

## Supporting Information

### Diffusion of Gold Nanorods Functionalized with Thermoresponsive Polymer Brushes

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Synthesis of PNIPAm-functionalized gold nanorods. Grafting density measurement of NIPAm-PNIPAm-SH brushes onto AuNRs by <sup>1</sup>H high-resolution magic-angle sample spinning (HRMAS) NMR spectroscopy. Analysis of  $g_1(t)$  decays by Inverse Laplace Transformation. Proton HR NMR spectra of NIPAm-PNIPAm-SH brushes onto AuNRs. AuNRs translational diffusivity measured by HRNMR spectroscopy.

#### **S1. Synthesis of PNIPAm-functionalized gold nanorods.**

*S1.1. Materials.* Tetrachlorauric (III) acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, >99.9 %), silver nitrate (AgNO<sub>3</sub>, 99.9999 %), hexadecyltrimethylammoniumbromide (CTAB, >99 %), L-ascorbic acid (reagent grade), sodium borohydride (NaBH<sub>4</sub>, >99 %), n-hexylamine (99 %), triethylamine (TEA, >99.5 %) and methyl acrylate (MA, 99 %) were purchased from Sigma-Aldrich and used as received. Dithiothreitol (DTT, >99 %) was purchased from abcr and stored in the fridge until use. Acetone (dry, 99.8 %), tetrahydrofuran (THF, dry, >99.9 %), 1,4-dioxane (dry, 99.5 %) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, dry, >99 %) were purchased from Acros Organics. Ethanol (EtOH, >99 %) was purchased from Sigma-Aldrich. N-Isopropylacrylamide (NIPAm, 97 %) was purchased from Sigma-Aldrich, recrystallized from

hexane and stored under nitrogen in the fridge until needed. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98 %) was purchased from Sigma-Aldrich, recrystallized from methanol and stored in the fridge until needed. 4,4'-Azobis(4-cyanovaleric acid (ACVA, >98 %) was purchased from Sigma-Aldrich and used as received. For the gold nanorod synthesis only deionized water (18.2 M $\Omega$ ·cm, 'PURELAB Plus', Veolia) was used. All glassware was extensively pre-cleaned and stored in an oven prior to use.

*SI.2. Polymer synthesis.* All PNIPAm types, i.e., BN-PNIPAm-SH<sup>1-3</sup> and NIPAm-PNIPAm-SH<sup>2,3</sup> with distinct molecular weight, were made by reversible addition-fragmentation chain-transfer polymerization (RAFT) of N-isopropylacrylamide (NIPAm) and post-polymerization modification by aminolysis. The same polymers were used as recently synthesized and published.<sup>1-3</sup>

*SI.3. AuNR synthesis.* CTAB-stabilized gold nanorods (AuNRs) were prepared according to literature.<sup>1,4</sup>

*SI.4. Functionalization of AuNRs with PNIPAm.* The complete surface functionalization of AuNR-CTAB with R-PNIPAm-SH (R = Bn or NIPAm-like), work-up of the PNIPAm-AuNRs dispersions and transfer to deuterated water was done as shown in [Ref 2](#).

**S2. Grafting density measurement of NIPAm-PNIPAm-SH brushes onto AuNRs by <sup>1</sup>H high-resolution magic-angle sample spinning (HRMAS) NMR spectroscopy.** We can define the grafting density of a PNIPAm brush tethered onto the surface of AuNRs by the relationship

$$\sigma = \frac{N_{PNIPAm}}{S_{AuNRs}}, \quad (S1)$$

where  $N_{PNIPAm}$  is the total number of polymer chains that forms brushes onto AuNRs having the number  $N_{AuNRs}$ , and the total area of  $S_{AuNRs}$ . It is assumed that all AuNRs have the same grafting density and therefore, no heterogeneous graft density is present. These assumptions lead to the inequality  $N_{PNIPAm} \geq N_{AuNRs}$ , and to the fact that ratio  $i = N_{PNIPAm}/N_{AuNRs}$ ,

fulfills the condition  $i=1,2,3\dots$ . Moreover, the polymer molecular weight and the size of AuNRs are assumed to be monodisperse.

