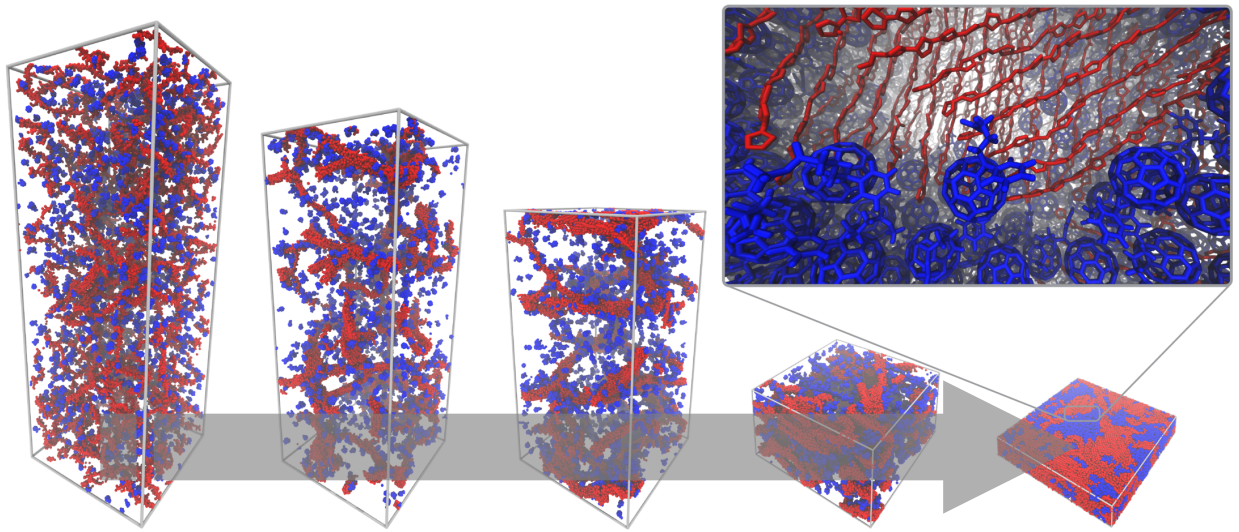
university of groningen
faculty of science and engineering
zernike institute for advanced materials

Martini Workshop 2017

Blends for Organic Photovoltaics



Riccardo Alessandri

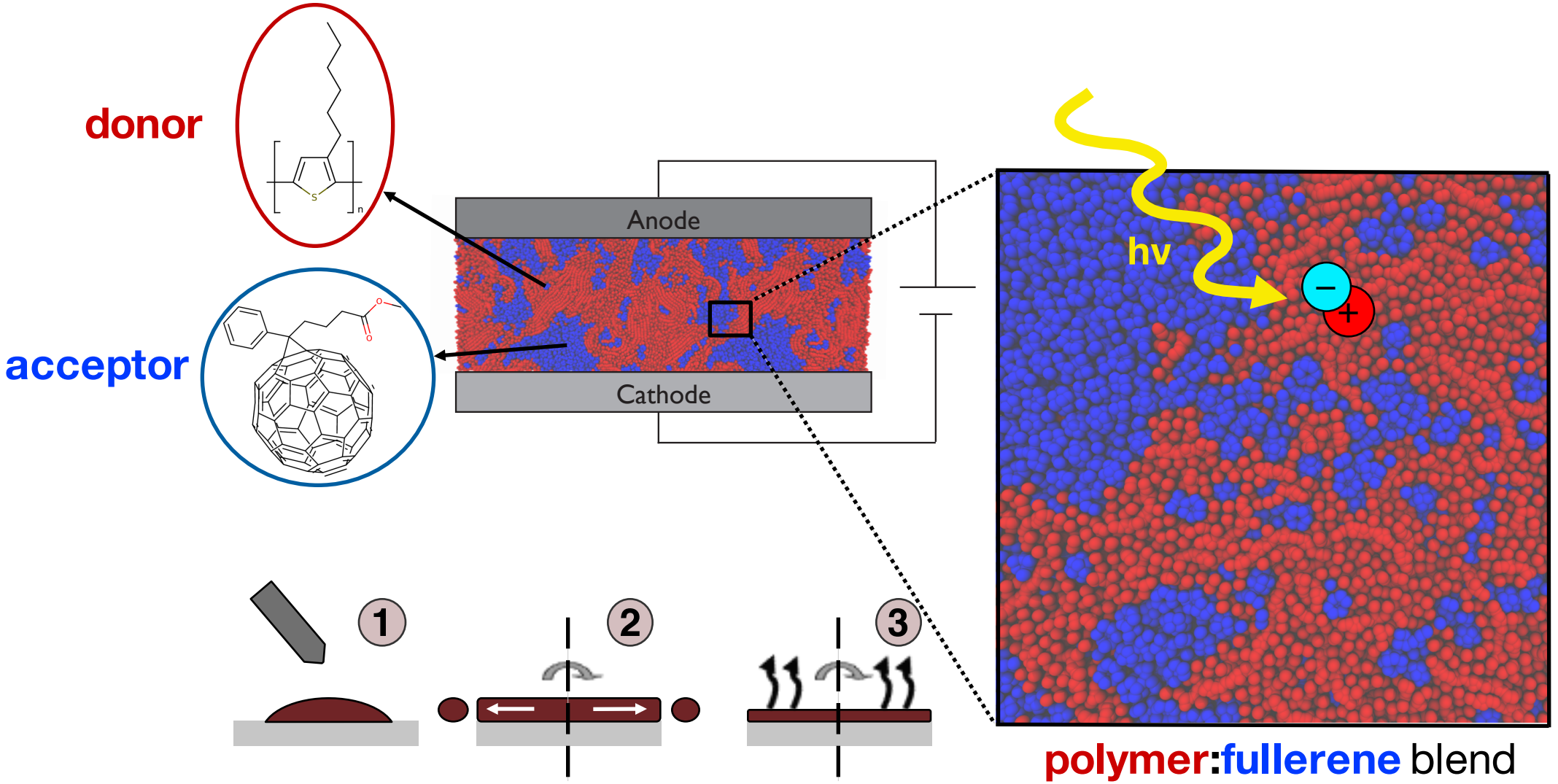
r.alessandri@rug.nl

24 / 08 / 2017

Outline

- **O**rganic **P**hoto**V**oltaics
- The **morphology** of OPV blends
- Building **Martini** models for an **OPV** system
  - The fullerene derivative : PCBM
  - The polymer : P3HT
- Solvent **evaporation** simulations
- **Results** for P3HT:PCBM
- Some **take home messages**

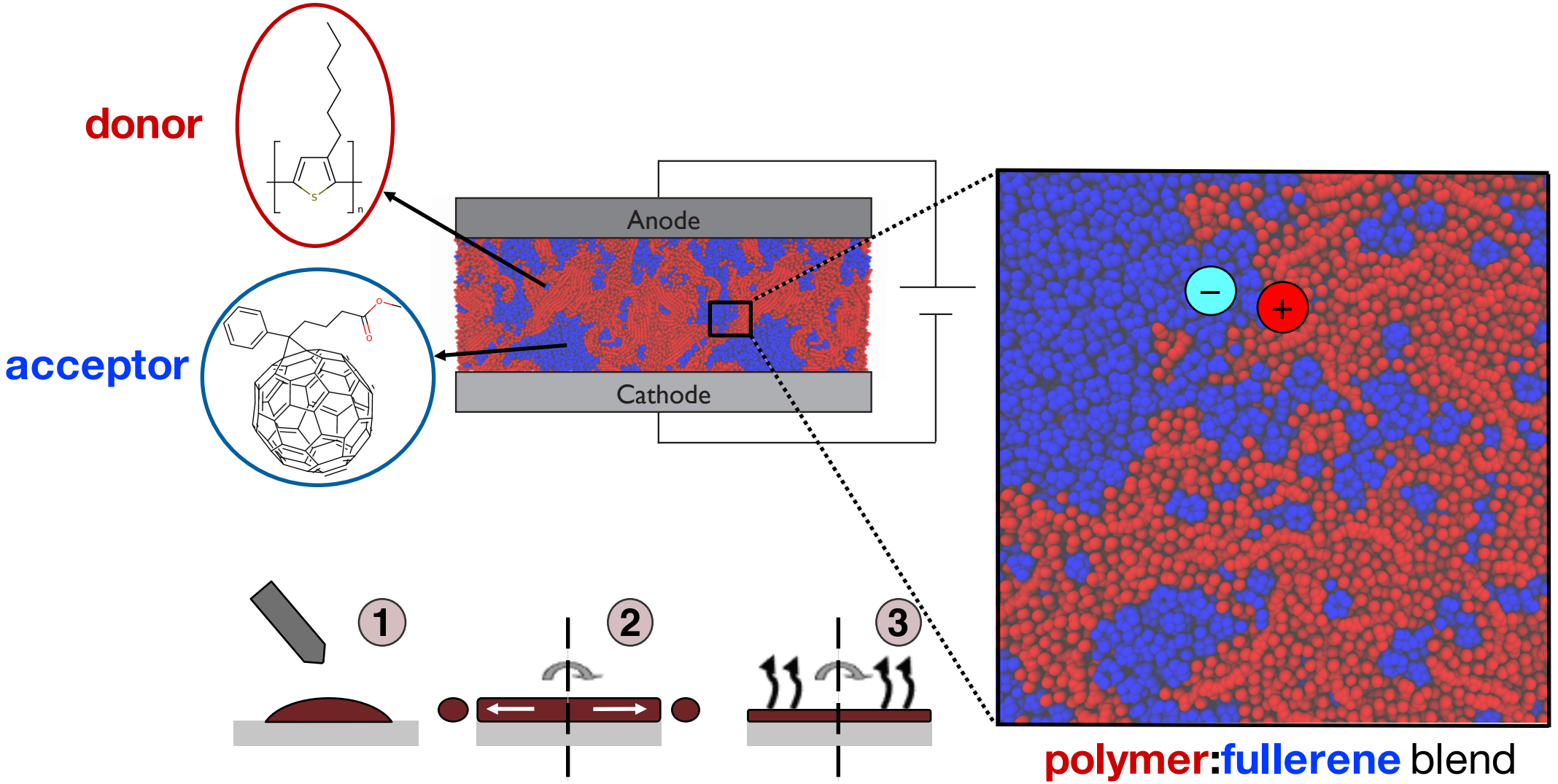
OPV in a nutshell



G. Yu *et al.*, *Science* **1995**, *270*, 1789

C. J. Brabec *et al.*, *Chem. Soc. Rev.* **2011**, *40*, 1185

OPV in a nutshell



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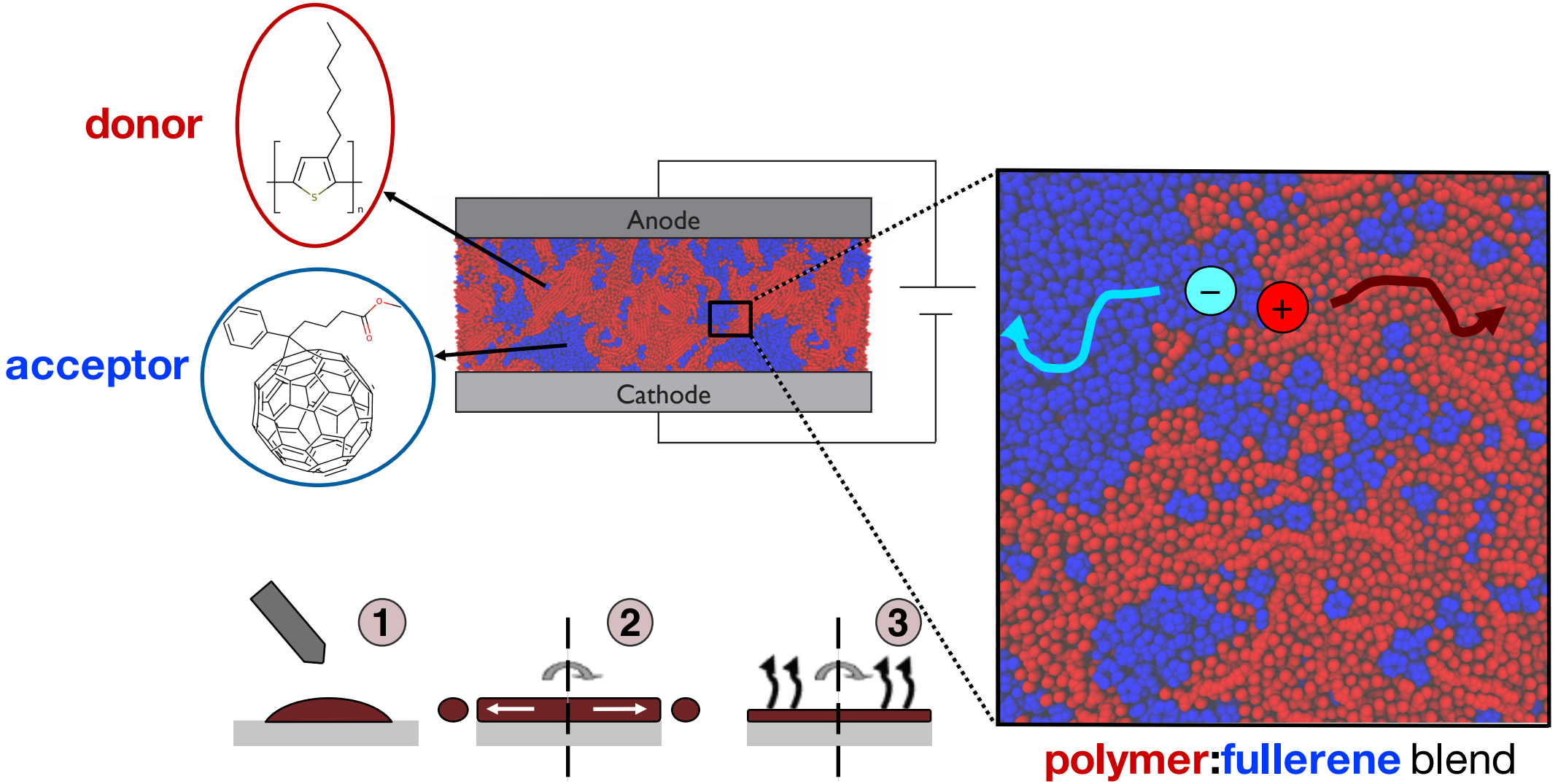
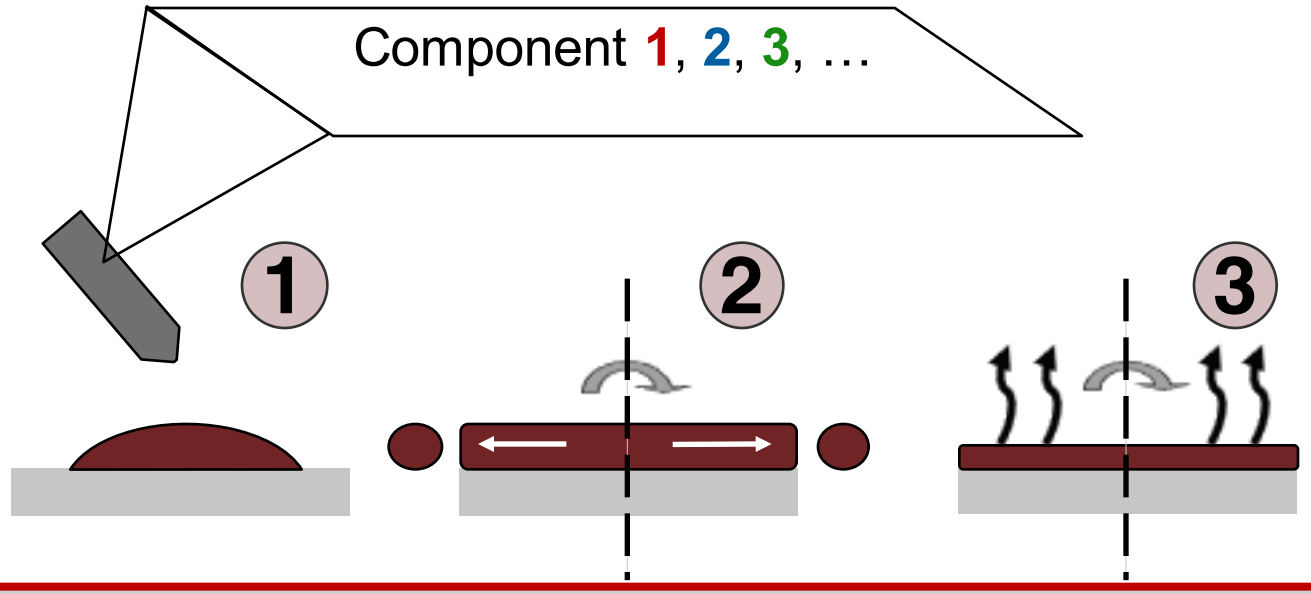
OPV in a nutshell



G. Yu *et al.*, *Science* **1995**, *270*, 1789

C. J. Brabec *et al.*, *Chem. Soc. Rev.* **2011**, *40*, 1185

The morphology



- *Trapped / quenched states*
- *Morphology not easy to resolve*
- *Very sensitive to processing conditions*
- *Cannot predict morphology*

Aims

*Get insights into **factors** determining the morphology from modeling*

- *Phase separation driving force*
- *Effect of molecular structure*
- *Effect of drying rate*
- *Effect of thermal annealing*
- *Effect of solvent*

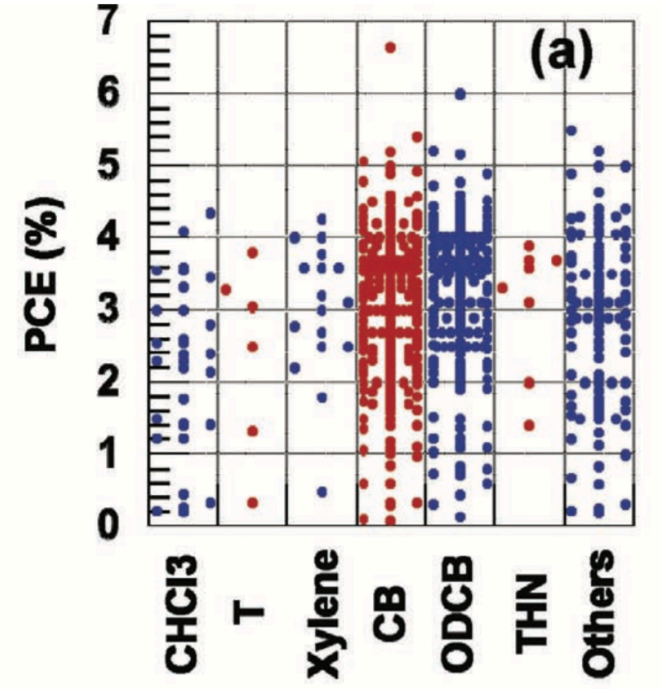
*Get **atom-resolved** structural information*

- *Packing, crystallinity*
- *Domains connectivity*
- *Molecular conformations at the interfaces (can be fed to more expensive calculations)*

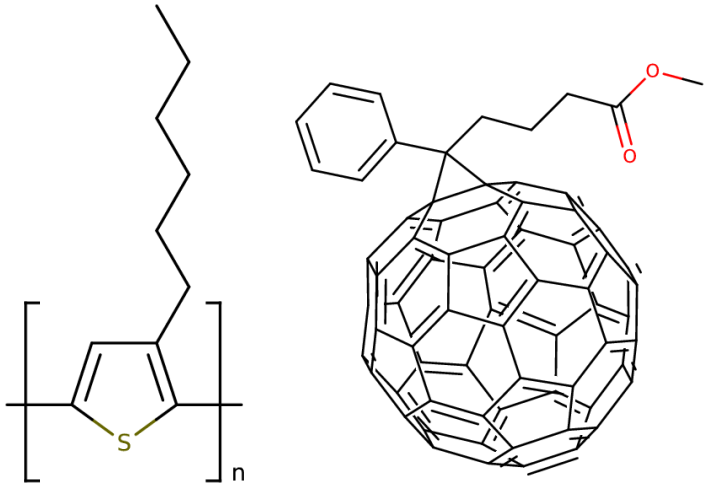
What do we need?

