Surface modification of MoS_2 nanoparticles with ionic liquid-ligands: Towards highly dispersed nanoparticles

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Supporting information

1. Synthesis and characterization of the ionic liquid 1 and the apolar ligand 2

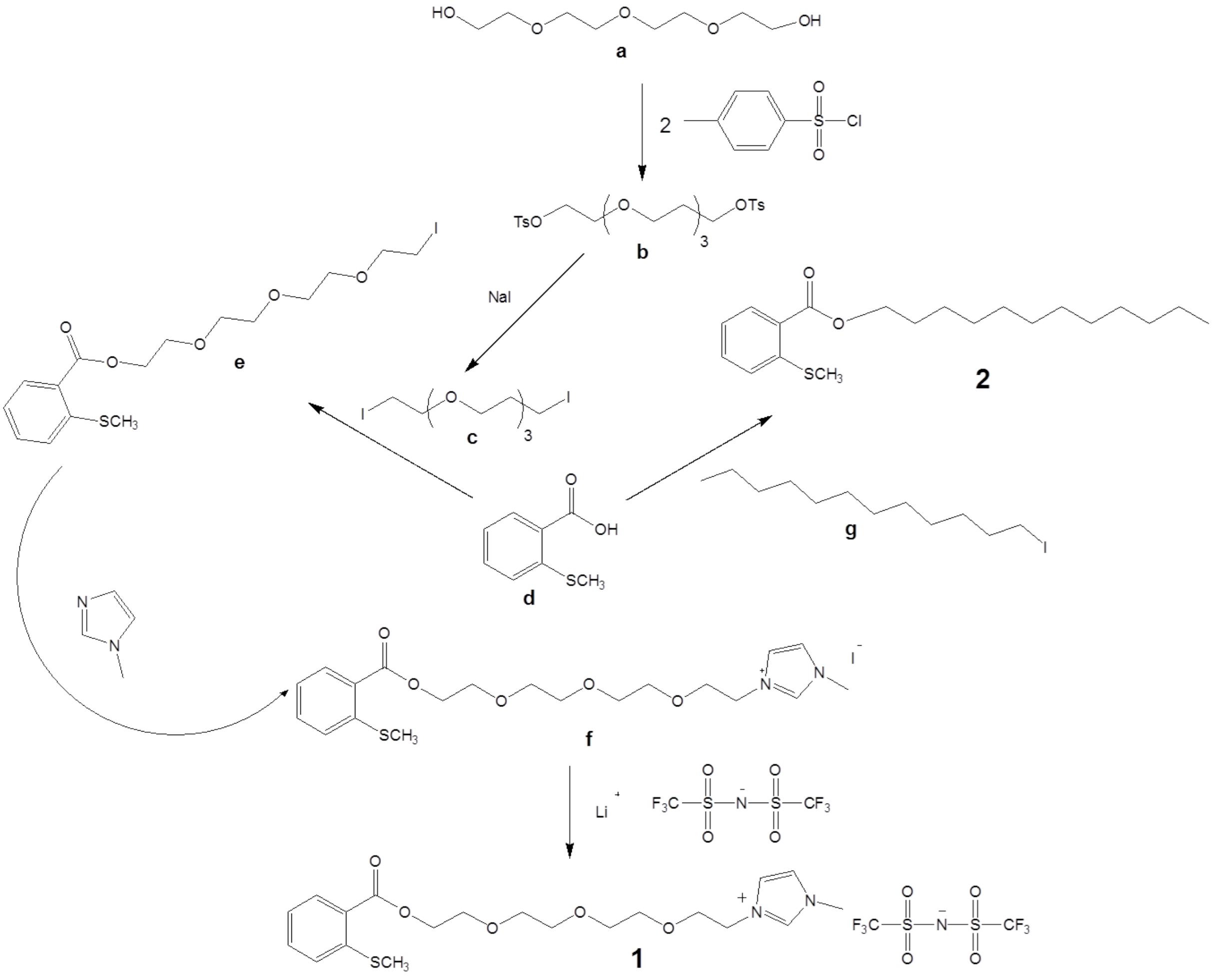

Fig. 1 Schematic presentation of the synthesis route towards IL 1 as well as its apolar counterpart 2

