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Copper(I) photosensitiser-silica nanoparticle assembly towards enhanced aqueous photoluminescence

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Abstract: Harnessing the luminescence potential of Cu(I) complexes in aqueous media is typically hindered by their poor photostability and altered properties. Here, we report the synthesis, engineering and morphological characterization of a hydrophobic homoleptic copper(I) complex entrapped into silica nanoparticles, Cu-I@SiO₂ (where “Cu-I” designates [Cu(2,9-diiodo-1,10-phenanthroline)₂]⁺), as a promising stabilisation strategy towards water-compatible, Cu(I) complex-based luminescence. The polyether chain-decorated nano-objects are spherical with an average diameter of ca. 10.8±1.9 nm. Upon dispersion in water, clear solution-like suspensions were obtained. Significantly, the aqueous suspensions photoluminesce ($\Phi_{em} = 5.10^{-4}$) upon excitation through the Metal-to-Ligand Charge-Transfer transition (MLCT) of the embedded copper(I) complexes. In contrast, the corresponding silica-free molecular complex dissolved in an aqueous environment revealed fully quenched emission. Finally, the use of Cu-I@SiO₂ suspensions as luminescent probes is reported, first by assessing their potential use as electrochemiluminescent probes, and second by monitoring the photoluminescence from Cu-I@SiO₂ in the presence of whole blood.

Keywords: dye doped silica nanoparticles; copper(I) complexes; direct microemulsion; electrochemiluminescence; photoluminescence; whole blood.

Introduction

There is a strong need for highly luminescent metal complexes that are low-cost and non-toxic for applications, from the detection of biomarkers of disease to display devices and photocatalysts.[1–7] Homoleptic copper(I)-diimine complexes $[\text{CuL}_2]^+$ (where L is 1,10-phenanthroline with bulky groups R at positions 2 and 9) are especially attractive because of their biocompatibility, non-cytotoxicity, wide availability and low-cost of starting materials which enable both biomedical and environmental applications. Importantly, homoleptic copper(I) complexes exhibit photoluminescence in the red to near infrared region (depending on R)[8–10] where biological samples have a lower absorbance, making the homoleptic complexes well suited for sensing in biological medium.

Towards the broad implementation of homoleptic copper(I) complexes, e.g. as molecular sensors in biological application,[11] two major issues should yet be tackled.

First, the excited state of $[\text{CuL}_2]^+$ complexes is known to be efficiently quenched in presence of water[9,12,13] or other nucleophilic species,[14] which are present in abundance in biological media.[15] This problematic quenching is due to the structural changes which occur upon light absorption by the complex in its Metal-to-Ligand Charge Transfer (MLCT) band. After excitation, an electron moves from the copper ion towards the coordinated ligand meaning that the oxidation state of the complex transiently changes from +I to +II. This is accompanied by a flattening of the coordination sphere, freeing up space above the formal Cu(II) ion, which can then coordinate virtually any kind of nucleophile, knowing that the preferred geometry of Cu(II) complexes is square pyramidal. This results in an important stabilization of the excited state energy levels leading to a premature efficient quenching of the excited state. While tethering bulky groups in 2,9-positions of 1,10-phenanthroline partially alleviates those issues, the photo-induced flattening and exciplex quenching remain effective in coordinating media (in THF,[16] acetonitrile[8,17] or water)[18] decreasing the emission quantum yield and lifetime of photo-excited copper(I) complexes.

Second, copper(I) complexes are kinetically unstable. The coordination sphere of copper(I) complexes is known to be labile[19–21] meaning that (apart from a few rare examples)[22] a complex with the typical structure $[\text{CuL}_2]^+$ is prone to ligand exchange at room temperature in solution in the presence of a competing ligand L', leading to a mixture of several structures ($[\text{CuL}_2]^+$, $[\text{CuLL}']^+$, $[\text{CuL}'_2]^+$) whose proportions depend of their respective formation constants. The presence of numerous potential ligands in biological media (e.g. thiols) may thus threaten the integrity of the complex's molecular structure.

Probably for these reasons, working with homoleptic copper(I) complexes $[\text{CuL}_2]^+$ in water, and *a fortiori* in biological media has been rarely reported. In 2018, Khnayzer et al. studied

the potential of a series of homoleptic copper(I) complexes in biological media in the frame of photodynamic therapy.[18] The goal was to use their excited triplet state to generate cytotoxic $^1\text{O}_2$. Importantly, of all studied complexes, only the very sterically strained $[\text{Cu}(\text{dstmp})_2]^+$ (where dstmp stands for 2,9-di-sec-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline, Figure S1a) proved to be photo-cytotoxic against cancer cells. The rationale was grounded in the lifetime of the excited state of $[\text{Cu}(\text{dsbtmp})_2]^+$ which is sufficiently long in aqueous medium (1.2 μs in a 1:1 mixture of acetonitrile and water) to allow reactivity with $^3\text{O}_2$. This is due to the bulky groups in positions 2, 3, 4, 7, 8 and 9 which protect the metal ion from nucleophilic attacks and limit the photo-induced flattening of the structure.[23,24] The other investigated complexes were less encumbered and exhibited severely quenched emission in the same conditions. This sole report on the photo-induced properties of homoleptic copper(I) complexes in biological media shows how crucial it is to protect the copper(I) ion from the environment in order to promote the excited state properties in aqueous medium.

A very interesting way to preserve and enhance the properties of $[\text{CuL}_2]^+$ complexes is to encapsulate them in a protective surrounding to retain their intrinsic excited-state properties without the influence from the external medium. Castellano et al. have recently reported copper(I) complexes encapsulated inside aqueous direct micelles and have shown that the emission lifetime of the assembly is still high (1.21 μs).[25] Another method consists in trapping copper(I) complexes inside a rigid silica matrix. For example, silica gel doped with $\text{Cu}(\text{bpy})_2^+$ (bpy is 2,2'-bipyridine) has been demonstrated to exhibit solid-state room temperature luminescence upon photo-excitation.[26] This is remarkable since $\text{Cu}(\text{bpy})_2^+$ is non luminescent. Corriu et al. have reported the immobilization of a derivative of luminescent $[\text{Cu}(\text{dap})_2]^+$ (where dap stands for 2,9-dianisyl-1,10-phenanthroline) which exhibits great stability vs. ligand exchange; unfortunately the photoluminescence properties have not been reported.[27] Heteroleptic copper(I) complexes have been immobilized in silica too.[28,29] De Cola and co-workers[29] have notably reported that such hybrid materials suspended in ethanol show enhanced photoluminescence compared to the isolated complexes in solution. However, in all the above cases, the emission properties are reported in the solid state or in suspensions that are highly light-scattering, due to the presence of large aggregates.

