Supporting Information:

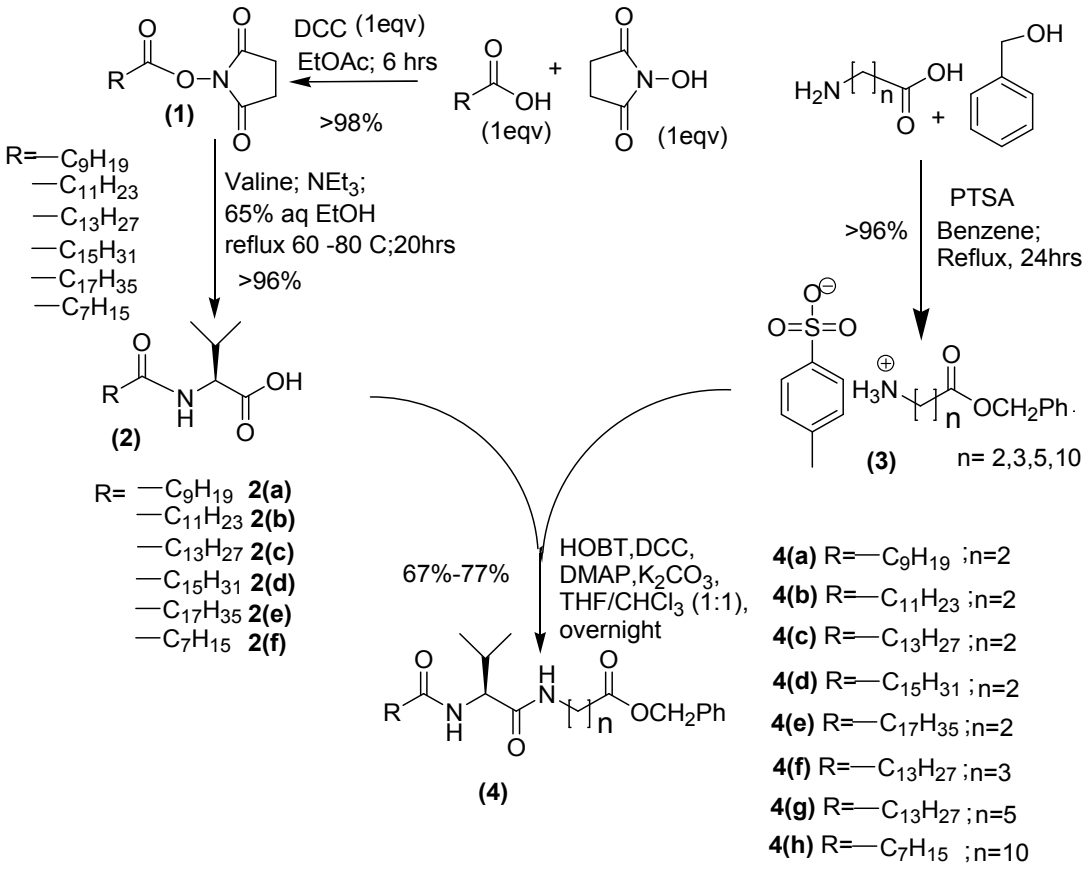
A systematic understanding of gelation self-assembly: Solvophobically assisted supramolecular gelation *via* conformational reorientation across amide functionality on a hydrophobically modulated dipeptide based ambidextrous gelator, N-*n*-acyl-(L)Val-X(OBn), (X = 1,ω-amino acid)

Saubhik Haldar and Koninika Karmakar*

Department of Chemistry, Jadavpur University, Kolkata 700 032, INDIA

Index

Scheme:


DCC (1eqv)
EtOAc; 6 hrs
>98%
(1)
(1eqv)
(1eqv)
R=—C9H19
—C11H23
—C13H27
—C15H31
—C17H35
—C7H15
Valine; NEt3;
65% aq EtOH
reflux 60 -80 C;20hrs
>96%
(2)
R= —C9H19 2(a)
—C11H23 2(b)
—C13H27 2(c)
—C15H31 2(d)
—C17H35 2(e)
—C7H15 2(f)
PTSA
>96%
Benzene;
Reflux, 24hrs
(3)
n= 2,3,5,10
67%-77%
HOBT,DCC,
DMAP,K2CO3,
THF/CHCl3 (1:1),
overnight
(4)
4(a) R=—C9H19 ;n=2
4(b) R=—C11H23 ;n=2
4(c) R=—C13H27 ;n=2
4(d) R=—C15H31 ;n=2
4(e) R=—C17H35 ;n=2
4(f) R=—C13H27 ;n=3
4(g) R=—C13H27 ;n=5
4(h) R=—C7H15 ;n=10

Synthetic procedure:

Synthesis of NHS ester of Fatty acids (1): To a solution of Fatty acid (1eqv) in 10 ml Ethyl acetate, N-hydroxysuccinimide (1eqv) was added followed by the addition of DCC (Dicyclohexylcarbodiimide) (1eqv) in 5 ml Ethyl acetate and the reaction stirred for 6-7 hrs. Completion of the reaction was confirmed byTLC.The reaction mixture was then filtered and the filtrate was concentrated under reduced pressure. The obtained residue was recrystallized from isopropanol and used for the next step without any further purification.(~98% yield).

Synthesis of N-Acyl-valine (2): To a solution of NHS ester of fatty acids (8.4 mmole, 1 eqv), (L)-Valine (1.2 eqv) in 40 ml of 65% aq Ethanol; Triethylamine (2.5 eqv) was added and put to reflux (60-80^{0}C) for 20 hrs. Then the reaction mixture was concentrated under reduced pressure and taken up in 25ml Ethyl acetate and washed sequentially with ice cold 1 (N) HCl (30 ml × 2), saturated brine solution (25 ml × 2).Organic layer was collected and dried over anhyd. Na_2SO_4 and evaporated under reduced pressure to give the desired product (~8.06mmol; ~96% yield; m.p= ~95-98^{0}C). The compoundswere used for the next step without any further purification.

2a: ^{1}HNMR (300 MHz,$CDCl_3$)-:δ::0.83-0.89 (t,C*H*$_3$ $(CH_2)_8$CONH-,3H), 0.89-0.98 (q, ($CH_3)_2$C*H*-CH (COOH)NH-, 7H), 1.1-1.3 (bs, CH_3 *(*$CH_2)_6$$CH_2CH_2$CONH-, 12H), 1.56-1.7 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-, 2H), 2.2-2.35 (t, CH_3 $(CH_2)_6CH_2CH_2$CONH-, 2H), 4.55-4.64 (q, -NHC*H* (COOH)CH $(CH_3)_2$, 1H), 5.89-5.99 (d, -N*H*-, 1H).

2b: ^{1}HNMR (300 MHz,$CDCl_3$)-:δ::0.88-0.92 (t,C*H*$_3$ $(CH_2)_{10}$CONH-,3H), 0.89-1.0 (q, ($CH_3)_2$C*H*-CH (COOH)NH-, 7H), 1.2-1.44 (bs, CH_3 *(*$CH_2)_8$$CH_2CH_2$CONH-, 16H), 1.56-1.7 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-, 2H), 2.21-2.35 (t, CH_3 $(CH_2)_8CH_2CH_2$CONH- , 2H), 4.55-4.61 (q, -NHC*H* (COOH)CH $(CH_3)_2$, 1H), 5.89-5.99 (d, -N*H*-, 1H).

2c: ^{1}HNMR (300 MHz,$CDCl_3$)-:δ::0.86-0.1 (t,*CH*$_3$ $(CH_2)_{12}$CONH-,3H), 0.89-1.0 (q, ($CH_3)_2$C*H*-CH (COOH)NH-, 7H), 1.2-1.45 (bs, $CH_3(CH_2)_{10}CH_2CH_2$CONH-, 20H), 1.56-1.7 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-, 2H), 2.23-2.35 (t, CH_3 $(CH_2)_{10}CH_2$*CH2CONH*- , 2H), 4.55-4.621 (q, -NHC*H* (COOH)CH $(CH_3)_2$, 1H), 5.89-5.99 (d, -N*H*-, 1H).

2d: ^{1}HNMR (300 MHz,$CDCl_3$)-:δ::0.89-0.1 (t,*CH*$_3$ $(CH_2)_{14}$CONH-,3H), 0.89-1.0 (q, ($CH_3)_2$CH-CH (COOH)NH-, 7H), 1.25-1.44 (bs, $CH_3(CH_2)_{12}CH_2CH_2$CONH-, 24H), 1.56-1.7 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-, 2H), 2.22-2.35 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-2, H), 4.55-4.61 (q, -NHC*H* (COOH)CH $(CH_3)_2$, 1H), 5.89-5.99 (d, -N*H*-, 1H).

2e: ^{1}HNMR (300 MHz,$CDCl_3$)-:δ::0.91-1.10 (t,C*H*$_3$ $(CH_2)_{16}$CONH-,3H), 0.89-1.0 (q, ($CH_3)_2$*CH*-CH (COOH)NH-, 7H), 1.2-1.46 (bs, $CH_3(CH_2)_{14}CH_2CH_2$CONH-, 28H), 1.56-1.7 (t, CH_3 $(CH_2)_{12}CH_2CH_2$CONH-, 2H), 2.23-2.35 (t, CH_3 $(CH_2)_{14}CH_2CH_2$CONH- , 2H), 4.55-4.611 (q, -NH*CH* (COOH)CH $(CH_3)_2$, 1H), 5.89-5.99 (d, -N*H*-, 1H).

Synthesis of p-toluenesulfonatesaltof 1-ω-Aminoacid benzylester (3): In 100ml of benzene a mixture of1,ω-Aminoacid(1 eqv), p-toluenesulfonic acid (PTSA).H_2O (1.1 eqv) and benzyl alcohol (2 eqv) was taken. After refluxing in Dean-Stark apparatus for 24hrs, 40 ml of diethyl ether was added to it with immediate precipitation of PTSA-salt of 1-ω-Aminoacid benzyl ester. The salt was then filtered, washed

with 10ml of dry diethyl ether and dried under reduced pressure. This compound was used for the next step without any further purification.(yield~96 %)

Synthesis of (4): To a solution of N-Acyl-(L)-valine (1 eqv) in 5ml of THF, Hydroxybenzotriazole (HOBt) (1.5 eqv) was added and kept on stirring in ice water bath at 0˚C.After 10mins of stirring, DMAP (1 eqv) and a solution of DCC (1.93 eqv) in 5 ml of $CHCl_3$ was added to it and kept stirring. Finally, after 15mins, K_2CO_3 (1.47 eqv) and PTSA-salt of 1-ω-Amino acid benzyl ester (1.2 eqv) was added and kept on stirring overnight at room temperture. The reaction mixture was then concentrated under reduced pressure and taken up in 30 ml $CHCl_3$ and washed sequentially with ice cold 1 (N) HCl (25 ml × 2), saturated brine (25 ml × 2).The organic layer was collected and dried over anhyd $Na_2SO_4$and then purified by silicagel (60-120 mesh) column chromatography in EtOAc/Petroleum ether solvent system of required ratios (~40% -60%) to get the desired product.

4a.Yield%=77%.^{1}HNMR (300 MHz, $CDCl_3$) : δ_H :: 0.875-0.918 (t, -NHCOCH$_2$CH$_2$ (CH$_2$)$_6$C*H*$_3$ and >CHCH (C*H*$_3$)$_2$, 9H), 1.27 (bs, -NHCOCH$_2$CH$_2$(C*H*$_2$)$_6$CH$_3$, 12H), 1.58-1.65 (m, -NHCOCH$_2$C*H*$_2$ (CH$_2$)$_6$CH$_3$,>CHC*H* (CH$_3$)$_2$,3H), 2.11-2.24 (t, -NHCOC*H*$_2$CH$_2$(CH$_2$)$_6$CH$_3$, 2H), 2.59-2.62 (t, -CONHCH$_2$C*H*$_2$COOCH$_2$Ph, 2H), 3.5-3.6 (m, CONHC*H*$_2$CH$_2$COOCH$_2$Ph, 2H), 4.17-4.2 (t, >C*H*CH (CH$_3$)$_2$, 1H), 5.09-5.1 (s, -CONHCH$_2$CH$_2$COOC*H*$_2$Ph, 2H), 6.11-6.13 (d,- N*H*COCH$_2$CH$_2$ (CH$_2$)$_6$CH$_3$), 1H), 6.52 (s, -CON*H*CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.26-7.35 (bs, aromatic, 5H).^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.42, 172.56, 171.41, 135.58, 128.62, 128.4, 128.2, 77.46, 77.04, 76.61, 66.54, 58.35 36.73, 36.67, 35.00, 33.96, 31.84, 31.19, 29.43, 29.32, 29.24, 25.74, 22.64, 19.12, 18.24, 14.07. ESI-MS (m/z) $C_{25}H_{40}N_2O_4$ (EXACT MASS= 432.3) 433.3(100%, $[M + H]^+$), 455.3(49%, $[M + Na]^+$).

