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New three- and four-armed flexible bridging ligands for use in metallosupramolecular chemistry: syntheses and X-ray structures

Justine R.A. Cottam, Peter J. Steel *

Chemistry Department, University of Canterbury, Christchurch, New Zealand

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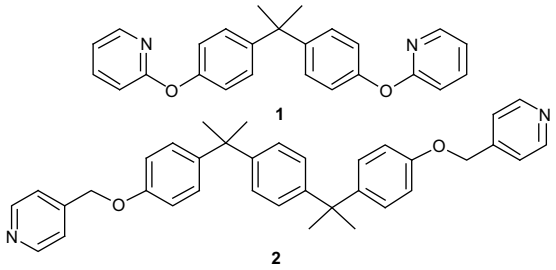
ABSTRACT

Preparations are described of twelve new tritopic and tetratopic ligands by coupling of two phenolic precursors with a range of heterocyclic units. X-ray crystal structures of four representative examples revealed the conformations in the solid state with the nitrogen donor atoms separated by distances ranging from 10.9 to 18.2 Å.

1. Introduction

The term metallosupramolecular chemistry[1,2] is used to describe the use of combinations of bridging organic ligands and metallic reagents for the construction of both discrete and polymeric assemblies with diverse architectures.[3–10] Originally, *rigid* bridging ligands were used for the rational construction of symmetrical polygons (squares, hexagons, etc.) and polyhedra (cubes, octahedra, dodecahedra, etc.). For some time, we have employed many *flexible* ligands that provide access to other less symmetrical topologies (helicates, rectangles, boxes, cages, etc.) that are not available to the more *rigid* ligands.[10] Recently[11] we reported the synthesis of a family of ditopic ligands by coupling commercially available bisphenols with various nitrogen heterocycles. For example, ligands **1** and **2** were made by reactions of bisphenols A and P with 2-bromopyridine and 2-chloromethylpyridine, respectively. By varying the starting bisphenol, the nature of the heterocycle and the presence or otherwise of additional methylene spacer groups, we were able to prepare a range of ligands that hold two metal centres apart by varying distances and use these for the preparation of a range of novel metallosupramolecular assemblies.[12]



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We now extend this design strategy to a range of three- and four-armed ligands derived from two commercially available phenolic precursors. These new ligands are potentially capable of bridging three or four metal centres. The syntheses of twelve such ligands are described along with the crystal structures of four representative examples.

2. Results and discussion

All the ligands were prepared by nucleophilic substitution reactions. Seven three-armed ligands were prepared from precursor **3** by substitutions of appropriate heterocyclic halides (**4**). Thus, compounds **5**–**6** were prepared by nucleophilic aromatic substitution reactions with 2-bromopyridine (**4a**), 2-chloropyrazine (**4b**), 2-chloroquinoline (**4c**) and 2-chloroquinoxaline (**4d**), respectively, (Scheme 1). These reactions were carried out in a refluxing sulpholane/toluene mixture, reaction conditions we have found to be particularly effective for the preparation of related ligands.[11,13] The methylene-expanded ligands **9**–**11** were prepared by phase-transfer-catalysed triple alkylation of **3** using 2-, 3- and 4-chloromethylpyridines (**4e**–**g**). Once again we have used these reaction conditions to prepare many structurally related ligands.[14,15]

The products were isolated by standard procedures and purified by recrystallisation. Isolated yields were generally good and are shown in Scheme 1. The compounds were all characterised by elemental analysis, mass spectrometry, melting point and by ^{1}H and ^{13}C NMR (see Experimental section). Full assignments of the ^{1}H NMR spectra were relatively straightforward, being aided by the symmetrical nature of the compounds. The separate spin systems of the various aromatic rings were readily identified by their integrals and cross-couplings and the individual protons of the heterocycles were assigned from their characteristic chemical shifts, spin–spin coupling and by comparison with the spectra from our own library of structurally related ligands containing these heterocycles.[10]

* Corresponding author. Tel.: +64 3 3642432; fax: +64 3 3642110.
E-mail address: peter.steel@canterbury.ac.nz (P.J. Steel).

