Supplementary Information for:

Quantum dots-imprinted polymers with size and shell-selective recognition properties

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Supplementary Methods

Materials

Chemicals. Methacrylic acid (MAA, 86.6g/mol) and ethylene glycoldimethacrylate (EGDMA, 198.22g/mol), obtained from VWR, were used without purification. The azobisisobutyronitril (AIBN, 164.21 g/mol), acetic acid and methanol were obtained from Sigma-Aldrich. 4-Aminothiophenol was purchased from Alfa Aesar. The CdSeTe/Zns core-shell organic and carboxylic quantum dots, with emission wavelength centered around 700 and 800 nm were purchased from life technologies. The poly(metyl methacrylate) (PMMA) rigid substrates were obtained from Weber Métaux Paris (~1 mm-thick).

Preparation of bulk QD@IPs. For the preparation of the homogenous imprinting solution, MAA (1.2 mL) as a functional monomer and carboxylic QDs (180 μL) as the template were added to 0.9 mL ethanol to allow the formation of the pre-polymerisation mixture. After 3 min, 0.06mL of EGDMA and 0.02g of AIBN were added in the mixture. The obtained solution was degassed by argon bubbling for 5 min before exposure to UV light at 365nm. After polymerization, a bulk QD@IPs macrogel disk was obtained, with a diameter of 20 mm and a thickness of *ca.* 4 mm. Bulk QD@IPs were kept in distilled water for 2h to remove the excessive amounts of unreacted monomers and free QDs. The reference non-imprinted polymer NIP was prepared similarly without the addition of the QDs template.

Preparation of QD@IP films on PMMA. The rigid PMMA surfaces were cut into slides of 2 cm×2 cm, then rinsed under sonication in methanol, water and methanol, in order to remove the organic residues and all impurities on the surface. 30μl of the prepolymerization mixture was then dropped on the clean PMMA surfaces. These substrates were then exposed to UV light in glass vessel, at room temperature for 2 hours to give a film of QD@IPs deposed in PMMA. The extraction of QDs was achieved in an aqueous solution of 4M acetic acid during 5h. The reference non-imprinted polymer NIP was prepared similarly without the addition of the QDs template. For the rebinding step, the surfaces were incubated in different concentrations of QDs for 20 min, then thoroughly washed with Milli-Q water using laboratory shaker for 20 min. Photopolymerization reaction was carried out in the ultraviolet processeur Spectrolinker XL 1500UV. It is a commercial reactor equipped with 6 tubes (8w). The wavelength is 365 nm and the intensity corresponds to 17.6mW/ cm^2.

Functionalization and characterization of QD$_{NH2}$. To obtain the amine-coated QDs (QD$_{NH2}$), most of the trioctylphosphine oxide (TOPO) was removed from the surface of the commercially available QDs. For this, the QDs were precipitated by addition of methanol and separated by centrifugation[4]. This step was repeated three times. Then, 1 mg of 4-aminothiophenol was added to the QDs dispersed in 1 mL of chloroform, and the resulting mixture was stirred for 24h at room temperature. Afterward, 0.4 mL of chloroform was added to the precipitate, followed by a centrifugation to remove the unreacted aminothiophenol. This process was repeated three times to obtain QD$_{NH2}$. Figure S0 (i) displays the ATR-FTIR spectra of QDs before precipitation (curve a)

