# New Ditopic and Tripodal 1,2,4-Triazole- and Tetrazole-Based Ligands for Coordination Chemistry

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*Received 12 October 2005; revised 15 December 2005*

**Abstract:** The practical synthesis of two new classes of polytopic azole-based ligands is reported. The synthesis of the precursor amines was achieved by substitution of a leaving group by an azide followed by reduction with triphenylphosphine and water. Another efficient method employs a Mitsunobu coupling with phthalimide allowing the conversion of a primary alcohol into a primary amine. The triazole and tetrazole were obtained by cyclization of these amine precursors. The first family consisted of ditopic ligands containing both 1-R-tetrazole and 4-R-1,2,4-triazole moieties linked by an alkyl spacer, while the second consists of branched ligands with three azole cycles linked to a benzene core through ether bonds. Both classes are suitable for building multidimensional polynuclear coordination assemblies and for the observation of thermal spin state crossover behavior with iron(II) ions.

**Key words:** ligands, heterocycles, Mitsunobu reaction, coordination chemistry

For years azole-based compounds have been of interest due to their application in medicinal chemistry.[1] They have also found application in many other important areas as fungicides,[1] color photography couplers,[2] plant growth regulators,[3] high energy density materials,[4] and herbicides and pesticides.[5,6] They have gained additional interest due to their use in coordination chemistry[7,8] with transition metals as molecular magnetic materials[8–10] and dye-molecules in regenerative solar cells.[11] More recently, the ability of ligands containing several azole moieties to build extended networks dragged these molecules into the field of coordination polymers.[12] Indeed, the octahedral coordination which can be assumed for many transition metals can arrange the bridging polycyclic azole ligands along three directions allowing the building of a 3-D molecular network (Figure 1).

This ability together with the occurrence of a spin crossover (SCO) for iron(II) azole coordination compounds made this class of ligands very attractive.[13] Indeed, the spin state of these materials can be switched by various external stimuli providing a basis for their potential use in display and memory devices.[14] This kind of arrangement was first reported for the model SCO coordination polymer tris(4,4′-bis-1,2,4-triazole)iron(II) diperchlorate.[15]

**SYNTHESIS** 2006, No. 9, pp 1504–1512
Advanced online publication: 11.04.2006
DOI: 10.1055/s-2006-926439; Art ID: T14205SS


The coordination chemistry of α,ω-bis(tetrazol-1-yl)alkanes and α,ω-bis(1,2,4-triazol-4-yl)alkanes is currently under investigation. Many of these ligands lead to multidimensional polynuclear assemblies when they are coordinated to transition metals of the first transition series (3d row).[16–19] Some of the iron(II) complexes with such ligands exhibit a SCO behavior on cooling to liquid nitrogen temperature.[12,16,18] These SCO properties vary depending both on the length and on the molecular arrangement of the spacer.

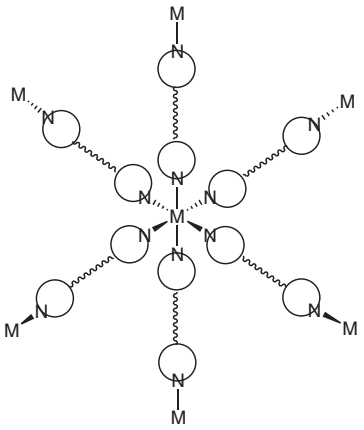



**Figure 1** Schematic view of a 3-D network made of polycyclic azoles linking together $3d^n$ transition metals

In the present work, the practical synthesis of novel mixed and branched 1,2,4-triazole and tetrazole ligands is reported (Schemes 1 and 2). The mixed ligands **a** contain both tetrazole and triazole rings linked by a flexible spacer while the branched ligands **d** and **e** are made of three azoles attached to a benzene core through an ether bond. Molecules **a** represent a new class of ditopic ligands, which may combine the coordinating properties of triazole and tetrazole. Up to now, only one example of a molecule containing both a 1-R-tetrazole and a 4-R-1,2,4-triazole has been reported, which was a tetrazole directly grafted onto a triazole but its synthesis could not be reproduced in our laboratory following the procedure given by Gaponik et al.[20] Only a few iron(II) complexes with tripodal azole ligands have been reported.[21–24] All the available crystal structures reveal mononuclear coordination compounds. These tripodal ligands, however, appear to be

suitable for promoting steep SCO behaviors. The target ligands **d** and **e** differ from the previously reported tripodal azole both by the nature of the core and the spacer, which links it to the heterocycles.

Since the alkylation of 1-*H*-1,2,4-triazole and 1-*H*-tetrazole in basic conditions leads mainly to 1-R-1,2,4-triazole and 2-R-tetrazole respectively,[25] the cyclization of the desired azole on a primary amine had to be considered as a general strategy. These cyclizations are extensively used nowadays as a common procedure for the synthesis of 4-R-1,2,4-triazole[5] and 1-R-tetrazole.[26] Therefore, two disconnections may be proposed for the synthesis of the target molecules **a** (Scheme 1). Route **A** involves the synthesis of 1-[ω-aminoalkyl]tetrazole **b**, followed by the cyclization of the 1,2,4-triazole; while path **B** requires the synthesis of 4-(ω-aminoalkyl)-1,2,4-triazole **c**. These two disconnections require starting from a primary alkylamine bearing a protected amine or a group, which may be easily converted into a primary amine, in the ω position. The protecting group chosen must be stable under the acidic conditions required for the synthesis of tetrazoles, as well resistant to hydrazine used for the preparation of triazoles.

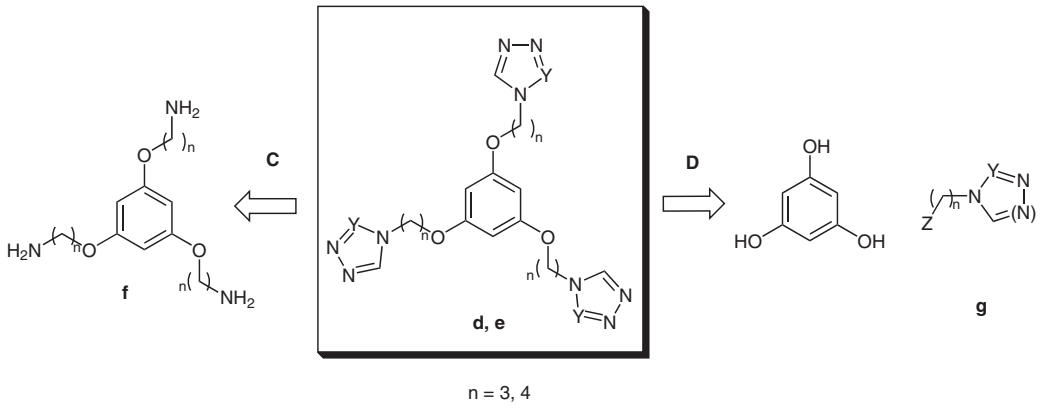

**Scheme 1** Retrosynthetic pathways for obtaining 1-(ω-[1,2,4]triazol-4-yl-alkyl)tetrazole **a**

The tripodal azoles **d** and **e** may be synthesized using either a divergent or a convergent approach (Scheme 2). The divergent approach requires the synthesis of the triamine **f** from the benzene core, as functionalization of the triamine would furnish the required azoles. Alternatively, the convergent pathway involves the grafting of the branch **g** onto the phloroglucinol core. Therefore, the end group of the alkyl branch (*Z*) must have the potential to undergo nucleophilic substitution.