4b.Yield=73%.^{1}HNMR (300 MHz, $CDCl_3$) : δ:: 0.87-0.91(t, -NHCOCH$_2$CH$_2$ (CH$_2$)$_8$C*H*$_3$ and >CHCH (C*H*$_3$)$_2$, 9H), 1.269 (bs, -NHCOCH$_2$CH$_2$(C*H*$_2$)$_8$CH$_3$, 16H), 1.63-1.74 (m, -NHCOCH$_2$C*H*$_2$ (CH$_2$)$_8$CH$_3$, >CHC*H* (CH$_3$)$_2$,3H), 2.11-2.2 (t, -NHCOC*H*$_2$CH$_2$(CH$_2$)$_8$CH$_3$, 2H), 2.58-2.62 (t, -CONHCH$_2$C*H*$_2$COOCH$_2$Ph, 2H), 3.5-3.63 (m, CONHC*H*$_2$CH$_2$COOCH$_2$Ph, 2H), 4.17-4.22 (t, >C*H*CH (CH$_3$)$_2$, 1H), 5.12 (s, -CONHCH$_2$CH$_2$COOC*H*$_2$Ph, 2H), 6.10-6.13 (d,- N*H*COCH$_2$CH$_2$ (CH$_2$)$_8$CH$_3$), 1H), 6.51(s, -CON*H*CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.37 (bs, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.2, 171.97, 171.35, 135.58, 128.62, 128.4, 128.3, 77.46, 77.04, 76.61, 66.61, 58.28 36.73, 34.9, 33.9, 31.8, 31.2, 29.6, 29.4, 29.32, 29.2, 25.74, 22.6, 19.12, 18.2, 14.09.ESI-MS (m/z) $C_{27}H_{44}N_2O_4$ (EXACT MASS= 460.33) 461.34(100%, $[M + H]^+$), 483.32(34%, $[M + Na]^+$).

4c.Yield=76%.^{1}HNMR (300 MHz, $CDCl_3$) : δ:: 1.1-1.25 (t, -NHCOCH$_2$CH$_2$ (CH$_2$)$_{10}$C*H*$_3$ and >CHCH (C*H*$_3$)$_2$, 9H), 1.57 (bs, -NHCOCH$_2$CH$_2$(C*H*$_2$)$_{10}$CH$_3$, 20H), 1.87-2.03 (m, -NHCOCH$_2$C*H*$_2$ (CH$_2$)$_{10}$CH$_3$,>CHC*H* (CH$_3$)$_2$,3H), 2.3-2.4 (t, -NHCOC*H*$_2$CH$_2$(CH$_2$)$_6$CH$_3$, 2H), 2.79-2.81 (t, -CONHCH$_2$C*H*$_2$COOCH$_2$Ph, 2H), 3.49 (s, CONHC*H*$_2$CH$_2$COOCH$_2$Ph, 2H), 4.19-4.32 (t, >C*H*CH (CH$_3$)$_2$, 1H), 5.12 (s, -CONHCH$_2$CH$_2$COOC*H*$_2$Ph, 2H), 6.12-6.13 (t,- N*H*COCH$_2$CH$_2$ (CH$_2$)$_{10}$CH$_3$), 1H), 6.63-6.651(t, -CON*H*CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.29-7.37 (m, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.27, 172.93, 171.407, 135.6, 128.62, 128.4, 128.28, 77.46, 77.041, 76.61, 66.59, 58.256, 36.7, 34.976, 33.99, 33.69, 31.9, 31.2, 29.63, 29.49, 29.33, 29.28, 25.75, 25.54, 25.544, 24.865, 24.77, 22.67, 19.13, 18.22, 14.09.ESI-MS (m/z) $C_{29}H_{48}N_2O_4$ (EXACT MASS= 488.36) 489.369(100%, $[M + H]^+$), 511.36(51%, $[M + Na]^+$).

4d.Yield=72%.^{1}HNMR (300 MHz, $CDCl_3$) : δ:: 0.875-0.918 (m, -NHCOCH$_2$CH$_2$ (CH$_2$)$_{12}$C*H*$_3$ and >CHCH (C*H*$_3$)$_2$, 9H), 1.27 (bs, -NHCOCH$_2$CH$_2$(C*H*$_2$)$_{12}$CH$_3$, 24H), 1.58-1.65 (m, -NHCOCH$_2$C*H*$_2$

$(CH_2)_{12}CH_3$,>CHC<u>*H*</u> $(CH_3)_2$,3H), 2.11-2.24 (t, -NHCOC<u>*H*</u>$_2$CH$_2$$(CH_2)_{12}CH_3$, 2H), 2.59-2.62 (t, -CONHCH$_2$C<u>*H*</u>$_2$COOCH$_2$Ph, 2H), 3.5-3.6 (m, CONHC<u>*H*</u>$_2$CH$_2$COOCH$_2$Ph, 2H), 4.17-4.2 (t, >C<u>*H*</u>CH $(CH_3)_2$, 1H), 5.09-5.1 (s, -CONHCH$_2$CH$_2$COOC<u>*H*</u>$_2$Ph, 2H), 6.11-6.13 (d,- N<u>*H*</u>COCH$_2$CH$_2$ $(CH_2)_{12}CH_3$), 1H), 6.52 (s, -CON<u>*H*</u>CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.26-7.35 (bs, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.6, 172.4, 171.8, 135.64, 128.6, 128.34, 128.18, 77.47, 77.05, 76.62, 66.53, 57.53, 41.35, 36.53, 35.02, 33.9, 33.47, 31.9, 29.67, 29.64, 29.61, 29.5, 29.33, 29.26, 25.64, 24.81, 22.82, 22.66, 22.20, 14.08.ESI-MS (m/z) $C_{31}H_{52}N_2O_4$ (EXACT MASS=516.37) 517.379 (100%, $[M + H]^+$), 539.37 (20%, $[M + Na]^+$).

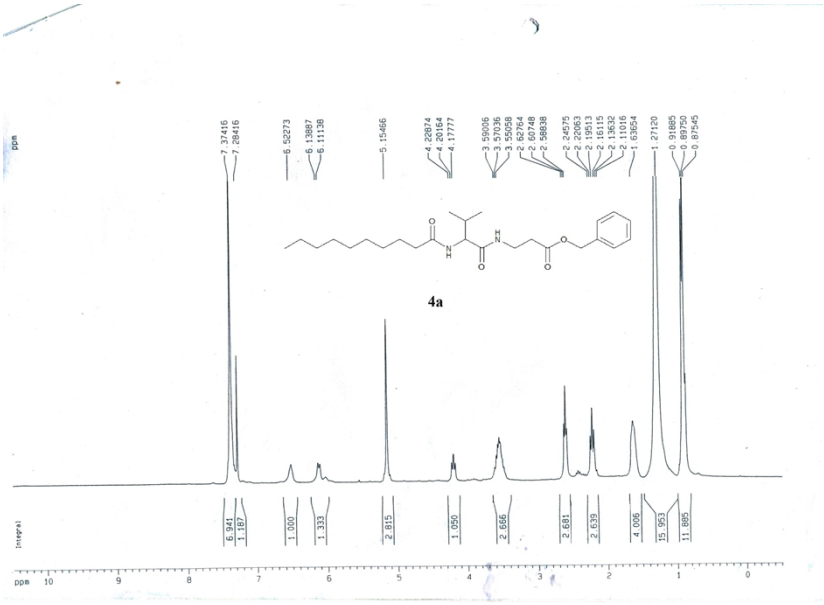
4e.Yield=69%.^{1}HNMR (300 MHz, $CDCl_3$) : δ:: 0.85-0.89(m, -NHCOCH$_2$CH$_2$ $(CH_2)_{14}$C<u>*H*$_3$</u> and >CHCH (C<u>*H*</u>$_3$)$_2$, 9H), 1.24 (bs, -NHCOCH$_2$CH$_2$(C<u>*H*</u>$_2$)$_{14}$CH$_3$, 28H), 1.6 (s, -NHCOCH$_2$C<u>*H*</u>$_2$ $(CH_2)_{14}CH_3$,>CHC<u>*H*</u> $(CH_3)_2$,3H), 2.14-2.19 (t, -NHCOC<u>*H*</u>$_2$CH$_2$$(CH_2)_{14}CH_3$, 2H), 2.56-2.60 (t, -CONHCH$_2$C<u>*H*</u>$_2$COOCH$_2$Ph, 2H), 3.5-3.54 (t, CONHC<u>*H*</u>$_2$CH$_2$COOCH$_2$Ph, 2H), 4.35-4.42 mt, >C<u>*H*</u>CH $(CH_3)_2$, 1H), 5.13 (s, -CONHCH$_2$CH$_2$COOC<u>*H*</u>$_2$Ph, 2H), 6.11-6.13 (d,- N<u>*H*</u>COCH$_2$CH$_2$ $(CH_2)_{14}CH_3$), 1H), 6.62 (s, -CON<u>*H*</u>CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.35 (bs, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.24, 172.56, 135.62, 128.62, 128.4, 128.3, 77.44, 77.21, 76.6, 66.68, 58.35 36.75, 34.97, 34.8, 34.13, 33.39, 31.9, 31.17, 29.68, 29.65, 29.61, 29.48, 29.34, 29.26, 25.73, 25.68, 22.68, 19.1, 18.2, 14.1.ESI-MS (m/z) $C_{33}H_{56}N_2O_4$ (EXACT MASS=544.42) 545.429(100%, $[M + H]^+$), 567.4(49%, $[M + Na]^+$).

4f.Yield=69%.^{1}HNMR (300 MHz, $CDCl_3$) : δ :: 0.85-0.91 (m, -NHCOCH$_2$CH$_2$ $(CH_2)_{10}$C<u>*H*$_3$</u> and >CHCH (C<u>*H*</u>$_3$)$_2$, 9H), 1.4 (bs, -NHCOCH$_2$CH$_2$(C<u>*H*</u>$_2$)$_{10}$CH$_3$, 20H), 1.58-1.65 (m, -NHCOCH$_2$C<u>*H*</u>$_2$ $(CH_2)_{10}CH_3$, >CHC<u>*H*</u> $(CH_3)_2$, 3H), 1.93-1.94 (t, -CONHCH$_2$C<u>*H*</u>$_2$CH$_2$COOCH$_2$Ph, 2H), 2.08-2.17 (t, -NHCOC<u>*H*</u>$_2$CH$_2$ $(CH_2)_{10}CH_3$, 2H), 2.55-2.59 (t, -CONHCH$_2$CH$_2$C<u>*H*</u>$_2$COOCH$_2$Ph, 2H), 3.44-3.59 (m, -CONHC<u>*H*</u>$_2$CH$_2$CH$_2$COOCH$_2$Ph, 2H), 4.37-4.39 (t, >*C<u>H</u>*CH $(CH_3)_2$, 1H), 5.132 (bs, -CONHCH$_2$CH$_2$CH$_2$COOC<u>*H*</u>$_2$Ph, 2H), 5.89 (s,- N<u>*H*</u>COCH$_2$CH$_2$ $(CH_2)_{10}CH_3$), 1H), 6.58 (s, -CON<u>*H*</u>CH$_2$CH$_2$CH$_2$COOCH$_2$Ph, 1H), 7.35 (bs, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.45, 173.26, 171.39, 135.75, 128.54, 128.32, 128.22, 77.45, 77.23, 77.03, 76.61, 66.44, 58.36, 38.92, 36.78, 36.70, 31.92, 31.76, 31.62, 30.95, 29.49, 29.35, 25.76, 24.61, 24.47, 22.68, 19.26, 14.11.ESI-MS (m/z) $C_{27}H_{44}N_2O_4$ (EXACT MASS= 502.38) 503.389 (100%, $[M + H]^+$), 525.38 (68%, $[M + Na]^+$), 541.3 (28%, $[M + K]^+$).

