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Supramolecular Approach to New Inkjet Printing Inks

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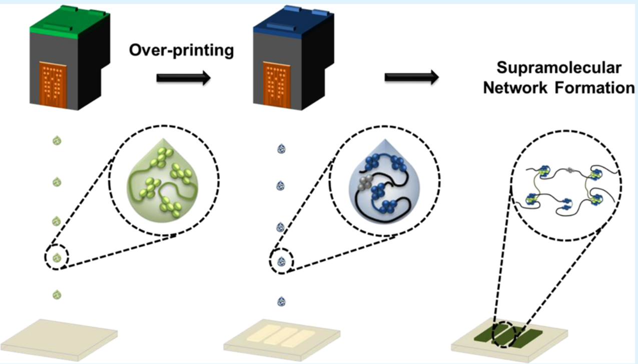
Supporting Information



ABSTRACT: Electronically complementary, low molecular weight polymers that self-assemble through tunable $\pi-\pi$ stacking interactions to form extended supramolecular polymer networks have been developed for inkjet printing applications and successfully deposited using three different printing techniques. Sequential overprinting of the complementary components results in supramolecular network formation through complexation of π-electron rich pyrenyl or perylenyl chain-ends in one component with π-electron deficient naphthalene diimide residues in a chain-folding polyimide. The complementary $\pi-\pi$ stacked polymer blends generate strongly colored materials as a result of charge-transfer absorption bands in the visible spectrum, potentially negating the need for pigments or dyes in the ink formulation. Indeed, the final color of the deposited material can be tailored by varying the end-groups of the π-electron rich polymer component. Piezoelectric printing techniques were employed in a proof of concept study to allow characterization of the materials deposited, and a thermal inkjet printer adapted with imaging software enabled in situ analysis of the ink drops as they formed and of their physical properties. Finally, continuous inkjet printing allowed greater volumes of material to be deposited, on a variety of different substrate surfaces, and demonstrated the utility and versatility of this novel type of ink for industrial applications.

KEYWORDS: *supramolecular, self-assembly, inkjet, charge transfer, polydiimide, polyethylene glycol*

INTRODUCTION

Inkjet printing is an attractive patterning technology[1−3] that is increasingly accepted for a wide variety of industrial and scientific applications. Fields such as graphics,[4] textiles,[5] electronics,[6−9] nanotechnology,[10,11] additive manufacturing,[2,12] and tissue engineering[13−15] utilize its ability to deposit liquid volumes as small as a picoliter, in well-defined arrays at precise locations while minimizing surface contamination.[1,16]

Commercially, the coding and marking of materials with information such as text or barcodes are of great importance to ensure traceability of products. High-throughput printing of tough and durable materials onto a variety of substrates, using either continuous inkjet (CIJ) or drop-on-demand (DOD) technologies, is necessary to deliver high volumes of printed data in a wide range of industrial settings. To achieve this, ink formulations containing high molecular weight polymers are used because of their strength and toughness, properties that ensure any coding or imaging applied to a surface is robust. However, a common issue with the use of high molecular weight, high-viscosity polymers is that they can block printer nozzles over time,[16] resulting in diminishing operational efficiency of the printer and significantly increased cost to the user. The molecular weight constraint also limits the range of materials available to ink formulators in their quest for improved on-substrate performance. A potential solution to this problem is the use of supramolecular chemistry to promote self-assembly of low molecular weight materials on a substrate surface. The resulting pseudo high molecular weight polymers can have many physicomechanical attributes in common with high molecular weight, covalently linked polymers.[17,18]

We have previously described a range of low-MW polymers, functionalized with complementary $\pi-\pi$ stacking motifs,[19−28] that enable formation of healable supramolecular network, and here we report that this approach can be applied to the development of new materials for inkjet printing. Low molecular weight polymers that are easily processed and can assemble via complementary $\pi-\pi$ stacking when deposited sequentially on a substrate surface have thus been designed, synthesized, and printed on a range of substrates. Not only do the $\pi-\pi$ stacking interactions lead to extended, supramolecular, polymer-like networks, but the resulting charge-transfer absorptions also yield strongly colored printed materials.[29−36]

