Electronic Supporting Information

Dispersible Microporous Di-block Co-polymer Nanoparticles via Polymerisation-Induced Self-Assembly

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Experimental

Materials

Poly(ethylene glycol) methyl ether (PEG, Mn 5000, PDI 1.09), anhydrous trimethylamine (TEA), 2-bromoisobutyryl bromide, dodecane thiol, potassium phosphate tribasic (K_3PO_4), Fumaronitrile (FN, 98 %) and potassium persulfate were all purchased from Sigma-Aldrich and used as received. Dry toluene was obtained in a method analogous to the one outlined by Grubbs.[1] Magnesium sulfate and carbon disulphide were purchased from Fischer and used as received. Divinylbenzene (DVB, technical grade 80 %) was passed through an alumina column in order to remove the inhibitor before use. Fumaronitrile (FN, 98 %) and 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98 %) were purchased from Sigma-Aldrich and used without further purification. All other chemicals were purchased from Sigma-Aldrich and used without any further purification.

Synthesis of PEG_{113}-Br

PEG_{113}-Br was prepared in a method similar to that reported by M. Liu and co-workers.[2] PEG_{113} (8 g, 1.6 mmol, 1 eq.) was dissolved in anhydrous toluene (100 mL) in a two-neck flask. TEA (0.32 mL, 2.3 mmol, 1.4 eq.) was added and the solution was cooled to 0 °C. 2-bromoisobutyryl bromide (0.26 mL, 2.1 mmol, 1.3 eq.) was added dropwise over the course of 1 h before being left to stir overnight at room temperature. The solvent was reduced before being precipitated into an excess of cold diethyl ether (200 mL). The crude product was dried under vacuum, dissolved in water before being extracted with DCM. The organic layers were collected, combined and dried over $MgSO_4$ and placed the fridge overnight to obtain the PEG_{113}-Br product (Yield = 87%. Found C: 53.78%, H: 9.07%, Expected C: 53.96%, H: 8.97%).

Synthesis of PEG-based macro-chain transfer agent (CTA)

The PEG-based macro-CTA was synthesised using a method adapted from a paper published by O'Reilly and co-workers.[3] Dodecane thiol (0.60 mL, 2.5 mmol, 1 eq.) was added to a stirred suspension of K_3PO_4 (0.53 g, 2.5 mmol, 1 eq.) in acetone (50 mL) and stirred for 10 minutes. Carbon disulphide (0.36 mL, 6 mmol, 2.5 eq.) was added to the suspension and left to stir for a further 10 minutes. PEG_{113}-Br (10 g, 2 mmol, 0.8 eq.) in acetone (30 mL) was added to the suspension which was left to stir overnight at room temperature. The solvent was removed by rotary evaporation precipitated into an excess of n-hexane twice and once into diethyl ether to ensure purity. The sample was dried in the vacuum oven overnight at 40 °C to afford the RAFT macro-CTA (Yield = 88%. Found C: 54.51%, H: 9.05%, S: 1.84%, Expected C: 54.52%, H: 9.13%, S: 1.80%).

Synthesis of HCPN-0.75

The insoluble porous polymer of FN/DVB was synthesised in an identical method to that reported by Li and co-workers.[4] DVB (0.26 g, 2 mmol, 1 eq.), FN (0.117 g, 1.5 mmol, 0.75 eq.) and toluene (10 mL) were all added to a 2-neck round bottom flask under nitrogen. The flask was heated to 80 °C and polymerisation was initiated through the addition of AIBN (3.8 mg, 0.023 mmol, 0.01 eq.). After 24 h the polymerisation was quenched and the solution poured into methanol to precipitate the polymer. The solid was washed with methanol and tetrahydrofuran (THF) and extracted from THF in Soxhlet apparatus for 16 h. The final product was collected and dried under vacuum at 60 °C.

$PEG_{113}DVB_{300}FN_{225}$ (RAFT only) *via* RAFT mediated polymerisation

A RAFT-mediated polymerisation route was employed utilising the PEG-based macro. The PEG-based macro CTA (0.13 g, 0.02 mmol, 1 eq.) and FN (0.35 g, 4.5 mmol, 225 eq.) were added to a 2-necked round bottom flask. The flask was evacuated and back-filled with nitrogen 3 times. Toluene (30 mL) and DVB (0.85 mL, 6 mmol, 300 eq.) were added to the flask to create a 5 % wt. solution. The solution was bubbled through with nitrogen gas to ensure the system was devoid of air before heating to 70 °C. Polymerisation was initiated through the addition of AIBN (0.66 mg, 0.004 mmol, 0.2 eq) and held at 70 °C for 24 h. The solid was washed with methanol and tetrahydrofuran (THF) and extracted from THF in Soxhlet apparatus for 16 h. The final product was collected and dried under vacuum at 60 °C.

$PEG_{113}DVB_{150}FN_{113}$ *via* RAFT mediated polymerisation induced self-assembly

The PEG-based macro CTA (0.13 g, 0.02 mmol, 1 eq.) and FN (0.175 g, 2.25 mmol, 113 eq.) were added to a 2-necked round bottom flask. The flask was evacuated and back-filled with nitrogen 3 times. Water and ethanol in a 60:40 ratio along with DVB (0.425 ml, 3 mmol, 150 eq.) were added to the flask to create a 1 % wt. solution. The solution was bubbled through with nitrogen gas to ensure the system was devoid of air before heating to 70 °C. Polymerisation was initiated through the addition of potassium persulfate (KPS, 1.08 mg, 0.004 mmol, 0.2 eq.) and held at 70 °C for 24 h. The product was isolated as a white solid through reprecipitation into diethyl ether before drying *in vacuo* at 40 °C for 16 h.

$PEG_{113}DVB_{300}FN_{225}$ *via* RAFT mediated polymerisation induced self-assembly

The PEG-based macro CTA (0.13 g, 0.02 mmol, 1 eq.) and FN (0.35 g, 4.5 mmol, 225 eq.) were added to a 2-necked round bottom flask. The flask was evacuated and back-filled with nitrogen 3 times. Water and ethanol in a 60:40 ratio along with DVB (0.85 ml, 6 mmol, 300 eq.) were added to the flask to create a 1 % wt. solution. The solution was bubbled through with nitrogen gas to ensure the system was devoid of air before heating to 70 °C. Polymerisation was initiated through the addition of potassium persulfate (KPS, 1.08 mg, 0.004 mmol, 0.2 eq.) and held at 70 °C for 24 h.

The product was isolated as a white solid through reprecipitation into diethyl ether before drying *in vacuo* at 40 °C for 16 h.

$PEG_{113}DVB_{600}FN_{450}$ *via* RAFT mediated polymerisation induced self-assembly
The PEG-based macro CTA (0.13 g, 0.02 mmol, 1 eq.) and FN (0.70 g, 9 mmol, 450 eq.) were added to a 2-necked round bottom flask. The flask was evacuated and back-filled with nitrogen 3 times. Water and ethanol in a 60:40 ratio along with DVB (1.70 ml, 12 mmol, 600 eq.) were added to the flask to create a 1 % wt. solution. The solution was bubbled through with nitrogen gas to ensure the system was devoid of air before heating to 70 °C. Polymerisation was initiated through the addition of potassium persulfate (KPS, 1.08 mg, 0.004 mmol, 0.2 eq.)and held at 70 °C for 24 h. The product was isolated as a white solid through reprecipitation into diethyl ether before drying *in vacuo* at 40 °C for 16 h.

