Supporting Information

Self-assembly of [2×2] grids and a hexagon using dipyrromethene ligands

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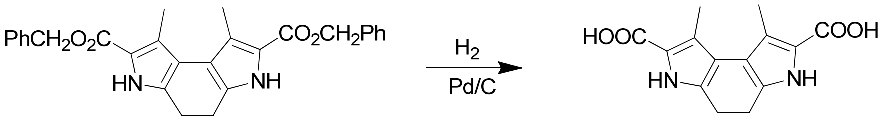
General information:

Unless otherwise noted, all starting materials and solvents were obtained from Aldrich, Fisher, Alfa Aesar or Oakwood and used without further purification. Thin-layer chromatography (TLC) was performed with Merck Silica Gel 60 F254. Column chromatography was performed using silica gel from Silicycle Chemical Division (particle size: 230-400 mesh). The gel permeation chromatography (GPC) was carried out on Bio-Beads S-X1 beads (200-400 mesh). ^{1}H NMR and ^{13}C NMR data were collected in d_6-DMSO or $CDCl_3$ on a Bruker Avance 300 MHz or a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to the residual non-deuterated solvent proton resonance as reference standard (d_6-DMSO at 2.50 ppm and 39.51 ppm for ^{1}H NMR and ^{13}C NMR, respectively; $CDCl_3$ at 7.27 ppm and 77.00 ppm for ^{1}H NMR and ^{13}C NMR). The low-resolution mass spectrometry (LRMS) and high-resolution mass spectrometry (HRMS) were taken on Kratos Concept IIHQ (EI), or Kratos MS50 (EI), or Bruker Esquire~LC (ESI) spectrometers. Mass spectra of the metal complexes were obtained by MALDI-TOF mass spectroscopy in the presence of an added matrix, 2-[(2 E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), on the Bruker Biflex IV instrument. UV-Visible spectra were recorded in chloroform at room temperature on a Cary 5000 scan spectrophotometer. Crystals of grid **9** and hexagon **11** were grown from a chloroform solution with hexane diffusion. The X-ray data were obtained on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected and integrated using Bruker SAINT software. The structures were solved by direct methods and refined with the SHELXTL crystallographic software package from Bruker-AXS.

Experimental procedure:



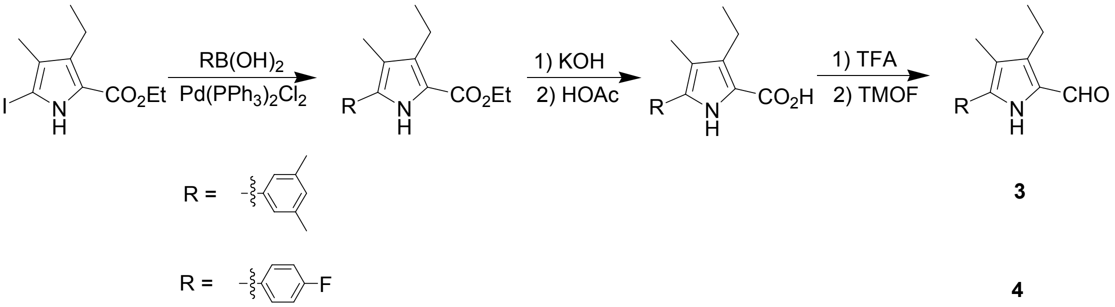
1

dihydropyrrolo[3,2-e]indole dibenzyl ester

dihydropyrrolo[3,2-e]indole dibenzyl ester was synthesized based on a previously reported procedure[1] to afford an off-white solid. Yield: (9.0 g, 36%); ^{1}H NMR (300MHz, DMSO-d_6) δ (ppm) 11.55 (br. s, 2H, NH), 7.32 - 7.46 (m, 10H, Ar-H), 5.27 (s, 4H, CH_2), 2.70 (s, 4H, CH_2), 2.46 (s, 6H, CH_3); EI MS (M^+): *m*/*z* 454; Anal. Calcd. for: $C_{28}H_{26}N_2O_4$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.39; H, 5.87; N, 6.50.

dihydropyrrolo[3,2-e]indole diacid (1)

To a mixture of dihydropyrrolo[3,2-e]indole dibenzyl ester (227 mg, 0.50 mmol) and 10 mol % palladium on activated carbon (50 mg) in a 250 mL round-bottom flask was added THF (75 mL) and MeOH (25 mL). The mixture was purged with hydrogen at 1 atm and stirred overnight. The reaction mixture was then filtered through Celite to remove the catalyst. The filtrate was carried on to the next step without further purification.



3

4

ethyl 5-(3,5-dimethylphenyl)-3-ethyl-4-methylpyrrole-2-carboxylate

Synthesized according to a previously reported procedure,[2] with some modification. To a mixture of ethyl 3-ethyl-5-iodo-4-methylpyrrole-2-carboxylate[3] (1.0 g, 3.26 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) and 3,5-dimethylphenylboronic acid (0.6 g, 4 mmol) in DME (30 mL) was added K_2CO_3 (1.38 g, 10 mmol, dissolved in minimum amount of water). The mixture was heated to 85˚C and stirred for 3 h. The reaction was allowed to cool, and the organic solvent was then removed *in vacuo*. The residue was treated with EtOAc (100 mL) and thoroughly washed with several portions of water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Flash chromatography on silica gel, eluting with

20% EtOAc in hexanes, afforded a yellow solid. Yield: (0.85 g, 92%); ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.81 (br. s, 1H, NH), 7.10 (s, 2H, Ar-H), 6.99 (s, 1H, Ar-H), 4.35 (q, J = 7.1 Hz, 2H, CH_2), 2.83 (q, J = 7.4 Hz, 2H, CH_2), 2.38 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 1.39 (t, J = 7.3 Hz, 3H, CH_3), 1.19 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 161.6, 138.3, 134.6, 133.1, 132.4, 129.1, 125.1, 117.8, 116.9, 59.8, 21.3, 18.4, 15.0, 14.5, 9.8; EI MS (M^+): *m/z* 285. HR-EI MS (M^+) *m/z* calcd for $C_{18}H_{23}NO_2$ 285.1729, found 285.1730.

