Supporting Information for:

Beyond Binary: Optical Data Storage with 0, 1, 2, and 3 in Polymer Films

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Synthesis

Scheme 1. Synthetic route for the synthesis of Dye 1 (top) and Dye 2 (bottom).

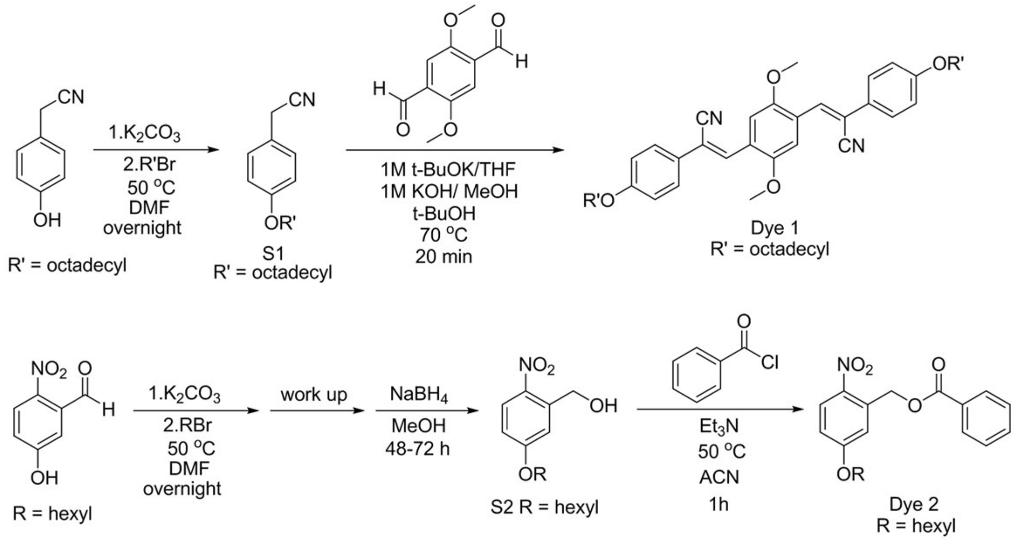
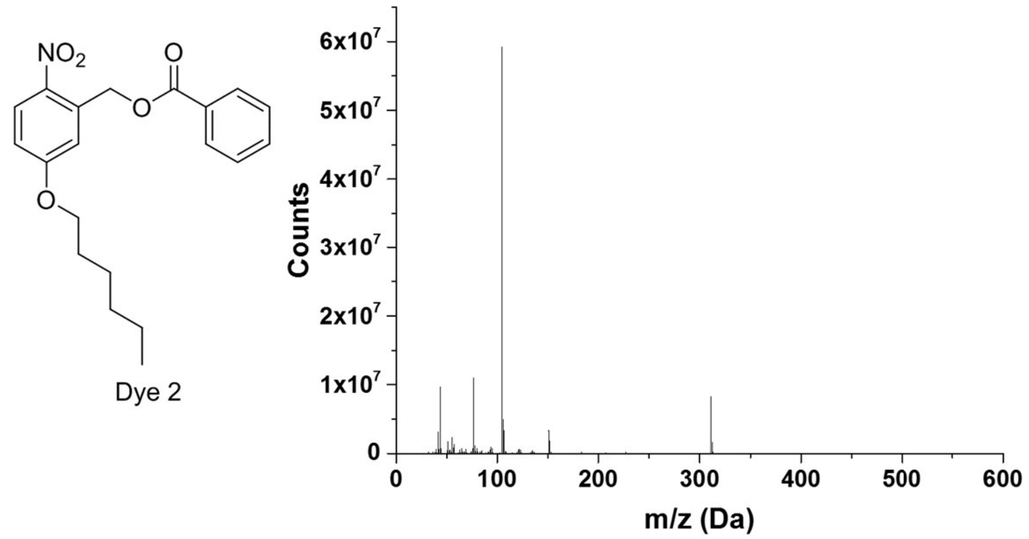
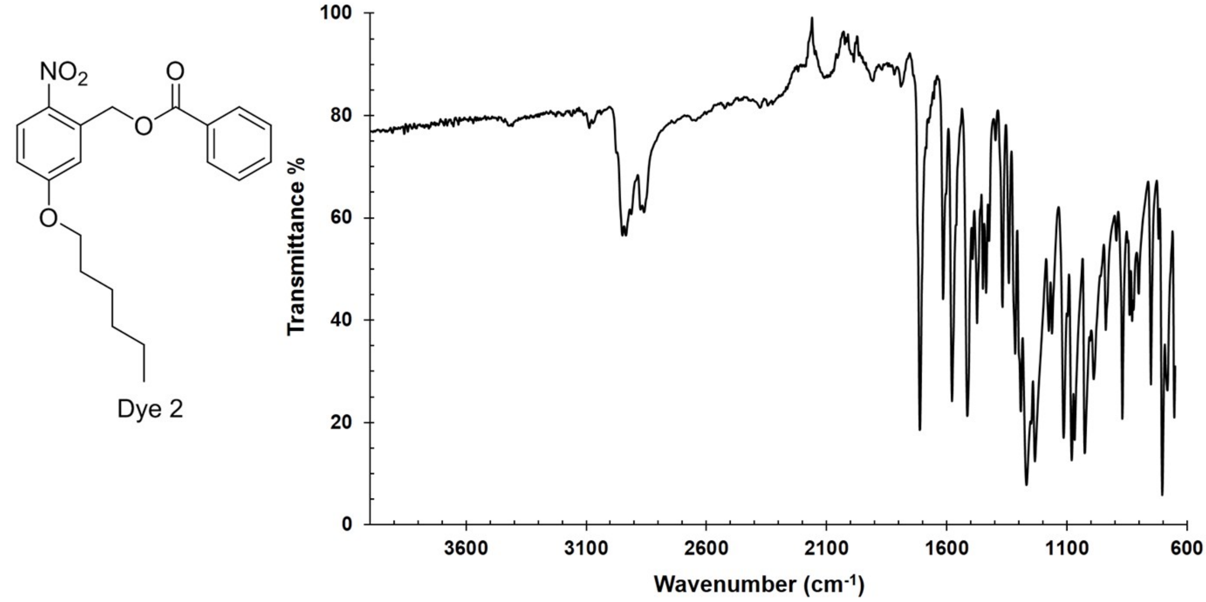


