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**PAPER** Paul H. J. Kouwer and Georg H. Mehl Hierarchical organisation in shapeamphiphilic liquid crystals **FEATURE ARTICLE** Slobodan Ž umer *et al.* Liquid crystal elastomer–nanoparticle systems for actuation



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### Hierarchical organisation in shape-amphiphilic liquid crystals<sup>†</sup>

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Shape-amphiphilic liquid crystals offer a route towards complex assemblies at the difficult 10 nanometer length scale. We present the preparation and mesomorphic characterisation of three novel shape amphiphiles based on azobenzenes. Their mesophases range from a simple nematic to complex lamellar phases of alternating layers of discotic and calamitic mesogens. In all smectic phases, the discotic and calamitic moieties are nanophase separated. As the different sub-layers start to tilt and/or display in-layer order independently, the mesophase assignment becomes more complex. Using temperature dependent X-ray diffraction we studied their characteristics.

#### Introduction

In liquid crystals order is combined with fluidity. The organisation in liquid crystals can be tuned at the molecular scale, but also much beyond that, on the macroscopic level, by using both alignment layers as well as external stimuli, such as magnetic, electric and optical fields. The control at multiple length scales makes liquid crystals ideal candidates for their use as active components or scaffolds in self-assembly processes.

Control over the organisation at the nanometer level has been targeted by many different routes. A classical approach is the combination of two incompatible units, inducing phase separation at the sub-molecular level. Incompatibility of ionic head groups and one or multiple aliphatic tails<sup>1,2</sup> forms the basis of selforganisation schemes of surfactants, which find wide application in industry and daily life, but also form the building blocks of complex systems in Nature. Over time, other schemes for nanophase segregation have also been developed, such as rigid/flexible systems (among which there are many thousands of liquid crystals), polar/apolar<sup>3</sup> and hydrocarbon/fluorocarbon<sup>4</sup> materials, as well as systems based on the differences of the shapes of the (sub)molecular units. Shape-amphiphilicity<sup>5</sup> is currently receiving increased attention. After it was shown that an appropriate choice of the molecular disc-rod geometry yielded rich phase behaviour,6 an increasing number of reports were published.<sup>7</sup>

A particularly attractive aspect of disc-rod geometries is that order at the 10 nm scale can be established. Although important for many photophysical processes, this length scale remains hard to target by either bottom-up or top-down approaches. The smectic disc-rod systems introduce two chemically different moieties that can carry individual functions. In addition, their order can be tuned independently. This forms an interesting basis for the design of complex self-assembly in bulk materials. Previously, we have shown a number of examples that show

1564 | J. Mater. Chem., 2009, 19, 1564-1575

a variety of mesophases, induced by the combination of discshaped and rod-shaped liquid crystals.<sup>6a,d</sup> In this contribution, we will discuss the organisation of a series of novel of shapeamphiphilic mesogens based on azobenzenes (see Fig. 1). Azobenzenes are well known to display *cis-trans* isomerisation upon irradiation with UV and visible light. In the field of liquid crystals, this property has been successfully applied to prepare photoalignment layers, but the versatility and easy accessibility of azobenzenes allow their application in many other fields requiring optical switching, for instance displays and optical



Fig. 1 Investigated disc-rod mesogens 1–3.

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recording.<sup>8</sup> Key in many applications, however, is the control of the organisation in these materials on the nanometer level. Our results show that highly organised systems can be achieved, while a high molecular mobility is maintained. The order in these systems can be fine-tuned by changing the discotic group and its functionality.

#### **Results and discussion**

#### Synthesis

The synthesis of the linked disc rod mesogens proceeded in a modular manner. Separately, the functionalised disc-shaped and rod-shaped mesogens were prepared. The calamitic moieties were linked using a gallic acid group and, in the final step of the synthesis, this trimer was coupled to the discotic mesogens. This modular approach was designed to generate a substantial number of shape-amphiphilic liquid crystal dimers from a limited number of starting materials, allowing a systematic study of the properties of this relatively new class of materials. Synthesis procedures and characterisation are provided in the ESI.<sup>†</sup>

The azobenzene mesogen was obtained in high yields by reacting the diazonium salt of 4-pentylaniline with phenol, see Scheme 1. The product was alkylated with an excess of dibromohexane under straightforward Williamson etherification conditions to yield **6**. Subsequent etherification under similar conditions with ethyl gallate yielded the "rod-trimer" mesogen **7**, which was fully characterised. Saponification of the carboxylic ester group under basic conditions yielded the free carboxylic acid **8** quantitatively. The poor solubility of **8** in a wide variety of organic solvents limited our ability to characterise the product and, hence, **8** was used in subsequent steps without further purification.

The bifunctional triphenylene was prepared *via* the classical biphenyl route,<sup>9</sup> see Scheme 2. Catechol was equipped with two undecyl spacers *via* a Williamson etherification and the aliphatic



Scheme 1 Synthesis of the linked-rod mesogens 7 and 8. Key: (*i*) 1. NaNO<sub>2</sub>, aq. HCl, 0 °C 1 hr, room temperature 1 hr; 2. PhOH, aq. NaOH, addition at room temperature, then heat to reflux 4 hrs, 86%. (*ii*) Br(CH<sub>2</sub>)<sub>6</sub>Br (excess), K<sub>2</sub>CO<sub>3</sub>, KI, butanone, heat reflux 16 hrs, 74%. (*iii*) K<sub>2</sub>CO<sub>3</sub>, KI, butanone, heat to reflux 16 hrs, 62%. (*iv*) 1. aq. KOH MeOH/THF (1:1), heat to reflux 4 hrs; 2. aq. HCl, quantitative.



