

ELECTRONIC SUPPLEMENTARY INFORMATION

Bifunctional hydrophobic ionic liquids: Facile synthesis by thiol-ene “click” chemistry

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General Procedure for the synthesis of mercaptopropylsilyl-functionalized ILs via thiol-ene reaction

In a dry 150 mL photochemical tube, 1 equiv. of *ene*-bearing ILs was added along with 0.5 equiv. of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone. Minimal amount (<1 mL) of solvent, 1:1 ratio of DCM and MeOH, was added and vigorously stirred until a homogenous solution was obtained. The photochemical tube was capped with a septum, purged with nitrogen, and then sealed with Parafilm. The 3-mercaptopropyltrimethoxysilane (MPTMS) was weighed into a syringe and added through the septum. The contents were stirred briefly and then irradiated with UV for 8h at room temperature under nitrogen atmosphere. The purification process was completed by washing the mixture with hexanes (6 × 30 mL) and dried under vacuum at 70°C for 12h. All of the synthesized ILs 1–16 were prepared using general procedure on a 500 mg scale.

IL 1:

Yield: >99%; ¹H NMR (DMSO-*d*₆, 500 Hz): δ_H 8.98 (s, 1H); 7.62 (d, 2H); 4.20 (t, 2H); 3.81 (s, 3H); 3.15 (s, 9H); 2.43 (t, 2H); 2.38 (t, 2H); 2.02 (t, 2H); 1.55 (m, 4H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ_C 136.92; 124.04; 122.60; 121.13; 118.57; 49.01; 48.23; 36.16; 30.62; 29.04; 29.01; 26.05 MS (EI): *m/z* 321.74 (M+2), 320.74 (M+1), 319.74 (M, calcd. 319.15).

IL 2:

Yield: >99%; ¹H NMR (DMSO-*d*₆, 500 Hz): δ_H 9.00 (s, 1H); 7.63 (d, 2H); 4.14 (t, 2H); 3.82 (s, 3H); 3.15 (s, 9H); 2.46 (t, 2H); 2.42 (t, 2H); 1.84 (m, 2H); 1.47-1.55 (m, 6H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ_C 136.80; 124.02; 122.58; 121.14; 118.57; 50.10; 49.01; 48.23; 36.15; 34.18; 29.62; 27.63 MS (EI): *m/z* 335.24 (M+2), 334.24 (M+1), 333.24 (M, calcd. 333.17).

IL 3:

Yield: 98%; ¹H NMR (DMSO-*d*₆, 500 Hz): δ_H 8.97 (s, 1H); 7.63 (d, 2H); 4.10 (t, 2H); 3.81 (s, 3H); 3.15 (s, 9H); 2.59 (t, 2H); 2.42 (t, 2H); 1.75 (m, 4H); 1.50 (m, 4H); 1.29 (m, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ_C 136.69; 123.98; 122.49; 121.13; 118.57; 49.13; 49.02; 36.10; 34.49; 31.29; 29.40; 28.90; 25.13; MS (EI): *m/z* 349.73 (M+2), 348.73 (M+1), 347.73 (M, calcd. 347.18).

IL 4:

Yield: >99%; ¹H NMR (DMSO-*d*₆, 500 Hz): δ_H 8.96 (s, 1H); 7.62 (d, 2H); 4.08 (t, 2H); 3.81 (s, 3H); 3.15 (s, 9H); 2.59 (t, 2H); 2.42 (t, 2H); 1.72 (m, 2H); 1.55 (m, 2H); 1.45 (m, 2H); 1.31 (m, 4H); 1.21 (m, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ_C 136.71; 123.98; 122.49; 118.57; 49.21; 36.12; 30.12; 31.29; 29.76; 29.36; 28.15; 25.65; MS (EI): *m/z* 363.18 (M+2), 362.18 (M+1), 361.18 (M, calcd. 361.20).

