Structure of Cyanine Dye Aggregates Observed by Scanning Tunneling Microscopy

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In solution and on a variety of substrates, the ability of spectral sensitizing dyes to form molecular aggregates with close intermolecular spacings and strong coupling is a well-known phenomenon. A given dye may form several different types of aggregates, which exhibits spectral shifts of ±100 nm from the monomer spectrum in the solution. Aggregate of dye absorbed on the surfaces of silver halide crystals is very important for spectral sensitization, so the structure of dye aggregates is attractive to photographic scientists. Extensive experimental[1—3] and theoretical[3,4] studies suggested that the basic structure of all aggregates was the same, but that in red-shifted J-aggregates, the slide angle α was small while that for the blueshifted H-aggregates approached 90°. These conclusions were obtained by indirect reasoning, to our knowledge, the actual intermolecular arrangements in these aggregates have never been observed directly.

Scanning tunneling microscopy (STM) developed in the 1980s as a new micro-technique is capable of observing individual atoms[5] or molecules[6,7]. We used CSTM 9000 (made in the Institute of Chemistry, Academia Sinica) to observe the structure of cyanine dye aggregates and obtained clear STM images with molecular resolution. We also determined the exact value of the slide angle.

Samples are a couple of thiacarbocyanine iodide. Fig. 1 shows the corresponding molecular structures of these dyes. The solution of dye (I) (in ethanol) and dye (II) (in

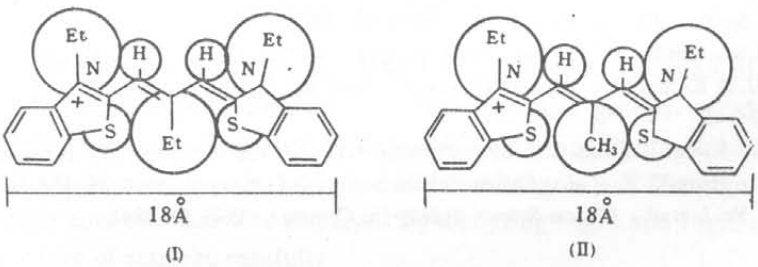

Fig. 1. Molecular structure of thiacarbocyanine iodide whose lengths are calculated from the standard bond length and bond angle.

methanol) was dropped, respectively, on the freshly stripped surface of pyrolytic graphite. After drying in the air, the samples were observed with STM.

Figs. 2 and 3 are respectively the STM images of dye (I) and dye (II). In these STM images, the white strips denote the dye molecules whose length is equal to the calculated value from the standard bond length and bond angle (about 18Å), and the width of the strip is equal to the thickness of the benzene ring (about 2.5Å). On the basis of these data we suggest that these molecules in ordered array are dye aggregates formed on the graphite surface. The slide angle α of dye (I) aggregate is 30°, while that of dye II is 50°. This is direct evidence that the mesosubstituents have influence on the structure of dye aggregates, which is in agreement with the conclusions drawn from spectroscopic[3] and X-ray[2] studies.

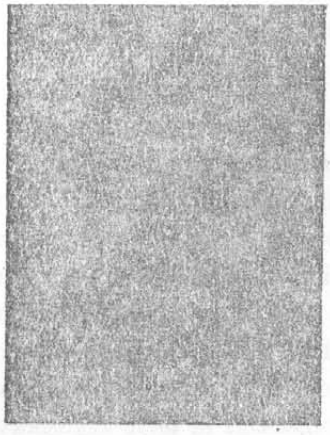

Fig. 2. STM image of dye (I) aggregate formed on the pyrolytic graphite surface. Scan area is 30 Å × 57 Å; tip bias, −16 mV; reference current, 0.72 nA.

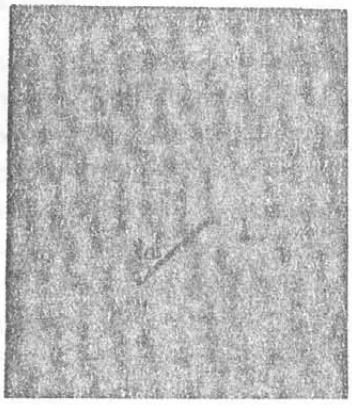

Fig. 3. STM image of dye (II) aggregate formed on the pyrolytic graphite surface. Scan area is 53 Å × 86 Å; tip bias, −15 mV; reference current, 0.66 nA.

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References

1 Steiger, R., Kitzing, R. & Junod, P., *J. Photogr. Sci.*, 1973, **21**: 107.
2 Douglas, L. Smith., *Photogr. Sci. and Eng.*, 1974, **18**: 309.
3 Emerson, E.S., Conlin, M.A., Rosenoff, A.E. *et al.*, *J. Phys. Chem.*, 1967, **71**: 2396.
4 Mcrae, E. G. & Kasha, M., *Physical Processes in Radiation Biology*, Academic Press Inc., New York, 1964, pp. 23—42.
5 Weimer, M., Krarar, J., Bai, C. & Baldeschwieler, J.D., *J. Vac. Sci. Technol.*, 1988, A6(2): 336.
6 Ruan, L.K., Heng, G.Z. *et al.*, *Chinese Science Bulletin* (in Chinese), 1990, **35**: 1649.
7 Bai, C.L., Ye, J. *et al.*, *Chinese Science Bulletin* (in Chinese), 1990, **35**: 1841.