

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/252155971>

# Controllable assembly and cycling conversion of various supramolecular aggregates of a cyanine dye

ARTICLE in APPLIED PHYSICS LETTERS · JANUARY 2011

Impact Factor: 3.3 · DOI: 10.1063/1.3535980

CITATIONS

7

READS

20

## 8 AUTHORS, INCLUDING:



**Hongxia Sun**

Chinese Academy of Sciences

33 PUBLICATIONS 286 CITATIONS

SEE PROFILE



**Jun-Feng Xiang**

Chinese Academy of Sciences

185 PUBLICATIONS 2,873 CITATIONS

SEE PROFILE



**Qianfan Yang**

Chinese Academy of Sciences

34 PUBLICATIONS 335 CITATIONS

SEE PROFILE



**Qiuju Zhou**

Université de Mons

21 PUBLICATIONS 285 CITATIONS

SEE PROFILE

## Controllable assembly and cycling conversion of various supramolecular aggregates of a cyanine dye

Hongxia Sun, Junfeng Xiang, Qianfan Yang, Qian Shang, Qiuju Zhou et al.

Citation: *Appl. Phys. Lett.* **98**, 031103 (2011); doi: 10.1063/1.3535980

View online: <http://dx.doi.org/10.1063/1.3535980>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v98/i3>

Published by the AIP Publishing LLC.

---

### Additional information on Appl. Phys. Lett.

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT



**MATERIAL SCIENCE RESEARCH  
AT 3K – MADE SIMPLE**

**MONTANA INSTRUMENTS**  
COLD SCIENCE MADE SIMPLE

**CLOSED CYCLE OPTICAL CRYOSTATS**

# Controllable assembly and cycling conversion of various supramolecular aggregates of a cyanine dye

Hongxia Sun, Junfeng Xiang, Qianfan Yang, Qian Shang, Qiuju Zhou, Yanxia Zhang, Guangzhi Xu, and Yalin Tang<sup>a)</sup>

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

(Received 1 November 2010; accepted 16 December 2010; published online 19 January 2011)

Constructing dye supramolecular aggregates and regulating their structures have been very important tasks in recent years due to their excellent properties and promising applications in many fields. In this paper, four kinds of aggregates have been constructed by using a cyanine dye under controllable conditions, and a simple method to realize a cycling conversion around these aggregates has been developed. To construct and regulate these aggregates were easily manipulated and identified, and could be directly observed with unaided eye. © 2011 American Institute of Physics. [doi:10.1063/1.3535980]

The supramolecular aggregates of cyanine dye have been given particular attention in recent years due to the excellent properties that their corresponding monomers do not show.<sup>1,2</sup> Countless devices have been proposed utilizing the unique properties of cyanine dye aggregates, for example the light harvesting systems for solar<sup>3</sup> and sensor devices,<sup>4</sup> electron or energy acceptors for excited donors,<sup>5</sup> components for nonlinear optics,<sup>6</sup> cavity quantum electrodynamics (QED) devices,<sup>7</sup> fast optical recording systems,<sup>8</sup> and storage of photoelectrons in silver nanoparticles.<sup>9</sup> One important issue to realize these applications is how to prepare a stable dye aggregate and regulate its aggregated structure.

Numerous methods to assemble dye aggregates have been described hitherto, with the most commonly used being the Langmuir–Blodgett technique<sup>10</sup> or the use of polymers,<sup>11</sup> nanocapsules,<sup>12</sup> and polyelectrolytes.<sup>13</sup> In addition, the matrices mainly used to form aggregate were the inorganic surfaces such as silver halide<sup>2,14,15</sup> or semiconductor surfaces.<sup>16</sup> However, the method to construct several different aggregates of a dye and achieve a cycling conversion among them have not been reported. In this work, we developed a simple method to construct four kinds of aggregates of a cyanine dye, 3,3'-di(3-sulfopropyl)-4,5,4',5'-dibenzo-9-methylthiacarbocyanine triethylammonium salt [MTC, Fig. 1(a)] and realize a cycling switch among these aggregates. One more interesting phenomenon worth noting was that the formation and conversion of these aggregates not only could be easily identified with observing their absorption spectra [Fig. 1(b)] but also could be directly judged with naked eye due to the different color for each aggregate [Fig. 1(c)], which could be useful for facilitating their application as chemical sensors.

