Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

High internal phase emulsion gels (HIPE-gels) from polymer dispersions reinforced with quadruple hydrogen bond functionality

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Experimental

Materials

Methyl methacrylate (MMA, Aldrich), and n-butyl acrylate (nBA, Aldrich), methacrylic acid (MAA, Aldrich) were destabilized by passing them over a column of basic aluminium before use, respectively. 2-amino-4-hydroxy-6-methylpyridine (98%), dibutyltindilaurate (95%), 1,6-diisocyanatohexane (98%), potassium persulfate (KPS, 99%) and Poly(ethylene glycol) methacrylate (PEGMA, average Mn~526g/mol) were purchased from Aldrich and used as received. All other chemicals were analytical grade and used as received. Deionized water was used in all experiments.

Synthesis of UPy functionalized PEGMA monomer

2-amino-4 hydroxy-6-methylpyrimidne (5.00g) was added in 1,6-diisocyanatohexane (40.37g,), and then the mixture was heated at 100^{o}C for 20h. 20ml of pentane was added and the resulting precipitate was filtered, and then washed with pentane for 3 times. The obtained white powder product was then dried at 60^{o}C in vacuo. After this, to a solution of polyethylene glycol methacrylate (2.63g, 5× 10^{-3}mol) in 60ml of anhydrous chloroform, the white powder above (1.76g) was added. After the addition of 3 drops of dibutyltindilaurate as catalyst, the mixture was heat at 60^{o}C for 20h. Another 60ml of chloroform was added after the reaction and then the mixture was filtered to remove any solids. The filtrate was concentrated back to ~60ml by rotation evaporation. ~1g of silica and 2 drops of dibutytindilaurate were added, the mixture was then heated at 60^{o}C for another 1h. The silica was removed by filter and the resulting solution was stored at 5^{o}C for the following reactions. Concentration:0.12g/ml. ^{1}H-NMR:13.1(s,1H,$CH_3CN\underline{H}$), 11.9(s,1H,$CH_2NH(C{=}O)N\underline{H}$),

10.0 (s,1H,$CH_2N\underline{H}(C=O)NH$), 6.1+5.6(s,2H,$C=C\underline{H}_2$), 5.8(s,1H,$C\underline{H}=CCH_3$), 3.6 (m, 40H,$C\underline{H}_2O$), 3.3(m, 2H, $NHCONHC\underline{H}_2$), 3.2(m,2H, $C\underline{H}_2NH(C=O)O$), 2.2(s, 3H, $CH=CC\underline{H}_3$), 1.9(s, 3H,$(C=O)CC\underline{H}_3$), 1.6-1.2(m, 8H, $CH_2C\underline{H}_2CH_2$). FTIR: ν 2926 and 2857 (CONH), 1699 (aryl C=O), 1668 (NCON). LC-MS (*m/z*): Cacld: 819.3; Found: 818.3 ($M\text{-}H^-$)

Synthesis of Rhodamine B piperazine methacrylamide

To a solution of Rhodamine B piperazine [1] (2 g, 3.64 mmol) in dry DCM (100 mL) cooled to 0°C, TEA (1.11g, 10.9 mmol) was added and the reaction was left to stir for 1hour. Methacryloyl chloride (0.970 g, 10.7 mmol) in 15mL DCM was added dropwise during 1 hour. The reaction was then raised to ambient temperature for a further 12 h. The volatiles were then removed under reduced pressure and the residue was purified by column chromatography using DCM/Et_3N (95/5), to give the rhodamine B piperazine methacrylamide as purple glassy solid in 80 % yield.

^{1}H NMR (400.03 MHz, $CDCl_3$, 298 K): δ = 1.20 (t, *J* = 7.0 Hz, 12H), 1.78 (s, 3H), 3.20-3.31 (m, 12), 3.54-3.61 (m, 8H), 4.9 (m, 1H), 5.14 (m, 1H), 7.07–7.15 (d, *J* = 9.5 Hz, 2H), 7.19–7.25 (m, 1H), 7.41–7.49 (m, 1H), 7.51–7.61 (m, 2H).

