Electronic Supplementary Information

Photo-controlled growth of dendrimer-based nanoparticles

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Contents

General Methods and Experimental procedures

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100MHz respectively using a Brüker AMX400 in $CDCl_3$ referenced to the solvent for both proton and carbon spectra. Elemental analyses (EA) were performed using a Thermofinnigan Flash EA 112 Series. Spectroscopic experiments were carried out in HPLC grade acetonitrile. UV/Vis absorption spectra were recorded in a Cary 100 spectrophotometer. Irradiations were carried out in degassed chloroform using a 200 W Xe/Hg Arc lamp coupled with a ThorLabs UG11 Colored Glass UV-Passing Filter, 275 - 375 or a Horiba Jobin Yvon H10 UV monochromator. Lamp light fluxes were determined by chemical actinometry using the classical ferrioxalate actinometer.[1] Photochemical quantum yields were determined by ^{1}H NMR spectroscopy for concentrated chloroform solutions and by UV-Vis spectroscopy for dilute solutions. Values were determined at conversion rates below 5%.

AFM images were acquired on an AFM Workshop TT-AFM instrument using vibrating mode in air. Samples were prepared by depositing 20 µL of an irradiated chloroform solution onto a freshly cleaved mica lamella which was dried overnight under reduced pressure.

For SEM imaging, a solution of **3** (1.5 mM) was irradiated for 180 min and centrifuged for 60 minutes at 12500 x g. The obtained pellet was, washed, dried under vacuum and deposited in silicon wafer substrate.

Synthesis

Coumarin tripodal chrompohore – Tris(2-(coumarin-3-amide)ethyl)amine (3)

To a stirred solution of 2 g (10.5 mmol) of coumarin-3-carboxylic acid (**1**) in dry chloroform, 2.5 g (21 mmol) of thionyl chloride were added dropwise for 5 min. The resulting mixture was refluxed for 12 hours. After cooling down to room temperature, dichloromethane (150 mL) was added and the solution was washed with water (20 mL) until no detection of gas evolution. The organic phase was then washed with 1% $NaHCO_3$ and dried with anhydrous $MgSO_4$. The solvent was removed by rotatory evaporation to yield 2 g (90%) of acyl chloride derivative **2** as a pale-yellow solid, which was used in subsequent reactions without purification.

To a solution of 2 g (9.5 mmol) of acyl chloride **2** in dry dichloromethane, 0.44 g (3 mmol) of dry tris(2-aminoethyl)amine and 1.38 g (10 mmol) of anhydrous potassium carbonate were added. The resulting mixture was refluxed while stirring for 12 hours. After cooling down to room temperature, the white solid was filtered off. The filtrate was diluted with 150 mL dichloromethane, washed with saturated $NaHCO_3$ and brine and dried with anhydrous $MgSO_4$. The organic phase was concentrated by rotatory evaporation and petroleum ether was added. The resulting precipitate was filtered off and washed with cold diethyl ether. The solid was dissolved in chloroform and reprecipitated through vapour diffusion of diethyl ether to yield 1.9 g (95%) of compound **3** as a pale yellow solid.

^{1}H NMR ($CDCl_3$) δ (ppm): 8.97 (m, 3H), 8.75 (s, 3H), 7.61-7.54 (m, 6H), 7.31 (t, J = 7.46 Hz, 3H), 7.10 (d, J = 8.32 Hz, 3H), 3.62-3.57 (m, 6H), 2.86 (t, J = 5.56 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm):

161.7, 161.0, 154.3, 147.5, 133.4, 129.7, 124.9, 119.0, 118.7, 116.4, 53.2, 38.2. EA calculated for $C_{36}H_{30}N_4O_9$: C 65.25; H 4.56; N 8.46; found: C 64.93; H 4.28; N 8.32.