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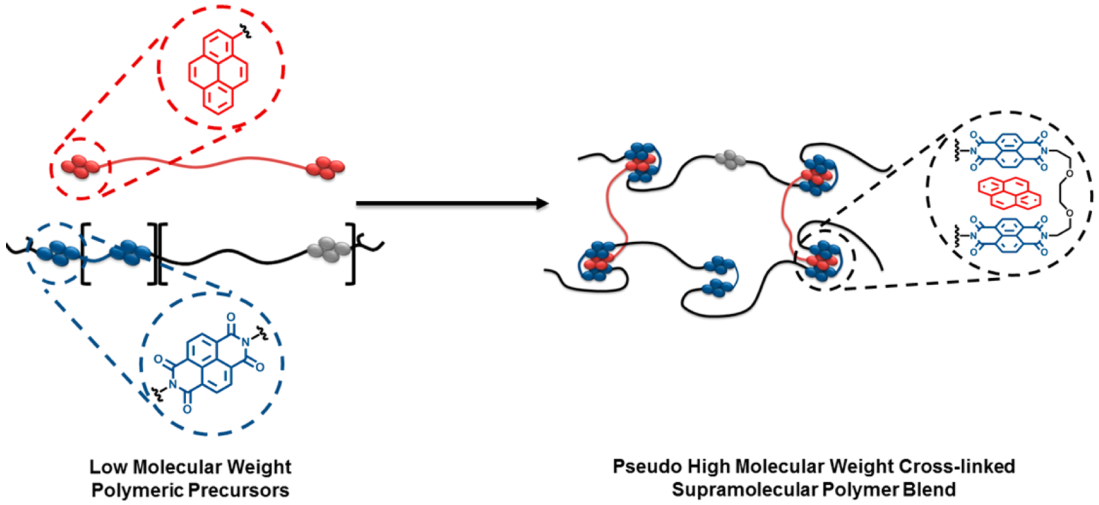
Scheme 1. Formation of Supramolecular Polymer Blends in Which Pyrenyl End-Groups (Shown in Red) Complex with a Chain-Folding Polydiimide (Blue/Black/Gray)[a]



[a]The naphthalene−diimide residues (gray) that are spaced by long PEG residues do not form chain-folding sequences.

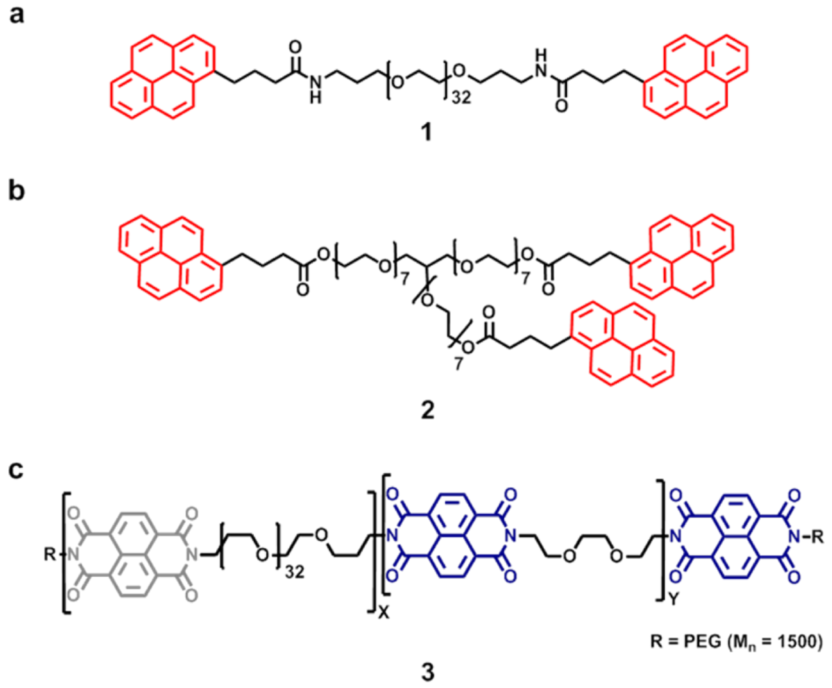


Figure 1. (a) Divalent (**1**) and (b) trivalent (**2**) pyrenyl-terminated π-electron rich polymers, synthesized by DCC-mediated coupling and used to print self-assembling polymer arrays. Pyrenyl moieties shown in red represent the π-electron rich end-groups. (c) The chain-folding polydiimide **3** has geometrically specific chain-folding naphthalene−diimide residues (blue) spaced by a linker derived from 2,2′-ethylenedioxy)bis(ethylamine). The naphthalene−diimide residues (gray) that are spaced by long polyethylene glycol residues do not form chain-folding sequences.

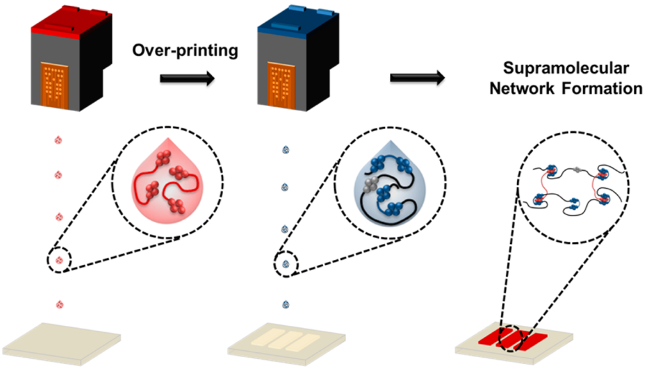
In this initial demonstration of the potential of supramolecular polymers for inkjet printing, difunctional and trifunctional polymers containing π-electron-rich pyrenyl-terminated moieties are combined with a complementary, chain-folding,[17,24,35−39] π-electron-deficient polydiimide (Scheme 1). We also report the ability to vary the charge-transfer colors produced by these supramolecular inkjet inks via structural modification of one of the blend components. This building block approach to supramolecular network generation holds significant potential for the development of new inkjet inks that possess tunable physical characteristics and colors.