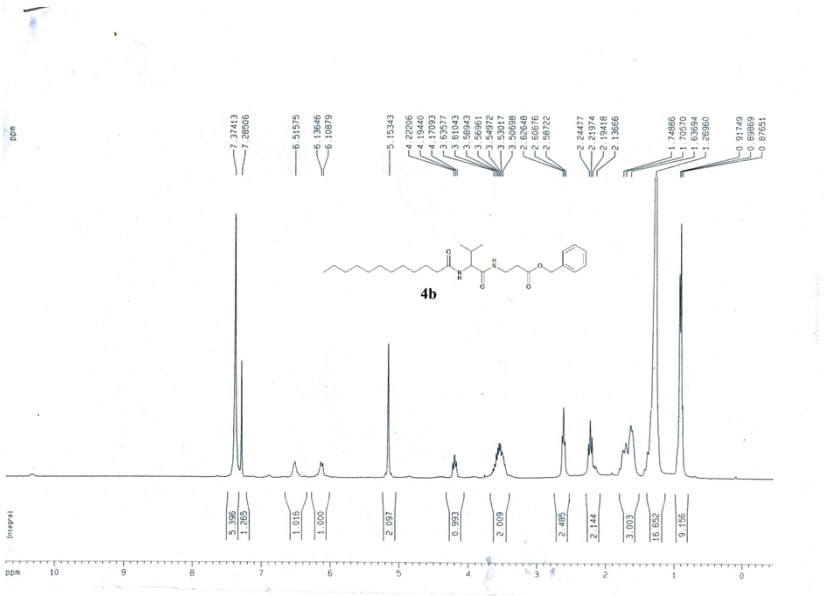
4g.Yield=69%.^{1}HNMR (300 MHz, $CDCl_3$) : δ :: 0.84-0.85 (m, -NHCOCH$_2$CH$_2$ $(CH_2)_{10}$C<u>*H*$_3$</u> and >CHCH (C<u>*H*</u>$_3$)$_2$, 9H), 1.25 (bs, -NHCOCH$_2$CH$_2$(C<u>*H*</u>$_2$)$_{10}$CH$_3$, -CONHCH$_2$CH$_2$(C<u>*H*</u>$_2$)$_2$CH$_2$COOCH$_2$Ph 24H), 1.6 (s, -NHCOCH$_2$C<u>*H*</u>$_2$(CH$_2$)$_{10}$CH$_3$, >CHC<u>*H*</u> $(CH_3)_2$, 3H), 1.780-1.788 (d, -CONHCH$_2$C<u>*H*</u>$_2$(CH$_2$)$_2$CH$_2$COOCH$_2$Ph, 2H), 2.08-2.2 (t, -NHCOC<u>*H*</u>$_2$CH$_2$ $(CH_2)_{10}CH_3$, 2H), 2.56-2.60 (t, -CONHCH$_2$CH$_2$(CH$_2$)$_2$C<u>*H*</u>$_2$COOCH$_2$Ph, 2H), 3.44-3.58 (m, -CONHC<u>*H*</u>$_2$CH$_2$(CH$_2$)$_2$CH$_2$COOCH$_2$Ph, 2H), 4.17-4.22 (t, >*C<u>H</u>*CH $(CH_3)_2$, 1H), 5.09-5.13 (s, -CONH(CH$_2$)$_5$COOC<u>*H*</u>$_2$Ph, 2H), 6.01-6.04 (d,- N<u>*H*</u>COCH$_2$CH$_2$ $(CH_2)_{10}CH_3$), 1H), 6.35 (s, -CON<u>*H*</u>(CH$_2$)$_5$COOCH$_2$Ph, 1H), 7.35 (bs, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.27, 172.93, 171.407, 135.58, 128.62, 128.4, 128.28, 77.46, 77.041, 76.61, 66.59, 58.256, 40.2, 36.73, 36.67, 35.00, 33.1, 31.84, 31.19, 29.63, 29.49, 29.33, 29.28, 25.74, 25.54, 22.64, 18.212, 17.124, 14.102.ESI-MS (m/z) $C_{27}H_{44}N_2O_4$ (EXACT MASS= 530.41) 531.419(100%, $[M + H]^+$), 553.421 (62%, $[M + Na]^+$).

4h.Yield=69%.^{1}HNMR (300 MHz, $CDCl_3$) : δ:: 0.846-0.934 (m, -NHCOCH$_2$CH$_2$ $(CH_2)_4$C<u>*H*$_3$</u> and >CHCH (C<u>*H*</u>$_3$)$_2$, 9H), 1.233-1.280 (m, -NHCOCH$_2$CH$_2$(C<u>*H*</u>$_2$)$_4$CH$_3$, -CONH(CH$_2$)$_2$(C<u>*H*</u>$_2$)$_7$CH$_2$COOCH$_2$Ph, 22H), 1.476-1.495 (d, -NHCOCH$_2$C<u>*H*</u>$_2$(CH$_2$)$_4$CH$_3$, -CONHCH$_2$CH$_2$(CH$_2$)$_6$C<u>*H*</u>$_2$CH$_2$COOCH$_2$Ph, 4H), 1.970-2.0 (m, >CHC<u>*H*</u> $(CH_3)_2$, 1H), 2.130-2.243 (m, -CONHCH$_2$C<u>*H*</u>$_2$(CH$_2$)$_7$CH$_2$COOCH$_2$Ph, 2H), 2.3-2.36 (m, -NHCOCH$_2$C<u>*H*</u>$_2$(CH$_2$)$_4$CH$_3$, 2H), 3.2-3.266 (m, -CONHC<u>*H*</u>$_2$(CH$_2$)$_9$COOCH$_2$Ph, 2H), 4.084-4.25

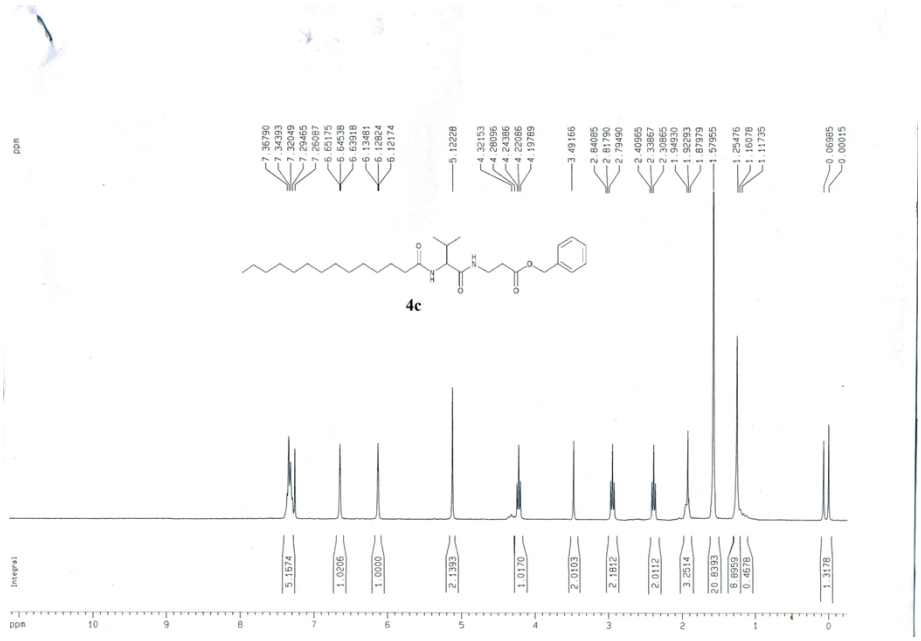
(m, >C*H*CH $(CH_3)_2$, 1H), 5.11 (s, -CONH$(CH_2)_{10}$COOC*H*$_2$Ph, 2H), 6.625-6.719 (m,- N*H*CO$(CH_2)_6CH_3$), -CON*H*$(CH_2)_{10}$COOCH$_2$Ph, 2H), 7.35 (s, aromatic, 5H). ^{13}C NMR(75 MHz, $CDCl_3$) :δ_C : 173.42, 172.56, 171.41, 135.58, 128.62, 128.4, 128.2, 77.46, 77.041, 76.61, 66.54, 58.35, 40.3, 36.73, 36.67, 35.00, 33.1, 31.84, 31.19, 29.7, 29.7, 29.43, 29.32, 29.24, 28.7 25.74, 22.64, 17.4, 17.1, 14.1.ESI-MS (m/z) $C_{27}H_{44}N_2O_4$ (EXACT MASS= 516.37) 517.379(100%, $[M + H]^+$), 539.39(58%, $[M + Na]^+$), 555.329(18% ,$[M + K]^+$).



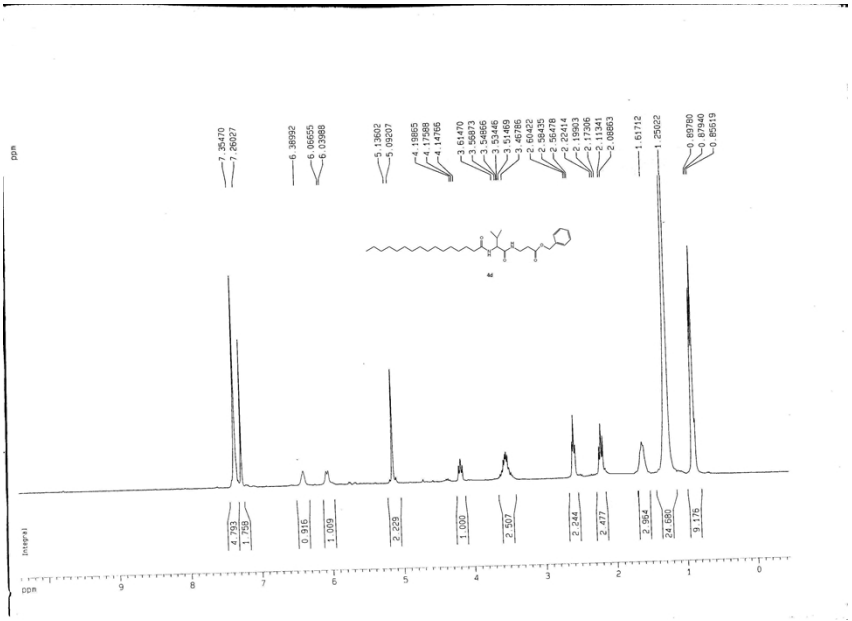
^{1}HNMR spectra of gelator **4a**.



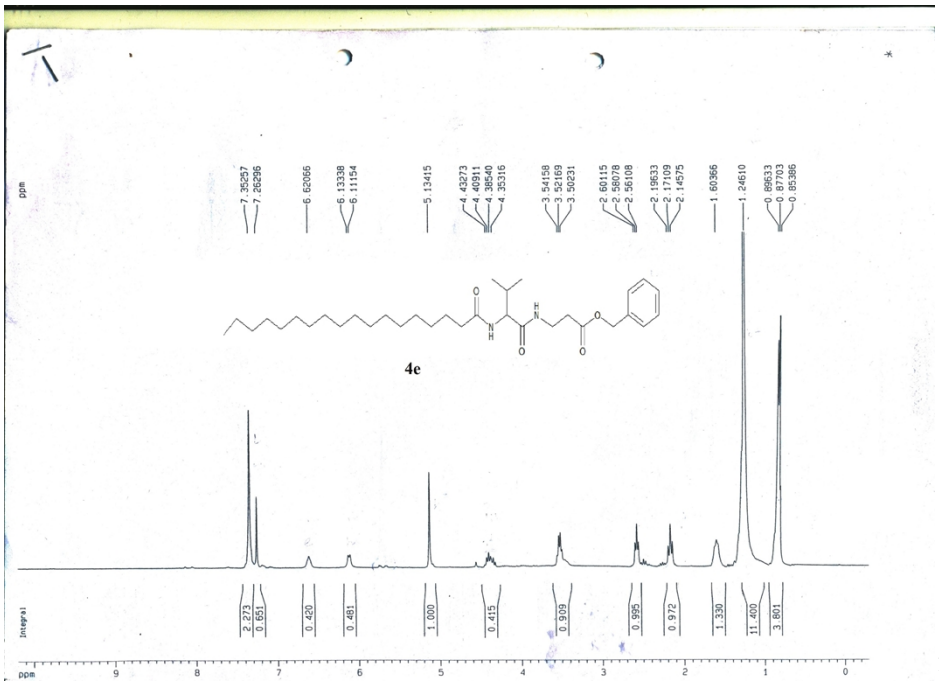
^{1}HNMR spectra of gelator **4b**.



^{1}HNMR spectra of gelator **4c**.

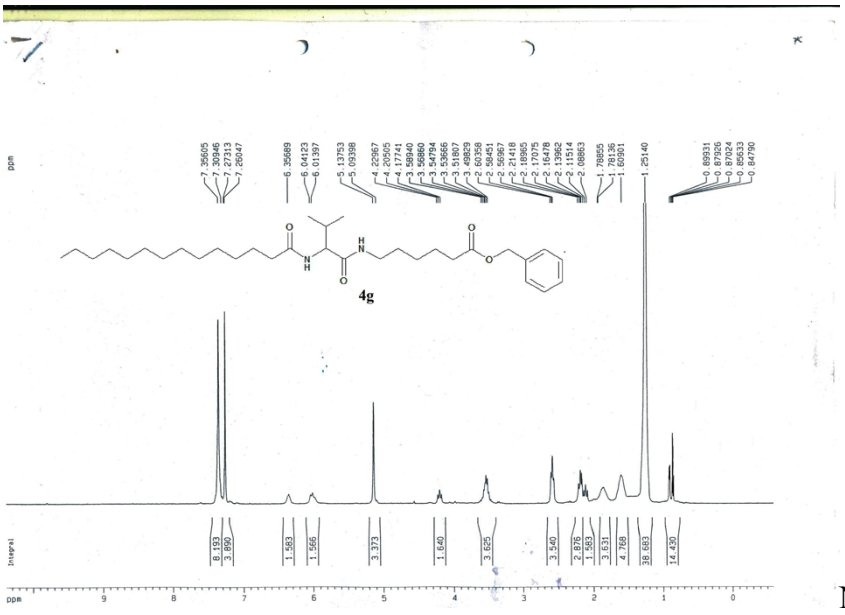


^{1}HNMR spectra of gelator **4d**.



