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Supporting Information

Fluorescent block copolymer micelles that can self-report on their assembly and small molecule encapsulation

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SUPPLEMENTARY TABLES

Table S1. Composition of solutions for FRET experiments shown in Figure 8.

Figure 8a	5	NR	H ₂ O	1,4-dioxane	Time after mixing
CLMs (t = 0)	82.8 µg, 2.5 nmol	-	2.5 ml	- ^a	-
CLMs + NR (t = 1)	82.8 µg, 2.5 nmol	80 ng, 0.25 nmol	2.5 ml	2.5 µl	1 min
CLMs + NR (t = 60)	82.8 µg, 2.5 nmol	80 ng, 0.25 nmol	2.5 ml	2.5 µl	60 min
NR	-	80 ng, 0.25 nmol	2.5 ml	2.5 µl	-
Figure 8c	3	NR	H ₂ O	1,4-dioxane	Time after mixing
NLMs (t = 0)	79.9 µg, 2.5 nmol	-	2.5 ml	-	-
NLMs + NR (t = 1)	79.9 µg, 2.5 nmol	80 ng, 0.25 nmol	2.5 ml	2.5 µl	1 min
NLMs + NR (t = 60)	79.9 µg, 2.5 nmol	80 ng, 0.25 nmol	2.5 ml	2.5 µl	60 min
NR	-	80 ng, 0.25 nmol	2.5 ml	2.5 µl	-
Figure 8d	5	RhB	H ₂ O	Time after mixing	
CLMs (t = 0)	82.8 µg, 2.5 nmol	-	2.5 ml	-	
CLMs + RhB (t = 1)	82.8 µg, 2.5 nmol	120 ng, 0.25 nmol	2.5 ml	1 min	
CLMs + RhB (t = 60)	82.8 µg, 2.5 nmol	120 ng, 0.25 nmol	2.5 ml	60 min	
RhB	-	120 ng, 0.25 nmol	2.5 ml	-	

^a The addition of 2.5 µl of 1,4-dioxane to CLMs was found to have no effect on the emission spectrum (see Figure S10).

SUPPLEMENTARY FIGURES

Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of P(*t*BA) (**1**). Integration of H1 was set to be equal to 3.00.

