

Hybrid organic/inorganic nanocomposite as a quasi-one-dimensional semiconductor under ambient conditions

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We describe here a novel hybrid organic/inorganic nanocomposite of hexahexyloxytriphenylene (HAT6) which is a columnar discotic liquid crystal and gold tetrachloride, an inorganic dopant, showing enhanced dc and ac electrical conductivity by several orders of magnitude at ambient conditions *vis-à-vis* the respective pure components. The composites at appropriate concentrations of the dopants retain the columnar hexagonal phase, which is confirmed by polarizing optical microscopy, differential scanning calorimetry, and x-ray scattering techniques. The UV-vis spectral studies show that the composites absorb in the entire visible range due to the formation of radical cations of the discotic molecules, making it a potential candidate for solar cell applications.

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I. INTRODUCTION

Ever since the discovery of disc-like molecules exhibiting columnar liquid crystalline properties,¹ there has been a great deal of interest in exploring its potential applications.² The discotic molecules generally consist of an aromatic core surrounded by aliphatic chains. Due to the strong π - π interaction between the aromatic cores and the weak interaction between the flexible aliphatic chains, the molecules can stack one over the other, forming columns. These columns can arrange in several ways forming columnar hexagonal, columnar rectangular, columnar oblique, columnar helical, or columnar plastic phases.³ Typical column-column distance in the columnar hexagonal phase is around 2–4 nm depending on the aliphatic chain length and the core-core distance within the column is around 0.35 nm with a length of a few tens of nanometers. This strong intracolumnar interaction and weak intercolumnar interaction contribute to the quasi-one-dimensional electrical conductivity along the columns.

The quasi-one-dimensional electrical conductivity in these discotic systems has been proposed for diverse applications in the areas including solar cells,⁴ molecular electronics,⁵ photovoltaic cells,⁶ and organic light emitting diodes.⁷ The efficiency of such devices depends on the band gap of the materials, which is typically about 4 eV for the discotic liquid crystals which therefore behave as insulators at normal conditions. On the other hand, they may be converted to useful semiconductors by doping with either electron rich or electron deficient molecules into the supramolecular order of the liquid crystalline phase. This of course means that the doping should be maintained at an optimum concentration in order to retain the liquid crystalline phase, while also be introducing sufficient electron or hole concentration into the liquid crystalline medium to increase the conductivity. Among them, the organic dopant trinitrofluorenone and several inorganic dopants such as iodine, aluminum chloride (AlCl₃), nitrosonium tetrafluoroborate (NOBF₄),

and gold nanoparticles have been proposed in the columnar liquid crystalline matrix.^{8–15} These dopants at low concentrations retain the columnar phase with enhancement in the electrical conductivity by several orders of magnitude. For the AlCl₃ and NOBF₄ doped systems, it has been shown that they form charge-transfer complexes with the discotic molecules. This results in the oxidation of the aromatic core of the discotic moiety with the formation of the radical cations, which enhances the electrical conductivity through the columns. For the NOBF₄ dopants, they may even intercalate within the column and can form a 1:1 complex.¹⁶ These complexes have better liquid crystalline order compared to the pure systems due to the strong electron donor-acceptor interactions within the column that originates from the sandwich-type structure. This is not the case with other dopants, which increase the entropy of the phase, thereby reducing the temperature range of liquid crystalline phase and disrupting the order at higher concentrations. Recently we have shown the enhancement in the electrical conductivity of the hexahexyloxytriphenylene (HAT6) and hexahexylthiotriphenylene (HHTT) systems that are doped with ferrocenium ions.¹⁷ The charge-transfer complex formed between the discotic molecules and the ferrocenium cation was shown to be responsible for the enhancement of electrical conductivity by hopping mechanism.

In the present paper, we study the charge-transfer complex formation of the discotic molecule, HAT6 with an inorganic dopant, gold tetrachloride (AuCl₄⁻), and the enhancement in both dc as well as ac electrical conductivity of the composites. For this organic/inorganic hybrid composite, we have observed a higher electrical conductivity in the columnar phase compared to the crystalline and isotropic phases. This large increase in conductivity was observed even under the ambient conditions in the absence of any inert atmosphere. This makes the system very interesting, as in most other discotic systems the conductivity experiments were carried out under rigorous anhydrous conditions in the pres-

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ence of either nitrogen or argon atmosphere or under applied magnetic field which is used for the alignment of the liquid crystals.^{8–16}

