

CdTe Nanocrystals Capped with a Tetrazolyl Analogue of Thioglycolic Acid: Aqueous Synthesis, Characterization, and Metal-Assisted Assembly

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ABSTRACT A novel ligand, 5-mercaptomethyltetrazole, is applied to the direct colloidal synthesis of highly luminescent (quantum yield of up to 60%) water-soluble CdTe nanocrystals. In the synthesis the 5-mercaptomethyltetrazole behaves analogously to the widely used thioglycolic acid, providing the additional advantage of solubility of the resulting nanocrystals in methanol. Moreover, the 5-mercaptomethyltetrazole-capped nanocrystals possess the unique ability to reversibly form fine 3D networks (hydrogels) upon the addition of metal salts.

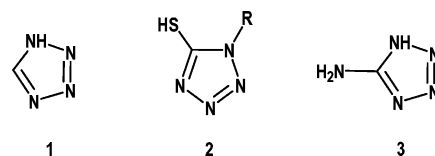
KEYWORDS: CdTe nanocrystals · aqueous synthesis · 5-mercaptomethyltetrazole · reversible 3D assembly

Tetrazoles are five-membered heterocyclic compounds containing four nitrogen atoms in the cycle and having the highest content of nitrogen among all organic substances, for example, 80 wt % for the simple tetrazole **1** (see Scheme 1). The presence of several nitrogen atoms of different types (pyrrole- and pyridine-like atoms) in the tetrazole ring determines their interesting physical and chemical properties.^{1,2} In spite of large positive enthalpies of formation, most of them are thermodynamically stable in the condensed phase, relatively weakly sensitive to impact and friction. Their donor nitrogen atoms can bind to various metal ions leading to stable complexes with diverse coordination modes of the heteroring which can be diversified by functional substituents. For this reason some tetrazoles are widely used in the surface treatment of various materials, in particular, 1-monosubstituted 5-thiotetrazoles **2** are used as corrosion inhibitors and photographic stabilizers.³ Most tetrazoles show high thermal stability below 200 °C while decompos-

ing at higher temperatures under formation of a high proportion of gaseous products.

This combination of properties allows the proposal of tetrazole derivatives as coating agents which can be controllably and completely removed from the different surfaces upon heating. In particular, they are attractive for the preparation of “naked” (organic surfactant free) nanostructures with high electroconductivity and catalytic activity.^{4–6} Recently, CdS and Au nanocrystals (NCs) capped with the 5-thiotetrazoles **2** (R = alkyl, phenyl) have been synthesized.^{7,8} It was shown that the ligand molecules can be removed from the surface of the NCs upon heating to ~250 to 270 °C. Moreover, CdS NCs capped with the 5-aminotetrazole **3** have been prepared and found to be successfully sintered into a continuous semiconductor thin film at temperatures as low as 230 °C.⁹

In addition, the tetrazol-5-yl group, –CN₄H, is a nonclassical isostere for the carboxylic group, –COOH. These functional groups have similar physicochemical properties and may be interchangeable, resulting in similar biological properties.¹⁰ Taking into account the above-mentioned isosterism, we decided to study novel tetrazole-based ligands, namely the 5-mercaptomethyltetrazole



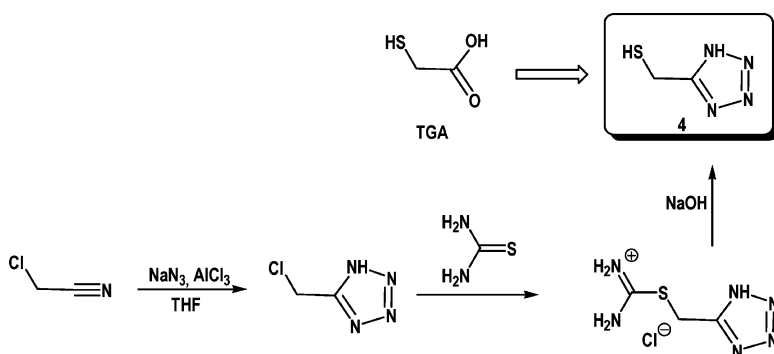
Scheme 1. Molecular structures of tetrazole (**1**) and its derivatives (**2**, **3**).

