Tetracarbene Ligands

International Edition: DOI: 10.1002/anie.201411006
German Edition: DOI: 10.1002/ange.201411006

Reversible Photochemical Modifications in Dicarbene-Derived Metallacycles with Coumarin Pendants**

Ying-Feng Han, Guo-Xin Jin, Constantin G. Daniliuc, and F. Ekkehardt Hahn**

Abstract: *Molecular rectangles were obtained from two bis-(NHC) ligands, each featuring two terminal coumarin groups and two Ag^+, Au^+, or Cu^+ ions. Upon UV irradiation ($\lambda = 365$ nm), the dinuclear complexes undergo photochemical modification through a [2+2] cycloaddition reaction of two adjacent coumarin moieties to give a macrocyclic tetra(NHC) ligand. The photodimerization of the coumarin pendants proceeds stereoselectively to give the syn-head-head isomers in all cases. Subsequent irradiation at $\lambda = 254$ nm initiates a photocleavage reaction with reconstitution of the initial dinuclear complexes with coumarin pendants.*

Photochemical modification (PCM) has recently been recognized as a useful method for the preparation of a variety of structures with interesting properties.[1–3] PCM has been shown to be broadly applicable to the preparation of various substituted metal–organic frameworks (MOFs)[1,2] and discrete assemblies[3] that would be difficult to obtain through standard synthetic protocols.

PCM, especially through photochemically induced [2+2] cycloaddition, has provided an efficient approach for the modification and functionalization of various complexes both in the solid state and in solution.[1a,2,3b,4–6] Based on the successful construction of organometallic molecular assemblies by using polydentate ligands with N-heterocyclic carbene donor functions,[7] we were recently able to perform PCM through photochemical [2+2] cycloaddition of rectangular metallacycles containing bridging dicarbene ligands with C–C double bonds as part of the metallacycle (**A**; Scheme 1).[8] These results indicate the suitability of $[M_2(\text{dicarbene})_2]^{2+}$ (M = Ag, Au) metallacycles as scaffolds for the photodimerization of olefinic bonds to yield cyclobutane units within the molecular rectangles (**B**), both in solution and in the solid state. While complexes of type **B** feature an internal cyclobutane unit obtained through [2+2] cycloaddition of internal olefinic bonds, we also became interested in utilizing $[M_2(\text{dicarbene})_2]^{2+}$ (M = Ag, Au) complexes with double bonds at carbene substituents (**C**), which upon [2+2] cycloaddition would lead to complexes featuring a macrocyclic ligand as in **D** (Scheme 1). Removal of the metal atoms from such assemblies could possibly lead to interesting new macrocycles.

As source of the double bonds for [2+2] cycloaddition, we selected a dicarbene ligand with two coumarin groups as in **C** (Scheme 1). The photodimerization of coumarin[9] has been studied in detail and the use of coumarin and its derivatives for the generation of polymers through [2+2] cycloaddition has been described.[10] Based on the reversible photodimerization–photocleavage reaction of coumarin, a promising controlled drug-release mechanism for coumarin-functionalized mesopourous silica substrates has been reported.[11]

In principle, the photodimerization of coumarin can afford *syn*-head-head (*syn*-HH), *syn*-head-tail (*syn*-HT), *anti*-head-head (*anti*-HH), and *anti*-head-tail (*anti*-HT) cyclobutanes (Scheme 2). Significant efforts have been directed towards the control of the stereochemistry of this [2+2] photodimerization reaction by using crystal engineering or packing within the solid state.[12] The stereoselective photodimerization of coumarin and its derivatives has been found to be efficiently controlled through confinement of the substrate within supramolecular hosts such as cucurbit[8]urils,[13] Pd nanocages,[14] and other hosts[15] in solution.

