

Alkynyl-Containing Discotic Liquid Crystal Molecules

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Under specific circumstances, organized columnar phases can be formed from the planar discoid shapes of the molecules that make up discotic liquid crystals. These materials offer unusual features because of their distinct columnar phase structure. They are utilized in organic semiconductors, liquid crystal magnetic materials, and photoelectric conversion. It has numerous applications, so researchers are paying more and more attention to it. In this paper, the effects of alkynyl groups on the properties of discotic liquid crystals at various positions are emphatically discussed. The main focus is on the alkynyl-containing discotic liquid crystal molecules and their properties reported in domestic and foreign literature in the past ten years.

Keywords: Discotic Liquid Crystal; Alkynyl Group; Organic Semiconductor; Polymers

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STUDIES have been conducted on the synthesis and characterization of discotic liquid crystal molecules of different configurations since Chandrasekhar (1) originally described the synthesis and characterization of discotic liquid crystal molecules in 1977. Thousands of different chemicals have been created thus far. A molecule with a planar discoid shape that can be ordered to produce a liquid crystal state when specific circumstances are met is known as a discotic liquid crystal molecule. The flexible components are primarily aliphatic long chains, whose function is to introduce perturbation factors into the rigid system and increase the solubility of the compound. It can be adjusted through the packing mode of these planar molecules under suitable conditions and promulgate the orderly arrangement in a one-dimensional direction. Many different types of rigid central cores exist, but the most common are poly(fused) ring aromatic hydrocarbons that achieve orderly arrangement in a one-dimensional direction through the interaction of plane molecules.

A distinct columnar phase structure can be formed by the

molecules of discotic liquid crystals. The molecules have one-dimensional order and are aligned in a direction perpendicular to the discoid plane in the columnar phase. The columnar arrangement forms a quasi-one-dimensional conjugated electron cloud distribution when the discotic mesogen itself exhibits electron conjugation. Because of their structural characteristics, discotic liquid crystals have promising futures as optoelectronic materials (2-5). Additionally, when compared to crystals with similar columnar stacking, the discotic liquid crystal system's defects are greatly reduced by the self-healing function caused by the perturbation of flexible chains and specific molecular mobility. The discotic liquid crystal molecules also reflect the fact that, as a semiconductor material, it has special advantages in carrier transport.

High order and good charge transport capabilities, a stable hexagonal columnar liquid crystal phase, and a broad mesogenic temperature range are the main determinants of the usefulness of discotic liquid crystal materials as optoelectronic and semiconductor materials. The phase state, phase transition temperature,

and stability of the phase state of the discotic compound can all be changed to satisfy these parameters. After the central core has been established, the structural modification of a discotic liquid crystal's performance also depends on changes to the flexible chain surrounding the core, such as altering the connection mode between the flexible chain and the core or the length of the flexible chain, adding functional groups, creating oligomers or polymers of the discotic liquid crystal (6-8). For instance, Rego (9) incorporated alkynyl groups directly into liquid crystal molecules, whereas Axenov et al. (10) used unsaturated alkynyl groups to produce liquid crystal compounds with low melting points, a wide temperature range of the mesogenic phase, and stable mesogenic phases. The substance exhibits good liquid crystallinity on the triphenylene core's stiff structure. This paper primarily introduces the alkynyl-containing discotic liquid crystals; the striking modifications in the mesogenicity and semi-conducting characteristics of various discotic central cores and dimers following the addition of alkynyl groups; and the development of polyalkyne-based discotic liquid crystal polymers.

Discotic Liquid Crystal Molecules

Discotic Liquid Crystals Based on Alkynyl

Benzene Ring Derivatives

Previous studies naturally focused on molecules made from a single benzene ring structure, since the benzene ring is the fundamental building block of aromatic chemicals. Numerous discotic liquid crystals of benzene derivatives have appeared since the initial finding of hexasubstituted ester-containing benzene derivatives in 1977.

