Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Self-Assembly and Multifunctionality in Peptide Organogels: Oil Spill Recovery, Dye Absorption and Synthesis of Conducting Biomaterials

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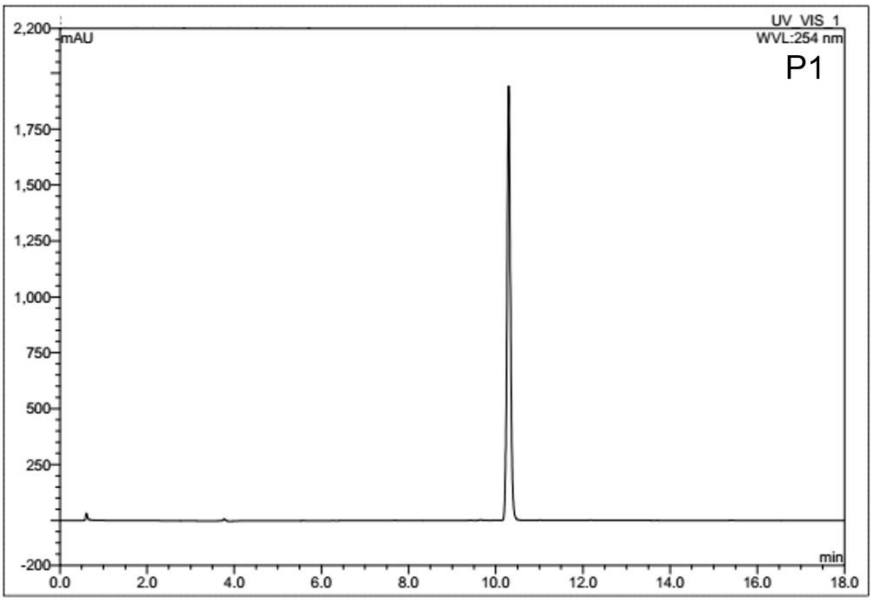

Figure S1. Analytical HPLC trace of the peptides P1.

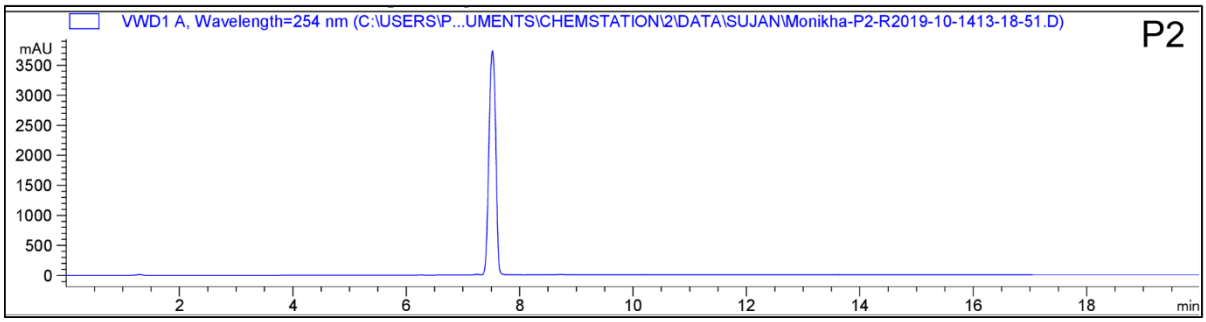

Figure S2. Analytical HPLC trace of the peptides P2.

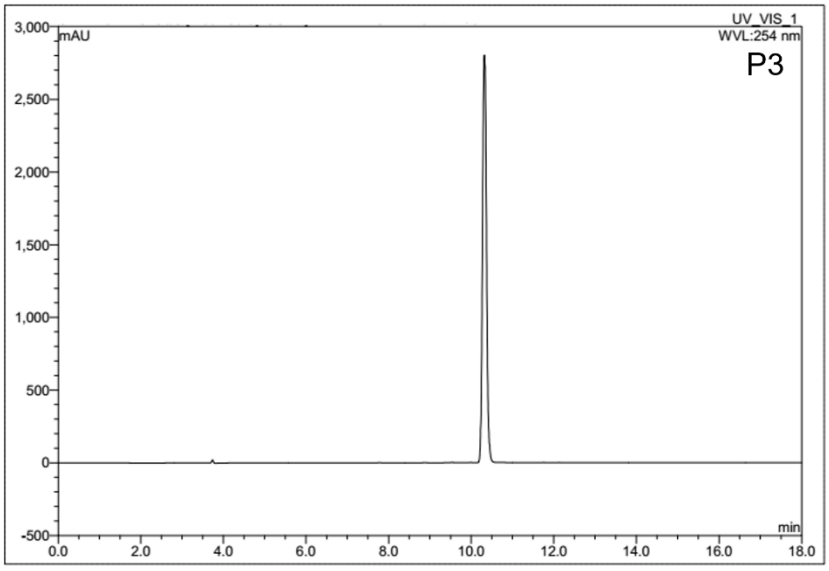

Figure S3. Analytical HPLC trace of the peptides P3.

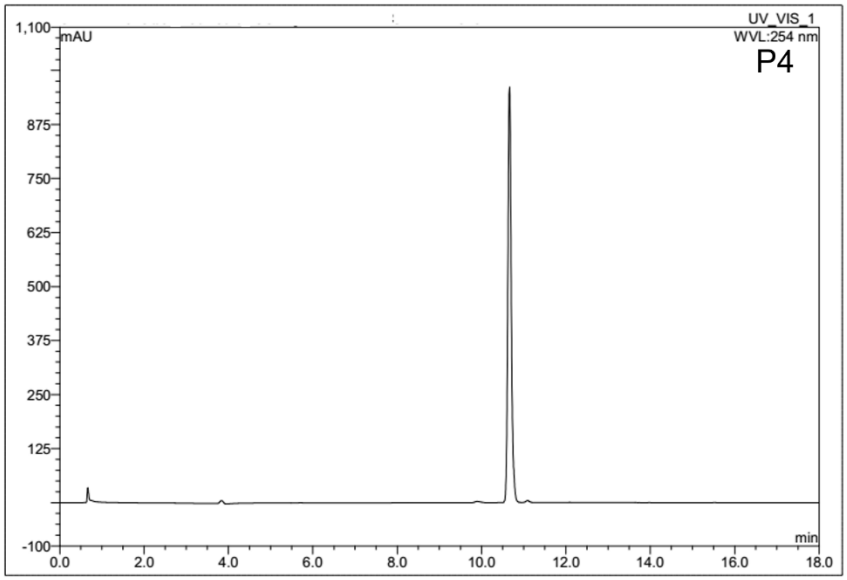

Figure S4. Analytical HPLC trace of the peptides P4.

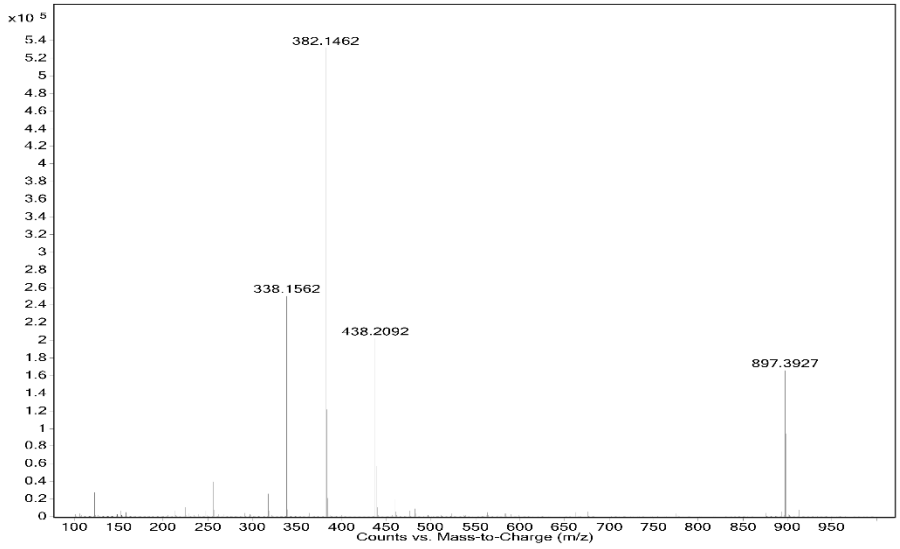

Figure S5: ESI-MS of P1

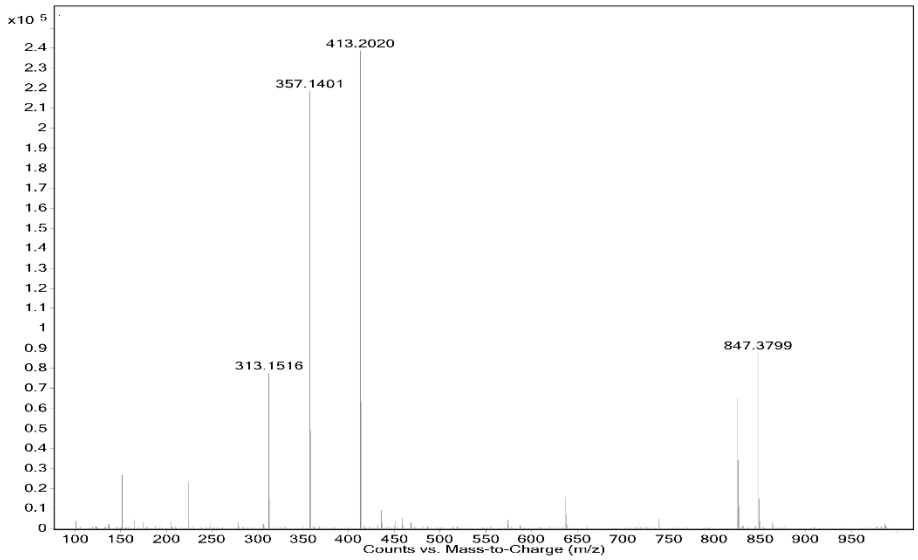

Figure S6: ESI-MS of P2.