■ RESULTS AND DISCUSSION

We have previously reported the preparation of a pyrenyl-terminated, divalent polymer **1** (Figure 1a, Supporting Information Figure S1) and its trivalent analogue **2** (Figure 1b, Supporting Information Figure S2) as part of a program to develop healable supramolecular blends with chain-folding polydiimides.[40] These telechelic polyethers were synthesized by DCC-mediated coupling of 1-pyrenebutyric acid with linear and branched PEGs to afford highly soluble polymers with π-electron rich end-groups. Previous studies have utilized chain-folding polydiimides with branched-alkyl termini[21−25,27,28] as complementary π-electron deficient polymers. Here we report a structurally related, chain-folding polydiimide **3**[41] (Figure 1c) with PEG terminal groups (Supporting Information Figure S3) which demonstrated improved solubility in solvents such as THF and ethanol and which thus enabled the new materials to be deposited via inkjet printing.

In order to produce self-assembled supramolecular networks from low-molecular weight polymers by inkjet printing, an overprinting approach was first investigated,[42,43] in which the complementary polymers are deposited sequentially on the substrate (Scheme 2).

Scheme 2. Overprinting of a π-Electron Rich Polymer with a π-Electron Deficient Polymer To Afford a Colored Supramolecular Network on the Substrate Surface



Before printing of the complementary supramolecular polymers, the solution characteristics of the individual polymers **1**, **2**, and **3** as well as their blends (**1** + **3**) and (**2** + **3**) were analyzed. Solutions of the respective polymers (10^{-4} M with respect to binding motifs) were formulated in THF/1,2-hexanediol (1:1 v/v) and filtered through a 5 μm microfiltration membrane. Dynamic solution viscosities (Figure S4) were then analyzed using a rolling-ball viscometer to investigate the presence of supramolecular interactions[44] and to ensure that the viscosity values fell within a suitable range for inkjet printing (approximately 2−12 cP). On blending of the solution containing the divalent pyrenyl polymer **1** (4.3 cP) with that containing the chain-folding polydiimide **3** (9.3 cP), a viscosity increase (to 10.8 cP) was observed in the resulting divalent blend solution (**1** + **3**), corresponding to a change in viscosity of 4.0 cP with respect to the mean viscosity of the two-component solutions (an estimated viscosity based on blending the two polymers if $\pi-\pi$ stacking interactions were not present). On blending the trivalent pyrenyl polymer **2** formulation (3.2 cP) with the chain-folding diimide **3** formulation, a red precipitate was produced, demonstrating the formation of an insoluble supramolecular network which was not amenable to printing in a preblended solution. These observations are consistent with previous studies[40] in which a divalent polymer blend showed a modest increase in viscosity while a much greater viscosity increase was observed when trivalent systems were blended.

Printing of the supramolecular polymer blends formed between either **1** or **2** and polydiimide **3** was carried out initially using a piezoelectric drop-on-demand inkjet printer (PIJ)[45] in which an electrical current changes the shape of a piezoelectric material within the printhead, creating a pressure pulse and thus ejecting a drop from the nozzle. Individual inkjet cartridges were filled with a membrane-filtered (0.5 μm) solution (3 mL) of the π-electron-rich polymer (**1** or **2**), which was deposited directly onto nonoptically brightened white card before overprinting with the π-electron deficient polymer formulation (**3**) from a separate cartridge. Formulations containing divalent **2** and trivalent **3** were deposited successfully onto the substrate under ambient conditions. Although the printed samples were essentially colorless to the naked eye (Figure 2a and Figure 2d), irradiation with a standard laboratory UV light source (254 nm) revealed a characteristic blue emission from the pyrenyl chain-ends[46] (Figure 2a′ and Figure 2d′) while also demonstrating sharply printed images. Separately, the chain-folding polydiimide **3** (Figure 2b and Figure 2e) was deposited under analogous conditions. The printed material was now pale brown in color

