Selective Coassembly of Aromatic Amino Acids to Fabricate Hydrogels with Light Irradiation-Induced Emission for Fluorescent Imprint

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Controlling the structural parameters in coassembly is crucial for the fabrication of multicomponent functional materials. Here a proof-of-concept study is presented to reveal the α-substituent effect of aromatic amino acids on their selective coassembly with bipyridine binders. With the assistance of X-ray scattering technique, it is found that individual packing in the solid state as well as bulky effect brought by α-substitution determines the occurrence of coassembly. A well-performed hydrogels based on the complexation between certain aromatic amino acids and bipyridine units are successfully constructed, providing unprecedented smart materials with light irradiation-triggered luminescence. Such hydrogels without the phase separation and photobleaching during light irradiation are able to behave fluorescent imprint materials. This study provides a suitable protocol in rationally designing amino acid residues of short peptides for fabricating self-assembled multicomponent materials. In addition, this protocol is useful in screening potential functional materials on account of diverse self-assembly behavior.

Recognition of amino acid residues is of vital importance in various biological events.[1] Inspired by typical enzyme–substrate interaction, many artificial systems have been developed to recognize amino acids.[2–5] Utilizing supramolecular chemistry protocols such as host–guest interactions, receptors like porphyrins,[2] cucurbit[n]urils,[3] crown ethers,[4] cyclen,[1] and acyclic thiourea[5] demonstrate capabilities to bind diverse chiral amino acids. These delicately modified cyclic or acyclic receptors are able to form complementary hydrogen bonds with specific amino acids in solution or the solid state. α-Positoned substituents on natural or chemically modified amino acids not only influence their binding with receptors, but also molecular stacking in aggregation and secondary folding structures of peptides.[6] Amino acid/short peptide derivatives represent an important branch of building blocks to fabricate advanced materials at micro/nanoscale due to their good biocompatibility, physiological activity, amphiphilicity, adaptability to ambient environment, and strong intramolecular interaction.[7,8] However, these features with property–structure relationship depend significantly on the type of amino acids or primary structure of amino acid sequences.[9] Therefore, great efforts have been paid to exploring the impact of amino acid variation.[10–13] To gain better understanding, Ulijn and co-workers[11] developed a dynamic peptide library where self-assembled morphology of short peptides with variable sequences could be likely predicted. Xu and co-workers[15] utilized amphiphilic tetrapeptides to explore the effect of different amino acid chiral centers on macroscopic supramolecular handedness of nanofibers. Their studies verified that the terminal amino acids dominate chiral orientation in the nanofiber formation.

In the aspect of fabricating functional materials, the combination of multiple components is way more effective than single component.[16–18] Likewise, the coassembly as a powerful methodology stands for the noncovalent linkage of organic molecules or polymers to build up ordered structures.[19,20] Noncovalent interactions between different components during the coassembly normally are π–π interactions, hydrogen/halogen bonding, electrostatic attraction and host–guest complexation, and so on.[21] Rationally applying these interactions to well control coassembly behavior, however, is still challenging. Self-sorting that represents the self-assembly of individual component could be a competitive pathway.[22] Thermodynamic and kinetic protocols are frequently employed to eliminate self-sorting competition in coassembled systems. Thermodynamic method focuses on enhancing intercomponent interaction such as the design of molecules with high structural similarity or strong oriented binding interaction, while kinetic one relies more on altering ambient conditions such as concentration or temperature.[23] For example, Stupp and co-workers designed peptide amphiphile analogs with same alkyl chains and amino acid sequences but different terminal groups to enhance the hydrogen bonding between components, showing excellent coassembly phenomenon.[24] Recently, they further implanted one fluorinated phenylalanine in peptide sequences to strengthen the anion–π interaction,
allowing for successful preparation of peptide/dodecanoic acid binary coassemblies.\[25\] We found that the coassembly behavior between pyrene and naphthalene dicarboximide appended glutamate building blocks was concentration-dependent (a kinetic control), and higher concentration would facilitate the coassembly and improve the intercomponent energy transfer.\[26\] In spite of these developments, the effect of amino acid type or $\alpha$-substituent structure on multicomponent self-assembly is still poorly understood. Unlike strong binding interaction between amino acids and other components,\[27\] relatively weak binding could be significantly influenced by self-sorting competition, which might result in a selectivity in various types of amino acid residues upon the coassembly with a weak binder. Thus, a better understanding of the effect is of vital importance in designing amino acid/short peptide-based multicomponent materials with desired functions.

