

NEXAFS Spectroscopic Study of Organic Photographic Dyes and Their Adsorbed States on AgCl and AgBr

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The near-edge X-ray absorption fine structure (NEXAFS) spectra were studied at the S K-edge using synchrotron radiation for various sulfur-containing organic photographic materials in the solid state and in the adsorbed states on AgCl and AgBr grains. The features in the spectra of neat solids were assigned by mutual comparison and polarization dependence. The spectra of merocyanine dyes containing thiocarbonyl group were drastically affected by the adsorption on AgCl and AgBr, with significant suppression of the peak corresponding to the excitation of the S 1s electron into the π^* orbital at the S=C bond. This change is interpreted as indicative that these compounds are adsorbed at the S atom in the thiocarbonyl group, such rearrangement of the chemical bonds leading to a contribution from the zwitterionic form with $S^- - C = N^+ <$ structure. By taking account of the area occupied by a molecule estimated from the measurements of the adsorption isotherm, a rather detailed picture emerged about the adsorbed state of this kind of dye. In contrast, the spectra of merocyanine and cyanine dyes containing sulfur in the five-membered aromatic ring showed little change by the adsorption on AgCl, indicating that the S atom is not the adsorption site or that the interaction between the molecule and AgCl is weak.

Introduction

In silver halide photography, many organic materials are added to the photographic emulsions to complement the performance of silver halide grains.¹ For example, the intrinsic sensitivity of silver halides is limited to the blue and ultraviolet region, beyond the bandgap of silver halides [2.6 eV (477 nm) for AgBr and 3.0 eV (413 nm) for AgCl]. This is only a small fraction of the visible region, and even black and white photography cannot be achieved with silver halides alone. To overcome this difficulty, a submonomolecular layer amount of dyes is adsorbed on the surface of silver halide grains, leading to the extension of their sensitivity to the absorption region of the adsorbed dyes (i.e. *spectral sensitization*).^{1,2} Further, J-aggregates of dye molecules are formed on the silver halide grain surfaces in appropriate cases, making the dye absorption spectra very sharp and intense. By using these effects, the reduction of their sensitive ranges into three principal colors becomes possible. Thus the technique of both monochromatic and color photography is based on the properties of these dyes adsorbed on silver halide grains.^{1,2}

For understanding and improving the function of these materials, the elucidation of their adsorption geometry on silver halides and the resultant interfacial electronic structure are

important. These states are also interesting from the basic viewpoint of the interaction between organic and ionic materials. Techniques such as X-ray photoelectron spectroscopy (XPS) and infrared absorption spectroscopy have been applied to the study of these systems,³ but only an incomplete understanding could be accomplished.

Recently, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is fast developing into a new branch of X-ray absorption spectroscopy for various applications in chemistry.⁴ In this spectroscopy, core electrons in a molecule are excited into various vacant orbitals by the absorption of soft X-ray radiation. Since the energies of the initial core orbitals are well separated among elements, one can selectively obtain element-specific information by examining the absorption edge of respective element. The core-electron excitation is subject to strict selection rules, and the spectra of oriented samples show significant dependence on the polarization of the incident light. This is a useful guideline for reliable peak assignments. Further, the high sensitivity achieved by employing the appropriate mode of measurement⁴ enables the study of adsorbed states and ultrathin films of organic materials on solid surfaces. Thus there have been several applications of NEXAFS to the study of the solid and adsorbed states of organic photographic materials^{5–9} by using synchrotron radiation, an excellent polarized light source.

Among the elements found in organic photographic materials, sulfur is one of the most interesting. It has a high affinity to silver ions in silver halides and often forms a part of π -conjugated system in the molecule. Smith et al.^{5,6} reported an

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extensive work on the S and Cl K-edge NEXAFS for the bulk solids of organic photographic materials and related compounds. In particular, the detailed polarization studies using single crystals and the investigation of Ag salts did much to clarify the nature of the observed spectral features. We have also reported NEXAFS measurements of sulfur-containing organic photographic materials in bulk solid at the S, N, and O K-edges,⁷ with special interest in the tautomerism in the thioamide group.

One of the most important aspects of these materials is the information about their submonomolecular layer adsorbed state on silver halides. We have already discussed briefly how the spectra of some dyes containing a thiocarbonyl group were drastically changed by the adsorption on AgCl, indicating their strong interaction with AgCl at this site.^{8,9} On the other hand, Smith et al.⁶ reported preliminary observations on their adsorbed state on AgBr sheets and claimed that the spectra of the adsorbed dyes show little indication of strong interaction between the adsorbed molecules and silver halide. However, these authors did admit that the sample characterization in their work has not yet been definite, leaving open the possibility of sampling not only of the substrate/adsorbate interface but also of a multilayer region of the "adsorbate". Thus the difference between our and their results might be due to sampling conditions. Therefore it should be useful to offer a full account of our work relating to the dyes adsorbed on silver halides, including the results of subsequent studies.

