Molecular modeling of the alkaline anionic exchange membranes for fuel cells

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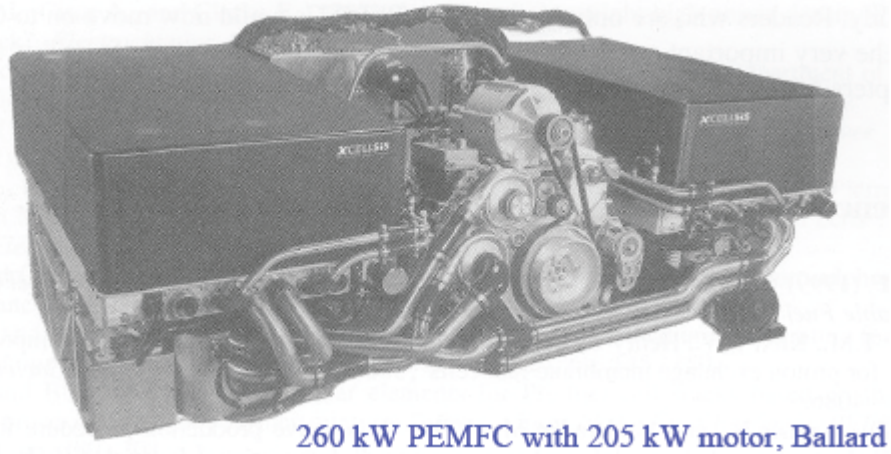
Kraków, February 28th, 2012

Proton Exchange Membrane Fuel Cells

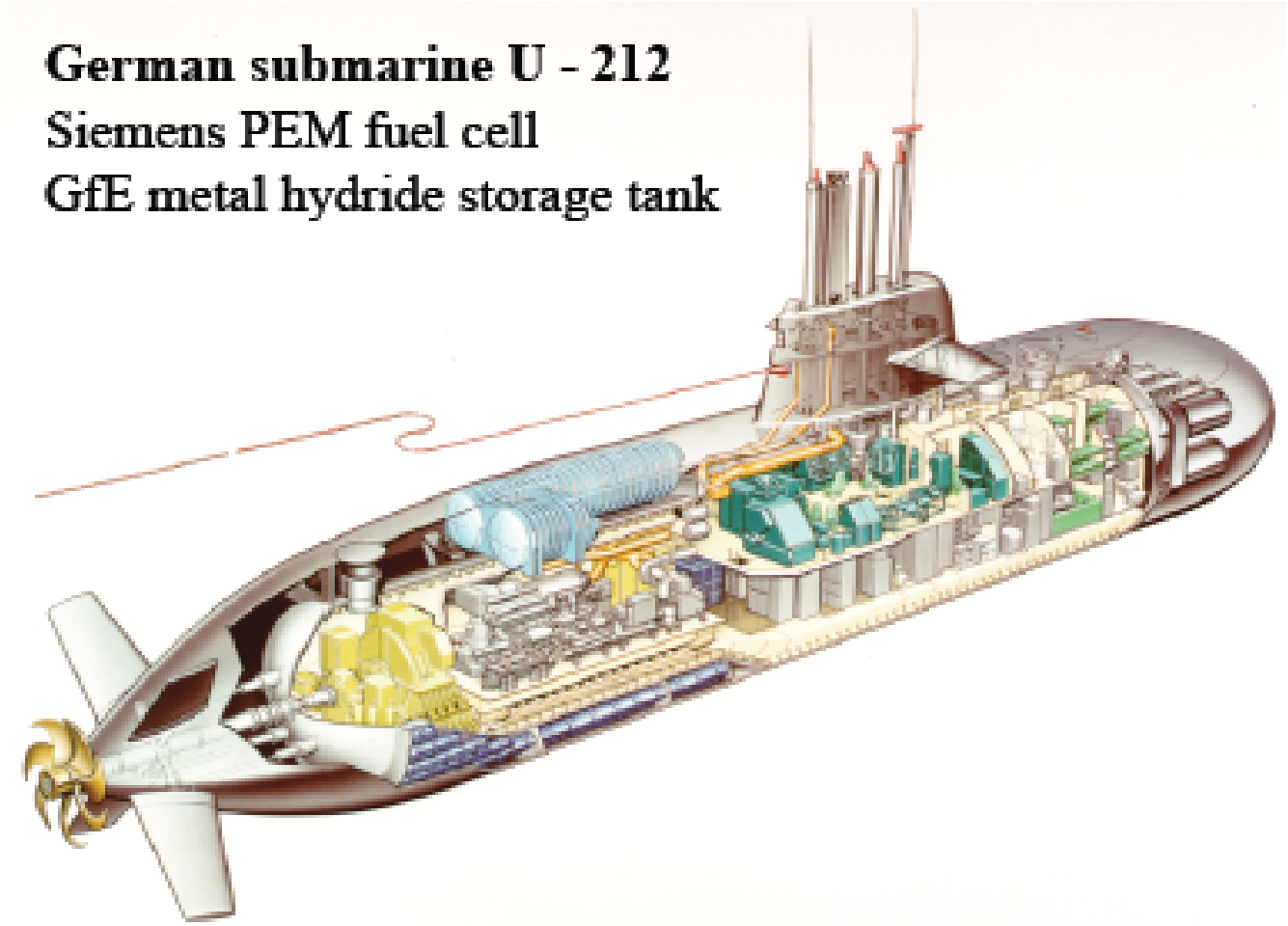
2004, 10 000 km
HydroGen3 (Opel Zafira)

http://www.gmeurope.com/marathon/

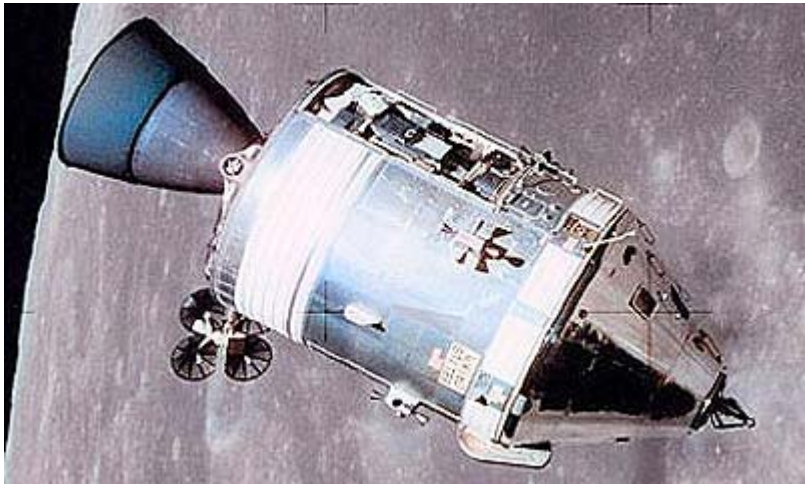


260 kW PEMFC with 205 kW motor, Ballard

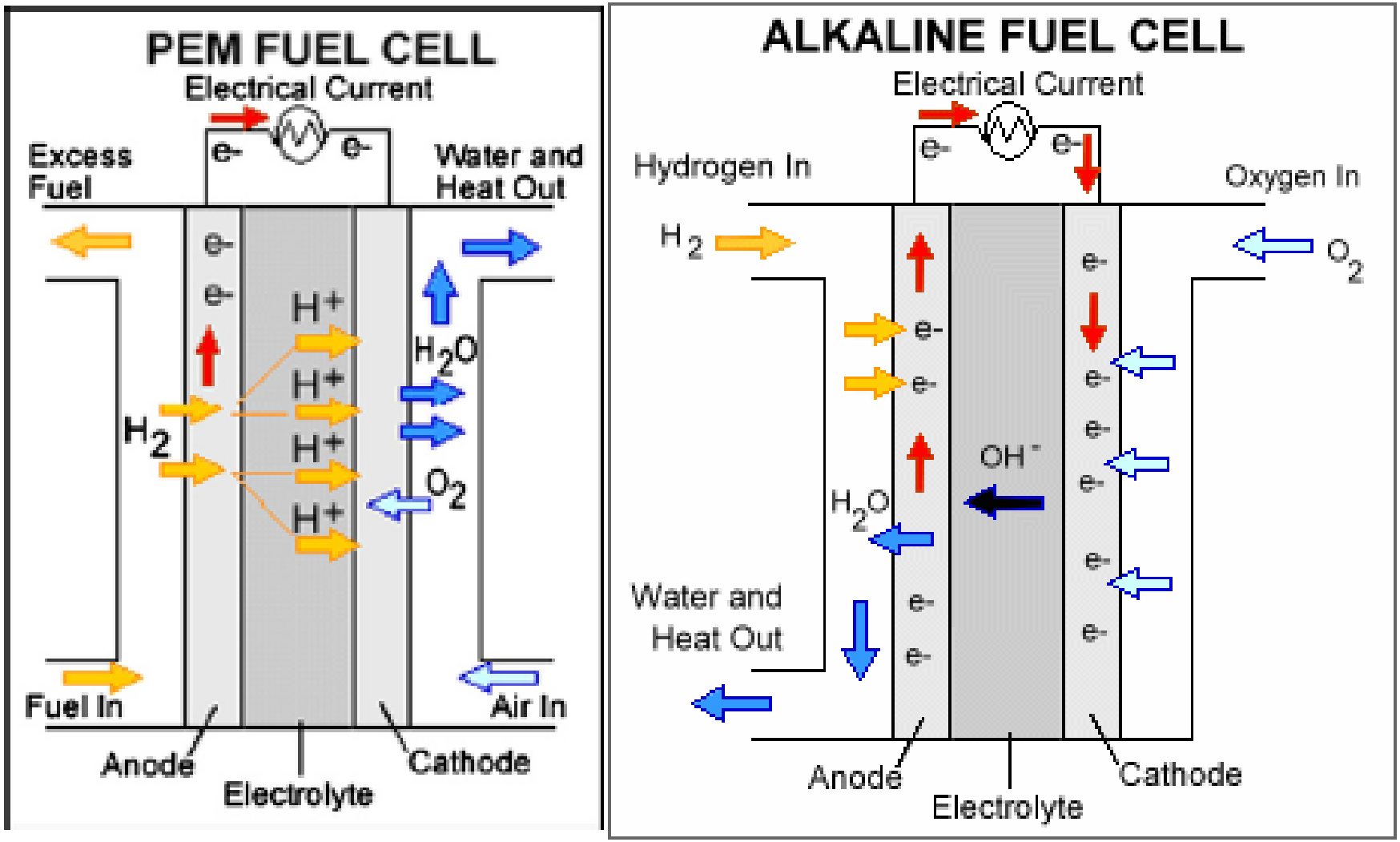
Proton Exchange Membrane Fuel Cells



Alkaline Fuel Cells

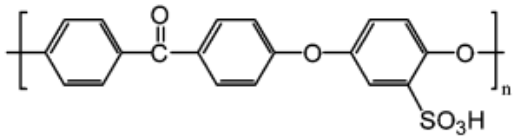


A Pratt & Whitney alkali fuel cell being assembled for an Apollo spacecraft, 1964

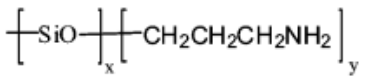


Schematic of a PEM and Alkaline fuel cell

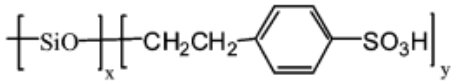
Chemical structures of several materials:



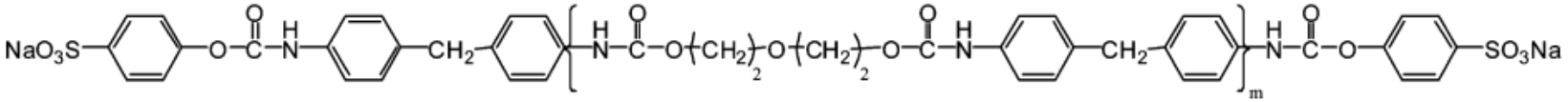
a) SPEEK



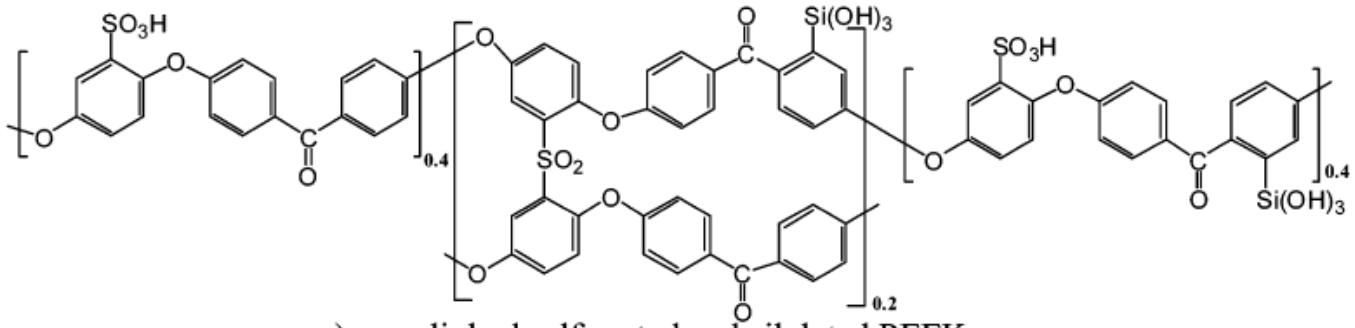
b) 3-aminopropyl functionalised silica



c) sulfonic acid functionalised silica

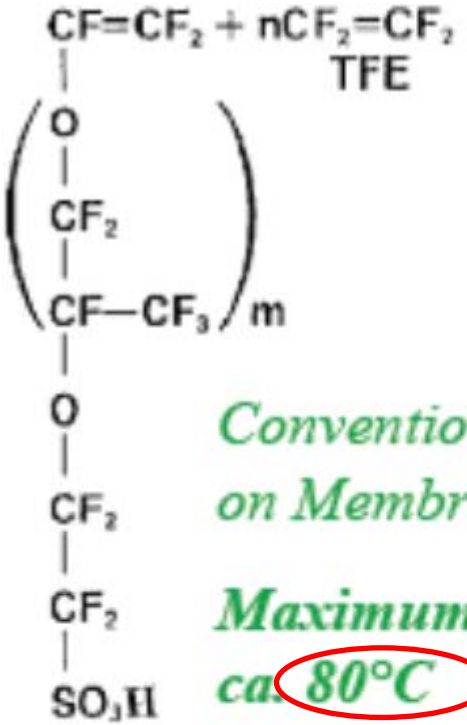


d) charged surface modifying macromolecule



e)cross-linked sulfonated and silylated PEEK

Which one is the best?



Conventional PEMFC are based on Membranes like Nafion

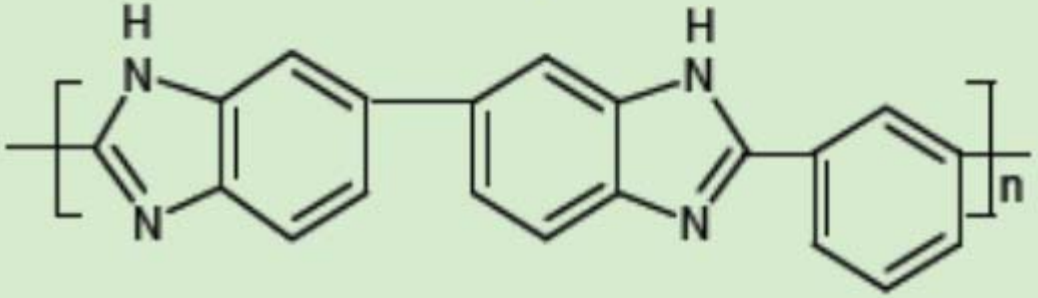
Maximum temperature ca. 80°C

Nafion

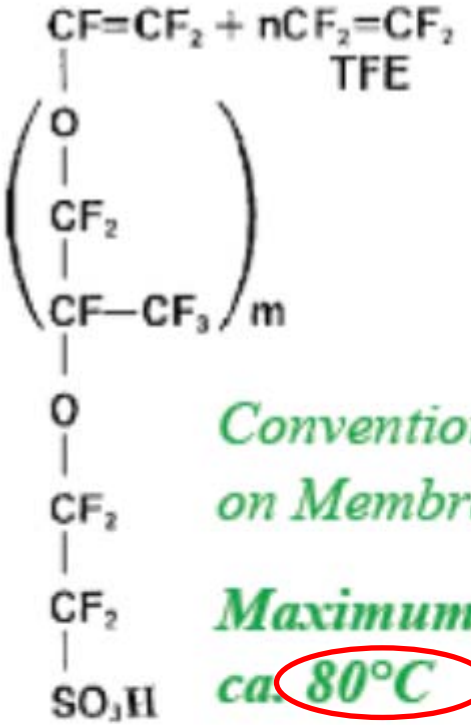
New membrane of PBI and phosphoric acid

Maximum temperature: ca. 200°C

PBI



Poly (2,2´-m-(phenylene)-5,5´-bibenzimidazole)



Past

Conventional PEMFC are based on Membranes like Nafion

Maximum temperature ca. 80°C

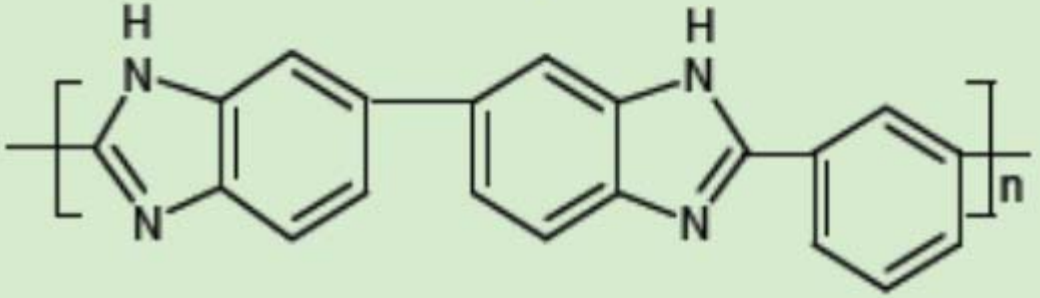
Nafion

FUTURE?

New membrane of PBI and phosphoric acid

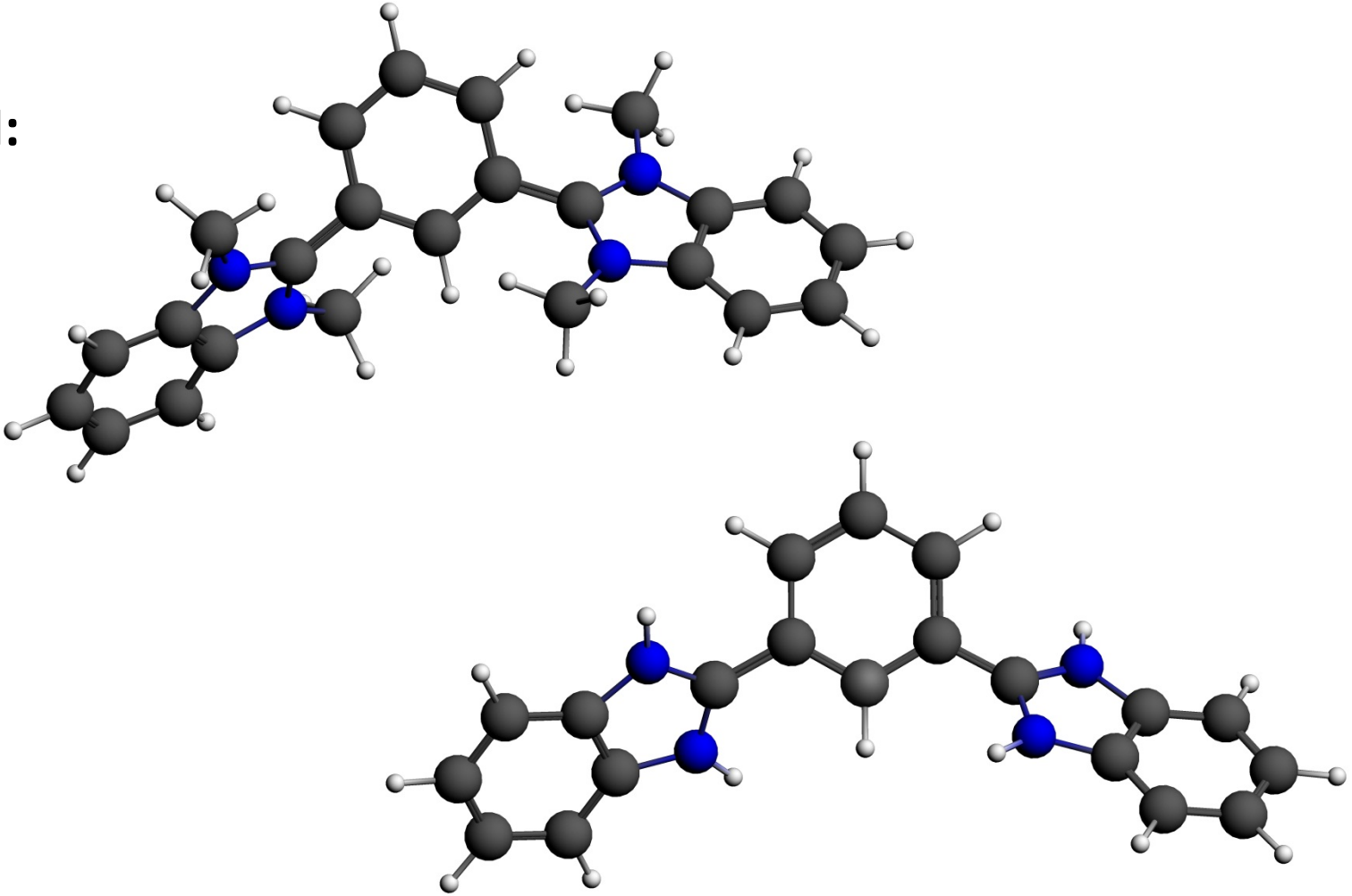
Maximum temperature: ca. 200°C

PBI

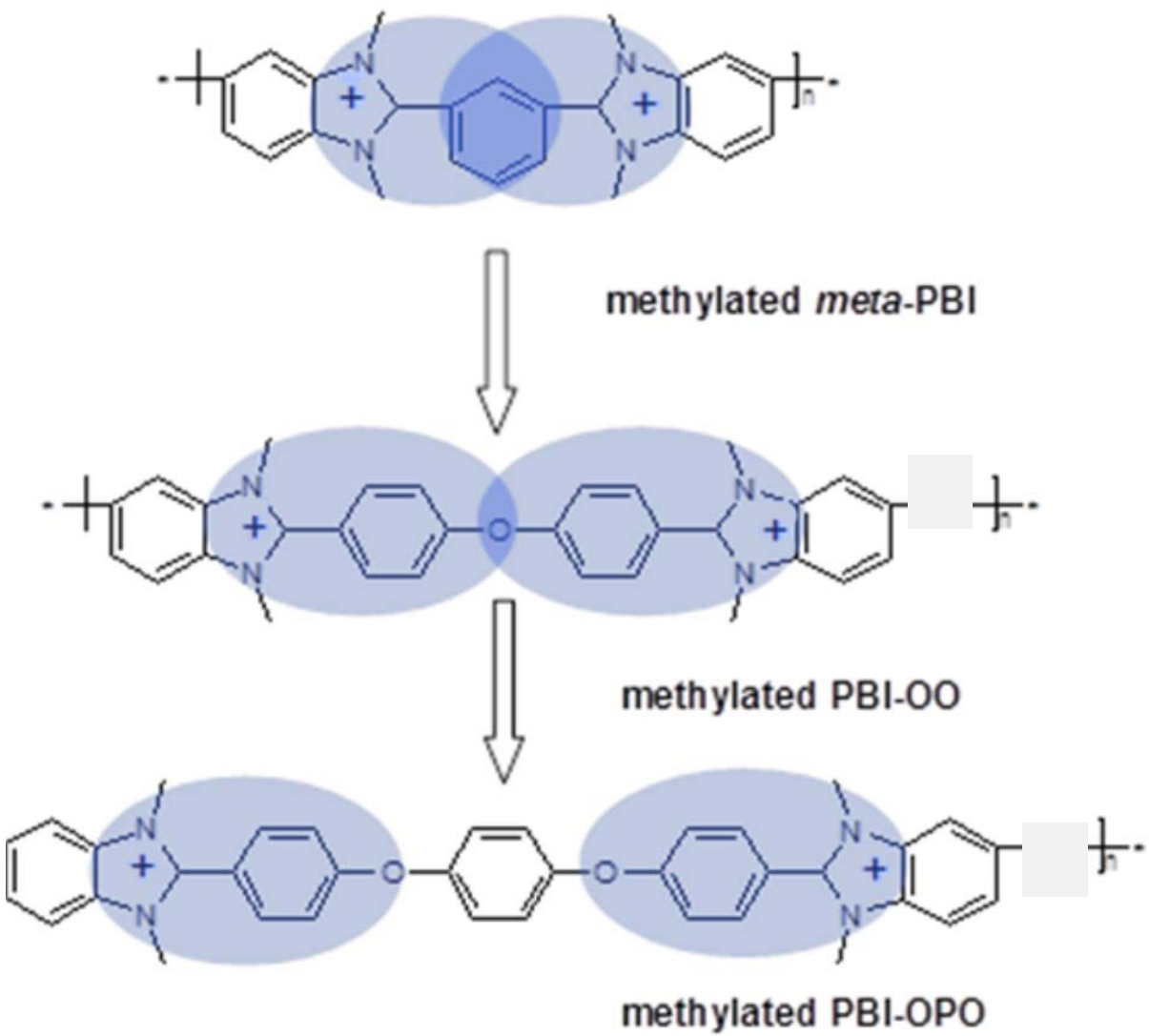


Poly (2,2´-m-(phenylene)-5,5´-bibenzimidazole)

PBI:

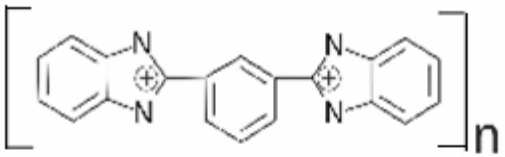


Dirk Henkensmeier, Hyoung-Juhn Kim, Hye-Jin Lee, Dong Hoon Lee, In-Hwan Oh, Seong-Ahn Hong, Suk-Woo Nam, Tae-Hoon Lim, Polybenzimidazolium based solid electrolytes, Macromolecular Materials and Engineering, 2011, 296, 899 - 908.