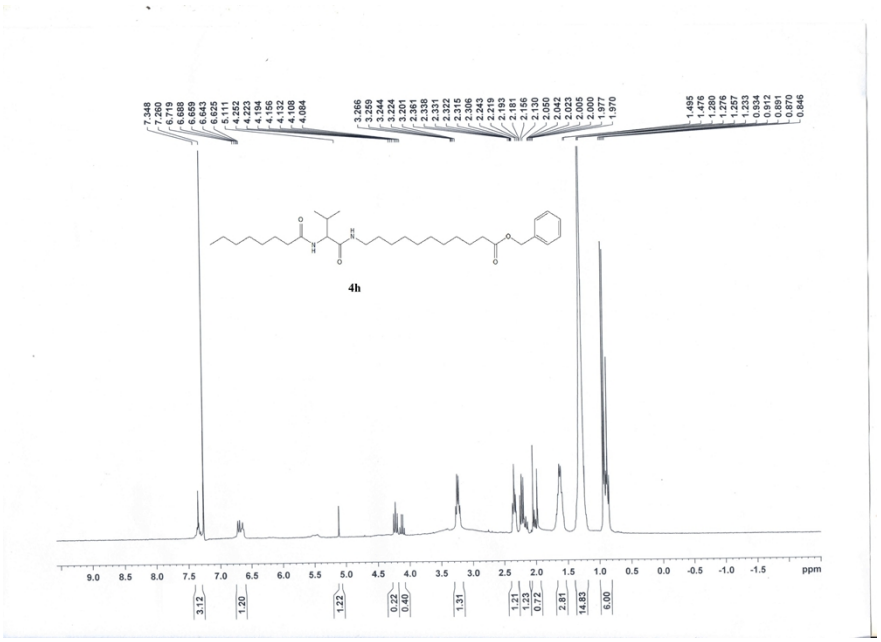
1

HNMR spectra of gelator **4e**.

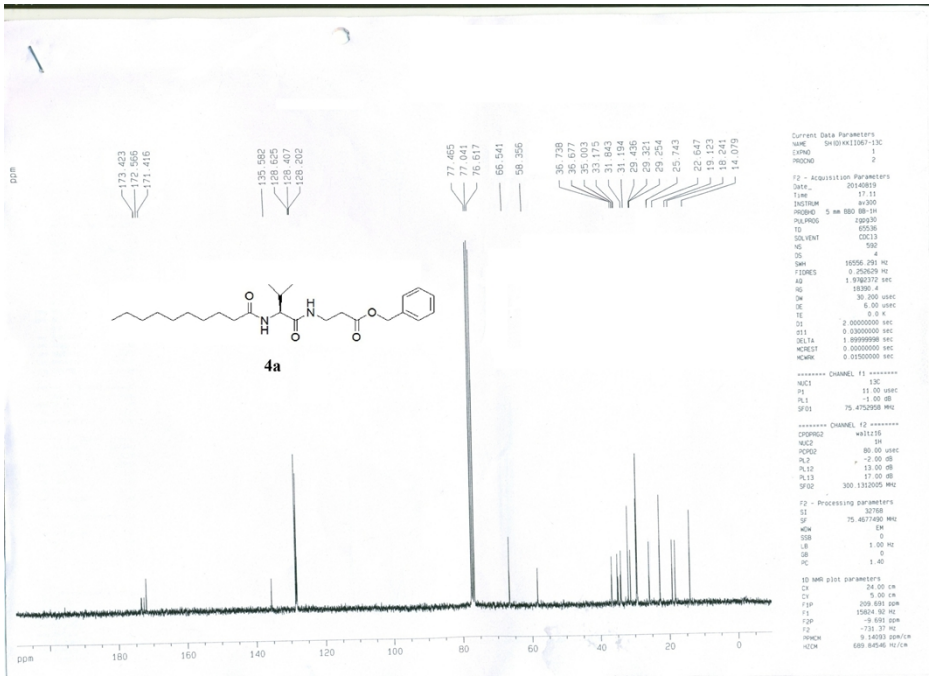


N

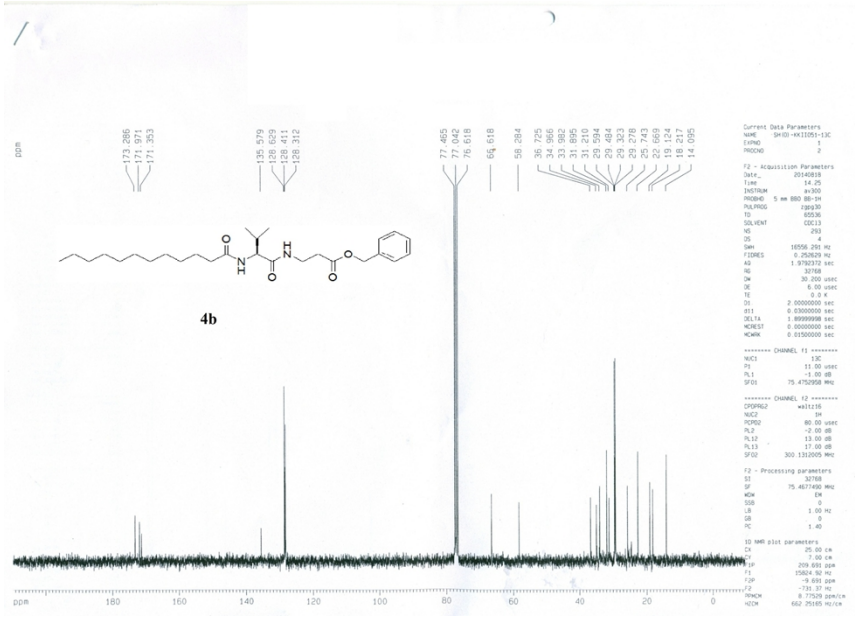
MR spectra of gelator **4g**.



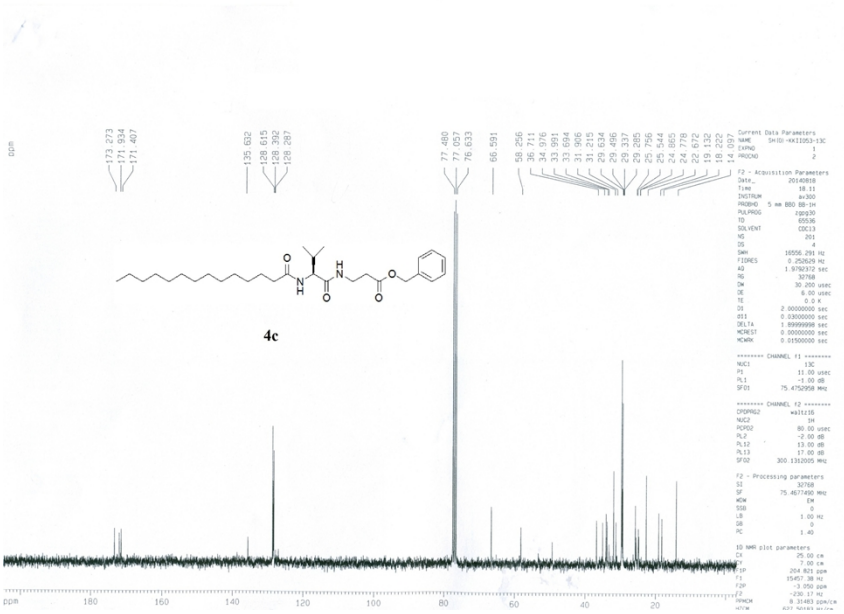
NMR spectra of gelator **4h**.



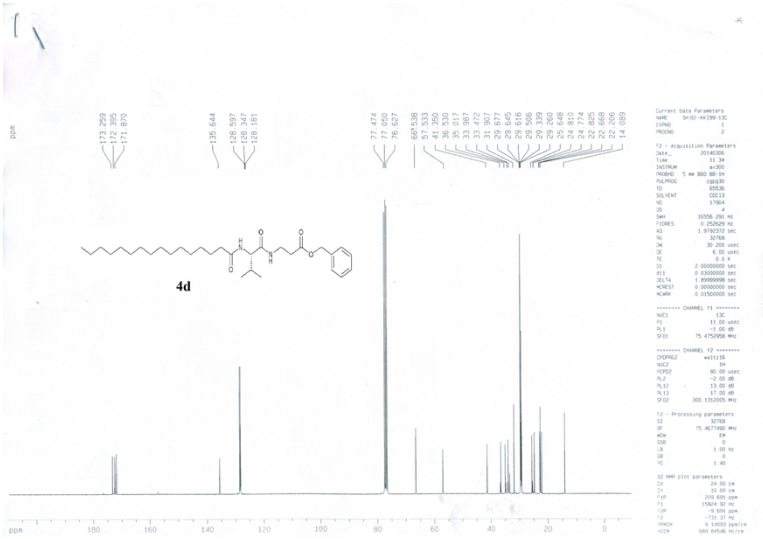
^{13}C NMR spectra of gelator **4a**.



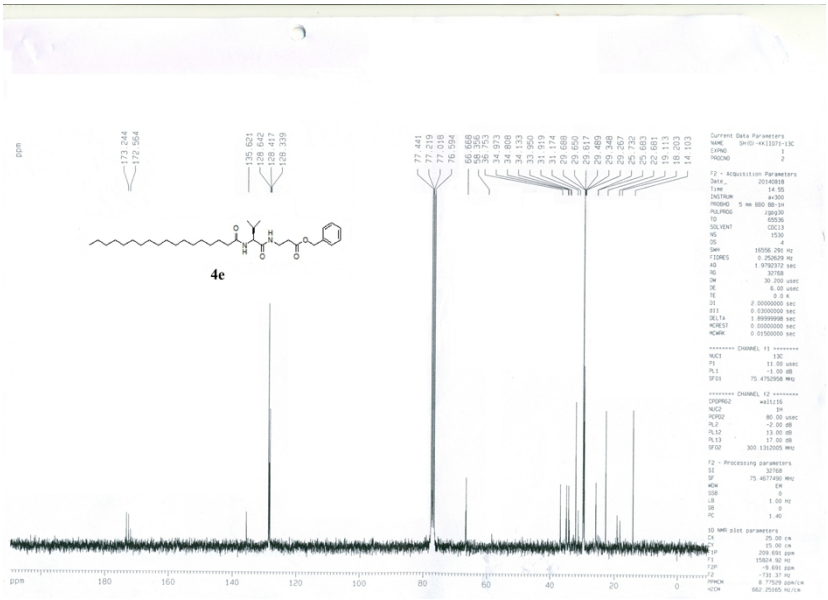
^{13}C NMR spectra of gelator **4b**.



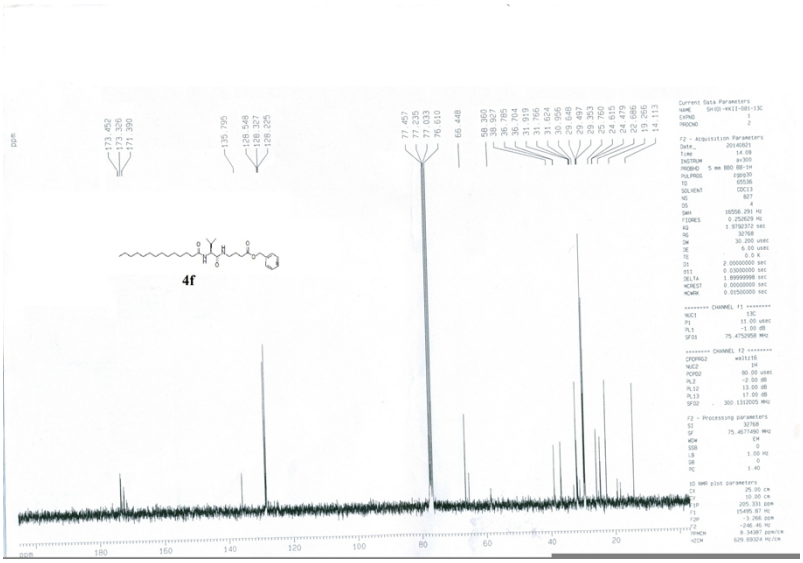
^{13}C NMR spectra of gelator **4c**.



