ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

On the non-innocence of the imidazolium cation in a rapid microwave synthesis of oleylamine-capped gold nanoparticles in an ionic liquid

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Experimental Section

Materials and Reagents

Oleylamine (O7805, technical grade, 70%), gold(III) chloride trihydrate (520918, ≥99.9% trace metal basis), toluene (244511, anhydrous, 99.8%), and methanol (34860, HPLC grade, ≥99.9%) were all purchased from Sigma-Aldrich (St. Louis, MO). The ionic liquids (ILs) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [Bmim][Tf_2N], 1-butyl-3-methylimidazolium trifluoroacetate, [Bmim][TFA], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_4mpy][Tf_2N], and 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_6mpy][Tf_2N] were made using details reported elsewhere.[1, 2] The preparation of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [Bmmim][Tf_2N] was also prepared following similar methods to those described in ref. 1.

Characterization Techniques

A Bruker AVIII 500 MHz NMR spectrometer was used to characterize the ionic liquids. All UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using 1 cm pathlength quartz cuvettes (Starna Cells, Inc., 23-Q-10). Transmission electron microscopy (TEM) studies were conducted on carbon coated copper grids (Ted Pella, Inc. 01814-F, support films, carbon type-B, 400 mesh copper grid) using a FEI Tecnai (F20 G2, Twin) microscope operated at a 200 keV accelerating electron voltage.

Conventional ("Hot-Injection") Synthesis of AuNPs

In a typical synthesis, 0.1 g (0.37 mmol) of oleylamine (OAm) and 1 g of ionic liquid were added to 5 mg (0.013 mmol) of gold(III) chloride trihydrate ($HAuCl_4$), which had been obtained by solvent evaporation of 0.50 mL of its 10 mg/mL EtOH stock solution, and this mixture was then injected into a hot solution (120 °C) of 0.2 g (0.74 mmol) OAm in 4 g of IL. The reaction proceeded for 1 h and was then allowed to cool naturally. Once cooled to room temperature, 10 mL of methanol was added to the solution and the particles were isolated by centrifugation (8000 rpm for 5 min). The supernatant was carefully discarded and this washing process was repeated two more times with 10 mL portions of methanol. The final product (AuNP pellet) was dispersed into 5 mL of toluene and transferred to a glass vial for dark storage.

[C_4mpy][Tf_2N] Recyclability in Conventional (Thermal) Synthesis

Initial reaction using fresh [C_4mpy][Tf_2N]

For the initial AuNP synthesis, the experimental steps were identical to those outlined above, however, after the first centrifugation, instead of discarding the supernatant, it was set aside while the resultant AuNPs were further washed one additional time. The collected supernatant (which consisted of [C_4mpy][Tf_2N], OAm, and methanol) was dried on a rotary evaporator to remove methanol and then a ^{1}H NMR spectrum was collected (Fig. S16) to determine the fate of the [C_4mpy][Tf_2N] and OAm. Based on NMR results, the amount of OAm was determined to be 9.67 mol% (relative to [C_4mpy][Tf_2N]) by comparing the intensities of the methyl group of OAm (δ = 0.90) with that of the IL (δ = 1.02). This OAm to [C_4mpy][Tf_2N] ratio was nominally the same as the initial ratio (9.47%), determined as follows:

$$\frac{\text{Moles OAm}}{\text{Moles IL}} = \frac{\dfrac{\text{Mass OAm}}{\text{Molecular weight OAm}}}{\dfrac{\text{Mass IL}}{\text{Molecular weight IL}}} = \frac{\dfrac{0.3\text{ g}}{267.5\text{ g/mol}}}{\dfrac{5\text{ g}}{422.41\text{ g/mol}}} = 0.0947 \times 100\% = 9.47\%$$

Additionally, on a mass basis (recovered mass/starting mass = 4.84 g/5.30 g), about 91% of the original [C_4mpy][Tf_2N] plus OAm mass was recovered.

Second reaction using recycled [C_4mpy][Tf_2N] medium

To test the recyclability of [C_4mpy][Tf_2N], 4.0 g of the recovered [C_4mpy][Tf_2N] + OAm mixture—simply denoted the [C_4mpy][Tf_2N] medium—was placed in a two-necked round-bottomed flask and heated to 120 °C. The remaining recovered mixture (0.84 g) plus 0.16 g of fresh [C_4mpy][Tf_2N] were added to 5 mg of $HAuCl_4$ which was then injected into the flask. UV-vis spectra and TEM images were collected for the resultant cleaned-up AuNPs (Figs. 2 and S15) and NMR analysis was conducted on the recycled [C_4mpy][Tf_2N] medium (Fig. S19). For the second reaction, about 96% of the original [C_4mpy][Tf_2N] medium was recovered on a mass basis (recovered mass/starting mass = 4.80 g/5.00 g).

Third reaction using twice-recycled [C_4mpy][Tf_2N] medium

The used [C_4mpy][Tf_2N] medium was recycled a second time following an identical protocol as above. That is, 4.0 g of the recovered [C_4mpy][Tf_2N] medium from the second reaction was placed into a two-neck round-bottom flask and heated to 120 °C. The remaining recovered mixture (0.80 g) and 0.20 g of fresh [C_4mpy][Tf_2N] were added to 5 mg of $HAuCl_4$ which was then injected into the flask. UV-vis and TEM analysis were conducted on the resultant AuNPs (Figs. 2 and S15).

Microwave Synthesis

In a typical synthesis, 0.3 g (1.11 mmol) of OAm and 1.0–5.0 g of IL were added to 5 mg (0.013 mmol) of $HAuCl_4$ (which had been obtained by solvent evaporation of 0.50 mL of its 10 mg/mL EtOH stock) and this mixture was placed into a 10 mL glass microwave vial. A commercial research-grade microwave reactor (CEM Corporation, Discover SP, Model # 909150) was set to pre-stir the solution for 1 min prior to ramping the temperature at an approximate rate of 1.58 °C/s to a final temperature of 50–120 °C, which was held for 10–120 s. All other microwave reactor parameters were kept at their default setting. Once the reaction was completed, 5 mL of methanol was added to the solution and the particles were isolated by centrifugation (8000 rpm for 5 min). This washing process was repeated two more times again using 5 mL portions of methanol. The final product was dispersed in 5 mL of toluene and transferred to a glass vial for storage. By adjusting experimental parameters (*i.e.*, the IL mass used, reaction temperature, reaction time) and monitoring the corresponding UV-vis profiles, a preliminary optimization of the MW reaction conditions was achieved: 0.3 g (1.11 mmol) of OAm and 5 mg (0.013 mmol) of $HAuCl_4$ in 2.5 g of IL for a 30 s MW reaction at 100 °C. Additionally, a control study was conducted in which OAm was omitted from the reaction. For this study, 5 mg of $HAuCl_4$ and 2.5 g of IL were microwave treated at 100 °C for 30 s. Upon cooling to room temperature, a single washing step was conducted in which 5 mL of methanol was added, vortexed, and the solution then centrifuged at 8000 rpm for 5 min. The supernatant was carefully decanted and the centrifuge tube rinsed with toluene. As shown in Table S2, neither the supernatant nor the purified sample displayed the plasmonic features expected for AuNP formation.

[C_4mpy][Tf_2N] Recyclability following Microwave Synthesis

In similar fashion to the conventional thermal reaction IL reusability studies described above, the [C_4mpy][Tf_2N] medium previously used for microwave reaction was dried via rotary evaporation to remove residual methanol. The recycled [C_4mpy][Tf_2N] medium was evenly distributed into two different microwave reaction vials each containing 5 mg of $HAuCl_4$. Fresh

OAm (0.3 g) was added to only one of the vials and then the individual mixtures were microwave heated at 100 °C for 30 s. Upon cooling, samples were washed with 5 mL of methanol followed by centrifugation at 8000 rpm for 5 min. The washing step was repeated and the final products dispersed into 5 mL of cyclohexane. Each purified sample was then transferred into two quartz cuvettes; *i.e.*, two cuvettes containing AuNPs made with addition of fresh OAm to the recycled [C_4mpy][Tf_2N] and two cuvettes of AuNPs prepared from once-used [C_4mpy][Tf_2N] alone. One cuvette of each sample type was then stored within a lab drawer at room temperature while the other was stored in a conventional freezer at –20 °C. All four cuvettes were sealed with Teflon caps and DuraSeal™ laboratory stretch film prior to storage.

AuNP Solvent Dispersibility and Storage Studies

For *dispersibility* studies, toluene was allowed to ambiently evaporate from the AuNPs, followed by attempts to re-disperse the dried AuNPs into a range of solvents (Table S3). For time-dependent studies of *storage stability*, AuNPs were stored in one of three physical states: (i) as a solvent dispersion at room temperature (kept in a lab drawer); (ii) as a frozen cyclohexane dispersion within a –20 °C freezer; or (iii) as a powder dried under ambient conditions (kept in a lab drawer). For the latter case, 0.15 mL of AuNPs in cyclohexane was pipetted into a small vial and the cyclohexane was allowed to evaporate in a fume hood. After a pre-defined time period, the dried sample was re-dispersed in 0.15 mL of cyclohexane and a UV-vis spectrum acquired to monitor the localized surface plasmon resonance (LSPR) band. This process of drying, re-dispersion, and UV-vis spectral acquisition was repeated at set time intervals to monitor temporal colloidal stability during “dry” storage.

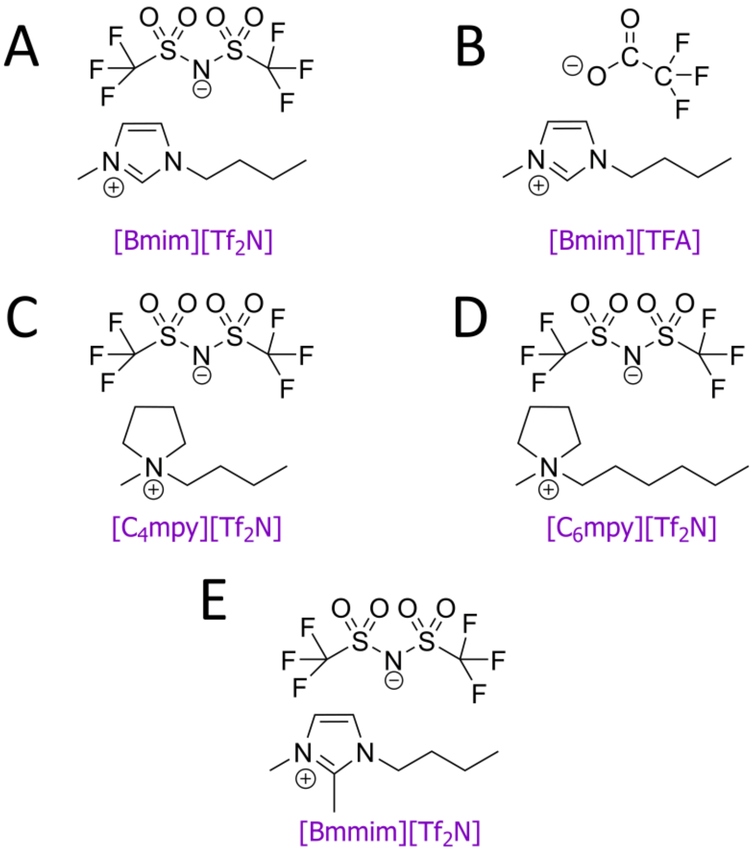


Fig. S1 Structures of the various ionic liquids tested within this work: (A) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [Bmim][Tf_2N], (B) 1-butyl-3-methylimidazolium trifluoroacetate, [Bmim][TFA], (C) 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_4mpy][Tf_2N], (D) 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_6mpy][Tf_2N], and (E) 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [Bmmim][Tf_2N].