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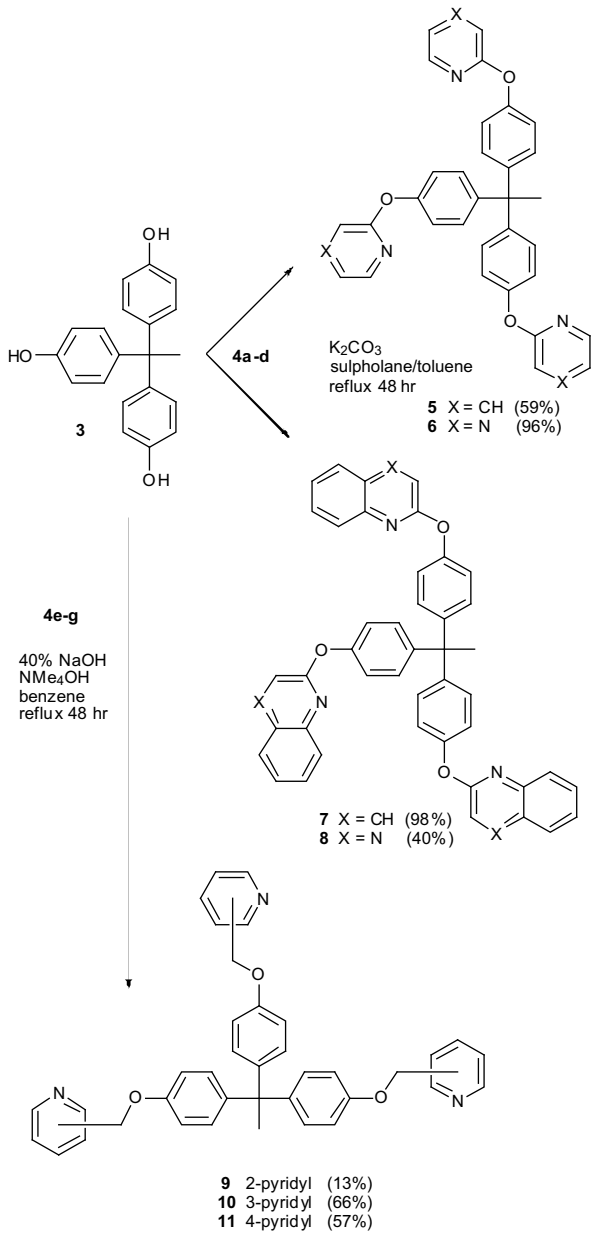


Scheme 1. Preparations of **5**–**11**.

Single crystal X-ray structure determinations were carried out on **5** and **11** to confirm their structures and to determine their conformations in the solid state, in order to gain some insight into the possible mode by which they might act as bridging ligands in supramolecular assemblies.

The X-ray structure of the 2-pyridyl ligand **5** is shown in Figure 1. It crystallises in the hexagonal space group $P6_3$ about a crystallographic threefold rotation axis with one third of the tripodal ligand in the asymmetric unit. The central quaternary carbon, the phenyl ring and the oxygen atom of the ligand are disordered over two sites, with the major component having 75% occupancy. In Figure 1 the minor component having 25% occupancy is not shown.

In the solid state the three benzene rings twist around the tetrahedral quaternary carbon atom in a propeller-like fashion with the methyl substituent pointing outwards. The three pyridine rings are tilted almost perpendicular to the meanplane of the closest benzene ring, with the internal nitrogen donor atoms all pointing inwards towards the centre of the adjacent benzene ring and the centre of the ligand. The distance between the pyridine nitrogen

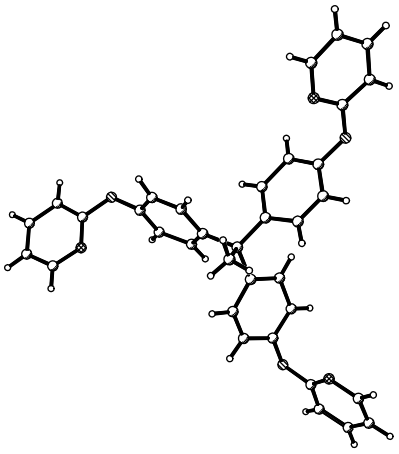


Figure 1. X-ray crystal structure of ligand **5**.

atoms within the ligand is 10.9 Å. In the extended structure there are edge-to-face interactions between aromatic rings as well as C–H···N interactions involving the pyridine rings.

