'From the Mole to the Molecule': Ruthenium Catalyzed Nitroarene Reduction Studied with 'Bench', High-Throughput and Single Molecule Fluorescence Techniques

by

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S1. Caracterization of the catalysts

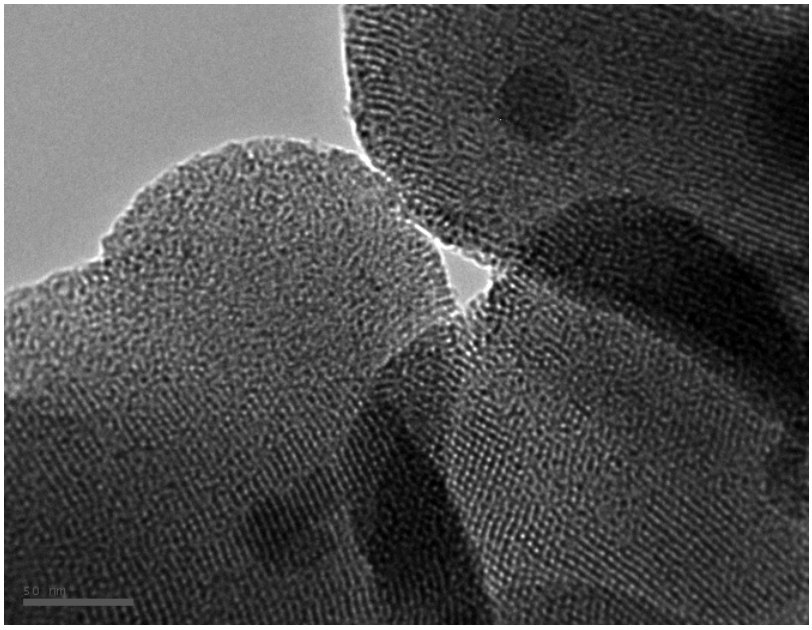


Figure S1 TEM image of Ru@MCM (size bar is 50 nm)

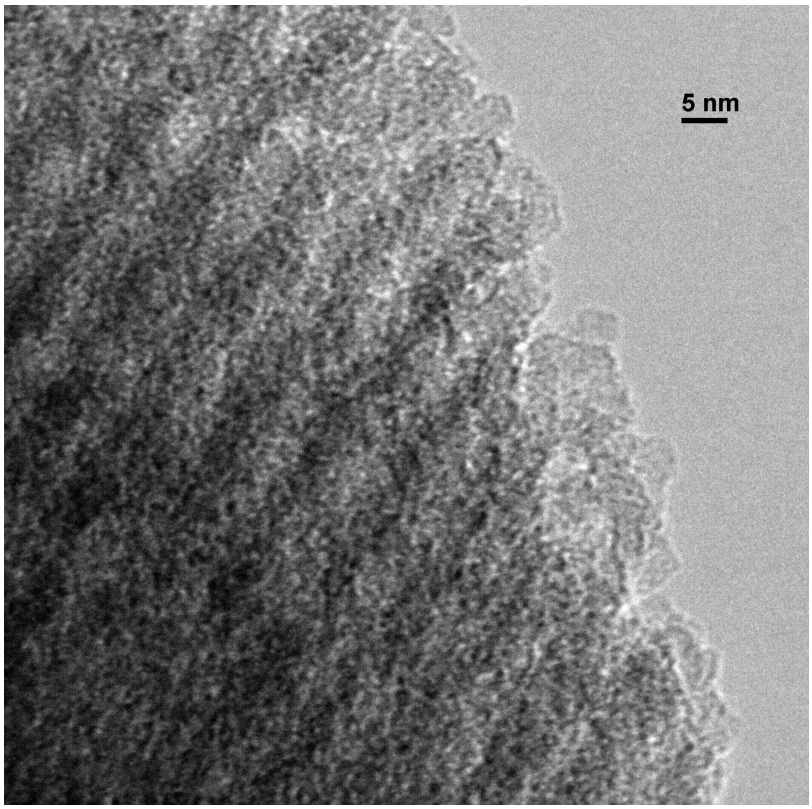


Figure S2 TEM image of Ru@SBA

Table S1. Structural properties of the catalysts

Sample	$A_{BET}(m^2/g)$	$V_p(cc/g)$
MCM-41	995	1.1
Ru@MCM	740	0.7
SBA-15	785	1.2
Ru@SBA	430	0.8

