Electronic Supplementary Information

In-situ synthesis of stimulus-responsive luminescent organic materials using a reactive inkjet printing approach

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Experimental

Materials: 1,4-Phenylenediacetonitrile (B2CN) was purchased from Alfa Aesar. Terephthaldehyde (TPA), 1-methyl-2-pyrrolidinone (NMP), potassium *tert*-butoxide (*t*-BuOK), benzaldehyde, anisaldehyde, formylbenzonitrile, biphenyl-4-carboxaldehyde, 2-thiophenecarboxaldehyde, 9-anthracenecarboxaldehyde, 4-nitrobenzaldehyde and ethylene glycol were purchased from Sigma Aldrich. Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning. (2Z,2′Z)-2,2′-(1,4-Phenylene)bis(3-(4-butoxyphenyl) acrylonitrile) (DBDCS),[1] 4-butoxybenzaldehyde (BA),[1] (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-phenylacrylonitrile) **(1)**,[2] (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4-methoxyphenyl)acrylonitrile) **(2)**,[3] (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(thiophen-2-yl)acrylonitrile) **(6)**[4] and CN-PPV[5] were prepared from the method described in the literatures. (2Z,2'Z)-2,2'-(1,4-Phenylene)bis(3-(4-propylphenyl)acrylonitrile) **(3)**, 4,4'-(1Z,1'Z)-2,2'-(1,4-phenylene)bis(2-cyanoethene-2,1-diyl)dibenzonitrile **(4)**, (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(biphenyl-4-yl)acrylonitrile) **(5)**, (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(anthracen-9-yl)acrylonitrile) **(7)** were prepared by employing similar synthetic procedures used for DBDCS.

Preparation of DBDCS, cyanostilbene derivatives and CN-PPV arrays by reactive inkjet printing: Preparation of microarrayed cyanostilbene derivatives are as follows. Three reactive inks (ink A: aromatic aldehyde (1.0 M) in NMP, ink B: B2CN (0.5 M) in 10% ethylene glycol-NMP, ink C: *t*-BuOK (1.0 M in water)) were prepared.

Microarrayed printing of the reactive inks was carried out with a piezoelectric dispensing system (GeSiM Nanoplotter 2.0, Germany). Each ink was dispensed (5 nl) on either a cleaned slide glass or a flexible PDMS film (75 x 25 mm) which was prepared by a standard method. The ink deposited solid substrate was placed in a dark place at room temperature (20 ^{o}C). Product formation was monitored by IR and NMR analyses. Samples for IR analysis were prepared by collecting the reaction mixture and grinding with KBr powder. Samples for NMR analysis were obtained by extracting the reaction mixture, collected at the designated time, with methylene chloride and drying over magnesium sulfate.

Conjugated polymer CN-PPV arrays were also prepared by employing a similar approach using three reactive inks (ink A: TPA (0.5 M) in NMP, ink B: B2CN (0.5 M) in 10% ethylene glycol-NMP, ink C: *t*-BuOK (1.0 M in water)).

1. S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675.
2. S.-J. Yoon and S.Y. Park, *J. Mater. Chem.*, 2011, **21**, 8338.
3. *US Pat.,* US 4197120, 1980.
4. J. Rault-Berthelot, C. Roze´, M.M. Granger, E. Raoult, *J. Electroanal. Chem.*, 1999, **466**, 144.
5. Y. Li, H. Xu, L. Wu, F. He, F. Shen, L. Liu, *J. Polym. Sci. Pol. Phys.*, 2008, **46**, 1105.