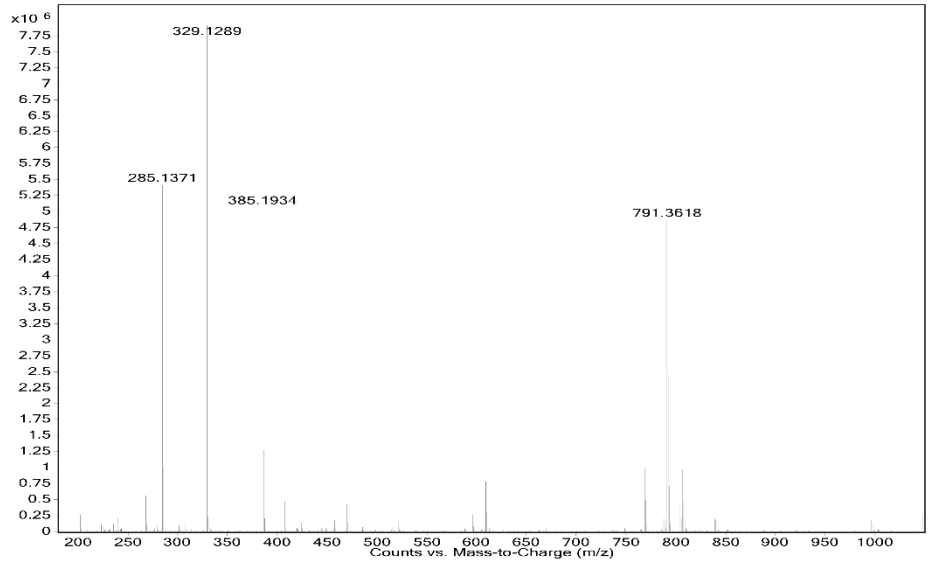

Figure S7: ESI-MS of P3.

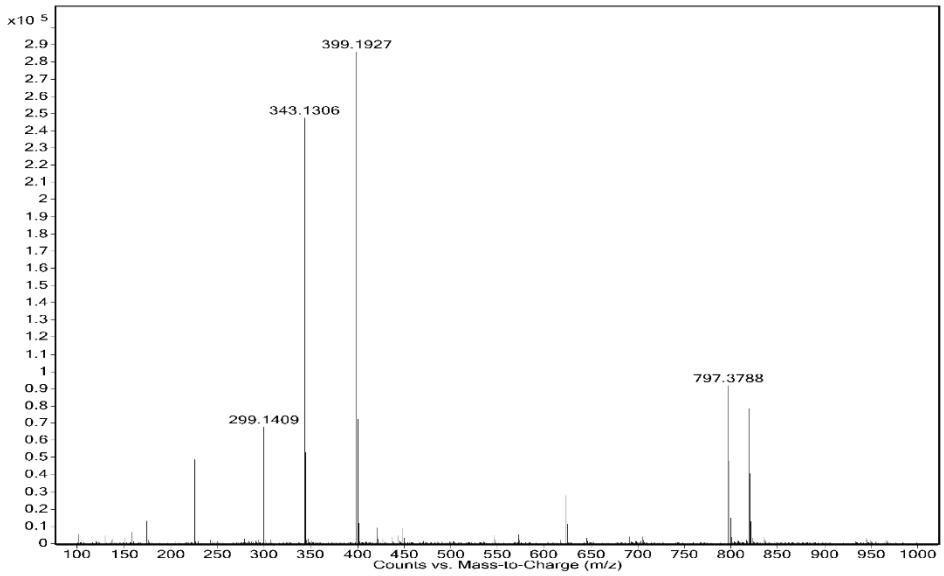

Figure S8: ESI-MS of P4.

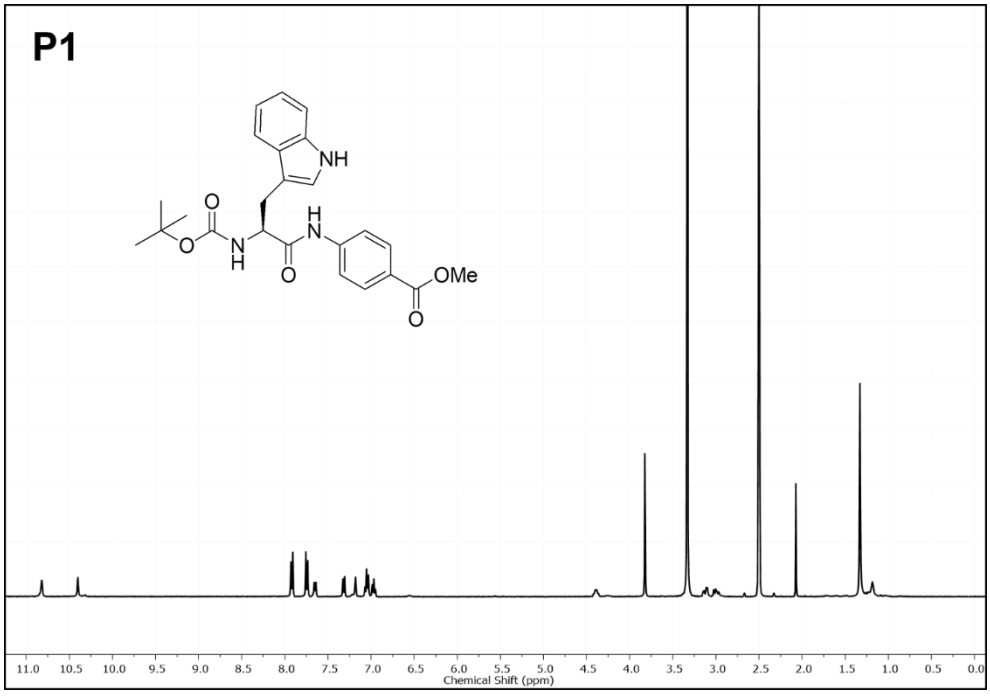

Figure S9: ^{1}H NMR spectra of P1.

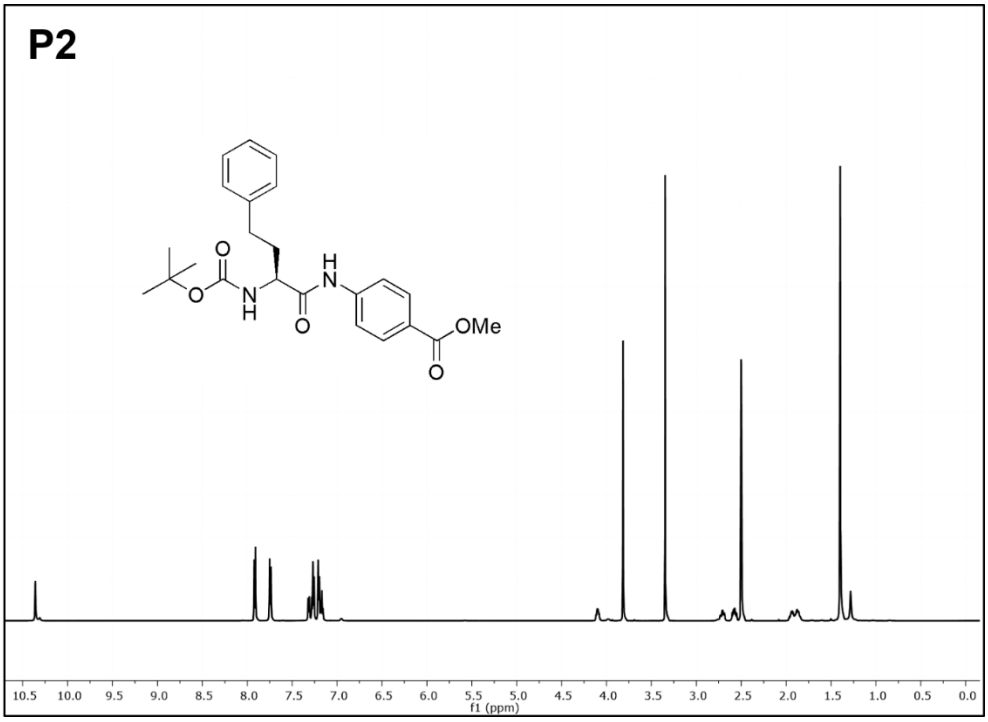

Figure S10: ^{1}H NMR spectra of P2.

