Electronic Supplementary Material (ESI) for Nanoscale.

Self-Assembled Polyoxometalate-Dendrimer Structures for Selective Photocatalysis

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Supporting Information

Experimental

POM-dendrimer assemblies were prepared as follows: Stock solutions of polyoxometalate cluster (W4) and poly(amidoamine) (PAMAM) dendrimer generation 4 (G4) were prepared by dissolving an appropriate amount of substance in deionized and filtered water of pH 3.5. Supramolecular assemblies were formed by mixing appropriate amounts of water, dendrimer and polyoxmetalate cluster stock solutions under stirring at pH 3.5 to yield loading ratios (molar ratio of POM cluster to molar concentration of primary amino groups of the dendrimer) of $0.03 \leq l \leq 0.85$. Before addition of dye stock solution the dendrimer-cluster assemblies were allowed to stand for at least 2 h to complete assembly formation. For small-angle neutron scattering POM-dendrimer assemblies were prepared accordingly using D_2O as solvent.

Methyl red stock solutions were prepared by dissolving an appropriate amount of substance in deionized and filtered water at pH 11. An appropriate amount of methyl red stock solution of pH 11 was then added to POM-dendrimer assemblies at pH 3.5 to yield $c(MR) = 3.80 \cdot 10^{-5}$ mol L^{-1}. No pH change was observed after addition of methyl red stock solution, the final pH of samples containing POM-dendrimer assemblies and methyl red was pH 3.5.

Dye stock solutions of methylene blue, alizarin yellow R and xylenol orange were prepared by dissolving an appropriate amount of substance in deionized and filtered water of pH 3.5. Addition of dye stock solutions to dendrimer-cluster assemblies were carried according to methyl red addition to yield $c(dye) = 3.80 \cdot 10^{-5}$ mol L^{-1}.

Light Scattering Measurements were carried out on an ALV CGS 3 goniometer with ALV 5000 correlator (ALV Germany) equipped with a HeNe laser with a wavelength of $\lambda = 632.8$ nm and 20 mW output power. Measurements covered an angular range of $30° \leq \theta \leq 150°$. Data analysis was carried out by converting the measured intensity autocorrelation function into the scattered electric field autocorrelation function using the Siegert relation. The electric field autocorrelation functions were further analyzed by regularized inverse LaPlace transformation using the program CONTIN by S. Provencher to yield the distribution of relaxation times.[1] From this, the apparent diffusion coefficient was calculated using the relation $D_{app} = q^{-2}\tau^{-1}$. By extrapolation to zero scattering vector square the diffusion coefficient was obtained. Via Stokes-Einstein relationship the diffusion coefficient was converted into the hydrodynamic radius R_H. The radius of gyration R_G was obtained using static light scattering.

UV-Vis spectra were recorded using a SHIMADZU UV Spectrophotometer (UV-1800) with a slit width of 1 nm using quart cuvettes from Hellma/ Müllheim with 1 and 10 cm path length. The spectral range covered 200 nm ≤ θ ≤ 800 nm.

Small-Angle Neutron Scattering (SANS) measurements were performed at the beamline D11 at Institut Laue Langevin (ILL), Grenoble, France. At D11, the following configurations were employed: sample-detector distances of d = 1.2 m, d = 8 m and d = 39 m were used at a wavelength of $\lambda = 6$ Å. All data were corrected for empty cell scattering, electronic background, detector uniformity and analyzed after subtracting solvent scattering and incoherent background. Error bars lie within 1-5% at low q and increase up to 15% at $0.9\ \mathrm{nm}^{-1} \leq q$.

ζ-potential measurements were carried out on a Zetasizer Nano ZS from Malvern Instruments. For each measurement five runs were performed. The Smoluchowski formula was used to calculate the ζ-potential from the electrophoretic mobility.

UV irradiation was performed using an UV-lamp with wavelengths of 254 nm and 366 nm.

