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PAPER

Photo-induced charge-transfer complex formation and organogelation by a tripeptide†

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A terminally protected tripeptide Boc–Phe–Phe–Tyr–OMe **1** and picric acid form a photo induced charge-transfer complex and organogels. The interactions between stacked aromatic units play a key role in the assembly process. UV light (366 nm) has been used as a source of energy to cleave and homogenize π-stacking in the supramolecular arrangement of peptide **1** and picric acid. CD, FT-IR, NMR and powder X-ray diffraction studies exhibit distinct structural changes before and after light irradiation. Field emission scanning electron microscopy of the xerogels reveal a morphological change caused by photo induced charge-transfer complex formation. The fluorescence spectroscopy as well as confocal microscopy studies show that these charge-transfer complexes have a significant red emission at 672 nm.

Introduction

Organogels are highly studied materials with wide range of applications like drug delivery,[1] thermo- and mechanoresponsive sensor materials,[2] ion-selective membranes,[3] and hardening liquid waste.[4] The noncovalent interactions such as π–π stacking, hydrogen bonding, metal-ion coordination, dipole–dipole interactions, and other van der Waals interactions are mainly responsible for the molecular self-assembly and the gelation process.[5] Different external stimuli like pH change,[6] solvent polarity,[7] light,[8] ultrasound,[9] ions,[10] enzymes,[11] and so forth are generally used to manipulate the structure and function of the gel. The gel phase is different from the solid or the liquid phase, and provides a novel platform for photochemical or photophysical process.[12] There is considerable interest in the development of gels responsive to external stimuli with a special focus on photo-responsive organogels. Recently, organogelators with interesting optical and electronic properties have been developed based on porphyrins,[13] phthalocyanines,[14] and conjugate oligomers.[15] Glycoluril has reported as a photo-responsive supergelator that can be switched reversibly from the gel to the sol state by light irradiation.[16]

As a part of our program aiming the fabrication of supramolecular materials,[17] herein we present the formation of photo induced two component organogel between peptide Boc–Phe–Phe–Tyr–OMe **1** and picric acid. The peptide itself forms a gel in various aromatic solvents like toluene, xylene, and 1,2-dichloro benzene. The doping of picric acid into the organogel is not enough to form the charge transfer complex. However, an external stimuli like exposure to UV light (366 nm) changes the colour of the organogel from pale green to brown.

Results and discussion

The terminally protected tripeptide Boc–Phe–Phe–Tyr–OMe **1** (Fig. 1) containing a C-terminal L-tyrosine residue has been synthesized by a conventional solution-phase methodology, purified, characterized and studied. The gelation propensities of the terminally protected tripeptide **1** has been studied in a variety of organic solvents by dissolving a small amount of the compound in 0.5 mL of the solvent under investigation by heating. Upon cooling the complete volume of solvent is immobilized and forms a transparent gel. We found that the tripeptide **1** forms thermoreversible transparent gels in various aromatic solvents including benzene, toluene, xylene and 1,2-dichlorobenzene (ESI Table 1†). The gelation has been confirmed by the inverted test tube method.[18] We have

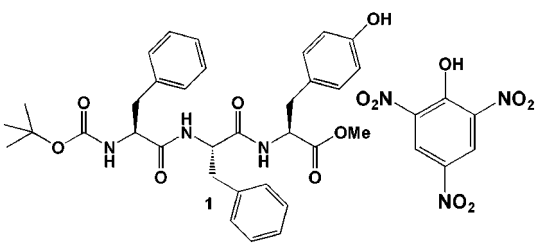

Fig. 1 The schematic presentation of the peptide **1** and picric acid.

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investigated the T_{gel} (gel to sol transition temparature) of tripeptide **1** in 1,2-dichlorobenzene (lowest MGC) which shows that the T_{gel} value increases as the concentration of the gelator increases (ESI Fig. 1†).

The reported peptide **1** is an electron rich compound and we were curious to examine its behaviour with an electron deficient system in gel state. One of the attractive properties of donor–acceptor organogels is their ability to assemble organic moieties in close proximity without forming a precipitate.[19] This may lead to potential applications in optics and electrochemistry because close packing of monomers improves conductivity and may provide improved and even nonlinear optical properties. We have incorporated an electron deficient molecule 2,4,6-trinitrophenol (picric acid) in the peptide **1** organogel. One interesting fact is that after mixing electron deficient picric acid with electron rich peptide **1** in 1,2-dichlorobenzene, the gel adopts the pale green colour of picric acid (Fig. 2d). Perhaps the addition of picric acid to the organogel is not enough to form the charge transfer complex. But, an exposure to external stimuli like UV light (366 nm) changes the colour of the organogel from pale green to dark brown (Fig. 2e). Hence, light acts as a source of activation energy and helps to form the charge transfer complex.