$PEG_{113}DVB_{1200}FN_{900}$ *via* RAFT mediated polymerisation induced self-assembly
The PEG-based macro CTA (0.13 g, 0.02 mmol, 1 eq.) and FN (1.40 g, 18 mmol, 900 eq.) were added to a 2-necked round bottom flask. The flask was evacuated and back-filled with nitrogen 3 times. Water and ethanol in a 60:40 ratio along with DVB (3.40 ml, 24 mmol, 1200 eq.) were added to the flask to create a 1 % wt. solution. The solution was bubbled through with nitrogen gas to ensure the system was devoid of air before heating to 70 °C. Polymerisation was initiated through the addition of potassium persulfate (KPS, 1.08 mg, 0.004 mmol, 0.2 eq.) and held at 70 °C for 24 h. The product was isolated as a white solid through reprecipitation into diethyl ether before drying *in vacuo* at 40 °C for 16 h.

Preparation of solutions for use in fluorescence studies
A 100 cm^3 stock solution containing 1 mg of polymer sample in methanol was prepared with an optical density of 0.2 (a.u). A 2.5 cm^3 aliquot of this solution was added to a glass cuvette which was used for the fluorescence studies. A separate 1 mM stock solution containing the quencher along with the polymer sample was also made up. This solution was added sequentially to the cuvette and the fluorescent quenching was observed.

Characterisation
Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin-Elmer Spectrum 100 fitted with an attenuated total reflectance tip (ATR). ^{1}H- and ^{13}C- NMR spectra were recorded on a 400 MHz Bruker Avance-400 spectrometer. Molecular weights (Mn) and polydispersity indices (PDI) were measured by gel permeation chromatography (GPC). THF was used as the eluent with a flow rate of 1 mL min^{-1} at 25 °C using polystyrene as the calibration standard. Universal calibration was applied employing Erma ERC-7512 refractive index detectors using Cirrus GPC-online software for analysis. Dynamic light scattering (DLS) of the polymer solutions

were carried out using a Malvern Zetasizer nanoZS instrument *via* the Stokes-Einstein equation which assumes perfectly monodisperse, non-interacting spheres.

Solid-State NMR samples were packed into 4 mm zirconia rotors and transferred to a Bruker Avance III HD spectrometer. 1D ^{1}H-^{13}C cross-polarisation magic angle spinning (CP/MAS) NMR experiments were measured at 125.76 MHz (500.13 MHz ^{1}H) at a MAS rate of 10.0 kHz. The ^{1}H $\pi/2$ pulse was 3.4 μs, and two-pulse phase modulation (TPPM) decoupling was used during the acquisition. The Hartmann-Hahn condition was set using hexamethylbenzene. The spectra were measured using a contact time of 2.0 ms. The relaxation delay D_1 for each sample was individually determined from the proton T_1 measurement ($D_1 = 5 \times T_1$). Samples were collected until sufficient signal to noise was observed, typically greater than 256 scans. The values of the chemical shifts are referred to that of TMS.

Scanning electron microscopy (SEM) images were collected on a Fei Inspect F50 Field Emission Gun SEM, run in secondary electron mode. Specimens were prepared by mounting onto carbon tape, supported on aluminium stubs. Transmission electron microscopy (TEM) studies were conducted using a Philips CM 100 instrument operating at 100 kV and equipped with a Gatan 1 k CCD camera. A diluted solution of the polymer material (0.10% w/w) was placed on carbon-coated copper grids, allowed to dry and then exposed to ruthenium(VIII) oxide vapor for 7 min at 20 °C prior to analysis. The ruthenium(VIII) oxide was prepared as follows: Ruthenium(IV) oxide (0.30 g) was added to water (50 g) to form a black slurry; addition of sodium periodate (2.0 g) with stirring produced a yellow solution of ruthenium(VIII) oxide within 1 min.[5]

Small-angle X-ray scattering (SAXS). SAXS data were collected using a laboratory SAXS instrument (Xeuss 2.0, Xenocs, France) equipped with a liquid gallium MetalJet X-ray source (Excillum, Sweden, wavelength $\lambda = 0.134$ nm), two sets of motorized scatterless slits for beam collimation and a Dectris Pilatus 1M pixel detector (sample-to-detector distance 6.335 m). SAXS patterns were collected over a q range of $0.011\ \text{nm}^{-1} < q < 1.0\ \text{nm}^{-1}$, where $q = (4\pi\sin\theta)/\lambda$ is the length of the scattering vector and θ is one-half of the scattering angle. Glass capillaries of 2 mm diameter were used as a sample holder and 6 data sets were collected over 10 min for each sample (empty capillary, methanol and 5% w/w polymer sample in methanol). Data were reduced (normalization and integration) using the Foxtrot software package supplied with the instrument and further analysed (background subtraction and data modelling) using Irena SAS macros for Igor Pro.[6]

Gas sorption measurements were performed using a micromeritics ASAP 2020 plus analyser employing high purity gases. Samples were degassed at 120 °C for 16 h under vacuum immediately prior to analysis. UV-Vis absorption spectra were taken on a Cary 5000 spectrophotometer. All steady-state fluorescence spectra were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer.

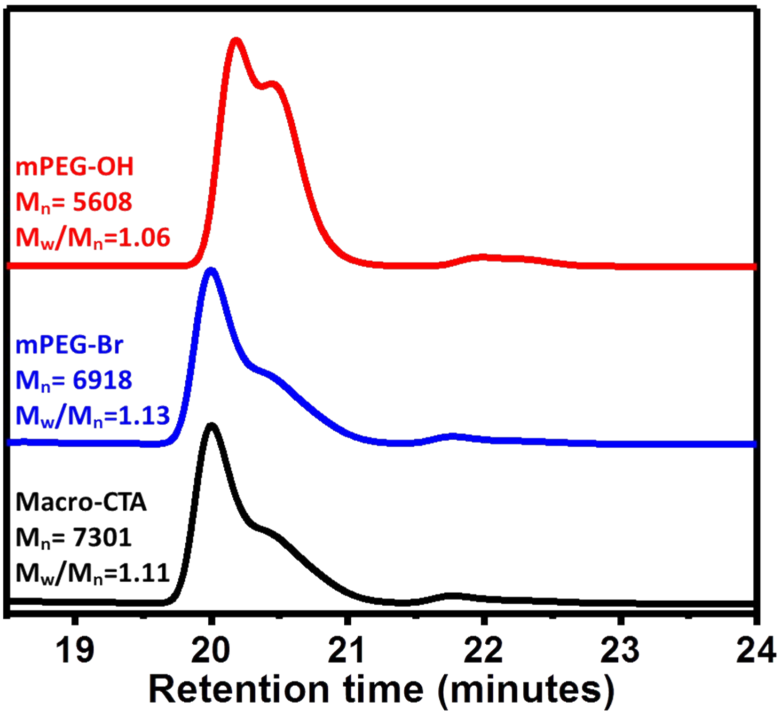


Figure S1. GPC chromatograms of mPEG-OH, mPEG-Br and PEG-CTA run against a PS standard detected by refractive index.

