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Monodispersive Linear Supermolecules Stabilizing Unusual Fluid Layered Phases

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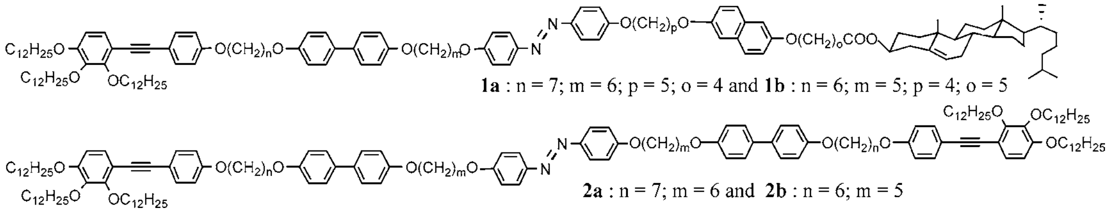
ABSTRACT



1a : n = 7; m = 6; p = 5; o = 4 and **1b** : n = 6; m = 5; p = 4; o = 5

2a : n = 7; m = 6 and **2b** : n = 6; m = 5

The first examples of monodisperse liquid crystalline pentamers, synthesized by covalently linking five mesogenic segments through four flexible spacers, exhibiting mono-/partially bilayered phases with unusual textures, as established by optical, calorimetric, and X-ray diffraction studies, are reported. Importantly, the two types of multifunctional pentamers, namely, unsymmetric and C_2 symmetric are soluble in organic solvents and exhibit analogous electrochemical features.

The creation of structurally diverse self-organizing functional single molecules, significant from both fundamental research and applications points of view, is a contemporary challenge for chemists.[1] This task, seems to be fulfilled, in part, by design and synthesis of multifunctional molecules stabilizing liquid-crystal (LC) phases, wherein they self-assemble into a variety of ordered fluid structures originating either from their parallel alignment or the nanosegregation of the immiscible molecular fragments,[2,3] which furnish, respectively, nematic (N) or layered (smectic: Sm) /columnar (Col) phases. For instance, some of these unique structures have the potential to serve as a soft medium for electron, ion, or molecular transporting, and in the fabrication of sensory, catalytic, and optical materials.[3−5] Of late, toward the further development of LCs with improved and tunable features, several giant molecular systems, called supermolecules, comprising covalently linked functional entities have been realized.[2c,5] Such LCs, unlike conventional (rodlike or disklike) systems, provide a variety of fluid structures with fascinating physical properties and functions.

One of the most important supermolecular examples are the linear oligomeric LCs (LOLCs) wherein two to several anisometric segments are covalently linked in end−end (axial) fashion to one another via flexible spacer(s).[6] Importantly, being monodisperse, their fluidity (viscosity) can be compared to those of low molar mass LCs but still displays transitional properties of polymers. So far, dimers,[6a−c] trimers,[6d,e] and tetramers[6f−h] comprising two, three, and four

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(1) (a) Lehn, J.-M. In *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, Germany, 2001. (b) Elemans, J. A. A. W.; Rowan, A. E.; Nolte, R. J. M. *J. Mater. Chem*. **2003**, *13*, 2661. (c) Kato, T. *Science* **2002**, *295*, 2414.

(2) (a) Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H. W.; Vill, V. In *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1998. (b) Tschierske, C. *J. Mater. Chem*. **2001**, *11*, 2647. (c) Tschierske, C. *Annu. Rep. Prog. Chem. Sect. C* **2001**, *97*, 191.

(3) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem*. **2006**, *45*, 38.

(4) Hamley, I. W. *Angew. Chem*. **2003**, *42*, 1692.

(5) Saez, I. M.; Goodby, J. W. *J. Mater. Chem*. **2005**, *15*, 26.

