SUPPORTING INFORMATION

Robust and Biocompatible Functionalization of ZnS Nanoparticles by Catechol-Bearing Poly(2-Methyl-2-Oxazoline)s

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Synthesis of Nitrodopamine hemisulfate. Dopamine hydrochloride (4 g, 0.021 mol) and sodium nitrite (5.1 g, 0.074 mol) were dissolved in ca. 120 ml of MilliQ water, kept at 0°C in an iced-bath and 20 ml of a 20% solution of H_2SO_4 were added dropwise. The brown reaction mixture formed was left to stir at room temperature overnight. Then, the mixture was filtered, washed with MilliQ water and cold methanol. The solid was then recrystallized from water at room temperature. After filtration, dark brown crystals were obtained and ^{1}H-NMR was performed, confirming the desired product.

Tribromodopamine hydrobromide. In detail, 3 g (0.019 mol) of bromine were dissolved in 15 ml of acetic acid and slowly added to 0.72 g of dopamine hydrochloride (0.004 mol) dissolved in 400 ml of acetic acid and left under stirring at RT for 4 hours. The purification was carried out by reprecipitation from acetone and hexane at 4°C. A white solid was collected by filtration and subsequently washed with pentane.

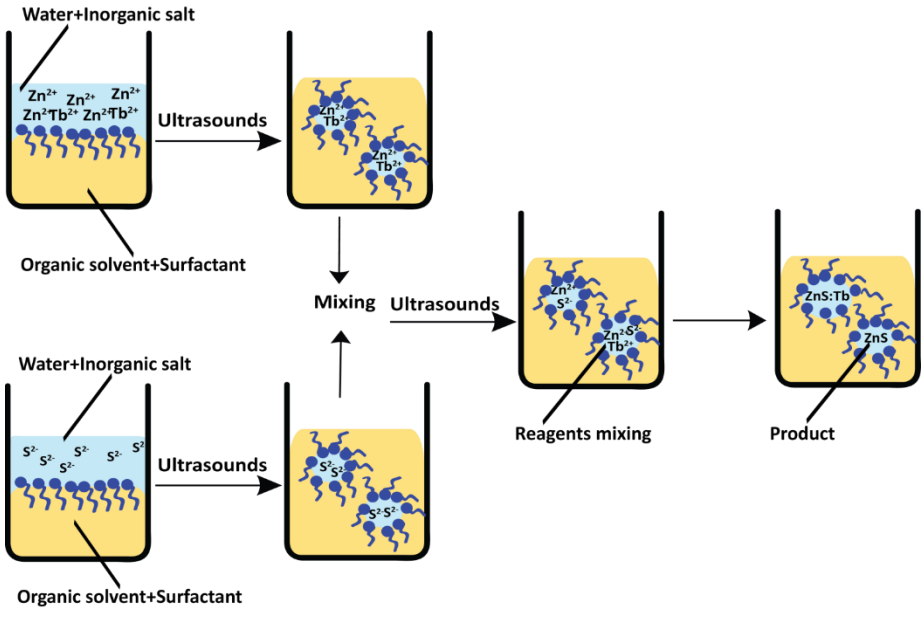

Figure S1. Miniemulsion process for the synthesis of ZnS and ZnS:Tb NPs.