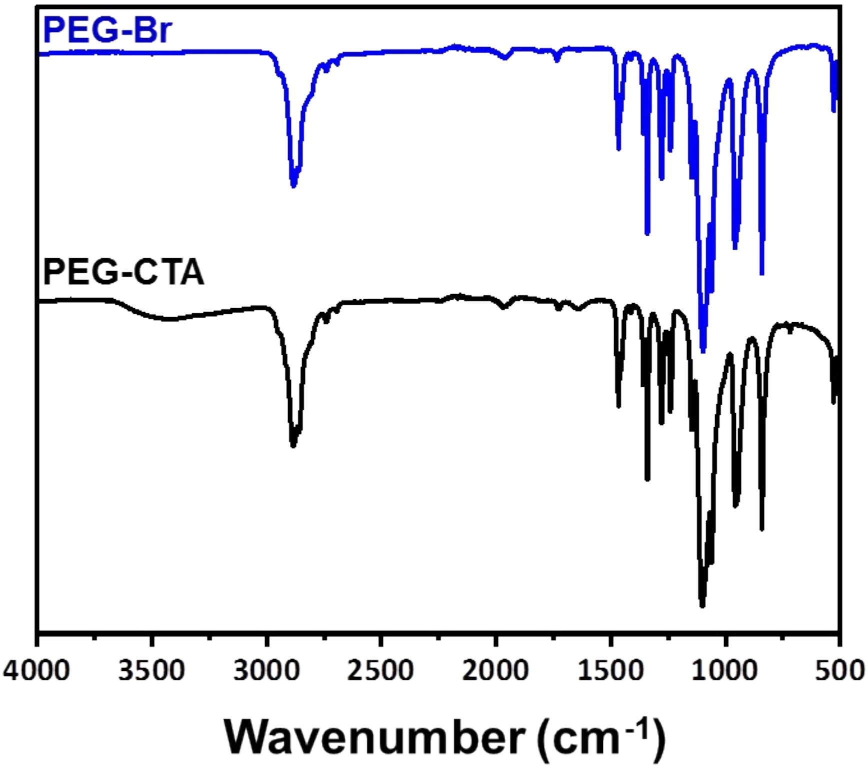


Figure S2. FTIR spectra of PEG-Br and PEG-CTA

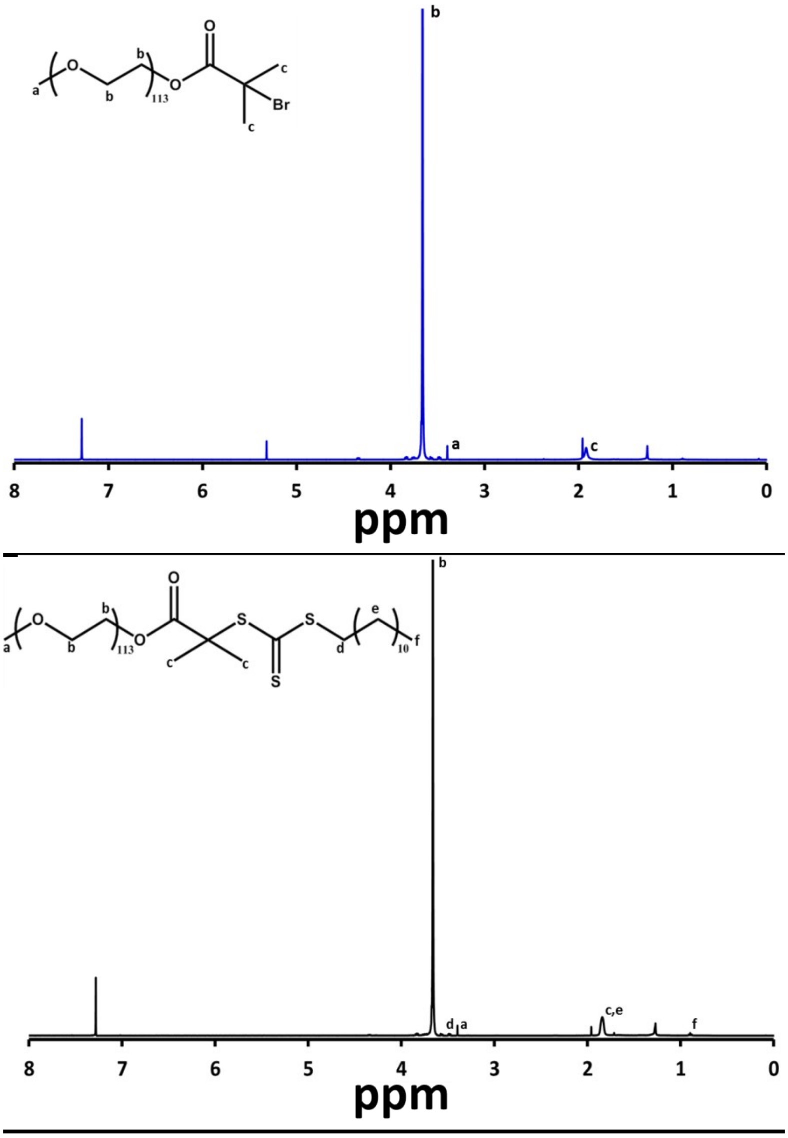
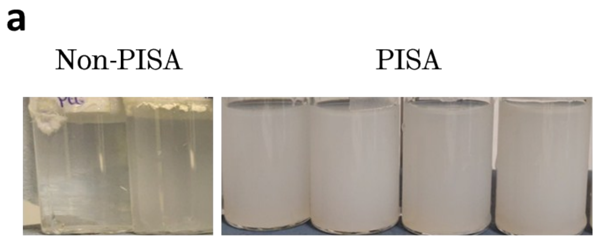
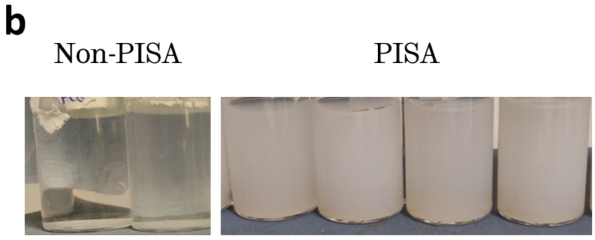


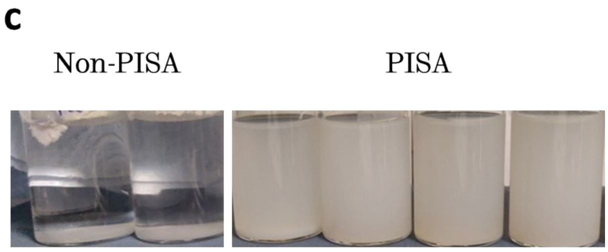
Figure S3. ^{1}H-NMR of PEG-Br (top) and PEG-CTA (bottom) in $CDCl_3$



30 mins sonication



24 hour undisturbed



1 week undisturbed

Figure S4. From left to right: HCPN-0.75, $PEG_{113}DVB_{300}FN_{225}$ (conventional RAFT solution), $PEG_{113}DVB_{150}FN_{113}$, $PEG_{113}DVB_{300}FN_{225}$, $PEG_{113}DVB_{600}FN_{450}$, and $PEG_{113}DVB_{1200}FN_{900}$ in methanol (a) immediately after 30 min sonication, (b) after 24 h and (c) after 1 week.