To determine the stoichiometric requirements of the two components upon gelation, T_{gel} is measured with increasing concentration of picric acid at a constant concentration of peptide **1** (46 mM). A plot of T_{gel} *vs.* the molar ratio of picric acid (ESI Fig. 2†) shows the maximum value T_{gel} at a 1 : 1 molar ratio of peptide **1** to picric acid. Also, we have investigated the MGC value of 1 : 1 mixture of **1** and picric acid in various aromatic solvents (ESI Table 2†). In the case of 1,2-dichloro benzene, the minimum gelation concentration (MGC) for the 1 : 1 mixture of compound **1** and picric acid is comparatively low. It is probable that the electron deficient 1,2-dichloro benzene is not forming a charge transfer complex with picric acid and rather acts only as a solvent.

To characterize the charge transfer complex formation UV/Visible absorption and emission experiments were carried out. The UV/Visible absorption spectra of peptide **1** ($c = 1 \times 10^{-5}$ M) in methanol shows a peak at 275 nm (ESI Fig. 3†). The addition of picric acid to the peptide **1** gel in 1,2-dichlorobenzene exhibits an absorption at 337 nm, (Fig. 2a) which is characteristic for picric acid. On exposure to UV light, a new absorption band appeared at 422 nm along with the 337 nm peak (Fig. 2b).

To obtain an insight into the photochemical properties of the light-induced charge-transfer organogel, fluorescence spectroscopy as well as confocal microscopy of the organogel were performed. As shown in Fig. 3, the photo-induced charge-transfer complex of peptide **1** and picric acid have an emission at 672 nm *i.e.* a red emission (excitation at 415 nm) along with a second emission at 435 nm in 1,2-dichlorobenzene. However, without light irradiation there is only an emission at 435 nm (Fig. 3, excitation at 415 nm), which is characteristic for picric acid. The emission quantum yield value (Φ_{em}) has been measured to be 0.19 (±10%).

Moreover, confocal microscopic images (Fig. 4) have confirmed the simultenious green emission (excitation at 488 nm) and red emission (excitation at 561 nm) from the photo-induced charge-transfer complex based organogel. Hence, now it is clear that the dark brown colour (Fig. 2e) of the light-stimulated organogel of compound **1** and picric acid is obtained by simultaneous green and red emission.

To determine if any chemical reaction takes place (formation of new compounds by light irradiation of the tyrosine phenolic OH, picric acid and 1,2-dichlorobenzene) or if the result is due to supramolecular arrangements of the components, the mass spectrum of the UV irradiated peptide picric acid organogel was recorded. The mass spectrum confirms the presence of the supramolecular complex of peptide **1** and picric acid rather than any new compounds (ESI Fig. 4†). A comparative study of the emission spectra of the organogel containing variable concentrations of picric acid with a constant peptide concentration (0.186 mM) in 1,2-dichlorobenzene have been performed. Fig. 5 shows that, with increasing concentration of picric acid in the system, the intensity of the emission at 672 nm increases.

To investigate the morphological changes of the organogel FE-SEM experiments were performed.[20] From Fig. 6a, one can consistently observe a network structure composed of fibrous aggregates for the peptide **1** xerogel from 1,2-dichlorobenzene. Fig. 6b shows that on addition of picric acid the fibrous structure is retained with some distortion. FE-SEM experiment shows that on exposure to UV light nanocrystal (length *ca* 100 nm) are

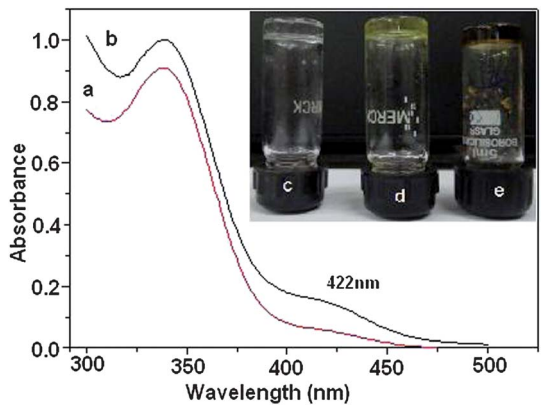

Fig. 2 UV/Vis spectra of peptide **1** and picric acid (a) before UV-light exposure and (b) after UV-light exposure in the gel state formed from 1,2 dichlorobenzene. (c) The transparent organogel of peptide **1** in 1,2-dichlorobenzene, (d) pale green gel after addition of picric acid and (e) dark brown gel after exposure to UV light.