NMR Spectra

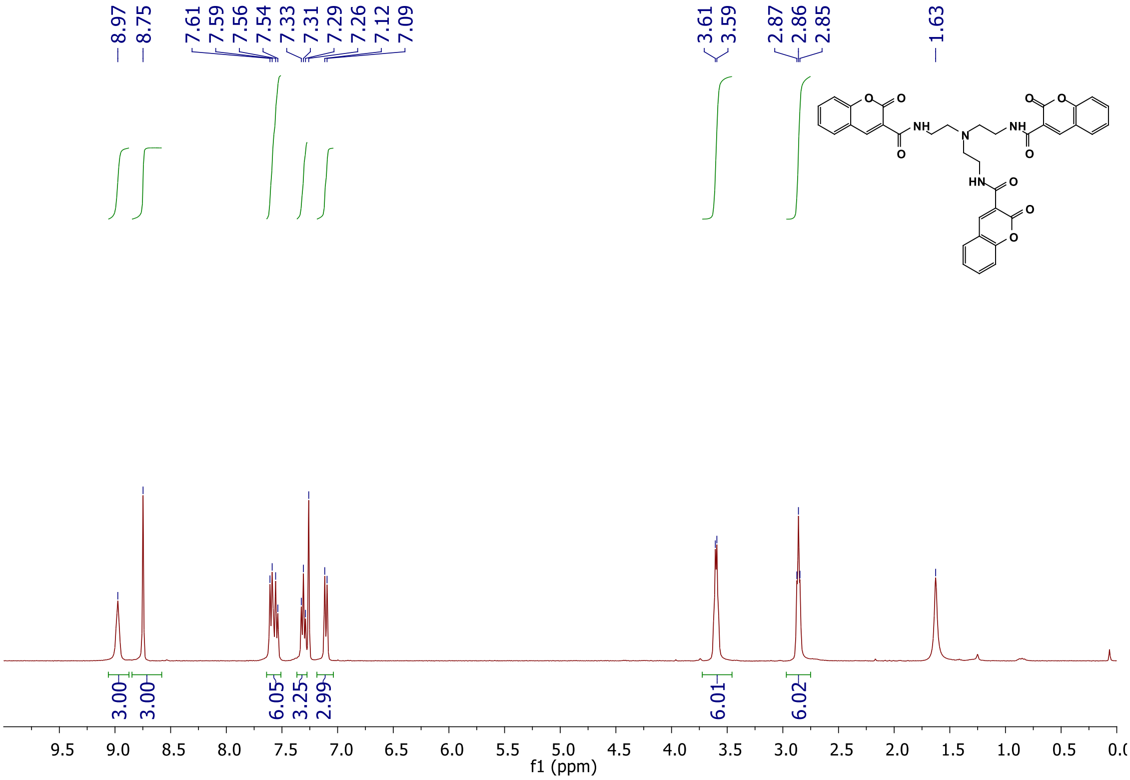

Fig. S1 – ^{1}H NMR spectrum of compound **3** in CDCl3

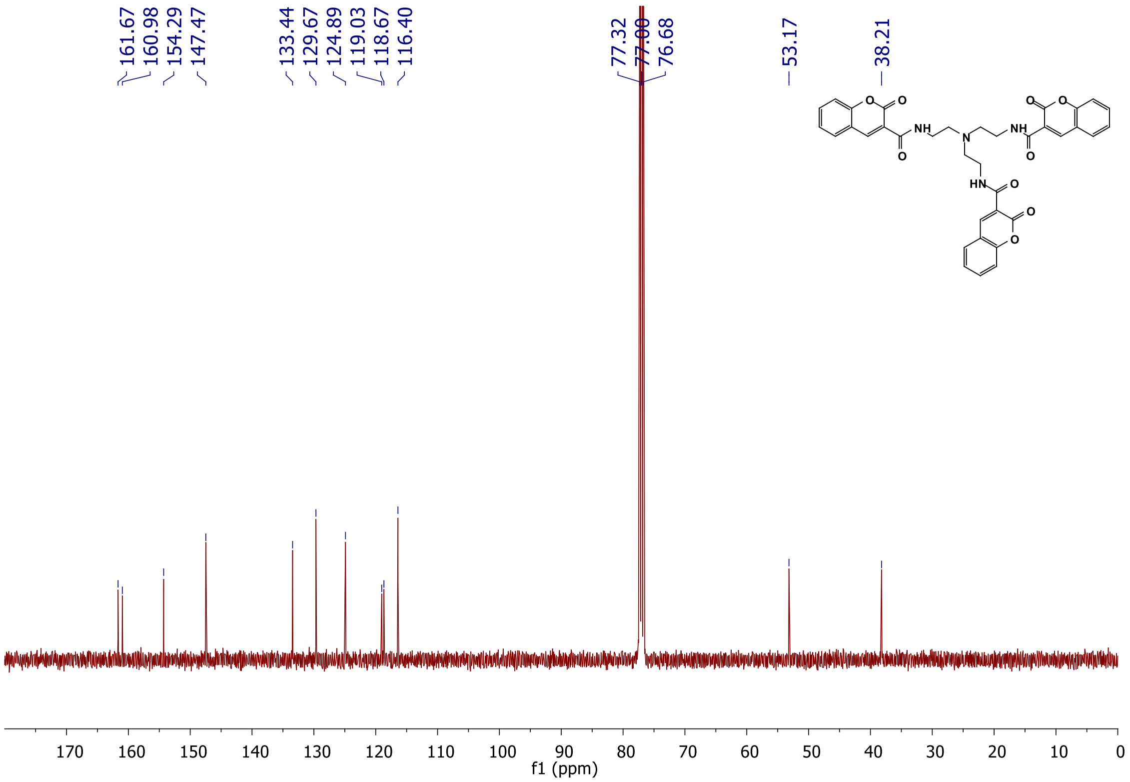

Fig. S2 – ^{13}C NMR spectrum of compound **3** in CDCl3

