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Phase-Dependent Photoluminescent Discotic Liquid Crystal Bearing Graphdiyne Substructure

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In recent years, graphdiyne and its derivatives with fascinating electro-optic properties have attracted tremendous scientific attention. Here we design and synthesize a graphdiyne-derived discotic liquid crystal material by decorating six wedge-shaped 3,4,5-tris(dodecyloxy)benzoate groups on the fundamental structural unit of graphdiyne, dehydrotribenzo[18]annulene core. This graphdiyne-derived liquid crystal material exhibits cubic phase and hexagonal columnar phase at varied temperatures. Most interestingly, this molecule displays a tunable phasedependent photoluminescence behavior. Under the irradiation of 365 nm wavelength ultraviolet light, the luminescent material emits pale blue, green and azure light in the cubic, hexagonal columnar and isotropic phases respectively. This graphdiynederived discotic liquid crystal with excellent optical characteristics might have application potentials in organic optoelectronic functional materials and devices.

Graphynes (GYs), a series of two-dimensional (2D) sp-sp² hybridized carbon allotropes, display fascinating electro-optic properties, such as high carrier mobility, excellent native band gap, anisotropic optical property, which have attracted tremendous scientific attention in recent years.^{1–3} As the most representative member of GY family, graphdiyne (GDY, Figure 1) with a 2D layered network structure formed by two conjugated triple bonds ($-C\equiv C-C\equiv C-)$ connecting aromatic carbon rings,^{4–7} exhibits great advantages in photo-related and electrochemical applications because of its unique atom arrangement, coexistence of sp- and sp²-hybridizations and extended π -conjugated system.^{8–10}

As schematically illustrated in Figure 1, the fundamental structural unit of GDY can be identified as dehydrotribenzo[18]annulene (DBA[18]) with a C_3 -symmetric axis. DBA[18] is a planar shape-persistent macrocyclic

molecule displaying particularly interesting self-assembly and optoelectronic properties.^{11,12} In addition, its shape-persistent macrocyclic derivatives have exhibited many fascinating characteristics in the fields of host-guest chemistry, supramolecular assembly, and crystalline materials. For example, multipore covalent organic framework (COF) materials constructed by DBA monomer units in the solid state were highly fluorescent because of the coplanar arrangement of DBA units.13-15 A series of DBA[18] derivatives have been investigated for self-assembly at the liquid-solid interface by scanning tunneling microscope, which displayed highly ordered 2D molecular networks with alkyl chain interdigitation patterns.¹⁶ Apparently, efficient and lamella spatial arrangements of the π -electron-conjugated molecules into well-defined nanometer-scaled structures of functional materials would dramatically enhance their inherent properties. Liquid-crystalline ordering offers the possibility of constructing well-organized π -conjugated materials.^{17–19}



Figure 1 The molecular structures of graphdiyne and the graphdiyne-derived liquid crystal molecule reported in this work.

As it is well known, liquid crystals (LCs) are an exceptional class of engineered molecular materials that can effectively control the self-assembly of π -conjugated units to obtain functional architectures.^{20,21} In particular, discotic LCs are able to spontaneously stack π -conjugated molecules into highly ordered periodic columns and then aggregate into 2D lattices through non-covalent interactions that can provide significant nanochannels for effective charge mobility, ion transportation,

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separation, filtration, adsorption and so on.^{22,23} However to our surprise, the incorporation of GDY substructure DBA[18] into discotic LCs has never been reported in literature before.

Here, we designed and synthesized a discotic LC material (named as GDYLC12) derived from the planar π -conjugated DBA[18]-core macrocyclic molecule, as shown in Figure 1. To arrange the DBA[18] core into a discotic LC, six wedge-shaped 3,4,5-tris(dodecyloxy)benzoate groups bearing 18 terminal alkoxy side chains were introduced in the building block core. The synthesis, mesomorphic property, optical behavior and electrochemical performances of GDYLC12 are investigated and described in this manuscript.



Scheme 1. Synthetic route of the dodecadehydrotribenzo[18]annulene-core discotic liquid crystal GDYLC12.

The synthetic route of the DBA[18]-core discotic LC molecule GDYLC12 is schematically illustrated in Scheme 1. The production of the target GDYLC12 started with a diiodination of 1,2-dimethoxybenzene with iodine and periodic acid in methanol to provide 1,2-diiodo-4,5-dimethoxybenzene (1),¹³ which was further engaged in a demethylation reaction through a BBr₃ activation to yield 1,2-dihydroxy-4,5diiodobenzene (2). Protection of the hydroxyl groups of compound 2 by using 3,4-dihydro-2H-pyran provided the intermediate 3. Palladium-catalyzed cross-coupling of the resulting diiodide 3 with (trimethylsilyl)acetylene (TMSA) proceeded smoothly at 50 °C to yield silyl-protected diethynyl arene 4, which was directly subjected to a deprotection of the trimethylsilyl group, affording the free diyne 5. In order to construct the DBA[18] framework, the key intermediate 6 was synthesized in a modest yield (22 %) through a cyclotrimerization reaction¹³ of the compound **5** catalyzed by cupric acetate monohydrate and pyridine in methanol and ether at 60 °C. Deprotection of the tetrahydropyranyl group of the compound 6 provided the DBA[18]-core 7. A substitution reaction of methyl gallate with 1-bromododecane and potassium carbonate in DMF offered 3,4,5tris(dodecyloxy)methyl benzoate (8), which was then engaged hydrolysis reaction produce 3,4,5in а to tris(dodecyloxy)benzoic acid (9) and further transformed into

