

Stimuli-Responsive Luminescent Liquid Crystals: Change of Photoluminescent Colors Triggered by a Shear-Induced Phase Transition**

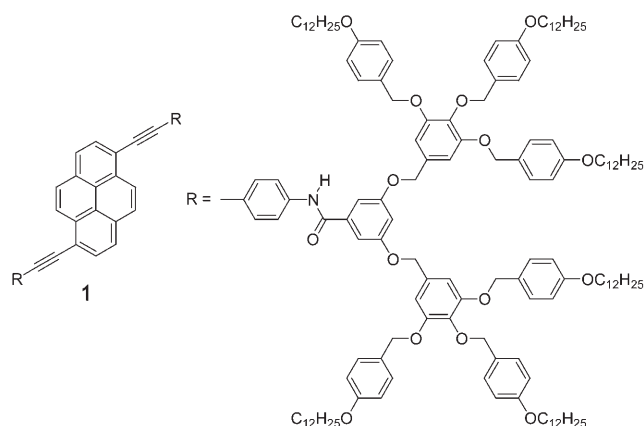
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Soft materials formed by molecular self-assembly have attracted much attention recently.^[1] Liquid crystals are one such soft material that combines ordered and dynamic states.^[2] These properties can be used to manufacture stimuli-responsive materials. The incorporation of photo-,^[3] electro-,^[4] and ion-functional^[5] moieties into liquid crystals leads to dynamic functional materials, the functions of which can be tuned by stimuli-induced structural changes. We are aiming to develop a new class of photo-functional nanostructured liquid crystals that respond to mechanical stimuli, and herein we report on a shear-induced liquid-crystalline (LC) phase transition of pyrene derivative **1** which induces a change of photoluminescent color. To date, only a limited number of LC materials have been reported to show shear-

induced phase transitions,^[6] and to the best of our knowledge no photo-functional liquid crystals that show a shear-induced LC phase transition associated with a change of their photoluminescent color have been prepared. Pyrene is a widely used probe due to its high fluorescent efficiency and excimer formation,^[7] and a number of pyrene derivatives have recently been reported to show LC behavior.^[8] We intend to use the LC order-order phase transitions of pyrene-based liquid crystals to control the luminescent properties of the ordered bulk materials. If the assembled structures of luminescent groups are changed by the phase transition, the photoluminescent properties of the materials could be tuned by external stimuli.^[9]

We expected that compound **1** should exhibit both columnar and cubic phases, although it is not easy to design for the induction of a cubic phase rationally.^[2d] These nanostructured liquid crystals are suitable for the arrangement of fluorophores. In compound **1**, two dendritic groups are linked to a central pyrene moiety by amide bonds. A variety of dendritic groups have been examined as LC molecular components,^[10–15] and the dendron having a methyl group at the focal point, which has a similar structure to that of the dendron introduced into **1**, has been reported to show a columnar phase.^[12] We have reported previously that dendritic H-bonded molecules with bulky substituents exhibit columnar–cubic phase transitions.^[16] The presence of hydrogen bonding in the ordered phases of **1** is expected to lead to formation of a one-dimensional chain structure.^[17]

Compound **1** was synthesized from 1,6-diethynylpyrene and the fan-shaped dendron by a Sonogashira coupling, which yielded a, transparent, orange viscous liquid that exhibits yellow photoluminescence. Compound **1** shows a thermotropic LC cubic phase that is optically isotropic from –35 °C to 175 °C on simple heating (Figure 1 a). The X-ray diffraction pattern of **1** at 160 °C (Figure 2 a) shows peaks at 53.8, 48.0, 44.1, and 31.1 Å with a reciprocal *d*-spacing ratio of $2:\sqrt{5}:\sqrt{6}:\sqrt{12}$ that correspond to (200), (210), (211), and (222) reflections, respectively, and are therefore indicative of a *Pm3n* cubic phase ($a = 107.6$ Å).^[16] Compound **1** exhibits yellow photoluminescence in the cubic phase (Figure 1 a), although the photoluminescent color changes from yellow to blue-green after the cubic–isotropic phase transition at 175 °C (Figure 1 a→b). The change of photoluminescent color from yellow to blue-green is triggered by mechanical shearing for **1** in the cubic phase (Figure 1 a→c). This change by the mechanical shearing is accompanied by the phase transition from the optically isotropic cubic phase to the birefringent phase.