Scheme 2 Synthesis of the bifunctional triphenylene 13. Key: (*i*)  $Br(CH_2)_{11}OH$ ,  $K_2CO_3$ , KI, butanone, heat to reflux 40 hrs. (*ii*) AcCl,  $C_5H_5N$ ,  $CH_2Cl_2$ , room temperature for 70 hrs, 67% over 2 steps. (*iii*) 1. FeCl<sub>3</sub>,  $CH_2Cl_2$ , room temperature for 20 hrs; 2. dry MeOH, 62%. (*iv*) Ethanol, *para*-toluenesulfonic acid, heat to reflux for 2 hrs, 98%.

alcohol functionalities were protected by acetyl groups from the oxidising conditions of the triphenylene reaction. Tetrahexyloxybiphenyl was prepared according to literature procedures.<sup>6d</sup> Oxidative coupling of **11** and **12** and subsequent removal of the acetyl protecting groups under acidic conditions yielded the bifunctional triphenylene **13**.

The synthesis of discotic mesogens 14 and 15 was described previously.<sup>6d,10</sup> Coupling of 13–15 with the linked rod-shaped mesogens 8 gave the target compounds 1–3 in moderate yields, see Scheme 3. We found that the linked disc-rods are readily soluble and straightforward to purify using standard column chromatography techniques

#### Thermal behaviour

The thermal behaviour of the novel linked disc-rod mesogens and their precursors was studied by differential scanning calorimetry (DSC, Fig. 2) and optical polarising microscopy (OPM, Fig. 3). The results are summarised in Table 1. Note that the mesomorphic properties of the mono-functional disc-shaped mesogens 14<sup>6d</sup> and 15<sup>10</sup> were published previously, but have been included here for comparison. Monofunctional triphenylene 14 exhibits a monotropic columnar phase, while 15 displays a broad, enantiotropic nematic phase. The bifunctional discotic mesogen 13 is not liquid crystalline and shows a melting



Scheme 3 Schematic representation of the synthesis of the target compounds 1–3. Key: (*i*) DCC, DMAP, pTSA, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 3–5 days, 42–65%.



Fig. 2 Normalised DSC traces of precursors 6 (blue) and 7 (green); and final products 1 (red, magnified  $2 \times$ ); 2 (orange) and 3 (purple). The (broad) glass transitions of 7 and 3 are visualised by magnifications of the DSC signal. The arrows indicate (small) transitions. Phases are indicated in the figure (cooling traces), monotropic phases between square brackets.

temperature of 82 °C. Both azobenzene precursors 6 (monomer) and 7 (trimer) show, on cooling from the isotropic phase, a narrow nematic range, followed by a SmA phase. The nematic phase of both materials is characterised by an optical schlieren texture and a small latent heat value at the nematic-isotropic phase transition: for 6  $\Delta H_{\rm N-I} = 0.9$  kJ mol<sup>-1</sup> and for 7  $\Delta H_{\rm N-I} =$ 2.1 kJ mol<sup>-1</sup> for three mesogens, which corresponds to 0.7 kJ per mol mesogen. Also, the latent heat at the SmA-N transition is roughly three times larger for trimer 7 than for 6. At lower temperatures 7 shows a small transition to a more ordered smectic phase and below room temperature a second order transition to a glassy phase, which effectively freezes in the order of the SmX phase. Monomer 6 crystallises at low temperatures and exhibits on cooling a similar, but monotropic, SmX phase due to slow crystallisation kinetics. Complete characterisation of the organisation in the higher ordered smectic phases of 6 and 7 has not been pursued.

The linked disc-rod mesogen 1, with the strongly nematogenic discotic mesogen attached, shows a narrow nematic phase at elevated temperatures. OPM experiments of the nematic phase initially show a grainy texture; however, after annealing overnight, just below the clearing temperature, the domains grow and a marbled texture can be observed (Fig. 3a). DSC experiments show the characteristically small latent heat at the clearing temperature, which was observed for all nematic linked disc-rod



Fig. 3 Optical polarising microscopy photographs of (a) 1 at T = 80 °C (N phase; marbled texture); (b) 2 at T = 75 °C (SmA phase; a grainy texture right and a homeotropically aligned texture left); (c) 2 at T = 65 °C (SmX phase; light birefringent grainy texture); and (d) 3 at T = 92 °C (SmA phase; focal conic texture).

mesogens that we prepared so far.<sup>6a,d,e</sup> At lower temperatures a highly organised lamellar structure is obtained, most likely a soft crystalline phase. Introduction of the triphenylene-based mesogen in the disc-rod mesogen changes the phase behaviour dramatically. The triphenylene moiety, usually organised in two-dimensional positionally ordered columnar mesophases, excludes the formation of the nematic phase entirely. Instead, a SmA phase is observed for both **2** and **3**. Microscopy experiments show a grainy texture, even after annealing (Fig. 3b and c), in combination with the formation of homeotropic areas. The large latent heat values at the smectic to isotropic transition ( $\Delta H_{\text{SmA-I}} = 24.3$  and 45.8 kJ mol<sup>-1</sup> for **2** and **3**, respectively) are indicators of the exceptionally high degree of order established in these optically conventional SmA phases. X-Ray diffraction measurements, discussed later in the paper, confirm this.

