(1) $[M^{+}+1]$, 242 (5) $[M^{+}]$, 197 (2), 183 (1), 169 (1), 157, (1), 143 (47), 128 (28), 117 (7), 104 (2), 91 (13), 77 (5), 57 (100), 41 (57).

Method B: Under an argon atmosphere, a mixture of zinc dust (0.85 g, 13 mmol), 1,2-dibromoethane (0.19 g, 1.0 mmol), and THF (2 mL) was heated in a three-necked flask to 60–70 °C for 2–3 min and then cooled to room temperature. Chlorotrimethylsilane (0.1 mL) was added, and the mixture was stirred at room temperature for 15 min. A solution of RI (12 mmol) in THF (10 mL) was then added, and the mixture was stirred for 12 h at 35 °C. The resulting RZnI solution was then added to another three-necked flask, in which $[NiCl_2(PPh_3)_2]$ (0.2 g, 0.3 mmol) and THF (2 mL) had been previously heated at 60 °C for 2 min. The resulting mixture was cooled to −18 °C. A solution of aldehyde (10 mmol) and chlorotrimethylsilane (20 mmol) in THF (10 mL) was added over a few minutes and the mixture was allowed to warm to room temperature. After stirring the mixture for 12 h, saturated aqueous solution of NH_4Cl (10 mL) and Et_2O (10 mL) were added and the mixture was stirred for 10 min. The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated. The product was isolated from the crude reaction mixture by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

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[18] Spectroscopic data for **7**: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (dd, $^3J(H,H) = 8.2$ Hz, $^3J(H,H) = 1.8$ Hz; 1 H), 6.89 (t, $^3J(H,H) = 7.4$ Hz; 1 H), 6.77 (d, $^3J(H,H) = 8.2$ Hz; 1 H), 5.09 (t, $^3J(H,H) = 6.0$ Hz; 1 H), 3.77 (s, 3 H), 1.58 (s, 2 H), 1.24 (s, 8 H), 0.84 (t, $^3J(H,H) = 6.6$ Hz; 3 H), 0.06 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.4$, 134.3, 127.4, 126.7, 120.4, 109.8, 68.3, 39.0, 31.8, 29.2, 26.0, 22.7, 14.1, 0.0 ppm; MS (70 eV): m/z (%): 296 (M^{+}+2, 0.5), 281 (5), 211 (100), 181 (5), 136 (4), 122 (4), 92 (4), 74 (16).

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Mechanistic Features, Cooperativity, and Robustness in the Self-Assembly of Multicomponent Silver(I) Grid-Type Metalloarchitectures

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Self-organization processes allow the spontaneous but controlled generation of complex organic or inorganic architecture on the basis of the molecular information stored in the components, and its processing through the interactional algorithms defined by specific molecular recognition events.[1, 2] Such processes connect input components with output entity(ies), with a fidelity/reliability depending on the robustness of the program, that is, its ability to resist interference from factors other than the directing/dominant coding interactions.

While in equilibrium conditions, the process ideally leads to the preferential formation of a given entity under thermodynamic control/pressure; input and output species may be linked by complex mechanistic pathways and involve the generation of kinetic species that may or may not be direct intermediates. Such is the case, for instance, in the final formation of the thermodynamically favored circular helicates following kinetically favored triple-helical complexes.[3]

Although it is crucial to gain insight into the mechanistic, thermodynamic, and kinetic features of the self-organization process, only few such studies have been reported.[4] Whereas the preferential, ideally exclusive, formation of a given entity is usually pursued, various factors may interfere with the dominant code and complicate the issue. Thus, considering the self-assembly of inorganic grid architectures, which makes use of specifically designed ligands and of strong metal-ion coordination interactions, $[2\times2]$-,[5] $[3\times3]$-,[6] and $[4\times4]$-[7] type entities form exclusively. However, with a pentadentate ligand, both an incomplete $[4\times5]Ag^{+}_{20}$ grid and a quadruple helicate are simultaneously generated in place of the full $[5\times5]Ag_{25}^{+}$ entity, because of the interplay of various structural factors.[8] On the other hand, such cases also stress that when different "Boltzmann species" are thus formed, provided they are well defined, diversity ensues, an attractive feature of multiple outputs[9] in a self-assembly process. To gain understanding of the self-organization pathways, it is first necessary to identify the species that may form and then try to define their role in the process. In particular, features such as

