Site-isolated, intermolecularly photocrosslinkable and patternable dendritic quinacridones†

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Received (in Berkeley, CA, USA) 29th January 2009, Accepted 23rd April 2009
First published as an Advance Article on the web 12th May 2009
DOI: 10.1039/b901897b

Quinacridone-cored dendrimers with photocrosslinkable cinnamate moieties on the periphery can be patterned down to 5 micron features while retaining luminescence.

We demonstrate here the formation of photopatternable thin films of dendritic quinacridones (Chart 1) which address the need for easily processed, patternable, emissive materials for application in organic light emitting diodes (OLEDs) and related thin film light sources. The quinacridone core is related to established (green emitting) dopants (*e.g.* **DMQA**) for aluminium quinolate-based OLEDs,[1] which enhance electroluminescence efficiency and stability of the OLED.

We have previously demonstrated site-isolation of this quinacridone core using [G0]–[G4] dendrimers, which increased the photoluminescence efficiency by 7-fold relative to *N*,*N*′-diisoamylquinacridone (**DIQA**),[2] a quinacridone derivative we developed as a dopant in solution-processed single layer OLEDs.[3,4] Because dendrimers are capable of site-isolating chromophores at their core, they have been used to effectively encapsulate photoactive, electroactive, and catalytic moieties.[5–11] Dendrimers have been incorporated into organic light emitting diodes (OLEDs) because the site-isolation of small molecule emitting chromophores prevents aggregation and self-quenching for films with high effective concentrations of the emissive core molecule.[12–18] Additionally, increased solubility lent by the dendritic structure renders these materials amenable to solution-processing of large area thin films.

Here, we have incorporated photoactivated cinnamate crosslinking groups onto the periphery of first and second generation quinacridone dendrimers, and demonstrate that standard photocrosslinking technology can be employed to create patterned thin films down to 6 nm in thickness, with lateral feature sizes as small as 5 μm. These cinnamate–quinacridone dendrimers are the first example of intermolecularly crosslinked emissive dendrimers for use in photopatterned luminescent thin film architectures.

The dendrimers prepared for this study consisted of a quinacridone core, benzyl aryl ether dendritic subunits, and cinnamate-based peripheral subunits. A cinnamic acid derivative was chosen for the periphery because it can be photocrosslinked without a chemical co-initiator, is chemically inert to the reaction conditions necessary for increase of generation, and the crosslinking can be monitored by UV spectroscopy.[19–21] The dendrimers were synthesized in a convergent fashion from the peripheral cinnamate moieties to a benzyl chloride at the focal point (ESI†). First and second generation dendrons (with benzyl chlorides at the focal point) were coupled to quinacridone (**QA**) under basic conditions (KOH–DMSO) to yield crosslinkable quinacridone dendrimers **1** and **2**, respectively (Chart 1). The temperature of these reaction mixtures was carefully maintained at the maximum necessary (55 °C) to deprotonate **QA** as indicated by a change from a violet suspension to a homogeneous blue solution. Temperatures in excess of this resulted in significant amounts of additional C-alkylation as evidenced by a higher MW peak in the gel permeation chromatogram (GPC) of the resulting product. A lower yield of **2** (15%) relative to **1** (65%) was attributed to poorer solubility of the [G2] dendron relative to the [G1] dendron in DMSO. Dendrimers **1** and **2** were both characterized by ^{1}H and ^{13}C NMR, MS, GPC, and combustion analysis.

Absorbance spectra of dendrimers **1** and **2** (Fig. 1) exhibited the expected cinnamate (295 and 310 nm) and quinacridone (512 nm) absorbance maxima. Photoluminescence (PL) spectra (λ_{ex} = 490 nm) in dilute chloroform solution (Fig. 1) show similar spectral profiles to **DIQA** with quinacridone absorbance λ_{max} of 512 nm and a Stokes shift of *ca.* 13 nm (Table 1). Quantum yields, measured *versus* a fluorescein standard, were 0.86 for **1** (compared with 0.85 for **DIQA**) and 1.0 for **2**. Linear Beer's law plots indicated that no solution aggregation existed up to *ca.* 10^{-3} M.

