Columnar Liquid Crystalline Assembly of a U-Shaped Molecular Scaffold Stabilized by Covalent or Noncovalent Incorporation of Aromatic Molecules

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ABSTRACT: We report on our serendipitous finding of the anomalous behavior of a novel liquid crystalline (LC) molecule $\mathbf{U_{H/H}}$, containing a U-shaped handle. While $\mathbf{U_{H/H}}$ itself shows a bicontinuous cubic (Cub$_{bi}$) phase, $\mathbf{U_{H/H}}$ in the presence of pyrene molecules as an external guest forms a hexagonal columnar (Col$_h$) phase without phase separation. Interestingly, even when the pyrene molecules were covalently attached to $\mathbf{U_{H/H}}$ ($\mathbf{U_{Py/Py}}$), the molecule exhibited a Col$_h$ phase, with a similar columnar geometry to that of $\mathbf{U_{H/H}}$ mixed with pyrene molecules (1–4 equiv.). This result means that no matter how the pyrene moieties are incorporated in the LC system, the resultant material exhibited a similar molecular assembly with a columnar geometry. This finding is interesting because $\mathbf{U_{H/H}}$ and pyrene molecules do not seem to have specific interactions or shape complementarity to form a columnar assembly, as in the case of $\mathbf{U_{Py/Py}}$. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**

KEYWORDS: bicontinuous cubic phase, hexagonal columnar phase, liquid crystal, luminescence, multi-component liquid crystal, molecular tweezers, pyrene

INTRODUCTION Columnar liquid crystals composed of multiple small molecules, where individual component molecules assemble anisotropically to form homogeneous liquid crystalline (LC) phases, have been attracting profound attention for their potential to exhibit unprecedented functional properties.[1] To provide such complex columnar LC materials, there are mainly two general requirements: (1) specific intermolecular interactions between the components, such as hydrogen bonding interactions,[2] ionic interactions,[3] and charge-transfer interactions;[4] and (2) complementary molecular shapes between the component molecules through host–guest complexation.[5] For example, shape-persistent star mesogens[6] with pyridine pendants, developed by Lehmann et al., can accept guest side-chain units with carboxylic acid moieties in their void spaces via hydrogen bonding.[6e] Interestingly, the guest side-chain unit without hydrogen bonding capability can also fill the space to form a homogeneous hexagonal columnar (Col$_h$) phase[7] with lower clearing temperature, owing to the appropriate shape and size of the cavity.[6e] LC mixture systems, where the components in an LC phase do not mutually satisfy both the requirements above, mostly lead to macrophase separation or the loss of the LC nature.

Herein, we report a new type of multi-component liquid crystals with a U-shaped handle[8] that can exhibit a Col$_h$ LC phase either by the external addition or the covalent attachment of pyrene moieties. This work started from our previous report on jumping behavior of a crystalline molecular tweezers having two pyrenyl head groups in the U-shaped handle (Compound **1**, Sch. 1).[9] As an extension of our interest in the tweezers-like molecular scaffold[8] toward novel functional materials, we designed $\mathbf{U_{Py/Py}}$ (Fig. 1) to confer LC nature to the scaffold by attaching a large benzyl ether dendrons[10] as a flexible side-chain to **1**. $\mathbf{U_{Py/Py}}$ itself assembled in a Col$_h$ manner in its LC mesophase (Fig. 3). In the course of detailed investigations of the columnar assembly of $\mathbf{U_{Py/Py}}$ by comparing with LC properties of $\mathbf{U_{Py/H}}$ (one pyrene head group attached to a U-shaped handle), $\mathbf{U_{H/H}}$ (U-shaped core alone) (Fig. 1), and their mixtures with pyrene molecules, we found that no matter how pyrene moieties are incorporated in the liquid crystals (i.e., covalently attached to U-shaped handle or noncovalently mixed with $\mathbf{U_{H/H}}$), they all formed Col$_h$ phase with a similar intercolumnar distances.

Additional supporting information may be found in the online version of this article.

This article is dedicated to Professor Mitsuo Sawamoto for his life-long outstanding achievements in polymer chemistry.

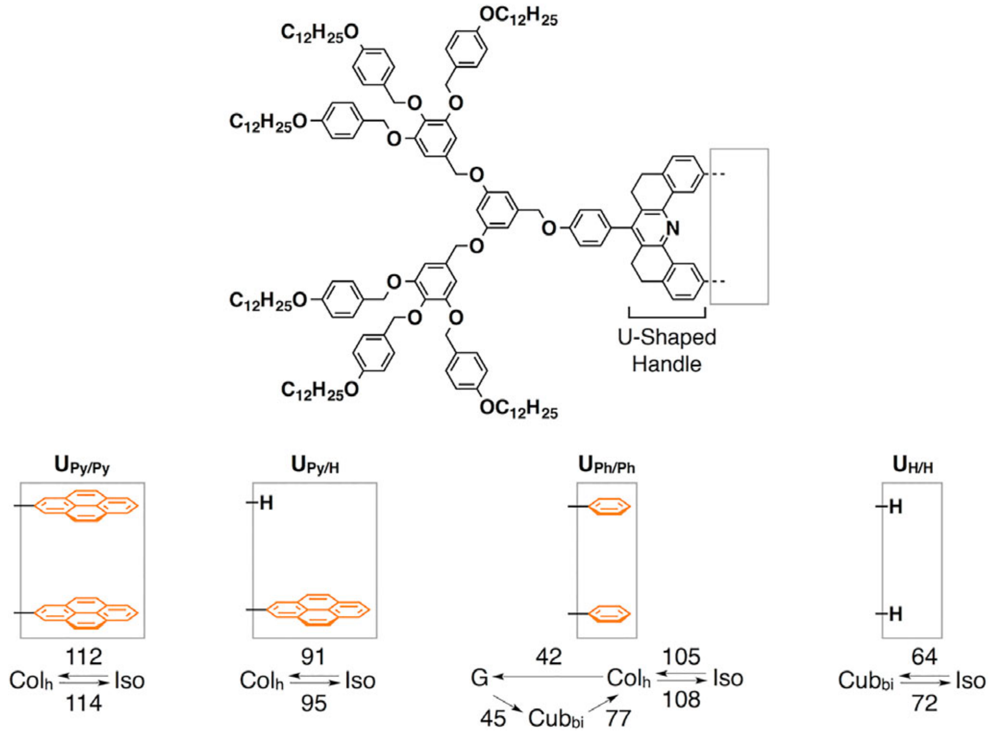


FIGURE 1 Chemical structures of the LC molecules in this report and the phase transition diagrams of those molecules (temperatures in °C; DSC at a scan rate of 10 °C min^{-1}). Col$_h$, G, Cub$_{bi}$, and Iso denote hexagonal columnar, glassy LC, bicontinuous cubic, and isotropic phases, respectively. Mesophases are determined by XRD studies shown in Figure 3 and Supporting Information, Figures S20–S23 and Tables S1–S4. [Color figure can be viewed at wileyonlinelibrary.com]