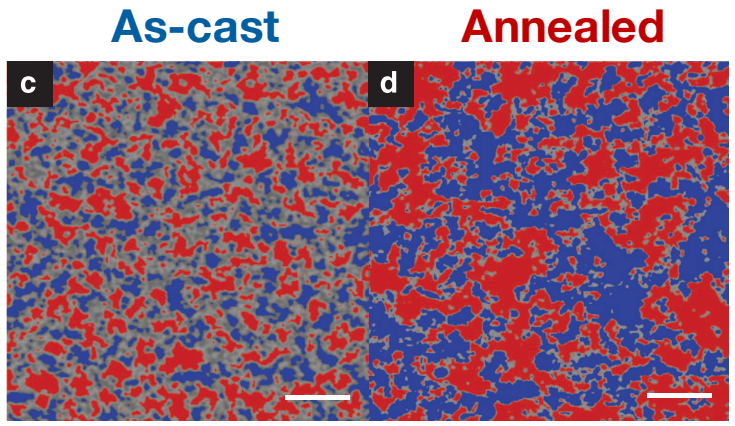
- **Martini models** for the OPV system
- Method to **generate the morphology**
- Ways to **compare to experiments**

P3HT:PCBM blend



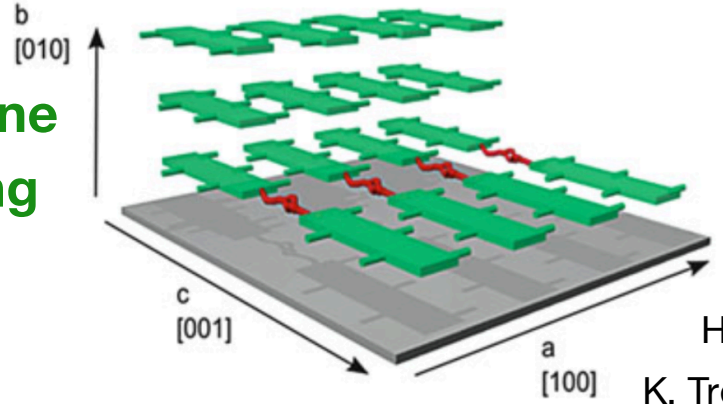
M. T. Dang *et al.*, *Adv. Mater.* **2011**, *23*, 3597

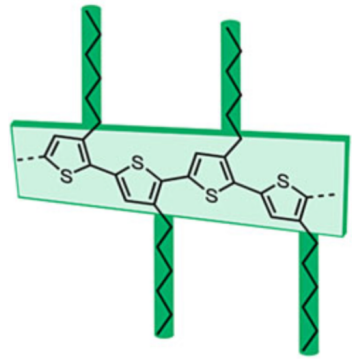




R. C. Masters *et al.*, *Nat. Comm.* **2015**, *6*

Backbone stacking

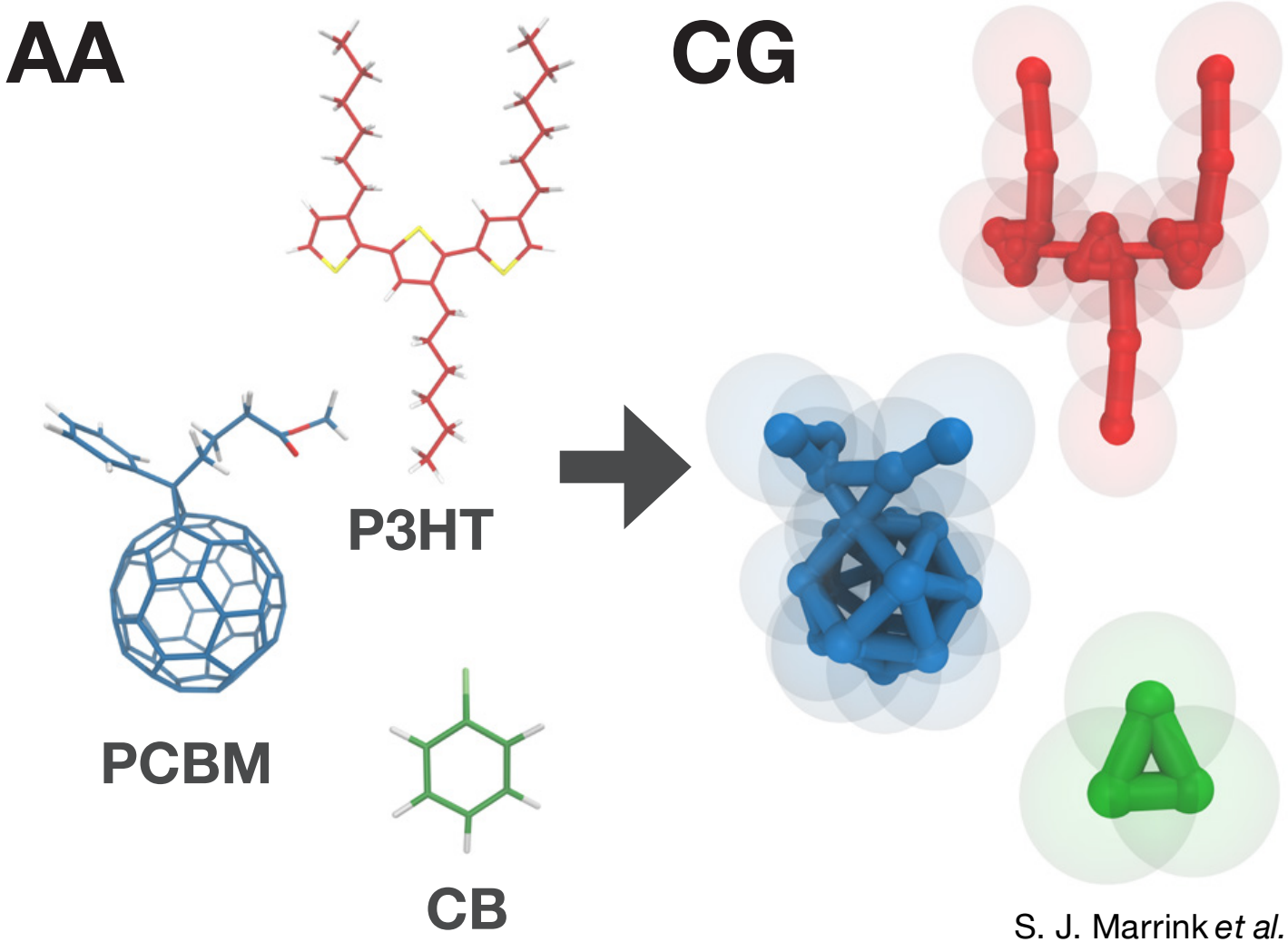




H. Sirringhaus *et al.*, *Nature* **1999**, *401*, 685

K. Tremel *et al.*, *Adv. Polym. Sci.* **2014**, *265*, 39

The Martini way



S. J. Marrink *et al.*, *JPCB* **2007**, *17*, 2311
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

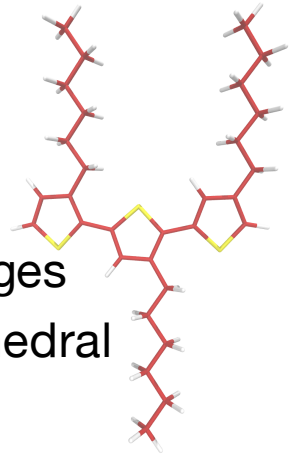
Atomistic force field details

P3HT

GROMOS 53A6[1] (AA)

HF/6-31G* DPA charges

QM-parametrized dihedral

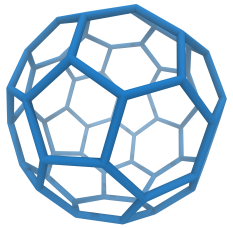


C_{60}

L. Monticelli model[2]

Parametrization based on so state properties

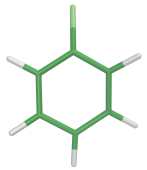
Good partitioning, density



CB

GROMOS 53A6[1] (AA)

HF/6-31G* DPA charges

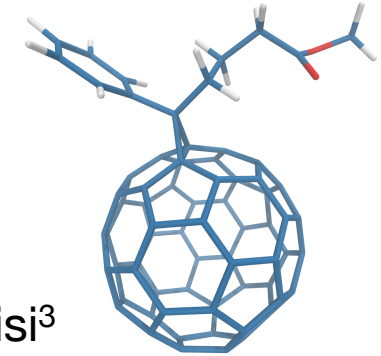


PCBM

GROMOS 53A6[1] (AA)

HF/6-31G* DPA charges

Dihedrals from Cheung&Troisi[3]

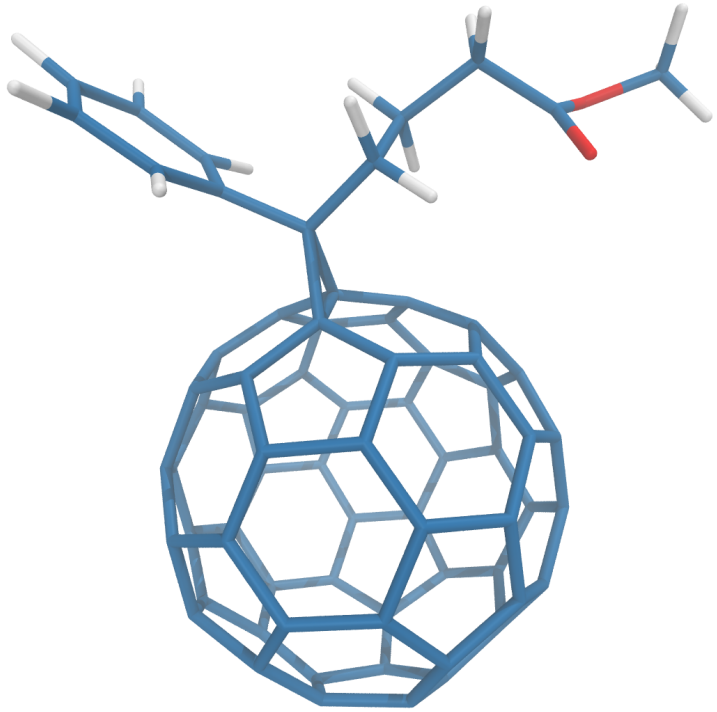


AA force fields for such molecules need checks!

[1]C. Oostenbrink et al., *J. Comput. Chem*. **2004**, *25*, 2656
[2]L. Monticelli, *JCTC* **2012**, *8*, 1370
[3]D. L. Cheung and A. Troisi, *JPCC* **2010**, *114*, 20479
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

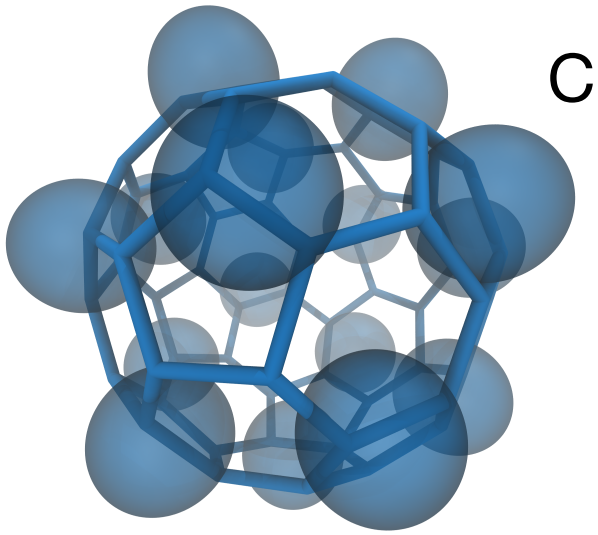
The fullerene model : mapping

- **Mapping**? Any existing Martini model?



PCBM

The fullerene model : mapping & nonbonded



CNP

C_{60}

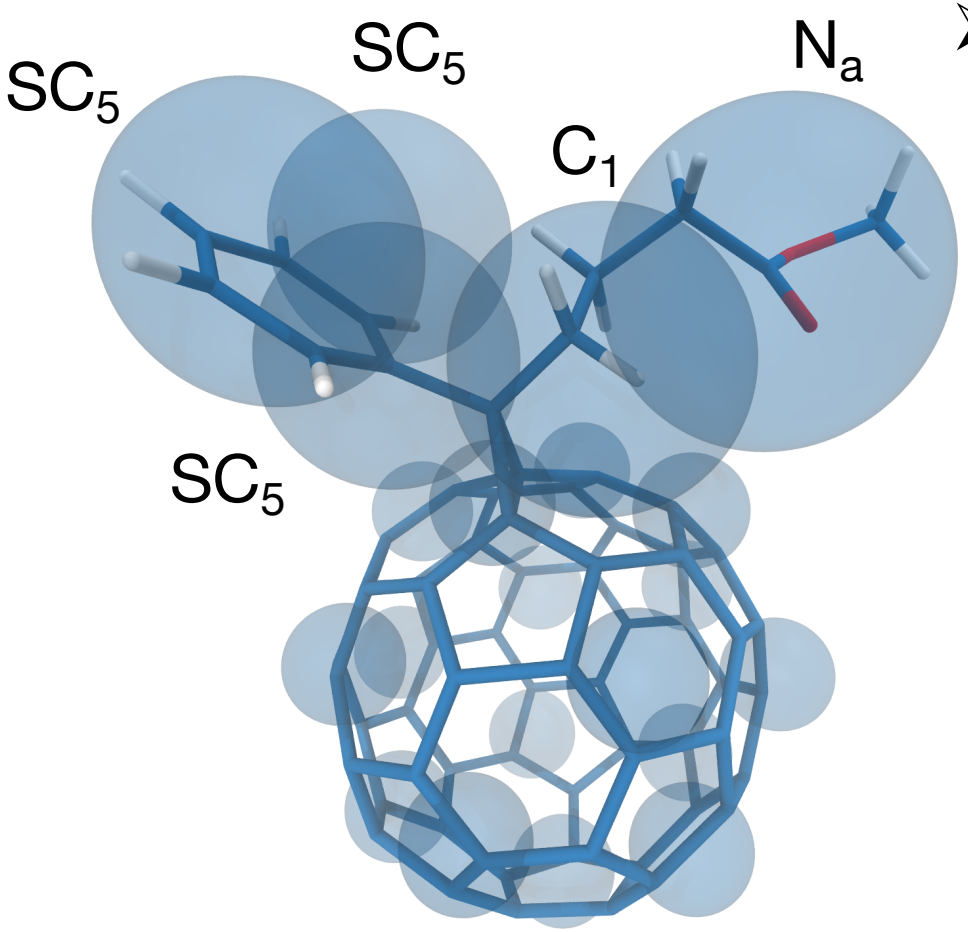
- **Mapping**? Any existing Martini model? **Yes!**
  - **16-beads model by Luca Monticelli**

    Parametrized based on:

    - partitioning (required a special **"CNP" bead**)
    - PMFs of dimerization in water and octane (comparing to the AA model – which was parametrized based on solid-state properties and partition free energies)

L. Monticelli, *JCTC* **2012**, *8*, 1370

The fullerene model : mapping & nonbonded

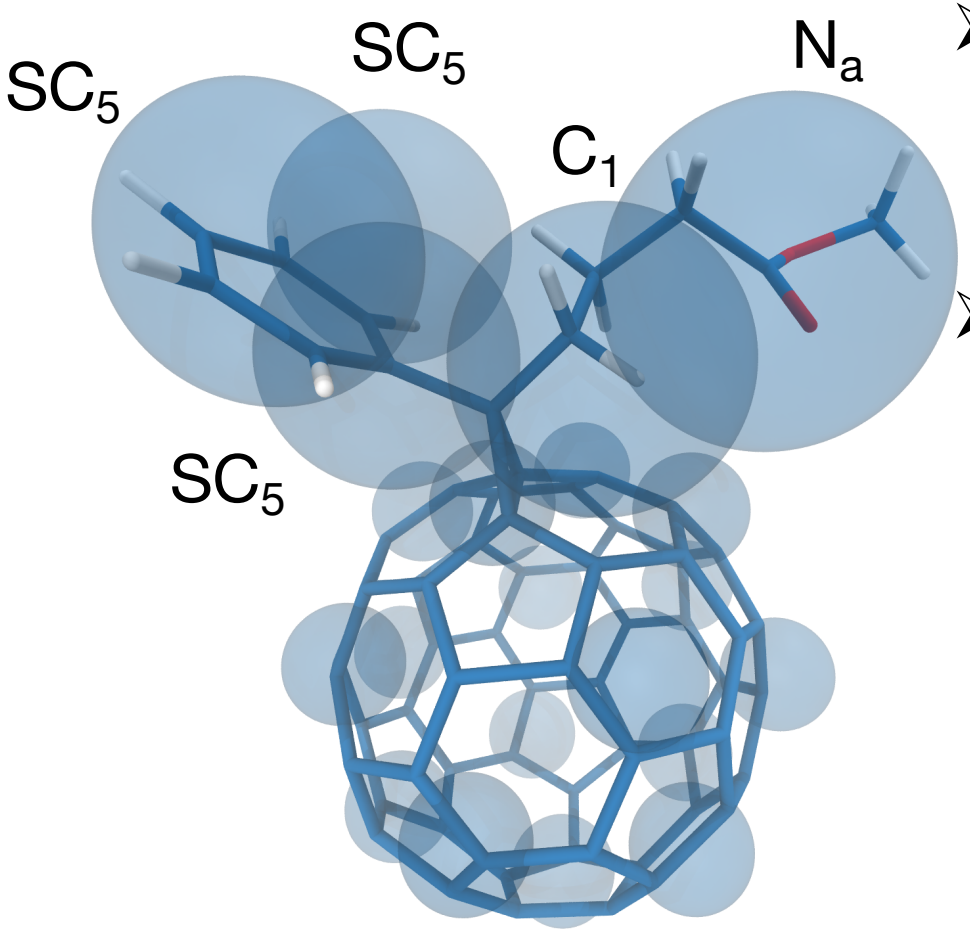


PCBM

- **Mapping**? Any existing Martini model? **Yes!**
  - **16-beads model by Luca Monticelli**
  - Other fragments are standard

