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Synthesis, characterization and mesomorphic properties of Ag(I) and Pd(II) complexes containing the pyridyl and tetrazoyl rings: crystal structure of $[C_{30}H_{46}N_{10}Ag\ ClO_4]$

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The synthesis of new monodentate heterocyclic ligands 5-(4-pyridyl)-2-alkyltetrazole (**L¹a,b**) and 4-[5-(2-alkyltetrazole)]aryl-4′-pyridinecarboxylate (**L²a,b,c**) containing two or three aromatic or heterocyclic rings (tetrazole, pyridine and benzene) and preparation of their corresponding silver(I) and palladium(II) complexes (**Ia,b,c** and **IIa,b,c**) are described. The thermal behaviour of the ligands and complexes was characterized by polarizing optical microscopy. The ligands and the complexes **Ia,b,c** and **IIc** showed no liquid crystalline phase. The complexes **IIa,b** showed mesomorphic behaviour, exhibiting smectic A enantiotropic mesomorphism X-ray diffraction measurements for complex **Ia** showed monodentate coordination of N-pyridine, and no coordination on the nitrogen atoms of the tetrazole ring.

1. Introduction

In the last 10–15 years, metallomesogen literature has increased several-fold and has been well reviewed [1, 2]. At present, there is much interest in the synthesis of metal-containing liquid crystals because of perceived advantages in combining the properties of liquid crystal systems with those of transition metals [3]. Metallomesogens have potential applications in optical devices; the basis for this prediction are the physical properties of metal complexes which are also assumed to be present in the metal mesogenic molecular skeleton. The synthesis of new mesogenic molecules with different ligands, metals or molecular geometries, is therefore a current subject of research.

Metal-containing compounds that exhibit thermotropic mesomorphism can be either coordination or organometallic complexes. In this work our interest is in coordination compounds and we describe the ability of monodentate heterocyclic ligands containing two or three of the aromatic ring structures tetrazole, pyridine and benzene, to generate mesomorphic behaviour [4]. We explored the influence of alkyltetrazole substituted at the terminal position of the ligands **L¹** and **L²** and the characterization of the mesomorphic properties of their Ag(I) complexes. With ligand **L²** we studied also the Pd(II) complex, **Ic**. We have also investigated the effect of the methoxy group as the lateral substituent in ligand **L²**. The effect of a lateral substituent is very well documented in the literature for organic mesogens and has been used as a useful strategy for modifying mesomorphism and consequently mesophase properties [5]. However, there are only limited studies involving mesogenic metal complexes containing lateral substituents [6]. Therefore, the possibility of using the methoxy group as a lateral substituent in **L²**, since this ligand contains three aromatic rings (a certain minimum size of the molecules is necessary for the investigation of the influence of lateral substitution [7]) represents a convenient strategy for decreasing the melting point of the complex.

The general structures of the new complexes are shown in figure 1.

2. Results and discussion

2.1. *Synthesis of the ligands* L^1 *and* L^2

The synthetic route used for preparation of ligands **L¹** and **L²** is shown in scheme 1. All the ligands synthesized were fully characterized by elemental analysis, NMR and IR spectroscopy. The synthetic route involved the formation of aryltetrazoles **2** and **4a,b** by the reaction of 4-cyanopyridine **1** or the corresponding hydroxyarylnitrile **3** with sodium azide, subsequent protection of the phenolic hydroxyl group and then alkylation of the tetrazole ring [8, 9]. The phenolic hydroxyl group was protected as an ester to prevent an O-alkylation reaction.

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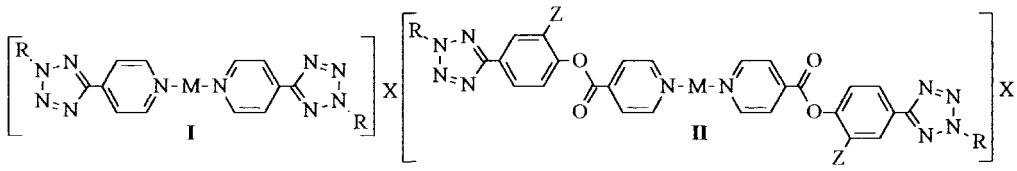


I **II**

a) M = Ag X = ClO_4 R = C_9H_{19}
b) M = Ag X = ClO_4 R = $C_{14}H_{29}$
c) M = Pd X = 2 OAc R = C_9H_{19}

a) M = Ag X = ClO_4 Z = H R = C_9H_{19}
b) M = Ag X = ClO_4 Z = H R = $C_{14}H_{29}$
c) M = Ag X = ClO_4 Z = CH_3O R = C_9H_{19}

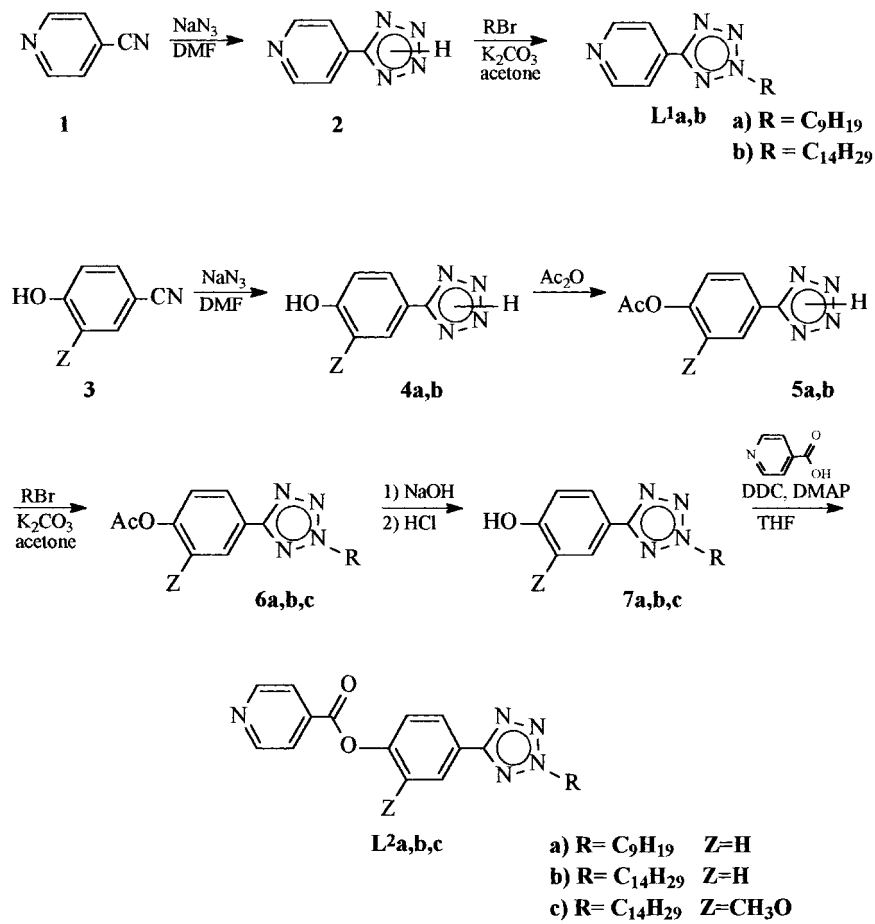
Figure 1. General structure of complexes of ligands L^1 and L^2.

