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ARTICLE TYPE

Supporting Information

Hierarchical Self-assembly of Amino Acid Derivatives into Stimuli-Responsive Luminescent Gels

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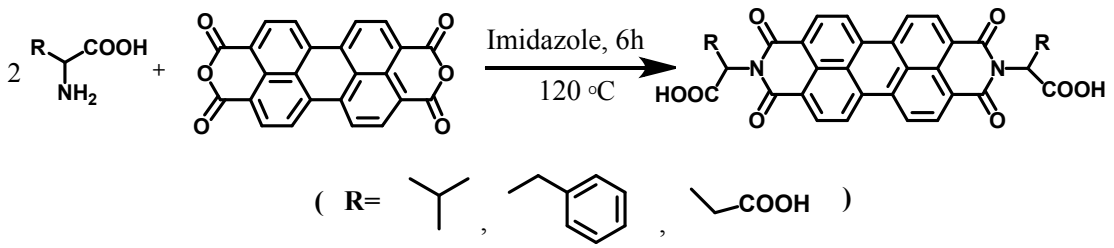
1）Synthesis and characterization of amino acid derivatives (PP, VP and AP)[S1,S2]



Scheme S1 Synthesis route of amino acid derivatives.

Synthesis of phenylalanine-functionalized perylene derivatives (PP)

0.392 g (1.0 mmol) perylene-3, 4, 9, 10-tetracarboxylic dianhydride, 0.330 g (2.0 mmol) L-phenylalanine and 2.0 g imidazole were heated at 120 °C for 6 hrs under nitrogen atmosphere. Then 50 mL of H_2O was poured into the hot mixture, refluxed for 6 hrs and cooled down, then added 1.0 moL/L HCl in dropwise till the mixture into acidity. Keeping the mixture in ambient temperatures overnight to let it precipitate out. The precipitate was filtered and washed with H_2O. The product was dried at room temperature to get mulberry powder (yield: 0.57g, 83%). The structure and purity of the product were confirmed by ^{1}H NMR, FT-IR and MS.

^{1}H NMR (400 MHz, DMSO-d, 20 °C, TMS, ppm): δ: 8.45 (d, 4.0 H), 8.31 (d, 4.0 H), 7.06-7.23 (m, 10.0 H), 5.92-5.95 (t, 2.0 H), 3.32-3.64 (d, 4.1 H).

FT-IR (KBr): 3473.0, 3413.7, 2927.2, 2602.6, 2356.0, 2320.0, 2009.0, 1696.2, 1645.5, 1591.1, 1505.2, 1438.8, 1400.5, 1349.2, 1252.4, 1129.2, 853.8， 805.9, 745.2, 699.2, 617.4 cm^{-1}.

MS (MALDI-TOF): 686.7 (calcd. 686.7, M)

Synthesis of valine-functionalized perylene derivatives (VP)

Similar procedure as like preparation of VP was followed for the synthesis of PP (yield: 0.51g, 87%).

^{1}H NMR (400 MHz, DMSO-d, 20 °C, TMS, ppm): δ: 8.61-8.62 (d, 4.0 H), 8.42-8.44 (d, 4.0 H), 5.18-5.20 (d, 2.0 H), 3.35-3.45 (m, 2.0 H), 1.26-1.28 (d, 6.0 H), 0.78-0.79 (d, 6.0 H).

FT-IR (KBr): 3460.3, 2963.9, 1698.3, 1656.6, 1591.9, 1434.2, 1401.7, 1342.4, 1252.5, 1174.3, 1124.1, 970.5, 854.8, 808.2, 748.1, 657.3.

MS (MALDI-TOF): 590.0 (calcd. 590.6, M)

Synthesis of aspartic-functionalized perylene derivatives (AP)

Similar procedure as like preparation of AP was followed for the synthesis of PP (yield: 0.49g, 79%).

^{1}H NMR (400 MHz, DMSO-d, 20 °C, TMS, ppm): δ: 8.37-8.56 (d, 4.1 H), 8.12-8.35 (d, 4.0 H), 6.02-6.06 (t, 2.0 H), 2.48-2.85 (d, 4.0 H).

