Supporting Information for:

Site-isolated, Intermolecularly Photocrosslinkable and Patternable Dendritic Quinacridones

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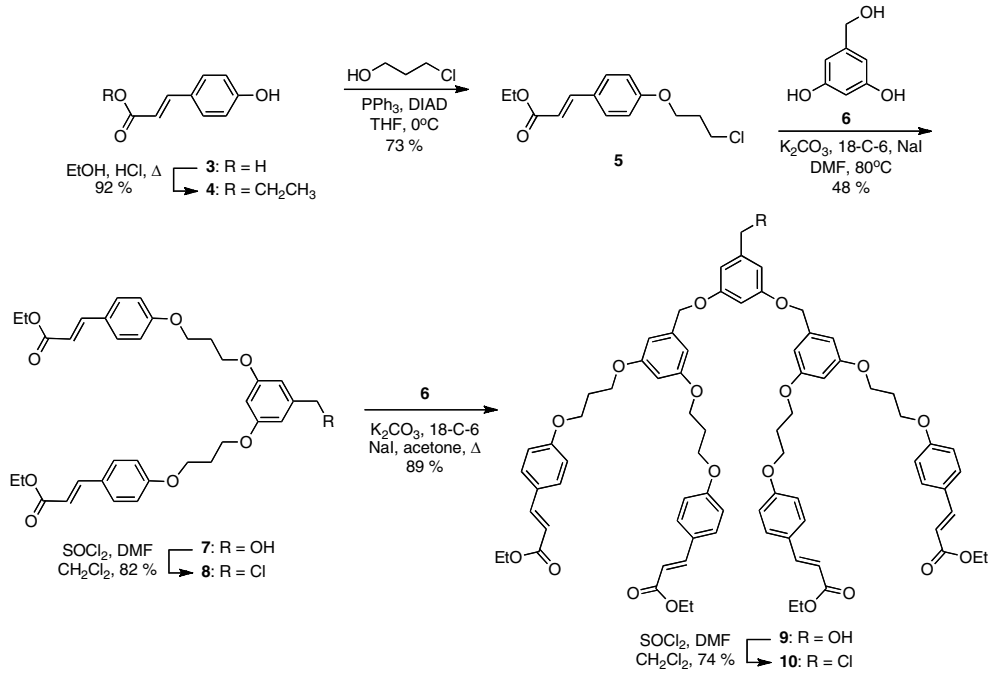
Synthesis of quinacridone dendrimers 1 and 2: Commercially available 4-hydroxycinnamic acid (**3**) was esterified and then coupled with 3-chloropropanol under Mitsunobu conditions to afford **5** in 67% yield over two steps. Alkylation of 3,5-dihydroxybenzyl alcohol (**6**) with **5** in DMF, followed by chlorination with thionyl chloride ($SOCl_2$) provided electrophilic first generation dendron **8**. Further homologation yielded second generation alcohol **9**, and subsequent chlorination yielded a second generation dendritic electrophile **10**.



Scheme S1. Synthesis of crosslinking dendrons.

Comparison of Absorbance Spectra of Chromophores: A comparison between the spectra for **1** and **2** with the absorbance spectra of **5** (scaled 4x and 8x, respectively, to account for the correct ratio of chromophores) verifies that the absorbance spectra of the dendrimers scale with the number of cinnamate moieties on their respective peripheries. Differences between the calculated and observed spectra can be attributed to non-zero absorption by the dendrons at ~310 nm and significant overlap between the 295 nm cinnamate band and both the dendron and the quinacridone bands.

