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Supplementary Materials

Pseudo-Planar Organic Heterojunctions by Sequential Printing of Quasi-Miscible Inks

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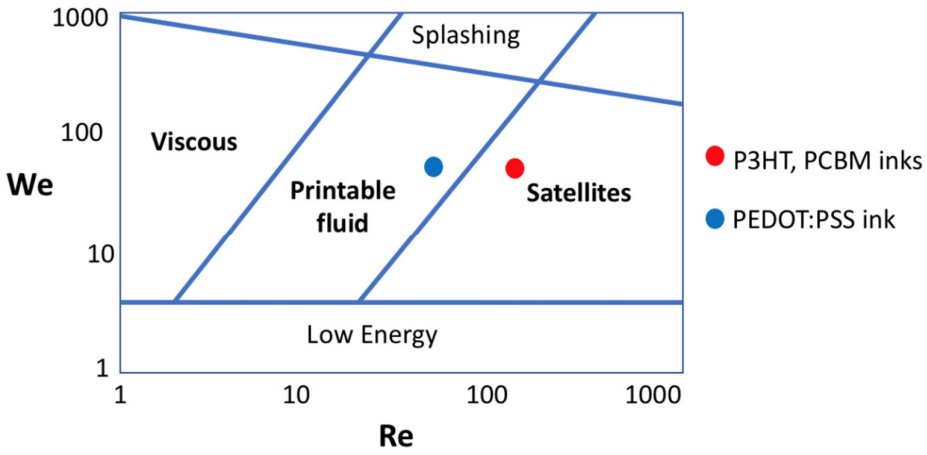

Figure S1. Derby plots for P3HT, PCBM and PEDOT:PSS inks prepared in this study.

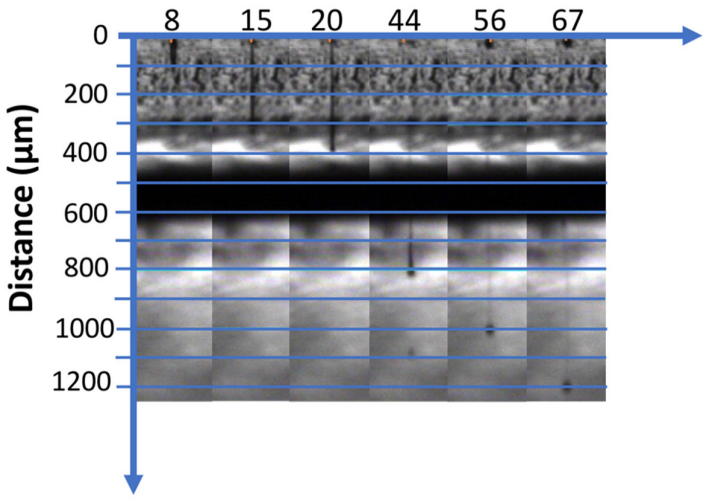

Figure S2. Stroboscopic images showing PEDOT:PSS ink deposition process at a jetting voltage equal to 23 V. The droplet is subjected to an elongation process which eventually does not lead to breakup.

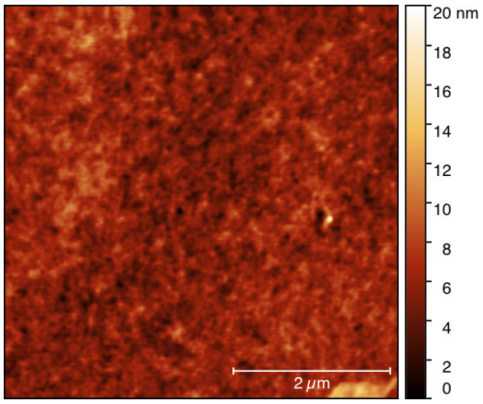

Figure S3. AFM characterization of the P3HT layer printed at 40 V.

