

Thienonaphtalimides as promising additive into organic solar cells

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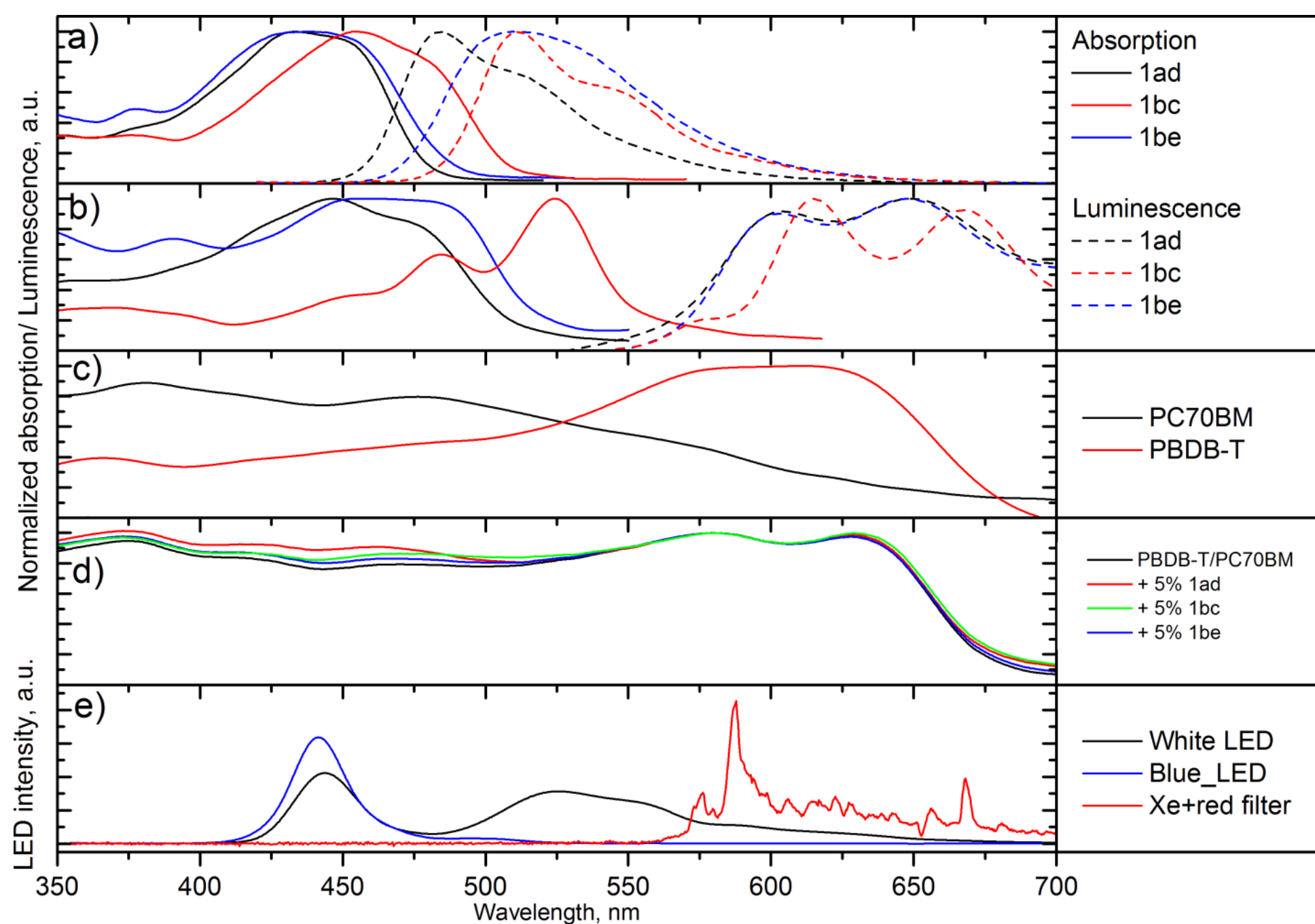
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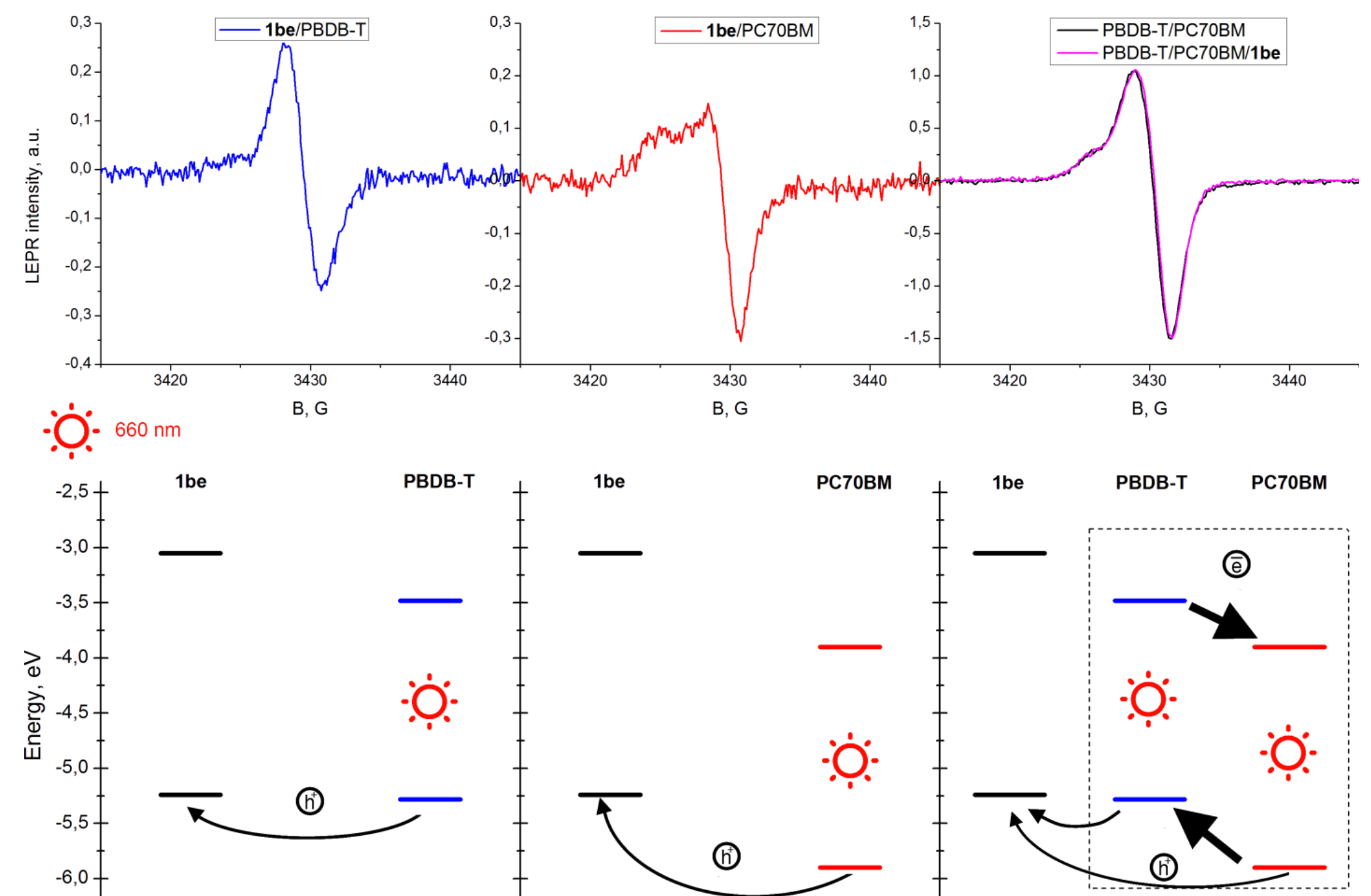
Search and application of new materials for organic photovoltaics (OPV) is promising field of investigation. Fundamental compounds such as poly(3-hexylthiophene) (P3HT) and fullerene derivative (PC60BM) have shown good performance in active layer of OPV, leading to PCE of 6 %, but for nowadays there are more perspective donors and acceptors. One of these are polymer PM6 and nonfullerene acceptor Y6 which allow to increase photovoltaic performance up to 15.7 % [1].