The methylene-expanded 4-pyridyl compound **11** crystallises in the triclinic space group P-1 (Fig. 2). Unlike **5** the asymmetric unit contains one whole ligand molecule and a disordered solvent molecule. The overall structure of ligand **11** is quite similar to that of **5** with the three benzene rings splayed in a propeller-like fashion about the central quaternary carbon atom core. However, each of the binding arms in the ligand adopts a different conformation. In two of the ligand arms, the pyridine rings lie almost perpendicular to the meanplanes of their adjacent benzene ring, whereas in the third ligand arm the pyridine and benzene ring lie approximately coplanar with one another. This destroys any potential higher internal symmetry. The two-atom methyleneoxy spacer groups all adopt a trans-periplanar arrangement, which is reflected in the C–C–O–C torsional angles of 165.6, 176.4 and 178.4°. Due to the incorporation of a 4-pyridyl group rather than 2-pyridyl, and the additional methylene spacer groups, the distances between the potentially coordinating nitrogen atoms are expanded to 16.8, 17.2 and 18.2 Å.

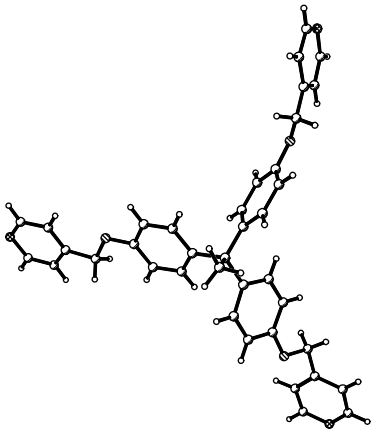
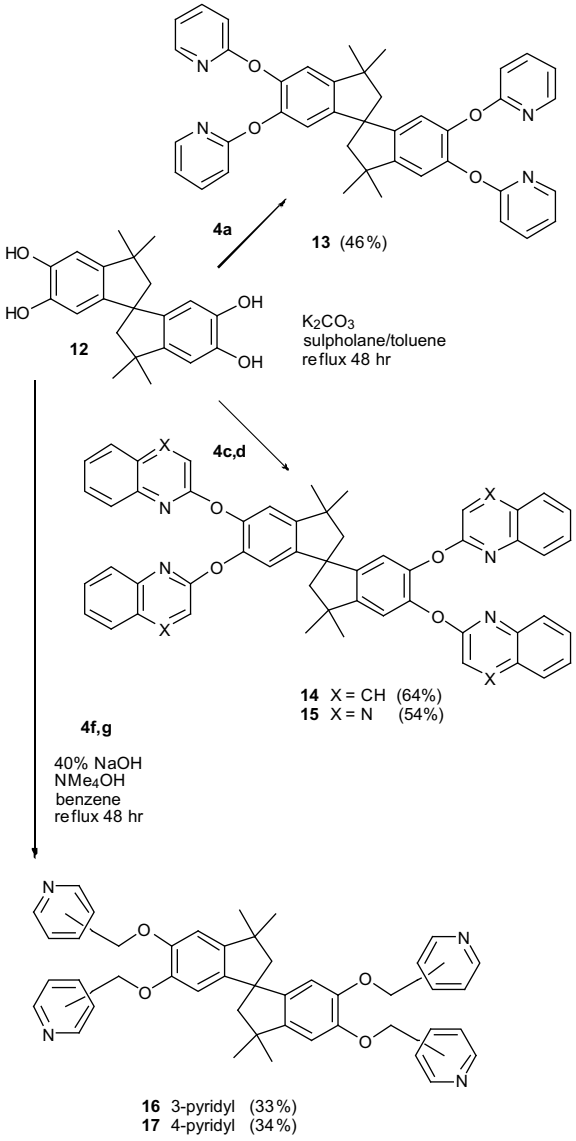


Figure 2. X-ray crystal structure of **11**.

We next turned our attention to the synthesis of new four-armed ligands and for this purpose employed the commercially available 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′,6,6′-tetrol (**12**) as the phenolic component. This was reacted with the seven halides **4** in the hope of making seven new four-armed ligands. In the event, only five of these reactions were successful (Scheme 2). The three potential ligands **13**–**15** have a single oxygen atom spacer

between the two components, whereas ligands **16** and **17** have two-atom spacer units. Curiously, reactions of **4** with 2-chloropyrazine (**4b**) and 2-chloromethylpyridine (**4e**) returned only the starting materials and failed to produce the desired products.



