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This Week's Citation Classic

Tani T & Kikuchi S. Calculation of the electronic energy levels of various photographic sensitizing and desensitizing dyes in emulsions. *Photogr. Sci. Eng.* **11**:129-44, 1967. [Inst. Industrial Science, Univ. Tokyo, Azabu-Shinyudocho, Tokyo, Japan]

In order to elucidate the mechanism of spectral sensitization in photography, electronic energy levels of various dyes adsorbed on AgBr were estimated in this paper through Hückel-approximation molecular orbital (HMO) calculation in correlation with polarographic and spectroscopic measurements of the dyes. [The *SCI*® indicates that this paper has been cited over 90 times since 1967.]

Tadaaki Tani
Research Laboratories, Ashigara
Fuji Photo Film Company
Minami-ashigara, Kanagawa 250-01
Japan

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"I was a postgraduate student in the laboratory of S. Kikuchi at the Institute of Industrial Science, University of Tokyo, from April 1963 to March 1968, and investigated, under his guidance, the mechanism of spectral sensitization in photography through electrochemical and quantum-chemical methods. In the laboratory, there was an atmosphere in which an attempt was being made to search for new direction in the field of photographic science by combining electrochemistry, photochemistry, and quantum chemistry. I was especially influenced by K. Honda's polarographic study of sensitizing dyes.

"There were two proposed mechanisms for spectral sensitization in photography: (1) electron transfer and (2) the energy transfer from excited dye molecules to silver halides.[1] Then, I considered that the determination of the electronic energy levels of various dyes with respect to those of AgBr was most important for elucidating the mechanism of spectral sensitization. I tried to do a Hückel-approximation molecular orbital (HMO) calculation of various dyes of photographic interests, and to correlate its result with those of polarographic and spectroscopic measurements of the dyes.

"The correlation of the lowest vacant electronic energy level (ε_{lv}) of those dyes with their polarographic half-wave reduction potential (E_{red}) was quite satisfactory, indicating that E_{red} and oxidation potential (E_{ox}) were correlated with ε_{lv} and the highest occupied level (ε_{ho}) of dye molecules, respectively. Those results enabled the estimation of the energy levels of those dyes adsorbed on AgBr.

"To the best of my knowledge, this paper was the first to do the HMO calculation of those dyes and to correlate its result with those of polarographic and spectroscopic measurements. This paper was also the first to give comprehensive energy levels of a wide range of dyes with sensitizing and desensitizing activities on AgBr, which were later confirmed by many groups of workers through various methods.[1]

"Plenty of knowledge on the electronic energy levels of dyes obtained from those investigations[1-3] indicated that spectral sensitization in photography principally took place by the electron transfer mechanism, and that the knowledge of the electronic energy levels of dyes was of great importance for spectral sensitization from both scientific and practical viewpoints. Presently, the measurement of E_{red} and E_{ox} and the HMO calculation are widely used to find the electronic energy levels of various dyes of photographic interests.[1]

"I was driven into the investigation, since my economic condition was such that I could not foresee my definite plan for living unless I could complete my thesis by the end of my postgraduate course.

"This paper was a main contribution to my thesis and to my receipt of the Progress Award of the Chemical Society of Japan in 1969, and also contributed to my receipt of the Journal Award in 1971 and the Fellowship Award in 1974 of the Society of Photographic Scientists and Engineers by leading to the proposal of the modified electron transfer mechanism for spectral sensitization."[2,3]

1. **West W & Gilman P B.** Spectral sensitivity and the mechanism of spectral sensitization. (James T H, ed.) *The theory of the photographic process.* New York: Macmillan, 1977. p. 251-90.
2. **Tani T, Kikuchi S & Honda K.** Modified electron transfer mechanism for spectral sensitization in photography. *Photogr. Sci. Eng.* **12**:80-9, 1968.
3. **Tani T.** Determination of electron affinity of dyes from polarogram and definition of electronegativity of dye molecules. *Photogr. Sci. Eng.* **14**:72-7, 1970.