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Xu, Y., Konrad, M. P., Lee, W. W. Y., Ye, Z., & Bell, S. E. J. (2016). A Method for Promoting Assembly of Metallic and Nonmetallic Nanoparticles into Interfacial Monolayer Films. *Nano Letters*, 16(8), 5255-5260. DOI: 10.1021/acs.nanolett.6b02418

**Published in:**  
Nano Letters

**Document Version:**  
Peer reviewed version

**Queen's University Belfast - Research Portal:**  
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# A Method for Promoting Assembly of Metallic and Non-Metallic Nanoparticles into Interfacial Monolayer Films

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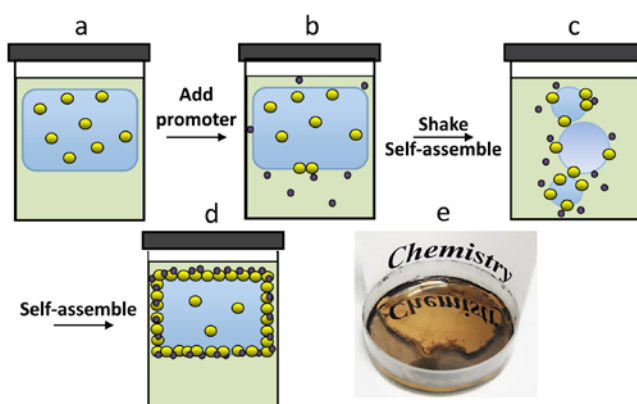
Abstract: 2-dimensional metal nanoparticle arrays are normally constructed at liquid-oil interfaces by modifying the surfaces of the constituent nanoparticles so that they self-assemble. Here we present a general and facile new approach to promoting such interfacial assembly without any surface modification. The method use salts which have hydrophobic ions of opposite charge to the nanoparticles, which sit in the oil layer and thus reduce the Coulombic repulsion between the particles in the organic phase, allowing the particles to sit in close proximity to each other at the interface. The advantage of this method is that since it does not require the surface of the particles to be modified it allows non-metallic particles including  $\text{TiO}_2$  and  $\text{SiO}_2$  to be assembled into dense interfacial layers using the same procedure as is used for metallic particles. This opens up a route to a new family of nanostructured functional materials.

KEYWORDS Self-assembly; 2-D arrays; liquid-liquid interface; charge screening

Self-assembly of nanoparticles (NPs) at liquid-liquid interfaces (LLI) offers a simple and graceful way to obtain defect-free 2-dimensional (2-D) array of NPs with numerous potential applications.<sup>[1-3]</sup> In early reports, silver particles of 10's of nm dimensions were assembled at the LLI to give highly reflective metal liquid-like films (MeLLFs).<sup>[4-6]</sup> This assembly was induced by attaching surfactant “modifiers” to the NPs which increased their hydrophobicity. More recently by modifying the hydrophobicity of the nanoparticles through careful selection of organic modifiers and performing contact angle measurements with dried MeLLFs obtained through a Langmuir-Blodgett method, Reincke et al. have shown that gold MeLLFs consisting of NPs with diameters between 8-40 nm had a near 90° contact angle at the interface.<sup>[7]</sup> This was supported by calculations of the partition of 10 nm NPs in liquid-oil systems, which showed that the NPs may only reside at the interface when the contact angle is close to 90°.<sup>[8]</sup> However, extending this contact angle tuning method to other NPs, particularly non-metals, is difficult since surface modification is often not straightforward and every new NP is effectively a special case.

More recently, molecular dynamics simulations of the assembly of charged 2 nm diameter gold NP monolayers at the interface of two immiscible electrolyte solutions under the influence of an external applied potential have brought interesting new insights. The simulations showed that the voltage-induced interfacial assembly process is accompanied by condensation of cationic counterions present in the oil phase onto the NPs, which shields their charge.<sup>[9]</sup> A similar effect was observed for highly hydrophilic charged silica NPs which were able to assemble at the liquid-liquid interface after reducing their charge by coagulating with their oppositely charged counter parts.<sup>[10]</sup> This is reminiscent of our observation that tetrabutylammonium nitrate ( $\text{TBA}^+\text{NO}_3^-$ ), which also has a cationic counterion, can be used to generate MeLLFs, although in this case the  $\text{TBA}^+$  cations do not absorb directly onto the particles.<sup>[11]</sup>