The dye aggregate was formed due to the interaction of short-range noncovalent forces, such as van der Waals or  $\pi$ - $\pi$  stacking interaction among the dye molecules.<sup>17</sup> The formation of the aggregates would arouse a strong redshifted or blueshifted effect on the electronic absorption spectra of dye solutions. Based on the absorption spectra, the aggregate whose absorption band is redshifted with respect to that of the monomer is named J-aggregate, while the one with blue-

shift is termed H-aggregate.<sup>18,19</sup> The aggregates were relatively sensitive to the environmental conditions, especially the medium composition.<sup>20,21</sup> Based on this factor, the construction and regulation of MTC aggregates were respectively performed under two conditions: in tris-HCl buffer solution without and with  $K^+$ .

MTC in methanol mainly existed in the form of monomer, whose absorption band was located at 573 nm (see Fig.

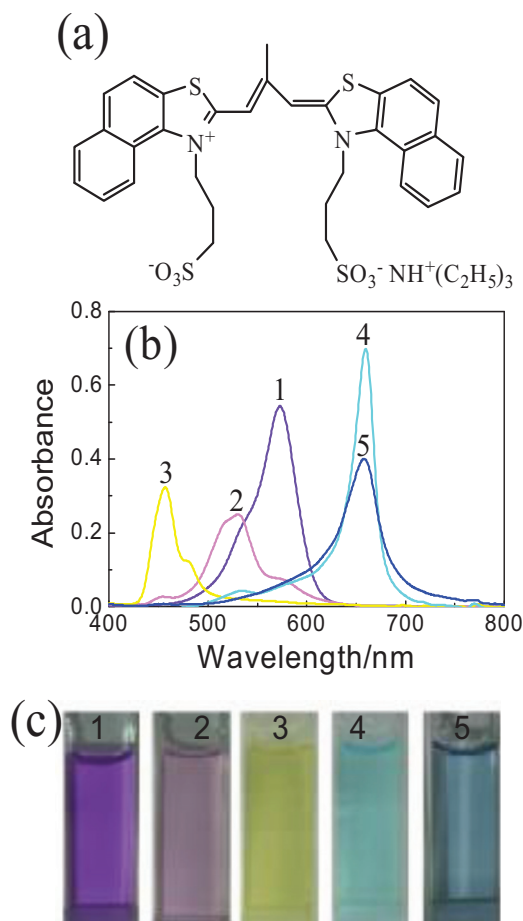


FIG. 1. (Color) (a) The molecular structure of MTC, (b) the absorption spectra of 5  $\mu$ M MTC in different states: (1) monomers, (2) H1-aggregates, (3) H2-aggregates, (4) J1-aggregates, and (5) J2-aggregates, and (c) the sample colors corresponding to above monomer and aggregates.

<sup>a)</sup>Electronic mail: tangyl@iccas.ac.cn.