II. EXPERIMENTAL SECTION

HAT6 was synthesized as reported earlier.¹⁸ Spectroscopic grade chloroauric acid, HAuCl_4 (Spectrochem), was used as received. The discotic molecules were dissolved in dichloromethane to which HAuCl_4 was added. A slow evaporation of the solvent results in the formation of a complex, which is easily identified by the immediate color change of the solution from pale yellow to dark green. Different compositions of HAuCl_4 with HAT6, 0.1% $\text{HAuCl}_4/\text{HAT6}$, 1% $\text{HAuCl}_4/\text{HAT6}$, and 5% $\text{HAuCl}_4/\text{HAT6}$ by weight were prepared.

The polarizing optical microscopy (POM) images were obtained using an Olympus POM instrument, coupled with a Mattler heater. The samples were sandwiched between a glass slide and a cover slip. The sample was heated to the isotropic phase, and the textures were imaged during cooling. The transition temperatures and associated enthalpy values of the liquid crystalline phase of the samples were determined by differential scanning calorimetry (DSC) (Perkin-Elmer, model Pyris 1D) at a scanning rate of $5\text{ }^\circ\text{C min}^{-1}$ for both heating and cooling. Small-angle x-ray scattering (SAXS) studies were carried out using an x-ray diffractometer (Rigaku, UltraX 18) operating at 50 kV and 80 mA using $\text{Cu K}\alpha$ radiation having a wavelength of 1.54 \AA . The samples were prepared by filling a capillary with the pure discotic systems or the composites and then sealing it. All the scattering studies were carried out at $80\text{ }^\circ\text{C}$, and the diffraction patterns were collected on a two-dimensional Marresearch image plate. A Perkin Elmer spectrophotometer with 1 cm path length cell was employed for the measurement of the UV-visible absorption spectra. Photoluminescence spectra were taken using a Fluoromax-4 (Horiba Jobin Yvon). The dc conductivity studies of the composites were carried out in indium tin oxide (ITO)-coated glass sandwich cells ($10\times 5\text{ mm}^2$) with a thickness close to $4\text{ }\mu\text{m}$. A slow cooling of the sample in the cell has been observed to results in the homeotropic alignment of the discotic molecules.^{19–22}

The alignment of the discotic liquid crystals has great influence in the measured conductivity, and this has been studied using different discotic cores such as triphenylene, phthalocyanine, and hexabenzocoronenes.^{23–26} The current measurements were carried out using a Keithley picoammeter (model 480) along with a constant dc voltage source and a temperature controller. Ionic conductivity measurements were carried out using a lock-in amplifier (Stanford Research Systems model SR830) at 1 kHz frequency. All the conductivity studies were carried out while cooling from the isotropic phase. The frequency response of the composite 1% $\text{HAuCl}_4/\text{HAT6}$ was carried out using the lock-in-amplifier, in the columnar hexagonal phase at a temperature of $80\text{ }^\circ\text{C}$. Cyclic voltammetry (CV) of pure HAT6 was carried out in dichloroethane solvent with 0.1M tetrabutyl ammonium tetrafluoroborate as a supporting electrolyte using a conventional three-electrode system. A model 263A potentiostat



FIG. 1. (Color online) Polarizing optical micrograph of the composite 1% $\text{HAuCl}_4/\text{HAT6}$, on cooling from the isotropic phase.

(EG&G) was employed for the studies using EChem software (EG&G). A platinum foil of area of 0.1 cm^2 was used as the working electrode and Ag/AgCl as a reference electrode. Another platinum foil of area of about 1 cm^2 constituted the auxiliary electrode. The redox peaks obtained for the samples were compared with ferrocene/ferrocenium reference system under identical conditions.

