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# Silica covering driven intensity enhancement and handedness inversion of the CPL signals of the supramolecular assemblies<sup>†</sup>

Pan Jiang,<sup>a</sup> Hongkun Li, <sup>b</sup>\*<sup>ab</sup> Wei Liu, <sup>b</sup><sup>a</sup> Yi Li, <sup>b</sup>\*<sup>a</sup> Baozong Li<sup>a</sup> and Yonggang Yang <sup>b</sup>\*<sup>a</sup>

A pair of Phe-Phe dipeptides with a tolane group were synthesized by introducing tolane with high emission efficiency to phenylalanine dipeptide. The sodium salts of the dipeptides were able to self-assemble into straight belts in a mixture of methanol and water. The supramolecular assemblies exhibited circularly polarized luminescence (CPL) properties. They can be used as templates to prepare dipeptide-based hybrid silicas through a supramolecular templating approach. The hybrid materials formed coiled nanoribbons, which showed a distinct and different morphology compared to supramolecular assemblies. Moreover, since silica covering can affect the packing structures of the tolane groups, the intensity of the CPL was enhanced and its handedness was inversed.

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## Introduction

Circularly polarized luminescence (CPL) refers to the phenomenon that a chiral luminescence system emits circularly polarized light with left or right rotation.<sup>1</sup> CPL-active materials have attracted a lot of attention in recent years for their potential applications in 3D displays,<sup>2</sup> photocatalytic asymmetric synthesis,<sup>3</sup> optical information storage,<sup>4</sup> and optical switches.<sup>5</sup> As is known, CPL activity is measured by the luminescence dissymmetry factor  $(g_{lum}), g_{lum} = 2(I_L - I_R)/(I_L + I_R)$ , where  $I_L$  and  $I_R$  are the intensities of the left- and right-handed circularly polarized emission, respectively. For practical applications, the luminescence efficiency, especially in the condensed phase, is another important parameter for evaluating the CPL performance. An exploration of efficient CPL-active materials with large  $g_{lum}$ values and high luminescence efficiency in the solid state is thus highly desirable. In recent years, various approaches have been reported to boost  $g_{lum}$  values, including Förster

<sup>b</sup> State Key Laboratory of Luminescent Materials and Devices, Key Laboratory of Luminescence from Molecular Aggregates of Guangdong Province, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou, 510640, China resonance energy transfer,<sup>6</sup> plasmon-resonance,<sup>7</sup> supramolecular assembly,<sup>8</sup> and liquid crystals.<sup>9</sup> In addition, CPL inversion is also a research hotspot in this field. Sign inversion of CPL in chiral systems shows enormous potential for the development of novel and well-defined functional optical devices. Plenty of factors, such as temperature,<sup>10</sup> stirring direction,<sup>11</sup> pH value<sup>12</sup> and solvent polarity,<sup>13</sup> may result in CPL inversion during the fabrication of CPL-active materials.

Supramolecular self-assemblies relying on weak noncovalent interactions, including hydrogen bonding, hydrophobic interactions, electrostatic interactions and  $\pi$ - $\pi$  stacking, provide an effective solution for accurately controlling the arrangement of building blocks and endowing the products with special functions.<sup>14</sup> By regulating external conditions intelligently, the size, shape and even handedness of self-assemblies are adjustable.<sup>15</sup> Sánchez and co-workers applied the sergeants-and-soldiers principle to the self-assembly of very simple *N*,*N'*-1,2-ethanediylbisbenzamides and realized an amplification of chirality.<sup>16</sup> Stupp *et al.* reported that the pH value, monomer concentration and proper functionalization of building blocks can result in different morphologies.<sup>17</sup>

Therefore, supramolecular self-assembly is a simple and efficient approach which can significantly amplify the circular polarization and realize CPL inversion.<sup>8,18</sup> Liu *et al.* reported enhanced and inversed CPL from photogenerated radical anions in dipeptide naphthalenediimide assemblies.<sup>18d</sup> Zheng *et al.* used a new concept of further assembly of helical self-assemblies to further boost the  $g_{lum}$  factor of CPL.<sup>19</sup> Zhang *et al.* synthesized a new chiral fluorescent molecule which can self-assemble into left-handed twist nanoribbons with a CPL