IL 5:

Yield: >99%; ¹H NMR (DMSO-*d*₆, 500 Hz): δ_H 9.08 (s, 1H); 7.74 (d, 1H); 7.67 (d, 1H); 4.14 (t, 2H); 3.84 (s, 3H); 3.16 (s, 9H); 2.42-2.49 (m, 4H); 1.74-1.78 (m, 2H); 1.46-1.58 (m, 4H); 1.22-1.32 (m, 4H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ_C 136.91; 124.03; 122.67; 121.20; 118.57; 49.20; 49.01; 36.13; 31.35; 29.77; 29.49; 28.41; 25.84; 23.51; MS (EI): *m/z* 377.76 (M+2), 376.76 (M+1), 375.76 (M, calcd. 375.21).

IL 6:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 8.98 (s, 1H); 7.69 (d, 1H); 7.55 (d, 1H); 4.14 (t, 2H); 3.88 (s, 3H); 3.16 (s, 9H); 2.40-2.48 (m, 4H); 1.70-1.78 (m, 6H); 1.34-1.58 (m, 8H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 136.43; 123.22; 122.33; 122.10; 118.22; 49.24; 48.99; 35.11; 32.55; 29.00; 28.57; 28.41; 28.11; 24.99; 23.26; MS (EI): m/z 391.88 (M+2), 390.88 (M+1), 389.88 (M, calcd. 389.23).

IL 7:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 7.57 (d, 2H); 4.06 (t, 2H); 3.72 (s, 3H); 3.16 (s, 9H); 2.55 (s, 3H); 2.43 (t, 4H); 1.47-1.68 (m, 14H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 144.56; 122.69; 121.18; 118.62; 49.01; 47.95; 35.01; 31.40; 29.46; 28.86; 28.57; 25.95; 23.96; MS (EI): m/z 405.43 (M+2), 404.43 (M+1), 403.43 (M, calcd. 403.24).

IL 8:

Yield: 97%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 9.04 (s, 1H); 7.67 (d, 2H); 4.12 (t, 2H); 3.82 (s, 3H); 3.16 (s, 9H); 2.41-2.47 (m, 4H); 1.74 (m, 2H); 1.57 (m, 2H); 1.46 (t, 2H); 1.16-1.34 (m, 10H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} MS (EI): 136.82; 124.00; 122.63; 121.17; 118.63; 50.09; 49.24; 49.03; 37.71; 36.13; 34.61; 31.42; 29.83; 29.17; 28.75; 25.98; 23.19; m/z 405.57 (M+2), 404.57 (M+1), 403.57 (M, calcd. 403.24).

IL 9:

Yield: 97%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 7.58 (d, 2H); 4.16 (t, 2H); 3.45 (s, 3H); 3.22 (s, 9H); 2.56 (s, 3H); 2.45 (m, 4H); 2.33 (t, 4H); 1.47-1.68 (m, 16H); 1.25 (s, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 143.33; 121.45; 121.01; 118.32; 48.41; 46.15; 35.12; 32.40; 30.46; 28.86; 28.57; 27.12; 26.45; 22.66; MS (EI): m/z 419.73 (M+2), 418.73 (M+1), 417.73 (M, calcd. 417.26).

IL 10:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 9.05 (s, 1H); 7.67 (d, 2H); 4.13 (t, 2H); 3.83 (s, 3H); 3.16 (s, 9H); 2.41-2.48 (m, 4H); 1.76 (t, 2H); 1.55 (m, 2H); 1.48 (t, 2H); 1.16-1.33 (m, 12H); ^{13}C NMR (DMSO- d_6 , 125 MHz): 136.84; 123.97; 123.63; 121.18; 118.62; 50.38; 49.25; 49.00; 36.15; 31.39; 29.80; 29.27; 29.17; 29.00; 28.76; 28.62; 25.91; 24.18; 23.47; 23.14; MS (EI): m/z 419.73 (M+2), 418.73 (M+1), 417.73 (M, calcd. 417.26).

IL 11:

Yield: 97%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 7.58 (d, 2H); 4.15 (t, 2H); 3.47 (s, 3H); 3.16 (s, 9H); 2.56 (s, 3H); 2.44 (m, 4H); 2.30 (t, 4H); 1.47-1.68 (m, 18H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 144.93; 122.44; 122.02; 118.44; 48.23; 46.55; 36.11; 34.43; 32.66; 29.16; 28.27; 27.44; 26.99; 26.15; 22.06; MS (EI): m/z 433.12 (M+2), 432.11 (M+1), 431.11 (M, calcd. 431.73).