The next step in our argumentation is related to the evaluation of the AuNRs volume and surface area. We consider in the following an AuNR with the length  $L$  of the cylindrical part and two hemisphere caps of radius  $R$ . The volume of the gold nanorod  $V_0$  is given by

$$V_0 = V_{cylinder} + 2V_{hemisphere}. \quad (S2)$$

From the above equation we can finally write

$$V_0 = \pi R^2 \left( L + \frac{4R}{3} \right). \quad (S3)$$

The total surface of one rod is obtained in a similar manner by adding the surface of cylinder and the surface of the two hemisphere, i.e.,

$$S_0 = 2\pi R(L + 2R). \quad (S4)$$

From the above equations we can evaluate the surface-to-volume ratio

$$\frac{S_0}{V_0} = \frac{6(L+2R)}{R(3L+4R)}. \quad (S5)$$

In our case the length ( $L$ ) and diameter ( $2R$ ) of AuNRs have been measured by TEM. The reported values are  $L = 70$  nm and  $2R = 16$  nm. From equation (S5) we finally get  $S_0/V_0=0.267$  nm<sup>-1</sup>.

Furthermore, we have to evaluate the total surface of AuNRs. For a mass  $m_{AuNRs}$  of AuNRs the total number of rods ( $N_{AuNRs}$ ) is given by

$$N_{AuNRs} = \frac{m_{AuNRs}}{\rho_{Au}V_0}, \quad (S6)$$

where  $\rho_{Au}$  is the gold density ( $\rho_{Au}=19.3$  g/cm<sup>3</sup> or  $\rho_{Au}=19.3 \times 10^{-18}$  mg/nm<sup>3</sup>), and  $V_0$  is the volume of a single AuNR given by Eq. (S3).

The total surface of AuNRs that will be grafted by the polymer is

$$S_{AuNRs} = N_{AuNRs}S_0, \quad (S7)$$

where  $S_0$  is given by Equation (S4).

Combining Eqs. (S3)-(S6), we get for the total surface of AuNRs that is grafted with PNIPAm

$$S_{AuNRs} = \frac{m_{AuNRs}}{\rho_{Au}} \frac{6(L+2R)}{R(3L+4R)}, \quad (S8)$$

and from Equation (S5) we yield

$$S_{AuNRs} = 1.38 \times 10^{16} m_{AuNRs} [mg] nm^2, \quad (S9)$$

where the quantity  $m_{AuNRs}$  is expressed in mg.

The number of partially deuterated water (HDO) will be used as an *in situ* reference for the  $^1H$  HRMAS NMR spectrum in the evaluation of the total number of grafted PNIPAm chains. For NMR brush samples we use 99.9 %  $D_2O$  that means only 0.1% from the total amount of  $D_2O$  is represented by HDO. The number of HDO molecules is given by

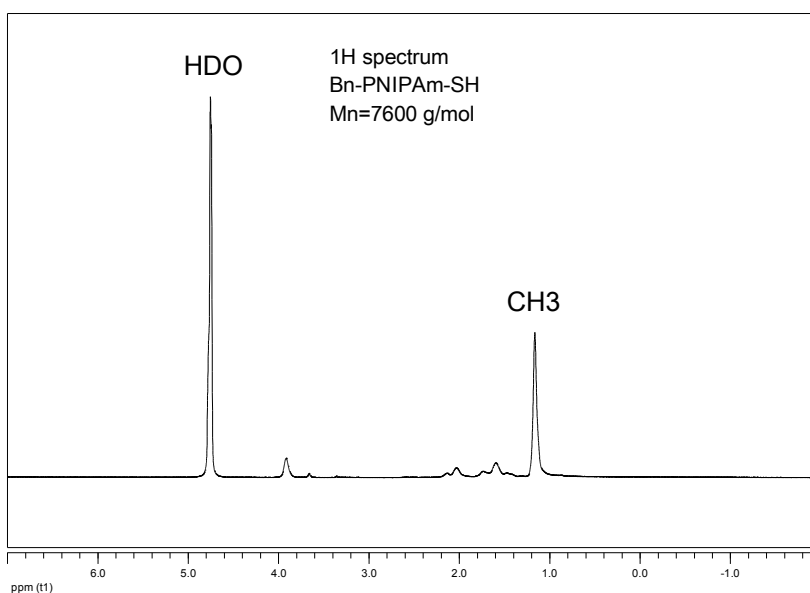
$$N_{HDO} \approx 3.17 \times 10^{19} \rho_{D_2O} V_{D_2O} [mL], \quad (S10)$$

