

# Binuclear Complexes Supported by a Tetrapyridyl Ligand with a Bending Anthraquinodimethane Linker

Takahiro Iwamoto,\* Yuta Sotome, and Youichi Ishii\*

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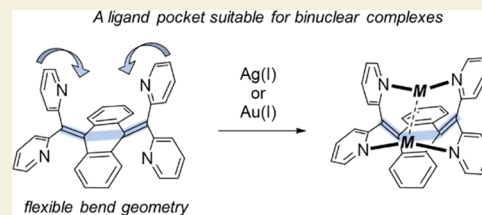
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**ABSTRACT:** A tetrapyridyl ligand with a bending anthraquinodimethane linker has been synthesized, and its complexation with coinage metals has been examined. The treatment of the ligand with Ag(I) and Au(I) cations afforded binuclear complexes, wherein the two metal centers were in close proximity to the inside space of the ligand. X-ray analyses corroborated with theoretical calculations indicated that the ligand has reasonable flexibility toward a bending deformation of the linker moiety to provide a ligand pocket suitable for the proximal binuclear complexes, even though such deformations accompany a non-negligible amount of energetic cost. On the other hand, treatment with 2 equiv of Cu(I) salt afforded a binuclear complex, in which both copper atoms were coordinated at the periphery of the ligand.

**KEYWORDS:** binuclear complex, gold, silver, copper, anthraquinodimethane



## INTRODUCTION

Binuclear complexes containing two metal atoms in close proximity have gained considerable attention due to their potential to enable unique molecular transformations, which are otherwise infeasible, through synergistic metal–metal effects.<sup>1</sup> Studies on binuclear systems have been performed for decades in transition metal chemistry, and many of them have made use of binucleating ligands with  $\mu$ -coordinating atoms/functionalities or a macrocyclic pocket to accumulate metal atoms.<sup>2</sup> More recent investigations from a synthetic viewpoint have been focused on bimetallic systems based on the design of elaborated binucleating ligands. One prevailing ligand design is construction of a well-organized ligand pocket to hold a binuclear center, thereby leading to the emergence of useful ligands for robust yet reactive proximal binuclear systems (Figure 1).<sup>1e</sup> Ligands based on 1,8-naphthyridine bearing donor units at the 2,7-positions represent one of the most useful scaffolds to create a variety of binuclear complexes including hetero-binuclear systems, and these complexes were found to exhibit unusual reactivity by cooperation of two metals.<sup>3–5</sup> Other recent examples include bidentate ligands with a *p*-terphenyl linker, which feature a arene–metal interaction stabilizing a binuclear core with a range of electronic states.<sup>6</sup> Furthermore, redox-active pyridinediimine ligands bridged by alkyl linkers have been reported, and the flexible alkyl linkers allow for dynamic changes in metal–metal distances.<sup>7</sup> These studies highlighted that the linker design is crucial not only for the construction of defined binuclear systems but also as a tunable factor to affect the extent of the metal–metal interaction and directly perturb the properties of the metal centers.

Overcrowded ethylenes have long been known to show out-of-plane structural deformation caused by severe steric hindrance. Tetraaryl-substituted anthraquinodimethane derivatives are among this type of compounds, most of which adopt a boat-like folded conformation in their ground state.<sup>8</sup> Such nonplanar bending geometries would provide an attractive scaffold to construct a three-dimensional coordination environment consisting of a conjugated system. However, to the best of our knowledge, no example has been known for binucleating ligands using an anthraquinodimethane linker. In this study, we have designed tetrapyridyl ligand **1** possessing an anthraquinodimethane linker (Figure 1b). Its complexations with coinage metals have been examined as a benchmark study to reveal the ability to construct a proximal binuclear system.

