Novel discotic mesogen: synthesis and liquid crystalline behavior of TAAB (tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine) derivatives with long alkoxy chains†

Seok Ho Kang,[a] Miok Kim,[a] Hyung-Kun Lee,[a] Yoon-Sok Kang,[b] Wang-Cheol Zin[b] and Kimoon Kim*[a]

[a] National Research Initiative Center for Smart Supramolecules, Department of Chemistry, and [b] Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, South Korea. E-mail: kkim@postech.ac.kr

Received (in Cambridge, UK) 9th November 1998, Accepted 27th November 1998

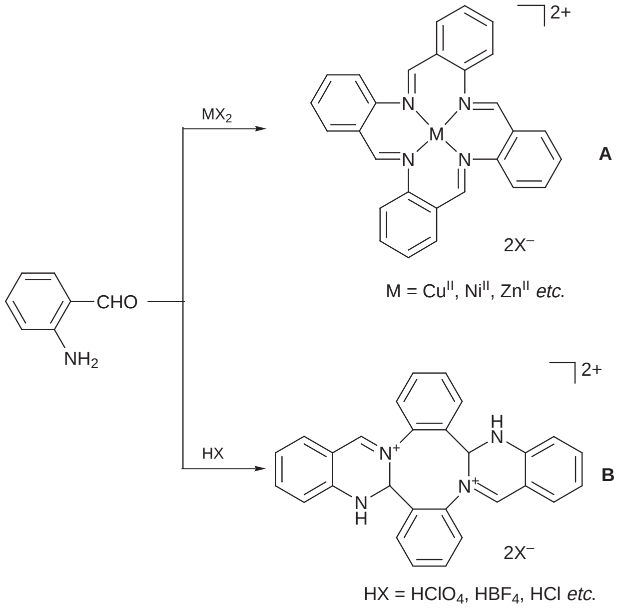
The self-condensation of 3,4-dialkoxy-2-aminobenzaldehyde (alkoxy = *n*-$C_8H_{17}O$, *n*-$C_{10}H_{21}O$ and *n*-$C_{12}H_{25}O$) in the presence of HBF_4 gives the tetrafluoroborate salt of diprotonated octaalkoxy-TAAB which exhibits a hexagonal columnar mesophase over a wide range of temperatures including room temperature.

Discotic liquid crystals are well-known examples of supramolecular assemblies based on self-organization.[1] The columnar arrangement of disk-like mesogens such as triphenylenes, porphyrins and phthalocyanines is a promising architecture for anisotropic materials with potential applications such as one-dimensional conductors,[2] photoconductors,[3] molecular wires and fibers,[4] light emitting diodes[5] and photovoltaic cells.[6]

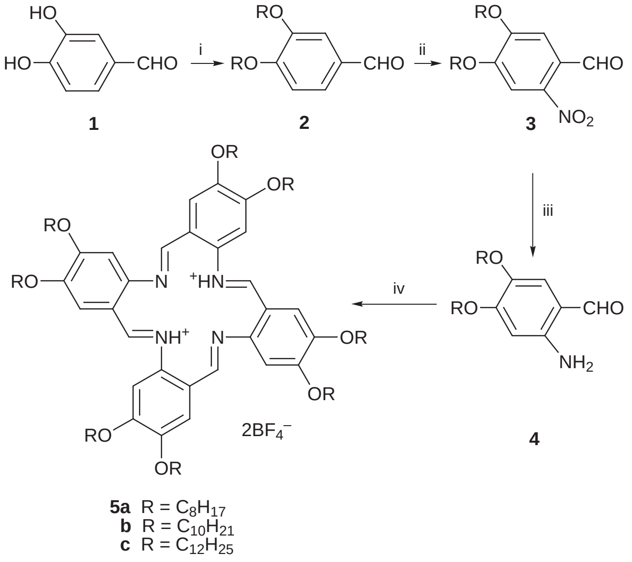
We are interested in studying new discotic mesogens.[7] Among the potential discotic mesogens we chose to examine was the macrocyclic compound tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]-tetraazacyclohexadecine (TAAB). Metal complexes of TAAB (**A**), which have been known for over three decades, are synthesized by the self-condensation reaction of *o*-aminobenzaldehyde in the presence of metal ions (Scheme 1).[8] Without metal ion templates, however, the self-condensation reaction produces various polycyclic compounds including the eight-membered ring macrocyclic compound 4b,5,15,16-tetrahydrodibenzo[3,4:7,8][1,5]diazocino[2,1-*b*:6,5-*b*]diquinazoline-11,22-diium ion (**B**)‡ (Scheme 1).[9] In fact, no metal-free TAAB derivatives have been reported until now. Furthermore, no liquid crystalline compound having a TAAB core is known. Herein we describe the first successful synthesis of metal-free TAAB derivatives having long alkoxy substituents on the phenyl rings and their liquid crystalline behavior.