Two thicknesses of thin films (*ca.* 300 nm and 6 nm by ellipsometry) of both **1** and **2** were made by spin-casting from *ca.* 10^{-6} M $CHCl_3$ solutions onto quartz. The 300 nm films were used to characterize the aggregation state of the chromophores before (Fig. 2) and after crosslinking (ESI†), and to investigate the conditions necessary for successful crosslinking (Fig. 3).

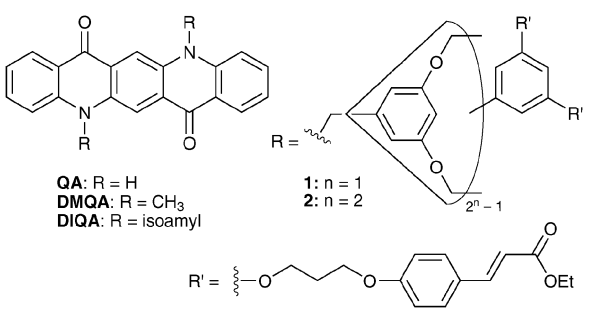

Chart 1 Quinacridone derivatives and dendrimers **1** and **2**.

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† Electronic supplementary information (ESI) available: Synthesis scheme, experimental procedures and characterization data for quinacridone dendrimers. See DOI: 10.1039/b901897b

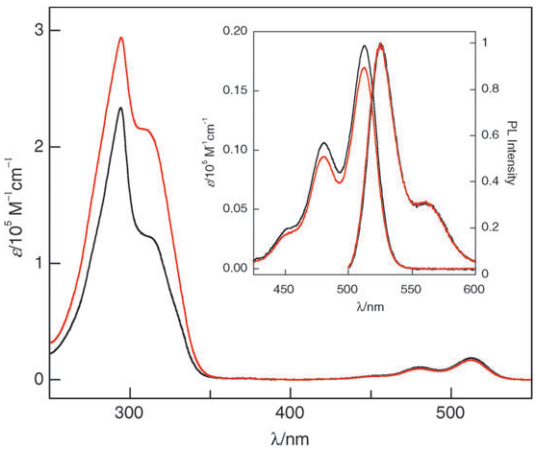

Fig. 1 Absorbance spectra ($CHCl_3$) of **1** (black) and **2** (red). Inset shows the absorbance and photoluminescence in the quinacridone region.

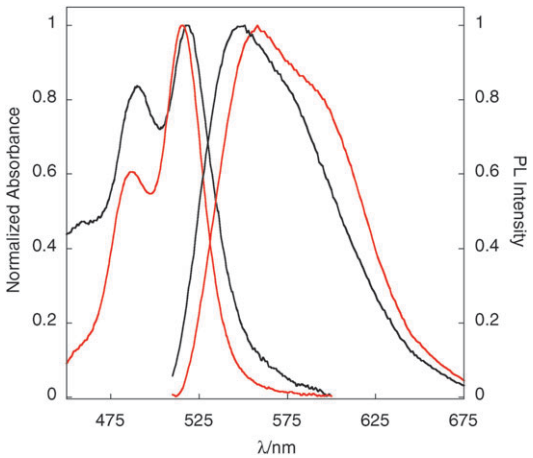

Fig. 2 Thin film (300 nm) absorbance and photoluminescence of **1** (red) and **2** (black).

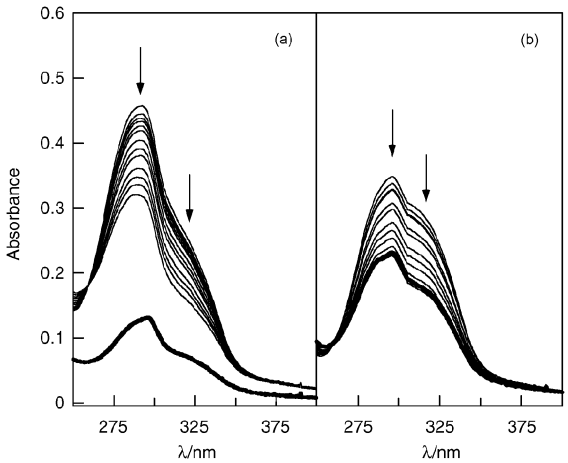

Fig. 3 Absorbance monitoring of crosslinking for (a) **1** and (b) **2** in 300 nm thin films. The dark lines are the spectra measured following wet development in $CHCl_3$.