## RESULTS AND DISCUSSION

The synthesis of ligand **1** was carried out by Stille coupling of 11,11,12,12-tetrabromo-9,10-anthraquinodimethane with 2-(tributylstannyl)pyridine (for details, see the [Experimental Section](#)).<sup>8</sup> An X-ray diffraction study revealed that ligand **1** has a bent geometry for the anthraquinodimethane unit, in which the bent angles of 140.7(1) and 141.3(1)° are comparable with those of similar types of tetraarylanthraquinodimethanes (Figure 2). As a result of the bending geometry of the anthraquinodimethane unit, two nitrogen atoms (N1, N3) of

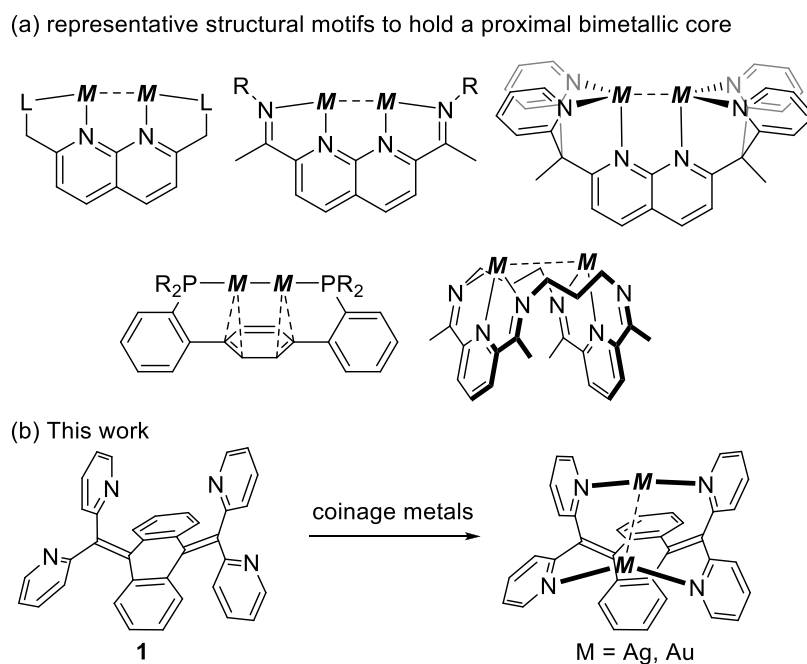
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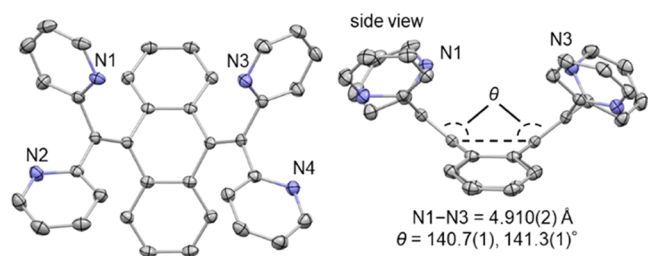
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**Figure 1.** Ligand pockets for bimetallic complexes containing two metals in close proximity.

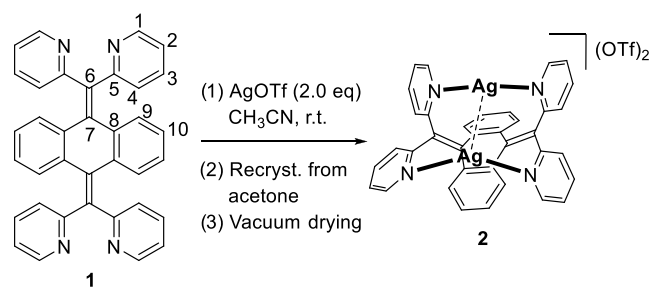


**Figure 2.** Solid-state structure of ligand **1** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. C: gray and N: purple.

the pyridyl groups pointing inward are located 4.910(2) Å apart from each other. One of the pyridyl rings in each (pyridyl)<sub>2</sub>C end group points inward, and the other outward in the solid state. On the other hand, in solution, the sharp and  $C_{2v}$  symmetric <sup>1</sup>H NMR spectrum of **1** indicates free rotation of the pyridyl groups.