EXPERIMENTAL

General

Unless otherwise noted, all the commercial reagents were used as received. Recycling preparative high-performance liquid chromatography (HPLC) was performed at room temperature using a 20 mm × 250 mm silica gel column (JAIGEL SIL SH043–10) on a Japan Analytical Industry Model LC-9201 HPLC system, equipped with a variable-wavelength UV–Vis detector. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL model JNM-ECA500II spectrometer, operating at 500 and 126 MHz for ^{1}H and ^{13}C NMR, respectively, where chemical shifts were determined with respect to tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR spectroscopy and CDCl$_3$ (δ 77.0 ppm) for ^{13}C NMR spectroscopy as internal standards. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Daltonics Autoflex™ speed spectrometer with dithranol as a matrix. The electronic absorption spectra were recorded on a JASCO V-670 UV/VIS/NIR spectrometer. The fluorescence spectra were recorded on a Jobin Yvon Horiba Spex Fluorolog 3 spectrometer. The absolute fluorescence quantum yields were recorded on a Hamamatsu C9920–02 absolute PL quantum yield measurement system. The fluorescence lifetimes were recorded by means of a typical time-correlated single-photon counting (TCSPC) method using a Hamamatsu Quantaurus-Tau C11367–02 fluorescence lifetime measurement system, where an internal LED (λ = 340 nm) was used as an excitation light source. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo DSC 1 differential scanning calorimeter. Polarized optical microscopy (POM) was performed on an OLYMPUS model BX51 optical polarizing microscope equipped with a Mettler FP-82HT hot stage. Photographs of the luminescence from the solids were taken by a Keyence VHX-5000 digital microscope under 365 nm UV light. The X-ray diffraction (XRD) experiments were carried out by using a synchrotron radiation X-ray beam, with a wavelength of λ = 1.08 Å on BL44B2 at the Super Photon Ring (SPring-8, Hyogo, Japan). A large Debye–Scherrer camera was used in conjunction with an imaging plate as a detector, and all the diffraction patterns were obtained with a 0.01° step in 2θ. During the measurements, all the samples placed into a 0.5-mm-thick glass capillary were rotated to obtain homogeneous diffraction patterns.

Synthesis of U$_{Py/Py}$

To a CH$_2$Cl$_2$ solution (900 mL) of **1**[9] (428 mg, 0.542 mmol) was added BBr$_3$ (10.8 mL of 1 M solution in CH$_2$Cl$_2$, 10.8 mmol) at −5 °C under Ar. After warming to 25 °C, the reaction mixture was stirred for 12 h. Then, saturated NaHCO$_3$ aq. was added to the mixture, and the mixture was successively acidified with 10% aq. HCl. The resulting mixture was then extracted with CH$_2$Cl$_2$, and the lower phase separated was collected. The organic extract was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to dryness, resulting in the phenol precursor as a yellow powder (384 mg), which was used for the next step without further purification.

A DMF solution (37.6 mL) of the crude phenol precursor obtained above (101 mg, 0.130 mmol), dendron **2**[10] (541 mg, 0.260 mmol), K_2CO_3 (56.4 mg, 0.408 mmol), and 18-crown-6 (4.10 mg, 0.0155 mmol) was stirred for 21 h at 80 °C under Ar. Then, the reaction mixture was poured into 150 mL of an ice/water mixture. The resulting mixture was extracted with CH_2Cl_2, and the lower separated phase was collected. The organic extract was washed with brine, dried over with Na_2SO_4, filtered, and evaporated to dryness. The residue was chromatographed on silica gel with hexane/CH_2Cl_2 (2/3) as the eluent, where the main fraction was collected and evaporated to dryness. The residue was subjected to recycling preparative HPLC (JAIGEL-SIL) with hexane/CH_2Cl_2 (2/3) as the eluent, at a flow rate of 9.9 mL min^{-1}, where the main fraction was collected and evaporated to dryness, resulting in $\mathbf{U}_{\mathbf{Py/Py}}$ as a white paste in 46% yield (2 steps, 185 mg, 0.0656 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 9.22 (d, J = 2.0 Hz, 2H), 8.53 (s, 4H), 8.11 (d, J = 7.5 Hz, 4H), 7.98–8.01 (m, 2H), 7.92 (d, J = 9.0 Hz, 4H), 7.86 (dd, J = 1.5 Hz, 7.5 Hz, 2H), 7.79 (d, J = 9.0 Hz, 4H), 7.40 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 9.0 Hz, 8H), 7.28 (d, J = 8.5 Hz, 4H), 7.17 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 8H), 6.75–6.77 (m, 10H), 6.61 (t, J = 2.0 Hz, 1H), 5.11 (s, 2H), 5.03 (s, 8H), 4.97 (s, 4H), 4.94 (s, 4H), 3.90–3.95 (m, 12H), 2.92–2.95 (m, 4H), 2.77–2.79 (m, 4H), 1.73–1.79 (m, 12H), 1.40–1.47 (m, 12H), 1.25–1.33 (m, 96H), 0.85–0.89 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 160.2, 158.9, 158.9, 158.0, 153.2, 149.7, 140.0, 139.4, 138.9, 138.4, 137.0, 135.8, 132.0, 131.3, 131.0, 130.2, 130.1, 129.8, 129.2, 129.1, 128.9, 128.1, 128.0, 127.6, 127.4, 125.6, 125.0, 124.8, 124.5, 123.6, 114.7, 114.6, 114.4, 114.1, 107.4, 106.6, 106.5, 101.5, 74.8, 71.2, 70.4, 70.0, 68.0, 67.9, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 27.7, 26.1, 25.7, 22.7, 14.1; MALDI-TOF-MS m/z calcd. For $C_{194}H_{236}NO_{15}$ $[M + H]^+$ 2819.77, found 2820.08; Anal. Calcd. for $C_{194}H_{235}NO_{15}$: C, 82.60; H, 8.40; N, 0.50. Found: C, 82.36; H, 8.33; N, 0.41.