#### Mixing studies of the nematic mesophases

Optical microscopy studies of contact samples of 1, 7 and 15 provided insight into the miscibility of the disc and rod-shaped species. Contact samples of 7 (calamitic) and 15 (discotic) showed homogeneous mixing in the isotropic phase at elevated temperatures. Upon cooling a broad region remained isotropic between the bulk mesophases of the two pure species. The isotropic range persisted at room temperature. This result shows

Table 1 Mesomorphic properties of the final products and the precursors

Mesogen	Mesophase behaviour <sup><i>a.b</i></sup>									
	CrX	72 (12.5)						N	81 (0.3)	I
2	Cr	43 (24.1)	$[SmY 43 (< 0.1)]^c$	SmX	69 (1.7)	SmA	81 (24.3)		~ /	Ι
3	G <sub>SmX</sub>	5		SmX	70 (4.4)	SmA	101 (45.8)			Ι
6	Cr	65 (29.2)			Ì, Î	SmA	79 (3.4)	Ν	84 (0.9)	Ι
7	G <sub>SmX</sub>	5		SmX	72 (2.3)	SmA	104 (8.1)	Ν	111 (2.1)	Ι
13	Cr	82 (57)			Ì, Î					Ι
14	Cr	55 (49)	$[Colh 51 (3.7)]^c$							Ι
15	Cr	132 (37)						Ν	246 (0.2)	Ι

<sup>*a*</sup> Transition temperatures in °C and corresponding latent heat values (between brackets) in kJ mol<sup>-1</sup>. <sup>*b*</sup> Abbreviations: Cr = crystalline;  $G_{SmX}$  = glassy phase with SmX texture frozen in; SmX/SmY = unknown smectic phase with in-layer positional order (see discussion); SmA = smectic A; N = nematic; I = isotropic. <sup>*c*</sup> Monotropic phase transition.

that, although 7 and 15 are miscible over the entire phase diagram, the formation of a nematic phase, or any other ordered phase for that matter, is strongly destabilised.

Contact samples of 1 and 7 showed (nearly) linear mixing behaviour, similar to what was observed for cyanobiphenyl systems.<sup>6b,c</sup> Also similar to these systems are the results of mixing studies between the linked disc-rod mesogen 1 with the discotic nematogen 15. In the centre of the phase diagram a minimum in the clearing temperature is found. By cooling the sample from the isotropic phase, initially a wide isotropic gap is observed, which slowly grows smaller by movement of both nematic-isotropic phase boundaries towards each other, see Fig. 4a–d. At T = 61°C, both nematic phases meet and a homogeneously mixed nematic phase is formed,<sup>6b,c</sup> see Fig. 4e. For 1/15, however, the nematic phase at this concentration is metastable and crystallises upon annealing, clearly seen in the reheated sample in Fig. 4f. The crystals appear exactly in the area of the minimum in the clearing temperature and slowly grow outward. After annealing, the crystalline phase melts in the reverse order; slowly from the sides to the centre area. A maximum clearing temperature of 91 °C is detected.

The monotropic phase behaviour of these mixtures hampered further investigation of the phase diagram in greater detail, but from the information available from the contact studies, a qualitative phase diagram can be sketched, see Fig. 5.

#### **X-Ray diffraction**

To further investigate the organisation of the new class of discrod liquid crystals, the materials were subjected to detailed X-ray diffraction (XRD) studies. The integrated diffractograms are shown as a function of the length of the scattering vector q:

$$q \equiv |\mathbf{q}| = \frac{4\pi \sin\theta}{n\lambda} \tag{1}$$

Here *d* is the spacing,  $\theta$  is half the diffraction angle, *n* is an integer and  $\lambda$  is the wavelength ( $\lambda = 1.54$  Å). Spacings were calculated from eq. (1) after fitting the intensities and determining the local maxima. Sharp peaks (Cr, SmX and small angle reflections in the SmA phase) were satisfactorily fitted with Gaussian distribution functions and diffuse peaks were fitted with Lorentzian functions. From the fits the half-width at half maximum (HWHM) of



**Fig. 4** Optical polarising microscopy photographs of contact samples of 1 (left) and **15** (right). Upon cooling from the isotropic phase with (rate: 1 °C min<sup>-1</sup>): (a) T = 78 °C; (b) T = 75 °C; (c) T = 70 °C; (d) T = 65 °C; and (e) T = 61 °C. All pictures taken at the same spot in the sample. Note that at lower temperatures the bulk of **15** and later also of **1** shows dark crystalline patches in the microscope. (f) The sample was annealed (2 hrs at 60 °C) and reheated to 78 °C, showing the monotropic crystals formed in the mixture sided by the isotropic regions of the mixture at different concentrations.



Fig. 5 Sketched phase diagrams of (left) 1/7 and (right) 1/15. Note that the relative fraction x was only estimated from contact sample experiments. 1/7 shows linear mixing between the two entities. The phase diagram of 1 and 15 shows a minimum in the clearing temperature at intermediate ratios and the induction of a crystalline phase with a maximum at a similar concentration. The latter can be supercooled giving rise to a narrow monotropic nematic phase (shaded area).

every reflection was determined, which is related to the extent of order in the mesophase, expressed by the correlation length  $\xi$  that can be calculated using the Scherrer equation:

$$\xi = 2\pi/\Delta q \tag{2}$$

where  $\Delta q$  is the half width of the reflection in reciprocal space.