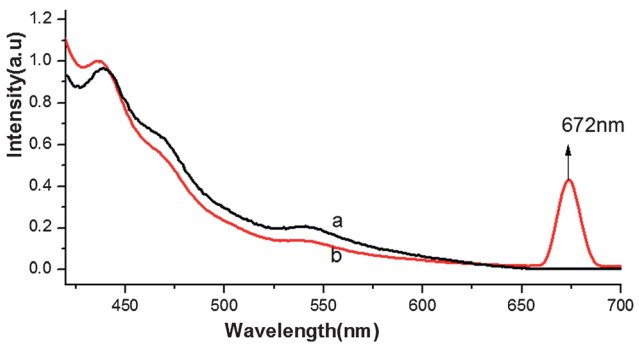

Fig. 3 Normalised emission plot of peptide **1** and picric acid (a) before light exposure (black line) and (b) after UV light exposure (red line), in gel state in 1,2-dichlorobenzene.

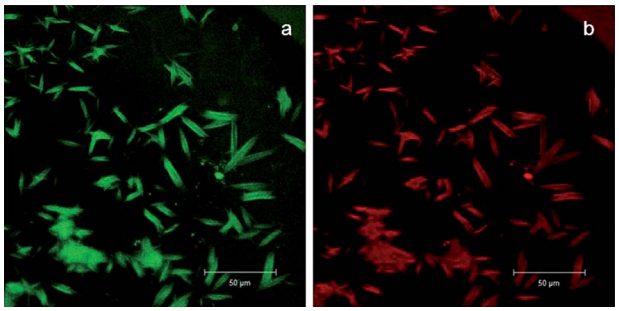

Fig. 4 Confocal micrograph of light irradiated organogel (from 1,2-dichlorobenzene) of peptide **1** and picric acid (a) green emission (excitation at 488 nm) and (b) red emission (excitation at 561 nm).

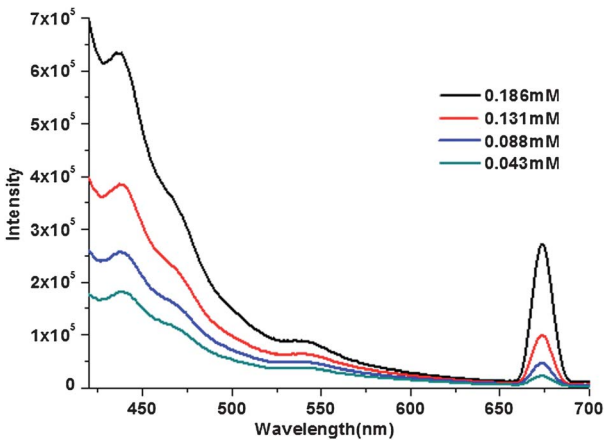

Fig. 5 Emission spectra of charge transfer complex (in gel state in 1,2-dichlorobenzene) with increasing picric acid concentration at constant peptide concentration (0.186 mM). $\lambda_{ex} = 415$nm.

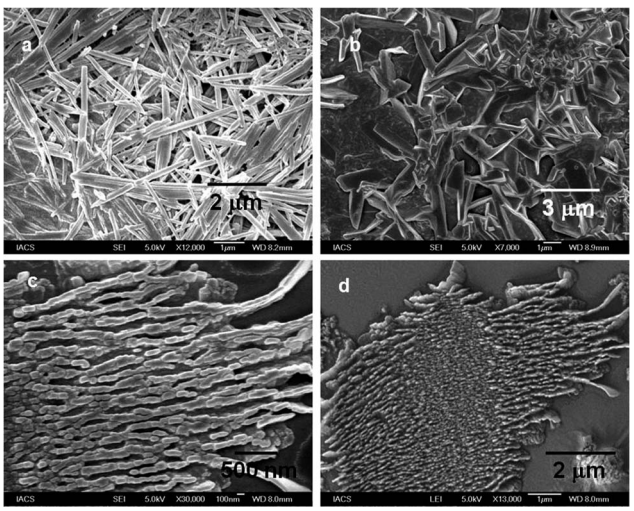

Fig. 6 FE-SEM images of (a) peptide **1** xerogel from 1,2-dichlorobenzene, (b) peptide **1** and picric acid xerogel from 1,2-dichlorobenzene before exposure to UV light, (c) and (d) peptide **1** and picric acid xerogel from 1,2-dichlorobenzene after UV light irradiation showing a linear array of nano crystals.

obtained (Fig. 6c and d). The nanocrystals are arranged in a linear array. The growth of nano crystal may be a causative factor for the transformation of transparent organogel to an opaque one.[21]

To gather information about the change of supramolecular arrangements of the components under UV irradiation, solution state ^{1}H NMR experiments were performed. Since the peptide contains a phenyl and a tyrosine ring, $CDCl_3$ is the appropriate solvent system to investigate the process by NMR. ^{1}H NMR was performed with the xerogel obtained from the peptide **1** picric acid organogel both before and after UV light irradiation. On light exposure, the peak of the NH of Phe(1) (6.21) and Phe(2) (6.37) has sifted to 6.15 and 6.30 respectively (Fig. 7). Before UV irradiation, the NMR spectrum is that of the peptide **1** and picric acid mixture. But after UV irradiation the shift of the characteristic peaks indicate that there is some change of environment caused by complex formation.