IL 12:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 9.04 (s, 1H); 7.66 (d, 2H); 4.11 (t, 2H); 3.83 (s, 3H); 3.15 (s, 9H); 2.41-2.49 (m, 4H); 1.75 (t, 2H); 1.57 (m, 2H); 1.46 (t, 2H); 1.15-1.35 (m, 14H); ^{13}C NMR (DMSO- d_6 , 125 MHz): 136.83; 123.98; 123.62; 121.17; 118.62; 49.26; 49.01; 36.15; 31.42; 29.82; 29.63; 29.38; 29.17; 29.02; 28.76; 28.62; 25.91; 24.18; 23.27; MS (EI): m/z 433.43 (M+2), 432.43 (M+1), 431.43 (M, calcd. 431.73).

IL 13:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 7.61 (d, 2H); 4.08 (t, 2H); 3.73 (s, 3H); 3.16 (s, 9H); 2.56 (s, 3H); 2.45 (m, 4H); 2.30 (t, 4H); 1.68 (m, 2H); 1.55-1.59 (m, 2H); 1.45-1.50 (m, 2H); 1.18-1.31 (m, 14H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 144.61; 122.72; 121.20; 118.64; 49.01; 47.95; 35.05; 31.43; 29.64; 28.27; 29.36; 28.94; 28.74; 26.04; MS (EI): m/z 447.95 (M+2), 446.95 (M+1), 445.95 (M, calcd. 445.29).

IL 14:

Yield: 97%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 8.98 (s, 1H); 7.62 (d, 2H); 4.22 (t, 4H); 3.16 (s, 18H); 2.45 (t, 4H); 2.33 (t, 4H); 2.11 (t, 4H); 1.57 (m, 8H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 136.33; 124.21; 122.93; 121.22; 118.41; 49.43; 37.11; 31.03; 30.11; 29.95; 26.87; ^{29}Si NMR (DMSO- d_6): δ_{Si} -41.84; MS (EI): m/z 543.80 (M+2), 542.80 (M+1), 541.80 (M, calcd. 541.23).

IL 15:

Yield: 98%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 4.13 (t, 2H); 3.44 (quart, 6H); 3.13 (s, 9H); 2.53 (t, 4H); 1.83 (m, 4H); 1.55 (m, 2H); 1.16 (t, 9H); ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 122.20; 118.64; 55.52, 52.63; 49.98; 48.95; 34.49; 34.36; 27.97; 23.39; 21.89; ^{29}Si NMR (DMSO- d_6): δ_{Si} -39.93; MS (EI): m/z 340.45 (M+2), 339.45 (M+1), 338.45 (M, calcd. 338.22).

IL 16:

Yield: 96%; ^1H NMR (DMSO- d_6 , 500 Hz): δ_{H} 7.17 (s, 5H), 6.75-6.98 (m, 10H); 4.20 (t, 2H); 3.16 (s, 9H); 2.49 (t, 4H); 2.04 (m, 2H); 1.56 (m, 4H). ^{13}C NMR (DMSO- d_6 , 125 MHz): δ_{C} 135.95; 125.77; 122.00; 120.8; 118.2; 115.6; 47.5; 34.6; 30.1; 29.1; 28.8; 28.4; 25.5; ^{29}Si NMR (DMSO- d_6): δ_{Si} -42.19; ^{31}P NMR (DMSO- d_6): δ_{P} 15.89; MS (EI): m/z 501.33 (M+2), 500.33 (M+1), 499.33 (M, calcd. 499.19).

Figure S1 shows an overlay view of the UV-Vis spectra of [allylmim][NTf₂] (0.03 M in methanol) as compared to the spectra of 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator (0.003 M in methanol). The analysis of λ_{max} at 334.6 nm demonstrates minimal overlap in the absorption bands of the photoinitiator and the starting material. The disparity in absorption supports the utilization for the UV light to drive the thiol-ene reaction, which proceeds *via* a radical mediated stepwise mechanism.

