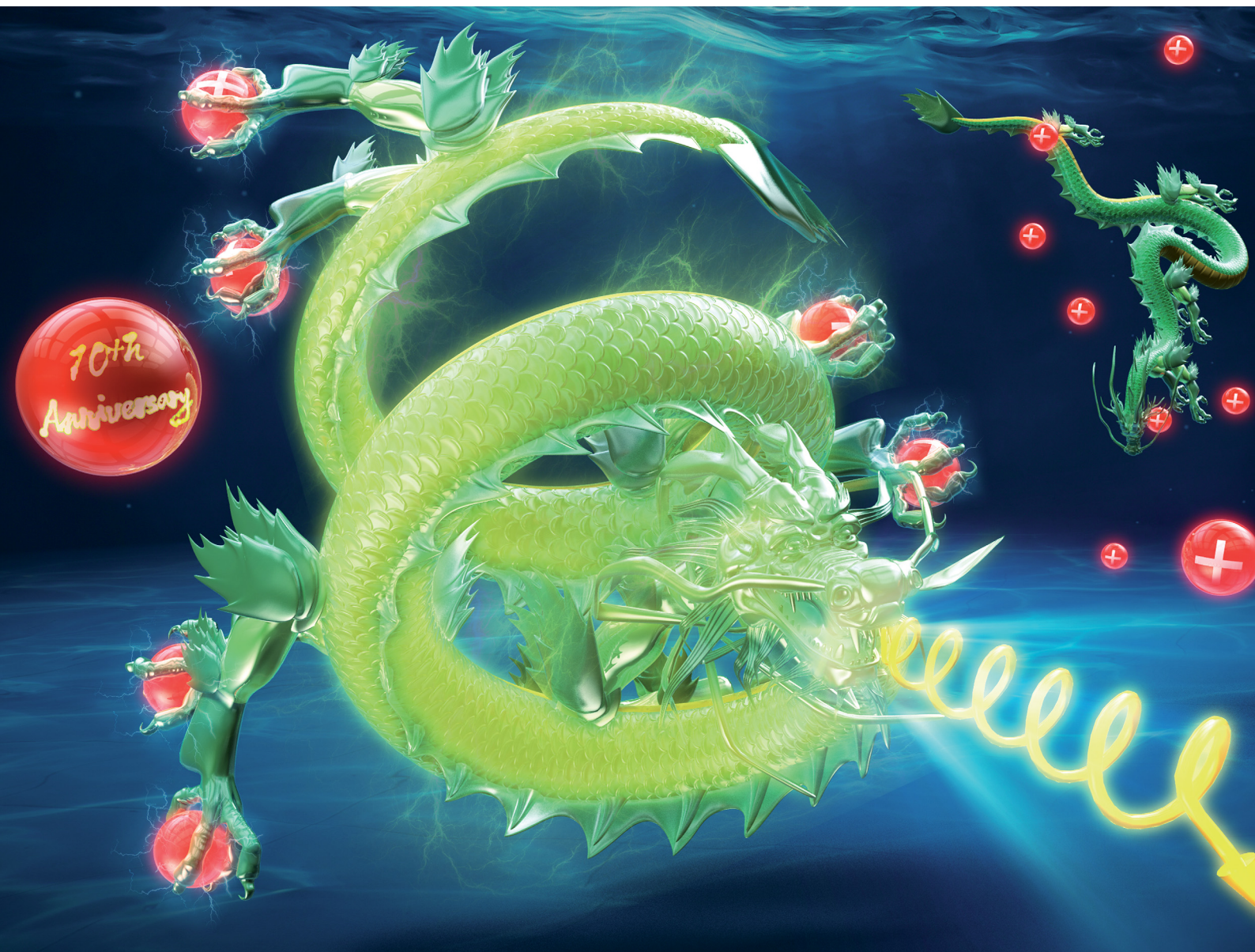


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**PAPER**

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Thermally stable and rewritable circularly polarized luminescent helical poly(diphenylacetylene): stabilization of macromolecular helicity memory *via* reversible ion-pair formation

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# Thermally stable and rewritable circularly polarized luminescent helical poly(diphenylacetylene)s: stabilization of macromolecular helicity memory *via* reversible ion-pair formation†

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Fluorescent poly(diphenylacetylene) (poly-**1-H**) bearing carboxy pendants forms a one-handed helical conformation upon thermal annealing in the presence of nonracemic chiral amines in water. This macromolecular helicity is retained (memorized) even after complete removal of the amines (*h*-poly-**1-H**); however, it is easily lost at high temperatures. In this study, we report an efficient stabilization of the helicity memory of *h*-poly-**1-H** even at high temperatures together with a significant enhancement in the solubility and fluorescent properties of *h*-poly-**1-H** using the reversible formation of an ion-pair complex with bulky ammonium or phosphonium cations. The ion-paired polymer with tetradecylammonium cations (*h*-poly-**1-A**<sub>10</sub>) nearly retained its helicity memory even after heating at 80 °C for 24 h or at 100 °C for 2 h in toluene, and significant enhancement in fluorescence quantum yield from 9% to 32% was observed. In addition, *h*-poly-**1-A**<sub>10</sub> formed a tough self-supporting film exhibiting strong CPL emission because of its helicity memory, and its ethanol solution could be used as a CPL ink. Because the stabilization of the helicity memory by noncovalent ion-pair formation is reversible, the ion-paired polymer could be reconverted to the original carboxylic-acid-type polymer while maintaining the helicity memory. Moreover, its macromolecular helicity can be repeatedly switched through heat treatment in the presence of the enantiomeric counterpart of the chiral amines and then further stabilized by the ion-pair formation.