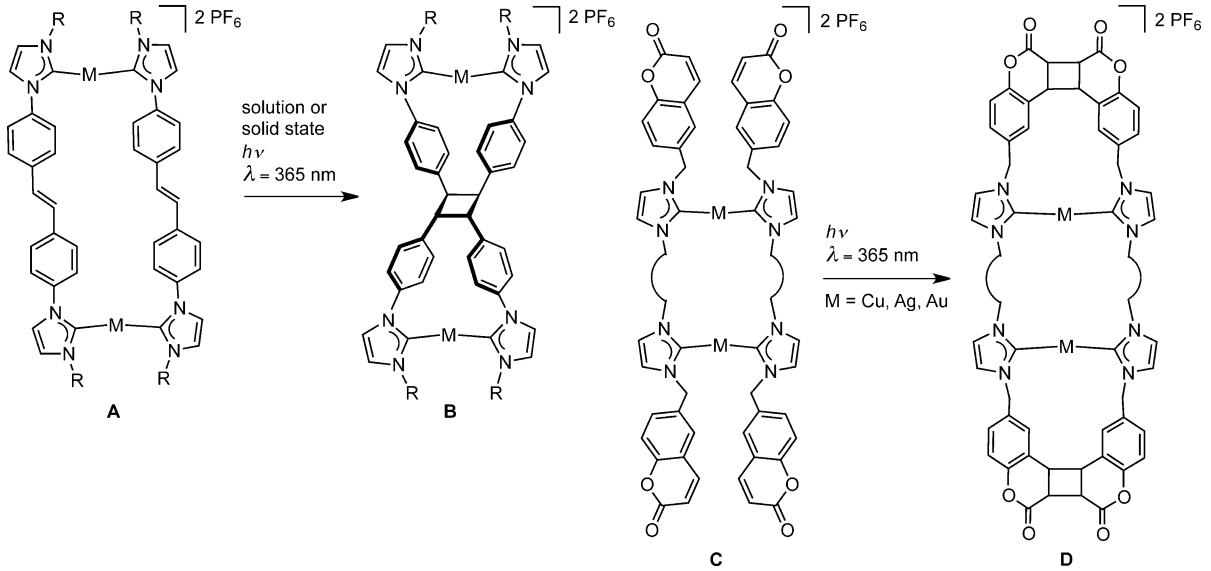
To our knowledge, coumarin has not been utilized as a functional group in metallosupramolecular assemblies, and the photochemical modification (PCM) of coumarin-functionalized metallosupramolecular assemblies has not been investigated to date. We became interested in such transformations becasue the coumarin groups in assemblies of type **C** (Scheme 1) would be preoriented for the stereoselective formation of head-head isomers in photochemically induced [2+2] cycloaddition reactions, thereby reducing the number of possible isomers from four to a maximum of two (Scheme 2).

Herein, we report the synthesis and characterization of a series of dinuclear Cu^I, Ag^I, and Au^I molecular rectangles of type **C** containing coumarin pendants (Scheme 3). Photochemically induced [2+2] cycloaddition reactions were performed with these complexes, thereby leading to new complexes featuring a macrocyclic coordinated tetracarbene ligand.

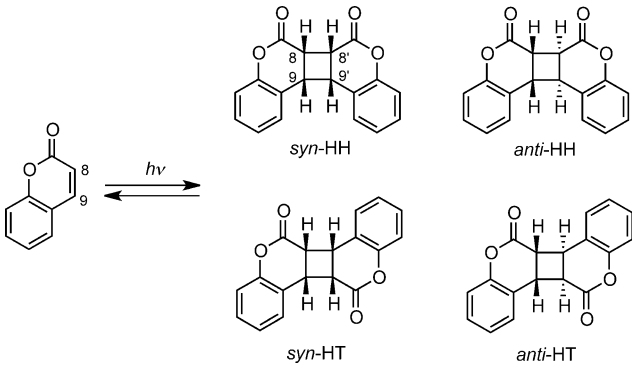
[*] Prof. Y.-F. Han, Prof. G.-X. Jin
Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University
220 Handan Road, 200433 Shanghai (P.R. China)
E-mail: yfhan1980@fudan.edu.cn
Prof. Y.-F. Han, Prof. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstraße 30, 48149 Münster (Germany)
E-mail: fehahn@uni-muenster.de
C. G. Daniliuc
Organische-Chemisches Institut
Westfälische Wilhelms-Universität Münster (Germany)

[**] The authors thank the Deutsche Forschungsgemeinschaft (SFB 858 and IRTG 2027) for financial support. Y.-F.H. thanks the Alexander von Humboldt Foundation and Shanghai Pujiang Program (14PJD006) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411006.



