

Synthesis of Tetra-, Hexa-, and Octanuclear Organozinc Ring Systems**

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Organozinc complexes attract widespread interest because of their usefulness as reagents in organic synthesis, catalysts for ring-opening polymerizations, in chemical-vapor synthesis of zinc oxide nanoparticles, and elsewhere.^[1–3] In spite of this interest, ring systems containing multiple organozinc centers still remain scarce.^[4] As part of our studies into ring formation by a number of N,N' and N,O-chelate ligands on treatment with main-group alkyls, we discovered that the use of the {Ph₂C(X)} group^[5] (X = O[−] or NH[−]) enabled us to isolate and structurally characterize novel tetra-, hexa-, and dodecanuclear organoaluminum ring systems.^[6]

Herein, we turn our attention to organozinc chemistry and find that use of this same motif allows easy access to new tetra-, hexa-, and octanuclear organozinc systems (**1**, **2**, and **3**, respectively, Scheme 1) with intriguing ring structures. Furthermore, these compounds serve as a useful entry point to other chemistry, for example reaction of **1** with *tert*-butyl lithium affords the remarkable cage complex **4**, which is built up from eight diphenylglycine-derived ligands through a combination of deprotonation and transfer of *tert*-butyl groups from lithium to zinc. Alkali-metal-containing zinc complexes often exhibit synergic effects, whereby the reactivity of zinc is greatly enhanced.^[7]

Addition of Et₂Zn (2.1 equiv) to α,α -diphenylglycine, Ph₂C(NH₂)CO₂H, in refluxing toluene results in evolution of ethane and affords, following workup, large colorless prisms of **1** in approximately 60% yield (Figure 1).^[8] Each zinc is four-coordinate with a Ph₂C(NH₂)CO₂ ligand chelating, through nitrogen and one oxygen, to one zinc center and bridging through the other oxygen to another; the coordination geometry is completed by an ethyl group. Throughout the structure the carboxylates bind in an *anti/syn* fashion. All the NH₂ groups are involved in intramolecular hydrogen bonds to a CO group attached to a neighboring zinc atom, and two

nitrogen centers, namely N(1) and N(3), each form an additional hydrogen bond to an acetonitrile molecule of crystallization. The core structure can thus be described as a wide, slightly puckered belt linked by pairs of Zn–O and N–H...O bonds. The ethyl groups are alternately up-down-up-down, with acetonitrile molecules hydrogen-bonded only to the “lower-rim” amines/amides. The ¹H NMR spectrum supports this formulation, with signals in the region δ = 0.03 to 0.99 ppm for the Zn–Et groups, whilst the signals for the NH₂ groups appear as two doublets at δ = 3.17 and 5.98 ppm, and assigned as *exo* and *endo* protons, respectively, in accordance with calixarene nomenclature. In the infrared spectrum, $\tilde{\nu}_{\text{NH}}$ stretching modes are detected at approximately 3327 (sharp), 3220, and 3138 cm^{−1} (both broad), and in the mass spectrum the peaks at *m/z* 1058 and 965 correspond to loss of diphenylglycine and diphenylglycine/ethylzinc, respectively, from the parent ion.

