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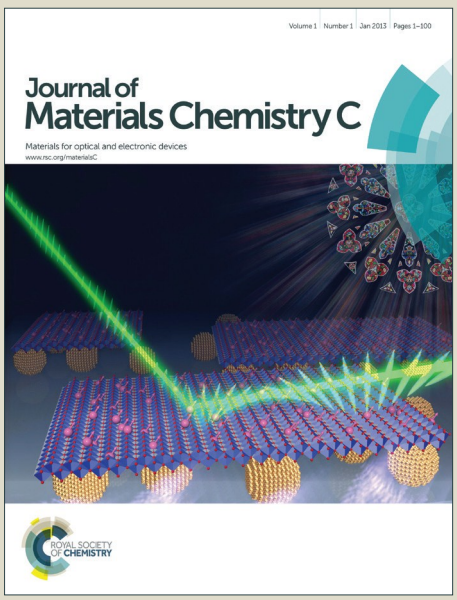

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ARTICLE TYPE

Controllable Multicolor Switching of the Oligopeptide-based Mechanochromic Molecules: From Gel Phase to Solid Powder

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A series of molecules with pyrene and rhodamine B as the color producing mechanophores that were linked by different spacers were synthesized and their mechanochromic properties were studied. Interestingly, we found that the molecule with diphenylalanine as a linker (PHE-2) showed a sequential multicolored switch from deep blue to bluish green and further to a reddish color, which was associated with the phase change from gel to xerogel as the solvent evaporated, and to a solid powder triggered by grinding. However, the gel and xerogel of the molecule with the link of pentaphenylalanine (PHE-5) exhibited the same deep blue color that switched to bluish green and further to a reddish powder by virtue of continuous grinding the xerogel sample in situ. The multicolored switch of PHE-2 and PHE-5 is realized by the variation of self-assembled structures, which induced the pyrene excimers transition from excimer 1 (deep blue) to excimer 2 (bluish green), and by the chemical reaction of rhodamine B from a spirolactam to a ring-opened amide (red). From the experimental results, we may conclude that the crucial point for controlling and tuning tricolored fluorescent switch of this system is to constrict the pyrene excimer in an overlapped packing mode, which can be achieved (1) by controlling the molecular structure; and (2) by confining the excimers of pyrene in a restricted environment.

Introduction

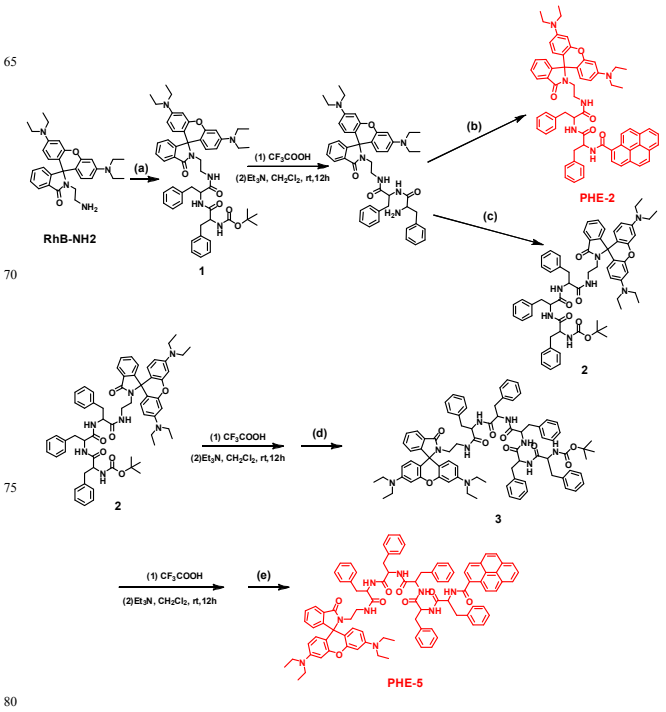
The development of organic fluorescent materials with tunable emissions to mimic the wonderful colors in nature has been a pursuit goal,[1] which is of great importance in fundamental research and in practical applications including photo switches,[2] light and display devices,[3] templates, sensors[4] and other related fields. To this end, much effort has been paid to seek simple and efficient ways for the fluorescent materials with high performance.[5] Recent advance in mechanochemistry provides an efficient strategy for tuning the luminescent properties of solid materials.[6] As reported, the molecular orientation and intermolecular interactions in the systems can be perturbed by external force, such as grinding, shearing, crushing, tension and hydrostatic pressure etc., which affords the materials to undergo a dramatic fluorescent emission color change.[7] Compared to other stimuli, mechanical stimulus may be less well progressed but it has the superiorities of simple operation process, environmentally clear and safe, and easy to be handled as a credible powder source in our daily life.[8] Up to now, a number of mechanochromic systems were reported, such as the aggregated organic molecules,[1b] liquid crystals,[1d] organometallic compounds,[1c] polymers[6b] and dye-doped polymers.[4c] However, to govern the force induced fluorescent color change in a controllable way rather than a serendipitous and random screening result remains in the preliminary stage with limited examples due to the absence of rational design concept. Moreover, the understanding of and the ability to modulate the molecular aggregation state are yet a challenging subject although it is very important for the development of mechanochromic materials.