Figure S1. Characterization of Dye 2 A) MS spectrum B) FTIR spectrum C) ^{1}H NMR (500 MHz) spectrum D) ^{13}C NMR (500 MHz) spectrum.

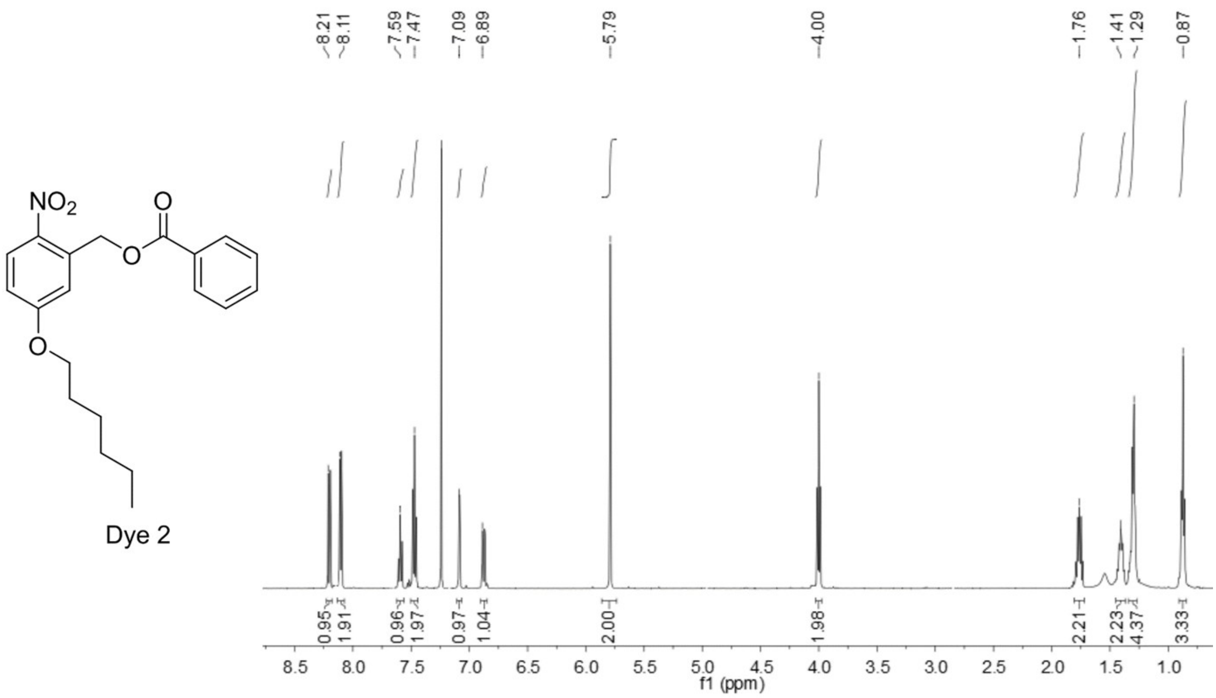
A)



B)

