

Electronic Supplementary Information for
Organometallic One-Pot Synthesis of ZnO Quantum Dots Coated by
Sulfoxides as L-Type Ligands

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1. Complementary characterization for neat DMF-processed ZnO QDs

Optical measurements – UV-Vis and photoluminescence (PL) spectroscopy

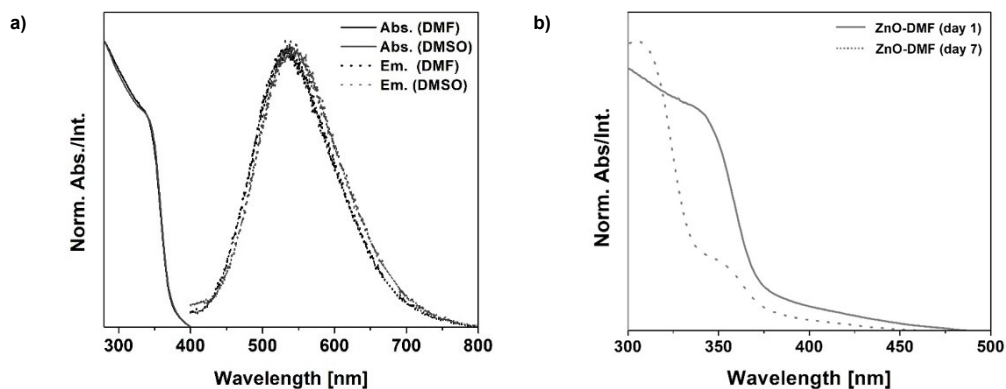


Figure S1. a) Normalized absorption (solid line) and emission spectra (dotted line) of as-prepared ZnO-DMF collected in DMF (black line) and in DMSO (grey line) solution; b) The absorption spectra of freshly prepared ZnO-DMF (solid line) and ZnO-DMF after 1 week of storage in DMF (dotted line).

Transmission Electron Microscopy (TEM) examination

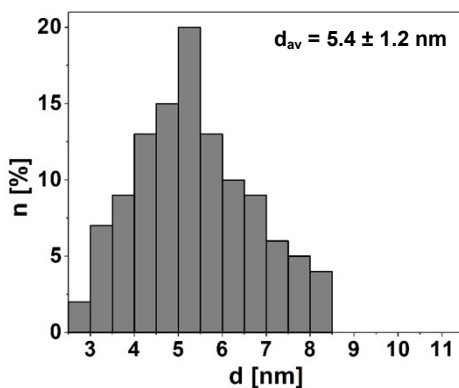


Figure S2. The size distribution of ZnO-DMF (based on the analysis of TEM images).

Dynamic Light Scattering (DLS) measurements

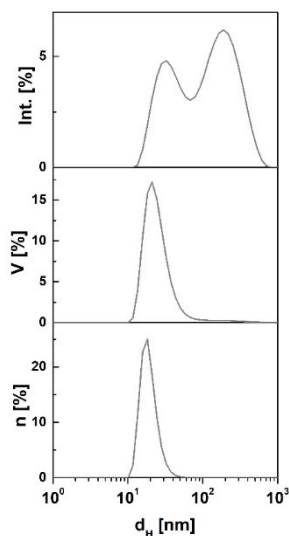


Figure S3. Intensity-averaged, volume-averaged and number-averaged size distribution of solvodynamic diameter of as-prepared ZnO-DMF obtained from the representative DLS measurements in DMF solution.

Fourier Transform Infrared (FTIR) spectroscopy

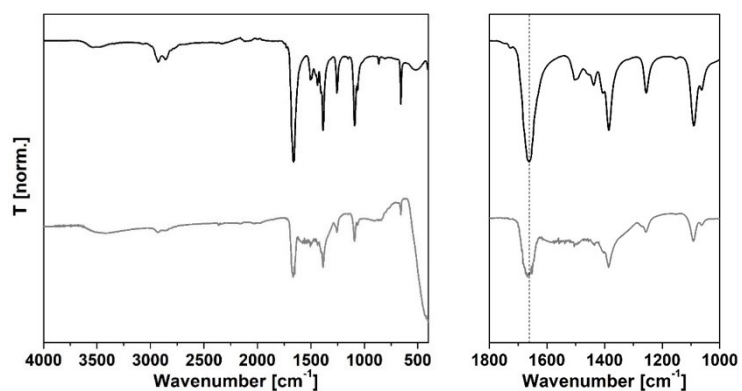


Figure S4. FTIR spectra of ZnO-DMF (grey line) and DMF (black line).

Thermogravimetric analysis (TGA)

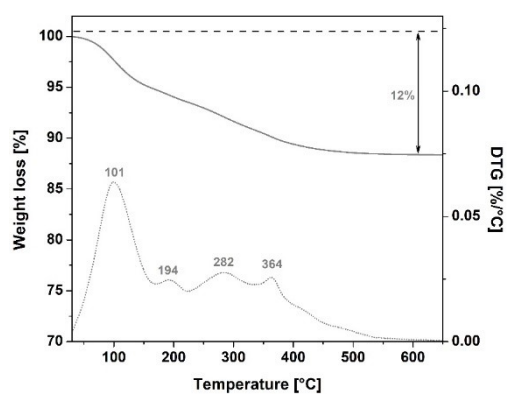


Figure S5. The TGA (solid line) and derivative thermogravimetric analysis (DTG) (dotted line) traces showing the decomposition of ZnO-DMF under synthetic air flow conditions.

2. Complementary characterization for neat DBSO-processed ZnO QDs

Optical measurements – UV-Vis and photoluminescence (PL) spectroscopy

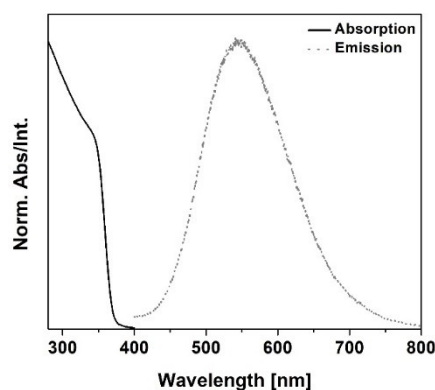


Figure S6. Normalized absorption (solid line) and emission spectra (dotted line) of as-prepared ZnO-DBSO collected in DMSO.

Transmission Electron Microscopy (TEM) examination

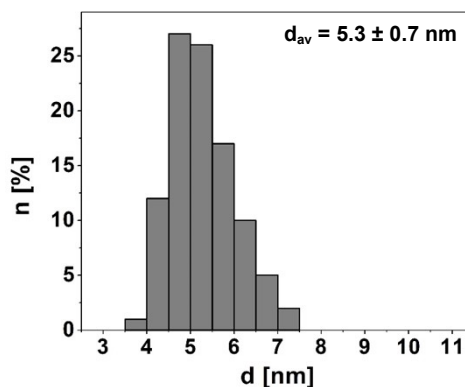


Figure S7. The size distribution of ZnO-DBSO (based on the analysis of TEM images).

Powder X-Ray Diffraction (PXRD) analysis

ZnO QDs' core size was calculated from the Scherrer's formula:

$$d_c = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

where:

d_c - diameter of ZnO QDs' core;

k - Scherrer's constant (shape factor), for sphere-like grains: $k=0.89$;

λ - the wavelength of X-rays, $\lambda = 1.54 \text{ \AA}$;

θ - Bragg diffraction angle;

β - is the full width at half-maximum (FWHM) of the diffraction peak corresponding to diffraction plane.

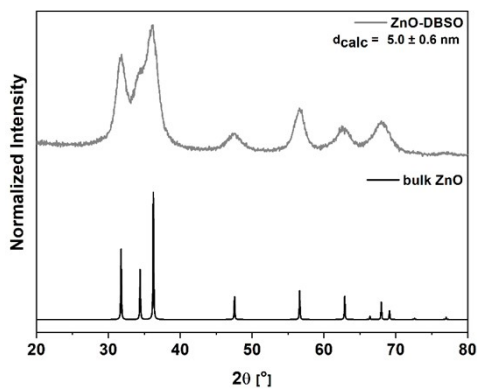


Figure S8. Powder X-ray diffraction pattern of **ZnO-DBSO** (grey line) in comparison with bulk ZnO pattern (black line) confirming wurtzite crystalline core structure.

Dynamic Light Scattering (DLS) measurements

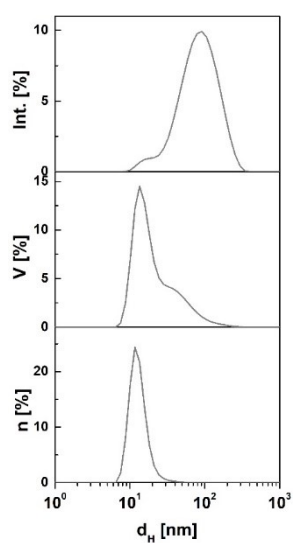


Figure S9. Intensity-averaged, volume-averaged and number-averaged size distribution of solvodynamic diameter of as-prepared **ZnO-DBSO** obtained from the representative DLS measurements in DMSO solution.

Thermogravimetric analysis (TGA)

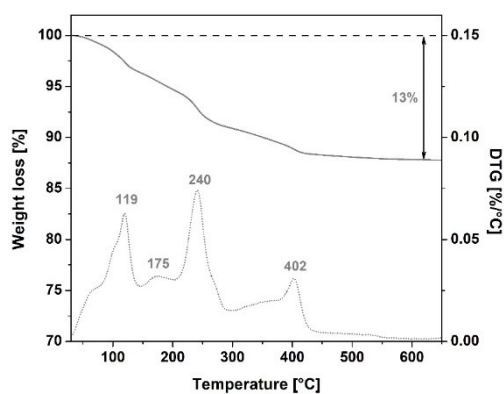


Figure S10. The TGA (solid line) and derivative thermogravimetric analysis (DTG) (dotted line) traces showing the decomposition of **ZnO-DBSO** under synthetic air flow conditions.

