

Complementary Hydrogen Bonding Between a Clicked C_3 -Symmetric Triazole Derivative and Carboxylic Acids for Columnar Liquid-Crystalline Assemblies**

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Click chemistry has received much attention in organic and polymeric materials chemistry, because it can provide a very efficient synthetic pathway for designing soft materials.^[1] To date, click chemistry has been mostly utilized to simply bridge organic building units into more complex architectures, such as dendrimers, block copolymers, and cyclic compounds.^[2] However, more attention is now paid to the functionality of click chemistry, and particularly in the use of the resulting triazole ring. As an interesting example, several research groups recently investigated the anion-binding properties of triazole derivatives, although some research regarding metal coordination were also reported.^[3] Craig et al. demonstrated that aryl triazole based oligomers can bind anions by utilizing the electropositive CH group of the triazole group.^[4] Contemporaneously, Hecht and Meudtner reported an unprecedented helix inversion in response to halide ions in triazole-linked foldamers,^[5] and Flood and Li observed a strong, selective affinity of shape-persisted triazolophanes for chloride ions.^[6] Such an anion-binding capability of clicked triazole-based compounds can be understood as privileged hydrogen bonding (H-bonding) between the anion and the CH group of the triazole ring.

Discotic liquid crystals (LCs) consisting of a flat aromatic core and flexible chains are known to form columnar mesophases. The columnar architecture formed by discotic LCs is very attractive because it provides a one-dimensional conducting pathway for electrons, photons, or energy.^[7] The

design of discotic LCs can be accomplished by supramolecular approaches. Among the possible non-covalent strategies, molecular recognition processes involving H-bonding interactions could be the most efficient way to build a rigid discotic mesogen by considering bonding directionality and strength.^[8]

In this regard, it would be interesting to design an H-bonding motif using a clicked triazole derivative for the construction of discotic LC materials. Considering the H-bonding capability of the triazole ring toward anions, we thought that the electropositive character of triazole hydrogen could allow an H-bonding formation with other H-acceptors, such as carbonyl and imidazole groups.^[9] Herein, we present novel H-bonded complexes (HBCs) consisting of a clicked C_3 -symmetric 1,3,5-tris(1-alkyl-1H-1,2,3-triazol-4-yl)benzene (TTB) unit with 3,4,5-trioctyloxybenzoic acids (TBAs) in a 1:3 stoichiometry (Figure 1). Taking into account the core structure of HBC, we suggest that the nitrogen atom in TTB can be an H-acceptor with respect to the donor from the terminal hydroxy group in TBA. The corresponding H-bonding is assigned as $\text{OH}^{\text{c}} \cdots \text{N}$. The aromatic hydrogen atoms in the triazolyl and benzenyl groups of TTB can also form H-bonding pairs with the carbonyl oxygen atom in TBA (depicted by $\text{CH}^{\text{a}} \cdots \text{O}$ and $\text{CH}^{\text{b}} \cdots \text{O}$ in Figure 1b). Owing to these complementary H-bonding interactions and the 1:3 stoichiometry, we intuitively thought that the HBC complexes would be conformationally rigidified, leading to supramolecular discs for the columnar stacking; any other stoichiometry is less likely to afford this organization.

To confirm the aforementioned conjectures, we initially performed the first-principles density functional calculations. We used the Gaussian03 package, the PBE-type gradient-corrected functional, and the B3LYP hybrid functional. The cc-pVDZ basis set was used with the counterpoise correction.^[10] The counterpoise-corrected binding energy between TTB and TBA was found to be 57.9 (48.2) kJ mol^{-1} when the PBE (B3LYP) functional was employed. This result confirms the known features of the PBE functional, which tends to overestimate H-bonding interactions.^[11] Nevertheless, the results clearly show that the three complementary H-bonds mediate the strong intermolecular binding between TTB and TBAs. The H-bond lengths are 1.70, 1.98, and 2.41 Å for $\text{OH}^{\text{c}} \cdots \text{N}$, $\text{CH}^{\text{a}} \cdots \text{O}$, and $\text{CH}^{\text{b}} \cdots \text{O}$, respectively. For comparison, we also calculated the interaction strength in the TBA dimer. The H-bond length in the TBA dimer is 1.53 Å, and the binding energy of the dimeric H-bonding association was calculated to be 36.7 (32.8) kJ mol^{-1} with the PBE (B3LYP)