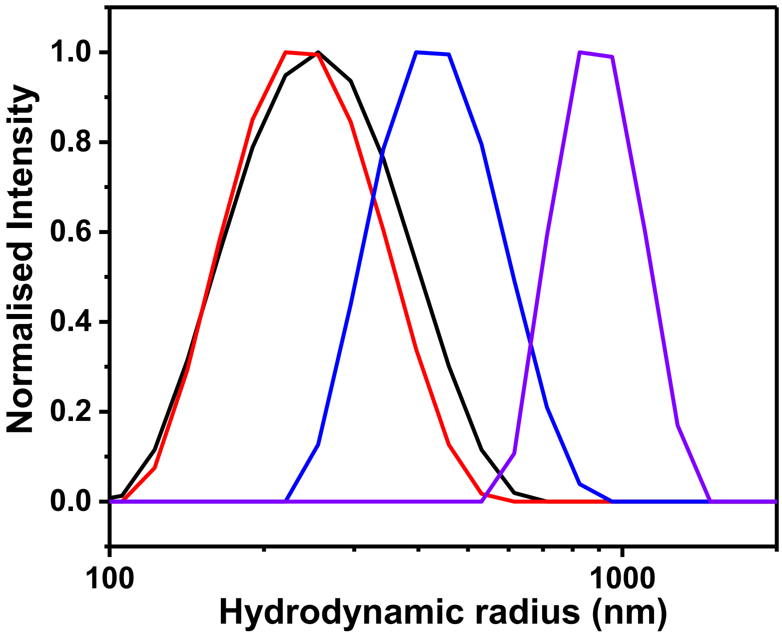


Figure S5. DLS data obtained after sonication of samples (PEG$_{113}$DVB$_{150}$FN$_{113}$, PEG$_{113}$DVB$_{300}$FN$_{225}$, PEG$_{113}$DVB$_{600}$FN$_{450}$, and PEG$_{113}$DVB$_{1200}$FN$_{900}$) for 30 minutes in methanol

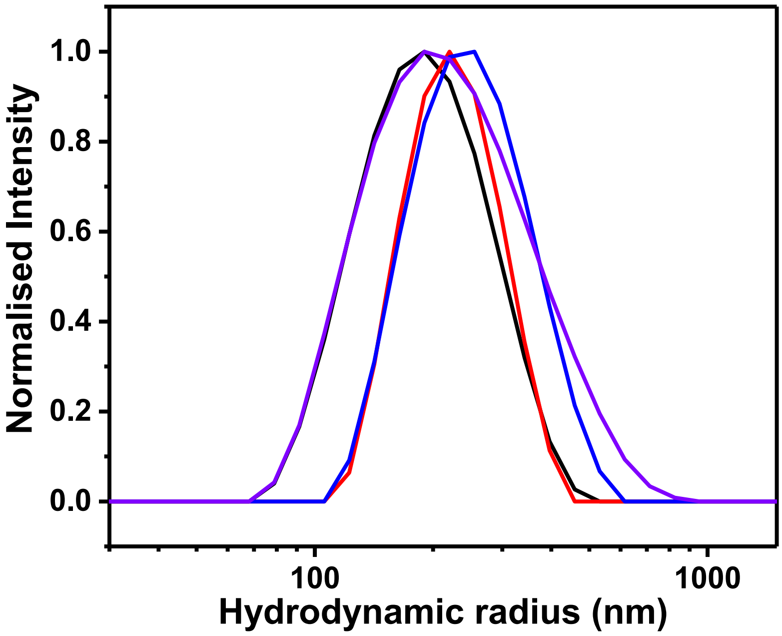


Figure S6. DLS data obtained after sonication of samples (PEG$_{113}$DVB$_{150}$FN$_{113}$, PEG$_{113}$DVB$_{300}$FN$_{225}$, PEG$_{113}$DVB$_{600}$FN$_{450}$, and PEG$_{113}$DVB$_{1200}$FN$_{900}$) for 3 hours in methanol

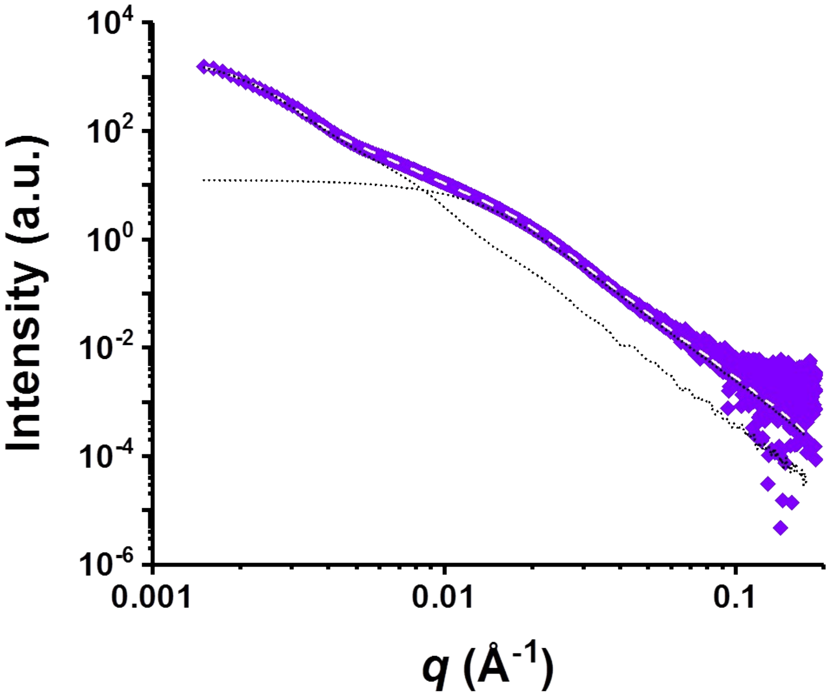


Figure S7. SAXS data for a 5% w/w dispersion of $PEG_{113}DVB_{96}FN_{72}$ particles in methanol (purple data), with overall fit to the two-population model (white dashed line) and each population of small and larger spheroids (dotted black lines).

Table S1. Summary of SAXS fittings for 5% w/w dispersions in methanol. D_1 is the primary particle diameter and D_{PY1} is the mean interaction distance between interacting primary particles. D_2 is the aggregate particle diameter and D_{PY2} is the mean interaction distance between interacting aggregate particles.

Sample	**D_1 / nm**	**D_{PY1} / nm**	**D_2 / nm**	**D_{PY2} / nm**
$PEG_{113}DVB_{150}FN_{113}$	27.0 ± 5.4	33.5	158 ± 61.7	239
$PEG_{113}DVB_{300}FN_{225}$	28.9 ± 7.0	33.8	174 ± 61.3	242
$PEG_{113}DVB_{600}FN_{450}$	24.0 ± 9.5	31.0	179 ± 36.2	279
$PEG_{113}DVB_{1200}FN_{900}$	25.4 ± 7.9	41.7	188 ± 50.0	256