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## Introduction

One-handed helical polymers are potential functional chiral materials such as chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC),<sup>1–4</sup> chiral sensors,<sup>5–7</sup> asymmetric catalysts,<sup>8,9</sup> and circularly polarized luminescent (CPL) materials<sup>10,11</sup> because of their excellent chiral recognition ability and chiroptical properties based on their helical chirality. To date, many artificial helical polymers with a controlled helix sense have been developed.<sup>12–16</sup> Recently, helical polymers capable of purposely

switching the helix sense through external stimuli have attracted significant attention,<sup>15,16</sup> which can be used as emerging functional chiral materials with switching functions based on the reversal of their helical chirality, such as switchable CSPs,<sup>17–19</sup> asymmetric catalysts,<sup>20–22</sup> and CPL,<sup>23</sup> which can switch the elution order of enantiomers, chirality of the target product, and CPL sign, respectively.

Poly(diphenylacetylene)s (PDPAs) are  $\pi$ -conjugated helical polymers that can form a one-handed helical conformation even in a solution.<sup>24,25</sup> PDPAs with a controlled helix sense can be used as practical chiral materials because of their excellent chemical and thermal stability and high fluorescence emission properties in solution and solid states.<sup>25–27</sup> Conventionally, PDPAs with a preferred-handed helical conformation are synthesized by polymerizing the corresponding optically active monomers or introducing optically active substituents into the pendants through polymer reaction followed by thermal annealing.<sup>28–38</sup>

On the other hand, we recently reported that PDPAs with a one-handed helical conformation can be prepared through

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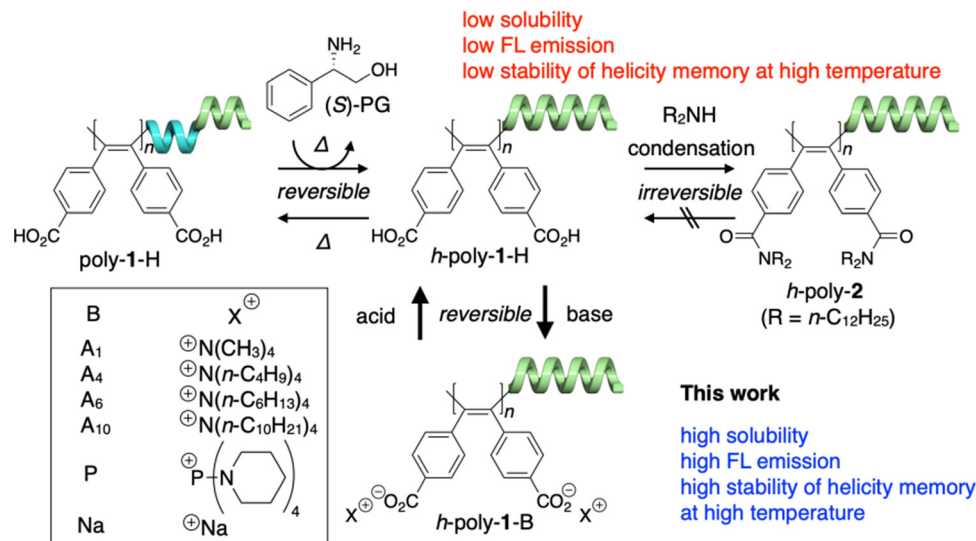


Fig. 1 Schematic illustrations of reversible modification of PDPA bearing carboxy pendants with macromolecular helicity memory (*h*-poly-1-H) through ion-pair formation of the carboxy pendants with achiral quaternary oniums (*h*-poly-1-B) and its irreversible modification by amidation of the carboxy pendants (*h*-poly-2).

noncovalent supramolecular chiral interactions with optically active guest compounds.<sup>39</sup> We demonstrated that optically inactive *cis*-stereoregular PDPA bearing carboxy pendant groups (poly-1-H) can fold into a one-handed helical conformation upon thermal annealing in water in the presence of nonracemic amines (Fig. 1). Moreover, the induced one-handed helical conformation can be maintained, or “memorized”, even after completely removing the nonracemic amines (*h*-poly-1-H), exhibiting clear CPL. Using this approach of helicity induction and memory, *h*-poly-1-H with the desired helix sense can be prepared using enantiomeric chiral amines as a helix inducer. Moreover, the helix sense of *h*-poly-1-H can be switched by noncovalently interacting with an opposite chiral amine followed by thermal annealing. The helicity memory of *h*-poly-1-H is relatively stable at temperatures lower than room but is easily lost at high temperatures in solution. In addition, *h*-poly-1-H has very low solubility in organic solvents and is soluble only in H<sub>2</sub>O–DMSO mixed solvents, and the quantum yield of *h*-poly-1-H was relatively low (2.5–9.3%). The solubility of *h*-poly-1-H in organic solvents and the stability of its helicity memory can be enhanced by introducing substituents into the pendants through amide linkages by condensation reactions with various amines using a condensation reagent at room temperature.<sup>40</sup> However, chemical modification of the pendants in *h*-poly-1-H by amidation is essentially irreversible, and switching the helix sense of *h*-poly-1-H (memory rewriting) using the enantiomeric opposite chiral amine is impossible. Thus, improving the thermal stability and solubility of helicity-memorized *h*-poly-1-H with simultaneous switching of the helix sense of the polymer backbone and without the irreversible chemical modification of the pendants is essential for the application of PDPAs with helicity memory to various switchable chiral materials,<sup>16</sup> typified by switchable CPL.<sup>41–43</sup>