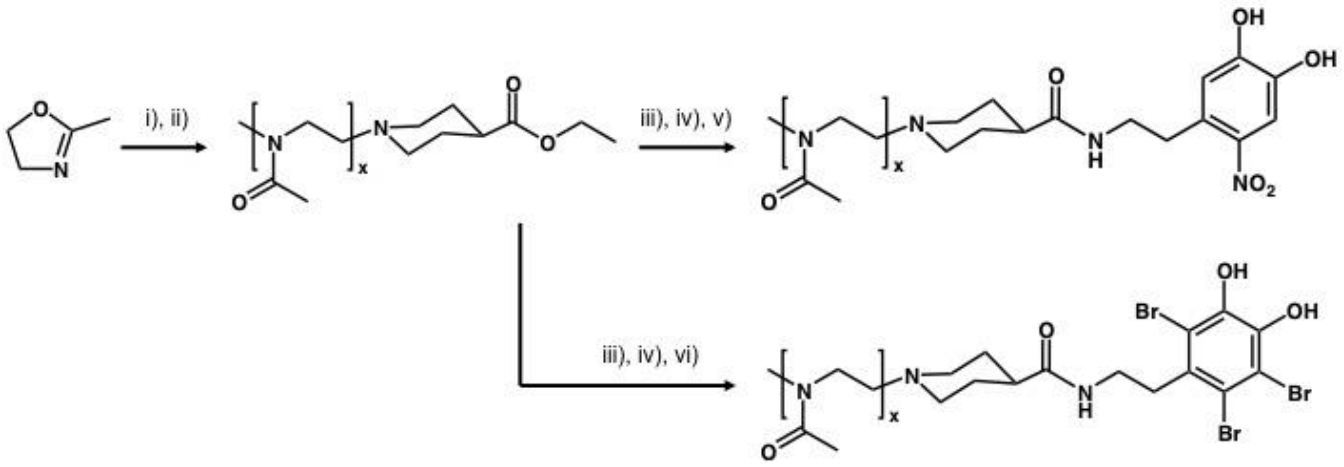

Figure S2. Synthesis of PMOXA(x)ND and PMOXA(x)BrD. i) MeOTf, dry ACN, 24h, 70 °C; ii) ethylisonipecotate, dry ACN, 48h, RT; iii) NaOH solution, pH 13, 24h, RT; iv) NHS, DCC, dry DMF, 24h, RT; v) ND, N.methylmorpholine, dry DMF, 24h, 0-25 °C; vi) BrD, N-methylmorpholine, dry DMF, 24h. 0-25 °C.

Table S1. Number- and weight-average absolute molecular weights, M_n and M_w, and dispersity ($Đ$) of PMOXA ligands measured by SEC.

Ligand precursor[a]	M_n **(g/mol)**	M_w **(g/mol)**	$Đ$
PMOXA(18)COOH	1500	1600	1.1
PMOXA(27)COOH	2300	2500	1.1
PMOXA(50)COOH	4500	4900	1.1
PMOXA(90)COOH	8000	9000	1.1

[a] theoretical (DP) expected from the monomer/initiator ratio during the synthesis

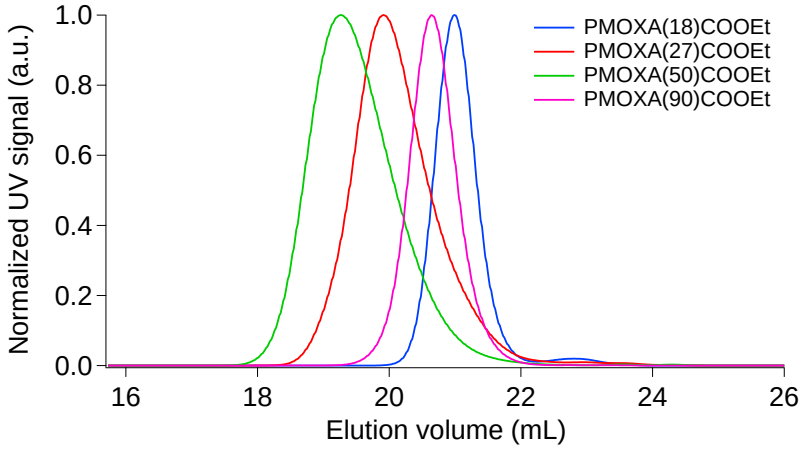

Figure S3. SEC elugrams of the different PMOXA ligands used for NPs functionalization.