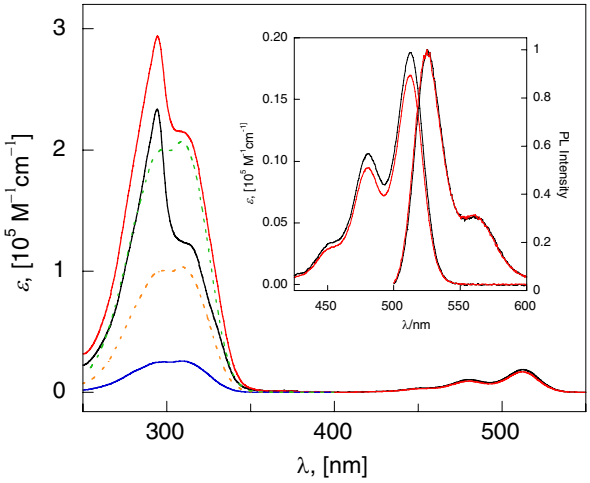


Figure S1. Absorbance spectra ($CHCl_3$) of **1** (black), **2** (red), **5** (blue), **5** x4 (orange dotted), and **5** x8 (green dotted). Inset shows the absorbance and photoluminescence in the quinacridone region of **1** (blue) and **2** (orange).

Additional AFM Images: Atomic force microscopy (AFM) images of the ca. 5 μm patterned dendrimer **2** (e.g. Figure S2) revealed that the lines of the pattern correspond well to the expected width of 5.2 μm as seen in an AFM of the Ronchi ruling mask (Figure S3). Also, the height of the patterned dendrimers was reduced to 17 nm, which is significantly lower than the pre-patterned film thickness as measured by ellipsometry (ca. 300 nm). This indicates that polymerization did not proceed through the entire film and

unreacted dendrimer was washed off during wet development. Finally, the patterns appear in rows with small (submicron) channels between the rows. This feature was not observed by fluorescence microscopy due to resolution limitations of the instrument except in the delamination image (Figure 4b) where the delaminated and readsorbed polymer appears as two strands per patterned line. The number of rows in AFM images ranges from 2 to 4 at different areas on the same patterned film, suggesting that they are the result of interference patterns of the irradiating light.

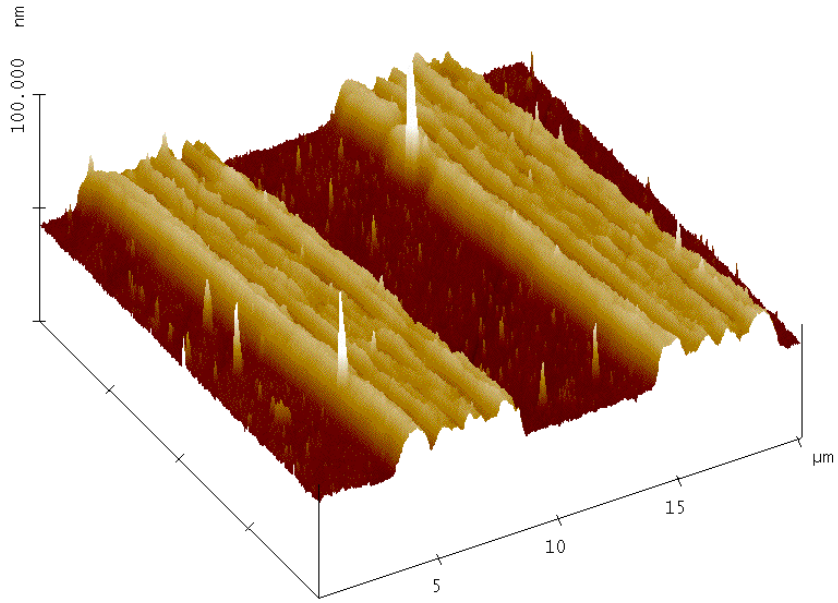


Figure S2. AFM image of patterned (through Rhonchi ruling) dendrimer **2**. Pre-patterned film thickness is ca. 300 nm.