5-(3,5-dimethylphenyl)-3-ethyl-4-methylpyrrole-2-carboxylic acid

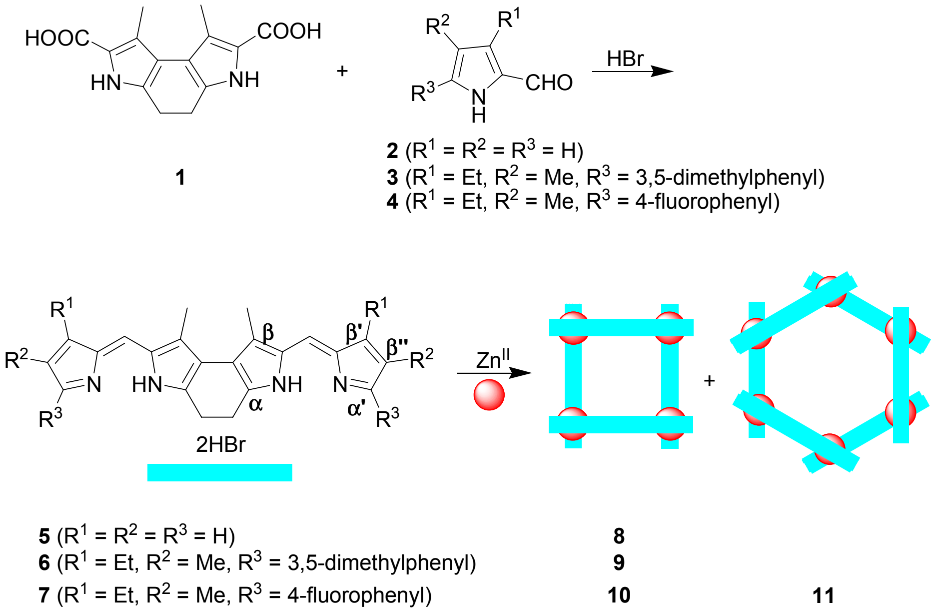
To a solution of ethyl 5-(3,5-dimethylphenyl)-3-ethyl-4-methylpyrrole-2-carboxylate (0.71 g, 2.5 mmol) in EtOH (30 mL) was added KOH (1.4 g, 25 mmol, dissolved in 5 mL water). The reaction mixture was refluxed for 3 h. After removal of the solvent, the residue was treated with 400 mL water, followed by addition of acetic acid to give a precipitate. The precipitate was filtered and washed with several portions of water to remove excess acetic acid to afford a grey solid. Yield: 0.50 g (78%); ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.87 (s, 1H, COOH), 7.11 (s, 2H, Ar-H), 7.01 (s, 1H, Ar-H), 2.86 (q, J = 7.6 Hz, 2H, CH_2), 2.38 (s, 6H, CH_3), 2.18 (s, 3H, CH_3), 1.20 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 166.3, 138.4, 136.8, 134.6, 132.2, 132.1, 129.4, 125.2, 117.5, 21.3, 18.4, 15.0, 9.8; EI MS (M^+): *m/z* 257. HR-EI MS (M^+) *m/z* calcd for $C_{16}H_{19}NO_2$ 257.1416, found 257.1417.

5-(3,5-dimethylphenyl)-3-ethyl-4-methylpyrrole-2-carbaldehyde (3)

According to a previously reported procedure,[4] some modifications were made for the synthesis of **3**. To a 50 mL round-bottom flask was added 5-(3,5-dimethylphenyl)-3-ethyl-4-methylpyrrole-2-carboxylic acid (0.42 g, 1.65 mmol) and TFA (3 mL). The reaction mixture was stirred for 15 mins before cooling to 0°C. The mixture was stirred for an additional 15 mins after slow addition of TMOF (2 mL) at 0°C. The reaction was poured into a well-stirred mixture of ice-water and CH_2Cl_2. The organic layer was washed with water, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and filtered. After removal of the organic solvent, the residue was purified by flash chromatography on silica gel, eluting with 30% EtOAc in hexanes, to give an off-white solid. Yield: (0.36 g, 90%); ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 9.62 (s, 1H, CHO), 9.11 (br. s, 1H, NH), 7.13 (s, 2H, Ar-H), 7.02 (s, 1H, Ar-H), 2.78 (q, J = 7.6 Hz, 2H, CH_2), 2.37 (s, 6H, CH_3), 2.18 (s, 3H, CH_3), 1.26 (t, J = 7.7 Hz, 3H, CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 176.8, 139.1, 138.4, 137.3, 131.6, 129.9, 128.1, 125.2, 117.6, 21.3, 17.2, 16.5, 9.7; EI MS (M^+): *m/z* 241. HR-EI MS (M^+) *m/z* calcd for $C_{16}H_{19}NO$ 241.1467, found 241.1467.

3-ethyl-5-(4-fluorophenyl)-4-methylpyrrole-2-carbaldehyde (4)

The same procedure was used as in the synthesis of **3**, starting from 4-fluorophenylboronic acid (0.56 g, 4 mmol) to afford **4** as a yellow solid. Yield: (0.35 g, 92%); ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 9.62 (s, 1H, CHO), 9.41 (br. s, 1H, NH), 7.46 - 7.52 (m, 2H, Ar-H), 7.15 (t, *J* = 8.6 Hz, 2H, Ar-H), 2.78 (q, *J* = 7.6 Hz, 2H, CH_2), 2.15 (s, 3H, CH_3), 1.26 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 176.9, 164.1, 160.9, 139.2, 136.2, 129.4, 129.3, 116.0, 115.7, 17.2, 16.5, 9.6; EI MS (M^+): *m/z* 231. HR-EI MS (M^+) *m/z* calcd for $C_{14}H_{14}NOF$ 231.1059, found 231.1059.



