

Electronic Supplementary Information

Light-responsive hybrid material based on luminescent core-shell quantum dots and steroidal organogels

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Table S1. Optical properties of the synthesized quantum dots.

NPs	λ_{ab} , (nm)	λ_{em} , (nm)	FWHM (nm)	Φ^a	Diameter (nm)	
					UV ^b	HRTEM
CT	519	529.0	28	9.3	2.55	2.6
CA	515	523.5	29	3.4	2.50	2.6
CST	519	532.6	27	55.0	2.55	4.0
CSA	513	529.4	28	46.4	2.48	4.7

^a Calculated using fluorescein as standard fluorophore, excitation at 465 nm.

^b Calculated using the maximum in the UV-visible spectra ¹

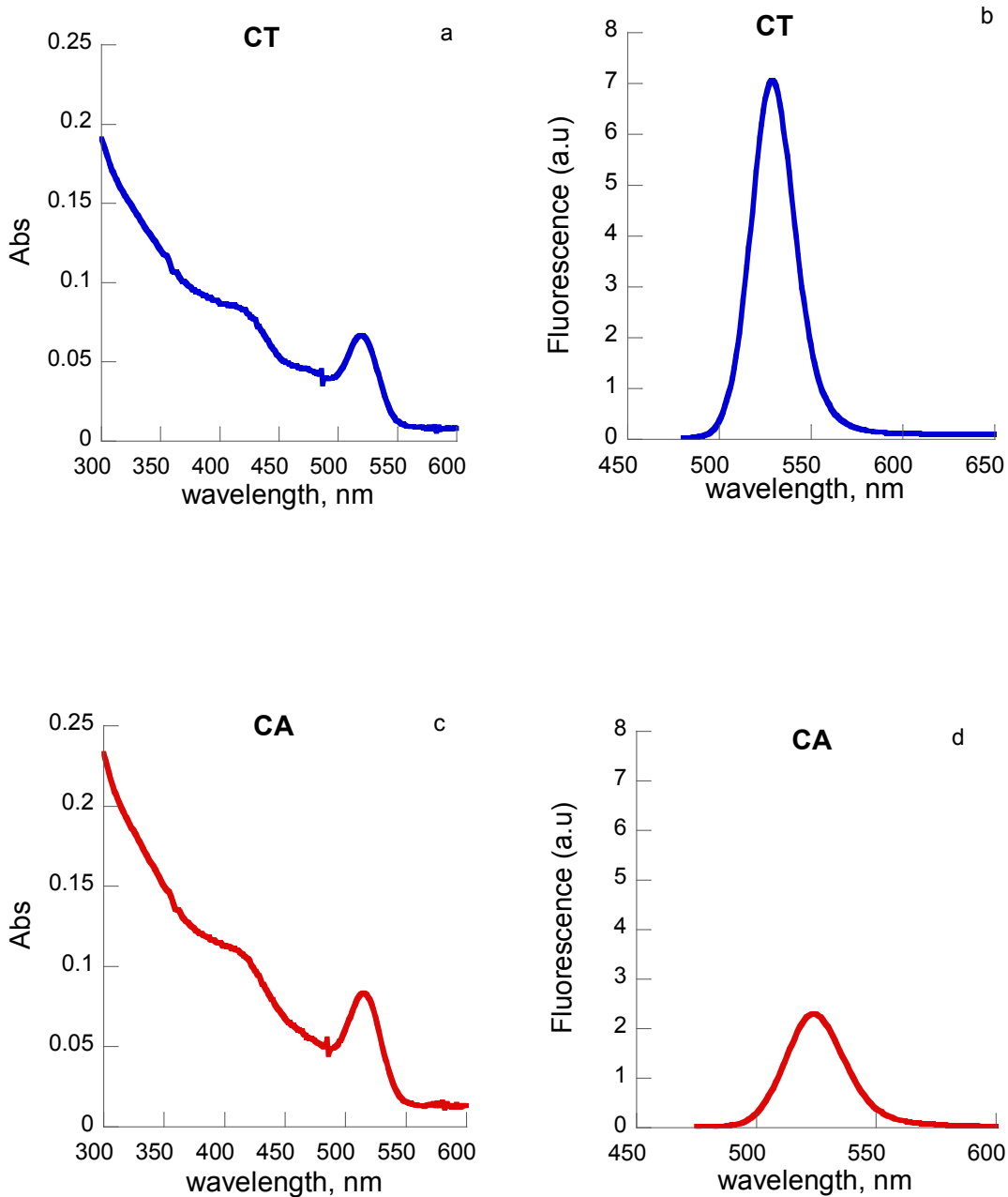


Figure S1: Absorption and emission spectra ($\lambda_{\text{exc}} = 465$ nm) of CT (a, b) and CA (c, d) with a concentration of 1×10^{-6} M in toluene.