S2. High-throughput reactions

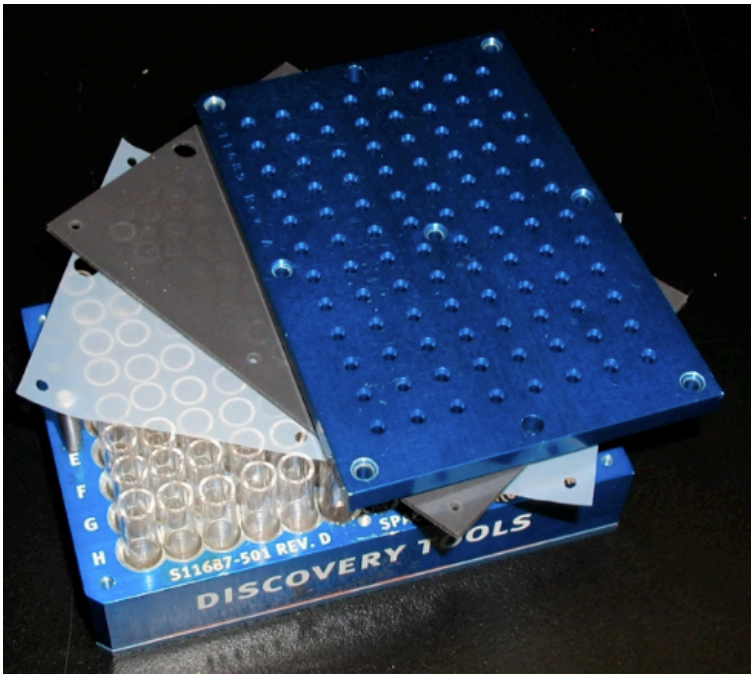


Figure S3 Screening plate containing 96 vials.

Figure S4 High-throughput facility during the addition of the reactants.