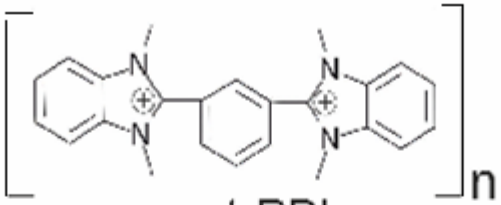


Dirk Henkensmeier, Hyeong-Rae Cho, Hyoung-Juhn Kim, Carolina Nunes Kirchner, Janine Leppin, Alexander Dyck, Jong Hyun Jang, EunAe Cho, Suk-Woo Nam, Tae-Hoon Lim, Polybenzimidazolium hydroxides - Structure, stability and degradation, Polymer Degradation and Stability, 2012, 97, 264 – 272.

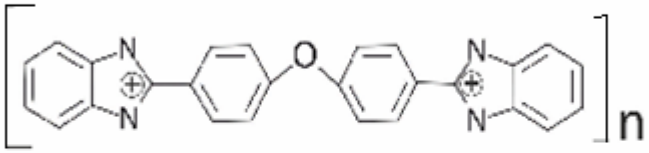
Results



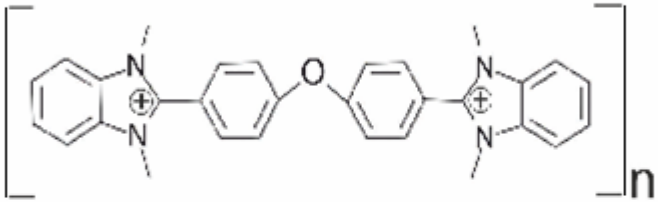
PBI



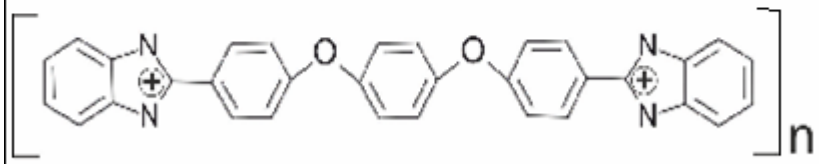
met-PBI



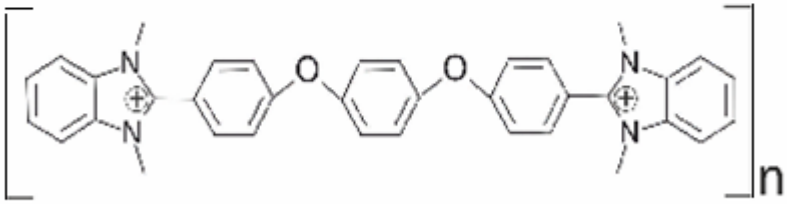
O-PBI



met-O-PBI



OO-PBI



met-OO-PBI

Modeling:

Static DFT calculations (ADF) for optimized structures

- the NMR calculations,
- charge distribution was studied by analysis of molecular electrostatic potential as well as Mullikien and Hirshfeld charges,
- anion bonding was analyzed by ETS-NOCV.

<u>Computational details</u>

- ADF (Amsterdam Density functional) program, version 2010.02; DFT (Density Functional Theory) with Becke88/Pedrew86 exchange-correlation functional; TZP basis, ZORA relativistic correction was used for I.

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We are grateful for the use of the "Zeus" supercomputer at Cracow.

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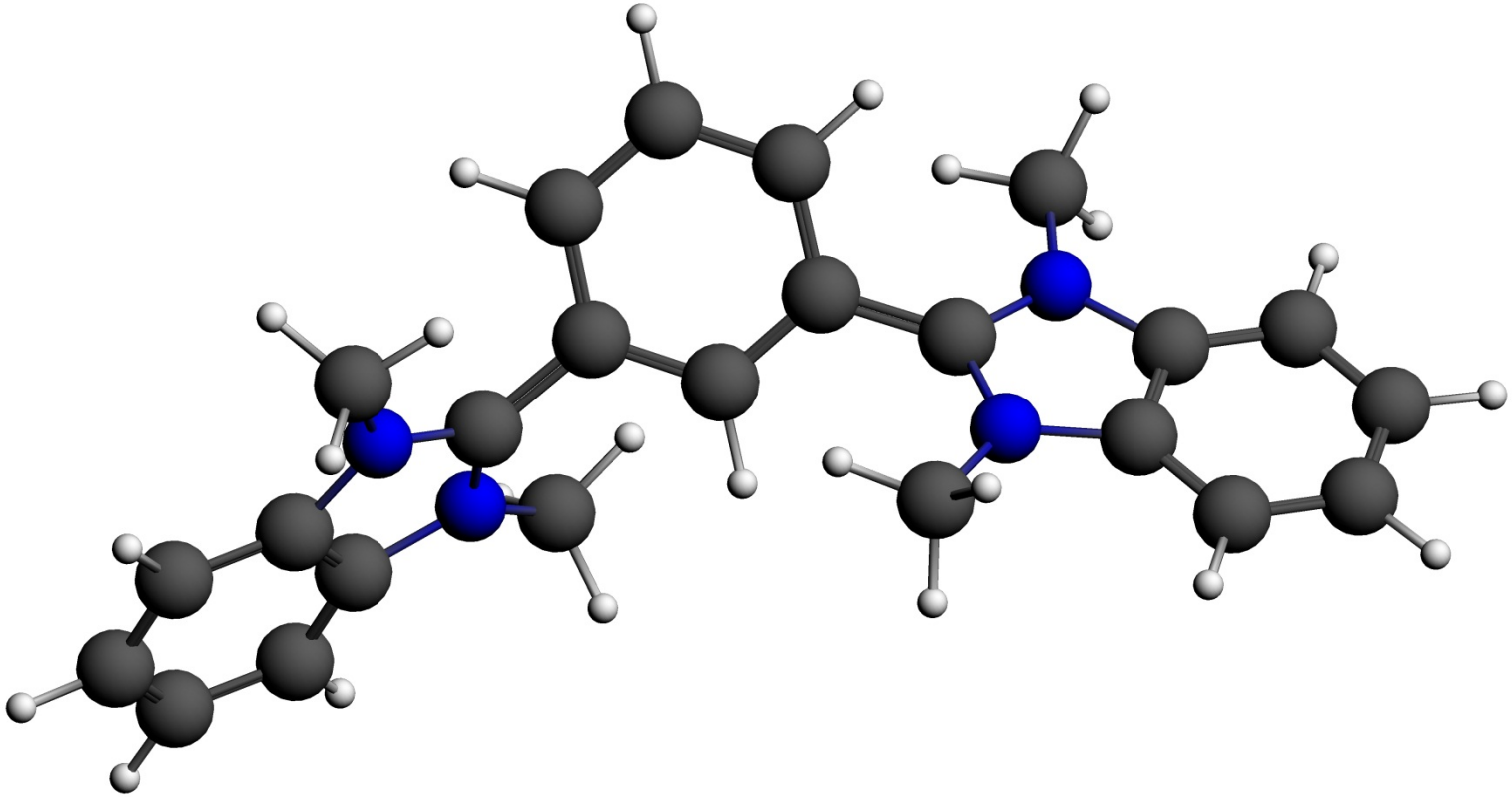
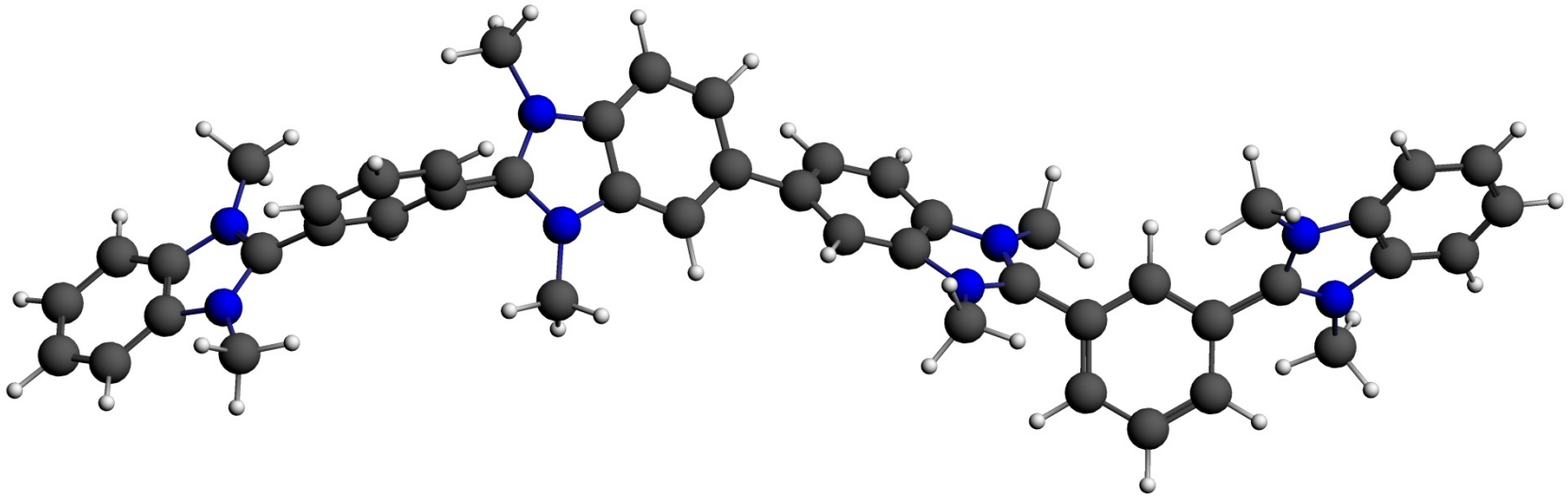
monomer

