# Supporting Information to: Structure of P3HT crystals, thin films, and solutions by UV/Vis spectral analysis

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## 1. LITERATURE SURVEY OF P3HT UV-VIS ABSORPTION DATA

TABLE S1: Experimentally observed absorption band energies of P3HT in eV reported in literature together with the ratio of intensities of the hypothetical "0-0" and "0-1" vibrational transitions, $I_{0-0}/I_{0-1}$, as discussed in, e.g., Spano et al. [1]; the mass of the polymer as well as the solvent is given whenever possible (entries in brackets indicate solvent used for spin coating).

| | | | "crystal" | | | "thin film" | | | | "solution" |
|---|---|---|---|---|---|---|---|---|---|---|
| source | $M_W$/kDa | solvent[a)] | 0-0 | 0-1 | $\frac{I_{0-0}}{I_{0-1}}$ | 0-0 | 0-1 | max | $\frac{I_{0-0}}{I_{0-1}}$ | max |
| Rahimi et al. (2014) [2]: | | | | | | | | | | |
| single crystal | 26.4 | n/a | 1.82 | 2.10 | 2.2 | - | - | - | - | - |
| thin film | ditto | (3HT) | - | - | - | 2.06 | 2.23 | 2.36 | 0.8 | - |
| solution | ditto | 3HT | - | - | - | - | - | - | - | 2.72 |
| Paquin et al. (2013) [3]: | | | | | | | | | | |
| thin film | 12.4 | (p-xylene) | - | - | - | 2.05 | 2.25 | 2.40 | 0.6 | - |
| thin film | 264.0 | (ditto) | - | - | - | 2.00 | 2.20 | 2.38 | 0.95 | - |
| Niles et al. (2012) [4]: | | | | | | | | | | |
| thin film | 50-65 | (toluene) | - | - | - | 2.06 | 2.24 | 2.39 | 0.65 | - |
| nanofibers | ditto | toluene | - | - | - | 2.01 | 2.19 | 2.36 | 1.0 | - |
| Scharsich et al. (2012) [5]: | | | | | | | | | | |
| solution (74mer) | 21.6 | $CHCl_3$ | - | - | - | - | - | - | - | 2.75 |
| solution (43mer) | 15.2 | $CHCl_3$ | - | - | - | - | - | - | - | 2.75 |
| solution (19mer) | 6.3 | $CHCl_3$ | - | - | - | - | - | - | - | 2.85 |
| solution (74mer) | 21.6 | 90 % EtAc | - | - | - | 2.05 | 2.22 | 2.35 | 0.8 | - |
| solution (43mer) | 15.2 | 90 % EtAc | - | - | - | 2.05 | 2.25 | 2.35 | 0.8 | - |
| solution (19mer) | 6.3 | 90 % EtAc | - | - | - | - | - | - | - | 2.65 |
| Hu et al. (2009) [6]: | | | | | | | | | | |
| solution | ?[b)] | THF | - | - | - | - | - | - | - | 2.78 |
| suspension | ditto | $THF/H_2O$ | - | - | - | 2.10 | 2.25 | 2.47 | 0.6 | - |
| Shrotriya et al. (2009) [7]: | | | | | | | | | | |

*continued on next page*

TABLE S1: (contd.) Experimentally observed absorption band energies of P3HT in eV reported in literature together with the ratio of intensities of the hypothetical "0-0" and "0-1" vibrational transitions, $I_{0-0}/I_{0-1}$, as discussed in, e.g., Spano et al. [1]; the mass of the polymer as well as the solvent is given whenever possible (entries in brackets indicate solvent used for spin coating).

| | | | "crystal" | | | "thin film" | | | | "solution" |
|---|---|---|---|---|---|---|---|---|---|---|
| source | $M_W$/kDa | solvent[a)] | 0-0 | 0-1 | $\frac{I_{0-0}}{I_{0-1}}$ | 0-0 | 0-1 | max | $\frac{I_{0-0}}{I_{0-1}}$ | max |
| thin film | ?[b)] | (DCB) | - | - | - | 2.17 | 2.39 | 2.51 | 0.7 | - |
| solution | ditto | DCB | - | - | - | - | - | - | - | 3.41 |
| Manceau et al. (2009) [8]: | | | | | | | | | | |
| thin film | ?[b)] | CB | - | - | - | 2.07 | 2.25 | 2.38 | 0.65 | - |
| Motaung et al. (2009) [9]: | | | | | | | | | | |
| solution | 64.0 | $CHCl_3$ | - | - | - | 2.12 | 2.30 | 2.45 | 0.8 | - |
| Cook et al. (2008) [10]: | | | | | | | | | | |
| thin film | 55 | (CB) | - | - | - | 2.05 | 2.23 | 2.39 | 0.6 | - |
| solution | ditto | CB | - | - | - | - | - | - | - | 2.72 |
| Clark et al. (2007) [11]: | | | | | | | | | | |
| solution | ?[b)] | $CHCl_3$ | - | - | - | - | - | - | - | 2.74 |
| solution, 70° C | ditto | isodurene | - | - | - | - | - | - | - | 2.74 |
| solution | ditto | isodurene | - | - | - | 2.03 | 2.20 | - | 0.93 | 2.70 |
| thin film | ditto | ($CHCl_3$) | - | - | - | 2.06 | 2.24 | 2.39 | 0.68 | - |
| thin film | ditto | (isodurene) | - | - | - | 2.05 | 2.20 | 2.36 | 0.81 | - |
| Kim et al. (2006) [12]: | | | | | | | | | | |
| thin film, 95.2 % rr | 21.9 | (CB) | - | - | - | 2.05 | 2.21 | 2.37 | 0.7 | - |
| thin film, 93.0 % rr | 31.9 | (CB) | - | - | - | 2.05 | 2.21 | 2.37 | 0.6 | - |
| thin film, 90.7 % rr | 45.9 | (CB) | - | - | - | 2.05 | 2.21 | 2.39 | 0.5 | - |

