

# Fabrication and Luminescence of Designer Surface Patterns with $\beta$ -Cyclodextrin Functionalized Quantum Dots *via* Multivalent Supramolecular Coupling

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Host–guest molecular interactions, well-known in the field of molecular biology, have been explored for supramolecular assembly of synthetic molecular and nanoscale components to obtain functional nanostructures.<sup>1–3</sup> The prerequisite for the assembly is that the constitutive building blocks have the structurally defined ability for molecular recognition. Directed host–guest assembly on surfaces allows one to build up hierarchical structures and integrate them into devices.<sup>3–6</sup> Preparation of well-defined surface assemblies was demonstrated for molecules,<sup>7,8</sup> dendrimers,<sup>9–11</sup> nanocolloids,<sup>12–14</sup> and proteins.<sup>6,15</sup> Host–guest interactions are reversible, either upon addition of guests (hosts) having higher binding constant to hosts (guests),<sup>16–18</sup> or by chemical or electrochemical reactions in the host–guest couples.<sup>10,19</sup> Host guest chemistry also offers the possibility for error correction.

Assembly of quantum dots (QDs) on surfaces is primarily explored in the context of their applications in optoelectronics<sup>20–22</sup> and sensing.<sup>23,24</sup> For supramolecular assembly in water the QDs must be coated with ligands that endow the QDs with colloidal stability in aqueous buffers and simultaneously display molecular recognition ability.<sup>23</sup> To this end, cyclodextrin-functionalized QDs are attractive materials as cyclodextrin is a well-known host of a

**ABSTRACT** Supramolecular microcontact printing was used to obtain controlled patterns consisting of quantum dots (QDs) functionalized at their periphery with  $\beta$ -cyclodextrin ( $\beta$ -CD) in combination with adamantyl terminated dendrimeric “glues”. Functionalization of core–shell CdSe/ZnS QDs was achieved by surface ligation. Immobilization of the QDs from solution onto glass substrates printed with (a) adamantyl-terminated poly(propylene imine) dendrimers and (b) *via* direct microcontact printing of QDs onto the dendrimer layer both yielded stable and robust multilayer structures. The stability of the patterns was primarily due to multivalent supramolecular host–guest interactions between  $\beta$ -CD located at the QD surface and adamantyl groups at the dendrimer periphery as the dendrimers acted as a “supramolecular glue”. The surface-immobilized QDs were capable of forming host–guest complexes with other molecules of interest at binding cavities not occupied by adamantyl groups. Complex formation with ferrocene-functionalized molecules at these sites led to partial quenching of the luminescence emission of QDs demonstrating the principle for sensing using the QD multilayer structures.

**KEYWORDS:** quantum dot · host–guest complex ·  $\beta$ -cyclodextrin · supramolecular glue · microcontact printing · ferrocene · luminescence quenching

multitude of small molecule guests binding to the CD cavity.<sup>23,25–32</sup> Binding of QDs *via* single host–guest complexes results in less stable structures as the stability of the QD layer is defined by a single supramolecular bond. Multivalent binding is therefore desired to provide stable supramolecular structures.<sup>13</sup> Additionally, well-defined patterns of QDs on relevant surfaces are often needed to provide spatially defined luminescent regions for example, for electrochromic displays<sup>20</sup> or a background reference in sensing applications.