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<sup>&</sup>lt;sup>a</sup> State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. E-mail: hkli@suda.edu.cn, liyi@suda.edu.cn, ygyang@suda.edu.cn

<sup>†</sup> Electronic supplementary information (ESI) available: XRD patterns of the organic self-assemblies before and after silica covering, CD spectra of tolane-1, emission spectra of (L, L)-T,  $\Phi_{\rm F}$  and  $g_{\rm lum}$  of materials. See DOI: 10.1039/d1nj01327k

#### Paper

property.<sup>20</sup> When ClO<sup>-</sup> ions were added into the system, the handedness of self-assemblies and the CPL signs were inversed. Moreover, using supramolecular self-assembly strategies, even achiral molecules can contribute to CPL amplification and inversion. Jin and co-workers prepared nanofiber-based chiral silica through a templating approach, where its chiral Information can transfer from silica hosts to achiral luminescent guests and they obtained CPL-active materials.<sup>21</sup> Feng *et al.* demonstrated that the handedness of the CPL of hydrogels can be efficiently inverted by achiral coumarin derivatives through noncovalent interactions.<sup>22</sup>

We have developed supramolecular templating approaches based on supramolecular self-assembly to fabricate helical organic-inorganic hybrid silicas.<sup>23</sup> For instance, we prepared two single-handed helical tetraphenylethylene (TPE)-bridged polybissilsesquioxane (TPE-silica) nanotubes with CPL activities, through a supramolecular templating approach using TPE-containing bis(triethoxysilane) as the precursor, and self-assemblies of chiral cationic amphiphilic compounds as the templates.<sup>23c</sup> In the process of preparation of hybrid materials, the achiral component co-assembles with the chiral templates, and the self-assemblies are trapped in silica nanostructures. It can be predicted that adding achiral molecules, such as an inorganic silica source, to chiral self-assembly systems may change the packing of the molecules. Herein, a pair of Phe–Phe dipeptides with a tolane group, (L, L)- and (D, D)-T, were synthesized (Fig. 1), whose supramolecular assemblies showed CPL properties and high fluorescence efficiency. Single-handed helical hybrid silicas, (L, L)- and (D, D)-T-SiO<sub>2</sub>, were fabricated through a dynamic supramolecular templating approach using the assemblies of (L, L)- and (D, D)-T as templates, respectively.<sup>24</sup> They exhibited enhanced luminescence efficiency and CPL activities with inversed handedness.

#### **Experimental section**

#### Materials

N-[(1,1-Dimethylethoxy)carbonyl]-L-phenylalanine (Boc-L-Phe-OH), N-[(1,1-dimethylethoxy)carbonyl]-D-phenylalanine (Boc-D-Phe-OH), and O-benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluorophosphate





(HBTU) were purchased from GL Biochem Ltd. (Shanghai, China). L-Phenylalanine methyl ester hydrochloride and p-phenylalanine methyl ester hydrochloride were purchased from Sam Chemical Technology Co., Ltd (Shanghai, China). 4-Ethynylanisole, methyl 4-iodobenzoate, copper(1) iodide, bis(triphenylphosphine)palladium dichloride (Pd 15.2%), 3aminopropyltrimethoxysilane, tetraethyl orthosilicate, (R)-(+)-1phenylethanol and (S)-(-)-1-phenylethanol were purchased from Aladdin Chemical Co., Ltd (Shanghai, China). N,Ndimethylformamide (DMF), methanol (MeOH), dichloromethane (DCM), triethylamine  $(Et_3N)$  and tetrahydrofuran (THF) were obtained from Chinasun Specialty Products Co., Ltd (Changshu, China). DMF, Et<sub>3</sub>N and DCM were dehydrated by treatment with calcium hydride for over 24 h and then redistilled. Trifluoroacetic acid (TFA) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

#### General procedures for the synthesis of compounds

Synthesis of tolane-1. Tolane-1 was synthesized according to the literature.  $^{\rm 25}$ 

