Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Nanoparticles decorated with folate based on a site-selective αCD-rotaxanated PEG-b-PCL copolymer for targeted cancer therapy

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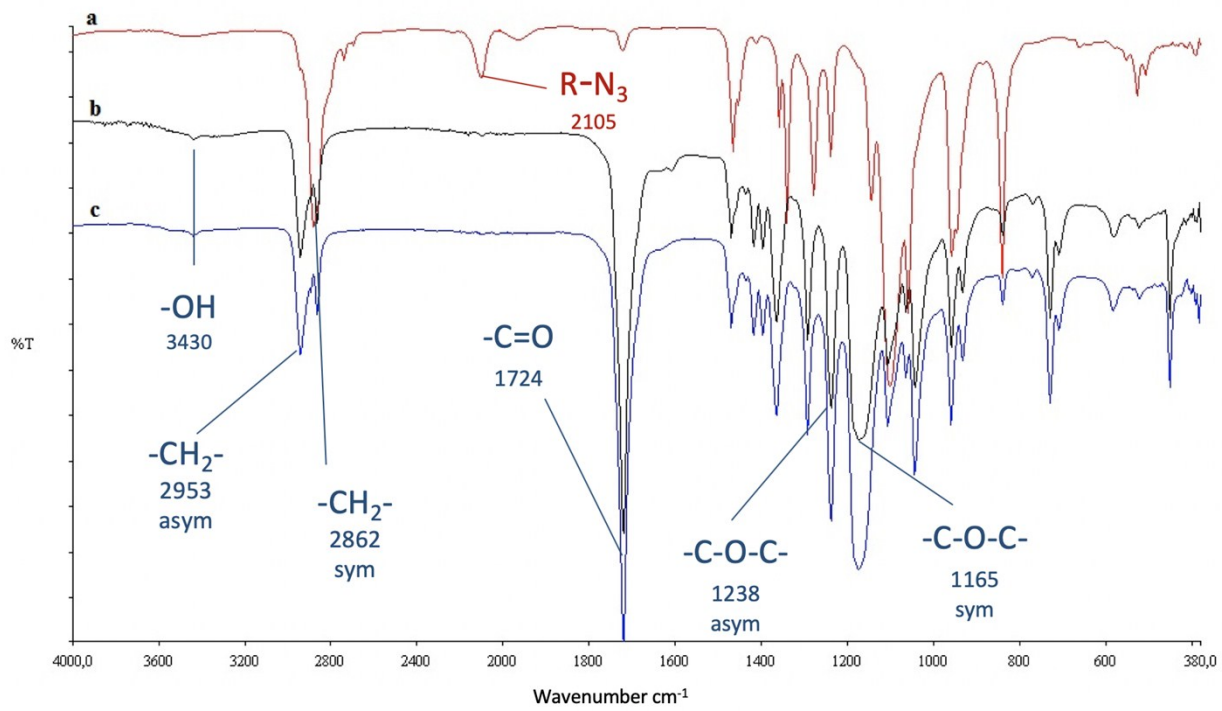


Figure S1. FTIR spectra of (a) TsO-PEG$_{1.5k}$-N$_3$, (b) R1, and (c) R2 with the assignment of diagnostic peaks. The spectra evidence the complete disappearance of the peak at 2105 cm^{-1}, corresponding to specific vibration of the azide group, in R1 and R2.