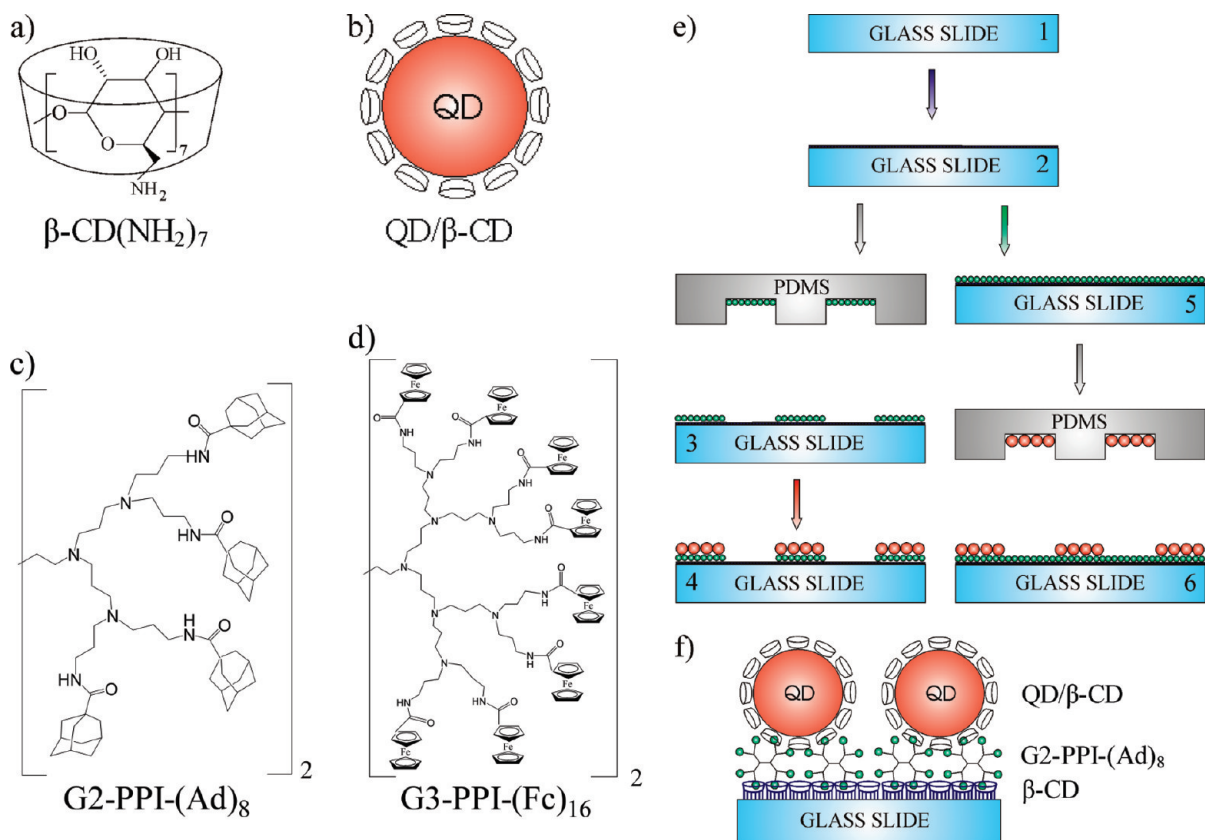
In this report we describe the fabrication of luminescent structures by selective

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**Figure 1.** Chemical structures of (a)  $\beta$ -cyclodextrin heptamine ( $\beta$ -CD(NH<sub>2</sub>)<sub>7</sub>), (b) QDs functionalized with  $\beta$ -CD(NH<sub>2</sub>)<sub>7</sub>, (c) adamantyl-terminated poly(propylene imine) dendrimer (2nd generation, G2-PPI-(Ad)<sub>8</sub>), and (d) ferrocenyl-terminated poly(propylene imine) dendrimers (3rd generation, G3-PPI-(Fc)<sub>16</sub>). (e) Scheme of the immobilization methods and (f) the structure of the resulting multilayer assembly. The numbers written on the glass slides represent the preparation steps and are explained in the main text.