Scheme 2. Preparations of **13**–**17**.

These new ligands differ from the others in the series in two respects. Firstly, these ligands are inherently chiral, although we have prepared racemic mixtures of the ligands. Secondly, the ligands have reduced symmetry relative to the other ligands we have used. Although they all have twofold rotation axes that relate the two halves of the ligand, the two heterocyclic rings within each half are not symmetry related and are therefore in different environments. We have previously discussed the problems associated with using such ligands in supramolecular chemistry[10] and this is probably why we have found that these ligands are less useful as bridging ligands.[12]

Once again the crystal structures of two representative examples were determined. The 2-pyridyl ligand **13** crystallises in the monoclinic space group $P2_1/c$ with a full molecule in the asymmetric unit (Fig. 3). The two catechol ring systems are oriented orthogonal to one another by virtue of the spiro ring junction. The four pyridyl ether arms are all oriented almost perpendicular to the meanplane of their adjacent catechol rings. The orientations of the pyridyl groups are such as to preserve a twofold rotation axis, although this is not crystallographically imposed. There is an intriguing alignment of two of the pyridine rings on opposite halves of the molecules that appears to result from an attractive π–π stacking interaction.

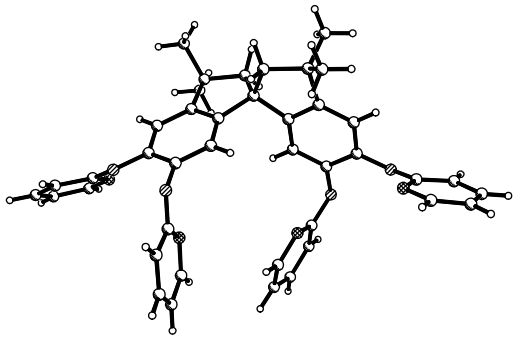


Figure 3. X-ray crystal structure of **13**.

The 2-quinolinyl analogue **14** crystallises in the orthorhombic space group Pnn2 with half a molecule in the asymmetric unit (Fig. 4). Thus, in this case the twofold symmetry is crystallographically imposed. As a consequence the pairs of nitrogen donors point in opposite directions, which may have important consequences for the way in which this ligand would bridge metal centres. In this structure the two quinoline rings within each half of the molecule are π–π stacked. In the solid state the two most distant nitrogen donors in **13** and **14** are separated by 11.1 and 11.7 Å, respectively.

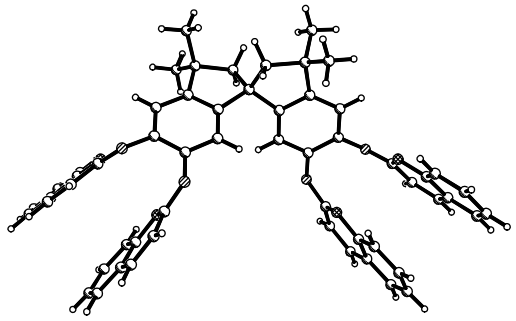


Figure 4. X-ray crystal structure of **14**.

3. Conclusion

The preparations of twelve new bridging ligands from two commercially available phenolic precursors, by coupling each with heterocyclic units, have been described. X-ray crystal structures of four representative examples revealed different conformations in the solid state with the terminal nitrogen donors being separated by distances ranging from 10.9 to 18.2 Å. Due to the flexible nature of these ligands, it is reasonable to speculate that they will adopt different conformations when bound to metals in their transition metal complexes. Nevertheless, the distances spanned by their bridging cores should remain constant. Metallosupramolecular assemblies derived from some of these ligands will be described elsewhere.

We believe that these compounds represent useful new additions to the library of multi-armed ligands that are presently available. Their inherent flexibility could conceivably provide access to topological assemblies not accessible to more established bridging ligands. Conventional three-armed ligands tend to be either planar, such as 2,4,6-tri(4-pyridyl)triazine, used to great effect

by Fujita and co-workers,[16] or tripodal, such as the tren-based ligands recently reviewed by Blackman.[17] Similarly, four-armed bridging ligands are usually classified as tetrahedral, such as tetra-(4-pyridyl)methane,[18] planar, such as tetra(4-pyridyl)porphyrins,[19] or based on rigid scaffolds such as calixarenes and cavitands.[20]

