ORGANIC
LETTERS

2011
Vol. 13, No. 4
764–767

A Mesogenic Triphenylene–Perylene–Triphenylene Triad

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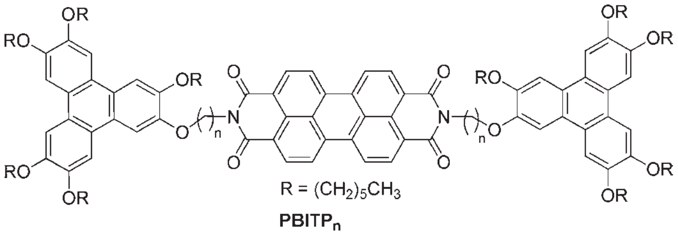
Received December 13, 2010

ABSTRACT



A straightforward synthesis of triphenylene–perylene–triphenylene triad structures has been achieved by using versatile triphenylene intermediates bearing a single oxyalkyl amine side chain. Among these, $PBITP_{10}$ showed a stable columnar mesophase implying favorably matched core–core separations in the structure. Importantly, the triad can be used as a vehicle for doping columnar triphenylene matrices with functional but incompatible perylene units and a mixture of hexahexyloxytriphenylene matrix doped with 0.1% $PBITP_{10}$ is homogeneous and liquid crystalline.

Discotic liquid crystals (DLCs) are promising candidates for use in organic electronic and optoelectronic devices because they readily self-assemble into ordered columnar structures that can in turn lead to efficient, directional charge migration.[1] For this reason they have potential applications for use in optoelectronic devices, such as thin film transistors, organic light emitting diodes (OLEDs), or photovoltaic devices.[2]

Triphenylene derivatives are among the most widely investigated discotic liquid crystals because they are robust and show a strong tendency for columnar mesophase formation. Synthetic advances have allowed a large array of symmetrical and unsymmetrically substituted derivatives to be prepared and evaluated, and the structural factors controlling mesophase formation in simple monomeric systems are now largely understood.[3] Furthermore,

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(1) (a) Adam, D.; Closs, F.; Frey, T.; Funhoff, D.; Haarer, D.; Ringsdorf, H.; Schuhmacher, P.; Siemensmeyer, K. *Phys. Rev. Lett.* **1993**, *70*, 457. (b) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141.

(2) (a) Freudenmann, R.; Behnisch, B.; Hanack, M. *J. Mater. Chem.* **2001**, *11*, 1618. (b) Seguy, I.; Destruel, P.; Bock, H. *Synth. Met.* **2000**, *111*, 15. (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119. (d) Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolbe, A.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. *Adv. Mater.* **2005**, *17*, 684.

(3) (a) Cammidge, A. N.; Bushby, R. J. *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. II, p 693. (b) Kumar, S. *Liq. Cryst.* **2004**, *31*, 1037. (c) Cammidge, A. N. *Philos. Trans. R. Soc., A* **2006**, *364*, 2697. (d) Cammidge, A. N.; Chausson, C.; Gopee, H.; Li, J.; Hughes, D. L. *Chem. Commun.* **2009**, 7375.

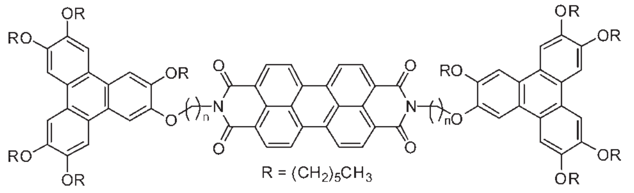
10.1021/ol103018v

columnar triphenylenes can spontaneously form highly aligned mesophases as thin films on solid substrates for device fabrication.[1,4,5]

Perylene is another important core for organic materials and several columnar mesophases have been observed in suitably functionalized structures.[6,7] Perylenes have received particular interest because of their absorption and emission properties in both solution and solid state. For example, Langhals[6a] and Jancy[6b] reported that perylene bisimide (PBI) has almost 100% fluorescence quantum yield in solution. Of particular interest is the use of combinations of aromatic/columnar structures in specific device architectures. For example, a perylene bisimide derivative has demonstrated an interesting photovoltaic performance of 2% in conjunction with hexabenzocoronene discotic materials.[2c] In thin film applications, such as OLEDS or PV devices, phase separation and immiscibility between organic components can be a desirable or indeed essential property. Other applications rely on doping the host columnar matrix with a complementary or active component. The columnar mesophases formed by discotic materials have a strong tendency to exclude other organics, even other mesogenic discogens, so it is normally impossible to introduce a low concentration dopant simply by mixing or formulation.