(6) (a) Imrie, C. T.; Henderson, P. A. *Curr. Opin. Colloid. Interface Sci.* **2002**, *7*, 298. (b) Tamaoki, N.; Moriyama, M.; Matsuda, H. *Angew. Chem.* **2000**, *39*, 509. (c) Mallia, A. V.; Tamaoki, N. *J. Mater. Chem*. **2003**, *13*, 219. (d) Imrie, C. T.; Henderson, P. A.; Seddon, S. M. *J. Mater. Chem*. **2004**, *14*, 2486. (e) Yelamaggad, C. V.; Hiremath, U. S.; Shankar Rao, D. S.; Krishna Prasad, S. *Chem. Commun*. **2000**, 57. (f) Yelamaggad, C. V.; Nagamani, S. A.; Hiremath, U. S.; Shankar Rao, D. S.; Krishna Prasad, S. *Liq. Cryst.* **2002**, *29*, 231. (g) Yelamaggad, C. V.; Nagamani, S. A.; Hiremath, U. S.; Shankar Rao, D. S.; Krishna Prasad, S. *Mol. Cryst. Liq. Cryst.* **2003**, *397*, 207. (h) Imrie, C. T.; Stewart, D.; Remy, C.; Christie, D. W.; Hamley, I. W.; Harding, R. J. M. *J. Mater. Chem*. **1999**, *9*, 2321.

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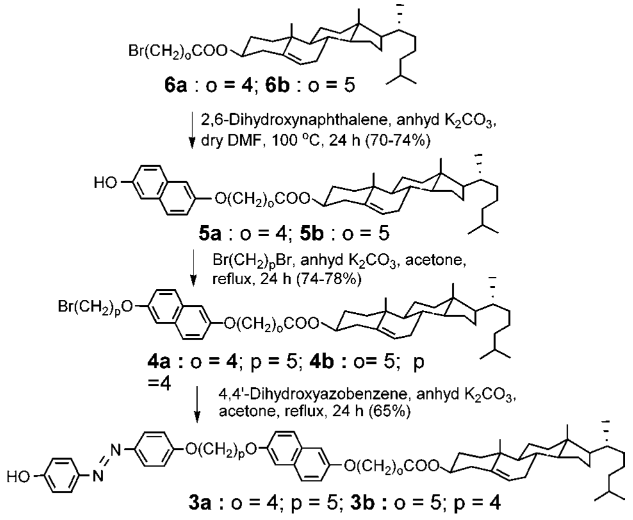
mesogens (separated by one, two, and three spacers), respectively, have been reported. These studies have demonstrated to an extent that by varying the chemical nature (functionality) of the constituent mesogens, as well as the length and parity of the spacer, a range of invaluable LOLCs exhibiting remarkable phase behavior, can be obtained.[6b−e] In fact, truly multifunctional LCs are the higher oligomers as they offer an elegant and innovative way of adding various requisite components. In addition, the organization of these giant molecules in the mesophase, appear to be rather intriguing.[6d−f] Despite such attractive features, the synthetic study has been limited to trimers and tetramers of symmetrical and nonsymmetrical types. In particular, investigations on the nonsymmetrical materials, in which the chemical nature of the constituent anisometric segments is different, have been scarcely reported. Surprisingly, the synthetic approaches to higher LOLCs, namely, pentamers, hexamers, etc. of any kind have not been, to our knowledge, reported hitherto. This can be ascribed to their immiscibility in organic solvents, making these LOLCs hard to purify.[7] Owing to their intrinsic structural diversity, the cumbersome synthetic pathways are necessary, which perhaps also impede their growth. Another important factor is that such designs may not support LC behavior.

