Supporting Information

Multicolored Emission and Lasing in DCM-Adamantane Plasma Nanocomposite Optical Films

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S1. ToF-SIMS Analysis

The structural characteristics of the DCM-ADA samples have been investigated by time-of-flight secondary-ion mass spectrometry (TOF-SIMS) using an instrument from Ion-ToF GmbH Germany. The sample was bombarded with a pulsed bismuth ion beam. The generated secondary ions were extracted with a 10 kV voltage and their time of flight, from the sample to the detector, was measured in a reflectron mass spectrometer. Typical analysis conditions in this work were 25 keV pulsed Bi+ ion beam at 45° incidence rastered over 500 × 500 μm². An electron flood gun for charge compensation was used during the measurements. Normalization of signals was carried out by using the total ion Intensity. DCM sublimated samples have been also measured as a reference. Adamantane mass spectrometry data from the bibliography is used as a reference NIST Chemistry WebBook database. (http://webbook.nist.gov/chemistry (accessed September 2015)) because adamantane powder is not stable under the ion beam of the ToF-SIMS spectrometer, being very rapidly sublimated.

The Tof-SIMS spectrum corresponding to a RPAVD film of adamantane has been published recently. The spectrum of an ADA sample is characterized by a series of intense peak groups in the region m/z < 100, the more intense peaks being centred at m/z = 41, 55, 67, 77, and 91. Additional peaks with a smaller intensity are also observed for m/z in the range between 100 and 250. Some small contribution can be observed at m/z at around 135 at the position where the most intense peak of adamantane (adamantane M+ molecular ion) is detected by conventional mass spectrometry of this molecule (molecular weight of adamantane = 136.23 uma) and at m/z = 136 (adamantane M++ H). The intensity of the peaks in the spectrum indicates that, in the RPAVD films, hydrogenated fragments with two, three, four, six, and seven carbon atoms are relatively abundant. This result very likely supports the fragmentation of the adamantane molecule during the thin-film deposition to form a solid organic film. Note that, in this case, some fragmentation produced by the ion beam during the measurement cannot be discarded. In addition, several peaks like those at m/z = 105, 121, and 165 and other small peaks visible for m/z > 100 are compatible with a partial oxidation of some of these fragments (e.g., like in C₇O₂H₅ fragments).
or the formation of bigger carbon aggregates than in the precursor molecule, suggesting the incorporation of some oxygen to the film and/or the formation of fragments bigger than the precursor (nonpolymerized) molecule. The first possibility agrees with the XPS analyses of the ADA samples as well as with previous XPS results dealing with the partial polymerization of different dye molecules where we could detect the incorporation into the film of some oxygen from the residual impurities of the chamber and due to post-deposition reactions with the atmosphere.\textsuperscript{1,2,24} shows the ToF-SIMS spectra corresponding to a selected set of DCM-adamantane nanocomposites. The spectrum of a DCM film and sublimated DCM layer are also included in the figure. The ToF-SIMS spectra of DCM and the sublimated DCM layer show two main peaks at \( m/z = 43 \) (CH\( 3 \)N\( 2 \)) and \( m/z = 288.8 \) corresponding to fragments of the DCM dye. These signals in the spectrum of the sublimated sample are more intense and clear. On the other hand, the DCM plasma nanocomposites show many additional and relatively intense peaks in the region of \( m/z = 20-150 \) that can be attributed to the fragmentation of DCM during the film deposition and the formation of the solid polymeric matrix.\textsuperscript{1, 2, 24} The DCM molecular weight is 303.36 uma, however the most intense band in the range of high masses is not observed at \( m/z = 303 \) (DCM M\( ++ \)H). Nevertheless, a low intense peak measured at \( m/z \approx 302 \) could indicate the presence of the molecular ion (DCM M\( + \)). Therefore, the DCM sample is formed by an organic matrix of DCM fragments, where some low-intensity peaks corresponding to integer DCM molecules embedded in the film can be detected.

The spectra corresponding to the DCM–adamantane films (samples DCM-ADA-1, DCM-ADA-2, DCM-ADA-4, DCM-ADA-6) show low intensity bands of adamantane and DCM molecular ions (\( m/z = 135, 302 \)) that confirm a low percentage of intact molecules. A group of intense peaks at \( m/z < 100 \), associated to C-H (O) in the polymeric matrix, prevails in the spectra of DCM and DCM-ADA films grown by RPAVD. Other less intensity fragments corresponding to precursor fragments are visible in the \( m/z \) range of 100 - 300.
Figure S1. Tof_SIMS of DCM-ADA films – ToF-SIMS spectra of A several films of the DCM-ADA series. The spectrum of DCM sublimated film and a picture of the DCM molecule are included as references.

The bands at m/z = 43 and 288 that are very intense in the DCM film and in the DCM sublimated spectra are not significant in DCM-ADA spectra. Thus, the interpretation of the ToF-SIMS results in the DCM–adamantane system is very similar to what has been discussed previously for the DCM and adamantane plasma homopolymers and in previous results recently published of similar materials. The films are obtained by a plasma fragmentation process involving the two molecules. There are integer DCM and adamantane molecules embedded in the solid matrixes and a certain percentage of oxygenated species are also present in the films.
Unfortunately, no quantitative results concerning the percentage of integer dyes as a function of the deposition conditions can be extracted from the ToF-SIMS analysis.

The ToF-SIMS spectra of the plasma nanocomposites are in all the cases dominated by fragments in the region m/z = 20 - 150 that have a relatively higher intensity as the percentage of adamantane in the films increases. These fragments are also present in the DCM films but are marginal in the spectra of the reference DCM and adamantane powder spectra. We attribute these fragments to the molecular precursor fragmentation processes during the thin film deposition by interaction with the plasma discharge. These processes lead to the formation of cross-linked organic matrices that are responsible of the thin film properties (i.e., optical properties, insolubility, thermal stability, etc.). Similar results have been obtained in other films prepared by a similar methodology.\textsuperscript{1-3}

Note that a certain degree of fragmentation occurs in the mass spectrometer during the analysis that can very likely be responsible of the very weak signals observed in the same region in the spectra of the reference molecules.

Figure S2. \( \nu_A + \nu_F \) vs. \( f(\varepsilon) + f(n) \) plot for different solvents reported in reference 4.
Table S1. Polarity dielectric and refractive index functions estimated for the RPAVD samples from linear fitting in Figure SX, and the excitation and emission maxima and VASE analysis of the samples. In case of sample DCM-ADA-6, the maximum of the excitation peak was determined after subtracting a spline baseline.

<table>
<thead>
<tr>
<th>Sample</th>
<th>f(ε)+f(n)</th>
<th>f(n)</th>
<th>f(ε)</th>
<th>f(ε)-f(n)</th>
<th>ε</th>
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<tr>
<td>DCM</td>
<td>0.688</td>
<td>0.255</td>
<td>0.433</td>
<td>0.177</td>
<td>10.6</td>
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<tr>
<td>DCM-ADA-1</td>
<td>0.657</td>
<td>0.250</td>
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<td>0.156</td>
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<td>DCM-ADA-2</td>
<td>0.641</td>
<td>0.245</td>
<td>0.396</td>
<td>0.151</td>
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<tr>
<td>DCM-ADA-3</td>
<td>0.626</td>
<td>0.250</td>
<td>0.376</td>
<td>0.126</td>
<td>5.5</td>
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<tr>
<td>DCM-ADA-4</td>
<td>0.594</td>
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<td>0.346</td>
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<td>DCM-ADA-5</td>
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<td>0.239</td>
<td>0.296</td>
<td>0.057</td>
<td>3.2</td>
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REFERENCES


