Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

2D and 3D Surface Photopatterning via Laser-Promoted Homopolymerization of a Perfluorophenyl Azide-Substituted BODIPY

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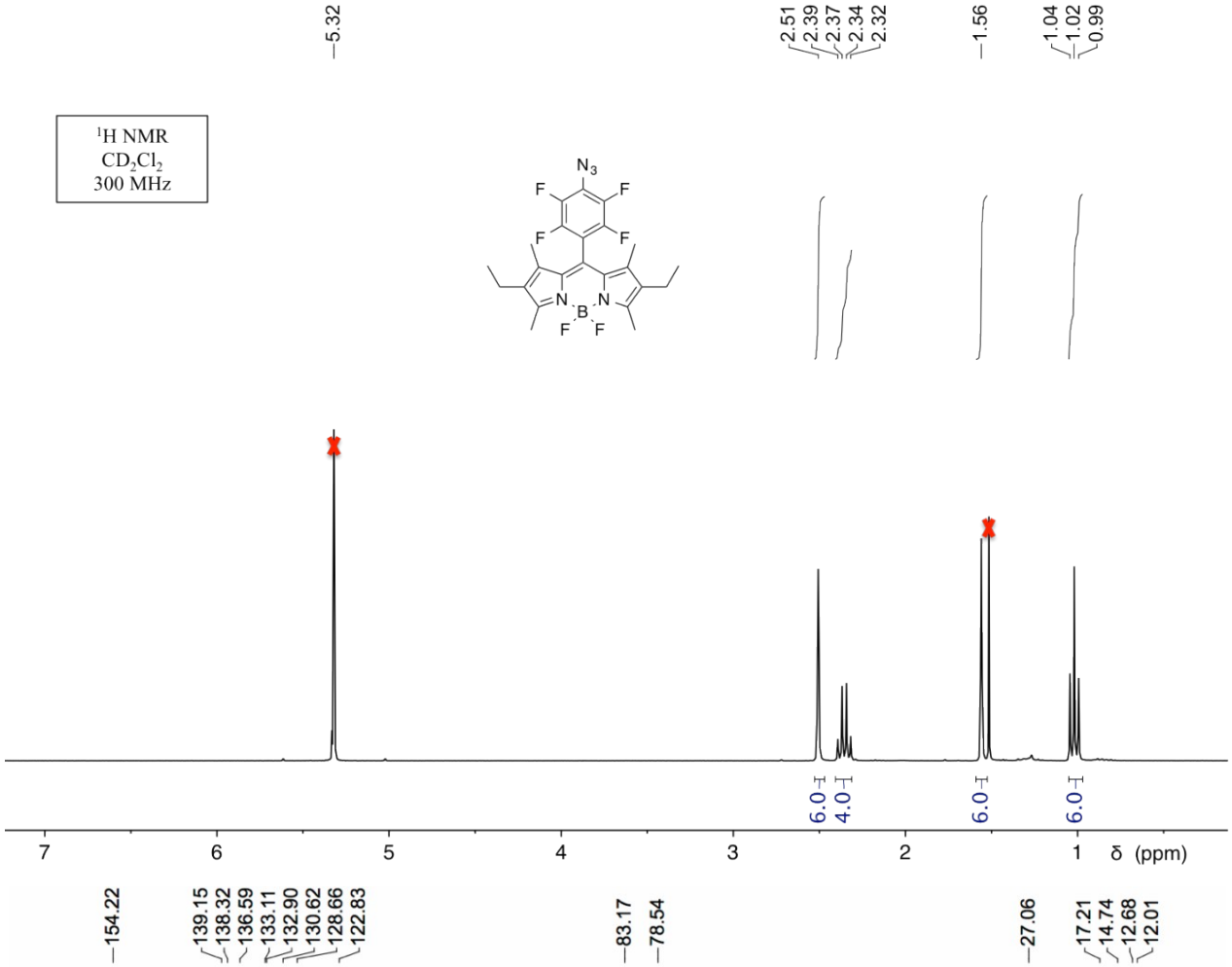
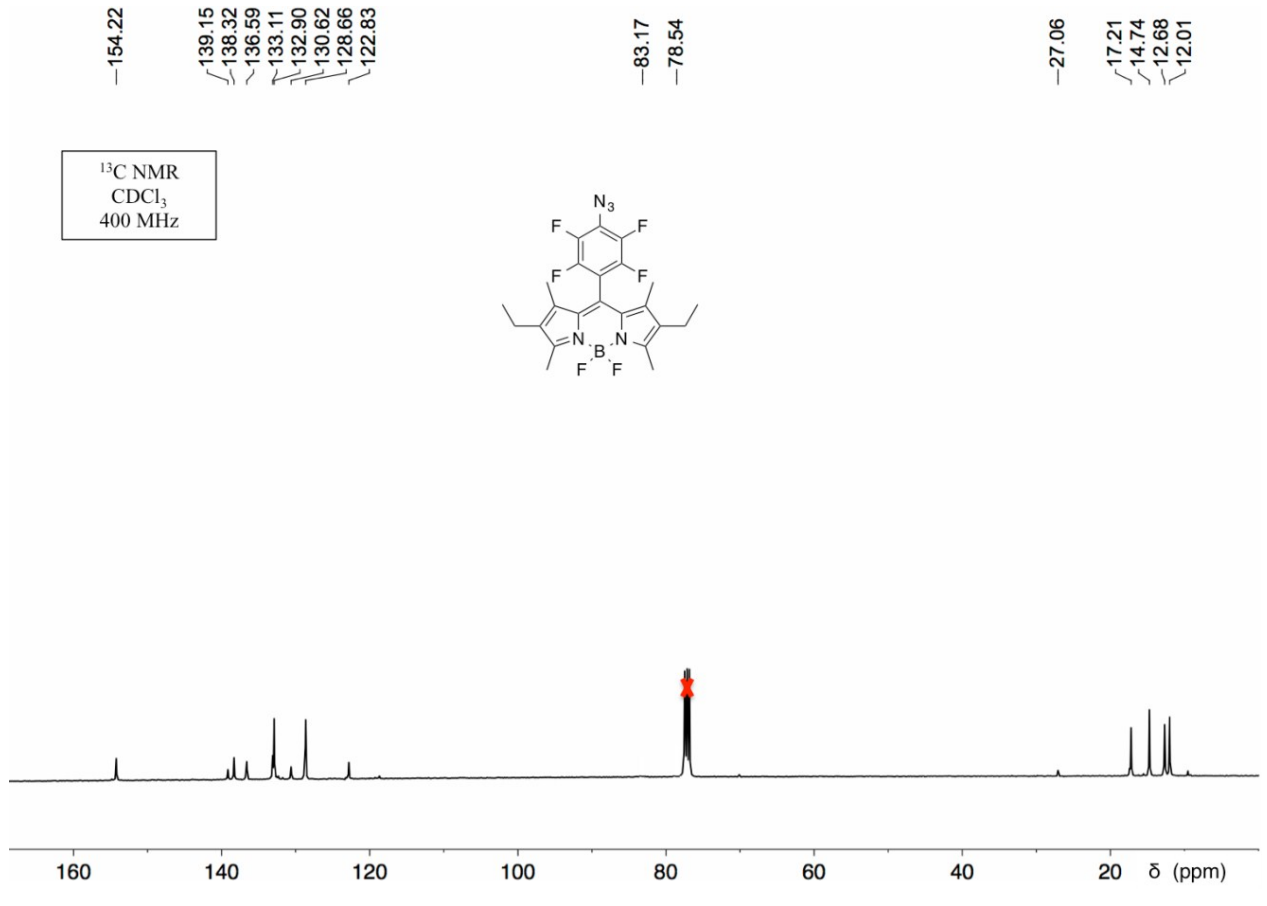
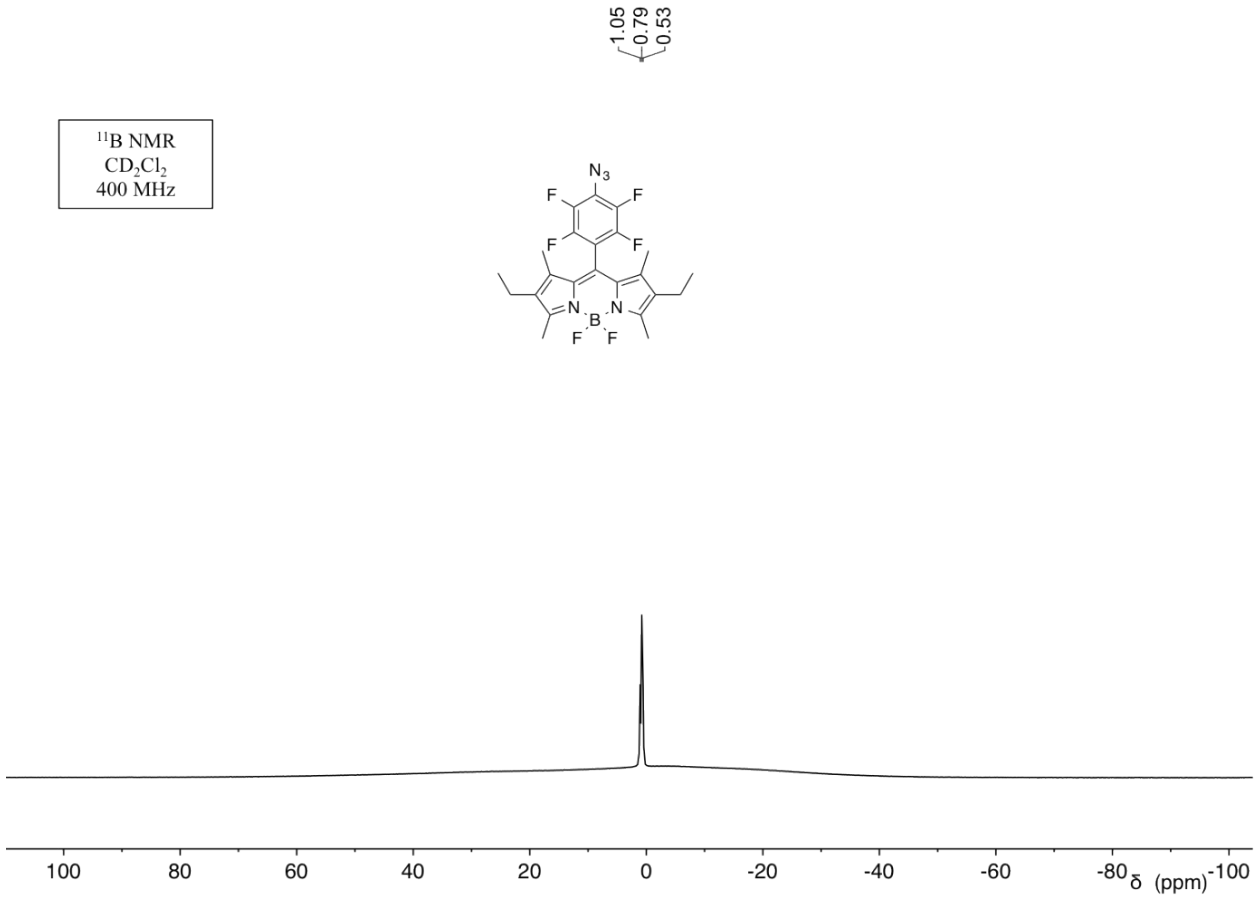
1. NMR spectra for 1

