Supporting Information

Self-assembling behaviour of a modified aromatic amino acid in competitive medium

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Synthesis of 4-Nitro-Phenylalanine (4NP)

4-Nitrophenylalanine was synthesized using the procedure reported in the literature[1]. 1.65 g (10 mmol) of L-phenylalanine was taken in a round bottom flask along with 2 mL conc. H_2SO_4 and mixed properly by a stirrer at the ice-cold condition. After 15 min, mixed acid (0.7 mL conc. H_2SO_4 and 0.7 mL conc. HNO_3) was added drop-wise with continuous stirring for 1 hr. Then, the solution was allowed to stir at room temperature for 4 hrs. The reaction mixture was poured into 100 mL ice-cold water with continuous stirring. The resulting solution was basified with liquor ammonia. The volume of the resulting solution was reduced until the precipitation appeared. The light yellow coloured solid mass was obtained and recrystallized in water. Shining needle-shaped crystal was grown in the water medium.

Yield: 1.2 g (55 %); M.P. : 247(±1) °C; ^{1}H NMR (300 MHz, DMSO-d_6, 60 °C): δ = 8.14-8.11 (m, 2H, Phe ring), 7.57-7.54 (m, 2H, Phe ring), 3.50-3.49 (m, 1H, α-H), 3.26-3.20 (m, 1H, β-H), 3.02-2.95 (m, 1H, β-H); MS (ESI): m/z calcd. for $C_9H_{10}N_2O_4$: 210.0641 $[M+H]^+$; found: 210.9858.

^{1}H NMR Spectra:

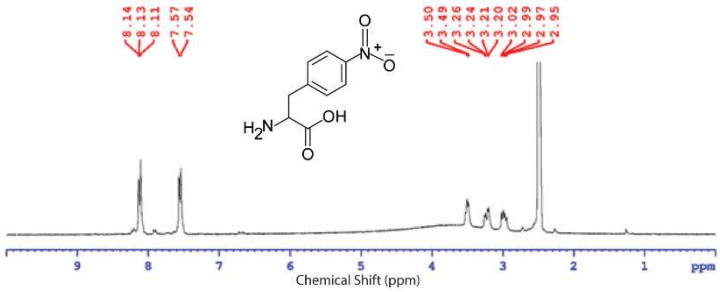


Fig. S1. ^{1}H NMR (300 MHz) spectrum of the 4-Nitro-Phenylalanine (4NP) in DMSO-d_6 at 60 °C.

Mass Spectrum

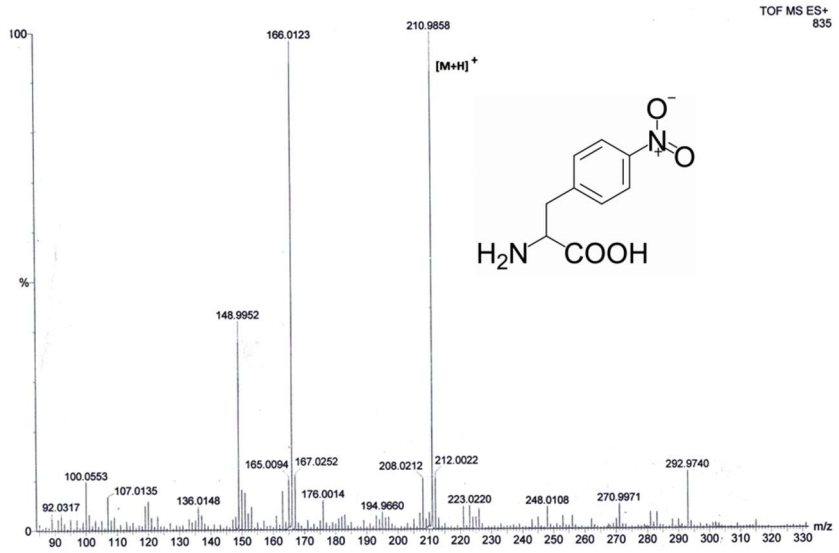


Fig. S2. HRMS spectrum of the 4-Nitro-Phenylalanine (4NP).