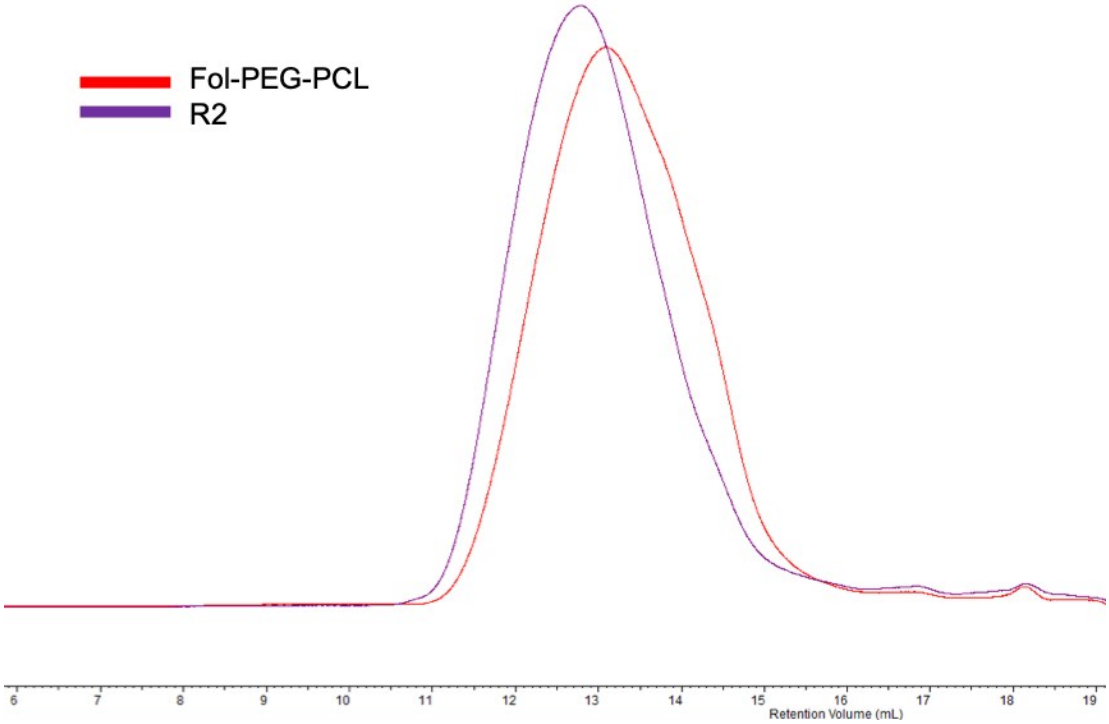
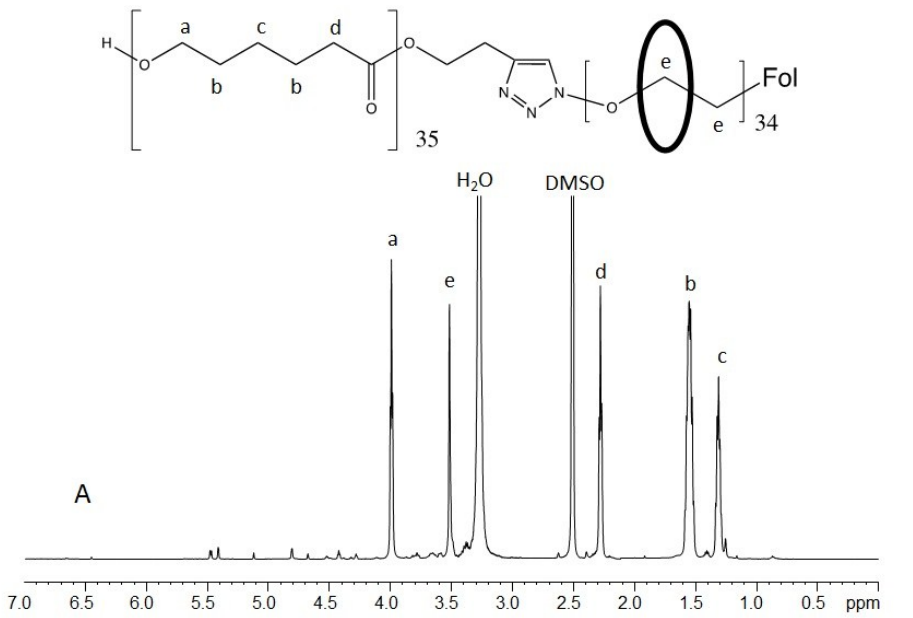


Figure S2. GPC curves (refractive index vs. retention volume, mL) of Fol-PEG$_{1k}$-PCL$_{4k}$ and R2. The mobile phase was THF.