Synthesis of (L, L)-T and (D, D)-T. BOC-L-Phe-L-Phe-OMe and 4-[(4-methoxyphenyl)ethynyl]benzoic acid were synthesized according to the literature.<sup>26,27</sup> The dipeptides were prepared by a manual liquid phase synthesis procedure. All four dipeptides were prepared by a manual liquid phase synthesis procedure. A solution of Boc-L-Phe-L-Phe-OMe (2.00 g, 4.70 mmol) in a mixture of DCM:TFA (1:1) was stirred for 2 h at room temperature. A white powder (L-Phe-L-Phe-OMe-TFA) was obtained after removing the solvents. To a solution of 4-[(4-methoxyphenyl)ethynyl]benzoic acid (3.17 mmol), L-Phe-L-Phe-OMe-TFA (4.70 mmol), and HBTU (1.78 g, 4.70 mmol) in DMF, 5  $\times$  equivalent of Et<sub>3</sub>N (5.09 mL, 36.5 mmol) was added under an N2 atmosphere and stirred at 50 °C for 12 h. Then, the solution was washed with 5.0 wt% NaHCO<sub>3</sub> aqueous solution. After filtering, the resulting ester was dried and the formed precipitate was obtained after being recrystallized from methanol. Then, a solution of NaOH (219 mg, 5.48 mmol) in water (5 mL) was added slowly to a stirred suspension of the ester (1.5 g, 2.74 mmol) in MeOH (50 mL). The reaction mixture was refluxed for 2 h. Then, it was cooled to room temperature and poured into distilled water (400 mL). The mixture was acidified with diluted hydrochloric acid, then filtered and washed to neutral. The crude product was dried in vacuo at 55 °C. The target product (L, L)-T was obtained after being recrystallized from methanol. The synthesis of (D, D)-T was the same as (L, L)-T.

Characterization of (I, I)-T. Mp 264.8 °C.  $[\alpha]_D^{20} = -67.2$  (c = 1.0, MeOH). FT-IR (cm<sup>-1</sup>): 3284 ( $\nu_{N-H}$ , amide A), 2215 ( $\nu_{C \equiv C}$ ), 1741 ( $\nu_{C = 0}$ , -COOH), 1626, 1602 ( $\nu_{C = 0}$ , amide I), 1532, 1514 ( $\nu_{N-H}$ , amide II). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , TMS)  $\delta_{H}$ : 2.59–3.13 (m, 4H; ArCH<sub>2</sub>CH), 3.76 (s, 3H; OCH<sub>3</sub>), 4.35–4.55 (m, 1H; CONHCHCOOH), 4.60–4.80 (m, 1H; CONHCHCONH), 6.96 (d, 2H; J = 8.1 Hz, ArH), 7.06–7.35 (m, 10H; ArH), 7.76 (d, 2H; J = 7.6 Hz, ArH), 7.48 (d, 2H; J = 8.2 Hz, ArH), 7.53 (d, 2H; J = 8.1 Hz, ArH), 8.29 (d, 1H; J = 7.4 Hz, CONHCHCOOH), 8.60 (d, 1H; J = 8.2 Hz, CONHCHCO), 12.78 (s, 1H; NHCHCOOH) ppm. MS (MALDI-TOF) m/z [M + 2Na]<sup>+</sup>, calculated: 591.215; found: 591.218. Elemental analysis: calculated

(for  $C_{34}H_{30}N_2O_5$ ), C 74.71, H 5.53, N 5.12%; found, C 74.43, H 5.83, N 4.99%.