*continued on next page*

TABLE S1: (contd.) Experimentally observed absorption band energies of P3HT in eV reported in literature together with the ratio of intensities of the hypothetical "0-0" and "0-1" vibrational transitions, $I_{0-0}/I_{0-1}$, as discussed in, e.g., Spano et al. [1]; the mass of the polymer as well as the solvent is given whenever possible (entries in brackets indicate solvent used for spin coating).

| | | | "crystal" | | | "thin film" | | | | "solution" |
|---|---|---|---|---|---|---|---|---|---|---|
| source | $M_W$/kDa | solvent[a)] | 0-0 | 0-1 | $\frac{I_{0-0}}{I_{0-1}}$ | 0-0 | 0-1 | max | $\frac{I_{0-0}}{I_{0-1}}$ | max |
| Brown et al. (2003) [13]: | | | | | | | | | | |
| thin film | ?[b)] | ($CHCl_3$) | - | - | - | 2.09 | 2.27 | 2.37 | 0.69 | - |
| thin film, regio-random | ditto | ($CHCl_3$) | - | - | - | 2.09 | 2.72 | 3.05 | 0.25 | - |
| this work: | | | | | | | | | | |
| solution | 65±10 | $CHCL_3$ | - | - | - | - | - | - | - | 2.75 |
| solution | ditto | 50 % EtAc | - | - | - | 2.03 | 2.17 | 2.37 | 0.89 | - |
| thin film | ditto | (CB) | - | - | - | 2.05 | 2.23 | 2.40 | 0.57 | - |
| Macchi et al. (2009): [14] | | | | | | | | | | |
| 4T[a)] | 0.33 | n-tDc | - | - | - | - | - | - | - | 3.19 |
| diMe-4T | 0.36 | ditto | - | - | - | - | - | - | - | 3.24 |
| tetraMe-4T | 0.39 | ditto | - | - | - | - | - | - | - | 3.51 |
| 4T, 4 K | 0.33 | ditto | - | - | - | 2.78 | 2.93 | 3.13 | 0.95 | - |
| diMe-4T, 4 K | 0.36 | ditto | - | - | - | 2.80 | 2.98 | 3.19 | 0.73 | - |
| tetraMe-4T, 4 K | 0.39 | ditto | - | - | - | 2.78 | 2.95 | 3.15 | 0.73 | - |

[a)] 3HT = 3-hexyl-thiophene, EtAc = ethylacetate, THF = tetrahydrofuran, CB = chlorobenzene, DCB = 1,2-dichlorobenzene, tDc = tetradecane, 4T = quaterthiophene [b)] not specified

## 2. COMPARISON OF RANGE-SEPARATED FUNCTIONALS

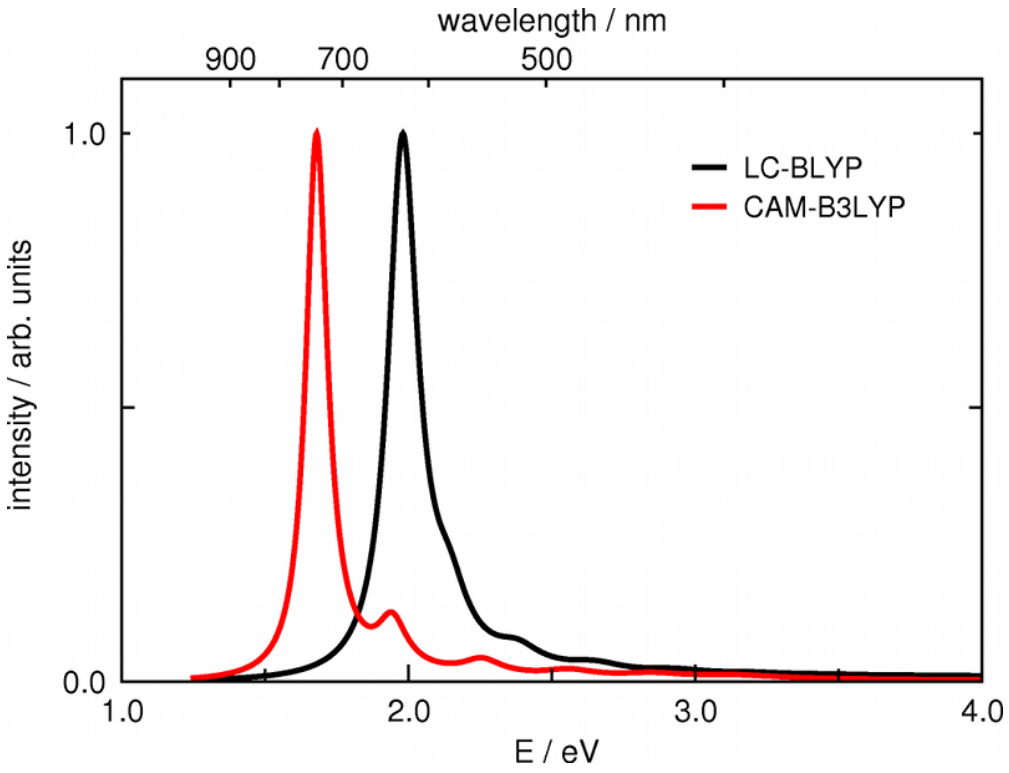


FIG. S1: Comparison of normalised TDDFT absorption spectra for a P3HT 32mer in planar crystal geonetry using the LC-BLYP and CAM-B3LYP functionals with the 6-31G* basis set. Hexyl groups were replaced by methyl groups.

