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Computational Design of Near-IR Absorbing Organic Materials for Light Harvesting Application

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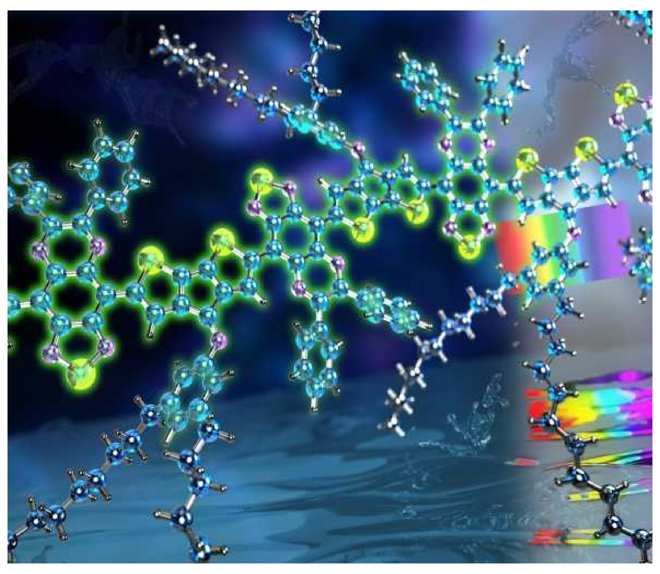
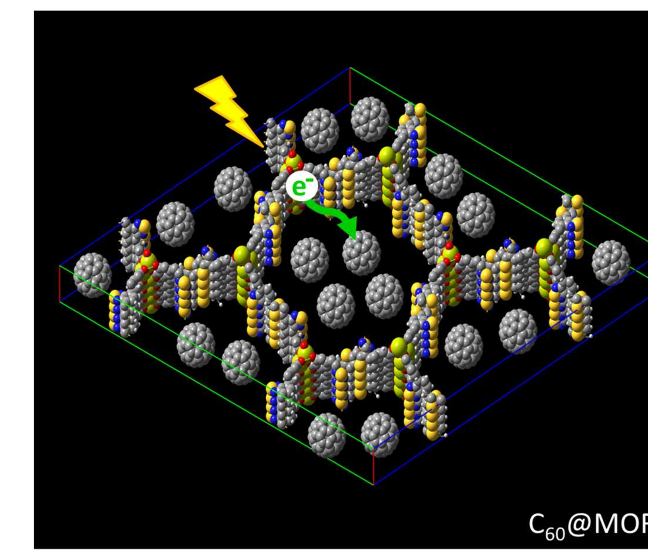
Abstract



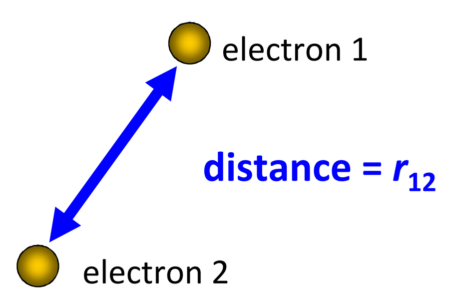
Foster, et. al.; *Macromol. Rapid Commun.*, 2014, 35, 1516

Organic and organic-inorganic hybrid materials demonstrate exceptional promise for next-generation electronic and optoelectronic applications due to their low production costs and flexibility in comparison to traditional inorganic materials (e.g. silicon). The growing interest in this technology mandates a fundamental understanding of the key factors governing their performance. First-principle calculations are poised to play a vital role in materials design because of the ability to rapidly screen materials for desired properties at low cost. We show that by judicious choice of the molecular building blocks precise control over the band/optical gaps can be achieved allowing for the design of conjugated polymers and metal-organic frameworks that have absorption spectrums extended into the near-infrared spectral region (> 1000 nm). The successes and shortcomings of predicting band/optical gaps using density functional theory will be addressed. Specifically, it will be shown that range-separated functionals yield results in good agreement with experiment and high level many-body methods.



M.E. Foster et. al., Chemical Science, 2014, 5, 2081-2090

Screened Hybrid Functionals for Solids / Periodic Systems



Range-separated functionals split the coulomb potential into short-range and long-range terms in attempt to recover the correct functional form of electron exchange at long-range; electron exchange now depends on electron distance.