Temperature dependent XRD measurements allowed us to analyse the evolution of the layer spacing in the different liquid crystal phases. The SmA phases of 2 and 3, as well as the SmX phase of 1, could be fitted satisfactorily with the empirically derived equation (3), commonly used to describe the temperature dependence of the tilt angle  $\theta_t$  of SmC phases:<sup>11</sup>

$$\theta_{\rm t}(T) = \kappa \left( \frac{T_{\rm Sm-Iso} - T}{T_{\rm Sm-Iso}} \right)^{\zeta} \tag{3}$$

Here  $\kappa$ , an empirical material parameter, is a fitting constant,  $T_{\text{Sm}\to\text{Iso}}$  is the transition temperature of the tilted smectic phase (commonly the SmC phase) and  $\zeta$  is the numerically determined critical exponent  $\zeta = 0.35$ .<sup>11</sup> Equation (4) defines the tilting angle as the ratio between the experimentally observed layer spacing d(T) and the layer spacing at zero tilt angle  $d_{\theta_1} = 0$ , *i.e.* the layer spacing that corresponds to the SmA phase and, in the case of limited interdigitation, to the molecular length.

$$\cos[\theta_{t}(T)] = \frac{d(T)}{d_{\theta_{t}=0}}$$
(4)

By combining equations (3) and (4) an expression for the layer spacing as a function temperature is obtained:

$$d(T) = d_{\theta_{t}=0} \cos\left[\kappa \left(\frac{T_{\text{Sm-Iso}} - T}{T_{\text{Sm-Iso}}}\right)^{\zeta}\right]$$
(5)

Equation (5) can be fitted to the experimental results from temperature dependent X-ray diffraction experiments using the free fitting parameters  $\kappa$  and  $d_{\theta_t} = 0$ . Although during the fitting procedure of the layer spacing at zero tilt ( $d_{\theta_t} = 0$ ) was set as a free fitting parameter, the resulting values for the molecular length (or twice the molecular length) have to match those obtained from molecular modelling studies. This correlation between layer spacings obtained from fits of the XRD data and those gained from calculated molecular lengths is an indication of the validity of this analytical approach.

In the higher ordered phases of **2** and **3**, the observed layer spacing showed a linear dependence on the temperature (equation 6), yielding values for both  $\alpha$  and  $\beta$ :

$$d(T) = \alpha + \beta T \tag{6}$$

The results of the X-ray diffraction measurements and the analysis will be discussed for all three final products individually.

The powder patterns of 1 in the isotropic, nematic and soft crystal phase are shown in Fig. 6. Fig. 7a shows the evolution of the radially integrated diffractograms with temperature. Quantitative results are summarised in Table 2. The diffraction pattern of 1 in the nematic phase shows weak alignment to the applied magnetic field. The pattern shows three diffuse halos at



**Fig. 6** Optical diffraction patterns of **1** at (a) 70  $^{\circ}$ C (CrX phase); (b) 80  $^{\circ}$ C (N phase) and (c) 100  $^{\circ}$ C (I phase).



**Fig. 7** (a) Integrated diffractograms of **1** as a function of temperature. Colour coding: red: isotropic; blue: nematic; orange: CrX. (b) Integrated diffraction patterns at T = 80 °C (blue) and T = 70 °C (orange). The inset shows the magnification of the two small angle reflections in the nematic phase, fitted by two Lorentzian distribution functions. (c) Temperature dependence of the layer spacing (open circles, left *y*-axis) and the correlation length (filled triangles, right *y*-axis). The solid line though the experimental data points represent a fit to equation (5).

small and wide angles (Fig. 6b). The wide angle reflection at 4.5 Å is attributed to the average distance between alkyl tails, convoluted with the distances along the short axes of the mesogenic components in the dyad (typically 4.5 Å for calamitics and 4.0–4.5 Å for discotics in the nematic phase). Two small angle halos are observed (see the inset in Fig. 7b) with spacings of 29.0 and 14.6 Å, respectively. Note that their different alignment to the magnetic field shows that B (14.6 Å) is not a higher harmonic of A, which also would not agree with a nematic organisation. The fact that both reflections are much smaller

 Table 2
 X-Ray diffraction data of 1 in the N and the CrX phase

T/°C	Phase	Reflection <sup>a</sup>	Peak shape <sup>b</sup>	$q/\mathrm{nm}^{-1}$	d/Å
80	N	А	d	2.2	29.0
		В	d	4.3	14.6
		$C_d$	d	14.0	4.5
70	CrX	002	S	1.14	55.0
		003	S	1.70	37.0
		004	S	2.26	27.8
		005	S	2.82	22.2
		007	S	3.96	15.9
		C <sub>d</sub>	d	14.4	4.4
		Cs	S	14.7	4.3
		D	S	15.7	4.0

<sup>*a*</sup> Reflections: Miller indices are used for layer reflections; diffuse reflections A–D are assigned: A, B = small angle reflection in the N phase (see inset in Fig. 7b);  $C_s/C_d = sharp/diffuse$  wide angle reflection in the SmX phase, always diffuse in the N and I phase; D = small wide angle reflection attributed to the face-to-face disc-disc distance. <sup>*b*</sup> d = diffuse, s = sharp.

than the total size of the dyad ( $\sim$ 55 Å as obtained from molecular modelling experiments) indicates that the discotic and calamitic components are homogeneously mixed in the nematic phase and no nanophase segregation between the two components occurs.

Upon cooling the sample, a highly ordered lamellar phase develops that shows multiple harmonics in the small angle area, see Fig. 7b. These (001) reflections and the absence of cross reflections highlight the strong one-dimensionality of the organisation in this phase. The non-uniform azimuthal distribution of the small angle reflections (Fig. 6a) shows that the alignment obtained in the high temperature nematic phase is retained. At wide angles the diffractogram is dominated by a single sharp reflection. Fitting of the experimental data reveals also a diffuse component under this peak. In addition, a shoulder is observed at 4 Å that was assigned to the face-to-face disc-disc distance (reflection D). Despite appearing rather sharp, its spacing and corresponding correlation length have characteristic values of a disordered (nematic-like) organisation.<sup>12</sup> The evolution of the layer spacing with temperature (Fig. 7c) shows a small but significant change. After fitting the experimental data to equation (5) an overall  $10^{\circ}$  tilt angle (averaged over the entire molecule) could be determined.