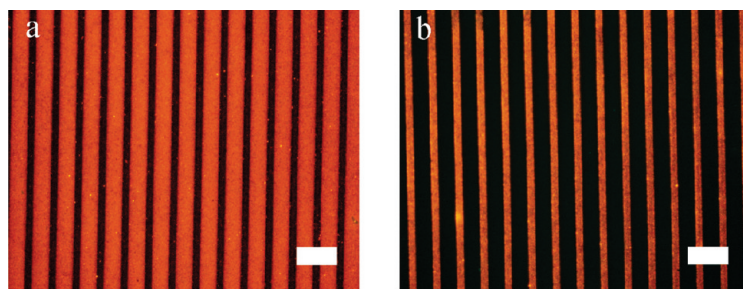
binding of functional dendrimers and  $\beta$ -CD modified QDs *via* supramolecular host–guest interactions. The stability of the assemblies is provided by multivalent interactions between the assembly components enabling the fabrication of multilayer structures. Microcontact printing of the assembly components is demonstrated to be an effective method in preparation of the assemblies. Additionally, we demonstrate that the unused hosts on the surface of the QDs allow for consecutive molecular recognition of other guest molecules to form more complex architectures. Robust platforms for luminescence sensing can be obtained when guests modulating the QD emission are used. In particular, we demonstrate that ferrocene functionalized dendrimers that bind to previously unoccupied cavities of the  $\beta$ -CD modified QDs effectively quench the QD luminescence modulating therefore the optical properties of the QD assemblies.

## RESULTS AND DISCUSSION

To create supramolecularly assembled patterns of QDs, proper functionalization of the QD surface and substrate is required. This is necessary for providing the relevant interactions between the respective pattern components. We chose multivalent host–guest complexation chemistry in aqueous solution to provide

stable, well-ordered layers. The QDs used for the assembly, therefore, should display high colloidal stability in aqueous buffers. We used commercially available carboxylate-functionalized CdSe/ZnS QDs with the first absorption peaks at 580 and 595 nm, respectively. The corresponding maxima of the emission of the QDs are located at 597 and 608 nm, respectively (see Figures S1 and S2 in the Supporting Information). The carboxylic groups at the surface of the QDs stabilize the nanoparticles in aqueous media and provide functionality for the binding of amino-terminated  $\beta$ -CD molecules (Figure 1a). Surface functionalization with  $\beta$ -CD was performed *via* an EDC-activated reaction between the carboxylic groups and amines. The resulting  $\beta$ -CD-modified QDs (QD/ $\beta$ -CD) (Figure 1b) show no significant changes in their absorption spectra; however, the luminescence decreases slightly (see Supporting Information).

To immobilize QD/ $\beta$ -CD on surfaces we chose materials based on their ability to form multivalent host–guest interactions, since such interactions are important to form kinetically stable assemblies.<sup>13</sup> The immobilization steps are schematically shown in Figure 1e. In the first step we create a monolayer of  $\beta$ -CD (2) on the glass substrate (1) (see Figure 1e). This  $\beta$ -CD layer serves as the multivalent anchoring platform for all subsequent immobilization steps and allows for ther-



**Figure 2.** Fluorescence images of (a) micropatterns of QDs/ $\beta$ -CD on glass substrate obtained by drop casting the QDs on microcontact printed G2-PPI-(Ad)<sub>8</sub> dendrimers and (b) by microcontact printing of the QDs onto a full G2-PPI-(Ad)<sub>8</sub> layer. The scale bars have a length of 25  $\mu$ m.

modynamically and kinetically stable positioning and patterning of molecules, for example dendrimers.<sup>1,9</sup>