III. RESULTS AND DISCUSSION

Figure 1 shows the polarizing optical micrographic texture obtained for the composite 1% $\text{HAuCl}_4/\text{HAT6}$. The focal conic texture exhibited by the nanocomposite confirms that it retains the columnar hexagonal liquid crystalline phase. We find that the higher concentrations of HAuCl_4 (for example, in a composite of 5% $\text{HAuCl}_4/\text{HAT6}$) lead to a phase separation and to the total disruption of the liquid crystalline phase. Figure 2 shows the DSC traces for the 0.1%, 1% and 5% of $\text{HAuCl}_4/\text{HAT6}$ composites. It is clear from the plots that the phase transition profiles are not significantly changed even after the addition of HAuCl_4 at low concentrations. We have also observed that the Col_h phase is destabilized at very high concentrations of HAuCl_4 (for samples above 5% of HAuCl_4) which is in accordance with the POM results. The DSC traces show that the phase transition temperatures shift to lower temperature with increasing dopant concentration. As expected, the enthalpy of the phase transition decreases as the dopant concentration increases. This is due to the fact that the dopants increase the entropy of the nanocomposite system and at higher concen-

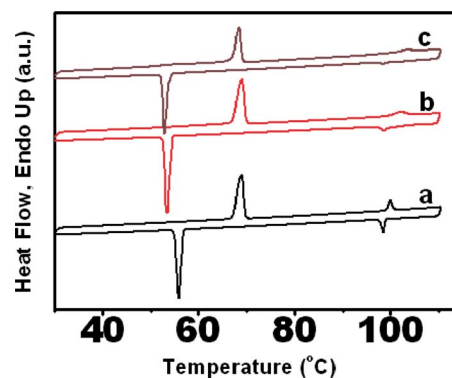


FIG. 2. (Color online) DSC traces for the composites: (a) 0.1% $\text{HAuCl}_4/\text{HAT6}$, (b) 1% $\text{HAuCl}_4/\text{HAT6}$, and (c) 5% $\text{HAuCl}_4/\text{HAT6}$.

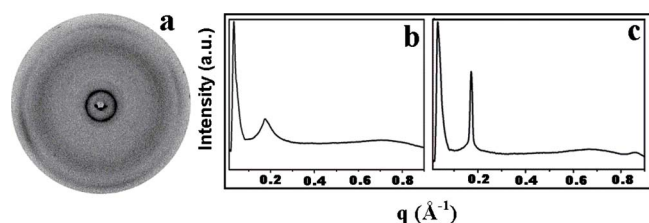


FIG. 3. (Color online) (a) SAXS profile for 1% HAuCl₄/HAT6 and the scattering vector vs intensity plot for (b) 0.1% HAuCl₄/HAT6 and (c) 1% HAuCl₄/HAT6 composites.

trations leads to the disruption of the liquid crystalline order. Moreover, as the concentration of HAuCl₄ increases, the concentration of HAT6 radical cation also correspondingly goes up. This weakens the π - π interaction within the column and leads to the destabilization of the liquid crystalline phase.

The liquid crystalline phase of the composites was further studied by the SAXS technique. The studies show that the intercolumnar separation is not disturbed by the addition of the dopants at lower concentrations. Figure 3 shows the diffraction pattern obtained for 1% HAuCl₄/HAT6 and the plot of scattering vector versus intensity for the composites 0.1% HAuCl₄/HAT6 and 1% HAuCl₄/HAT6. The diffraction pattern and the plots show the typical peaks of such systems and the d -value was measured to be 19.2 \AA , which is in agreement with the values for the pure HAT6 previously reported in the literature. The different peaks in both the plots follow the order $1 : \sqrt{3} : 2$, which confirms that the columnar hexagonal order is retained even after the addition of the dopants into the matrix.

UV-visible absorbance studies of the composites were carried out in dichloromethane with the neat solvent as the reference. Figure 4 shows the spectra of all the composites. The peaks at 430, 580, 630, and 830 nm are clear and can be attributed to the presence of HAT6 radical cation formed by the oxidation of HAT6 by AuCl₄⁻ ions.²⁷ The process of oxidation of HAT6 by AuCl₄⁻ results in a composite of the radical cation, (HAT6)⁺, and the reduced complex of monovalent gold, AuCl₂⁻. A very strong absorbance was observed at 360 nm. These bands have been attributed to the symmetrically allowed transitions.¹⁸ The peak at 280 nm (not shown in the figure) is assigned to the pure HAT6 molecule corresponding to a band gap of about 4.4 eV. The significant ab-

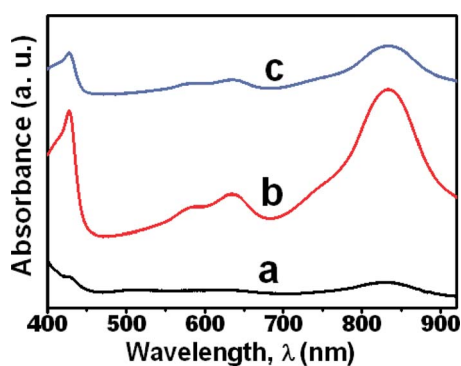


FIG. 4. (Color online) UV-vis spectra for the samples: (a) 0.1% HAuCl₄/HAT6, (b) 1% HAuCl₄/HAT6, and (c) 5% HAuCl₄/HAT6.

