PFO-BPy-SWCNT Hybrid Systems for Organic Solar Cells

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Introduction

Single walled carbon nanotubes (SWCNT) are promising candidates for photovoltaic (PV) active layers[1-3] in organic solar cells. To obtain high on/off current ratios, enriched semiconducting SWCNT solutions not containing metallic SWCNT are favourable. Solubilizers[4] are found to selectively disperse SWCNTs. The copolymer of 9,9-di-octylfluorenyl-2,7-diyl and bipyridine (PFO-BPy) delivers dispersions containing 97% (6,5)-SWNT[5]. The first part of our theoretical investigations is focused on modeling the PFO-BPy-SWCNT hybrid system to gain information about the geometries and interactions. We hope to find explanations for the selective adsorption of the polymer on the chiral (6,5)-SWCNT. In a second step we are focused on the absorbance and electron-hole dynamics to understand the hybrid system and tune its optical absorption.

Methodology

All total energy calculations and structure optimizations have been performed with the real-space density functional theory (DFT) code GPAW[6], which is based on the projector augmented wave method. We use a grid spacing of 0.2 Å for representing the density and wave functions, and the PBE exchange and correlation functional[7].

The spectra were modelled from the transition dipole matrix elements, which were calculated within linear response time dependent DFT[8]. Only singlet states were considered.
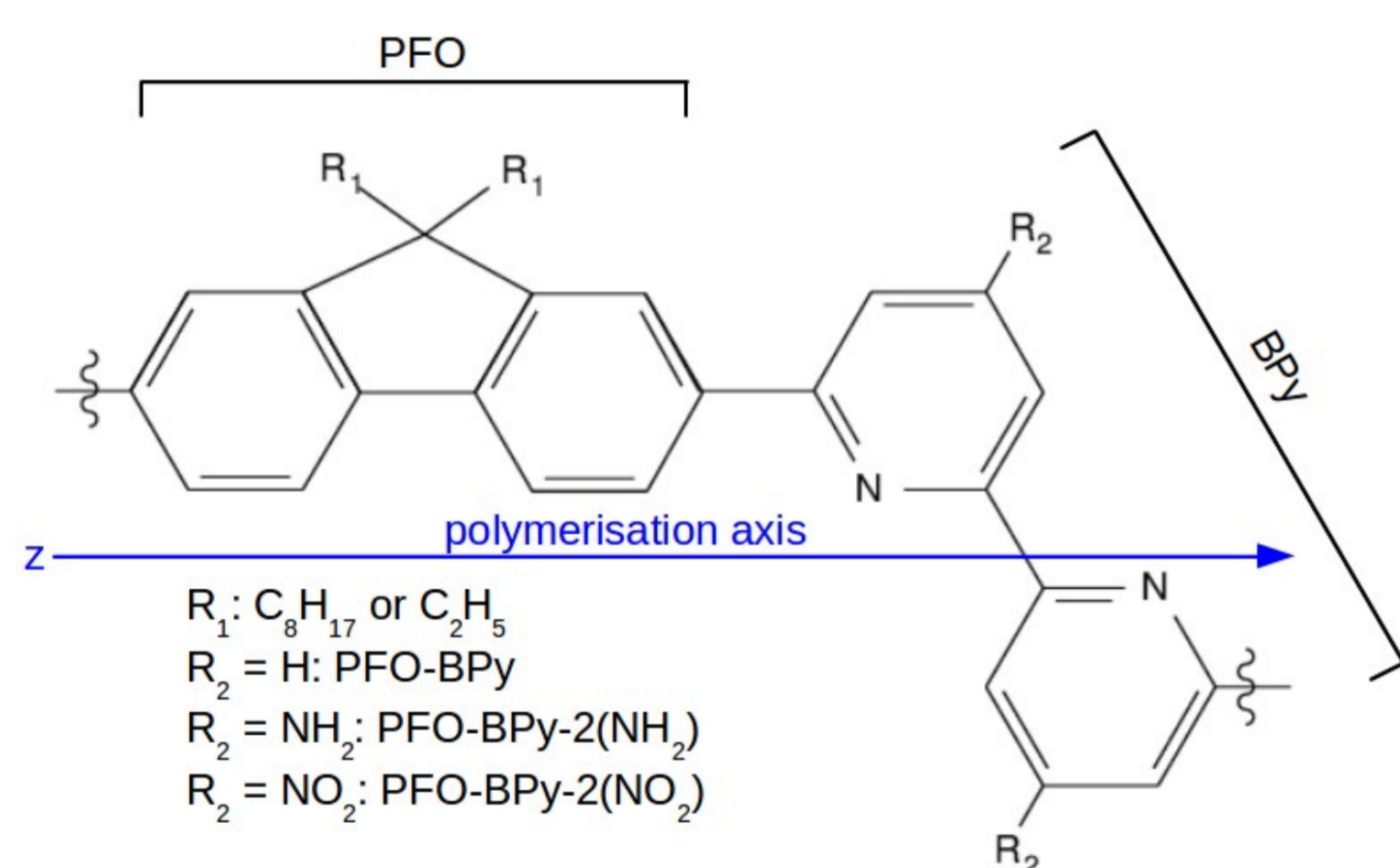