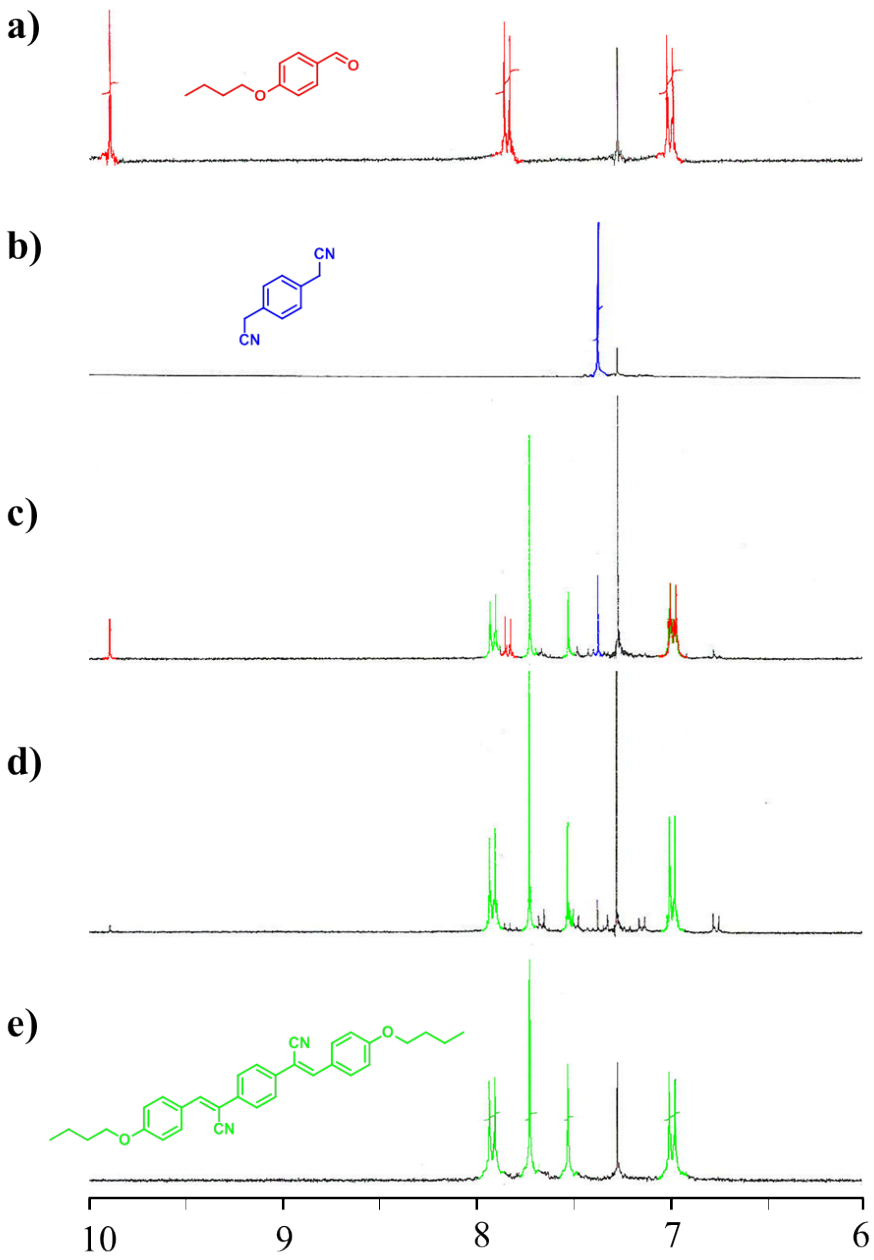

Fig. S1 ^{1}H NMR spectra of 4-butoxybenzaldehyde (BA) (a), 1,4-phenylenediacetonitrile (B2CN) (b), reaction mixture obtained 5 h (c) and 24 h (d) after inkjet printing and independently prepared DBDCS (e). Samples for NMR analysis were obtained by extracting the reaction mixture, collecting at the designated time with methylene chloride, and drying over magnesium sulfate.

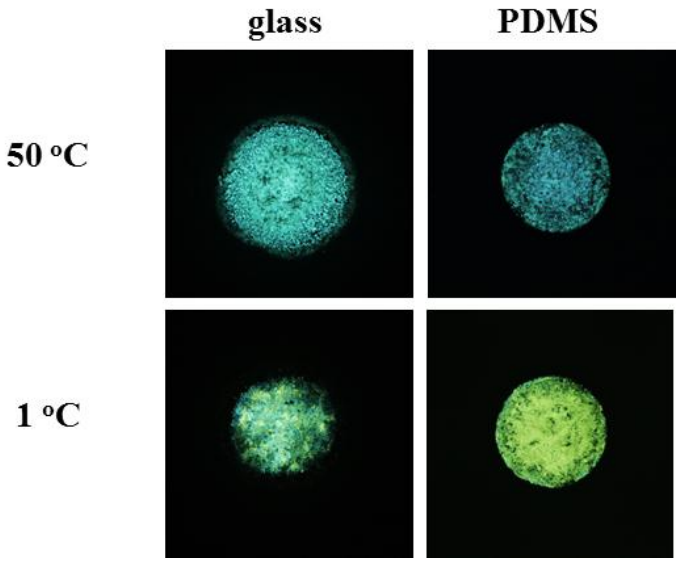

Fig. S2 Fluorescence microscope images of DBDCS spots obtained after 24 h at different temperature conditions on glass and PDMS films (excitation wavelength: 330-385 nm).

