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Synthesis and study of hybrid hydrogen-bonded bent-core liquid crystal complexes containing C_{60}- and Si-based proton donors†

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Novel hydrogen-bonded (H-bonded) C_{60}- and Si-based bent-core liquid crystal (LC) complexes containing a bent-shape proton acceptor and C_{60}- and Si-based single/double armed proton donors were synthesized and mingled to produce hybrid H-bonded LC complexes. The SmCP phases were able to be introduced in the hybrid LC complexes with a very high C_{60}-based moiety up to 90 mol%. Among our H-bonded LC complexes, the hybrid LC complexes with low contents of the C_{60}-based moiety (≤ 24 mol%) possessed the highest spontaneous polarization value (ca. 494 nC/cm²), the widest mesophase range (40.8°C) and the lowest saturated electric field (8.8 Vpp/μm). Under electric fields of modified triangle waveforms, both series of hybrid H-bonded LC complexes displayed an anti-ferroelectric (AF) to a ferroelectric (FE) polar switching as the C_{60}-based moiety increased up to 24-50 mol%. Therefore, the hybrid H-bonded LC complexes containing a broad molar ratio (0-90 mol%) of C_{60}-based moiety revealed a tunable route for the electro-optical applications of C_{60}-based H-bonded liquid crystals.

Introduction

Buckyball (also named as buckminsterfullerene or [60]fullerene) is a structure of truncated icosahedron with formula C_{60}, which was first synthesized by Kroto et al. in 1985. The buckyball structure displays various special properties, such as observable wave-particle duality, superconductivity, non-linear optical property and high electronic affinity. Moreover, with proper surface modification, its derivatives showed extensive applications, e.g., hydration, hydrogenation, halogenation, oxygenation, cycloadition, free radical reaction, photoreaction, endohedral metallofullerenes, catalyst, biomedical sensor/therapy and electron acceptor. The arrangements of charge transporting materials (e.g., buckyballs) were drawn much attention recently due to the improving of charge transfer in molecular electronics. By attaching to mesogens, [60]fullerene could be aligned via liquid crystalline mesophases, and the methods were luxuriant (including some cost-effective ways) to enhance the arrangements of buckyballs. With the advantages of easy manipulating and flexible ratio-control (also reported as an effective conduit for charge transfer), hydrogen-bonds (H-bonds) were our aim to be introduced to the C_{60}-based liquid crystal (LC) systems. The electro-optical properties of fullerene-based LCs have been determined in the smectic and columnar phases, accompanied with the molecular arrangements as well as the orientations of π-conjugated cores in mesophases to provide essential information for practical appearances. However, the electro-optical performance of C_{60}-based LCs are rare, especially for those with H-bonds. Therefore, the combination of H-bonding, bent-core LCs, and fullerenes in this study are required for further investigations on their mesomorphic and electro-optical aspects. However, to our best knowledge, no hybrid H-bonded C_{60}-based liquid crystals have been synthesized up to date, which may be resulted from the weak H-bonding between donor and acceptors as well the strong aggregation of C_{60} nanoparticles (NPs) to disturb the arrangements of mesogens. Therefore, an efficient blending method was applied to induce and stabilize the mesophases of H-bonded C_{60}-based LCs in our research. Moreover, LCs with ferro- and anti-ferroelectricities were utilized to reinforce the control of the applied electric fields as well as strengthen the photovoltaic effect on charge transporting materials. According to the previous research of Ros et al., covalent-bonded bent-core LCs based on [60]fullerene displayed broad ranges of SmCP phases and novel physical properties. Hence, as shown in Figs. 1 and 2,
Various H-bonded C60-based bent-core complexes, i.e., FIA100 and FIIA100 (analogue IIA100 without C60 as a comparison), were synthesized and investigated in this study, where a bent-shaped proton acceptor NBF14 and the corresponding proton donors FIA, FIA and IIA were prepared. In addition, the previously reported H-bonded Si-based bent-core complex FIIA100 containing the proton donor SiA was utilized as a LC host to mix with Au-based covalent bent-core dopant in order to facilitate the smectic alignment of Au-nanoparticles by electric fields. Furthermore, the Si-based bent-core LC complex FIIA100 in this survey was also mingled with both H-bonded C60-based bent-core complexes FIA100 and FIIA100 to induce and even extend the mesophase ranges of the hybrid H-bonded bent-core LCs.

