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

Rachel Méallet-Renault, Robert Pansu, Sonia Amigoni-Gerbier and Chantal Larpent*

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**

Corresponding Author

Prof. C. Larpent
SIRCOB, UMR CNRS 8086,
Université de Versailles St Quentin en Y.,
45 Avenue des Etats-Unis, 78035 Versailles Cedex, France.
Fax: 33 139254452; E-mail: larpent@chimie.uvsq.fr ; Fax: 33 139254452;

Synthesis and spectroscopy of Mesityl-BODIPY dye 1

1 was synthesized using the conventional method from 2,4-dimethyl-3-ethylpyrrole 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 Cu^{II} (complexation yield > 95%) as well as Zn^{II}, Ni^{II}, Co^{II} (complexation yields 70-80%).

The Cu-binding capacity of the **CNL** nanolatex is 0.54 mmol Cu^{II} /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 $Cu(NO_3)_2$, 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 Cu^{II} in dilute medium).

Figure S1 : Spectrophotometric titration of CNL with $Cu(NO_3)_2$ 0.01M.

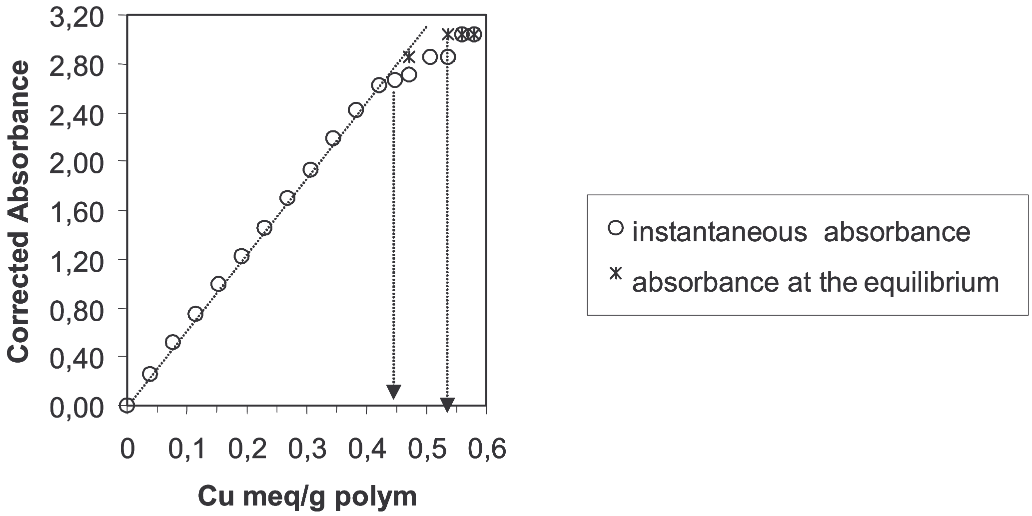
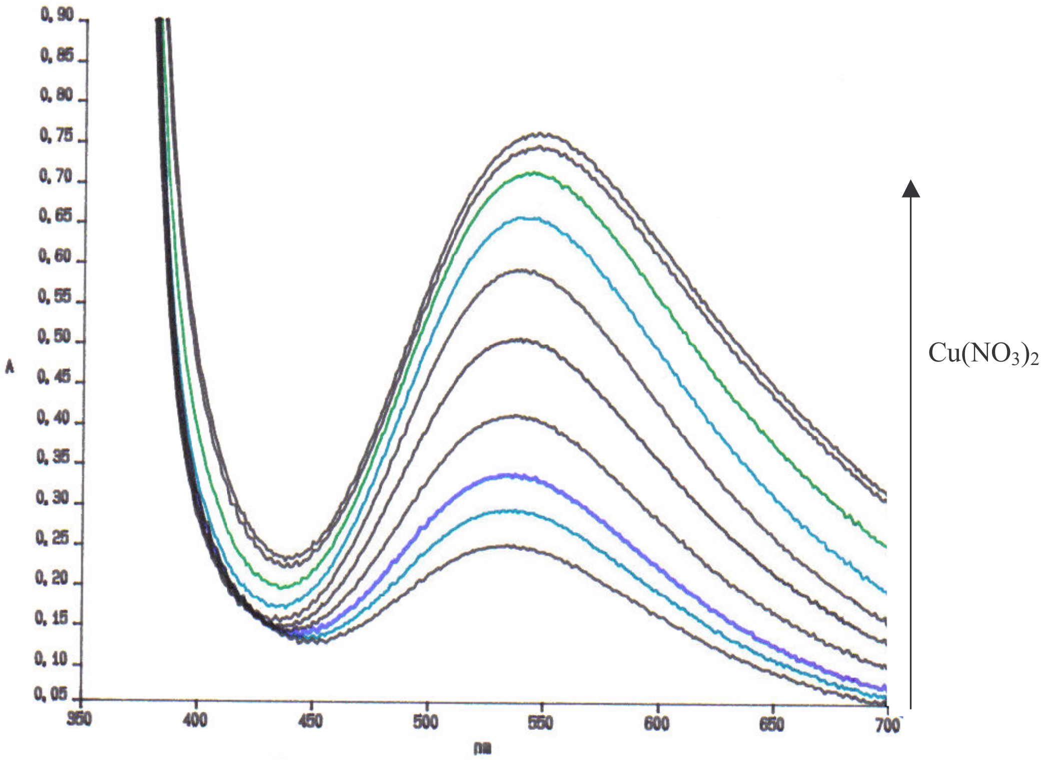


