Sol-Gel Materials:
Tetraethyl orthosilicate (TEOS): 99.999% - Aldrich
Millipore water: 17.7-17.8 – Barnstead Epure
Ethanol – 95% - Aaper Alcohol
Phosphoric Acid: 85% - EMD

Sol-Gel Preparation:
In a 2 mL micro centrifuge tube: ethanol, then TEOS, then water, then 1% H₃PO₄ were combined. They were mixed with a vortexer, tightly sealed, and stored in the dark to gel (18-20 hours). Volumes were delivered with micropipettes and are as follows:

- Ethanol: 633.8 µL
- TEOS: 317.5 µL
- Millipore Water: 180.0 µL
- 1% H₃PO₄: 3.51 µL

Thin Film Preparation/ Spin Coating:
After the 18-20 hours of time allotted for the sol to gel, the sol-gel was mixed again prior to thin film preparation. Using a micropipette, 80 µL of sol-gel was delivered onto a 25 x 25 mm cover slip (Fisherfinest Premium Cover Glass) and spin coated into a thin film at 6100 rpm for 110 seconds.

Spin Coater: Laurell Technologies – Model WS-400A-6NPP/LITE

Cover Slip Preparation: Acetone wash, 5 x Millipore rinse, 10% NaOH wash, 5 x Millipore rinse, Store in Millipore water. During each washing the cover slips are sonicated for 30 minutes. On fifth rinse, cover slips are sonicated for 5 minutes prior to next washing step.

Fig. 2 (c) Shown above are the absorption spectra for the longer post spin coating delay samples; post doped cover slip, and pre doped thin films which were overlapped in Figure 2 (a). Interestingly, the ratio Dimer/Monomer decreases with post spin coating delay.

Preliminary Profilometry Measurements for Film Thickness:
Thin films were prepared as above, subjected to controlled PSCD, submerged in aqueous solution, subsequently removed and blown dry. Using a razor blade, a strip of gel was then removed from the thin films in a “snow plow” fashion. Using a XP-2 stylus Profilometer by Ambios Technology the step height was then measured. The scan speed was 0.05 mm/s with a measured length of 0.8 mm, the applied force was 0.5 mg, and the range was 10 µm. Samples were usually measured the same day of preparation. Each thickness was the average of quadruple measurements taken from 2 different spots yielding a total of 8 values per film. The average thickness was determined to be 190±10 nm.
Calculations: Relative increases in doping and approximate concentration.
The degree of relative doping was determined by calculating the ratio of R6G loaded in a kinetically-dope film to
that in a pre-doped film prepared from a liquid sol containing 0.5 mM R6G. Molar extinction coefficients (ε) for
R6G monomer and dimer at 500 nm and 531 nm are estimated from references 1. Calculations are based on the
following parameters:

\[
\begin{align*}
\varepsilon_{\text{monomer}}^{(500)} &= 30,000 \, \text{M}^{-1} \, \text{cm}^{-1} \\
\varepsilon_{\text{dimer}}^{(500)} &= 94,000 \, \text{M}^{-1} \, \text{cm}^{-1} \\
\varepsilon_{\text{monomer}}^{(531)} &= 78,300 \, \text{M}^{-1} \, \text{cm}^{-1} \\
\varepsilon_{\text{dimer}}^{(531)} &= 31,000 \, \text{M}^{-1} \, \text{cm}^{-1}
\end{align*}
\]

Assumption: pre-doped film thickness = kinetically-doped film thickness = \( l \)

Given that:

\[
\begin{align*}
\text{At 500 nm: } A_{500}^{\text{kinetically-doped}} &= \frac{\varepsilon_{\text{monomer}}^{(500)} (30,000) + \varepsilon_{\text{dimer}}^{(500)} (94,000)}{\varepsilon_{\text{monomer}}^{(500)} l} = 0.8875 \\
\text{At 531 nm: } A_{531}^{\text{kinetically-doped}} &= \frac{\varepsilon_{\text{monomer}}^{(531)} (78,300) + \varepsilon_{\text{dimer}}^{(531)} (31,000)}{\varepsilon_{\text{monomer}}^{(531)} l} = 0.6844
\end{align*}
\]

Solve for the two linear equations which give:

\[
\begin{align*}
\frac{\varepsilon_{\text{monomer}}^{(500)}}{\varepsilon_{\text{dimer}}^{(500)}} &= \frac{A_{531}^{\text{kinetically-doped}} - A_{500}^{\text{kinetically-doped}}}{A_{500}^{\text{kinetically-doped}} - A_{531}^{\text{kinetically-doped}}} = \frac{5.73 \times 10^{-6}}{l} \\
\frac{\varepsilon_{\text{dimer}}^{(500)}}{\varepsilon_{\text{dimer}}^{(531)}} &= \frac{A_{531}^{\text{kinetically-doped}} - A_{500}^{\text{kinetically-doped}}}{A_{500}^{\text{kinetically-doped}} - A_{531}^{\text{kinetically-doped}}} = \frac{7.61 \times 10^{-6}}{l} \\
\frac{\varepsilon_{\text{R6G}}^{(500)}}{\varepsilon_{\text{dimer}}^{(531)}} &= \frac{5.73 \times 10^{-6}}{l} + \frac{7.61 \times 10^{-6}}{l} = \frac{2.10 \times 10^{-5}}{l} \\
\text{ratio} &= \frac{2.10 \times 10^{-5}/l}{1.43 \times 10^{-7}/l} = 146
\end{align*}
\]

Assuming \( l = 190 \) nm

\[
\begin{align*}
\frac{\varepsilon_{\text{dimer}}^{(500)}}{\varepsilon_{\text{dimer}}^{(531)}} &= \frac{2.10 \times 10^{-5}}{1.90 \times 10^{-5}} = 1.100 \text{ mM}
\end{align*}
\]

The extinction coefficients are in \( \text{M}^{-1} \, \text{cm}^{-1} \), and the path length of the film thickness in centimeters.¹
**Leaching Test:**

Presented above are both the heated and non-heated thin films after 5 days aging. Both had been doped by the developed method prior to aging.

Shown above: **Non-heated** film after one hour of extraction in water.

Shown above: **Heated** film after one hour of extraction in water.

Shown above: **Non-heated** film after one hour of extraction in ethanol.

Shown above: **Heated** film after one hour of extraction in ethanol.