CD is an excellent method of determining the change of supramolecular arrangements. CD spectra of peptide **1** picric acid complex in acetonitrile before UV exposure (Fig. 8b) have positive bands at 205 nm and 225 nm. Fig. 8c exhibits the significant change after UV irradiation and a new negative band at 215 nm has appeared. Moreover, after light irradiation, a two fold increase of intensity of the positive band at 225 nm is observed.

Further information on the change of supramolecular arrangements of the peptide **1** and picric acid under different conditions was obtained from the FT-IR studies.[22] The FT-IR spectra of peptide **1** and picric acid before UV irradiation (Fig. 9a) have bands at 3288 cm^{-1} (N–H stretching vibrations) and 1648 cm^{-1} (C=O stretching vibrations) indicating presence of hydrogen bonded conformation.[23] After exposure to UV light those bands have shifted at 3293 cm^{-1} and 1636 cm^{-1} exhibiting a structural change by the complex formation (Fig. 9b).[24]

The powder X-ray diffraction (PXRD) data of the xerogels indicate a large difference of molecular arrangement in the 1 : 1 peptide **1**–picric acid gel before and after UV irradiation (ESI Fig. 4†). A peak corresponding to a *d*-spacing of 4.85 Å

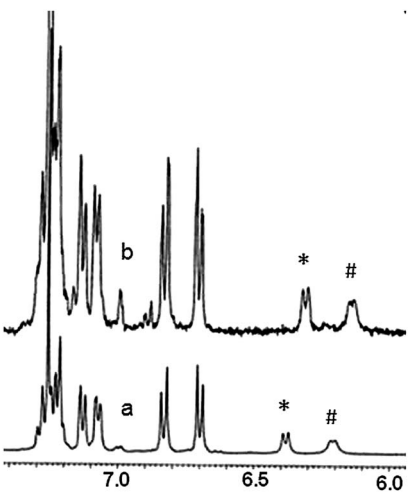

Fig. 7 Part of the ^{1}H NMR spectra of the peptide **1** and picric acid 1 : 1 complex in $CDCl_3$ (a) before UV light exposure and (b) after UV light exposure, showing the up field shifting of peaks.

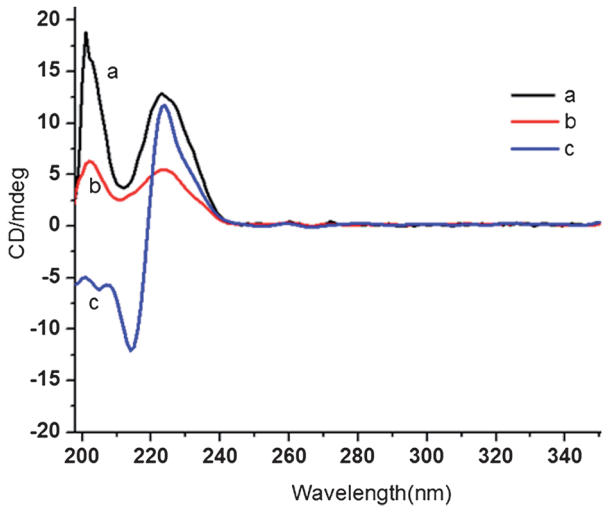

Fig. 8 Solution state CD spectra of (a) pure peptide **1** in acetonitrile, (b) peptide **1** and picric acid 1 : 1 complex before light exposure, (c) peptide **1** and picric acid 1 : 1 complex after UV exposure showing the conformational change in acetonitrile.

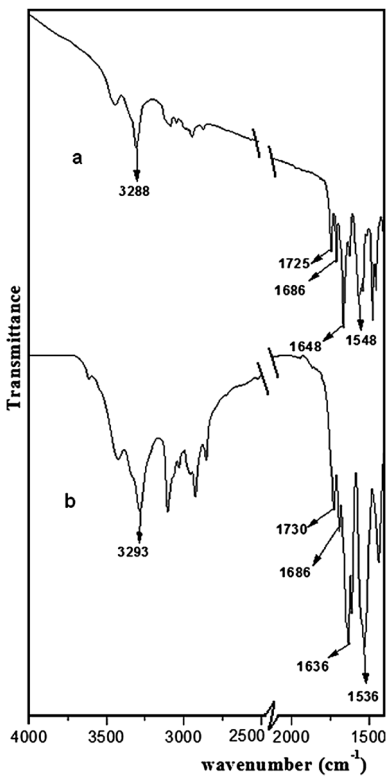

Fig. 9 Solid state FT-IR spectra of xerogel of (a) peptide **1** and picric acid 1 : 1 complex before light exposure and (b) peptide **1** and picric acid 1 : 1 complex after UV exposure showing the conformational change.

