

# Layered Inorganic/Organic Photographic Composites: Novel Strategies for Delivering Active Chemistries to Photographic Media

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## Abstract

We demonstrate several synthetic design strategies for assembling layered inorganic/organic photographic composites. Design emphasis is placed upon assembling multiple functionalities into complex chemical structures. Two general design strategies employed in the authors' laboratory are demonstrated, including intercalation chemistry and organic/inorganic self-assembly. Materials prepared by the above strategies are used to develop a novel approach for sequestering and, later delivering, functional chemistry into photographic media. The approach relies upon intercalation chemistry—a reversible process whereby atoms, molecules, macromolecules, and polymers can be inserted into the interstices of a layered matrix. We demonstrate that layered materials are able to effectively sequester photographically useful molecules in aqueous and gelatin environments, and we further demonstrate that the absorbed molecules can later be released from the interlayer region to perform a desired photochemical function. We have established two general release mechanisms by which intercalated functional chemistry can be sequestered and delivered via a chemical switch. The process has significant potential as a general method for the controlled, temporal release of materials of photographic significance.

## Introduction

Modern materials chemistry is marked by a persistent evolution toward materials of greater and greater complexity and function. Examples of such efforts include the design of self-assembled materials, composite materials, nanostructured materials, and inorganic/organic hybrids.<sup>1,2</sup> Chemical methodologies for producing these materials are quickly improving. We describe novel approaches that allow these methodologies to be extended to include a silver halide/organochemistry in which the organic moiety is chosen to serve a specific photographic function, and we demonstrate the first examples of such materials. Further, we show that complex inorganic/organic hybrid materials can be prepared utilizing photographic molecules such as color developers, inhibitors, electron transfer agents, etc., as the organic sub-lattice. Last, we have identified

mechanisms whereby photographically useful molecules may be sequestered (rendered inactive) within the interlayer spaces of layered materials and later released (rendered active) via a pH switch. The goal of this research is to produce materials that possess a plurality of photographic functionalities for applications in conventional, thermal, inkjet, and other imaging modalities. As a result of their molecular nature, we hope that such materials might enable conventional and alternative imaging technologies with very fast image-access rates.

## Methods

### Self-Assembly

One method for the preparation of inorganic/organic composites utilizes the assembly of alternating inorganic and organic frameworks via coulomb stabilization. In this manner, a counter-charged organic sub-lattice stabilizes “pieces” or “slices” of an inorganic sub-lattice that has a net charge. It is possible to imagine such an arrangement in a silver halide structure, as depicted below, in which [111] slices of the silver halide lattice are stabilized by alternating layers of organic cations. This synthetic strategy relies on the identification of a suitable solvent system. Three possible systems exist for silver halide, including aqueous acid, aqueous alkali halide, and organic bases such as DMF. To date, we have chosen to work solely with aqueous mineral acids.

We show that when silver halides are reacted with amine-functionalized organic molecules in aqueous acid, a wide variety of composite silver halide/organic hybrid materials can be prepared. The structural variety and extent of this chemistry is determined largely by the size, charge, and periodicity of the organic molecules. Furthermore, we have shown that such hybrid materials can be prepared with photographically useful molecules such as developers<sup>3</sup>. An example of such material is a crystal structure  $\text{Ag}_2\text{Br}_6(\text{CD-2})_2\cdot 2\text{H}_2\text{O}$ , where Ag = yellow, Br = green, N = blue, O = red (Fig. 2), and CD-2 is a commercial color developer molecule. This structure consists of alternating layers of  $[\text{Ag}_2\text{Br}_6]^{4-}$  clusters and bi-protonated developer molecules  $[\text{CD-2}\cdot 2\text{H}^+]^{2+}$ . The ability of the developer molecule to

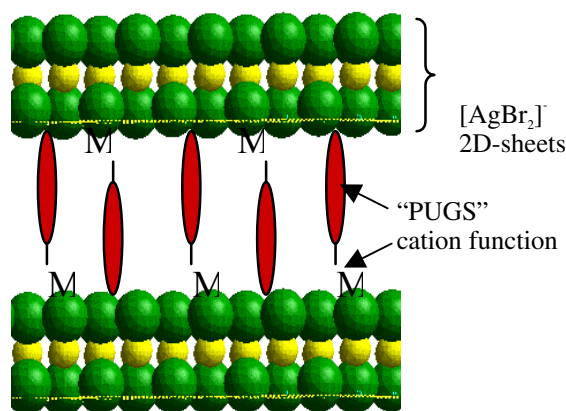
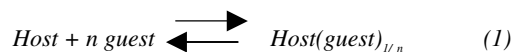


Figure 1. A hypothetical AgX-organo hybrid structure containing photographically useful groups (PUGS)

reduce silver halide is completely shut down because of the protonation of the amine functions. However, the potential of the developer may be “switched on” by a change in pH of the system. The “switch-ability” is demonstrated by the observation that gelatin suspensions of this material immediately turn black upon addition of a few drops of base and that coatings of this material with silver halide can be developed imagewise by suspension in 2.5 % aqueous NaOH, in just 5–10 seconds at room temperature.

