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Preparation and Property Manipulation of High Efficiency Circularly Polarized Luminescent Liquid Crystal Polypeptides

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Circularly polarized luminescence (CPL) materials show great potential applications in asymmetric synthesis, chemical sensors, biological probes, 3D displays and other fields. However, the preparation of high efficiency circularly polarized luminescent materials with high solid fluorescence quantum yield and large glum value is still a challenge. This article creatively combines the construction strategy of CPL materials and side-chain chiral liquid crystal polymer materials to engineer a series of new CPL-active side-chain chiral liquid crystal polymers (named PGAC-m, m is the spacer length, m = 4, 6, 10). The chiral poly (L-glutamate) with α -helical secondary structure is devised as the backbone, and the cyanostilbene with aggregation-induced emission enhancement (AIEE) characteristics is applied as luminescent mesogen pendants, which is covalently linked to backbone by different spacer length. The phase structure and the photophysical properties of PGAC-m were characterized in detail. The experimental results show that PGAC-m can self-assemble to form lamellarordered chiral smectic C (SmC*) phase structure and show typical AIEE characteristics with high solid-state quantum yield. The chirality of polypeptides can be transferred to cyanostilbene, which makes PGAC-m emit circularly polarized light. Meanwhile, the chiral helix structure of PGAC-m can effectively enlarge the glum value, and therefore PGAC-m show high solid quantum yield and large g_{lum} value. Interestingly, the photophysical properties of PGAC-m can be regulated by changing the spacer length. The solid fluorescence quantum yield of PGAC-m decrease gradually with the increase of spacer length, while the gium value show the opposite change rule. The maximum solid fluorescence quantum yield and gium value of PGAC-m can achieve 34.1% and 4.5×10^{-2} , respectively.

Introduction

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Circularly polarized luminescence (CPL) refers to the phenomenon that chiral luminescent materials emit different left-handed and right-handed circularly polarized light. The study for CPL materials is conducive to reveal the excited state structure information of chiral luminescent materials, and look insight into the chirality generation, transfer and amplification mechanism.¹ Owing to the multifaceted promising applications, such as circularly polarized organic light-emitting diodes,² information security encryption,³ asymmetric synthesis,⁴ CPL switch⁵⁻⁸ and CPL sensing and probing, etc,⁹ CPL materials have become one of the research hotspots in the luminescence field. The luminescence dissymmetry factor (g_{lum}) and fluorescence quantum yield are important parameters for characterization of circularly polarized luminescent materials. The g_{lum} value is acquired by g_{lum} = 2 (I_L-I_R) / (I_L + I_R), where I_L and I_R are lefthanded and right-handed circularly polarized light intensity. In

order to promote real applications, the researchers are being devoted to develop CPL materials with high fluorescence quantum yield and large g_{lum} value.

Recently, considerable focuses have been attracted into organic CPL-active materials.¹⁰⁻¹² It is proved to be an effective strategy to integrate chiral structure into fluorescent molecules to construct organic CPL-active materials.¹³ From the perspective of molecular weight, organic CPL-active materials can be divided into small-molecule CPL-active organic materials and polymer-based CPL-active organic materials.¹² At present, small-molecule CPL organic materials have been widely studied and have harvested many excellent achievements.¹¹ Polymer-based CPL organic materials possess the inherent advantages of polymers and exhibit better processing capacity, film-forming performance as well as thermal stability, which dramatically expand the practical applications range of CPL materials.

Doping is an effective method to engender polymer-based organic CPL materials. The conventional approach is to embed achiral luminescent polymers guest into a chiral-nematic LC matrix¹⁴ or embed chiral dopants guest into achiral-nematic luminescent polymers matrix.¹⁵⁻¹⁷ The strong CPL signals can be induced by intermolecular interactions between achiral fluorescence polymers and chiral moieties. Compared with the host-guest doped polymer-based CPL materials, the organic CPL materials fabricated from non-doped chiral luminescent