The synthesis of metal free, octaalkoxy-TAAB compounds **5a–c** is shown in Scheme 2. 3,4-Dihydroxybenzaldehyde **1** was alkylated with alkyl bromide (alkyl = *n*-octyl, *n*-decyl and *n*-dodecyl) and subsequently converted into the corresponding 2-nitrobenzaldehyde by nitration. The key step for the synthesis of TAAB derivatives is the reduction of the 3,4-dialkoxy-2-nitrobenzaldehyde **3**. The proper choice of reducing agent is crucial because these reduction reactions are undoubtedly complicated by competing inter- and intra-molecular condensation reactions. Attempts to reduce **3** with previously-used reducing agents such as titanium(III) chloride and ferrous sulfate gave none of the desired product, while sodium sulfide gave only a 10% yield. However, the 3,4-dialkoxy-2-aminobenzaldehyde **4** could be prepared by hydrogenation of **3** with H_2 and Pd/C in 60–83% yield. In contrast to 2-aminobenzaldehyde, the dialkoxyaminobenzaldehydes are stable at room temperature; their stability increases with increasing alkyl chain length.

The self-condensation of **4** using HBF_4 in refluxing EtOH gives the tetrafluoroborate salt of diprotonated octaalkoxy-TAAB (**5a–c**) in 14–21% yield. The products have been characterized by NMR, UV–VIS, IR and mass spectroscopy and gave satisfactory elemental analyses.§ Their simple ^1H and ^{13}C NMR spectral patterns are consistent with the 16-membered



Scheme 1



Scheme 2 *Reagents and conditions*; i, RBr, K_2CO_3, acetone; ii, HNO_3, $NaNO_2$, CH_2Cl_2; iii, H_2, Pd/C (10%), CH_2Cl_2, room temp.; iv, HBF_4, EtOH, reflux.

---

† Synthetic and spectroscopic data for **2–5** and a photograph of the texture of **5c** under a polarizing microscope at 70 °C is available from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/93

Table 1 Phase behavior of **5a–c**[a]

Compound	Transition	T/°C	ΔH/J g^{-1}	Lattice constant/Å
5a	K–D$_{hd}$	−4.3	2.17	25.46
	D$_{hd}$–I	271[b]		
5b	K–D$_{hd}$	2.8	5.23	27.69
	D$_{hd}$–I	263[b]		
5c	K–D$_{hd}$	22.5	22.64	29.62
	D$_{hd}$–I	249[b]		

[a] Transition temperatures and enthalpies were determined by DSC (scan rate 10 °C min^{-1}). K, crystalline phase; D$_{hd}$, hexagonal columnar phase; I, isotropic phase. [b] Transition observed only by polarizing microscopy.

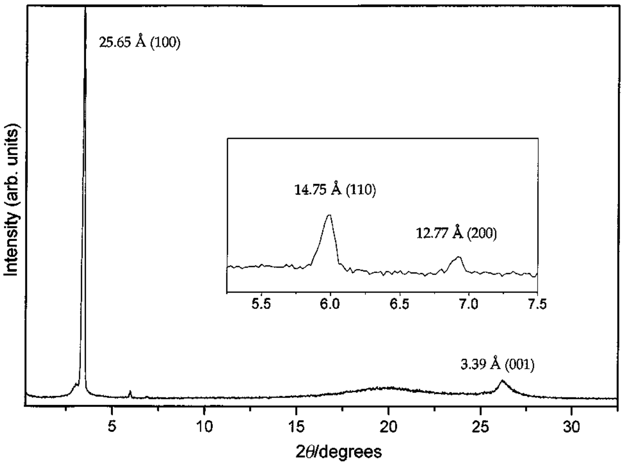


Fig. 1 X-Ray diffraction pattern of **5c** taken at room temperature.

TAAB core being in a diprotonated form. This is in sharp contrast to the fact that the self-condensation of simple 2-aminobenzaldehyde under the same conditions yields **B** having an eight-membered ring core (Scheme 1). This is the first example of the self-condensation reaction of an *o*-aminobenzaldehyde without metal ion templates leading to the formation of the 16-membered macrocyclic TAAB core. The electron-donating alkoxy substituents appear to stabilize the diprotonated TAAB core in **5**.

The diprotonated TAAB derivatives **5a–c** show mesomorphic behavior over a wide range of temperatures as revealed by differential scanning calorimetry (DSC), polarizing microscopy and X-ray diffraction measurements (Table 1). For example, **5c** shows a columnar mesophase at room temperature and transforms into an isotropic liquid at 249 °C. These transitions are not observed by DSC due to the low isotropic transition enthalpy, but are observed by polarizing microscopy. In optical microscopy a pseudo-focal conic texture is observed, which is typical for columnar mesophases. The compound starts decomposing just above the clearing point.

