

HOPE-PV 2020 School

# Comparison of non-fullerene acceptors: How geometry influences electronic transport

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## Acknowledgments

### Collaborations

Sergei Tretiak (theory, LANL)

Martin Seifrid (experiment, U Toronto)

S Halaby, M Martynowycz, Z Zhu; S Tretiak, AZ, T Gonen, M Seifrid,  
Microcrystal Electron Diffraction for Molecular Design of Functional  
Non-Fullerene Acceptor Structures, submitted to Chem Mater

Pavel Troshin (Skoltech)

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Anna Koehler (U Bayreuth/Volkswagen)

**Skoltech**

Skolkovo Institute of Science and Technology

**RSF**

Russian  
Science  
Foundation

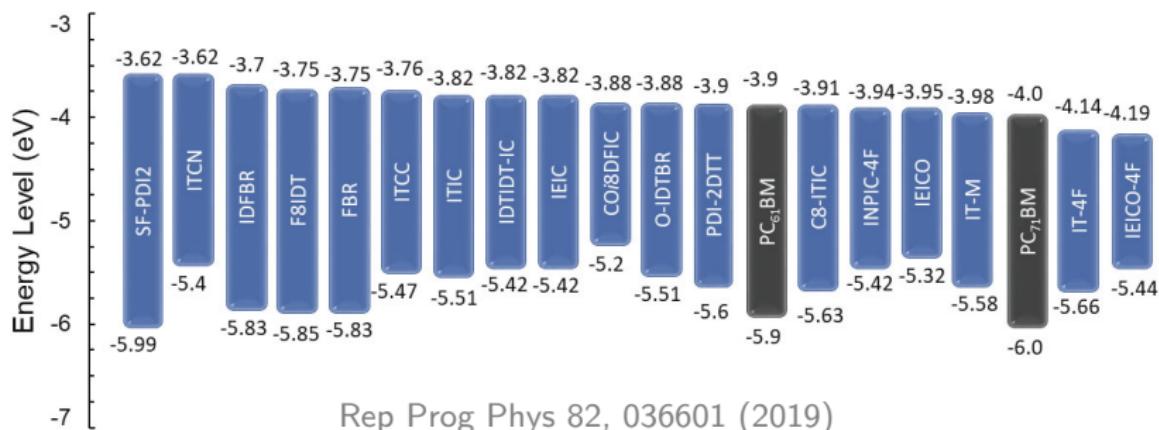


# Motivation

A historical view on progress in organic photovoltaics:

- 6% – utilizing known materials such as P3HT/PCBM
- 12% – major advance in design of electron donor material
- 18% – major advance in design of electron acceptor material

Now a lot of non-fullerene acceptors (**NFA**) are known:



Rep Prog Phys 82, 036601 (2019)

*With A-D-A intramolecular structure, NFAs showed a new type of intermolecular electronic connectivity, illustrating that our understanding of possible intermolecular packings is limited*

# Outline

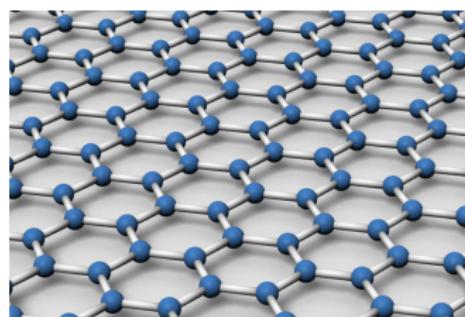
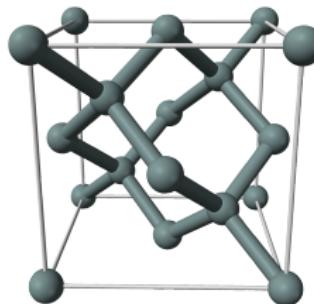
- Geometry of intermolecular packings:  
trade off between connectivity and processability
- Methodology: arguing reliability of first principle modeling
- Comparison of NFAs from charge transport perspective