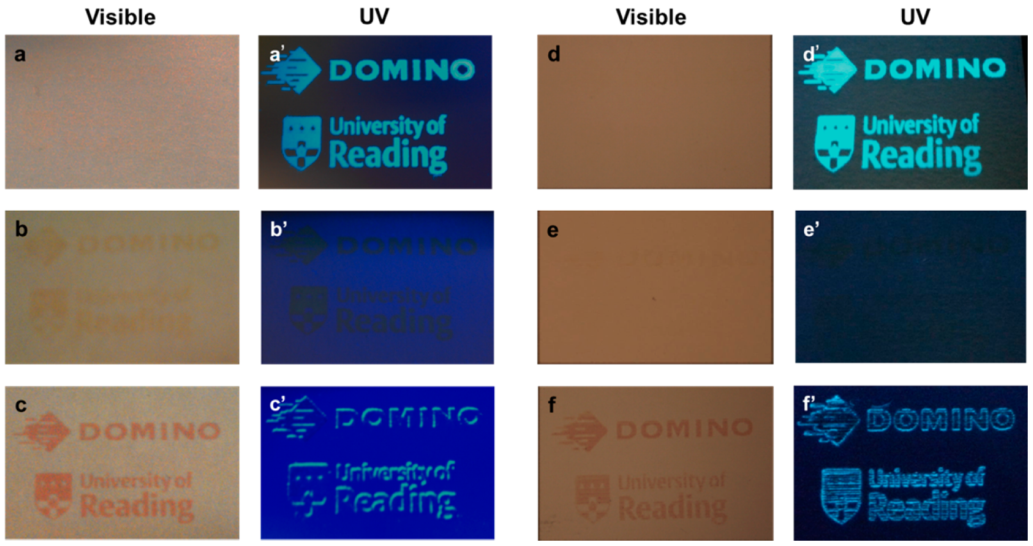


Figure 2. Images of the printed pyrenyl samples under visible (a, d) and short wavelength UV light (a′ and d′) showing the formation of colored charge-transfer complexes (c, f) from electronically complementary polydiimide (b, b′, e, e′) moieties within the supramolecular polymer architecture. Quenching of pyrenyl emissions in the overprinted samples (c′, f′) is observed under short wavelength UV light. Note that images b and b′ and e and e′ represent the printing of **3** on two different occasions under analogous conditions.

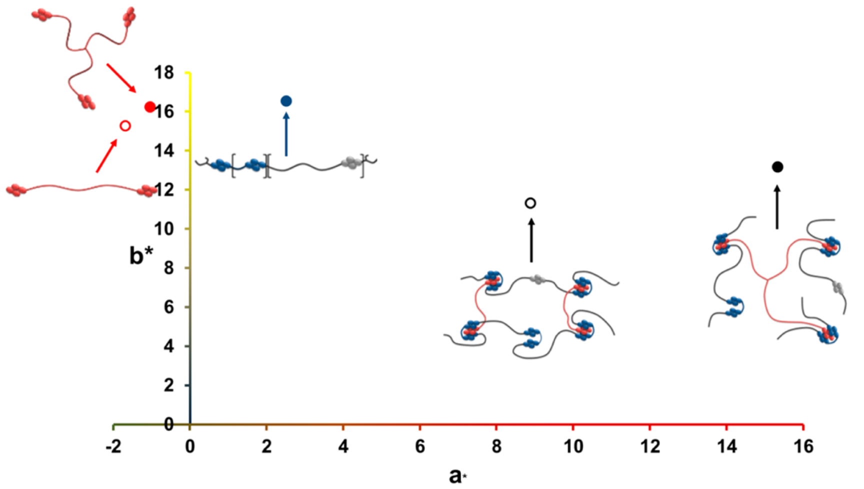
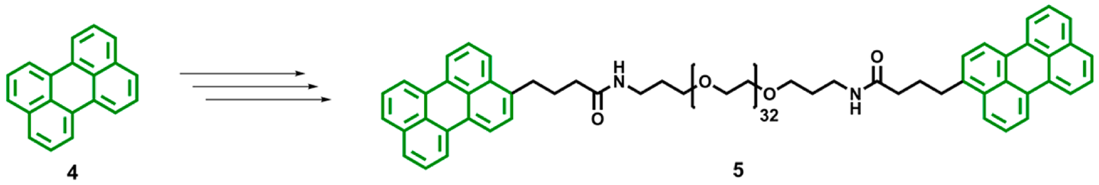


Figure 3. Color space analysis of the printed samples, demonstrating the marked shifts in the value of a^* in the overprinted materials.

Scheme 3. Structures of Perylene 4 and the Divalent Perylene-Terminated Polyethylene Glycol 5



under visible light, but no significant fluorescence was evident on irradiating with UV light at 254 nm (Figure 2b′ and Figure 2e′). On overprinting of the polydiimide with solutions of either the divalent pyrenyl-terminated **1** (Figure 2c) or trivalent pyrenyl **2** (Figure 2f), a distinct red color resulted from sequential deposition of the two essentially colorless precursors. This color arises from a charge-transfer absorption[29−36] resulting from $\pi-\pi$-stacking between the chain-folding diimide and electronically complementary pyrenyl residues[47,48] and immediately indicates formation of an extended supramolecular polymer network. Upon irradiating the overprinted samples with short wavelength UV light (254 nm), the pyrenyl emissions were seen to be quenched as a result of the charge-transfer complexation (Figure 2c′ and Figure 2f′). Owing to the tolerances of the movable surface on which the substrate is mounted, a slight misalignment was observed in the overprinted samples which can be visualized by persistent pyrenyl emissions.