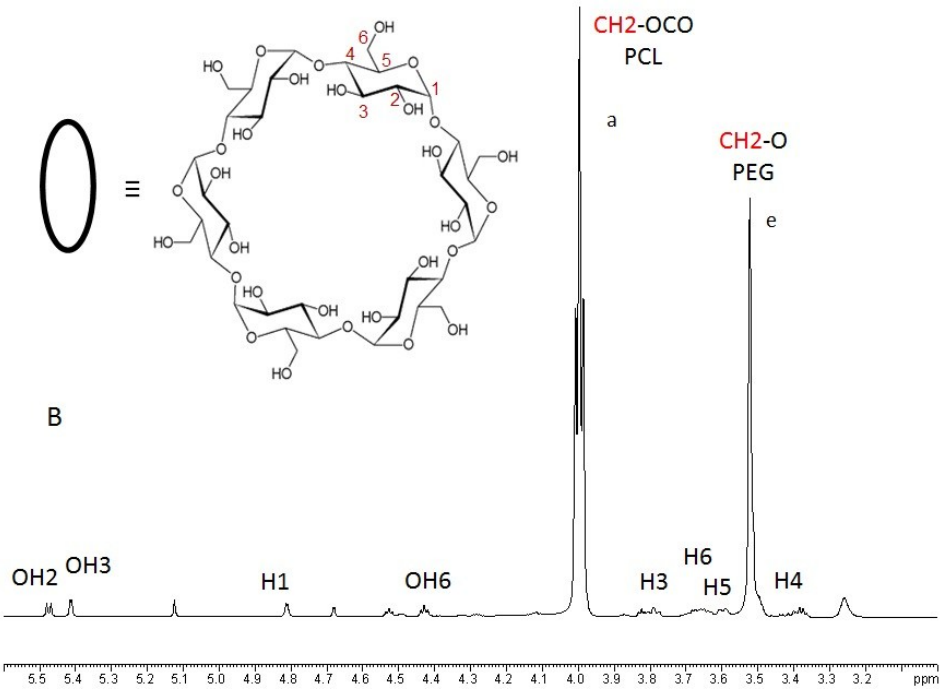


Figure S3. A. ^{1}H NMR spectrum of R1 in d6-DMSO with the designation of polymer peaks. B. ^{1}H NMR spectrum of R1 in d6-DMSO with the designation of αCD peaks. The sugar ring positions are numbered on one unit of the αCD chemical structure reported in the figure.

TGA analysis

The thermal stability of pure copolymer and rotaxanes was investigated by TGA. Increase in thermal stability is a striking feature for the formation of PEG-αCD inclusion complex. The thermogravimetric curve of Fol-$PEG_{1.5k}$-b-PCL_{4k} (Figure S4) follows a two-step decomposition process which starts around 250°C. According to literature,[1] PEG starts to degrade above 280°C, which corresponds to the second stage in the curve of Fol-$PEG_{1.5k}$-b-$PCL_{4k.}$, whereas the first stage is relative to PCL degradation.[2] The profile of both rotaxanes shows a one stage thermal decomposition starting around 290°C for R2 and above 300°C for R1. The higher incipit of degradation of R1 with respect to R2 was attributed to the crystalline organisation of threaded αCDs in the channel-like structure, as assessed by WAXD analysis, which further contributes to increasing the thermal stability.

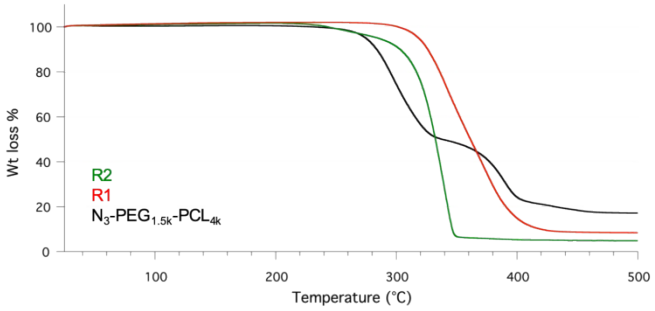
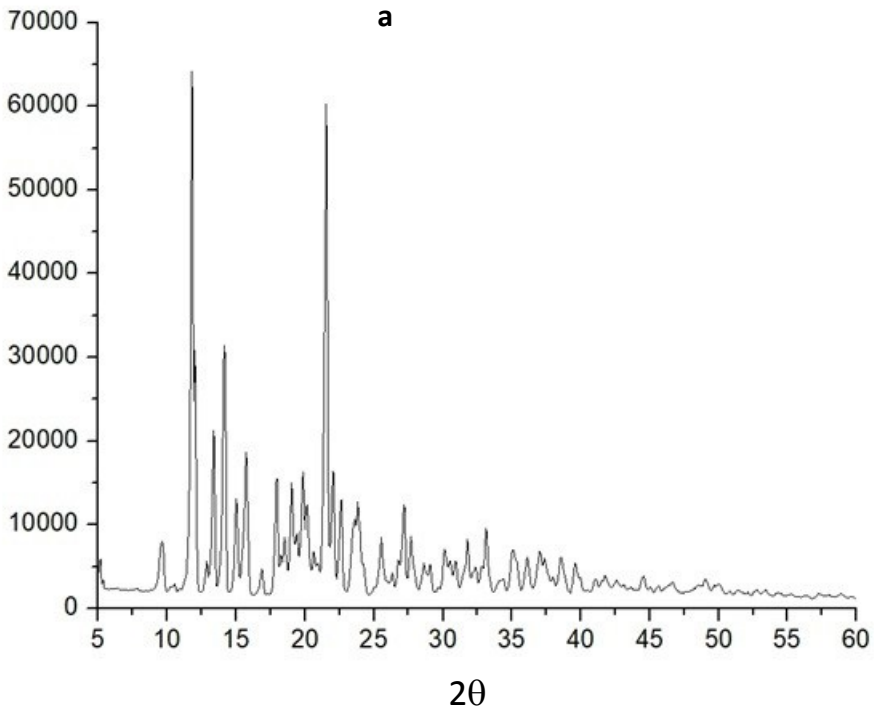