(2θ = 18.27°) accompanied by another peak at 10.06 Å (2θ = 8.8°) indicates the cross β-sheet structure of peptide **1**.[25] The disappearance of this peak and increase of intensity of another peak at 4.04–3.56 Å (2θ = 23.5°) is characteristic of a π–π stacking interaction, clearly indicating the formation of the charge–transfer complex after light irradiation.

To study the electrochemical properties of the charge-transfer complex system, cyclic voltammetry was performed. The electrochemical oxidation of Tyr is well-known and the oxidation peak is found to be kinetically irreversible, connected with radical formation.[26] From the cyclic voltametric study, the oxidation potential of tripeptide **1** (1.57 V, Fig. 10a) decreases to 1.47 V (Fig. 10b) in the 1 : 1 complex with picric acid. On UV light exposure, the value further decreases to 1.36 V (Fig. 10c). The results clearly indicates the effect of charge-transfer complex formation by photo irradiation.

Geometry optimizations and vibrational frequency analyses were carried out without any symmetry constraints at the level of density functional theory (DFT) based methods as implemented in the electronic structure program Gaussian 03.[27] We have used the Beck's three parameter hybrid exchange functional[28] combined with the Lee–Yang–Parr non-local correlation function abbreviated as B3LYP.[29] The split-valence basis set with diffuse functions, namely 6-311+G, have been employed for all atoms. Vibrational frequencies were calculated for optimized molecular structures to verify that no negative frequencies were present for minimum energy structures. However the DFT studies on the peptide **1**–picric acid complex show that the complex is highly stable due to charge transfer and π–π interactions (3.44 Å between picric acid and Tyr and 3.66 Å between picric acid and Phe(2)). The HOMO to LUMO energy differences of peptide **1** and picric acid are 29.08 kcal mol^{-1} and 22.12 kcal mol^{-1} respectively. Whereas the energy difference between the HOMO of peptide **1** and the LUMO of picric acid is 7.75 kcal mol^{-1}, which is significant for this complex formation. Fig. 11 exhibits the molecular orbital diagram of the complex.

We have synthesized another tripeptide Boc–Phe–Phe–Paba–OMe **2** (Paba = *p*-aminobenzoic acid) containing both electron rich (donor) and electron deficient (acceptor) aromatic moieties. This peptide also forms thermoreversible transparent gels in various aromatic solvents including benzene, toluene and 1,2-dichlorobenzene. But this tripeptide failed to form any photo induced charge-transfer complex with picric acid. From X-ray crystallography, it is evident that the asymmetric unit contains two molecules of peptide **2** (namely A and B) and there is no intramolecular hydrogen bond or intermolecular hydrogen bond between molecules A and B.[30] The backbone torsion angles

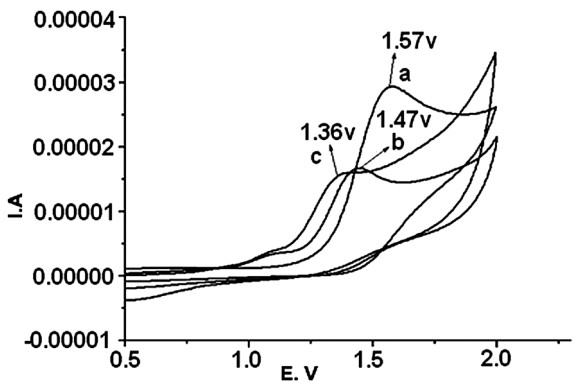

Fig. 10 Voltammograms of (a) peptide **1**, (b) peptide **1** with picric acid before UV irradiation and (c) peptide **1** with picric acid after light exposure.

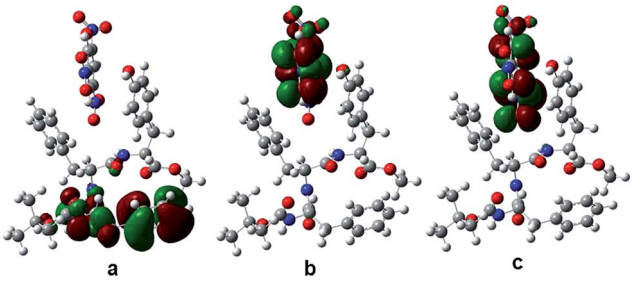

Fig. 11 Molecular orbital diagram of the peptide **1**–picric acid complex showing (a) HOMO, (b) LUMO and (c) LUMO + 1.

