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Routes to novel mono- and bis-tetrazole compounds: synthesis, spectroscopic and structural characterization†

Cite this: DOI: 10.1039/c3nj00090g

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Received (in Montpellier, France) 22nd January 2013,
Accepted 25th January 2013

DOI: 10.1039/c3nj00090g

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Relatively easy-to-run synthetic routes to new mono- [1-(2-(4,5-dihydro-1*H*-imidazol-1-yl)ethyl)-1*H*-tetrazole (**1**) and 3-(2-(1*H*-tetrazol-1-yl)ethyl)oxazolidin-2-one (**13**)], and bis-tetrazole [*N*,*N*-bis(2-(1*H*-tetrazol-1-yl)ethyl)-formamide (**2**), bis(2-(1*H*-tetrazol-1-yl)ethyl)amine (**3**), *N*-(2-(1*H*-tetrazol-1-yl)ethyl)-*N*-(2-(2-(1*H*-tetrazol-1-yl)-ethylamino)ethyl)formamide (**5**), N^1,N^2-bis(2-(1*H*-tetrazol-1-yl)ethyl)ethane-1,2-diamine (**6**), *N*,*N*′-(2,2′-azanediylbis(ethane-2,1-diyl))bis(*N*-(2-(1*H*-tetrazol-1-yl)ethyl)formamide) (**8**) and N^1-(2-(1*H*-tetrazol-1-yl)ethyl)-N^2-(2-(2-(1*H*-tetrazol-1-yl)ethylamino)ethyl)ethane-1,2-diamine (**9**)] ligands have been developed. **2** (whose crystal structure is described), **3**, **5**, **6**, **8** and **9** are of particular interest as precursors for further functionalization due to the aldehyde and secondary amine functions, while **2**, **5**, **8** and **13** are potential synthons for the formation of ditopic ligands for metal–organic framework construction. Unexpected instability of Boc under basic and nucleophilic conditions at high temperature followed by fragmentation of *tert*-butyl 2-chloroethyl(2-(2-chloroethylamino)ethyl)carbamate (**14**) and *tert*-butyl 2,2′-azanediylbis(ethane-2,1-diyl)bis(2-chloroethylcarbamate) (**15**) afforded **13**, whose crystal structure is presented.

Introduction

Tetrazoles belong to a class of molecules that are found to be useful in various sectors as drugs,[1] explosives,[2] sensors,[3] and even for pancreatic cancer treatment.[4] In coordination chemistry, these molecules can be encountered in one of the most fascinating class of materials of modern crystal engineering in so-called metal–azolate frameworks[5] and azole coordination polymers,[6] which are of ever increasing interest due to the richness of properties that can be expected including spin crossover,[7–9] long range magnetic ordering,[10] porosity,[11–13] solar cooling,[14] *etc.* Among these materials, tetrazole building blocks play a prominent role, considering their potential coordination modes.[15] For instance, a Cu^{II} metal–organic framework $[Cu(L)(OH)]BF_4$ made of the asymmetric 1-[3′-(1,2,4-triazol-4-yl)-propyl]tetrazole (**L**) was recently reported. This material presents strong antiferromagnetic interactions leading to a globally diamagnetic material.[16] According to X-ray analysis, **L** connects four Cu^{II} ions, where the 1,2,4-triazole and tetrazole units exhibit a bridging bis-monodentate μ_2-*N*1,*N*2 and a unique μ_2-*N*2,*N*3 coordination mode, respectively. Thus, design of new tetrazole scaffolds, in particular those containing one or more functional units, is of current interest, with the goal to extend dimensionality of the target crystal networks.

In the frame of our long time interest in the preparation of azole-containing molecules, in particular with tetrazole functions,[7,17–22] we and others have largely focused on the synthesis of simplest bis-tetrazoles with alkane spacers,[17–19,23] applying successfully the Kamiya patent.[24] We herein report new synthesis strategies for mono- and bis-tetrazole molecules that could act as potential ligands of metal complexes.