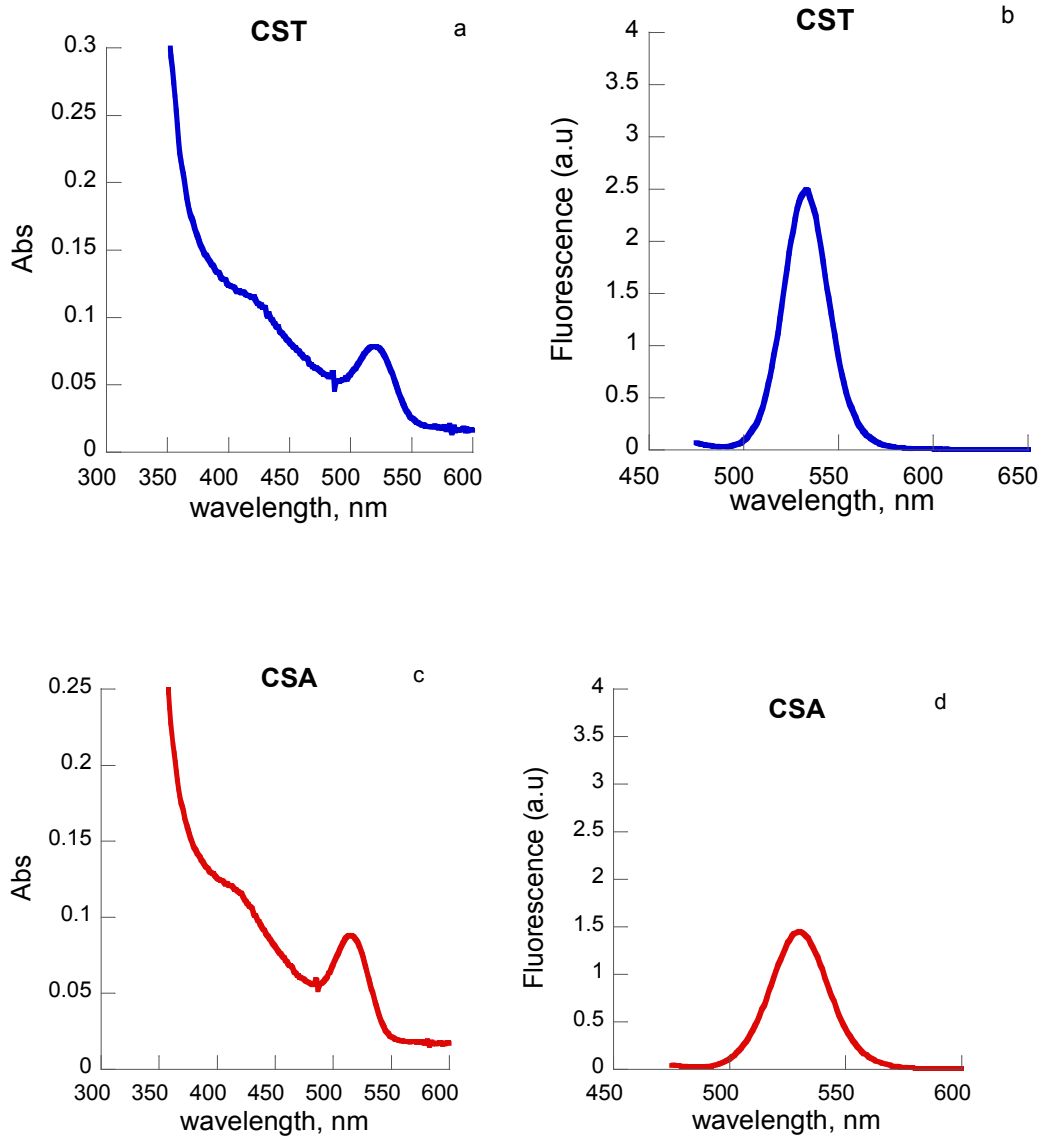


Figure S2: Absorption and emission spectra ($\lambda_{\text{exc}} = 465$ nm) of CST (a, b) and CSA (c, d) with a concentration of 1.1×10^{-6} M in toluene.

HTEM images of QDs

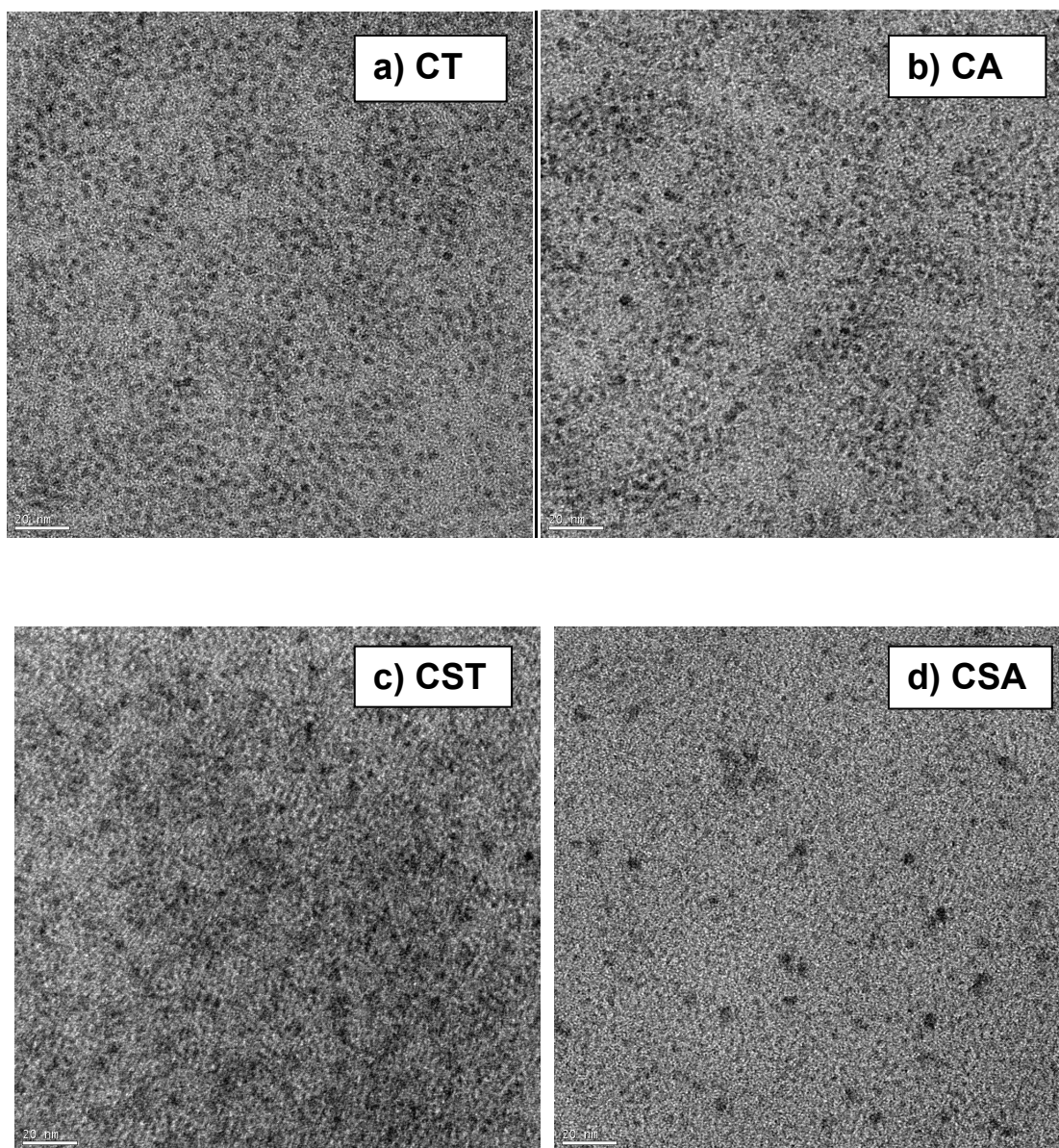


Figure S3: High resolution transmission electron microscopy of quantum dots: a) CT, b) CA, c) CST and d) CSA. Scale bar 20 nm.

