Fluorescent Nanostructures: Direct Laser Writing of Nanosized Oligofluorene Truxenes in UV-Transparent Photoresist Microstructures (Adv. Mater. 7/2009)

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Direct Laser Writing of Nanosized Oligofluorene Truxenes in UV-Transparent Photoresist Microstructures

By *Alexander J. C. Kuehne,* David Elfström, Allan R. Mackintosh, Alexander L. Kanibolotsky, Benoit Guilhabert, Erdan Gu, Igor F. Perepichka, Peter J. Skabara,* Martin D. Dawson,* and Richard A. Pethrick**

Recently, the incorporation of nanoscaled inorganic components into organic photoresist hosts to produce photocurable composite materials, has been reported.[1] Combining highly processable photoresists with nanoscaled inorganic quantum dots or nanocrystals in this way creates an attractive method for the production of photonic-device structures, including single-photon sources, waveguides, and lasers.

Due to the recognized incompatibilities between functional organic light-emitting molecules and conventional photolithography materials, the fabrication of all-organic microstructures presents a significant technological challenge.[2] In this paper, we report the incorporation of nanosized oligofluorene truxenes into a novel UV-transparent organic photoresist material, as an alternative approach to fluorescent nanocomposites. Oligofluorene truxenes are a new class of monodisperse organic light-emitting molecules.[3] The blending of oligofluorene truxenes and a UV-transparent photoresist enables photoprocessing of individually dispersed nanoscopic organic light-emitting molecules within a microstructured UV-transparent matrix. These blends will allow the creation of all-organic optical-device structures for a wide range of photonic applications.

It is well known that the incorporation of inorganic quantum dots into photoresists reduces the speed of polymerization relative to the pure resist.[1a] The reduction in rate is partially attributed to the effects of the competing absorption of the quantum dots with the photoacid generator (PAG) that initiates the polymerization process. In sharp contrast, the incorporation of the organic oligofluorene truxene into the UV photoresist leads to large increases in the rate of polymerization. The observed increase in rate is due to a photoinduced electron transfer (PET) from the photon harvested by the oligofluorene truxenes to the PAG.[4]

In the ideal matrix, the spectral properties of the oligofluorene truxene should be unaltered by the nature of the photoresist matrix. It should also act as an encapsulant, to inhibit photo-oxidation of the organic light-emitting molecules and allow the creation of appropriate optical structures for device fabrication.

Here, we examine the spectral properties of novel oligofluorene truxene photoresist composites, and show easy processability of the composite by direct laser writing (DLW) of waveguide-type structures. The laser-written structures are characterized using optical microscopy and scanning electron microscopy (SEM).

Most commercial negative-photoresist materials are based on aromatic entities, which impart to the resist desirable properties for semiconductor processing, but are not ideal as a matrix for light-emitting materials. The π–π interaction between aromatic units generates the desired high viscosity for spin-coating. However, these aromatic units limit the transparency of the matrix, and provide a possible source of energy transfer and quenching. A resist such as SU-8 has acceptable transparency above 360 nm. However, below this wavelength it absorbs almost all of the energy. In addition, aromatic groups can induce solvatochromic shifts in π-conjugated light-emitting molecules.[5] In a previous paper, we reported the development of an epoxy-based photoresist that achieves transparency down to 300 nm in a film 20 μm thick.[6] However, as a result of the polarity of the glycidyl ether groups in the cyclohexyldiglycidyl ether (CHDG) photoresist, it is difficult to achieve miscibility of the fluorene molecules, which tend to form large aggregates and are less effective photoemitters.

In this paper, we report on a novel UV-transparent negative photoresist system based on 1,4-cyclohexyldimethanol divinyl ether (CHDV, see Fig. 1). Cross-linking in this system is achieved via the vinyl ether moieties instead of using glycidyl ether groups. CHDV is less polar than CHDG, and more readily solvates fluorene light-emitting molecules. When a proton is produced from the decomposition of the PAG, the vinyl ether moieties polymerize, to produce a carbon-based backbone with pending vinyl ether groups (see Fig. 1, structure 4), and extended polymerization leads to the creation of a cross-linked network. The absence of aromatic groups in CHDV creates a matrix that is passive, and allows transmission of light down to about 240 nm. The PAG of choice was a *para*-octyloxy-functionalized diphenyliodonium hexafluoroantimonate. The *para*-octyloxy chain pro-

