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Photoactive Hybrid Gelators Based on a Luminescent Inorganic $[Cu_4I_4]$ Cluster Core

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The formation of supramolecular self-assemblies of low-molecular-weight gelators (LMWGs) is an attractive and elegant way to organize, through spontaneous aggregation, small molecules at the micro- and nanoscale level into stimuli-responsive soft materials.[1] The discovery of new organogels that are sensitive to external stimuli is very appealing for tailored applications in biosciences, molecular electronics, sensing, or as confined reaction media and templates for well-defined inorganic materials.[2] Metal-based gelators (metallogelators) have also emerged recently, affording smart gels in which the metal plays a central role and leads to new functional materials.[3] Introduction of metal centers provides new properties such as magnetism,[4] catalytic activity[5], and luminescence,[6] properties that can be triggered by external stimuli such as the temperature. Despite the increasing number of gelation motifs being discovered, it remains a challenge to reliably predict the gelation capability of a compound, especially with nonconventional linear or disc-shaped gelators. New gelation motifs are, however, highly desirable from both fundamental and practical standpoints. Few polymetallic coordination complexes, such as the linear $Pt_2LL'_2$,[7] cylindrical Pd_2L_2[8] and Ag_3L_3,[9] triangular M_3L_3[10] (M = Au, Cu, Ag), or Zn_4L_4 grid[11] compounds (L = organic ligand), have been incorporated as cores in LMWGs. Recently, polyoxometallate-containing supramolecular gels have also been reported but hybrid gelators based on coordination clusters remain rare.[12]

Tetracopper(I) clusters formulated $[Cu_4X_4L_4]$ (X = Cl, Br, I; L = organic ligand) are well known for their rich photophysical properties.[13] The molecular structure of these cubane-type clusters is formed by four copper and four halide atoms alternatively occupying the corners of a cube (Figure 1). Their remarkable photoluminescence properties, especially their emission, are sensitive to environmental conditions such as temperature,[14] rigidity of the medium[15], or pressure,[16] and make these clusters particularly appealing for the synthesis of stimuli-responsive materials exhibiting original optical properties. First-row transition-metal compounds are also attractive from an economical point of view as they are less toxic and more readily available than noble metal complexes. In this context, functionalization of tetrahedrally coordinated $[Cu_4I_4L_4]$ clusters with ligands able to induce gelation should give rise to a new class of hybrid gelators leading to materials with intriguing structural and photophysical properties.

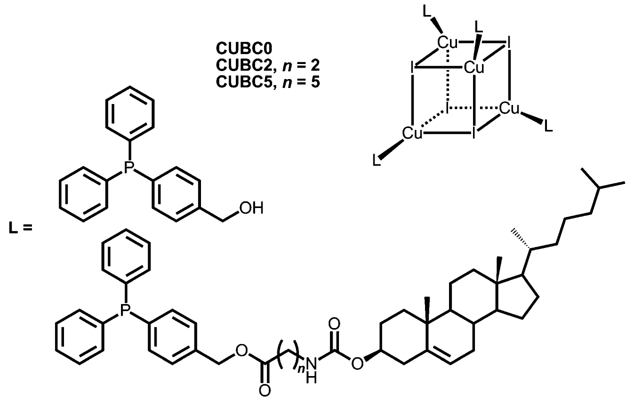

Figure 1. Structure of the $[Cu_4I_4L_4]$ cubane clusters functionalized with cholesteryl phosphine ligands, CUBC*n* (n = 2, 5), and with (4-(diphenylphosphino)phenyl)methanol phosphine, CUBC0.

Here, we report on the first series of hybrid LMWGs based on the $[Cu_4I_4]$ cubane core functionalized by rationally designed cholesteryl-based phosphine ligands. Cholesterol derivatives are well-known gelation motifs and hydrogen-bonding motifs have also been introduced to further stabilize the molecular aggregation in solution.[17] The gels of clusters obtained after cooling hot clear solutions present an

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original nanosized globular structure, which is highly emissive and exhibits luminescence thermochromism with a temperature-dependent emission. Moreover, by taking advantage of the luminescence rigidochromism properties of the cubane clusters, the gelation process was also monitored in situ.