In the CrX phase, the system is clearly highly organised, but has no three-dimensional positional order, required for a formal crystal phase. The correlation length of the layer spacing is constant, but not very high ( $\xi_{002}/d_{002} = 6.9$ ), which indicates that the organisation in the CrX phase is more or less frozen in and that the molecules have a limited mobility. In this sense, the CrX phase may very well be a one-dimensional equivalent to the twodimensional columnar plastic phase, which is frequently observed for discotic liquid crystals. Fig. 8 summarises the structures of the two phases observed for 1.

The magnetic field in our XRD setup was too weak to align the SmA phase displayed by 2 and only azimuthally isotropic diffraction rings were obtained. The radially integrated spectra as a function of temperature are shown in Fig. 9; a summary of the reflections in the different phases is given in Table 3. In the isotropic phase, 2 shows only two diffuse halos.



Fig. 8 Sketch of the order in the mesophases of 1 (l = 55 Å). (a) Mixed nematic. Although biaxiality is likely at small length scales as a result of the large aspect rations of the components, we have no direct evidence for the formation of a biaxial nematic phase. (b) CrX: bilayered lamellar phase with in-layer organisation of both the calamitic and the discotic species (L = 110.9 Å). We have insufficient evidence to reliably discuss the tilt angles observed in the different layers, their correlation between subsequent layers or the correlation of the columnar phase normal (perpendicular to the smectic phase normal) between different layers.



Fig. 9 XRD results of 2. Integrated diffractograms of 2 as a function of temperature: (a) full pattern; (b) zoom of the small angle area. Colour coding: red: isotropic; light blue:  $SmA_d$ ; blue:  $SmA_2$ ; green: SmX; purple SmY (monotropic); orange: crystal.

 Table 3
 X-Ray diffraction data of 2 in both SmA phases and the higher ordered SmX and SmY phases

T/°C	Phase	Reflection <sup>a</sup>	Peak shape <sup>b</sup>	$q/\mathrm{nm}^{-1}$	d/Å
81	interdigitated SmA <sub>d</sub>	001	S	0.95	66.1
	u	002	s	1.87	33.6
		003	S	2.79	22.5
		004	S	3.71	16.9
		В	d	3.89	16.2
		С	d	14.5	4.3
79	bilayer SmA <sub>2</sub>	$002^{c}$	S	1.08	58.4
		003	S	1.58	39.8
		004	S	2.12	29.7
		005	S	2.65	23.8
		В	d	3.66	17.1
		007	S	3.71	17.0
		С	d	14.5	4.3
51	SmX	002	S	1.08	58.2
		003	S	1.58	39.8
		004	S	2.14	29.4
		005	S	2.64	23.8
		В	d	3.62	17.4
		007	S	3.72	16.9
		Cd	d	14.4	4.4
		C <sub>s</sub>	S	14.7	4.27
40	SmY	002	S	1.09	57.7
		003	S	1.58	39.7
		004	S	2.14	29.3
		005	S	2.65	23.7
		В	d	3.63	17.3
		007	S	3.72	16.9
		Cd	d	14.5	4.3
		Ċs	s	14.7	4.27

<sup>*a*</sup> Reflections: Miller indices are used for layer reflections; diffuse reflections B and C are assigned: B = reflection in layers of discotic moieties in SmA or SmX phase; C = wide angle reflection with a diffuse (C<sub>d</sub>) or sharp (C<sub>s</sub>) component. <sup>*b*</sup> d = diffuse, s = sharp. <sup>*c*</sup> Additional SAXS measurements elucidated the (small) fundamental reflection as well:  $q_{001} = 0.54$  nm<sup>-1</sup> and  $d_{001} = 116$  Å (T = 79 °C).

The difference with the SmA phase is striking. Many high order reflections are observable in the small angle area. The diffuse reflection in the wide angle area confirms the absence of long-range in-layer order, confirming the phase structure to be a SmA phase. A zoom of the small angle area (Fig. 9b) shows clearly the higher harmonics. Under the sharp reflections in the small angle area, a diffuse reflection, indexed B, is observed which is attributed to the packing of the discotic groups within the layer (best seen in Fig. 10). The diffuse character of this reflection highlights the short range positional order that is associated with the organisation of the discotic moieties. In other words, the two-dimensional organisation of the discotic moieties inside the layered structure is either isotropic or, more likely due to their large aspect ratio, nematic-like. Either way, the organisation will always be confined between two layers of calamitic mesogens and communication (i.e. long-range orientational order) between two adjacent layers of discotics seems unlikely.

Interestingly, the (006) reflection is entirely missing from the diffractogram, which we, at this moment, cannot explain by any means other than a non-systematic absence from the diffraction experiment. It is, however, noted that the (006) reflection is missing in the SmX phase of dyad 1 too.<sup>13</sup> The fundamental (001) reflection corresponds to a spacing >100 Å and is positioned behind the beam stop of our setup. It was observed at 117 Å

а



**Fig. 10** Integrated diffraction patterns at T = 79 °C (top), T = 80 °C (middle, both SmA phases coexisting) and T = 81 °C, all fitted by multiple Gaussian functions as well as one Lorentzian function (at  $q \sim 3.8 \text{ mm}^{-1}$ ). The pattern at 80 °C is a mixture of the SmA<sub>2</sub> phase at 79 °C and the SmA<sub>d</sub> at 81 °C. The solid lines represent the fits of the diffractograms, all obtained by a single multi-peak fitting procedure.<sup>14</sup>

 $(T = 79 \ ^{\circ}\text{C})$  during experiments recorded with a SAXS setup, albeit low in intensity compared to the (002) reflection.