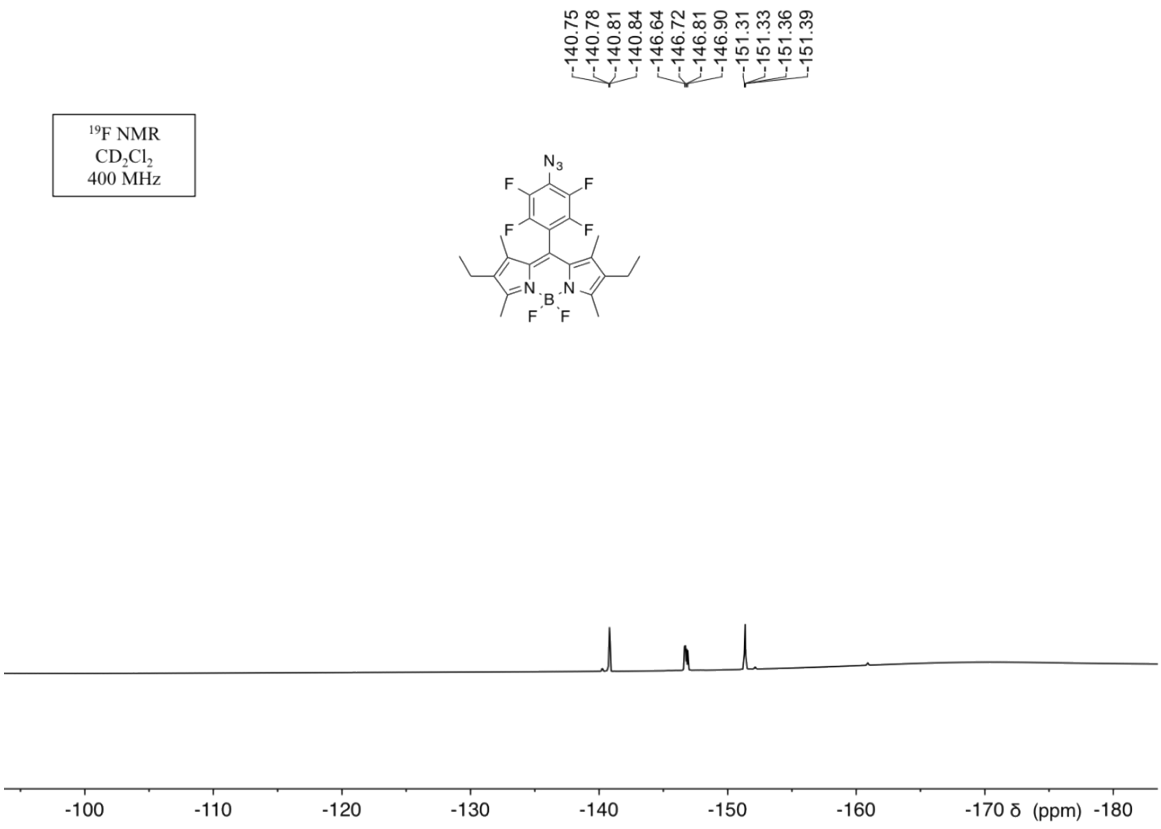




^{11}B NMR
CD_2Cl_2
400 MHz



^{19}F NMR
CD_2Cl_2
400 MHz



2- UV-Vis and fluorescence studies

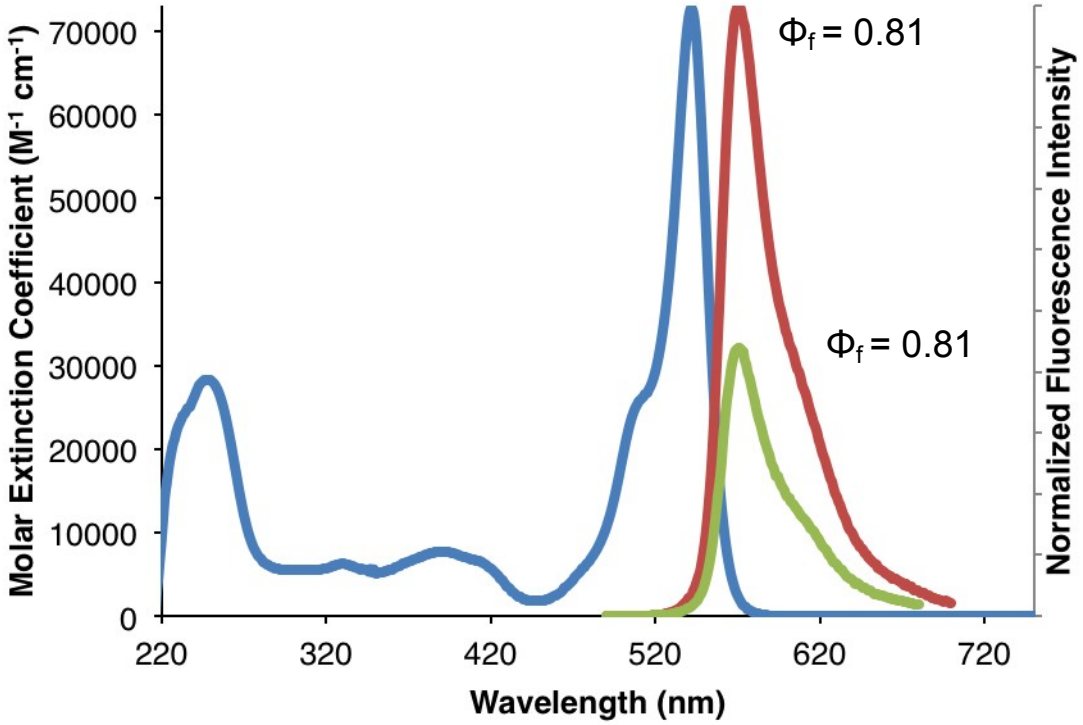


Figure S1. Electronic absorption spectra (blue line), emission spectra with λ_{ex} = 470 nm (red line) and 350 nm (green line) of BODIPY **1** in toluene.

Fluorescence Quantum Yield.

The fluorescence and reaction quantum yield were determined in quartz cells in acetonitrile, were degassed by multiple freeze-pump-thaw cycles and then blowtorch sealed. The luminescence quantum yield [S1] (Φ) of the optically dilute solutions were calculated according to the equation $\Phi = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which Φ_r refers to the quantum yield reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent. Fluorescein ($\Phi_f = 0.95$[S2]) in 0.1 M NaOH (aq.) and the pentafluorophenyl BODIPY synthon ($\Phi_f = 0.99$[S1]) in acetone, were used as the standards.

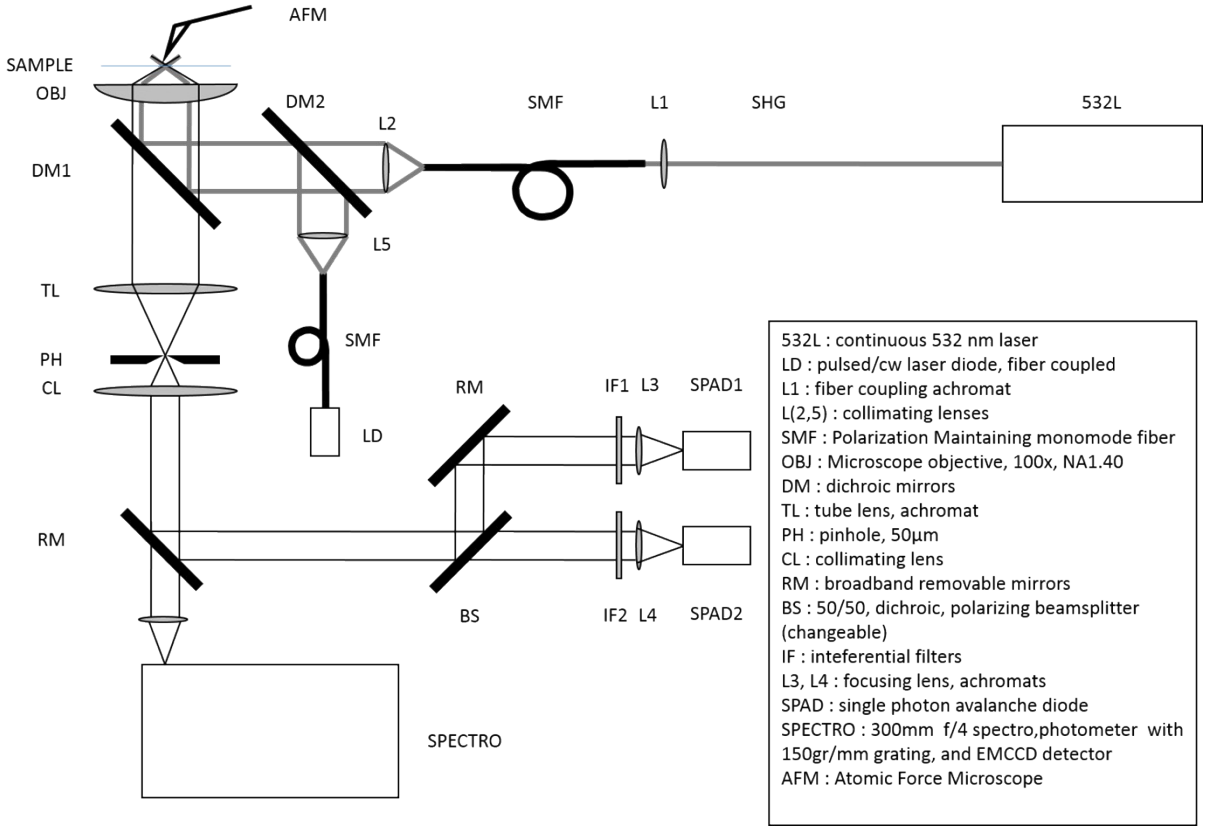
References

[S1] D. E. Eaton, *Handbook of Organic Photochemistry*, Vol 1; Scaiano, J. C., Ed.; CRC : Boca Raton, FL, 1989.

