Electronic Supplementary Material (ESI) for ChemComm.

'Clickable' ZnO Nanocrystals: Superiority of Organometallic Approach over Inorganic Sol-Gel Procedure

Agnieszka Grala,[a,b] Małgorzata Wolska-Pietkiewicz,[a] Wojciech Danowski,[a] Zbigniew Wróbel,[b] Justyna Grzonka,[b,c,d] and Janusz Lewiński*[a,b]

[a] Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland
[b] Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] Warsaw University of Technology, Faculty of Materials Science and Engineering, Wołoska 141,
02-507 Warsaw, Poland
[d] Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland
* The corresponding author: lewin@ch.pw.edu.pl

Table of Contents:

1. General considerations.

Precursor synthesis and the click reaction on the surface of NCs were conducted in an argon atmosphere using standard Schlenk techniques. THF, used as a solvent, was dried and distilled from sodium−potassium alloy and benzophenone prior to use. All reagents were purchased from commercial vendors and used in a dry argon atmosphere.

2. Precursor synthesis and preparation of *una*-ZnO NCs.

An appropriate amount of 10-undecynoic acid (182 mg, 1 mmol) was dissolved in THF (4 mL) and cooled to −78 °C in an argon atmosphere. Then Et_2Zn (0,5 mL of a 2 M solution in hexane, 1 mmol) was added dropwise under vigorous stirring. The reaction was gradually warmed up to the room temperature. After 3 hours the reaction mixture was exposed to the air and consequently stirred for 3 days. Subsequently, the liquid residual was evaporated in a vacuum, redispersed in THF. Then, as obtained NCs were precipitated using hexane, centrifuged, dried in vacuum and redispersed again in 4 mL of THF for further processing (solution A). The same synthetic procedure was applied for preparation of *una*-ZnO NCs used for characterization.

3. The *click reaction* – preparation of *tr*-ZnO NCs.

The proper amount of S-(3-azidopropyl)thioacetate (1 mmol) was mixed with the catalytic amount of $[Cu(C_{12}H_8N_2)[P(C_6H_5)_3]_2]NO_3)\cdot 1/2\ CH_2Cl_2$ (18 mg, 0.02 mmol) cooled down to -20 ºC and kept in vaccum for 1 h in order to remove the oxygene. Then the mixture was warmed up to the room temperature and dissolved in THF (solution B). The solution B was added to the solution A and stirred in the argon atmosphere for 1 h. After that time the reaction mixture was filtered and treated with hexanes. As obtained NCs were centrifuged, washed again with THF, precipitated with hexane and dried in vacuum. Additionally, we run a blind test to demonstrate that the cycloaddition reaction cannot take place without the presence of Cu(I) ions.

4. UV-Vis spectroscopy.

Optical absorption (UV-Vis) spectra for ZnO NPs colloidal suspension in THF, DMSO were collected on Hitachi U-2910 spectrophotometer. A standard quartz cell (Hellma) with a 10 mm path length was used and rinsed with proper solvent before each run. Photoluminescence (PL) measurements were carried out using HITACHI Fluorescence Spectrophotometer F-7000.

5. HRTEM characterization.

Size, shape and morphology of the nanocrystals were examined by High-Resolution Transmission Electron Microscopy (HRTEM). Nanocrystal samples were drop-cast (THF or DMSO solution) onto 300-mesh, holey carbon-coated copper grids (Quantifoil). Afterward, the excess solvent evaporated at room temperature. Nanocrystal samples were imaged using a C_s corrected scanning transmission electron microscope (STEM, HITACHI HD2700, 200 kV).

6. ^{1}H NMR analysis.

The ^{1}H NMR spectra were acquired on Varian Mercury 400 MHz spectrometer at 298 K and chemical shifts are internally referenced to $CDCl_3$ calculated relative to TMS. Chemical shifts are expressed in δ (ppm). ^{1}H NMR, δ ppm: (a) *una*-ZnO NCs 1.31-1.40 (m, CH_2, 8H), 1.51 (m, CH_2, 2H), 1.62 (m, CH_2, 2H), 1.93 (≡CH, 1H), 2.16 (m, CH_2, 2H), 2.34 (t, CH_2, 2H); (b) *tr*-ZnO NCs 1.26-1.30 (m, CH_2, 8H), 1.63 (br, CH_2, 2H), 1.92 – traces (s, ≡CH, 1H), 2.19 (m, CH_2, 2H), 2.31 (CH_2, 2H), 2.34 (s, CH_3, 3H), 2.70 (t, CH_2, 2H), 2.86 (t, CH_2, 2H), 4.37 (t, CH_2, 2H), 7.34 (s,=CH-N, 1H); (c) free acid – *una*-H1.31 and 1.38 (s_{br} and m, CH_2, 8H), 1.50 (m, CH_2, 2H), 1.62 (m, CH_2, 2H), 1.93 (≡CH, 1H), 2.16 (m, CH_2, 2H), 2.34 (t, CH_2, 2H). Note that signals from deprotoneted acid on the surface of NCs are slightly broadened (Figure S6).

