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Room-Temperature Redox-Active Liquid Crystals Composed of Tetraazanaphthacene Derivatives

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Ordered superstructures fabricated by self-organization can be achieved through programmed molecular design, using non-covalent intermolecular interactions such as hydrogen bonding, coordination, electrostatic attraction, and van der Waals forces at equilibrium in the experimental system.[1–5] A liquid-crystalline (LC) state constructed from assembled molecules can form self-organized superstructures even in thin films because the arrangement of molecules in the LC state already forms an ordered superstructure by intermolecular interactions such as the hydrophobic attraction of long alkyl chains.[6–10] Some LC molecules with π-conjugated polycyclic frameworks and certain long-chain alkyl substituents not only self-organize into low-dimensional ordered superstructures but also have a high charge-carrier mobility through the π-stacking structures when a bias voltage is applied.[11,12] Further, LC molecule have the potential to compensate for high carrier-transport through an ordered superstructure in the LC films because of a self-healing behavior which reduces grain boundaries and structural defects by molecular fluctuation.[13,14]

Interestingly, *N*-heteroacenes, in which N atoms partially replace C atoms in a π-conjugated polycyclic oligoacene framework (e.g., pentacene),[15,16] behave as electron acceptors due to the presence of electronegative imino-N atoms. These compounds are therefore good candidates for *n*-type semiconductors capable of transporting electrons. 5,6,11,12-Tetraazanaphthacene (TANC), an *N*-heteroacene with four N atoms that was previously reported by our group,[17–19] also functions as an electron acceptor, having reversible two-step, two-electron transfer peaks ($E^1_{1/2} = -0.66$ V and $E^2_{1/2} = -1.20$ V vs. Ag/Ag^+ in acetonitrile).[19] We also observed a field-effect transistor (FET) activity for a TANC thin film prepared by a vapor deposition process.[19] However, the FET activity decreased due to the independent and isolated growth of crystalline domains on the surface over time. A molecular conductor with high conductivity ($50\,\mathrm{S\,cm^{-1}}$ at room temperature), formed from TANC radical anions and copper ions, has been also reported.[17] The TANC radical anions, as bridging ligands, coordinate to Cu ions present in mixed valence states (Cu^+/Cu^{2+}) to produce a conductive metal-coordination polymer with d–π interactions similar to the Cu-Me_2DCNQI system.[21]

Herein, we have investigated the effects of the introduction of long alkyl chains into TANC and fluoflavin (FFV, a reduced precursor of TANC[22]), which develop LC states based on their π-conjugated frameworks. By these modifications, we are able to prepare two redox-active room-temperature LC materials: **1a** with an oxidized TANC framework and **2a** with a reduced FFV skeleton. Thin films with columnar molecular arrays are easily fabricated from these LC materials, in which **1a** and **2a** are aligned parallel to the shearing direction by application of a shearing mechanical stress. Moreover, upon the addition of the strong base 1,8-diazabicycloundec-7-ene (DBU), a mixture of **1a** and **2a** generates a TANC radical anion by the disproportionation of an electron from the FFV to the TANC framework. To the best of our knowledge, for an *N*-heteroacene framework, only a smectic LC state based on dipole moments has been reported.[23] However, this is the first report on the formation of the columnar LC state of **1a** and **2a** at room temperature through self-organization.

Figure 1 shows the molecular structures of **1** and **2** bearing racemic branched alkoxy chains **a** and linear chains **b** at the 4- and 5-positions of the π-conjugated acene frameworks. The introduction of long-chain alkoxy groups prevents the growth of single-crystal domains that hinder the passage of an electric current in FET activity. Compounds **2a** and **2b** were prepared by the thermal condensation of 2,3-diamino-4,5-dialkoxybenzene and 2,3-dichloroquinoxaline in ethylene glycol. Compounds **1a** and **1b** were prepared by the respec-

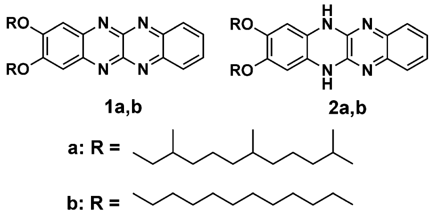

Figure 1. Molecular structures of **1a** and **2a** with racemic branched long chain alkoxy groups, and **1b** and **2b** with linear ones.