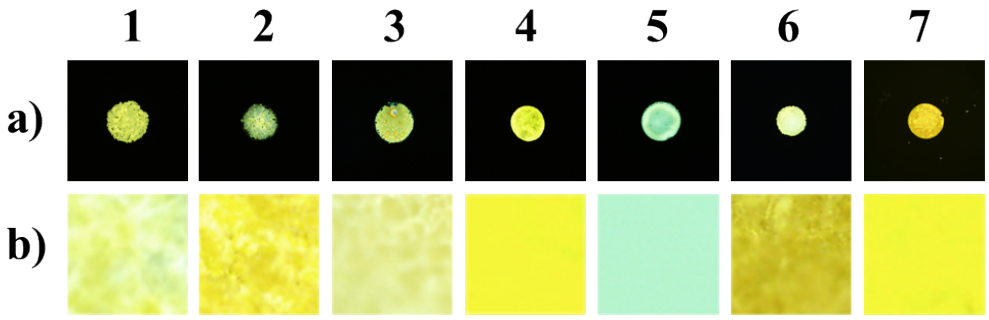

Fig. S3 Fluorescence microspoce images of cyanostilbene derivatives obtained by reactive inkjet printing system on PDMS film (a), and independently prapraed products (b).

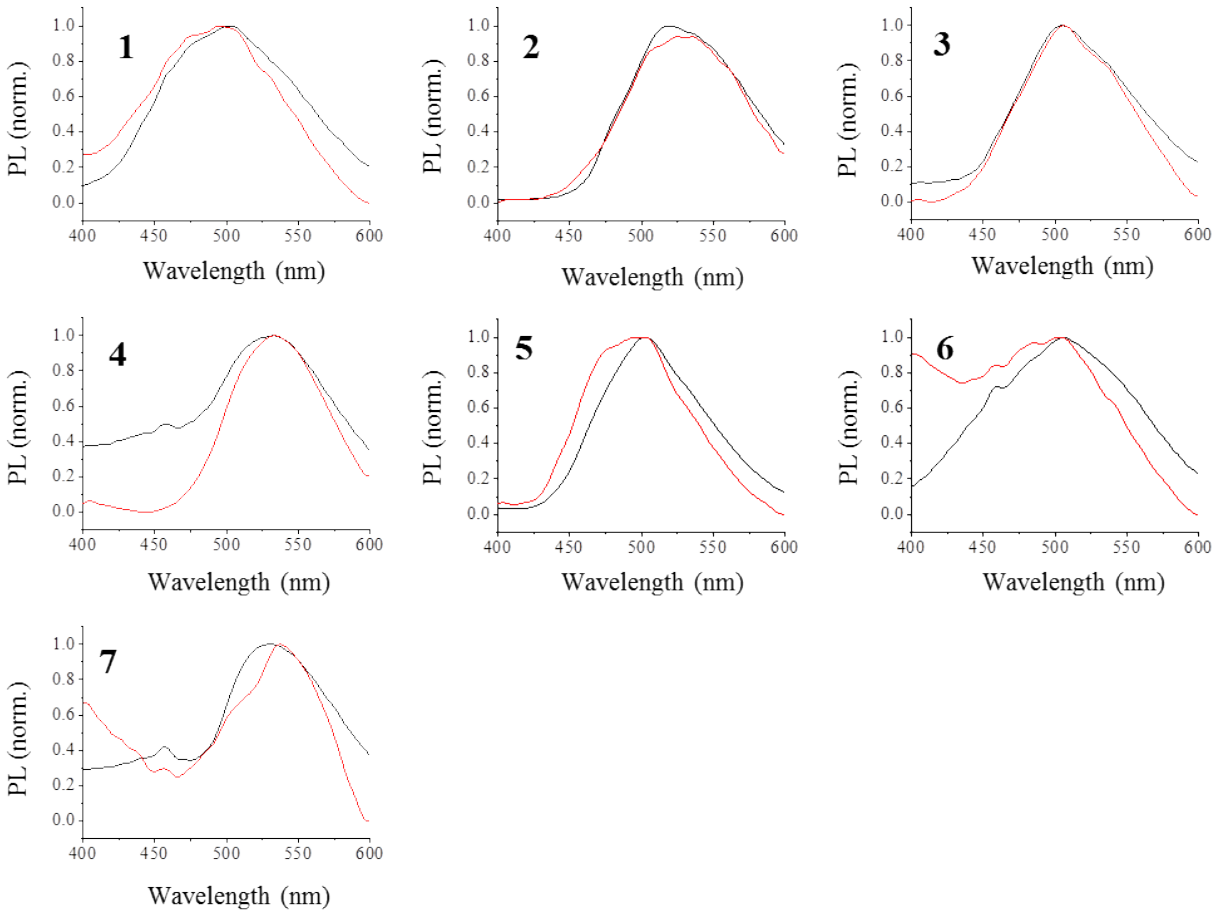

Fig. S4 PL spectra of reaction mixture of some selected cyanostilbene derivatives obtained 24 h after inkjet printing on PDMS film (red line) and independently