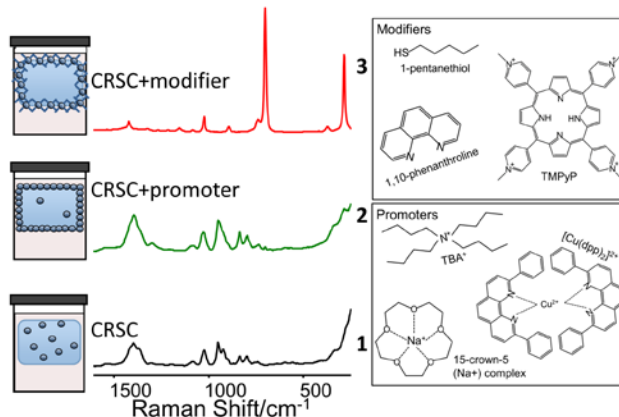
Here we provide extensive experimental evidence that  $\text{TBA}^+\text{NO}_3^-$  is merely a single example of a new class of “promoter” compounds, which promote interfacial assembly by altering the electrostatic forces between the particles rather than by altering hydrophobicity of the NPs’ surfaces like “modifiers”. By combining the “modifier” and “promoter” mechanisms, we are now able to explain the various well known methods to induce self-assembly of nanoparticle arrays at the liquid-liquid interface. Furthermore, this understanding has allowed us to control the interfacial assembly process to the extent that not only metal NPs but also alloys, mixed particle composites and even non-metallic NPs can be assembled without any surface modification of the particles.



**Figure 1.** Schematic representations of promoter-induced self-assembly of charged colloidal NPs at LLI (**a-d**). The blue layer and the olive green layer represent water and oil, respectively. The oil layer wraps around the water layer due to the surface of the reaction vessel being hydrophobic. Gold and purple spheres represent nanoparticles and promoter ions, respectively. (**e**) Photograph of a reflective gold MeLLF shown *in-situ*.

Typically, interfacial 2-D arrays were assembled through vigorous shaking of aqueous NP colloid with immiscible oil and a small concentration of promoter or modifier (see Figure 1 and

experimental section for full details). We have used surface-enhanced Raman spectroscopy (SERS) to study the metal NPs in the parent solution before and after interfacial assembly, since it allows the chemical composition of the surface of the enhancing material to be measured *in situ*. For example, in citrate-reduced silver colloid (CRSC), which is widely used in MeLLF formation,<sup>[7, 12]</sup> the NPs are stabilised by a surface layer of negatively charged citrate ions which can be observed by SERS (Figure 2). However, when the aqueous colloid is shaken with dichloromethane (DCM) and 1-pentanethiol to create a MeLLF, the SERS signal of the NPs in the interfacial array changes to that of the 1-pentanethiol modifier which has bound to the surface and increased the hydrophobicity. Indeed it was observations of this type that were used to support the “modifier” mechanism. This experiment can be repeated using a wide range of chemically disparate modifiers which give their own characteristic SERS spectra in the MeLLF, since they adsorb or bind to the particle surface (Table S1).<sup>[12-14]</sup> However, when  $\text{TBA}^+\text{NO}_3^-$  was used to induce MeLLF formation the SERS spectrum of the MeLLF did not show any  $\text{TBA}^+$  bands, it remained the same in the interfacial array as it was in the parent colloid. This observation was unexpected since the MeLLF can only form when  $\text{TBA}^+\text{NO}_3^-$  is added, if just the parent colloid and DCM are shaken together and allowed to settle the two immiscible phases separate with the NPs remaining dispersed in the aqueous layer. Moreover, further investigation revealed that this was not a special case, as direct *in situ* SERS measurement of MeLLFs formed with the aid of other compounds revealed that some which were initially reported as modifiers actually act as promoters (Table S1).



**Figure 2.** SERS spectra of the parent CRSC (1) compared with spectra of MeLLFs prepared from the same CRSC with a promoter, TBA<sup>+</sup> (2) and a modifier, 1-pentanethiol (3). As shown in schematics on the left, unlike modifiers that attach to the surface of the NPs, promoters do not change the surface chemistry of the NPs. A diversity of modifiers and promoters can be applied as shown on the right and in Table S1.