Synthesis of bis-1,11-(p-toluenesulfonyloxy)-3,6,9-trioxaundecane (b)

The synthesis was accomplished according to the procedure from Shao et al.[1]. TEG (5 g, 25.74 mmol) and 4-toluenesulfonyl chloride (11 g, 57.70 mmol, 3 equiv.) were transferred into a round bottom flask and suspended in triethylamine (200 mL). The reaction mixture was stirred at room temperature over night. The solvent was removed and the product extracted with ethylacetate, thereafter dried over Na_2SO_4. The yellow crude product was obtained after filtration and evaporation of solvent with further purification via column chromatography (silica gel, EtOAc/hexane 1:1) to give the pure product. Yield: 96 % (4.8 g).Appearance: colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.72 (m, 4H), 7.25 (dd, J= 8.59 Hz, 0.64 Hz, 4H), 4.04-4.08 (m, 4H), 3.58-3.62 (m, 4H), 3.44-3.50 (m, 8H), 2.35 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 144.83 (s, 2C), 133.01 (s, 2C), 129.83 (s, 4C), 127.95 (s, 4C), 70.64 (d, J= 22.93 Hz, 8C), 69.28 (s, 4C), 68.69 (s, 4C), 21.64 (s, 2C).

Synthesis of diiodotetraethylene glycol (c)

The synthesis was achieved modifying the procedure from Shao et al.[1]. Sodium iodide (4.38 g, 3 mol equiv.) and TPTEG (**b**, 4.9 g, 9.74 mmol) were suspended in acetone (100 mL) in a round bottom flask. The mixture was heated at 40°C under reflux over night. The solvent was removed thereafter and the product was extracted with dichloromethane and washed with brine. The solvent was evaporated and the product was obtained. Yield: 82.5 % (4.0 g).Appearance: yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.70 (t, J= 6.89, 4H), 3.61 (s, 8H), 3.20 (t, J= 6.89 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 77.26 (s, 2C), 77.00 (s, 2C), 76.75 (s, 2C), 2.96 (s, 2C).

Synthesis of 2-(methylthio) benzoic acid (d)

2-(Methylthio)benzoic acid (**d**) was synthesized according to the procedure of Huynh et al.[2], with further modifications to achieve desired result. Accordingly, thiosalicylic acid (15.42 g, 0.119 mol) was suspended in methanol (40 mL) at zero degrees under an inert atmosphere and further deprotonated with 1.9 M NaOH. The solution was allowed to stir for 15 mins. and methyl iodide (8.72 g, 0.14 mol) was added dropwise. The reaction mixture was allowed to stir for 2 h at zero degrees, thereafter, a good portion of the solvent was removed and the rest acidified with 1 M HCl (pH= 1), washed with brine and dried over magnesium sulfate. After filtration, the solvent was evaporated and the obtained white product was dried in vacuo. Yield: 68 % (11.56 g). Appearance: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 11.78 (s, 1H), 8.08 (d, J= 9.35 Hz, 1H), 7.45 (t, J= 7.71 Hz, 1H), 7.23 (d, J= 8.12 Hz, 1H), 7.13 (t, J= 7.07 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 171.33 (s, 1C), 144.37 (s, 1C), 133.32 (s, 1C), 132.49 (s, 1C), 125.50 (s, 1C), 124.43 (s, 1C), 123.54 (s, 1C), 15.58 (s, 1C).

Synthesis of 1-[2-(methylthio)benzoyl]-11-iodo-3,6,9-trioxaundecane (e)

2-(methylthio) benzoic acid (**d**) (0.25 g, 1.48 mmol) was suspended in acetone (30 mL) and deprotonated with two fold excess of ceasium carbonate (2 equiv., 0.98 g, 2.96 mmol) followed by the addition of diiodotetraethylene glycol (**c**) (3 equiv., 4.44 mmol, 1.84 g). The reaction mixture was heat to 45°C and refluxed for 24 h after which the solvent was removed. The residue was acidified and the product extracted with ethylacetate. The solvent was evaporated to obtain the product in a yield of 85 % (1.7 g). Appearance: yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.03 (dd, J= 7.97, 1.45 Hz, 1H), 7.47 (m, 1H), 7.28 (s, 1H), 7.15 (m, 1H), 4.48 (dd, J= 5.51, 4.30 Hz, 2H), 3.84 (dd, J= 5.41, 4.40 Hz, 2H), 3.62-3.75 (m, 10H), 3.24 (t, J= 6.58 Hz, 2H), 2.45 (s, 3H).

