View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: D. Haldar, D. Podder, S. Roy Chowdhury and S. Nandi, *New J. Chem.*, 2019, DOI: 10.1039/C8NJ05578E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

5 6 7

12 13

000 L Burley

39

-<mark>≆</mark>40

ā41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

www.rsc.org/



Debasish Podder,^a Srayoshi Roy Chowdhury,^a Sujay Kumar Nandi^a and Debasish Haldar*^a

New Journal of Chemistry

A novel series of tripeptide based low molecular weight super-organogelators were synthesized and characterized. Four tripeptides with diverse steric crowding at the central amino acid residue were studied. From these series, only sterically less hindered peptide 1 and peptide 3 formed organogel in different saturated hydrocarbons, crude oil, and aromatic solvents. In diesel, the peptides formed gel at 1 wt% i.e. act as super-organogelators. Interestingly both the peptides gel show high stability and remarkable self-healing property. As the peptides have electron rich phenyl system, the corresponding gel also interact with cationic dyes and can remove selectively cationic dyes from the waste water. The super-gelators have very high efficiency to solidify only the oil from a biphasic mixture of oil-water. Due to the high solubility of the super-gelators in non-toxic organic solvent ethanol, the solution is easy to handle and just by spraying the ethanol solution over oil-water mixture be able to perform gelling function at room temperature. The trapped water under the organogel can be pumped out and the oil can be recovered from the organogel by vacuum distillation. So, the supergelators can be used as a low cost, non toxic, room temperature easy to use material for the oil-spill recovery.

Introduction

Supramolecular gels are semi-solid like materials that can encapsulate a large amount of solvent.¹⁻⁴ These gels are also known as low molecular weight gels² (LMWG) which are basically composed of elastic entangled fiber network obtained by self-assembly of building blocks through various non-covalent interactions such as hydrogen bonding, π - π stacking, dipole-dipole interactions, and Van der Waals interactions.⁵⁻⁹ These gels are responsive to different external stimuli like temperature, pH, solvent polarity, light, ultrasound, and salts. ^{10-28} These make supramolecular gels suitable for various applications such as in the field of sensing, pharmaceutics, catalysis, actuating, charge transport, reaction media, dye absorption and oil spill recovery.²⁹⁻³⁵ Although there is a large number of reports of low molecular weight organogelators, still discovery of a new organogelator having low biphasic minimum gelling concentration (BMGC) at ambient environment is challenging.³⁶⁻³⁷

Dyes are essential for the textile industry but they have been found to pollute water which causes harmful effects on the environment. There are various methods such as carbon black adsorption, chemicoagulation, sedimentation, advanced oxidation procedure to remove dyes from waste water.³⁸⁻⁴¹ However, these processes have some disadvantages. Thus, removal of dyes from waste water is highly demanding.

Since last century, oil spill accidents have occurred around the world during oil transportation by ships or from natural calamities in oil fields and pipelines. Due to the oil spill, marine oil pollution is the most alarming issue and is a serious threat to the marine life and marine ecosystem.42 Phase-selective organogelator which can selectively solidify the oil layer from the oil-water biphasic mixture can be a useful solution to this problem. Toward this goal, three research groups (Sureshan, Zeng and Chaudhuri) have carried out impressive works, 43-46 with many different phase-selective organogelators, that can work either in powder form or in solution phase due to their high solubility in non-toxic organic solvents.⁴⁷⁻⁵² But the amount of expensive gelator is the major stumbling block. So, we need to develop a super-organogelator that will form gel with low BMGC at ambient condition.

Previously we have reported the self-assembly behaviour of the dipeptide Boc-Phe-Phe-OMe by X-ray crystallography and various microscopic techniques.53 This compound formed an opaque gel in xylene by heating-cooling technique but the minimum gel concentration (MGC) was very high (40mg/ml). In 2008 Li and co-workers reported the formation of selfassembled organogel by NH₂-Phe-Phe-COOH.⁵⁴ Ulijn and coworkers have reported the gelation behaviour of Fmoc protected Phenylalanine and its derivatives.⁵⁵⁻⁵⁹ Recently, We have introduced different achiral spacers between two phenylalanine residues and study their stimuli-responsive behaviour.⁶⁰⁻⁶¹ In this regards here we have designed and synthesized a series of tripeptides keeping phenylalanine residue at two terminal positions and introducing different α amino acids with increasing steric hindrance at the α -carbon as spacers between two phenylalanine residues (Fig.1). The peptides contain phenylalanine, alanine, α -amino isobutyric