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polymers are unnecessary to consider the troubles of stability and compatibility existing in doping systems, and thus it also acquires extensive researches. At present, the research on the non-doped organic CPL polymers is mainly focused on the chiral conjugated polymer.¹⁸⁻²² The conjugated polymer can inherently emit fluorescence, and the introduction of chiral building blocks into the conjugated polymers provides an effective avenue to generate CPL-active polymers. However, the majority of traditional rigid conjugated backbones only emit fluorescence in dilute solutions. The fluorescence intensity is greatly reduced or even unable to emit fluorescence when aggregate owing to aggregation-caused quenching (ACQ) effect, which is greatly restrict its application. Recently, relevant researches concerning CPL-active chiral conjugated polymers with AIE core have been gradually reported,²³⁻²⁷ which overcomes the luminescence quenching defects of traditional chiral conjugated polymers in solid state. In 2018, Tang and Li et al prepared a chiral conjugated polymer with the backbone composed of TPE and chiral alanine by azido-alkynyl click polymerization.27 The obtained polymer showed typical aggregation-induced CPL emission with a solidstate g_{lum} value of 4.5 \times 10^-3. At present, most of the reported g_{lum} value of chiral conjugated polymers is in the range about $10^{-5} \sim 10^{-3}$. It remains challenging to construct CPL-active polymer materials with larger glum value and higher solid fluorescence quantum yield.

Chiral liquid crystal is a kind of liquid crystal with spiralstacking phase structure,²⁸ which endows the chiral liquid crystal with unique photophysical properties, such as selective reflection, optical rotation, circular dichroism, etc.²⁹⁻³⁰ Meanwhile, the spiral structure formed by the self-assembly of chiral liquid crystal can achieve chiral amplification effect. Therefore, chiral liquid crystal is an ideal medium to generate CPL-active materials with high g_{lum} value. Relevant research results prove that chiral luminescent LC exhibits great advantages in the construction of CPL-active materials with high g_{lum} value. ^{5-6, 16, 31-34} At present, there are only a few kinds of non-doped CPL chiral liquid crystal polymers, which are low in solid fluorescence quantum yield and difficult to regulate in properties. Non-doped CPL chiral liquid crystal polymers with high solid quantum yield and large g_{lum} is rarely reported.

Based on the above fact, this article creatively combines the construction strategy of CPL-active materials and side-chain chiral liquid crystal polymer materials, and takes cyanostilbene with aggregation-induced emission enhancement (AIEE) characteristics as the luminescent mesogen,³⁵⁻⁴⁰ chiral poly (Lglutamate) with α -helical conformation⁴¹⁻⁴² as the backbone to prepare a novel CPL-active side-chain chiral liquid crystal polymers PGAC-m (the chemical structure is shown in Scheme 1, m is the spacer length). The chirality of polypeptides can be transferred to cyanostilbene, which makes PGAC-m emit circularly polarized light. The self-assembly process of chiral liquid crystal polymers is used to amplify the glum value. The AIEE property of cyanostilbene is used to avoid the fluorescence quenching of PGAC-m in solid state. Therefore, circularly polarized luminescent chiral liquid crystals with high solid quantum yield and large g_{lum} will be obtained. The



influence of spacer length on the aggregation structure and photophysical properties of PGAC-m will be also elucidated. This work unfolds a new insight to harvest non-doped CPL polymer materials with high solid quantum yield and large g_{lum} value, and also provides theoretical guidance for the preparation of new high-performance circularly polarized luminescent materials.

Experimental section

Materials

All including 4-hydroxyacetonitrile, reagents cyanobenzaldehyde, L-Glutamic acid (L-Glu), ethylenediamine tetraacetic acid (EDTA), triphosgene, triethylamine (TEA), tetramethyl guanidine, 1, 4-dibromobutane, 1. 6dibromotexaneand as well as 1, 10-dibromodecane were purchased from Aladdin Reagent Co. and utilized without further purification. Glu-Cu was prepared in our laboratory. THF was refined via sodium metal to remove trace amounts of water. DMF was dried with molecular sieve activated under high temperature before use. NaHCO₃, NaOH, copper acetate and the other solvents were commercially available from Aladdin Reagent Co.

