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The positive effect on hole transport behaviour in anisotropic gels consisting of discotic liquid crystals and hydrogen-bonded fibres†

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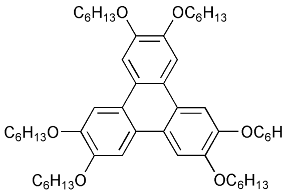
The hole mobility of a discotic liquid-crystalline triphenylene compound is enhanced by the gelation with hydrogen-bonded fibrous aggregates.

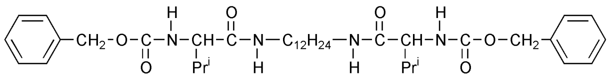
Liquid crystals are functional materials that possess anisotropic molecular order and fluidity.[1] Liquid-crystalline (LC) charge transport materials have attracted attention because of their potential for future electric functional devices.[2–9] The control of the self-assembled structures for these materials is of importance for the enhancement of such properties.

Recently, as a new class of LC materials, LC physical gels have been prepared from calamitic liquid crystals and hydrogen-bonded molecular aggregates.[10–13] Significant electro-optical properties have been observed for the nematic physical gels.[11] The molecular motion of the nematic liquid crystals has been improved by the formation of microphase-separated states.[11] Our intention is to introduce such microphase-separated structures into the discotic LC materials to tune their electric function. Here we report that the hole mobility of a discotic LC triphenylene compound is enhanced by the gelation with hydrogen-bonded fibrous aggregates.

Triphenylene compound **1** exhibits a discotic hexagonal columnar (D_h) phase between 68 and 100 °C. Two L-amino acid derivatives **2** and **3**,[14] which are able to gelate organic solvents and calamitic liquid crystals, have been chosen as gelators. The discotic LC gels are formed when the mixtures of the discotic compound (**1**) and the gelators are cooled from the isotropic liquid states. Fig. 1a and c show the polarised optical photomicrographs of the gels based on **2** and **3** at 76 °C. The different morphologies are observed for these gels because of the different phase sequence of the mixtures as given in Table 1. For the mixture of **1** and **3** (**1**/**3**), the fibrous aggregation of **3**

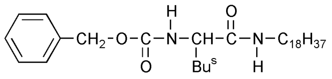


1



$$C_6H_5\text{-}CH_2\text{-}O\text{-}\underset{\|}{\overset{}{C}}(=O)\text{-}N(H)\text{-}CH(Pr^i)\text{-}C(=O)\text{-}N(H)\text{-}C_{12}H_{24}\text{-}N(H)\text{-}C(=O)\text{-}CH(Pr^i)\text{-}N(H)\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}C_6H_5$$

2



$$C_6H_5\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}N(H)\text{-}CH(Bu^s)\text{-}C(=O)\text{-}N(H)\text{-}C_{18}H_{37}$$

3

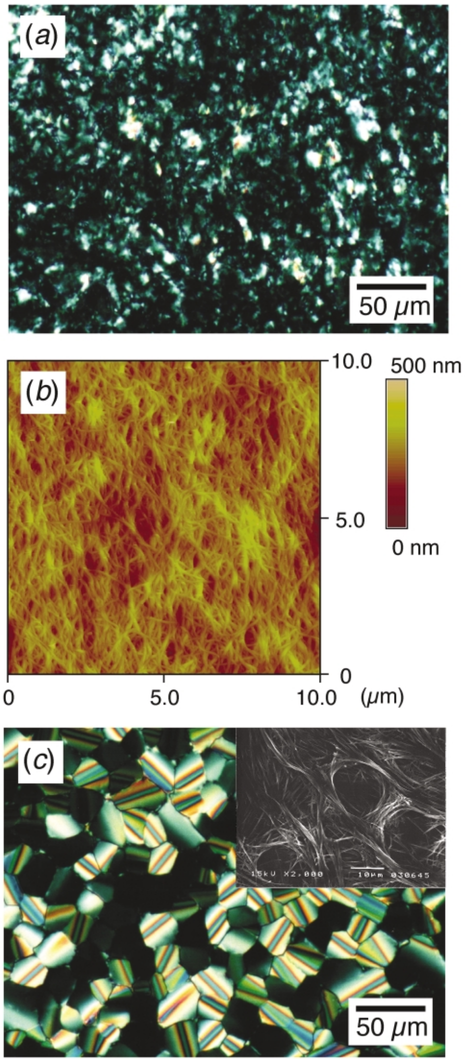


Fig. 1 (a) Polarised optical photomicrograph of **1**/**2** at 76 °C; (b) AFM image of the xerogel obtained from **1**/**2**; (c) Polarised optical photomicrograph of **1**/**3** at 76 °C. Inset: SEM image of the xerogel obtained from **1**/**3**.