By using Wolff-Kishner reduction and a palladium-catalyzed coupling reaction, Kumar et al. created branched alkyl-substituted hexaethynylbenzene derivatives, which displayed a nematic discotic liquid crystal phase at room temperature and increased the viewing angle of the liquid crystal display (11). Additional research found that the substituents' and connecting atoms' chain length affects how these compounds behave in liquid crystals. Such molecules can also have their liquid crystal behavior controlled by adding electron acceptors, which results in charge transfer effects on the molecules (12).

According to Varshney et al. (13), the achiral alkyl branch of the radioactive polyalkynyl benzene series forms a columnar phase (Col), although the regular alkoxy branch also forms a columnar phase (Col). When chiral alkoxy branches are present, a chiral nematic-discotic phase (ND*) forms in addition to the nematic-discotic phase (ND). The phase transition temperature was successfully decreased to room temperature by the "molecular symmetry effect," and the charge transfer complex and 2,4,7-trinitrofluoren-9-one (TNF) produced a univariate hexagonal columnar phase (Colh). Further utilizing these compounds' molecular rotational characteristics for effective charge transfer was done by Lee et al. (14). Hennrich et al. investigated highly polarizable C₃-symmetric 1,3,5-trialkynyl benzene series and discovered that these compounds not only exhibited the tetragonal columnar phase (Colr), Colh, and ND phases, but also intense fluorescence, a clear Stokes shift, and general photoconductivity (15). Triethynylbenzene was used by Ryu et al. to cre-

ate star-shaped 1,3,5-trialkynylbenzene derivatives. At room temperature, they noticed a CO₂ phase and a vertical alignment tendency (16).

Phenylene and Acetylene Macrocycles

Fischer et al. created the first macrocyclic compounds in 1994 (17). Macrocycles have rigid alkyne or lower alkyne units that serve as bridges and aromatic or antiaromatic groups at the margins. Macrocycles typically have a triangular or hexagonal form. The smallest macrocyclic compounds have been created by Seo et al., who also confirmed how side chains affect mesogenicity (18).

Large triangular and hexagonal compounds were created by Li et al. (19) and Fritzsche et al. (20), using the Sonogashira-Hagihara and oxidative glaser coupling processes, respectively. The phenylene spacing and the existence of aryl groups in the edge unit allowed for the detection of the Colr, Colh, and ND phases for the cyclic trimer. While self-assembling into the Colh and Colr phases, hexagonal macrocyclic compounds display more conventional liquid crystallinity.

The optoelectronic characteristics of triangular compounds were investigated by Luo et al. (21). Triangular compounds are an ideal material for creating photoelectric switches since they can not only produce nA-type photocurrent but also have an on/off ratio of 103. Kato et al. reported shape-stable macrocyclic compounds with phenanthrenes in the corners of triangles, tetraalkoxy-phenanthrene-mixed dehydro(n)rotaxenes (or quadrilaterals) (22). While the comparable antiaromatic rotaxenes lack any discernible fluorescence features, some rotaxenes are luminous.

Discotic Liquid Crystals with Alkynyl Functional Groups

Liquid Crystals with a Discotic Phenylene Structure

Triphenylene discoid molecules are among the most studied discotic liquid crystal materials because of their advantages of simple synthesis and processing and low melting point. A hard planar triphenylene core and many flexible chains surround the rigid core in such liquid crystal molecules. This triphenylene molecule exhibits enhanced charge and exciton transport capabilities along the direction of the column axis and is easily converted into a columnar liquid crystal phase. The main application-related issues for discotic liquid crystal materials to be resolved are extending the temperature range of the liquid crystal phase and decreasing the melting point, which may be primarily accomplished by altering the molecular structure.

To explore the effect of structural elements on the development, nature, and stability of discotic triphenylene mesophases, Andrew et al. synthesized several polysubstituted triphenylenes with a combination of alkynes and alkoxy groups (23). Their findings demonstrated that when triphenylene contains two alkynes, the columnar mesophase activity can really be improved; but, when four or six alkynes are present, the mesophase behavior is completely inhibited.

