Title: Metal-Ion-Induced Spontaneous Formation of a Photocurrent-Generating Surface-Bound Complex in the Ninhydrin Reaction

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This study was aimed at examining the effects of metal ions on the classical ninhydrin reaction. During the process, a surface-bound species was incidentally discovered, and its structure and properties were characterized. It was hypothesized that metal–amino acid coordination would delay color development and generate a metal-containing adsorbed complex. Histidine was used as a model amino acid to evaluate the effect of zinc ions. The relationship between zinc concentration and color development time was analyzed, and adsorption behavior was examined under varying immersion conditions. The adsorbed species was evaluated using absorption spectroscopy and dissolution studies involving EDTA. Zinc coordination considerably delayed color development. In the presence of zinc, a red species spontaneously formed a stable ultrathin film (~80 nm) on glass substrates upon simple immersion for approximately 30 min, exhibiting strong adhesion. The absorption maximum of the adsorbed layer differed from that of Ruhemann's purple. After EDTA treatment, the peak shifted to coincide with Ruhemann's purple, indicating a zinc-centered coordination structure incorporating a Ruhemann's purple moiety. Following air oxidation, which decolorized the dissolved layer, reintroduction of ninhydrin regenerated the color reaction, confirming the presence of amino acid components. These results indicate that the surface-bound species corresponds to a His–Zn–Ruhemann's purple coordination complex. When incorporated into an electrochemical cell, the complex generated a photocurrent of 276 μA in a 4 cm2 cell under cloudy sunlight. These findings suggest that the complex may serve as a novel functional material, with potential applications including titanium-free dye-sensitized solar cells.