

Laser direct write printing of sensitive and robust light emitting organic molecules

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We examine the effects of three laser direct-write (LDW) printing techniques on 9-anthracenemethanol and tris(8-hydroxyquinoline)aluminum (Alq₃) organic luminophores in order to link the differences in transfer mechanism to the resulting material properties. Degradation can occur where laser light and elevated temperatures are transferred to the molecules, such as those printed via matrix-assisted or thin metal absorptive layer LDW. In contrast, thick film polyimide absorbing layer techniques eliminate damage in these sensitive materials by shielding them from excessive heat and laser illumination. © 2009 American Institute of Physics.

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Laser direct write (LDW) has emerged as an important approach for printing a broad range of materials in user defined patterns.^{1–3} In its earliest implementations, the back surface of a donor substrate containing the material of interest is irradiated by a pulsed-laser, causing volatilization and ejection of the desired material to a receiver substrate placed directly beneath.^{4,5} Aspiring to print a broader range of complex rheological liquids (“inks”), researchers turned their attention to engineering ways of protecting the active material from the potentially harmful effects of this energetic approach. Materials such as organic and biological molecules are particularly vulnerable, where the specific transfer mechanism can lead to damage in these sensitive systems.

Common realizations of LDW printing consist of direct matrix absorption (DMA),^{6–8} thin metal film absorptive (MFA) layer,^{9–12} and thin or thick polymer film absorptive (PFA) layer.^{13–15} The DMA approach employs volatile and laser-absorbing solvents that decompose under pulsed illumination, resulting in volatile by-products that eject the remaining ink from the sacrificial substrate.¹⁶ It is argued that the nonabsorbing solute is unaffected by the laser process, thus permitting the deposition of inorganic and organic materials.^{6,16} The MFA approach employs a metal or metal oxide thin film as a sacrificial absorbing layer.^{9–11} The metal film is intended to prevent direct interaction between photons and transfer agent, acting as a dynamic release layer through either thermal, thermoacoustic, melting, or ablative-type mechanisms.^{4,10,17–19} The PFA approach uses an absorbing polymer layer, which either undergoes photodecomposition (e.g., a thin triazene layer) or mechanical deformation (e.g., thick film polyimide absorbing layer). The thin film triazene polymer minimizes the amount of laser energy absorbed in the transfer material due to the short absorption depth (47 nm at $\lambda=308$ nm) in the UV compared to its thickness (~ 100 nm) and the low decomposition temperature. This allows vaporization and subsequent material transfer at low incident fluences.^{13,14,20,21} In contrast, thick film polyimide

absorbing layer transfers exploit the photophysical and mechanical properties of the film by keeping it intact during the entire transfer process.¹⁵ The polymer undergoes rapid plastic deformation thereby imparting momentum to the overlaying ink layer. Once the polymer stops expanding, the ink continues moving forward toward the receiver substrate enabling the material transfer. Thus, the transferred material is constantly shielded from any hot expanding gases or laser light and is protected from contamination due to the absorbing species.

In this letter we examine the connection between organic luminophore degradation and laser transfer mechanism by photoluminescence (PL) and nuclear magnetic resonance (NMR) spectroscopy. Standard matrix-assisted and thin titanium absorbing layer LDW techniques are tested alongside a thick film polyimide absorbing layer. Two luminophores are selected based on their sensitivity to heat and ultraviolet radiation. On the sensitive end of the scale is the blue fluorophore, 9-anthracenemethanol (AM), while the more robust transition metal based counterpart is the green fluorescing tris(8-hydroxyquinoline)aluminum (Alq₃).

AM (97%, Acros Organics) and Alq₃ (99.995%, Sigma Aldrich) are added to N-methyl-2-pyrrolidone (NMP) ($1/\alpha = 1.6$ cm) at a concentration of 30 mg/ml, heated at 75 °C for 5 min to dissolve the luminophore, and subsequently allowed to cool, forming our ink. Donor substrates for matrix-assisted transfers are glass slides, whereas donor substrates for titanium layer transfers are glass slides with a 50 nm sputter-coated layer of titanium. Donor substrates for thick

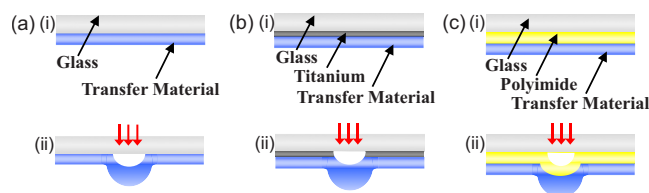


FIG. 1. (Color online) Conceptualization of LDW printing mechanism (i) before and (ii) during initial stages of material transfer. (a) DMA, (b) thin MFA layer with titanium, and (c) thick PFA layers.