In this contribution, we propose to prepare and characterize clear suspensions of silica nanoparticles which embed homoleptic copper(I) complexes, to promote their excited state properties in aqueous and biological media (Figure 1). The complex $[\text{Cu}(2,9\text{-diiodo-1,10-phenanthroline})_2]^+$ **Cu-I⁺** was elected as a benchmarking Cu-based luminophore for its luminescence in the near-IR and long-lived excited state (> 100 ns).[30] We selected a direct microemulsion method for the silica nanoparticles synthesis, templated by the Pluronic F127

polymer [31–35] which is known to lead to very stable (several months) clear aqueous suspensions.[36,37] The obtained hybrid nano-objects feature long-lived (> 100 ns) near infrared luminescence in water, which has led us to investigate their potential as electrochemiluminescent probes and as luminophores in whole blood samples.

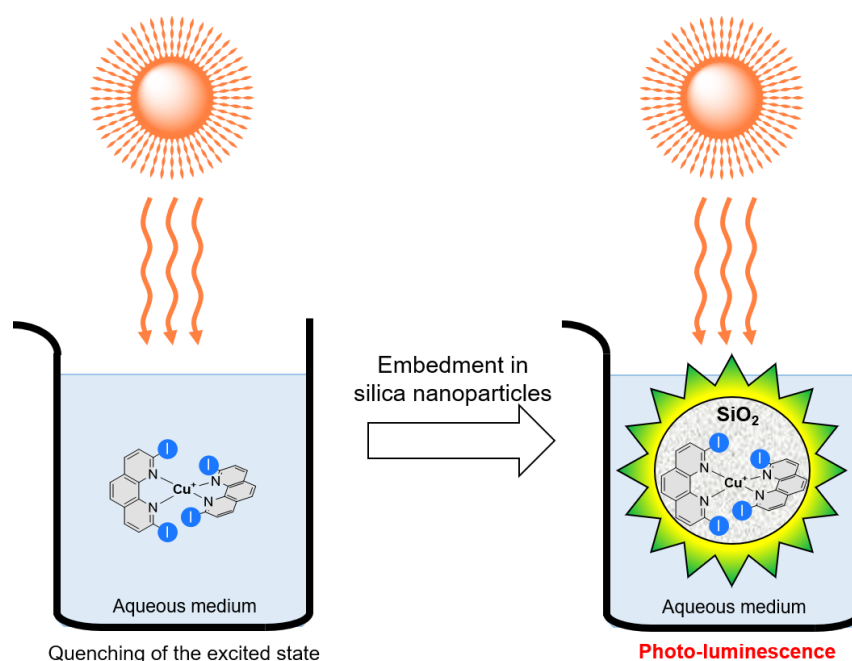


Figure 1. Strategy developed to enhance the emission quantum yield and lifetime of $[\text{CuL}_2]^+$ complexes in aqueous medium.

Results and discussion

Synthesis and morphological study

The synthesis of the PEG-decorated silica nanoparticles doped with Cu-I^+ was adapted from the literature.[31] First, direct micelles (oil-in-water) are formed, behaving as nano-reactors where the sol-gel process takes place. F127 is used as a surfactant for the preparation of the micelles. F127 is a poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethyleneglycol) triblock copolymer which acts as an amphiphilic species because the ethyleneglycol chains on each side of the structure are hydrophilic, while the central propyleneglycol chain is hydrophobic. In water, the F127 polymer chains arrange in micelles where each macromolecule can be seen as a hairpin (Figure 2).

The BARF^- salt ($\text{BARF}^- = \text{tetrakis}[3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}]\text{borate}$) of Cu-I^+ (Figure S1b, synthesis detailed in the supporting information) has been prepared in good yield (~70%). In comparison to the usual PF_6^- counter ions, BARF^- dramatically increases the hydrophobicity of

the complex (e.g., the BARF^- salt of Cu-I^+ is soluble in diethyl ether, whereas the PF_6^- salt of the same complex is insoluble) and helps to ensure the efficient trapping of the Cu-I^+ complexes at the core of the micelle. While the BARF^- salt of Cu-I^+ is totally insoluble in water, orange transparent aqueous solutions of the micelles are obtained. Next, the organic silica precursor tetraethoxysilane (TEOS) is added and the sol-gel process is catalysed by HCl. Knowing that copper(I) complexes can be unstable in presence of acid, we have first controlled the stability of the micelles in the presence of different amounts of aqueous HCl. The micellar suspension, initially deep orange, turns colourless after a few minutes for $[\text{HCl}] > 0.18 \text{ mM}$, probably because Cu-I^+ gets destroyed *via* protonation of the 2,9-diiodo-1,10-phenanthroline ligand and subsequent disruption of the coordination scaffold. Thus, the concentration of HCl has been set at 0.18 mM in all experiments. TEOS is finally added into the mixture and the hydrolysis-condensation reaction is allowed to run for 6 hours under strong stirring. During this time, no significant colour change is observed. Finally, dimethoxydimethylsilane is added as a capping agent to stop the growth of the nanoparticles.[31] Clear orange suspensions of Cu-I^+ doped silica nanoparticles (Cu-I@SiO_2) are obtained (Figure 3a). Excess HCl, TEOS or F127 are removed by dialysis and ultrafiltration (see SI for experimental details). Importantly, the colour of the suspension does not change after the ultrafiltration steps, and the filtrates are always colourless. In addition, attempts to extract the copper(I) complexes from the aqueous suspensions using 2-octanol have been unsuccessful.[31] This shows that the Cu-I^+ molecules are mostly embedded inside the silica nanoparticles and not dispersed within the outer shell of surfactants. The aqueous suspensions of Cu-I@SiO_2 are stable when shelved in ambient daylight for more than six months.