Herein, we present our studies on selective coassembly of bipyridines and aromatic amino acids as a proof-of-concept research. The aromatic amino acids we employed are fluorenylmethyl (Fmoc) group protected L-type glycine (Gly), alanine (Ala), isoleucine (Lle), glutamic acid (Glu), phenylalanine (Phe), and tryptophan (Trp), as well as modified amino acids including aspartic acid benzyl ester (Asp), O-tert-butyl-serine (Sert), and aspartic acid 4-tert-butyl ester (Aspt).\[28a\] We chose 4,4$' \text{-dipyridyl (BP)} and 1,2-di(4-pyridyl)ethylene (BPE) to potentially bind with carboxylic groups of amino acids via hydrogen bonding (Scheme 1).\[28b\] The binding of bipyridines during solution-processed self-assembly shows a selectivity to amino acids. The selectivity is basically determined by two factors, one of which is the number of intermolecular hydrogen bonds in individual solid state, and another is steric effect of substituents like tert-butyl group (Scheme 1c). Binding and self-assembly of various amino acid/bipyridine complexes give rise to diverse phases on the basis of individual packing parameters. The BPE-Phe complex favors 1D growth during the self-assembly to afford high-quality hydrogels with light-responsiveness. Although luminescent organogels could be readily fabricated via the self-assembly of organic luminophores\[29a,b\] or organic/inorganic hybridization, the construction of luminescent self-standing hydrogels is often difficult on account of inevitable fluorescent quenching in water.\[29c–e\] Significantly, the present study provides an excellent example on the fabrication of light-triggered luminescent hydrogels. Upon UV light irradiation (254 nm), BPE in coassembled arrays could undergo the isomerization into its cis-isomer with greatly enhanced emission.\[30\] After sufficient irradiation, the hydrogel could still retain its phase integrity with partial disassociation, enabling the construction of ordered multicomponent gels with light-triggered luminescence.

The self-assembly of aromatic amino acids and bipyridine moieties was conducted by dispersing a small portion of mixture in water miscible organic solvent like methanol into water phase. Though the variation of organic solvent/water ratio has a certain influence on the aggregation of building blocks, the effect was minimized in the present

**Scheme 1.** a) Molecule structures of aromatic amino acids as hydrogen bonding donors. b) Chemical structures of bipyridines as hydrogen bonding acceptors. c) Illustration of two pathways during the self-assembly of aromatic amino acids with bipyridines, i.e., separate assembly (pathway I) and coassembly (pathway II), which are intimately related to hydrogen bonding sites of aromatic amino acids and steric hindrance effect. d) Self-assembly of Phe and BPE produces high-quality hydrogels with light-triggered fluorescent emission property.
study by controlling organic solvent ratio normally less than 10 vol%. Further observations indicate that a slight variation of organic solvent fraction (for example, from 5 to 10 vol%) had a negligible effect on morphologies and bulk aggregation behavior. All applied samples exhibited emulsion appearance in the first place, followed by aging process (24 h normally) to transform into different kinds of phases including precipitates and gels. In order to have a better understanding regarding the interaction between Fmoc-amino acid and bipyridines, we obtained a single crystal of Gly-BP in aqueous media. As shown in Figure 1a, Gly and BP form a sandwiched structure, showing a layered or lamellar topology along a axis with a d-spacing value of 23 Å. Within the sandwich structure, one BP molecule binds two Gly molecules via hydrogen bonding (1.7 Å), indicating the binding ratio between amino acids and bipyridines is 2:1. The plane surface of BP is almost vertical to fluorine moiety to give the zig-zag complexes. Each supramolecular complex (BP-2Gly) is noncovalently connected by interamide hydrogen bonding (2.2 Å), interbipyridine π–π stacking (3.3 Å), and interfluorine interaction (3.6 Å). Thus, expanded supramolecular units afford intersectional stacks with lateral ones, giving a lamella structure eventually.