To quantify the color changes on overprinting complementary formulations, color space analysis was undertaken using a GretagMacbeth SpectroEye instrument. Figure 3 shows a two-dimensional representation of the resulting analysis. On the a^* axis, negative values characterize colors tending toward green whereas positive values tend toward red, and the b^* axis represents colors tending toward blue (negative values) or yellow (positive values). It was found that the two printed pyrenyl terminated polymer formulations (**1** or **2**) have similar color characteristics (divalent, $a^* = -1.7$, $b^* = 15.3$; trivalent, $a^* = -1.0$, $b^* = 16.2$). When these solutions were overprinted with the chain-folding polydiimide ($a^* = 2.5$, $b^* = 16.6$), a red image appeared as a result of the charge-transfer absorption, and consequently, a dramatic shift toward higher a^* values was observed. The divalent blend was seen to shift to an a^* value of 8.9, while a greater increase was demonstrated by the trivalent blend ($a^* = 15.3$) as a consequence of the increased density of discrete charge-transfer complexes. The l^* coordinate (Figure S5) allows for a representation of darkness, from white (100) to black (0). While the divalent **1** and trivalent **2** pyrenyl polymer formulations are extremely pale in color (l^* of 92.3 and 93.8, respectively) as seen in the printed images (Figure 2), upon overprinting with the chain-folding polydiimide ($l^* = 86.6$), a decrease in l^* values were observed for both the divalent supramolecular blend ($l^* = 82.3$) and trivalent supramolecular blend ($l^* = 77.8$), indicating a darker image was formed.

Fluorescence spectroscopy was also carried out on the printed samples. Analysis at increasing excitation wavelength revealed the characteristic emission bands for the pyrenyl excimer emission centered at 470 nm, with the greatest intensity being observed for excitation at 345 nm.[46] This excimer emission is more prominent in the spectrum of the trivalent polymer **2** (Figure S6d) than in that of divalent polymer **1** (Figure S6a), as consequence of the increased effective concentration of pyrenyl residues. When **1** or **2** was overprinted with the fluorescence-inactive polydiimide **3** (Figure S6b), the excimer pyrenyl emissions were completely quenched[20,22,23,49] (Figure S6c and Figure S6e), confirming complementary $\pi-\pi$ stacking in the deposited material.

Previous studies[50] have also demonstrated the use of perylene, **4**, as an alternative π-electron rich moiety for use in healable supramolecular polymer blends. Interestingly, the charge-transfer complexes formed between perylene and the chain-folding diimide produce green solutions. This color was also retained in the solid state when films of the polymer blend were drop-cast, demonstrating promise for use as a polymer in the current application. A divalent perylene-terminated polyether **5** was synthesized (Scheme 3, Figures S7−S10) as described previously[50] from perylene, **4**.

The solution characteristics of the individual polymers (in THF/1,2-hexanediol, 1:1 v/v, 10^{-4} M with respect to binding motifs) as well as of the blend were analyzed as described above

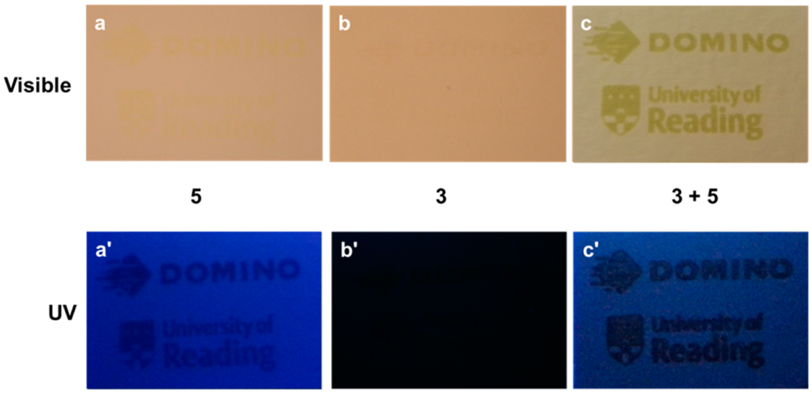


Figure 4. Images of the printed samples of **3**, **5**, and (**3** + **5**) under visible light (a, b, c) and short wavelength UV light (a′, b′, c′) revealing the formation of green charge transfer complexes from electronically complementary moieties within the supramolecular polymer network.

for the pyrenyl systems. Dynamic viscosity measurements (Figure S11) revealed that on blending the divalent perylenyl polymer **5** formulation (4.1 cP) with the chain-folding polydiimide **3** formulation (9.3 cP), a viscosity increase (11.3 cP) was observed in the resulting solution of the supramolecular polymer blend (**3** + **5**). The increase corresponds to a change in viscosity of 4.6 cP with respect to the mean viscosity of the individual components. These observations are consistent with previous studies[40] and with those demonstrated here by the divalent pyrenyl polymer blend (**1** + **3**, 10.8 cP), demonstrating the new formulations were suitable for deposition by way of a piezoelectric drop-on-demand inkjet printer (PIJ).