Notably, with a minor molar ratio of SiA100 (i.e., 10 mol%), the hybrid H-bonded bent-core LC complex containing both Si-based FIIA100 and C60-based FIA100 were able to display SmCP phases, and the electro-optical as well as mesomorphic properties could be manipulated and optimized via the blending ratio of the Si- and C60-based complexes, which could be more easily controlled than the covalent-bonded C60-based LC systems.

Experimental

Synthesis. Synthetic steps of components FIA, FIIA, IIA, SiA and NBF14 are shown in Scheme S1 in the Supporting Information. Chemical characterization data of FIA, FIIA, IIA, SiA and NBF14 are provided below:

4-(12-(4-(1-methylfulleropyrroolidin-2-yl)phenoxo)dodecyloxy)benzoic acid, (FIA). 1H NMR (300 MHz, CDCl3) δ (ppm): 8.00 (d, J = 9.0 Hz, 2H), 7.40 (m, 4H), 6.88 (d, 2H), 4.96 (d, J = 9.0 Hz, 1H), 4.87 (s, 1H), 4.22 (d, J = 9.0 Hz, 1H), 4.01-3.92 (m, 4H), 2.78 (s, 3H), 1.75 (m, 4H), 1.36-1.23 (m, 16H). 13C NMR (75 MHz, CDCl3) δ (ppm) = 26.26, 29.38, 29.84, 30.60, 34.49, 40.29, 66.61, 68.23, 68.48, 70.22, 114.37, 114.81, 122.50, 124.73, 128.35, 128.95, 136.08, 139.83, 140.16, 140.41, 141.79, 141.94, 142.08, 142.25, 143.4, 144.65, 144.87, 144.97, 145.39, 145.5, 145.59, 145.76, 146.03, 146.46, 146.55, 147.07, 147.32, 147.55, 159.44, 163.32, 166.49. Anal. Calcd for C41H32N03Si: C, 90.01; H, 2.86; N, 0.99. MS (FAB- m/z): 1173.3 (exact mass); found, 1174.6.

Fig. 1 Molecular structures of proton donors FIA, FIIA, IIA and IIA as well as a proton acceptor NBF14.

Fig. 2 (a) H-bonded bent-core complexes FIA100, FIIA100, SI100 and IIA100; (b) hybrid LC complexes FIA50 and FIIA50 containing 50% molar ratio of SI100 and 50% molar ratio of FIA100 and FIIA100, respectively.
Sample preparation. The H-bonded complexes were prepared by dissolving proton acceptor NBF14 and proton donors FIA, FIAA, SIA or IIA with equimolar amounts of pyridyl and benzoic acid groups in anhydrous tetrahydrofuran (THF). After each LC mixture was slowly evaporated at room temperature, the THF was completely removed in vacuum for 24 h, and then the hybrid LC complexes were obtained.

Characterization. $^1$H and $^{13}$C NMR spectra were verified with Varian Unity 300 MHz spectrometer. Mass spectra and elemental analyses were determined with Micromass TRIO-2000 GC-MS and Perkin-Elmer 240C elemental analyzer, respectively. MALDI-TOF measurements were carried out on AutoFlex III MALDI mass spectrometer (Bruker Daltonics, Germany). Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer Spectrum 100 Series with pressed KBr pellets. Mesophase patterns, enthalpies of mesophase transitions and X-ray diffraction (XRD) were measured with polarized optical microscope (POM, Leica DMLP; equipped with a hot stage, Linkam TMS-94/LET350), differential scanning calorimeter (DSC, Perkin Elmer Diamond; rate 5°C/min of heating or cooling) and synchrotron X-ray radiation (at beamlines BL13A1, BL17A1 and BL01C2 at National Synchrotron Radiation Research Center, NSRRC, Taiwan), respectively. Typical X-ray scattering patterns were obtained with detectors (marCCD165 or mar345 image plates) for 1 to 30 seconds. The scattering angles were calibrated with two standard samples of silver benenate and silicon with beam diameter 0.5 mm for the 10-keV beam ($\lambda = 0.124$ nm$^{-1}$). The electro-optical properties were measured with prepared samples injected in commercially non-rubbed indium-tin-oxide (ITO) cells (mesophase state; thickness 9 μm; active area 0.25 cm$^2$). With a digital oscilloscope (Tektronix TDS-3012B) connected to a high-power amplifier (Gwinstek) and a function generator (Tektronix AFG 3021), measurements of spontaneous polarization were made with a modified triangular-wave method at a frequency of 50 Hz (see Fig. S1 in the Supporting Information).$