The promoters, like the modifiers, are chemically diverse and include transition metal complexes and crown ethers, as well as organic salts (Figure 2 and Table S1). However, despite this diversity, all the promoters that successfully induce formation of MeLLFs from negatively charged NPs have a common feature, they are all salts of hydrophobic cations. Simple water soluble metal halide salts do not act as successful promoters, nor do amphiphilic salts with hydrophobic anions. Conversely, we have found that MeLLFs can only be formed from positively charged NPs (see below) if the promoters are salts with hydrophobic anions. Therefore an essential quality for a successful promoter is that it contains a hydrophobic ion carrying an opposite charge to the NPs, which in turn suggests that in these systems the key interaction is between the nanoparticles at the interface and oppositely-charged ions in the oil phase. For simplicity, in the

following discussion we will concentrate on the case where the particles are negatively charged but all arguments work equally well for positively charged particles and anionic promoters.

The SERS data show that the promoters are not adsorbed onto the surface of the particles, or sufficiently close to be enhanced but they still need to be localised near the interface if they are to electrostatically interact with the nanoparticle film (see below). Inductively coupled plasma optical emission spectroscopy (ICPOES) measurements of the change in concentration of promoter which was initially added in the oil phase showed that approximately half the promoter was lost from the bulk organic phase on MeLLF formation (Table S2). Since the hydrophobic promoter cations would prefer to stay in the organic phase and SERS measurements have also conclusively shown that the promoters do not adsorb directly onto the NPs, this leaves the solution near the organic side of the interface as the only region where they can be located. It is clearly the promoters near the interface which stabilise the MeLLFs since the films remain intact even when the bulk organic phase containing the excess promoter is replaced with pure solvent. It should not be surprising that these promoter cations are attracted to sit near the interface since in the MeLLF the interface is completely covered with negatively charged particles.

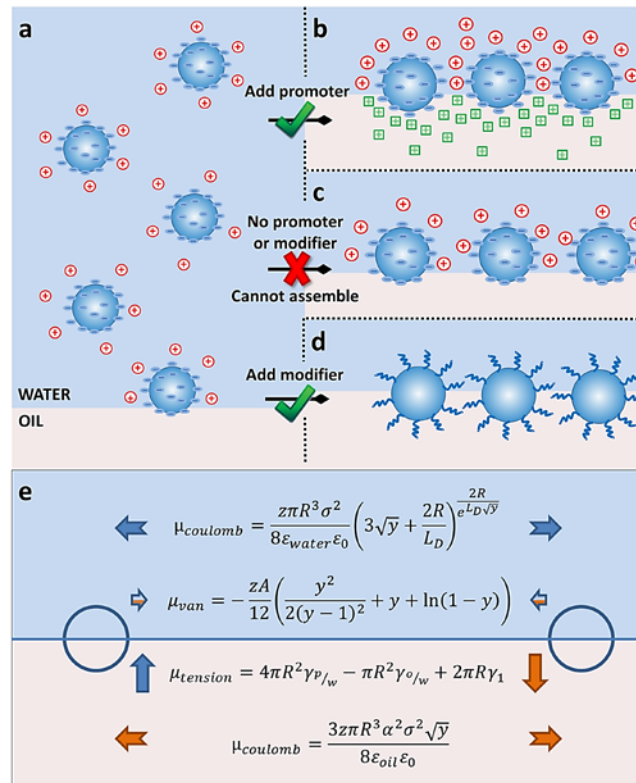
As shown in Figure 3e, for the case of particles which have a  $90^\circ$  contact angle with both phases, the main forces determining the total energy of a system of charged particles sitting at a LLI are the interfacial surface tension, Coulombic repulsion between the particles (which has 2 components that act through the aqueous and oil phases) and van der Waals attraction between the particles.<sup>[15-18]</sup> It should be noted that van der Waals attraction between NPs will also change along with the surrounding environment. However, this change is relatively small and van der Waals force is always attractive regardless of the NPs being in water or oil. Therefore van der Waals attractions between NPs from both phases were discussed together. In the absence of promoter or

modifier the particles predominantly reside in the aqueous phase (Figure 3a). The total free energy can be reduced by allowing some particles to move to the interface to reduce the interfacial energy,<sup>[19]</sup> but this can only proceed to the extent that the reduction in interfacial energy exceeds or equals the increased Coulombic repulsion between the NPs caused by localising them at the interface. Since the Coulombic repulsion is large, the number of particles which sit at the interface is low. Addition of a low (ppm) concentration of hydrophilic salts reduces the Coulombic repulsion in the aqueous phase but not in the oil phase. The result is that even after prolonged shaking, no change could be observed. The majority of the NPs remained dispersed in the colloid (Figure 3a) rather than assembling at the interface (Figure 3c), even though this would reduce the interfacial energy.