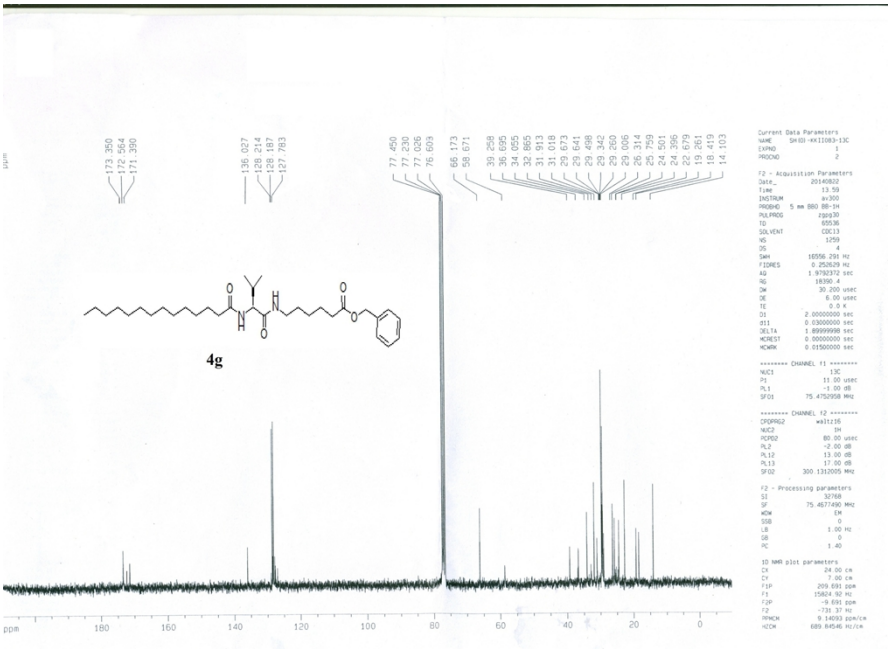
^{13}C NMR spectra of gelator **4d**.



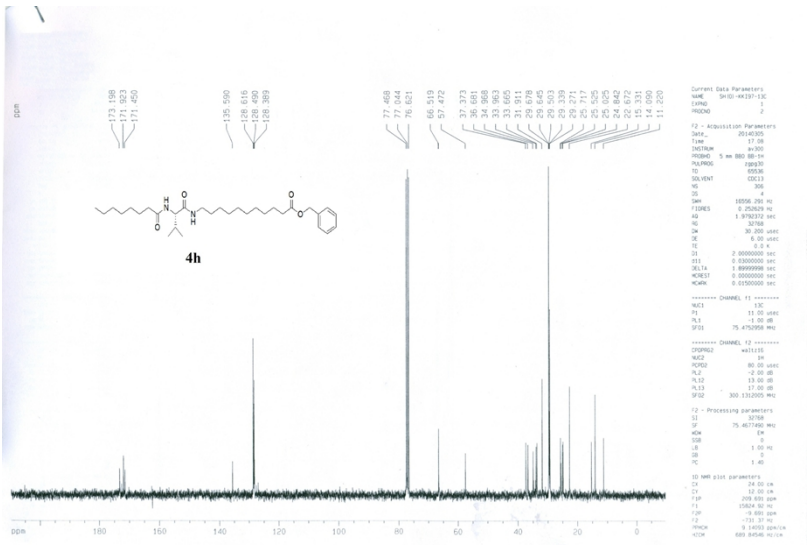
^{13}C NMR spectra of gelator **4e**.



^{13}C NMR spectra of gelator **4f**.



^{13}C NMR spectra of gelator **4g**.



^{13}C NMR spectra of gelator **4h**.

Table S1.. Gelation number and Gel to Sol phase transition temperature (T_{gel})of gelators in different solvents

	(4a)		(4b)		(4c)		(4d)		(4e)		(4f)		(4g)		(4h)	
c LogP→	5.726		6.611		7.544		7.942		9.153		8.172		9.117		8.285	
SOLVENTS	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**	**GN**	**T_g**
Benzene	30	32.8	231	33.8	243	35.8	322	40.9	312	37.6	56	33.1	96	34.1	WG	
O-Xylene	32	32.6	188	33.6	196	35.6	265	41.3	232	36.4	48	33.1	87	34	143	33.8
Toluene	22	32.4	173	33.4	174	35.7	202	41.4	183	36	44	33.3	89	33.8	112	33.5
O-DCB	30	33.2	174	33.2	181	36.2	199	44.2	193	36.2	-	-	-	-	WG	-
Anisole	21	32	66	32	73	35.5	85	39.1	79	36	55	33.4	87	33.9	155	33.9
P E	s		54	33.7	52	36.1	64	58.8	62	38	s	-	s	-	s	-
Hexane	410	33.9	398	33.1	270	37.1	240	42.1	113	38.8	144	34.6	185	36.5	s	-
Cyclohexane	124	33	157	33.9	200	35.6	302	42.5	295	38.9	140	34.2	149	34.5	s	-
THF	s	-	s	-	s	-	s	-	s	-	s	-	s	-	s	-
$CHCl_3$	s	-	s	-	s	-	s	-	s	-	s	-	s	-	s	-
Dioxane	s	-	s	-	s	-	s	-	s	-	s	-	s	-	s	-
Acetonitrile	107	33.4	532	34.1	551	35.5	863	47.9	762	38.7	184	34.1	375	34.9	217	34.5
EtOAc	17	32.1	104	33.3	159	36.1	216	38	154	37.1	93	33.8	116	34.2	108	33.4
DMF	s	-	112	31.8	143	35.3	165	30.5	154	37.4	-	-	-	-	-	-
DMSO	60	32.3	215	33.4	234	36.2	258	54.3	253	37.8	155	33.8	229	34.3	102	34
Acetone	68	32.5	135	33.5	225	35.5	487	44.2	150	37.8	153	33.7	220	33.9	s	-
Nitromethane	319	33.6	729	34.9	836	36.8	2981	49.8	680	38.1	788	34.9	823	35.7	-	-
MeOH	74	32.1	271	33.1	310	35.8	500	51	333	36.5	101	33.4	164	33.8	s	-
80% aq MeOH	225	33.8	559	34.5	758	36.4	999	39.8	851	38	556	34.9	598	35	s	-
70% aq MeOH	114	33.6	456	34.2	695	36	886	39.5	710	37.8	434	34.5	502	34.9	s	-
50% aq MeOH	93	33.5	392	34	477	35.8	656	39.1	521	37.7	331	33.9	379	34	s	-
40% aq MeOH	s	-	s	-	s	-	s	-	s	-	s	-	s	-	s	-
EtOH	66	32	127	33.4	150	35.4	364	50	141	37.2	94	33.4	111	33.8	s	-
80% aq EtOH	231	33.8	691	34.5	953	36.3	1377	41.2	1091	38.2	667	34.8	722	34.8	s	-
70% aq EtOH	104	33.7	511	34.1	550	35.9	959	39.9	898	37.9	225	34.2	312	34.1	s	-
2-Propanol	s	-	77	33.5	89	35.2	113	35.9	110	36.2	55	33.6	94	33.9	s	-
Butanol	s	-	84	33.7	101	35.5	187	36.4	132	36.6	84	33.4	112	34.6	s	-
50% aq EG	is	-	is	-	is	-	is	-	is	-	is	-	is	-	is	-
50% aq Glycerol	is	-	is	-	is	-	is	-	is	-	is	-	is	-	is	-

O-DCB= O-Dichlorobenzene P E= Petroleum ether EG= Ethylene Glycol

Rheology:

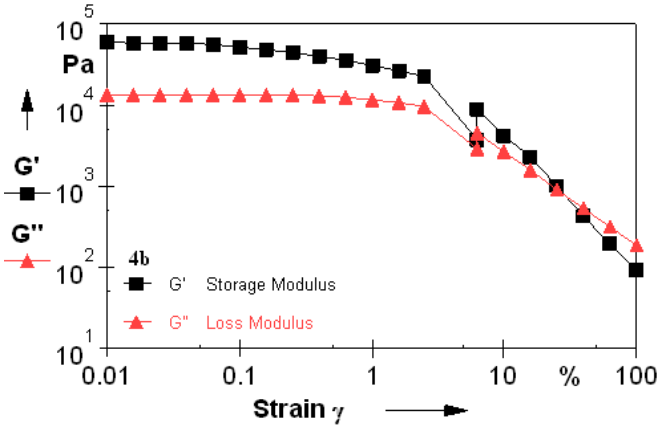


Figure S1.Strain amplitude sweep experiment (ω at 10rads/sec) for **(4b)** in acetonitrile.

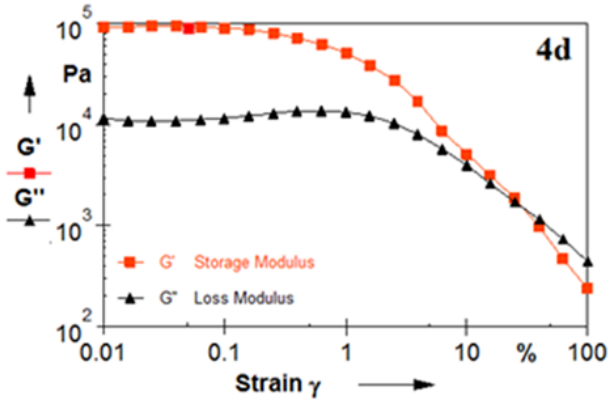


Figure S2.Strain amplitude sweep experiment (ω at 10rads/sec) for **(4d)** in acetonitrile.

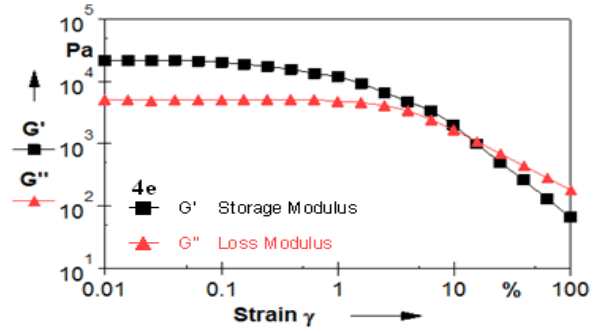


Figure S3.Strain amplitude sweep experiment (ω at 10rads/sec) for **(4e)** in acetonitrile

Continuation of Rheology….

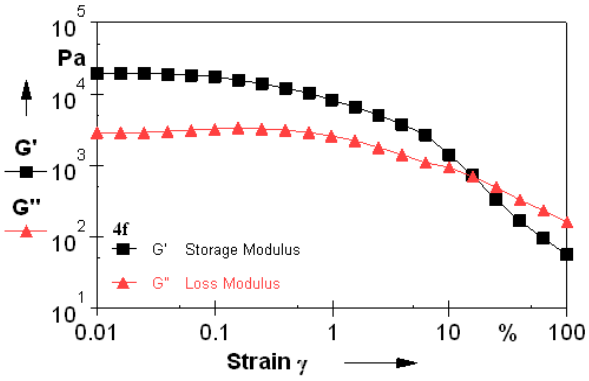


Figure S4.Strain amplitude sweep experiment (ω at 10rads/sec) for **(4f)** in acetonitrile.

Thermal stability

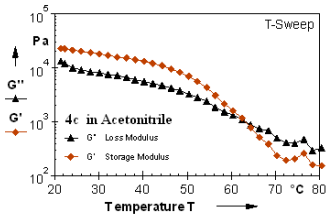


Figure S5.Temperature sweep experiment for **(4c)** in acetonitrile

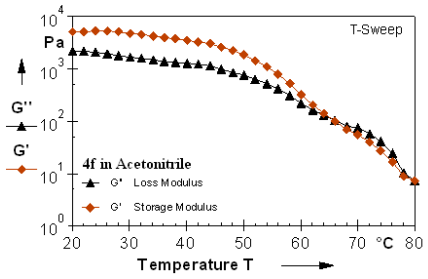


Figure S6.Temperature sweep experiment for **(4f)** in acetonitrile

Continuation of Thermal Stability…..

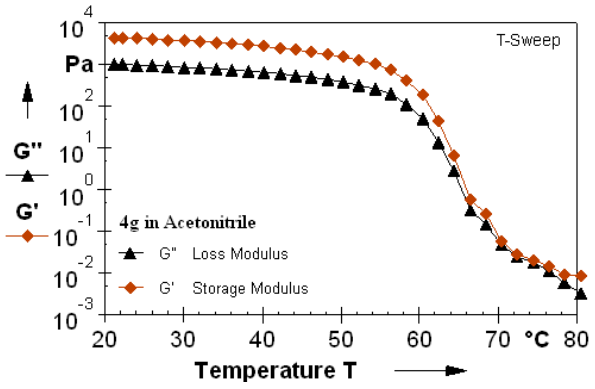


Figure S7.Temperature sweep experiment for **(4g)** in acetonitrile

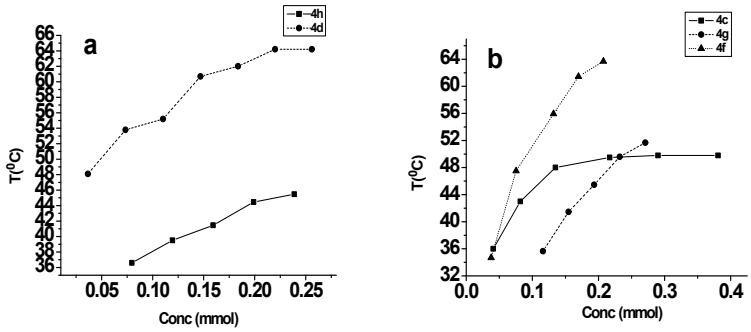


Figure S8.T_{gel} (°C) versus concentration (mmoles) plots for gelators of (a) SET-II and (b) SET-III in Acetonitrile.