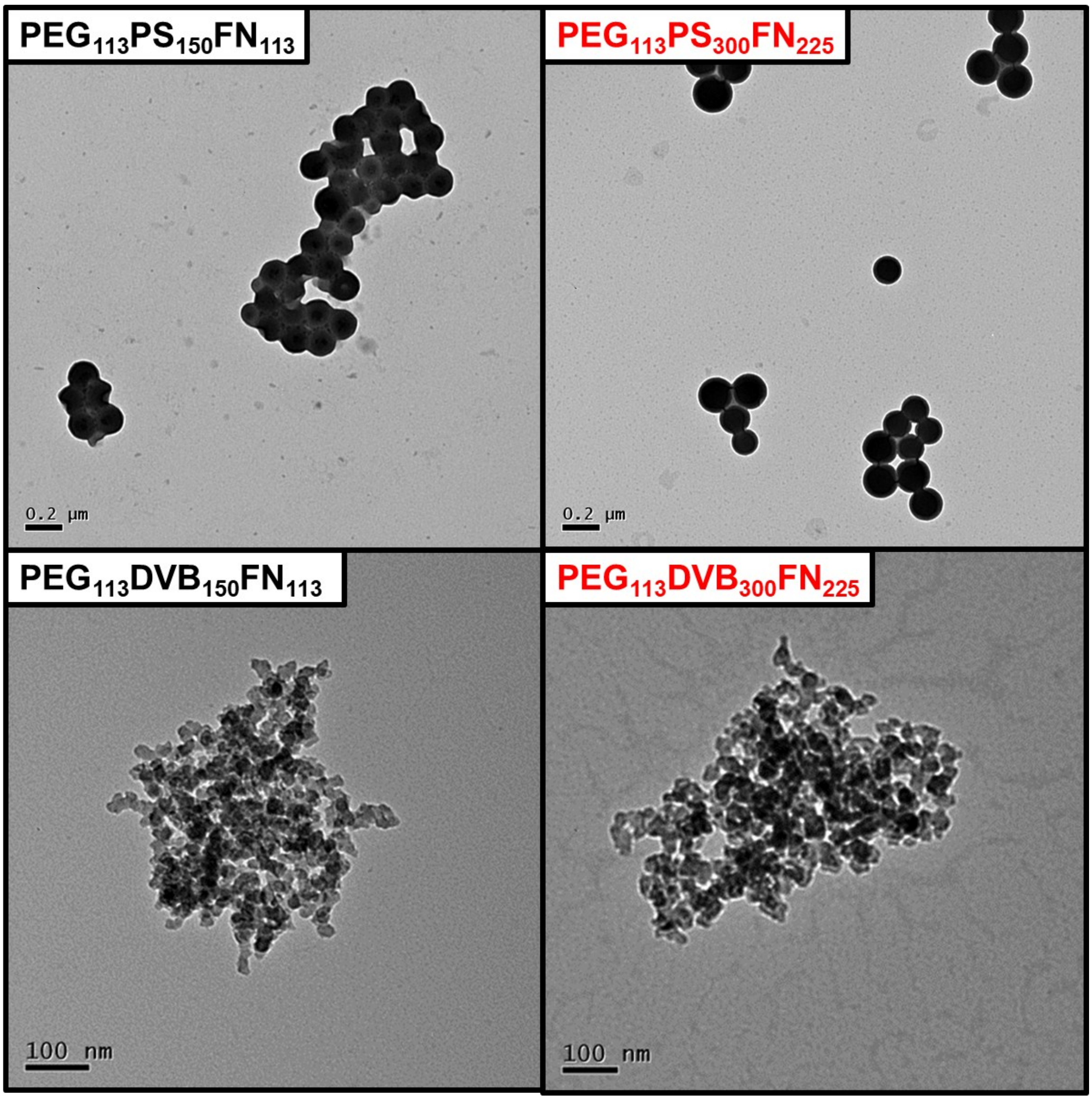


Figure S8. TEM images comparing morphology of styrene (top) and DVB (below) analogues

Table S2. Table showing the hydrodynamic diameters of the DVB and PS samples

Sample	**Hydrodynamic diameter (nm)**	
	X = DVB	**X = PS**
$PEG_{113}X_{150}FN_{113}$	204	224
$PEG_{113}X_{300}FN_{225}$	219	202
$PEG_{113}X_{600}FN_{450}$	230	315
$PEG_{113}X_{1200}FN_{900}$	262	254

Table S3. Hydrodynamic radii of each sample when dispersed in various solvents

Sample	Solvent						
	$CHCl_3$/ nm	DCM/ nm	Toluene/ nm	MeOH/ nm	THF/ nm	CH_3CN/ nm	Acetone/ nm
$PEG_{113}DVB_{150}FN_{113}$	2163	2223	2111	204	242	200	245
$PEG_{113}DVB_{300}FN_{225}$	2592	2299	2840	219	352	207	352
$PEG_{113}DVB_{600}FN_{450}$	1757	1940	1326	230	420	320	375
$PEG_{113}DVB_{1200}FN_{900}$	1074	3868	978	262	568	376	461

Table S4. Elemental analysis values found for each sample synthesised

Sample	% Carbon		% Hydrogen		% Nitrogen		% Sulfur	
	Theoretical	Found	Theoretical	Found	Theoretical	Found	Theoretical	Found
$PEG_{113}DVB_{150}FN_{113}$	78.01	80.74	5.66	6.88	14.68	7.31	0.08	0.79
$PEG_{113}DVB_{300}FN_{225}$	78.55	82.22	5.58	6.75	15.03	7.64	0.04	0.37
$PEG_{113}DVB_{600}FN_{450}$	78.84	85.18	5.53	7.11	15.20	4.94	0.02	0.26
$PEG_{113}DVB_{1200}FN_{900}$	78.98	83.82	5.51	6.87	15.29	6.83	0.01	0.45

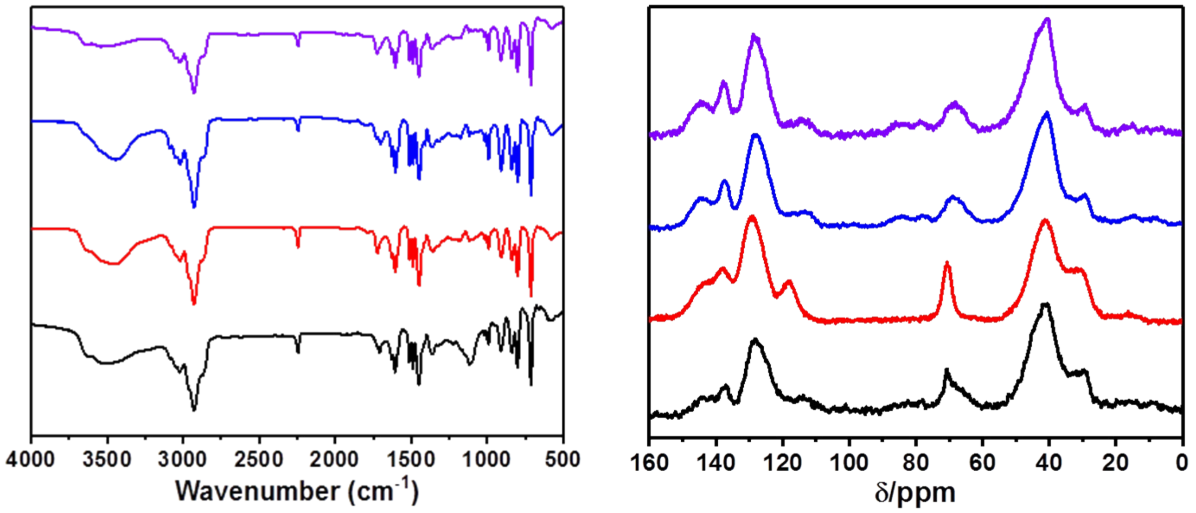


Figure S9. (Left) FTIR spectra and (Right) Solid state ^{13}C CP/MAS NMR of $PEG_{113}DVB_{150}FN_{113}$, $PEG_{113}DVB_{300}FN_{225}$, $PEG_{113}DVB_{600}FN_{450}$, and $PEG_{113}DVB_{1200}FN_{900}$