In this paper, we report NEXAFS studies of dyes in the bulk and the adsorbed states on AgCl grains at the S K-edge, using well-characterized specimens. The comparison of the spectra of these states clearly demonstrates the existence of a strong interaction with silver halide for dyes containing a thiocarbonyl group. For one of these dyes, we also performed experiments on the dye/AgBr interface and obtained similar results with those for the dye/AgCl interface. From the combination of the NEXAFS studies and the study of the adsorption isotherm to silver halide, a rather detailed picture of the adsorbed state of this class of dyes has emerged. The implication of such adsorption geometry on spectral sensitization is also discussed in relation to the interfacial electronic structure obtained by UV photoelectron spectroscopy.^{9,10}

Experimental Section

Samples. Materials used explained are shown in Chart 1. They are merocyanine dyes (**1–10**), cyanine dyes (**11–14**), and a reference compound 2-mercaptobenzimidazole (MBIZ) (**15**). They were synthesized in Ashigara Research Laboratories according to the literature cited in ref 11, except for MBIZ, which was commercially purchased from Wako Chemical. The purities of these materials exceeded 99%, as assessed by elemental analysis and liquid chromatography. The NEXAFS samples for the bulk solid were prepared by rubbing their powder on Ag sheets or by vacuum evaporation on Cu sheets of 50–100 nm thicknesses.

The powder of AgCl for NEXAFS experiments was precipitated by mixing and digesting 1 N aqueous solution of silver nitrate and potassium chloride at 60 °C for 1 h and washing precipitates with water more than 10 times. The concentration of Cl[−] ion was kept higher than that of Ag⁺ during mixing. The specific surface area of the grains was determined as 0.34 m²/g by means of a Quantasorb surface area analyzer. For the preparation of the NEXAFS specimen of dyes adsorbed on these grains, a methanolic solution of the dye in question was added to an aqueous suspension of AgCl powder, which was then agitated at 45 °C for 2 h. The AgCl powder with dyes adsorbed was separated from the suspension, washed by water, and then

dried in a draft chamber. As described later, the dye adsorption is of Langmuir type, leading to saturated adsorption under this condition. The spectra of MBIZ were recorded for a single crystal of 4 × 9 × 1.5 mm³.

As for AgBr specimens in NEXAFS measurements, we prepared AgBr films with a thickness of 50 nm by vacuum evaporation on a Ag sheet. The evaporated AgBr film was immersed in a methanolic solution of merocyanine dye and washed by water in a way similar to the case of AgCl powder.

Adsorption Isotherms. Detailed studies of adsorption isotherms to cubic AgCl and AgBr grains in photographic emulsions were performed for dye **4** in order to determine the occupied area per molecule on the grain surface. The AgCl and AgBr grains (average edge lengths 0.63 and 0.73 μm, respectively) in aqueous gelatin solutions (i.e., emulsions) were prepared by a controlled double-jet method.¹² Methanolic solutions of the dye were added to the emulsions, which were then agitated at 40 °C for 20 min. With the aid of an enzyme, the grains with the dye adsorbed were separated from the phase of an aqueous gelatin solution in a centrifuge. The concentration of the dye in the solution (*c*) was derived from the absorbance of the solution determined by a recording spectrometer (Shimadzu UV-360) and used for calculating the amount of the dye adsorbed (*m*).

NEXAFS Measurements. The actual AgCl samples for the NEXAFS measurements were prepared by pressing AgCl powder with adsorbed dyes into disks.

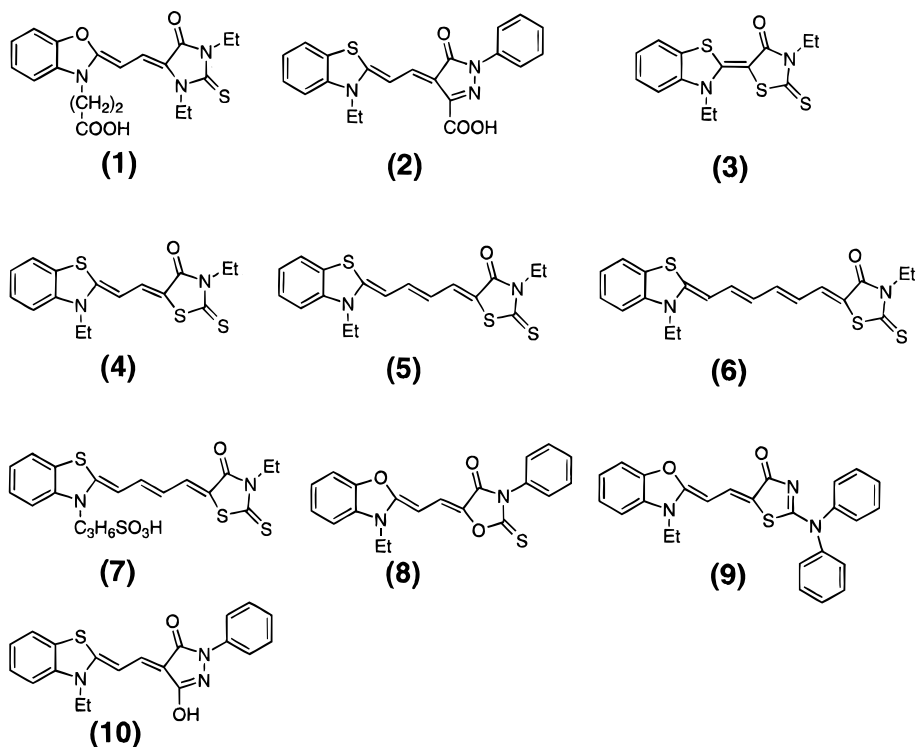
NEXAFS spectra were measured on BL-11B and 2A soft X-ray beamlines at the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) with synchrotron radiation from a bending magnet (11B)^{14,15} or an undulator (2A)^{16–18} monochromatized by a double-crystal monochromator. The resolution with an InSb(111) (BL-11B) or a Si(111) (BL-2A) crystal in the S K-edge region was about 1.0 and 0.3 eV, respectively. The spectra were measured in the photon energy region 2460–2510 eV, and the photon energy was calibrated by taking the lowest energy peak of K₂SO₄ to be at 2481.7 eV.¹⁹ The spectra in Figures 1, 3, 4(I–III) and those in Figures 2, 4(IV, V), 5 were measured at BL-11B and at BL-2A, respectively.

