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# Selective encapsulation and enhancement of the emission properties of a luminescent Cu(I) complex in mesoporous silica

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*We describe a synthetic approach to prepare new luminescent silica-based materials through the encapsulation of a neutral copper(I) complex inside the pores of mesoporous silica nanoparticles (MSN). Interestingly the compound is present, in the solid state, as two polymorphs, blue and yellow emissive, and in solution it shows a pale yellow color that is also mirrored by an emission in the yellow-orange region of the electromagnetic spectrum. The X-ray structures of single crystals have been obtained for both polymorphs. The complex encapsulation in MSN is achieved by its entrapment inside micelles followed by condensation of the silica source. Interestingly, the entrapment leads to the isolation of only one species. Indeed, the compound inside the MSN exhibits remarkable photophysical properties, showing an intense blue emission in solution and in the solid state. Powder X-ray diffraction of the hybrid materials proves that the complex entrapped in MSN is indeed the blue polymorph. The confinement provides not only a method to isolate only one form of the complex, but also a certain rigidity, more stability of the system by protection of the complex from undesirable oxidation, leading to a highly emissive material possessing a photoluminescence quantum yield of 65 %.*

**Keywords**: *copper complex • silica • encapsulation • luminescence • polymorph*

## Introduction

*The use of confined spaces to enhance photophysical properties and stability is an emerging field that is attracting the interest of scientists.[1, 2] Different techniques can be used to encapsulate luminescent molecules in porous materials: post-synthetic grafting in the pores after the particle is formed; insertion of the desired emitter in the template used for the formation of the porous silica;[3, 4] or derivatization of the emitting unit itself in order to obtain a surfactant.[5, 6] The encapsulation could lead to superior performance of the luminescent materials[7, 8] and to a better stability of the emitters due to the space constrain and the rigidity of the surrounding environment. Indeed, the rigidity and isolation from the environment can enhance the emission and extend the excited state lifetime. In this respect, Corma et al. demonstrated that the entrapment of a ruthenium complex in zeolites was able to enhance the stability of a Light-Emitting Electrochemical Cell.[9] More recently, our group developed an iridium based surfactant which, when immobilized in MSNs, resulted to be protected by dioxygen quenching and exhibiting enhanced photophysical properties.[5] Such approach was extended to rare-earth based molecules, with for instance lanthanide*

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*complexes that have been studied extensively over the past decades. The complexes were covalently bounded to the silica matrix[10, 11] or just diffused by their physical encapsulation into the pores of zeolites,[12, 13] to obtain emissive hybrid materials. Indeed, these systems exhibit interesting improvement in terms of photo-stability, chemical stability and thermo-stability.[14] So far, however, such an approach has been restricted to the use of rather expensive and non-ecologically friendly metals. The possibility to replace the rare metals with more abundant emitters has recently been the subject of many studies and in particular copper complexes are promising candidates.[15] The interest in Cu(I) compounds, beyond the availability of copper on earth, is related to their interesting properties: good tunability of their emission colors,[16-18] long-lived $^3$MLCT excited states, low cost and a relatively friendly impact to the environment.[19] Nevertheless, an improvement of their photoluminescence quantum yield (PLQY), and even more stringent, a better stability, are required in order to apply such emitters in optical devices. In addition, many copper complexes crystallize as a mixture of polymorphs. Separation of the different crystals is often difficult and in solution the compounds display properties which are frequently not the one corresponding to the desired polymorph.*

*To overcome all these issues, encapsulation of the complexes inside inorganic porous matrices could be an interesting approach, and to the best of our knowledge no attempt to obtain a single species, from mixture of different forms (isomers or polymorphs) has been reported.*

*In this paper, we describe a novel strategy to isolate only one of the possible polymorphs of a luminescent* **Cu(I)** *complex, which indeed exists as two emissive (blue and yellow) forms. The approach is related to the insertion, through hydrophobic interactions, of the luminescent complex,* **Cu(I)** *(***Figure 1** *and* **Scheme 1***) in the micelles formed by the surfactant CTAB (hexadecyltrimethylammonium bromide), used as a template for the condensation of mesoporous silica nanoparticles. Upon formation of the porous particles the entrapped complex shows a great stability and enhanced photophysical properties. Interestingly we demonstrate that we are able to form only one polymorph of the complex inside the silica pores, which is the desired highly emissive blue species.*