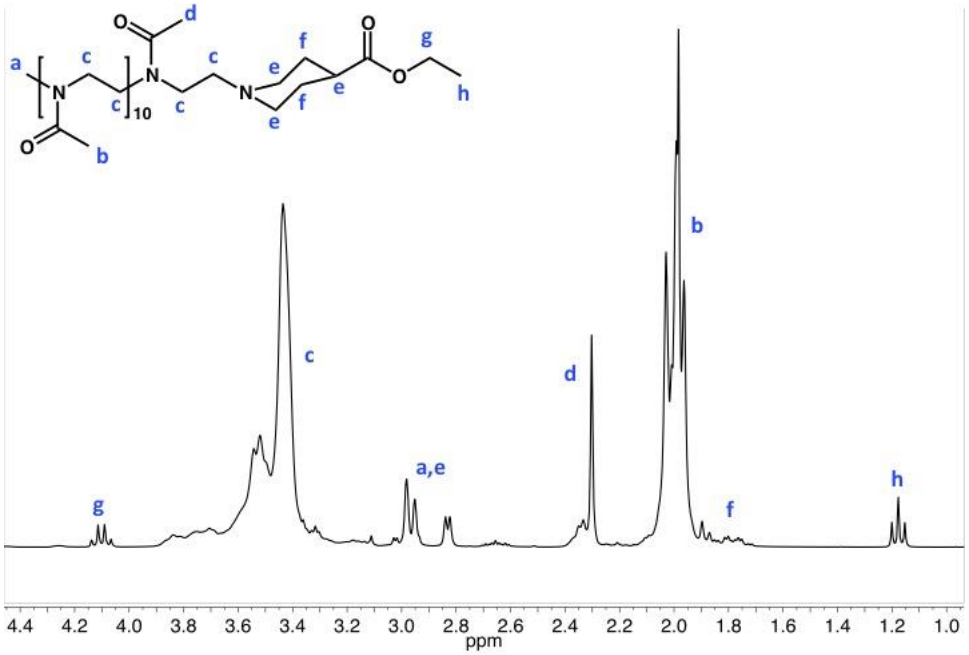

Figure S4. [1]H-NMR(300 MHz) spectrum of PMOXA(18)COOEt in D_2O. δ = 4.1 (q, 2H, C(O)O$\underline{CH_2}CH_3$), 3.6-3.3 (m, 70H, N-$\underline{CH_2CH_2}$), 3.1-2.8 (m, 3H, N-$\underline{CH_3}$ initiator ; 4H, N-$\underline{CH_2}$ terminating agent), 2.2 - 1.95 (m, 53H, C(O)$\underline{CH_3}$), 1.8 (m, 4H, C(O)CH$\underline{CH_2}$ terminating agent), 1.2 (t, 3H, C(O)OCH$_2\underline{CH_3}$) ppm.

