

Room-Temperature Columnar Liquid Crystals from Hydrogen-Bonded Dendritic Assemblies

Sivakumar Irla,* Velayudhan A. Raghunathan, and Sandeep Kumar*

Cite This: *ACS Omega* 2026, 11, 48361–48372

Read Online

ACCESS |



Metrics & More

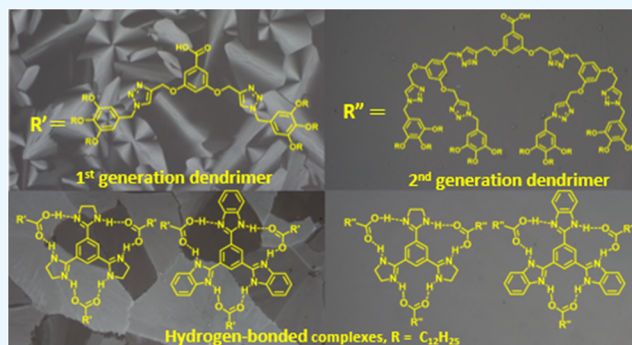


Article Recommendations



Supporting Information

ABSTRACT: Dendrimers represent a distinctive class of synthetic macromolecules with broad utility across soft matter, materials science, nanotechnology, and biomedical sciences. In this study, we describe the synthesis of carboxylic acid-functionalized first and second-generation dendrimers using CuAAC (copper-catalyzed azide, alkyne cycloaddition) click chemistry. Dendrimers exhibit thermotropic mesomorphic behavior and form robust hydrogen-bonded supramolecular complexes with benzotriazole or benzimidazole derivatives. Notably, the hydrogen-bonded complexes also exhibit mesomorphism. Interestingly, some of these exhibit a room-temperature columnar hexagonal mesophase and transition to cubic phases. By underscoring the pivotal role of noncovalent interactions in modulating liquid-crystalline order, this work provides a systematic investigation of the mesomorphic properties of all of the newly synthesized dendrimers and their supramolecular assemblies.



INTRODUCTION

Liquid crystals (LCs) represent a unique state of matter intermediate between conventional liquids and crystalline solids, combining molecular mobility with long-range orientational order to give rise to distinctive optical and electrical properties that have been widely explored for use in display technologies, sensors, and functional materials.^{1,2} The ability to tune mesophase behavior through precise molecular design has made liquid crystals a central focus in both fundamental research and advanced materials science. Dendrimers constitute a unique class of synthetic macromolecules characterized by a highly branched, monodisperse, and three-dimensional architecture.^{3–5} Although widely studied in synthetic polymer chemistry, dendritic motifs are also abundant in nature; for example, the dense array of dendritically branched setae on gecko feet provides exceptional adhesion through maximized surface contact and weak intermolecular interactions.⁶ Inspired by such natural systems, the design and synthesis of dendritic compounds have become an important focus in modern organic chemistry.⁷ Synthetic dendrimers mimic natural branching motifs while offering precisely controlled architectures and high functional-group densities, making them ideal candidates for advanced materials with tailored physical and chemical properties.^{8,9} Since their discovery in the late 1970s, dendrimers have attracted considerable interest in materials science, biomedical sciences, catalysis, sensing, liquid-crystalline systems, and advanced functional materials.^{10–13}

Among functional dendrimers, liquid crystal dendrimers (LC dendrimers) have attracted particular attention for their ability to combine molecular order with structural flexibility. Several approaches have been developed to induce liquid-crystalline behavior in dendritic polymers.¹³ The most common methods involve functionalizing dendrimer peripheries with mesogenic or promesogenic units that drive self-assembly into ordered mesophases.¹⁴ Beyond covalent design, dendrimers and dendrons can also be organized into supramolecular architectures through noncovalent interactions, including van der Waals, ionic, π – π , dipolar, and hydrogen bonding. Microsegregation of incompatible structural units, strongly influenced by branching topology, can likewise generate liquid-crystalline mesophases.^{15–20} Consequently, dendrimers exhibit a wide range of mesophases, including nematic, smectic, columnar, cubic, bicontinuous cubic, and spheroidal cubic phases in both thermotropic and lyotropic systems.^{12,21–23} Cubic phases are broadly classified into two main types: bicontinuous cubic phases, which consist of two interpenetrating continuous networks separated by a curved interface and typically adopt Ia3d space group symmetry,

Received: May 1, 2026

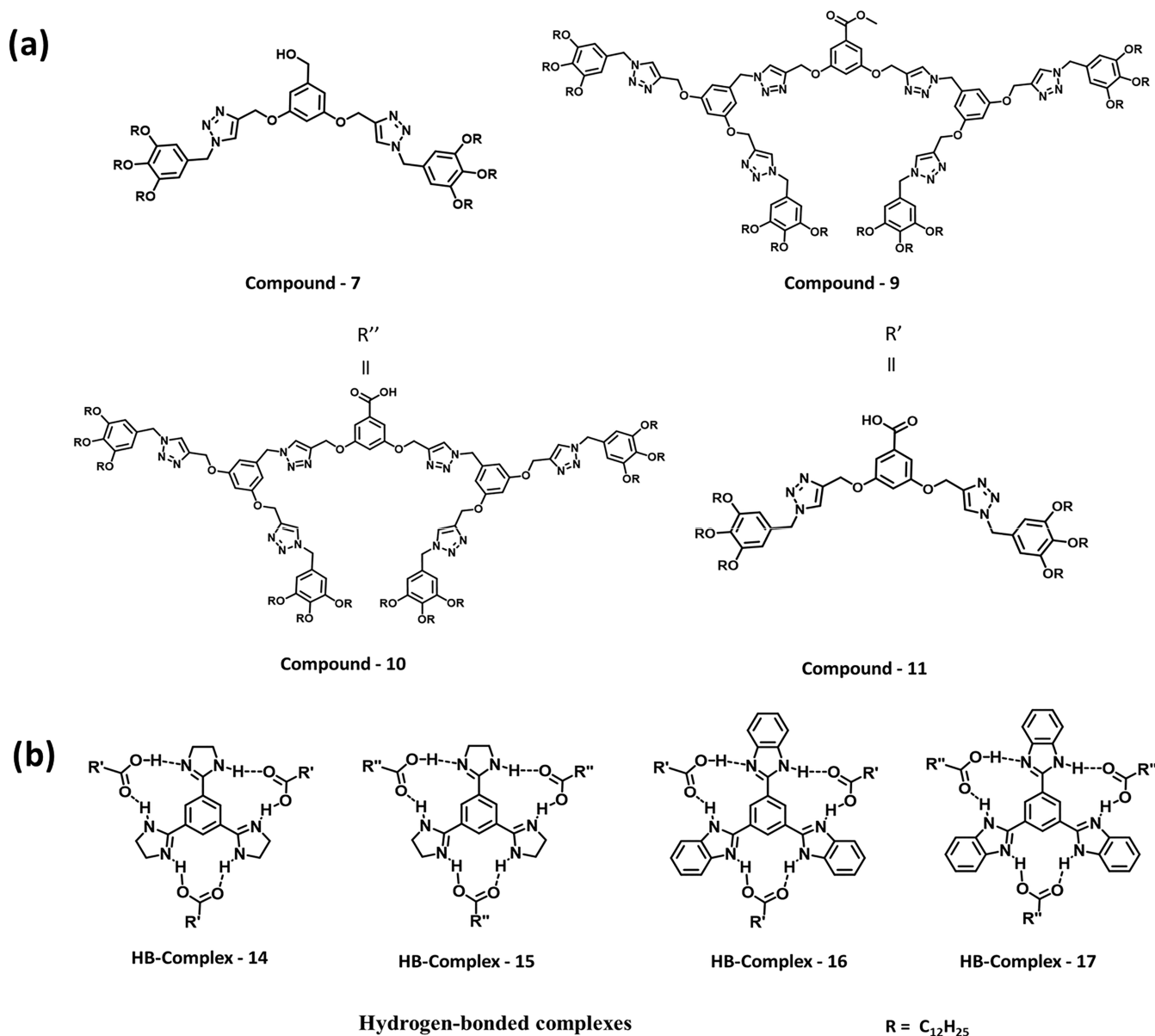
Revised: July 17, 2026

Accepted: July 22, 2026

Published: August 1, 2026



Scheme 1. (a) Liquid Crystalline Dendrimers; (b) Hydrogen-Bonded (HB) Complexes



and micellar or columnar cubic phases, which arise from the packing of discrete aggregates into a cubic lattice and most commonly adopt $Pm3n$ or $Im3m$ space group symmetry. Both types are optically isotropic under polarizing optical microscopy and can be distinguished by systematic absence analysis of X-ray diffraction data.^{23–25} Cubic phases of $Pm3n$ symmetry have been widely reported in dendritic and polycatenar systems.^{1,14} Dendritic architectures can also form three-dimensional mesophases such as tetragonal and quasi-liquid-crystalline phases with high rotational symmetry, underscoring their remarkable ability to generate complex, tunable liquid-crystalline structures that are difficult to obtain with conventional low-molecular-weight mesogens.^{24,26}