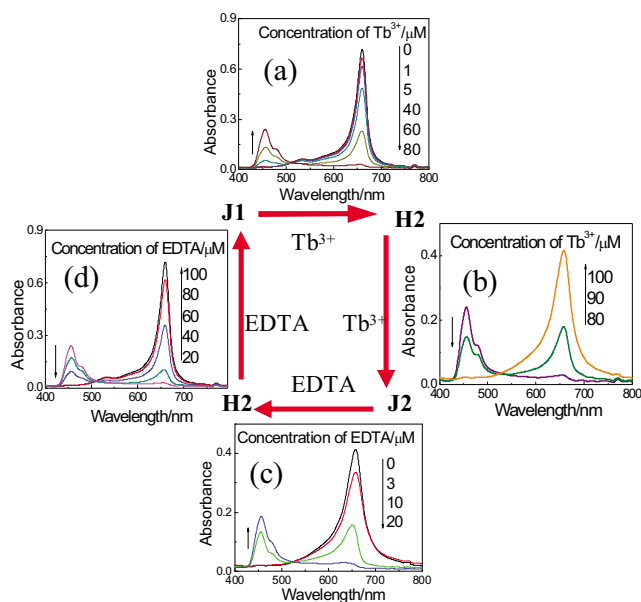


FIG. 2. (Color online) The schematic illustration of the cycling transition from J1-aggregate to reverted J1-aggregate of 5  $\mu\text{M}$  MTC with the presence of 15 mM KCl in tris-HCl buffer (pH 7.0). The conversions of MTC aggregate from J1 to H2, H2 to J2, J2 to H2, and H2 to J1 with increasing amount of  $\text{Tb}^{3+}$  or EDTA were orderly exhibited in the absorption spectra a-d.

S1 in Ref. 22). In tris-HCl buffer solution without  $\text{K}^+$ , MTC formed an H-aggregate (H1-aggregate) with a broad absorption band at 525 nm (see Fig. S1 in Ref. 22). Adding terbium ions in, the absorption band of the H1-aggregate disappeared and a relatively narrow absorption band appeared at 455 nm [see Fig. S2(a) in Ref. 22], meaning another H-aggregate (H2-aggregate) formation. The H2-aggregate could be further converted to a J-aggregate (J2-aggregate) with the absorption band greatly redshifted to 650 nm [see Fig. S2(b) in Ref. 22] by adding more  $\text{Tb}^{3+}$ . All these results indicated that MTC assembling in the absence of  $\text{K}^+$  could realize the conversion from H1-aggregate to H2-aggregate and J2-aggregate by adding terbium ions.

In tris-HCl buffer solution containing  $\text{K}^+$ , MTC formed another J-aggregate (J1-aggregate), which also showed an absorption band at 650 nm (see Fig. S3 in Ref. 22). It could be observed that the color of the J1-aggregate was different from that of the J2-aggregate. Comparing the absorption spectra of J1- and J2-aggregates, we found they had different spectral shapes and half widths, and the half width of the J-band in the presence of  $\text{Tb}^{3+}$  was about twice [see Fig. S2(b) in Ref. 22] as that with  $\text{K}^+$  (see Fig. S3 in Ref. 22). Moreover, the J2-aggregate of MTC- $\text{Tb}^{3+}$  shows an additional shoulder at  $\sim 560$  nm probably due to the absorbance of the residual monomers. These different phenomena may be the reason for the different colors of the J1- and J2-aggregates [Fig. 1(b)].

The J1-aggregate was converted to H2-aggregate and J2-aggregate by adding  $\text{Tb}^{3+}$  [Figs. 2(a) and 2(b)]. Moreover, the H2-aggregate and J1-aggregate (reverted J1-aggregate) [Figs. 2(c) and 2(d)] could be orderly reconstructed from the J2-aggregate by adding ethylene diamine tetraacetic acid (EDTA), an excellent ligand to terbium ions and other rare earth elements.<sup>23,24</sup> Comparing the absorption spectra of the two J1-aggregates [Figs. 2(a) and 2(d)] and two H2-aggregates [Figs. 2(b) and 2(c)] respectively in this system,

TABLE I. The particle sizes obtained using DLS for kinds of aggregates in freshly prepared solution at room temperature.

Aggregate	Z-average (nm)	Peak 1 diameter (nm)	Peak 2 diameter (nm)	PDI
H1-aggregate	735.6	395.0	121.6	0.792
H2-aggregate	177.1	183.4	...	0.350
J1-aggregate	203.5	273.9	...	0.341
J2-aggregate	3371	1532	5386	0.482
Reverted J1-aggregate	201.6	509.4	...	0.425