Kwak *et al.* reported that the fluorescent properties and solubility of anionic PDPA with sulfonic acid pendants can be

improved by forming an ion-pair complex with ammonium cations with long alkyl chains.<sup>44</sup> We envisaged that the stability of the macromolecular helicity memory in *h*-poly-1-H, as well as its solubility and fluorescent properties, could be simultaneously improved through noncovalent ion-pair complex formation with various cations. In this study, we converted *h*-poly-1-H to the corresponding ion-pair complexes with various ammonium or phosphonium cations, and the effects of the structure of the counter cations on the stability of helicity memory at high temperatures, solubility in various solvents, film-forming ability, and fluorescent properties were investigated.

## Results and discussion

*h*-Poly-1-H, maintaining the induced helical conformation as helicity memory, was prepared according to a previously reported method (Fig. 1).<sup>39</sup> Poly-1-H was heated in water in the presence of (*S*)-phenylglycinol ((*S*)-PG) to induce a left-handed helical conformation, followed by acidification with hydrochloric acid to remove (*S*)-PG and isolate *h*-poly-1-H. In H<sub>2</sub>O–DMSO (1/1, v/v), isolated *h*-poly-1-H exhibited an intense induced circular dichroism (ICD) with a negative first Cotton effect in the polyene backbone region ( $\Delta\epsilon_{1st} = -22.5$ ), indicating the formation of a left-handed helical conformation (Fig. 2a). The helix-sense excess of *h*-poly-1-H was estimated to be 88% based on the ICD intensity.<sup>39</sup>

*h*-Poly-1-H was soluble in H<sub>2</sub>O–DMSO mixtures; however, it was almost insoluble in water, DMSO, and other common organic solvents (Table 1). In contrast, the sodium salt of *h*-poly-1-H (*h*-poly-1-Na) exhibited high solubility in water, suggesting that the low solubility of *h*-poly-1-H in solvents is due to the strong intermolecular hydrogen bonds between the

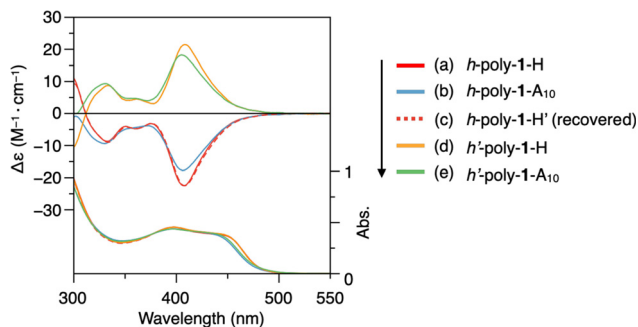


Fig. 2 CD and absorption spectra of (a) as-prepared *h*-poly-1-H in H<sub>2</sub>O–DMSO (1/1, v/v), (b) *h*-poly-1-A<sub>10</sub> in MeOH, (c) *h*-poly-1-H' after ion-pair deformation from *h*-poly-1-A<sub>10</sub> in H<sub>2</sub>O–DMSO (1/1, v/v), (d) *h'*-poly-1-H in H<sub>2</sub>O–DMSO (1/1, v/v), and (e) *h'*-poly-1-A<sub>10</sub> in MeOH, measured at 25 °C. [Polymer] = 1.0 mM.

Table 1 Solubility of *h*-Poly-1-H and *h*-Poly-1-B in various solvents<sup>a</sup>

Run	Polymer	Solubility <sup>a</sup>					
		H <sub>2</sub> O (78.3) <sup>b</sup>	DMSO (46.5) <sup>b</sup>	MeOH (32.7) <sup>b</sup>	THF (7.58) <sup>b</sup>	Toluene (2.38) <sup>b</sup>	Hexane (1.88) <sup>b</sup>
1	<i>h</i> -poly-1-H	×	×	×	×	×	×
2	<i>h</i> -poly-1-A <sub>1</sub>	○	×	○	×	×	×
3	<i>h</i> -poly-1-A <sub>4</sub>	○	○	○	△	×	×
4	<i>h</i> -poly-1-A <sub>6</sub>	×	○	○	○	○	×
5	<i>h</i> -poly-1-A <sub>10</sub>	×	△	○	○	○	○
6	<i>h</i> -poly-1-A <sub>10</sub> (40)	×	×	○	○	△	△
7	<i>h</i> -poly-1-A <sub>10</sub> (20)	×	×	○	×	×	×
8	<i>h</i> -poly-1-P	○	○	○	○	△	×
9	<i>h</i> -poly-1-Na	○	×	△	×	×	×

<sup>a</sup> ○:soluble, △:partially soluble, ×:insoluble, 1 mg mL<sup>-1</sup>, at room temperature (ca. 25 °C). <sup>b</sup> Relative permittivity at 25 °C cited from ref. 45.