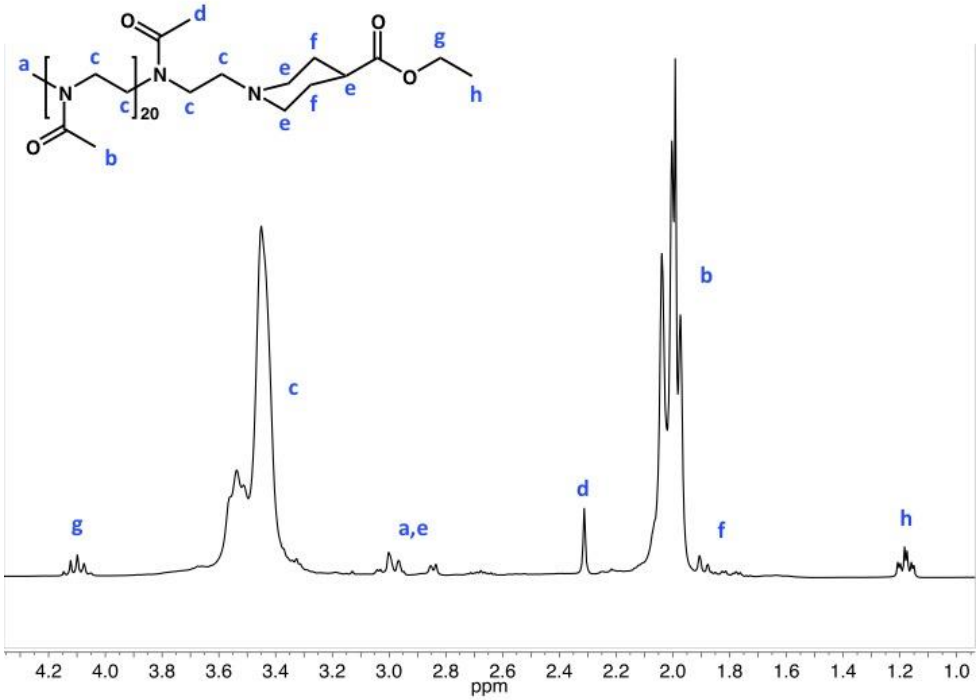

Figure S5. [1]H-NMR(300 MHz) spectrum of PMOXA(27)COOEt in D_2O. δ = 4.1 (q, 2H, C(O)O$\underline{CH_2}CH_3$), 3.6-3.3 (m, 89H, N-$\underline{CH_2CH_2}$), 3.1-2.8 (m, 3H, N-$\underline{CH_3}$ initiator ; 4H, N-$\underline{CH_2}$ terminating agent), 2.2 - 1.95 (m, 69H, C(O)$\underline{CH_3}$), 1.8 (m, 4H, C(O)CH$\underline{CH_2}$ terminating agent), 1.2 (t, 3H, C(O)OCH$_2\underline{CH_3}$) ppm.

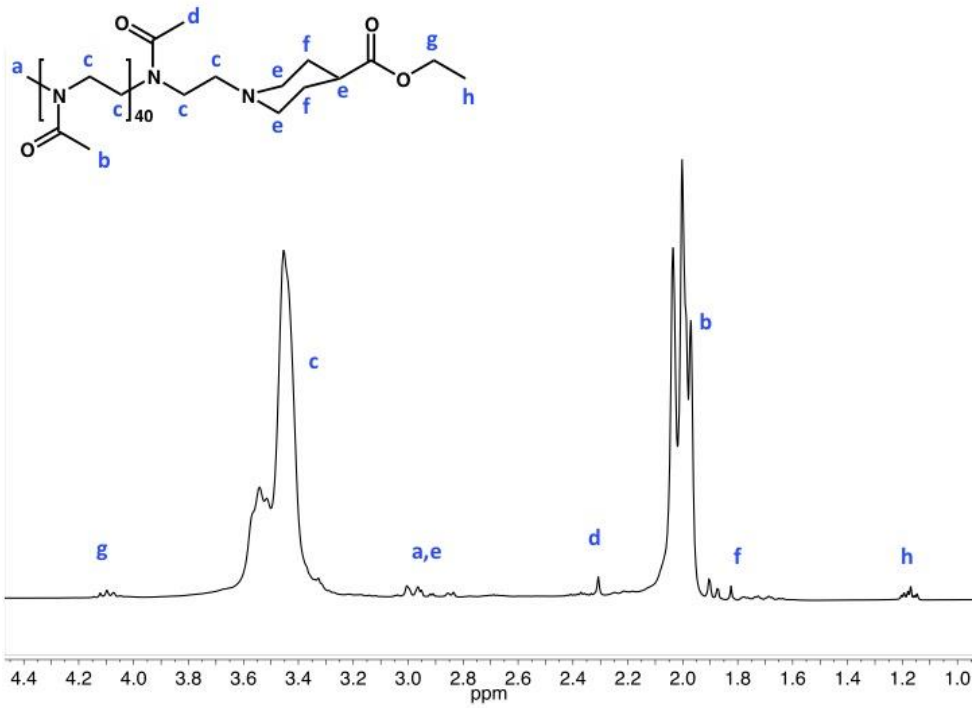

Figure S6. ^{1}H-NMR(300 MHz) spectrum of PMOXA(50)COOEt in D_2O. δ = 4.1 (q, 2H, C(O)O$\underline{CH_2}CH_3$), 3.6-3.3 (m, 225H, N-$\underline{CH_2CH_2}$), 3.1-2.8 (m, 3H, N-$\underline{CH_3}$ initiator ; 4H, N-$\underline{CH_2}$ terminating agent), 2.2 - 1.95 (m, 163H, C(O)$\underline{CH_3}$), 1.8 (m, 4H, C(O)CH$\underline{CH_2}$ terminating agent), 1.2 (t, 3H, C(O)OCH$_2\underline{CH_3}$) ppm.