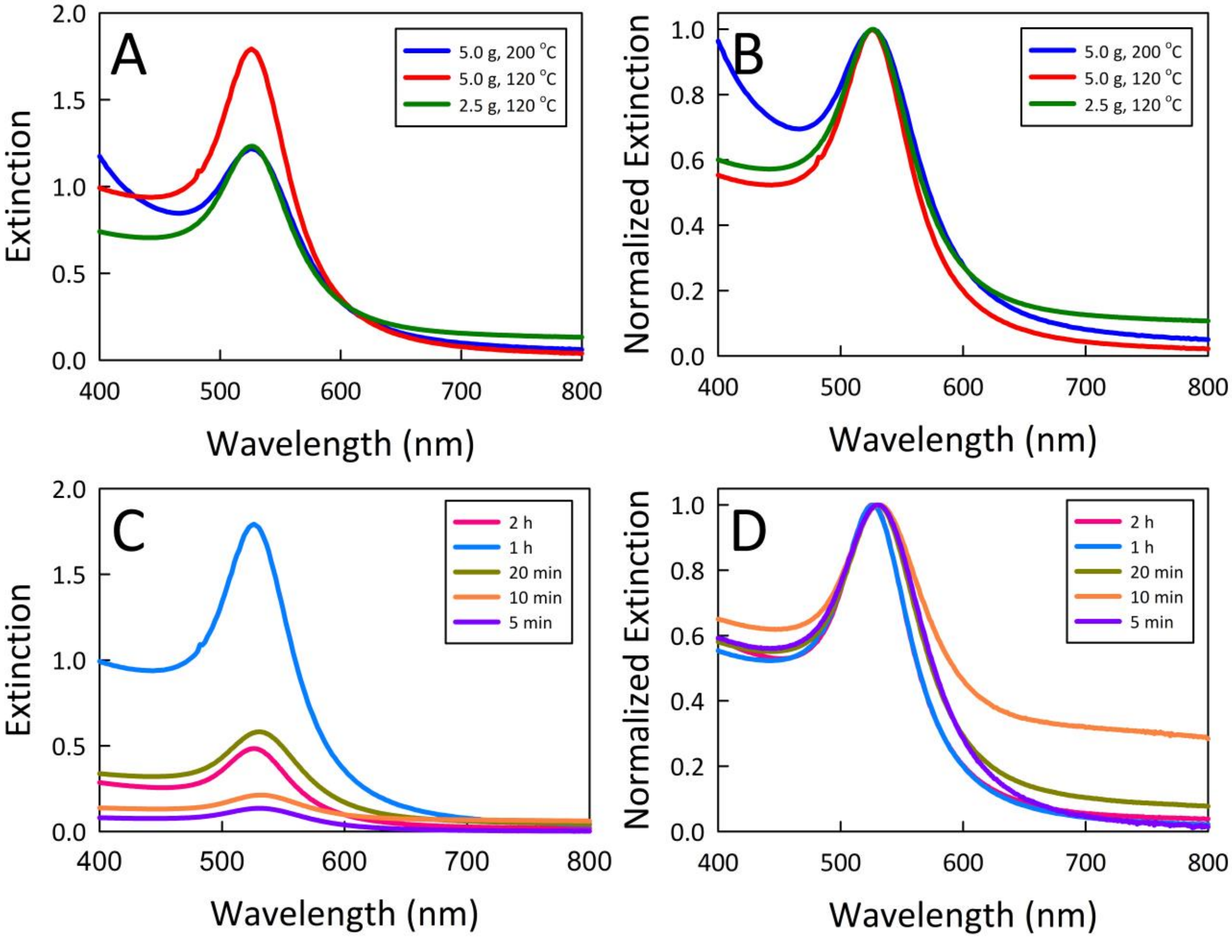


Fig. S2 Conventional approach optimizations of the reaction temperature and [C_4mpy][Tf_2N] quantity (A) as well as the reaction time (C). The corresponding normalized extinction plots are provided in panels B and D. Note that for optimization of the reaction time (panels C and D), the reactions were conducted at 120 °C using 5.0 g of [C_4mpy][Tf_2N].

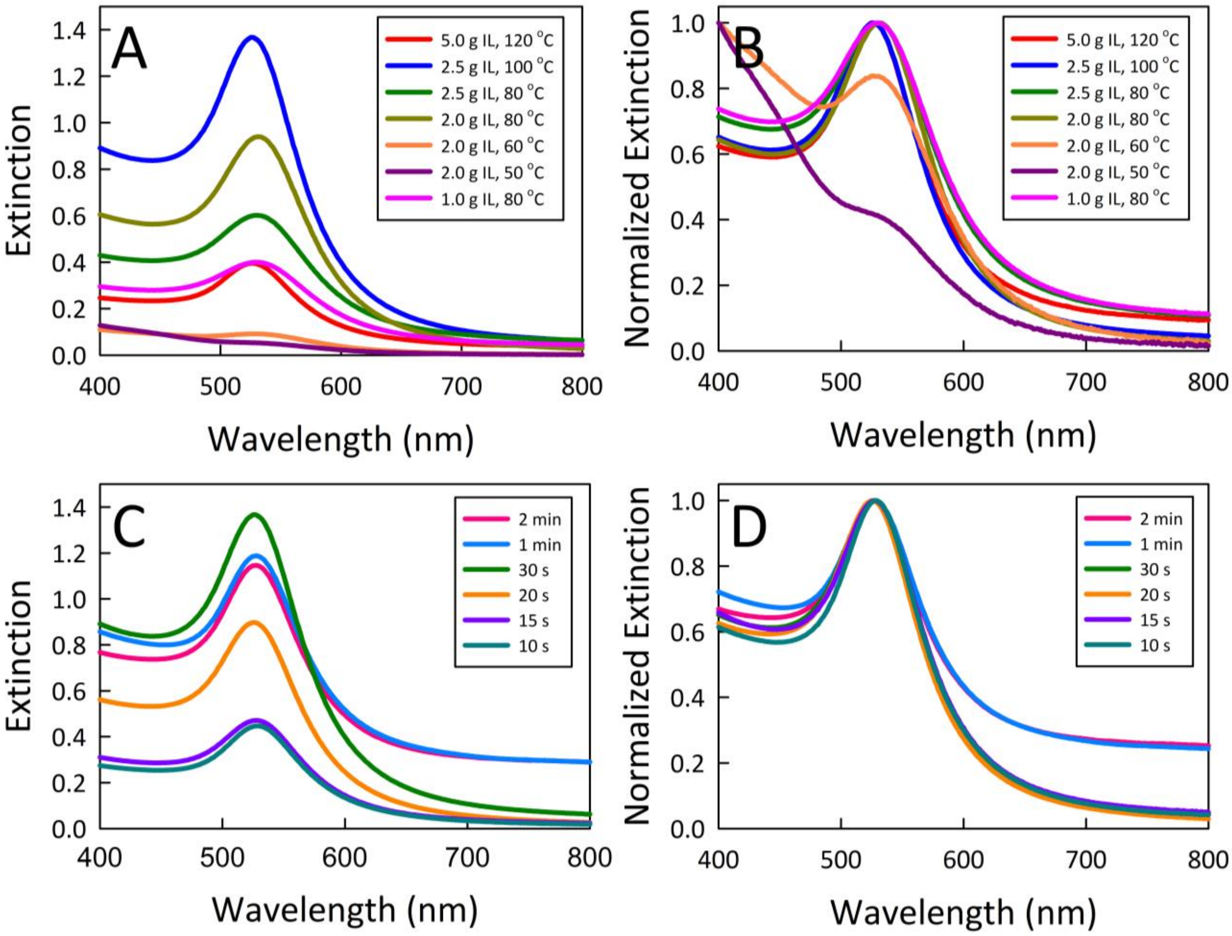


Fig. S3 Microwave approach optimizations of the reaction temperature and [C_4mpy][Tf_2N] quantity (A) as well as the reaction time (C). The corresponding normalized extinction plots are provided in panels B and D. Note that for the optimization of the reaction time (panels C and D), the reactions were conducted at 100 °C using 2.5 g of [C_4mpy][Tf_2N].

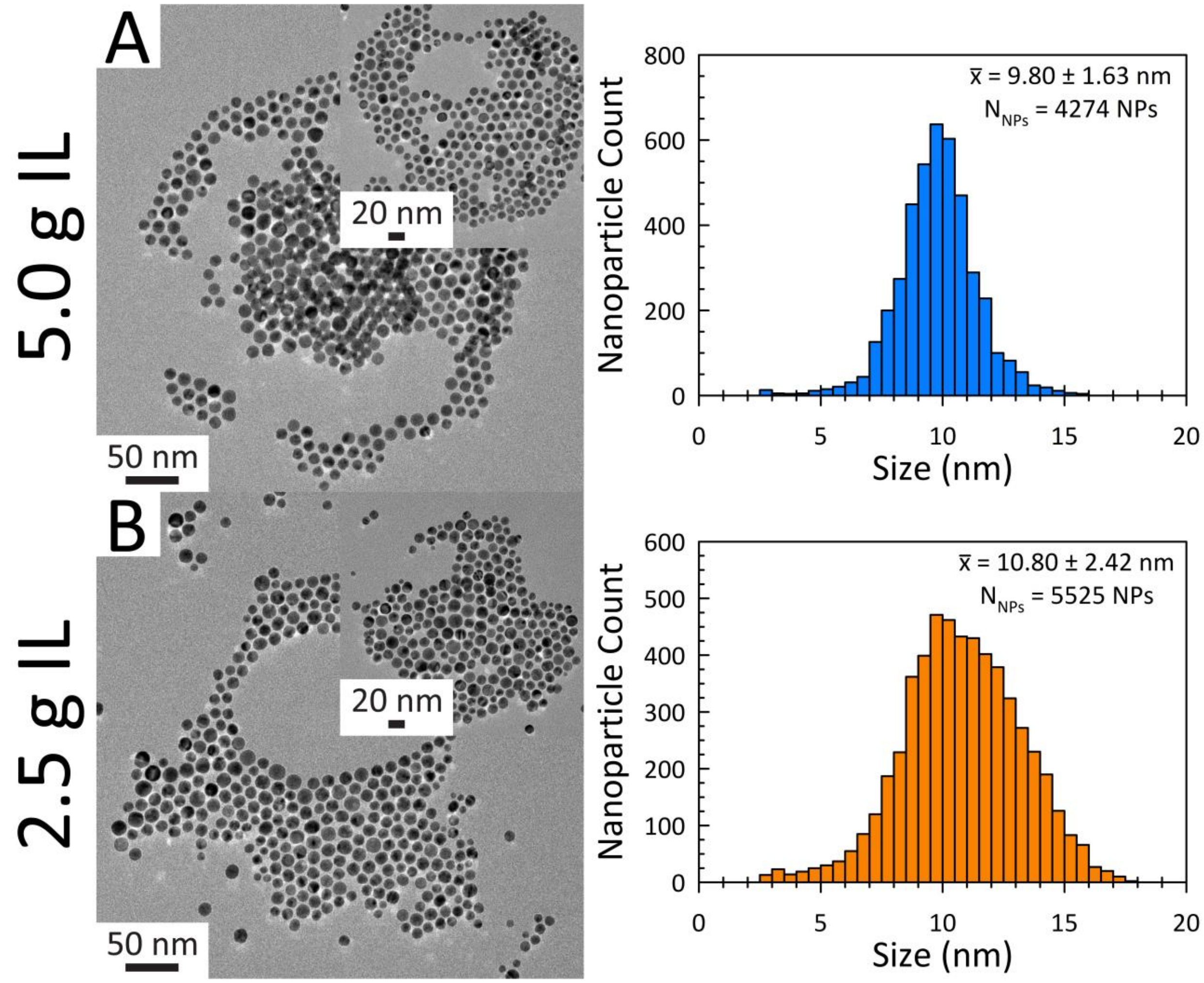


Fig. S4 Representative TEM images of AuNPs synthesized through the conventional method using (A) 5.0 g of [C_4mpy][Tf_2N] and (B) 2.5 g of [C_4mpy][Tf_2N]. The respective histograms are shown to the right of the TEM images. Decreasing the quantity of IL employed led to a ~10% larger average AuNP diameter and greater polydispersity.