Additional Results

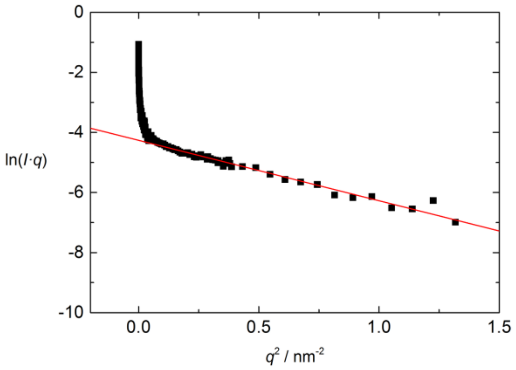

Figure S1: Cross-section Guinier plot of SANS data of POM-dendrimer assemblies with *l* = 0.7 and c(dendrimer) = $3.52 \cdot 10^{-5}$ mol L^{-1}: the linear dependence indicates locally cylindrical structures.

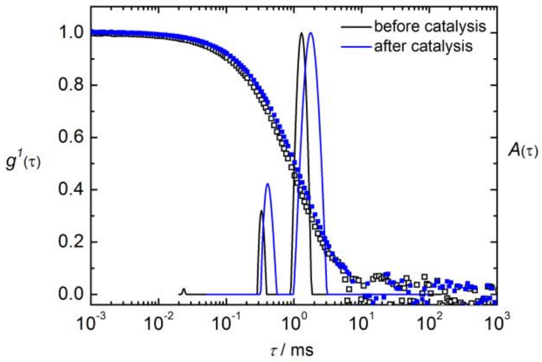

Figure S2: Dynamic light scattering from POM-dendrimer assemblies of *l* = 0.7 in presence of MR: Electric field autocorrelation function $g^1(\tau)$ and distribution of relaxation times $A(\tau)$ before catalysis (black) and after catalysis (blue) showing a nearly constant assembly size; c(MR) = $3.80 \cdot 10^{-5}$ mol L^{-1}, c(POM) = $1.35 \cdot 10^{-4}$ mol L^{-1}.

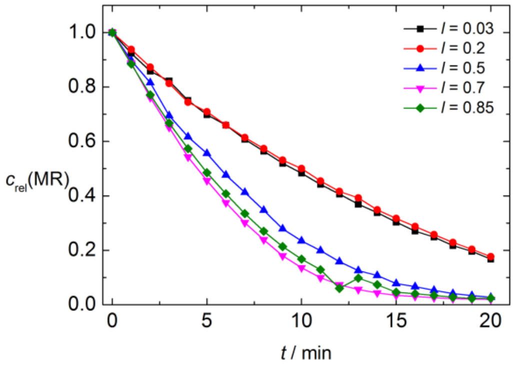

Figure S3: Time-dependent relative methyl red concentration for dendrimer-cluster assemblies of a loading ratio range $0.03 \leq l \leq 0.85$.