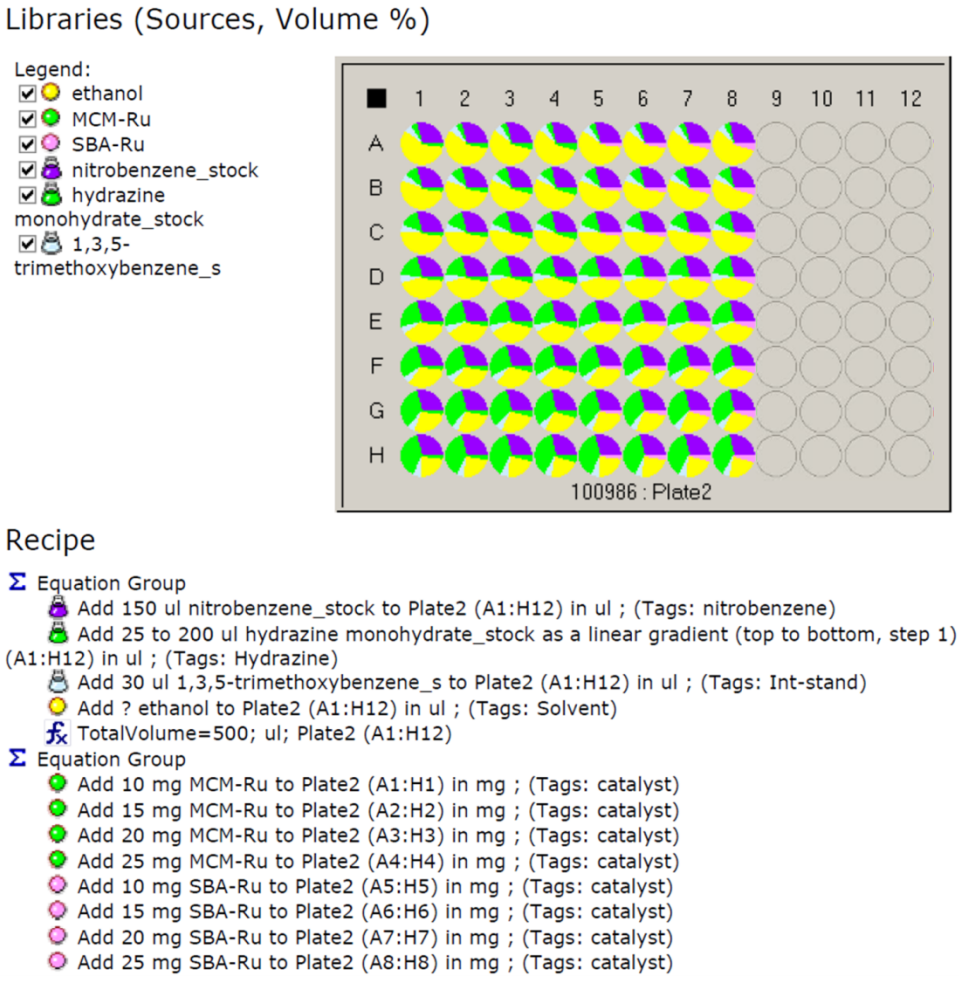


Figure S5 Screening plate to test the catalytic activity of the different materials as a function of the amount of catalyst and hydrazine in the reduction of nitrobenzene.

S3. UV-Vis Absorption and Emission Spectroscopy:

Absorbance and emission spectra of NN-1 and AN-2 are shown in the main text. It is important to note that these are spectra of a dilution of each and not directly the reaction mixtures. The dilution was used so that both the starting material and products were not at high enough concentrations to affect the emission measurements. At this dilution the solutions have matched absorbance at 406.5 nm, which was used as the excitation wavelength in emission experiments to ensure equal excitation of both compounds. Under 406.5 nm excitation the emission spectra of NN-1 and AN-2 were recorded as shown. The maximum counts in emission were not only red shifted, but were 7x higher for AN-2 than NN-1. For this reason reaction solutions became brighter upon excitation during the reaction. For completion, the lifetime of NN-1 and AN-2 were also recorded and are shown below. The data fit well first order kinetics for the first 90% of the decay traces with lifetimes of 11.0 and 9.7 ns for NN-1 and AN-2, respectively.