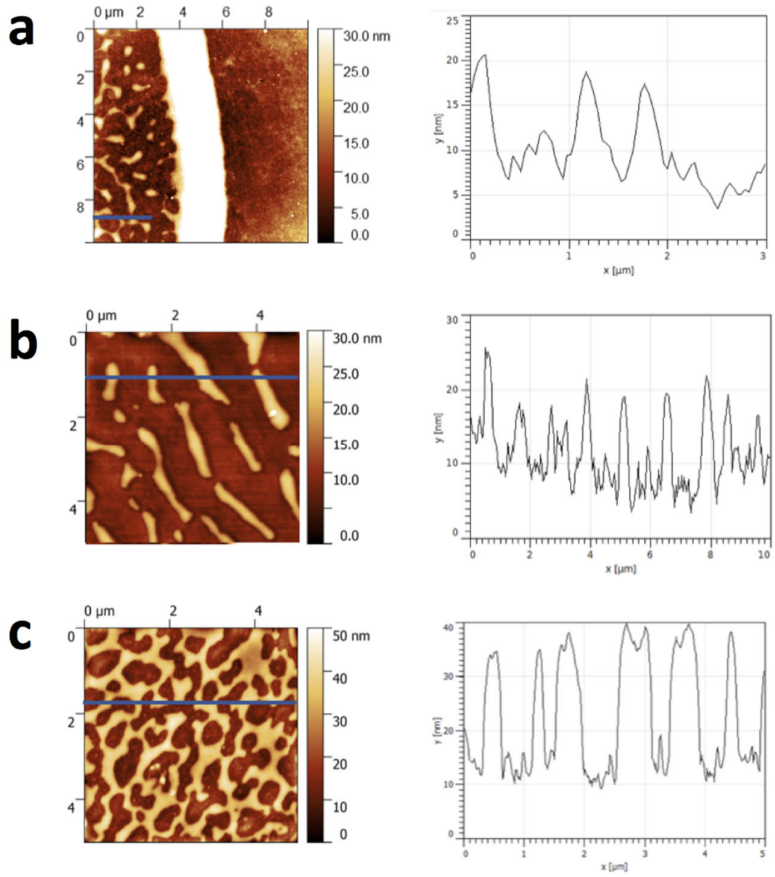

Figure S4. Section analysis of the (**a**) border of the P3HT layer (27 V jetting voltage); border of the P3HT-PCBM layer, being the PCBM layer printed at 27 V (**b**) or 40 V (**c**).

Table S1. Solvents used for printed solar cells.

Printing Materials	Printing Medium	References
Carbon nanomaterials	Isopropanol	[1]
	Water/propylene glycol	[2]
Inorganic dopants	Alcohols, water, and their mixtures	[3]
Metals or Metal Oxides	Acetonitrile	[4]
	Alcohols	[5,6]
	DMF	[7]
	DMSO	[8–10]
	Glycols	[3,11,12]
	Glycols mixtures	[13,14]
	Hexanethiol/dodecanethiol	[15]
	Triton X-100	[16]
	Water	[17]
	Water mixtures	[14,18,19]
Minerals (chalcopyrite)	o-Xylene/indane/tetrahydronaphthalene	[20]
	Ethanol/ethanolamine	[21]
	Ethylene glycol mixtures	[13,21–23]
P3HT:PCBM	Halogenated aromatic solvents (chlorobenzene, o-dichlorobenzente) and their mixtures	[24–30]
	Chlorobenzene	[31]
PEDOT:PSS	Ethylene glycol mixtures	[32,33]
	Water	[28]
Perovskites	Alcohols	[34,35]
	γ-Butyrolactone	[36,37]
	DMF	[38–44]
	DMSO / γ-butyrolactone	[45,46]
	DMF/DMSO mixtures	[47–49]
Polymers	Chloroform/trichloroethylene	[50]
	DMSO	[51]
	Water	[52,53]
	Various solvents/mixtures	[54,55]

Table S2. Summary of the Mean values of the OSC performances obtained from three different measurements; the standard deviation around the mean value of each parameter is reported in brackets.