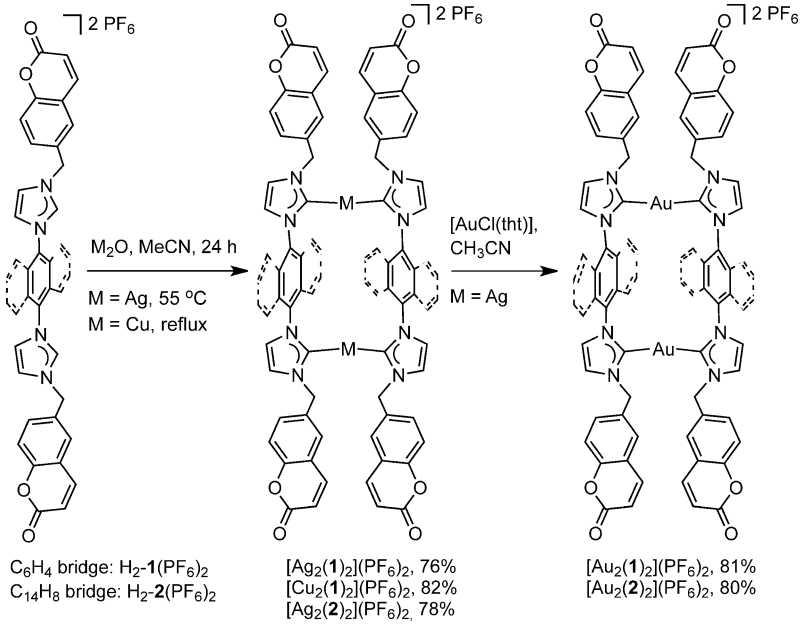
Scheme 1. Photochemically initiated [2+2] cycloaddition of double bonds within or outside of the metallacycle of $[M_2(\text{dicarbene})_2]^{2+}$ cations.



Scheme 2. Isomers resulting from the photodimerization of coumarin.

The coumarin-substituted diazolium salts H_2-**1**$(PF_6)_2$ and H_2-**2**$(PF_6)_2$ were synthesized through alkylation of 1,4-bis(1-imidazolyl)-benzene and 9,10-bis(1-imidazolyl)anthracene, respectively, with 6-bromomethylcoumarin followed by anion exchange with NH_4PF_6 in methanol (see the Supporting Information). The subsequent reaction of equimolar amounts of Ag_2O with H_2-**1**$(PF_6)_2$ or H_2-**2**$(PF_6)_2$ in acetonitrile gave the dinuclear silver tetracarbene complexes $[Ag_2(\mathbf{1})_2](PF_6)_2$ and $[Ag_2(\mathbf{2})_2](PF_6)_2$, respectively, in good yields (Scheme 3). Formation of the molecular rectangles was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, with the latter showing a resonance for the C_{NHC} carbon atom in all cases, as well as by high resolution mass spectrometry (see the Supporting Information). Similarly, the reaction of Cu_2O with H_2-**1**$(PF_6)_2$ in acetonitrile resulted in the formation of the dicopper tetracarbene metallacycle $[Cu_2(\mathbf{1})_2](PF_6)_2$.