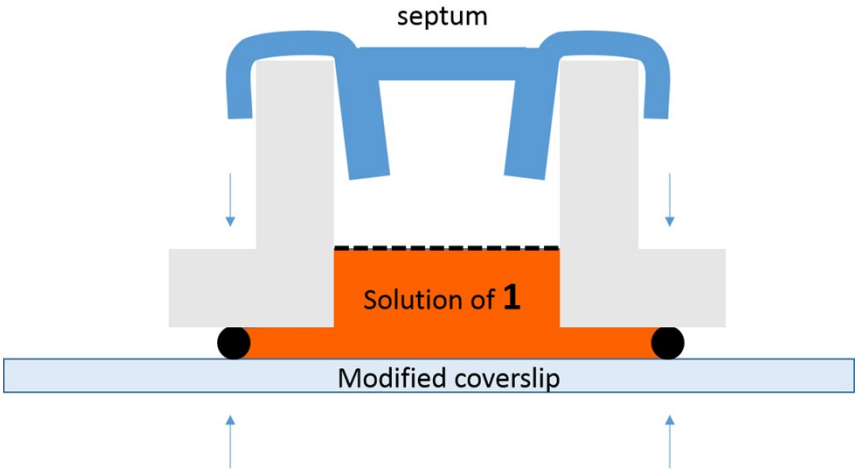
[S2] J. H. Brannon, D. J. Magde, *J. Phys. Chem.* **1978**, *82*, 705.

3. Patterning processes

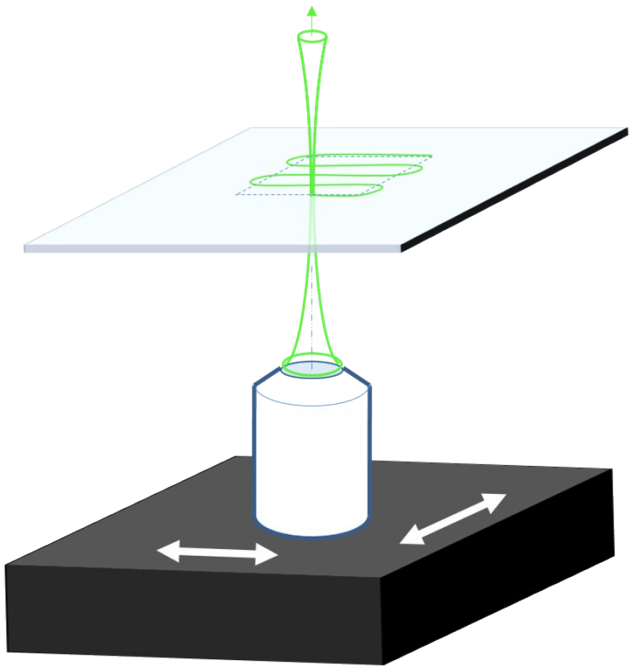
3.1 Microscopy set-up



Scheme S1. Temporally and spectrally-resolved confocal fluorescence microscopy coupled to an atomic force microscopy setup.



Scheme S2. Section view of the sample holder for patterning. The cavity is made of Teflon™, and is pressed mechanically against the seal (represented by the blue arrows). The dashed line represents approximately the level of solution during the process.



Scheme S3. Patterning process.

3.2 Imaging

Confocal microscopy (CFM):

The same confocal microscopy setup (scheme S2) was used to analyze the fluorescent patterns obtained. The pulsed 375 nm laser diode was used as the excitation source. The fluorescence was collected by the objective and transmitted by the 80T/20R beamsplitter before a long-pass filter with 405 nm cutoff wavelength rejected the backscattered excitation light. The light was then focused onto a 50 µm pinhole by a tube lens prior to being diverted either onto Single Photon Avalanche Diodes (SPILLARs) for confocal lifetime imaging, or onto a fiber-coupled emission spectrometer (Andor, SR303i) equipped with an EMCCD camera (Andor, Newton) for confocal hyperspectral imaging. The scanning of the sample was performed by the same piezo stages than for the patterning.

CFM fluorescence intensity normalization:

Due to the fact that a CFM can be operated in varying acquisition conditions, normalization of intensities is necessary for quantitative comparisons. In the context of this article, intensities are normalized according to:

$$I_{norm}(cts.nW^{-1}.s^{-1}). = \frac{pixel\ counts}{imaging\ excitation\ power\ \times\ integration\ (=pixel)\ time}$$

Lifetimes measurements:

For the FLIM images, the rainbow color-scale is applied to an average lifetime calculated by a "FastFLIM" algorithm, defined as the barycenter (i.e the weighted average arrival time of the photons) of the TCSPC decay curve corresponding to a pixel, minus an arbitrary zero-time, defined as the time of highest derivative (steepest increase) in the onset of the decay curve corresponding to the overall image:

$$\tau_{avg} = \frac{\sum_{i=0}^{n}(t_i \cdot y_i)}{\sum_{i=0}^{n}(y_i)} - \max_{t_0 \geq t \geq t_n}\left(\frac{\delta y}{\delta t}\right) \quad (1)$$

Where n is the number of TCSPC channels, y_i is the number of photons counted in the channel i and t_i is the time of channel i.

