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COMMUNICATION

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

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We have prepared luminescent organic materials by a reactive inkjet printing system. A stimulus (vapour/heat)-responsive fluorescent dye as well as a luminescent conjugated polymer were readily generated by printing of an aldehyde, a phenylenediacetonitrile, and potassium *t*-butoxide.

Owing to its unique advantages including low reagent consumption and direct patterning ability, inkjet printing technology has been actively employed for the preparation of organic materials and devices.¹⁻³ For instance, inkjet printing-based fabrication of light emitting conjugated polymer film,^{4,5} metallo-copolymer film,⁶ conducting polymer circuit⁷⁻⁹ and OLED,^{10,11} have been already invented. We also reported electrochromic display,¹² anti-counterfeiting^{13,14} and volatile organic vapor sensors¹⁵ based on this technology. Especially interesting is the reactive inkjet printing (RIP) system which utilizes chemically reactive materials as ink sources.^{10,11,16,17} Reactive inkjet printing enables preparation of functional materials on specific locations by *in-situ* chemical synthesis from printed reagents. Fabrication of metal and metal oxide derived patterns has been achieved using the emerging drop-on-demand inkjet printing method.¹⁸⁻²⁴ In addition, there have been some fascinating examples for the RIP-based synthesis of organic materials including polyacrylate libraries,²⁵⁻³⁰ polyurethane³¹⁻³² as well as poly(9-vinylcarbazole)³³ and poly-radical.³⁴ Especially, the concept of overprinting for the fabrication of a materials library is interesting since it allows to investigate the features of various components in one set of experiment.^{25-30,35} Herein, we report synthesis of a variety of fluorescent cyanostilbene derivatives as well as a solid-state fluorescent conjugated polymer using the RIP technology. In addition, fabrication of patterned fluorescent molecular arrays that undergo a solvatochromic/thermochromic transition was also proved. In order to test the feasibility of *in-situ* synthesis of

stimulus-responsive luminescent organic materials, a cyanostilbene derivative (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4-butoxyphenyl) acrylonitrile) (DBDCS) has been selected in the initial phase of this investigation (Fig. 1). DBDCS has been already reported in the literature and its vapor-chromic and thermochromic phenomena in the solid state are also well described.³⁶ We envisioned that inkjet printing of 4-butoxybenzaldehyde (BA), 1,4-phenylenediacetonitrile (B2CN) and potassium *tert*-butoxide (*t*-BuOK) results in the generation of the desired DBDCS by a condensation reaction (Fig. 1). The product formation was monitored by IR and NMR analyses. The stimulus-responsive nature of the *in-situ* generated DBDCS was probed by exposing the reaction product to organic vapor and thermal annealing.

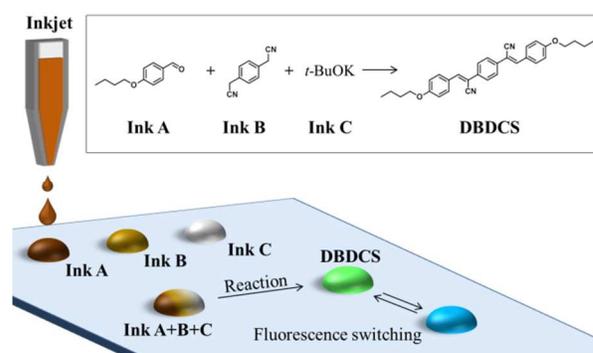


Fig. 1 Schematic illustration for the preparation of DBDCS using a reactive inkjet printing (RIP) method.

Three reactive inks are prepared (ink A: BA (1.0 M) in *N*-methyl-2-pyrrolidone (NMP), ink B: B2CN (0.5 M) in 10% ethylene glycol-NMP, ink C: *t*-BuOK (1.0 M in water). The polar solvent NMP is chosen to facilitate the condensation reaction. In addition, a small amount of ethylene glycol was added to the NMP to retain a wetted state of the droplets and to

guarantee enough reaction time. The relatively nonvolatile NMP and ethylene glycol result in no coffee ring effect and also allowed uniform spots which are hard to obtain with volatile organic solvents. To dispense three prepared inks on a specific area, we used a piezoelectric dispensing system (GeSiM Nanoplotter, Germany). Owing to its high reproducibility and accuracy, three prepared reactive inks can be dropped (5 nl) at the same location on the substrate.

In an effort to verify DBDCS generation from the inkjet-printed chemical reaction, IR spectroscopic monitoring was performed (Fig. 2). It is clear that the distinct bands corresponding to the aldehyde carbonyl (C=O) and cyanide (C≡N) groups at 1694 and 2248 cm^{-1} respectively, decrease 5 h after inkjet printing. It should be noted that the band at 2169 cm^{-1} observed after 5 h reaction (Fig. 2c) is presumably due to the intermediate formation and disappears after 24 h (Fig. 2d). It is clear that the starting BA and B2CN are almost consumed and the desired product is formed after 24 h reaction at 20 °C (Fig. 2d and 2e). The reaction progress was also monitored with ^1H NMR spectroscopy which confirmed the formation of DBDCS as the only noticeable major product (Fig. S1†).