The morphology of Gly-BP and Gly-BPE was characterized by scanning electron microscopy (SEM; Figure 1b,c). Gly-BP and Gly-BPE self-assembled into micro/nanoscale rods and ribbons with approximate widths of 0.8 and 1 µm, respectively. Clearly, the complexation with bipyridine enhances the growth of Gly backbone in 3D scale rather than 1D.[27b] The self-assembly between Gly and BP was also studied by small and wide angle X-ray scattering (SAXS and WAXS) techniques as shown in Figure 1d. The pristine Gly assembly in water showed the first-order peak at 0.33 Å⁻¹ (d = 1.9 nm), which gradually disappeared when 0.5 molar equivalent BP was added, in a good agreement with the molar ratio of 2:1 revealed by single crystal analysis. In the meantime, a new scattering peak at 0.277 Å⁻¹ (d = 2.3 nm) appeared in the presence of only 0.1 equivalent BP, which could be assigned as (001) plane of lamellar structure,[31f] and the deviation value Δd = 0.4 nm is contributed by BP-packed arrays inside the sandwich structure. BPE is also capable of binding Gly during the self-assembly, exhibiting similar scattering peaks. Due to relatively longer molecular length of BPE as compared to BP, scattering peaks demonstrate slight shifts to lower vector (q) region. The structure evolution of Gly with an increasing amount of BP was also well revealed by the WAXS patterns, where (002) and (003) planes could be clearly observed in consistent with simulated patterns (Figure S1, Supporting Information).

Figure 1. a) Single crystal structure and packing of Gly-BP complex. In the packing mode, Gly and BP are marked in blue and red, respectively, and hydrogen was omitted for clarity. Representative SEM images of self-assembled b) Gly-BP and c) Gly-BPE complexes (5 × 10⁻³ M, 0.5 equiv.). d) SAXS and WAXS patterns of different samples with variable BP or BPE molar ratios.
In addition to Gly, we expanded our study to other aromatic \(\alpha\)-amino acids. The existence of various types of \(\alpha\)-positioned substituents may have a considerable influence on their recognition capability to bipyridines during the coassembly. Ala, of which amino acid domain is modified with a methyl group when compared to Gly, showed nanoribbon assemblies with BP or BPE revealed by SEM (Figure S2a,b, Supporting Information). However, the aspect ratio of Ala-BPE assembly is much larger than that of Ala-BP, and Ala-BPE favors the growth more along 2D axis. Ala-BP and Ala-BPE showed no scattering peaks in SAXS patterns. Yet at wide angle region, peaks of Ala-BP with different molar ratios are almost identical to simulated patterns of Ala single crystal, without the observation of new peaks or major peak shifts, suggesting that Ala tends to form individual aggregation in the presence of BP. On the contrary, pristine peaks were replaced by new peaks in the presence of BPE, and the first two peaks with distances of 1.13 and 0.8 nm are close to the (002) and (003) planes of a lamellar structure. Glu owns two carboxylic acid groups capable of binding two bipyridines \([27a]\). Entangled nanofibers with diameters around 50 and 100 nm could be observed under SEM for Glu-BP and Glu-BPE assemblies, respectively (Figure S3a,b, Supporting Information). Though the nanofibers seem significantly intertwined, the aggregation of Glu-BP and Glu-BPE generates metastable hydrogels, and only part of water would be gelled, probably due to low aggregation number and relatively good water solubility of Glu and its complexes. Demonstrated in Figure S3c (Supporting Information), xerogels exhibit scattering peaks at 0.24 \(\AA^{-1}\) \((d = 2.6 \text{ nm} \ \text{for Glu-BP})\) and 0.22 \(\AA^{-1}\) \((d = 2.85 \text{ nm for Glu-BPE})\) in SAXS patterns, which are different from that of pristine hydrogel solely formed by Glu \((d = 2.45 \text{ nm})\), implying that Glu is able to bind with two bipyridines during the coassembly. However, less informative peaks in their WAXS patterns may be due to relatively low resolution. Then, hydrogels were casted to thin films for WAXS characterization (Figure S3d, Supporting Information). Both of Glu-BP and Glu-BPE assemblies display a diffraction peak around 6.3° with a distance of 1.4 nm, which could be designated as the second-order peak (002), implying lamellar molecular arrangement of hydrogen-bonded complexes.