## Lattice geometry:

Trade off between connectivity and processability

For good charge transport we should have maximum electronic connectivity (3D for bulk materials, 2D for 2D materials)

- Bandwidth is proportional to coordination number
- Robustness of transport with respect to disorder



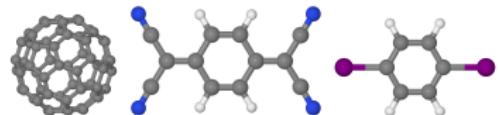
However, best solution processable organic semiconductors usually have poor electronic connectivity (e.g. amorphous polymers)

- Contain electron-insulating solubilizing groups
- Polycrystalline organic materials usually have poor morphology
- No efficient synthesis of all-organic frameworks

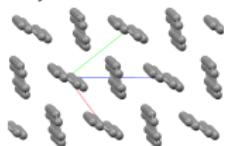
# Basic crystalline motifs in organic semiconductors

(with mobility  $\gtrsim 1 \text{ cm}^2/\text{V}\cdot\text{s}$ )

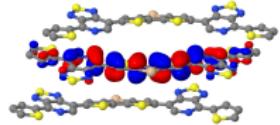
- “Hydrogen-poor” small molecules  
(often 3D connectivity but limited molecular design)



- Herringbone packing  
(2D connectivity but small couplings, pentacene)



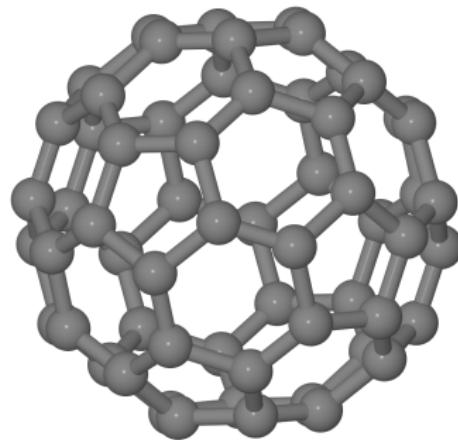
- $\pi$ -stacking  
(large couplings but 1D, many A-D-A donors)



- All-organic frameworks  
(large couplings and 2D/3D connectivity but no efficient synthesis and processing)

## C<sub>60</sub> has superior 3D electronic connectivity

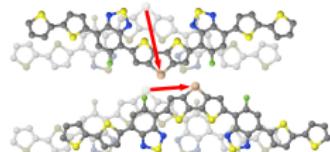
Competitive NFA must be as good electron transporter as PCBM



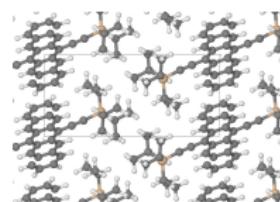
- FCC lattice with coordination number 12
- High density of states at LUMO (triply degenerate)
- But electronics couplings are moderate:  $\sim 30$  meV
- Functionalized fullerenes might be different

# Complex crystalline motifs in organic semiconductors (with mobility $\gtrsim 1 \text{ cm}^2/\text{V}\cdot\text{s}$ )

- Slipped  $\pi$ -stack  
(1D but with long electron transfer, T1)

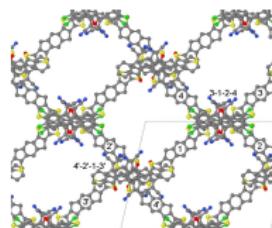


- $\pi$ -stacking + herringbone motifs  
(anisotropic 2D, rubrene)