Hexabromotriphenylene was used by Wang and coworkers

ers to create a series of six symmetrically substituted triphenylene derivatives (24). In addition to extending the range of triphenylenes' long-type conjugation, six symmetrical substituents can also improve the compounds' solubility. It is shown that the various substituents of the discoid molecules affect the electronic properties and mesophases by contrasting their properties and examining the relationship between the structural properties. It is demonstrated that the extended conjugation length affects the triphenylene derivatives by comparing the absorption and photoluminescence spectra of these pure compounds, and the photoluminescence spectra of the absorption wavelengths show a significant increase with increasing conjugation length. According to the electrochemical characteristics of these compounds, HTP3 and HTP4 have lower LUMO levels than HTP1 and HTP2, which may be a result of the phenyl group's addition, which lengthens the conjugation and increases the electron delocalization.

In order to investigate the effects of flexible chains on the phase state, phase transition temperature, and phase stability, Zhao et al. created flexible chains containing unsaturated groups around triphenylene (25). Their findings showed that the target compounds all exhibit an ordered hexagonal-columnar mesogenic phase. The terminal alkynyl chain compound series has the highest melting point, while the terminal alkenyl flexible chain compound series has a lower melting point than the terminal alkynyl flexible chain compound series. The highest clearing point and largest mesogenic temperature range were found in the vinyloxy flexible chain compound series, and the clearing point rose noticeably as the number of unsaturated ether chains increases.

Although hexa(phenylethynyl)triphenylene's self-organized ND phase is uncommon in discotic liquid crystals, its broad bandgap energy precludes its use in organic electronics. The triphenylene derivative not only displayed an ND phase but also relatively low bandgap energy of 2.53 eV when a thiophene unit was added at the periphery via a Suzuki–Miyaura and Sonogashira cross-coupling process to offset this effect.

Discotic Hexabenzene-Like Liquid Crystals

Hexabenzocoronene (HBC) is a macrocyclic aromatic molecule with a diameter of 0.15 nm that is made up of 42 carbon atoms bound together by covalent bonds. By employing a transition metal-catalyzed cyclization technique to create HBC derivatives with chiral and racemic groups, Fechtenkter et al. discovered that the compounds' solubility and processing characteristics were enhanced and that their crystal phase changed to a columnar phase (26). At temperatures below room temperature, the compound can enter the columnar phase area; however, the clearing threshold is not reached until 400 °C. While the structurally related p-dodecylphenylacetylene substituted HBC showed corresponding phase transitions at 15 °C and 80 °C, it was clear that the addition of the connecting arm, the ethynyl group, had an impact on the compound's phase transition temperature.

Hexa-hexabenzopyridine/perylene diimide dimers with covalent bonds were created by Dössel et al. as a fundamental model for checking energy and electron transfer procedures (27). While unstable, compounds made of columnar polymers can

display photoluminescence. For the purpose of preventing direct charge recombination, the connecting section of the dyad is not conjugated. Because there is no electron contact between the donor and acceptor, this type of star-shaped doublet transports holes and electrons along the column-oriented channel, potentially as a result of coaxial line acting on the crystal field effect.

Liquid Crystal Made of Perylene Diimide

The majority of perylene imide compounds are soluble in typical organic solvents due to the fused-ring conjugated system and molecular planarity of perylene imide compounds, which improve the interaction of massive bonds between molecules and raise the lattice energy. Such compounds can be given various functional groups to increase their solubility. The Sonogashira coupling process has been used to create perylene imide (PBI) derivatives with benzyne substituents in the bay position. By identifying absorption peaks and distinct electronic vibrational processes, the manufactured doublet exhibits a distinct red shift. Effective charge transfer from electron-rich substituents to electron-deficient PBI nuclei is made possible by these substituents. The PBI ethynyl (dimethylaminophenyl) substituent exhibits a significant donating property, according to the spectrum characteristics.

Discotic Liquid Crystals That Resemble Porphyrins

By using a "click" reaction, symmetric octa(thioalkane) nitrogen-containing porphyrins terminated by azide or acetylene groups, respectively, can be cross-linked into Langmuir membranes, according to Belviso et al. (28) and Kayal et al. (29). Or the COOH phase was created by thermally activating the azide-alkyne cycloaddition. Surprisingly, crosslinking had minimal impact on the mesophase.