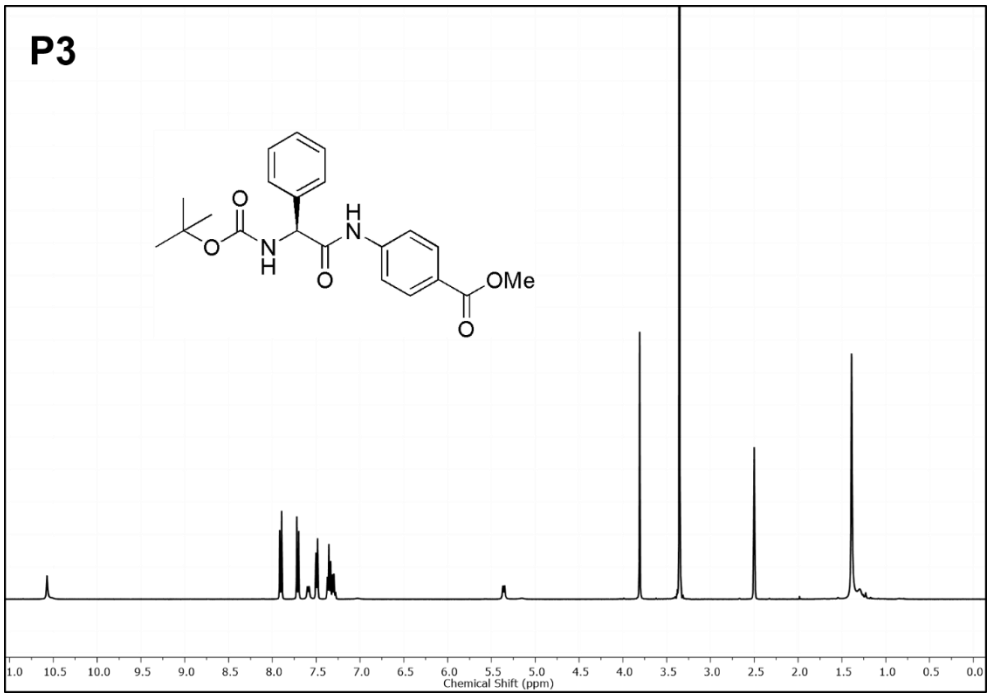

Figure S11: ^{1}H NMR spectra of P3.

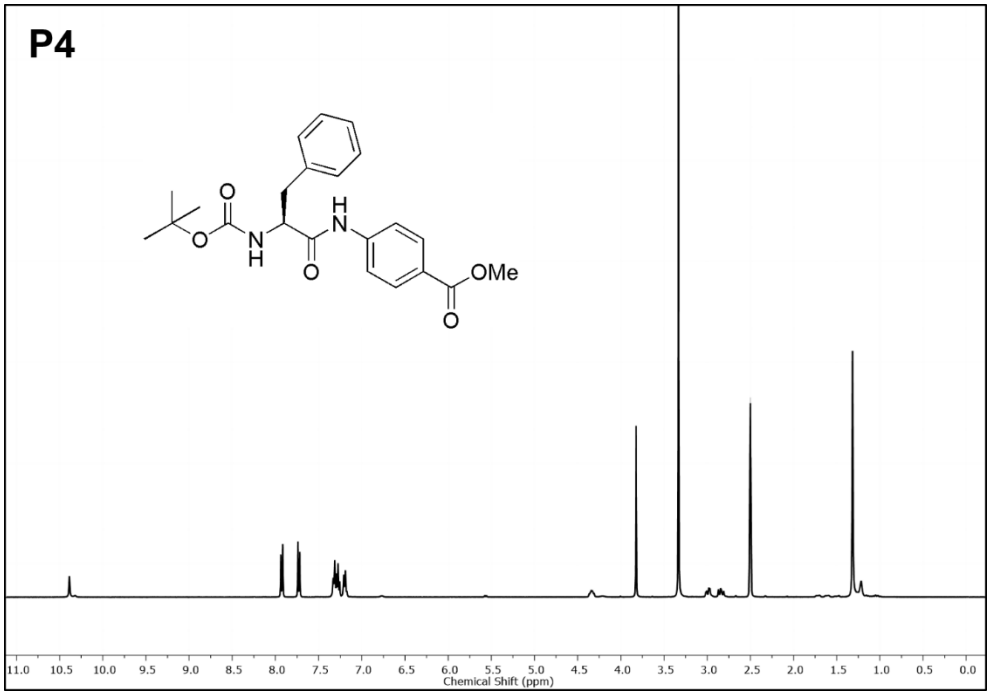

Figure S12: ^{1}H NMR spectra of P4.

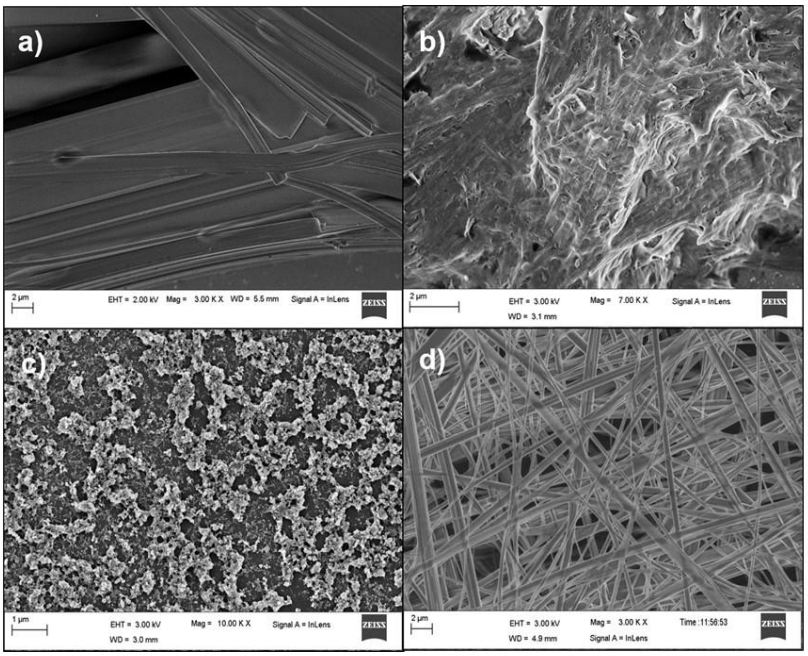

Figure S13: FESEM images of (a) P1, (b) P2, (c) P3 and (d) P4 in 1,2-DCB solution.

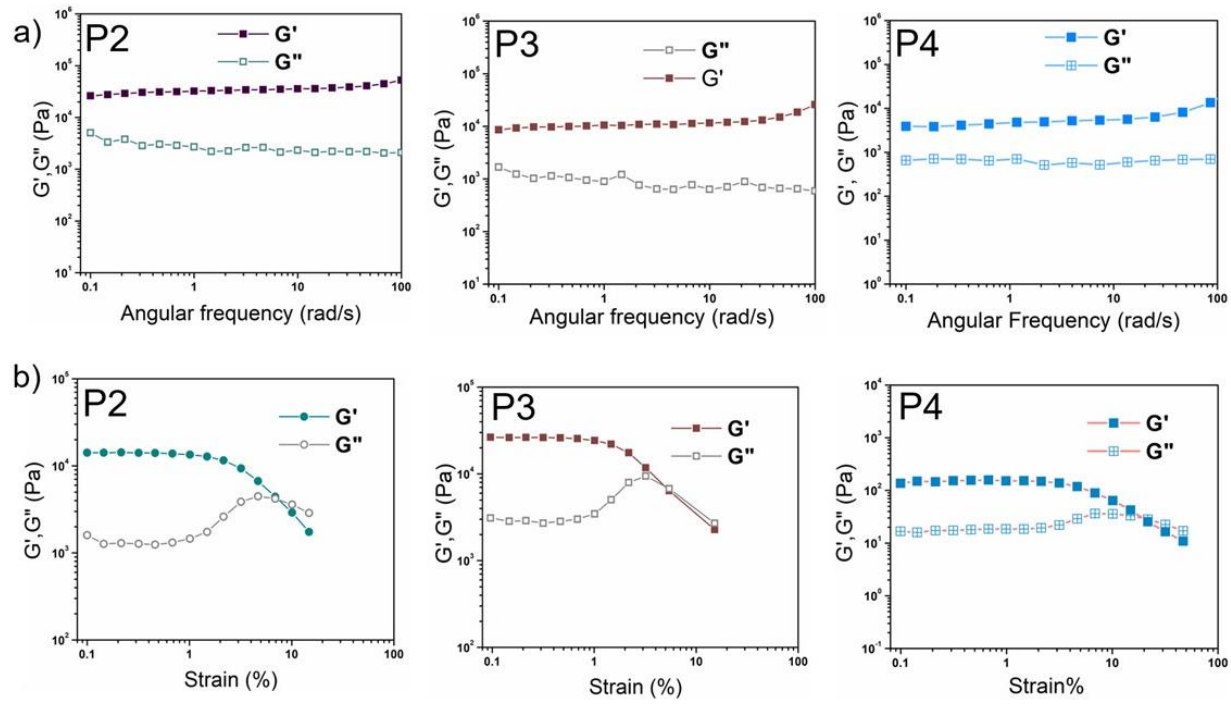

Figure S14: Rheology of P2-P4 xerogels. Strain dependence and (b) Frequency dependence of the dynamic storage moduli (G′) and the loss moduli (G″) of organogel from P2-P4 in 1,2-DCB at 1 % w/v.