prepared products (black line). Chemical structures are shown in Fig. 5.

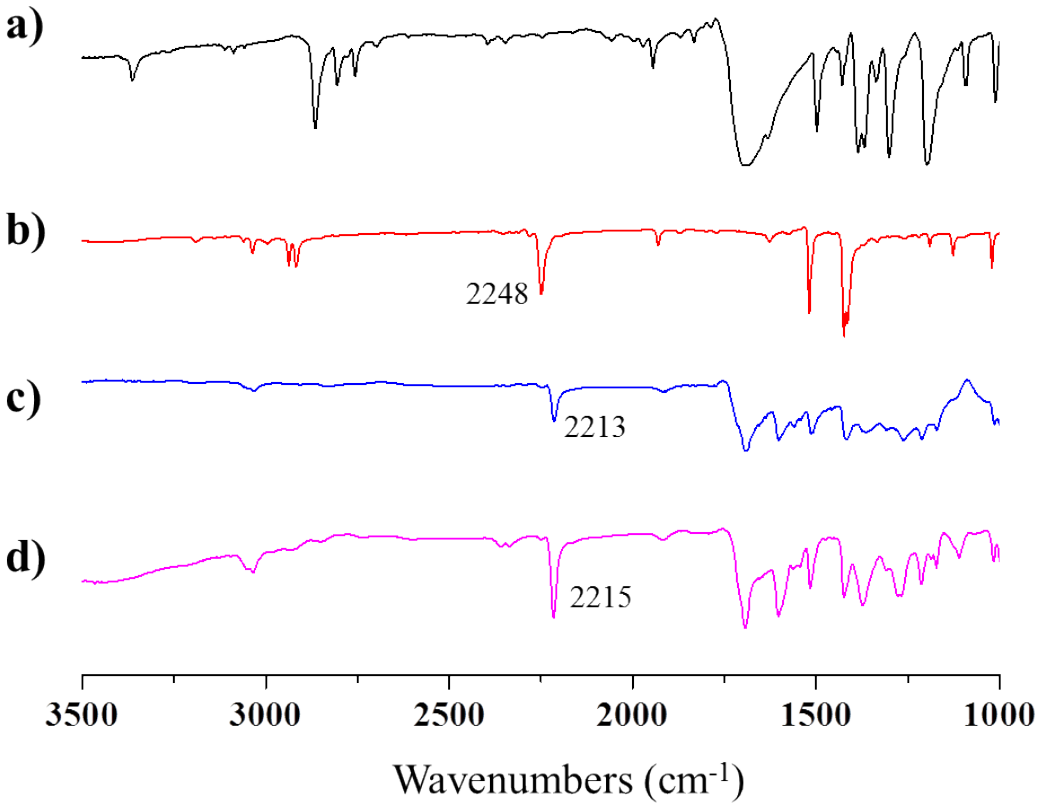

Fig. S5 FT-IR spectra of terephthaldehyde (TPA) (a), 1,4-phenylenediacetonitrile (B2CN) (b) reaction mixture 24 h after printing (c) and independently prepared CN-PPV (d). The sample for IR analysis after 24 h reaction was prepared by collecting the reaction mixture and grinding with KBr powder.