Table S2 Photophysical properties of the QD-OG1 hybrids

QD or QD-OG1	λ_{em} (nm)	Φ^a	τ_{av} (ns)	K_r $10^6 s^{-1}$	K_{nr} $10^6 s^{-1}$
CT	529.0	9.1	-	-	-
CT-OG1	529.0	0	-	-	-
CA	523.5	3.4	160.9	0.21	6.0
CA-OG1	523.5	0.9	29.1	0.33	34.0
CST	532.6	55.0	69.6	7.90	6.46
CST-OG1	532.6	25.7	45.2	5.75	16.4
CSA	529.4	46.4	152.3	3.02	3.5
CSA-OG1	529.4	11.7	60.9	1.92	14.5

^a Calculated using fluorescein as standard fluorophore, excitation at 465 nm.

Values of k_r and k_{nr} in table S2 were obtained according to the fluorescence lifetime equation S1 combined with equation S2 (Lakowicz, Principles of Fluorescence Spectroscopy, 3rd edition). The average lifetime τ_{av} obtained for the multiexponential luminescence decay was used in both equations.

$$\tau_{av} = \frac{1}{(k_r + k_{nr})} \quad \text{Equation S1}$$

$$\phi = \frac{k_r}{k_r + k_{nr}} = \tau_{av} \cdot k_r \quad \text{Equation S2}$$

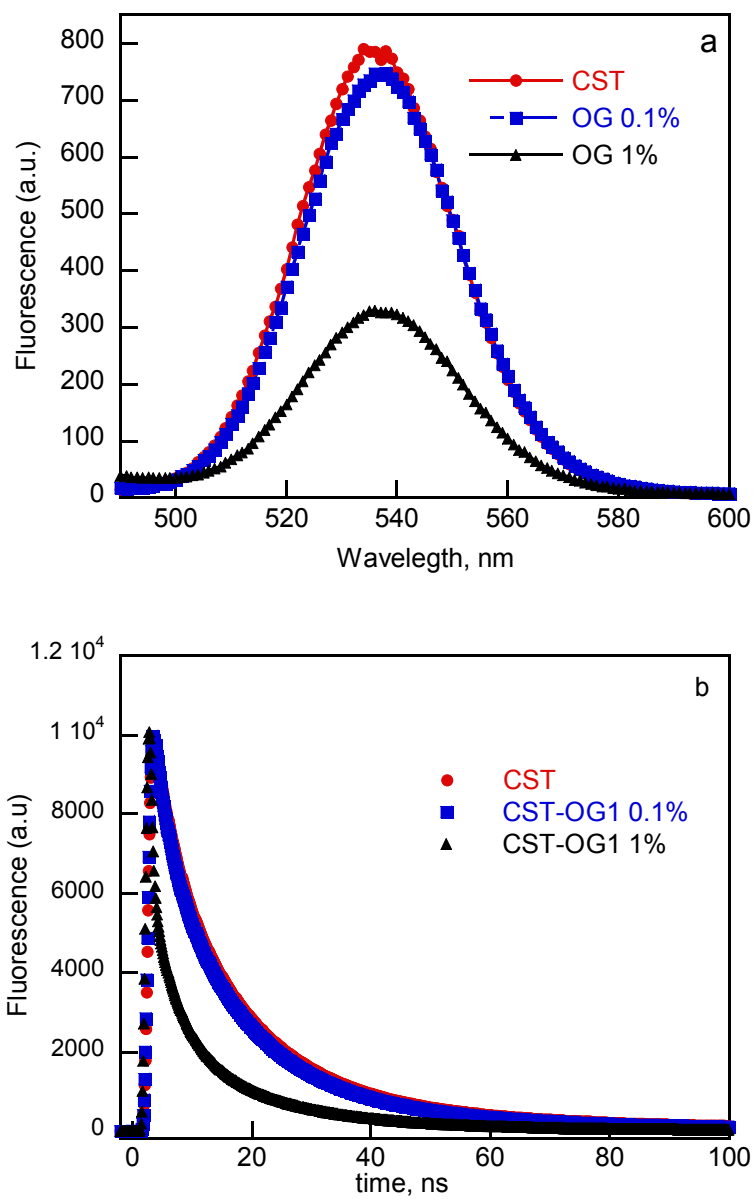


Figure S4 a) Fluorescence emission spectra and b) fluorescence kinetic trace of **CST** in *n*-hexane, **CST+ OG1** (0.1 wt.% in *n*-hexane) and **CST-OG1** (1 wt.% in *n*-hexane). $\lambda_{\text{exc}} = 457 \text{ nm}$

Table S3 Photophysical properties of CST at increasing concentration of OG1 in chloroform.