4. Experimental

4.1. General experimental

^{1}H NMR spectra were recorded on Varian Unity 300 or Varian 500 spectrometers at 23 °C with a 3 mm probe operating at 300 MHz or 500 MHz. Spectra were recorded in $CDCl_3$ and referenced relative to the internal standard Me_4Si. ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer operating at 75 MHz and referenced against the solvent signal at 77.10 ppm. Electrospray (ES) mass spectra were recorded using a Micromass LCT-TOF mass spectrometer, with a probe operating at 3200 V and a cone voltage of 30 V. Samples were dissolved in 1:1 acetonitrile/water, and spectra acquired using source and desolvation temperatures of 80 °C and 150 °C, respectively. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell microanalytical laboratory, University of Otago, Dunedin.

Unless otherwise stated, reagents were obtained from commercial sources and used as supplied. Solvents were purified by standard literature procedures and freshly distilled as required. 2-Chloroquinoxaline **6d** was prepared by a literature procedure.[21]

4.2. General reaction procedures

4.2.1. Method A. A mixture of **3** or **12** (1 equiv) and potassium carbonate (7 equiv) was stirred in a solution of sulpholane/toluene (10 ml:5 ml) at room temperature under argon for 45 min. The haloazine **4a–d** (3 or 4 equiv) was added and the mixture was heated to reflux at ~180 °C under argon for 48 h. The resulting mixture was poured into a solution of 7% aqueous sodium hydroxide solution (~30 ml). This was then extracted with chloroform and the extracts were combined and reduced in vacuo to give the crude product in a sulpholane solution. This was added to acetone, heated, treated with decolourising charcoal and filtered. The acetone was removed in vacuo to give the product in a saturated sulpholane solution. Just enough water was added to precipitate the crude product, which was then recrystallised from acetone/water solution to give the pure product. Typically, these reactions were carried out on a scale that delivered 1–2 g of purified ligand.

4.2.2. Method B. A mixture of **3** or **12** (1 equiv), the appropriate chloromethylpyridine/HCl **4e–g** (3 or 4 equiv), 40% aqueous tetrabutylammonium hydroxide (6 drops), 40% aqueous sodium hydroxide (7 ml) and benzene (25 ml) was refluxed (~80 °C) for 48 h. The organic layer was then separated, dried over Na_2SO_4 and concentrated in vacuo to give a crude solid or oil, which was then purified by recrystallisation. Again, reaction scales were such as to furnish 1–2 g of purified ligand.

4.3. Physical and spectral properties

*4.3.1. Compound **5**.* Method A from **3** and **4a**. Pale yellow solid. Yield 59%. Mp 152–155 °C. Anal. Found: C, 78.14; H, 5.21; N, 7.70. Calcd for $C_{35}H_{27}N_3O_3$: C, 78.19; H, 5.06; N, 7.82. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.19 (3H, d, H6′), 7.64 (3H, t, H4′), 7.17 (6H, d, H3, H5), 7.05 (6H, d, H2, H6), 6.96 (3H, t, H5′), 6.89 (3H, d, H3′), 2.19 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.47, 152.30, 147.68, 144.93, 139.43, 129.94, 120.05, 118.49, 111.64, 51.43, 30.76. ESI-MS: Found MH^+=538.2141; $C_{35}H_{28}N_3O_3$ requires MH^+=538.2131.

*4.3.2. Compound **6**.* Method A from **3** and **4b**. White crystalline solid. Yield 96%. Mp 178.5 °C. Anal. Found: C, 71.16; H, 4.51; N, 15.36. Calcd for $C_{32}H_{24}N_6O_3$: C, 71.10; H, 4.47; N, 15.55. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.42 (3H, s, H3′), 8.28 (3H, s, H6′), 8.27 (3H, s, H5′), 7.21 (6H, d, H3, H5), 7.10 (6H, d, H2, H6), 2.24 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.92, 151.25, 145.51, 141.04, 138.48, 135.89, 129.99, 120.33, 51.54, 30.74. ESI-MS: Found MH^+=541.1966; $C_{32}H_{25}N_3O_3$ requires MH^+=541.1988.