Synthesis of 4

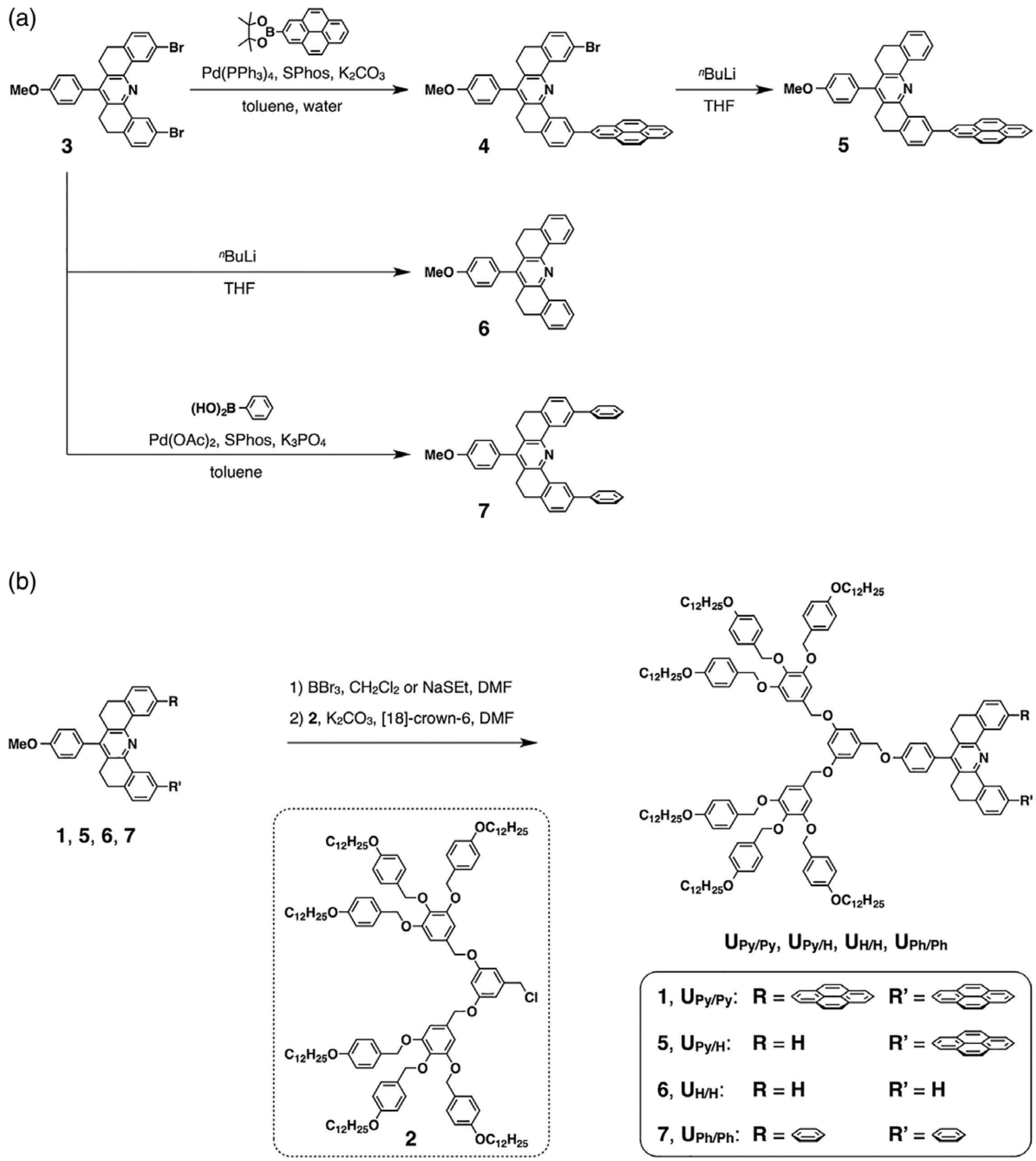
To a toluene solution (25.0 mL) of **3**[9] (221 mg, 0.404 mmol), after being degassed by Ar bubbling for 30 min, were added 4,4,5,5-tetramethyl-2-pyren-2-yl-[1,3,2]dioxaborolane (2-(Bpin)pyrene)[11] (128 mg, 0.390 mmol), 1.0 mM K_2CO_3 aq. (2.50 mL, 2.50 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (35.5 mg, 0.0865 mmol), and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (45.4 mg, 0.0393 mmol) under a gentle flow of Ar, and the resulting mixture was stirred at 80 °C for 28 h. After the mixture was allowed to cool to 25 °C, saturated aq. $NaHCO_3$ was added. The resulting mixture was extracted with toluene, and the upper separated phase was collected. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was chromatographed on silica gel with hexane/CH_2Cl_2 (2/1) as the eluent, where the main fraction was collected and evaporated to dryness, resulting in **4** as a white powder in 16% yield (41.9 mg, 0.0627 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 9.06 (d, J = 2.0 Hz, 1H), 8.72 (d, J = 2.5 Hz, 1H), 8.58 (s, 2H), 8.20 (d, J = 7.5 Hz, 2H), 8.20 (d, J = 9.0 Hz, 2H), 8.13 (d, J = 9.5 Hz, 2H), 8.00–8.03 (m, 1H), 7.86 (dd, J = 2.0 Hz, 7.8 Hz, 1H), 7.41–7.43 (m, 2H), 7.17 (d, J = 9.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H), 2.92–2.95 (m, 2H), 2.76–2.82 (m, 4H), 2.69–2.72 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 159.1, 150.3, 148.9, 147.5, 140.4, 139.0, 137.3, 137.2, 136.6, 135.7, 131.6, 131.4, 131.1, 130.1, 129.9, 129.6, 129.5, 129.1, 128.4, 128.3, 128.2, 127.7, 127.7, 125.8, 125.0, 124.7, 124.6, 123.9, 123.8, 121.0, 114.0, 55.3, 27.9, 27.7, 26.0, 25.7; MALDI-TOF-MS m/z calcd. For $C_{44}H_{31}BrNO$ $[M + H]^+$ 668.16, found 668.64.

Synthesis of 5

To a THF solution (15.0 mL) of **4** (41.0 mg, 0.0613 mmol) was added ^{n}BuLi (70.0 μL of 2.66 M solution in hexane, 0.184 mmol) at −78 °C under Ar. After the reaction mixture was stirred for 1 h at −78 °C, MeOH (18 μL) was added. After warming to 25 °C, the reaction mixture was stirred for 15 h. Then, drops of water were added to the solution at 0 °C. After the organic solvents were evaporated, CH_2Cl_2 and water were added to the resultant solid. The resulting mixture was extracted with CH_2Cl_2, and the lower phase separated was collected. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/CH_2Cl_2 (2/1) as eluent, where the main fraction was collected and evaporated to dryness under reduced pressure. The residue was reprecipitated from $CHCl_3$/MeOH, resulting in **5** as a white solid in 74% yield (26.7 mg, 0.0452 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 9.07 (d, J = 2.5 Hz, 1H), 8.60 (dd, J = 1.0 Hz, 7.5 Hz, 1H), 8.55 (s, 2H), 8.18–8.22 (m, 4H), 8.13 (d, J = 9.5 Hz, 2H), 8.00–8.03 (m, 1H), 7.83 (dd, J = 1.8 Hz, 7.3 Hz, 1H), 7.39–7.42 (m, 2H), 7.31 (td, J = 1.5 Hz, 7.3 Hz, 1H), 7.22 (d, J = 7.0 Hz, 1H), 7.18 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 3.91 (s, 3H), 2.93–2.96 (m, 2H), 2.85–2.87 (m, 2H), 2.76–2.79 (m, 2H), 2.70–2.73 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 159.0, 150.2, 150.0, 147.3, 140.4, 139.3, 137.9, 137.2, 136.0, 135.3, 131.5, 131.1, 129.9, 129.9, 129.5, 129.4, 128.7, 128.3, 128.2, 127.7, 127.7, 127.4, 127.1, 125.8, 125.4, 125.0, 124.8, 124.6, 123.9, 123.8, 114.0, 55.3, 28.2, 28.0, 25.9, 25.9; MALDI-TOF-MS m/z calcd. For $C_{44}H_{32}NO$ $[M + H]^+$ 590.25, found 590.66.

Synthesis of $\mathbf{U}_{\mathbf{Py/H}}$

To a CH_2Cl_2 solution (10 mL) of **5** (26.0 mg, 0.0440 mmol) was added BBr_3 (150 μL of 1 M solution in CH_2Cl_2, 0.150 mmol) at −5 °C under Ar. After warming to 25 °C, the reaction mixture was stirred for 7 h. Saturated aq. $NaHCO_3$ was added to the mixture, and the mixture was acidified with 10% HCl aq. The resulting mixture was then extracted with CH_2Cl_2, and the lower phase was separated and collected. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel



SCHEME 1 Synthesis of LC molecules containing a U-shaped handle ($\mathbf{U_{Py/Py}}$, $\mathbf{U_{Py/H}}$, $\mathbf{U_{H/H}}$, and $\mathbf{U_{Ph/Ph}}$) and their precursors (**5**, **6**, and **7**).

using hexane/CH_2Cl_2 (1/5) as the eluent, where the main fraction was collected and evaporated to dryness under reduced pressure, resulting in the phenol precursor as a white powder (20.0 mg), which was used for the next step without further purification.