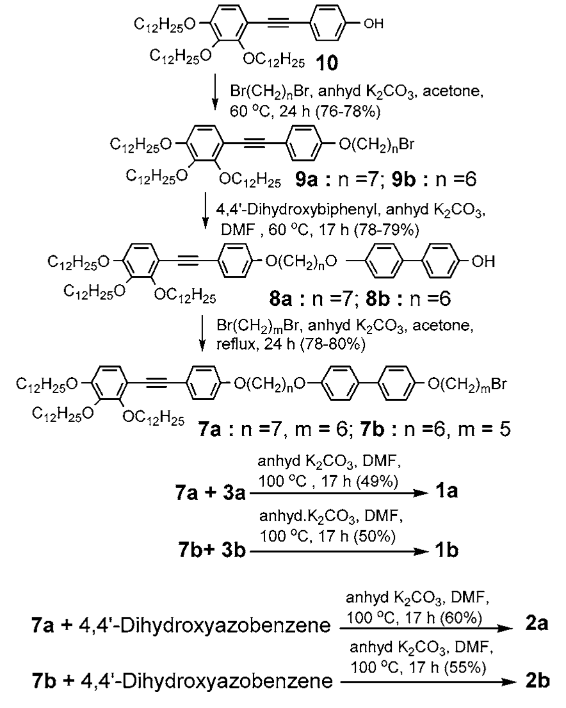
Here we report the first successful endeavor of design and synthesis of mesomorphic, as well as soluble, giant pentamers composed of five mesogenic segments interlinked through four flexible spacers varying in their length and parity. The design is considered to provide functional diversity and maximize the probability of mesophase formation. In particular, two sets of both nonsymmetric, **1a**,**b**, and C_2 symmetric, **2a**,**b**, pentamers have been synthesized. The pentamers **2a**,**b** comprise tolane (half-disc),[6f,g] biphenyl (promesogenic,),[2a] azobenzene (photoactive)[8] mesogenic cores; whereas pentamers **1a**,**b** contain cholesterol (chiral, promesogenic, thermochromic,)[9] and naphthalene (mesogenic, kinked)[10] entities, additionally. The synthesis of pentamers **1a**,**b** and **2a**,**b** required the preparation of key precursors **3a**,**b** and **7a**,**b**. Schemes 1 and 2 illustrate the synthesis of these as well as target molecules. Williamson ether synthesis protocol was used for all the transformations.[11] Cholesteryl ω-bromoalkanoates (**6a**,**b**),[6g] were reacted with 3-fold excess of 2,6-dihydroxynaphthalene to obtain monofunctionalized naphthols **5a**,**b,** which, on refluxing with $\propto,\omega$-dibromoalkanes, yielded monobromides **4a**,**b**. Treatment of 4,4′-dihydroxyazobenzene[6g] in large excess with **4a**,**b** furnished **3a**,**b**. Scheme 1 depicts the above-mentioned reaction sequences. As shown in Scheme 2, the condensation of diphenylacetylene (tolane) **10**,[6g] with 3-fold excess of dibromoalkanes led to bromides **9a**,**b**, which reacted with 4,4′-dihydroxybiphenyl in excess to obtain **8a**,**b.** These phenols were converted to **7a**,**b**. Finally, pentamers **1a**,**b** and **2a**,**b** were obtained in almost excellent yieds by reacting **7a**,**b** with **3a**,**b** and **7a**,**b** with 4,4′-dihydroxyazobenzene, respectively.

Scheme 1. Synthesis of Key Intermediates **3a**,**b**



All the intermediates were thoroughly purified by column chromatography, while the pentamers were purified by repeated recrystallization in hot DMF. The pentamers were found to be readily soluble in some of the common organic solvents. The UV−visible spectrum, of **1a**,**b** showed absorption maxima at 318 and 355−358 nm, while **2a**,**b** showed an absorption maximum at 360 nm. The ^{1}H and ^{13}C NMR

Scheme 2. Synthesis of Precursors **7a**,**b** and Target Pentamers



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(7) For example, several linear pentamers prepared earlier in our laboratory were found to be insoluble solids with very high melting points.

(8) (a) Ikeda, T.; Sasaki, T.; Iehimura. K. *Nature* **1993**, *361*, 428. (b) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shino, T.; Ikeda, T.; Tamai, N. *J. Am. Chem. Soc.* **1997**, *117*, 7791. (c) Mallia, A.V.; Tamaoki, N. *Chem. Commun.* **2004**, 2538. (d) Nair, G. G.; Krishna Prasad, S.; Yelamaggad, C. V. *J. Appl. Phys.* **2000**, *87*, 2084.

(9) (a) Tamaoki, N. *Adv. Mater.* **2001**, *13*, 1135. (b) Mallia, A. V.; Tamaoki, N. *Chem. Soc. Rev.* **2004**, *33*, 76.

(10) (a) Lauk, U. H.; Skrabal, P.; Zollinger, H. *Helv. Chim. Acta* **1985**, *68*, 1406. (b) Duffy, W. L.; Jones, J. L.; Kelly, S. M.; Minter, V.; Tuffin, R. *Mol. Cryst. Liq. Cryst.* **1999**, *332*, 91.