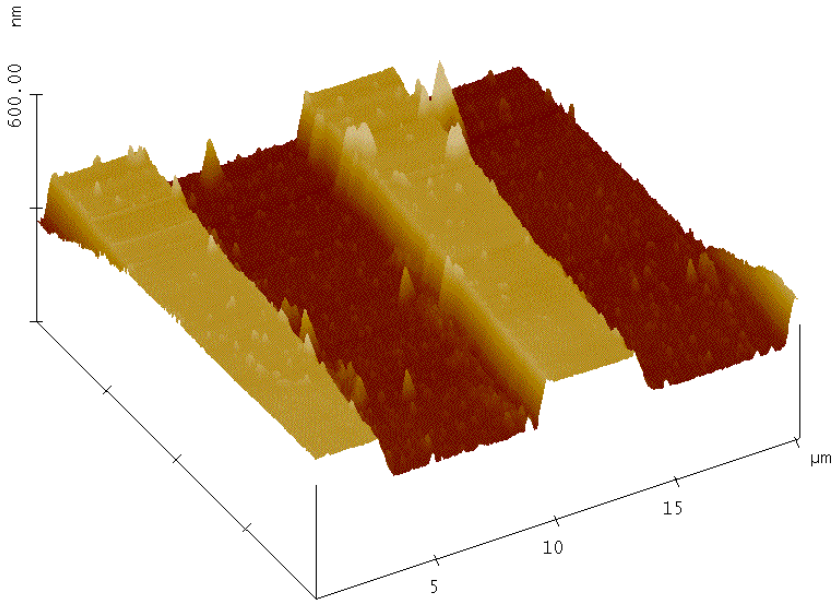


Figure S3. AFM image of Rhonchi Ruling (chrome lines on glass) showing 5 μm line spacings.

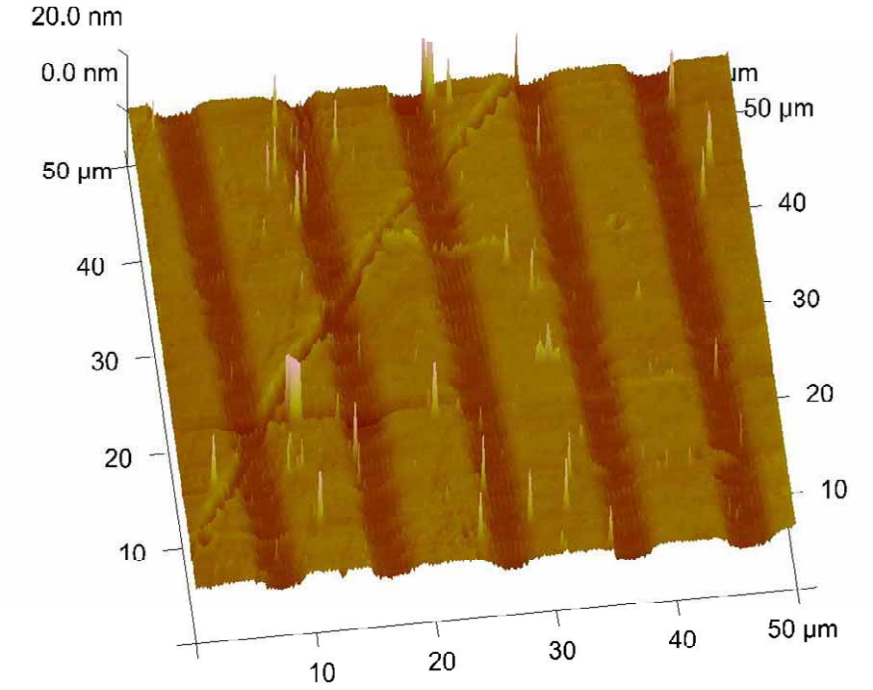


Figure S4. AFM image of patterned (through Rhonchi ruling) dendrimer **2**. Pre-patterned film thickness is ca. 6 nm.

Experimental procedures:

Synthesis of molecules:

NMR spectroscopy was performed using either a Bruker AM-250 or a Bruker DRX-500 spectrometer available at the University of Arizona. Mass spectrometry (MS) was performed by the MS Instrument Facility at the University of Arizona. Elemental analysis for C, H, and N was performed by NuMega in San Diego, CA. Acetone, CH_2Cl_2, and DMF were dried over crushed 3Å molecular sieves. All other needed reagents were purchased from readily available suppliers and used as received. Flash chromatography was performed according to the method of Still and coworkers[1] with 40-63 μm silica gel (EMD Chemicals, Inc.). TLC was performed on precoated plates containing a fluorescent indicator (Silica Gel 60 F_{254}, EMD Chemicals, Inc.).