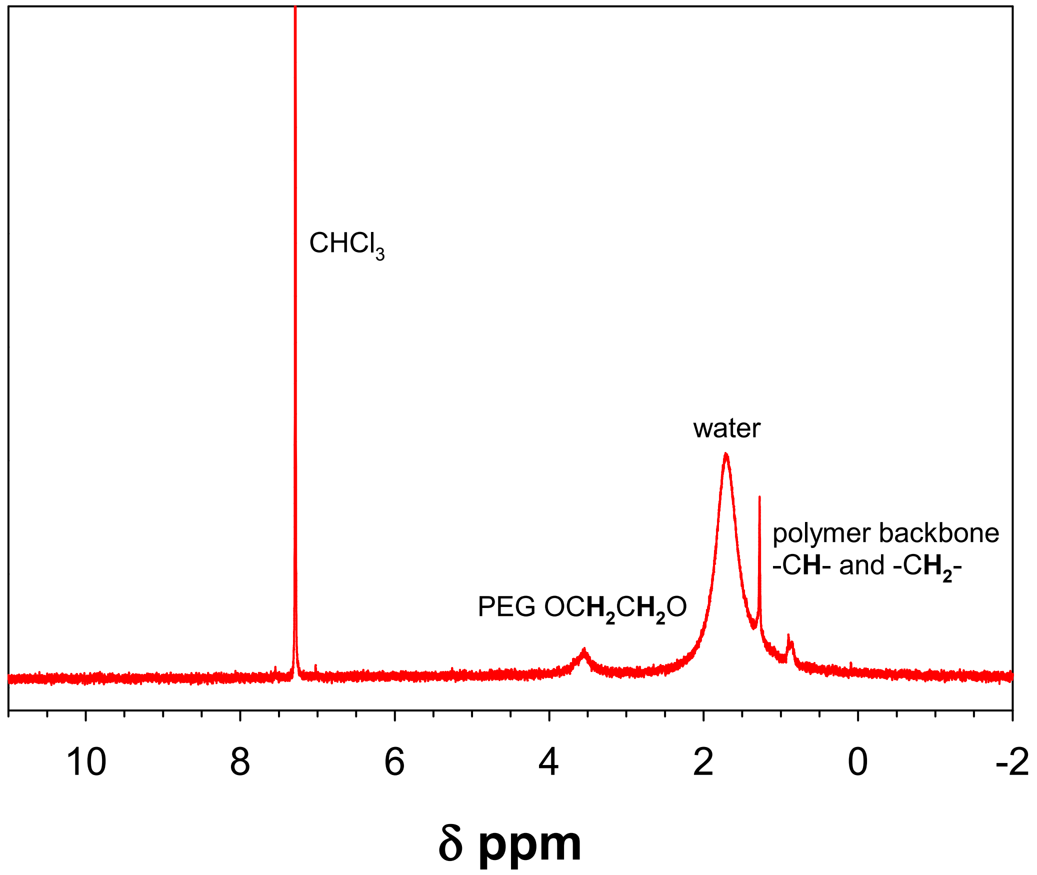


Figure S10. Solution phase ^{1}H-NMR of $PEG_{113}DVB_{300}FN_{225}$, in $CDCl_3$.

Table S5. Reported BET surface areas of other solution processable porous polymers published in the literature

Sample	**SA_{BET} (m^2/g)**	**REF**
$PEG_{113}DVB_{150}FN_{113}$	244	This work
$PEG_{113}DVB_{300}FN_{225}$	270	This work
$PEG_{113}DVB_{600}FN_{450}$	409	This work
$PEG_{113}DVB_{1200}FN_{900}$	400	This work
SHCP-3	158	7
SHCP-4	355	7
SHCP-5	530	7
SCMP-1	505	8
TPDC-BZ	610	9
PHCPN	133	10
CzBDP	180	11
Poly(DCDM)-395	646	12
xPCMS-g-PDMAEMA	562	13
xPCMS-g-PNIPAM	596	13

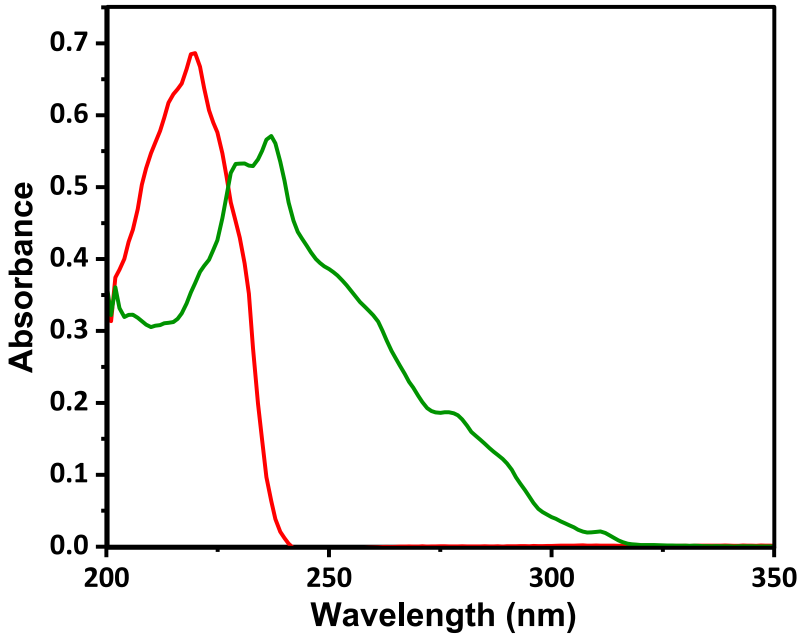


Figure S11. UV-Vis spectra of FN and DVB monomers in methanol

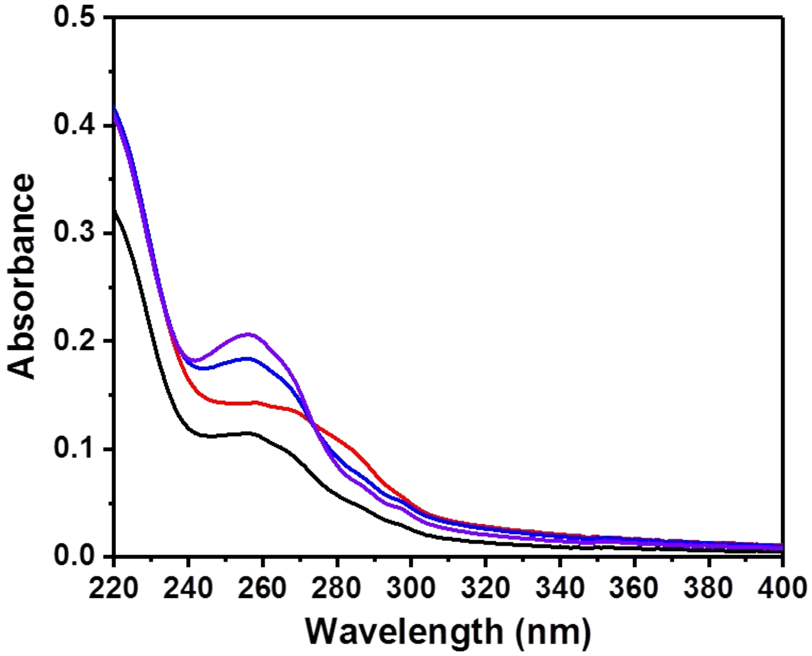


Figure S12. UV-Vis spectra of $PEG_{113}DVB_{150}FN_{113}$, $PEG_{113}DVB_{300}FN_{225}$, $PEG_{113}DVB_{600}FN_{450}$, and $PEG_{113}DVB_{1200}FN_{900}$in methanol

