Organogel-quantum dots hybrid materials displaying fluorescence sensitivity and structural stability towards nitric oxide

Prashant D. Wadhavane, M. Angeles Izquierdo,* Francisco Galindo, M. Isabel Burguete and Santiago V. Luis*

Universitat Jaume I, Departamento de Química Inorgánica y Orgánica, Av. Sos Baynat, s/n, E-12071 Castellón (Spain); E-mail: mizquier@.uji.es; luiss@uji.es

Index Page

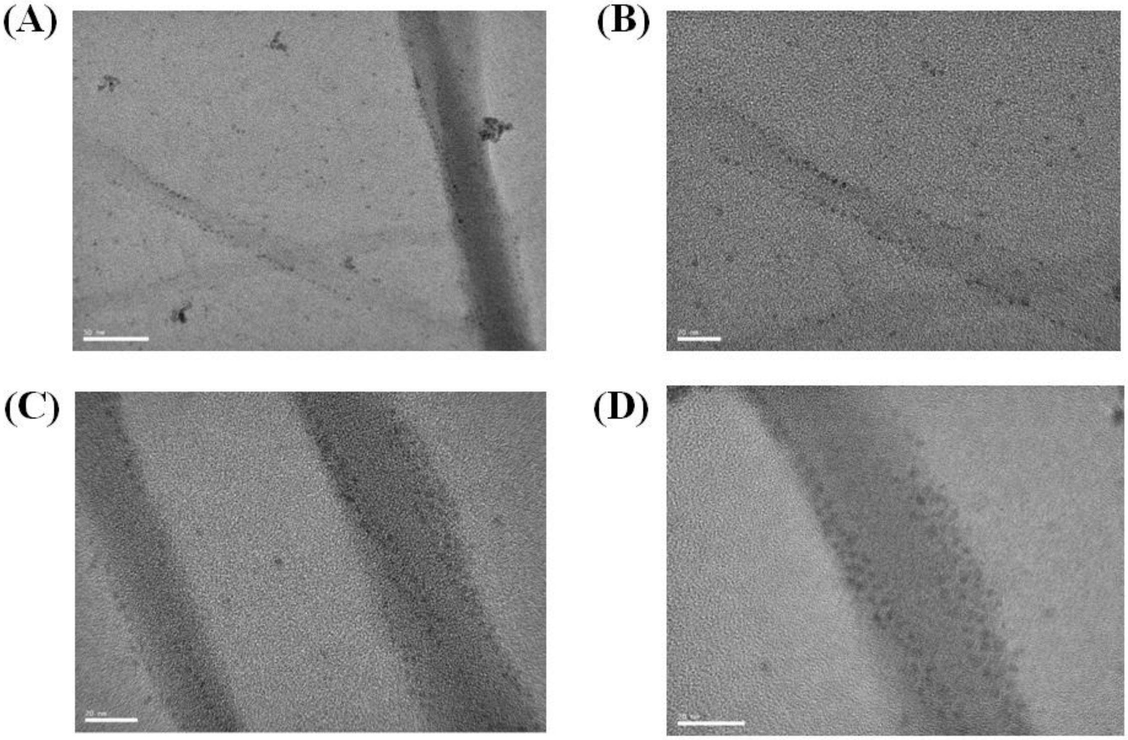

Figure S1. TEM micrographs of the fibrilar structure of the cyclophane **1** xerogel containing CdSe/ZnS QDs.

Scalebar is: A) 50 nm, B) 20 nm, C) 20 nm, D) 20 nm.