Cholesteryl phosphine ligands were synthesized from (4-(diphenylphosphino)phenyl)methanol[18] and cholesteryl chloroformate by using classical organic reactions for peptides syntheses. Two phosphine ligands were studied with different spacer lengths between the triphenylphosphine moiety and the cholesteryl group. The spacer varies with the length of the alkyl chain ($n=2, 5$) between the ester and the carbamate linkers (Figure 1). Reaction of CuI with the ligand in dichloromethane afforded the corresponding [$Cu_4I_4L_4$] clusters, namely CUBC*n* ($n=2, 5$), as a white powder in relatively good yields (>60%, see the Supporting Information). For comparison, the CUBC0 cluster with the benzyl alcohol precursor phosphine (Figure 1) was also synthesized. Its molecular structure, determined by single-crystal X-ray diffraction analysis, is represented in Figure 2 and consists of a distorted [Cu_4I_4] cube with each copper atom coordinated by one phosphine ligand. All the clusters were characterized by elemental analysis, FTIR, UV/Vis, ^{31}P and ^{1}H NMR spectroscopy (see the Supporting Information). Coordination complexes based on copper(I) halides are known to form a variety of structural motifs with the same ligand.[19] In our case, the formation of the functionalized [Cu_4I_4] core in CUBC2 and CUBC5 was ascertained by solid-state ^{31}P magic angle spinning (MAS) NMR spectroscopy, which showed signals similar to the reference tetranuclear cluster CUBC0 (Figure S1 in the Supporting Information). The formation of the cubane core is also confirmed by the luminescence thermochromism properties of the clusters (see below).

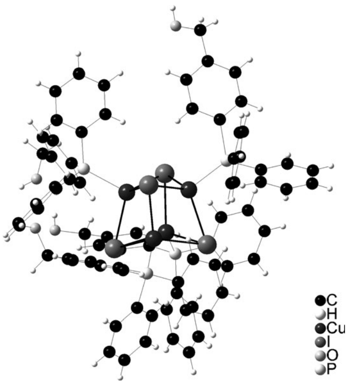

Figure 2. Molecular structure of [$Cu_4I_4(PPh_2(C_6H_4)CH_2OH)_4$] cubane cluster (CUBC0).

The gelation ability of CUBC*n* ($n=2, 5$) was evaluated in various polar, nonpolar, protic, and nonprotic solvents by the "stable to inversion of a test tube" method (Table S2 in the Supporting Information). Whereas CUBC5 was unable to form a gel, CUBC2 was revealed to be a good gelator of cyclohexane (minimum gelation concentration, MGC = 12.5 gL^{-1}). Stable and robust gels (Figure 3a), displaying a thermally reversible sol-to-gel phase transition, were obtained from hot cyclohexane solutions. The entire volume of solvent was immobilized and could support its own weight without collapsing. Surprisingly, with only three additional methylene groups, CUBC5 gave only an insoluble suspension and failed to form a gel. This result highlights the subtlety of the gelation process and the difficulty of prediction. The colorless gel of CUBC2 appeared slightly scattering under white light and isotropic between cross-polarizers (Figure S2 in the Supporting Information). Upon UV irradiation at 312 nm, the gel was highly luminescent, exhibiting a green emission (Figure 3b). Epifluorescence microscopy revealed the presence of a green luminescent cottony fiber-like structure inside the solvent (Figure 4b). The thermochromic luminescence properties of the gel were revealed upon cooling down. Under the same UV excitation, the room-temperature green emission becomes blue when the sample is immersed in liquid nitrogen (Figure 3c).

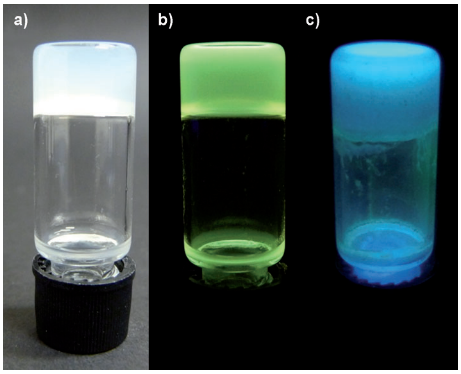

Figure 3. Gelation test in cyclohexane (20 gL^{-1}). The gel does not flow when the vial is turned upside-down. Photos of CUBC2 gel at a) room temperature in ambient light, b) room temperature under UV irradiation at 312 nm (green emission), and c) after cooling in liquid nitrogen and under UV irradiation at 312 nm (blue emission).

