ESRF	**Experiment title:** Structural synergies between conjugated polymers and nonfullerene acceptors: a key to improve photovoltaic stability?	**Experiment number**: MA-5752
Beamline: BM28-XMaS	**Date of experiment**: from: 31/01/2023 to: 05/02/2023	**Date of report**: 31/03/2023
Shifts: 15	**Local contact(s)**: Oier Bikondoa	*Received at ESRF:*

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Report:

The system of study is a photovoltaic blend of two organic molecules: the conjugated polymer PM6 and the small, semiconducting molecule Y6. The idea of this experiment was to study the crystallization of this PM6:Y6 system using different ratios of both materials and different solvents. Usually, with this kind of photovoltaic systems, it is found that the optimal configuration is the one which contains a slightly higher quantity of acceptor (Y6) and deposited from a solution which is chloroform with a tiny quantity of a secondary solvent with a higher boiling point. It is understood that using a secondary solvent as an additive improves the efficiency of the device by inducing a subtle phase separation and crystallization on the acceptor, which, usually, it is convenient.

The main insight we extracted from this experiment is that, within the PM6:Y6 system, the acceptor (Y6) is able to diffuse and crystallize, essentially, if it is predominant over the polymer and also, aided by the presence of the additive. In **Figure 1,** there is an example of GIWAXS patterns associated with a temperature ramp over a Y6-predominant bulk heterojunction in the presence of additive. In this case, the acceptor crystallizes once the system reaches 220°C. Most likely, the system is able to evolve at a lower temperature.

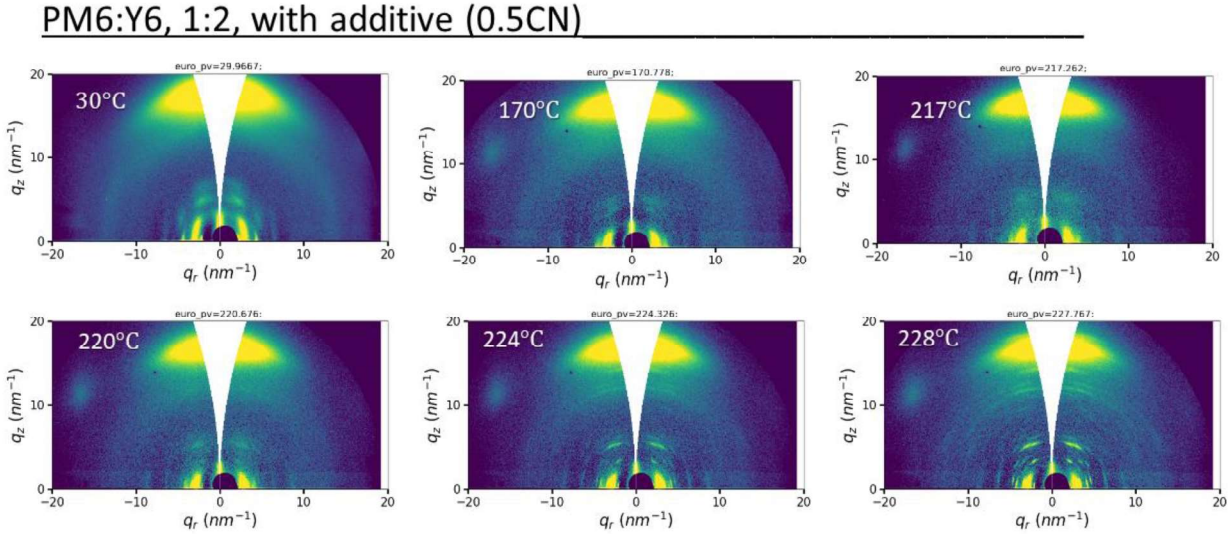

Figure 1. GIWAXS patterns from PM6:Y6 (1:2) with additive, measured at different temperatures close to Y6 crystallization temperature.

On the other hand, we bring the same system without any additive up to degradation temperatures (~280°C) to prove that the acceptor does not crystallize at all, even when it doubles the mass of the polymer (**Figure 2**).