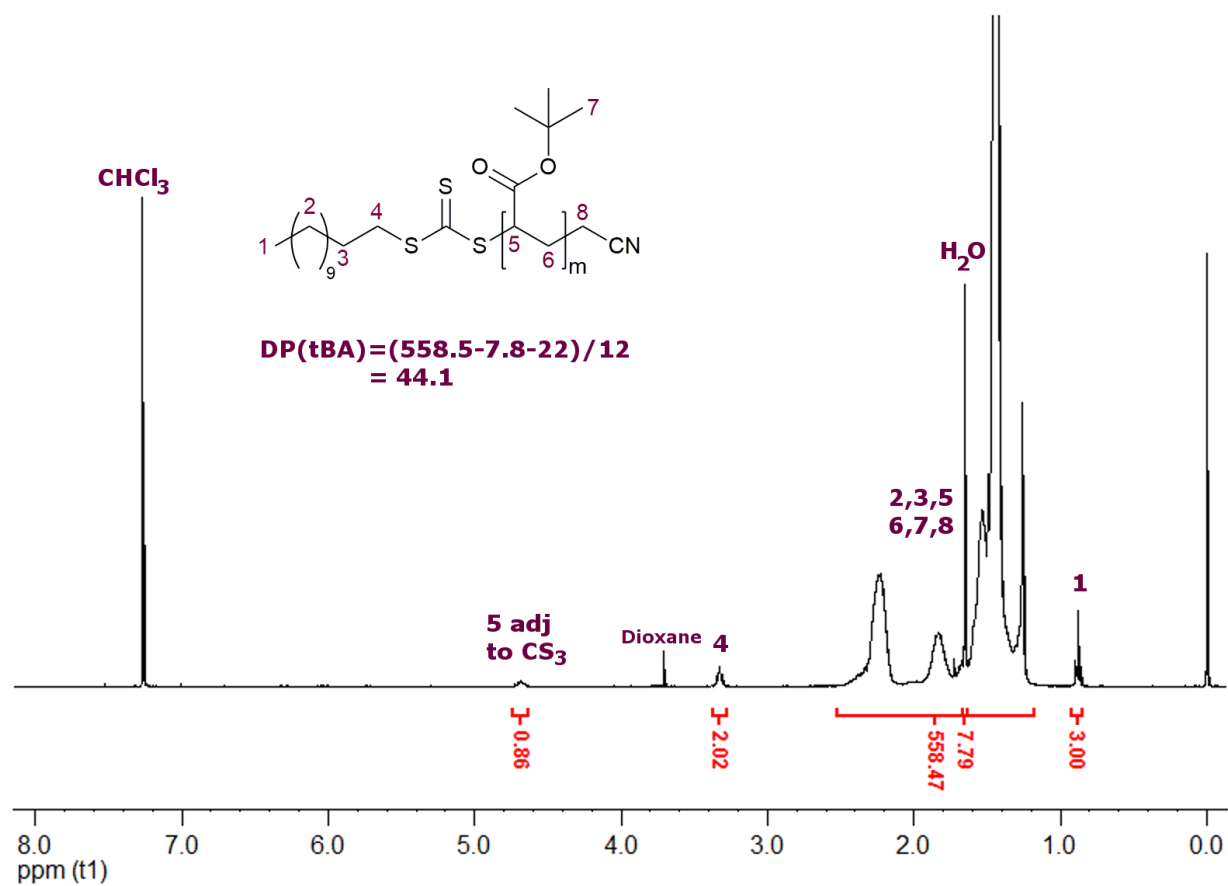


Figure S2. ^1H NMR spectrum (400 MHz, CDCl_3) of $\text{P}(t\text{BA-co-DTMA})$ (**2**). Integration of H1 was set to be equal to 3.00.