A desirable strategy for inducing or tuning liquid-crystalline behavior in dendritic systems is to exploit noncovalent interactions. Among these, hydrogen bonding has emerged as one of the most versatile tools owing to its directionality, strength, and reversibility. It plays a central role in both chemistry and biology and has been extensively used to induce,

stabilize, and modulate mesophases in liquid-crystalline systems.^{1,2,27} Previous studies by Kato and co-workers demonstrated hydrogen-bond-derived smectic and columnar mesophases in folic acid-based systems, while glutamic acid-derived dendritic architectures have shown similarly rich mesomorphic behavior.^{28–30} Donor–acceptor systems, such as carboxylic acids paired with pyridines, benzimidazoles, benzotriazoles, heptazine, and other nitrogen-containing heterocycles, have been widely explored in this context.^{31–36} Such supramolecular approaches enable assembly, reduce synthetic complexity, and enhance stimuli responsiveness. Columnar mesophases formed by disc-shaped molecules are particularly significant owing to their excellent electro-optical properties, making them attractive candidates for optoelectronic applications.^{37,38} Carboxylic acid-functionalized dendrimers are particularly well suited for such complexation, as they engage in strong, directional hydrogen bonding with suitable acceptor molecules, thereby significantly modifying molecular shape, intermolecular interactions, and phase

symmetry to tune liquid-crystalline order and thermal stability. Despite these advances, systematic investigations that address the combined influence of dendrimer generation and hydrogen-bond-driven supramolecular assembly on mesomorphic behavior remain scarce.³⁹

In parallel, synthetic methodologies for dendrimer construction have evolved significantly.⁴⁰ CuAAC (copper-catalyzed azide–alkyne cycloaddition) click chemistry has emerged as one of the most reliable and efficient routes, enabling precise control over molecular architecture.^{41–44} Dendrimers prepared via CuAAC click chemistry have proven to be robust platforms for liquid-crystalline and supramolecular materials.^{45,46} When combined with peripheral carboxylic acid functionalities, dendrimers synthesized via CuAAC click chemistry become particularly attractive candidates for hydrogen-bonded mesogenic systems. Hydrogen-bonded complexes formed between carboxylic acids and these heterocycles have been reported to exhibit stable liquid-crystalline phases, including nematic, smectic, and columnar ordering.^{47–52} Despite these advantages, the incorporation of carboxylic acid groups into dendritic frameworks and the resulting effects on mesomorphic behavior remain underexplored.

Herein, we report the synthesis of first- and second-generation carboxylic acid–functionalized dendrimers via CuAAC click chemistry and their supramolecular assembly with benzotriazole and benzimidazole derivatives, yielding hydrogen-bonded liquid-crystalline systems. Both dendrimers and their 1:3 hydrogen-bonded complexes exhibit thermotropic mesomorphic behavior, showing the transitions between hexagonal columnar (Col_h) and cubic ($\text{Pm}3n$) mesophases. Notably, some supramolecular complexes display stable columnar mesophases at room temperature. The insights gained from this study provide valuable guidelines for the rational design of functional dendritic liquid crystals and supramolecular soft materials for advanced applications in optoelectronics, sensing, and responsive systems.

RESULTS AND DISCUSSION

Design and synthesis of a novel class of carboxylic acid-functionalized dendrimers, like first and second generations, and hydrogen-bonded complexes were shown in Scheme S1. The dendrimers were prepared by incorporating two (5-(azidomethyl)-1,2,3-tris(dodecyloxy)benzene) units onto a central resorcinol core via CuAAC click chemistry.⁵³ Benzotri(imidazole) derivatives (compounds 12 and 13) were then prepared according to the literature procedures.^{54,55} All compounds were purified by column chromatography on silica gel (100–200 mesh), followed by repeated reprecipitation using suitable analytical-grade solvents. The chemical structures of all compounds were confirmed by ^1H NMR, ^{13}C NMR spectroscopy, and elemental analysis. The detailed synthetic scheme, procedures, and characterization data are given in the Supporting Information. The hydrogen-bonded LC complexes were prepared by dissolving the carboxylic acid derivatives and benzotri(imidazole) derivatives in $\text{MeOH}/\text{CHCl}_3$ and stirring for 2 h, followed by solvent removal. Spectroscopic analysis (FT-IR and ^1H NMR, ^{13}C NMR) and thermal analysis (DSC) confirmed the formation of the supramolecular complexes. The synthesized dendrimers exhibit thermotropic mesomorphic behavior, displaying the columnar hexagonal (Col_h) and cubic ($\text{Pm}3n$) phases. Notably, the hydrogen-bonded complexes exhibit a stable hexagonal columnar mesophase at room

temperature, which transforms into a cubic ($\text{Pm}3n$) phase at elevated temperatures.

The structure of all dendrimers (7, 9, 10, 11) and their corresponding hydrogen-bonded (14–17) liquid crystalline (LC) materials are shown in Scheme 1, and the thermal stability of all LC compounds was evaluated by thermogravimetric analysis (TGA). Each sample was subjected to a heating scan at $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere to assess the compound's thermal stability. All compounds exhibit thermal stability, showing no significant weight loss up to approximately $335\text{ }^\circ\text{C}$. Beyond this temperature, gradual decomposition occurred between 350 and $475\text{ }^\circ\text{C}$, with major degradation completed by around $520\text{ }^\circ\text{C}$. The thermal stability of all the compounds is much higher than their isotropic (Iso) temperature. This indicates that all compounds have excellent thermal stability. The TGA thermograms of dendrimers and hydrogen-bonded complexes are given in Figure 1.

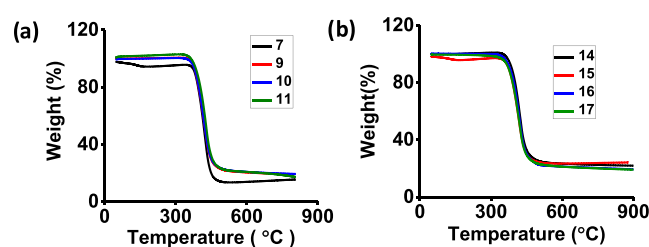


Figure 1. (a) TGA thermograms of liquid-crystalline dendrimers, (b) TGA thermograms of hydrogen-bonded (HB) complexes.

The liquid-crystalline (LC) behavior of the dendrimers was investigated using polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray diffraction (SAXS). All the compounds exhibited enantiotropic mesophase behavior. POM textures (Figure 2) recorded upon cooling from the isotropic (Iso) phase revealed focal-conic patterning for compounds 7 and 11, characteristic of columnar hexagonal (Col_h) mesophase. In contrast, Compounds 9 and 10 exhibit optically isotropic textures characteristic of the cubic mesophase. DSC data of 7, 9, 10, and 11 show the enantiotropic mesophase between a high-temperature isotropic (Iso) phase and a low-temperature crystalline (Cr) phase.

Compounds 7 and 11 show two transition peaks corresponding to the single Col_h mesophase. Compound 7 exhibits a transition from the crystalline (Cr) phase to the columnar hexagonal (Col_h) mesophase at $61.9\text{ }^\circ\text{C}$, and becomes isotropic (Iso) at $81.7\text{ }^\circ\text{C}$. Upon cooling from the isotropic (Iso) phase, the Col_h mesophase reappears at $78.7\text{ }^\circ\text{C}$, followed by crystallization. Compound 11 similarly exhibits a Cr to Col_h transition at $38.4\text{ }^\circ\text{C}$ and becomes isotropic at $98.2\text{ }^\circ\text{C}$. Upon cooling, the Col_h mesophase reappears at $94.4\text{ }^\circ\text{C}$, followed by crystallization.

In contrast, compounds 9 and 10 exhibit two transition peaks corresponding to the single-cubic mesophase, which belongs to the $\text{Pm}3n$ space group. Compound 9 transitions from Cr to Col_c at $75.1\text{ }^\circ\text{C}$ and becomes isotropic (Iso) at $98.7\text{ }^\circ\text{C}$. Upon cooling from the isotropic (Iso) phase, the cubic ($\text{Pm}3n$) mesophase reappears at $83.1\text{ }^\circ\text{C}$. Compound 10 transitions from Cr to cubic ($\text{Pm}3n$) at $97.7\text{ }^\circ\text{C}$ and becomes isotropic at $159.5\text{ }^\circ\text{C}$. Upon cooling, the cubic ($\text{Pm}3n$) mesophase reappears at $156.0\text{ }^\circ\text{C}$, followed by crystallization.