Alkylation with the appropriate alkyl bromide followed by deprotection furnished the 5-(4-pyridyl)-2-alkyltetrazoles **L^1a,b** or the 5-(4-hydroxyphenyl)-2-alkyltetrazoles **7a,b,c**.

The tetrazolate anion is an ambidentate system in which alkylation reactions can occur at the N-1 or N-2 positions, the relative proportions of which depend upon the conditions of the alkylation and the influence of the 5-substituent. However, in our case, spectroscopic evidence suggests that the N-2 anion in the tetrazole ring is the nucleophile in alkylation. The regioselectivity in alkylation was confirmed by analysis of ^{13}C NMR chemical shifts of the C5 carbon atom in the tetrazole ring. For the ligands **L^1a,b** and **L^2a,b,c** the chemical shift for C5 varied from 163.5 to 162.7 ppm. A comparison of these values with those found by Butler *et al.* [10, 11] in similar systems is in agreement with the chemical shifts of the regioisomer N-2. This regioselectivity is due to the large steric hindrance at the N-1 position considering the size of the alkylating agents used.

2.2. *Silver and palladium complexes*

The complexes were prepared accordingly to reaction scheme 2. The reactions were carried out by stirring two equivalents of the corresponding ligand **L^1a,b** or **L^2a,b,c** with one equivalent of silver perchlorate in methanol solution at room temperature, or with one equivalent



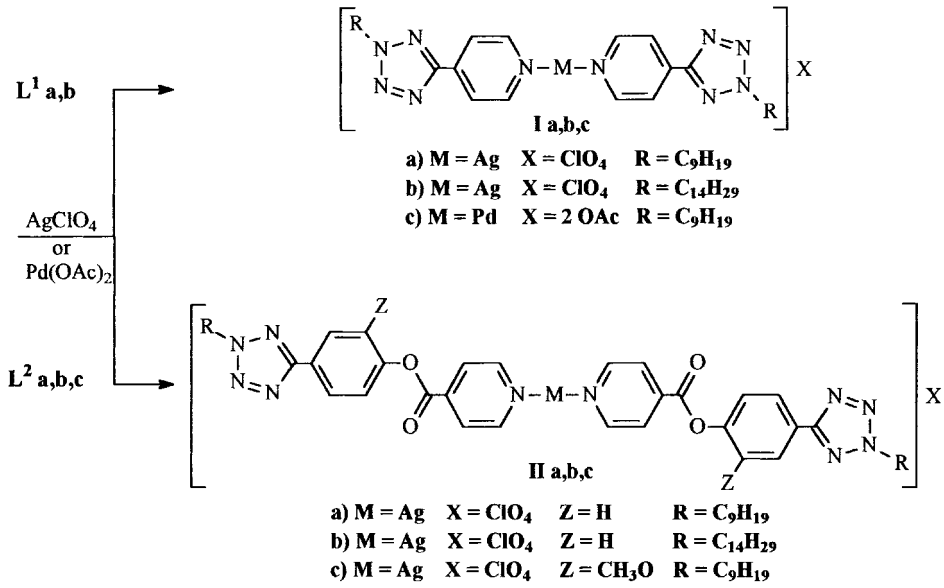
1 **2** **L^1a,b** **a)** R = C_9H_{19} **b)** R = $C_{14}H_{29}$

3 **4a,b** **5a,b**

6a,b,c **7a,b,c**

L^2a,b,c **a)** R= C_9H_{19} Z=H **b)** R= $C_{14}H_{29}$ Z=H **c)** R= $C_{14}H_{29}$ Z=CH_3O

Scheme 1.



Scheme 2.

of palladium diacetate in acetic acid solution at 90°C. The ligands **L¹** or **L²** contain four N-donor atoms, one N-pyridyl and three nitrogen atoms of the tetrazole ring, which are capable of acting as coordination sites. Structural studies have shown that tetrazole and its derivatives have a rich variety of coordination modes with transition metals [8, 12, 13]. With the ligands **L¹** or **L²**, the nitrogen atoms of the tetrazole ring may act in one of three distinct coordination modes: (a) formation of the organo-metal compound, (b) bidentate coordination, (tetrazole may be bridging) and (c) monodentate nitrogen coordination, in addition to monodentate N-pyridyl coordination [14, 15]. However, in the case of Ag(I) only a monodentate nitrogen coordination mode through the N-tetrazole or N-pyridine should be possible since Ag(I) preferentially stabilizes linear compounds with coordination number 2.

The analytical and NMR spectroscopic data for the complexes are consistent with mononuclear $Ag(\mathbf{L})_2X$ and $[Pd(\mathbf{L}_2X_2]$ stoichiometry with monodentate coordination of the pyridine. The complexes and free ligand have similar spectra, but small differences in the aromatic region indicate that complexation has been achieved. For example, the ^{1}H NMR spectra for the complexes **Ia,b,c** or **IIa,b,c** in the AA′XX′ system, pyridyl ring, $\Delta\nu/J > 10$, the protons on the carbons *ortho* to the nitrogen of the pyridine ring were shifted to higher frequencies by a few tenths of ppm, relative to their positions in the spectra in the free ligands, while the carbons *ortho*, *meta* and *para* to the ring nitrogen were shifted to higher frequencies by 1.41–2.71 ppm. The Pd(II) complex was further characterized by the presence of an additional singlet at around 1.88 ppm due to the methyl protons of the acetate anion. The purity of the ligands and complexes was confirmed by elemental analysis.

In all cases of the Ag(I) complexes no coordination of the nitrogen atoms of the tetrazole ring was observed; the monodentate coordination products of N-pyridine were isolated and the structure of complex **Ia** was confirmed by an X-ray diffraction study.

2.3. *Crystal structure determination of complex* ***Ia***

To see if intermolecular interactions were of potential importance in determining the phase behaviour of our materials, we undertook structure determination of the complexes. Unfortunately, all attempts to grow single crystals suitable for X-ray analysis were unsuccessful except for complex **Ia**, for which a colourless crystalline solid was obtained from 1-butanol.

Figure 2 shows the structure of **Ia** and the labelling scheme. The overall molecular shape is S-like and nearly flat. Table 1 gives crystallographic data; structure refinement and selected bond distances and bond angles are given in table 3.