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[**] This work was supported by a Grant-in-Aid for Creative Scientific Research of “Invention of Conjugated Electronic Structures and Novel Functions” (grant no. 16GS0209) (T.K.) from the Japan Society for the Promotion of Science (JSPS) and the Global COE Program for Chemistry Innovation (T.K. and Y.S.) from the Ministry of Education, Culture, Sports, Science and Technology. We thank Prof. K. Araki and Dr. T. Mutai for measuring the emission lifetimes.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

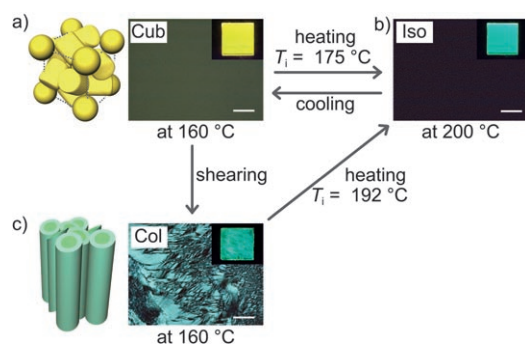


Figure 1. The change of photoluminescent color exhibited by **1** and the respective polarized microscopic images: a) in the cubic phase at 160 °C, b) in the isotropic phase at 200 °C, and c) in the shear-induced columnar phase at 160 °C. Scale bar: 100 μm . The photoluminescent images of **1** sandwiched between quartz substrates under UV irradiation at 365 nm observed in each condition are shown in the inset of each polarized microscopic image. T_i : LC–isotropic phase-transition temperature.

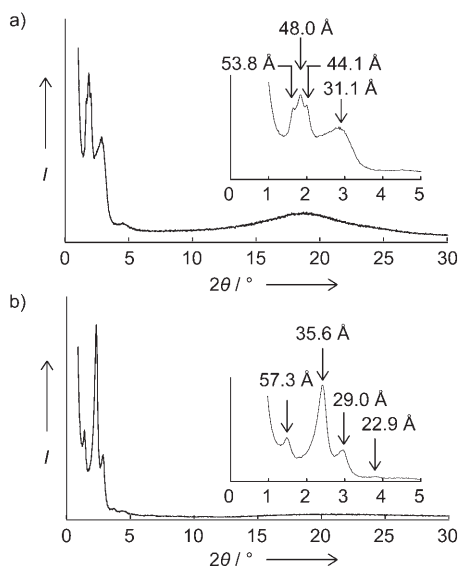


Figure 2. X-ray diffraction patterns of **1**: a) in the cubic phase at 160 °C and b) in the shear-induced columnar phase at 160 °C.

X-ray diffraction measurements performed at 160 °C after the shearing (Figure 2b) indicate that a shear-induced cubic–columnar phase transition has occurred. The diffractions observed for **1** in the small angle region after the shearing can be ascribed to the (11), (02), (22), and (41) reflections of a $P2/a$ rectangular columnar phase ($a = 96.7$, $b = 71.2$ Å) which is stable and does not exhibit an isothermal transition back to the cubic phase. Further heating of **1** leads to a columnar–isotropic phase transition at 192 °C with no formation of a cubic phase (Figure 1c→b). Once compound **1** has formed the isotropic state it does not return to the columnar phase on simple cooling without mechanical shearing. The observed increase of LC–Iso transition temperature and the transition enthalpy (see the Supporting Information) suggest that the shear-induced columnar phase is thermodynamically more

stable than the $Pm3n$ cubic phase. These results imply that the cubic phase exhibited by **1** is a metastable LC phase.

The optical properties of **1** in the cubic (160 °C), shear-induced columnar (160 °C), and isotropic (200 °C) phases were examined by absorption and emission spectroscopy (Figure 3). The absorption bands for compound **1** in the shear-induced and cubic LC phases are observed in the 350–470 nm

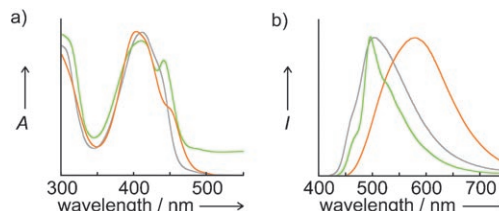


Figure 3. a) Absorption and b) emission spectra of **1** in the cubic phase at 160 °C (orange line), in the shear-induced columnar phase at 160 °C (green line), and in the isotropic phase at 200 °C (gray line).