Inkjet deposition of solutions onto nonoptically brightened white card was carried out using a membrane-filtered (0.5 μm) solution (3 mL) of the π-electron-rich perylene terminated polymer, overprinted with the π-electron deficient chain-folding polydiimide formulation under ambient conditions. The printed sample of the perylene terminated polymer **5** alone was a faint yellow color when examined under visible light (Figure 4a). Irradiation with a standard laboratory UV light source (254 or 310 nm) did not reveal the characteristic blue emission from the perylene moieties[46] in the solid state (Figure 4a′), although the polymer was observed to fluoresce in solution prior to deposition. One possible explanation for this unexpected result is self-quenching of the perylene fluorescence in the solid state, once deposited. Lemmetyinen et al. have reported[51] an analogous result in which Langmuir–Blodgett films containing pyrene-labeled phospholipids undergo self-quenching of the pyrene chromophores in close proximity. The chain-folding polydiimide **3** was also deposited under analogous conditions, exhibiting a pale brown color under visible light (Figure 4b) and no significant fluorescence (Figure 4b′) on irradiating with UV light (254 nm). On overprinting the polydiimide **3** with a solution of the perylene-terminated polymer **5** (Figure 4c), an intense green color was observed (from deposition of two pale brown/yellow solutions). This color change is the consequence of a charge-transfer absorption resulting from $\pi-\pi$ stacking between the electronically complementary chain-folding diimide and perylene residues, indicating formation of an extended supramolecular polymer network. Upon irradiation of the overprinted samples with long wavelength UV light (310 nm), perylene fluorescence was not observed (Figure 4c′). Spectroscopic studies of model compounds[50] have demonstrated fluorescence quenching of perylene by a chain-folding bis-diimide in solution, which would presumably also take place in the deposited solid once the perylene aggregates had been dispersed by the formation of charge-transfer complexes.

Color space analysis (Figure S12) was also used to confirm the distinct color change upon overprinting. It was observed that the color characteristics of the perylene terminated polymer **5** (a^* = −7.9, b^* = 53.6) were at high b^* values indicating the sample was yellow, with a slight green hue evidenced from the negative a^* character. When the solutions were overprinted with the chain-folding polydiimide **3** (a^* = 0.9, b^* = 14.7) a green image was developed as a result of the charge-transfer absorption, and so a shift toward lower a^* values was observed (a^* = 11.8, b^* = 41.1). Although showing only a modest shift to negative a^* values, the sample displayed a stronger green color, while a dramatic loss of the yellow (b^*) characteristic of the printed samples also can be attributed to the formation of a supramolecular charge-transfer complex between electronically complementary binding motifs (**3** + **5**). The l^* coordinate also gave an indication as to the darkness of the deposited material. The perylene terminated polymer **5** was pale in color (l^* = 87.4), which correlated well with visual inspection of the printed images. While the chain-folding polydiimide **3** was slightly darker (l^* = 84.1), a large decrease in l^* values was observed for the supramolecular blend **3** + **5** (l^* = 74.7).

An additional technique to confirm the presence of supramolecular interactions between electronically complementary polymers in the printed samples was fluorescence spectroscopy (Figure S13). Previous studies[40] with pyrenyl moieties as end-groups have utilized this technique to great effect, but in the current system, the perylene chain ends did not fluoresce in the solid state as confirmed by visual inspection of the printed samples (Figure 4). It is possible that self-quenching was the result of microphase separation between the polymer midblock and the perylene residues at the chain termini, bringing the aromatic units into close proximity and allowing good orbital overlap between neighboring perylene moieties. The chain-folding polydiimide was fluorescence-inactive as previously described, while the overprinted blend was also fluorescence inactive. Thus, by varying the π-electron rich chromophore in the self-assembled complex, we have demonstrated that tuning of charge-transfer band may be achieved by structural modification, an approach that could be utilized to generate a palette of different printed colors; the analogous anthracene complex, for example, is blue.