*4.3.3. Compound **7**.* Method A from **3** and **4c**. Yellow crystalline solid. Yield 98%. Mp 170 °C. Anal. Found: C, 80.03; H, 5.26; N, 5.72. Calcd for $C_{47}H_{33}N_3O_3\cdot H_2O$: C, 79.98; H, 5.00; N, 5.95. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.12 (3H, d, H4′), 7.83 (3H, d, H8′), 7.74 (3H, d, H5′), 7.61 (3H, t, H7′), 7.43 (3H, t, H6′), 7.26 (12H, m, H2, H3, H5, H6), 7.08 (3H, d, H3′), 2.28 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.49, 152.00, 146.35, 145.23, 139.82, 129.88, 129.80, 127.85, 127.33, 125.66, 124.86, 120.45, 112.73, 51.59, 30.91. ESI-MS: Found MH^+=688.2609; $C_{47}H_{34}N_3O_3$ requires MH^+=688.2600.

*4.3.4. Compound **8**.* Method A from **3** and **4d**. Yellow solid. Yield 40%. Mp 160 °C. Anal. Found: C, 73.60; H, 4.64; N, 11.13. Calcd for $C_{44}H_{30}N_6O_3\cdot 1^1/_2\ H_2O$: C, 73.63; H, 4.63; N, 11.71. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.70 (3H, s, H3′), 8.06 (3H, d, H8′), 7.81 (3H, d, H5′), 7.65 (6H, m, H6′, H7′), 7.28 (12H, m, H2, H3, H5, H6), 2.33 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.75, 151.05, 145.74, 139.95, 139.58, 139.23, 130.41, 129.96, 128.90, 127.72, 127.50, 120.60, 51.73, 30.92. ESI-MS: Found MH^+=691.2489; $C_{44}H_{31}N_6O_3$ requires MH^+=691.2458.

*4.3.5. Compound **9**.* Method B from **3** and **4e**. White crystalline solid. Yield 13%. Mp 92 °C. Anal. Found: C, 78.91; H, 5.73; N, 7.15. Calcd for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5.74; N, 7.25. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.58 (3H, d, H6′), 7.72 (3H, t, H4′), 7.68 (3H, d, H3′), 7.23 (3H, m, H5′), 6.99 (6H, d, H3, H5), 6.89 (6H, d, H2, H6), 5.17 (6H, s, CH_2), 2.10 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.29, 156.36, 149.05, 142.07, 136.74, 129.59, 122.49, 121.17, 113.89, 70.49, 50.55, 30.64. ESI-MS: Found MH^+=580.2596; $C_{38}H_{34}N_3O_3$ requires MH^+=580.2600.

*4.3.6. Compound **10**.* Method B from **3** and **4f**. Orange solid. Yield 66%. Mp 133 °C. Anal. Found: C, 78.46; H, 5.78; N, 7.20. Calcd for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5.74; N, 7.25. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.67 (3H, s, H2′), 8.58 (3H, d, H6′), 7.77 (3H, d, H4′), 7.32 (3H, m, H5′), 7.02 (6H, d, H3, H5), 6.87 (6H, d, H2, H6), 5.05 (6H, s, CH_2), 2.11 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.41, 149.32, 148.90, 142.24, 135.30, 132.57, 129.66, 123.48, 113.93, 67.45, 50.64, 30.71. ESI-MS: Found MH^+=580.2591; $C_{38}H_{34}N_3O_3$ requires MH^+=580.2600.

*4.3.7. Compound **11**.* Method B from **3** and **4g**. Orange solid. Yield 57%. Mp 135 °C. Anal. Found: C, 78.47; H, 5.85; N, 7.39. Calcd for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5.74; N, 7.25. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.60 (6H, d, H2′, H6'), 7.33 (6H, m, H3′, H5'), 7.00 (6H, d, H3, H5), 6.84 (6H, d, H2, H6), 5.04 (6H, s, CH_2), 2.10 (3H, s, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.22, 149.88, 146.31, 142.30, 129.68, 121.48, 113.95, 68.08, 50.64, 30.69. ESI-MS: Found MH^+=580.2592; $C_{38}H_{34}N_3O_3$ requires MH^+=580.2600.