For lifetimes shown in table 1 and of **1** in solution, the reported average lifetime results from fittings of the decay curves to multi-exponential models with IRF (Instrumental Response Function) reconvolution, according to the equations:

$$y(t) = irf(t) \otimes \sum_{i=0}^{m \leq 4}\left(A_i \cdot e^{-t/\tau_i}\right) + bkg \quad (2)$$

$$\tau_{int} = \frac{\sum_{i=0}^{m}\left(A_i \cdot {\tau_i}^2\right)}{\sum_{i=0}^{m}(A_i \cdot \tau_i)} \quad (3)$$

Where the parameter i denotes this time the term number in the multi-exponential model, and irf(t) is the instrumental response function measured by a reconstruction algorithm (PicoQuant© SymPhoTime© software) from a decay recorded from **1** in diluted (10^{-6} M) solution.

Atomic Force Microscopy (AFM)

An Asylum MFP3D bio AFM was coupled to the IX71 inverted optical microscope so that the tip apex could be visualized through the coverslip which allowed to retrieve and target the patterns. The AFM

consisted in a head holding the tip and driving it in the vertical (Z) direction while a piezo (XY) stage held the coverslip. It was operated in alternative contact mode with a soft cantilever (OMCL-AC240TS ; spring constant k = 2 N/m ; resonance frequency f = 70kHz ; tip radius = 7 nm)

4. Characterization of the patterns

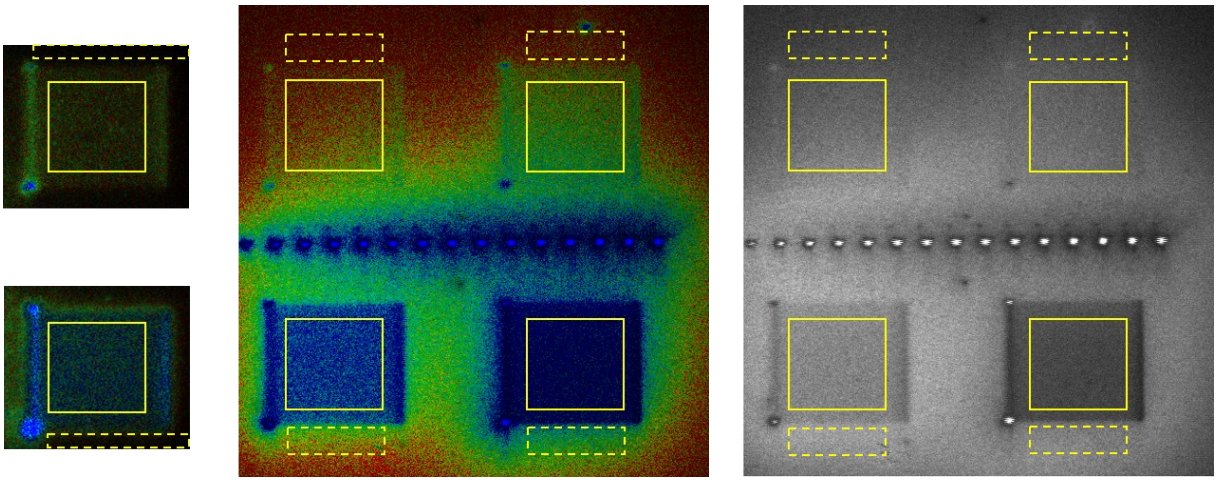


Figure S2: ROIs used for the lifetime and intensity analyses. Left: patterns of Figure 2 in the article. Center and right: patterns of Figure1.

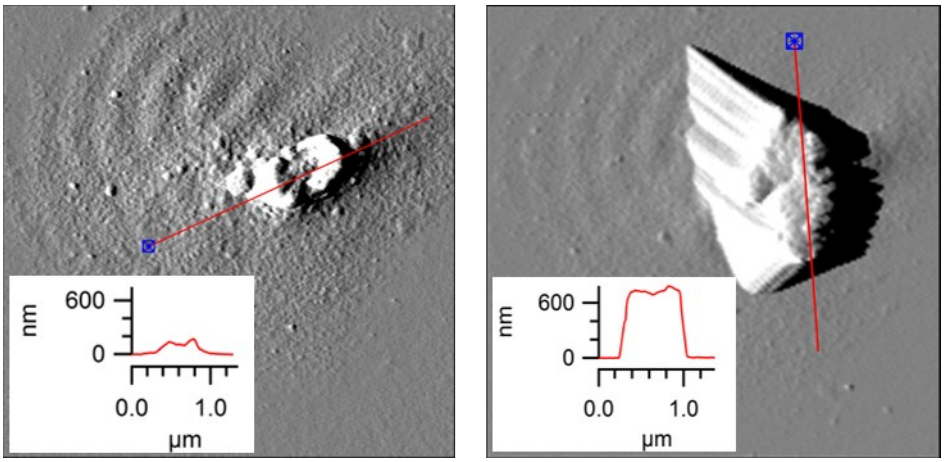


Figure S3. AFM amplitude images of pillars patterned from a 50 mM solution of **1** in toluene on a PEG-coated glass coverslip. Left: 3 s irradiation; right: 14 s irradiation (reproduction of Figure 1c).