## Results and Discussion

*The hydrophobic* **Cu(I)** *complex, isolated as a yellow emissive powder, has been previously prepared in our laboratory.[20] As some other organometallic copper(I) complexes,[21, 22] it tends to crystallize in different polymorphs. The two forms have been isolated by slow evaporation of EtOH leading to both yellow emitting crystals[‡],* **Cu(I) yellow** *and blue-green emitting crystals,* **Cu(I) blue,** *and their single crystal X-ray structures was resolved (***Figure 1***). In the single unit cell, we observe a different orientation of the phenyl rings of the phosphine, and more interestingly, the packing of the molecules is quite different for the two forms (for details, see the Electronic Supporting Information). The different packing of the complexes is indeed responsible for the different emission colors of the crystals.*

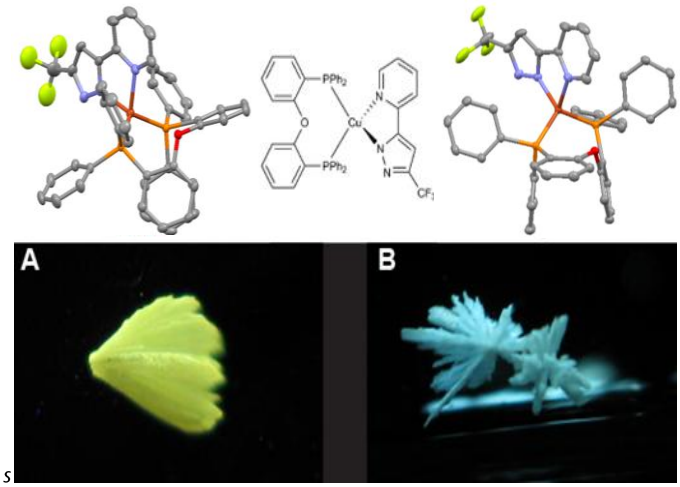


**Figure 1.** *Chemical formula (middle-top), and the crystals under UV illumination (366 nm): (A) Cu(I) yellow and above its X-ray structure; (B) Cu(I) blue and above its X-ray structure.*

*However, once dissolved in organic solvents, both the polymorphs possess only one emission present is yellow/orange region of the spectrum. The photophysical properties of the complex in solution and the precipitate (solid state) are depicted in Table 1. Absorption and emission spectra were recorded at room temperature in deaerated dichloromethane and the luminescence is shown in* **Figure 2A** *(see* **Figure S1** *for the excitation spectra). The compound absorbs in the UV region due to the intraligand ($^1$LC, 300 nm) transition involving the ligands*

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*coordinated to the Cu ion and in particular the pyridine pyrazole*