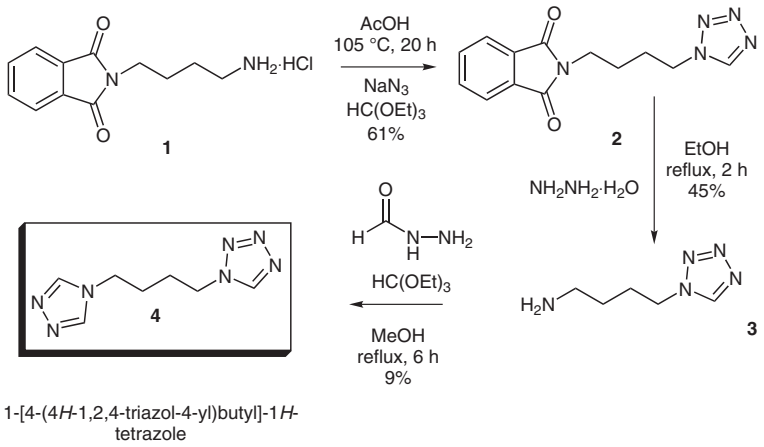
Our initial approach involved the synthesis of **a** through the disconnection **A** (Scheme 3). A convenient way to intermediate **b** is to start from a monoprotected α,ω-bisaminoalkane. Thus, *N*-(4-aminobutyl)phthalimide hydrochloride (**1**) was prepared from the commercially available *N*-(4-bromobutyl)phthalimide, according to a described procedure: the bromide was substituted by an azide group, which was subsequently reduced under acidic conditions.[27]

Then, the amino group was converted into tetrazole **2** according to a standard procedure using triethylorthoformate and sodium azide in acetic acid.[26] Next, the phthalimide moiety was removed using hydrazine to yield the amine **3**. Finally, we attempted to reach the target compound **4** employing the procedure described by Bayer et al. for the preparation of 4-substituted 1,2,4-triazoles.[5] Unfortunately, despite the fact that a large amount of the cyclized compound could be identified in the crude product, by $^1$H NMR spectroscopy, purification by column chromatography on silica gel did not afford the product **4** in good yield (9%) due to the very high polarity of the 4-R-1,2,4-triazole motif.

Therefore, approach **A** was dismissed because of the loss of yield at the final step, and disconnection **B** was examined (Scheme 1). The synthesis of intermediate **c** was considered starting from the known precursor 4-(3′-hydroxypropyl)-1,2,4,-triazole (**5**, Scheme 4). This was prepared according to the method of Bayer et al.[5] as previously reported.[28] The use of anhydrous conditions and freshly prepared monoformyl hydrazine enabled us to increase the reported yield by ten percent (51% vs 41%). The Mitsunobu coupling[29] of alcohol **5** with phthalimide gave compound **6**, which after deprotection by hydrazine furnished the free amine **7**. The final step leading to the tetrazole compound **8** was carried out using the method of Kamiya et al.[26] The synthesis of **8** through the retrosynthetic path **B** did not require any purification step involving column chromatography. Accordingly, the final product **8** was obtained in good yield (32%). As for the other tetrazole cyclizations described in the text (**2**, **12**, **14**), $^1$H NMR spectroscopy gives evidence of high cy-




**Scheme 2** Divergent **C** and convergent **D** approaches for the synthesis of the target ligands **d** and **e** (Y = CH, **d**; Y = N, **e**)

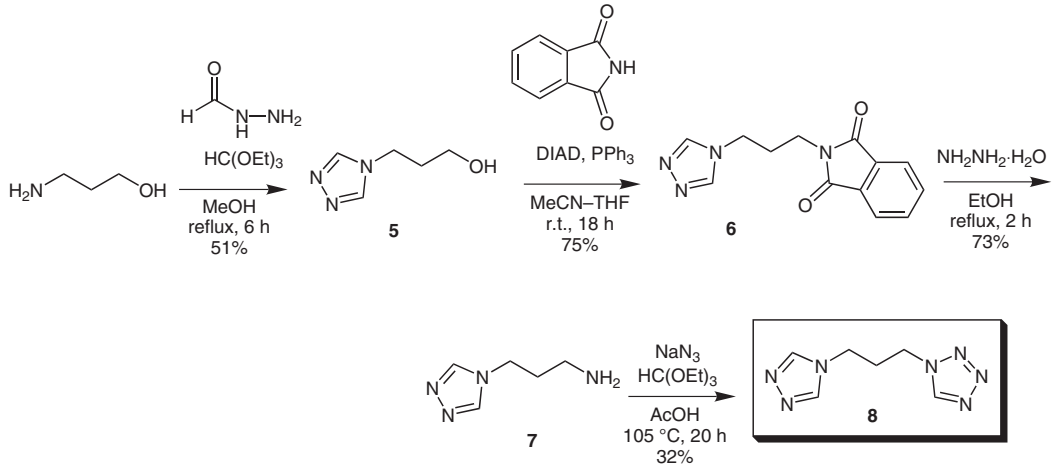



**Scheme 3** Multistep synthesis of 1-(4′-[1,2,4]triazol-4-yl-butyl)tetrazole (**4**) using approach **A**

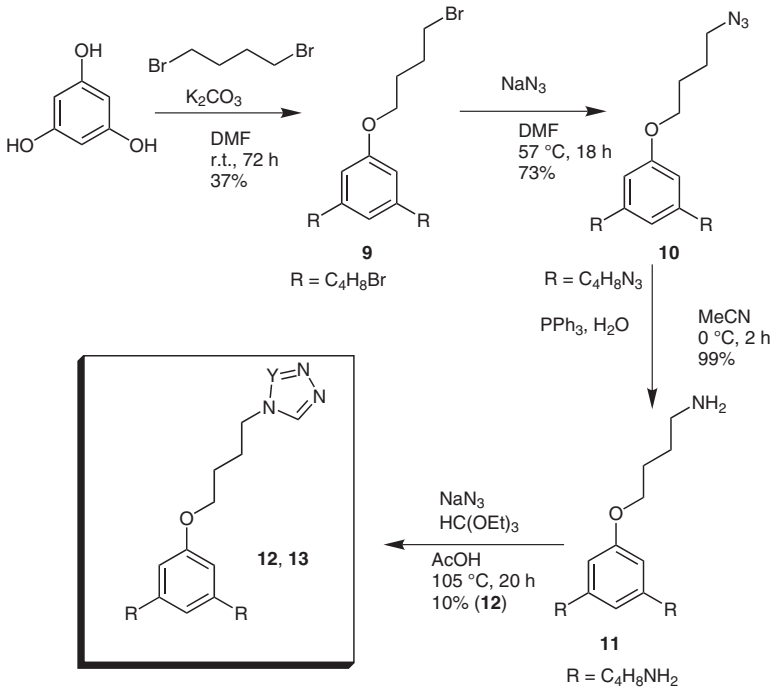
clization rates indicating that the loss of yield can be attributed to our purification procedures.