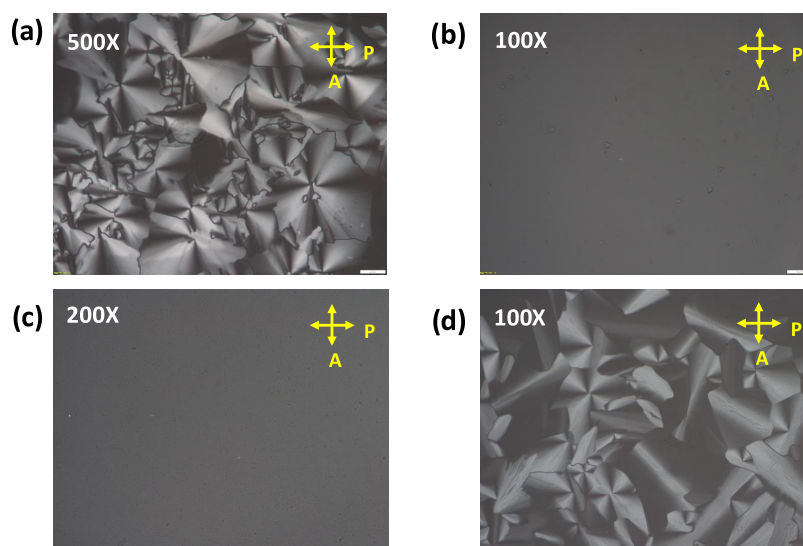


Figure 2. Birefringence texture observed under POM for (a) Compound 7 at 95 °C, (b) Compound 9 at 80 °C, (c) Compound 10 at 135 °C, (d) Compound 11 at 78 °C, at different temperatures upon cooling from the isotropic (Iso) phase.

All DSC thermograms are shown in Figure 3, and the phase transition temperatures and enthalpy values are presented in Table 1

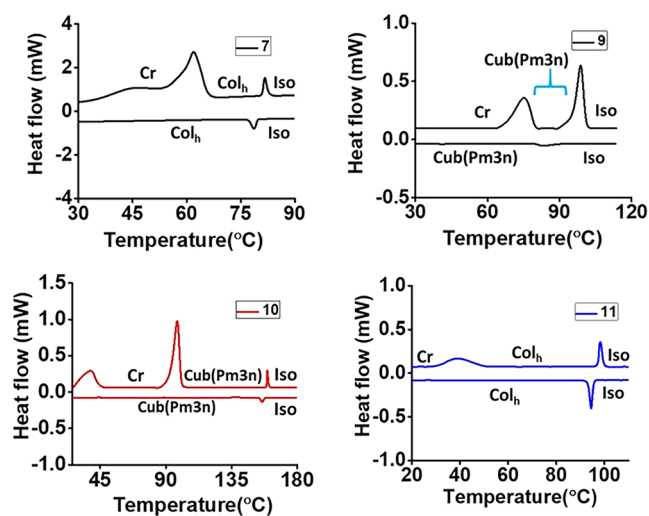


Figure 3. DSC thermograms obtained for the 7, 9, 10, and 11 derivatives showing phase transitions during heating and cooling cycles at the scan rate of 10 °C min⁻¹.

Table 1. Phase Transition Temperatures (°C), Enthalpy Changes, [J/g] of Dendrimers and Hydrogen-Bonded Complexes at the Time of Heating and Cooling Obtained from DSC^a

compound	heating	cooling
7	Cr 61.9 [20.77] Col _h 81.7 [1.90] Iso	Iso 78.7 [−1.25] Col _h
9	Cr 75.1 [10.40] cubic (<i>Pm3n</i>) 98.7 [10.92] Iso	Iso 83.1 [−0.33] cubic (<i>Pm3n</i>)
10	Cr 97.7 [22.49] cubic (<i>Pm3n</i>) 159.5 [1.10] Iso	Iso 156.0 [−0.66] cubic (<i>Pm3n</i>)
11	Cr 38.4 [1.42] Col _h 98.2 [1.04] Iso	Iso 94.4 [−1.04] Col _h

^aCr—Crystalline phase; Col_h—Columnar hexagonal phase; cubic (*Pm3n*) phase; Iso—Isotropic.

To further confirm the supramolecular assembly of 7, 9, 10, and 11, small-angle X-ray scattering (SAXS) experiments were carried out. The X-ray diffractograms of all the compounds are shown in Figure 4. Compounds 7 and 11 are found to exhibit

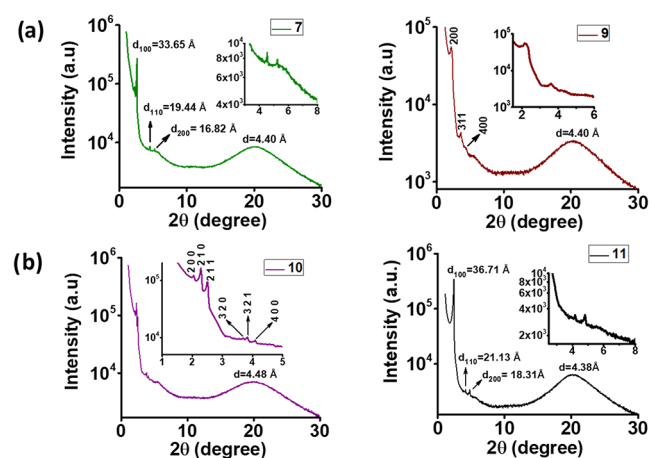


Figure 4. (a) X-ray diffraction patterns of the hexagonal phase of compound 7 at 65 °C (on heating), and the cubic phase of compound 9 at 30 °C (on cooling from the isotropic phase), (b) X-ray diffraction patterns of the hexagonal phase of compound 11 at 25 °C (on cooling from the isotropic phase), and cubic phase of compound 10 at 135 °C (on heating).

the hexagonal columnar (Col_h) phase upon cooling from the isotropic (Iso) phase, as evidenced by sharp diffraction peaks in the small-angle region, whose spacings (*d*) are in the ratio 1:1/√3:1/2. In the wide-angle region, the diffractograms exhibit broad peaks at *d* = 4.3–4.50 Å, corresponding to the molten alkyl chains. The lattice parameter (*a*) is 38.85 Å and 42.37 Å for 7 and 11, respectively. From the lattice parameter, the number of molecules occupying each slice of a column is estimated to be 2. The X-ray diffractograms of compound 9 at 30 °C and compound 10 at 135 °C show multiple peaks in the small-angle region. These can be indexed on a *Pm3n* cubic lattice, and the lattice parameters (*a*) are estimated to be 84.44 Å and 86.84 Å, respectively. For compounds 9 and 10, the

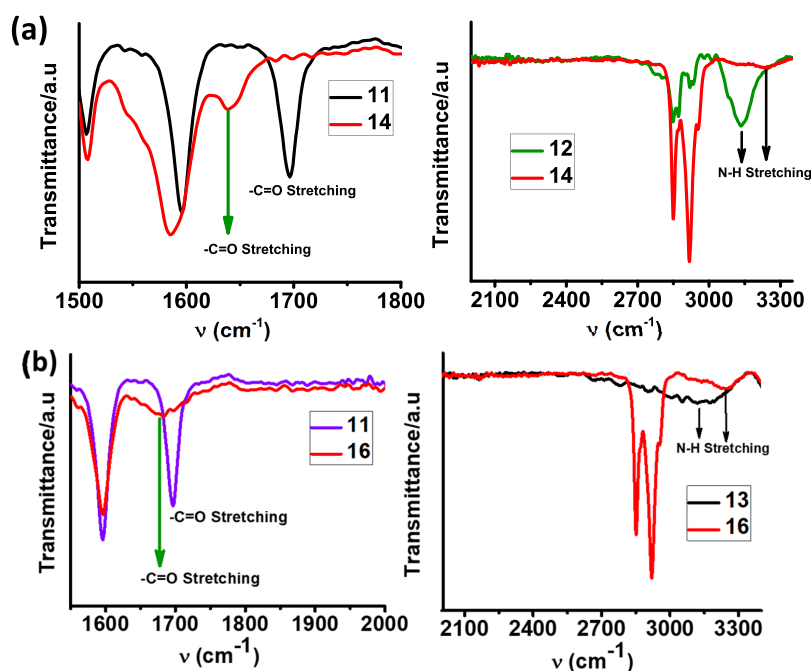


Figure 5. FTIR spectra: comparison in the –NH and C=O stretching region. (a) Pure components of 11 and 12, and their H-bonded complex of 14. (b) Pure components of 11 and 13, and their H-bonded complex of 16.

number of molecules per unit cell in the cubic lattice is 104 and 114, respectively. The *d*-spacings of these compounds and their Miller indices are given in Table 3, along with the lattice parameters.

Detailed study of the hydrogen-bonded complexes

Hydrogen-bonded complexes were prepared using 1:3 ratios of benzotriimidazole derivatives to first and second-generation carboxylic acid-functionalized dendrimers. Complex 14 was prepared by dissolving compound 12 with 10, and complex 15 by dissolving compound 12 with dendrimer 11, both in MeOH/CHCl₃ (1:4 v/v), stirring for 2 h at room temperature, and removing the solvents under reduced pressure. Complex 16 was prepared by dissolving compound 13 with 10, and Complex 17 by dissolving compound 13 with 11, both in MeOH/CHCl₃ (2:3 v/v), followed by stirring for 3 h at 60 °C and subsequent solvent removal. The chemical structure of dendrimers, benzotriimidazole derivatives, the resulting hydrogen-bonded complexes, and schematic representations are shown in Scheme S1. The formation of the hydrogen-bonded complexes was confirmed by FT-IR and NMR spectroscopy along with thermal analysis. The detailed synthetic scheme, procedures, and full characterization data are provided in the Supporting Information. All complexes exhibit enantiotropic liquid crystalline behavior over a wide temperature range, reflecting the strong, stable hydrogen-bonding interaction between compounds 12 or 13 and dendrimers 10 or 11.

