ELECTRONIC SUPPORTING INFORMATION (ESI)

QDs decorated with thiol-monomer ligands as new multicrosslinkers for the synthesis of smart luminescent nanogels and hydrogels.

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Table S1. Photophysical properties[a] and nanoparticle sizes[b] of the hybrid nanoparticles in dichloromethane solution.

Entry	sample	$\lambda_{abs.max}$ (nm)	$\lambda_{em.max.}$ (nm)	Φ_F	$^c\Phi_{F\ rel.}$	Size (nm)
1	QD_1	560.9	570.5	0.031	1	3.3*
2	QD_1@AcSEMA	558.9	568.6	0.209	6.7	3.4 ± 0.9
3	QD_2	507.9	520.8	0.015	1	2.5*
4	QD_2@AcSEOMA	474.8	510.0	0.032	2.1	7.2 ± 1.0

[a]Maximum absorption wavelength ($\lambda_{abs.max}$), maximum emission wavelength ($\lambda_{em.max}$), emission quantum yield taking as reference DCMSP in ethanol (Φ_F= 0.435) for QD_1 [1] or to fluorescein in basic water (Φ_F= 0.92) for QD_2[2], [c]emission quantum yield related ($\Phi_{F\ rel.}$) to the parent CdSe@TOPO (QD_n) ($\Phi_{F\ rel}$). [b]Measured by dynamic light scattering (DLS) in diluted dichloromethane solutions. *Nanoparticle sizes estimated as a function of their photophysical properties as it was described by Yu *et al.*[3].

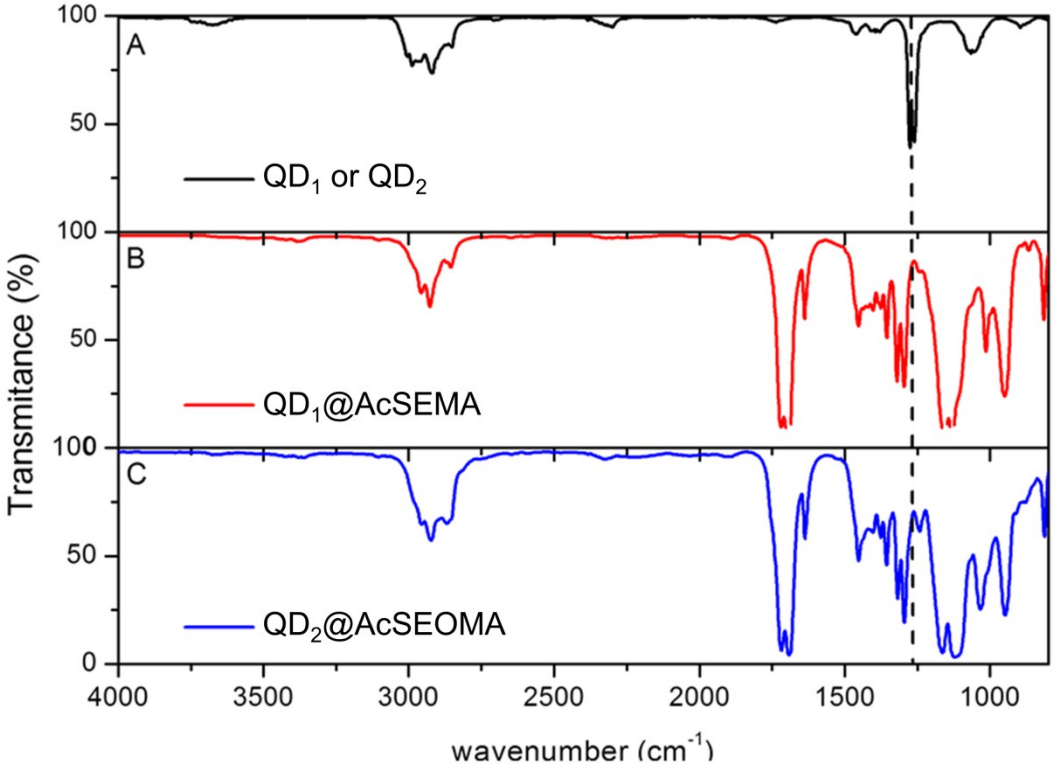

Figure S1. FTIR-ATR spectra of A) QD_1@TOPO or QD_2@TOPO. B) QD_1 after ligand exchange with AcSEMA and dialysis. C) QD_2 after ligand exchange with AcSEOMA and dialysis.