region (Figure 3a). These bands are similar except for the additional peak observed at 440 nm for the shear-induced columnar phase. The band for the shear-induced columnar phase ($\lambda_{\text{max}} = 496$ nm) in the emission spectrum of **1** (Figure 3b) is blue-shifted with respect to that of **1** in the cubic phase at 160 °C ($\lambda_{\text{max}} = 579$ nm). This spectral shift corresponds to the change of photoluminescent color from yellow to blue-green (Figure 1a→c). The emission bands of **1** in the shear-induced columnar and isotropic phases are observed in the same region (450–700 nm). These spectral features may be indicative of the monomeric emission of **1** in the shear-induced columnar phase. The emission band observed in the cubic phase is broader and less structured than that for the shear-induced columnar phase, which is attributed to excimer formation of the pyrene moieties in the cubic phase. This excimer formation is confirmed by the fact that the emission lifetime for the cubic phase is longer than that for the shear-induced columnar phase (see the Supporting Information). This observation shows that the emitting species for the cubic and shear-induced columnar phases are different. The excimer formation of compound **1** is also supported by the results of previous studies on the excimer emission of several 1,6-diethynylpyrene derivatives.^[18] The spectroscopic measurements for **1** therefore show that mechanical shearing disturbs the excimer formation of the 1,6-diethynylpyrene moieties of **1** and leads to a blue-green photoluminescence for the shear-induced columnar phase.

The self-assembled structures in the cubic and shear-induced columnar phases were also studied by IR spectroscopy (Figure 4). The IR spectra for **1** in both the cubic and shear-induced columnar phases show that the amide groups are involved in the formation of hydrogen bonds and no free amide C=O or N–H groups are present (Figure 4b,c). The C=O stretching band observed for **1** in the cubic phase shifts from 1655 to 1645 cm^{-1} upon shear-induced cubic–columnar phase transition. This shift indicates that the weaker H-bonded state in the cubic phase changes to a stronger H-bonded state in the shear-induced columnar phase. In

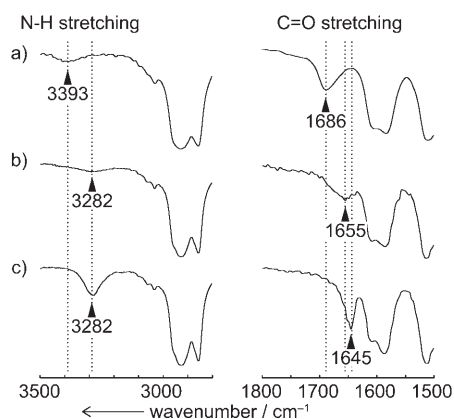


Figure 4. IR spectra of **1** in different phases: a) isotropic (210°C); b) cubic (160°C); c) shear-induced columnar (160°C).

addition, the peaks corresponding to the C=O and N–H stretches observed in the shear-induced columnar phase become sharper than those observed in the cubic phase (Figure 4b,c). These observations also suggest that mechanical shearing induces a change in the self-assembled structures of **1** at a molecular level.

Proposed structures for the self-assembled cubic and shear-induced columnar phases of **1** are shown in Figure 5. Compound **1** forms micellar structures in the $Pm3n$ cubic

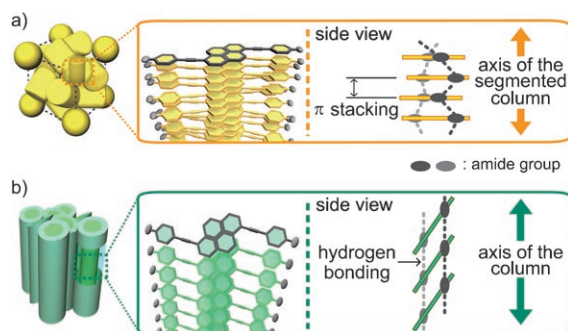


Figure 5. Illustrations of the assembly of **1** in the cubic phase (a) and in the shear-induced columnar phase (b). The dendritic side-chains of **1** are omitted in the middle and right-hand images of the assembled luminescent cores.

phase (Figure 5a, left); a number of LC compounds have been reported to exhibit micellar cubic phases.^[12,16,19] Each micelle in the micellar cubic phase of **1** consists of a segmented column formed by approximately 20 individual molecules. The number of molecules forming each micelle was calculated based on the results of the X-ray measurements (see the Supporting Information). Similar segmented columnar structures in a micellar cubic phase have been reported previously.^[16,19] The segmented columnar structures in the cubic phase of **1** result from hydrogen bonding between the amide groups of adjacent molecules and the formation of π -stacked structures of the emission cores (Figure 5a, middle and right). This type of self-assembly for **1** leads to yellow excimer emission. Compound **1** should be arranged in

disordered stacks in these segmented columns (Figure 5a, middle and right). This proposed self-assembled structure is supported by the fact that the length between the H-bonded amide groups is generally longer than the distance between the adjacent arenes that form π -stacked structures.^[20]