The spectra were measured in a vacuum chamber evacuated to 10^{−6} Pa range. The spectra of the bulk samples were measured in the total electron yield mode (TEY).⁴ The amount of emitted photoelectrons was measured as the drain current from the sample. It was amplified by a picoammeter, converted to a train of pulses by a VF converter, and counted by a counter. The incident photon intensity was measured as the drain current from a nickel or copper mesh inserted in the light path. The obtained photoemission yield as a function of photon energy is known to be a good replica of the absorption spectrum.⁴

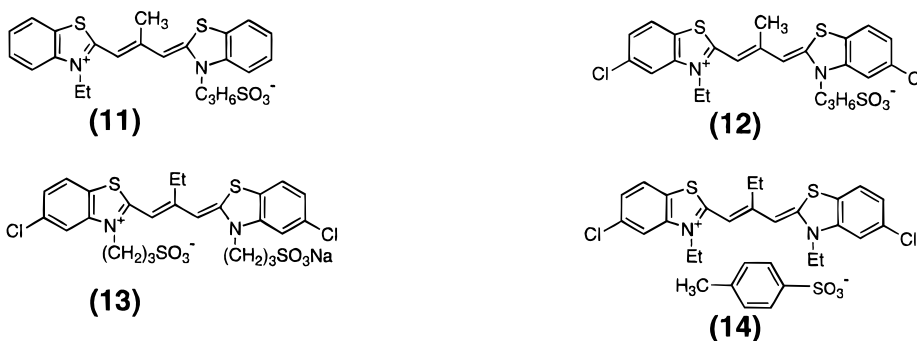
In the case of the adsorbed states, the amount of the adsorbed dye molecules per surface area is small, and only one or a few S atom(s) are contained in a large organic molecule. For overcoming this difficulty, we employed fluorescence yield detection⁴ using a UHV-compatible gas proportional counter,¹⁵ combined with the use of AgCl powder samples. Since many dye molecules on the large area of powder surfaces could be probed by virtue of the large penetrating depth of incident and fluorescence photons, we could obtain spectra with rather good signal-to-background ratio. On the other hand, we could not get spectra of good quality for AgBr powder samples, since the energy resolution of the proportional counter was not sufficiently high to distinguish between the weak S K-fluorescence from the dye and the strong Br L-fluorescence from AgBr powder.

CHART 1: Compounds Studied in This Work

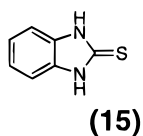
Merocyanines



Cyanines



Reference



To reduce the ratio of Br L-fluorescence to S K-fluorescence we reduced the total amount of AgBr in the specimen by using dye adsorbed on very thin evaporated film of AgBr (50 nm thick) instead of AgBr powder of thousands of nanometers size. With these samples, we could obtain spectra of reasonable quality.

One difficulty in the high-energy spectroscopy of Ag halides is the radiation damage of the sample, as observed in previous XPS experiments.³ This effect was not so severe in experiments using synchrotron radiation from a bending magnet (BL-11B), but we observed some damage when we employed intense radiation from the undulator (BL-2A). This effect could be reduced to almost negligible level by cooling the sample below 120 K with liquid nitrogen.

Results and Discussion

Spectra of Dye Solids. In the upper part of Figure 1 we show the S K-edge NEXAFS spectra of the solids of merocyanine dyes 1–7. They exhibit three characteristic spectral features, labeled A–C. The peak energies are 2470–2471 eV (peak A), 2473–2474 eV (peak B), and 2480.5 eV (peak C). The feature B consists of the main peak and a shoulder on the higher energy side. On the other hand, the sulfur atoms in these dyes can be classified by the local chemical structure into three types (see Chart 1), i.e., (i) thia type S (–S–) in the aromatic five-membered ring, (ii) thiocarbonyl type S (S=C), and (iii) sulfo type S (–SO₃H).