1

2 ($R^1 = R^2 = R^3 = H$)
3 (R^1 = Et, R^2 = Me, R^3 = 3,5-dimethylphenyl)
4 (R^1 = Et, R^2 = Me, R^3 = 4-fluorophenyl)

5 ($R^1 = R^2 = R^3 = H$) **8**
6 (R^1 = Et, R^2 = Me, R^3 = 3,5-dimethylphenyl) **9**
7 (R^1 = Et, R^2 = Me, R^3 = 4-fluorophenyl) **10** **11**

bisdipyrrin ligand (5)

To a solution of freshly prepared **1** (0.050 mmol) in THF (75 mL) and MeOH (25 mL) was added **2** (48 mg, 0.50 mmol), followed by the addition of 33% hydrogen bromide in acetic acid (1.0 mL). The solution immediately turned from colourless to dark purple. The solution was stirred for 1 h, and the organic solvent was then removed *in vacuo* to give black solid. The black solid was redissolved in $CHCl_3$ (75 mL) and MeOH (25 mL), and another portion of **2** (48 mg, 0.50 mmol) was added, followed by the addition of 33% hydrogen bromide in acetic acid (1.0 mL). The reaction mixture was stirred for 4 h at room temperature. Removal of the solvent *in vacuo* gave the crude product. To this crude product was added just enough chloroform and methanol to form a homogeneous solution, and then diethyl ether was added to precipitate the product, which was collected by filtration and rinsed with more diethyl ether to give a black solid. Yield: (200 mg, 80%); ESI MS $(M+H)^+$: *m/z* 341.3; HR-ESI MS $(M+H)^+$: *m/z* calcd for $C_{22}H_{21}N_4$: 341.1766; found: 341.1758. UV/Vis ($CHCl_3/CH_3OH$ = 2/1) λ_{max} nm (A): 583.0 (1.115).

bisdipyrrin ligand (6)

The same procedure was used as in the synthesis of **5**, starting from **3** (242 mg, 1.0 mmol) to afford a black solid. Yield: (346 mg, 87%); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 14.27 (br. s, 2H, NH), 12.52 (br. s, 2H, NH), 7.56 (s, 4H, Ar-H), 7.28 (s, 2H, Ar-H), 7.14 (s, 2H, *meso*-H), 3.50 (s, 4H, CH_2), 2.78 (d, J = 7.0 Hz, 4H, CH_2), 2.65 (s, 6H, CH_3), 2.44 (s, 12H, CH_3), 2.20 (s, 6H, CH_3), 1.24 (t, J = 7.6 Hz, 6H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 156.0, 154.8, 150.4, 138.1, 134.3, 132.8, 128.1, 128.0, 127.8, 126.9, 123.5, 120.8, 119.3, 29.6, 22.2, 21.3, 18.9, 16.2, 10.7; ESI MS $(M+H)^+$: *m*/*z* 633.6; HR-ESI MS $(M+H)^+$: *m*/*z* calcd for $C_{44}H_{49}N_4$: 633.3957; found: 633.3943. UV/Vis ($CHCl_3$) λ_{max} nm (logε): 647.0 (5.24).

bisdipyrrin ligand (7)

The same procedure was used as in the synthesis of **5**, starting from **4** (232 mg, 1.0 mmol) to afford a black solid. Yield: (350 mg, 90%); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 14.25 (br. s, 2H, NH), 12.61 (br. s, 2H, NH), 7.93 (s, 4H, Ar-H), 7.32 (s, 2H, *meso*-H), 7.22 (t, J = 7.6 Hz, 4H, Ar-H), 3.48 (s, 4H, CH_2), 2.77 (d, J = 5.9 Hz, 4H, CH_2), 2.66 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 1.23 (br. s, 6H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 156.5, 152.9, 150.6, 134.9, 132.4, 132.3, 128.2, 126.8, 124.6, 123.3, 119.9, 116.0, 115.7, 22.2, 18.8, 16.1, 13.6, 10.6; ESI MS $(M+H)^+$: *m*/*z* 613.5; HR-ESI MS $(M+H)^+$: *m*/*z* calcd for $C_{40}H_{39}N_4F_2$: 613.3143; found: 613.3148. UV/Vis ($CHCl_3$) λ_{max} nm (logε): 644.0 (5.31).

[2×2] Zn^{II} grid (8)

According to a previously reported procedure,[5] some modifications were made for the synthesis of **8**. To a solution of **5** (50 mg, 0.1 mmol) in $CHCl_3$/MeOH (20 mL/10 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (33 mg, 0.15 mmol) in MeOH (1 mL), followed by addition of a solution of NaOAc (82 mg, 1 mmol) in MeOH (1 mL). After stirring overnight, the solvent was removed by rotary evaporation. The crude compound was purified by flash chromatography on silica gel, eluting with CH_2Cl_2, to give the target Zn^{II} complex as a dark green solid, and the remainder is composed of unidentified polymeric material. Yield: 7.5 mg (19%); ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.18 (s, 8H, pyrrole-H), 7.16 (s, 8H, pyrrole-H), 6.99 (d, J = 3.5 Hz, 8H, *meso*-H), 6.34 (dd, J = 3.7, 1.4 Hz, 8H, pyrrole-H), 2.53 (s, 24H, CH_3), 2.28 (dq, J = 10.6, 6.6 Hz, 16H, CH_2); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) 164.2, 145.4, 140.1, 138.0, 133.7, 128.4, 126.7, 123.4, 115.3, 25.0, 13.1; MALDI-TOF calcd. 1615.2, found 1615.2 [$(M)^+$]; Anal. Calcd. for: $C_{88}H_{72}N_{16}Zn_4$: C, 65.44; H, 4.49; N, 13.88. Found: C, 65.33; H, 4.59; N, 13.63; UV/Vis ($CHCl_3$) λ_{max} nm (logε): 575.0 (5.63) and 613.0 (5.53).