Different polycondensed compounds were probed in organic electronics and one of the most famous type of chemical compounds is perylene- and naphtalimides. In our lab donor molecules were synthesized based on thienonaphtalimides, bridged with various π -linkers. As it was found, additive of 5 % of **3** into PBDB-T/PC70BM active layer leads to small increment of PCE (from 17.57 % to 17.68 %), which could be explained by amplification of crystallinity of donor polymer PBDB-T.

Optical Properties



EPR Measurements



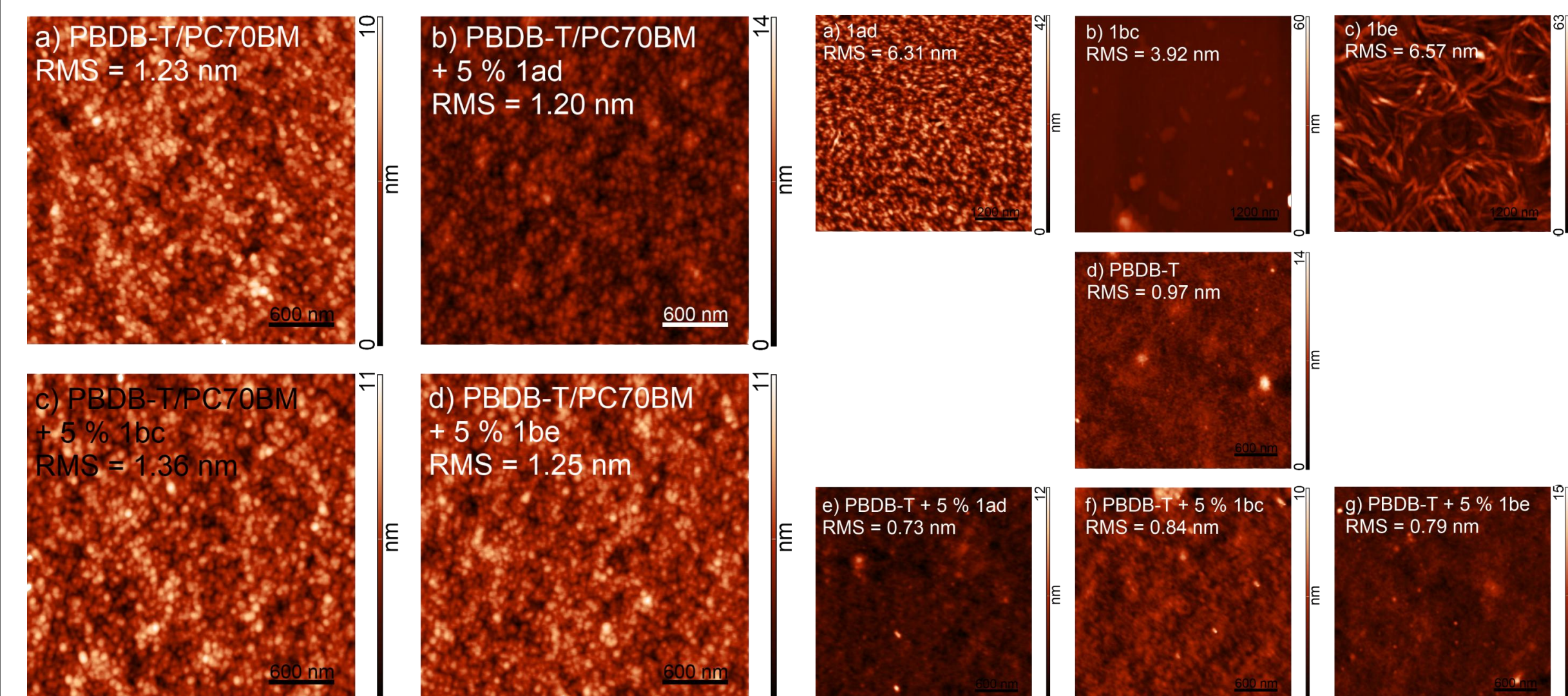
Compounds containing fluorene or carbazole bridge have quite similar shape and position of spectra but extinction coefficient is two times higher for the first one (fig. X and table X) which could be related to a presence of less donor fragment.

The highest luminescence quantum yield of 66% in solution was observed for **1be**, which could be attributed to a presence of heteroatom in central core. In thin films, all spectra are red-shifted due to formation of J-aggregates and large Stokes shift takes place. Given phenomenon is known to appear in compounds, which performs to form highly ordered structures (aggregates) due to strong intermolecular interactions in solid state [2].