XC Functional Form

$$E_{XC} = a\,E_x(\mu HF, SR) + (1-a)\,E_x(\mu DFT, SR) + E_x(DFT, LR) + E_c(DFT)$$

a=%HF (0.25 for HSE06)

μ = range separation parameter (0.11 Borh^{-1} for HSE06)

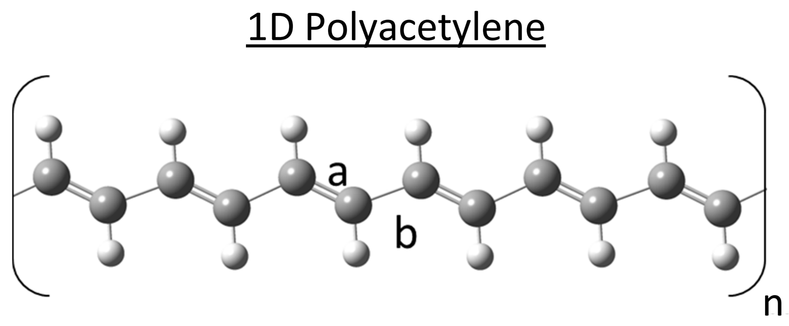
$$\frac{1}{\mathbf{r}_{12}} = \underbrace{\frac{1-\mathrm{erf}(\mu\cdot\mathbf{r}_{12})}{\mathbf{r}_{12}}}_{\text{short-range}} + \underbrace{\frac{\mathrm{erf}(\mu\cdot\mathbf{r}_{12})}{\mathbf{r}_{12}}}_{\text{long-range}}$$

μ = range separation parameter (1/Bohr)

- 100% Short-range Hartree-Fock (HF) can not correctly describe metallic behavior in periodic solids
- Electron correlation and dielectric effects screen/cancel long-range HF (screening length ~5 Å)
- Example functionals: HSE03, HSE06, M11
- This is the opposite to what was good for molecules!

XC Functional and the Relationship between Bandgap and Bond Length Alternation (BLA)

1D Polyacetylene



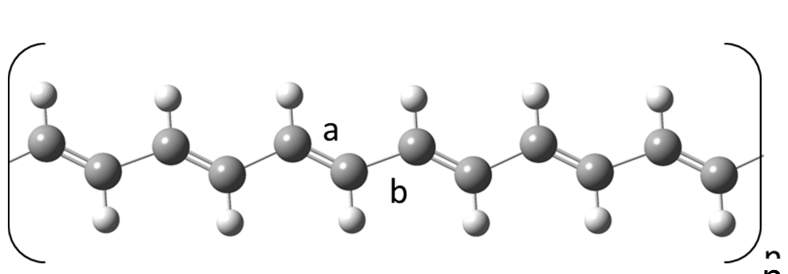
BLA = b – a

Optimized Geometry

	Band Gap (eV)	BLA (Å)
HF	7.2	0.123
PBEh (PBE0)	**1.5**	**0.060**
HSE06	0.8	0.050
PBE	0.1	0.015

Experimental Band Gap = 1.2 eV; BLA = 0.08 Å

- Bandgap is directly correlated to the Bond Length Alternation; bandgap approaches zero as BLA approaches zero
- Hartree-Fock (HF) theory over **localizes** electrons causing a large BLA and bandgap
- GGA-DFT (PBE) over **delocalizes** electrons causing a small BLA and bandgap
- PBEh (global hybrid; 25% HF exchange) preforms the best but BLA and bandgap are underestimated
- HSE06 (screened hybrid functional) underestimates BLA; as a results, the bandgap