We first examine simple dyes containing an S atom of a single type. Dye 1 has only a thiocarbonyl S. The peaks A and B

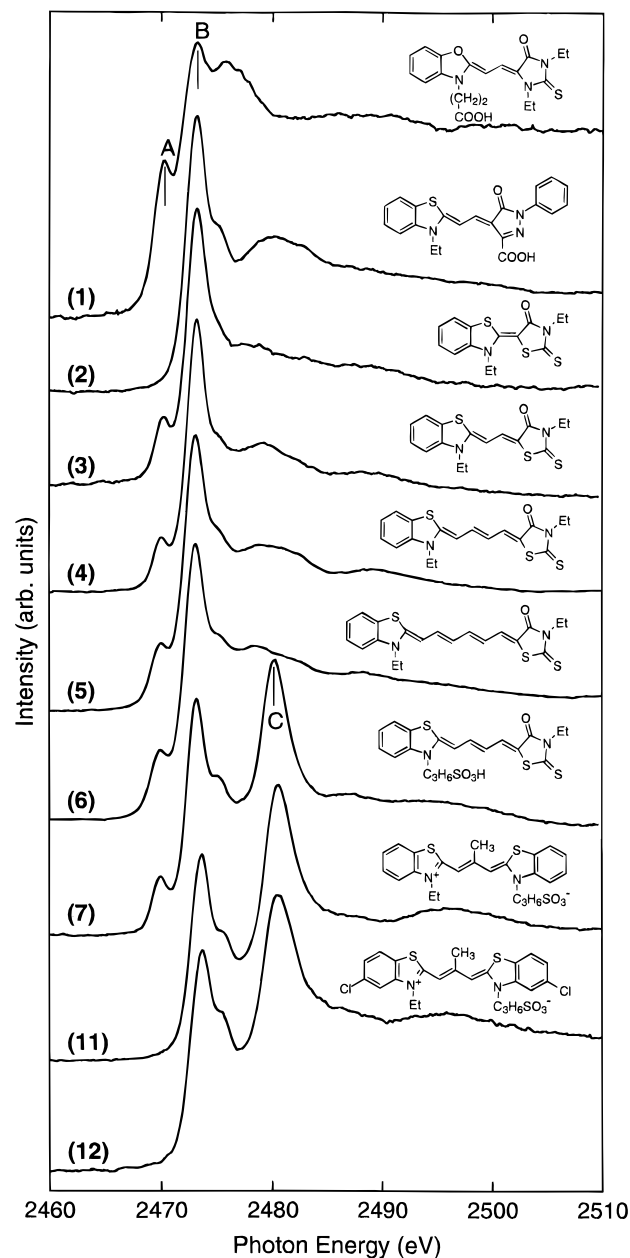


Figure 1. S K-edge NEXAFS spectra of merocyanine dyes (**1–7**) and cyanine dyes (**11** and **12**) in the solid state.

can be assigned to the transitions from S 1s to $\pi^*(S=C)$ and $\sigma^*(S-C)$ orbitals, respectively, by comparison with the results of extensive studies of thioamides.⁷ This assignment is confirmed by the polarization dependence of the peak corresponding to A in the spectra of a single crystal of MBIZ (**15**) shown in Figure 2. This peak appears strongly when the electric vector of the incident light is inclined to the molecular plane, indicating that it is a S 1s to $\pi^*(S=C)$ excitation. The assignments of the higher energy features than A and B in the spectrum of Figure 1 are not clear at present.²¹

Next we turn to dye **2**, which has only a thia type S. The lowest energy peak B should contain the transition from the S 1s orbital to the σ^* orbital localized on the S–C bond ($\sigma^*(S-C)$). Also we expect that it may contain the contribution from the excitation to the π^* orbital in the aromatic five-membered ring including the S atom. The lowest energy peak in the spectrum of thiophene, in which the sulfur atom is also included in an aromatic ring, actually consists of two excitations to $\sigma^*(S-C)$ and π^* orbitals.^{22,23} These assignments for the excita-

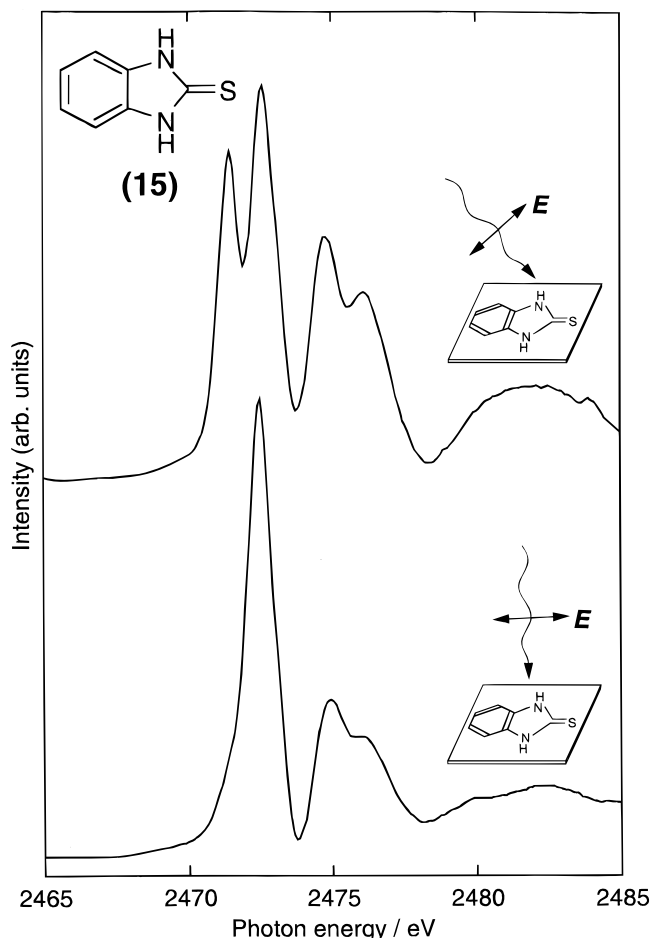


Figure 2. Polarization dependence of the NEXAFS spectra of a MBIZ (**15**) single crystal with the electric vector of the incident light nearly parallel (lower) and inclined (upper) to the molecular plane.²¹ The angle between the electric vector and the molecular plane is 2.8° (lower) and 42.2° (upper), respectively.

tions of thia and thio type S atoms also agree with those reported by Smith et al.^{5,6} for similar dyes and dye intermediates from extensive polarization measurements and the measurements of Ag salts.