However, this balance of forces can be changed by adding a promoter such as  $\text{TBA}^+\text{NO}_3^-$  (or one of the others shown in Figure 2 and Table S1) which has a hydrophobic cation.  $\text{TBA}^+$  has a finite free energy of transfer between oil and water on the order of ca. 0.5 eV.<sup>[20]</sup> Dissolving amphiphilic salts of this type in an immiscible liquid-liquid system creates an interfacial potential and leads to the formation of regions on each side of the interface enriched in hydrophobic cations and hydrophilic anions. In the current case, the presence of the promoter cations at the oil side of the interface stabilises any NPs which partially submerge into the oil phase (Figure 3b) by screening the Coulombic repulsion between the negatively charged surfaces of the NPs in the oil layer, which means it is no longer the simple unscreened repulsion term (Figure 3e). The reduction in Coulombic repulsion, combined with the van der Waals attraction, allows the particles to pack closely together at the interface where they sit at a distance determined by the balance between the 2 forces in much the same way as is observed for salt-induced aggregation of metal NPs into 3-D clusters in simple aqueous solution. Importantly, this mechanism explains how the promoters can



cause assembly of NPs at the interface without adsorbing directly onto them. This mechanism is entirely different from that illustrated in Figure 3d where the surface of the particles is covered by strongly bonded modifiers which change their hydrophobicity ( $\gamma_{p/w}$ ) and/or the surface charge density ( $\sigma$ ).<sup>[21]</sup> The adsorption of NPs to the liquid-liquid interface is normally kinetically controlled relying on the Brownian motion of the NPs. Thus an external force (shaking) is applied to accelerate this process by bringing the NPs to the interface.



**Figure 3.** When aqueous colloid is mixed with immiscible oil, a few NPs are driven to the interface by the reduction of interfacial energy, while strong electrostatic repulsion keeps most NPs dispersed in the aqueous phase (a). Self-assembly (c) cannot be achieved. The addition of promoters (b) or modifiers (d) significantly weakens electrostatic repulsion between neighboring NPs by providing charge screening or removing NPs' surface charge. (e) Shows the forces

balancing two charged colloidal NPs with a contact angle of  $90^\circ$  between the two liquid phases.

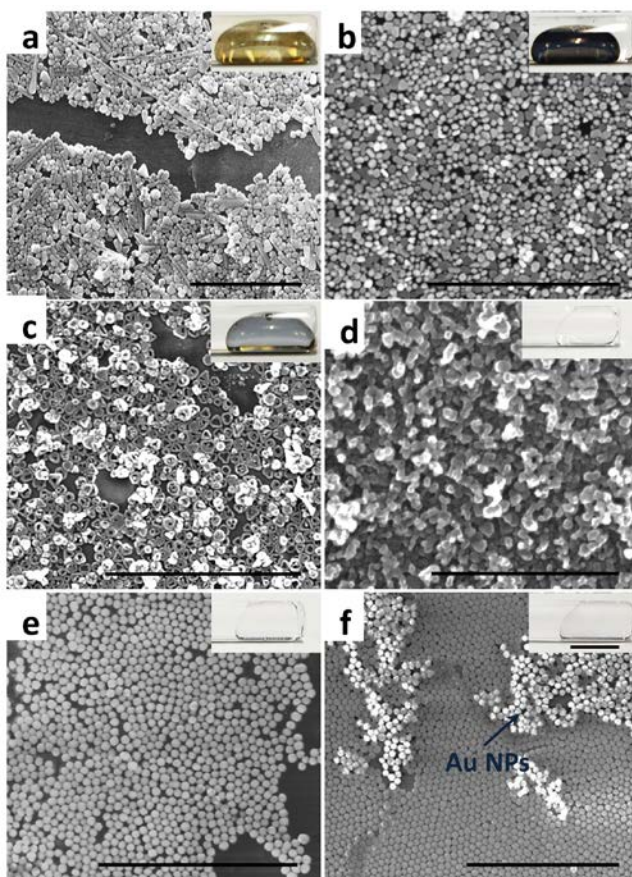
Definitions of symbols are given in Table S4.