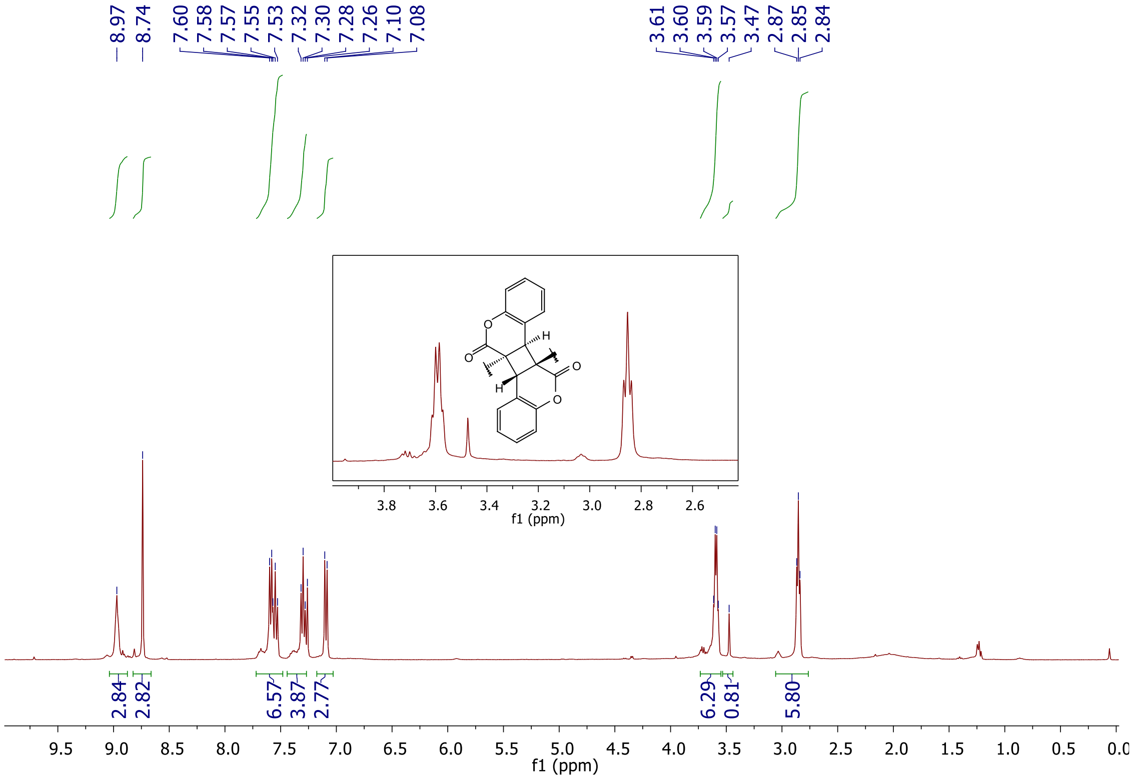

Fig. S3 – ^{1}H NMR spectrum of compound **3** in CDCl3 after irradiation at 330 nm for 30 min.

Dynamic Light Scattering