Comparison of normalized absorbance spectra of 300 nm thin films of dendrimers **1** and **2** to solution spectra confirms non-aggregating chromophore cores brought about by dendron-induced site-isolation (Fig. 2). Decreasing PL λ_{max} (Table 1) and narrower peak widths in thin film PL spectra for dendrimers **1** and **2** indicate decreased amounts of red-shifted (excimer) emission with increasing generation. Interestingly, the PL λ_{max} of both **1** and **2** are blue-shifted compared to the *t*Bu[G3] quinacridone dendrimer reported previously by us,[2] although the PL efficiencies are somewhat lower. Although the cinnamate dendrons provide physical encapsulation of the chromophores so that aggregation is prevented, it is likely that the dendrons do not spatially isolate the chromophores at sufficient distances to prevent self-quenching which lowers the PL efficiency.

The 300 nm thin films of dendrimers **1** and **2** were subjected to irradiation (λ = 310 nm, 6 nm slits) using a 75 W Xe arc lamp. The solid state [2 + 2] photodimerization of cinnamic acid and its derivatives is easily monitored by changes in the UV absorbance (λ_{max} = 310–315 nm).[19–21] Continuous irradiation clearly showed a decrease in the cinnamate peaks in the UV for both **1** (30% overall decrease of 292 nm, λ_{max}) and **2** (40% overall decrease at 292, λ_{max}) after 90 minutes (Fig. 3). The decrease in cinnamate absorbance is most likely due to *both* $E \rightarrow Z$ isomerization as well as [2 + 2] photodimerization. During wet development ($CHCl_3$ for 3 minutes), a major portion of the film of **1** washed away leaving only 28% of the original absorbing cinnamate peak, while the film of **2** exhibited no change in absorbance subsequent to wet development. These results were the same even after extended wet development (18 hours) for **2**. Hence, dendrimer **1** was only moderately successful in achieving a crosslinked film, while **2** formed an insoluble network. Longer irradiation times provided similar results with incomplete crosslinking of **1** in all cases. Several trials determined that at least a 40% loss of cinnamate absorbance was necessary to form an insoluble network for dendrimer **2**. This 40% loss corresponded to *ca.* 60–90 minutes of irradiation depending on film thickness (thicker films required longer irradiation times).

Photoluminescence measurements of dendrimer **2** in 300 nm films indicated an integrated loss of emission of *ca.* 20% after

Table 1 Photophysical characterization of **1** and **2** in $CHCl_3$ solution and thin film (in parentheses)

	MW/g mol^{-1}	$\lambda_{max,Abs}$/nm	$\lambda_{max,PL}$/nm	10^{-4} $\varepsilon_{\lambda max}$/M^{-1} cm^{-1}	Φ_{fl}[a]	Film PL efficiency[b]
DIQA	452.6	524 (498)	537 (594)	1.79	0.85	1
[G1], **1**	1485.7	512 (516)	526 (558)	1.78	0.86	4.1
[G2], **2**	2903.3	512 (519)	525 (551)	1.68	1.0	6.4
*t*Bu[G3][2]	5259.4	513 (516)	526 (567)	1.78	1.0	6.8

[a] Measured *versus* a fluorescein standard (Φ_{fl} = 0.95) 0.1 M aq. NaOH solution. [b] Measured by integrating the corrected PL spectrum (λ_{ex} = 470 nm) and dividing by the absorbance at 470 nm. This value was then divided by the analogous value for a **DIQA** film.

