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## Beyond binary: optical data storage with 0, 1, 2, and 3 in polymer films†

Peiran Wei,‡ Bowen Li,‡ Al de Leon and Emily Pentzer \*

The evergrowing amount of data created and collected is met with the increased need to store this data. In compliment to improving data storage capabilities using engineering controls such as decreased pixel size (*i.e.*, Blu-ray) or 3-D pixels (*i.e.*, voxels), chemistry-based approaches are required to move beyond current limitations and meet our future needs. Herein, we present a new methodology to optically store data in a quaternary code of 0, 1, 2, 3 in a commodity polymer containing a low loading of two small molecules, and using heat and UV light to write, and read fluorescence output. The as-prepared film is non-fluorescent (0), and can be written through a wooden or metal mask with thermal treatment (1), light treatment (2), or both (3), giving three different colours of fluorescence under UV irradiation. The flexible polymer film remains colourless and transparent under ambient light after patterning, retains the stored data after exfoliation with sandpaper, and can be removed from the substrate and mechanically deformed without detriment to the pattern. This straightforward and scalable system demonstrates the use of simple and robust chemical reactions to improve data storage capabilities and has the potential to exponentially increase information density.

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## Introduction

As the amount of data generated has increased exponentially in the past few decades, the demand for scalable and portable information storage devices likewise grows.<sup>1,2</sup> To meet these needs, novel engineering-based approaches have been pursued, including magnetic storage devices,<sup>2–4</sup> optical data storage (ODS),<sup>2,5</sup> and flash memory.<sup>6</sup> Among these, ODS attracts both academic and industrial interest due to low cost,<sup>7,8</sup> high capacity,<sup>7,9</sup> and high data stability.<sup>3,7</sup> Typical ODS techniques that are reproducible and commercially used rely on a binary data system (0, 1),<sup>2,7,10</sup> accessed, for example, by locally changing the optical properties of the medium, as in compact discs (CDs). Tremendous research and development efforts have been expended to increase capacity by decreasing the size of the laser spot and thus decrease the physical size of the unit of data stored (*i.e.*, storage unit of 800 nm for CD to 150 nm for Blu-ray).<sup>5,9</sup>

More recent successes improving ODS using engineering approaches include patterning of 3-D pixels, called voxels by using multilayer films and nonlinear excitation.<sup>4,11–13</sup> For example, Singer and coworkers reported a co-extrusion process to fabricate a film of 23 layers of poly(ethylene terephthalate glycol modified)

(PETG) in which every-other layer contained a thermo-responsive small molecule dye; data was then written using a confocal Blu-ray laser to give a fluorescent binary code in 3D.<sup>14,15</sup> In a similar vein, Belfield and coworkers reported a 3D ODS system composed of a polymer matrix containing an acid sensitive, two-photon-absorbing dye and a photoacid generator; this system allowed for fluorescent data to be recorded in voxels, as written by a two-photon process, up to eight layers thick.<sup>5</sup> While these systems are promising, transformative innovations in storage techniques beyond engineering controls are necessary to meet the requirements for the scalable and portable storage of data.

An attractive approach to next generation ODS systems is based on an output higher order than binary (0, 1), particularly ternary (0, 1, 2) or quaternary (0, 1, 2, 3) codes. Such systems could be accessed by the concurrent use of multiple responsive units in one material, in which each unit responds to unique stimuli to result in complimentary outputs. A range of stimuli can be used to trigger outputs, including mechanical force,<sup>16–18</sup> small molecule additives (*e.g.*, CO<sub>2</sub>, NO<sub>x</sub>),<sup>19,20</sup> and applied voltage,<sup>21–25</sup> among others; furthermore, potential outputs include changes in solubility,<sup>26</sup> second harmonic generation signal,<sup>27</sup> and production of small molecules. Perhaps one of the most simplistic and readily accessible stimuli/output systems is heat and/or light as stimulus (thermo- and photo-responsive) and output of colour change (absorption or emission).<sup>28–31</sup> Common photo-responsive systems include spiropyrans and diarylethenes, and their derivatives,<sup>32,33</sup> which reversibly undergo colour change based on electrocyclic reactions catalyzed by light; for example, Yam and

Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106,  
USA. E-mail: ehp24@case.edu

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‡ These authors contribute equally.