69.62; H, 10.05. MS (m/z) 378.26 (exact mass); found, 378 (M$^+$).

Results and discussion

Molecular Structures and Phase Behavior of Synthesized Complexes. As shown in Fig. 2a, single-armed H-bonded bent-core complexes FIA100 and SIA100$^{41}$ are composed of proton donor FIA (or SIA) and acceptor NBF14 with 1:1 molar ratio; while double-armed H-bonded bent-core complexes FIA100 and IIA100 consist of proton donor FIA (or IIA) and acceptor NBF14 with 1:2 molar ratio. The existence of H-bonded in the mesophases can be proved by temperature-variant FTIR spectroscopy (see the Supporting Information). Among these H-bonded bent-core complexes, upon cooling only SIA100 and IIA100 processed the smectic CP (SmCP) and smectic C (SmC) phases, respectively. However, the C$_{60}$-based H-bonded bent-core complexes FIA100 and FIA100 did not display any mesophases in contrast to their C$_{60}$-based covalent-bonded analogues,$^{37}$ while the mesophases were hindered by the stronger aggregation tendency of C$_{60}$ with weaker H-bonds in the H-bonded complexes (i.e., FIA100 and FIA100). Therefore, SIA100 was introduced to the H-bonded C$_{60}$-based bent-core complexes (FIA100 and FIA100) to extend the mesophase ranges of the hybrid H-bonded bent-core complexes. As illustrated in Fig. 2b, binary complex FIA50 was prepared from FIA, SIA and NBF14 with 1:1:2 molar ratio and binary complex FIA50 was produced by FIA, SIA and NBF14 with 1:2:4 molar ratio. In general, binary complexes FIAx and FIAx were denoted as x % molar ratio of C$_{60}$-based bent-core proton donor (i.e., $x = 4, 24, 50, 76, 90$ and $100$). For example, since a double-armed proton donor FIA bearing two --COONBF$_4$ functional groups would be H-bonded with two pyridyl moieties of proton acceptor NBF$_14$ (see Fig. 2b and Table S1 of the Supporting Information). In addition, the relationship for x values and weight percents (wt%) of C$_{60}$-based bent-core complexes are also presented in Table S1 in order to compare with our previous research.$^{41}$ As shown in Table 1 and Fig. 3, the broadest mesophase ranges (upon cooling) of binary complexes FIAx and FIAx were both extended from 33.4°C (SIA100) to 40.8 (at $x = 24$) and 37.6°C (at $x = 50$), respectively. The POM images of typical broken-fan textures of the SmCP phase for $x = 24$ were shown in Fig. S2 of the Supporting Information.