A



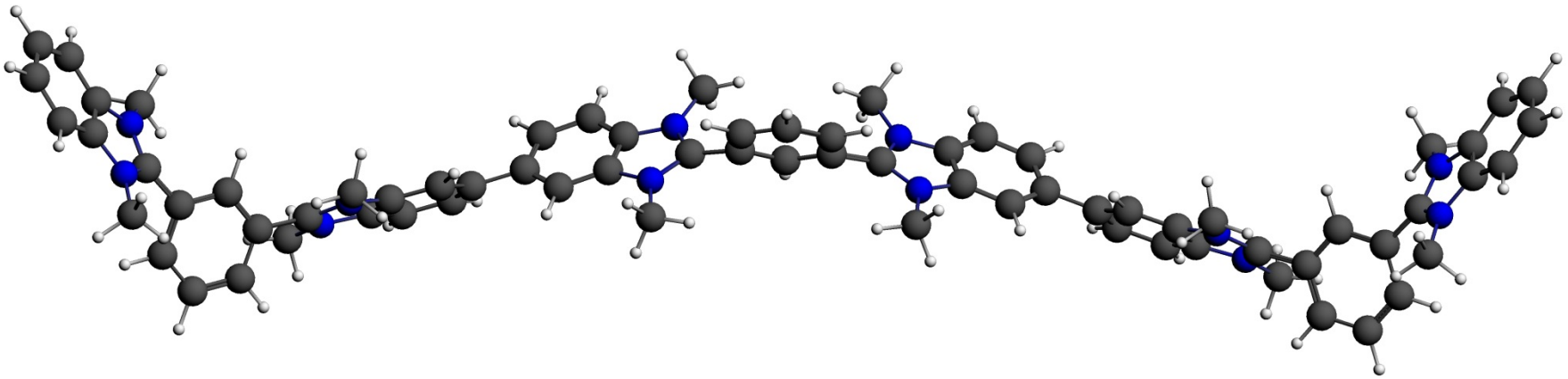
A

dimer



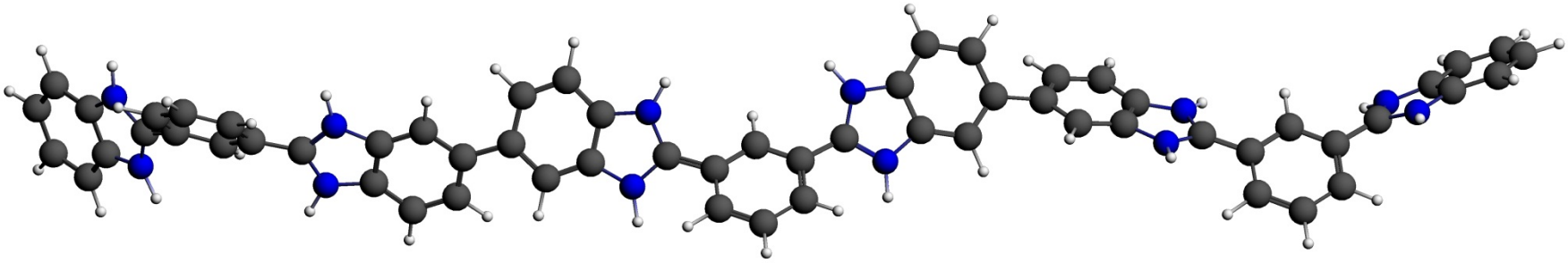
A

trimer

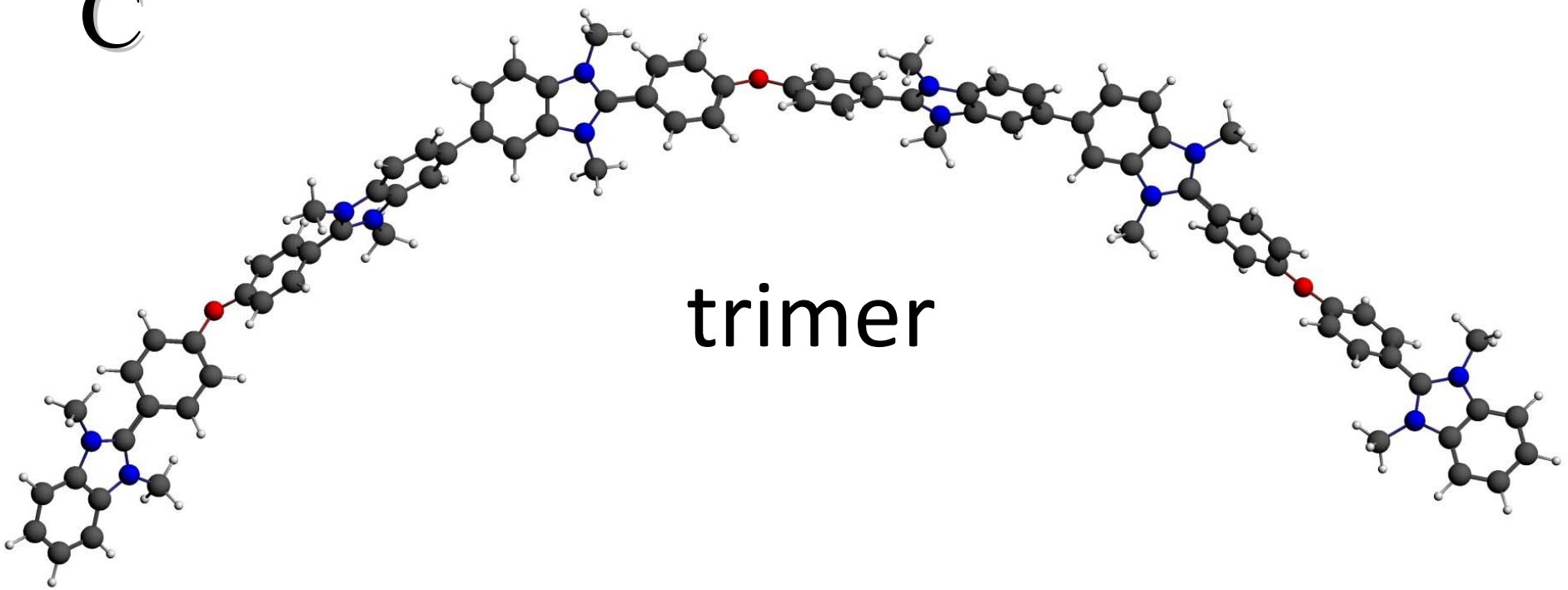


B

trimer

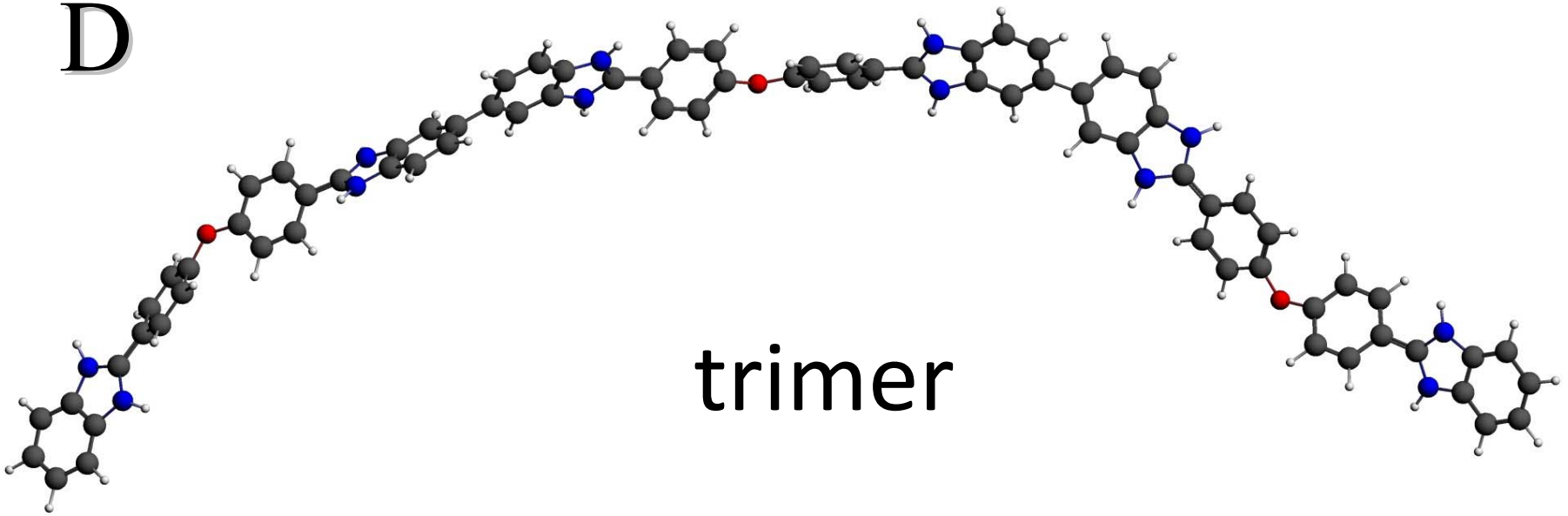


C



trimer

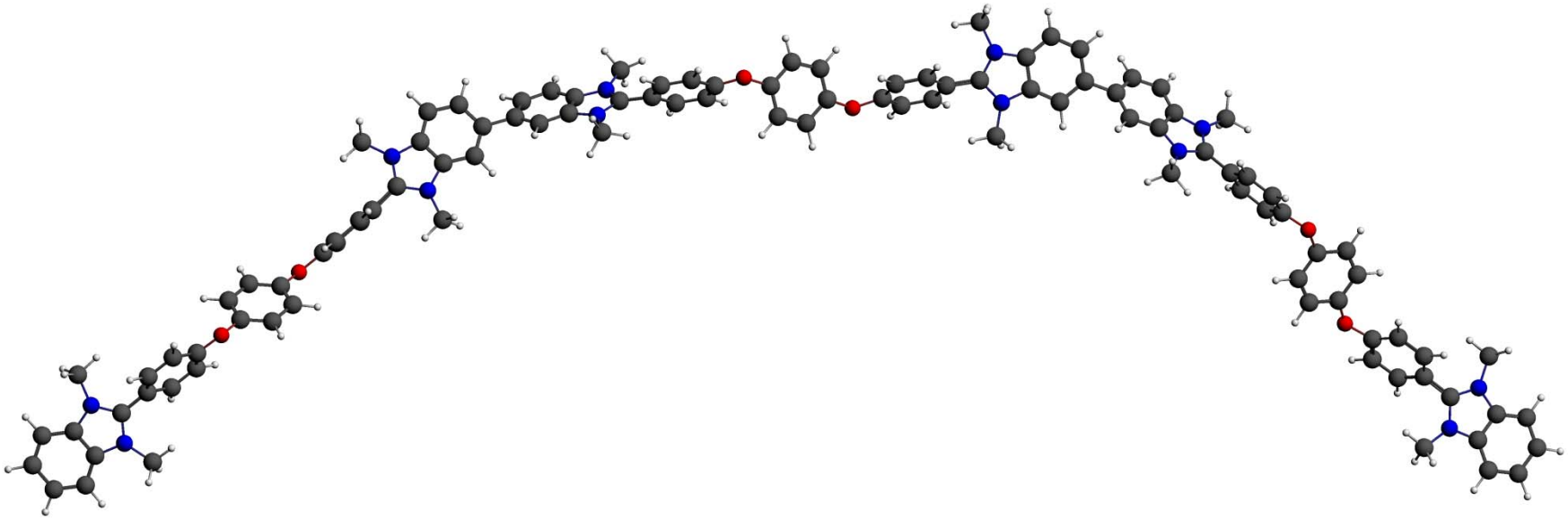
D



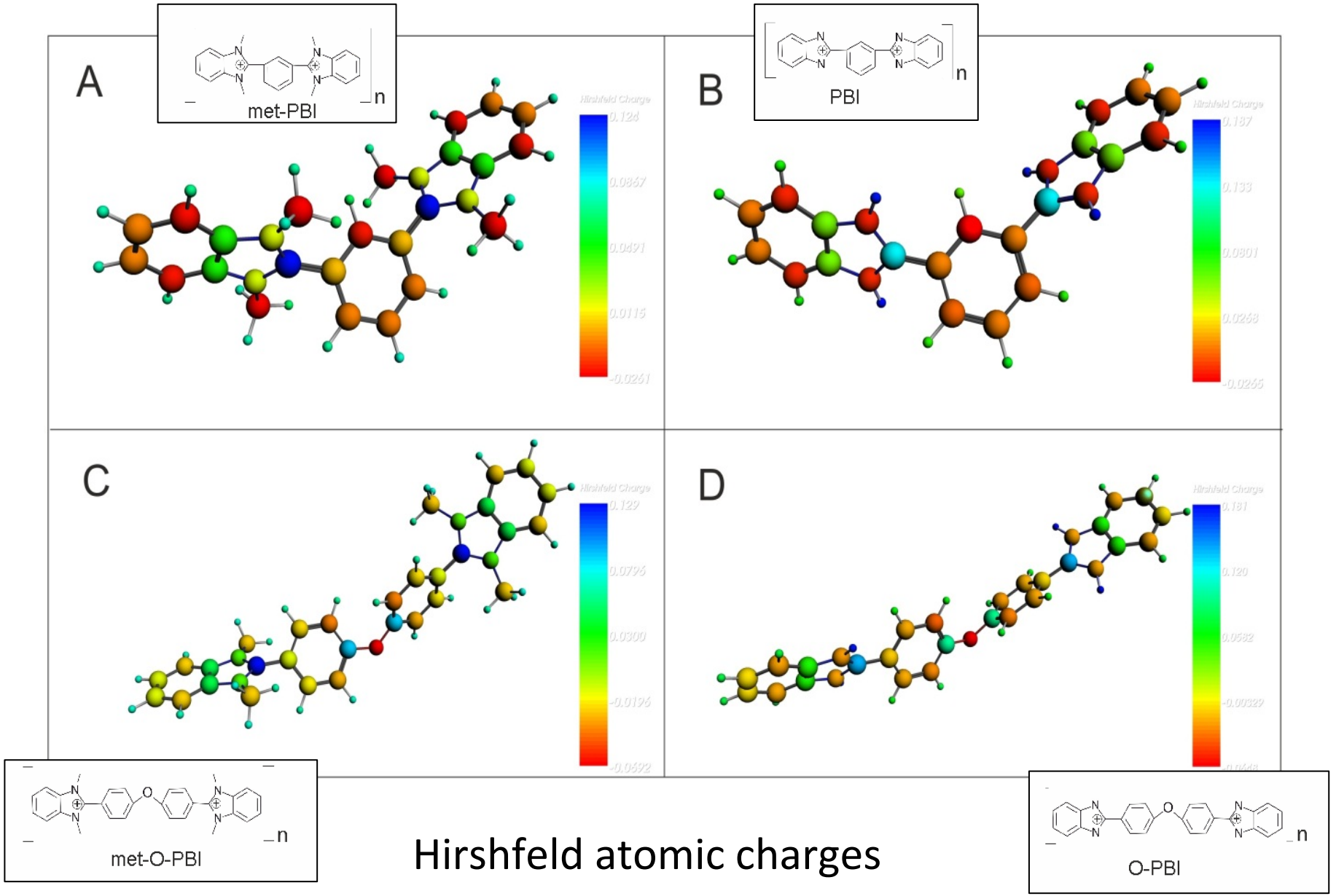
trimer

E

trimer

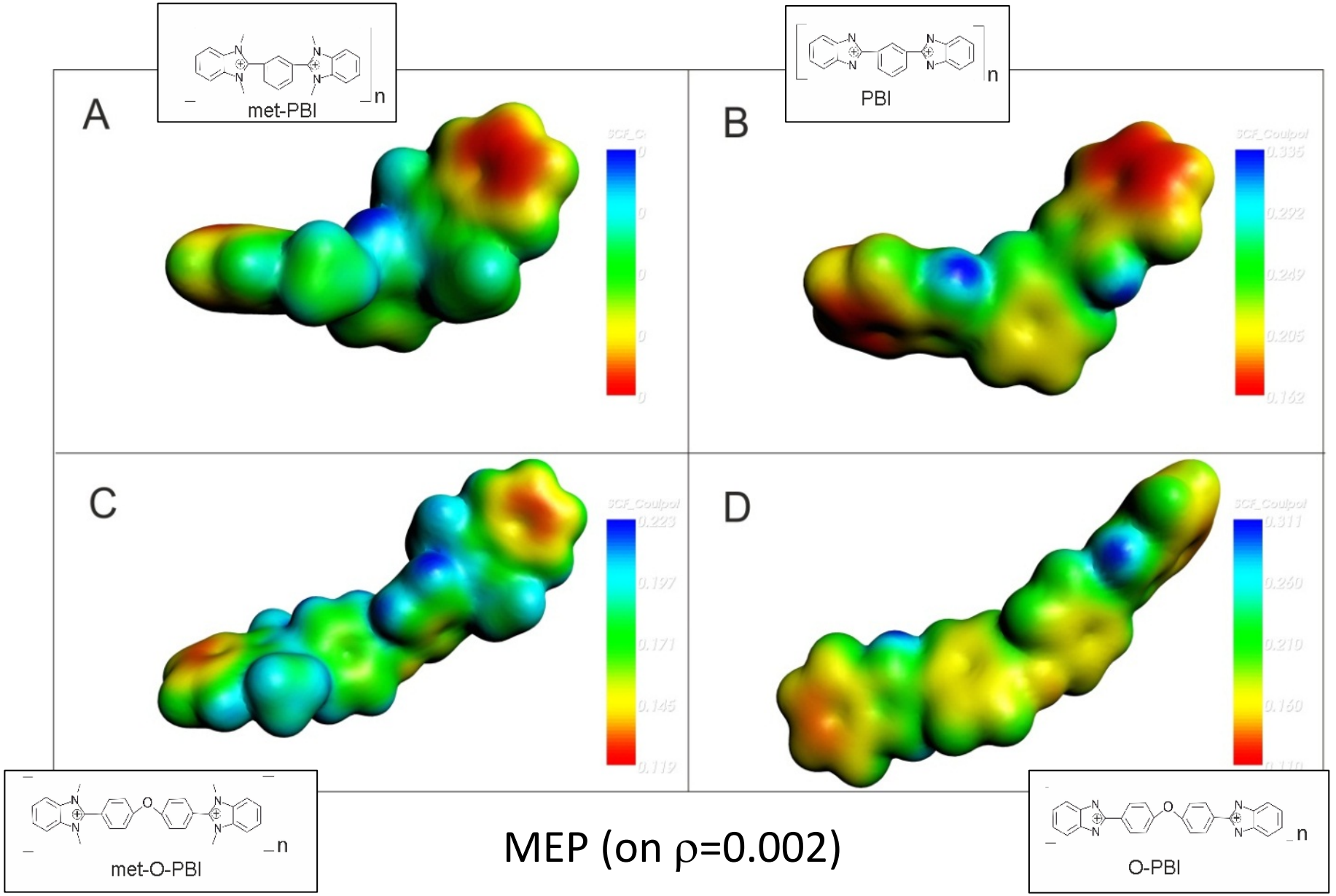


Charge distribution



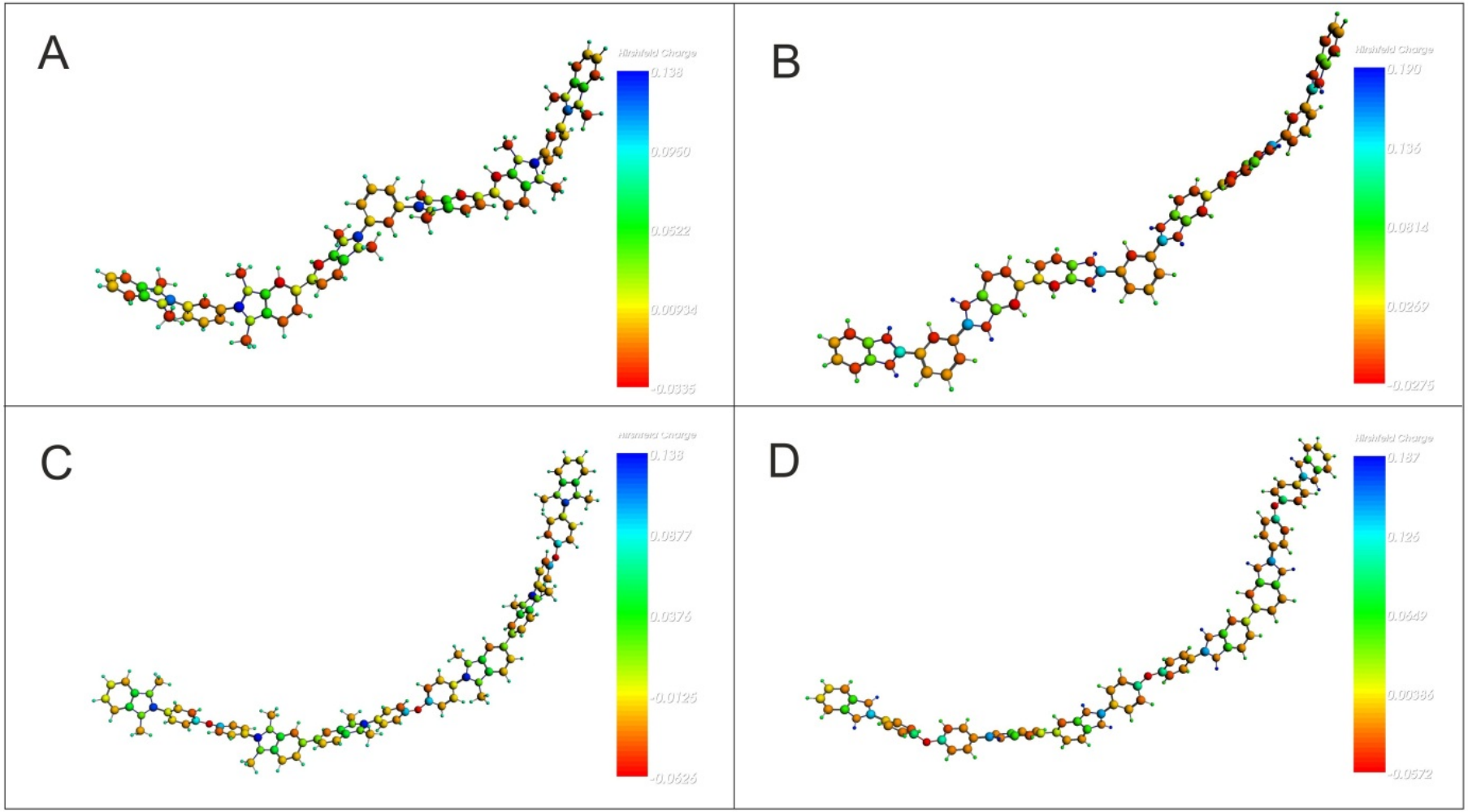
Hirshfeld atomic charges

Charge distribution



MEP (on ρ=0.002)

Charge distribution



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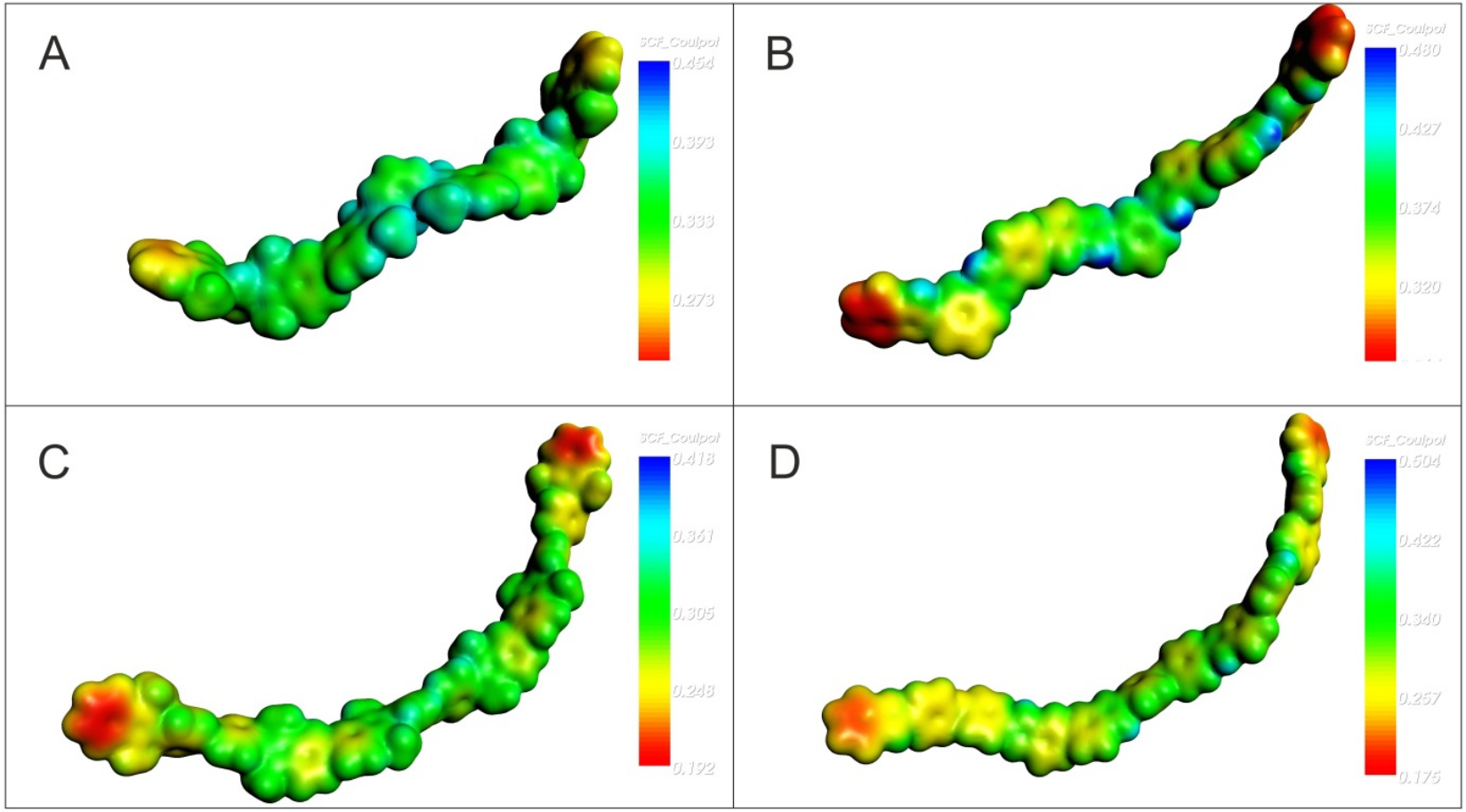
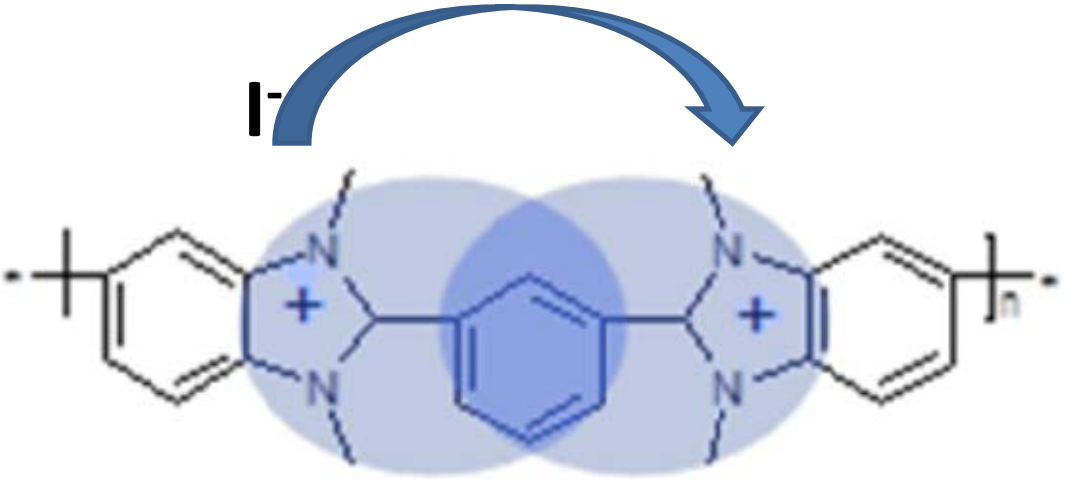
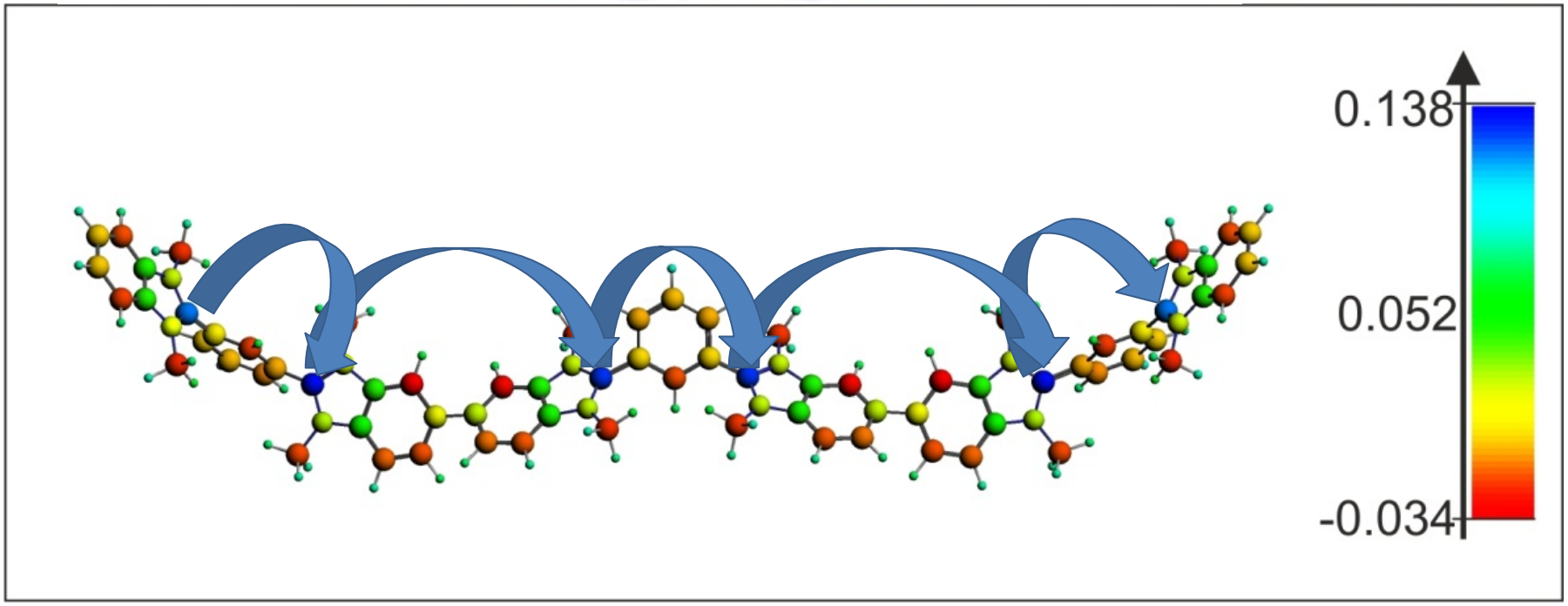


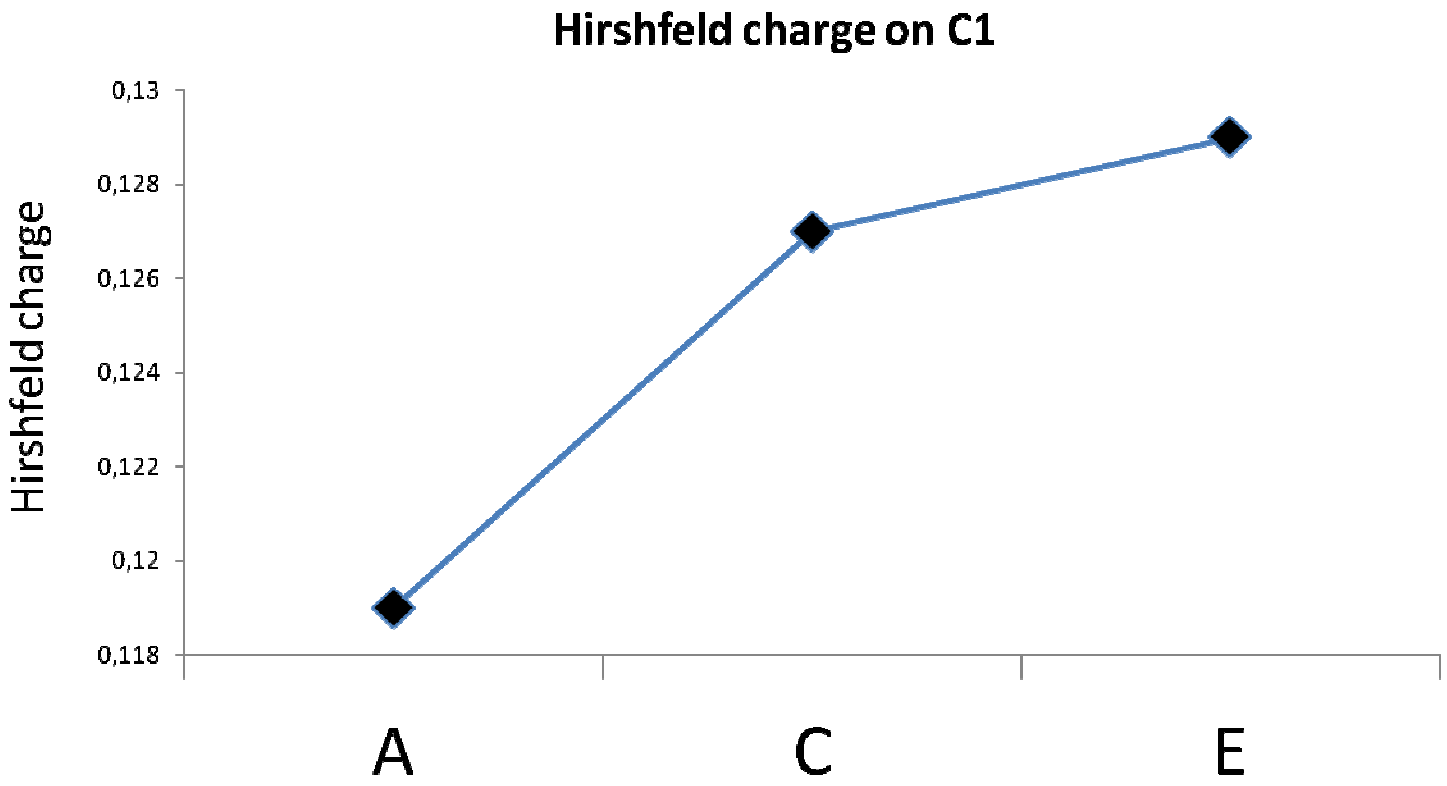
MEP (on ρ=0.002)

Anion conductivity

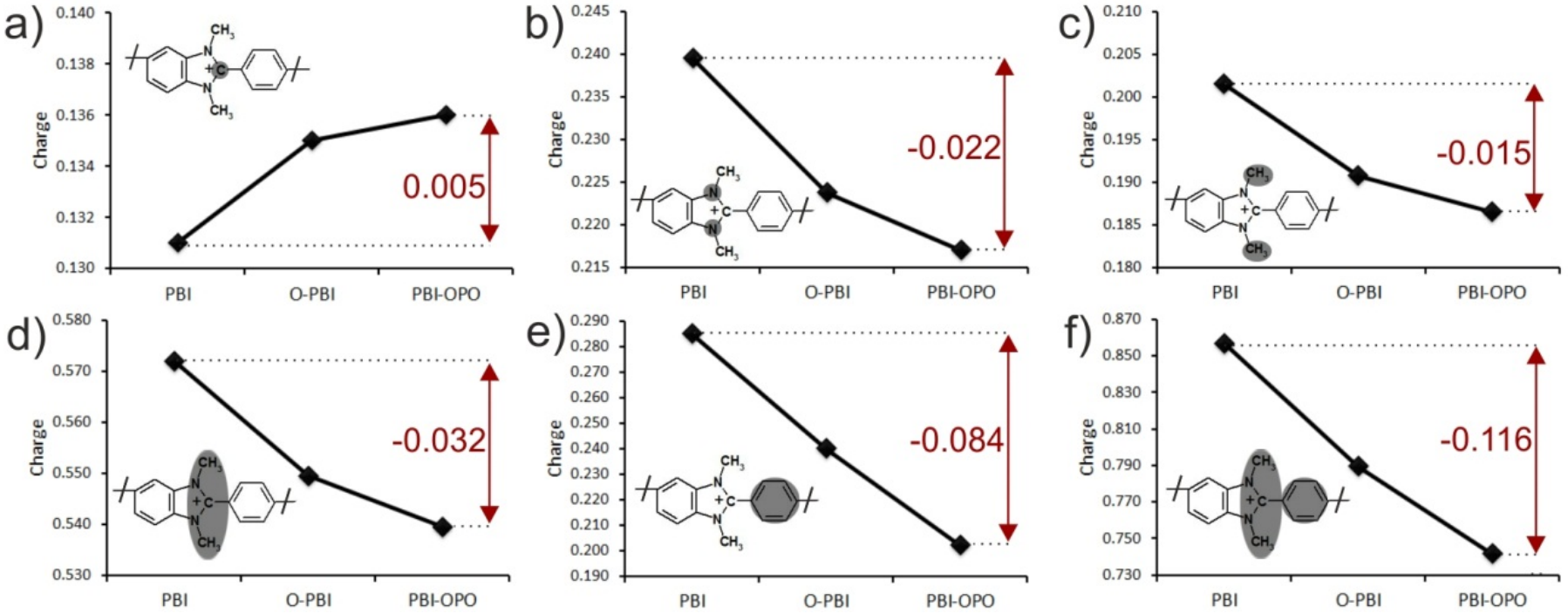


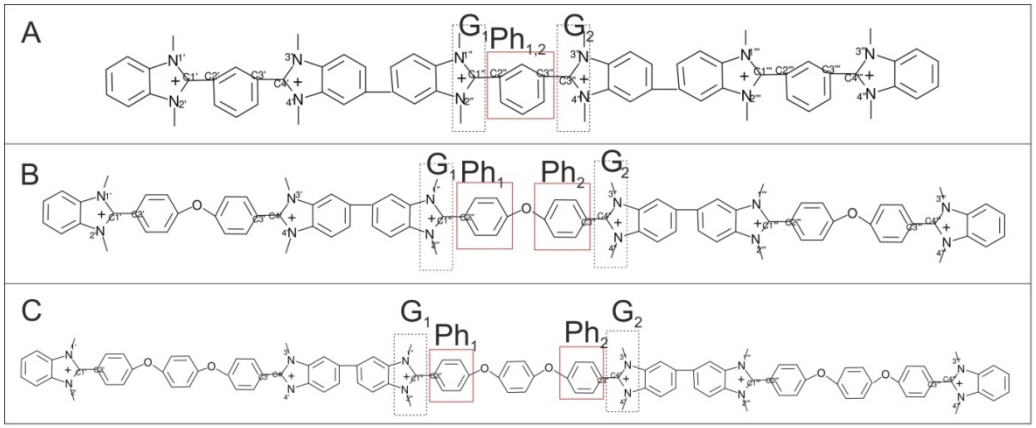


Charge distribution



Charge distribution





Interactions with anions

Molecular Dynamic Born-Oppenheimer aproach:

CP2K program:
• version 2.1.397;
• Quickstep; DFT with Padé representation of LDA (local density approximation);
•GPW (gaussian and plane waves methods) DZVP-MOLOPT-GTH and GTH-PADE with cutoff: 280 Ry;
•thermostat: Nosé–Hoover (T=5K,300K).

We are grateful for the use of the "Zeus" supercomputer at Cracow.