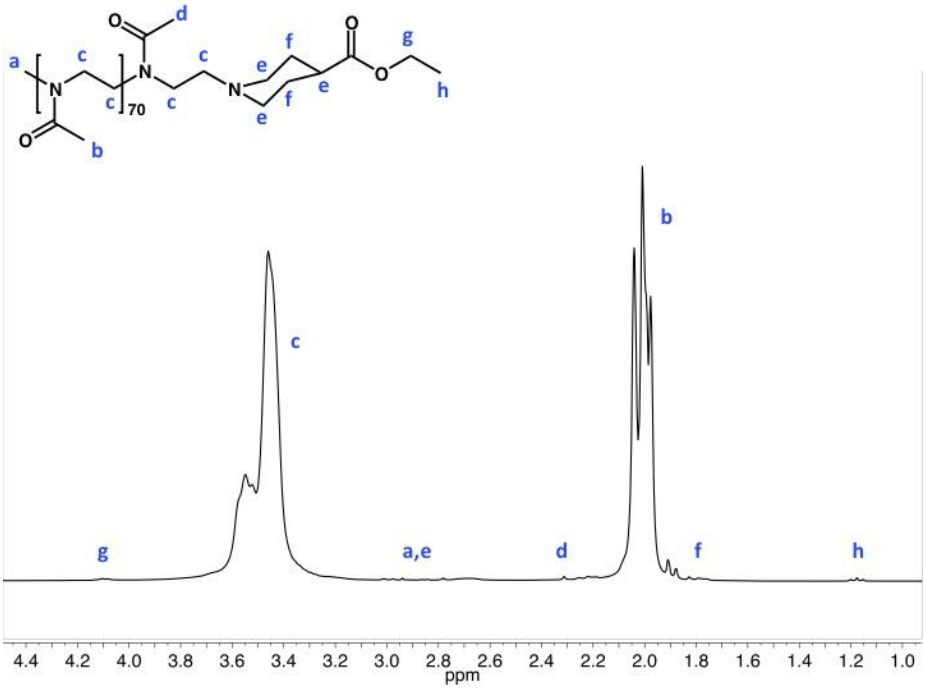

Figure S7. ^{1}H-NMR(300 MHz) spectrum of PMOXA(90)COOEt in D_2O. δ = 4.1 (q, 2H, C(O)O$\underline{CH_2}CH_3$), 3.6-3.3 (m, 381H, N-$\underline{CH_2CH_2}$), 3.1-2.8 (m, 3H, N-$\underline{CH_3}$ initiator ; 4H, N-$\underline{CH_2}$ terminating agent), 2.2 - 1.95 (m, 279H, C(O)$\underline{CH_3}$), 1.8 (m, 4H, C(O)CH$\underline{CH_2}$ terminating agent), 1.2 (t, 3H, C(O)OCH$_2\underline{CH_3}$) ppm.

