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Abstract: Tetranuclear copper-iodide cluster consisting of a $\{Cu_4I_4\}$ cubane and diphenylphosphine ligand has been found as a highly stable precursor for further post-functionalization through hydrophosphination reaction. UV irradiation of the cluster in the presence of various alkenes allows direct functionalization of the latter, giving access to a wide range of copper cubane complexes, a source of molecular diversity for luminescent materials. Such a strategy provided access to the first example of water-soluble luminescent cubane copper iodide.

Introduction

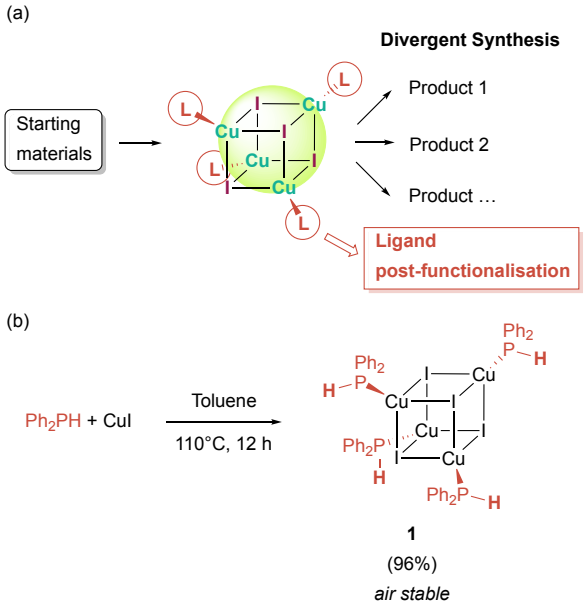
Being able to generate molecular diversity in a simple and rapid way by chemical synthesis is essential to identify and optimize new properties of interest. For example, high-throughput screening and combinatorial chemistry are two representative examples of strategies that can rapidly lead to the discovery of new drugs. These approaches are proving to be very effective in this field but are not necessarily applicable to other areas, such as transition metal materials for example. An approach more adapted to molecular materials, especially with transition metal complexes, may be divergent synthesis, since it allows for rapid generation of libraries of compounds, which is in contrast to traditional target-driven linear or convergent synthesis.[1] However, divergent synthesis involves post-functionalization steps, which is a challenging route because metal complexes are potentially reactive molecules that generally do not tolerate further manipulation.

In the field of photoactive materials, there is a growing interest in systems based on earth-abundant and non-expensive transition metals, also owing to their potential applications in different fields of photochemistry.[2,3] In this regard, copper has rapidly emerged as a metal of choice motivated by its low toxicity, low cost and abundancy.[4,5] In particular, tetranuclear copper-iodide clusters of general formula $[Cu(\mu_3\text{-}X)L]_4$ consisting of a $\{Cu_4X_4\}$ cubane core (X = halogen) and ligands (L = nitrogen or phosphorus-based ligand) located apically are attractive entities because of their intriguing photophysics combined with their extensive stimuli responsive properties.[6] Light-emitting devices based on copper-cubane derivatives have also been reported recently.[7] They also have been successfully applied for the development of low cost highly luminescent inks with different colors that cover the whole visible spectrum range.[8]

Since these systems constitute an unprecedented family of luminescent stimuli-responsive compounds and materials, the control and modulation of their physical and photophysical properties is highly sought. The properties of such particular polynuclear complexes are associated with the four apical ligands that influence both the metallophilic interactions within the cubane and the inter-cluster interactions (aggregation-induced emission properties for example).[9,10] Little chemical modification on the ligand may greatly influence the overall behavior of the material (Scheme 1a).

In this context, the development of modular approaches aiming at introducing chemical diversity straightforwardly onto a luminescent scaffold is of great importance for their further application as photofunctional material. In particular, strategies enabling the direct chemoselective functionalization onto preformed metal complexes are attractive for an easy access to a large library of luminescent compounds and it would be a strong asset to facilitate the development of such emerging materials. Indeed, post-functionalization of coordination compounds has long been understudied because it was thought that complexes were incompatible with chemical transformations by nature.[11]

Herein, a highly stable copper cubane featuring photoreactive P-H bonds can react with various alkenes to produce a large range of interesting copper complexes. The proposed post-functionalization strategy offers easy access to molecular diversity in future developments of potentially luminescent materials.