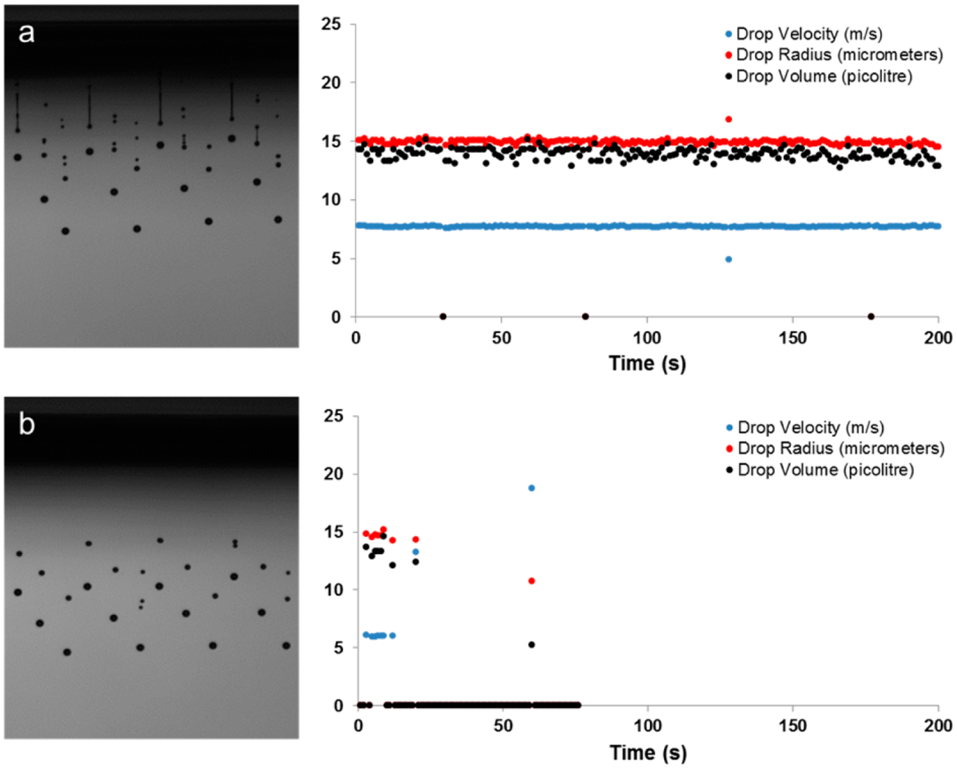


Figure 5. Stroboscopic images and JetXpert analysis of (a) the divalent pyrenyl formulation and (b) the chain-folding polydiimide formulation. Imaging of the drops allows the JetXpert software to calculate the physical characteristics of the droplets formed. The gray area at the very top of each image is the printhead, viewed side on and parallel to the cartridge.

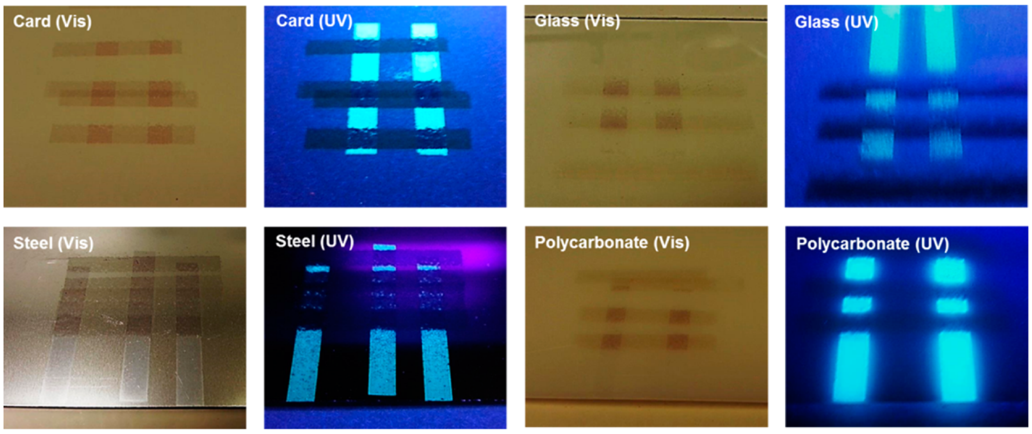


Figure 6. Supramolecular polymers deposited on a variety of substrate surfaces by continuous inkjet printing. The trivalent pyrenyl **2** formulation was deposited initially, before the substrate was rotated through 90°, and the chain-folding diimide **3** formulation then overprinted. Where the printed lines intersect, red $\pi-\pi$-stacked interpolymer complexes are formed between the electronically complementary moieties, and fluorescence quenching is also observed.

To study the formation of droplets from the printhead, a thermal inkjet (TIJ)[2,52] drop-on-demand printer adapted with a JetXpert analysis suite for in situ drop-in-flight measurements was used. Samples of divalent pyrenyl polymer **1** and chain-folding polydiimide **3** were formulated as described above, and 20 mL of each solution was loaded into individual cartridges for analysis. As a result of the low viscosity of the formulation containing the trivalent pyrenyl polymer **2**, this material could not be printed, the viscosity characteristics being outside the operating window of the printer. Samples of the other polymer formulations were printed continuously for up to 3 min, and the drop radii, volumes, and velocities were measured. The divalent pyrenyl polymer formulation demonstrated steady drop formation (Figure 5a) in triplicate from the three rows of nozzles, each firing at a set time delay, although satellite drops and ligaments were also observed owing to imperfect breakup of the drops. Analysis of the stroboscopically illuminated ink drops of the divalent pyrenyl formulation (**1**) gave the average drop velocity (7.7 ms^{-1}), average drop radius (14.9 μm), and average volume (13.9 pL) of the observed droplets. The chain-folding polydiimide solution (**3**) exhibited similar parameters while printing (average velocity of 8.2 ms^{-1}, average radius of 14.7 μm, average volume of 12.3 pL), although the drops were produced with fewer satellites and ligaments (Figure 5b). The stability of the jet of polydiimide **3** was observed to diminish after 80 s, at which point the drops were no longer detectable by the parameters of the software, although still being produced visually.