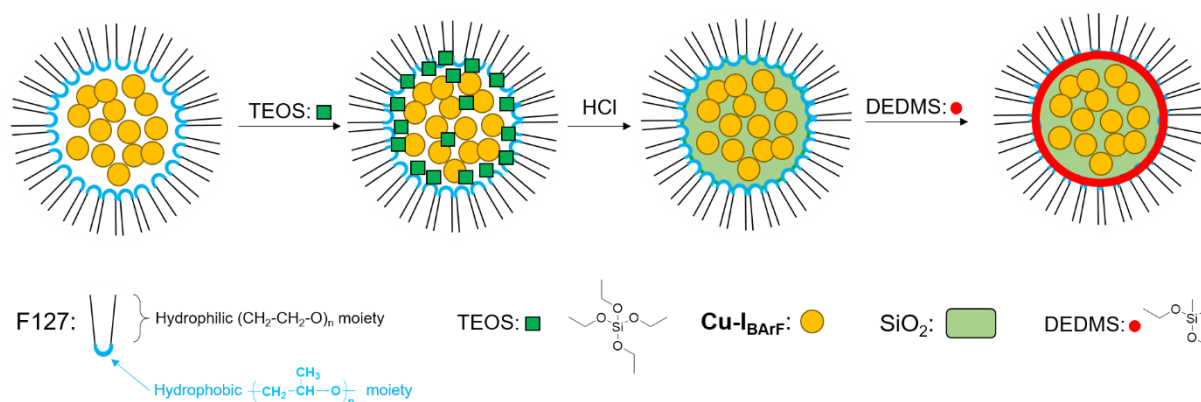


Figure 2. Synthesis of the Cu-I@SiO_2 nanoparticles

ICP-MS measurements have yielded a Si:Cu mole ratio of 1065. A loading of ca. 15 copper(I) complexes is estimated to be trapped inside each nanoparticle. This result is consistent with previous reports on related systems.[34] Transmission Electron Microscopy (TEM) pictures reveal that the Cu-I@SiO_2 materials consist of homogeneous, spherical

nanoparticles of 10.8 nm in Feret diameter with a standard deviation of 1.9 nm (Figure 3b and Figure S2). Dynamic light scattering (DLS, Figure S3) experiments show that there is a population of nanoparticles with sizes ranging between 10 and 20 nm, with a maximum population at ca. 12-13 nm and a rather low polydispersity index, as previously observed in related works.[31,34] The nanoparticles diameter measured with TEM is smaller than the one retrieved from DLS measurements, as expected since the presence of trapped surfactant molecules protruding out of the inorganic silica core are taken in account by DLS (hydrodynamic diameter), whereas TEM only shows the inorganic cores of the nanoobjects.

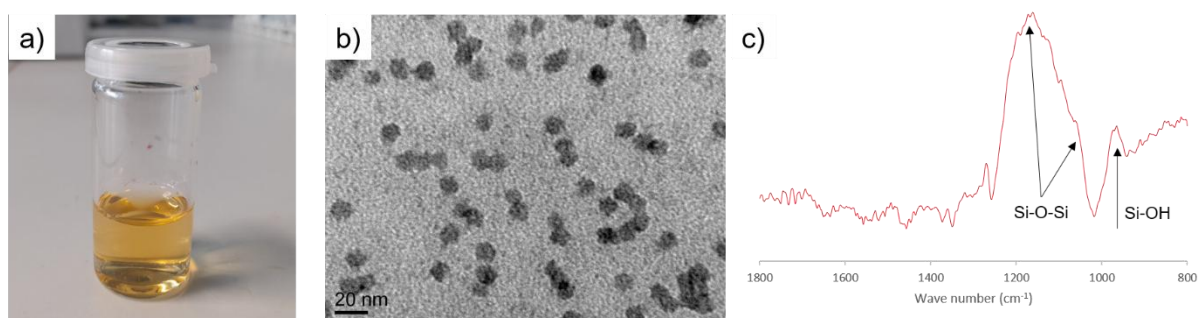


Figure 3. a) Picture of the aqueous suspensions of Cu-I@SiO₂. b) TEM picture of Cu-I@SiO₂. c) Subtraction of the FT-IR spectrum of the micelles from the FT-IR spectrum of Cu-I@SiO₂.

FT-IR spectra of the aqueous suspensions of Cu-I@SiO₂ have been measured by ATR (Figures 3c and S4). Subtracting the FT-IR spectrum of the pure F127 micelles in water from the FT-IR spectrum of Cu-I@SiO₂ reveals transitions at 1050-1150 cm⁻¹ and 950 cm⁻¹ ascribed to Si-O-Si (TO-LO) and Si-OH vibration modes of amorphous silica materials, respectively. The latter suggests high superficial density of O-H typically observed for nanoparticles with high specific area (Figure 3c).[38] The spectral features of the embedded copper complexes are not intense enough to be observed. Overall, the morphological study confirms that the **Cu-I**⁺ complexes are embedded inside the silica nanoparticles.

Optical properties

UV-Vis spectroscopy

The obtained aqueous suspensions of Cu-I@SiO₂ have been characterized by UV-Vis absorption spectroscopy (Figure 4a) and compared to that of **Cu-I**⁺ (BArF⁻ salt) in CH₂Cl₂. Both spectra are dominated by a MLCT transition at 480 nm, typical of homoleptic copper(I)-diimine complexes.[10,30] As can be seen in Figure 4a, the light scattering is negligible for Cu-I@SiO₂, reflecting the transparency of the solution. The clear match in shape and maximum absorption wavelength between the two traces infers that the complex within Cu-

I@SiO₂ is virtually unaffected by the silica environment despite the solvent discrepancy (see the black and red lines in Figure 4a). This is often the case for DDSN prepared by the direct micro-emulsion method.[31,32,39]