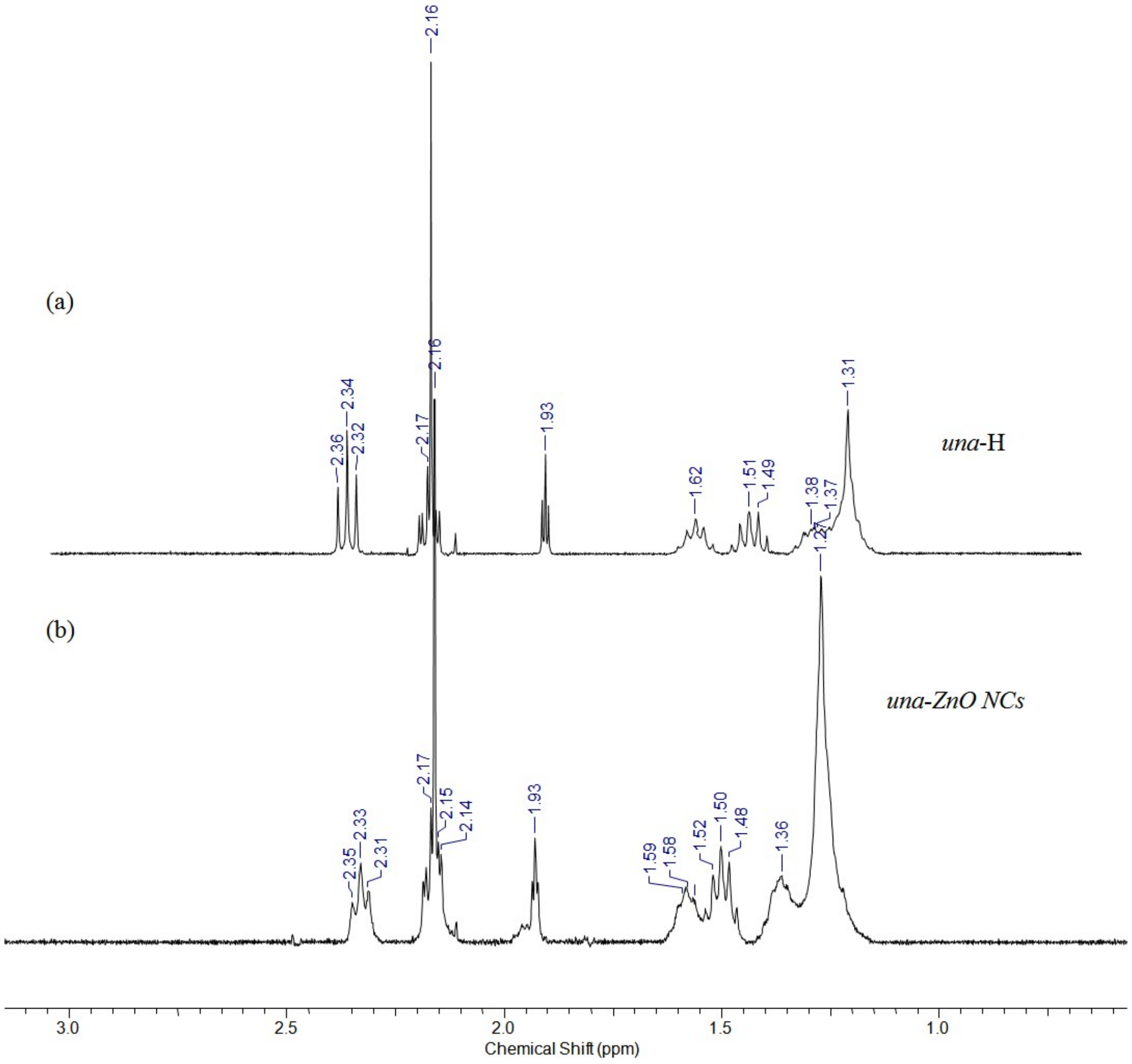


Fig. S6 The ^{1}H NMR spectra of: (a) 10-undecynoic acid (*una*-H) and (b) *una*-ZnO NCs.

