Chirality-Enabled Liquid Crystalline Physical Gels with High Modulus but Low Driving Voltage

Huan Ruan,[†] Guannan Chen,[†] Xiaoyu Zhao,[†] Yong Wang,[†][®] Yonggui Liao,[†][®] Haiyan Peng,^{*,†}[®] Chuan-Liang Feng,[‡][®] Xiaolin Xie,^{*,†}[®] and Ivan I. Smalyukh^{§,||}[®]

[†]Key Lab for Material Chemistry of Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

 ‡ School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, China

[§]Department of Physics and Materials Science and Engineering Program, University of Colorado at Boulder (CUB), Boulder, Colorado 80309, United States

^{II}Sino-US Joint Research Center on Liquid Crystal Chemistry and Physics, HUST and CUB, Wuhan 430074, China

Supporting Information

ACS APPLIED MATERIALS

& INTERFACES

ABSTRACT: Self-supporting liquid crystalline physical gels with facile electro-optic response are highly desirable, but their development is challenging because both the storage modulus and driving voltage increase simultaneously with gelator loading. Herein, we report liquid crystalline physical gels with high modulus but low driving voltage. This behavior is enabled by chirality transfer from the molecular level to three-dimensional fibrous networks during the self-assembly of 1,4-benzenedicarboxamide phenylalanine derivatives. Interestingly, the critical gel concentration is as low as 0.1 wt %. Our findings open doors to understanding and exploiting the role of chirality in organic gels.



KEYWORDS: chirality, liquid crystal, physical gel, high modulus, low driving voltage

1. INTRODUCTION

Supramolecular gels, an important class of soft materials, are comprised of intertwined three-dimensional (3D) solid networks within a fluidic surrounding host.¹⁻⁵ Typically, the 3D networks are formed by gelators that are first homogeneously dissolved or dispersed in a solvent at high temperature and then cooled down to fix the shape and microstructure.⁶ The solvent can be either organic or inorganic.^{7,8} As a common inorganic solvent, water has been used for a long time to form hydrogels for meeting the mechanical and biocompatibility requirements in bio-applications (e.g., cell cultivation and tissue engineering).9-15 Hydrogels are easy to form because water usually mediates the 3D network formation via hydrogen bonding.¹⁶ Gel formation in organic solvent is also common but often more challenging.¹⁷ A strong intermolecular interaction among gelator molecules is a basic prerequisite for robust gels.¹ Too strong interactions between the gelator and solvent produce sol rather than gel, whereas with too week interactions the gelator cannot homogeneously dissolve in the solvent.^{19,20} In addition, it is also challenging to enable added functions to an organic gel.

Since the Kato's seminal work on the nematic liquidcrystalline (LC) physical gels,²¹ gels with anisotropic organic solvent have sparked a great deal of attention.²² Because of the thermosensitive anisotropic characteristic of the fluidic liquid crystals (LCs),23-27 and the soft noncovalent bonding of gel networks,⁶ both order-disorder and sol-gel phase transitions can be readily observed in LC physical gels.¹⁸ Thus, it is possible to realize quick response of LC physical gels to electric field,²⁸ light,^{29,30} heat,³¹ magnetic field,³² and so forth. In addition, LC physical gels promise applications in large-area, ultra-thin, flexible LC displays, where mechanical robustness and facile electro-optic responses are needed.³³ Cooling methods,³⁴ solvent polarity,³⁵ metal ions,³⁶ gelator substitutes,³⁷ alignment conditions^{38,39} and other factors show remarkable influences on the microstructure and performance of LC physical gels. Thus, constant efforts have been devoted to boost the mechanical resistance or to lower down the driving voltage of LC physical gels. For instance, Nair and coworkers described that the monodisperse chiral peptide gelator was able to afford organogels with an excellent elasticity and fast response.⁴⁰ Chen and co-workers realized a highperformance light scattering display by adding a relatively

Received: August 22, 2018 Accepted: November 13, 2018 Published: November 13, 2018



Figure 1. (a) Chemical structures of LPF, DPF, and 5CB. (b) LC gels with 0.5 wt % LPF (i), 0.5 wt % DPF (ii), and suspension with 0.5 wt % racemate (LPF and DPF in a 1:1 mol ratio, iii). Golden ellipses represent the LC molecules while the helical wires signify the gelator assemblies.

small amount (<0.5 wt %) of POSS gelator into the LC host.⁴¹ Interestingly, this gel was able to exhibit good optical performance even when stretched up to 145%. Yamamoto and co-workers also prepared a polydivinylbenzene microparticle/LC composite gel, and disclosed its outstanding selfsupporting and repetitive recovery capabilities.⁴² Wood and co-workers realized "self-quenchable defect glass" with high modulus by dispersing polymethylmethacrylate microspheres in 4-pentyl-4'-cyanobiphenyl (5CB).43 Yet, despite the amazing progress in the development of LC physical gels, obtaining high modulus while maintaining low driving voltage still remains a grand challenge. This hurdle arises because a large amount of gelators are generally required to define the mechanical toughness to a LC physical gel, but the increase of gelator loading prompts increased driving voltage due to the increased area of interfaces.