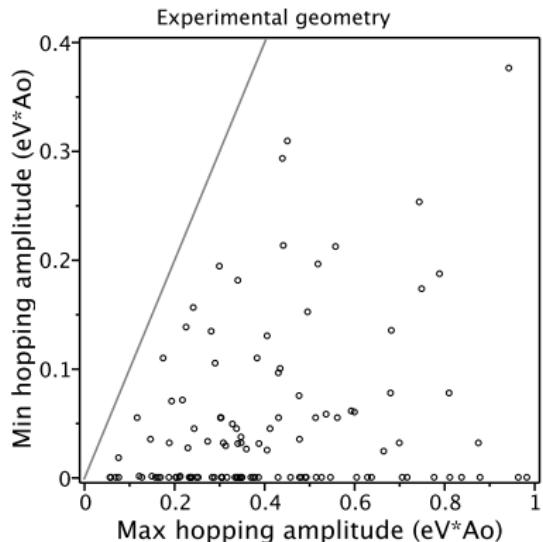
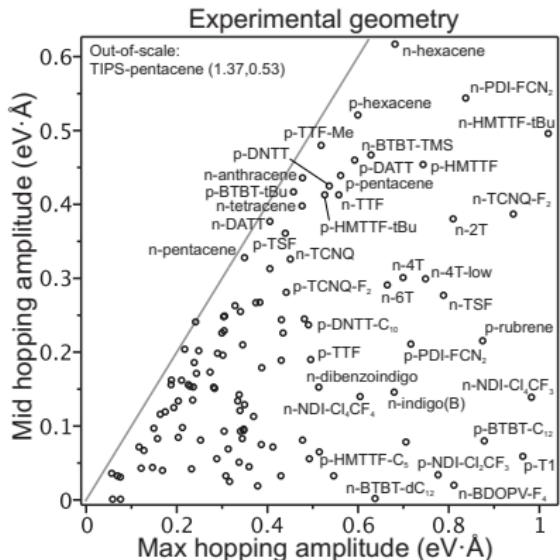


- Brickwork  
(2D with large couplings, TIPS-pentacene)

- *Wire mesh – to be discussed here*  
(3D connectivity, many NFAs)



# Map of known organic semiconductors



*Mostly 1D or 2D conductivity*

*Known 3D networks are “hydrogen-poor” small molecules like TCNQ except for relatively large C<sub>60</sub>*

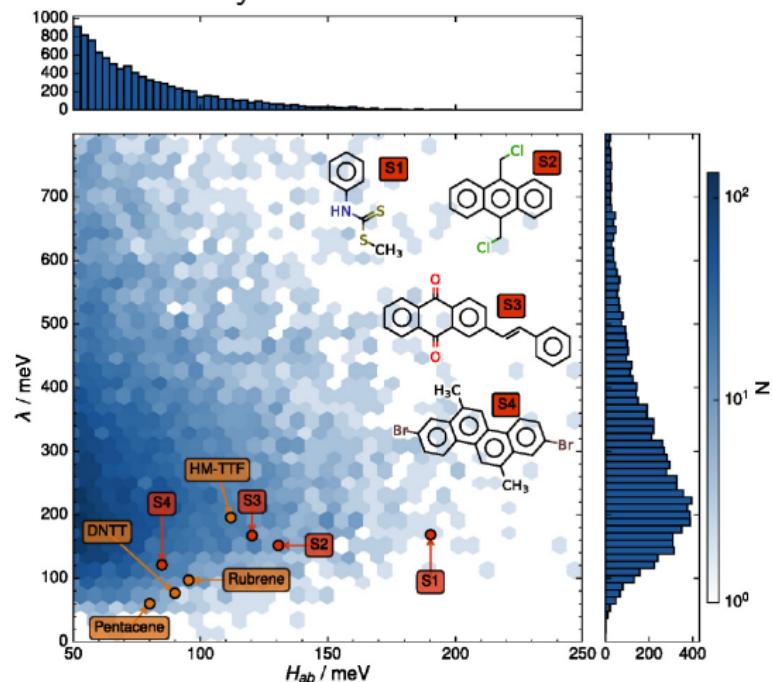
# How large are electronic couplings?