We previously reported a multicolored co-aggregate and a single organic molecule whose color changed sequentially from blue to green and to reddish in response to an external force.[9] The multicolored emission could be tuned simply by different packing of the chromophores and a force-induced ring-opening reaction. What puzzles us is how to make such a tricolored switching in a controllable way but not a serendipitous result and whether we can conduct such a molecular system to achieve controllable multicolored change by altering molecular structure or via modulating the phases of a compound. With this in mind, we designed the molecules with pyrene and rhodamine B as the color producing mechanophores which bridged by different spacers and examined their mechanochromic properties. In our previous work, we found that when the chromophores of pyrene and rhodamine B were linked by tetraphenylalanine as a spacer, it could change colors from blue to bluish-green and further to a reddish color. [9a] However, no tricolored switch was observed when the linking spacer was an aliphatic chain due to its softer nature and the stability of the sandwich packing of pyrene units, indicating that the spacer played an important role in the color switch.[10] We then designed and synthesized the molecules with combined alanine and phenylalanine fragments as the links (Supporting Information, Scheme S1). As a result, these molecules showed either no tricolored transition or only inconspicuous color change (Figure S1&S2). Hence, we built spacers by using different phenylalanine units to introduce rigid benzene rings in the structure for expecting the achievement of

controllable arrangement of dimeric pyrene units. Moreover, we tried to fabricate the gel phase from these molecules for creating a restrict environment to further confine the molecular packing mode. For a short and clear description, herein we mainly focus on the mechanochromic properties of the molecules with diphenylalanine (PHE-2) and pentaphenylalanine (PHE-5) as the spacers (the molecule PHE-1 with one phenylalanine as a spacer is shown in Scheme S1. It only showed two colors' change by grinding and did not discussed in this article), from which we may further understand the multicolored switch related to the molecular structures and different phases of a compound, and find a simple and efficient way for controlling the multicolored switch. PHE-2 was constructed with diphenylalanine as a spacer to link pyrene and rhodamine B at each side. It could form a fluorescent gel in organic solvent. Notably, an orderly color change of PHE-2 from deep blue to bluish green and further to a reddish color was observed, which was associated with the phase change from gel to xerogel as the solvent evaporated, and to a solid powder triggered by force. For advancing our knowledge on the structure-emission relationship, PHE-5 with the same chromophores but using pentaphenylalanine as a spacer was synthesized (PHE-5). The luminescent gel of PHE-5 showed deep blue color while its xerogel maintained the same color, which behaved differently from PHE-2. Upon continuous force perturbation, the deep blue color of the PHE-5 xerogel sample changed to bluish green and further to reddish. Such results evidence clearly that the arrangement of molecules correlates with (1) the molecular structure and (2) the molecules' existing environment, and indicate that the molecular spacer and the phase structure conduct the distinct chromophores packing and in consequence the emission characteristics. To the best of our knowledge, there are few reports in literature showing the controllable multicolored change by altering molecular structure and by adjusting molecular arrangement in different phases. Moreover, turning the gel phase with different colors[11] and developing stimuli-responsive xerogels are rarely described even though the ultrasound and mechanical stress driven/responsive organogels have been examined and summarized recently.[12] For example, J. B. Beck and S.J. Rowan used reversible metal-ligand interactions to construct the metallo-supramolecular gel-like systems with mechano-responsive property by showing a thixotropic (shear-thinning) behavior.[13] N. Clarke and J. W. Steed et al. prepared the simple copper (II) bromide-based metallogels that transformed from weak gel-like materials to robust gels upon shearing.[14] Such force perturbation transformed the system to a 3D gel network.