Compounds **3–6** contain both thia type S and thiocarbonyl type S. Due to the local nature of core excitation, we expect that the spectra of these dyes should primarily be the overlap of the contributions from the two types of S atoms, which are similar to the spectra of dyes **1** and **2**. As a result, the intensity ratio of peak A to B is expected to be smaller for dyes **3–6** than for **1**. This is actually the case, as seen in Figure 1. There is little change among the spectra of dyes **3–6** with systematically changing the methine chain length.

The merocyanine dye **7** contains a sulfo type S atom, as well as thia type and thiocarbonyl type S atoms. Its spectrum is similar to those of **3–6** except for the intense peak C, which can be assigned to the S 1s to t_2^* excitation in the SO_3^{2-} group.²⁴ The high excitation energy is due to the bonding with the electron-withdrawing O atoms. Corresponding high-energy peaks also appear in many compounds with sulfonato and sulfonyl groups.²⁴

In the lower part of Figure 1, we also show the spectra of two cyanine dyes **11** and **12**. The peaks B and C can be similarly ascribed to the excitations at the thia and sulfonato types of S atoms, as in the case of merocyanine dyes. Although we do not show the full spectra of other merocyanine dyes **8–10** and cyanine dyes **13** and **14**, they could also be assigned in a similar way.

Spectra of Adsorbed Dyes on Silver Halides. After establishing the correspondence between the local environments of S atoms and the peaks in the spectra, we now examine the adsorbed states, with attention to the relation between the adsorption behavior of dyes and their chemical structure.

To begin with we note that there have been several experimental findings suggesting that dyes containing a thiocarbonyl type S are adsorbed to silver halides at this S atom. First, dyes containing a C=S double bond have high adsorptivity, which implies that the C=S part has a strong interaction with a silver halide.²⁴ Second, the adsorption of these dyes decreases the ionic conductivity of cubic AgBr grains in photographic emulsion. This can be interpreted as that the dye is adsorbed to the surface Ag⁺ sites, preventing the formation of interstitial Ag⁺ ions responsible for ionic conduction.²⁵ These are, however, indirect evidence, and more direct information is desired. Trials by X-ray photoelectron spectroscopy (XPS), or ESCA, have suggested the change of the spectra in the S 2s and 2p region, but severe radiation damage and charging prevented a definite conclusion.³

(i) *Adsorbed States on AgCl.* In Figure 3a, the NEXAFS spectra of two simple merocyanine dyes **1** and **2** adsorbed on AgCl are shown for comparison with the spectra of bulk solids. For dye **2**, which contains a thia type S, the spectra show almost no change on adsorption, suggesting that either the S atom is not the adsorption site or the interaction between the S atom and AgCl is weak. On the other hand, for dye **1**, which contains a thiocarbonyl type S, we see a drastic change of the NEXAFS spectrum from that of solid dye, with much decreased intensity of peak A corresponding to the $\pi^*(\text{S}=\text{C})$ resonance. This clearly demonstrates that the thiocarbonyl part is the adsorption site, leading to significant change of the chemical bonding around the S atom. A similar effect of adsorption on the NEXAFS spectrum is seen for other merocyanine dyes **8** to **10** as shown in Figure 4 (I, II, and III). The spectra of the thiocarbonyl-containing dye **8** show a change similar to that for **1**, while those of dyes containing thia type S, **9** and **10**, are little affected. Although previously in a preliminary report⁸ we stated that peak A disappears, careful examination revealed that it actually does not completely disappear, as seen from the expanded spectra of the low-energy region in Figure 3b. Later we shall discuss this point further, together with the results for the adsorbed state on AgBr.

In Figure 4(IV, V), we show the spectra of the two cyanine dyes **13** and **14** with thia type S. The spectrum of dye **13** was little affected on its adsorption to AgCl powder, indicating a state of adsorption similar to that for the merocyanines with thia type S atoms. The spectrum of the dye **14** adsorbed on AgCl is apparently different from that of the solid even for the cooled sample, with regards to the weak intensity of the peak at around 2480 eV. However, this decrease can be ascribed to the loss of the tosyl anion responsible for this peak, due to the washing treatment after the adsorption. The spectrum at the lower energy region is little affected by the adsorption. In Figure 4b, we also show the spectra of the adsorbed state for samples at room temperature (RT) (short dashed line). We see an additional shoulder (arrowed) at the lower energy side of the peak A of each compound, which demonstrates the effect of radiation damage by intense synchrotron radiation from the undulator.