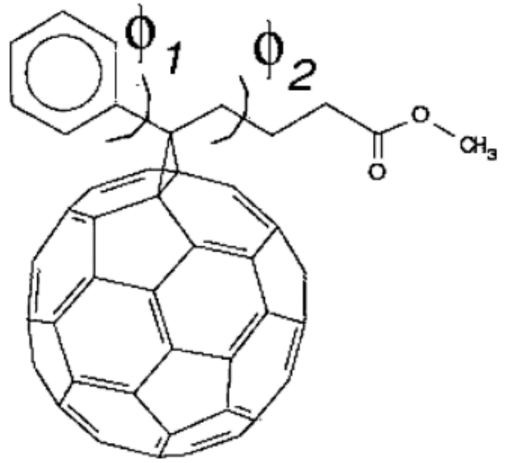
L. Monticelli, *JCTC* **2012**, *8*, 1370
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

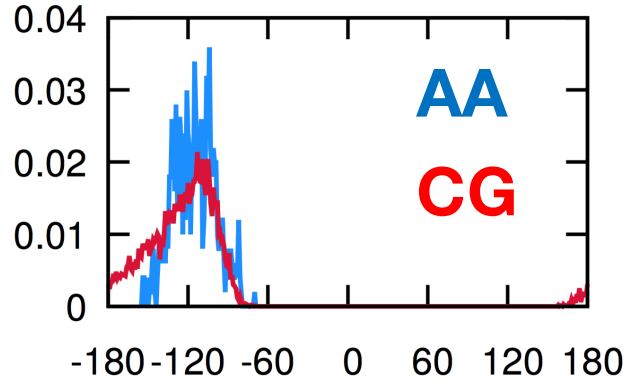
The fullerene model : bonded



PCBM

- **Mapping**? Any existing Martini model? **Yes!**
  - **16-beads model by Luca Monticelli**
  - Other fragments are standard
- Any peculiar **bonded parameters**?
  - Dihedrals from Cheung & Troisi for the AA force field





L. Monticelli, *JCTC* **2012**, *8*, 1370
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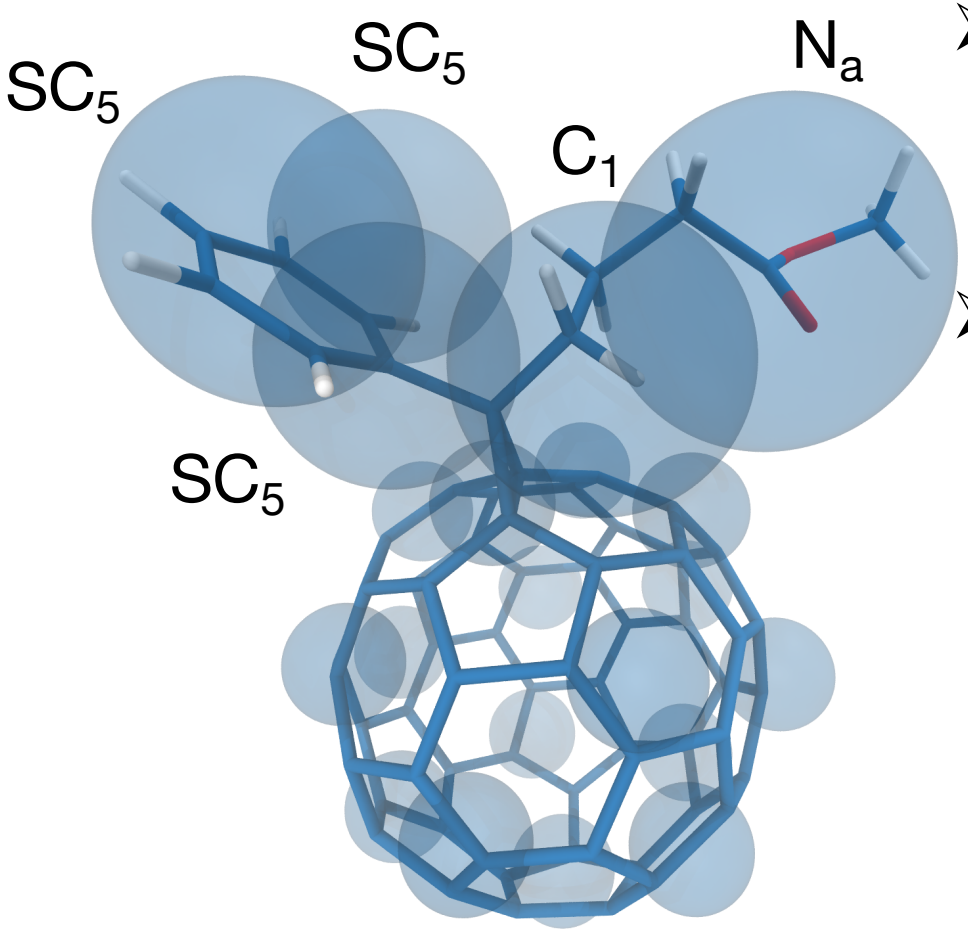
D. L. Cheung and A. Troisi, *JPCC* **2010**, *114*, 20479

The fullerene model : bonded

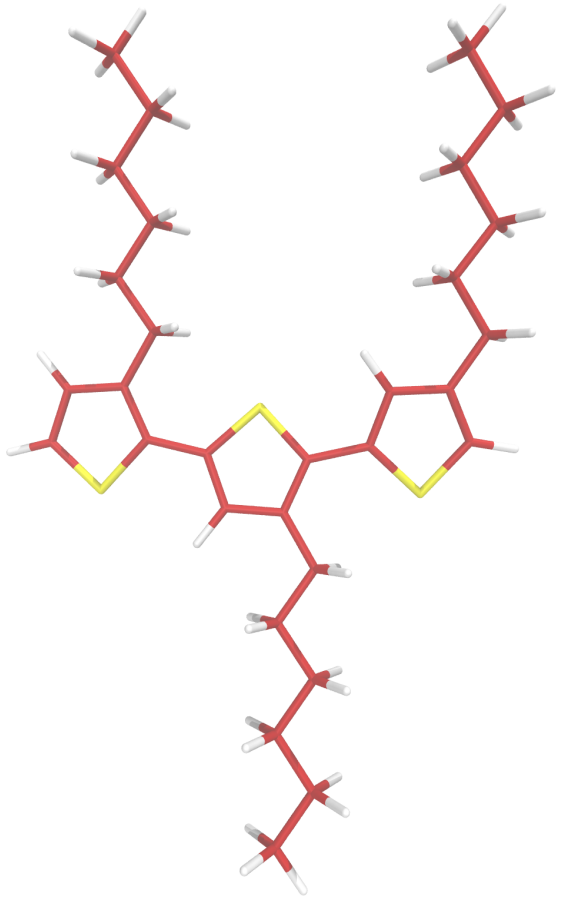


PCBM

- **Mapping**? Any existing Martini model? **Yes!**
  - **16-beads model by Luca Monticelli**
  - Other fragments are standard
- Particular **bonded**?
  - Dihedrals from Cheung & Troisi
  - Dihedrals to prevent side chain rotation around sp^3 carbon

L. Monticelli, *JCTC* **2012**, *8*, 1370
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697
D. L. Cheung and A. Troisi, *JPCC* **2010**, *114*, 20479

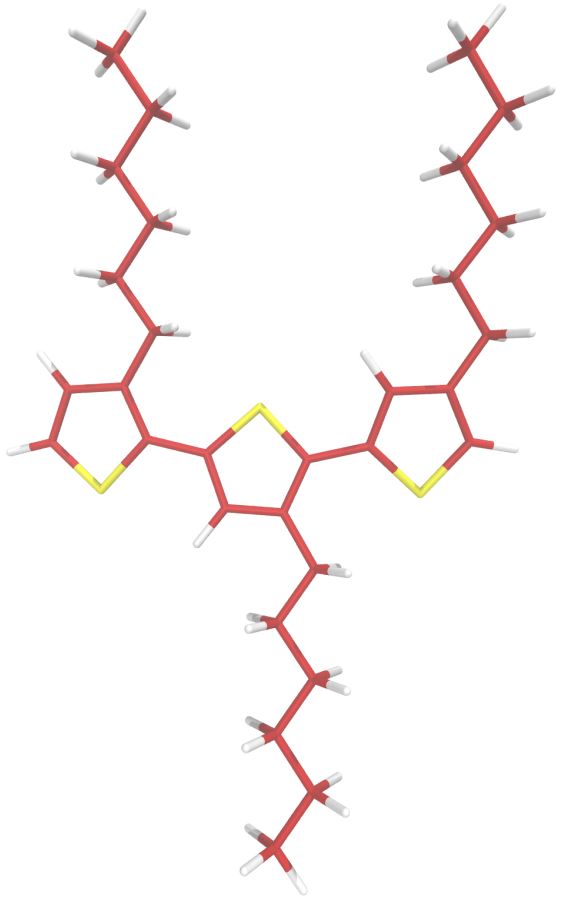
The polymer model : mapping



P3HT
(trimer)

- **Mapping**? Any existing Martini model?

The polymer model : mapping



P3HT
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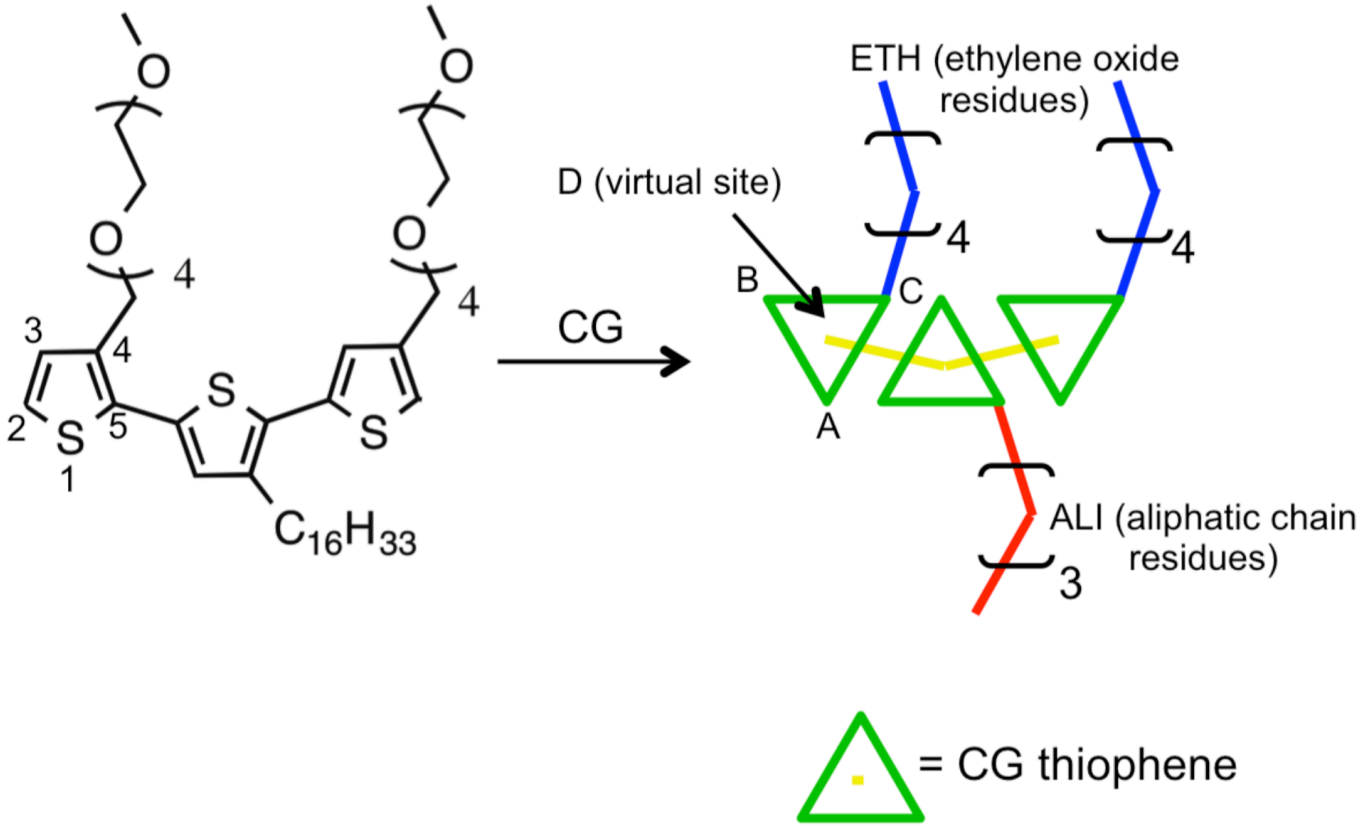
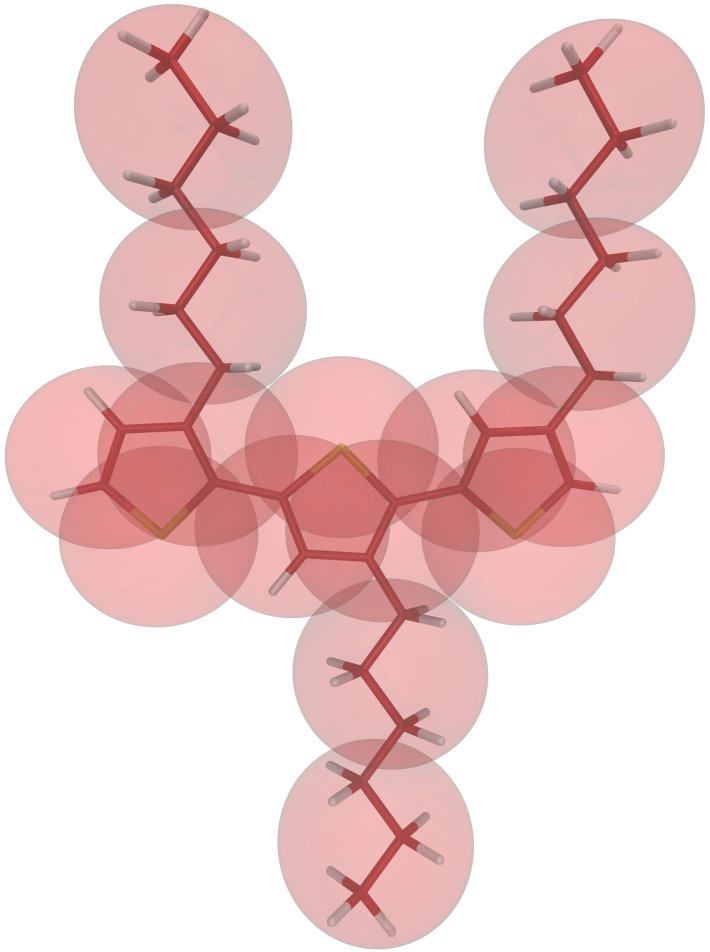


D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**

The polymer model : mapping



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(trimer)

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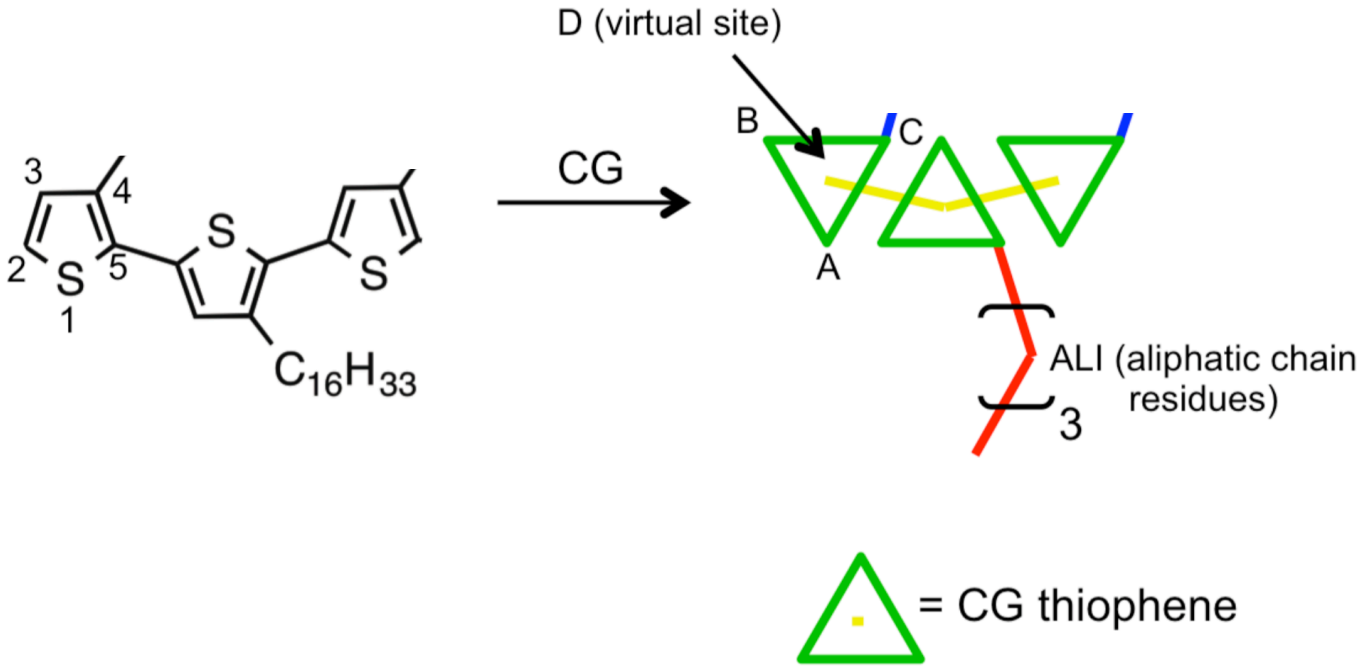
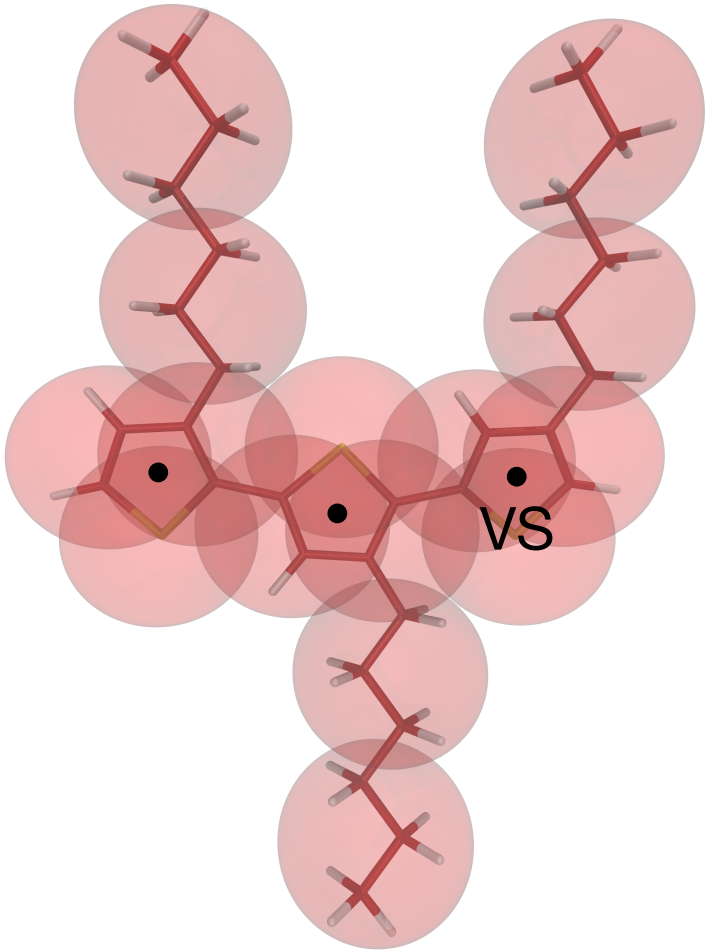


