**Supplementary Information**

**Origin of fullerene-induced vitrification of fullerene:donor polymer photovoltaic blends and its impact on solar cell performance**

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**Figure S1.** Thermal behaviour of PCE11 (i.e. PffBT4T-2OD), [60]PCBM and a 1:1 blend of them. Here, as systems were drop-cast at 25 °C, a noticeable cold crystallisation exotherm is observed for the binary also in this scenario, while such an exothermic feature is again missing in the neat components.