Both $[Ag_2(\mathbf{1})_2](PF_6)_2$ and $[Ag_2(\mathbf{2})_2](PF_6)_2$ reacted through transmetalation with two equivalents of [AuCl(tht)] in acetonitrile to give the dinuclear gold complexes $[Au_2(\mathbf{1})_2](PF_6)_2$ and $[Au_2(\mathbf{2})_2](PF_6)_2$, respectively, in excellent yields of about 80%. Multinuclear NMR spectroscopy (^1H, $^{13}C\{^1H\}$, ^{19}F and ^{31}P) and mass spectrometry confirmed the formation of these complexes. Among the indications for the successful transmetalation is the slight downfield shift of the C_{NHC} resonances when going from the silver(I) to the gold(I) NHC complexes. HRMS spectrometry also shows the formation of the dinuclear gold(I) cations $[Au_2(\mathbf{1})_2]^{2+}$ and



Scheme 3. Preparation and transmetalation of dicarbene-derived molecular rectangles. tht = tetrahydrothiophene.

$[Au_2(\mathbf{2})_2]^{2+}$ as strong peaks with the proper isotope distribution.

An X-ray diffraction analysis with crystals of $[Au_2(\mathbf{2})_2](PF_6)_2$ confirmed the formation of a dinuclear complex with four pendant coumarin groups (Figure 1). All metric parameters in the $[Au_2(\mathbf{2})_2]^{2+}$ cation (Au–C_{NHC} 2.004(9)–2.021(9) Å, C_{NHC}-Au-C_{NHC} 172.8(4) and 173.9(4)°) fall within the range previously observed for $[Au_2\{(bis)NHC)\}_2]^{2+}$ cations[7,8,16] and related linearly coordinated $\{Au(NHC)_2\}$ moieties.[7c]

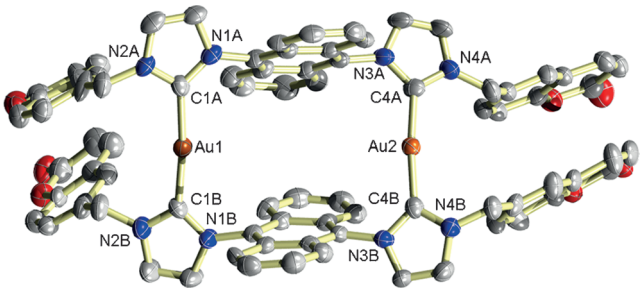


Figure 1. Molecular structure of the dication $[Au_2(\mathbf{2})_2]^{2+}$ in $[Au_2(\mathbf{2})_2](PF_6)_2$ crystals (ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1–C1A 2.017(9), Au1–C1B 2.007(9), Au2–C4A 2.004(9), Au2–C4B 2.021(9); C1A-Au1-C1B 173.9(4), C4A-Au2-C4B 172.8(4).

As observed previously, the N3,N3′ substitution pattern of the dicarbene ligand influences the geometry of dinuclear $[M_2\{(bis)NHC)\}_2]^{2+}$ complexes[8] and interactions between the coumarin substituents in $[Au_2(\mathbf{2})_2]^{2+}$ lead to a slight rotation of one $\{Au(NHC)_2\}$ unit relative to the other. The orientation of the two adjacent coumarin units is not exactly coplanar. They do, however, interact through π-stacking interactions with distances between the midpoints of the C8=C9 bonds (Figure 2) of about 4.2 Å. This orientation of the coumarin units is expected to favor the exclusive formation of the *syn*-head-head [2+2] cycloaddition product upon irradiation.

Irradiation of the dinuclar complexes $[M_2(\mathbf{1})_2](PF_6)_2$ (M = Ag, Cu, Au) and $[M_2(\mathbf{2})_2](PF_6)_2$ (M = Ag, Au) with a mercury lamp ($\lambda = 365$ nm, ambient temperature) in [D$_6$]DMSO or CD_3CN led exclusively to formation of the *syn*-head-to-head cycloaddition products $[M_2(\mathbf{3})](PF_6)_2$ and $[M_2(\mathbf{4})](PF_6)_2$, respectively (Scheme 4, see the Supporting Information for experimental details). Irradiation times between 16 h and 36 h were required to maximize the yield of the [2+2] cycloaddition products.