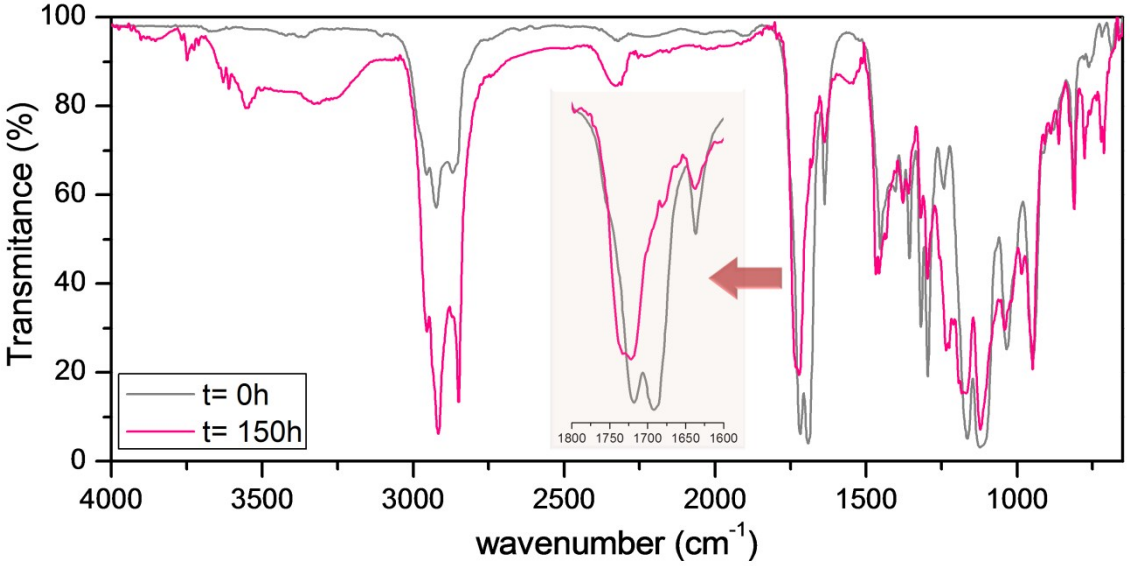

Figure S2. FTIR-ATR spectra corresponding to QD_2@TOPO in the presence of AcSEOMA before hydrolysis (grey line) and QD_2@SEOMA hybrids, after 150h of hydrolysis reaction, in the presence of sodium methoxide (pink line).