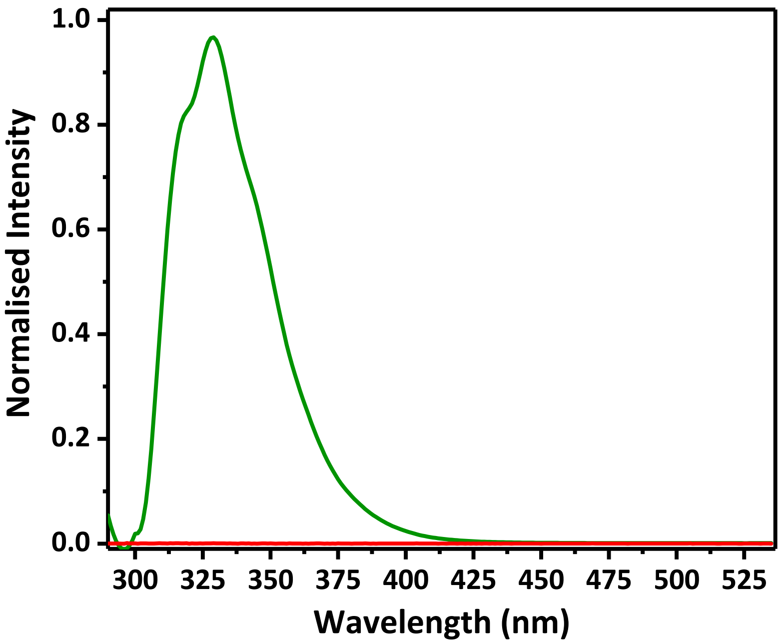


Figure S13. Normalised emission spectra of a methanol solution of FN (λ_{ex} = 220 nm) and DVB (λ_{ex} = 237 nm) monomer

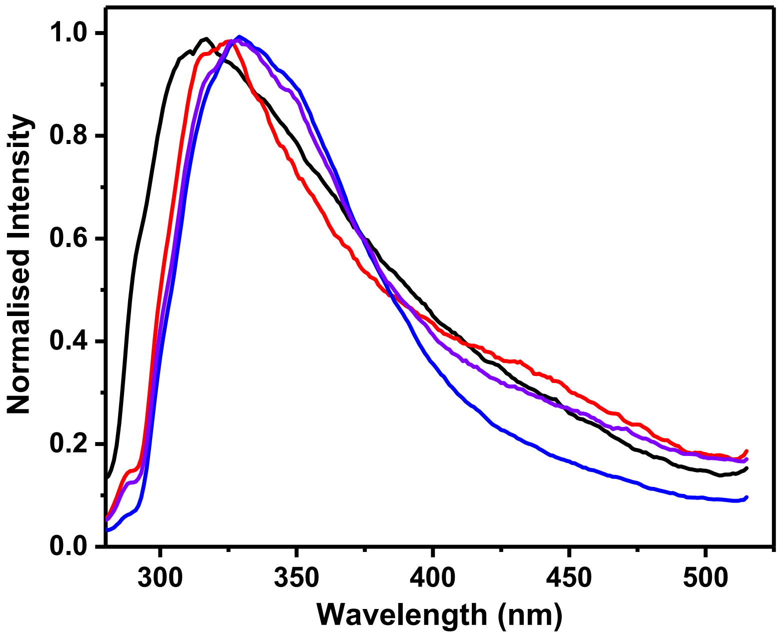


Figure S14. Normalised emission spectra (λ_{ex} = 260 nm) of $PEG_{113}DVB_{150}FN_{113}$, $PEG_{113}DVB_{300}FN_{225}$, $PEG_{113}DVB_{600}FN_{450}$, and $PEG_{113}DVB_{1200}FN_{900}$ in methanol

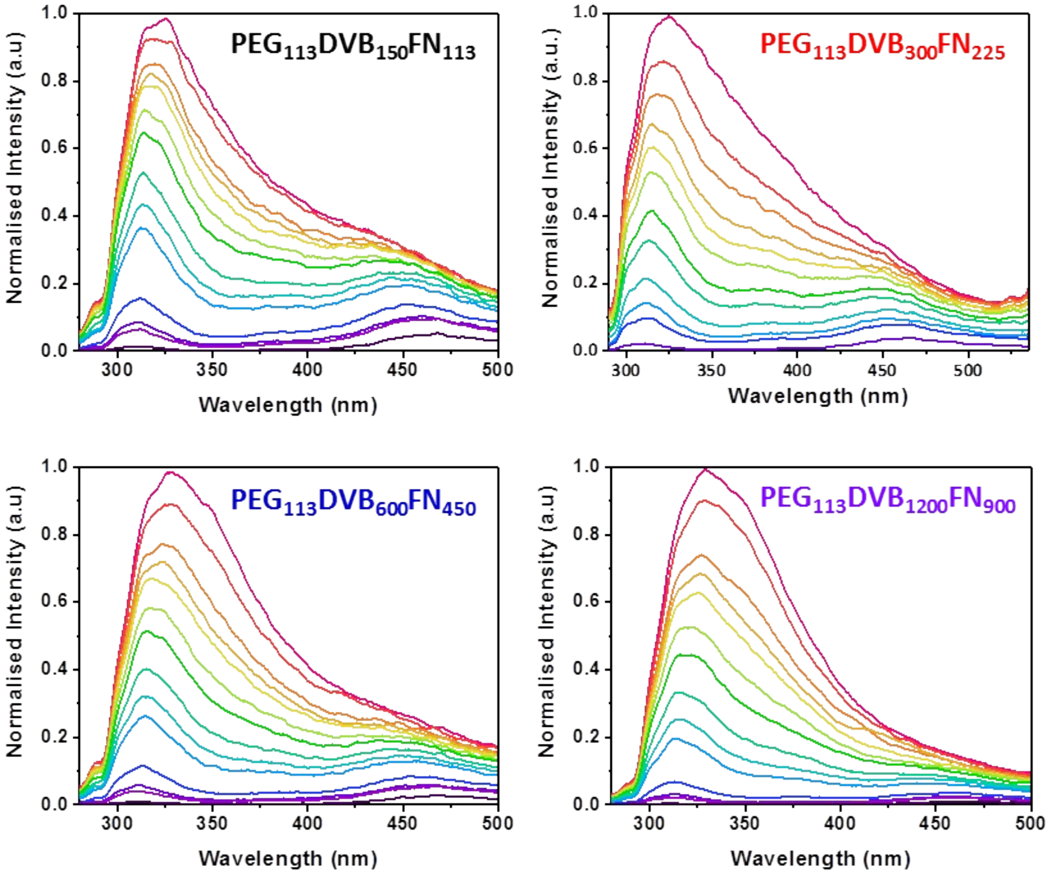


Figure S15. Normalised emission spectra (λ_{ex} = 260 nm, λ_{em} = 326) of $PEG_{113}DVB_{150}FN_{113}$, $PEG_{113}DVB_{300}FN_{225}$, $PEG_{113}DVB_{600}FN_{450}$, and $PEG_{113}DVB_{1200}FN_{900}$ upon addition of increasing amounts of picric acid in methanol

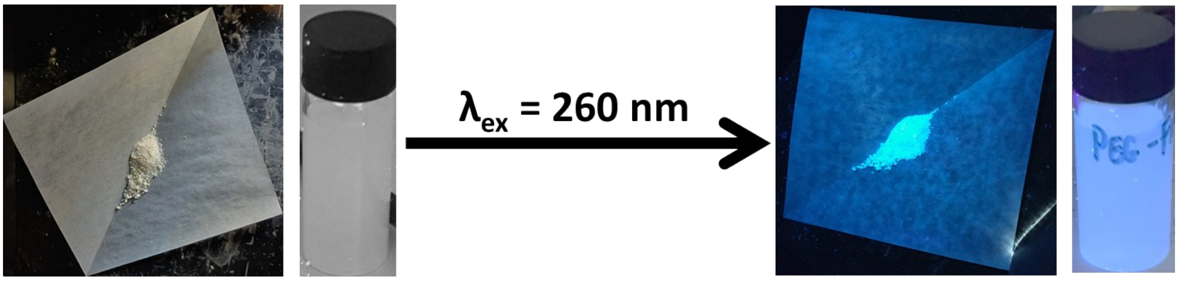


Figure S16. Imagine highlighting the fluorescence of the sample when exposed to UV light (λ_{ex} = 260 nm, λ_{em} = 326)

