Electronic Supplemental Information (ESI)

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

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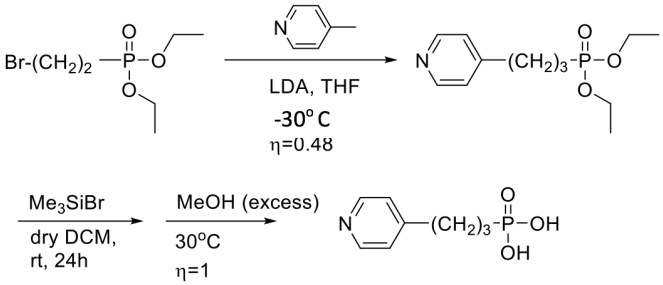
Synthesis of (3-(pyridin-4-yl)propyl)phosphonic acid was performed in two steps as shown in scheme S1.



Scheme S1.

Synthesis of diethyl (3-(pyridine-4-yl)propylphosphonate. 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 $MgSO_4$ and concentrated. The crude product was purified by column chromatography (SiO_2, dichloromethane: methanol, 24 : 1 (v : v)). The fractions with $R_f = 0.15$ were separated to give 1.91 g of diethyl (3-(pyridine-4-yl)propylphosphonate (η = 0.48).

^{1}H NMR (500 MHz, $CDCl_3$) 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)(OC*H*$_2$CH$_3$)$_2$) , 2.72 (t, *J* = 7.6 Hz, 2H, PyC*H*$_2$CH$_2$~), 1.96 (m, 2H, PyCH$_2$C*H*$_2$~), 1.79 – 1.69 (m, 2H, Py(CH$_2$)$_2$ C*H*$_2$ ~), 1.32 (t, *J* = 7.1 Hz, 6H, ~ P(O)(OCH$_2$C*H*$_3$)$_2$).
^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 150.03; 149.76; 123.90; 61.57 (d, *J* = 6.2 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).
^{31}P NMR (161 MHz, $CDCl_3$) δ (ppm): 31.23.

Synthesis of (3-(pyridin-4-yl)propyl)phosphonic acid. (3-PPA) Diethyl (3-(pyridine-4-yl)propylphosphonate (1.91g, 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 Me_3SiBr 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.
^{1}H NMR (400 MHz, CD_3OD) 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, PyC*H*$_2$CH$_2$~), 2.24 (m, 2H, PyCH$_2$C*H*$_2$~), 1.77 – 1.68 (m, 2H, Py(CH$_2$)$_2$ C*H*$_2$ ~).
^{13}C NMR (125 MHz, CD_3OD) 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).
^{31}P NMR (161 MHz, $CDCl_3$) δ (ppm): 27.34.

ESI-HRMS m/z 202.0629 [M+1] (calcd. average mass for $C_8H_{12}NO_3P$: 201.0555)

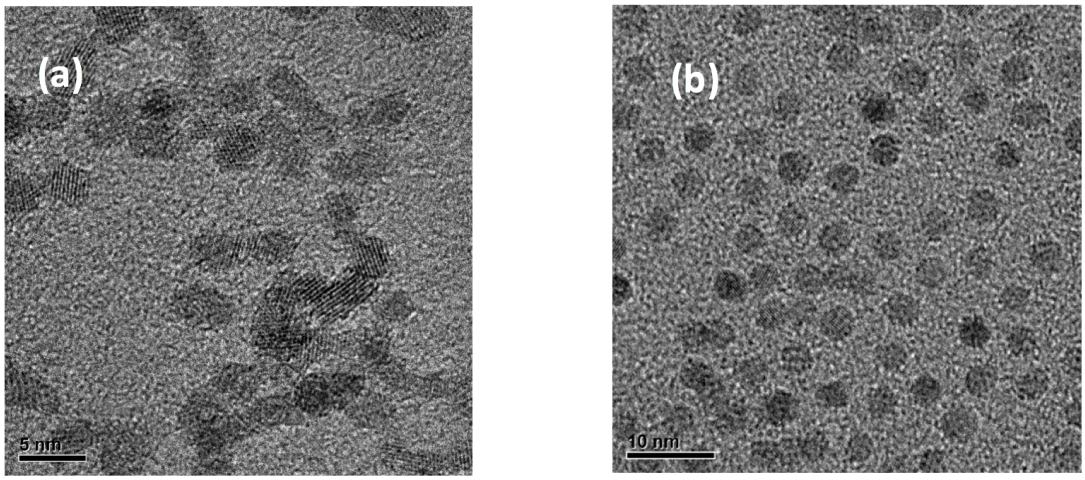


Figure S1. TEM images of ZrO_2 nanoparticles (a) before functionalization, average particle size =3.49 nm (B) after functionalization with 3-PPA, average particle size =3.41 nm