Synthesis of 1-[2-(methylthio)benzoyl]-11-(3-methyl-1H-imidazolium-1-yl)-(3,6,9-trioxaundecane) iodide (f)

1-[2-(methylthio)benzoyl]-11-iodo-3,6,9-trioxaundecane (**e**) (1.71 g, 3.78 mmol) was dissolved in a small amount of of water and then 1-methylimidazole (10 mL, 10 fold excess) was added. The reaction mixture was heated to 105°C for 48 h under reflux and an inert atmosphere. The solvent was removed and the brownish liquid was dried on vacuum line. Purification was accomplished by column chromatography (silica gel, chloroform: methanol, 2:1). Yield: 84 % (1.43 g). Appearance: brownish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 9.69 (s, 1H), 7.97 (dd, J= 8.85, 1.56 Hz, 1H), 7.68 (t, J= 1.75 Hz, 1H), 7.56-7.47 (m, 1H), 7.29 (d, J= 8.11 Hz, 1H), 7.18 (m, 2H), 3.97 (s, 3H), 3.74 (m, 14H), 3.48 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 143.41 (s, 1C), 137.20 (s, 1C), 133.00 (s, 1C), 131.27 (s, 1C), 126.25 (s, 2C), 124.55 (s, 1C), 123.79 (s, 1C), 123.72 (s, 1C), 123.55 (s, 2C), 122.42 (s, 1C), 70.51 (s, 1C), 70.19 (d, J= 4.62 Hz, 1C), 69.17 (s, 1C), 68.73 (s, 1C), 63.92 (s, 1C), 49.68 (s, 1C), 36.62 (s, 1C), 15. 67 (s, 1C).

Synthesis of 1-[2-(methylthio)benzoyl]-11-(3-methyl-1H-imidazolium-1-yl)-(3,6,9-trioxaundecane) bis (trifluoromethanesulfonyl) imide (1)

The synthesis of 1-[2-(methylthio)benzoyl]-11-(3-methyl-1H-imidazolium-1-yl)-(3,6,9-trioxaundecane) bis (trifluoromethanesulfonyl) imide (**1**) was performed by dissolving 1-[2-(methylthio)benzoyl]-11-(3-methyl-1H-imidazolium-1-yl)-(3,6,9-trioxaundecane) iodide (**f**) (1.62 g, 3.01 mmol), in a small amount of water/acetone (total volume: 25 mL) with simultaneous addition of Li-Tf_2N (0.86 g, 3.01 mmol). The reaction mixture was heated to 40°C and stirred for 24 h under inert atmosphere. The solvent was removed afterwards and the obtained ionic liquid was dissolved in dichloromethane and washed with cold water for several times. The solvent was evaporated and the ionic liquid was dried in vacuo. Yield: 96 % (1.37 g). Appearance: light brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$)δ ppm: 8.80 (s, 1H), 7.96 (dd, J= 7.84, 1.57 Hz, 1H), 7.48-7.50 (m, 2H), 7.28 (d, J= 8.17 Hz, 1H), 7.14-7.16 (m, 2H), 4. 25 (d, J= 9.22 Hz, 2H), 3.87 (s, 3H), 3.81-3.58 (m, 14H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)δ ppm: 166.23 (s,1C), 143.36 (s, 1C), 136.64 (s, 1C), 136.34 (s, 1C), 132.95 (s, 1C), 131.23 (s, 1C), 126.28 (s, 1C), 124.48 (s, 1C), 123.70 (t, J= 98.12 Hz, 79.92 Hz, 2C), 122.71 (s, 1C), 121.38 (s, 1C), 118.19 (s, 1C), 109.99 (s, 1C), 70.46 (s, 1C), 70.15 (s, 1C), 69.05 (s, 1C), 68.48 (s, 1C), 63.87 (s, 1C), 49.68 (s, 1C), 36.22 (s, 1C), 15.45 (s, 1C).