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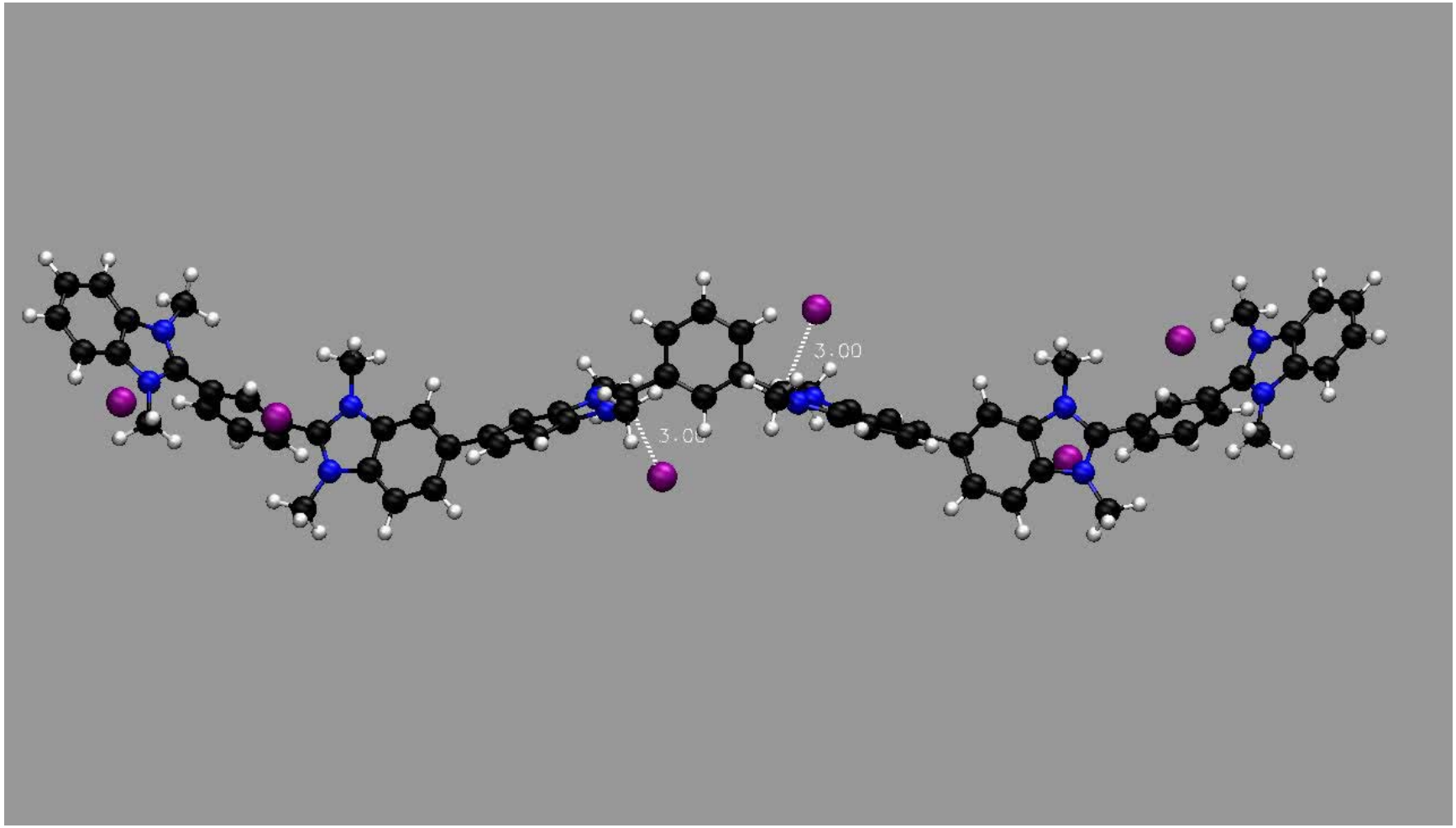
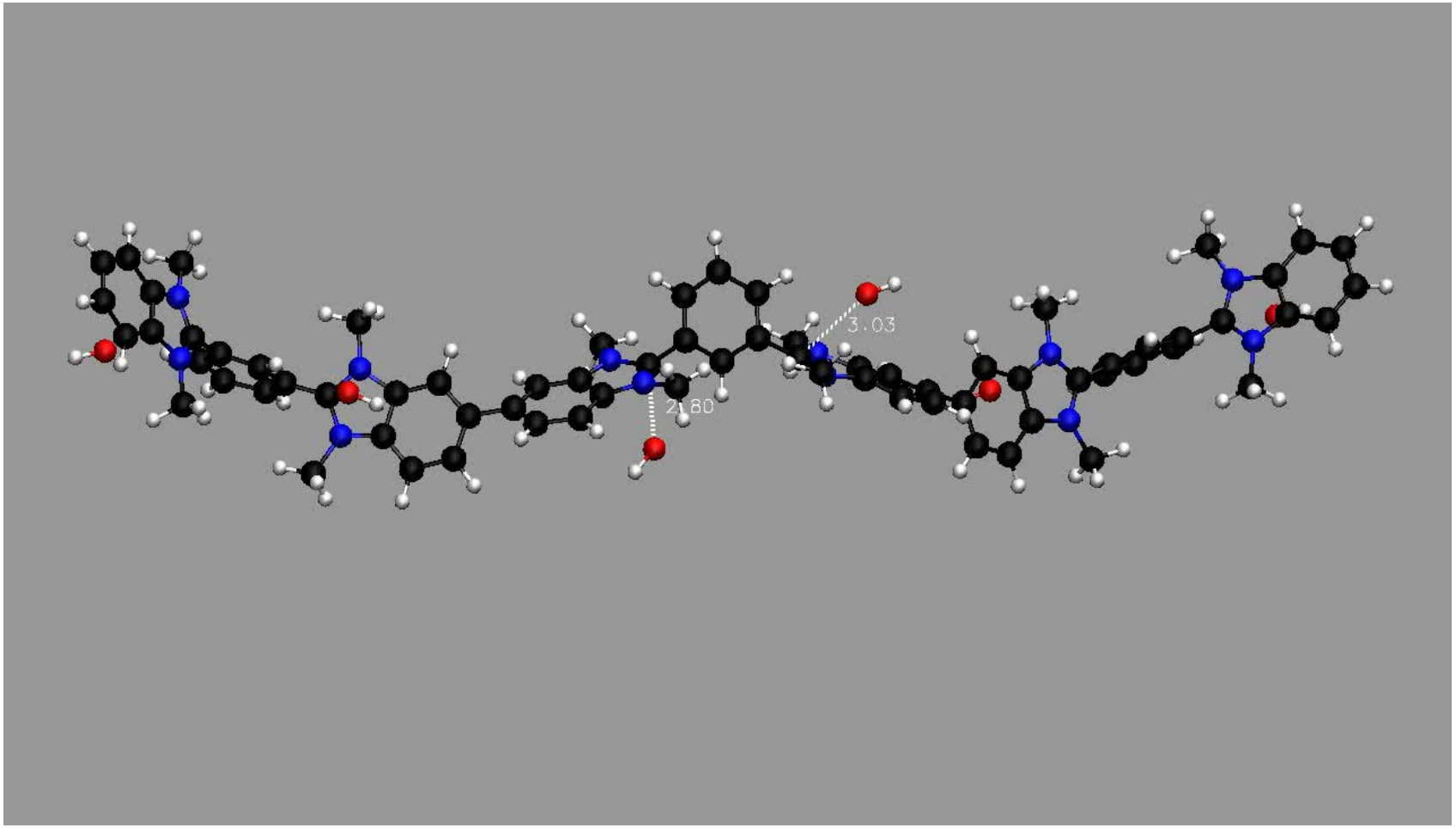
Interactions with anions



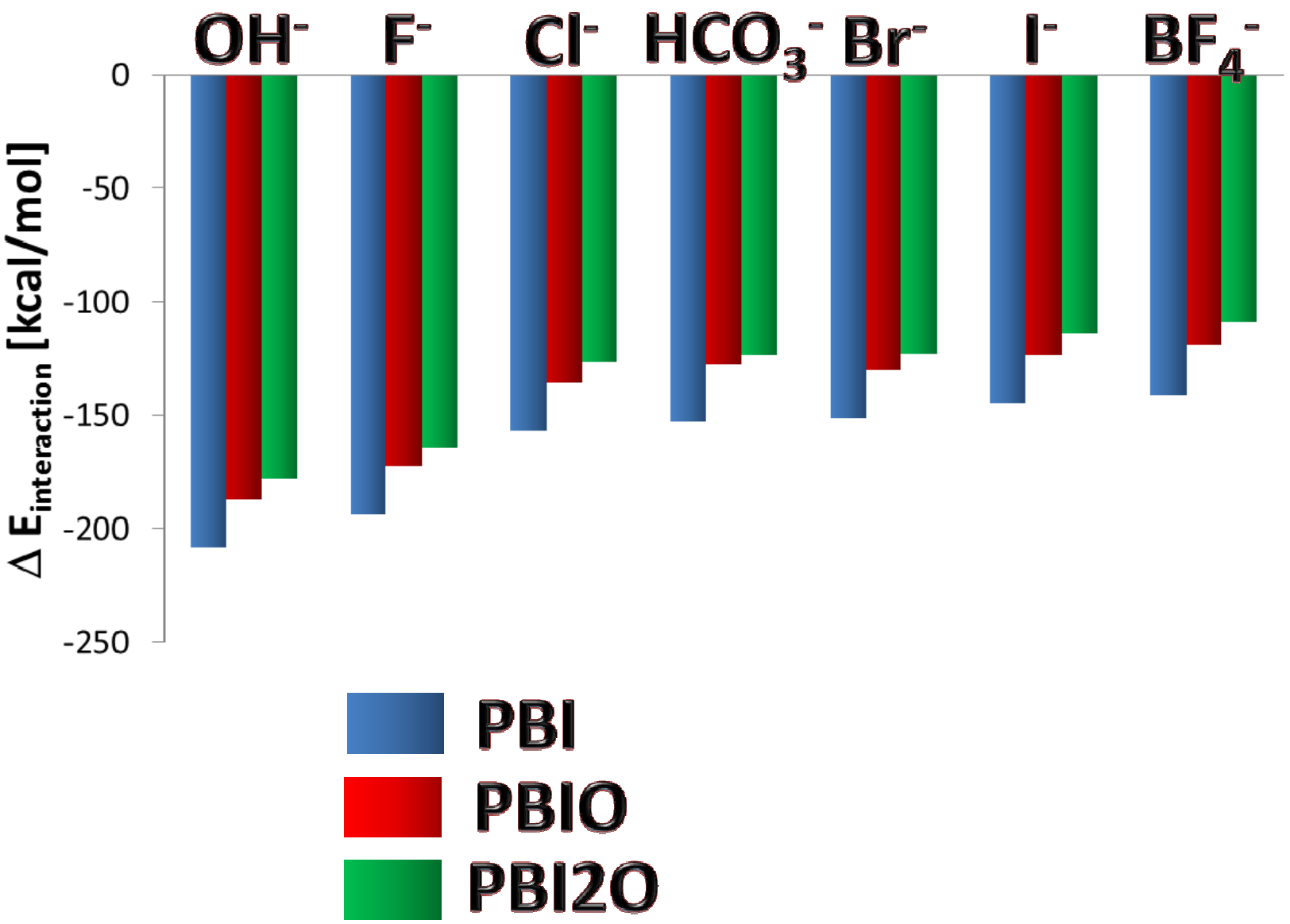
Trimer A^{6+} + $6I^{-}$

Interactions with anions



Trimer A^{6+} + 6 OH^-

Interactions with anions



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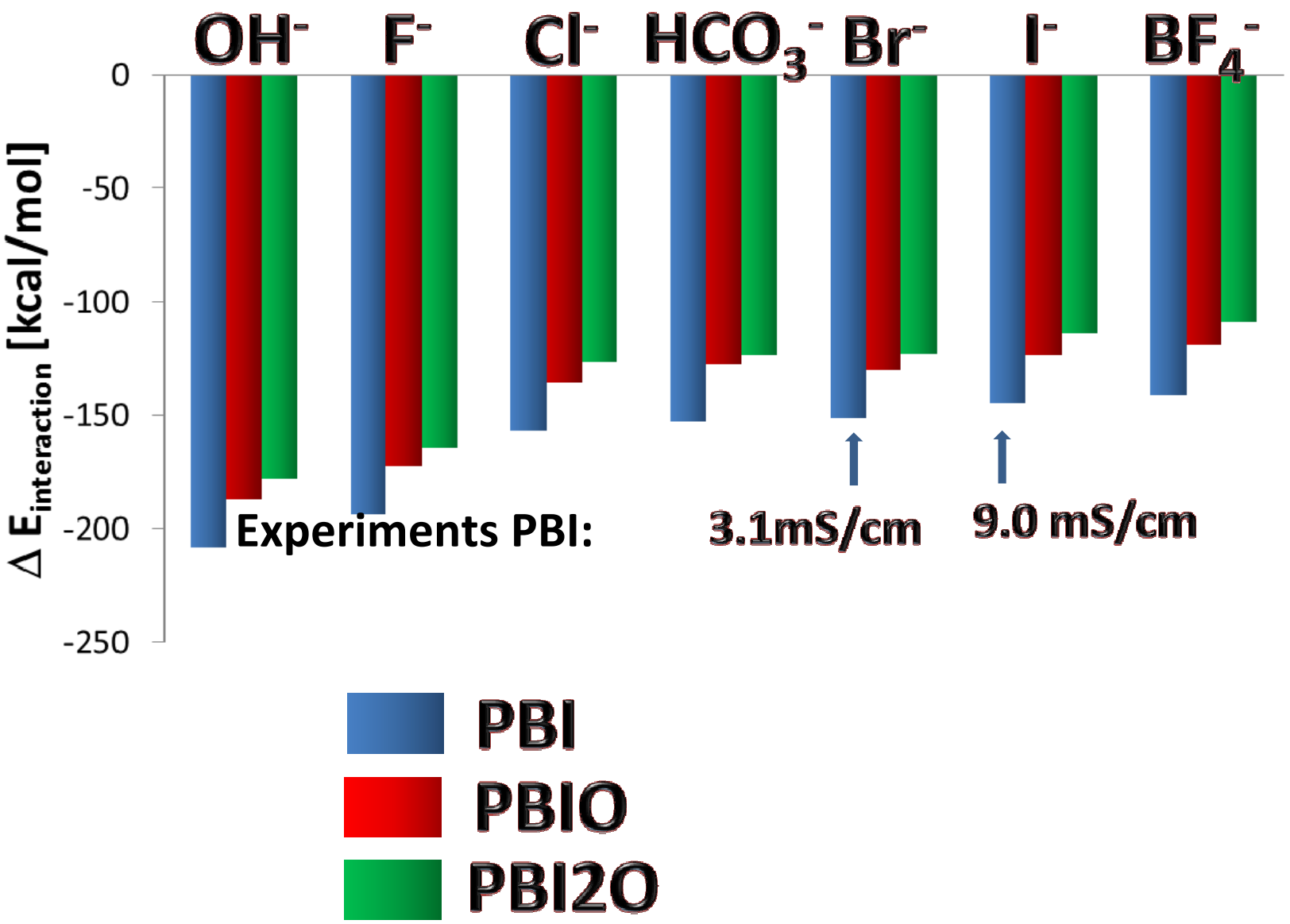

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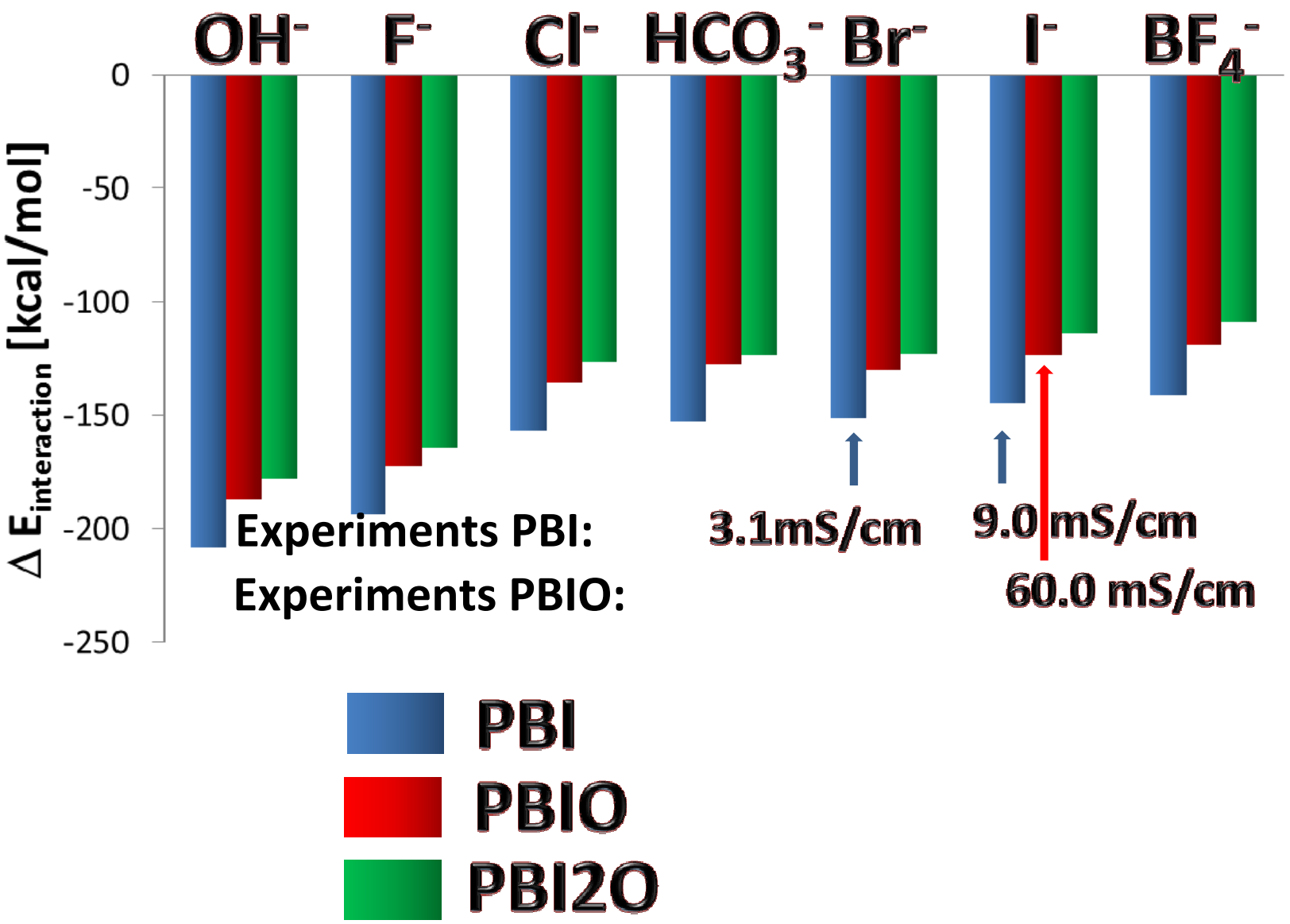

Interactions with anions

	$\Delta E_{Pauli}/6$	$\Delta E_{elstat}/6$	$\Delta E_{orb}/6$	$\Delta E_{bonding}/6$	$\Delta E_{dis}/6$	$\Delta E_{total}/6$
A	$PBI^{6+} + 6\ OH^-$	415,81	-445,23	-280,15	-309,57	101,5	-208,05
	$PBI^{6+} + 6\ Cl^-$	59,46	-244,96	-45,78	-231,28	74,6	-156,68
	$PBI^{6+} + 6\ I^-$	37,35	-224,15	-26,46	-213,26	68,5	-144,67
	$PBI^{6+} + 6\ HCO_3^-$	31,13	-228,14	-26,91	-223,93	71,2	-152,64
	$PBI^{6+} + 6\ BF_4^-$	17,23	-202,56	-14,40	-199,73	58,8	-140,89
C	$PBIO^{6+} + 6\ OH^-$	416,01	-411,25	-276,82	-272,06	85,2	-186,80
	$PBIO^{6+} + 6\ Cl^-$	67,25	-212,23	-49,67	-194,65	59,6	-135,03
	$PBIO^{6+} + 6\ I^-$	44,59	-197,41	-30,55	-183,37	60,1	-123,19
	$PBIO^{6+} + 6\ HCO_3^-$	34,22	-182,40	-27,92	-176,11	48,6	-127,45
	$PBIO^{6+} + 6\ BF_4^-$	16,91	-177,27	-13,87	-174,24	55,4	-118,77
E	$PBI2O^{6+} + 6\ OH^-$	418,25	-393,36	-279,82	-254,94	77,5	-177,41
	$PBI2O^{6+} + 6\ Cl^-$	70,61	-197,22	-52,56	-179,17	52,6	-126,56
	$PBI2O^{6+} + 6\ I^-$	46,94	-178,18	-32,38	-163,62	49,6	-113,93
	$PBI2O^{6+} + 6\ BF_4^-$	16,46	-154,66	-13,57	-151,77	42,7	-109,03

Interactions with anions

	ΔE_{Pauli} /6	ΔE_{elstat} /6	ΔE_{orb} /6	$\Delta E_{bonding}$ /6	ΔE_{dist} /6	ΔE_{total} / 6
A PBI^{6+} + 6 OH^-	415,81	-445,23	-280,15	-309,57	101,51	-208,05
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$PBIO^{6+}$ + 6 I^-	44,59	-197,41	-30,55	-183,37	60,18	-123,19
$PBIO^{6+}$ + 6 HCO_3^-	34,22	-182,40	-27,92	-176,11	48,66	-127,45
$PBIO^{6+}$ + 6 BF_4^-	16,91	-177,27	-13,87	-174,24	55,47	-118,77
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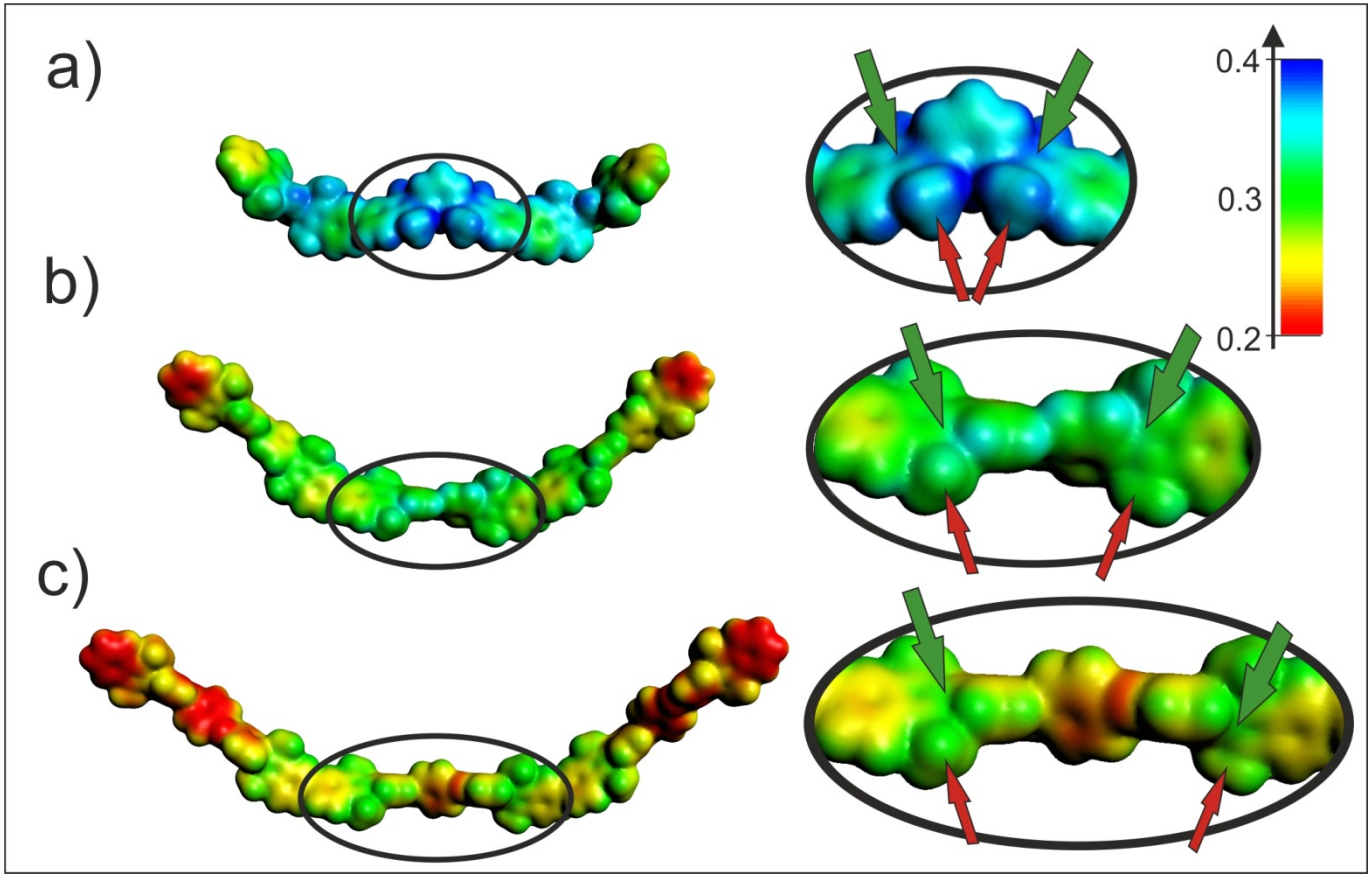
$PBI2O^{6+}$ + 6 I^-	46,94	-178,18	-32,38	-163,62	49,68	-113,93
$PBI2O^{6+}$ + 6 BF_4^-	16,46	-154,66	-13,57	-151,77	42,74	-109,03

Interactions with anions



MEP (on ρ=0.002)

