Construction of Azo-conjugated Metal Complex Films on Surface and Their Photo and Redox Behaviors

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We have studied the synthesis and physical properties of azo-conjugated transition metal complexes for the purpose to clarify how the photoisomerization reaction is affected by the nature of metal centers and also how the physical properties of the complexes are changed by the photoisomerization reaction. In a series of studies we have found several unique behaviors of azo-conjugated metal complexes that have not been observed in regular organic azobenzenes [1]. For example, it has been discovered that the trans/cis ratio of the azobenzene-attached bipyridine ligands in their cobalt complex is reversibly altered by a combination of photoirradiation with a single UV light source and the reversible redox change between Co(II) and Co(III) [2, 3]. On the other hand, the trans/cis ratio of 3-ferrocenylazobenzene is reversibly altered by a combination of photoirradiation with a single green light source and the reversible redox change between Fe(II) and Fe(III) [4].

In the present study, we report the fabrication of such redox-active photochromic metal complexes on the electrode surface and investigate their physical properties. The monolayer and multiplayer films of azobenzene-attached bis(terpyridine)cobalt complexes were prepared using a combination of 2,2':6',2''-terpyridine (tpy) ligand SAM formation and stepwise metal-tpy coordination reactions using Co(II) ions and azobenzene-bridged bis(terpyridine) ligands in addition with the redox reactions (Figure 1). By this method several tens of metal complex layers can be constructed, and the layer formed exhibited photoisomerization behavior in dry conditions.

Self-assembled monolayer films of a disulfide derivative of 3-ferrocenylazobenzene was facilely fabricated on gold electrode (Figure 2). We could observe photoisomerization behavior of SAMs on Au/ITO/quartz substrates under dry condition with irradiation at 365 nm (π–π^* band), whereas significant photoisomerization behavior was not detected in case of using green light.

Redox-combined isomerization of these films will be also given in this presentation.

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References

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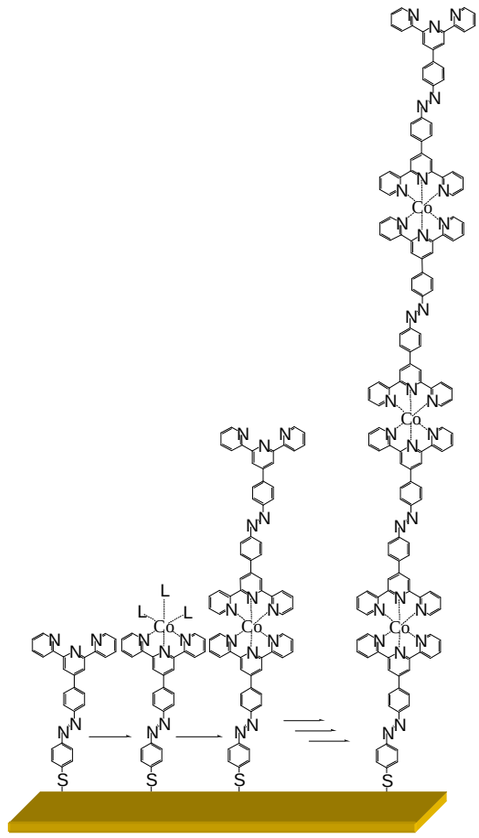

Figure 1. A fabrication method of azobenzene-bridged bis(terpyridine)cobalt comple layers.

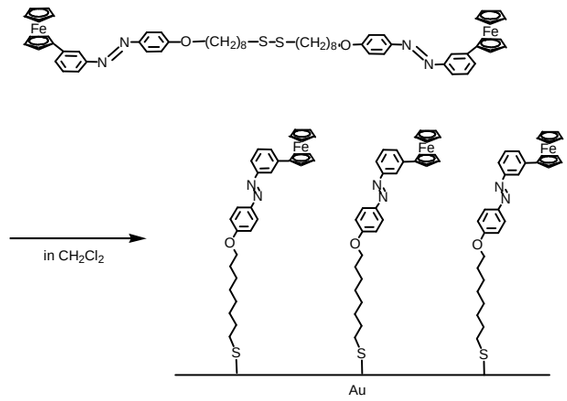

Figure 2. A fabrication method of 3-ferrocenyl-azobenzene SAMs on Au.