As mentioned in the introduction, the coordination sphere of copper(I) complexes is labile in coordinating solvents. We anticipated that the coordination sphere of **Cu-I**⁺, when immobilized inside the silica matrix, would be less sensitive to ligand scrambling. In order to test this hypothesis, potassium cyanide, a good competitor ligand in copper(I) coordination chemistry[40–42] has been added to a solution of molecular **Cu-I**⁺ and to a suspension of Cu-I@SiO₂ while monitoring the evolution of their UV-Vis spectra. In both cases, the MLCT collapses indicating that the coordination sphere of the **Cu-I**⁺ is broken and that colourless [Cu(CN)₄]³⁻ is formed. However, the reaction is instantaneous in the case of “free” **Cu-I**⁺ (Figure S5a) while several minutes (> 10 mn) are necessary to monitor the complete disappearance of the signal at 480 nm in the case of Cu-I@SiO₂ (Figure S5b). This demonstrates that the silica network grown around the **Cu-I**⁺ complexes is porous and that competitive ligands can penetrate the F127 layer and the walls of silica leading to ligand scrambling. When a larger competitive ligand such as bathocuproine disulfonic acid sodium salt **bphen**_{SO₃Na} is used, virtually no ligand exchange is observed for several hours, even in presence of a strong excess of **bphen**_{SO₃Na} (ca. 80 equivalents, Figure S6a) while it is again instantaneous when the free complex **Cu-I**⁺ is put in presence of more than 4 equivalents of **bphen**_{SO₃Na} (Figure S6b). Those results suggest that the efficacy of ligand exchange depends on the diffusion of the competitive ligands within the crown of F127 and through the pores of silica.

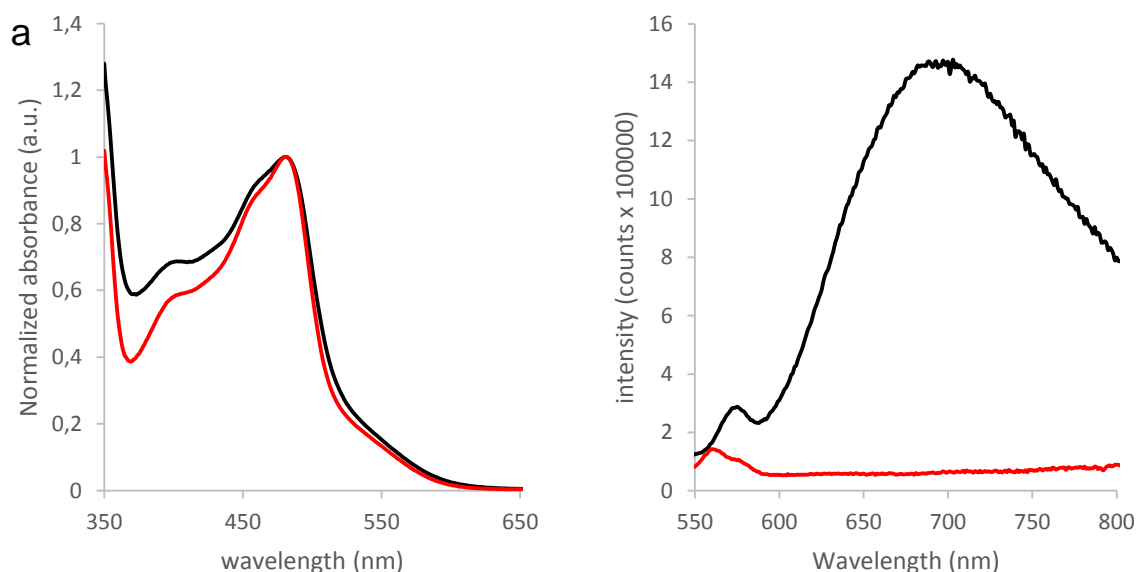


Figure 4. a) Absorption spectra of Cu-I@SiO₂ in water (black line) and **Cu-I**⁺ in CH₂Cl₂ (BARF⁻ salt, red line). b) Emission spectra of Cu-I@SiO₂ (degassed water, black line), **Cu-I**⁺ (PF₆⁻ salt in a 1:1 mixture of water and acetonitrile, red line). Excitation wavelength set at 480 nm, optical density of 0.2 at 480 nm. Addition of acetonitrile was necessary to dissolve **Cu-I**⁺ in aqueous environment.

Fluorescence spectroscopy

The luminescence properties of the suspensions were examined (Figures 4b and S7). Aqueous suspensions of Cu-I@SiO₂ exhibit a broad luminescence signal at ca. 700 nm when excited at 480 nm, very similar in shape and position to the emission signal recorded for **Cu-I**⁺ in dichloromethane solutions. Conversely, the emission of the excited complex in aqueous environment is completely quenched (Figure 4b). This suggests that the copper(I) complexes are protected from water molecules when confined inside the silica nanostructure. The emission quantum yield is estimated at 0.5×10^{-3} (see SI for experimental details) about a third of that of **Cu-I**⁺ in CH₂Cl₂ (1.4×10^{-3}). This could be ascribed to an uneven distribution of the copper(I) complexes. While some are buried deep inside the nanoparticle, others are situated on the surface and could therefore be more exposed to water and exciplex quenching thus leading to an overall smaller averaged emission quantum yield. Second, as indicated by the addition of CN⁻, the silica structure is porous and water molecules can likely penetrate and reach some complexes, promoting the fast deactivation of the excited state of embedded **Cu-I**⁺. In addition, water and CH₂Cl₂ molecules could be trapped inside the silica walls during the synthesis. Notwithstanding the rather weak emission quantum yield of Cu-I@SiO₂, those results prove that entrapment of a modest luminophore like **Cu-I**⁺ in silica, with little steric hindrance compared to [Cu(dsbtmp)₂]⁺, allows to preserve its excited state properties in aqueous media.

Time correlated single photon counting (TC-SPC) has been used to estimate the emission lifetime of Cu-I@SiO₂. The decay of the latter (Figure S8) contains several phases. Four different exponentials are necessary to fit the experimental decay, probably due to the fact that complex molecules are closely packed and immobilized in various positions and local microenvironments inside the nanoparticles, thus leading to heterogeneity. Although a short average lifetime of 45 ns could be retrieved, a long-lived phase with a lifetime of 148 ns (12% of the overall signal) comparable to the value obtained for the free complex in dichloromethane (Figure S9) could be identified. In line with the comments above, the longer-lived emission traces can be associated to excited complexes insulated from the external media, while shorter-lived emission traces likely stem from populations of excited complexes which are diversely exposed to quenchers (e.g., water molecules) whether they diffuse in the nanoparticles or they are trapped within the silica structure.