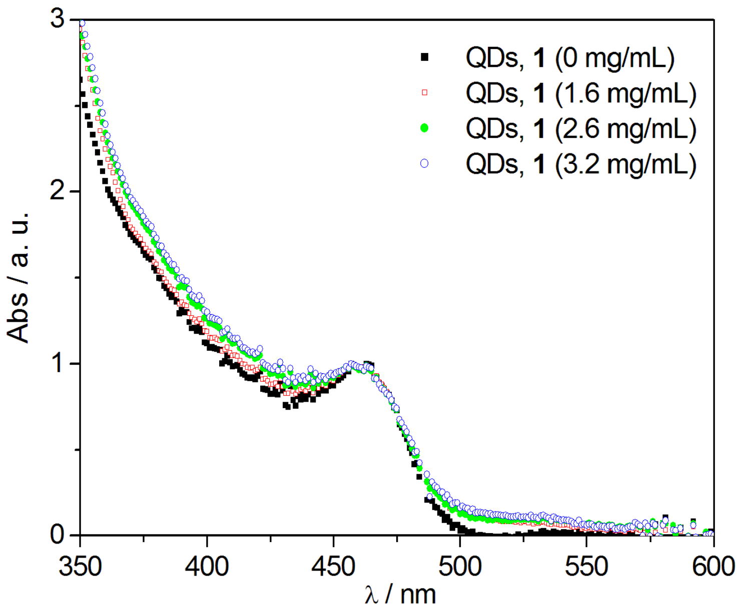

Figure S2. Absorption spectra of samples prepared in toluene containing CdSe/ZnS QDs (0.45 μM) and different concentrations of organogelator **1**. The absorption spectra have been corrected at 600 nm and normalized at 457 nm to allow comparison of the shape and position of the absorption maxima.

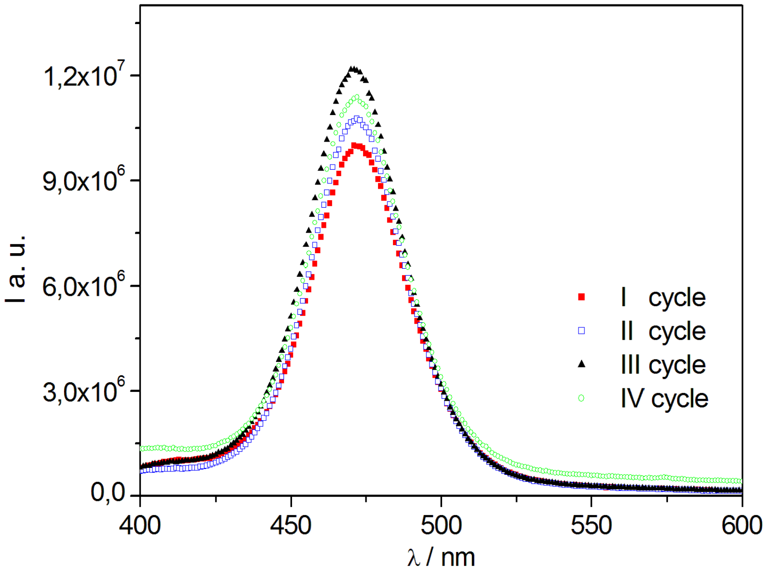

Figure S3. Emission spectra of samples prepared in toluene containing CdSe/ZnS QDs (0.75 μM) and organogelator **1** (2.7 mg/mL) (λ_{exc} = 366 nm). The organogels were heated to achieve a clear solution, followed by cooling to room temperature to reform the gel. The cycle was repeated four times in the same cuvette and the emission spectra of the samples were measured 30 minutes after formation of the organogel.