### Intercalation Chemistry

Intercalation chemistry is the insertion of molecules or atoms into the interstices, layers, or channels of host materials with maintenance of the structural features of the host.<sup>3</sup> There are many materials capable of such chemistry including clays, metal hydrogen phosphates, layered double hydroxides, etc. Intercalation normally proceeds by one of three mechanisms: (1) ion-exchange, (2) acid/base interaction, or (3) charge transfer. The guest atoms or molecules are thus reversibly bound to the host lattice as shown in Eq. 1.



The reaction may be reversed by the introduction of an ion for which the host has a greater affinity, or in the case of acid/base interactions, by a suitable change in pH.

We take advantage of this chemistry by utilizing very active or “hot” photographic chemistry as the guest molecules of the above host intercalation compounds. The active chemistry, such as color developers, nucleators, electron transfer agents (ETAs), or silver ion, is thus sequestered by the solid host and presumably rendered inactive. When coated in film, paper, or other formulations, the guest molecules can be released via pH switch to perform a function in a particular imaging system. The

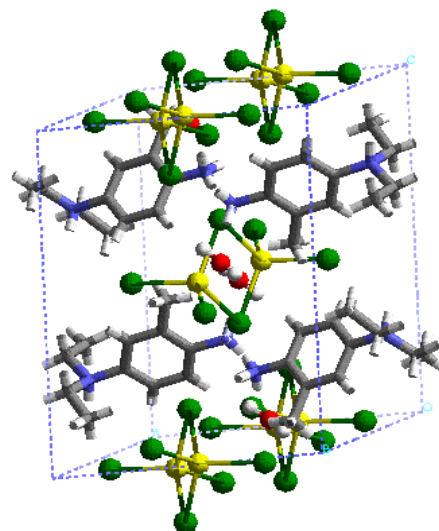


Figure 2. Crystal structure of  $\text{Ag}_2\text{Br}_6(\text{CD-2})_2 \cdot 2\text{H}_2\text{O}$  highlighting the  $[\text{Ag}_2\text{Br}_6]^{4+}$  cluster binding.

main requirements of the host lattice are that it be colorless, photographically inert, nanoparticulate in size, and relatively inexpensive. Fortunately, there are many solid hosts available that meet these requirements. Hybrid materials as represented by compounds like the structures above offer some unique opportunities for potential imaging applications. These materials provide silver and photochemistry dispersed and confined on a molecular level and, further, provide a pathway for the chemistry to be “switched on” as desired. Such materials might have applications in “fast access” film systems or dry systems in which a switch is provided by a material that thermally decomposes to release active chemistry. To further demonstrate our approach, let us examine a few specific examples.

## Results

The metal hydrogen phosphates are a class of layered compounds represented by the general structure  $\text{M}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ; where M = Ti, Sn, Zr and Ge. These materials are able to reversibly intercalate a wide variety of ions, e.g.,  $\text{Ag}^+$ , organic molecules, (such as amines, quaternary ammonium ions, amides), and others.<sup>4</sup> The structure of the host shown below consists of metal-oxygen layers sheathed on either side by  $\text{PO}_4$  tetrahedra, which are capped in the interlayer region by a proton. This proton is highly acidic and may be reversibly ion-exchanged with a variety of cations, or it is free to bind materials such as organic bases. Thus, the structure is held together by weak Van der Waals forces along the interlayer axis, which leads to the remarkable intercalation and ion exchange properties of the host. We have utilized this chemistry to demonstrate that a wide variety of photographic molecules may be reversibly ion-exchanged or intercalated into the metal hydrogen phosphates.

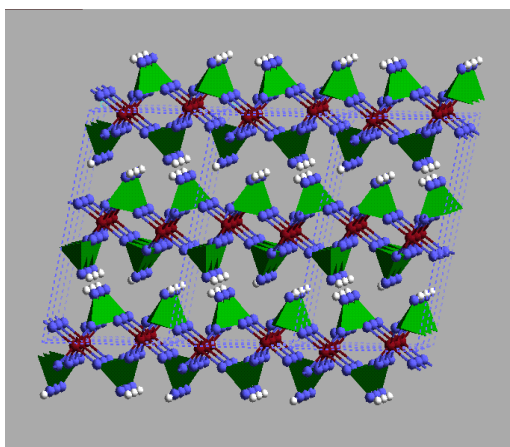
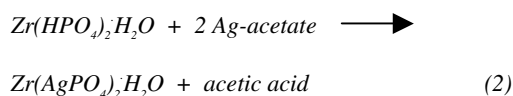


Figure 3. Crystal structure of  $Zr(HPO_4)_2 \cdot H_2O$ .