D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

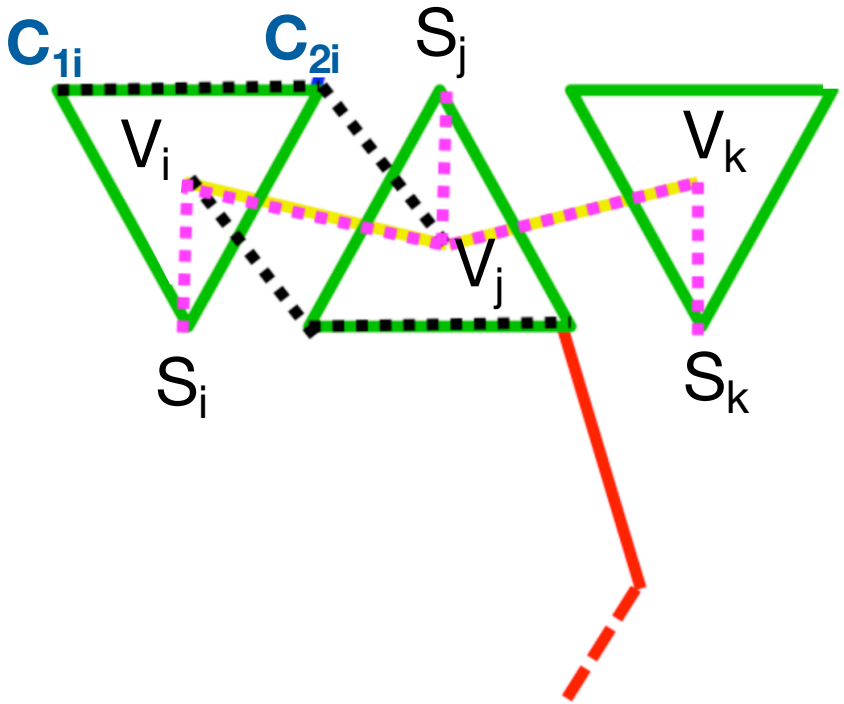
The polymer model : bonded

VS = virtual site



P3HT
(trimer)

- **Mapping**? Any existing Martini model? **Yes!**
- Which **bonded parameters** can we use?
  - **Polythiophene backbone**



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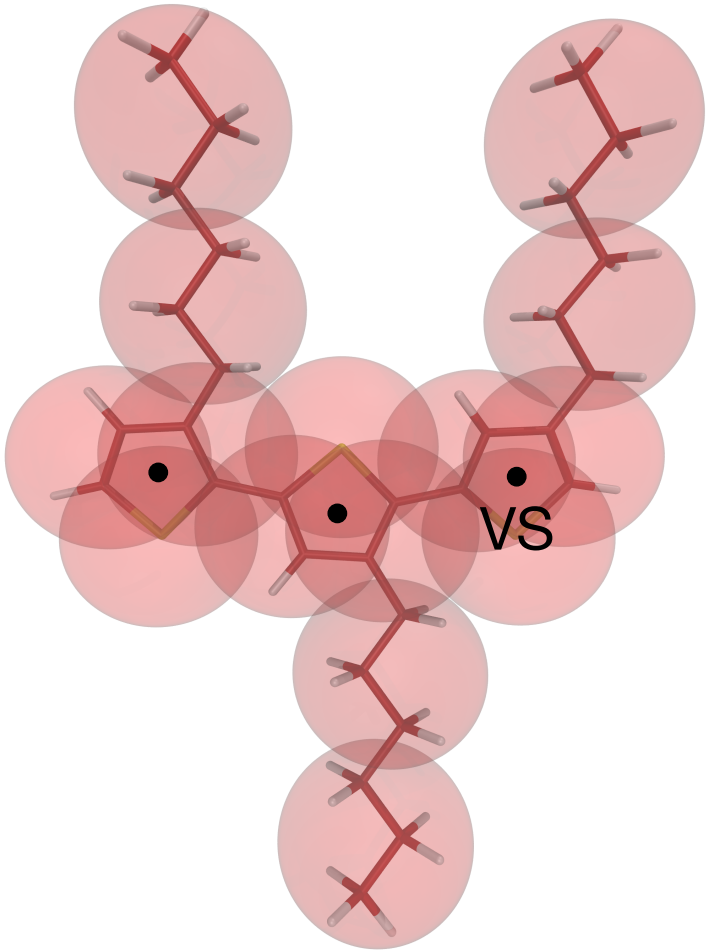

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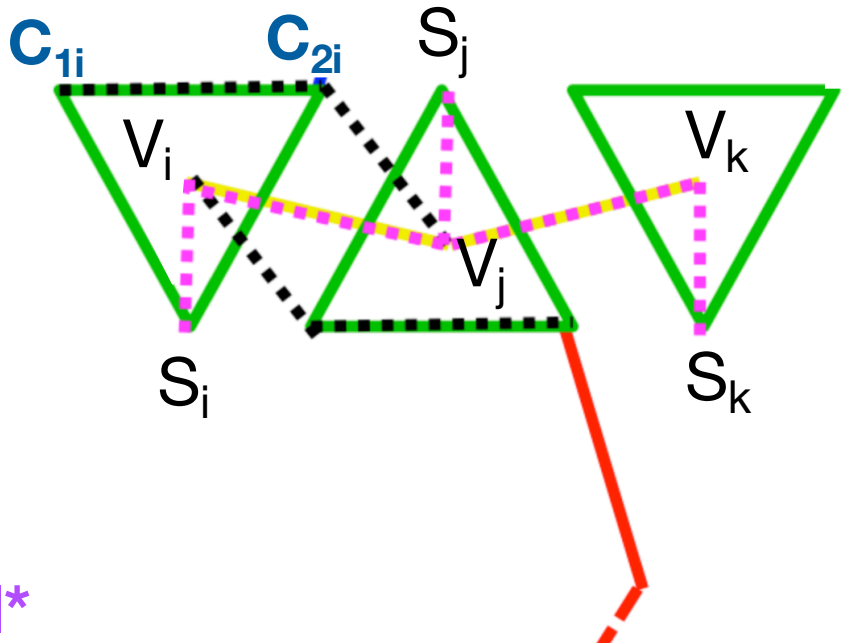
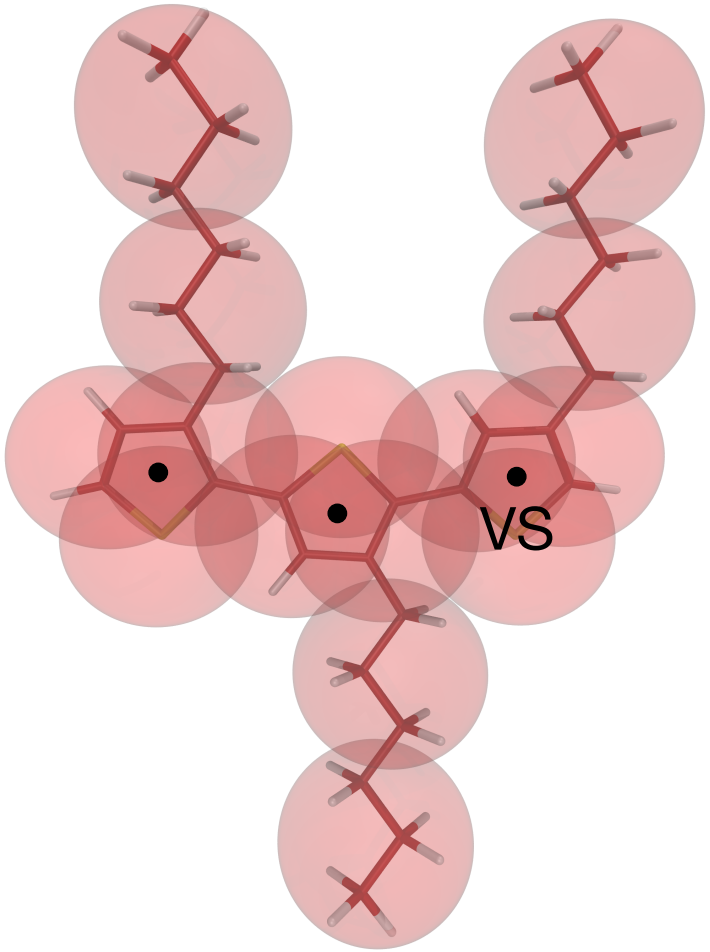


- **VS connection**
- **C-C-VS angles**
- **VS-assisted dihedral***

*M. Bulacu *et al.*, *J. Chem. Theory Comput.* **2013**, 9, 3282
D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

The polymer model : bonded

VS = virtual site



P3HT
(trimer)

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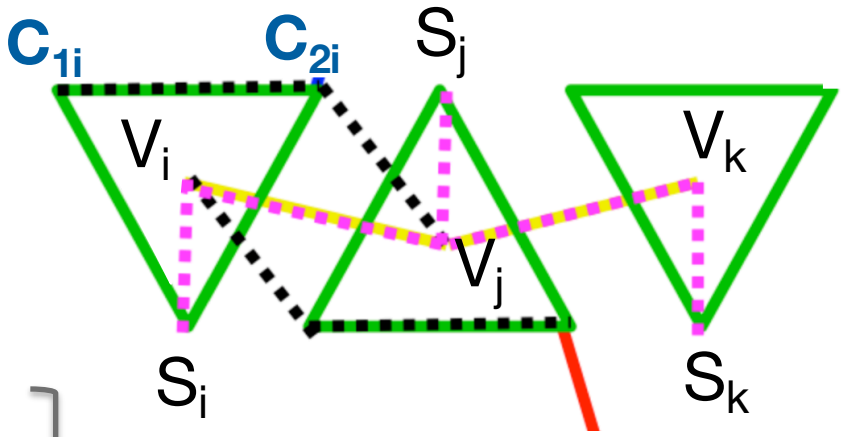
- Which **bonded parameters** can we use?
  - **Polythiophene backbone**



- **VS connection**
- **C-C-VS angles**
- **VS-assisted dihedral***

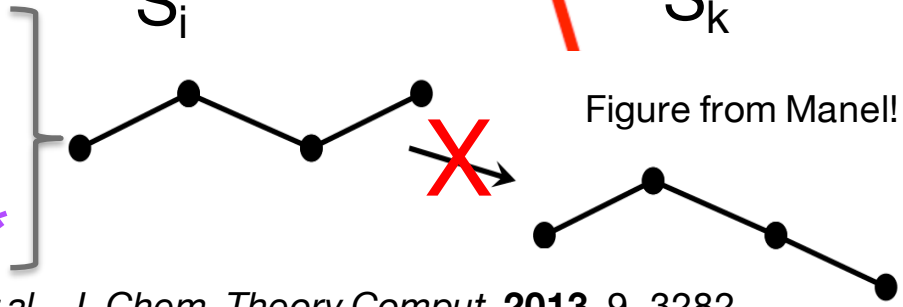


Figure from Manel!

*M. Bulacu *et al.*, *J. Chem. Theory Comput.* **2013**, 9, 3282
D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
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The polymer model : bonded

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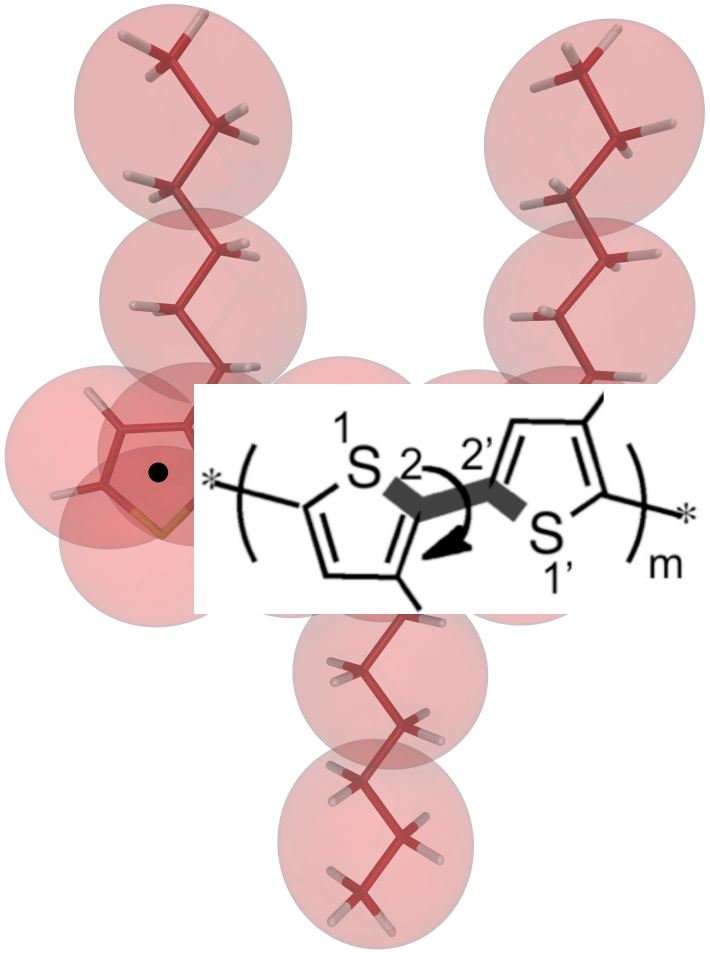
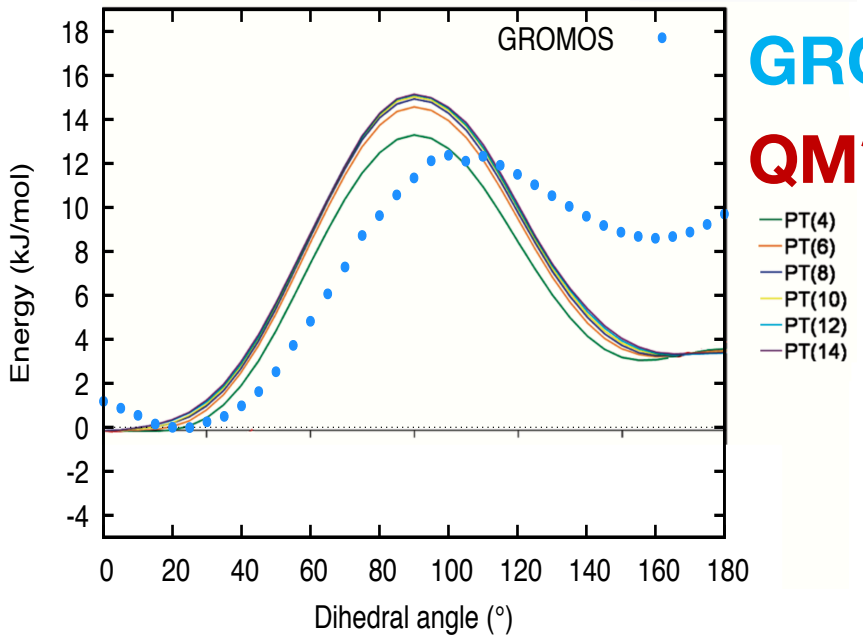


P3HT
(trimer)

➢ **Dihedrals** between π-conjugated fragments



GROMOS 53A6 (ATB)

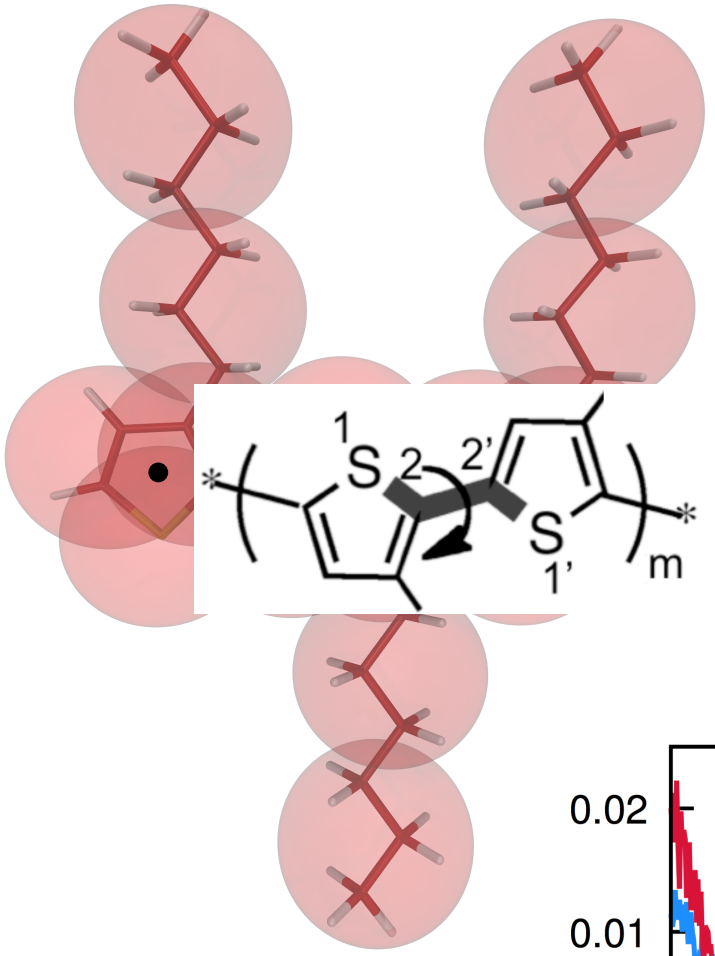
QM**

1. Reference data
2. Compare to standard AA and correct (i.e., fit) if needed

S. B. Darling and M Sternberg, *J. Phys. Chem. B* **2009, *113*, 6215
D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

