

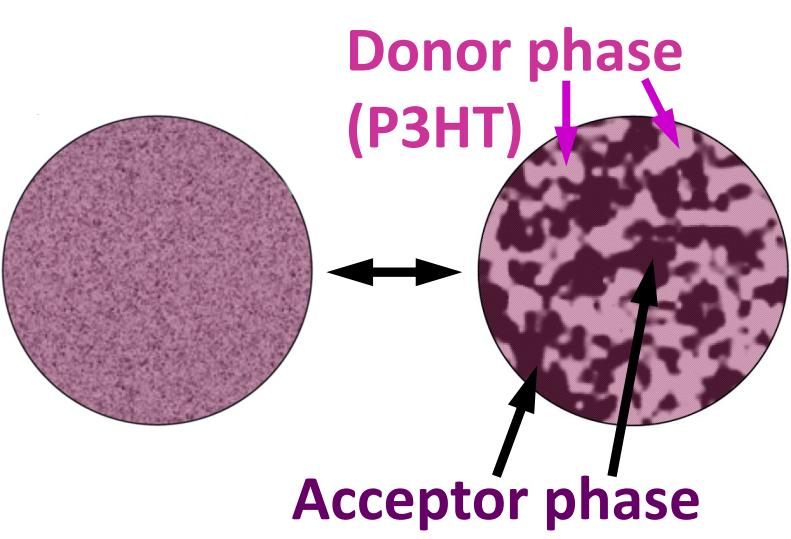
Concentration Dependence of the Self-Assembly of Poly(3-hexylthiophene)

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Introduction and Objective

The molecular orientation and morphology of conjugated polymer-based bulk-heterojunction (BHJ) composites are critical to the device performance. Recently, aggregates and nanofibers of poly(3-hexylthiophene) (P3HT) have received attention as an attractive method for controlled organization of the donor and acceptor constituents into nanoscale phase-separated domains.

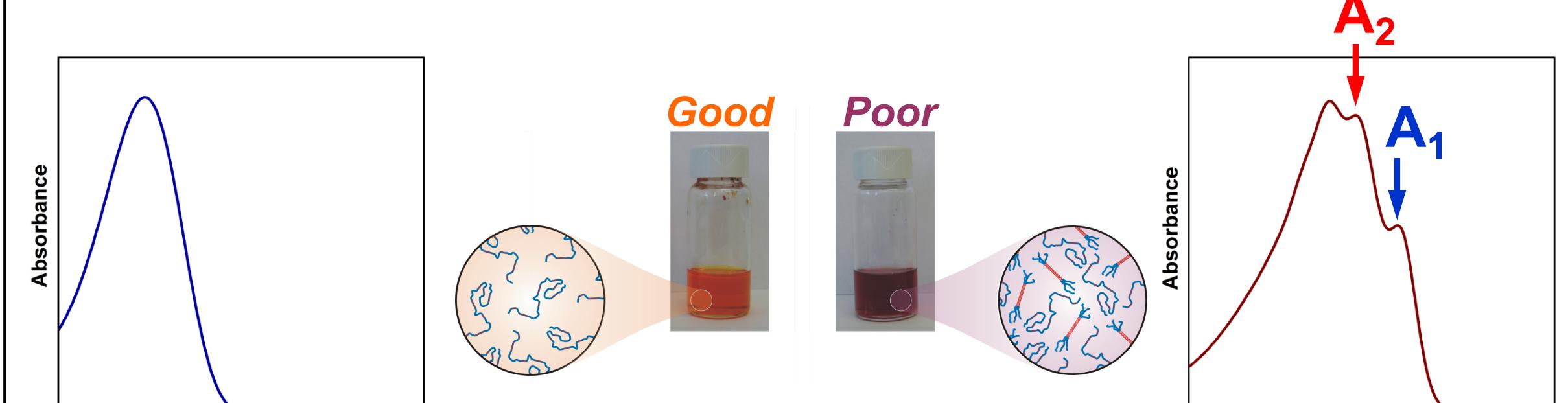


We are using binary solvent mixtures to direct the assembly of P3HT into H- and J-aggregates, which have significantly different optical and electronic properties. The assembly of these aggregates plays a critical role in determining the photophysics, the behavior of excitons within the P3HT nanostructures, and the solid-state crystallinity of P3HT in the BHJ composite.

