Supramolecular Liquid Crystal Nanocomposites Based on Carboxylic Acid - Pyridine Hydrogen Bonds

M. Roohnikan, A. Lindner-D'Addario, V. Toader, A. Rey, D. Tan, T. Friščič and L. Reven

QUEBEC CENTRE FOR ADVANCED MATERIALS, DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY, 801 SHERBROOKE ST. W., MONTREAL QC H3A 0B8

Synthesis of (3-(pyridin-4-yl)propyl)phosphonic acid was performed in two steps as shown in scheme S1.

Scheme S1.

Synthesis of diethyl (3-(pyridine-4-yl)propyl)phosphonate. Lithium diisopropyl amide (LDA) (18.5 ml, 1.2 eq.) was added dropwise to a solution 4-methyl pyridine (Sigma Aldrich) (1.5 ml, 15.25 mmol, 1 eq.) in 30 ml dry THF at -30°C under an inert atmosphere. After the reaction mixture was stirred at low temperature for 3 h, diethyl 2-bromoethyl phosphonate (2.85 ml, 15.25 mmol, 1 eq.) was added as a solution in 20 ml dry THF. The reaction mixture was allowed to reach room temperature overnight then was portioned between water and chloroform. The organic layer was separated, dried over MgSO4 and concentrated. The crude product was purified by column chromatography (SiO2, dichloromethane: methanol, 24 : 1 (v : v)). The fractions with Rf = 0.15 were separated to give 1.91 g of diethyl (3-(pyridin-4-yl)propyl)phosphonic acid (η = 0.48).

1H NMR (500 MHz, CDCl3) δ (ppm): 8.51 (d, J = 5.4 Hz, 2H, H ortho to N), 7.13 (d, J = 5.8 Hz, 2H, H meta to N), 4.17 – 4.02 (m, 4H, ~ P(O)(OCH2CH2)2), 2.72 (t, J = 7.6 Hz, 2H, PyCH2CH2~), 1.96 (m, 2H, PyCH2CH2~), 1.79 – 1.69 (m, 2H, Py(CH2)2CH2~), 1.32 (t, J = 7.1 Hz, 6H, ~ P(O)(OCH2CH3)2).

13C NMR (500 MHz, CDCl3) δ (ppm): 150.03; 149.76; 123.90; 61.57 (d, J = 7.6 Hz); 35.6 (d, J = 15 Hz); 25.04 (d, J = 142.08 Hz); 23.13 (d, J = 5.03 Hz); 16.47 (d, J = 6.2 Hz).

31P NMR (161 MHz, CDCl3) δ (ppm): 31.23.

Synthesis of (3-(pyridin-4-yl)propyl)phosphonic acid. (3-PPA) Diethyl (3-(pyridine-4-yl)propyl)phosphonate (1.91 g, 7.44 mmol, 1 eq.) was dissolved in 29 ml dichloromethane under an inert atmosphere. Trimethylsilyl bromide (2.95 ml, 22.34 mmol, 3 eq.) was added dropwise and the reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure together with the excess Me3SiBr and to the residue methanol was added. The mixture was heated at 30°C for 4h. The solvent was removed under vacuum to give 1.49 g of (3-(pyridin-4-yl)propyl)phosphonic acid.

1H NMR (400 MHz, CD3OD) δ (ppm): 8.67 (d, J = 6.8 Hz, 2H, H ortho to N), 7.85 (d, J = 6.4 Hz, 2H, H meta to N), 3.02 (t, J = 7.6 Hz, 2H, PyCH2CH2~), 2.24 (m, 2H, PyCH2CH2~), 1.77 – 1.68 (m, 2H, Py(CH2)2CH2~).

13C NMR (125 MHz, CD3OD) δ (ppm): 161.63, 142.49, 126.56, 35.82 (d, J = 27.6 Hz), 26.25 (d, J = 138.4), 23.33 (d, J = 5.03 Hz).

31P NMR (161 MHz, CDCl3) δ (ppm): 27.34.

ESI-HRMS m/z 202.0629 [M+1] (calcd. average mass for C9H12NO3P: 201.0555)
Figure S1. TEM images of ZrO$_2$ nanoparticles (a) before functionalization, average particle size =3.49 nm (B) after functionalization with 3-PPA, average particle size =3.41 nm

$^1$H NMR of free ligands

$^1$H NMR of functionalized NPs

Figure S2. $^1$H NMR spectra of 3-(pyridin-4-yl)propylphosphonic acid (3-PPA) in CD$_3$OD and 3-PPA adsorbed on ZrO$_2$ NPs in D$_2$O.

The attachment of 3-PPA to the ZrO$_2$ ligands is verified by the broadening and shifting of the proton signals as compared to the unbound ligand where the assignment of the peaks is based on the chemical shifts and splittings as detailed in the proceeding synthesis section. As typically observed, the proton signal (e) closest to the surface bound phosphonate group is broadened into the baseline beyond detection.
Figure S3. TGA data for the ZrO$_2$ NPs functionalized with 3-PPA through exchange (left) and milling (right).

**Oleic acid stabilized ZrO$_2$ NPs:**

**TGA data**: 73% residual (ZrO$_2$) and 27% organic (OA)

Surface area of 1 g of 3.5 nm dia. ZrO$_2$ NPs:

\[
\text{surface per NP} \times \text{NPs per g} = 4\pi r^2 \times \left( \frac{1g \ ZrO_2}{\text{mass of 1 NP}} \right) = 4\pi r^2 \times \left( \frac{1g \ ZrO_2}{\text{vol of 1 NP} \cdot d_{ZrO_2}} \right) = 4\pi (1.75nm)^2 \left( \frac{1g \ ZrO_2}{1.28 \times 10^{-19} g/\text{NP}} \right) = 38.48 \text{nm}^2 \times 7.81 \times 10^{18} \text{NPs} = 3.01 \times 10^{20} \text{nm}^2/\text{g}
\]

Surface area of the ZrO$_2$ NPs in 1 g of ZrO$_2$-OA NPs:

\[
0.73g \times 3.01 \times 10^{20} \text{nm}^2/\text{g} = 2.19 \times 10^{20} \text{nm}^2/\text{g}
\]

Number of OA ligands, MW= g/mol in 1 g of ZrO$_2$-OA NPs:

\[
0.27g/282g \cdot \text{mol}^{-1} \times 6.022 \times 10^{23} \cdot \text{mol}^{-1} = 5.77 \times 10^{20} \text{ligands}
\]

Surface area per ligand = \(2.19 \times 10^{20} \text{nm}^2/5.77 \times 10^{20} \text{ligands} = 0.38 \text{nm}^2\)

**ZrO$_2$-pyr NPs produced by milling, starting with oleic acid stabilized ZrO$_2$ NPs:**

**TGA data**: 86.7% residual (ZrO$_2$) and 13.3% organic (3-PPA)

Surface area of the ZrO$_2$ NPs:

\[
0.867g \times 3.01 \times 10^{20} \text{nm}^2/\text{g} = 2.61 \times 10^{20} \text{nm}^2
\]

Number of 3-PPA ligands, MW=199 g/mol:

\[
0.133g/199g \cdot \text{mol}^{-1} \times 6.022 \times 10^{23} \cdot \text{mol}^{-1} = 4.02 \times 10^{20} \text{ligands}
\]

Surface area per ligand = \(2.61 \times 10^{20} \text{nm}^2/4.02 \times 10^{20} \text{ligands} = 0.65 \text{nm}^2\)
Figure S4. POM of 2 wt% ZrO$_2$-pyr NP in 4CA for (a) slow cooling, 0.1 deg/min. and (b) fast cooling, 1 deg./min.