pendant carboxy groups. We converted *h*-poly-1-H to the corresponding ion-pair complex with various ammonium or phosphonium cations (*h*-poly-1-B) to improve its solubility in various organic solvents and water. *h*-Poly-1-B was prepared by mixing *h*-poly-1-H with an equimolar amount of quaternary ammonium hydroxide (A<sub>*n*</sub>OH, where “*n*” represents the number of carbons in (n-C<sub>*n*</sub>H<sub>2*n*+1</sub>)<sub>4</sub>N) or tetrapiperidinophosphonium hydroxide (POH) to carboxylic acid groups at room temperature in methanol (MeOH), followed by removal of MeOH under reduced pressure. *h*-Poly-1-A<sub>1</sub> and *h*-poly-1-A<sub>4</sub> prepared from tetramethylammonium hydroxide (A<sub>1</sub>OH) and tetrabutylammonium hydroxide (A<sub>4</sub>OH), respectively, were soluble in MeOH as well as water. *h*-Poly-1-A<sub>6</sub> and *h*-poly-1-A<sub>10</sub> prepared from tetrahexylammonium hydroxide (A<sub>6</sub>OH) and tetradecylammonium hydroxide (A<sub>10</sub>OH) with long alkyl chains, respectively, were insoluble in water but soluble in toluene, THF, and MeOH. In particular, *h*-poly-1-A<sub>10</sub> exhibited good solubility in various hydrocarbon solvents, including *n*-hexane. *h*-Poly-1-P, prepared from the quaternary phosphonium salt POH, exhibited amphiphilic properties and good solubility in water as well as organic solvents, including DMSO, MeOH, and THF, and it was partially soluble in toluene.

The IR spectrum of *h*-poly-1-A<sub>10</sub> exhibits an intense peak around 2900 cm<sup>-1</sup> attributed to the C–H stretching of the decyl group (Fig. S1, ESI<sup>†</sup>). However, the peak at 1720 cm<sup>-1</sup> corresponding to the C=O stretching of the CO<sub>2</sub>H group, which was observed for *h*-poly-1-H, was not detected for *h*-poly-1-A<sub>10</sub>. In contrast, partially ion-paired *h*-poly-1-A<sub>10</sub>(20) and *h*-poly-1-A<sub>10</sub>(40) prepared from *h*-poly-1-H using 0.2 and 0.4 equivalents of A<sub>10</sub>OH, respectively, exhibited clear peaks at 1720 cm<sup>-1</sup> and 2900 cm<sup>-1</sup>. These results indicate that almost all pendant carboxy groups in *h*-poly-1-H were converted to the ion-pair complexes in *h*-poly-1-A<sub>10</sub>. In the <sup>1</sup>H NMR spectrum of *h*-poly-1-A<sub>10</sub>, peaks corresponding to the alkyl group of the A<sub>10</sub> cation were observed as very broad signals, indicating that A<sub>10</sub> forms ion pairs with the polymer (Fig. S2B, ESI<sup>†</sup>). Furthermore, *h*-poly-1-A<sub>10</sub> was reconverted to the original carboxylic-acid-type polymer (*h*-poly-1-H') by adding an excess amount of trifluoroacetic acid (TFA), as confirmed by the <sup>1</sup>H NMR and IR measurements (Fig. S1 and S2C, ESI<sup>†</sup>). Partially ion-paired *h*-poly-1-A<sub>10</sub>(40) was fully soluble in THF and MeOH and partially soluble in nonpolar solvents such as toluene and *n*-hexane, whereas less ion-paired *h*-poly-1-A<sub>10</sub>(20) was soluble only in MeOH. These results show that the ion-pair formation with A<sub>10</sub> cation can enhance the solubility of *h*-poly-1-H in organic solvents, leaving 60% of the pendants as free carboxylic acid groups.

The CD and absorption spectra of *h*-poly-1-A<sub>10</sub> in MeOH are shown in Fig. 2b. Compared to *h*-poly-1-H, *h*-poly-1-A<sub>10</sub> exhibited a slight blue shift of the peak in the main-chain absorption region, and its ICD intensity of the first Cotton ( $\Delta\epsilon_{1st} = -17.8$ ) was approximately 20% lower than that of *h*-poly-1-H. This could be because compared to *h*-poly-1-H, *h*-poly-1-A<sub>10</sub> forms a helical conformation with a slightly different helical pitch due to steric hindrance between the bulky A<sub>10</sub> cations in the side chains.<sup>39</sup> However, the CD and absorption spectra of *h*-poly-1-H', which was reconverted to the carboxylic-acid-type polymer by treating *h*-poly-1-A<sub>10</sub> with TFA, were same as those of *h*-poly-1-H (Fig. 2c). These results show that *h*-poly-1-H can be reversibly interconverted to *h*-poly-1-A<sub>10</sub>, stably maintaining the helicity memory. Recovered *h*-poly-1-H' with left-handed helicity memory was subsequently heated in water in the presence of (*R*)-PG instead of (*S*)-PG as the chiral guest, followed by acidification using hydrochloric acid to remove (*R*)-PG. Consequently, the isolated polymer (*h'*-poly-1-H) exhibited a complete mirror-imaged CD spectrum with a positive first Cotton effect ( $\Delta\epsilon_{1st} = 21.5$ ), indicating the formation of the opposite right-handed helical conformation (Fig. 2d). As expected, *h'*-poly-1-A<sub>10</sub>, which was prepared from *h'*-poly-1-H and A<sub>10</sub>OH, also exhibited a mirror-imaged CD spectrum to that of *h*-poly-1-A<sub>10</sub> ( $\Delta\epsilon_{1st} = 18.2$ ) (Fig. 2e). This demonstrates that *h*-poly-1-H can be reversibly converted to the ion-pair complex *h*-poly-1-B while maintaining the helicity memory, and the helicity of *h*-poly-1-H (or *h'*-poly-1-H) can be reversibly switched by heating it in water in the presence of the opposite enantiomeric guest compound.