The formation of the hydrogen-bonded complexes was confirmed by using FTIR. Notably, the infrared spectra of the obtained H-bonded complexes are not simple superpositions of the spectra of the individual components, indicating the presence of specific intermolecular interactions. The FTIR spectra of 11, 12, and 13, and their corresponding H-bonded complexes 14 and 16, are shown in Figure 5, while the spectra of compounds 10, 12, and 13 and their hydrogen-bonded complexes 15 and 17 are presented in Figure S1. The N–H stretching band of the 12 (benzotriimidazole) derivative is

observed at 3134 cm^{−1}. Upon complexation, this band becomes significantly weaker and shifts to higher wavenumbers (3238 cm^{−1}), clearly reflecting its involvement in hydrogen bonding. Pronounced changes are also observed in the carbonyl stretching region. In the free carboxylic acid dendrimers, the C=O stretching band at 1696 cm^{−1} corresponds to the hydrogen-bonded dimeric form. After complexation with compound 12, this dimeric C=O band completely disappears, and a new broadened C=O stretching band appears at 1639 cm^{−1}, shifted to lower wavenumbers, consistent with the formation of intermolecular hydrogen bonds between compounds 11 and 12. Similar spectral changes are observed for the remaining hydrogen-bonded complexes, further confirming the establishment of strong hydrogen-bonding interactions.

The selectivity of hydrogen bonding in the complexes was further confirmed by the complete disappearance of the homodimeric C=O band around 1700 cm^{−1} upon complexation, confirming that carboxylic acid homodimerization is completely replaced by selective heterodimer formation with the benzotriazole or benzimidazole units. The triazole rings introduced by CuAAC click chemistry are not expected to compete significantly as hydrogen-bond acceptors, as the triazole nitrogens are weaker hydrogen-bond acceptors than benzotriazole or benzimidazole nitrogens due to their lower basicity.⁵⁶ This confirms that hydrogen bonding occurs selectively between the carboxylic acid groups of the dendrimers and the benzotriazole or benzimidazole units rather than with the triazole rings or through homodimerization. The characteristic C=O and N–H stretching frequencies of compounds 10–13 and all hydrogen-bonded complexes (14–17) are summarized in Table S1.

Further evidence for hydrogen-bond formation between the benzotriimidazole derivatives and the first- and second-generation dendrimers was obtained from ¹H NMR spectroscopy. The NMR spectra of hydrogen-bonded complexes 14

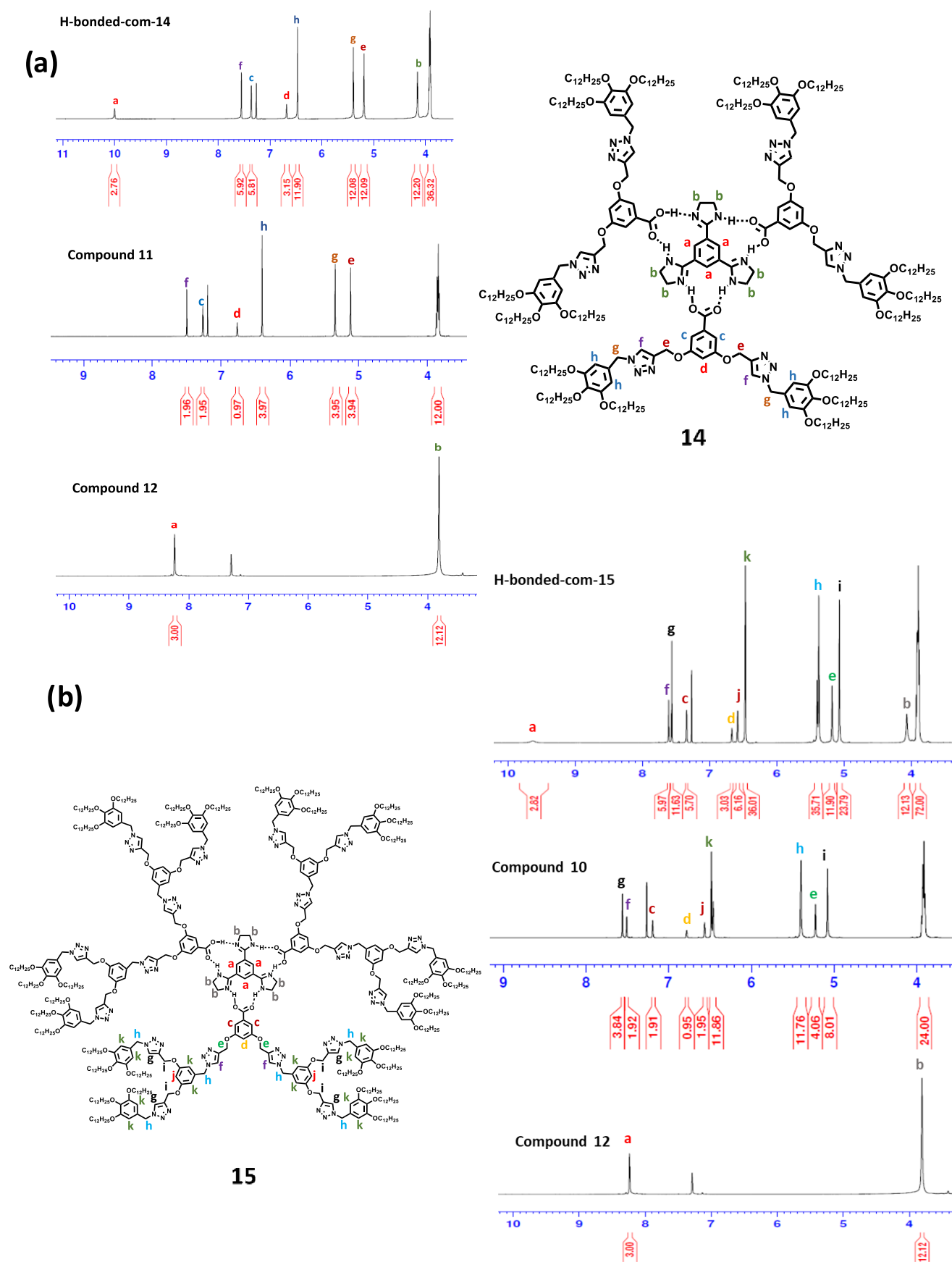


Figure 6. (a) Comparative ^1H NMR studies of pure compounds 11 and 12, and the hydrogen complex 14. (b) Comparative ^1H NMR studies of pure compounds 10 and 12, and the hydrogen complex 15. (a) Comparative ^1H NMR studies of 11, and 12 pure compounds and, hydrogen complex of 14 (b) Comparative ^1H NMR studies of 10, and 12 pure compounds and, hydrogen complex of 15.

and **15** were recorded in CDCl_3 , whereas those of complexes **16** and **17** were recorded in CDCl_3 and in a 1:1 mixture of CDCl_3 and $\text{DMSO}-d_6$, respectively. Comparative NMR analyses of individual compounds and their H-bonded complexes of **14** and **15** are given in Figures 6 and S2. Integration of the characteristic proton signals confirms the expected stoichiometry of the supramolecular complexes, consistent with the designed hydrogen-bonded assemblies between the dendrimers and benzotriazole or benzimidazole derivatives. In addition, clear chemical shift changes are observed for the aromatic (Ha) and methylene (Hb) protons of the benzotriazole or benzimidazole units upon complexation. Direct observation of the N–H and COOH protons is not feasible under these conditions, as these protons undergo significant broadening due to strong intermolecular hydrogen bonding interactions and fast dynamic exchange within the supramolecular complex; therefore, hydrogen bonding is inferred from the downfield shifts of neighboring aromatic and methylene protons.

In the free benzotriazole derivative **12**, the Ha and Hb protons appear at 8.23 and 3.80 ppm, respectively. Upon formation of the hydrogen-bonded complex **14**, these signals shift downfield to 9.99 and 4.15 ppm, respectively, reflecting deshielding caused by strong intermolecular hydrogen bonding. Similar downfield shifts are observed for the corresponding protons in complex **15**. Comparable spectral changes are also detected for complexes **16** and **17**, with minor variations attributable to differences in dendrimer generation and solvent environment. Overall, the consistent downfield shifts and maintained proton integration ratios across all complexes provide strong ^1H NMR evidence for the formation of stable hydrogen-bonded supramolecular assemblies, in good agreement with previously reported systems.