Recently, chirality has drawn special attention in hydrogels and LCs to enable attractive structures and unique functions.^{9–12,44–49} For instance, molecular chiral gelators are able to self-assemble into chiral nanohelix with strong supramolecular chirality.²⁰ More importantly, the nanohelix is capable of further transferring chirality and excited energy to an achiral acceptor, giving rise to amplified chirality in the gels and greatly enhanced circularly polarized luminescence. In addition, it has been reported that cells adhere more tightly and grow faster in the L-type hydrogels than in the D-type hydrogels, demonstrating the great significance of chirality.¹⁰ Comprehensive reviews by Liu and colleagues have summarized the effect of chirality on the supermolecular gel behavior, including chiral recognition, chiral amplification, chiral separation, chiral inversion, and so forth. 50-52 Yet, the chirality effect on LC physical gel properties is rarely considered. Herein, inspired by the chirality-amplified optical functions from Liu's group, we hypothesized that a robust LC physical gel with high storage modulus but low driving voltage could be enabled by employing chiral gelators. To demonstrate a proof of concept, the 1,4-benzenedicarboxamide phenylalanine derivatives were employed as the gelators,⁹⁻¹¹ and 5CB was used as the LC host medium. The chemical structures of the chosen enantiomers [e.g., left-handed 1,4-benzenedicarboxamide phenylalanine derivative (LPF) and right-handed 1,4benzenedicarboxamide phenylalanine derivative (DPF)] and LC are shown in Figure 1a. Interestingly, both LPF and DPF are able to mediate LC physical gels, independently, but their racemate fails to do so (Figure 1b). The chiral gel networks are self-assemblies of LPF or DPF molecules primarily driven by

intermolecular hydrogen bonding and $\pi - \pi$ stacking.^{16,53,54} Up to 10⁴ Pa of storage modulus and as low as 0.5 V/ μ m of threshold driving voltage were achieved simultaneously in the new chiral LC gels. Our chiral LC physical gels open a door to utilizing the chirality effects in organic gel media.

2. EXPERIMENTAL SECTION

2.1. Materials. The nematic LC (i.e., 5CB) was purchased from Shijiazhuang Chengzhi Yonghua Display Material Co., Ltd., China. No further purification was conducted before use.

2.2. Synthesis of Gelators (e.g., LPF and DPF). Gelators were synthesized according to the previously reported procedures.⁹

2.3. Preparation of LC Physical Gels. Gelators (0.5-2.5 mg) were initially added into transparent capped vials, followed by the addition of LC 5CB (0.5 g) in each vial. Upon heating to 150 °C, the gelators were completely dissolved in the isotropic 5CB. The hot solution was cooled down to 25 °C under the ambient condition, giving rise to uniform LC physical gels. The critical gel concentration (CGC) of both enantiomers (e.g., LPF and DPF) was determined to be 0.1 wt %.

2.4. Differential Scanning Calorimetry. The phase transition behavior of LC physical gels was recorded using differential scanning calorimetry (DSC) (Q2000, TA Instruments, USA). Gels (2 mg) were added into an aluminum liquid pan that was then placed on the DSC sample holder. Another empty aluminum pan was used as the reference. Following this, they were heated from zero to 150 °C at a ramp rate of 10 °C·min⁻¹ under the N₂ gas atmosphere. After being isothermally kept at 150 °C for 3 min, the sample was cooled down to 0 °C with the identical ramp rate. The phase transition temperature and enthalpy were recorded during cooling. The sol–gel phase transition was determined using the falling-ball method.⁵⁵

2.5. Rheology Measurement. The viscoelasticity of LC physical gels was characterized on a rheometer (MCR 302, Anton Paar, Austria) that was equipped with a controlled thermal stage. Before measurement, gels were reshaped in a thickness of 0.5 mm between two parallel circular plates (PP25), by heating to 150 °C and subsequently cooling to 25 °C. Shearing on gels was performed within the linear viscoelastic region after allowing to stand for 10 min. During the dynamic strain sweep, angular frequency $\omega = 10$ rad·s⁻¹ and strain $\gamma = 0.01-100\%$, whereas in the dynamic frequency sweep, the parameters were: strain $\gamma = 0.05\%$ and $\omega = 0.1-100$ rad·s⁻¹.

2.6. Scanning Electron Microscopy. Microstructures and morphologies of LC physical gels were observed by field emission scanning electron microscopy (SEM) (Sirion 200, FEI Corp., The Netherlands) with an accelerating voltage of 10 or 15 kV. To improve the image contrast, the LC was removed away by *n*-hexane. In general, LC gels were heated into their solution state and dropped on a clean silicon wafer, followed by completely cooling down to room temperature and immersing in *n*-hexane for 48 h. Finally, xerogels were dried in air and sputtered with a thin layer of platinum on their top surfaces for SEM characterization.



Figure 2. (a) CD signals of LPF (black) and DPF (red) in ethanol with a concentration of 2×10^{-3} M. No gel was formed. (b) CD signals of LPF gel (black), DPF gel (red), and racemate (blue) in 5CB with a content of 0.5 wt % for each. (c) Schematic illustration on the chirality transfer mechanism of LC physical gels (the golden ellipses represent LC molecules).

2.7. Circular Dichroism. Circular dichroism (CD) spectra were collected using a JASCO J-815CD spectrometer with a resolution of 1.0 nm. Prior to characterization, LC gels were heated to the solution state and then transferred into square quartz cells with an inner gap thickness of 2 mm. To collect the CD spectra of LPF and DPF molecules, 0.5 mg of their powders were dissolved in 0.5 mL of ethanol and then transferred into a quartz cell (inner gap: 1 mm), respectively.

