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Supramolecular assembly of fluorescent phasmidic diacetylene and its photopolymerization†

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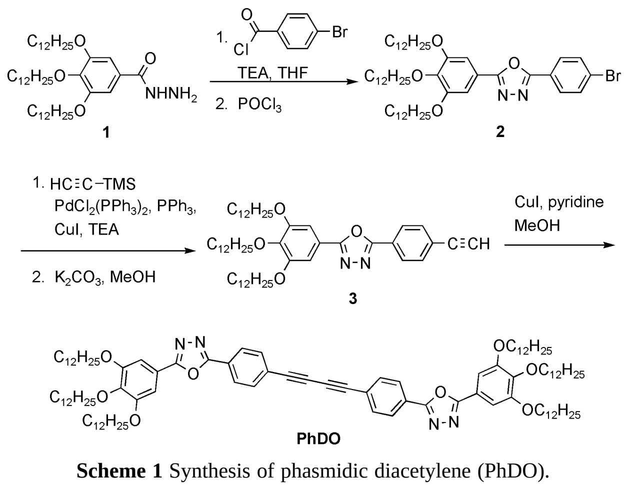
The closed micellar triclinic structure of a fluorescent phasmidic diacetylene (PhDO) has been fixed by topochemical photopolymerization which induced fluorescence quenching to offer a novel method of image photopatterning.

Topochemical polymerization of mesogenic diacetylenes is one of the interesting research topics related to supramolecular science[1] and molecular electronics[2] since polymerization in the liquid crystalline (LC) state provides a promising pathway to obtain organized macromolecules. To date, a number of mesogenic diacetylenes exhibiting nematic, smectic, and columnar phases have been studied to determine fundamental structure–property correlations.[2–4] Here we report a new type of mesogenic diacetylene, *i.e.* a phasmidic diacetylene bearing a strongly fluorescent conjugated oxadiazole unit (PhDO). Phasmidic or polycatenar molecules are generally composed of a rod-like core and two endgroups of half-disk shape possessing two or three flexible tails, where each component is joined by polar linkages with transverse dipole moments such as ester or amide groups. Consequently these molecules can be thought of as hybrid materials of calamitic and discotic LCs and thus exhibit various mesophases including nematic, smectic, and columnar phases as well as cubic, tetragonal and orthorhombic three-dimensional phases.[5]

The chemical structure of PhDO is characterized by the presence of a diacetylene unit in the center of the calamitic core and two oxadiazole linkages between the core and the endgroups (Scheme 1). In addition to the role as a polar linkage, the heteroaromatic oxadiazole unit provides π-electron conjugation throughout the rigid part. Herein are described the synthesis and self-assembling properties of PhDO. As a promising application arising from the fully conjugated nature of PhDO, absorption and fluorescence image patterning by photoirradiation is also demonstrated in this work.



Scheme 1 Synthesis of phasmidic diacetylene (PhDO).

Scheme 1 shows the structure and the synthetic procedures of PhDO. The oxadiazole ring was formed by the reaction of acid hydrazide (**1**) with bromobenzoyl chloride and subsequent dehydration in $POCl_3$, to give **2**. Acetylene compound **3** was obtained by ethynylation of **2** with (trimethylsilyl)acetylene in the presence of $PdCl_2(PPh_3)_2$, PPh_3, and CuI in triethylamine, followed by removal of the trimethylsilyl group by K_2CO_3 in methanol. The final product PhDO was readily prepared by oxidative self-coupling of **3** with CuI in pyridine/methanol and isolated by column chromatography on silica gel (ethyl acetate) in high yield (92%).† The isolated PhDO was further purified by recrystallization from ethyl acetate and subsequent reprecipitation from ethyl acetate into *n*-hexane to give a high level of purity for the study of self-assembling properties.