3. Characterization of adduct-type $[\text{Et}_2\text{Zn}(\text{L})]$ precursors

Nuclear Magnetic Resonance (NMR) spectroscopy

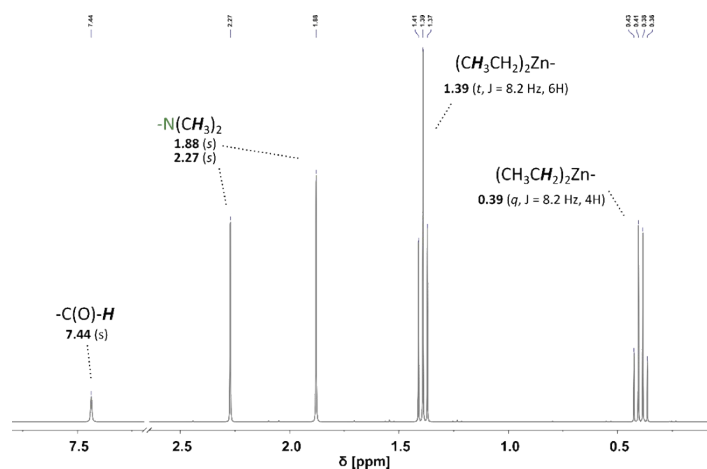


Figure S11. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{DMF})]$ in C_6D_6 .

$[\text{Et}_2\text{Zn}(\text{DMF})]$: ^1H NMR (C_6D_6 , 400 MHz, 303 K): $\delta = 0.39$ (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 1.39 (t, $(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 1.88 (s, $(\text{CH}_3)_2\text{N-}$), 2.27 (s, $(\text{CH}_3)_2\text{N-}$), 7.44 (s, $-\text{C}(\text{O})-\text{H}$); ^{13}C NMR (C_6D_6 , 400 Hz, 303 K): $\delta = 5.41$ ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 11.30 ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 30.74 ($(\text{CH}_3)_2\text{N-}$), 35.31 ($(\text{CH}_3)_2\text{N-}$), 162.57 ($-\text{C}(\text{O})-\text{H}$) ppm.

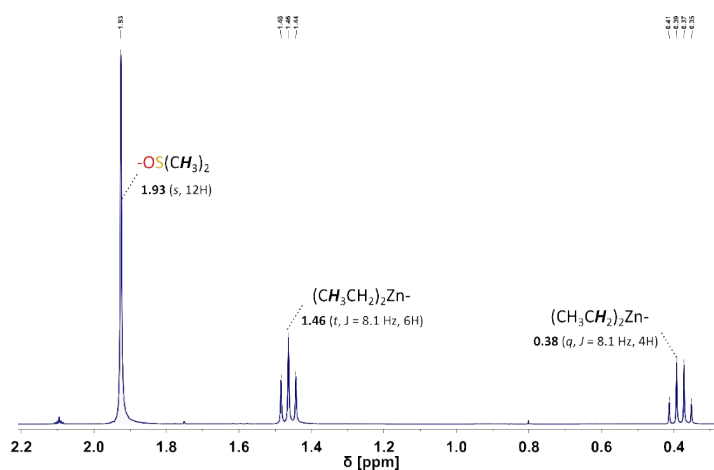


Figure S12. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{DMSO})]$ in toluene-d_8 .

$[\text{Et}_2\text{Zn}(\text{DMSO})]$: ^1H NMR (toluene-d_8 , 400 MHz, 303 K): $\delta = 0.38$ (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 1.46 (t, $(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 1.93 (s, $(\text{CH}_3)_2\text{SO-}$) ppm; ^{13}C NMR (toluene-d_8 , 400 MHz, 303 K): $\delta = 5.32$ ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 12.44 ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 40.30 ($(\text{CH}_3)_2\text{SO-}$) ppm.

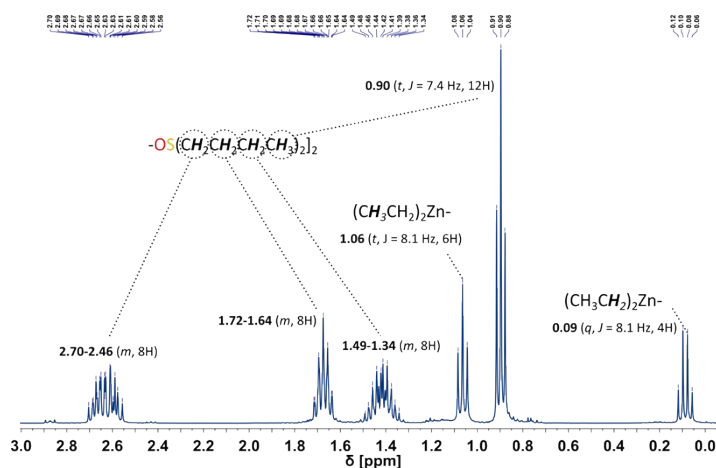


Figure S13. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{DBSO})]$ in CDCl_3 .

$[\text{Et}_2\text{Zn}(\text{DBSO})]$: ^1H NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 0.09$ (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 0.90 (t, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$), 1.06 (t, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 1.34-1.49 (m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$) 1.64-1.72 (m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$), 2.46-1.70 (m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$) ppm; ^{13}C NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 5.58$ ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 10.87 ($(\text{CH}_3\text{CH}_2)_2\text{Zn-}$), 13.57 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$), 21.98 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$), 24.54 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$), 51.80 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SO-}$) ppm.

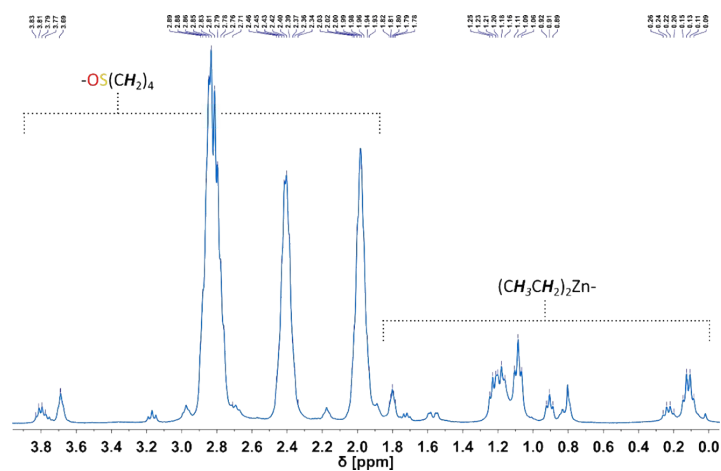


Figure S14. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{TMSO})]$ in CDCl_3 .

$[\text{Et}_2\text{Zn}(\text{TMSO})]$: ^1H NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 0.12$, 0.23 (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 1.09, 1.20 (t, $\text{CH}_3\text{CH}_2\text{Zn}$), 1.93-2.03, 2.34-2.46, 2.71-2.89 (m, $-\text{CH}_2-$ groups); ^{13}C NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 25.48$, 54.46 ppm.

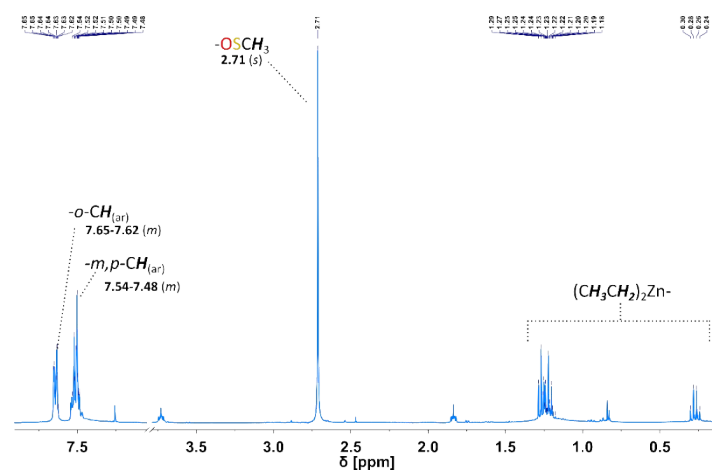


Figure S15. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{MPSO})]$ in CDCl_3 .

$[\text{Et}_2\text{Zn}(\text{MPSO})]$: ^1H NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 0.27$ (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 1.18-1.29 (m, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 2.71 (s, CH_3SO), 7.48-7.54 (m, $-m,p-\text{CH}_{(\text{ar})}$), 7.62-7.65 (m, $-o-\text{CH}_{(\text{ar})}$) ppm; ^{13}C NMR (CDCl_3 , 400 MHz, 303 K): $\delta = 1.14$, ($(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 13.27 ($(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 43.85 (CH_3SO), 123.45 ($-o-\text{CH}_{(\text{ar})}$), 129.30 ($-m-\text{CH}_{(\text{ar})}$), 130.99 ($-p-\text{CH}_{(\text{ar})}$), 145.60 ppm.

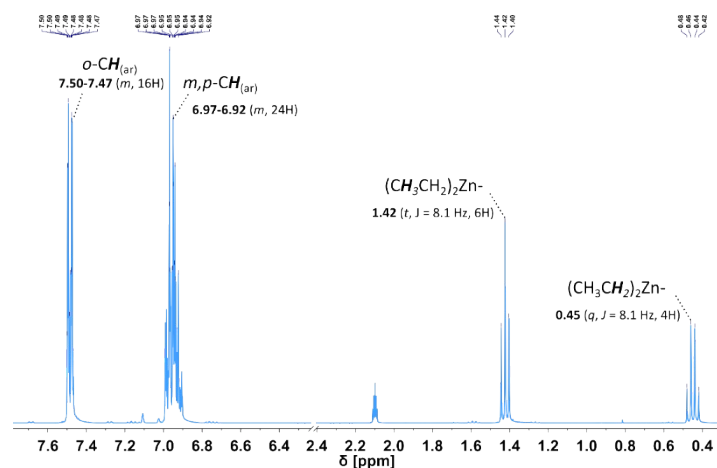


Figure S16. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{DPSO})]$ in $\text{toluene-}d_8$.

