

Revised

Supporting Information

An Additional Fluorenylmethoxycarbonyl (Fmoc) Moiety in Fmoc-functionalized L-Lysine induces pH-controlled ambidextrous gelation with significant advantages

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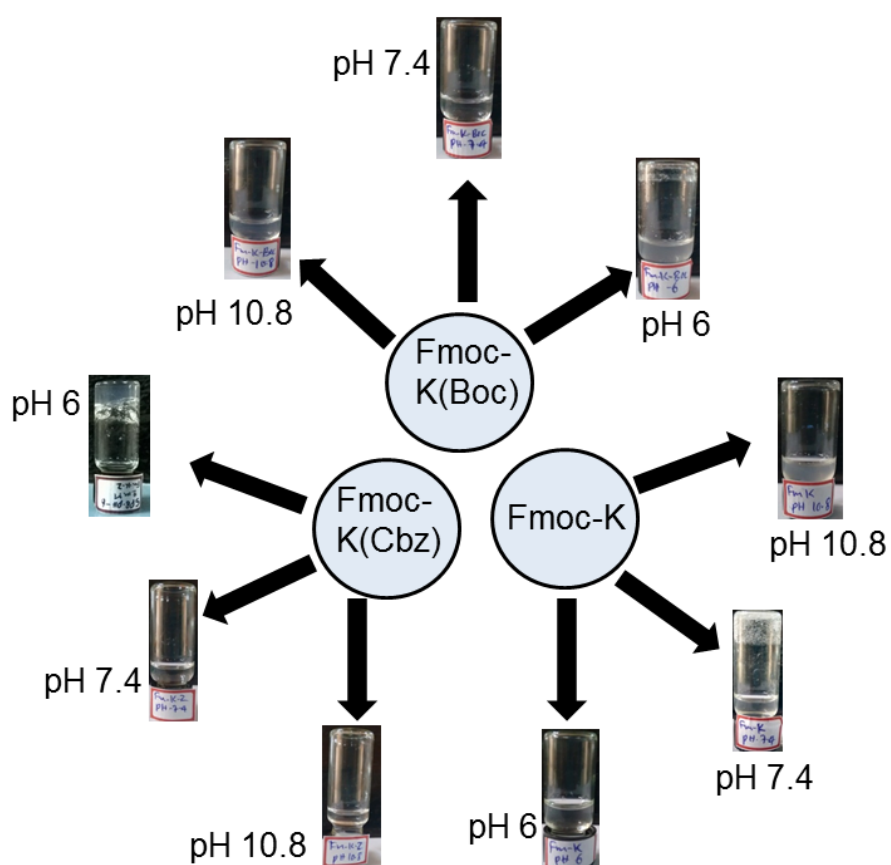


Figure S1: Digital images of Fmoc-K(Boc), Fmoc-K(Cbz) and Fmoc-K hydrogelation test at different pHs.