7. FTIR spectroscopy.

The infrared spectra were recorded on a FT-IR Perkin-Elmer System 2000 spectrometer. Abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. (a) *una*-ZnO NCs [cm^{-1}]: 453 (s), 527 (vw), 582 (vw), 643 (w), 678 (w), 723 (w), 747 (w), 789 (vw), 843 (vw), 956 (vw), 1034 (vw), 1063 (vw), 1096 (vw), 1207 (vw), 1215 (vw), 1273 (vw), 1312 (vw), 1341 (w), 1358 (w) 1397 (m), 1409 (w), 1456 (m), 1530 (vs), 1600 (w), 2120 (wv), 2849 (w), 2920 (w), 3281 (w); (b) *tr*-ZnO NCs [cm^{-1}]: 445 (s), 450 (s), 629 (w), 676 (vw), 727 (vw), 750 (vw), 801 (vw), 863 (vw), 954 (w) 1053 (w), 1112 (w), 1137 (w), 1220 (vw), 1306 (vw), 1357 (w), 1406 (m), 1416 (m), 1439 (m), 1545 (m), 1590 (m), 1694 (w), 2853 (w), 2926 (w), 3083 (vw), 3138 (vw).

8. Powder X-ray diffraction studies.

Powder XRD data were collected on a Siemens D5005 diffractometer (Bruker AXS). Measurements employed Ni-filtered Cu Kα radiation of a copper sealed tube charged with 40kV voltage and 40mA current and Bragg-Brentano geometry with beam divergence of 1 deg. in the scattering plane. The sample was spread over surface of a porous glass plate fixed to the sample holder. Diffraction patterns were measured in the range of 5-80 degrees of scattering angle by step scanning with step of 0.02 degree.

