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# The Electronic Effects of Ligands on Metal-Coordination Geometry: A Key Role in the Visual Discrimination of Dimethylaminopyridine and its Application towards Chemo-switch †

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**Due to its special coordination ability to Cu(II)-terpyridine complexes, a simple and straightforward visual recognition of *p*-DMAP out of its analogues has been realized via selective metallogel collapse. In combination the selective gel collapse and self-healing property of metallohydrogel 1a, its potential application towards chemo-switch is also demonstrated.**

Due to their broad applications in chemistry and material sciences, functional molecular gels have drawn considerable attentions.[1,2] In comparison with organogels, less-studied metallogels represent one of the most intriguing "smart" materials,[3] because the incorporation of transition metals into gelator molecules not only integrates the metal characteristics (including conductive, redox, catalytic or luminescent properties) into the gel, but also provides an additional subtle control of the molecular assembly. Among non-covalent weak interactions, metal-metal interactions constitute a main driving force leading to metallogel formations.[3a] Therefore, structural modification by suitable guest molecules might handicap or assist these metal interactions to allow a control over metallogel, indicating metallogels as a conceptually new platform for the visual molecular discrimination.[1d] With this in mind, our group firstly realized an unprecedented visual discrimination of enantiomers of chiral phosphines via metallogels based on platinum pincer complexes.[4]

Subsequently, our research was extended to metallo-hydrogels derived from terpyridine metal complexes to explore their potential applications in the visual recognition.[5] It was suggested that the balance of metal-metal interaction, π-π stacking and hydrogen bonding between the gelator and water molecules exhibits crucially impact on the gel. In combination the special coordination ability of Cu(II) ion to the *N*-ligands with our metal-ligand interaction blocking strategy, the addition of bulky terpyridines or bidentate ligands like bipyridines into the metallo-hydrogel **1a** resulted in gel collapse after the chlorides substitution and ligand chelation (Fig. 1a).[5b,c] In contrast to a plenty of examples on chemical triggering organogels, exploration of less-studied intriguing metallogels towards molecular switches still constitute a challenging task.[6] Accordingly, the feasibility of these terpyridine metallogels towards photo- and chemo-switches have been also demonstrated.[5a,b] Besides the multidentate ligands, mono-dentate pyridine (Py) and its derivatives are considered as a class of the most important ligands.[7] However, in general, the less-hindered mono-dentate ligands like Py are considered as an unlikely option to control the gel properties. Following our recent research interests in exploring novel pincer metal complexes towards sensing, catalysis and material sciences,[4,5,8,9] herein, we would like to probe the responsive behaviors and feasibility of metallo-hydrogels based on Cu(II) pincer complexes (**1-5**) with additional mono-dentate pyridine derivatives (Fig. 1b). Along with determining the intrinsic correlation between the metal coordination geometry and molecular assembly, their potential application towards chemo-switch was also demonstrated.

As we previous reported, terpyridine complex **1a** is readily to gelate water even without heating and cooling operation. The critical gelater concentration is 0.25 wt%, therefore, complex **1a** is regarded as a super hydrogelgelator.[5c] In consideration of its coordination propensity to Cu(II) ion, Py was selected to investigate its impact on high thermo-stable metallo-hydrogels **1a** (1 wt%, the corresponding gel−sol phase-transition temperature is 74 °C). After the addition of 1 equiv. Py upon metallogel **1a** (1 wt%), no obvious collapsing was observed. Increasing the amount of Py to 12 equiv., a gel collapse was finally realized after the identical operations. A variety of pyridine derivatives were then screened. However, only the addition of 4-dimethylaminopyridine (*p*-DMAP) led to instant gel collapse without heating, other pyridine derivatives were fail to achieve the
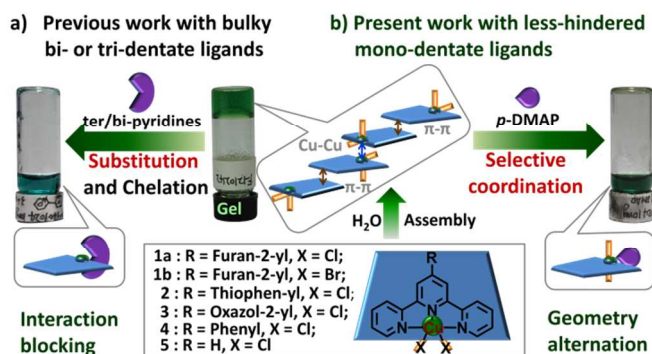


**Fig. 1**. Control over metallo-hydrogel collapse via different strategies: a) halide substitution with a bulky multi-dentate ligand and ligand chelation; b) selective coordination with a mono-dentate ligand.