[2×2] Zn^{II} grid (9)

The same procedure was used as in the synthesis of **8**, starting from **6** (71 mg, 0.1 mmol). The crude compound collected from flash chromatography on silica gel, was then purified using gel permeation chromatography eluting with toluene. The target Zn^{II} grid was obtained as a dark green solid, and the remainder is composed of unidentified polymeric material. Yield: (4.9 mg, 7.0%); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 6.74 (s, 8H, *meso*-H), 6.63 (s, 8H, Ar-H), 6.57 (s, 16H, Ar-H), 2.50-2.58 (m, 16H, CH_2), 2.45 (s, 24H, CH_3), 2.14-2.20 (m, 16H, CH_2), 1.99 (s, 48H, CH_3), 1.88 (s, 24H, CH_3), 1.13 (t, J = 7.6 Hz, 24H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 160.7, 157.1, 142.9, 138.3, 136.6, 135.6, 129.5, 128.3, 126.0, 122.6, 121.1, 120.5, 29.7, 25.3, 21.1, 18.4, 16.1, 13.0, 10.1; MALDI-TOF calcd. 2785.0, found 2784.7 [$(M)^+$]; UV/Vis ($CHCl_3$) λ_{max} nm (logε): 625.0 (5.68) and 661.0 (5.66).

[2×2] Zn^{II} grid (10) and hexagon (11)

The same procedure was used as in the synthesis of **9**, starting from **7** (74 mg, 0.1 mmol) to afford dark green solids, and the remainder is composed of unidentified polymeric material.

grid (10): Yield: 6.2 mg (9.2%); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 6.88 (dd, J = 7.9 and 5.5 Hz, 16H, Ar-H), 6.81 (s, 8H, *meso*-H), 6.61 (t, J = 8.6 Hz, 16H, Ar-H), 2.56-2.65 (m, 16H, CH_2), 2.49 (s, 24H, CH_3), 2.15 (s, 16H, CH_2), 1.88 (s, 24H, CH_3), 1.17 (t, J = 7.5 Hz, 24H, CH_3); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm) 161.0, 155.7, 144.0, 138.5, 135.7, 131.6, 130.8, 129.6, 122.8, 121.2, 121.1, 114.3, 114.1, 29.7, 25.2, 18.4, 16.5, 12.8, 10.1; MALDI-TOF calcd. 2704.5, found 2704.3 [$(M)^+$]; UV/Vis ($CHCl_3$) λ_{max} nm (logε): 620.0 (5.44) and 657.0 (5.42).

hexagon (11): Yield: 1.6 mg (2.4%); ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 6.95 (dd, J = 8.5 and 5.6 Hz, 24H, Ar-H), 6.79 (s, 12H, *meso*-H), 6.57 (t, J = 8.5 Hz, 24H, Ar-H), 2.69 (q, J = 7.0 Hz, 24H, CH_2), 2.32 (s, 36H, CH_3), 1.98 (s, 36H, CH_3), 1.86 (s, 24H, CH_2), 1.19 (t, J = 7.6 Hz, 36H, CH_3); MALDI-TOF calcd. 4056.8, found 4056.4 [$(M)^+$]; UV/Vis ($CHCl_3$) λ_{max} nm (logε): 618.0 (5.59) and 655.0 (5.58).

Intermolecular CH/π interactions and fluorine-fluorine interaction for hexagon 11

Three types of noncovalent interactions can be observed involving the α'-4-fluorophenyl groups from three neighbouring molecules in the same layer. Type A and B are both intermolecular CH/π interactions, and CH···centroid distances are 3.4 and 3.3 Å, respectively. By contrast, type C is the fluorine-fluorine interation with F-F distance of 3.6 Å (Fig.1).[6] Due to its S_6 symmetry, another five interaction subunits exist for each molecule. Consequently, all the α'-4-fluorophenyl rings in one molecule are involved in at least one type of interaction. In addition, another fluorine-fluorine interaction can be detected between the neighbouring molecules belonging to the adjacent layers with F-F distance of 4.1 Å (Fig. 2). Therefore, in total six F-F interactions can be found between one molecule in the middle layer and the six surrounding molecules (three are in the upper layer while three in lower layer). Generation of the channel structure may receive considerable contributions from sum of the aforementioned intermolecular noncovalent interactions.

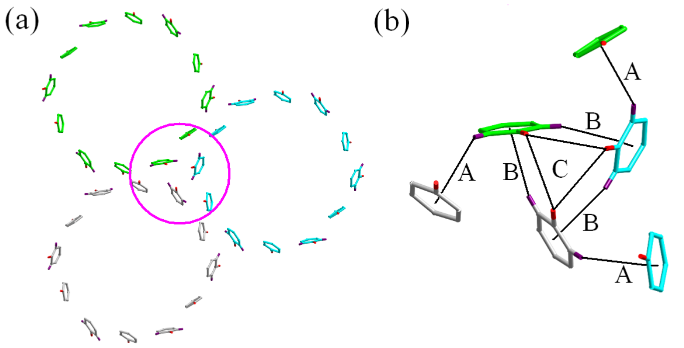


Fig. 1 Packing of hexagon **11** only phenyl rings in one layer: (a) top view; (b) three types (A to C) of noncovalent interactions showed in an enlarged interaction subunit (F in violet and H in red).