[*] Dr. A. J. C. Kuehne, Prof. P. J. Skabara, Prof. R. A. Pethrick,
Dr. A. R. Mackintosh, Dr. A. L. Kanibolotsky
WestCHEM, Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street, Glasgow G1 1XL (UK)
E-mail: alexander.kuhne@strath.ac.uk; peter.skabara@strath.ac.uk;
r.a.pethrick@strath.ac.uk

Prof. M. D. Dawson, D. Elfström, B. Guilhabert, Dr. E. Gu
Institute of Photonics, University of Strathclyde
106 Rottenrow, Glasgow G4 0NW (UK)
E-mail: m.d.dawson@strath.ac.uk

Dr. I. F. Perepichka
Centre for Materials Science
Faculty of Science and Technology
University of Central Lancashire
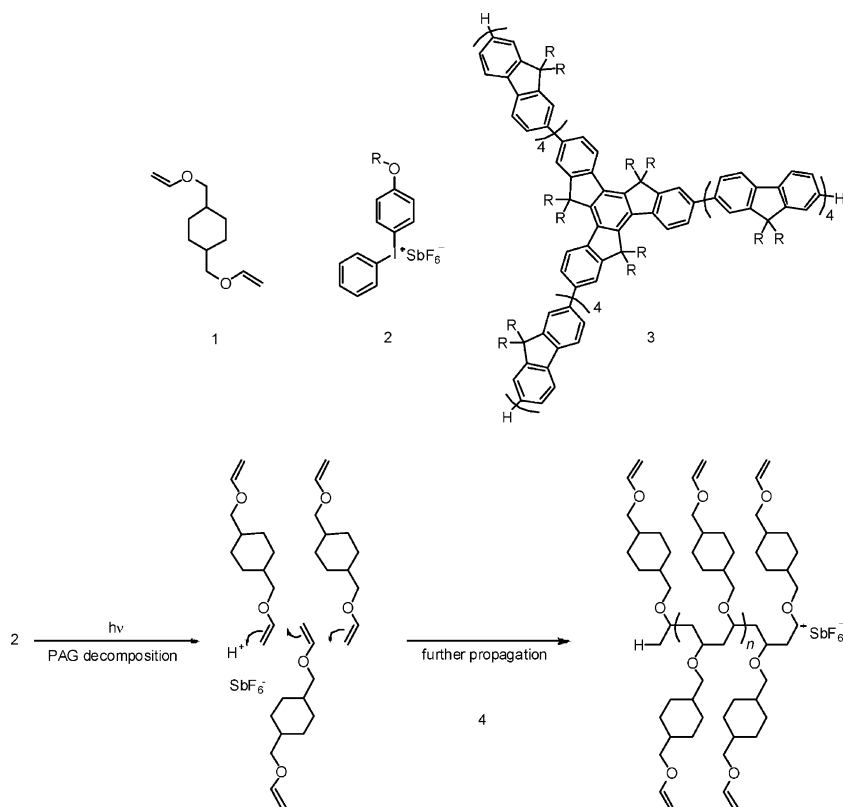Preston PR1 2HE (UK)

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Figure 1. 1) 1,4-Cyclohexanedimethanol divinyl ether, 2) 4-octyloxy diphenyliodonium hexafluoroantimonite (PAG), with R as an octyl chain, 3) oligofluorene truxenes T4, with R as a hexyl chain, and 4) photoinduced cationic polymerization mechanism for CHDV.

vides improved solubility in the nonpolar CHDV photoresist matrix. The peak absorption for PAG is at ∼250 nm, as determined from a solution in acetonitrile (see Fig. 2a). The absorption at 225 nm is due to $\pi \rightarrow \pi^*$ transitions in the conjugated phenyl rings of the PAG. Photocuring pure CHDV with PAG requires a deep UV wavelength for initiation. After cure, the CHDV photoresist has over 90% transparency at 250 nm for a 2.6 μm thick film (see Fig. 2a). The high transparency of the photoresist material in the UV spectrum enables complete photoexcitation of the incorporated fluorescing molecules.