To investigate the effect of ion-pair formation on the stability of the helicity memory, the solutions of *h*-poly-1-H and *h*-poly-1-A<sub>6</sub> were heated at 80 °C, and their time-dependent CD intensity changes ( $\Delta\epsilon_{1st}^{(t)}/\Delta\epsilon_{1st}^{(0)}$ ) were measured. When

**Table 2** Stability of helicity memory of *h*-Poly-1-H, *h*-Poly-1-B, and *h*-Poly-2 in solvents at different temperatures<sup>a</sup>

Run	Polymer	Solvent	Temperature (°C)	$\Delta\epsilon_{1st}^{(24)}/\Delta\epsilon_{1st}^{(0)}$ (%) <sup>a</sup>
1	<i>h</i> -poly-1-H	H <sub>2</sub> O–DMSO (1/1, v/v)	80	4.0
2	<i>h</i> -poly-1-A <sub>6</sub>	DMSO	80	103
3	<i>h</i> -poly-1-A <sub>6</sub>	DMSO	100	70
4	<i>h</i> -poly-2	toluene	80	85
5	<i>h</i> -poly-1-A <sub>10</sub>	toluene	80	103
6	<i>h</i> -poly-1-A <sub>10</sub>	toluene	100	87
7	<i>h</i> -poly-1-A <sub>10</sub> (40)	toluene	100	87
8	<i>h</i> -poly-1-Na	H <sub>2</sub> O	50	10
9	<i>h</i> -poly-1-A <sub>1</sub>	H <sub>2</sub> O	50	47
10	<i>h</i> -poly-1-A <sub>4</sub>	H <sub>2</sub> O	50	60
11	<i>h</i> -poly-1-P	H <sub>2</sub> O	50	73
12	<i>h</i> -poly-1-Na	H <sub>2</sub> O	25	55
13	<i>h</i> -poly-1-P	H <sub>2</sub> O	25	100

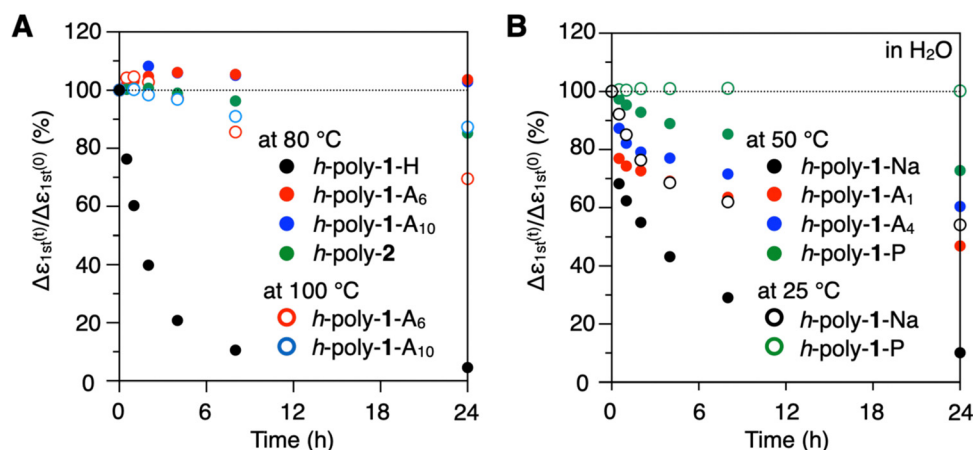
<sup>a</sup> Ratio of ICD intensities measured at 25 °C before and after standing the solutions at various temperatures for 24 h.

*h*-poly-1-H was heated at 80 °C in H<sub>2</sub>O–DMSO (1/1, v/v) for 24 h, its ICD intensity was reduced to 4% (run 1 in Table 2, Fig. 3A, and Fig. S3A, ESI<sup>†</sup>). On the other hand, when the DMSO solution of *h*-poly-1-A<sub>6</sub> was heated at 80 °C, its ICD intensity hardly changed even after 24 h (run 2 in Table 2, Fig. 3A and Fig. S3B, ESI<sup>†</sup>). These results show that *h*-poly-1-A<sub>6</sub> behaves as a static helical polymer that hardly undergoes racemization even at 80 °C.<sup>16</sup> Thus, the stability of the helicity memory in *h*-poly-1-H can be significantly enhanced by the formation of an ion-pair complex with quaternary ammonium cations even at high temperatures. During the initial stage of heating, *h*-poly-1-A<sub>6</sub> exhibited a slight change in the absorption spectrum, which was not observed for *h*-poly-1-H (Fig. S3A and B, ESI<sup>†</sup>). This slight change in the absorption spectrum of *h*-poly-1-A<sub>6</sub> is presumably due to a slight change in its conformation to a thermodynamically more stable one after the formation of the

ion-pair complex.<sup>46</sup> Furthermore, when *h*-poly-1-A<sub>6</sub> was heated in DMSO at 100 °C for 24 h, its ICD intensity was reduced to approximately 70% (run 3 in Table 2, Fig. 3A and Fig. S3C, ESI<sup>†</sup>). However, the <sup>1</sup>H NMR spectra of *h*-poly-1-A<sub>6</sub> before and after heating at 80 °C and 100 °C showed no changes, indicating that the ion-pair complex of PDPA is chemically stable even at high temperatures (Fig. S4, ESI<sup>†</sup>).