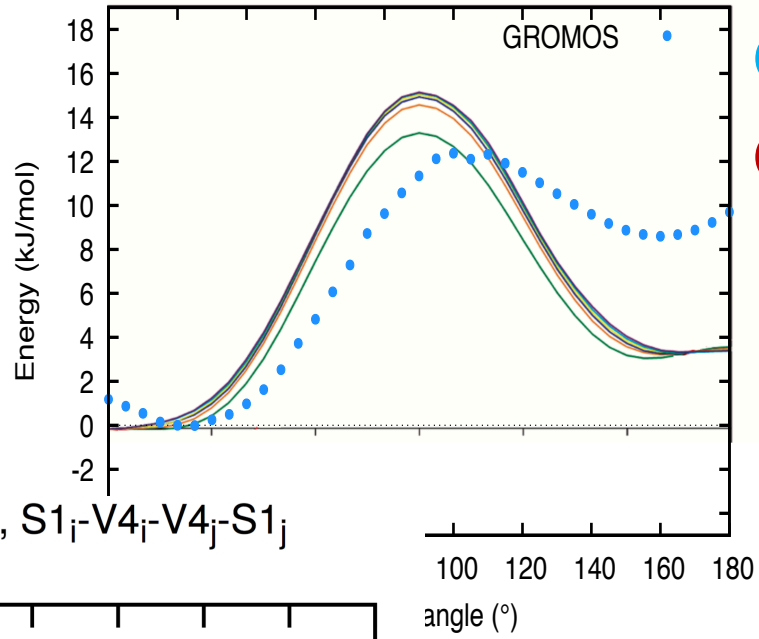
The polymer model : bonded

VS = virtual site

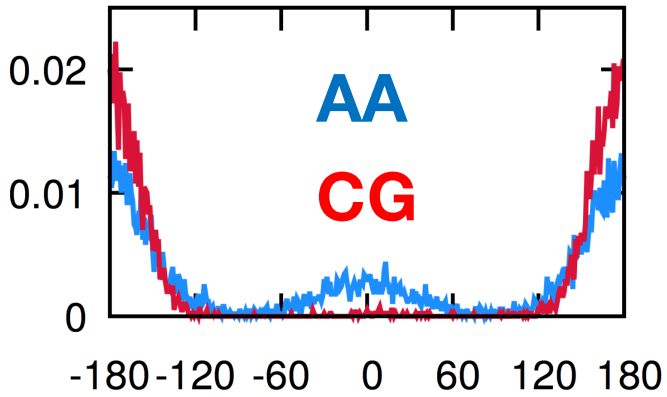


P3HT
(trimer)

➢ **Dihedrals** between π-conjugated fragments



Φ_1, $S1_i$-$V4_i$-$V4_j$-$S1_j$



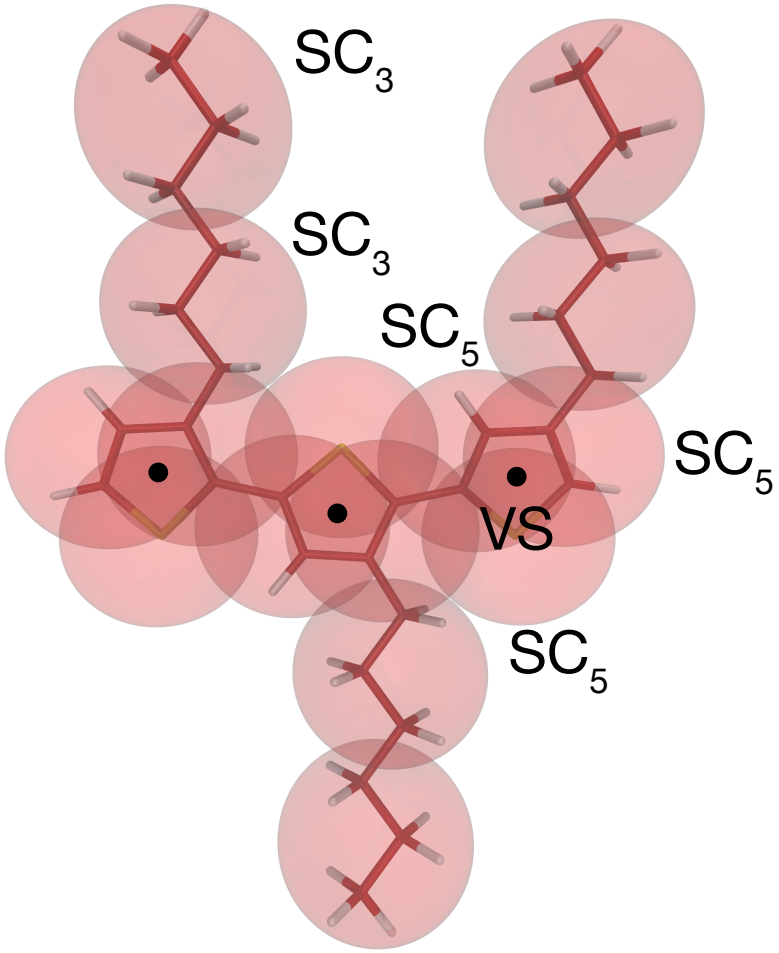
GROMOS 53A6 (ATB)

QM**

1. Reference data
2. Compare to standard AA and correct (i.e., fit) if needed
3. Implement the same (or re-tune) a bit in the CG model (depends also on the mapping)

arling and M Sternberg, *J. Phys. Chem. B* **2009**, *113*, 6215
D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

The polymer model : nonbonded



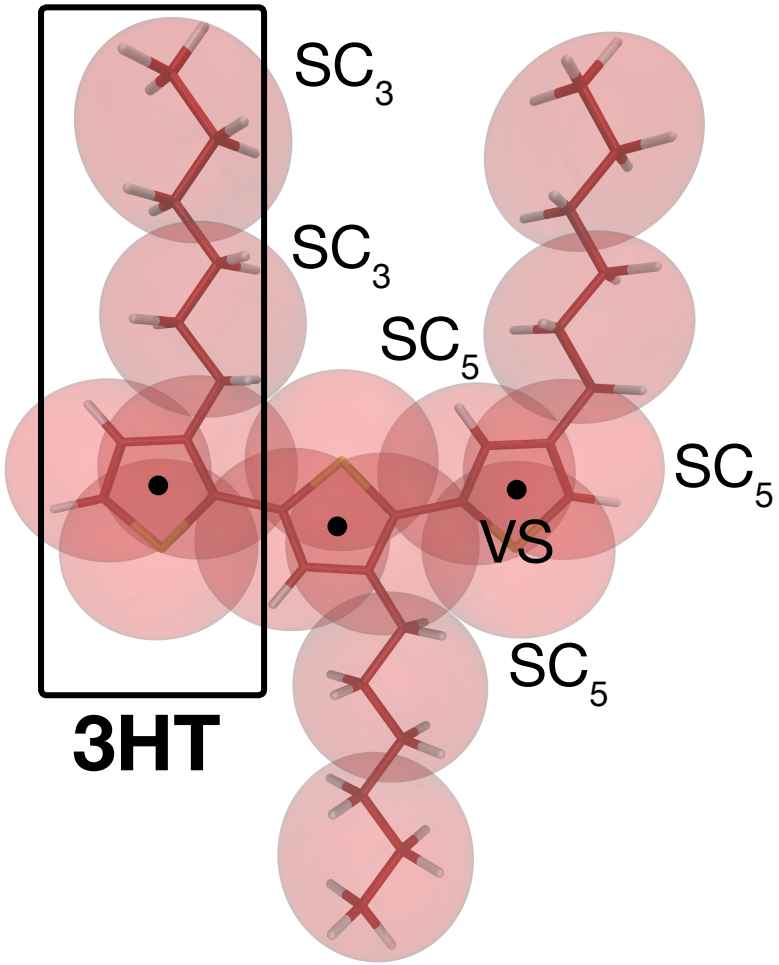
P3HT
(trimer)

- **Mapping**? Any existing Martini model? **Yes!**
- Which **bonded parameters** can we use? Some.
- **Nonbonded parameters**?

1. Pick bead flavours based on the Martini bible*
2. Validate your choices:
   - Tune nonbonded interactions of different fragments of the polymer (TI, PMF – see next)
   - Experimental targets for a polymer (radius of gyration / hydrodynamic radius, persistence length, …)

*S. J. Marrink *et al.*, *JPCB* **2007**, *17*, 2311

The polymer model : nonbonded

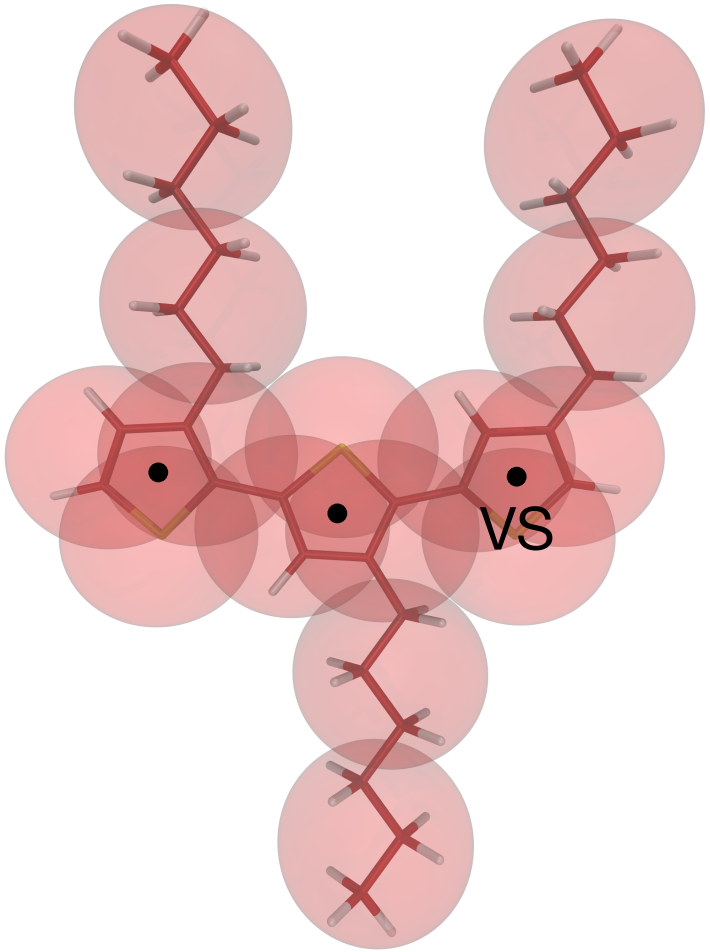


- **Mapping**? Any existing Martini model? **Yes!**
- Which **bonded parameters** can we use? Some.
- **Nonbonded parameters**?

1. Pick bead flavours based on the Martini bible*
2. Validate your choices:
   - Tune nonbonded interactions of different fragments of the polymer (TI, PMF – see next)
   - Experimental targets for a polymer (radius of gyration / hydrodynamic radius, persistence length, …)

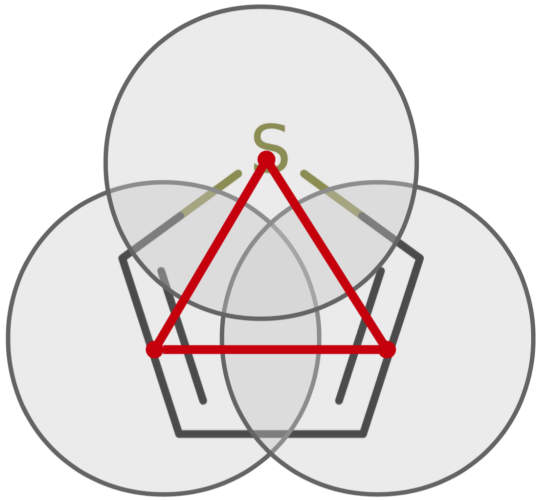
*S. J. Marrink *et al.*, *JPCB* **2007**, *17*, 2311

The polymer model : nonbonded



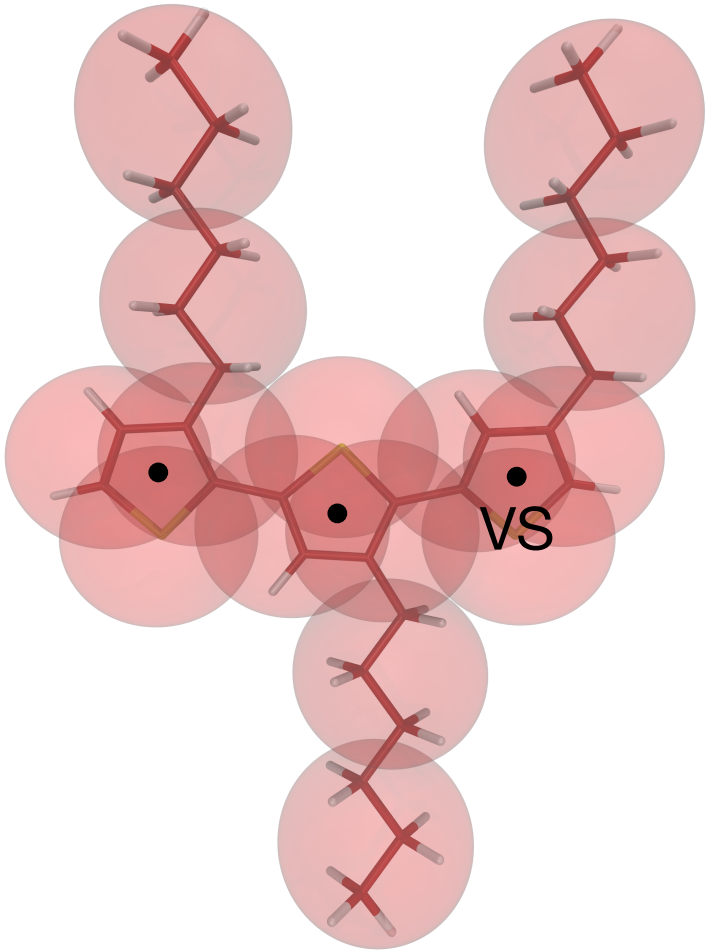
P3HT
(trimer)

- The available* **thiophene** model used *tweaked* interactions to fix the stickiness of the model



*D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

The polymer model : nonbonded



P3HT
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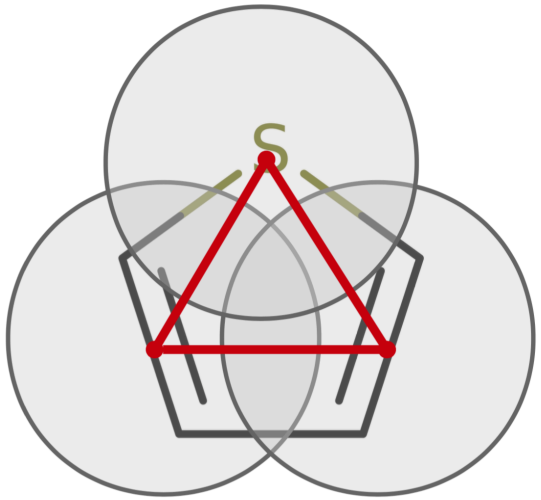
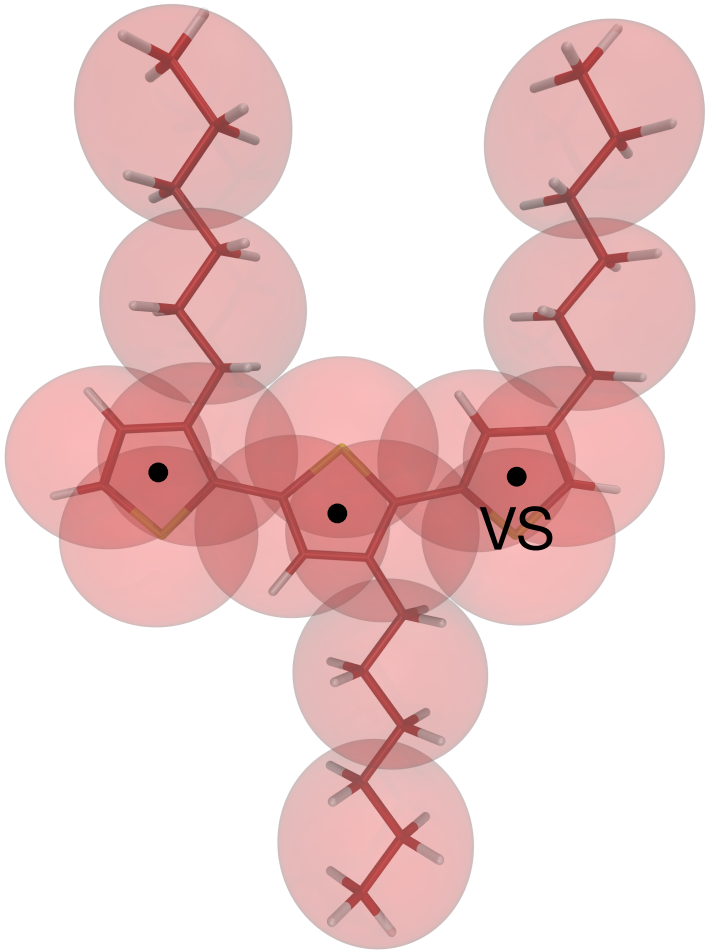


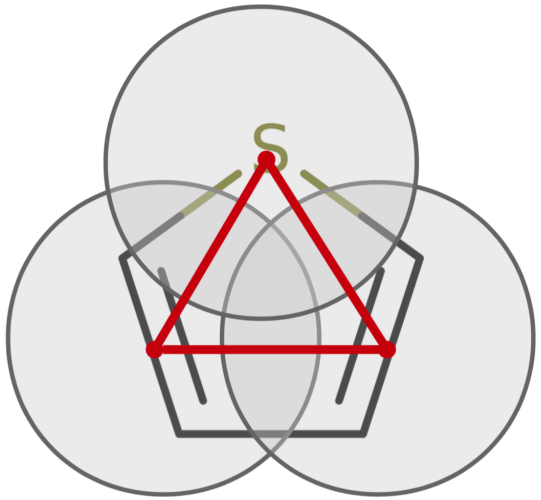
*D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

The polymer model : nonbonded



P3HT
(trimer)