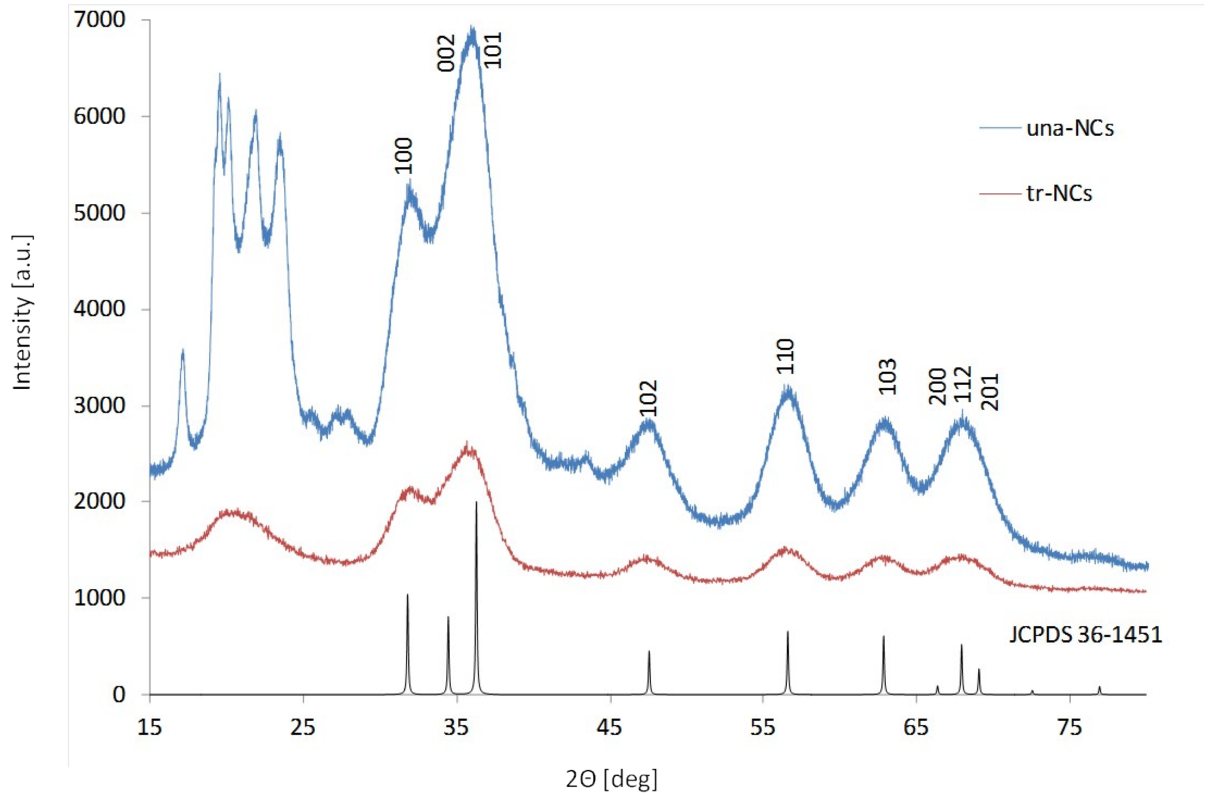


Fig. S8 The powder X-ray diffraction patterns of *una*-ZnO NCs and *tr*-ZnO NCs.

9. Dynamic Light Scattering.

Hydrodynamic diameter of NPs was determined by Dynamic Light Scaterring (DLS) performed on Malvern Zetasizer Nano Z. Solutions of *una*-ZnO NCs and *tr*-ZnO NCs in $CHCl_3$ were filtered before the analysis through a 0.2 micron filter to remove any dust particles.