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Scheme 2. Synthesis of 5-mercaptomethyltetrazole.

(5-HSCH₂Tz) **4** (see Scheme 2) as a substitute of thioglycolic acid (TGA) which is widely used as a capping agent in the aqueous synthesis of colloidal semiconductor NCs such as CdTe, Cd_{1-x}Hg_xTe, ZnSe, and Zn_{1-x}Cd_xSe.^{11–15}

Here we present an aqueous synthesis and characterization of CdTe NCs capped with the tetrazolyl analogue of TGA. Moreover, a simple type of controllable 3D assembly of synthesized NCs into gel-like networks initiated by metal ions is reported.

RESULTS AND DISCUSSION

The size of the CdTe/5-HSCH₂Tz NCs is controlled by the duration of reflux and can easily be monitored by absorption and photoluminescence (PL) spectroscopy (see Figure 1). Five min after the beginning of the reflux a clearly resolved absorption maximum of the first electronic transition of the CdTe NCs appears at ~470 nm. These NCs possess green band-edge emission with a PL maximum at ~510 nm. These maxima are shifted to ~590 nm in absorption and to ~610 nm in PL spectra after 92 h of reflux, indicating growth of NCs. As is seen from Figure 1, some absorbance spectra show quite well-resolved shoulders corresponding to second and even third electronic transitions, whereas

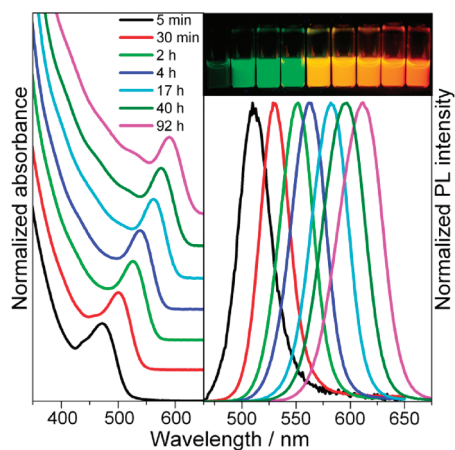


Figure 1. Absorption and PL ($\lambda_{\text{ex}} = 450$ nm) spectra of CdTe/5-HSCH₂Tz NCs taken as prepared. The inset shows a photograph of the photoluminescence color change of the NC colloid (under UV lamp, $\lambda_{\text{ex}} = 365$ nm) during the synthesis.

usually water-based CdTe NCs exhibit only the first one. The appearance of more than one electronic transition in the absorption spectra is clear evidence for good monodispersity and crystallinity of the NCs obtained. One more proof of their good quality is the high photoluminescence quantum yield (PL QY) which amounts to 60% for the as prepared CdTe NC colloid after 92 h of reflux.

The PL bands are sufficiently narrow (full widths at half-maximum are in the range of 32–47 nm) indicating again the relatively narrow size distribution of the NCs. The Stokes shift lies in the range of ~20 to 30 nm and is very similar to that of TGA-capped NCs. According to the sizing curve for thiol-capped CdTe NCs,¹² the average size of the CdTe/5-HSCH₂Tz nanoparticles increases during the synthesis from 2.1 to 3.3 nm. The crystallinity of the nanoparticles and their quasi-spherical shape are evidenced from high resolution transmission electron microscopy (TEM) observations (Figure 2). X-ray diffraction (XRD) analysis shows that the NCs belong to the cubic (zinc blende) structure. However, the positions of the XRD reflexes are intermediate between the values for the cubic CdTe and the cubic CdS phases (Figure 3). This fact might be explained by the incorporation of sulfur into the growing NCs due to partial hydrolysis of the thiol, which was earlier observed in the synthesis of CdTe NCs capped with TGA.^{11,12} Thus, 5-HSCH₂Tz demonstrates behavior very similar to TGA in the synthesis of CdTe.