Results and discussion

Organic syntheses

We have involved diethylenetriamine, triethylenetetramine and tetraethylenepentamine as starting materials for the possible formation of corresponding bis(2-(1*H*-tetrazol-1-yl)ethyl)amine (**3**), N^1,N^2-bis(2-(1*H*-tetrazol-1-yl)ethyl)ethane-1,2-diamine (**6**) and N^1-(2-(1*H*-tetrazol-1-yl)ethyl)-N^2-(2-(2-(1*H*-tetrazol-1-yl)ethylamino)-ethyl)ethane-1,2-diamine (**9**) with NaN_3 and $HC(OEt)_3$ (Schemes 1–3).[24]

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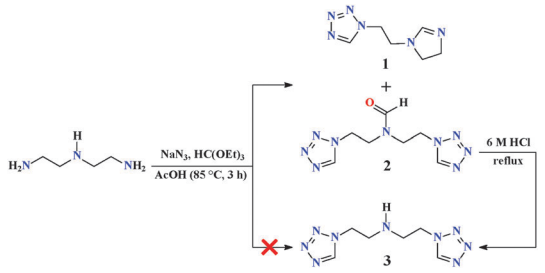
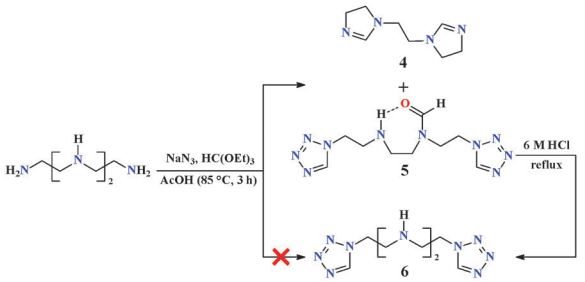
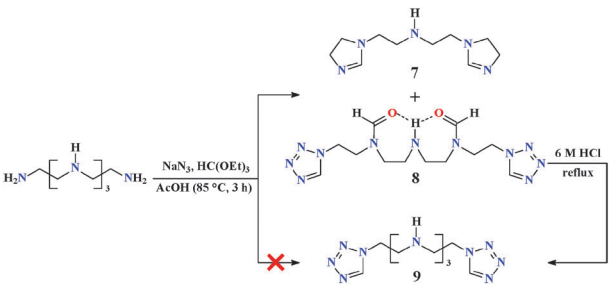
† Electronic supplementary information (ESI) available: Tables S1 and S2. CCDC 905036 (**2**) and 905035 (**13**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00090g



Scheme 1



Scheme 2



Scheme 3

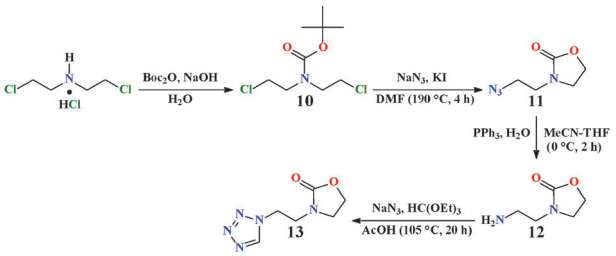
The higher nucleophilic character of the secondary amine group compared to the terminal primary amine functions leads however mostly to the formation of cyclic monoformamidine *N*,*N*-bis(2-(1*H*-tetrazol-1-yl)ethyl)formamide (**2**) and *N*-(2-(1*H*-tetrazol-1-yl)ethyl)-*N*-(2-(2-(1*H*-tetrazol-1-yl)ethylamino)ethyl)formamide (**5**) or bis-formamidine *N*,*N*′-(2,2′-azanediylbis(ethane-2,1-diyl))bis(*N*-(2-(1*H*-tetrazol-1-yl)ethyl)formamide) (**8**) derivatives.

Compounds 1-(2-(4,5-dihydro-1*H*-imidazol-1-yl)ethyl)-1*H*-tetrazole (**1**) (Scheme 1), 1,2-bis(4,5-dihydro-1*H*-imidazol-1-yl)-ethane (**4**) (Scheme 2) and bis(2-(4,5-dihydro-1*H*-imidazol-1-yl)-ethyl)amine (**7**) (Scheme 3) were isolated by crystallization from the reaction mixture (yield: 27, 43 and 39%, respectively). The formation of **1**, **4** and **7** is favoured by the formation of the five-membered cyclic formamidine group.

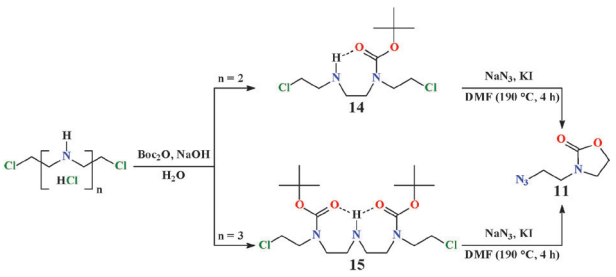
Molecules **2**, **5** and **8** were thus obtained during an attempt to isolate the target bis-tetrazoles **3**, **6** and **9** by column chromatography (Schemes 1–3). Bis-tetrazoles **2** (whose crystal structure has been solved, *vide infra*), **5** and **8** are probably obtained from the opening of the formamidine cycles of **1**, **4** and **7** with the further interaction with $HC(OEt)_3$. Hydrolysis of the amide functions of **2**, **5** and **8** under acidic conditions (6 M HCl) leads finally to the target bis-tetrazoles **3**, **6** and **9** (Schemes 1–3).