Optical transient absorption spectroscopy

To explore in depth the behaviour of the excited state of the copper(I) complex inside the silica nanoparticle, optical transient absorption spectra have been recorded following excitation with 500 nm laser pulses (400 nJ/pulse, 300 fs instrument response, see Supporting Information for additional details). The transient spectra and dynamics of Cu-I@SiO₂ solutions in water are similar to those of **Cu-I**⁺ solutions in dichloromethane (PF₆⁻ salt) on the sub-picosecond to nanosecond timescales (Figure 5a).[30] The excited-state absorption (ESA) following excitation is initially broad and featureless, centred at about 540 nm with a weak absorption extending to wavelengths greater than 700 nm. The negative signal at wavelengths less than 500 nm reflects the ground-state bleach of the MLCT transition. Throughout the first 30 ps, the ESA narrows and blue shifts at the peak position to ~530 nm. The ESA features at time delays greater than 30 ps are spectrally better resolved, with a peak near 545 nm and shoulder near 515 nm and weak absorption extending to wavelengths greater than 700 nm. These transient features then decay monotonically on the hundreds of nanoseconds timescale (Figures 5a and S10a) as revealed by transient absorption measurements performed on the nanosecond to microsecond timescales (500 nm excitation, 800 nJ/pulse, 1.2 ns instrument response).

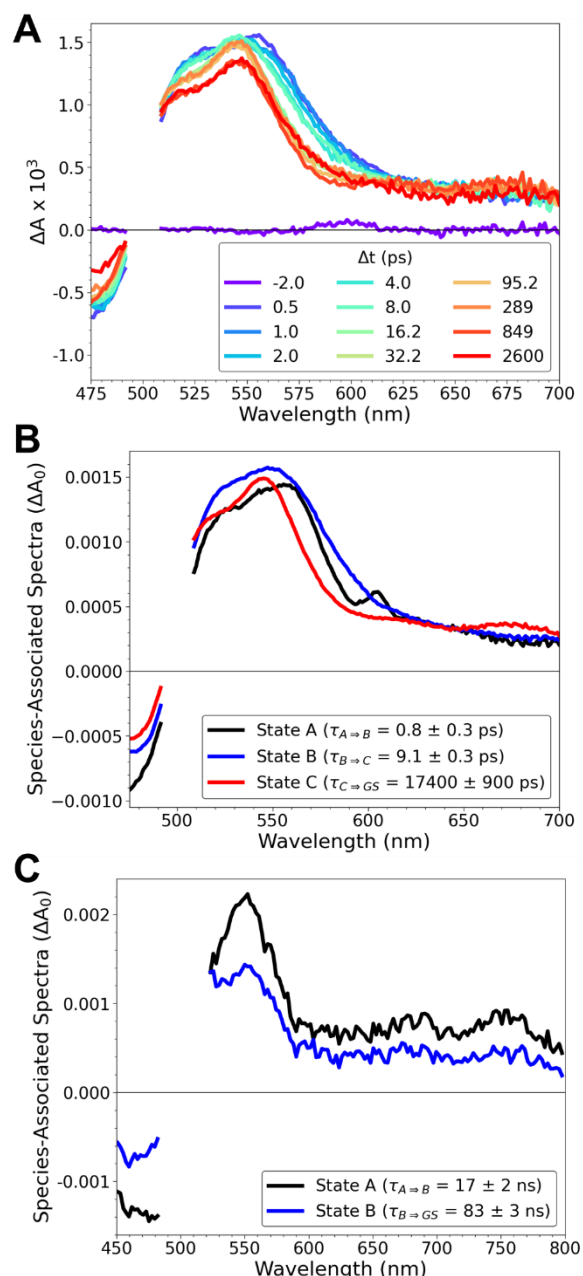


Figure 5. a) Transient absorption spectra for a solution of Cu-I@SiO₂ in water at select time delays following 500 nm excitation (400 nJ/pulse). Species-associated spectra obtained via global kinetic analysis of the b) femtosecond and c) nanosecond transient absorption data using sequential first-order kinetic models. Optimized time constants for the conversion from one state to the next are provided in the legends.

The TA data for Cu-I@SiO₂ solutions in water have been treated with global kinetic analysis using a sequential first-order kinetic mechanism (see Supporting Information for more details). The femtosecond transient absorption data are fit to an A → B → C → GS (ground state) model where **Cu-I** complexes are promoted from the GS to state A by the 500 nm laser pulses and then relax back to the GS according to the prescribed pathway. The

nanosecond transient absorption data are fit to an $A \rightarrow B \rightarrow \text{GS}$ model. The species-associated spectra and corresponding population curves are provided in Figures 5b and S10 for the femtosecond measurements and Figures 5c and S11 for the nanosecond measurements. Following excitation at 500 nm, the ESA feature increases slightly as the excited-state population transfers from state A to state B with $\tau_{A \rightarrow B} \approx 0.8$ ps. This timescale and change in ESA are consistent with the pseudo-Jahn-Teller excited-state structural distortion driven by coordination geometry differences for Cu(I) ion in the ground state and Cu(II) in the MLCT excited state. The transition from state B to state C with $\tau \approx 9.1$ ps—shown by the ESA shifting to shorter wavelengths and becoming more resolved—corresponds to relaxation of the excited-state population from a $^1\text{MLCT}$ excited state to the lowest energy $^3\text{MLCT}$ excited state. The nanosecond transient absorption results reveal that the $^3\text{MLCT}$ excited state relaxes back to the ground state with bi-exponential dynamics ($\tau \approx 17$ ns and $\tau \approx 83$ ns). This is consistent with the multi-exponential decay of the photoluminescence and provides further evidence that the **Cu-I** complexes experience a distribution of microenvironments in the SiO_2 matrix.