$[\text{Et}_2\text{Zn}(\text{DPSO})]$: ^1H NMR ($\text{toluene-}d_8$, 400 MHz, 303 K): δ =): δ = 0.45 (q, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 1.42 (t, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 6.92-6.97 (m, $-m,p\text{-CH}_{(\text{ar})}$), 7.50-7.47 (m, $-o\text{-CH}_{(\text{ar})}$) ppm; ^{13}C NMR ($\text{toluene-}d_8$, 400 MHz, 303 K): δ = 5.84 ($(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 11.70 ($(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 124.71 ($o\text{-CH}_{(\text{ar})}$), 129.24 ($m\text{-CH}_{(\text{ar})}$), 130.67 ($p\text{-CH}_{(\text{ar})}$), 147.12 ($-C_{(\text{ar})}\text{-SO}$) ppm.

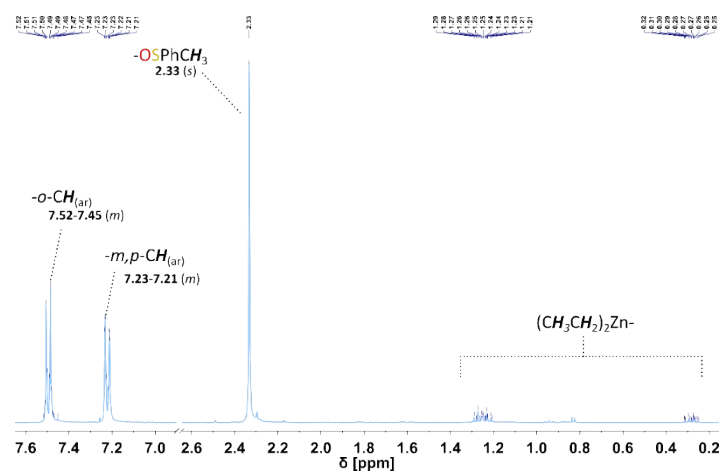


Figure S17. ^1H NMR spectra of $[\text{Et}_2\text{Zn}(\text{DTSO})]$ in CDCl_3 .

$[\text{Et}_2\text{Zn}(\text{DTSO})]$: ^1H NMR (CDCl_3 , 400 MHz, 303 K): δ = 0.29 (m, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 1.25 (m, $(\text{CH}_3\text{CH}_2)_2\text{Zn}$), 2.33 (s, CH_3SO), 7.21-7.23 (m, $-m,p\text{-CH}_{(\text{ar})}$), 7.45-7.52 ($-o\text{-CH}_{(\text{ar})}$); ^{13}C NMR (CDCl_3 , 400 MHz, 303 K): δ = 21.34 (CH_3Ph), 124.90, 129.94 ($o\text{-CH}_{(\text{ar})}$ ($m\text{-CH}_{(\text{ar})}$), 141.44 ($p\text{-CH}_{(\text{ar})}$), 142.51 ($-C_{(\text{ar})}$) ppm

4. Complementary characterization for ZnO QDs obtained through L-type protector-assisted synthesis

Optical measurements – UV-Vis and photoluminescence (PL) spectroscopy

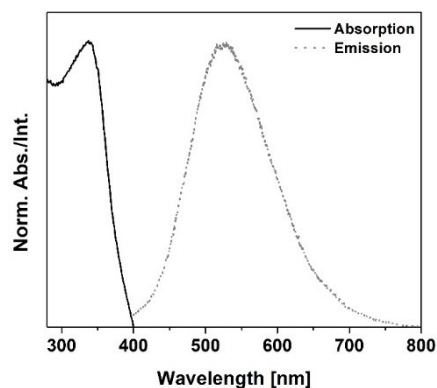


Figure S18. Normalized absorption (solid line) and emission spectra (dotted line) of prepared ZnO-DMF' QDs collected in DMSO.

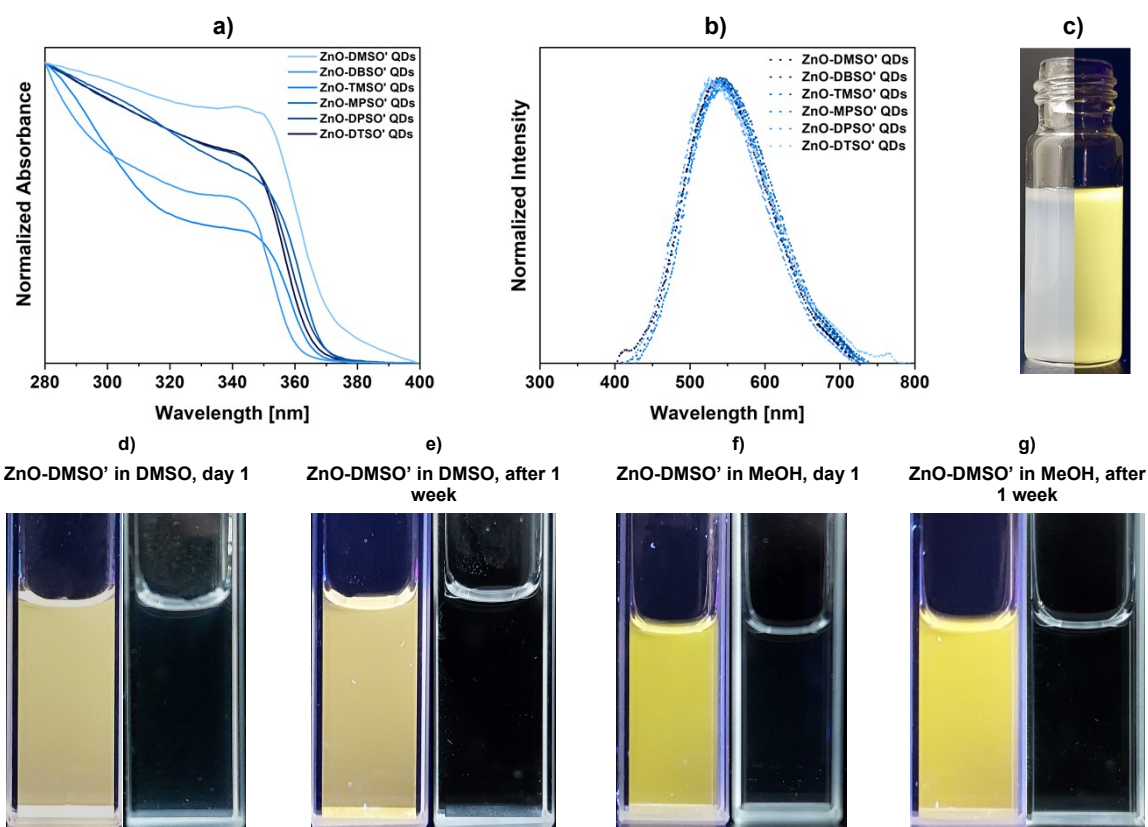


Figure S19. Normalized absorption (a) and emission (b) spectra of prepared ZnO-DMSO', ZnO DBSO', ZnO-TMSO', ZnO-MPSO', ZnO-DPSO', ZnO-DTSO' collected in DMSO and (c) photographs of ZnO-DMSO' suspension in DMSO (1 mg/mL) under visible and 365 nm UV light; the photographs of ZnO-DMSO' colloids under UV light (left) and under daylight (right) formed in DMSO (d – freshly filtered, e – after 1 week of storage) and in methanol (f – freshly filtered, g – after 1 week of storage), filtered through 0.45 μ m PTFE syringe filter.

Powder X-Ray Diffraction (PXRD) analysis

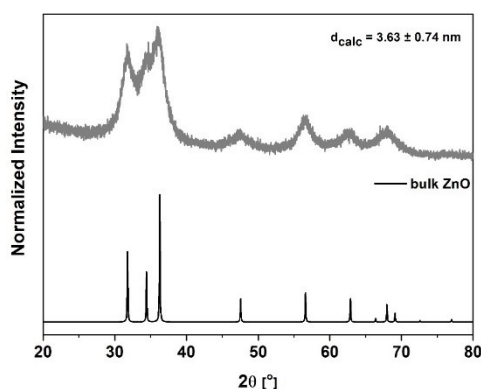


Figure S20. Powder X-ray diffraction pattern of ZnO-DMF⁺ (grey line) in comparison with bulk ZnO pattern (black line) confirming wurtzite crystalline core structure.

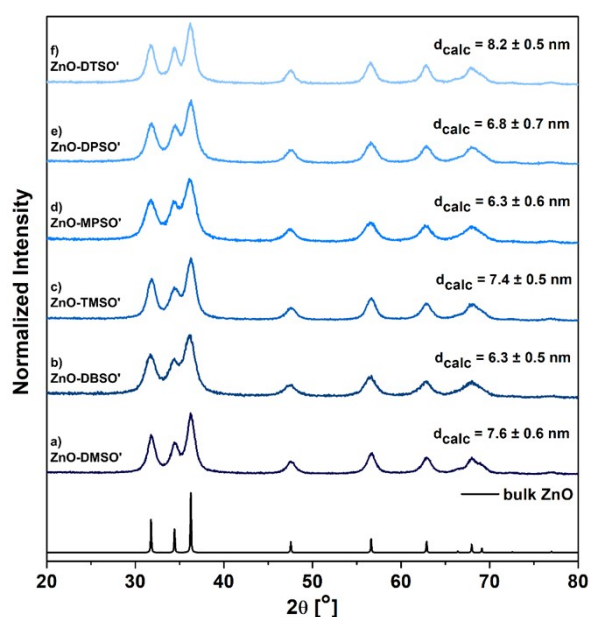


Figure S21. Powder X-ray diffraction patterns of a) ZnO-DMSO⁺, b) ZnO-DBSO⁺, c) ZnO-TMSO⁺, d) ZnO-MPSO⁺, e) ZnO-DPSO⁺, f) ZnO-DTSO⁺ in comparison with bulk ZnO pattern (black line) confirming wurtzite crystalline core structure.