- The **thiophene** model



AA bond distance ≈ 0.20 nm

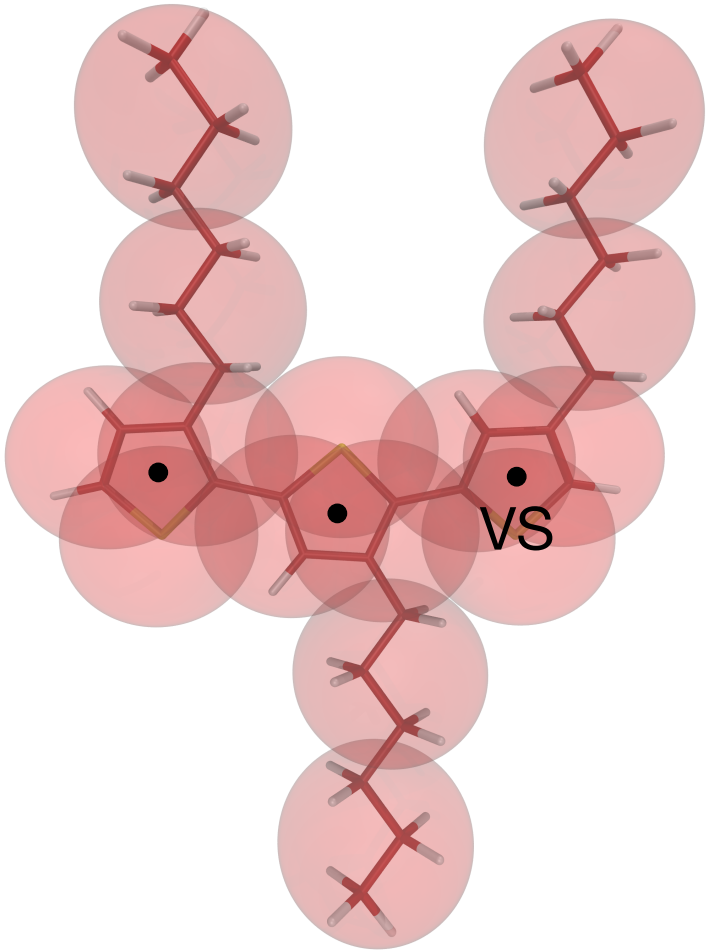
~~**CG bond distance = 0.20 nm**~~

CG bond distance = 0.24 nm

Liquid, good density, good partitioning (see next), good dimerization

D. Janeliunas, Ph. D. Dissertation, TU Delft **2014**
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

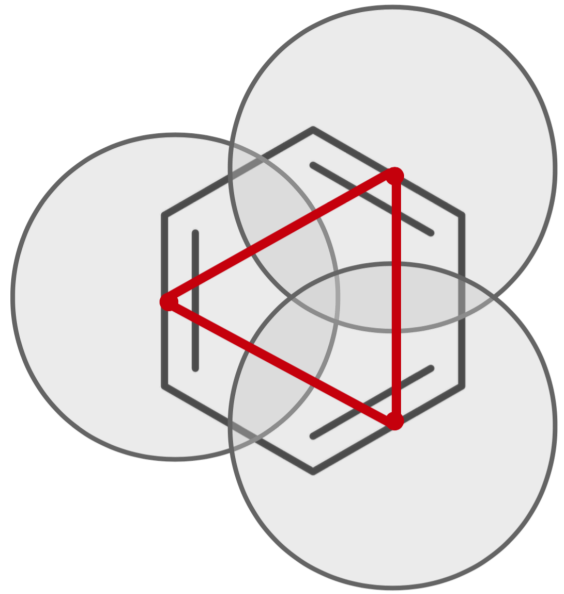
The polymer model : nonbonded



P3HT
(trimer)

➢ The **thiophene** model

benzene



balance between a good density and keeping benzene liquid

AA bond distance ≈ 0.21-0.22 nm

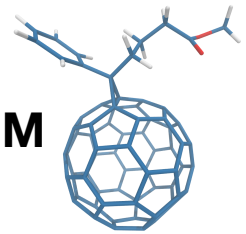
CG bond distance* = 0.27 nm

*S. J. Marrink *et al.*, *JPCB* **2007**, *17*, 2311
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

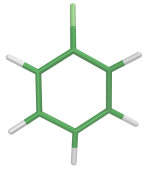
Validation I : densities

3HT

PCBM



CB



	exp.	CG	AA
3HT	0.94	0.95	1.02
PCBM	∼1.50	1.37	1.55
CB	1.10	0.90	1.08

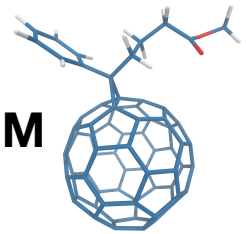
solid (slow dynamics!)

R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

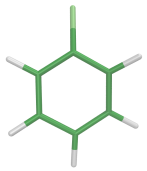
Validation II : free energies of transfer

3HT

PCBM



CB



		$\Delta G_{HD \rightarrow W}$			$\Delta G_{HD \rightarrow BENZ}$		
	CG model	**exp**	**CG**	**AA**	**exp**	**CG**	**AA**
thiophene	SC5-SC5-SC5	**10**	12	13	**-**		
hexane	SC3-SC3	**26**	25	25	**-**		
benzene	SC5-SC5-SC5	**12**	11	13	**–3**	0	–3
CB	SC4-SC4-SC5	**16**	18	18	**–2**	1	–3
C_{60} *	16 x CNP	**97**	75	92	**–9**	–10	-

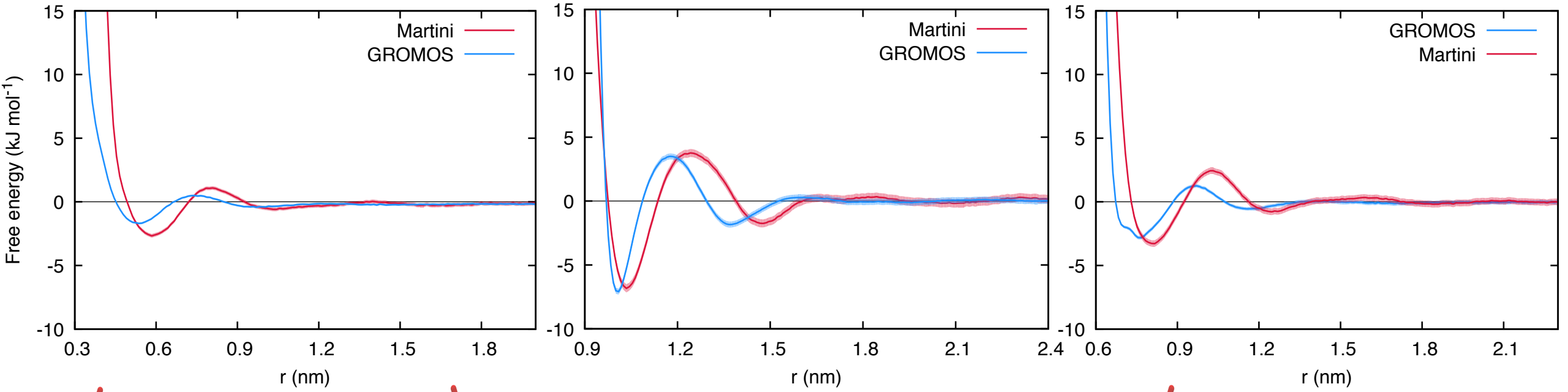
* Data from L. Monticelli, *JCTC* **2012**, *8*, 1370 (**octane** instead of hexadecane).

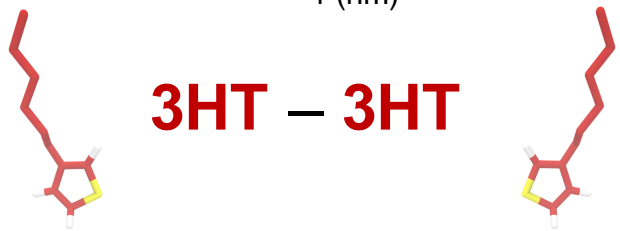
Validation III : PMF of dimerization in CB

Umbrella Sampling:

150 ns (each AA window)

500 ns (each CG window)





3HT – 3HT

PCBM – PCBM

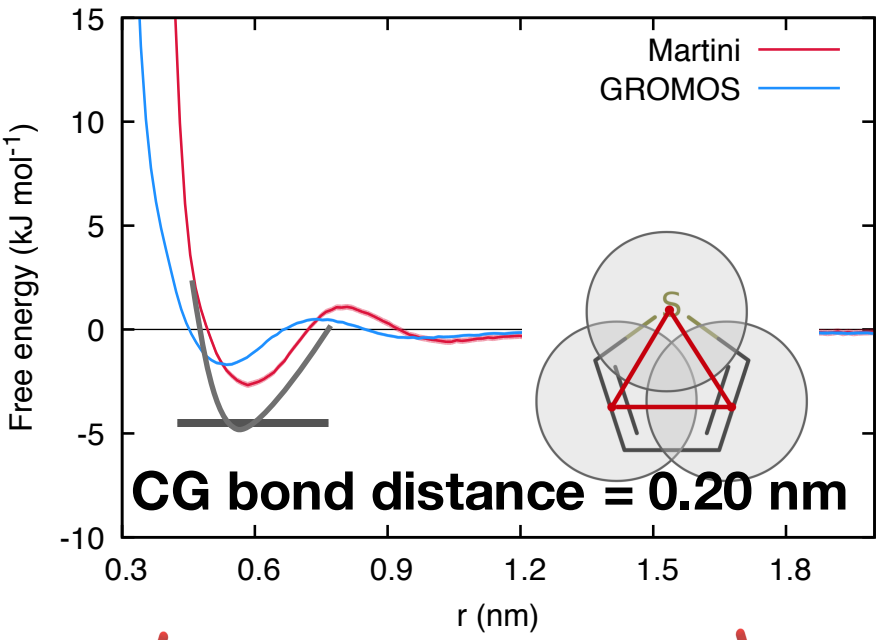
3HT – PCBM

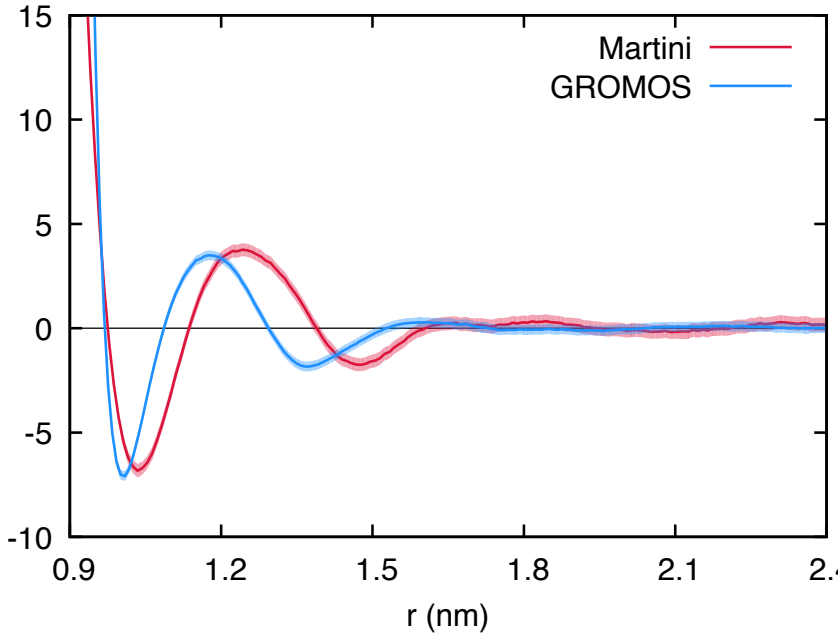
Validation III : PMF of dimerization in CB

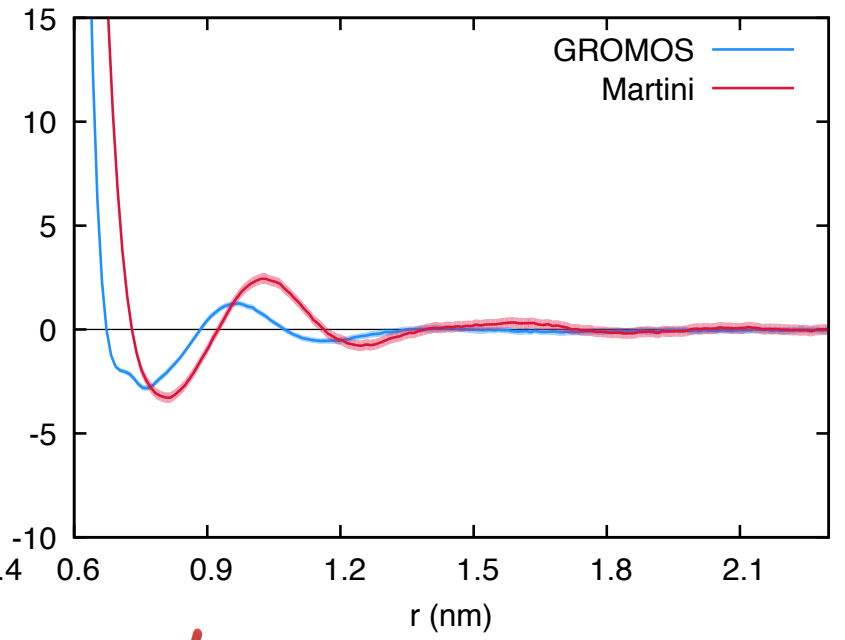
Umbrella Sampling:

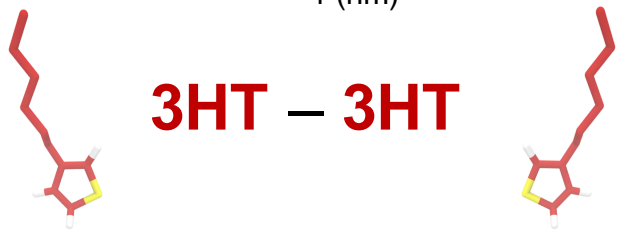
150 ns (each AA window)

500 ns (each CG window)



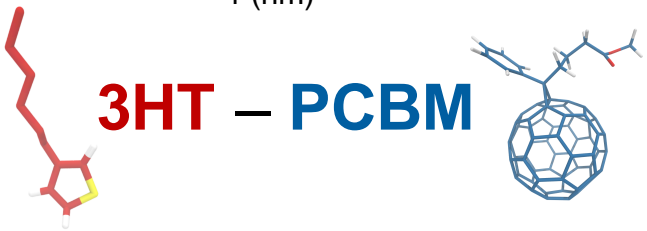






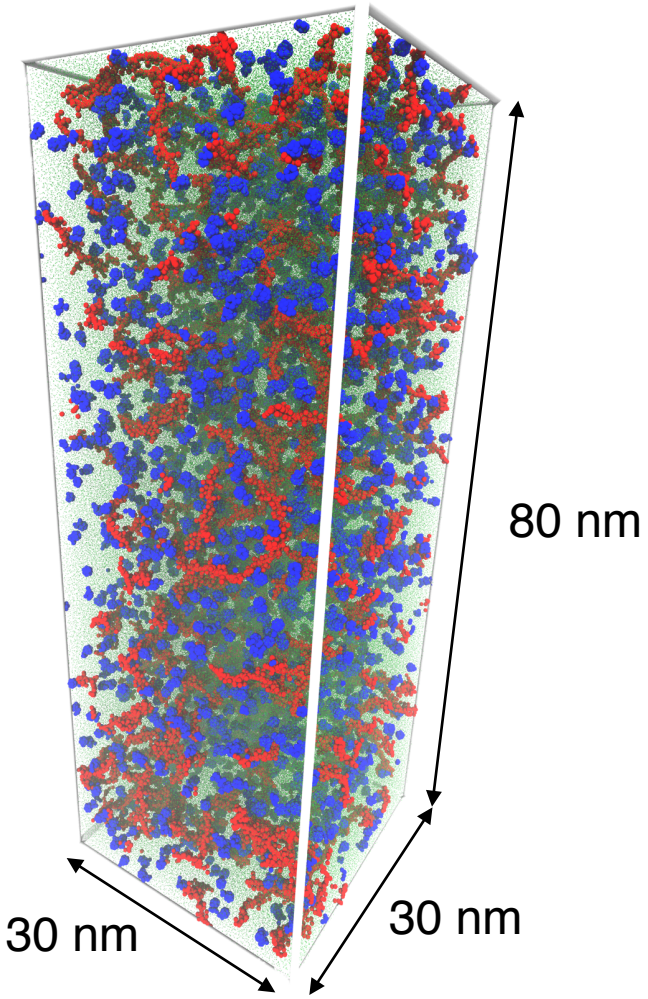
3HT – 3HT

PCBM – PCBM



3HT – PCBM

Solvent evaporation simulations*



P3HT(48-mer) : PCBM : CB

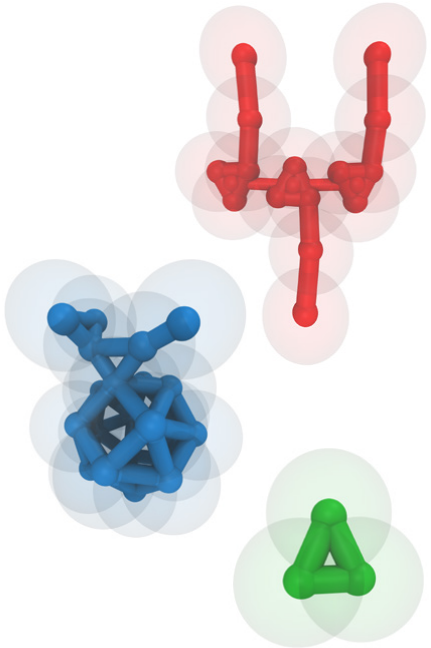
(> 1 million CG particles)

classical **MD**

3D pbc

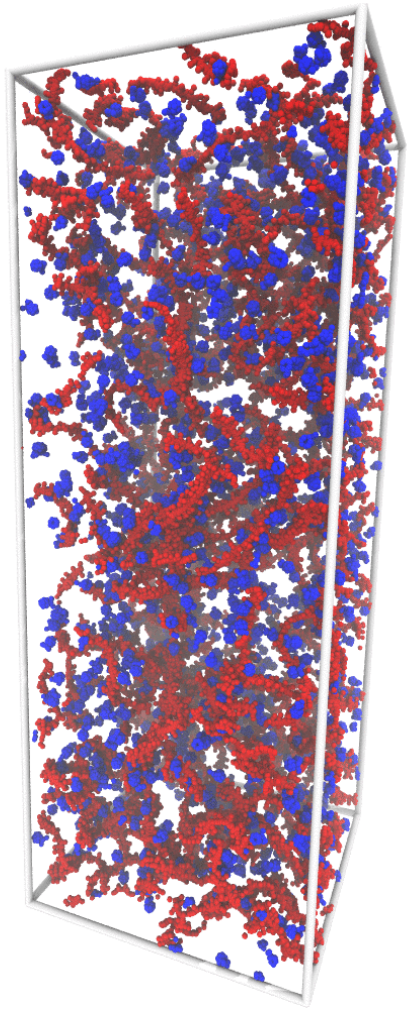
~2% of the **solvent is removed** randomly from the box every 15 ns