*4.3.8. Compound **13**.* Method A from **12** and **4a**. White crystalline solid. Yield 46%. Mp 169–171 °C. Anal. Found: C, 75.75; H, 5.47; N, 8.63. Calcd for $C_{41}H_{36}N_4O_4$: C, 75.91; H, 5.59; N, 8.64. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.08, 8.00 (4H, d, H6′, H6″), 7.53, 7.02 (4H, t, H4′, H4″), 7.02 (2H, s, H4), 6.87, 6.83 (4H, t, H5′, H5″), 6.81 (2H, s, H7), 6.68, 6.62 (4H, d, H3′, H3″), 2.44 (2H, d, H2a), 2.38 (2H, d, H2b), 1.38 (6H, s, H8), 1.37 (6H, s, H9). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.19,

Table 1
Crystal data and X-ray experimental details

Compound	**5**	**11**	**13**	**14**
Empirical formula	$C_{35}H_{27}N_3O_3$	$C_{39}H_{33}N_3O_3$	$C_{41}H_{36}N_4O_4$	$C_{57}H_{44}N_4O_4$
Formula weight	537.60	591.68	648.74	848.96
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Hexagonal	Triclinic	Monoclinic	Orthorhombic
Space group	$P6_3$	P-1	$P2_1/c$	Pnn2
Unit cell dimensions				
a (Å)	14.0521(3)	6.7134(4)	16.6512(5)	11.1349(3)
b (Å)	14.0521(3)	13.0108(9)	10.3247(3)	18.1266(4)
c (Å)	8.1827(5)	19.2362(16)	21.1705(5)	11.1145(2)
α (°)	90	109.752(2)	90	90
β (°)	90	94.467(3)	112.797(1)	90
γ (°)	120	96.779(2)	90	90
Volume (Å^3)	1399.3(1)	1557.8(2)	3355.3(2)	2243.33(9)
Z	2	2	4	2
Density (calculated) (mg/m^3)	1.276	1.261	1.284	1.257
Absorption coefficient (mm^{-1})	0.082	0.080	0.084	0.079
F(000)	564	624	1368	892
Crystal size (mm^3)	0.70×0.25×0.05	0.62×0.17×0.04	0.45×0.35×0.10	0.45×0.43×0.08
Theta range for data collection (°)	2.90–27.45	1.13–25.05	2.38–25.05	2.59–25.05
Reflections collected	20,714	14,729	51,569	23,598
Independent reflections [*R*(int)]	1141 [0.0845]	5491 [0.0426]	5942 [0.0414]	2106 [0.0491]
Data/restraints/parameters	1141/1/167	5491/0/417	5942/0/442	2106/1/294
Goodness-of-fit on F^2	1.028	1.114	1.043	1.048
R_1 [$I>2\sigma(I)$]	0.0430	0.0553	0.0447	0.0261
wR_2 (all data)	0.1168	0.1517	0.1163	0.0683

163.13, 149.51, 147.35, 147.31, 147.24, 144.97, 144.64, 138.98, 138.89, 119.09, 118.05, 117.91, 116.49, 110.72, 110.47, 59.39, 57.37, 43.40, 31.54, 30.18. ESI-MS: Found MH^+=649.2793; $C_{41}H_{37}N_4O_4$ requires MH^+=649.2815.

4.3.9. Compound ***14***. Method A from **12** and **4c**. Yellow solid. Yield 64%. Mp 196–197 °C. Anal. Found: C, 79.82; H, 5.37; N, 6.49. Calcd for $C_{57}H_{44}N_4O_4\cdot{}^1/_2\ H_2O$: C, 79.79; H, 5.29; N, 6.53. ^{1}H NMR (500 MHz, $CHCl_3$): *δ* 8.12, 8.04 (4H, d, H4′, 4H″), 7.91, 7.82 (4H, d, H8′, H8″), 7.62, 7.54 (4H, d, H5′, H5″), 7.47, 7.42 (4H, t, H7′, H7″), 7.32, 7.27 (4H, t, H6′, H6″), 7.18 (2H, s, H4), 7.05 (2H, s, H7), 6.92, 6.87 (4H, d, H3′, H3″), 2.56 (2H, d, H2a), 2.49 (2H, d, H2b), 1.46 (6H, s, H8), 1.44 (6H, s, H9). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 161.88, 161.18, 149.47, 147.30, 146.11, 146.06, 144.90, 144.58, 139.28, 139.18, 129.36, 127.61, 127.58, 127.06, 127.02, 125.47, 125.41, 124.43, 124.31, 119.54, 116.76, 112.12, 111.88, 59.50, 57.49, 51.08, 43.51, 31.59, 30.26. ESI-MS: Found MH^+=849.3450; $C_{57}H_{45}N_4O_4$ requires MH^+=849.3441.