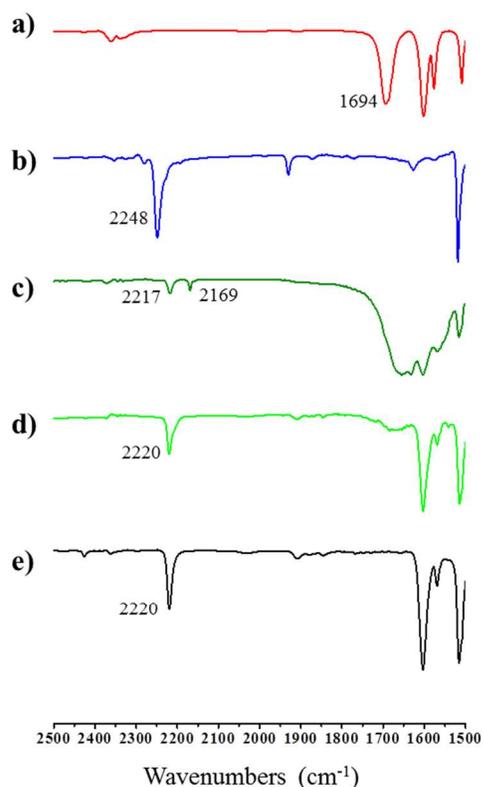


Fig. 2 FTIR spectra of BA (a), B2CN (b) and reaction mixture obtained after 5 h (c) and 24 h (d) at 20 °C. FTIR spectrum of independently prepared DBDCS (e)

In order to fabricate DBDCS patterns, three starting ink solutions were dispensed in the form of aligned dot arrays. The microarray synthesis was conducted on glass and polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) substrates. Optical and fluorescence images were obtained

after a 24 h reaction (Fig. 3). As shown in Fig 3a, the DBDCS microarrays prepared on the glass substrate emitted a blue-green fluorescence (excitation: 330-385 nm). We also fabricated the DBDCS patterns on a PDMS film which display a yellow-green emission (Fig. 3b). DBDCS can exist in two different phases; a blue-emitting B-form and green-emitting G-form.³⁶ The two phases are switchable and a B-to-G transformation occurs by organic vapor and a reverse G-to-B transition by thermal annealing. Interestingly, we have observed a substrate-dependent phase control of the DBDCS arrays. Thus, the B-form of DBDCS was generated predominantly when the glass substrate was used while the G-form of the product was obtained with the PDMS substrate. It seems like the property of the substrate plays a significant role. Thus, the hard surfaced glass substrate enables fast evaporation of the solvent and results in the formation of B-form DBDCS. In contrast, the soft and flexible nature of PDMS allows penetration of the DBDCS molecules inside the polymer matrix and affords slow molecular packing of DBDCS during evaporation of the solvent, yielding the G-form of the product. This was confirmed by preparing DBDCS at different conditions. Thus, preparation of DBDCS at 50 °C resulted in the formation of B form of the dye on both glass and PDMS substrates. In contrast, lowering the reaction temperature to 1 °C afforded generation of B/G mixture (glass substrate) and G form (PDMS substrate) of the product (Fig. S2†).

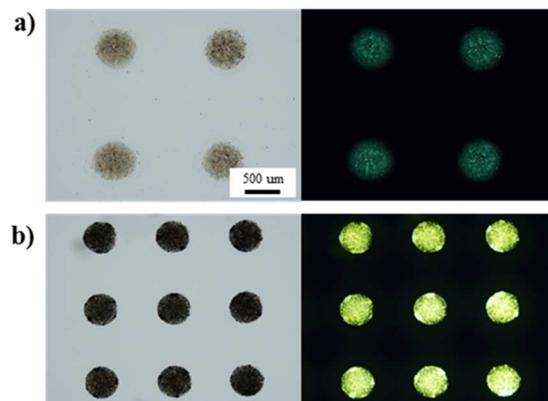


Fig. 3 Optical (left) and fluorescence (right) microscopic images of DBDCS arrays obtained from the in-situ inkjet synthesis on glass (a) and PDMS (b) substrates (λ_{ex} =330-385 nm).