The single-armed binary complexes FIAx displayed lower crystallization temperatures (SmCP-Cr) than their double-armed analogues FIAx, which could be attributed to the colligative property of C$_{60}$-based complexes. Notably, although most binary complexes possessed monotropic mesophase, only binary complexes FIA90 and FIA90 containing a very high content of C$_{60}$-based H-bonded bent-core complexes demonstrated narrow mesophase temperature ranges 11.4 and 10.8°C, respectively (see Fig. 3b). Importantly, higher uptake loads of C$_{60}$-based component can be blended into the binary complexes FIAx and FIAx (i.e., $x = 50, 76$ and 90 without phase separation) than our previous Au-based covalent-bonded bent-core dopant (phase separation occurred at larger than 20 wt%) in SIA100. Therefore, an effective hybrid method for high contents of H-bonded C$_{60}$-based bent-core complexes was introduced in this study. In addition, by increasing the content of C$_{60}$-based moiety to moderate values, the polarity of the SmCP phase varied sequentially from antiferroelectricity to ferroelectricity in the binary complexes FIAx and FIAx (at $x = 24 ~ 50$, see Fig. 3, which was also discussed in the section "Electro-Optical Properties").
Molecular structures based on X-ray analysis. In order to decipher the molecular structures of the C₄₀-based bent-core complexes, FIAx and FIIAx were probed with powder XRD measurements (see Table S2 of the Supporting Information). The C₄₀-based bent-core complexes FIAx and FIIAx possess one set of sharp peaks in small angle and broad diffuse scattering signals in wide angle regions indicating a smectic lamellar order of uniformly mixed systems coupled with similar orders of lateral intermolecular distances, respectively (e.g., x = 50 shown in Figs. 4a-4c). Sharp peaks indexed as (01) in the small-angle region at the associated d-spacing values of d₁ with 46 ~ 50 Å for hybrid complexes FIAx and FIIAx, which were shorter than the calculated molecular lengths of FIA100 FIIAx and SIA100 (MM+ method, 65 ~ 76 Å) indicating the existence of tilted angles examined in bent-core hybrid complexes (see Table S2). Furthermore, no interdigitated structures are revealed due to the observation of one set ordered diffraction pattern only, and d-spacing values of FIAx and FIIAx in Fig. 4c reflected a sequentially descending intensity from (01) to (02) and (03), which indicated simple monolayer organizations instead of C₄₀ aggregation-induced bilayer structures with the strongest intensity indexed at (02). Both hybrid complexes FIAx and FIIAx possessed similar mesophases of SmCP because of the monolayer structure, rather than a bilayer structure induced by the competitions between Si-based nanosegregations and H-bonding.

![Fig. 4 Proposed molecular orders and XRD patterns of (a) FIA50 and (b) FIIAx as well as (c) both 1-D XRD integrations; (d) the d-spacing values of FIAx (black), FIIAx (white) and SIA100 (gray) at T = T_{iso-SmCP} - 10°C upon cooling.](image)

The d-spacing values of hybrid complexes FIAx and FIIAx with same x values were almost the same, except for x = 90 with the largest d-spacing difference possibly due to different measured temperatures (see Fig. 4d and Table 1). Therefore, inferred from the monolayer structures characterized by the XRD measurements of FIAx and FIIAx, the decreased d-spacing...
value of SmCP with increasing $C_{60}$ molar ratio might be mainly attributed to the reduced measured temperature in each hybrid complex, which also suggested that no NP-induced nanosegregations occurred in FIAx and FIIAx.