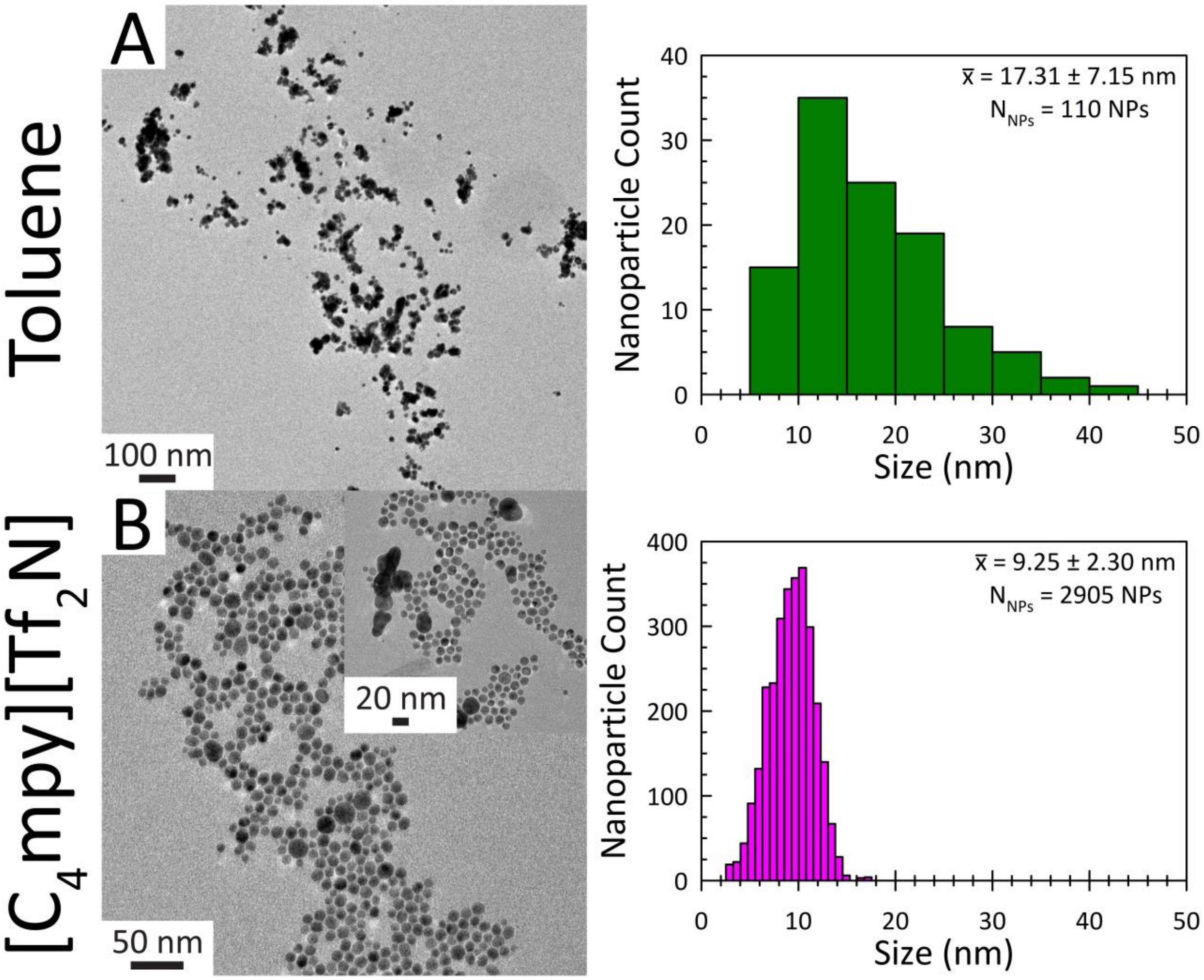


Fig. S5 Representative TEM images of AuNPs synthesized via the microwave method using (A) toluene or (B) [C_4mpy][Tf_2N] as the solvent. The synthetic conditions were as follows: 5 mL of toluene or 5 g of IL were heated at 120 °C for 30 s in the presence of Au precursor. When employing toluene, the resultant AuNPs were large, irregular structures that were highly aggregated while [C_4mpy][Tf_2N] produced AuNPs that were comparable to those generated following a conventional thermal method (see Fig. S4).

Table S1. Images of the resulting post-reaction solutions when varying the [C_4mpy][Tf_2N] quantity and the synthesis temperature in the microwave approach. At temperatures of 80 °C or higher, all [C_4mpy][Tf_2N] quantities tested showed clear evidence of AuNP formation while temperatures lower than 60 °C produced lighter colored samples, potentially indicating minor formation of AuNPs. The studies employing toluene displayed slight or no indication of the successful formation of colloidally-stable AuNPs.

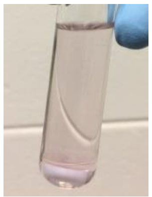
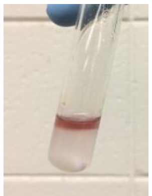
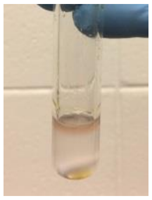
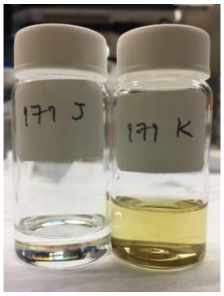
Temp	**[C_4mpy][Tf_2N]**				**Toluene**
	5 g	**2.5 g**	**2.0 g**	**1.0 g**	
120 °C					5 mL toluene 
100 °C					
80 °C					1 mL toluene 
60 °C					
50 °C					

Table S2. Images of a microwave heating control study in which only $HAuCl_4$ and $[C_4mpy][Tf_2N]$ were microwave treated (*i.e.*, OAm was omitted from the reaction mixture). Upon purification of the post-reaction sample (far-right panel), it was evident that without OAm present in the reaction mixture colloidally-stable AuNPs were not formed (left vial in the right most panel). The deep brown color of the solution after reaction (middle panel) and dark yellow color of the supernatant (right vial in the far-right panel) are attributed to the browning/degradation of the IL and/or any unreduced $HAuCl_4$, respectively.

Before reaction	**After reaction**	**Left: purified sample; Right: supernatant**
		

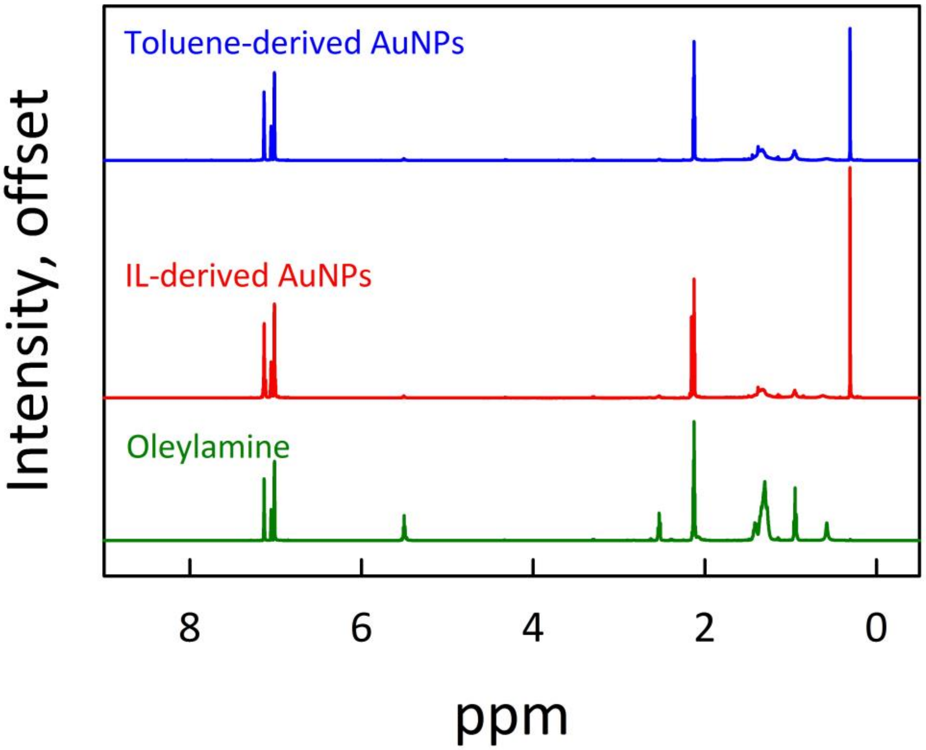


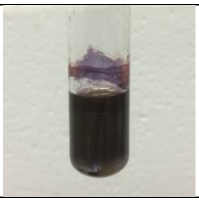
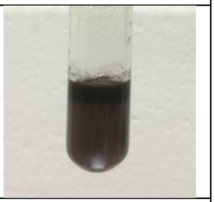
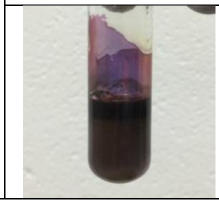
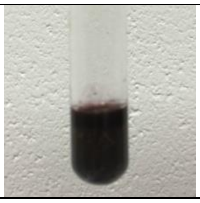
Fig. S6 ^{1}H NMR spectra of (bottom to top) OAm, [C_4mpy][Tf_2N]-derived AuNPs, and toluene-derived AuNPs in toluene-d_8 which demonstrate that the AuNPs are capped primarily by native OAm and not by its putative oxidation product (*i.e.*, oleylamide). Each spectrum was normalized to the toluene singlet peak at δ = 2.1 ppm.

Table S3. Dispersibilities of MW-generated AuNPs within different organic solvents.

Solvent	Yes/No	Note
Toluene	Yes	These products gave ruby-red dispersions.
Hexane	Yes	
Cyclohexane	Yes	
Chloroform	Yes	
Fluorobenzene	Yes	
Tetrahydrofuran	Yes	
Triethylamine	Yes	
Methanol	No	
Ethanol	No	
Dimethylformamide	No	
Acetonitrile	No	
Dimethyl sulfoxide	No	These two products were not promptly dispersed in the solvents: they required sonication and yielded just pale pink dispersions.
Ethylene glycol	No	
[a] $[P_{14,666}][Tf_2N]$	No	
[b] $[P_{14,666}][C_7SO_3]$	No	

[a] $[P_{14,666}][Tf_2N]$ = trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide
[b] $[P_{14,666}][C_7SO_3]$ = trihexyltetradecylphosphonium 1-heptanesulfonate

Table S4. Images of AuNP products obtained immediately after synthesis in $[C_4mpy][Tf_2N]$ for reaction time optimization using a microwave approach. All reactions were conducted with 2.5 g of $[C_4mpy][Tf_2N]$ at 100 °C.