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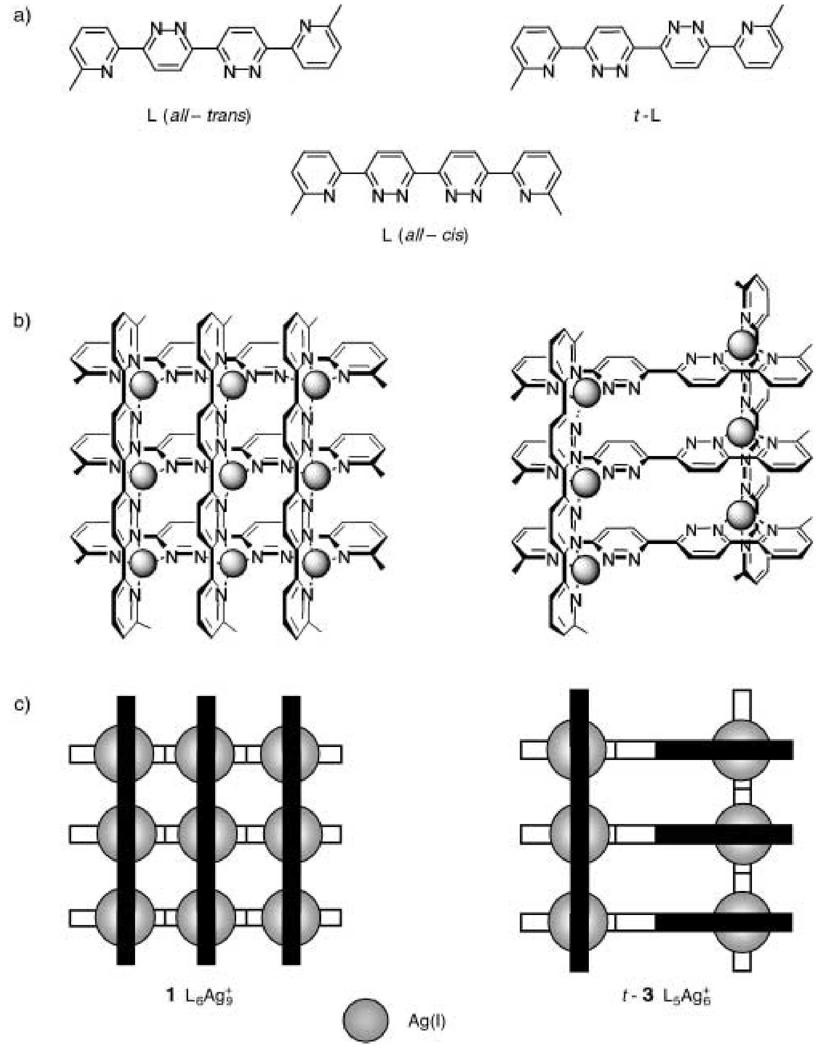

Figure 1. a) Definition of the form of the ligand L used; b) structures of the grid complexes **1** and *t*-**3**; c) schematic representations of the grid complexes; the white bars denote the parts of the ligands "behind" the silver cations, and the black bars represent those "in front".

nonlinearity, cooperativity, and structural switching events are of great interest.

The self-assembly of the [3 × 3]-grid-type complex $L_6Ag^{+}_{9}$ (**1**; Figure 1) from the tritopic L ligand and Ag^I ions was reported earlier.[6] We have now investigated the nature of the species which is progressively generated as increasing amounts of metal ions are added to a solution of the ligand,[10] monitoring the evolution of the resulting mixtures by ^1H and ^{109}Ag NMR spectroscopy.[11] Noting that there may be several assembly pathways and assuming that the final multiligand multimetallic entity **1** builds up by stepwise connection of ligand molecules and metal ions, the identified species of lower ligand numbers and nuclearities should lie on the self-assembly hypersurface, either directly on the mechanistic pathway or on a bifurcation.