coworkers reversibly patterned a polymer matrix containing functionalized diarylethene, with excellent fatigue resistance.<sup>34</sup> Although thermo-responsive systems are not as ubiquitous, an elegant data storage system was reported by Weder and coworkers based on an alkyl-substituted oligophenylene-vinylene small molecule in a polymer matrix. Heat was used to control the aggregation state of the molecule in the polymer; the as processed film was fluorescent due to solubility of the molecule within the polymer host, but after heating above the  $T_g$  of the polymer, the film was no longer fluorescent as the small molecule diffused through the matrix and formed excimers.<sup>35</sup> Likewise, Takeoka and coworkers tailored the chemistry of a polymer-based system to prepare a material that can be stimulated with heat and light to control the colour of the material under ambient conditions. The well-known thermo-responsive polymer poly(*N*-isopropyl acrylamide) (PNIPAM) was partially functionalized with azobenzene units, then porous hydrogels were prepared and careful selection of temperature and light irradiation was used to tune the colour over the visible region.<sup>36</sup> While these systems reveal the crucial role chemical composition plays in a material's response to stimulus, further innovations in materials are required to transform the field of data storage. Indeed, a single system that utilizes two orthogonal stimuli to access two or more unique and complimentary outputs is an attractive approach to moving beyond a binary code (0, 1) to ternary (0, 1, 2) or quaternary (0, 1, 2, 3).

Herein, we present a quaternary data storage system using orthogonally stimuli-responsive small molecule dyes in a film of commodity polymer. This system is composed of a poly(methyl methacrylate) (PMMA) film containing <0.04 wt% of two small molecules: **Dye 1** which is thermally responsive and becomes fluorescent upon heating the film to 120 °C and **Dye 2** which is photo-responsive and becomes fluorescent upon irradiation with 365 nm light.<sup>37,38</sup> Before stimulus is applied, the polymer film is transparent, colourless, and without fluorescence (Fig. 1, left); upon photo-irradiation ultramarine fluorescence is observed, upon thermo-irradiation green fluorescence is observed, and upon both thermo- and photo-irradiation cyan fluorescence is observed, yet the film remains transparent and nearly colourless under ambient conditions (Fig. 1, right). Wooden or metal masks (Fig. 1, center) can be used to pattern films quickly and efficiently with spatial resolution of 300 μm for both dyes, and the patterns

remain after exfoliation or submersion of the film in boiling water. This straightforward and scalable system demonstrates a novel, chemistry-based method using easily accessible materials, which has the potential to transform data storage capabilities by using higher order code, especially with specialized light and heat sources (*i.e.*, lasers).

## Result and discussion

The commodity polymer PMMA was chosen as the polymer matrix for the two dyes due to its ready availability, ease of process, and solubility of both small molecules in the matrix. **Dye 1** (Fig. 2A) is a known cyano-substituted oligo(*p*-phenylene vinylene) developed by Weder and co-workers, and was prepared following the reported procedure.<sup>35</sup> The thermo-responsivity of **Dye 1** is based on its aggregation state in a polymer film; its excimer (*i.e.*, aggregate) form is non-fluorescent and its monomeric form is fluorescent. Thus, the solubility of **Dye 1** in the polymer matrix, as well as the mobility of polymer chains can be used to dictate the fluorescence output. A film prepared by blade coating PMMA containing 0.04 wt% of **Dye 1** is non-fluorescent due to aggregation of the small molecule at this concentration and under these processing conditions; however, post-deposition thermal annealing of the polymer film allowed molecules of **Dye 1** to diffuse away from each other through the polymer matrix, and removal of the heat source quenched the molecular movement such that the monomeric form of **Dye 1** was trapped, and green fluorescence was realized. **Dye 2** (Fig. 2B) is an *o*-nitrobenzyl ester of benzoic acid prepared following standard reactions (see ESI†); these tailored esters undergo Norrish Type II radical cleavage under UV irradiation (mechanism in ESI†) and the linkage is commonly used to change the solubility of macromolecules.<sup>39</sup> This reaction produces a fluorescent byproduct, an *o*-nitro benzaldehyde, which has not been substantially investigated or utilized in previous studies.<sup>40</sup> A recent report from our group illustrated incorporation of an *o*-nitrobenzyl ester functionalized phthalocyanine in polymer films, and used this system to pattern fluorescence using UV light.<sup>41</sup> The structure and purity of **Dye 1** and **Dye 2** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, and mass spectrometry (see ESI†). Moreover, **Dye 1** is stable under UV irradiation and **Dye 2** is thermally



**Fig. 1** Overview of work presented herein: transparent and non-fluorescent PMMA film containing two orthogonally responsive dyes, use of a wooden mask and thermal and photo stimuli to give a transparent film with fluorescent pattern and data storage in 0 (no fluorescence), 1 (green fluorescence), 2 (aquamarine fluorescence), and 3 (blue fluorescence). Polymer film is 3 cm × 5 cm; main image shows film under UV light and insets show full film under ambient light.