The \(\alpha\)-position of Trp is a benzpyrole group that is a potential hydrogen bonding donor to bipyridine or other acceptors. The aggregation of Trp-BP and Trp-BPE gives rise to particle morphology with diameters around 2 \(\mu\text{m}\) and several hundreds of nanometers, respectively (Figure S4a,b, Supporting Information). Expectedly, both of SAXS and WAXS patterns indicate the existence of amorphous molecular stacks in these particle assemblies. The presence of benzpyrole possibly results in multiple and disordered interactions between Trp and bipyridine, responsible for the formation of amorphous structures. According to our previous studies \([27b]\) regarding ordered Trp assembly that forms micro/nanoplates in water, it is believed that these bipyridines are capable of identifying Trp. Next, the coassembly and self-sorting behavior between Phe and bipyridine were investigated (Figure 2a–e). No scattering peaks were observed in the SAXS pattern of Phe-BP, and its WAXS pattern was identical to simulated Phe sole assembly, indicating that Phe adopts individual

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**Figure 2.** a) SAXS and b) WAXS patterns of Phe-BP and Phe-BPE assemblies. c) FT-IR spectra of Phe-BP and Phe-BPE assemblies. Representative SEM images of self-assembled d) Phe-BP and e) Phe-BPE complexes.
aggregation rather than binding with BP (Figure 2a,b). In contrast, hump peaks at d = 2.24, 1.13, and 0.74 nm with a ratio of 1:0.5:0.33 were present in SAXS pattern of Phe-BPE, suggesting that Phe-BPE could coassemble into lamellar phase. Morphological studies were in consistent with X-ray scattering results. The formation of microscale fibers with 1 µm in diameter and tens of micrometers in length further confirms the self-sorted individual assembly of Phe with BP. Phe-BPE generates nanofibers with a mean diameter of 50 nm, providing intertwined networks to immobilize water for the formation of hydrogels. For the rest of applied amino acids, only Asp could bind with bipyridines, and Lle, Sert, and Aspt showed negative binding capabilities to both of BP and BPE based on morphological and SAXS/WAXS studies (Figures S5–S7, Supporting Information).

Fourier transform infrared spectroscopy (FT-IR) was further utilized to verify the diverse interaction between these amino acids and bipyridines. As shown in Figure 2c and Figure S8 (Supporting Information), the band at a range of 1720–1730 cm$^{-1}$ could be assigned as hydrogen-bonded carboxylic acids (=O–H type hydrogen bonding), which represent the presence of self-organized individual building blocks. The absence of this band means that carboxylic groups are likely bound by bipyridine groups (N–H type hydrogen bonding). FT-IR spectra are in good agreement with our conclusions from SAXS/WAXS studies.

The diverse complexation and molecular packing parameters between bipyridines and aromatic amino acids are summarized in Table 1. In applied aromatic amino acids, only Gly, Asp, Trp, and Glu were able to bind BP. Although Phe and Ala were insensitive to BP, they were capable of binding BPE. But the binding of Ala and Phe with BPE seems weaker than that of other amino acids like Gly, which was well supported by X-ray scattering results. The first-order scattering peak of Ala-BPE is missing and the locations of the 2nd and 3rd peaks exhibit certain dependency on BPE molar ratios. Only hump peaks were found in scattering patterns of Phe-BPE, meaning the absence of long-range ordered molecular packing arrays. Comparatively weak binding interaction between Phe-BPE possibly leads to the occurrence of flaws and defects that shall hinder the expansion to other dimensions, resulting in the formation of 1D gel fibers with high aspect ratio. In Table 1, another pronounced phenomenon is that all coassemblies adopt lamellar arrangements at mesoscale (designated as L$β$ phase, due to the ordered molecular packing inside layers).