and after immobilization of 4-aminothiophenol (curve b). The latter exhibits two bands at 1618 et 1283 cm^{-1} characteristic of the deformation mode of N-H in NH$_2$ and C-N in aromatic vibration[5], confirming the immobilization of amino groups. The strong band centered at 781cm^{-1} is characteristic of out-of-plane NH$_2$ bending[6]. In addition, the fingerprint of aromatic group, characteristic of C=C bond, was observed at 1593 cm^{-1}. Figure S0 (ii) displays the photoluminescence spectra of QD$_{NH2}$.
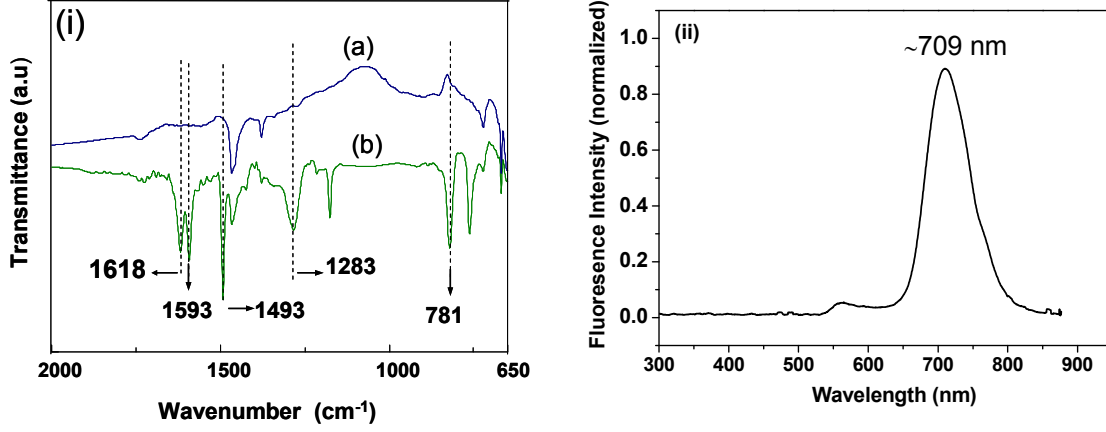
Figure S0. (i) ATR-FTIR spectra of organic QDs (a) after cleaning in methanol and (b) after immobilization of amino functions (QD$_{NH2}$) **(ii)** Fluorescence spectrum of QD$_{NH2}$.

Measurements of the equilibrium swelling ratio. The equilibrium swelling ratio were measured on non-imprinted and imprinted hydrogels, in distilled water at pH= 7 at room temperature, using the following relation (1) and (2):

$$v_{2r} = \left(1 + \frac{\left[\frac{m_r}{m_d} - 1\right]\rho 2}{\rho 1}\right)^{-1} \tag{1}$$

$$v_{2s} = \left(1 + \frac{\left[\frac{m_s}{m_d} - 1\right]\rho 2}{\rho 1}\right)^{-1} \tag{2}$$

Where m_r and m_d are the weights of the hydrogels after preparation (relaxed state) and after drying, respectively, and ρ_1 and ρ_2 are the densities of the solvent (ρ_1 = 1 for water) and polymer network (ρ_2 = 1.33 for PMAA), respectively. Here, m_s is the weight of the swollen hydrogel at equilibrium. The weight of the hydrogels was taken over a single-pan digital microbalance (sensitive to ± 0.01 mg). Finally, v_{2r} corresponds to the polymer volume fraction in the gel immediately after preparation (relaxed state), and v_{2s} to the polymer volume fraction of the swollen gels (swollen state).

Estimation of the mesh size. The structural parameter used to describe the size of the recognitive pores is the correlation length ξ[1] (or mesh size) which corresponds to the linear distance between two adjacent cross-links and was calculated using the following relation:

$$\xi = v_{2s}^{-\frac{1}{3}} \left(\frac{2C_n \bar{M}_c}{M_r}\right)^{1/2} \iota \tag{3}$$

In this expression, C_n is the Flory characteristic ratio[2] equal to $C_{n(PMAA)}$ = 14.6. $\bar{M}_c$ is the number average molecular weight between cross-links and M_r is the molecular weight of the repeating units in the polymer chain. l is the length of the bond along the polymer backbone (for methacrylates polymers, l = 1.54 Å). $\bar{M}_c$ can be obtained from the following expression:

$$\bar{M}_c = -\frac{\left(1 - \frac{2}{\varphi}\right)V_1\rho 2 \, v_{2r}^{\frac{2}{3}} \, v_{2s}^{\frac{1}{3}}}{ln\,(1 - v_{2s}) + v_{2s} + \chi v_{2s}^{2}} \tag{2}$$

where V_1 is the molar volume of the solvent, $V_1 = 18$ cm^3 moL^{-1}; φ is the number branches originating from a cross-linking site, $\varphi = 3$; and the Flory interaction parameter, $\chi = 0.54$.

The results of these calculations are presented in Table 1 and are quite revealing of the modifications of porosity induced by the imprinting process, with ξ values noticeably higher for QDs-free QD@IPs as compared to NIPs.