It should be noted that bis-tetrazoles **5** and **8** contain one and two formamide functions, respectively (Schemes 2 and 3). This might be explained by the formation of intramolecular linear hydrogen bonds in the structure of **5**, and bifurcated hydrogen bonds, in the structure of **8**, which protect the neighbouring NH group for further interaction (Schemes 2 and 3).

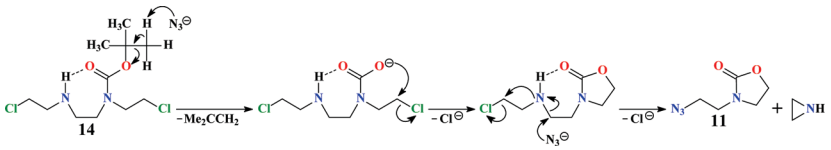
The above described strategy suffers however from the low yield of the desired products **3**, **6** and **9** (yield: 5, 13 and 8%, respectively). To overcome this disadvantage, the secondary amine groups were first protected by the reaction of 2,2′-dichloroethylamine hydrochloride with Boc_2O under basic conditions leading to the formation of *tert*-butyl bis(2-chloroethyl)-carbamate (**10**), *tert*-butyl 2-chloroethyl(2-(2-chloroethylamino)-ethyl)carbamate (**14**) and *tert*-butyl 2,2′-azanediylbis(ethane-2,1-diyl)bis(2-chloroethylcarbamate) (**15**) (Schemes 4 and 5). Compounds **14** and **15** contain one and two carbamate functions, respectively (Scheme 5), which might be explained by the formation of intramolecular linear hydrogen bonds, in the structure of **14**, and bifurcated hydrogen bonds, in the structure of **15**, similar to those found in the structures of **5** and **8** (Schemes 2 and 3). The terminal chlorine atoms of **10**, **14** and **15** were substituted by the azide groups with the aim to obtain corresponding bis-azides. However, due to the basic character of the azide anion, a terminal hydrogen atom of the *tert*-butyl group was abstracted by azide leading to the elimination of the isobutene group with the subsequent elimination of the chloride atom by the carbamate. Thus, 3-(2-azidoethyl)oxazolidin-2-one (**11**) was formed in all cases (Schemes 4 and 5). The instability of Boc under substitution conditions of chlorine leading to **11** is surprising taking into account the extreme resistance of Boc towards basic and nucleophilic reagents.[25] The Boc deprotection



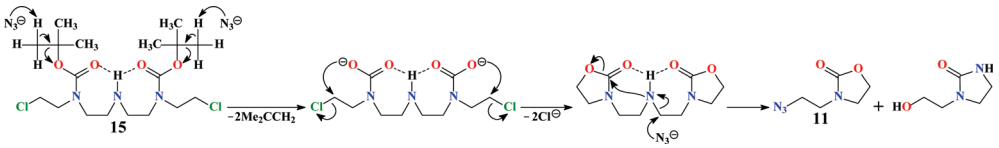
Scheme 4



Scheme 5



Scheme 6



Scheme 7

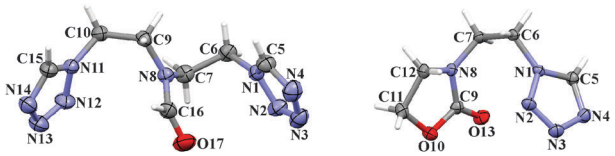


Fig. 1 Thermal ellipsoid (50%) plot of **2** (left) and **13** (right).

by a E_2 mechanism as described in Schemes 6 and 7 for **14** and **15** has not been used in the common literature of total syntheses up to now.

The fragmentation of **14** and **15** under such substitution conditions, which is also described in Schemes 6 and 7, is both unexpected and unprecedented.

The product **11** was considered as an intriguing precursor for the further formation of the corresponding tetrazole. Thus, synthetic conditions have been optimized and high temperature accompanied by the presence of KI were found to be the most appropriate conditions. Indeed, the iodine atom promotes the *trans*-halogenation, providing a better leaving group, while high temperature conditions favour the removal of isobutene. The azide group of **11** was subsequently reduced using PPh_3 and water to afford 3-(2-aminoethyl)oxazolidin-2-one (**12**), whose amine group was further involved in the tetrazole cyclization by reacting with NaN_3 and $HC(OEt)_3$ leading to 3-(2-(1*H*-tetrazol-1-yl)ethyl)oxazolidin-2-one (**13**) (Scheme 4), whose crystal structure has been determined (*vide infra*).