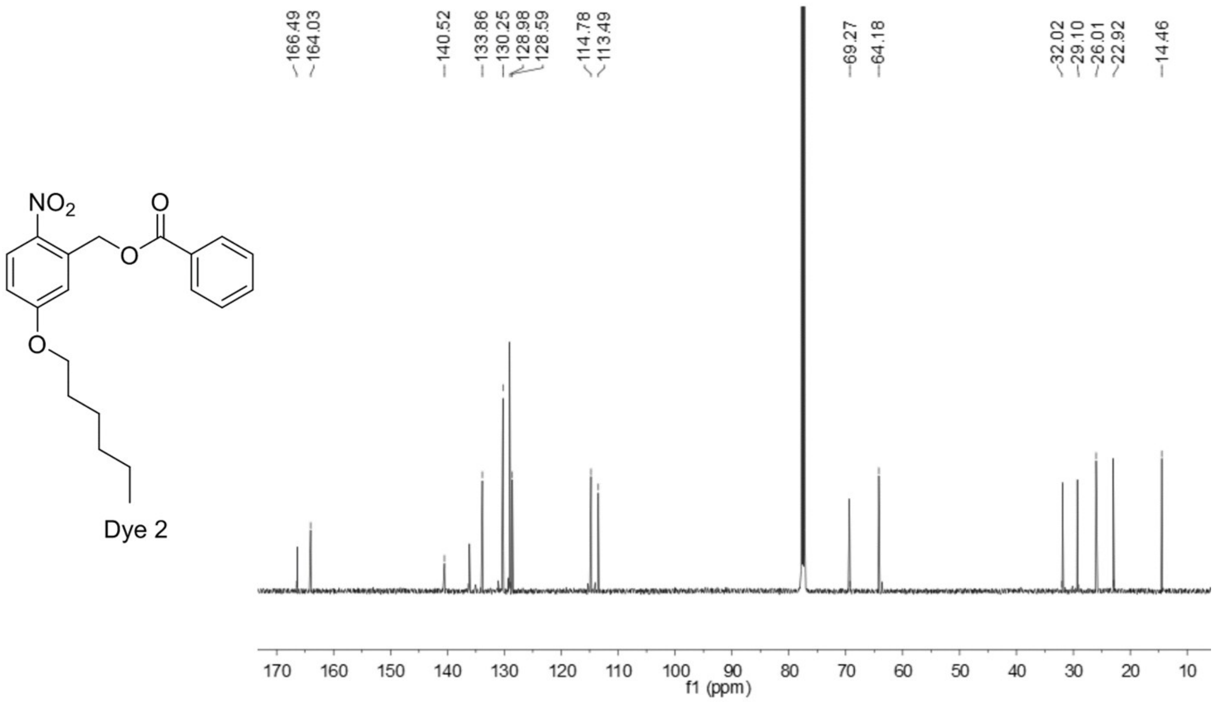


C)



8.21
8.11
7.59
7.47
7.09
6.89
5.79
4.00
1.76
1.41
1.29
0.87
NO_2
O
O
O
Dye 2
0.95
1.91
0.96
1.97
0.97
1.04
2.00
1.98
2.21
2.23
4.37
3.33
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

D)



166.49
164.03
140.52
133.86
130.25
128.98
128.59
114.78
113.49
69.27
64.18
32.02
29.10
26.01
22.92
14.46
NO_2
O
O
O
Dye 2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S2. Orthogonal responsivity of Dye 1 and Dye 2 to heat and light- Dye 1 is stable to UV radiation and Dye 2 is thermally stable to ~265 °C A) Photograph under ambient light of **PMMA-D1** before and after 30 min of irradiation with 365 nm light; B) Photograph of **PMMA-D1** under UV light before and after 30 min of irradiation with 365 nm light; C) UV-Vis absorption spectra of **PMMA-D1** before (blue trace) and after (red trace) 30 min of irradiation with 365 nm light; D) 2D fluorescence spectra of **PMMA-D1** before and after 30 min of irradiation with 365 nm light; E) thermogravimetric analysis (TGA) weight loss profile of **Dye 2** (data collected under a nitrogen atmosphere).