Though other cocrystals were failed to obtain, the X-ray scattering results clearly demonstrate the molecular arrangements in co-assemblies similar to Gly-BP (except for Trp). Our previous studies have revealed that Fmoc-amino acids favor two pathways in the aggregation through the complexation of melamine with strong duplex hydrogen bonding under a 1:1 ratio, resulting in diversified morphologies (columnar and lamellar). However, the simplex molecular arrangement obviously elucidates that the binding modality as well as the stacks of complexes is fixed, independent to the variation of amino acids and bipyridines.

Once aromatic amino acids and bipyridines are triggered to aggregate, they basically follow two pathways including individual assembly (self-sorting) and coassembly. The balance between these two pathways might be partially influenced by the number and strength of noncovalent interactions in aggregated state. We here assume that only strong interactions such as hydrogen bonding and π–π stacking could dominate the assembly. As we discussed above, the lamellar structure was supported by three hydrogen bonding interactions (Figure 1), i.e., carboxylic acid–pyridine (1.7 Å), carbonyl–hydrogen (2.2 Å), and hydrogen–carbonyl (2.2 Å). Figure 3a displays the individual solid state structures and noncovalent interaction sites of some aromatic amino acids. All these building blocks (except Ala) form shoulder to shoulder (–) π–π stacking interaction with adjacent fluorene moieties, where distances are ranged from 3.5 to 3.7 Å. Due to the participation of water, Ala forms five hydrogen bonds with water and adjacent Ala. Phe owns two π–π stacking interactions on fluorene and benzene groups, apart from which, Phe molecules are linked via interamide and intercarboxylic acid hydrogen bonding. Lle could form one π–π stacking and four hydrogen bonds with each other. Therefore, for Ala, Phe, and Lle, it is reasonable to speculate that they tend to individually aggregate via strong noncovalent interactions (pathway I) rather than forming weak complexes with bipyridines (three hydrogen bonding sites). For the other three listed building blocks, they only form two intermolecular hydrogen bonds (Asp and Aspt have one more intramolecular hydrogen bonding rather than intermolecular interactions).

Table 1. Summary of self-assembly and complexation behavior for different aromatic amino acids.

<table>
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<tr>
<th>Item</th>
<th>BP-Gly</th>
<th>BP-Ala</th>
<th>BP-Asp</th>
<th>BP-Phe</th>
<th>BP-Glu</th>
<th>BP-Trp</th>
<th>BP-Lle</th>
<th>BP-Sert</th>
<th>BP-Aspt</th>
</tr>
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<td>P</td>
</tr>
<tr>
<td>Complexation</td>
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<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
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<td>A</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<td>12.6</td>
<td>15.4</td>
<td>17.1</td>
</tr>
<tr>
<td>Item</td>
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<td>BPE-Ala</td>
<td>BPE-Asp</td>
<td>BPE-Phe</td>
<td>BPE-Glu</td>
<td>BPE-Trp</td>
<td>BPE-Lle</td>
<td>BPE-Sert</td>
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<td>12.6</td>
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Note: P, precipitate; PG, partial gel; G, gel; L$β$, highly ordered packing arrangement of lamellar mesostructure; A, amorphous/disordered packing arrangement; nd, not detected. For those did not form complexes with bipyridines, periodic packing arrays are identical to their single crystal structures, and thus they were not listed in the table. The Sert-BPE assembly behavior remained unknown due to the formation of unanalyzable precipitates with high viscoelasticity.
According to our experimental observations, only Asp was successfully bound by bipyridines (pathway II), while Sert and Aspt produced individual assemblies with high fidelity. On top of that, the effect of bulky steric hindrance should be taken into account. Although Aspt and Sert are lack of multiple non-covalent interactions in the aggregation stage, their complexes with bipyridines may have the difficulty to stack on account of bulky effect of tertiary butyl group. We found that the mixture of Sert and BPE failed to generate well-defined aggregates for analysis, just giving unanalyzable viscous precipitates, which verified our assumption about the steric effect. In addition, BPE was easier to form complexes with applied amino acids (Table 1). We believe that different binding capability is originated from the difference of their water solubility. BP possesses better water solubility than that of BPE due to its shorter hydrocarbon fragment. The competition of solvation effect to the coassembly (de-solvation process) would be much stronger for BP than that of BPE in aqueous media. As a consequence, it