We have previously reported that the pendant carboxy group of *h*-poly-1-H can be converted to an amide group while retaining its helicity memory.<sup>39,40</sup> Therefore, *h*-poly-2 bearing long alkyl chains through amide linkages in the side chain was synthesized through the reaction between *h*-poly-1-H and didodecylamine (2) at room temperature using a condensing reagent, and the stability of its helicity memory in solution was investigated (Fig. 1). When *h*-poly-2 was heated in toluene at 80 °C for 24 h, its ICD intensity decreased to 85% of its initial value (run 4 in Table 2, Fig. 3A and Fig. S3D, ESI<sup>†</sup>). Consequently, ion-paired *h*-poly-1-A<sub>6</sub> had a more stable helicity memory stability than *h*-poly-2, where alkyl chains with the same carbon number as that in *h*-poly-1-A<sub>6</sub> were introduced in the pendant *via* a covalent bond. The stability of the helicity memory in *h*-poly-2 at 80 °C did not change, regardless of its concentration, whereas that of *h*-poly-1-A<sub>6</sub> decreased with decreasing concentration under the same conditions due to the dissociation of the ion-paired side chain (Fig. S5, ESI<sup>†</sup>). However, increasing the concentration of the A<sub>6</sub> cation in DMSO by adding the tetrahexylammonium bromide (A<sub>6</sub>B) suppressed the decrease in the stability of the helicity memory of *h*-poly-1-A<sub>6</sub> even under more diluted conditions. Therefore, the steric hindrance between the bulky ammonium cations forming ion-pairs in the pendants plays an important role in stabilizing helicity memory.

Similar to *h*-poly-1-A<sub>6</sub>, *h*-poly-1-A<sub>10</sub> also exhibited highly stable helicity memory, maintaining 103% and 87% of the initial ICD intensities after heating in toluene at 80 °C and 100 °C for 24 h, respectively (runs 5 and 6 in Table 2, Fig. 3A and



**Fig. 3** (A) Time-dependent ICD intensity changes ( $\Delta\epsilon_{1st}^{(t)}/\Delta\epsilon_{1st}^{(0)}$ ) of *h*-poly-1-H in H<sub>2</sub>O–DMSO (1/1, v/v) at 80 °C, *h*-poly-1-A<sub>6</sub> in DMSO at 80 °C and 100 °C, *h*-poly-1-A<sub>10</sub> in toluene at 80 and 100 °C, and *h*-poly-2 in toluene at 80 °C. (B) Time-dependent ICD intensity changes ( $\Delta\epsilon_{1st}^{(t)}/\Delta\epsilon_{1st}^{(0)}$ ) of *h*-poly-1-Na, *h*-poly-1-A<sub>1</sub>, *h*-poly-1-A<sub>4</sub>, and *h*-poly-1-P at 25 and 50 °C in water. All CD measurements were performed at 25 °C after standing at designated temperatures. [Polymer] = 1.0 mM.

**Table 3** Fluorescence quantum yields ( $\Phi_{\text{FL}}$ ) of *h*-Poly-1-H, *h*-Poly-1-B, and *h*-Poly-2<sup>a</sup>

Run	Polymer	Solvent	$\Phi_{\text{FL}}^a$
1	<i>h</i> -poly-1-H	H <sub>2</sub> O–DMSO (1/1, v/v)	9.3 <sup>b</sup>
2	<i>h</i> -poly-1-A <sub>6</sub>	toluene	20
3	<i>h</i> -poly-1-A <sub>10</sub>	toluene	32
4	<i>h</i> -poly-1-A <sub>10</sub> (40)	toluene	26
5	<i>h</i> -poly-2	toluene	23
6	<i>h</i> -poly-1-Na	H <sub>2</sub> O	2.5 <sup>b</sup>
7	<i>h</i> -poly-1-P	H <sub>2</sub> O	4.5

<sup>a</sup>  $\Phi_{\text{FL}}$  values were calculated by using quinine sulfate as a reference substance (see supporting information). <sup>b</sup> See ref. 39.

Fig. S3E, ESI<sup>†</sup>). Interestingly, *h*-poly-1-A<sub>10</sub>(40), in which only 40% of the pendant carboxy groups formed an ion-pair complex with A<sub>10</sub> cations, also exhibited similar stability of the helicity memory to that of *h*-poly-1-A<sub>10</sub> in toluene at 100 °C (run 7 in Table 2 and Fig. S3F, ESI<sup>†</sup>). These results indicate that *h*-poly-1-H can be converted into a static helical polymer that does not undergo helix inversion at high temperatures ( $\geq 80$  °C) by noncovalent ion-pair formation with bulky A<sub>6</sub> and A<sub>10</sub> cations.