Temp	Time			
	30 s	20 s	15 s	10 s
100 °C				
	Time			
	1 min	2 min		
				

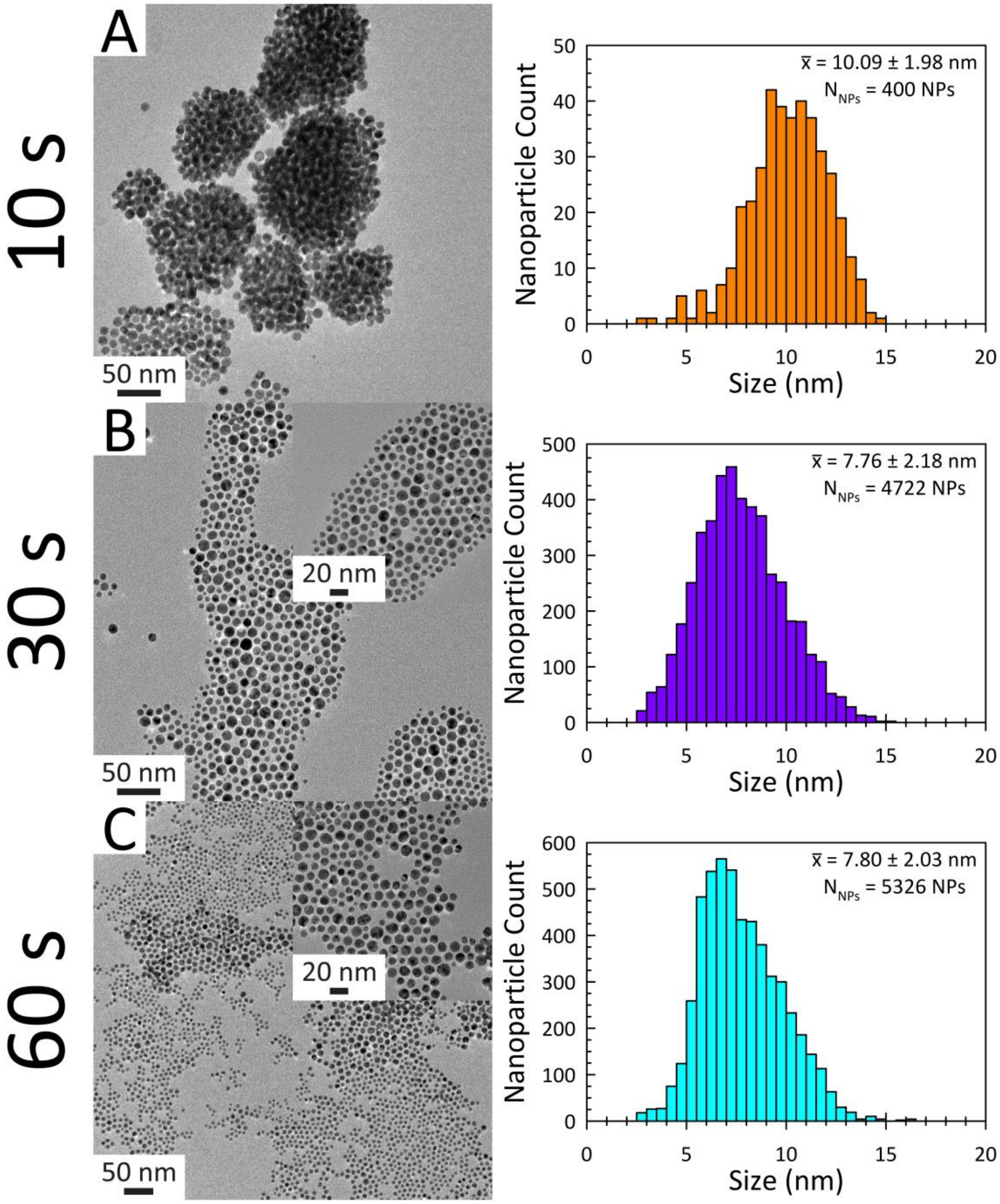


Fig. S7 Representative TEM images of AuNPs synthesized in [C_4mpy][Tf_2N] using the microwave method, where the samples (containing 2.5 g of IL) were microwave treated at 100 °C for (A) 10 s, (B) 30 s, or (C) 60 s. The results demonstrate the following: 1) AuNPs comparable to results from a conventional method can be obtained for microwave heating of the sample for only 10 s; 2) longer reaction times using these synthetic conditions produced AuNPs that were, on average, approximately 2.3 nm smaller than a 10 s treatment; and 3) cutting the IL quantity in half from 5.0 g to 2.5 g and decreasing the synthesis temperature from 120 °C to 100 °C yielded smaller AuNPs than the original synthetic conditions (compare Figs. S5B and S7B).

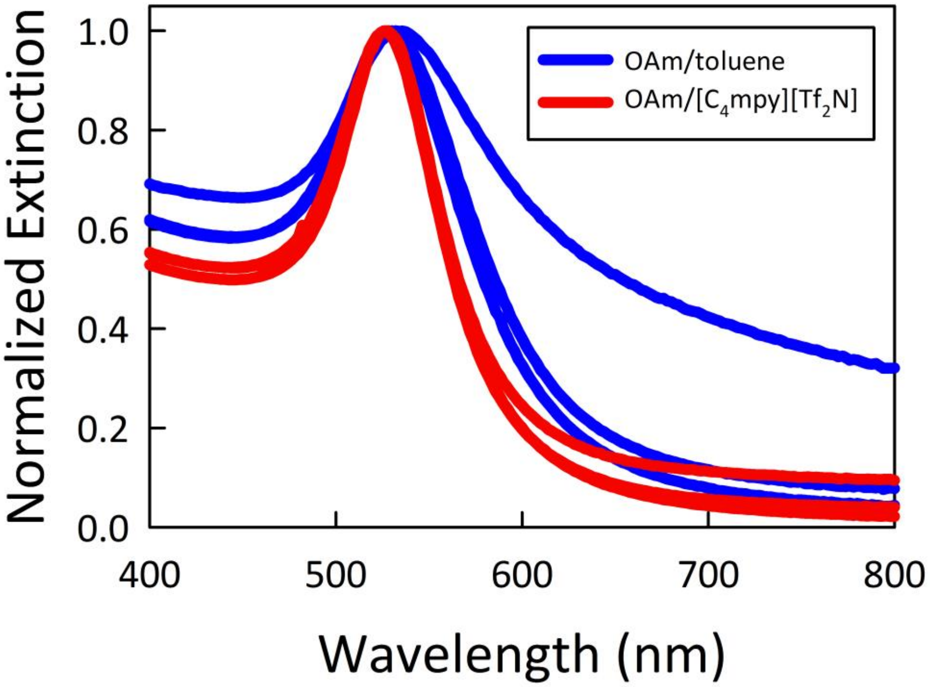


Fig. S8 Normalized absorbance spectra of the resultant AuNP solutions from a conventional approach employing either [C_4mpy][Tf_2N] (red curves) or toluene (blue curves) as the reaction medium. The results of three representative reactions in each solvent system are shown. The spectra demonstrate that, in our approach, AuNPs can be more reproducibly generated when using [C_4mpy][Tf_2N] as the reaction solvent. Additionally, the spectral profiles of the LSPRs allude to the formation of smaller, more uniform AuNPs when generated in [C_4mpy][Tf_2N].

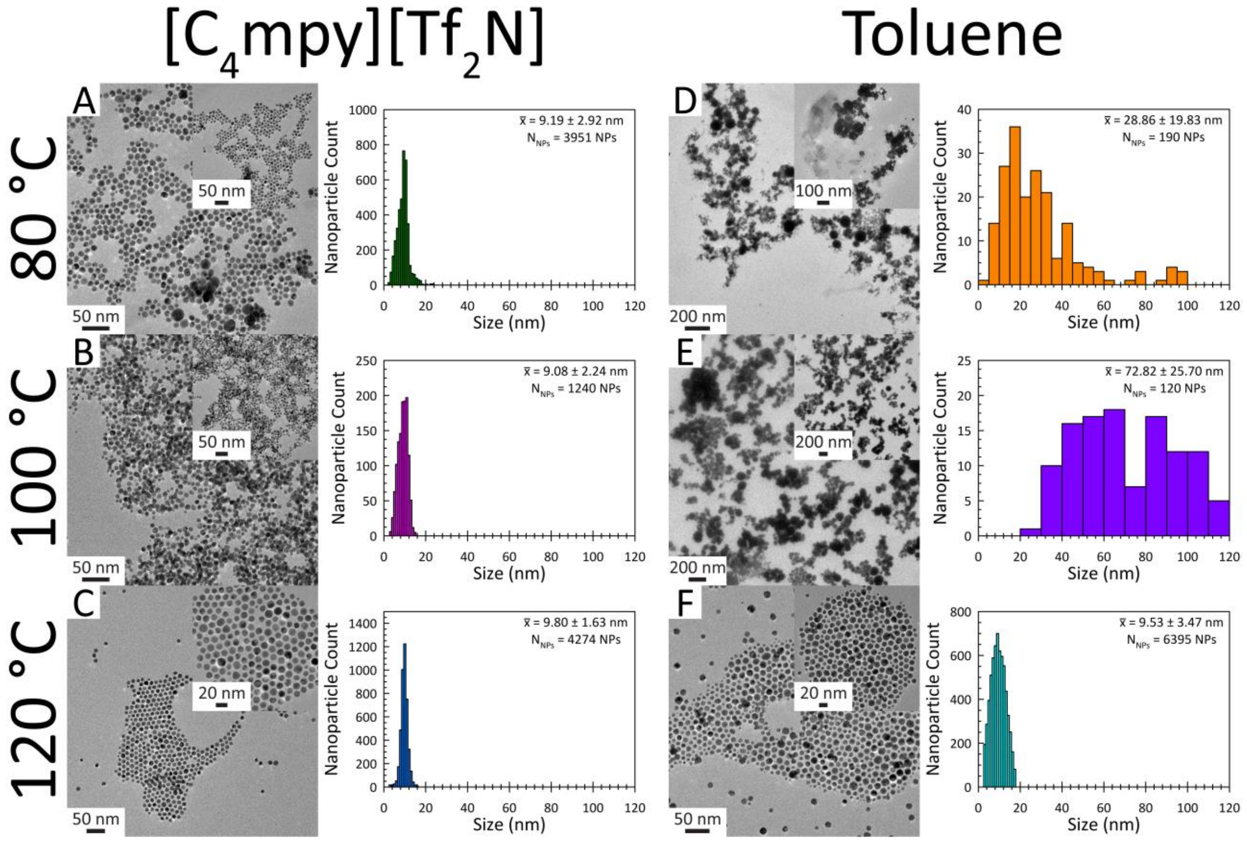


Fig. S9 Representative TEM images of AuNPs synthesized at (A and D) 80 °C, (B and E) 100 °C, and (C and F) 120 °C using the conventional method using either (A–C) 5 g of [C_4mpy][Tf_2N] or (D–F) 5 mL of toluene as the solvent. The average AuNP size for the temperature-dependent synthesis of AuNPs in [C_4mpy][Tf_2N] remained nominally the same regardless of the temperature employed, while the polydispersity of the AuNPs decreased with increasing temperature. Conversely, when toluene was used as the solvent, only a synthesis temperature of 120 °C led to the formation of AuNPs comparable in size and polydispersity to the AuNPs synthesized in [C_4mpy][Tf_2N], while lower temperatures resulted in large, polydispersed, and highly aggregated AuNPs, highlighting the advantages of employing IL over conventional organic solvents. The AuNP histograms are provided to the right of their respective TEM images.