^{a.} Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur -741246, West Bengal, India E-mail: deba h76@yahoo.com; deba h76@iiserkol.ac.in

⁺ Electronic Supplementary Information (ESI) available: [Peptide synthesis, NMR spectroscopy, rheology curves, Figure ESI S1-S35, peptide single crystals (CCDC 1855060)]. See DOI: 10.1039/x0xx00000x

ARTICLE

1 2

3

4

5

6

7

8

9

10

11

12

13

0000 February

<u>3</u>9

-<mark>≆</mark>40

ā 41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 acid, phenylglycine and 1-Aminocyclohexanecarboxylic acid (Fig. 1). Peptides 2 and 4 are more sterically hindered than 1 and 3. Among these peptides, only tripeptides 1 and 3 formed transparent organogel in various aromatic solvents and saturated hydrocarbons. The transparent gels have significant self-healing property. These peptides 1 and 3 also exhibit phase selective gelation of oil from a biphasic mixture of oil and water and can be used for oil spill recovery. As the the super-gelators are high solubility in non-toxic organic solvent ethanol, the solution is easy to handle and just by spraying the ethanol solution over oil-water mixture be able to form organogel at room temperature. The trapped water under the organogel can be pumped out and the oil can be recovered from the organogel by vacuum distillation.



Fig. 1. The schematic representation of tripeptides 1-4.

Results and discussion

We have designed and synthesized four tripeptides Boc-Phe-XXX-Phe-OMe (XXX = Alanine/ α -Aminoisobutyric acid/ Phenyl glycine/ 1-Aminocyclohexanecarboxylic acid) (Fig.1). Steric crowding at the α -carbon of the central amino acid spacer gradually increases from peptide **1** to peptide **4**. We wish to study the effect of the spacer in the tripeptide self-assembly. The reported tripeptides have been synthesized by conventional solution phase methodology. The final compounds have been purified and characterized by ¹H-NMR, ¹³C-NMR, FT-IR and Mass spectrometry analysis. First we have

2 | J. Name., 2012, 00, 1-3

Journal Name

done the Solid state FT-IR of all the peptides 1-4, to know the backbone conformation and self-assembly batter 79/From FT24R spectroscopy, for peptides 1 and 3, there are intense bands at 3302 cm⁻¹ and 3306 cm⁻¹ respectively which are responsible for the hydrogen bonded NH. But in case of peptides 2 and 4, there are bands at 3427 cm⁻¹ and 3395 cm⁻¹ respectively along with 3283 cm⁻¹ and 3323 cm⁻¹ bands that indicates all the NH are not hydrogen bonded (ESI Figure 1). Hence, backbone structures and hydrogen bonding patterns of peptides 1 and 3 are similar whereas peptides 2 and 4 are structurally close. Peptide 2 was characterized by X-ray Crystallography. Peptide 2 crystallizes with one molecule in the asymmetric unit from methanol-water solution by slow evaporation. The peptide adopts a kink like structure (Fig. 2). There is no intramolecular hydrogen bond. The important torsion angles are listed in ESI Table 1. In higher order packing peptide 2 self-assembles through intermolecular hydrogen bonding (N7-H7....O2, 2.02Å, 2.87Å, 169°, 1+x,y,z) to form a column-like structure (ESI Figure 2).



Fig. 2. The ORTEP diagram of peptide 2.

Initially, the gelation abilities of all the peptides were checked in various organic solvents by dissolving 10 mg of compound in 1 ml of different organic solvents. Peptide 1 and Peptide 3 were found to form transparent gels (Fig 3 and ESI Figure 3) in different aromatic solvents like xylene, o-xylene, p-xylene, mxylene, toluene, benzene (Electron donating solvents) as well as chlorobenzene, 1,2-dichlorobenzene (Electron withdrawing solvents) and different saturated hydrocarbons like petrol, diesel, kerosene, mustard oil, body oil, olive oil, crude oil by heating-cooling technique only (ESI Figure 4 and Fig.4). But peptide 2 and peptide 4 failed to form gels in any organic solvent as well as in oil. For peptides 1 and 3, the spacer i.e the central amino acid between the two phenylalanine residues containing one hydrogen atom along with one methyl group in case of peptide 1 and one phenyl group in case of peptide 3.