Beyond the device applications, we aim to learn more about the fundamental solvent-P3HT interactions and assembly mechanisms of P3HT. Here we use absorbance spectroscopy to investigate the effect of P3HT concentration on the structural order of P3HT nanostructures and the extent (%) of aggregation in a series of binary solvent mixtures. This will help us understand more about how the properties of the solutions impact the properties of the solid state thin films made from these aggregate dispersions.

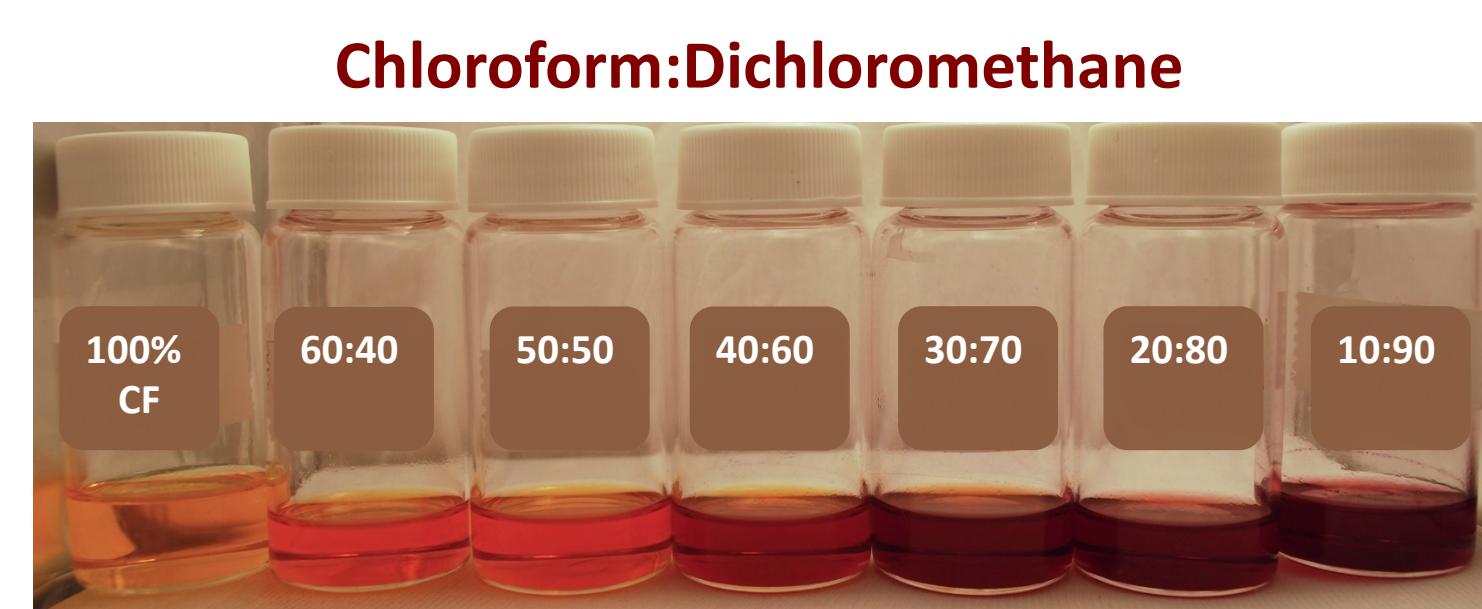
Experimental Methods

Absorbance spectroscopy and atomic force microscopy measurements were conducted on P3HT aggregate dispersions and thin films using binary solvent mixtures composed of varying amounts of "good" and "poor" solvents.



Two Good Solvents	One Poor Solvent
Chloroform (CF) and Toluene (Tol)	Dichloromethane (DCM)

P3HT solutions with varying CF:DCM and Tol:DCM volume fractions were prepared and allowed to age in the dark for 24 hours. We used solutions with 0.05 mg·mL⁻¹ and 0.1 mg·mL⁻¹ concentrations of P3HT.



