Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for
Defect-controlled softness, diffusive permeability, and mesh-topology of metallo-supramolecular hydrogels

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Materials

Four-arm hydroxy-terminated poly(ethylene glycol) (pEG), M_w = 20 kg mol^{-1}, further denoted as 4-arm 20K, and 8-arm hydroxy-terminated pEG, M_w = 40 kg mol^{-1}, denoted as 8-arm 40K, were purchased from Creative PEG Works (NC, USA), and re-precipitated in cold diethyl ether before further use. Potassium hydroxide (KOH) flakes (90%) and 4'-Chloro-2,2':6',2''-terpyridine (99%) were purchased from Sigma Aldrich. Extra dry dimethyl sulfoxide (DMSO, + 99.7% over molecular sieve) is purchased from Acros Organics. Sodium chloride (NaCl, ≥ 99.5%), dichloromethane (DCM, ≥ 99.8%), and diethyl ether (≥ 99.5%) were purchased from Fisher Scientific. Zinc nitrate hexahydra-te (98%) is purchased from Alfa Aesar.

Syntheses

Terpyridine-functionalized 4-arm and 8-arm polymer precursors.

The hydroxyl termini of the star-shaped pEG polymers were converted to terpyridine units by the following Williamson type ether synthesis (**SI1**).

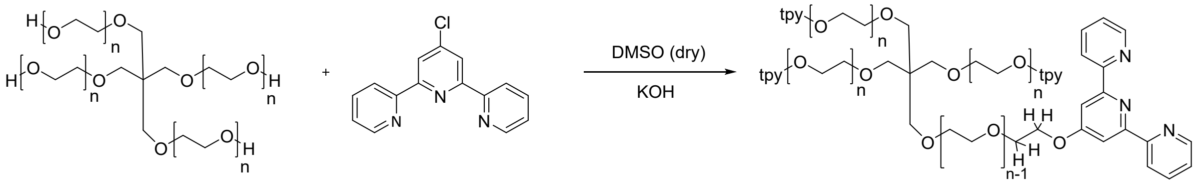

Figure SI1. Reaction route for the synthesis of tetra-arm pEG-terpyridine. The functionalization of 8-arm pEG-terpyridine is analogous.

Before use, the pEG was purified and therefore melted at 60 °C, cooled to 40 °C, dissolved in DCM, precipitated in diethyl ether, and dried under vacuum. KOH (0.056 g, $1 \cdot 10^{-3}$ mol, 20 eq.) was dried in a flask for 1 h under reduced pressure, and dry DMSO (20 mL) was added in inert N2-atmosphere. To this suspension, 4-arm pEG (M_w = 20 kg mol^{-1}, 1 g, $5 \cdot 10^{-5}$ mol, 1 eq.) was added. The reaction mixture was stirred under nitrogen counter flow at 60 °C for 1 h. Afterwards, 4'-Chloro-2,2':6',2''-terpyridine (0.1340 g, $5 \cdot 10^{-4}$ mol, 10 eq.) was added, and the reaction was stirred at 60 °C for another 48 h. After cooling to room temperature, the reaction mixture was add-ed dropwise to cold water (200 mL) and a small amount of white precipitate was filtered off. To the liquid phase, brine (200 mL) was added, and the aqueous solution was washed three times with DCM (200 mL). The organic phases were collected, dried with sodium sulphate, and concentrated under vacuum. Afterwards, the polymer was precipitated in ice-cold diethyl ether (500 mL). The white powder was collected and dried under vacuum overnight. The same reaction conditions were applied to functionalize the 8-arm 40K pEG-OH, but the reaction was performed twice to achieve a high degree of terpyridine functionalization. The degree of functionalization of terpyridine was quantified by NMR and was found to be 95% (4-arm 20K) and 90% (8-arm 40K), respectively (**SI2-SI3**).