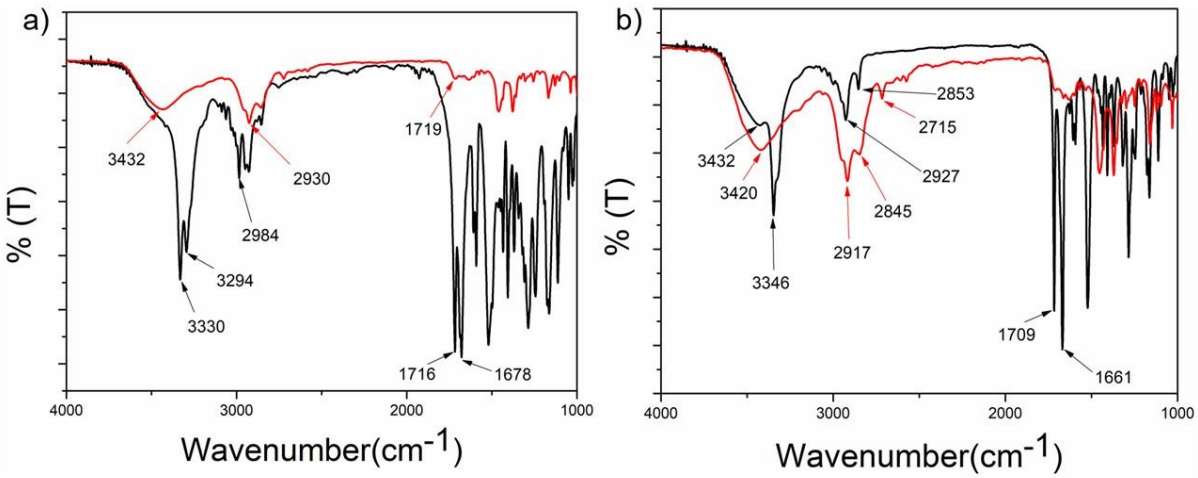

Figure S15: Superimposition of the FT-IR spectra of (a) P3 and (b) P4 in their powder and xerogel states.

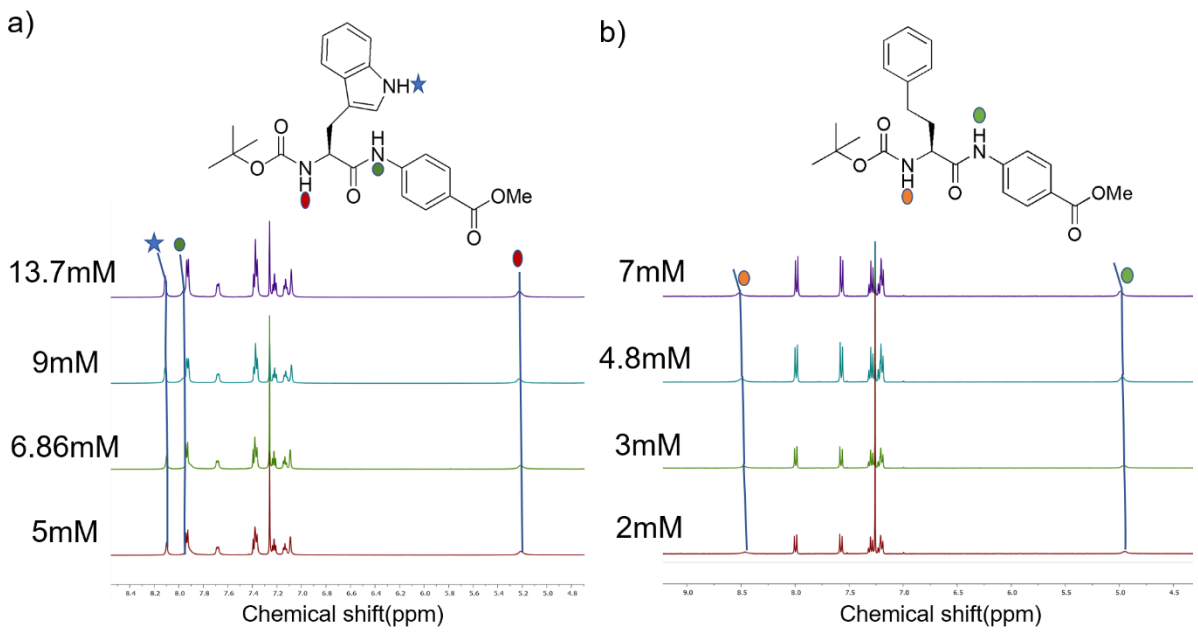

Figure S16: NH region of the stacked ^{1}H NMR spectra of the peptides (a) P1 and (b) P2 in $CDCl_3$ at different concentrations which are lower, equal and higher than the MGC of the solution.

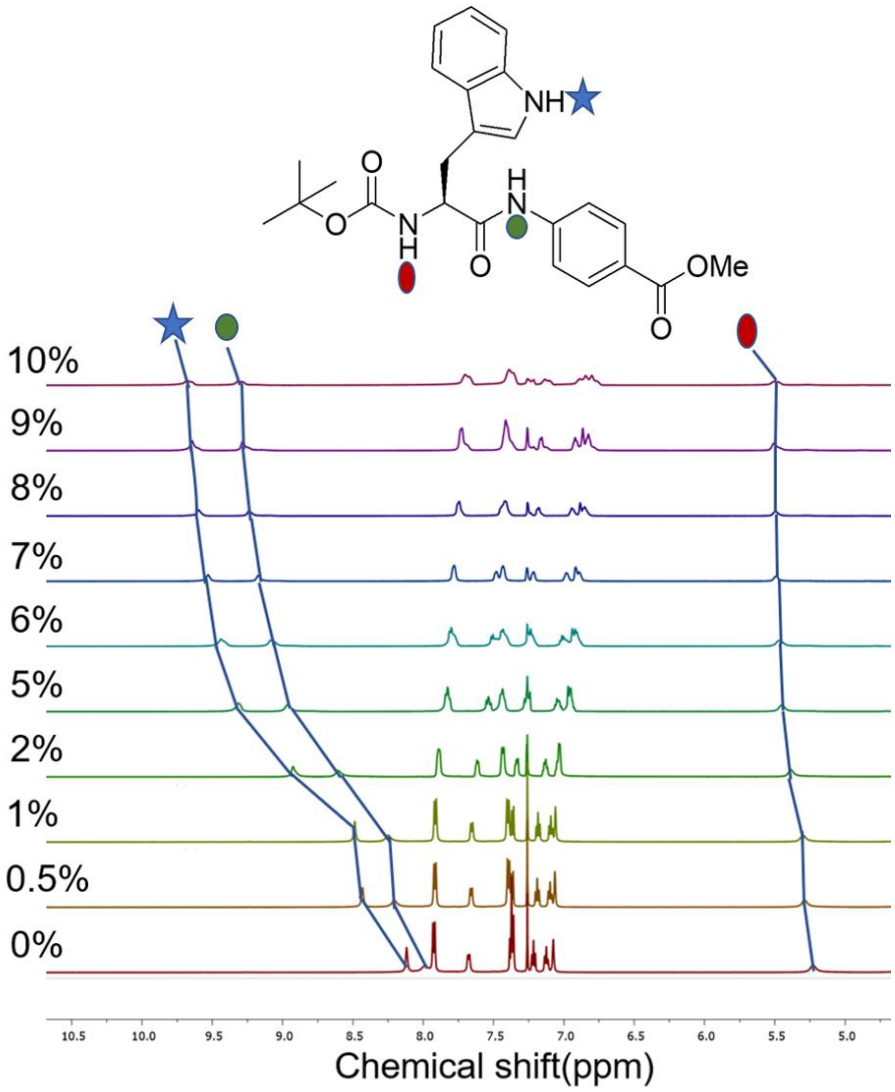

Figure S17: Stacked NH region of the ^{1}H NMR spectrum obtained upon addition of increasing amounts of DMSO-d_6 to the $CDCl_3$ solution of P1.