2.8. Electro-Optic Characterization. The electro-optic performance of LC physical gels was analyzed on a LC display parameter tester (LCT-5016C, North LC Engineering Research and Development Centre, China). A halogen lamp was used as the light source. Characterization was performed in the transmission mode and 1 kHz AC electric field was applied to drive the device. Prior to measurement, LC gels were heated into the solution state and then added into LC cells with indium tin oxide coating on the inner surface (cell gap: 10 μ m). This process was implemented through capillary action. After cooling down to 25 °C, the LC gel device was ready for measurement. During characterization, most of the incident light was scattered in the absence of electric field while going through the LC gel device when the electric field exceeded the Frederiks threshold. The threshold voltage $(V_{\rm th})$ and saturated voltage $(V_{\rm sat})$ referred to the voltages applied on the device when the transmittance reached 10% and 90% of the normalized maximum transmittance, respectively. Meanwhile, the contrast ratio (CR) was defined as $CR = 10 \log \left(\frac{TE_{max}}{TE_{min}}\right)$, where TE_{max} was the maximum transmittance while TE_{min} was the minimum transmittance.⁵⁶ The rise time τ_{on} and decay time au_{off} under the electric field were defined as the duration required to reach 90% and 10% of the normalized maximum

transmittance, respectively, upon applying and removing the electric field.

3. RESULTS AND DISCUSSION

3.1. Gelation Capability of LPF and DPF in 5CB. An LC gel is a soft matter system in which fluidic LC is interpenetrated by a 3D nonfluidic solid network. The threshold loading is referred as CGC. A gelator shows a high gelation capability if possessing a low CGC. Hereto, the reported CGC in LC gels is higher than 0.15 wt %.37 In addition, a storage modulus of more than 10⁴ Pa is regarded to be the value required to enable the self-supporting capability in a gel.⁴³ Thus, a high gelator loading of more than 1.0 wt % is usually needed in those LC gels to meet the mechanical requirements because of their relatively low gelation capability. In a LC physical gel, a high loading of the gelator generally prompts a high driving voltage. It is challenging to lower down the CGC by improving the gelation capability in a LC gel. Fortunately, chirality-induced helical stacking has been disclosed to be able to lower down the configurational energy.^{57,58} Interestingly, both LPF and DPF, with a strong chirality,⁹ realize LC gels with a low CGC of 0.1 wt %. The CGC value is much smaller than that of many other gelators.³² To further demonstrate the proof of concept, chiral LPF, DPF and achiral racemate (e.g., LPF and DPF in a 1:1 mol ratio) were loaded in the LC 5CB with a gelator concentration of 0.5 wt %. As displayed in Figure 1b, both LPF and DPF are able to generate stable LC gels, while no gel can be formed with their



Figure 3. SEM images of (a) xerogel with 0.5 wt % LPF, (b) xerogel with 0.5 wt % DPF, and (c) solid fiber with 0.5 wt % racemate (e.g., LPF and DPF in a 1:1 mol ratio). LCs were removed by *n*-hexane prior to SEM characterization.



Figure 4. DSC curves upon cooling of (a) LPF gels and (b) DPF gels with different gelator contents. T_{IN} signifies the isotropic-nematic phase transition temperature.

racemate. Only a suspension is obtained with the racemate. The result indicates the importance of chirality to enable a remarkable gelation capability, as reported previously.⁵⁹ Notably, it is a different story in hydrogels. The same racemate composed of 1,4-benzenedicarboxamide phenylalanine derivatives is able to form hydrogels.¹⁰ It is easy to understand that, in a hydrogel, both water and gelators participate in the physical network via intermolecular hydrogen-bonding.¹⁶ Neither LPF nor DPF generates hydrogen bonding with the hydrophobic SCB.²¹

3.2. Chirality of LPF and DPF Gels. To get a deeper understanding on the chirality of LC gels, CD characterization was conducted. As displayed in Figure 2a, both LPF and DPF dissolved in ethanol exhibit clear CD signals, indicating remarkable chirality. The LPF molecules show positive peak absorption at 219 nm, whereas negative peak absorption at 243 nm. By contrast, the DPF molecules show similar peak absorptions at the same wavelengths, but in opposite directions. The negative and positive cotton effects for LPF and DPF, respectively, are supposed to be induced by the $\pi - \pi$ stacking of phenyl chromophores.⁵⁹ Interestingly, a red shift of \sim 100 nm on the peak absorptions is noted when LC gels are formed with LPF and DPF (Figure 2b). In addition, the peak absorption intensity at 352 nm becomes 100 times larger than that at 320 nm. The results indicate that the chirality has transferred from the molecular level to macrostructures during the self-assembling process, and chiral amplification occurs synchronously. A possible chiral transfer and amplification mechanism during the self-assembly process is illustrated in Figure 2c. Notably, no CD signal is detectable in the racemic system (e.g., LPF and DPF in a 1:1 mol ratio). The results show that, during the self-sorting process of a racemate, the two enantiomers are assembled alternatively. The result is consistent with the fact that the heterochiral interactions of LPF and DPF are stronger than those of homochiral ones.^{60,61}

3.3. Microstructures of LPF and DPF Gels. To show clear evidence to the chiral structures of LC gels, SEM studies were implemented. To enhance the image contrast, the LC was removed away by n-hexane from the LC gels prior to characterization, leaving xerogels. Clearly, there exist tangled self-assembled helical fibers in the chiral gels (Figure 3a,b). Particularly, the LPF fibers spiral clockwise while DPF fibers spiral counterclockwise because of their distinct chirality of LPF and DPF.⁹ In addition, the diameter of DPF fibers (e.g., 55 nm) appears to be nearly twice larger than that of LPF fibers (e.g., 28 nm). To understand why there is a diameter difference, we studied the purity of LPF and DPF using proton nuclear magnetic resonance spectroscopy (¹H NMR) and polarimetry. ¹H NMR spectra indicate no chemical shift difference between LPF and DPF (Figures S1 and S2 in the Supporting Information). The specific rotation (α) value of LPF and DPF is measured to be -980° and $+964^{\circ}$ (Figure S3 in the Supporting Information), respectively, indicating a similar optical purity for LPF and DPF. Because DPF is found to be much easier to be dissolved in 5CB, in compassion with LPF, we speculate that the solubility difference is a plausible reason for the diameter difference of the fibrous network. Thicker fibers are expected to result in stronger mechanical performance to LC gels, which may further influence the phase transition, rheological behaviors, and electro-optic performance.⁶² In contrast, neither 3D fiber networks nor spiral structures are observed in the racemate system (Figure 3c), which is in good agreement with the CD results. Moreover, cholesteric fingerprint texture and phase are observed in the LC gels at a high loading of gelators (Figure S4 in the Supporting Information), which is believed to be another reason for the gel global chirality.