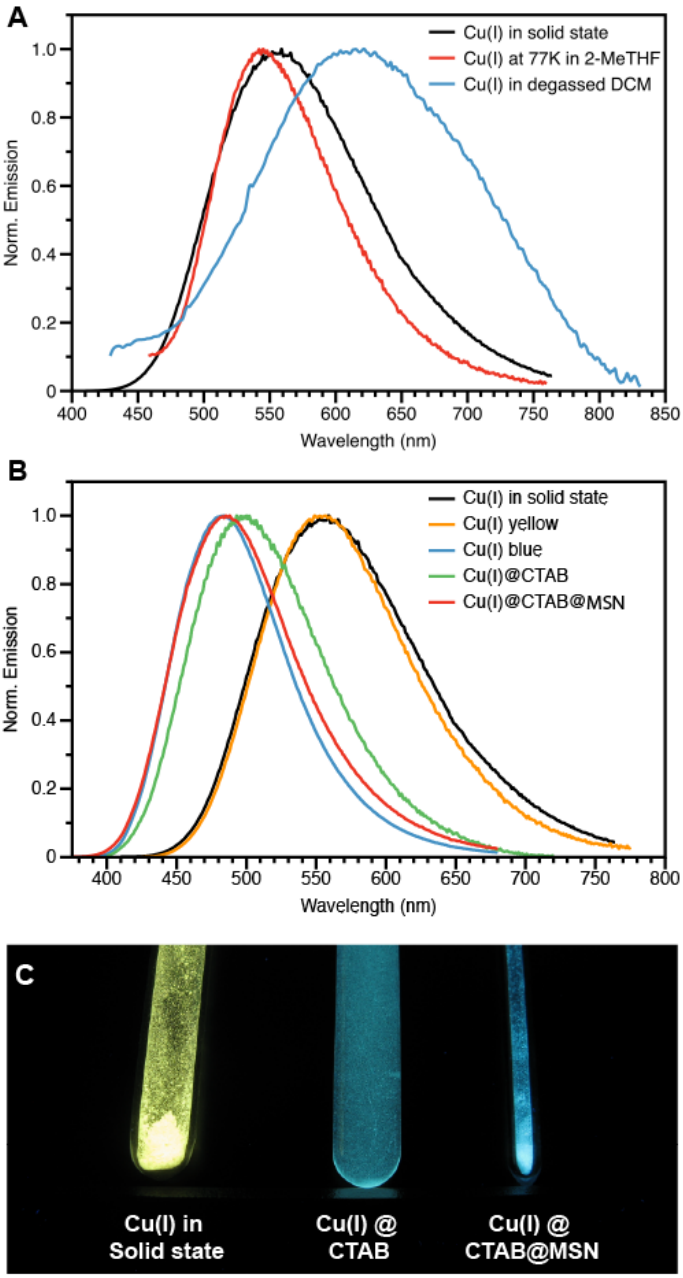


**Figure 2.** *Emission spectra of pure complex (A), emission spectra in different environments (B), and digital photograph of the luminescence complex in the different environment (C). For A and B $\lambda_{Exc}$ = 375 nm, for C excitation with UV lamp $\lambda_{Exc} \approx$ 366 nm. The spectrum of Cu(I)@CTAB@MSN was recorded in solid state.*

*ligand has transitions at lower energy than the phosphines. At longer wavelength, we can observe the spin allowed metal to ligand charge transfer ($^1$MLCT, 350 nm) bands corresponding to the d→π* transitions involving the pyridine ligand. Excitation at 360 nm leads to broad unstructured emission bands, that for the dichloromethane solution has a maximum at about 630 nm. The emission has a triplet MLCT nature, as also reported for similar Cu(I) complexes emission.[23] Unsurprisingly, the distortion between the ground state and the excited state occurs easily in solution, which leads to a low emission quantum yield, even in degassed solvents such as DCM and short excited state lifetime (see* **Table 1***).*

*Also, the low temperature emission in a 2-MeTHF matrix, at 77K, presents a featureless band, at higher energy than the fluid solution. Such a blue shift confirms the charge transfer character of the*

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**Table 1.** *Photophysical properties of the copper complexes in solution, as precipitate, and inside mesoporous silica at different condition.*

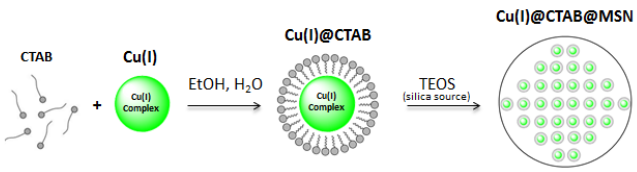
| | $\lambda_{em}$(nm) | $\Phi_{Ph}$(%) | Lifetime 298 K (μs) | |
|---|---|---|---|---|
| **Cu(I)** *in degassed DCM* | *617* | *0.08* | *0.133 (100%)* | |
| **Cu(I)** *precipitate* | *550* | *10.* | *10.8(31%)* | *4.8 (69%)* |
| **Cu(I) yellow** | *549* | *10.* | *14.3(72%)* | *4.9 (28%)* |
| **Cu(I)** *at 77K in 2-MeTHF* | *545* | *n.a.*[a] | *170 (100%)* | |
| **Cu(I)@CTAB** | *498* | *9.5* | *23.0(74%)* | *6. (26%)* |
| **Cu(I)@CTAB@MSN (solid state)** | *488* | *65* | *23.3(78%)* | *4.4 (22%)* |
| **Cu(I) blue** | *484* | *64* | *23.7(73%)* | *6.1 (27%)* |