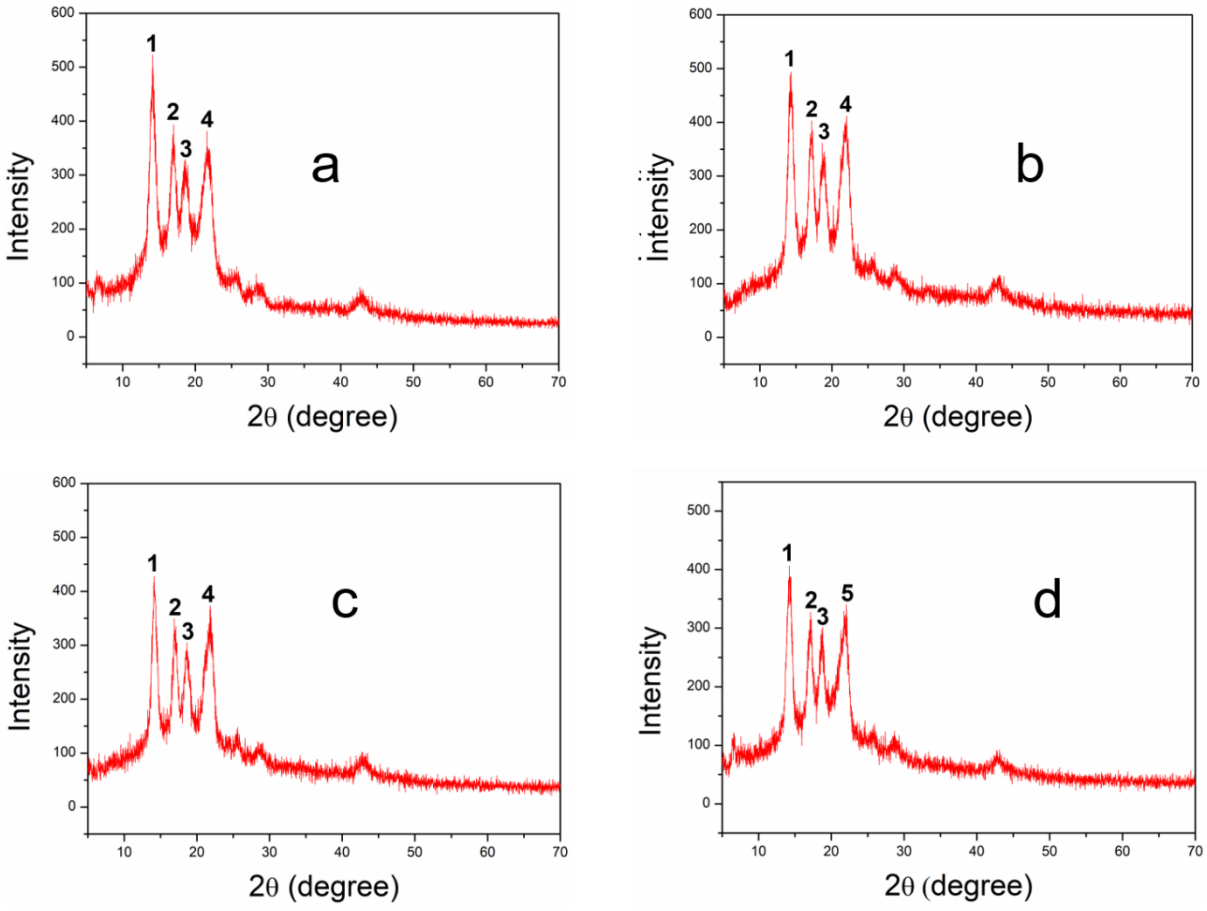

Figure S18: PXRD of xerogels of peptides (a) P1, (b) P2, (c)P3 and (d) P4.

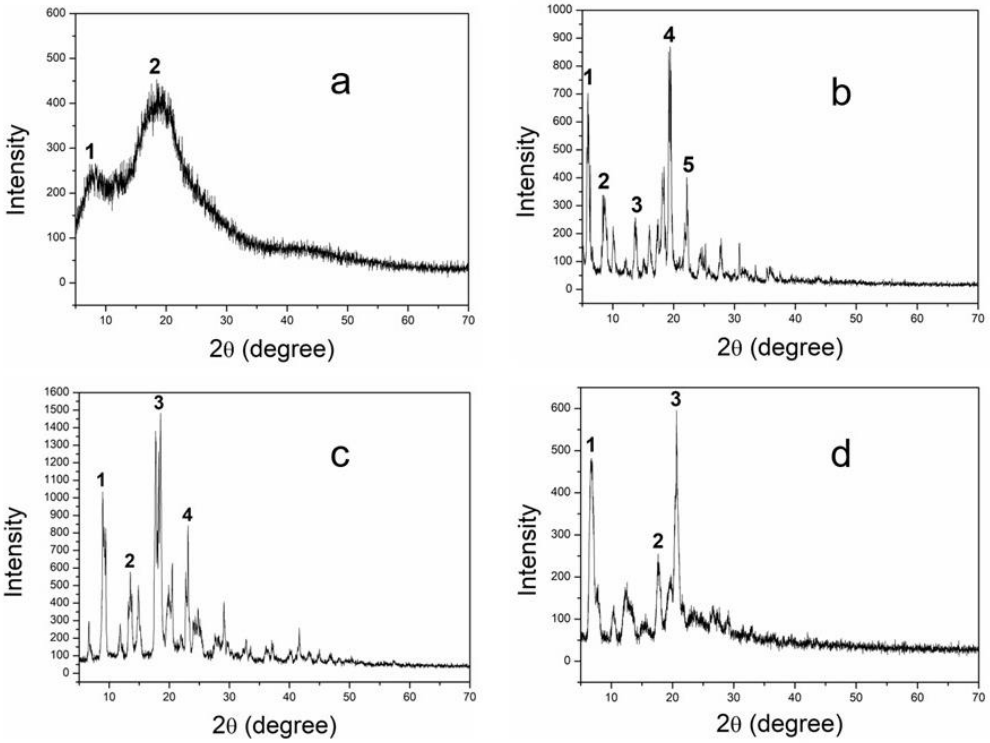

Figure S19: PXRD of peptides in powdered state. (a) P1, (b) P2 (c) P3 and (d) P4.

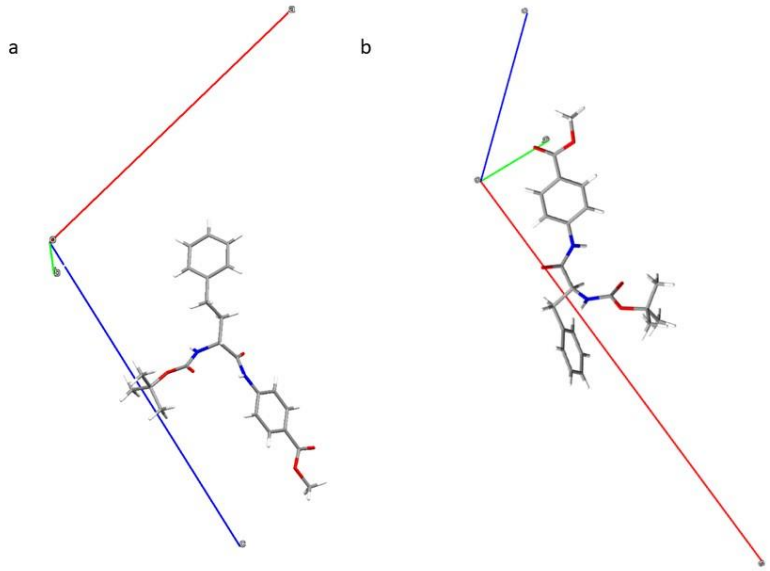

Figure S20: Asymmetric unit cell in the crystals of (a) P2 and (b) P4.

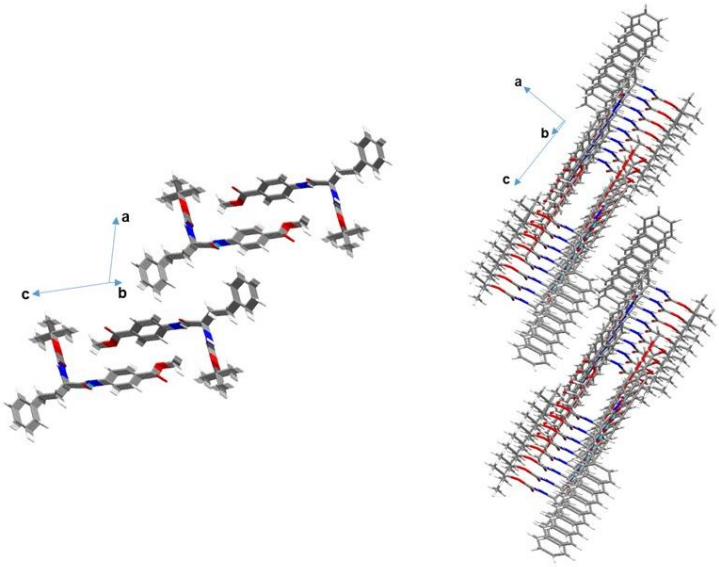

Figure S21: Packing in the crystals of P2.

