Mesoscopic string structures of thiacyanine J aggregates in solution

Hiroshi Yao,*† Mayumi Omizo and Noboru Kitamura

Division of Chemistry, Graduate School of Science, Hokkaido University, Nishi 8, Kita 10, Kita-ku, Sapporo 060-0810, Japan

Received (in Cambridge, UK) 19th January 2000, Accepted 28th March 2000
Published on the Web 13th April 2000

Mesoscopic string structures of single 5,5′-dichloro-3,3′-disulfopropyl thiacyanine J aggregates produced in an aqueous solution were observed directly by both fluorescence microscopy and microspectroscopy.

J aggregates are specific organic dye assemblies discovered by Jelley and Scheibe,[1,2] and characterized by a narrow and intense absorption band that shows a bathochromic shift compared to the relevant monomer band.[3] On the basis of such optical characteristics, the aggregates have been often used as spectral sensitizers in photography.[4] Recent interest has also focused on the ability of J aggregates to exhibit coherent excitation phenomena which provide large optical nonlinearities.[5,6] Since the aggregate structure reflects highly on its spectroscopic properties such as the spectral line shape and peak energy, detailed investigations of the structures and/or morphologies of *single* aggregates are of primary importance. Previous studies demonstrated that a pseudoisocyanine (PIC) dye produces J aggregates at a mica/solution interface, and the single aggregate has a three-dimensional disk-like island structure in the mesoscopic size range as elucidated by tapping mode AFM (atomic force microscopy) in solution.[7,8] On the other hand, although structural and/or morphological differences are expected between the J aggregates at a solid/liquid interface and those produced in bulk solution,[9] details have been poorly understood since a real structure of the aggregates in solution have not been observed *in situ*. In this study, we report a direct observation of single thiacyanine J aggregates in an aqueous solution by both fluorescence microscopy and microspectroscopy.

Sample solutions were prepared by dissolving a 5,5′-dichloro-3,3′-disulfopropyl thiacyanine sodium salt [abbreviated as TC; chemical structure shown in the inset of Fig. 1; Nippon Kankoh-Shikiso Kenkyusho (99%)] in an aqueous NaCl (5.0 mM) solution under moderate heating (<60 °C). Fluorescence microscope images were obtained by using a CCD camera (Hitachi, Remote Eye) set on an optical microscope (Nikon, Optiphoto-2). Fluorescence spectroscopy under the microscope was conducted by using a polychromator–multichannel photodetector set (Hamamatsu Photonics, PMA-11) equipped on the microscope.[10] An Xe beam (Hamamatsu Photonics, L2273) passed through an interference filter (KL-45, Toshiba Glass) or an Ar^+ laser beam (Coherent, Innova 70) at 454.5 nm were used as the excitation sources for fluorescence imaging and spectroscopy, respectively. A sharp-cut filter (Y-47, Toshiba Glass) was mounted in front of the CCD camera–photodetector set to eliminate scattering light of the excitation beam. Measurements were performed at room temperature.

Fig. 1 shows the absorption and fluorescence spectra of TC in aqueous NaCl solutions at different concentrations ([TC] = 0.2, 0.1, 0.05 and 0.03 mM) with a set optical path length of 300 μm. When the concentration of TC is >0.05 mM, the absorption spectrum [Fig. 1(a)] showed a sharp and intense J band at *ca.* 464 nm in addition to the monomer (430 nm) and dimer bands (408 nm). The peak position and line width of the J band was constant under these concentrations, indicating that the internal structure of the J aggregate was unchanged. The fluorescence spectrum [Fig. 1(b)] does not show a Stokes shift, which is characteristic of J aggregates.[11]