Interactions with anions

A

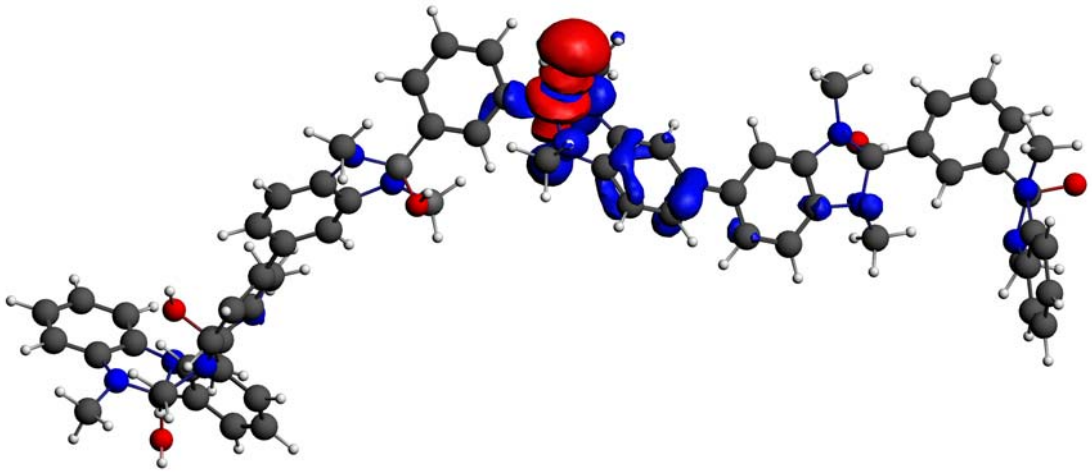
C

E

	$\Delta E_{Pauli}/6$	$\Delta E_{elstat}/6$	$\Delta E_{orb}/6$	$\Delta E_{bonding}/6$	$\Delta E_{dist}/6$	$\Delta E_{total}/6$
$PBI^{6+} + 6\ OH^-$	415,81	-445,23	-280,15	-309,57	101,51	-208,05
$PBI^{6+} + 6\ Cl^-$	59,46	-244,96	-45,78	-231,28	74,60	-156,68
$PBI^{6+} + 6\ I^-$	37,35	-224,15	-26,46	-213,26	68,59	-144,67
$PBI^{6+} + 6\ HCO_3^-$	31,13	-228,14	-26,91	-223,93	71,29	-152,64
$PBI^{6+} + 6\ BF_4^-$	17,23	-202,56	-14,40	-199,73	58,84	-140,89
$PBIO^{6+} + 6\ OH^-$	416,01	-411,25	-276,82	-272,06	85,26	-186,80
$PBIO^{6+} + 6\ Cl^-$	67,25	-212,23	-49,67	-194,65	59,62	-135,03
$PBIO^{6+} + 6\ I^-$	44,59	-197,41	-30,55	-183,37	60,18	-123,19
$PBIO^{6+} + 6\ HCO_3^-$	34,22	-182,40	-27,92	-176,11	48,66	-127,45
$PBIO^{6+} + 6\ BF_4^-$	16,91	-177,27	-13,87	-174,24	55,47	-118,77
$PBI2O^{6+} + 6\ OH^-$	418,25	-393,36	-279,82	-254,94	77,53	-177,41
$PBI2O^{6+} + 6\ Cl^-$	70,61	-197,22	-52,56	-179,17	52,61	-126,56
$PBI2O^{6+} + 6\ I^-$	46,94	-178,18	-32,38	-163,62	49,68	-113,93
$PBI2O^{6+} + 6\ BF_4^-$	16,46	-154,66	-13,57	-151,77	42,74	-109,03

Interactions with anions

$A+OH^-$: ETS-NOCV analysis



ΔE^1_{orb}=-245.70 kcal/mol

Interactions with anions

	$\Delta E_{Pauli}/6$	$\Delta E_{elstat}/6$	$\Delta E_{orb}/6$	$\Delta E_{bonding}/6$	$\Delta E_{dis}/6$	$\Delta E_{total}/6$
A	$PBI^{6+} + 6\ OH^-$	415,81	-445,23	-280,15	-309,57	101,5	**-208,05**
	$PBI^{6+} + 6\ Cl^-$	59,46	-244,96	-45,78	-231,28	74,6	**-156,68**
	$PBI^{6+} + 6\ I^-$	37,35	-224,15	-26,46	-213,26	68,5	**-144,67**
	$PBI^{6+} + 6\ HCO_3^-$	31,13	-228,14	-26,91	-223,93	71,2	**-152,64**
	$PBI^{6+} + 6\ BF_4^-$	17,23	-202,56	-14,40	-199,73	58,8	**-140,89**
C	$PBIO^{6+} + 6\ OH^-$	416,01	-411,25	-276,82	-272,06	85,2	**-186,80**
	$PBIO^{6+} + 6\ Cl^-$	67,25	-212,23	-49,67	-194,65	59,6	**-135,03**
	$PBIO^{6+} + 6\ I^-$	44,59	-197,41	-30,55	-183,37	60,1	**-123,19**
	$PBIO^{6+} + 6\ HCO_3^-$	34,22	-182,40	-27,92	-176,11	48,6	**-127,45**
	$PBIO^{6+} + 6\ BF_4^-$	16,91	-177,27	-13,87	-174,24	55,4	**-118,77**
E	$PBI2O^{6+} + 6\ OH^-$	418,25	-393,36	-279,82	-254,94	77,5	**-177,41**
	$PBI2O^{6+} + 6\ Cl^-$	70,61	-197,22	-52,56	-179,17	52,6	**-126,56**
	$PBI2O^{6+} + 6\ I^-$	46,94	-178,18	-32,38	-163,62	49,6	**-113,93**
	$PBI2O^{6+} + 6\ BF_4^-$	16,46	-154,66	-13,57	-151,77	42,7	**-109,03**

Interactions with anions

	$\Delta E_{Pauli}/6$	$\Delta E_{elstat}/6$	$\Delta E_{orb}/6$	$\Delta E_{bonding}/6$	$\Delta E_{dis}/6$	$\Delta E_{total}/6$
A	$PBI^{6+} + 6\ OH^-$	415,81	-445,23	-280,15	-309,57	101,51	**-208,05**
	$PBI^{6+} + 6\ Cl^-$	59,46	-244,96	-45,78	-231,28	74,6	**-156,68**
	$PBI^{6+} + 6\ I^-$	37,35	-224,15	-26,46	-213,26	68,5	**-144,67**
	$PBI^{6+} + 6\ HCO_3^-$	31,13	-228,14	-26,91	-223,93	71,2	**-152,64**
	$PBI^{6+} + 6\ BF_4^-$	17,23	-202,56	-14,40	-199,73	58,8	**-140,89**
C	$PBIO^{6+} + 6\ OH^-$	416,01	-411,25	-276,82	-272,06	85,2	**-186,80**
	$PBIO^{6+} + 6\ Cl^-$	67,25	-212,23	-49,67	-194,65	59,6	**-135,03**
	$PBIO^{6+} + 6\ I^-$	44,59	-197,41	-30,55	-183,37	60,1	**-123,19**
	$PBIO^{6+} + 6\ HCO_3^-$	34,22	-182,40	-27,92	-176,11	48,6	**-127,45**
	$PBIO^{6+} + 6\ BF_4^-$	16,91	-177,27	-13,87	-174,24	55,4	**-118,77**
E	$PBI2O^{6+} + 6\ OH^-$	418,25	-393,36	-279,82	-254,94	77,5	**-177,41**
	$PBI2O^{6+} + 6\ Cl^-$	70,61	-197,22	-52,56	-179,17	52,6	**-126,56**
	$PBI2O^{6+} + 6\ I^-$	46,94	-178,18	-32,38	-163,62	49,6	**-113,93**
	$PBI2O^{6+} + 6\ BF_4^-$	16,46	-154,66	-13,57	-151,77	42,7	**-109,03**

Interactions with anions

	$\Delta E_{Pauli}/6$	$\Delta E_{elstat}/6$	$\Delta E_{orb}/6$	$\Delta E_{bonding}/6$	$\Delta E_{dis}/6$	$\Delta E_{total}/6$
A	$PBI^{6+} + 6\ OH^-$	415,81	-445,23	-280,15	-309,57	101,51	**-208,05**
	$PBI^{6+} + 6\ Cl^-$	59,46	-244,96	-45,78	-231,28	74,66	**-156,68**
	$PBI^{6+} + 6\ I^-$	37,35	-224,15	-26,46	-213,26	68,59	**-144,67**
	$PBI^{6+} + 6\ HCO_3^-$	31,13	-228,14	-26,91	-223,93	71,29	**-152,64**
	$PBI^{6+} + 6\ BF_4^-$	17,23	-202,56	-14,40	-199,73	58,84	**-140,89**
C	$PBIO^{6+} + 6\ OH^-$	416,01	-411,25	-276,82	-272,06	85,29	**-186,80**
	$PBIO^{6+} + 6\ Cl^-$	67,25	-212,23	-49,67	-194,65	59,65	**-135,03**
	$PBIO^{6+} + 6\ I^-$	44,59	-197,41	-30,55	-183,37	60,15	**-123,19**
	$PBIO^{6+} + 6\ HCO_3^-$	34,22	-182,40	-27,92	-176,11	48,66	**-127,45**
	$PBIO^{6+} + 6\ BF_4^-$	16,91	-177,27	-13,87	-174,24	55,47	**-118,77**
E	$PBI2O^{6+} + 6\ OH^-$	418,25	-393,36	-279,82	-254,94	77,52	**-177,41**
	$PBI2O^{6+} + 6\ Cl^-$	70,61	-197,22	-52,56	-179,17	52,69	**-126,56**
	$PBI2O^{6+} + 6\ I^-$	46,94	-178,18	-32,38	-163,62	49,69	**-113,93**
	$PBI2O^{6+} + 6\ BF_4^-$	16,46	-154,66	-13,57	-151,77	42,74	**-109,03**

Conclusions:

- ETS-NOCV analysis indicates the strengthening of polymer-anion bond in the order:

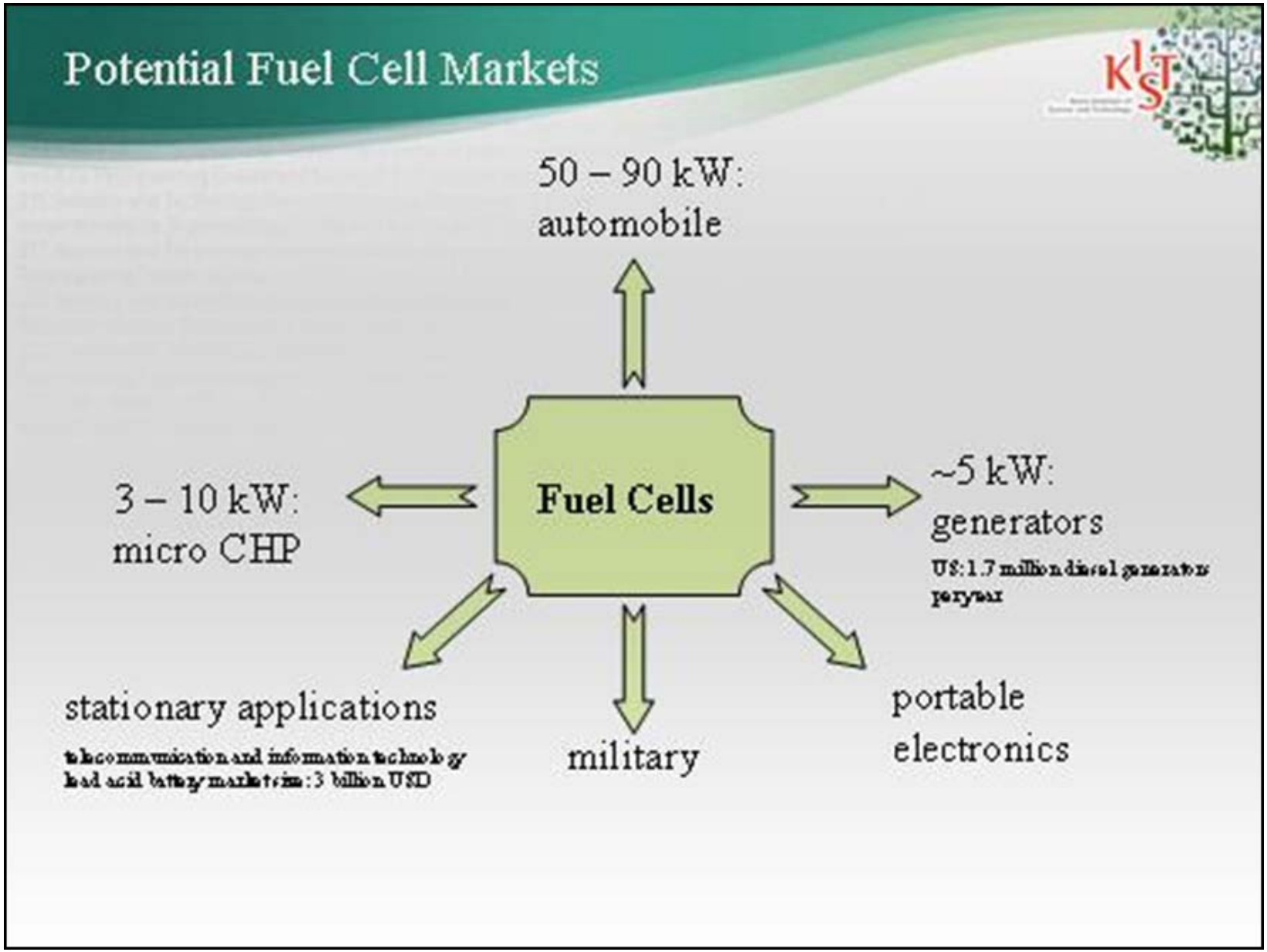
  PBI2O < PBIO << PBI

- Hydroxide bonding is characterized by a high value of orbital interaction term (ca. -280 kcal/mol) which indicates formation of the covalent bond, while for other ions the respective values are substantially smaller (between -14 and -46 kcal/mol), corresponding to ionic interactions without substantial charge transfer.

- Results of the calculations rationalize the differences in experimental NMR spectra for various anions, as well as the experimental conductivity trends.

Thank you very much

Potential Fuel Cell Markets



Platinum is used in fuel cells

US DOE goal for 2015:
0.2 g Pt / kW stack power

11 million cars in Korea Stack power 90 kW → 198 t platinum are needed

	2011 metal price for 18 g (0.2g Pt/kW = 90 kW)	World production
Platinum	1120 USD	200 t (2008)
Palladium	417 USD	206 t (2008)
Silver	24 USD	20,800 t (2008)
Cobalt	0.7 USD	57,500 t (2006)
Nickel	0.4 USD	1,284,000 t (2005)

Korea: 1 year production

Germany: 4 years

Europe: 21 years

China: 7 years
(But: China has 19.3% of world population!)

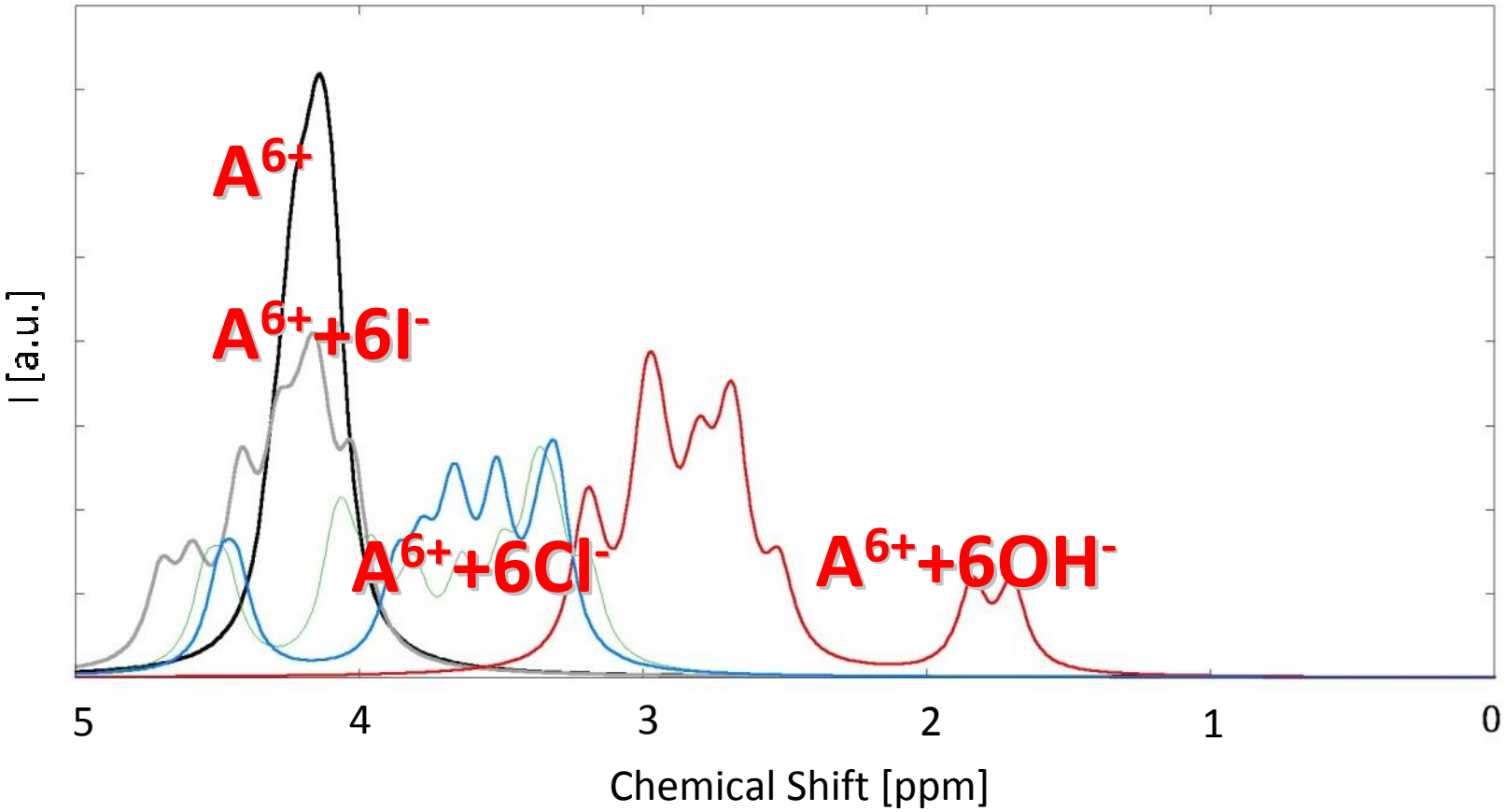
World: > 1,000,000,000 cars

→100 times world production of platinum is needed

→Current catalytic converters have about 3 – 7 g Pt

AFC

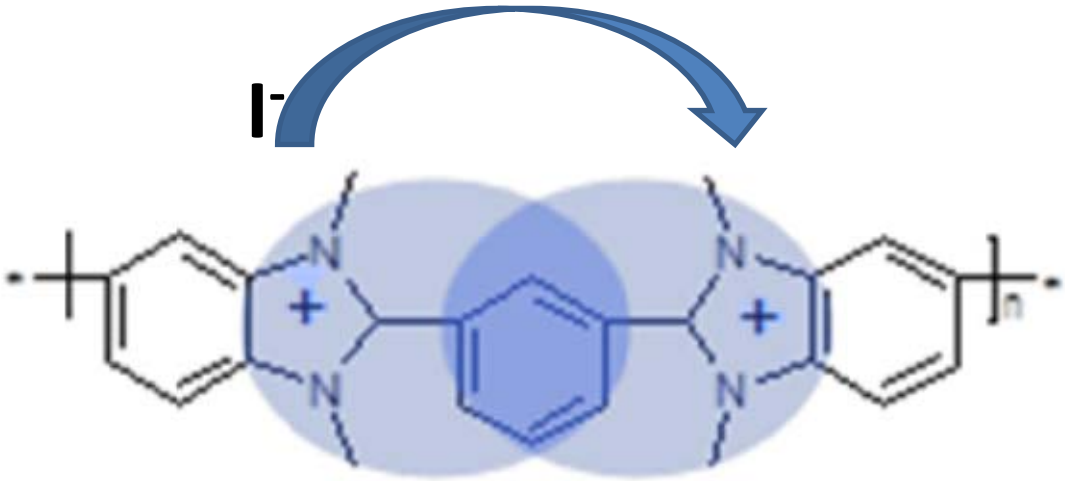
NMR calculations



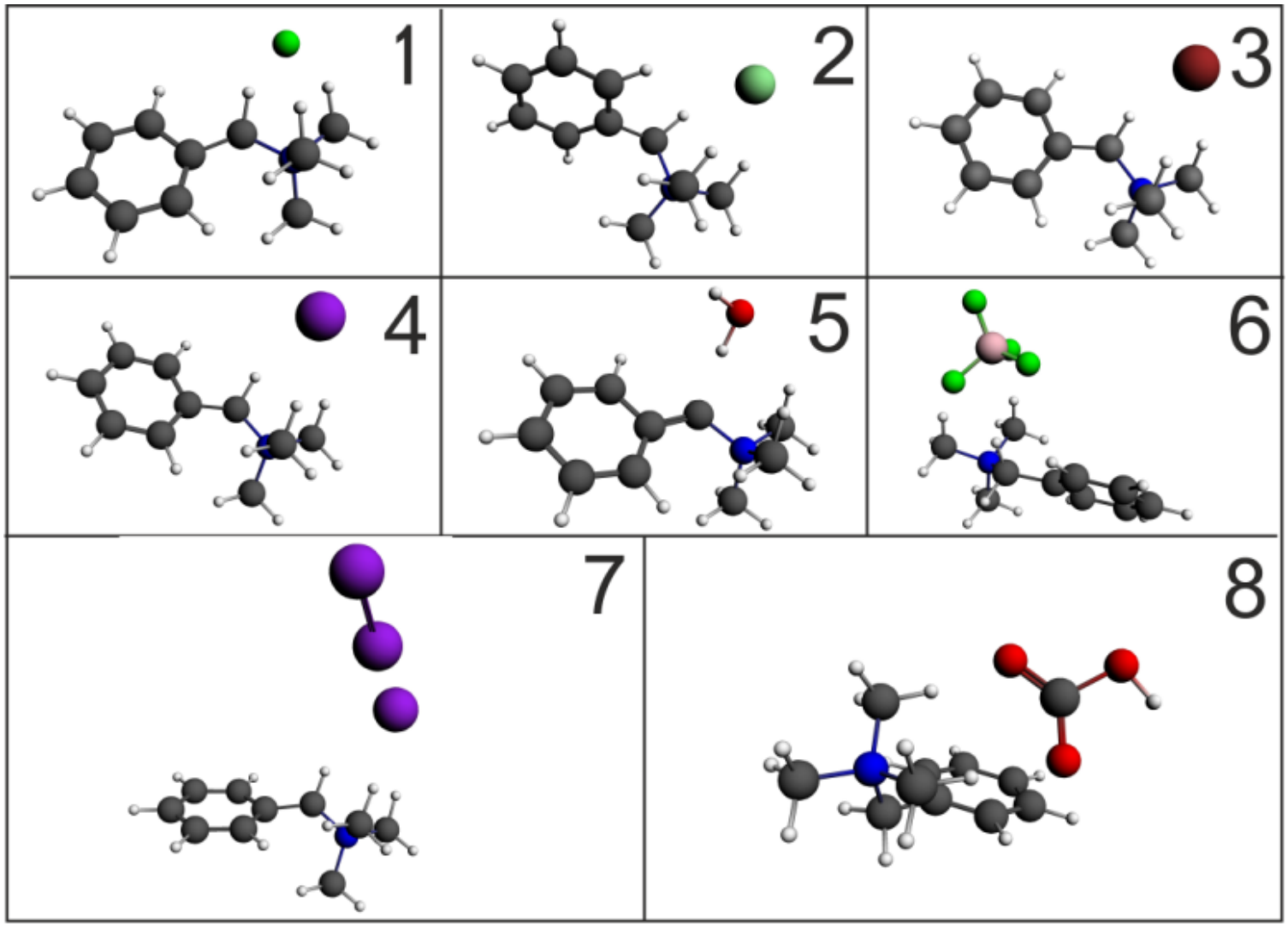
Next step:

Calculation of conductivity makes use of:
•model of ions conductivity in liquid,
•transition state theory (barrier)