Characterization of (b, b)-T. Mp 261.3 °C.  $[\alpha]_D^{20} = +67.6$  (c = 1.0, MeOH). FT-IR (cm<sup>-1</sup>): 3295 ( $\nu_{N-H}$ , amide A), 2216 ( $\nu_{C \equiv C}$ ), 1741 ( $\nu_{C = 0}$ , -COOH), 1629, 1602 ( $\nu_{C = 0}$ , amide I), 1534, 1514 ( $\nu_{N-H}$ , amide II). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , TMS)  $\delta_{H}$ : 2.59–3.13 (m, 4H; ArCH<sub>2</sub>CH), 3.76 (s, 3H; OCH<sub>3</sub>), 4.35–4.55 (m, 1H; CONHCHCOOH), 4.60–4.80 (m, 1H; CONHCHCONH), 7.00 (d, 2H; J = 7.5 Hz, ArH), 7.09–7.40 (m, 10H; ArH), 7.52 (d, 2H; J = 7.6 Hz, ArH), 7.57 (d, 2H; J = 8.0 Hz, ArH), 7.80 (d, 2H; J = 7.1 Hz, ArH), 8.36 (d, 1H; J = 7.4 Hz, CONHCHCOOH), 8.65 (d, 1H; J = 7.7 Hz, CONHCHCO), 12.82 (s, 1H; NHCHCOOH) ppm. MS (MALDI-TOF) m/z [M + 2Na]<sup>+</sup>, calculated: 591.215; found: 591.238. Elemental analysis: calculated (for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>), C 74.71, H 5.53, N 5.12%; found, C 74.96, H 5.64, N 4.90%.

#### Preparation of self-assemblies and hybrid silicas

**Preparation of organic self-assemblies.** 10 mg of (L, L)-T/(D, D)-T (0.0183 mmol) was dissolved in 1.4 mL of pre-made aqueous NaOH (0.0366 mmol) solution (MeOH/H<sub>2</sub>O = 1:1, v/v). A white gel was instantly formed from the reaction mixture which was kept under static conditions at 0 °C for 12 h.

**Preparation of hybrid silicas.** 10 mg of (L, L)-T/(D, D)-T (0.0183 mmol) was dissolved in 1.4 mL of pre-made aqueous NaOH (0.0366 mmol) solution (MeOH/H<sub>2</sub>O = 1:1, v/v). The reaction mixture was kept under static conditions at 0 °C for 30 minutes. Then, APTMS (10  $\mu$ L, 0.0426 mmol) was added under vigorous stirring at 0 °C. Thirty seconds later, TEOS (30  $\mu$ L, 0.134 mmol) was added. One minute later, stirring was stopped. The reaction mixture was kept at 0 °C for 12 h.

#### General methods

The morphology study was performed on a Hitachi S-4800 field emission scanning electron microscope (Ibaraki prefecture, Japan) with an acceleration voltage of 3.0 kV. Before the FE-SEM images were taken, platinum was sputtered on the surface of the xerogel samples for 70 seconds to improve the conductivity and prevent the charging effect. Transmission electron microscopy (TEM) images were taken on a Tecnai G220 instrument operating at 200 kV. Circular dichroism (CD) and UV-vis spectroscopy studies were performed on a JASCO J-815 circular dichroism spectrometer (Tokyo, Japan) under a nitrogen atmosphere. CD and UV-vis spectra were recorded within a wavelength range from 200 to 600 nm with a bandwidth of 1.0 nm, a 1.0 nm-interval and an average scanning speed of 100 nm min<sup>-1</sup>. To eliminate the effect of linear dichroism, the CD spectra of the solid samples were measured using a plate holder which makes the samples rotate 360° in 22.5° increments. The fluorescence spectroscopy and quantum yields were performed on an Edinburgh Instrument FLS 980 (Edinburgh Instruments, UK), where the excitation wavelength was 320 nm. CPL spectra were measured on a JASCO CPL-300 (Tokyo, Japan). To eliminate the effect of linearly polarized luminescence, the CPL spectra of the solid samples were measured using a plate holder which makes the samples rotate  $360^{\circ}$  in  $22.5^{\circ}$  increments. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) analysis was

performed on a Varian NMR 400 spectrometer (Palo Alto, USA). Elemental analysis was performed on a PerkinElmer series II CHNS/O analyzer 2400 (Waltham, Massachusetts, USA). Mass spectra (MS) were obtained using an UltrafleXtreme MALDI TOF/TOF spectroscope (Bruker, USA). FT-IR spectra were recorded using a Bruker V70 spectrometer (Germany). Wide-angle X-ray diffraction (WAXRD) patterns were recorded using an X'Pert-Pro MPD X-ray diffractometer (Almelo, Netherlands) with Cu-Ka radiation (1.542 Å) and an Ni filter at room temperature. Optical rotation was measured with a RUDOLPH Autopol IV.