(cinn$_2$[G1])$_2$quinacridone (1). A mixture of quinacridone (403 mg, 1.29 mmol), KOH (472 mg, 8.40 mmol), and DMSO (20 mL) was heated with stirring under Ar to 55 °C for 1.5 h. A solution of **8** (2.0 g, 2.2 mmol) in DMSO (10 mL) was then added and the reaction mixture was maintained at 55 °C for 21 h. Additional KOH (113 mg, 2.02 mmol) and NaI (35 mg, 0.24 mmol) were added and the reaction was continued for another 36 h. The reaction mixture was allowed to cool to ambient temperature, diluted with $CHCl_3$ (200 mL), and washed with H_2O (2 x 100 mL), sat. NH_4Cl (100 mL), and sat. NaCl (100 mL). The organic fraction was dried (Mg_2SO_4), filtered, and the filtrate was concentrated in vacuo to ca. 100 mL. Slow addition of this solution to rapidly stirring MeOH (700 mL) resulted in the precipitation of a red solid. The red solid was filtered, washed with copious amounts of MeOH and then purified by column chromatography (dryload, 9:1 CH_2Cl_2/Et_2O). Reprecipitation from $CHCl_3$ into MeOH afforded **1** (1.237

g, 65%) as a red solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.58 (s, 2 H), 8.46 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.67 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 2 H), 7.58 (d, *J* = 16.0 Hz, 4 H), 7.43 and 6.85 (AA'BB' pattern, *J* = 8.5 Hz, 16 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 7.27 (t, *J* = 7.5 Hz, 2 H), 6.42 (m, 6 H), 6.27 (d, *J* = 16.0 Hz, 4 H), 5.66 (br s, 4 H), 4.20 (q, *J* = 7.0 Hz, 8 H), 4.10 (t, *J* = 6.0 Hz, 8 H), 4.08 (t, *J* = 6.0 Hz, 8 H), 2.17 (pentet, *J* = 6.0 Hz, 8 H), 1.30 (t, *J* = 7.0 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) 178.2, 167.3, 160.8, 160.5, 144.2, 142.9, 137.8, 136.9, 134.9, 129.6, 127.8, 127.2, 126.5, 121.4, 121.3, 115.7, 115.3, 114.8, 113.9, 104.6, 100.1, 64.5, 64.4, 60.3, 29.1, 14.4; MS (MALDI, dithranol) *m/z* 1484.77 (M^+, $C_{90}H_{88}N_2O_{18}$ requires 1484.60), 1507.78 ($M + Na^+$, $C_{90}H_{88}N_2O_{18}Na$ requires 1507.59); Anal Calcd for $C_{90}H_{88}N_2O_{18}$: C, 72.76; H, 5.97; N, 1.89. Found: C, 72.38; H, 5.81; N, 2.11.

(cinn$_4$[G2])$_2$quinacridone (2). A mixture of quinacridone (46 mg, 0.15 mmol), powdered KOH (41 mg, 0.73 mmol), and DMSO (8 mL) was heated with stirring under Ar to 55 °C for 5 h. **10** (0.505 g, 0.379 mmol) was then added and the reaction mixture was maintained at 55 °C for 65 h. The reaction mixture was allowed to cool to ambient temperature, diluted with $CHCl_3$ (200 mL), and washed with H_2O (2 x 100 mL), sat. NH_4Cl (100 mL), and sat. NaCl (100 mL). The organic fraction was dried (Mg_2SO_4), filtered, and the filtrate was concentrated in vacuo to ~30 mL. Slow addition of this solution to rapidly stirring MeOH (200 mL) resulted in the precipitation of a red solid. Purification of the red solid by column chromatography (dryload, 1:1 Hex/EtOAc to remove impurities then switched to 4:1 CH_2Cl_2/Et_2O to remove product) followed by an additional precipitation from CH_2Cl_2/Hex (1:1) into MeOH afforded **2** (64 mg, 15%) as a red solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.50 (s, 2 H), 8.44 (dd, *J* = 8.0, 1.5 Hz, 2 H),