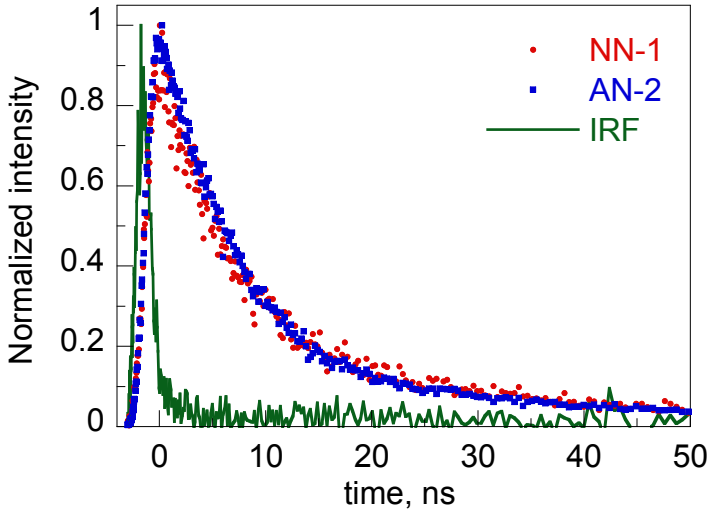
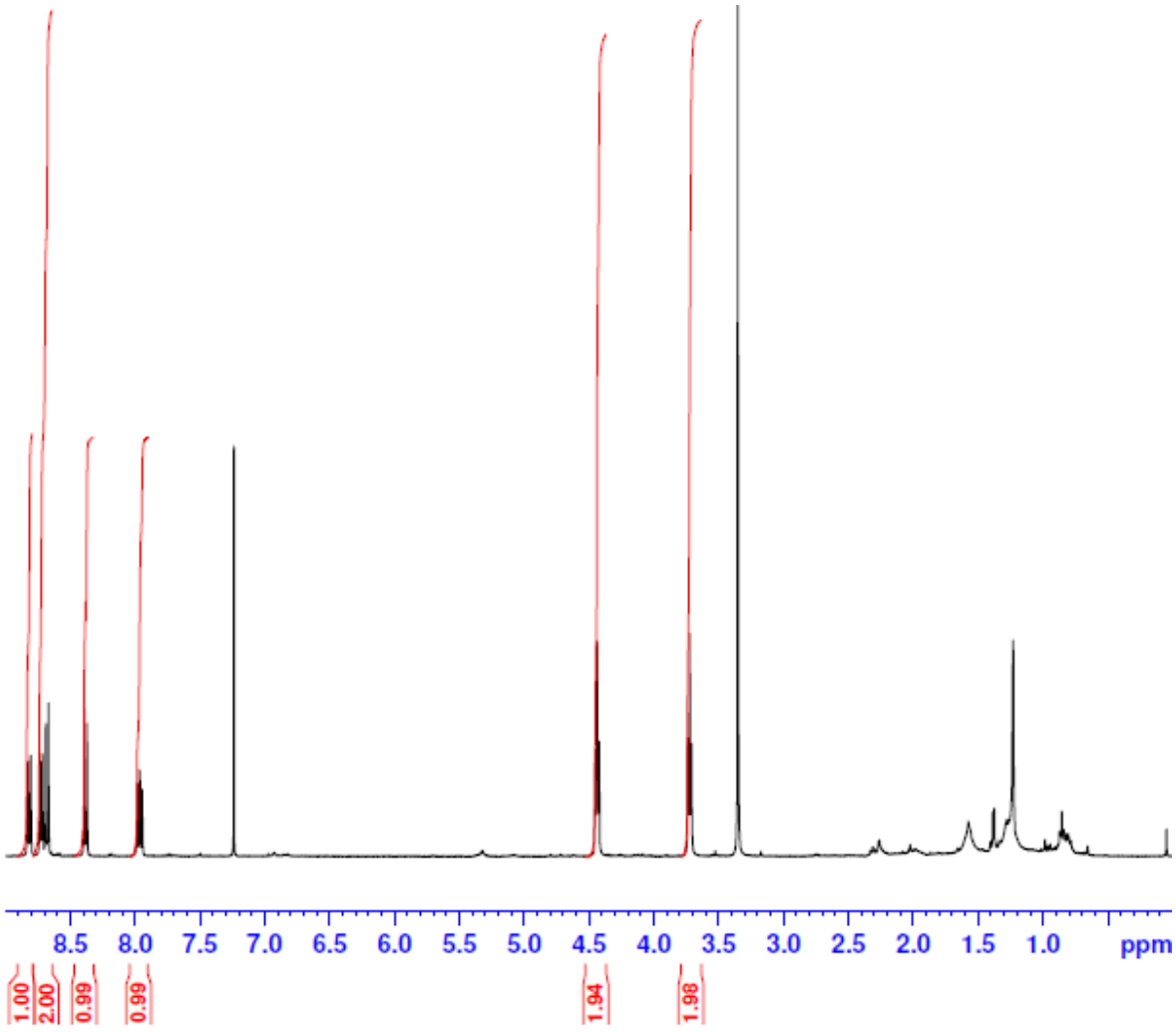


Figure S6 Emission decay traces obtained upon excitation (λ_{exc} = 425 nm) of methanolic solutions of NN-1 (recorded at 485 nm) and AN-2 (recorded at 525 nm) under air. Lamp profile is also included.

