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Regulating a two-dimensional metallo-supramolecular self-assembly of multiple outputs

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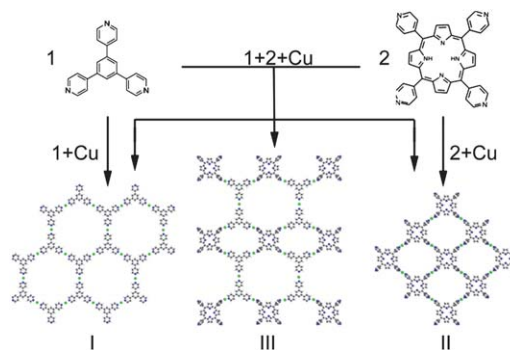
On a Au(111) surface, a mixture of two types of molecular ligands assembles with Cu generating two homogeneous and one heterogeneous metallo-supramolecular structures owing to same pyridyl–Cu–pyridyl coordination. The proportion of the three phases in the output structures is regulated by adjusting the ratio of the two components in the input molecular mixture. As the ratio approaches the stoichiometric value of the heterogeneous structure, one of the ligands is 100% incorporated in the heterogeneous phase, manifesting a unique amplification behaviour in this multiple output self-assembly.

Supramolecular self-assembly allows for the bottom-up fabrication of highly complex materials with interesting chemical and physical functions and properties.^{1–3} In recent decades, metallo-supramolecular self-assembly has been investigated extensively due to the fact that organic ligands can be specifically designed to assemble metal–organic structures providing novel structures and properties.^{4–11} In metallo-supramolecular assembly, the self-assembly protocol experiences reversible forming and breaking of coordination bonds, which enables self-organization, self-recognition and self-selection among ligands and metal ions driven by thermodynamics and/or kinetics.^{12–19} However, accurate design and full control of the self-assembly process are still challenging. Especially for systems involving multiple building units, the self-assembly often introduces multiple phases in final products, expressing less-controlled output structures.^{13,14,20–25}

The self-assembly in nature nevertheless exhibits highly selective and spontaneous build-up of specific outputs.^{2,3,26–28} Besides thermodynamic and kinetic effects, other factors including component concentration, steric effects, template effects, *etc.* may influence self-assembled structures too. In this paper, we report how to regulate a multiple-output 2D metallo-supramolecular self-assembly by adjusting the ratio of the components of the input molecular mixture. As illustrated in Scheme 1, three metallo-supramolecular coordination network structures (I, II and III) invoking the same pyridyl–Cu–pyridyl binding emerge from the self-assembly of the mixture of two pyridyl ligands (1: 1,3,5-trispyridylbenzene (TPyB),

2†: 5,10,15,20-tetra(4-pyridyl) porphyrin (TPyP)) and Cu. The phases I and II are homogeneous structures that contain a single type of ligands, whereas the phase III is a heterogeneous structure which contains both ligands. By adjusting the ratio of the two ligands of the input molecular mixture, the proportion of the phase III in the output structures was enhanced in a way that 100% of compound 2 participated this phase, *i.e.*, realizing an absolutely amplified self-assembly.^{13,14}

Our previous work reported that compound 1 (or 2) alone coordinated with Cu forming the homogeneous structure of the phase I (or II) on the Au(111) surface.^{29,30} The structures of both phases adopt a two-fold linear pyridyl–Cu–pyridyl bonding algorithm. When both compounds are present in the self-assembly, this bonding configuration possibly results in a heterogeneous phase where both ligands are organized in an ordered hybrid structure. We conducted experiments in which a mixture of compounds 1 and 2 was deposited onto the Au(111) substrate together with Cu. Fig. 1a shows that the two homogeneous phases, the phase I and phase II networks, are formed. High resolution images of the two phases are shown in Fig. 1b and c, respectively, displaying the phase II rhombus network of 2 and the phase I honeycomb network of 1. Besides the phase I and II networks, a new network structure, denoted as phase III, was found. As shown in the high-resolution image in Fig. 1d, this new phase comprises straight boundaries of the adjacent phase I and phase II networks. A tentative model manifest the molecular structure of the phase III in Fig. 1e, where a stripe of the phase I



Scheme 1 Compounds 1 (1,3,5-trispyridylbenzene (TPyB)) and 2 (5,10,15,20-tetra(4-pyridyl) porphyrin (TPyP)) and three network phases I, II and III stabilized by Cu–pyridyl–pyridyl coordination.