Figure 3. a) Strong noncovalent interaction sites of several aromatic amino acids in their individual solid states where red line represents hydrogen bonding and blue line stands for the π–π stacking. Single crystals of Gly and Glu were failed to obtain. b) A schematic representation of selective modulation in amino acid mixtures. c) SAXS patterns of selective modulation in multiple component systems. d) Summary of selective modulation capability of Gly or Glu by BP in the presence of other building blocks.
Figure 4. a) Normalized emission spectra of solution sample (Phe:BPE = 1:0.5, 5 × 10⁻³ m) in methanol as well as gel samples with different BPE molar ratios (5 × 10⁻³ m) excited at 290 nm, inset of which shows digital images of Phe-BPE mixture in methanol (solution) and water (gel). b) Dynamic oscillatory strain sweep of gel samples (concentration of Phe: 5 × 10⁻³ m) with variable BPE molar ratios (frequency = 1 rad s⁻¹). c) BPE molar ratio-dependent storage modulus of gels.

is more favorable for BPE to bind some aromatic amino acids than BP.

Based on differential selectivity of these aromatic amino acids to bipyridines, we aimed to achieve selective modulation of one component in multiple building block mixtures (Figure 3b). This task could be challenging owing to potential interplay between building blocks. At molecular scale, these amino acids shall aggregate into coassembled packing arrays on account of significant structural similarity. At macroscopic scale, the preformed micro/nanofibers of one component have possibilities to block the aggregation of another. Even such, we screened potential candidates for selective noncovalent modulation and discrimination. BP with better selectivity was applied as the main modulator to tune the assembly of Gly, Glu, and Asp. Multicomponent self-assemblies were triggered by dispersing mixtures of amino acids and BP (0.5 equiv.) in methanol into water, followed by 24 h incubation before characterizations. Asp failed to generate well-defined aggregates in the presence of other amino acids. SAXS/WAXS characterizations were performed to evaluate the selective modulation. In the mixture of Gly-Ala/BP, Gly-Lle/BP, Gly-Sert/BP, and Gly-Asp/BP, we identified scattering peaks of Gly-BP aggregate and sole aggregates of Ala, Lle, Sert, and Asp (Figure 3c and Figure S9b, Supporting Information). The analysis of Glu-Lle/BP and Glu-Asp/BP showed the same results (Figure S9a,b, Supporting Information). In these multicomponent systems (Figure 3d), Gly and Glu could be selectively modulated by BP (or BPE; Figure S10, Supporting Information). Although ordered aggregates were observed in some systems such as Glu-Phe/BP, Glu-Ala/BP, and Gly-Phe/BP (Figure S9, Supporting Information), the scattering peaks indicate the emergence of new molecular stacking arrays, which might be ascribed to the interference of other components. The interference between amino acids during the self-assembly could be more intense in three-component systems or more. It is hard for three-component systems to produce long-range ordered aggregates, giving only amorphous structures just like the Gly-Ala-Phe/BP system (Figure S9b, Supporting Information).