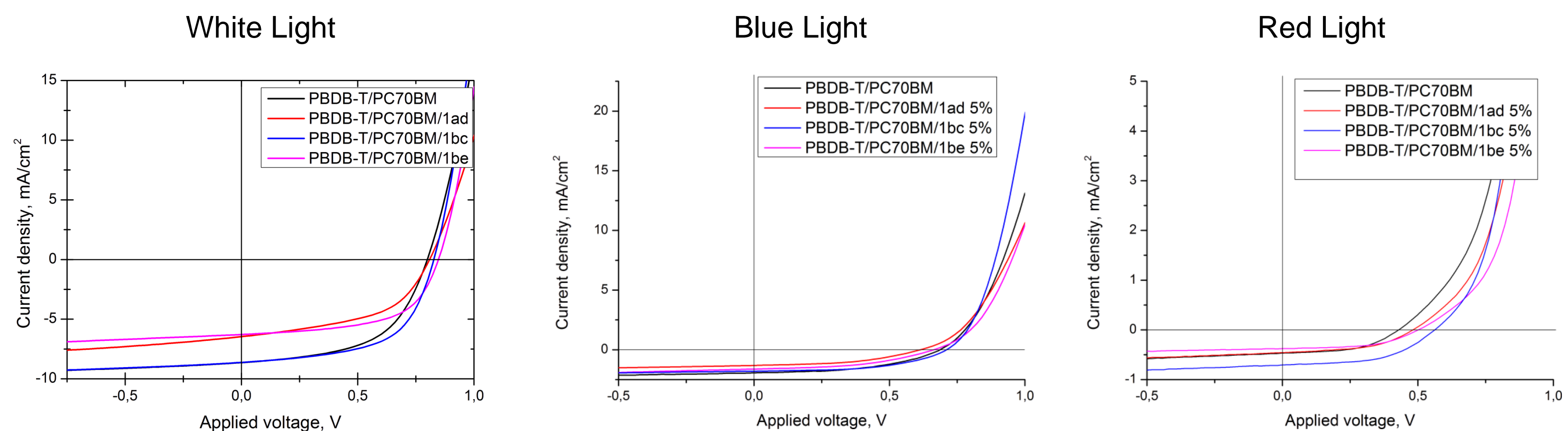
Under light illumination exciton formation in PBDB-T takes place, leading to hole transfer from HOMO (donor) to HOMO (acceptor). Strong line with center at 3429.5 G is attributed to superposition of PBDB-T negative polaron and cation-radical of **1be**. Similar situation was observed for **1be**/PC70BM blend but PC70BM presented as anion-radical because of lower energies of HOMO and LUMO orbitals than of **1be** and PC70BM absorb microwave at lower magnetic field. Also it was found that increased gap between HOMO levels which should promote hole transfer does not affect significantly on LEPR signal intensity. Morphology of PBDB-T/PC70BM without NI is smooth (RMS = 1.23 nm) and uniform and PC70BM crystallites with size of ~ 90 nm formed on the top of film. Adding small amounts of NI into blend did not affect on surface of composite what was unexpected. The only change was enhanced aggregation of fullerene (white seeds) on the top of PBDB-T/PC70BM/**1bc** (5 %) which could slightly increase J_{sc} .

Surface of PBDB-T film is very smooth (RMS = 0.97 nm) and the size of domains is about of 30–40 nm. Adding 5 % of NI leads to increased amount of aggregates, probably of PBDB-T. We suggest that ability of **1bc** to form less crystalline phase has a favorable effect on regularity of PBDB-T by alkyl-alkyl chain interactions between PBDB-T and **1bc**, which confirms previously observed phenomenon of an increased intensity absorption peak of PBDB-T in 610–640 nm region.

Atomic Force Microscopy



J-V curves of OPV devices



Conclusions

As it was revealed by set of different physical and chemical methods our novel NI-like are electron donor, which prefer to slightly enhance PC70BM aggregation on the top of surface and change the morphology of PBDB-T layer. Also high enough absorption and luminescence of thienonaphtalimides affect on OPV performance, which depends on content of NI in active layer. Using different spectra of light source it is possible to estimate the impact of optical and morphological properties of ternary composites. Thus, optical absorption and/or luminescence of NI leads to slight increase of PCE in case of **1bc** (blue light excitation). On the other hand, morphological factors strongly increase of PCE up to two times with respect to binary PBDB-T/PC70BM composite (red light).

References

- [1] J. Yuan et al, Joule 2019, 3, pp. 1140–1151.
- [2] R. Ahmed et al, J. Phys. Chem. C 2021, 126, pp. 423–433.