^{13}C NMR (100.59 MHz, $CDCl_3$, 298 K): δ = 12.50, 18.12, 41.34, 46.01, 47.17, 52.19, 52.88, 96.11, 113.52, 114.32, 125.40, 127.51, 129.77, 129.99, 130.06, 130.46, 131.91, 135.17, 136.02, 155.44, 155.70, 157.54, 167.12, 167.22.

High resolution MS-ES calc. for $C_{36}H_{43}ClN_4O_3$ (M+): 614.30; found: 579.75 (M-Cl).

Fluorescence spectrometry of the Rhodamine B monomer solution in water was performed to obtain the emission spectrum (**Fig S8**). Abs= 564nm and Em= 583nm

Emulsion copolymerization of UPy functionalized monomer

A solution of sodium hydrogen carbonate (0.2g, 150ml) was poured into a 250ml reactor, and then degassed monomers MMA (2.43g, 0.0243mol), BA (3.11g, 0.0243mol) and rhodamine piperazine amide methacrylate (0.001g) were added with PEGMA-UPy macromonomer (0.6g in 5ml of chloroform) under nitrogen atmosphere. The mixture was heated 70^{o}C. After purging with N_2 for 30min, potassium persulfate (0.129g, 4.75× 10^{-4}mol) dissolved in 5ml water was injected to initiate the emulsion polymerization. The reaction was kept for 6h. After that, the latex particles were purified through dialysis for a week. For the preparation of reference PMMA-PBA-PMAA latex particles, we adapt the same route excepting using MAA (0.2g) instead of PEGMA-UPy monomer. The average hydrodynamic diameters of particles were determined by dynamic light scattering (DLS, Malvern Zetasizer Nano) and shown in **Fig.S1**and **Fig.S2**.

HIPE-organogel preparation

The high internal phase emulsion organogels were prepared typically by hand-shaking a mixture of toluene (0.2ml) and PMMA-PBA-PUPy latex dispersion (0.1wt% concentration, 0.8ml) containing sodium chloride (0.05g) for only 5 seconds. Alternatively the HIPE organogels were prepared by placing the mixture on a vortex mixer (Fisherbrand, Whirlimixer) for less than 10 seconds.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker spectrometer using $CDCl_3$ as solvent. Fourier transform infrared spectroscopy (FT-IR) spectra were collected using Pekin-Elmer Spectrum 100 at ambient temperature. Mass spectra were recorded on a Bruker Esquire2000 (ESI) liquid chromatography-mass spectrometry.

For SEM observations, HIPE gels were transferred onto silica wafers and dried over night at room temperature and then coated with Au before taking images on a Zeiss Supra 55VP FEGSEM microscope. Confocal imaging was performed on a Zeiss LSM 510 confocal microscope. Lasers with wavelengths of 514nm and 480nm were used to excite rhodamine labelled particles and hostasol in toluene, respectively. Rheological experiments were taken at 20°C on a Malvern Kinexus Rheometer using plate geometry. The temperature was set to ±0.01°C in accuracy by using Julabo a temperature instrument. All rheological measurements were performed twice to ensure reproducibility. Diffusion analysis of Rhodamines B dye in a HIPE gel was performed on a Perkin Elmer Lamda-45 UV-VIS spectrophotometer.