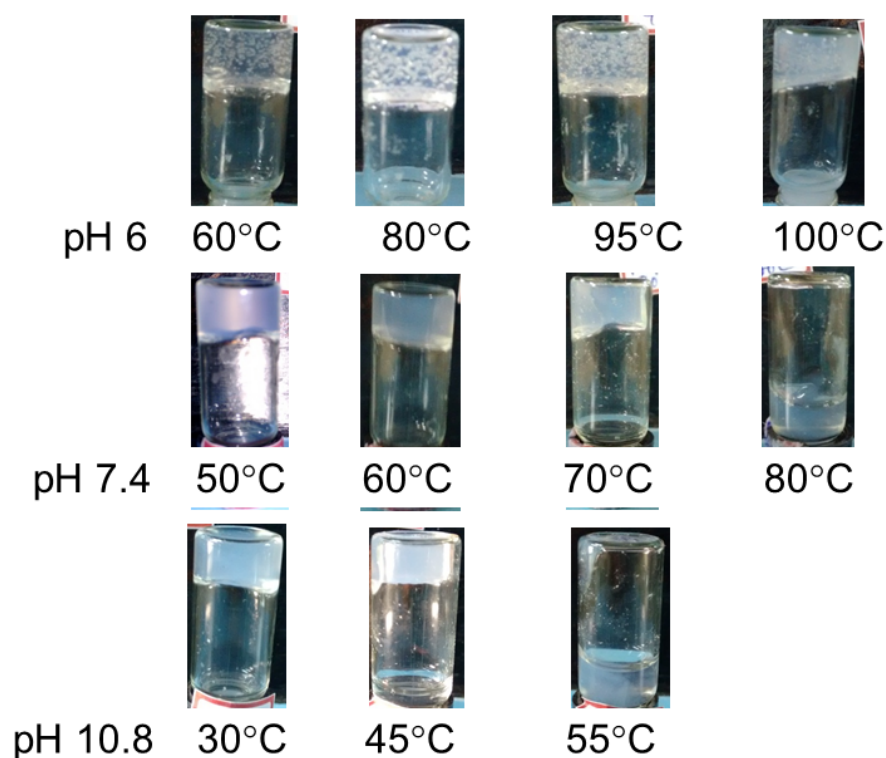


Figure S2: Digital images shows the effect of temperature on the Fmoc-K(Fmoc) hydrogels formed at different pH. The thermal stability of the Fmoc-K(Fmoc) hydrogels (5 mM, pH 6.0, 7.4 and 10.8) were tested by vial inversion method. Fmoc-K(Fmoc) hydrogels were prepared as described in earlier in the material and method section. The Fmoc-K(Fmoc) hydrogels were kept in a water bath and the temperature was increased from room temperature to desired temperature. The hydrogel was kept at the desired temperature for 10 mins.

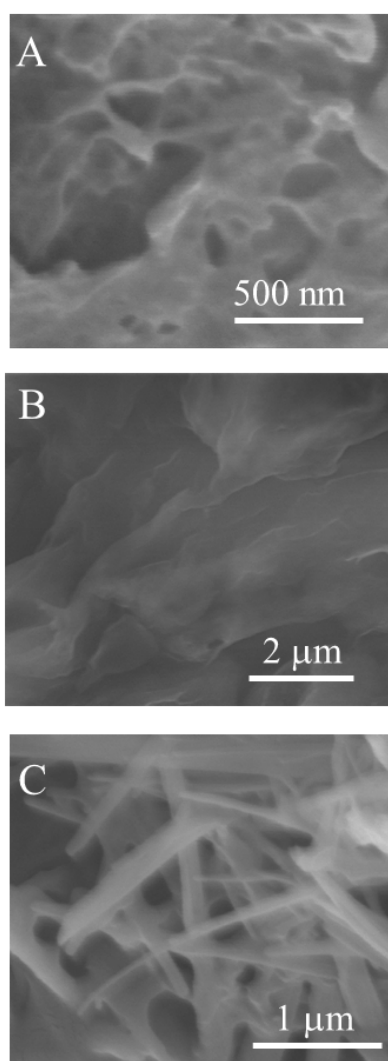


Figure S3: SEM images of lyophilized hydrogel of Fmoc-K(Fmoc) formed at pH 6.0 (A), pH 7.4 (B) and pH10.8 (C).