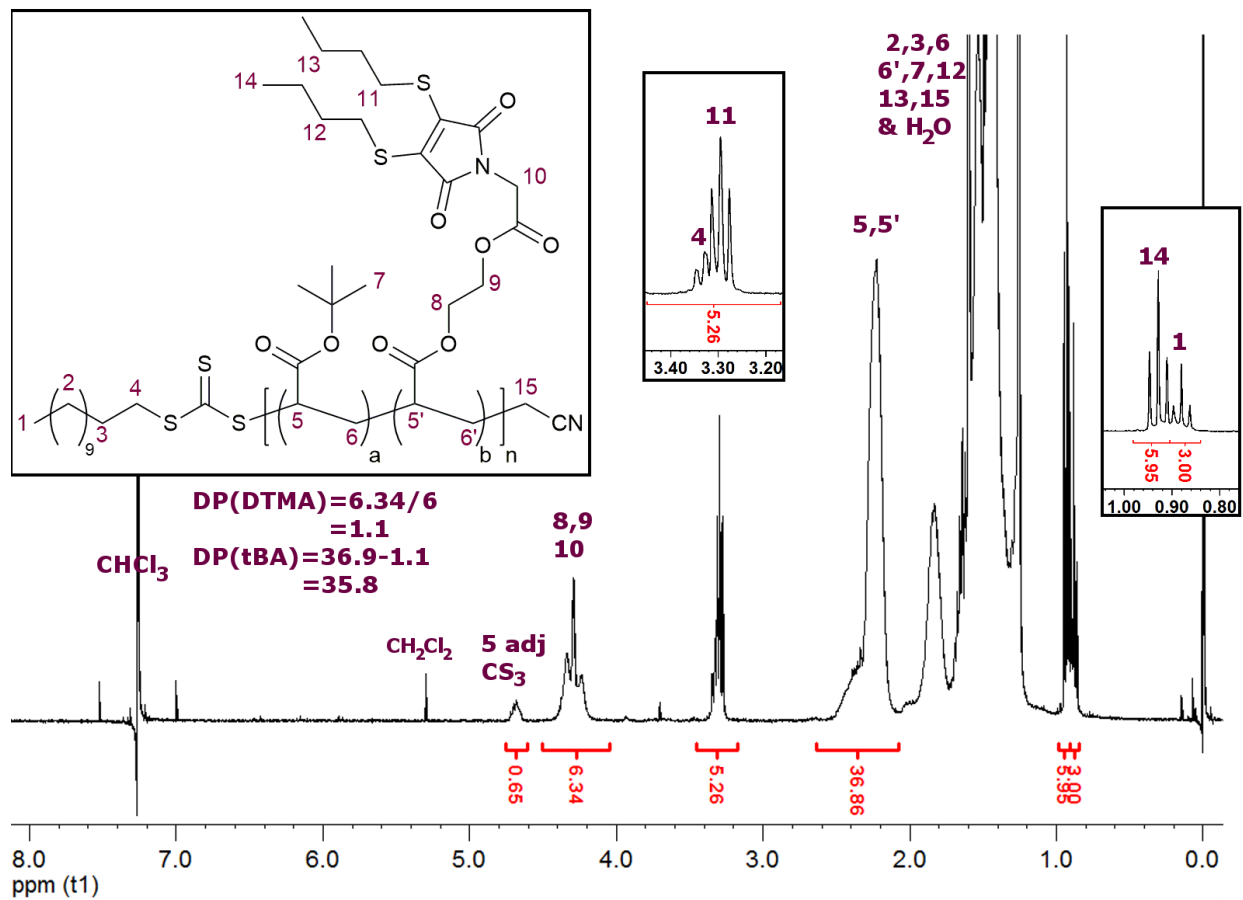


Figure S3. Three-dimensional chromatogram of **2** obtained by SEC using a PDA detector and THF as eluent.

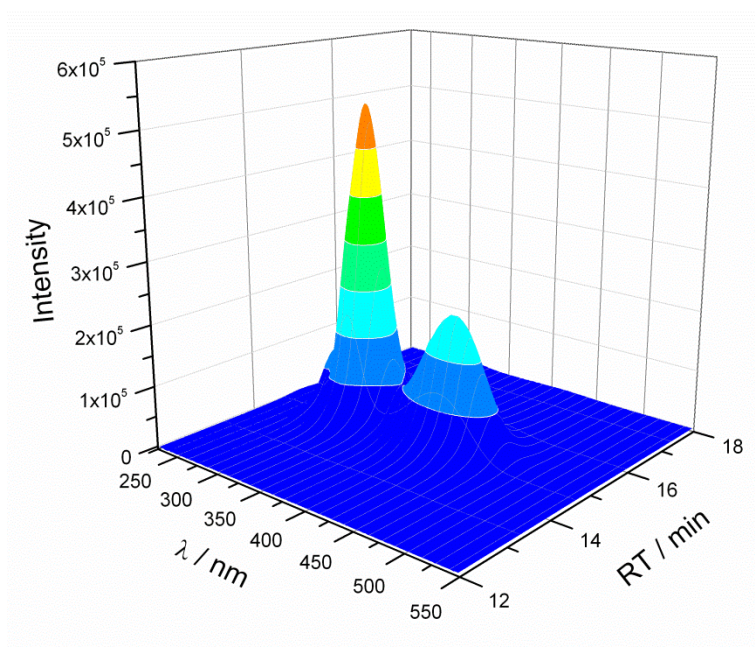


Figure S4. ^1H NMR spectrum (400 MHz, CDCl_3) of P(TEGA)-*b*-P(*t*BA) (**3**). Combined integration of H2,3,5,5',6,6',12,13 was set to be equal to the combined integration of H4&11 + (558.5-7.8-2).