7.62 (ddd, *J* = 8.3, 7.3, 2.0 Hz, 2 H), 7.58 (d, *J* = 16.0 Hz, 8 H), 7.44 and 6.87 (AA'BB' pattern, *J* = 9.0 Hz, 32 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.23 (t, *J* = 7.5 Hz, 2 H), 6.53 (t, *J* = 2.0 Hz, 2 H), 6.47 (d, *J* = 1.5 Hz, 4 H), 6.43 (d, *J* = 2.0 Hz, 8 H), 6.31 (t, *J* = 2.0 Hz, 4 H), 6.27 (d, *J* = 16.0 Hz, 8 H), 5.64 (br s, 4 H), 4.86 (s, 8 H), 4.19 (q, *J* = 7.0 Hz, 16 H), 4.10 (t, *J* = 6.0 Hz, 16 H), 4.01 (t, *J* = 6.0 Hz, 16 H), 2.16 (pentet, *J* = 6.0 Hz, 16 H), 1.30 (t, *J* = 7.0 Hz, 24 H); ^{13}C NMR (125 MHz, $CDCl_3$) 178.0, 167.2, 160.6, 160.5, 160.1, 144.1, 142.9, 138.9, 137.8, 136.8, 134.7, 129.6, 127.7, 127.2, 126.4, 121.4, 121.2, 115.7, 115.2, 114.8, 113.8, 105.7, 105.0, 100.9, 70.1, 64.5, 64.3, 60.3, 29.1, 14.4; MS (MALDI, dithranol) *m/z* 2901.93 (M^+, $C_{174}H_{176}N_2O_{38}$ requires 2902.19). Anal Calcd for $C_{174}H_{176}N_2O_{38}$: C, 71.98; H, 6.11; N, 0.96. Found: C, 71.59; H, 6.24; N, 1.27.

Ethyl (*E*)-4-hydroxycinnamate (4). Compound **4**[2] was prepared from (*E*)-4-hydroxycinnamate **(3)** according to the literature.

Ethyl (*E*)-4-(3-chloropropoxy)cinnamate (5). To a solution of **4** (0.546 g, 2.84 mmol), 3-chloropropanol (330 mg, 3.59 mmol), and triphenylphosphine (PPh_3) (0.748 g, 2.84 mmol) in THF (5 mL) on an ice bath under Ar was added diisopropylazodicarboxylate (DIAD) (0.580 g, 2.89 mmol) via syringe. After stirring for 4 h, the reaction mixture was concentrated in vacuo and the residue was recrystallized (x3) from MeOH to afford **5** (0.530 g, 73%) as colorless crystals: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.8 Hz, 1 H), 7.47 and 6.91 (AA'BB' pattern, *J* = 8.8 Hz, 4 H), 6.31 (d, *J* = 16.0 Hz, 1 H), 4.25 (q, *J* = 7.3 Hz, 2 H), 4.15 (t, *J* = 6.0 Hz, 2 H), 3.75 (t, *J* = 6.3 Hz, 2 H), 2.25 (pentet, *J* = 6.3 Hz, 2 H), 1.33 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (63 MHz, $CDCl_3$) 167.3, 160.4, 144.1, 129.7, 127.4, 115.8, 114.8, 64.3, 60.3, 41.3, 32.0, 14.3.

Anal. calcd for $C_{14}H_{17}ClO_3$: C, 62.57; H, 6.38; MS (ESI) *m/z* 269.1 ($M+H^+$). Found: C, 62.32; H, 6.58%