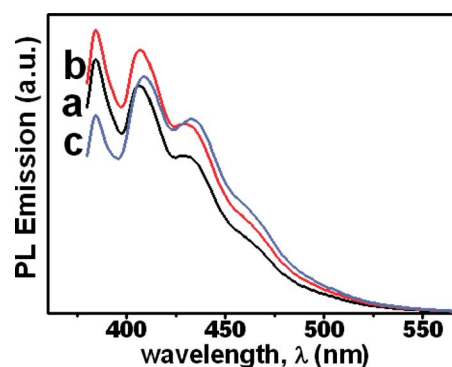


FIG. 5. (Color online) Photoluminescence emission spectra at an excitation at 360 nm for (a) pure HAT6, (b) 0.1% HAuCl₄/HAT6, and (c) 1% HAuCl₄/HAT6 systems.

sorbance by the composites throughout the visible range in the spectrum is quite interesting and points to its potential as a solar absorber.²⁸

Both photoluminescence emission and excitation spectra of the composites were taken in dichloromethane medium at a concentration of 1 mg/3 ml. Figure 5 shows the emission spectra at an excitation wavelength of 360 nm (the highest intensity peak in the UV-vis spectra for the pure HAT6). The emissions were observed at three wavelengths, 383, 406, and 433 nm. The intensity among these three was found to be highest for the 406 nm peak. Figure 6 shows the excitation spectra for the 406 nm band. Three excitation wavelengths were observed at 361, 353, 340, and a weak shoulder band at 300 nm corresponding to a band gap of 3.43, 3.51, 3.64, and 4.08 eV, respectively. The peaks can be assigned to the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, and $S_0 \rightarrow S_4$ transitions. It has been shown that the photoexcitation spectral lines such as $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ are symmetrically forbidden for the single discotic molecule, while the aggregation of the molecules makes them symmetrically allowed.²⁹

Figure 7 shows the temperature dependence of the dc conductivity for the composites during cooling from the isotropic phase. The electrical conductivity of pure HAT6 was $< 10^{-10}$ S/m and was below the lower limit of measurement in our setup. The plots in Fig. 7 show the variation in electrical conductivity with temperature for 0.1% AuCl₄⁻/HAT6 and 1% AuCl₄⁻/HAT6 composites. It can be seen from the plots that the conductivity increases by several orders of

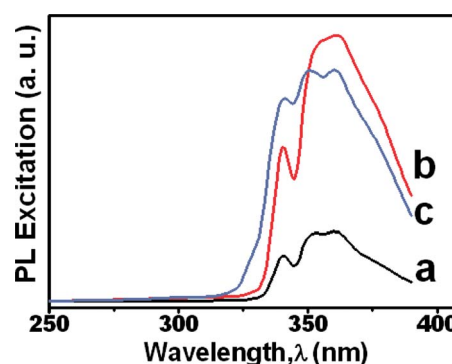


FIG. 6. (Color online) Photoluminescence excitation spectra for the emission band at 406 nm for the samples: (a) pure HAT6, (b) 0.1% HAuCl₄/HAT6, and (c) 1% HAuCl₄/HAT6 systems.

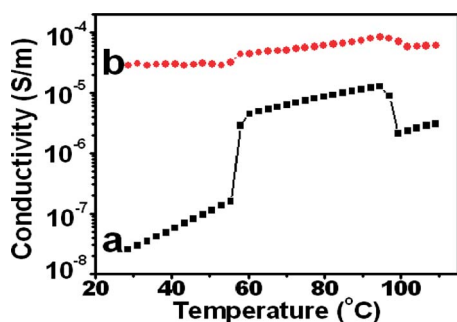


FIG. 7. (Color online) Plots of dc conductivity values as a function of temperature for the composites: (a) 0.1% HAuCl₄/HAT6 and (b) 1% HAuCl₄/HAT6.

magnitude after the doping. It can be seen that there is a clear and significant change in the electrical conductivity at the temperatures corresponding to phase transitions. We have observed that the conductivity of the crystalline phase is very much lower than the columnar hexagonal phase. We previously reported a similar behavior for the ferrocenium composite with HAT6 and HHTT.¹⁷ We attribute this remarkable enhancement in dc conductivity in the present system to the formation of HAT6⁺ radical cations along the columns which provides a quasi-one-dimensional path for the transport of charges. In the isotropic phase, the conductivity again decreases due to the disruption of the columns indicating that the major contribution for the conductivity comes from the columnar hexagonal order of the composites. This unusual behavior makes the present system unique in its manifestation of quasi-one-dimensional conductivity in the liquid crystalline phase.

