Metal-chelating nanoparticles as selective fluorescent sensor for Cu$^{2+}$

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Supplementary Information

Synthesis and spectroscopy of Mesityl-BODIPY dye 1
Synthesis of cyclam-functionalized nanoparticles CNL (Spectrophotometric titration of CNL with Cu(NO$_3$)$_2$ and Absorption spectra of CNL + Cu(NO$_3$)$_2$).
Loading of CNL with dye 1: preparation of fluorescent complexing nanolatex FCNL
Spectroscopic analysis of fluorescent nanolatex FCNL
$^1$H and $^{13}$C NMR spectra of dye 1

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Synthesis and spectroscopy of Mesityl-BODIPY dye 1

1 was synthesized using the conventional method from 2,4-dimethyl-3-ethylypyrrole and 2,4,6-trimethylbenzaldehyde.1

In dichloromethane, the absorption maximum wavelength is 526 nm with a molar extinction coefficient of 58000 mol.L⁻¹.cm⁻¹. Emission maximum wavelength is 535 nm. Absorption and excitation spectra are identical.

Synthesis of cyclam-functionalized nanoparticles CNL

The aqueous suspension of metal-binding nanoparticles (cyclam-functionalized nanolatex CNL) was prepared according to the previously described procedure.2 A microemulsion consisting of a mixture of styrene (600 µL), divinylbenzene (740 µL), N-vinylbenzylcyclam (400mg), DMPA (radical photoinitiator, 140 mg, 0.05mol/mol of monomers) in 40 mL of a 15 %wt solution of dodecyltrimethylammonium bromide (DTAB) in water was polymerized under white light irradiation at 20°C for 15h. The stable translucent nanolatex CNL was used without further purification for dye loading and spectroscopic studies.

Final polymer content 4%wt. The diameter of the particles was deduced from QELS and TEM analyses.

Metal-binding capacity was deduced from metal uptakes. CNL binds Cu²⁺ (complexation yield > 95%) as well as Zn²⁺, Ni²⁺, Co²⁺ (complexation yields 70-80%).

The Cu-binding capacity of the CNL nanolatex is 0.54 mmol Cu²⁺ /g polymer (2.16 10⁻² mol/L of suspension, almost complete complexation of the cyclam residues).

Spectrophotometric titration of the Cu-Cyclam complex (absorption wavelength 536nm, figure S2) upon addition of a dilute 0.01M solution of Cu(NO₃)₂, shown in figure S1, indicates that about 0.45 mmol Cu per g polymer are instantaneously complexed in dilute solution (18 mmol/L of suspension). That means that about 85% of the cyclam residues are involved in a rapid solution-like complexation process (instantaneous complexation of Cu²⁺ in dilute medium).
Figure S1: Spectrophotometric titration of CNL with Cu(NO$_3$)$_2$ 0.01M.

![Graph showing corrected absorbance vs Cu meq/g polym.](image)

- ○: instantaneous absorbance
- ×: absorbance at the equilibrium

Figure S2: Absorption spectra of CNL + Cu(NO$_3$)$_2$ 0.01M.

![Graph showing absorption spectra.](image)
Loading of CNL with dye 1: preparation of fluorescent complexing nanolatex FCNL
1 has been encapsulated by swelling: Swelling experiments were performed by adding a small aliquot (12μL) of a solution of 1 in dichloromethane to 300μL of the as-prepared nanolatex CNL followed by evaporation of the solvent (24h at room temperature). Various loading concentrations have been used. The amount of encapsulated dye was quantified from the absorbance of 1 at 528.5 nm. The maximum load is about 85μmol/g polymer (i.e. 100 molecules of 1 per particle).

The present study was performed on a fluorescent nanolatex FCNL containing 59μmol/g polymer, well below the maximum loading. No leakage of 1 has been observed over 1 month.

Spectroscopy
A U.V.-vis. Varian CARY 500 spectrophotometer was used. Excitation and emission spectra were measured on a SPEX Fluorolog-3 (Jobin-Yvon). A right-angle configuration was used. Optical density of the samples was checked to be less than 0.1 to avoid reabsorption artefacts.

Time-resolved spectroscopy: The fluorescence decay curves were obtained with a time-correlated single-photon-counting method using a titanium-sapphire laser (82 MHz, repetition rate lowered to 4 MHz thanks to a pulse-peaker, 1 ps pulse width, a doubling crystals is used to reach 495 nm excitation) pumped by an argon ion laser. The Levenberg-Marquardt algorithm was used for non-linear least squares fits.

Spectroscopic analysis of fluorescent nanolatex FCNL:
Fluorescent metal-complexing nanolatex FCNL (59μmol 1/g polymer) was diluted 1000 times in pure water before spectroscopic analyses.

Characteristics of the FCNL sample studied:
- Polymer content: 40mg/L
- Remaining surfactant DTAB: 0.014%wt (0.45 10^{-3} M). The concentration of remaining surfactant is well below its critical micelle concentration (54 10^{-3} M, 16.6g/L, 1.66%wt) so that micellar solubilization of the dye can be neglected.
- Dye content: 59μmol 1/g polymer, 2.36 10^{-6} mol/L of FCNL. About 75 molecules of dye per particle.
- Cyclam content: 0.54mmol/g polymer, 2.16 10^{-5} mol/L of FCNL, about 700 molecules per particle. About 1.8 10^{-5} mol of cyclam per liter of FCNL are involved in a rapid complexation process (about 600 molecules per particle).
The calculated Förster radius is about 2.1-2.3 nm. The non linear variation of \( I_0/I \) with Cu concentration can be interpreted by the presence of two populations of fluorophores.\(^3\) A modified Stern-Volmer plot (see figure S3 below) shows that 80% of dye molecules can be quenched (accessible dyes) and that only 20% of the fluorophores are not accessible for energy transfer : the distance between these dyes and the complexes is larger than the Förster radius.\(^5\)

Assuming that \( I \) is distributed all over the particle volume, this is in acceptable agreement with the volume fractions of the core 20-25% (internal radius about 5 nm, not accessible for energy transfer) and the shell 75-80% (thickness 3nm).

\(^5\) According to the Perin’s model that states that beyond a critical radius no quenching occurs and within that radius quenching occurs with 100% efficiency.

**Figure S3 : Modified Stern-Volmer Plot : \( I_0/(I_0-I) \) vs \( 1/[Cu] \)**

\[ \frac{I_0}{I_0 - I} = \frac{1}{f} + \frac{1}{f \cdot K \cdot [Cu - \text{Complex}]} \]

\( f \) = fraction of accessible dye ; \( K \) = Stern-Volmer Constant

Fitting parameters : \( f = 0.8 \); \( K = 3.3 \times 10^6 \) (+/- 0.4 \( 10^6 \))

**References**

$^1$H NMR spectrum of dye 1 (300MHz, CDCl$_3$)
$^{13}$C NMR spectrum of dye 1 (75 MHz, CDCl$_3$)