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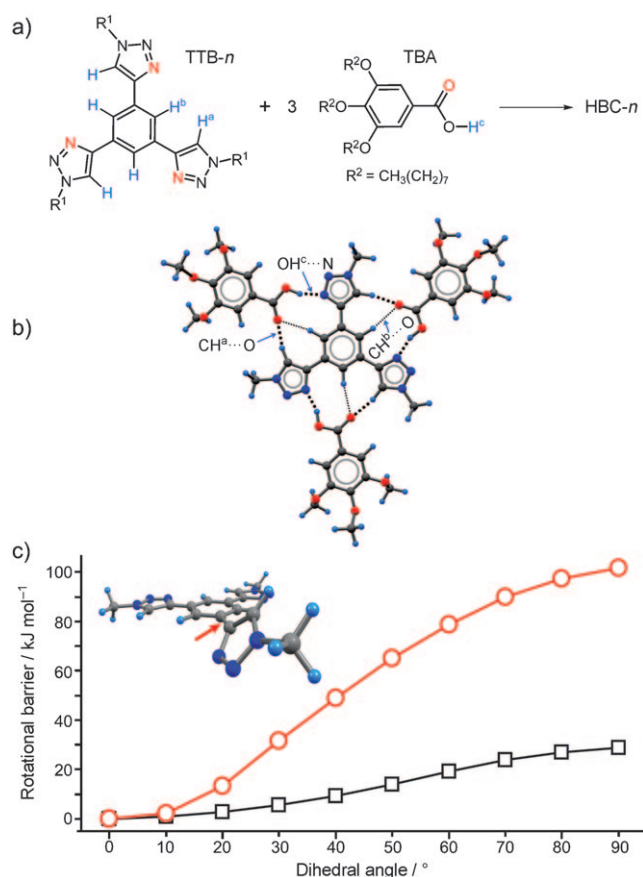


Figure 1. a) Molecular structures of TTB-*n* and TBA. b) Optimized geometry of HBC-*n* by complementary H-bonding. HBC-1: R¹ = CH₃-(CH₂)₇, HBC-2: R¹ = CH₃-(CH₂)₉; HBC-3: R¹ = CH₃-(CH₂)₁₁. H-bonding between TTB and TBA are depicted with dotted lines. c) Rotational energy barriers of TTB (□) and HBC (○) as a function of dihedral angle with respect to the C–C bond (indicated by the red arrow). For clarity, alkyl groups are represented using methyl groups in (b) and (c). C gray, N blue, O red, H small blue spheres.

functional. This result indicates that the TBAs exhibit some amount of energy gains in the HBC formation.

The preference for the disc-like configuration of HBC can be explained by the rotational energetics of the triazolyl group of TTB. Using the abovementioned computational method, we first fully optimized the geometries and then rigidly rotated the triazolyl group with respect to the central benzene group. Figure 1c shows that the rotational barrier increases significantly when HBC consists of TTB with three TBA units. This obviously originates from the complementary H-bonding. If we consider the first-order Arrhenius-type reaction $v = v_0 \exp(-\Delta E/k_B T)$, the rotation of the triazolyl group is largely suppressed in HBC even if the rotation in isolated TTB were marginally allowed (Figure 1c).

The preparation of TTB was performed by a click reaction of 1-azidoalkane and 1,3,5-triethynylbenzene using CuSO₄·5H₂O and sodium ascorbate as catalysts (Supporting Information, Scheme S1).^[2] TBA was prepared by sequential alkylation and hydrolysis reactions as described elsewhere.^[12] The obtained TTBs and TBA were characterized by ¹H and ¹³C NMR spectroscopy, elemental analysis, and gel perme-

ation chromatography (GPC). All of the experimental data fit well with the designed molecular structure (see the Supporting Information). As analyzed by differential scanning calorimetry (DSC), each of TTB and TBA alone exhibited no LC phase. HBCs were obtained by mixing TTB with TBA in a 1:3 molar ratio in chloroform followed by slow evaporation of the solvent at reduced pressure.

The formation of CH^a...O and CH^b...O H-bonds was indicated by IR and ¹H NMR spectroscopy. The C=O stretching vibration in TBA appears at 1685 cm⁻¹ (Figure 2a), which indicates dimeric H-bonding.^[12] Conversely, the carbonyl band in HBC-1 shifted to 1703 cm⁻¹, which is lower than that (1733 cm⁻¹) of the free carboxylic acid.^[12] This result suggests that the carbonyl group still interacts with a different H-bonding donor, presumably CH^a of the triazole in TTB. Furthermore, the shift to the lower frequency of 1703 cm⁻¹ may confirm that the carbonyl groups form hydrogen bonds with CH^a, which is a weaker H-bonding donor than the OH group from the carboxylic acid. To corroborate this, the ¹H NMR signals in CDCl₃ solutions were examined (concentration of all samples: 9.87 × 10⁻² M). As shown in Figure 2b, the signal from the hydrogen atom CH^a of the triazole in TTB-1 appeared at δ = 7.97 ppm, but it shifted at δ = 8.09 ppm for HBC-1. The signal for the hydrogen atom CH^b of the central benzene unit is also shifted slightly downfield in HBC-1. Therefore, a more realistic HBC structure can be described by considering that the carbonyl group is associated with the triazolyl hydrogen atom as well as the benzene hydrogen atom, although the stronger H-bonding is involved in the triazolyl hydrogen atom. This NMR result is consistent with their H-bonding lengths presented in the above-mentioned simulation data.