Method: MD with constraints

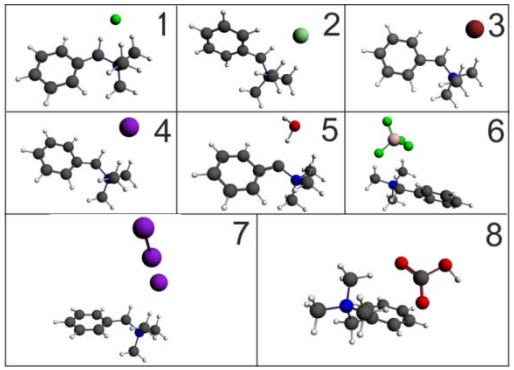


Interactions of triton with anions



Interactions of triton with anions

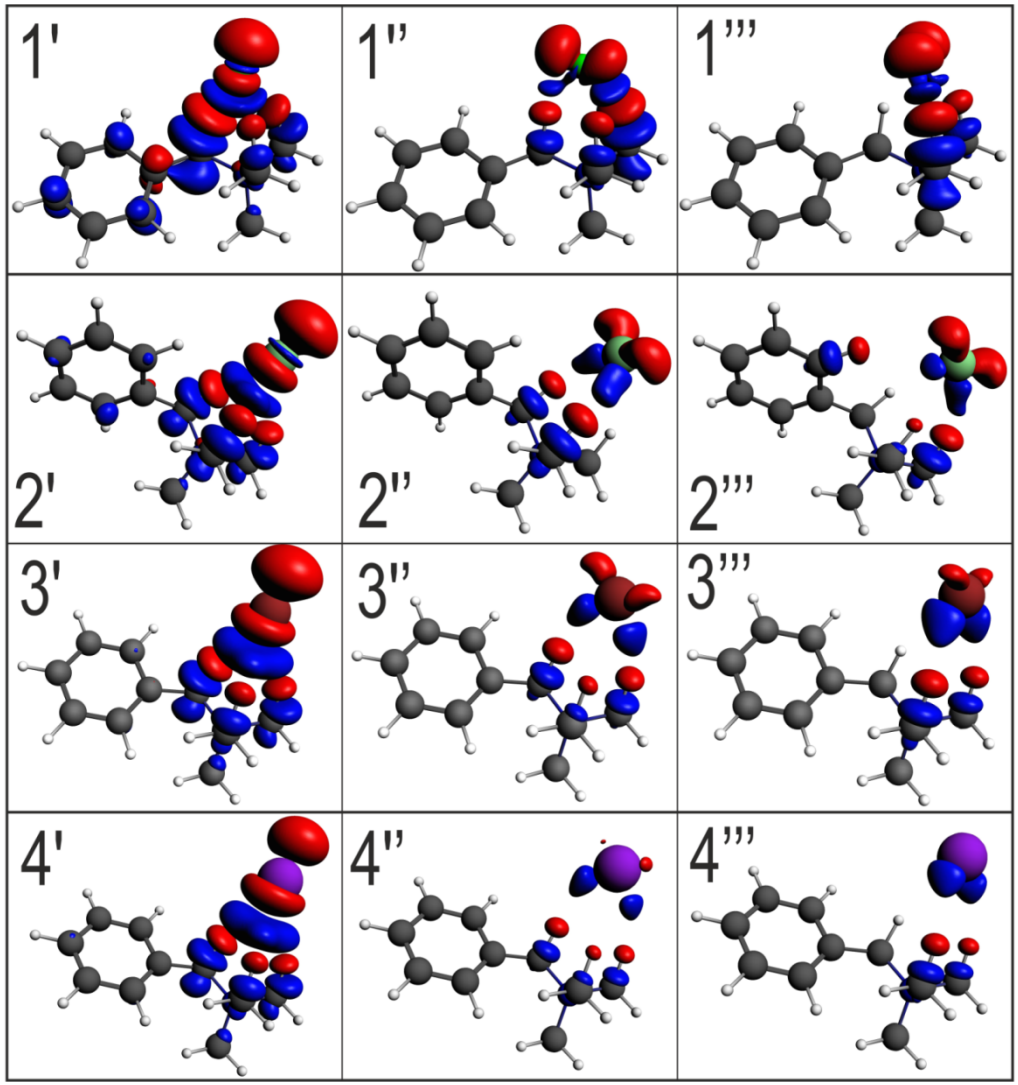
Out of plane	E_{Pauli}	E_{elstat}	E_{orb}	$E_{bonding}$	E_{dist}	$E_{interaction}$
$Triton^{+}+F^{-}$	57,25	-133,28	-50,87	-126,91	2,88	-124,03
$Triton^{+}+Cl^{-}$	32,44	-101,67	-28,41	-97,63	-6,43	-104,06
$Triton^{+}+Br^{-}$	32,40	-97,12	-26,57	-91,29	0,65	-90,64
$Triton^{+}+I^{-}$	29,83	-90,25	-22,94	-83,36	0,50	-82,86
$Triton^{+}+I_3^{-}$	14,45	-68,60	-12,17	-66,32	-6,82	-73,14
$Triton'+H_2O$	28,50	-24,46	-16,78	-12,74	-117,20	-129,94
$Triton^{+}+HCO_3^{-}$	30,11	-94,82	-23,07	-87,77	-3,73	-91,50
$Triton^{+}+BF_4^{-}$	22,10	-86,30	-16,91	-81,11	0,51	-80,60

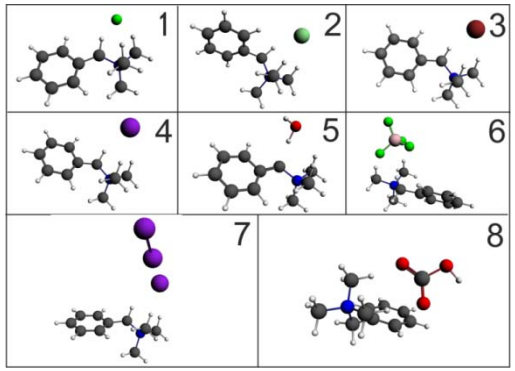


Interactions with anions

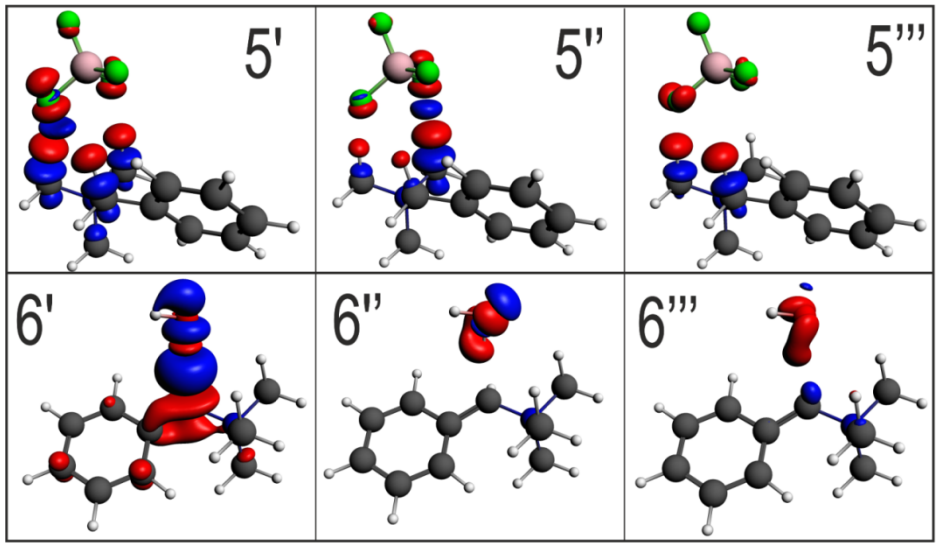
	ΔE_{Pauli}	$\Delta E_{Pauli}/6$	ΔE_{elstat}	$\Delta E_{elstat}/6$	ΔE_{orb}	$\Delta E_{orb}/6$	$\Delta E_{Bonding}$	$\Delta E_{bonding}/6$	$\Delta E_{dist}/6$	$\Delta E_{total}/6$
A	$PBI^{6+} + 6\ OH^-$	2494,88	415,81	-2671,37	-445,23	-1680,90	-280,15	-1857,40	-309,57	101,51	-208,05
	$PBI^{6+} + 6\ Cl^-$	356,78	59,46	-1469,77	-244,96	-274,66	-45,78	-1387,65	-231,28	74,60	-156,68
	$PBI^{6+} + 6\ I^-$	224,09	37,35	-1344,87	-224,15	-158,78	-26,46	-1279,55	-213,26	68,59	-144,67
	$PBI^{6+} + 6\ HCO_3^-$	186,77	31,13	-1368,85	-228,14	-161,48	-26,91	-1343,57	-223,93	71,29	-152,64
C	$PBI^{6+} + 6\ BF_4^-$	103,35	17,23	-1215,36	-202,56	-86,39	-14,40	-1198,40	-199,73	58,84	-140,89
	$PBIO^{6+} + 6\ OH^-$	2496,08	416,01	-2467,50	-411,25	-1660,92	-276,82	-1632,33	-272,06	85,26	-186,80
	$PBIO^{6+} + 6\ Cl^-$	403,51	67,25	-1273,40	-212,23	-298,01	-49,67	-1167,90	-194,65	59,62	-135,03
	$PBIO^{6+} + 6\ I^-$	267,55	44,59	-1184,43	-197,41	-183,31	-30,55	-1100,19	-183,37	60,18	-123,19
	$PBIO^{6+} + 6\ HCO_3^-$	205,31	34,22	-1094,42	-182,40	-167,53	-27,92	-1056,64	-176,11	48,66	-127,45
	$PBIO^{6+} + 6\ BF_4^-$	101,44	16,91	-1063,62	-177,27	-83,23	-13,87	-1045,41	-174,24	55,47	-118,77
E	$PBI2O^{6+} + 6\ OH^-$	2509,52	418,25	-2360,18	-393,36	-1678,94	-279,82	-1529,61	-254,94	77,53	-177,41
	$PBI2O^{6+} + 6\ Cl^-$	423,66	70,61	-1183,32	-197,22	-315,36	-52,56	-1075,02	-179,17	52,61	-126,56
	$PBI2O^{6+} + 6\ I^-$	281,65	46,94	-1069,05	-178,18	-194,29	-32,38	-981,69	-163,62	49,68	-113,93
	$PBI2O^{6+} + 6\ BF_4^-$	98,78	16,46	-927,95	-154,66	-81,42	-13,57	-910,59	-151,77	42,74	-109,03

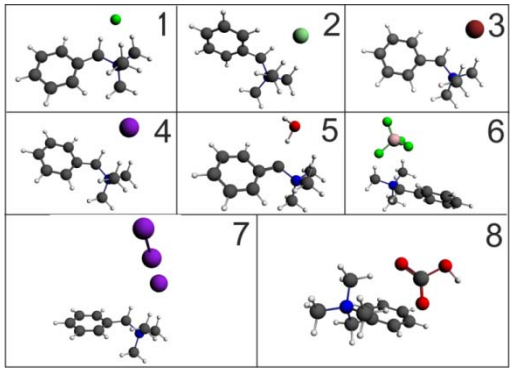
Interactions of triton with anions

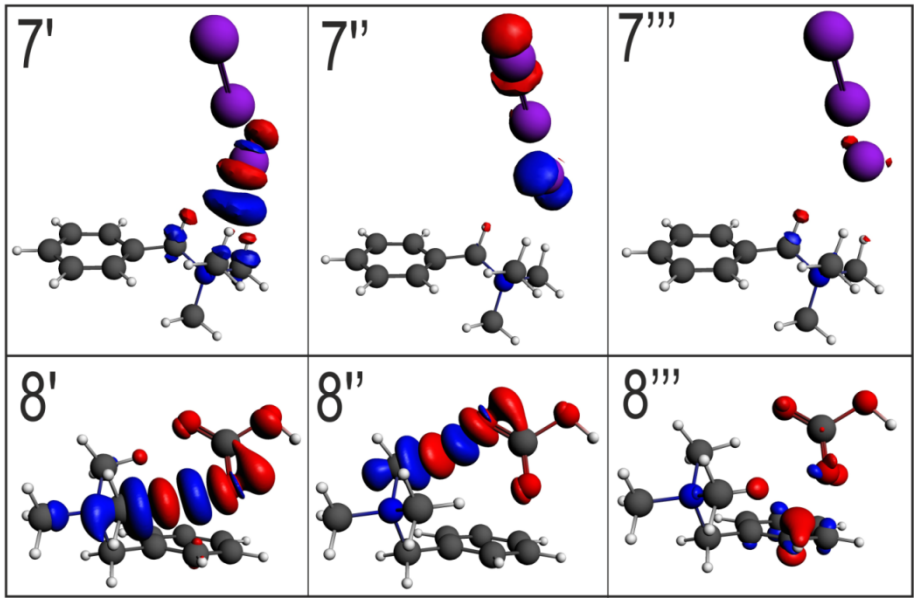




Interactions of triton with anions







Stable Hydroxide:

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Communication

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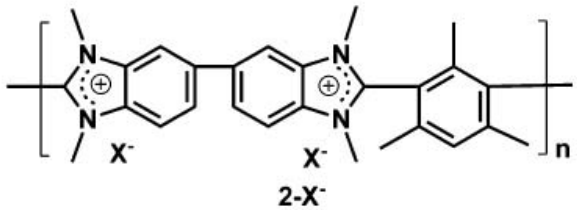
A Stable Hydroxide-Conducting Polymer

Owen D. Thomas, Kristen J. W. Y. Soo, Timothy J. Peckham, Mahesh P. Kulkarni, and Steven Holdcroft*

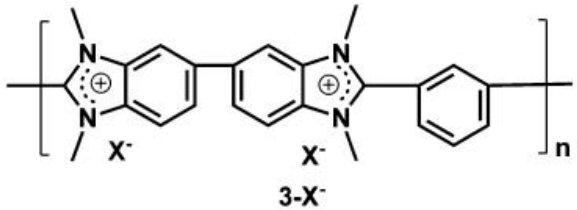
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Supporting Information

ABSTRACT: A stable hydroxide-conducting membrane based on benzimidazolium hydroxide and its analogous anion-exchange polymer is reported for the first time. The molecular and polymeric analogues possess unprecedented hydroxide stability in neutral and KOH solutions as the soluble benzimidazolium salt, made possible by steric crowding around the benzimidazolium C2 position, which is usually susceptible to nucleophilic attack by OH^-. The polymers were cast and insolubilized for the purpose of forming membranes by blending with a poly(benzimidazole) followed by hydroxide-activated electrostatic interactions. The resulting membranes possess ionic (OH^-) conductivities of up to 13.2 mS cm^{-1} and represent a new class of anion-exchange polymers and membranes.



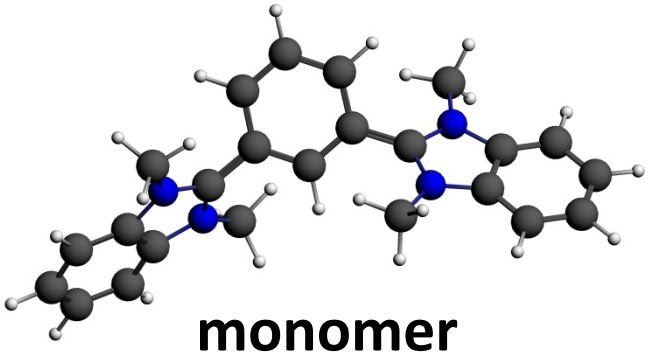
2-X^-



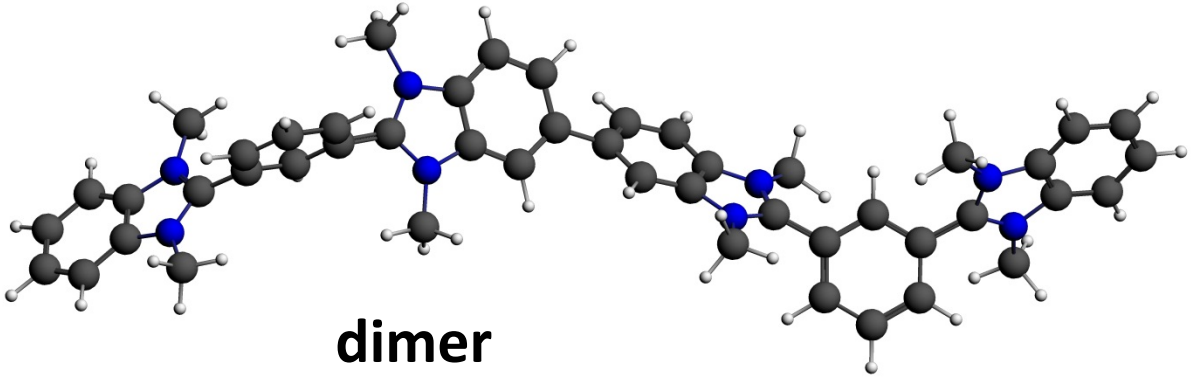
3-X^-

Figure 1. Poly[2,2′-(*m*-mesitylene)-5,5′-bis(*N*,*N*′-dimethylbenzimidazolium)] (Mes-PDMBI, 2-X^-) and poly[2,2′-(*m*-phenylene)-5,5′-bis(*N*,*N*′-dimethylbenzimidazolium)] (PDMBI, 3-X^-).

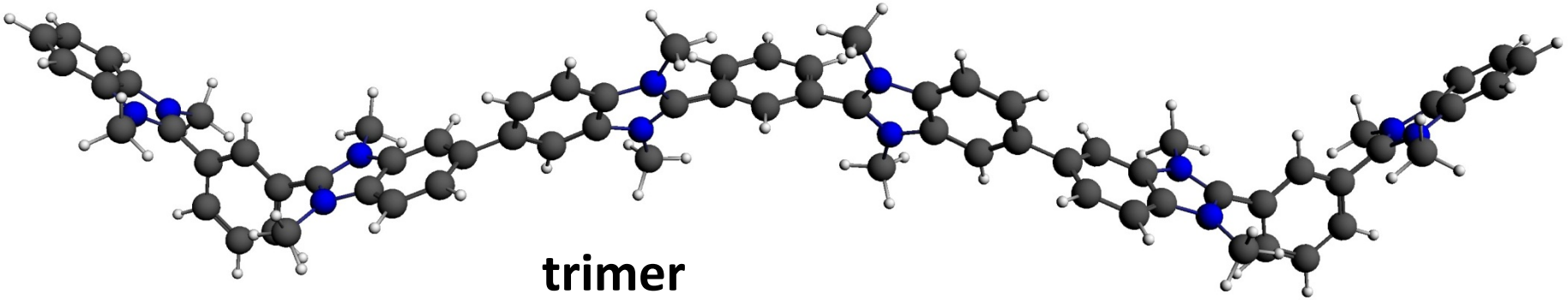
PBI:



monomer

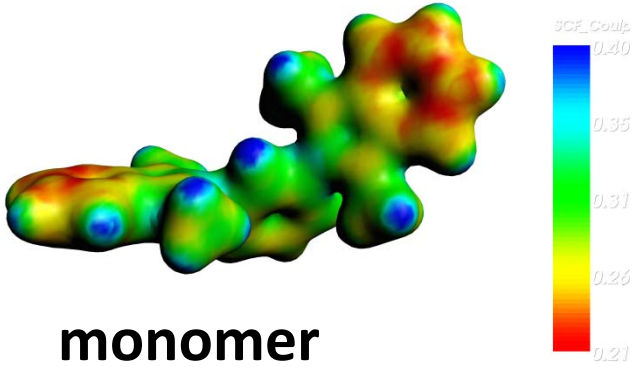


dimer

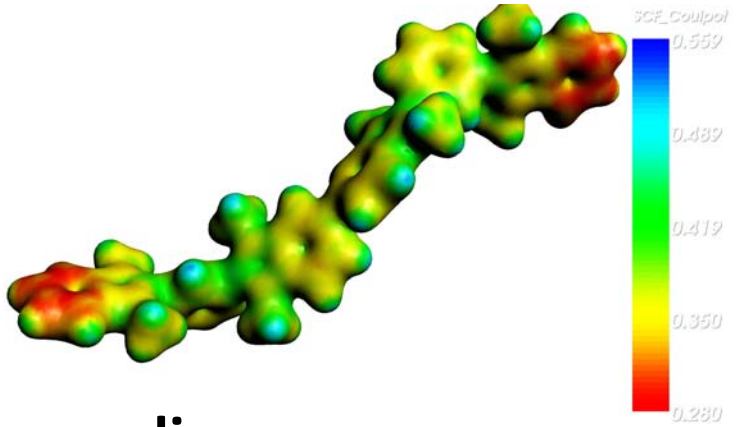


trimer

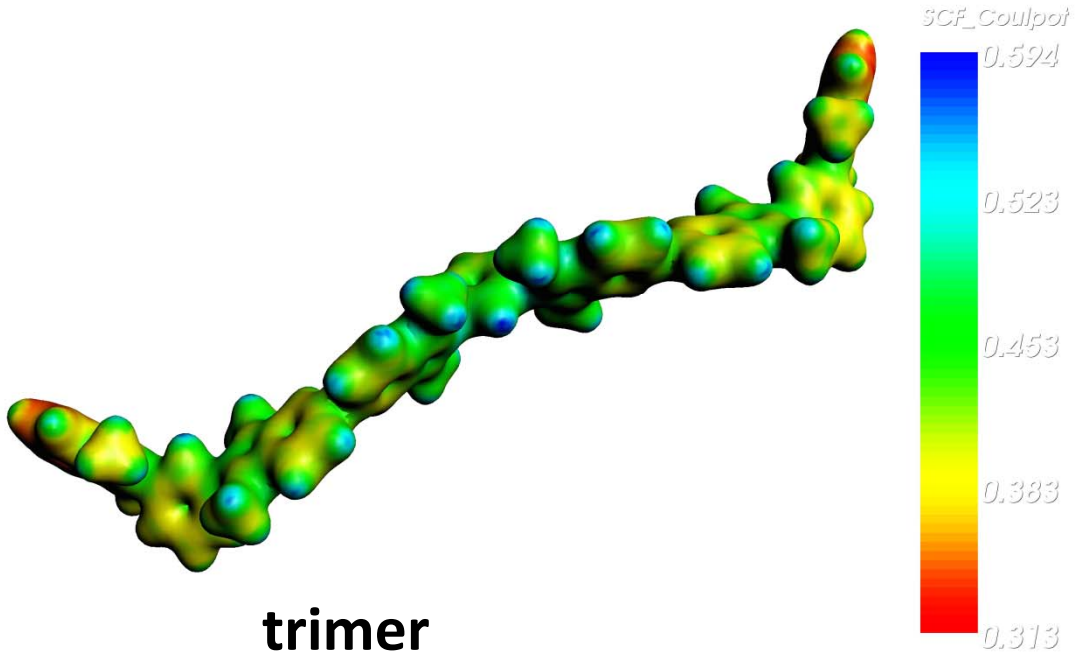
MEP for PBI:



monomer

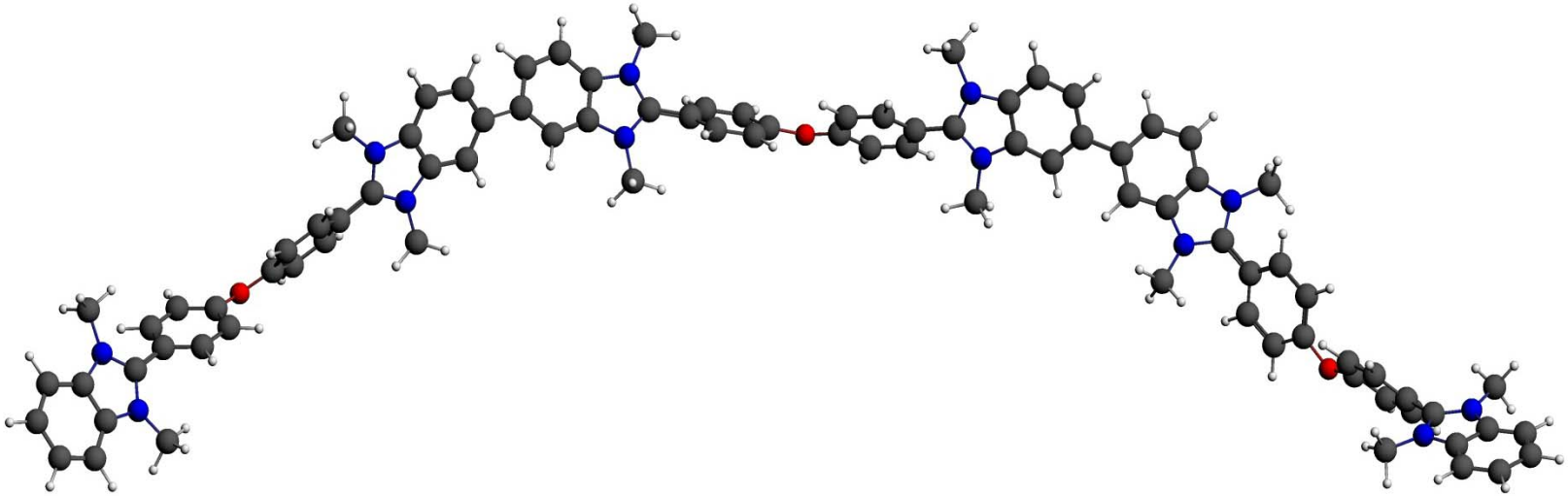


dimer

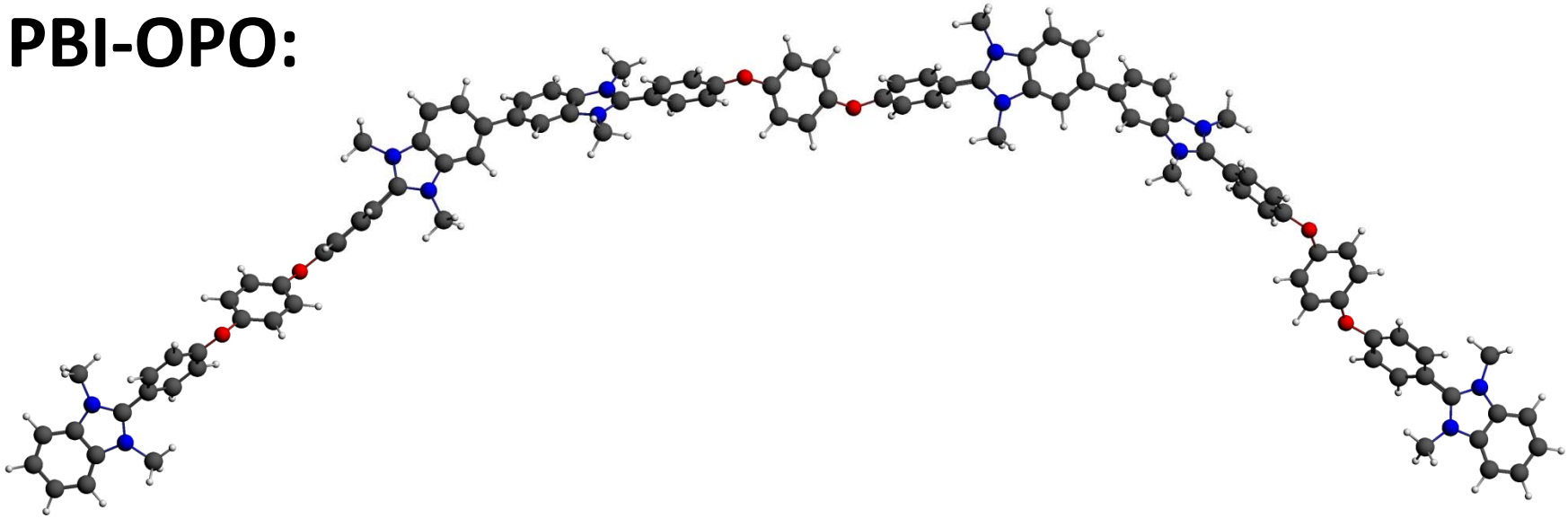


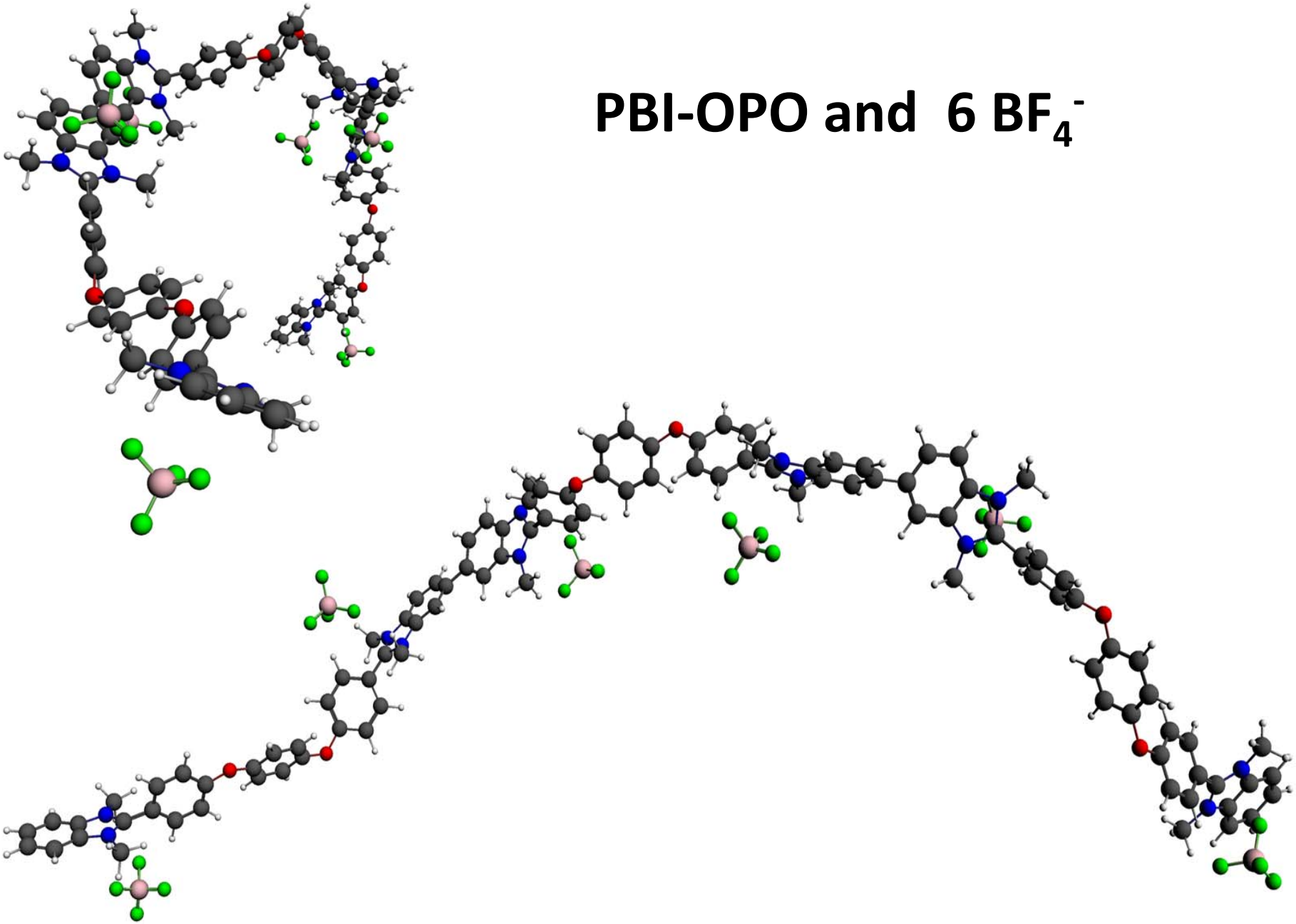
trimer

PBI-OO:

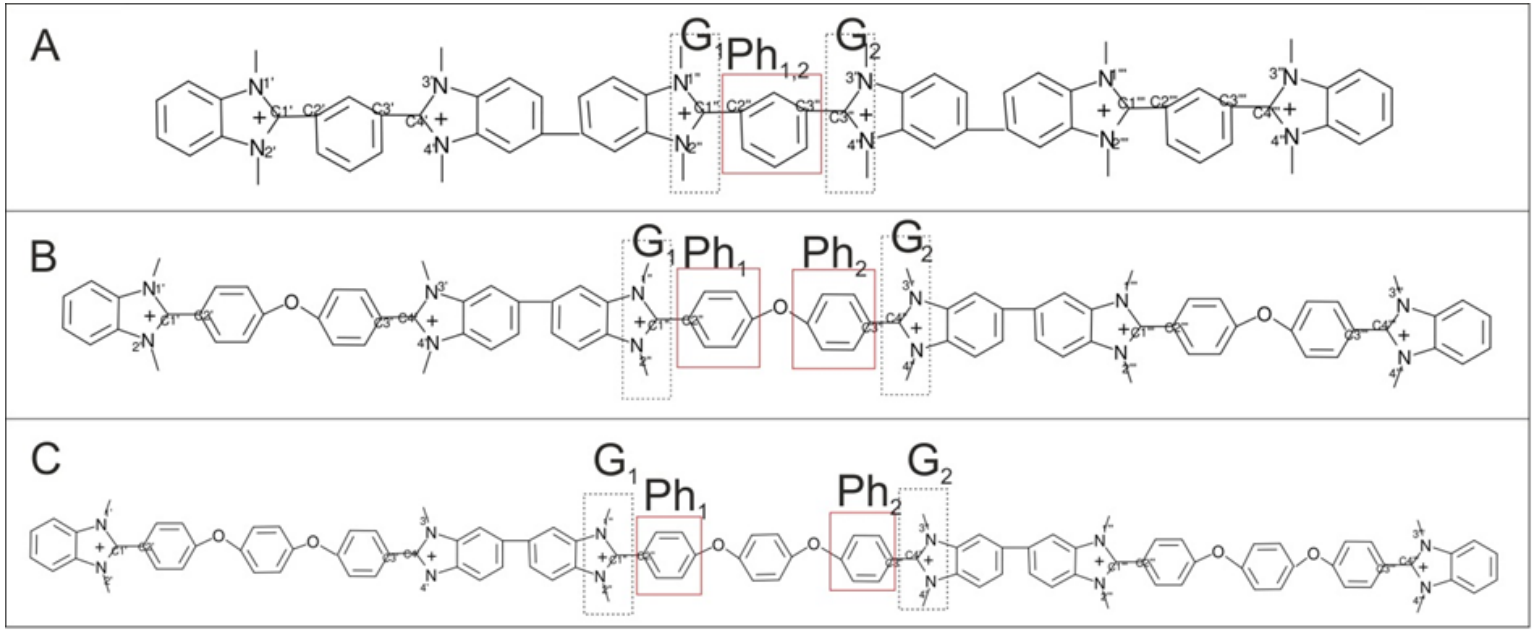


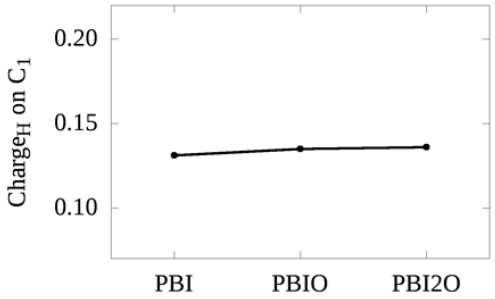
PBI-OPO:

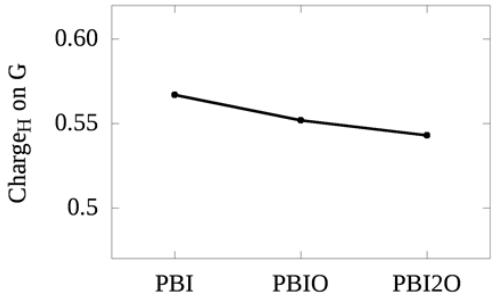


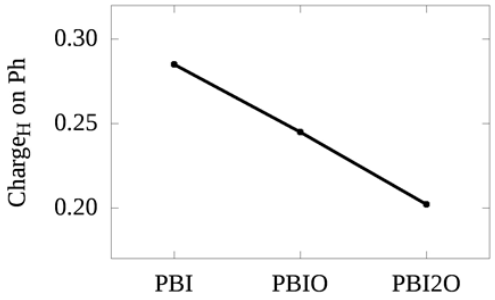


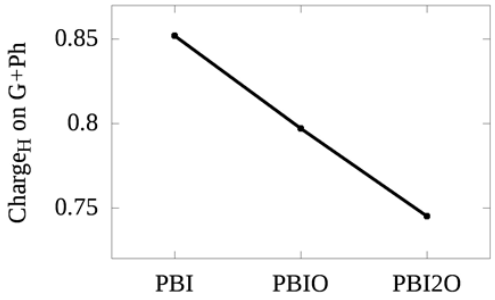
PBI-OPO and 6 BF_4^-


A
G1
Ph1,2
G2
B
G1
Ph1
Ph2
G2
C
G1
Ph1
Ph2
G2


Charge$_H$ on C$_1$
0.20
0.15
0.10
PBI
PBIO
PBI2O


Charge$_H$ on G
0.60
0.55
0.5
PBI
PBIO
PBI2O

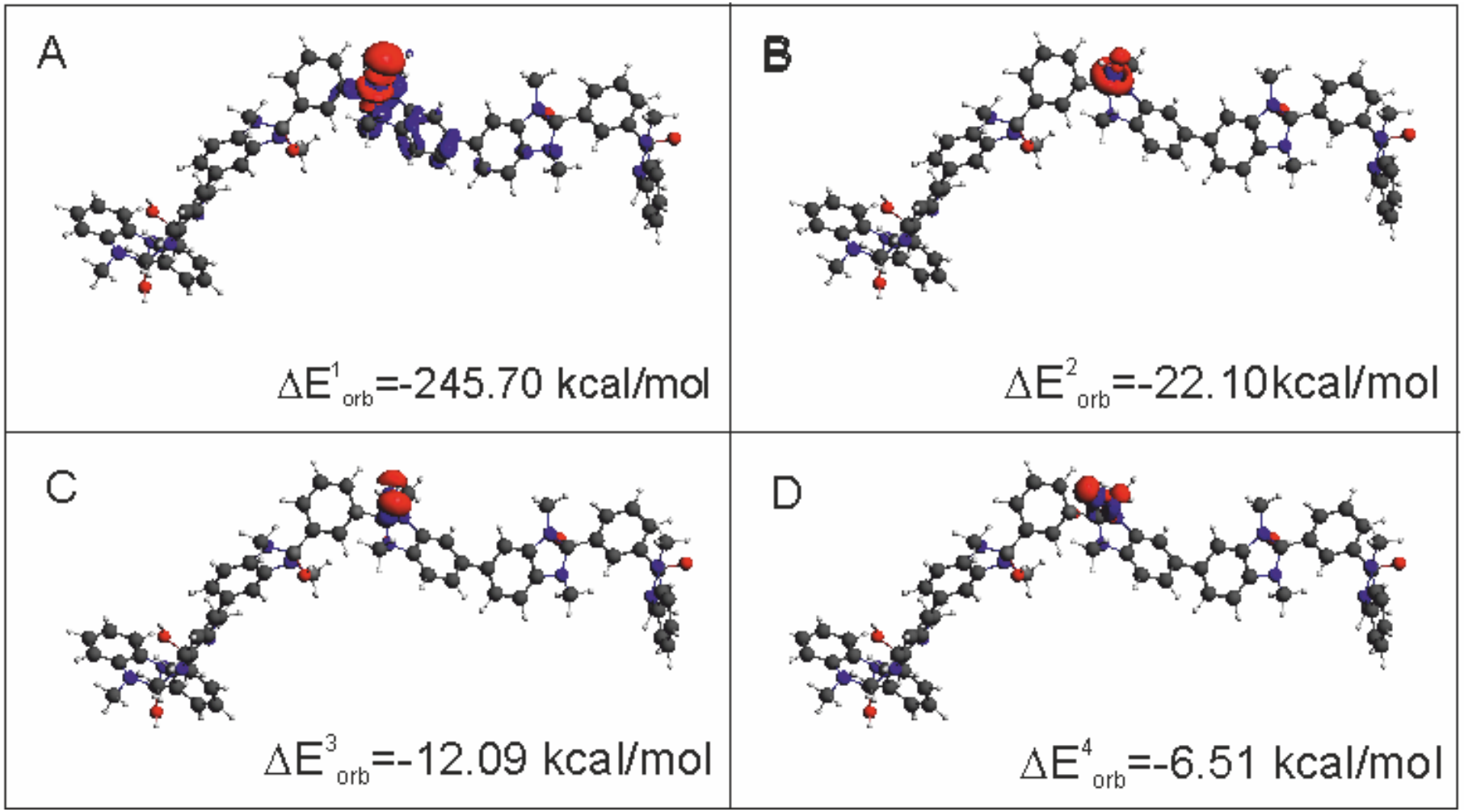

Charge$_H$ on Ph
0.30
0.25
0.20
PBI
PBIO
PBI2O

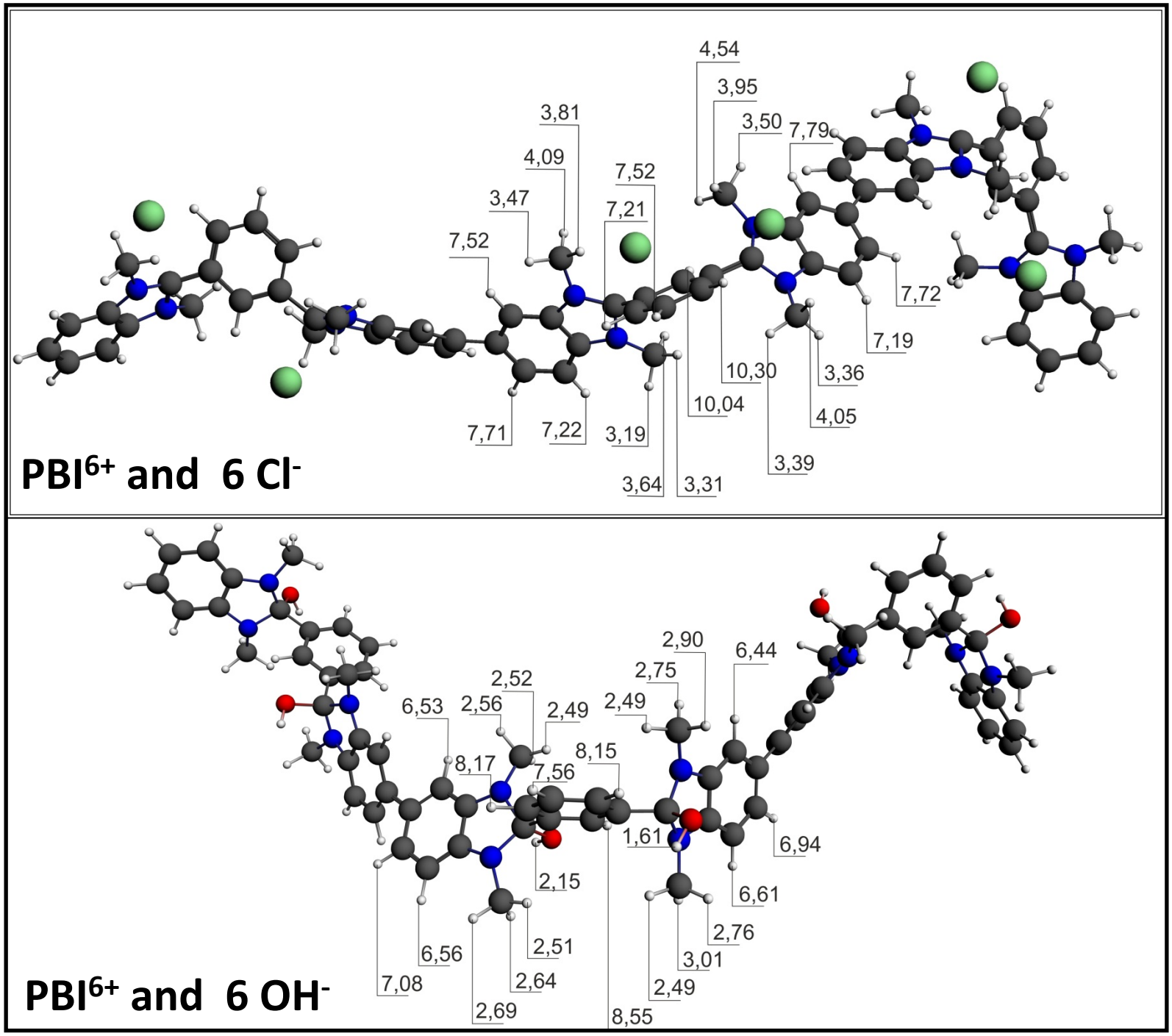

Charge$_H$ on G+Ph
0.85
0.8
0.75
PBI
PBIO
PBI2O

ETS

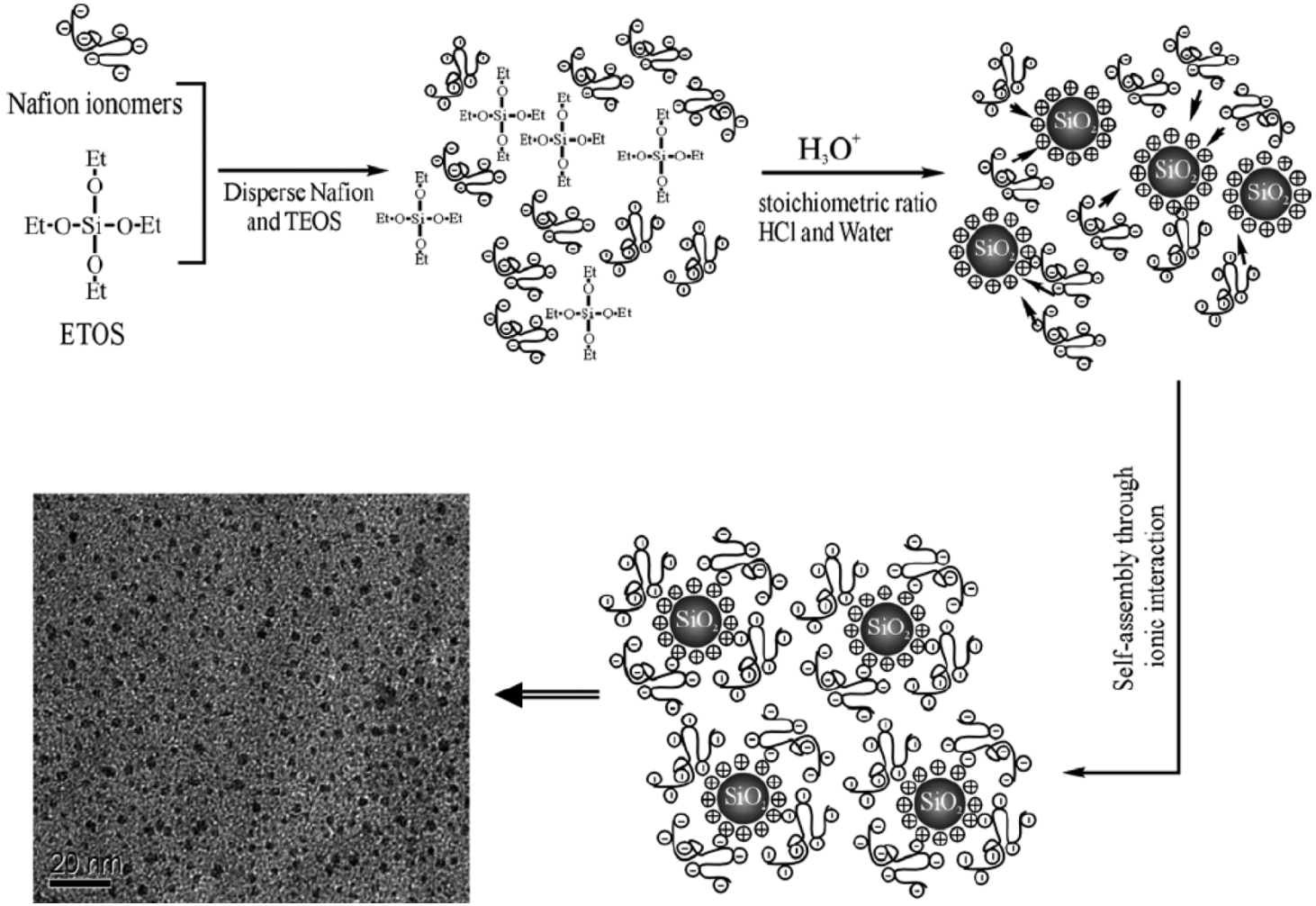
[kcal/mol]	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	$\Delta E_{Bonding}$	ΔE_{dist}	ΔE_{total}	ΔE_{total} / 6
PBI^{6+} + 6 OH^-	2494,88	-2671,37	-1680,90	-1857,40	609.06	**-1248.30**	-208,05
PBI^{6+} + 6 Cl^-	356,78	-1469,77	-274,66	-1387,65	447.60	**-940.08**	-156,68
PBI^{6+} + 6 I^-	224,09	-1344.87	-158,78	-1279,55	411.54	**-868.02**	-144,67
PBI^{6+} + 6 BF_{4-}	103,35	-1215,36	-86,39	-1198,40	353.04	**-845.34**	-140,89
PBI-OO^{6+} + 6 OH^-	2496,08	-2467,50	-1660,92	-1632,33	511.56	**-1120.8**	-186,80
PBI-OO^{6+} + 6 Cl^-	403,51	-1273,40	-298,01	-1167,90	357.72	**-810.18**	-135,03
PBI-OO^{6+} + 6 I^-	267,55	-1184,43	-183,31	-1100,19	361.08	**-739.14**	-123,19
PBI-OO^{6+} + 6 BF_4^-	101,44	-1063,62	-83,23	-1045,41	332.82	**-712.62**	-118,77
PBI-OPO^{6+} + 6 OH^-	2509,52	-2360,18	-1678,94	-1529,61	465.18	**-1064.46**	-177,41
PBI-OPO^{6+} + 6 Cl^-	423,66	-1183,32	-315,36	-1075,02	315.66	**-759.36**	-126,56
PBI-OPO^{6+} + 6 I^-	281,65	-1069,05	-194,29	-981,69	298.08	**-683.58**	-113,93
PBI-OPO^{6+} + 6 BF_4^-	98,78	-927,95	-81,42	-910,59	256.44	**-654.18**	-109,03

NOCVs

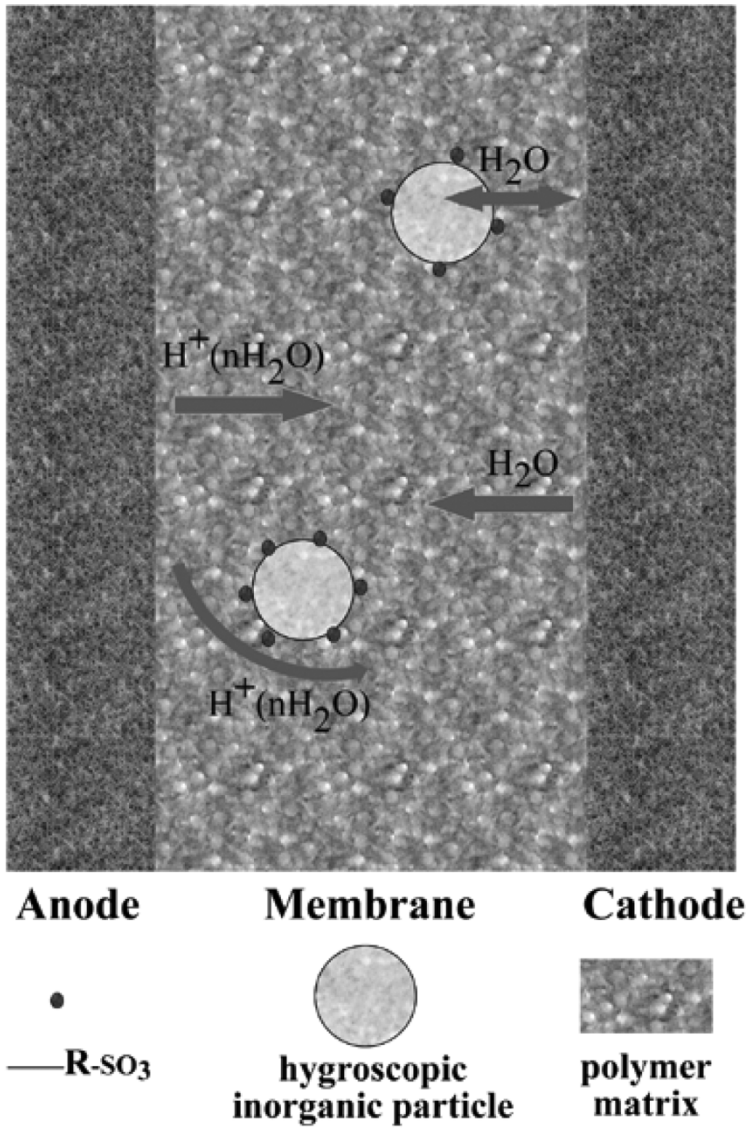

A
ΔE^{1}_{orb}=-245.70 kcal/mol
B
ΔE^{2}_{orb}=-22.10kcal/mol
C
ΔE^{3}_{orb}=-12.09 kcal/mol
D
ΔE^{4}_{orb}=-6.51 kcal/mol