## 3. ENVIRONMENTAL EFFECTS

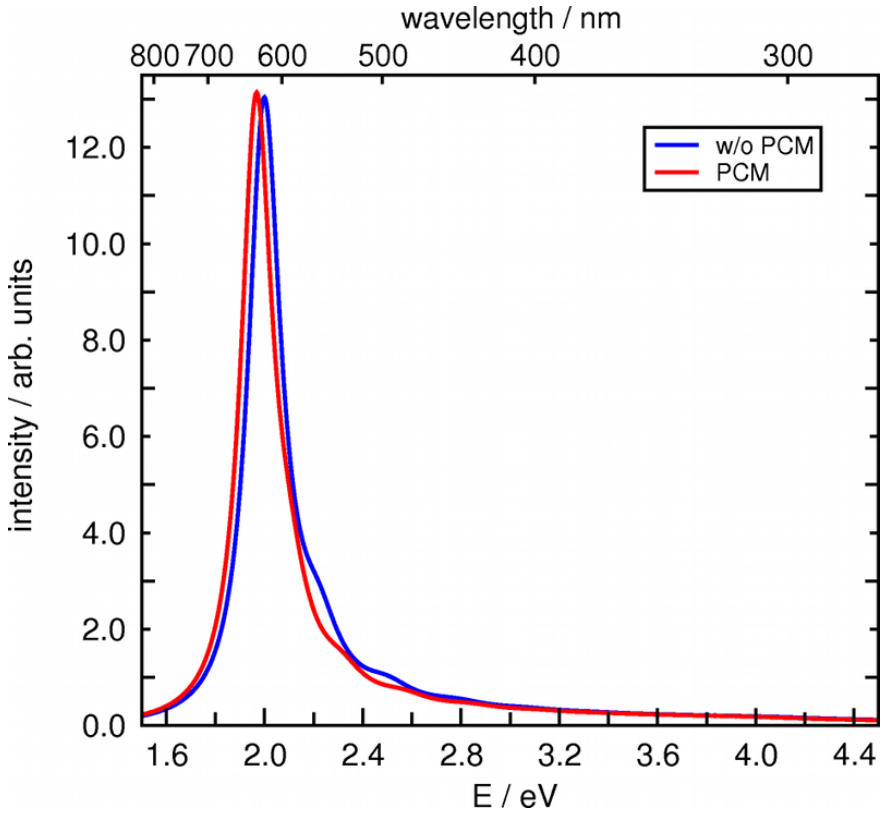


FIG. S2: Crystal spectrum calculated using TDDFT/LC-BLYP/6-31G* with and without the PCM model for the environment. Hexyl groups were replaced by methyl groups.

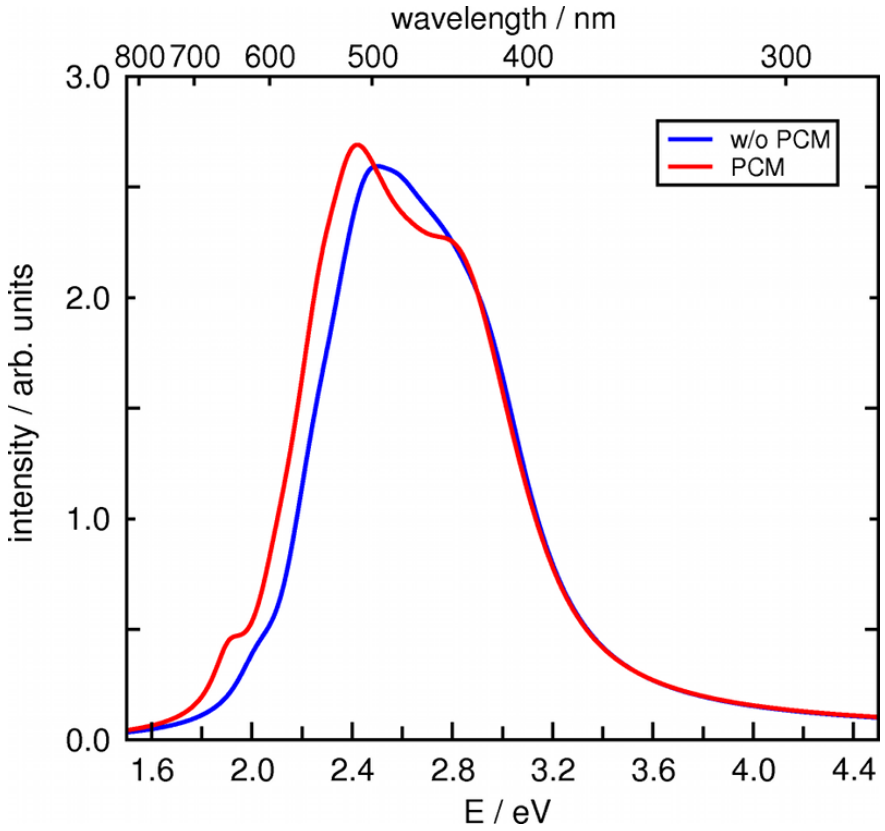


FIG. S3: Averaged thin film spectra calculated using TDDFT/PBE0/6-31G* with and without the PCM model for the solvent.