Scheme 1. (a) General molecular structure of $[Cu_4I_4L_4]$ copper iodide cubanes. Modulation of the physical and photophysical properties by varying the nature of the ligand; (b) Synthesis of copper(I) cubane **1**.

Results and Discussion

The synthesis of the cubane $[Cu(\mu_3\text{-}I)(PPh_2H)]_4$ **1** is depicted in Scheme 1b. Copper iodide was heated in presence of diphenyl phosphine in toluene which gave the tetranuclear species in 96% yield. Interestingly, whereas diphenylphosphine PPh_2H is highly reactive and should be stored under N_2, the resulting Cu complex displays exceptional stability under air (up to 250 °C as deduced from thermogravimetric analysis). Crystals suitable for X-ray diffraction analysis were grown and Fig. 1 displays the molecular structure of the cubane. The bond distances and angle mean values for **1** are within the range of reported values for this type of clusters coordinated by phosphine ligands. The mean Cu-Cu distance is 2.87 Å which is greater than the sum of the van der Waals (2.80 Å).[12]

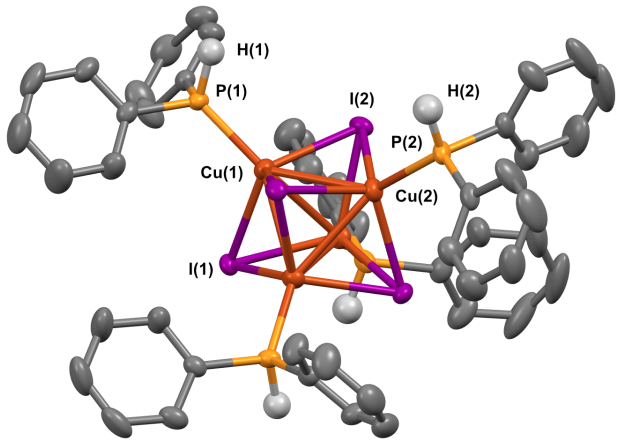
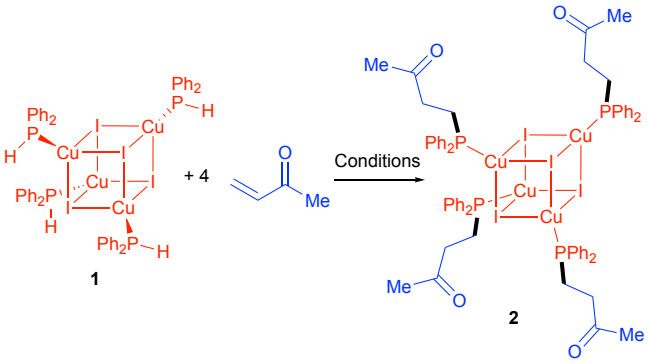


Figure 1. Molecular structure of tetranuclear copper complex $[Cu(I)(PPh_2H)]_4$ **1**. Selected bond lengths (Å): P(1)-H(1), 1.29(3); P(2)-H(2), 1.26(4). Average bond lengths (Å) Cu-I, 2.682; Cu-Cu, 2.884; Cu-P, 2.251.