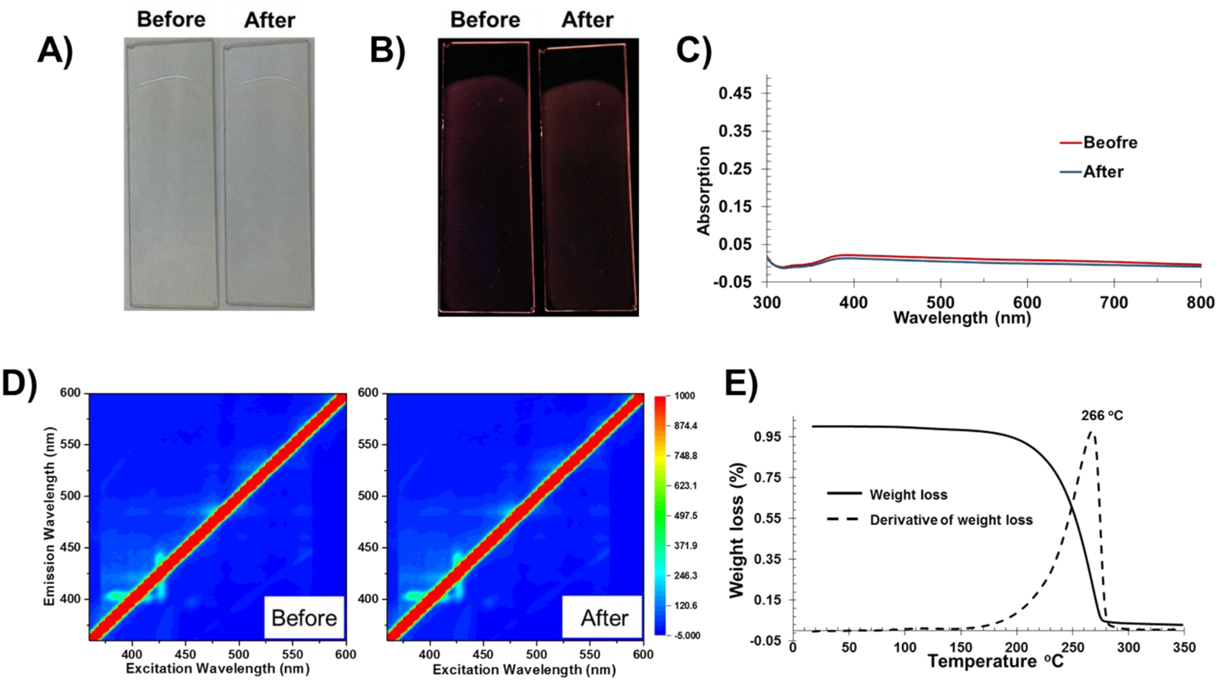


Figure S3. UV-Vis absorption spectra of **PMMA-D1** and **PMMA-D2** before and after stimuli is applied demonstrates no major increase in absorption for the patterned species. Each film sample contains only one dye.

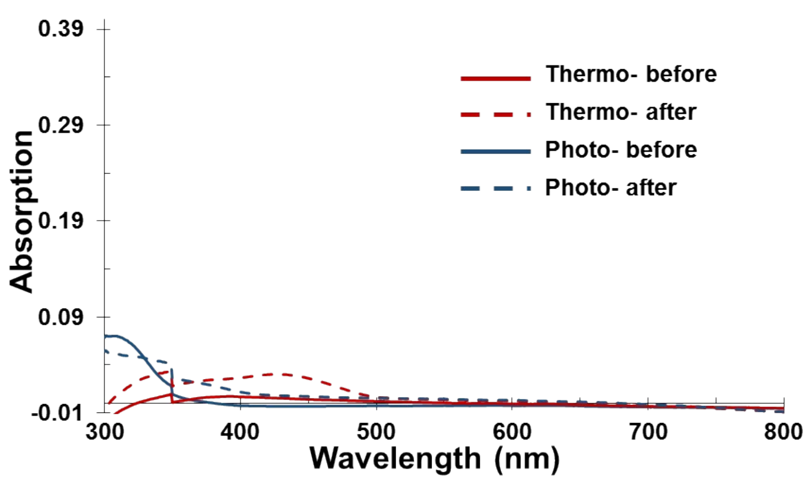


Figure S4. Morphology of **PMMA-D1-D2** before and after patterning does not change after treatment with heat or light. A) Photograph of film under UV light before patterning; B) Photograph of film under UV light after patterning C) 2D morphology spectrum of film before patterning; D) 2D morphology spectrum of film after patterning; E) Height profile of trace 1 (red) before and after patterning; F) Height profile of trace 2 (green) before and after patterning; G) Height profile of trace 3 (blue) before and after patterning; H) 3D morphology spectrum of film before patterning; I) 3D morphology spectrum of film after patterning.