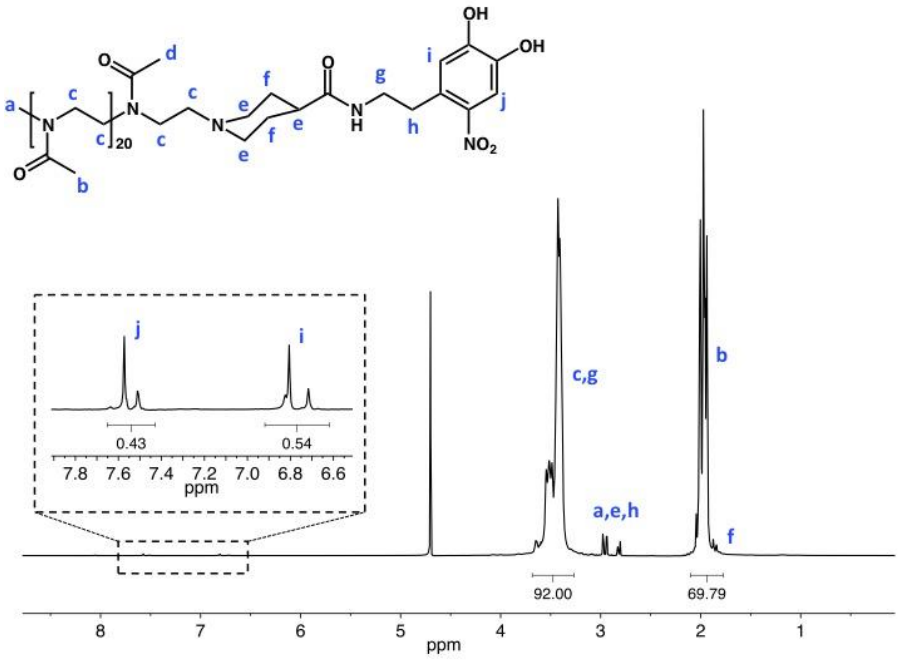

Figure S8. ^{1}H-NMR(500 MHz) spectrum of PMOXA(27)ND in D_2O, reported as example. The efficient coupling with ND is confirmed by the presence of the aromatic signals (i and j) at 6.8 and 7.5 ppm. δ = 7.6 (s, 1H, Ar), 6.8 (s, 1H, Ar), 4.1 (q, 2H, C(O)O$\underline{CH_2}CH_3$), 3.6-3.3 (m, 92H, N-$\underline{CH_2CH_2}$ and N-$\underline{CH_2}CH_2$-Ar), 3.1-2.8 (m, 3H, N-$\underline{CH_3}$ initiator ; 4H, N-$\underline{CH_2}$ terminating agent and N-$CH_2\underline{CH_2}$-Ar), 2.2 - 1.95 (m, 69H, C(O)$\underline{CH_3}$), 1.8 (m, 4H, C(O)CH$\underline{CH_2}$ terminating agent), 1.2 (t, 3H, C(O)OCH$_2\underline{CH_3}$) ppm.

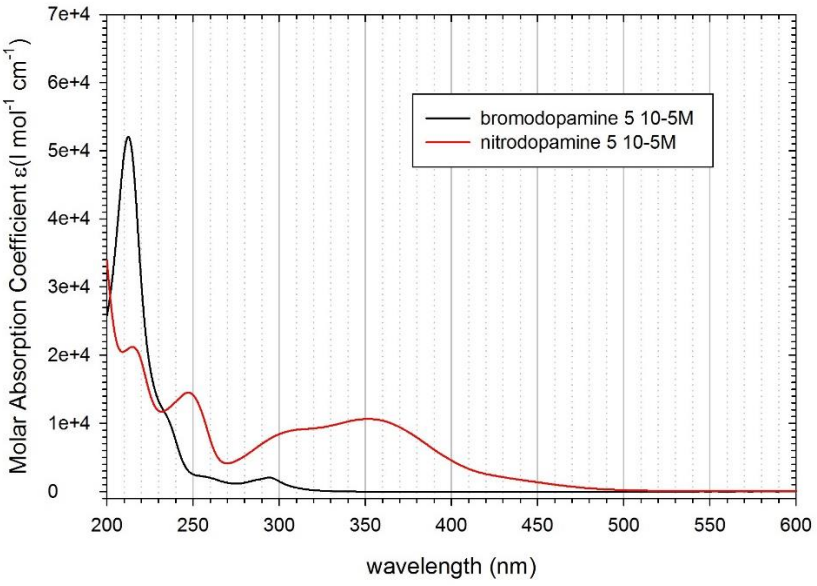

Figure S9. UV absorption spectra of 50 μM solutions of ND and BrD in water.