In the next phase of this investigation, we focused on the feasibility of fluorescence switching of DBDCS prepared by reactive inkjet printing. Exposing tetrahydrofuran (THF) vapor to a glass substrate containing the B-form of DBDCS spot resulted in the generation of the G-form of DBDCS (Fig. 4a, top). Heat treatment (120 °C, 30 min) of the THF-exposed glass afforded recovery of the initial B-form. This process can be reversibly controlled by an alternative heating and solvent exposure process. Similar results were obtained with a DBDCS spot on a PDMS substrate (Fig. 4a, bottom). Unlike the glass substrate, the PDMS matrix allows movement of DBDCS molecules inside the polymer matrix. Accordingly, repeated

solvent and heat treatment cycles resulted in the partial destruction of the fluorescent spot. Monitoring of the B-to-G phase transition by photoluminescence (PL) spectra indicated that the emission maximum shifted from 496 to 505 nm (Fig. 4b).

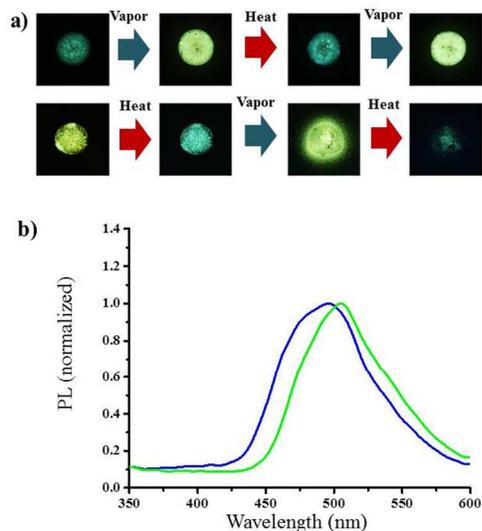


Fig. 4 Fluorescence microscope images of DBDCS spots prepared on glass (top) and PDMS (bottom) upon solvent/heat treatment. (b) PL spectra of B- (blue line) and G (green line)-phases of DBDCS ($\lambda_{\text{ex}}=330$ nm). The emission spectrum for the G-form of DBDCS was obtained by exposing THF to the B-form DBDCS prepared on a glass substrate.

The versatility of our system was further proved by preparing a variety of luminescent cyanostilbene derivatives (Fig. 5). As shown in Fig. 5, the RIP method allowed a facile synthesis of cyanostilbene derivatives with unsubstituted (1), electron rich (2,3) as well as an electron poor (4) substituent. In addition, aldehydes derived from phenyl (5), thienyl (6) and anthracene (7) groups were also converted to the desired products without difficulty. It should be noted that we were not able to obtain the cyanostilbene derivative with 4-nitrobenzaldehyde. 4-Nitrobenzaldehyde was found to be ineffective with the plotting solvent NMP while the desired product was formed in ethanol when the conventional solution based synthesis was carried out. The cyanostilbene derivatives displayed in Fig. 5 are also prepared independently using the conventional solution phase synthesis to compare emission features. Fluorescence microscopic images confirm that the RIP-based approach is affordable for the preparation of diverse luminescent cyanostilbene derivatives (Fig. S3[†]). In addition, the photoluminescence spectra of some cyanostilbene derivatives that are prepared by RIP were matched with those obtained from independent methods (Fig. S4[†]).

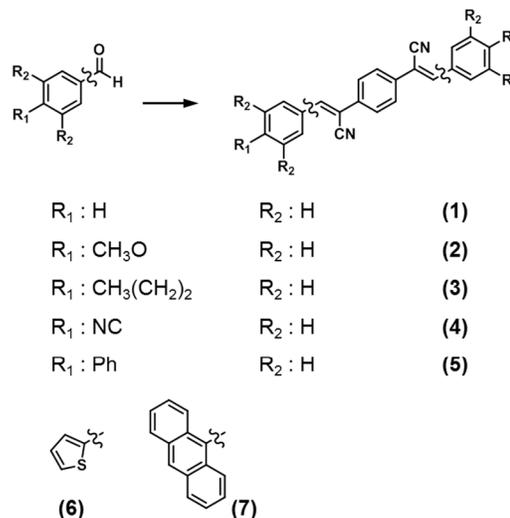
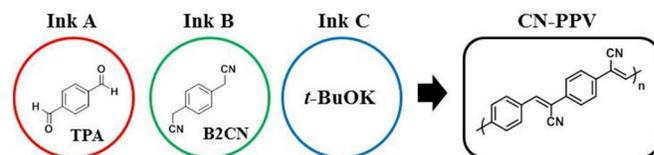


Fig. 5 Structures of cyanostilbene derivatives prepared by the reactive inkjet printing method.

The scope of the reactive inkjet printing is not limited to the preparation of small molecular luminescent materials. We have successfully applied this method to the *in-situ* synthesis of a luminescent conjugated polymer. As shown in Scheme 1, condensation reaction between terephthalaldehyde (TPA) and B2CN in the presence of base yielded a cyano-substituted conjugated polymer poly(phenylenevinylene) (CN-PPV).