A DMF solution (8.00 mL) containing the crude phenol precursor obtained above (20.0 mg, 0.0347 mmol), dendron **2**[10] (183 mg, 0.0879 mmol), K_2CO_3 (17.6 mg, 0.127 mmol), and 18-crown-6 (1.20 mg, 0.00588 mmol) was stirred for 54 h at 80 °C under Ar. The reaction mixture was poured into 40 mL of ice/water. The resulting mixture was extracted with CH_2Cl_2, and the lower phase separated was collected. The organic extract was washed with brine, dried over with Na_2SO_4, filtered, and evaporated to dryness. The residue was chromatographed on silica gel with hexane/CH_2Cl_2 (2/5) as the eluent, where the main fraction was collected and evaporated to dryness, resulting in $\mathbf{U_{Py/H}}$ as a white paste in 15% yield (2 steps, 11.4 mg, 0.00435 mmol). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 9.07 (d, J = 2.5 Hz, 1H), 8.60 (dd, J = 1.0 Hz, 8.0 Hz, 1H), 8.55 (s, 2H), 8.18–8.22 (m, 4H), 8.13 (d, J = 9.0 Hz, 2H), 8.00–8.03 (m, 1H), 7.83 (dd, J = 1.8 Hz, 7.8 Hz, 1H), 7.38–7.41 (m, 2H), 7.32 (d, J = 8.5 Hz, 8H), 7.28 (d, J = 8.5 Hz, 4H), 7.20 (d, J = 7.0 Hz, 1H), 7.17 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 8H), 6.75–6.77 (m, 10H), 6.60 (t, J = 2.3 Hz, 1H), 5.10 (s, 2H), 5.03 (s, 8H), 4.96 (s, 4H), 4.94

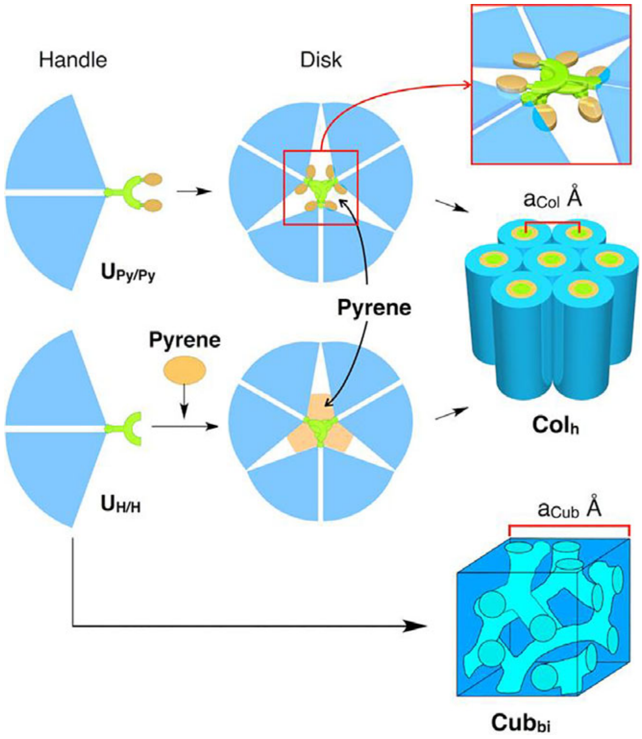


FIGURE 2 Schematic illustration of the stacking of U-shaped handles observed in both Col_h and Cub_{bi} LC assemblies of the LC molecules in this report. [Color figure can be viewed at wileyonlinelibrary.com]

(s, 4H), 3.90–3.96 (m, 12H), 2.90–2.93 (m, 2H), 2.82–2.85 (m, 2H), 2.74–2.77 (m, 2H), 2.69–2.72 (m, 2H), 1.73–1.80 (m, 12H), 1.41–1.47 (m, 12H), 1.25–1.34 (m, 96H), 0.86–0.89 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 160.2, 158.9, 158.9, 158.2, 153.2, 140.4, 139.3, 139.2, 138.4, 137.8, 137.7, 137.2, 136.0, 135.3, 132.0, 131.5, 131.1, 130.2, 130.0, 129.8, 129.4, 129.4 129.2, 128.9, 128.7, 128.3, 128.2, 127.7, 127.4, 125.8, 125.4, 125.0, 125.0, 124.7, 124.6, 123.9, 123.8, 114.9, 114.6, 114.4, 114.1, 107.4, 106.5, 106.5, 101.5, 74.8, 71.2, 70.4, 70.1, 68.0, 68.0, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 27.7, 29.4, 29.3, 29.3, 26.0, 26.0, 22.7, 14.1; MALDI-TOF-HRMS *m/z* calcd. For $C_{178}H_{228}NO_{15}$ $[M + H]^+$ 2619.7031, found 2619.7041.

Synthesis of 6

To a THF solution (16.0 mL) of **3**[9] (300 mg, 0.548 mmol) was added ^{n}BuLi (1.30 mL of 2.66 M solution in hexane, 3.46 mmol) at −78 °C under Ar. After the reaction mixture was stirred for 1 h at −78 °C, MeOH (270 μL) was added. After warming to 25 °C, the reaction mixture was stirred for 18 h. Then, drops of water were added to the solution at 0 °C. After the organic solvents were evaporated, CH_2Cl_2 and water were added to the resultant solid, and the resulting mixture was extracted with CH_2Cl_2. The lower phase was collected. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was recrystallized from $CHCl_3$/MeOH, resulting in **6** as white prisms in 91% yield (193 mg, 0.496 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.57 (dd, *J* = 1.5 Hz, 7.3 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30 (td, *J* = 1.2 Hz, 7.4 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 2.81–2.84 (m, 2H), 2.66–2.69 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 159.0, 150.0, 147.2, 137.8, 135.4, 129.9, 129.9, 129.2, 128.6, 127.4, 127.0, 125.3, 113.9, 55.3, 28.2, 25.8; MALDI-TOF-MS *m/z* calcd. For $C_{28}H_{24}NO$ $[M + H]^+$ 390.19, found 390.45.

Synthesis of $U_{H/H}$

To a DMF solution (20 mL) of **6** (40.4 mg, 0.104 mmol) was added NaSEt (240 mg, 2.86 mmol) at 25 °C under Ar. After warming to 140 °C, the reaction mixture was stirred for 1 h. Then, the reaction mixture was poured into saturated aq. $NaHCO_3$, and the mixture was acidified with 10% HCl aq. The resulting mixture was extracted with CH_2Cl_2, and the lower phase was collected. The organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane/AcOEt (3/1) as eluent, where the main fraction was collected and evaporated to dryness under reduced pressure, resulting in phenol precursor as a white powder (39.6 mg), which was used for the next step without further purification.