Ligand **1** was first subjected to complexation with AgOTf in acetonitrile. Treatment of ligand **1** with 2 equiv of AgOTf in acetonitrile provided a single product judging from <sup>1</sup>H NMR analysis. In the <sup>1</sup>H NMR spectrum of the resulting complex, four pyridyl groups were observed equivalently, and signals for the hydrogen atoms H1, H2, and H3 (the atom labeling is shown in Figure 3) were shifted to a lower magnetic field by 0.17–0.24 ppm in comparison with those of the parent ligand. Recrystallization from (CH<sub>3</sub>)<sub>2</sub>CO/Et<sub>2</sub>O afforded complex **2**(OCMe<sub>2</sub>) as colorless crystals. Crystals of **2**(OCMe<sub>2</sub>) gave off the acetone molecule on drying under vacuum, and the <sup>1</sup>H NMR spectrum of the dried sample revealed the absence of coordinated molecules such as acetone and water.

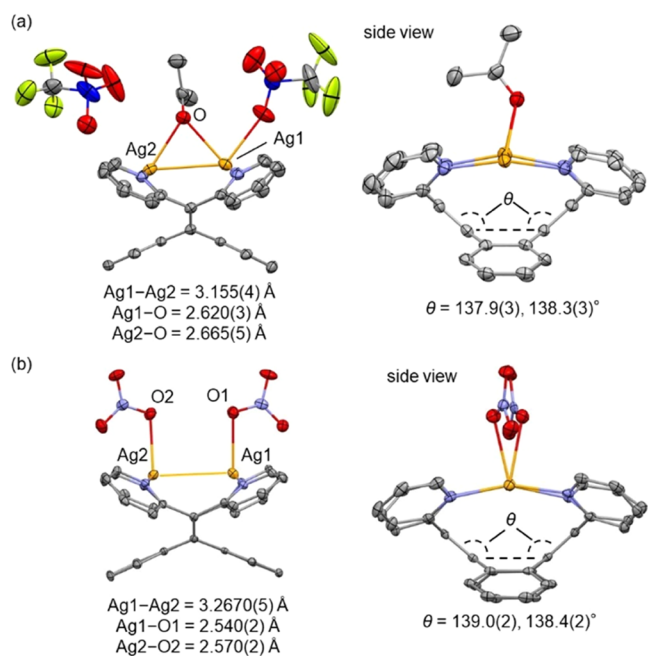
Single crystals suitable for X-ray analysis were obtained by layering an acetone solution of the complex with chlorobenzene (Figure 4a). The solid-state structure featured two silver atoms in close proximity, which are supported inside the ligand scaffold. Argentophilic interaction was corroborated by the Ag–Ag distance of 3.155(4) Å, which was shorter than the



**Figure 3.** Complexation of ligand **1** with AgOTf.

sum of their van der Waals radii (3.44 Å) and lie within the range of previously observed argentophilic interaction (2.71–3.65 Å).<sup>9</sup> A disordered silver atom was observed on the site of one silver atom (Ag1) with an occupancy of 8% (see the Supporting Information), and the Ag1<sub>disordered</sub>–Ag2 distance was 3.50(3) Å. Each silver atom is coordinated with two pyridyl moieties in a pseudo-trans fashion (N–Ag–N angles = 157.2(1) and 145.6(2)°), and the resulting binuclear core is bridged by one acetone molecule. Moreover, one silver atom (Ag1) was coordinated with the counteranion. There is little interaction between the silver centers and the anthraquinodimethane unit, judging from the shortest Ag–C distance of 3.121(5) Å.<sup>10</sup> This complexation inside the ligand scaffold induces deformation of the anthraquinodimethane core; the bent angles were found to be 137.9(3) and 138.3(3)° in complex **2**(OCMe<sub>2</sub>), which are smaller than those of the free ligand (right side). Such deformation results in the decrease of the distances between two pyridine units (N...N = 4.297(3) and 4.227(4) Å), which allows for the present coordination in a pseudo-trans fashion.

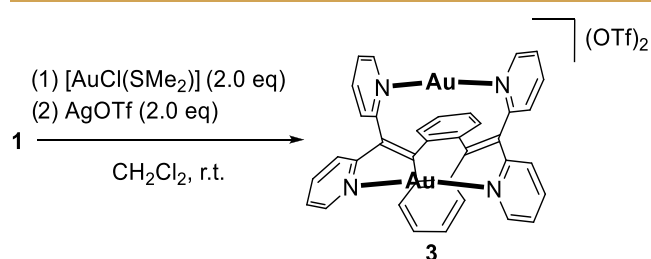
The above-mentioned type of  $\mu_2$ -solvent coordination toward a binuclear silver core has been known in several reports,<sup>11</sup> some of which showed that the solvent bridge helped to hold the Ag<sub>2</sub> core. To clarify the effect of solvent coordination on the formation of the present bimetallic complex, we examined the synthesis of a bimetallic Ag