To get more insight into the nature of the objects at the origin of the gelation phenomenon, SEM and TEM analyses were performed on CUBC2 xerogel obtained by freeze-drying the corresponding gel. SEM images reveal the presence of a dense 3D network of short interlocked beaded-like filaments with an average diameter of 40–60 nm (Figures 4a and S3 in the Supporting Information). TEM analyses confirm this three-dimensional globular network (Figures 4c and S4 in the Supporting Information), which is responsible for the gelation of the solvent. The formation of this extended globular superstructure must arise from hierarchical self-assembly processes in which nanospherical particles created at an early state of gel formation fused to form such an unusual network.[20] The [Cu_4I_4] cubane structure and the tetrahedral arrangement of the cholesterol moieties must prevent a facile packing of the clusters into ex-

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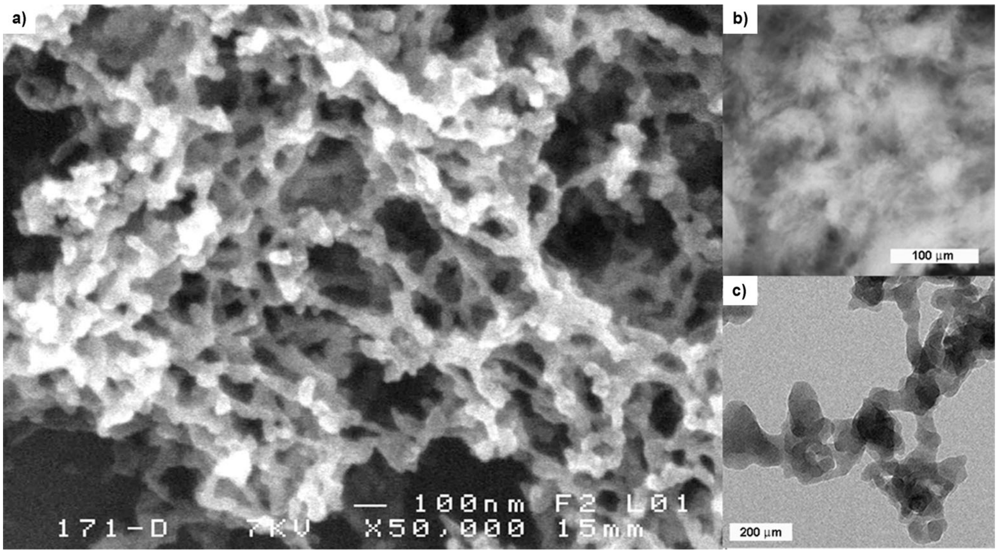

Figure 4. a) SEM image of CUBC2 xerogel deposited on silicon wafer. b) Drop of CUBC2 gel in cyclohexane (20 $g L^{-1}$) observed by optical microscopy under UV irradiation at 340–380 nm (green emission). c) TEM photograph of a diluted xerogel of CUBC2 deposited on carbon-coated copper grid.

tended columnar aggregates as is commonly observed for the formation of fibers or ribbons.

FTIR analyses revealed the role of hydrogen bonding in the gel formation (see the Supporting Information). In $CHCl_3$, the two stretching $\upsilon_{C=O}$ bands at 1731 and 1712 cm^{-1} are attributed to unbound ester and carbamate functions, respectively, whereas the free NH functions are found at 3454 cm^{-1}. For the gel, xerogel, and solid, the presence of a more marked shoulder at 1699 cm^{-1} ($\upsilon_{C=O}$) and a new band at 3351 cm^{-1}(υ_{NH}), show that part of the carbonyl and NH functions are engaged in hydrogen bonding (Figures S5 and S6 in the Supporting Information). Thus, the formation of the globular aggregates responsible for gel formation is likely directed by hydrogen bonds between the spacers and van der Waals interactions between the cholesteryl groups of the ligands. No π–π stacking of the phenyl groups is present in the crystal structure of CUBC0, so this interaction must be limited in the gel. Likewise, direct involvement of the [Cu_4I_4] core in intermolecular interactions seems to be unfavorable owing to the steric hindrance of the surrounding ligands. X-ray diffraction experiments performed on the gels and xerogels confirm that the superstructure leading to the gel formation is preserved upon freeze-drying (Figure S7 in the Supporting Information), in agreement with FTIR analyses.