(Ethylcinnamate)$_2$[G1]-OH (7). A mixture of **5** (50.3 g, 187 mmol), **6** (13.1 g, 93.4 mmol), K_2CO_3 (35.8 g, 259 mmol) and DMF (100 mL) was stirred at ambient temperature for 20 h under Ar. 18-Crown-6 (30 mg, 0.12 mmol) was added and the reaction was heated to 80 °C for 56 h. Additional K_2CO_3 (6.5 g, 47 mmol) and NaI (70 mg, 0.47 mmol) were added and the mixture was maintained at 80 °C for an additional 24 h. The reaction mixture was cooled, filtered, and the filtrate was partitioned between H_2O (100 mL) and CH_2Cl_2 (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with H_2O (2 x 100 mL) and sat. NaCl (2 x 100 mL), dried (Mg_2SO_4), filtered, and the filtrate was concentrated in vacuo. Recrystallization of the residue from acetone afforded **7** (27.3 g, 48%) as a colorless solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 2 H), 7.45 and 6.89 (AA'BB' pattern, *J* = 8.5 Hz, 8 H), 6.52 (d, *J* = 2.5 Hz, 2 H), 6.39 (t, *J* = 2.5 Hz, 1 H), 6.30 (d, *J* = 16.0 Hz, 2 H), 4.61 (d, *J* = 6.0 Hz, 2 H), 4.25 (q, *J* = 7.5 Hz, 4 H), 4.17 (t, *J* = 6.0 Hz, 4 H), 4.14 (t, *J* = 6.0 Hz, 4 H), 2.25 (pentet, *J* = 6.0 Hz, 4 H), 1.63 (t, *J* = 6.0 Hz, 1 H), 1.33 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.3, 160.6, 160.2, 144.2, 143.4, 129.7, 127.2, 115.8, 114.8, 105.3, 100.6, 65.3, 64.5, 64.3, 60.3, 29.2, 14.4; MS (ESI) *m/z* 627.3 ($M+Na^+$), 1230.8 ($2M+Na^+$). Anal. calcd for $C_{35}H_{40}O_9$: C, 69.52; H, 6.67. Found: C, 69.27; H, 7.10.

(Ethylcinnamate)$_2$[G1]-Cl (8). A solution of **7** (1.05 g, 1.73 mmol), DMF (8 drops), and CH_2Cl_2 (25 mL) was allowed to stir under Ar at ambient temperature while thionyl chloride (260 mg, 2.20 mmol) was added via syringe. After stirring for 1.5 h, sat.

$NaHCO_3$ (15 mL) was added to quench the reaction and the mixture was allowed to stir for 1 h. After separating the aqueous layer, the organic layer was washed with sat. $NaHCO_3$, H_2O, and sat. NaCl (15 mL each), dried (Mg_2SO_4), filtered, and the filtrate was concentrated to a colorless solid. Flash chromotography (19:1 CH_2Cl_2/Et_2O) of the solid followed by recrystallization from EtOH afforded **8** (0.89 g, 82%) as a fluffy white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 2 H), 7.45 and 6.89 (AA'BB' pattern, *J* = 8.5 Hz, 8 H), 6.53 (d, *J* = 2.0 Hz, 2 H), 6.42 (t, *J* = 2.0 Hz, 1 H), 6.30 (d, *J* = 16.0 Hz, 2 H), 4.48 (s, 2 H), 4.25 (q, *J* = 7.0 Hz, 4 H), 4.17 (t, *J* = 6.0 Hz, 4 H), 4.13 (t, *J* = 6.0 Hz, 4 H), 2.25 (pentet, *J* = 6.0 Hz, 4 H), 1.33 (t, *J* = 7.0 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.3, 160.5, 160.1, 144.1, 139.5, 129.6, 127.3, 115.8, 114.8, 107.3, 101.4, 64.4, 64.3, 60.3, 46.2, 29.1, 14.3; MS (ESI) *m/z* 645.3 ($M+Na^+$), 1266.7 ($2M+Na^+$). Anal. calcd for $C_{35}H_{39}ClO_8$: C, 67.46; H, 6.31. Found: C, 67.31; H, 6.73.