Synthesis of dodecyl 2-(methylthio) benzoate (2)

The synthesis of dodecyl 2-(methylthio) benzoate (**2**) was accomplished in a similar way as product (**e**) by suspending 2-(methylthio) benzoic acid (**d**) (2 g, 11.89 mmol) in 30 mL of acetone and deprotonating with a two-fold excess of Cs_2CO_3 (7.74 g, 2 equiv., 23.7 mmol) followed by the addition of 1-iodododedacane (3.52 g, 1 equiv., 11.89 mmol). The reaction mixture was heated to 45°C and refluxed under inert atmosphere. The solvent was removed and the residue was acidified and the product was extracted with ethylacetate. Yield: 90 % (1.8 g). Appearance: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.00 (d, J= 7.81 Hz, 1H), 7.49 (m, 1H), 7.32 (m, 1H), 7.19 (m, 1H), 4.35 (t, J= 6.37 Hz, 2H), 2.48 (s, 3H), 1.77 (m, 2H), 1.39 (m, 18H), 0.91 (t, J= 6.85 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm: 170.80 (s, 1C), 166.64 (s, 1C), 166.52 (s, 1C), 133.28 (s, 1C), 132.46 (s, 1C), 132.35 (s, 1C), 131.22 (d, J= 9.38 Hz, 1C), 124.41 (d, J= 15.52 Hz, 1C), 123.48 (d, J= 18.79 Hz, 1C), 65.29 (s, 1C), 32.02 (d, J= 24.51 Hz, 1C), 28.95 (s, 6C), 26.11 (d, J= 3.39 Hz, 2C), 22.70 (s, 1C), 15.61 (s, 1C), 14.12 (s, 1C).

2. Preparation and modification of MoS_2 NPs

Preparation of unfunctionalized MoS_2 nanoparticles[3]

For the synthesis of MoS_2 nanoparticles, thiourea (0.69 g, 9 mmol) was dissolved in 30 mL of water and added to sodium molybdate (0.72 g, 3 mmol). The ionic liquid N-butyl-N'-methylimidazolium-chloride ([bmim][Cl]) (1 g, 5.7 mmol) was subsequently dissolved in 20 mL of water and added to the reaction flask. The reaction was purged with gas and then acidified with 0.1 N HCl (pH<1). The reaction mixture was refluxed under inert atmosphere at 180°C for 24 h. After cooling to room temperature, the solution was centrifuged and obtained nanoparticles washed several times with water.

After evaporation of water, the nanoparticles were dried in oven at 50°C. Size (obtained from DLS): 12.2 nm (radius), 24.4 nm (diameter). Yield: 98 % (1.38 g).

Functionalization of bare MoS_2 nanoparticles with the ionic liquid IL-ligand-1

MoS_2 nanoparticles were functionalized by transferring the ionic liquid (ligand-**1**) (0.086 g, 0.12 mmol) and MoS_2 NPs (0.020 g, 0.12 mmol) into a round bottom flask containing methanol. The reaction mixture was refluxed for 48 h. The obtained NPs were washed with methanol and water and dried in oven overnight at 50°C.

Functionalization of bear MoS_2 nanoparticles with ligand-2

The functionalization of MoS_2 NPs with hydrophobic compound (ligand-**2**) was achieved through the same process as previous, where the ligand (**2**) (0.051 g, 0.12 mmol) and the MoS_2 NPs (0.020 g, 0.12 mmol) were transferred into a round bottom flask containing methanol (20 mL). The reaction mixture was heated under reflux for 48 h. The obtained nanoparticles were washed with toluene and dried in an oven at 50°C.

Preparation of amphiphilic MoS_2 nanoparticles with hydrophilic IL-ligand 1 and the hydrophobic ligand (2)

Functionalization of the bare NPs with an equimolar ratio of the IL-ligand (**1**) and the ligand (**2**) was done by putting the bear MoS_2 NPs (0.040 g, 0.25 mmol) into a round bottom flask containing methanol with stirring. This was followed by the addition of the hydrophilic IL-ligand (**1**) (0.5 equiv., 0.086 g) and the ligand (**2**) (0.5 equiv., 0.051 g). The reaction mixture was heated and allowed to stir under reflux for 60 h. The obtained NPs were washed several times with methanol and water to remove unreacted ligands.