**Electro-Optical Properties.** The electro-optical properties were investigated from the saturated spontaneous polarization ($P_s$) values obtained via non-rubbed ITO-sandwiched cells to avoid the influence of polyimide layers to ferroelectricity. Under electric fields of modified triangle waveforms, both FIAx and FIIAx displayed an anti-ferroelectric (AF) to a ferroelectric (FE) polar switching as $C_{60}$ increased. The responsive current signals at the zero-voltage position declined and even vanished as the molar ratio of $C_{60}$-based moiety with $x \geq 50$ (see the orange rectangle area marked in Figs. 5a-5b), indicating a ferroelectric polar switching, where the SmCP range was maximized at $x = 24$ (see Table 1). According to the previous research, bent-core complexes processed anti-ferroelectric polar switching behavior due to the easy-stacking of bent-shaped molecules with anti-ferroelectric order from neighboring layers, but the anti-polar packing could be diminished via NPs aggregated at the smectic layer interfaces. Hence, the switching from anti-ferroelectric to ferroelectric polar order along with $C_{60}$ ratio can be realized from the aggregation of NPs at the interfaces of smectic layers. The trends of $P_s$ values and the saturated $P_s$ values at certain electric fields of hybrid complexes FIAx and FIIAx are described in Fig. S7. As shown in Fig. Sc, as the $C_{60}$-based moiety increased, both $P_s$ values of hybrid complexes FIAx and FIIAx increased to be saturated at minor $C_{60}$ doped ranges of $x = 4 \sim 24$, which are higher than $0.356$ nC/cm$^2$ of SIA100 (at $x = 0$) and reached the largest $P_s$ values of 494 and 490 nC/cm$^2$ (both at $x = 4$) for FIAx and FIIAx series, respectively. In addition, the $P_s$ values of FIAx and FIIAx dropped continuously to become smaller at higher $C_{60}$ doped ranges of $x = 50 \sim 90$. Similarly, in contrast to FIIAx with the same x values, FIAx (at $x \geq 24$) possessed lower $P_s$ values due to higher $C_{60}$-based moieties. The minor doping effect of $C_{60}$-based moiety on promoted $P_s$ values could be attributed to the reinforced separation of induced dipoles by the NP dopants under electric fields. The saturated electric field ($E_{sat}$) was defined as the electric field at 90% of saturated $P_s$ values (see Fig. S3 of the Supporting Information), and the lowest $E_{sat}$ values of FIAx and FIIAx series were obtained at 8.8 and 12.0 Vpp/μm for FIA4 and FIIA24, respectively (see Fig. Sd), which were possibly due to the easy driving tendencies of the decreased packing order in the mesophases with minor $C_{60}$-based contents. By further increasing the ratio of $C_{60}$-based moiety, the field induced dipole reorientation was restricted by higher viscosities of the mesophases with higher $C_{60}$-based contents and led to low $P_s$ values and high $E_{sat}$ values. Notably, the saturated $P_s$ value of SIA100 decayed to half values for FIAx and FIIAx series at relatively high ratios of $C_{60}$-based moiety, i.e., FIAx at $x \geq 76$ (i.e., 84 wt%, see Table S1), and FIIAx at $x \geq 90$ (i.e., 92 wt%), which happened in our previous report on Au-based LC composite at 5 wt% of NPs (a relatively low ratio of surface-modified Au NPs). Moreover, in contrast to a low wt% (5 wt%) of surface-modified Au NPs in the previous Au-based LC composite, the AF-FE switching behavior happened at a higher content of surface-modified C60 (x = 50, i.e., 63 wt% and 56 wt% for FIAx and FIIAx, respectively) in both hybrid LC complexes. Finally, unlike the phase separation induced in the previous Au-based LC composite containing ~ 20 wt% content of surface-modified Au NPs, much higher contents of surface-modified C60 still could be miscible in both FIAx and FIIAx series at x = 90 (i.e., 94 and 92 wt%, respectively), which could be useful to utilize hybrid LC complexes with high contents of surface-modified C60. Therefore, the anti-ferroelectric (AF) to a ferroelectric (FE) polar switching behavior as well as optimized $P_s$ and $E_{sat}$ values could be introduced by adjusting the contents of surface-modified C60 in the hybrid LC complexes.

**Conclusion**

Single- and double-armed $C_{60}$-based H-bonded bent-core complexes (FIA100 and FIIA100) were mixed with Si-based H-bonded bent-core LC SIA100 successfully to induce ferroelectric and anti-ferroelectric mesophases, where the hybrid $C_{60}$-based H-bonded LC complexes are synthesized and reported for the first time. Adjusting various molar ratios of surfacemodified $C_{60}$ in the hybrid H-bonded bent-core LC complexes, the transition temperatures and ranges of the SmCP phases could be reduced and extended, respectively. Compared with Au-based LC composites, much higher contents of surface-modified C60 could be miscible in both...
hybrid LC complexes FIAx and FIIAx series at x = 90 (i.e., 94 and 92 wt%, respectively). The anti-ferroelectric (AF) to a ferroelectric (FE) polar switching behavior occurred in the hybrid LC complexes with moderate molar ratios of C80-based moiety. The electro-optical properties, such as Pₘ and Eₘₘ values, could be manipulated and optimized via the blending ratio of the Si- and C80-based complexes, which could be more easily controlled than the covalent-bonded C80-based LC systems.

Acknowledgements

The financial support of this project is provided by the Ministry of Science and Technology (MOST) in Taiwan through MOST 103-2113-M-009-018-MY3 and 103-2221-E-009-215-MY3. We also thank Drs. Ming-Tao Lee and Hwo-Shuen Sheu for the assistance of measuring XRD at 13A1 and 01C2 in National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

References and notes