(Ethylcinnamate)$_4$[G2]-OH (9). A mixture of **8** (1.4 g, 2.3 mmol), **6** (154 mg, 1.10 mmol), K_2CO_3 (478 mg, 3.46 mmol), 18-crown-6 (50 mg, 0.19 mmol), and NaI (104 mg, 0.692 mmol) in acetone (50 mL) was maintained at reflux for 25 h under Ar, and then filtered. The filtrate was concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (50 mL), washed with H_2O, sat. NH_4Cl, H_2O, and sat. NaCl (25 mL each), dried (Mg_2SO_4), filtered, and concentrated in vacuo to a colorless foam. Purification of the foam by column chromatography (9:1 CH_2Cl_2/Et_2O) followed by recrystallization in CH_2Cl_2/EtOH afforded **9** (1.3 g, 89 %) as a colorless solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 4 H), 7.43 and 6.88 (AA'BB' pattern, *J* = 9.0 Hz, 16 H), 6.59 (d, *J* = 2.5 Hz, 2 H), 6.56 (d, *J* = 2.5 Hz, 4 H), 6.50 (t, *J* = 2.0 Hz, 1 H), 6.41 (t, *J* = 2.5 Hz, 2 H), 6.28 (d, *J* = 16.0 Hz, 4 H), 4.91 (s, 4 H), 4.62 (d, *J* = 6.0 Hz, 2 H), 4.24 (q, *J* = 7.0 Hz,

8 H), 4.16 (t, *J* = 6.0 Hz, 8 H), 4.13 (t, *J* = 6.0 Hz, 8 H), 2.24 (pentet, *J* = 6.0 Hz, 8 H), 1.82 (t, *J* = 6.0 Hz, 1 H), 1.32 (t, *J* = 7.0 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.3, 160.5, 160.2, 160.0, 144.2, 143.5, 139.2, 129.7, 127.2, 115.7, 114.8, 105.9, 105.6, 101.3, 100.9, 69.9, 65.2, 64.5, 64.3, 60.3, 29.2, 14.3; MS (ESI) *m/z* 1335.5 ($M+Na^+$). Anal. calcd for $C_{77}H_{84}O_{19}$: C, 70.41; H, 6.45. Found: C, 69.97; H, 6.95.

(Ethylcinnamate)$_4$[G2]-Cl (10). A solution of **9** (1.3 g, 0.97 mmol), DMF (5 drops), and CH_2Cl_2 (50 mL) was allowed to stir under Ar at ambient temperature while thionyl chloride (160 mg, 1.4 mmol) was added via syringe. After stirring for 1.5 h, sat. $NaHCO_3$ (30 mL) was added to quench the reaction and the mixture was allowed to stir for 1 h. After separating the aqueous layer, the organic layer was washed with sat. $NaHCO_3$, H_2O, and sat. NaCl (30 mL each), dried (Mg_2SO_4), filtered, and the filtrate was concentrated to a colorless solid. Purification of the solid by column chromotography (SiO_2, dryload, 9:1 CH_2Cl_2/Et_2O) afforded **10** (0.96 g, 74%) as a fluffy colorless solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 4 H), 7.44 and 6.89 (AA'BB' pattern, *J* = 8.5 Hz, 16 H), 6.60 (d, *J* = 2.0 Hz, 2 H), 6.56 (d, *J* = 2.0 Hz, 4 H), 6.53 (t, *J* = 2.0 Hz, 1 H), 6.42 (t, *J* = 2.0 Hz, 2 H), 6.28 (d, *J* = 16.0 Hz, 4 H), 4.93 (s, 4 H), 4.49 (s, 2 H), 4.24 (q, *J* = 7.0 Hz, 8 H), 4.16 (t, *J* = 6.0 Hz, 8 H), 4.14 (t, *J* = 6.0 Hz, 8 H), 2.24 (pentet, *J* = 6.0 Hz, 8 H), 1.57 (s, 1H), 1.32 (t, *J* = 7.0 Hz, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.3, 160.5, 160.2, 159.9, 144.2, 139.6, 139.0, 129.7, 127.3, 115.8, 114.8, 107.6, 105.9, 102.1, 100.9, 70.0, 64.5, 60.3, 46.3, 29.2, 14.3; MS (ESI) *m/z* 1353.4 ($M+Na^+$). Anal. calcd for $C_{77}H_{83}ClO_{18}$: C, 69.44; H, 6.28. Found: C, 69.13; H, 6.60.