Further evidence for hydrogen bond formation was obtained from ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of the free first-generation dendrimer **11**, the carbonyl carbon of the carboxylic acid group appears at 170.08 ppm. Upon formation of the hydrogen-bonded complexes, this signal shifts downfield to 172.83 ppm in complex **14** and 172.12 ppm in complex **16**, consistent with the involvement of the carbonyl group in intermolecular hydrogen bonding with the benzotriazole or benzimidazole units. For the second-generation dendrimer **10**, the carbonyl carbon signal is not observed in the free dendrimer, which is commonly encountered for high molecular weight dendrimers due to the low relative concentration of the carbonyl carbon, its quaternary nature, and long relaxation times. Notably, upon complexation with benzotriazole or benzimidazole derivatives, the carbonyl carbon becomes clearly visible at ~ 170 ppm in complexes **15** and **17**, providing strong additional evidence for the formation of hydrogen-bonded assemblies. These observations are fully consistent with the FTIR and ^1H NMR data.

The H-bonded supramolecular complexes with liquid-crystalline properties were analyzed using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). Compounds **14**–**17** were all found to be mesomorphic. Compounds **14** and **16** display two distinct mesophases: columnar hexagonal (Col_h) and cubic ($\text{Pm}3n$). Whereas complexes **15** and **17** exhibit only the cubic ($\text{Pm}3n$) mesophase. DSC thermograms (Figure 7) were used to investigate the mesophase behavior of all complexes. Compounds **14** and **16** clearly show three transition peaks associated with the two mesophases. Both complexes exhibit

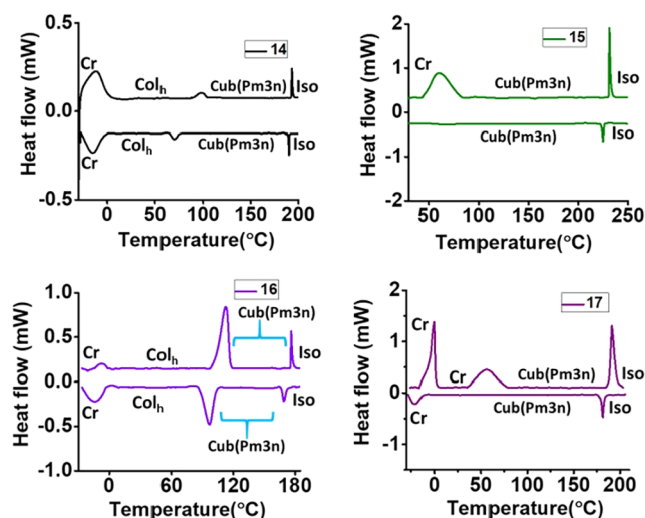


Figure 7. DSC thermograms obtained for the **14**, **15**, **16**, and **17** derivatives showing phase transitions during heating and cooling cycles at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$.

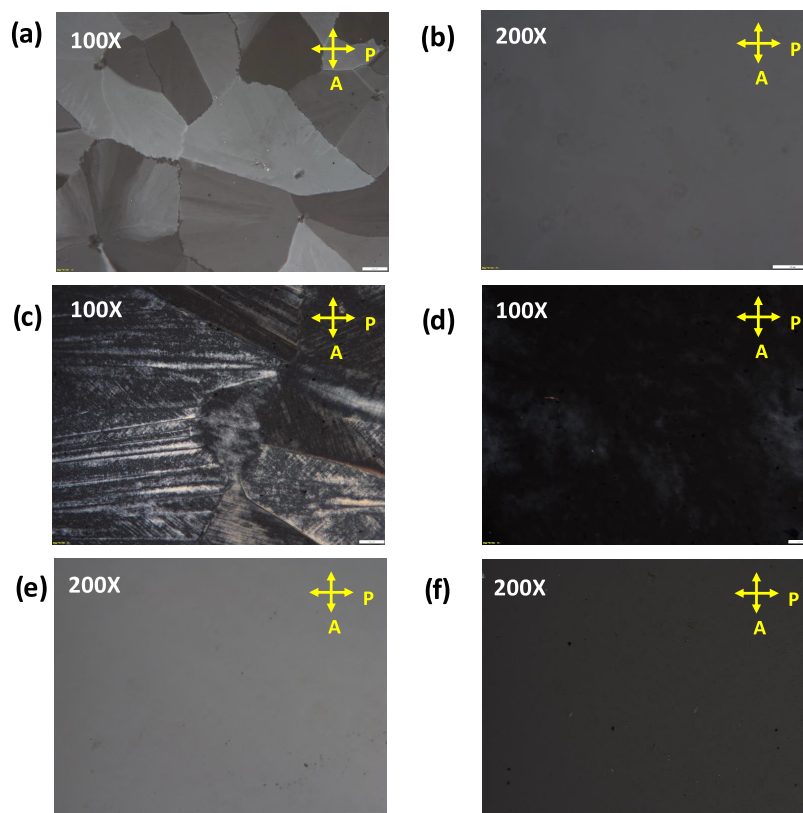
the columnar hexagonal (Col_h) mesophase at room temperature, and the transition temperatures are 97.84 and $112.52\text{ }^\circ\text{C}$, which become isotropic (Iso) at 193.22 and $176.17\text{ }^\circ\text{C}$, respectively. Upon cooling from the isotropic (Iso) phase, cubic ($\text{Pm}3n$) mesophase appears at $190.19\text{ }^\circ\text{C}$ for **14** and $168.90\text{ }^\circ\text{C}$ for **16**. Further cooling results in the re-emergence of the columnar hexagonal (Col_h) mesophase at 69.46 and $96.82\text{ }^\circ\text{C}$, followed by crystallization (Cr) below $-10\text{ }^\circ\text{C}$. Compounds **15** and **17** exhibit two transition peaks corresponding to the single mesophase. Both show broad melting temperatures at 60.55 and $0.41\text{ }^\circ\text{C}$, respectively, and become isotropic (Iso) at 231.27 and $191.18\text{ }^\circ\text{C}$, respectively. Upon cooling from the isotropic (Iso) phase, the cubic ($\text{Pm}3n$) phase appeared at 224.95 and $181.38\text{ }^\circ\text{C}$, respectively, and remained unaltered to room temperature. Additionally, Compound **17** shows a sharp transition on heating at $0.4\text{ }^\circ\text{C}$ corresponding to the melting of the crystalline phase, followed by a broad transition at $55.37\text{ }^\circ\text{C}$ attributed to a crystal-to-crystal (Cr $\rightarrow$ Cr') transition, reproducibly observed across multiple heating runs, before entering the cubic ($\text{Pm}3n$) phase. The cubic ($\text{Pm}3n$) – Iso clearing transition appears at $191.1\text{ }^\circ\text{C}$ as a single, well-resolved peak. The observed phase transition temperatures and corresponding enthalpy values are summarized in Table 2.

The transition temperatures and enthalpies of H-bonded complexes were investigated using DSC and further validated by POM. Liquid-crystalline textures were examined under crossed polarizers upon cooling from the isotropic (Iso) phase. Complexes **14** and **16** exhibit two distinct mesophases. Upon cooling, both display the optically isotropic texture over the ranges 190 to $69\text{ }^\circ\text{C}$ and 168 to $96\text{ }^\circ\text{C}$, respectively, characteristic of the cubic ($\text{Pm}3n$) mesophase. Further cooling leads to the appearance of plate-like textures corresponding to the columnar hexagonal (Col_h) mesophase. In contrast, Compounds **15** and **17** show only an optically isotropic texture upon cooling from the isotropic (Iso) phase, indicative of a single cubic ($\text{Pm}3n$) mesophase. All the POM textures are shown in Figure 8. Repeated heating–cooling cycles revealed no evidence of phase segregation, demonstrating that the supramolecular complexes remain intact and stable, likely due to strong hydrogen-bonding interactions.

Table 2. Phase Transition Temperatures (°C), Enthalpy Changes, [J/g] of Dendrimers and Hydrogen-Bonded Complexes at the Time of Heating and Cooling Obtained from DSC^a

compound	heating			cooling		
14	Cr −10.8 [3.89]	Col _h 97.8 [0.80]	Cubic (<i>Pm3n</i>) 193.2 [0.46]	Iso 190.1 [−0.35]	Cubic (<i>Pm3n</i>) 69.4 [−1.45]	Col _h −14.8 [−3.42]
15	Cr 60.5 [18.87]	Cubic (<i>Pm3n</i>) 231.2 [2.47]	Iso	Iso 224.9 [−0.76]	Cubic (<i>Pm3n</i>)	
16	Cr −5.6 [4.51]	Col _h 112.5 [8.77]	Cubic (<i>Pm3n</i>) 176.1 [0.73]	Iso 168.9 [−0.74]	Cubic (<i>Pm3n</i>) 96.8 [−6.51]	Col _h −11.6 [−4.36]
17	Cr −0.41 [5.40]	Cr' 55.37 [4.28]	cubic (<i>Pm3n</i>) 191.1 [4.40]	Iso 181.3 [−1.07]	Cubic (<i>Pm3n</i>) −20.8 [−1.18]	Cr

^aCr—Crystalline phase; Cr'—Crystal, Col_h—Columnar hexagonal phase; cubic (*Pm3n*); Iso—Isotropic.