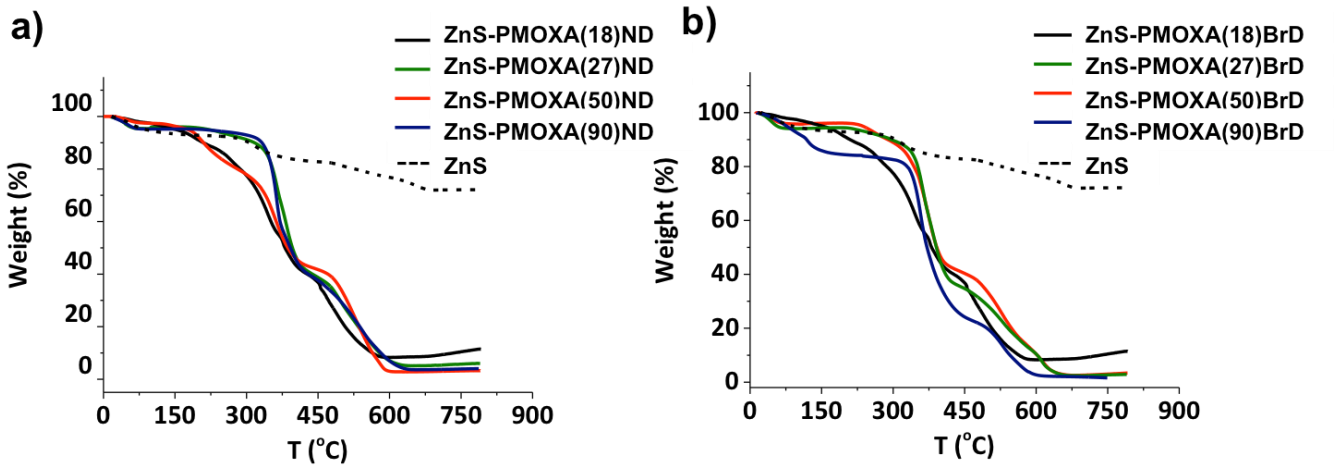

Figure S10. Thermogravimetric analysis for ZnS-PMOXAND (a) and ZnS-PMOXABrD (b).

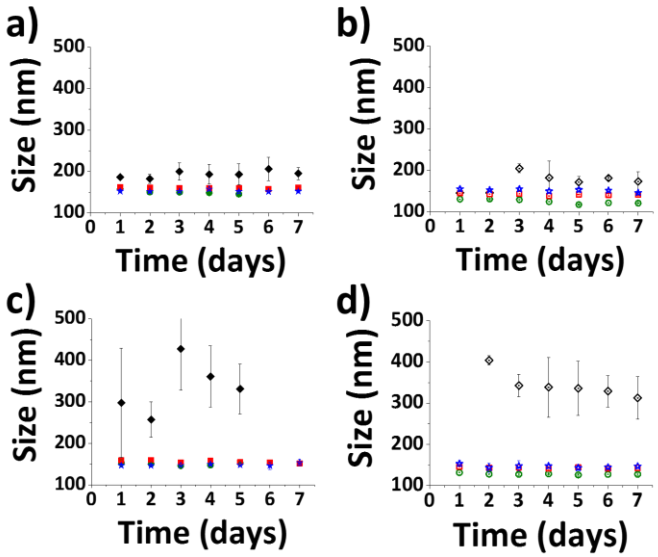

Figure S11. HD values of ZnS-PMOXA(x)ND in water (a) and PBS (c); ZnS-PMOXA(x)BrD in water (b) and PBS (d) as a function of the storage time. ZnS-PMOXA(18) (black markers); ZnS-PMOXA(27) (green markers); ZnS-PMOXA(50) (red markers); ZnS-PMOXA(90) (blue markers).

Table S2. Average hydrodynamic radius measured from DLS measurements after 9 months of storage at 4 ºC.

Sample	**Average HD intensity distribution (nm) after 9 month storage in water at 4 ºC**
ZnS-PMOXA(18)ND	sedimented
ZnS-PMOXA(18)BrD	sedimented
ZnS-PMOXA(27)ND	137±87 (96%) 5426±289 (4%)
ZnS-PMOXA(27)BrD	sedimented
ZnS:-PMOXA(50)ND	170±78 (100%)
ZnS-PMOXA(50)BrD	142±70 (100%)
ZnS-PMOXA(90)ND	140±50 (100%)
ZnS-PMOXA(90)BrD	108±22 (100%)