The [3 × 3] $L_6Ag^{+}_{9}$ grid (**1**) forms immediately and cleanly when a stoichiometric amount of silver(I) is added to a solution of the ligand L (Ag^+/L 9/6). To obtain good reference points, the ^1H and ^{109}Ag NMR spectroscopic data for **1** itself were first analyzed in detail. In agreement with the earlier spectral results,[6] they allowed a clear identification, by their characteristic chemical shift, of three types of silver cations: "corner", "edge", and "center".

Progressive addition of $AgCF_3SO_3$ to a solution of ligand L leads to very pronounced changes in the ^1H NMR spectrum over the titration range until the stoichiometry of **1** is reached, at which only this grid complex is present (Figure 2).

At a low Ag^+/L ratio a mixture of many species is observed, most of which could not be identified, except for one type of complex which predominates at Ag/L ≈ 1:1 and presents characteristic ^1H NMR signals, spread into the $\delta = 6.5-7.0$ ppm and 9.7 ppm regions (Figure 2a). The ^{109}Ag NMR spectroscopic data comprise two signals corresponding to Ag^+ ions in the "corner" position and one signal for an ion in an "edge" position. Together with the detailed analysis of the ^1H NMR spectroscopic measurements,[11] the results point to the presence, among other species, of at least two complexes of $L_nAg_n^+$ type, probably having an intertwined structure and with all ligands in a transoid arrangement around the central C–C bond. The complexes could be a triangular $L_3Ag_3^+$ and a square $L_4Ag_3^+$[14] species, in analogy to earlier observations of coexisting Cu^I complexes of such types (see structures **2**($n = 3$) and **2**($n = 4$), Figure 3).[15, 16]

At $Ag^+/L \approx 6:5$, another discrete complex is almost exclusively formed (Figure 2c). Extensive

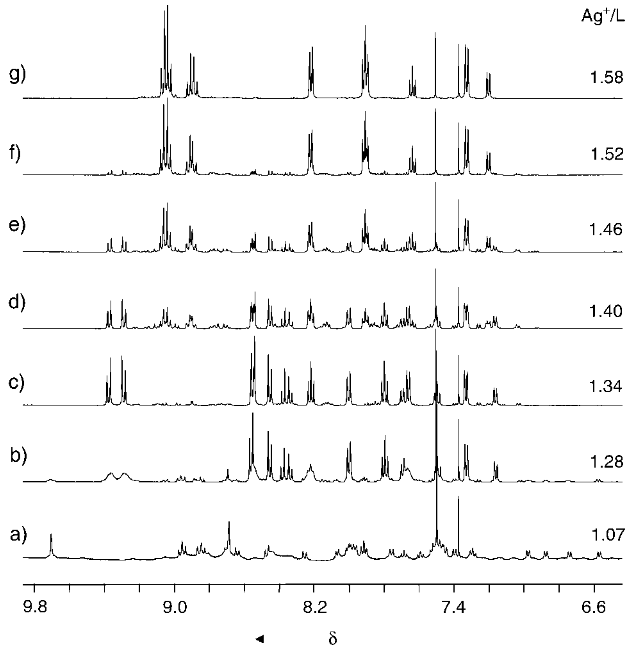

Figure 2. 500 MHz ^1H NMR spectra of ligand L in the course of the titration by $AgCF_3SO_3$; solvent: $CDCl_3/CD_3NO_2$ 25/75. The spectra c) and g) at ratios 1.34 and 1.58 correspond to almost pure $L_5Ag_6^+$, **3**, and $L_6Ag_9^+$, **1**, respectively. Because of the small quantities of salt introduced, there may be a significant discrepancy between the Ag^+/L ratio indicated and the actual stoichiometry of the species observed, e.g. for **3**, $L_5Ag_6^+$, traces b) and c).