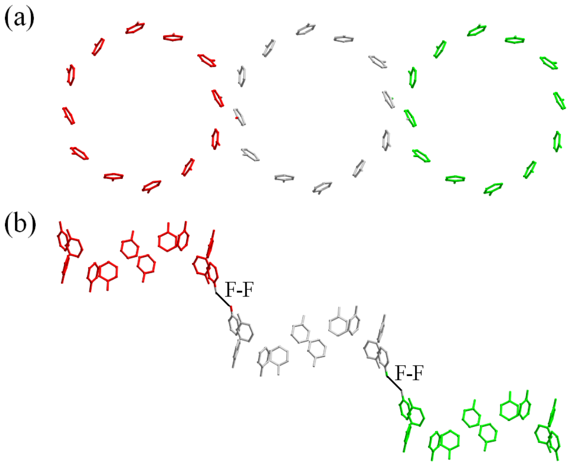
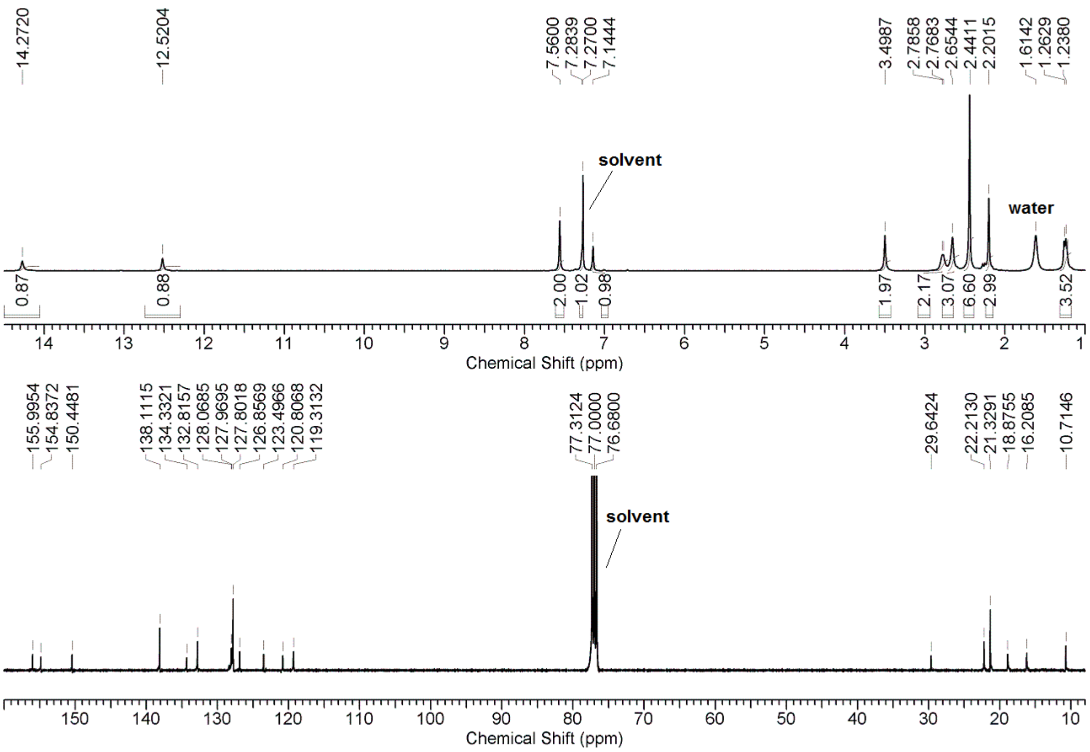


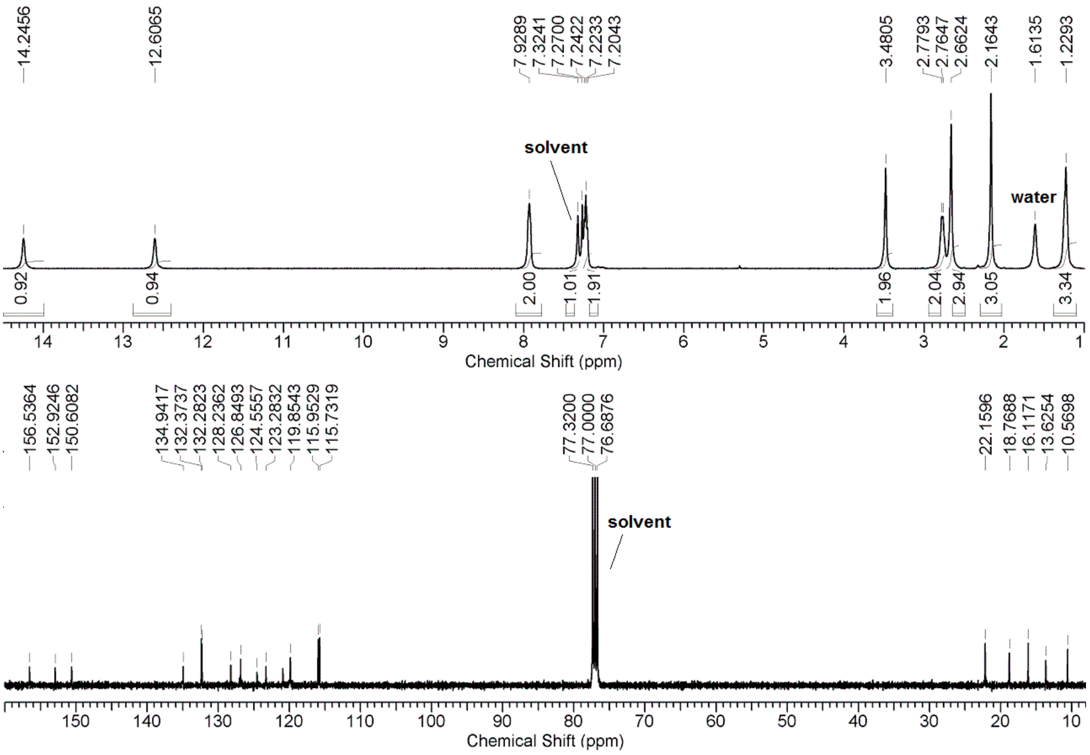
Fig. 2 Packing of hexagon **11** with only phenyl rings in three consecutive layers: (a) top view and (b) side view with F-F interactions displayed. H atoms are omitted for clarity.