(ϕ_1, ψ_1, ϕ_2 and ψ_2) of peptide **2** are in the parallel β-sheet region of the Ramachandran diagram. But the overall the peptide backbone adopts a kink like shape including the *p*-aminobenzoic acid moiety. From Fig. 12, it can be seen that there are strong intramolecular π–π interaction (shortest C–C distance is 3.464 Å for molecule A and 3.545 Å for molecule B) between the Phe(1) and Paba(3) residues. The Phe(1) ring is acting as the donor and the electron deficient Paba(3) ring is the acceptor. The light irradiation has been failed to cleave this strong intramolecular π-stacking. As a result there is no photo induced charge transfer complex formation between peptide **2** and picric acid.

Experimental

General

All L-amino acids were purchased from Sigma chemicals. HOBt (1-hydroxybenzotriazole) and DCC (dicyclohexylcarbodiimide) were purchased from SRL.

Peptide synthesis

The peptides were synthesized by conventional solution-phase methods using a racemization free fragment condensation strategy. The Boc group was used for N-terminal protection and the C-terminus was protected as a methyl ester. Couplings were mediated by dicyclohexylcarbodiimide/1-hydroxybenzotriazole (DCC/HOBt). Deprotection of the methyl ester was performed using the saponification method. The intermediates were characterized by 500 MHz and 400 MHz ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and mass spectrometry. The final compound was fully characterized by 500 MHz ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy (125 MHz, 100MHz), mass spectrometry, and FT-IR spectroscopy. The peptides were purified by column chromatography using silica (100–200 mesh size) gel as stationary phase and an *n*-hexane–ethyl acetate mixture as eluent.

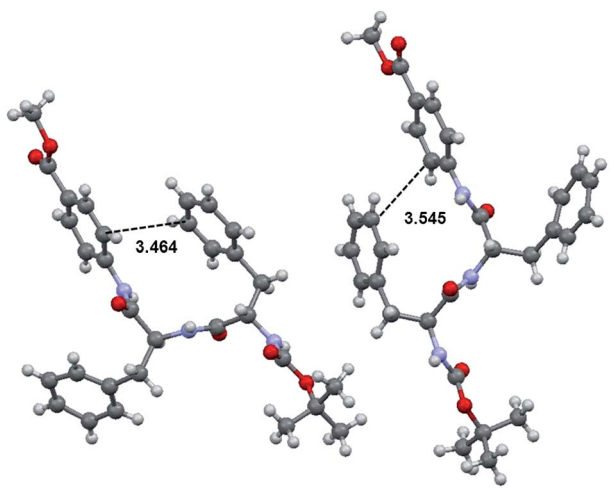

Fig. 12 The crystal structure of tripeptide **2**. Intramolecular π–π interactions are shown as a dotted line.

(a) Boc–Phe(1)–OH (3). A solution of L-phenylalanine (3.30 g, 20 mmol) in a mixture of dioxane (40 mL), water (20 mL) and 1 M NaOH (20 mL) was stirred and cooled in an ice-water bath. Di-*tert*-butylpyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 20–30 mL, cooled in an ice-water bath, covered with a layer of ethyl acetate (about 50 mL) and acidified with a dilute solution of $KHSO_4$ to pH 2–3 (Congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and drier over anhydrous Na_2SO_4 and evaporated in a vacuum. The pure material was obtained as a waxy solid. Yield 4.87 g, (18.35 mmol, 91.78%).

^{1}H NMR (DMSO-d_6, 500 MHz, δ in ppm); 12.75 (br, 1H, COOH); 7.28–7.09 (m, 5H, aromatic ring protons); 7.11–7.09 (d, 1H, J = 10 Hz, Phe NH); 4.09–4.01 (m, 1H, CαH Phe); 3.02–2.87(m, 2H, CβH Phe),1.36 (s, 9H, Boc). ^{13}C NMR (DMSO-d6, 125 MHz, δ in ppm): 173.57, 155.41, 138.00, 129.05, 128.09, 126.27, 80.24, 55.10, 36.39, 20.73. FT-IR: (cm^{-1}) 3336.62, 2980.24, 2928.43, 1718.09, 1508.24, 1396.37, 1368.93, 1252.56, 1165.90, 1053.15, 1028.98.