For the tripodal targets (strategy **C**), the synthesis of **d** and **e** was first considered through the functionalization of triamine **f** derived from phloroglucinol (Scheme 2). The intermediate **9**, already described by Curtis et al.,[30] was synthesized by Williamson alkylation according to a more convenient procedure inspired by the method described by Nithyanandhan et al.[31] for tris-5-bromopentyl phloroglucinol (Scheme 5). Then the bromide was substituted by azide to afford **10**. Reduction of **10** was attempted using both catalytic hydrogenation and triphenylphosphine and water to yield the amine **11**; the procedure with triphenylphosphine was more convenient and gave a higher yield. The key intermediate **11** could also be synthesized by grafting *N*-(4-bromobutyl)phthalimide onto phloroglucinol to give tris-4-*N*-butylphthalimide phloroglucinol, which was subsequently treated with hydrazine. The Williamson alkylation of phloroglucinol by *N*-(4-bromobutyl)phthalimide was achieved, however, in poor yield and this route was abandoned. The cyclization of triamine **11** to azoles was attempted using standard conditions.[5,26] $^1$H NMR spectroscopy of the crude mixtures indicated that tetrazole **12** formed but not triazole **13**. Tetrazole **12** was isolated in very small quantities, while the synthesis of **13** was not achieved. Hence, the convergent approach (strategy **D**) was investigated (Scheme 6).

For practical reasons, ω-hydroxyalkylazoles were used as precursors to **g** (see, Scheme 2). The synthesis of **5** was optimized based on the synthesis of **8**. The reaction of 3-amino-1-propanol with sodium azide and triethyl orthoformate in acetic acid gave the acetylated product **14**. Saponification of **14** under mild conditions afforded the desired tetrazole **15** in good yield. Since activation of the terminal alcohols through their conversion into mesylates or tosylates did not allow subsequent substitution, the grafting of the alcohols through a Mitsunobu coupling[29] was considered. Thus, phloroglucinol reacted with **5** and



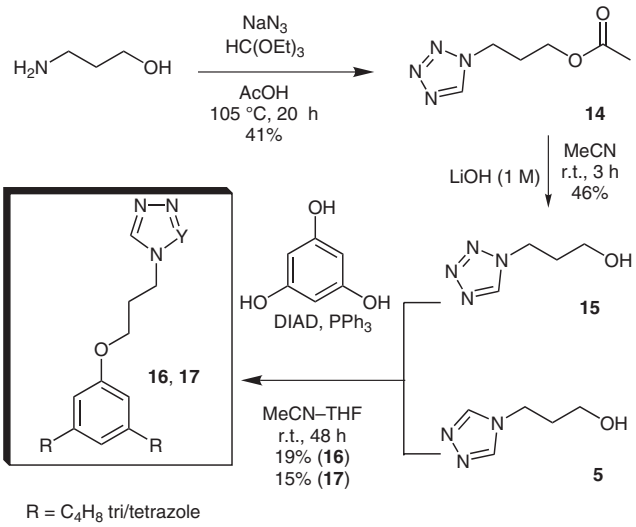

**Scheme 4** Multistep synthesis of **8** through disconnection **B**




**Scheme 5** Divergent approach **C** for the synthesis of tripodal tetrazole **12** and triazole **13**; Y = N, tetrazole; Y = CH, triazole

**15** according to a procedure described for the coupling of imidazoline with phenol (addition of a mixture of alcohol and nucleophile to the preformed betaine).[32] The reaction was followed by $^1$H NMR spectroscopy, looking specifically at the chemical shifts of the aromatic protons. We noticed that successive addition of three fractions of the preformed betaine to a 1:3 mixture of phloroglucinol and ω-hydroxyalkylazole improved the rate of substitution. In this way, the tripodal ligands **16** and **17** were obtained. The high polarity of the triazole made purification difficult, resulting in low yields for the tripodal ligands **16** and **17**; fortunately, the low number of steps compensated for this drawback.

With the required ligands in hand we next looked at the synthesis of a coordination compound with such ligands. One equivalent of iron(II) tetrafluoroborate hexahydrate was mixed with three equivalents of tris-3-[1,2,4]triazol-4-yl-propyl phloroglucinol (**16**, trptrz) in MeOH yielding a white powder **18** with the formula $[Fe(trptrz)_2](BF_4)_2 \cdot 5H_2O$. Pouring liquid nitrogen onto this powder induced a weak color change to pink precluding a possible spin state crossover for the iron(II) ions on cooling. The magnetic properties of **18** were thus investigated over the temperature range (4–300 K). Figure 2 shows the temperature dependence of the $\chi_M T$ product, $\chi_M$ being the molar magnetic susceptibility. This product is proportional to the total spin state of the complex providing the possibility of tracking a spin conversion from the high-spin (HS) state ($S = 2$) to the low-spin state ($S = 0$) when the sample is cooled. A gradual spin conversion centered at the transition temperature $T_{1/2}$ ca. 140 K was observed. The spin conversion is clearly evidenced when looking at the $^{57}$Fe Mössbauer spectrum recorded at this temperature that reveals HS and LS iron(II) ions. Mössbauer parameters [$\delta_{LS} = 0.541(2)$ mm/s, $\Delta E_Q^{LS} = 0.190(4)$ mm/s; $\delta_{HS1} = 1.106(2)$ mm/s, $\Delta E_Q^{HS1} = 3.116(4)$ mm/s and $\delta_{HS2} = 1.076(2)$ mm/s, $\Delta E_Q^{HS2} = 2.520(4)$ mm/s] are similar to those reported for iron(II) polynuclear SCO compounds with μ-$N_1$,$N_2$-triazole[33] ligands suggesting presumably a coordination polymer or an oligomer, which may spray in several dimensions rather than a mononuclear complex with chelating triazole ligands.