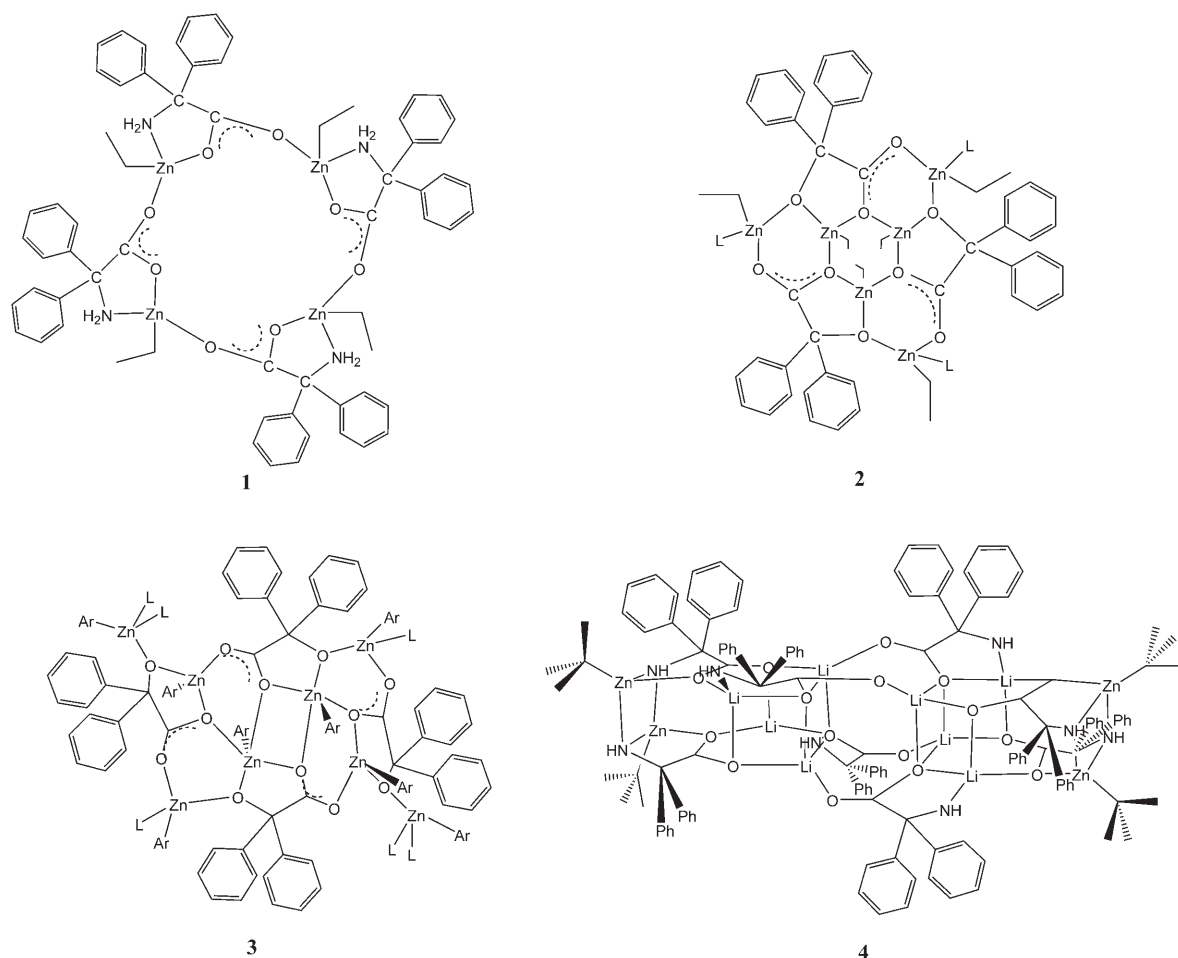
In contrast to the organoaluminum chemistry, in which both diphenylglycine and the related pro-ligand benzilic acid, Ph₂C(OH)CO₂H, gave products with identical structural motifs, the use of benzilic acid with Et₂Zn afforded small colorless prisms in about 9% yield, which were shown by X-ray crystallography using synchrotron radiation^[9,10] to be a trimeric hexanuclear product **2**. The rather low yield is believed to be a consequence of the limited solubility of **2** in acetonitrile; attempts to crystallize **2** from other solvents met with no success. The molecular structure of this acetonitrile solvate **2** is shown in Figure 2a. The central Zn₃O₃ ring has a chair conformation, and the three Zn₂O₃C rings each have that of a folded envelope; these six-membered rings are linked by the CPh₂ group derived from the benzilic acid to form a further three five-membered rings. There are two types of zinc center: as in **1**, each zinc center retains an ethyl group, the three central zinc atoms are further coordinated to only oxygen atoms derived from the benzilic acid pro-ligand (one hydroxy, two carboxylate), whilst the outer three zinc centers (Zn(4), Zn(5) and Zn(6)) are bound by two oxygen atoms from the benzilic acid pro-ligand (one hydroxy, one carboxylate), an ethyl group, and an acetonitrile binds to complete the structure. The binding of the carboxylate groups can be described as *anti/syn/syn* with the three zinc centers protruding out of the carboxylate plane (O(2)/O(5)/O(8)) by about 0.93 (Zn(1)), 0.87 (Zn(2)), and 0.84 (Zn(3)) Å, resulting in a bowl-type structure overall. The view of the structure shown in Figure 2b emphasizes how **2** can be viewed as an “inorganic cup”.