Inkjet Printed Component	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF	PCE (%)
P3HT:PCBM PHJ	0.67 (±0.33)	0.33 (±0.07)	0.30 (±0.03)	0.062 (±0.02)
P3HT:PCBM BHJ	2.92 (±0.07)	0.58 (±0.03)	0.33 (±0.01)	0.56 (±0.05)
PEDOT:PSS HTL + P3HT:PCBM BHJ	3.76 (±1.30)	0.45 (±0.04)	0.26 (±0.07)	0.44 (±0.20)

References

1. Dodoo-Arhin, D.; Howe, R.C.T.; Hu, G.; Zhang, Y.; Hiralal, P.; Bello, A.; Amaratunga, G.; Hasan, T. Inkjet-printed graphene electrodes for dye-sensitized solar cells. *Carbon* **2016**, *105*, 33–41, doi:10.1016/j.carbon.2016.04.012.
2. Kastner, J.; Gnatiuk, I.; Wagner, M.; Holzinger, D.; Rudelstorfer, V.; Hesser, G.; Fuchsbauer, A.; Hild, S. Grinded nano-graphite inkjet inks for application in organic solar cells. *Nanotechnology* **2019**, *30*, 45601, doi:10.1088/1361-6528/aae67a.
3. Stüwe, D.; Mager, D.; Biro, D.; Korvink, J.G. Inkjet technology for crystalline silicon photovoltaics. *Adv. Mater.* **2015**, *27*, 599–626, doi:10.1002/adma.201403631.
4. Lee, D.H.; Chang, Y.J.; Herman, G.S.; Chang, C.H. A general route to printable high-mobility transparent amorphous oxide semiconductors. *Adv. Mater.* **2007**, *19*, 843–847, doi:10.1002/adma.200600961.