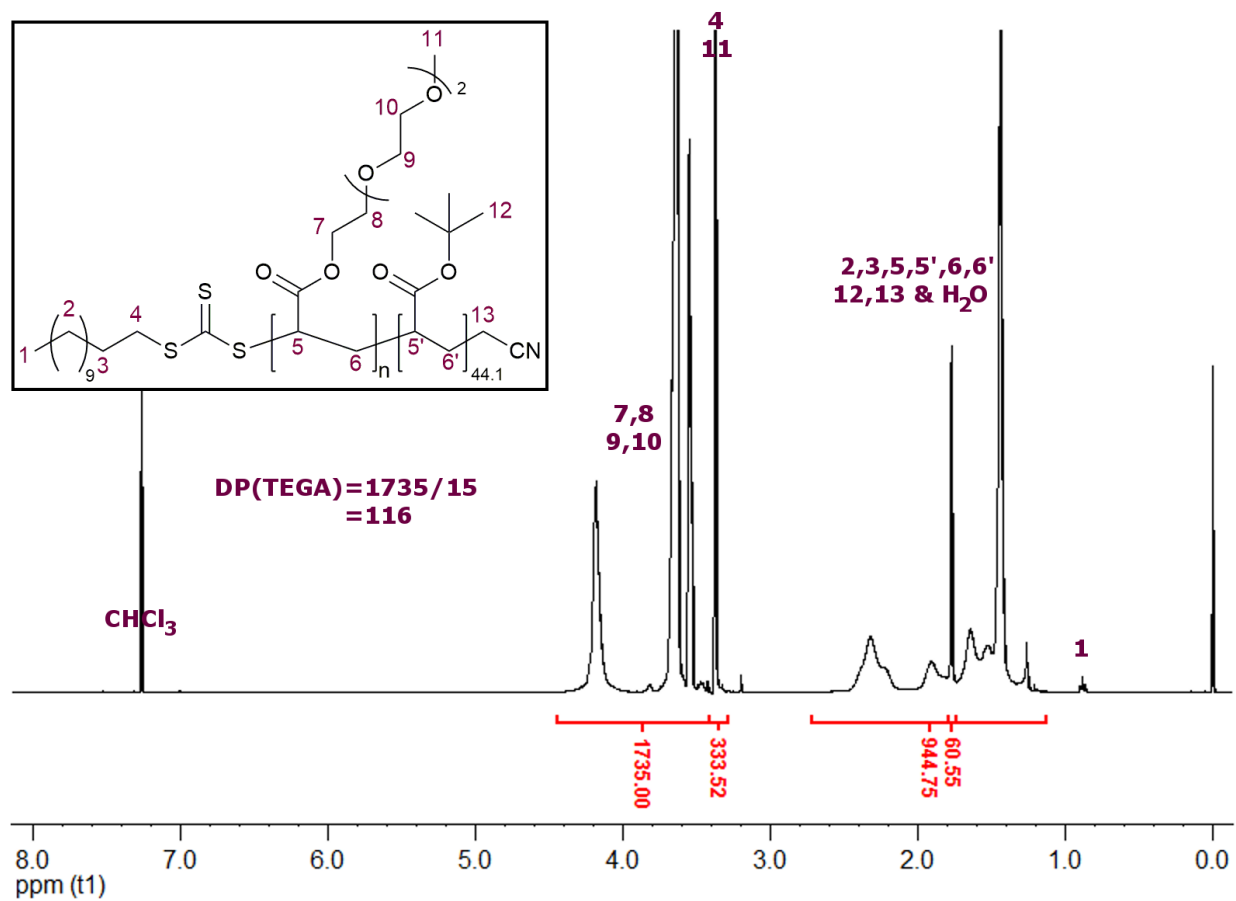


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3) of $\text{P}(\text{TEGA-co-DTMA})\text{-}b\text{-P}(t\text{BA})$ (**4**).

Integration of H1 was set to be equal to 3.00.