While these transient spectra and dynamics are generally typical of solutions of Cu(I) bisphenanthroline complexes, **Cu-I*** specifically,[30] encapsulating the photosensitizer in the SiO_2 nanoparticles led to several distinctions compared to the solution phase behaviours. Most notably, $^3\text{MLCT}$ lifetimes longer than 1 ns are rarely observed for copper(I) bisphenanthroline complexes in coordinating solvents. Transient interactions between the excited-state Cu(II) centre and solvent molecules are proposed to stabilize the excited-state and facilitate rapid relaxation to the ground state. Thus, the about 45 ns average lifetime of the $^3\text{MLCT}$ state for solutions of Cu-I@ SiO_2 in water highlights the role the SiO_2 matrix has in reducing the unproductive Cu(II)-solvent interactions. Additionally, the intersystem crossing observed here for solutions of Cu-I@ SiO_2 in water is slightly faster than that for solutions of **Cu-I*** in dichloromethane—9 ps vs 11 ps, respectively. Faster intersystem crossing has been observed for copper(I) bisphenanthroline complexes with bulky substituents at the 2,9-positions of the phenanthroline ligands that restrict the excited-state structural distortions. While the 9 ps intersystem crossing (ISC) time constant for Cu-I@ SiO_2 suspensions in water is not substantially shorter than that of **Cu-I*** solutions in dichloromethane, our results suggest that embedding the **Cu-I*** complexes in the SiO_2 matrix further restricts the excited-state structural distortions. The similar ISC time constant for Cu-I@ SiO_2 suspensions in water and **Cu-I*** in dichloromethane agrees with earlier studies where the time constants for the Jahn-Teller distortion and ISC were shown to be inner shell processes with little change by the media.[43–46]

Electrochemical Properties

To further investigate the impact of the entrapment on the Cu complex properties, the electrochemical behaviour of Cu-I@SiO₂ has been recorded in aqueous solution (0.1 M LiClO₄) and compared to that of the free metal complex in solution in organic media (CH₂Cl₂, 0.1 M tetra-*n*-butylammonium hexafluorophosphate). The complex shows a quasi-reversible oxidation process at approximately +1.26 V vs. SCE corresponding to the copper-centred oxidation.[30] Figure 6 shows the voltammograms obtained for Cu-I@SiO₂ at a glassy carbon electrode. Consistent with the behaviour observed for the complex in solution, a well-defined peak corresponding to the one-electron oxidation of the metal centre is observed with a formal potential, E° , of 1.064 ± 0.025 V vs. Ag/AgCl (3.5M KCl). Taking into account the differences in reference electrodes, this represents a shift of approximately 235 mV in a negative potential direction when the complex is incorporated within the silicate nanoparticles. This shift is consistent with the metal complex being thermodynamically easier to oxidise and is likely to arise from the higher dielectric constant inside the nanoparticles, due to the diffusion of water molecules ($\epsilon_r = 78$) inside the structure, compared to CH₂Cl₂ ($\epsilon_r = 9$). The peak-to-peak separation is 183 ± 20 mV which is significantly larger than the value of 57 mV expected for a reversible electron transfer under semi-infinite linear diffusion control. Moreover, the ratio of the cathodic peak current, i_{pc} , to the anodic peak current, i_{pa} , varies from 0.62 at 10 mVs^{-1} to 0.52 at 1000 mVs^{-1} . This quasi-reversible response could arise either from a slow heterogeneous electron transfer or from a following chemical reaction, e.g., oxidation state dependent changes in the coordination sphere of the metal complex. The observation that the reaction is less reversible at higher scan rates where one would expect any chemical reaction following electron transfer to occur to a lesser extent, suggests that the slow heterogeneous electron transfer is the most significant factor. However, there is some degradation of the metal complex when it is oxidised, e.g., i_{pa} decreases by $15 \pm 5\%$ over 10 repeated cycles at 10 mV s^{-1} .

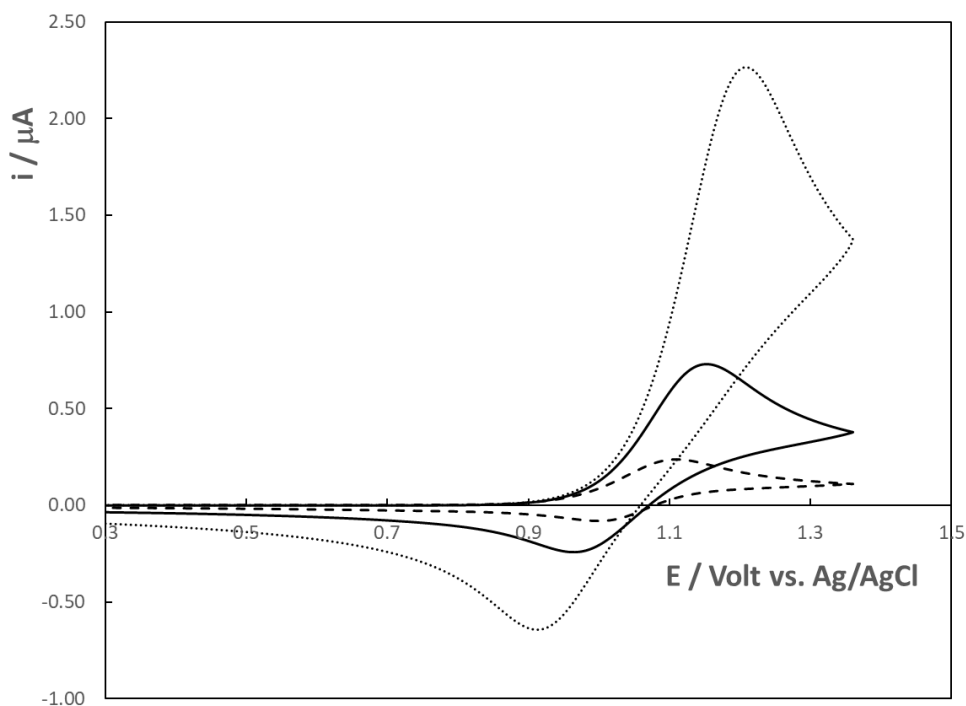


Figure 6. Cyclic voltammograms of an aqueous suspension of Cu-I@SiO₂ at a glassy carbon electrode where the supporting electrolyte is 0.1 M LiClO₄. The scan rates are 1 V s⁻¹, ——— 0.1 V s⁻¹ and - - - - 0.01 V s⁻¹.