We reasoned that a possible general approach to addressing this issue would be to fuse the discotic (triphenylene) and functional aromatic component (perylene) in a covalent manner. Phase separation is then impossible in such a homogeneous system and a doped matrix can be produced so long as mesophase formation is retained. In this letter we report the fusion of discotic triphenylenes onto a central perylene bisimide unit to give triphenylene−perylene−triphenylene triads.

Hexasubstituted triphenylenes generally have a strong tendency to form columnar mesophases so long as the link atom can conjugate to the core (alkoxides are the most widely employed).[3c] In twinned and oligomeric assemblies of triphenylene discotics, columnar mesophase formation is only retained if the link groups are flexible and compatible with the intercolumn separation.[8] Rigid linkers lead to nematic mesophases in some cases.[9] For example, Freudenmann et. al synthesized a conjugated−bridged triphenylene dimer having a large spectral red-shift[2a] used in OLEDs but liquid crystalline properties were lost. On the other hand, Mao reported a triphenylene dimer bridged by a phenylene carbamate linkage and flexible spacers for application as a charge transporting layer in an organic electroluminescent device and found that the flexible spacer and the hydrogen bonds contributed to generate organized thin films.[10] In our design of fused triphenylene−perylene systems we therefore chose simple hydrocarbon linkers of varying length. The final triad design is shown in Figure 1.



PBITPn, **n** = 2, 4,6,10

Figure 1. Target triphenylene−perylene−triphenylene triads **PBITP$_n$**.

Perylene bisimide derivatives are most conveniently prepared by reaction between commercially available 3,4:9,10-perylene-*tetra*-carboxylic acid dianhydride (**19**) and 2 equiv of a primary amine. Simple, short-chain derivatives are known to be poorly soluble, however, so we selected a route that would introduce the highly substituted triphenylenes onto the perylene in the final step so that any solubility and purification issues were avoided. The synthesis therefore required a discotic triphenylene bearing a single amine on the end of one side chain. The synthesis of the key precursors is shown in Scheme 1. The synthesis requires monohydroxypentahexyloxy triphenylene **3** and we recently reported a convenient protocol that allows such intermediates to be prepared easily in a single step via a mixed cyclization between hexyloxphenol and 1,2-bishexyloxybenzene using iron chloride.[11]

Potassium phthalimide was alkylated[12] with dibromoalkane in a statistical synthesis to give convenient access to masked bromoalkylamines that were employed to alkylate monohydroxytriphenylene **3**. The triphenylene amine precursors were then prepared by deprotection using Ing−Manske reaction conditions[13] This sequence worked well for all medium and long chain lengths but failed in the synthesis of the ethylamine intermediate during the triphenylene alkylation step. For this amine an alternative synthesis was employed, shown in Scheme 2. Monohydroxy triphenylene **3** was alkylated with 1,2-dibromoethane under phase transfer conditions and the resulting bromide **16** treated with potassium phthalimide. Deprotection with hydrazine proceeded smoothly to yield the

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(4) (a) Vauchier, C.; Zann, A.; Le Barney, P.; Dubois, J. C.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 103. (b) Kawata, K. *Chem. Rec.* **2002**, *2*, 59. (c) Wang, J.; He, Z.; Zhang, Y.; Zhao, H.; Zhang, C.; Kong, X.; Mu, L.; Liang, C. *Thin Solid Films* **2010**, *518*, 1973.

(5) Li, J.; He, Z.; Zhao, H.; Kong, X.; Gopee, H.; Xu, M.; An, X.; Jing, X.; Cammidge, A. N. *Pure Appl. Chem.* **2010**, *82*, 1993.

