Magnetic Nanobeads as Support for Zinc(II)–Cyclen Complexes: Selective and Reversible Extraction of Riboflavin

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Supporting Information

1. NMR spectra  S2
2. IR-ATR spectra  S3
3. TEM pictures  S4
4. Additional UV- and fluorescence-spectra, binding studies  S4

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1. NMR spectra

$^1$H-NMR
(300 MHz, CDCl$_3$)

$^{13}$C-NMR
(75.5 MHz, CDCl$_3$)
2. IR-ATR spectra

![IR Spectra](image)

**Figure S1.** IR Spectra depicting the nucleophilic substitution of the benzyl chloride moieties in 3 with sodium azide and the subsequent attachment of the cyclen ligand followed by complexation with Zn(II).
3. TEM pictures

![TEM pictures](image1.png)  ![TEM pictures](image2.png)

**Figure S2.** TEM pictures of polymer-encapsulated Fe/C nanoparticles before the functionalization with zinc(II)-cyclen complexes (3, left) and after the functionalization (7, right). No substantial changes between the pictures are noticeable.

4. Additional UV- and fluorescence-spectra, binding studies

![UV and fluorescence spectra](image3.png)

**Figure S3.** Absorption- (left) and emission- (right) measurements to determine the loading of the functionalized particles. Solution of riboflavin (30 µm, —), solution after treatment with 7 (—), and recovery of riboflavin from 7 (—). 200 mL of a riboflavin solution (30 µM) and 20 mg of 7 were used. To recover the riboflavin the particles were washed with 100 ml diluted HCl. From the differences in the intensities a loading of ~ 0.16 mmol/g was calculated.
Figure S4. Absorption- (left) and emission- (right) measurement of the polymer coated particles 3 lacking the zinc(II)-cyclen complexes. The solution of riboflavin (10 μm, —) and the solution after treatment with 3 (—) is depicted. Only a negligible amount of riboflavin is adsorbed by the particles.

Figure S5. Binding- and release of riboflavin to Zn(II)-cyclen-functionalized Co/C nanoparticles 13. Absorption spectra (left) as well as emission spectra (right) are shown. Solution of riboflavin (10 μm, —), solution after treatment with 13 (—), and recovery of riboflavin from 13 (—).
Figure S6. Absorption- (left) and emission- (right) measurement of non-functionalized Co/C particles. Solution of riboflavin (10 μm, —), solution after treatment with particles (—), and recovery of riboflavin (—). The addition of riboflavin onto the nanoparticle surface is observed to some extent, which cannot be reversed.

Figure S7. Absorption- (left) and emission- (right) measurements of a riboflavin solution stirred with Zn(II)-biscyclen functionalized nanobeads 18. Solution of riboflavin (10 μm, —), solution after treatment with 18 (—), and recovery of riboflavin from 18 (—). The biscyclen-tagged particles do reversibly adsorb riboflavin, however, at a reduced efficiency.