3.4. Phase Diagram of Chiral LC Physical Gels. During the formation of LC physical gels, there are two independent thermo-reversible phase transitions, that is, isotropic-nematic transition and sol-gel transition. A phase diagram based on

DSC analysis describes these behaviors. As displayed in Figure 4, when cooling down the LC gels from 150 to 0 °C, only one exothermal peak at 33 °C is observed, for both LPF and DPF gels, regardless of their content (e.g., from 0.1 to 0.5 wt %) in 5CB. This phase transition is ascribed to the isotropic–nematic transition of 5CB. Interestingly, the change of phase transition enthalpy (e.g., ~4.3 J/g) is negligible when varying the gelator loading from 0.1 to 0.5 wt %, indicating a small effect of confinement of the fibrous gel network on the LC order parameter. This weak confinement is envisioned to offer a low driving voltage. Notably, no sol–gel transition is detected by DSC, probably because of the low content of gelator. Sol–gel transition is usually clear in DSC with a high gelator loading,³⁷ yet only under 0.5 wt % of LPF or DPF can be completely dissolved in 5CB.

To characterize the sol-gel phase transition, further study using the falling-ball method was implemented.^{55,63} As shown in Figure 5, the temperature of sol-gel phase transition (T_{SG})



Figure 5. Phase diagram of LPF/5CB and DPF/5CB LC gels.

is much higher than that of isotropic-nematic transition $(T_{\rm IN})$. The phase diagram indicates a consecutive phase transition from isotropic liquid to isotropic gel and then to nematic gel upon cooling. In addition, distinct from the gelator-

independent $T_{\rm IN}$, the $T_{\rm SG}$ continuously increases from ~100 to ~140 °C with the augmentation of gelator content from 0.1 to 0.5 wt %. The high value of $T_{\rm SG}$ indicates a good thermal stability. The $T_{\rm SG}$ of DPF is always slightly higher than that of LPF, implying a subtle higher gelation capability of DPF. This observation is in good accordance with the thicker DPF fiber in 3D networks (Figure 3).

3.5. Dynamic Rheological Behaviors of LPF and DPF LC Physical Gels. Gels provide a mechanical support to the fluidic LCs, which is expected to enable flexible LC devices. Mechanical resistance of LC gels to external forces can be easily characterized by dynamic rheological shearing. In general, dynamic frequency sweep within the linear viscoelastic region at 25 °C was exerted. As shown in Figure 6, the addition of LPF and DPF facilitates the formation of LC gels. These gels hold a nearly one order of magnitude higher storage modulus (G') than loss modulus (G''). Both G' and G''continuously increase with an augmentation of gelator content from 0.1 to 0.5 wt %. Interestingly, up to 10⁴ Pa of storage modulus is obtained when loading 0.5 wt % DPF, which is much higher than that of many other gels at the same loading concentration.⁴⁰ The outstanding mechanical performance with a storage modulus higher than 10⁴ Pa promises good mechanical properties to LC gels.⁴³

As well accepted,³⁷ the storage modulus of a gel increases with an increase of gelator content, and eventually levels off. The relation can be quantitatively described by a sigmoidal curve with Gompertz function⁶⁴

$$G' = G'_{s} e^{-e^{-k(c-c_{0})}}$$
(1)

where the $G'_{\rm S}$ is the saturated modulus, c_0 stands for the inflection point, and k signifies a constant. Interestingly, with good nonlinearly overlaid fits over the experimental data, 2.1 × 10⁴ and 2.8 × 10⁴ Pa of $G'_{\rm S}$ for LPF and DPF gels, respectively, and an identical c_0 of 0.5 wt % for both LPF and DPF LC gels are obtained. The results indicate that both LPF and DPF gels



Figure 6. Frequency sweep curves of LC gels with different gelator contents: (a) storage modulus (G') and (c) loss modulus (G'') for LPF/5CB gels, (b) storage modulus and (d) loss modulus for DPF/5CB gels.



Figure 7. Threshold voltage (V_{th}) and saturated voltages (V_{sat}) of LC physical gels with (a) LPF and (b) DPF, and response time under the electric field of LC physical gels with (c) LPF and (d) DPF, respectively. An alternative current (ac) voltage at a frequency of 1 kHz was used to drive the LC devices. The peak-to-peak amplitude was 100 V when driving LC gels, whereas it was 50 V when driving the pure 5CB.

are potentially able to reach the saturation platform at a higher gelator loading. However, more gelators cannot be dissolved in 5CB.