we could find that they are completely identical, probably the H2- and the J1-aggregate reconstructed by adding EDTA being similar to the original H2- and J1-aggregate. One more interesting phenomenon could also support this conclusion: the molar ratio between EDTA and  $\text{Tb}^{3+}$  in the whole system was just 1:1 (both of them were 100  $\mu\text{M}$ ), meaning all the  $\text{Tb}^{3+}$  has been chelated and isolated from the aggregates and thus facilitated the reversion of J1-aggregate. Besides, the concentration of EDTA needed to finish the switch from J2-aggregate to H2-aggregate was 20  $\mu\text{M}$ , and thus the  $\text{Tb}^{3+}$  concentration subtracting that has been chelated by EDTA should be 80  $\mu\text{M}$ , identical to the amount needed to complete the conversion from J1-aggregate to H2-aggregate, indicating both of the two H2-aggregates existed in the similar  $\text{Tb}^{3+}$  conditions, thus they probably were also similar in conformation.

The sample solution was also measured by dynamic light scattering (DLS) method<sup>25,26</sup> to obtain the size distribution of these aggregates and further confirm the recovery of these aggregates in this cycling system. Table I summarized the size information for each aggregate including Z-average diameter, major peak diameter, and polydispersity index (PDI). The PDI value reflected the polydispersity of these aggregates. Among these aggregates, H1-aggregate and J2-aggregate had a much higher PDI value than other aggregates indicating their larger polydispersity, which was in accordance with the appearance of their two bands (see Fig. S4 in Ref. 22). Z-average diameter was used to estimate the size of each aggregate. J2-aggregate had a maximal Z-average, 3.37  $\mu\text{M}$ , and the Z-average value for the other aggregates was not more than 1  $\mu\text{M}$ . In fact, the size for these aggregates except for J2-aggregate was mainly concentrated in the range of 200–500 nm according to the peak diameter. The size of the reverted J1-aggregate was much smaller than that of J2-aggregate and was close to that of J1-aggregate, which strongly supported the recovery of J1-aggregate in the cycling system.

Due to the nonfluorescence of H-aggregates,<sup>27</sup> the sample solutions containing J-aggregates were further measured by laser confocal scanning microscopy (LCSM) [Figs. 3(a)–3(d)]. The wavelength of 559 nm was used to excite the MTC dyes. All the samples containing aggregates exhibited elliptic or rounded spots. These spots should be attributed to the aggregates because the MTC monomer solution sample showed no obvious graphic character. Moreover, J1- and J2-aggregate solutions also exhibited images when excited at 635 nm (see Fig. S5 in Ref. 22), further supporting this conclusion because the MTC monomer had no fluorescence when excited at this wavelength (see Fig. S6 in Ref. 22). The images of these aggregates exhibited scattered spots with



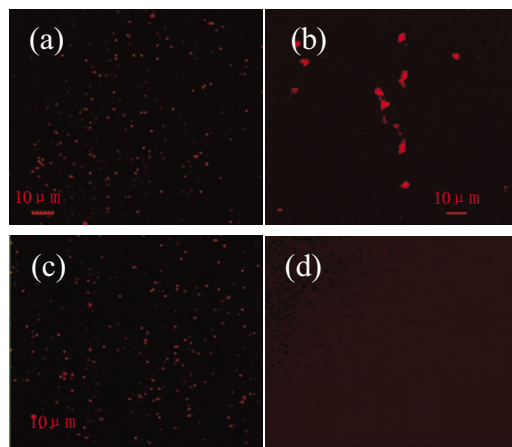


FIG. 3. (Color online) The LCSM images of (a) J1-aggregate, (b) J2-aggregate, (c) reverted J1-aggregate, and (d) MTC monomer excited at 559 nm.

uniform size, and the spot sizes of J2-aggregate were much bigger than that of the J1-aggregate and the reverted J1-aggregate, while the J1-aggregate had the similar spot size with that of the reverted J1-aggregate, which was consistent with the results of DLS. Moreover, the fact that the images for J1-aggregate and reverted J1-aggregate were similar also supported the recovery of J1-aggregate in this cycling system.