The single-crystal structure consists of two parallel monomeric molecules of the complex, separated by a Ag … Ag distance of 3.353(1) Å. The Ag ion is coordinated by two ligand molecules in an approximately linear arrangement through the pyridine nitrogen atoms: N … Ag … N 176.4(1)°, Ag … N5′ 2.145(3) Å, Ag … N5 2.147(3) Å. An inversion centre exists between each Ag cation, where each Ag interacts weakly by secondary interactions with two different oxygen atoms of the

Table 1. Crystal data and structure refinement for bis[5-(4-pyridyl)-2-nonyltetrazole]silver(I) perchlorate.

Empirical formula	$C_{30}H_{46}AgClN_{10}O_4$
Formula weight	754.09
Crystal system	Triclinic
Space group	$P_{1\searrow}$
a (Å)	7.806(2)
b (Å)	11.171(2)
c (Å)	20.627(4)
α (°)	83.34(3)
β (°)	79.40(3)
γ (°)	85.63(3)
Volume (Å^3)	1753.3(6)
Z	2
D_{calc} (g cm^{-1})	1.428
μ (mm^{-1})	0.70
$F(000)$	784
Crystal size (mm^3)	0.42 × 0.36 × 0.13
Theta range (°)	2.59 to 25.00
Unique reflections	6171 [$R_{int} = 0.0243$]
Refinement method	Full-matrix least-squares on F^2
Parameters/restraints	434/65
Extinction coefficient	0.0029(5)
GOOF (on F^2)	1.037
$R1$ [$I > 2\sigma(I)$][a]	0.0377
wR_2 (all data)[b]	0.1023
Residual in D-map (e Å^{-3})	0.446 and −0.455

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$.
[b] $wR_2 = \{\Sigma \, [w(F_o^2 - F_c^2)^2] / \Sigma \, [w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o^2) + (0.0466P)^2 + 0.9636P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

perchlorate anions, Ag…O4 2.896(3) Å and Ag…O3i 3.187(4) Å, leading to a centrosymmetric molecule. This secondary interaction is also responsible for the non-linear arrangement, figure 3. The pyridyl and tetrazoyl rings are essentially coplanar and the dihedral angles between their least-squares planes are 10.1(1)° and 11.1(1)°. The two pyridyl fragments which lie mutually *trans* to the silver atoms are twisted relative to one another by 8.5(1)°.

2.4. *Thermal properties*

The ligands **L^{1}a,b** and **L^{2}a,b,c** show no liquid crystalline phases. The absence of mesogenic properties of the tetrazole derivatives may tentatively be attributed to the presence of the pentagonal tetrazole ring which produces a non-linear substitution and thereby an accentuated molecular curvature which inhibits liquid crystal formation. The same behaviour was observed in the complexes **Ia,b,c**, where the length of the mesogenic rigid core is increased from 7.2 Å (for the free ligand) to 16.7 Å, more than double. Even so, none of the complexes were liquid crystals.

Finally, we tried to obtain liquid crystalline phases by variation of the structure of the ligands, **L^{2}a,b** and formation of the complexes **IIa,b**. The idea was to increase the rigid core length of the ligand by incorporating an additional six-membered ring linked by a carboxylic group into the rigid core increasing the length from 12.5 Å in the free ligand to 27.4 Å in the complexes. With a lateral methoxy group it was observed that the liquid crystalline phase is totally suppressed in complex **IIc**, and the melting point increases by about ten degrees.

The phase transition temperatures and optical textures were studied by polarising optical microscopy (POM). The identification of the mesophases on the basis of optical texture results is summarized in table 2.

Only complexes **IIa,b** show mesomorphic behaviour. On cooling the isotropic liquid, the smectic A (SmA) phase appears as *batônnets* forming a focal-conic texture. This SmA phase was easily confirmed by the partial appearance of homeotropic texture, without subjecting the samples to mechanical stress. In this phase, the molecule may spontaneously align normal to the surface, giving a dark essentially textureless field between crossed polarizers.

The mesomorphic behaviour of these complexes can easily be explained if it is assumed that the distortion of molecular shape is reduced somewhat because the tetrazole ring is shifted to the terminal position of the rigid aromatic core. At this position the flexible *n*-alkyl chain allows partial compensation of the molecular bend, and the ratio of length to width is also increased. Another contribution to mesomorphism is the presence of a carboxylic group that undergoes intermolecular interaction owing to the dipole moment of the ester group across the molecular axis, and is widely used for the construction of liquid crystalline materials.

3. Experimental

All reagents used in the synthesis were purchased from Aldrich Chemical Company (USA) and solvents were used as received from E. Merck. Elemental analyses were performed using a Perkin-Elmer model 2400 instrument. Infrared spectra were recorded on a Perkin-Elmer model 781 spectrometer in KBr disk or film. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC-200F spectrometer at 200 MHz and 50.4 MHz, respectively. Chemical shifts are reported relative to tetramethylsilane

Table 2. Thermal behaviour of the metal complexes **IIa,b,c**; transition temperatures in °C.

Complex	R	Cr		SmA		I
IIa	C_9H_{19}	•	174.0	•	203.8	•
IIb	$C_{14}H_{29}$	•	178.4	•	202.2	•
IIc	C_9H_{19}	•	183.5	—	—	•