Calculated core sizes of ZnO-L QDs - summary

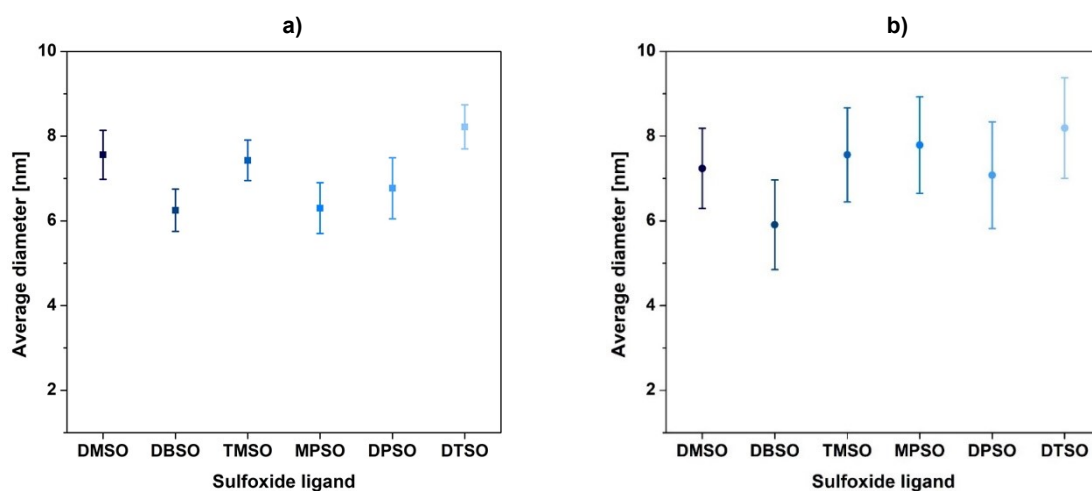


Figure S22. The representation of ligand-independent core size of the respective ZnO-DMSO⁺, ZnO-DBSO⁺, ZnO-TMSO⁺, ZnO-MPSO⁺, ZnO-DPSO⁺, ZnO-DTSO⁺ derived from (a) PXRD and (b) TEM data.

Shape analysis of ZnO QDs – 2D plots

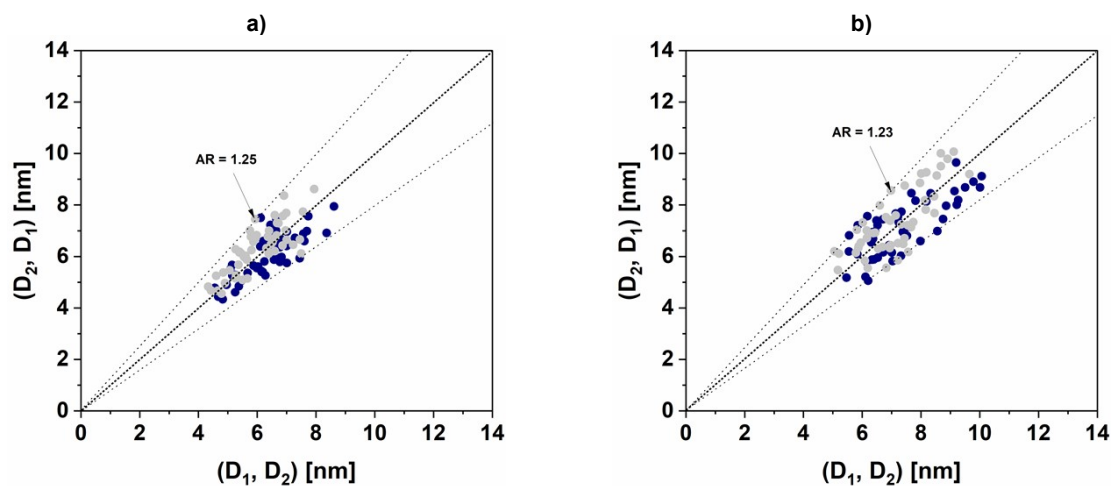


Figure S23. 2D plots of shape analysis for a) ZnO-DMSO' and b) ZnO-DPSO' derived from TEM data. Notations: D_1 – length, D_2 – width of QD.¹

Dynamic Light Scattering (DLS) analysis

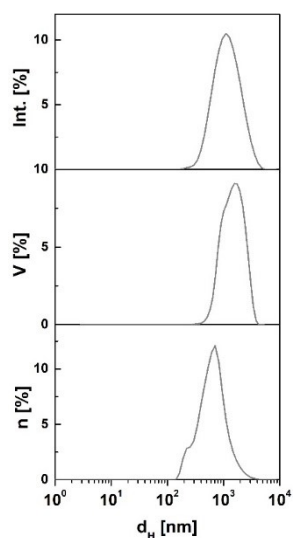


Figure S24. Intensity-averaged, volume-averaged and number-averaged size distribution of solvodynamic diameter of as-prepared **ZnO-DMF'** obtained from the representative DLS measurements in THF.

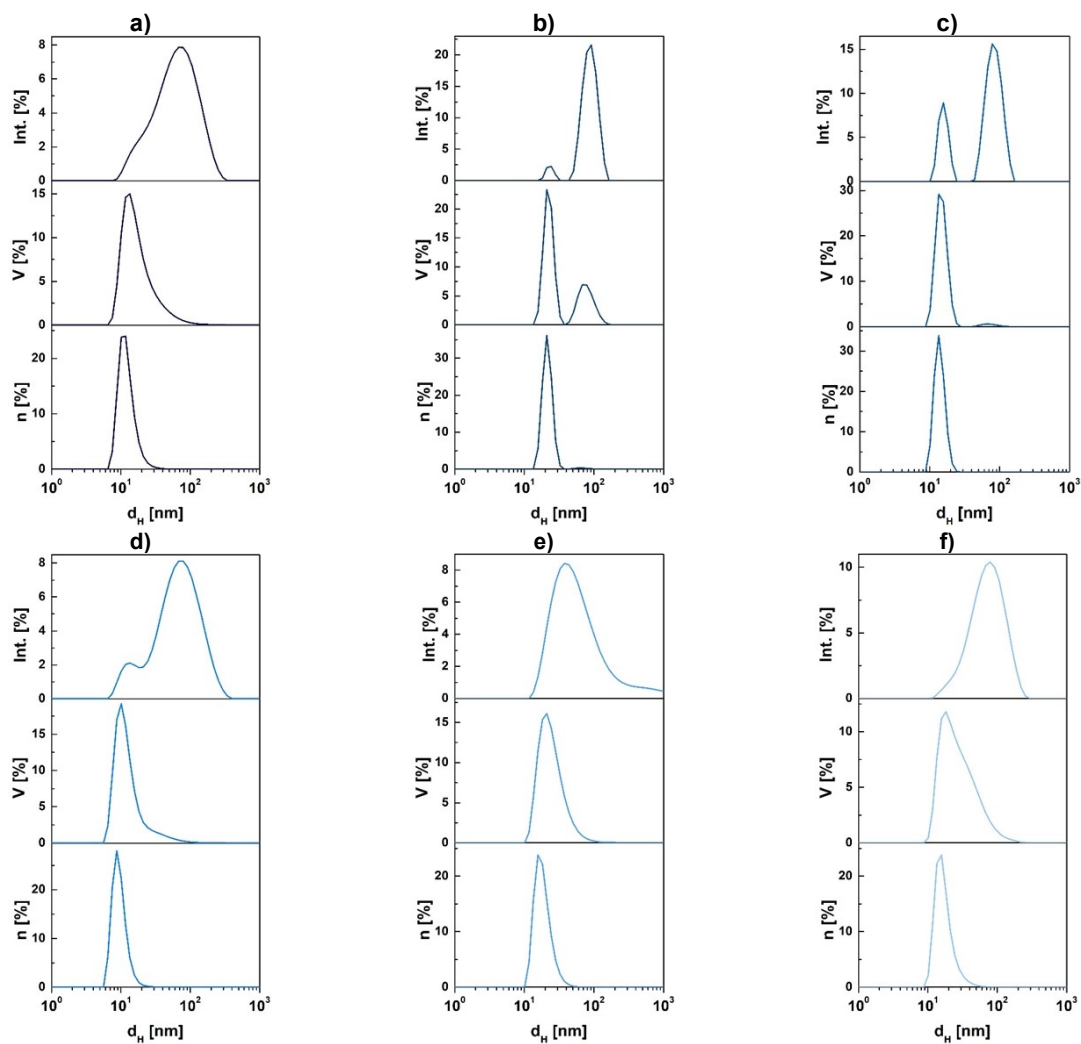


Figure S25. Intensity-averaged, volume-averaged and number-averaged size distribution of solvodynamic diameter of as-prepared of (a) **ZnO-DMSO'**, (b) **ZnO-DBSO'**, (c) **ZnO-TMSO'**, (d) **ZnO-MPSO'**, (e) **ZnO-DPSO'** and (f) **ZnO-DTSO'** obtained from the representative DLS measurements in DMSO.

Nuclear Magnetic Resonance (NMR) spectroscopy

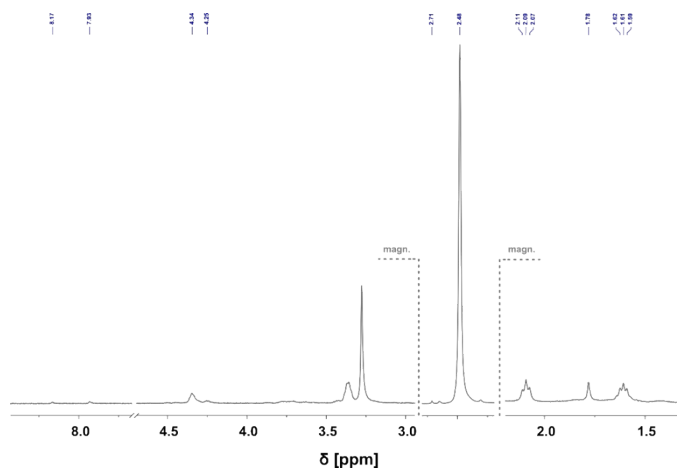


Figure S26. ¹H NMR spectra of ZnO-DMF¹ in DMSO-d₆.