A further interesting structural change was detected close to the transition from the isotropic liquid. As the SmA phase is formed at 81 °C, peak positions of the small angle reflections are remarkably different from those at 79 °C and at lower temperatures, see Fig. 10. Analysis shows that the structure of the SmA phase changes rapidly on cooling. The layer spacing at 80 °C was found to be 64 Å, which corresponds to a lamellar phase, where both the discotic and calamitic moieties are separated in sublayers but where the two classes of mesogenic groups are completely interdigitated (SmA<sub>d</sub>). The SmA phase that forms at 79 °C and below has a layer spacing of 117 Å, which corresponds to a bilayered structure of stretched mesogens (SmA2). The correlation lengths  $\xi$  of the lattice spacings of the SmA<sub>d</sub> and  $SmA_2$  phase are 457 and 359 Å, respectively. With the difference in the one dimensional lattice, this translates into 7.0 layers in the SmA<sub>d</sub> phase and only 6.1 layers in the SmA<sub>2</sub> phase. Although the material displays a higher degree of (one-dimensional) ordering in the SmA<sub>d</sub> phase, the substantial free volume it costs (based on a simple molecular model) causes the system to reorganise into the interdigitated bilayered phase at lower temperatures. This transition is a clear marker of the subtle forces and interactions that are involved in the phase formation in these shape-amphiphilic liquid crystals.



**Fig. 11** Temperature dependence of the layer spacing (open circles, left *y*-axis) and the correlation length (filled triangles, right *y*-axis). The colour coding of Fig. 9 has been used again. The solid lines through the experimental data points represent linear fits (soft crystal SmY and SmX phases) and a fit using equation (5) in the SmA<sub>2</sub> phase.

Fig. 11 shows how the layer spacing and the correlation length develop with temperature. Phase transitions are easily recognised as a discontinuity in the layer spacing and the related values for the correlation lengths (or the temperature derivatives thereof). Interestingly, at 81 °C in the SmA phase, the layer spacing shows a maximum, after which it gradually decreases on cooling; the common behaviour typically observed for a tilted phase. In fact, the experimental data of the (narrow) SmA<sub>2</sub> phase is best fitted with equation (5) that is often used to describe SmC phases. In the lower temperature SmX and monotropic SmY phase, the layer spacing shows a linear relation with temperature. The inflection point in  $d_{002}$  and  $\xi_{002}$  clearly marks the phase transition that initially was missed in the DSC experiments because of its small latent heat.

The soft-crystal CrZ phase at low temperatures is characterised by a number of additional reflections that do not correspond to a simple lamellar structure. In this phase the five (00l)reflections remain present, albeit with different intensities, indicating that this phase also possesses a strongly layered character. The limited number of cross reflections, however, do not allow us to index and characterise this phase further. The disappearance of the diffuse reflection B at 17 Å and the appearance of sharp reflections in this area point towards a change in the organisation of the triphenylene moieties at the SmY-CrZ transition, which we attribute to their organisation in columns. If one assumes that the direction of column formation is uncorrelated between the layers, a macroscopically highly disordered three-dimensional structure is expected. The reduced spacing of these reflections associated with the discs with lowering the temperature may indicate some tilting of the discs with respect to the layer normal, which in turn explains the continuing reduction of the layer spacing, also in the three-dimensional ordered phase, see Fig. 11.

The phase behaviour of **2** is graphically summarised in Fig. 12. In the  $\text{SmA}_d$  and  $\text{SmA}_2$  phases, the system shows a well-defined periodicity without in-layer positional order. The decrease in the layer spacing upon cooling is a signature of tilt within one of the layers (or both). This, in combination with the presence of homeotropic optical textures, is a signature of De Vries-type SmA phases,<sup>15</sup> as will be discussed later. At the transition to the SmX



Fig. 12 Sketch of the order in the mesophases of 2 (l = 58 Å). (a) SmA<sub>d</sub>: bilayer SmA phase wherein both layers are completely interdigitated (L = 66 Å). (b) SmA<sub>2</sub>: bilayer SmA phase without interdigitation (L = 118.5 Å). (c,d) SmX, SmY: bilayered lamellar phase with one of the layers showing positional order and further tilting of the mesogens in the layer. (e) Suggested crystal phase. It is important to stress that for all smectic phases shown here there is no correlation between the layers of the tilt angles of the mesogens or direction of the phase normal in the 2D ordered discotic layers.

phase, the layer of azobenzenes moieties shows in-layer positional order, while the XRD evidence suggests that the organisation in the layer of discotic mesogens does not change considerably.



**Fig. 13** Integrated small angle diffractograms of **3** at 90 °C (top) and 30 °C (bottom). The diffractograms are fitted by multiple Gaussian functions and two Lorentzian functions. The individual peaks fits are shown in orange lines, the cumulative fit function as a solid red line. The inset shows the small angle region as a function of temperature. Colour coding: red: isotropic; blue: SmA<sub>d</sub>; green: SmX.

In other words, this points toward an assembly behaviour where the sub-layer of the calamitic mesogens exhibits a soft crystal structure whereas the discotic sub-layer is still disordered or, at most, oriented in nematic like domains. The rapid further decrease in layer spacing in the monotropic SmY phase indicates an additional tilting process that could originate from the discotic moieties. The Cr phase at room temperature shows in-layer organisation in both the calamitic and the discotic layer.

The XRD pattern of 3 shows fewer features than observed for the dimers 1 or 2. It was not possible to align 3 in a magnetic field and as a result only azimuthally isotropic reflections were observed. Radially integrated spectra at different temperatures are shown in Fig. 13 and XRD data in different phases are given in Table 4.