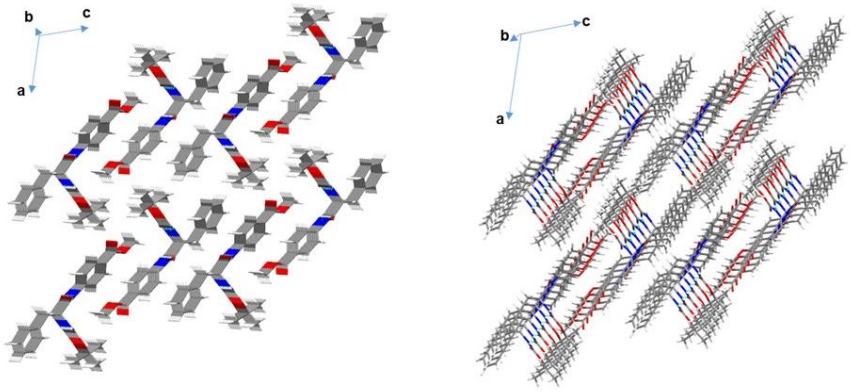

Figure S22: Packing in the crystals of P4.

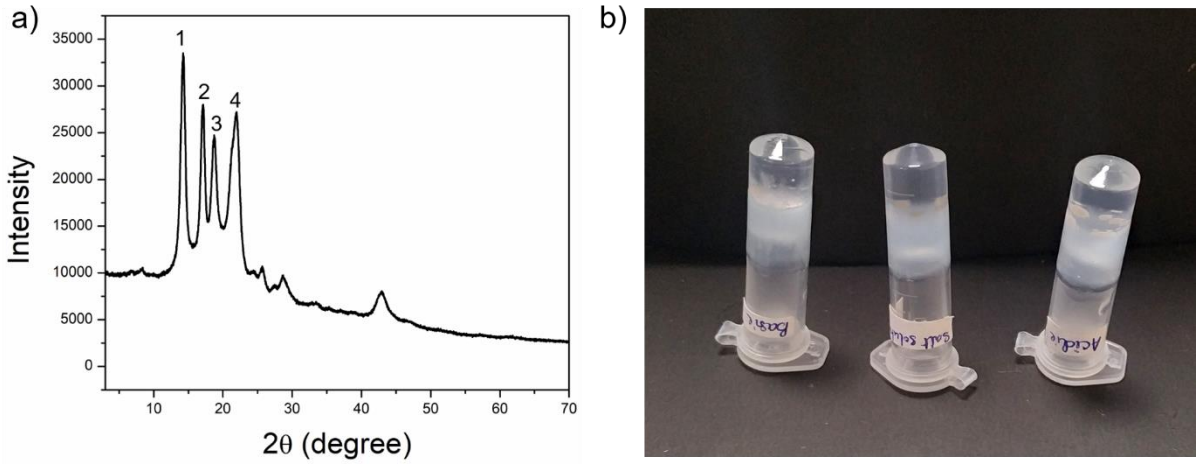

Figure S23: a) PXRD of P1 xerogel in kerosene and b) gelation of P1 in kerosene in the presence of acidic, salt solution and basic solution.

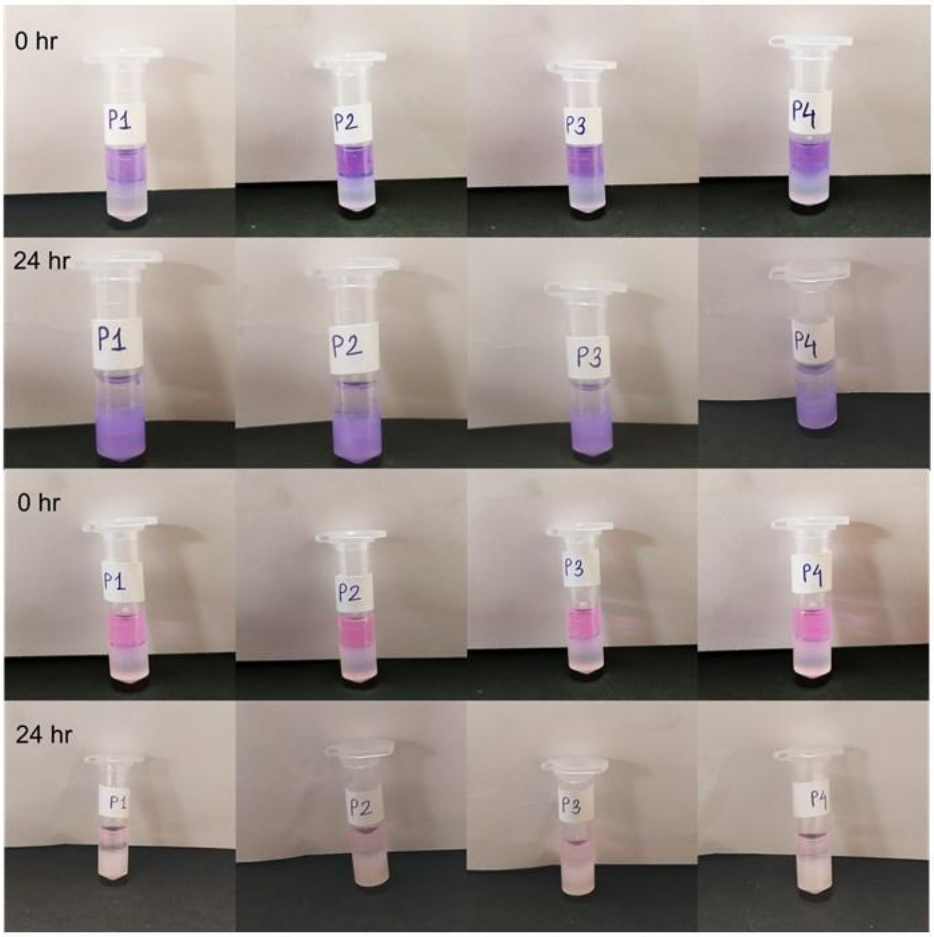

Figure S24: Absorption of cationic dyes CV and RB by organogels P1-P4.

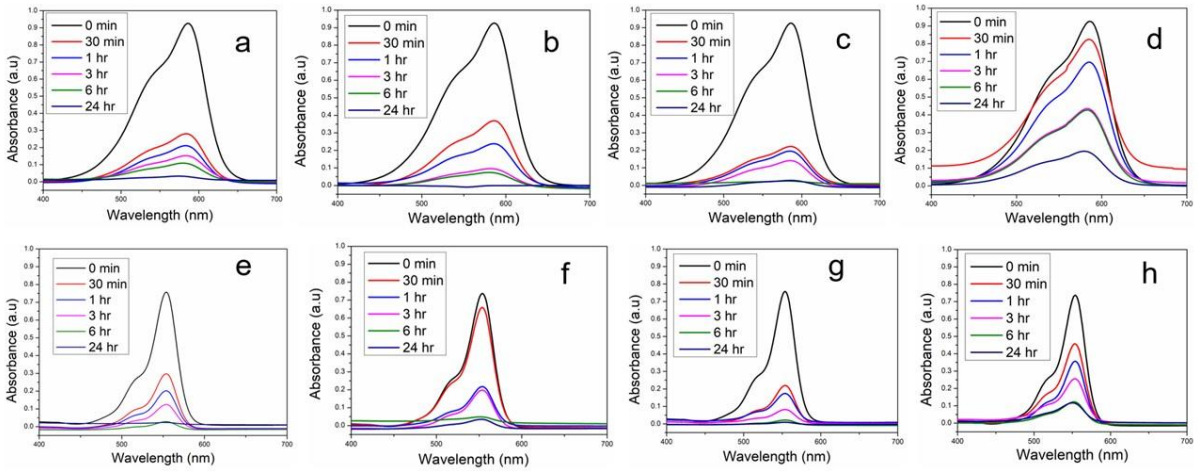

Figure S25: Absorption of dyes by organogels P1-P4 studied by UV spectroscopy. Time dependent absorption spectra of the supernatant solution containing CV (a-d) and RB (e-h) incubated with organogels formed by P1-P4 respectively in 1,2-DCB

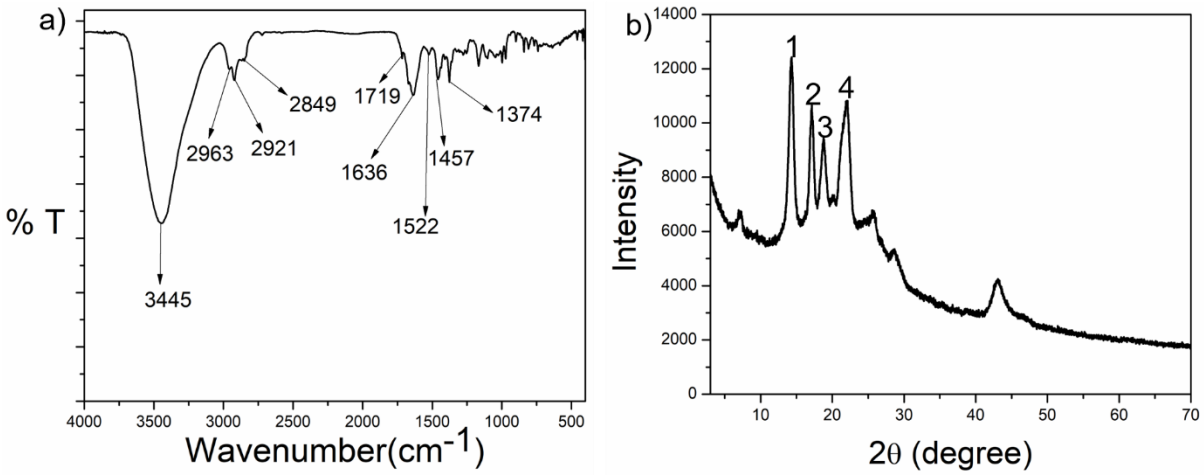

Figure S26: a) FT-IR of RGO-P1 hybrid xerogel and b) PXRD of RGO-P1 hybrid organogel.