Figure S2 : Absorption spectra of CNL + $Cu(NO_3)_2$ 0.01M.



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:

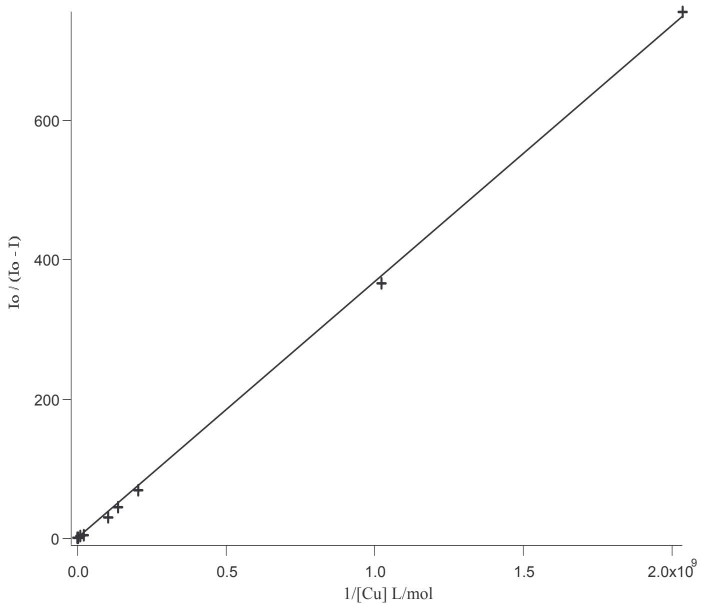
- Polymer content : 40mg/L
- Remaining surfactant DTAB : 0.014%wt (0.45 10^{-3} M). The concentration of remaining surfactant is well below its critical micelle concentration (54 10^{-3} M, 16.6g/L, 1.66%wt) so that micellar solubilization of the dye can be neglected.
- Dye content : 59µmol **1**/g polymer, 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.[$]

Assuming that **1** 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).