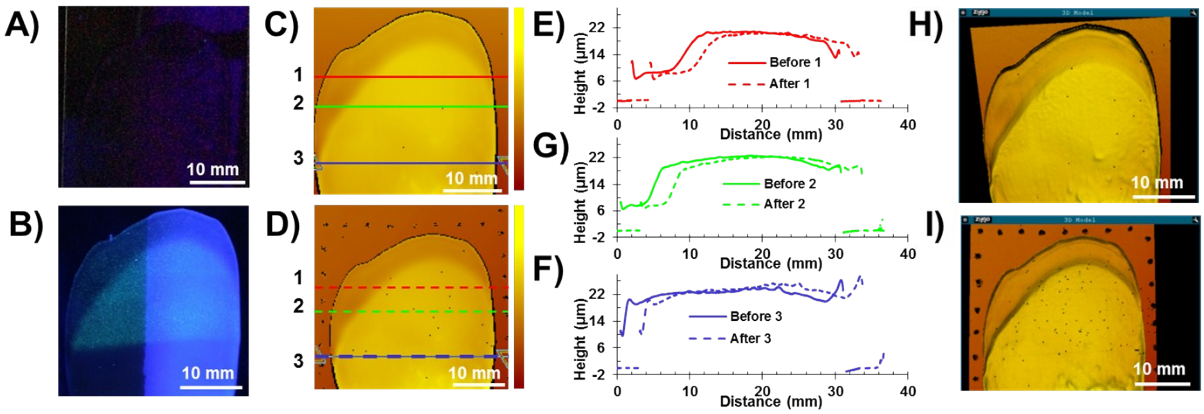


Figure S5. Evaluation of the dependence of fluorescence intensity and wavelength on duration of exposure to stimuli for **PMMA-D1** (right) and **PMMA-D2**) shows fluorescence increases with exposure to stimuli, but wavelength does not change. Top left: Photograph under UV light of **PMMA-D1** showing influence of different extents of thermal radiation (120 °C) realized using a wooden mask; Top right: Photograph under UV light of **PMMA-D2** showing influence of different extents of light irradiation (365 nm) realized using a wooden mask; Middle left: Maximum fluorescence intensity of **PMMA-D1** film as a function of time in seconds exposed to heat (120 °C) corresponding to image above; Middle right: Maximum fluorescence intensity of **PMMA-D2** after different times of exposure to heat (λ_{ex} = 330 nm) corresponding to image above; Bottom left: Fluorescence emission spectra of **PMMA-D1** film as a function of time in minutes exposed to UV light (365 nm); Bottom right: Fluorescence emission spectra of **PMMA-D2** after different times of exposure to UV light (λ_{ex} = 330 nm).