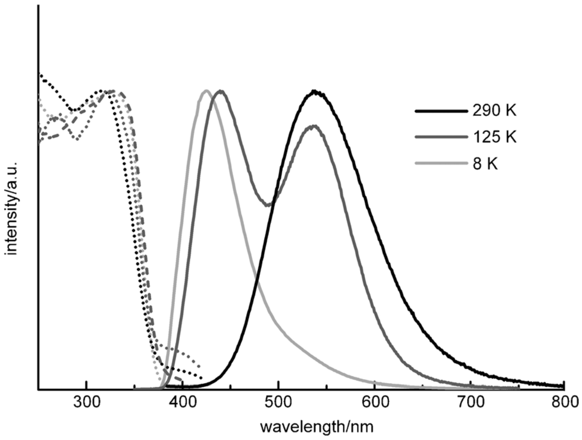

Figure 5. Luminescence spectra of CUBC2 gel at 290, 125, and 8 K. Normalized emission spectra (solid lines) have been recorded at $\lambda_{ex}=300$ nm and corresponding excitation spectra at $\lambda_{em}=540$ nm (dotted black and middle grey lines) and at $\lambda_{em}=425$ nm (dashed middle grey and dotted light grey lines).

The photoluminescence spectra of the CUBC2 gel were recorded from 290 K to 8 K (see the Supporting Information, Figures S8–10 and corresponding data in Table S3). At 290 K, the emission spectrum displays a broad band centered at $\lambda_{max}=535$ nm (Figure 5, $\lambda_{ex}=300$ nm), corresponding to the bright green emission observed in Figure 3b ($\Phi_{absolute\ internal}=7\,\%$; $\tau_1=0.13$ µs (97 %), $\tau_2=1.3$ µs (3 %) at 300 nm). By lowering the temperature, this band (LE for low energy) progressively decreases in intensity with the concomitant appearance of a new emission band at higher energy $\lambda_{max}=435$ nm (HE for high energy). At 125 K, the intensities of the two bands are almost equal and the excitation spectra recorded for both emissions are quite similar with maxima at $\lambda_{max}=330$ nm (Figure 5). Below 100 K, the LE band is completely absent and only the HE band at $\lambda_{max}=425$ nm is visible, leading to the blue emission observed for the sample cooled in liquid nitrogen (Figure 3c). When the sample is progressively warmed up to room temperature (290 K), the green emission of the LE band is recovered, indicating a completely reversible phenomenon. Note, the luminescence properties of CUBC2 in the xerogel and in the powder are similar to the ones observed in the gel state (Table S3 and Figures S8–10 in the Supporting Information). The thermochromism observed is characteristic of the [$Cu_4I_4L_4$] copper iodide cubane clusters with two emission bands (LE and HE), the relative intensities of which vary with temperature. Based on previous theoretical and experimental studies, these bands are attributed to different excited states.[21] The LE band is assigned to a ^{3}CC cluster-centered state (combination of an iodide-to-copper charge transfer transition (XMCT) and a copper-centered Cu d→s, p transition), whereas the HE band is attributed to an iodide,copper-to-phosphine ligand charge-transfer transition (^{3}X,MLCT). By exhibiting the typical thermochromic luminescence of copper iodide clusters, this study also confirms that the $[Cu_4I_4L_4]$ cubane structure is preserved in the gel, a fact that is also true in the cases of the xerogel and powder.

Copper iodide clusters can also display luminescence rigidochromic properties with a change in the emission wavelength and intensity depending on the rigidity of the local environment.[13b] This phenomenon is attributed to the variable extent of the molecular distortions of the ^{3}CC state relative to the ground state, an effect that is influenced by constraints imposed by the medium.[22] Upon excitation, strong geometrical relaxation of the ^{3}CC state occurs owing to electron redistribution associated with large distortions of the $[Cu_4I_4]$ core that is revealed by a large Stokes shift. This effect is commonly observed as a blue shift of the emission along with a large increase in intensity when solutions of clusters are solidified.[15] Here, this property has been exploited in order to probe the gelation process of CUBC2 during the sol–gel transition. A suspension of CUBC2 in cyclohexane (20 g L^{-1}) was heated at 65 °C until a clear solution was obtained and the emission spectra were recorded upon cooling down (Figure 6). At the beginning of the cooling process, a gradual increase of the emission intensity is observed and is likely attributed to a growing process in which the clusters form semirigid spherical nanoparticles. Note that the luminescence of a $CHCl_3$ solution of the cluster at the same concentration (20 g L^{-1}) at room temperature is too weak to be measured. This means that aggregates of clusters are already present in cyclohexane solution even at 65 °C. After 11 min (30 °C), the observed sudden and rapid increase of the luminescence intensity can be associated with confinement of the cluster in a dense and rigid 3D globular network at the origin of gel formation. After 25 min (25 °C), the emission characteristics of the highly luminescent gel remain stable with time, meaning that the gelation process is finished at this point under these experimental conditions. A shift in the emission wavelength is also observed during gelation, changing from 580 to 535 nm. According to the rigidochromism phenomenon, this blue shift is due to the confinement of the clusters in a more rigid environment leading to conformational states at higher energy compared with a liquid state with fewer environmental constraints. The strong intensity increase (by a factor of 60) observed during gelation can be attributed to limited nonradiative phenomena through decreased fluxionality in the more rigid gel state associated with enhanced scattering.[13b] The effect of temperature on the luminescence changes observed can be ruled out as cooling a solution of clusters lead to a red shift of the emission.[23] Passing from an almost nonluminescent liquid state to a brightly emissive gel state, the cluster, thus, appears as a probe for the gelation phenomenon. This study confirms the hierarchical process of gel formation occurring through the assembly of the clusters into a globular rigid matrix, the driving forces of which are van der Waals interactions and hydrogen bonds between the ligands.