3.6. Electro-Optic Properties of LC Physical Gels with LPF and DPF. Because the LC is immobilized by the gel network with tiny interfacial confinement, LC physical gels display significant potential for low-voltage electro-optic display in the light-scattering mode. As displayed in Figure 7, LC gels with both LPF and DPF exhibit high contrast electrooptic switching between the light scattering (field-off) and light transmission (field-on) states. The former is caused by the refractive index mismatch between LC droplets and the fibrillar network, whereas the latter results from the uniform LC orientation along the electric field. For the gels with 0.1 to 0.5 wt % of LPF or DPF, the threshold voltage $(V_{\rm th})$ and saturated voltage (V_{sat}) increase slightly with the gelator content (Table 1). In addition, the switch-on time (τ_{on}) and switch-off time (au_{off}) of these LC gels are longer than those of LC gels with 1,3:2,4-di-O-benzylidene-D-sorbitol.³⁷ However, the responsive time of the gels has a tendency to reduce as the gelator content

Table 1. Electro-Optic Properties of LPF and DPF LC Physical Gels

gelator type	content (wt %)	$V_{ m th} \ ({ m V} \cdot \mu { m m}^{-1})$	$V_{\rm sat}$ (V· μ m ⁻¹)	CR	$ au_{ m on} \ (m ms)$	${ au_{ m off} \over (m ms)}$
LPF	0.1	0.4	2.9	6.6	4.0	432
LPF	0.2	0.5	3.0	8.3	4.5	418
LPF	0.3	0.6	3.7	10.6	4.5	380
LPF	0.4	0.5	3.5	11.1	4.0	340
LPF	0.5	0.5	3.6	11.8	4.5	287
DPF	0.1	0.4	2.9	7.7	4.5	390
DPF	0.2	0.5	2.9	8.4	4.5	369
DPF	0.3	0.6	3.5	9.4	4.0	330
DPF	0.4	0.6	4.7	10.1	4.5	287
DPF	0.5	0.5	4.3	11.2	5.0	233

increases. The anchoring energies between the network and LCs play a crucial role in the electro-optic performance of LC gels. The thicker nanofibers result in larger anchoring energies, giving rise to the higher driving voltage and faster switch-off response. As aforementioned, the gelation capability of both LPF and DPF is so strong that our gels can still have a very high modulus even at a very low gelator concentration. Lower content of gelator provides few interfaces and lower anchoring energy, and thus affording a lower driving voltage. Clearly, the mechanical performance of LC gels with LPF or DPF is superior in comparison with other reported LC gels at the same loading,³⁷ and the driving voltage is much lower than that of other gels with similar mechanical performance.

4. CONCLUSIONS

Two types of LC chiral physical gels were formulated with enantiomers (e.g., LPF and DPF, respectively). Both LPF and DPF enabled robust LC gels at a low gelator loading (e.g., 0.1-0.5 wt %). In addition, the DPF was found to form thicker fibrous structures than LPF at the same concentration, which contributed to a slightly higher thermodynamic stability and mechanical resistance. As high as 10⁴ Pa of storage modulus while as low as 0.5 V/ μ m of threshold driving voltage were obtained at a loading of 0.5 wt % of DPF. Chiral structures were found to be significant to form these LC gels with high modulus but low driving voltage, and the racemate with half LPF and half DPF was not able to afford any LC gels. Our chiral LC gels with high mechanical performance but low driving voltage promise low-voltage flexible display. This research may also provide a framework for understanding the fundamental structure-property relation based on chiral materials.

ACS Applied Materials & Interfaces

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b14488.

¹H-NMR spectrum of LPF in DMSO-d₆, ¹H-NMR spectrum of DPF in DMSO-d₆, specific rotation (α) value of LPF and DPF, and POM images of LC gels with LPF and DPF, respectively, at 25 °C (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: hypeng@hust.edu.cn (H.P.). *E-mail: xlxie@hust.edu.cn (X.X.).

ORCID 6

Yong Wang: 0000-0003-4704-5436 Yonggui Liao: 0000-0003-2943-1501 Haiyan Peng: 0000-0002-0083-8589 Chuan-Liang Feng: 0000-0001-6137-5568

Xiaolin Xie: 0000-0001-5097-7416

Ivan I. Smalyukh: 0000-0003-3444-1966

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge support from the NSFC (51433002, 51503045 and 51773073), the NSF of Hubei Scientific Committee (2016CFA001), the Fundamental Research Funds for the Central Universities (2017KFYXJJ165, 2015ZDTD005), and the technical support from the HUST Analytical and Testing Center. I.I.S. acknowledges support of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award ER46921, contract DE-SC0010305 with the University of Colorado Boulder.

REFERENCES

(1) Liu, Q.; Smalyukh, I. I. Liquid Crystalline Cellulose-Based Nematogels. Sci. Adv. 2017, 3, No. e1700981.

(2) Ji, X.; Wu, R.-T.; Long, L.; Guo, C.; Khashab, N. M.; Huang, F.; Sessler, J. L. Physical Removal of Anions from Aqueous Media by Means of a Macrocycle-Containing Polymeric Network. J. Am. Chem. Soc. 2018, 140, 2777-2780.

(3) Yan, X.; Cook, T. R.; Pollock, J. B.; Wei, P.; Zhang, Y.; Yu, Y.; Huang, F.; Stang, P. J. Responsive Supramolecular Polymer Metallogel Constructed by Orthogonal Coordination-Driven Self-Assembly and Host/Guest Interactions. J. Am. Chem. Soc. 2014, 136, 4460-4463.

(4) Ji, X.; Shi, B.; Wang, H.; Xia, D.; Jie, K.; Wu, Z. L.; Huang, F. Supramolecular Construction of Multifluorescent Gels: Interfacial Assembly of Discrete Fluorescent Gels through Multiple Hydrogen Bonding. Adv. Mater. 2015, 27, 8062-8066.

(5) Yan, X.; Xu, D.; Chi, X.; Chen, J.; Dong, S.; Ding, X.; Yu, Y.; Huang, F. A Multiresponsive, Shape-Persistent, and Elastic Supramolecular Polymer Network Gel Constructed by Orthogonal Self-Assembly. Adv. Mater. 2012, 24, 362-369.

(6) Kato, T.; Hirai, Y.; Nakaso, S.; Moriyama, M. Liquid-Crystalline Physical Gels. Chem. Soc. Rev. 2007, 36, 1857-1867.