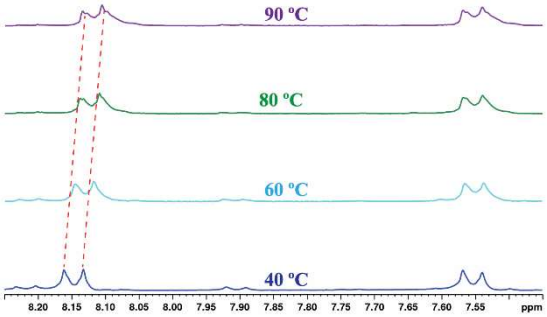


Fig. S3. Temperature dependent ^{1}H NMR experiment of 4NP in DMSO-d_6. The gelator concentration in the gel is 0.6 % (w/v).

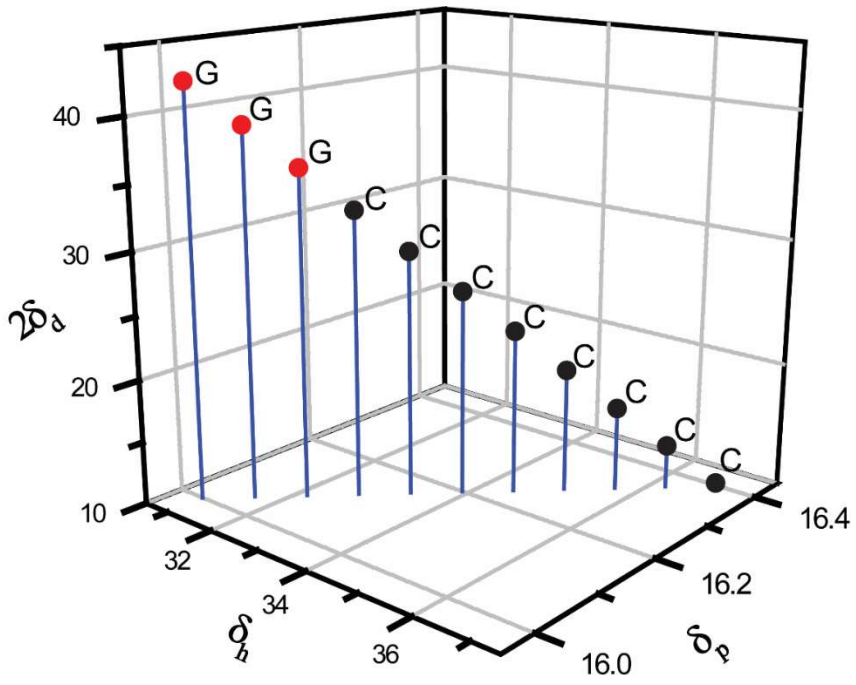


Fig. S4. Solubility for 4NP, represented in Hansen space. Here gel state represent by 'G' and crystal state represent the 'C'. Here, 2.0 mg of 4NP was dissolved in 1.0 ml of mixed solvents.