[a] *not measured due to instrumental limitation.*

*emission and due to the lack of solvent stabilization, of the polar excited state, a rather large shift is observed (***Figure 2A***). The excited state decays with a monoexponential kinetics and the luminescence lifetime is much longer than in solution, confirming the triplet nature of the emissive state. The emission of the precipitate, obtained by simple precipitation of the complex from solution, is very similar to the low temperature luminescence (***Figure 2A***). The emission quantum yield is higher than in solution and the excited state lifetime in the microsecond regime. Interestingly, the two crystalline species, polymorphs* **Cu(I) yellow** *and* **Cu(I) blue** *display a biexponential excited state lifetimes and have very different values, as also reflected in the emission quantum yields that for the blue emissive crystals reach 65%. All the main photophysical data are reported in* **Table 1**.

*In order to study the behavior of the emitters in a confined space in solution, and to understand which of the species would form by interaction with an hydrophobic environment, we have dissolved the* **Cu(I)** *(5mg) in a minimum amount of EtOH, (2 ml) and added to 15 ml of an aqueous CTAB solution (1.8x10*$^{-3}$ *M), well above the critical micelle concentration. The complex, due to its hydrophobic nature, is easily entrapped inside the micelles, creating complex-CTAB hybrid micelles,* **Cu(I)@CTAB**, *that can be used as template for the sol-gel synthesis of mesoporous silica nanoparticles (***Scheme 1***). To understand the role of the micelle formation on the photophysical behavior, we compared the emission of a solution of the emitter with the one after formation of the hybrid micelles. The complex, which emits at 550 nm as a powder, once dissolved in ethanol (5·10*$^{-4}$ *M) does not exhibit any appreciable luminescence, most likely due to the coordination of the solvent to the distorted excited state geometry of the* **Cu(I)**. *The micellar solution of the complex,* **Cu(I)@CTAB**, *on the other hand, displays a rather intense blue emission (***Figure 2B***) and its excited state lifetime is longer than in DCM solution. This blue emission, absent in DCM solution and in the powder, resembles the emission in the crystalline phase of the blue polymorph,* **Cu(I) blue**. *This finding suggests that the micelle surrounding the hydrophobic compound creates not only a non-polar shell, that could be partially responsible for the strong blue shift in such solution, but also pre-organizes the packing of the complex in order to stabilize the formation of the* **Cu(I) blue** *species in a rather rigid environment.*

*After the addition of tetraethyl orthosilicate (TEOS), the hydrolysis-condensation mechanism takes place and mesoporous silica nanoparticles with pores containing the complex-CTAB micelles are obtained (***Figure 3** *and* **Scheme 1***). Due to the sensitivity of the Cu(I) complexes towards oxidation and reduction, we developed mild synthesis conditions, such as ambient processing temperature and almost neutral pH. For this reason, a weak base, like tris(hydroxymethyl) aminomethane,*[24] *was used to ensure the formation of micelles at pH close to 8.*




**Scheme 1.** *Schematic representation of encapsulation of copper complex in mesoporous silica nanoparticles.*

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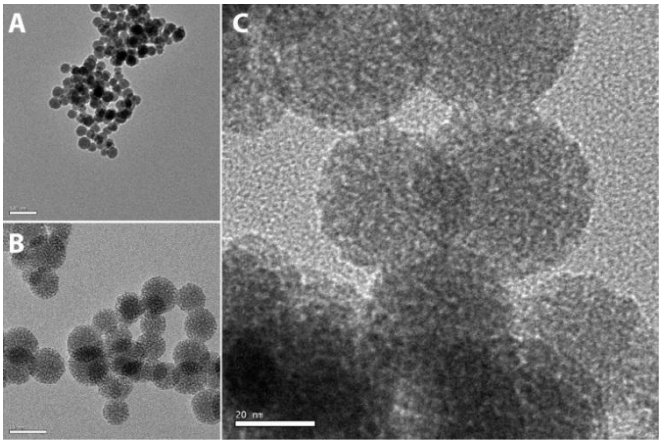


**Figure 3.** *(A-C) Typical TEM images of Cu(I)@CTAB@MSN with different magnifications. Scale bar equals to 100, 50 and 20nm, respectively.*