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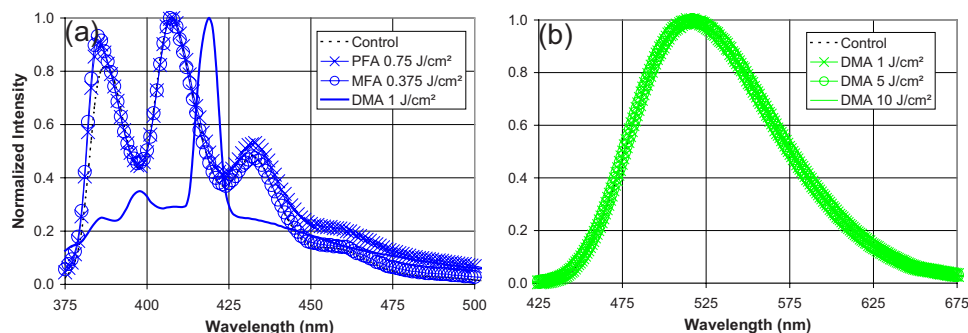


FIG. 2. (Color online) PL spectra of (a) AM showing significant damage when printed via DMA (1 J/cm²) but no apparent damage using either MFA (0.375 J/cm²) or PFA (0.75 J/cm²) approaches. An undamaged spectrum of (b) Alq₃ material printed via DMA transferred at higher fluences can be seen for the Alq₃ molecule.

film polyimide transfers are produced as described in our earlier work, wherein a polyamic acid precursor is coated on glass and spun to a final thickness of 6 μm .¹⁵ 30 μl of the luminophore ink is pipetted onto donor substrates and spread with a wirecoater (Gardner #6), producing a liquid layer thickness of about 10 μm . Donor substrates are inverted and placed 150 μm above a precleaned receiver glass substrate. This assembly is placed on a vacuum chuck situated on an XYZ translation stage allowing for computer programmable motion control. A frequency tripled Nd:YVO₄ laser ($\lambda = 355$ nm, $\tau = 15$ ns) is used to irradiate the back of the donor substrate, focused to a diameter of 50 μm at the glass/absorbing material interface. The laser forward transfer processes employed in this work are shown schematically in Fig. 1.

In order to investigate material degradation, closely spaced droplets are printed onto a glass receiver using each laser printing technique, forming a continuous film with a footprint of 5×2 cm² in the “wet” state. Laser fluences are chosen such that the transfers from each technique produce similar post transfer droplet dimensions. Fluences of 1, 0.375, and 0.75 J/cm² are selected for DMA, MFA, and PFA, respectively, which correspond to circular droplets of 250 μm in diameter. The deposited materials are then washed off of their glass acceptor slides with acetonitrile into quartz cuvettes, until no visible residue remains on the slides. All samples are subsequently degassed via argon bubbling. Control samples are prepared by adding a few drops of the original luminophore ink to a quartz cuvette containing acetonitrile. Emission spectra are recorded using a spectrometer equipped with two monochromators and a photomultiplier tube detector. Right angle exposure is used in all experiments. The source wavelength is set at 400 nm for Alq₃ and 350 nm for AM. Spectra are normalized by peak intensity.

To further investigate the plausible degradation of transferred molecules, NMR spectra are recorded at room temperature. Samples are prepared by rinsing the deposited material off their glass acceptor slides with 1/2 ml of deuterated acetone. The solution is recirculated over the glass slide until no visible residue remains.

Figure 2(a) shows laser transferred and control PL spectra for AM. A strong decrease in luminescence at signature wavelengths is evident in the spectrum that is deposited by matrix-assisted laser transfer (FI=1 J/cm²). This is a clear indication of damage to the molecular structure. However one notes that neither the titanium nor polyimide absorbing layer transfers produce signs of degradation visible by PL.

In order to validate the claim that the transfer mechanisms associated with thin titanium and thick polyimide ab-

sorptive layers do not cause organic luminophore degradation, NMR spectra are acquired. Due to aliphatic interference from the transfer solvent (NMP) at low chemical shift values, the most revealing portion of the spectra is the aromatic region, from ~ 6.5 to 9 ppm. Accordingly, this portion is highlighted in Fig. 3. As expected, significant damage is apparent in the AM luminophore transferred via DMA (FI = 1 J/cm²) compared to the control, as shown in Figs. 3(d) and 3(a), respectively. Molecular degradation comes in the form of oxidation, a by-product of elevated temperatures and excessive UV exposure.^{22,23} Although luminophore molecules are in direct contact with higher temperature volatilized solvent, the NMR data do not allow one to isolate the effects of thermal decomposition and photo-oxidation.

NMR studies of AM molecules transferred using thin titanium metal layers, show clear indication of molecular degradation [Fig. 3(c)]. This is in direct contrast to the PL spectra shown in Fig. 2(a). Under these experimental conditions, (FI=0.375 J/cm²) transfer occurs through complete vaporization of the metal layer, forming a high temperature and high pressure plume in direct contact with transfer material suggesting a thermal damage mechanism [Fig. 1(b)]. However, the possibility of UV-catalyzed damage cannot be ruled out since there is still significant photon penetration through the thin Ti films of approximately 20% of the initial laser energy. These results show that it is possible to induce