Results and discussion

The designed compounds PHE-2 and PHE-5 were synthesized in a similar way by using rhodamine B (the ring-opened form) as a starting reagent that reacted with ethylenediamine to afford the compound in a spirolactam form[15] (RhB-NH2, Scheme 1); then a standard DCC coupling of RhB-NH_2 and Boc-protected diphenylalanine (Boc-PHE-PHE-OH) gave the intermediate 1; the desired spacers were obtained by removing the Boc group of 1 and then linking it with the Boc-PHE-OH and Boc-PHE-PHE-OH; finally, the target molecules were obtained through connecting 1-pyrenecarboxylic acid with the spacer chains. The synthetic route and the structures of PHE-2 and PHE-5 are shown in Scheme 1. ^{1}H NMR, ^{13}C NMR and HRMS measurements were used to verify the structure and purity of them. The detailed synthetic procedures and characterization of the corresponding molecules are described in the Supporting Information.



Reaction conditions: (a) Boc-PHE-PHE-OH(purchased), DCC, HOBt, ice-salt bath, 48h; (b) 1-pyrenecarboxylic acid, DCC, HOBt, DMAP, ice-salt bath, 96 h. (c) Boc-PHE-OH, DCC, HOBt, ice-salt bath, 48 h; (d) Boc-PHE-PHE-OH, DCC, HOBt, ice-salt bath, 72 h; (e) 1-pyrenecarboxylic acid, DCC, HOBt, DMAP, ice-salt bath, 96 h.

Scheme 1. The synthesis of PHE-2 and PHE-5.

In order to investigate the multicolored switching of these compounds, the gelation ability of PHE-2 and PHE-5 was examined in different organic solvents for restricting the molecules in a confined environment. To avoid evaporation of the liquid components, gels were prepared in a sealed vial (i.d ≈ 1 cm). The weighed PHE-2 and PHE-5 were heated to a homogeneous solution. Then, the vial was placed at room temperature for a sufficient time. If the cooled samples were not visually phase-separated and did not flow perceptibly when the vials were inverted, they were considered to be gels. The gelation ability of the compounds is summarized in Table 1. As observed, both PHE-2 and PHE-5 displayed good solubility in the polar solvents of dichloromethane, chloroform and dimethylformamide (DMF), however, they formed precipitates in the nonpolar solvent of n-hexane and in the high polar solvent of methanol. PHE-2 also dissolved in acetone and tetrahydrofuran (THF), whereas PHE-5 precipitated in acetone. PHE-2 only formed a transparent gel in ethyl acetate at a concentration of 14.6 mg·mL^{-1} (Figure 1a). In comparison, PHE-5 gelated in THF at a higher concentration of 43.1 mg·mL^{-1} and formed an opaque gel in the mixed solvent of CH_2Cl_2/ethyl acetate (3:1, v/v) at a concentration of 12.6 mg·mL^{-1} (Figure 1c). This difference in gelation behavior indicates that PHE-5 is a more polar compound due to more amide fragments included in its spacer.

The morphologies of the xerogels obtained from PHE-2 in ethyl acetate and PHE-5 in the CH_2Cl_2/ethyl acetate were observed by transmission electron microscopy (TEM). The

xerogels exhibited highly developed and intertwined fibrous networks with a large aspect ratio (length over width). TEM images showed that the fiber density of PHE-2 gel was higher than that of PHE-5 gel. The interconnected fibers from PHE-2 were hundreds of nanometers long and approximately 15 nm wide (Figure 1b), and the fibrous networks of PHE-5 showed above several micrometers in length and approximately 50 nm in width (Figure 1d).