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tive oxidation of **2a** and **2b,** with PbO_2 in $CHCl_3$ (see the Supporting Information).

Unsubstituted FFV molecules are nearly insoluble in organic solvents except for DMSO and DMF. However, the long-chain alkoxy substituents of **2a** and **2b** conferred high solubility in various organic solvents, including $CHCl_3$, acetone, ethyl acetate, and even *n*-hexane.

Of the four compounds, the UV/Vis spectrum of **1a** displays the lowest energy absorption maximum at 440 nm in CH_2Cl_2, which is bathochromically shifted as compared to that of **2a** at 419 nm (Figure S1, Supporting Information). This indicates that π-conjugation in **1a** is expanded by the oxidation of **2a**: the 20π electron system of **2a** is converted into the 18π one of **1a** with Hückel aromaticity,[15] and the electronic character of the system is changed from the antiaromatic species **2a** to the aromatic **1a**.[15] The behavior of **1b** and **2b** is very similar to that of **1a** and **2a**.

The LC behavior of **1a** and **2a** is summarized in Table 1, together with the phase transition behavior of **1b** and **2b**. By differential scanning calorimetry (DSC), as shown in Figure S2 in the Supporting Information, **1a** and **2a** maintain columnar LC phases at room temperature, and their phase transitions from isotropic liquids to columnar LC phases on cooling have broad peak temperatures at 35.7 °C and 73.4 °C, respectively. The transition temperature for the formation of the LC phase of **1a** is much lower than that of **2a**, despite having similar mesogenic cores. The IR spectrum of **2a** in the columnar LC state has an intense broad peak related to the ν(NH) stretching vibration around 3200 cm^{-1}, which is characteristic of an intermolecular H-bond of the N−H···N type connecting the FFV frameworks of **2a** (Figure S3, Supporting Information). On heating, when the phase transition occurs from the columnar LC phase to the isotropic liquid, the intensity of the ν(NH) peak for **2a** decreases. By contrast, the IR spectrum of **1a** shows no change in the analogous peak in relation to an intermolecular H-bond before or after the phase transition (Figure S4, Supporting Information). The intermolecular H-bonds between the FFV frameworks of **2a** would stabilize the formation of the columnar LC state. In contrast, **1b** and **2b**, with linear chain alkoxy groups, exhibit no LC phases, and their phase transitions from isotropic liquids to the crystalline phase are observed as sharp peaks at 183.5 and 169.9 °C, respectively.

Table 1. Liquid-crystalline behavior of **1** and **2**.

Compound	Phase transition[a]
1a	$\mathrm{Col_h}$ 73.6 (8.30) Iso[b]
1b	Cr 183.5 (38.78) Iso
2a	$\mathrm{Col_t}$ 130.6 (3.79) Iso[b]
2b	Cr 169.9 (11.21) Iso

[a] Phase transition temperatures (°C) and enthalpy changes in parentheses (kJ mol^{-1}) were determined by DSC measurements at the second cycle at a scanning velocity of 10 °C min^{-1}. $\mathrm{Col_h}$: hexagonal columnar; $\mathrm{Col_t}$: tetragonal columnar; Cr: crystalline; Iso: isotropic. [b] No distinct transition peaks were detected by DSC measurement above −100 °C.