(7) Kato, T. Self-Assembly of Phase-Segregated Liquid Crystal Structures. Science 2002, 295, 2414-2418.

(8) Kouwer, P. H. J.; Koepf, M.; Le Sage, V. A. A.; Jaspers, M.; van Buul, A. M.; Eksteen-Akeroyd, Z. H.; Woltinge, T.; Schwartz, E.; Kitto, H. J.; Hoogenboom, R.; Picken, S. J.; Nolte, R. J. M.; Mendes,

E.; Rowan, A. E. Responsive Biomimetic Networks from Polyisocyanopeptide Hydrogels. Nature 2013, 493, 651-655.

(9) Liu, G.-F.; Zhu, L.-Y.; Ji, W.; Feng, C.-L.; Wei, Z.-X. Inversion of the Supramolecular Chirality of Nanofibrous Structures through Co-Assembly with Achiral Molecules. Angew. Chem., Int. Ed. 2016, 55, 2411-2415.

(10) Liu, G.-F.; Zhang, D.; Feng, C.-L. Control of Three-Dimensional Cell Adhesion by the Chirality of Nanofibers in Hydrogels. Angew. Chem., Int. Ed. 2014, 53, 7789-7793.

(11) Liu, G.-F.; Ji, W.; Wang, W.-L.; Feng, C.-L. Multiresponsive Hydrogel Coassembled from Phenylalanine and Azobenzene Derivatives as 3D Scaffolds for Photoguiding Cell Adhesion and Release. ACS Appl. Mater. Interfaces 2015, 7, 301-307.

(12) Dou, X.-Q.; Feng, C.-L. Amino Acids and Peptide-Based Supramolecular Hydrogels for Three-Dimensional Cell Culture. Adv. Mater. 2017, 29, 1604062.

(13) Sano, K.; Ishida, Y.; Aida, T. Synthesis of Anisotropic Hydrogels and Their Applications. Angew. Chem., Int. Ed. 2018, 57, 2532-2543.

(14) Wang, W.; Zhang, Y.; Liu, W. Bioinspired Fabrication of High Strength Hydrogels from Non-Covalent Interactions. Prog. Polym. Sci. 2017, 71, 1-25.

(15) Rosales, A. M.; Vega, S. L.; DelRio, F. W.; Burdick, J. A.; Anseth, K. S. Hydrogels with Reversible Mechanics to Probe Dynamic Cell Microenvironments. Angew. Chem., Int. Ed. 2017, 56, 12132-12136.

(16) Liu, G.; Li, X.; Sheng, J.; Li, P.-Z.; Ong, W. K.; Phua, S. Z. F.; Ågren, H.; Zhu, L.; Zhao, Y. Helicity Inversion of Supramolecular Hydrogels Induced by Achiral Substituents. ACS Nano 2017, 11, 11880-11889.

(17) Jiang, H.; Zhang, L.; Chen, J.; Liu, M. Hierarchical Self-Assembly of a Porphyrin into Chiral Macroscopic Flowers with Superhydrophobic and Enantioselective Property. ACS Nano 2017, 11, 12453-12460.

(18) Kato, T.; Mizoshita, N.; Kishimoto, K. Functional Liquid-Crystalline Assemblies: Self-Organized Soft Materials. Angew. Chem., Int. Ed. 2006, 45, 38-68.

(19) Sun, Y.; Li, S.; Zhou, Z.; Saha, M. L.; Datta, S.; Zhang, M.; Yan, X.; Tian, D.; Wang, H.; Wang, L.; Li, X.; Liu, M.; Li, H.; Stang, P. J. Alanine-Based Chiral Metallogels via Supramolecular Coordination Complex Platforms: Metallogelation Induced Chirality Transfer. J. Am. Chem. Soc. 2018, 140, 3257-3263.

(20) Yang, D.; Duan, P. F.; Zhang, L.; Liu, M. H. Chirality and Energy Transfer Amplified Circularly Polarized Luminescence in Composite Nanohelix. Nat. Commun. 2017, 8, 15727.

(21) Kato, T.; Kutsuna, T.; Hanabusa, K.; Ukon, M. Gelation of Room-Temperature Liquid Crystals by the Association of a Trans-1,2bis(amino)cyclohexane Derivative. Adv. Mater. 1998, 10, 606-608.

(22) van der Asdonk, P.; Kouwer, P. H. J. Liquid Crystal Templating as an Approach to Spatially and Temporally Organise Soft Matter. Chem. Soc. Rev. 2017, 46, 5935-5949.

(23) Chen, G.; Ni, M.; Peng, H.; Huang, F.; Liao, Y.; Wang, M.; Zhu, J.; Roy, V. A. L.; Xie, X. Photoinitiation and Inhibition under Monochromatic Green Light for Storage of Colored 3D Images in Holographic Polymer-Dispersed Liquid Crystals. ACS Appl. Mater. Interfaces 2017, 9, 1810-1819.

(24) Ni, M.; Chen, G.; Sun, H.; Peng, H.; Yang, Z.; Liao, Y.; Ye, Y.; Yang, Y.; Xie, X. Well-Structured Holographic Polymer Dispersed Liquid Crystals by Employing Acrylamide and Doping ZnS Nanoparticles. Mater. Chem. Front. 2017, 1, 294-303.

(25) Ni, M. L.; Peng, H. Y.; Xie, X. L. Structure Regulation and Performance of Holographic Polymer Dispersed Liquid Crystals. Acta Polym. Sin. 2017, 10, 1557-1573.