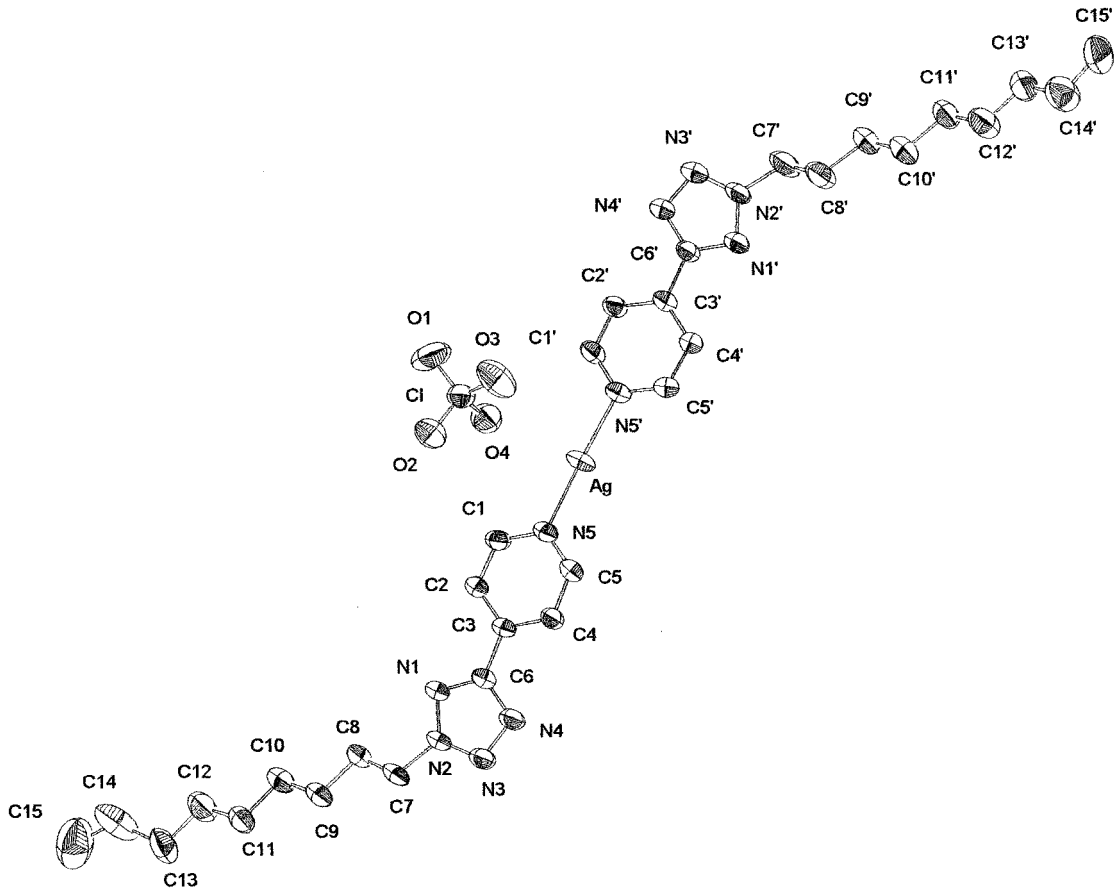


Figure 2. ZORTEP drawing with labelling scheme showing the asymmetric unit contents found in the crystal structure determination of complex **Ia**, $[C_{30}H_{46}N_{10}Ag{-}ClO_4]$. Ellipsoids are at 40% probability level; hydrogen atoms are omitted for clarity.

and in units of ppm. Textures and transition temperatures for compounds were observed by POM using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP 82 heating stage.

3.1. *X-ray data collection and structure refinement*

For the X-ray analysis, a colourless crystal of **Ia** was isolated and mounted on a CAD-4 diffractometer employing a graphite monochromator, Mo-K_α radiation ($\lambda = 0.71073$ Å). Cell constants were determined by centering 25 reflections in the theta range 9.70°–13.25°. Intensities of 6520 reflection were collected using $\omega/2\theta$ scan at room temperature. All reflections were corrected for Lorenz and polarization factors. An absorption correction based on 7 ψ-scans were also applied [16], with maximum and minimum transmission factors of 0.95659 and 0.82643, respectively. The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXS97 and SHELXL97 programs [17]. All heavy atoms were refined anisotropically, whereas H atoms were added at their calculated positions and included in the structure factor calculations using a riding model. There are 2 disordered carbon atoms in the unprimed carbon chain, where the C14 and C15 atoms have two alternative positions. The site occupation for these atoms were refined and they were 0.45(3) for C14 and C15 and 0.55(3) for C14* and C15*. A view of molecular structure was obtained with the ZORTEP program [18]. Further information on crystal structure and refinement is listed in tables 1 and 3.

3.2. *Preparation of materials*

3.2.1. *5-(4-Pyridyl)tetrazole* ***2***

This was prepared by a literature method [19] and recrystallized from ethanol/water to give a yellow solid, yield 70.0% (9.9 g), m.p. 261.0–263.4°C (lit. 254°C) [19]. IR (KBr, cm^{-1}) ν_{max}: 3058, 2530, 2110, 2024, 1632, 1528, 1438, 1388, 846.

3.2.2. *5-(4-Pyridyl)-2-alkyltetrazoles* ***L*^{1}

A solution of 5 g (34 mmol) 5-(4-pyridyl)tetrazole **2**, the appropriate alkyl bromide (34.0 mmol), 4.76 g (34.0 mmol) potassium carbonate in cyclohexanone (100 ml) was heated at reflux for 56 h. After cooling to

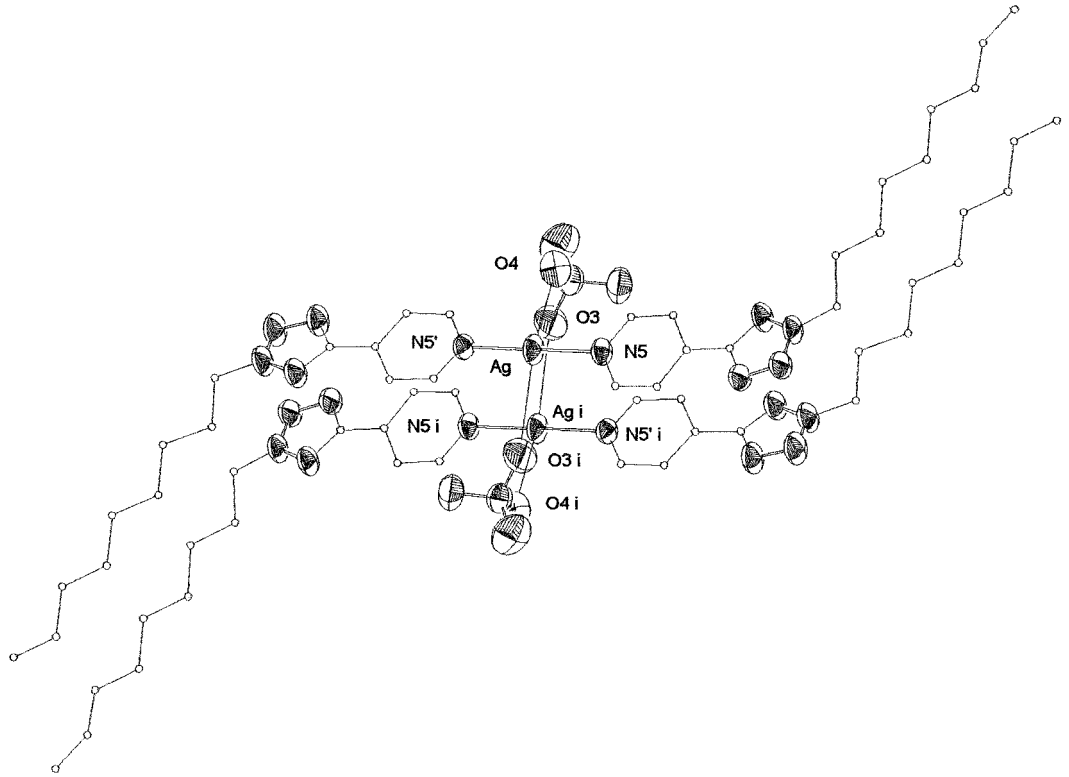


Figure 3. A view of complex **Ia** showing the weak interactions between Ag cation complex units and the perchlorate counterions. The C atoms are shown in arbitrary size and H atoms are omitted for clarity. Atoms labelled with i were generated by the symmetry operation $-x, -y, -z$.