The X-ray diffraction (XRD) pattern of **1a** at 25 °C reveals three reflection peaks at 42.0 Å (100), 24.2 Å (110), and 21.0 Å (200) in the low-angle 2θ region with the reciprocal *d*-spacing ratio of 1:$\sqrt{3}$:2 (Figure 2). These results imply that **1a** self-assembles into a hexagonal columnar LC structure.[7] Meanwhile, **2a** exhibits two reflection peaks at 32.4 Å (100) and 22.9 Å (110) with the reciprocal *d*-spacing ratio of 1:$\sqrt{2}$, which indicates self-assembly into a tetragonal columnar LC structure.[7] Furthermore, the intercolumnar distance of 48.5 Å in the LC phase of **1a** at 25 °C is larger than that of 32.4 Å in **2a**. This result suggests that each adjacent TANC moiety of **1a** connects in a head-to-head formation with weak H-bonds of a CH···N type to form a 1D π-stacking column (Figure S5, Supporting Information). Meanwhile, **2a** also forms a 1D π-stacking column in the LC state, similarly to **1a**. However, each adjacent FFV moiety of **2a** is connected with strong H-bonds of the N-H···N type in the lateral direction, thereby giving an alternative inversion arrangement (Figure S5, Supporting Information). A similar example, in which LC molecules based on imidazole frameworks self-assembled into a tetragonal columnar structure analogous to **2a** through strong H-bonds of the N−H···N type has been reported.[24] Moreover, their intercolumnar distances of 48.5 Å for **1a** and 32.4 Å for **2a** in the columnar LC phases, as estimated by XRD measurements, are shorter than the fully extended molecular length of approximately 56 Å for **1a** and 43 Å for **2a** (Figure S5, Supporting Information). The interdigitation of alkoxy chains between the neighboring columns would occur in the columnar LC phases.

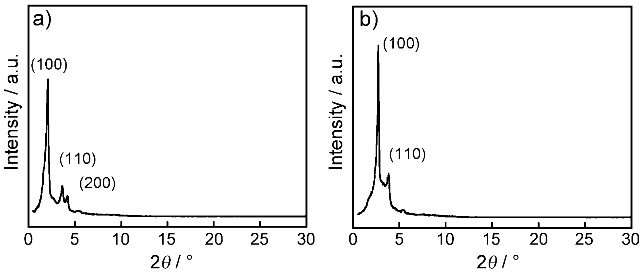

Figure 2. X-ray diffraction patterns of two LC states at room temperature: (a) **1a** in the hexagonal columnar structure and (b) **2a** in the tetragonal columnar structure.

Macroscopically, the uniaxial alignments of these two columnar LC structures are achieved by shearing **1a** and **2a** between sandwiched glass plates at room temperature. Observations by polarized light microscopy revealed that **1a** and **2a** tend to align parallel to the shearing direction. As shown in Figure 3, the birefringence of the aligned samples of **1a** and **2a** alternately changes between light and dark upon a 45° rotation under the crossed Nicols condition (Figure 3 and Figure S6, Supporting Information).[25]

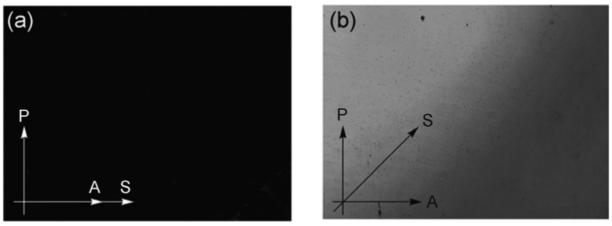

Figure 3. Polarized optical photomicrographs of the uniaxially aligned **1a** in the hexagonal columnar phase at room temperature by mechanical shearing. Rotating the sample by 45° gives periodic dark (a) and bright (b) images under the crossed Nicols condition. Arrows indicate the directions of the mechanical shearing (S), polarizer (P), and analysis (A) axes.

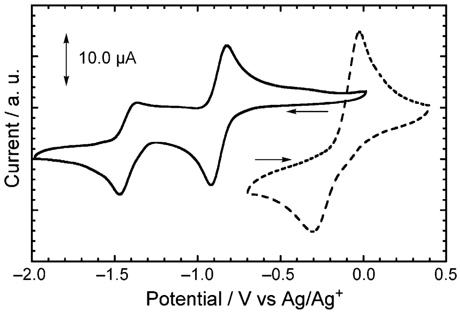

Figure 4. Cyclic voltammograms of **1a** (solid line) and **2a** (dashed line) at 1.0 mM in CH_2Cl_2 (**1a**) and DMF (**2a**) solutions of $n\text{Bu}_4\text{NPF}_6$ (0.10 M), at a scanning velocity of 100 $\text{mV}\,\text{s}^{-1}$.