**Table 1.** Structural Parameters of the QD@IP$_S$ and NIP Hydrogels

| Hydrogels	v_{2r}	v_{2s}	$\bar{M}_c$ (g mol^{-1})	ξ (Å)
QD@IP$_S$	0.24	0.17	1980	71
NIP	0.45	0.23	1060	48

Instrumentation

Fluorescence measurements. Fluorescence spectra were carried out using a LY473III-100 laser with a wavelength of 473 nm, a power of 100 mW and an excitation spot size of about 4 mm on the sample. The fluorescence intensity was detected in the direction perpendicular to the PMMA plates coated by the QD@IPs and NIP, with a spectrometer (Avantes AVS –S2000). The spectral resolution was 2 nm. All spectra are the result of the average of seven measurements on different areas of the sample.

FT-IR Spectroscopy Attenuated Total Reflection- ATR measurements. ATR-FTIR spectra were recorded with a germanium ATR accessory (Jasco ATR PR0470-H) using JASCO FT/IR-6100 Fourier Transform Infrared Spectrometer, equipped with MCT (mercury−cadmium−telluride) detector. Each spectrum results from the accumulation of 1000 interferograms with a 4 cm^{-1} resolution. The spectrometer is permanently purged with dry and low carbon dioxide before recording the spectra.