**Figure 4.** Solid-state structure of (a) complex **2**(OCMe<sub>2</sub>) and (b) **1**-(AgNO<sub>3</sub>)<sub>2</sub> with thermal ellipsoids at 50% probability. Counteranions are omitted for clarity in the side view of complex **2**(OCMe<sub>2</sub>). C: gray, N: blue, Ag: orange, O: red, S: deep blue, and F: green.

complex without a bridging molecule. Instead of AgOTf, the use of AgNO<sub>3</sub> was found to provide a similar type of binuclear silver complex, in which two NO<sub>3</sub> anions coordinated to the respective silver centers to prevent solvent bridging (Figure 4b). In this case, the Ag–Ag distance is slightly longer than that of complex **1**, yet is still within the range of argentophilic interaction (Ag–Ag = 3.2670(5) Å). Therefore, we found that ligand **1** can hold the Ag<sub>2</sub> core even in the absence of the assistance of a bridging molecule.

Ligand **1** also proved to be suitable for the synthesis of a binuclear gold complex (Figure 5). The treatment of ligand **1**

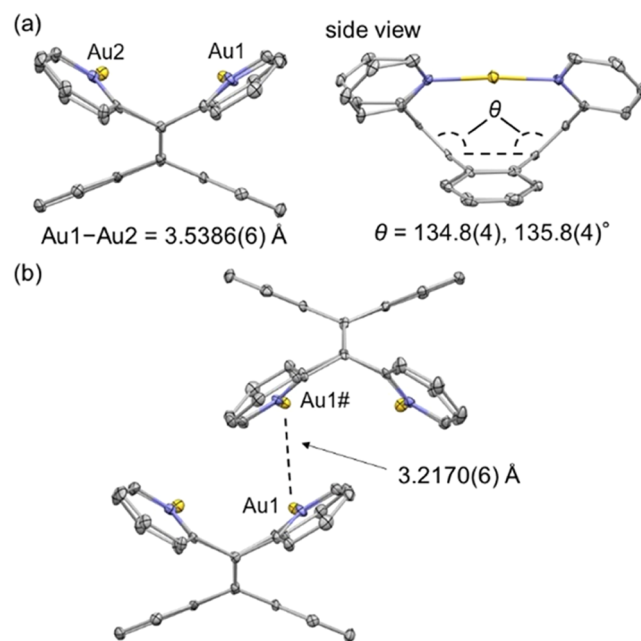


**Figure 5.** Synthesis of binuclear gold complex **3**.

with 2.0 equiv of [AuCl(SMe<sub>2</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> followed by anion exchange with AgOTf resulted in quantitative formation of binuclear gold complex **3**. Note that the reaction outcome is significantly affected by the synthetic procedure probably due to the practical issue at the generation of a cationic Au species;<sup>12</sup> when a CH<sub>2</sub>Cl<sub>2</sub> solution of [AuCl(SMe<sub>2</sub>)<sub>2</sub>] is first treated with AgOTf and then allowed to react with **1**, the yield of **3** was much lower (50% NMR yield), and formation of an unidentified byproduct was observed.

A crystallographic study revealed that both two gold atoms are located inside the ligand pocket; however, unlike **2**, the Au–Au distance of 3.5386(6) Å is longer than the sum of their

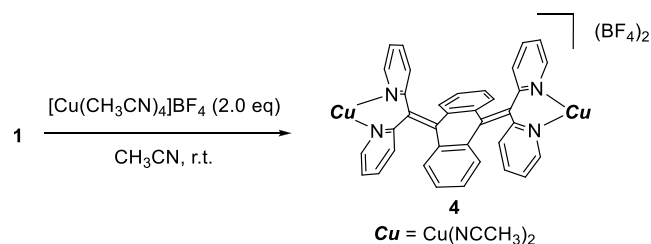
van der Waals radii (3.32 Å) as well as the common aurophilic interaction distances (2.50–3.50 Å).<sup>13</sup> Thus, the aurophilic interaction within the binuclear core of **3** would be of small importance. Instead, an intermolecular aurophilic interaction along with  $\pi$ – $\pi$  interactions between pyridyl units is observed in a stacked arrangement (Figure 6b). As observed for complex



**Figure 6.** (a) Solid-state structure of complex **3** with thermal ellipsoids at 50% probability. Hydrogen atoms and counteranions are omitted for clarity. C: gray, N: blue, and Au: yellow. (b) Intermolecular aurophilic interaction in **3**.