Spectroscopic and structural characterization

All obtained tetrazoles and intermediate products were fully characterized by ^{1}H NMR spectroscopy and mass-spectrometry, and their compositions were established by elemental analysis.

Recrystallization of **2** and **13** from hot methanol leads to the formation of X-ray suitable crystals, whose structures were refined in the monoclinic space group $P2_1/a$. The molecular structures of **2** and **13** are shown in Fig. 1, while the selected bond lengths and angles are listed in Tables S1 and S2 in ESI,† respectively. No significant intra- and intermolecular interactions have been found for both structures. Packing of **2** and **13** is shown in Fig. 2 and 3, respectively. It is worth noting that the *N*,*N*-diethylformamide spacer in the structure of **2** exhibits a $g^+g^+g^+g^+$ conformation (Fig. 1).

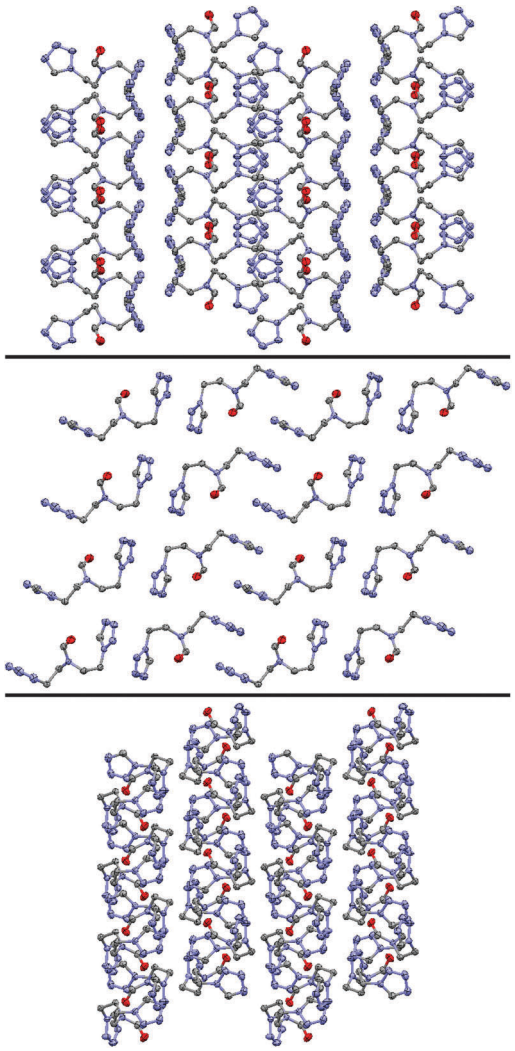


Fig. 2 Thermal ellipsoid (30%) plot of packing of **2** along the *0a* (top), *0b* (middle) and *0c* (bottom) axes. H-atoms were omitted for clarity.

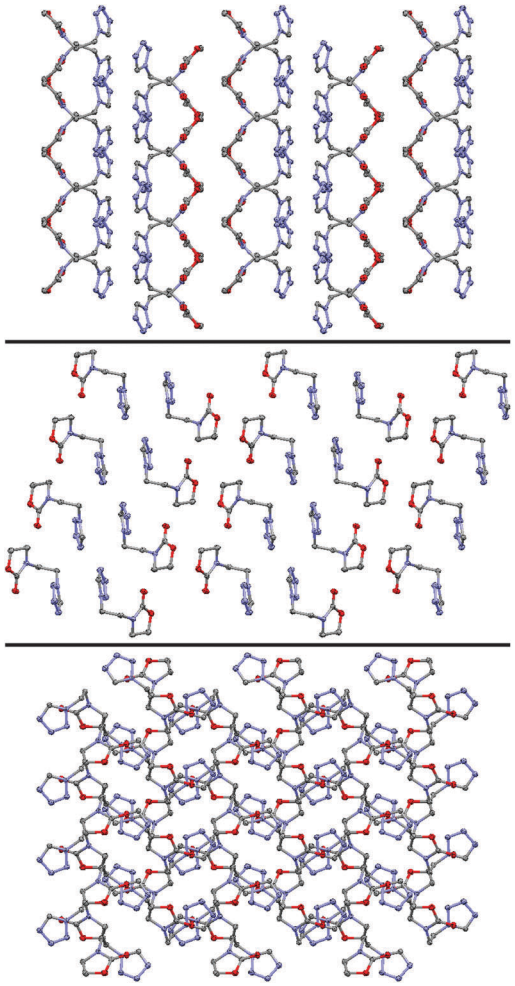


Fig. 3 Thermal ellipsoid (50%) plot of packing of **13** along the *0a* (top), *0b* (middle) and *0c* (bottom) axes. H-atoms were omitted for clarity.