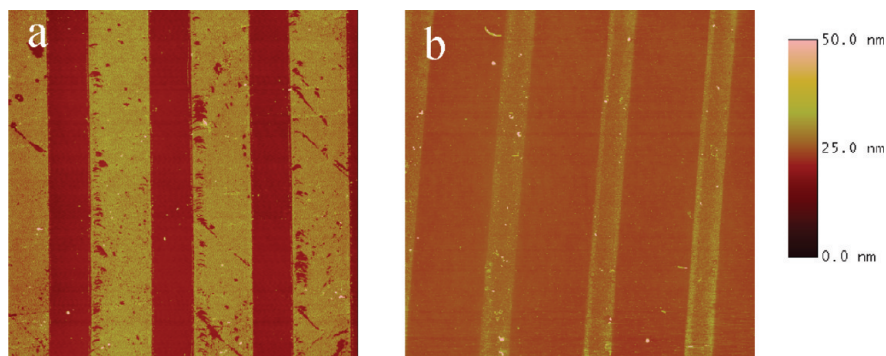
We have explored two complementary methods for the supramolecular pattern building with QDs. In the first method a layer of adamantyl-terminated dendrimers (G2-PPI-(Ad)<sub>8</sub>) (Figure 1c) on  $\beta$ -CD functionalized substrate is formed by microcontact printing ( $\mu$ CP) (3).<sup>33</sup> Owing to the high number of functional units on the periphery of the G2-PPI-(Ad)<sub>8</sub> the dendrimers bind multivalently to the  $\beta$ -CD layer.<sup>12</sup> Additionally, there are many adamantyl groups left exposed to the solution, which are available for complexation with other hosts. QDs bearing surface-immobilized  $\beta$ -CD can therefore also bind by multivalent interactions to the adamantyl-functionalized G2-PPI-(Ad)<sub>8</sub> dendrimers. The QD attachment to the G2-PPI-(Ad)<sub>8</sub> layer is performed by simply casting a drop of a QD water solution onto the functionalized surface (4). Immobilization of QD/ $\beta$ -CD is highly selective to G2-PPI-(Ad)<sub>8</sub> leaving a background  $\beta$ -CD layer in the non-pattern region.

The fluorescence emission from the QD/ $\beta$ -CD pattern is shown in Figure 2a. The 10  $\mu$ m fluorescent lines and 5  $\mu$ m spacings correspond to the pattern of the PDMS stamp used to print the G2-PPI-(Ad)<sub>8</sub> dendrimers. This result indicates that the QDs were attached to the substrate selectively only to the areas where the G2-PPI-(Ad)<sub>8</sub> molecules were previously printed. The average pattern height measured by AFM (Figure 3a) is equal to  $\sim$ 10 nm, which approximately corresponds to the combined height of the G2-PPI-(Ad)<sub>8</sub> and QD/ $\beta$ -CD

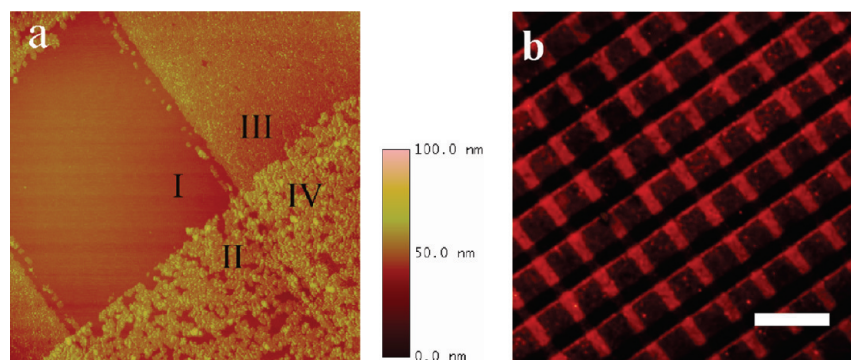
layers. Additionally, AFM imaging proved unequivocally that QDs did not attach directly to the  $\beta$ -CD layer.

The second fabrication method was based on direct printing of QD/ $\beta$ -CD onto glass slides covered with G2-PPI-(Ad)<sub>8</sub> (5). The  $\beta$ -CD-modified glass substrate was first immersed in a 10 mM solution of G2-PPI-(Ad)<sub>8</sub>. After drying, a PDMS stamp inked with QD/ $\beta$ -CD was brought into contact with the substrate (6). Following stamp removal the excess of QD/ $\beta$ -CD was rinsed off with a PBS buffer. Fluorescence image of the resulting pattern is shown in Figure 2b (5  $\mu$ m lines and 10  $\mu$ m spacing on the PDMS stamp). The height of the QD patterns, as obtained from the AFM image (Figure 3b) is equal to  $\sim$ 6 nm, in good agreement with the estimated size of the QD/ $\beta$ -CD conjugate. Similarly to the first method the fluorescence and AFM (Figure 3b) imaging revealed that there were no QDs present in the space between the printed lines. This means that there was no substantial diffusion of the QDs across the G2-PPI-(Ad)<sub>8</sub> functionalized surface after microcontact printing. This is primarily due to the high molar mass of the QDs and to the multivalent nature of the QD attachment to the substrate.