goal (Fig. 2c). Among pincer complexes **1b-5** with different substituents at 4'-position, only complexes **1b** and **4**, gelated water to form stable hydrogels (1 wt%, Fig. 2a). However, regardless of the phase, all selected samples rapidly transferred into clear green solutions after the addition of 1 equiv. *p*-DMAP. Delightedly, blue-green rectangular single crystals **6a-8**, which are suitable for X-ray analysis, were gradually grown from the corresponding solutions (Fig. S7-S12).
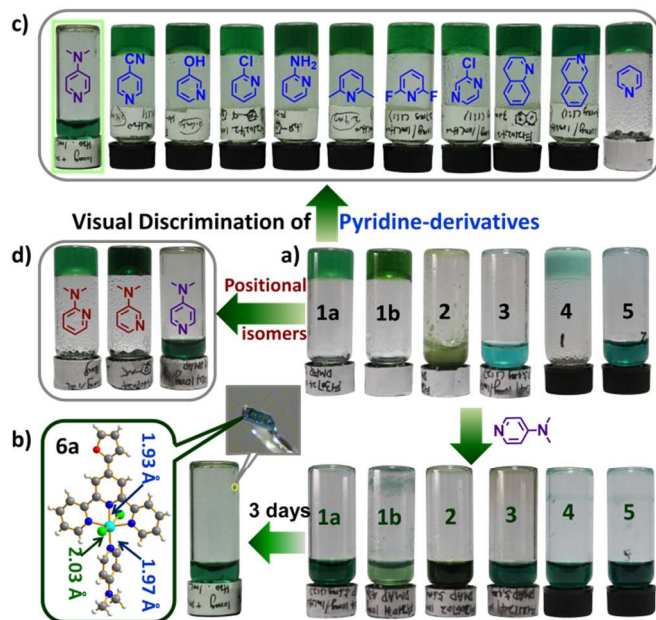


**Fig. 2**. a) Gelation test with Cu-pincer complexes **1-5** and additional *p*-DMAP; b) a crystal growth of adduct **6a** in situ from the collapsed sol [**1a**+*p*-DMAP] and the relative molecular structure of complex **6a**; selective metallo-hydrogel **1a** (1 wt%) collapse with c) additional pyridine derivatives or d) DMAP positional isomers.

As shown in Fig. 2b, the Cu(II) center of complex **6a** adopted a six-coordination geometry, in which the Py-ring was almost perpendicular to the terpyridine plane. The bond distance of Cu-$N_{DMAP}$ was slightly longer than that of the central Cu-$N_{tpy}$. (1.97 Å *vs.* 1.93 Å); and two side Cu-$N_{tpy}$ bonds were equal (2.03 Å). The Cl ligands occupied the axial positions, however, the difference between these two Cu-Cl bonds was significant: one was 2.68 Å and the other was 3.23 Å. The elongated octahedral geometry of complex **6a** clearly indicated there is a strong Jahn-Teller effect,[10] which would significantly enhance the complex stability. Although there were obvious π-π interactions (between the furan ring and one of the arm Py-ring of the second molecule, 4.01 Å), no evident Cu-Cu interactions were found, due to the special elongated octahedral geometry (Fig. S8). Distorted octahedral geometries, similar bond lengths and interactions were also found in the crystal structures of complexes **7** and **8** (Fig. S9-S12). With the data obtained so far, we may presume that *p*-DMAP was inclined to coordinate with Cu(II) center resulting in six-coordination adducts with elongated octahedral geometry, which efficiently interrupted the possible Cu-Cu interaction[5b,c], leading to the gel collapse. Additionally, UV-vis studies also supported the selective coordination ability of *p*-DMAP towards pincer Cu(II) complexes (Fig. S16-S18).

Taking account of dimethylamino group (Me₂N) as a strong electron-donating group, which readily enhances the electron density on *para*-N atom and its coordination ability, a series of pyridine derivatives with *para*-substituents, such as isonicotinonitrile (*p*-CNP), 4-diethylaminopyridine (*p*-DEAP), 4-(4-morpholinyl)-