OG (% w/v)	τ_{av} (ns)	Φ_F	Area	$k_r \cdot 10^6 s^{-1}$	$K_{nr} \cdot 10^6 s^{-1}$
0	58.1	0.5501	28675.51	9.47	7.74
0.5	53.6	0.4549	23713.04	8.49	10.17
1	52.62	0.3622	18881.79	6.89	12.12
1.5	49.59	0.3090	16109.48	6.23	13.93
2	49.02	0.2865	14935.65	5.84	14.55
2.5	50.05	0.2630	13712.6	5.25	14.73
3	47.2	0.2423	12630.43	5.13	16.05

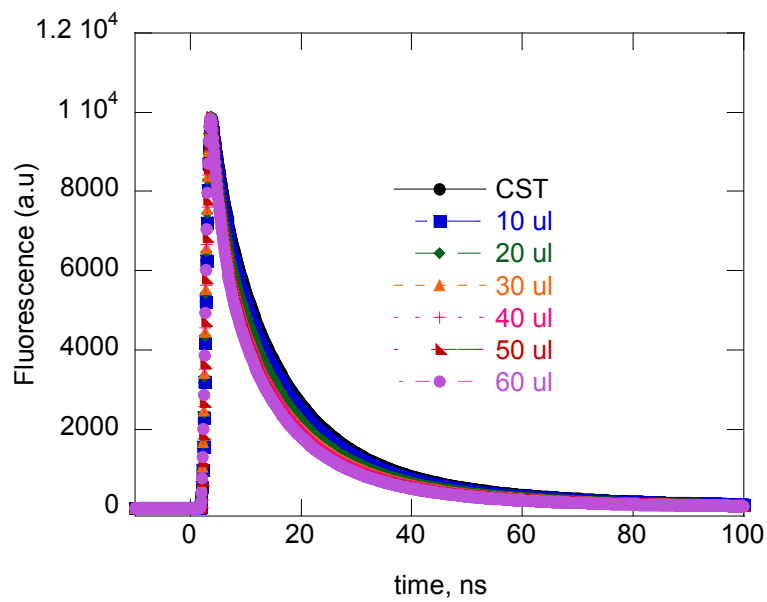


Figure S5 Fluorescence lifetime of **CST** in solution, at increasing concentration of **OG1** in chloroform. $\lambda_{\text{exc}} = 457 \text{ nm}$

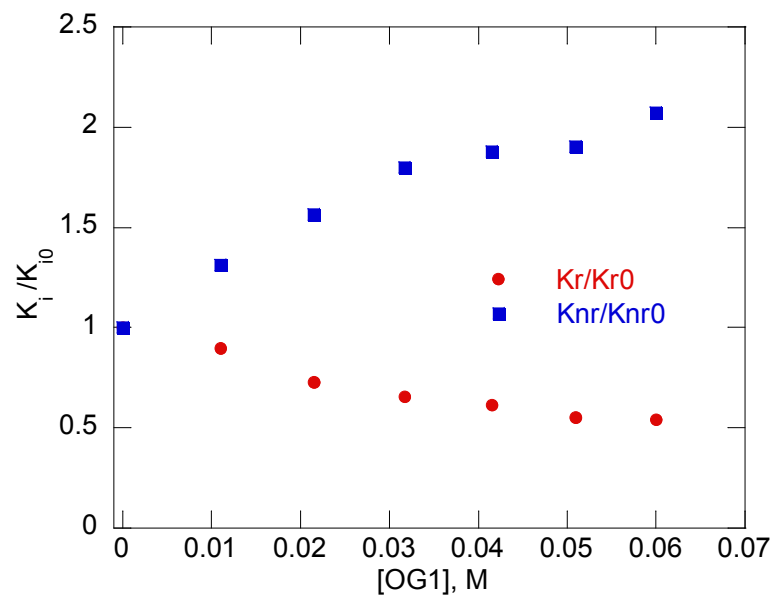


Figure S6 Ratio of radiative and non-radiative rate constant values of CST in the presence of increasing concentrations of OG1 in chloroform.

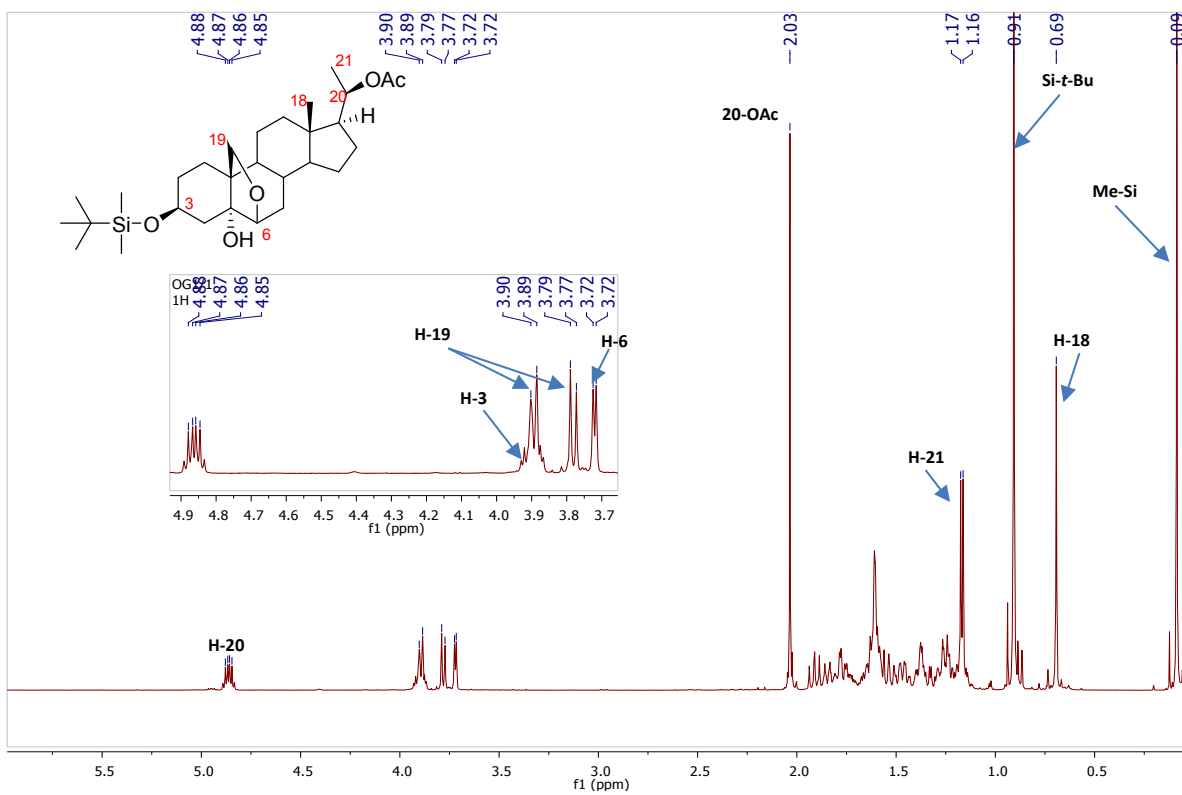


Figure S7. ¹H NMR (500 MHz) CDCl₃ (OG1)