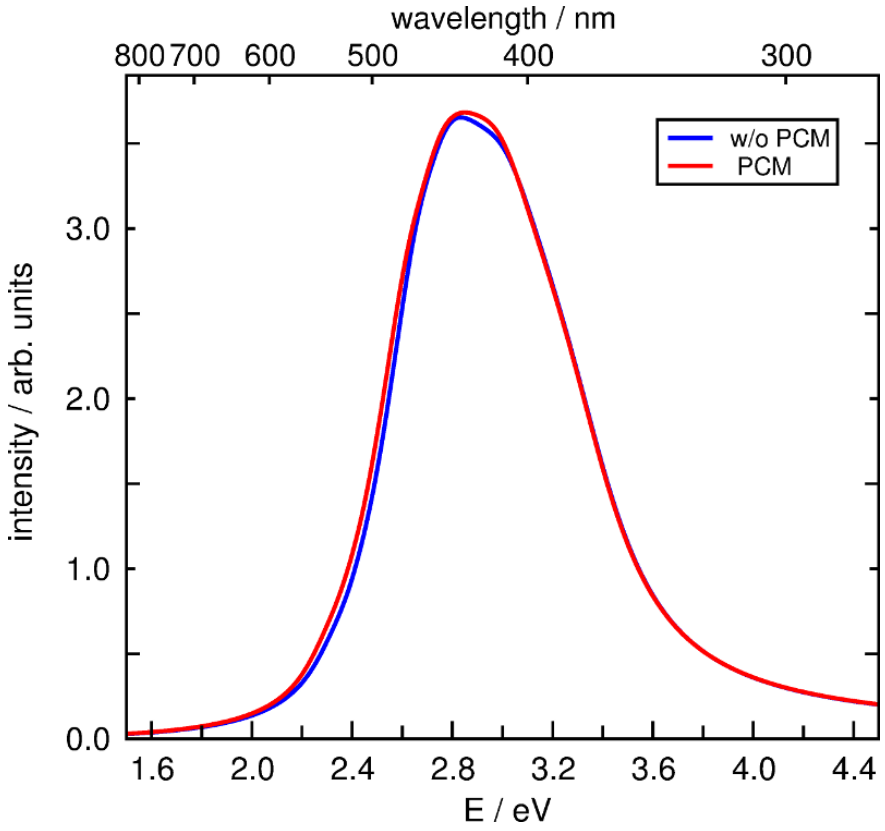


FIG. S4: Averaged solution spectra calculated using TDDFT/PBE0/6-31G* with and without the PCM model for the solvent.

## 4. FRONTIER MOS OF THIN FILM STRUCTURES

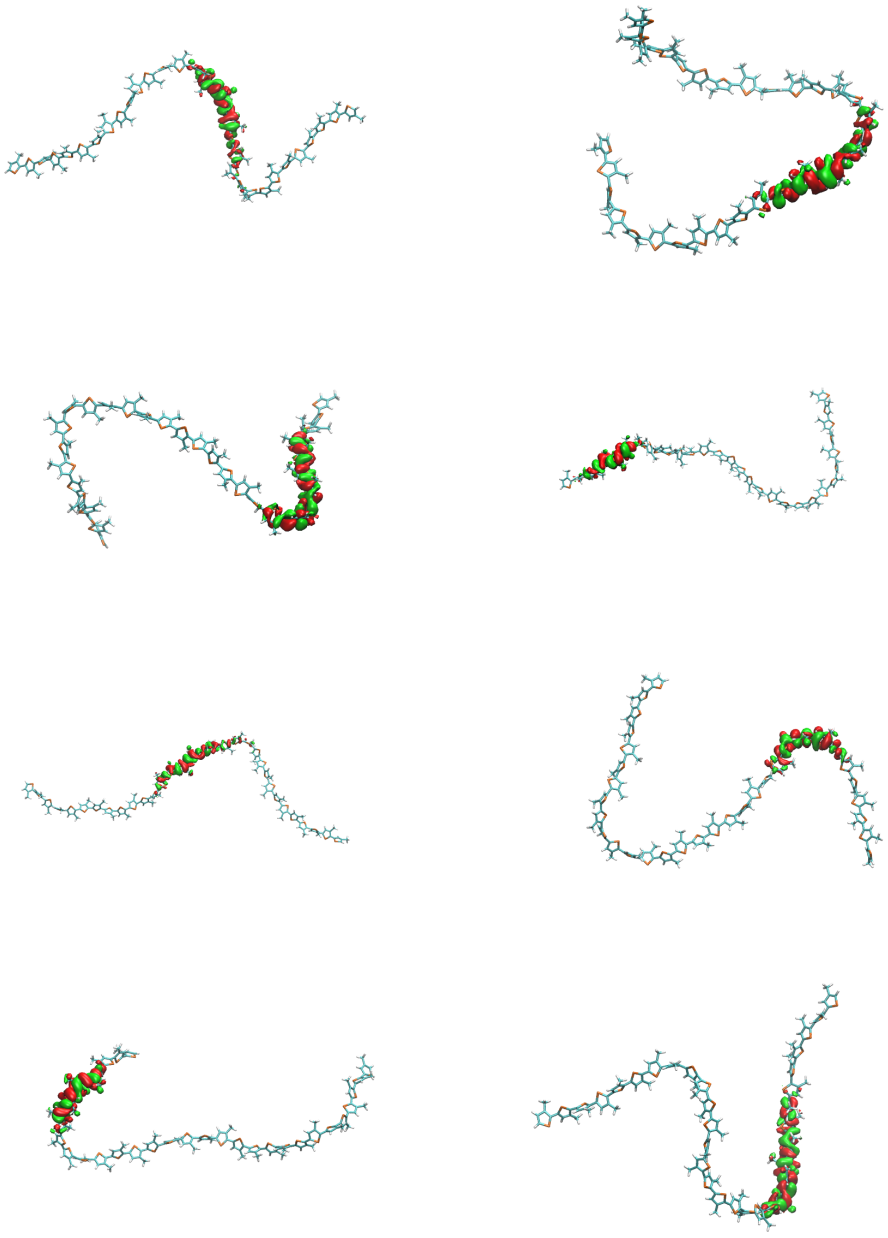

FIG. S5: Highest occupied molecular orbitals (HOMOs) of randomly selected amorphous P3HT chains calculated with PBE0/6-31G*.