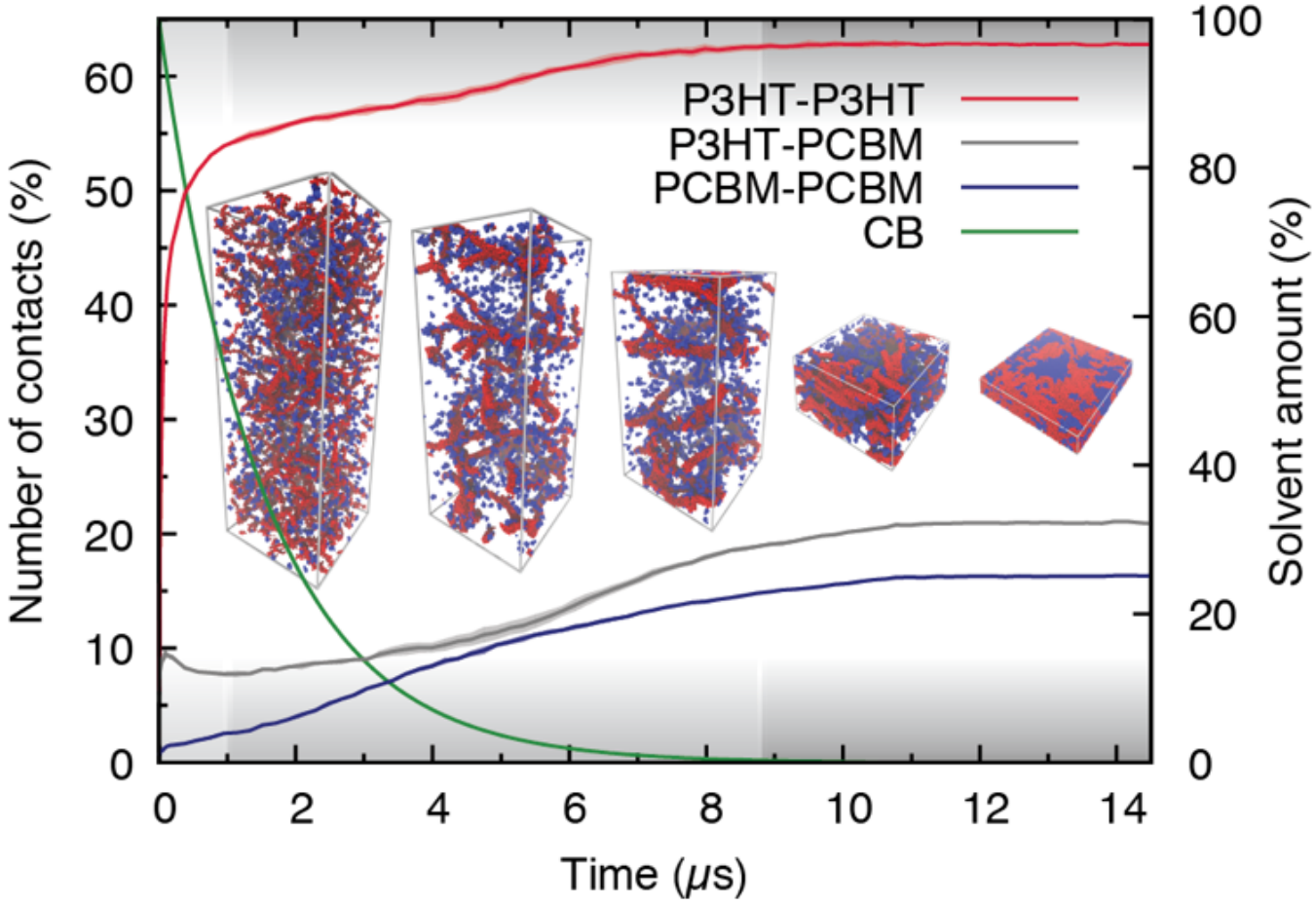
pressure coupling only **along z**



*CK Lee and CW Pao, *JPCC* ***2014***, *118*, 1124

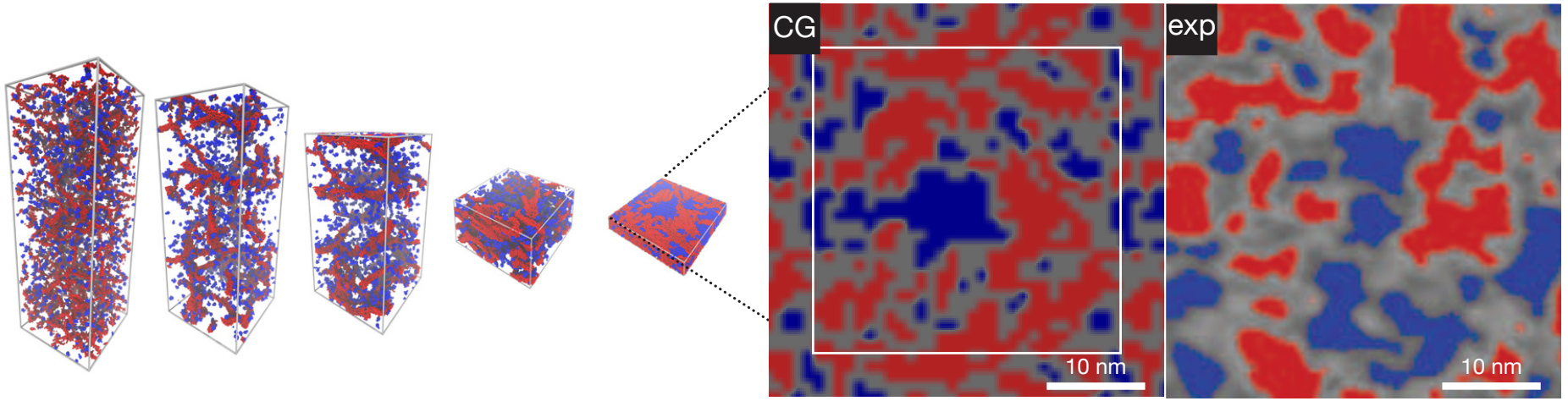
Morphology evolution during solvent evaporation





R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

Morphology evolution during solvent evaporation



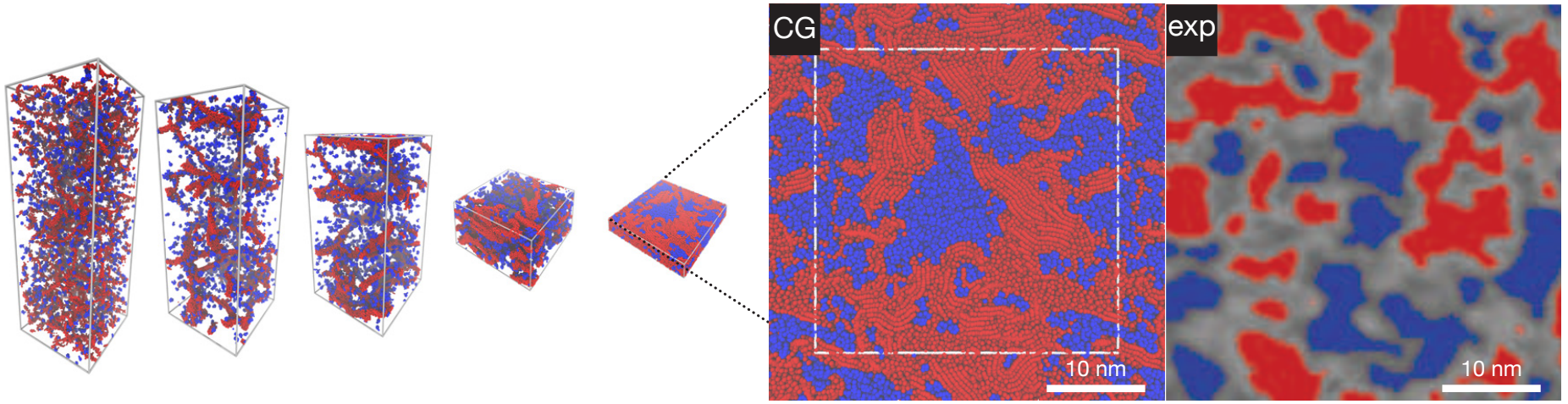
CG "blurred" **EF-SEM image**

RC Masters *et al.*,
Nat. Commun. ***2015***

Qualitative agreement with literature experimental data.

R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

Morphology evolution during solvent evaporation



CG-particle resolved **EF-SEM image**

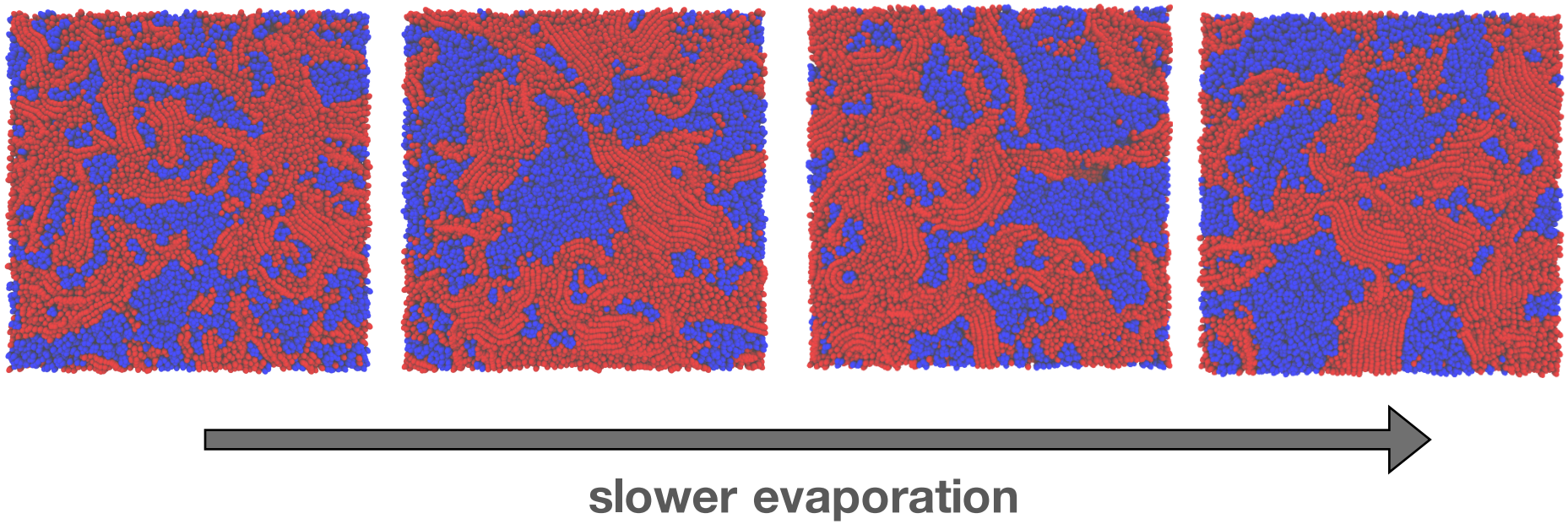
RC Masters *et al.*, *Nat. Commun.* ***2015***

Script to perform evaporation simulations available at http://cgmartini.nl/

Qualitative agreement with literature experimental data.

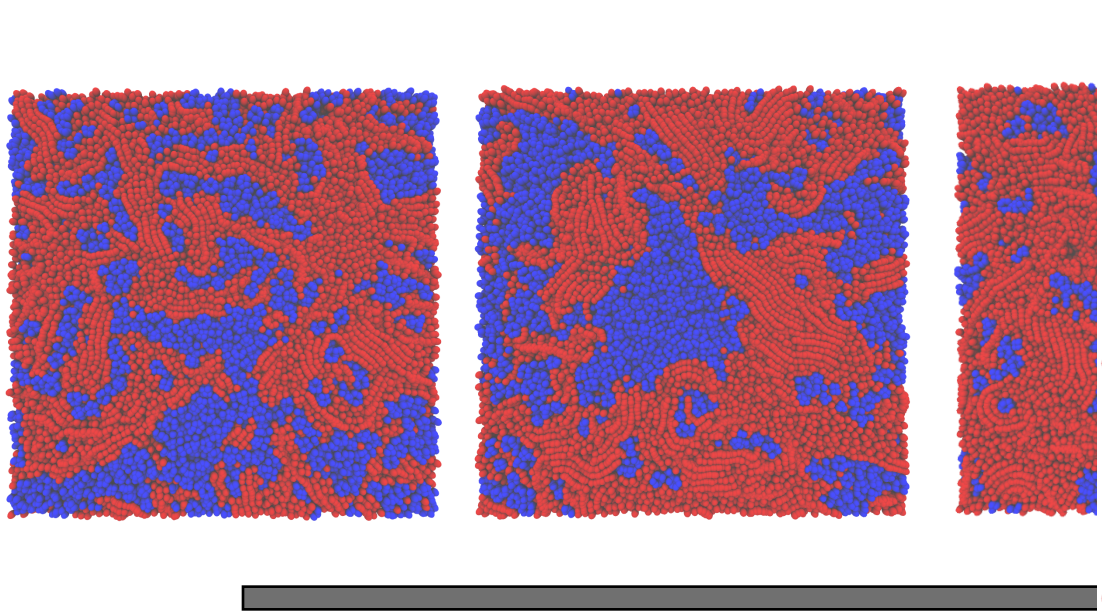
R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

Effect of drying rate

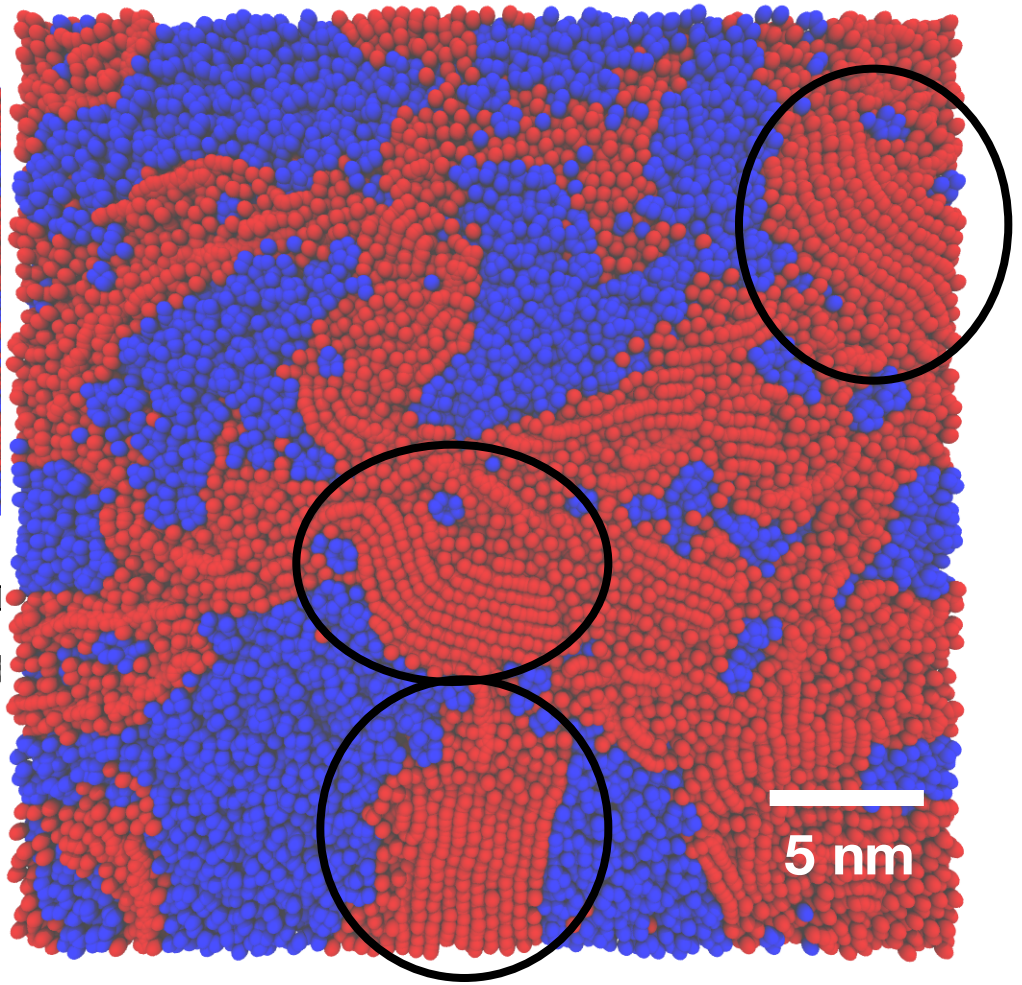


Slower drying increases phase separation as it gives P3HT more time to self-organize.

Effect of drying rate



slower evapora



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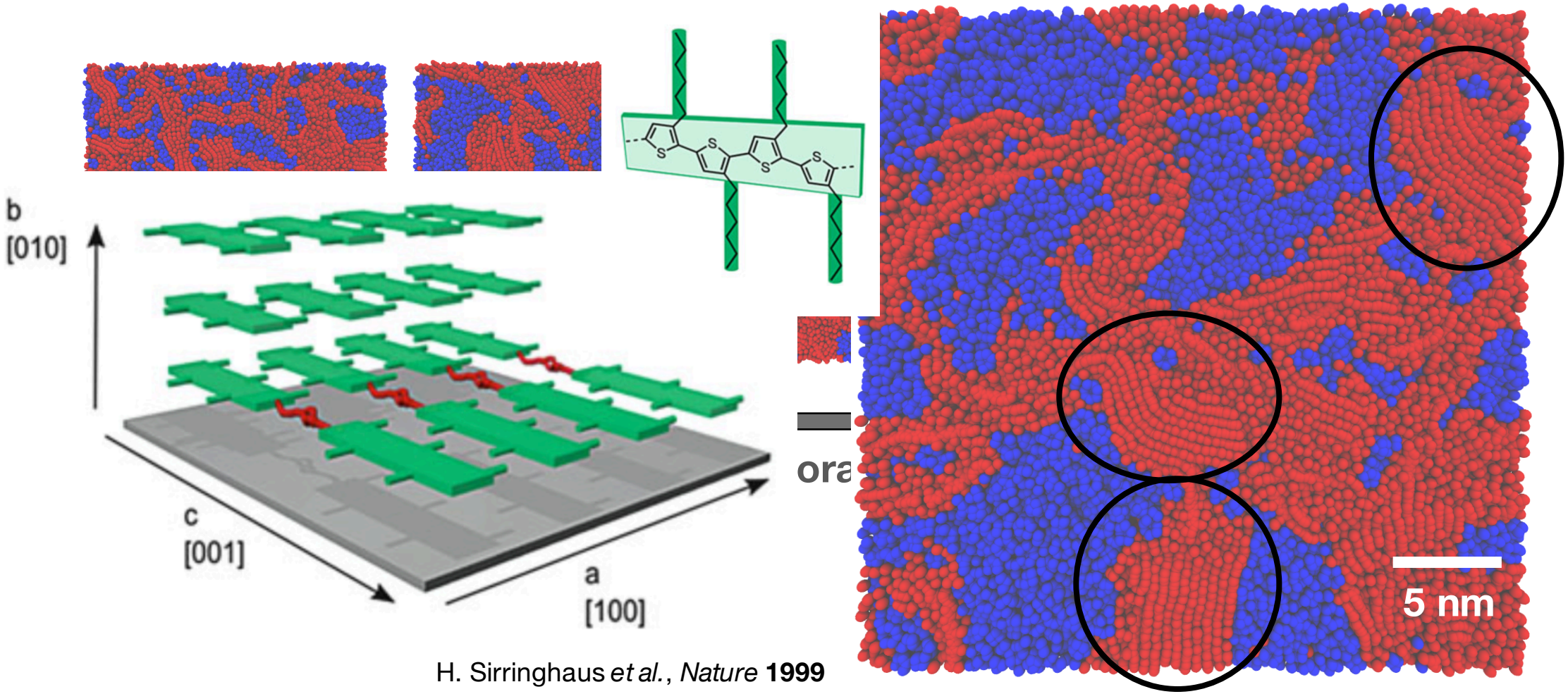
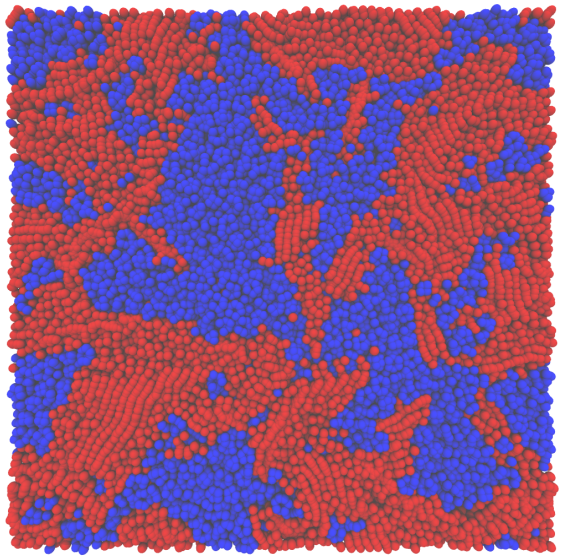