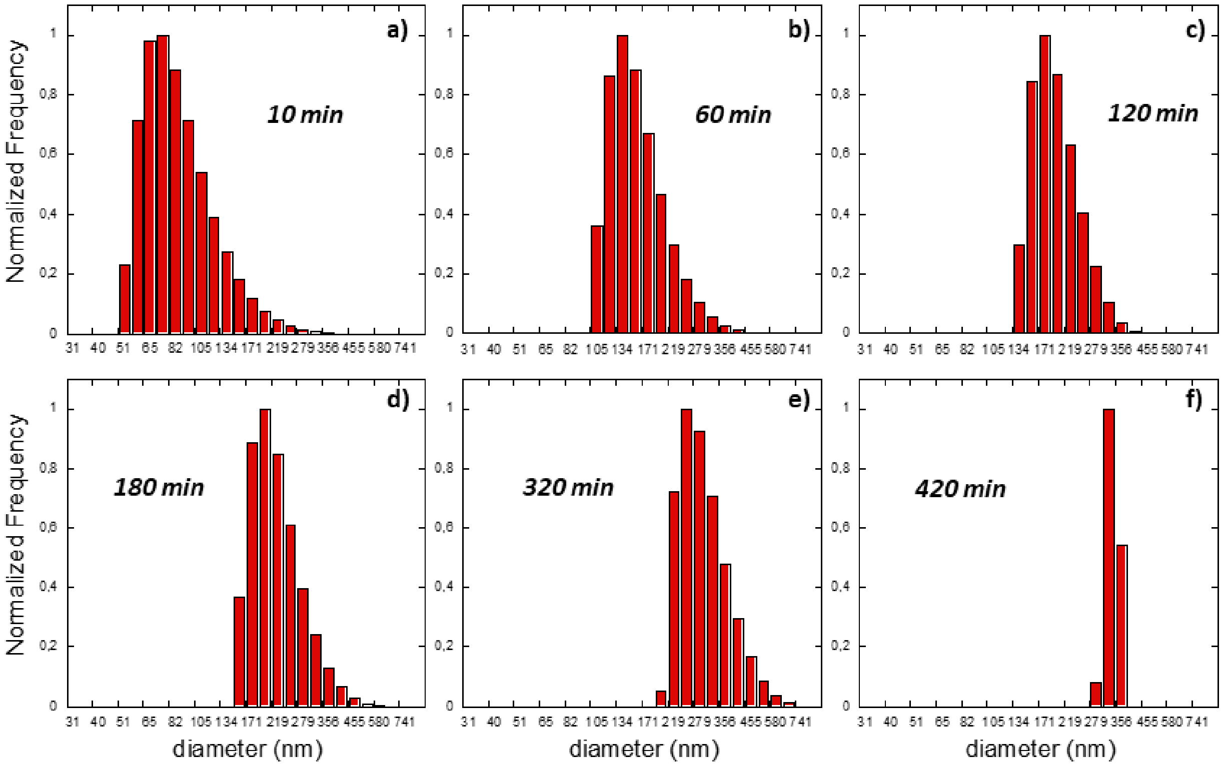

Fig. S4 – Histograms obtained in DLS measurements of a solution of **3** in chloroform irradiated at 330 nm for 10 (a), 60 (b), 120 (c), 180 (d), 320 (e) and 420 (f) minutes.