^{1}H NMR and ^{13}C NMR spectra of ligand 6-7 and complex 8-11:

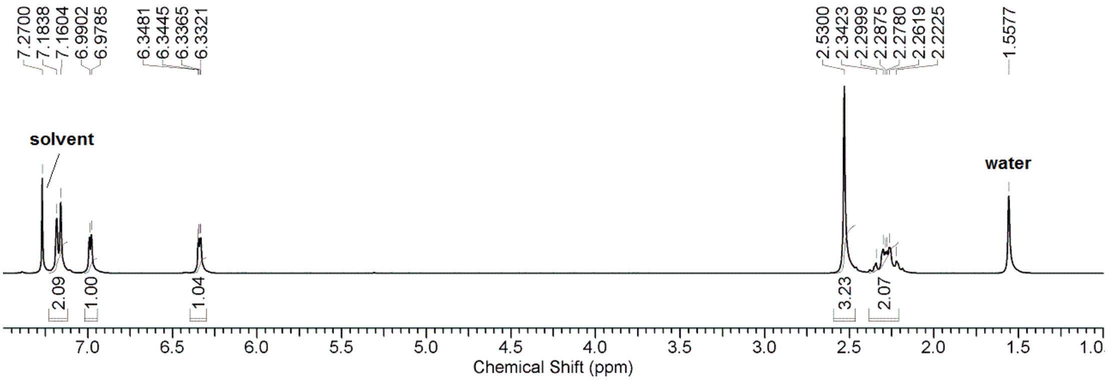
^{1}H NMR and ^{13}C NMR spectra of ligand **6**

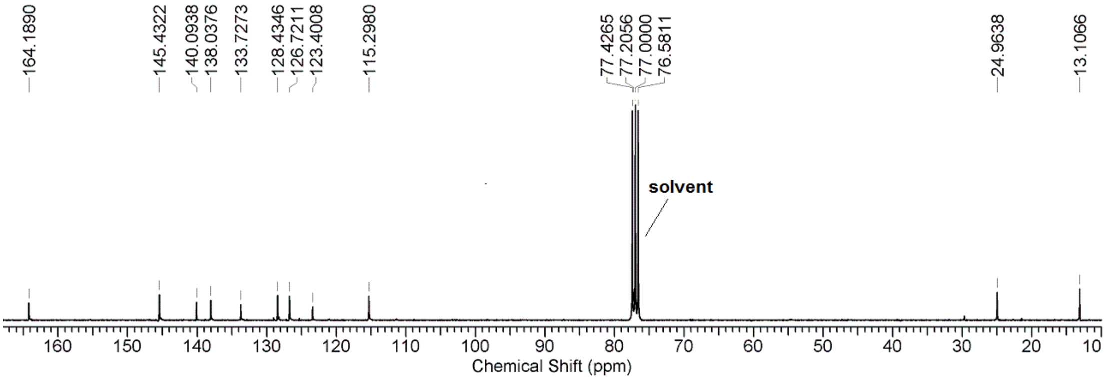


^{1}H NMR and ^{13}C NMR spectra of ligand **7**

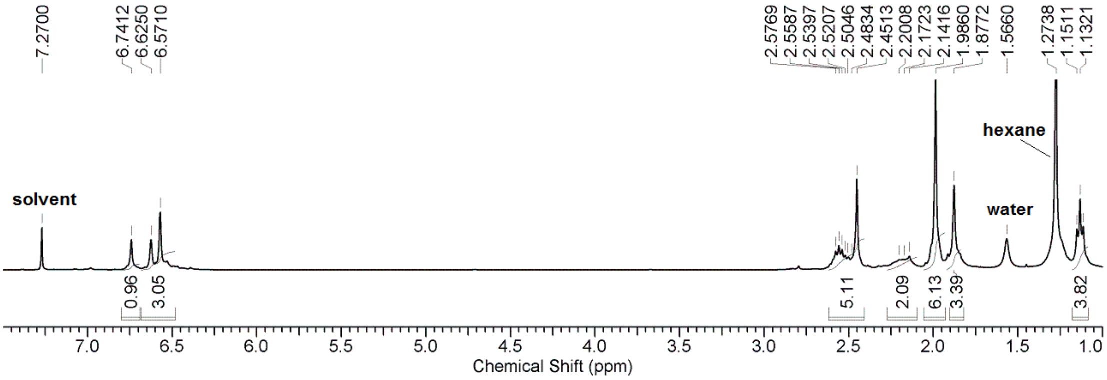


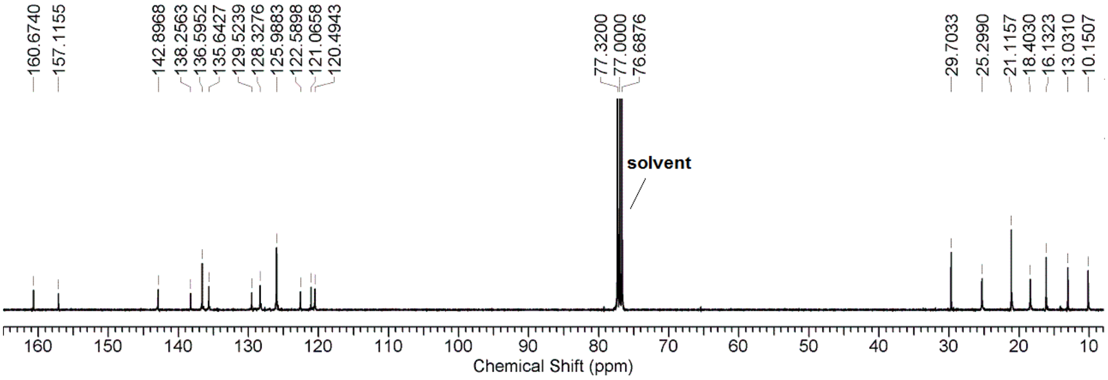
^{1}H NMR and ^{13}C NMR spectra of grid **8**