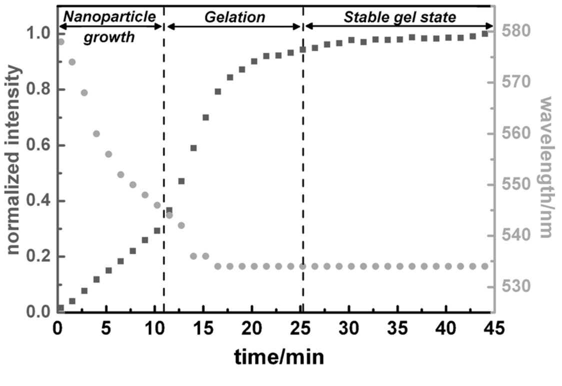

Figure 6. Time-dependent emission wavelength and intensity measured upon cooling a hot solution of CUBC2 at 20 g L^{-1} in cyclohexane, to room temperature ($\lambda_{ex} = 300$ nm).

To conclude, original hybrid gelators based on the $[Cu_4I_4]$ cubane cluster core have been obtained by the design of specific phosphine ligands. The highly emissive gels exhibit luminescence thermochromism properties. The formation of a 3D dense globular network resulting from the aggregation of nanoparticles is responsible for the observed gelation. The hierarchical self-assembly process at the origin of the nanoparticles formation is currently under investigation (SAXS, rheology, etc.) to elucidate the cluster packing in this superstructure. The specific structural and photophysical properties of the gels are retained in the xerogels, giving access to a new family of optically active materials of high specific surface with potential sensing and catalytic applications. The rigidochromic luminescence properties of the copper iodide clusters lead to an on/off system for which the emission is exalted in the gel state. These clusters exhibiting luminescent properties sensitive to the rigidity of the environment appear as original probes to precisely study gelation mechanisms and studies for this purpose are ongoing. More generally, the present example paves the way for the design of original functional materials based on nonconventional copper halide metallogelators.

Experimental Section

Experimental procedures for the synthesis of the ligands and clusters, characterization data, additional microscopy images of the xerogels, and temperature-dependent spectroscopic studies of the xerogels and powders are available in the Supporting Information. A color version of Figure 4 is also available in the Supporting Information. CCDC-953833 contains the supplementary crystallographic data for this paper (CUBC0). These data can be obtained free of charge from The Cam-

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bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_;request/cif.

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Keywords: cluster compounds · gels · metallogelators · rigidochromic luminescence · thermochromic luminescence

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[1] R. G. Weiss, P. Terech, *Molecular Gels, Materials With Self-Assembled Fibrillar Networks*, Springer, Dordrecht, **2006**.

[2] S. Banerjee, R. K. Das, U. Maitra, *J. Mater. Chem.* **2009**, *19*, 6649–6687.

[3] M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.

[4] a) O. Roubeau, A. Colin, V. Schmitt, R. Clérac, *Angew. Chem.* **2004**, *116*, 3345–3348; *Angew. Chem. Int. Ed.* **2004**, *43*, 3283–3286; b) R. Perochon, P. Davidson, S. Rouzière, F. Camerel, L. Piekara-Sady, T. Guizouarn, M. Fourmigué, *J. Mater. Chem.* **2011**, *21*, 1416–1422.

[5] a) Y. R. Liu, L. He, J. Zhang, X. Wang, C. Y. Su, *Chem. Mater.* **2009**, *21*, 557–563; b) Y. He, Z. Bian, C. Kang, Y. Cheng, L. Gao, *Chem. Commun.* **2010**, *46*, 3532–3534.