The light-emitting molecules used in this study were the oligofluorene truxene designated T4.[3] The molecules consist of a truxene core with three pendant quaterfluorene units (see Fig. 1, structure 3). The CHDV photoresist system is miscible with these oligofluorene truxenes, which are approximately 4 nm in radius, and exerts little or no solvatochromic shift on the spectra of these molecules. The lack of a solvatochromic shift is in contrast to that observed when the oligofluorene truxene is dispersed in toluene. The T4 oligofluorene truxenes show very efficient blue photoluminescence with a high fluorescence quantum yields in both solution and the solid state (86% and 60% respectively).[3a] Figure 2b compares the absorption spectra for T4 as a solid film, in solution, and in the cured CHDV matrix, demonstrating similarity of the T4 in cured CHDV spectrum with that of the solution spectrum. The absorption maxima for T4 are at 372 nm in the solid state, 373 nm in toluene, and 371 nm in the polymerized CHDV, respectively. However, the emission spectra

in the various states exhibit significant differences (see Fig. 2b). The emission maximum of the T4 toluene solution peaks at 413 nm, and for T4 incorporated in the polymerized CHDV matrix the maximum is at 411 nm. The maximum of the solid T4 film is red-shifted by ∼30 nm, at 440 nm. Blending the T4 molecules into the CHDV photoresist system and curing the film produces an emission spectrum for the oligofluorene truxenes, which is comparable to that in toluene solution. The spectrum of T4 in the CHDV matrix is broadened with respect to its solution spectrum, due to greater vibronic interactions of the fluorescing molecules with the polymer matrix, indicating that the T4 molecules are monodisperse and ''pseudo-solvated'' within the solid CHDV matrix. Larger aggregates of oligofluorene truxenes would produce a red-shifted spectrum of shape similar to that of the solid-state spectrum.[5,7]

When oligofluorene truxenes are incorporated into the CHDV photoresist system, PAG can be activated at the absorption wavelengths of the truxenes, which are at much lower energies than its own absorption maximum. PET from the light-emitting molecule to the PAG leads to photolysis of the PAG at lower energies than its usual absorption wavelength. Here, an electron is excited to the LUMO of the T4 at a value of −2.14 eV, and is transferred into the LUMO of the PAG, which has a value of −3.72 eV. The iodonium initiator, hence, gets reduced from a cation to a radical. To relax, the radical electron can now return to the ground state of the T4, or relax through a follow-up reaction that involves scission of the C–I bond, and hence the decomposition of the PAG (an energy diagram of the process is available in the Supporting Information).[4] The LUMO of the PAG was determined by cyclic voltametry against ferrocene as internal standard. The HOMO and LUMO levels of T4 were taken from reference [3a].

This transfer mechanism as a result of the incorporation of the oligofluorene truxenes is very effective in enhancing the rate of cure, and allows irradiation at 368 nm, whereas the neat photoresist material requires irradiation at 254 nm. If neat CHDV with PAG is irradiated at 368 nm, no cure of the resin is observed. The observed high rate of reaction when the oligofluorene truxenes are present is consistent with their photon harvesting ability, activating all the PAG molecules at essentially the same time.[8]

The essentially low-polarity CHDV matrix appears to effectively protect the T4 molecules from photo-oxidation. Normally, fluorene molecules, when exposed to atmospheric oxygen, are subject to photo-oxidation, and form fluorenone moieties that shift the fluorescence spectrum towards the green.[9] Recent work in our laboratories suggests that the encapsulation of fluorene-based molecules within a polymer matrix reduces the diffusion of oxygen and suppresses photo-oxidation.[10]