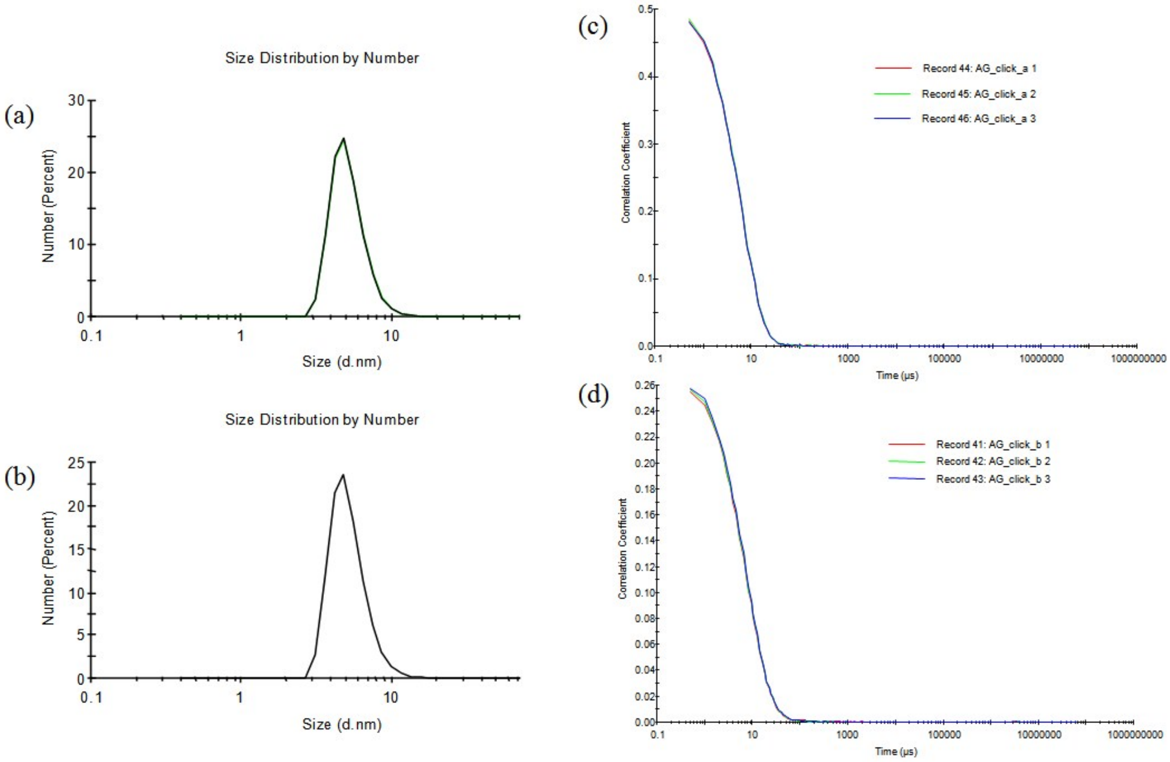
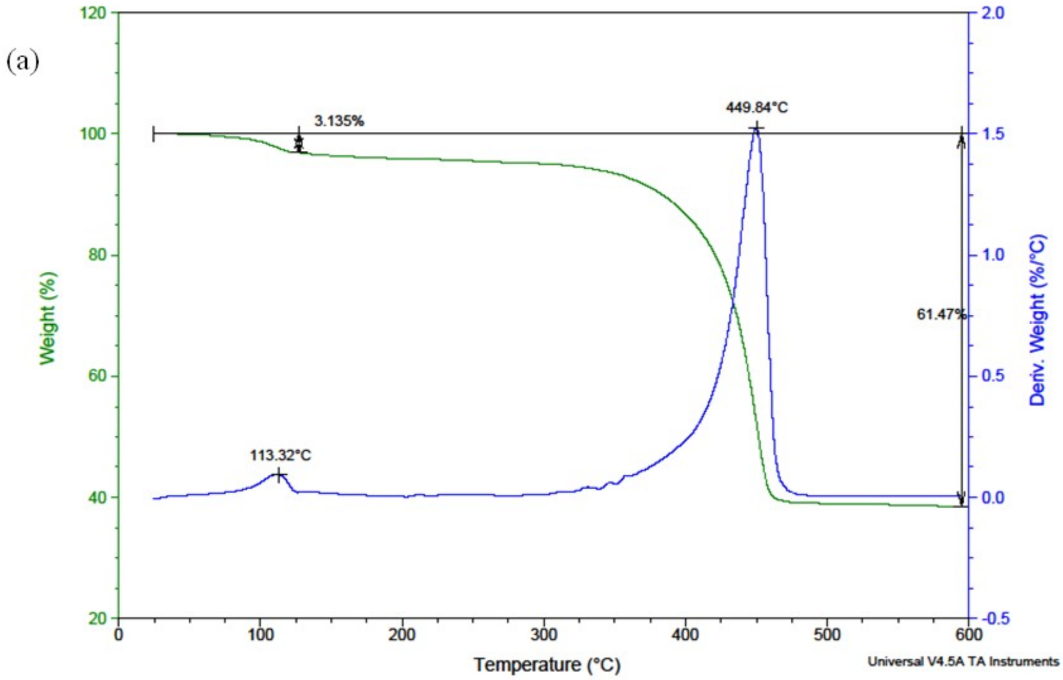
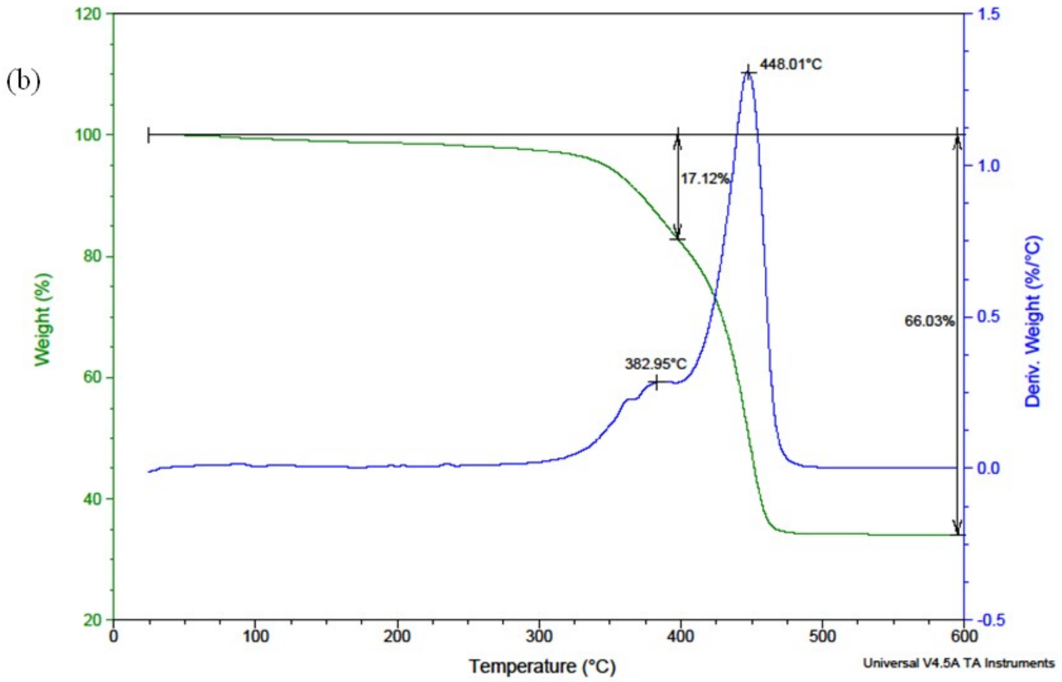


Fig. S9 Dynamic Light Scattering measurements for: (a) *una*-ZnO NCs, (b) *tr*-ZnO NCs; raw correlation data for (c) *una*-ZnO NCs, (d) *tr*-ZnO NCs.