Figure S4. TGA curves of Fol-$PEG_{1.5k}$-b-PCL_{4k} and rotaxanated copolymers.

References

1. X. Du, H. Wang, X. Cheng, Z. Du, *RSC Adv.* 2016, **6,** 42643.
2. O. Persnaire, M. Alexandre, P. Degèe, P. Dubois, *Biomacromolecules*, 2001, **2**, 288.



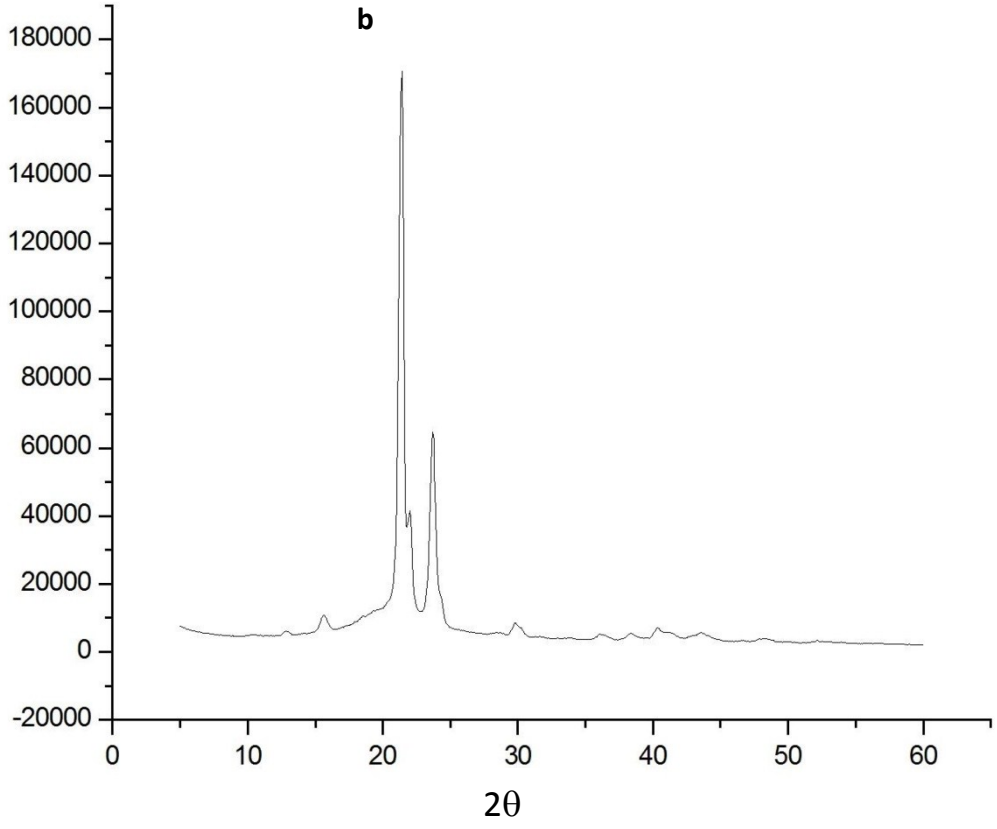


Figure S5. XRD diffractogram of αCD (a) and butynyl-PCL_{4k} (b)