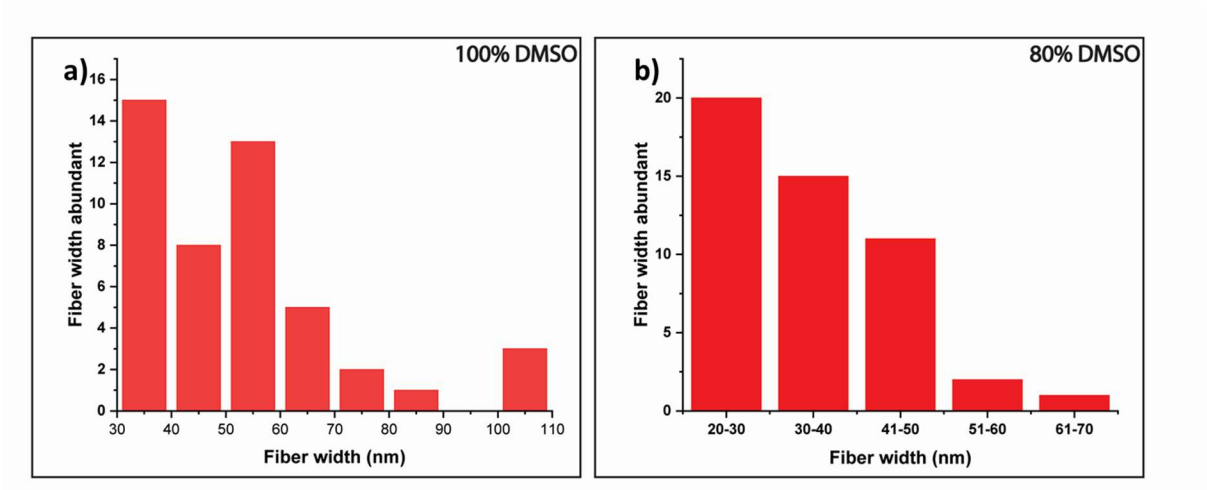


Fig. S5. Distribution of 4NP fiber diameter from FE-SEM images (**Fig 6**) with help of Image-J Software.

Table S1. Crystal data and refinement parameters for 4NP and comparative data for phenylalanine

Name	4-Nitro Phenylalanine (4NP)	Phenylalanine (Phe)[2]
Formula	$C_9H_{10}N_2O_4$, H_2O	$C_9H_{11}NO_2$
Crystal System	Monoclinic	Monoclinic
Space group	P 1 2_1 1	$P2_1$
a (Å)	6.241(5)	6.0010 (5)
b(Å)	5.293(4)	30.8020 (17)
c (Å)	15.726(9)	8.7980 (4)
α(°)	90	90
β(°)	101.19(2)	90.120
γ(°)	90	90
V (Å^3)	509.6(6)	1626.24 (17)
Z	8	8
D_{calc} (g.cm^{-3})	1.487	
μ(MoK$_\alpha$) (mm^{-1})	0.123	
F000	240	
Temperature (K)	293	
Radiation MoK$_\alpha$ (Å)	0.71073	
Theta Min-Max (°)	2.6, 25.1	
Dataset	-7 : 7 ; -6 : 6 ; -18 : 18	
Tot., Uniq. Data, R(int)	12375, 1818, 0.219	
Observed data, I > 2σ(I)	1728	
Nref, Npar	1818, 154	
R, wR2, S	0.0772, 0.2010, 1.07	
Max. and Av. Shift/Error	0.00, 0.00	
Min. and Max. Resd. Dens. [e/Å^3]	-0.30, 0.26	
CCDC No.	1961522	
'w=1/[\s^2^(Fo^2^)] where P=(Fo^2^+2Fc^2^)/3'		

Table S2. Different bond lengths (Å) present in **4NP**

O7-C10	1.246(6)	C11-C12	1.539(6)
O8-C10	1.252(6)	C13-C14	1.393(7)
O11-H11A	0.85(9)	C13-C12	1.501(7)
O11-H11B	0.83(12)	C13-C18	1.381(7)
N9-H9A	0.8900	C16-C15	1.376(7)
N9-H9B	0.8900	C16-C17	1.370(7)
N9-H9C	0.8900	C15-H15	0.9300
N9-C11	1.481(6)	C15-C14	1.388(8)
O10-N8	1.213(6)	C14-H14	0.9300
O9-N8	1.225(7)	C17-H17	0.9300
N8-C16	1.465(7)	C17-C18	1.388(8)
C10-C11	1.527(6)	C12-H12A	0.9700
C11-H11	0.9800		