XRD :

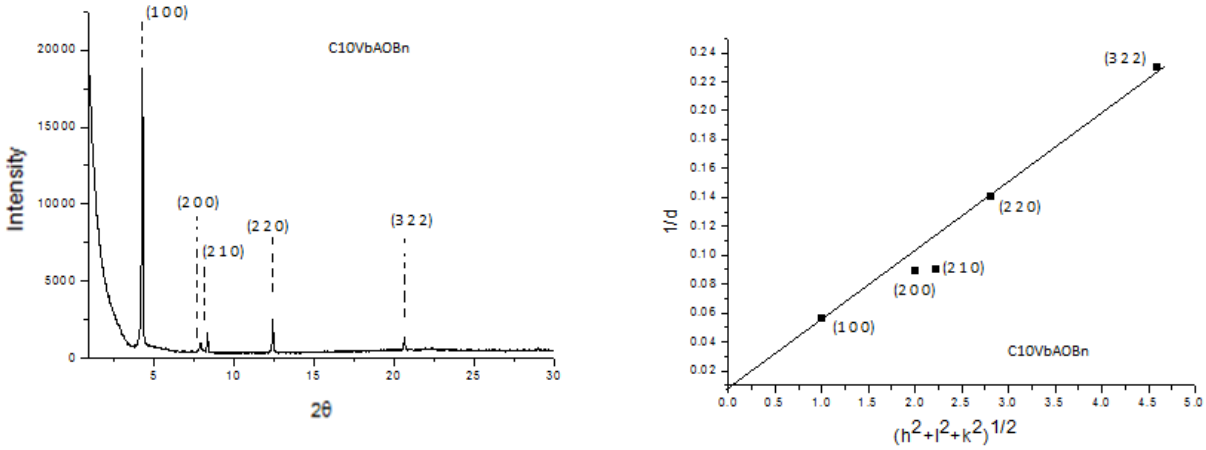


Figure S9**.** XRD profile of xerogels (intensity vs. 2θ) for **4a** in acetonitrile and itscorresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

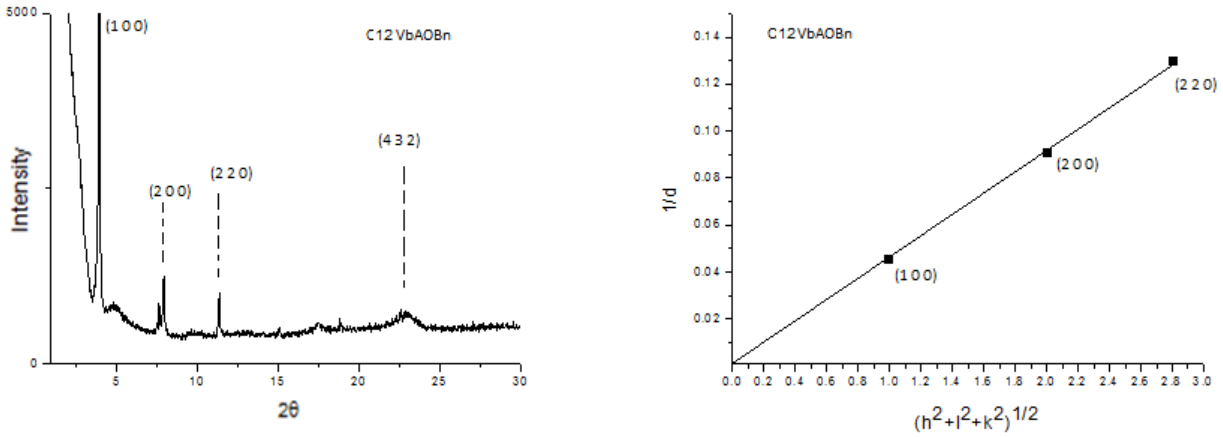


Figure S10.XRD profile of xerogels (intensity vs. 2θ) for **4b** in acetonitrile and its corresponding plotof d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

Continuation of XRD….

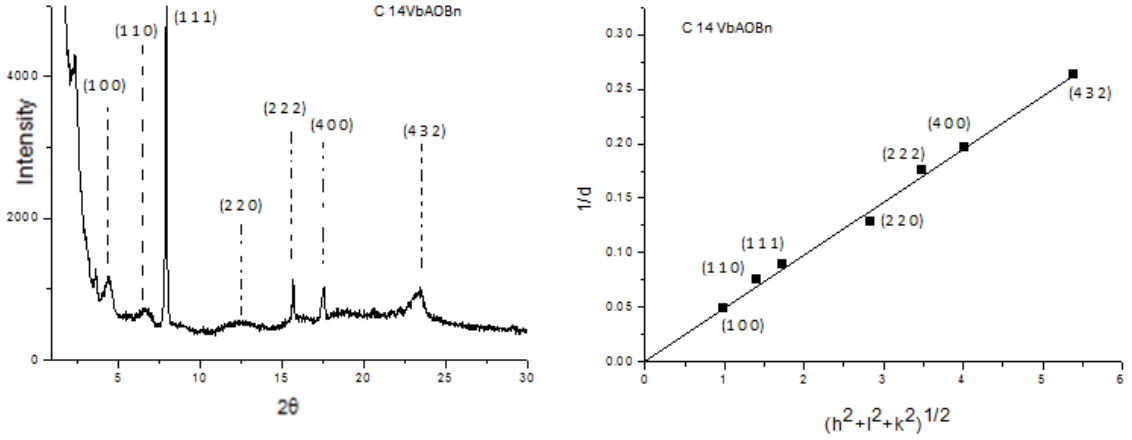


Figure S11.XRD profile of xerogels (intensity vs. 2θ) for **4c** in acetonitrile and its corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

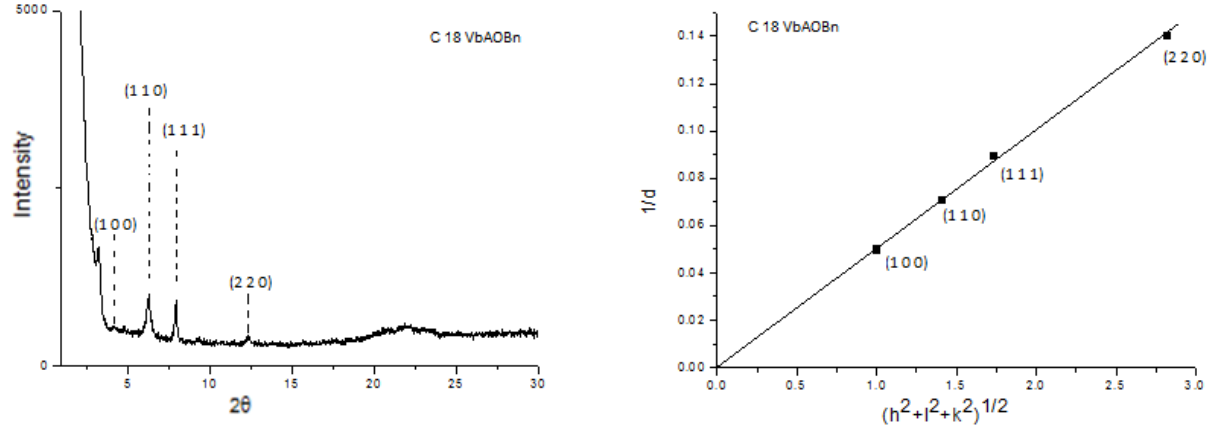


Figure S12. XRD profile of xerogels (intensity vs. 2θ) for **4e** in acetonitrile and its corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

Continuation of XRD….

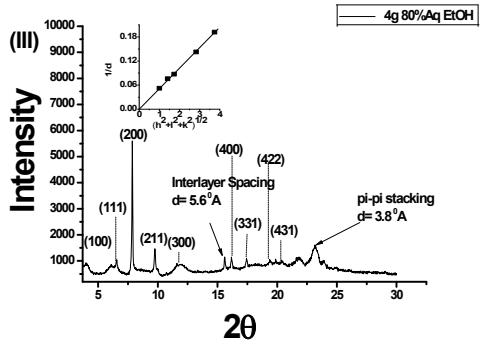


Figure S13.XRD profile of xerogels (intensity vs. 2θ) for **4g** in 80%(v/v) Ethanol.H_2O and its corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$ (at inset).

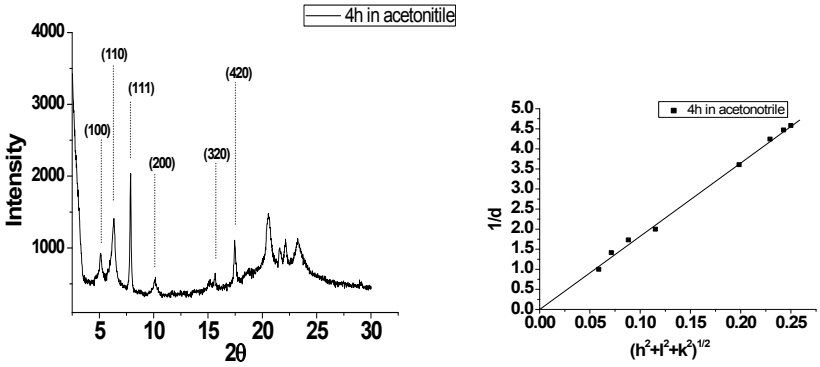


Figure S14.XRD profile of xerogels (intensity vs. 2θ) for **4h** in acetonitrile andits corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

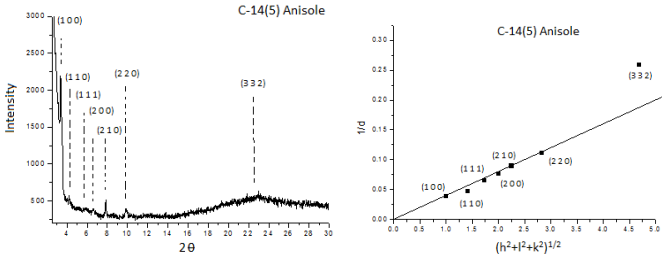


Figure S14.XRD profile of xerogels (intensity vs. 2θ) for **4g** in anisole andits corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$

Continuation of XRD…..

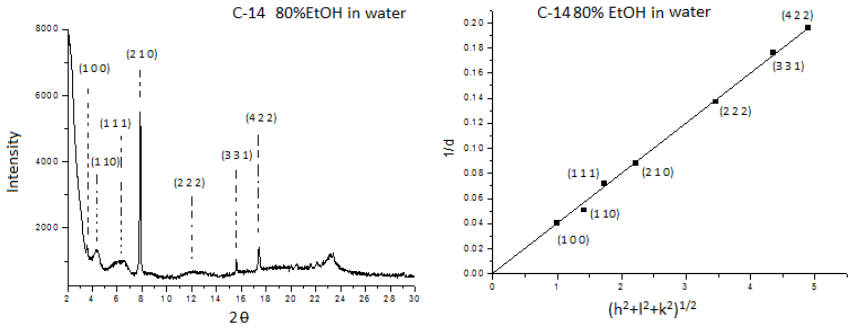


Figure S15.XRD profile of xerogels (intensity vs. 2θ) for **4c** in 80% aq. EtOHandits

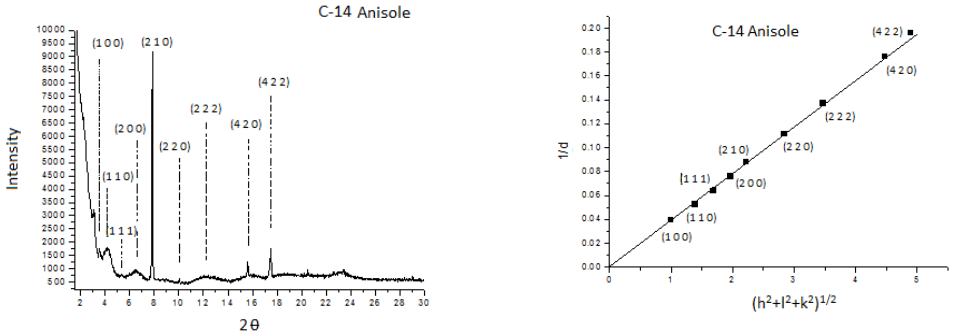


Figure S16.XRD profile of xerogels (intensity vs. 2θ) for **4c** in Anisoleandits corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.