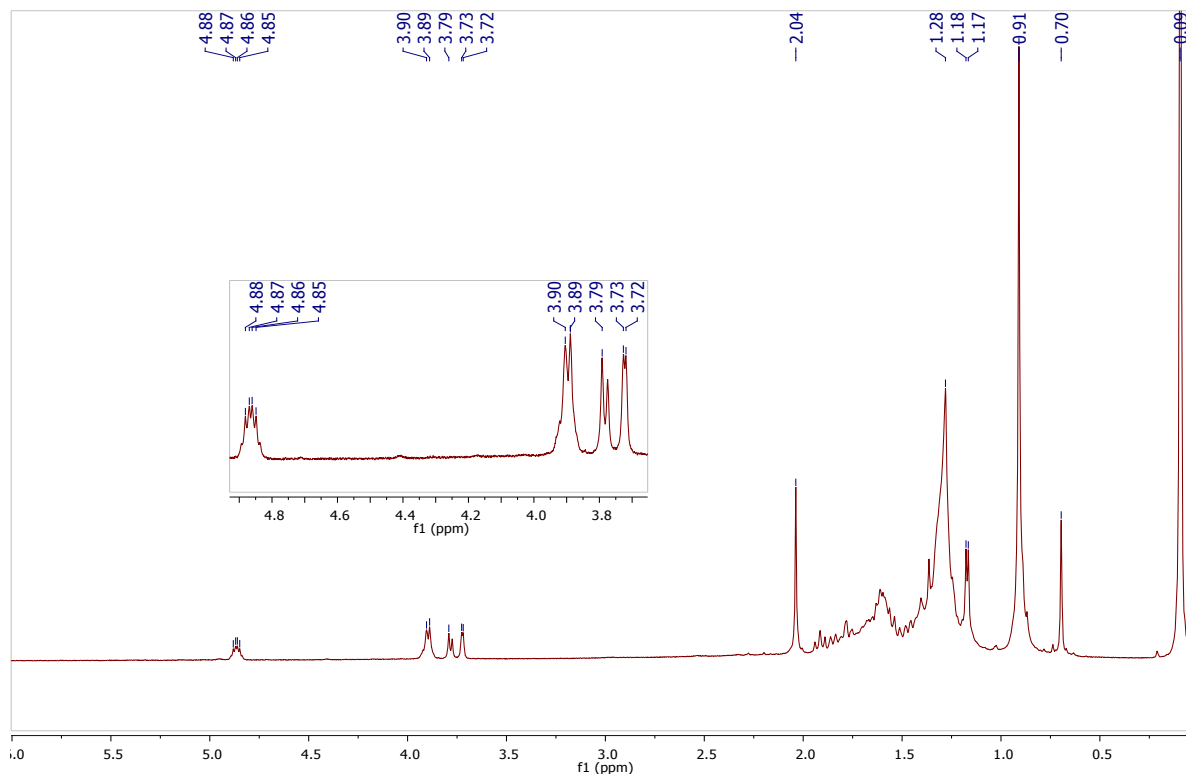


Figure S8. ¹H NMR (500 MHz) CDCl₃ CST-OG1

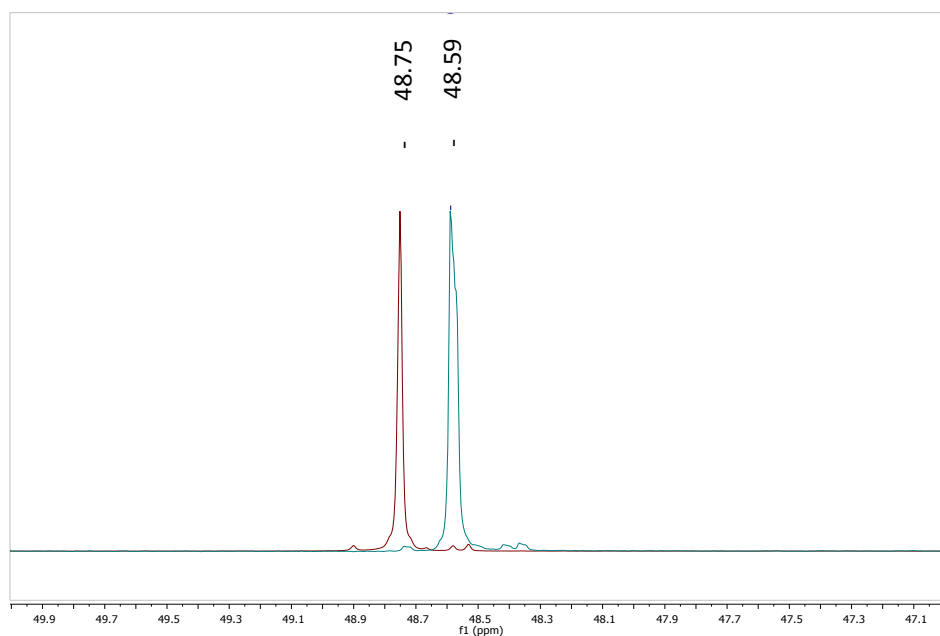
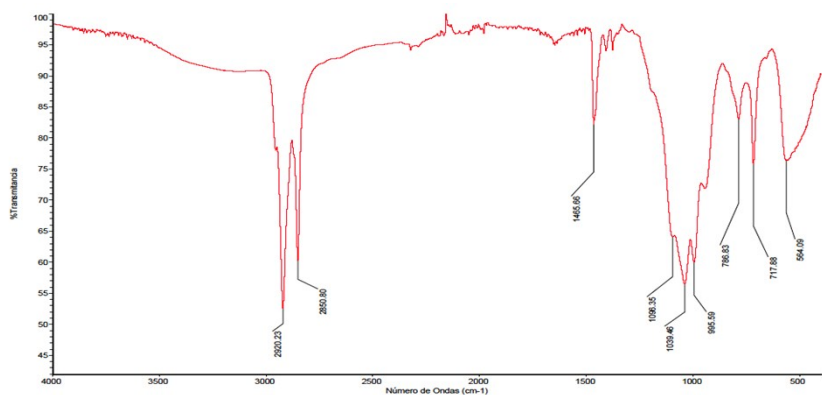
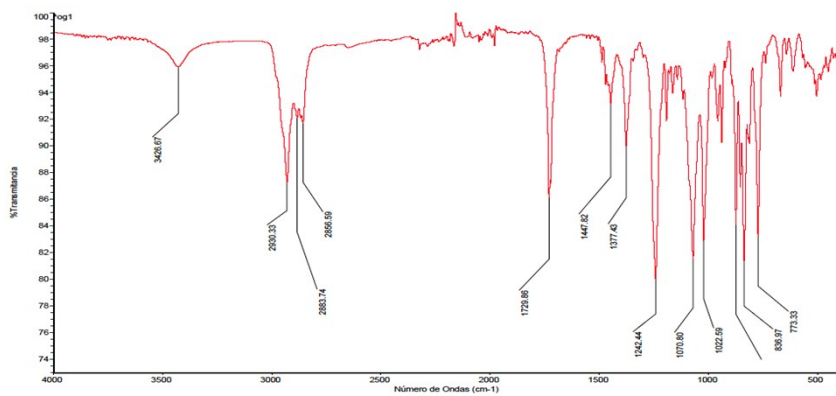