Figures 3b and d illustrate two extreme cases, but MeLLF formation may be induced by a combination of both mechanisms.<sup>[6, 22]</sup> For example, some of the transition metal complexes used in early MeLLF studies were hydrophobic electrolytes that could provide charge screening but also could adsorb onto the particles, so they can potentially act as both promoter and modifier.

Since the promoter induced self-assembly mechanism relies on simple electrostatic interactions with unmodified particles, it is a remarkably general method for forming MeLLFs from charged metal NPs. In principle, the minimum amount of promoter required to induce self-assembly would be the amount needed to adequately screen the Coulombic repulsion between the particles and this will depend on many conditions such as the size of the interface, the morphology and surface properties of the NPs; the particle concentration etc. However, in practice this uncertainty is not a problem, a reasonable excess of promoter can be used routinely with all the particles without perturbing the system since the excess cations simply remain in the bulk solvent (as shown by ICP). This allowed us to successfully assemble MeLLFs composed of NPs formed from different metals with completely different morphologies, surface species and zeta potentials (from ca. -20 mV to -60 mV), as shown in Figures 4 and S1. Of course, if very high concentrations of promoter were necessary, the change in bulk ionic strength might lead to unwanted aggregation of the NPs in the aqueous phase. However, we found that even for colloids with a high  $\zeta$  of -60 mV, a promoter concentration of ca.  $4 \times 10^{-3}$  M of TBA<sup>+</sup> in the oil phase was sufficient, which is well below the concentration that gives uncontrolled aggregation. Also, since the primary role of the

oil phase is to provide a high energy interface with water, a diverse range of organic solvents, from hexadecane to chloroform (Table S3) can be used.

The promoter-induced method can also be applied to form 2-D arrays of metal alloys at the liquid-liquid interface. Figure 4c shows 2-D assemblies of negatively charged silver-gold nano-boxes formed with the aid of  $\text{TBA}^+$  promoters. Furthermore, positively charged NPs (created by modifying the negatively charged NPs) can be assembled into 2-D arrays using promoters containing a negatively charged hydrophobic anion such as tetraphenylborate ( $\text{TPB}^-$ ) (Figure S2).



**Figure 4.** (a-c) show MeLLFs formed with polygonal citrate reduced silver NPs, near spherical citrate reduced gold NPs (ca. 65 nm diameter) and silver-gold alloy nano-boxes respectively. (d-e) show NP 2-D arrays formed with polygonal titanium oxide NPs and spherical silica NPs (ca. 50 nm diameter). (f) shows a composite 2-D array formed with spherical gold (ca. 20 nm

diameter) and silica NPs. In images a, c and e areas of the samples with cracks were deliberately chosen to show the monolayer nature of the NP arrays. Scale bars in SEM images represent 1  $\mu\text{m}$ . Images in the top right corners show the particle films *in situ*, where they wrap a droplet of organic solvent which is sitting in water (scale bar representing 1 cm is shown in f).

Importantly, the charge screening method can be extended to the assembly of non-metallic NPs at the interface since it should work for any colloidal NP with a non-zero  $\zeta$ . Figure 4e shows a densely-packed monolayer of commercial silica NPs ( $\zeta = -47$  mV), assembled using  $\text{TBA}^+$  as the promoter. Similarly, P25  $\text{TiO}_2$  particles, which are widely used as photo-catalysts and under our experimental conditions carry a positive surface charge ( $\zeta = +50$  mV), were assembled into 2-D arrays using anionic  $\text{TPB}^-$  (Figure 4d).