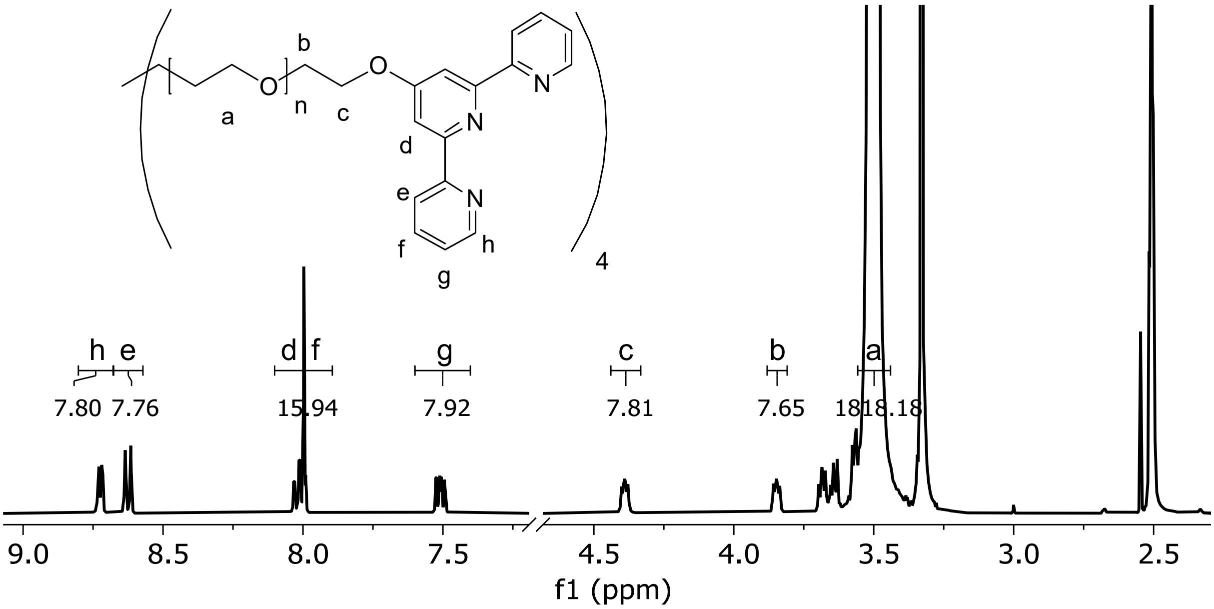

Figure SI2. ^{1}H-NMR of the 4-arm pEG-terpyridine (20K) in DMSO.