A sample with a direct-laser-written structure of T4 in a CHDV blend did not show any change in its emission spectrum after 6 months of exposure to air and ambient light. A neat T4 film
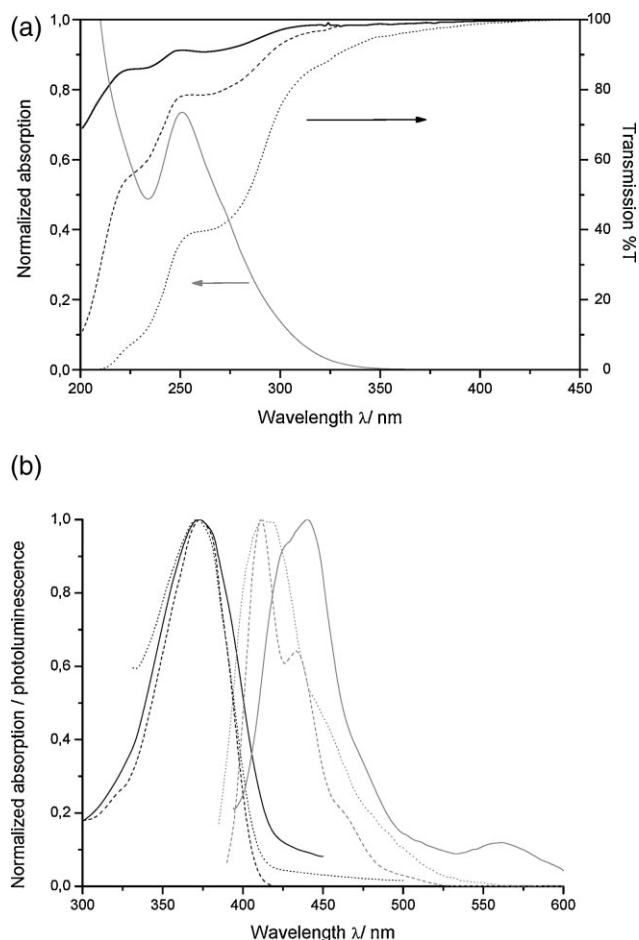
Figure 2. a) Transmission spectra of different thicknesses of CHDV with 1 wt% of PAG: 2.6 μm (solid black), 7.0 μm (dashed black), 11.0 μm (dotted black), and normalized absorption spectrum of PAG in acetonitrile (gray). b) Normalized absorption and photoluminescence spectra of a solid T4 film (solid black and gray), T4 in a toluene solution (dashed black and gray), and T4 pseudosolvated within a CHDV polymer matrix (dotted black and gray).

spin-coated from toluene and the laser-written T4/CHDV structure were exposed to radiation from a 368 nm UV lamp. After a radiation dose of 187.2 J cm^{-2}, the spectrum of the neat T4 film was dominated by a broad peak with a maximum at ~550 nm, which can be attributed to fluorenone formation due to photo-oxidation of the fluorene moiety.[9] The spectrum of the laser-written T4/CHDV structure, however, shows only minor changes (spectra are supplied in the Supporting Information). We can hence conclude that CHDV films containing the fluorene molecules exhibit very good stability and color retention compared to neat T4 films.

In this study, cure of the T4/CHDV mixture was achieved using a standard amount of 1.0 wt% PAG. The photoinitiator was first dissolved in the same amount of toluene wt/wt for compatibilization and to improve solubility in the CHDV photoresist. Use of more than 1.0 wt% of PAG leads to a reduction in the resolution of the pattern, and does not shorten the cure time significantly. The photopatterned structures adhered well to the substrate during and after the wash-off

process. However, the full pattern was transferred in an ''adhesive-tape transfer test''. In this study, no surface treatment of the substrate was applied. The adhesion of the structures could be further increased by use of an adhesion promoter before DLW. The full pattern was transferred onto the tape, and was intact after transfer, which implicates good mechanical properties of the cured T4/CHDV composites in terms of structural rigidity (a microscopy image of the transferred pattern can be found in the Supporting Information).