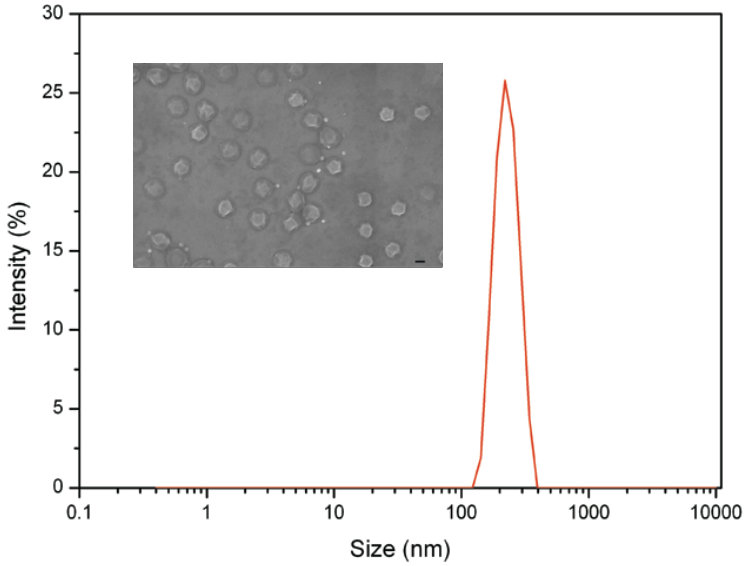

Fig. S1 Intensity-average hydrodynamic diameter of PMMA-PBA-PUPy latex particles by dynamic light scattering (average size: 223nm, PDI: 0.025). Insert: SEM image of latex particles at room temperature, scale bar: 200nm.

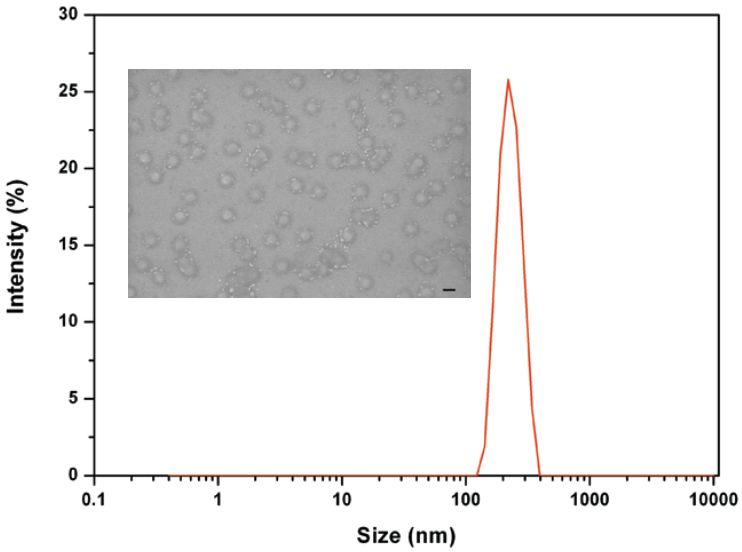

Fig. S2 Intensity-average hydrodynamic diameter of the soft PMMA-PBA-PMAA latex particles by DLS (average size: 235nm, PDI: 0.012). Insert: SEM image of the melted latex particles at room temperature, scale bar: 200 nm.

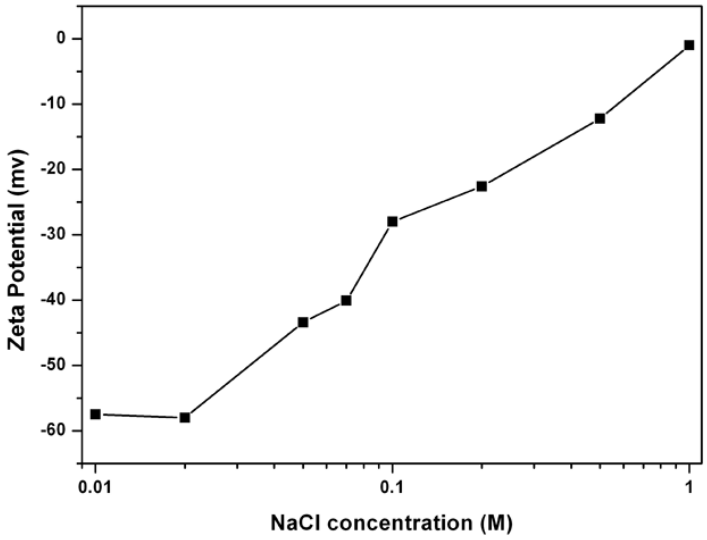

Fig. S3 Zeta potential of PMMA-PBA-PUPy latex particles as a function of NaCl concentration.