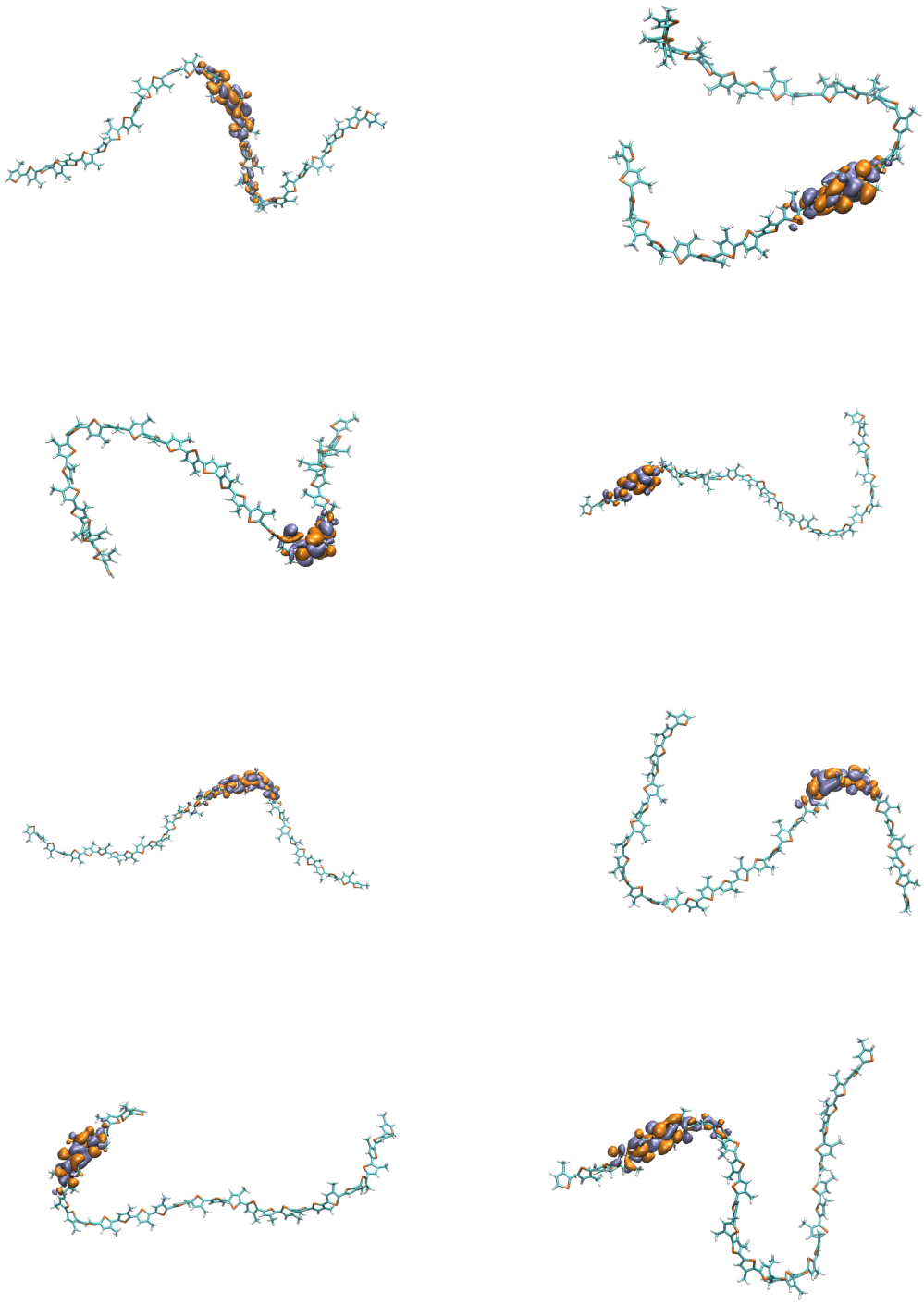

FIG. S6: Lowest unoccupied molecular orbitals (LUMOs) of randomly selected amorphous P3HT chains calculated with PBE0/6-31G*.

## 5. FRONTIER MOS OF SOLUTION STRUCTURES

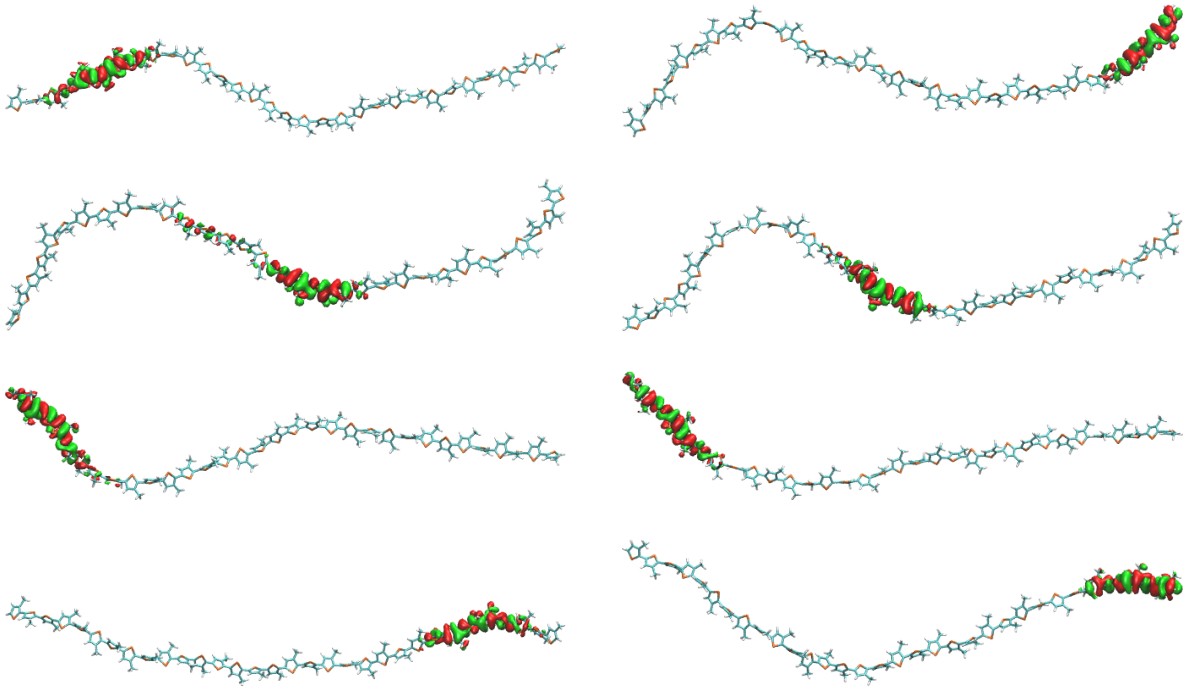

FIG. S7: Highest occupied molecular orbitals (HOMOs) of randomly selected solute P3HT chains calculated with PCM/PBE0/6-31G*.