Interestingly, addition of trimethylaluminum (2 equiv) to a toluene solution of **1** resulted in the previously characterized dodeca-aluminum complex [(Ph₂C(NH)CO₂)₂(Me₂Al)(MeAl)]₄(AlMe₂)₄ as the only crystalline product, and

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Scheme 1. Complexes **1–4** (Ar = C₆F₅, L = MeCN).

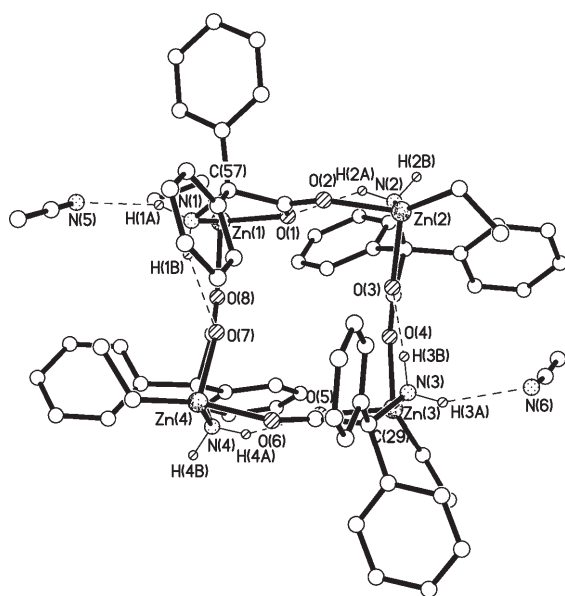


Figure 1. Molecular structure of **1**. Non-carbon atoms are labeled, and only NH hydrogen atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–O(1) 2.0649(14), Zn(1)–O(8) 2.0633(14), Zn(1)–N(1) 2.0786(17), Zn(1)–C(57) 1.969(2); C(57)–Zn(1)–O(8) 113.91(8), C(57)–Zn(1)–O(1) 127.53(8), O(1)–Zn(1)–O(8) 100.71(6).

similar treatment of complex **2** afforded the known $[(\text{Ph}_2\text{C}(\text{O})\text{CO}_2)_2(\text{Me}_2\text{Al})(\text{MeAl})](\text{AlMe}_2)_2$;^[6] both products were identified by ¹H NMR spectroscopy and X-ray crystallography (unit cell determination).

Treatment of benzoic acid with two equivalents of (C₆F₅)₂Zn-toluene in toluene afforded, following workup, a white solid in about 47% yield. Crystals suitable for X-ray diffraction using synchrotron radiation^[9,11] formed slowly on allowing the solution to stand for a long time at ambient temperature. There is half of a centrosymmetric molecule of **3** and three acetonitrile molecules of crystallization in the asymmetric unit. There are four different types of zinc center (see Figure 3): zinc atoms Zn(1), Zn(3), and Zn(4) are distorted tetrahedral with NO₂C, O₃C, and N₂OC coordination environments, respectively, whilst Zn(2) is best described as adopting a square-based pyramidal geometry with a C₆F₅ group at the apex and an O₄ base. The structure comprises a central, planar Zn₂O₂ diamond, with each of these zinc atoms also being part of a six-membered Zn₂O₂C₂ ring. The carboxylate binding in **3** resembles that in **2**, namely *anti/syn*. The inorganic core grows out from this diamond in opposite directions such that a Zn₂O₃C and two ZnO₂C₂ rings link to give an overall extended “chair-like” conformation with respect to the zinc atoms. The remaining two zinc