Table 3. Selected bond lengths and angles for bis[5-(4-pyridyl)-2-nonyltetrazole]silver(I) perchlorate. Symmetry code: $^{i}\ -x, -y, -z$

Ag–N5′	2.145(3)
Ag–N5	2.147(3)
Ag–O4	2.896(3)
Ag–O3^{i}	3.187(4)
N5′–Ag–N5	176.4(1)
N5′–Ag–O4	91.2(1)
N5–Ag–O4	90.2(1)
N5′–Ag–O3^{i}	89.8(1)
N5–Ag–O3^{i}	90.0(1)
O4–Ag–O3^{i}	160.37(9)

room temperature, the solid formed was filtered off. The solution was concentrated in a rotary evaporator and the residue distilled to give the pure product.

3.2.2.1. *5-(4-Pyridyl)-2-nonyltetrazole* ***L^{1}a***. Distillation at 180°C (0.5 mm Hg) gave a yellow liquid, yield 70.0% (6.5 g). IR (KBr, cm^{-1}) ν_{max}: 2926, 2856, 1612, 1460, 1420, 836, 754. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.76$ (d, $J = 6.0$ Hz, 2H, $-C_5H_4N$), 8.02 (d, $J = 6.0$ Hz, 2H, $-C_5H_4N$), 4.68 (t, $J = 7.1$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.07 (m, 2H, $-NCH_2C\underline{H}_2$), 1.30 (m, 12H, $-CH_2-$), 0.87 (t, $J = 6.7$ Hz, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 162.7$ ($-CN_4-$), 150.4, 134.7, 120.5, 53.2 ($-NCH_2-$), 31.5, 29.1, 29.0, 28.9, 28.6, 26.1, 22.4 (7C, $-CH_2-$, nonyl chain), 13.8 (1C, $-CH_3$). CHN: found C 65.98, H 8.32, N 25.73; requires C 65.90, H 8.48, N 25.62%.

3.2.2.2. *5-(4-Pyridyl)-2-tetradecyltetrazole* ***L^{1}b***. Distillation at 195°C (0.4 mm Hg) or recrystallization from acetonitrile/water gave a yellow solid, yield 75.0% (7.9 g), m.p. 49.3°C. IR (KBr, cm^{-1}) ν_{max}: 2920, 2848, 1610, 1466, 1422, 836, 770, 750. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.76$ (d, $J = 6.0$ Hz, 2H, $-C_5H_4N$), 8.02 (d, $J = 6.0$ Hz, 2H, $-C_5H_4N$), 4.68 (t, $J = 7.1$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.10 (m, 2H, $-NCH_2N\underline{H}_2-$), 1.25 (m, 22H, $-CH_2-$), 0.88 (t, $J = 6.7$ Hz, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 162.7$ ($-CN_4-$), 150.4, 134.7, 120.5, 53.2 ($-NCH_2-$), 31.5, 29.1, 29.0, 28.9, 28.6, 26.1, 22.4 (12C, $-CH_2-$, tetradecyl chain), 13.8 (1C, $-CH_3$). CHN: found C 69.63, H 9.96, N 20.29; requires C 69.45, H 10.13, N 19.95%.

3.2.3. *5-(4-Hydroxyaryl)tetrazoles* ***4***

A suspension of 0.15 mol of 4-hydroxyarylnitrile **3**, 37.5 g (0.60 mol) of sodium azide, and 30.9 g (0.60 mol) of ammonium chloride in 100 ml of dimethylformamide was stirred overnight at 160°C. After cooling, the solvent

was concentrated in a rotary evaporator and the reaction mixture poured into 250 ml of ice/water and acidified with hydrochloric acid. The white precipitate was isolated by filtration, washed with ice water and recrystallized.

3.2.3.1. *5-(4-Hydroxyphenyl)tetrazole* ***4a***. Recrystallization from water gave a white solid, yield 80.0% (19.4 g), m.p. 241.8°C. IR (KBr, cm^{-1}) ν_{max}: 3420, 2710–2630 (broad), 1614, 1414, 1280, 840. ^1H NMR (200 MHz, DMSO-d_6) $\delta = 10.30$ (br s, 1H, −OH), 7.95 (d, $J = 8.4$ Hz, 2H, $-C_6H_4-$), 7.05 (d, $J = 8.4$ Hz, 2H, $-C_6H_4-$), 4.65 (br s, 1H, $-CN_4H$). CHN: found C 54.28, H 5.16, N 31.68; requires C 54.13, H 5.12, N 31.33%.

3.2.3.2. *5-(4-Hydroxy-2-methoxyphenyl)tetrazole* **4b**. Recrystallization from water gave a white solid, yield 61.0% (5.5 g), m.p. 215.6–217.1°C. IR (KBr, cm^{-1}) ν_{max}: 3410, 2710–2630 (broad), 1608, 1514, 1250, 840. ^1H NMR (200 MHz, DMSO-d_6) $\delta = 9.81$ (br s, 1H, −OH), 7.58 (d, $J = 1.7$ Hz, 1H, $-C_6H_3-$), 7.50 (dd, $J = 8.1$ Hz, $J = 1.7$ Hz, 1H, $-C_6H_3-$), 6.97 (d, $J = 8.1$ Hz, 1H, $-C_6H_3-$), 3.87 (s, 3H, $-OCH_3$), 3.51 (br s, 1H, $-CN_4H$). CHN: found C 52.28, H 5.37, N 27.09; requires C 52.17, H 5.45, N 27.04%.

3.2.4. *5-(4-Acetoxyaryl)tetrazoles* ***5***

To a suspension of 5-(4-hydroxyaryl)tetrazole **4** (50 mmol) in 30 ml of water was added a solution of 3M sodium hydroxide until the solid was completely dissolved. Ice and acetic anhydride (5 ml, 53 mmol) were then added and the mixture vigorously stirred for 10 to 15 min. The reaction mixture was acidified with hydrochloric acid. The acetate was isolated by filtration, washed with cool water and recrystallized.

3.2.4.1. *5-(4-Acetoxyphenyl)tetrazole* ***5a***. Recrystallization from ethanol/water gave a white solid, yield 98.0% (10 g), m.p. 182°C. IR (KBr, cm^{-1}) ν_{max}: 2716–2620 (broad), 1754, 1614, 1502, 1212, 912. ^1H NMR (200 MHz, DMSO-d_6) $\delta = 8.18$ (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 7.49 (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 6.21 (br s, 1H, $-CN_4H$), 2.39 (s, 3H, CH_3CO_2-). CHN: found C 54.82, H 5.10, N 25.59; requires C 54.79, H 5.06, N 25.46%.

