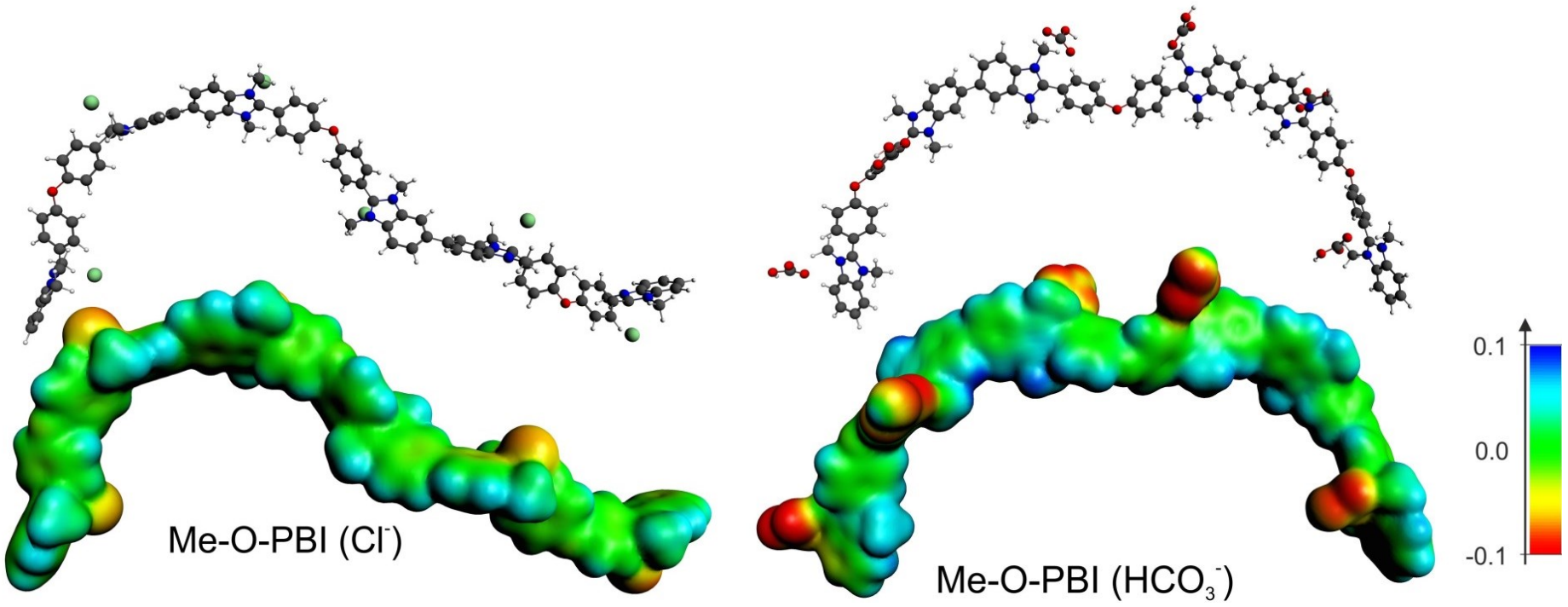


	$\Delta E_{interaction}$	$\Delta E_{dist} + \Delta E_{elstat} + \Delta E_{Pauli}$	ΔE_{orb}
$Me\text{-}O\text{-}PBI^{6+} + 6\ Cl^-$	-128.68	-85.39	-43.30
$Me\text{-}O\text{-}PBI^{6+} + 6\ HCO_3^-$	-120.61	-99.52	-21.09
$Me\text{-}O\text{-}PBI^{6+} + 6\ I^-$	-116.23	-92.66	-23.57
		'non-covalent'	'covalent'

lowest $|\Delta E_{orb}|$:

lowest charge transfer ion → polymer

11:14



lowest $|\Delta E_{orb}|$: lowest charge transfer ion → polymer resulting in the highest charge separation

Main Conclusion

The increased solvation energy observed for the system with bicarbonate ions (compared to the polymer interacting with iodide and chloride ions), results from the increased electrostatic interaction with the solvent, which primarily originates from the increased charge separation observed for this system.

More details:

Dirk Henkensmeier, Hyeongrae Cho, Mateusz Brela, Artur Michalak, Alexander Dyck, Wiebke Germer, Ngoc My Hanh Duong, Jong Hyun Jang, Hyoung-Juhn Kim, Nam-Suk Woo, Tae-Hoon Lim*; Anion conducting polymers based on ether linked polybenzimidazole (PBI-OO);* **International Journal of Hydrogen Energy**, 2014, 39 (6), pp 2842–2853.

Wiebke Germer, Janine Leppin, Carolina Nunes Kirchner, Hyeongrae Cho, Hyoung-Juhn Kim, Dirk Henkensmeier, Kwan-Young Lee, Mateusz Brela, Artur Michalak and Alexander Dyck, *Phase Separated Methylated Polybenzimidazole (O-PBI) Based Anion Exchange Membranes*, **Macromolecular Materials and Engineering**, 2015,

Thank you very much

$PBI^{6+}+6Cl^{-}+726\ H_2O$