The formation of dinuclear complexes bearing the macrocyclic tetracarbene ligand **3** or **4** was unambiguously established by ^{1}H NMR spectroscopy for all cases listed in Scheme 4. For example, the ^{1}H NMR spectrum of complex $[Au_2(\mathbf{1})_2](PF_6)_2$ (Figure 3, top) features the characteristic doublet resonances for the protons H_a and H_b at $\delta = 6.31$ and 7.70 ppm, respectively. Upon irradiation ($\lambda = 365$ nm), the intensity of these doublet resonances diminishes and after 18 h, two multiplets at $\delta = 4.04$ and 4.15 ppm, indicative of the formation of complex $[Au_2(\mathbf{3})](PF_6)_2$ featuring a *syn*-HH cyclobutane ring, are observed (Figure 3, bottom). Additionally, the protons of the methylene bridge linking the coumarin to the NHC in $[Au_2(\mathbf{1})_2](PF_6)_2$ (H_j, $\delta =$ 5.34 ppm) become diastereotopic upon the [2+2] cycloaddition and in $[Au_2(\mathbf{3})](PF_6)_2$ give rise to two doublets at $\delta = 5.12$ and 5.34 ppm. Similar observations were made for all of the complexes listed in Scheme 4 (see the Supporting Information).

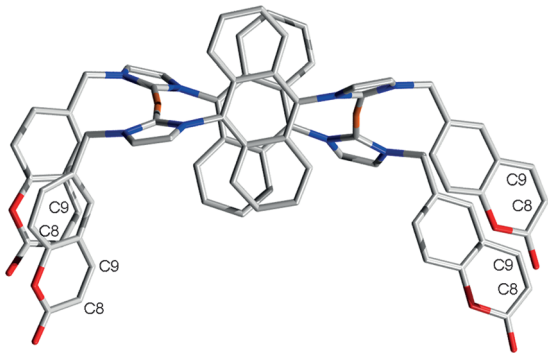
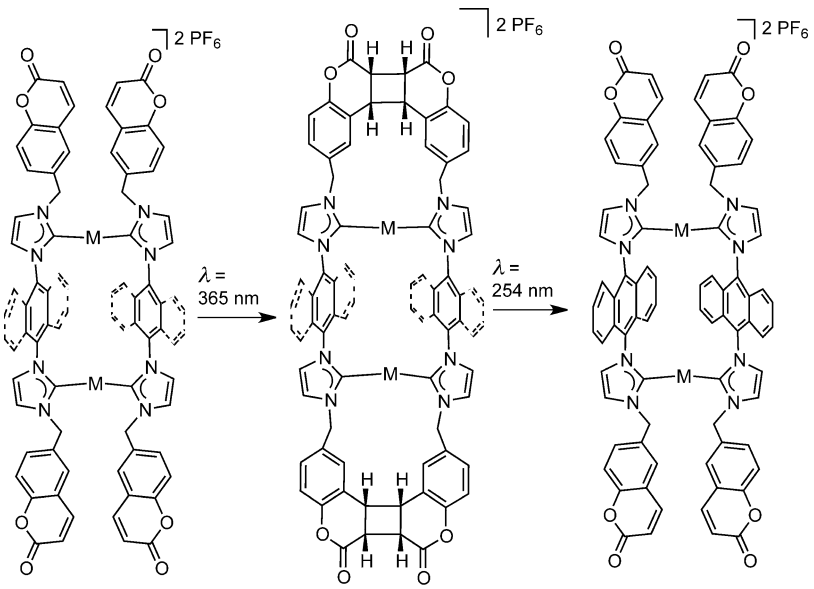


Figure 2. Molecular structure of the dication $[Au_2(\mathbf{2})_2]^{2+}$ showing the orientation of the coumarin rings.

The *syn*-HH stereochemistry of the photodimerization products was established through comparison of the ^{1}H NMR



Scheme 4. Double [2+2] cycloaddition in dinuclear complexes.