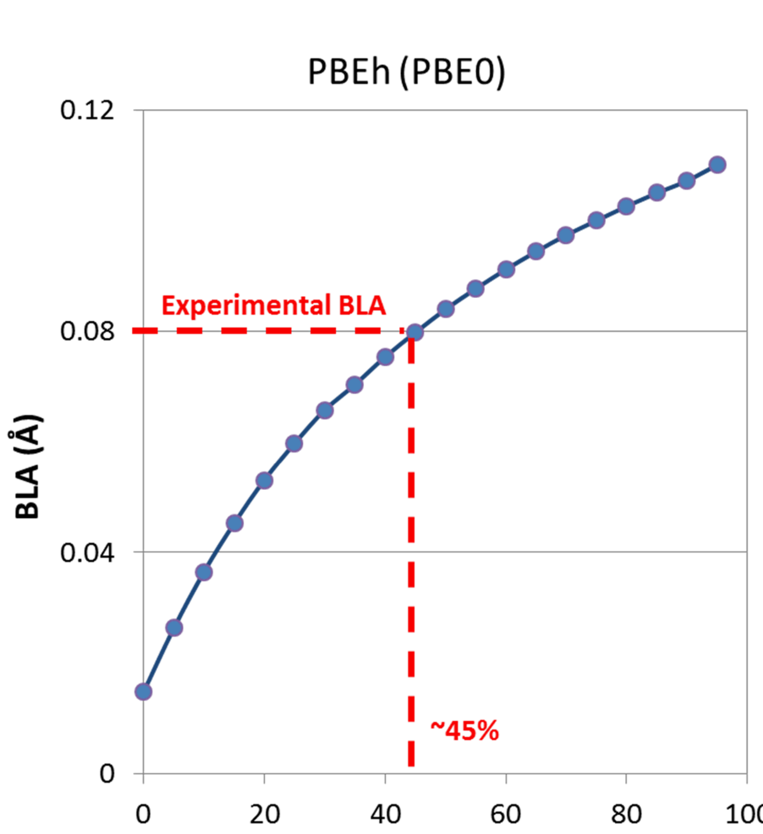


BLA = b – a = 0

Fixed Geometry (BLA = 0)

	Band Gap (eV)	BLA (Å)
HF	4.3	0
PBEh (PBE0)	0.3	0
HSE06	**0.0**	**0**
PBE	**0.0**	**0**

- Fundamentally, the bandgap must go to ZERO as the bond length alternation goes to ZERO
- HF and PBEh fail the test; this can catastrophically effect predictions for narrow bandgap materials
- GGA (PBE) and screened hybrid functionals (HSE06) satisfy this fundamental condition

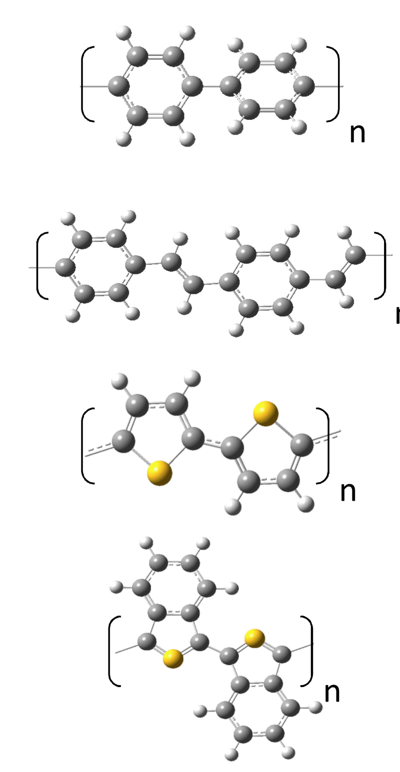


- Correct BLA can be achieved for by optimizing the faction of HF exchange
- Correct BLA is achieved for polyacetylene with 45% HF exchange (PBE45) but the bandgap is too large (2.72 eV)
- Single-point HSE06 calculation on PBEh(45% HF) yields exact bandgap for polyacetylene (1.2 eV)

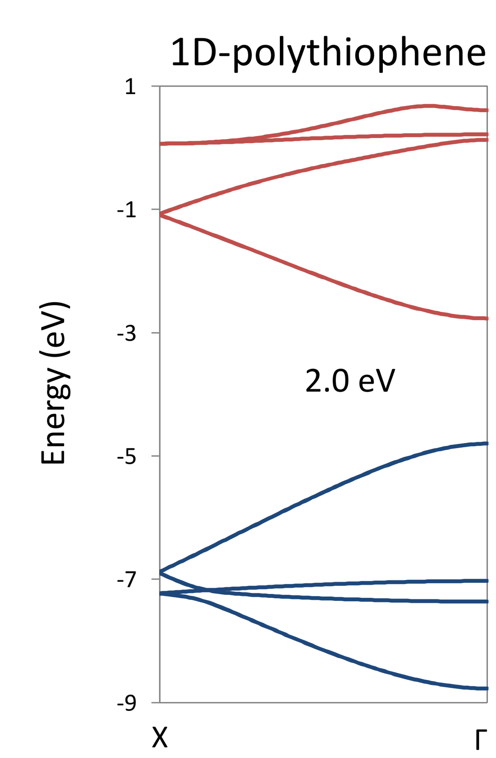
Proposed Method For Predicting Bandgaps Of Periodic Systems

1. Optimize geometry using PBEh functional with 45% HF exchange (PBE45)
2. Preform single-point HSE06 calculation on optimized PBE45 geometry