4.3.10. Compound ***15***. Method A from **12** and **4d**. Yellow solid. Yield 54%. Mp 244–245 °C. Anal. Found: C, 72.84; H, 4.68; N, 12.69. Calcd for $C_{53}H_{40}N_8O_4.H_2O$: C, 73.09; H, 4.86; N, 12.87. ^{1}H NMR (500 MHz, $CHCl_3$): *δ* 8.46, 8.38 (4H, s, H3′, H3″), 7.94, 7.86 (4H, d, H8′, H8″), 7.52, 7.50 (4H, d, H5′, H5″), 7.45, 7.38 (6H, m, H6′, H6″, H7′, H7″), 7.23 (2H, s, H4), 7.13 (2H, s, H7), 2.60 (2H, d, H2a), 2.53 (2H, d, H2b), 1.50 (6H, s, H8), 1.48 (6H, s, H9). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 156.17, 150.30, 147.87, 143.81, 143.44, 139.71, 139.64, 139.49, 139.42, 138.31, 138.14, 130.15, 130.08, 128.74, 128.63, 127.38, 127.35, 127.20, 119.64, 116.83, 104.68, 59.37, 57.57, 51.10, 43.68, 31.55, 30.19. ESI-MS: Found MH^+=853.3275; $C_{53}H_{41}N_8O_4$ requires MH^+=853.3251.

4.3.11. Compound ***16***. Method B from **12** and **4f**. White solid. Yield 33%. Mp 104–105 °C. Anal. Found: C, 74.44; H, 6.27; N, 7.44. Calcd for $C_{45}H_{44}N_4O_4\cdot H_2O$: C, 74.44; H, 6.41; N, 7.75. ^{1}H NMR (500 MHz, $CHCl_3$): *δ* 8.68, 8.58 (4H, d, H2′, H2″), 8.56, 8.50 (4H, d, H6′, H6″), 7.80, 7.70 (4H, d, H4′, H4″), 6.78 (2H, s, H4), 6.37 (2H, s, H7), 5.15, 4.96 (8H, s, H7′, H7″), 2.31 (2H, d, H2a), 2.15 (2H, d, H2b), 1.33 (6H, s, H8), 1.30 (6H, s, H9). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 149.33, 149.22, 148.93, 148.46, 148.31, 145.63, 143.28, 135.34, 135.33, 132.81, 132.68, 123.47, 123.35, 110.88, 108.78, 69.27, 69.15, 59.37, 57.40, 43.25, 31.50, 30.35. ESI-MS: Found MH^+=705.3446; $C_{45}H_{45}N_4O_4$ requires MH^+=705.3441.

4.3.12. Compound ***17***. Method B from **12** and **4g**. Yellow solid. Yield 34%. Mp 98 °C. Anal. Found: C, 74.99; H, 6.66; N, 6.47. Calcd for $C_{45}H_{44}N_4O_2\cdot{}^1/_2$ EtOAc: C, 75.38; H, 6.46; N, 7.48. ^{1}H NMR (500 MHz, $CHCl_3$): *δ* 8.61, 8.54 (8H, d, H2′, H2″, H6′, H6″), 7.42, 7.32 (8H, d, H3′, H3″, H5′, H5″), 6.75 (2H, s, H4), 6.33 (2H, s, H7), 5.18, 4.97 (8H, s, H7′, H7″), 2.30 (2H, d, H2a), 2.04 (2H, d, H2b), 1.31 (6H, s, H8), 1.29 (6H, s, H9). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 149.66, 149.54, 148.20, 148.03, 146.69, 146.55, 145.66, 143.16, 121.56, 110.39, 108.32, 69.67, 69.56, 59.32, 57.41, 43.24, 31.55, 31.43, 30.32. ESI-MS: Found MH^+=705.3471; $C_{45}H_{45}N_4O_4$ requires MH^+=705.3441.

4.4. Crystallography

Crystal data and experimental details of the data collections and structure refinements are listed in Table 1. Data were collected with a APEX CCD area detector, using graphite monochromatised Mo Kα radiation (*λ*=0.71073 Å). Almost complete spheres of data were collected. The structures were solved by direct methods using SHELXS,[22] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[23] Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 728092–728095). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

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