The complexation between BPE and amino acids enables the fabrication of photoresponsive hydrogel materials. Molecular packing of Phe-BPE, Glu-BP, and Glu-BPE complexes leads to the hydrogel formations. Among these three systems, Phe-BPE hydrogel possesses better performance over others in terms of water retention, colloidal stability, uniformity (phase continuity), and transparency. Phe self-assembled into white precipitates with microscale fibers, and turbid gel could be formed with the addition of only 0.1 molar equiv. BPE (Figure S11, Supporting Information). After adding more than 0.3 molar equiv. BPE, hydrogels became transparent. It should be noted that, the transparency shrinks with the increase of Phe concentration, having a critical gel concentration about 2 × 10⁻¹ m, suggesting that it is a supergel with ultrahigh water content. The UV absorption of Phe-BPE falls in the region of 250–350 nm, showing a slight red shift in aqueous media as compared to that in methanol, indicative of J-type π– π stacking between aromatic moieties (Figure S12a, Supporting Information). Attributed to J-type π– π stacking during the coassembly, peaks in 1H NMR spectra of Phe and BPE became wide and hump ones after the gelation (Figure S12b, Supporting Information), demonstrating a high-fidelity coassembly process. The π– π interaction is further confirmed by a significant red shift in emission spectra upon the gelation (Figure 4a). Noted that the peak located at the region of 400–500 nm belongs to the combination of BPE emission and fluorene excimer emission caused by π– π stacking. The BPE molar ratio-dependent emission spectra (0.4 to 1.0 equiv.) demonstrate a gradual decrease in relative intensity of this peak upon the increase of BPE. Because BPE with a stilbene core has aggregation-induced-emission (AIE) property, the decreased intensity implies the disassociation of self-assembled structures. We then utilized the rheology to monitor the molar ratio-dependent mechanical strength variations (Figure 4b,c). All the gels exhibit long linear viscoelastic strain in dynamic oscillatory strain sweep from 0.01% to 10% where storage modulus (G') is about 1 order of magnitude larger than loss modulus (G'″), implying typical rheological behavior of gels. The G' value (representing elastic performance) of the sample with 0.5 equiv. BPE is about 4.7 kPa, which gradually shrinks to ≈1 kPa with 1 equiv. BPE (Figure 4c). The decrease of mechanical strength reflects the reduction of fiber density and effective crosslinking between gel nanofibers. This observation is very likely aroused by the disassociation of assemblies, which is in consistent with emission studies. Oscillatory strain sweep also reveals the concentration-dependent mechanical strengthen behavior of gels (Figure S13a, Supporting Information). In addition, the independence of modulus on applied
frequency from 0.1 to 100 rad s\(^{-1}\) elucidates the stability of Phe-BPE gels.\[38\]

We further carried out studies on the photoresponsiveness of the Phe-BPE gels. The obtained hydrogels own considerable transparency, allowing for the penetration of light. In addition, BPE could undergo trans to cis isomerization under light irradiation. Supramolecular gels with photoresponsiveness have been extensively investigated on the basis of photosensitive organic species including azobenzene, spiropyran, diarylethene, and so on.\[39\] In contrast, stilbene analogs have advantages such as good stability after photoisomerization, and tunable luminescence over the mentioned molecules.\[40\] At a low concentration, BPE could disperse in methanol and water phase, giving negligible fluorescence. After UV light irradiation at 254 nm, the fluorescence intensity in methanol elevated significantly in methanol and water (Figure 5a and Figure S14a, Supporting Information), and the maximum emission was varied slightly, showing a bright blue luminescent color (relative quantum yield \(\Phi\) increased from 0.91% to 13.19% in water). Original absorption peak at 292 nm shifted to 244 nm after sufficient UV light irradiation. Then, we tested the luminescent variation in the hydrogel state. Figure 5b demonstrates gradual fluorescent intensity enhancement of the hydrogel sample after light irradiation (10 min irradiation time interval (\(\Phi\) increased from 0.0125% to 0.121%). Different from that in dilute solution state, UV light irradiated gels apparently displayed green luminescent color (main peak at 480 nm), possibly due to relatively high concentration and binding with Phe. It was believed that the photoisomerization could cause light irradiation-induced emission (Figure 5c). Free rotation of BPE double bond would transform the absorbed energy into thermal radiation rather than luminescence, reminiscent of typical AIE phenomenon of tetraphenyl ethylene. Nevertheless, the present light-induced emission enhancement performed on ordered hydrogels indicates several advantages over AIE-based fluorescent turn-on systems (see more discussions in the Supporting Information). After
the photoisomerization, however, steric hindrance caused by smaller dihedral angle shall hinder and restrict the free rotation of ethylene bond, giving higher quantum yield in turn.\[41\] This speculation was further supported by $^1$H NMR spectra (Figure S14b, Supporting Information). After the irradiation, BPE peaks at higher chemical shifts were observed, revealing that BPE switched its conformation rather than forming fused dimer.