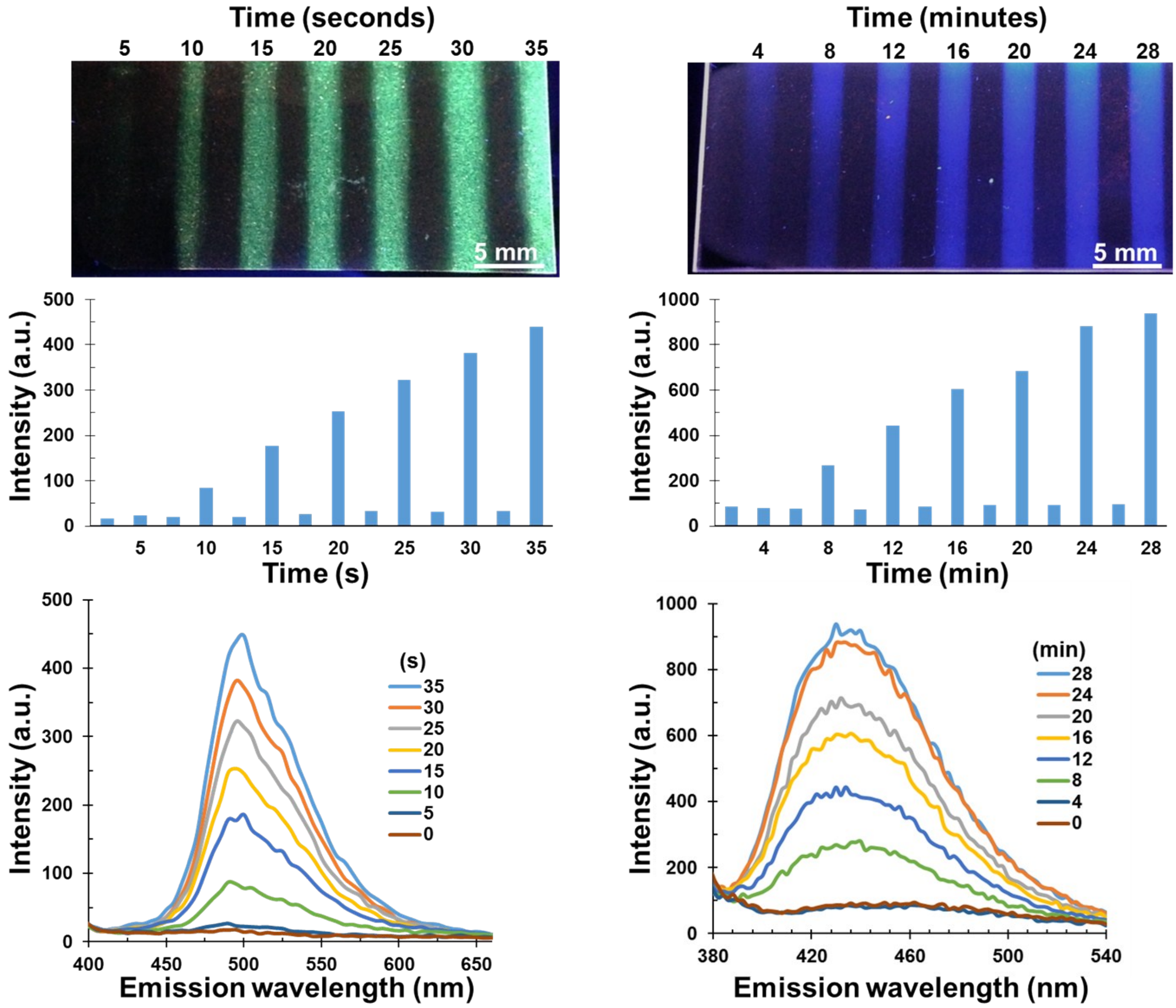


Figure S6. Photograph of dual patterned **PMMA-D1-D2** demonstrates the possible size of patterning using masks: A) Film under UV light after being patterned with wooden slits; B) Optical image of film under UV light after patterning with heat using a wire mesh; C) Optical image for **PMMA-D2** after patterning with light using a wire mesh as a mask. Scale bar on the insets of B and C are 5 mm, demonstrating the large surface area possible.

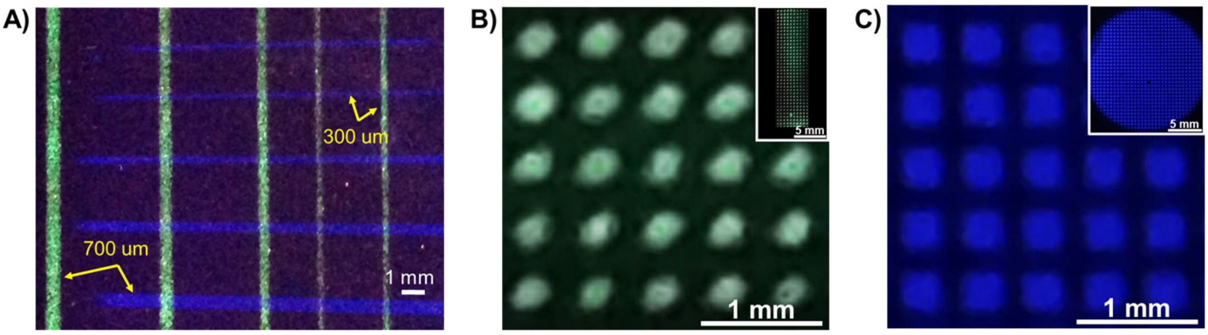


Figure S7. Optical image of **PMMA-D1-D2** under UV light and morphology before and after exfoliation with sand paper show that pattern can still be read after removal of ~50% of the material. A) Photograph of film under UV light before (left) and after (right) mechanical exfoliation; B) 3D morphology spectra of film before (left) and after (right) exfoliatoin; C) Height profile of green trace drawn in A and B before and after exfoliation.