Intermolecular Excitonic Coupling Analysis

$$\frac{A_1}{A_2} = \frac{n_1}{n_2} \cdot \left(\frac{1 - \frac{J}{\omega_p} e^{-S} \sum_{v>0} S^v}{1 - \frac{J}{\omega_p} e^{-S} \sum_{v=1} S^v} \right)^2$$

J = Resonant excitonic coupling ($J = 0.25 \cdot W$)
 n_i = Refractive index of the solvent
 ω_p = Phonon frequency
 S = Huang-Rhys Factor
 v = Excited-state vibrational level

The equation relates the A_1/A_2 peak ratios to the interchain excitonic coupling (J) and structural order within the P3HT aggregates., where smaller J -values ($A_2 < A_1$) are indicative of more structural order.

Extent of Aggregation

We use a Beer's law to determine the amount (%) of P3HT that actually forms aggregates.

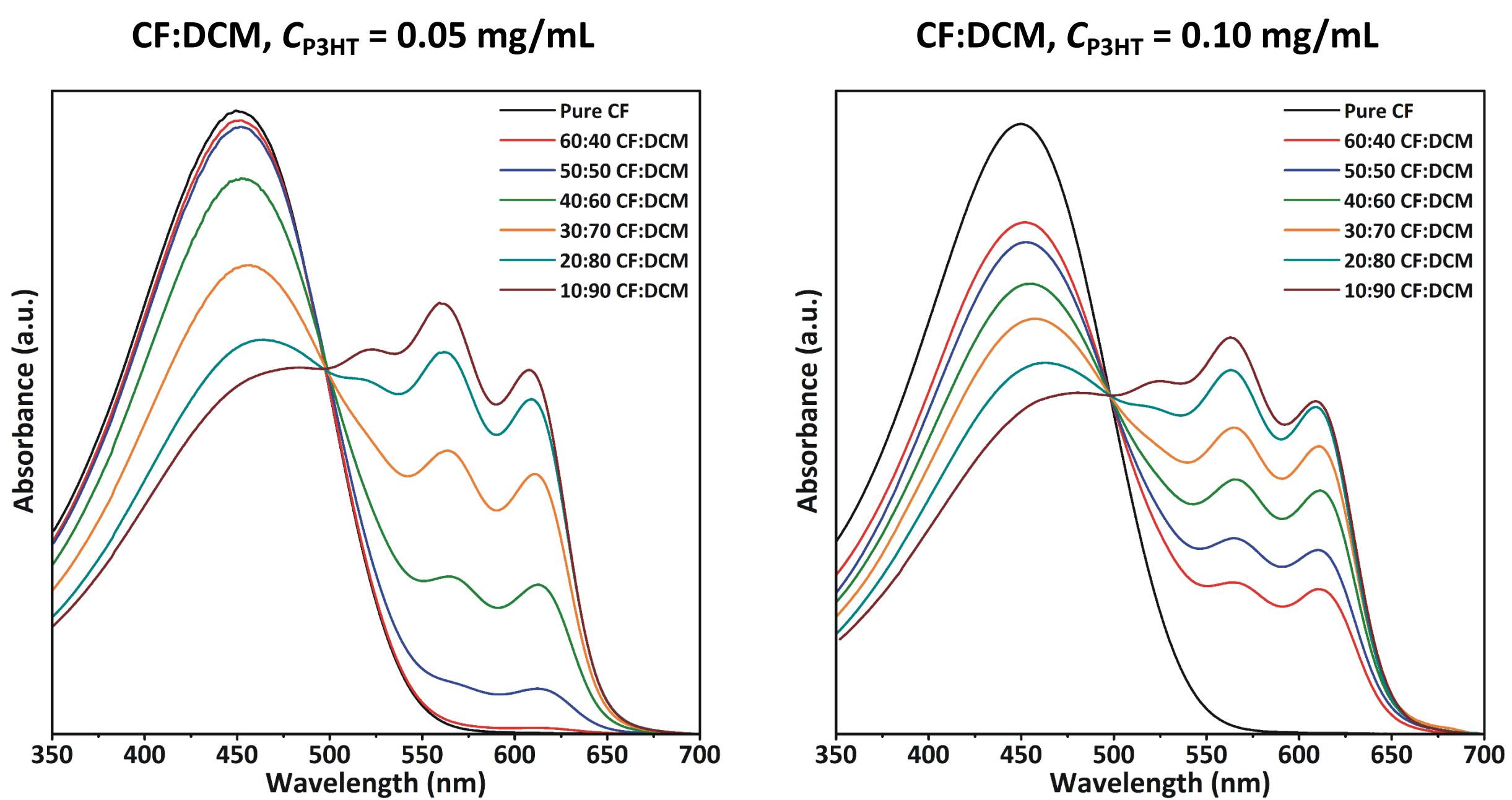
$$A = \epsilon \ell C_{P3HT}$$

$$F = -\frac{\Delta A_{\text{amorphous}}}{\Delta A_{\text{aggregate}}} = \frac{\epsilon_{\text{amorphous}}}{\epsilon_{\text{aggregate}}}$$

$$\% \text{Aggregation} \approx \frac{A_{\text{aggregate}}}{A_{\text{aggregate}} + (A_{\text{amorphous}} / F)} \times 100$$