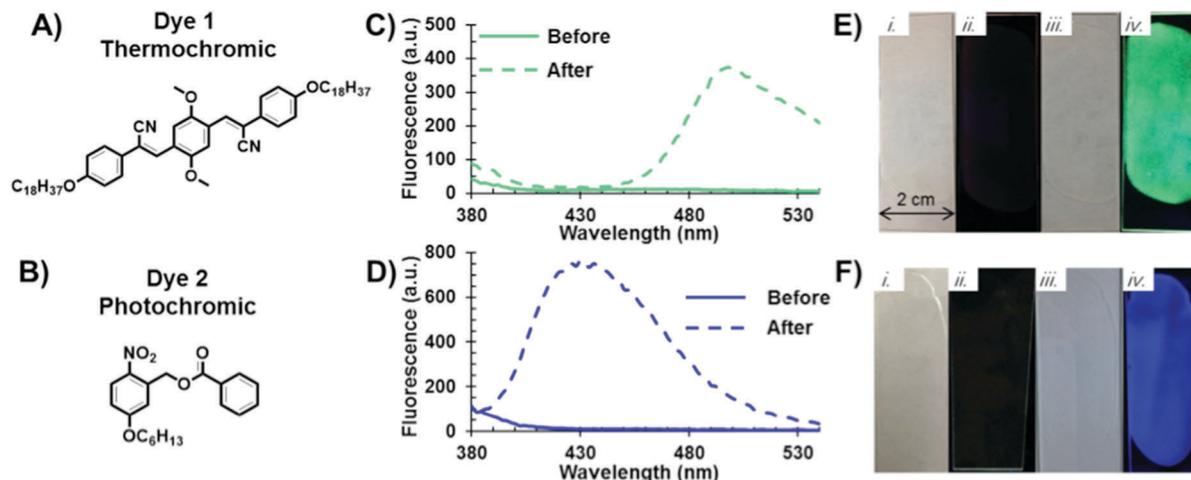


Fig. 2 (A and B) Chemical structures of **Dye 1** and **Dye 2**; (C and D) emission spectra before and after applied stimuli for **PMMA-D1** and **PMMA-D2** ( $\lambda_{\text{ex}} = 365$  nm); (E and F) photographs **PMMA-D1** and **PMMA-D2** under ambient light before (i) and after (iii) after applied stimuli, and under UV light before (ii) and (iv) after applied stimuli.

stable up to  $>200$  °C (Fig. S2, ESI<sup>†</sup>), suggesting the dyes will be orthogonally responsive when incorporated into a single polymer film.

To study the responsivity of each dye, PMMA films containing only **Dye 1** or only **Dye 2** were prepared by blade coating (referred to as **PMMA-D1** and **PMMA-D2**). A range of concentrations of the dyes was evaluated, and optimal loadings were determined to be 0.01 wt% for **Dye 1** and 0.04 wt% for **Dye 2**, with film thickness of  $\sim 40$   $\mu\text{m}$ . Both films were nearly colourless, transparent, and non-emissive under UV light (i and ii of Fig. 2E and F). Heating **PMMA-D1** to 120 °C for 5 seconds using an air heat gun rendered the film green fluorescent under UV light (Fig. 2E(iv)), due to a change in aggregation state of the molecule (excimer to monomer). UV irradiation of **PMMA-D2** led to a film with ultramarine fluorescence (Fig. 2F(iv)), attributed to the *o*-nitrosobenzaldehyde compound produced upon a Norrish Type II reaction;<sup>40,41</sup> of note, the strength of the UV light source determines the required time of exposure for fluorescence activation (e.g., 10 minutes for a hand held UV lamp or 1 minute using a Bluepoint irradiator from Honle UV America). **PMMA-D1** and **PMMA-D2** showed emission maxima at 510 nm and 430 nm, respectively (Fig. 2C and D,  $\lambda_{\text{ex}} = 365$  nm), with little overlap in emission. After application of the stimuli, both films remained transparent and colourless under ambient conditions (Fig. 2E(iii) and F(iii)). As the two dyes respond to two different stimuli and show distinct emission profiles, incorporation of both dyes into the same polymer film should lead to orthogonal fluorescence outputs based on the stimuli used, provided the dyes do not unfavorably interact with each other by forming charge transfer complexes or undergoing fluorescence resonance energy transfer (FRET).