The ac conductivity behavior of these composites shown in Fig. 8 is also interesting as the values are quite high and are comparable to that of dc conductivity values. This is very important from the point of view of understanding the mechanism of conductance. It has been previously observed that the addition of dopants such as AlCl₃ and iodine increases the ionic conductivity of the columnar phase by about a million times.^{9,19} The present systems behave in a similar manner exhibiting an increase in both the ionic conductivity as well as dc conductivity. Figure 8 (inset) shows a plot of ionic conductivity as a function of frequency. It can be seen from the plot that the ionic conductivity is almost constant at the low frequency region while increasing rapidly

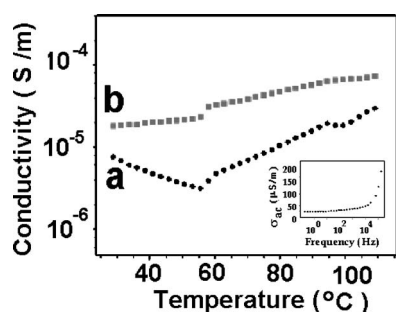


FIG. 8. Plots of ionic conductivity values as a function of temperature for the composites: (a) 0.1% HAuCl₄/HAT6 and (b) 1% HAuCl₄/HAT6. The inset shows the ac conductivity (σ_{ac}) of 1% HAuCl₄/HAT6 as a function of frequency.

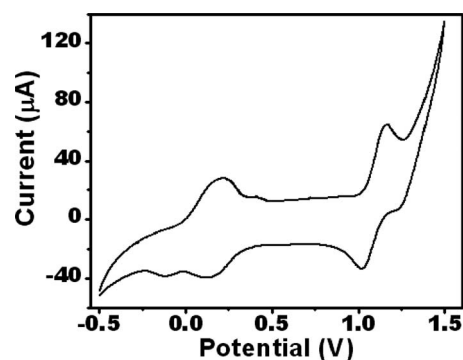


FIG. 9. Cyclic voltammogram of HAT6 in 0.1M tetrabutylammonium tetrafluoroborate in dichloroethane. The potential shown is with respect to Ag/AgCl reference electrode.

at higher frequencies. We find that the conductivity follows a $\omega^{0.8}$ dependence at high frequencies and this has been attributed to the hopping or tunneling of charge carriers⁹ within the columns while the frequency-independent conductivity at low frequencies is attributed to slower transition rates due to the structural defects within the columns.³⁰ The enhancement in ac conductivity can be attributed either to the presence of ionic dopants or due to the formation of radical cations in the system. Previously, using AlCl₃/HAT6 composites, it was proposed that the contribution of the counterions to the ionic conductivity was significantly less compared to the electronic migrations, since the counterions would be almost frozen between the alkyl chains of the discotic molecules.⁹ We have earlier observed that doping with ferrocenium tetrafluoroborate did not increase the ionic conductivity even though it forms a charge-transfer complex with the discotic molecules.¹⁷ In the present system, the dopants form charge-transfer complex, thereby generating radical cations of the discotic molecules. From these observations, it is inferred that the very high ionic conductivity of the present composites can be attributed to the formation of radical cations of HAT6.

The CV of pure HAT6 in dichloroethane with 0.1M tetrabutylammonium tetrafluoroborate as the supporting electrolyte is shown in Fig. 9. The first peak during the forward cycle in the CV corresponds to the oxidation of HAT6 to HAT6 radical cation, which occurs at -0.35 V with respect to ferrocene/ferrocenium reference electrode. The second peak seen in the figure at high positive potential is due to the formation of oxides of Pt on the electrode surface. At this positive potential triphenylene is also oxidized, but merges with the PtO peak and therefore could not be resolved in the CV. We have also found in another experiment that the oxidation of gold to its oxides takes place at $+0.64$ V versus ferrocene/ferrocenium reference electrode (not shown in the figure). In other words, the potential of oxidation of the HAT6 to HAT6 radical cation occurs at far more negative potential compared to that of gold. This large difference in the potentials of oxidation of these two species (HAT6 and Au) shows that the formation of HAT6 radical cation is energetically favored by the reduction of Au³⁺ to Au⁺. On the other hand, the absence of any surface plasmon band in

the UV-vis spectra of the nanocomposite rules out the possibility of the complete reduction to gold nanoparticles by HAT6.