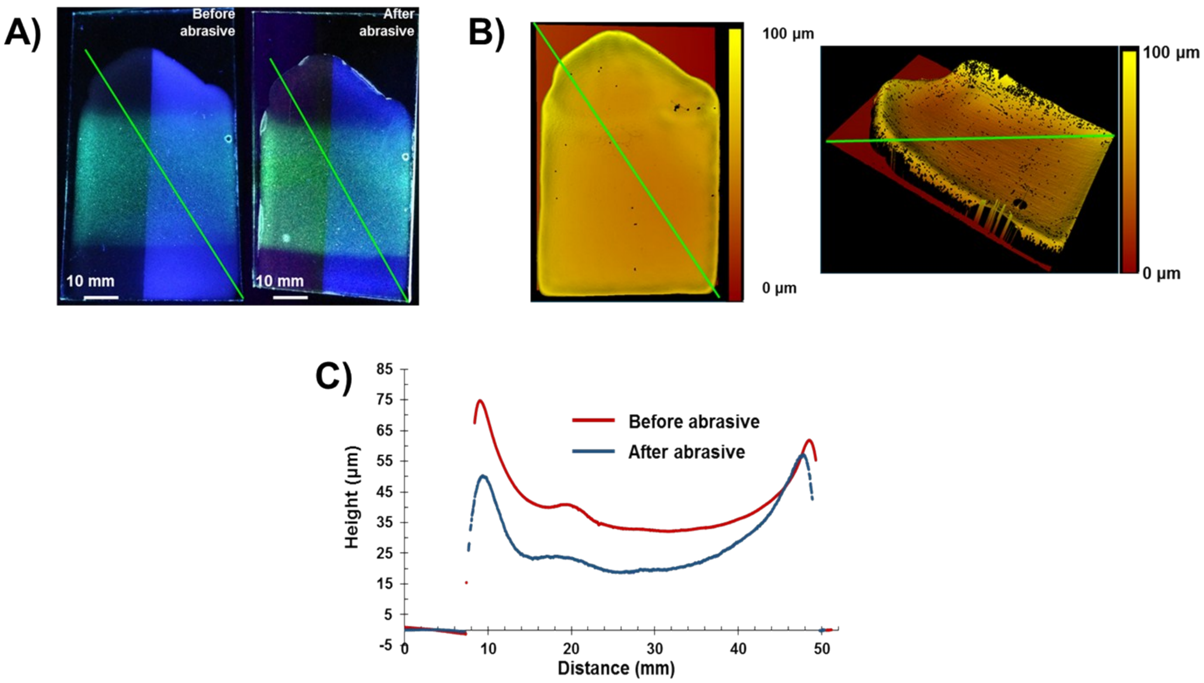


Figure S8. Wooden masks prepared by laser cutting and used for patterning miRNA and owl. Into films of **PMMA-D1-D2**.

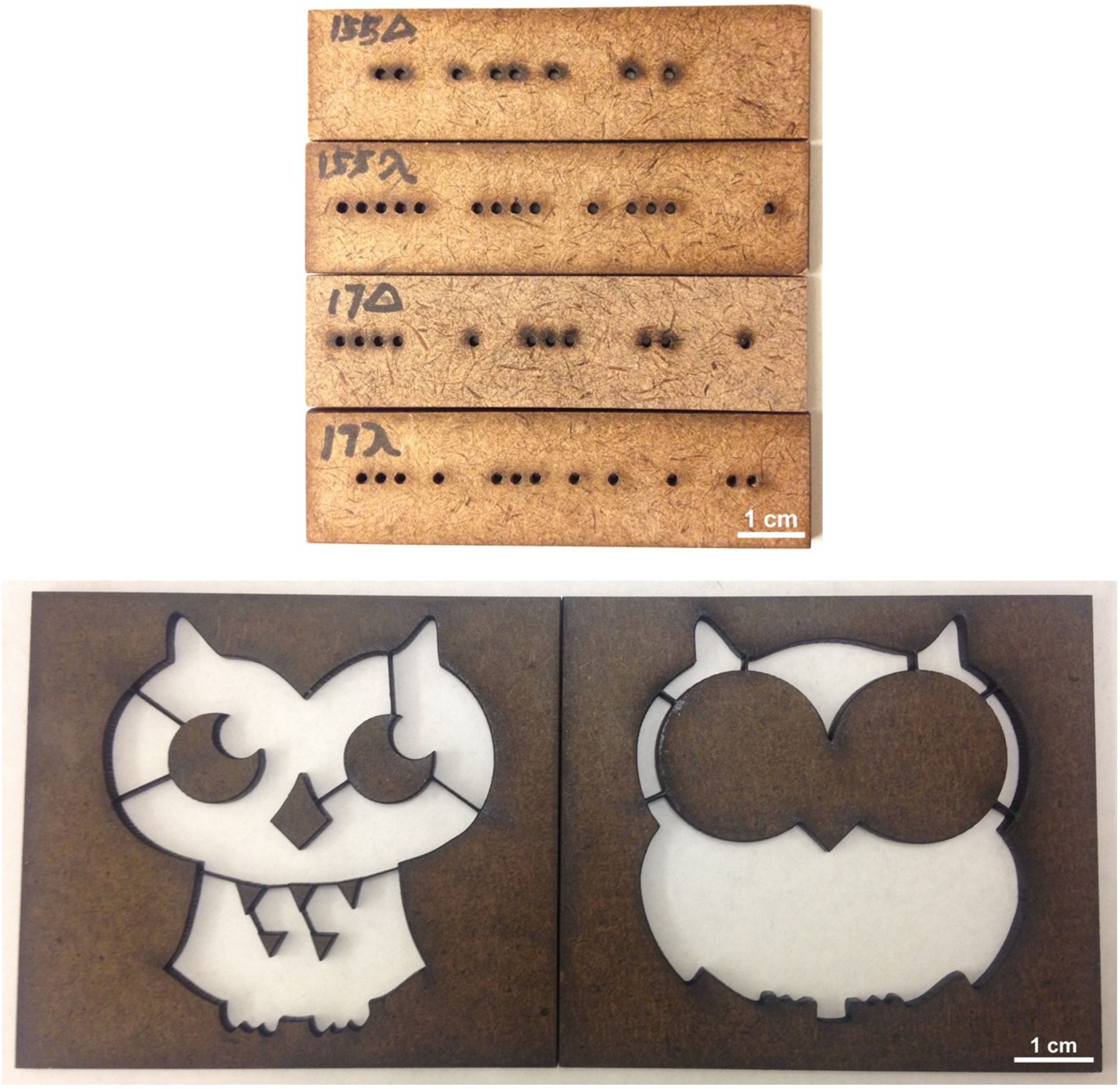
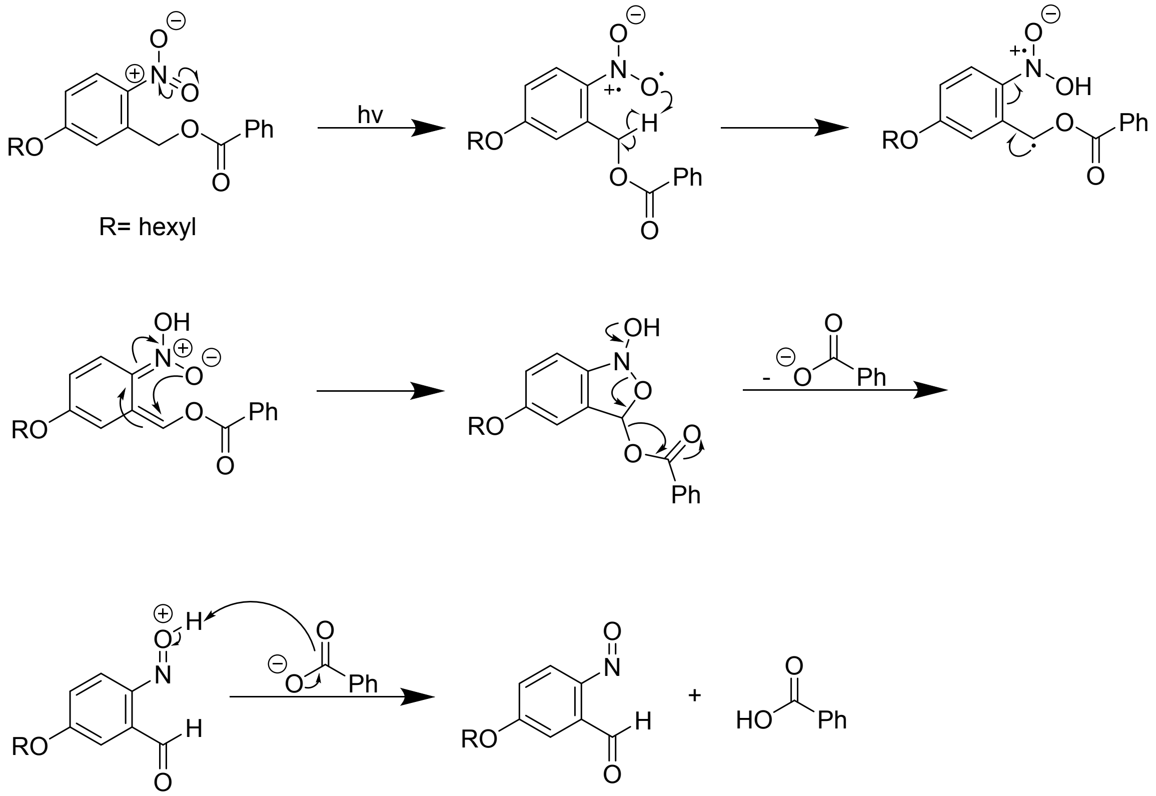