Figure 3: PFO-BPy aligned in three different orientations with respect to the (6,6)-SWCNT: (a) xz-plane perpendicular to the SWCNT axis; (b) yz-plane perpendicular to the SWCNT axis; (c) yx-plane perpendicular to the SWCNT axis.

Hetero Junction

The calculations revealed that the polymer units are interacting with the SWCNTs in all the orientations shown in figure 3, were the hetero junction showed in 3 (c) is the lowest in energy. Recent polarized absorption spectroscopy[9] showed the polymer only absorbs light polarized parallel to that absorbed by the SWCNT (figure 4). Since the SWCNTs only absorb light polarized along the tube axis, this suggests that the orientation shown in figure 3 (c) is the most probable. This is as well consistent with the results from our DFT calculations including Van der Waals.

Figure 4: Results of polarized absorbtion spectroscopy of PFO-BPy (6,5)-SWCNT probe in polysterene matrix.

Setup

The chemical structure of the examined PFO-BPy polymers were calculated in the config-uration shown in figure 1. Further, the second repetition unit was turned around the polymerisation axis by 180° before being attached to the pyridine. On this structure we are able to perform periodic calculations.

Figure 1: Chemical structure of one repetition unit PFO-BPy $(PFO-BPy)_1$ and its functionalised derivatives.