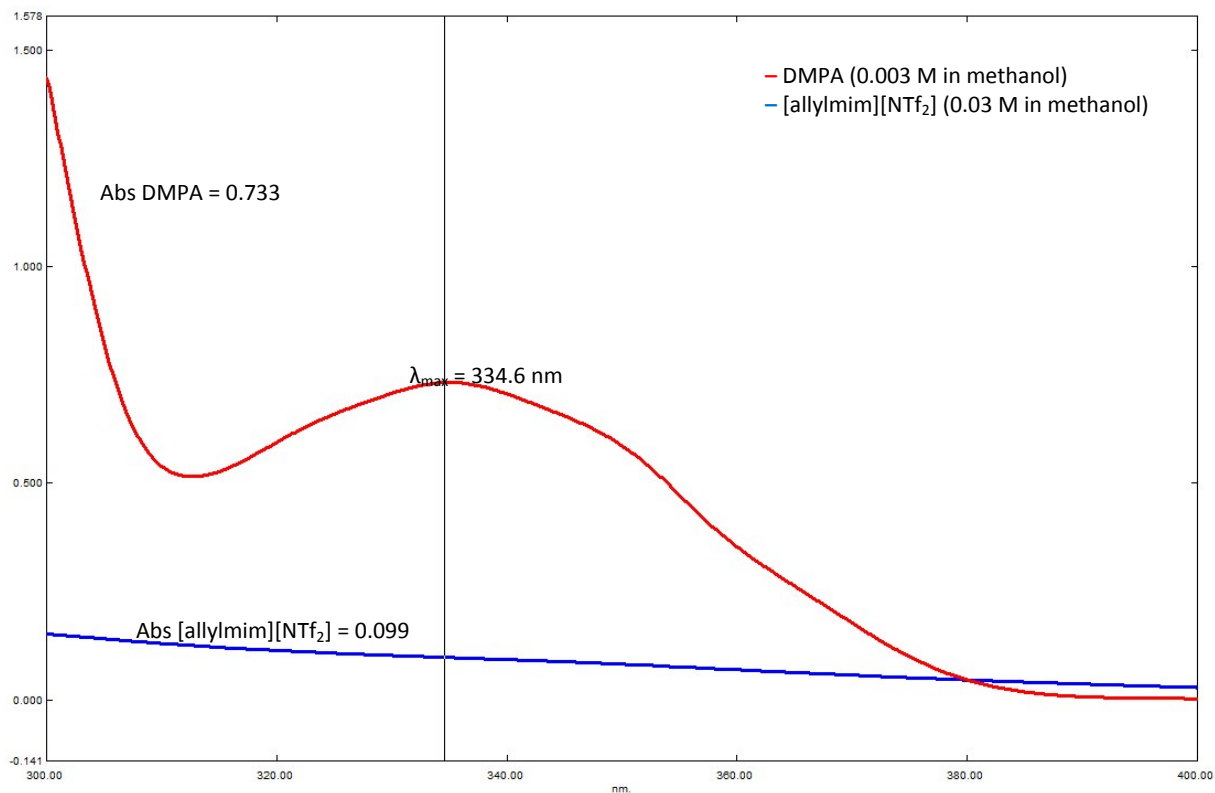


Figure S1. UV-Vis spectra of 0.03 M [allylmim][NTf₂] in methanol (blue line) and 0.003 M DMPA in methanol (red line) absorbance versus wavelength in nm.

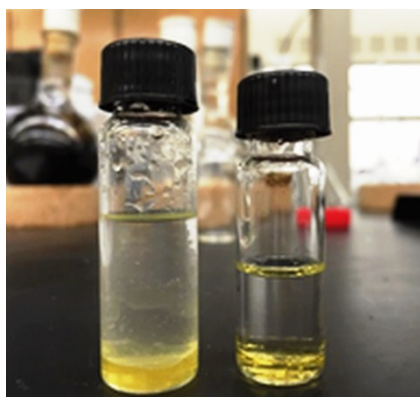


Figure S2. Immiscibility of IL 1 in H₂O (left) and hexanes (right). IL 1 is the bottom phase in both.