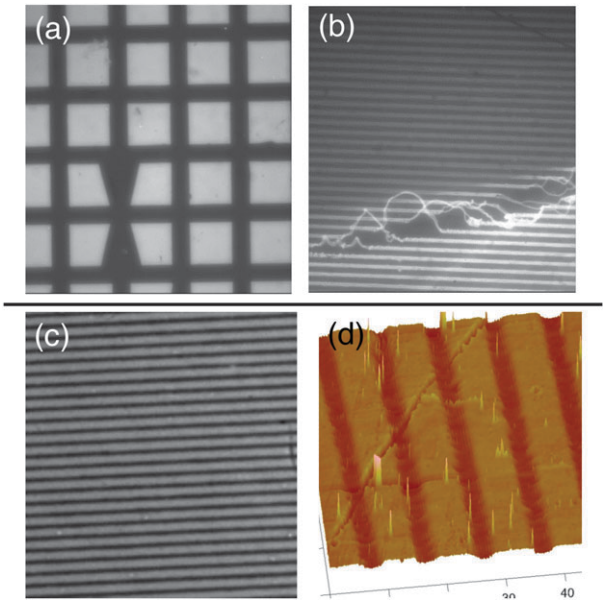

Fig. 4 Fluorescence microscopy images (a), (b), and (c) of patterned dendrimer **2**: (a) was made from TEM grids (*ca.* 85 μm feature sizes), while (b) and (c) are 5 μm lines; (b) shows an area in which the dendrimer has become delaminated and then re-adsorbed to the surface; (c) is 5 μm lines patterned on a *ca.* 6 nm thin film; (d) is an AFM image (full images in ESI†) of 5 μm patterned lines of dendrimer **2** on a *ca.* 6 nm thin film.

crosslinking and wet development. This corresponded to a similar 20% decrease in quinacridone absorbance during crosslinking (ESI†), suggesting that PL loss was solely due to degradation of the film during crosslinking and that loss of emission due to red-shifting was negligible. Since the bulk of the site-isolation properties of the material remain intact, observed loss in emission is not detrimental to the usefulness of the material in luminescent thin film architectures.

We next produced features from our 300 nm thick dendrimer thin films with pattern sizes ranging from 5 to 85 μm. Films (with *ca.* 85 μm feature sizes) were produced by irradiation (310 nm for 90 minutes) of a film masked with a transmission electron microscopy (TEM) copper grid and subsequent wet development in $CHCl_3$. Patterns of dendrimer **2** visualized under a fluorescence microscope (535 nm excitation filter; 615 nm emission filter) exhibited resolved lines with sharp edges (Fig. 4a). These positive tone images have dark areas with no emissive material and light areas of patterned dendrimer. Patterns were produced with *ca.* 5 μm features using a Ronchi ruling (5 μm chrome lines on glass) as a photomask (Fig. 4b). Irradiation times were increased to *ca.* 3 h to account for the low transparency of glass at 310 nm (<10%). Image (b) also shows an area where dendrimer desorption and subsequent readsorption occurred. Remarkably, the crosslinked dendrimer network remained intact in all areas and no disruption of the integrity of the material was observed, indicating a high tensile strength.

Using the conditions for crosslinking determined by the experiments on the 300 nm films, we next patterned the ultra thin films (*ca.* 6 nm) of **2** using a Ronchi ruling mask and characterized them by fluorescence microscopy and AFM. Fluorescence microscopy images of the patterned 6 nm films (Fig. 4c) are identical to those obtained after patterning 300 nm films (Fig. 4b). However, differences were observed by AFM. Whereas the 300 nm films were found to contain channels after patterning and wet development (ESI†), the ultra thin films showed no evidence of channels within the patterned rows (Fig. 4d). We believe that this is due to complete polymerization through the entire thickness of the 6 nm film. The similar thickness of the ultra thin film before and after crosslinking (*ca.* 6 nm), as well as the similar RMS surface roughness, is a further evidence of complete polymerization. In the 300 nm films, the majority of material is removed upon wet development due to incomplete polymerization.

Dendrimers can simultaneously serve multiple roles in a complex system due to their varied yet discrete architecture. The dendrimers presented herein contain all the necessary components that render them easily processed, patternable, emissive materials for the fabrication of stand-alone emissive thin film light sources. These materials indicate enhanced utility for dendrimers in OLEDs and other solution-processed, multilayer luminescent devices.

The authors acknowledge the National Science Foundation (DMR-0120967) for support.

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