The mechanism of salt-induced J-aggregation of cyanine dyes is the replacement of the organic cation of a cyanine dye by the metal ion of the added inorganic salt.<sup>28</sup> This mechanism can be also applied to MTC J-aggregation induced by  $K^+$ . In NMR spectra, the addition of KCl caused the  $CH_3$  and  $CH_2$  signals of MTC exhibiting highly resolved triplet and quartet patterns, suggesting that  $K^+$  has penetrated into the aggregates and replaced the triethylammonium ions (see Fig. S7 in Ref. 22).<sup>29,30</sup> The further transition of the J-aggregate induced by  $Tb^{3+}$  probably was due to the replacement of  $K^+$  by  $Tb^{3+}$ , which is a more efficient coordinated ion with dye molecules than  $K^+$ .<sup>31,32</sup>

In summary, two kinds of H- and J-aggregates of a cyanine dye MTC have been fabricated under different conditions. Multiple transitions between H1 and H2, H1 and J1, J1 and H2, H2 and J2 aggregates as well as a cycling transition around J1, H2, and J2 aggregates have been achieved by adding  $K^+$ ,  $Tb^{3+}$ , and EDTA. The features of these supramolecular aggregates have further been characterized through DLS and LCSM methods. The absorption spectra of the MTC monomers and different aggregates were greatly sensitive to their transition, and the color of MTC was also changed with every transition, which endows the MTC and its aggregates great advantages in optical application such as molecular probe. Recently, we have made great progress in recognizing some specific DNA and protein structures by the cyanine dye aggregates.<sup>33–36</sup> The excellent properties of these aggregates would encourage us to further investigate their aggregation mechanism and application as molecular probe.