(ii) *Adsorbed State on AgBr.* In Figure 5, the NEXAFS spectrum of the thiocarbonyl type merocyanine dye **1** adsorbed on AgBr evaporated film is shown in comparison with the spectrum of the bulk solid. The spectra show similar change by adsorption to that of **1** on AgCl powder, with reduction of

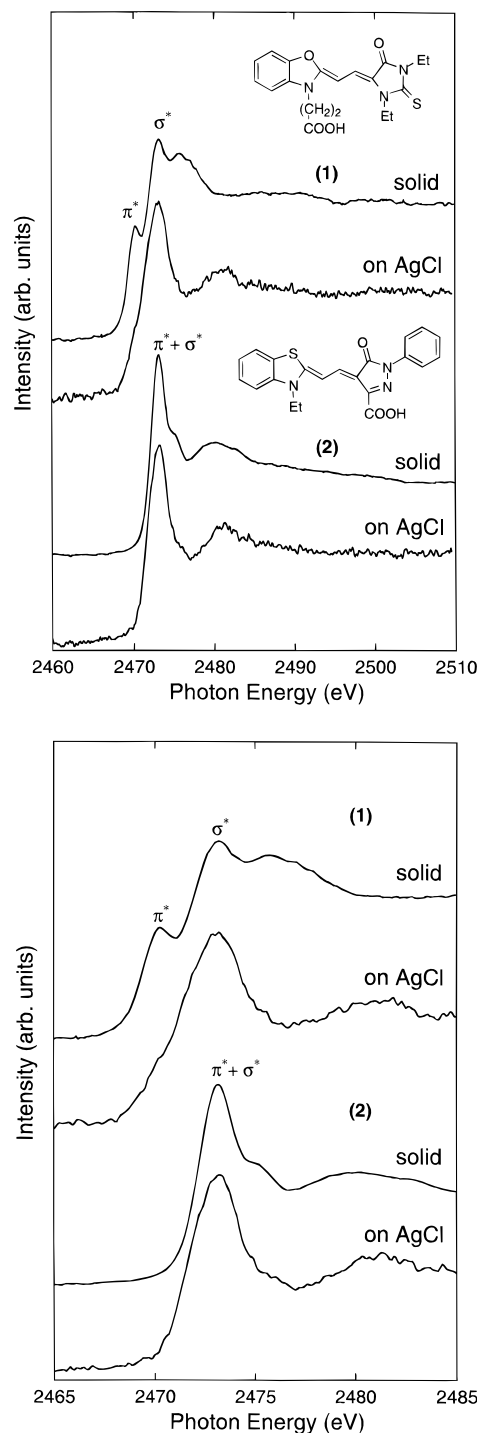


Figure 3. S K-edge NEXAFS spectra of dyes **1** and **2** in the solid state and in the adsorbed state on AgCl powder: (a) full spectra, (b) the expanded spectra of the low-energy region. The samples of the adsorbed state were cooled with liquid nitrogen for preventing the radiation damage by synchrotron radiation.

the intensity of the peak A assigned to the $\pi^*(\text{S}=\text{C})$ resonance. The feature at about 2470 eV is better resolved in these spectra than those in Figure 3 in AgCl, due to the difference in the energy resolution of the beamlines used. Still we suppose that the behavior of this dye is essentially similar for the adsorption on AgCl and AgBr.

The present results do not agree with those in ref 6 for merocyanine dye on a AgBr sheet crystal prepared by submerging it in aqueous solution. In the latter, the spectra of the dye on AgBr showed little change from that of bulk solid, suggesting either the physical nature of adsorption or the lack of participa-

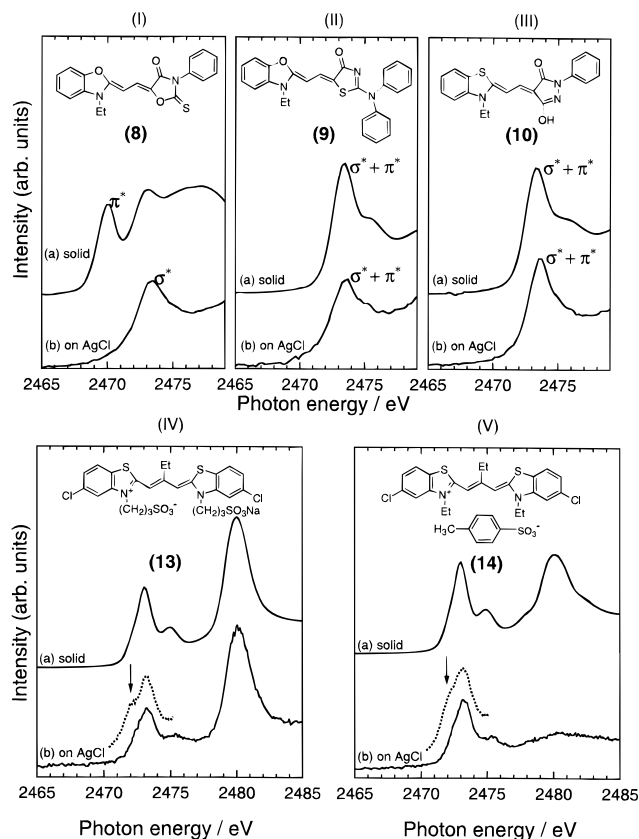


Figure 4. S K-edge NEXAFS spectra of merocyanine dyes [(I) dye 8, (II) dye 9, and (III) dye 10] and the cyanine dyes [(IV) dye 13 and (V) dye 14] in the solid state (a) and in the adsorbed state on AgCl powder (b). The samples of the adsorbed state were cooled with liquid nitrogen for preventing radiation damage by synchrotron radiation from the undulator.