(For charge transport we need good geometrical connectivity and large couplings)

Intramolecular are  $\sim 1$  eV

Synthetic Metals 259, 116231 (2020); Solar Energy 198, 605 (2020)

Intermolecular are usually  $< 100$  meV:



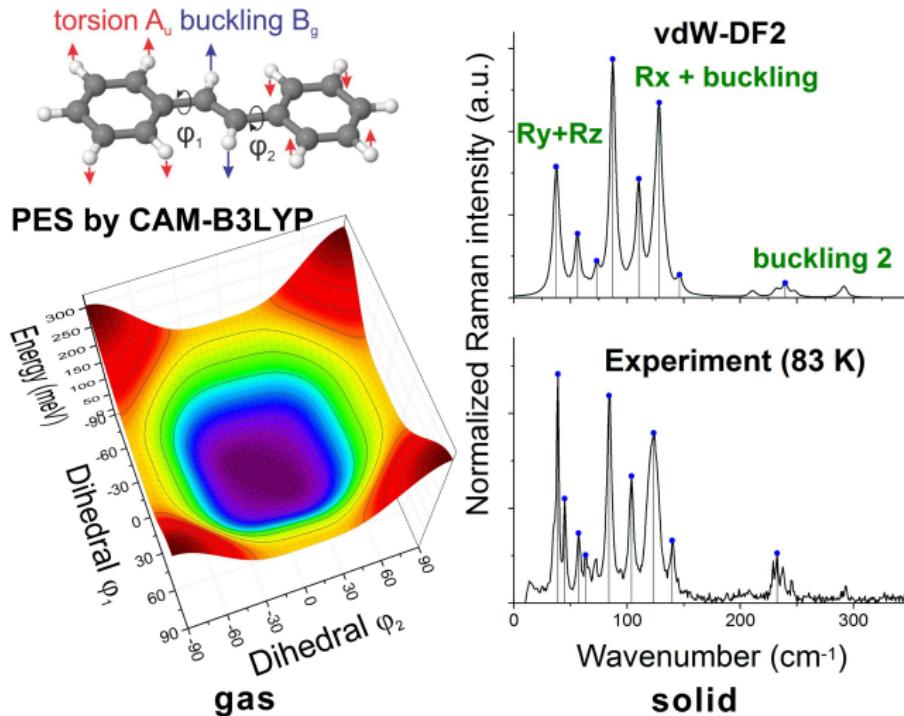
J Phys Chem Lett 7, 3973 (2016)

# Outline

- Geometry of intermolecular packings:  
trade off between connectivity and processability
- Methodology: arguing reliability of first principle modeling
- Comparison of NFAs from charge transport perspective

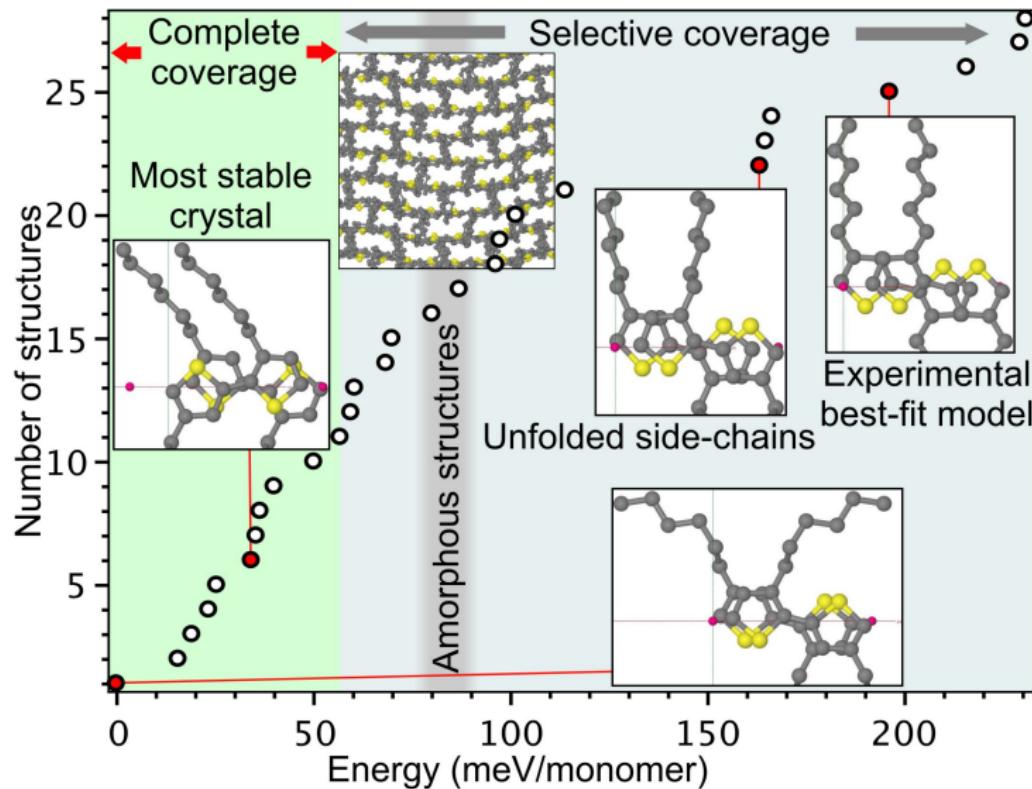
# Accuracy of intramolecular geometry: BLA and dihedrals