Kinetics of Liquid Phase Crystallization

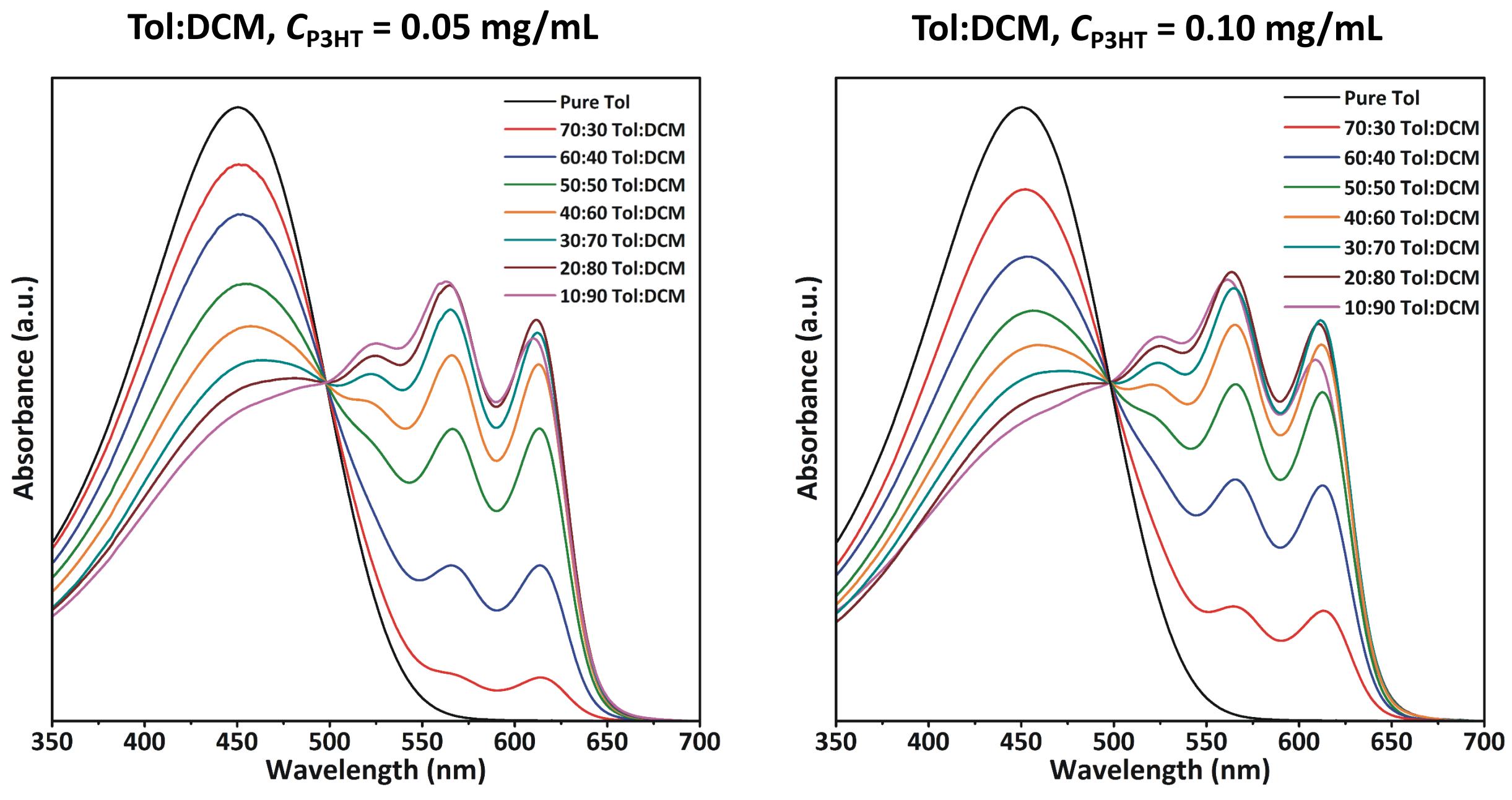
Chloroform:Dichloromethane Dispersions



Solvent	J/meV	%Agg
CF:DCM 10:90	10.9	47
CF:DCM 20:80	8.3	41
CF:DCM 30:70	4.7	28
CF:DCM 40:60	1.0	16
CF:DCM 50:50	-0.2	6
CF:DCM 60:40	-10.7	2
CF:DCM 70:30	---	0

The lower P3HT concentration can produce highly ordered aggregates ($J < 0$), but only in very small amounts (extent of aggregation < 10%).

Toluene:Dichloromethane Dispersions



Solvent	J/meV	%Agg
Tol:DCM 10:90	9.8	44
Tol:DCM 20:80	5.9	39
Tol:DCM 30:70	4.1	35
Tol:DCM 40:60	1.8	30
Tol:DCM 50:50	0.1	25
Tol:DCM 60:40	-2.1	17
Tol:DCM 70:30	-4.9	10

Solvent	J/meV	%Agg
Tol:DCM 10:90	14	53
Tol:DCM 20:80	8.7	50
Tol:DCM 30:70	4.9	45
Tol:DCM 40:60	3.0	40
Tol:DCM 50:50	0.9	34
Tol:DCM 60:40	0.5	25
Tol:DCM 70:30	-0.6	14

The Tol:DCM solvent exhibits notable aggregation in the 70:30 mixture, even at the lower P3HT concentration.

- We know that chloroform is a better solvent for P3HT than toluene.