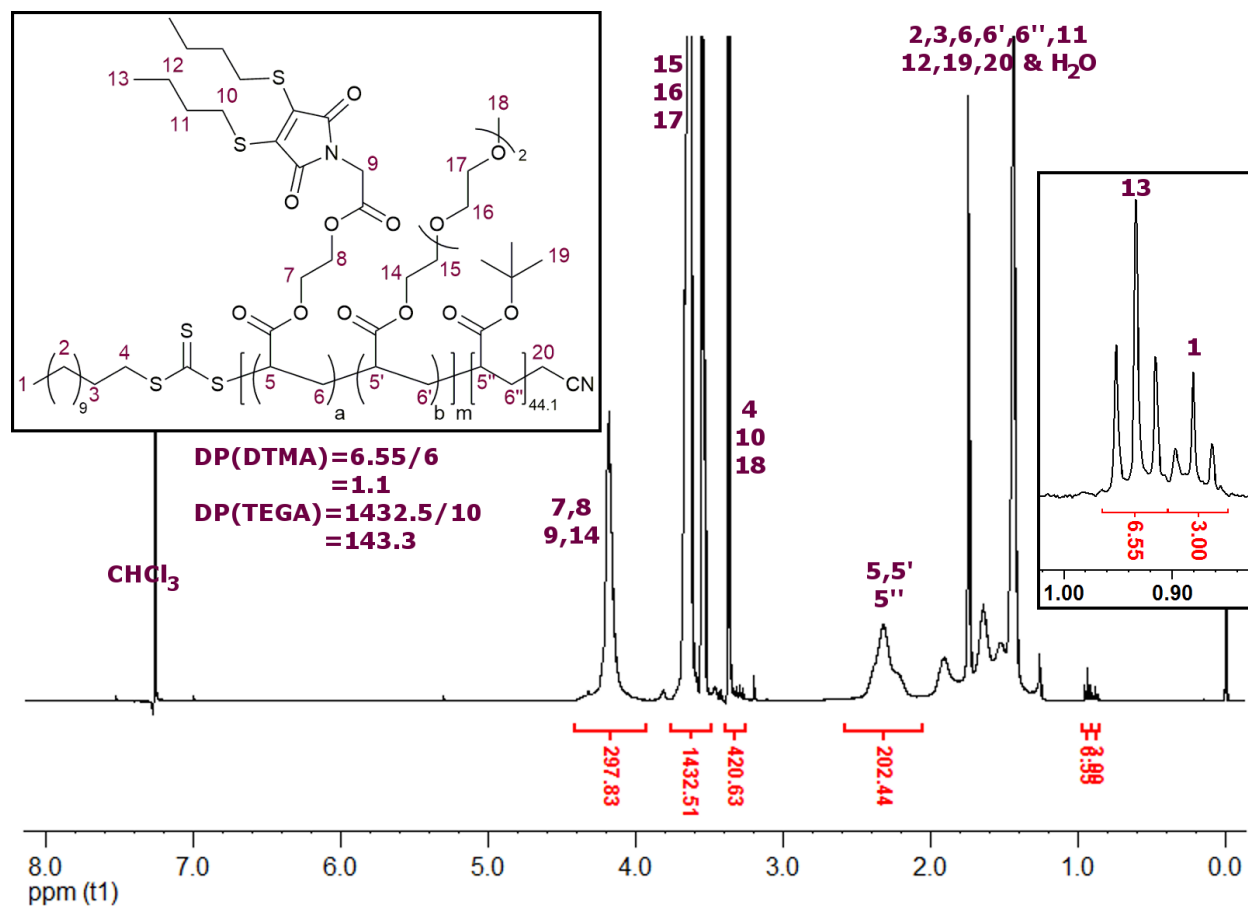


Figure S6. ^1H NMR spectrum (400 MHz, CDCl_3) of $\text{P}(\text{TEGA-co-DTMA})\text{-}b\text{-P}(t\text{BA})$ (**5**).
 Combined integration of H1&H4 was set to be equal to 8.95.