Stilbene and PPV: J Phys Chem Lett 10, 3232 (2019)



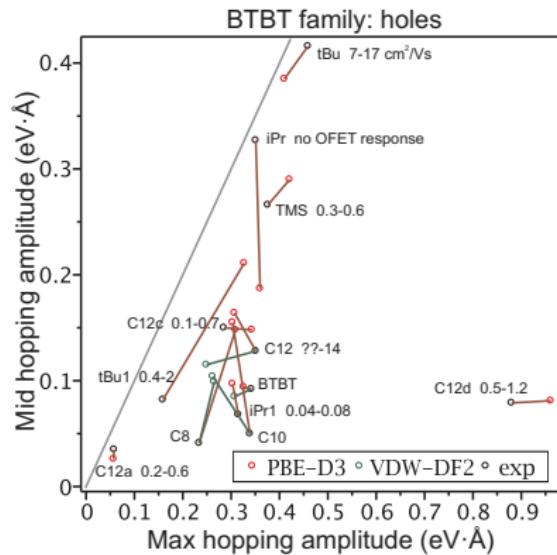
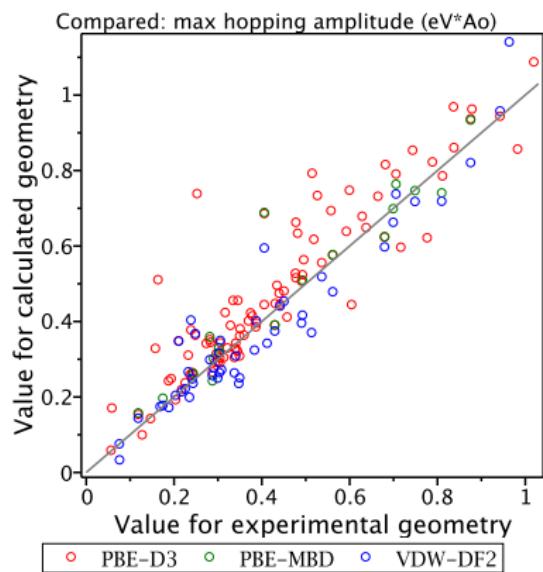
# Accuracy of intermolecular geometry: packing topology

P3HT: J Phys Chem C 122, 9141 (2018)



# Accuracy of crystal geometry for calculation of mobility

Hopping amplitudes\* for 50 crystals including all high- $\mu$  [Chem Soc Rev 47, 422 (2018)]



$$\mu = 0.95 \frac{D(t^2)}{W(T)^2} \frac{\text{cm}^2}{\text{V}\cdot\text{s}}, \text{ square root of eigenvalues of } D(t^2) \text{ are hopping amplitudes}$$