Table S3. Different bond angles (°) present in **4NP**

H11A O11 H11B	98(7)	C15 C14 C13	120.4(5)
H9A N9 H9B	109.5	C15 C14 H14	119.8
H9A N9 H9C	109.5	C16 C17 H17	121.0
H9B N9 H9C	109.5	C16 C17 C18	118.0(5)
C11 N9 H9A	109.5	C18 C17 H17	121.0
C11 N9 H9B	109.5	C11 C12 H12A	108.8
C11 N9 H9C	109.5	C11 C12 H12B	108.8
O10 N8 O9	122.8(5)	C13 C12 C11	113.9(4)
O10 N8 C16	118.8(5)	C13 C12 H12A	108.8
O9 N8 C16	118.4(5)	C13 C12 H12B	108.8
O7 C10 O8	125.1(4)	H12A C12 H12B	107.7
O7 C10 C11	118.9(4)	C13 C18 C17	121.4(5)
O8 C10 C11	116.0(4)	C13 C18 H18	119.3
N9 C11 C10	110.5(4)	C17 C18 H18	119.3
N9 C11 H11	108.1	C15 C14 C13	120.4(5)
N9 C11 C12	109.6(4)	C15 C14 H14	119.8
C10 C11 H11	108.1	C16 C17 H17	121.0
C10 C11 C12	112.3(4)	C16 C17 C18	118.0(5)
C12 C11 H11	108.1	C18 C17 H17	121.0
C14 C13 C12	121.5(4)	C11 C12 H12A	108.8
C18 C13 C14	119.0(5)	C11 C12 H12B	108.8
C18 C13 C12	119.5(5)	C13 C12 C11	113.9(4)
C15 C16 N8	119.4(5)	C13 C12 H12A	108.8
C17 C16 N8	117.9(5)	C13 C12 H12B	108.8
C17 C16 C15	122.7(5)	H12A C12 H12B	107.7
C16 C15 H15	120.7	C13 C18 C17	121.4(5)
C16 C15 C14	118.6(5)	C13 C18 H18	119.3
C14 C15 H15	120.7	C17 C18 H18	119.3
C13 C14 H14	119.8		

Table S4. C–H···π distance present in **4NP**.

C–H→Cg	**H..Cg (Å)**	**C..Cg (Å)**	**<C-H..Cg (°)**
C12-H12A -> Cg1	2.823	3.707(6)	152

Table S5. Hydrogen bonding distances (Å) and angles (°) present in **4NP**

Donor (D)-H···Acceptor (A)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**< D–H···A (°)**
N(9)-H(9A)...O(7)	0.89	2.21	2.909(6)	135
N(9)H(9A)...O(11)	0.89	2.45	3.098(7)	130
N(9)-H(9B)...O(11)	0.89	1.89	2.771(6)	173
N(9)-H(9C)...O(8)	0.89	1.88	2.759(6)	168
O(11)-H(11A)...O(7)	0.85(8)	1.88(8)	2.715(6)	165(7)
O(11)-H(11B)...O(7)	0.83(10)	2.59(11)	3.292(6)	143(8)
O(11)-H(11B)...O(8)	0.83(10)	2.02(10)	2.807(6)	158(10)

Crystallographic data

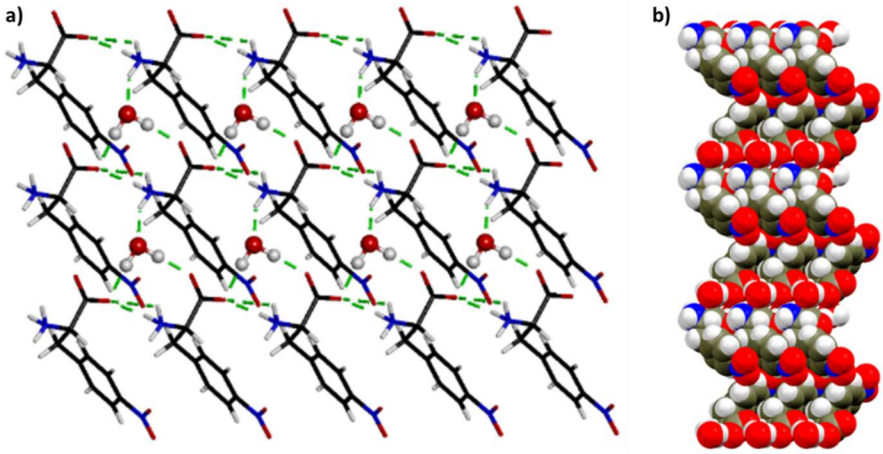


Fig. S6. a) Hydrogen bonding interaction pattern of 4NP with water molecule. **b**) Space fill model of 4NP.