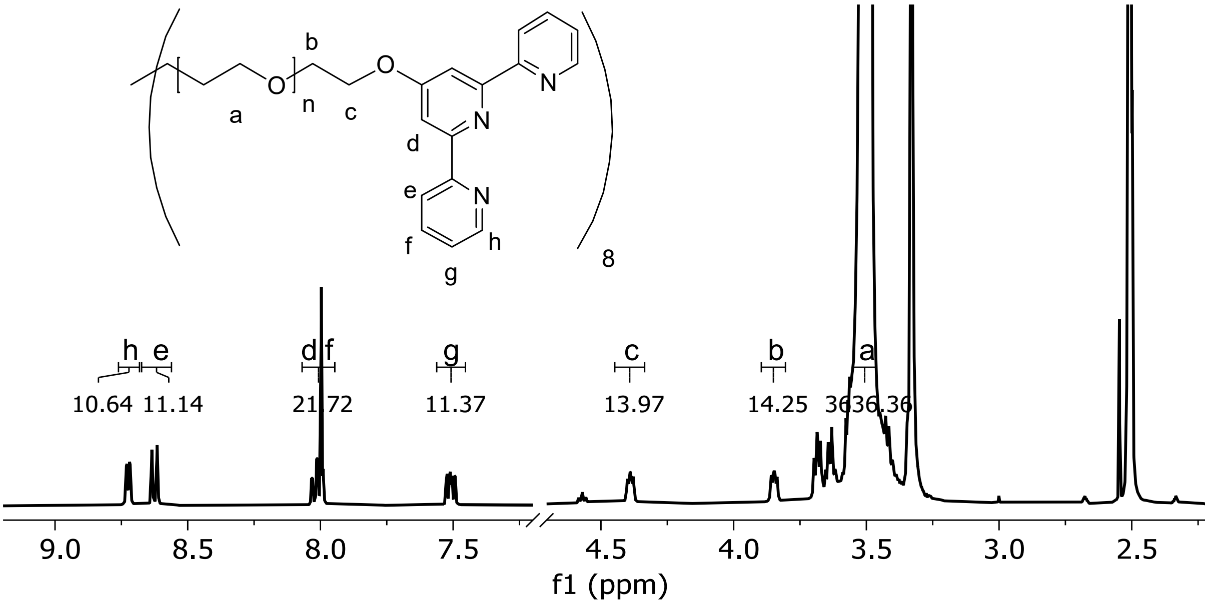

Figure SI3. ^{1}H-NMR of the 8-arm pEG-terpyridine (40K) in DMSO.

Fluorescence-labelled polymer tracer for FRAP measurements.

To measure polymer self-diffusion coefficients by FRAP experiments, a fluorescently active dye molecule has to be attached to the polymer building blocks of interest. In addition to that, it is of major importance that the dye-labelled 4-arm polymers quantitatively contain terpyridine end-groups on each arm. These polymer tracers were synthesized according to a previously described procedure [1] and are visualized in **SI4**. In summary, hydroxy-terminated tetra-arm pEG-OH with a molar mass of 20 kg mol^{-1} was reacted with epicholorhydrin to obtain epoxy-terminated polymers. The subsequent ring-opening with sodium azide yielded in hydroxyl-azide-pEG that further reacted with propargyl-terpyridine in a copper-free Huisgen click reaction. The remaining hydroxyl groups were activated via reaction with p-nitrophenylchloroformate and through addition of (S)-(+)-4-(3-aminopyrrolidino)-7-nitrobenzofurazan (NBD), the final fluorescence-labelled tracer polymers were obtained. Un-reacted excess dye was removed via size exclusion chromatography in methanol using a Sephadex$^{\text{TM}}$ LH-20 column. The degree of terpyridine functionalization was determined by NMR to be 89% (**SI5**).