Figure 4 shows the cyclic voltammograms of **1a** and **2a** in CH_2Cl_2 and DMF solutions (0.1 M $n\text{Bu}_4\text{NPF}_6$), respectively. **1a** exhibits a reversible two-step, two-electron transfer. By scanning from 0 V, two redox potentials in **1a** are observed at $E^1_{1/2} = -0.89$ V and $E^2_{1/2} = -1.44$ V (vs. Ag/Ag^+), which are characteristic of the formation of the radical anion and dianion of the TANC framework, respectively. In contrast, **2a** shows a quasi-reversible redox peak at $E^1_{1/2} = -0.17$ V (vs. Ag/Ag^+) with two electron transfers. No LC-TANC radical anion is observed in the cyclic voltammogram for **2a** due to a broadened peak with two electron transfers (**1b** and **2b** show a similar behavior: $E^1_{1/2} = -0.89$ V and $E^2_{1/2} = -1.44$ V for **1b** and $E^1_{1/2} = -0.24$ V for **2b**). The difference in the electrochemical behavior between **1a** and **2a** (or **1b** and **2b)** probably originates in a PCET (proton-coupled electron transfer) effect of the NH groups of **2a**, as in 1,4-hydroquinone derivatives.[26] The CVs of 1,4-hydroquinone derivatives produce a broadened peak with two electron transfers after the addition of the base and acetate. The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO}) of **1** and **2** can be approximately evaluated from the $E^1_{1/2}$ potentials in the cyclic voltammograms and the absorption edge of the UV/Vis spectra, respectively (Table S1, Supporting Information). The E_{LUMO} values for **1a** and **1b** are comparable to those of LC hexaazatriphenylene[27] and LC perylene tetracarboxylic acid bisimide,[28] which are used as *n*-type organic semiconductors based on their electron acceptor properties. Furthermore, the E_{HOMO} of **2a**, despite the influence of PCET, indicates that **2a** is a better electron donor than the representative electron donors tetrathiafulvalene (TTF) and ferrocene and, hence, can be a suitable candidate for a *p*-type semiconductor.

The LC mixture of **1a** and **2a** is incapable of forming charge-transfer LC complexes. However, the addition of a strong base such as DBU generates a TANC radical anion under anaerobic conditions, probably through an electron disproportionation reaction between **1a** and **2a**.[17] After the reaction, the ESR spectrum of the mixture of **1a** and **2a** shows a typical peak ($g = 2.00428$) originating from TANC radical anions at room temperature (Figure 5). It is expected that in the LC mixture of **1a** and **2a**, the TANC radical anion would be generated because of a charge-transfer reaction triggered by the addition of a proton-withdrawing molecule as a strong base. In fact, the LC mixture also becomes ESR-active after the addition of excess DBU. However, the generated TANC radical anion is very unstable in air and decomposes quickly.

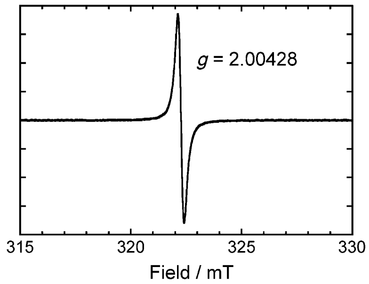

Figure 5. ESR spectrum of the anionic radical of TANC at room temperature under aerobic conditions.

In conclusion, two *N*-heteroacene LC materials based on TANC and FFV frameworks with mesogenic cores, **1a** and **2a**, were prepared. Compounds **1a** and **2a** form 1D π-stacked hexagonal and N-H···N H-bonded tetragonal columnar LC structures, respectively, over a wide range of temperatures, including room temperature. Furthermore, the electron disproportionation reaction between **1a** and **2a** under strongly basic conditions generates TANC radical anions. In the future, we seek to prepare a thin-film LC electron conductor based on the isolated LC-TANC radical anions.