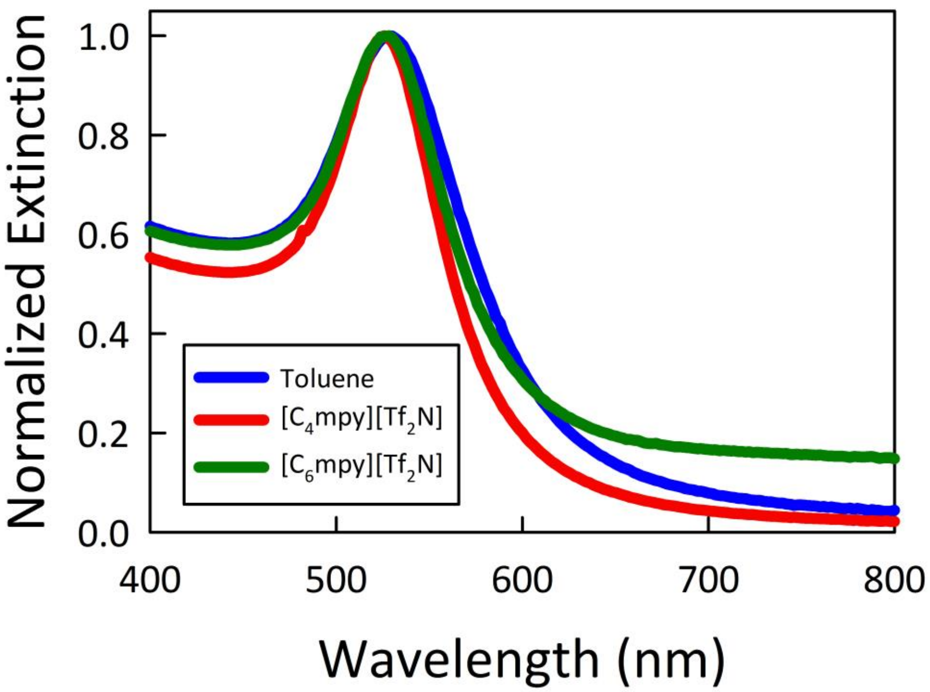
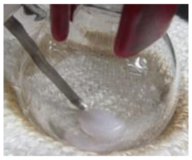
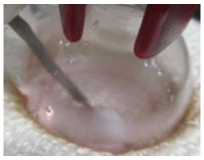
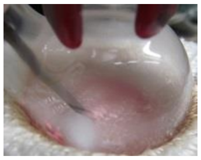
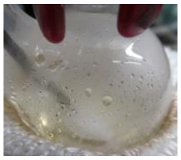
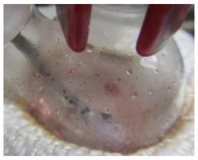


Fig. S10 UV-vis spectral comparison of AuNPs synthesized using the conventional method and either toluene, [C_4mpy][Tf_2N], or [C_6mpy][Tf_2N] as the solvent. Employing [C_6mpy][Tf_2N] as the solvent resulted in a comparable spectral profile to results obtained when conducting the reaction in [C_4mpy][Tf_2N] or toluene, suggesting that the resultant AuNPs are likely of a similar size and polydispersity.

Table S5. Pictorial timeline of the solution color evolution when employing various ILs in a conventional (thermal) synthesis. Samples prepared using imidazolium-based ILs showed no indication of AuNP formation, changing in color from clear to a light yellow, a common observation accompanying IL degradation. In contrast, reactions employing pyrrolidinium-based ILs produced a pale pink color shortly after injection of the gold precursor, indicating AuNP formation. Indeed, following purification, the resulting samples showed visual evidence for successful AuNP formation (*i.e.*, plasmonic features).

	[Bmim][Tf$_2$N]	**[Bmim][TFA]**	**[C$_4$mpy][Tf$_2$N]**	**[C$_6$mpy][Tf$_2$N]**
Before injection of the gold precursor				
After injection (< 60 s)				
After 1 h				
Final purified sample (the samples in the cuvettes were 3-fold diluted from the purified sample)				

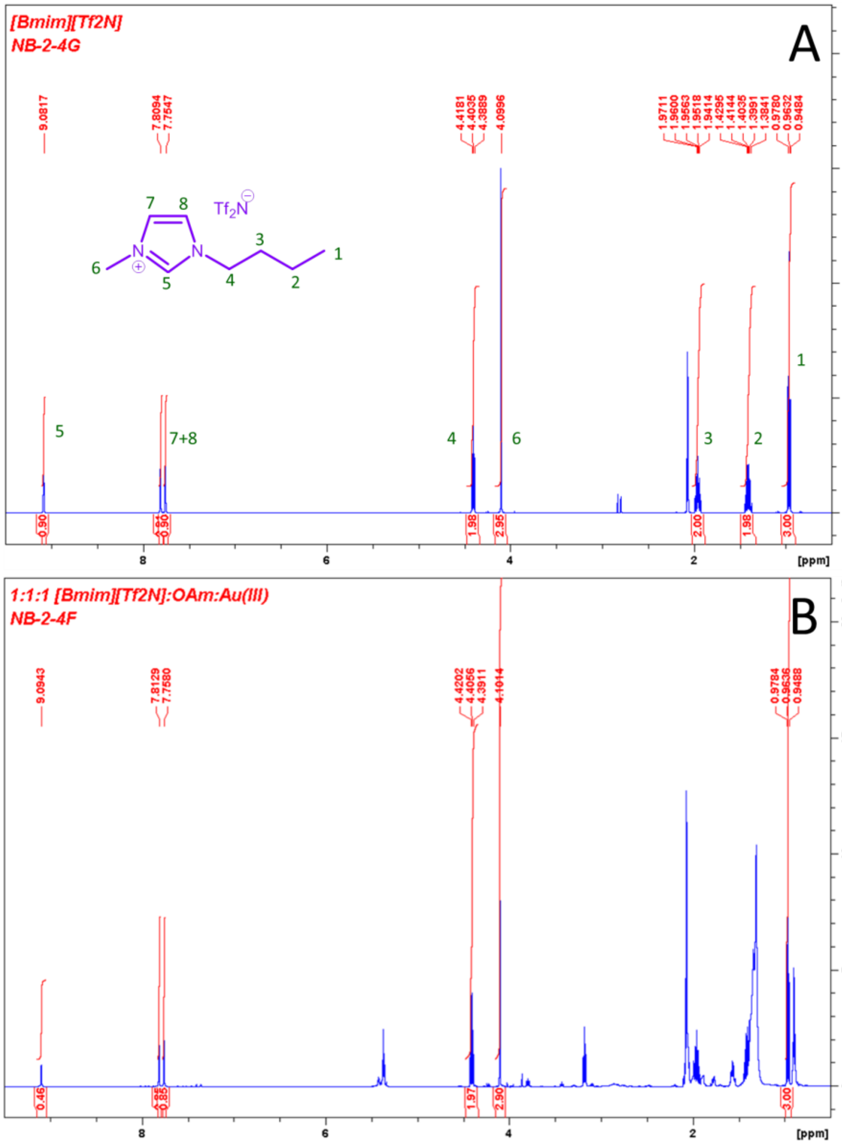


Fig. S11 (A) ^{1}H NMR spectrum of [Bmim][Tf$_2$N] (500 MHz, acetone-*d*$_6$, [ppm]): δ = 9.08 (s, 1H), 7.80 (s, 1H), 7.75 (s, 1H), 4.41-4.38 (t, 2H, *J* = 7.3 Hz), 4.09 (s, 3H), 1.97-1.94 (m, 2H), 1.42-1.38 (m, 2H), 0.97-0.94 (t, 3H, *J* = 7.4 Hz). (B) ^{1}H NMR spectrum of a 1:1:1 molar mixture of [Bmim][Tf$_2$N]:OAm:HAuCl$_4$. Integration of the peak attributed to the C-2 proton on the imidazolium cation (labeled as position 5 in panel A) demonstrates that when [Bmim][Tf$_2$N] is in the presence of equivalents of both OAm and HAuCl$_4$, the intensity of the C-2 proton peak drops roughly 2-fold.

Table S6. Pictures of the resultant AuNP samples generated via a microwave-mediated synthesis in the presence of ILs based on an imidazolium cation. These results demonstrate the lack of successful AuNP formation when employing [Bmim][Tf_2N] as solvent whereas the C-2 methylated version, [Bmmim][Tf_2N], affords apparent AuNP formation due to the reduced ability of the $[Bmmim]^+$ cation to inactivate OAm in this reaction. This outcome is corroborated spectrally in Fig. S12B below.

Reaction contents	Before heating	After heating	Product in toluene
OAm **[Bmim][Tf_2N]**			
OAm **[Bmim][Tf_2N]** **$HAuCl_4$**			
OAm **[Bmmim][Tf_2N]** **$HAuCl_4$**			

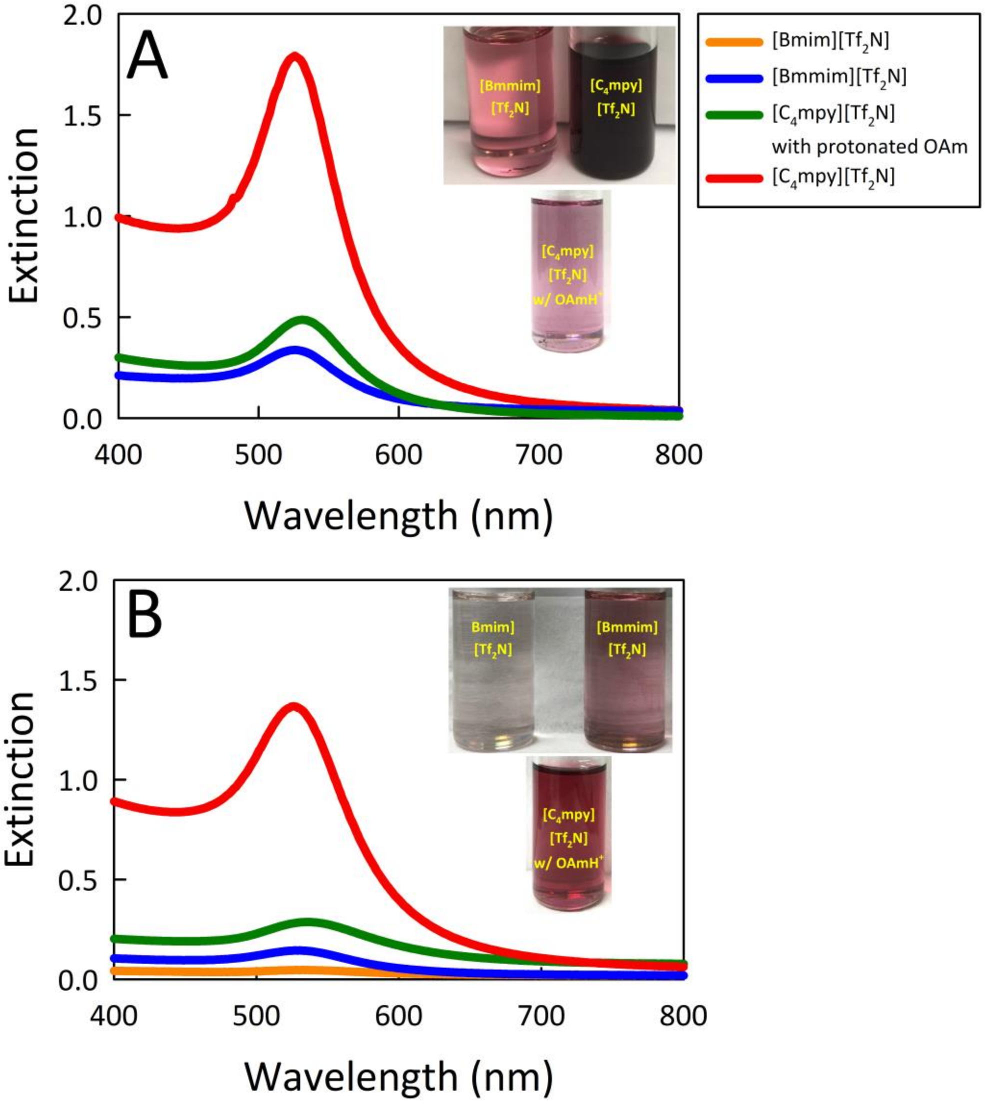
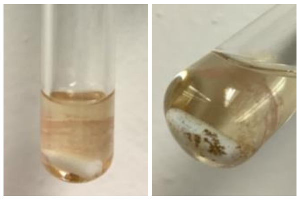


Fig. S12 UV-vis spectral comparison between AuNPs synthesized in the presence of oleylammonium chloride (OAmHCl) via (A) a conventional approach versus (B) a microwave-mediated approach. In both cases, employing OAmHCl (instead of OAm) within [C$_4$mpy][Tf$_2$N] resulted in drastically lower LSPR intensities. This outcome is consistent with protonation of OAm leading to a decrease in its strength as a reducing agent toward HAuCl$_4$. Although hardly definitive, deprotonation at the C-2 site of the imidazolium ring (with concomitant carbene formation and protonation of OAm) is a plausible explanation for the poor reactivity of OAm in [Bmim][Tf$_2$N]. The upper legend applies to both panels. Note that OAmHCl generation was achieved by adding 92.7 µL of HCl (*conc.*) to the reaction mixture (*ca.* one equiv relative to OAm).