The present composites have very high dc conductivity, which is comparable to the systems earlier reported for the columnar systems doped with gold nanoparticles^{11,31} or ferrocenium ions.¹⁷ The dc conductivity of columnar discotic systems may arise either due to the hole hopping or electron tunneling mechanism. In the present case, due to the facile formation of the radical cations of HAT6, the hopping mechanism should be more favored. The fact that the ionic conductivity of the doped system is also quite significant and comparable to dc conductivity means that the HAT6 radical cations are the dominant charge carriers in the composite.

It was shown by Boden *et al.*²⁰ that the conductivity is dominated by hole mobility, on the basis of the work function difference between the ITO and HAT6 with the cell configuration of ITO/HAT6/ITO. The hopping mobility is weakly dependent on the temperature while the electron mobility is temperature dependent with activation energy (E_a) that follows the form²⁰

$$\mu_b^e \sim \mu_0 e^{-E_a/kT},$$

where μ_b^e is the electron mobility at temperature T , μ_0 is the mobility at absolute zero, and k is the Boltzmann constant.

The activation energies for the conductivity in the liquid crystalline phase of the present systems are calculated from the Arrhenius plots of conductivity (σ) as a function of ($1/T$). For the 0.1% HAuCl₄/HAT6 composite, the activation energy E_a was measured to be 0.35 eV, and that for 1% HAuCl₄/HAT6, it was 0.2eV. These values are significantly lower than the reported value of about 0.5 eV for the pure HAT6 system^{19,32,33} and phthalocyanine system³⁴ with electron transport as the dominant charge transport phenomenon. This supports the hopping mechanism as a dominant mode of transport of the charge carriers in these doped systems. Moreover, as the concentration of the dopant, HAuCl₄ is increased from 0.1% to 1%, the concentration of HAT6 radical cations resulting from charge-transfer process also increases correspondingly. This increase in the concentration of HAT6 radical cations further lowers the activation energy for the conductance and provides a facile transport pathway for the charge transport in the composites.

IV. CONCLUSION

The systems described here show very high ionic conductivity that is comparable to the dc conductivity values. Systems with very high electronic as well as ionic conductivities may provide several promising advantages over systems with only electronic or ionic conductivity. Moreover, the photon absorption of the present system in the full visible region makes it an interesting candidate for the solar cells. A higher absorption in the near IR region is more promising as the sun emits a major flux in this region, which increases the external quantum efficiency for the solar cell and photovoltaic device applications.³⁵⁻³⁷ Since the high conductivity of the present system originates from the columnar arrangement of the hexagonal phase under normal ambient conditions, it

may help to overcome some of the major problems associated with the quenching of charge carriers by moisture that is observed in similar systems.