*The obtained particles were characterized by electron microscopy, dynamic light scattering (DLS), X-ray Photoelectron Spectroscopy (XPS), small-angle X-ray scattering (SAXS) and Nitrogen sorption isotherms (for details, see the Electronic Supporting Information). The resulting mesoporous materials which encapsulate the copper complex* **Cu(I)@CTAB@MSN***, have average diameter of 30 nm as estimated from the TEM images (***Figure 3***). DLS revealed a very high mono-dispersity of the nanoparticles (***Figure S2***) and from electron microscopy images, we can observe that the particles with and without* **Cu(I)** *complex entrapped, possess an identical morphology (***Figure S3** *for particles without* **Cu(I)***). The presence and the effect of the Cu(I) complex inside the micelles was confirmed by nitrogen sorption experiments (***Figure S4D***). Indeed, we observed an increase of the pore size for the particles containing the complex. The small-angle X-ray scattering (SAXS) patterns are shown in* **Figure S4A***. These* **Cu(I)@CTAB@MSN** *samples exhibit analogous single broad peaks and absence of diffraction peaks at higher angles, which is attributed to the incomplete order of the mesopores in the particles and to the absence of degradation of the copper complex inside the pore.*

*To confirm the integrity and the chemical nature of the copper complex inside mesoporous silica, $^{19}F$ CP-MAS NMR spectra were recorded (***Figure S5***) and showed the presence of a single species. The XPS measurements reveal that the copper species is indeed Cu(I) and is not oxidized to Cu(II) (***Figure S4B***). This analysis is particularly important since during the encapsulation into the silica pores degradation of the copper complex can occur, as well as oxidation of the copper ion, resulting in a non-luminescent product.*

*The photophysical properties of the encapsulated Cu complex have been studied in solid state and in solution by suspending the mesoporous silica, with the entrapped complex, in ethanol (***Figure 2B***). Indeed, upon formation of the particles only a further small hypsochromic shift is observed on the solid-state sample compared with the micelles, but a dramatic change in the emission quantum yields was recorded (PLQY=65%). The solid and the mixture in suspension possess identical properties indicating that the complex is completely isolated in the mesoporous silica, and it is in a rigid environment, that prevent radiationless deactivation. Interestingly we observe that are able to form only the* **Cu(I) blue** *species inside the silica by comparing the photophysical properties. It is important to mention that* **Cu(I)@CTAB@***MSN in solid state or in ethanolic suspension display the same emission profile.*

*As a conclusive evidence that we obtained a copper complex inside mesoporous silica having the same structure as the* **Cu(I) blue** *polymorphs, we measured the sample by powder XRD. The XRD patterns (***Figure 4***) clearly show that* **Cu@CTAB@MSN** *has the same pattern as the powder XRD peaks of the blue emissive crystal,* **Cu(I)blue** *with additional amorphous feature coming from the silica contribution.*

*After removing the template surfactant (CTAB) and the complex from the pores by calcination technique, at 550°C, we could analyze the geometry and size of the pores. Both samples (***CTAB@MSN** *and* **Cu(I)@CTAB@MSN***) have similar isotherm sorption patterns, meaning that they possess the same cylindrical pore geometry (Figure S4C). The encapsulation of the copper complex did not alter significantly the formation of CTAB classical micellar structure templating the pore of the silica. However, when looking carefully to the pore size distribution, we could observe the formation of larger pore size (6-9 nm) after the encapsulation of the copper complex in analogy of pore enlargement using organic molecules (Figure S4D).[25] This result supports the hypothesis that the copper compounds are entrapped in the center of the micelles, determining an enlargement of the system. Also, the mobility of the micellar system, was demonstrated by removing the template by Soxhlet extraction in boiling ethanol. Indeed, we could not detect by XPS the presence of Cu, P and F atoms after this treatment, excluding the entrapment of the complex in*
*the silica framework.*