where the density of deuterated water is  $\rho_{D_2O} = 1.107 \text{ g/cm}^3$  at 25 °C, and  $V_{D_2O}$  is the volume of deuterated water in mL. Finally, we can write

$$N_{HDO} \approx 3.51 \times 10^{19} V_{D_2O} [mL]. \quad (S11)$$

The grafting density can be measured by knowing the number of PNIPAm chains in brushes. This objective can be reached by  $^1H$  HRMAS NMR spectroscopy. We will assume in the following that by the purification process applied at the end of grafting procedure that none of the PNIPAm are present as free chains. Furthermore, the  $^1H$  HRMAS NMR spectrum is measured in the swollen state of the brush, i.e., below the lower critical solution temperature (LCST). For our brushes we made the measurements around 20 °C and for this propose a NMR spectrometer with a high magnetic field should be used (for instance, like in our case 16.4 T, i.e., 700 MHz for proton). This will lead to preferentially stretched PNIPAm brushes having increased lateral mobility. Hence,  $^1H$  NMR spectrum in the aliphatic region (see [Figure S1](#)) will show well resolved peaks especially for the  $CH_3$  groups of *N*-isopropyl at  $\delta = 1.2$  ppm. Furthermore, the  $^1H$  NMR peak of HDO ( $\delta = 4.8$  ppm) will be distinct from the

peaks of PNIPAm. The closest peak to the HDO is that of *N*-isopropyl CH at  $\delta = 3.9$  ppm. As a consequence of this good spectral resolution the integral intensities of HDO and methyl groups can be evaluated accurately leading to the possibility to measure the number of grafted PNIPAm chains using as reference the number of HDO molecules. We can mention that the NIPAm monomer unit has two CH<sub>3</sub> groups that mean the total number of six protons per monomer. As an example, we consider the case of benzyl end functionalized PNIPAm with molecular weight  $M_n = 7600 \text{ g mol}^{-1}$ . The <sup>1</sup>H HRMAS spectrum is shown in **Figure S1**.



**Figure S1.** <sup>1</sup>H HRMAS spectrum in the aliphatic region of Bn-PNIPAm-SH brushes ( $M_n = 7600 \text{ g/mol}$ ) onto AuNRs measured at temperature of 23 °C with a NMR spectrometer operating at the frequency of 700 MHz.

The integral area ( $I$ ) under NMR peaks is proportional with the number of protons that corresponds to the total number of molecules (HDO) and those in the methyl groups. We define the ratio ( $r$ ) of the integrals under CH<sub>3</sub> and HDO peaks by

$$r = \frac{I_{CH_3}}{I_{HDO}}. \quad (\text{S12})$$

In terms of the total number of NIPAm monomer units which corresponding to the total number of grafted PNIPAm chains we can write

$$r = \frac{6N_{totalNIPAm}}{N_{HDO}}. \quad (\text{S13})$$

Finally, we get

$$N_{total\ NIPAm} = \frac{rN_{HDO}}{6}. \quad (S14)$$

Combining Eqs. (S11) and (S14) we can write

$$N_{total\ NIPAm} = 5.85 \times 10^{18} rV_{D2O} (mL). \quad (S15)$$

The number of NIPAm monomer units  $n_{monomers}$  in a polymer chain of PNIPAm with molecular weight  $M_n$  is given by

$$n_{monomers} = \frac{M_n}{M_{n,monomer}}, \quad (S16)$$

where  $M_{n,monomer}$  is the molecular weight of a NIPAm monomer unit ( $M_{n,monomer} = 113.16\text{ g mol}^{-1}$ ). Hence, the total number of PNIPAm polymer chains that forms brushes can be written from Eqs. (S15) and (S16)

$$N_{PNIPAm} = \frac{N_{total\ NIPAm}}{n_{monomers}}, \quad (S17)$$

and finally

$$N_{PNIPAm} = 6.62 \times 10^{20} \frac{rV_{D2O} [mL]}{M_n [\frac{g}{mol}]}. \quad (S18)$$