Table 4	X-ray	diffraction	data	of 3	in	the	SmA <sub>d</sub>	and	the	SmX	phase
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T/°C	Phase	Reflection <sup>a</sup>	Peak shape <sup>b</sup>	$q/\mathrm{nm}^{-1}$	ď/Å
90	$SmA_d$	002	8	1.35	46.4
		004	S	2.70	23.3
		006	S	3.9	15.9
		В	d	4.05	15.5
		С	d	14.4	4.4
24	SmX	002	S	1.38	45.6
		004	S	2.74	23.0
		В	d	3.97	15.8
		006	S	4.09	15.4
		$C_d$	S	14.4	4.4
		C <sub>s</sub>	d	14.82	4.24

<sup>*a*</sup> Reflections: Miller indices are used for layer reflections; diffuse reflections B and C are assigned: B = reflection in layers of discotic moieties in SmA or SmX phase; C = wide angle reflection with a diffuse ( $C_d$ ) or sharp ( $C_s$ ) component. <sup>*b*</sup> d = diffuse, s = sharp.

In the SmA phase three layer spacings are observed, the first reflection (d = 49 Å) represents a spacing considerably smaller that the molecular length (l = 58 Å). The absence of a strong fundamental reflection in 1 and 2 encouraged us to interpret the XRD results of 3 analogously. This interpretation fits duly with a bilayered structure, but now with only the discotic mesogens completely interdigitated (SmA<sub>d</sub>). Considering that in 3 the cross section of the discotic groups was designed to be approximately half of that of the calamitic groups, this assembly model is very plausible. The first strong reflection in the small angle area is then the (002) reflection and further reflections are the higher harmonics. It is remarkable that for 3 (and in contrast to other disc-rod systems, presented here and before) only the even harmonics are observed.<sup>16</sup>

Fig. 13 shows the integrated diffractogram at 90 °C and the fits of the reflections. As described earlier for **2**, the small angle area shows, in addition to the sharp lamellar spacings, a diffuse halo at around 17 Å, assigned to the two-dimensional isotropic or nematic-like organisation of the discotic moieties. This reflection remains present (and diffuse) in the lower temperature SmX phase (Fig. 13). The major difference between the XRD patterns in the SmA<sub>d</sub> and the SmX phase in **3** is the sharpening of the wide angle reflection, which suggests the formation of in-layer organisation of the azobenzene mesogens. The inset in Fig. 13 shows a zoom of the small angle area with temperature measured on a SAXS setup. No small angle reflection could be observed. Even at low temperatures, the small angle region of the diffractogram remains unaltered.<sup>19</sup>

The temperature effect on the layer spacing (Fig. 14) shows a very similar picture to that observed for **2**. In the SmA<sub>d</sub> phase, the (002) spacings are satisfactorily fitted to equation (5). A high  $R^2$  value of the fit could be obtained because of the large temperature window of the SmA<sub>d</sub> phase, when compared to **2**. Incidentally this result strengthened our view that the layer spacing of the SmA phase of **2** can also be described best using equation (5). In the SmX phase, the layer spacing of **3** shows a linear dependence with temperature. At the transition, the correlation length of the layer spacing does not change considerably. It can be observed that the value for  $\xi_{002}$  in **3** ( $\xi_{002}/d_{002} =$ 14.4 at T = 90 °C) is much larger than for **1** or **2** ( $\xi_{002}/d_{002} = 6.1$  at



**Fig. 14** Temperature dependence of the layer spacing ( $\bigcirc$ , left *y*-axis) and the correlation length ( $\blacktriangle$ , right *y*-axis). Solid lines in the experimental data points represent data fits (power law in the SmA<sub>d</sub> phase, linear in the SmX phase). The same colour coding as in Fig. 9 was used.



**Fig. 15** Sketch of the order in the mesophases of 3 (l = 58 Å). (a) SmA<sub>d</sub>: bilayer SmA phase wherein the layer with the discotic mesogens is completely interdigitated. (b) SmX: lamellar phase similar to the SmA with in-layer positional order in the layer with the calamitic mesogens.

T = 79 °C). This enhanced lamellar organisation may be one of the reasons why further in-layer organisation is disfavoured, and hence no higher ordered phases are observed for **3**. A graphical interpretation of the mesophases of **3** is shown in Fig. 15.

#### Organisation and tilting in the smectic phases

The presence of the specific XRD reflections from the discotic moiety (reflections B and D) in the products allows us to evaluate the organisation of the different layers individually.<sup>17</sup> The pronounced difference in the organisation of the adjacent layers highlights a nomenclature problem in the identification of mesophases that consist of alternating layers of ordered calamitic mesogens (*e.g.* SmI or SmF phases) with disordered (nematic or isotropic) discotic mesogens.<sup>18</sup> Current procedures use miscibility studies for proper nomenclature, but for this class of complex materials such methods cannot be applied for mesophase assignment. In addition, we believe that calamitic or discotic mesogens with conventional mesophases may readily mix with these complex assemblies by simply inserting the liquid crystal into the appropriate layer, thereby expanding the layers without affecting the symmetry of the system.

Additionally, our microscopy results indicate the presence of optically uniaxial phases, whilst the XRD experiments show on cooling decreasing layer spacing for all lamellar phases. This behaviour is characteristic of so-called De Vries phases<sup>15</sup> in which the mesogens are tilted with respect to the layer normal, but as the direction of the tilt in subsequent layers is uncorrelated, the phases appear uniaxial under crossed polarisers. Cooling in a De Vries mesophase commonly results in a minor increase in the tilt angle and therefore a minor decrease in the layer spacing (as observed for **1–3**). In the design of materials exhibiting a De Vries SmA phase, the correlation between the layers is reduced by separating the mesogens with small incompatible blocks

Table 5 Fitting results of the temperature dependence of the layer spacing of 1-3