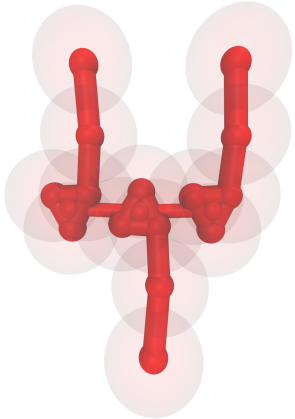
H. Sirringhaus *et al.*, *Nature* **1999**

K. Tremel *et al.*, *AdvPolymSci* **2014**

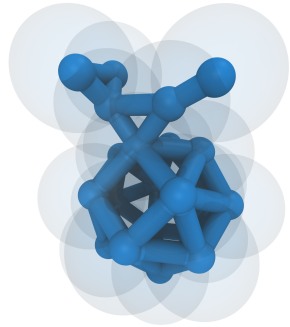
Effect of thermal annealing



as-cast

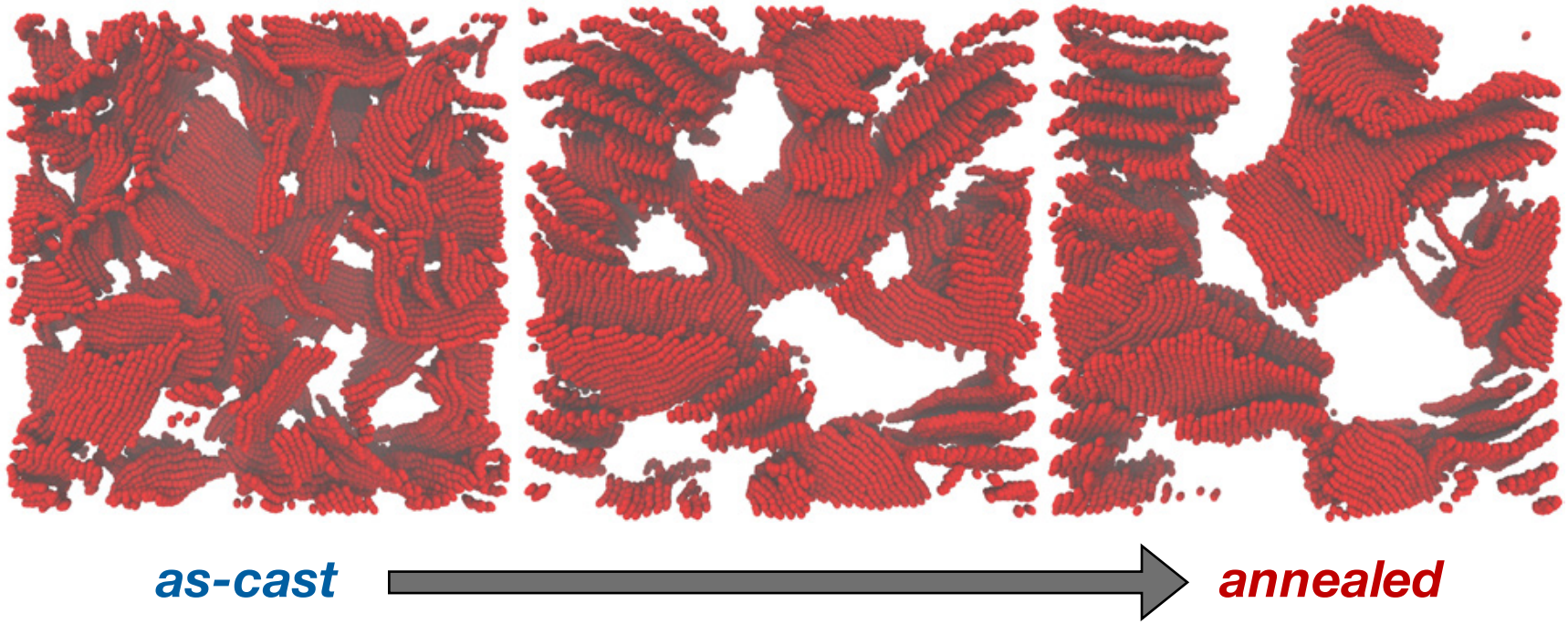


P3HT



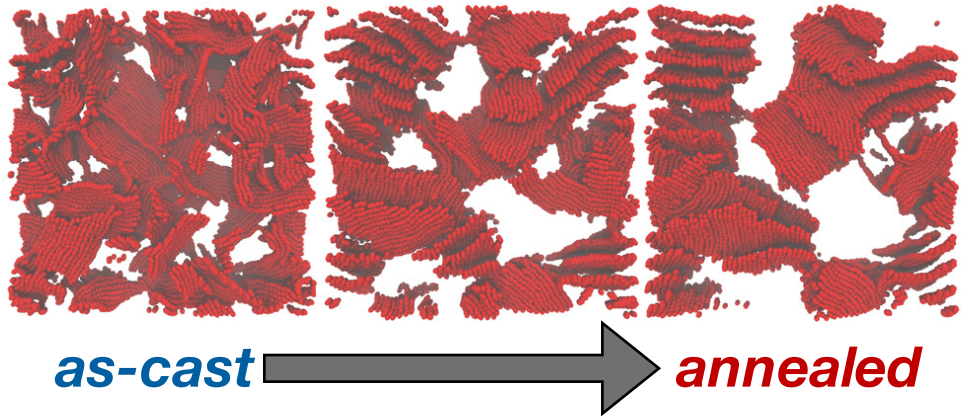
PCBM

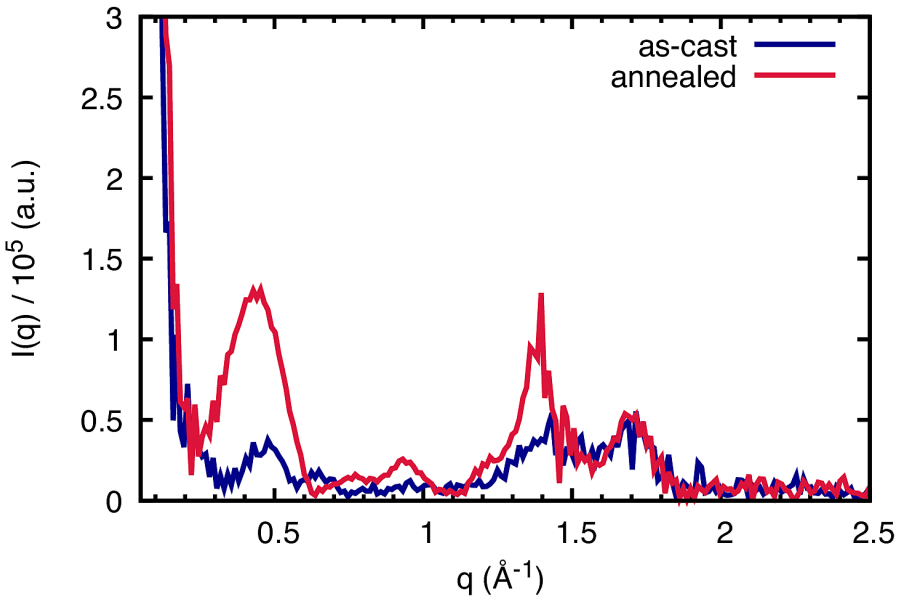
Effect of thermal annealing



Local domain segregation and crystallinity increase upon annealing.

Effect of thermal annealing

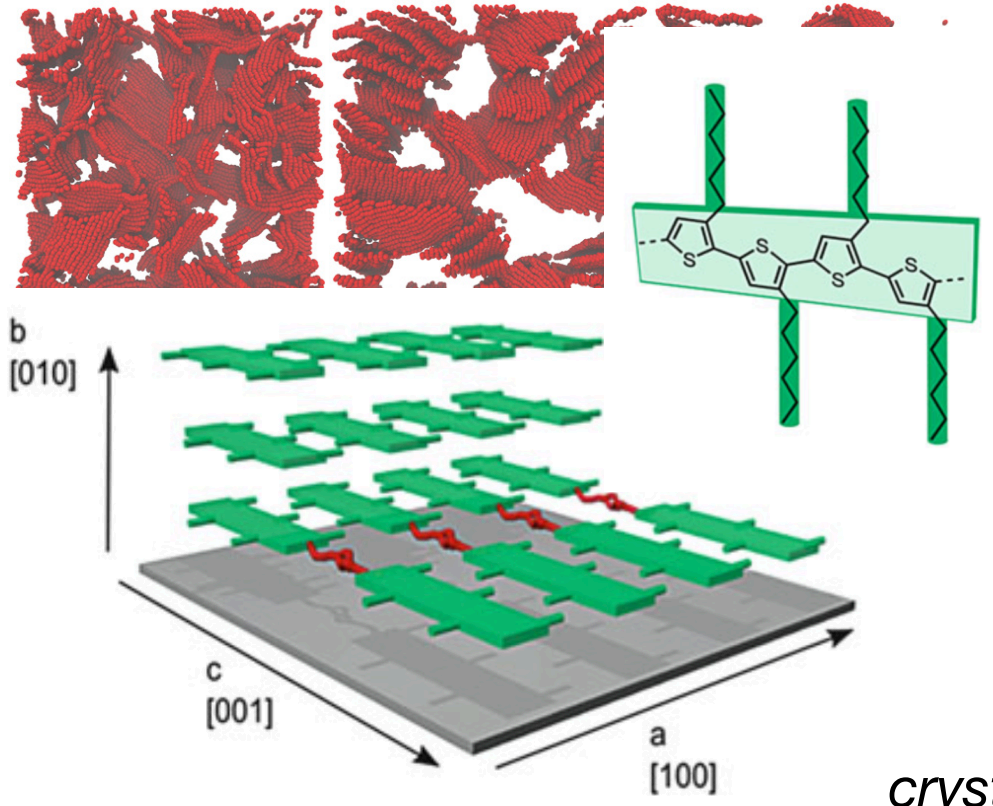


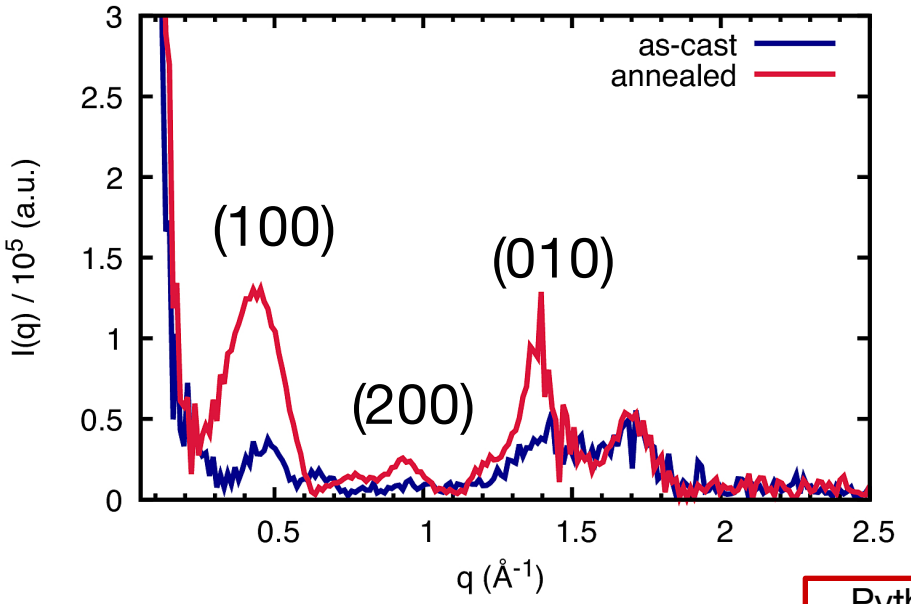


Local domain segregation and crystallinity increase upon annealing.

R. Alessandri *et al.*, *JACS* **2017**, *139*, 3697

Effect of thermal annealing



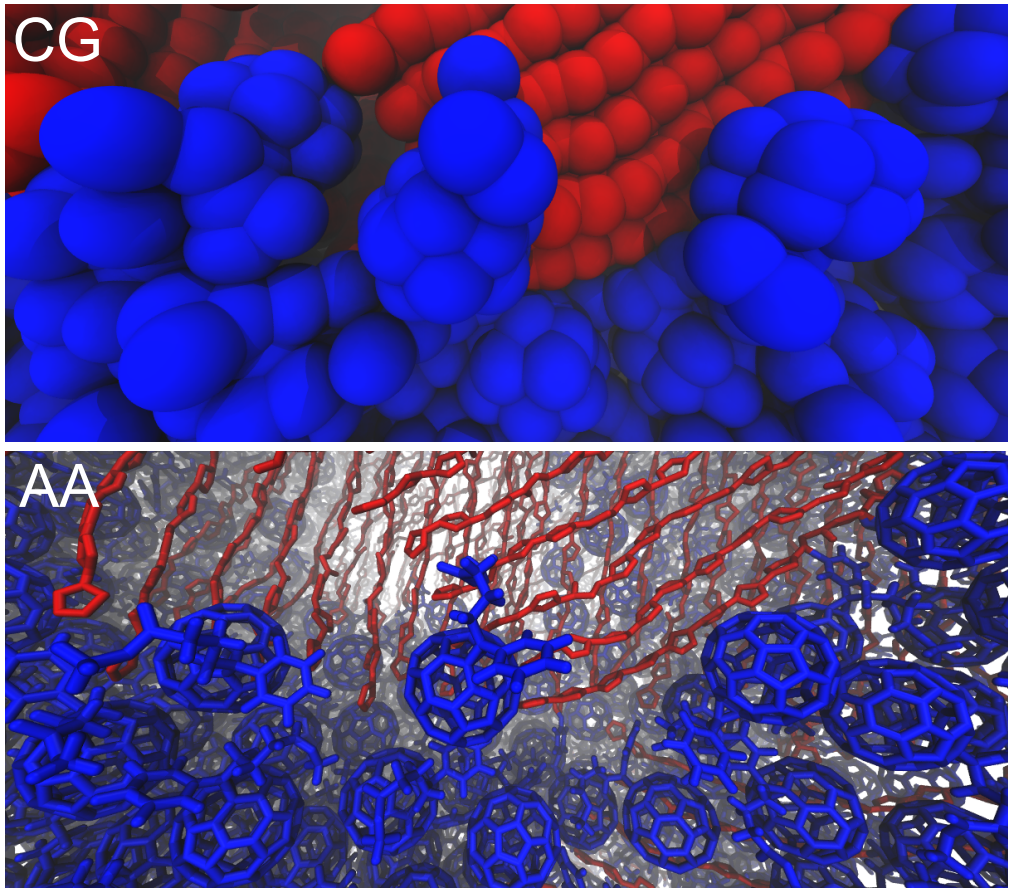


crystallinity increase upon annealing.

Python notebook with code to compute the scattering curves available at http://cgmartini.nl/

Computed scattering curves in qualitative agreement with experiments.

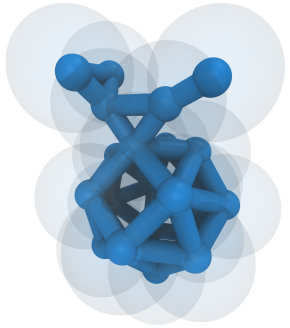
Backmapping

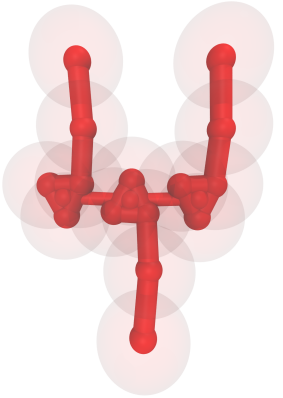


- Resolve structures at the interfaces
- Atomistic structures available for advanced quantum chemical calculations

* T. A. Wassenaar *et al.*, *JCTC* **2014**, 10, 676

Take home messages (I)

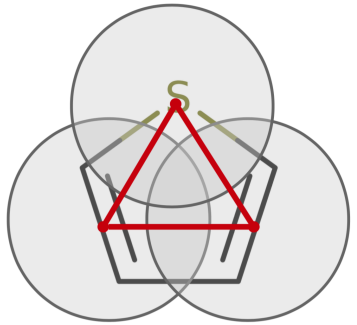




➢ (Polymers and fullerenes) *parametrization*:

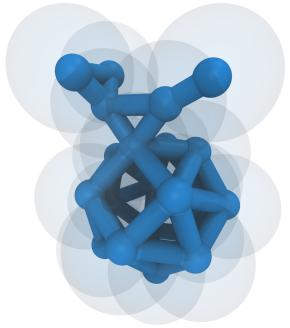
- Check (→ QM) **dihedrals** involving rotation around bonds connecting conjugated fragments or exotic (e.g., C_{60}) groups

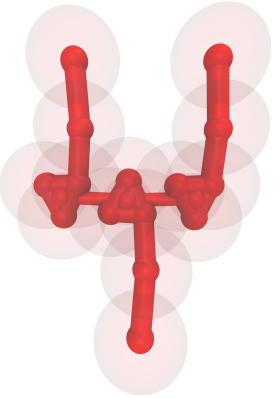
- Carefully check partitioning & dimerization behaviors when you need to use lot of **S-beads**



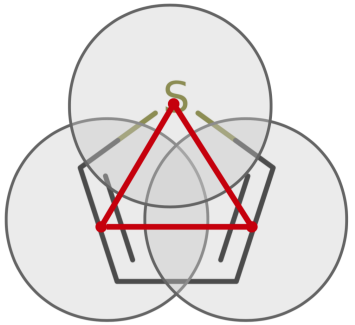
- **Don't use to short bond lengths** (~ don't overmap): having perfectly matching bonded distributions doesn't always make your CG model better (you can *inflate* your S-beads fragment a bit)

Take home messages (II)





- (Polymers and fullerenes) *parametrization*:
  - **Time consuming**: use the literature and build on top of models other people built. If then you're not satisfied, you can always improve it, but it can give you a great starting point. This also helps Martini models transferability



- Keep in mind the *limitations*:
  - Length scales (polymer MW, system size, …)
  - Time scales (CG vs experimental drying time)