The graft density of linear PNIPAm polymer onto AuNRs can be evaluated from Eqs. (S1), (S9), and (S18). Finally, we can write

$$\sigma = 4.797 \times 10^4 \frac{rV_{D2O} [mL]}{m_{AuNRs} [mg] M_n [\frac{g}{mol}]}, \frac{chains}{nm^2}. \quad (S19)$$

We apply the approach described above to the series of NIPAm end functionalized PNIPAm brushes onto AuNR (hereafter NIPAm-PNIPAm-SH) with different molecular weight. The ratios of  $V_{D2O}/m_{AuNRs}$  used in dispersion preparation are given in [Table S1](#).

**Table S1. Ratio  $V_{D2O}/m_{AuNRs}$  Versus  $M_n$  for NIPAm-PNIPAm-SH Brushes onto AuNRs.**

$M_n$ [g mol <sup>-1</sup> ]	$V_{D2O}$ [mL]	$m_{AuNRs}$ [mg]	$V_{D2O}/m_{AuNRs}$ [mL/mg]
4000	0.4380	17.5	0.025

8000	0.4676	18.7	0.025
12500	0.4050	16.2	0.025
30000	0.4600	18.4	0.025
45000	0.5200	20.8	0.025

The ratios  $r$  (Eq. (S12)) for the same series measured from  $^1\text{H}$  HRMAS NMR spectra are given in [Table S2](#).

**Table S2. Ratio  $r$  from  $^1\text{H}$  HRMAS NMR Spectra Versus  $M_n$  for NIPAm-PNIPAm-SH Brushes onto AuNRs.**

$M_n$ [g mol $^{-1}$ ]	$I_{\text{CH}_3}$	$I_{\text{DHO}}$	$r$
4000	1	27.8	0.0359
8000	1	7.8	0.1284
12500	1	4.2	0.2369
30000	1	10.4	0.0961
45000	1	1.6	0.6097

From Equation (S19) and the above Tables we obtain the grafting density for NIPAm-PNIPAm-SH brushes onto AuNRs (see [Table S3](#))

**Table S3. Grafting Density  $\sigma$  Versus  $M_n$  for NIPAm-PNIPAm-SH Brushes onto AuNRs.**

$M_n$ [g/mol]	$\sigma^*$ [chains/nm $^2$ ]
4000	0.011
8000	0.019
12500	0.023

30000	0.0038
45000	0.016

\*Estimated errors of the order of 20%.

Furthermore, we can also evaluate the number of chains grafted onto a single rod. The surface of a AuNRs is given by  $S_0 = 2\pi R(L + 2R)$ , where in our case  $L=70$  nm and  $2R=16$  nm. From these values we get  $S_0=4321$  nm<sup>2</sup>. Finally, for the number of tethered PNIPAm chains onto one AuNR denoted by  $n_{PNIPAm}$  we get  $n_{PNIPAm} \approx 48$  chains, for  $M_n = 4000$  g/mol and for  $M_n = 12500$  g/mol,  $n_{PNIPAm} \approx 99$  chains (see also [Table S3](#)).