Conclusions

In summary, we have developed syntheses of mono-tetrazole **1** and bis-tetrazoles **2**, **3**, **5**, **6**, **8** and **9**. Unexpected instability of Boc under basic and nucleophilic conditions at high temperature followed by fragmentation of **14** and **15** afforded the mono-tetrazole **13**, whose crystal structure is presented. All obtained tetrazole compounds are of potential interest as ligands for the formation of coordination polymers with an advanced set of properties, in particular spin crossover behaviour in the case of Fe^{II} complexes.[7] Furthermore, the bis-tetrazoles **2**, **3**, **5**, **6**, **8** and **9** are of particular interest as precursors for further functionalization due to the formamide and secondary amine functions. Moreover, molecules **2**, for which the crystal structure is described, **5**, **8** and **13** might be interesting synthons for the formation of novel ditopic ligands for use in metal–organic frameworks.[21,22]

Experimental

General procedures

Infrared spectra in KBr were recorded using a BioRad FTS 135 spectrometer in the range 400–3600 cm^{-1}. ^1H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C. Mass spectra were recorded on a Thermo Finnigan LCQ Ion Trap spectrometer using APCI mode by detecting positive ions. Elemental analyses were carried out at the University College of London (UK).

Syntheses

1-(2-(4,5-Dihydro-1*H*-imidazol-1-yl)ethyl)-1*H*-tetrazole (1), 1,2-bis(4,5-dihydro-1*H*-imidazol-1-yl)ethane (4) and bis(2-(4,5-dihydro-1*H*-imidazol-1-yl)ethyl)amine (7). Acetic acid (60 mL) was slowly added to a mixture of diethylenetriamine, triethyl enetetramine or tetraethylenepentamine (0.1 mol; 10.3, 14.6 and 18.9 g, respectively), NaN_3 (14.3 g, 0.22 mol) and $HC(OEt)_3$ (53.3 g, 0.36 mol). The reaction mixture was heated at 85 °C for 3 h and cooled. Then concentrated HCl (22 mL) was added. The solvent was then removed *in vacuo*. The obtained yellow or yellowish brown oil was dissolved in MeOH–ethyl acetate (1 : 1, v/v) and filtered. The corresponding product was precipitated as a white or beige powder on standing.

1. Yield: 4.49 g (27%). ^1H NMR (D_2O), δ: 4.04 (br. s, 4H, CH_2, ethylene spacer), 4.14 (t, $^3J_{H,H}$ = 5.6 Hz, 2H, CH_2, dihydroimidazol), 4.89 (t, $^3J_{H,H}$ = 5.6 Hz, 2H, CH_2, dihydroimidazol), 8.26 (s, 1H, CH, dihydroimidazol), 9.34 (s, 1H, CH, tetrazole) ppm. MS (*m*/*z*): 167.0 $[M + H]^+$. Anal. Calc. for $C_6H_{10}N_6$ (166.19): C 43.36, H 6.07, N 50.57. Found: C 43.83, H 6.07, N 50.15%.

4. Yield: 7.15 g (43%). ^1H NMR (D_2O), δ: 4.11 (s, 4H, CH_2, ethylene spacer), 4.19 (t, $^3J_{H,H}$ = 5.7 Hz, 4H, CH_2, dihydroimidazol), 4.97 (t, $^3J_{H,H}$ = 5.7 Hz, 4H, CH_2, dihydroimidazol), 8.17 (s, 2H, CH, dihydroimidazol) ppm. MS (*m*/*z*): 167.2 $[M + H]^+$. Anal. Calc. for $C_8H_{14}N_4$ (166.23): C 57.81, H 8.49, N 33.71. Found: C 57.69, H 8.58, N 33.64%.

7. Yield: 8.16 g (39%). ^1H NMR (D_2O), δ: 3.89 (d. t, $^3J_{HNCH}$ = 6.2 Hz, $^3J_{H,H}$ = 5.8 Hz, 4H, NCH_2, ethylene spacer), 4.27 (d. t, $^3J_{HNCH}$ = 5.9 Hz, $^3J_{H,H}$ = 5.8 Hz, 4H, CH_2, ethylene spacer), 4.05 (t, $^3J_{H,H}$ = 5.6 Hz, 4H, CH_2, dihydroimidazol), 4.90 (t, $^3J_{H,H}$ = 5.6 Hz, 4H, CH_2, dihydroimidazol), 8.29 (s, 2H, CH, dihydroimidazol) ppm. MS (*m*/*z*): 209.1 $[M + H]^+$. Anal. Calc. for $C_{10}H_{19}N_5$ (209.29): C 57.39, H 9.15, N 33.46. Found: C 57.54, H 9.03, N 33.35%.