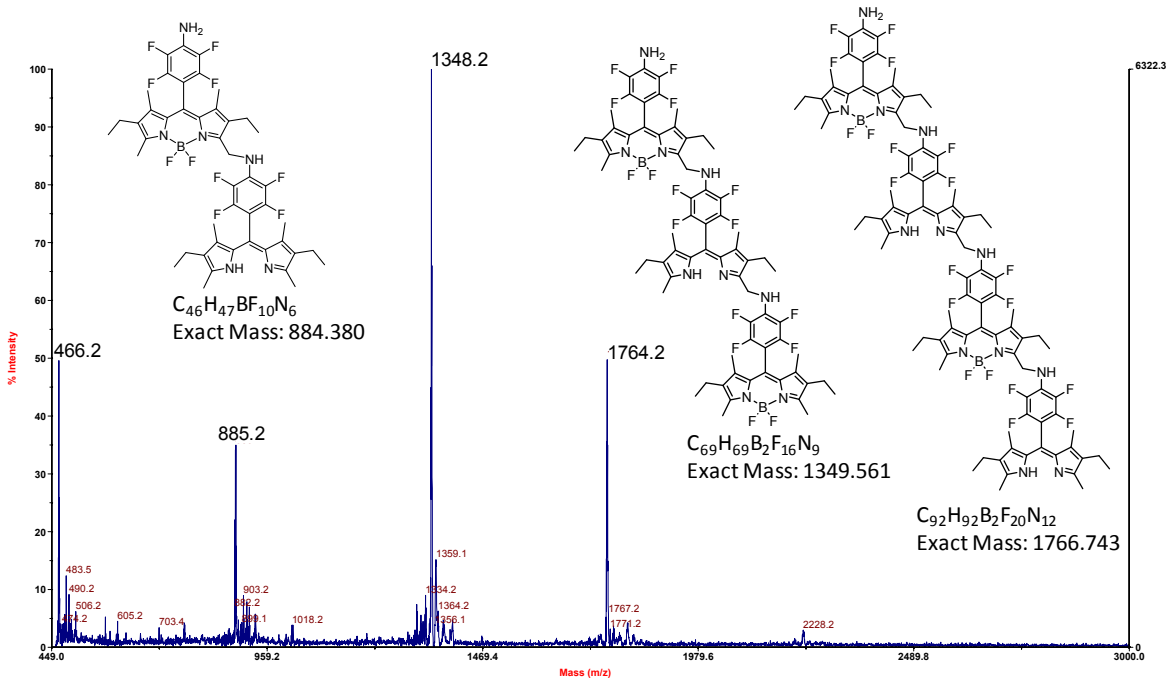


Figure S4. MALDI-TOF spectrum (DCTB matrix) of a solution of **1** in CD_2Cl_2 (0.5 mL in a NMR tube, 10 mM) after irradiation for 18 h at 320-390 nm with a low pressure Hg lamp (Type TLC, 365 nm, 6W) placed at ~ 20 cm of the tube. Tentative structures of the oligomers, among other possible ones, that were formed.

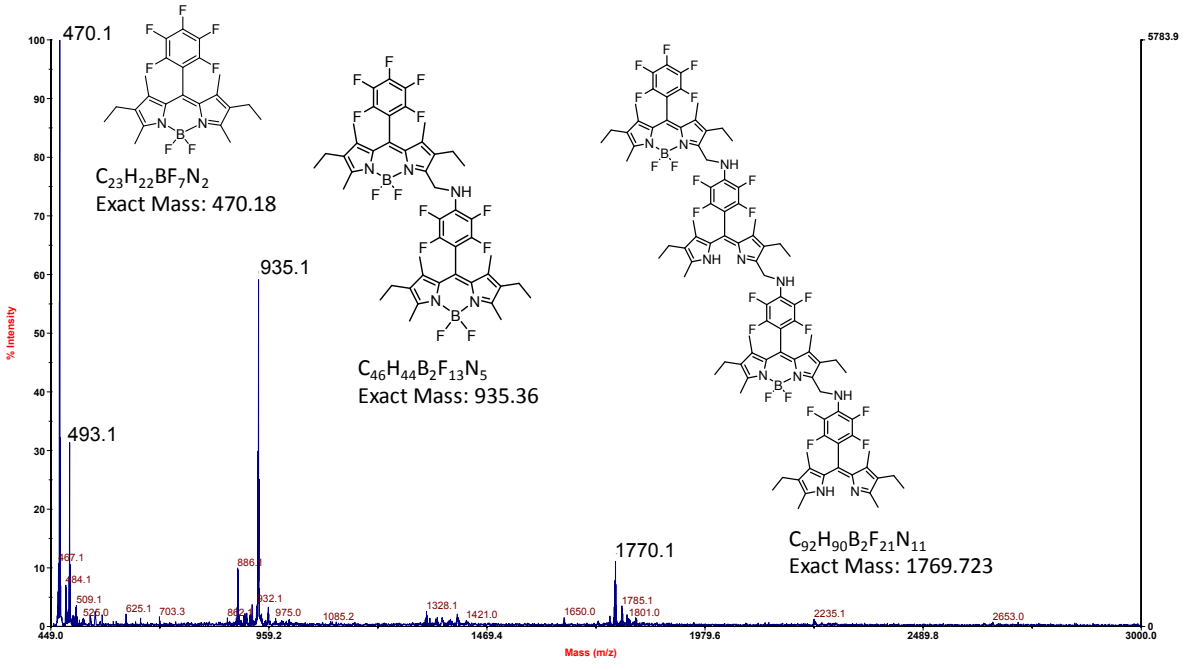


Figure S5. MALDI-TOF spectrum (DCTB + Na matrix) of a mixture of **1** and **2** in CD_2Cl_2 (0.5 mL in a NMR tube,10 mM each) after irradiation for 12 h at 320-390 nm with a low pressure Hg lamp (Type TLC, 365 nm, 6W) placed at ~ 20 cm of the tube. Tentative structures of the oligomers, among other possible ones, that were formed.