**Scheme 6** Convergent approach **D** for the synthesis of the tripodal triazole **16** and tetrazole **17**; Y = N, tetrazole; Y = CH, triazole

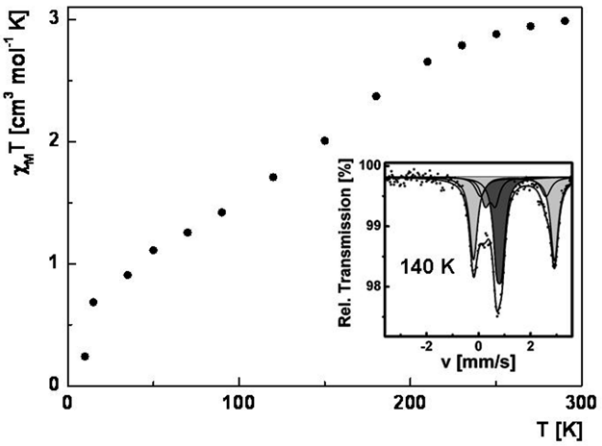



**Figure 2** $\chi_M T$ vs. T plot for $[Fe(trptrz)_2](BF_4)_2 \cdot 5H_2O$ (**18**). The inset shows the $^{57}Fe$ Mössbauer spectrum recorded at 140 K. The signals in grey, black, and dark grey refer to a HS-Fe(II) doublet, LS-Fe(II) singlet, and LS-Fe(III) doublet.

The incomplete character of the conversion at low temperature, revealing HS iron(II) ions, is shown by the non-zero value of $\chi_M T$ around 50 K. This spin conversion is also incomplete at room temperature as revealed by Mössbauer spectroscopy that shows LS iron(II) ions and by the low value of $\chi_M T$ at room temperature. Below 50 K a subsequent decrease of $\chi_M T$, that is not associated with the SCO phenomenon itself, is observed. This magnetic behavior is attributed to conjugated effects of spin orbit coupling and expected structural deformation of the coordination sphere of the remaining HS iron(II) ions which triggers a decrease of $\chi_M T$ due to the splitting of the Zeeman components of the $^5T_{2g}$ ground state.[34,35] Spin crossover behavior has also been observed for iron(II) coordination compounds with ligands **6**–**8**, **14**, and **15** and is expected for compounds with ligands **2**–**4**, **12**, **13**, and **17**. Such investigations are in progress in our laboratories.

The large scale synthesis of a new class of polytopic ligands containing both 1-R-tetrazole and 4-R-1,2,4-triazole moieties was achieved. The use of triazole precursors allowed us to avoid any purification steps involving column chromatography thus leading to good yields. On the other hand, the synthesis of tripodal triazole and tetrazole with a benzene core was achieved through a convergent approach, preferred to the divergent strategy. The procedures described for obtaining **8**, **16**, and **17** may be easily extended to other alkyl spacers since the convenient syntheses of 4-(ω′-hydroxyalkyl)-1,2,4-triazoles and 1-(ω′-hydroxyalkyl)tetrazoles have been described.[5,6,36] In addition, we found that the most efficient way to obtain (poly)amines was the substitution of a leaving group by azide followed by its reduction with triphenylphosphine and water. Also, a convenient way to convert a primary alcohol into a primary amine (when classical procedures for the activation of alcohol failed) was exemplified. This procedure, based on the Mitsunobu coupling with phthalimide took advantage of the poor solubility of the phthalimide derivatives to separate them from the by-products of the Mitsunobu coupling (that are soluble in acetonitrile–THF and alcohols). Finally, an iron(II) coordination compound with ligand **16** exhibiting thermally induced SCO behavior has been prepared. The coordination mode of **16** is presumably tridentate, contrary to recently prepared triazoles having poly(benzyl ether) dendrons that are bidentate leading to one dimensional SCO chains.[37] The coordination of tetrazole and 1,2,4-triazole based ligands described in this work with $3d^n$ transition metals is currently under investigation in our laboratory.

Solvents were dried prior to use. Reagents (Aldrich, Acros, or Fischer) were used as received. PE used had a bp range of 40–60 °C. Melting points were determined on an oil bath Büchi device. IR spectra were collected on a BioRad FTS 135 spectrometer on KBr pellets for solids and between NaCl plates for oils. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on Varian Gemini 200-92 (200 MHz) and Bruker 500 MHz Avance spectrometers. TMS and sodium 3-(trimethylsilyl)-1-propane sulfonate were used as internal references in $CDCl_3$ and $D_2O$, respectively. For other solvents, the residual solvent peak was used as the internal reference. Mass spectra were recorded on a Thermo Finnigan LCQ Ion Trap spectrometer, in APCI or ESI mode, detecting positive ions. HRMS were carried out on a Micromass Qtof2 spectrometer in ESI mode detecting positive ions. TLC was performed on precoated silica gel 60 $F_{254}$ plates purchased from Merck. The spots were visualized either using a ROC UV lamp (254 nm) or iodine vapor. Column chromatography was performed on silica gel 60 (63–200 mesh, Merck). Elemental analyses were carried out at the Service Central d'Analyse du CNRS (Vernaison, France) and at the University College of London (UK).

The synthesis of complex **18** was performed under standard Schlenk procedures under an argon stream. The solvent content of complex **18** was determined by thermogravimetric analysis (TGA) in air at the heating rate of 10 °C/min using a Mettler Toledo TGA/SDTA851e analyzer. Magnetic susceptibility was measured in the temperature range 4–290 K using a Quantum design MPMS-5S SQUID magnetometer. Magnetic data were corrected for diamagnetic contributions, which were estimated from Pascal's constants. The powdered sample was loaded into a gelatin capsule. $^{57}Fe$ Mössbauer spectra were recorded in transmission geometry with a $^{57}Co(Rh)$ radioactive source. The samples were sealed in aluminum foil and mounted in a nitrogen cryostat. The spectra were fitted using Recoil 1.05 Mössbauer Analysis Software.[38] Isomeric shifts are given relative to α-iron.

**Formic Hydrazide**

$HCO_2Et$ (76.5 mL, 1.0 mol, 1 equiv) was mixed carefully with hydrazine monohydrate (49 mL, 1.2 mol, 1.2 equiv) in MeOH (200 mL). The reaction mixture was heated to reflux for 1 h. The solvent was removed under reduced pressure to give a pale-yellow oil, which crystallized on standing. The white crystals were washed with PE and dried under high vacuum at 40 °C.

Yield: 51.4 g (85%); mp 54–55 °C (lit.[39] 54 °C).

**2-[4-(1*H*-Tetrazol-1-yl)butyl]isoindoline-1,3-dione (2)**

Hydrochloride **1**[27] (1.50 g, 5.94 mmol, 1 equiv), $NaN_3$ (0.39 g, 5.92 mmol, 1 equiv), and $HC(OEt)_3$ (2.7 mL,16.23 mmol, 2.75 equiv) were mixed at r.t., then AcOH (15 mL) was added. The resulting mixture was heated to 105 °C and stirred for 20 h. AcOH was removed under reduced pressure, the resulting yellow solid was dissolved in hot MeCN (15 mL), and the non-soluble by-products were removed by filtration. The solution was purified by chromatography [$CH_2Cl_2$ (300 mL) → $CH_2Cl_2$–EtOAc, 1:1] to afford the product as a pale-yellow solid.