***N*,*N*-Bis(2-(1*H*-tetrazol-1-yl)ethyl)formamide (2), *N*-(2-(1*H*-tetrazol-1-yl)ethyl)-*N*-(2-(2-(1*H*-tetrazol-1-yl)ethylamino)ethyl)formamide (5) and *N*,*N*′-(2,2′-azanediylbis(ethane-2,1-diyl))bis(*N*-(2-(1*H*-tetrazol-1-yl)ethyl)formamide) (8).** The synthetic procedure is the same as that for **1**, **4** and **7**. However, the resulting yellow or yellowish brown oil was dissolved in MeOH (3 mL) and chromatographed on silica gel by elution first with ethyl acetate and then with MeOH. The fraction eluted with MeOH was collected and the solvent was then removed *in vacuo*. The obtained oil was dissolved in MeOH (20 mL) and diethyl ether (10 mL) was added. The product was obtained as brownish needles (**2**) or yellowish brown fine crystalline solids (**5** and **8**) on standing.

2. Yield: 1.19 g (5%). ^1H NMR (DMSO-d_6), δ: 3.73 (t, $^3J_{H,H}$ = 5.3 Hz, 4H, CH_2, ethylene spacer), 4.64–4.71 (m, 4H, CH_2 ethylene spacer), 7.53 (s, 1H, CHO), 9.36 (s, 1H, CH, tetrazole), 9.38 (s, 1H, CH, tetrazole) ppm. MS (*m*/*z*): 238.0 $[M + H]^+$. Anal. Calc. for $C_7H_{11}N_9O$ (237.22): C 35.44, H 4.67, N 53.14. Found: C

35.97, H 4.64, N 53.34%. Crystals of **2** suitable for single crystal X-ray analysis were obtained by dissolving the product (0.02 g) in hot MeOH (2 mL) with further slow evaporation of the solvent.

5. Yield: 3.64 g (13%). ^{1}H NMR (DMSO-d_6), δ: 3.58–4.82 (m, 12H, CH_2, ethylene spacer), 7.63 (s, 1H, CHO), 9.37 (s, 1H, CH, tetrazole), 9.42 (s, 1H, CH, tetrazole), 11.84 (br. s, 1H, NH) ppm. MS (*m*/*z*): 281.1 $[M + H]^+$. Anal. Calc. for $C_9H_{16}N_{10}O$ (280.29): C 38.57, H 5.75, N 49.97. Found: C 38.68, H 5.61, N 49.88%.

8. Yield: 2.93 g (8%). ^{1}H NMR (DMSO-d_6), δ: 3.62 (t, $^3J_{H,H}$ = 5.5 Hz, 4H, CH_2, ethylene spacer), 3.85 (t, $^3J_{H,H}$ = 5.4 Hz, 4H, CH_2, ethylene spacer), 4.26 (t, $^3J_{H,H}$ = 5.6 Hz, 4H, CH_2, ethylene spacer), 4.37 (t, $^3J_{H,H}$ = 5.6 Hz, 4H, CH_2, ethylene spacer), 7.76 (s, 2H, CHO), 9.32 (s, 1H, CH, tetrazole), 9.34 (s, 1H, CH, tetrazole), 12.28 (br. s, 1H, NH) ppm. MS (*m*/*z*): 367.3 $[M + H]^+$. Anal. Calc. for $C_{13}H_{24}N_{11}O_2$ (366.41): C 42.61, H 6.60, N 42.05. Found: C 42.74, H 6.54, N 42.13%.

Bis(2-(1*H*-tetrazol-1-yl)ethyl)amine hydrochloride (3·HCl), N^1,N^2-bis(2-(1*H*-tetrazol-1-yl)ethyl)ethane-1,2-diamine dihydrochloride (6·2HCl) and N^1-(2-(1*H*-tetrazol-1-yl)ethyl)-N^2-(2-(2-(1*H*-tetrazol-1-yl)ethylamino)ethyl)ethane-1,2-diamine trihydrochloride (9·3HCl). HCl (6 M, 10 mL) was added to **2**, **5** or **8** (0.22 mmol; 0.052, 0.062 and 0.081 g, respectively) and the mixture was refluxed overnight. The solvent was then removed *in vacuo*. The product was obtained as pale yellow or pale brown oil.