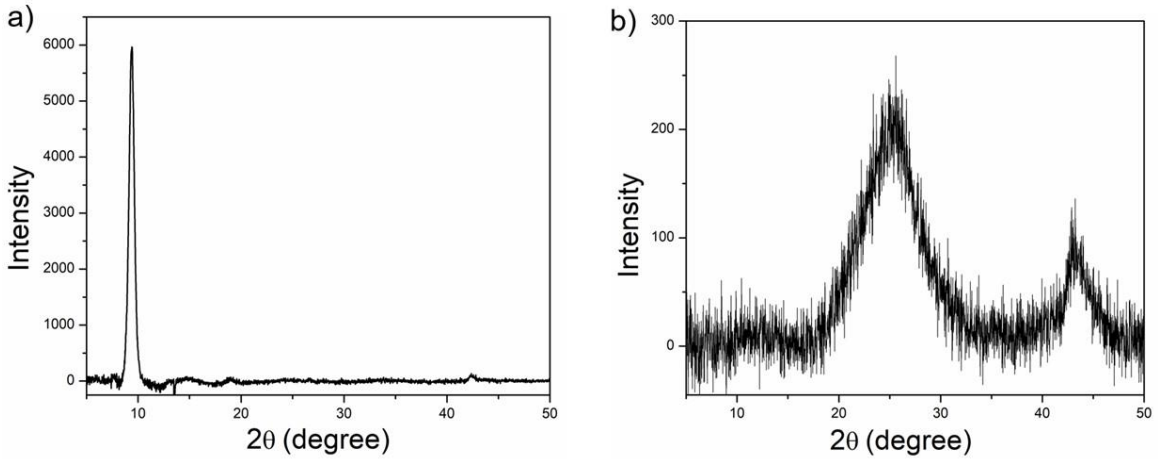

Figure S27: PXRD of a) graphene oxide and b) RGO incorporated into the hybrid organogels.

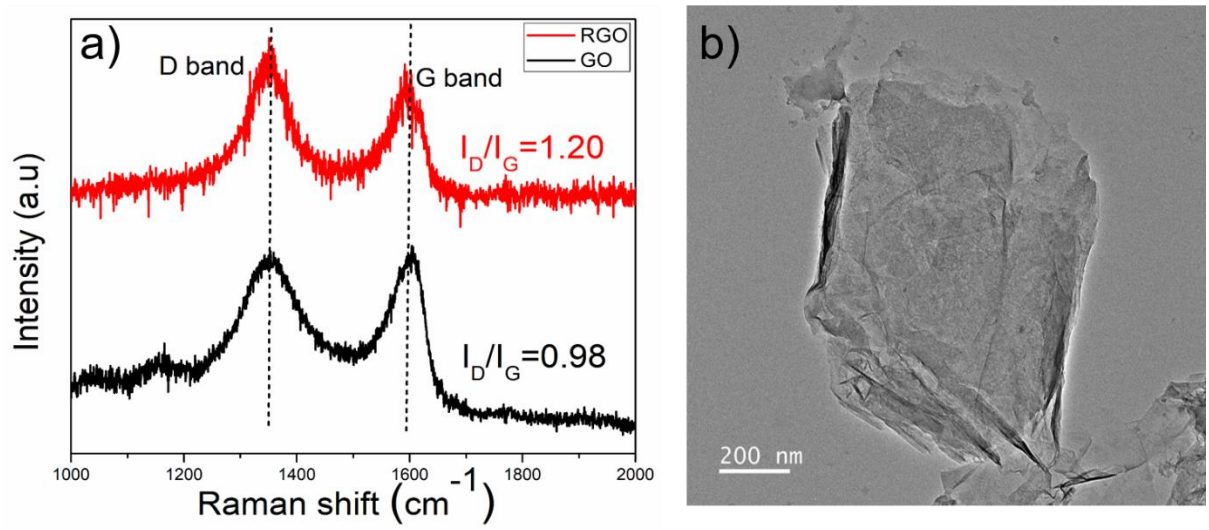

Figure S28: a) Raman spectra of GO and RGO. b)TEM image of RGO

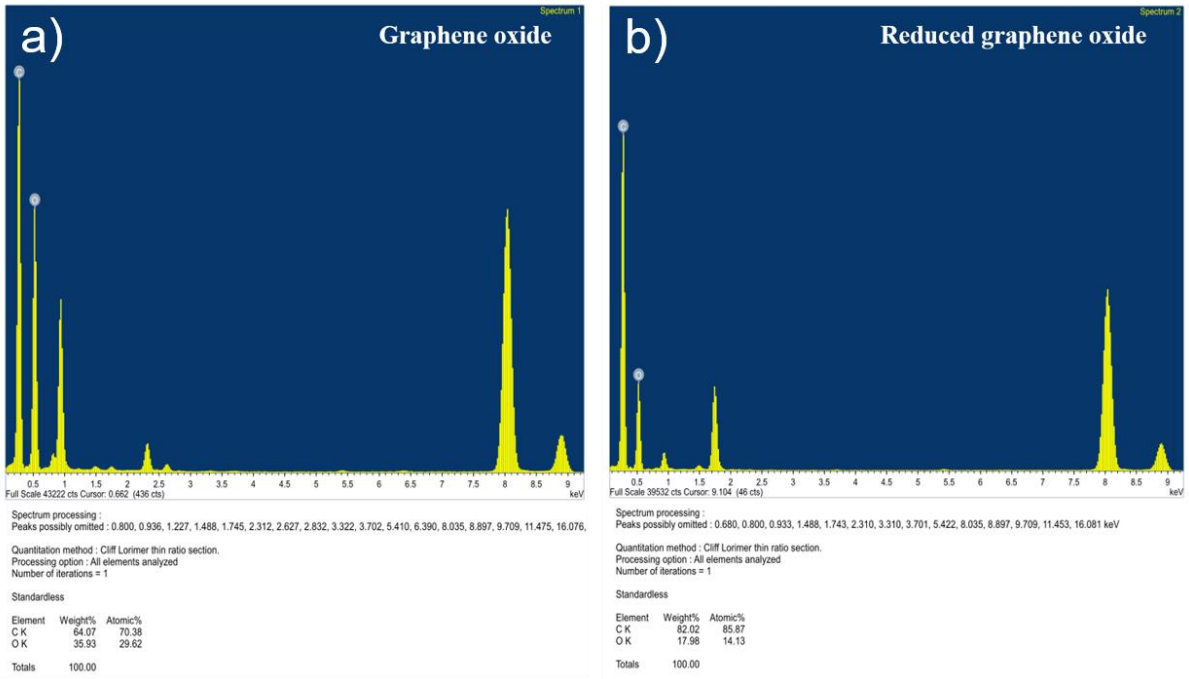

Figure S29: a) EDX analysis of GO and b) EDX analysis of RGO.