Colloidal solutions of CdTe NCs capped with tetrazole **4** are stable and for more than a year do not

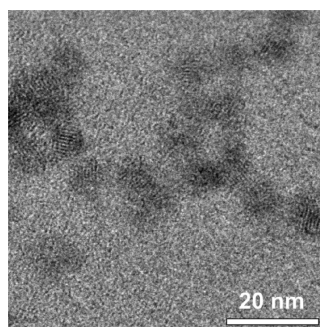


Figure 2. High-resolution TEM image of CdTe/5-HSCH₂Tz NCs after 92 h of growth.

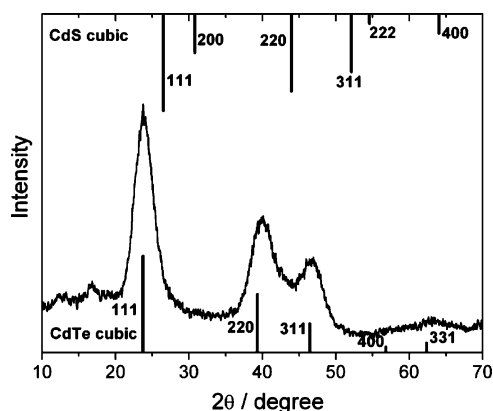


Figure 3. XRD pattern of CdTe/5-HSCH₂Tz NCs. The line diffraction patterns show the bulk cubic CdTe and CdS reflexes (JCPDS cards 15-770 and 10-454, respectively).

change their optical properties being kept under air in the dark. The NCs can be precipitated out of solution by first concentrating the solution followed by the addition of 2-propanol. In contrast to CdTe NCs capped with TGA the NCs obtained here are soluble in methanol. This is a very important property since it extends the options for further processing of the NCs, for example, the formation of uniform thin films by casting or spin-coating or for the fabrication of nanocomposites with silica, alumina, *etc.* materials commonly processed by sol-gel technology from short-chain alcohol dispersions.

Currently there is considerable interest in assembling NCs in one way or the other. The assembly approaches existing provide possibilities to form 1D, 2D, and 3D nanostructures which are attractive for use in optoelectronics and photovoltaics.¹⁶ Gels and aerogels assembled from colloidal light-emitting NCs represent an emerging class of materials bridging the nano- and the macro-world.^{17–19} Recently, the photochemically assisted preparation of highly porous gels and aerogels of aqueous CdTe NCs capped with TGA was reported.²⁰ On the other hand, the use of coordinating ligands opens the possibility of metal-assisted assembly as was shown in an example of gold nanoparticles functionalized with pyridine derivatives.^{21,22}

Applying 5-mercaptomethyltetrazole as a capping agent for CdTe NCs creates a quick and reproducible approach for the preparation of NC gels. We found that the addition of an aqueous solution of cadmium acetate to the CdTe/5-HSCH₂Tz NC colloids leads to the formation of hydrogels (Figure 4). Hydrogels are formed on the bottom of the flask within relatively short times (from a few seconds up to 2–3 weeks, depending on the amount of cadmium acetate used). This method offers a facile and highly reproducible interconnection of nanoparticles leading to a multibranching network. Moreover, the technique developed does not involve any sophisticated processing like chemical destabilization of

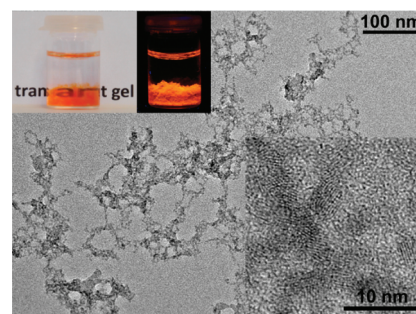


Figure 4. TEM and HRTEM images of a CdTe NC hydrogel fragment dried on a TEM grid. Inset: a typical true-color image of a CdTe hydrogel under day light (left) and under UV lamp excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$) (right).