The shear-induced cubic–columnar phase transition of **1** at 160°C results in the formation of non-segmented columnar structures (Figure 5b, left). The stronger H-bonded states (Figure 4c) that are not observed in the cubic phase are formed in these columnar structures (Figure 5b, middle and right). Each molecule in these structures is expected to form hydrogen bonds to adjacent molecules with a distance of around 5 Å. This proposed assembled structure of **1** (Figure 5b) is supported by previous reports on the crystal structures of some arenedicarboxamides,^[21] where the diamides that pack in one-dimensional tapes are translationally related and each molecule is H-bonded to two adjacent molecules with a separation of 5 Å. Moreover, the arenes of these compounds are not overlapping.^[21] In light of these crystal structures, compound **1** with a similar structure may assemble into the linear H-bonded structures shown in Figure 5b, which should result in interference with the excimer formation of the 1,6-diethynylpyrene moieties of compound **1**. The blue-green photoluminescence for the shear-induced columnar phase is observed because of these self-assembled structures.

In summary, we have found that compound **1** shows a shear-induced LC order–order transition from a micellar cubic to a columnar phase; this transition is accompanied by a change of the luminescent color. The micellar cubic phase exhibited by **1** is a metastable LC phase. This isothermal transition from metastable to stable phases may be useful for dynamically changing the properties of functional liquid crystals. The concept of metastable liquid crystals is very useful for the development of a variety of stimuli-responsive materials.

Received: January 12, 2008

Revised: March 19, 2008

Published online: June 2, 2008

Keywords: liquid crystals · nanostructures · photoluminescence · self-assembly · supramolecular chemistry

- [1] a) Special issue on supramolecular chemistry and self-assembly: *Science* **2002**, 295, 2395–2421; b) I. W. Hamley, *Angew. Chem.* **2003**, 115, 1730–1752; *Angew. Chem. Int. Ed.* **2003**, 42, 1692–1712; c) *Supramolecular Polymers*, 2nd ed. (Ed.: A. Ciferri), Taylor & Francis, London, **2005**.
- [2] a) *Handbook of Liquid Crystals* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**; b) *Thermotropic Liquid Crystals* (Ed.: G. W. Gray), Wiley, Chichester, **1987**; c) T. Kato, *Science* **2002**, 295, 2414–2418; d) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, 118, 44–74; *Angew. Chem. Int. Ed.* **2006**, 45, 38–68; e) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, 119, 4916–4973; *Angew. Chem. Int. Ed.* **2007**, 46, 4832–4887; f) C. Tschierske, *J. Mater. Chem.* **2001**, 11, 2647–2671.