A DMF solution (13.0 mL) of the crude phenol precursor obtained above (20.6 mg, 0.0549 mmol), dendron **2**[10] (173 mg, 0.0831 mmol), K_2CO_3 (22.0 mg, 0.159 mmol), and 18-crown-6 (2.30 mg, 0.0113 mmol) was stirred for 22 h at 80 °C under Ar. The reaction mixture was poured into 60 mL of ice/water. The resulting mixture was extracted with CH_2Cl_2, and the lower phase was collected. The organic extract was washed with brine, dried over with Na_2SO_4, filtered, and evaporated to dryness. The residue was chromatographed on silica gel with hexane/AcOEt (5/1) as the eluent, where the main fraction was collected and evaporated to dryness. The residue was further chromatographed on silica gel with hexane/CH_2Cl_2 (1/2) as the eluent, where the main fraction was collected and evaporated to dryness, resulting in $\mathbf{U_{H/H}}$ as a white paste in 26% yield (2 steps, 34.6 mg, 0.0143 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, ppm): δ 8.57 (dd, *J* = 1.0 Hz, 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.27–7.32 (m, 14H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 8H), 6.74–6.77 (m, 10H), 6.59 (t, *J* = 2.0 Hz, 1H), 5.07 (s, 2H), 5.02 (s, 8H), 4.95 (s, 4H), 4.93 (s, 4H), 3.90–3.95 (m, 12H), 2.79–2.82 (m, 4H), 2.65–2.68 (m, 4H), 1.74–1.80 (m, 12H), 1.41–1.47 (m, 12H), 1.26–1.34 (m, 96H), 0.86–0.89 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, ppm): δ 160.2, 158.9, 158.9, 158.2, 153.2, 150.0, 147.1, 139.3, 138.4, 137.8, 135.4, 132.0, 130.3, 130.2, 130.0, 129.8, 129.2, 129.1, 128.9, 128.6, 127.4, 127.0, 125.3, 114.8, 114.4, 114.1, 107.4, 106.5, 101.5, 74.8, 71.2, 70.4, 70.0, 68.0, 68.0, 31.9, 29.7, 29.6, 29.4, 29.3, 29.3, 28.1, 26.1, 25.8, 22.7, 14.1; MALDI-TOF-MS *m/z* calcd. For $C_{162}H_{220}NO_{15}$ $[M + H]^+$ 2419.65, found 2419.51; Anal. Calcd. for $C_{162}H_{219}NO_{15}$: C, 80.39; H, 9.12; N, 0.58. Found: C, 80.42; H, 9.20; N, 0.63.

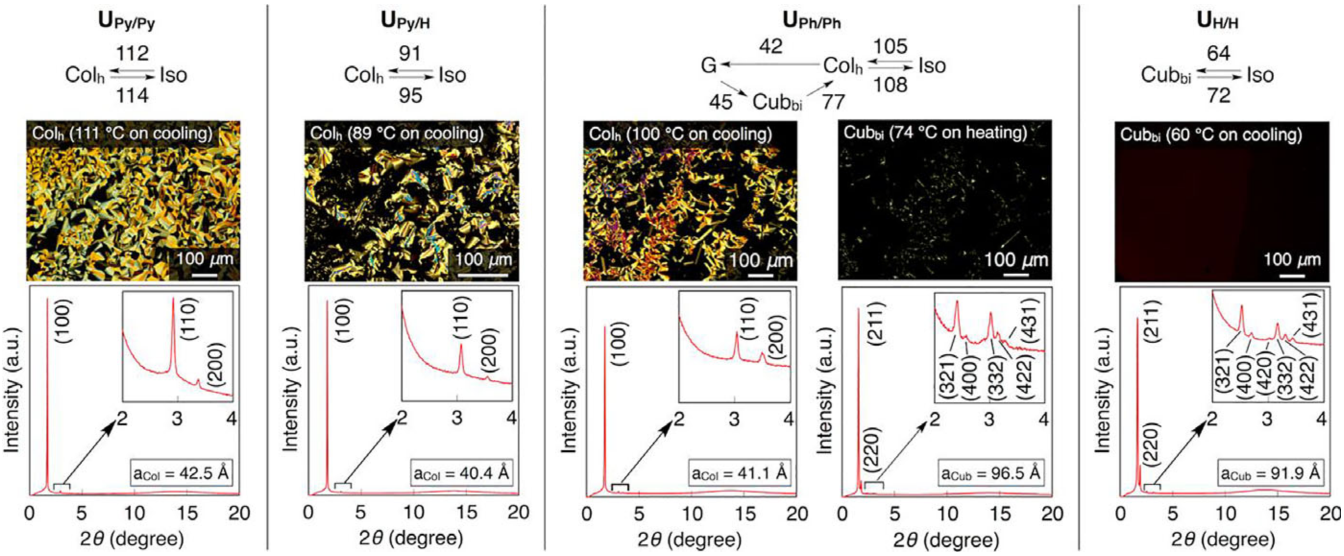


FIGURE 3 A series of characterization data for $\mathbf{U_{Py/Py}}$, $\mathbf{U_{Py/H}}$, $\mathbf{U_{Ph/Ph}}$, and $\mathbf{U_{H/H}}$ in the LC phase. Each column contains a phase transition diagram (temperature in °C; DSC at a scan rate of 10 °C min^{-1}), a POM image, and an XRD pattern. Col$_h$, G, Cub$_{bi}$, and Iso denote hexagonal columnar, glassy LC, bicontinuous cubic, and isotropic phases, respectively. The numbers in parentheses in XRD patterns are Miller indexes assigned to each diffraction peak. The XRD patterns were taken at 110 °C (for $\mathbf{U_{Py/Py}}$), 87 °C (for $\mathbf{U_{Py/H}}$), 99 °C (for the Col$_h$ phase of $\mathbf{U_{Ph/Ph}}$), 70 °C (for the Cub$_{bi}$ phase of $\mathbf{U_{Ph/Ph}}$), and 60 °C (for $\mathbf{U_{H/H}}$). [Color figure can be viewed at wileyonlinelibrary.com]

Synthesis of 7

To a toluene solution (1.00 mL) of **3**[9] (30.2 mg, 0.0552 mmol), after being degassed by Ar bubbling for 30 min, were added phenylboronic acid (17.1 mg, 0.140 mmol), K_3PO_4 (231 mg, 1.09 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (5.30 mg, 0.0129 mmol), and palladium acetate (Pd(OAc)$_2$) (2.0 mg, 0.00891 mmol) under a gentle flow of Ar, and the resulting mixture was stirred at 80 °C for 8 h. After the mixture was allowed to cool to 25 °C, it was filtered with Celite and a pad of silica. The filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from CHCl$_3$/MeOH, resulting in **7** as a white powder in 84% yield (25.0 mg, 0.0462 mmol). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, ppm): δ 8.86 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 6.5 Hz, 4H), 7.57 (dd, J = 2.3 Hz, 7.8 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.35–7.38 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H), 2.87–2.90 (m, 4H), 2.71–2.74 (m, 4H); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C, ppm): δ 159.0, 150.0, 147.3, 141.3, 139.8, 137.0, 135.7, 129.9, 129.9, 129.4, 128.7, 127.9, 127.2, 127.1, 123.9, 114.0, 55.3, 27.9, 25.9; MALDI-TOF-MS m/z calcd. For $C_{40}H_{32}NO$ [M + H]$^+$ 542.25, found 542.64.

Synthesis of $\mathbf{U_{Ph/Ph}}$

To a DMF solution (15 mL) of **7** (33.0 mg, 0.0610 mmol) was added NaSEt (159 mg, 1.89 mmol) at 25 °C under Ar. After warming to 140 °C, the reaction mixture was stirred for 1 h. The reaction mixture was poured into saturated aq. NaHCO$_3$, and the mixture was acidified with 10% HCl aq. The resulting mixture was extracted with CH$_2$Cl$_2$, and the lower phase was collected. The organic extract was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to dryness under reduced pressure, resulting in the phenol precursor as a white powder (34.8 mg), which was used for the next step without further purification.