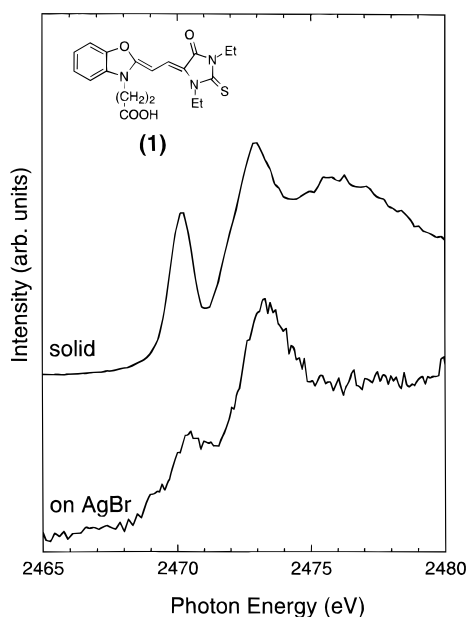


Figure 5. S K-edge NEXAFS spectra of dye 1 in the solid state and in the adsorbed state on evaporated AgBr film.

tion of the S atom in the direct molecule–AgBr bonding. However, their results are in contradiction with the observations about adsorption and ionic conduction described above. A probable origin of the difference between ref 6 and our work is the amount of dye on the Ag halide surface. As the authors of ref 6 themselves admit, it might be probable that the sampled part may be a multilayer region containing dye molecules

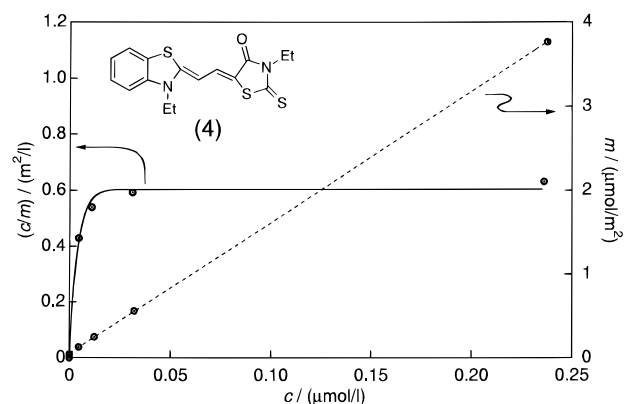


Figure 6. Adsorption isotherm of dye 4 to cubic AgCl grains with average edge length of $0.63 \mu\text{m}$ in an aqueous gelatin solution at 40°C for 20 min, where m is the (amount of the dye adsorbed)/(surface area of the grains) and c is the concentration of the dye in the solution phase (solid line). Langmuir plot of the adsorption isotherm (dashed line).

without the substrate/adsorbate interface. In our case, on the other hand, the studies of the adsorption isotherm described below showed Langmuir type behavior,¹³ which clearly demonstrates that adsorption cannot proceed beyond monolayer coverage.¹³ Therefore the amount of dye adsorbed in the NEXAFS samples presently studied for AgCl is a submonomolecular layer, which is similar to the real photographic applications. In this case, all the dye molecules were in direct contact with the AgCl surface. When multilayers of dyes are deposited on AgCl, many molecules are not in contact with the surface, and an entirely different result might come out.

Adsorption Geometry and Chemical Bonding of Thiocarbonyl Dyes. As explained above, the NEXAFS spectra of the dyes with a thiocarbonyl group point to the adsorption to AgCl and AgBr at the S atom in this group, with a large change of chemical bonding. With auxiliary information from the adsorption isotherm measurements, we can deduce more details about the adsorption geometry and chemical bonding.

In Figure 6 (solid line), the adsorption isotherm is shown for dye 4 on AgCl grains with average edge length of $0.63 \mu\text{m}$, in an emulsion at 40°C . The concentration of the dye c , the amount of dye adsorbed m , and the saturated amount of dye adsorbed M follow the Langmuir type relation

$$c/m = c/M + b \quad (1)$$

where b is a constant.

By replotting the data as a relation between c/m vs c , we obtain Figure 6 (dashed line). According to eq 1, the slope of the straight line in Figure 6 (dashed line) gives the values of M and the area/adsorbed molecule as $2.14 \mu\text{mol}/\text{m}^2$ and 77.6 \AA^2 , respectively. Similar measurements for cubic AgBr grains with average edge length of $0.73 \mu\text{m}$ in an emulsion of 40°C gave values of $2.7 \mu\text{mol}/\text{m}^2$ and 61.4 \AA^2 , respectively. The similar area/molecule for AgCl and AgBr suggests a similar way of adsorption on the two silver halides.