the initial colloid or its photochemical treatment. Our approach is easily up-scalable and provides the option of the production of large amounts of gels/aerogels. The 3D structures obtained are optically transparent and maintain the emission properties of the original nanocrystals (see Figure 4, inset). The HRTEM image clearly shows the random orientation of the NCs and their networking in the gel structure. Owing to the retention of the crystalline lattices of single NCs the resulting network still keeps the optical and electronic properties of its building blocks.²³

Absorption and PL spectra of the original NC colloid and of the hydrogel formed are shown in Figure 5a. The position of the first absorption maximum of the gel is virtually unaltered compared to that of the initial colloid. At the same time, the PL maximum shifts for about 15 nm to longer wavelengths most probably because of energy transfer from smaller NCs (donors) to larger ones (acceptors), as also suggested by PL lifetime measurements (Figure 5b). The difference between the PL decays of the initial CdTe NCs and the hydrogel is clear: the emission of the hy-

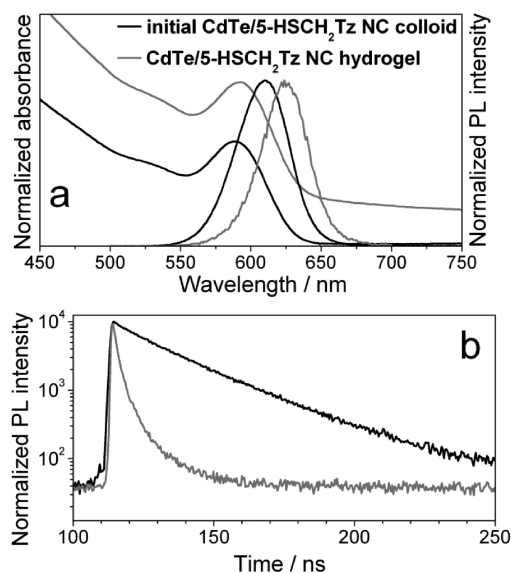
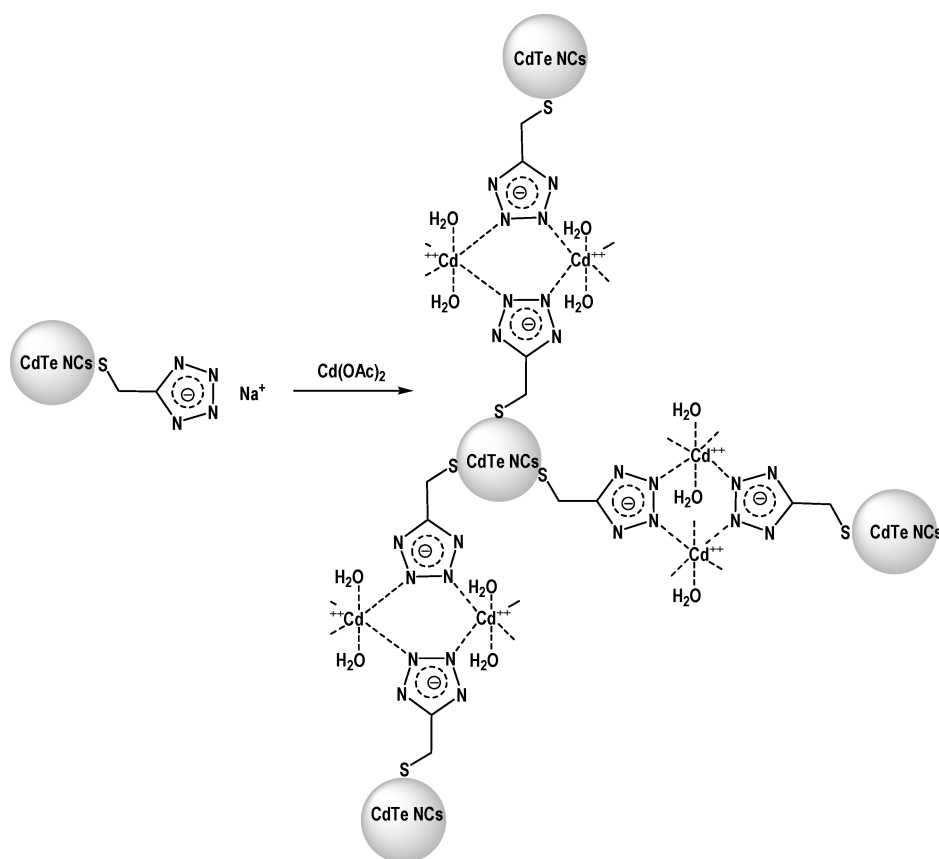