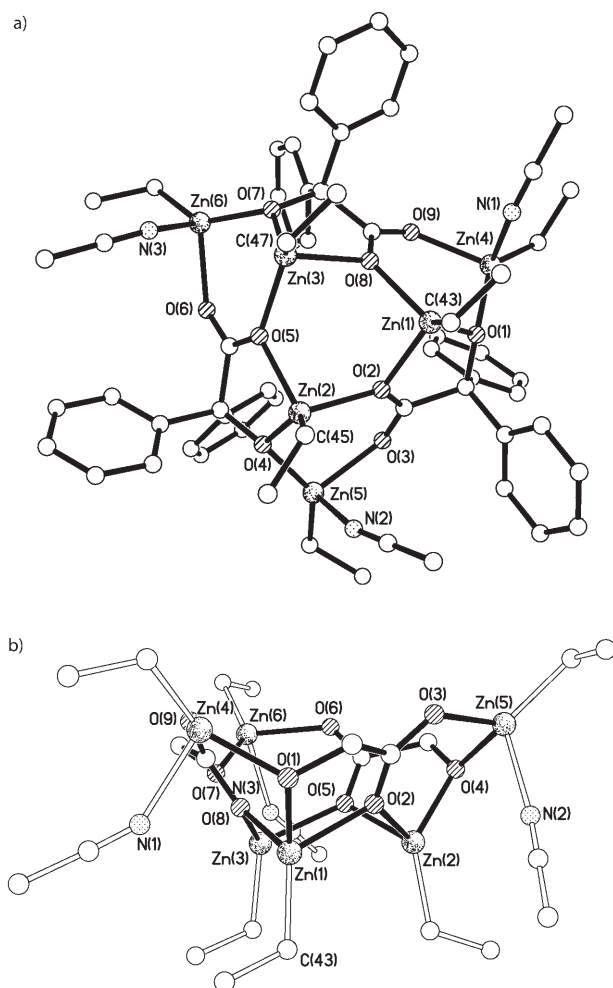


Figure 2. a) Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–O(1) 1.9710(9), Zn(1)–O(2) 2.0937(9), Zn(1)–O(8) 2.1073(9), Zn(1)–C(43) 1.9634(15), Zn(6)–O(6) 2.0823(10), Zn(6)–O(7) 1.9505(9), Zn(6)–N(3) 2.1981(14); Zn(1)–O(2)–Zn(2) 114.52(4), O(6)–Zn(6)–O(7) 95.50(4). b) Side view of **2** emphasizing the cup-like structure (phenyl groups removed for clarity).

centers, Zn(4) and Zn(4A), are “pendant” and bound at either end of the inorganic core to O(6) and O(6A), respectively. There is extensive intramolecular π – π stacking in **3**, with that involving the phenyl rings at C(9)/C(23) and the C₆F₅ rings at Zn(1)/Zn(4), respectively, having a distance of about 3.3 Å. A distance of approximately 3.4–3.6 Å separates the two C₆F₅ rings at Zn(1) and Zn(4), which are slightly offset. There is also an edge-to-face interaction between the rings at C(17) and at C(3A), with a hydrogen-to-centroid distance of 3.01 Å. These intramolecular interactions are reminiscent of those observed recently for the complex [Zn(C₆F₅)₂NH(CH₂Ph)]₂.^[12] Interestingly however, in **3** there is no intermolecular π – π stacking.

Complexes **1–3** serve as convenient entry points into new organozinc chemistry. Our preliminary reactivity studies on **1** have yielded an intriguing heterobimetallic cage complex on reaction with *tert*-butyl lithium. Small crystals of **4** suitable for an X-ray study using synchrotron radiation^[9,13] were grown

