Supporting information

From Discrete Linear $^{t}Bu_2Zn$ Molecules to 1D Coordination Polymers and 2D Fabrics

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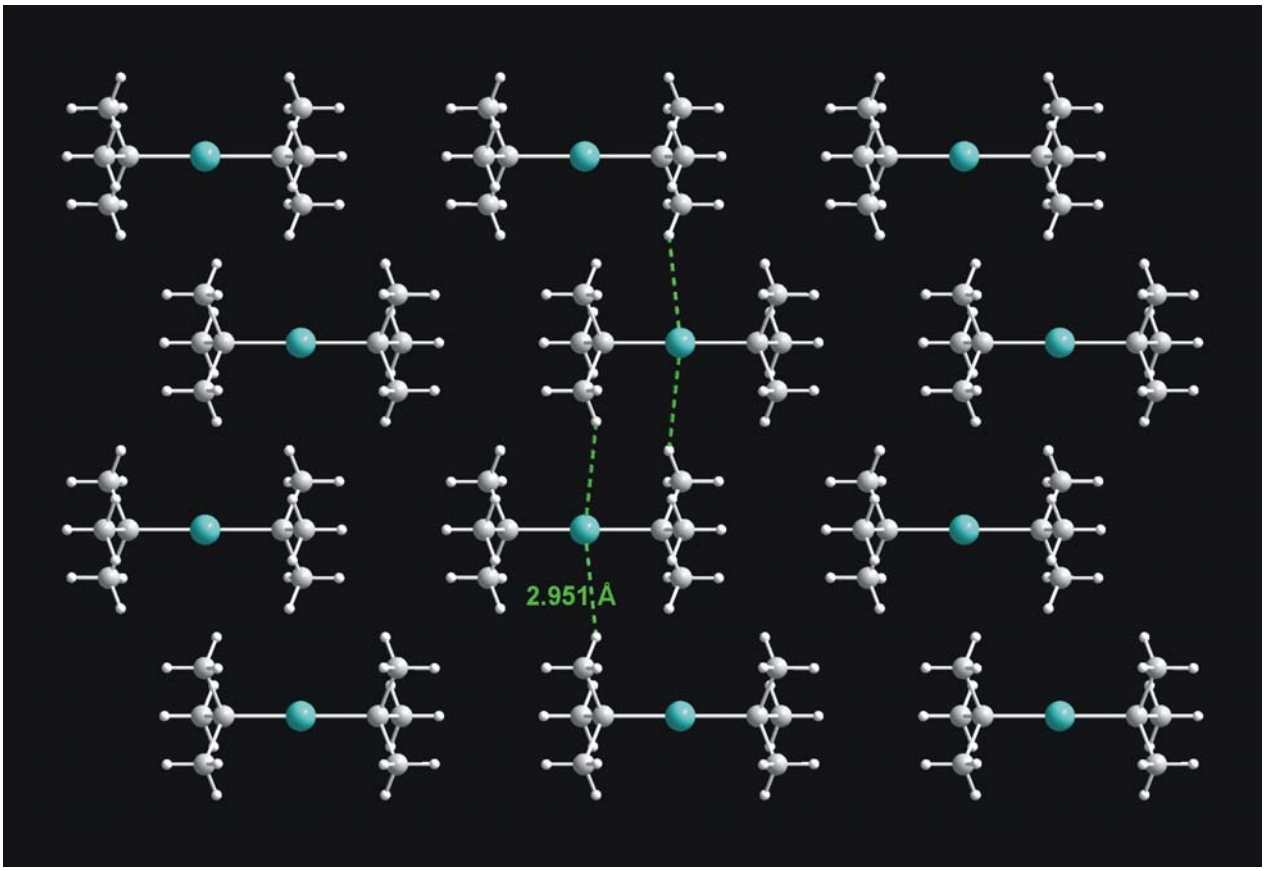
Figure S1. Crystal packing for **1** viewed along *a* axis.



Experimental Section

General Remarks:

All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. NMR spectra were recorded on a Varian Mercury 400 spectrometer.

Synthesis and characterization

[Zn^{t}Bu$_2$] (**1**): Di-*tert*-butylzinc was prepared according the literature procedure.[1] Colorless crystals of **1** suitable for X-ray single-crystal determination were obtained by sublimation at 30°C under vacuum ($5 \cdot 10^{-2}$ Torr).