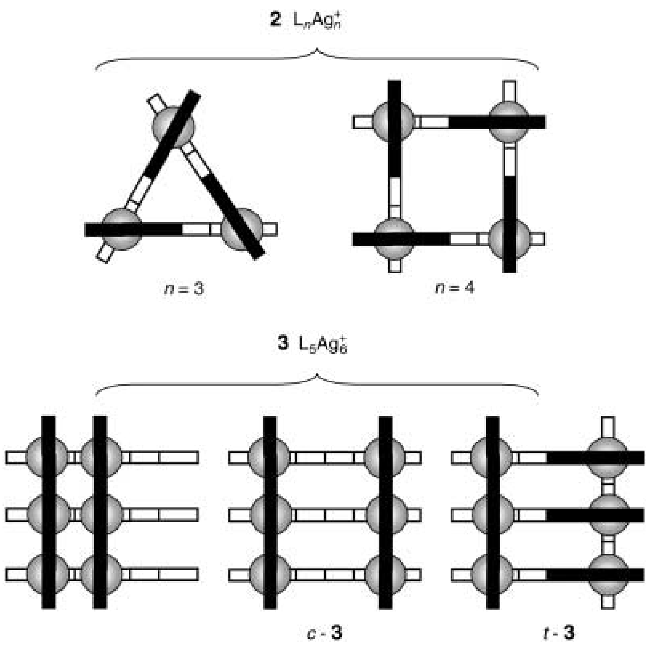

Figure 3. Schematic representation of different forms of the two types of species $L_nAg_n^+$, **2** ($n=3, 4$), and $L_5Ag_6^+$, **3**; in the complex **3**, bottom left, the terminal pyridine units of the horizontal ligands are expected to be in a transoid orientation to the neighboring pyridazine. For **2**, only forms with “corner” Ag^+ ions are shown.

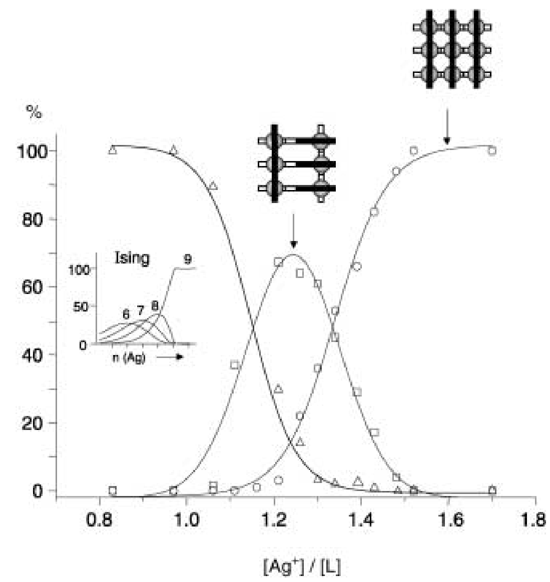

Figure 4. Distribution curves of the species **1**, $L_6Ag_9^+$, (○), the *t*-**3** form of $L_5Ag^+{}_6$ (□) and all the others (△; by difference) in the course of the titration of L by $AgCF_3SO_3$ in CD_3Cl/CD_3NO_2 25/75, determined by integration of characteristic 200 MHz ^1H NMR signals for the two complexes. The inset shows part of the distribution curves of the species containing 6–9 silver ions for a statistical non-cooperative Ising model with nine independent sites.

measurements and analysis of ^1H and ^{109}Ag 2D NMR spectra and relaxation times allow the unambiguous identification of the complex as a species of $L_5Ag_6^+$ composition, in agreement with the titration stoichiometry. The silver NMR spectroscopic data indicate the presence of two sets of ^{109}Ag-coupled proton signals corresponding to “corner” and “edge” silver cations, respectively. Together with the ^1H NMR spectroscopic data[17] and taking into account that the transoid conformation around the central C–C bond in L is much preferred over the cisoid one,[12, 13] the structure *t*-**3** (see Figure 1 b,c) can be assigned to $L_5Ag_6^+$; in *t*-**3**, the ligands in the set of three (shown as “horizontal”) are in the form *t*-L, presenting a transoid conformation around the central C–C bond, whereas the other two ligands (shown as “vertical”), are in the cisoid form *c*-L. The ^1H NMR spectrum in Figure 2 b displays exchange-broadened signals for the two cisoid ligands of the *t*-**3** species. A 2D exchange map shows that the partner(s) in this ligand-exchange reaction is (are) a different species from the $L_nAg_n^+$ complexes mentioned above. This process allows the formation of the *c*-$L_5Ag^+{}_6$ (*c*-**3**) entity (Figure 3) which is a prerequisite for the generation of the final grid $L_6Ag_9^+$ (**1**; see also below).[16]