Due to the low viscosity (5.62 cP) of the CHDV, the creation of spin-cast films is not possible, because the CHDV is dewetting the substrate, and an alternative approach to pattern generation was carried out. For direct laser writing, a borosilicate glass substrate used for its near UV transparency was brought into contact with the T4/CHDV photoresist mixture, which had been placed in a polytetrafluoroethylene (PTFE) basin (a schematic of the setup can be found in the Supporting Information). The structures were written face down through the substrate, with the sample stage translated under a fixed optical beam position by computer-controlled X–Y–Z translation stages. Using this direct laser writing approach, patterns were created with 0.5 wt%, 1.0 wt%, and 5.0 wt% of T4 in CHDV. Because of the PET from T4 to the photoacid, the polymerization of CHDV occurs very rapidly, and writing was carried out at very high speeds. In this study, the writing speed was maintained at a constant rate of 1.5 mm s^{-1}, and the output power of the 375 nm gallium nitride diode laser source was varied between 40 μW, 80 μW, 120 μW, and 160 μW, in order to study the effect on the feature size and resolution that could be achieved. After laser writing, the borosilicate glass slide was lifted from the basin, and excess photoresist removed by washing in toluene. The dimensions achieved were extracted from microscope images, and hence represent the width at the bottom. The values are listed in Table 1. It can be seen that increasing the laser intensity produces a broader line, whilst a change in the T4 concentration from 0.5 wt% to 1.0 wt% produces only a small increase in line width. The resolution, however, is reduced with a 5.0 wt% content of T4. Changing the concentration of T4 will influence the light-harvesting characteristics of the resist, and allow for more PAG molecules to be activated and, hence, a greater chance of 'dark'-polymerization, where reaction occurs outside the illuminated region as a consequence of proton migration from the illuminated zone. When more PAG molecules are initiated, there is a greater chance of active polymerization centres propagating beyond the illuminated zone, and reduced overall resolution.[11] Figure 3 shows optical microscopy images of the 1.0 wt% T4 series in the CHDV photoresist system under ambient and UV illumination. The images show a uniform blue fluorescence throughout the laser-written lines, indicating that a homogeneous dispersion of

Table 1. Line-widths of T4/CHDV microstructures.

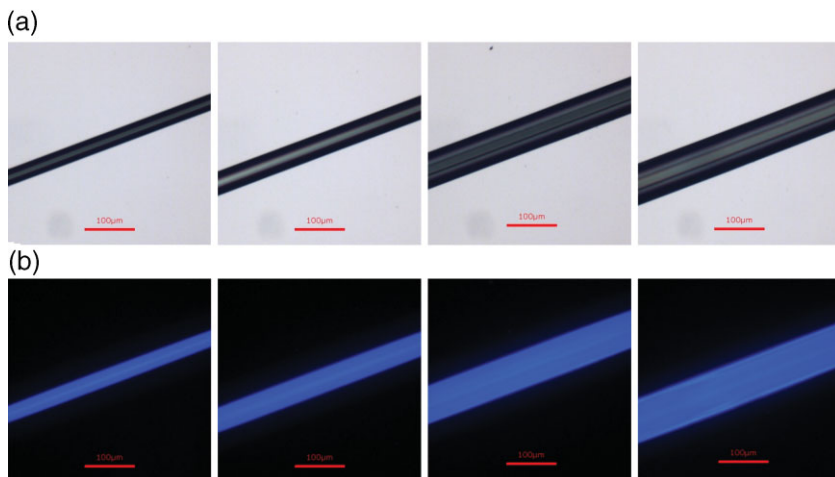| Laser output power	0.5 wt % T4 in CHDV	1 wt % T4 in CHDV	5 wt % T4 in CHDV
40 μW	35 μm	35 μm	50 μm
80 μW	45 μm	50 μm	80 μm
120 μW	70 μm	70 μm	100 μm
160 μW	90 μm	95 μm	120 μm