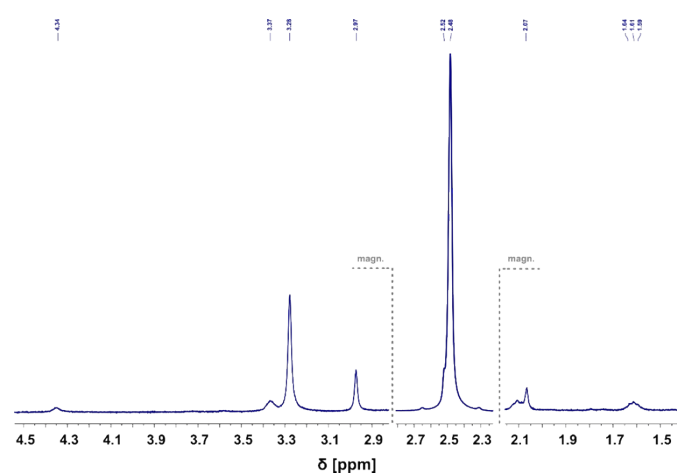


Figure S27. ¹H NMR spectra of ZnO-DMSO¹ in DMSO-d₆.

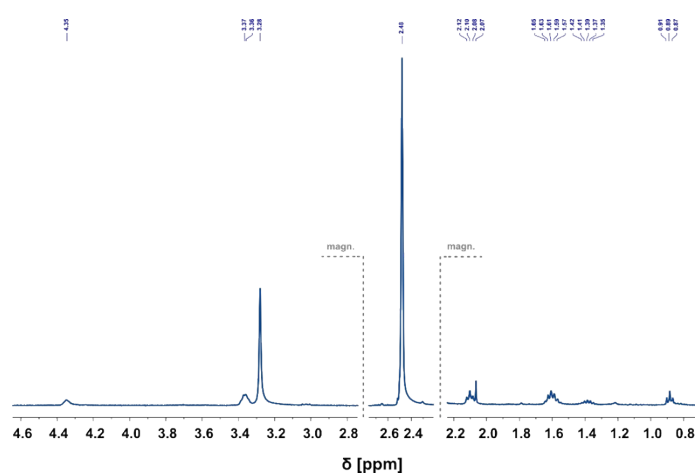


Figure S28. ¹H NMR spectra of ZnO-DBSO¹ in DMSO-d₆.

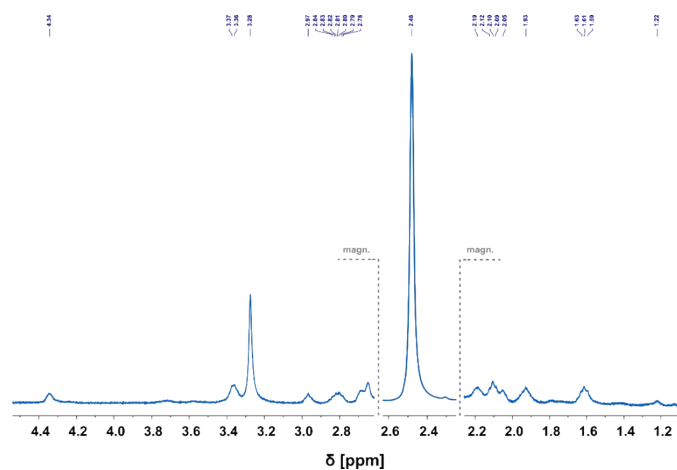


Figure S29. ^1H NMR spectra of $\text{ZnO-TMSO}^{\text{I}}$ in DMSO-d_6 .

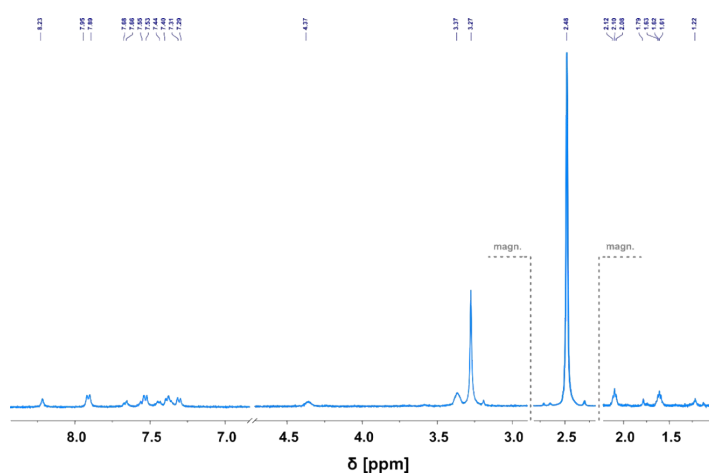


Figure S30. ^1H NMR spectra of $\text{ZnO-MPSO}^{\text{I}}$ in DMSO-d_6 .

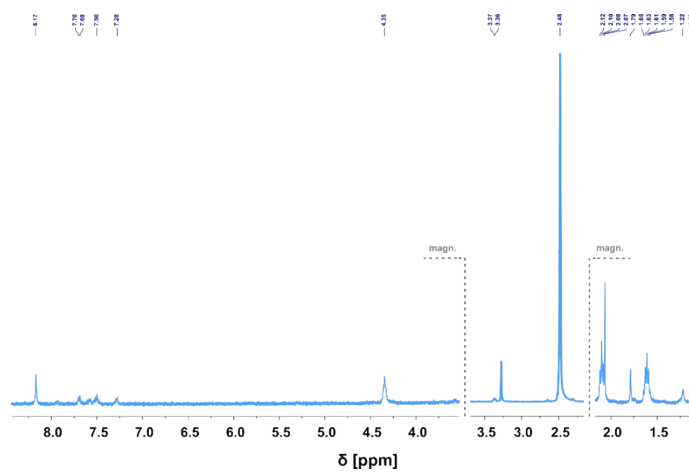


Figure S31. ^1H NMR spectra of $\text{ZnO-DPSO}^{\text{I}}$ in DMSO-d_6 .

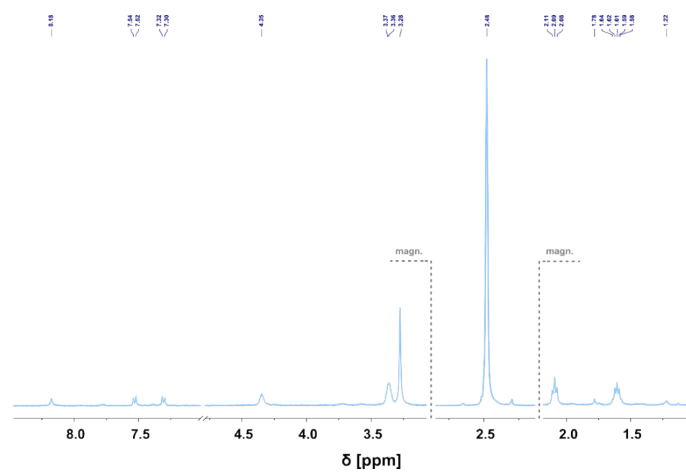


Figure S32. ^1H NMR spectra of ZnO-DTSO' in DMSO-d_6 .

Fourier Transform Infrared (FTIR) spectroscopy

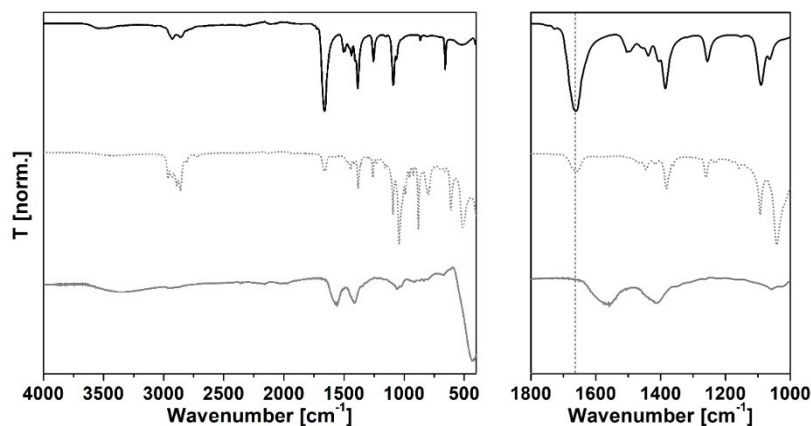


Figure S33. FTIR spectra of **ZnO-DMF'** (dark grey line), the corresponding organometallic adduct-type precursor **[Et₂Zn(DMF)]_x** (dotted line) and pure DMF (black line).

DMF: IR (ATR): $\nu = 3539$ (vw), 3482 (vw), 3073 (vw), 2926 (vw), 2856 (vw), 2775 (vw), 2328 (vw), 1726 (vw), 1663 (vs), 1502 (w), 1440 (w), 1385 (s), 1256 (m), 1152 (vw), 1092 (s), 1063 (m), 865 (w), 805 (vw), 658 (m), 518 (w), 404 (w) cm^{-1} ;

[Et₂Zn(DMF)]_x: IR (ATR): $\nu = 3421$ (vw), 2962 (w), 2933 (w), 2893 (w), 2858 (m), 2806 (vw), 2719 (vw), 2125 (vw), 1920 (vw), 1661 (w), 1445 (vw), 1418 (vw), 1383 (w), 1260 (w), 1229 (vw), 1158 (vw), 1093 (s), 1041 (vs), 989 (m), 958 (w), 924 (w), 881 (vs), 798 (m), 662 (w), 611 (s), 516 (vs) cm^{-1} .

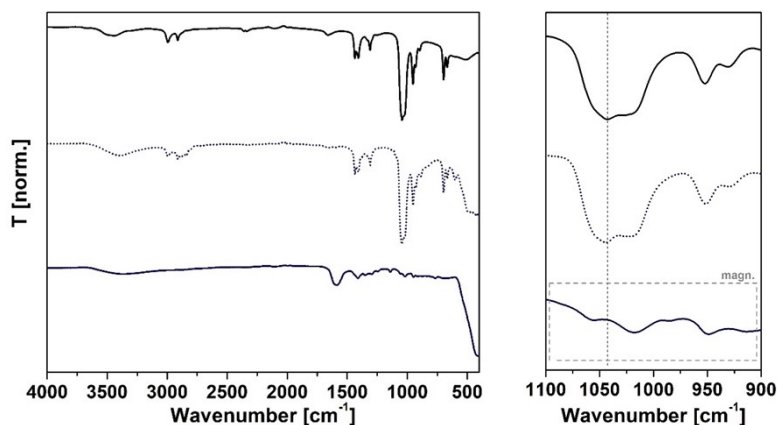


Figure S34. FTIR spectra of **ZnO-DMSO'** (blue line), the corresponding organometallic adduct-type precursor **[Et₂Zn(DMSO)]_x** (dotted line) and pure pro-ligand (black line).

