

A Nickel(II)-Gold(I) D-Penicillamate Coordination System with Multiple Switching in Color, Magnetism, and Chirality

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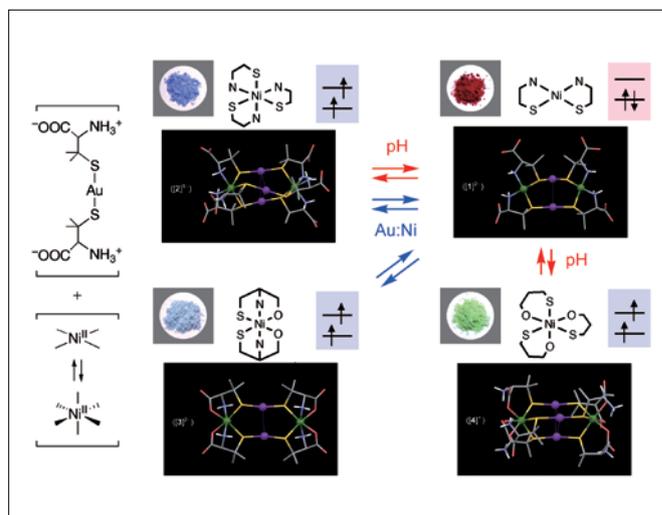
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▶ No. 24 in "100 Papers Selection" (p. 60)

The design and creation of molecular systems that show chemical and physical changes in response to external stimuli are a topic of current interest. A common approach to create such systems is to combine multifunctional organic and/or inorganic ligands with transition metal ions that adopt flexible geometrical and electronic structures. Nickel(II) ion is promising as a metal component of switching systems because it can take several coordination geometries, such as octahedron and square plane, which are convertible to each other with the concomitant changes in spin-state and color.

We found that four different polynuclear complexes ($[1]^{2-}$, $[2]^{5-}$, $[3]^{2-}$, and $[4]^+$) are chirally selected from Ni^{II} and $[Au(D-Hpen)_2]^-$ ($D-H_2pen = D$ -penicillamate) that serves as a chiral multidentate metalloligand, thanks to the flexible geometries of Ni^{II} and the versatile coordination modes of D -pen bound to Au^I . Complexes $[2]^{5-}$, $[1]^{2-}$, and $[3]^{2-}$ are interconvertible in response to the $Ni^{II} / [Au(D-pen)_2]^{3-}$ ratio, whereas $[2]^{5-}$, $[1]^{2-}$, and $[4]^+$ are interconvertible in response to solution pH. Note that $[1]^{2-}$ has square-planar, achiral Ni^{II} centers with a low-spin d^8 configuration, while $[2]^{5-}$, $[3]^{2-}$, and $[4]^+$ have octahedral, chiral Ni^{II} centers with a high-spin configuration. Thus, $[1]^{2-}$ is triply reversible with $[2]^{5-}$, $[3]^{2-}$, and $[4]^+$, accompanied not only by the readily detectable color change, but also by the drastic switches in magnetism and chirality. To our knowledge, such a multiply reversible switching system in multiple phenomena is unprecedented. The creation of other dynamic switching systems through the use of multifunctional chiral metalloligands in combination with two or more transition metal ions with manifold geometrical and electronic properties is promising.



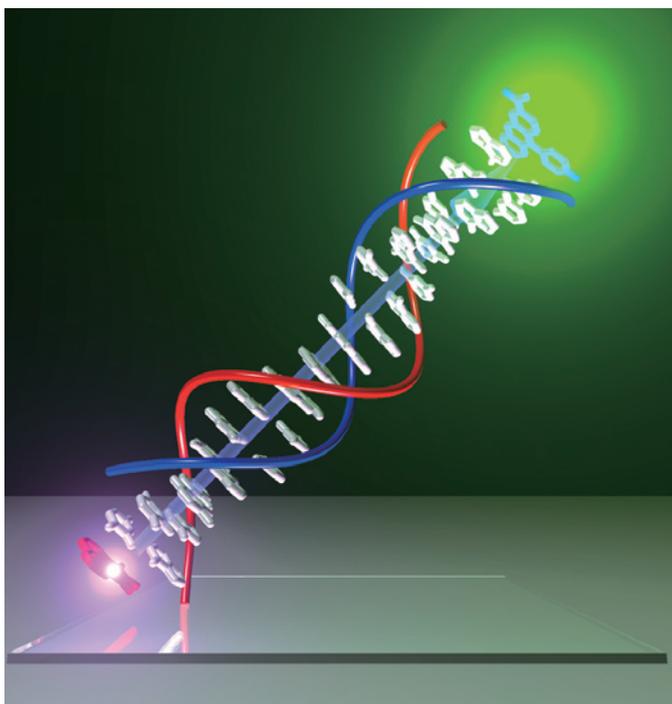
Single-Molecule Observation of DNA Charge Transfer

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Charge transfer through double helical DNA is mediated by the π -stacked array of base pairs, and highly depends upon the electronic interaction between base pairs which reflects the difference in the base composition and sequence. In order to investigate the charge transfer process of individual DNA molecules and the optical readout of DNA information at the single molecule level, we performed the single-molecule detection of DNA charge transfer process using single-molecule fluorescence spectroscopy. The charge transfer process through DNA, leading to the oxidation of the fluorescent dye, was monitored from the on-off signal change of the dye after the charge injection by the excitation of a photosensitizer. We found that a charge generated by the excitation of the photosensitizer migrates through DNA and leads to the oxidative decomposition of the fluorescent dyes, resulting in the fluorescent signal changes. The photobleaching efficiency by the DNA charge transfer specifically depended upon the base sequence, suggesting the discrimination of the individual DNA information. On the basis of this approach, the optical readout of a single-base mismatch contained in a target DNA was performed at the single molecule level. As expected, the single base mismatches strongly suppressed the photobleaching efficiency compared to the match sequence, although it depends on the position in the sequence. The mismatch effect on the photobleaching efficiency by DNA charge transfer allowed us to detect a mutation of the target DNA in the BRCA1 sequence, providing a novel method to identify the mutation and SNPs from individual DNA molecules by utilizing DNA chip technology. In addition, our approach for the single molecule detection of the DNA charge transfer can be applied to clarify the function of the DNA charge transfer on the DNA-protein complex, and would become a useful method for a better understanding of the biological consequences of the DNA charge transfer.