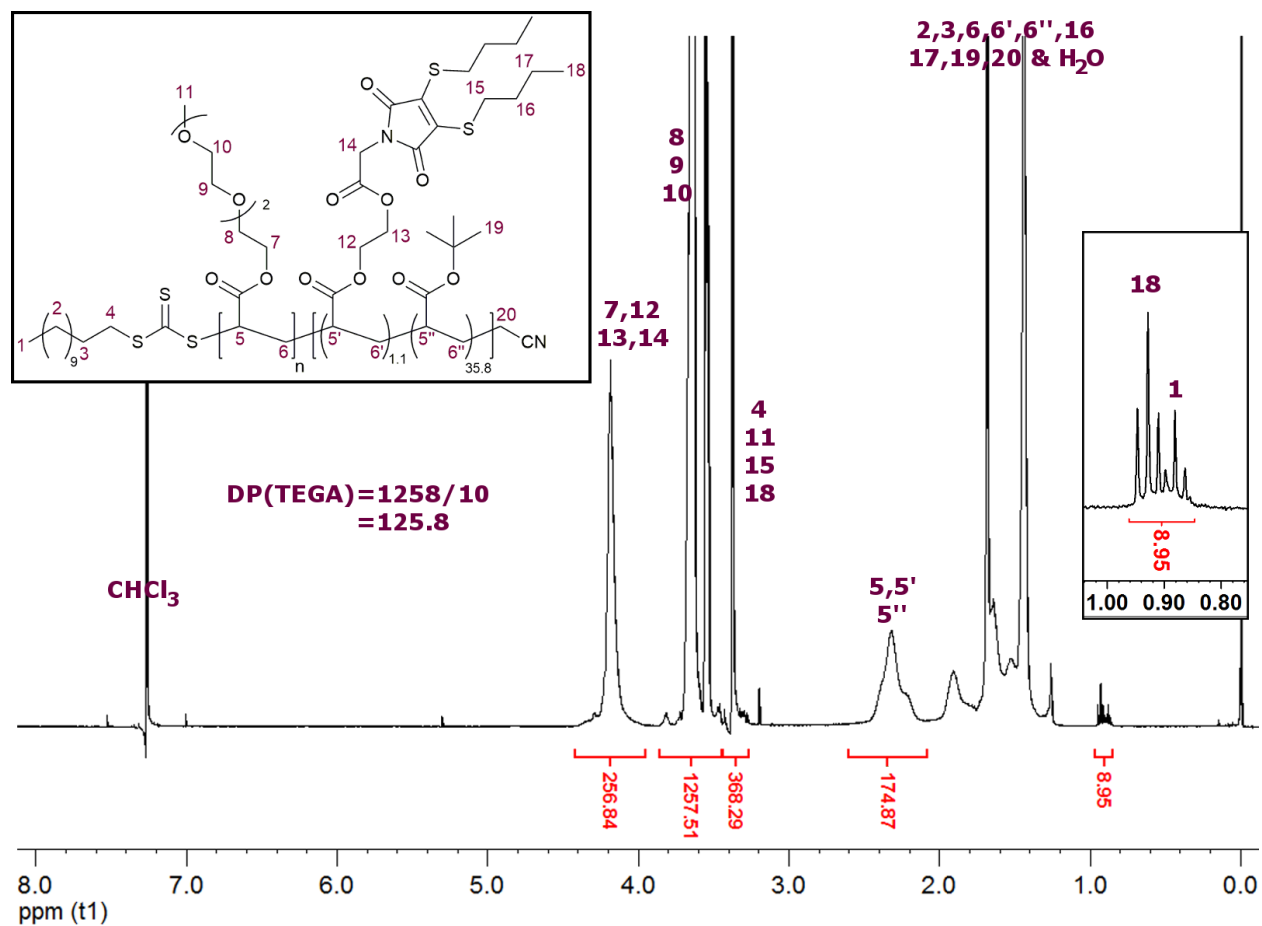


Figure S7. Plots to determine D (left hand side) and plots to determine M_w (right hand side) for; a & b) SLMs; c & d) CLMs; e & f) NLMs.