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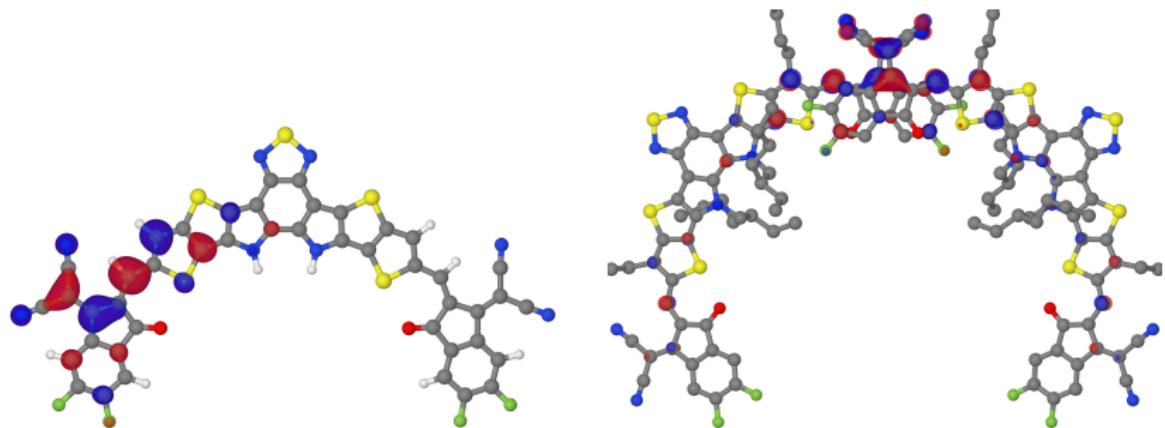
## How do we compare

- Experimental geometry is usually not very accurate for electronic structure calculations  
    ⇒ DFT-D optimized geometry (PBE-D3/PAW400)
- Electronic couplings are calculated in dimer approximation with two states per molecule (CAM-B3LYP/6-31G\*)
- Errors in calculation of charge carrier mobility might be large  
    ⇒ we compare descriptors of charge transport:
  - ▶ Electronic bandwidth (end-to-end and mean square root)
  - ▶ Hopping amplitudes (coupling multiplied by hopping distance):

$$\mu = 0.95 \frac{D(t^2)}{W(T)^2} \frac{\text{cm}^2}{\text{V}\cdot\text{s}}, \text{ square root of eigenvalues of } D(t^2) \text{ are hopping amplitudes}$$

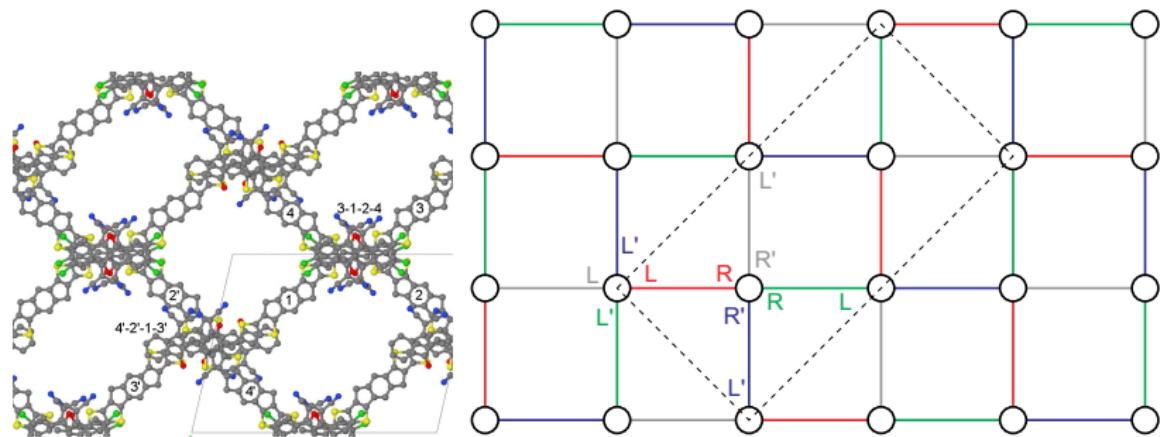
# A-D-A molecules and their $\pi$ -stacking

Example of Y6



# Wire mesh intermolecular packings

A-D-A molecules interconnected via  $\pi$ -stacking of A-units



- The topology of interconnections has complex 3D pattern
- Breaking some contacts breaks 3D connectivity
- Breaking L-R symmetry breaks 3D connectivity (see above)