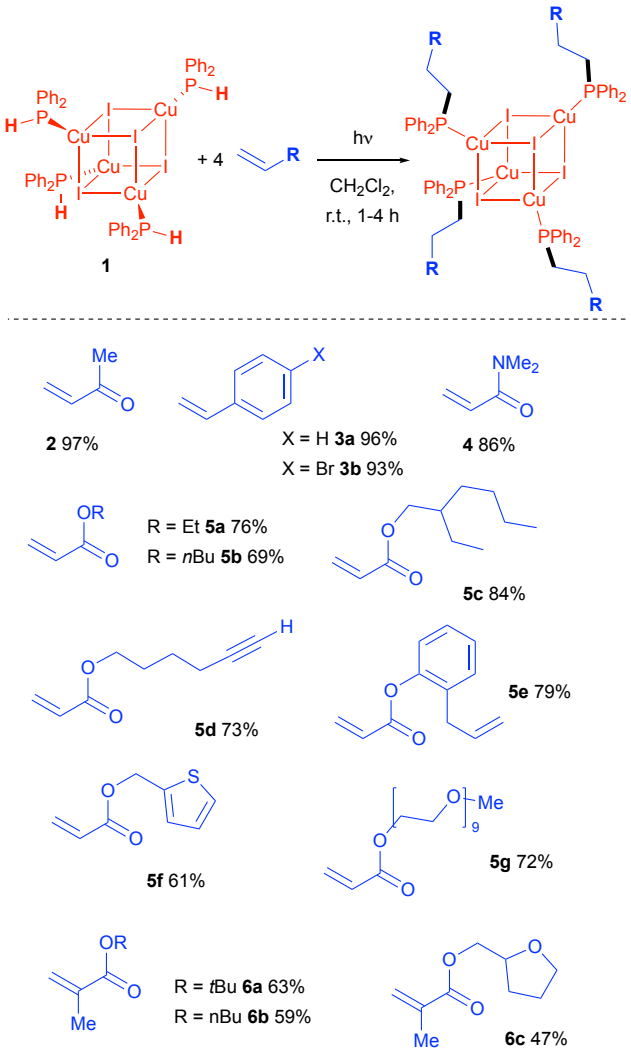
Although exceptionally stable, we anticipated that the P-H functions could be activated to allow a direct hydrophosphination reaction onto alkene substrates. Hydrophosphination of methyl vinyl ketone was examined first (Scheme 2) to generate the functionalized cubane **2**, a complex that we recently synthesized starting from CuI and the corresponding tertiary phosphine.[13] Interestingly, traces of cubane **2** were observed when dissolving compound **1** in methyl vinyl ketone at room temperature for 12 hours, demonstrating its reactivity (entry 1). The conversion could be improved by heating and 18% of conversion were observed after 12 h in refluxing acetonitrile (entry 2). Finally, the mixture was irradiated with a UV lamp at λ_{exc} = 365 nm for 1 hour at ambient temperature (entry 3), resulting in complete conversion of methyl vinyl ketone as deduced from ^{1}H NMR analysis. The fully functionalized cubane could be isolated in 97% by precipitation in cyclohexane.[14]



Entry	Conditions	Conversion
1	methyl vinyl ketone (solvent), r.t. 12 h.	**<1%**
2	methyl vinyl ketone (4.2 eq.), acetonitrile, 70 °C, 12 h.	**18%**
3	methyl vinyl ketone (4.2 eq.), CH_2Cl_2, hν, 1 h.	**97%**

Scheme 2. Reactivity of tetranuclear copper complex $[Cu(\mu_3\text{-}I)(PPh_2H)]_4$ **1** toward methyl vinyl ketone (Entry 3: λ_{exc} = 365 nm).

In order to demonstrate the utility of this method, we have applied the procedure to a variety of alkene substrates as shown in Scheme 3. Methyl vinyl ketone (**2**), styrene (**3a-b**), acrylamide (**4**), acrylate (**5a-f**) and methacrylate derivatives (**6a-c**) were tested with success, giving the corresponding products with isolated yields ranging from 47% (**6c**) to 97% (**3**). Interestingly, it is possible to functionalize **1** with acrylates bearing alkyne or inactivated alkene: compounds **5d** and **5e** were obtained in 73% and 79% yield, respectively. Thiophene-based compounds are widely studied in materials science and technology: cubane **1** could be functionalized with acrylate **5f** bearing a thiophene moieties. Poly(ethylene glycol) methyl ether acrylate is used to create biocompatible homopolymer used as material for biomedical applications. The post-functionalization with such a type of monomer is also possible (**5g**) thus providing the possibility of creating potentially biocompatible materials. Therefore, a whole molecular diversity is offered which will make it possible to quickly identify some molecules of interest for various potential applications.



Scheme 3. Scope of the direct hydrophosphination of tetranuclear copper complex $[Cu(\mu\text{-}I)(PPh_2H)]_4$ **1** (Isolated yield). Reaction conditions: dichloromethane as solvent, r.t., λ_{exc} = 365 nm, reaction time: 1 h for compound **3** and 4 h for all other compounds listed.