3.2.4.2. *5-(4-Acetoxy-2-methoxyphenyl)tetrazole* ***5b***. Recrystallization from ethanol/water gave a white solid, yield 94.0% (6.3 g), m.p. 202.8–203.8°C. IR (KBr, cm^{-1}) ν_{max}: 2980–2652 (broad), 1754, 1508, 1270, 1212, 1020, 866. ^1H NMR (200 MHz, DMSO-d_6) $\delta = 7.85$ (d, $J = 1.7$ Hz, 1H, $-C_6H_3-$), 7.74 (dd, $J = 8.2$ Hz, $J = 1.7$ Hz, 1H, $-C_6H_3-$), 7.43 (d, $J = 8.2$ Hz, 1H, $-C_6H_3-$), 3.98 (s, 3H, $-OCH_3$), 3.61 (br s, 1H, $-CN_4H$), 2.39 (s, 3H, CH_3CO_2-). CHN: found C 53.02, H 5.29, N 22.51; requires C 53.11, H 5.26, N 22.48%.

3.2.5. *5-(4-Acetoxyaryl)-2-alkyltetrazoles* ***6***

A solution of 5-(4-acetoxyaryl)tetrazole **5** (8.0 mmol), the appropriate alkyl bromide (8.0 mmol), potassium carbonate (8.0 mmol) in cyclohexanone (100 ml) was heated at reflux for 56 h, cooled to room temperature and the solid formed was filtered. The solution was concentrated in a rotary evaporator and the residue recrystallized from ethanol/water to give the pure product.

3.2.5.1. *5-(4-Acetoxyphenyl)-2-nonyltetrazole* ***6a***. Recrystallization from ethanol/water gave a white solid, yield 70.0% (1.8 g), m.p. 53.0–54.1°C. IR (KBr, cm^{-1}) ν_{max}: 2716, 1754, 1502, 1282, 912. CHN: found C 65.45, H 7.99, N 16.98; requires C 65.33, H 7.83, N 16.86%.

3.2.5.2. *5-(4-Acetoxyphenyl)-2-tetradecyltetrazole* ***6b***. Recrystallization from ethanol/water gave a white solid, yield 75.0% (2.4 g), m.p. 61.2–62.5°C. IR (KBr, cm^{-1}) ν_{max}: 2716, 1754, 1502, 1282, 912. CHN: found C 68.95, H 9.09, N 14.01; requires C 68.87, H 8.96, N 13.93%.

3.2.5.3. *5-(4-Acetoxy-2-methoxyphenyl)-2-tetradecyltetrazole* ***6c***. The crude product was used without further purification or characterization.

3.2.6. *5-(4-Hydroxyaryl)-2-alkyltetrazoles* ***7***

A solution of 5-(4-acetoxyaryl)-2-alkyltetrazole **6** (8.0 mmol) in 50 ml of ethanol and a solution of potassium hydroxide (8.0 mmol KOH in 10 ml water) was heated at reflux for 4 h. After cooling to room temperature the reaction mixture was poured into 100 g of ice and acidified with hydrochloric acid. The aqueous mixture was shaken three times with ether. The ether extracts were washed with water, dried over sodium sulphate and the solvent evaporated. The crude product was recrystallized.

3.2.6.1. *5-(4-Hydroxyphenyl)-2-nonyltetrazole* ***7a***. Recrystallization from ethanol gave a white solid, yield 78% (1.8 g), m.p. 72.0°C. IR (KBr, cm^{-1}) ν_{max}: 3144, 2924, 2852, 1614, 1460, 842. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.00$ (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 6.97 (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 4.62 (t, $J = 7.2$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.05 (quint., 2H, $-NCH_2C\underline{H}_2-$), 1.30 (m, 12H, $-CH_2-$), 0.87 (t, $J = 6.3$ Hz, 3H, $-CH_3$). ^{13}C NMR (50.4, $CDCl_3$) $\delta = 164.9$ ($-CN_4-$), 158.2, 128.6, 119.4, 116.0, 53.3 ($-NCH_2-$), 31.9, 29.6, 29.3, 28.9, 26.3, 22.7 (7C, $-CH_2-$, nonyl chain), 14.1 (1C, $-CH_3$). CHN: found C 66.68, H 8.41, N 19.45; requires C 66.54, H 8.33, N 19.31%.

3.2.6.2. *5-(4-Hydroxyphenyl)-2-tetradecyltetrazole* ***7b***. Recrystallization from ethanol gave a white solid, yield 83% (2.4 g), m.p. 81.5°C. IR (KBr, cm^{-1}) ν_{max}: 3151, 2922, 2850, 1614, 1464, 910, 840. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.01$ (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 6.97 (d, $J = 8.7$ Hz, 2H, $-C_6H_4-$), 4.62 (t, $J = 7.2$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.05 (quint., 2H, $-NCH_2C\underline{H}_2-$), 1.25 (m, 22H, $-CH_2-$), 0.87 (t, $J = 6.3$ Hz, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.9$ ($-CN_4-$), 158.2, 128.6, 119.4, 116.0, 53.3 ($-NCH_2-$), 31.9, 29.6, 29.3, 28.9, 26.3, 22.7 (12C, $-CH_2-$, tetradecyl chain), 14.1 (1C, $-CH_3$). CHN: found C 70.39, H 9.59, N 15.67; requires C 69.98, H 9.46, N 15.43%.

3.2.6.3. *5-(4-Hydroxy-3-methoxyphenyl)-2-tetradecyltetrazole* ***7c***. Recrystallization from hexane gave a white solid, yield 60.0% (2.17 g), m.p. 53.5°C. IR (KBr, cm^{-1}) ν_{max}: 3244, 2922, 2848, 1602, 1488, 1282, 880, 794, 760. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 7.66$ (m, 2H, $-C_6H_3-$), 6.99 (d, $J = 7.9$ Hz, 1H, $-C_6H_3-$), 4.61 (t, $J = 7.2$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 3.98 (s, 3H, $-OCH_3$), 2.05 (m, 2H, $-NCH_2C\underline{H}_2-$), 1.25 (m, 22H, $-CH_2-$), 0.87 (t, $J = 6.6$ Hz, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 165.7$, 165.0, 164.9 ($-CN_4-$), 121.2, 120.1, 115.5, 109.9, 56.8 ($-OCH_3$), 53.3 ($-NCH_2-$), 32.6, 30.3, 30.2, 30.0, 29.6, 27.0, 26.6, 23.3 (12C, $-CH_2-$, tetradecyl chain), 14.8 (1C, $-CH_3$). CHN: found C 68.05, H 9.39, N 14.46; requires C 68.11, H 9.34, N 14.42%.