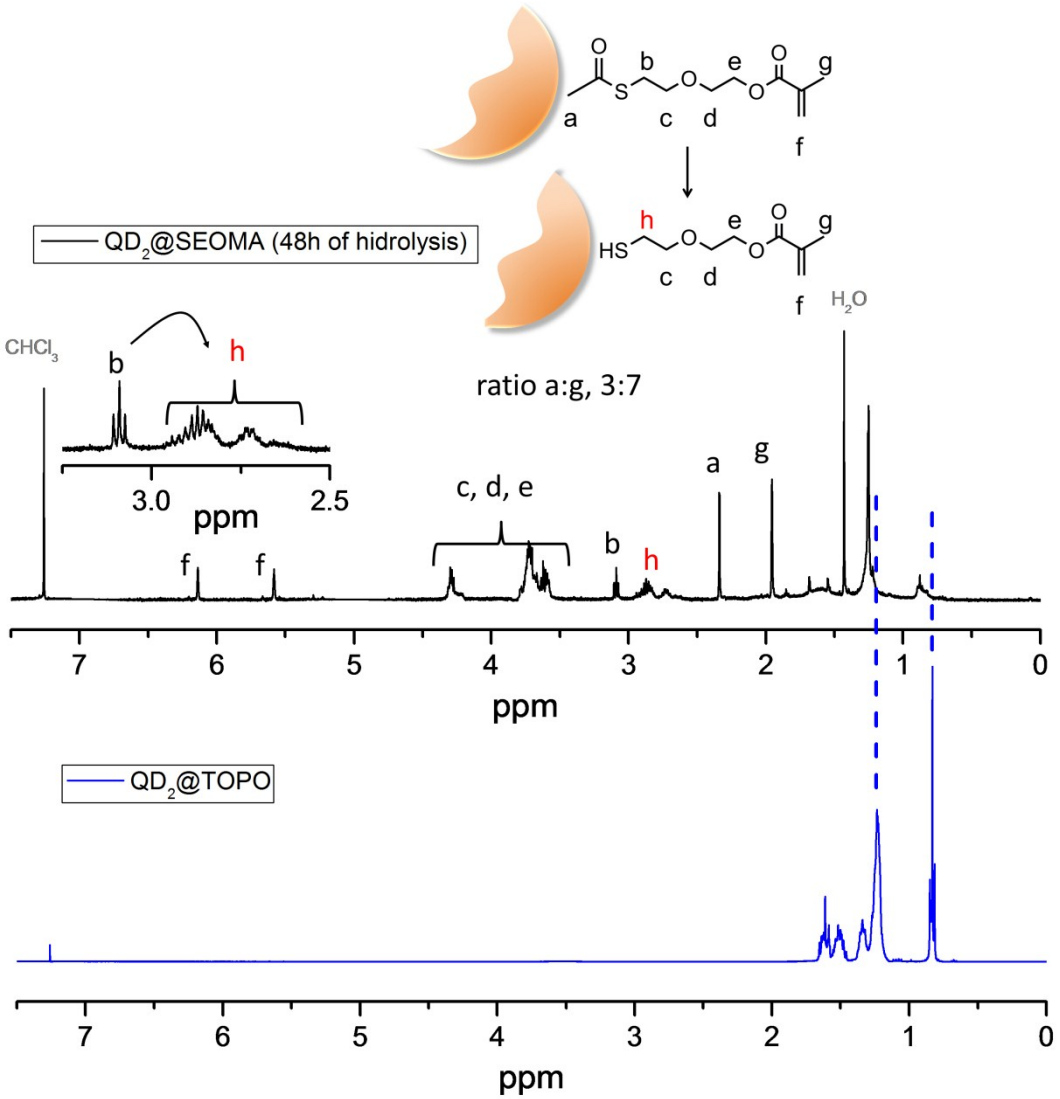

Figure S3. ^{1}H-NMR of QD_2@SEOMA sample after 48h of hydrolysis where two species (AcSEOMA and SEOMA) linked to the nanoparticle surface coexist. The ^{1}H-NMR of pristine QD_2@TOPO is included at the bottom to check the efficiency of the ligand exchange reaction.