Measurements and characterizations

Chemical structure and purity information of monomers MNCA-m and polymers PGAC-m were obtained by a Bruker ARX400 MHz spectrometer. The molecular weight of small molecule compound was measured by a Bruker Biflex III MALDI-TOF instrument. GPC 120 instrument was applied to measure the number-average molecular weight (Mn) and the molecular weight distribution (PDI) of PGAC-m using DMF as solvent. The flow rate is 1.0 mL min⁻¹ at 80 $^\circ \!\! \mathbb{C}$. Therom Scientific Nicolet 6700 FT-IR instrument was employed to monitor the conversion degree of monomers and preliminarily determine the spatial configuration of the PGAC-m. The decomposition temperature of PGAC-m were measured by a TGA Q50 under N₂ atmosphere with a scanning rate of 10 $^\circ\mathrm{C}$ min⁻¹. The liquid crystal textures of PGAC-m were observed by a Mettler FP82 polarizing microscope (POM) with a hot stage. The phase transition temperature of polymers PGAC-m was measured by a TA Q10 DSC with the scanning rate of 10 $^\circ \!\! C$ min⁻¹ during the heating and cooling process. The phase structure of polymers PGAC-m was confirmed by an Anton Paar SAXSess. The preparation process of PGAC-m test samples are described as follows: PGAC-m were heated to above their clear point temperature with a heating rate of 10 $^\circ \!\! \mathbb C$ min⁻¹, and then cooled to 30 $^\circ \! \mathbb{C}$ with a cooling rate of 5 $^\circ \! \mathbb{C}$ min⁻¹ to obtain the test samples. The UV-Vis absorption spectra of polymers PGAC-m were recorded on a Cary 100

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spectrophotometer instrument. The circular dichroism (CD) spectra were recorded by a JASCO J-810 spectrophotometer. The fluorescence spectra of polymers PGAC-m were measured by a PTI Qm40 fluorescence spectroscopy. Circularly polarized luminescence (CPL) tests were carried out on a JASCO CPL-300 instrument. The fluorescence quantum yields of PGAC-m in solid state were measured by FLS980 fluorescence spectroscopy with integral sphere. Zetasizer nano ZS90 particle size analyzer was applied to gauge the average particle size.

Preparation of monomers and polymers

The synthetic process of monomers MNCA-m and polymers PGAC-m with different spacer length (m = 4, 6, and 10) are shown in Fig.1. The specific synthetic methods and structural characterizations are elaborated by choosing MNCA-4 and PGAC-4 as representative. The synthetic methods of MNCA-4 and PGAC-4 are as follows.

of Synthesis of compound 1. blend 4-А hydroxyphenylacetonitrile (20.0 g, 0.15 mol), K₂CO₃ (62.3 g, 0.45 mol), catalytic amount of KI and 1, 4-dibromobutane (65.0 g, 0.31 mol) were dissolved in 250 mL acetone. The mixtures were heated to 70 $^\circ\!\mathrm{C}$ and stirred for 10 hours. When the reaction was almost complete, the insoluble solid was removed by suction filtration. The filtrate was evaporated by rotary evaporator to get crude product. The crude product was further purified by column chromatography using petroleum ether and CH_2Cl_2 (v : v = 1 : 1) as eluent to get the target product as a white solid (35.0 g). Yield: 87.5%. ¹H NMR (δ, ppm, CDCl₃): 7.23-7.21 (d, 2H, Ph-H); 6.90-6.87 (d, 2H, Ph-H); 3.97-3.94 (m, 2H, -OCH2-); 3.68 (s, 2H, -CH2CN); 3.45-3.41 (m, 2H, -CH₂Br); 1.92-1.76 (m, 4H, -CH₂-); Mass Spectrometry (MS) (m/z) [M] calcd for C₁₂H₁₄BrNO, 267.06; found 267.16.

Synthesis of compound 2. A round-bottomed flask (500 mL) were added with compound 1 (30.0 g, 0.12 mol), CH₃ONa (6.0 g, 0.11 mol) and 120 mL ethanol. 4-Cyanobenzaldehyde (14.6 g, 0.11 mol) was dissolved in 120 mL ethanol and then handed over into a 250 mL constant pressure drop funnel, which was slowly added into the round-bottomed flask. After that, the mixtures were stirred at room temperature for 3 hours. Abundant yellow solid powder precipitated out, and the precipitate was separated by suction filter and washed three times with ethanol. The precipitate was collected and dried in vacuum to gain the pure product with pale yellow solid (31.5 g). Yield: 69%. ¹ H NMR (δ, ppm, CDCl₃): 7.95-7.93 (d, 2H, Ph-H); 7.75-7.73 (d, 2H, Ph-H); 7.64-7.62 (d, 2H, Ph-H); 7.42 (s, 1H, -CH=); 6.98-6.95 (d, 2H, Ph-H); 4.05-4.02 (m, 2H, -OCH₂-); 3.51-3.49 (m, 2H, -CH₂-Br); 2.09-1.98 (m, 4H, -CH₂-); Mass Spectrometry (MS) (m/z) [M] calcd for $C_{20}H_{17}BrN_2O$, 380.05; found 380.16.