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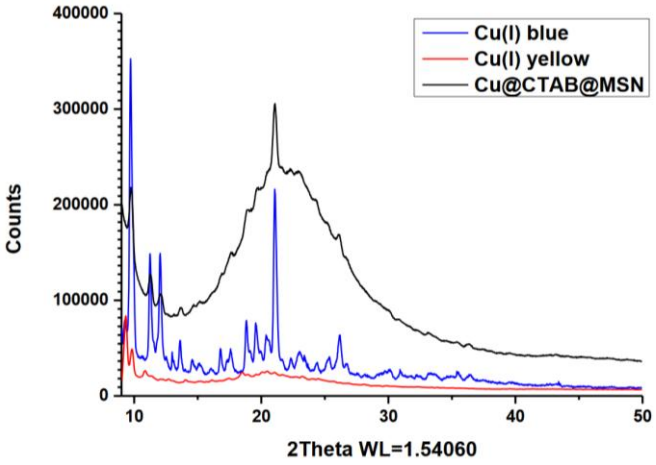


**Figure 4.** *XRD pattern of the Cu@CTAB@MSN (black line), Cu(I) blue (blue line) and Cu(I) Yellow (Red line).*

## Conclusions

*In conclusion, we demonstrated that using mesoporous silica as confinement system for a neutral Cu(I) complex, which possess two polymorphic structures with very different emission properties, it is possible to entrap only one. Interestingly the species that is selectively encapsulated correspond to the blue luminescent Cu(I) complex, and it is already present during the micelle template formation and it is further stabilized and rigidified once the mesoporous silica is synthesized. The resulting hybrid material, featuring a high photoluminescence quantum yield (65%), has been fully characterized. Moreover, powder X-ray diffraction proves that only the blue emissive polymorph is inside the MSN. This strategy can surely be applied to other complex mixture of different polymorphs or isomers since the entrapping could discriminate only one of them through supramolecular interactions.*

## Experimental Section

### *Materials and characterization*

*All the chemicals were purchased from Sigma Aldrich, Tokyo Chemical Industry and Alfa Aesar and used without any further purification.*

### *Synthesis of Cu(I) complex*

*Precursor $[(CH_3CN)_4Cu]PF_6$ (213 mg, 0.57 mmol, 1 equiv.) and POP (310 mg, 0.58 mmol, 1 equiv.) were dissolved in 20 mL of degassed DCM. After one hour of stirring at room temperature under a $N_2$ atmosphere, 5-trifluoromethyl-3-(2´´-pyridyl)-pyrazole, 3-trifluoromethyl-5-(2´-pyridyl)-1H-pyrazole (123 mg, 0.58 mmol, 1 equiv.) is added. The reaction is stirred overnight and 15 mL of a solution of $Na_2CO_3$ 1M is added. The organic layer was separated and then dried over $Na_2SO_4$, filtered and the solvent evaporated under reduced pressure. Chromatography in silica gel and $CH_2Cl_2$ as eluent gave the final pure product as a yellowish powderYield: 67%. HRMS calc. for the compound $C_{45}H_{33}CuN_3OP_2F_3$ 813.13; found 814.14 ([M+H]).*

*$^1$H NMR (300 MHz, $CDCl_3$) δ= 7.72 (d, 1H); 7.61-7.46 (m, 5H); 7.31 (m, 3H); 7.19-7.02 (m, 14H); 6.95-6.82 (m, 6H); 6.78- 6.76 (m, 3H); 6.65 (t, 1H). $^{31}$P NMR: (300 MHz, $CDCl_3$) δ= -13.62; $^{19}$F NMR: (300MHz, $CDCl_3$) δ= -59.43.*

*Synthesis of Cu@CTAB@MSN*

*The molar composition used was 1 TEOS: 0.070 CTAB: 0.26 $NH_2C(CH_2OH)_3$: 265 $H_2O$: 5.5 EtOH. Typically, 5 mg of the complex is dissolved in 2 mL of EtOH and a solution of 80 mg of CTAB and 100 mg of THMAM in 15 mL of water is added. After 5 minutes of stirring, 700 µL of TEOS was added quickly to the mixture. The reaction was carried out at room temperature overnight under magnetic stirring at 750 rpm. The final pH was around 8. After centrifugation, washing several times with ethanol and drying under vacuum, a fine white powder was collected.*

## Supplementary Material

*Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.*

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## Author Contribution Statement

*L.D., Y.A., E.A.P., P. C., C.R., C.B., have performed the experiments K.R. has done the crystallographic studies, L.D.C. and E.A.P. have written the paper.*

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