**Figure 8.** Birefringence texture observed under POM for a compound: (a, b) Compound 14 at 80 and 130 °C, (c, d) Compound 16 at 90 and 140 °C, (e) Compound 15 at 140 °C, (f) Compound 17 at 150 °C at different temperatures upon cooling from the isotropic (Iso) phase.

The liquid crystalline phase behavior of the hydrogen-bonded complexes (14, 15, 16, and 17) was examined using X-ray diffraction (XRD) upon cooling from the isotropic (Iso) phase. The X-ray diffraction patterns of the H-bonded complexes of 14 and 16 are shown in Figure 9. Consistent with the DSC and POM analysis, these complexes exhibit two distinct mesophases. Accordingly, X-ray diffraction studies were carried out at temperatures corresponding to the two mesophases. Compounds 14 exhibits four sharp peaks at 50 °C, and compound 16 exhibits six sharp peaks at 28 °C in the small-angle region. Their spacings are in the ratio of 1:1/√3:1/2:1/√7:1/√9:1/√13, corresponding to the columnar hexagonal (Col_h) mesophase. The lattice parameter (*a*) is found to be 48.57 Å and 51.57 Å, respectively. The wide-angle region exhibits two broad peaks, one at around 4.3 Å corresponding to the molten alkyl chain. Additionally, core–core peaks observed at 3.44 Å and 3.57 Å for compounds 14 and 16, respectively, indicate π – π stacking interactions between the aromatic units in the dendritic framework and benzotriazole or benzimidazole derivatives. Such interactions are well-known to contribute to the stability of columnar mesophases.^{37,38} Furthermore, the broad peaks at 4.3–4.5 Å,

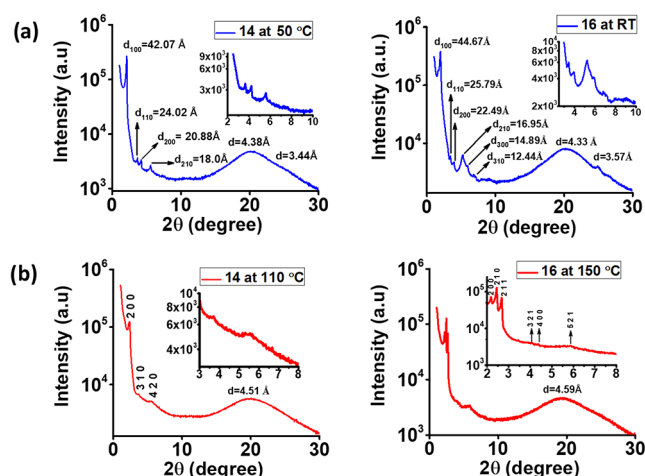


Table 3. Layer Spacings Obtained from XRD Patterns for 7, 11, 14, and 16^a

compounds	T (°C)	d-spacing(Å)	phase	parameters
7	65	33.65 (1 0 0), 19.44 (1 1 0), 16.82 (2 0 0) 4.41	Col _h	$a = 38.85 \text{ Å}$ $S_h = 1307.44 \text{ Å}^2$ $V_h = 5765.84 \text{ Å}^3$ $Z = 2.1$
9	30	42.22 (2 0 0), 25.15 (3 1 1), 20.94 (4 0 0), 4.40	Cubic (Pm3n)	$a = 84.44 \text{ Å}$ $Z = 104.4$
10	135	43.42 (2 0 0), 38.65 (2 1 0), 35.25 (2 1 1), 23.88 (3 2 0), 23.05 (3 2 1), 21.58 (4 0 0), 4.48	Cubic (Pm3n)	$a = 86.84 \text{ Å}$ $Z = 114.0$
11	25	36.71 (1 0 0), 21.13 (1 1 0), 18.31 (2 0 0) 4.38	Col _h	$a = 42.38 \text{ Å}$ $S_h = 1555.43 \text{ Å}^2$ $V_h = 6812.81 \text{ Å}^3$ $Z = 2.4$
14	50	42.07 (1 0 0), 24.02 (1 1 0), 20.88 (2 0 0), 15.80 (2 1 0), 4.40, 3.44	Col _h	$a = 48.57 \text{ Å}$ $S_h = 2042.99 \text{ Å}^2$ $V_h = 7027.89 \text{ Å}^3$ $Z = 0.8$
14	110	37.69 (2 0 0), 23.73 (3 1 0), 16.50 (4 2 0), 4.51	Cubic (Pm3n)	$a = 75.38 \text{ Å}$ $Z = 50.7$
15	186	46.96 (2 0 0), 41.75 (2 1 0), 38.49 (2 1 1), 25.56 (3 2 1), 23.53 (4 0 0), 4.50	Cubic (Pm3n)	$a = 93.93 \text{ Å}$ $Z = 46.85$
16	28	44.67 (1 0 0), 25.79 (1 1 0), 22.49 (2 0 0), 16.95 (2 1 0), 14.89 (3 0 0), 12.44 (3 1 0), 4.33, 3.57	Col _h	$a = 51.58 \text{ Å}$ $S_h = 2304.05 \text{ Å}^2$ $V_h = 8225.48 \text{ Å}^3$ $Z = 0.9$
16	150	40.56 (2 0 0), 36.36 (2 1 0), 33.18 (2 1 1), 21.65 (3 2 1), 20.22 (4 0 0), 15.09 (5 2 1), 4.59	Cubic (Pm3n)	$a = 81.12 \text{ Å}$ $Z = 61.4$
17	170	64.86 (2 0 0), 46.16 (2 2 0), 41.27 (3 1 0), 37.74 (2 2 2), 32.51 (4 0 0), 29.15 (4 2 0), 26.65 (4 2 2), 25.50 (5 0 0), 24.69 (5 1 1), 23.06 (4 4 0), 18.95 (6 3 1), 18.09 (7 1 1), 17.09 (7 2 2), 4.54	Cubic (Pm3n)	$a = 129.73 \text{ Å}$ $Z = 121.78$

^aHexagonal: (lattice area $S_h = (\sqrt{3}/2)a^2$; lattice volume $V_h = S_h h_c$ (h_c if h_c is not observed); No. of molecules per slice of column (Z) = $N_A \rho V_h / M$; N_A = Avogadro's number; ρ = density; a = lattice parameter; h_c = core core peak; h_a = chain peak; M = molecular weight). Cubic (Pm3n): a = lattice parameter; No. of molecules per unit cell in the cubic lattice (Z) = $a^3 \rho N_A / M$; ρ it is assumed to be 1 g cm^{-3} .

corresponding to molten dodecyloxy ($C_{12}H_{25}$) alkyl chains, suggest that London dispersion forces (LDF) from the large number of peripheral chains also contribute to mesophase stabilization through microsegregation between the rigid aromatic core and the flexible alkyl periphery.^{1,12} All the sharp peaks in the small-angle region can be indexed on the two-dimensional hexagonal lattice. The number of molecules per slice of the column (Z) was calculated from the XRD data and was found to be very close to 1. At elevated temperatures, both the compounds 14 and 16 show a few sharp peaks in the small-angle region, with their d -spacings in the ratio of $2:\sqrt{10}:\sqrt{20}$ and $2:\sqrt{5}:\sqrt{6}:\sqrt{14}:\sqrt{16}:\sqrt{30}$, respectively, that corresponds to the (2 0 0), (3 1 0), (4 2 0) and (2 0 0), (2 1 0), (2 1 1), (3 2 1), (4 0 0), (5 2 1) reflections from a cubic lattice belonging to the space group $Pm3n$. The broad peak shown at 4.5 Å in the wide-angle region corresponds to the molten alkyl chains. The lattice parameters (a) of these compounds are 75.38 and 81.12. The number of molecules in the unit cell of the cubic lattice is 51 and 81. The d -spacings of these compounds and their Miller indices are given in Table 3, along with the lattice parameters.

For compounds 15 and 17, the X-ray diffractograms show that the supramolecular assembly exists in the $Pm3n$ cubic phase. Multiple sharp peaks are observed in the small-angle region, in the ratios of $2:\sqrt{5}:\sqrt{6}:\sqrt{14}:\sqrt{16}$ and $2:\sqrt{8}:\sqrt{10}:\sqrt{12}:\sqrt{16}:\sqrt{20}:\sqrt{24}:\sqrt{25}:\sqrt{27}:\sqrt{32}:\sqrt{46}:\sqrt{51}:\sqrt{57}$, which can be indexed on the $Pm3n$ cubic lattice. The lattice

parameter (a) of the cubic phase is found to be 93.93 Å and 129.73 Å , respectively, for compounds 15 and 17. In the wide-angle region, a broad peak is observed at 4.5 Å , corresponding to molten alkyl chains. The number of molecules in the unit cell of the cubic lattice is 47 and 122. The details of the indexing are given in Table 3, and the X-ray diffractograms are presented in Figure 10. X-ray data from the cubic phase of all compounds can be indexed on the $Pm3n$ space group and are given in Table S2.