- [3] a) K. Ichimura, *Chem. Rev.* **2000**, *100*, 1847–1873; b) T. Ikeda, *J. Mater. Chem.* **2003**, *13*, 2037–2057; c) T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem.* **2007**, *119*, 512–535; *Angew. Chem. Int. Ed.* **2007**, *46*, 506–528; d) F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549.
- [4] a) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141–143; b) M. Funahashi, N. Tamaoki, *ChemPhys-Chem* **2006**, *7*, 1193–1197; c) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747; d) R. J. M. Nolte, *Liq. Cryst.* **2006**, *33*, 1373–1377; e) S. Xiao, M. Myers, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald, C. Nuckolls, *Angew. Chem.* **2005**, *117*, 7556–7560; *Angew. Chem. Int. Ed.* **2005**, *44*, 7390–7394.
- [5] a) K. Binnemans, *Chem. Rev.* **2005**, *105*, 4148–4204; b) C. F. van Nostrum, S. J. Picken, A.-J. Schouten, R. J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965; c) K. Kishimoto, M. Yoshio, T. Mukai, M. Yoshizawa, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2003**, *125*, 3196–3197; d) M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2004**, *126*, 994–995; e) M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2006**, *128*, 5570–5577.
- [6] a) C. R. Safinya, E. B. Sirota, R. J. Plano, *Phys. Rev. Lett.* **1991**, *66*, 1986–1989; b) P. T. Mather, A. Romo-Uribe, C. D. Han, S. S. Kim, *Macromolecules* **1997**, *30*, 7977–7989; c) C. Pujolle-Robic, L. Noirez, *Nature* **2001**, *409*, 167–171; d) V. Schmitt, F. Lequeux, A. Pousse, D. Roux, *Langmuir* **1994**, *10*, 955–961; e) J. Yamamoto, H. Tanaka, *Phys. Rev. Lett.* **1996**, *77*, 4390–4393.
- [7] a) F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587–614; b) B. Xing, C.-W. Yu, K.-H. Chow, P.-L. Ho, D. Fu, B. Xu, *J. Am. Chem. Soc.* **2002**, *124*, 14846–14847; c) G. Jones II, V. I. Vullev, *Org. Lett.* **2001**, *3*, 2457–2460; d) L. M. Ilharco, A. M. Santos, M. J. Silva, J. M. G. Martinho, *Langmuir* **1995**, *11*, 2419–2422.
- [8] a) T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, *Angew. Chem.* **2001**, *113*, 2119–2122; *Angew. Chem. Int. Ed.* **2001**, *40*, 2060–2063; b) S. A. Benning, T. Hassheider, S. Keuker-Baumann, H. Bock, F. Della Sala, T. Frauenheim, H.-S. Kitzerow, *Liq. Cryst.* **2001**, *28*, 1105–1113; c) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shivanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *419*, 384–387; d) A. Hayer, V. de Halleux, A. Köhler, A. El-Garouhy, E. W. Meijer, J. Barberá, J. Tant, J. Levin, M. Lehmann, J. Gierschner, J. Cornil, Y. H. Geerts, *J. Phys. Chem. B* **2006**, *110*, 7653–7659; e) Y. Kamikawa, T. Kato, *Org. Lett.* **2006**, *8*, 2463–2466.
- [9] Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520–1521.
- [10] G. H. Mehl, *Angew. Chem.* **2005**, *117*, 678–679; *Angew. Chem. Int. Ed.* **2005**, *44*, 672–673.
- [11] a) K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1993**, *115*, 11496–11505; b) D. A. Tomalia, J. M. J. Fréchet, *J. Polym. Sci. Part A* **2002**, *40*, 2719–2728.
- [12] a) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2001**, *123*, 1302–1315; b) V. Percec, E. Aqad, M. Peterca, M. R. Imam, M. Glodde, T. K. Bera, Y. Miura, V. S. K. Balagurusamy, P. C. Ewbank, F. Würthner, P. A. Heiney, *Chem. Eur. J.* **2007**, *13*, 3330–3345.
- [13] D. Guillon, R. Deschenaux, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 515–525.
- [14] I. M. Saez, J. W. Goodby, *J. Mater. Chem.* **2005**, *15*, 26–40.
- [15] J. Barberá, B. Donnio, L. Gehringer, D. Guillon, M. Marcos, A. Omenat, J. L. Serrano, *J. Mater. Chem.* **2005**, *15*, 4093–4105.
- [16] a) T. Kato, T. Matsuoka, M. Nishii, Y. Kamikawa, K. Kanie, T. Nishimura, E. Yashima, S. Ujiie, *Angew. Chem.* **2004**, *116*, 2003–2006; *Angew. Chem. Int. Ed.* **2004**, *43*, 1969–1972; b) Y. Kamikawa, M. Nishii, T. Kato, *Chem. Eur. J.* **2004**, *10*, 5942–5951; c) Y. Kamikawa, M. Nishii, T. Kato, *Mol. Cryst. Liq. Cryst.* **2005**, *435*, 755–765.
- [17] a) T. Kato, *Struct. Bonding (Berlin)* **2000**, *96*, 95–146; b) T. Kato, Y. Hirai, S. Nakaso, M. Moriyama, *Chem. Soc. Rev.* **2007**, *36*, 1857–1867.
- [18] a) H. Abe, Y. Mawatari, H. Teraoka, K. Fujimoto, M. Inouye, *J. Org. Chem.* **2004**, *69*, 495–504; b) H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu, M. Inouye, *Chem. Eur. J.* **2006**, *12*, 824–831; c) H. Shimizu, K. Fujimoto, M. Furusyo, H. Maeda, Y. Nanai, K. Mizuno, M. Inouye, *J. Org. Chem.* **2007**, *72*, 1530–1533.
- [19] K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *Angew. Chem.* **1997**, *109*, 2188–2190; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2087–2089.
- [20] a) M. L. Bushey, A. Hwang, P. W. Stephens, C. Nuckolls, *J. Am. Chem. Soc.* **2001**, *123*, 8157–8158; b) T.-Q. Nguyen, M. L. Bushey, L. E. Brus, C. Nuckolls, *J. Am. Chem. Soc.* **2002**, *124*, 15051–15054.
- [21] a) F. D. Lewis, J.-S. Yang, C. L. Stern, *J. Am. Chem. Soc.* **1996**, *118*, 12029–12037; b) F. D. Lewis, J.-S. Yang, *J. Phys. Chem. B* **1997**, *101*, 1775–1781.