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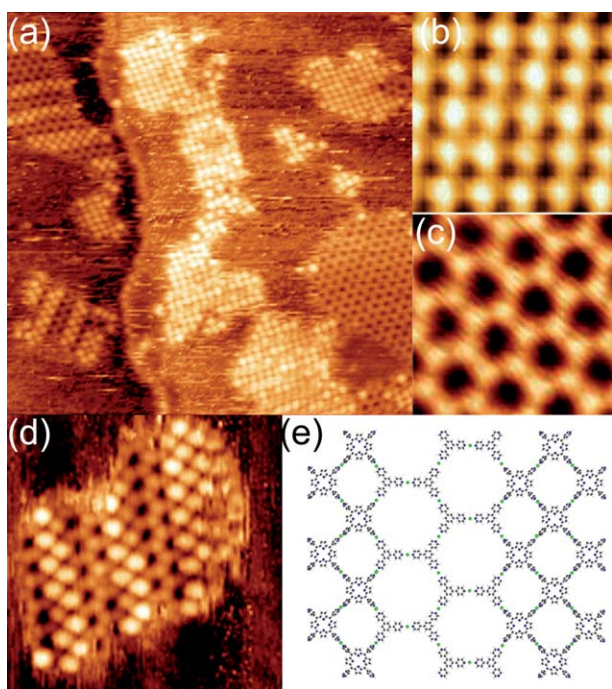


Fig. 1 (a) A typical STM topograph of the sample obtained at 300 K annealing shows three types of phases—I, II and III—highlighted by the high resolution STM images (b), (c) and (d). (Scales: (a) 100 nm × 100 nm; (b and c) 10 nm × 10 nm; (d) 30 nm × 30 nm.) (e) A tentative model corresponding to phase III networks. Colours: C, gray; N, blue; H, white; Cu, green. Data acquisition conditions: (a) $U = -1.46$ V, $I = 0.37$ nA; (b) $U = 1.26$ V, $I = 0.42$ nA; (c) $U = -1.48$ V, $I = 0.43$ nA; (d) $U = -1.45$ V, $I = 0.37$ nA.

network in the middle is connected to two stripes of the phase II network through pyridyl–Cu–pyridyl coordination. We propose the similarity between the dimensions of two homogeneous structures (the lattice constant along the longer diagonal direction of the phase II rhombus network is 2.82 nm, and the lattice constant of the phase I network is 2.73 nm) allows the formation of the boundary lines at the interfaces of the two network phases.

Next, we discuss how to enhance the proportion of the heterogeneous phase III in the output structures, *i.e.* to realize its amplification. We use the percentage of the compound 1 (or 2) involved in the phase I (or the phase II) and the phase III to quantitatively describe the proportion of the three phases in the output structures. In the following discussion, [1] or [2] defines the total amount of compound 1 or 2 involved in Cu–pyridyl coordination; [1<I] or [2<II] defines the total amount of compound 1 or 2 that participates in the phase I or phase II structure; [1<III] or [2<III] defines the total amount of compound 1 or 2 that participates in the phase III structure. We varied the ratio of the two compounds [2]/[1] of the input molecular mixture by adjusting the deposition time of the two molecules. To examine the thermodynamic and kinetic effects, we varied the self-assembly temperature by annealing the samples at different conditions. We acquired STM data of the output structures and conducted statistical analysis accordingly. Table 1 summarizes the results based on the STM data of three experimental trials with different input molecular ratios. Each trial was subjected to two annealing treatments: the first annealing at 450 K for a short time (1 minute) and the second annealing at 450 K for a long time (10 minutes). The color

bars shown in Table 1 represent the percentages of the two ligands participating in the three phases in the output structures. The left column shows the results of an input molecular mixture of [2]/[1] = 2.01. At 300 K, only marginal percentages of molecules (9% of compound 1 and 2% of compound 2) were involved in the phase III. After the first annealing treatment, 50% of compound 1 was involved in the phase III. After the second annealing, this value reached 59%. These results suggest at 300 K, the heterogeneous phase was kinetically hindered and the thermal annealing at 450 K enhanced the heterogeneous phase. However, further enhancement of the phase III was not achieved with the longer thermal annealing. The middle column shows the results of an input molecular mixture of [2]/[1] = 1.51. This mixture gives similar results to the first trial: after the 450 K annealing the phase III networks contain about half of compound 1. The right column shows the results of an input molecule mixture of [2]/[1] = 0.34. At 300 K, 15% of compound 2 participated in the phase III. Upon the first 450 K annealing, 100% of compound 2 participated in the phase III, indicating compound 2 molecules were totally consumed in the phase III structure while the phase II was entirely suppressed. Therefore in contrast to the previous two trials, under this condition, the compound 2 was 100% expressed in the heterogeneous phase III, *i.e.*, this phase was absolutely amplified in the self-assembly.