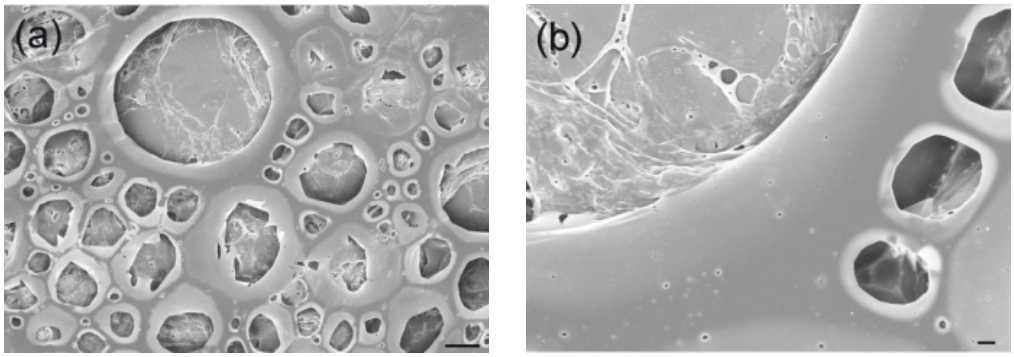

Fig. S4 (a) SEM image of HIPE-organogel prepared using 80% aqueous 0.1wt% UPy functionalized particle dispersion and 20% toluene after drying in air at room temperature, scale bar: 20μm, (b) zoom-in SEM image, scale bar: 2 μm

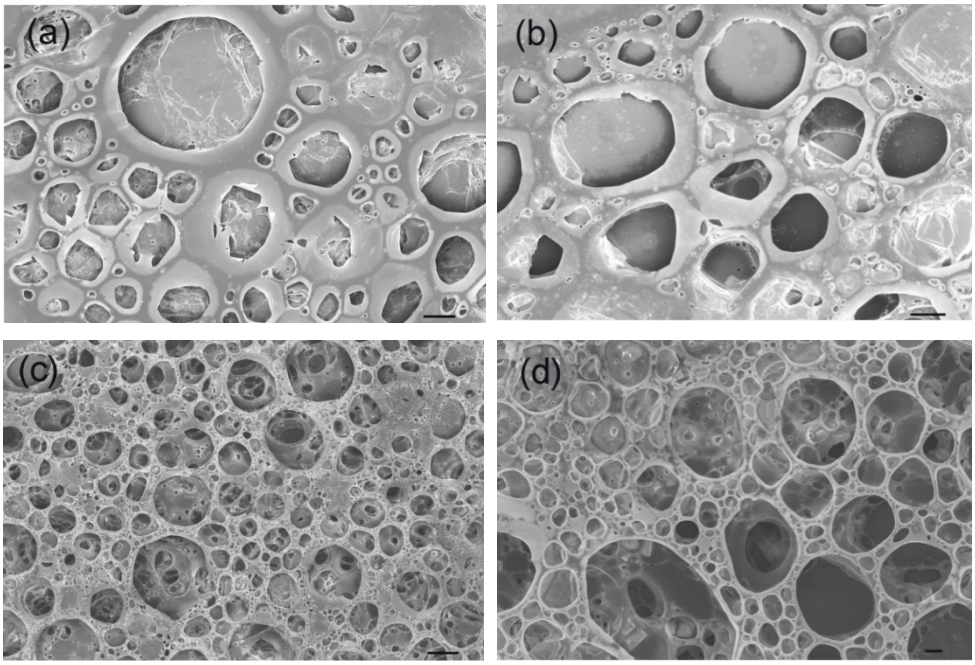

Fig. S5 SEM images of HIPE gels with internal phase volume fraction (80%) at different colloidal particle concentrations, (a) 0.1%, (b) 0.5%, (c) 1%, all scale bars: 20μm, and (d) 5%, scale bars: 2μm.