(11) See Supporting Information for details.

spectra obtained were found to be in complete consonance with the proposed structure; FAB mass and microanalytical data further confirmed the molecular structure (SI) of pentamers. The LC behavior of these compounds was probed by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) studies; the phase transition temperatures and associated enthalpy values obtained are shown in Table 1.

Table 1. Phase Sequence, Transition Temperatures (°C),[a] and Enthalpies (J/g) of Pentamers **1a**,**b** and **2a**,**b** (Heating/Cooling)

1a: Cr 131.7 [39.4] M_1 164.6 [12.7] I 163.3 [12.4] M_1 92.5 [23.6] Cr
1b: Cr 132.3 [14.9] M_1 198.3 [14.1] I 193 [15.9] M_1 88.5 [1.5] Cr
2a: Cr 158.1 [17] M_2 174.7 [11.1] I 173.7 [11.8] M_2 147.8 [23.9] Cr
2b: Cr 99.7[b] [39.4] M_2 154.2 [11.2] I 153.4 [10] M_2 96.3 [4.9] Cr

[a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C/min. [b] Cr to Cr transitions was observed at 78.3 [4.8]. Cr = Crystal, M_1= A monolayer smectic phase; M_2 = An intercalated smectic phase; I = Isotropic phase

Despite the fact that the unsymmetrical pentamers **1a**,**b** possess a different set of spacers, they displayed an identical enantiotropic mesophase (M_1) phase. However, a pronounced alternation can be seen for the isotropic (I) to M_1 phase-transition temperatures; pentamer **1b** exhibits a higher value than **1a** indicating that the overall molecular shape of the latter system is bent. Compound **1a** or **1b** placed between a glass slide and cover slip, upon heating, melt into the M_1 phase with a nonspecific texture, which remains unaltered till the clearing point. The melting and clearing temperatures seen by POM are in good agreement with the DSC peaks; the large enthalpy values associated with these transitions are indicative of the M_1 phase being a highly ordered mesophase. Slow cooling (0.5−1 °C/min) of the liquid led to the formation of M_1 exhibiting a low birefringent mosaic texture (Figure 1a), which on shearing transforms to a pseudoisotropic texture indicating that the molecules **1a**,**b** prefer homeotropic alignment. The low birefringence mosaic texture may suggest the phase to be the smectic Q (SmQ) phase.[12] However, as we shall see later, the XRD studies do not support this conjecture. On cooling the sample at a rate of 3−5 °C/min from the isotropic phase, a nonspecific pattern (Figure 1b) was formed. Notably, the usage of slides treated for planar or homeotropic orientations yielded identical textures indicating that any aligning influence of the substrate is ineffective for the M_1 phase. The electrical switching studies revealed that the M_1 phase is apolar.

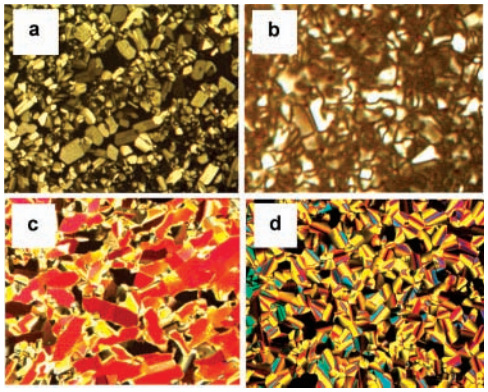

Figure 1. Microphotographs of the textures obtained for the mesophases of pentamers: (a) M_1 phase at 158 °C of **1a** obtained during slow cooling; (b) M_1 phase at 134 °C of **1a** formed during fast cooling; (c) **2a** at 170 °C; (d) **2b** at 147 °C.