Yield: 0.975 g (61%); mp 143–145 °C; $R_f$ 0.4 (EtOAc–$CH_2Cl_2$, 1:1).

IR (KBr): 3457 (w), 3148 (w), 2951 (w), 2874 (w), 1767 (m), 1767 (m), 1708 (s), 1610 (w), 1485 (w), 1467 (m), 1441 (m), 1405 (s), 1374 (m), 1340 (m), 1237 (m), 1189 (m), 1165 (m), 1119 (m), 1098 (m), 1075 (m), 1047 (s), 963 (m), 917 (m), 859 (m), 728 (s), 660 (w), 620 (w), 552 (w), 533 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.69–1.83 (m, 2 H), 1.94–2.05 (m, 2 H), 3.76 (t, *J* = 6.7 Hz, 2 H), 4.53 (t, *J* = 7.2 Hz, 2 H), 7.72–7.82 (m, 2 H), 7.84–7.88 (m, 2 H), 8.65 (s, 1 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 25.6, 27.2, 36.7, 47.6, 123.6, 132.2, 134.3, 142.6, 168.5.

MS: *m*/*z* calcd for $C_{13}H_{14}N_5O_2$ [M + $H^+$]: 272.11; found: 272.1.

Anal. Calcd for $C_{13}H_{13}N_5O_2$ (271.28): C, 57.56; H, 4.83; N, 25.82. Found C, 57.44; H, 4.82, N, 25.56.

**4-(1*H*-Tetrazol-1-yl)butylamine (3)**

Tetrazole **2** (60 mg, 0.22 mmol, 1 equiv) and $NH_2NH_2{\cdot}H_2O$ (40 μL, 0.82 mmol, 3.7 equiv) in EtOH (10 mL) were heated to reflux for 2 h. After removal of the phthalhydrazide by filtration, the solvent was removed under reduced pressure to give a pale-yellow solid. To ensure that all phthalhydrazide was removed, MeCN (10 mL) was added, the resulting solution was filtered, and concentrated; this process was carried out three times to afford pure **3**.

Yield: 14 mg (45%).

IR (KBr): 3104 (m), 2944 (m), 2868 (m), 1639 (s), 1571 (s), 1482 (s), 1442 (s), 1368 (m), 1315 (m), 1170 (m), 109 (m), 1023 (w), 970 (m), 883 (w), 836 (w), 772 (w), 749 (w), 722 (w), 700 (w), 679 (w), 663 (w), 653 (w), 561 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, DMSO, 298 K): δ = 1.38–1.52 (m, 2 H), 1.84–1.97 (m, 2 H), 2.71 (t, *J* = 7.0 Hz, 2 H), 4.57 (t, *J* = 7.1 Hz, 2 H), 9.2 (s, 1 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 27.2, 29.9, 41.1, 48.2, 142.5.

MS: *m*/*z* = 142 [M + $H^+$].

HRMS: *m*/*z* calcd for $C_5H_{12}N_5$ [M + $H^+$]: 142.1092; found: 141.1091.

**1-[4-(4*H*-1,2,4-Triazol-4-yl)butyl]-1*H*-tetrazole (4)**

Freshly prepared anhyd formic hydrazide (25 mg, 0.42 mmol, 1 equiv) and $HC(OEt)_3$ (0.2 mL, 1.20 mmol, 2.9 equiv) in MeOH (10 mL) were heated to reflux for 2 h, then **3** (60 mg, 0.42 mmol, 1 equiv) in anhyd MeOH (5 mL) was added dropwise, and the mixture was kept at reflux for a further 4 h. After removal of the solvent under reduced pressure, the resulting pink oil was dissolved in a small amount of EtOH and purified by chromatography (EtOAc → *i*-PrOH → EtOH) to afford **4** as a white solid.

Yield: 7 mg (9%); $R_f$ 0.25 (EtOH).

$^1H$ NMR (200 MHz, DMSO, 298 K): δ = 1.61–1.85 (m, 4 H), 4.06 (t, *J* = 6.5 Hz, 2 H), 4.48 (t, *J* = 6.6 Hz, 2 H), 8.51 (s, 2 H), 9.40 (s, 1 H).

**3-(4*H*-1,2,4-Triazol-4-yl)propan-1-ol (5)[28]**

Freshly prepared anhyd formic hydrazide (30.81 g, 0.51 mol, 1 equiv) and $HC(OEt)_3$ (102 mL, 0.61 mol, 1.2 equiv) in MeOH (650 mL) were heated to reflux for 2 h, then 3-aminopropan-1-ol (39.2 mL, 0.51 mol, 1 equiv) was added dropwise, and the mixture was kept at reflux for a further 4 h. The solvent was subsequently removed under reduced pressure to give a pink oil, which was left at –18 °C overnight to afford white needles. The needles were removed by filtration and washed with cold acetone. Finally, the white compound was dried under reduced pressure.

Yield: 32.74 g (51%); mp 61–64 °C.

IR (KBr): 3330 (s), 3108 (m), 2928 (m), 2874 (m), 1678 (vs), 1538 (s), 1462 (m), 1388 (m), 1188 (s), 1062 (s), 987 (w), 959 (w), 923 (w), 875 (w), 715 (w), 637 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.99–2.09 (m, 2 H), 3.25 (br s, 1 H, OH), 3.65 (t, *J* = 5.9 Hz, 2 H), 4.25 (t, *J* = 6.7 Hz, 2 H), 8.24 (s, 2 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 33.1, 42.2, 57.8, 143.3.

**2-[3-(4*H*-1,2,4-Triazol-4-yl)propyl]isoindoline-1,3-dione (6)**

$PPh_3$ (3.12 g, 11.88 mmol, 1.5 equiv) in anhyd MeCN–THF (1:1, 20 mL) were cooled to 0 °C, DIAD (2.34 mL, 11.88 mmol, 1.5 equiv) was added with stirring, and the mixture was stirred for 10 min. Then a mixture of phthalimide (1.158 g, 7.87 mmol, 1 equiv) and **5** (1 g, 7.87 mmol, 1 equiv) in MeCN–THF (1:2, 20 mL) was added, the mixture was allowed to warm to r.t., and then stirred overnight. The white precipitate formed was removed by filtration and recrystallized from $H_2O$ (10 mL) to afford pale-yellow sharp plates.

Yield: 1.513 g (75%); mp 176–178 °C.

IR (KBr): 3444 (w), 3137 (m), 3107 (m), 3041 (w), 2965 (w), 1760 (s), 1703 (s), 1521 (m), 1441 (m), 1399 (s), 1365 (m), 1346 (s), 1186 (s), 1118 (m), 1075 (m), 1030 (m), 969 (m), 810 (w), 726 (m), 531 (m), 631 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 2.15–2.28 (m, 2 H), 3.76 (t, *J* = 6.3 Hz, 2 H), 4.10 (t, *J* = 7.0 Hz, 2 H), 7.77–7.81 (m, 2 H), 7.85–7.89 (m, 2 H), 8.34 (s, 2 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 30.4, 34.8, 42.9, 123.6, 132, 134.5, 143, 168.5.