To demonstrate the feasibility of individually stimulating **Dye 1** and **Dye 2** in the same polymer film, a PMMA film containing both dyes was prepared by blade coating from an ethyl acetate solution (referred to as **PMMA-D1-D2**). The 40  $\mu\text{m}$  thick film was divided into four quadrants by exposing the right half of

the film to UV irradiation (365 nm), and the bottom half of the film to heat (120 °C), and shown in Fig. 3A. The top left quadrant of **PMMA-D1-D2** is untreated, and shows no fluorescence under UV light, as expected. The bottom left quadrant of **PMMA-D1-D2** is exposed to only heat and showed a green fluorescence similar to that observed for **PMMA-D1**, while the top right quadrant is only exposed to UV light and showed an

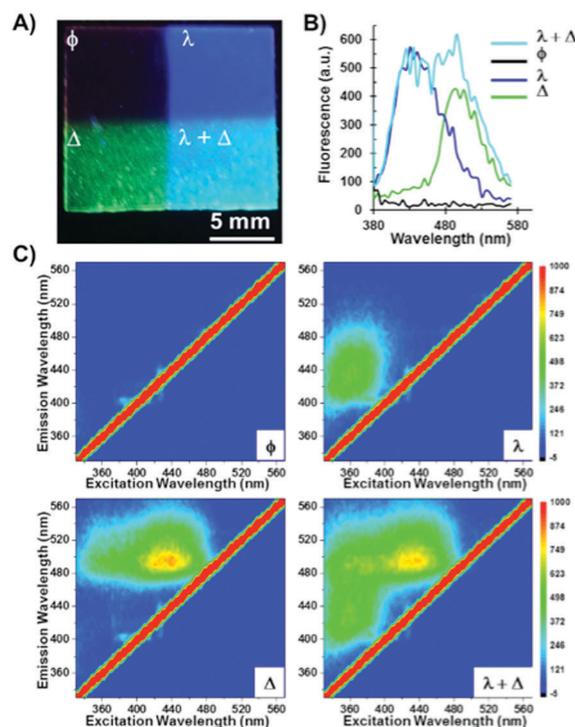


Fig. 3 (A) Photograph under UV light of **PMMA-D1-D2** that has been patterned with light and heat; (B) fluorescence spectra of the four different quadrants of **PMMA-D1-D2** shown in A ( $\lambda_{\text{ex}} = 365$  nm); (C) excitation–emission scans of the four different quadrants of **PMMA-D1-D2** shown in A.

ultramarine fluorescence, similar to **PMMA-D2**. Gratefully, the bottom right quadrant of **PMMA-D1-D2**, which is exposed to both heat and light, showed cyan fluorescence, unique to any other quadrant. The emission spectra and excitation–emission scans of the four quadrants illustrate that fluorescence of the heat-treated and light-treated quadrants can be attributed solely to **Dye 1** and **Dye 2**, that fluorescence of the quadrant treated with both light and heat is a composite of the two dyes, and that all quadrants can be easily distinguished from each other (Fig. 3C). The combined (*i.e.*, composite) fluorescence of **Dye 1** and **Dye 2** in **PMMA-D1-D2** is likely possible because only a small amount of each dye is present; thus, energy transfer between the two molecules does not dominate, as with FRET, in which one dye absorbs the emission of the other, nor do the dyes interact as a charge transfer complex. As expected, **PMMA-D1-D2** remains transparent and colourless under ambient light after patterning, and the morphology of the polymer film does not change (Fig. S3 and S4, ESI<sup>†</sup>). The results presented in Fig. 3 demonstrate that **Dye 1** and **Dye 2** can be incorporated into the same polymer film and individually stimulated to give a quaternary code of 0, 1, 2, and 3 (no fluorescence, green fluorescence, ultramarine fluorescence, and cyan fluorescence).

To study the dependence of fluorescence intensity and wavelength on extent of exposure to stimuli, **PMMA-D1** was heated for time intervals from 5 to 35 seconds and **PMMA-D2** was irradiated with 365 nm light for time intervals from 4 to 28 minutes using a handheld UV lamp. As seen in Fig. 4A and C, extent of exposure to stimulus (heat or light) influences the resulting fluorescence intensity, but not the wavelength of fluorescence for each system (Fig. 4B, D and Fig. S5, ESI<sup>†</sup>). Fig. 5A shows patterning of **PMMA-D1-D2** under exposure to light and heat for different extents of time, and the white box indicates the quadrant of the film with the four colours that can most easily be differentiated by the naked eye. A CIE (Commission Internationale de l'Éclairage) chromaticity diagram (Fig. 5B) reveals that areas

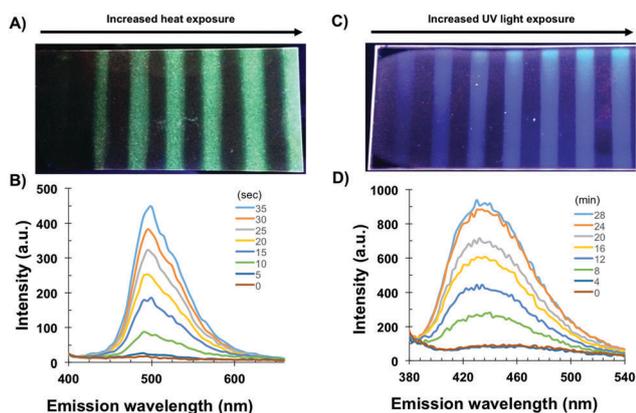


Fig. 4 (A) Photograph under UV light of **PMMA-D1** showing influence of different extents of thermal radiation (120 °C from 0–35 seconds); (B) emission spectra for sections of **PMMA-D1** exposed to varied duration of heat as shown in A; (C) photograph under UV light of **PMMA-D2** showing influence of different extents of UV light irradiation (365 nm) using a handheld UV lamp from 0–28 minutes); (D) emission spectra for sections of **PMMA-D2** exposed to varied duration of UV light as shown in B.