Figure 5. Absorbance and emission ($\lambda_{\text{ex}} = 450 \text{ nm}$) spectra (a) and PL decay ($\lambda_{\text{ex}} = 470 \text{ nm}$) curves (b) of the CdTe/5-HSCH₂Tz NC colloid and of the resulting hydrogel.



Scheme 3. Mechanism proposed for the gelation of CdTe/5-HSCH₂Tz NCs.

drogel decays much faster being accompanied by PL quenching. In this case, the formation of the 3D network leads to the appearance of additional channels for nonradiative deactivation through fast energy transfer analogous to that in clusters of CdTe NCs electrostatically bound by Ca ions.²⁴ The proximity of the nanoparticles incorporated into the network allows for both Förster and Dexter energy transfer mechanisms. An additional reduction of the emission lifetime by gelation of the NCs could be induced by enhanced energy transfer from originally luminescent quantum dots to “dark” ones which are commonly present in NC ensembles.²⁵

A most likely mechanism of the formation of the gel state is the cross-linking of individual NCs by the complexation of tetrazolate units with additional cadmium cations as is shown in Scheme 3. The tetrazolate anion which is generated by deprotonation of the 5-monosubstituted tetrazole (for tetrazole **1** pK_a = 4.8) under basic conditions is known to be a bridging ligand which can coordinate with metal ions *via* two, three, or four nitrogen atoms.^{3,26} It was shown that the coordination by the N2 and N3 atoms of the tetrazole ring is energetically favored.²⁷ Such bridging coordination is realized in various supramolecular systems²⁸ as well as in some polynuclear tetrazolate complexes (see ref 29 and the literature cited therein) causes the formation of

gels in aqueous solutions of La(III),³⁰ Fe(III), Rh(III), Co(II), and Ni(II)²⁷ 5-R-tetrazolates. In accordance to this we have also successfully used Ni²⁺ ions to initiate the gelation of 5-HSCH₂Tz-capped CdTe NCs (results not shown here). Interestingly, the formation of Cd²⁺-5-HSCH₂Tz polymeric complexes occurred already in the state of the preparation of the precursor solution which was indicated through a significantly increased viscosity of the reaction mixture. However, these complexes were decomposed upon the injection of H₂Te.

Attempting to prove the crucial role of the tetrazolate unit in the gelation process we repeated the synthetic procedure replacing the capping ligand, tetrazole **4** with TGA. However, no evidence was gained for gel formation of the CdTe/TGA NCs by the addition of Cd²⁺. Only some quenching of the PL was observed which previously was explained by energy transfer from smaller NCs to larger ones during their clustering (formation of small aggregates) initiated by divalent ions.^{24,31,32}

According to the proposed mechanism of gelation, the NC network formation should be reversible *via* the displacement of the tetrazole units from the coordination sphere of Cd²⁺ by even stronger ligands. In order to prove this concept we performed an experiment on the reversible gelation employing the strong complexation agent ethylenediaminetetraacetic acid (EDTA). As deduced from the inspec-