10. Thermogravimetric analysis.

TGA were carried out using a TA Instruments Q600 under a flow of argon, to max 600°C, at a heating rate of 5°C•min^{-1} (flow rate of 100 mL/min). Open alumina crucibles with 5 mm in diagonal were used.





-

(c)

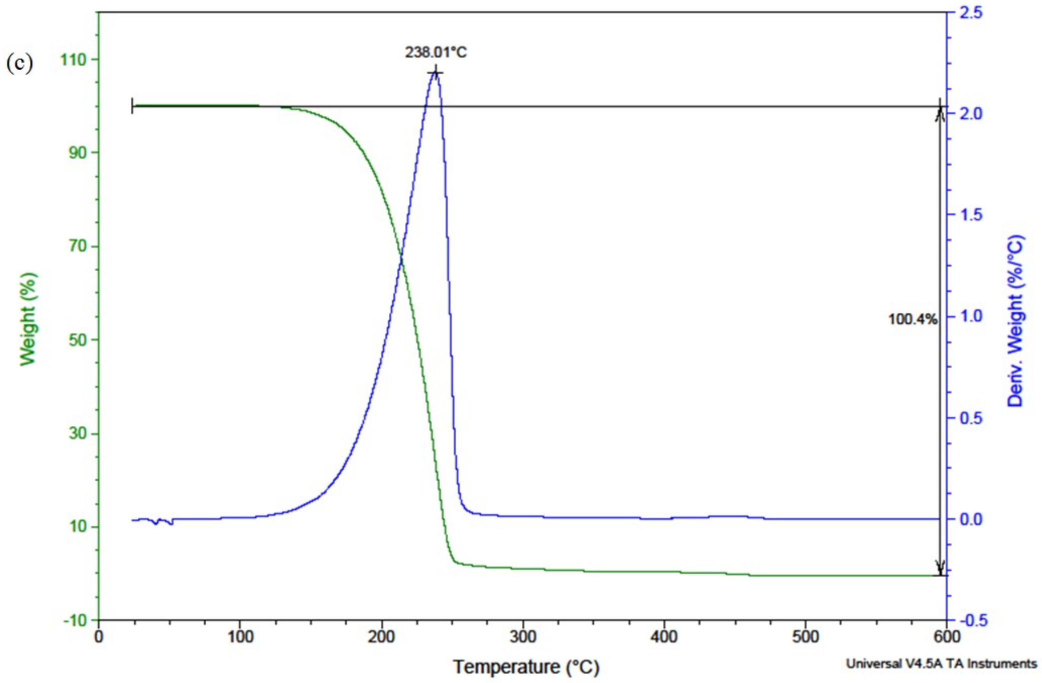


Fig. S10 TGA analysis of: (a) *una*-ZnO NCs, (b) *tr*-ZnO NCs, (c) *una*-H.

11. Synthesis of ZnO NCs by inorganic sol-gel metod.

inorgA-ZnO NCs *synthesis.* To ethanolic solution of $Zn(OAc)_2$ (184 mg, 1 mmol, 5 mL EtOH), 10-undecynoic acid (182 mg, 1 mmol) dissolved in 5 mL EtOH was added. The reaction mixture was stirred for 3 h at 80 ºC. After that time the reaction mixture was cooled down to 0 ºC and the ethanolic solution of $LiOH \cdot H_2O$ was added (63 mg, 1.5 mmol, 15 mL EtOH). The reaction was stirred overnight at room temperature. The resulting *inorgA*-ZnO NCs were separated from the solution, washed twice with EtOH and dried in vacuum.