Figure S9. ^{31}P NMR (202.5 MHz, CDCl_3) superimposed spectra, in green TOPO (20 mM) FWHM: 6.3Hz and brown TOPO (20 mM) + **OG1** (20 mM) FWHM: 3.2 Hz.

a)



b)



c)

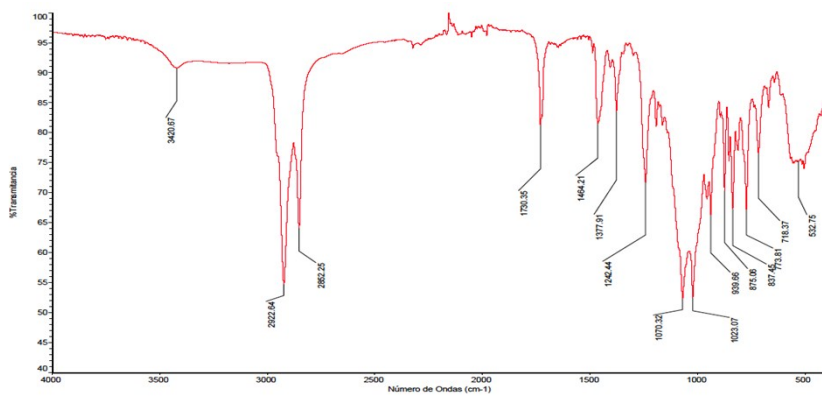


Figure S10. FT-IR spectra of a) CST b) OG1 and c) OG1-CST.

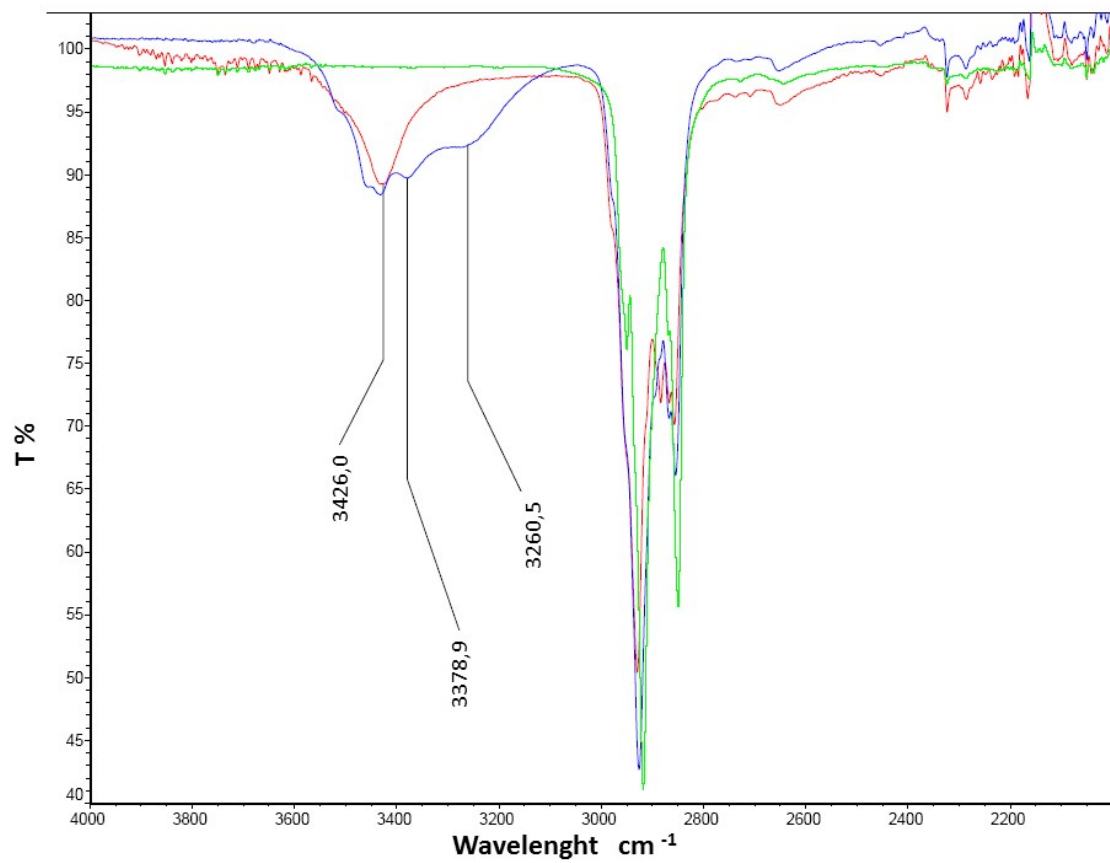


Figure S11. FT- IR spectra of **OG1** (red), **TOPO** (green) and **TOPO+OG1** mixture (blue).