Table S7. Pictures of attempted AuNP synthesis (conventional and microwave reaction routes) in [Bmim][Tf_2N]. In these experiments, sodium borohydride ($NaBH_4$) was added to the *post-reaction* mixture as a strong reducing agent to establish whether unreacted $HAuCl_4$ remained. When employing a conventional approach, addition of $NaBH_4$ produced large black flecks (sample #1), a clear demonstration that a portion (or all) of the Au(III) remained after reaction with OAm. When employing microwave heating, the addition of $NaBH_4$ generated large, flake-like structures (sample #2). Interestingly, a control study excluding OAm resulted in the apparent reduction of $HAuCl_4$ to form flakes and electroless plating onto the vial walls, even without $NaBH_4$ addition (sample #3). While some $HAuCl_4$ reduction took place in the latter microwave study, colloidally-stable AuNPs were not accessible in [Bmim][Tf_2N] with or without OAm addition.

Sample description	Appearance of sample	Appearance after sample purification
#1: Conventional heating of OAm, and $HAuCl_4$ in [Bmim][Tf_2N] with **$NaBH_4$ added post-reaction**		
#2: Microwave heating of OAm and $HAuCl_4$ in [Bmim][Tf_2N] with **$NaBH_4$ added post-reaction**		
#3: Microwave heating of $HAuCl_4$ in [Bmim][Tf_2N] **(no $NaBH_4$ added post-reaction)**		

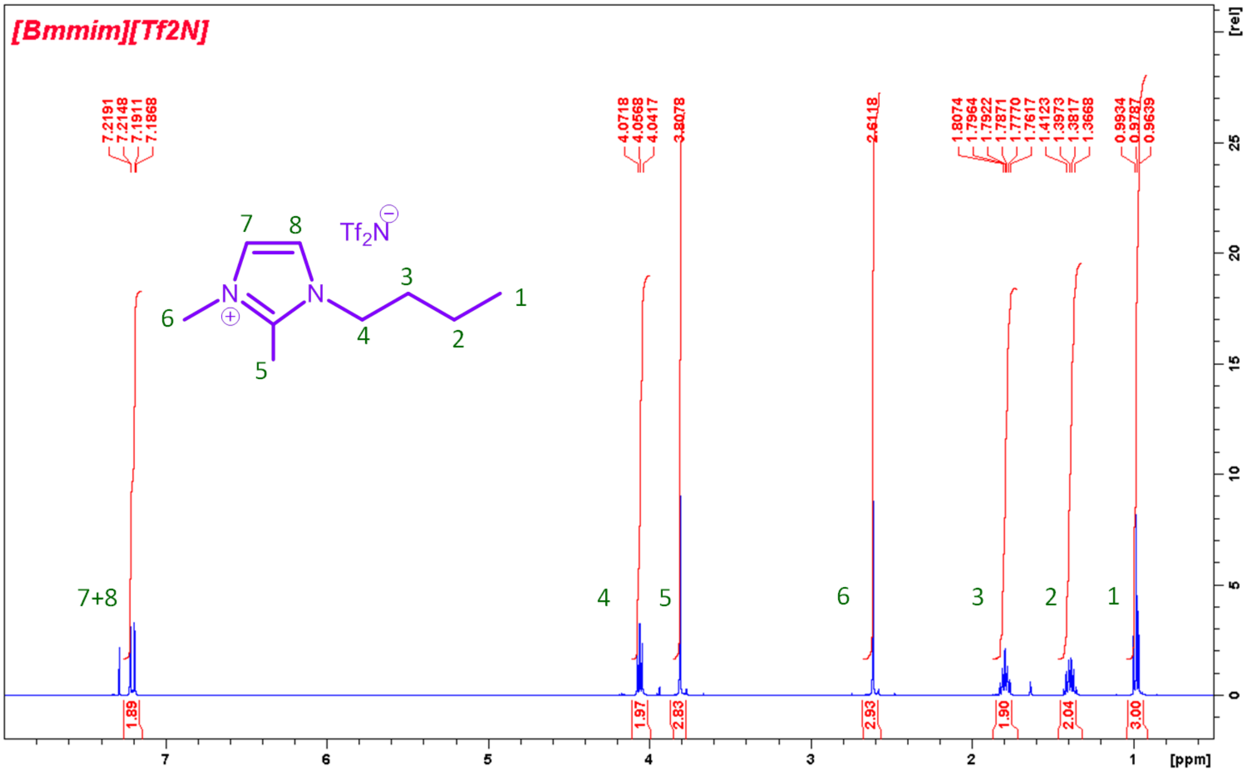


Fig. S13 ^{1}H NMR spectrum of [Bmmim][Tf$_2$N] (500 MHz, CDCl$_3$, [ppm]): δ = 7.21-7.18 (m, 2H), 4.07-4.04 (t, 2H, J = 7.5 Hz), 3.80 (s, 3H), 2.61 (s, 3H), 1.80-1.76 (m, 2H), 1.41-1.36 (m, 2H), 0.99-0.96 (t, 3H, J = 7.4 Hz).

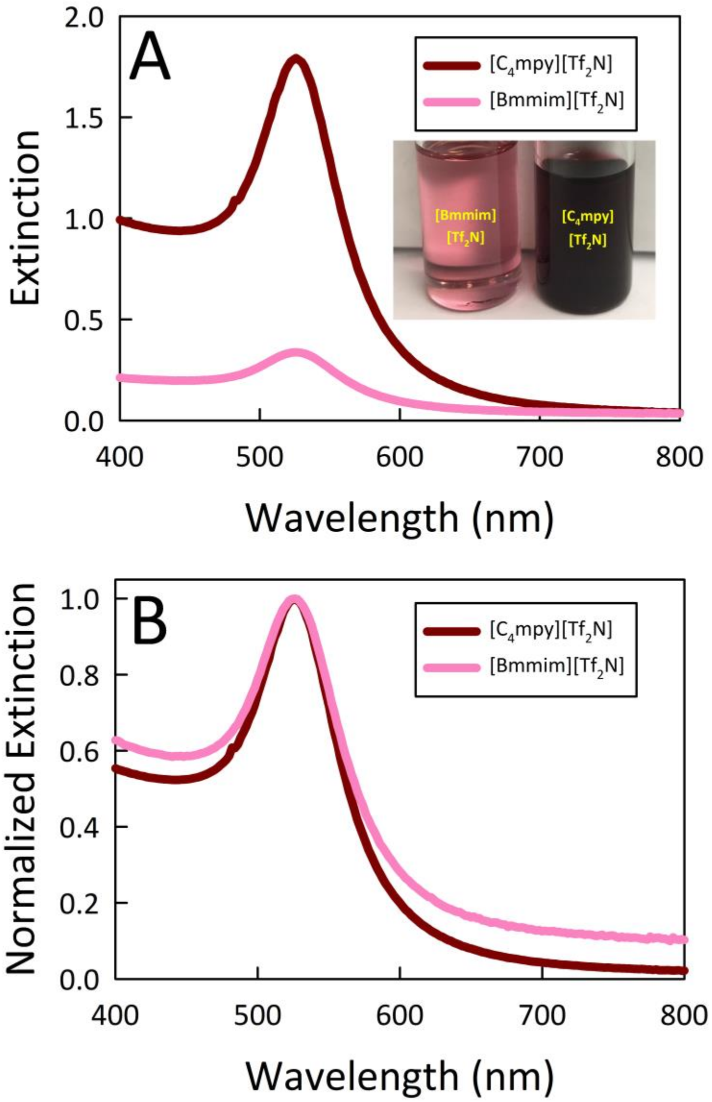


Fig. S14 (A) UV-vis spectral comparison between AuNPs synthesized in [C$_4$mpy][Tf$_2$N] and [Bmmim][Tf$_2$N] illustrating the dramatic difference in the quantity of AuNPs generated in these two different ILs. The current results also highlight the fact that, when the hydrogen at the C-2 position of [Bmim]$^+$ is replaced with a methyl group, the resulting [Bmmim]$^+$ is more compatible with AuNP formation. Note that the spectrum of the [C$_4$mpy][Tf$_2$N]-derived AuNPs was collected on a sample diluted 3-fold from the original sample shown in the inset of the upper panel. While the maximum absorbance value for the AuNPs synthesized in these two ILs differs drastically, normalized absorbance profiles shown in panel B indicate clear similarities, although AuNPs synthesized in [Bmmim][Tf$_2$N] display obvious spectral tailing from 550 to 800 nm, a feature likely arising from growth of somewhat larger AuNPs possessing greater heterogeneity.

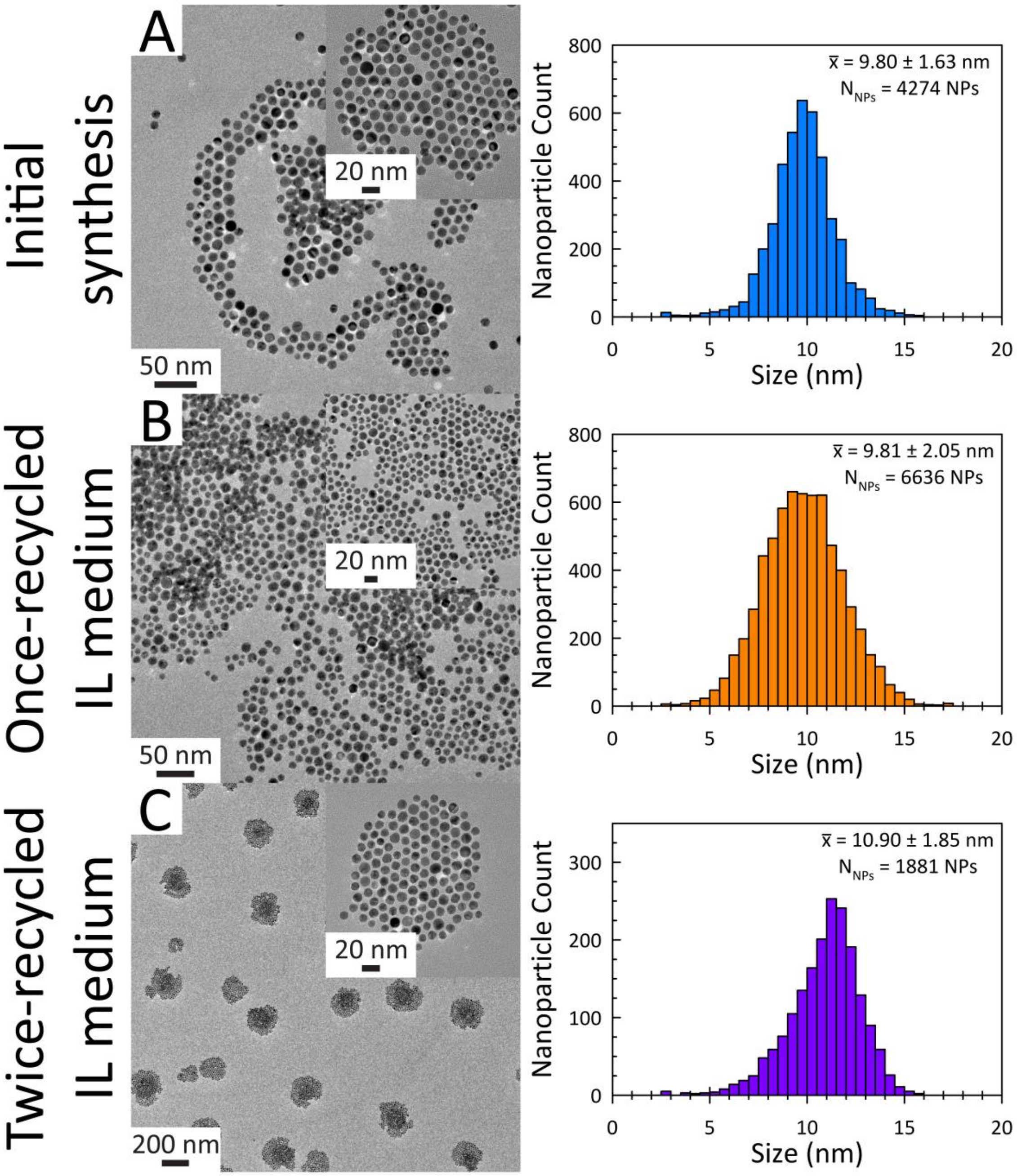


Fig. S15 Representative TEM images of AuNPs synthesized via the conventional method using (A) fresh [C_4mpy][Tf_2N] and the same medium (B) once- and (C) twice-recycled. The resulting AuNP size distribution for the initial synthesis and the first recycling are similar, although the average AuNP size increased slightly after the [C_4mpy][Tf_2N] medium was recycled a second time.