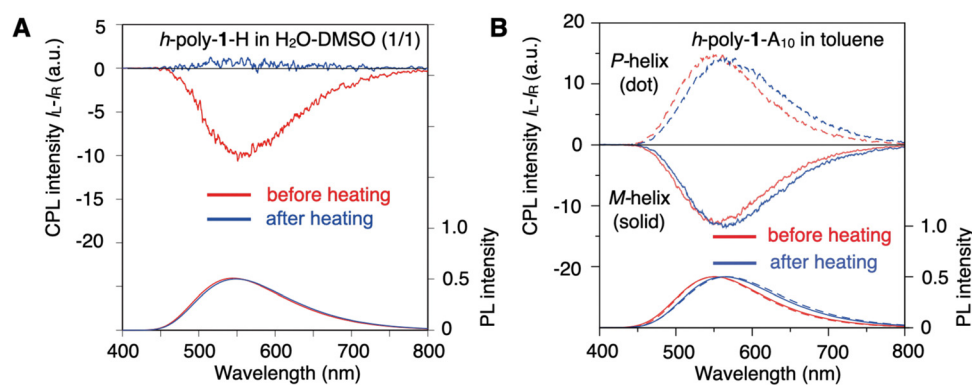
The effect of ion pairing on the stability of helicity memory of *h*-poly-1-B in water was also investigated (Fig. 3B). Water-soluble *h*-poly-1-Na, *h*-poly-1-A<sub>1</sub>, *h*-poly-1-A<sub>4</sub>, and *h*-poly-1-P were heated in water at 50 °C for 24 h and their ICD intensities before and after heating were compared. As a result, the stability of helicity memory in water increased in the following order: *h*-poly-1-Na < *h*-poly-1-A<sub>1</sub> < *h*-poly-1-A<sub>4</sub> < *h*-poly-1-P (runs 8–11 in Table 2, Fig. 3B and Fig. S6A–D, ESI<sup>†</sup>). Thus, the thermal stability of the helicity memory of *h*-poly-1-B increased by the formation of an ion-pair complex with bulky cations in water. The ICD intensity of *h*-poly-1-Na in water decreased to 55% of the initial value after 24 h, even at 25 °C, whereas that of *h*-poly-1-P in water remained unchanged (runs 12 and 13 in Table 2, Fig. 3B and Fig. S6E, F, ESI<sup>†</sup>). Hence, it was demonstrated that the helix inversion hardly occurs at 25 °C, even in water, by selecting an adequately bulky phosphonium cation as the counter cation.

Similar to the previous report by Kwak *et al.*,<sup>44</sup> *h*-poly-1-B ion-paired with hydrophobic cations showed increased

fluorescence emission compared with *h*-poly-1-H. The fluorescence quantum yield ( $\Phi_{\text{FL}}$ ) of *h*-poly-1-H in H<sub>2</sub>O–DMSO (1/1, v/v) was 9.3% (run 1 in Table 3),<sup>39</sup> while that of *h*-poly-1-A<sub>6</sub> in toluene increased to 20% (run 2 in Table 3). The  $\Phi_{\text{FL}}$  of *h*-poly-1-A<sub>10</sub> containing bulkier A<sub>10</sub> (compared to A<sub>6</sub>) as the counter cation increased to 32% in toluene (run 3 in Table 3). The  $\Phi_{\text{FL}}$  of partially ion-paired *h*-poly-1-A<sub>10</sub>(40) in toluene was 26%, which is significantly higher than that of *h*-poly-1-H (run 4 in Table 3). In contrast, *h*-poly-2 modified with hydrophobic long alkyl chains through an amide linkage showed almost the same  $\Phi_{\text{FL}}$  (23%) as that of *h*-poly-1-A<sub>6</sub> in toluene (run 5 in Table 3). Thus, the solubilization of *h*-poly-1-H in organic solvents by the formation of an ion-pair complex with hydrophobic cations is as effective as the introduction of hydrophobic groups through covalent bonding, which stabilizes the helicity memory and enhances the fluorescence properties. However, the  $\Phi_{\text{FL}}$  of *h*-poly-1-P in water was 4.5%, which is slightly higher than that of *h*-poly-1-Na (2.5%), suggests that the effect of the counter cations on the fluorescence properties in water was less noticeable than that in organic solvents (runs 6 and 7 in Table 3).

*h*-Poly-1-H exhibited CPL emission at approximately 550 nm based solely on the memorized helicity.<sup>39</sup> However, when *h*-poly-1-H was heated in H<sub>2</sub>O–DMSO (1/1, v/v) at 80 °C for 24 h, the helicity memory was almost lost, resulting in no CPL emission (Fig. 4A). In contrast, the luminescence dissymmetry factor ( $g_{\text{lum}}$ ) value of ion-paired left- (*M*-) and right-handed (*P*-) *h*-poly-1-A<sub>10</sub> before and after heating at 100 °C for 24 h in toluene were same (*i.e.*,  $2.0 \times 10^{-3}$ ) (Fig. 4B). This indicates that the CPL emission was maintained even after heating. The observed red shift of the FL and CPL spectra after heating probably results from a slight conformational change during the initial stage of heating, as also observed in the CD and absorption spectra mentioned above (Fig. S3E, ESI<sup>†</sup>). Thus, these results demonstrate that ion-paired *h*-poly-1-A<sub>10</sub> can function as a thermally stable CPL material.