Although the crystal structure analysis on dye 4 by X-ray diffraction was reported,^{28–30} the details of atomic positions are not available from these references. Therefore we borrowed the structure of 3-ethyl-5-[2'-(3'-ethylbenzoxazolyldiene)ethylidene]rhodanine, in which the S atom in the benzthiazole ring of dye 4 is substituted by an O atom. The reported structure by X-ray diffraction³¹ agrees well with that of dye 4 including that the molecule is in the trans form. The structure of dye 4 deduced in this way is shown in Figure 7a. By allotting van der Waals radii to the atoms in the molecule and assuming the

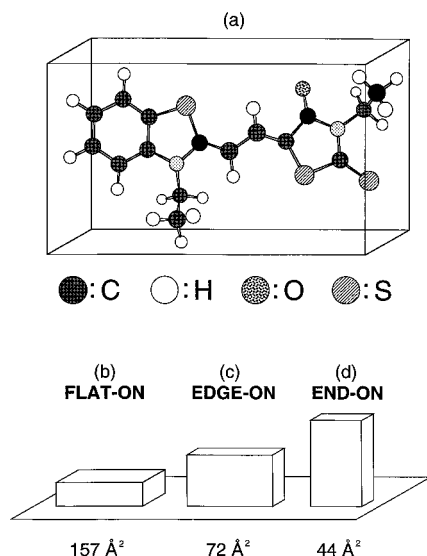


Figure 7. Molecular structure of dye **4** derived from the X-ray diffraction results³¹ (a) and the three typical adsorption orientations deduced from it: (b) flat-on, (c) edge-on, and (d) end-on. The area per molecule for each case is shown in units of Å².

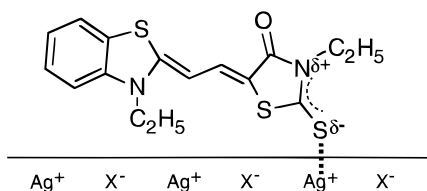


Figure 8. Estimated adsorption geometry and chemical bonding of dye **4** adsorbed on silver halide. X⁻ denotes the halide ion (Cl⁻ or Br⁻).

thickness of the dye molecule to be 4.5 Å, we can approximate the shape of the dye with a rectangular body. From such a molecular shape, we can suppose probable dye orientations on the grain surface to be flat-on, edge-on, and end-on³² and estimate the area/molecule for these orientations to be 157, 72, and 44 Å², respectively, as shown in Figures 7b–d. Thus the observed value of area/molecule is close to that expected for the edge-on geometry. By combining the information from NEXAFS and adsorption isotherm experiments, the adsorption geometry in Figure 8 can be deduced.

Reference 6 reported an independent trial for studying orientation by the polarization dependence of the S and Cl K-edge spectra of another merocyanine dye on AgBr. Although the authors deduced edge-on orientation, we again note that their sample on AgBr may not correspond to the adsorbed state with submonomolecular layer coverage.

In the NEXAFS spectra of this class of dyes in Figures 3, 4, and 5 we see the reduction of the intensity of peak A corresponding to the excitation from S 1s to the $\pi^*(C=S)$ orbital. This is indicative that the double-bond nature of the CS bond is slightly modified to that of a single bond, corresponding to the partial occupation of the π^* orbital by the intramolecular polarization of the electron cloud. Such a change can be reasonably explained when we assume the adsorption at the C=S site onto the Ag⁺ ion of silver halides. This will induce the rearrangement of the chemical bond of the S=C–N structure into a zwitterionic S⁻–C=N⁺ structure. Thus the actual chemical bonding in the adsorbed dye will be like that depicted in Figure 8, which is between these two extreme structures.

From the polarized chemical bonding in Figure 8, we expect the formation of a dipole layer at the surface of silver halides

adsorbed with thiocarbonyl dyes, with the positive charge at the vacuum side. This will lead to the lowering of the vacuum level of silver halides by dye adsorption. Actually, our study of the electronic structure of thiocarbonyl dye/AgCl and dye/AgBr interfaces by UV photoelectron spectroscopy (UPS)^{9,10} revealed a large lowering of the vacuum level on the order of 1 eV. At least some part of this lowering may be due to the oriented dipole formed by the polarized dye molecules, besides the possible contribution from the transfer of electrons from the dye molecules to silver halides and the surface reconstruction of Ag halides by adsorption.

Conclusion

In this work, we have shown that NEXAFS spectroscopy at the S K-edge can be effective in the study of the adsorption of S-containing organic photographic dyes on silver halides. In particular, carefully prepared samples of a submonomolecular layer of merocyanine dyes with a thiocarbonyl group showed drastic changes in NEXAFS spectra upon adsorption to AgCl and AgBr. The analysis of the change, together with other information, offered a rather detailed picture about the adsorption geometry and chemical bonding of the adsorbed state. In contrast, dyes containing sulfur in the aromatic five-membered ring showed little change of the NEXAFS spectra on adsorption on AgCl, indicating that the sulfur atom is not the adsorption site or that the interaction of the dye with AgCl is not so strong.

Such an assignment of the adsorption site may also be possible by XPS, but NEXAFS has advantages over XPS in that (i) NEXAFS provides direct information such as the detection of an unsaturated bond by π^* resonance, (ii) NEXAFS is free from the difficulty of energy calibration due to sample charging in XPS, and (iii) radiation damage can be smaller than in conventional XPS experiments, possibly because of the weaker photon flux in NEXAFS or the absence of sample heating by X-ray tubes close to the specimen. The last consideration is important to radiation-sensitive materials such as photographic systems.

Thus the present study has clearly demonstrated the usefulness of NEXAFS for the study of the adsorbed states of large functional organic molecules adsorbed on inorganic solid surfaces.

Moreover, direct determination of molecular orientation of dyes might become possible by measuring the polarization dependence of the NEXAFS spectra at these edges, if we can prepare dye samples adsorbed on well-defined flat surfaces (e.g. (100) or (111) surfaces) of AgX single crystals. Although the preparation of such surfaces is rather difficult, we are now making an effort in this direction.

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