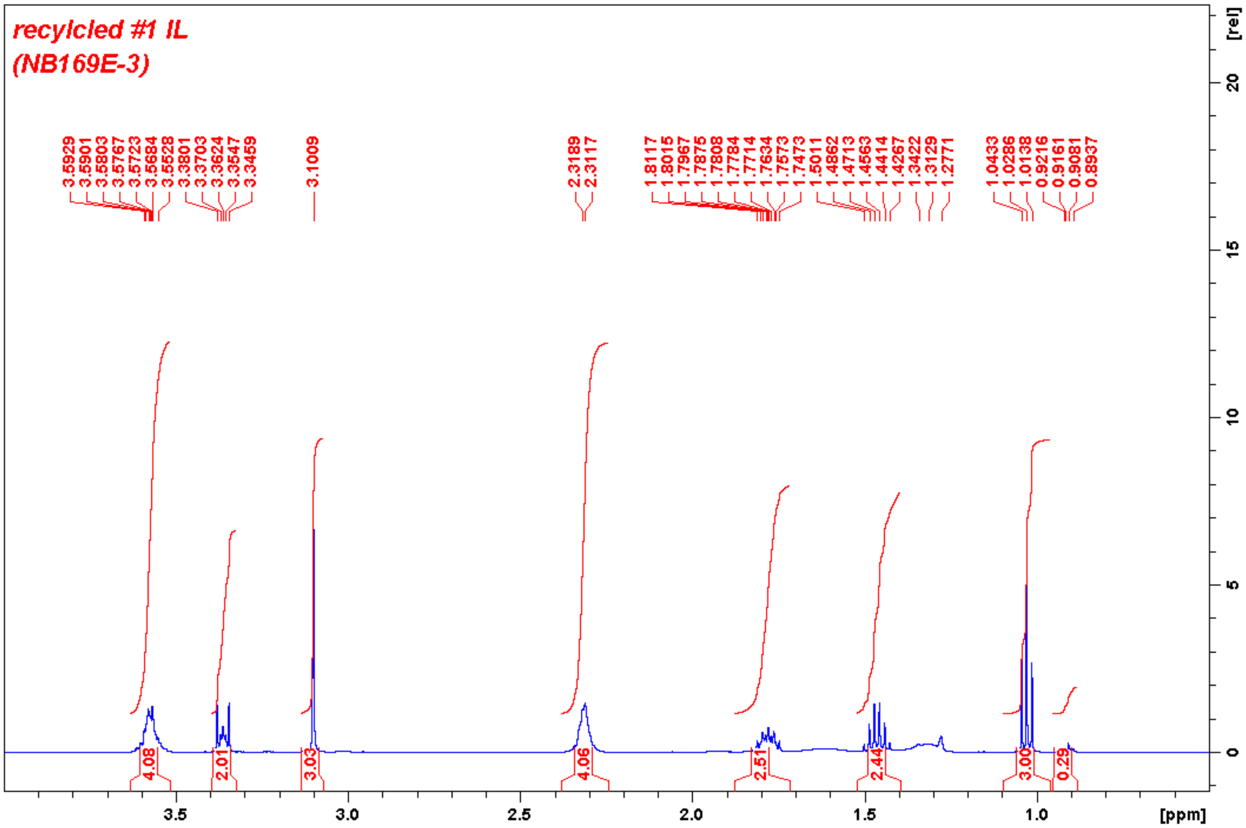


Fig. S16 ^{1}H NMR spectrum of the once-recycled [C_4mpy][Tf_2N] medium. The integrated intensity of the methyl group of OAm (δ = 0.90) was compared with that of the [C_4mpy]$^+$ terminal methyl group (δ = 1.02; $(CH_2)_3CH_3$) to determine the molar ratio of OAm to IL. The OAm amount was determined to be 9.67 mol% (relative to [C_4mpy][Tf_2N]), which is nominally the same as the starting ratio of 9.47%.

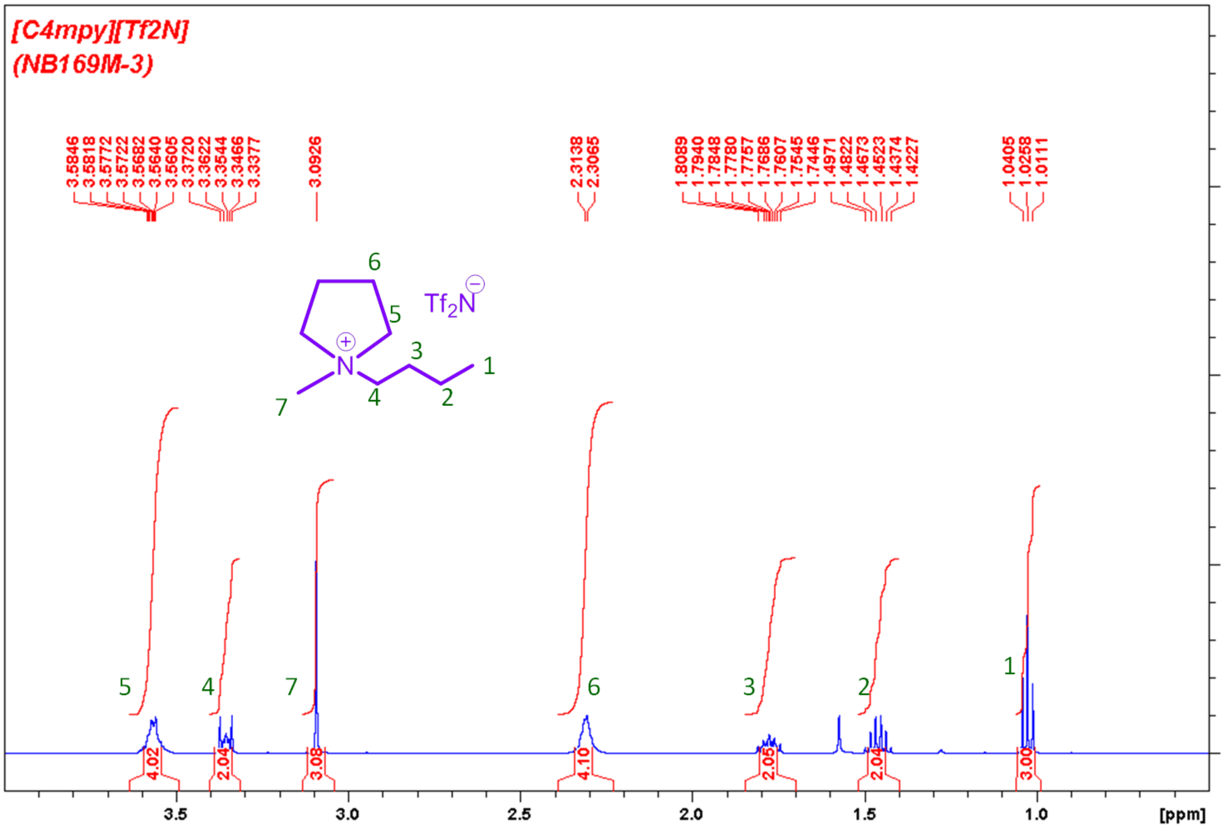


Fig. S17 ^{1}H NMR spectrum of [C$_4$mpy][Tf$_2$N] (500 MHz, CDCl$_3$, [ppm]): δ = 3.58-3.56 (m, 4H), 3.37-3.33 (m, 2H), 3.09 (s, 3H), 2.31-2.30 (d, 4 H, *J* = 3.7 Hz), 1.80-1.74 (m, 2H), 1.49-1.42 (m, 2H), 1.04-1.01 (t, 3H, *J* = 7.4 Hz).

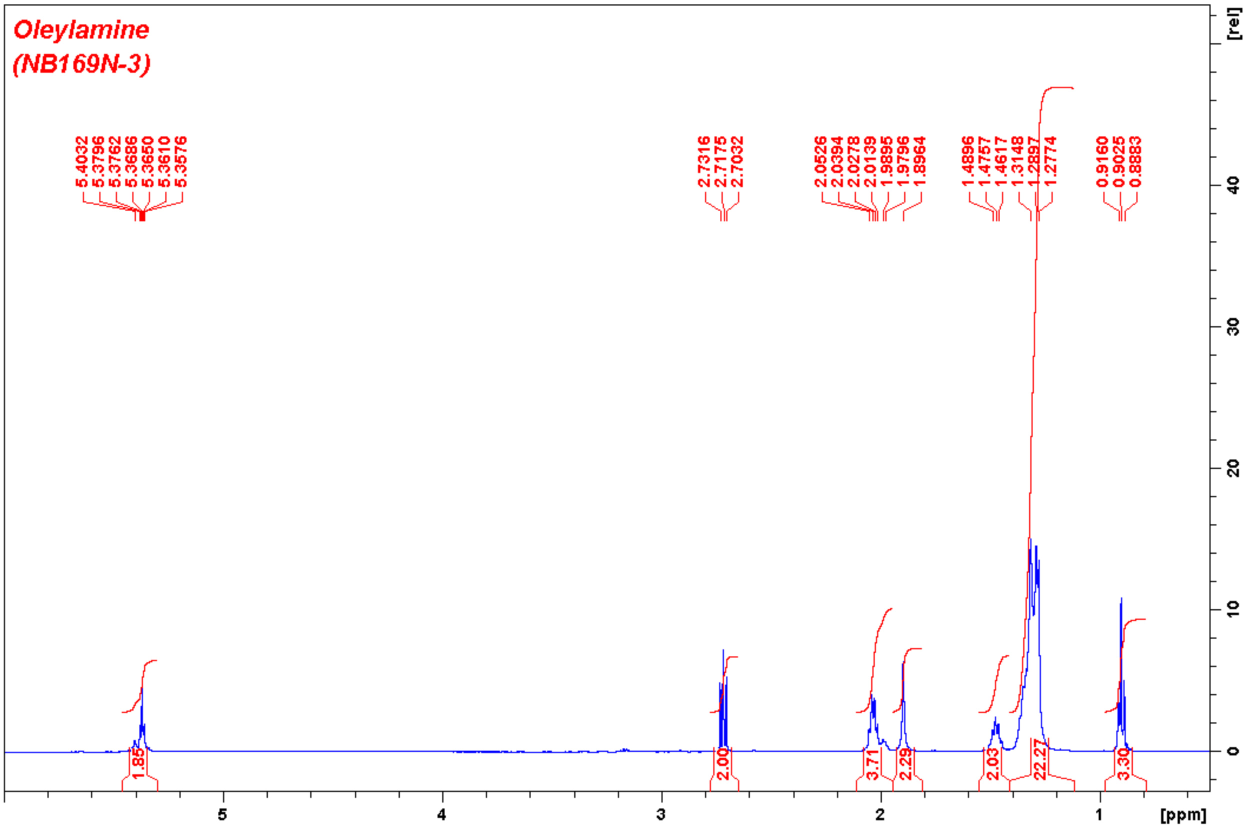


Fig. S18 ^{1}H NMR spectrum of OAm (500 MHz, $CDCl_3$, [ppm]): δ = 5.40-5.35 (m, 2H), 2.73-2.70 (t, 2H, *J* = 7.1 Hz), 2.05-1.97 (m, 4H), 1.89 (s, 2H), 1.48-1.46 (t, 2H, *J* = 7.0 Hz), 1.31-1.27 (m, 22H), 0.91-0.88 (t, 3H, J = 6.8 Hz).