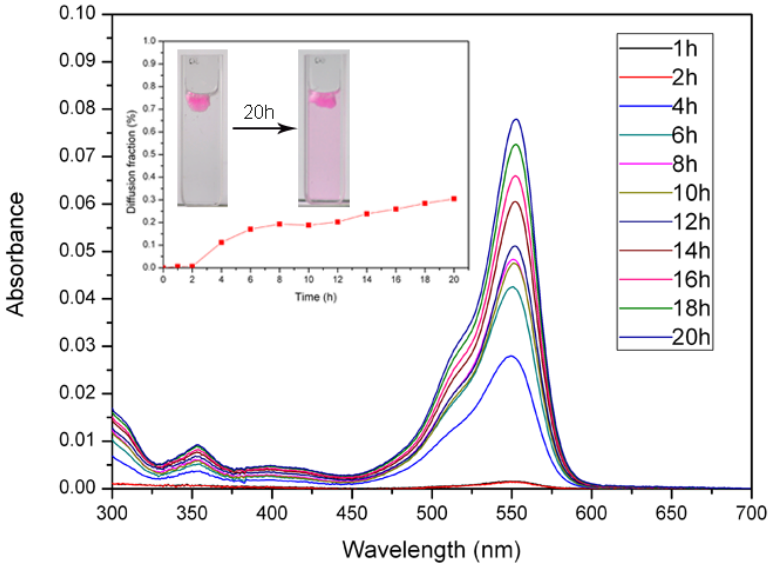

Fig. S6 UV-Vis spectra of diffusion intensity of rhodamine B dye in pure water which was originally loaded in HIPE gels, the inset plots diffusion fraction vs time showing the diffusion rate of rhodamine B from the internal water phase of HIPE gels to outside pure water.

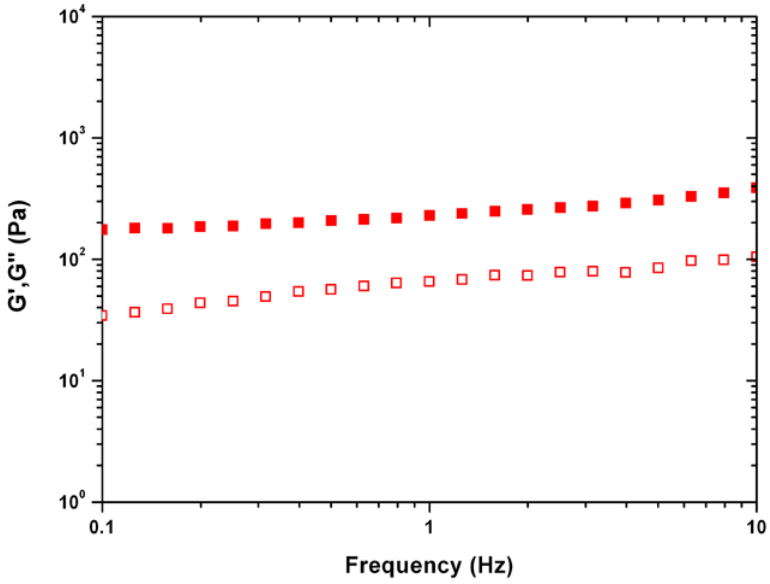

Fig. S7 Storage modulus (solid symbol) and loss modulus (open symbol) of the emulsion stabilized by 1wt% of PMMA-PBA-PMAA latex particles as a function of frequency in the oscillatory frequency sweep.

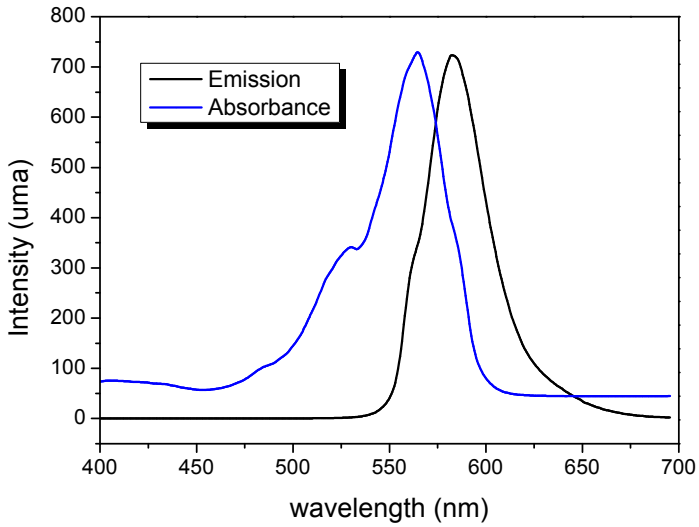

Fig. S8 Absorbance and emission spectra of Rhodamine B piperazine methacrylamide in aqueous solution.

References

1 T. Nguyen and M. B. Francis, *Org. Lett.*, 2003, **5**, 3245