Electrochemiluminescence Properties

Richter and co-workers have shown that [Cu(2,9-dimethyl-1,10-phenanthroline)₂]⁺ can generate electrochemiluminescence (ECL) in aqueous, nonaqueous, and mixed solvent solutions using tri-*n*-propylamine, TPrA, as an oxidative-reductive co-reactant.[47] Figure 7 shows that the Cu-I@SiO₂ nanoparticles can generate electrochemiluminescence at a potential that coincides with the oxidation of the Cu⁺ metal centre.

This result is significant since the molecular complex does not show any optically driven emission in a water/acetonitrile mixture. The observation of ECL only at potentials where the metal centre is oxidised at the electrode surface contrasts with the archetypal ruthenium tris bipyridyl [Ru(bpy)₃]²⁺-TPrA ECL system.[48–50] In the [Ru(bpy)₃]²⁺ system, electrogenerated TPrA^{•+} radical can chemically oxidise the Ru²⁺ centre causing ECL to be observed at relatively less positive potentials due to the highly exergonic reaction of TPrA^{•+} with Ru³⁺ despite the fact that the applied potential is not sufficiently positive to electrochemically oxidise Ru²⁺ directly at the electrode surface. The fact that ECL is observed indicates that copper centres within the nanoparticles can be oxidised and that the co-reactant can permeate the particles at least to some extent. This evidences that, despite the fact that **Cu-**

I^+ complexes are embedded within a silica matrix, electron transfers at an electrode/nanoparticle interface are possible.

However, the intensity of the ECL observed is extremely low, approximately 750-fold lower on a per molecule basis, than that observed for solution phase $[\text{Ru}(\text{bpy})_3]^{2+}$ under the same conditions. This result could arise due to differences in the excited-state properties of the encapsulated complex or differences in the rate of heterogeneous electron transfer. The standard rate of heterogeneous electron transfer measured for the copper containing nanoparticles in this work is $2.1 \pm 0.5 \times 10^{-3} \text{ cm.s}^{-1}$ which is only a factor of approximately ten lower than that observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ in solution, i.e., slow heterogeneous electron transfer from the Cu^+ centres is not the only cause of the low ECL intensities observed. Importantly, the emission quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\phi_{\text{em}} = 0.042$ in degassed water)[51] is roughly 300 times larger than the one of Cu-I@SiO_2 , another likely reason to rationalize the weak ECL signal observed for these doped nanoparticles.

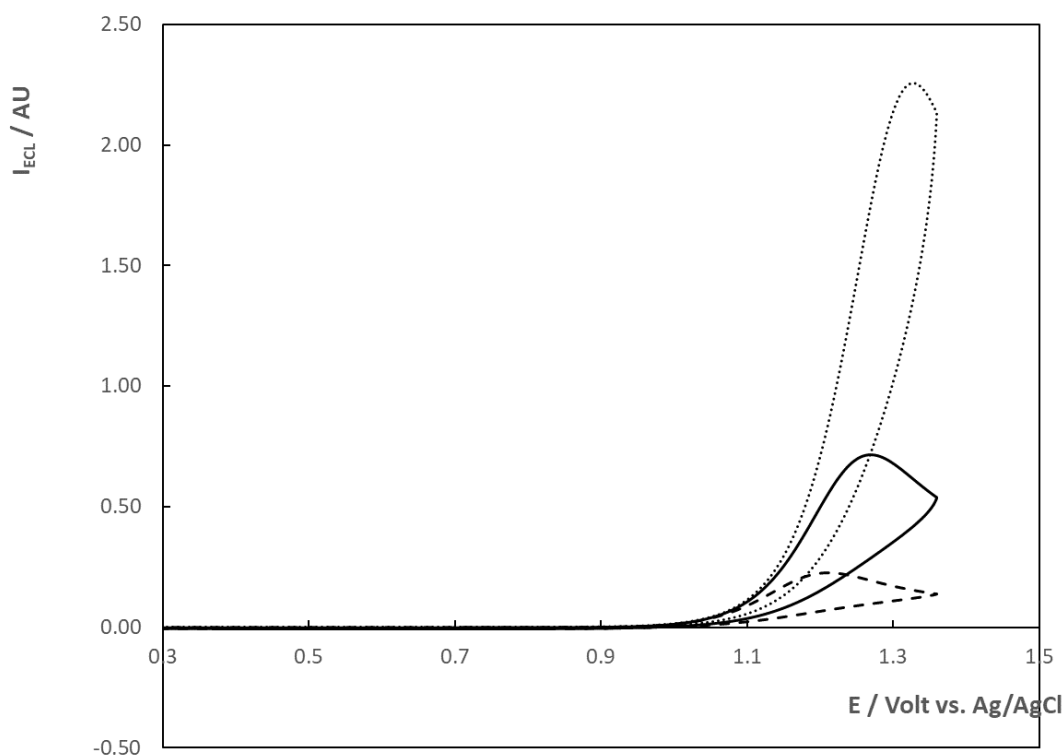


Figure 7. Potential dependence of the electrochemiluminescence intensity observed for a $6 \mu\text{M}$ aqueous suspension of Cu-I@SiO_2 at a glassy carbon electrode where the supporting electrolyte is 0.1 M LiClO_4 . The scan rates are $\cdots\cdots\cdots 1 \text{ V s}^{-1}$, $\text{—} 0.1 \text{ V s}^{-1}$ and $\text{- - - -} 0.01 \text{ V s}^{-1}$.

Proof of concept in a bio-application: photoluminescence in whole blood

The availability of photoluminescent probes that produce detectable emission from within a medium as complex and coloured as blood is important in the field of bio-diagnostics.[52,53] Since the Cu-I@SiO₂ emits towards the near-infrared region where whole blood becomes more transparent (Figure S12), this prompted us to study the influence of whole blood on the emission properties of Cu-I@SiO₂.