pyridine (*p*-MPP), 4-methoxy pyridine (*p*-MOP) and 4-methylpyridine (4-MeP), as well as two *p*-DMAP positional isomers (*o*-DMAP or *m*-DMAP), were selected to test their gel collapse ability (Fig. 2d and S6). Upon the addition of 1 equiv. *p*-DEAP on the top of gel **1a**, instant gel collapsing was also observed. However, other pyridines all failed to collapse the gel. The B3LYP density functional theory (DFT) calculations at 6-31G(d) level were carried out with Gaussian 09 package to probe the mechanism, in which the nucleophilicity of tetracyanoethylene (TCE) was used as the reference.[12-14] The HOMO, LUMO energies, the global nucleophilicity indexes (*N*) and charges at N atom of the selected pyridines were compiled in the Table 1. Unlike *p*-CNP, Py, *p*-MeP and *p*-MOP (entries 1-4, Table 1), *p*-DMAP and *p*-DEAP were assigned as the strong nucleophiles (entries 6 and 9, Table 1). Due to the electron-withdrawing property of oxygen atom, the *N* value of *p*-MPP was inferior to those of *p*-DMAP and *p*-DEAP (Table 1).
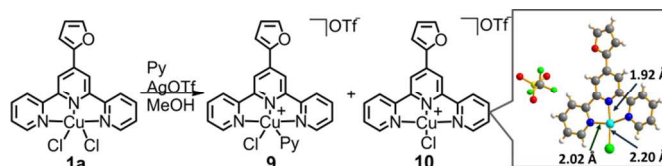


**Scheme 1.** Synthesis of planar pincer complex **10** and its crystal structure.

In order to explain the gel collapse with 12 equiv. Py, we aimed to synthesize the complex **9** (Scheme 1), in which one Cl ligand was substituted by Py. However, when 1 equiv. silver triflate (AgOTf) and 2 equiv. Py in methanol at room temperature were reacted with complex **1a**, instead of complex **9**, a distorted square planar four-coordination Cu(II) complex **10** was obtained, which was confirmed by the X-ray crystal structure obtained by direct evaporation of complex **10** in methanol. In comparison to complex **6a**, similar Cu-$N_{tpy}$ bond lengths (1.92 Å and 2.02 Å) were observed. However, the length of Cu-Cl in the structure of complex **10** was only 2.20 Å. Obvious π-π and Cu-Cu interactions between the molecules were found, which was much shorter than what observed in the crystal of complex **1a** (3.71 Å *vs.* 4.10 Å, Fig. S13 and 14)[5c]. Due to the efficient molecular packing[11], compound **10** hardly gelated any selected organic solvents and water.

**Table 1.** The calculated global properties of selected nucleophiles.[a]

| Entry | R-Py | HOMO | LUMO | *N* | Charge at N atom (*e*) |
|---|---|---|---|---|---|
| 1 | *p*-CNP | 0.2797 | -0.0763 | 1.51 | -0.432 |
| 2 | Py | 0.2526 | -0.0225 | 2.25 | -0.452 |
| 3 | *p*-MeP | 0.2496 | -0.0183 | 2.33 | -0.458 |
| 4 | *p*-MOP | 0.2450 | -0.0076 | 2.46 | -0.476 |
| 5 | *p*-MPP | 0.2156 | -0.0044 | 3.26 | -0.481 |
| 6 | *p*-DMAP | 0.2055 | 0.0059 | **3.54** | -0.490 |
| 7 | *o*-DMAP | 0.1939 | -0.0070 | 3.85 | -0.519 |
| 8 | *m*-DMAP | 0.1934 | -0.0075 | 3.87 | -0.438 |
| 9 | *p*-DEAP | 0.2025 | 0.0049 | 3.62 | -0.493 |
| 10 | Piperidine | 0.2090 | 0.0825 | 3.44 | -0.691 |
| 11 | *p*-DMAP•TFA | 0.2530 | -0.0287 | **2.23** | -0.460 |

[a] HOMO, LUMO in au; global nucleophilicity (*N*), values in eV.

Using natural bond orbital (NBO) analysis,[15] the charges on N atom of *p*-DMAP and *p*-DEAP were also calculated, which were much higher than what observed with other pyridine derivatives. In the cases of *o*- and *m*-DMAP, the global nucleophilicity *N* value were almost equal to each other (entries 7 and 8, Table 1). Especially, the charge on N atom of *o*-DMAP was the richest among three positional isomers (-0.519 *vs.* -0.438 and -0.490, Table 1), however, *o*-DMAP was ineffective to collapse the gel **1a**. After

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detailed energy optimization of three possible isomers **6a-c** formed by complex **1a** and *p*-, *m*- or *o*-DMAPs at M06/6-31+G(d) with SDD (on Cu) level,[16] respectively, the adduct **6a** was calculated as the most stable isomer (Table S26, Fig. S15). Although, the free energy for isomer **6c** was little lower than that of **6a** in 0.6 kcal/mol, the distance of $N_{DMAp}$-Cu (3.70 Å) as well as steric hindrance between -$NMe_2$ group and terpyridine skeleton suggested that complex **6c** was thermodynamically unstable.