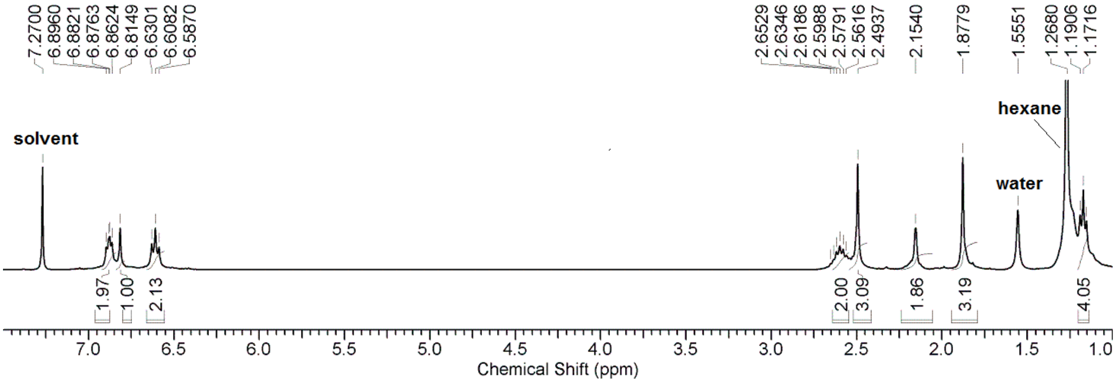


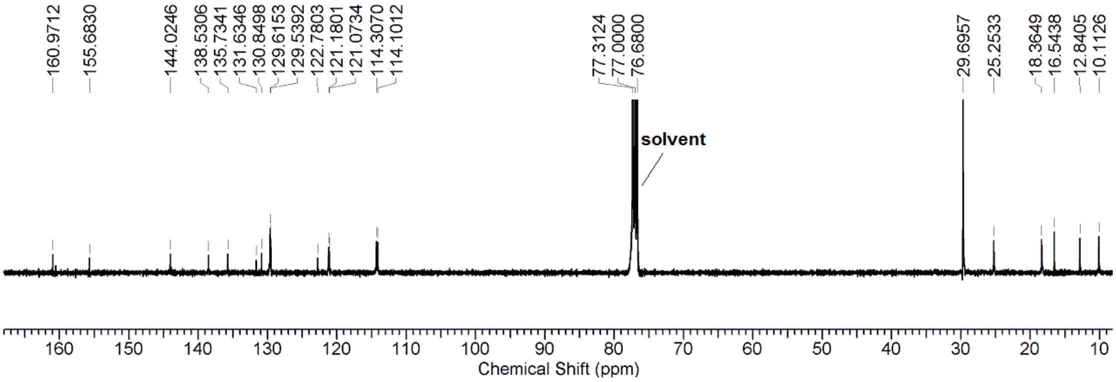
^{1}H NMR and ^{13}C NMR spectra of grid **9**



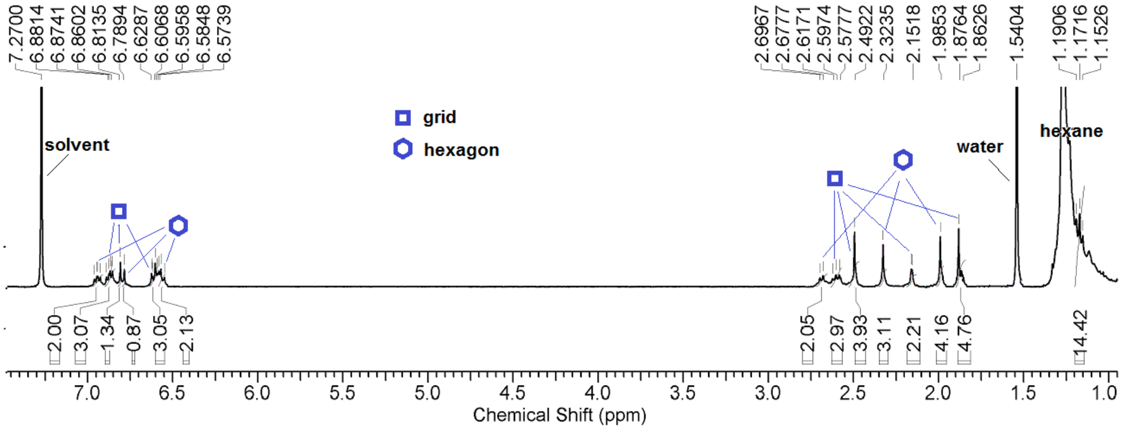


^{1}H NMR and ^{13}C NMR spectra of grid **10**



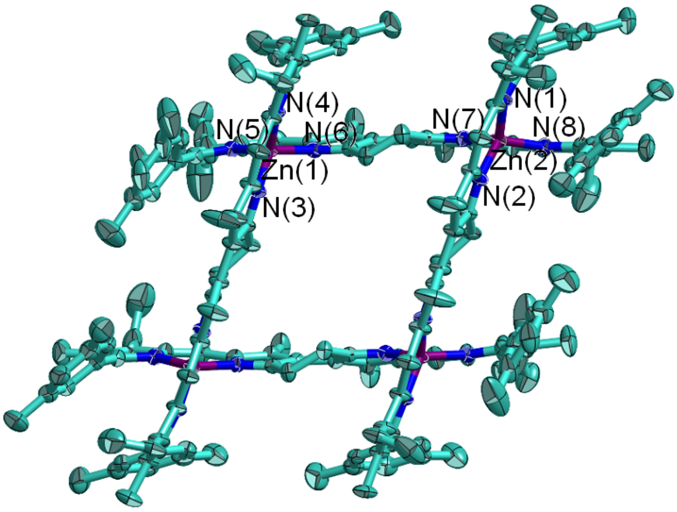


^{1}H NMR spectrum of hexagon **11**



Selected crystal data and details of data collection for 9 and 11:

1. Crystal data for grid 9



Experimental

Data Collection

A green prism crystal of $C_{176}H_{184}N_{16}Zn_4{\cdot}5C_6H_{14}$ having approximate dimensions of 0.40 × 0.44 × 0.55 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of -100.0 $\pm$ 0.1°C to a maximum 2θ value of 55.9°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