The emission behavior in the complexes of aromatic amines and carboxylic acids is strongly dependent upon the H-bonding strength.^[13] Thus, OH^c...N was examined by the steady-state fluorescence spectra of TTB-1, TBA, and HBC-1 using the bulk and solution samples with excitation λ_{ex} at 265 nm. In contrast to the emission maxima (λ_{max}) below 345 nm in the bulk emission spectra of TTB-1 and TBA, HBC-1 showed a considerably red-shifted spectrum with λ_{max} = 383 nm (Figure 2c). This suggests the formation of a remarkable H-bonding motif (OH^c...N), although the detailed dynamics are ambiguous at the present moment. This formation was further confirmed by comparing the emission spectra of HBC-1 detected in cyclohexane (C₆H₁₂) and a cyclohexane/ethanol mixture (1:1 v/v; Figure 2d). Similar to the bulk HBC sample, the sample in apolar cyclohexane also exhibited a red-shifted emission with λ_{max} = 375 nm. In contrast, the spectrum detected in the ethanol/cyclohexane solution was slightly red-shifted to λ_{max} = 358 nm, evidently because protic ethanol hindered the OH^c...N between TTB and TBA.

On the basis of these spectroscopy and simulation results, it is obvious that the central disc of the HBCs has an extended rigid core with disc-like geometry. The disc-like structure would be a prerequisite for columnar packing of discotic LC molecules. We then checked the thermotropic LC behavior of HBCs. LC formation of the HBCs was analyzed using DSC and polarized optical microscopy (POM) techniques (for

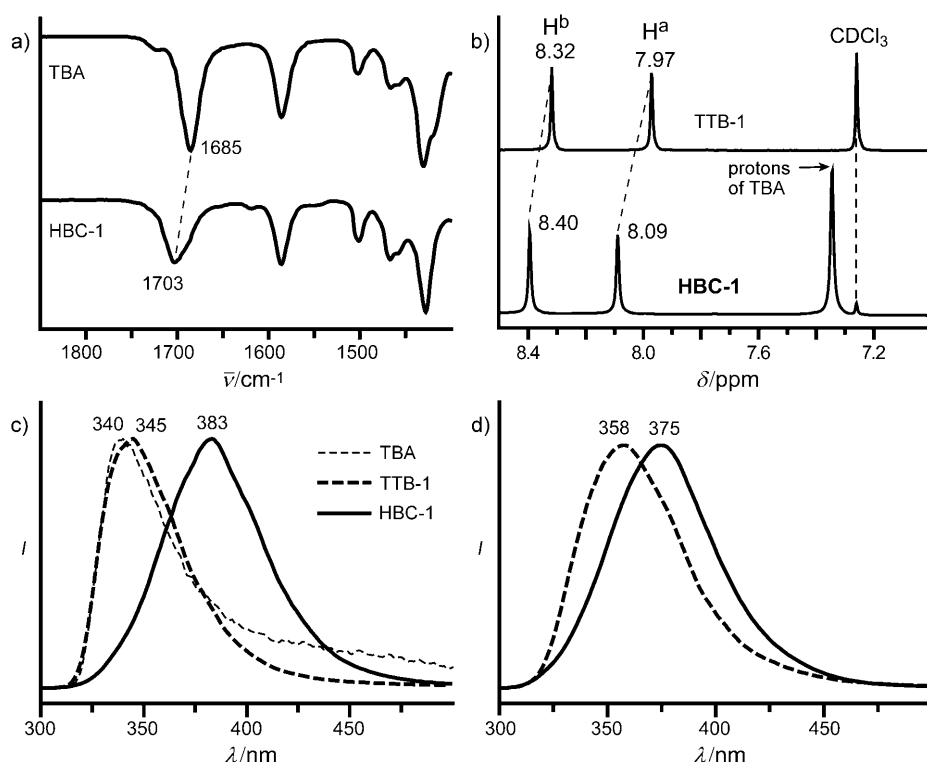


Figure 2. a) IR absorption spectra of TBA and HBC-1; b) ^1H NMR spectra of TTB-1 and HBC-1 in CDCl_3 ; c) emission spectra of TBA, TTB-1, and HBC-1 in the bulk; and d) emission spectra of HBC-1 in cyclohexane (C_6H_{12} , —) and a $\text{EtOH}/\text{C}_6\text{H}_{12}$ mixture (1:1 v/v, ----).