inorgB-ZnO NCs *synthesis. The click reaction.* 'As prepared' *inorgA*-ZnO NCs were redispersed in dry THF under an inert argon atmosphere (solution B). 1 mmol of S-(3-azidopropyl)thioacetate was mixed with the catalytic amount of $[Cu(C_{12}H_8N_2)[P(C_6H_5)_3]_2]NO_3) \cdot 1/2\ CH_2Cl_2$ (18 mg, 0.02 mmol), cooled down to -20º C and kept in vaccum for 1 h in order to remove the oxygene. Then the mixture was warmed up to the room temperature and dissolved in THF (solution B). The solution B was added to the solution A and stirred in the argon atmosphere for 1 h. After that time the reaction mixture was filtered and treated with hexanes. 'As obtained' *inorgB*-ZnO NCs were centrifuged, wash again with hexane and dried in vacuum.

12. ^{1}H NMR spectra for *inorgA*-ZnO and *inorgB*-ZnO NCs.

δ ppm: (a) *inorgA*-ZnO NCs 1.28-1.38 (m, CH_2, 8H), 1.53 (m, CH_2, 2H), 1.65-1.58 (m, CH_2, 2H), 1.92 (s, ≡CH, 1H), 2.17 (m, CH_2, 2H), 2.34 (t, CH_2, 2H), (impurities – 2.43 and 2.09 ppm); (b) *inorgA*-ZnO NCs 0.87 (t, CH_2, 2H), 1.25-1.31 (m, CH_2, 8H), 1.63 (br, CH_2, 2H), 2.15 (s, CH_2, 2H), 2.20 (m, CH_2, 2H), 2.34 (s, CH_3, 3H), 2.87 (t, CH_2, 2H), 4.38 (m, CH_2, 2H), 7.43 (s,=CH-N, 1H).