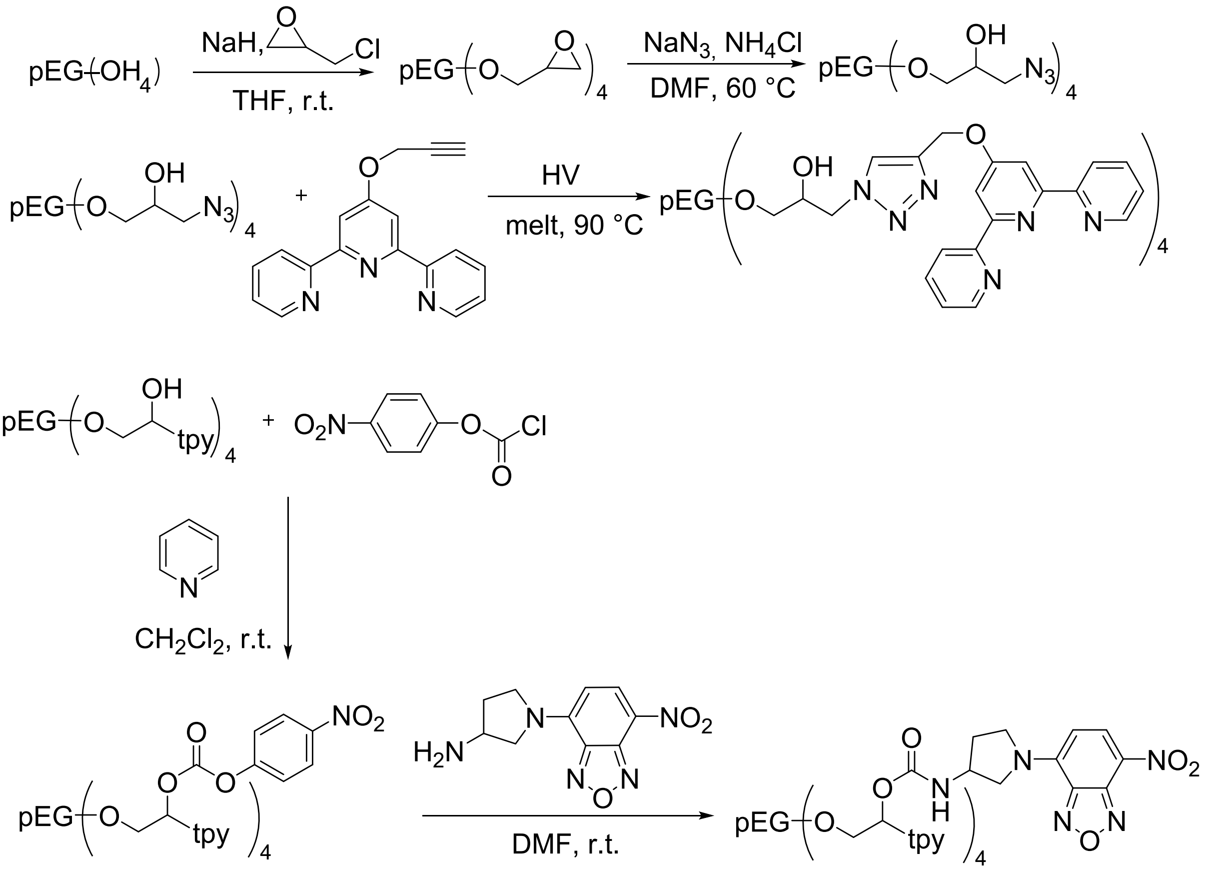

Figure SI4. Reaction route for the dye-labelled tetra-arm pEG-terpyridine (20K) tracer molecules.

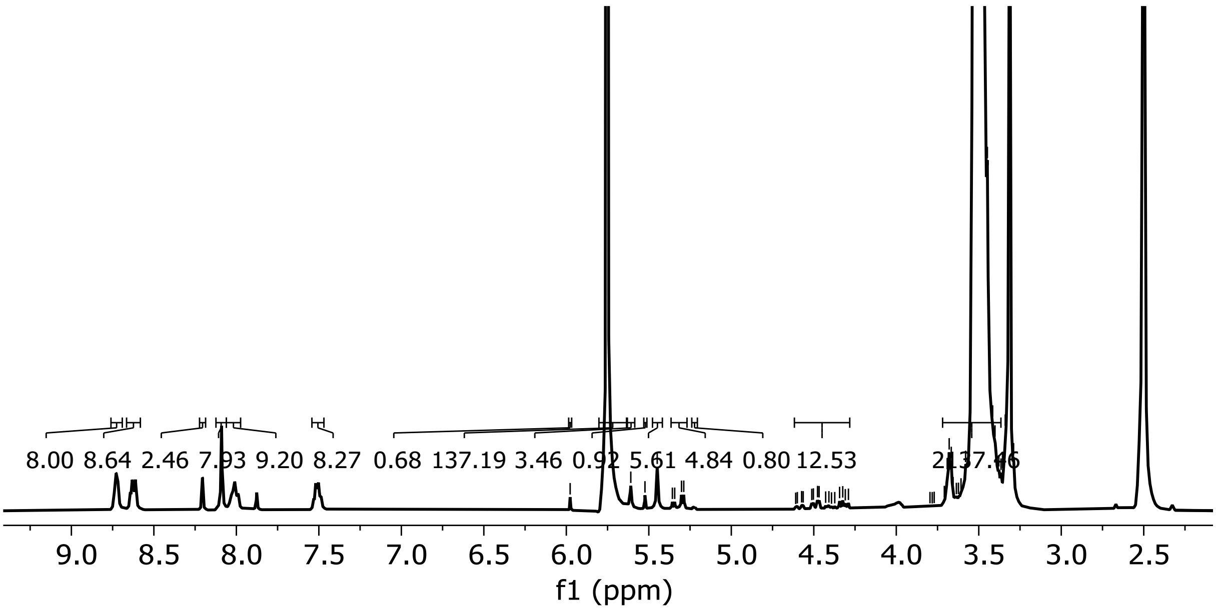

Figure SI5. ^{1}H-NMR of the 4-arm pEG-terpyridine (20K) tracer molecules in DMSO.

References

[1] S. Tang, A. Habicht, S. Li, S. Seiffert and B. D. Olsen, Macromolecules, 2016, 49, 5599–5608.