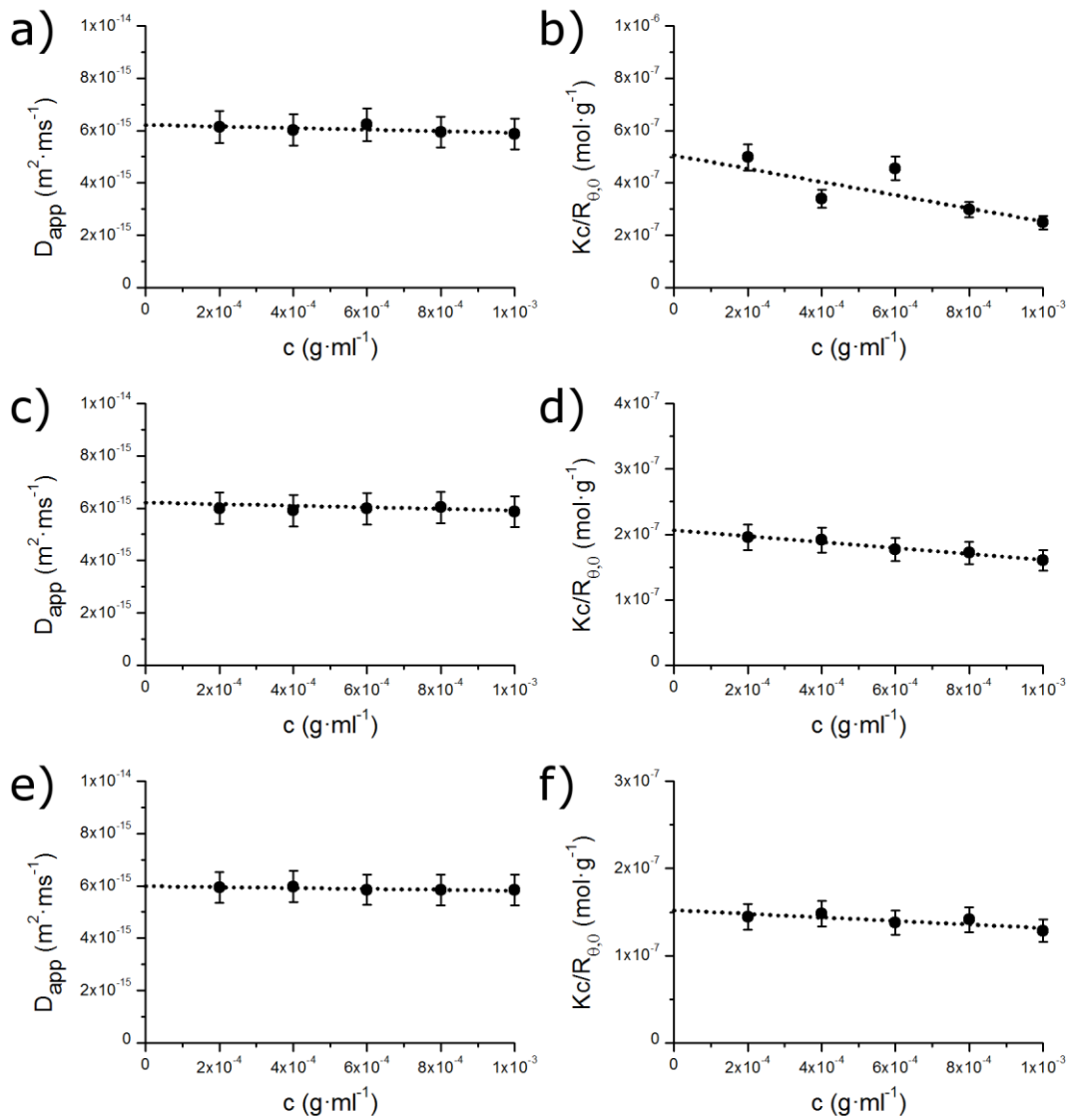


Figure S8. FLIM image of the thin film formed from a) 4 micelles (SLMs); and b) 5 micelles (CLMs). Scale bars = 200 μm .