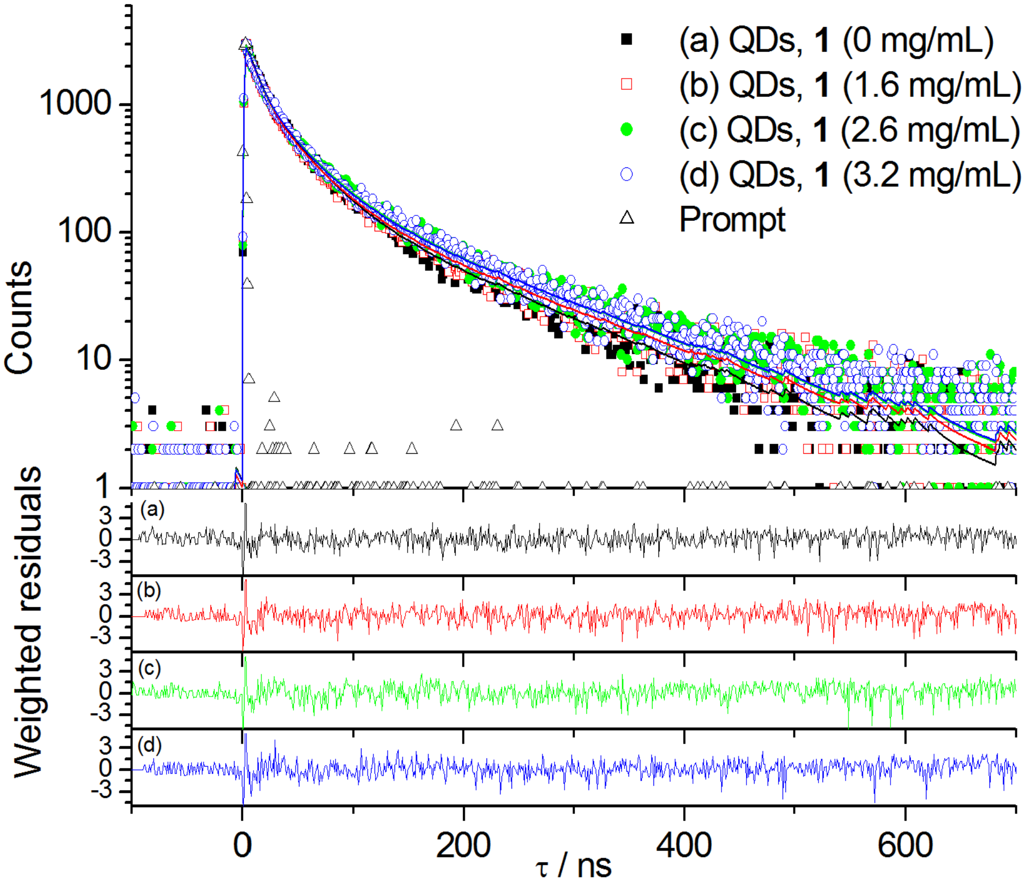

Figure S4. Fluorescence decay traces and weighted residuals of CdSe/ZnS QDs (0.45 μM) in toluene and toluene organogel containing different concentrations cyclophane **1** (λ_{exc} = 372 nm, λ_{em} = 480 nm). The incident light pulse is also shown (open triangles).

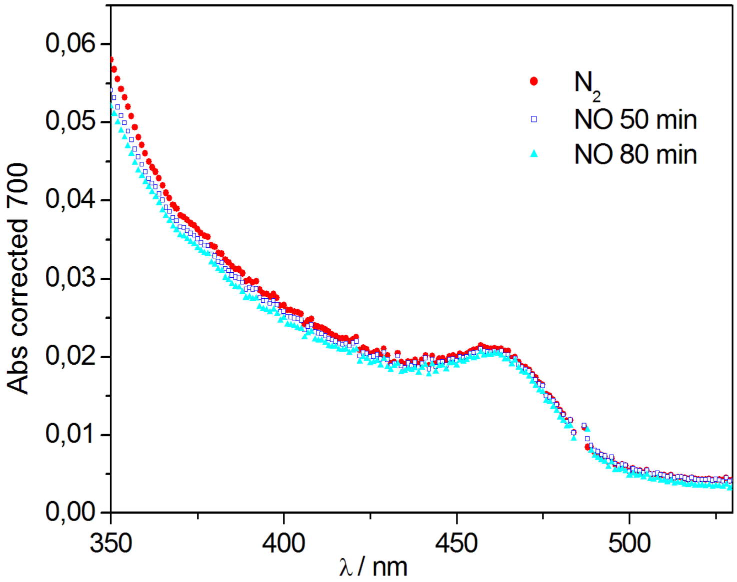

Figure S5. Absorption spectra of the CdSe/ZnS QDs (0.45 μM) in the toluene organogel of cyclophane **1** (2.6 mg/mL) before and after addition of NO (1.5 %).