## Results and discussion

The gel-forming abilities of (L, L)- and (D, D)-T were explored. Since they were poorly soluble in water or aqueous solution of NaOH, they could not self-assemble to form hydrogels. (L, L)and (D, D)-T can cause physical gels in an NaOH (1.04 g L<sup>-1</sup>) solution of a mixture of methanol and water (1:1, v/v) at 0 °C. The field-emission scanning electron microscopy (FE-SEM) images indicated that the sodium salts of (L, L)- and (D, D)-T assembled into straight belts (Fig. 2a and b). The organic selfassemblies were covered by silica through a dynamic templating approach using 3-aminopropyltrimethoxysilane (APTMS) as the co-structure-directing agent and tetraethoxysilane (TEOS) as the silica source. Interestingly, the obtained hybrid silicas, (L, L)- and (D, D)-T-SiO<sub>2</sub>, were right- and left-handed coiled nanoribbons, respectively (Fig. 2c–f). Their helical pitches were about 1.0  $\mu$ m.

To understand the formation of the coiled structure, FE-SEM images of the reaction mixture were taken after different reaction times (Fig. 3). After the addition of APTMS and TEOS, APTMS co-assembled with the gelator, and twisted nanoribbons were identified at the terminals of the belts. With an extension of the reaction time, all of the belts transformed to twisted nanoribbons, and coiled nanoribbons were then formed. At the same time, silica oligomers originated from TEOS adsorbed on the surfaces of the coiled nanoribbons and copolymerized with the APTMS molecules. A schematic illustration of the formation of right- and left-handed coiled nanoribbons is shown in Fig. 4. Due to this morphological transformation from straight belt to coiled ribbon, the neighbouring tolane groups were proposed to pack in a twisted structure within the coiled nanoribbons.

To understand the organization of the tolane groups before and after silica covering, the wide angle X-ray diffraction (WAXRD) patterns of the xerogels of the sodium salts of (L, L)and (D, D)-T and the hybrid silicas were taken (Fig. S1, ESI†). For the xerogels, many sharp peaks were identified, indicating an ordered structure. The distance between neighbouring tolane groups was about 0.37 nm. For the hybrid silicas, the intensity of the diffraction peaks was low. The molecules did not pack in a long-range order. The distance between neighbouring tolane groups was about 0.41 nm. This molecular packing difference can drive the difference in optical activity.



**Fig. 2** (a–d) FE-SEM images of the xerogels of the self-assemblies of the sodium salts and organic–inorganic hybrid silicas. (a) (L, L)-**T**, (b) (D, D)-**T**, (c) (L, L)-**T-SiO<sub>2</sub>** and (d) (D, D)-**T-SiO<sub>2</sub>**. (e and f) TEM images of the organic–inorganic hybrid silicas. (e) (L, L)-**T-SiO<sub>2</sub>** and (f) (D, D)-**T-SiO<sub>2</sub>**.

To study the optical activity of the gelators before and after silica covering, CD and UV-vis absorption spectra were measured at a concentration of 7.14 g  $L^{-1}$  (Fig. 5). The UV



Fig. 4 Schematic illustration of the formation of right- and left-handed coiled nanoribbons.

absorption bands at a wavelength longer than 300 nm originated from the tolane group. The CD signals of the enantiomers present mirror symmetry. For (L, L)-T, a broad and weak positive CD signal was identified at  $\sim$  418 nm, and a negative one was identified at 338 nm. According to the exciton chirality method, the sign of the signal at the longer wavelength determines the exciton chirality.<sup>14a</sup> The negative CD signal at 320 nm originated from the electron transition within the tolane group under a chiral surrounding condition. To confirm the origin of the CD signals, the CD spectra of tolane-1 in (R)and (S)-1-phenylethanol were taken at a concentration of  $10^{-4}$  M (Fig. S2, ESI<sup>†</sup>). The results confirmed that the CD signal at  $\sim$  320 nm originated from the electron transition within the tolane group. After being covered by silica, the intensity of the CD signals decreased sharply (Fig. 5b). For (L, L)-T-SiO<sub>2</sub>, an obvious broad positive signal was identified at 363 nm. Moreover, the intensity ratio of the signals at 342 and 323 nm was increased. The neighbouring tolane groups are proposed to pack in a twisted structure.