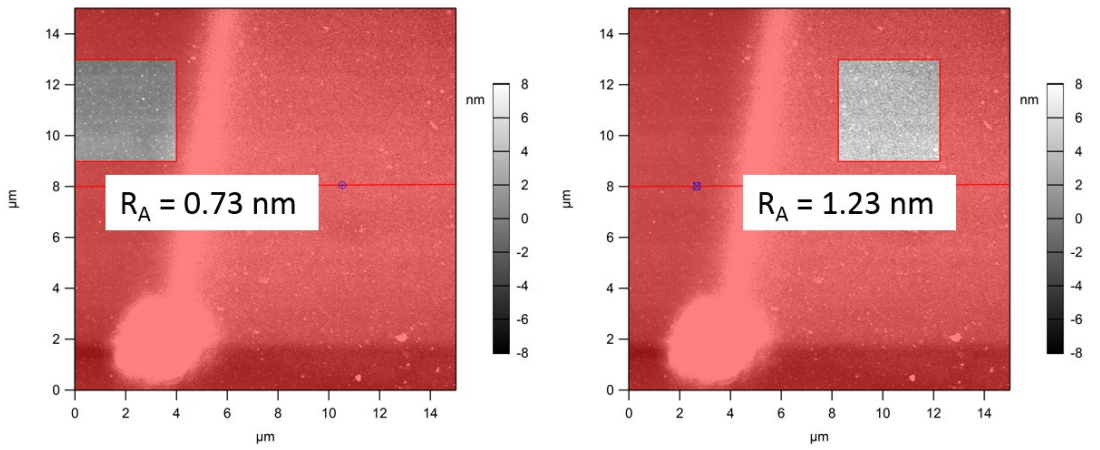


Figure S6. AFM height images of bottom square pattern of Figure 2a showing the ROIs considered for the roughness analysis. R_A is the arithmetic average roughness.

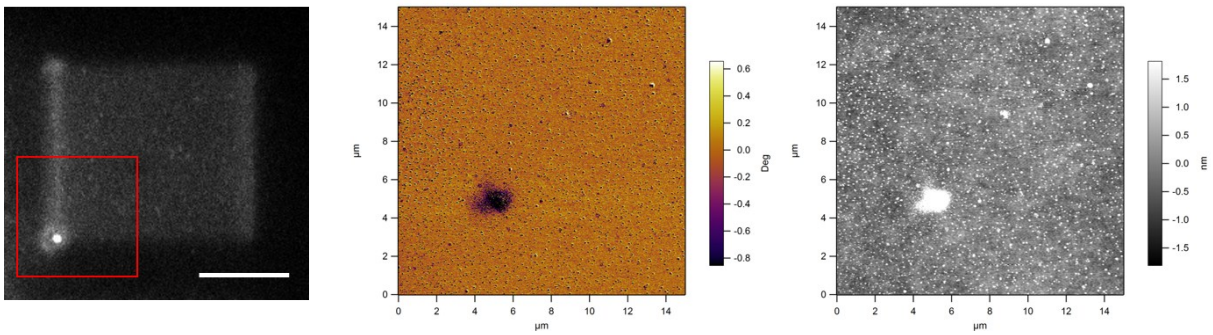


Figure S7. Left: fluorescence intensity, reproduction of the upper image of Figure 2a, i.e. the square patterned at 0.89 µW, showing the area analyzed by AFM (red square); scale bar = 10 µm. Phase (center) and topography (right) AFM images, where the only detectable feature is the brighter corner due to the laser kept fixed for seconds at the end of the patterning procedure (see section 3.3).

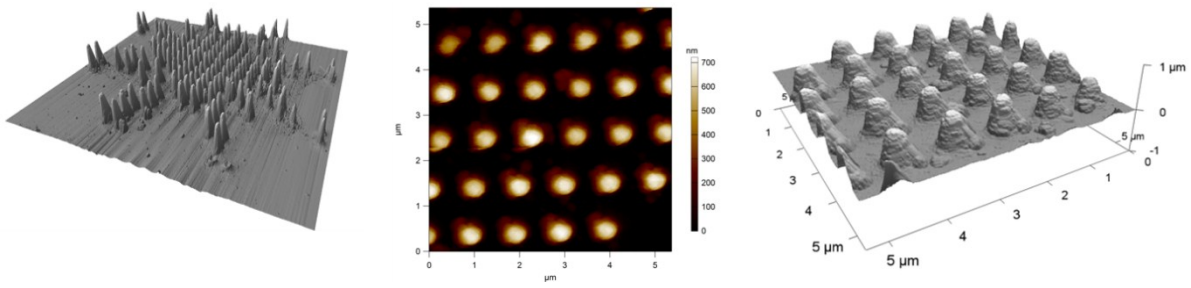


Figure S8. AFM pillars height analysis of the patterned sun figure. Left: 3D representation of the AFM topography image of the entire sun pattern. Center: AFM zoom on the central region, topography image, and, right: corresponding 3D representation.