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- ¹S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana, J. Phys.* **9**, 471 (1977).
- ²N. Boden, R. J. Bushby, J. Clements, and B. Movaghar, *J. Mater. Chem.* **9**, 2081 (1999).
- ³S. Kumar, *Chem. Soc. Rev.* **35**, 83 (2006).
- ⁴S. Sergeyev, W. Pisula, and Y. H. Geerts, *Chem. Soc. Rev.* **36**, 1902 (2007).
- ⁵S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, and M. Tosoni, *Angew. Chem., Int. Ed.* **46**, 4832 (2007).
- ⁶L. S. Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, and J. D. MacKenzie, *Science* **293**, 1119 (2001).
- ⁷I. Seguy, P. Destruel, and H. Bock, *Synth. Met.* **111-112**, 15 (2000).
- ⁸V. S. K. Balagurusamy, S. K. Prasad, S. Chandrasekhar, S. Kumar, M. Manickam, and C. V. Yelamagadd, *Pramana, J. Phys.* **53**, 3 (1999).
- ⁹N. Boden, R. J. Bushby, and J. Clements, *J. Chem. Phys.* **98**, 5920 (1993).
- ¹⁰N. Boden, R. J. Bushby, A. N. Cammidge, J. Clements, R. Luo, and K. J. Donovan, *Mol. Cryst. Liq. Cryst.* **261**, 251 (1995).
- ¹¹S. Kumar, S. K. Pal, P. S. Kumar, and V. Lakshminarayanan, *Soft Matter* **3**, 896 (2007).
- ¹²N. Boden, R. J. Bushby, and J. Clements, *J. Mater. Sci.: Mater. Electron.* **5**, 83 (1994).
- ¹³G. B. M. Vaughan, P. A. Heiney, J. P. McCauley, Jr., and A. B. Smith III, *Phys. Rev. B* **46**, 2787 (1992).
- ¹⁴S. Chandrasekhar and V. S. K. Balagurusamy, *Proc. R. Soc. London, Ser. A* **458**, 1783 (2002).
- ¹⁵N. Boden, R. J. Bushby, J. Clements, M. V. Jesudason, P. F. Knowles, and G. Williams, *Chem. Phys. Lett.* **152**, 94 (1988).
- ¹⁶D. Markovitsi, H. Bengs, and H. Ringsdorf, *J. Chem. Soc., Faraday Trans.* **88**, 1275 (1992).
- ¹⁷P. S. Kumar, S. Kumar, and V. Lakshminarayanan, *J. Phys. Chem. B* **112**, 4865 (2008).
- ¹⁸S. Marguet, D. Markovitsi, P. Millie, H. Sigal, and S. Kumar, *J. Phys. Chem. B* **102**, 4697 (1998).
- ¹⁹N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan, and T. Kreouzis, *Phys. Rev. B* **52**, 13274 (1995).
- ²⁰N. Boden, R. J. Bushby, J. Clements, and B. Movaghar, *J. Appl. Phys.* **83**, 3207 (1998).
- ²¹S. H. Eichhorn, A. Adavelli, H. S. Li, and N. Fox, *Mol. Cryst. Liq. Cryst.* **397**, 347 (2003).
- ²²J. K. Vij, A. Kocot, and T. S. Perova, *Mol. Cryst. Liq. Cryst.* **397**, 231 (2003).
- ²³H. Fujikake, T. Murashige, M. Sugibayashi, and K. Ohta, *Appl. Phys. Lett.* **85**, 3474 (2004).
- ²⁴H. Iino, J. Hanna, R. J. Bushby, B. Movaghar, B. J. Whitaker, and M. J. Cook, *Appl. Phys. Lett.* **87**, 132102 (2005).
- ²⁵H. Iino, Y. Takayashiki, J. i. Hanna, R. J. Bushby, and D. Haarer, *Appl. Phys. Lett.* **87**, 192105 (2005).
- ²⁶M. Kastler, F. Laquai, K. Mullen, and G. Wegner, *Appl. Phys. Lett.* **89**, 252103 (2006).
- ²⁷N. Boden, R. J. Bushby, J. Clements, and R. Luo, *J. Mater. Chem.* **5**, 1741 (1995).
- ²⁸I. A. Levitsky, W. B. Euler, N. Tokranova, B. Xu, and J. Castracane, *Appl. Phys. Lett.* **85**, 6245 (2004).
- ²⁹V. Duzhko, H. Shi, K. D. Singer, A. N. Semyonov, and R. J. Twieg, *Langmuir* **22**, 7947 (2006).
- ³⁰E. O. Arikainen, N. Boden, R. J. Bushby, J. Clements, B. Movaghar, and A. Wood, *J. Mater. Chem.* **5**, 2161 (1995).
- ³¹L. A. Holt, R. J. Bushby, S. D. Evans, A. Burgess, and G. Seeley, *J. Appl. Phys.* **103**, 063712 (2008).
- ³²D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, *Phys. Rev. Lett.* **70**, 457 (1993).

- ³³L. D. A. Siebbeles and B. Movaghar, *J. Chem. Phys.* **113**, 1609 (2000).
- ³⁴J. F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser, and S. J. Picken, *Liq. Cryst.* **6**, 577 (1989).
- ³⁵G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nature Mater.* **4**, 864 (2005).
- ³⁶W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).
- ³⁷M. M. Wienk, M. G. R. Turbiez, M. P. Struijk, M. Fonrodona, and R. A. J. Janssen, *Appl. Phys. Lett.* **88**, 153511 (2006).