Temperature (°C) ± 0.1 °C	Density (g/cm ³) ± 0.0005 g/cm ³	Viscosity (mPa.s)
0.0	1.3953	728.160 ± 0.05
20.0	1.3768	201.550 ± 0.03
40.0	1.3563	73.247 ± 0.01
60.0	1.3389	34.169 ± 0.06
80.0	1.322	18.917 ± 0.05
100.0	1.3051	11.811 ± 0.04

Table S1. Dynamic viscosity and density data of IL **1**. Precision associated with viscosity measurements is given as the standard deviation of ten runs.

The viscosity data for **1** was fit to the Vogel-Fulcher-Tamman (VTF) expression (Equation 1) while the density data were fit to a simple quadratic expression (Equation 2) in temperature.

Equation 1
$$\eta \text{ (mPa.s)} = \eta_{\infty} \exp\left(\frac{k}{T - T_0}\right)$$

Equation 2
$$\rho \text{ (g/cm}^3\text{)} = D_1 + D_2 T \text{ (K)} + D_3 T \text{ (K)}^2$$

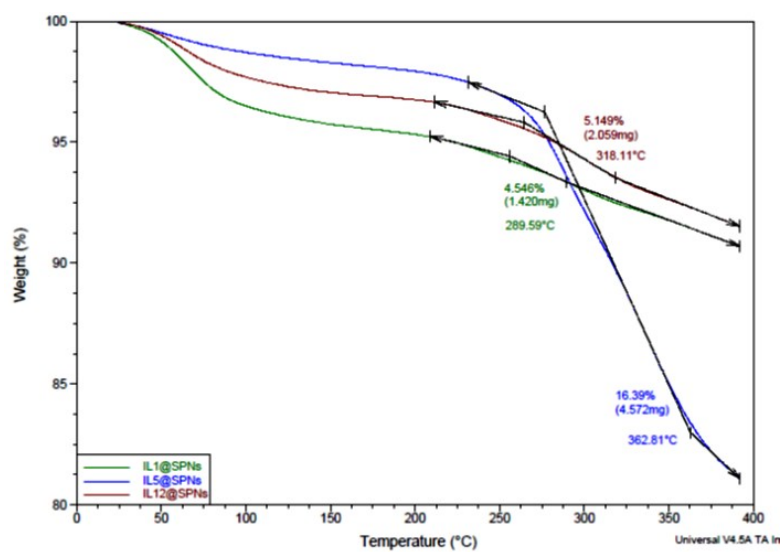


Figure S3. TGA curves of magnetite SPNs coated with bare ILs **1**, **5** and **12**.

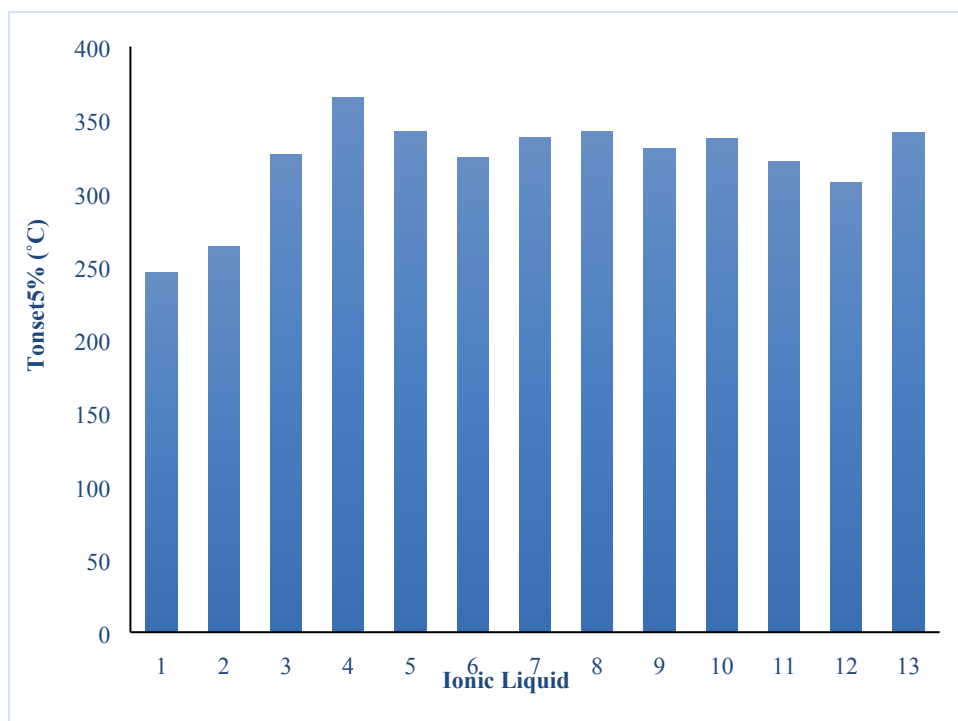


Figure S4. Decomposition temperatures ($T_{\text{onset5\%}}$) of imidazolium-based ILs **1-13**