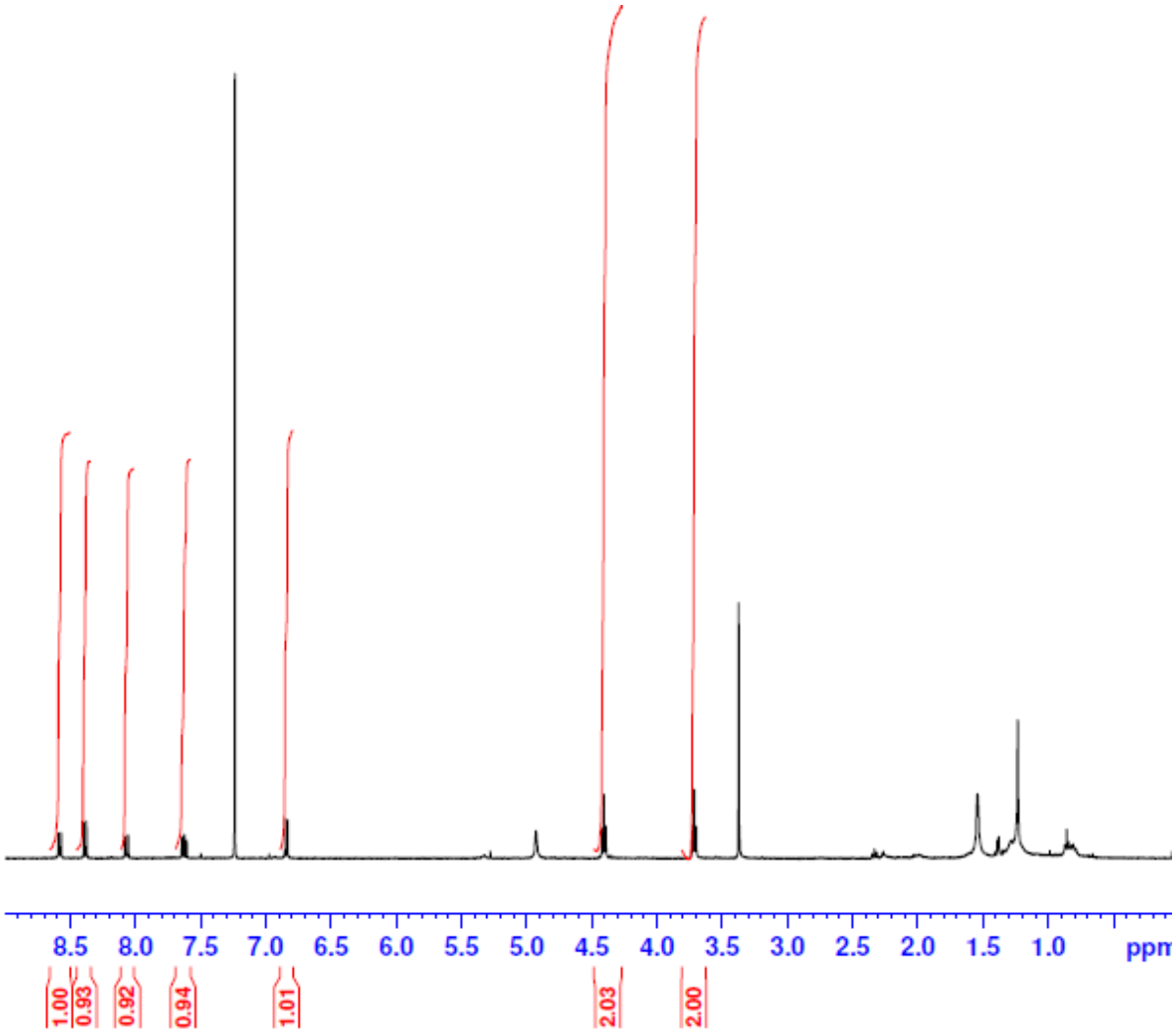
S4. NMR Spectroscopy:

In order to determine the identity as well as quantify the conversion of the reaction in scheme 1, 1H NMR spectra of **NN-1** as well as reaction solutions were obtained. The spectra are shown here with relevant hydrogen atom lines indicated.