FT-IR (KBr): 3437.8, 2942.5, 2364.1, 1898.8, 1864.4, 1689.9, 1433.8, 1400.6, 1381.0, 1266.8, 1176.6, 1132.7, 881.1, 808.1, 749.4, 633.9 cm^{-1}.

MS (MALDI-TOF): 622.1 (calcd. 622.5, M)

2) Additional Gelation properties in various solvents

Table S1 Gelation properties in various solvents.[a]

Solvents/system	BP	PP	VP	AP
n-Hexane	I	I	I	I
THF	S	P	P	P
Acetone	S	P	P	P
Ethanol	S	S	P	P
Acetonitrile	P	P	P	I
DMF	S	S	S	S
H2O	P	I	I	I
DMSO	S	S	S	S
Chloroform	I	I	I	I
Acetic acid	S	P	P	P
1, 4-Dioxane	S	P	P	P
Mixed solvent 1[b]	S	P	P	P
Mixed solvent 2[c]	S	P	P	P

[a] G = gel, S = Solution, P = precipitation, I=insoluble. [b]volume ratio of acetonitrile-1, 4- dioxane (2: 1), [c]Volume ratio of ethanol-1, 4- dioxane (2: 1). The critical gelation concentrations of the gelators are given in parentheses [%w/v]

3) Additional photos of gels

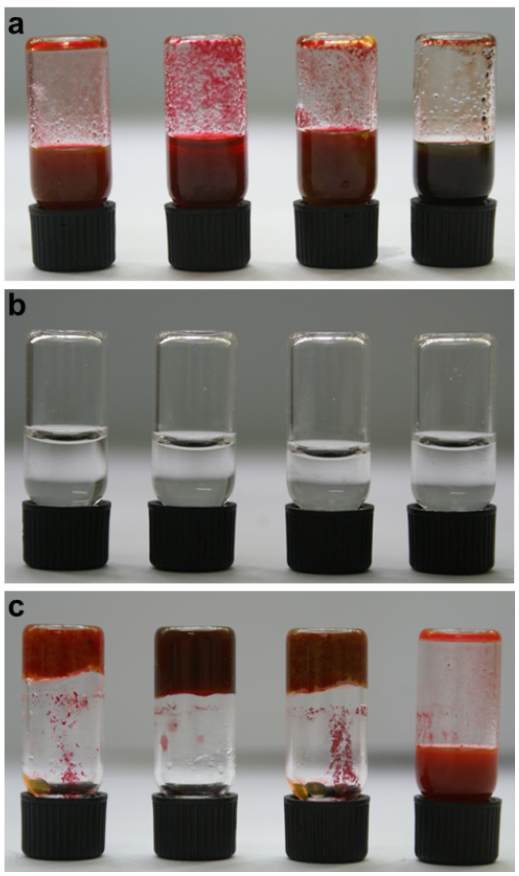


Fig. S1 (a) Optical images of pure compounds in different solvents, from left to right, PP solution in acetic acid, VP solution in mixed solvent 1, VP solution in mixed solvent 2 and AP solution in THF. (b) Photo of BP solution in acetic acid, mixed solvent 1, mixed solvent 2 and THF. (c) Photo of PP/BP=1: 2 in acetic acid, VP/BP=1: 2 in mixed solvent 1, VP/BP=1: 2 in mixed solvent 2, AP/BP=1: 2 in THF.