The C_2 symmetric pentamers **2a**,**b** consisting of different sets of four spacers exhibit enantiotropic single mesophases differing slightly in their textures. However, the miscibility as well as XRD studies revealed that the structures of these phases are indistinguishable. Thus, it may be sensible to consider that both pentamers stabilize an identical mesophase, which we abbreviate as M_2 phase. Compound **2a** when placed between either treated or untreated glass slides and cooled from isotropic liquid, exhibits the M_2 phase appearing initially as tiny batonnets[11] but coalescing to a pattern as shown in Figure 1c. The pentamer **2b** exhibited the M_2 phase for which the mosaic texture having coffee bean like objects (Figure 1d) were noted. Here again, the substrate effects are negligible. Unlike for the M_1 phase, highly birefringent nonspecific patterns are obtained upon shearing the M_2 phase of both the compounds. Thus, optical textural features seem to rule out the likelihood of M_1 and M_2 phase being conventional smectic phases, rather they point to highly ordered unusual structures.

XRD experiments were carried out in the M_1 and M_2 phases using unaligned samples. The XRD pattern obtained in the M_1 phase of both pentamers (**1a**,**b**), were very similar and showed two sharp reflections in the low-angle region with the spacing (d) value for the first one being an exact multiple of the second (Table 2) suggesting a layered structure. In addition, a diffuse peak seen in the wide angle region with d values of about 4.7 Å for both the compounds proves the fluid nature of the phase. The layer spacing of the first reflection obtained is close to the molecular length of **1a**,**b** estimated from the all-trans conformation. This implies that the molecules form a monolayered orthogonal smectic structure. Thus, assigning the M_1 phase to the

Table 2. The Layer Spacings (d/Å) Obtained in the Mesophases, the Estimated All-Trans Molecular Length (L/Å) of Four Pentamers, and the Ratio of d to L

entry (temp/°C)	mesophase	d_1, d_2 (Å)[a]	L (Å)[b]	d/L
1a (150 °C)	M_1	88.5, 43.9	91	0.97
1b (160 °C)	M_1	94.22, 47.16	94	1
2a (160 °C)	M_2	83.04, 39.93	120	0.69
2b (140 °C)	M_2	80.35, 38.56	115	0.70

[a] The spacings determined by X-ray diffraction. [b] Molecular lengths estimated by CS Chem Draw 3D Ultra 9 software.

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(12) (a) Nguyen, H. T.; Ismaili, M.; Isaert, N.; Achard, M. F. *J. Mater. Chem.* **2004**, *14*, 1560. (b) Pansu, B. *Pramana* **2003**, *61*, 285. (c) Levelut, A.-M.; Hallouin, E.; Bennemann, D.; Heppke, G.; Lotzsch, D. *J. Phys. II Fr.* **1997**, *7*, 981.

aforementioned SmQ phase, reported to have a highly tilted structure,[12] can be undoubtedly ruled out. Figure 2a depicts the schematic representation of the local molecular organization within the monolayer smectic (M_1) phase. It can be imagined that within a layer, these long molecules organize in an antiparallel fashion wherein the bulky cholesteryl segment of a molecule moves closer to the alkyl tail regime of the adjacent molecule to reduce the excluded volume. Thus, the M_1 phase appears to be a new monolayered smectic modification given the fact it possesses unique textural pattern.

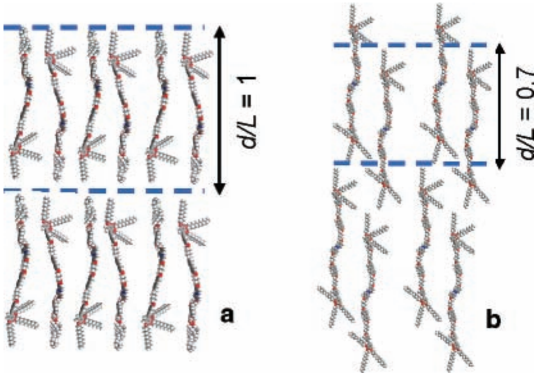

Figure 2. Schematic representation of the self-assembly of pentamers **1b** in a monolayered phase (a) and **2b** in an intercalated layered phase (b).