A DMF solution (13.0 mL) of the crude phenol precursor obtained above (23.1 mg, 0.0438 mmol), dendron **2**[10] (144 mg, 0.0692 mmol), K$_2$CO$_3$ (19.8 mg, 0.143 mmol), and 18-crown-6 (1.90 mg, 0.00931 mmol) was stirred for 23 h at 80 °C under Ar. The reaction mixture was poured into 60 mL of ice/water. The resulting mixture was extracted with CH$_2$Cl$_2$, and the lower phase was collected. The organic extract was washed with brine, dried over Na$_2$SO$_4$, filtered, and evaporated to dryness. The residue was chromatographed on silica gel with hexane/AcOEt (5/1) as the eluent, where the main fraction was collected and evaporated to dryness. The residue was further chromatographed on silica gel with hexane/CH$_2$Cl$_2$ (1/2) as the eluent, where the main fraction was collected and evaporated to dryness, resulting in $\mathbf{U_{Ph/Ph}}$ as a white paste in 48% yield (2 steps, 49.8 mg, 0.0194 mmol). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, ppm): δ 8.86 (d, J = 2.5 Hz, 2H), 7.76 (d, J = 7.0 Hz, 4H), 7.56 (dd, J = 2.3 Hz, 7.8 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.35–7.38 (m, 2H), 7.31 (d, J = 8.5 Hz, 8H), 7.26–7.29 (m, 6H), 7.15 (d, J = 9.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 8H), 6.74–6.77 (m, 10H), 6.60 (t, J = 2.0 Hz, 1H), 5.09 (s, 2H), 5.02 (s, 8H), 4.95 (s, 4H), 4.93 (s, 4H), 3.90–3.95 (m, 12H), 2.84–2.87 (m, 4H), 2.70–2.73 (m, 4H), 1.73–1.80 (m, 12H), 1.41–1.47 (m, 12H), 1.26–1.35 (m, 96H), 0.86–0.89 (m, 18H); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C, ppm): δ 160.2, 158.9, 158.9, 158.2, 153.2, 150.0, 147.2, 141.3, 139.8, 139.3, 138.4, 136.9, 135.7, 132.0, 130.3, 130.2, 130.0, 129.8, 129.4, 128.9, 128.7, 127.9, 127.2, 127.0, 114.9, 114.4, 114.1, 107.4, 106.5, 101.5, 74.8, 71.2, 70.4, 70.1, 68.0,

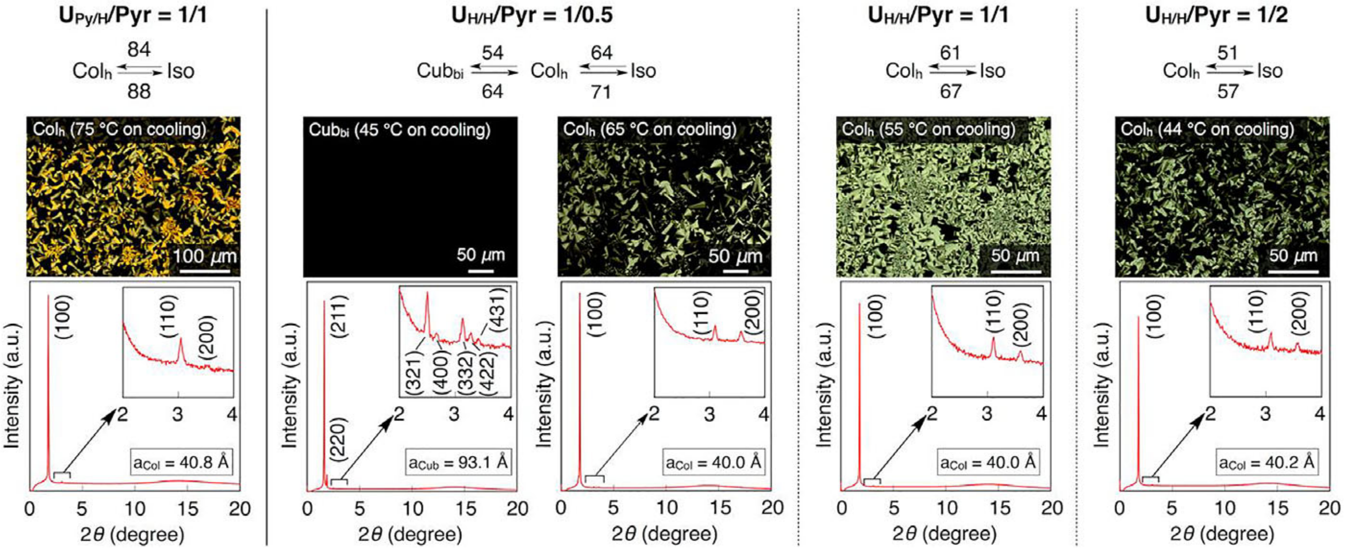


FIGURE 4 A series of characterization data for the binary mixtures of $\mathbf{U_{Py/H}}$**/Pyr** = 1/1, $\mathbf{U_{H/H}}$**/Pyr** = 1/0.5, $\mathbf{U_{H/H}}$**/Pyr** = 1/1, and $\mathbf{U_{H/H}}$**/Pyr** = 1/2 (molar ratio) in LC phase. Each column contains a phase transition diagram (temperature in °C; DSC at a scan rate of 10 °C min^{-1}), a POM image, and an XRD pattern. Col$_h$, Cub$_{bi}$, and Iso denote hexagonal columnar, bicontinuous cubic, and isotropic phases, respectively. The numbers in parentheses in XRD patterns are Miller indexes assigned to each diffraction peak. The XRD patterns were taken at 75 °C (for $\mathbf{U_{Py/H}}$**/Pyr** = 1/1), 45 °C (for the Cub$_{bi}$ phase of $\mathbf{U_{H/H}}$**/Pyr** = 1/0.5), 58 °C (for the Col$_h$ phase of $\mathbf{U_{H/H}}$**/Pyr** = 1/0.5), 58 °C (for $\mathbf{U_{H/H}}$**/Pyr** = 1/1), and 50 °C (for $\mathbf{U_{H/H}}$**/Pyr** = 1/2). [Color figure can be viewed at wileyonlinelibrary.com]

68.0, 31.9, 29.7, 29.6, 29.4, 29.3, 29.3, 27.8, 26.1, 25.9, 22.7, 14.1; MALDI-TOF-MS *m/z* calcd. For $C_{174}H_{228}NO_{15}$ $[M + H]^+$ 2571.71, found 2571.87; Anal. Calcd. for $C_{174}H_{227}NO_{15}$: C, 81.23; H, 8.89; N, 0.54. Found: C, 80.88; H, 9.16; N, 0.54.

RESULTS AND DISCUSSION

$\mathbf{U_{Py/Py}}$ was synthesized from the methoxy-substituted precursor **1**[9] (Sch. 1). Subsequent deprotection of the methoxy unit followed by a Williamson etherification reaction with a benzyl chloride-terminated Percec-type dendron[10] gave $\mathbf{U_{Py/Py}}$. This molecule was unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy (Supporting Information, Figs. S1 and S2) and MALDI-TOF-MS. The differential scanning calorimetry (DSC) profile of $\mathbf{U_{Py/Py}}$ showed a phase transition at 112 and 114 °C for the cooling and heating processes, respectively (Supporting Information, Fig. S10). Polarized optical microscopy (POM) of $\mathbf{U_{Py/Py}}$ on cooling from its isotropic melt displayed a fan texture at 111 °C (Fig. 3), which is characteristic of a Col$_h$ LC mesophase. Synchrotron radiation X-ray diffraction (XRD) analysis of $\mathbf{U_{Py/Py}}$ at 110 °C showed diffraction peaks, with *d* spacings of 36.8, 21.2, and 18.4 Å (Supporting Information, Fig. S20 and Table S1), which were indexed as (100), (110), and (200) diffractions of a Col$_h$ assembly, with an intercolumnar distance of 42.5 Å (Fig. 3).