4) Additional SEM images

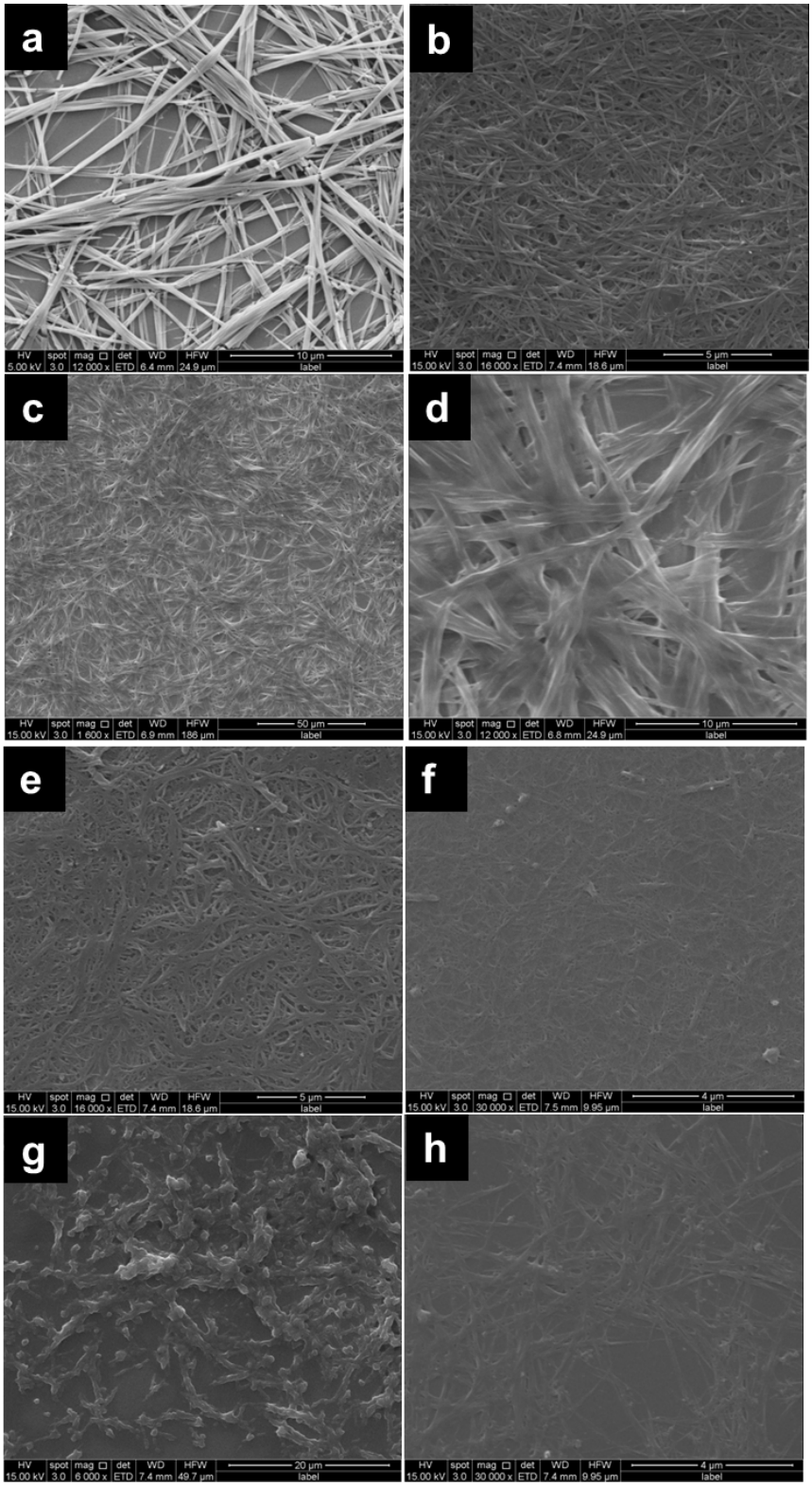


Fig. S2 SEM images, （a）for PP/ BP =1: 2 gel ([PP] = 5×10^{-4} M) in THF, (b) for VP/ BP =1: 2 gel ([VP] =10^{-2} M) in mixed solvent 2; (c) for PP/ BP =1: 2 gel ([PP] =10^{-2} M) in acetic acid in larger scale, (d) for PP/ BP =1: 2 gel ([PP] =10^{-2} M) in acetic acid in small scale; (e) for VP/ BP =1: 2 gel ([VP] =10^{-2} M) in mixed solvent 1, (f) for VP/ BP =1: 2 gel ([VP] =5×10^{-4} M) in mixed solvent 1; (g) for AP/ BP =1: 2 gel ([AP] =10^{-2} M) in THF, (f) for AP/ BP =1: 2 gel ([AP] =5×10^{-4} M) in THF.