MS: *m*/*z* calcd for $C_{13}H_{13}N_4O_2$ [M + $H^+$]: 257.1; found: 257.1.

Anal. Calcd for $C_{13}H_{12}N_4O_2$ (256.26): C, 60.93; H, 4.72; N, 21.86, O, 12.48. Found: C, 60.99; H, 4.92; N, 21.74; O, 12.48.

**3-(4*H*-1,2,4-Triazol-4-yl)propylamine (7)**

Triazole **6** (5.40 g, 21.07 mmol, 1 equiv) and $NH_2NH_2{\cdot}H_2O$ (2.20 mL, 22.26 mmol, 1.05 equiv) in EtOH (40 mL) were heated to reflux for 2 h. After removal of the phthalhydrazide by filtration at r.t., the solvent was removed under reduced pressure to give a pale-yellow solid. To ensure that all phthalhydrazide was removed, MeCN (10 mL) was added, the resulting solution was filtered, and concentrated; this process was carried out three times to afford pure **7**.

Yield: 1.941 g (73%).

IR (NaCl): 3378 (s), 3120 (s), 2958 (s), 2358 (m), 2165 (w), 1646 (m), 1540 (s), 1488 (s), 1388 (m), 1321 (s), 1189 (s), 1079 (m), 993 (m), 636 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CD_3OD$, 298 K): δ = 1.85–1.99 (m, 2 H), 2.59 (t, *J* = 7.0 Hz, 2 H), 4.16 (t, *J* = 7.2 Hz, 2 H), 8.52 (s, 2 H).

$^{13}C$ NMR (50 MHz, $CD_3OD$, 298 K): δ = 34.6, 39.6, 44.2, 144.8.

MS: *m*/*z* = 127.1 [M + $H^+$].

HRMS: *m*/*z* calcd for $C_5H_{11}N_4$ [M + $H^+$]: 127.0983; found: 127.0985.

**1-[3-(4*H*-1,2,4-Triazol-4-yl)propyl]-1*H*-tetrazole (8)**

AcOH (40 mL) was added to a mixture of triazole amine **7** (2.65 g, 21.00 mmol, 1 equiv), $NaN_3$ (1.37 g, 21.00 mmol, 1 equiv), and $HC(OEt)_3$ (4 mL, 24.05 mmol, 1.15 equiv). The reaction mixture was heated to 105 °C and stirred for 20 h. AcOH was removed under reduced pressure, the resulting yellow solid was dissolved in hot MeCN, and the non soluble by-products were removed by filtration. MeCN was subsequently removed under reduced pressure and the yellow solid was dissolved in MeOH (30 mL). Upon addition of $Et_2O$ (90 mL), the product precipitated as a white powder, which was collected by filtration and dried under reduced pressure.

Yield: 1.22 g (32%); mp > 200 °C.

IR (KBr): 3117 (m), 3092 (m), 3004 (w), 2962 (w), 1700 (w), 1675 (w), 1537 (s), 1489 (m), 1458 (m), 1432 (w), 1385 (m), 1365 (w), 1344 (w), 1257 (w), 1209 (m), 1185 (s), 1169 (s), 1107 (s), 1079 (m), 1058 (m), 1040 (w), 974 (s), 952 (m), 913 (m), 863 (m), 839 (w), 768 (m), 723 (m), 694 (w), 665 (m), 639 (s) $cm^{-1}$.

$^1H$ NMR (200 MHz, $D_2O$, 298 K): δ = 2.45–2.69 (m, 2 H), 4.25 (t, *J* = 7.0 Hz, 2 H), 4.58 (t, *J* = 7.3 Hz, 2 H), 8.51 (s, 2 H), 9.17 (s, 1 H).

$^{13}C$ NMR (50 MHz, $CD_3OD$, 298 K): δ = 31.5, 43.6, 46.5, 144.8, 145.

MS: *m*/*z* = 180.0 [M + $H^+$].

Anal. Calcd for $C_6H_9N_7$ (179.18): C, 40.22; H, 5.06; N, 54.72. Found: C, 40.22; H, 5.03; N, 54.75.

**1-(4-Bromobutoxy)-3,5-bis(4-bromobutyl)benzene (9)**

Benzene-1,3,5-triol (2 g, 15.86 mmol, 1 equiv) in DMF (12 mL) was added over a period of 20 min to a solution 1,4-dibromobutane (8.2 mL, 68.66 mmol, 4.3 equiv) and finely ground anhyd $K_2CO_3$ (8.60 g, 153.27 mmol, 9.6 equiv) in DMF (40 mL). The mixture was stirred at r.t. for 72 h. Toluene (20 mL) was added to the reaction mixture, the resulting mixture was filtered, and the solvent was removed under reduced pressure. The resulting brown oil was then dissolved in $CH_2Cl_2$ (20 mL), the organic phase was successively washed with brine (3 × 20 mL) and $H_2O$ (3 × 20 mL), and dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure to give an oil, which was dissolved in hexane–EtOAc (9:1), and purified by column chromatography (hexane–EtOAc, 9:1) to afford the product as a transparent oil.

Yield: 3.12 g (37%); $R_f$ 0.21 (hexane–EtOAc, 9:1).

IR (NaCl): 2943 (m), 2871 (m), 2847 (w), 1598 (s), 1461 (m), 1438 (m), 1384 (m), 1223 (m), 1161 (s), 1064 (m), 888 (w), 816 (m), 753 (w), 681 (w), 643 (w), 560 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.84–2.13 (m, 12 H), 3.48 (t, *J* = 6.5 Hz, 6 H), 3.95 (t, *J* = 5.8 Hz, 6 H), 6.00 (s, 3 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 27.8, 29.4, 33.4, 66.9, 93.9, 160.8.

**1-(4-Azidobutoxy)-3,5-bis(4-azidobutyl)benzene (10)**

Trialkyl benzene **9** (550 mg, 1.28 mmol, 1 equiv) and $NaN_3$ (1.90 g, 29.23 mmol, 23 equiv) in DMF (18 mL) were heated to 57 °C overnight. Then toluene (10 mL) was added, the resulting solution was filtered, and concentrated; this process was carried out three times to afford the product as a yellow oil.

Yield: 0.391 g (73%).

IR (NaCl): 2942 (m), 2875 (m), 2095 (s), 1599 (m), 1463 (m), 1388 (m), 1352 (m), 1281 (m), 1255 (m), 1163 (s), 1067 (m), 719 (m), 681 (w), 636 (w), 595 (w), 556 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.65–1.95 (m, 12 H), 3.35 (t, *J* = 6.3 Hz, 6 H), 3.95 (t, *J* = 5.9 Hz, 6 H), 6.05 (s, 3 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 26.0, 26.7, 51.4, 67.5, 94.4, 161.0.