Tolane derivatives are usually highly emissive in both solution and solid state.<sup>28</sup> The emission spectra of (L, L)-T in the methanol/water mixtures with different water fractions ( $f_w$ ) are displayed in Fig. S3 (ESI†). (L, L)-T showed purple fluorescence with a band at 418 nm in methanol. With an increase in the  $f_w$  values (<60%), the emission intensity decreased gradually. Moreover, the emission maximum red-shifted to 443 nm with



Fig. 3 FE-SEM images of hybrid silicas taken after different aging times. (a–f) (L, L)-**T-SiO<sub>2</sub>**, (g–l) (D, D)-**T-SiO<sub>2</sub>**. Note that 'before' refers to before adding TEOS and APTMS, 'after' refers to after adding TEOS and APTMS.



Fig. 5 CD and UV-vis spectra of (a) the self-assemblies of the sodium salts and (b) the hybrid silicas.

Abs

Abs

550

550

an increase in the polarity of the solvent, that could be attributed to the intramolecular charge transfer (ICT) between the electron donor (-OCH<sub>3</sub>) and the electron acceptor (-COOH).<sup>28b,29</sup> The increased  $f_w$  raised the polarity of the system and stabilized the charge separation, and thus drove the equilibrium to the ICT state. As the  $f_w$  value increased continuously ( $f_w > 60\%$ ), the emission intensity increased progressively, and the emission maximum blue-shifted to 400 nm, showing aggregation-induced emission (AIE) characteristics. This demonstrates that (L, L)-T exhibited both ICT and AIE features in the methanol/water mixtures. Due to the competition between the ICT and AIE effects, the highest intensity was not recorded at an  $f_w$  of 90%. The fluorescence quantum yields ( $\Phi_{\rm F}$ ) of (L, L)- and (D, D)-T in methanol measured using an integrating sphere were 34.6% and 34.7%, respectively (Table S1, ESI†).

Photographs of the (L, L)-T solution in methanol and physical gel in an NaOH  $(1.04 \text{ g L}^{-1})$  solution of a mixture of MeOH and  $H_2O$  (1:1, v/v) and (L, L)-T-SiO<sub>2</sub> powder are shown in Fig. 6. All the samples emitted purple light at about 380 nm under 365 nm UV light. The emission spectra of the xerogels of the selfassemblies and hybrid silica powders are given in Fig. 7a. The  $\Phi_{\rm F}$ values of (L, L)-T, (D, D)-T, (L, L)-T-SiO<sub>2</sub> and (D, D)-T-SiO<sub>2</sub> are 53.1%, 51.7%, 56.7% and 56.3%, respectively (Table S1, ESI<sup>†</sup>). The values of the hybrid silicas are higher than those of the selfassemblies. This may be due to the fact that the inorganic matrix can greatly restrict the intramolecular motions of tolane units, and protect the fluorophors from coming into contact with reactive oxygen species.<sup>30</sup> It is worth noting that the  $\Phi_{\rm F}$  values of hybrid silicas, (L, L)-T-SiO<sub>2</sub> and (D, D)-T-SiO<sub>2</sub>, are higher than those (26.2% and 21.2%) of TPE-Silicas in our previous work.<sup>23c</sup>

The intense fluorescence and molecular chirality of the tolane-conjugated dipeptides prompted us to investigate the CPL properties of their self-assemblies before and after silica





Fig. 6 Photographs of the (L, L)-T solution in methanol at a concentration of  $1.0 \times 10^{-4}$  M and physical gel at a concentration of 7.14 g L<sup>-1</sup> in an NaOH (1.04 g  $L^{-1}$ ) solution of a mixture of MeOH and H<sub>2</sub>O (v/v = 1/1) under (a) natural and (b) 365 nm UV light and those of the (L, L)-T-SiO<sub>2</sub> powder under (c) natural and (d) 365 nm UV light.



