SUPPORTING INFORMATION

Unidirectional and crystalline organic semiconductor microwire

arrays by solvent vapor annealing with PMMA as the assisting layer

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(a)	60°C	(b)	65°C
	5 <u>0 µm</u>		5 <u>0 µm</u>
(c)	70°C	(d)	75℃
		SHE S	SHE
	5 <u>0 μm</u>	11.11	5 <u>0 μm</u>

Figure S1. OM image of C6-DPA arrays after PASVA treatment for different temperatures.



Figure S2. OM image of C6-DPA arrays for different SVA treatment times.



Figure S3. OM image of C6-DPA films on SiO₂/Si and PMMA/SiO₂/Si after SVA with horizontal substrates. Both films are snowflake-like with no microwires formed.



Figure S4. (a) AFM image of spin-coated PMMA with a concentration of 0.5 mg.ml⁻¹ after SVA. (b)The thickness of PMMA is about 2.5nm.



Figure S5. (a) OM images of the PASVA approach with different semiconductors and different

polymers as the assisting layer. All semiconductors and polymer were used with a concentration of 0.5 mg/ml.

The formation of crystal arrays by the PASVA approach needs to meet two prerequisites. First, the solubility of both the semiconductor and the polymer should be good in the chosen solvent. Second, there should be spontaneous vertical phase separation and after the vertical phase separation the semiconductor layer should be on top of the polymer layer. In our system (C6-DPA/PMMA), both the semiconductor and the polymer show good solubility in the chose solvent (toluene). It has been reported that when organic semiconductor/PMMA mixture film underwent SVA spontaneous vertical phase separation occurred (Adv. Mater. 2010, 23, 523). That is to say, out material system meets the two prerequisites for a successful PASVA approach.

Another two semiconductors (Perylene and TIPS-Pentacene) and another two polymers (polystyrene and polyvinyl pyrrolidone) has also been investigated. As can be seen from Fig. S5, although PS show good solubility in toluene, no microribbons were obtained. Here, we tentatively ascribe the failure to the unsuccessful phase separation of the semiconductor/PS mixture. As for PVP, it show poor solubility in both toluene and THF, clearly no microribbons can be obtained.