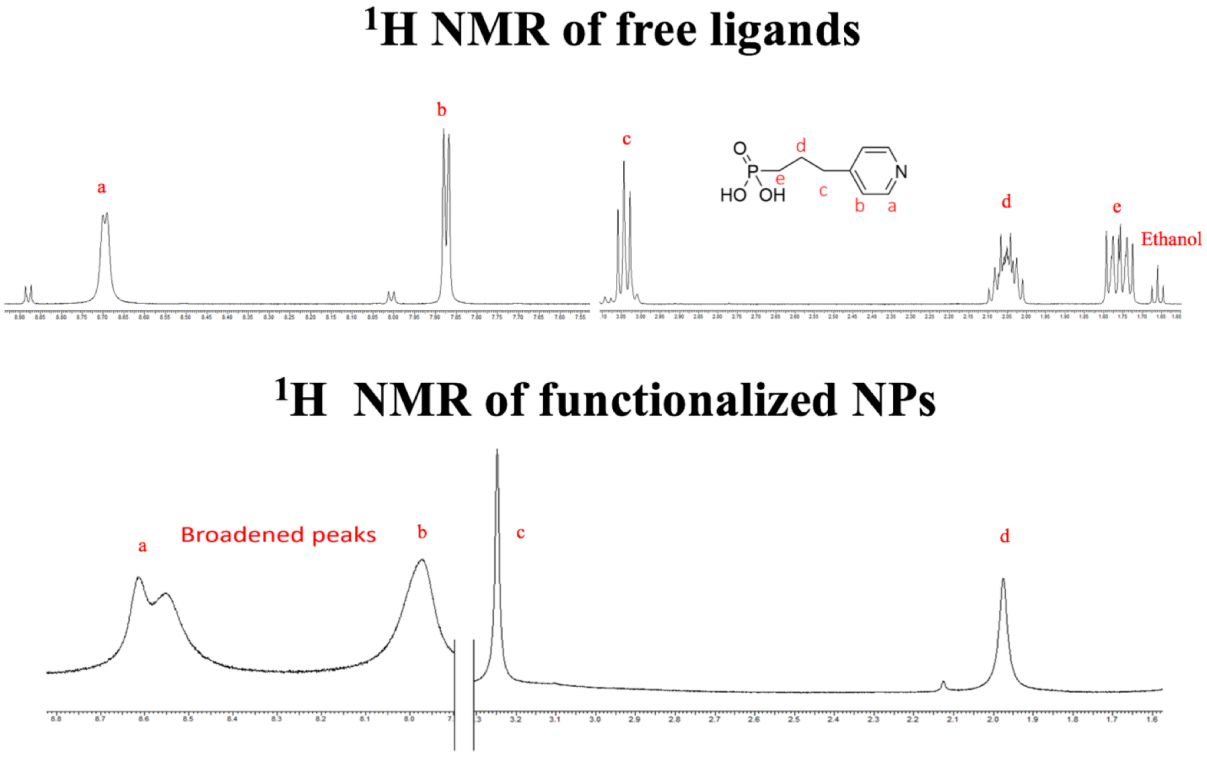
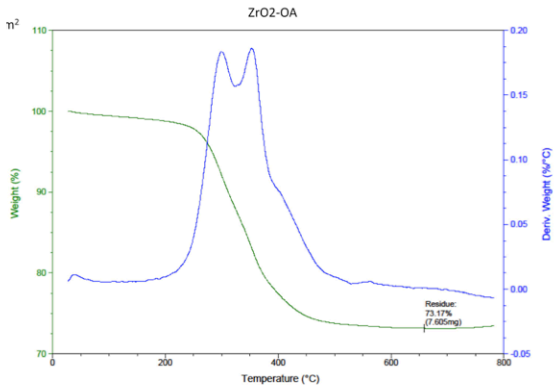
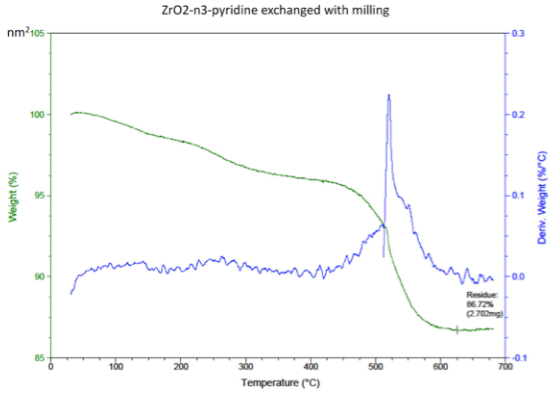


Figure S2. ^{1}H NMR spectra of 3-(pyridin-4-yl)propyl)phosphonic acid (3-PPA) in CD_3OD and 3-PPA adsorbed on ZrO_2 NPs in D_2O.