DMSO: IR (ATR): $\nu = 3445$ (vw), 2992 (m), 2911 (m), 2822 (vw), 2087 (vw), 1990 (vw), 1954 (vw), 1641 (vw), 1437 (m), 1405 (m), 1333 (vw), 1309 (w), 1293 (vw), 1052 (vs), 1041 (vs), 1031 (vs), 1019 (vs), 953 (m), 930 (w), 894 (vw), 696 (m), 666 (w), 648 (vw), 416 (vw) cm^{-1}

[Et₂Zn(DMSO)]_x: IR (ATR): $\nu = 3394$ (vw), 2995 (vw), 2970 (vw), 2937 (vw), 2911 (vw), 2887 (vw), 2843 (vw), 2809 (vw), 2322 (vw), 1657 (vw), 1601 (vw), 1437 (w), 1406 (w), 1375 (vw), 1332 (vw), 1309 (w), 1228 (w), 1162 (vw), 1134 (vw), 1093 (vw), 1043 (vs), 1019 (vs), 952 (m), 931 (w), 888 (w), 835 (w), 695 (m), 667 (w), 601 (w), 494 (s), 423 (s) cm^{-1} .

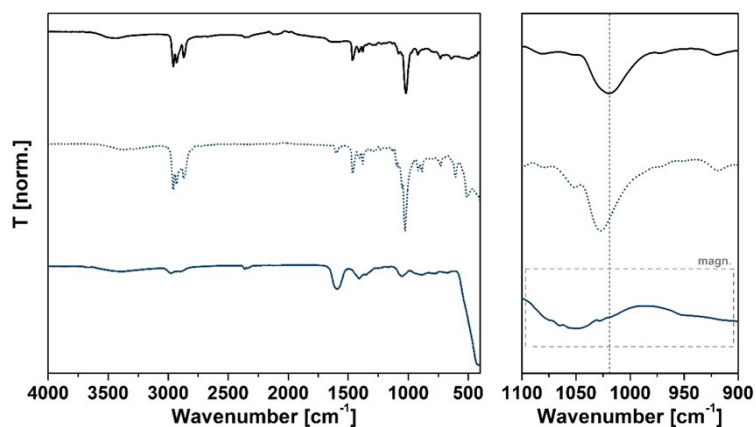


Figure S35. FTIR spectra of ZnO-DBSO' (blue line) the corresponding organometallic adduct-type precursor [Et₂Zn(DBSO)]_x (dotted line) and pure pro-ligand (black line).

DBSO: IR (ATR): $\nu = 3437$ (vw), 2957 (m), 2929 (m), 2869 (m), 2117 (vw), 2085 (vw), 1994 (vw), 1632 (vw), 1581 (vw), 1465 (m), 1409 (w), 1380 (w), 1342 (w), 1295 (w), 1269 (w), 1221 (vw), 1183 (vw), 1132 (vw), 1079 (w), 1019 (vs), 969 (w), 920 (w), 895 (w), 873 (w), 805 (w), 782 (w), 732 (m), 697 (w), 641 (m), 512 (m), 501 (m), 455 (m), 427 (w) cm⁻¹

[Et₂Zn(DBSO)]_x: IR (ATR): $\nu = 3375$ (vw), 3296 (vw), 2958 (m), 2930 (m), 2905 (w), 2872 (w), 2807 (vw), 2726 (vw), 1596 (vw), 1464 (w), 1409 (vw), 1381 (w), 1342 (vw), 1294 (vw), 1272 (vw), 1228 (vw), 1182 (vw), 1131 (vw), 1099 (w), 1078 (w), 1050 (m), 1027 (vs), 972 (w), 949 (w), 918 (w), 885 (w), 807 (vw), 784 (vw), 730 (w), 700 (vw), 634 (w), 606 (w), 510 (s), 454 (m) cm⁻¹.

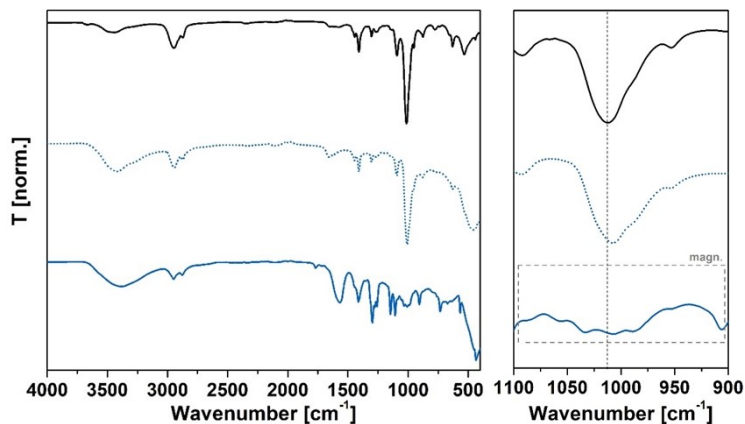


Figure S36. FTIR spectra of ZnO-TMSO' (blue line), the corresponding organometallic adduct-type precursor [Et₂Zn(TMSO)]_x (dotted line) and pure pro-ligand (black line).

TMSO: IR (ATR): $\nu = 3664$ (vw), 3450 (vw), 2943 (w), 2873 (vw), 2359 (vw), 2328 (vw), 2108 (vw), 1901 (vw), 1648 (vw), 1596 (vw), 1445 (vw), 1408 (w), 1305 (vw), 1268 (vw), 1252 (vw), 1148 (vw), 1133 (vw), 1094 (w), 1012 (vs), 951 (w), 892 (vw), 874 (vw), 774 (vw), 734 (vw), 658 (vw), 631 (w), 531 (w), 441 (vw) cm⁻¹

[Et₂Zn(TMSO)]_x: IR (ATR): $\nu = 3419$ (w), 3288 (vw), 2943 (w), 2872 (vw), 2108 (vw), 1659 (vw), 1614 (vw), 1552 (vw), 1460 (vw), 1445 (vw), 1409 (w), 1304 (vw), 1263 (vw), 1145 (vw), 1134 (vw), 1094 (w), 1007 (vs), 953 (m), 889 (w), 877 (w), 781 (w), 770 (w), 658 (w), 630 (m), 529 (s), 461 (vs) cm⁻¹.

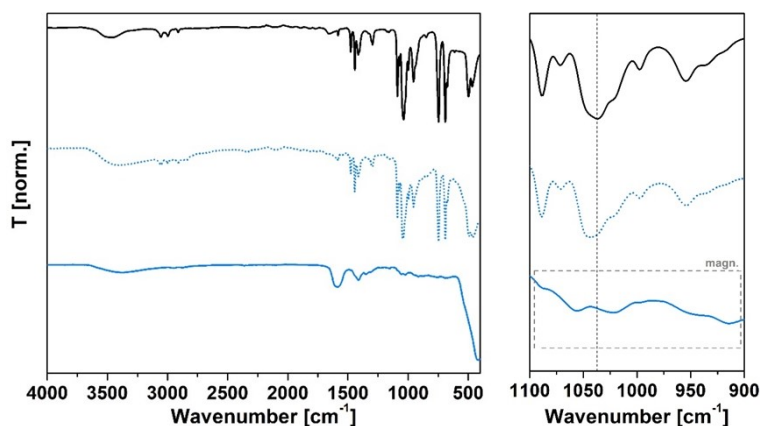


Figure S37. FTIR spectra of ZnO-MPSO' (blue line), the corresponding organometallic adduct-type precursor [Et₂Zn(MPSO)]_x (dotted line) and pure pro-ligand (black line).

(MPSO): IR (ATR): $\nu = 3077$ (w), 3054 (w), 2984 (w), 2903 (w), 1891 (vw), 1816 (vw), 1771 (vw), 1672 (vw), 1607 (vw), 1581 (vw), 1474 (w), 1442 (m), 1420 (w), 1408 (w), 1361 (vw), 1331 (vw), 1303 (w), 1287 (vw), 1172 (vw), 1158 (vw), 1089 (s), 1067 (m), 1033 (vs), 1019 (s), 995 (m), 969 (m), 951 (s), 918 (w), 857 (vw), 745 (vs), 689 (vs), 682 (s), 612 (vw), 491 (s), 467 (s), 406 (vw) cm⁻¹

[Et₂Zn(MPSO)]_x: IR (ATR): $\nu = 3406$ (w), 3162 (vw), 3056 (w), 2996 (vw), 2969 (vw), 2911 (vw), 2879 (vw), 2842 (vw), 2673 (vw), 2356 (vw), 2331 (vw), 2118 (vw), 2085 (vw), 1953 (vw), 1886 (vw), 1812 (vw), 1767 (vw), 1667 (vw), 1602 (vw), 1581 (vw), 1544 (vw), 1500 (vw), 1476 (w), 1442 (m), 1413 (w), 1403 (w), 1368 (vw), 1327 (vw), 1304 (vw), 1295 (w), 1237 (vw), 1174 (vw), 1154 (vw), 1088 (s), 1071 (m), 1043 (vs), 1018 (s), 996 (s), 954 (s), 937 (m), 885 (w), 847 (w), 746 (vs), 690 (vs), 673 (m), 611 (w), 591 (m), 532 (m), 495 (vs), 464 (vs) cm⁻¹.