5. Kim, J.; Na, S.I.; Kim, H.K. Inkjet printing of transparent InZnSnO conducting electrodes from nano-particle ink for printable organic photovoltaics. *Sol. Energy Mater. Sol. Cells* **2012**, *98*, 424–432, doi:10.1016/j.solmat.2011.11.050.
6. Singh, A.; Gupta, S.K.; Garg, A. Inkjet printing of NiO films and integration as hole transporting layers in polymer solar cells. *Sci. Rep.* **2017**, *7*, 1775, doi:10.1038/s41598-017-01897-9.
7. Oh, Y.; Lee, S.-N.; Kim, H.-K.; Kim, J. UV-assisted chemical sintering of inkjet-printed TiO_2 photoelectrodes for low-temperature flexible dye-sensitized solar cells. *J. Electrochem. Soc.* **2012**, *159*, H777–H781, doi:10.1149/2.011210jes.
8. Lin, X.; Kavalakkatt, J.; Lux-Steiner, M.C.; Ennaoui, A. Inkjet-printed $Cu_2ZnSn(S, Se)_4$ solar cells. *Adv. Sci.* **2015**, *2*, 1500028, doi:10.1002/advs.201500028.
9. Uhl, A.R.; Katahara, J.K.; Hillhouse, H.W. Molecular-ink route to 13.0% efficient low-bandgap $CuIn(S,Se)_2$ and 14.7% efficient $Cu(In,Ga)(S,Se)_2$ solar cells. *Energy Environ. Sci.* **2016**, *9*, 130–134, doi:10.1039/c5ee02870a.
10. Lin, X.; Madhavan, V.E.; Kavalakkatt, J.; Hinrichs, V.; Lauermann, I.; Lux-Steiner, M.C.; Ennaoui, A.; Klenk, R. Inkjet-printed CZTSSe absorbers and influence of sodium on device performance. *Sol. Energy Mater. Sol. Cells* **2018**, *180*, 373–380, doi:10.1016/j.solmat.2017.09.003.
11. Hersh, P.A.; Curtis, C.J.; van Hest, M.F.A.M.; Kreuder, J.J.; Pasquarelli, R.; Miedaner, A.; Ginley, D.S. Inkjet printed metallizations for $Cu(In_{1-x}Ga_x)Se_2$ photovoltaic cells. *Prog. Photovoltaics Res. Appl.* **2011**, *19*, 973–976, doi:10.1002/pip.1105.
12. Na, S.-I.; Park, D.-W.; Kim, S.-S.; Yang, S.-Y.; Lee, K.; Lee, M.-H. ITO-free flexible polymer solar cells with ink-jet-printed Ag grids. *Semicond. Sci. Technol.* **2012**, *27*, 125002, doi:10.1088/0268-1242/27/12/125002.
13. Lin, X.; Klenk, R.; Wang, L.; Köhler, T.; Albert, J.; Fiechter, S.; Ennaoui, A.; Lux-Steiner, M.C. 11.3% efficiency $Cu(In,Ga)(S,Se)_2$ thin film solar cells via drop-on-demand inkjet printing. *Energy Environ. Sci.* **2016**, *9*, 2037–2043, doi:10.1039/C6EE00587J.
14. Yadav, B.S.; Dey, S.R.; Dhage, S.R. Effective ink-jet printing of aqueous ink for $Cu(In,Ga)Se_2$ thin film absorber for solar cell application. *Sol. Energy* **2019**, *179*, 363–370, doi:10.1016/j.solener.2019.01.003.
15. Barbé, J.; Eid, J.; Ahlswede, E.; Spiering, S.; Powalla, M.; Agrawal, R.; Del Gobbo, S. Inkjet printed $Cu(In,Ga)S_2$ nanoparticles for low-cost solar cells. *J. Nanoparticle Res.* **2016**, *18*, 379, doi:10.1007/s11051-016-3686-5.
16. Bernacka-Wojcik, I.; Senadeera, R.; Wojcik, P.J.; Silva, L.B.; Doria, G.; Baptista, P.; Aguas, H.; Fortunato, E.; Martins, R. Inkjet printed and "doctor blade" TiO2 photodetectors for DNA biosensors. *Biosens. Bioelectron.* **2010**, *25*, 1229–1234, doi:10.1016/j.bios.2009.09.027.
17. Cranton, W.M.; Wilson, S.L.; Ranson, R.; Koutsogeorgis, D.C.; Chi, K.; Hedgley, R.; Scott, J.; Lipiec, S.; Spiller, A.; Speakman, S. Excimer laser processing of inkjet-printed and sputter-deposited transparent conducting SnO_2:Sb for flexible electronics. *Thin Solid Films* **2007**, *515*, 8534–8538, doi:10.1016/j.tsf.2007.03.118.