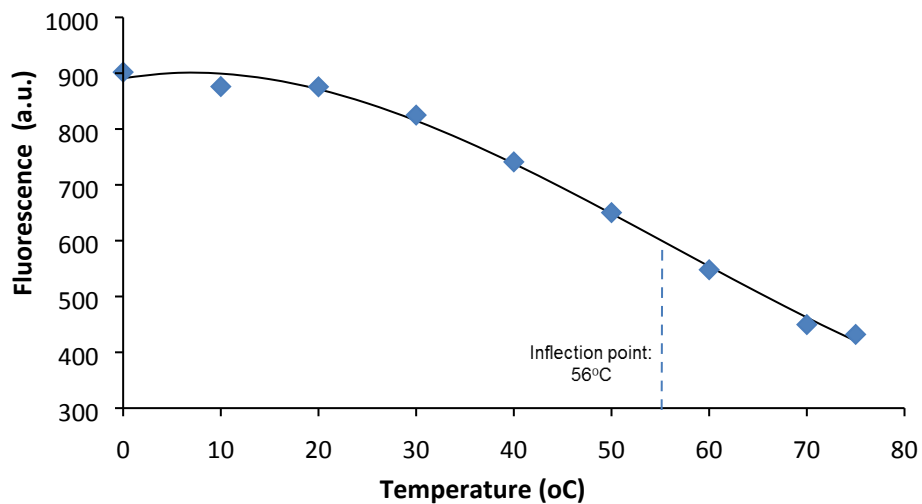


Figure S12: Variation of the CST-OG1 fluorescence with the temperature Maximum values for the fluorescence emission spectra of QD-CST in solution and in the organogel from *n*-hexane; λ_{exc} = 400 nm. Temperature was raised from 0 to 75°C. Concentrations in the OG1-CST hybrid: OG1 1 wt. %, QD-CST 1.14 μ M. The Tg value could be measured at the inflection point (Tg = 56 °C).

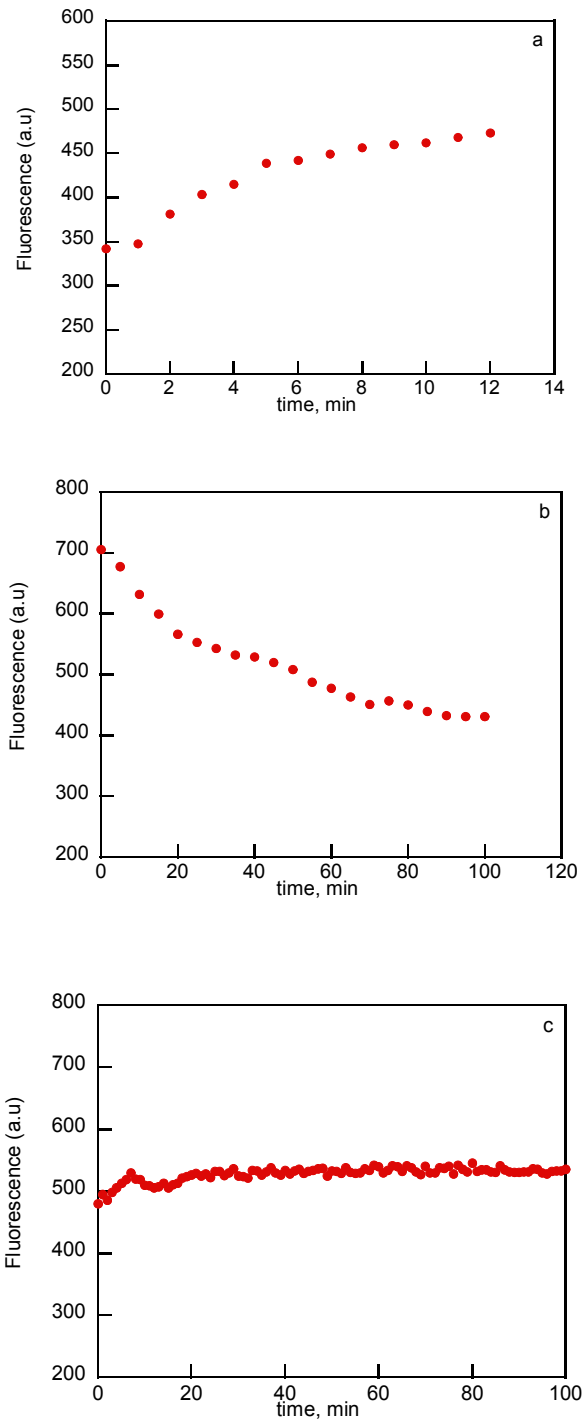


Figure S13: Effect of small amount of a) acetone (50 μ l), b) water (20 μ l) and c) *n*-hexane (150 μ l) on the luminescence properties of the CST-OG1.

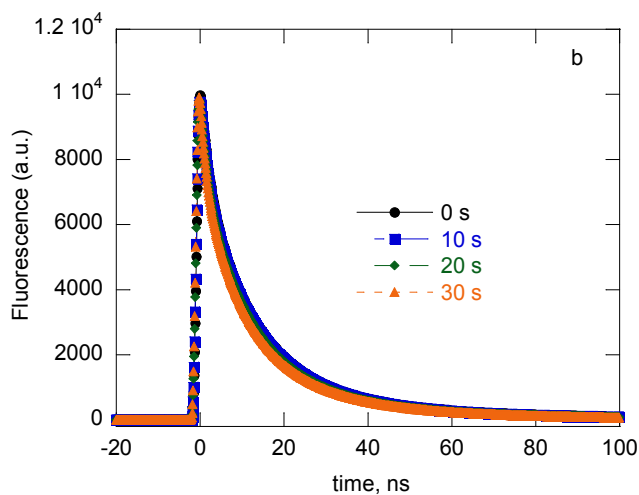
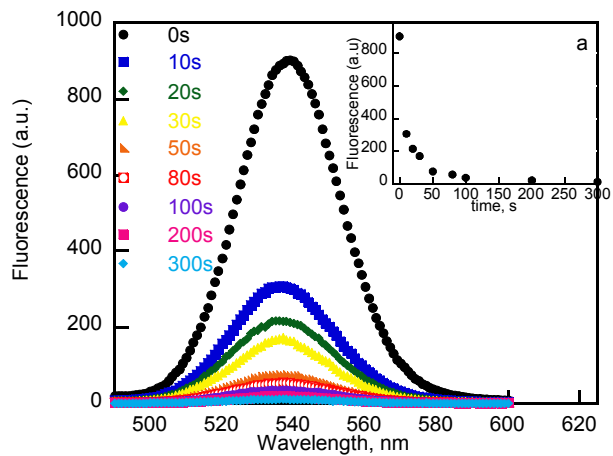


Figure S14 Fluorescence quenching of CST in the presence of DAE (2.5 mM) at different irradiation time with UV light (340 nm), quenching efficiency = 95%. a) Fluorescence spectra, inset fluorescence intensity at 537 nm vs. irradiation times; and b) Fluorescence kinetic traces.