Transition Dipole Moment

Figure 2 shows the calculated absorbance spectrum of a PFO-BPy polymer consisting of three repetition units (PFO-BPy)$_3$. These results show that in the UV region the polymer absorbs light polarized along the polymerisation axis, i.e. in the z-direction.
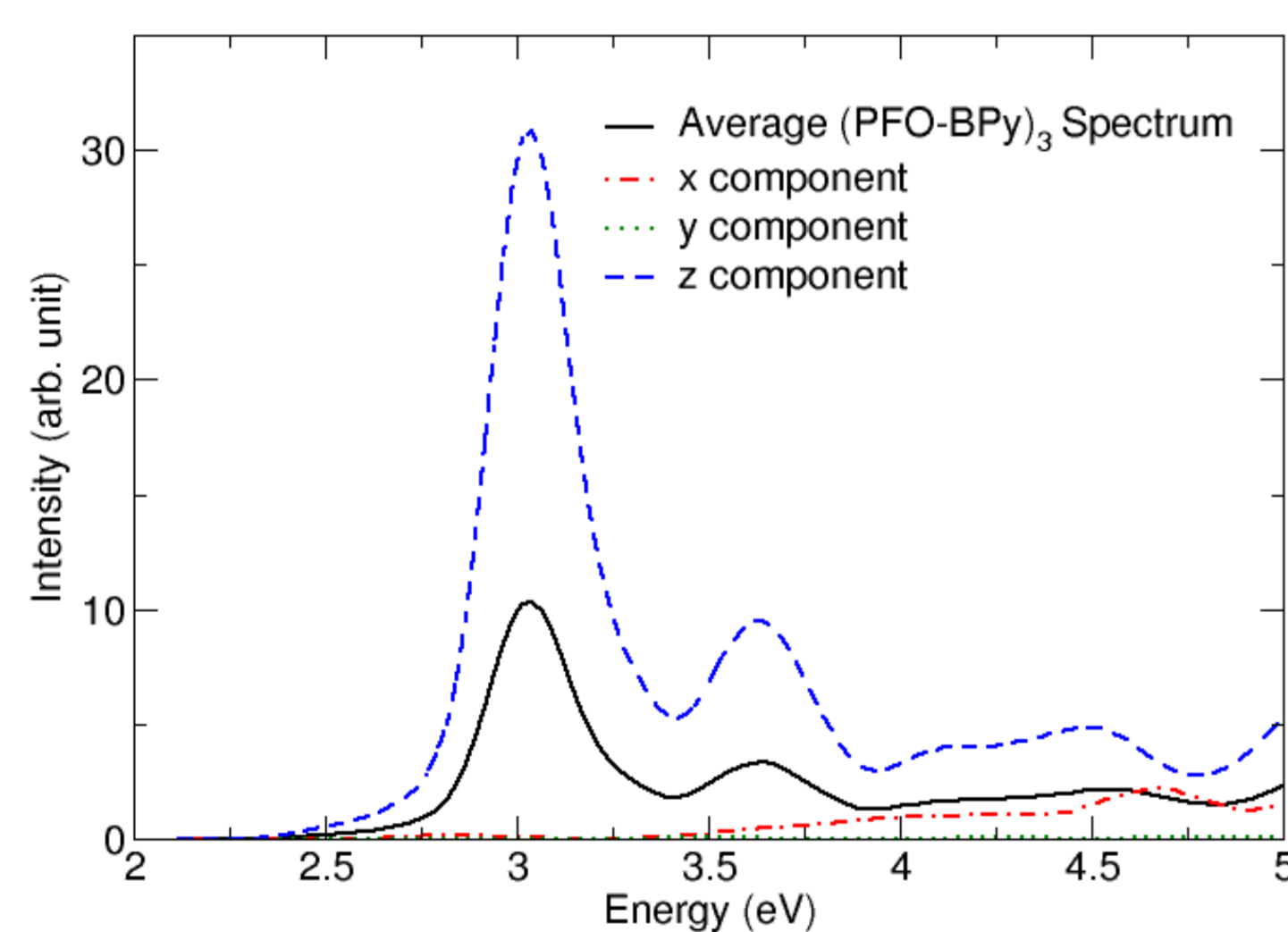