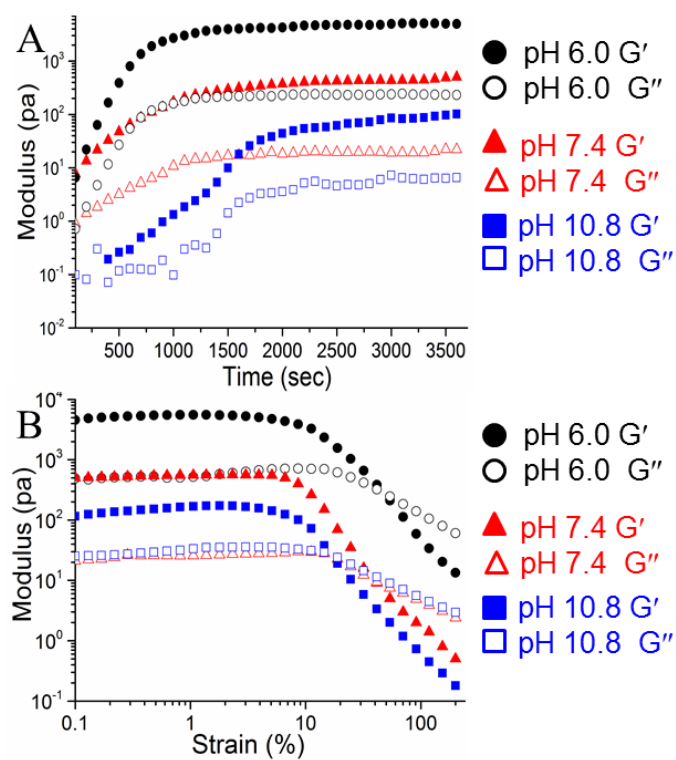


Figure S4: Time sweep (A) and amplitude sweep (B) test of Fmoc-K(Fmoc) hydrogels formed at pH 6.0, 7.4 and 10.8.

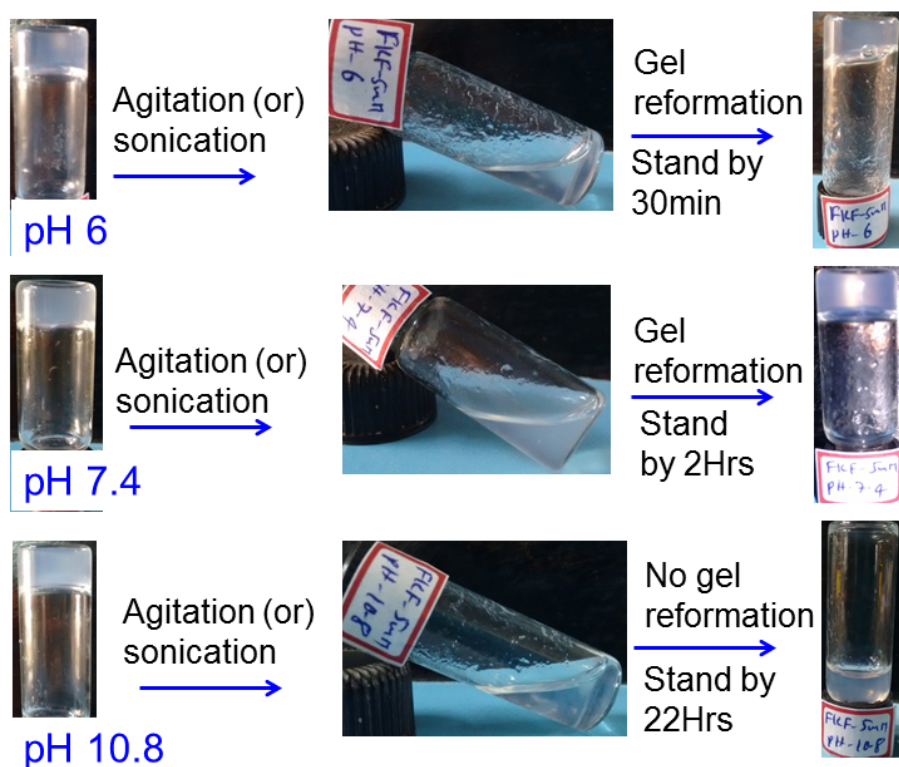


Figure S5: Digital images show the effect of agitation on the recovery of hydrogel (Thixotropic property) of Fmoc-K(Fmoc)hydrogels (5mM, pH 6.0, 7.4, and 10.8). Agitation was done manually. Fmoc-K(Fmoc) hydrogel exhibits thixotropic property at pH 6.0 and 7.4 while it doesn't at pH 10.8. Similar result was noticed when sonication was done instead of agitation.