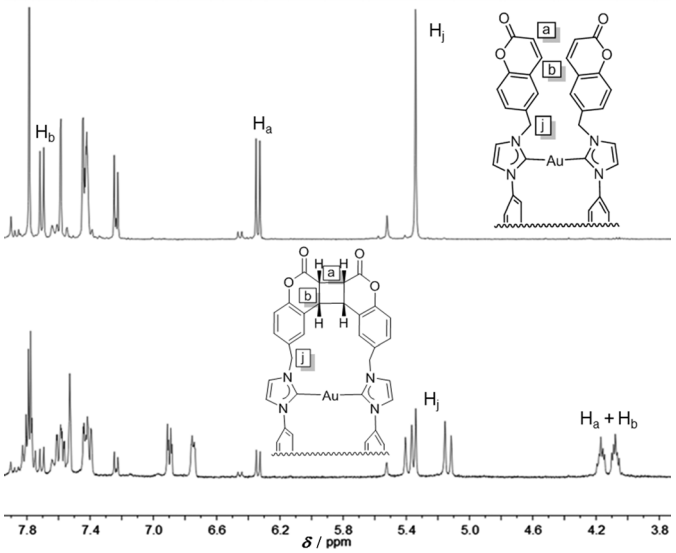


Figure 3. ^{1}H NMR spectra of $[Au_2(\mathbf{1})_2](PF_6)_2$ and the [2+2] cycloaddition product $[Au_2(\mathbf{3})](PF_6)_2$ (both in CD_3CN).

resonances for the H_a and H_b protons to those of known 6-alkylcoumarins before and after photodimerization.[17] The conversion in the [2+2] cycloaddition reaction was estimated by comparing the intensity of the H_a resonance of the starting materials ($\delta \approx 6.4$ ppm) to the intensity of the resonance for the cyclobutane protons H_a and H_b ($\delta \approx 4.1$–4.2 ppm). An extension of the irradiation time did not affect the stereochemistry of the reaction product but increased the conversion to up to 100% (for $[Au_2(\mathbf{4})](PF_6)_2$). However, decomposition of some complexes was noted after irradiation for 12 h, thus limiting the attainable yields, particularly for the light-sensitive silver complexes (see the Supporting Information). The complexes $[Ag_2(\mathbf{4})](PF_6)_2$ and $[Au_2(\mathbf{4})](PF_6)_2$ were isolated after photodimerization. Although photodimerization can take place in both an intra- and intermolecular fashion, MALDI-TOF experiments with the isolated complexes do not support the occurrence of intermolecular photodimerization. Photodimerization of the anthracene moieties was also not observed.

Cyclobutane derivatives formed through the [2+2] cycloaddition of coumarins are known to undergo photocleavage upon irradiation with UV light.[10] Irradiation of an acetonitrile solution of $[Au_2(\mathbf{4})](PF_6)_2$ at $\lambda = 254$ nm (ambient temperature) led to an absorption at $\lambda = 322$ nm in the UV/Vis spectrum, which is consistent with the presence of free coumarin groups and thus of photoinduced cleavage of the cyclobutane to reconstitute the original complex $[Au_2(\mathbf{2})_2](PF_6)_2$ (see the Supporting Information).

We present herein the self-assembly of a series of dicarbene-derived metallacycles ($M = Ag^I$, Cu^I, Au^I) bearing pendant coumarin groups. In the dinuclear metallacycles, pairs of coumarin pendants from different ligands exist in close proximity and upon irradiation they stereoselectively form *syn*-HH cyclobutanes with high conversion rates. As a result of the double [2+2] cycloaddition, new tetracarbene macrocycles coordinated to two M^I centers were obtained. Given the generally facile liberation of imidazolium salts from silver NHC complexes,[8] a series of macrocyclic imidazolium-based cyclophanes might result from the liberation of the tetracarbenes **3** and **4** from their silver complexes. Such cyclophanes have recently attracted interest as chemosensors for the sensing of RNA in living cells,[18] and research along these lines is in progress.

Keywords: carbenes · coumarin · photochemical activation · photodimerization · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4958–4962
Angew. Chem. **2015**, *127*, 5042–5046

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Received: November 13, 2014
Revised: January 8, 2015
Published online: February 25, 2015