$$C_{P3HT}(\text{pure CF}) \approx 15 \text{ mg/mL}$$

$$C_{P3HT}(\text{pure Tol}) \approx 1 \text{ mg/mL}$$

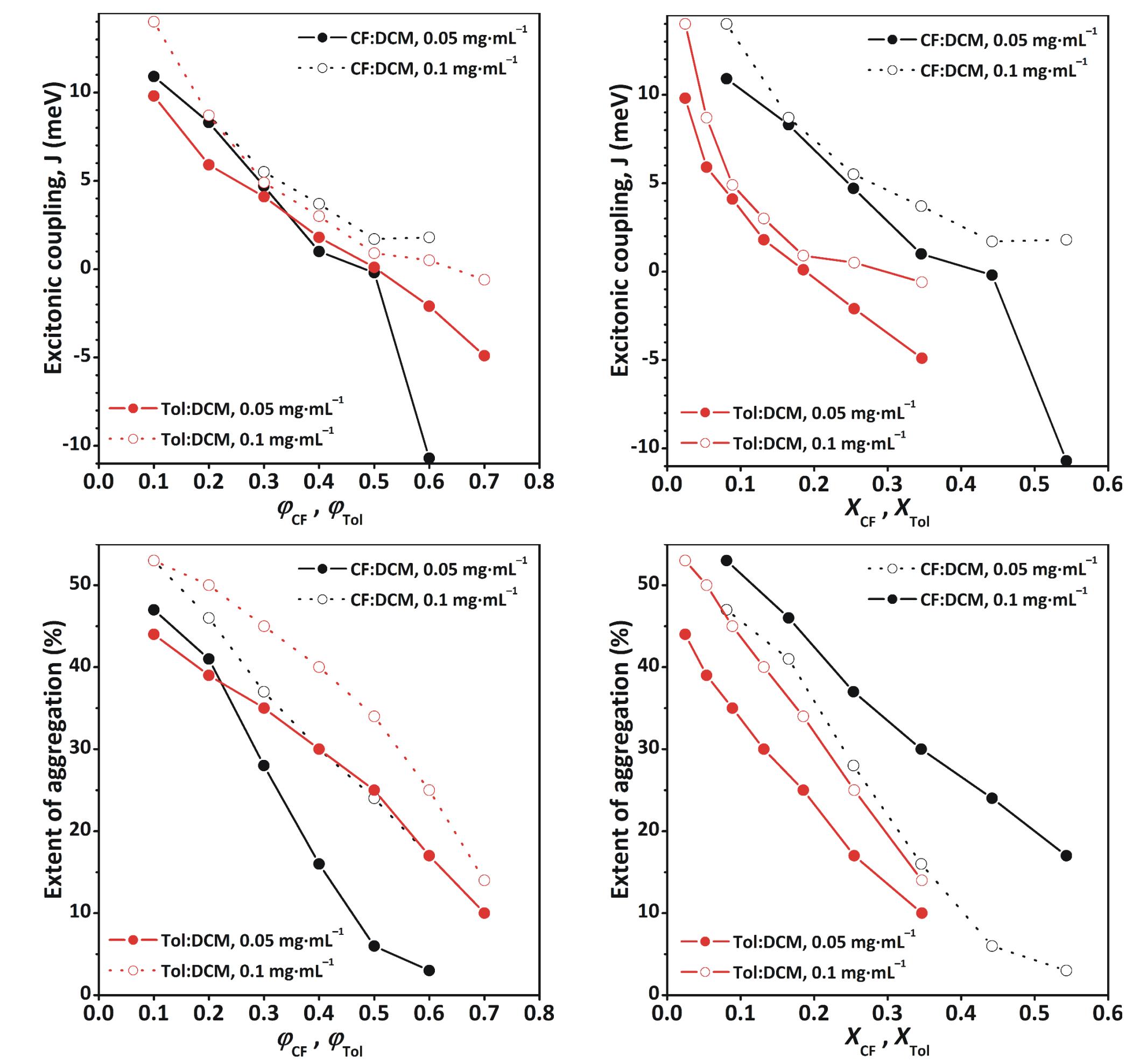
In CF:DCM solvents, the extent of aggregation is more sensitive to P3HT concentration when the mixtures have higher compositions of CF

Interestingly, in blends with higher amounts of DCM (< 30:70) the J values and extent of aggregation are comparable for both CF:DCM and Tol:DCM mixtures

It appears that when a "threshold" composition of DCM is reached in the solvent blend the "goodness" of the good solvent (CF and Tol) does not significantly impact the extent of aggregation or the structural order (J values) of the aggregates.

Absorbance Spectra of P3HT Films (cont.)

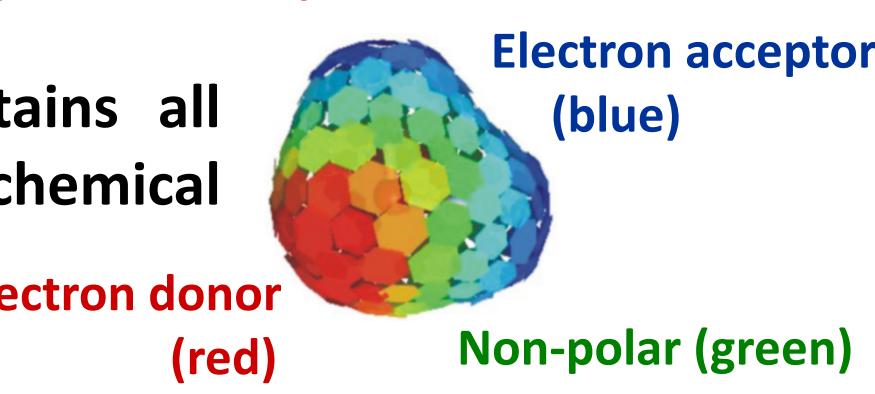
The disparity (or similarity) between the J values and extent of aggregation is emphasized when plotted against the mole fraction (X) and volume fraction (ϕ) of the good solvent.



It is unclear whether it is best to evaluate these two quantities in terms of X or ϕ .