Further addition of salt leads to the conversion of this intermediate **3** into the final $L_6Ag_9^+$ [3 × 3] grid (**1**) displaying its characteristic spectrum. It is seen in the distribution diagram for the two main species identified (**1** and **3**; Figure 4) that the formation of $L_6Ag_9^+$ is highly nonlinear. Examination of the proton NMR spectra indicates that there are only small amounts $\leq 10\,\%$ of other, intermediate, complex(es) formed along the path from **3** to **1**, which cannot interconvert directly but must undergo dissociation/reassociation processes with rotation around the central C–C bond of three L ligands. These minor species may be other forms of $L_5Ag_6^+$ (see Figure 3). The behavior observed implies overall positive cooperativity in the formation of $L_6Ag_9^+$ from $L_5Ag_6^+$, with three Ag^+ ions and a ligand molecule binding in a single overall step. In contrast, assuming an Ising model with nine independent (non-cooperative) sites, the distribution curves would demonstrate the formation of the complexes with seven and eight cations, which were not observed in the course of the titration.

Addition of salt much beyond the $L_6Ag_9^+$ stoichiometry, up to four equivalents (six ions to one ligand), did not lead to further changes in the ^1H NMR spectrum. Thus, the final [3 × 3] grid (**1**) is stable to a large excess of Ag^+ ions. This behavior indicates that the $L + Ag^+$ system displays high *robustness*[18] with respect to formation of $L_6Ag_9^+$. Conversely, the intermediate entity $L_5Ag_6^+$, which appears and disappears without being directly on the pathway, may be considered as an *anomaly*, as it exists only in a restricted range of Ag^+ concentrations during the process.

Figure 3 shows a selection of the complexes of type $L_nAg_n^+$ (**2**) and $L_5Ag_6^+$ (**3**) among the many complexes of different compositions and structures that can, in principle, form in the course of the titration.

Formally, conversion of the *trans* species *t*-$L_5Ag_6^+$ (*t*-**3**) into the corresponding *cis* form *c*-$L_5Ag_6^+$, (*c*-**3**; Figure 3), where three transoid ligands (*t*-L) become cisoid ones (*c*-L), generates three complexation sites and triggers the binding of three Ag^I ions and a ligand L molecule in a single overall step. *c*-$L_5Ag_6^+$ is expected to be about 20 kcal mol^{-1} less stable than *t*-$L_5Ag^+{}_6$.[12] On the other hand, the complexation of a single Ag^+ ion by a 9,10-phenanthroline (phen) and a 2,2′-bipyridine (bipy) unit may be estimated to provide an association free energy of about 15 kcal mol^{-1}, so that binding of three Ag^I ions and a ligand L (*all-trans*) by c-$L_5Ag^{+}{}_6$ to form $L_6Ag^{+}{}_9$ should correspond to about 45 kcal mol^{-1} binding free energy.[19] This gross estimate[19b] does not take into account the weaker binding to a pyridazine nitrogen compared to a pyridine one, nor the electrostatic interactions between the charged coordination sites, nor the stacking interactions between the ligands.