Fig. 7 (a) Emission and (b) CPL spectra of the xerogels of the sodium salts of the dipeptides and hybrid silicas, (c) CD and UV-vis, and (d) CPL spectra of (L, L)- and (D, D)-T solution in methanol at a concentration of  $1.0 \times 10^{-4}$  M,  $\lambda_{\rm ex} = 320 \ \rm nm$ 

covering. As expected, both the xerogels of the sodium salts of the dipeptides and the hybrid silicas showed CPL activity. Almost mirror images were observed in the CPL spectra (Fig. 7b). The  $g_{lum}$  values of the xerogels of the sodium salts of (L, L)-T and (D, D)-T were calculated to be about  $-2.3 \times 10^{-3}$ and +1.1  $\times$  10<sup>-3</sup>, respectively, whereas the  $g_{lum}$  values of (L, L)-T-SiO<sub>2</sub> and (D, D)-T-SiO<sub>2</sub> were about  $+4.4 \times 10^{-3}$  and  $-5.4 \times 10^{-3}$ . respectively (Table S2, ESI<sup>†</sup>). It should be noted that the  $|g_{lum}|$ values of the hybrid silicas are higher than those of the xerogels, and TPE-silica ( $-0.6 \times 10^{-3}$  and  $+1.6 \times 10^{-3}$ ).<sup>23c</sup> Furthermore, the CPL spectra of the xerogels and hybrid silicas exhibited inversed signals. The difference in the packing structures of the tolane groups within the xerogels and hybrid silicas should drive these phenomena. Within the xerogels, the neighbouring tolane groups stack in a parallel or an antiparallel structure. Then, straight ribbons are formed. Since the neighbouring tolane groups do not stack in a chiral manner, the handedness of the CPL signals of the xerogels should be driven by the chiral surrounding condition formed by the Phe-Phe dipeptide residues. Within the hybrid silica with

a coiled morphology, the neighbouring tolane groups stack in a chiral manner. The handedness of the CPL signals of the hybrid silicas should be mainly dominated by the stacking handedness of the neighbouring tolane groups.

For a better understanding of the origin of the CPL signals, CD and CPL spectra of (L, L)- and (D, D)-T were measured in methanol at a concentration of  $1.0 \times 10^{-4}$  M. As shown in Fig. 7c, the CD signal at 315 nm originated from the electron transition within the tolane group and no CD signals were observed at longer wavelength, indicating that there was no chiral stacking among the tolane groups. The CPL spectra showed that (L, L)- and (D, D)-T in methanol exhibited weak negative and positive signals, respectively (Fig. 7d). The signs of the signals were the same as those of their CD signals. The CD and CPL signals at long wavelength should originate from the electron transition within the tolane group.

## Conclusions

In summary, we have prepared a pair of tolane-conjugated dipeptides, (L, L)-T and (D, D)-T, and two single-handed helical hybrid silicas, (L, L)-T-SiO<sub>2</sub> and (D, D)-T-SiO<sub>2</sub>, through a dynamic supramolecular templating approach. The xerogels of the self-assemblies of the sodium salts of (L, L)-T and (D, D)-T showed good CPL performance with  $g_{\text{lum}}$  values of  $-2.3 \times 10^{-3}$  and  $+1.1 \times 10^{-3}$ , and the  $\Phi_{\text{F}}$  values of 53.1% and 51.7%, respectively. (L, L)-T-SiO<sub>2</sub> and (D, D)-T-SiO<sub>2</sub> exhibited enhanced CPL activities with inversed handedness ( $+4.4 \times 10^{-3}$  and  $-5.4 \times 10^{-3}$ ), and high fluorescence efficiency with  $\Phi_{\text{F}}$  values of 56.7% and 56.3%, respectively. It was found that silica covering induced intensity enhancement and handedness inversion of the CPL signals of the supramolecular assemblies, due to the change of the arrangement of the tolane groups.

## Conflicts of interest

There are no conflicts to declare.

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