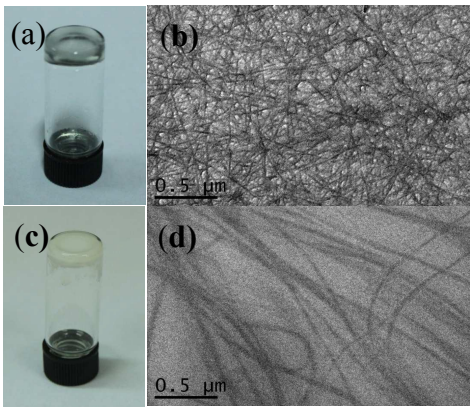


Figure 1.The pictures of gels from (a) PHE-2 and (c) PHE-5; TEM images of (b) PHE-2/ethyl acetate xerogel and (d) PHE-5 xerogel obtained from mixed solvent of CH_2Cl_2/ethyl acetate. The samples were prepared on a copper grid covered with carbon film.

Of much interest is that PHE-2 shows a sequential tricolored switch in different states. The PHE-2 gel in ethyl acetate emitted a deep blue color under UV-light. When the solvent was evaporated, we observed a piece of film-like xerogel with a bluish green color. Sequentially, grinding the film-like xerogel in situ with a spatula, a reddish solid powder was obtained (Figure 2a-2c). However, PHE-5 displayed different behavior. It gelated in a mixed solvent of CH_2Cl_2/ethyl acetate (3:1, v/v). The gel exhibited a deep blue color and this color retained as the solvent was removed from the system. Upon slightly grinding and further force disturbance in situ, we observed that the deep blue color of PHE-5 xerogel transformed to a bluish green solid and to a reddish powder sequentially (Figure 2d-g). We used the Confocal Laser Scanning Microscopy (CLSM) to further monitor the emission colors of PHE-2 and PHE-5 xerogels. Evidently, the fibers of PHE-2 gave a bluish green color (Figure 2h), while the fibrous networks from PHE-5 displayed the deep blue emission (Figure 2i). The visualized color change of gels and xerogels from PHE-2 and PHE-5 is an interesting but rarely described example, which confirms that (1) pyrene units may be arrayed by a similar way in both gel phase assemblies, however they adopt different packing patterns when the solvents are eliminated; (2) the gel phase provides a restrict space in which pyrene units are confined to arrange in a partially overlapped mode; (3) the molecular structure is crucial for modulating the chromophores packing.

The fluorescent measurement was performed to evidence the distinct emission of PHE-2 and PHE-5 in different states. Firstly, we measured the emission of PHE-2 solution in ethyl acetate at a concentration of 9.8 $mg \cdot mL^{-1}$. As a result, we found that the solution of PHE-2 exhibited an emission band at 404 nm, which was assigned to the monomeric emission of pyrenyl moiety. For the gel sample of PHE-2, a peak at 410 nm with a shoulder was observed, while the emission wavelength dramatically red-shifted to 480 nm with enhanced emission intensity (τ=53.62 ns) when the gel became to the xerogel. We also measured the emission of the as-prepared solids of PHE-2 that showed the emission at 480 nm, according with the PHE-2 xerogel. As a result of in situ grinding, the xerogel exhibited a new peak at 585 nm with a reddish color (Figure 3a). As for the sample of PHE-5, the gel in the mixed solvent emitted at 429 nm. This peak red-shifted only 6 nm and centered at 435 nm when the solvent was removed. Slightly grinding the dried gel with a spatula, a red-shifted luminescence band at 465 nm with a bluish green color (τ=58.34 ns) was observed. Further with heavy force disturbance, a new peak at 580 nm was detected for a reddish powder (Figure 3b).

Table 1. Gelation behavior of PHE-2 and PHE-5 in the common organic solvents at room temperature.