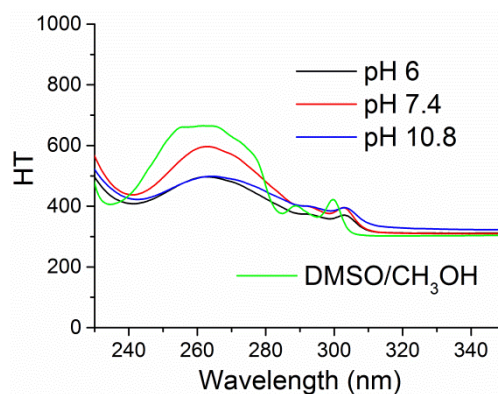


Figure S6: Change in HT, associated with the CD spectra of Fmoc-K(Fmoc) hydrogels at different pH and in DMSO/CH₃OH mixture, as a function of wavelength. Concentration of Fmoc-K(Fmoc) was 2 mM and the path length of the quartz cell was 0.5 mm.

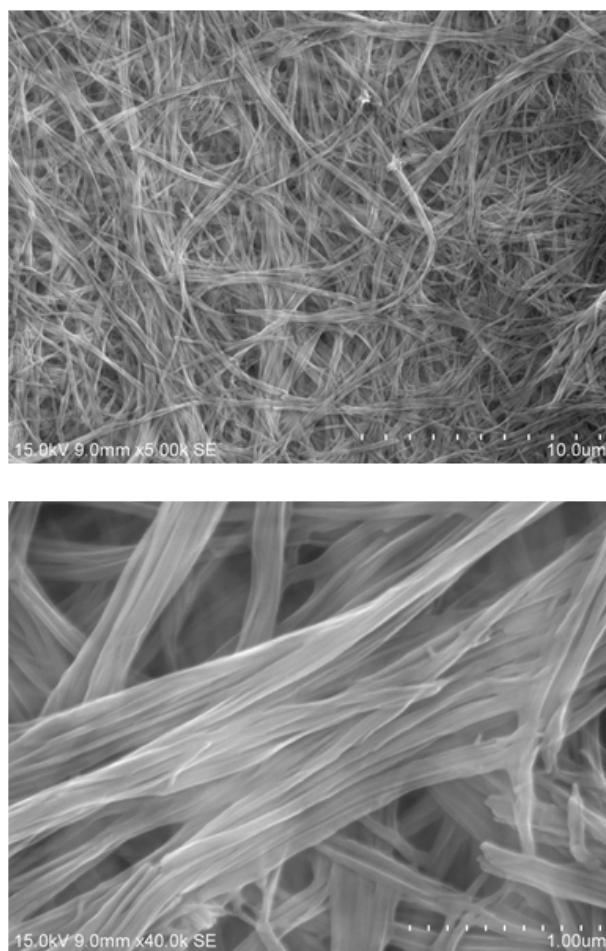


Figure S7: FESEM images of Fmoc-K(Fmoc) organogel formed in CH₃OH. FESEM images were collected on Hitachi SU6600. A small amount of organogel was dried at room temperature on an aluminium foil followed by gold-coating.