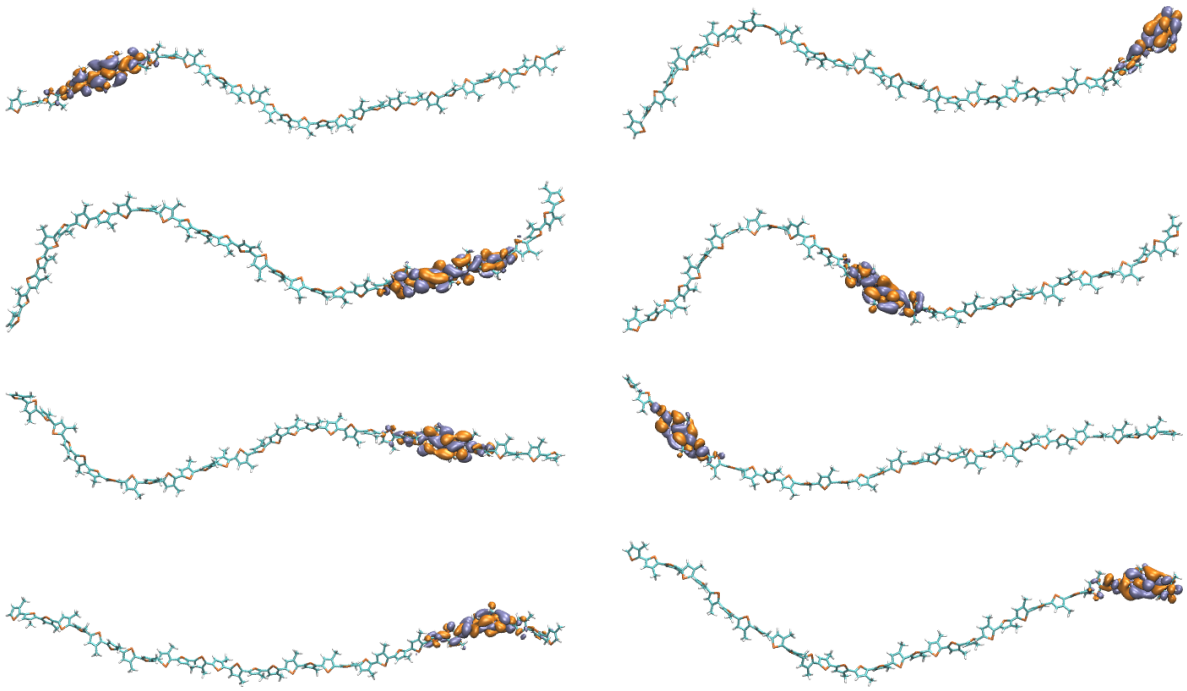

FIG. S8: Highest unoccupied molecular orbitals (LUMOs) of randomly selected solute P3HT chains calculated with PCM/PBE0/6-31G*.

## 6. FRONTIER ORBITALS OF 3-ME-THIOPHENE

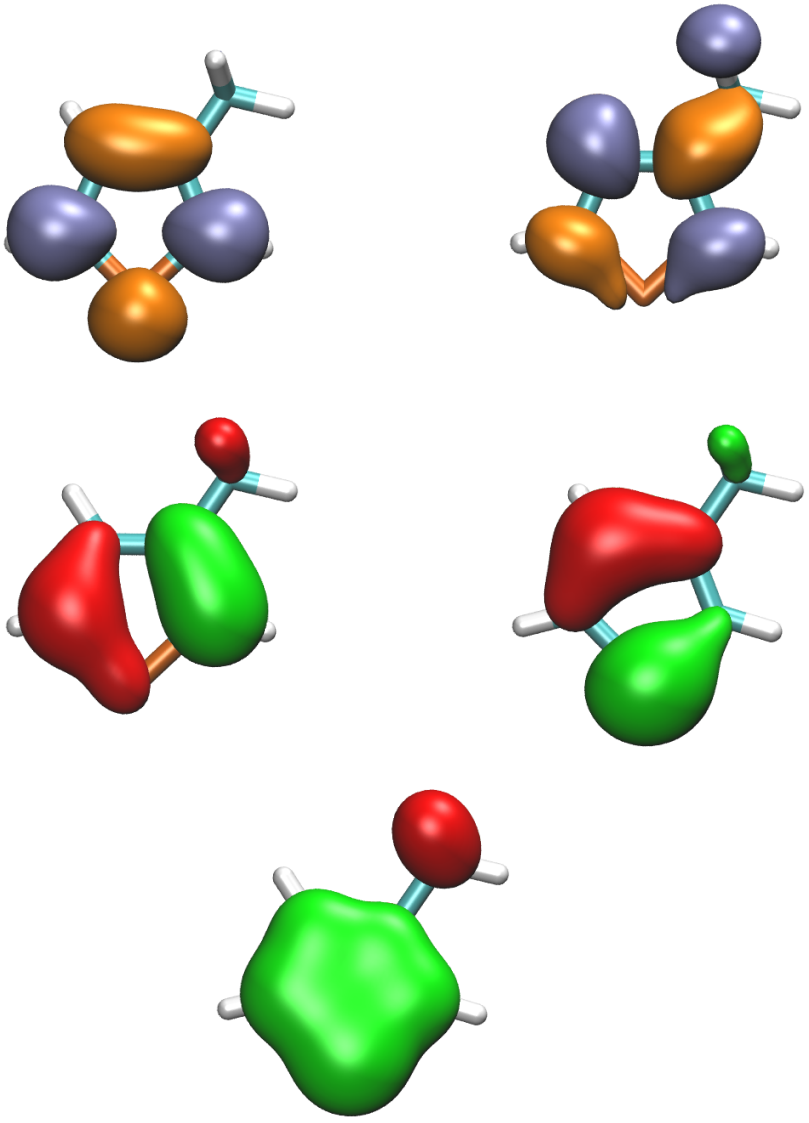


FIG. S9: Frontier orbitals of 3-Methyl-thiophene calculated with B3LYP/6-31G* showing the nodal structure of the $\pi$-system MOs.