Solvent	PHE-2 CGC[a]	PHE-5 CGC[a]
Ethyl acetate	G(14.6)	P
Dichloromethane	S	S
Chloroform	S	S
DMF	S	S
n-Hexane	P	P
Methanol	P	P
Acetone	S	P
Tetrahydrofuran	S	G(43.1)
Dichloromethane/ Ethyl acetate (3:1,v/v)	n.d.	G(12.6)

[a] G, P and S denote gelation, precipitation and solution, respectively. n.d. denotes no data. The critical gelation concentration (CGC, $mg \cdot mL^{-1}$) is shown in parentheses and S represents no gel formed below 100 $mg \cdot mL^{-1}$.

We propose that the deep blue and bluish green emissions of PHE-2 arise from different packing of pyrene units in the gel and xerogel states. As known, the partially overlapping packed dimeric units of pyrene emit at shorter wavelength with a deep blue color, low quantum yield and short lifetime (E1). E1 is an unstable excimer and usually exists in a restricted environment, such as crystals and viscous liquid. The stable excimer of pyrene (E2) shows at longer wavelength with a bluish green color, higher quantum yield and longer lifetime due to the sandwich packing with enhanced π-π interaction.[16] In our case, the gel phase of PHE-2 resembles that of a restricted environment, which limits the movement of pyrene units and impels them to adopt a partially overlapped packing mode although few E2 may be coexisted with E1 in the PHE-2gel phase, thus to give a deep blue color. With the solvent withdrawn, the pyrene units may slip to a sandwich arrangement with the bluish green emission for achieving a thermodynamic steady state. Such color change indicates a transformation of pyrene excimers from E1 to E2 in the system. The unchanged deep blue color of PHE-5 gel and xerogel implies that the pyrene excimers are fixed in the orientation of partially overlapped packing in the system. This result correlates to the molecular structure of PHE-5 with a pentaphenylalanine spacer which further astricts the movement of

pyrene units as compared to PHE-2 with diphenylalanine as a link. That means the spacer of pentaphenylalanine constrains the pyrene units to be partially overlapping packed either in the restrict gel phase or in the xerogel state. As for the reddish color of the ground PHE-2 and PHE-5 xerogel samples, it is due to a force-induced chemical transformation of rhodamine B from a spirolactam into a ring-opened amide.

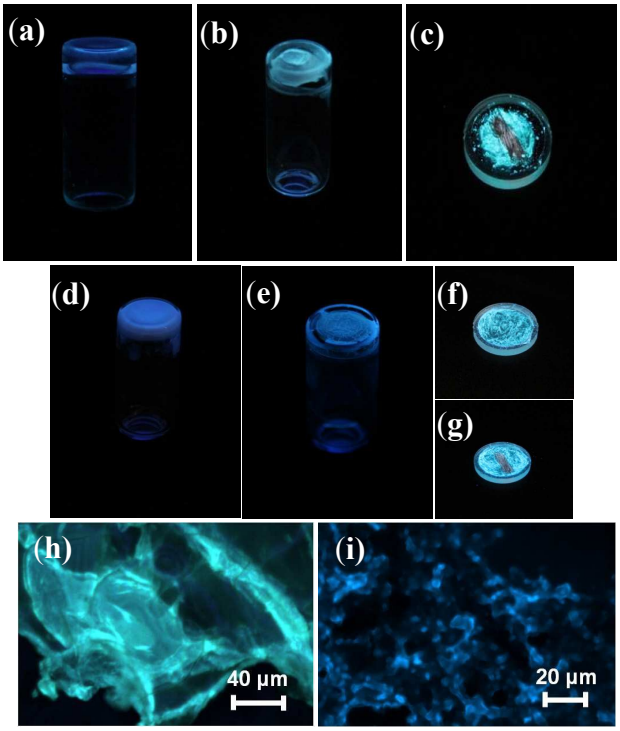


Figure 2. The pictures of (a) PHE-2 gel; (b) PHE-2 xerogel; (c) PHE-2 xerogel after grinding; (d) PHE-5 gel; (e) PHE-5 xerogel; (f) PHE-5 xerogel after slightly grinding; (g) PHE-5 xerogel after further grinding; (h) CLSM image of PHE-2 xerogel and (i) CLSM image of PHE-5 xerogel. The pictures (a-g) were taken under UV light.