3·HCl. ^{1}H NMR (D_2O), δ: 3.71 (t, $^3J_{H,H}$ = 5.9 Hz, 4H, CH_2, ethylene spacer), 4.93 (t, $^3J_{H,H}$ = 5.9 Hz, 4H, CH_2, ethylene spacer), 9.26 (s, 2H, CH, tetrazole) ppm. MS (*m*/*z*): 210.0 $[M - Cl]^+$. Anal. Calc. for $C_6H_{12}ClN_9$ (245.67): C 29.33, H 4.92, N 51.31. Found: C 29.14, H 5.17, N 51.42%.

6·2HCl. ^{1}H NMR (D_2O), δ: 3.82 (t, $^3J_{H,H}$ = 5.8 Hz, 4H, CH_2, ethylene spacer), 4.11 (t, $^3J_{H,H}$ = 5.8 Hz, 4H, CH_2, ethylene spacer), 4.87 (t, $^3J_{H,H}$ = 5.9 Hz, 4H, CH_2, ethylene spacer), 9.29 (s, 2H, CH, tetrazole) ppm. MS (*m*/*z*): 289.6 $[M - Cl]^+$. Anal. Calc. for $C_8H_{18}Cl_2N_{10}$ (325.20): C 29.50, H 5.58, N 43.07. Found: C 29.37, H 5.51, N 43.14%.

9·3HCl. ^{1}H NMR (D_2O), δ: 3.67 (t, $^3J_{H,H}$ = 5.9 Hz, 4H, CH_2, ethylene spacer), 3.78 (t, $^3J_{H,H}$ = 5.9 Hz, 4H, CH_2, ethylene spacer), 4.16 (t, $^3J_{H,H}$ = 5.7 Hz, 4H, CH_2, ethylene spacer), 5.02 (t, $^3J_{H,H}$ = 5.7 Hz, 4H, CH_2, ethylene spacer), 9.27 (s, 2H, CH, tetrazole) ppm. MS (*m*/*z*): 369.1 $[M - Cl]^+$. Anal. Calc. for $C_{10}H_{24}Cl_3N_{11}$ (404.73): C 29.68, H 5.98, N 38.07. Found: C 29.82, H 6.08, N 38.19%.

3-(2-Azidoethyl)oxazolidin-2-one (11). A solution of **10**, **14** or **15** (0.033 mol; 8.0, 9.4 and 14.1 g, respectively), which were obtained by the similar procedure as described in ref. 20, NaN_3 (4.7 g, 0.072 mol) and KI (5.5 g, 0.033 mol) in DMF (100 mL) was refluxed for 4 h and cooled. To the resulting mixture toluene (100 mL) was added and the solution was filtered. The solvent was then removed *in vacuo*. The obtained orange oil was dissolved in water (20 mL) and extracted with diethyl ether (3 × 20 mL) and then with ethyl acetate (3 × 20 mL). The latter fraction was collected and dried with $MgSO_4$. The solvent was then removed *in vacuo*. The product was obtained as dark brown oil or a beige fine crystalline solid.

11. Yield: 2.16 g (42%), using **10**; 1.91 g (37%), using **14**; 2.47 g (48%), using **15**. ^{1}H NMR ($CDCl_3$), δ: 3.44 (t, $^3J_{H,H}$ = 5.1 Hz, 2H, CH_2, ethylene spacer), 3.53 (t, $^3J_{H,H}$ = 5.1 Hz, 2H, CH_2, ethylene spacer), 3.69 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH_2, oxazolidin-2-one), 4.36 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH_2, oxazolidin-2-one) ppm. MS (*m*/*z*): 157.0 $[M + H]^+$. Anal. Calc. for $C_5H_8N_4O_2$ (156.14): C 38.46, H 5.16, N 35.88. Found: C 38.48, H 5.27, N 35.65%.

3-(2-Aminoethyl)oxazolidin-2-one (12). A solution of **11** (0.0064 mol, 1 g) was added drop-wise to a cold solution of PPh_3 (2.1 g, 0.008 mol) in MeCN–THF (1 : 1, v/v; 40 mL). The reaction mixture was stirred for 2 h and water (25 mL) was added. MeCN and THF were then removed *in vacuo* and the mixture was filtered. Water was then removed *in vacuo*. The product was obtained as a pale yellow liquid. Yield: 0.77 g (92%). ^{1}H NMR (DMSO-d_6), δ: 1.80 (br. s, 2H, NH_2), 2.72 (t, $^3J_{H,H}$ = 6.3 Hz, 2H, CH_2, ethylene spacer), 3.17 (t, $^3J_{H,H}$ = 6.3 Hz, 2H, CH_2, ethylene spacer), 3.44 (t, $^3J_{H,H}$ = 8.1 Hz, 2H, CH_2, oxazolidin-2-one), 4.24 (t, $^3J_{H,H}$ = 8.1 Hz, 2H, CH_2, oxazolidin-2-one) ppm. MS (*m*/*z*): 131.1 $[M + H]^+$. Anal. Calc. for $C_5H_{10}N_2O_2$ (130.15): C 46.14, H 7.74, N 21.52. Found: 46.29, 7.68, N 21.60%.