In the $L_5Ag^{+}{}_6$ entity, the ligands in the set of three, shown as "horizontal", must be all three either in the t-L or in the c-L form, as in t-**3** and c-**3** respectively; no species with mixed forms $[(c\text{-L})_2(t\text{-L})]$ or $[(c\text{-L})(t\text{-L})_2]$ can exist. Thus, cooperativity lies on one hand in the simultaneous "preparation" of the three central sites for binding and on the other hand in the fact that in the incoming L molecule all three sites are rigidly connected, so that binding to one of them forces binding to the other two.[20] Conversion of one site in t-$L_5Ag^{+}{}_6$ from t into c implies $t \rightarrow c$ conversion of the other two, which amounts to an effective increase in affinity from no binding at these two sites to binding at two single phen-type sites (about $2 \times (20/2)$ kcal mol^{-1}).[19] This factor formally represents the free-energy term $\Delta\Delta G$ by which the affinity of the $L_5Ag_6^+$ species for further Ag^+ binding is raised when the first site becomes occupied.[21] It may be regarded as the coupling between the first binding event and the two subsequent ones. Such a value is qualitatively in line with the very uneven species distribution (Figure 4), in which the starting t-$L_5Ag^{+}{}_6$ and the final $L_6Ag^{+}{}_9$ are highly predominant and the two intermediate species containing seven and eight Ag^+ ions only form in a (very) small amount. These features imply a high cooperativity between the sites, corresponding to a switching process between the two entities.[22] Positive cooperativity has been observed in helicate formation[23] as well as in other nonbiological systems.[4b, 24] In view of the complexity of the conversion of $L_5Ag_6^+$ into $L_6Ag_9^+$, it is not possible at this stage to provide a more quantitative analysis of the cooperativity[21, 22] nor to analyze it in terms of site-specific contributions.[25]

The present results provide insight into the nature of the species that may be involved in the mechanistic pathway(s) for the self-assembly of the [3 × 3] metallogrid (**1**) and also hint at how complex such a process is. The results reveal the robustness of the structural program leading to **1**, as well as the overall cooperative nature of the system. Both characteristics, together with the reversible exploration of the free-energy hypersurface, are of basic significance for the dynamic behavior of supramolecular devices and materials.[18]

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[10] As the grid complex **1** forms and is stable in nitromethane, but is destroyed in coordinating solvents such as acetonitrile, the titrations were performed in a mixture of $CDCl_3/CD_3NO_2$ 25:75 for solubility reasons. The presence of small amounts of water does not significantly affect the formation of the grids. Typical procedure: A suspension of the ligand (5.4 mg; 15.9 μmol) was prepared in 500 μL of the solvent $CDCl_3/CD_3NO_2$ 25/75. Half of the amount of $AgCF_3SO_3$ salt required for generating the [3 × 3] grid (3 mg; 12 μmol) was initially added to solubilize all the ligand. The titrating agent was a solution containing a 3-fold excess of $AgCF_3SO_3$ (18 mg; 71.5 μmol) with respect to the stoichiometry of the complete grid, in 250 μL of the same solvent, containing the amount of ligand (2.7 mg; 8 μmol) required to keep its concentration constant during the titration. Aliquots (10 μL) of the metal salt solution were added to the ligand and the ^1H NMR spectra were recorded after each addition, when the thermodynamic equilibrium was assumed to be reached (no change in the NMR spectrum). $CDCl_3$ was filtrated over basic alumina, then kept over molecular sieves 3 Å; CD_3NO_2 was dried over molecular sieves. The ligand and silver triflate were dried under vacuum and heating, and the silver salt was protected from light.

[11] ^1H NMR spectra were recorded on a Bruker AC 200 or Bruker ARX 500 spectrometer. The ^{109}Ag NMR signals were observed by a $^1H/^{109}Ag$ 2D HMBC gradient-accelerated procedure on a BRUKER ARX 500 spectrometer using a 5 mm inverse broadband probe and nominal 90° pulses of 36 μs for ^{109}Ag nuclei and 10 μs for ^1H nuclei. Although no long-range $^1H/^{109}Ag$ spin coupling is observed in 1D ^1H NMR spectra, correlations between hydrogen atoms and silver atoms are observed with transfer delays in the range 0.1 – 0.2 s.