3

4

5

6

7

8

9

10

11

12

13

ARTICLE

Journal of Chemistry Accepted

Fig.3. Transparent gels of peptide 1 in different aromatic solvents.

Gelation was confirmed by the inverted vial method (Fig 3). The minimum gel concentrations for peptide 1 and 3 are very less compared to the only Boc-Phe-Phe-OMe. Here the MGC varies in the range 2.5 mg-6 mg/ml for peptide 1 and 2.2-4.8 mg/ml for peptide 3. For both the peptides, the gels from xylene having lowest MGC and the gels from chlorobenzene having highest MGC. Minimum gelation concentrations of all the reported gels are summarized in ESI Table 2. Surprisingly the MGC for the gels in various oils were much lower compared to those in aromatic solvents. In different oils, the MGC for Peptide 1 and 3 varies from 1.2-2.1 mg/ml and 1.4-2.1 mg/ml respectively and are summarized in ESI Table 2. So, the peptides 1 and 3 can act as super-gelators for diesel and petrol.

As gelation in crude oil is highly demanding, we have also checked the gelation of peptide 1 and peptide 3 in crude oil. Peptide 1 and peptide 3 can successfully form gel in crude oil by normal heating-cooling technique (ESI Figure 5.)

gel is sufficiently strong to tolerate the weight about 150 gm DOI: 10.1039/C8NJ05578E (Fig. 5).

Further, we have synthesized other three tripeptides by replacements of phenylalanine with Leucine, Valine and Alanine and studied their gelation behavior in diesel. 44,46,48 We have used leucine, valine and alanine as a terminal amino acid for peptide 5, peptide 6 and peptide 7 respectively. From these three peptides only leucine containing 5 forms gel in diesel but at higher MGC and BMGC compare to peptide 1. MGC is 8 mg/ml and BMGC is 17.3 mg/ml for peptide 5. The peptides 6 and 7 failed to form gel in diesel. So, from all of these peptides, peptide **1** has lower MGC and BMGC in diesel.

The mechanical strength of the gel was measured by rheology experiments. Storage modulus (G') and loss modulus (G") are the main two factors in rheology where G' represents the elastic response and G" represents the viscous behaviour of the gel. We have prepared the gel of peptides 1 and 3 in xylene and performed oscillatory frequency sweep experiment. In a typical frequency sweep experiment, the variation of G' and G" is monitored as a function of angular frequency at a constant strain 0.01%. For both peptides 1 and 3 gels G' is greater than G" and did not cross each other over the entire the range of angular frequency, which indicates that the gels are elastic in nature (Fig. 6). We have also performed the rheology experiment of the gel from diesel (ESI Figure. 6)



Fig. 6. Rheology of organogel in Xylene of (a) peptide 1 and (b) peptide 3. The storage modulus G' of the gel (1 wt%) was found to be larger than the loss modulus G" indicates an elastic rather than viscous material.

The morphologies of the gels were examined by optical microscope. The optical microscopic images of peptide 1 xerogels exhibit elongated fiber-like morphologies (ESI Figure 7). To better understand the morphologies of the gels, FE-SEM is a wonderful technique. From FE-SEM, xerogels of peptide 1 obtained from different solvents show the branch of



Water Diesel

Fig. 5. The peptide 3 gel in diesel is sufficiently strong to tolerate the weight of 150 gm water. $CoCl_2$ was added to water for clarity.

We have also measured the T_{gel} (gel to sol transition temperature) for the reported gels (ESI Table 3). For both the peptides 1 and 3, T_{gel} of gels from the aromatic organic solvents are lower than the gels in oils. For both the peptides, with increasing peptide concentration T_{gel} increases. All the organogels are thermo-reversible. The gels are stable up to 2 months without loss of transparency, colour, and shape. The

Journal Name

nanorods or nanofibers of length up to few micrometers (Fig. 7). The nanofibers are interlinked to produce a 3D network that can entrap solvents. However, the xerogels of peptide **3**

exhibit fibers of small length (ESI Figure 8).