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Keywords: cyclic voltammetry • electron acceptor • liquid crystals • radicals • self-assembly

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[1] W. Pisula, X. Feng, K. Müllen, *Adv. Mater.* **2010**, *22*, 3634.
[2] J. D. Hartgerink, E. Beniash, S. I. Stupp, *Science* **2001**, *294*, 1684.
[3] B. H. Northrop, Y. R. Zheng, K. W. Chi, P. J. Stang, *Acc. Chem. Res.* **2009**, *42*, 1554.
[4] J. J. Storhoff, C. A. Mirkin, *Chem. Rev.* **1999**, *99*, 1849.
[5] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491.
[6] T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44; *Angew. Chem. Int. Ed.* **2006**, *45*, 38.
[7] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832.
[8] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, K. Siemensmeyer, *Phys. Rev. Lett.* **1993**, *70*, 457.
[9] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485.
[10] B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* **2009**, *109*, 6275.
[11] S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902.
[12] M. Funahashi, *Polym. J.* **2009**, *41*, 459.
[13] A. Benito-Hernández, U. K. Pandey, E. Cavero, R. Termine, E. M. García-Frutos, J. L. Serrano, A. Golemme, B. Gómez-Lor, *Chem. Mater.* **2013**, *25*, 117.
[14] J. Cornil, V. Lemaur, J. P. Calbert, J. L. Brédas, *Adv. Mater.* **2002**, *14*, 726.
[15] U. H. F. Bunz, J. U. Engelhart, B. D. Linder, M. Schaffroth, *Angew. Chem.* **2013**, *125*, 3898; *Angew. Chem. Int. Ed.* **2013**, *52*, 3810.
[16] U. H. F. Bunz, *Chem. Eur. J.* **2009**, *15*, 6780.
[17] M. Tadokoro, S. Yasuzuka, M. Nakamura, T. Shinoda, T. Tatenuma, M. Mitsumi, Y. Ozawa, K. Toriumi, H. Yoshino, D. Shiomi, K. Sato, T. Takui, T. Mori, K. Murata, *Angew. Chem.* **2006**, *118*, 5268; *Angew. Chem. Int. Ed.* **2006**, *45*, 5144.
[18] M. Tadokoro, M. Nakamura, T. Anai, T. Shinoda, A. Yamagata, Y. Kawabe, K. Sato, D. Shiomi, T. Takui, K. Isoda, *ChemPhysChem* **2011**, *12*, 2561.
[19] K. Isoda, M. Nakamura, T. Tatenuma, H. Ogata, T. Sugaya, M. Tadokoro, *Chem. Lett.* **2012**, *41*, 937.
[20] S. Yasuzuka, K. Murata, H. Yoshino, T. Fujimoto, M. Shimotori, M. Nakamura, M. Tadokoro, *J. Phys. Soc. Jpn.* **2006**, *75*, 014704.
[21] R. Kato, H. Kobayashi, A. Kobayashi, *J. Am. Chem. Soc.* **1989**, *111*, 5224.
[22] Y. Akimoto, *Bull. Chem. Soc. Jpn.* **1956**, *29*, 460.
[23] A. E. Riley, G. W. Mitchell, P. A. Koutentis, M. Bendikov, P. Kaszynki, F. Wudl, S. H. Tolbert, *Adv. Funct. Mater.* **2003**, *13*, 531.
[24] S. H. Seo, J. H. Park, J. Y. Chang, *Langmuir* **2009**, *25*, 8439.
[25] M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2004**, *126*, 994.
[26] T. M. Alligrant, J. C. Alvarez, *J. Phys. Chem. C* **2011**, *115*, 10797.
[27] B. Gao, J. Li, M. Li, Y. Cheng, L. Wang, *ChemPhysChem* **2009**, *10*, 3197.
[28] M. Funahashi, A. Sonoda, *Org. Electron.* **2012**, *13*, 1633.

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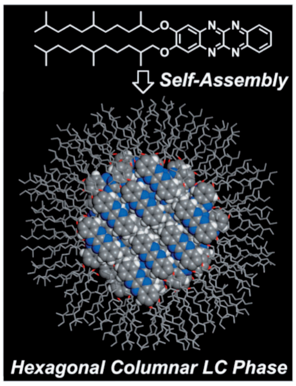
Liquid-crystalline (LC) *N*-heteroacenes, tetraazanaphthacene (TANC), and fluoflavin (FFV) were synthesized, and their self-assembly into columnar LC structures at room temperature was investigated. LC TANC and LC FFV functioned as an electron acceptor and electron donor, respectively. A TANC/FFV LC mixture showed ESR activity in the presence of a strong base.



Liquid Crystals

Kyosuke Isoda, Tomonori Abe, Makoto Tadokoro** ______ ■■■■–■■■■

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