(6) (a) Langhals, H. *Helv. Chim. Acta* **2005**, *88*, 1309. (b) Jancy, B.; Asha, S. K. *J. Phys. Chem. B* **2006**, *110*, 20937.

(7) Wicklein, A.; Lang, A.; Much, M.; Thelakkat, M. *J. Am. Chem. Soc.* **2009**, *131*, 14442.

(8) (a) Kumar, S. *Liq. Cryst.* **2005**, *32*, 1089. (b) Cammidge, A. N.; Gopee, H. *Liq. Cryst.* **2009**, *36*, 809. (c) Li, J.; He, Z.; Gopee, H.; Cammidge, A. N. *Org. Lett.* **2010**, *12*, 472.

(9) (a) Kumar, S.; Varshney, S. K. *Org. Lett.* **2002**, *4*, 157. (b) Zhang, L.; Gopee, H.; Hughes, D. L.; Cammidge, A. N. *Chem. Commun.* **2010**, *46*, 4255.

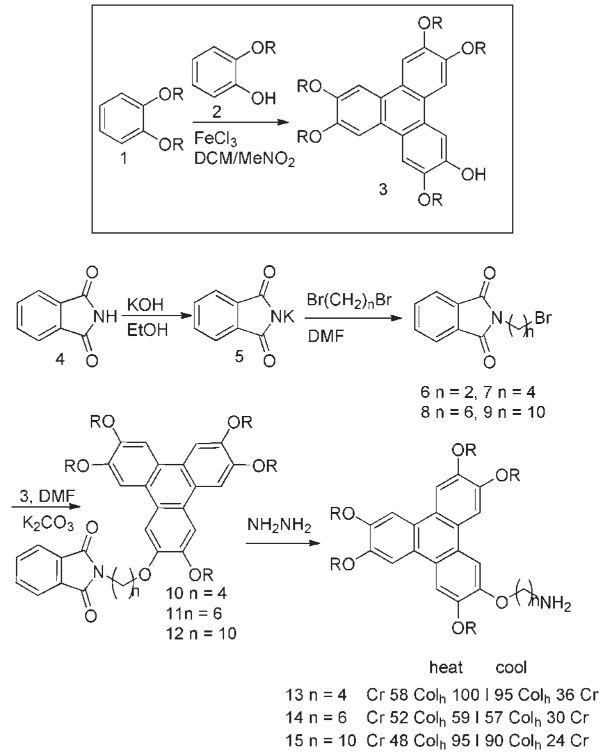
(10) Mao, H.; He, Z.; Wang, J.; Zhang, C.; Xie, P.; Zhang, R. *J. Lumin.* **2007**, *122−123*, 942.

(11) Kong, X.; He, Z.; Gopee, H.; Jing, X.; Cammidge, A. N. *Tetrahedon Lett.* **2011**, *52*, 77.

(12) Salzberg, P. L.; Supniewski, J. V.; Whitmore, F. C.; Benedict, H. C. *Org. Synth.* **1941**, *1*, 119.

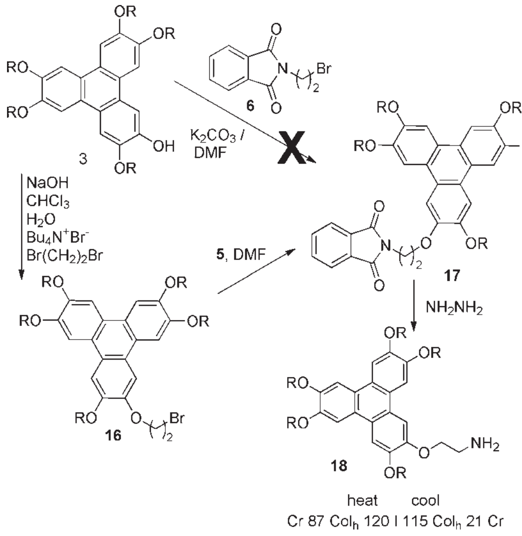
(13) (a) Ueda, T.; Ishizaki, K. *Chem. Pharm. Bull.* **1967**, *15*, 228. (b) Khan, M. N. *J. Org. Chem.* **1995**, *60*, 4536.

