Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information:
Solvent-driven interactions between hydrophobically coated nanoparticles

1 Flory-Huggins parameter determination using the Hansen parameters or Hildebrand parameters as solubility parameters

Since the thiol part of the ligands is attached to the surface, the computation has been done using hexane parameters for 2C6 and n-dodecane parameters for 2C12. According to the regular solution theory, the Flory-Huggins interaction parameter can be expressed, as in polymer science, as a function of the Hansen solubility parameters of both solvent and ligand (labeled 1 and 2):

$$\chi_{12} = \frac{v}{RT}\left[(\delta_{1d}-\delta_{2d})^2 + 0.25(\delta_{1p}-\delta_{2p})^2 + 0.25(\delta_{1hb}-\delta_{2hb})^2\right] \tag{1}$$

where v is the solvent molar volume and the different parameters are related to the dispersive contribution (d), polar one (p) and hydrogen-bonding one (hb). Hildebrand approach has also been used to predict the Flory-Huggins parameters:

$$\chi_{12} = \frac{v}{RT}[(\delta_1-\delta_2)^2] + 0.34 \tag{2}$$

where the Hildebrand parameter corresponds to the dispersive Hansen parameter. The absolute values of the Flory parameter estimated by both approaches are quite different but the global tendency is the same and toluene is the less good solvent or even bad solvent of the list.

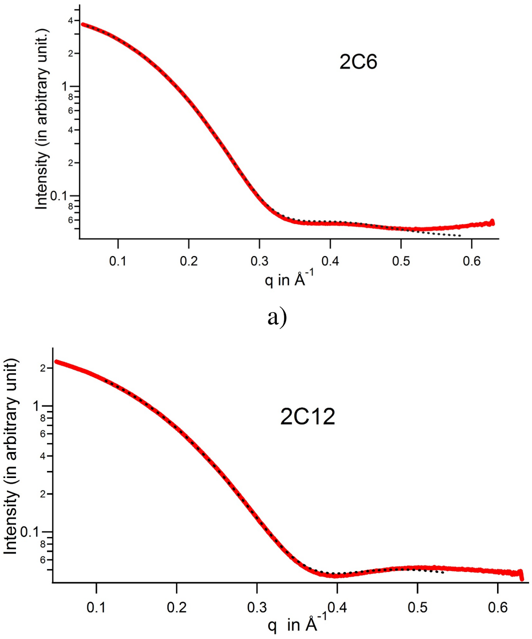
	Hansen parameters in MPa$^{1/2}$				Hildebrand parameter in MPa$^{1/2}$
Solvent	δ_d	δ_p	δ_{hb}		δ
n-hexane	14.9	0	0		14.9
n-dodecane	16.1	0	0		16.1
n-heptane	15.3	0	0		15.3
Cyclohexane	16.8	0	0.2		16.8
n-hexadecane	16.3	0	0		16.3
Toluene	18.2	1.4	2		18.2

Flory parameter	2C6 Hansen	2C6 Hildebrand	2C12 Hansen	2C12 Hildebrand
n-dodecane	0.126	0.49	0.000	0.34
n-heptane	0.009	0.35	0.038	0.39
Cyclohexane	0.157	0.5	0.022	0.36
n-hexadecane	0.231	0.57	0.005	0.34
Toluene	0.473	0.804	0.217	0.51

2 Characterization of Gold Nanoparticles

The core diameter of the gold NPs has been measured using Small Angle X-ray Scattering (SAXS). At low concentration, the structure factor is equal to 1 and the intensity is only related to the NP form factor. Only the gold core diameter can be measured with this technique since there is not enough contrast between the ligands and the solvent. The gold diameter distribution (mean size $\overline{D}$ and polydispersity p) has been determined considering a Schulz distribution $P(D,\overline{D},p)$ and using the NIST programs for fitting (http://www.ncnr.nist.gov/).

$$P(D,\overline{D},p) = \left(\frac{1}{p^2}\right)^{\frac{1}{p^2}} \left(\frac{D}{\overline{D}}\right)^{(\frac{1}{p^2}-1)} \frac{exp^{-\frac{1}{p^2}\frac{D}{\overline{D}}}}{\overline{D}\,\Gamma(\frac{1}{p^2})}. \tag{3}$$



a)

b)

Figure 1: SAXS pattern on dilute suspensions (1w% in n-dodecane) of 2C6 (a) and 2C12 (b) nanoparticles. The black dotted line is the best fit: with 2.4 nm mean diameter and 16% polydispersity for the 2C6 nanoparticules and with 2.25 nm mean diameter and 11% polydispersity for the 2C12 nanoparticules. Performed on Swing beamline (Soleil, FRANCE).

3 Method for extracting the structure factor from the measured radial intensity

The intensity $I(q)$ scattered by a NPs suspension is fitted for large q ($q > 0.2$ Å^{-1}) using a fit function

$$f(q) = A + B * FF(D, p) \tag{4}$$

related to the form factor $FF(D, p)$ of spheres with diameter D and polydispersity p, as given by the Schulz-Hardy distribution. A is some background taken as independent of q , B is related to the NPs concentration through scattering but also absorption. The structure factor for all values of q is then extracted using:

$$S(q) = (I(q) - A)/(B * FF(D, p)) \tag{5}$$

This procedure sets the value of $S(q)$ close to 1 for $q > 0.2$ Å^{-1}. Typical error on $S(q)$ can be estimated to 5%.

In order to remove the contribution from kapton windows on the D2AM beam line, the intensity $I(q)$ has been corrected by substracting the intensity scattered by pure solvent, normalized by the transmission and the exposure time.

4 Estimation of the interaction energy for 2C12 NPs modeled as hard spheres when suspended in cyclohexane and in toluene

The apparent hard sphere diameter D_{HSa} determined using the Percus-Yevick approximation depends on the solvent: $D_{HSa2} = 4.4$ nm in cyclohexane and $D_{HSa1} = 4.05$ nm in toluene. Since the apparent diameter D_{HSa} is larger than the diameter D_{HSe} predicted by considering full interpenetration of extended chains ($D_{HSa} > D_{12} + \ell_{12} = 2.2 + 1.6$ nm), the mixing energy for a distance between the NPs equal to this apparent diameter is given by Eq. 2. It can be easily computed using the Flory-Huggins parameter deduced from the Hansen solubility parameters: $\chi = 0.022$ for cyclohexane and $\chi = 0.22$ for toluene.

solvent	cyclohexane	toluene
χ	0.022	0.22
Solvent volume V_S in nm^3	0.179	0.177
Shell extension L=ℓ in nm	1.6	1.6
Ligand volume fraction in the shell	0.42	0.42
Hard sphere diameter	4.4 nm	4.05 nm
Ligand mixing energy in kT unit	1.6	1.75
van der Waal energy in kT unit	-0.05	-0.09