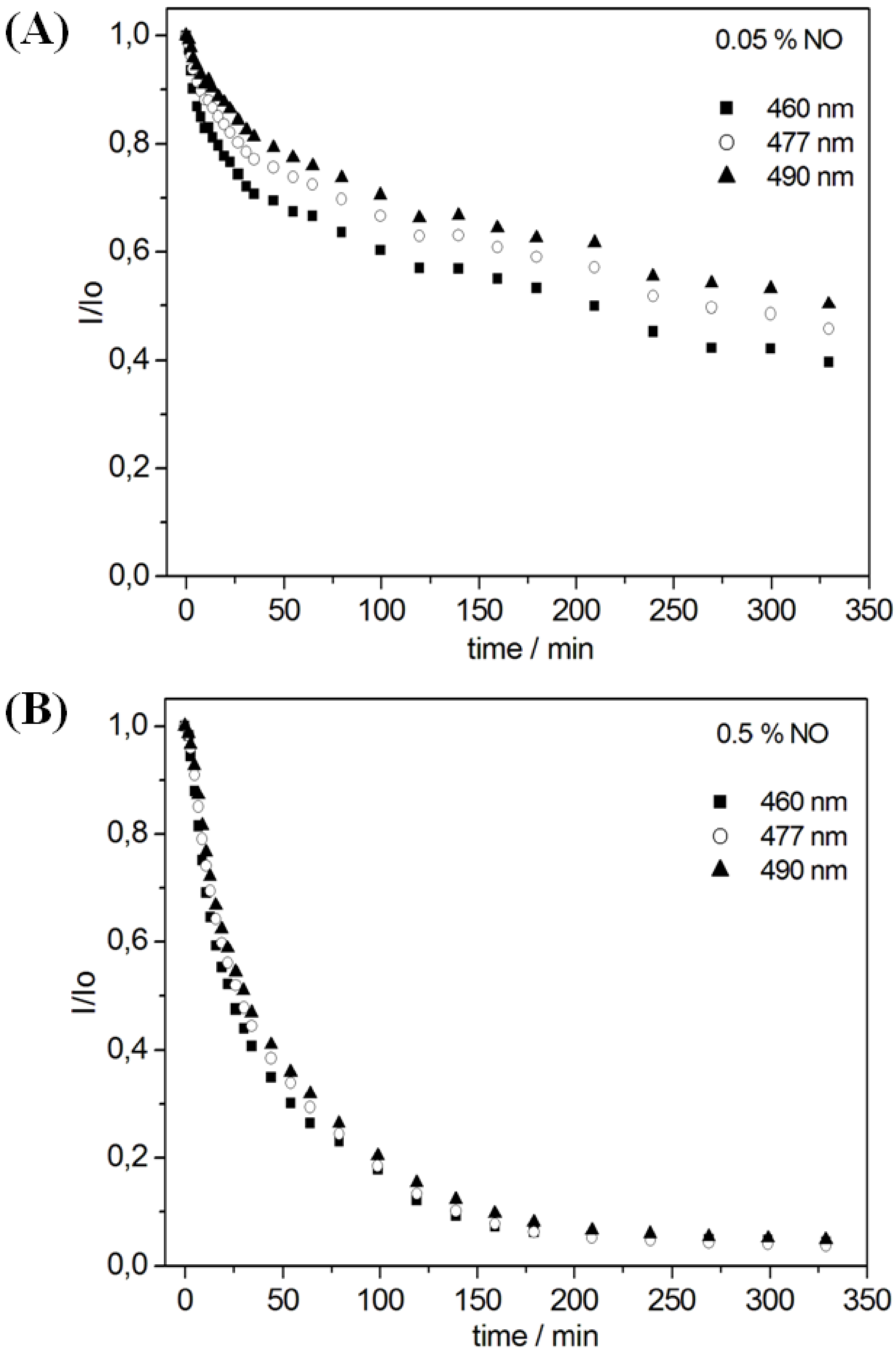

Figure S6. Evolution along the time of the fluorescence intensity at different emission wavelengths (460 nm, 477 nm and 490 nm) of the QDs (0.45 μM) in the toluene organogel of cyclophane **1** (2.6 mg/mL) in the presence of different concentrations of NO: A) 0.05 % NO, B) 0.5 % NO.