[12] In 2,2′-bipyridine, the transoid form is calculated to be about 6 – 8 kcal mol^{-1} more stable than the cisoid one.[13] The difference in stability between these two forms should be at least as large in the 3,3′-bipyridazine unit present in L. As a consequence, the $L_5Ag_6^+$ species t-**3** of C_{2h} symmetry, with a transoid conformation around the central C–C bond of the three neighboring t-L ligands, should be about 20 kcal mol^{-1} more stable than the corresponding C_{2v} species c-**3**, in which the same three ligands are in the cisoid form represented in

structure *c*-L (see Figure 1). Similar considerations hold for the complexes $L_nAg_n^+$ (**2** Figure 3, top).

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[17] These data involve a) mutual relaxation cross-peaks between the methyl groups of the three transoid ligands, and b) significant differences in T_1 relaxation times of the central pyridazine hydrogens in the transoid (2.1 s) and in the cisoid (1.3 s) ligands.

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[19] a) As a first approximation, one may assume that free bipy and 9,10-phenanthroline (phen) are models for binding to a transoid and a cisoid site respectively in ligand L. Then, binding of one free ligand L (*all-trans*) and three Ag^+ ions to the $L_5Ag_6^+$ species *c*-**3** may be estimated to amount to a free energy of about 45 kcal mol^{-1}, corresponding to the formation of three mixed-ligand Ag^+(bipy,phen) complexes, which would each provide a binding free energy of $[Ag^+(bipy)_2/2 + Ag^+(phen)_2/2] = 10/2 + 20/2 = 15$ kcal mol^{-1}.[19c] Note that the difference between binding of Ag^+ to a single phen and a single bipy (20-10)/2 = 5 kcal mol^{-1} should compare to a cisoid into transoid conversion that is, 6–8 kcal mol^{-1};[12] b) we realize that this data "torturing" may already be going too far… Molecular-mechanics Universal-Force-Field calculations provide an energy difference of about 50 kcal mol^{-1} between *c*-**3** and *t*-**3**; E. Ruiz, unpublished work. *Ab initio* calculations on different complexes have been undertaken; G. Corongiu, P. Nava, work in progress; c) this corresponds to complexation in acetonitrile: W. J. Peard, R. T. Pflaum, *J. Am. Chem. Soc.* **1958**, *80*, 1593.

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Electrochemical Modulation of Fluorophore Emission on a Nanostructured Gold Film**

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Fluorophore-bound gold nanoparticles can serve as a probe in biological systems, provide basic understanding of molecular-level interactions of a surface-bound organic moiety,[1–4] and contribute to the development of biological tracers as well as optoelectronic devices.[5–8] In a fluorophore–gold nanoassembly the charge transfer interaction between the two components plays an important role as it dictates the pathways by which the excited state deactivates. For example, in the case of 1-aminomethylpyrene the transfer of lone-pair electrons to gold nanoparticles led to a fluorescence enhancement.[9] On the other hand, the fluorescence emission of a pyrenylthiol ((1-pyrenyl)-6-oxaheptanethiol) was quenched through charge transfer upon binding to the gold nanoparticles.[10]

Gold nanoparticles capped with organic molecules have a unique ability to retain the charge when subjected to an electric field. Their ability to display quantized charging has been demonstrated by Murray and coworkers.[6, 11] Control of charging of the gold nanocore thus becomes an important factor if one is interested in modulating the interaction between the gold nanocore and a surface-bound fluorophore. In order to systematically assess the effect of charging on the photochemistry of surface-bound molecules, we have conducted spectroelectrochemical measurements using nanostructured gold films that were functionalized with a pyrenylthiol and have succeeded in modulating the fluorescence using an externally applied electrochemical bias. The possibility of achieving electrochemical modulation of the fluorescence of a gold-surface-bound fluorophore opens up new avenues to design sensors, displays, and biological probes.

Earlier studies have shown that fluorophores bound to bulk metal surfaces are nonfluorescent.[1, 12–14] Both energy transfer and electron transfer processes are considered to be major deactivation pathways for the excited fluorophore on metal surfaces. Our recent study has shown the possibility of achieving a photoinduced electron transfer in colloidal suspensions of pyrenylthiol-functionalized gold nanoparti-

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