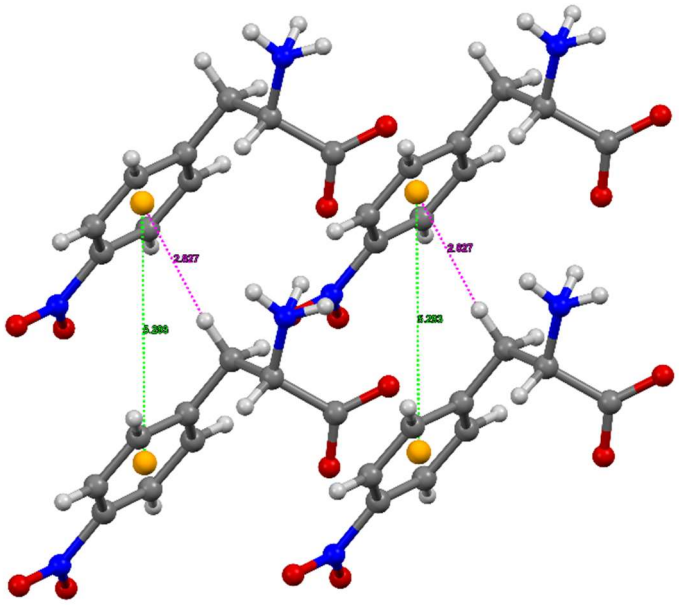


Fig. S7. π-π stacking interaction and C-H···π interaction pattern of 4NP.

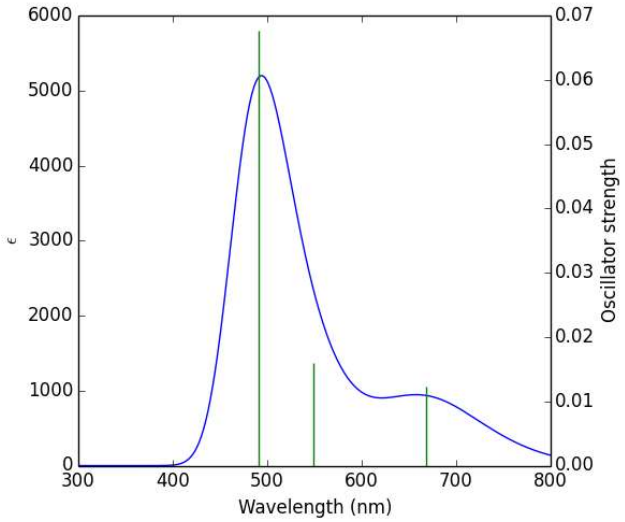
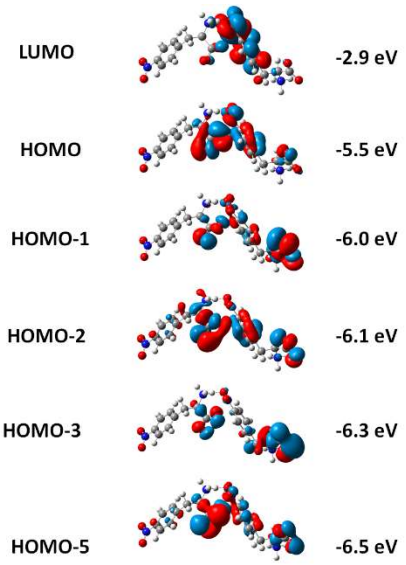


Fig. S8. UV-vis spectra of 4NP in DMSO environment obtained from TD-DFT calculations.



No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	668.73	0.0123	HOMO->LUMO (93%)	H-1->LUMO (2%)
2	548.91	0.0159	H-2->LUMO (70%), H-1->LUMO (27%)	H-5->LUMO (2%)
3	490.83	0.0676	H-2->LUMO (26%), H-1->LUMO (62%)	H-5->LUMO (3%), H-3->LUMO (2%), HOMO->LUMO (5%)

Fig. S9. Orbital pictures of different orbitals involved in various electronic transitions.

1. F. Bergel and J. A. Stock, *Journal of the Chemical Society (Resumed)*, 1954, 2409-2417.
2. E. Mossou, S. C. M. Teixeira, E. P. Mitchell, S. A. Mason, L. Adler-Abramovich, E. Gazit and V. T. Forsyth, *Acta Crystallographica Section C*, 2014, **70**, 326-331.