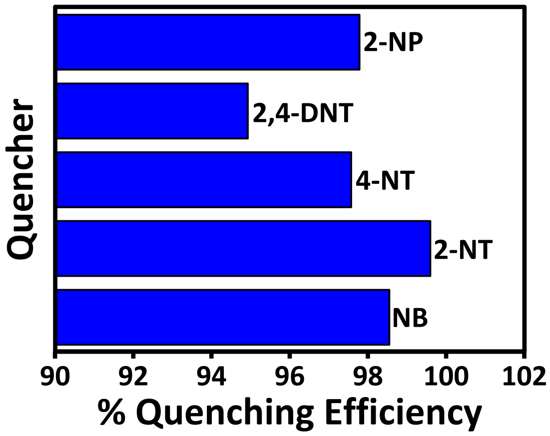


Figure S17. Quenching efficiency of $PEG_{113}DVB_{300}FN_{225}$ upon addition of 2-nitrophenol (2-NP, 52 ppm), 2,4-dinitrophenol (2,4-DNT, 68 ppm), 4-nitrotoluene (4-NT, 51 ppm), 2-nitrotoluene (2-NT, 39 ppm) and nitrobenzene (NB, 35 ppm)

Table S6. % Quenching upon addition of 38 ppm of picric acid to a 0.1 mg/mL solution of sample in methanol

Sample	Amount added	% Quenching
$PEG_{113}DVB_{150}FN_{113}$	38 ppm	> 99
$PEG_{113}DVB_{300}FN_{225}$	38 ppm	> 99
$PEG_{113}DVB_{600}FN_{450}$	38 ppm	> 99
$PEG_{113}DVB_{1200}FN_{900}$	38 ppm	> 99

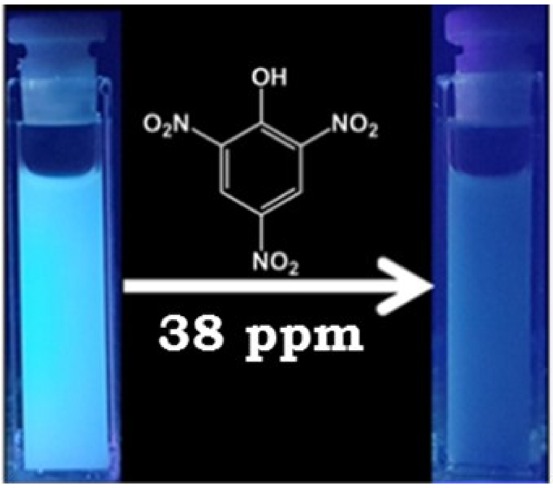


Figure S18. Fluorescence quenching of $PEG_{113}DVB_{300}FN_{225}$ upon addition of 38 ppm of picric acid demonstrating the efficacy of the sample to act as a chemosensor towards picric acid.

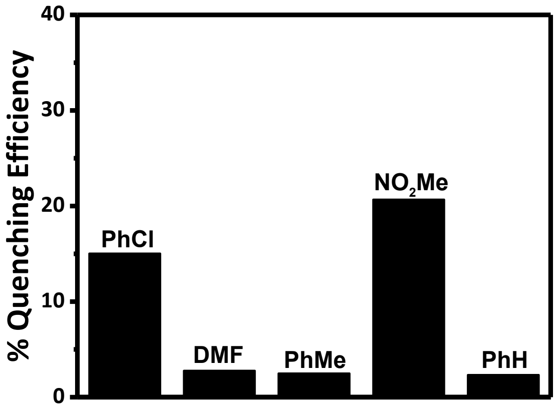


Figure S19. Quenching efficiency of $PEG_{113}DVB_{300}FN_{225}$ upon addition of chlorobenzene (PhCl, 42 ppm), N,N'-dimethylformamide (DMF, 27 ppm), toluene (PhMe, 42 ppm), nitromethane (NO_2Me, 23 ppm) and benzene (PhH, 30 ppm)

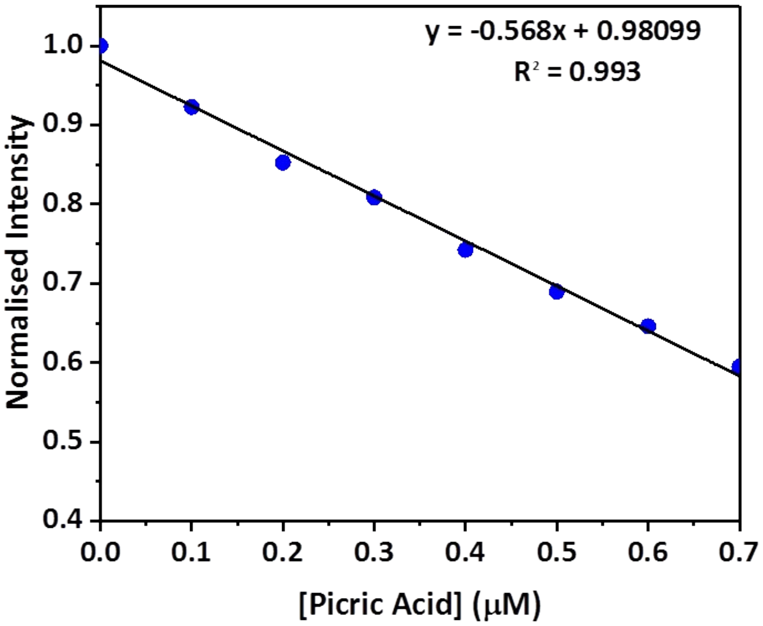


Figure S20 Fluorescence intensity of $PEG_{113}DVB_{300}FN_{225}$ upon excitation at 275 nm as a function of picric acid concentration over a low concentration range. Top right of the image shows the linear fit equation along with the R^2 value. Standard deviation was found to be 0.13966

The limit of detection (LoD) for the system was derived using the following equation:

$$LoD = {}^{3\ x\ \sigma}/_{K}$$

Where, σ is the standard deviation of the intensity and K is the slope of the graph.

Hence, for picric acid, the LoD is:

$$LoD = {}^{3\ x\ 0.10907}/_{0.568}$$

$$LoD = 0.73\ uM = 169\ ppb$$

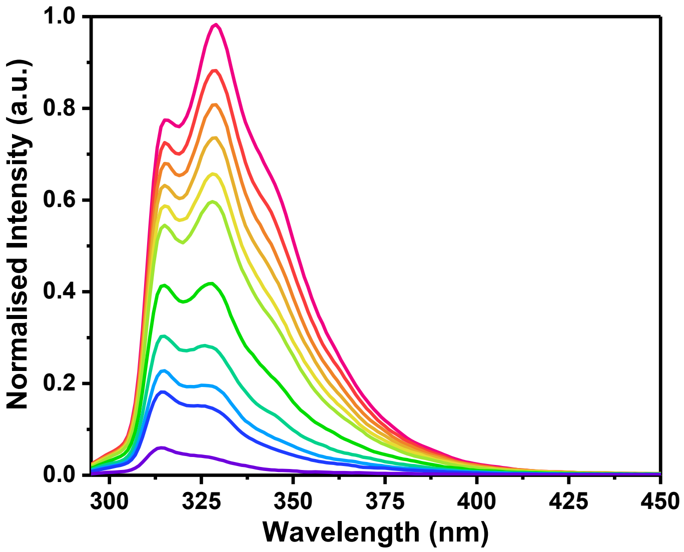


Figure S21. Fluorescence quenching of DVB monomer in methanol solution when exposed to increasing amounts of picric acid

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