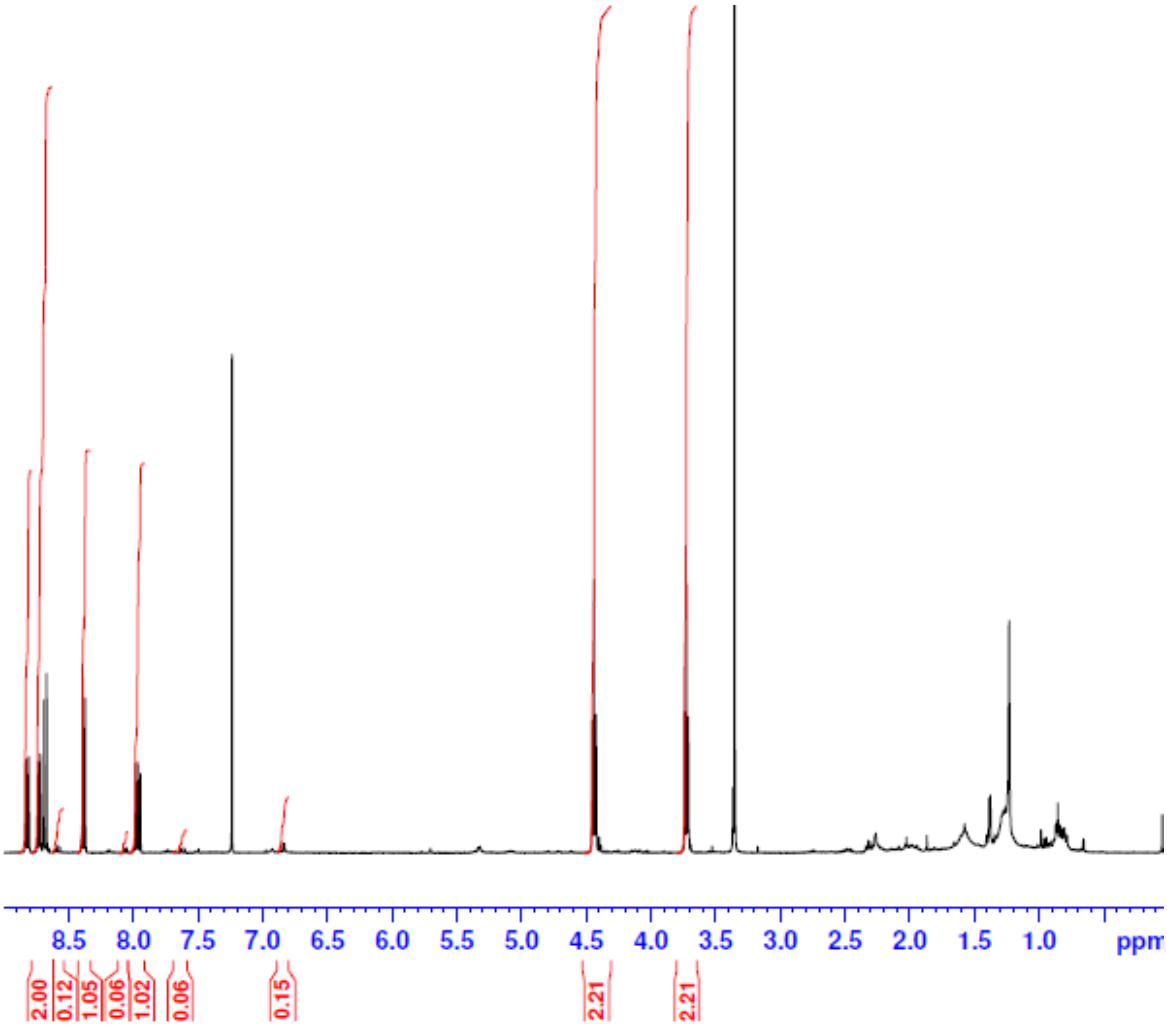
^{1}H NMR Spectrum of NN-1 Alone:



^{1}H NMR Spectrum of Reaction Solution After 100 % Conversion of NN-1 to AN-2:



^{1}H NMR Spectrum of Reaction Solution after *ca.* 6 % Conversion of NN-1 to AN-2 with a H_2 Atmosphere Over the Ru/SBA Catalyst (entry 4, Table 2):



S5. Single Molecule Imaging:

White light, TIRF and FLIM images of the products are reported in the main text. Here we show that similar data was obtained with 375 nm excitation to selectively excite the starting material; top left – white light image, top right – TIRF image, bottom left – FLIM image and bottom right – comparative FCS traces of the solution and catalyst spots as indicated. The FCS curves shown here have a lower signal to noise than the final product due to the lower quantum yield of emission of the starting material. However, it is clear that the starting material has a much longer diffusion time in catalyst spots than the SM freely diffusing.