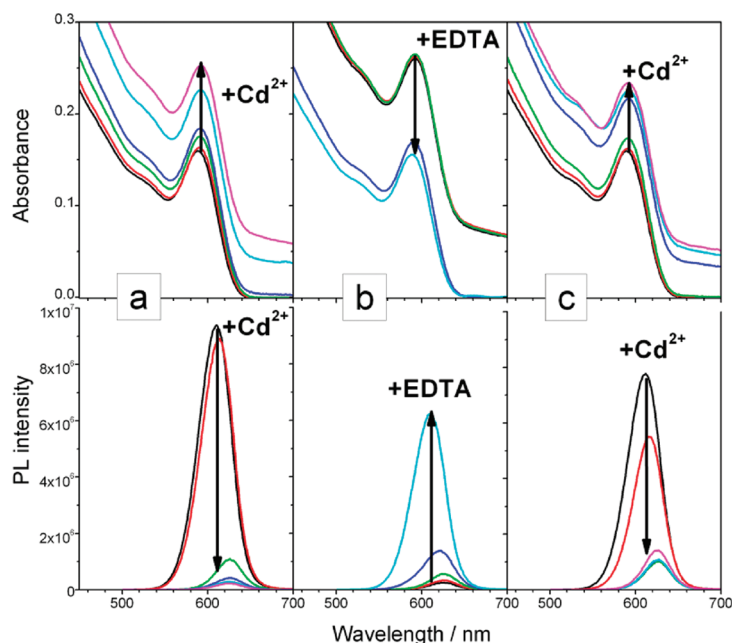


Figure 6. Absorbance (top panels) and emission (bottom panels) ($\lambda_{\text{ex}} = 450$ nm) spectra of CdTe/5-HSCH₂Tz NC colloid (the concentration of the NCs is 2×10^{-6} M) measured upon a stepwise addition of Cd²⁺ ions into the initial colloid (a) and into the by EDTA regenerated colloid (c), (b) NC solution regeneration after step a by the addition of EDTA. The arrows indicate increased Cd²⁺ or EDTA concentration ranging from 0 to 5×10^{-7} M.

tion of the absorption spectra presented in Figure 6b, the addition of the same amounts of EDTA as previously used for Cd²⁺ leads to the complete decomposition of the 3D structure: after the addition of the EDTA aliquot the scattering gel dispersion becomes absolutely transparent confirming the absence of networks or larger aggregates of nanoparticles. During the gelation the PL intensity decreases significantly (see Figure 6a and Supporting Information, Figure S11). The regeneration of the colloidal solution upon the addition of EDTA is accompanied by a recovery of the emission intensity of the system as well as a return of PL maximum to its origi-

nal position. A complete regaining of emission intensity however is not achievable since the equilibration requires quite long times and the interaction of the EDTA molecules with the NC surface may lead to the formation of additional trap states on the NC surfaces. Nevertheless, at least 80% of the initial emission intensity is retained after two cycles of gelation–regeneration. As demonstrated in Figure 6c, a further injection of Cd²⁺ ions again induces interconnection of the NCs. Thus, reversible gelation occurs owing to the selective competitive complexation of Cd²⁺ ions by ligands possessing different electron-donation abilities.

CONCLUSIONS

We have developed an aqueous synthesis of highly luminescent (quantum yield of up to 60%) CdTe NCs employing the novel ligand 5-mercaptomethyltetrazole as a stabilizer. Besides strong emission and superb stability the 5-mercaptomethyltetrazole-capped NCs are soluble in methanol which opens additional degrees of freedom in their processing. Using these NCs, a convenient and facile method of assembling of 3D nanostructures was developed. A driving force for the formation of a gel network is a cross-linking of individual NCs by complexation of the tetrazolate unit with cadmium(II) cations added. This approach allows the reproducible and easily upscaleable fabrication of 3D semiconductor networks maintaining the optical properties of the initial NCs. Moreover, the unique ability of reversible gelation was introduced by the competitive complexation of Cd ions by a stronger ligand such as EDTA. We believe that this technique will open ways for the controllable preparation of hybrid semiconductor1–semiconductor2 and semiconductor–metal 3D structures which may find applications as light-harvesting and energy-transporting systems in nanophotonics and photovoltaics.