For the detailed understanding of the columnar assembly of $\mathbf{U_{Py/Py}}$, the LC properties of $\mathbf{U_{Py/H}}$, $\mathbf{U_{H/H}}$, and $\mathbf{U_{Ph/Ph}}$ (Fig. 1) were investigated. These molecules were synthesized from the corresponding methoxy-substituted precursors (**5**, **6**, and **7** in Sch. 1) in the same way as the synthesis of $\mathbf{U_{Py/Py}}$. Analogous to $\mathbf{U_{Py/Py}}$, $\mathbf{U_{Py/H}}$ with one pyrenyl head group also exhibited a Col$_h$ phase below 91 °C on cooling (DSC, Supporting Information, Fig. S11). Its intercolumnar distance of 40.4 Å (Fig. 3 and Supporting Information, Fig. S21 and Table S2) calculated from the XRD pattern at 87 °C was slightly shorter than that of $\mathbf{U_{Py/Py}}$ at 110 °C (42.5 Å, Fig. 3). Meanwhile, $\mathbf{U_{H/H}}$ exhibited a bicontinuous cubic (Cub$_{bi}$) phase with $Ia\overline{3}d$ space group[12] below 64 °C on cooling (DSC, Supporting Information, Fig. S12), with a lattice constant of 91.9 Å at 60 °C (XRD, Fig. 3 and Supporting Information, Fig. S22 and Table S3). $\mathbf{U_{Ph/Ph}}$, with two phenyl head groups, exhibited a Col$_h$ LC mesophase between 105 and 42 °C on cooling (DSC, Supporting Information, Fig. S13) with an intercolumnar distance of 41.1 Å (99 °C, XRD, Fig. 3) and a Cub$_{bi}$ LC mesophase ($Ia\overline{3}d$) between 45 and 77 °C on heating (Supporting Information, Fig. S23 and Table S4). These characterizations of the LC molecules demonstrated that the geometries of an LC assembly are determined by the size of the head groups; the larger head groups (pyrenyl) formed a Col$_h$ assembly, and the smaller head groups (hydrogen) formed a Cub$_{bi}$ assembly (Fig. 2).

Interestingly, the addition of one or two equivalents of pyrene molecules as a guest to Cub$_{bi}$ liquid crystal of $\mathbf{U_{H/H}}$ formed a homogeneous Col$_h$ LC assembly. Mixtures of $\mathbf{U_{H/H}}$ with one equivalent of pyrene ($\mathbf{U_{H/H}}$**/Pyr** = 1/1) and two equivalents of pyrene ($\mathbf{U_{H/H}}$**/Pyr** = 1/2) were prepared by the slow-evaporation of $CHCl_3$ solutions, and their LC properties were investigated (DSC: Supporting Information, Figs. S16 and S17; POM: Fig. 4; XRD: Fig. 4 and Supporting Information, Figs. S26 and S27 and Tables S7 and S8). Both the mixtures exhibited Col$_h$ LC mesophases, with intercolumnar distances of 40.0 Å (58 °C for $\mathbf{U_{H/H}}$**/Pyr** = 1/1 in Fig. 4) and 40.2 Å (50 °C for

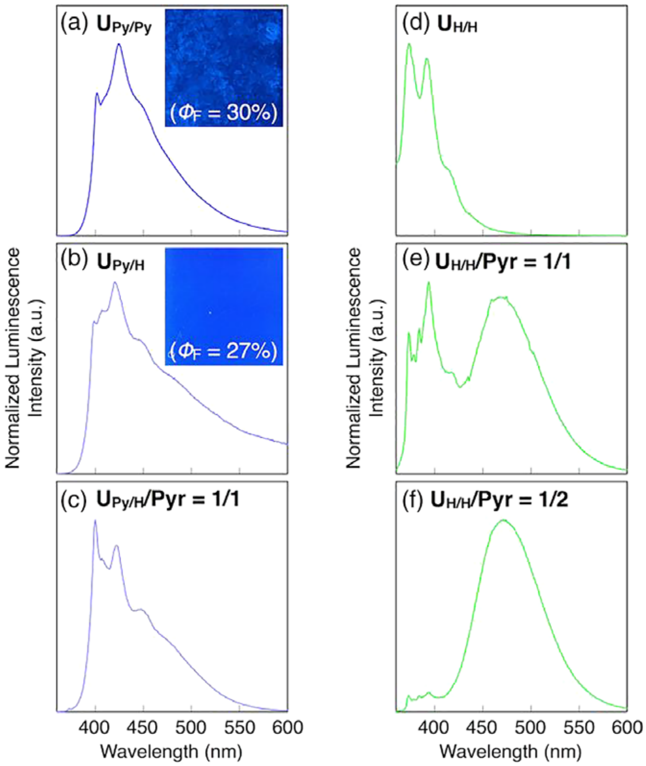


FIGURE 5 Luminescence spectra (λ_{ex} = 340 nm) of film samples of (a) $\mathbf{U_{Py/Py}}$, (b) $\mathbf{U_{Py/H}}$, (c) $\mathbf{U_{Py/H}/Pyr}$ = 1/1, (d) $\mathbf{U_{H/H}}$, (e) $\mathbf{U_{H/H}/Pyr}$ = 1/1, and (f) $\mathbf{U_{H/H}/Pyr}$ = 1/2. The insets in (a) and (b) show photographs of emission from film samples of (a) $\mathbf{U_{Py/Py}}$ and (b) $\mathbf{U_{Py/H}}$ under 365 nm UV light. Φ_F denotes absolute luminescence quantum yield. The film samples were prepared by sandwiching the LC molecules by two quartz flats and cooled from its isotropic melt to 25 °C at a rate of 5 °C min^{-1}. [Color figure can be viewed at wileyonlinelibrary.com]

$\mathbf{U_{H/H}/Pyr}$ = 1/2 in Fig. 4). These intercolumnar distances are close to those of $\mathbf{U_{Py/Py}}$ (42.5 Å, Fig. 3), $\mathbf{U_{Py/H}}$ (40.4 Å, Fig. 3), and $\mathbf{U_{Ph/Ph}}$ (41.1 Å, Fig. 3) in their Col$_h$ LC mesophases. Similarly, $\mathbf{U_{Py/H}}$ incorporated with one equivalent of pyrene molecule as a guest ($\mathbf{U_{Py/H}/Pyr}$ = 1/1) exhibited a Col$_h$ phase, with an intercolumnar distance of 40.8 Å (75 °C, Fig. 4). The series of investigations above clarified that the intercolumnar distances of a Col$_h$ phase are independent of how the pyrene moieties are incorporated in the LC system. From these observations, we propose in Figure 2 and Figure S38 in the Supporting Information a model of columnar assembly of $\mathbf{U_{Py/Py}}$ based on the stacking of the U-shaped handle, where one column stratum consists of three molecules.[13] In this model, the center of disk is the U-shaped handle, and the pyrene head groups overhang from the center. Even in the mixture systems, such as $\mathbf{U_{H/H}/Pyr}$ = 1/1, $\mathbf{U_{H/H}/Pyr}$ = 1/2, and $\mathbf{U_{Py/H}/Pyr}$ = 1/1, the guest pyrene molecules resided around the center, resulting in similar Col$_h$ geometries to $\mathbf{U_{Py/Py}}$ (Fig. 2). This model is consistent with a previous report that the benzyl-ether dendron employed in this study forms a disk with three molecules for the construction of a columnar structure.[10c] If we suppose that the average height of the column stratum is three times of the average π-stacking distance (three times of 3.4 Å[14]) and the density of the LC molecule is 1.0 g cm^{-3}, as reported in a reference using the same benzyl-ether dendron,[10c] the number of molecules used for making one disk can be calculated to be 3.4, 3.3, and 3.5 for $\mathbf{U_{Py/Py}}$, $\mathbf{U_{Py/H}}$, and $\mathbf{U_{Ph/Ph}}$, respectively. These results also support the model (Fig. 2).