(26) Peng, H.; Bi, S.; Ni, M.; Xie, X.; Liao, Y.; Zhou, X.; Xue, Z.; Zhu, J.; Wei, Y.; Bowman, C. N.; Mai, Y.-W. Monochromatic Visible Light "Photoinitibitor": Janus-Faced Initiation and Inhibition for Storage of Colored 3D Images. J. Am. Chem. Soc. 2014, 136, 8855-8858.

ACS Applied Materials & Interfaces

(27) Peng, H.; Chen, G.; Ni, M.; Yan, Y.; Zhuang, J.; Roy, V. A. L.; Li, R. K. Y.; Xie, X. Classical Photopolymerization Kinetics, Exceptional Gelation, and Improved Diffraction Efficiency and Driving Voltage in Scaffolding Morphological H-PDLCs Afforded Using a Photoinitibitor. *Polym. Chem.* **2015**, *6*, 8259–8269.

(28) Zhao, Y.; Tong, X. Light-Induced Reorganization in Self-Assembled Liquid Crystal Gels: Electrically Switchable Diffraction Gratings. *Adv. Mater.* **2003**, *15*, 1431–1435.

(29) Zhao, D.; Ouyang, D.; Jiang, M.; Liao, Y.; Peng, H.; Xie, X. Photomodulated Electro-Optical Response in Self-Supporting Liquid Crystalline Physical Gels. *Langmuir* **2018**, *34*, 7519–7526.

(30) Moriyama, M.; Mizoshita, N.; Yokota, T.; Kishimoto, K.; Kato, T. Photoresponsive Anisotropic Soft Solids: Liquid-Crystalline Physical Gels Based on a Chiral Photochromic Gelator. *Adv. Mater.* **2003**, *15*, 1335–1338.

(31) Yabuuchi, K.; Rowan, A. E.; Nolte, R. J. M.; Kato, T. Liquid-Crystalline Physical Gels: Self-Aggregation of a Gluconamide Derivative in Mesogenic Molecules for the Formation of Anisotropic Functional Composites. *Chem. Mater.* **2000**, *12*, 440–443.

(32) Kempe, M. D.; Scruggs, N. R.; Verduzco, R.; Lal, J.; Kornfield, J. A. Self-Assembled Liquid-Crystalline Gels Designed from the Bottom Up. *Nat. Mater.* **2004**, *3*, 177–182.

(33) Leaw, W. L.; Mamat, C. R.; Triwahyono, S.; Jalil, A. A.; Bidin, N. Liquid Crystal Physical Gel Formed by Cholesteryl Stearate for Light Scattering Display Material. *J. Colloid Interface Sci.* **2016**, *483*, 41–48.

(34) Abe, H.; Kikuchi, H.; Hanabusa, K.; Kato, T.; Kajiyama, T. Morphology Control of Liquid Crystalline Composite Gels Based on Molecular Self-Assembling Kinetics. *Mol. Cryst. Liq. Cryst.* **2003**, *399*, 1–15.

(35) Abe, H.; Kikuchi, H.; Hanabusa, K.; Kato, T.; Kajiyama, T. Improvement of Light Switching Contrast of Liquid Crystalline Composite Gel by Adding Polar Organic Solvent. *Mol. Cryst. Liq. Cryst.* **2003**, 399, 43–52.

(36) Cardinaels, T.; Hirai, Y.; Hanabusa, K.; Binnemans, K.; Kato, T. Europium(III)-Doped Liquid-Crystalline Physical Gels. *J. Mater. Chem.* **2010**, *20*, 8571–8574.

(37) Bi, S.; Peng, H.; Long, S.; Ni, M.; Liao, Y.; Yang, Y.; Xue, Z.; Xie, X. High Modulus and Low-Voltage Driving Nematic Liquid-Crystalline Physical Gels for Light-Scattering Displays. *Soft Matter* **2013**, *9*, 7718–7725.

(38) Mizoshita, N.; Hanabusa, K.; Kato, T. Self-Aggregation of an Amino Acid Derivative as a Route to Liquid-Crystalline Physical Gels - Faster Response to Electric Fields. *Adv. Mater.* **1999**, *11*, 392–394.

(39) Mizoshita, N.; Hanabusa, K.; Kato, T. Fast and High-Contrast Electro-Optical Switching of Liquid-Crystalline Physical Gels: Formation of Oriented Microphase-Separated Structures. *Adv. Funct. Mater.* **2003**, *13*, 313–317.

(40) Nair, G. G.; Prasad, S. K.; Bhargavi, R.; Jayalakshmi, V.; Shanker, G.; Yelamaggad, C. V. Soft Glass Rheology in Liquid Crystalline Gels Formed by a Monodisperse Dipeptide. *J. Phys. Chem.* B 2010, *114*, 697–704.

(41) Chen, S.; Luo, X.; He, H.; Tong, X.; Wu, B.; Ma, M.; Wang, X. Stretchable Light Scattering Display Based on Super Strong Liquid Crystalline Physical Gels with Special Loofah-Like 3D Gel Networks. *J. Mater. Chem. C* **2015**, *3*, 12026–12031.

(42) Yamamoto, T.; Yoshida, M. Viscoelastic and Photoresponsive Properties of Microparticle/Liquid-Crystal Composite Gels: Tunable Mechanical Strength Along with Rapid-Recovery Nature and Photochemical Surface Healing Using an Azobenzene Dopant. *Langmuir* **2012**, *28*, 8463–8469.

(43) Wood, T. A.; Lintuvuori, J. S.; Schofield, A. B.; Marenduzzo, D.; Poon, W. C. K. A Self-Quenched Defect Glass in a Colloid-Nematic Liquid Crystal Composite. *Science* **2011**, *334*, 79–83.