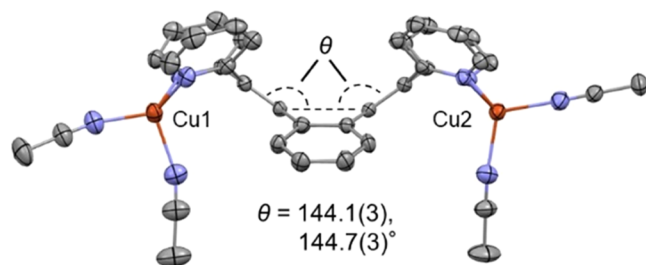
**2**, the bent angle of the anthraquinodimethane unit decreased to 134.8(4) and 135.8(4)<sup>o</sup> from those of the parent ligand, and thus, induced-fit complexation accompanying the bending deformation works effectively. Since <sup>1</sup>H NMR analysis of the complex showed that all pyridyl units were equivalent even at –40 °C, the dimeric structure of **3** with intermolecular Au–Au interaction is considered to be labile in solution.

Complexation with 2.0 equiv of [Cu(Me<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> in acetonitrile was finally examined to afford binuclear copper complex **4** (Figure 7). X-ray analysis indicated that the



**Figure 7.** Synthesis of binuclear copper complex **4**.

coordination site in **4** is completely different from those of **2** and **3** (Figure 8). Each copper atom is located at the periphery of ligand **1** and subjected to coordination by the two neighboring pyridyl units to form a 6-membered chelate with a boat-like conformation. In addition, the coordination of two acetonitrile molecules results in a distorted tetrahedral geometry of the copper centers ( $\tau_4 = 0.84$  for Cu1 and 0.88



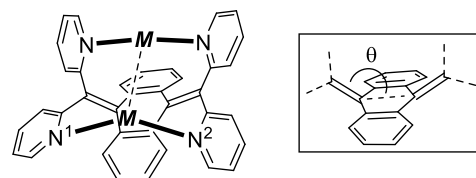
**Figure 8.** Solid-state structure of complex **4** with thermal ellipsoids at 50% probability. Hydrogen atoms and counteranions are omitted for clarity. C: gray, N: blue, and Cu: orange.

for Cu2).<sup>14</sup> Unlike complexes **2** and **3**, the bent angles of the anthraquinodimethane moiety become slightly larger than those of ligand **1** (144.1(3) and 144.7(3)°). Although the observed outward coordination might be induced by the coordination of acetonitrile molecules, the examination of less coordinating solvents was hampered due to the low solubility of complex **4** in such solvents (CH<sub>2</sub>Cl<sub>2</sub>, THF, and MeOH).

It is noteworthy that silver complex **2** likely shows bimodal coordination behavior in solution judging from the comparison of the <sup>1</sup>H NMR spectra of complexes **2–4**; the <sup>1</sup>H NMR spectra of complex **2** in the coordinating CD<sub>3</sub>CN solvent are highly similar to those of copper complex **4**, while in less coordinating solvents such as CD<sub>3</sub>OD, complex **2** exhibits NMR spectra similar to those of complex **3** (see the Supporting Information). Therefore, we believe that silver complex **2** switches the inward and outward coordination modes depending on the coordinating ability of the solvent. In the case of gold and copper complexes, such bimodal coordination behavior has not been observed.