Synthesis of Glu-Cu. A mixture of L-Glu (14.7 g, 100 mmol) and 375 mL deionized water were added into a 1000 mL round-bottomed flask. The mixtures were stirred at 70 $^{\circ}$ C for 2 hours to obtain an uniform clear solution. Copper acetate (18.6 g, 103.0 mmol) was dissolved in a beaker containing 375 mL deionized water, and then was slowly added into the above-mentioned 1000 mL round-bottomed flask. After that, the reaction mixtures were stirred at room temperature for 48



hours. Lots of blue powder were gradually precipitated out and purified by suction filter. The filter cake was washed sequentially with deionized water, ethanol and ether, and then dried in vacuum to obtain the blue solid powder product (22 g). Yield: 91%.

Synthesis of compound 3. A mixture of Glu-Cu (2.3 g, 4.7 mmol), L-Glu (1.4 g, 9.5 mmol), 1.5 mL deionized water and 8 mL DMF were added into a 1000 mL round-bottomed flask. Tetramethyl guanidine (2.5 mL) was slowly added and then the mixtures were stirred at room temperature for 2 hours to obtain a blue clear solution. Compound 2 (7.6 g, 20 mmol) was dissolved in 30 mL DMF and poured into the blue clear solution. The mixture was heated at 40 $^{\circ}$ C for 48 hours in the dark. After that, 400 mL acetone was poured into the round-bottomed flask and stirred for 30 minutes to fully dissolve impurity. The insoluble was isolated via vacuum filter and added into a newly prepared EDTA disodium salt solution (3.6 g EDTA, 2.1 g NaHCO₃, 30 mL H₂O), which was stirred for 4 hours to fully remove copper. Finally, a yellow-green solid was obtained (4.5 g). Yield: 48%.

Synthesis of monomer MNCA-4. Compound 3 (2.0 g, 4.5 mmol), triphosgene (0.9 g, 3.0 mmol) and 120 mL refined THF were added into a 500 mL round-bottomed flask. The mixture was heated at 50 $^\circ\!\mathrm{C}$ for 24 hours. With the process of reaction, the reaction system gradually turned to a clear and transparent solution. After cooling, the mixture were slowly added into the dry n-hexane to give a yellow solid, which was then dissolved in a small amount of THF and further purified by column chromatography to give pure monomer MNCA-4 as a yellow solid (1.3 g). Yield: 65%. ¹H NMR (δ , ppm, CDCl₃): 7.98-7.95 (d, 2H, Ph-H); 7.81-7.79 (d, 2H, Ph-H); 7.66-7.63 (d, 2H, Ph-H); 7.46 (s, 1H, -CH=); 6.99-6.95 (d, 2H, Ph-H); 6.45 (s, 1H, -NH-); 4.41-4.38 (t, 1H, -CHNH-); 4.23-4.21 (m, 2H, -OCH₂-); 4.23-4.21 (m, 2H, -OCH₂-); 2.58-2.54 (m, 2H, -CH₂-); 2.27-2.12 (m, 2H, -CH₂-); 1.94-1.90 (m, 4H, -CH₂-); Mass Spectrometry (MS) (m/z) [M] calcd for C₂₆H₂₃N₃O₆, 473.18; found 473.13.

Synthesis of PGAC-4. The polymer PGAC-4 was obtained by ring opening polymerization of N-Carboxyanhydride (NCA) using TEA as the initiator. The specific operation steps were described as follows: MNCA-4 (0.5 g, 1.2 mmol), refined DMF

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(4 mL) and TEA (1.3 mg, 0.012 mmol) were successively added into a glass polymerization tube. The polymerization tube was frozen by liquid nitrogen and then was vacuumed for 5 min to remove oxygen. After that, nitrogen was injected. After three cycles, the polymerization tube was sealed and reacted at 30°C for 24 hours with vigorously stirring. When the reaction was completed, the glass polymerization tube was opened and the reaction mixtures were slowly added into 300 mL methanol through a disposable syringe. The yellow powder solid precipitate was collected and dried in vacuum to gain the desired polymer PGAC-4 with a yield of 71%. The similar method was adopted to prepare PGAC-6 and PGAC-10 according to preparation route elaborated in Fig.1.