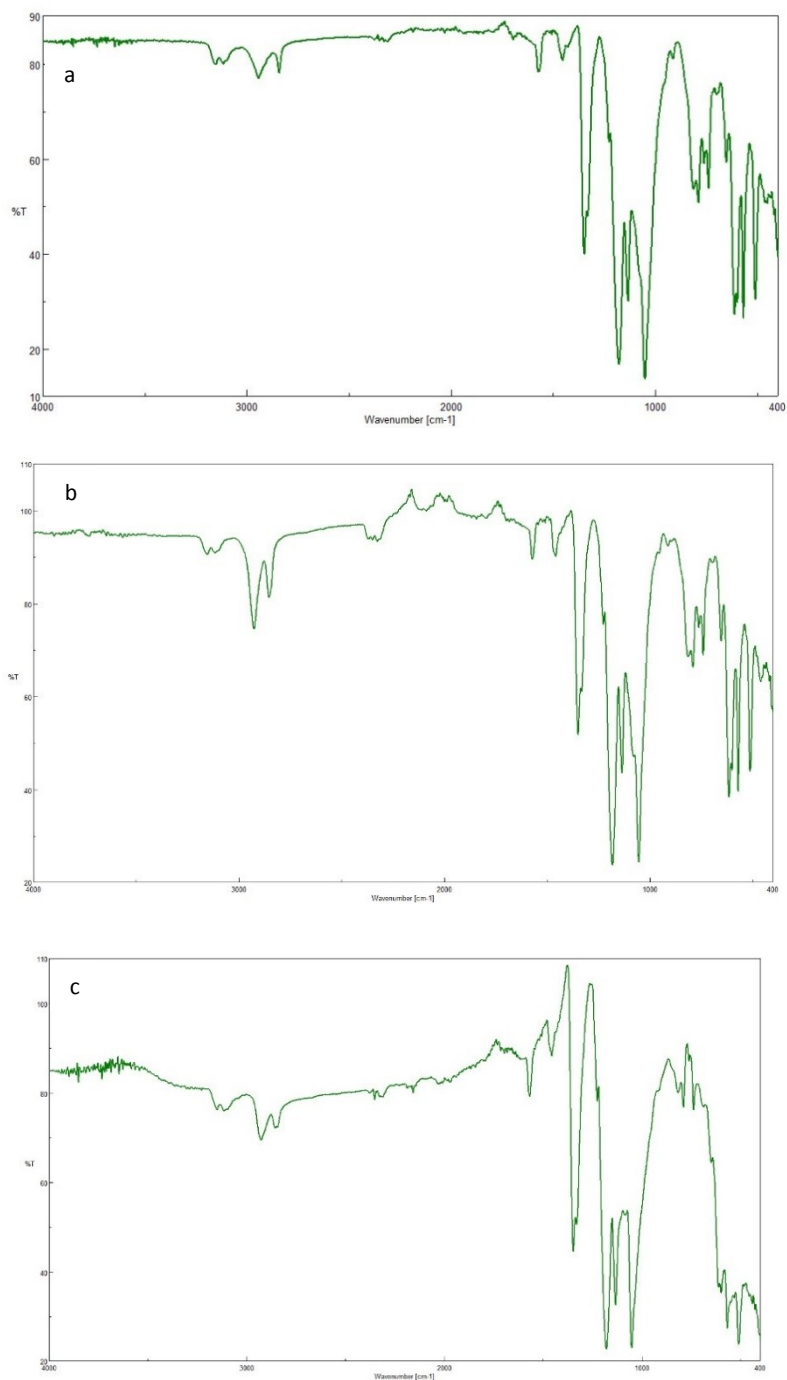


Figure S5. FT-IR spectra of IL **1**@SPNs-OA (a), IL **5**@SPNs-OA (b) and IL **12**@SPNs-OA (c). The spectra verify that all of the ILs were successfully immobilized onto the surface of oleic-acid coated SPNs. A key indication that silanes have been covalently immobilized on the nanoparticle surface is the presence of a new Si-O-Si stretching vibration between 1060 and 1140 cm^{-1} .