In order to clarify the mesomorphism of these compounds, we performed X-ray diffraction experiments at room temperature. The X-ray diffraction pattern (Fig 1) of the mesophase of **5c** shows a set of sharp reflections in the small-angle region which correspond to reciprocal spacings in a ratio of $1:\sqrt{3}:\sqrt{4}$. These peaks were assigned to the (100), (110) and (200) reflections from a hexagonal arrangement with a lattice constant a = 29.62 Å. In the wide-angle region, X-ray diffraction measurement also shows two broad and diffuse rings. The first one corresponds to a spacing of 4–5 Å, which is related to the liquid-like correlation between the molten aliphatic chains. The second ring at 3.39 Å is presumably related to the periodic stacking of the macrocyclic subunits within the columns. A molecular mechanical calculation suggests that the diprotonated TAAB core has a saddle-shaped conformation similar to those for metal complexes of unsubstituted TAAB reported earlier.[8b] The saddle-shaped macrocycles are stacked along the column with a mean interplanar distance of 3.39 Å. The columns are in turn arranged in a two-dimensional hexagonal array.

In summary, we synthesized novel discotic liquid crystals containing the macrocyclic TAAB core. The key to the successful synthesis of the stable diprotonated TAAB core is the introduction of electron–donating alkoxy substituents. The long alkoxy chains stabilize not only the precursor 3,4-dialkoxy-2-aminobenzaldehyde but also the diprotonated TAAB core formed by self-condensation of the precursor. These macrocyclic compounds exhibit hexagonal columnar mesophases over a wide range of temperatures including room temperature, demonstrating that the saddle-shaped macrocyclic core may be successfully used as a new discotic mesogen. These novel liquid crystalline materials may have interesting physical properties which are currently under investigation. The successful syntheses of the metal-free TAABs open up new possibilities for synthesizing a variety of metal complexes using these compounds as ligands. We are also working along this line.

This work was supported by the Creative Research Initiative Program (the Korean Ministry of Science and Technology). The X-ray diffraction measurements were performed at the Pohang Accelerator Laboratory (Beamline 3C2). We thank Mr Woo Sung Jeon for molecular mechanical calculations and Professor G. V. Smith for helpful suggestions in preparation of the manuscript.

Notes and references

‡ Old literature (ref. 8,9) refers to compound **B** as (TAAB)(HBF$_4$)$_2$ or [(TAAB)H$_2$][BF$_4$], but these abbreviations are misleading because the macrocycle core **B** is different from that of **A**.

§ All the compounds have been fully characterized by ^{1}H NMR, UV–VIS, IR and mass spectroscopy and gave satisfactory elemental analyses. *Selected data* for **5c**: δ_H(CDCl$_3$, 300 MHz) 0.87 (t, 24H, CH$_3$), 1.44 [m, 144H, (CH$_2$)$_9$], 1.73 (m, 16H, CH$_2$), 3.83 (q, 16H, OCH$_2$), 6.42 (s, 4H, Ar), 6.58 (s, 4H, Ar), 7.96 (s, 4H, N=CH); δ_C(CDCl$_3$, 75 MHz) 14.51, 23.13, 24.91, 26.56, 29.75, 29.89, 30.24, 30.33, 32.40, 69.39, 69.66, 99.92, 117.70, 119.87, 124.68, 138.44, 149.29, 154.71, 157.56; ν_{max}(KBr)/cm^{-1} 1635 (C=C), 1555 (C=N); *m/z* (FAB) 1887.7 (M + H$^+$ − 2HBF$_4$); Calc. for $C_{124}H_{214}N_4O_8B_2F_8$: C, 72.21; H, 10.46; N, 2.72. Found: C, 71.97; H, 10.32; N, 2.84.

1 S. Chandrasekar, in *Advances in Liquid Crystals*, ed. G. H. Brown, Academic Press, New York, vol. 5, 1982; C. Destrade, P. Foucher, H. Gasparoux, N-H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121; S. Chandrasekar, *Liq. Cryst.*, 1993, **14**. 3.
2 N. Boden, R. Bissell, J. Clements and B. Movaghar, *Liq. Crystal. Today*, 1996, **6**, 1.
3 J. Simmerer, B. Glusen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K. H. Etzbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf and D. Haarer, *Adv. Mater.*, 1996, **8**, 815.
4 C. F. van Nostrum and R. J. M. Nolte, *Chem. Commun.*, 1996, 2385; E. J. Osburn, A. Schmidt, L. K. Chau, S. Y. Chen, P. Smolenyak, N. R. Armstrong and D. F. O'Brian, *Adv. Mater.*, 1996, **8**, 926.
5 T. Christ, B. Glusen, A. Greiner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 48.
6 C.-Y. Liu, H.-L. Pan, M. A. Fox and A. J. Bard, *Science*, 1993, **261**, 897.
7 S. J. Kim, S. H. Kang, K.-M. Park, H. Kim, W.-C. Zin, M.-G. Choi and K. Kim, *Chem. Mater.*, 1998, **10**, 1889.
8 (*a*) J. S. Skuratowicz, I. L. Madden and D. H. Busch, *Inorg. Chem.*, 1977, **16**, 1721; (*b*) A. J. Jircitano, R. I. Sheldon and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3022.
9 F. Seidel and W. Dick, *Ber. Dtsch. Chem. Ges.*, 1927, **60**, 2018; J. D. Goddard and T. Norris, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 211; P. G. Owston and L. S. Shaw, *Acta Crystallogr.*, 1988, **B44**, 39.

Communication 8/08739C