Mesogen	<i>ľ⁴/</i> Å	Phase	fitting parameters eq. (6)		fitting parameters eq. (5)			
			α/Å	$\beta/mÅ~K^{-1}$	$d_{002}(\theta_{\rm t}=0)/{\rm \AA}$	κ	$R^{2}/\%$	$\theta_t^{\ b}/^{\circ}$ at $(T/^{\circ}C)$
1	55.0	$CrX^c$	_	_	$55.0 \pm 0.1$	$0.43 \pm 0.01$	99.5	10.2(30)
2	58.0	$SmA_2^{c,d}$	$58.02 \pm 0.07$	$4.7\pm0.9$	$58.4 \pm 0.1$	$0.16 \pm 0.01$	71/76	2.7(70)
		$\mathrm{Sm}\mathrm{X}^{\overline{d}}$	$57.63 \pm 0.02$	$12 \pm 1$			99.7	6.8(48)
		$SmY^d$	$55.45\pm0.06$	$57 \pm 1$		_	99.0	9.9(36)
3	48.9	$SmA_d^c$			$46.4 \pm 0.1$	$0.28\pm0.02$	99.4	6.8(62)
		$SmX^d$	$41.24\pm0.05$	$15 \pm 2$	—	_	99.9	10.3(30)

<sup>*a*</sup> Molecular length *l* is calculated after minimisation of the (stretched) structure in Chem3D; for **3**, the full molecular length is 58.0 Å (same as **2**), but after considering full interdigitation of the discotic moieties a smaller value is calculated. <sup>*b*</sup> Tilt angle  $\theta_t$  determined from equation (5) or as the cosine of  $d_{002}(T)/d_{002}(\theta_t = 0)$ , the latter a result of the fitting procedure of a higher temperature phase. <sup>*c*</sup> Fit using equation (5). <sup>*d*</sup> Fit using equation (6).

(*e.g.* siloxanes and perfluorinated materials) at the terminal end of the tails.<sup>20</sup> The present case with a discotic mesogen positioned at the end of the tail could, in principle, be considered an extreme example of the above approach.

Table 5 summarises the observed tilting behaviour of 1–3 as determined by fitting the XRD analysis. Experimental layer spacings were either fitted linearly or to equation (5).<sup>11</sup> It is interesting to see that the different lamellar phases show rather different temperature dependences for the constants  $\beta$  and  $\kappa$  associated with the layer spacing, which in the absence of a wider set of materials and considering that the measured values are averages over both (different) moieties in the molecule is not surprising.

One of the fitting parameters of equation (5) is  $d_{\theta_t} = 0$ , which corresponds to the stretched molecular length of the mesogen *l* (taking into account interdigitation for **3**). For all materials, the fits give values close to those gained from calculating the fully extended molecular conformations. From these values and the experimental layer spacing, it is possible to deduce a tilt angle  $\theta_t$ , which, for all materials, is rather low. However, one has to take into account that this calculated tilt angle is an average value for the entire molecule. In the case that only part of the mesogen, for instance the azobenzene moieties, are tilting, the actual tilt will be much larger than the calculated average values. As an example, when only the azobenzene units are responsible for the observed tilt in the CrX phase of **1**, their tilt can be considered to be ~18°.

Tilting of one of the two layers, or indeed of both of the layers, is a straightforward means for the system to improve packing density by reducing small discrepancies in the cross sections of the discotic and calamitic layers. Therefore, this submolecular cross sectional ratio should be considered a key parameter to direct mesophase formation in such complex materials.

#### Conclusions

We have presented three novel liquid crystalline shapeamphiphiles based on azobenzenes and different discotic moieties. With a strong nematogen, like those based on pentakis(phenylethynyl)phenol, the shape-amphiphile exhibits a nematic phase, where the discs and rods are homogeneously mixed. This nematic phase is miscible with the nematic phases of the precursors, albeit that the mixture with the discotic nematogen shows a strong suppression of the clearing temperature in the phase diagram. The shape-amphiphiles with triphenylene groups show a variety of smectic phases. The highest temperature smectic phase is characterised by a relatively low viscosity, a homeotropic texture, sharp layer reflections and the absence of sharp wide angle reflections. All features are characteristic of a SmA phase. The ratio in cross sections of the rods and the disc determines the details of packing inside the layers: partly interdigitated for **3** and bilayer for **2**. Although the organisation of the azobenzene rods fits very well with the classical picture of a SmA phase, the discs inside the layer are forced into a two-dimensional structure, resulting in a SmA<sub>biax</sub> type organisation, dependent on the correlation length of the orientation order. Another example of such a structure has been recently published.<sup>21</sup>

The smectic phases at lower temperature are all characterised by some extent of in-layer organisation observed from the XRD experiments. However for 2 and 3 the limited number of reflections (only one) does not allow at present t the organisation in the azobenzene layer to be established (scattering from the discotic mesogens remains diffuse).

Notable is that in the systems where sub-layers of rods and discs occur, on further cooling the rod containing sub-layers organize first into higher ordered structures, whereas the disc rich sub-layers remain in a less ordered structure. We believe that this can be tuned by selecting proper disc-rod combinations.

Moreover, the combination of a uniaxial appearance in microscopy experiments and a slightly decreasing layer spacing with temperature suggests that all observed smectic phase have a De Vries-type character. This is not surprising, as the tilt directions of adjacent calamitic layers are expected to be completely uncorrelated due to the presence of the layer disordered discotics. It is noted that such behaviour is closely connected to that of liquid crystal dimers forming bilayer SmA phases.<sup>22</sup>

In short, we have presented three new members of the class of shape-amphiphiles exhibiting rich mesophase behaviour. The characterisation and phase assignment of the shape-amphiphiles is still in its infancy, but the advantages of such materials are apparent: combining an exceptionally high degree of organisation at the 10 nm level with the advantages that liquid crystals offer.

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