Can be illustrated with LEGO blocks – each block is a molecule



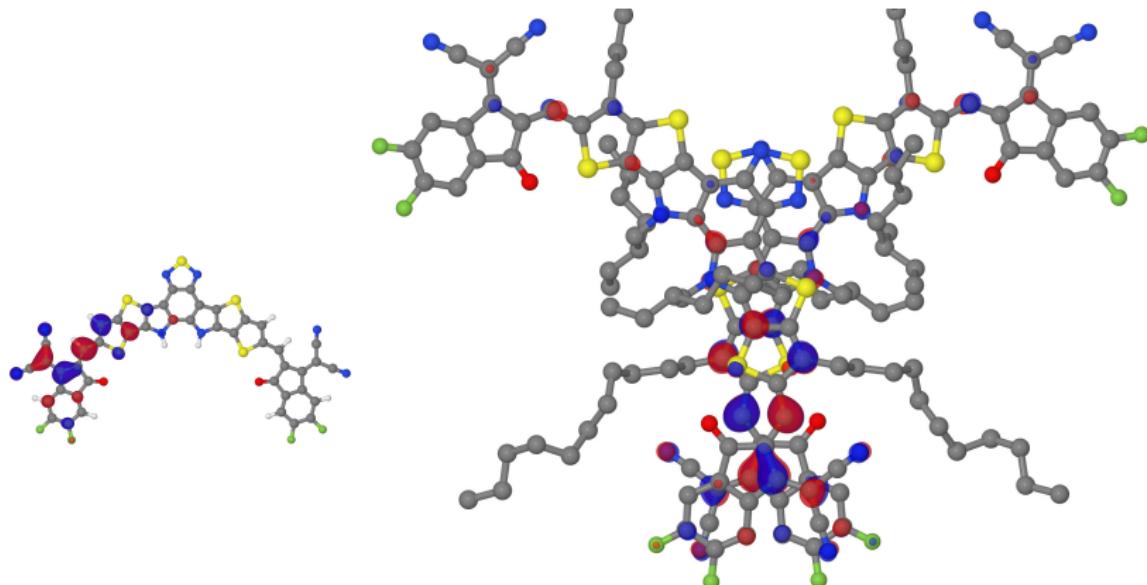
## Comparison: NFAs and some reference systems

system		$\eta_1$	$\eta_2$	$\eta_3$	geometry
1D systems					
R24	h	0.33	0.06	0.03	$\pi$ -stack
T1	h	1.23	0.01	0.00	slipped stack
EH-IDTBR	e	1.32	0.22	0.03	slipped stack
ITIC-Th	e	0.94	0.08	0.00	slipped stack
ITIC-1Cl	e	0.74	0.07	0.00	broken mesh
2D systems					
hexacene	h	0.75	0.65	0.04	herringbone
TIPS-pentacene	e	1.39	0.53	0.00	brickwork
3D systems					
C60	e	$\sim$ 0.4	$\sim$ 0.4	$\sim$ 0.4	fcc
F2-TCNQ	e	0.94	0.39	0.38	3D
<b>o-IDTBR</b>	e	1.04	0.35	<b>0.19</b>	wire mesh
<b>Y6</b>	e	0.99	0.92	<b>0.39</b>	wire mesh
3D models (100 meV couplings)					
<b>o-IDTBR model</b>		0.99	0.39	0.33	wire mesh

$\eta_{1,2,3}$  are hopping amplitudes in eV·Å

## Why Y6 is exceptional

- All intermolecular couplings are large (in contrast to o-IDTBR)
- Large-area overlap due to corner-like molecular shape



# Summary

- Fine tuning of intermolecular contacts in novel NFAs allows for creation of materials with robust 3D electronic connectivity
- Example of structural variations within the wire mesh packing topology suggests to look for other solution processable architectures with more robust 3D connectivity
- See more details in article [Chem Mater 33, 966 \(2021\)](#)