The different arrangement of pyrene units invariably associates with the molecular self-assembled structures. Hence, differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) measurements were employed to further elucidate the microstructures of the fibrous networks from PHE-2 and PHE-5. Very interestingly, significant differences were detected. The DSC profiles of PHE-5 xerogel showed an endothermic peak and an exothermic peak in the heating and cooling cycles at 175 ^{o}C and 162 ^{o}C, respectively. In contrast, PHE-2 xerogel only exhibited an endothermic peak at 136 ^{o}C in the first heating cycle, implying a recrystallization of PHE-5 upon cooling from the melt (Figure S3). The SAXS profile of PHE-2 assemblies displayed two major diffraction peaks with the scattering vector ratio of 1 : 2, verifying a lamellar packing with a d spacing of 1.58 nm (Figure 3c), smaller than the calculated molecular size of PHE-2 (Figure S5a). As PHE-2 xerogel showed bluish green color, pyrene units in the lamellar structure were face-to-face arranged in a sandwich pattern that was transformed by sliding the partially overlapped dimeric pyrene units. While SAXS profile of PHE-5 showed two major diffraction peaks at the low angle, whose scattering vector ratio was 1 : √3 that could be ascribed to (100), (110) reflection of a hexagonal columnar packing (Figure 3d). The calculated column diameter was 2.42 nm, which corresponded to the optimized geometry of PHE-5 with the molecular length of 2.06 nm (Figure S6a). In such an assembled structure, most of the pyrenyl moieties were partially overlapped with each other, which led to a deep blue emission. Obviously, the different stacking modes of molecules in the gel and xerogel samples reasonably resulted in different emission colors. Moreover, the SAXS profiles of ground PHE-2 and PHE-5 samples exhibited the disappearance of diffraction peaks, indicating the damage of self-assembled lamellar and columnar architectures (Figure S4). It meant that the ground samples with either a bluish green color or a reddish color were amorphous.

We deduce two molecular models of the lamellar mode and the hexagonal columnar packing according to the experimental results as shown in the Supporting Information (Figure S5&S6). As the lamellar period is smaller than twice the extended molecular length of PHE-2, interdigitated bilayer may be easily formed via intermolecular hydrogen bonds and π-π stacking interactions. We suppose that pyrenyl units in PHE-2 gel phase are constrained yet to be partially overlapping packed in a layered pattern, thus the pyrene moieties are liable to slip for achieving a more stable face-to-face arrangement. As the PHE-5 gel emitted a blue color at 429 nm, most of the pyrenyl groups in the hexagonal columnar pattern were speculated to be arrayed on one side to match the partly overlapped packing mode. The column may grow by a helical-like manner with pyrenyl units in the center and rhodamine B branches at the outside. In such a packing way, by comparison, pyrenyl units are in a more restricted environment which may obstruct them to adopting a sandwich arrangement only by removing the solvent from the system.

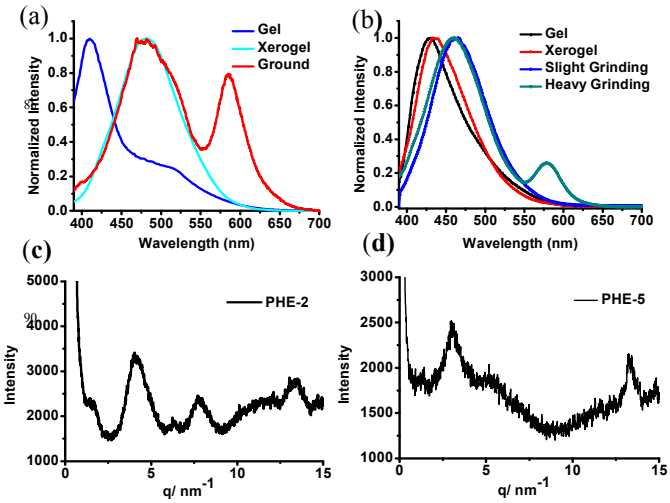


Figure 3. Fluorescent spectra of (a) PHE-2 gel, xerogel and the same sample upon grinding; (b) PHE-5 gel, xerogel and the same sample upon slightly and heavily grinding (λex= 365 nm); SAXS patterns of (c) PHE-2 xerogels and (d) PHE-5 xerogels before grinding.