18. Cherrington, R.; Hughes, D.J.; Senthilarasu, S.; Goodship, V. Inkjet-printed TiO2 nanoparticles from aqueous solutions for dye-sensitized solar cells (DSSCs). *Energy Technol.* **2015**, *3*, 866–870, doi:10.1002/ente.201500096.
19. Brisse, R.; Faddoul, R.; Bourgeteau, T.; Tondelier, D.; Leroy, J.; Campidelli, S.; Berthelot, T.; Geffroy, B.; Jousselme, B. Inkjet printing NiO-Based p-type dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 2369–2377, doi:10.1021/acsami.6b12912.
20. Eggenhuisen, T.M.; Galagan, Y.; Biezemans, A.F.K.V.; Slaats, T.M.W.L.; Voorthuijzen, W.P.; Kommeren, S.; Shanmugam, S.; Teunissen, J.P.; Hadipour, A.; Verhees, W.J.H.; et al. High efficiency, fully inkjet printed organic solar cells with freedom of design. *J. Mater. Chem. A* **2015**, *3*, 7255–7262, doi:10.1039/c5ta00540j.
21. Wang, W.; Su, Y.-W.; Chang, C. Inkjet printed chalcopyrite $CuIn_xGa_{1-x}Se_2$ thin film solar cells. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2616–2620, doi:10.1016/j.solmat.2011.05.011.
22. Wang, L.; Lin, X.; Ennaoui, A.; Wolf, C.; Lux-Steiner, M.C.; Klenk, R. Solution-processed In_2S_3 buffer layer for chalcopyrite thin film solar cells. *EPJ Photovoltaics* **2016**, *7*, 70303, doi:10.1051/epjpv/2016001.
23. Yadav, B.S.; Ranjan Day, S.; Dhage, S.R. Chalcopyrite CIGS absorber layer by inkjet printing for photovoltaic application. *Mater. Today Proc.* **2017**, *4*, 12480–12483, doi:10.1016/j.matpr.2017.10.047.
24. Hoth, C.N.; Choulis, S.A.; Schilinsky, P.; Brabec, C.J. High photovoltaic performance of inkjet printed polymer:fullerene blends. *Adv. Mater.* **2007**, *19*, 3973–3978, doi:10.1002/adma.200700911.
25. Aernouts, T.; Aleksandrov, T.; Girotto, C.; Genoe, J.; Poortmans, J. Polymer based organic solar cells using ink-jet printed active layers. *Appl. Phys. Lett.* **2008**, *92*, 33306, doi:10.1063/1.2833185.
26. Hoth, C.N.; Schilinsky, P.; Choulis, S.A.; Brabec, C.J. Printing highly efficient organic solar cells. *Nano Lett.* **2008**, *8*, 2806–2813, doi:10.1021/nl801365k.
27. Hoth, C.N.; Choulis, S.A.; Schilinsky, P.; Brabec, C.J. On the effect of poly(3-hexylthiophene) regioregularity on inkjet printed organic solar cells. *J. Mater. Chem.* **2009**, *19*, 5398–5404, doi:10.1039/B823495G.
28. Eom, S.H.; Park, H.; Mujawar, S.H.; Yoon, S.C.; Kim, S.S.; Na, S.I.; Kang, S.J.; Khim, D.; Kim, D.Y.; Lee, S.H. High efficiency polymer solar cells via sequential inkjet-printing of PEDOT:PSS and P3HT:PCBM inks with additives. *Org. Electron.* **2010**, *11*, 1516–1522, doi:10.1016/j.orgel.2010.06.007.
29. Sun, Y.; Zhang, Y.; Liang, Q.; Zhang, Y.; Chi, H.; Shi, Y.; Fang, D. Solvent inkjet printing process for the fabrication of polymer solar cells. *RSC Adv.* **2013**, *3*, 11925–11934, doi:10.1039/C3RA22659J.
30. Sumaiya, S.; Kardel, K.; El-Shahat, A. Organic solar cell by inkjet printing—An overview. *Technologies* **2017**, *5*, 53, doi:10.3390/technologies5030053.
31. Espinosa, N.; García-Valverde, R.; Urbina, A.; Lenzmann, F.; Manceau, M.; Angmo, D.; Krebs, F.C. Life cycle assessment of ITO-free flexible polymer solar cells prepared by roll-to-roll coating and printing. *Sol. Energy Mater. Sol. Cells* **2012**, *97*, 3–13, doi:10.1016/j.solmat.2011.09.048.