CONCLUSION

In summary, first and second-generation carboxylic acid-functionalized dendrimers were successfully synthesized via CuAAC click chemistry and assembled with benzotriazole or

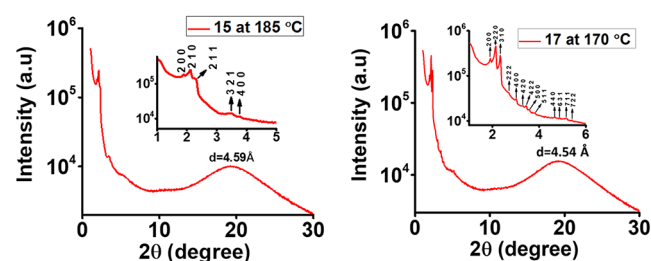


Figure 10. X-ray diffraction patterns of 15 at 185 °C and 17 at 170 °C , in the cubic phase.

benzimidazole derivatives through hydrogen bonding to form well-defined supramolecular liquid crystalline systems. Hydrogen bonding has been employed to induce mesomorphism in liquid-crystalline systems, primarily yielding nematic, smectic, or columnar phases. The present work demonstrates, to the best of our knowledge, for the first time that hydrogen-bonded complexes of carboxylic acid–functionalized dendrimers with benzotriazole or benzimidazole derivatives can induce both columnar hexagonal and cubic mesophases within the same supramolecular system, with the mesophase type governed by dendrimer generation. The first-generation dendrimers, containing carboxylic acid and hydroxyl groups, exhibit a columnar hexagonal (Col_h) mesophase, while the second-generation dendrimers bearing carboxylic acid and ester functionalities display a cubic ($\text{Pm}3n$) mesophase, as evidenced by POM, DSC, and X-ray diffraction analysis. This generation dependence is retained in the hydrogen-bonded complexes: complexes derived from the first-generation dendrimer (14 and 16) exhibit a columnar hexagonal mesophase at room temperature with a transition to a cubic phase at elevated temperature, whereas complexes derived from the second-generation dendrimer (15 and 17) retain only the cubic phase across the entire mesomorphic range, mirroring the behavior of the parent dendrimers. This consistent generation-dependent mesophase switching, in both the dendrimers and their hydrogen-bonded complexes, represents a systematic and tunable approach to controlling liquid-crystalline phase behavior, distinct from previously reported hydrogen-bonded dendritic systems. The formation of stable 1:3 hydrogen-bonded complexes was confirmed by FTIR and ^1H NMR spectroscopy, and all complexes retain mesomorphic order. Most significantly, complexes 14 and 16 exhibit stable room-temperature mesomorphism, a practical feature not observed in previously reported hydrogen-bonded dendrimer systems. Taken together, these results show that combining controlled dendrimer generation with hydrogen-bond-driven supramolecular assembly offers a route to tunable, room-temperature mesomorphic dendritic liquid crystals, with potential applications in switching devices, optical data storage, and optoelectronics.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.6c04985>.

Experimental procedures, synthetic scheme, ^1H and ^{13}C NMR spectra, IR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Sivakumar Irla — Raman Research Institute, Soft Condensed Matter, Bangalore 560080, India; Present Address: Department of Industrial Engineering, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States; orcid.org/0000-0002-0096-8156; Email: iss133@pitt.edu

Sandeep Kumar — Raman Research Institute, Soft Condensed Matter, Bangalore 560080, India; Department of Chemistry and Biochemistry, Sharda School of Engineering and Science, Sharda University, Greater Noida 201310, India; Email: skumar.sandeep@gmail.com

Author

Velayudhan A. Raghunathan — Raman Research Institute, Soft Condensed Matter, Bangalore 560080, India; orcid.org/0000-0002-9213-1811

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.6c04985>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to sincerely thank K.N.Vasudha and Dr. H.T.Srinivasa for their help with the operation of spectrometers, diffractometers, and NMR.

■ REFERENCES

- (1) Tschierske, C. Liquid crystal engineering—new complex mesophase structures and their relations to polymer morphologies, nanoscale patterning and crystal engineering. *Chem. Soc. Rev.* **2007**, *36* (12), 1930–1970.
- (2) Lehn, J.-M. Supramolecular Chemistry—Scope and Perspectives. Molecules, Supermolecules, and Molecular Devices (Nobel Lecture). *Angew. Chem., Int. Ed.* **1988**, *27* (1), 89–112.
- (3) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A New Class of Polymers: Starburst-Dendritic Macromolecules. *Polym. J.* **1985**, *17* (1), 117–132.
- (4) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol. *J. Org. Chem.* **1985**, *50* (11), 2003–2004.
- (5) Hawker, C. J.; Frechet, J. M. J. Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. *J. Am. Chem. Soc.* **1990**, *112* (21), 7638–7647.
- (6) Autumn, K.; Liang, Y. A.; Hsieh, S. T.; Zesch, W.; Chan, W. P.; Kenny, T. W.; Fearing, R.; Full, R. J. Adhesive force of a single gecko foot-hair. *Nature* **2000**, *405* (6787), 681–685.
- (7) Dykes, G. M. Dendrimers: a review of their appeal and applications. *J. Chem. Technol. Biotechnol.* **2001**, *76* (9), 903–918.
- (8) Abbasi, E.; Aval, S. F.; Akbarzadeh, A.; Milani, M.; Nasrabadi, H. T.; Joo, S. W.; Hanifepour, Y.; Nejati-Koshki, K.; Pashaei-Asl, R. Dendrimers: synthesis, applications, and properties. *Nanoscale Res. Lett.* **2014**, *9* (1), No. 247.
- (9) Zeng, F.; Zimmerman, S. C. Dendrimers in Supramolecular Chemistry: From Molecular Recognition to Self-Assembly. *Chem. Rev.* **1997**, *97* (5), 1681–1712.
- (10) B Undre, S.; R Pandya, S.; Kumar, V.; Singh, M. Dendrimers As Smart Materials For Developing The Various Applications In The Field Of Biomedical Sciences. *Adv. Mater. Lett.* **2016**, *7* (7), S02–S16.
- (11) Astruc, D.; Boisselier, E.; Ornelas, C. Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, Photonics, and Nanomedicine. *Chem. Rev.* **2010**, *110* (4), 1857–1959.
- (12) Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. Liquid crystalline dendrimers. *Chem. Soc. Rev.* **2007**, *36* (9), 1495–1513.
- (13) Peng, H.; Liu, X.; Wang, G.; Li, M.; Bratlie, K. M.; Cochran, E.; Wang, Q. Polymeric multifunctional nanomaterials for theranostics. *J. Mater. Chem. B* **2015**, *3* (34), 6856–6870.
- (14) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. Dendron-Mediated Self-Assembly, Disassembly, and Self-Organization of Complex Systems. *Chem. Rev.* **2009**, *109* (11), 6275–6540.
- (15) Guillon, D.; Deschenaux, R. Liquid-crystalline dendrimers. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6* (6), 515–525.