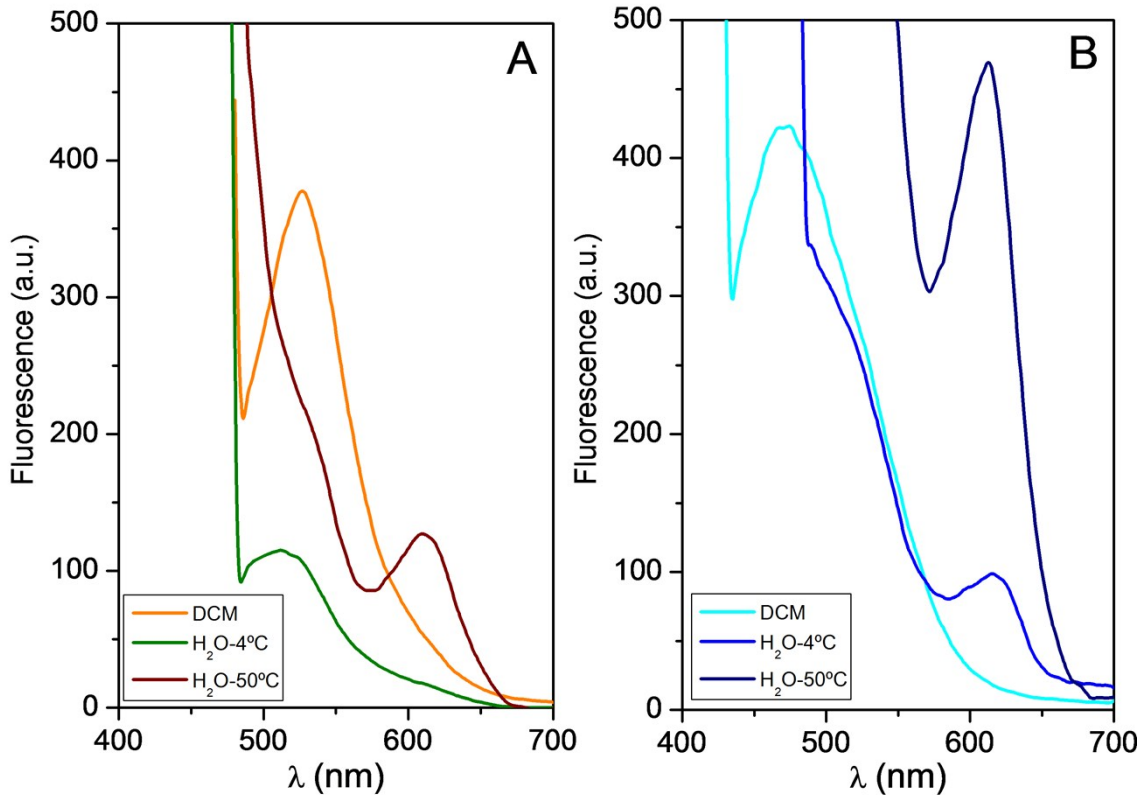

Figure S4. Fluorescence spectra of hybrid QD@nanogels based on A) SEMA and B) SEOMA in dichloromethane (DCM) solutions and in water solution at pH 7.0 at two temperatures (4°C and 50°C), below and above the collapsing temperature of the nanogels. (All the emission spectra of samples were recorded under 450 nm of wavelength excitation except QD@SEOMA@pMEO$_2$MA nanogels in DCM which was excited at 400 nm due their blue shift emission).

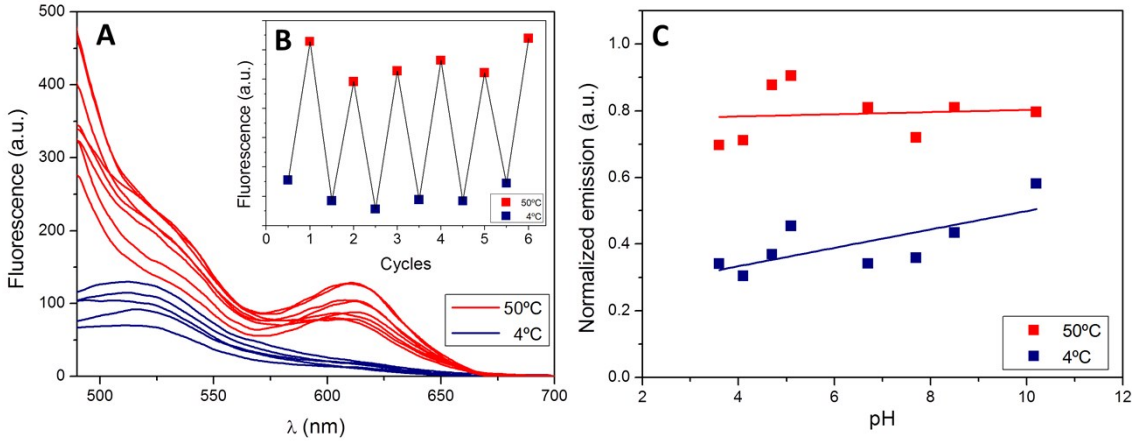

Figure S5. A) Fluorescence emission spectra evolution of hybrid nanogels of QD@SEMA@pMEO$_2$MA in water solution at pH 7.0 recorded after heating the sample above (50°C) and below (4°C) the Tc for different and B) consecutive cycles. C) Evolution of the normalized emission fluorescence with pH and temperature.