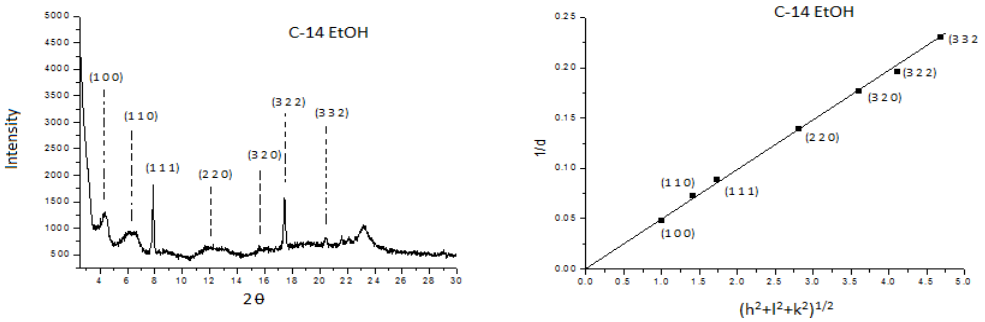
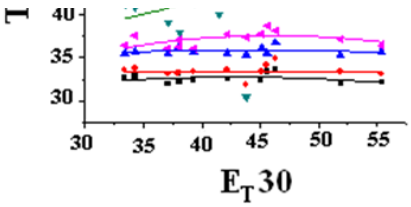


Figure S17.XRD profile of xerogels (intensity vs. 2θ) for **4c** in EtOHandits corresponding plot of d^{-1} vs. $\sqrt{(h^2+l^2+k^2)}$.



Solvent effect**:**

Figure S18. E_{T30} versus $T_g$plot of gelator **4a, 4b, 4c, 4d** and **4e** in different solvents.

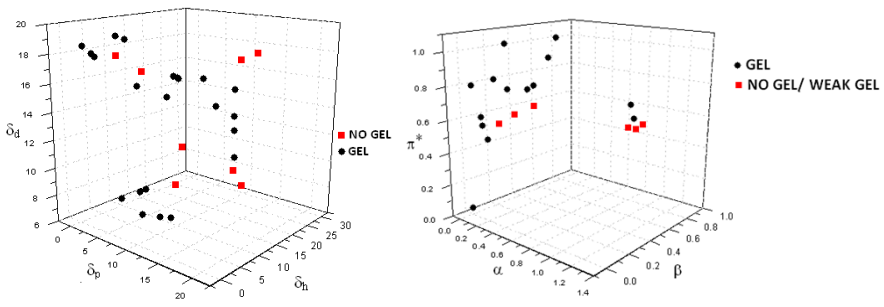


Figure S19.3D plots of Hansen and Kamlet Taft parameters at different solvent for **4a-4g** gelators.

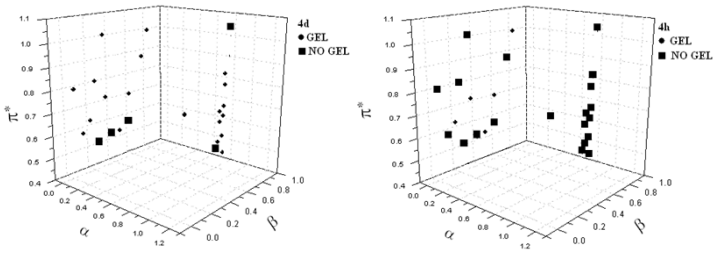


Figure S20.Comparison of 3D plots of Kamlet Taft parameters at different solvents for **4d-4h** gelators.

Continuation of Solvent effect….

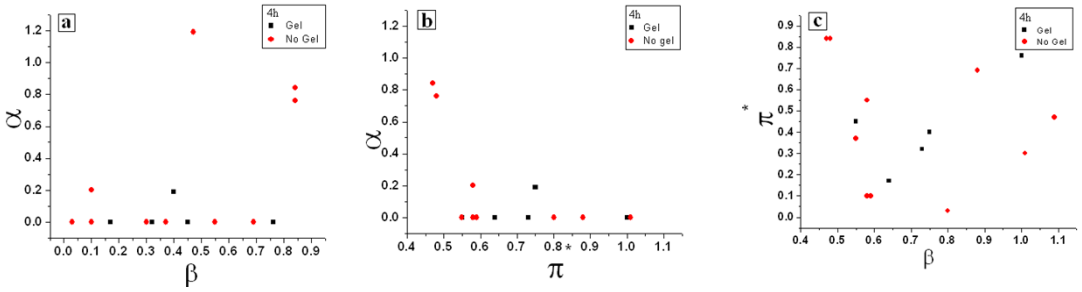


Figure S22.Plots of

Figure S21.Plots of $\delta_p$vsδ_h, $\delta_d$vsδ_h and $\delta_p$vsδ_d (HSP) for gelator **4h [**gelation is found in solvents with lower δ_h values, i.e., solvents with lower H-bonding capability].

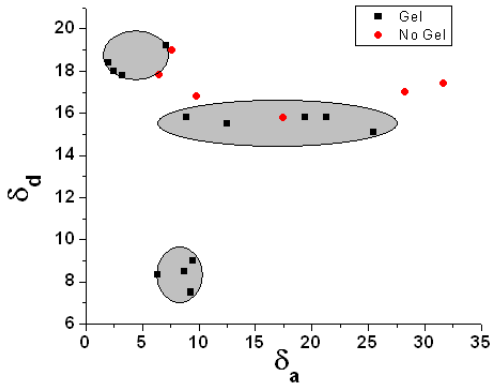


Figure S23.Plots of $\delta_d$vsδ_h for gelators**4a-4g**.

Continuation of Solvent effect….

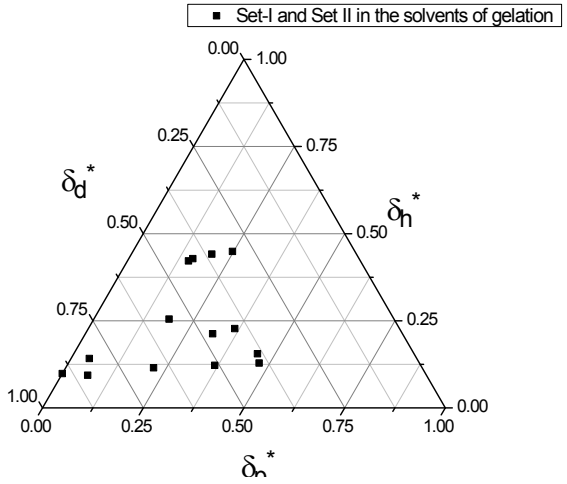


Figure S24.Teas plot of Hansen Parameters for gelators of Set-I and Set –II in solvents of gelation.

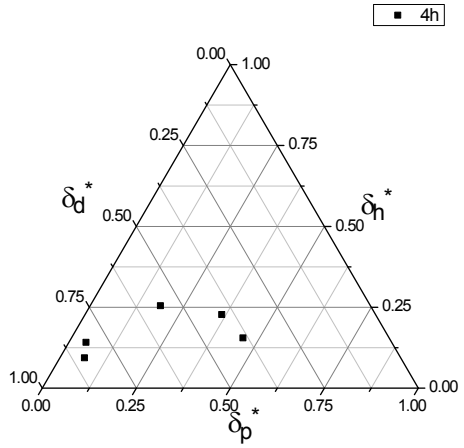


Figure S25.Teas plot of Hansen Parameters for **4h** in solvents of gelation.

CD

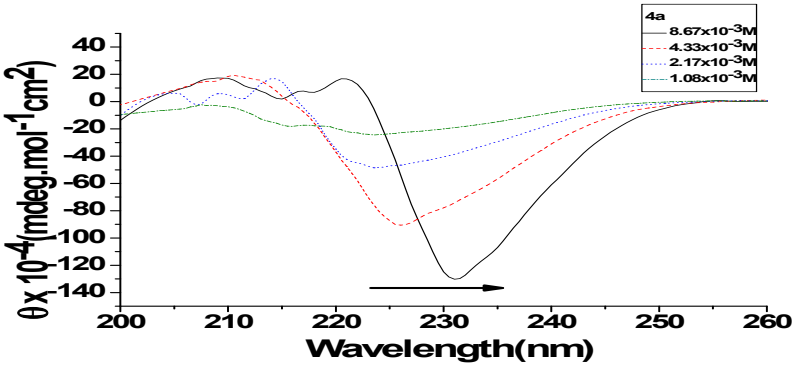


Figure S26.CD spectra of **4f** at different concentrations.

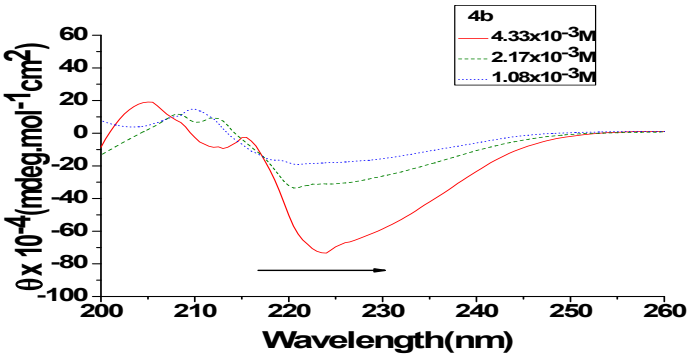


Figure S27.CD spectra of **4f** at different concentrations.

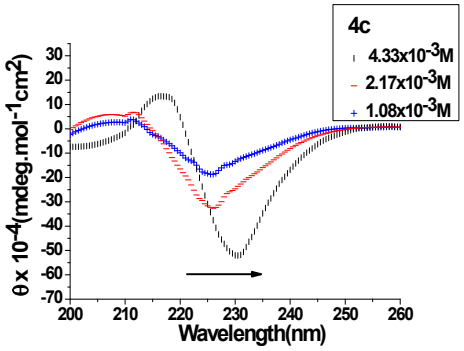


Figure S28.CD spectra of **4f** at different concentrations.

Continuation of CD…..

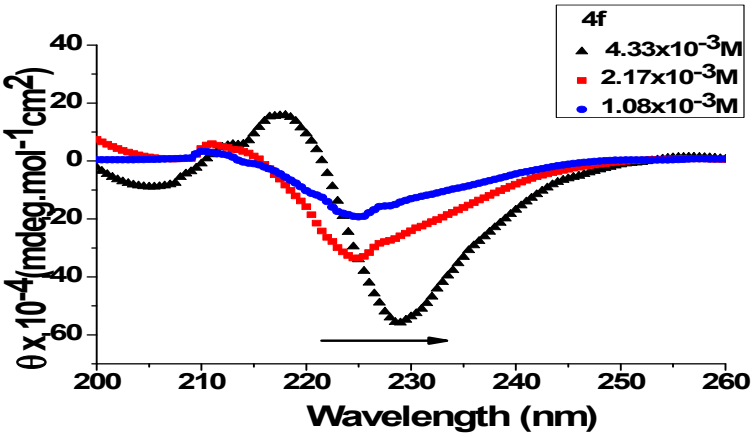


Figure S29.CD spectra of **4f** at different concentrations.

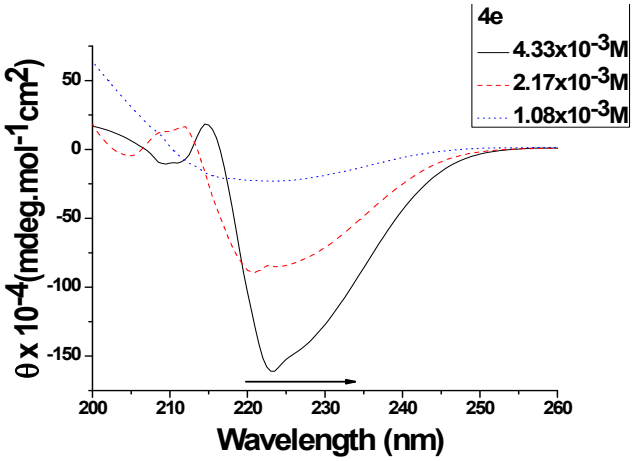


Figure S30.CD spectra of **4f** at different concentrations.

FT-IR spectra:

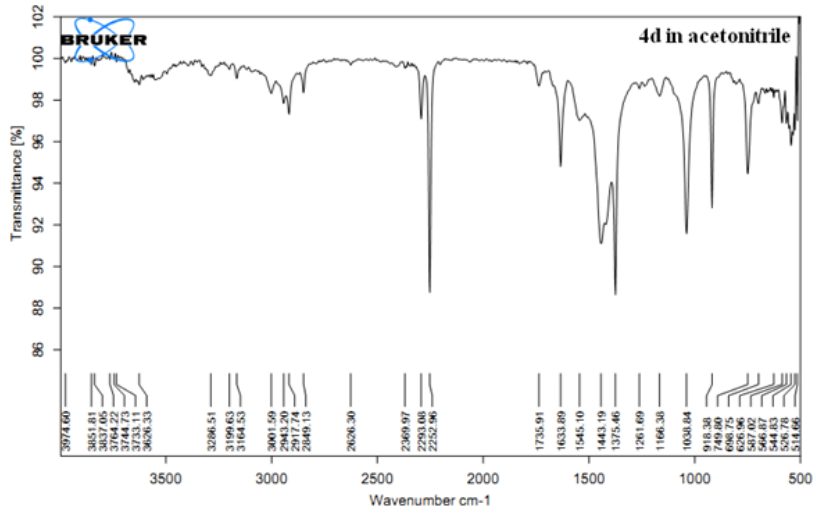


Figure S31.IR spectra of gelator **4d** in acetonitrile in gel state.