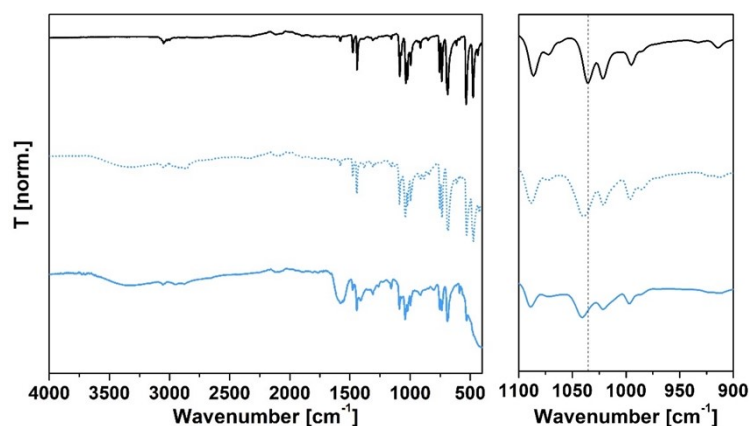


Figure S38. FTIR spectra of ZnO-DPSO' (blue line), the corresponding organometallic adduct-type precursor $[\text{Et}_2\text{Zn}(\text{DPSO})]_x$ (dotted line) and pure pro-ligand (black line).

(DPSO): IR (ATR): $\nu = 3064$ (w), 3052 (m), 3048 (m), 3034 (w), 3018 (w), 2999 (m), 2988 (w), 2900 (w), 2887 (w), 2119 (w), 2068 (w), 1899 (w), 1810 (w), 1609 (w), 1582 (w), 1575 (w), 1474 (s), 1440 (s), 1395 (w), 1377 (w), 1339 (w), 1329 (w), 1312 (w), 1304 (w), 1295 (w), 1275 (w), 1247 (w), 1241 (w), 1225 (w), 1175 (w), 1167 (w), 1155 (w), 1087 (vs), 1071 (m), 1059 (w), 1036 (vs), 1021 (vs), 995 (s), 982 (m), 933 (w), 913 (m), 856 (w), 849 (w), 839 (w), 756 (s), 735 (vs), 693 (vs), 685 (vs), 667 (m), 613 (w), 588 (vw), 563 (vw), 532 (vs), 475 (vs), 435 (w), 417 (vw) cm^{-1}

$[\text{Et}_2\text{Zn}(\text{DPSO})]_x$: IR (ATR): $\nu = 3327$ (vw), 3079 (vw), 3053 (vw), 3036 (vw), 3018 (vw), 2997 (vw), 2965 (vw), 2928 (vw), 2887 (vw), 2855 (vw), 2807 (vw), 2719 (vw), 2657 (vw), 2328 (vw), 2116 (vw), 2086 (vw), 2064 (vw), 2000 (vw), 1986 (vw), 1950 (vw), 1897 (vw), 1880 (vw), 1806 (vw), 1762 (vw), 1705 (vw), 1656 (vw), 1604 (vw), 1577 (vw), 1543 (vw), 1530 (vw), 1477 (w), 1442 (m), 1379 (vw), 1332 (vw), 1307 (vw), 1290 (vw), 1266 (vw), 1234 (vw), 1173 (vw), 1157 (vw), 1129 (vw), 1088 (m), 1073 (w), 1039 (m), 1021 (m), 997 (m), 986 (m), 966 (w), 949 (w), 925 (w), 913 (w), 884 (w), 853 (w), 842 (w), 754 (s), 734 (s), 690 (vs), 682 (vs), 613 (w), 590 (w), 562 (w), 530 (vs), 484 (vs), 474 (vs), 424 (s) cm^{-1} .

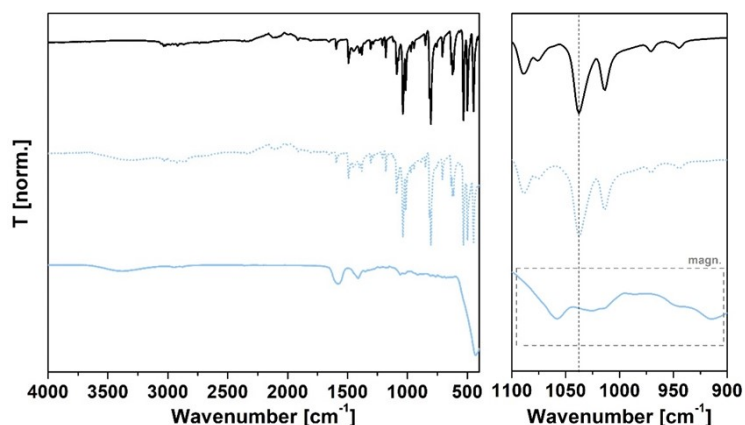


Figure S39. FTIR spectra of ZnO-DTSSO' (blue line), the corresponding organometallic adduct-type precursor $[\text{Et}_2\text{Zn}(\text{DTSSO})]_x$ (dotted line) and pure pro-ligand (black line).

(DTSSO): IR (ATR): $\nu = 3058$ (w), 3035 (m), 3019 (m), 2977 (m), 2949 (m), 2919 (m), 2866 (m), 2739 (w), 2113 (w), 1995 (w), 1915 (w), 1809 (w), 1658 (w), 1650 (w), 1593 (w), 1573 (w), 1491 (m), 1450 (m), 1401 (m), 1380 (m), 1355 (w), 1305 (w), 1285 (w), 1250 (w), 1210 (w), 1179 (m), 1117 (w), 1088 (m), 1074 (m), 1036 (vs), 1013 (s), 971 (w), 943 (w), 849 (w), 813 (s), 803 (vs), 756 (w), 707 (w), 697 (vw), 634 (w), 623 (m), 615 (m), 534 (vs), 498 (s), 447 (vs), 407 (vw) cm^{-1}

$[\text{Et}_2\text{Zn}(\text{DTSSO})]_x$: IR (ATR): $\nu = 3320$ (vw), 3057 (vw), 3034 (vw), 3021 (vw), 2973 (vw), 2919 (vw), 2863 (vw), 2737 (vw), 2675 (vw), 2351 (vw), 2328 (vw), 2297 (vw), 2112 (vw), 2087 (vw), 1998 (vw), 1914 (vw), 1808 (vw), 1652 (vw), 1594 (vw), 1574 (vw), 1493 (w), 1452 (w), 1399 (w), 1381 (w), 1356 (vw), 1305 (vw), 1284 (vw), 1246 (vw), 1211 (vw), 1181 (w), 1157 (vw), 1117 (vw), 1088 (m), 1075 (w), 1038 (vs), 1013 (s), 969 (w), 944 (w), 885 (vw), 847 (w), 814 (s), 805 (vs), 756 (w), 708 (w), 698 (w), 680 (vw), 634 (m), 621 (m), 616 (m), 558 (w), 530 (vs), 499 (vs), 444 (vs) cm^{-1} .

Thermogravimetric analysis (TGA)

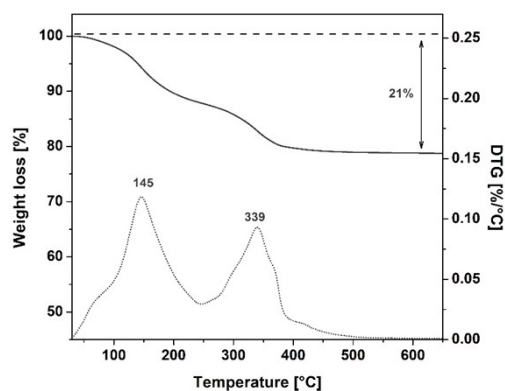


Figure S40. The TGA (solid line) and derivative thermogravimetric analysis (DTG) (dotted line) traces showing the decomposition of **ZnO-DMF'** under synthetic air flow conditions.