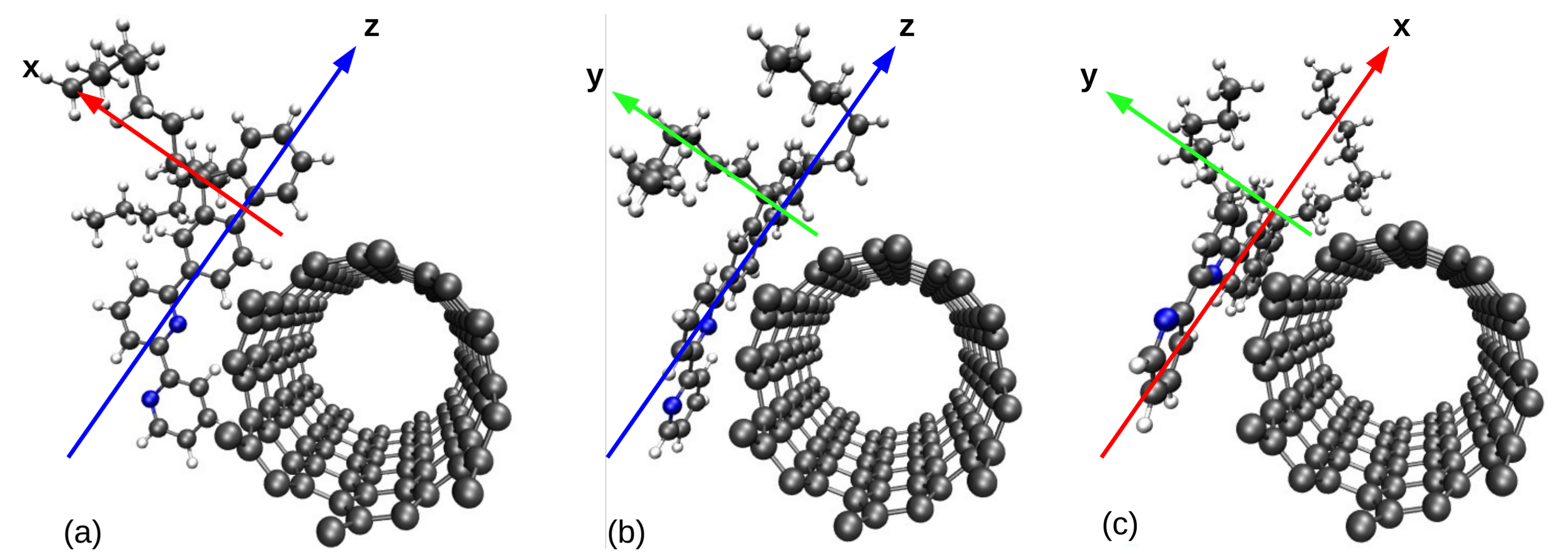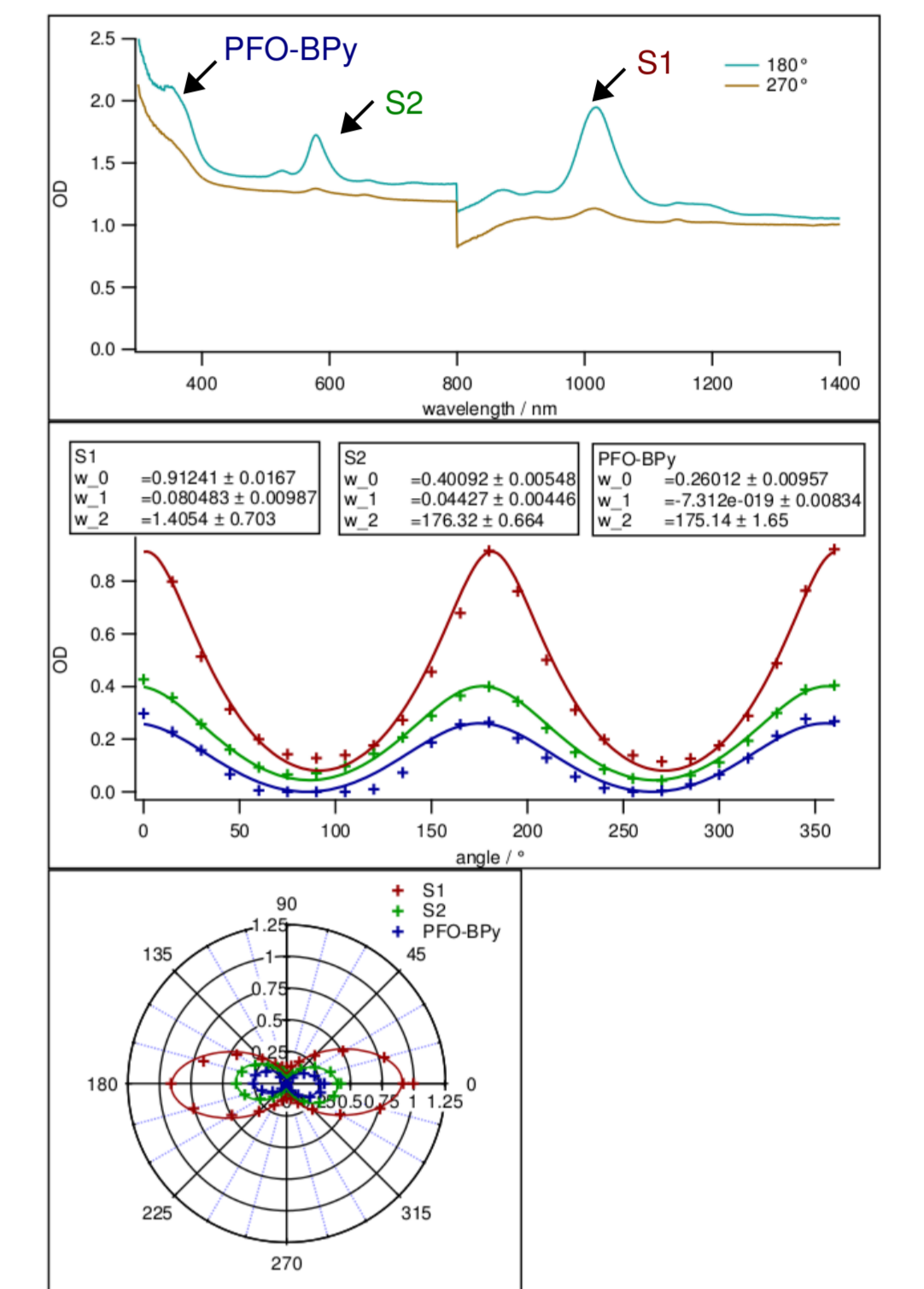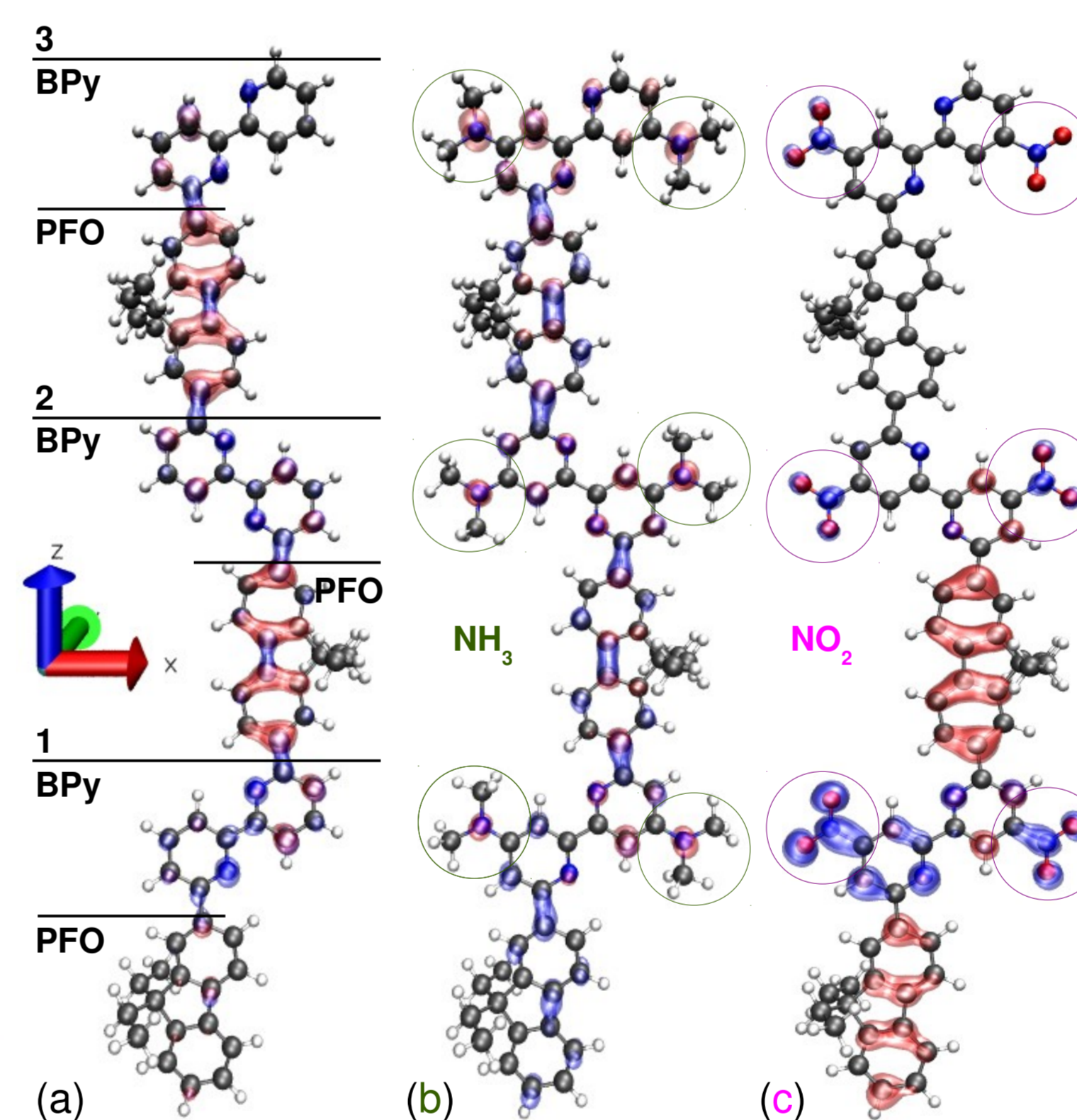