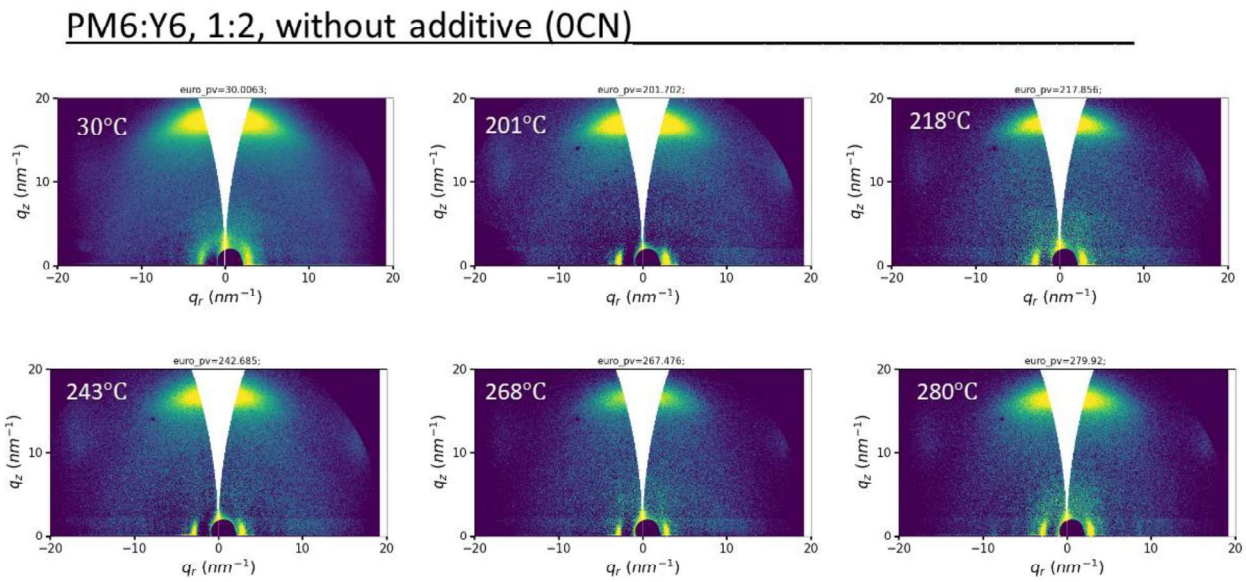

Figure 2. GIWAXS patterns from PM6:Y6 (1:2) without additive, at different temperatures until Y6 degradation temperature.

We tested the same temperature ramp over a range of different donor:acceptor ratios with and without additive and found that, virtually, the acceptor is able to diffuse and crystallize only if its predominant and after being deposited from the mixture of solvent. In the rest of the cases, the Y6 is so well blended with PM6 that the diffusion is forbidden or extremely slow to crystallize during the experimental time (**Figure 3**). This finding has important consequences for the study of the stability of organic solar cells, since instability is their main drawback.

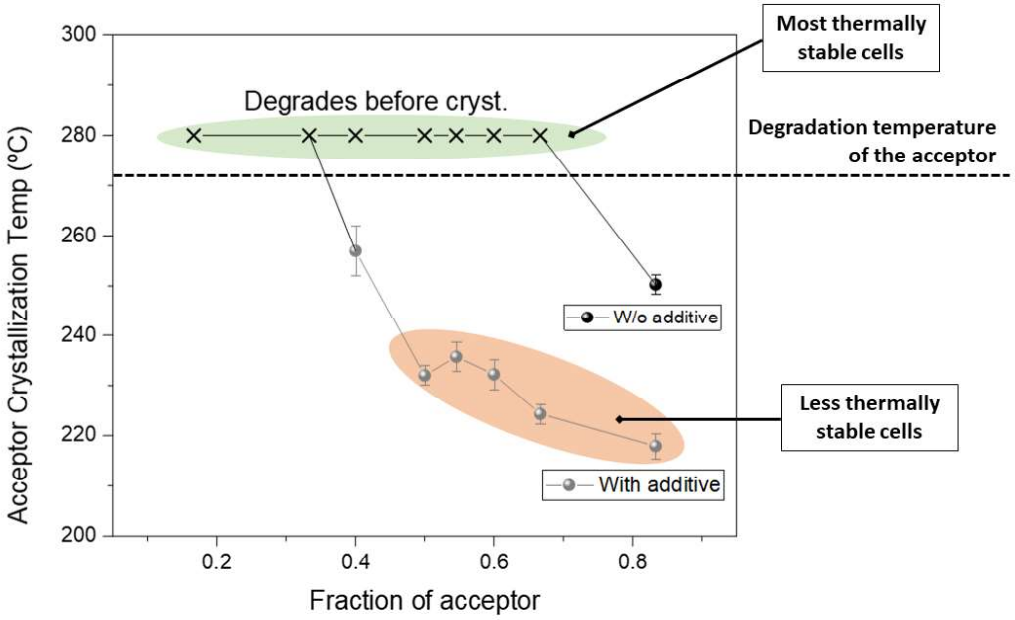

Figure 3. Crystallization temperature of Y6 within PM6:Y6 system, with different donor:acceptor ratios, with and without additive.

It is known already that the diffusion of acceptor molecules out of the polymer matrix is an important source of instability for organic solar cells. With these results, we are proving how, inside the same system, the thermodynamics between polymer and small molecule may be dramatically different upon changing their relation. In this sense, we speculate (not proved), that the most efficient solar cells (higher Y6 content with additive) are, paradoxically, the lest stable ones, at least, from a thermodynamical perspective. We will continue studying this effect by testing the efficiency in real solar cells.