Of the 160278 reflections that were collected, 21591 were unique (R_{int} = 0.051); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[7] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.82 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[8]), with minimum and maximum transmission coefficients of 0.682 and 0.792, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[9]. The material crystallizes with one half-molecule related to another by rotation about a two-fold axis. Additionally, the material crystallizes with 2.5 molecules of n-hexane in the asymmetric unit. Two of these hexane molecules were successfully modeled (albeit, with some disorder in one molecule), a third, however, residing in a channel produced by adjacent Zn4 complexes, could not be modeled properly. The PLATON/SQUEEZE[10] program was used to produce a 'solvent-free' data set (at least solvent-free at the site mentioned above). DFIX and SADI constraints were used to maintain reasonable geometries for the remaining disordered solvent fragments (hexane). The final formula includes the missing hexane molecule. For the given disordered hexane, it results overall in slightly less than one molecule since one part of it lies over a symmetry site. Finally, one ethyl substituent was also disordered and was modeled in two orientations. All non-hydrogen atoms except some of those in the disordered n-hexane were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[11] on F^2 was based on 21591 reflections and 1020 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

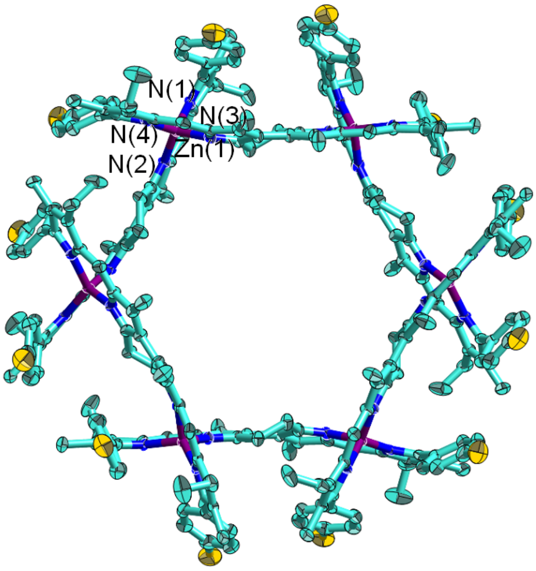
$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.106$$

$$wR2 = [\, \Sigma \, (w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.185$$

The standard deviation of an observation of unit weight[12] was 1.12. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.85 and –0.39 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[13]. Anomalous dispersion effects were included in Fcalc[14]; the values for Δf' and Δf" were those of Creagh and McAuley[15]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[16]. All refinements were performed using the SHELXTL[17] crystallographic software package of Bruker-AXS.

2. Crystal data for hexagon 11



Experimental

Data Collection

A green tablet crystal of $C_{240}H_{216}N_{24}F_{12}Zn_6 \cdot 3.24CHCl_3$ having approximate dimensions of 0.11 × 0.22 × 0.40 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX II diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of $-170.0 \pm 0.1^{\circ}C$ to a maximum 2θ value of 50.1°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 60.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

Of the 50795 reflections that were collected, 7126 were unique ($R_{int} = 0.046$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[7] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 7.63 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[8]), with minimum and maximum transmission coefficients of 0.800 and 0.921, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[9]. The material crystallizes with one partially occupied site containing chloroform. Refining this molecule's population gave a value of 0.54. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[11] on F^2 was based on 7126 reflections and 467 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.081$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2} = 0.186$$

The standard deviation of an observation of unit weight[12] was 1.09. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.83 and –0.54 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[13]. Anomalous dispersion effects were included in Fcalc[14]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[15]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[16]. All refinements were performed using the SHELXL-97[17] via the WinGX[18] interface.

Table S1. Crystal data and structure refinement for grid **9**

Temperature	-100.0 ± 0.1°C
Empirical Formula	$C_{206}H_{254}N_{16}Zn_4$
Formula Weight	3215.73
Crystal Colour, Habit	green, prism
Crystal Dimensions	0.40 × 0.44 × 0.55 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 24.936(3) Å
	b = 12.9012(17) Å
	c = 28.201(4) Å
	$\alpha = 90.0^{\circ}$
	$\beta = 95.206(6)^{\circ}$
	$\gamma = 90.0^{\circ}$
	V= 9035(2) Å^{3}
Space Group	*P* 2/*n* (#13)
Z value	2
Reflections collected	21591
Independent reflections	12724
Goodness of Fit Indicator	1.07
Final R Indices [$I>2\sigma(I)$]	*R*1 = 0.059, w*R*2 = 0.161
R indices (all data)	*R*1 = 0.106, w*R*2 = 0.185

Table S2. Crystal data and structure refinement for hexagon **11**

Temperature	-170.0 $\pm$ 0.1°C
Empirical Formula	$C_{243.24}H_{219.24}N_{24}F_{12}Cl_{9.72}Zn_6$
Formula Weight	4443.34
Crystal Colour, Habit	green, tablet
Crystal Dimensions	0.11 × 0.22 × 0.40 mm
Crystal System	trigonal
Lattice Type	primitive
Lattice Parameters	a = 24.236(2) Å
	b = 24.236(2) Å
	c = 11.8480(6) Å
	$\alpha = 90.0^{o}$
	$\beta = 90.0^{o}$
	$\gamma = 120.0^{o}$
	V= 6026.8(6) $Å^3$
Space Group	*P* -3 (#147)
Z value	1
Reflections collected	7126
Independent reflections	5647
Goodness of Fit Indicator	1.09
Final R Indices [I>2σ(I)]	*R*1 = 0.062, w*R*2 = 0.171
R indices (all data)	*R*1 = 0.081, w*R*2 = 0.186

Optical properties:

Table S3. Spin-allowed ligand-centered transition band λ_{max1}(nm) and metal-to-ligand charge transfer transition band λ_{max2} (nm) for ligand **6-7** and complex **8-11**

Compound	$\lambda_{max1}/\log\varepsilon_1$	$\boldsymbol{\lambda_{max2}/\log\varepsilon_2}$
ligand **6**	647/5.24	—
ligand **7**	644/5.31	—
grid **8**	575/5.63	613/5.53
grid **9**	625/5.68	661/5.66
grid **10**	620/5.44	657/5.42
hexagon **11**	618/5.59	655/5.58

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11. Least Squares function minimized: $\Sigma w(Fo^2 - Fc^2)^2$
12. Standard deviation of an observation of unit weight: $[\Sigma w(Fo^2 - Fc^2)^2 / (No – Nv)]^{1/2}$

Where: No = number of observations, Nv = number of variables

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