Significantly, the steady state emission spectra of Cu-I@SiO₂ ($\lambda_{exc} = 481$ nm) can be recorded when aliquots of whole blood are added to the suspension (Figure 8a) albeit decreasing in intensity at high blood concentration. This observation, made with a weakly luminescent species such as Cu-I@SiO₂, clearly demonstrates the benefits of having an emission band centred in the blood transparency window. Eventually, the emission band blue shifts and gets distorted in presence of 40 μ L of whole blood (ca. 1.4% of the total volume). This distortion is likely due to the superimposition of the photoluminescence signal from blood (Figure S13). The decrease of the intensity could be due to some absorption of the emitted light by blood (although the absorbance of the samples at 680 nm remains low, Figure S14), loss of emitted light by scattering (due to the presence of large bodies in whole blood) or to partial absorption of excitation light by blood (absorbance at 481 nm is above 0.8 in presence of blood, Figure S14) instead of Cu-I@SiO₂ (absorbance at 481 nm is 0.2 before addition of blood, Figure S14). Unexpected secondary interactions between the numerous constituents of whole blood and Cu-I@SiO₂ could also be important (as we experienced that the silica nanoparticle is porous).

Measuring the time-resolved emission decays of those complex mixtures by time-correlated single photon counting (TC-SPC) enables the monitoring of long-lived emission decays selectively originating from the Cu-I@SiO₂ nanoparticles. In addition, the kinetic traces can be accumulated over long periods allowing to improve the signal-to-noise ratio. As shown in Figure 6b, the Cu-I@SiO₂ long-lived decays are virtually unaffected in the presence of 20 or 40 μ L of whole blood. The long-lived emission decay of Cu-I@SiO₂ could even be observed for a 1:1 mixture of blood and Cu-I@SiO₂ suspension (Figure S15). This is quite remarkable, first because fluorescence in presence of whole blood is usually performed on diluted blood samples (e.g., 5%).[53] Second, the fact that the luminescence of a rather weak luminophore like Cu-I@SiO₂ can still be monitored in a complex and concentrated blood sample demonstrates that homoleptic copper(I) complexes can certainly play a role in biomedical sensing when they are efficiently protected from the external environment by a silica “armour”, under the shape of a stable transparent aqueous suspension.

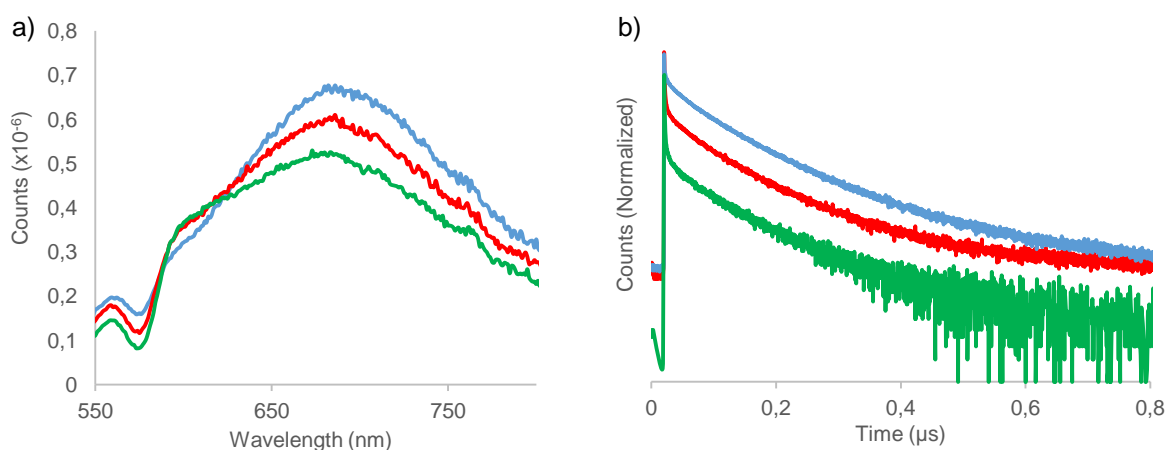


Figure 8. a) Steady-state emission spectra of Cu-I@SiO₂ suspension (excitation at 480 nm) in presence of 20 and 40 µL of whole blood. Excitation at 480 nm, volume of the analysed aqueous suspension of Cu-I@SiO₂: 2.9 mL. b) Emission decays of Cu-I@SiO₂ suspensions (excitation at 438 nm) in absence (blue trace) and in presence of 20 (red trace) and 40 µL (green trace) of whole blood.

Conclusion

In this article, we have reported that trapping luminescent copper (I) complexes inside a protective silica matrix, decorated with PEG chains, leads to stable aqueous suspensions of coloured nanoparticles Cu-I@SiO₂. The solution-like behaviour of the latter (high transparency, limited light scattering) enables in-depth characterisation and diverse applications. Electrochemical and optical studies suggest that the silica around copper (I) complexes is porous and that small molecules like H₂O can diffuse into the nanoparticles albeit to a very limited extent and with rather slow kinetics. However, the aqueous suspensions are photoluminescent although water is an efficient quencher of the excited state for the free molecular complexes. This demonstrates that the trapped copper (I) complexes are nevertheless still partially shielded from the external medium.

We explored the potential of the Cu-I@SiO₂ nanoparticles in two fields showing relevance towards luminescent probes for biodiagnostic applications. First, we measured the ECL intensity of the suspension in presence of TPrA as co-reagent. The signal, albeit weak, can be clearly monitored and paves the way towards the development of ECL-based assays using copper(I) homoleptic complexes as near infrared luminophores. Second, considering that the emission of Cu-I@SiO₂ lies within the blood transparency window, we performed a preliminary photoluminescence study of the latter in whole blood. Although the emission band is significantly affected by blood, TC-SPC measurements allowed to observe a long-

lived luminescence signal, opening interesting opportunities for the future development of luminescent probes and their detection by fluorescence lifetime imaging microscopy (FLIM). Accordingly, the application of this strategy to more luminescent copper (I) complexes is highly desirable to facilitate data acquisition. Work on this matter is ongoing in our team.

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