(44) Liu, G.; Sheng, J.; Wu, H.; Yang, C.; Yang, G.; Li, Y.; Ganguly, R.; Zhu, L.; Zhao, Y. Controlling Supramolecular Chirality of Two-Component Hydrogels by J- and H-Aggregation of Building Blocks. *J. Am. Chem. Soc.* **2018**, *140*, 6467–6473. (45) Liu, J.; Yuan, F.; Ma, X.; Auphedeous, D.-i. Y.; Zhao, C.; Liu, C.; Shen, C.; Feng, C. The Cooperative Effect of Both Molecular and Supramolecular Chirality on Cell Adhesion. *Angew. Chem., Int. Ed.* **2018**, *57*, 6475–6479.

(46) Wang, F.; Feng, C.-L. Metal-Ion-Mediated Supramolecular Chirality of L-Phenylalanine Based Hydrogels. *Angew. Chem., Int. Ed.* **2018**, *57*, 5655–5659.

(47) Qin, L.; Gu, W.; Wei, J.; Yu, Y. Piecewise Phototuning of Self-Organized Helical Superstructures. *Adv. Mater.* **2018**, *30*, 1704941.

(48) Li, J.; Zhang, Z.; Tian, J.; Li, G.; Wei, J.; Guo, J. Dicyanodistyrylbenzene-Based Chiral Fluorescence Photoswitches: An Emerging Class of Multifunctional Switches for Dual-Mode Phototunable Liquid Crystals. *Adv. Opt. Mater.* **2017**, *5*, 1700014.

(49) Zheng, Z.-g.; Li, Y.; Bisoyi, H. K.; Wang, L.; Bunning, T. J.; Li, Q. Three-Dimensional Control of the Helical Axis of a Chiral Nematic Liquid Crystal by Light. *Nature* **2016**, *531*, 352–356.

(50) Zhang, L.; Wang, T.; Shen, Z.; Liu, M. Chiral Nanoarchitectonics: Towards the Design, Self-Assembly, and Function of Nanoscale Chiral Twists and Helices. *Adv. Mater.* **2016**, *28*, 1044– 1059.

(51) Han, J.; You, J.; Li, X.; Duan, P.; Liu, M. Full-Color Tunable Circularly Polarized Luminescent Nanoassemblies of Achiral AIEgens in Confined Chiral Nanotubes. *Adv. Mater.* **2017**, *29*, 1606503.

(52) Zhang, L.; Qin, L.; Wang, X.; Cao, H.; Liu, M. Supramolecular Chirality in Self-Assembled Soft Materials: Regulation of Chiral Nanostructures and Chiral Functions. *Adv. Mater.* **2014**, *26*, 6959– 6964.

(53) Feng, C.-L.; Dou, X.; Zhang, D.; Schönherr, H. A Highly Efficient Self-Assembly of Responsive C_2 -Cyclohexane-Derived Gelators. *Macromol. Rapid Commun.* **2012**, 33, 1535–1541.

(54) Dou, X.; Li, P.; Zhang, D.; Feng, C.-L. C_2 -Symmetric Benzene-Based Hydrogels with Unique Layered Structures for Controllable Organic Dye Adsorption. *Soft Matter* **2012**, *8*, 3231–3238.

(55) Cheng, W.; Zhao, D.; Qiu, Y.; Hu, H.; Wang, H.; Wang, Q.; Liao, Y.; Peng, H.; Xie, X. Robust Multi-Responsive Supramolecular Hydrogel Based on a Mono-Component Host-Guest Gelator. *Soft Matter* **2018**, *14*, 5213–5221.

(56) Liu, Y. J.; Sun, X. W.; Liu, J. H.; Dai, H. T.; Xu, K. S. A Polarization Insensitive 2x2 Optical Switch Fabricated by Liquid Crystal-Polymer Composite. *Appl. Phys. Lett.* **2005**, *86*, 041115.

(57) Zerrouki, D.; Baudry, J.; Pine, D.; Chaikin, P.; Bibette, J. Chiral Colloidal Clusters. *Nature* **2008**, *455*, 380–382.

(58) Rößler, U. K.; Bogdanov, A. N.; Pfleiderer, C. Spontaneous Skyrmion Ground States in Magnetic Metals. *Nature* **2006**, 442, 797– 801.

(59) Cao, H.; Zhu, X.; Liu, M. Self-Assembly of Racemic Alanine Derivatives: Unexpected Chiral Twist and Enhanced Capacity for the Discrimination of Chiral Species. *Angew. Chem., Int. Ed.* **2013**, *52*, 4122–4126.

(60) Smith, D. K. Lost in Translation? Chirality Effects in the Self-Assembly of Nanostructured Gel-Phase Materials. *Chem. Soc. Rev.* **2009**, *38*, 684–694.

(61) Jędrzejewska, H.; Szumna, A. Making a Right or Left Choice: Chiral Self-Sorting as a Tool for the Formation of Discrete Complex Structures. *Chem. Rev.* **201**7, *117*, 4863–4899.

(62) Mizoshita, N.; Suzuki, Y.; Kishimoto, K.; Hanabusa, K.; Kato, T. Electrooptical Properties of Liquid-Crystalline Physical Gels: A New Oligo(Amino Acid) Gelator for Light Scattering Display Materials. J. Mater. Chem. 2002, 12, 2197–2201.

(63) Lin, K.-Y.; Wang, D.-M.; Lai, J.-Y. Nonsolvent-Induced Gelation and Its Effect on Membrane Morphology. *Macromolecules* **2002**, *35*, 6697–6706.

(64) Krishnan, A. S.; Vargantwar, P. H.; Spontak, R. J. Thermorheological Behavior of Coexisting Physical Networks: Combining SAFIN and SAMIN Organogels. *Soft Matter* **2012**, *8*, 12025–12033.