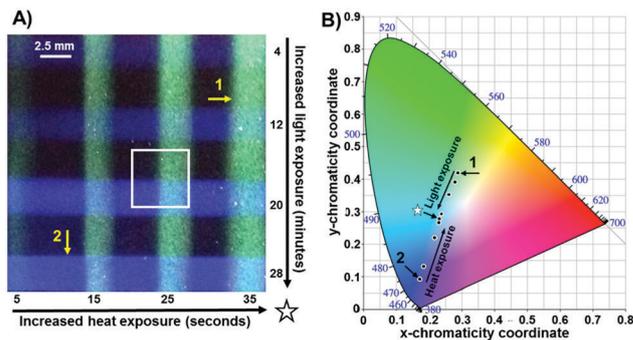
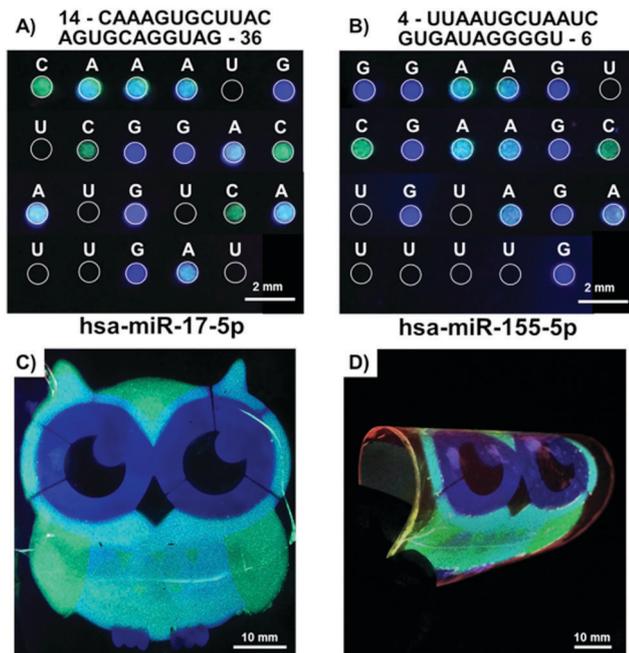


Fig. 5 (A) Photograph of **PMMA-D1-D2** after different duration of exposure to light and heat, the white box indicates the four colours most easily distinguished by the naked eye; (B) the CIE chromaticity diagram, which shows the fluorescence colour changes of **PMMA-D1-D2** with different extents of exposure to stimuli.

of the film exposed to both light and heat shown in Fig. 5A have varied fluorescence colour (as well as intensity). For example, **PMMA-D1-D2** exposed to heat for 15 seconds and UV light for 28 minutes has an RGB value of (108, 202, 180), while exposure to heat for 35 seconds and UV light for 12 minutes gives an RGB value of (105, 162, 242). Thus, the fluorescence signature of the cyan colour of **PMMA-D1-D2** can be tuned by varying the extent of exposure to heat and light, increasing possible fluorescence signatures.

The quaternary code provided by our system can be paralleled to DNA or RNA nucleotides, with, *e.g.*, A = 0, C = 1, G = 2, and T(U) = 3. Two different microRNA (miRNA) sequences, hsa-miR-17-5p and hsa-miR-155-5p, were easily patterned in PMMA films using wooden masks. These masks were prepared from a 2.5 mm thick piece of wood using a laser cutter to give patterns of holes 1 mm in diameter separated by 1.2 mm (see ESI<sup>†</sup>); one mask was used to expose specific regions of **PMMA-D1-D2** to light and the other mask used for selective exposure to heat. The written fluorescence patterns shown in Fig. 6A and B can be read under UV light: no treatment (black = U), heat only treatment (green = C), light only treatment (ultramarine = G), and treatment with heat and light (cyan = A). Given this code and size of the data storage units (1 mm), the sequence can easily be read with the naked eye. Moreover, an image processing program written with MATLAB was used to read the RGB profile of each spot and readily gave the correct sequence of miRNA (MATLAB code is available in ESI<sup>†</sup>), indicating the high contrast of colour between the four fluorescent outputs.