(b) Boc–Phe(1)–Phe(2)–OMe (4). 4.5 g (16.96 mmol) of Boc–Phe–OH was dissolved in 25 mL dry DCM in an ice-water bath. H–Phe–OMe was isolated from 7.31 g (33.92 mmol) of the corresponding methyl ester hydrochloride by neutralisation, subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed immediately by 3.49 g (16.96 mmol) dicyclohexylcarbodiimide (DCC) and 2.59 g (16.96 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 48 h. DCM was evaporated and the residue was dissolved in ethyl acetate (60 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCl (3 × 50 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) and dried over anhydrous sodium sulphate and evaporated in a vacuum to yield Boc–Phe(1)–Phe(2)–OMe as a white solid.

Yield 5.56 g (13.03 mmol, 76.82%). M.P. 121–122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm): 7.27–6.89 (m, 10H, aromatic ring protons). 6.19–6.18 (d, 1H, J = 5 Hz, NH1); 4.85 (m, 1H, CαH Phe1); 4.71–4.70 (d, 1H, J = 5 Hz, NH2); 4.25 (m, 1H, CαHPhe2); 3.59 (s, 3H, OMe); 3.02–2.93 (m, 4H, CβH Phe1, CβH Phe2); 1.35(s, 9H, Boc); ^{13}C NMR (125MHz, $CDCl_3$, δ in ppm): 171.36, 170.76, 155.30, 136.50, 129.23, 127.13, 80.24, 55.65, 53.28, 38.27, 31.94, 29.72. FT-IR: (cm^{-1}) 3330.85, 3063.74,

3033.66, 2987.73, 2973.66, 2926.79, 2855.47, 1745.20, 1698.16, 1666.37, 1604.89, 1522.35, 1497.14, 1445.66.

(C) Boc–Phe(1)–Phe(2)–OH (5). To 4.4 g (10.31 mmol) of Boc–Phe(1)–Phe(2)–OMe, 25 mL MeOH and 2 M 15 mL NaOH were added and the progress of saponification was monitored by thin layer chromatography (TLC). The reaction mixture was stirred. After 10 h, methanol was removed under vacuum; the residue was dissolve in 50 mL of water, and washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1 M HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts were pooled, dried over anhydrous sodium sulphate, and evaporated under vacuum to obtained compound as a white solid. Yield 3.5 g (8.49 mmol, 82.30%).

^{1}H NMR (DMSO-d_6, 500 MHz, δ in ppm); 12.75 (broad peak, 1H, COOH); 8.14–8.12 (d, 1H, J = 10 Hz, NH2); 7.34–7.21(m, 10H, aromatic ring proton); 6.95–6.93 (d, 1H, J = 10 Hz, NH1); 4.52–4.49 (m, 1H, CαH Phe1); 4.23–4.19 (m, 1H, CαH Phe2); 3.16–3.12 (m, 2H, CβH Phe1); 3.02–2.94 (m, 2H, CβH Phe2); 1.33 (s, 9H, Boc); ^{13}C NMR (125MHz, DMSO-d_6, δ in ppm): 172.76, 171.84, 155.15, 137.67, 129.15, 128.05, 126.51, 78.51, 56.45, 54.55, 53.78, 39.85, 27.59. FT-IR: (cm^{-1}) 3339.51, 3030.84, 2978.61, 2928.46, 1691.18, 1664.23, 1524.12, 1454.93.

(d) Boc–Phe(1)–Phe(2)–Tyr(3)–OMe (1). 1 g (2.42 mmol) Boc–Phe–Phe–OH was dissolved in 4 mL DCM in an ice-water bath. H–Tyr–OMe 1.12 g (4.84 mmol) was isolated from the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and concentrated to 7 mL. Then it was added to the reaction mixture, followed immediately by 0.499 g (2.42 mmol) dicyclohexylcarbodiimide (DCC) and 0.370 g (2.42 mmol) HOBt. The reaction mixture was allowed to come to room temperature was stirred for 72 h. The residue was taken in 30 mL ethyl acetate and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 2 M HCL (3 × 50 mL), brine (2 × 50 mL), then 1 M sodium carbonate (3 × 50 mL) and brine (2 × 50 mL) and dried over anhydrous sodium sulfate and evaporated under vacuum to yield the tripeptide **1** as a white solid. Purification was done by silica gel column (100–200 mesh size) and ethyl acetate and hexane 1 : 2 as the eluent. Yield 1.2 g (2.03 mmol, 84.09%). M.P. 143–145 °C.