Immobilized QD/ $\beta$ -CD should be capable to form host–guest complexes with other molecules of interest. In particular we show that the formation of specific host–guest complexes on the surface of QDs can modulate the emission of the QDs. In our previous works we demonstrated that ferrocene moieties in close proximity to the QD surface efficiently quench the QD luminescence.<sup>18,34</sup> To check whether a similar



**Figure 3.** AFM height images of QDs/ $\beta$ -CD patterns on glass substrate obtained by (a) drop casting the QDs on microcontact printed G2-PPI-(Ad)<sub>8</sub> dendrimers and (b) by microcontact printing of the QDs onto a full G2-PPI-(Ad)<sub>8</sub> layer. Scan sizes are 50  $\mu$ m  $\times$  50  $\mu$ m.



**Figure 4.** (a) AFM height image of the cross patterns: (I) primary  $\beta$ -CD layer, (II) printed adamantane dendrimers with QD/ $\beta$ -CD on top, (III) ferrocene dendrimers on top of the  $\beta$ -CD layer, (IV) ferrocene dendrimers printed on top of the QD/ $\beta$ -CD/G2-PPI-(Ad)<sub>8</sub> layer. Scan size is  $10\ \mu\text{m} \times 10\ \mu\text{m}$ . (b) Fluorescence image of a QDs/ $\beta$ -CD pattern cross-printed with G3-PPI-(Fc)<sub>16</sub> dendrimers. The luminescence of the QDs in the cross-printed regions visibly decreased. The length of the scale bar is  $30\ \mu\text{m}$ .

quenching takes place also in the system described here, we chose dendrimers functionalized with ferrocene at the periphery (G3-PPI-(Fc)<sub>16</sub>) (Figure 1d).<sup>10,11</sup> These dendrimers can be solubilized in water under the conditions of low pH and in the presence of cyclodextrin. Multiple functionalities at the dendrimer periphery should provide a stable multivalent attachment to the QD/ $\beta$ -CD layers.

For subsequent experiments we chose the patterns prepared *via* the first method using a homogeneous  $\beta$ -CD substrate with printed adamantyl “glue”. Here the QD stripes were obtained by attachment from solution, and in between the stripes there was a  $\beta$ -CD layer exposed. The G3-PPI-(Fc)<sub>16</sub> dendrimers were microcontact-printed perpendicularly across the QD/ $\beta$ -CD stripes. The resulting cross-patterns were characterized by fluorescence and AFM microscopy.

A representative AFM height image of the cross-printed sample is shown in Figure 4a. There are four planes with different heights corresponding to the primary  $\beta$ -CD layer (I), printed adamantane dendrimers with QD/ $\beta$ -CD on top (II), ferrocene dendrimers on top of the  $\beta$ -CD layer (III), and ferrocene dendrimers printed on top of the QD/ $\beta$ -CD/G2-PPI-(Ad)<sub>8</sub> layer (IV). The mean values of the height for each region with respect to region I are equal to  $\sim 10\ \text{nm}$  (II),  $\sim 3\ \text{nm}$  (III), and  $\sim 13\ \text{nm}$  (IV). The height difference between regions I and III corresponds approximately to the estimated height of the G3-PPI-(Fc)<sub>16</sub> dendrimers. Accordingly, the height difference between regions IV and II is the same as between regions I and III. These results indicate that the transfer of the dendrimers to the surface was successful and that the QD layer was not compromised by the cross stamping of G3-PPI-(Fc)<sub>16</sub>. In particular, there was no lift-off of the QDs upon contact with the

dendrimer-coated stamp. By providing stable multivalent binding between the respective components it was possible therefore to obtain multilayer structures.