The M_2 phase of pentamers **2a**,**b** displayed similar XRD patterns. In addition to a wide angle peak with *d* values of about 4.5 Å, they contained two sharp reflections in the small-angle region. The *d* values of these low-angle reflections (Table 2) suggest a lamellar structure for the M_2 phase. The layer spacing, as shown in Table 2, is much lower than the estimated molecular length indicating that the M_2 phase is an intercalated smectic phase. Such an arrangement, as shown in Figure 2b, perhaps originates from the electrostatic quadrupolar interaction between the dissimilar anisometric segments as well as from the mechanism that excludes volume or space filling constraints. Apparently, the M_2 phase also seems to be a distinct lamellar phase as it displays unusual textures.

The solution electrochemistry of these four pentamers was investigated. The oxidation and reduction potentials were measured by cyclic voltametry (CV) at a scanning rate of 0.05 mVs^{-1} for the millimolar solutions of pentamers in dichloromethane. All the four giant molecules displayed an identical and reproducible cyclic voltammograms.[11] These voltammograms are characterized by two oxidation waves centered on $E_{1ox} = 1.22$ and $E_{2ox} = 1.78$ V and a reduction wave centered on $E_{red} = -1.26$ V (Table 3). In these molecular architectures, it is rather complicated to specify which of the molecular fragments causes the electrochemical behavior. Nonetheless, owing to their identical redox behavior it is reasonable to deduce that the tolane and/or azobenzene fragments are responding. The band gap (ΔE) between the frontier orbitals was determined from the CV by taking the difference between the onset of oxidation and reduction potential.[13,14] The ΔE was also estimated from the red edge of the longest wavelength absorption, $\lambda_{\text{red edge}} =$ 500 nm in the UV−vis spectra.[11,14] Apparently, ΔE deduced from the methods are comparable implying that these compounds genuinely possess electroactivity.

Table 3. Electrochemical[a] Properties of Pentamers **1a**,**b** and **2a**,**b**

entry	E^b_{1ox}	E^b_{2ox}	E^b_{red}	E^b_{HOMO}	$E^{c,d}_{LUMO}$	ΔE^c_{CV}	$\Delta E^{c,e}_{UV}$
1a	1.17	1.76	−1.21	5.87	3.49	2.38	2.49
1b	1.19	1.83	−1.35	5.89	3.35	2.54	2.49
2a	1.26	1.72	−1.25	5.96	3.45	2.5	2.49
2b	1.26	1.86	−1.23	5.96	3.47	2.49	2.48

[a] Experimental conditions: Pt-disc working electrode, Pt-rod counter electrode, Ag/AgCl in saturated LiCl solution as reference electrode, $(Bu)_4NPF_6$ (0.1 M), room temperature. [b] In volts (V). [c] In electron volts (eV). [d] Estimated from the onset oxidation and reduction potential (vs Ag/Ag^+) plus 4.7 (see ref 11). [e] Band gap determined from the red edge of the longest wavelegnth in the UV−vis absorption of pentamers.

In conclusion, the syntheses, characterization, and mesomorphism of the first examples of multifunctional unsymmetric and C_2 symmetric pentamers comprising five mesogenic segments interlinked through four flexible spacers varying in their length and parity, are reported. Apart from devising synthetic feasibility, their physical properties have been improved by rendering them soluble in organic solvents and by self-organizing to exhibit mesomorphism. The C_2 symmetric pentamers possess tolane, biphenyl, and azobenzene cores, while unsymmetrical ones contain cholesterol and naphthalene entities, additionally. These monodispersive supermolecules have been evidenced to self-assemble into monolayered or intercalated phases, which appear to be rather new smectic modifications given the fact they possess unique textural pattern. Besides this, they possess electrochemical activity. Indubitably, this approach offers a unique way to design a multifunctional material which can bridge the gap between low molar mass and polymeric LCs, with enhanced functional capability and ease of processability.

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Supporting Information Available: Synthetic procedures and characterization data of all intermediates and target molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Leeuv, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met*. **1997**, *87*, 53. (b) Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 3284. (c) Wang, H.-Y.; Feng, J.-C.; Wen, G.-A.; Jiang, H.-J.; Wan, J.-H.; Zhu, R.; Wang, C.-M.; Wei, W.; Huang, W. *New J. Chem.* **2006**, *30*, 667.

[14] Kanibolotsky, A. L.; Berridge, R.; Skabara, P.; Perepichka, J.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.