In concentrated solutions, distinctive opalescence was observed. Therefore, fluorescence microscopy was conducted to examine the microstructures of the TC J aggregates. Fig. 2 shows fluorescence microscope images at [TC] $\geqslant$ 0.05 mM, above which the J band appears and mesoscopic string structures were clearly observed. Since a characteristic fluorescence image was not detected below 0.05 mM, the strings distributed in solution were considered to be J aggregates of TC. To the best of our knowledge, this is the first observation of mesoscopic J aggregates in a solution phase. The length of the string was several tens of μm while the width was very narrow; sub- or a few μm. This string structure of the J aggregate is probably due to anisotropic interactions between TC molecules in solution (*i.e.* quasi-one-dimensional stacking interactions), different from that of PIC J aggregates observed at a solid/liquid interface.[7,8] A single string is likely to bend in an arc form, suggesting that the mesoscopic J aggregate is flexible and polycrystalline-like. The fluorescence images also show that morphologies of the aggregates were dependent on the TC concentration. With a decrease in the concentration, the density of the string decreased while the length of the aggregate was slightly increased. The results are probably due to lower supersaturation at a low concentration which leads to generation of fewer nuclei, and the string would grow to a larger size; *cf.* microcrystallite formation processes. It is worth noting, furthermore, tha single J aggregates could be optically trapped by

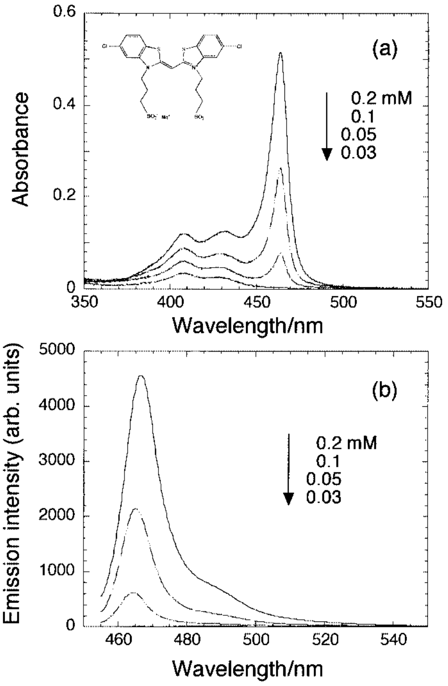

Fig. 1 Absorption (a) and fluorescence (b) spectra of TC in an aqueous NaCl solution ([NaCl] = 5 mM): optical path length = 300 μm.

---

† Present address: Department of Material Science, Faculty of Science, Himeji Institute of Technology, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan. E-mail: yao@sci.himeji-tech.ac.jp

DOI: 10.1039/b000548g

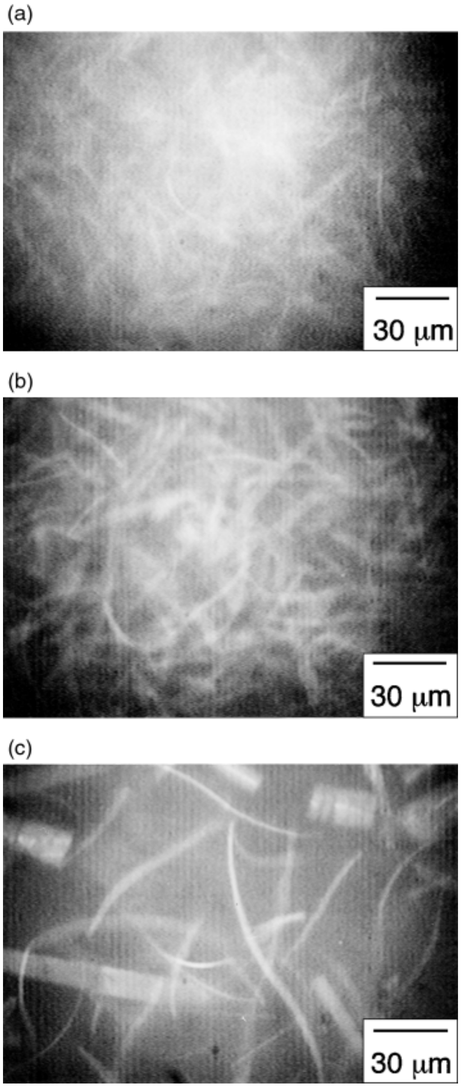

Fig. 2 Fluorescence microscope images of the TC J aggregates in aqueous NaCl solutions. (a), (b) and (c) show images at [TC] = 0.2, 0.1 and 0.05 mM, respectively. The mesoscopic strings correspond to the TC J aggregates.

a focused laser beam at 1064 nm (optical tweezers) and details will be described elsewhere.[12]