- (16) Elemans, J. A. A. W.; Boerakker, M. J.; Holder, S. J.; Rowan, A. E.; Cho, W.-D.; Percec, V.; Nolte, R. J. M. Plastic- and liquid-crystalline architectures from dendritic receptor molecules. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99* (8), 5093–5098.
- (17) Stebani, U.; Lattermann, G. Unconventional mesogens of hyperbranched amides and corresponding ammonium derivatives. *Adv. Mater.* **1995**, *7* (6), 578–581.
- (18) Cameron, J. H.; Facher, A.; Lattermann, G.; Diele, S. Poly(propyleneimine) dendromesogens with hexagonal columnar mesophase. *Adv. Mater.* **1997**, *9* (5), 398–403.
- (19) Vera, F.; Luis Serrano, J.; Sierra, T. Twists in mesomorphic columnar supramolecular assemblies. *Chem. Soc. Rev.* **2009**, *38* (3), 781–796.
- (20) Rowan, S. J.; Mather, P. T. Supramolecular Interactions in the Formation of Thermotropic Liquid Crystalline Polymers. In *Liquid Crystalline Functional Assemblies and Their Supramolecular Structures*; Kato, T., Ed.; Springer: Berlin Heidelberg, 2008; pp 119–149.
- (21) Bitan-Cherbakovsky, L.; Libster, D.; Ottaviani, M. F.; Aserin, A.; Garti, N. Structural Behavior and Interactions of Dendrimer within Lyotropic Liquid Crystals, Monitored by EPR Spectroscopy and Rheology. *J. Phys. Chem. B* **2012**, *116* (8), 2420–2429.
- (22) Bitan-Cherbakovsky, L.; Libster, D.; Aserin, A.; Garti, N. Complex Dendrimer–Lyotropic Liquid Crystalline Systems: Structural Behavior and Interactions. *J. Phys. Chem. B* **2011**, *115* (42), 11984–11992.
- (23) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. Rational Design of the First Spherical Supramolecular Dendrimers Self-Organized in a Novel Thermotropic Cubic Liquid-Crystalline Phase and the Determination of Their Shape by X-ray Analysis. *J. Am. Chem. Soc.* **1997**, *119* (7), 1539–1555.
- (24) Ungar, G.; Liu, Y.; Zeng, X.; Percec, V.; Cho, W.-D. Giant Supramolecular Liquid Crystal Lattice. *Science* **2003**, *299* (5610), 1208–1211.
- (25) Seddon, J. M. Structure of the inverted hexagonal (HII) phase, and non-lamellar phase transitions of lipids. *Biochim. Biophys. Acta, Rev. Biomembr.* **1990**, *1031* (1), 1–69, DOI: 10.1016/0304-4157(90)90002-T.
- (26) Zeng, X.; Ungar, G.; Liu, Y.; Percec, V.; Dulcey, A. E.; Hobbs, J. K. Supramolecular dendritic liquid quasicrystals. *Nature* **2004**, *428* (6979), 157–160.
- (27) Savyasachi, A. J.; Kotova, O.; Shanmugaraju, S.; Bradberry, S. J.; O'Maille, G. M.; Gunnlaugsson, T. Supramolecular Chemistry: A Toolkit for Soft Functional Materials and Organic Particles. *Chem* **2017**, *3* (5), 764–811.
- (28) Kato, T.; Frechet, J. M. J. A new approach to mesophase stabilization through hydrogen bonding molecular interactions in binary mixtures. *J. Am. Chem. Soc.* **1989**, *111* (22), 8533–8534.
- (29) Gray, G. W.; Jones, B. Mesomorphism and chemical constitution. Part I. The n-alkoxynaphthoic acids. *J. Chem. Soc.* **1954**, *0*, 683–686.
- (30) Kato, T.; Frechet, J. M. J. Stabilization of a liquid-crystalline phase through noncovalent interaction with a polymer side chain. *Macromolecules* **1989**, *22* (9), 3818–3819.
- (31) Brienne, M.-J.; Gabard, J.; Lehn, J.-M.; Stibor, I. Macroscopic expression of molecular recognition. Supramolecular liquid crystalline phases induced by association of complementary heterocyclic components. *J. Chem. Soc., Chem. Commun.* **1989**, No. 24, 1868–1870.
- (32) Felekis, T.; Tziveleka, L.; Tsiourvas, D.; Paleos, C. M. Liquid Crystals Derived from Hydrogen-Bonded Supramolecular Complexes of Pyridinylated Hyperbranched Polyglycerol and Cholesterol-Based Carboxylic Acids. *Macromolecules* **2005**, *38* (5), 1705–1710.
- (33) Didehban, K.; Namazi, H.; Entezami, A. Triazine-based Dendrimers as Liquid Crystals: Synthesis and Characterization. *Iran. Polym. J.* **2009**, *18*, 731–741.
- (34) Lehmann, M. Star Mesogens (Hekates)—Tailor-Made Molecules for Programming Supramolecular Functionality. *Chem. — Eur. J.* **2009**, *15* (15), 3638–3651.
- (35) Xu, J.; Ling, T. C.; He, C. Hydrogen bond-directed self-assembly of peripherally modified cyclotriphosphazenes with a homeotropic liquid crystalline phase. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (14), 4691–4703.
- (36) Bala, I.; Gupta, S. P.; Kumar, S.; Singh, H.; De, J.; Sharma, N.; Kailasam, K.; Pal, S. K. Hydrogen-bond mediated columnar liquid crystalline assemblies of C₃-symmetric heptazine derivatives at ambient temperature. *Soft Matter* **2018**, *14* (30), 6342–6352.
- (37) Kumar, S. Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.* **2006**, *35* (1), 83–109.
- (38) Kumar, S. *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers*; CRC Press, 2011.
- (39) Lugger, S. J. D.; Houben, S. J. A.; Foelen, Y.; Debijs, M. G.; Schenning, A. P. H. J.; Mulder, D. J. Hydrogen-Bonded Supramolecular Liquid Crystal Polymers: Smart Materials with Stimuli-Responsive, Self-Healing, and Recyclable Properties. *Chem. Rev.* **2022**, *122* (5), 4946–4975.
- (40) Moore, J. S. Dendritic molecules: Concepts, syntheses, perspectives. By G. R. Newkome, C. N. Moorefield, F. Vögtle, VCH, Weinheim 1996, xi, 261 pp., hardcover, DM 198.00 ISBN 3–527–29325–6. *Adv. Mater.* **1997**, *9* (9), 761.
- (41) Tiwari, V. K.; Jaiswal, M. K.; Rajkhowa, S.; Singh, S. K. Click Chemistry in Dendrimer Synthesis. In *Click Chemistry*; Tiwari, V. K.; Jaiswal, M. K.; Rajkhowa, S.; Singh, S. K., Eds.; Springer Nature: Singapore, 2024; pp 297–334.
- (42) Franc, G.; Kakkar, A. Dendrimer design using CuI-catalyzed alkyne–azide “click-chemistry”. *Chem. Commun.* **2008**, No. 42, 5267–5276.
- (43) Franc, G.; Kakkar, A. K. “Click” methodologies: efficient, simple and greener routes to design dendrimers. *Chem. Soc. Rev.* **2010**, *39* (5), 1536–1544.
- (44) Wu, P.; Malkoch, M.; Hunt, J. N.; Vestberg, R.; Kaltgrad, E.; Finn, M. G.; Fokin, V. V.; Sharpless, K. B.; Hawker, C. J. Multivalent, bifunctional dendrimers prepared by click chemistry. *Chem. Commun.* **2005**, No. 46, 5775–5777.
- (45) Guerra, S.; Nguyen, T. L. A.; Furrer, J.; Nierengarten, J.-F.; Barberá, J.; Deschenaux, R. Liquid-Crystalline Dendrimers Designed by Click Chemistry. *Macromolecules* **2016**, *49* (9), 3222–3231.
- (46) Concellón, A.; Termine, R.; Golemme, A.; Romero, P.; Marcos, M.; Serrano, J. L. High hole mobility and light-harvesting in discotic nematic dendrimers prepared via ‘click’ chemistry. *J. Mater. Chem. C* **2019**, *7* (10), 2911–2918.
- (47) Barberá, J.; Puig, L.; Serrano, J. L.; Sierra, T. Structural Study on Columnar Mesophases Consisting of H-Bonded Supramolecules. *Chem. Mater.* **2004**, *16* (17), 3308–3317.
- (48) Xiong, J.-F.; Luo, S.-H.; Huo, J.-P.; Liu, J.-Y.; Chen, S.-X.; Wang, Z.-Y. Design, Synthesis, and Characterization of 1,3,5-Tri(1H-benzo[d]imidazol-2-yl)benzene-Based Fluorescent Supramolecular Columnar Liquid Crystals with a Broad Mesomorphic Range. *J. Org. Chem.* **2014**, *79* (17), 8366–8373.
- (49) Lugger, J. A. M.; Mulder, D. J.; Bhattacharjee, S.; Sijbesma, R. P. Homeotropic Self-Alignment of Discotic Liquid Crystals for Nanoporous Polymer Films. *ACS Nano* **2018**, *12* (7), 6714–6724.
- (50) Bhattacharjee, S.; Lugger, J. A. M.; Sijbesma, R. P. Pore size dependent cation adsorption in a nanoporous polymer film derived from a plastic columnar phase. *Chem. Commun.* **2018**, *54* (68), 9521–9524.
- (51) Lugger, J. A. M.; Sijbesma, R. P. Easily Accessible Thermotropic Hydrogen-Bonded Columnar Discotic Liquid Crystals from Fatty Acid–Tris-Benzoimidazolyl Benzene Complexes. *ChemistryOpen* **2016**, *5* (6), 580–585.
- (52) Bögels, G. M.; Lugger, J. A. M.; Goor, O. J. G. M.; Sijbesma, R. P. Size-Selective Binding of Sodium and Potassium Ions in Nanoporous Thin Films of Polymerized Liquid Crystals. *Adv. Funct. Mater.* **2016**, *26* (44), 8023–8030.
- (53) Krishnan, N.; Ameen, M. A. H.; Atchimnaidu, S.; Perumal, D.; Golla, M.; Krishna, J.; Varghese, R. Self-assembly of tetraphenyl-ethylene-based dendron into blue fluorescent nanoparticles with

aggregation induced enhanced emission. *J. Chem. Sci.* **2018**, *130* (10), No. 141.

(54) Yang, H.; Chen, J.-M.; Sun, J.-J.; Yang, S.-P.; Yu, J.; Tan, H.; Li, W. Syntheses, crystal structures and magnetic properties of three novel cobalt(ii) complexes containing imidazole derivative groups. *Dalton Trans.* **2009**, No. 14, 2540–2551.

(55) Lee, H. Y.; Park, J.; Lah, M. S.; Hong, J.-I. A hamburger-shaped helical stacking of disk-shaped ligands mediated by silver(ii) ions. *Chem. Commun.* **2007**, No. 47, 5013–5015.

(56) Laurence, C.; Brameld, K. A.; Graton, J.; Le Questel, J.-Y.; Renault, E. The pKBHX Database: Toward a Better Understanding of Hydrogen-Bond Basicity for Medicinal Chemists. *J. Med. Chem.* **2009**, *52* (14), 4073–4086.