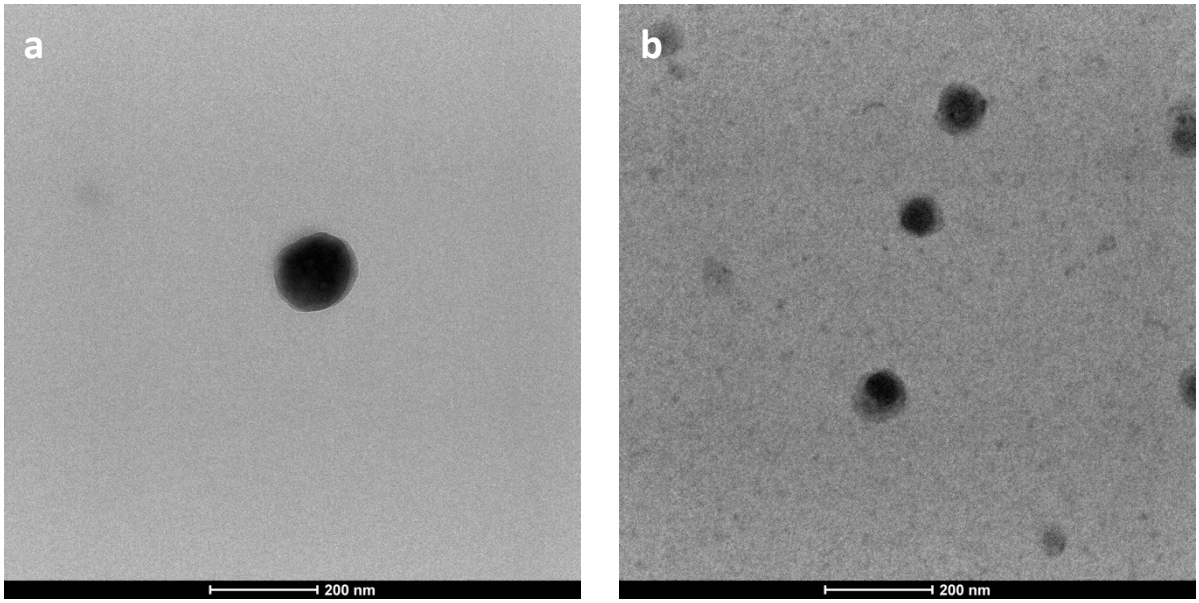


Figure S 6. Representative TEM micrographs of Fol-NPs 20% (a) and R1-NPs 20% (b)

Table S1. Properties of Nile-Red loaded NPs. Nile Red actual loading was determined by dissolving 1 mg of NPs in 1 mL of THF/DMSO solution 1/1 and the samples analyzed by fluorescence, against a calibration curve of Nile Red prepared in the same solvents.

Formulation code	D_H (nm)	P.I.	ζ (mV)	Nile Red Actual loading (mg NR/100 mg NPs)
ntNPs	96.6	0.1	-14.3	0.78
Fol-NPs 10%	124.2	0.2	-25.3	0.65
Fol-NPs 20%	129.7	0.2	-22.4	0.72
R1-NPs 10%	146.3	0.2	-28.9	0.80
R1-NPs 20%	149.5	0.2	-27.1	0.79

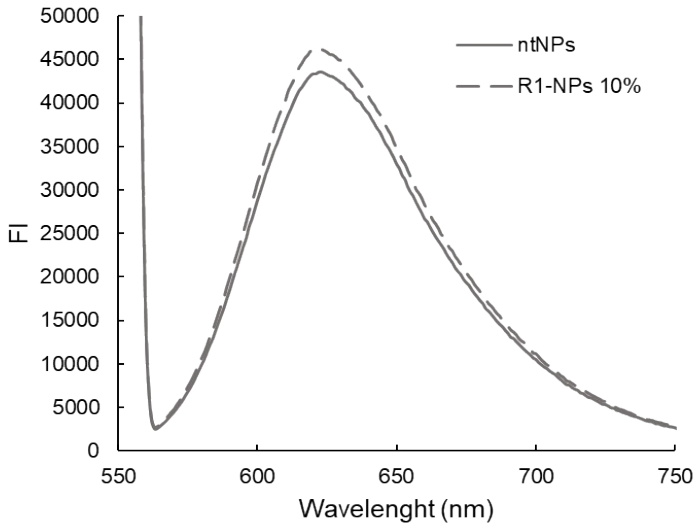


Figure S7. Fluorescence emission spectra (λ_{ex} 552 nm) of ntNPs and R1-NPs 10% loaded with Nile Red.