MS: *m*/*z* = 418.0 [M + $H^+$].

Anal. Calcd for $C_{18}H_{27}N_9O_3$ (417.48): C, 51.79; H, 6.52; N, 30.20; O, 11.50. Found: C, 52.51; H, 6.63; N, 29.74; O, 11.69.

**4,4′-[5-(4-Aminobutoxy)-1,3-phenylene]dibutylamine (11)**

Triazide **10** (160 mg, 0.38 mmol, 1 equiv) and $PPh_3$ (340 mg, 1.30 mmol, 3.4 equiv) in MeCN (10 mL) were stirred for 2 h. Then $H_2O$ (10 mL) was added, stirring continued for a further 2 h, and the reaction mixture was concentrated to 5 mL under reduced pressure. After filtration, the residual water was removed under reduced pressure to afford the triamine as a pale-yellow oil.

Yield: 99%.

IR (NaCl): 3250 (m), 2942 (m), 2875 (m), 1597 (s), 1465 (m), 1389 (m), 1340 (w), 1309 (w), 1262 (w), 1165 (s), 1064 (m), 922 (w), 819 (m), 750 (w), 723 (w), 686 (w), 543 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.75 (m, 12 H), 2.70 (t, *J* = 6.3 Hz, 6 H), 3.3 (br s, 6 H, $NH_2$) 3.86 (t, *J* = 6.4 Hz, 6 H), 5.99 (s, 3 H).

$^{13}C$ NMR (50 MHz, $D_2O$, 298 K): δ = 26.5, 28.2, 42.1, 70.7, 97.9, 163.1.

MS: *m*/*z* = 340.1 [M + $H^+$].

HRMS: *m*/*z* calcd for $C_{18}H_{34}N_3O_3$ [M + $H^+$]: 340.2600; found: 340.2596.

**1,1′-[4,4′-{5-[4-(1*H*-Tetrazol-1-yl)butoxy]-1,3-phenylene}bis(butane-4,1-diyl)]bis(1*H*-tetrazole) (12)**

Triamine **12** (710 mg, 1.58 mmol, 1 equiv), $NaN_3$ (380 mg, 5.84 mmol, 3.7 equiv), and $HC(OEt)_3$ (2 mL, 12 mmol, 7.6 equiv) were dissolved in AcOH (35 mL), the resulting mixture was heated to 105 °C for 20 h. Then the solvent was removed under reduced pressure to give a brown oil which solidified on standing. The brown solid was dissolved in $CH_2Cl_2$ (10 mL), the resulting solution was filtered in order to remove insoluble by-products, and then purified by column chromatography (EtOAc–MeCN, 4:1). The product was recovered as a yellow semi-solid.

Yield: 80 mg (10%); $R_f$ 0.25 (EtOAc–MeCN, 4:1).

IR (KBr): 3145 (m), 2955 (m), 2930 (m), 2880 (m), 1614 (s), 1589 (s), 1460 (m), 1387 (m), 1169 (s), 1152 (s), 1112 (m), 1100 (m), 1060 (m), 970 (w), 925 (w), 894 (m), 864 (m), 818 (m), 798 (w), 783 (w), 736 (w), 720 (w), 677 (m), 662 (m), 641 (m), 594 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 1.74–1.92 (m, 6 H), 2.05–2.25 (m, 6 H), 3.96 (t, *J* = 5.6 Hz, 6 H), 4.55 (t, *J* = 7.0 Hz, 6 H), 6.01 (s, 3 H), 8.67 (s, 3 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 26.1, 27.1, 48.2, 67.2, 94.5, 142.7, 160.7.

MS: *m*/*z* = 499.2 [M + $H^+$].

Anal. Calcd for $C_{21}H_{30}N_{12}O_3$ (498.55): C, 50.59; H, 6.07; N, 33.71. Found: C, 50.91; H, 5.95; N, 33.31.

**3-(1*H*-Tetrazol-1-yl)propyl Acetate (14)**

AcOH (20 mL) was added to a mixture of 3-aminopropan-1-ol (3.8 mL, 49.68 mmol, 1 equiv), $NaN_3$ (3.25 g, 49.99 mmol, 1 equiv), and $HC(OEt)_3$ (10 mL, 60.12 mmol, 1.2 equiv). The resulting mixture was heated for 20 h at 105 °C. The reaction mixture was then cooled to r.t., filtered, and the solvent was removed under reduced pressure to give a yellow oil, which solidified on standing. The yellow solid was then dissolved in MeCN (15 mL), the resulting solution was filtered in order to remove insoluble by-products, and then purified by column chromatography (EtOAc) to give a colorless oil.

Yield: 3.52 g (42%); $R_f$ 0.45 (EtOAc).

IR (KBr): 2951 (m), 2888 (m), 1734 (m), 1666 (s), 1567 (s), 1391 (m), 1254 (m), 1174 (w), 1107 (w), 1054 (m), 972 (w), 653 (w), 612 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, $D_2O$, 298 K): δ = 2.38–2.51 (m, 2 H), 4.26 (t, *J* = 5.9 Hz, 2 H), 4.80 (t, *J* = 6.7 Hz, 2 H), 9.36 (s, 1 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 20.7, 28.9, 45.5, 60.7, 143.0, 170.8.

MS: *m*/*z* = 170.9.

Anal. Calcd for $C_6H_{10}N_4O_2$ (170.17): C, 42.35; H, 5.92; N, 32.92. Found: C, 42.51; H, 5.80; N, 32.89.

**3-(1*H*-Tetrazol-1-yl)propan-1-ol (15)**

A mixture of acetate **14** (11 g, 64.64 mmol, 1 equiv) in MeCN (350 mL) and 1 M aq LiOH (350 mL 5.4 equiv) was stirred at r.t. overnight. Then, the reaction mixture was concentrated under reduced pressure, the resulting white solid was extracted with EtOAc (200 mL), and then concentrated to give a yellowish oil, which was purified by column chromatography (EtOAc–MeOH, 9:1) to afford a colorless oil.

Yield: 3.774 g (46%); $R_f$ 0.27 (EtOAc–MeOH, 9:1).

IR (NaCl): 3380 (s), 3434 (m), 2951 (m), 2885 (m), 2093 (w), 1655 (m), 1634 (m), 1488 (m), 1423 (m), 1371 (w), 1579 (vw), 1241 (vw), 1172 (s), 1108 (s), 1062 (s), 971 (m), 937 (w), 912 (w), 873 (m), 812 (vw), 708 (w), 655 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 298 K): δ = 2.03–2.16 (m, 2 H), 3.56 (t, *J* = 5.6 Hz, 2 H), 4.55 (t, *J* = 6.7 Hz, 2 H), 8.78 (s, 1 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$, 298 K): δ = 31.8, 45.1, 57.9, 143.2.

MS: *m*/*z* = 128.9 [M + $H^+$].