3.2.7. *4-[5-(2-Alkyltetrazole)]aryl-4′-pyridinecarboxylates* $\boldsymbol{L^2}$

Isonicotinic acid (0.626 g, 5.08 mmol) was heated under reflux with thionyl chloride (20 ml) for 4 h, immediately after distillation. Excess thionyl chloride was removed in a rotary evaporator, and the isonicotinic chloride added in portions to a solution of the appropriate 5-(4-hydroxyaryl)-2-alkyltetrazole **7** (5.08 mmol) in pyridine. This mixture was heated at reflux for 12 h. After cooling to room temperature the reaction mixture was poured into 10 g of ice/water; the product was isolated by filtration, washed with ice water and recrystallized.

3.2.7.1. *4-[5-(2-Nonyltetrazole)]phenyl-4′-pyridinecarboxylate* $\boldsymbol{L^2a}$. Recrystallization from ethanol gave a white solid, yield 60.0% (8.0 g), m.p. 55.5–56.2°C. IR (KBr, cm^{-1}) ν_{max}: 2916, 2848, 1740, 1466, 1296, 756. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.88$ (d, $J = 5.8$ Hz, 2H, $-C_5H_4N$), 8.25 (d, $J = 8.6$ Hz, 2H, $-C_6H_4-$), 8.03 (d, $J = 5.8$ Hz, 2H, $-C_5H_4N$), 7.36 (d, $J = 8.6$ Hz, 2H, $-C_6H_4-$), 4.65 (t, $J = 7.1$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.07 (m, 2H, $-NCH_2C\underline{H}_2-$), 1.30 (m, 12H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.2$ ($-CO_2-$), 163.5 ($-CN_4-$), 151.9, 150.9, 136.6, 128.3, 125.9, 123.2, 122.0, 53.3 ($-NCH_2-$), 31.8, 29.4, 29.2, 28.9, 26.4, 22.6 (7C, $-CH_2-$, nonyl chain), 14.8 (1C, $-CH_3$). CHN: found C 67.17, H 6.94, N 17.85; requires C 67.05, H 6.88, N 17.70%.

3.2.7.2. *4-[5-(2-Tetradecyltetrazole)]phenyl-4′-pyridinecarboxylate* $\boldsymbol{L^2b}$. Recrystallization from ethanol gave a white solid, yield 62.0% (9.7 g), m.p. 95.8–97.2°C. IR (KBr, cm^{-1}) ν_{max}: 2916, 2848, 1740, 1466, 1296, 756. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.88$ (d, $J = 5.8$ Hz, 2H, $-C_5H_4N$), 8.25 (d, $J = 8.6$ Hz, 2H, $-C_6H_4-$), 8.02 (d, $J = 5.8$ Hz, 2H, $-C_5H_4N$), 7.37 (d, $J = 8.6$ Hz, 2H, $-C_6H_4-$), 4.66 (t, $J = 7.1$ Hz, 2H, $-NC\underline{H}_2CH_2-$), 2.07 (m, 2H, $-NCH_2C\underline{H}_2-$), 1.30 (m, 22H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.2$ ($-CO_2-$), 163.5 ($-CN_4-$), 151.9, 150.9, 136.6, 128.3, 125.9, 123.2, 122.0, 53.3 ($-NCH_2-$), 31.8, 29.4, 29.2, 28.9, 26.4, 22.6 (12C, $-CH_2-$, tetradecyl chain), 14.1 (1C, $-CH_3$). CHN: found C 69.98, H 8.07, N 15.14; requires C 69.91, H 7.99, N 15.01%.

3.2.7.3. *4-[5-(2-Tetradecyltetrazole)]-2-methoxyphenyl-4′-pyridinecarboxylate* $\boldsymbol{L^2c}$. The crude product was used without further purification or characterization.

3.2.8. *Preparation of silver(I) complexes*

A mixture of 1.0 mmol of ligand ($\mathbf{L^1a,b}$ or $\mathbf{L^2a,b,c}$), 0.5 mmol of silver perchlorate monohydrate and methanol (20 ml) was stirred for 20–30 min. The precipitate formed was filtered and recrystallized.

3.2.8.1. *Bis[5-(4-pyridyl)-2-nonyltetrazole]silver(I) perchlorate* ***Ia***. Recrystallization from 1-butanol gave a white solid, yield 90.0% (0.34 g), m.p. 126°C. IR (KBr, cm^{-1}) ν_{max}: 2926, 2856, 1612, 1460, 1144, 1114, 1088, 838, 754. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.85$ (d, $J = 6.0$ Hz, 4H, $2-C_5H_4N$), 8.00 (d, $J = 6.0$ Hz, 4H, $2-C_5H_4N$), 4.66 (t, $J = 7.2$ Hz, 4H, $2-NC\underline{H}_2CH_2-$), 2.07 (m, 4H, $2-NCH_2C\underline{H}_2-$), 1.30 (m, 24H, $12-CH_2-$), 0.86 (t, $J = 6.6$ Hz, 6H, $2-CH_3$). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 161.4$ (2C, $2-CN_4-$), 152.8, 137.2, 122.0, 53.7 (2C, $2-NCH_2-$), 31.8, 29.3, 29.2, 29.2, 28.9, 26.4, 22.6 (14C, $14-CH_2-$, nonyl chains), 14.1 (2C, $2-CH_3$). CHN: found C 48.47, H 6.25, N 17.14; requires C 47.78, H 6.15, N 18.57%.

3.2.8.2. *Bis[5-(4-pyridyl)-2-tetradecyltetrazole]silver(I) perchlorate* ***Ib***. Recrystallization from isopropanol gave a white solid, yield 70.0% (0.38 g), m.p. 128.5°C. IR (KBr, cm^{-1}) ν_{max}: 2954, 2918, 2848, 1624, 1434, 1108, 1082, 1028, 844, 756, 718, 620. ^1H NMR (200 MHz, $CDCl_3$) $\delta = 8.88$ (d, $J = 6.1$ Hz, 4H, $2-C_5H_4N$), 8.07

(d, $J = 6.1$ Hz, 4H, 2−C_5H_4N), 4.68 (t, $J = 7.2$ Hz, 4H, 2−NC$\underline{H}_2CH_2$−), 2.09 (m, 4H, 2−$NCH_2C\underline{H}_2$−), 1.32 (m, 44H, 22−CH_2−), 0.88 (t, $J = 6.1$ Hz, 6H, 2−CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 161.4$ (2C, 2−CN_4−), 152.8, 137.2, 122.0, 53.7 (2C, 2−NCH_2−), 31.8, 29.3, 29.2, 29.2, 29.2, 28.9, 26.4, 22.6 (24C, 24−CH_2−, tetradecyl chain), 14.1 (2C, 2−CH_3). CHN: found C 53.81, H 7.41, N 15.60; requires C 53.72, H 7.44, N 15.66%.