5) Rheological data

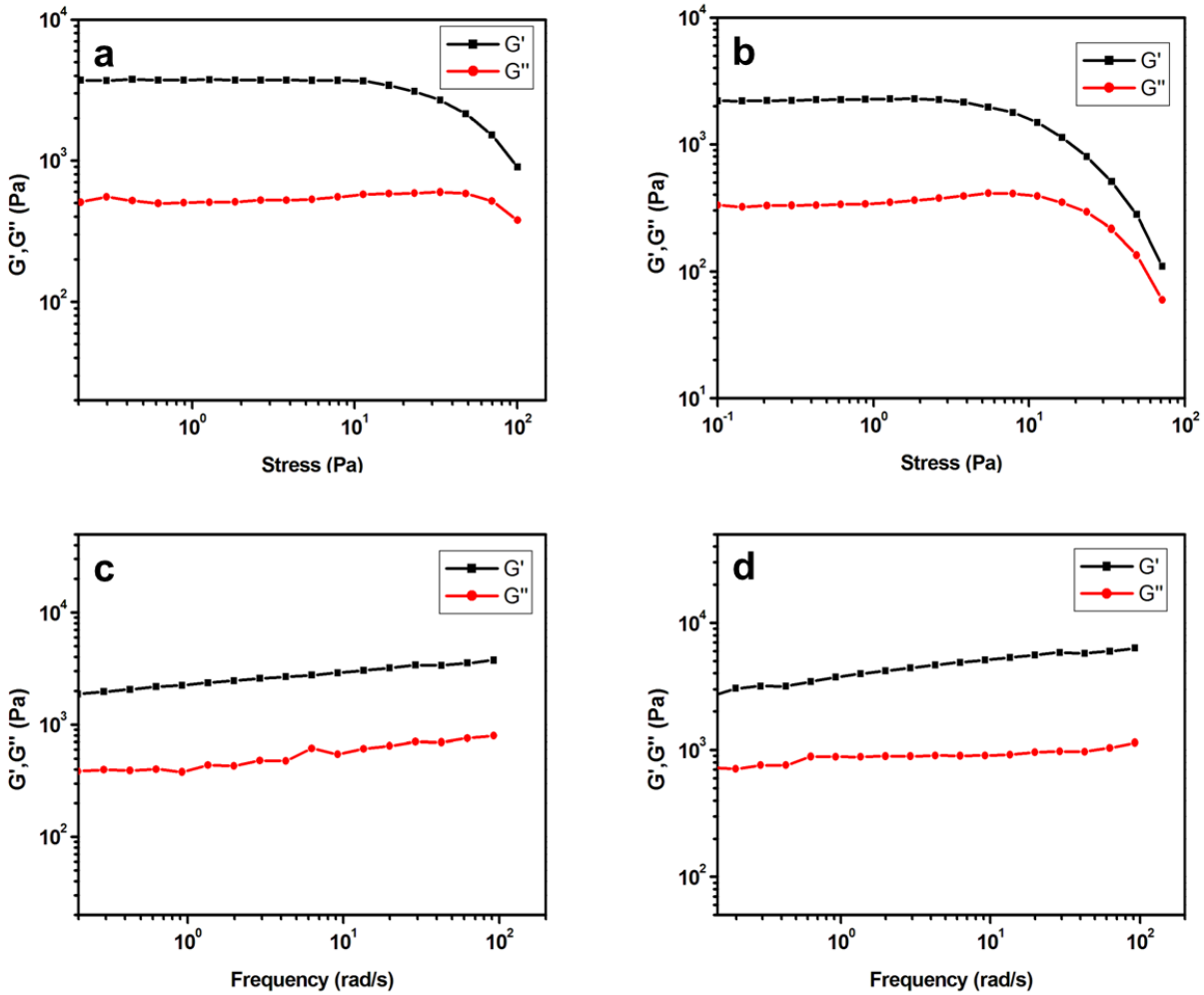


Fig. S3 (a) Stain sweep of the VP/BP gel in mixed solvent 1 at a frequency of 6.28 rad s^{-1}; (b) Stain sweep of the VP/BP gel in mixed solvent 2 at a frequency of 6.28 rad s^{-1}; (c) frequency sweep of the VP/BP gel in mixed solvent 1 at a strain of 0.1%; (d) frequency sweep of the VP/BP gel in mixed solvent 2 at a strain of 0.1%