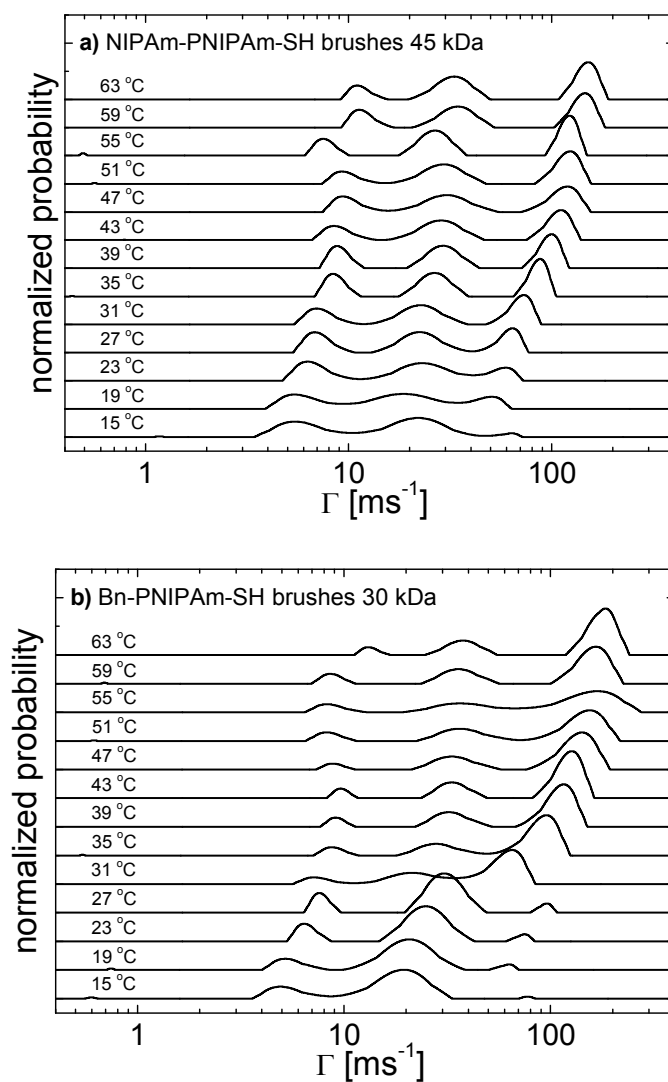
We can conclude that the measurement of the graft density of polymer brushes by <sup>1</sup>H HRMAS NMR spectroscopy is straightforward as long as separated and narrow peaks are detected in the high-resolution spectrum.<sup>5</sup> To fulfill this conditions (i) the graft density has not to be very high such that segmental interchain interactions does not broaden NMR peaks and (ii) the thermoresponsive brush has to be measured in the swollen regime having stretched chains.

The graft density can be correlated to the brush height and the polymer molecular weight.<sup>6,7</sup> Ishida and Biggs<sup>8</sup> investigated temperature-induced structural changes of PNIPAm layer grafted onto silicon wafers substrate in aqueous solution using AFM and quartz crystal microbalance with dissipation. For the layer grafted on silica a number average molecular weight was 655 kDa with the polydispersity of 2.4. The dry thickness of the grafted layer measured with an ellipsometer was 7.6 nm. The grafting density calculated from thickness and molecular weight data assuming the dry density value of PNIPAm to be 1.269 g/cm<sup>3</sup> was 0.0088 chains/nm<sup>2</sup>, that is about 0.01 chains/nm<sup>2</sup>.<sup>8</sup> This value is in the agreement with that reported in [Table S3](#). Furthermore, polystyrene brushes on gold nanospheres with the diameter between 20-80 nm, have a grafting density determined by TGA in the range 0.085-0.003 chain/nm<sup>2</sup>.<sup>9</sup>



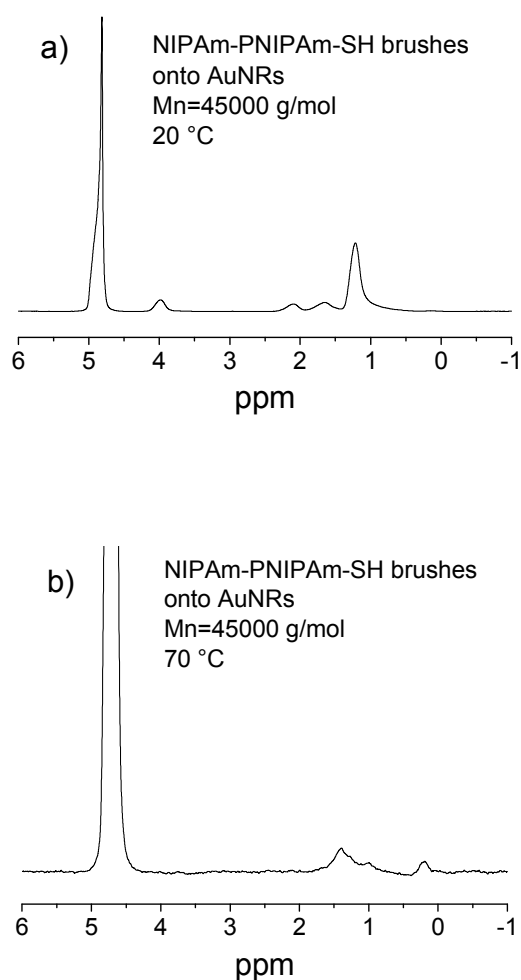
A source of errors in NMR measurements of grafting density could be related to the presence of broad NMR resonance like that of HDO molecules inside of the brush especially close to the surface that are not visible in the NMR spectrum. Moreover, the monomers close to the grafted surface could have also a broad NMR signal and will be buried in the baseline noise. We shall mention that modern solid-state NMR spectrometers operating at high magnetic field have short dead time (about 1  $\mu$ s) that allows detection of the broad NMR signals and therefore, partially reducing the above source of errors.