## 7. INDIVIDUAL UV-VIS SPECTRA OF THIN FILM STRUCTURES

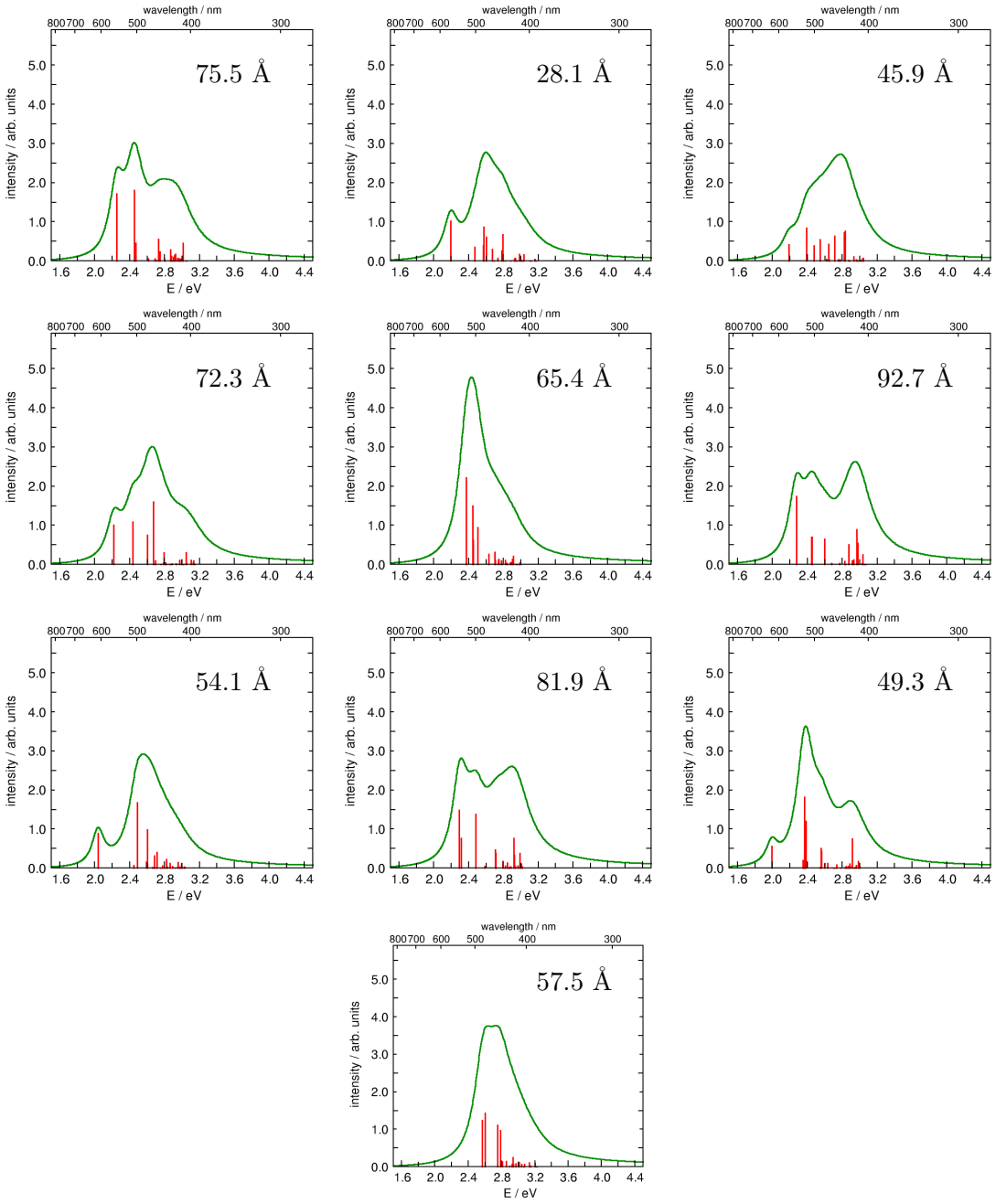


FIG. S10: P3HT thin film: individual TDDFT/6-31G* UV-vis spectra of the 10 selected structures. Band shape (green) obtained from calculated line spectrum (red) with Lorentzian broadening (FWHM = 50 nm). The end-to-end distance given in each graph shows no obvious correlation with the spectral shape or position.