Resolution of patterning using masks and stability of fluorescence patterns in **PMMA-D1-D2** films was then evaluated. Using a wire mesh, light and heat could each be used to pattern 300  $\mu\text{m}$  circular signals with 200  $\mu\text{m}$  between each other (Fig. S6, ESI<sup>†</sup>), demonstrating that transport of heat or light does not place a lower limit on resolution at these length scales. Masks with slits from 700 to 350  $\mu\text{m}$  were also fabricated using a laser cutter and used to pattern **PMMA-D1-D2**; in this system, both green and ultramarine lines were readily observed, though the cyan fluorescence could not be readily distinguished by the naked eye due to the small area of the colour (Fig. S6, ESI<sup>†</sup>). The use of masks



**Fig. 6** All patterns were prepared by using irradiation with heat for 25 seconds and irradiation with light for 20 minutes. (A) miRNA (hsa-mir-17-5p) patterned in four different fluorescent colours (no treatment, thermal, photo, photo + thermal); (B) miRNA (hsa-mir-155-5p) patterned in four different fluorescent colours (no treatment, thermal, photo, photo + thermal), which can be read using a MATLAB program; (C) optical image of a patterned owl; (D) polymer film with owl peeled from the substrate and mechanically bent. The yellow-orange fluorescence on the edge of the film in D is due to the weak fluorescence of **Dye 1** excimer.

places a lower limit on resolution for this system, which will ultimately be overcome by decreasing the spot size of the light/heat source to improve resolution (*i.e.*, use of lasers or AFM tip). Patterned **PMMA-D1-D2** could be removed from the glass substrate and no change in the pattern was observed after mechanical deformation, such as scrolling and bending (Fig. 6D and Video S1, ESI<sup>†</sup>). This free standing film could be soaked in boiling water (Video S2, ESI<sup>†</sup>), and written on with a permanent marker, again without detriment to the tailored pattern. Moreover, unlike data storage in commercial CD/DVD systems, **PMMA-D1-D2** stores information throughout the polymer matrix, and patterns are easily legible even after removing ~50% of the polymer film from the surface by exfoliation with sand paper (Fig. S7, ESI<sup>†</sup>). These tests demonstrate that patterned **PMMA-D1-D2** is robust to many conditions, and in fact the fluorescence pattern can be read continuously under a handheld UV lamp without detriment up to ~25 minutes. The pattern can be destroyed by irradiation with strong UV light or heat from a hotplate (>110 °C) or heat gun, providing a means for catastrophic data removal.

## Conclusion

In summary, we have reported a new, chemistry-based system to improving optical data storage using a quaternary code (0, 1, 2, 3) by incorporating orthogonally responsive small molecules in a commodity polymer film. This approach is in direct

compliment to engineering approaches, including decreased pixel size and patterning of voxels. In the as prepared PMMA film containing **Dye 1** and **Dye 2**, no fluorescence is observed; however, after heating **Dye 1** becomes green fluorescent and after irradiation **Dye 2** becomes ultramarine fluorescent, and upon stimulation with both heat and light the film shows cyan fluorescence. Before and after patterning, the polymer film is transparent and colourless under ambient conditions, and the pattern can only be observed under UV light. We further demonstrate the influence of extent of exposure to stimuli on intensity and colour of fluorescence and use optimized conditions to pattern miRNA sequences. Excellent resolution of patterning can be realized using masks (to ~300 μm), patterns are stable to many conditions, and the patterns can be destroyed under proper stimuli. This novel data storage system makes use of readily accessible materials and data can be stored rapidly and efficiently. This work provides a new approach to next generation data storage methods, with on-going work focusing on improving resolution by tailoring the light/heat source and optimizing 3D data storage opportunities.

## Experimental

### Materials and instrumentation

All reagents were purchased from commercial suppliers. 5-Hydroxy-2-nitrobenzaldehyde, hexyl bromide, diethyl ether, sodium hydroxide, dimethylformamide (DMF), methanol, triethylamine, benzoyl chloride, 4-hydroxyphenylacetonitrile, octadecyl bromide, ethanol, *tert*-butanol, 2,5-dimethoxyterephthalaldehyde, potassium hydroxide, chloroform, and magnesium sulfate were purchased from Sigma Aldrich. Ethyl acetate and tetrahydrofuran (THF) were obtained from Fisher Scientific. Potassium carbonate and potassium *tert*-butoxide were ordered from Acros Organics. Acetonitrile, sodium borohydride, and poly(methyl methacrylate) (PMMA) were purchased from VWR, Oakwood Chemicals, and Arkema Chemicals V920, respectively.