After UV light irradiation, the turbidity of the hydrogel was elevated with the emergence of macroscopic aggregates, showing certain microphase separation within gel phase (inset of Figure 5b). Due to the self-confinement, no further phase transition occurred with prolonged irradiation time after 2 h. The gel still remained its overall integrity with sufficient irradiation.\[42\] The UV light treated gel, after being air dried, was characterized by SAXS experiments (Figure S15a, Supporting Information). The location of original (001) peak was barely changed, while the weakened intensity elucidates that the Phe-BPE nanofibers in gel were partially disassociated. FT-IR spectral results verified the disassembly of nanofibers after the irradiation (Figure S15b, Supporting Information), and the band at 1720 cm$^{-1}$ became more intense in comparison to pristine sample, indicative of the disassociation of Phe-BPE complex. Partial disassembly of the gel by photoisomerization was also reflected by the decrease of gel mechanical strength (Figure S15c, Supporting Information). 30 min irradiation led to considerable storage modulus decrease from 5 to $\approx$3 kPa. Thanks to the gel integrity, it allows for the fabrication of hydrogels with light irradiation-induced emission. From Figure 5b, we could clearly observe the emergence of green emission from nonemissive gel in cuvette triggered by 2 h light irradiation. Utilizing this protocol, we successfully achieved spatial fluorescent patterning in hydrogel substrates.\[43\] By designing photomasks of tinfoil that was encapsulated on the hydrogel surfaces in petri dishes, patterned hydrogel materials were obtained upon light irradiation (Figure 5d,e). The patterning was flexible, and both of a word “NTU” and a star shape were imprinted on hydrogels. The patterns were able to be detected under natural or UV light contributed by the increased turbidity and greatly enhanced green fluorescence. This fluorescent patterning was also rewritable. The patterned hydrogels could be recovered to almost original state by aging for 2 weeks in sealed petri dish (Figure 5d). The recovery might be attributed by dynamic component exchange between UV treated and untreated areas inside the gel system,\[44\] demonstrating a sort of self-erasable or self-healing behavior. SEM images of UV treated and untreated hydrogel areas exhibit diverse morphologies (Figure 5e,f). The well-ordered nanofiber networks were destructed in the UV treated areas, giving rise to massive fibers at microscale, probably originated from the Phe sole self-assembly after the complex disassociation.

In summary, we have investigated the $\alpha$-substitution influence of aromatic amino acids on the coassembly behavior with bipyridines (BP-BPE). The applied amino acids with diverse structures show the selectivity toward the complexation with BP-BPE during the aggregation. The results reveal that steric effect and hydrogen bonding are intimately associated with the selectivity. This protocol also facilitates to the development of smart hydrogel materials. The Phe-BPE complex could self-assemble into high-quality hydrogel. Upon UV light irradiation, nonemissive hydrogel could be transformed into a hydrogel with green color luminescence, allowing for fluorescent patterning in gel matrix. While it is very challenging to achieve light-responsive materials with the conversion from nonemission to strong emission, our design based on hydrogels would cast new light on the fabrication of novel smart materials.

**Experimental Section**

Experimental details including the preparation and characterization of self-assemblies could be found in the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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