Figure 2: Calculated average absorbance spectrum of $(PFO-BPy)_3$ (black) and its components of the transition dipole moment in x (red), y (green), and z (blue).

Figure 5: Electron (blue) and hole (red) of (a) $(PFO-BPy)_3$, (b) $(PFO-BPy-2(NH_3))_3$, and (c) $(PFO-BPy-2(NO_2))_3$.

Electron-Hole-Pair

In figure 5 the polymer's electron (blue) and hole (red) densities for the transitions assigned in figure 6 are presented. For electron donating functional groups (b) the electron (blue) is spread throughout the π system, while for electron withdrawing groups (c) the density is mostly located on the functional groups. In agreement with these results, we observed an increasing separa-tion for the electron and hole from electron donating to electron withdrawing groups in different calculations.

Tuning of Absorbace

The absorbance spectra of $(PFO-BPy)_3$, $(PFO-BPy-2(NH_3))_3$, and $(PFO-BPy-2(NO_2))_3$ are shown in figure 6. The polymer including biprydine functionalised with nitro groups shows a bathochromic shifted absorbance peak around 1.76 eV.
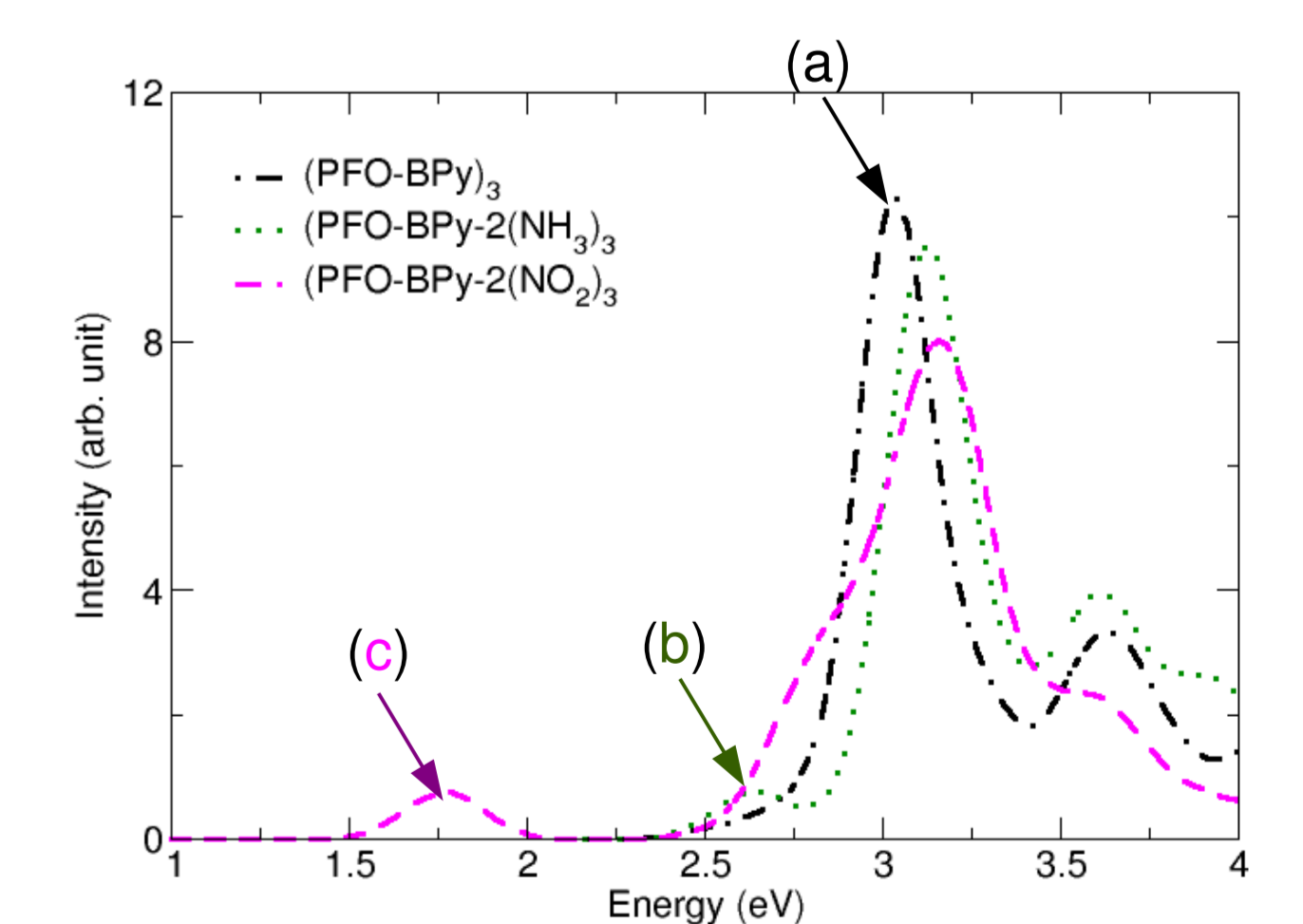

Figure 6: Absorbance spectra of $(PFO-BPy)_3$, $(PFO-BPy-2(NH_3))_3$, and $(PFO-BPy-2(NO_2))_3$.

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Conclusions

We have demonstrated *in silico* that the transition dipole moment of PFO-BPy lies along the polymerisation axis. Comparison with recent experimental results suggests that the polymer is aligned to the tube. We also find PFO-BPy polymers functionalised by electron withdrawing groups, i.e. NO_2, provide the largest red shift.

Here we provide a pathway towards the design of new materials for organic solar cells. This work was carried out in collaboration with Florian Spaeth and Tobias Hertel, whom we thank for stimulating discussions.