3,4,5-tris(dodecyloxy)benzoyl chloride (**10**). The Art desired discotic molecule GDYLC12 (**11**) was Successfully of the parely through an esterification reaction of the compound **7** with acyl chloride **10** in presence of trimethylamine at 40 °C.





thermotropic liquid crystalline properties The and mesomorphic structure of DBA[18]-core molecule GDYLC12 were investigated by utilization of polarized optical microscopy differential scanning calorimetry (DSC), (POM). and temperature-varied small- and wide-angle X-ray scattering (SAXS-WAXS) measurements. Thermal stability of GDYLC12 was characterized using thermogravimetric analysis (TGA) under N2 atmosphere, the initial thermal decomposition temperatures (T_d, 5 % weight loss) of GDYLC12 was ca. 341 °C (Figure S25), which demonstrated a good thermal stability over a broad temperature range. Under POM observation (Figure 2a), GDYLC12 exhibited a room-temperature dendritic-like growth aggregates upon cooling from the isotropic melt, which was the characteristic of thermotropic columnar mesophase. The X-ray diffractogram of GDYLC12 showed three reflections in the small-angle region at 15 °C (Figure 2d), which consisted of a sharp scattering peak at *d*-spacing of 35.2 Å, and two weak peaks at d-spacing of 20.2 Å, 17.5 Å. The above peaks were assigned to 100, 110 and 200 signals respectively, with a relative d-spacing ratio of 1: $\sqrt{3}$: 2, which revealed the characteristic reflections of hexagonal columnar (Col_b) phase, with a lattice constant a = 40.6 Å. Furthermore, the liquid like packing of peripheral aliphatic alkoxy chains were confirmed by a broad halo at 4.4 Å in the wide-angle region. When GDYLC12 was cooled to below -10 °C, the birefringent texture vanished as shown in Figure S31 and Video S1, implying that an optically isotropic cubic phase might appear at low temperature.²⁴⁻²⁸ Moreover, the X-ray diffractogram was significantly different, a sharp scattering peak at 35.5 Å and four weak peaks at 24.3 Å, 20.5 Å, 17.7 Å, 15.8 Å were observed at -10 °C. A relative *d*-spacing ratio of 1: $\sqrt{2}$: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{5}$, was indexed to the pattern of the cubic (Cub) phase with a

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Pm3m lattice.^{29–32} As illustrated in Figure 2b, the DSC diagram of GDYLC12 manifested two enantiotropic phase transitions, corresponding to a Cub-to-Col_h transition around –6 °C and a Col_h-to-isotropic transition around 42.7 °C upon heating process. On the cooling process, a relatively large hysteresis of Col_h-to-isotropic phase transition was observed, which was attributed to the high viscosity of discotic LC molecule.^{33,34} The proposed packing models for the Cub and Col_h phases are shown in Figure S32. Overall, the above measurement results confirmed that the GDY-derived discotic mesogen GDYLC12 had a broad range of liquid crystalline phase and could retain its mesophase even at very low temperature.

UV-Vis absorbance and fluorescence of the discotic mesogen GDYLC12 were investigated in both solution and spin-coated thin film. As illustrated in Figure 3a, the UV-Vis spectrum of GDYLC12 solution showed a short wavelength absorption band with two peaks at around 317 and 339 nm. This absorption band was ascribed to π - π * transition localized on the DBA[18] core. The long wavelength absorption band showed two peaks at around 367 nm and 377 nm, which was assigned to $n-\pi^*$ transition derived from the alkoxyphenyl fragments. The fluorescence spectrum of GDYLC12 showed an emission band centered at 434 nm with a shoulder peak at 422 nm. A large stokes shift of 95 nm was observed for this LC molecule in solution. It should be noted that GDYLC12 emitted a dark blue fluorescence in dilute solution upon excitation at 365 nm UV light as shown in Figure 3a (inset), the absolute fluorescence quantum yield (Φ_F) was ca. 78.7 % (conc. = 1.0 X 10⁻⁵ mol/L). UV-Vis absorption spectra of the spin-coated GDYLC12 thin film showed a similar curve shape at varied temperatures (Figure 3b), although the relative absorbance gradually increased along with the temperature rising from -20 °C to 60 °C.



Figure 3. (a) UV-Vis and fluorescence spectra (λ_{ex} = 350 nm) collected from GDYLC12 in chloroform solution (conc. = 1.0×10^{-5} mol/L) at room temperature. Inset: fluorescent image of GDYLC12 solution taken under 365 nm UV illumination. (b) UV-Vis spectra of the spin-coated thin film of GDYLC12 measured at different temperatures. Inset: absorbance at 384 nm of (b).