Two important questions remain regarding the ability of the previously mentioned materials to deliver chemistry to photographic and other imaging systems: (1) How well do these materials sequester? (i.e., isolate chemistry from other imaging elements in the system), and (2) How facile is the release of these materials upon a pH, or other, switch? We chose the silver ion intercalate of zirconium hydrogen phosphate, prepared according to Eq. 2, as a model system to address these questions.



We added a level series of  $Zr(AgPO_4)_2 \cdot H_2O$  to an emulsion melt containing AgBr, gelatin, surfactant and other addenda, and measured the release of  $Ag^+$  from the nanoparticulate by monitoring pAg; the results are given below.

Figure 4 shows the nominal additional silver added as  $Zr(AgPO_4)_2 \cdot H_2O$  to a AgBr photographic emulsion (diamonds) and that detected as free silver ion using a silver ion electrode (squares).

The graph indicates that, at the highest level, less than 0.2 % of the silver ion nominally added as  $Zr(AgPO_4)_2 \cdot H_2O$  is released into the melt.

A simple photographic experiment in which  $Zr(AgPO_4)_2 \cdot H_2O$  nanoparticles are coated as addenda in a sulfur-only sensitized AgBr/I T-Grain emulsion coated at 75 mg/ft<sup>2</sup>, with 300 mg/ft<sup>2</sup> gelatin and 150 mg/ft<sup>2</sup> 76FU coupler, indicates the facileness of  $Ag^+$  ion release from the host upon pH switch (i.e., development). See sensitometry below (Fig. 5). The data below indicate that  $Ag^+$  is being

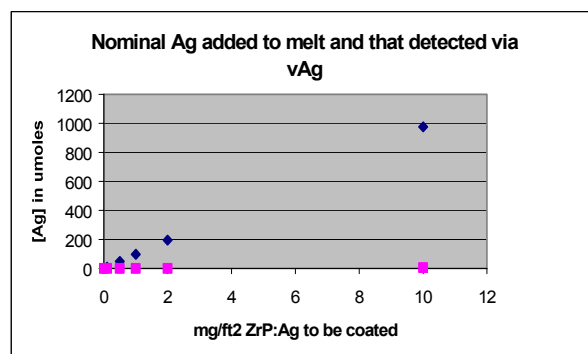


Figure 4. Nominal Ag added to a AgBr photographic emulsion (diamonds) and that detected as free silver ion via a silver ion electrode.

released to the emulsion in the timeframe of development as both speed and density are increasing. Other data, not shown, indicate that if an equivalent amount of silver ion is introduced via  $AgNO_3$ , considerable fog results in the system. These results again are consistent with the assessment that the silver ions are sequestered, reasonably well, by the host lattice.

This talk will overview our work to date, including the sequester and release of organic chemistry such as color developers into photographic systems.

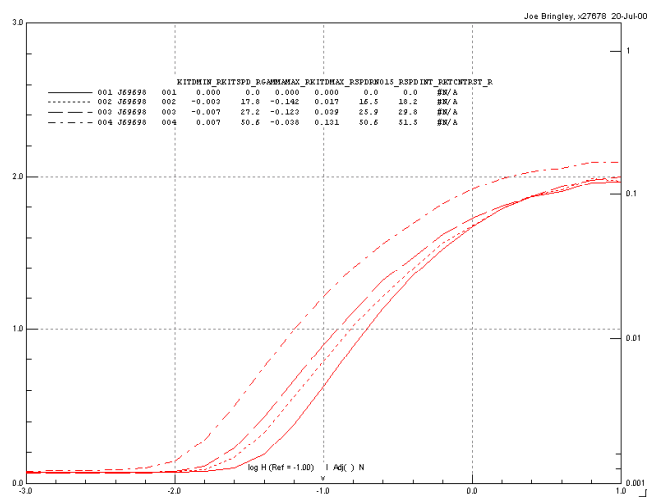


Figure 5. Sensitometry data for  $Zr(AgPO_4)_2$  coated as addenda in 75 mg/ft<sup>2</sup> of a AgBr emulsion. The solid line is the check (zero level) experiment.

## References

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## Biography

Joseph Bringley received a Ph.D. in physical chemistry from the University of Virginia in 1988. His thesis work

involved the study and synthesis of pseudo low-dimensional semiconducting materials and the preparation of high-temperature superconducting materials. Dr. Bringley was a visiting NATO scientist at the Universite de Montpellier in Montpellier, France in 1988 and was a post-doctoral fellow at the IBM Thomas J. Watson Research Laboratories from 1989-1991. He joined Eastman Kodak Company in 1991 and has since worked toward the discovery and development of new photographic and radiographic imaging materials. Dr. Bringley has published thirty-four refereed scientific papers and holds forty-four U.S. Patents.