Results and discussion

Structural characterization of MNCA-m and PGAC-m

Monomers MNCA-m and polymers PGAC-m were obtained according to the synthetic route showed in Fig.1. The chemical structures of MNCA-m were confirmed by ¹H NMR, mass spectrum and ¹³C NMR. Fig.2 (a) displays the ¹H NMR spectrum of MNCA-4. The spectrum showed that all hydrogen atoms in the molecular structure can be found the corresponding chemical shift peaks. Moreover, the area ratio of the peaks is basically consistent with the number ratio of the corresponding hydrogen atoms, which indicated that the pure MNCA-4 is obtained. Mass spectrum (Fig.2 (b)) and ¹³C NMR (Fig.2 (c)) also confirmed the purity of MNCA-4. Fig.2 (d) shows the ¹H NMR spectrum of PGAC-4. Compared with MNCA-4, the corresponding proton peaks of PGAC-4 became wider due to the decreased proton activity after polymerization. Besides, the chemical shift peak of -NH on the N-carbonyl anhydride of MNCA-4 is found to have thoroughly disappeared, indicating that TEA successfully initiates NCA ring opening polymerization of MNCA-4. The chemical structure of the other monomers and polymers were also confirmed by similar methods, and the characterization results are shown in Fig. S1.

FT-IR spectrometer was applied to monitor whether the conversion of MNCA-4 is complete after the polymerization, and confirm the secondary structure of PGAC-m. Fig.3 shows the FT-IR spectra of MGAC-4 and PGAC-4. After polymerization, the stretching vibration peaks of -C=O on N-carbonyl anhydride located at 1850 cm⁻¹ and 1780 cm⁻¹ are completely disappeared. The stretching vibration peak (amide I) located at 1657 cm⁻¹ and the deformation vibration peak (amide II) located at 1548 cm⁻¹ belong to polymer PGAC-4, indicating that MNCA-4 have been unreservedly converted into PGAC-4. In addition, it can be concluded that PGAC-4 present thoroughly α -helical conformation in solid state according to the position of the amide I and amide II.43 The FT-IR spectra of PGAC-6 and PGAC-10 are exhibited in Fig.S2. The results indicate that PGAC-6 and PGAC-10 also exhibit α -helical conformation in solid state.



Fig.2 (a) The ¹H NMR spectrum of MNCA-4 in $CDCl_3$; (b) The mass spectrum of MNCA-4 in $CDCl_3$; (c) The ¹³C NMR of MNCA-4 in DMSO-d₆; (d) The ¹H NMR spectrum of PGAC-4 in DMSO-d₆.



GPC instrument was applied to measure the M_n and PDI of PGAC-m. The results are elaborated in Table 1 and corresponding GPC curves are shown in Fig.S3. The M_n of all polymers is more than 3.5×10^4 g mol⁻¹ to reduce the influence of M_n on the phase transition temperature and phase structure. The GPC curves are symmetrical single peak with narrow distribution, indicating that the target polymers have been successfully prepared.

Table 1 GPC, TGA and DSC test results of PGAC-m					
Polymers	M _n (×10 ⁴) ^a	PDI ^a	Т _і (°С) ^ь	T _g (℃) ^b	T _d (°C) ^c
PGAC-4	3.7	1.20	143	127	341
PGAC-6	4.7	1.19	140	121	331
PGAC-10	5.2	1.28	137	104	349

^a Obtained from the GPC instrument.

^b Measured by DSC instrument.

^c Obtained by TGA Q50 instrument.

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Thermal stability of PGAC-m

The thermal stability of PGAC-m was characterized by TGA instrument. The thermal decomposition curves are recorded in Fig.4 and the detailed data is listed in Table 1. As can be seen from the TGA curves, the thermal decomposition temperature (defined as the temperature at which the mass fraction is reduced by 5 wt%) of all polymers is above 330 $^{\circ}$ C, which indicates that PGAC-m exhibit good thermal stability.