Scheme 1. Preparation of Triphenylene with Primary Amine Groups (n = 4, 6, and 10)



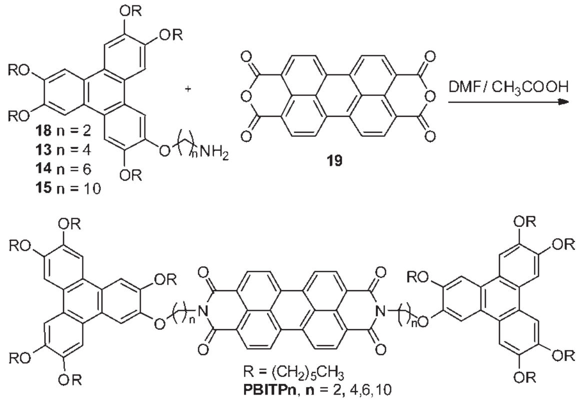
target primary amine **18**. Triphenylene amines **13**−**15** and **18** are versatile and useful precursors for grafting discotic mesogenic units onto further functional moieties. They are interesting in their own right. When cooled from the isotropic liquid they form columnar mesophases with characteristic textures when viewed under a polarizing optical microscope. Further cooling tends to lead to a glassy structure that slowly crystallizes.

Scheme 2. Alternative Synthesis of Triphenylene Amine **18**



The final triphenylene−perylene−triphenylene triads (**PBITP$_n$**) were prepared in a single efficient step from triphenylene amines **13**−**15** and **18** by reaction with 3,4:9,10-perylene-*tetra*-carboxylic dianhydride **19** by using a trace of glacial acetic acid as a catalyst and a modification of the procedure developed by Rohr[14] in which the triphenylene amines were employed as the limiting reactants (Scheme 3).

Scheme 3. Synthesis of Triphenylene−Perylene−Triphenylene Triads



Thermotropic mesophase behavior of the triads was investigated by using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). **PBITP$_2$**, **PBITP$_4$**, and **PBITP$_6$** showed only crystalline phases with their melting temperatures reduced as the length of the flexible spacer increased, and this behavior is typical for systems that combine two different discotic units. **PBITP$_{10}$** is unique in the series and particularly interesting because it does form a surprisingly stable liquid crystal phase below around 165 °C and shows a texture typical of a columnar hexagonal (Figure 2). There is clearly a subtle structural balance required in such linked systems. In this case there is a match beween the separation required in columns formed solely by triphenylenes (the triphenylene core plus OC_6H_{13}) and the triphenylene−perylene separation (the broader perylene core is compensated by a $-OC_{10}H_{12}O-$ bridge). Figure 2 also depicts a cartoon of the triad structure and a likely arrangement of the units within a columnar mesophase. It could also be speculated that charge transfer interactions could stabilize the columnar arrangement but there is no evidence for any such interaction from solution-state UV−visible spectroscopy. Indeed, the triads show preserved fluorescence from the perylene core providing a further indication for absence of charge-transfer or other significant face-to-face interactions that would be expected to cause complete quenching.

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[14] Rohr, U.; Kohl, C.; Müllen, K.; Van de Craats, A.; Warman, J. *J. Mater. Chem.* **2001**, *11*, 1789.