Supplementary figures
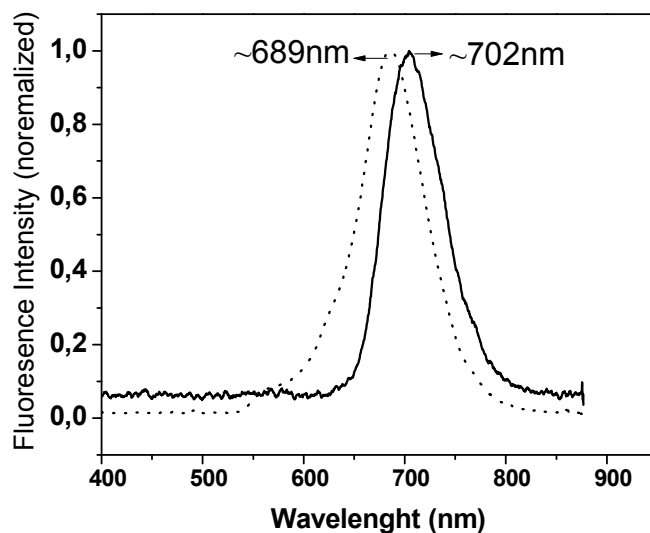
Figure S1. Fluorescence spectra of carboxylic QDs dropped on a glass plate (full line) or trapped in the polymer matrix film (dotted line).
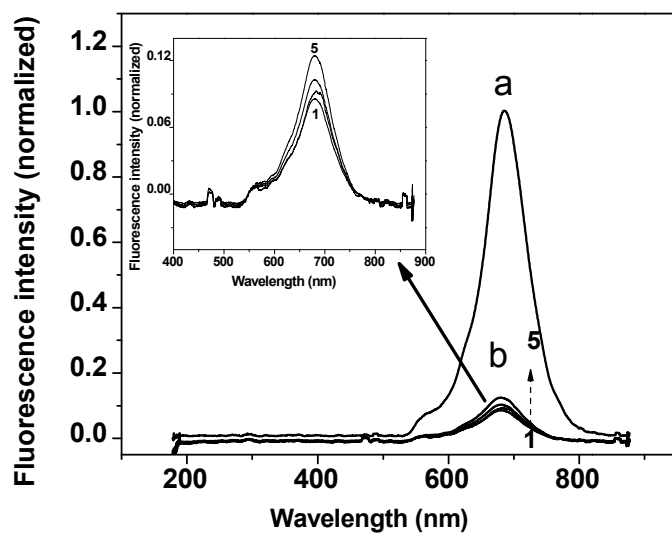
Figure S2. Normalized Fluorescence spectra of QD@IPs films (a) before extraction of QDs (b) after extraction of QDs. The spectra marked with numbers from 1 to 5 correspond to the results of five successive uptake-extraction cycles.
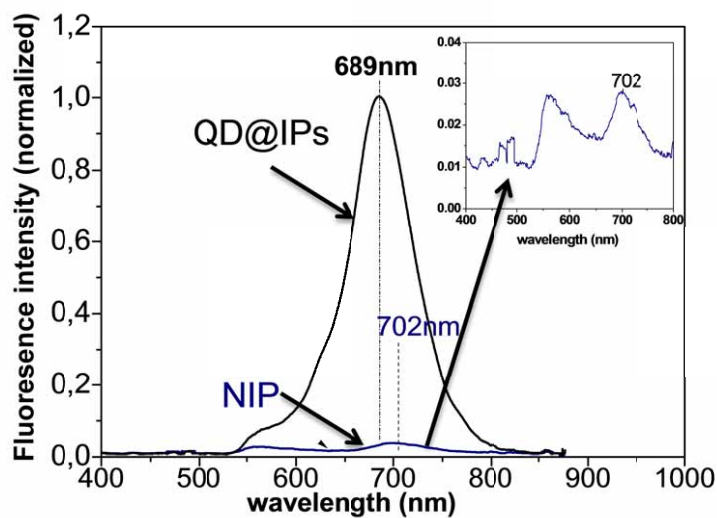
Figure S3. Normalized fluorescence spectra of QD@IPs and NIP films after incubation with QDs ([QDs] = 1µM).
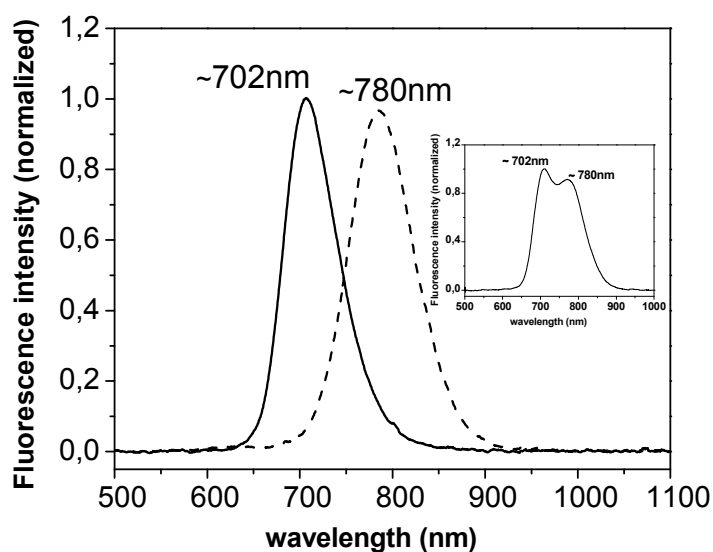
Figure S4. Fluorescence spectra of QDs (full line) and QD$_{size}$ (dashed line). In insert is shown the corresponding fluorescence spectrum of a mixture (50%/50%) of QDs and QD$_{size}$ dropped on a glass plate.
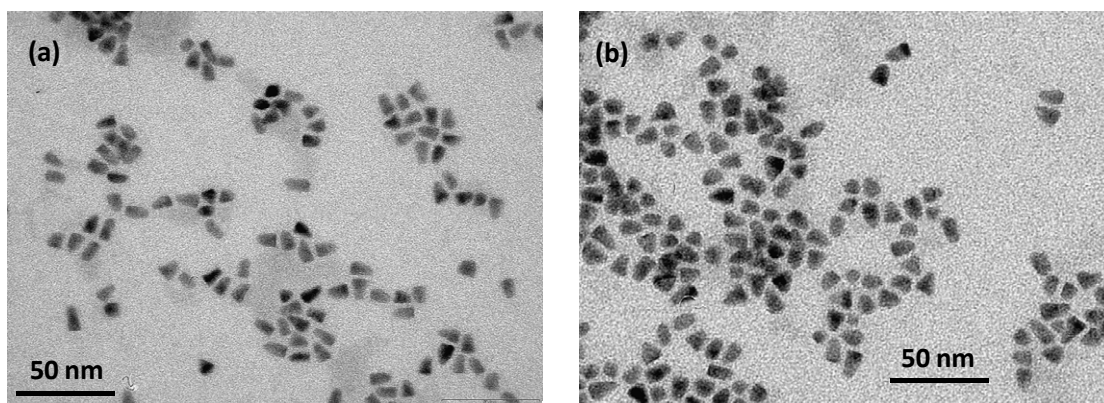
Figure S5: TEM images of (a) QD$_{size}$ and (b) QDs.

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