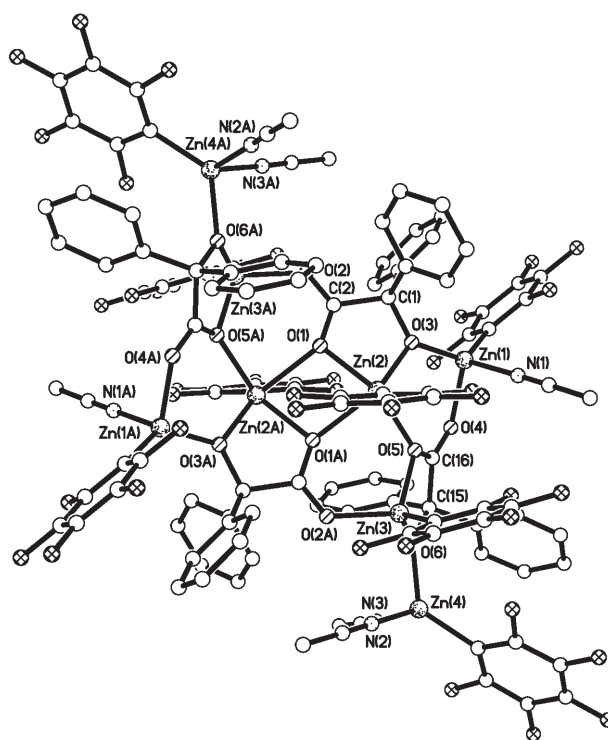


Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–O(3) 1.934(5), Zn(1)–O(4) 2.009(5), Zn(2)–O(3) 2.101(4), Zn(2)–O(1) 2.082(5), Zn(2)–O(5) 2.130(5), Zn(2)–O(1A) 2.284(4), Zn(3)–O(6) 1.960(5), Zn(3)–O(2A) 1.988(5), Zn(3)–O(5) 2.054(4), Zn(4)–O(6) 1.944(5); O(3)–Zn(1)–C(29) 130.1(3), O(3)–Zn(1)–O(4) 103.01(19), C(29)–Zn(1)–O(4) 109.3(3), C(35)–Zn(2)–O(3) 124.7(2), C(35)–Zn(2)–O(1) 109.8(2), O(3)–Zn(2)–O(1) 79.53(18), O(3)–Zn(2)–O(5) 93.69(19), O(1)–Zn(2)–O(5) 137.44(17), O(6)–Zn(3)–C(41) 131.1(3), O(6)–Zn(3)–O(2A) 102.29(19), O(6)–Zn(3)–O(5) 81.87(18), O(2A)–Zn(3)–O(5) 105.88(18), O(6)–Zn(4)–C(47) 128.6(3), Zn(2)–O(1)–Zn(2A) 106.56(18), Zn(1)–O(3)–Zn(2) 122.0(2), Zn(3)–O(5)–Zn(2) 109.3(2), Zn(4)–O(6)–Zn(3) 118.1(2). Symmetry operator A = –x, –y, –z.

from toluene at 0°C (Figure 4). The cage lies on the twofold axis *b* and contains four zinc centers and eight lithium centers, which are linked together by eight Ph₂C(NH)CO₂ ligands in *anti/syn/syn* fashion. Each zinc has a distorted tetrahedral coordination environment and is bound by an oxygen and two nitrogen atoms of diphenylglycine-derived ligands together with a bulky *tert*-butyl group. This group arises from transfer of the lithium reagent to zinc, as in the reaction of the Zn₄N₈ cage complex [(ZnEt(NMe₂)NH)₄] with *tert*-butyl lithium.^[14]

All the lithium centers are four-coordinate with either an O₄ (Li(2) and Li(4)) or O₃N (Li(1) and Li(3)) coordination environment. The connectivity of the “inorganic” core of **4** can be described as a coordination oligomer, which has been “capped” at either end by *tert*-butyl groups. The NH groups in **4** do not engage in hydrogen bonding.

In summary, we have shown that use of the {Ph₂C(X)} group, X = O[–] or NH[–], in organozinc chemistry allows access to some remarkable new complexes with fascinating structures. Further studies will focus on the coordinating properties of these new compounds.