3. Optimization of the reaction conditions regarding surface modification of MoS_2 NPs

Surface modification of MoS_2 NPs with ionic liquid-ligand 1

Weight ratio ligand/NP	**Reaction duration**	**Grafting density [chain/nm^2]**
1:1	2days	0.089
1:1	3 days	0.141
3:1	2 days	0.080
3:1	3 days	0.090
5:1	2 days	0.082
1:2	2 days	0.013
2:1	2 days	0.077

Surface modification of MoS_2 NPs with ligand 2

Weight ratio ligand/NP	**Reaction duration**	**Grafting density [chain/nm^2]**
1:1	2days	0.093
1:1	3days	0.161
3:1	2days	0.130
3:1	3days	0.109
5:1	2days	0.088
5:1	3days	0.091
1:2	2days	0.037

4. DLS analysis of MoS_2 NPs:

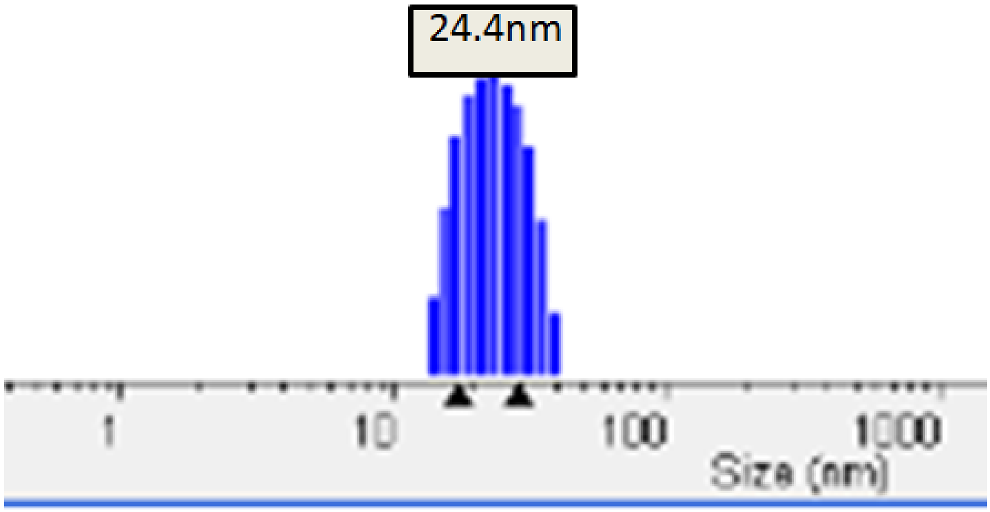

Fig. 1 Size distribution of bare MoS_2

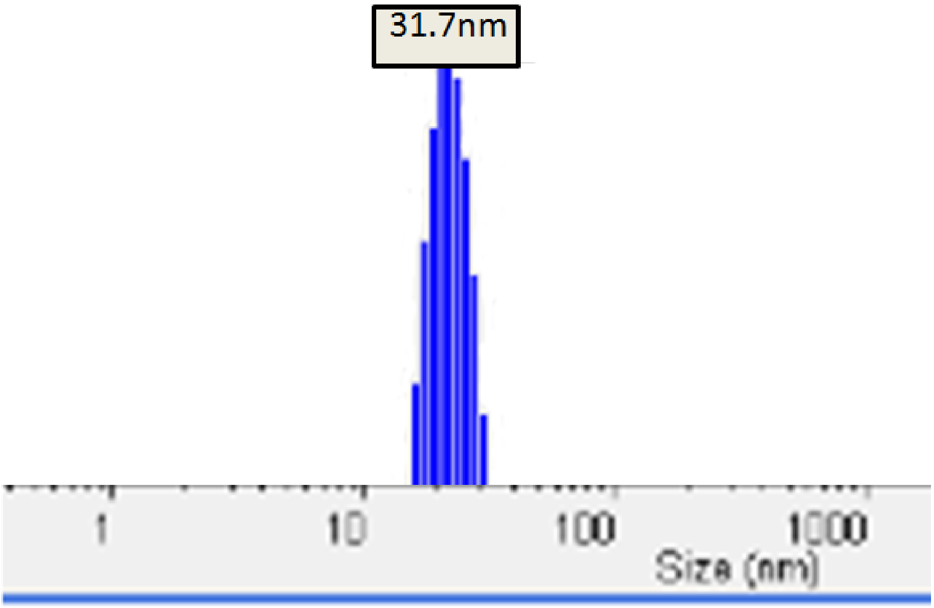

Fig. 2 Size distribution of modified MoS_2 with ionic liquid 1

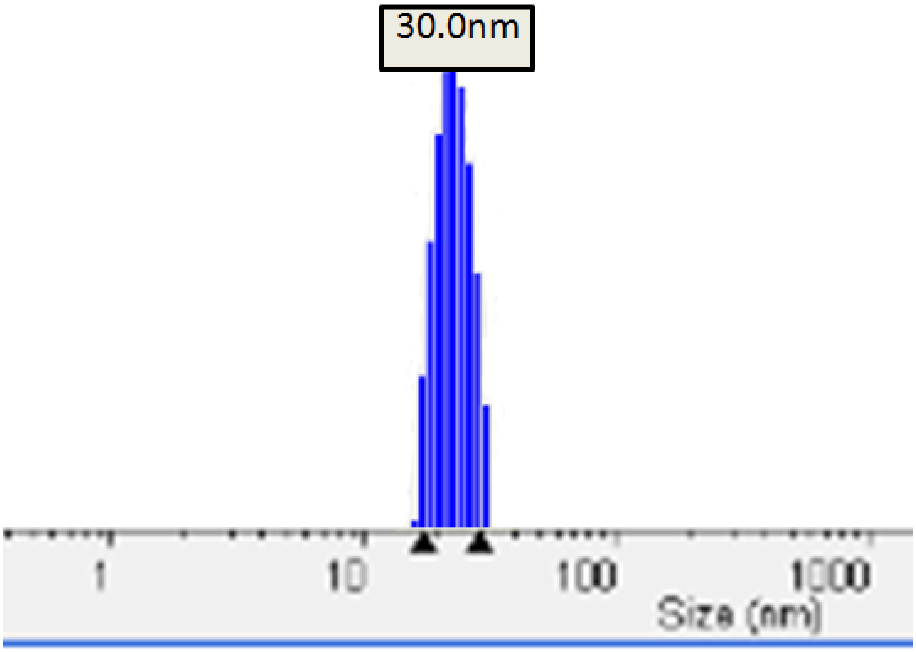

Fig. 3 Size distribution of modified MoS_2 with hydrophobic ligand 2

5. TGA analysis of MoS_2 NPs

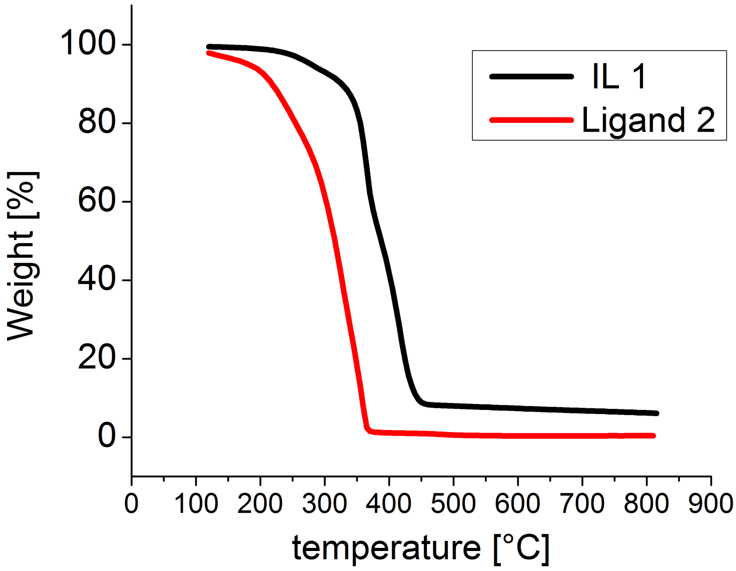

Fig. 4 TGA curve of pure IL-ligand 1 and ligand 2

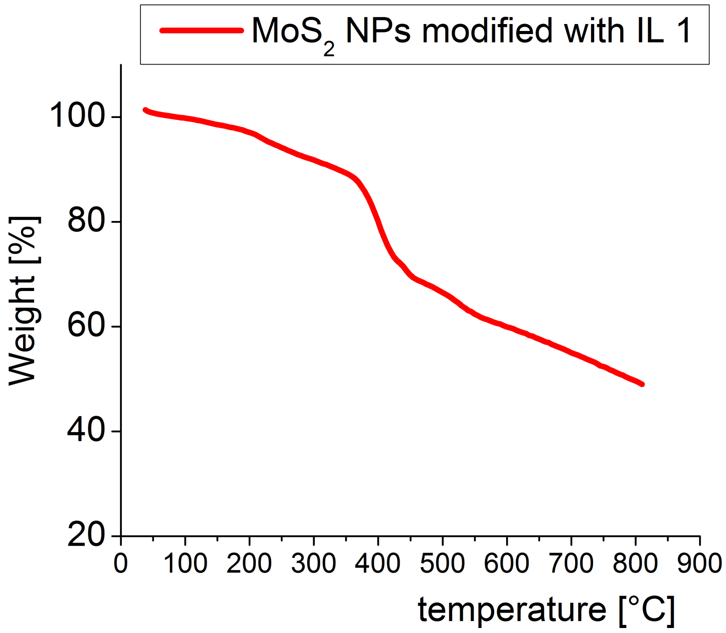

Fig. 5 **TGA curve of modified MoS_2 with IL-ligand 1**