To further evaluate the utility of the ink formulations developed in this work, continuous inkjet printing (CIJ)[53] was next investigated as a technique for depositing greater volumes of material and accessing a wider variety of substrates. This type of printing, in which the ink is recycled in a closed loop system and deposited by selectively deflecting single drops from the droplet stream created at the printhead, is used in a variety of industrial settings as a high-speed coding and marking tool. Although the resolution of the printed image is not as high as that which can be achieved with other inkjet printers, the faster printing speeds associated with the technology, coupled with the increased number of substrate-types that can be marked, account for CIJ printing being used in some 90% of coding applications.[16]

To achieve successful deposition of the supramolecular polymers by CIJ, a number of additives were required including salts (to provide conductivity and so enable drops to be charged and deflected) and viscosity modifiers.[16] The trivalent pyrenyl polymer **2** was selected for deposition along with the chain-folding polydiimide **3**, as this combination had demonstrated the most promising results in PIJ printing studies through the formation of more densely "cross-linked" supramolecular networks.[40] Jettable formulations of polymers **2** and **3** (4.8% w/v) were produced using a solvent blend comprising THF (71.0% v/v), 1,2-hexanediol (7.9% v/v), and ethanol (3.9% v/v). Lithium nitrate (4.8% w/v) was added to the formulation to provide conductivity, and cellulose acetate butyrate [M_n = 16 000 Da] (7.6%, w/v) was used to modify the solution viscosity. These formulations had viscosities of 3.99 cP (**2**) and 5.41 cP (**3**), respectively, while the conductivities of 552 μS cm^{-1} (**2**) and 515 μS cm^{-1} (**3**) allowed for use in a CIJ printer fitted with a 75 μm nozzle. Multiple lines of the trivalent pyrenyl **2** were deposited on a variety of substrates including nonoptically brightened white card, polycarbonate, glass, and steel (Figure 6) before perpendicularly overprinting with the chain-folding polydiimide **3**. Visual inspection of the intersection between the two printed patterns revealed the familiar red color indicative of the $\pi-\pi$ stacking interaction. The pale brown color of the chain-folding polydiimide **3** was observed on all surfaces, but the trivalent pyrenyl polymer **2** was visible only on the steel substrate. Irradiation with short-wavelength UV light (254 nm) demonstrated quenching of the pyrenyl emissions on all substrates, as previously seen when printing on the nonoptically brightened white card using the piezoelectric printer. These results greatly widen the scope for printing supramolecular polymers on a range of different substrates for a variety of applications.

CONCLUSIONS

New supramolecular polymers have been developed for inkjet printing applications and successfully deposited using three different printing techniques. By sequential overprinting of the two complementary polymer solutions, a self-assembled supramolecular network is formed on the substrate surface, thus producing a pseudo high molecular weight polymer from two complementary low molecular weight precursors. Furthermore, this delivery system produces self-colored images without the need for dyes or pigments and with scope for further colors to be developed through tuning of the charge transfer absorption. Visual inspection of the materials deposited by PIJ printing showed that overprinting the π-electron rich pyrenyl polymer (**1** or **2**) or perylenyl polymer (**5**) with the π-electron deficient chain-folding polydiimide **3** resulted in a distinct red (**1** + **3** or **2** + **3**) or green (**3** + **5**) color as a result of the charge transfer absorption between electronically complementary residues. Examination of the overprinted samples under short wavelength UV light demonstrated fluorescence quenching of the chromophore emissions through complexation on the printed substrate surface. These results were further quantified by color space analysis and fluorescence spectroscopy on the printed materials. A TIJ printer was then used to monitor droplet formation and the physical properties of the droplets formed. The formulation containing the divalent pyrenyl polymer **1** was selected for examination owing to its favorable viscosity characteristics, demonstrating stable printing over an extended period, while drop breakup was seen to be improved in the chain-folding polydiimide **3** formulation with fewer satellites and ligaments being formed when compared to polymer **1**. Finally, a CIJ printer was used to deposit larger volumes of formulations containing **2** and **3**, affording high levels of supramolecular "cross-linking". Polymers were printed onto a variety of substrates with retention of the supramolecular interactions, demonstrating the versatility and potential of supramolecular polymer systems in inkjet applications using a variety of printing techniques.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details, including characterization of the polymers described and additional data figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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