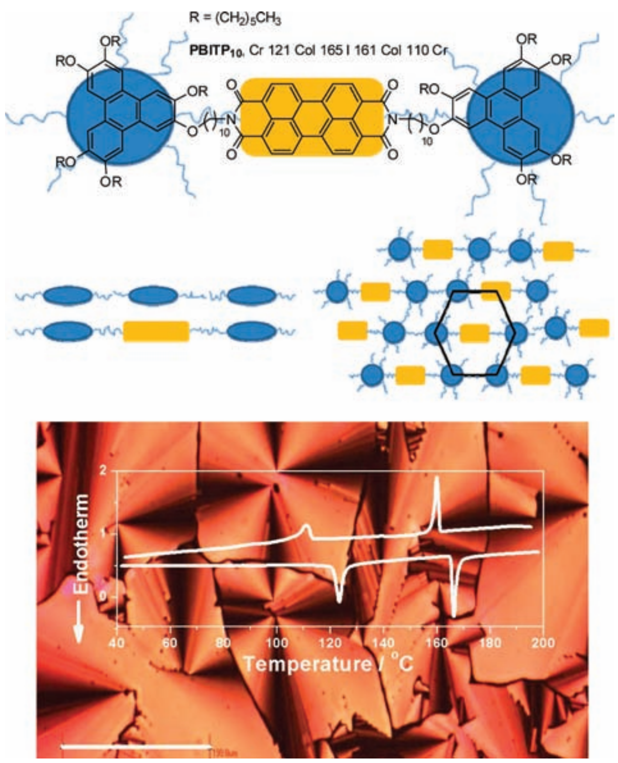

Figure 2. A cartoon representation of **PBITP$_{10}$** and its likely arrangement in the columnar mesophase, and the mesophase texture from **PBITP$_{10}$** at 160 °C observed by polarizing optical microscopy (scale bar = 200 μm). Thermal transitions from DSC are inset.

The absorption spectrum of the triad shows essentially a combination of the absortion spectra for the isolated triphenylene[7] and perylene units.[9] Fluorescence spectroscopy, however, shows that there is communication between the different units in the excited state. Observing fluorescence from the perylene, the profile of the excitation spectrum for the triad essentially follows the absorption spectrum, unambiguously confirming that excitation of the triphenylene leads to emission from the central perylene.

Observation of a stable columnar phase for **PBITP$_{10}$** suggested the potential for using the triad as a vehicle for introducing incompatible functional components into the columnar matrices of the parent hexaalkoxytriphenylenes without inducing phase separation. Hexahexyloxytriphenylene (HAT6) was used as host material. In its pure state it forms a columnar mesophase between 70 and 100 °C. Doping with triad **PBITP$_{10}$** led to a suppression of the clearing temperature. A sample doped with 2% **PBITP$_{10}$** remained an isotropic liquid when cooled to 75 °C at which point slow crystallization began. The same observation resulted from the 0.5% doped sample but in both cases the outcomes were interesting because there was no phase separation between the triad and HAT6, with crystals forming from the doped mixture. Significant transition suppression was observed when an even lower doping concentration was employed (0.1%) but importantly in this case cooling to 76 °C led to formation of a columnar mesophase, again with no separation of the triad from its matrix. The mesophase structure was retained (as a glass) down to room temperature.

In summary, a straightforward synthesis of triphenylene–perylene–triphenylene triad structures has been achieved by using versatile triphenylene intermediates bearing a single oxyalkyl amine side chain. The final triad structures with linking chain lengths of 2, 4, and 6 methylene units are nonmesogenic, but the triad with decyl linkers forms a stable columnar mesophase below 165 °C. As such it is a rare example of a columnar material comprising significantly different cores. There is no evidence for charge transfer or other ground state interactions and the stability of the columnar structure is likely to arise through favorably matched core–core separations. The fluorescence of the central perylene core is preserved, and the excitation spectrum clearly demonstrates that excitation of the triphenylene leads to emission from the perylene. Importantly, the triad can be used as a vehicle for doping columnar triphenylene matrices with functional but incompatible perylene units. Doping hexahexyloxytriphenylene with 0.1% of mesogenic triad **PBITP$_{10}$** gives a columnar phase below 76 °C with no separation of the triad from its host matrix. These results suggest this approach to incorporation of functional components in columnar materials can be more widely applied so long as careful design principles are used to match the core and linker structures.

Acknowledgment. X.K. thanks the China Scholarship Council, Ministry of Education. This work is supported by the funds from NSFC (20674004), ISTCP (2008DFA61420), and the 111 project (B08002).

Supporting Information Available. Experimental procedures and compound characterization data and absorption and fluorescence spectra for **PBITP$_{10}$**. This material is available free of charge via the Internet at http://pubs.acs.org.