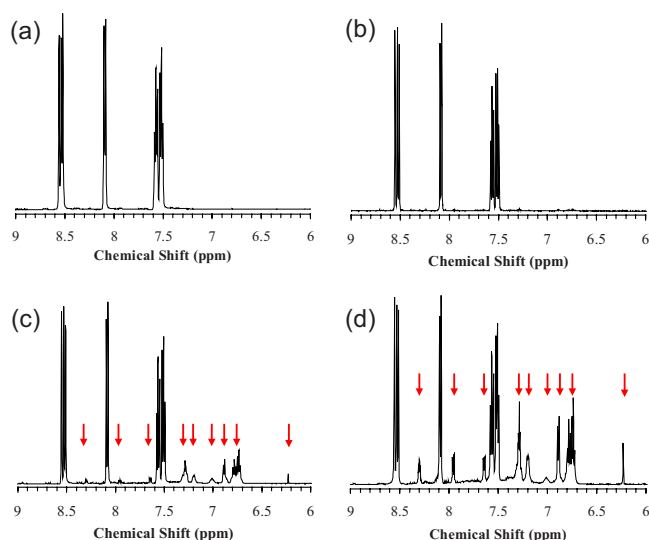


FIG. 3. (Color online) NMR spectra of AM for (a) control and printed using (b) PFA (0.75 J/cm²), (c) MFA (0.375 J/cm²), and (d) DMA (1 J/cm²) transfer techniques. Arrows indicate degradation products present in MFA and DMA. No peaks exist in control or PFA.

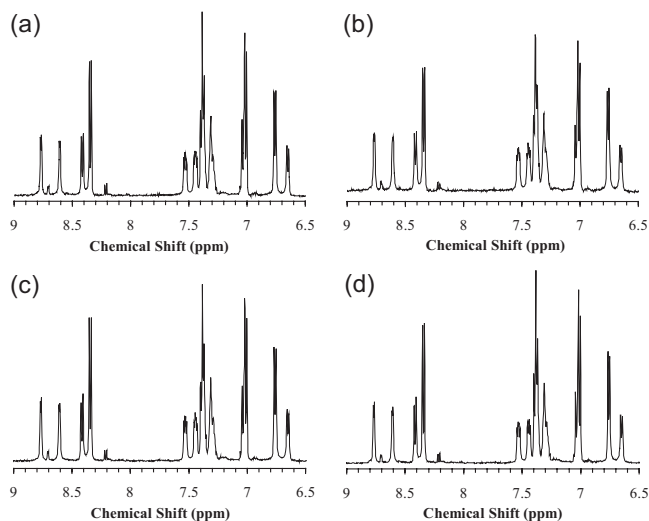


FIG. 4. NMR spectra of Alq₃ for (a) control and printed using DMA at (b) 1 J/cm², (c) 5 J/cm², and (d) 10 J/cm². No degradation is visible at any of these fluences.

nonluminescent damage in organic semiconducting molecules that avoid detection by PL studies.

The mechanism of transfer-associated with thick film polyimide layers [Fig. 3(b)] does not produce any signs of material degradation, in agreement with the PL spectra. This suggests that the thick film polyimide layer prevents exposure of the transfer cargo to both UV irradiation and elevated temperatures. The transfer mechanism associated with this technique (Fl=0.75 J/cm²) is characterized by an intact polymer layer undergoing mechanical deformation to expel the overlying material [Fig. 1(c)].¹⁵

Based on these results for AM, one is tempted to conclude that since the molecules of interest are in direct thermal contact with the vaporized species and experience direct exposure to the high energy ultraviolet irradiation during DMA and thin MFA LDW, these approaches necessarily lead to damage in organic and biological materials. However, in the case of Alq₃ the PL (not shown) indicates no apparent degradation at identical fluences as AM, regardless of the transfer technique used. Furthermore, matrix-assisted laser transfers of Alq₃ are conducted at higher laser fluences and show no variations in the resulting PL spectra, even at the highest fluence of 10 J/cm², as shown in Fig. 2(b). It appears that the greater resistance to thermal and UV oxidation for Alq₃ helps preserve this molecule during transfer, even under the harshest of laser conditions. Based on the absence of damage, one can infer that the effective maximum temperature achieved during the transfer process remains below 350 °C.

An identical series of NMR comparisons are performed for Alq₃ samples transferred using each laser based technique at identical fluences as those for AM, and in all instances, no material degradation is detected. Matrix-assisted laser deposited samples are subsequently created using the same range of laser fluences corresponding to those in Fig. 2(b). In all cases, the resulting NMR spectra are identical to the nonlaser-transferred control sample, regardless of laser fluence (Fig. 4).

In summary this work presents a correlation between transfer mechanisms associated with three LDW printing

techniques, and the damage they impart on organic luminophores. Damage is present in AM molecules printed via matrix absorption and thin titanium absorptive layer techniques, both of which impart the heat and UV light needed to drive oxidation and degrade the molecular properties. Although in some cases the PL spectrum shows strong luminescence at the appropriate wavelengths, the more quantitative NMR studies indicate that the material was in fact damaged. In contrast, a thick film polymer absorbing layer which undergoes mechanical deformation to induce forward transfer, can print contamination-free AM luminophores. In the case of Alq₃, the greater photo and thermal stability enable it to survive all three transfer mechanisms. This provides important information about the maximum effective temperature associated with the different mechanisms, in particular, direct matrix-assisted processes.

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