Scheme 1 Ink components and a conjugated polymer obtained from reactive inkjet printing.

Inkjet printing of these reactive inks on a glass substrate afforded patterned luminescent microarrays (Fig. 6a and 6b). Versatility of the method was also proved by fabricating arrayed patterns of the conjugated polymer on a flexible PDMS film (Fig. 6c and 6d). FTIR spectroscopic monitoring of the reaction indicates that the starting TPA and B2CN disappeared 24 h after inkjet printing at 20 °C (Fig S5[†]). Comparison of the FTIR spectrum of the conjugated polymer obtained from the inkjet printing with that of CN-PPV independently prepared from the conventional solution synthesis demonstrates the efficiency of the reactive inkjet printing method. In addition, the photoluminescence (PL) spectrum of the product obtained from the inkjet method (Fig. 6e, red line) is almost identical with the one prepared by the solution based approach (Fig. 6e, black line). The molecular weight of the polymer was difficult to obtain owing to the insoluble nature of the polymer.

However, comparison of the emission spectra displayed in Fig. 6e suggests that at least oligomeric conjugated materials are produced by the reactive inkjet printing, since a red shifted emission centred at 635 nm was observed. The complete disappearance of the starting materials by the IR analysis is additional supporting evidence for the formation of the polymeric materials.

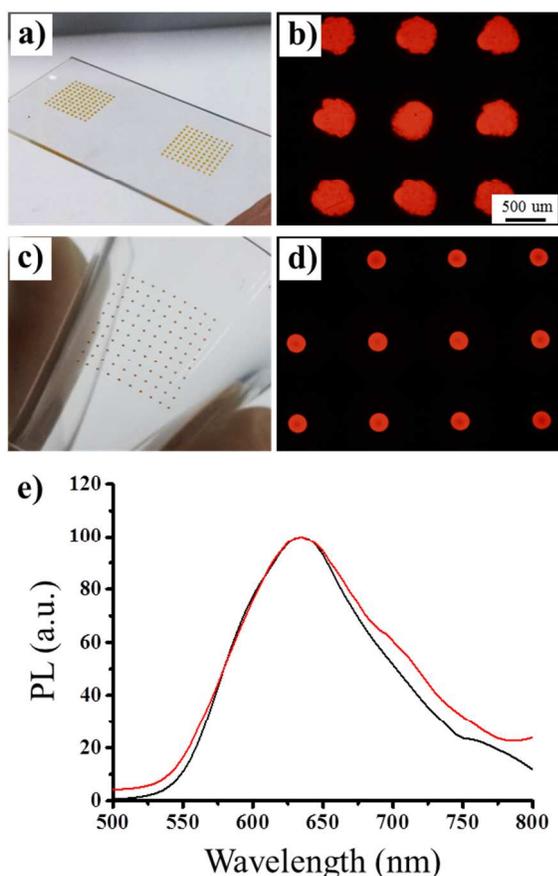


Fig. 6 (a,b) Photograph (a) and fluorescence microscopic image (b) of CN-PPV arrays prepared on a glass substrate at 20 °C. (c,d) Photograph (c) and fluorescence microscopic image (b,d) of CN-PPV arrays prepared on a PDMS film ($\lambda_{\text{ex}}=510\text{-}550$ nm). (e) Photoluminescence (PL) spectra of CN-PPV prepared by reactive inkjet printing (red line) and conventional solution phase synthesis (black line) ($\lambda_{\text{ex}}=470$ nm).

Conclusion

We have utilized a reactive ink system to fabricate fluorescent organic molecular arrays. Inkjet printing of aromatic aldehyde, aromatic nitrile, and base solutions afforded the efficient synthesis of a luminescent cyanostilbene derivative DBDCS by an *in-situ* condensation reaction. The reaction was probed by IR, and NMR analyses and a clean product formation was observed after a 24 h reaction. The luminescent cyanostilbene derivative displayed two different phases (B- and G-forms) depending on the substrate used. The B-form product was obtained when a

glass substrate was employed, while the G-form cyanostilbene was produced when the reactive inkjet printing was carried out on a PDMS film. Regardless of the substrate used, the *in-situ* prepared DBDCS shows vapor-chromic and thermo-chromic behaviors. Cyanostilbene derivatives library also was fabricated by employing various aromatic aldehydes. Fluorescent materials library also was readily prepared through *in-situ* condensation reaction of reactive inks. Facile synthesis of a luminescent conjugated polymer is an additional meritorious feature of this reactive inkjet method. The straightforward approach described above should be useful for the preparation of various stimulus-responsive organic materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, NMR, IR and PL diagrams. See DOI: 10.1039/b000000x/

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Abstract for TOC

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