Figure 4 depicted temperature-dependent fluorescence emission of the spin-coated GDYLC12 thin film in three distinct states (Cub phase, Col_h phase and isotropic phase). As demonstrated in Figure 4b, in the cubic phase below -6 °C, the maximum emission wavelength appeared at ca. 439 nm and showed no distinct change as the temperature elevated. Next, in the Col_h phase centered at 20 °C, the emission spectrum had a significant red shift (λ_{max} = 499 nm) compared to that in the Cub phase. As the temperature was elevated further to the isotropic liquid phase (above 42.7 °C), the emission maximum of GDYLC12 was blue-shifted and appeared at 440 nm (Figure 4c). These varied emission wavelengths were related to the

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mesophase-regulated molecular stacking structures to The stacking variation was confirmed by temperature dependent X-ray scattering experiment, which exhibited the varied diffraction peaks in the small-angle region (1° ~ 5°) and the obvious diffraction peak shift in the wide-angle region (12° ~ 17°) in the temperature range from 15 °C to −10 °C (Figure 2d). Hence, the remarkable red shift may be attributed to the molecular arrangement alteration during the phase transition from Cub phase to Col_h phase.^{35–37} Compared with the condensed intracolumnar packing in Col_h phase, the unconsolidated stacking of aromatic cores in both the optically isotropic Cub phase and the isotropic phase resulted in the lesser interchromophoric π - π interactions, which induced strong blue-shifted emission. Therefore, the fluorescence color could be tuned via altering the temperature/phase-dependent molecular stacking structures. Some typical images of GDYLC12 thin film upon heating from the Cub phase to the isotropic state were provided in Figure 4a. Under UV light of 365 nm wavelength, the green light emission at 20 °C in the ordered Col_h columnar phase was in striking contrast to the pale blue emission at -20 °C in the Cub phase and the azure light appeared at 60 °C in the isotropic liquid phase, respectively. As expected, the CIE chromaticity diagram showed the analogously luminescent color changes of GDYLC12 thin film at -20 °C, 20 °C and 60 °C (Figure S33). Overall, a remarkable phase-dependent photoluminescence behavior of the GDY-derived LC molecule was modulated by the temperature-regulated intracolumnar stacking variation.



Figure 4. (a) Fluorescence images of GDYLC12 thin film under 365 nm UV illumination at -20 °C (left), 20 °C (middle) and 60 °C (right) respectively. Fluorescence spectra (λ_{ex} = 350 nm) of the spin-coated GDYLC12 thin film from (b) -20 to 20 °C, and (c) 20 to 60 °C.

The existence of intracolumnar stacking interactions was further confirmed by the corresponding fluorescence decay profiles, the decay lifetime in solid state about 10.48 ns for GDYLC12 was found to be higher than that in dilute chloroform (ca. 1.78 ns) at room temperature (Figure S35,36). The restricted intramolecular motions and effective π -electronic delocalization determined the relatively slow deactivation process in solid state. In addition, a reduced fluorescence lifetime in organic solvent may be caused by the non-radiative deactivation process, which derived from the intramolecular motion of a flexible structural component.

Electrochemical properties of GDYLC12 were investigated by cyclic voltammetry (CV) experiments employing the classical

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three-electrode method, and the detailed protocols are depicted in the Supporting Information (Figure S39). Reversible oxidation and reduction potentials of GDYLC12 were approximately 0.11 V and -1.19 V in the range of $-2.0 \approx 2.0$ V, while those of compound ${\bf 7}$ were approximately 0.20 V and -1.06 V. The energy levels of the highest and lowest occupied molecular orbital (HOMO and LUMO) were calculated, according to the formulae $E_{HOMO} = - (E_{onset}^{ox} - E_{Fc/Fc+} + 4.8) eV$, E_{LUMO} = - ($E_{onset}{}^{red}$ - E $_{Fc/Fc+}$ + 4.8) eV and ΔE_{caled} = E_{LUMO} - $E_{HOMO}.{}^{38,39}$ The HOMO and LUMO energy values of GDYLC12 were found to be -4.80 eV and -3.50 eV with an optical band gap of 1.30 eV, while HOMO and LUMO energy values of compound 7 were found to be about -4.89 eV and -3.63 eV with an optical band gap of 1.26 eV. Hence, the experimental results indicated that GDYLC12 possessed a narrow optical band gap. Compared with compound 7, GDYLC12 exhibited an enhanced HOMO and LUMO energy level, and a slightly broader energy band gap, which was ascribed to the larger conjugation system of GDYLC12.

In conclusion, we reported a C_3 -symmetric GDY-core discotic LC molecule bearing six symmetrical wedge-shaped 3,4,5tris(dodecyloxy)benzoate groups with 18 flexible alkyl chains. This mesogen can self-assemble into cubic and hexagonal columnar microstructures over a broad temperature range, and possesses superior luminescence property and low optical band gap energy. Most significantly, this GDY-derived discotic LC material displays а tunable phase-dependent photoluminescence behavior, which have potential applications in optoelectronic functional materials. We hope that this work would bring a new perspective for the development and application of GDY-derived materials.

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