ARTICLE

1 2

3

4

5

6

7

8

1399 1399 1399

ā41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 these solutions were placed in vials containing gel of pentide 1 in xylene. However, the gel matrix selectively dentraps that forme dyes from the aqueous medium. The dye absorption study of the gelator was very fast and monitored by Uv-Vis spectroscopy as a function of time (Fig. 10). Within 24 h more than 95% removal of the dyes was observed. As the peptide is electron-rich due to presence of aromatic rings and the amide



Fig. 7. FE-SEM images of the xerogels of peptide 1 from (a) 1,2-dichlorobenzene (b) m-Xylene (c) Toluene (d) Xylene (e) p-Xylene and (f) o-Xylene.

To further investigate the morphologies of gels in different organic solvents, AFM experiment was performed. The AFM images of the xerogel obtained from different organic solvents show nanorods like morphologies for the peptide 1 with almost similar size and shape (Fig. 8).



Fig. 8. AFM images of the xerogels of peptide 1 obtained from (a) 1,2-Dichlorobenzene (b) Toluene and (c) p-xylene.

More interestingly these gels exhibit amazing self-healing⁶²⁻⁶³property. When a cylindrical gel was cut into several small pieces and joined together, the gel pieces were found to integrate into a single cylindrical block within 15 minutes. When dye-doped (Rhodamine 6G) gel pieces were combined with undoped gel pieces in an alternative manner, the flow of the dye from doped to the undoped pieces confirmed the diffusion of the dye to the undoped portion that indicates the dynamic flow of the solvent through the joining point (Fig. 9). The self-healing may be due to dynamic equilibrium between the generation of the new fibers and the disconnection of the old fibers and that governs the reformation of gel.

It is interesting to note that the gel of the peptide **1** has enormous potential to absorb toxic organic dyes. There are various types of dyes like cationic, anionic and neutral. For this purpose, 1 mM solution of dyes rhodamine 6G (cationic), methyl violet (cationic), methyl orange (anionic), and pyrocatechol violet (neutral) was prepared. Then, 1 mL of



Fig. 9 Alternate arrangement of Rhodamine 6g-doped and undoped gel cylinders that self-heal to form a single cylinder with sufficient mechanical strength and the diffusion of the dye from doped to the undoped portion of the gel.

bonds, it has an attractive interaction with the cationic dyes but not with anionic or neutral dyes. The peptide 1 gel can be reused several times for the cationic dye removal with almost same efficiency.



We have examined the phase selective gelation of both the peptides **1** and **3** from oil-water mixture. Primarily we have investigated phase selective gelation by standard heating cooling technique. We have added 2.5 mg of peptide **1** in the mixture of water and diesel (each 1 ml) and warmed the solution for solubilizing the peptide. Then the mixture was kept to cool at room temperature and instantly within 2 minutes diesel layer was solidified above the water. However, heating-cooling in phase-selective gelation is an inappropriate

3

4

5

6

7

8

9

10

11

12

13

39

<u>≆</u>40

ā41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

Journal Name

technique for practical application such as oil-spill recovery due to the high flammability of most oils.^{35,64} To avoid such incident, a room temperature alternative procedure has developed. BMGC of Peptide 1 and Peptide 3 for diesel are 2.5 mg/ml and 3.6 mg/ml respectively. In this protocol, 20 mg of peptide 1 was dissolved in 1 mL of ethanol. This aliquot was injected at the interface of the diesel–water mixture (5ml diesel and 10ml water) (Fig. 11) at room temperature. Immediately diesel layer formed gel keeping the water phase intact at room temperature. We have introduced an injection syringe through the self-healing gel layer to the water layer and removed the water completely. Finally, by vacuum distillation process we recovered the diesel and collect the super organogelator. The material cost of the peptide 1 is INR 30/gm which is lower than reported diesel gelators.