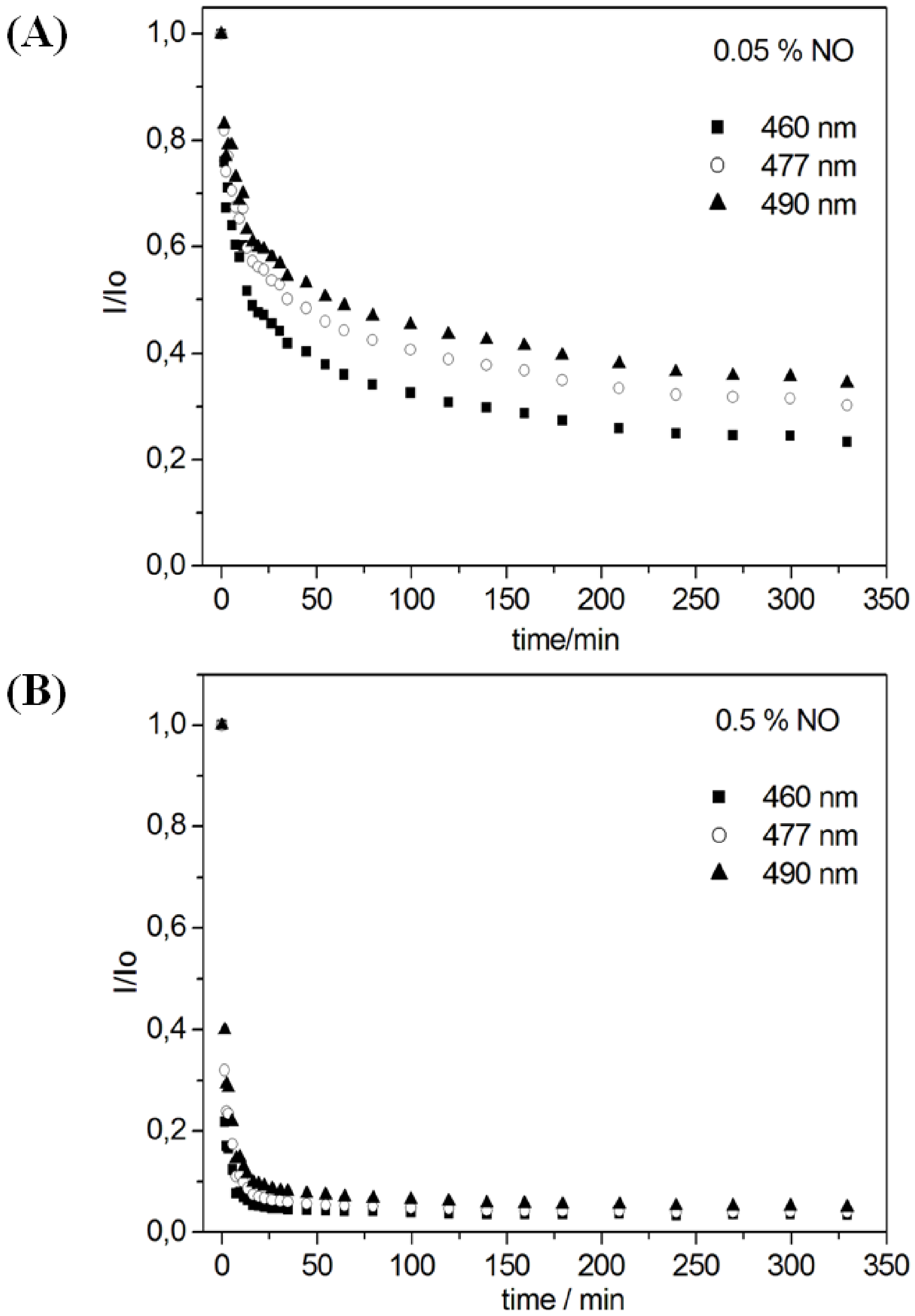

Figure S7. Evolution along the time of the fluorescence intensity at different emission wavelengths (460 nm, 477 nm and 490 nm) of the QDs (0.45 μM) in toluene in the presence of different concentrations of NO: A) 0.05 % NO, B) 0.5 % NO.