TABLES:

Table S1: Gelation properties of peptides P1-P4. OG: Opaque Gel, TNS: Translucent Gel, S: Soluble

Solvents	P1 State/MGC(%w/v)/T_{gel}(ºC)	P2 State/MGC(%w/v)/T_{gel}(°C)	P3 State/MGC(%w/v)/T_{gel}(ºC)	P4 State/MGC(%w/v)/T_{gel}(ºC)
Chloroform	OG/0.20/52	OG/0.20/50	OG/0.30/32	OG/0.20/45
1,2 DCB	TNS/0.4/69	TNS/0.30/62	TNS/0.40/78	TNS/0.40/76
Toluene	Transparent/0.20/50	Transparent/0.20/63	Transparent/0.25/75	Transparent/0.10/62
Benzene	Transparent/0.25/52	Transparent/0.20/57	Transparent/0.20/56	Transparent/0.30/51
THF	OG/0.35/55	OG/0.20/70	OG/0.35/40	OG/0.20/40
Chlorobenzene	Transparent/0.35/50	Transparent/0.20/47	Transparent/0.35/71	TNS/0.40/43
ACN	S	-	S	S
Dioxane	S	-	S	S
DMF	S	-	S	-
Ethanol	S	S	S	S
DMSO	S	S	S	S
Methanol	S	-	S	S
n-heptane	-	S	-	-

Table S2: Interplaner distances in the xerogels obtained from PXRD

Xerogels	Peak 1		Peak 2		Peak 3		Peak 4	
	2θ (degree)	d(Å)	2θ (degree)	d(Å)	2θ (degree)	d(Å)	2θ (degree)	d(Å)
P1 (DCB solvent)	14.121	6.265	17.041	5.191	18.641	4.754	21.601	4.109
P2 (DCB solvent)	14.321	6.179	17.181	5.154	18.901	4.689	22.041	4.028
P3 (DCB solvent)	14.121	6.265	16.861	5.252	18.641	4.754	21.841	4.064
P4 (DCB solvent)	14.241	6.212	17.161	5.162	18.841	4.704	22.061	4.024
RGO-P1 hybrid (DCB solvent)	14.199	6.232	17.081	5.18501	18.652	4.751	21.993	4.037
P1 (Kerosene oil)	17.093	5.185	18.690	4.7428	21.88	4.0579	25.645	3.4695

Table S3 Crystallographic parameters of P2 and P4

Parameters	P2	P4
Molecular formula	C_{23} H_{28} N_2 O_5	C_{22} H_{26} N_2 O_5
Formula weight	412.47	398.45
Crystal system	Monoclinic	Monoclinic
Crystallizing solvent	Methanol/H_2O	Methanol/H_2O
Space group	I 2 (5)	C 2 (5)
a/Å	20.281(9)	27.13(2)
b/Å	5.226(3)	5.227(4)
c/Å	22.662(10)	15.424(12)
α/°	90	90
β/°	105.39(5)	105.46(4)
γ/°	90	90
V/ Å^3	2316(2)	2108(3)
Z	4	4
Density/g cm^{-3}	1.183	1.255
Molecules/asym.unit	1	1
R1	0.0829	0.1036
wR2	0.1971	0.2240
CCDC No.	1961451	1961450

Table S4 Torsion angles (deg) for the peptides of P2 and P4

Peptide	Residue	ϕ	θ_1	θ_2	θ_3	ψ
P2	HPhe PABA	95.83 30.06	178.55	1.41	179.36	89.48 180.0
P4	Phe PABA	-98.44 -35.70	-177.73	2.35	-179.25	92.06 178.54

Table S5: Intermolecular H-bond parameters for peptide P2 and P4

Peptide	Donor (N)	Acceptor (O)	N----O (Å)	H----O (Å)	<N-H----O (deg)
P2	N1 (PABA) N2'(HPhe)	O1'(HPhe) O4 (Boc-CO)	3.027 3.086	2.259 2.269	148.90 158.46
P4	N1 (PABA) N2'(Phe)	O3'(Phe) O4 (Boc-CO)	3.034 3.040	2.265 2.217	149.40 159.77

Table S6: Gelation ability of P1 in fuels

P1	MGC(w/v)	T_{gel}
Kerosene	0.6%	91º C
Petrol	1.5%	75º C
Diesel	1.5%	84º C

Table S7: Dye absorption efficiencies of the organogels P1-P4

Gelators	CV(%)	RB(%)
P1	92.94	98.57
P2	95.66	97.70
P3	89.00	99.60
P4	91.87	53.55

Synthesis of Boc amino acids:

Amino acid (1 equiv.) was dissolved in 5N NaOH and stirred; temperature was maintained at 0 ℃. To the stirred solution Boc anhydride (1.2 equiv.) dissolved in 1,4-dioxane was added. The pH of the reaction was maintained around 12 and was allowed to stir overnight under ice-cooled condition. After that dioxane and water was evaporated completely *in vacuo*. To the reaction mixture water was added until it completely dissolved and washed with 50 ml ethyl acetate (3X) to ensure removal of excess Boc anhydride. The aqueous layer was taken and

acidified with 6N HCl (pH = 2). Then it was extracted with 50 ml ethyl acetate (3X) and washed with brine solution. The organic layer was dried over anhydrous Na_2SO_4 and was finally evaporated to get the Boc protected amino acid. This was used for synthesis without further purification.

All the four Boc protected amino acids namely Boc-W-OH, Boc-homo-Phe-OH, Boc-Phg-OH and Boc-F-OH were synthesized by the above procedure.

Synthesis of PABA-methyl ester:

Para amino Benzoic acid (PABA) (1 equiv.) was taken in a dry round bottom flask (RB). Into it required amount of dry methanol was added. The RB was kept in inert atmosphere. Into the reaction mixture, $SOCl_2$ (1.5 equiv.) was added drop-wise and the reaction mixture was stirred for another 40 minutes under ice cooled condition. After 40 minutes the reaction mixture was refluxed for 4 hours. After four hours the reaction mixture was cooled down and then evaporated to get the PABA methyl ester. This was used for synthesis without further purification.

Synthesis of dipeptide P1:

Boc-W-OH (1 equiv.) was taken in an RB and dissolved in dry THF. The reaction mixture was put in an ice bath with mechanical stirring. Para amino benzoic acid methyl ester (2 equiv.) was taken in a beaker and dissolved in water. Then this aqueous solution was basified with $NaHCO_3$ solution. After that the reaction mixture was extracted with ethyl acetate (3X). The organic layer was collected, washed with brine solution and dried over anhydrous Na_2SO_4 and evaporated *in vacuo* till a concentrated solution of free base was obtained. This free base was added into the reaction mixture containing Boc-W-OH along with simultaneous addition of DCC (1 equiv.) and HOBt (1 equiv.) and was allowed to stir overnight. The reaction mixture was evaporated completely by using rota-vapour. Cold acetonitrile was added to the residue and the solution were kept in ice cold condition for 10 minutes. After that DCU was filtered which precipitated out in acetonitrile and the solution was concentrated *in vacuo*. Ethyl acetate was added to the residue and was washed with 2N HCl and then 10% Na_2CO_3 solution. This was followed by a brine solution wash. The ethyl acetate layer was collected and anhydrous Na_2SO_4, passed through it. Finally, the ethyl acetate was collected in and evaporated *in vacuo* to get P1. P2, P3 and P4 were synthesized by identical methods.

Purification of the peptides:

The dipeptides were purified using column chromatography over silica gel using solvent systems 40% ethyl acetate in hexane for P1, 25% for both P2 and P4, 30% for P4 respectively.

Post purification all the peptides were characterized using HPLC (Figure S1-4), ESI-MS (Figure 5-8) and ^{1}H NMR (Figure 9-12).

Preparation of graphene oxide:

Graphene oxide (GO) was synthesized following the modified Hummers' method. 1g of graphite powder was added to 50 ml of concentrated sulphuric acid taken in a conical flask while maintaining the temperature between 0-5° C followed by the addition of 6g potassium permanganate (KMnO4) to the above mixture under constant stirring. The conical was then transferred to a water bath where it was maintained at 35° C for 2 hours. In the next step the conical flask was again transferred to an ice bath where 100 ml of DI water was slowly added under vigorous stirring. Lastly 8 ml of hydrogen peroxide (H_2O_2) was added to this diluted mixture to obtain a yellow coloured slurry, which was washed with 20% HCl followed by acetone until the pH increased above 5. The as obtained GO powder was then dispersed in DI water.

Preparation of reduced graphene oxide:

100 ml of 0.5 mg/ml of GO dispersion in water was taken in a reagent bottle and heated at about 70 °C followed by addition of 3 ml liquid ammonia and 40 µL of hydrazine hydrate. The resultant mixture turned blackish in colour and was further heated for another 30 minutes to obtain the reduced graphene oxide.

Characterization of RGO:

The pXRD of GO and rGO contained a peaks at 2θ = 9.5° and 25.6, corresponding to a d spacings of 9.29 Å and 3.47 Å respectively. The larger interplaner distances in GO were attributed to the functional groups present in the basal plane of GO. The smaller interplaner distances in rGO indicated closely packed 2D sheets in the case of rGO compared to that of GO (ACS Appl. Mater. Interfaces 2017, 9, 19417−19426).

Raman spectra of synthesized RGO gave a characteristic D and G band at 1351 and 1595 cm^{-1} respectively (Figure S28). The ratio of the intensities of D and G bands was 1.18 which was in compliance with the standard reports (ACS Appl. Mater. Interfaces 2017, 9, 19417−19426)

RGO was further characterized using TEM (Figure S28). TEM image of RGO exhibited several layers of thick flakes, each of a few micrometers in size.

EDX analysis of graphene oxide and reduced graphene oxide has been done to estimate the wt% of Carbon and oxygen in the samples. While the C and O % were 64.07%. and 35.93% for graphene oxide, it was 82.02% and 17.98% for RGO (Figure S29).