Fig. 11. Removal of diesel from water. (a) Diesel layer above water. (b) Addition of ethanol solution of peptide 1. (c) The phase selective gel. (d) Insertion of injection syringe in to water layer through gel. (e) Suction of water in syringe. (f) Collection of water and (g) Separated water and organogel.

Experimental

General

All L-amino acids (L-phenylalanine, 2-aminoisobutyric acid, Lalanine, L-phenylglycine and 1-Aminocyclohexanecarboxylic acid) were purchased from Sigma chemicals. HOBt (1hydroxybenzotriazole) and DCC dicyclohexylcarbodiimide) were purchased from SRL.

Peptide Synthesis

All the peptides were synthesized by conventional solution phase methods by using racemization free fragment condensation strategy. The Boc group was used for N-terminal protection and the C-terminus was protected as a methyl ester. Deprotections of methyl ester were performed using saponification method. Couplings were mediated by dicyclohexylcarbodiimide/1hydroxybenzotriazole (DCC/HOBt). All of the intermediates were characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and mass spectrometry. The final compounds were fully characterized by 500 MHz, 400MHz ¹H NMR spectroscopy, ¹³C NMR spectroscopy (125 MHz, 100MHz), mass spectrometry and B spectroscopy J05578E

NMR Experiments

All NMR experiments were performed on a Jeol 400 MHz or Bruker 500 MHz spectrometer. Compound concentrations were in the range 1-10 mM in CDCl₃ and DMSO-*d*₆.

FT-IR Experiments

FT-IR spectroscopy in solid-state was performed with a Perkin Elmer Spectrum RX1 spectrophotometer using KBr disk method.

Absorption spectroscopy

The absorption spectra of peptides were measure on a Perkin Elmer UV/Vis spectrometer (Lambda 35) using quartz cell having 1 cm path length.

Mass Spectrometry

Mass spectrometry was carried out on a Waters Corporation Q-Tof Micro YA263 high-resolution mass spectrometer by electrospray ionization (positive-mode).

Polarised optical Microscope

A small amount of solution of the compound was placed on a clean glass cover slip and then dried by slow evaporation, then visualized at $40 \times$ magnification (Olympus optical microscope equipped with polarizer and CCD camera).

Field Emission Scanning Electron Microscopy

Field emission-scanning electron microscopy (FE-SEM) was performed to examine the morphologies of the synthesized peptides. A drop of peptide solution was casted on a clean microscopic glass slide and dried under vacuum. The samples were gold-coated, and the images were captured in an FE-SEM apparatus (Jeol Scanning Microscope-JSM-6700F).

Atomic force microscopy

The morphology of the reported compound was investigated by atomic force microscopy (AFM). A drop of the sample solution were placed on a clean microscope cover glass and then dried by slow evaporation. The material was then allowed to dry under vacuum at 30° C for two days. Images were taken with an NTMDT instrument, model no. AP-0100 by semicontact-mode

Gelation

1.5 mg of compound was dissolved in 1 mL of various organic solvents like different aromatic solvents like xylene, o-xylene, p-xylene, m-xylene, toluene, benzene (Electron donating solvents) as well as chlorobenzene, 1,2-dichlorobenzene (Electron withdrawing solvents) and different saturated hydrocarbons like petrol, diesel, kerosene, mustard oil, body oil, olive oil, crude oil by heating-cooling technique only. Homogeneous gel was formed.

Rheology Experiments

To examine the thixotropic behaviour and mechanical strength of the gel, we have done rheological measurements on a MCR 102 rheometer (Anton Paar, Modular Compact Rheometer) by a steel parallel plate geometry having 40 mm diameter at 20 °C. The rheometer was attached to a Peltier circulator thermo cube in order to control the temperature accurately. The storage modulus (G') and loss modulus (G") of the gel were then recorded by using the setup.