DSC analysis of PhDO gave only an endothermic peak at 88 °C (ΔH = 17.1 J g^{-1}) on heating and thermal polymerization was not observed up to 200 °C. On cooling two exothermic peaks were observed at 87 °C (ΔH = −0.3 J g^{-1}) and 75 °C (ΔH = −19.1 J g^{-1}). The former exotherm with small ΔH is ascribable to the monotropic transition to mesophase and the latter to the crystal transition. In the mesophase cooled from the isotropic melt, the sample is highly viscous and showed an optically isotropic phase between the crossed polarizers, similar to the cubic phase. After annealing in the mesophase, a birefringent texture was formed very slowly and turned into a mosaic-like texture on cooling to room temperature by crystallization.† To know the nature of the self-organization, X-ray diffraction (XRD) analysis was carried out by using synchrotron radiation (the Pohang Accelerator Laboratory). In the mesophase cooled from the isotropic melt, PhDO showed a number of sharp reflections in the small-angle region and a poorly resolved broad halo in the wide-angle region (Fig. 1a). From these reflections the mesophase structure could be assigned as a triclinic $P1$ lattice with cell parameters of a = 51.8, b = 44.1, c = 42.4 Å, α = 83.45, β = 114.1, and γ = 105.21°.† Taking into account the self-assembly characteristics of phasmidic molecules that agglomerate into supramolecular aggregates consisting of a few molecules which in turn organize into higher-order form,[5] we presume that each triclinic lattice point is filled up with a closed micellar aggregate formed by PhDO molecules. The average number of molecules in each aggregate is calculated to be 29 from the lattice constants and density of PhDO. Consequently the mesophase of PhDO can be defined as a closed micellar triclinic phase and the most probable model of it is illustrated in Fig. 1b: the inner core of the closed micelle is constructed by the rigid rod part of PhDO and separated from adjacent ones by space-filling flexible tails. Although several micellar mesophases have already been reported for a few systems such as carbohydrates, dendritic and

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† Electronic Supplementary Information (ESI) available: synthetic details, polarized optical micrographs, characterization of XRD, XRD after polymerization, IR spectra, and absorption change during photopolymerization. See http://www.rsc.org/suppdata/cc/b3/b306015b/

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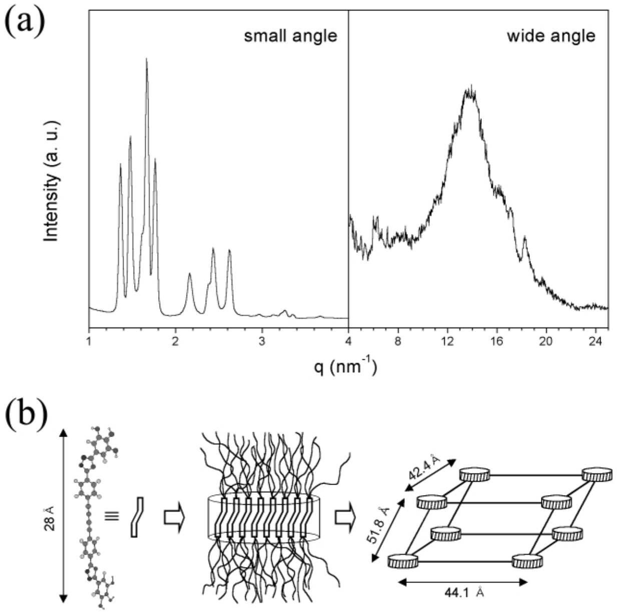

Fig. 1 XRD patterns of PhDO representing the triclinic mesophase (a, 80 °C on cooling) and a possible model for assembly of PhDO in the triclinic lattice (b). The length of the rigid part (28 Å) was calculated using Mopac 97 (PM3 parameter).

rod–coil molecules, all of them are cubic phases with spherical micelles or are organized into a non-cubic three-dimensional lattice with tetragonal symmetry.[6–8] To the best of our knowledge, PhDO is the first example showing a micellar triclinic mesophase among phasmidic and rod–coil molecules. Though the reason is not clear at this point, the deviation from cubic structure seems to imply that the micelle formed by the double-bent PhDO molecules (see the structure in Scheme 1) is of non-spherical, anisotropic shape as is illustrated in Fig. 1b.