Figure 4b shows a fluorescence image of QDs cross-patterned with G3-PPI-(Fc)<sub>16</sub> dendrimers. In the areas where these dendrimers are in contact with QD/ $\beta$ -CD the luminescence of the nanoparticles visibly decreased. The QDs in the areas with no G3-PPI-(Fc)<sub>16</sub> printed on top retained their original luminescence. The quenching effect clearly observed in fluorescence imaging is due to the formation of host–guest complexes between the ferrocenyl groups and the immobilized  $\beta$ -CD hosts at the QD surface. The quenching mechanism likely involves a charge transfer process between photoexcited QDs and the ferrocene groups.<sup>34</sup> Modulation of the QD optical properties in the multilayer structures was therefore shown and it represents a proof-of-principle for molecular sensing of water-soluble species able to bind to the  $\beta$ -CD cavity.

## CONCLUSIONS

We described two methods for the immobilization of water-soluble  $\beta$ -CD-functionalized QDs on planar surfaces based on multivalent supramolecular interactions. The  $\beta$ -CD molecules on the QD surface were available for subsequent host–guest complexation with molecules of interest. In particular, the luminescence of QDs was modulated by introducing ferrocene-functionalized dendrimers by cross printing on top of the QD layer. In regions where the ferrocenyl dendrimers formed host–guest complexes with  $\beta$ -CD-functionalized QDs the luminescence intensity decreased, likely due to a photoinduced charge transfer between the ferrocene and QDs.

## EXPERIMENTAL SECTION

**Materials.** Carboxylate-functionalized core–shell CdSe/ZnS EviTag600 and eFluor605 quantum dots were obtained from Evident Technologies (New York, U.S.) and eBioscience (San Diego,

U.S.), respectively. 3-Aminopropyl triethoxysilane (APTES), *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (TPEDA), 1,4-phenylene diisothiocyanate (DITC), and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) were purchased from Al-

drich. PBS buffer solution (pH = 7.4) was obtained from B. Braun Melsungen AG (Melsungen, Germany).  $\beta$ -Cyclodextrin heptamine ( $\beta$ -CD(NH<sub>2</sub>)<sub>7</sub>), adamantyl-terminated poly(propylene imine) (2nd generation, G2-PPI-(Ad)<sub>8</sub>), and ferrocenyl-terminated poly(propylene imine) (3rd generation, G3-PPI-(Fc)<sub>16</sub>) dendrimers were synthesized according to previously reported procedures.<sup>10,35,36</sup> For all the experiments Milli-Q water with resistivity higher than 18 M $\Omega$  cm was used.

**Synthesis of  $\beta$ -CD Modified QDs.** A 50  $\mu$ L portion of a PBS buffer solution containing carboxylated QDs (EviTag600 or eFluor605, 10  $\mu$ M) was mixed with 200  $\mu$ L of EDC ( $1 \times 10^{-4}$  g) and the solution was stirred for 30 min. Subsequently, 250  $\mu$ L of  $\beta$ -CD(NH<sub>2</sub>)<sub>7</sub> ( $2 \times 10^{-4}$  g) was added to the mixture and the mixture was shaken overnight. The resulting materials were purified by ultracentrifugation (40000 rpm, 30 min) or used as prepared.