FTIR spectra were obtained using an Agilent Cary 630 FTIR in ATR mode and diamond on ZnSe crystal. MALDI-TOF measurements were accomplished with Bruker autoflex III TOF/TOF200. An UVGL-68 Handheld UV lamp was used for all UV irradiation. Morphology of films was measured by Zygo NewView 7300 profilometer. Masks used for patterning the films were prepared using a Universal ILS12.150D laser cutter. UV-vis spectra were obtained using an Agilent Cary 5000 UV-vis-NIR spectrophotometer. Fig. 4D was generated by program CIE1931xy.V.1.6.0.2. All photographs were taken by iPhone 5c.

Fluorescence experiments were carried on Agilent Cary Eclipse fluorescence spectrophotometer. For Fig. 2C, experiments were performed with excitation wave length of 330 nm, scanning from 330–540 nm; excitation and emission slits were set to 5 nm, excitation was performed in increments of 3 nm and detector voltage was 700 V. For Fig. 2D, parameters were the same as Fig. 2C, but the detector voltage was 650 V. For Fig. 3B and C, parameters were same as Fig. 2D but the scan range was 330–600 nm. For Fig. S2D (ESI<sup>†</sup>), experiments were performed

with excitation wave length of 330 nm, scanning from 360–600 nm; excitation and emission slits were set to 5 nm, excitation was performed in increments of 3 nm and detector voltage was 600 V. For Fig. S6A (ESI<sup>+</sup>), instruments were set as same parameters with Fig. S2D (ESI<sup>+</sup>), but detector voltage was 700 V. Fig. S6B (ESI<sup>+</sup>) the detector voltage was 675 V.

## Synthesis

### Preparation of 4-octadecyloxyphenylacetonitrile (compound S1)<sup>35</sup>.

A 50 mL round bottom flask was loaded with a magnetic stir bar, 4-hydroxyphenylacetonitrile (200 mg, 1.50 mmol), potassium carbonate (538 mg, 3.90 mmol), and anhydrous DMF (25 mL), and the reaction vessel was capped and placed under a nitrogen atmosphere. Octadecyl bromide (550 mg, 1.65 mmol) was then added by injection using syringe and the mixture stirred overnight at 50 °C using an oil bath. After complete consumption of 4-hydroxyphenylacetonitrile (as determined by TLC on silica gel using a mobile phase of 6:1 hexane:ethyl acetate), the crude reaction mixture was poured into water (100 mL) and extracted with diethyl ether (2 × 100 mL). The combined organic layers were then washed with deionized water (1 × 100 mL), and brine (1 × 100 mL). After drying over MgSO<sub>4</sub>, solvent was removed under reduced pressure and the crude product was suspended in ethanol (~25 mL) and then washed on a Buchner funnel under reduced pressure with ethanol (3 × 100 mL) to give pure product as light yellow solid. Yield = 88%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.19–7.20 (d, 2H), 6.86–6.87 (d, 2H), 3.91–3.94 (t, 2H), 3.65 (s, 2H), 1.73–1.78 (m, 2H), 1.40–1.44 (m, 2H), 1.24–1.33 (m, 28H), 0.85–0.88 (t, 3H).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 14.3, 22.9, 23.0, 26.2, 29.4, 29.6, 29.6, 29.7–29.9, 68.3, 115.2, 118.4, 121.7, 129.2, 159.1.

GC-MS (EI): *m/z* 382 (M<sup>+</sup>), 189, 114, 92, 88, 78, 64, 50, 38, 36, 24, 9.

**Preparation of (2Z,2'Z)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(2-(4-(octadecyloxy)phenyl)acrylonitrile) (Dye 1)<sup>35</sup>.** A 50 mL round bottom flask was loaded with a magnetic stir bar, compound S1 (471 mg, 1.22 mmol), 2,5-dimethoxyterephthalaldehyde (108 mg, 0.56 mmol), and anhydrous DMF (25 mL), and the reaction vessel was capped and placed under a nitrogen atmosphere. A solution of potassium *tert*-butoxide in THF (1.0 M, 0.15 mL) and potassium hydroxide in methanol (1.0 M, 1.5 mL) were then added by injection using syringe and the mixture stirred for 20 min at 70 °C using an oil bath. The crude reaction mixture turned orange. After 20 min, the crude reaction mixture was filtered on filter paper by using Buchner funnel under reduced pressure and washed with methanol (3 × 100 mL) to give pure product as orange solid. Yield = 96%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.84–7.86 (s, 2H), 7.60–7.62 (d, 4H), 6.92–6.94 (m, 4H), 3.96–3.98 (t, 4H), 3.92–3.93 (s, 6H), 1.76–1.81 (m, 4H), 1.16–1.33 (m, 64H), 0.83–0.86 (t, 6H).

MALDI-TOF: *m/z* 928 (M<sup>+</sup>).