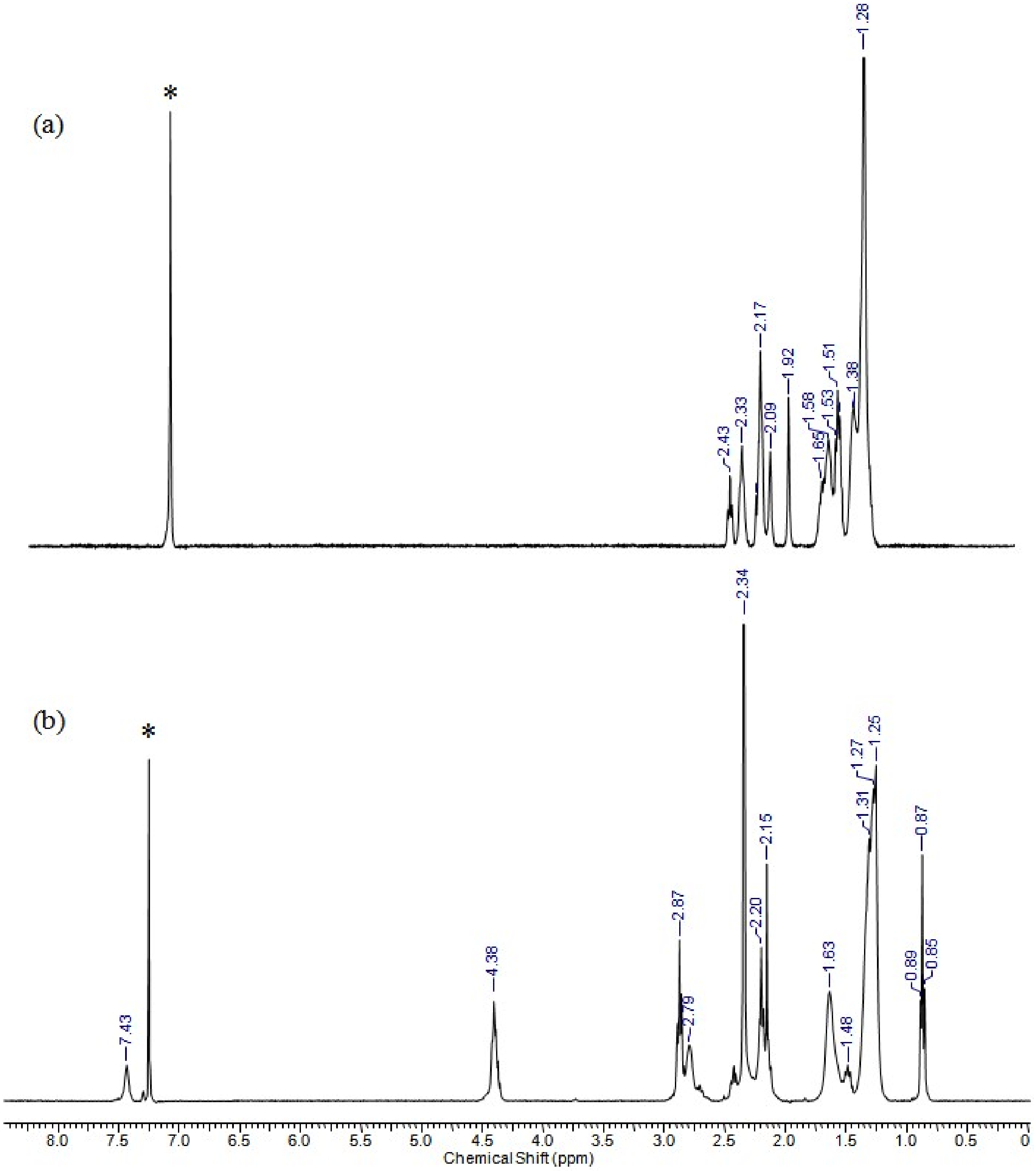


Fig. S12 ^{1}H NMR spectra of: (a) *inorgA*-ZnO NCs and (b) *inorgB*-ZnO NCs after the click reaction, * $CDCl_3$.

13. PXRD patterns for *inorgA*-ZnO and *inorgB*-ZnO NCs.

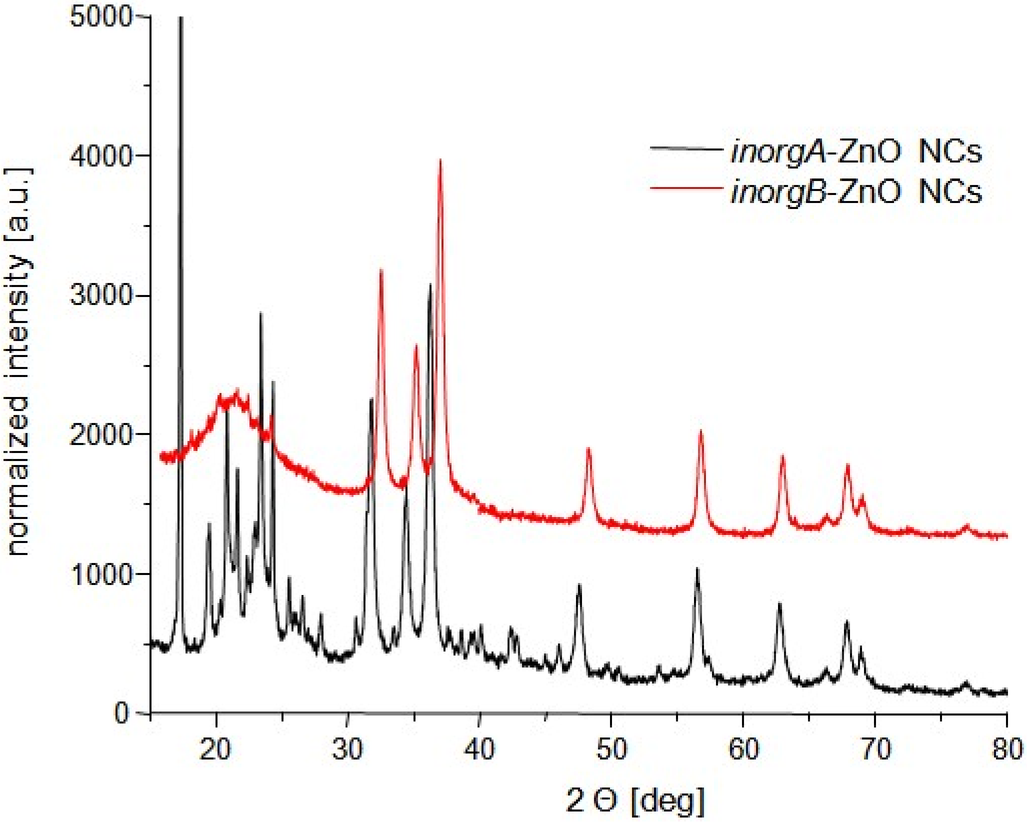


Fig. S13 PXRD patterns of: *inorgA*-ZnO NCs (black line) and *inorgB*-ZnO NCs after the click reaction (red line).