[6] a) F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549; b) V. K.-M. Au, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2012**, *51*, 7537.

[7] a) W. Lu, Y.-Y. Law, J. Han, S. S.-Y. Chui, D.-L. Ma, N. Zhu, C.-M. Che, *Chem. Asian J.* **2008**, *3*, 59–69; b) J. Zhang, X.-D. Xu, L.-J. Chen, Q. Luo, N.-W. Wu, D.-X. Wang, X.-L. Zhao, H.-B. Yang, *Organometallics* **2011**, *30*, 4032–4038.

[8] T. Naota, H. Koori, *J. Am. Chem. Soc.* **2005**, *127*, 9324–9325.

[9] X. Wei, X. Li, Z. Yang, J. Lan, G. Gao, Y. Xue, J. You, *Chem. Sci.* **2012**, *3*, 359–363.

[10] a) A. Kishimura, T. Yamashita, T. Aida, *J. Am. Chem. Soc.* **2005**, *127*, 179–183; b) A. Kishimura, T. Yamashita, K. Yamaguchi, T. Aida, *Nature Mater.* **2005**, *4*, 546–549; c) S. A. Joshi, N. D. Kulkarni, *Chem. Commun.* **2009**, 2341–2343.

[11] J. G. Hardy, X. Cao, J. Harrowfield, J.-M. Lehn, *New J. Chem.* **2012**, *36*, 668–673.

[12] a) B. Liu, J. Yang, M. Yang, Y. Wang, N. Xia, Z. Zhang, P. Zheng, W. Wang, I. Lieberwirth, C. Kuebel, *Soft Matter* **2011**, *7*, 2317–2320; b) L. Zhang, B. Marzec, R. Clérac, Y. Chen, H. Zhang, W. Schmitt, *Chem. Commun.* **2013**, *49*, 66–68.

[13] a) A. Barbieri, G. Accorsi, N. Armaroli, *Chem. Commun.* **2008**, 2185–2193; b) P. C. Ford, E. Cariati, J. Bourasssa, *Chem. Rev.* **1999**, *99*, 3625–3627; c) V. W.-W. Yam, K. K.-W. Lo, *Chem. Soc. Rev.* **1999**, *28*, 323–334.

[14] a) M. Radjaipour, D. Oelkrug, *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 159; b) C. Tard, S. Perruchas, S. Maron, X. F. Le Goff, F. Guillen, A. Garcia, J. Vigneron, A. Etcheberry, T. Gacoin, J.-P. Boilot, *Chem. Mater.* **2008**, *20*, 7010.

[15] D. Tran, J. L. Bourassa, P. C. Ford, *Inorg. Chem.* **1997**, *36*, 439.

[16] S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin, J.-P. Boilot, *J. Am. Chem. Soc.* **2010**, *132*, 10967.

[17] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George, *Angew. Chem.* **2006**, *118*, 470–474; *Angew. Chem. Int. Ed.* **2006**, *45*, 456–460.

[18] a) O. Herd, A. Hessler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69–76; b) R. A. Leising, J. J. Grzybowski, K. J. Takeuchi, *Inorg. Chem.* **1988**, *27*, 1020–1025.

[19] R. Peng, M. Li, D. Li, *Coord. Chem. Rev.* **2010**, *254*, 1–18.

[20] L. Yang, L. Luo, S. Zhang, X. Su, J. Lan, C.-T. Chen, J. You, *Chem. Commun.* **2010**, *46*, 3938–3940.

[21] S. Perruchas, C. Tard, X. F. Le Goff, A. Fargues, A. Garcia, S. Kahlal, J.-Y. Saillard, T. Gacoin, J.-P. Boilot, *Inorg. Chem.* **2011**, *50*, 10682.

[22] Upon excitation, strong geometrical relaxation of the ^{3}CC state occurs owing to electron redistribution associated with large distortions of the [Cu_4I_4] core that is revealed by the large Stokes shift.

[23] a) K. R. Kyle, C. K. Ryu, J. A. DiBenedetto, P. C. Ford, *J. Am. Chem. Soc.* **1991**, *113*, 2954; b) I. Roppolo, E. Celasco, A. Fargues, A. Garcia, A. Revaux, G. Dantelle, F. Maroun, T. Gacoin, J.-P. Boilot, M. Sangermano, S. Perruchas, *J. Mater. Chem.* **2011**, *21*, 19106.

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