**Preparation of 5-hexyloxy-2-nitrobenzyl alcohol (compound S2)<sup>38,40</sup>.** Compound S2 was synthesized by a tandem *O*-alkylation and carbonyl reduction: a 50 mL round bottom flask was loaded with a magnetic stir bar, 5-hydroxy-2-nitrobenzaldehyde (2 g, 12 mmol), potassium carbonate (5 g, 36 mmol), and anhydrous

DMF (25 mL), and the reaction vessel was capped and placed under a nitrogen gas atmosphere. 1-Bromo-hexane (3 g, 18 mmol) was then added and the mixture stirred overnight at 50 °C heated using an oil bath. After complete consumption of 5-hydroxy-2-nitrobenzaldehyde (as determined by TLC on silica gel using a mobile phase of 6:1 hexanes:ethyl acetate), the crude reaction mixture was poured into aqueous NaOH (1 M, 100 mL) and extracted with diethyl ether (2 × 100 mL). The combined organic layers were then washed with deionized water (1 × 100 mL), and brine (1 × 100 mL). After drying over MgSO<sub>4</sub>, solvent was removed under reduced pressure and the crude oil was dissolved in methanol (25 mL) in a round bottom flask equipped with a magnetic stir bar. Then, NaBH<sub>4</sub> (3.2 g, 84 mmol) was added and the reaction mixture was left to stir for 2–3 days at room temperature. After complete consumption of 5-hydroxy-2-nitrobenzaldehyde (as determined by TLC on silica gel using a mobile phase of 6:1 hexanes:ethyl acetate), the reaction mixture was diluted with DI water (100 mL) and the product extracted with diethyl ether (2 × 100 mL). The combined organic layers were dried over MgSO<sub>4</sub> and solvent was removed under reduced pressure to give a yellow solid. Flash chromatography on silica gel using a gradient eluent of hexane:ethyl acetate (10:0 to 10:1 to 0:10). TLC: R<sub>f</sub> (6:1 v/v hexane:ethyl acetate) = 0.3. Yield = 86%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.15–8.16 (d, 1H), 7.18 (s, 1H), 6.85–6.87 (dd, 1H), 4.96 (s, 2H), 3.93–3.94 (t, 2H), 2.54 (s, 1H), 1.77–1.82 (m, 2H), 1.42–1.48 (m, 2H), 1.29–1.36 (m, 4H), 0.88–0.9 (t, 3H).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 14.0, 22.5, 25.5, 28.9, 31.4, 63.1, 68.9, 113.5, 114.8, 128.0, 140.1, 163.9.

GC-MS (EI): *m/z* 253 (M<sup>+</sup>), 152, 123, 107, 95, 80, 69, 57, 55, 43.

### Preparation of 5-hexyloxy-2-nitrobenzyl benzoate (Dye 2).

A 50 mL round bottom flask was loaded with magnetic stir bar, then compound S2 (361 mg, 1.43 mmol) was added. Acetonitrile (25 mL) was added and the reaction vessel was capped and placed under a nitrogen environment. Benzoyl chloride (100 mg, 0.71 mmol) was added by injection using syringe, followed by addition of two drops of triethylamine. The mixture was left to stir for 1 h at 50 °C using an oil bath to heat. After complete consumption of compound S2 (as determined by TLC on silica gel using a mobile phase of 8:1 hexanes:ethyl acetate), the crude reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (2 × 100 mL). The combined organic layers were then washed by DI water (1 × 100 mL), and brine (1 × 100 mL), then dried over MgSO<sub>4</sub> and solvent removed under reduced pressure to give a light yellow solid. TLC: R<sub>f</sub> (8:1 v/v hexane:ethyl acetate) = 0.6. Yield = 90%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.19–8.21 (d, 1H), 8.10–8.11 (d, 2H), 7.58–7.61 (t, 1H), 7.46–7.49 (t, 3H), 7.08–7.09 (d, 1H), 6.86–6.89 (dd, 1H), 1.73–1.81 (m, 2H), 1.38–1.44 (m, 2H), 1.28–1.32 (m, 4H), 0.86–0.89 (t, 3H).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 14.5, 22.9, 26.0, 29.1, 32.0, 64.2, 69.3, 113.5, 114.8, 128.6, 129.0, 130.2, 133.9, 140.5, 164.0, 166.5.

GC-MS (EI): *m/z* 311 (M + -NO<sub>2</sub>), 150, 105, 77, 43, 41.

## Film preparation

**Preparation of poly(methyl methacrylate) (PMMA) films of Dye 1 and Dye 2.** In a 100 mL beaker, PMMA (20 g) was dissolved in ethyl acetate (60 mL) followed by addition of solid **Dye 1** (2 mg) and/or **Dye 2** (8 mg). The solution was sonicated for 5 minutes, then centrifuged for 10 minutes. Films were then prepared by blade coating with a 0.2 mm height onto glass slides.

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