

Face-selective decoration of an organic single crystal toward photochemical devices

Nami Tokunaga,^a Yuzo Fujiki,^a Seiji Shinkai^{ab} and Kazuki Sada^{*a}

Received (in Cambridge, UK) 28th April 2006, Accepted 18th July 2006

First published as an Advance Article on the web 2nd August 2006

DOI: 10.1039/b606085d

Face-selective decoration of a single crystal constructed from 1-pyrenemethylammonium chloride by an anionic porphyrin dye is reported. CLSM observations indicated that the {001} face of the single crystal was selectively coated by the anionic porphyrin (TPPS). This novel achievement could be the first step for preparation of multi-component composite materials mediated by anisotropy of organic single crystals toward photochemical devices.

Single crystals of organic molecules have been well known as functional materials with anisotropic electronic and magnetic properties in bulk, and their crystal faces have different morphology and chemical properties. Adhesion of organic molecules or inorganic materials to the specific crystal faces has been discussed with respect to control of growth or dissolution of organic crystals.¹ More recently, dyeing crystals by incorporation of dye molecules into a parent crystal has attracted much attention,² and controlled aggregation of inorganic mesocrystals by organic crystal templates has recently been discussed for the formation of inorganic superstructures as models of biomineralization.³ However, less attention has been paid to the utility of crystal surfaces for the preparation of composite materials based on organic crystals as nuclei.^{4,5} Here, we focused on anisotropic decoration of organic single crystals by selective interaction with additives toward photochemical devices. This paper demonstrates the selective decoration of an organic dye onto the single crystal of 1-pyrenemethylammonium chloride (**1**) as a mother single crystal by electrostatic interaction. The pyrene group of **1** was expected to be less soluble in aqueous media, and the chloride anion on the crystal surface should exchange easily with organic anions in solution. As adsorbents, some porphyrin dyes, TPPS (tetra(4-sulfonatophenyl)porphyrin sodium salt) and TMPyP (tetrakis(*N*-methylpyridiniumporphyrin) tetra *p*-toluenesulfonate) were used for selective decoration (Fig. 1).

Recrystallization of **1** from hot ethanol gave pale yellow crystals with a rectangular box shape. X-Ray crystallographic analysis revealed the orientation of the crystal axis, the Miller indices of the crystal faces, and molecular packing of **1** as shown in Fig. 2.† The largest rectangular face was assigned as {001} or {00 $\bar{1}$ }, and the side long one was {010} or {0 $\bar{1}$ 0}, respectively. The packing diagram indicated that the crystal of **1** is formed by the bilayer

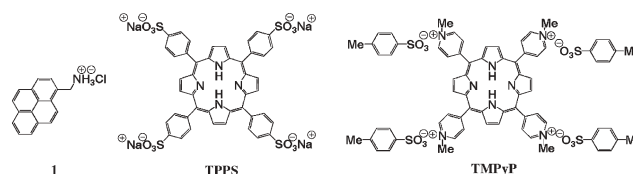


Fig. 1 Molecular structure of **1**, TPPS and TMPyP.

structure with alternating stacking of pyrene layers and ion-pair layers. The former are constructed by π - π and CH- π interactions between the pyrene groups, and the latter are formed by a two-dimensional hydrogen bond network between the ammonium cations and the chloride anions that run parallel to the {001} face. Therefore, the {001} faces should be either the hydrophobic surface or the hydrophilic surface due to exposure of the pyrene groups or the ionic groups. On the other hand, the {010} faces are the hydrophobic surface with hydrophilic stripes that run *ca.* 15 Å apart. Then, a single crystal (*ca.* 775 × 25 × 75 μm) of **1** was mounted in a glass capillary by silicon grease and dipped into the dye solution (*ca.* 2.0 mM) for a quick moment. After washing in distilled water, the crystal was analyzed by a confocal laser scanning microscope (CLSM) as shown in Fig. 3. We used two lasers for excitation, 364 and 543 nm. The former was suitable for the pyrene group of the parent crystal and Soret band of the porphyrin, and the latter only for a Q-band of the porphyrin. Under microscope observation, the crystal surfaces became slightly

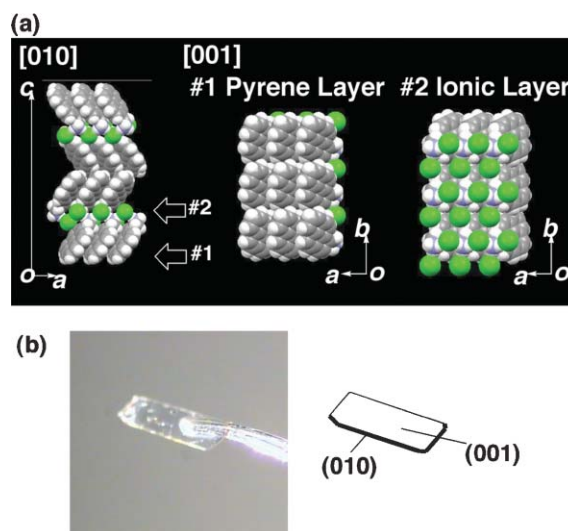


Fig. 2 (a) Crystal packing of **1** and (b) micrograph of a single crystal with the Miller indices of crystal surfaces.

^aDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka, Japan. E-mail: sadatcm@mbox.nc.kyushu-u.ac.jp; Fax: +81-92-802-2820; Tel: +81-92-802-2821

^bCenter of Future Chemistry, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka, Japan

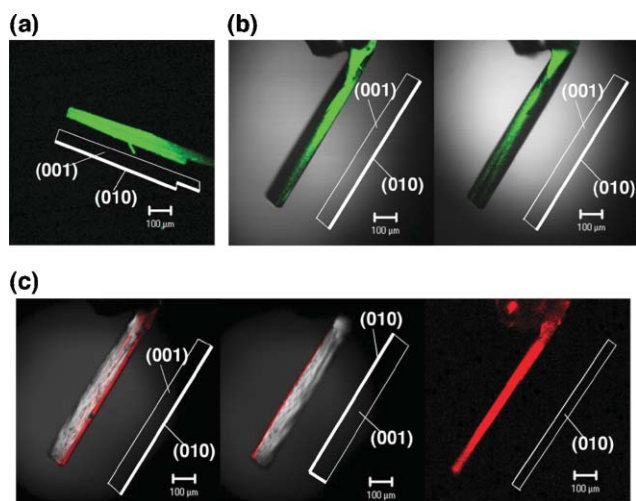


Fig. 3 CLSM images of crystals of **1**: (a) **1** only ($\lambda_{\text{ex}} = 364$ nm), (b) decorated by TPPS ($\lambda_{\text{ex}} = 364$ nm), and (c) decorated by TPPS ($\lambda_{\text{ex}} = 543$ nm).

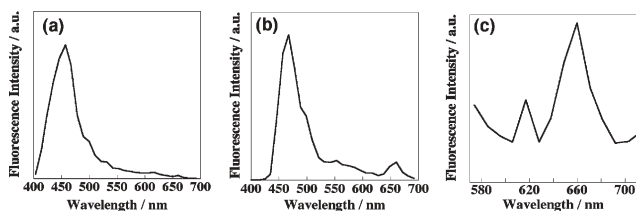


Fig. 4 Fluorescence spectra of crystals of **1**: (a) **1** only ($\lambda_{\text{ex}} = 364$ nm), (b) decorated by TPPS ($\lambda_{\text{ex}} = 364$ nm), and (c) decorated by TPPS ($\lambda_{\text{ex}} = 543$ nm).

rough, but the shapes of the crystals remained unchanged. For the cationic **TMPyP**, no adhesion was observed under the current dipping conditions. However, the anionic **TPPS** was adsorbed onto the surfaces of **1**. Before adsorption of **TPPS**, the whole crystal faces emitted brightly due to emission from the pyrene by the excitation at $\lambda_{\text{ex}} = 364$ nm, whereas the excitation at $\lambda_{\text{ex}} = 543$ nm provided no emission. The fluorescence maximum at 460 nm as shown in Fig. 4 was assigned for emission of the pyrene group and no fluorescence of the porphyrin was observed. On the other hand, the dipped crystal had a different photochemical process. The excitation at 543 nm indicated that the crystal emitted only from the $\{010\}$ and $\{0\bar{1}0\}$ faces. Other surfaces had no fluorescence at this excitation. It is noteworthy that the larger $\{001\}$ and $\{00\bar{1}\}$ faces had mostly no fluorescence. The fluorescent peak of porphyrin at 660 nm was observed in the fluorescence spectra excited at 543 nm. Since the excitation at 364 nm can be adopted for both excitation of pyrene and porphyrin, the whole crystal faces emitted brightly and the fluorescence maxima were observed both at 460 and 660 nm. These results strongly suggest that the porphyrin was adsorbed selectively on the $\{010\}$ and $\{0\bar{1}0\}$ faces of **1**. The four sulfonate groups of **TPPS** are just suitable for adsorption on the hydrophilic surface with ionic hydrophilic stripes. The distance between the two sulfonate groups at the 5 and 15 positions is around 15 Å and this is similar to those between the ionic hydrophilic stripes on the $\{010\}$ and $\{0\bar{1}0\}$ faces.