To gain an insight into the coordination modes, we assessed the structural parameters of silver, gold, and copper complexes by DFT calculations at the B3LYP-GD3BJ/6-311G\*\**-*SDD level of theory. Notably, calculations with the treatment of acetonitrile as an implicit solvent by the SMD model showed that a proximal binuclear structure was more stable than the corresponding distal binuclear structures in the case of all metals (see the Supporting Information). On the other hand, calculations with the treatment of acetonitrile as an explicit solvent provided different results; the outward coordination is more thermodynamically favorable than the inward coordination for silver and copper complexes ( $\Delta G = 22.4$  and  $27.4$  kcal/mol, respectively), while the inward structure is more stable than the outward one with a  $\Delta G$  of 0.4 kcal/mol for the gold complex. In these calculations, with the consideration of acetonitrile coordinations, the optimized gold complex with the distal binuclear structure contains two coordinated acetonitrile molecules, whereas coordinations of four acetonitrile molecules are found in the distal silver and copper complexes. Thus, the difference in the coordination numbers dramatically affects the stability of the outward complex, though the number of coordination molecules still remains obscure from the experimental viewpoint.

The optimized proximal binuclear structures of Ag and Au complexes were almost identical to that obtained by X-ray analyses, and slight differences in several structural parameters may be ascribed to the packing effect in the crystal state (Figure 9). Of importance, the bent angle of the anthraquinodimethane unit is almost identical to that obtained by X-ray analyses. Energy costs for such structural



| M  | distances (Å) <sup>a</sup> |      |                                  | $\theta^a$ | energy cost for ligand deformation |
|----|----------------------------|------|----------------------------------|------------|------------------------------------|
|    | M---M                      | N-M  | N <sup>1</sup> ---N <sup>2</sup> |            |                                    |
| Cu | 2.75                       | 1.95 | 3.80                             | 133.3      | 17.8 kcal/mol                      |
| Ag | 3.13                       | 2.18 | 4.29                             | 138.1      | 15.9 kcal/mol                      |
| Au | 3.22                       | 2.09 | 4.15                             | 134.5      | 20.0 kcal/mol                      |

<sup>a</sup>Averaged values.

**Figure 9.** DFT calculations of the proximal binuclear copper, silver, and gold complexes.

deformations were estimated by single-point energy calculations of the ligand moiety in the complexes. The obtained energy costs for silver and gold complexes are 15.9 and 20.0 kcal/mol, respectively, and these non-negligible amounts of energy costs may be attributed to the rigid structure of a conjugated anthraquinodimethane unit consisting of sp<sup>2</sup> carbons. Nonetheless, the present study revealed that anthraquinodimethane-based ligand **1** has reasonable flexibility toward the bending deformation to thereby provide a ligand pocket suitable to access the proximal bimetallic complexes.

In the case of the copper complex, a similar binuclear structure was estimated, whose Cu–Cu distance of 2.75 Å is close to twice the van der Waals radius (2.80 Å). Owing to the smaller atomic radius of the copper atom, formation of a proximal binuclear complex requires a smaller ligand pocket in comparison to the silver and gold complexes, as shown by the shorter Cu–N bond, the closer N<sup>1</sup>...N<sup>2</sup> separation, and the smaller bent angle of the anthraquinodimethane unit. However, the deformation energy is lower than that in the gold complex. Thus, the energy costs for the ligand deformation would not be a dominant factor in determining the preference for the outward coordination in the copper complex. In addition to the solvent effects (vide supra), we now assume that the higher propensity of Ag(I) and Au(I) to adopt a low coordination number and a linear structure might play an important role in constructing complexation inside the ligand scaffold. Further experimental and theoretical studies are needed to unveil the bimodal coordination behavior.

## CONCLUSIONS

As a ligand for proximal binuclear complexes, we here designed a tetrapyridyl compound with an anthraquinodimethane linker. Its coordination behavior has been assessed by complexation with coinage metals in conjunction with DFT calculations. As a result, in addition to the inherent bent geometry of the linker unit, ligand **1** was found to have a reasonably bending deformation ability and consequently served as a multitopic ligand capable of accommodation of two silver or gold metal centers in the defined proximal space. In comparison to the previously reported elaborated ligands for binuclear complexes, ligand **1** constructed the silver and gold complexes in unique coordination modes; each metal center was coordinated with donor units in a pseudo-trans fashion, and the linker unit hardly took part in the coordination with metal centers. Elucidation of reactivities of these complexes and application





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