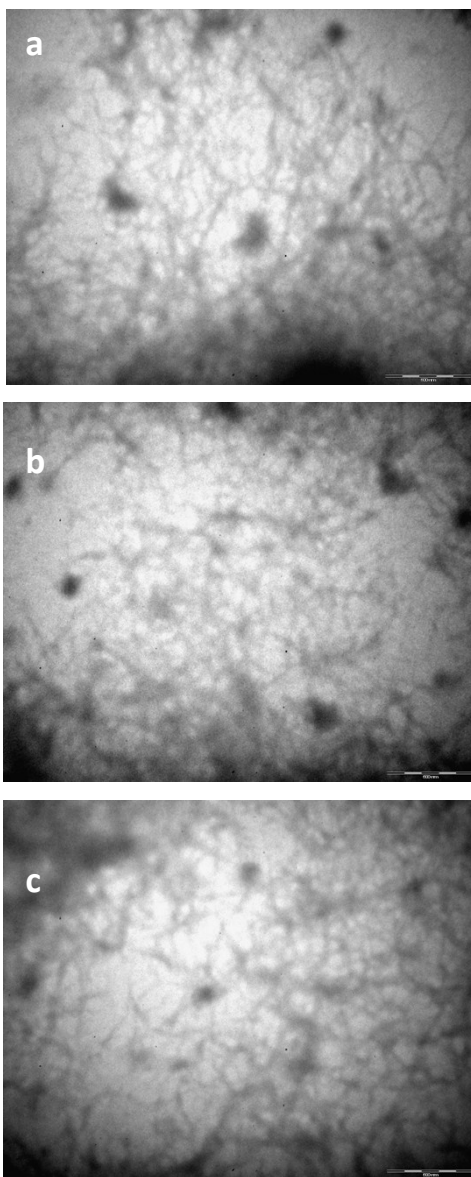


Figure S15 TEM images of CST-OG1 hybrid in the presence of DAE a) before and b) after photoswitching experiment. c) Morphology control of a Xerogel of OG1 after irradiation (conditions of the photoswitching experiment).

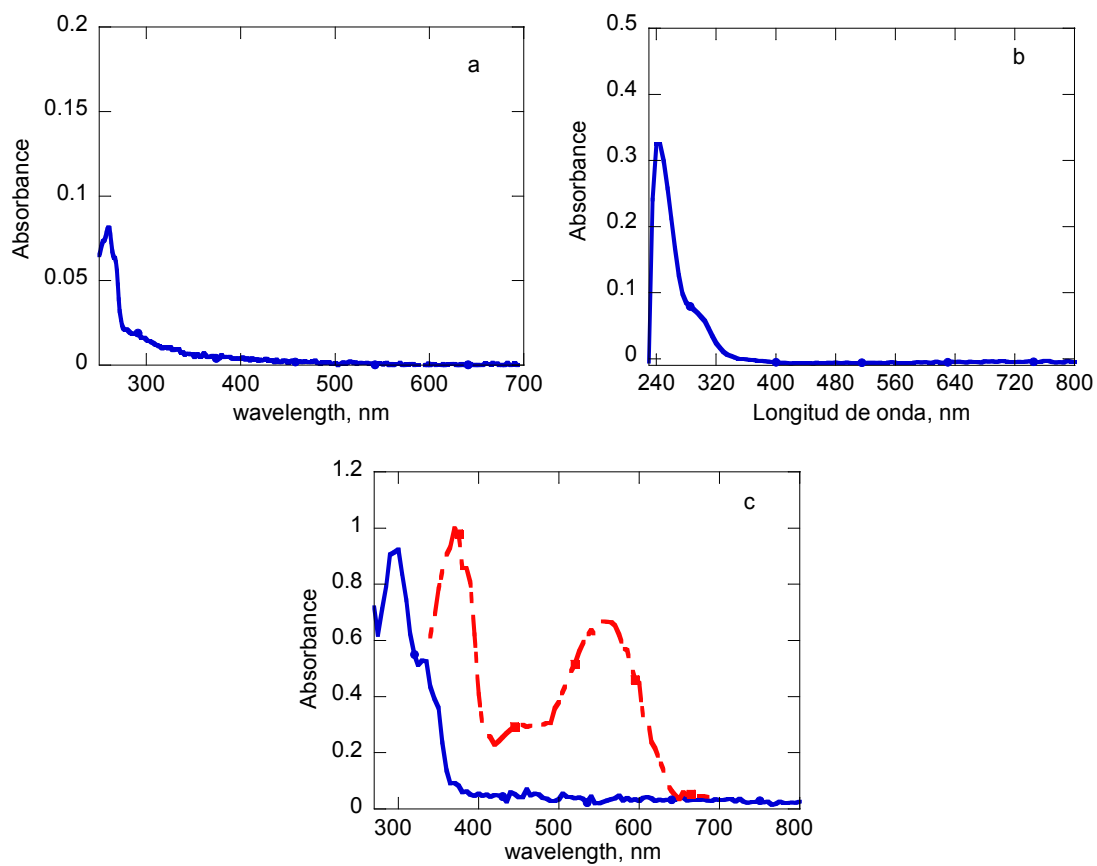


Figure S16 UV-visible absorption spectra of a) TOPO in *n*-hexane, b) OG1 in dichloromethane and c) OPEN form of DAE (blue line) and CLOSE form of DAE (red line) in dichloromethane.

1. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chemistry of Materials*, 2003, **15**, 2854-2860.