## 8. INDIVIDUAL UV-VIS SPECTRA OF SOLUTION STRUCTURES

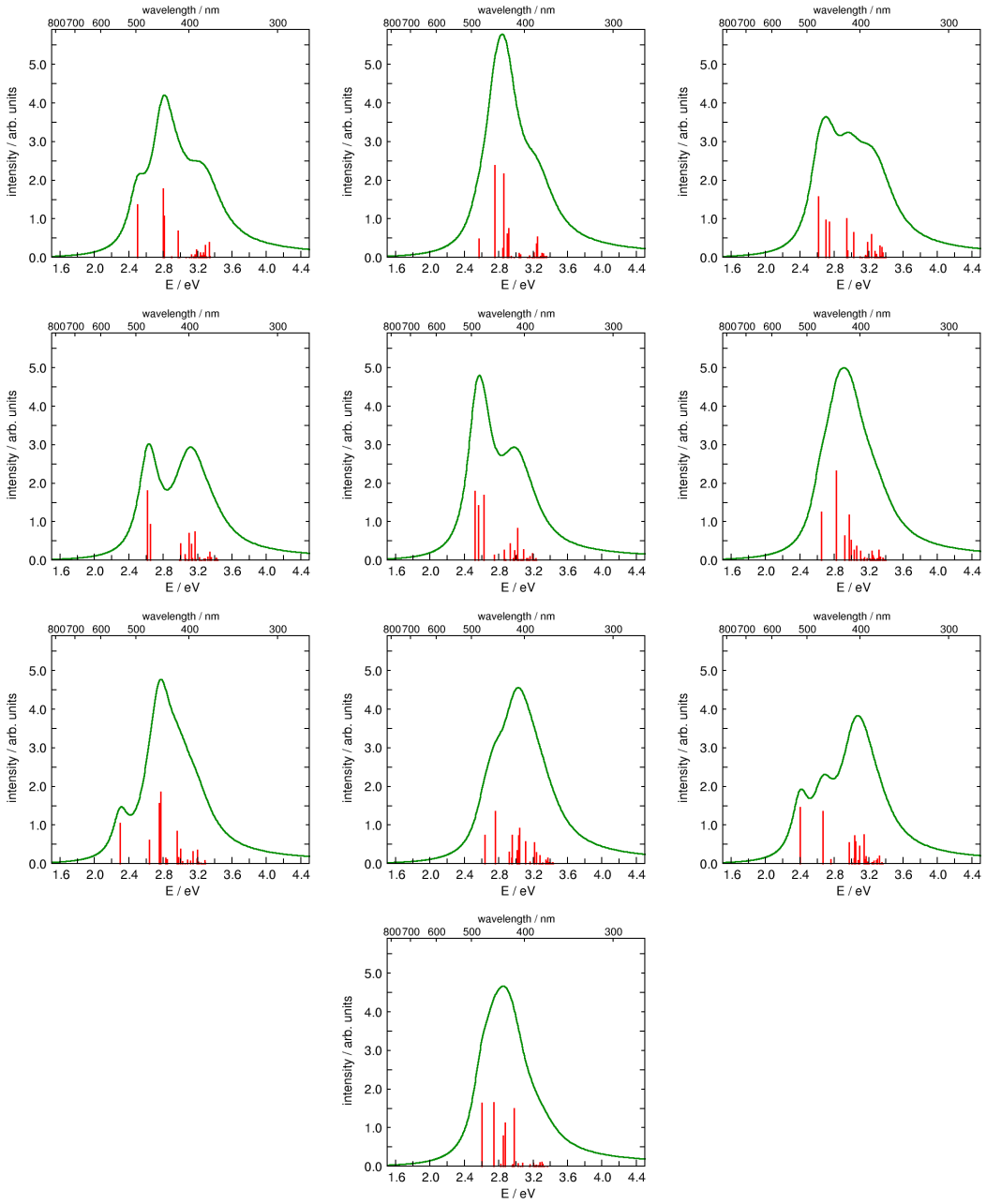


FIG. S11: P3HT solution: individual TDDFT/6-31G* UV-vis spectra of the 10 structures. Band shape (green) obtained from calculated line spectrum (red) with Lorentzian broadening (FWHM = 50 nm).

## 9. DECOMPOSITION OF EXPERIMENTAL MIXED SOLVENT SPECTRA

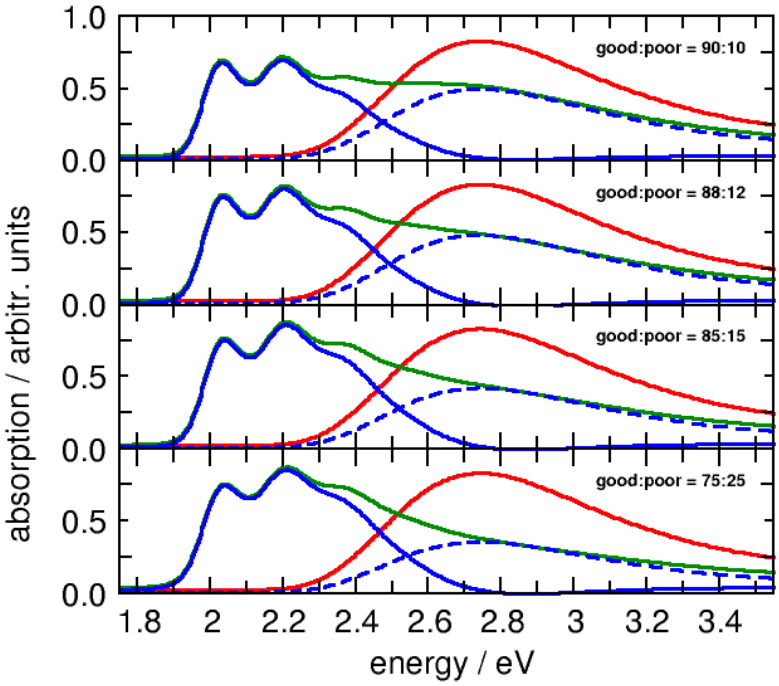


FIG. S12: Decomposition of experimental UV-vis spectra (green) in mixed solvent according to Scharsich et al. [5]. Pure 'thin film' spectrum (solid blue line) results by subtracting contribution (dashed blue line) of 'pure' solution (red).

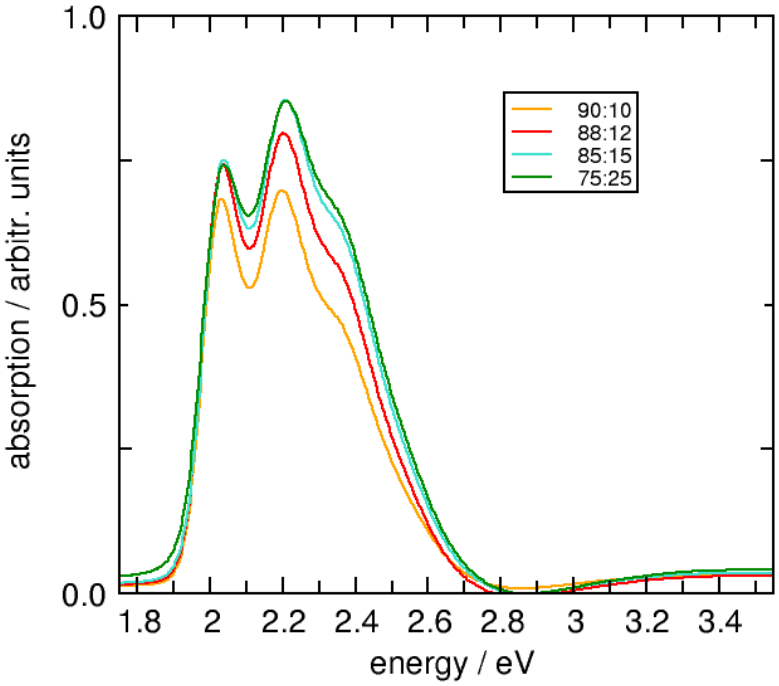


FIG. S13: Comparison of pure 'thin film' spectra obtained by the decomposition presented in Fig. S12 for different ratios of 'poor' and 'good' solvent.

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