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.



Footprint ~ 0.38 nm^2



Footprint ~ 0.65 nm^2

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:

$$\text{surface per NP} \times \text{ NPs per g} = 4\pi r^2 \times \left\{\frac{1g\ ZrO_2}{mass\ of\ 1\ NP}\right\} = 4\pi r^2 \times \left\{\frac{1g\ ZrO_2}{vol\ of\ 1\ NP \cdot d_{ZrO_2}}\right\}$$

$$= 4\pi(1.75nm)^2\left(\frac{1g\ ZrO_2}{\frac{4}{3}\pi(1.75nm)^3 \cdot 5.7\times10^{-21}g \cdot nm^3}\right) = 4\pi(1.75nm)^2\left(\frac{1g\ ZrO_2}{1.28\times10^{-19}g/NP}\right)$$

$$= 38.48nm^2 \times 7.81\times10^{18}NPs = 3.01\times10^{20}nm^2/g$$

Surface area of the ZrO_2 NPs in 1 g of ZrO_2-OA NPs:
$0.73g \times\ 3.01\times10^{20}\ nm^2/g = 2.19\times10^{20}nm^2/g$

Number of OA ligands, MW= g/mol in 1 g of ZrO_2-OA NPs:
$0.27g/282g \cdot mol^{-1} \times 6.022\times10^{23} \cdot mol^{-1} = 5.77\times10^{20}ligands$

surface area per ligand = $2.19\times10^{20}nm^2/5.77\times10^{20}ligands = \mathbf{0.38\ nm^2}$

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:
$0.867g \times\ 3.01\times10^{20}\ nm^2/g = 2.61\times10^{20}nm^2$
Number of 3-PPA ligands, MW=199 g/mol:
$0.133g/199g \cdot mol^{-1} \times 6.022\times10^{23} \cdot mol^{-1} = 4.02\times10^{20}ligands$

surface area per ligand = $2.61\times10^{20}nm^2/4.02\times10^{20}ligands = \mathbf{0.65\ nm^2}$

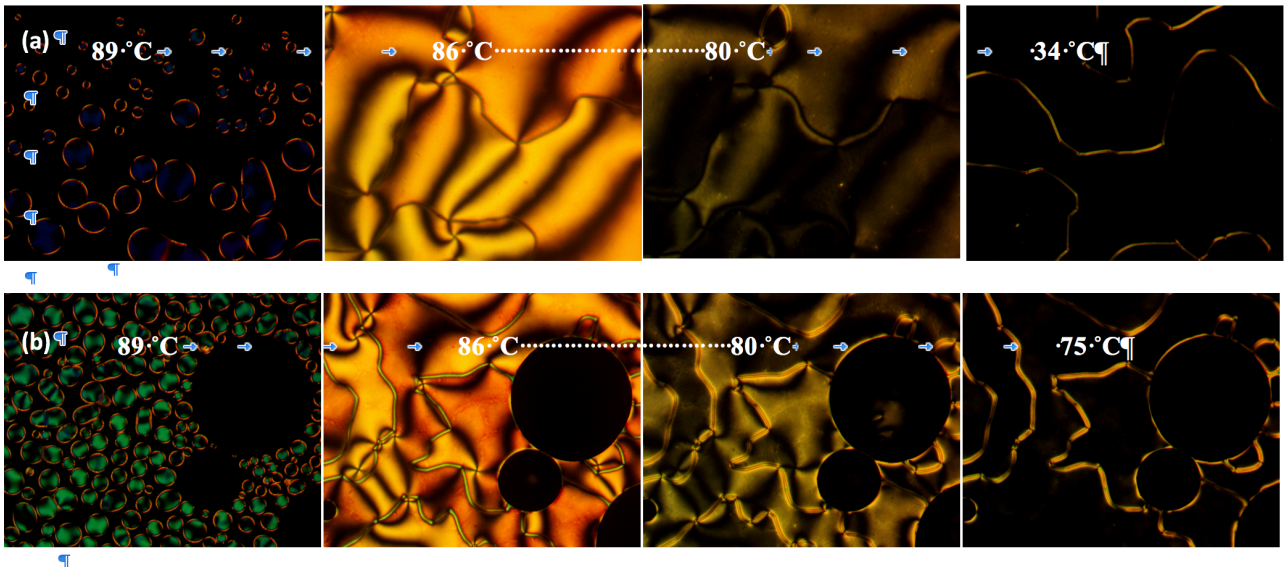


Figure S4. POM of 2 wt% ZrO_2-pyr NP in 4CA for **(a)** slow cooling, 0.1 deg/min. and **(b)** fast cooling, 1 deg./min.