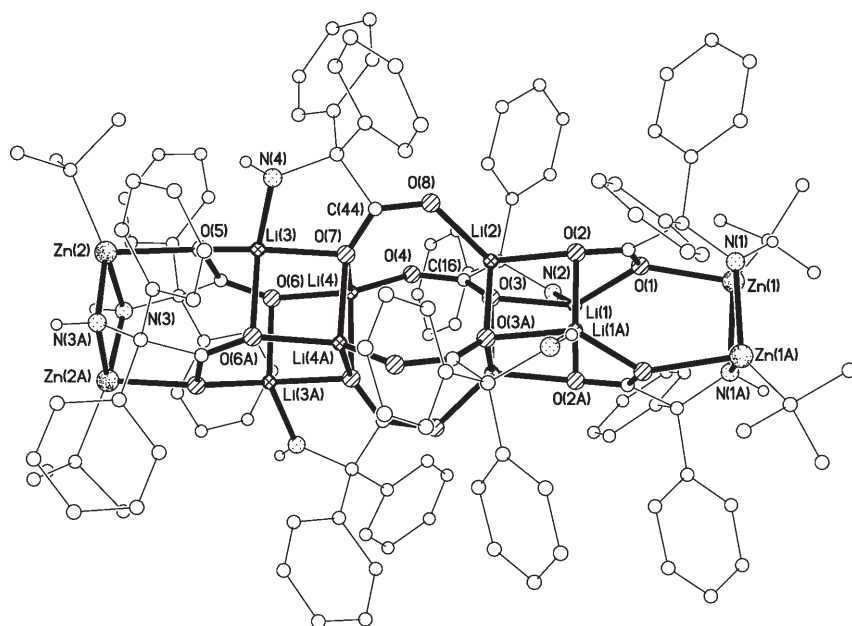


Figure 4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–O(1) 2.158(3), Zn(1)–N(1) 2.051(4), Zn(1)–N(1A) 2.090(4), Li(1)–O(1) 1.917(7), Li(1)–N(2) 2.012(8), Li(1)–O(3) 1.973(7), Li(1A)–O(2) 2.056(8), Li(2)–O(3) 1.986(8), Li(2)–O(8) 1.890(8), Li(2)–O(3A) 2.020(10), N(1)–Zn(1)–N(1A) 90.42(15), O(1)–Zn(1)–N(1) 79.51(12), Zn(1)–N(1)–Zn(1A) 89.30(15), Zn(1)–O(1)–Li(1) 129.5(2), Li(1)–O(3)–Li(2) 99.6(3), Li(4)–O(4)–C(16) 131.2(5), Li(1)–N(2)–C(15) 107.2(3), Li(2)–O(8)–C(44) 129.8(4), O(7)–C(44)–O(8) 125.2(4). Symmetry operator A = $-x, y, -z + 3/2$.

Experimental Section

All manipulations were performed under nitrogen using standard Schlenk techniques and dried, deoxygenated solvents.

1: 2,2'-diphenylglycine (2.00 g, 8.80 mmol) and Et_2Zn (18.50 mL, 1.0 M in hexanes, 18.50 mmol) were heated under reflux in toluene (30 mL) for 12 h. Following removal of volatiles in vacuo, the residue was extracted into warm acetonitrile (40 mL). The solution as allowed to stand at ambient temperature, affording **1** as large colorless blocks. Yield: 1.83 g, 61%; elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{88}\text{N}_4\text{O}_8\text{Zn}_4 \cdot 2\text{MeCN}$: C 59.8, H 5.5, N 6.2; found: C 59.7, H 5.4, N 6.0; IR: $\tilde{\nu}$ = 3327 (sharp), 3220 and 3138 $\nu(\text{NH}_2)$, 1606 and 1581 cm^{-1} $\nu(\text{CO})$ broad; ^1H NMR (CDCl_3 , 400 MHz, 298 K): δ = 7.81–7.14 (5 × m, 40H, arylH), 5.98 (d, 4H, $^3J_{\text{HH}} = 10.4$ Hz, *endo*- NH_2), 3.17 (d, 4H, $^3J_{\text{HH}} = 10.4$ Hz, *exo*- NH_2), 2.43 (s, 1.5H, $^1/2\text{MeCN}$), 0.99 (t, 12H, $^3J_{\text{HH}} = 7.6$ Hz, CH_3), 0.03 ppm (m, 8H, $^3J_{\text{HH}} = 7.6$ Hz, CH_2); ES-MS: 1058 [$M^+ - \text{Ph}_2\text{C}(\text{NH}_2)\text{CO}_2\text{H}$], 994 [$M^+ - \text{Ph}_2\text{C}(\text{NH}_2)\text{CO}_2\text{H} - \text{Zn}$], 965 [$M^+ - \text{Ph}_2\text{C}(\text{NH}_2)\text{CO}_2\text{H} - \text{ZnEt}$], 739 [$M^+ - 2\text{Ph}_2\text{C}(\text{CO}_2\text{H}) - (\text{NH}_2) - \text{ZnEt}$].

2: As for **1**, but using benzoic acid (2.00 g, 8.76 mmol) and Et_2Zn (1.80 mL, 17.56 mmol), affording **2** as small colorless prisms at 0°C. Yield: 0.38 g, 9%; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{69}\text{N}_3\text{O}_9\text{Zn}_6 \cdot 2\text{MeCN}$: C 49.7, H 5.2, N 2.9; found: C 49.8, H 5.0, N 2.7; IR: $\tilde{\nu}$ = 2361 $\nu(\text{CN})$, 1576 cm^{-1} $\nu(\text{CO})$ broad; ^1H NMR (CDCl_3 , 400 MHz, 298 K): δ = 7.78–6.43 (overlapping m, 30H, arylH), 1.91 (bs, 9H, MeCN), 1.24–0.53 ppm (overlapping m, 30H, Et); ES-MS: 1258 [$M^+ - 4\text{MeCN} - \text{Et}$], 1217 [$M^+ - 5\text{MeCN} - \text{Et}$], 922 [$M^+ - 5\text{MeCN} - \text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H} - \text{ZnEt}$], 666 [$M^+ - 5\text{MeCN} - \text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H} - \text{ZnEt} - \text{Et}$], 601 [$M^+ - 5\text{MeCN} - \text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H} - 2\text{ZnEt}$].