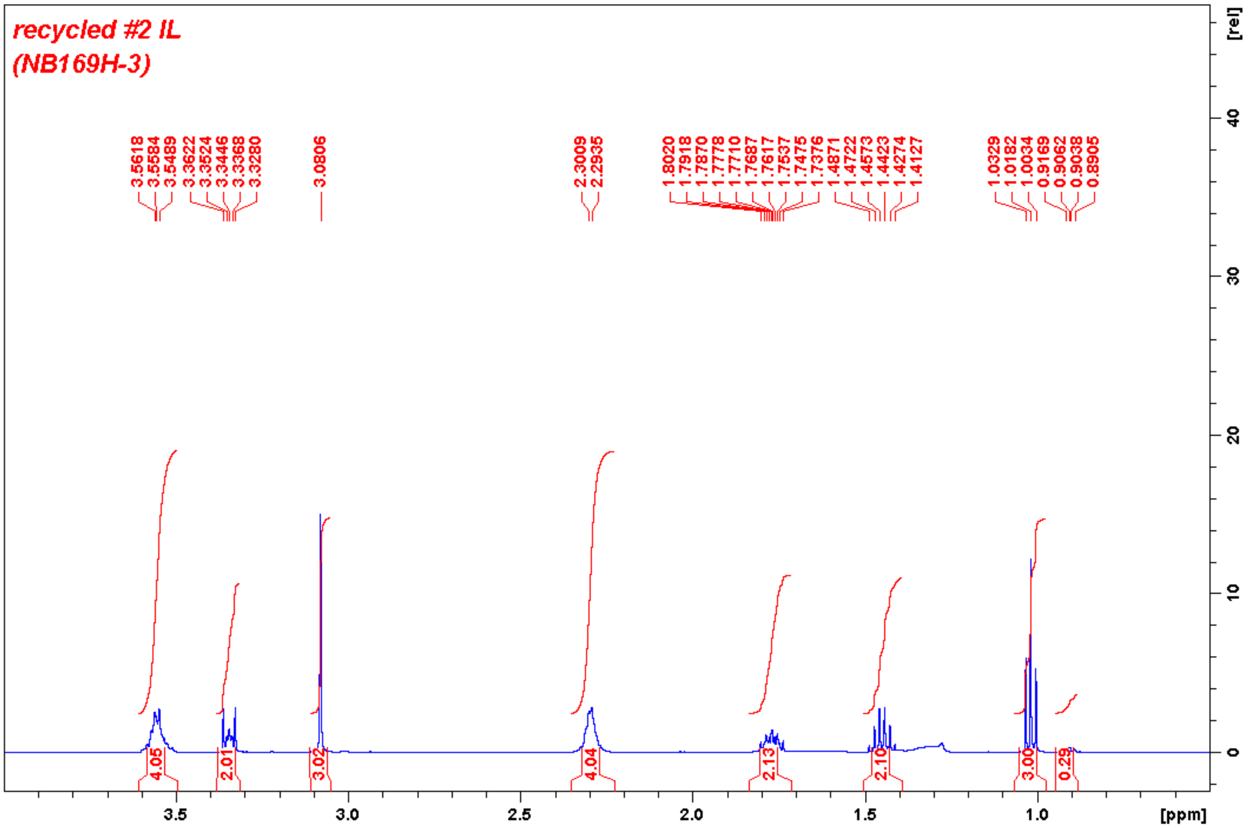


Fig. S19 ^{1}H NMR spectrum of the twice-recycled [C_4mpy][Tf_2N] medium. The integrated intensity of the methyl group of OAm (δ = 0.90) was compared with that of the [C_4mpy]$^+$ terminal methyl group (δ = 1.02; $(CH_2)_3CH_3$) to determine the molar ratio of OAm to IL. The OAm amount was determined to be 9.67 mol% (relative to [C_4mpy][Tf_2N]), which is nominally the same as the initial amount (9.47%).

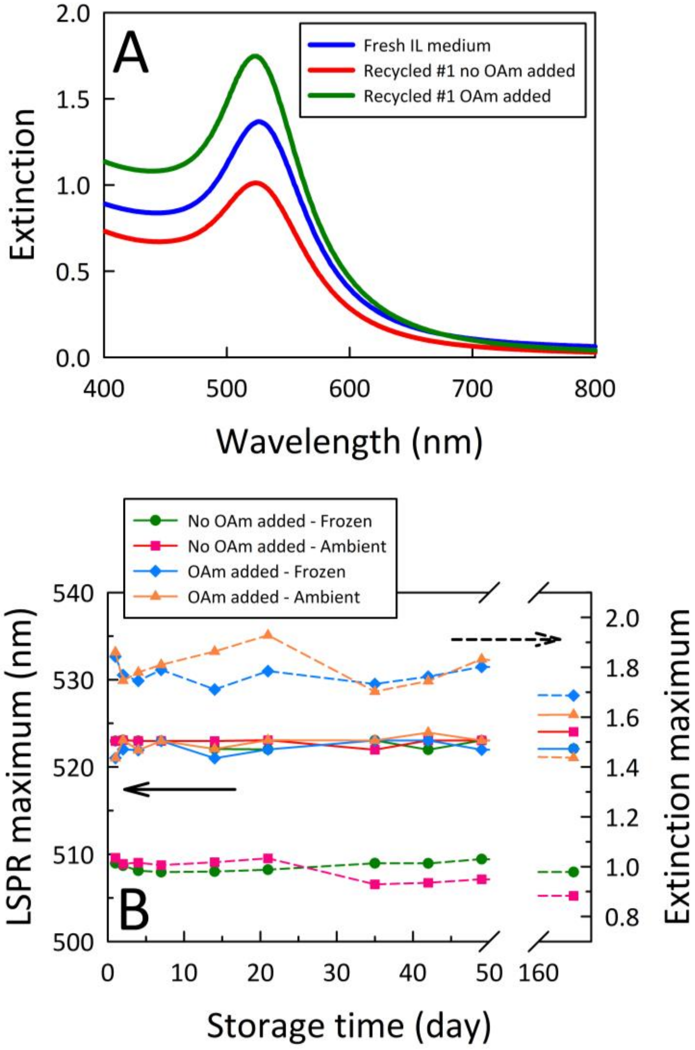


Fig. S20 (A) UV-vis spectra comparing AuNPs synthesized following our microwave approach (100 °C, 30 s) and using fresh or once-recycled [C_4mpy][Tf_2N] media, where the once-recycled medium was used as-is or supplemented with additional OAm. Interestingly, the once-recycled [C_4mpy][Tf_2N] medium containing supplemental OAm resulted in a more-intense LSPR band, a result that can be attributed to additional AuNP formation, however, the origin of this outcome remains unclear. (B) The effect of storage conditions {*i.e.*, room temperature (denoted "Ambient") or in a –20 °C freezer ("Frozen")} on cyclohexane-dispersed AuNPs produced **using once-recycled [C_4mpy][Tf_2N]** or once-recycled [C_4mpy][Tf_2N] supplemented with fresh OAm. AuNPs made in once-recycled [C_4mpy][Tf_2N] remain colloidally stable for at least 160 days (at which point the study was terminated), regardless of storage conditions, in contrast to results obtained for AuNPs synthesized via a conventional thermal approach.

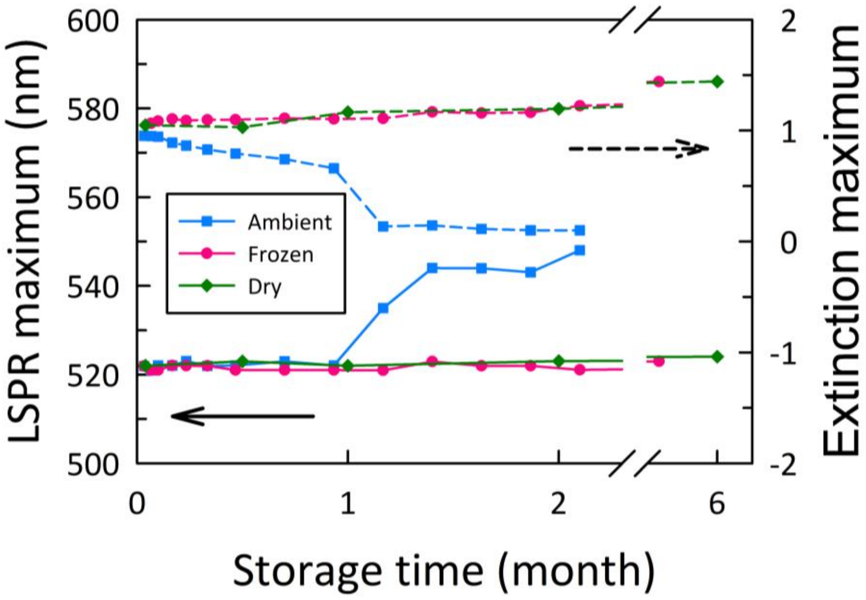
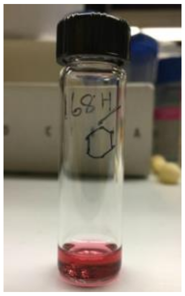
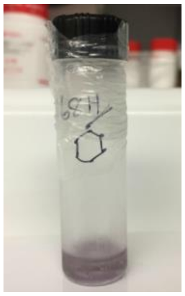


Fig. S21 Effects of storage conditions on the colloidal stability of cyclohexane-dispersed AuNPs made in 2.5 g of **fresh [C_4mpy][Tf_2N]** (MW reaction parameters: 100 °C, 30 s), assessed by monitoring the time-resolved LSPR maximum and corresponding extinction values. When storing samples at ambient conditions in cyclohexane, the AuNPs began to destabilize immediately and within a month colloidal stability was largely compromised. In contrast, storage of the AuNPs in frozen cyclohexane (–20 °C) or in a dry state at ambient temperature significantly improved longevity, with the AuNPs remaining colloidally stable for at least a full 6 months (the duration of the study).

Table S8. Images of AuNPs dispersed in cyclohexane prior to freezing, in the frozen state, and immediately upon thawing.

As-synthesized product	**Frozen product**	**Thawed product**
		

1. A. K. Burrell, R. E. D. Sesto, S. N. Baker, T. M. McCleskey and G. A. Baker, *Green Chem.*, 2007, **9**, 449-454.
2. H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G. A. Baker, J. F. Wishart, A. J. Benesi and M. Maroncelli, *J. Phys. Chem. B*, 2008, **112**, 81-92.