Theory: COSMO-RS

Conductor-like Screening MOdel for Real Solvents (COSMO-RS) calculations

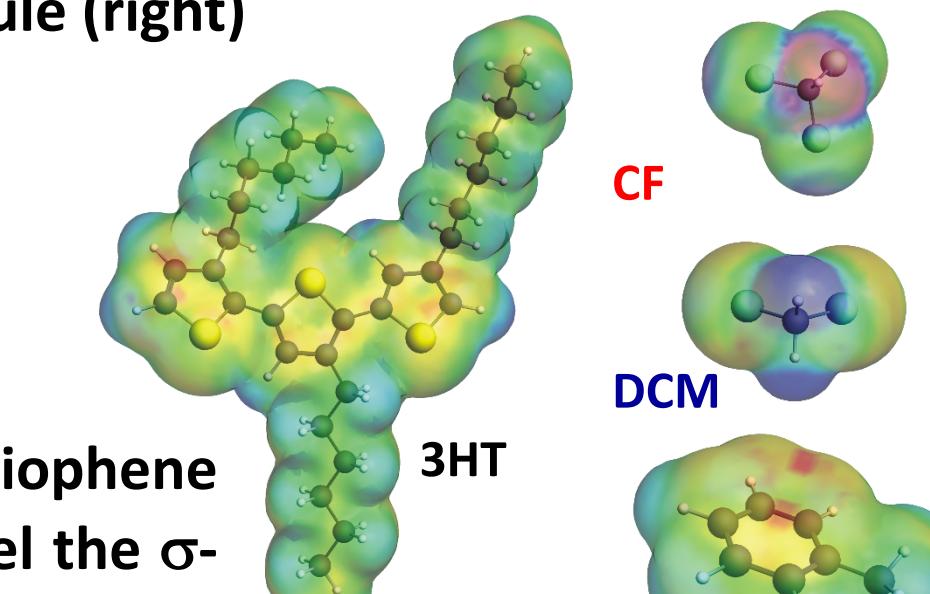


The screening charge density surface (σ -surface) contains all relevant information for COSMO-RS to calculate the chemical potential, μ

- A molecule (right) is represented by its σ -surface.

Interactions are based on surface segments, with screening charge σ

- σ -profile (σ distribution): histogram of charged surface segments of a molecule (right)