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† Electronic supplementary information (ESI) available: transient photocurrents for **1**, **1**/**2** and **1**/**3**. See http://www.rsc.org/suppdata/cc/b1/b111380c/

occurs after **1** enters the LC state on cooling. In this case, the aggregates of compound **3** develop in the boundary of the LC domains because the LC phase of **1** and the isotropic liquid phase of **3** are immiscible. Consequently, the domain size is approximately 30 μm for the gels of **1** and **3** (Fig. 1c). In contrast, for **1**/**2**, gelator **2** forms hydrogen-bonded aggregates in the isotropic state at 133 °C. In this miscible mixture, the fibres are able to form finer networks (Fig. 1b), which results in the formation of the LC domains in the submicrometer level (Fig. 1a).

The hole mobility (μ) of the discotic gels with different sizes of phase-separated structures has been measured by the time-of-flight method.‡ For the discotic phase of **1** alone showing homeotropic alignment in the cell, the hole mobility has been determined to be 4.5×10^{-4} cm^2 V^{-1} s^{-1}. This value is in good agreement with that reported in the literature.[4] Interestingly, the hole mobility of **1**/**2** in the discotic LC gel state is 1.2×10^{-3} cm^2 V^{-1} s^{-1}, which is nearly three times higher than that of **1** alone. Fig. 2 shows the hole mobility for **1**, **1**/**2** and **1**/**3** as a function of temperature on cooling. Both **1**/**2** and **1**/**3** show hole mobilities, which are independent of electric field strength and temperature. Such behaviour is similar to that of **1** alone. We assume that the finely dispersed solid networks of **2** effectively suppress the fluctuations of the LC molecules and enhance the molecular order of the columnar structure, leading to the positive effect on the hole transport behaviour.§ This effect seems to be similar to the case of the plastic mesophase.[6] It should be noted that enhancement of the hole mobilities is observed for the gel even though the partial disorder of the homeotropic alignment is caused by the gelation. For **1**/**3**, the phase separation forms the carrier transport paths comprising of the neat liquid crystal forming the larger domain as seen in Fig. 1c. In this case, the enhancement of the hole transport behaviour due to gelation does not occur.

In summary, appropriate tuning of microphase-separated morphologies of the discotic LC gels leads to the fabrication of new organic materials that transport carriers efficiently.

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Table 1 Phase transition behaviour of the single components and the mixtures of **1** containing 3.0 wt% of **2** and **3** on cooling

Sample	Phase transition temperature[a]/°C						
1	I	98	D$_h$	54	Cr		
2	I	146	Cr				
3	I	95	Cr				
1/2	I	133	Gel	97	LC (D$_h$) Gel	57	Cr
1/3	I	88	D$_h$ + I[b]	79	LC (D$_h$) Gel	60	Cr

[a] Phase behaviour determined by optical polarising microscopy and differential scanning calorimetry (5.0 °C min^{-1}). I: isotropic; D$_h$: discotic hexagonal; Cr: crystalline. [b] Gelator **3** in the isotropic state and the LC domains show phase separation.

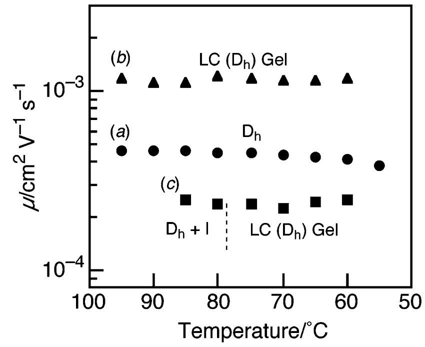

Fig. 2 Plot of the hole mobility μ *versus* temperature in an electric field of 4.0×10^4 V cm^{-1}: (a) **1**; (b) **1**/**2**; (c) **1**/**3**.

Notes and references

‡ The transit time t_T of photogenerated holes traversing the LC layer was determined from an inflection point in a double logarithmic plot of transient photocurrent as a function of time. Hole mobility μ was calculated from the equation, $\mu = d/E \cdot t_T$, where d is a sample thickness ($\approx$ 30 μm) and E an electric field strength.

§ We have confirmed that the hydrogen-bonded fibre itself does not function as a conducting path by measuring the value of μ in the isotropic gel state of **1**/**2** (130–100 °C). The mobility is in the order of 10^{-6} cm^2 V^{-1} s^{-1}, which corresponds to that of the isotropic phase of **1**.

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