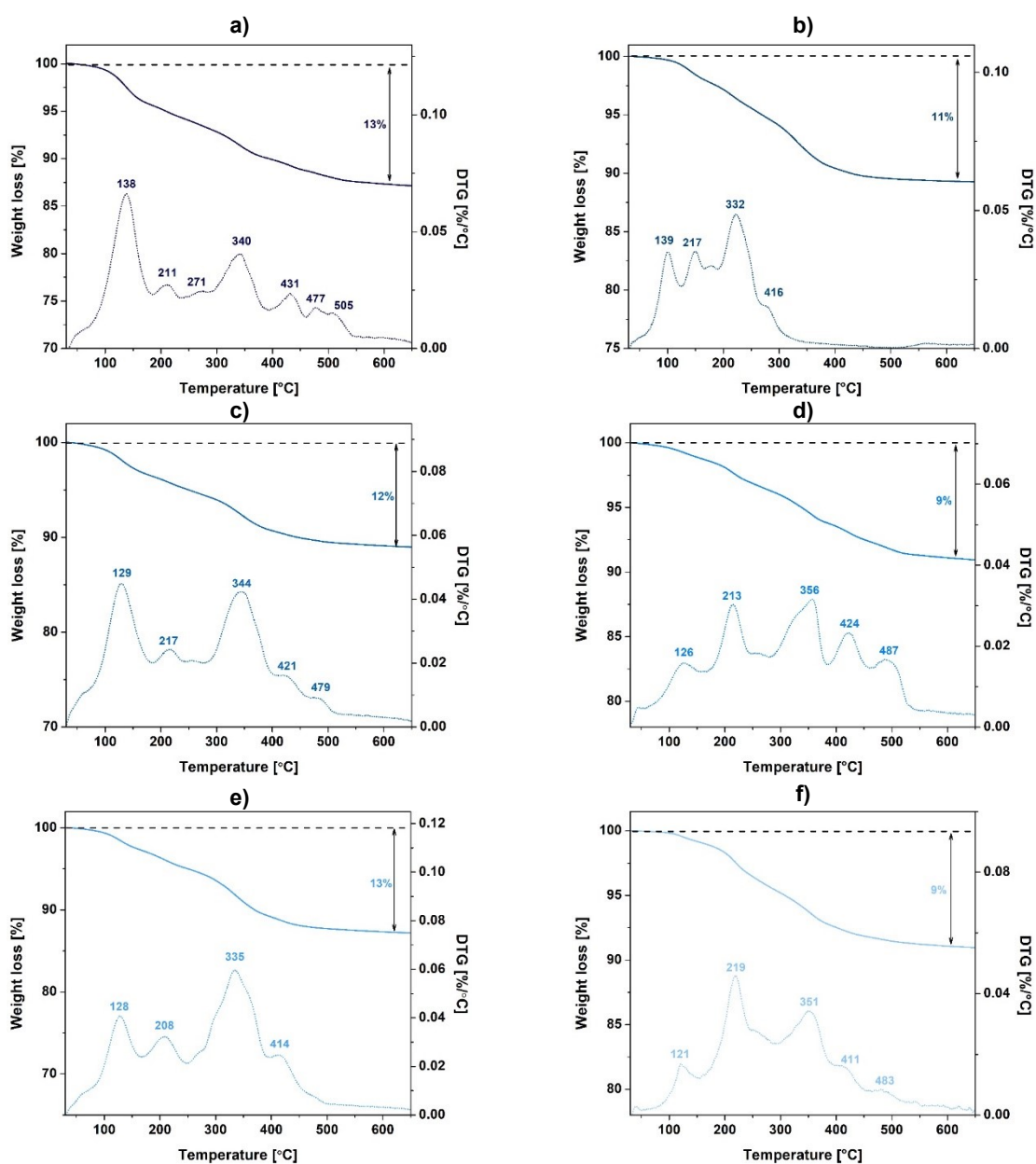


Figure S41. The TGA (solid line) and derivative thermogravimetric analysis (DTG) (dotted line) traces showing the decomposition of (a) **ZnO-DMSO'**, (b) **ZnO-DBSO'**, (c) **ZnO-TMSO'**, (d) **ZnO-MPSO'**, (e) **ZnO-DPSO'** and (f) **ZnO-DTSO'** under synthetic air flow conditions.

5. Additional information and calculations for TGA, DLS and optical data

Ligand content determined from TGA data

The number of bound ligands per unit surface area (i.e., the grafting density, σ) is a critical feature to consider especially in terms of designing functionalized nanomaterials. The relative mass of organic ligand and the mass of the pure ZnO QDs were found from the experimental TGA data. Note that TGA is an effective method which provide insight into the true value of the grafting density as well as the magnitude of the methodological systematic errors.²

Grafting density (σ) was calculated as follows:

$$\sigma = \frac{n_l}{n_{QDs} \times S_{QDs}}$$

where:

n_l – number of ligands attached to ZnO QDs' core

n_{QDs} – number of ZnO cores

S_{QDs} – surface area of spherical QD (πr^2)

$$n_l = \frac{wt\%_l}{m_l} = \frac{wt\%_l \times N_A}{MW_l}$$

$wt\%_l$ – weight loss percentage (from TGA results)

N_A – Avogadro's number

m_l – ligand mass

MW_l – ligand molar mass

$$n_{QDs} = \frac{wt\%_{QDs}}{m_{QDs}} = \frac{wt\%_{QDs}}{\rho_{ZnO} \times V_{QD}}$$

$wt\%_{QDs}$ – weight percentage of the core (100% - $wt\%_l$)

ρ_{ZnO} – density of bulk ZnO

V_{NC} – volume of a single spherical QD ($\frac{4}{3}\pi r^3$)

r – radius of QD

For the determination of ligand coverage (exclusively organic layer) excluding water molecules or hydroxyl groups, the weight loss corresponding to the water content from TGA results has been subtracted from the value applied in equation. Grafting density excluding water content was calculated by modifying the equation as follows:

$$n_l^* = \frac{wt\%_l^*}{m_l} = \frac{(wt\%_l - wt\%_{H_2O}) \times N_A}{MW_l}$$

n_l^* – number of organic ligands attached to ZnO QDs' core

$wt\%_l^*$ – weight loss percentage (from TGA results)

$wt\%_{H_2O}$ – weight loss percentage attributed to water molecules (from TGA results)

$$n_{QDs}^* = \frac{wt\%^*_{QDs}}{m_{QDs}} = \frac{wt\%^*_{QDs}}{\rho_{ZnO} \times V_{QD}}$$

n_{QDs}^* – recalculated number of ZnO cores

$wt\%^*_{QDs}$ – weight percentage of the core (100% - $wt\%_l^*$)

The results from TGA and grafting density calculations for each sample of ZnO QDs are presented in Tables S2-3.

Table S1. The results of TGA measurements and calculated grafting density of ZnO-DMF, ZnO-DBSO and ZnO-DMF'.

| Sample name | ZnO-DMF | ZnO-DBSO | ZnO-DMF' |
|-------------|---------|----------|----------|
|-------------|---------|----------|----------|

| | | | |
|--|-----------|----------|------|
| Ligand coverage [%] | 11.7/6.4* | 12.3/8.6 | 21.4 |
| Grafting density [ligand/nm ²] | 4/2* | 2/2* | 7/3* |

*value excluding water/OH content

Table S2. The results of TGA measurements and calculated grafting density of sulfoxide-coated **ZnO-L QDs**.

| Sample name | ZnO-DMSO' | ZnO-DBSO' | ZnO-TMSO' | ZnO-MPSO' | ZnO-DPSO' | ZnO-DTSO' |
|--|-----------|-----------|-----------|-----------|------------|-----------|
| Ligand coverage [%] | 12.9/8.5* | 11.1/9.1* | 11.8/8.3* | 9.6/8.3* | 13.3/10.6* | 9.6/8.8* |
| Grafting density [ligand/nm ²] | 8/5* | 3/2* | 5/4* | 3/2* | 3/2* | 2/2* |

*value excluding water/OH content

DLS results - summary

Table S3. The values of polydispersity index (Pdl) and Z-average of investigated ZnO QDs.

| Sample name | ZnO-DMF | ZnO-DBSO | ZnO-DMF' |
|--------------------------------------|--------------------------|--------------------------|--------------------------|
| Pdl | 0.488 ¹ | 0.263 ¹ | 0.181 ³ |
| Z-average | 71.50 ¹ | 68.76 ¹ | 1030 ³ |
| ζ -potential [mV] ² | 25.2 ± 4.05 ² | 26.0 ± 3.87 ² | 31.7 ± 4.07 ² |

Table S4. The values of polydispersity index (Pdl) and Z-average of investigated ZnO-L QDs.

| Sample name | ZnO-DMSO' | ZnO-DBSO' | ZnO-TMSO' | ZnO-MPSO' | ZnO-DPSO' | ZnO-DTSO' |
|--------------------------------------|------------|-------------|-------------|-------------|-------------|-------------|
| Pdl ¹ | 0.398 | 0.149 | 0.466 | 0.415 | 0.284 | 0.227 |
| Z-average ¹ | 51.17 | 75.37 | 42.70 | 47.98 | 45.95 | 61.30 |
| ζ -potential [mV] ² | 36.2 ± 4.0 | 35.4 ± 4.56 | 31.5 ± 4.77 | 31.9 ± 4.34 | 35.6 ± 4.34 | 37.2 ± 4.94 |

Measurements performed in ¹ - DMSO, ² - water.

Optical measurements – summary

All the luminescence decay curves for ZnO QDs are fitted with a fourth-order exponential function described with the following equation:

$$I(t) = A_1 \exp\left(\frac{-t}{T_1}\right) + A_2 \exp\left(\frac{-t}{T_2}\right) + A_3 \exp\left(\frac{-t}{T_3}\right) + A_4 \exp\left(\frac{-t}{T_4}\right)$$

Table S5. PL lifetimes (excitation wavelength – 340 nm) of ZnO QDs performed in the solid state.

| Sample name | | ZnO-DMF | ZnO-DBSO | ZnO-DMF' |
|--|---------------------|-------------------------|--------------------------|--------------------------|
| PL decay time τ [ns (% contribution)] | T_1 | 9.8 (80.0) | 28.5 (78.1) | 21.0 (69.1) |
| | T_2 | 40.2 (17.8) | 114.5 (12.3) | 67.8 (22.0) |
| | T_3 | 254.6 (1.7) | 925.6 (7.6) | 708.7 (5.9) |
| | T_4 | 791.1 (0.5) | 3166.1 (2.0) | 2586.4 (3.0) |
| | $\langle T \rangle$ | $\langle 204.1 \rangle$ | $\langle 1590.2 \rangle$ | $\langle 1554.3 \rangle$ |
| χ^2 | | 1.15 | 1.04 | 1.01 |

$T_{1,n}$ – PL decay components, $\langle T \rangle$ - mean value of PL decay time.

Table S6. PL lifetimes (excitation wavelength – 340 nm) of ZnO-L QDs performed in the solid state.

| Sample name | | ZnO-DMSO' | ZnO-DBSO' | ZnO-TMSO' | ZnO-MPSO' | ZnO-DPSO' | ZnO-DTSO' |
|--|---------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| PL decay time τ [ns (% contribution)] | T_1 | 22.6 (70.0) | 27.8 (80.2) | 20.2 (61.9) | 18.9 (65.1) | 24.7 (73.4) | 21.9 (69.3) |
| | T_2 | 66.7 (23.6) | 111.3 (11.3) | 58.9 (29.5) | 62.1 (26.9) | 77.8 (17.6) | 68.5 (21.9) |
| | T_3 | 674.9 (4.8) | 780.2 (6.0) | 743.3 (6.8) | 712.9 (5.7) | 751.8 (6.5) | 719.3 (6.7) |
| | T_4 | 2345.2 (1.6) | 2875.8 (2.5) | 2649.1 (1.8) | 2604.7 (2.3) | 2731.9 (2.5) | 2639.8 (2.1) |
| | $\langle T \rangle$ | $\langle 1154.1 \rangle$ | $\langle 1586.8 \rangle$ | $\langle 1283.3 \rangle$ | $\langle 1424.1 \rangle$ | $\langle 1506.4 \rangle$ | $\langle 1375.7 \rangle$ |
| χ^2 | | 1.03 | 0.95 | 1.06 | 0.93 | 1.01 | 0.95 |

*Gauss fitting, $T_{1,n}$ – PL decay components, $\langle T \rangle$ – mean value of PL decay time.

6. References

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- 2 D. N. Benoit, H. Zhu, M. H. Lillierose, R. A. Verm, N. Ali, A. N. Morrison, J. D. Fortner, C. Avendano and V. L. Colvin, *Anal. Chem.*, 2012, **84**, 9238–9245.