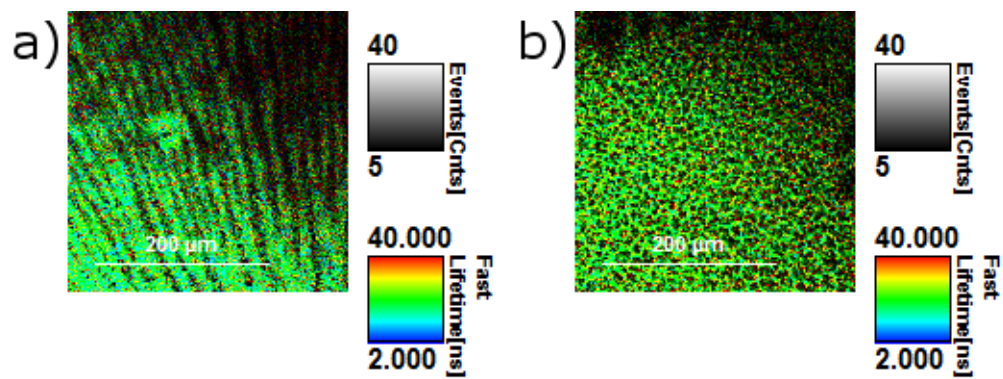


Figure S9. Emission at 515 nm and 610 nm of CLMs for the first 30 s after addition of NR.

$\lambda_{\text{ex}} = 422 \text{ nm}$.

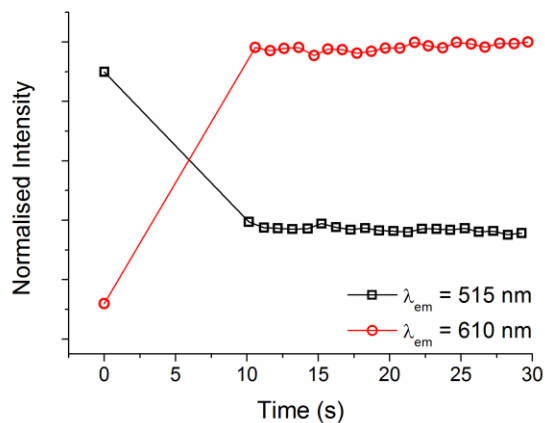
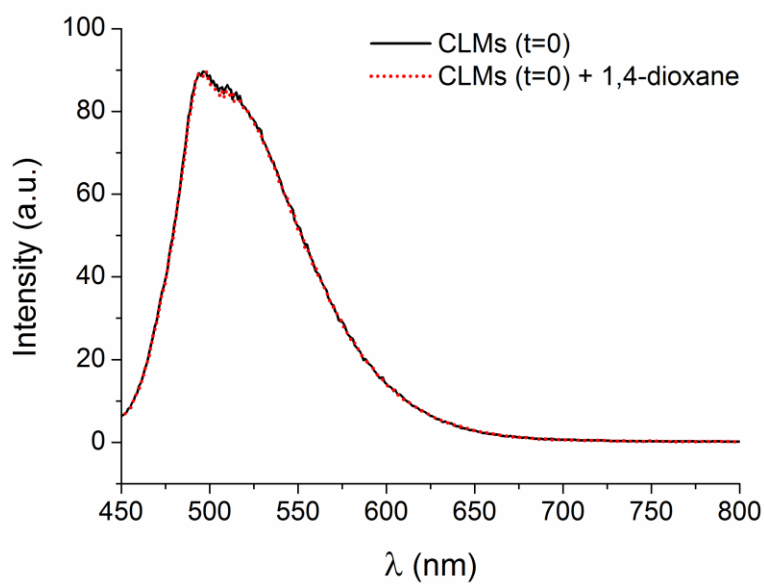


Figure S10. Emission spectra of CLMs (2.5 ml, [DTM] = 1 μM) before and after the addition of 2.5 μl 1,4-dioxane.



REFERENCES

- (1) Hua, F.; Jiang, X.; Li, D.; Zhao, B. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2454.
- (2) Robin, M. P.; O'Reilly, R. K. *Chem. Sci.* **2014**, *5*, 2717.
- (3) Nicolai, T.; Brown, W.; Johnsen, R. M.; Stepanek, P. *Macromolecules* **1990**, *23*, 1165.
- (4) Colombani, O.; Ruppel, M.; Burkhardt, M.; Drechsler, M.; Schumacher, M.; Gradzielski, M.; Schweins, R.; Müller, A. H. E. *Macromolecules* **2007**, *40*, 4351.
- (5) Esker, A. R.; Mengel, C.; Wegner, G. *Science* **1998**, *280*, 892.