Phase structure and phase transition behavior of PGAC-m

The phase structure and phase transition behavior of PGACm were examined in detail. The phase textures can be visually observed through POM instrument. To remove thermal history, all polymers were heated to 160 $^\circ$ C , and then were cooled to 20 $^\circ$ C . The heating and cooling rate were set to 10 $^\circ$ C min^-1. POM images of PGAC-m were captured during the cooling process. The typical images are shown in Fig.5. Obvious birefringence phenomenon and typical smectic phase textures appeared during the cooling process, which directly indicates that PGAC-m can self-assemble into smectic phase structure.

The differential scanning calorimetry (DSC) was employed to measure the glass transition temperature (T_g) and clearing point temperature (T_i) of polymers PGAC-m. For consistency with POM test conditions, all polymers were heated to 160 °C and then cooled to 20 °C. After that, all polymers were heated to 160 °C again. The heating and cooling rate were set to 10 °C min⁻¹. The second DSC heating curves were recorded in Fig.6 and the test results are exhibited in Table 1. The obvious endothermic peaks at 143 °C, 140 °C and 137 °C are observed, which belong to the phase transition temperature from liquid crystal phase to isotropic phase of PGAC-4, PGAC-6, and PGAC-10, respectively. The glass transition temperature and clearing point temperature decreased with the increase of spacer length, implying that longer spacer is beneficial to the movement of polymer segments.³⁷

To better understand the phase structures of the resulting polymers, small-angle X-ray scattering (SAXS) test was manipulated. The test samples were heated to above their clearing point temperature, and then cooled to 30 $^{\circ}$ C with the rate of 5 $^{\circ}$ C min⁻¹. The SAXS patterns were recorded at 30 $^{\circ}$ C and the test results are exhibited in Fig. 7. As observed, all

polymers showed obvious peaks. For PGAC-4 and PGAC 6 the scattering vectors ratio of the two peaks 91^{10} and 92^{11} is 32.72. For PAGC-10, the scattering vectors ratio of the five peaks is 1 : 2:3:4:5. The results confirm that PGAC-m with different spacer length can form lamellar-ordered smectic structure, which is consistent with POM test results. The layer spacing values are also calculated according to 2π / q. For PGAC-4, its first-order diffraction peak is located at 2.25 nm⁻¹, and the corresponding layer spacing is 2.79 nm. The theoretical molecular length obtained from Material Studio is about 2.42 nm. Therefore, there should be an inclination angle between the mesogenic unit and the bedding planes, implying that PGAC-4 adopt a double-layer smectic C molecular packing. According to similar calculation method, we presume that polymer PGAC-m can also self-assemble into double-layer smectic C phase structure. Moreover, with the increase of spacer length, the inclination angles decrease gradually. Comprehensive consideration of POM, DSC and SAXS test results, we speculate that the possible molecular stacking arrangements of PGAC-m are as presented in Fig.8.





Fig.5 POM images of PGAC-4 obtained at 130 $^{\circ}$ C (a), PGAC-6 obtained at 125 $^{\circ}$ C (b), PGAC-10 obtained at 120 $^{\circ}$ C (c). (Magnification: ×200).



Fig.6 DSC curves of PGAC-m during the second heating process with a heating rate of 10 $^\circ\!C$ min 1.



Fig.7 SAXS patterns of PGAC-m recorded at 30°C.



Fig.8 The schematic illustration of possible molecular stacking arrangements of PGAC-m.

Photophysical properties of PGAC-m

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The photophysical properties of PGAC-m were also characterized in details. Fig.9 (a) and Fig.9 (b) display the UV absorption spectra of PGAC-m in thin film state and in dilute DMF solution, respectively. As shown in Fig.9 (a), PGAC-m with different spacer length shows the similar UV absorption spectra. The absorption peaks are located at about 350 nm, which belongs to the π - π * transition of cyanostilbene moiety. In DMF solution, the PGAC-m also shows the similar UV absorption spectra. However, the absorption peaks shift to 343 nm (Fig.9 (b)), indicating that cyanostilbene shows twisted conformation in dilute DMF solution.