Finally, we show that densely packed composites can also be prepared. Figure 4f shows a monolayer gold-silica composite prepared using a mixed aqueous phase containing both silica and gold NPs. A similar silver-silica composite is shown in Figure S3. Interestingly, in the mixed monolayers the two different kinds of NPs formed domains, possibly because of the van der Waals forces between NPs of the same type being more attractive than those between dissimilar particles.<sup>[23]</sup> Composite materials based on metal oxides in close contact with noble metal nanoparticle are interesting because of their potential for plasmon-induced hot electron generation.<sup>[24]</sup>

In summary, we report a novel method, supported with a detailed mechanism, to assemble vastly different NP 2-D arrays using promoters that provide charge screening between the particles at the interface instead of modifying their surface chemistry. The self-assembly system is remarkably

simple, consisting of only three components: the colloidal suspension of charged NPs, another immiscible liquid phase and a low concentration of promoter. NP 2-D arrays have immense potential as catalytic, photonic and conducting devices, they are also considered as basic building blocks for more sophisticated functional nano-devices. Because this approach allows for assembly of unmodified metal and non-metal NPs, it opens up an even broader range of applications than are possible with conventional 2-D metal NP arrays.

*Methods. Materials.* All chemicals used were ACS reagents purchased from Aldrich Ltd. and used without further purification unless otherwise stated. Silver nitrate and gold (III) chloride hydrate were of 99.9999% purity. SiO<sub>2</sub> colloid was obtained from nanoComposix Inc. 4-tert-butylcalix[4]arenetetramethylester, [Ru(BPY)<sub>3</sub>]Cl<sub>2</sub>, and TiO<sub>2</sub> colloid (40 wt%) were the kind gifts of Prof. M. A. McKervey, Dr. N. C. Fletcher and Prof. A. Mills, respectively. All experiments used low TOC (<3.0 ppb) 18.2 MΩcm water.

*Colloid preparation.* CRSC, citrate-reduced gold colloid (CRGC), hydroxylamine-reduced silver colloid (HRSC), borohydride-reduced silver colloid (BRSC) and silver-gold nano-boxes were prepared following literature methods.<sup>[25-30]</sup> The pHs of these colloids were slightly acidic ranging from 6-7. Highly mono-disperse CRGC with a mean particle diameter of 50 nm was obtained from BBI Solutions and used without any further modification. SiO<sub>2</sub> colloid was diluted by 10<sup>3</sup> with DDI water before being used. TiO<sub>2</sub> colloid was diluted by 2 × 10<sup>3</sup> with DDI water. Concentrated HCl (aq.) was used to tune the pH of the colloid to ca. 2 to give the colloid a highly positive ζ (ca. +50 mV).<sup>[31]</sup>

Mercaptopropenesulfonate (MPS) functionalized negatively charged BRSC and silver-gold nano-boxes were obtained by adding 1% (v/v) 10<sup>-3</sup> M MPS (aq.). The excess MPS and other ionic

species were removed by centrifugation and resuspension in DDI water. The process was repeated several times if necessary. The final  $\zeta$  varied for each batch but was always strongly negative at ca. -30 mV.

Positively charged colloids were prepared by functionalizing the colloids used above with thiocholine as reported in literature with slight modifications.<sup>[32]</sup> Prior to thiol modification, all colloids (apart for HRSC) were capped with  $\text{Br}^-$  by adding 2% (v/v) 0.01 M KBr (aq.) then centrifuged and resuspended in DDI water to remove excess ions. The process was repeated until peaks of the initial capping agents on the NPs could not be seen in the SERS spectrum of the colloid. The resulting colloid was added dropwise over 10 min into vigorously stirred 1% (v/v)  $10^{-4}$  M thiocholine (aq.). The resulting colloid was centrifuged to remove aggregates. The supernatant was centrifuged once more and resuspended in DDI water to give the final positively-charged colloid. The final  $\zeta$  varied for each batch but was always strongly positive at ca. +25 mV.

Centrifugation conditions varied for NPs of different size. For colloids consisting of NPs < 20 nm diameter, centrifugation was carried out at 4000 rcf for 1.5 h; for ca. 20-60 nm colloids centrifugation was carried out at 3200 rcf for 1 h; for > 60 nm colloids, centrifugation was carried out at 3000 rcf for 1h. For removal of aggregates, all colloids were centrifuged at 1000 rcf for 5 min.