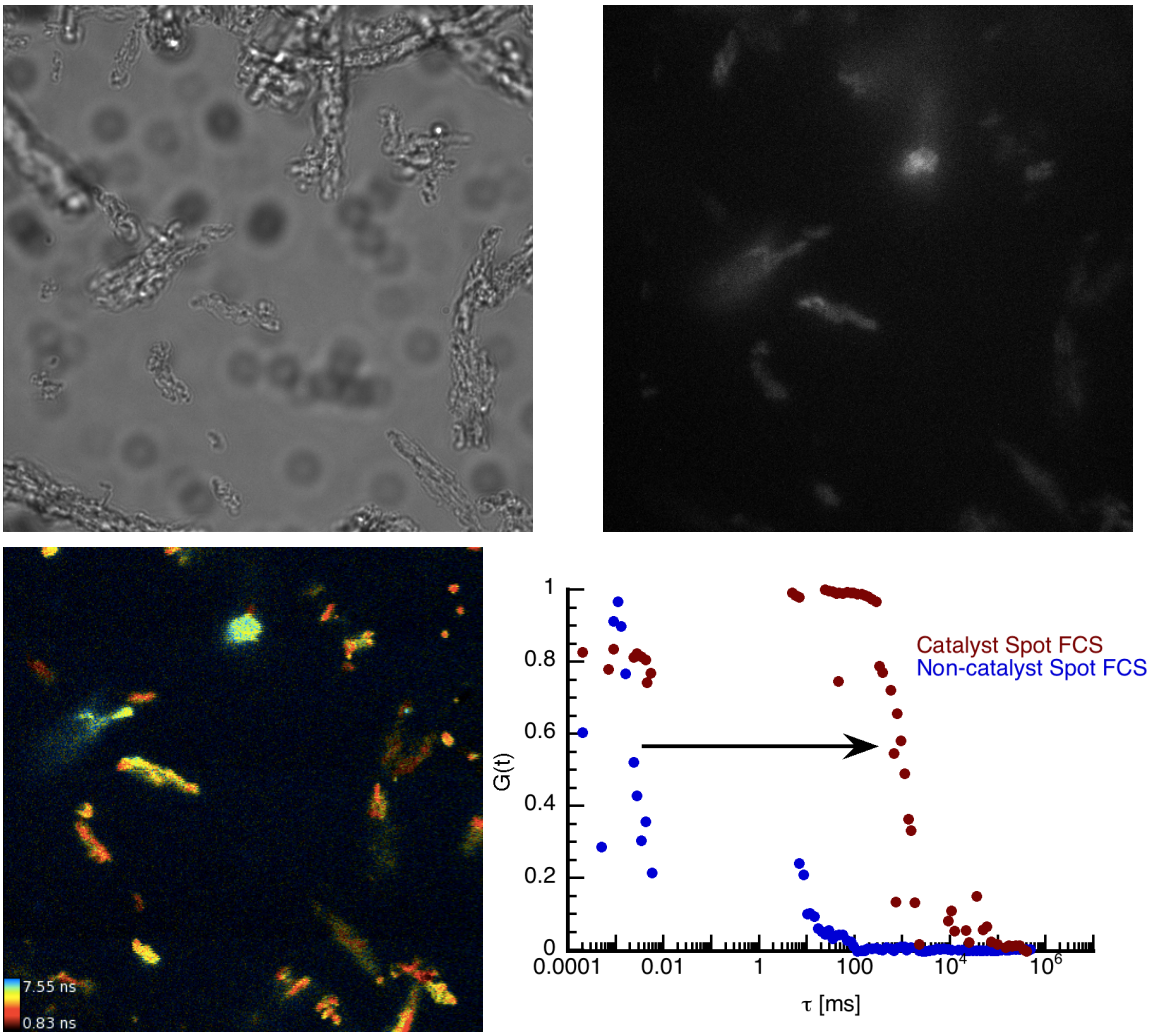


Figure S7 Images of the same region of catalyst during the reduction of NN-1 to AN-2, top left: white light image, top right: TIRF image, bottom left: FLIM image. Bottom right: representative FCS traces of catalyst and non-catalyst spots upon 375 nm excitation.

S6. TIRF Videos

The TIRF image in the top right of Figure S5 is a single frame, but the images can be taken in sequence as 'movies' as described below.

The videos show fluctuations in light intensity at the position of the catalyst, which are consistent with the proposed mechanism where NN-1 is reduced to AN-2 at the catalyst. The product has an increased emission quantum yield and is more excitable (higher absorbance) at 480 nm (imaging excitation wavelength), and therefore, appears brighter when compared with the starting material.

Video A. Movie of the reaction of NN-1 at room temperature, where increased light intensity corresponds to AN-2 emission, imaged with TIRF microscopy using 480 nm excitation and corresponding the same location and 50 seconds time as in Figure 6.

Video B. Same conditions as in Video A, but showing a separate section of the sample.

Note: Videos are of the .AVI type and are available as separate files. They have been compressed so that they only use about 1Mb each. An appropriate player compatible with AVI videos is required.

References

1) A. Carrillo, L. Schmidt, M. L. Marin and J. C. Scaiano, Catal. Sci. Tech., 2014, 4, 435.