32. Galagan, Y.; Coenen, E.W.C.; Sabik, S.; Gorter, H.H.; Barink, M.; Veenstra, S.C.; Kroon, J.M.; Andriessen, R.; Blom, P.W.M. Evaluation of ink-jet printed current collecting grids and busbars for ITO-free organic solar cells. *Sol. Energy Mater. Sol. Cells* **2012**, *104*, 32–38, doi:10.1016/j.solmat.2012.04.039.
33. Galagan, Y.; Coenen, E.W.C.; Abbel, R.; van Lammeren, T.J.; Sabik, S.; Barink, M.; Meinders, E.R.; Andriessen, R.; Blom, P.W.M. Photonic sintering of inkjet printed current collecting grids for organic solar cell applications. *Org. Electron.* **2013**, *14*, 38–46, doi:10.1016/j.orgel.2012.10.012.
34. Lee, J.-W.; Na, S.-I.; Kim, S.-S. Efficient spin-coating-free planar heterojunction perovskite solar cells fabricated with successive brush-painting. *J. Power Sources* **2017**, *339*, 33–40, doi:j.jpowsour.2016.11.028.
35. Liang, C.; Li, P.; Gu, H.; Zhang, Y.; Li, F.; Song, Y.; Shao, G.; Mathews, N.; Xing, G. One-step inkjet printed perovskite in air for efficient light harvesting. *Sol. RRL* **2018**, *2*, 1700217, doi:10.1002/solr.201700217.
36. Hashmi, S.G.; Martineau, D.; Li, X.; Ozkan, M.; Tiihonen, A.; Dar, M.I.; Sarikka, T.; Zakeeruddin, S.M.; Paltakari, J.; Lund, P.D.; et al. Air processed inkjet infiltrated carbon based printed perovskite solar cells with high stability and reproducibility. *Adv. Mater. Technol.* **2017**, *2*, 1600183, doi:10.1002/admt.201600183.
37. Hashmi, S.G.; Tiihonen, A.; Martineau, D.; Ozkan, M.; Vivo, P.; Kaunisto, K.; Ulla, V.; Zakeeruddin, S.M.; Grätzel, M. Long term stability of air processed inkjet infiltrated carbon-based printed perovskite solar cells under intense ultra-violet light soaking. *J. Mater. Chem. A* **2017**, *5*, 4797–4802, doi:10.1039/C6TA10605F.
38. Wei, Z.; Chen, H.; Yan, K.; Yang, S. Inkjet printing and instant chemical transformation of a CH3NH3PbI3/nanocarbon electrode and interface for planar perovskite solar cells. *Angew. Chem. Int. Ed.* **2014**, *53*, 13239–13243, doi:10.1002/anie.201408638.
39. Bag, M.; Jiang, Z.; Renna, L.A.; Jeong, S.P.; Rotello, V.M.; Venkataraman, D. Rapid combinatorial screening of inkjet-printed alkyl-ammonium cations in perovskite solar cells. *Mater. Lett.* **2016**, *164*, 472–475, doi:10.1016/j.matlet.2015.11.058.
40. Gheno, A.; Huang, Y.; Bouclé, J.; Ratier, B.; Rolland, A.; Even, J.; Vedraine, S. Toward highly efficient inkjet-printed perovskite solar cells fully processed under ambient conditions and at low temperature. *Sol. RRL* **2018**, *2*, 1800191, doi:10.1002/solr.201800191.
41. Alamri, A.M.; Leung, S.; Vaseem, M.; Shamim, A.; He, J. Fully inkjet-printed photodetector using a graphene/perovskite/graphene heterostructure. *IEEE Trans. Electron Devices* **2019**, *66*, 2657–2661, doi:10.1109/TED.2019.2911715.
42. Chen, S.; Zhang, L.; Yan, L.; Xiang, X.; Zhao, X.; Yang, S.; Xu, B. Accelerating the screening of perovskite compositions for photovoltaic applications through high-throughput inkjet printing. *Adv. Funct. Mater.* **2019**, *29*, 1905487, doi:10.1002/adfm.201905487.