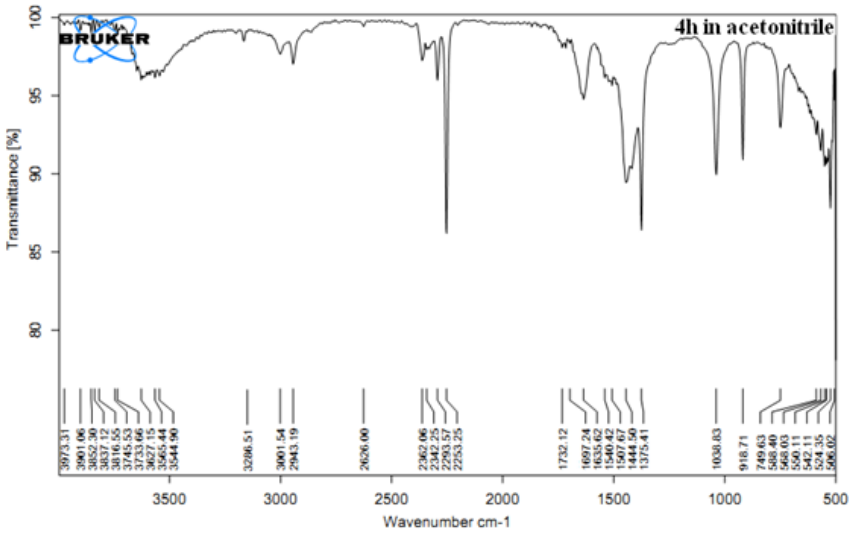


Figure S32**.** IR spectra of gelator **4h** in acetonitrile in gel state.

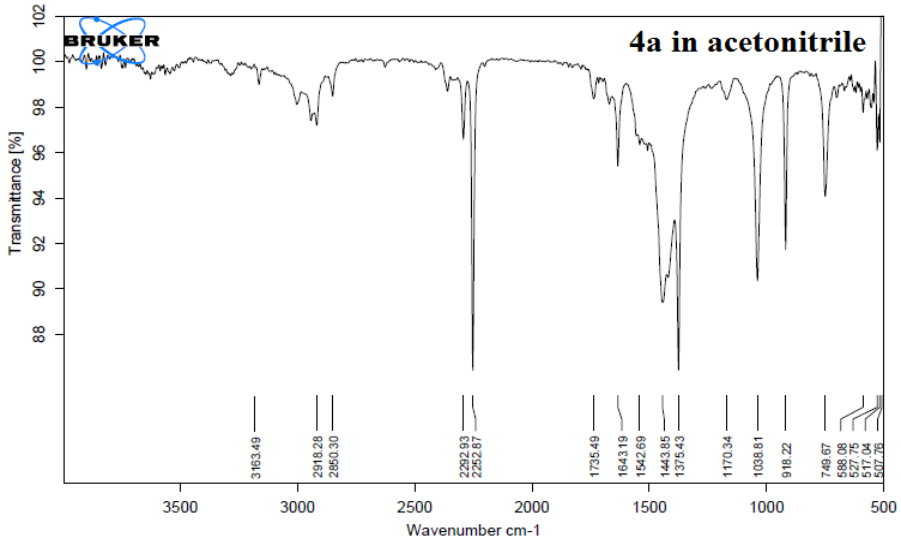


Figure S33.IR spectra of gelator **4a** in acetonitrile in gel state.

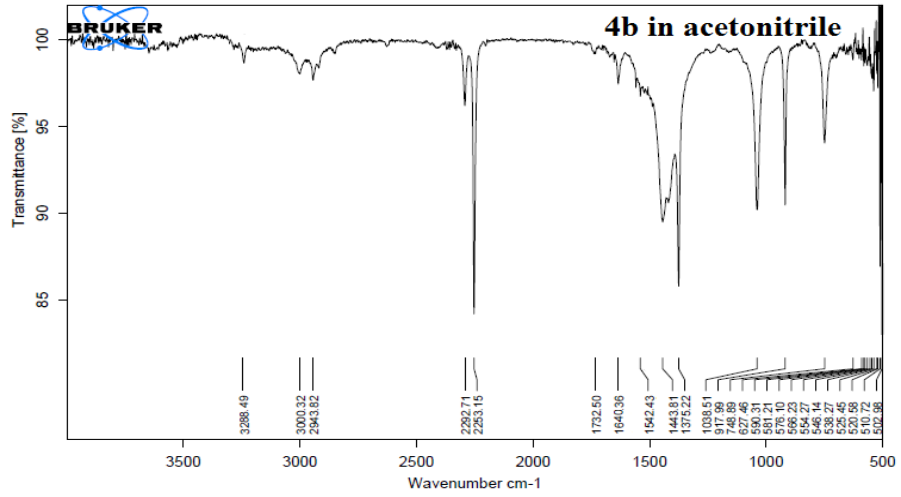


Figure S34**.** IR spectra of gelator **4b** in acetonitrile in gel state.

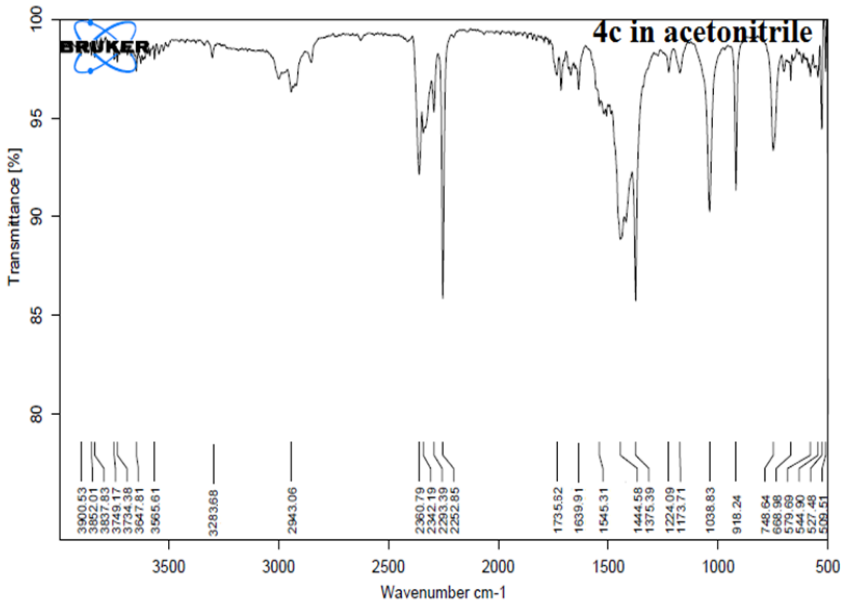


Figure S35.IR spectra of gelator **4c** in acetonitrile in gel state.

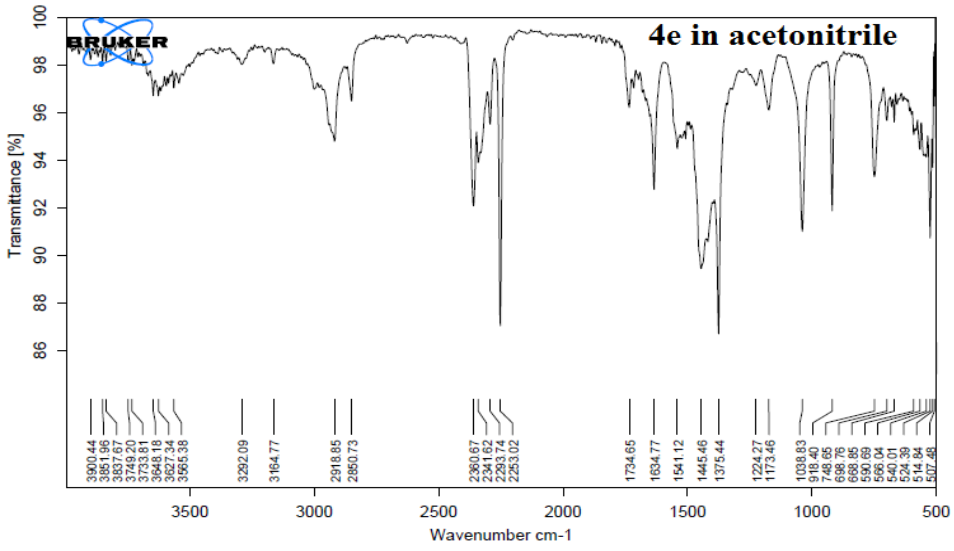


Figure S36**.** IR spectra of gelator **4e** in acetonitrile in gel state.

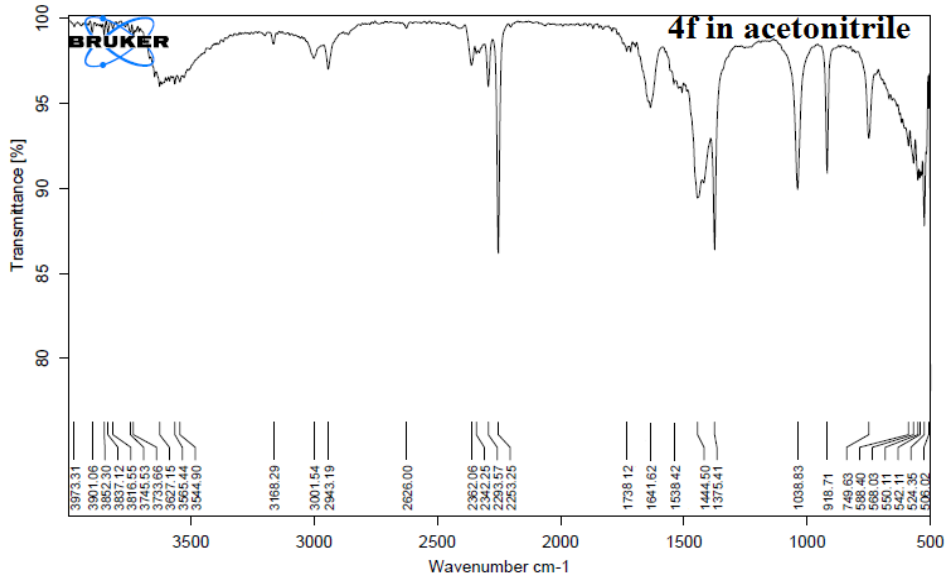


Figure S37.IR spectra of gelator **4f** in acetonitrile in gel state.

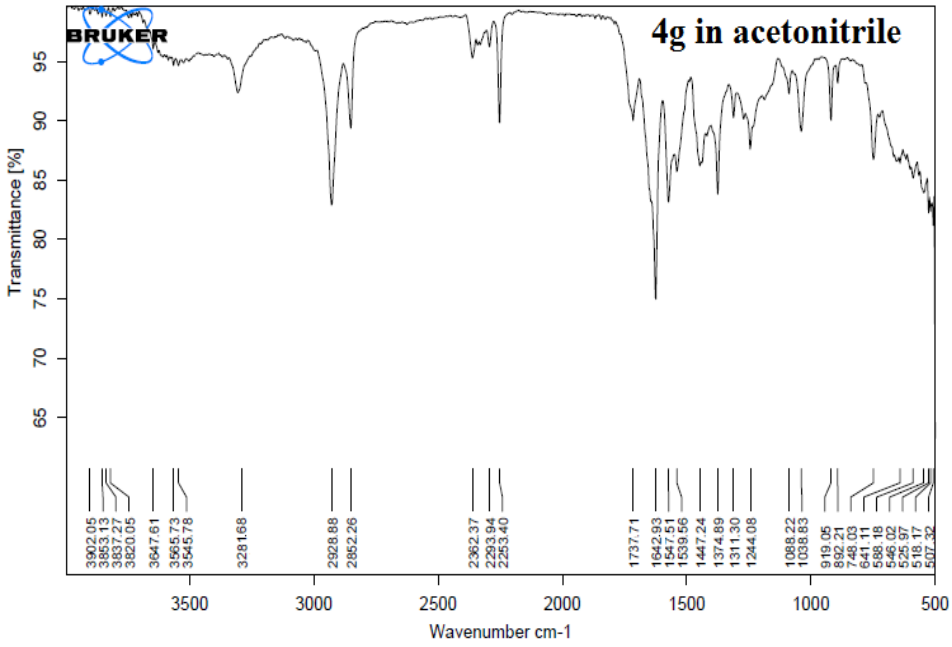


Figure S38**.** IR spectra of gelator **4g** in acetonitrile in gel state.