Figure 3. Microscopy images of fluorescing microstructures with 1 wt% T4 and 1 wt% PAG, written with a laser, observed using optical microscopy with a) white-light illumination and b) 368 nm illumination, written at 40 μW, 80 μW, 140 μW, and 160 μW (from left to right).
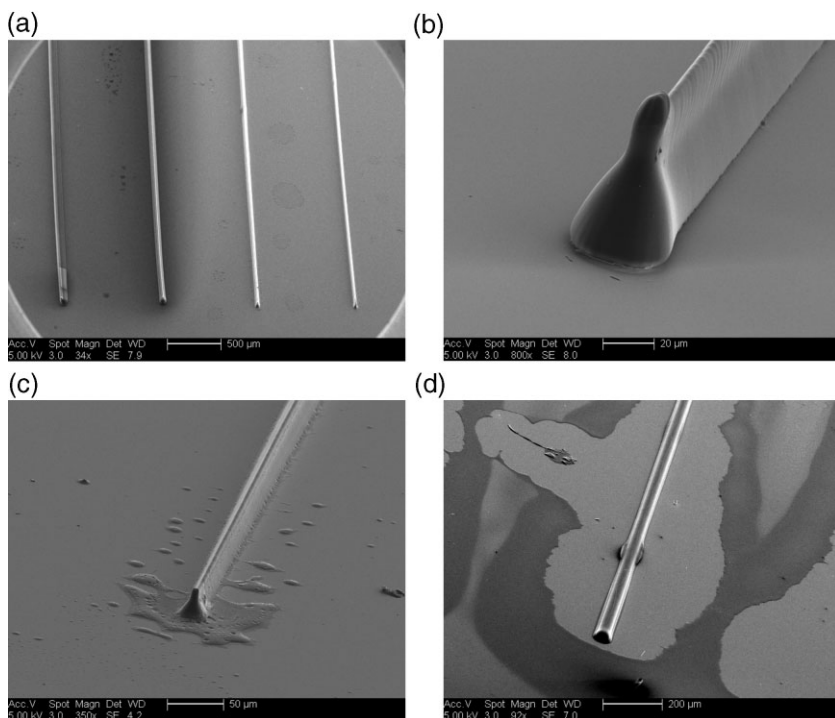

Figure 4. Scanning electron microscopy images of different percentages of T4 in CHDV: a) image of the 0.5 wt% T4 sample with four lines written at 160 μW, 140 μW, 80 μW, and 40 μW from left to right; b) close up image of the line written at 40 μW into the 0.5 wt% T4 in CHDV blend; c) image of the line written at 40 μW into the 1.0 wt% T4 in CHDV blend; d) image of the line written at 40 μW into the 5.0 wt% T4 in CHDV blend.

due to residues of the composite, from incomplete wash-off. Examination of the structure of the line produced with the lowest T4 concentration (i.e., 0.5 wt%) indicates a good aspect ratio and smooth walls. The thicker features that can be seen at the end of the structure are due to an exposure time lag when starting and stopping the stage and opening and closing the laser-beam shutter. The shape of the feature reflects as much the shape of the optical beam as the effects of the polymerization process on the feature structure. The 'upside-down chalice' shape of the structures in the blends of 0.5 and 1.0 wt% is assumed to be a result of the high sensitivity of the resist material, due to the light-harvesting character of the T4. When writing into the resist, face down through the substrate, the focal point of the laser beam lies beyond the substrate. After the focal point, convergence of the beam occurs, and combined with the high sensitivity of the resist, the observed shape in the material represents the profile of the laser beam. This is not apparent in the 5.0 wt% T4/ CHDV blend. With the higher loading of the photon-harvesting T4, the composite absorbs more strongly, and limits the extent to which the laser beam penetrates into the resist composite in the PTFE basin. Hence, in the 5.0 wt% T4/CHDV blend, no activation of the PAG occurs beyond the focal point of the laser, leading to a half-cylindrical shape of the written line. In conclusion, a higher content in photon-harvesting T4 leads to greater absorption, and hence structures that have a lower aspect ratio. With lower T4 contents, the laser beam can penetrate deeper into CHDV/T4 blend, and hence produce structures that have a higher aspect ratio. This effect defines the shape of the structure, whereas dark-polymerization, which occurs after the direct-laser-writing step, reduces the overall resolution of the structures.

Figure 5 shows a more complicated pattern created, under computer control of the translation stages, as a 4:5 Lissajous structure using 1 wt% of T4 in the CHDV resist. When the laser power was limited to 0.4 μW, and PAG content was reduced to 0.1 wt%, a line width of 2.5 μm was achieved.

This paper presents the cure characteristics of a photoresist material, which contains fluorene-based light-emitting molecules. The absorption and fluorescence spectra of the oligofluorene derivative indicate that a homogeneous dispersion of the T4 molecules is achieved throughout the CHDV matrix. Apparent environmental protection of the T4 molecules from oxygen, combined with the short cure time, render these novel photo-cross-linkable composites of CHDV and T4 highly attractive for applications in organic optoelectronics.
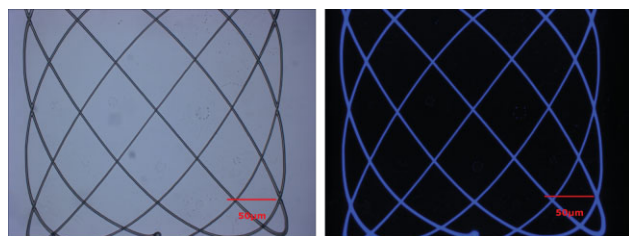
the T4 in the CHDV was achieved, consistent with the spectroscopic characteristics.