In recent decades, developments in molecular biology and microscopy techniques have made it possible to visually detect molecules in living systems.[15] Among the variety of reactions, alkyne-azide "click" chemistry has been identified as a conjugation reaction of choice and the identification of new tools for potential biological targets remains topical.[16] In this direction, the cubane **5d** is of interest since the alkyne-containing acrylate may be post-functionalized using click-strategy, thus offering potential easy fluorescence labeling.[17] We found that the complex reacts rapidly within minutes in the presence of 4 equiv. of benzyl azide with no need of additional catalyst, as deduced from NMR and mass spectrometry experiments (Eq. 1, see SI for details). Although more work is needed to identify the exact mechanism of the reaction, it seems most likely that the system undergoes an autocatalytic mechanism, with cubane being the catalyst of the reaction.[18,19]

5d + 4 Bn-N_3 $\xrightarrow[\text{min.}]{CH_2Cl_2,\ \text{r.t.}}$ $[Cu_4I_4][\text{phosphine triazole}]_4$ (1)

Among examples displayed in Scheme 3, complex **5g** decorated with poly(ethylene glycol) (PEG) chains constitutes a novel family of cubane, since it exhibits unprecedented solubility in water.

The peculiar photoluminescence properties of this class of cupper-iodine clusters and the remarkable solubility in aqueous environment of derivative **5g** prompted us to investigate the photophysical properties of this latter, as a proof of principle of the proposed straightforward post-functionalization strategy. At a first stage, compound **5g** was investigated in diluted aqueous solution . The electronic absorption and emission are displayed in Figure 2b and the corresponding data are listed in the ESI (Table S1). Upon excitation at λ_{exc} = 300 nm, diluted H_2O solution of **5g** display an intense, broad and featureless photoluminescence band with emission maxima centered at λ_{em} = 595 nm. This emission is attributable to a radiative process from a triplet excited state with admixed cluster-centered (^{3}CC) and halogen-to-ligand charge transfer (^{3}XLCT) nature, in comparison with related copper-iodine cubane clusters of $\{Cu(\mu_3\text{-}I)(phosphane)\}_4$ general structure.[11] An irreversible and slow photodegradation of the sample was observed upon cycling photoluminescence spectra, which hampered deeper investigation by means of time-resolved techniques. Nevertheless, observation of photoluminescence in solution is surprising and unprecedented for copper-iodide cubane, to the best of our knowledge. Lack of solution photoluminescence is typically attributed to the reduced chemical stability of the cluster due to the flexible nature of the metal-iodine scaffold and ligand dissociation in fluid solution.[20] These processes appeared to be favorably suppressed in solution samples of **5g** most likely due to the shielding effect imparted by the multiple oligo-ethyleneglycol chains onto the luminescent tetra-metallic core that also provide an amphiphilic character to the compound. As consequence, radiative de-excitation becomes now competitive over non-radiative intra- and inter-molecular (dissociative) processes. This finding of switching-on effect on the luminescence in amphiphilic metal complexes is in agreement with other systems reported in the literature.[21]

Interestingly, the neat PEG-cubane cluster **5g** obtained as a colorless oil after synthesis, displays stable photoluminescence centered at 595 nm with moderate intensity (photoluminescence quantum yield = 6%) with long-lived excited-state lifetime (τ_{av} = 1.88 μs) as typical of formally spin-forbidden triplet emission from ^{3}CC/^{3}XLCT band (see Table SI in SI)

Dynamic light scattering (DLS) was also used for studying sizes of nanoparticle in water (Figure 2c). The signal was monodisperse and the particle size was found to be around 9 nm which is consistent with single cubane clusters.[22] Increasing the concentration in solution did not affect the results suggesting no aggregation under these conditions. Replacing water by organic solvent such as CH_2Cl_2 leads to loss of signal by DLS measurement and loss of luminescence, suggesting a dynamic intermolecular exchange process of the copper atoms.[19a]