*Protocol for interfacial self-assembly.* Self-assembly was carried out at room temperature. MeLLFs,  $\text{SiO}_2$ ,  $\text{TiO}_2$  2-D arrays and 2-D composites were obtained by vigorously shaking 5 mL of aqueous colloid with 3 mL of organic solvent (normally DCM) in the presence of 1.3 mL of  $10^{-6}$ - $10^{-3}$  M of modifier/promoter for 1-3 minutes (40 minutes in the case of 1-dodecanthiol). For consistency the volume ratio between oil and aqueous colloid was always 3:5 unless otherwise stated. However this volume ratio is not strictly required for self-assembly. Drops of emulsion

with NPs at the interface would form and coalesce together, leading to the formation of a 2-D film at the liquid-liquid interface. Non-water soluble modifiers were dissolved in the organic solvent before mixing. Water soluble modifiers were normally added directly to the aqueous-oil mixture. MeLLFs were prepared *in situ* in a cylindrical, stoppered quartz vials which were regularly treated with saturated NaOH (aq.) solution (~12 hours) and thoroughly washed to ensure that their surfaces were hydrophilic. With these sample containers the MeLLFs formed so that the films surrounded the organic phase at the bottom. For assembly of 2-D composites, the aqueous phase consisted of a mixture of diluted silica colloid with CRGC (CRSC). The volume ratio between diluted silica colloid and CRGC (CRSC) prepared in house was 1:1. The volume ratio between diluted silica colloid and commercial CRGC was 1:4.

*Instrumentation.* Conventional optical images were taken with a Nikon COOLPIX L820. SEM was performed with a Quanta FEG 250 at an acceleration voltage of 20 kV under high chamber vacuum (under  $8 \times 10^{-5}$  mbar) with standard SEM copper tape or carbon tape as background. All images of samples containing SiO<sub>2</sub> NPs were acquired under low chamber vacuum (0.9 mbar). SEM samples were made by lifting MeLLFs horizontally from the interface with a thin polystyrene substrate. Zeta potential measurements were carried out on a Zetasizer Nano ZS (Malvern Instruments Ltd., U.K.). SERS spectra were obtained using a 785 nm benchtop Raman spectrometer (Avalon Instruments, RamanStation) operated in 180° backscattering configuration with a horizontal excitation/collection axis. The spectra of the MeLLFs were collected by focusing the laser onto the vertical section of the film which lay against the side walls of the containers. This minimized any potential scattering from the aqueous phase, which in some cases also contained colloidal nanoparticles that had not been drawn into the film (see Figure 2d). ICPOES measurements were run on a Perkin Elmer Optima 4300 DV Inductively Coupled Plasma Optical

Emission Spectrometer in conjunction with a Perkin Elmer AS-93 plus autosampler. Three MeLLF samples were prepared for investigation. Each sample consisted of 6.86 mL of DCM, 140  $\mu$ L of  $5 \times 10^{-5}$  M non-aqueous solution of  $[\text{Cu}(\text{dmp})_2]\text{BF}_4$  (total concentration of the modifier in the sample  $\sim 1 \times 10^{-6}$  M) and 12 mL of CRSC. On shaking, the NPs assembled at the interface, forming a reflective MeLLF. The upper (aqueous) phase was then removed using a glass pipette until the liquid/liquid interface broke and the organic phase was exposed to the air. 5 mL of the organic phase was then immediately removed and poured into a 5 mL volumetric flask. The solutions obtained this way were evaporated naturally over the next three days. Subsequently, the residue remaining on the bottom of the vessels was dissolved in 10 % solution of MeOH and then analysed.

#### ASSOCIATED CONTENT

**Supporting Information.** This material is available free of charge via the Internet at <http://pubs.acs.org> or from corresponding author.

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##### **Funding Sources**

M.P.K. was supported by an ESF research studentship.

##### **Notes**

The authors declare no competing financial interests.

#### ACKNOWLEDGMENT



We thank Prof. A. P. de Silva for his valuable suggestions on the manuscript, Prof. M. A. McKerverey, Dr. N. C. Fletcher and Prof. A. Mills for 4-tert-butylcalix[4]arenetetramethylester, [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> and TiO<sub>2</sub> colloid, respectively.

## ABBREVIATIONS

Nanoparticles, NPs; liquid-liquid interfaces, LLI; 2-dimensional, 2-D; metal liquid-like films, MeLLFs; tetrabutylammonium nitrate, TBA<sup>+</sup>NO<sub>3</sub><sup>-</sup>; surface-enhanced Raman spectroscopy, SERS; citrate-reduced silver colloid, CRSC; dichloromethane, DCM; Inductively coupled plasma optical emission spectroscopy, ICPOES; tetraphenylborate, TPB<sup>-</sup>.

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