6) FTIR results

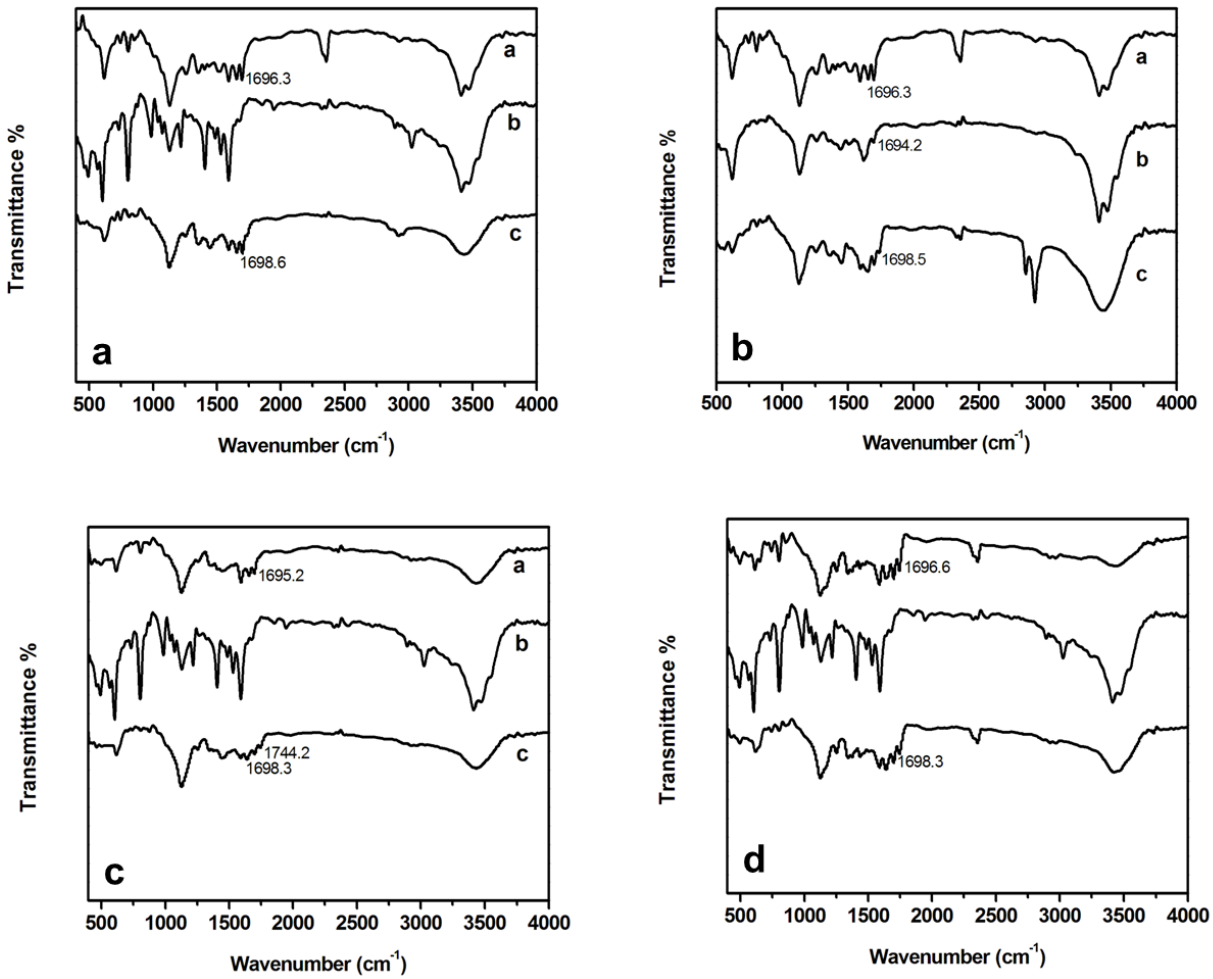


Fig. S4 （a）FT-IR spectra diluted with KBr for a-PP/BP=1:2 dried gel, b-pure BP, c-pure PP, the solvent of gel is THF; (b) FT-IR spectra for a-PP/BP=1: 2 dried gel, b- PP/BP=1:1 dried gel and c-PP/BP=2: 1dried gel, the solvent of gel is THF; (c) FT-IR spectra for a-VP/BP=1:2 dried gel, b-pure BP, c-pure VP, the solvent of gel is mixed solvent 1; (d) FT-IR spectra for a-VP/BP=1:2 dried gel, b-pure BP, c-pure VP, the solvent of gel is mixed solvent 2.