EXPERIMENT

All the chemicals used were of analytical grade or of the highest purity available. All the solutions were prepared using Milli-Q water (Millipore) as the solvent.

Synthesis of 5-Mercaptomethyltetrazole. 5-HSCH₂Tz has been synthesized by the cycloaddition of sodium azide to chloroacetonitrile followed by the replacement of the chlorine atom with the hydrosulfide group under treatment with thiourea (see Scheme 2). The new ligand was characterized by elemental analysis, ¹H and ¹³C NMR spectroscopy (see Supporting Information). It presents a white solid melting at 69–70 °C. Differential scanning calorimetry and thermogravimetric analysis showed that 5-HSCH₂Tz undergoes decomposition above ~140 °C with two exothermic peaks at ~200 °C and ~230 °C (Supporting Information, Figure S12).

Synthesis of CdTe/5-HSCH₂Tz NCs. In a typical synthesis of CdTe NCs capped with tetrazole **4** 0.3 g (0.72 mmol) of Cd(ClO₄)₂ · 6H₂O was dissolved in 30 mL of water, and 0.21 g (1.81 mmol) of 5-mercaptomethyltetrazole was added under stirring, followed by adjusting the pH to 11.5 by dropwise addition of an appropriate amount of 1 M NaOH solution. The solution was placed into

a three-necked flask fitted with a septum and valves and was de-aerated by bubbling argon through for 30 min. Under stirring, H₂Te gas (generated by the reaction of 0.07 g (0.16 mmol) of Al₂Te₃ lumps with an excess amount of 1 N H₂SO₄) was passed through the solution (molar ratio of Cd²⁺/Te²⁺/5-HSCH₂Tz = 1.5/1/3.75) together with a slow argon flow for nearly 20 min. Further refluxing at 100 °C under open-air conditions led to the nucleation and growth of the NCs.

Preparation of CdTe/5-HSCH₂Tz NC Hydrogels and Their Degelation. Hydrogels were obtained by the addition of Cd(OAc)₂ aqueous solution (10^{-2} M) to the reprecipitated NC colloids (concentration of NCs is 2×10^{-6} M) at a molar ratio of NCs/Cd²⁺ = 2–8/1 depending on the time of gelation. Hydrogels were redissolved back to colloidal form by the addition of an aliquot of 10^{-2} M EDTA aqueous solution (pH 12 by addition of 1 M NaOH) equal to the Cd²⁺ concentration in the gelled sample.

Characterization of the NCs. UV–vis absorption spectra were recorded using a Cary 50 spectrophotometer (Varian Inc., Palo Alto CA). Fluorescence measurements were performed with a FluoroMax-4 spectrofluorometer (HORIBA Jobin Yvon Inc., Edi-

son, NJ). Time resolved PL spectra were measured on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc., Edison, NJ) using a 200 ps pulsed laser diode emitting at 470 nm. All spectra were measured at room temperature. The PL QY of the NCs was evaluated according to the procedure described in details recently³³ using Rhodamin 101 (PL QY = 96%) and Rhodamin 6G (PL QY = 95%) as reference standards.

Samples for TEM were prepared by dropping diluted NC colloids or gel dispersions in methanol onto copper grids coated with a thin Formvar-carbon film with subsequent evaporation of the solvent. TEM imaging was carried out on a Tecnai T20 microscope operating at 200 kV (FEI).

Powder XRD measurements were performed with a D5000 diffractometer (Siemens, Munich, Germany, Cu K α radiation). Samples for XRD were obtained by placing finely dispersed powders of NCs on a standard Si wafer.

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Supporting Information Available: Detailed synthesis protocols and characterization of 5-mercaptopethyltetrazole, photograph of an initial CdTe/5-HSCH₂Tz NC colloid, hydrogel dispersion, and degelated colloid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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