Crosslinking experiments:

Thin films of the dendrimers were formed by spin-casting from a 10^{-6} M chloroform solution onto quartz slides. Films were then crosslinked at 315 nm using a 75 W Xe Arc lamp. At certain time intervals, irradiation was discontinued and the UV/Vis spectrum of the film was recorded. After a set period of time, the film was removed from the photolyzer, dipped in a chloroform solution, and then final UV/Vis and photoluminescence measurements were made.

Patterning experiments:

Patterning experiments were performed on thin films by either sandwiching copper TEM grids (ca. 85 μm feature size) between the thin film containing dendrimer and a blank quartz slide. When smaller feature sizes were desired, a Rhonchi ruling (chrome lines on glass, ca. 5 μm lines) was pressed against the dendrimer thin film and irradiation proceeded through the mask and thin film.

Fluorescence microscopy images were acquired with a Nikon Eclipse TE 2000-U microscope using a 10× (N. A. 0.25) objective. A Cascade 512b ICCD camera (Roper Scientific) with the acquisition program Winview/32 (version 2.5, Roper Scientific) was used to capture and process the images.

The AFM used for this study was a Digital Instruments Bioscope, based on a Nanoscope IV, consisting of a Dimension SPM head mounted on a Nikon Eclipse TE 2000-U microscope. Height data was obtained for all of the samples using unmodified MikroMasch DP-18 HiRES probes.

Additional data:

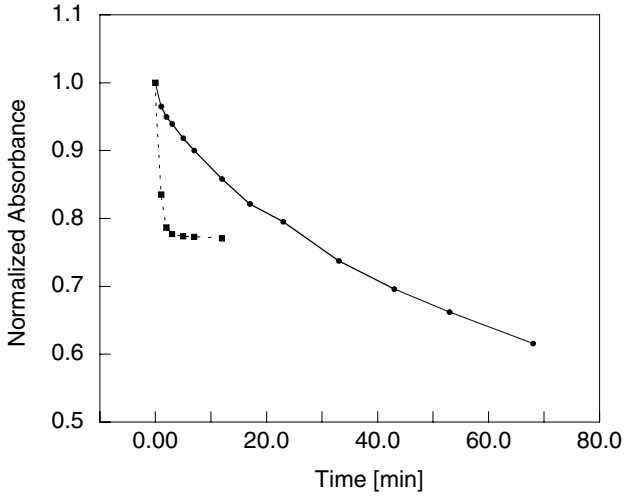


Figure S5. Solution (dashed line) versus thin film (solid line) photolysis of dendrimer **1**.

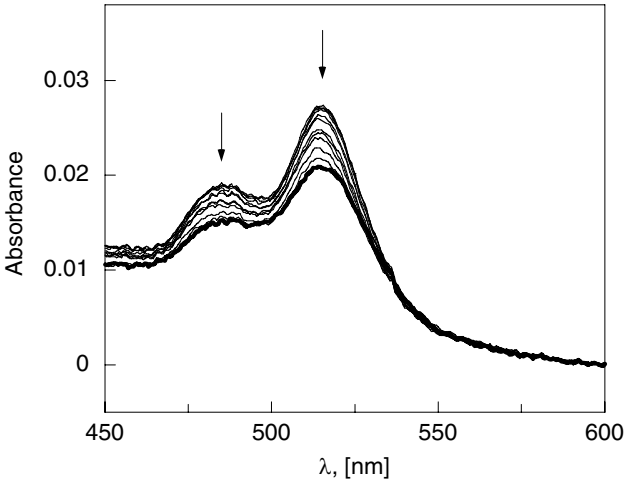


Figure S6. Absorbance monitored during the crosslinking of **2** in the quinacridone region showing ca. 20% degradation of the film during photolysis. The dark line is the spectra measured following wet development.

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] Cernerud, M.; Reina, J. A.; Tegenfeldt, J.; Moberg, C. *Tetrahedron-Asymmetr.* **1996**, *7*, 2863.