Discotic Liquid Crystal Dimer

Two stiff mesogens that are either the same or distinct are joined by bridges make up a liquid crystal dimer. Compared to conventional small-molecule liquid crystals, it has unusual physical characteristics. The discotic state is improved by the compound's abundance of mesogenic phase states as well as some liquid crystal dimer compounds' polymer features, such as glass transition during phase transition. the usefulness of organic semiconductor materials like liquid crystals. As an alternative to changing the flexible chains around the triphenylene mesogens to produce stable columnar phases, bridge chains are used to join the two triphenylene molecular mesogens, giving rise to triphenylene dimer compounds.

By the Pd-catalyzed self-coupling reaction of terminal alkynes, Zhao and coworkers (30) generated diphenylbutadiyne bridged triphenylene discotic liquid crystal dimers and a series of functionalized discotic liquid crystal monomers. According to their results of the thermogravimetric analysis (TGA), it has good thermal stability and starts to break down at around 370 °C. All monomer and dimer compounds were discovered using polarized light microscopy and differential scanning calorimetry to be columnar phase liquid crystals that were in liquid crystal phase at room temperature. The molecule also possesses very stable columnar packing, high-definition brilliant spots, and a

broad mesogenic phase range. It is proven that joining two discotic mesogens with a semi-rigid bridge chain can stabilize the columnar phase to some extent. A comparison of the literature reveals that the central bridge chain's rigidity has a significant impact on the triphenylene discotic liquid crystal dimer's mesogenicity and that the rigidity of the central bridge chain of diphenylbutadiyne is advantageous for the molecules' orderly stacking.

Through the Sonogashira coupling and cyclization procedure, Zhao et al. also created a (D-A-D) trimers using triphenylene as the electron donor and perylene diimide as the electron acceptor (31). Due to effective molecular autonomous ordering, all trimers self-assemble to create layered columnar tilting phases that can give rise to highly separated donor-acceptor (D-A) heterojunction structures. By stacking hexabenzophthalimide to create an electron transport channel and using electron-rich striphenylene as a hole transient pathway, a so-called p-n heterojunction is constructed and proven for the first time at the molecular level.

Polymer Liquid Crystal

A polymer liquid crystal is a polymer created by joining mesogens together chemically. It combines the benefits of polymer stability and liquid crystal's optoelectronic capabilities. Due to their functional side chains, monosubstituted side-chain liquid crystal polyalkynes have numerous application possibilities in the fields of electricity and optics.

By using a Rh(nbd)₂Cl₂/Et₃N catalyst system, Xing et al. successfully polymerized the monomers in a solution of

tetrahydrofuran by changing the bond length of the spacer to the main chain of polyalkyne (32). It dissolves readily in common organic solvents due to its low molecular weight. The yield is extremely high and can reach 84%. All polymers have very high thermal decomposition temperatures, and when heated to 300 °C, there is no degradation. While the polymer's X-ray diffraction peak is sharpest when the spacer length is a methylene group of five carbons, corresponding to the development of mixed columnar liquid crystals, the tailed triphenylene having four carbons exhibits a hexagonal columnar phase. It has been discovered that the packing of mesogens and the structure of triphenylene polymers are both significantly influenced by the length of the alkyl chain.

Conclusion

This paper mainly introduces the remarkable changes in the mesogenicity and semiconducting properties of discotic liquid crystal molecules of polyalkyne-based discotic liquid crystal polymers, as well as the significant changes in the mesogenicity and semiconducting properties of discotic liquid crystals containing alkynyl structures and various central cores and dimers after the modification of alkynyl groups. Although thousands of compounds have been published and more than four decades have passed since the discovery of discotic liquid crystals, the study of discotic liquid crystals containing alkynyl groups is still in its infancy. How to increase the order degree of the discotic liquid crystal's columnar phase and how to enhance its film-forming properties are now the two primary issues in the field of discotic liquid crystal materials. ■

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