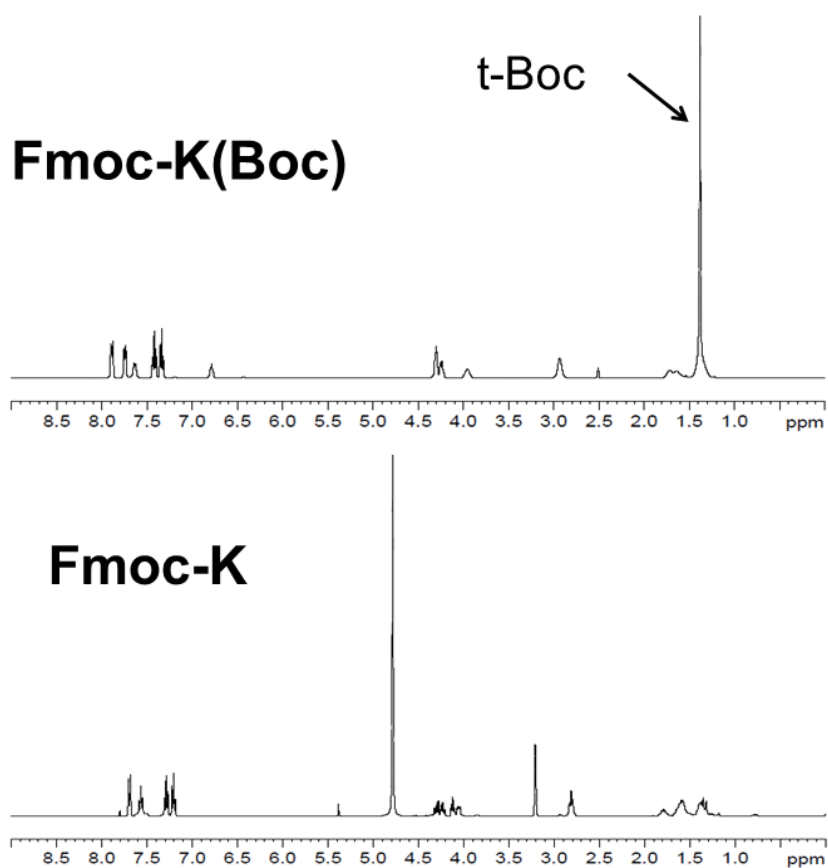


Figure S8: ^1H NMR spectra of Fmoc-K(Boc) and Fmoc-K in DMSO-d_6 and CD_3OD , respectively.

Table S1. Summary of hydrogelation and organogelation test of different Lysine-based LMW compounds

	pH /solvent	Nature of solution	Morphology	MGC (wt)	MGT (hrs)
Hydrogels					
Fmoc-K(Fmoc)	6.0	Transparent gel	Skin-like Fibrous nature	0.5% (0.1%)	5min (2hrs)
	7.4	Translucent gel	Smooth scaffold	0.5% (0.1%)	5min (2hrs)
	10.8	Translucent gel	Non-porous scaffold	0.5% (0.1)	~5min (>2hrs)
Fmoc-K(Cbz)	6.0	Transparent gel	nd	0.1%	>2
	7.4	Clear solution	-	-	-
	10.8	Clear solution	-	-	-
Fmoc-K(Boc)	6.0	Precipitate	nd	-	-
	7.4	Clear solution	-	-	-
	10.8	Clear solution	-	-	-
Fmoc-K	6.0	Clear solution	-	-	-
	7.4	Precipitate (sticky)	nd	-	-
	10.8	Precipitate	-	-	-
Organogels					
Fmoc-K(Fmoc)	CHCl ₃	Opaque gel	Bundles of fibrils	2%	1*
	CH ₂ Cl ₂	Opaque gel	Bundles of fibrils	2%	1*
	CH ₃ OH	Opaque gel	Bundles of fibrils	2%	1*

nd-not determined. MGT-minimum gelation time. *maximum 1 hr.

Table S2: Summary of organogelation of Fmoc-K(Fmoc) in different solvents.

Solvents	Fmoc-K(Fmoc) solubility in organic solvents at RT	Nature of the solution after annealing	Relative Polarity of the solvent
Cyclohexane	Insoluble	Ppt	0.006
Hexane	Insoluble	Ppt	0.009
Heptane	Insoluble	Ppt	0.012
Toluene	p.soluble	O.gel*	0.099
Chloroform	p.soluble	O.gel	0.259
Dichloromethane	p.soluble	O.gel	0.309
Tetrahydrofuran	soluble	Clear	0.207
Acetone	Soluble	Clear	0.355
DMF	Soluble	Clear	0.386
Acetonitrile	Insoluble	Insoluble	0.460
DMSO	Soluble	Clear	0.444
Methanol	p.soluble	O.gel	0.762

p.soluble= partially soluble; O.gel= Opaque gel; Highlighted in yellow indicates Fmoc-K(Fmoc) organogels formed within an hr at room temperature (RT) and studied in the current work. *requires longer time (days) to form organogel.

Table S3 Different vibrational frequencies (cm^{-1}) of Fmoc-K(Fmoc) hydrogels and organogels.

	C=O (COOH)	C=O (Fmoc)
DMSO- d_6	$\sim 1725^*$	1714
Hydrogel		
pH 6.0	1723	1690
pH 7.4	1717	1693
pH 10.8	nv	1693
Organogel		
CHCl_3	1712	1689
CH_2Cl_2	1707	1690
CH_3OH	1732	1689

nv-not visible (overlapped with C=O (Fmoc)), *overlapped with Fmoc C=O