43. Prajongtat, P.; Sriprachuabwong, C.; Wongkanya, R.; Dechtrirat, D.; Sudchanham, J.; Srisamran, N.; Sangthong, W.; Chuysinuan, P.; Tuantranont, A.; Hannongbua, S.; et al. Moisture-resistant electrospun polymer membranes for efficient and stable fully printable perovskite solar cells prepared in humid air. *ACS Appl. Mater. Interfaces* **2019**, *11*, 27677–27685, doi:10.1021/acsami.9b05032.
44. Shi, L.; Meng, L.; Jiang, F.; Ge, Y.; Li, F.; Wu, X.; Zhong, H. In situ inkjet printing strategy for fabricating perovskite quantum dot patterns. *Adv. Funct. Mater.* **2019**, *29*, 1903648, doi:10.1002/adfm.201903648.
45. Mathies, F.; Abzieher, T.; Hochstuhl, A.; Glaser, K.; Colsmann, A.; Paetzold, U.W.; Hernandez-Sosa, G.; Lemmer, U.; Quintilla, A. Multipass inkjet printed planar methylammonium lead iodide perovskite solar cells. *J. Mater. Chem. A* **2016**, *4*, 19207–19213, doi:10.1039/C6TA07972E.
46. Xie, M.; Lu, H.; Zhang, L.; Wang, J.; Luo, Q.; Lin, J.; Ba, L.; Liu, H.; Shen, W.; Shi, L.; et al. Fully solution-processed semi-transparent perovskite solar cells with ink-jet printed silver nanowires top electrode. *Sol. RRL* **2018**, *2*, 1700184, doi:10.1002/solr.201700184.
47. Li, P.; Liang, C.; Bao, B.; Li, Y.; Hu, X.; Wang, Y.; Zhang, Y.; Li, F.; Shao, G.; Song, Y. Inkjet manipulated homogeneous large size perovskite grains for efficient and large-area perovskite solar cells. *Nano Energy* **2018**, *46*, 203–211, doi:10.1016/j.nanoen.2018.01.049.
48. Mathies, F.; Eggers, H.; Richards, B.S.; Hernandez-Sosa, G.; Lemmer, U.; Paetzold, U.W. Inkjet-printed triple cation perovskite solar cells. *ACS Appl. Energy Mater.* **2018**, *1*, 1834–1839, doi:10.1021/acsaem.8b00222.
49. Huckaba, A.J.; Lee, Y.; Xia, R.; Paek, S.; Bassetto, V.C.; Oveisi, E.; Lesch, A.; Kinge, S.; Dyson, P.J.; Girault, H.; et al. Inkjet-printed mesoporous TiO2 and perovskite layers for high efficiency perovskite solar cells. *Energy Technol.* **2019**, *7*, 317–324, doi:10.1002/ente.201800905.
50. Pede, D.; Serra, G.; De Rossi, D. Microfabrication of conducting polymer devices by ink-jet stereolithography. *Mater. Sci. Eng. C* **1998**, *5*, 289–291, doi:10.1016/S0928-4931(97)00056-8.
51. Madigan, C.F.; Hebner, T.R.; Sturm, J.C.; Register, R.A.; Troian, S. Lateral dye distribution with ink-jet dye doping of polymer organic light emitting diodes. *MRS Proc.* **2000**, *625*, 123, doi:10.1557/PROC-625-123.
52. Rowe, C.W.; Katstra, W.E.; Palazzolo, R.D.; Giritlioglu, B.; Teung, P.; Cima, M.J. Multimechanism oral dosage forms fabricated by three dimensional printing. *J. Control. Release* **2000**, *66*, 11–17, doi:10.1016/S0168-3659(99)00224-2.
53. Gribkova, O.L.; Kabanova, V.A.; Tameev, A.R.; Nekrasov, A.A. Ink-jet printing of polyaniline layers for perovskite solar cells. *Tech. Phys. Lett.* **2019**, *45*, 858–861, doi:10.1134/S1063785019090050.
54. de Gans, B.-J.; Duineveld, P.C.; Schubert, U.S. Inkjet printing of polymers: state of the art and future developments. *Adv. Mater.* **2004**, *16*, 203–213, doi:10.1002/adma.200300385.
55. Tekin, E.; de Gans, B.-J.; Schubert, U.S. Ink-jet printing of polymers–from single dots to thin film libraries. *J. Mater. Chem.* **2004**, *14*, 2627–2632, doi:10.1039/B407478E.