Photopolymerization of PhDO was investigated with a sample quenched from the mesophase to room temperature using a high pressure Hg lamp (polychromic, 14 mW at 365 nm). We noted that the XRD pattern after quenching remained identical to that of the mesophase, identifying the frozen state of the mesophase due to the suppressed crystallization by high viscosity. Interestingly, after exposure for 30 min the polymerized sample retained the XRD pattern of its monomer mesophase apart from a small reduction of the intra- and intermicellar distances. The differences of XRD peaks are smaller than 0.03 nm^{-1} in q spacing.† In the IR spectrum, absorbances at 2148 and 2222 cm^{-1} from carbon–carbon triple bonds decreased significantly after irradiation, from which the conversion was estimated as *ca.* 33%.† Accordingly, the obtained products are oligomers with a degree of polymerisation of *ca.* 10, inevitably resulting from the limited numbers of molecules within the closed micelle. Maintenance of the supramolecular structure of monomer assembly after polymerization is a rare case for diacetylene mesogens.[4] According to the proposed micellar structure of PhDO, the reason for the virtually unchanged supramolecular nanostructure of polymer may be as follows: topochemical polymerization occurs within the closed micelle due to the suitable stacking distance of diacetylenes (4.6 Å), while intermicellar reaction is completely limited by the isolating effect of flexible tails. Consequently only a small shrinkage in micelle size is allowed by polymerization, which does not lead to changes in the supramolecular structure. Importantly such a polymerization-induced fixation of micellar structure without intermicellar connection provides a simple and potential method to prepare nano-size polymeric particles; investigations into this are being carried out in our group.

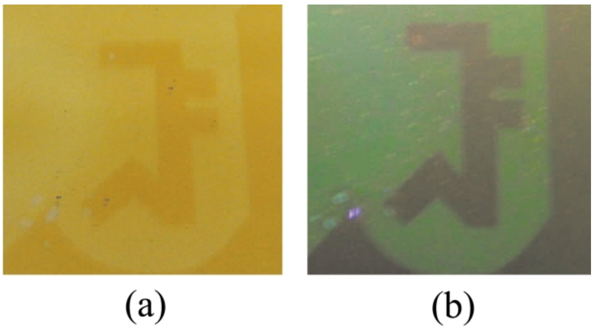
(a) (b)

Fig. 2 Absorption (a) and fluorescence (b) patterns obtained by irradiating the frozen mesophase sandwiched between two glass substrates through nega-type photomask. The pictures were taken without and with excitation at 365 nm, respectively.

PhDO is a fluorescent mesogen due to the full conjugation in its rigid part. Its chloroform solution gives a strong greenish blue emission while in the mesophase the emission is red-shifted and slightly reduced in intensity due to mesogen stacking, as reported for similar mesogens.[9] During photopolymerization in the frozen mesophase, the original pale yellow color of PhDO gradually turned brown with a remarkable increase in visible absorption.† Moreover the fluorescence originating from the conjugated oxadiazole unit was completely queched after polymerization probably due to complete self-absorption by the polydiacetylene backbone with strong and enlarged visible absorption. Though color changes upon increased absorption are common, fluorescence emission and its change in diacetylene polymerization is a rare case. Thus these optical characteristics of PhDO suggest a novel application of diacetylene polymerization, *i.e.* image photopatterning. Fig. 2 shows photographs of absorption (a) and fluorescence (b) patterns obtained by illumination through nega-type photomask, where dark and non-fluorescent parts were photopolymerized. The pattern resolution is estimated to be far below 10 μm which is the limitation of our photomask.

In summary, a novel phasmidic mesogen, PhDO, was found to form a micellar triclinic mesophase and proved to be a new type of fluorescent diacetylene capable of fixing the mesophase structure by topochemical polymerization. Fluorescence image patterning by photopolymerization was demonstrated.

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