ARTICLE

1

Journal Name

View Article Online

DOI: 10.1039/C8NJ05578E

2 3 4 5 6 7 8 9 10 11 12 13 ഷ്ട്ര3 ষ্ট4 000 L Burley <u>3</u>9 <u>≆</u>40 ā 1 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59

60

X-ray crystallography

Diffraction quality white crystals of peptide **2** were obtained from methanol-water solution by slow evaporation. Intensity data were collected with MoK α radiation by Bruker APEX-2 CCD diffractometer. Data were processed using Bruker SAINT package. The structure solution and refinement were performed by SHELX97. Refinement of non-hydrogen atoms was performed using anisotropic thermal parameters. Crystal data of Peptide 1: C₂₈H₃₇N₃O₆, Mw = 511.61, P1 21/C 1, a = 5.9854(3) Å, b = 19.6802(8) Å, c = 23.5930(16) Å, α = 90°, β = 90°, γ = 90°, V = 2779.1(3) Å3, Z = 4, dm = 1.22 Mg m-3, , R1 = 0.0537 and wR2 = 0.1548 CCDC 1855060 contains the crystallographic data for the crystals respectively.

Self-Healing Study

We have prepared two set of cylindrical gel (dye doped and dye undoped) by dissolving 30 mg of peptide **1** in 6 ml of xylene in test tube. We have used Rhodamine 6G dye for doping. Then we cut both the gel cylinder (dye doped and dye undoped) into small pieces using a blade and arranged them in an alternative manner in close pack.

Dye removal study

To check the dye absorption ability of the organogel, initially we have prepared a organogel by dissolving 5 mg of peptide **1** in 1 ml of xylene. Then we have placed 1 ml of different dye solution (1mM) in vials containing the gel. The dye absorption ability of the gel was monitored by Uv-Vis spectroscopy. We have taken out 0.01 ml of aqueous solution containing the dyes and dilute it up to 1ml and measured the absorbance and follow the same procedure with different time interval.

Phase-selective gelation

In a typical phase-selective gelation experiment conducted at room temp, 20 mg of peptide 1 was dissolved in 1 mL of ethanol. This aliquot was injected at the interface of the diesel–water mixture (5ml diesel and 10ml water).

Conclusions

In conclusion, we have designed and synthesized a new class of super-gelators that can separate oil by phase-selective gelation of oil from water-oil mixture at room temperature. The super-gelators are high soluble in non-toxic organic solvent ethanol, the ethanol solution is easy to handle and just by spraying the ethanol solution over oil-water mixture be able to perform gelling function at room temperature. The trapped water under the gel can be pumped out without disturbing the gel. Finally, the oil can be recovered from the organogel by vacuum distillation. The organogel show high stability and significant self-healing property. As the peptides have electron rich phenyl groups, the corresponding gels also exhibit interactions with cationic dyes and can remove those cationic dyes selectively from the waste water. So, the supergelators can be used as a low cost, non toxic, room temperature easy to use material for the oil-spill recovery and water cleaning. The results are promising and environmentally benign.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge IISER Kolkata, India, for financial assistance. D. Podder and S. K. Nandi thanks CSIR, India for research fellowship. S. R. Chowdhury acknowledges the IISER-K, India for fellowship.