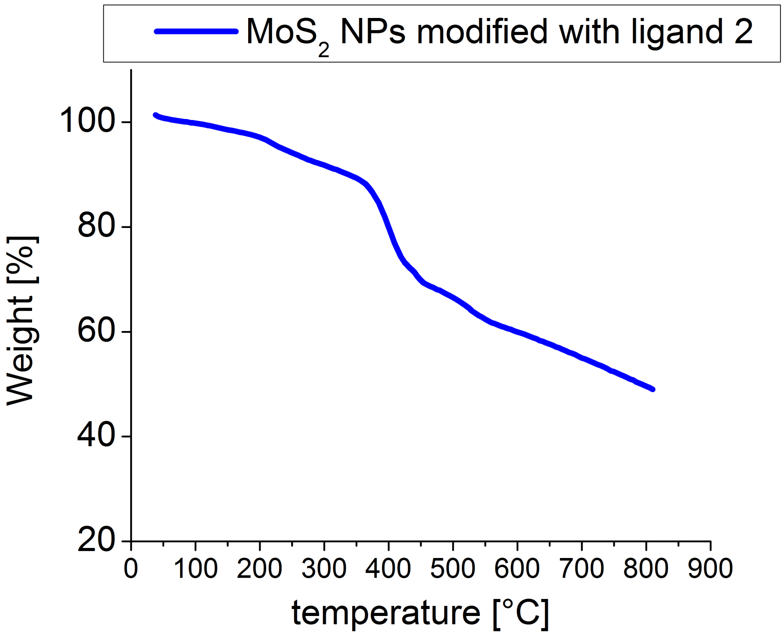

Fig. 6 **TGA curve of modified MoS_2 with ligand 2**

6. IR analysis of MoS_2 NPs

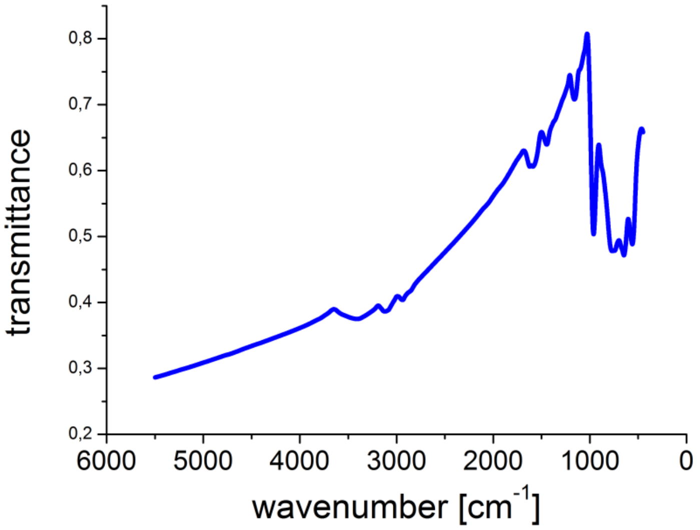

Fig. 7 IR spectrum of bare MoS_2 NPs

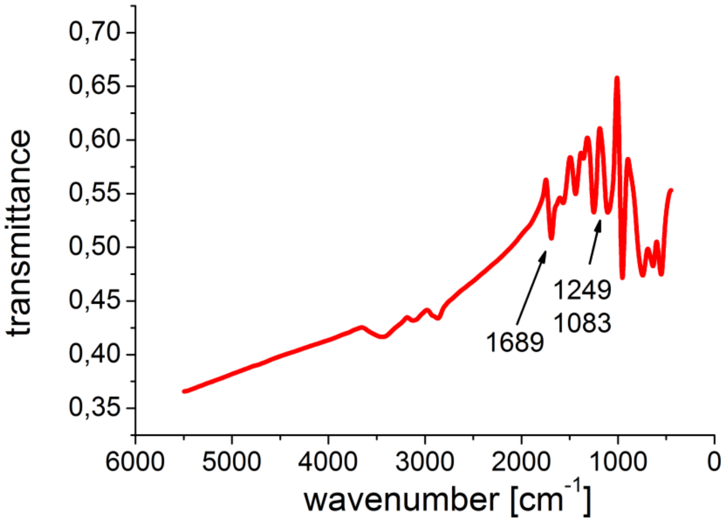

Fig. 8 IR spectrum of modified MoS_2 with ionic liquid-ligand 1

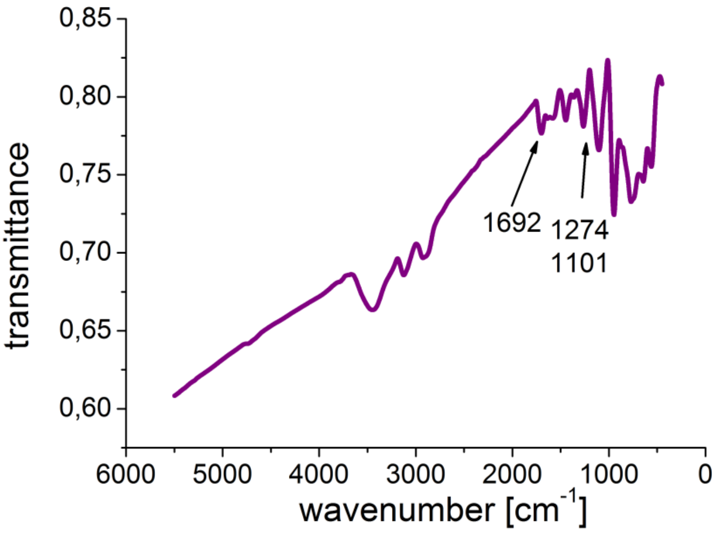

Fig. 9 IR spectrum of “amphiphilic” MoS_2

7. Preparation of microemulsions

Table 1: Composition of [EMIM][$BuSO_4$]/decaline-microemulsions.

Entry	decaline (g)	[emim] [$BuSO_4$] (g)	total mass (g)	NPs (mg)	observations
1	0.179	2.11	2.29	4.4	microemulsion
2	0.358	1.872	2.23	4.5	microemulsion
3	0.538	1.638	2.18	4.6	microemulsion
4	0.717	1.404	2.12	4.7	bi/triphasic
5	0.896	1.171	2.07	4.8	bi/triphasic
6	1.075	0.936	2.01	4.9	bi/triphasic
7	1.254	0.702	1.96	5.1	bi/triphasic
8	1.434	0.468	1.90	5.3	bi/triphasic
9	1.613	0.234	1.85	5.4	bi/triphasic

1. M. Shao, P. Dongare, L. N. Dawe, D. W. Thompson and Y. M. Zhao, *Org. Lett.*, 2010, **12**, 3050-3053.
2. H. V. Huynh, C. H. Yeo and G. K. Tan, *Chem. Commun.*, 2006, **0**, 3833-3835.
3. H. Luo, C. Xu, D. B. Zou, L. Wang and T. K. Ying, *Mater. Lett.*, 2008, **62**, 3558-3560.