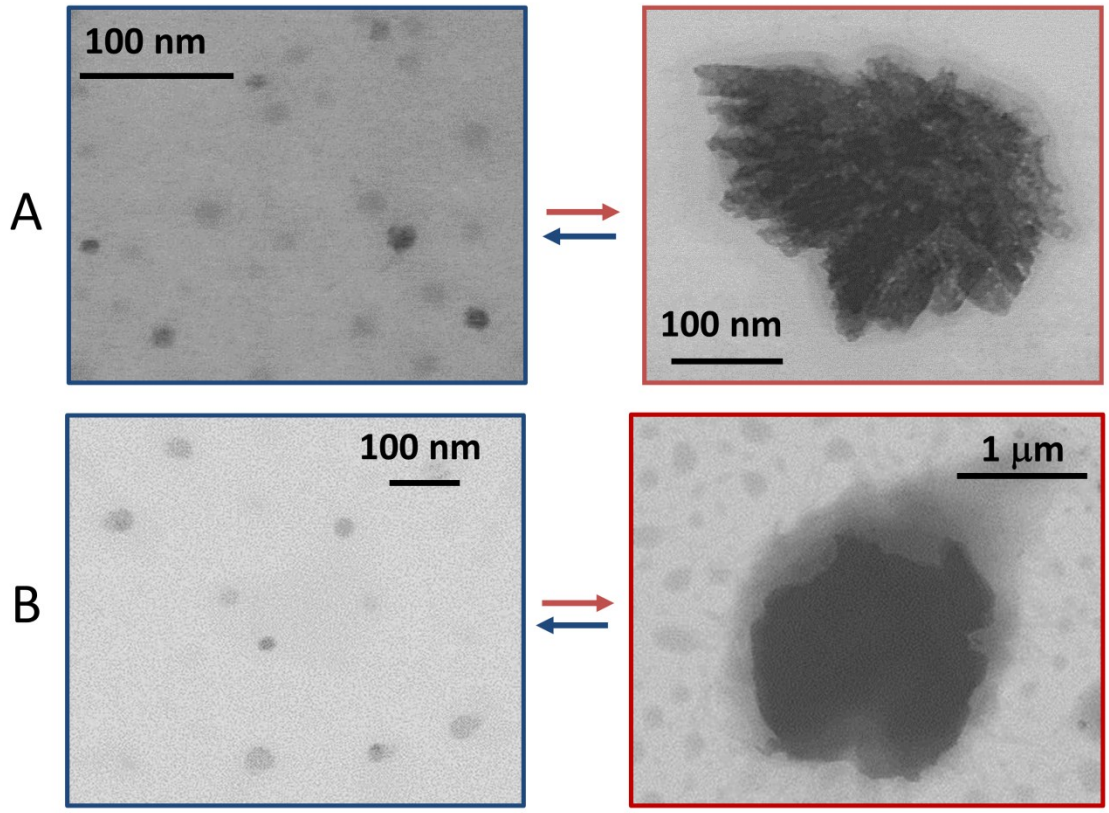

Figure S6. Representative sTEM images at 4ºC and 50ºC from water solutions of A) QD@SEMA@pMEO$_2$MA at pH 7 and B) QD@SEOMA@pMEO$_2$MA nanogeles at pH 9.

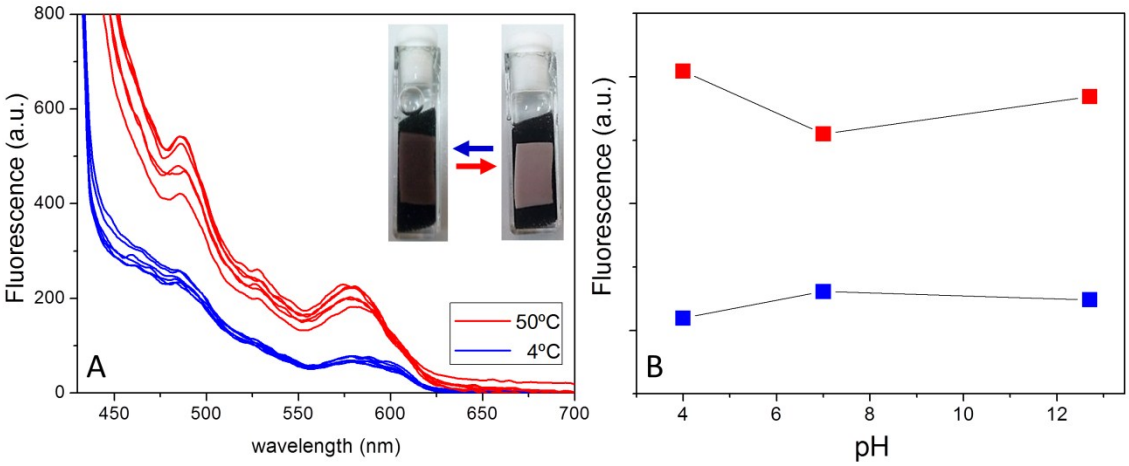

Figure S7. A) Evolution of the fluorescence emission spectra of the hybrid hydrogels of QD@SEMA-pMEO$_2$MA-2 wt% soaked in phosphate buffer at pH 4 during different and successive cycles of cooling (4°C) and heating (50°C). *Inset*: real photograph of the same hydrogel recorded at the two temperatures is included. B) Variation of the normalized fluorescence emission as a function of the pH and temperature of the medium.

Table S2. Equilibrium swelling (Q_∞) of hydrogels based on MEO_2MA crosslinked with different amounts of hybrid nanoparticles of QD@SEMA or QD@SEOMA obtained in water solutions at pH 7 and 4°C.

Hydrogel	Crosslinker amount (wt%)	Q_∞ (%)
QD@SEMA-$pMEO_2MA$	1	398
	2	308
	3	-
QD@SEOMA-$pMEO_2MA$	1	504
	2	737
	3	719

References

1. K. Rurack and M. Spieles, *Analytical Chem.*, 2011, **83**, 1232-1242.
2. D. Magde, R. Wong and P. G. Seybold, *Photochemistry and Photobiology*, 2002, **75**, 327-334.
3. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.