[$] *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]



(+) : experimental points, line: calculated

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

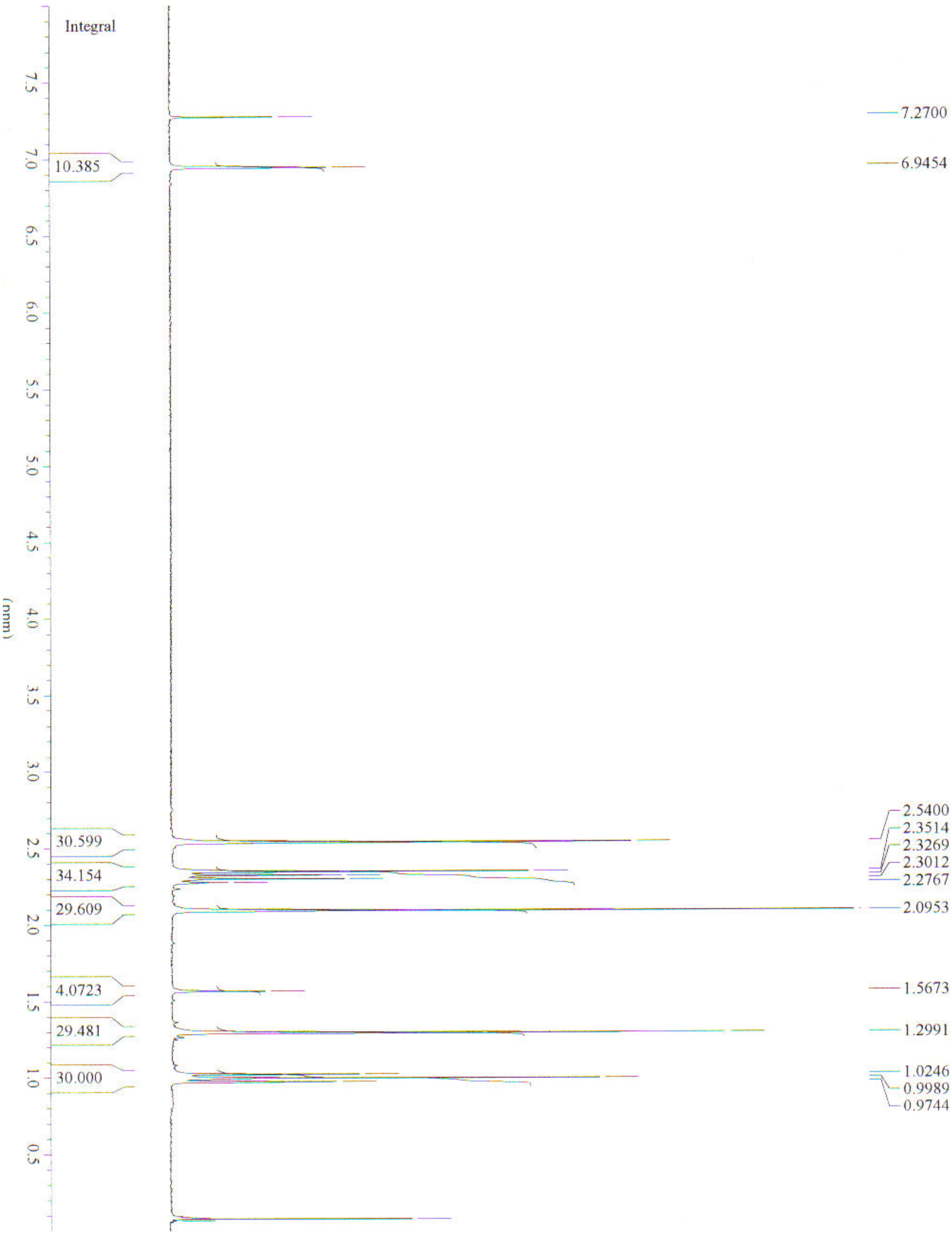
f = fraction of accessible dye ; K = Stern-Volmer Constant

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

References

1. M. Kollmannsberg, T. Gareis, S. Heinl, J. Breu and J. Daub, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1333-1335.
2. S. Amigoni-Gerbier, S. Desert, T. Gulik-Kryswicki and C. Larpent, *Macromolecules*, 2002, **35**, 1644-1650.
3. K. Nakashima, S. Tanida, et al., *J. Photochem. Photobiol. A : Chemistry*, 1998, **117**, 111-117.

[1]H NMR spectrum of dye 1 (300MHz, $CDCl_3$)



^{13}C NMR spectrum of dye 1 (75 MHz, $CDCl_3$)