Anal. Calcd for $C_4H_8N_4O$ (128.13): C, 37.49; H, 6.29; N, 43.73. Found: C, 37.87; H, 6.23; N, 43.39.

**4,4′-{3,3′-[5-(3-(4*H*-1,2,4-Triazol-4-yl)propoxy]-1,3-phenylene}bis(propane-1,3-diyl))bis(4*H*-1,2,4-triazole) (16)**

A solution of $PPh_3$ (2.43 g, 9.25 mmol, 3.5 equiv) in anhyd MeCN–THF (1:1, 20 mL) was cooled to 0 °C. Then DIAD (1.82 mL, 9.25 mmol, 3.5 equiv) was added and the resulting mixture was stirred for 10 min. A mixture of benzene-1,3,5-triol (0.34 g, 2.66 mmol, 1 equiv) and **5** (1 g, 7.86 mmol, 3 equiv) in MeCN (15 mL) was added and the mixture allowed to warm to r.t. The reaction mixture was stirred for 48 h, filtered, and the solvent was removed under reduced pressure. The resulting yellow solid was then dissolved in $CH_2Cl_2$–$H_2O$ (1:1, 40 mL), the organic phase was extracted with $H_2O$ (2 × 20 mL), and the combined aqueous fractions were concentrated under reduced pressure to give a brown oil. The resulting oil was dissolved in MeOH and purified by chromatography (EtOAc→MeOH) to afford a yellowish oil.

Yield: 0.234 g (19%); $R_f$ 0.11 (MeOH).

IR (NaCl): 3112 (m), 2949 (m), 2883 (m), 1708 (w), 1600 (s), 1537 (m), 1466 (m), 1390 (m), 1185 (s), 1164 (s), 1070 (m), 985 (w), 955 (w), 863 (m), 824 (m), 637 (m) $cm^{-1}$.

$^1H$ NMR (200 MHz, $CD_3OD$, 298 K): δ = 2.20–2.36 (m, 6 H), 3.93 (t, *J* = 5.8 Hz, 6 H), 4.34 (t, *J* = 6.7 Hz, 6 H), 5.99 (s, 3 H), 8.54 (s, 6 H).

$^{13}C$ NMR (125 MHz, $CD_3OD$, 298 K): δ = 30.2, 43.1, 65.3, 94.3, 145.3, 160.8.

MS: *m*/*z* = 455.3 [M + $H^+$].

HRMS: *m*/*z* calcd for $C_{21}H_{28}N_9O_3$ [$M^+$]: 454.2315; found: 454.2302.

**1,1′-{3,3′-[5-(3-(1*H*-Tetrazol-1-yl)propoxy]-1,3-phenylene}bis(propane-1,3-diyl)bis(1*H*-tetrazole) (17)**

A solution of $PPh_3$ (2.060 g, 7.85 mmol, 3 equiv) in anhyd MeCN–THF (1:1, 20 mL) was cooled to 0 °C. DIAD (1.55 mL, 7.87 mmol, 3 equiv) was added and the resulting mixture was stirred for 10 min. Then a mixture of benzene-1,3,5-triol (0.330 g, 2.62 mmol, 1 equiv) and **5** (1.01 g, 7.86 mmol, 3 equiv) in MeCN (10 mL) was added, the resulting mixture allowed to warm to r.t., and stirred for 48 h. Then the solvent was removed under reduced pressure and the resulting brown oil was dissolved in a small amount of EtOAc. The white precipitate formed on stirring was removed by filtration. After removal of EtOAc under reduced pressure, a small amount of acetone was added, and the product precipitated as a beige semi-solid upon addition of $Et_2O$.

Yield: 180 mg (15%).

IR (KBr): 3127 (m), 2958 (m), 2800 (m), 1615 (s), 1588 (s), 1457 (m), 1159 (s), 1107 (m), 1068 (m), 964 (w), 912 (w), 879 (w), 823 (w), 802 (w), 681 (m), 600 (w) $cm^{-1}$.

$^1H$ NMR (200 MHz, DMSO-$d_6$, 298 K): δ = 2.22–2.34 (m, 6 H), 3.94 (t, *J* = 5.8 Hz, 6 H), 4.61 (t, *J* = 6.8 Hz, 3 H), 6.01 (s, 3 H), 9.41 (s, 3 H).

$^{13}C$ NMR (50 MHz, DMSO-$d_6$, 298 K): δ = 28.8, 45.0, 64.6, 94.2, 144.2, 160.1.

MS: *m*/*z* = 457.0 [M + $H^+$].

Anal. Calcd for $C_{18}H_{24}N_{12}O_3$ (456.47): C, 47.36; H, 5.30; N, 36.82. Found: C, 47.00; H, 5.48; N, 36.51.

**Bis[4,4′-[3,3′-{5-[3-(4*H*-1,2,4-triazol-4-yl)propoxy]-1,3-phenylene}bis(propane-3,1-diyl)]bis(4*H*-1,2,4-triazole)]iron(II) Ditetrafluoroborate Pentahydrate (18)**

$Fe(BF_4)_2 \cdot 6H_2O$ (74 mg, 0.22 mmol, 1 equiv) in MeOH (5 mL) was added to a solution of **16** (300 mg, 0.66 mmol, 3 equiv) in MeOH (3 mL) and the resulting mixture was stirred for 2 h. The white precipitate formed was collected by filtration and dried under reduced pressure.

Yield: 153 mg (61%).

IR (KBr): 3439 (m, br), 3127 (m), 2949 (w), 2884 (w) 1600 (s), 1545 (m), 1462 (m), 1394 (m), 1190 (m, sh), 1166 (s), 1068 (s), 878 (w), 833 (w), 634 (m) $cm^{-1}$.

TGA: solvent content, 4.22%; decomposition > 250 °C.

Anal. Calcd for $C_{42}H_{64}N_{18}O_{11}FeB_2F_8$ (1226.46): C, 41.13; H, 5.25; N, 20.56; Fe, 4.55. Found: C, 40.83; H, 4.65; N, 20.14; Fe, 4.72.

## Acknowledgment

We gratefully acknowledge financial support through a Fonds Special de Recherche to the Université catholique de Louvain and the Fonds pour la Recherche dans l'Industrie et dans l'Agriculture for a doctoral grant for Y. Boland. J. Marchand-Brynaert is senior research associate of the FNRS (Belgium). L. Piraux is thanked for providing access to a SQUID magnetometer and G. Zhou for recording the magnetic data.

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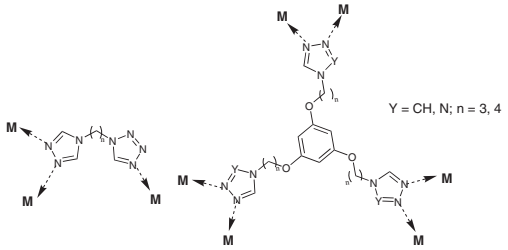


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