Interestingly, both $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ in their Col$_h$ LC states displayed a deep blue luminescence.[15] In CHCl$_3$, $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ in electronic absorption spectroscopy showed fine vibronic absorption bands assignable to the absorption of pyrene (Supporting Information, Figs. S32 and S33).[16] The luminescence spectra of $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ in CHCl$_3$ upon excitation at 340 nm likewise displayed a fine vibronic structure, with three emission maxima (Supporting Information, Figs. S34 and S35).[15] The film samples of $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$, upon excitation at 340 nm, explicitly displayed luminescence peaks at 425 nm and 421 nm, respectively [Fig. 5(a,b)], without any obvious excimer peaks, and showed deep blue-color emissions [Fig. 5(a,b), insets].[15] We monitored the luminescence decay profiles (Supporting Information, Figs. S36 and S37) of $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ at six different emission wavelengths, 400, 420, 440, 460, 480, and 500 nm, upon excitation at 340 nm (Supporting Information, Tables S11 and S12). For $\mathbf{U_{Py/Py}}$, the luminescence decay profiles at 400 nm and 420 nm, which are at around the peak of the luminescence spectrum [425 nm, Fig. 5(a)], could be fit by one or two components without rise time (Supporting Information, Table S11 and Fig. S36), indicating that the luminescence profile was dominated by the emission from nonstacked pyrenyl head groups.[15] This was also the case in the luminescence decay profiles of $\mathbf{U_{Py/H}}$ (Supporting Information, Table S12 and Fig. S37), where the decay profiles at 400, 420, and 440 nm could be fit by one component without rise time. These spectral features indicate that the pyrenyl moieties most likely exist as a monomeric species. Notably, none of the previously reported pyrene-containing LC materials[17] displayed deep blue-color emissions ($\lambda_{em,max}$ = 425 nm for $\mathbf{U_{Py/Py}}$ and 421 nm for $\mathbf{U_{Py/H}}$) in bulk. Therefore, the luminescence behaviors of $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ were quite distinctive.

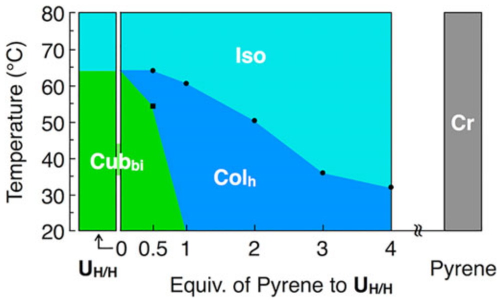


FIGURE 6 Phase diagram of the mixtures of $\mathbf{U_{H/H}}$ with guest pyrene molecules ($\mathbf{U_{H/H}/Pyr}$ = 1/x) with x = 0, 0.5, 1, 2, 3, and 4 (phase transition temperatures (in °C; DSC on cooling at a scan rate of 10 °C min^{-1}) versus molar equivalent of guest pyrene molecules). $\mathbf{U_{H/H}/Pyr}$ = 1/0 means $\mathbf{U_{H/H}}$ alone without any guest molecules. Col$_h$, Cub$_{bi}$, Cr, and Iso denote hexagonal columnar, bicontinuous cubic, crystal, and isotropic phases, respectively. [Color figure can be viewed at wileyonlinelibrary.com]

Luminescence spectroscopy for the film samples of mixtures, $\mathbf{U_{Py/H}}$**/Pyr** = 1/1, $\mathbf{U_{H/H}}$**/Pyr** = 1/1, and $\mathbf{U_{H/H}}$**/Pyr** = 1/2, provided information about how guest pyrene disks are incorporated in the parent LC molecules. In the case of $\mathbf{U_{Py/H}}$**/Pyr** = 1/1, the luminescence spectrum [Fig. 5(c)] was similar to that of $\mathbf{U_{Py/H}}$ [Fig. 5(b)], without the distinctive broad luminescence peak at ~470 nm. This result indicated that pyrene molecules and pyrenyl head groups do not form excimers.[15] The mixtures $\mathbf{U_{H/H}}$**/Pyr** = 1/1 and $\mathbf{U_{H/H}}$**/Pyr** = 1/2 both showed broad luminescence peaks at ~470 nm [Fig. 5(e,f)], which were not observed in luminescence spectra of $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$ [Fig. 5(a,b)]. These broad peaks could be due to an excimer emission from the guest pyrene molecules, indicating that the guest molecules in the LC medium have positional freedom to form an excimer.

The summary of phase transition behaviors of the mixtures of $\mathbf{U_{H/H}}$ and pyrene molecules at different molar ratios is shown in Figure 6. DSC traces, POM images, and XRD patterns of these mixtures are shown in Figure 4 and the Supporting Information (DSC: Supporting Information, Figs. S15–S19; POM: Supporting Information, Figs. S30 and S31; XRD: Supporting Information, Figs. S25–S29 and Tables S6–S10). First, a mixture of $\mathbf{U_{H/H}}$ with 0.5 equivalent of pyrene ($\mathbf{U_{H/H}}$**/Pyr** = 1/0.5) was prepared. Interestingly, this mixture exhibited a Cub_{bi} LC mesophase below 54 °C (DSC, Supporting Information, Fig. S15), with a lattice constant of 93.1 Å at 45 °C (Fig. 4 and Supporting Information, Fig. S25 and Table S6) together with a Col_{h} LC mesophase with a lattice constant of 40.0 Å at 58 °C (Fig. 4 and Supporting Information, Fig. S25 and Table S6) in a very narrow temperature range between 64 and 54 °C on cooling. This result indicates that at least one equivalent of guest pyrene is required to convert the original Cub_{bi} LC mesophase of $\mathbf{U_{H/H}}$ completely to a Col_{h} LC mesophase. Interestingly, upon further addition of the guest pyrene molecules ($\mathbf{U_{H/H}}$**/Pyr** = 1/2, 1/3, and 1/4), POM images of the samples showed homogeneous fan textures (Fig. 4 and Supporting Information, Figs. S30 and S31). The XRD patterns of the sample were consistent with Col_{h} assemblies (Supporting Information, Tables S8–S10), without any peaks assignable to crystalline guest pyrene (Supporting Information, Figs. S27–S29). This observation indicates that $\mathbf{U_{H/H}}$ has a large capability to incorporate guest molecules.

CONCLUSIONS

In conclusion, we developed a novel LC molecule $\mathbf{U_{H/H}}$, bearing a U-shaped handle, that exhibited a Cub_{bi} phase. In the presence of pyrene molecules as an external guest, $\mathbf{U_{H/H}}$ formed the Col_{h} phase without phase separation. Columnar assemblies with similar intercolumnar distances were observed in the LC molecules $\mathbf{U_{Py/Py}}$ and $\mathbf{U_{Py/H}}$, where pyrene moieties were covalently attached to the U-shaped handle. This study demonstrates a potential use of guest molecules to form multi-component liquid crystals to control the LC assembly. Incorporation of other functional guest molecules to $\mathbf{U_{H/H}}$ is now under investigation in our research group.

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13 Note that a model comprising a dimeric core (length = ~ 29 Å), as reported in ref. 9, exceeds the size of the column diameter (~40 Å) obtained in this study. See Fig. S38 for details.

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