^{1}H NMR ($CDCl_3$, 500 MHz, δ in ppm): 7.29–6.69 (m, 14H, aromatic ring proton); 7.05–7.04 (d, 1H, J = 5 Hz, NH1); 6.43–6.41 (d, 1H, J = 10 Hz, NH2); 6.38–6.36 (d, 1H, J = 10 Hz, NH3); 4.77–4.75 (m, 1H, CαH Phe1); 4.70–4.68 (m, 1H, CαH Phe2); 4.57–4.56 (m, 1H, CαH Tyr); 3.67 (s, 3H, OMe); 3.03–2.84 (m, 6H, CβH Phe1,CβH Phe2, CβH Tyr3); 1.39 (s, 9H, Boc); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 171.42, 170.04, 161.21, 155.48, 136.34, 130.32, 129.42, 128.73, 127.02, 115.79, 80.68, 70.10, 55.69, 53.54, 49.29, 37.97, 33.88, 29.71. FT-IR (cm^{-1}): 3305.85, 3063.24, 3029.20, 2929.15, 2851.88, 1738.06, 1687.78, 1648.47, 1517.25. ESIMS: m/z 612.45, [M+Na]$^+$; M_{calcd} 589.27.

NMR experiments

All solution state NMR studies were carried out on a Brüker AVANCE 500 MHz and Jeol JNM-ECS 400 MHz spectrometer at 298 K. Compound concentrations were in the range 1–10 mmol in $CDCl_3$ and $(CD_3)_2SO$.

FTIR spectroscopy

All reported solid-state FTIR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique.

Mass spectrometry

Mass spectra were recorded on a Q-Tof Micro YA263 high-resolution (Waters Corporation) mass spectrometer by positive-mode electrospray ionization.

Circular dichroism (CD) spectroscopy

Solution state CD study of peptide **1** in acetonitrile has been carried out before and after UV irradiation on a JASCO J-815-150S instrument at a temperature of 25 °C.

Fluorescent spectroscopy

Fluorescent spectrum of the reported compounds were recorded at different concentration in 1,2-dichlorobenzene on a fluorescent spectrometer (Perkin Elmer) and at excitation wavelength 415nm.

Confocal microscopy

The organogels from peptide **1** and picric acid in 1,2-dichlorobenzene, before and after UV light exposure were drop cast on glass slide and then dried under vacuum, and images were taken.

Field emission scanning electron microscopy

Morphologies of all reported gel materials were investigated using field emission scanning electron microscopy (FE-SEM). The organogels were dried and platinum coated and the micrographs were taken in an FE-SEM apparatus (Jeol Scanning Microscope-JSM-6700F).

UV/Vis spectroscopy

UV/Vis absorption spectra were recorded on a Perkin Elmer UV/Vis spectrophotometer.

Gelation study

The gel forming ability of synthetic tripeptide **1** with or without picric acid were studied in different organic solvents. 5–20 mg of the corresponding compound was added in 0.5 ml of solvent under investigation and made a clear solution by heating. The gel appeared on cooling. The gel melting temperature of the resultant organogel were determined by the inverted test tube method.

Cyclic voltametry

The cyclic voltametry was carried out using Princeton Applied Research Potentiostat/Galvanostat Model/236A. All experiments were performed in the three-electrode mode using an Ag/AgCl as a reference electrode and a platinum wire as counter

electrode. The CV experiments were recorded by scanning the potential from 0.50 to +2.0 V (*vs.* Ag/AgCl), employing a scan rate of 50 mV s^{-1} under a N_2 atmosphere. Measurements were recorded in 5 mL of CH_3CN, with 0.1 M $(Bu_4N)ClO_4$ (TBAPC) as the supporting electrolyte.

Powder X-ray diffraction (PXRD)

The PXRD patterns of xerogel obtained from 1 : 1 mixture of peptides **1** and picric acid before and after UV light exposure were studied (Rigaku parallel beam optics attachment). The instrument was operated at 35 kV and 30 mA current using Ni-filtered Cu-Kα radiation and was calibrated with a standard silicon sample. Samples were scanned from 5μ to 45μ (2θ) at the step scan mode (step size 0.03μ, preset time 2 s) and the diffraction patterns were recorded using a scintillation scan detector.

Computational studies

Geometry optimizations and vibrational frequency analyses were carried out without any symmetry constraints at the level of density functional theory (DFT) based methods using the electronic structure program Gaussian 03. The Beck's three parameter hybrid exchange functional combined with the Lee–Yang–Parr non-local correlation function abbreviated as B3LYP has used for calculation. The split-valence bases set with diffuse functions, namely 6-311+G, have been employed for all atoms. Vibrational frequencies were calculated for optimized molecular structures to verify that no negative frequencies were present for minimum energy structures.

Conclusions

In conclusion, we have demonstrated the fabrication of a novel light induced organogel by a simple noncovalent supramolecular approach. UV light has been used as a source of energy to cleave and homogenize π-stacking and formation of charge-transfer complex in an organogel medium. The photo irradiation has changed the morphology of the organogel from fiber network to nanocrystals array with a significant red emission. This photo-induced soft material may have potential application in the fabrication of optoelectronic devices.

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