[Zn^{t}Bu$_2$][1,2-bis(4-pyridyl)ethane] (**2**): To a stirred solution of 1,2-bis(4-pyridyl)ethane (0.138 g, 0.75 mmol) in 5 mL THF the solution of Zn^{t}Bu$_2$ in THF (0.135 g, 0.75 mmol) was added dropwise at -78°C. After the addition was completed the reaction mixture was allowed to warm to room temperature, then the volatiles were removed *in vacuo* afforded the yellow residue. Compound **2** is soluble in THF, and also sparingly soluble in aromatic solvents. Square yellow crystals of **2** were obtained from a THF/toluene solution at 0 °C after 4 hours (0,253 g, 93%). ^{1}H NMR (400 MHz, THF-d$_8$): δ = 0.97 (s, 18H, Zn-C(CH$_3$)$_3$), 2.70 (s, 4H, -(CH$_2$)$_2$-), 6.90 (d, 4H, Ar), 8.30 (d, 4H, Ar) ppm.

[Zn^{t}Bu$_2$][1,2-bis(4-pyridyl)ethylene] (**3**): Compound **3** was prepared in similar manner to **2** using 1,2-bis(4-pyridyl)ethylene (0.136 g, 0.75 mmol) in 5 mL THF the solution of Zn^{t}Bu$_2$ in THF (0.135 g, 0.75 mmol). Needlelike dark red crystals of the resulting product were obtained from a THF solution at 0 °C after 4 hours (0,244 g, 90%). ^{1}H NMR (400 MHz, toluene-d$_8$): δ = 1.26 (s, 18H, Zn-C(CH$_3$)$_3$), 6.48 (s, 2H, -(CH)$_2$-), 6.70 (d, 4H, Ar), 8.36 (d, 4H, Ar) ppm.

X-ray Structure Determination.

Single crystals of **1**, **2** and **3** suitable for X-ray diffraction studies were placed in nujol in an inert atmosphere at -50°C. Then cooled crystals were directly moved to a goniometer head and cooled to -173°C.

Crystal data for **1,** $^{t}Bu_2Zn$, $C_8H_{18}Zn$: M = 179.59, crystal dimensions 0.60 × 0.45 × 0.20 mm^3, orthorhombic, space group P nma (no. 62), a = 10.3370(3) Å, b =9.5680(2) Å, c = 9.7300(2) Å, U = 962.34(4) Å^3, Z = 4, F(000) = 384, D_c = 1.240 g m^3, T = 100(2)K, μ(Mo-Kα) = 2.479 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 23.00°, 713 unique reflections. The structure was solved by direct methods using the SHELXS972 program and was refined by full matrix least–squares on F^2 using the program SHELXL97.3 H-atoms were included in idealized positions and refined isotropically. Refinement converged at $R1$ = 0.0299, $wR2$ = 0.0714 for all data and 49 parameters ($R1$ = 0.0259, $wR2$ = 0.0695 for 610 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.188. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.69/-0.30 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC - 622313. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **2,** $[^{t}Bu_2Zn\ (bpe)]_n$, $C_{20}H_{30}N_2Zn$: M = 363.83, crystal dimensions 0.45 × 0.35 × 0.20 mm^3, tetragonal, space group I 41/acd (no. 142), a = 16.2170(11) Å, b = 16.2170(11) Å, c = 29.604(3) Å, U = 7785.6(10) Å^3, Z = 16, F(000) = 3104, D_c = 1.242 g m^3, T = 100(2)K, μ(Mo-Kα) = 1.263 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 21.24°, 1089 unique reflections. The structure was solved by direct methods using the SHELXS97[2] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[3] H-atoms were

included in idealized positions and refined isotropically. Refinement converged at $R1$ = 0.0704, $wR2$ = 0.0768 for all data and 108 parameters ($R1$ = 0.0304, $wR2$ = 0.0687 for 613 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 0.890. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.18/-0.35 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC - 622314. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **3,** $[^tBu_2Zn\ (bpene)]_n$, $C_{20}H_{28}N_2Zn$: M = 361.81, crystal dimensions 0.50 × 0.45 × 0.30 mm^3, orthorhombic, space group P nna (no. 52), a = 14.6890(6) Å, b = 16.4720(6) Å, c = 8.3540(12) Å, U = 2021.3(3) Å^3, Z = 4, F(000) = 768, D_c = 1.189 g m^3, T = 100(2)K, μ(Mo-Kα) = 1.216 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 24.70°, 1724 unique reflections. The structure was solved by direct methods using the SHELXS97[2] program and was refined by full matrix least–squares on F^2 using the program SHELXL97.[3] H-atoms were included in idealized positions and refined isotropically. Refinement converged at $R1$ = 0.0555, $wR2$ = 0.0685 for all data and 130 parameters ($R1$ = 0.0288, $wR2$ = 0.0640 for 1190 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 0.966. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.41/-0.34 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC - 622315. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(1) Lehmkuhl, H.; Olbrychs, O. *Liebigs Ann. Chem.* **1975**, 1162.

(2) ”SHELXS-97, Program for Structure Solution”: Sheldrick, G.M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

(3) Sheldrick, G. M. SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.