No accessibility of **TPPS** to the $\{001\}$ and $\{00\bar{1}\}$ faces suggests that the hydrophobic pyrenyl layer was exposed on these surfaces and that the π - π and CH- π interactions between the pyrene and porphyrins are not strong enough to associate with each other.

In conclusion, we demonstrated face-selective decoration of a single crystal of **1** by dipping in an aqueous solution of **TPPS**. The electrostatic interaction between the cationic crystals and anionic dyes plays an important role for adhesion on the crystal surface, and the anisotropic adhesion is attributed to the molecular arrangement of the hydrophobic and anionic groups on the crystal surfaces. Recent advances of crystal engineering⁶ enable us to design the specific crystal surfaces, and the complementary arrangement of the adsorbents should give us the next advancement, *i.e.*, face-selective decoration. This should provide the multi-component composite materials mediated by anisotropy of organic single crystals. Introduction of the chromophores into the molecular structure of the parent crystals and the adsorbents would provide us various photochemical devices. Further trials for fluorescence energy transfer or quenching by electron transfer are under investigation.

We thank the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) for financial support for K. S. and S. S. A part of this work was supported by the 21st Century COE Program (MEXT), and “Functional Innovation of Molecular Informatics” for Y. F. and S. S. We thank Prof. I. Hamachi, Dr A. Ojida and Mr S. Matsumoto at Kyoto University for CLSM observation.

Notes and references

† X-Ray crystallographic data for **1**: $C_{17}H_{14}ClN$, $M = 267.75$, orthorhombic $P2_12_12_1$, $a = 4.8026(15)$ Å, $b = 7.891(3)$ Å, $c = 35.162(11)$ Å, $V = 1332.6(7)$ Å³, $T = 298$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.271$ mm⁻¹, $D_{\text{calcd}} = 1.33$, 105311 reflections measured, 3736 unique which were used in all calculations. $R_1 = 0.063$ ($I > 2.0 \sigma(I)$), $wR_2 = 0.161$ (all data). All structures solved by direct methods and refined using SHELXS-97 with anisotropic thermal parameters for non-hydrogen atoms. CCDC 606956. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606085d

- 1 L. Addadi, Z. Berkovitch-Yellin, I. Weissbuch, J.-v. Mil, L.-J. W. Shimon, M. Lahav and L. Leiserowitz, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 466; I. Weissbuch, R. Popovitz-Biro, M. Lahav and L. Leiserowitz, *Acta Crystallogr.*, 1995, **B51**, 115; I. Weissbuch, M. Lahav and L. Leiserowitz, *Cryst. Growth Des.*, 2003, **3**, 125.
- 2 B. Kahr and R. W. Gurney, *Chem. Rev.*, 2001, **101**, 893; J. B. Benedict, P. M. Wallace, P. J. Reid, S.-H. Jang and B. Kahr, *Adv. Mater.*, 2003, **15**, 1068; A. Barbon, M. Bellinazzi, J. B. Benedict, M. Brustolon, S. D. Fleming, S.-H. Jang, B. Kahr and A. L. Rohl, *Angew. Chem., Int. Ed.*, 2004, **43**, 5328.
- 3 H. Coelfen and M. Antonietti, *Angew. Chem., Int. Ed.*, 2005, **44**, 5576; S. Guo, L. Konopny, R. Popovitz-Biro, H. Cohen, H. Porteau, E. Lifshitz and M. Lahav, *J. Am. Chem. Soc.*, 1999, **121**, 9589; V. Hensel, A. Godt, R. Popovitz-Biro, H. Cohen, T.-R. Jensen, K. Kjaer, I. Weissbuch, E. Lifshitz and M. Lahav, *Chem.-Eur. J.*, 2002, **8**, 1413.
- 4 M. Kreiner, B. D. Moore and M.-C. Parker, *Chem. Commun.*, 2001, 1096; M. Kreiner, G. Fuglevand, B. D. Moore and M.-C. Parker, *Chem. Commun.*, 2005, 2675; M. Murugesan, D. Cunningham, J.-L. Martinez-Albertos, R.-M. Vrcelj and B. D. Moore, *Chem. Commun.*, 2005, 2677.
- 5 Y. Fujiki, N. Tokunaga, S. Shinkai and K. Sada, *Angew. Chem., Int. Ed.*, 2006, **45**, 4764.
- 6 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; G. R. Desiraju, *Angew. Chem., Int. Ed.*, 1995, **34**, 2311; M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313; D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, **7**, 1.