7）Fluorescence data

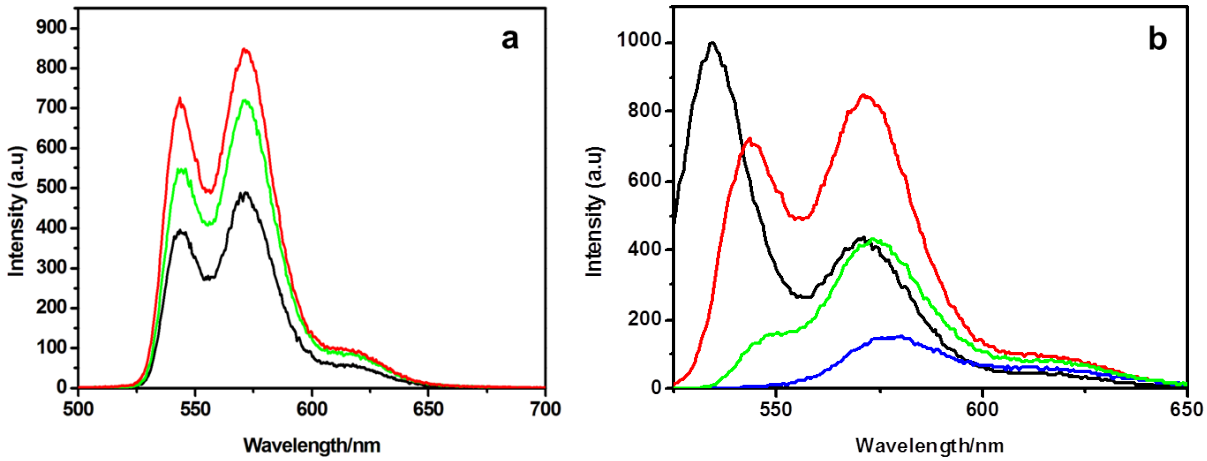


Fig. S5 (a) Fluorescence spectra of PP with different molar equivalent of BP at room temperature, [PP] = 10^{-5} M, λex=486 nm, [pathlength = 5 mm]. (Red line for PP/BP=1:2, green line for PP/BP=1:1, black line for PP/BP=2:1.); (b) Concentration dependent fluorescence spectra of PP/ BP = 1: 2 system at 20 ℃ at high concentration. (Black line for [PP] = 10^{-5} M, red line for [PP] = 10^{-4} M, green line for [PP] = 5 × 10^{-4} M, blue line for [PP] = 10^{-3} M.)

8) Additional photos of gels tuned by triethylamine

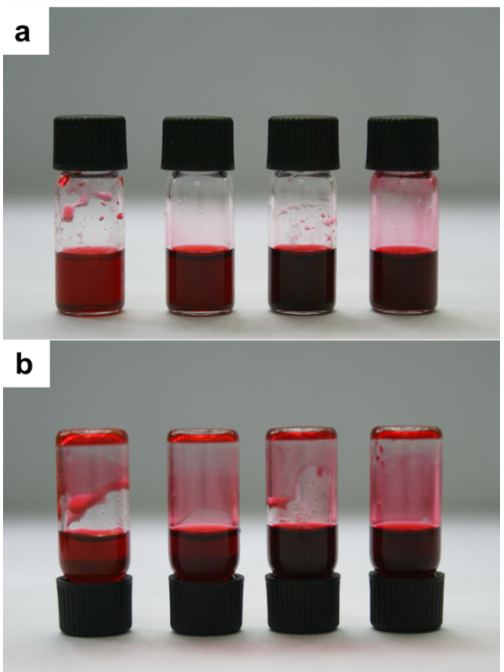


Fig. S6 (a) Upright optical images of gel tuned by triethylamine in different solvents, from left to right， PP/BP-TEA in acetic acid, VP/BP-TEA in mixed solvent 1, VP/BP-TEA in mixed solvent 2, AP/BP-TEA in THF; (b) Inverted optical images of gel tuned by triethylamine in different solvents, from left to right， PP/BP-TEA in acetic acid, VP/BP-TEA in mixed solvent 1, VP/BP-TEA in mixed solvent 2, AP/BP-TEA in THF.

9) References

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