Fig. 3 shows fluorescence spectra observed for a single string and at the periphery of the string {[TC] = 0.05 mM, corresponding to Fig. 2(c)}. The excitation beam diameter was *ca.* 10 μm, and the measurements were conducted at various positions in the string. However, the spectral band shape did not change with the observation position in the string. Since the spectrum was quite similar to that in Fig. 1(b), the strings seen in Fig. 2 were concluded to be TC J aggregates.[13] It is noteworthy that fluorescence was scarcely observed at the outer periphery of the strings, indicating that TC in an aqueous solution produces exclusively mesoscopic-size J aggregates.

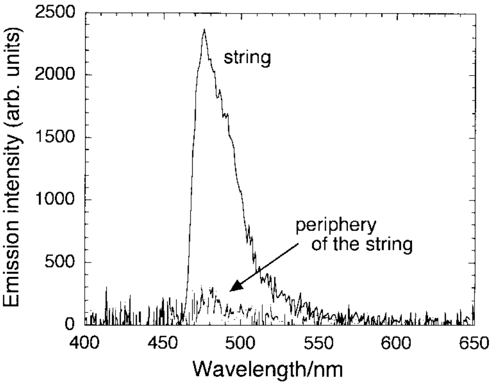

Fig. 3 Fluorescence spectra observed for a *single* string of TC J aggregates and at the periphery of the string: concentration of TC = 0.05 mM.

Recently, the structures of TC J aggregates with different counter cations in solution have been studied by synchrotron XRD and NMR spectroscopy by Tiddy *et al.*[14,15] The results suggested that the J aggregates involve thousands of molecules, which generate a liquid-crystalline lamellar phase composed of ordered dyes and water layers in an aqueous solution. If similar morphologies are also expected in our system, the observed single string could show a lamellar phase, and the water content could be more than *ca.* 95%, which would probably be the origin of the flexibility of the aggregates. Thus, detailed microstructures of the J aggregates are worth studying by various local sensing tools such as AFM and SNOM (scanning near-field optical microscopy), and work along such lines is now in progress.

Notes and references

1 E. E. Jelley, *Nature*, 1936, **138**, 1009; 1937, **139**, 631.
2 G. Scheibe, *Angew. Chem.*, 1936, **49**, 563; 1937, **50**, 212.
3 K. Norland, A. Ames and T. Taylor, *Photogr. Sci. Eng.*, 1970, **14**, 296.
4 A. H. Herz, *The Theory of the Photographic Process*, ed. T. H. James, Macmillan, New York, 4th edn., 1977, ch. 10.
5 E. Hanamura, *Phys. Rev. B*, 1988, **37**, 1273.
6 F. C. Spano, J. R. Kuklinski and S. Mukamel, *J. Chem. Phys.*, 1991, **94**, 7534.
7 H. Yao, S. Sugiyama, R. Kawabata, H. Ikeda, O. Matsuoka, S. Yamamoto and N. Kitamura, *J. Phys. Chem. B*, 1999, **103**, 4452.
8 S. S. Ono, H. Yao, O. Matsuoka, R. Kawabata, N. Kitamura and S. Yamamoto, *J. Phys. Chem. B*, 1999, **103**, 6909.
9 V. Czikkely, H. D. Försertling and H. Kuhn, *Chem. Phys. Lett.*, 1970, **6**, 11.
10 H. Yao, H. Ikeda and N. Kitamura, *Langmuir*, 1997, **13**, 1996.
11 A slight red-shift of the fluorescence peak wavelength of the J aggregate was observed depending on the TC concentration. The result is due to re-absorption effects of the fluorescence.
12 H. Yao, M. Omizo and N. Kitamura, to be submitted.
13 Since a Y-47 filter was mounted in front of the photodetector set, the fluorescence spectrum in the shorter wavelength region was somewhat distorted.
14 G. J. T. Tiddy, D. L. Mateer, A. P. Ormerod, W. J. Harrison and D. J. Edwards, *Langmuir*, 1995, **11**, 390.
15 W. J. Harrison, D. L. Mateer and G. J. T. Tiddy, *J. Phys. Chem.*, 1996, **100**, 2310.