Cyanostilbene is a typical AIEE-active group, and the prepared polymers PGAC-m are anticipated to retain the AIEE properties. As verification, the fluorescence spectrometer was performed to investigate the emission behavior of PGAC-m in DMF-H₂O mixtures with different water fraction (f_w). PGAC-4 is selected as an example to describe this process. Fig.10 (a) shows the emission spectra of PGAC-4 in DMF-H₂O mixtures with different water fraction. Firstly, weak luminescence intensity is observed in pure DMF, and the fluorescence emission peak is located in at 462 nm. When the water fraction increases to 20%, the fluorescence emission peak of



Fig.9 UV-Vis absorption spectra of PGAC-m in the film state (a) and in DMF solution (b) (Concentration = 1×10^{-5} mol L⁻¹).

PGAC-4 shifts from 462 nm to 493 nm. Subsequently, the wavelength corresponding to the fluorescence emission peak remains basically unchanged. In the whole process, the fluorescence intensity increases with the increase of water fraction. When the water fraction is 97%, the fluorescence intensity reaches the maximum value. At this time, the fluorescence intensity is 4 times of that in pure DMF solution (Fig.10 (b)). To better understand this enhanced emission behavior, dynamic light scattering (DLS) measurement of PGAC-4 was carried out (Fig.S4(e)). The average diameter increases significantly from 16 nm (f_w = 0%) to 847 nm (f_w = 90%), indicating that PGAC-4 gradually aggregate to form nanoparticle suspensions with the addition of water, which results in the molecular configuration planarization from twisted structure to coplanar structure. This planarization configuration is in favour of J-aggregation formation and restrains non-radiative transition, leading to the enhanced emission behavior.^{36, 44} The UV-visible absorption spectra of PGAC-4 with different water fraction also reveal aggregation process (Fig.S4(f)). The illustrations in Fig.10 (b) are the luminescent pictures of the PGAC-4 in the pure DMF solution, in the mixed DMF-H₂O solutions with water fraction of 20% and 97%, and in solid state, respectively. All the pictures were taken under 365 nm UV light. These illustrations further confirm the enhanced emission behavior and red shift phenomenon. The fluorescence test results suggest that PGAC-4 exhibits AIEE properties. Similarly, PGAC-6 and PGAC-10 are also successfully endowed with AIEE properties and their emission spectra are displayed in Fig.S4. The luminescence

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Fig.10 (a) Emission spectra of PGAC-4 in DMF-H₂O mixtures with different water fraction; (b) Plots of I/I₀ values versus water fraction of PGAC-4; (c) Fluorescence spectrum of PGAC-4 in thin film state. Excitation wavelength = 365 nm. Concentration = 1×10^{-5} mol L⁻¹. The inserted pictures were taken under 365 nm UV light.

emission spectrum of PGAC-4 in thin film state was also measured. As observed from Fig.10 (c), the emission peak is located at approximately 478 nm.

Chiral optical properties of PGAC-m

What is known to us is that circular dichroism (CD), reflecting the absorption differences of left-handed and righthanded light, can be applied to investigate structural information concerning ground electronic state of chiral fluorescent materials. To judge whether the chirality of poly (Lglutamate) backbone has been transferred to cyanostilbene pendants, we investigated the CD spectra of PGAC-m in two states at room temperature, including in pure DMF solution and in glassy liquid crystal film. After heating the polymer sample to a temperature above its clearing point temperature, the film is uniformly pressed, and then slowly cooled to room temperature to obtain the glassy liquid crystal film. No CD signals were detected in pure DMF solution for all polymers (Fig.S5), implying that cyanostilbene may adopt random orientation conformation, causing racemization in DMF solution.^{33, 45} However, in glassy liquid crystal film, the

resulting polymers exhibit striking cotton effects at around 350 nm (Fig.11 (b), Fig.11 (c) and Fig.11 (d)), Which belongs to the absorption of cyanostilbene moiety (Fig.11 (a)). The test results show that the chirality of poly (L-glutamate) is successfully transferred to cyanostilbene and induced the formation of preferred-handed screw conformation. Taking comprehensive into account CD and SAXS test results, we deem that PGAC-m form helix-arranged chiral smectic C (SmC*) phase structure, which is well maintained in the glassy state.





Fig.12 CPL spectra of PGAC-m in glassy liquid crystal film (a) PGAC-4; (b) PGAC-6; (c) PGAC-10; (d) Corresponding luminescence dissymmetry factor (g_{lum}) spectra. Excitation wavelength = 350 nm.