Scanning Electron Microscopy

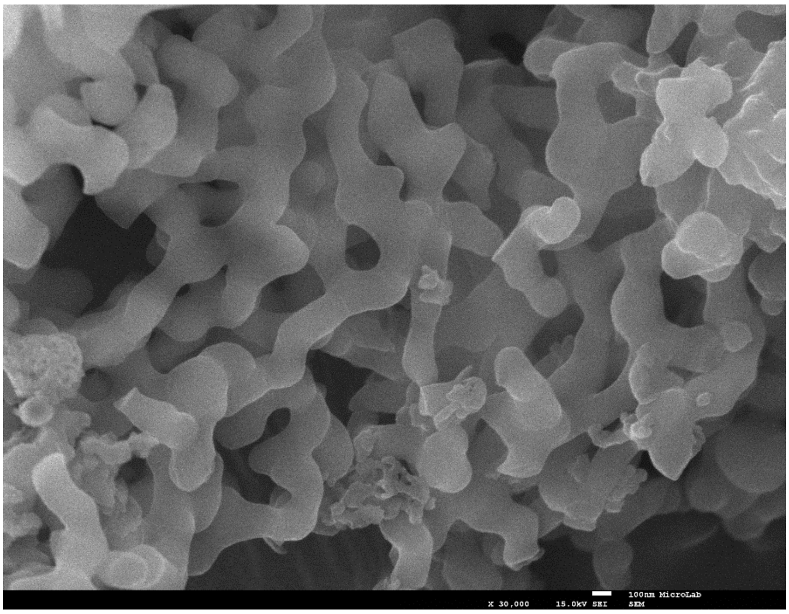

Fig. S5 – SEM image of nanoparticles obtained by centrifugation of a solution of **3** in chloroform irradiated at 330 nm for 180 minutes. Scale is 100 nm.

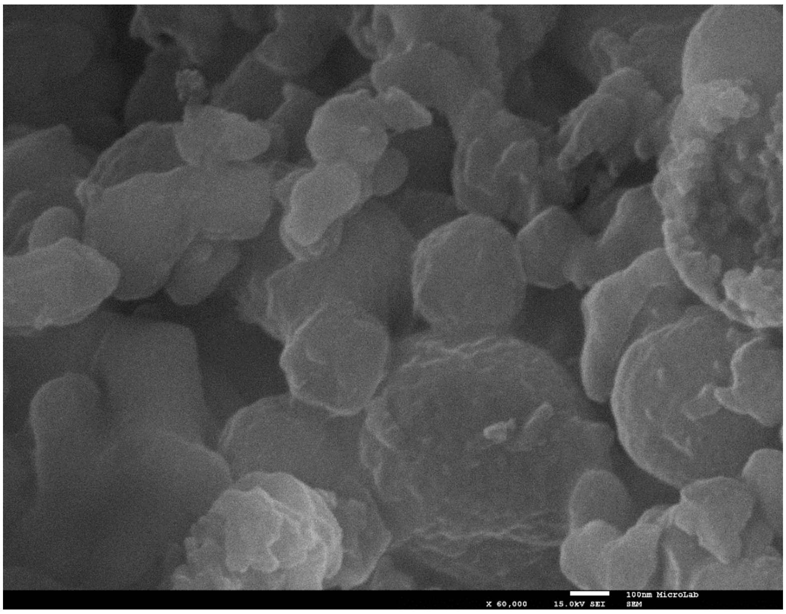

Fig. S6 – SEM image of nanoparticles obtained by centrifugation of a solution of **3** in chloroform irradiated at 330 nm for 180 minutes. Scale is 100 nm.

The SEM images show aggregated particles obtained by irradiation of **3**, forming fibre-like structures. The aggregation is suggested to have occurred due to centrifugation of irradiated suspensions. The cross-section diameter and node size in these fibres is consistent with the particle size measured by DLS for the same irradiation conditions.

References

1. C.G. Hatchard, C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518-536