3-(2-(1*H*-tetrazol-1-yl)ethyl)oxazolidin-2-one (13). Acetic acid (38 mL) was slowly added to a mixture of **12** (0.0058 mol, 0.75 g), NaN_3 (0.46 g, 0.007 mol) and $HC(OEt)_3$ (2.31 g, 0.0156 mol). The reaction mixture was heated at 105 °C for 20 h and cooled. The solvent was then removed *in vacuo*. The obtained yellow oil was dissolved in hot ethyl acetate (3 mL). The resulting solution was kept at −18 °C until an orange or pale brown powder was precipitated. The product was filtered off and dissolved in hot MeOH (3 mL). The resulting solution was kept at 18 °C until a pale orange powder was precipitated. Yield: 0.93 g (88%). ^{1}H NMR ($CDCl_3$), δ: 3.38 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH_2, oxazolidin-2-one), 3.81 (t, $^3J_{H,H}$ = 5.7 Hz, 2H, CH_2, ethylene spacer), 4.28 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, CH_2, oxazolidin-2-one), 4.73 (t, $^3J_{H,H}$ = 5.7 Hz, 2H, CH_2, ethylene spacer), 8.97 (s, 1H, CH, tetrazole) ppm. MS (*m*/*z*): 184.0 $[M + H]^+$. Anal. Calc. for $C_6H_9N_5O_2$ (183.17): C 39.34, H 4.95, N 38.23. Found: C 39.18, H 4.92, N 38.14%. Crystals suitable for single crystal X-ray analysis were obtained by dissolving of **13** (0.02 g) in hot MeOH (2 mL) with further slow evaporation of the solvent.

X-Ray crystallography

The X-ray data for **2** and **13** were collected at 293 and 120 K, respectively, using an MAR345 image plate and Mo–Kα (λ = 0.71069 Å) radiation. The unit cell parameters were refined using all the collected spots after the integration process. The data were not corrected for absorption, but the data collection mode partially takes the absorption phenomena into account. All structures were solved by direct methods using SHELX97[26] and refined by full-matrix least-squares on F^2 using SHELX97.[26] All non-hydrogen atoms were refined with anisotropic temperature factors. All H-atoms were localized by Fourier-difference synthesis. The H-atoms were included in the refinement with a common isotropic temperature factor; when calculated, they were refined using appropriate riding models. Figures were generated using the program Mercury.[27]

Crystal data for 2. $C_{17}H_{11}N_9O$, M_r = 237.25 g mol^{-1}, monoclinic, space group $P2_1/a$, a = 12.849(3), b = 5.378(2), c = 16.169(5) Å, β = 102.50(2)°, V = 1090.8(6) Å^3, Z = 4, ρ = 1.445 g cm^{-3},

μ(Mo–Kα) = 0.109 mm^{-1}, reflections: 4521 collected, 1525 unique, R_{int} = 0.055, R_1(all) = 0.0430, wR_2(all) = 0.1144.

Crystal data for 13. $C_6H_9N_5O_2$, M_r = 183.18 g mol^{-1}, monoclinic, space group $P2_1/a$, a = 10.619(3), b = 5.430(2), c = 14.639(5) Å, β = 108.69(2)°, V = 799.6(5) Å^3, Z = 4, ρ = 1.522 g cm^{-3}, μ(Mo–Kα) = 0.119 mm^{-1}, reflections: 12338 collected, 1620 unique, R_{int} = 0.057, R_1(all) = 0.0400, wR_2(all) = 0.1231.

Acknowledgements

This work was funded by the Fonds National de la Recherche Scientifique-FNRS (FRFC 2.4508.08, 2.4537.12) and ARC Louvain. We thank the Fonds pour la Recherche dans l'Industrie et dans l'Agriculture for a doctoral scholarship allocated to Y.B., and the F.R.S.-FNRS (Belgium) and WBI (Belgium) for post-doctoral positions allocated to D.A.S. and M.G.B. We are also grateful to the COST action MP1202. ''Rational design of hybrid organic–inorganic interfaces: the next step towards advanced functional materials''.

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