To confirm our assumption of lamellar and helical-like columnar packing modes from PHE-2 and PHE-5 molecules, we run the Circular Dichroism (CD) measurement of the PHE-2 and PHE-5 samples at different temperatures. It was found that PHE-5 sample gave a negative signal at 275 nm and a broad band from 345 nm to 376 nm, in accordance with the phenylalanine and pyrenyl moieties in the aggregates. These signals disappeared when the temperature increased to 60 ^{o}C (Figure 4b). Such results support our speculation that the PHE-5 molecules adopt an ordered helical-like column packing in the gelation process. Differently, the PHE-2 sample exhibited a strong negative signal at 290 nm at room temperature, mainly attributed to the π-π transition of the phenylalanine residues (Figure 4a). This signal decreased and finally disappeared with increasing the temperature to 60 ^{o}C (Figure 4b), thus indicating the establishment of a chiral

lamella pattern in the gelation process. In addition, we found that the solution sample of PHE-2 showed the characteristic stretching absorption band of amide I band at 1670 cm^{-1}, while in the xerogel state, amide I band split into two bands at 1680 cm^{-1} and 1635 cm^{-1} (Figure S7), which implied that the amide bonds in the fibrous networks from PHE-2 were possibly related to an anti-parallel β-sheet-like conformation. This result was in accordance with that reported previously in the literature.[17]

The hydrogen bonding of the amide groups and the π-π stacking of phenyl groups may play the key roles in the aggregated structures of PHE-2 and PHE-5. Fourier transform infrared spectroscopy (FTIR) measurement was performed to further confirm the self-assembled structures at the molecular level. For the xerogels of PHE-2 and PHE-5, the characteristic stretching absorption band of the hydrogen bonded form of amide N-H groups was observed at about 3290 cm^{-1}, which is considerably lower than the position of the absorption band for a free N-H group (ca. 3400 cm^{-1}). Upon mechanical grinding, these bands gradually weakened and broadened, indicating the destruction of hydrogen bonds and the conversion from the ordered structures to the amorphous phase (Figure S7 and S8).

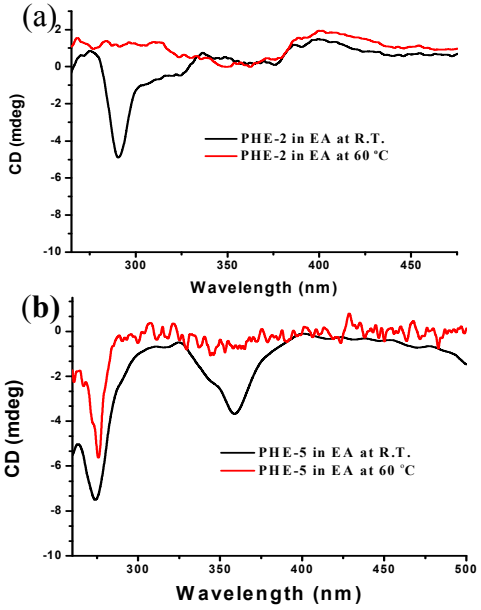


Figure 4. CD spectra of (a) PHE-2 and (b) PHE-5 samples in ethyl acetate at different temperatures.

The tricolored luminescence switching of PHE-2 and PHE-5 samples is reversible but behaved differently. The deep blue color of PHE-5 could be fully recovered by heating the reddish powder at 170 °C for several minutes (Figure S9). Such phenomenon was quite different from the molecule with a spacer of tetraphenylalanine as we reported previously. The recovery of deep blue color of that molecule required heating and solvent treating. Dissimilarly, the reddish powder of PHE-2 could only convert to a bluish green color but not a deep blue emission by heating it at the conditions mentioned above. In addition, by fuming with solvents, the bluish-green emission of PHE-2 couldn't recover to deep-blue color because the excimer of pyrene with a sandwich packing is more stable due to the enhancement of π-π interaction. Dissolving the recovered powder in solvents (ethyl acetate or CH_2Cl_2/ethyl acetate), the gels with deep blue color could be obtained again (Figure S10).