4,54
3,95
3,50
7,79
3,81
4,09
7,52
3,47
7,21
7,52
7,72
7,19
10,30
3,36
10,04
4,05
7,71
7,22
3,19
3,39
3,64
3,31
PBI6+ and 6 Cl-
2,90
6,44
2,75
2,52
6,53
2,56
2,49
2,49
8,17
7,56
8,15
1,61
6,94
2,15
6,61
2,76
6,56
2,51
3,01
7,08
2,64
2,49
2,69
8,55
PBI6+ and 6 OH-

Material-Nafion:



Scheme for the formation of the Nafion−SiO2 nanoparticles by self-assembly method. The inset shows the transmission electron microscopy (TEM) micrograph of the self-assembled Nafion−SiO2 nanoparticles.117 Reprinted with permission from ref 117. Copyright 2007 Elsevier



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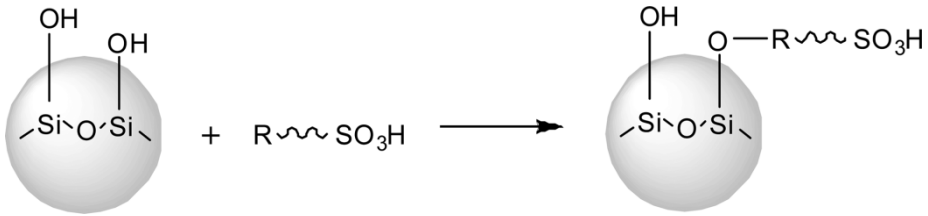
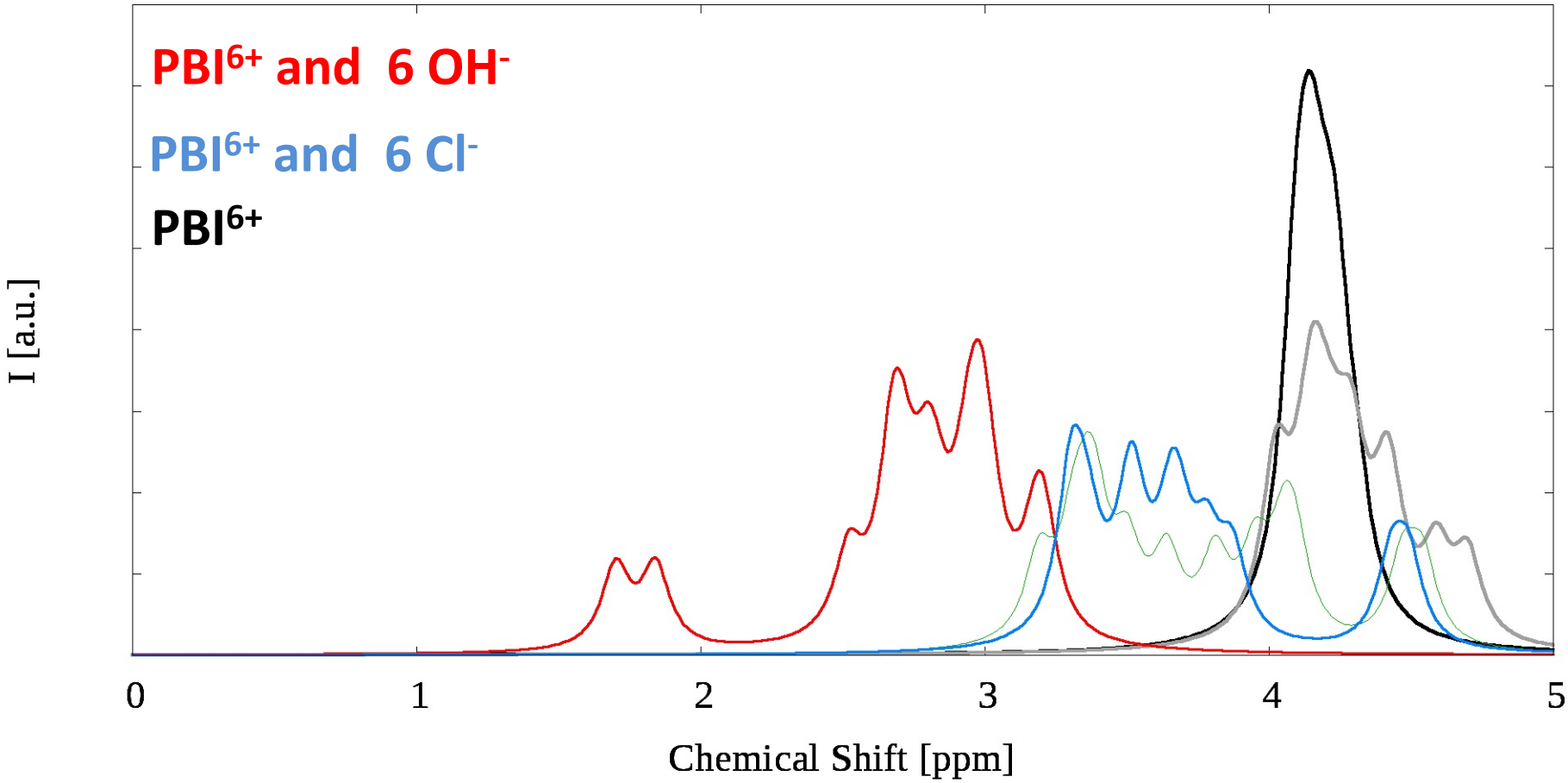
Schematic diagram of water and proton transport in Nafion membrane modified by inorganic fillers with hygroscopic and proton conductive properties.

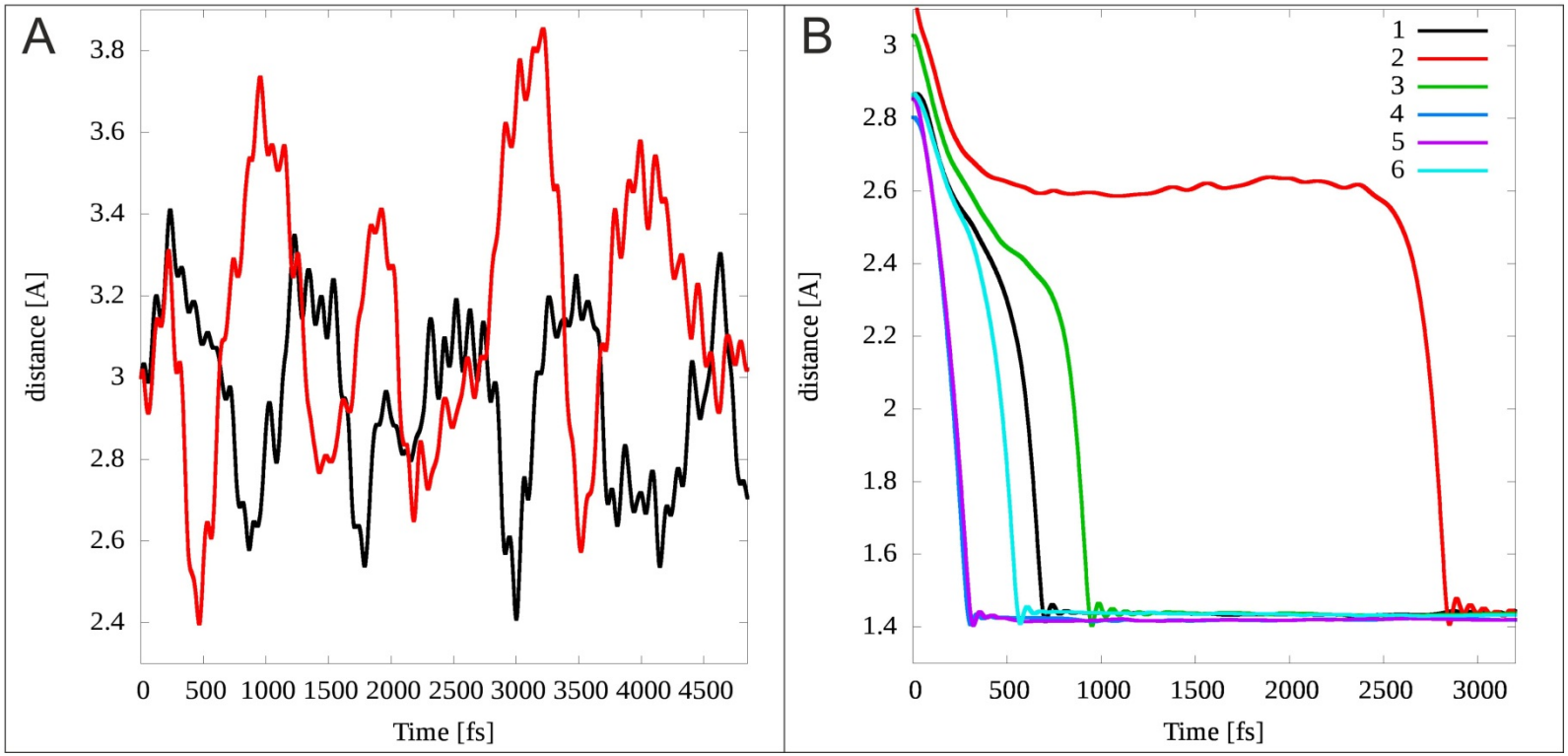


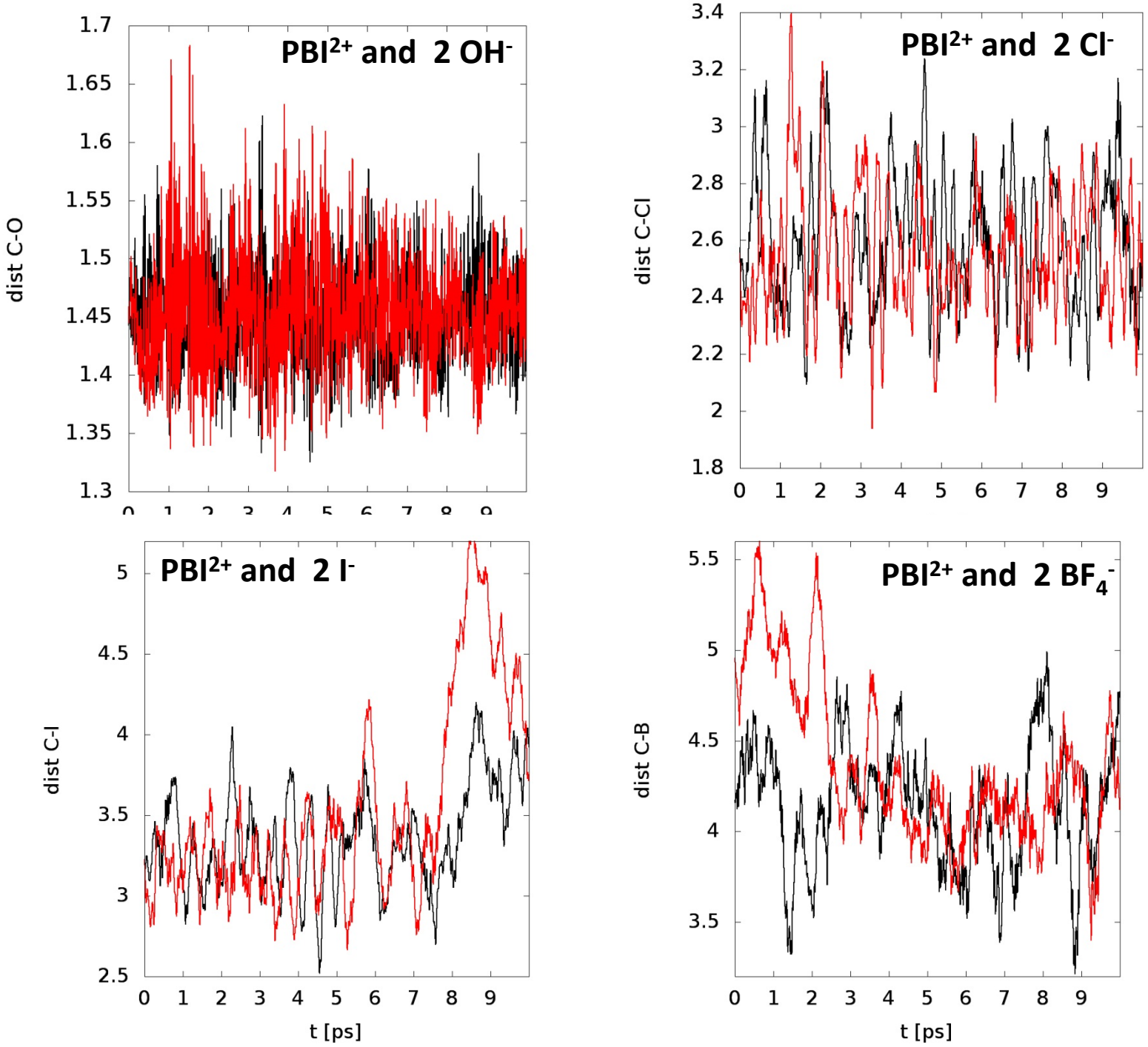
Schematic diagram of the silica particles modified by sulfonic acid groups.


PBI6+ and 6 OH-
PBI6+ and 6 Cl-
PBI6+
I [a.u.]
0
1
2
3
4
5
Chemical Shift [ppm]

PBI^{6+} and 6 I^-

PBI^{6+} and 6 OH^-




PBI2+ and 2 OH-
dist C-O
PBI2+ and 2 Cl-
dist C-Cl
PBI2+ and 2 I-
dist C-I
PBI2+ and 2 BF4-
dist C-B
t [ps]
t [ps]

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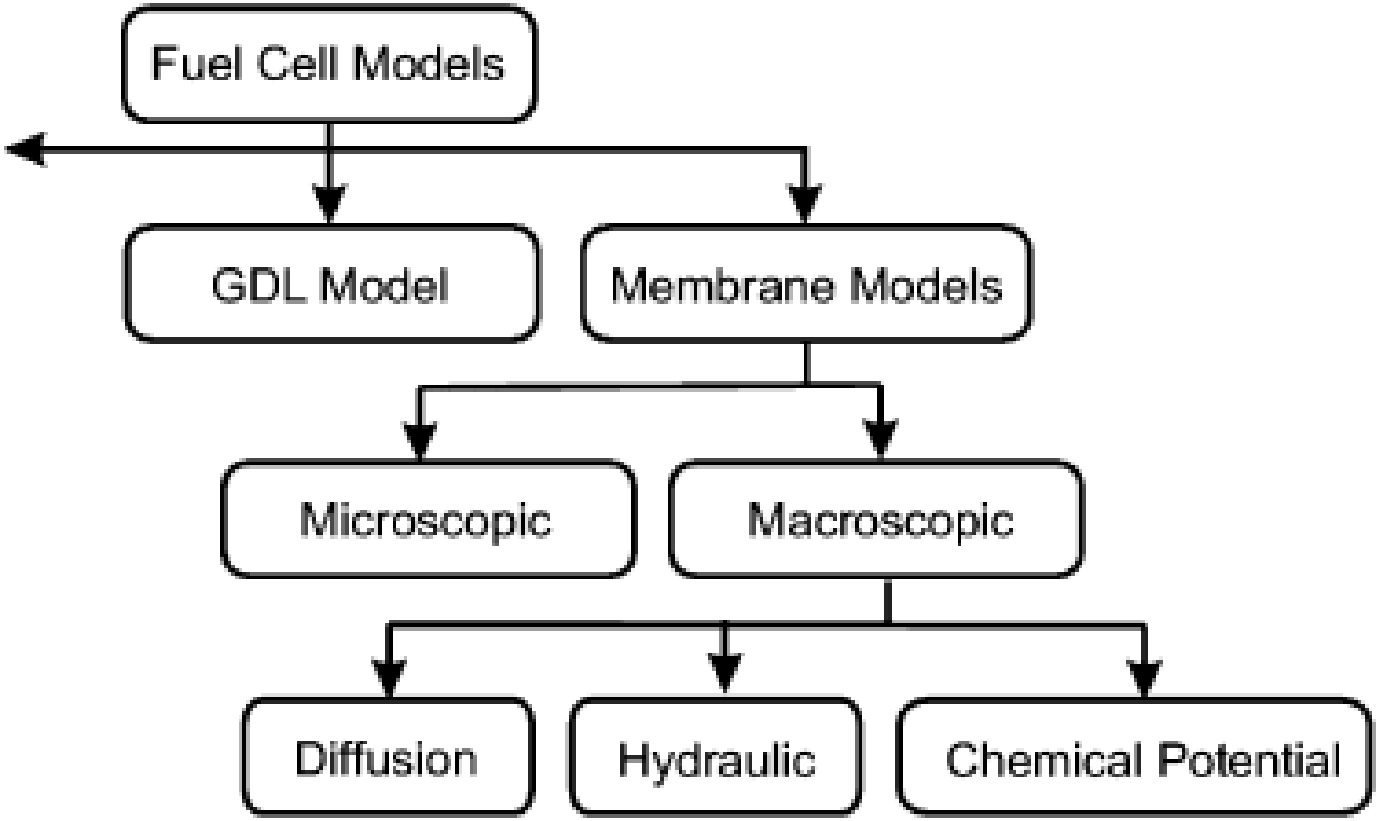
NARODOWA STRATEGIA SPÓJNOŚCI

FNP
Fundacja na rzecz Nauki Polskiej

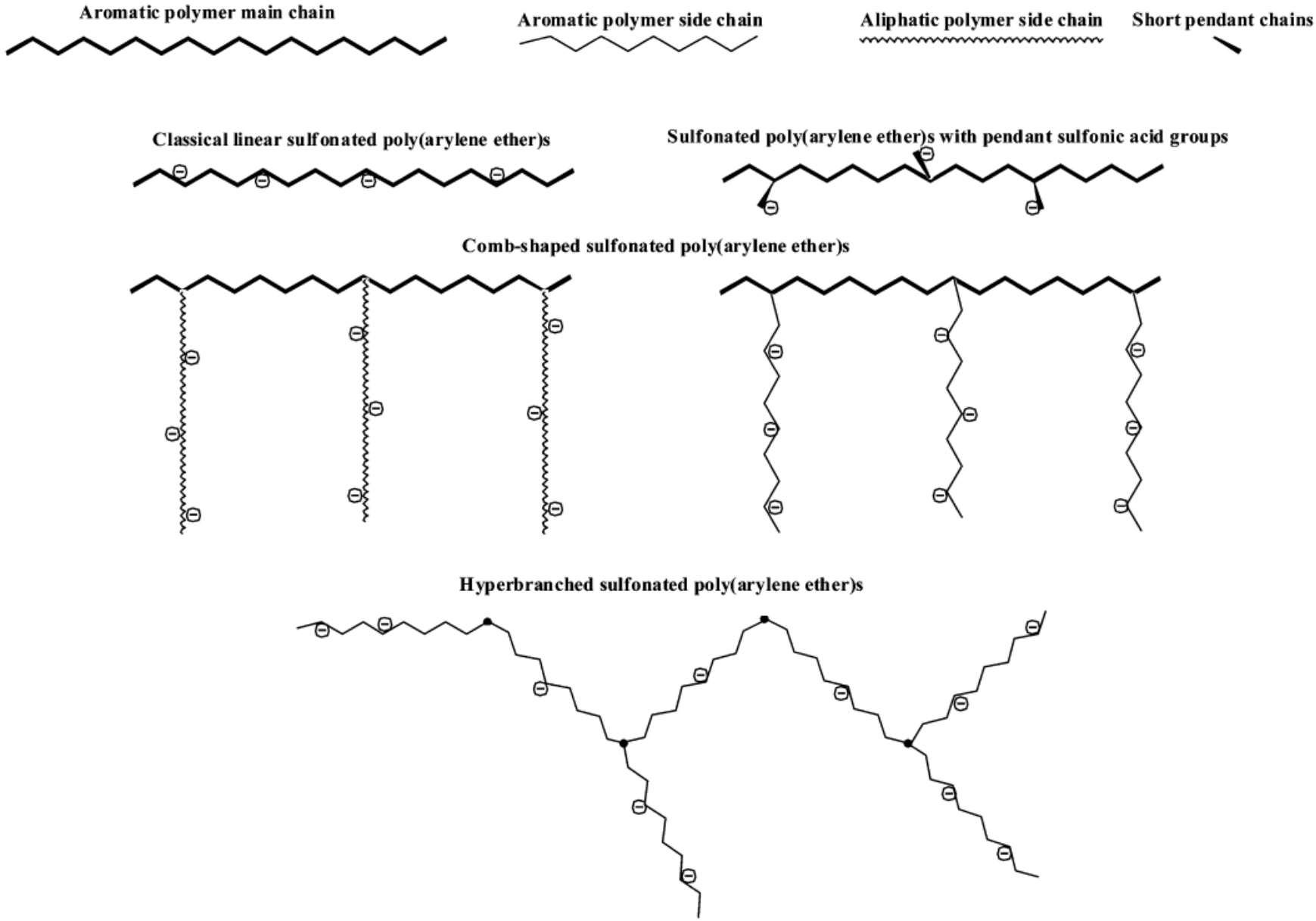
UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ ROZWOJU REGIONALNEGO

Modeling of Proton Exchange Membrane Fuel Cells

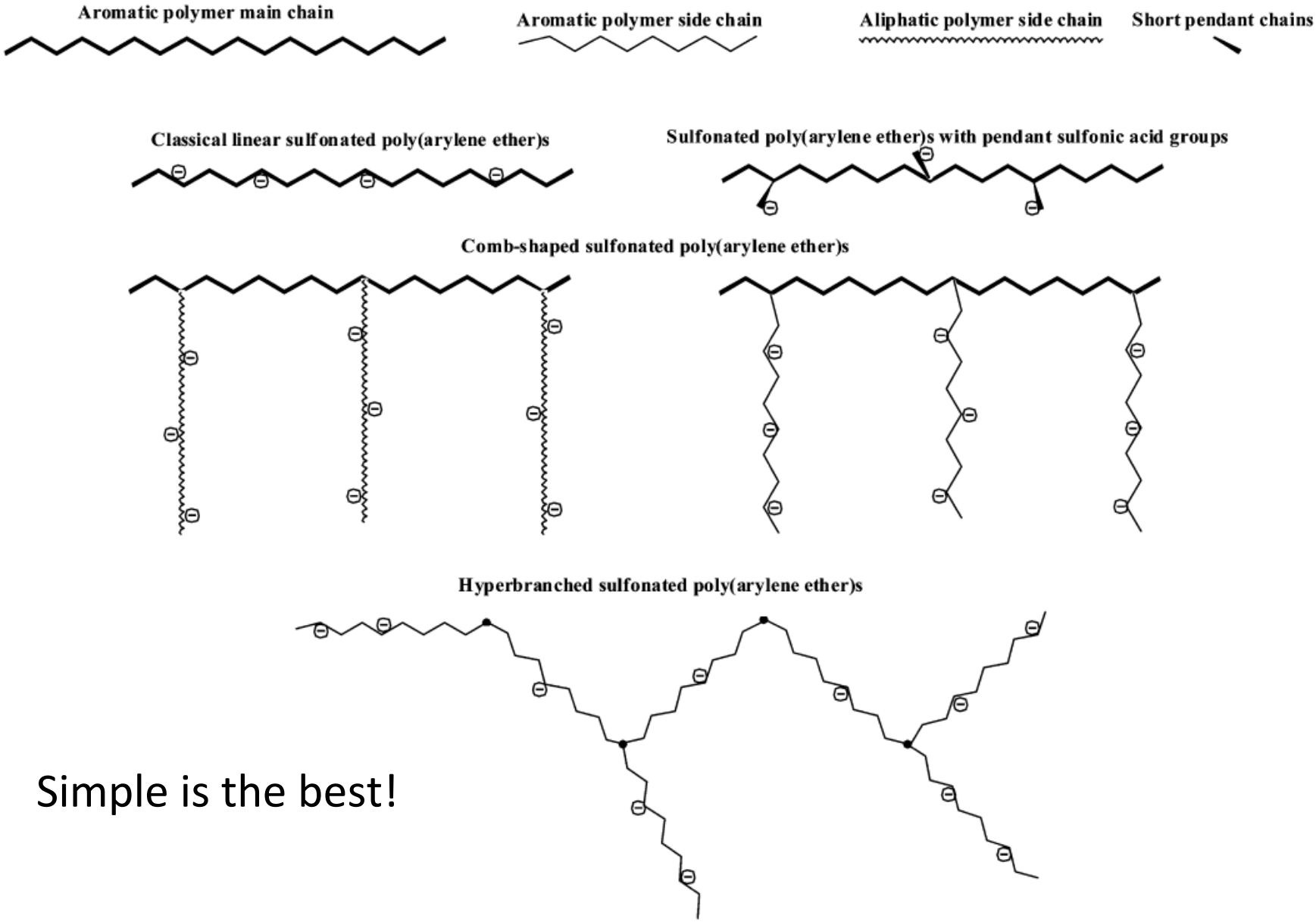


N. Djilali, Energy 32 (2007) 269–280

Why PBI?


Aromatic polymer main chain
Aromatic polymer side chain
Aliphatic polymer side chain
Short pendant chains
Classical linear sulfonated poly(arylene ether)s
Sulfonated poly(arylene ether)s with pendant sulfonic acid groups
Comb-shaped sulfonated poly(arylene ether)s
Hyperbranched sulfonated poly(arylene ether)s

Why PBI?



Simple is the best!