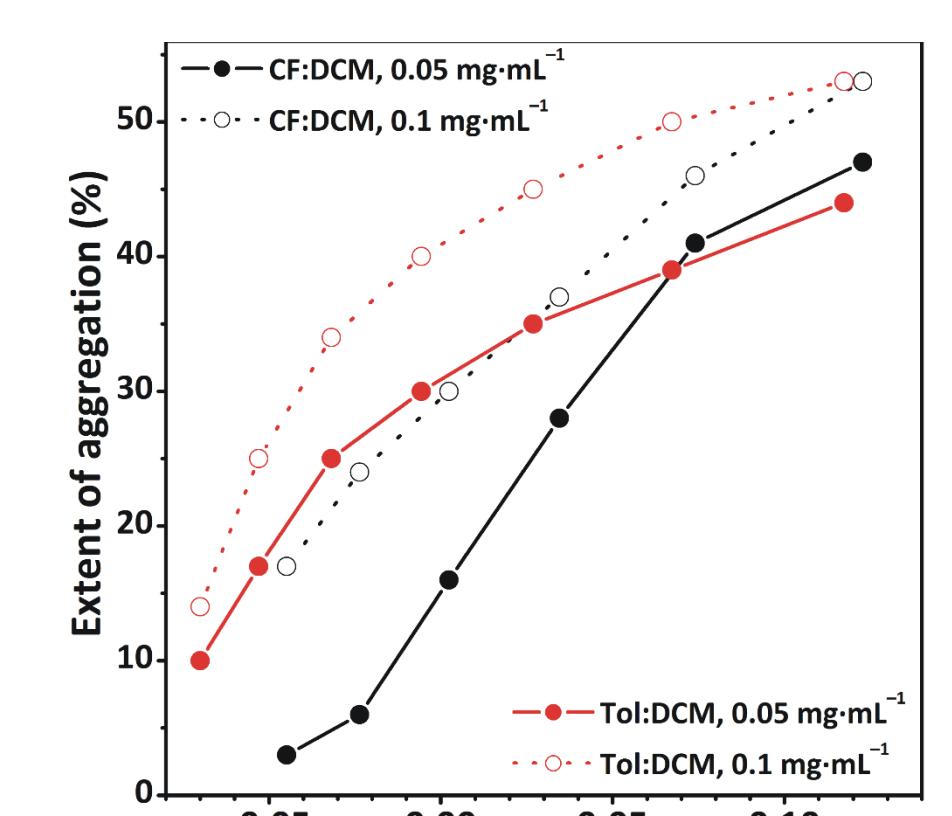
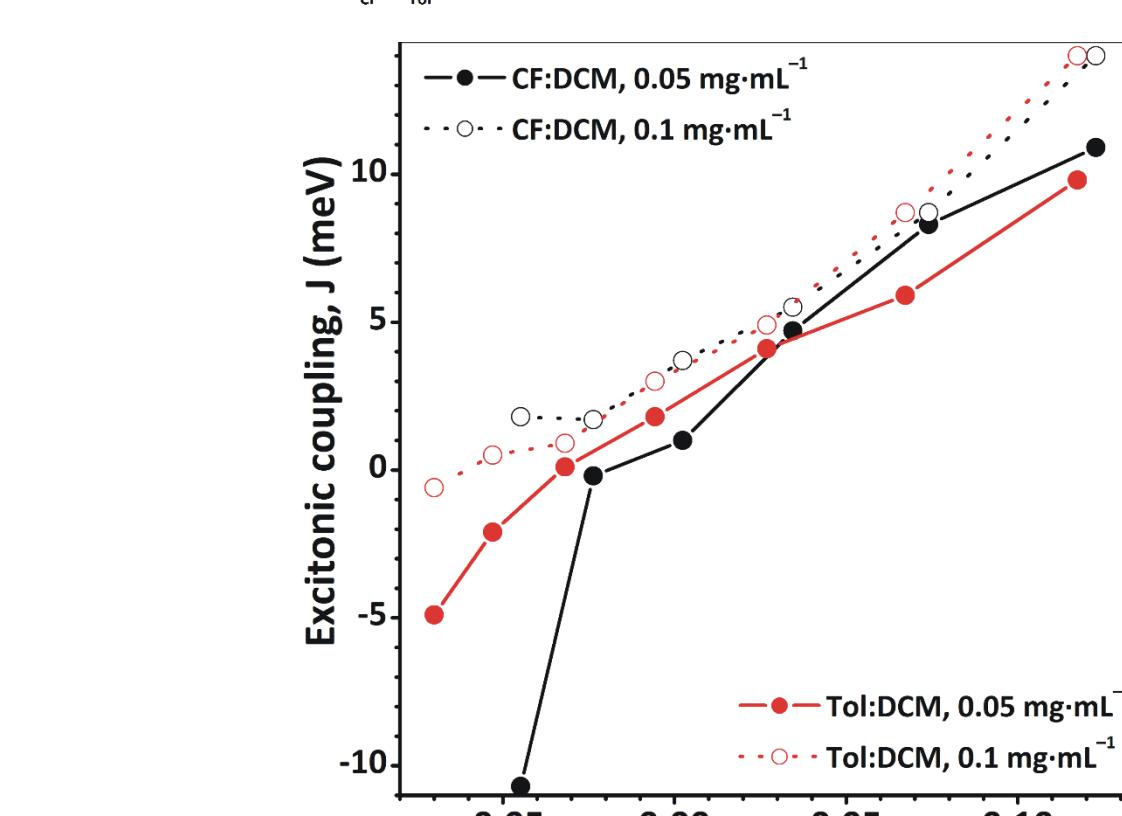
We used a 3-hexylthiophene trimer (3HT) to model the σ -surface of P3HT

Activity Coefficients (γ): Solubility and Stability (Ideality) of the Solutions

The chemical potential, μ , and mole fraction solubility, X_s , of a solute in solution is related to the activity coefficient, γ ,

$$\mu_i^{(\text{solution})} = \mu_i^{(\text{pure})} + RT \cdot \ln(\gamma)$$

$$\ln(X_s) = -\ln(\gamma) + \frac{\Delta H_{\text{fus}}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)$$



Acknowledgements

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