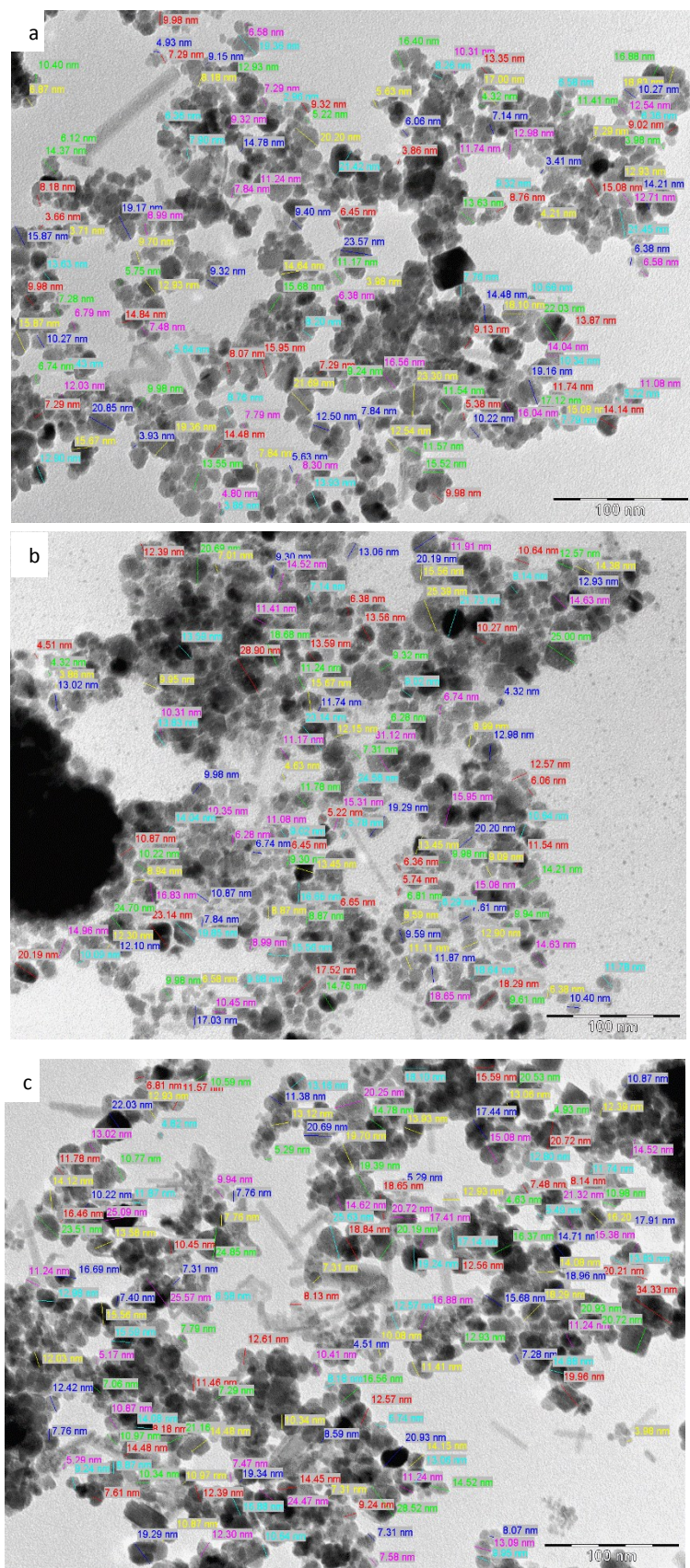


Figure 6S. TEM images of a) IL 1@SPNs-OA, 1, b) IL 5@SPNs-OA, c) IL 12@SPNs-OA.