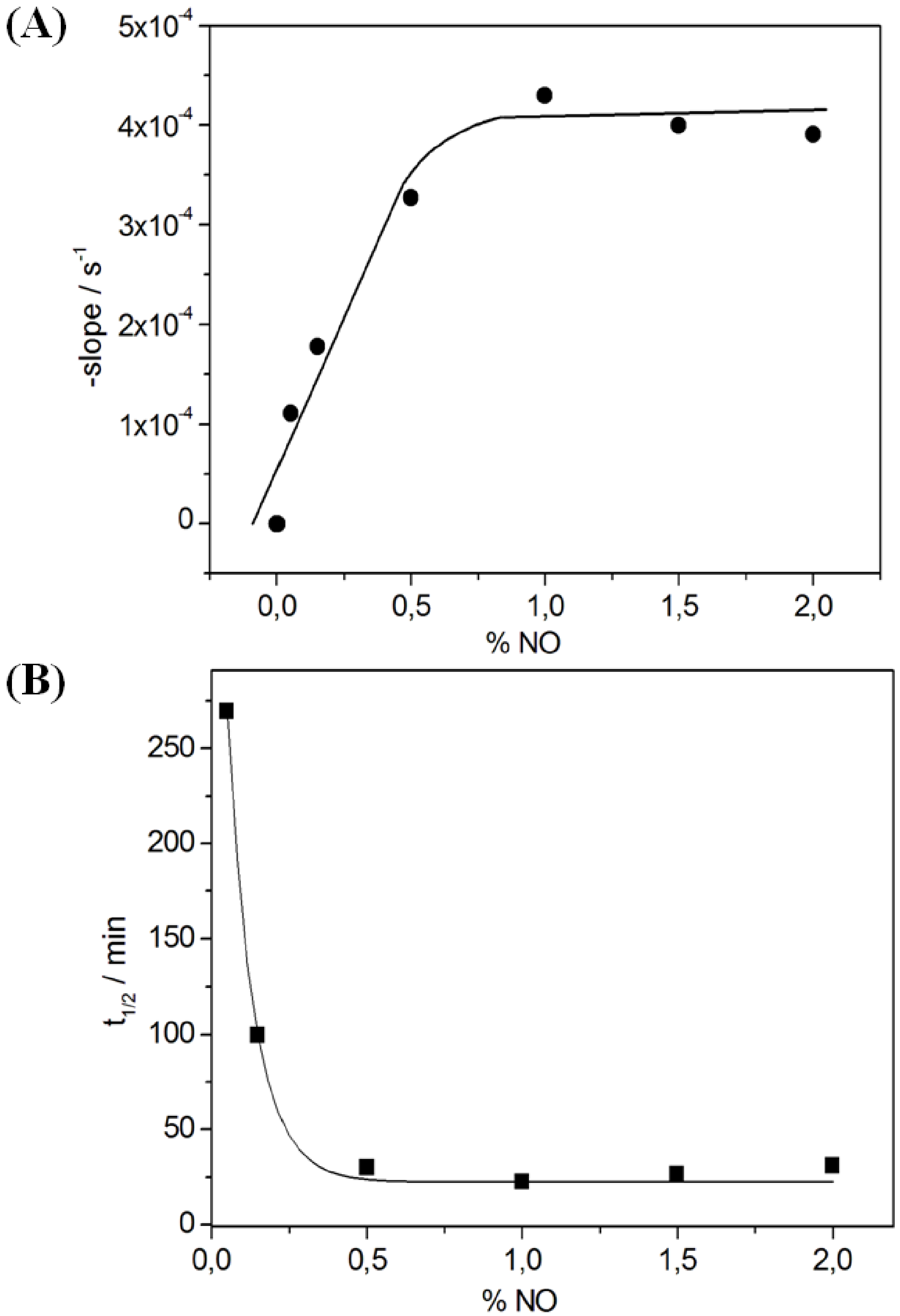

Figure S8. A) Comparative representation of the apparent rate (r) of quenching of the fluorescence of the QDs for different concentrations of NO in the toluene organogel-QDs composite. B) Comparative representation of the time at which the emission of the QDs at 477 nm was reduced 50 % relative to the initial intensity ($t_{1/2}$) due to quenching of the fluorescence of the QDs for different concentrations of NO in the toluene organogel-QDs composite. Samples containing toluene, cyclophane **1** (2.6 mg/mL) and CdSe/ZnS QDs (0.45 μM).

Table S1 Quantum dots sensitivity towards nitric oxide

Media	NO (% vol)	$t_{1/2}$ (min)	$-r \times 10^{-4}$ (s^{-1})
Organogel[a]	0.05	269.5	1.1
Organogel[a]	0.15	99.5	1.8
Organogel[a]	0.5	30.0	3.3
Organogel[a]	1	22.5	4.3
Organogel[a]	1.5	26.5	4.0
Organogel[a]	2	31.0	3.9
Toluene[b]	0.05	34.5	6.6
Toluene[b]	0.1	9.5	18.0
Toluene[b]	0.5	< 1.5	53.0
Toluene[b]	1	< 1.5	40.0

[a] Samples containing CdSe/ZnS QDs (0.45 μM) in the toluene organogel of cyclophane **1** (2.6 mg/mL). [b] Samples containing CdSe/ZnS QDs (0.45 μM) in toluene.