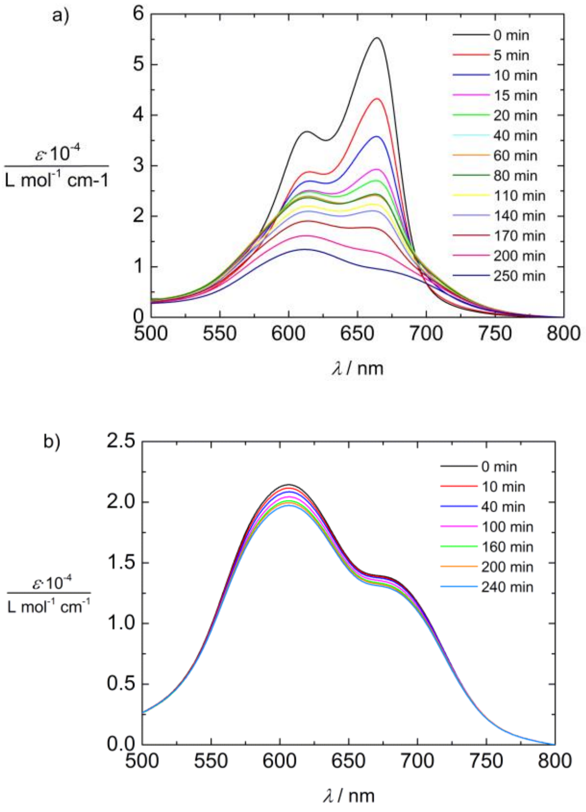

Figure S4: UV-Vis analysis of methylene blue degradation: a) Time-dependent UV-Vis spectra of methylene blue degradation in presence of POM-dendrimer assemblies with $l = 0.7$; b) UV-Vis spectra of methylene blue degradation in presence of W4; c(MB) = $3.80 \cdot 10^{-5}$ mol L^{-1}, c(POM) = $1.35 \cdot 10^{-4}$ mol L^{-1}.

Table S1: Loading ratio dependent degradation of methylene blue in presence of POM-dendrimer assemblies after 280 min of UV irradiation, *c*(MB) = $3.80 \cdot 10^{-5}$ mol L^{-1}, *c*(POM) = $1.35 \cdot 10^{-4}$ mol L^{-1}.

loading ratio	*l* = 0.03	*l* = 0.2	*l* = 0.5	*l* = 0.7	*l* = 0.85
dye degradation	22 %	47 %	65 %	83 %	65 %

Similar to what is observed for the degradation of the positively charged methyl red, an activity increase is observed with increasing POM-dendrimer ratio up to *l* = 0.7. Going to higher loading ratio results in a decrease of the activity.

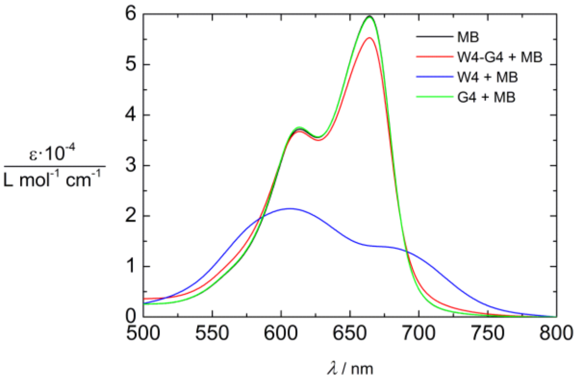

Figure S5: UV-Vis spectra of pure methylene blue (black curve), POM-dendrimer assemblies with *l* = 0.7 with methylene blue (red curve) and methylene blue in presence of POM (blue curve) and dendrimer (green curve); c(MB) = $3.80 \cdot 10^{-5}$ mol L^{-1}, c(POM) = $1.35 \cdot 10^{-4}$ mol L^{-1}.

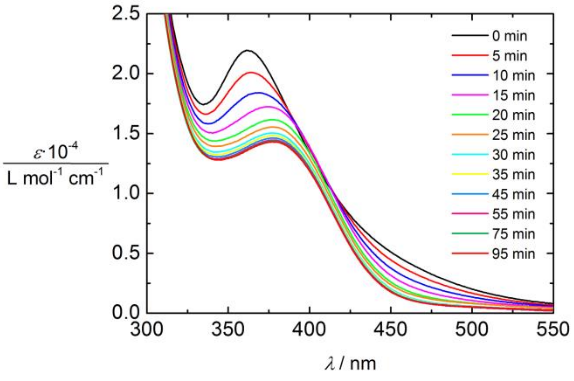

Figure S6: UV-Vis analysis of alizarin yellow R degradation: Time-dependent UV-Vis spectra of alizarin yellow R degradation in presence of POM-dendrimer assemblies assemblies with *l* = 0.7; c(AY) = $3.80 \cdot 10^{-5}$ mol L^{-1}, c(POM) = $1.35 \cdot 10^{-4}$ mol L^{-1}.

[1] S. W. Provencher, *Comput. Phys. Commun.* **1982**, *27*, 229-242.