Based on the above results and analysis, the mechanically induced multicolored switch of PHE-2 and PHE-5 samples in different states could be summarized as follows: both of the gels of PHE-2 and PHE-5 emitted deep blue luminescence because of the partially overlapped packing of pyrene excimers either in a lamellar or in a helical-like hexagonal column, indicating the pyrene moieties were confined in the gel phase. Upon removing the solvent, the assembled lamellar structure of PHE-2 slipped, which led to a sandwich stacking of pyrene units and resulted in the transition of excimers from E1 to E2 with the bluish green color. However, the assembled column structure of PHE-5 could not be altered by eliminating the solvent, and the variation of excimers from E1 to E2 in such a system was triggered by virtue of external force perturbation. Sequentially, extreme force perturbation induced a reddish color, which was due to the ring-opening reaction of rhodamine B from a spirolactam to a ring-opened amide. From the aforementioned results, we may conclude that the crucial point for controlling and tuning tricolored fluorescent switch of phenylalanine oligopeptide-based system is to constrict the pyrene excimer in an overlapped packing mode, which can be achieved (1) by controlling the molecular structure; and (2) by confining the excimers of pyrene in a restricted environment.

Conclusions

In summary, we report two organic molecules of PHE-2 and PHE-5 with the same chromophores of pyrene and rhodamine B but different number of phenylalanine units as the spacers. The fluorescent gels could be constructed from either a signal molecule of PHE-2 or a signal molecule of PHE-5. The PHE-2 gel exhibited sequential multicolored fluorescent emission with the gel changing to xerogel by removing the solvent and further to a solid powder by grinding. However, the variation of deep blue color of PHE-5 sample required external force action. Upon continuous grinding in situ, a bluish green color and further to a reddish powder was observed. The multicolored switch of PHE-2 and PHE-5 is realized by the variation of self-assembled structures, which induced the pyrene excimers transition from E1 with a deep blue color to E2 showing a bluish green emission; and by the ring-opening reaction of rhodamine B from a spirolactam to a ring-opened amide. In order to control the tricolored switch of this system, the crucial point is to constrict the pyrene excimer in an overlapped packing mode either by controlling the molecular structure or by confining the excimers of pyrene in a restricted environment. These results may not only reveal the relationship between the supramolecular structure and photophysical property, but also provide a broad perspective for the design of novel multicolored mechanochromic materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of experimental sections, including synthesis, characterization, spectra, SAXSS patterns and optical images]. See DOI: 10.1039/b000000x/

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Controllable Multicolor Switching of the Oligopeptide-based Mechanochromic Molecules: From Gel Phase to Solid Powder

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A series of molecules with pyrene and rhodamine B as the color producing mechanophores that were linked by different spacers were synthesized and their mechanochromic properties were studied. Interestingly, we found that the molecule with diphenylalanine as a linker (PHE-2) showed a sequential multicolored switch from deep blue to bluish green and further to a reddish color, which was associated with the phase change from gel to xerogel as the solvent evaporated, and to a solid powder triggered by grinding. However, the gel and xerogel of the molecule with the link of pentaphenylalanine (PHE-5) exhibited the same deep blue color that switched to bluish green and further to a reddish powder by virtue of continuous grinding the xerogel sample in situ. The multicolored switch of PHE-2 and PHE-5 is realized by the variation of self-assembled structures, which induced the pyrene excimers transition from excimer 1 (deep blue) to excimer 2 (bluish green), and by the chemical reaction of rhodamine B from a spirolactam to a ring-opened amide (red). From the experimental results, we may conclude that the crucial point for controlling and tuning tricolored fluorescent switch of this system is to constrict the pyrene excimer in an overlapped packing mode, which can be achieved (1) by controlling the molecular structure; and (2) by confining the excimers of pyrene in a restricted environment.