Notes and references

- 1 P. Dastidar, Chem. Soc. Rev., 2008, **37**, 2699–2715.
- 2 N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821–836.
- 3 G. Yu, X. Yan, C. Han and F. Huang, *Chem. Soc. Rev.*, 2013, **42**, 6697–6722.
- 4 S. Bera and D. Haldar, J. Mater. Chem. A, 2016, 4, 6933– 6939.
- 5 A. Harada, R. Kobayashi, Y. Takashima, A. Hashidzume and H. Yamaguchi, *Nature Chemistry*, 2011 **3**, 34-37.
- 6 T. Park and S. C. Zimmerman, J. Am. Chem. Soc., 2006, 128, 11582-11590.
- 7 A. Ajayaghosh and V. K. Praveen, Acc. Chem. Res., 2007, 40, 644–656.
- 8 S. Tanaka, M. Shirakawa, K. Kaneko, M. Takeuchi and S. Shinkai, *Langmuir*, 2005, **21**, 2163-2172.
- 9 T. Tu, W. Fang, X. Bao, X. Li, and K. H. Dotz, Angew. Chem. Int. Ed., 2011, 50, 6601–6605.
- 10 N. Fujita, Y. Sakamoto, M. Shirakawa, M. Ojima, A. Fujii, M. Ozaki, and S. Shinkai, J. Am. Chem. Soc., 2007, **129**, 4134-4135.
- 11 S. Xiao, Y. Zou, M. Yu, T. Yi, Y. Zhou, F. Li and C. Huang, *Chem. Commun.*, 2007, **0**, 4758-4760.
- 12 J. J. D. Jong, L. N. Lucas, R. M. Kellogg, J. H. V. Esch and B. L. Feringa, *Science*, 2004, **304**, 278-281.
- 13 W. Cai, G. T. Wang, Y. X. Xu, Xi, K. Jiang, and Z. T. Li, *J. Am. Chem. Soc.*, 2008, **130**, 6936-6937;
- 14 Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang, and C. Huang Chem. Mater., 2006, **18**, 2974-2981;
- 15 S. Maity, P. Jana and D. Haldar, CrystEngComm, 2011, 13, 3064-3071.
- 16 O. J. Dautel, M. Robitzer, J. P. L. Porte, F. S. Spirau, and J. J. E. Moreau J. Am. Chem. Soc., 2006, **128**, 16213-16223;
- 17 P. Xue, R. Lu, G. Chen, Y. Zhang, H. Nomoto, M. Takafuji and H. Ihara, *Chem.Eur. J.*, 2007, **13**, 8231.
- 18 D. Bardelang, Soft Matter, 2009, 5, 1969-1971.
- 19 G. Cravotto and P. Cintas, *Chem. Soc. Rev.*, 2009, **38**, 2684-2697.
- 20 C. Dou, D. Li, H. Gao, C. Wang, H. Zhang and Y. Wang, Langmuir, 2010, 26, 2113-2118.
- 21 T. Naota and H. Koori, J. Am. Chem. Soc., 2005, **127**, 9324-9325.
- 22 K. Isozaki, H. Takaya and T. Naota, Angew. Chem., Int. Ed., 2007, 46, 2855-2857.
- 23 B. V. Gangar, K. Nagarajan, R. V. Krishnan and A. B. Pandit, Ultrason. Sonochem., 2011, 18, 250-257.
- 24 X. Wang, J. Kluge, G. G. Leisk and D. L. Kaplan, *Biomaterials*, 2008, **29**, 1054-1064.
- 25 M. Zhang, L. Meng, X. Cao, M. Jiang and T. Yi, Soft Matter, 2012. 8, 4494-4498.
- 26 H. Maeda, Chem.Eur. J., 2008, 14, 11274-11282;
- 27 A. Ajayaghosh, P. Chithra and R. Varghese, *Angew. Chem., Int. Ed.*, 2007, **46**, 230- 233;