- <sup>1</sup>H. Kashida, H. Asanuma, and M. Komiyama, *Angew. Chem., Int. Ed.* **43**, 6522 (2004).
- <sup>2</sup>B. J. Walker, G. P. Nair, L. F. Marshall, V. Bulovi, and M. G. Bawendi, *J. Am. Chem. Soc.* **131**, 9624 (2009).
- <sup>3</sup>W. Yang, F. Wan, Y. Wang, and C. Jiang, *Appl. Phys. Lett.* **95**, 133121 (2009).
- <sup>4</sup>R. M. Jones, L. Lu, R. Helgeson, T. S. Bergstedt, D. W. McBranch, and D. G. Whitten, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 14769 (2001).
- <sup>5</sup>F. Meng, K. Chen, H. Tian, L. Zuppiroli, and F. Nuesch, *Appl. Phys. Lett.* **82**, 3788 (2003).
- <sup>6</sup>F. Würthner, S. Yao, T. Debaerdemaeker, and R. Wortmann, *J. Am. Chem. Soc.* **124**, 9431 (2002).
- <sup>7</sup>J. R. Tischler, M. S. Bradley, V. Bulovic, J. H. Song, and A. Nurmikko, *Phys. Rev. Lett.* **95**, 036401 (2005).
- <sup>8</sup>A. Naber, U. C. Fischer, S. Kirchner, T. Dziomba, G. Kollar, L. F. Chi, and H. Fuchs, *J. Phys. Chem. B* **103**, 2709 (1999).
- <sup>9</sup>J. Hranisavljevic, N. M. Dimitrijevic, G. A. Wurtz, and G. P. Wiederrecht, *J. Am. Chem. Soc.* **124**, 4536 (2002).
- <sup>10</sup>Y. Hirano, A. Maio, and Y. Ozaki, *Langmuir* **24**, 3317 (2008).
- <sup>11</sup>J. Zhang and J. R. Lakowicz, *J. Phys. Chem. B* **109**, 8701 (2005).
- <sup>12</sup>C. S. Peyratout, H. Möhwald, and L. Dähne, *Adv. Mater.* **15**, 1722 (2003).
- <sup>13</sup>E. Rousseau, M. M. Koetse, M. Van der Auweraer, and F. C. De Schryver, *Photochem. Photobiol. Sci.* **1**, 395 (2002).
- <sup>14</sup>S. B. Brichtkin, M. A. Osipova, T. M. Nikolaeva, and V. F. Razumov, *High Energy Chem.* **39**, 442 (2005).
- <sup>15</sup>K. Hosoi, A. Hirano, and T. Tani, *J. Appl. Phys.* **90**, 6197 (2001).
- <sup>16</sup>F. Nüesch, J. E. Moser, V. Shklover, and M. Grätzel, *J. Am. Chem. Soc.* **118**, 5420 (1996).
- <sup>17</sup>A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, and G. B. Behera, *Chem. Rev.* **100**, 1973 (2000).
- <sup>18</sup>T. Miyagawa, M. Yamamoto, R. Muraki, H. Onouchi, and E. Yashima, *J. Am. Chem. Soc.* **129**, 3676 (2007).
- <sup>19</sup>A. Eisfeld and J. S. Briggs, *Chem. Phys.* **324**, 376 (2006).
- <sup>20</sup>V. F. Kamalov, I. A. Struganova, and K. Yoshihara, *J. Phys. Chem.* **100**, 8640 (1996).
- <sup>21</sup>I. A. Struganova, S. Morgan, and H. Lim, *J. Phys. Chem. B* **106**, 11047 (2002).
- <sup>22</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3535980> for supporting figures for MTC and its aggregates measured by using absorption spectra, DLS, CLSM, and fluorescence spectra.
- <sup>23</sup>J. C. Stern, J. E. Sonke, and V. J. M. Salters, *Chem. Geol.* **246**, 170 (2007).
- <sup>24</sup>T. V. Ternovaya, V. P. Shelest, N. V. Gerasimenko, and E. L. Il'nitskaya, *Theor. Exp. Chem.* **21**, 418 (1985).
- <sup>25</sup>U. Kätzel, M. Vorbau, M. Stintz, T. Gottschalk-Gaudig, and H. Barthel, *Part. Part. Syst. Charact.* **25**, 19 (2008).
- <sup>26</sup>U. Nöbbmann, M. Connah, B. Fish, P. Varley, C. Gee, S. Mulot, J. Chen, L. Zhou, Y. Lu, F. Sheng, J. Yi, and S. E. Harding, *Biotechnol. Genet. Eng. Rev.* **24**, 117 (2007).
- <sup>27</sup>J. S. Kim, R. Kodagahly, L. Strekowski, and G. Potanoy, *Talanta* **67**, 947 (2005).
- <sup>28</sup>W. J. Harrison, D. L. Mateer, and G. J. T. Tiddy, *J. Phys. Chem.* **100**, 2310 (1996).
- <sup>29</sup>T. D. Slavnova and A. K. Chibisov, *J. Phys. Chem. A* **109**, 4758 (2005).
- <sup>30</sup>J. Xiang, X. Yang, C. Chen, Y. Tang, W. Yan, and G. Xu, *J. Colloid Interface Sci.* **258**, 198 (2003).
- <sup>31</sup>A. K. Chibisov, H. Görner, and T. D. Slavnova, *Chem. Phys. Lett.* **390**, 240 (2004).
- <sup>32</sup>A. K. Chibisov, T. D. Slavnova, and H. Görner, *Nanotech. Russ.* **3**, 19 (2008).
- <sup>33</sup>Q. Yang, J. Xiang, S. Yang, Q. Li, Q. Zhou, A. Guan, X. Zhang, H. Zhang, Y. Tang, and G. Xu, *Nucleic Acids Res.* **38**, 1022 (2010).
- <sup>34</sup>Q. Yang, J. Xiang, S. Yang, Q. Zhou, Q. Li, Y. Tang, and G. Xu, *Chem. Commun. (Cambridge)* **2009**, 1103.
- <sup>35</sup>Y. Zhang, J. Xiang, Y. Tang, G. Xu, and W. Yan, *ChemPhysChem* **8**, 224 (2007).
- <sup>36</sup>Q. Yang, J. Xiang, Q. Li, W. Yan, Q. Zhou, Y. Tang, and G. Xu, *J. Phys. Chem. B* **112**, 8783 (2008).