Fig. 2a is a representative STM image of the phase III structure formed at the 100% enhancement, showing large size islands of rectangular networks (this structure co-existed with the phase I networks (not shown here) that were formed by the remaining 32% of compound 1 molecules). As shown in the high resolution STM image in Fig. 2b, columns of compound 2 molecules (larger ones) are linked by dimers of compound 1 (smaller ones), forming a rectangular lattice. The rectangular frame in Fig. 2b marks the unit cell of the heterogeneous phase with lattice constants of 2.89 nm and 3.48 nm along two orthogonal directions. The structural model in Fig. 2c illustrates that the unit cell of this phase contains two molecules of 1, one molecule of 2 and five Cu atoms. Comparing with Fig. 1d and e, one should note the rectangular structure here is an extreme case of the boundary lines of the adjacent homogeneous phases: the phase I stripe is reduced to a column of dimers of compound 1 and the phase II stripe is reduced to a column of single molecules of compound 2. This structure is likely energetically more stable than the phase III structure shown in Fig. 1d as the lattice mismatch of the phase I and

Table 1 Compound percentages involved in the different phases depending upon the compound ratios and annealing treatments^a

[2]/[1]	[1<I]/[1], [1<III]/[1]; [2<III]/[2], [2<II]/[2]		
	2.01	1.51	0.34
300K	81%, 9%; 2%, 98%	—	90%, 10%; 15%, 85%
450K(1st)	50%, 50% 13%, 87%	46%, 54% 18%, 82%	32%, 68%; 100%, 0
450K(2nd)	41%, 59% 15%, 85%	66%, 34% 11%, 89%	—

^a Blue bars present [1<I]/[1]; green bars present [1<III]/[1]; red bars present [2<III]/[2] and black bars present [2<II]/[2]. Gray bars mean the data in these conditions are not available.

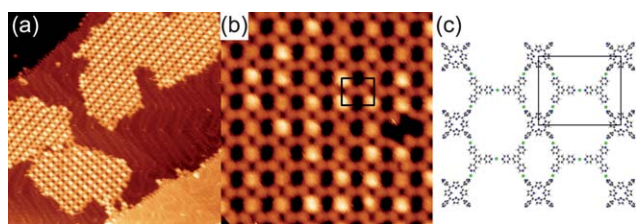


Fig. 2 (a) An overview STM image (100 nm × 100 nm) showing the enhancement of the phase III networks. (b) A high resolution image (22.8 nm × 22.8 nm) of the phase III networks. The black frame marks the unit cell. (Data acquisition conditions: (a) $U = -1.51$ V, $I = 0.31$ nA; (b) $U = -1.48$ V, $I = 0.51$ nA.) (c) The structural model of the phase III network with the unit cell highlighted by a black frame. (Colours: C: gray, N: blue, H: white, Cu: green.)

the phase II network structures introduces the excess bonding energy in the later one.

Now we discuss the mechanism of the enhancement of the heterogeneous phase. As the three phases are constructed by the same pyridyl–Cu–pyridyl coordination of comparable bonding configuration, we exclude the thermodynamic effects as the major driving force for the enhancement. Secondly, since the equilibrium had been likely reached after the second annealing, the kinetic effects can be excluded too. Some early studies suggested the effect of the void size or the component density plays a role in determining the phase self-selection behaviour of supramolecular systems.¹⁹ However, in the current system, the three phases are of comparable surface density of molecular coverage. The size of the phase III unit cell is 10.0 nm², which is exactly the same as the sum of the unit cells of the phase I (6.4 nm²) and II (3.6 nm²) structures. In a single phase III unit cell, the number of compounds **1**, **2** and Cu is 2, 1 and 5, which is equivalent to the sum of the quantities of these components in the phase I (the number of component **1** and Cu is 2 and 3) and II (the number of component **2** and Cu is 1 and 2) unit cells. So, the partition of the phase III structure into phase I and II leads to an equal total network area and equal molecular density. These facts exclude the effect of network size or the component density playing a role in the enhancement.

Note the enhancement of the heterogeneous phase is achieved when $[2]/[1]$ is 0.34 in the input molecular mixture. This value is close to the normal stoichiometry $[2]/[1]$ ratio of the phase III structure, 0.50, compared with the other two input mixtures. Hence we propose the ratio of the two compounds in the initial input molecular mixture must be close to the normal stoichiometry of the heterogeneous structure to realize the enhancement of this phase in the self-assembly. In contrast, if the compound ratio is far from the normal stoichiometry, for example, 2.01 or 1.51, the enhancement of the heterogeneous phase cannot be achieved.

In conclusion, we have demonstrated the amplification effect in a 2D supramolecular coordination self-assembly system of multiple output structures. Three structural phases co-exist from the self-assembly of a mixture of two molecular ligands and Cu. The heterogeneous phase is enhanced when the ratio of the two compounds in the input molecular mixture is close to the normal stoichiometry of this phase.

Acknowledgements

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Notes and references

† Experimental method: a Au(111) single crystal was cleaned by cycles of Ar ion sputtering and annealing at 900 K in an ultrahigh vacuum system. Cu atoms were evaporated from a Cu source by an electron-beam evaporator. After Cu deposition, compounds **1** and **2** were evaporated at 473 K and 663 K, respectively, from an organic molecular beam evaporator onto the Au(111) sample held at room temperature. Cu dosage was overdosed to avoid the possible deficiency of Cu atoms in the coordination self-assembly. All STM scanning was performed in constant-current mode at room temperature *in situ* (Omicron).

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