DSC second-heating and first-cooling curves of HBCs, see the Supporting Information, Figure S5). In contrast to the non-mesogenic TTB-*n* and TBA, all HBCs displayed LC phases, although they showed different mesomorphic behavior depending on the thermal process. HBC-1 and HBC-2 showed monotropic LC phases exclusively on cooling, while HBC-3 formed an enantiotropic LC phase (appearing on both heating and cooling).

To identify the LC phases, we investigated the POM textures of HBCs on slow cooling (2°Cmin^{-1}) from the isotropic melt. All of the HBCs showed a similar optical texture with dendritic domains, which are typically observed in the hexagonal columnar LC phase of discotic LCs (Figure 3a; Supporting Information, Figure S6).^[14] Notably, upon annealing, some dark areas did not become birefringent. Instead, finger-like contours were observed between two parallel polarizers, indicating the perpendicular alignment of columns to the glass substrate (Figure 3b). This homeotropic orientation may be attributed to the polar interaction between the heteroatoms on the HBC aromatic core and the glass surface.^[15]

Finally, the microstructural details in the LC phases were analyzed by small- and wide-angle X-ray scattering (SAXS and WAXS) experiments. Samples were slowly cooled from the isotropic liquid by keeping the same thermal condition performed in the POM observations. Like the similarity in the POM texture, they exhibited analogous X-ray scattering patterns, although HBC-1 showed only a strong reflection in its SAXS spectrum (Supporting Information, Figure S7). As a

representative SAXS result, HBC-2 displayed two sharp reflections between which two broad reflections were observed (Figure 3c). The reflections can be indexed as the (100), (110), (200), and (210) planes of a 2D hexagonal columnar structure. In the WAXS data, along with the halo reflection of molten alkyl peripheries at 4.4 Å , the LC phase showed another broad shoulder near 3.5 Å (Figure 3d). The shoulder-like reflection may be attributed to the intracolumnar stacking of H-bonded cores, and it disappeared in the liquid state. Consequently, it can be said that the supramolecular discs mediated by the complementary H-bonding stack on top of each other to form one-dimensional cylinders that self-organize into a two-dimensional hexagonal lattice.

In summary, we verified the complementary H-bonding between a C_3 -symmetric triazole derivative and carboxylic acids by

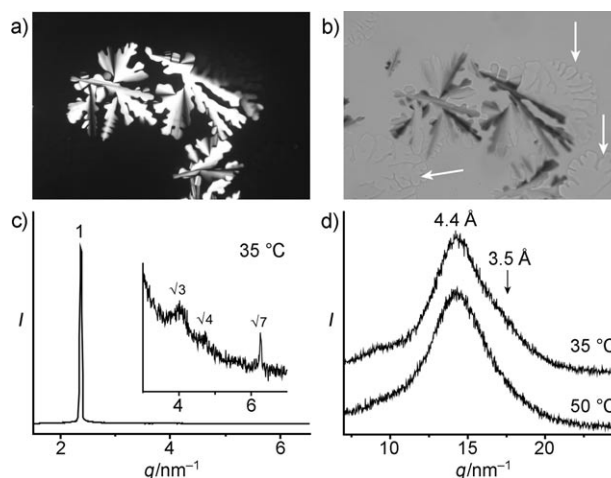


Figure 3. a,b) POM textures of HBC-3 (white arrows indicate columnar domains with homeotropic orientations); c) SAXS and d) WAXS spectra of HBC-2. Images in (a) and (b) were taken when two polarizers were crossed and parallel, respectively.

spectroscopy and simulation studies. With the aid of the H-bonding, the complexes have an extended mesogenic disc. On the basis of the POM and X-ray scattering results, we demonstrated the formation of 2D hexagonal columnar LC phases in the melt. Notably, to the best of our knowledge, the HBCs in this study are the first example of a “clicked” triazole being employed as an H-bonding motif (bearing the hydrogen donor and acceptor) for LC materials. The molecular design

concept reported herein could provide a supramolecular pathway applicable for electronics and nanoporous organic materials owing to the columnar morphology and the dynamic nature of the H-bonding.

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