Piperidine has similar nucleophilicity (3.44 *vs.* 3.54, Table 1) and higher $pK_a$ value (11.21 *vs.* 9.70, Table S25) than that of *p*-DMAP. However, the addition of 1 equiv. piperidine failed to collapse metallogel **1a**, which may reveal that the coordination ability of guest molecule plays predominant effects on the gel formation/collapse rather than its $pK_a$ value. With this clue in mind, alternation of the electron density of the guest is expected to provide a control over gel collapse and reformation. Therefore, trifluoroacetic acid (TFA) was chosen for this purpose. As we expected, a gel reformation of the collapsed sol [**1a**+*p*-DMAP] (1 wt%) was observed upon addition of 1 equiv. TFA (Fig. 3). Using ^{1}H NMR spectroscopy, upon addition of 1 equiv. TFA into a $CDCl_3$ solution of *p*-DMAP, the proton signals related to $Me_2N$ group were obviously downfield shifted (eg. -C$H_3$ shifted from 2.99 to 3.22 ppm), while no obvious shift was observed for the α-protons of the pyridine ring (Fig. S29). With additional TFA, there was no change observed, and it clearly indicated that TFA only selectively protonated the $Me_2N$ group, which was quite different to the previous reports.[17] After protonation, the *N* value was decreased from 3.54 to 2.23 (entry 11, Table 1), which was even inferior to that of Py. Hence, *p*-DMAP•TFA was readily to dissociate from complex **6a**. To our delight, we successfully realized the reversible gel-to-sol phase transition more than twenty times. In consideration of the gel-reformation of the sol [**1a**+100 equiv. *p*-DMAP] being still observed upon addition of 100 equiv. TFA, this new metallo-hydrogel chemo-switch system should be highly fatigue-resistance.[1d,5a] Furthermore, the gel re-formation process was further investigated by SEM and TEM. Unlike the nanoparticle morphology observed with metallo-hydrogel **1a**,[5c] dense long nanofiber networks were observed in all re-formed metallo-hydrogels [**1a**+*p*-DMAP/TFA] (Fig. 3b, ESI†). In contrast, bulky rectangular crystalline rods were found in all collapsed sols [**1a**+*p*-DMAP/TFA+*p*-DMAP] (Fig. 3a, ESI†).
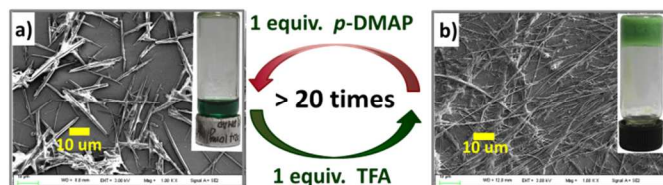


**Fig. 3.** Gel collapse and reformation process by adding *p*-DMAP and TFA, subsequently. SEM images of: a) collapsed sol [**1a**+*p*-DMAP/TFA+*p*-DMAP] and b) reformed gel [**1a**+*p*-DMAP/TFA].

In summary, a simple, convenient and straightforward visual discrimination of *p*-DMAP out of its positional isomers and other analogues has been realized by using metallo-hydrogels based on pincer terpyridine Cu(II) complexes via selective gel collapsing. In assistance with single crystal analysis, theoretical calculation, NMR, SEM and TEM morphology studies, the electron property of pyridine derivatives plays a crucial role on the highly selective coordination to Cu(II) center. The resulted six-coordination adduct with octahedral geometry apparently

blocks the Cu-Cu interaction leading to the gel collapse. In combination this selective coordination ability of mono-dentate pyridine derivatives and the self-healing ability of metallo-hydrogel **1a**, the reversible gel-to-sol phase transition has been achieved more than 20 times by the addition of *p*-DMAP and TFA, subsequently. The inspiring outcome highlights their feasibility towards chemo-switch.

## Notes and references

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR, ^{13}C NMR and ESI-MS spectra, single crystal study, DFT theoretical calculation , SEM and TEM morphologies. See DOI: 10.1039/c000000x/

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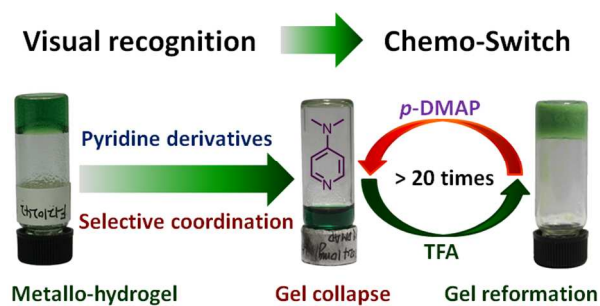


Visual discrimination of *p*-DMAP has been demonstrated via metallo-hydrogel collapse by alternation the geometry of Cu(II)-terpyridine complexes after selective ligand coordination, subsequently; their feasibility towards chemo-switch has been also realized.

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