Considering that the resulting polymers can not only form spiral-stacked SmC*, but also possess high emission efficiency, which create a suitable CPL emission environment. Reasonably, PGAC-m is expected to generate CPL emission in glassy liquid crystal film. Inspired by this, we investigated the CPL properties of PGAC-m in DMF solution and in glassy liquid crystal film by JASCO-CPL-300 instrument. PGAC-4 is selected as an example to illustrate the CPL properties. Similar to CD test results, the CPL signal is also silent in DMF solution (Fig.S6). It's inspiring that strong CPL signal at 458 nm is detected in

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glassy liquid crystal film (Fig.12 (a)). The corresponding glime value can achieve 4.5×10^{-2} (Fig.12 (d)),¹⁰ which is rarely reported. The g_{lum} value is larger than that of most reported non-doped CPL-active polymer materials, the comparison data of g_{lum} values and quantum yields with those reported in literatures are given in Table S1. This large glum value of PGAC-4 is acquired by the self-assembly of chiral liquid crystals, which shows amplification effect. Although the amplification effect is not prominent in comparison with the glum value of reported emissive chiral nematic liquid crystal systems, it shows a great superiority in fluorescence quantum yield (which will be discussed in the following part). Similarly, PGAC-6 and PGAC-10 also exhibit silent CPL signals in DMF solution (Fig.S7 and Fig.S8), while evident CPL signals are detected in glassy liquid crystal film (Fig.12 (b) and Fig.12 (c)). Impressively, the CPL properties can be manipulated by changing spacer length. The g_{lum} value decreases with the increase of spacer length (Fig.12 (d)), which is attributed to the "decoupled effect" between the chiral poly (L-glutamate) backbone and cyanostilbene side group. The shorter the spacer length, the more efficient the chiral transfer from poly (L-glutamate) to cyanostilbene, and the larger the g_{lum} value.

The fluorescence quantum yield in solid state

The fluorescence quantum yield is an important indicator for evaluating CPL property, and the high solid quantum yield of luminescence is conducive to promote the practical application of CPL materials. Therefore, we measured the solid quantum yield of PGAC-m, and also explored the influence of spacer length on the solid fluorescence quantum yield of PGAC-m. As observed from Fig.13, all the resulting polymers possess relatively high solid quantum yields, and the solid quantum yield increases with the increase of spacer length. The fluorescence quantum yields of PGAC-4, PGAC-6 and PGAC-10 are 30.2%, 32.8% and 34.1%, respectively. This enhanced solid fluorescence quantum yield is mainly caused by decoupling effect,³⁷ which means that the long space is conducive to the aggregation of cyanostilbene group, and extend the conjugation of α -cyanostilbene to improve the solid quantum vield of PGAC-m.



Fig.13 The solid fluorescence quantum yields of PGAC-m (excitation wavelength = 365 nm).

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Conclusions

In this article, we have creatively constructed a series of novel CPL-active side-chain chiral liquid crystal polymers PGACby integrating poly (L-glutamate) backbone m and cyanostilbene pendants through different spacer length. The influence of spacer length on the phase structure and the photophysical properties of PGAC-m were studied in detail. Experiment results showed that the resulting polymers PGACm can self-assemble to form helix-arranged chiral smectic C (SmC*) phase. The clearing point temperature of PGAC-m decreases with the increase of spacer length. All polymers exhibited typical AIEE characteristics, and the solid fluorescence quantum yields of PGAC-m increases with the increase of spacer length. The solid fluorescence quantum yield solid-state of PGAC-10 can achieve 34.1%. The chirality of poly (L-glutamate) is successfully transferred to cyanostilbene and PGAC-m can emit strong circularly polarized light in glassy liquid crystal film. Moreover, the CPL properties can be manipulated by changing the spacer length. The glum value decreases with the increase of spacer length, and g_{lum} value of PGAC-4 can achieve 4.5×10^{-2} . To the best knowledge, this is the first report concerning non-doped CPL-active polymer materials fabricated from side-chain chiral luminescent liquid crystal polymer. This work unfolds a new insight to harvest non-doped CPL polymer materials with high solid quantum yield and large g_{lum} value, and also provides theoretical guidance for the preparation of new high-performance circularly polarized luminescent materials.

Conflicts of interest

There are no conflicts to declare.

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A series of novel high efficiency CPL-active side-chain chiral ^{DGL} 101039/DOTC03276J crystal polypeptides were constructed.