A self-supporting film of ion-paired *h*-poly-1-A<sub>10</sub> was produced by casting the solution in organic solvents, such as acetone (Fig. 5B). The CD and CPL spectra of the cast films prepared on quartz plates from the acetone solutions of *M*- and



**Fig. 4** (A) CPL (top) and PL (bottom) spectra of *h*-poly-1-H before (red) and after (blue) heating at 80 °C for 24 h in H<sub>2</sub>O–DMSO (1/1, v/v), measured at 25 °C. (B) CPL (top) and PL (bottom) spectra of *M*- (solid line) and *P*-helical (dot line) *h*-poly-1-A<sub>10</sub> before (red) and after (blue) heating at 100 °C for 24 h in toluene, measured at 25 °C. Excited at 350 nm, [polymer] = 1.0 mM.



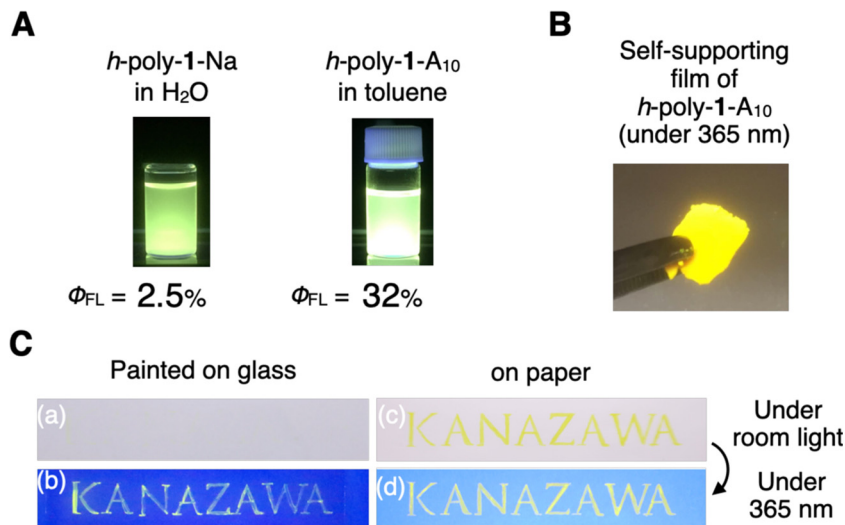


Fig. 5 Photographs of (A) *h*-poly-1-Na in H<sub>2</sub>O and *h*-poly-1-A<sub>10</sub> in toluene and (B) *h*-poly-1-A<sub>10</sub> self-supporting film under UV light (365 nm). (C) Photographs of letters painted with *h*-poly-1-A<sub>10</sub> in ethanol on (a and b) glass and (c and d) paper under (a and c) room light and (b and d) UV light.

*P*-*h*-poly-1-A<sub>10</sub> showed mirror-imaged spectra (Fig. S7 and S8, ESI<sup>†</sup>). The CPL spectra of the cast film before and after heating at 100 °C for 24 h were same (Fig. S8, ESI<sup>†</sup>). Furthermore, *h*-poly-1-A<sub>10</sub> exhibited good solubility in ethanol; thus the ethanol solution of *h*-poly-1-A<sub>10</sub> can be used as a CPL ink to paint letters on materials such as glass and paper (Fig. 5C). In contrast, for the solutions of *h*-poly-1-H in H<sub>2</sub>O–DMSO mixed solvents, preparing self-supporting films or using them as a CPL ink is difficult. Therefore, the solubilization of *h*-poly-1-H in organic solvents by the formation of an ion-pair complex with cations containing long alkyl chains is a powerful method not only for stabilizing the helicity memory of *h*-poly-1-H but also for the application of *h*-poly-1-H as a CPL material.

## Conclusion

In conclusion, PDPA bearing carboxy pendants with helicity memory were successfully converted into ion-paired complexes with various counter cations while maintaining the helicity memory. Obtained ion-paired PDPA with bulky ammonium cations, such as tetradecylammonium (A<sub>10</sub>), showed significantly high stability of the helicity memory at high temperatures, high solubility in various organic solvents, and improved fluorescent properties without any chemical modification of the pendant carboxy groups *via* covalent bonding. Because ion-pair formation by noncovalent interactions is reversible, ion-paired PDPA can be reversibly reconverted to the original carboxylic-acid-type polymer while retaining its helical memory. Moreover, the helix sense of the polymer backbone can be reversibly and repeatedly switched upon its thermal annealing in the presence of the opposite enantiomeric amine. Partially ion-paired PDPA, where approximately 40% of the pendant carboxy groups were ion-paired with A<sub>10</sub>, exhibited almost the same stability of the helicity memory of the fully ion-paired PDPA in toluene at 100 °C. This suggests that the introduction

of various functional groups into the remaining 60% of the carboxy pendants while imparting high solvent solubility and high stability of helicity memory to the carboxylic-acid-type PDPA with the helicity memory. PDPA with high solubility in organic solvents and ion-paired with long-chain alkylammonium cations can be cast from a solution to form a self-supporting film with a strong CPL emission and can also be used as a CPL ink.

This reversible and comprehensive method to improve the stability of helicity memory, solubility in solvents, and fluorescence properties of the carboxylic-acid-type PDPA with helicity memory by ion-pair formation is very powerful and promising for the development of functional chiral materials based on macromolecular helicity memory, such as asymmetric catalysts and CSPs for enantioseparation as well as CPL materials. In our laboratory, we are working on the development of chiral materials based on PDPA with helicity memory utilizing this ion-pair formation method.

## Conflicts of interest

The authors declare no competing financial interest.

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