**Preparation of  $\beta$ -CD Monolayer.**  $\beta$ -CD monolayers on glass were obtained as described previously by Onclin *et al.*<sup>37</sup> Microscope cover slides (Deckglaser, 24  $\times$  24 mm<sup>2</sup>, Menzel-Glaser) were activated with Piranha solution (concentrated H<sub>2</sub>SO<sub>4</sub> mixed with 33% H<sub>2</sub>O<sub>2</sub> in a volume ratio of 3:1; *Warning! Piranha solutions must be handled with caution as they may unexpectedly detonate.*) for 20 min to form a hydroxyl layer on the surface. The substrates were intensively rinsed with Milli-Q water and dried under N<sub>2</sub>. The substrates were then put into a high vacuum desiccator together with 0.1 mL of TPEDA. After overnight incubation, the slides were rinsed with ethanol and dichloromethane to remove excess of silanes and subsequently dried with a nitrogen stream. The attachment of 1,4-phenylene diisothiocyanate was performed in a 20 mM solution of toluene at 60  $^{\circ}$ C during 2 h. Samples were thoroughly rinsed with toluene and dried in a nitrogen flow. The  $\beta$ -CD attachment was performed during 2 h in an aqueous solution of  $\beta$ -cyclodextrin-heptamine (0.1 mM, pH = 7) at 60  $^{\circ}$ C. Samples were thoroughly rinsed with water and dried in a nitrogen flow.<sup>38,39</sup>

**Microcontact Printing of Functionalized Dendrimers.** Stamps were prepared by casting a 10:1 (v/v) mixture of poly(dimethylsiloxane) (PDMS) and curing agent (Sylgard 184, Dow Corning) onto a silicon master with a  $10 \times 5 \mu\text{m}^2$  and  $5 \times 10 \mu\text{m}^2$  pattern spacing. After overnight curing at 60  $^{\circ}$ C, the stamps were oxidized by oxygen plasma for 1 min and subsequently inked by casting a drop of a 1 mM aqueous solution of G2-PPI-(Ad)<sub>8</sub> or G3-PPI-(Fc)<sub>16</sub> dendrimers onto the stamp for 10 min. Before printing, the stamps were blown dried in a stream of nitrogen. The stamps were brought into conformal contact with the substrate for 10 min. After stamp removal, the printed substrates were rinsed with water and dried with nitrogen.

**Immobilization of QDs on Functionalized Glass Slides.** Immobilization of QD/ $\beta$ -CD on the glass surface was performed using two different procedures (Figure 1e). In the first procedure, 100  $\mu$ L of a  $10^{-6}$  M QD solution was deposited on the glass slide **3** patterned previously with G2-PPI-(Ad)<sub>8</sub> (**2**). After 10 min the substrate was rinsed with a PBS buffer and dried under N<sub>2</sub> resulting in pattern **4**.

In the second procedure the QDs were microcontact printed directly onto the G2-PPI-(Ad)<sub>8</sub> functionalized glass slide **5**. The QDs (100  $\mu$ L,  $10^{-6}$  M) were casted onto the PDMS stamp and after 10 min dried under N<sub>2</sub>. The PDMS stamp was brought into contact with the substrate slide for 5 min and carefully removed. Finally, the glass slides were washed with PBS buffer and dried under N<sub>2</sub> resulting in pattern **6**.

**Methods.** The absorption spectra of the QD solutions were measured with a Varian Cary 300 UV–vis spectrophotometer. The photoluminescence spectra were measured with an Edinburgh XE-900 spectrofluorometer ( $\lambda_{\text{ex}} = 500$  nm). Fluorescence imaging was performed using an inverted fluorescence microscope (Olympus IX71) equipped with a mercury lamp (U-RLF-T) and a digital camera (Olympus DP70). Olympus filter cube U-MWG was used to filter the excitation and emission light ( $\lambda_{\text{ex}} \leq 350$  nm,  $\lambda_{\text{em}} \geq 420$  nm). Topography imaging of the coated glass substrates was performed at ambient conditions in air with a NanoScope III atomic force microscope (Veeco/Digital Instruments, Santa Barbara, CA) equipped with a J-scanner. A single beam Si cantilever with a nominal spring constant of 42 nN/nm (Nanosensors, Germany) was used for imaging in the tapping mode.

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**Supporting Information Available:** Absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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