3: As for **1**, but using benzoic acid (2.00 g, 8.76 mmol) and $(\text{C}_6\text{F}_5)_2\text{Zn}$ -toluene (8.61 g, 17.52 mmol) affording **3** as a white solid. Yield: 3.37 g, 47% (based on benzoic acid); elemental analysis calcd (%) for $\text{C}_{116}\text{H}_{58}\text{F}_{40}\text{N}_6\text{O}_{12}\text{Zn}_8$: C 46.3, H 1.9, N 2.8; found: C 47.0, H 2.1,

N 2.1; IR: $\tilde{\nu}$ = 2353, 2312 $\nu(\text{CN})$, 1614, 1586, 1505 cm^{-1} $\nu(\text{CO})$; ^1H NMR ($[\text{D}_6]\text{DMSO}$, 400 MHz, 298 K): δ = 7.47–6.87 (5 × bm, 40H, arylH), 2.07 ppm (s, 13.5H, 4.5MeCN); ^{19}F NMR ($[\text{D}_6]\text{DMSO}$, 282.4 MHz, 298 K): δ = –114.3 (m, 4F, *o*-F), –115.9 (m, 4F, *o*-F), –116.4 (m, 4F, *o*-F), –139.5 (m, 1F), –154.9 (t, $J_{\text{FF}} = 16.9$ Hz, 1F), –157.6 (bs, 2F), –159.0 (t, $J_{\text{FF}} = 22.5$ Hz, 3F), –162.5 (overlapping m, 15F), –165.4 ppm (bt, 4F, *m*-F); MS (MALDI): 1840 [$M^+ - 2[\text{Zn}(\text{C}_6\text{F}_5)(\text{NCMe})_2] - 3\text{C}_6\text{F}_5 - \text{MeCN}$], 1799 [$M^+ - 2[\text{Zn}(\text{C}_6\text{F}_5)(\text{NCMe})_2] - 3\text{C}_6\text{F}_5 - 2\text{MeCN}$].

4: *t*BuLi (1.76 mL, 1.7 M in pentane, 3.00 mmol) was added to **1** (1.00 g, 0.73 mmol) in THF at –78°C, the system was slowly allowed to warm to ambient temperature and then stirred for 12 h. Following removal of volatiles in vacuo, the residue was taken up in toluene (20 mL) and stored at 0°C to afford **4** as small colorless prisms. Yield: 0.21 g, 24% (based on diphenylglycine-derived ligand); elemental analysis calcd (%) for $\text{C}_{131.5}\text{H}_{128}\text{Li}_8\text{N}_8\text{O}_{16}\text{Zn}_4$: C 66.0, H 5.4, N 4.7; found: C 65.7, H 5.1, N 4.7; IR: $\tilde{\nu}$ = 3336, 3164 $\nu(\text{NH})$, 1603 cm^{-1} $\nu(\text{CO})$ broad; ^1H NMR (CDCl_3 , 400 MHz, 298 K): δ = 7.76–6.45 (bm, 82.5H, arylH + arylH_{toluene}), 3.67 (bs, 8H, NH), 2.35 (s, 1.5H, $\text{CH}_3\text{toluene}$), 1.13 ppm ($\text{C}(\text{CH}_3)_3$); MS (MALDI): 2271 [$M^+ - \text{Zn} - t\text{Bu}$], 2206 [$M^+ - 2\text{Zn} - t\text{Bu}$], 1980 [$M^+ - 2\text{Zn} - t\text{Bu} - 2\text{Li}$], 1973 [$M^+ - 2\text{Zn} - t\text{Bu} - 3\text{Li}$], 1923 [$M^+ - 2\text{Zn} - t\text{Bu} - 2\text{Li}$], 1743 [$M^+ - 3\text{Zn} - 4t\text{Bu} - 2\text{Li}$].