Figure S9. Mechanism for the light induced cleave o-nitrobenzyl ester to give fluorescent nitroso-benzaldhyde and benzoic acid byproduct.



Script of MATLAB program which transform image to miRNA sequence

```
clear; clc;
[filename,path]=uigetfile;
RGB1=imread(strcat(path,filename));
RGB=zeros(23,3);
for i1=38:61:1433
    RGB0=[0 0 0];
    for j1=i1-2:i1+2
        for j2=50-2:50+2
            RGB0=RGB0+im2double(squeeze(RGB1(j2,j1,:))');
            RGB1(j2,j1,:)=[255 255 255];
        end
    end
    RGB((i1-38)/61+1,:)=RGB0/25;
end
disp('RGB values:');
disp(RGB*255);
imshow(RGB1);
result=[];
for k=1:23
    if (RGB(k,2)*255>130&&RGB(k,3)*255<187); result=[result,' C']; end
    if (RGB(k,2)*255<130&&RGB(k,3)*255>187); result=[result,' U']; end
    if (RGB(k,2)*255>130&&RGB(k,3)*255>187); result=[result,' A']; end
    if (RGB(k,2)*255<130&&RGB(k,3)*255<187); result=[result,' G']; end
end
disp('Results:');
disp(result);
```

References

[1] Chem. Mater. 2006, 18, 946-955
[2] ACS Macro Lett. 2012, 1, 825-929
[3] Li, Wei, de Leon, Frey, Pentzer. *Tailored phthalocyanine dye with photo-responsive solubility, color, and fluorescence in solution and the solid state*. Submitted.