### S3. Analysis of $g_i(t)$ decays by Inverse Laplace Transformation.



**Figure S2.** Normalized probability of relaxation rates  $\Gamma$  obtained by Inverse Laplace transform of autocorrelation functions  $g_1(t)$  for (a) NIPAm-PNIPAm-SH ( $M_n = 45000 \text{ g mol}^{-1}$ ) and (b) Bn-PNIPAm-SH brushes ( $M_n = 30000 \text{ g mol}^{-1}$ ) onto AuNRs measured by DLS in the temperature range of 15 °C-63 °C. We can evaluate the peaks corresponding to  $\Gamma_1$  and  $\Gamma_2$  relaxation rates from the values of  $D_T$  and  $D_R$  shown in Figure 3 (main text) and  $q = 2.63 \times 10^7 \text{ m}^{-1}$ . The first and the third probability peak from the left to right hand side correspond to  $\Gamma_1$  and  $\Gamma_2$  relaxation rates, respectively.

#### S4. Proton HR NMR spectra of NIPAm-PNIPAm-SH brushes onto AuNRs.



**Figure S3.** Proton HRMAS spectra of NIPAm-PNIPAm-SH brushes onto AuNRs (5 wt% in  $D_2O$ ) measured at 20 °C (a) and 70 °C (b). The temperature-induced phase transition at 70 °C is revealed by the broadening of the  $^1H$  peaks in the aliphatic region that reduces the intensity of  $CH_3$  ( $\delta = 1.2 \text{ ppm}$ ),  $CH_2$  ( $\delta = 1.6 \text{ ppm}$ ), and  $CH$  ( $\delta = 3.9 \text{ ppm}$ ) peaks.

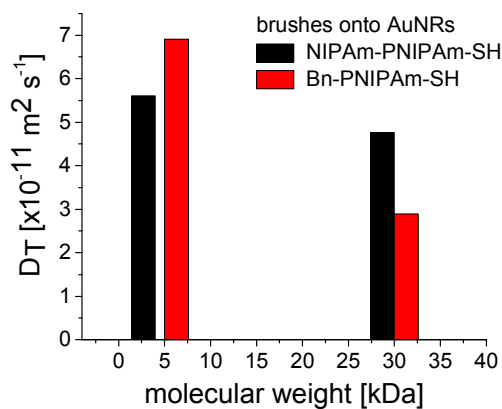
**S5. Transition temperature and changes in entropy for PNIPAm brushes onto AuNRs with NIPAm and Bn end groups measured by effective hydrodynamic radius.**

**Table S4. Transition Temperature ( $T_t$ ) and Normalized Change in Entropy  $|\Delta S|/k_B$ , Obtained by the Fits of z-Temperature Dependences with Two-State Model (Eq. (12), main text).**

Sample	$M_n$ [g mol <sup>-1</sup> ]	$T_t$ [°C] <sup>a</sup>	$ \Delta S /k_B$ <sup>a</sup>
NIPAm-PNIPAm-SH brushes onto AuNRs	12500	27.0	129.4
	45000	25.6	117.7
Bn-PNIPAm-SH brushes onto AuNRs	10000	25.0	138.4
	30000	28.5	122.2

<sup>a</sup>The estimated errors are of the order of 20%.

**S6. AuNRs Translational Diffusivity Measured by HRNMR Spectroscopy.**



**Figure S4.** Translational diffusivities of AuNRs with NIPAm-PNIPAm-SH and Bn-PNIPAm-SH brushes for two molecular weights. The NMR diffusometry measurements were made at 20 °C.

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