3

4

5

6

7

8

9

10

11

12

13

39

÷<u>₹</u>40

ā 1

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59 60

- Journal Name
- 28 H. J. Kim, J. H. Lee and M. Lee, Angew. Chem., Int. Ed., 2005, 44, 5810-5814.
- 29 P. Terech and R. G. Weiss, Chem. Rev., 1997, 97, 3133–3160.
- 30 A. R. Hirst, B. Escuder, J. F. Miravet, and D. K. Smith, *Angew. Chem. Int. Ed.* 2008, **47**, 8002 8018.
- 31 S. S. Babu, S. Prasanthkumar, and A. Ajayaghosh, Angew. Chem. Int. Ed. 2012, **51**, 1766–1776
- 32 D. K. Kumar and J. W. Steed, *Chem. Soc. Rev.*, 2014, **43**, 2080-2088
- 33 F. Aparicio, E. Matesanzb and L. Sanchez, Chem. Commun., 2012, 48, 5757–5759.
- 34 G. O. Lloyd and J. W. Steed. *Nature Chemistry*, 2009, **1**, 437-442.
- 35 S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan and G. John, Angew. Chem., 2010, **122**, 7861–7864.
- 36 J. H. V. Esch and B. L. Firinga, Angew. Chem. Int. Ed. 2000, 39, 2263-2266.
- 37 J. H. V. Esch, Langmuir 2009, 25, 8392–8394.
- 38 C.A. Basha, N.S. Bhadrinarayana, N. Anantharaman, and K.M. M. S. Begum, J. Hazard. Mater, 2008, 152, 71–78.
- 39 M. Bayramoglu, M. Kobya, O.T. Can. and M. Sozbir, Sep. Purif. Technol., 2004, 37, 117–125.
- 40 O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu, Chemosphere, 2004, 62, 181–187.
- 41 A. Pirkarami and M. E. Olya, Journal of Saudi Chemical Society, 2017, 21, 179–186.
- 42 M. Schrope, Nature, 2011, 472, 152–154.
- **43** A. M. Vibhute, V. Muvvala, and K. M. Sureshan, *Angew. Chem. Int. Ed.*, 2016, **55**, 7782 –7785.
- 44 J. Li, Y. Huo and H. Zeng, J. Mat. Chem. A, 2018, 6, 10196– 10200.
- 45 S. Datta, S. Samanta and D. Chaudhuri, J. Mat. Chem. A, 2018, 6, 2922-2926.
- 46 C. Ren, J. Shen, , F. Chen and H. Zeng, *Angew. Chem. Int. Ed.*, 2017, **56**, 3847-3851.
- 47 C. Ren, F. Chen, F. Zhou, J. Shen, H. Su, and H. Zeng, Langmuir, 2016, 32, 13510–13516.
- **48** Y. Ohsedo, *Polymer advanced technologies*. 2016, **27**, 704-711.
- 49 C. Ren, G. H. B. Ng, H. Wu, K. H. Chan, J. Shen, C. Teh, J. Y. Ying, and H. Zeng, *Chem. Mater*. 2016, **28**, 4001–4008.
- 50 S. Mukherjee, C. Shang, X. Chen, X. Chang, K. Liu, C. Yu and Y. Fan, *Chem. Commun.*, 2014, **50**, 13940-13943.
- 51 D. Wang, J. Niu, Z. Wang, and J. Jin, *Langmuir*, 2015, **31**, 1670–1674.
- 52 S. Bhattacharya and Y. K. Ghosh, *Chem. Commun.*, 2001, **0**, 185–186.
- 53 S. Bera, P. Jana, S. K. Maity, and D. Haldar, *Cryst. Growth Des.* 2014, **14**, 1032–1038.
- 54 X. Yan, Y. Cui, Q. He, K. Wang, and J. Li, *Chem. Mater.* 2008, **20**, 1522–1526.
- A. M. Smith, R. J. Williams, C. Tang, P. Coppo, R. F. Collins, M. L. Turner, A. Saiani, and R. V. Ulijn, *Advanced Material*, 2008, 20, 37-41.
- 56 N. A. Dudukovic and C. F. Zukoski, *Langmuir*, 2014, **30**, 4493–4500.
- 57 V. Singh, K. Snigdha, C. Singh, N. Sinhad and A. K. Thakur, Soft Matter, 2015, **11**, 5353—5364.
- 58 C. Tang, R. V. Ulijn, and A. Saiani, *Langmuir*, 2011, **27**, 14438– 14449.
- 59 W. Liyanage and B. L. Nilsson, Langmuir 2016, 32, 787–799.
- 60 A. Pramanik, A. Paikar and D. Haldar, *RSC Adv.*, 2015, **5**, 53886–53892.
- 61 A. Pramanik, A. Paikar, K. Maji and D. Haldar, *RSC Adv.*, 2016, **6**, 59851–59857.
- 62 Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrınyi, P. H. Dussault, Y. Osada and Y. M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 8114-8131
 - This journal is © The Royal Society of Chemistry 20xx

- 63 A. Vidyasagar, K. Handore, and K. M. Sureshan, Angew. Chem. Int. Ed. 2011, 50, 8021 – 8024.. DOI: 10.1039/C8NJ05578E
- 64 T. Kar, S. Mukherjee and P. K. Das, New J. Chem., 2014, 38, 1158–1167.

Bublisked on ULFebruary 2018, Rowalowder UNW estern Skutury University an 211/2019 1:24122 MA

TOC Graphic

Tripeptide based super-organogelators: structure and function

Debasish Podder, Srayoshi Roy Chowdhury, Sujay Kumar Nandi and Debasish Haldar*

The peptide based super-gelators are highly soluble in non-toxic organic solvent ethanol, the solution is easy to handle and just by spraying the ethanol solution over oil-water mixture be able to form organogel at room temperature.