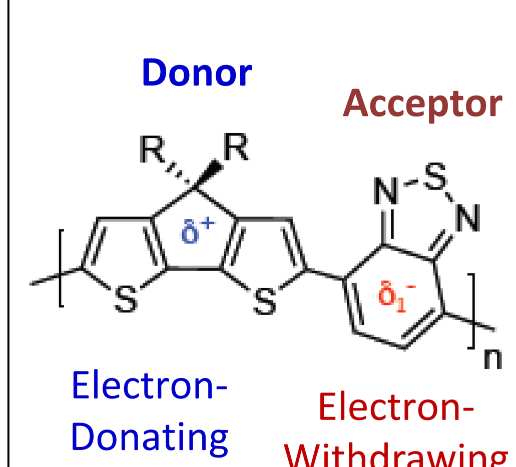
Validating HSE06//PBE45 Approach

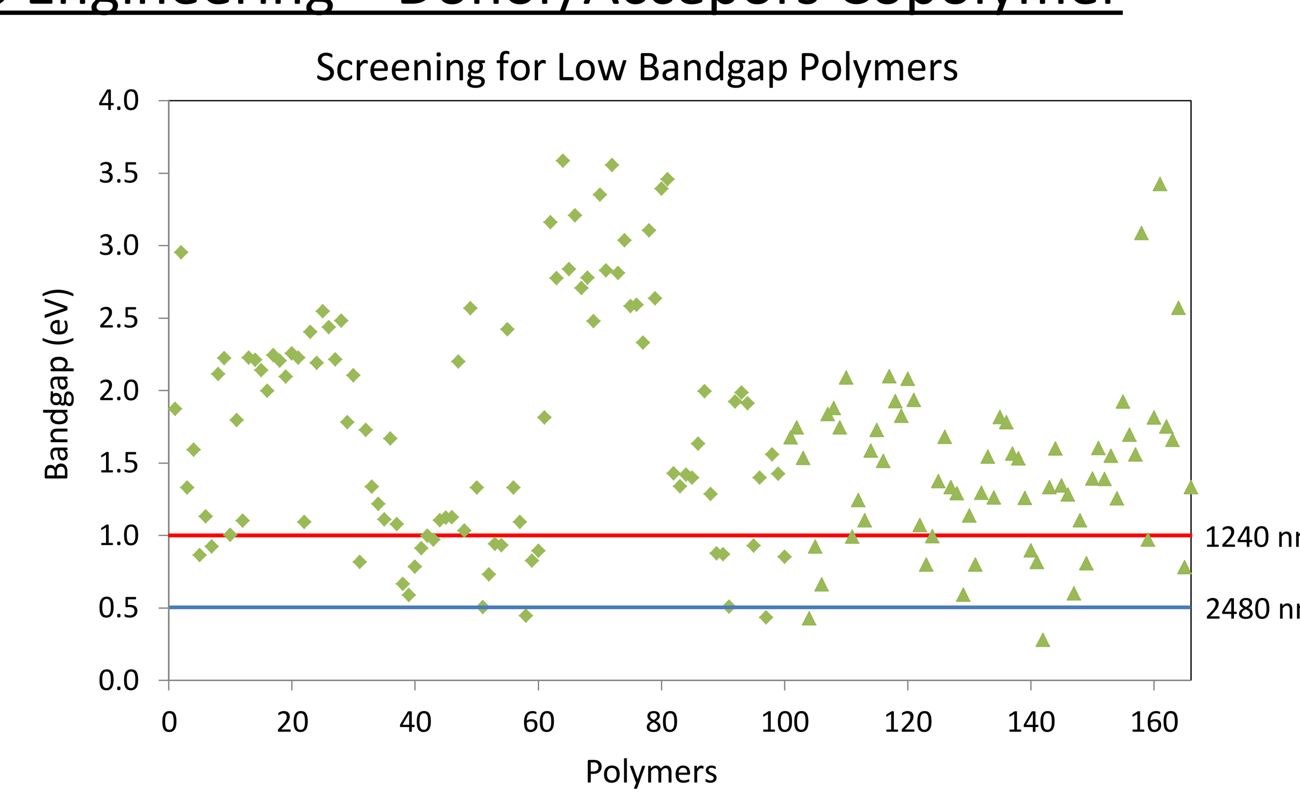


Polymer 1	Exp.	3.2 eV
	HSE06//PBE45	3.5 eV
Polymer 2	Exp.	2.5 eV
	HSE06//PBE45	2.2 eV
Polymer 3	Exp.	2.0 eV
	HSE06//PBE45	2.0 eV
Polymer 4	Exp.	1.0 eV
	HSE06//PBE45	0.9 eV