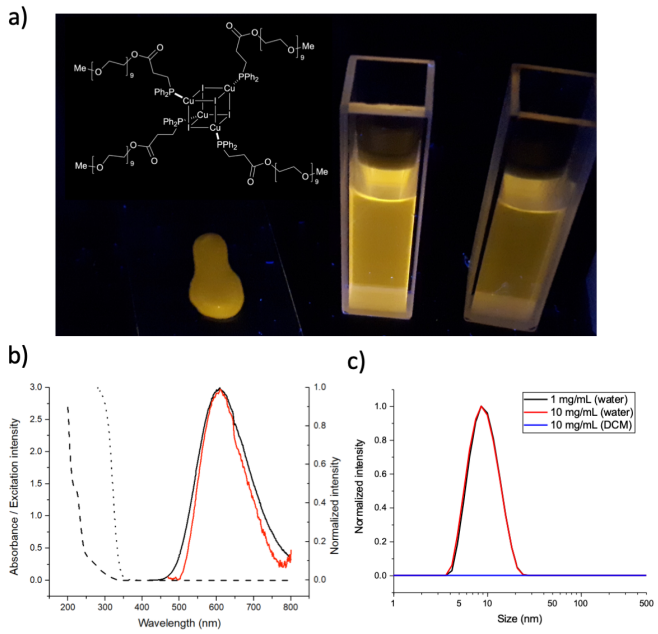


Figure 2. (a) Complex **5g** in pure form (on a glass plate, *left*) and in water at 10^{-3} M and 10^{-4} M (*right*) under UV radiation. (b) Emission spectra as neat oil (red solid trace) and in air-equilibrated aqueous solution at 2.10^{-4} M upon excitation at 300 nm (black solid trace). Excitation spectra (300 nm, black dotted trace) at 2.10^{-4} M and UV-Vis spectra (black dashed trace) at 2.10^{-5} M in air-equilibrated aqueous solution. (c) DLS analysis of complex **5g** in water or in dichloromethane as solvent.

Conclusion

In summary, copper-iodide diphenylphosphine cubane is a highly stable precursor, which can be activated under UV light to generate molecular diversity in the field of cubane copper chemistry. The post-functionalization occurs under smooth conditions at room temperature and the corresponding products were isolated in high yields. We envisage that this study can open up an avenue to use copper cubanes in emissive devices.

Experimental Details

Cubane $[Cu(\mu_3\text{-}I)(PPh_2H)]_4$ 1. Copper(I) Iodide (500 mg, 2.62 mmol), diphenylphosphine (500 mg, 2.68 mmol) and dry toluene (8 mL) were placed in a flame-dried Schlenk tube under argon. The solution was heated at 100 °C during 12 hours. Then the mixture was cool down to room temperature and the solvent was removed under vacuum. The solid residue was dissolved in CH_2Cl_2 and the solution was poured into Et_2O. The complex precipitated instantaneously and was filtered and washed several times with Et_2O. The product was dried under vacuum. White powder (947 mg), yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 16H), 7.31 (br t, J = 7.4 Hz, 8H), 7.28 (br td, J = 7.5, 1.3 Hz, 16H), 5.83 (d, $J_{P\text{-}H}$ = 255 Hz, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2 (d, $J_{C\text{-}P}$ = 13 Hz, CH), 130.4 (d, $J_{C\text{-}P}$ = 29 Hz, C), 129.7 (CH), 128.7 (d, $J_{C\text{-}P}$ = 9 Hz, CH). ppm; ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$): δ: -40.2 (br) ppm; FTIR: ν_{max} (pure, diamond orbit) = 2975, 1476, 1437, 1089, 887, 819, 725, 686 cm^{-1}; ATG: 5% weight loss at 257 °C HRMS (ESI): m/z calcd for $[C_{48}H_{43}Cu_4I_4P_4]^+$: 1502.5672, Found: 1502.5672.

CCDC Deposition Number 2063316 for copper complex **1**.

Direct hydrophosphination of tetranuclear copper complex $[Cu(\mu\text{-}I)(PPh_2H)]_4$ 1. General Procedure: Complex **1** was placed in a flame-dried Schlenk tube under argon and was dissolved in dry dichloromethane and (concentration 50 $mg.mL^{-1}$). Four equivalents of the acrylate derivative was added and the solution was irradiated at λ = 365 nm with a LED lamp for 4 hours (except for compound **3**: 1 hour). Then the mixture was cooled down to the room temperature and the solvent was removed under vacuum. The solid residue was dissolved in CH_2Cl_2 and the solution was poured into Et_2O or n-Hexane. The complex precipitated instantaneously and was filtrated and washed several times with Et_2O and *n*-hexane. The product was then dried under vacuum. For analytical data of all compounds, see Supporting Information.

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Keywords: copper complexes • coordination chemistry • luminescence • phosphine • reactivity

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