The SEM images of the laser-written structures (Fig. 4) show in more detail the structure of the T4/CHDV series written at 40 μW. The thin-film patches in the images of Figure 4c and d are

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Figure 5. 4:5 Lissajous structure written in CHDV with 1 wt% T4 and low laser intensity 0.4 μW, resulting in a line width of 2.5 μm.

We have shown facile processability of the composite by direct laser writing, resulting in structures with tunable size down to 2.5 μm, smooth side walls, and high aspect ratios.

Experimental

Materials and Instruments: The oligofluorene truxene T4 was synthesized by A. L. K., I. F. P., and P. J. S., and the synthetic route can be found elsewhere [3]. CHDV and solvents were purchased from Sigma–Aldrich and used without further purification. *Para*-octyloxy-functionalized diphenyliodonium hexafluoroantimonate was purchased from ABCR.

UV-vis Absorption Spectroscopy: Spectra were taken using a Perkin Elmer Lambda 20 UV/Vis spectrophotometer. Deposited T4 films were recorded on a 1 mm thick quartz wafer spin-coated from a 20 mg mL^{-1} toluene solution at 1000 rpm. CHDV and T4/CHDV composites with 1 wt% PAG were drop-cast onto quartz wafers. Solutions were taken in toluene in a quartz cuvette of 10 mm path length.

Photoluminescence Spectroscopy: Spectra were recorded using a Perkin Elmer LS 50B fluorescence spectrometer in a quartz cuvette of 10 mm path length, and for the solid films from a quartz wafer. The same samples as for the UV-vis absorption analysis were used.

Microscopy Images: Microscopy images were taken using a CCD camera (Q-imaging Inc.) mounted onto an inverted fluorescent microscope (Nikon Eclipse TE2000-U) with a set of 10×/0.25NA, 20×/0.5NA Plan Flour objectives. Fluorescent images were taken using a UV-2A filter cube, to filter out the excitation source.

Scanning Electron Microscopy: For SEM imaging, carbon was evaporated onto the laser-written structures using a BAL-TEC CED 200 carbon evaporator, and the structures were examined using a FEI Sirion field-emission SEM.

Direct Laser Writing: The setup consisted of a GaN diode laser (15 mW @ 374 nm, circularized and collimated output beam with a spot size of 1 μm in diameter in the focal point) with a variable neutral density filter wheel, a mechanical shutter (minimum open time 10 ms), and a beam expander. A microscope objective (N.A. 0.4) was controlled by a piezo objective-translational stage (400 μm range, sub-nanometer precision). The sample was placed onto a X–Y sample-translation stage (25 mm × 25 mm range, ∼1 μm precision, 1.5 mm s^{-1} max speed). The system was controlled through a CCD camera imaging system and a control PC operating the shutter and stages.

Sample Preparation: Direct Laser Writing: For sample preparation, the borosilicate cover slides (near UV transparent) were thoroughly cleaned in a standard procedure using an ultrasonic bath in acetone and then methanol (3–5 min each). The cover glasses were then rinsed with deionized water, and subsequently treated in an isopropanol ultrasonic bath and rinsed again, dried with a spinner at 8 000 rpm for 30 s, and then left on a hotplate at ∼100 °C for at least 20 min. The composite is prepared

by carefully weighing desired ratios of CHDV, PAG, and oligofluorene truxenes, and ultrasound is used to facilitate mixing and dispersion of the T4. The composite is pipetted into a shallow (∼500 μm deep) 10 mm × 10 mm basin in a block of PTFE plastic. The clean cover glass is placed over the basin with care taken not to capture any air bubbles. The sample is placed under the objective. The writing was carried out by moving the sample while the shutter was open. The laser beam is static. After direct laser writing, the structures were developed by taking the cover slide from the plastic block and washing off in toluene for 5–10 s.

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