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- [8] Crystal data for **1**: $C_{68}H_{74}N_6O_8Zn_4$, $M_r = 1364.81$, monoclinic, space group $P2_1/c$, colorless, $0.84 \times 0.61 \times 0.45 \text{ mm}^3$, $a = 14.9705(7)$, $b = 16.9228(8)$, $c = 25.9541(12) \text{ \AA}$, $\beta = 91.756(2)^\circ$, $V = 6572.2(5) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.379 \text{ g cm}^{-3}$, $\mu = 1.500 \text{ mm}^{-1}$, 56079 data measured on a Bruker SMART 1000 CCD diffractometer, 15751 independent, ($R_{\text{int}} = 0.0348$), which were used in all the calculations, $wR2 = 0.0888$ (all data), $R1 = 0.0329$ (for 12492 data with $F^2 > 2\sigma(F^2)$), 4978 parameters, largest difference map features within $\pm 0.548 \text{ e \AA}^{-3}$. Ethyl group C(61)/C(62) was modeled as disordered over 2 sets of positions. Refined with restraints on geometry and displacement parameters, major/minor = 78.4:21.6(7)%.^[13b]
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- [10] Crystal data for **2**: $C_{64}H_{75}N_5O_9Zn_6$, $M_r = 1450.51$, orthorhombic, space group $P2_12_12_1$, colorless, $0.25 \times 0.25 \times 0.09 \text{ mm}^3$, $a = 12.083(2)$, $b = 19.653(4)$, $c = 27.898(6) \text{ \AA}$, $V = 6625(2) \text{ \AA}^3$, $T = 151(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.454 \text{ g cm}^{-3}$, $\mu = 2.194 \text{ mm}^{-1}$, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monochromator, $\lambda = 0.6765 \text{ \AA}$, 74156 reflections measured, 21477 unique ($R_{\text{int}} = 0.0356$) which were used in all the calculations. The final $wR2 = 0.0544$ (all data) and $R1 = 0.0216$ (for 20962 data with $F^2 > 2\sigma(F^2)$), 769 parameters, largest difference map features within $\pm 0.569 \text{ e \AA}^{-3}$.^[13b]
- [11] Crystal data for **3**: $C_{128}H_{76}F_{40}N_{12}O_{12}Zn_8$, $M_r = 3256.96$, triclinic, space group $P\bar{1}$, colorless, $0.07 \times 0.04 \times 0.03 \text{ mm}^3$, $a = 14.106(6)$, $b = 15.238(6)$, $c = 17.382(7) \text{ \AA}$, $\alpha = 101.279(5)$, $\beta = 108.299(5)$, $\gamma = 103.605(5)^\circ$, $V = 3298(2) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 1$, $\rho_{\text{calcd}} = 1.640 \text{ g cm}^{-3}$, $\mu = 1.549 \text{ mm}^{-1}$, synchrotron radiation at Daresbury Laboratory, Station 16.2 SMX, silicon 111 monochromator, $\lambda = 0.7848 \text{ \AA}$, 24476 reflections measured, 12765 unique ($R_{\text{int}} = 0.0933$) which were used in all the calculations. The final $wR2 = 0.2558$ (all data) and $R1 = 0.0935$ (for 12765 data with $F^2 > 2\sigma(F^2)$), 908 parameters, largest difference map features within $\pm 1.747 \text{ e \AA}^{-3}$.^[13b]
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- [13] a) Crystal data for **4**: $C_{131.5}H_{128}Li_8N_8O_{16}Zn_4$, $M_r = 2393.42$, monoclinic, space group $C2/c$, colorless, $0.10 \times 0.08 \times 0.06 \text{ mm}^3$, $a = 27.6536(16)$, $b = 24.6622(15)$, $c = 24.7281(15) \text{ \AA}$, $\beta = 120.214(2)^\circ$, $V = 14573.5(15) \text{ \AA}^3$, $T = 120(2) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.091 \text{ g cm}^{-3}$, $\mu = 0.706 \text{ mm}^{-1}$, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monochromator, $\lambda = 0.6751 \text{ \AA}$, 49220 reflections measured, 11232 unique ($R_{\text{int}} = 0.0533$) which were used in all the calculations. The final $wR2 = 0.2320$ (all data) and $R1 = 0.0704$ (for 7822 data with $F^2 > 2\sigma(F^2)$), 893 parameters, largest difference-map features within $\pm 0.451 \text{ e \AA}^{-3}$. The *tert*-butyl group on Zn(2) was modeled with methyl groups split over 2 sets of positions (major/minor = 78.3:21.7(13)%). Three of the phenyl groups are two-fold disordered, and in each case the *ipso*-C is common to both components, while the other five ring carbons are split over two sets of positions (at C(23) major/minor = 81.2:18.8(7)%; C(45) major/minor = 69.3:30.7(5)%; C(51) major/minor = 69.3:30.7(5)%). Platon squeeze was used to model a disordered toluene molecule.^[15] b) CCDC 638661–CCDC 638664 (**1–4**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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