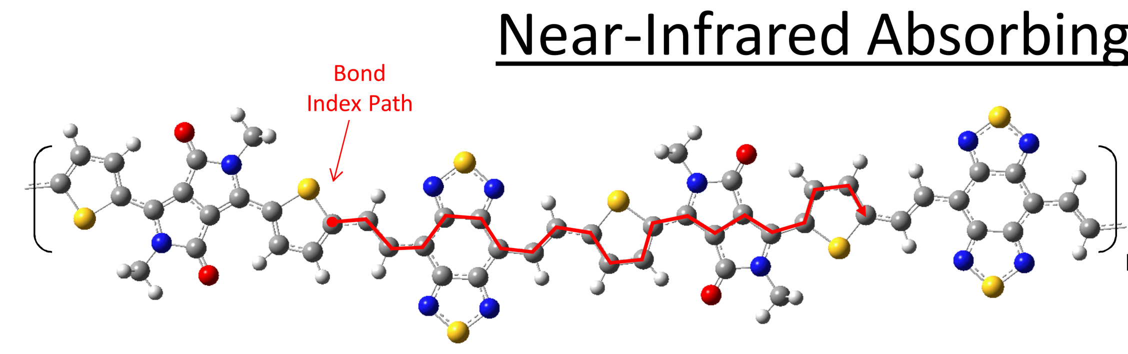
Bandgap Engineering – Donor/Accepors Copolymer

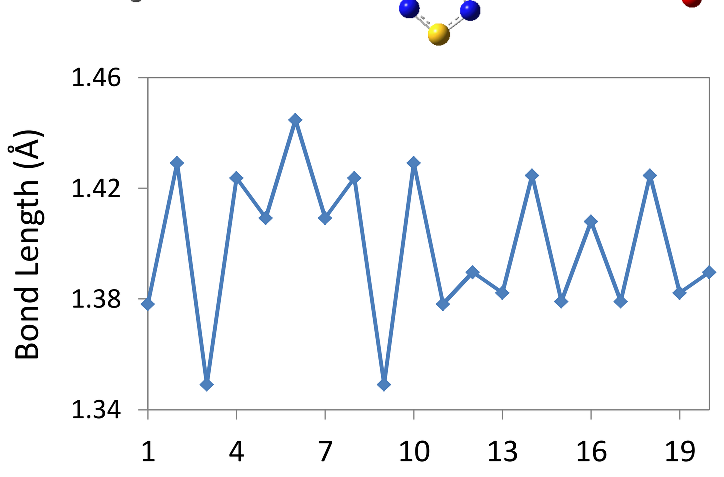




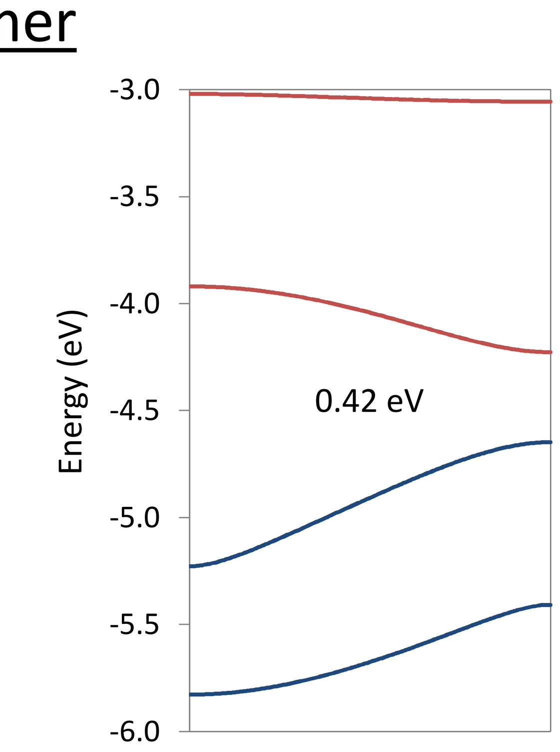
Creating a narrow bandgap polymer requires choosing a donor/acceptor combination that minimizes the bond length alternation (BLA)

Near-Infrared Absorbing Polymer





Avg. Bond Length = 1.399 Å
STDEV Bond Length = 0.027 Å
Max. BLA = 0.080 Å
Min. BLA = 0.035 Å
Avg. BLA = 0.007 Å



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