3.2.8.3. *Bis{4-[5-(2-nonyltetrazole)]phenyl-4′-pyridinecarboxylate}silver(I) perchlorate* ***IIa***. Recrystallization from 1-butanol/ethanol gave a white solid, yield 60.7% (0.30 g), Cr 174.0 SmA 203.8 I (°C). IR (KBr, cm^{-1}) ν_{max}: 2918, 2850, 1740, 1464, 1286, 1198, 1116, 1092, 1048, 756. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 9.00$ (d, $J = 6.1$ Hz, 4H, 2−C_5H_4N), 8.2 (d, $J = 8.6$ Hz, 4H, 2−C_6H_4−), 8.11 (d, $J = 6.1$ Hz, 4H, 2−C_5H_4N), 7.37 (d, $J = 8.6$ Hz, 4H, 2−C_6H_4−), 4.67 (t, $J = 7.2$ Hz, 4H, 2−NC$\underline{H}_2CH_2$−), 2.06 (m, 4H, 2−$NCH_2C\underline{H}_2$−), 1.30 (m, 24H, 12−CH_2−), 0.88 (t, 6H, 2−CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.0$ (2C, 2−CN_4−), 162.4, (2C, 2−CO_2−), 152.8, 151.7, 138.4, 128.4, 125.7, 124.5, 122.0, 53.6 (2C, 2−NCH_2−), 31.8, 29.3, 29.2, 28.9, 26.4, 22.6 (14C, 14−CH_2−, nonyl chains), 14.1 (2C, 2−CH_3). CHN: found C 53.95, H 4.12, N 15.21; requires C 53.70, H 4.51, N 14.23%.

3.2.8.4. *Bis{4-[5-(2-tetradecyltetrazole)]phenyl-4′-pyridinecarboxylate}silver(I) perchlorate* ***IIb***. Recrystallization from ethanol gave a white solid, yield 60.0% (0.20 g), Cr 178.4 SmA 202.2 I (°C). IR (KBr, cm^{-1}) ν_{max}: 2920, 2851, 1740, 1464, 1289, 1201, 1114, 1090, 1050, 757. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 9.02$ (d, $J = 6.1$ Hz, 4H, 2−C_5H_4N), 8.25 (d, $J = 8.6$ Hz, 4H, 2−C_6H_4−), 8.10 (d, $J = 6.1$ Hz, 4H, 2−C_5H_4N), 7.39 (d, $J = 8.6$ Hz, 4H, 2−C_6H_4−), 4.66 (t, $J = 7.2$ Hz, 4H, 2−NC$\underline{H}_2CH_2$−), 2.07 (m, 4H, 2−$NCH_2C\underline{H}_2$−), 1.32 (m, 44H, 22−CH_2−), 0.89 (t, 6H, 2−CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.0$ (2C, 2−CN_4−), 162.4, (2C, 2−CO_2−), 152.8, 151.8, 138.4, 128.4, 125.7, 124.5, 122.0, 53.6 (2C, 2−NCH_2−), 31.8, 29.3, 29.2, 28.9, 26.4, 22.7 (24C, 24−CH_2−, tetradecyl chain), 14.1 (2C, 2−CH_3). CHN: found C 56.85, H 6.42, N 13.12; requires C 57.16, H 6.57, N 12.34%.

3.2.8.5. *Bis[4-[5-(2-tetradecyltetrazole)]-2-methoxyphenyl-4′-pyridinecarboxylate]silver(I) perchlorate* ***IIc***. Recrystallization from ethanol gave a white solid, yield 60.7% (0.30 g), m.p. 181.7–184°C. IR (KBr, cm^{-1}) ν_{max}: 2918, 2855, 1742, 1606, 1476, 1276, 1204, 1180, 1122, 1084, 1030, 755. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.94$ (d, $J = 6.0$ Hz, 4H, 2−C_5H_4N), 8.13 (d, $J = 6.0$ Hz, 4H, 2−C_5H_4N), 7.73 (s, 2H, 2−C_6H_4−), 7.70 (d, $J = 8.0$ Hz, 2H, 2−C_6H_4−), 7.14 (d, $J = 8.0$ Hz, 2H, 2−C_6H_4−), 4.60 (t, $J = 6.7$ Hz, 4H, 2−NC$\underline{H}_2CH_2$−), 3.84 (s, 6H, $2CH_3O$−), 2.00 (m, 4H, 2−$NCH_2C\underline{H}_2$−), 1.24 (m, 44H, 22−CH_2−), 0.80 (t, $J = 6.3$ Hz, 6H, 2−CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 164.2$ (2C, 2−CN_4−), 161.7 (2C, 2−CO_2−), 151.6, 151.2, 140.7, 139.0, 126.9, 125.0, 123.1, 119.4, 110.9, 56.1 (2C, 2−OCH_3), 53.4 (2C, 2−NCH_2−), 31.9, 29.6, 29.5, 29.3, 28.9, 26.3, 22.6 (24C, 24−CH_2−, tetradecyl chains), 14.1 (2C, 2−CH_3). CHN: found 53.05, H 4.58, N 14.39; requires C 52.91, H 4.63, N 13.42%.

3.2.9. *Preparation of bis[5-(4-pyridyl)-2-nonyltetrazole]-palladium(II) diacetate* ***Ic***

A mixture of 0.27 g (1.0 mmol) of 5-(4-pyridyl)-2-nonyltetrazole $\mathbf{L^1a}$ 0.11 g (0.5 mmol) of palladium(II) acetate and glacial acetic acid (20 ml) was heated at reflux under a nitrogen atmosphere for 3 days. The mixture was cooled to room temperature and the precipitate formed was filtered and recrystallized from isopropanol to give a white solid, yield 68.0% (0.23 g), m.p. 152.9°C. IR (KBr, cm^{-1}) ν_{max}: 2920, 2852, 1626, 1462, 1434, 1360, 1304, 854, 694. ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 8.85$ (d, $J = 6.6$ Hz, 4H, 2−C_5H_4N), 8.09 (d, $J = 6.6$ Hz, 4H, 2−C_5H_4N), 4.69 (t, $J = 7.1$ Hz, 4H, 2−NC$\underline{H}_2CH_2$−), 2.06 (m, 4H, 2−$NCH_2C\underline{H}_2$−), 1.88 (s, 6H, $2C\underline{H}_3CO$), 1.29 (m, 24H, 12−CH_2−), 0.88 (t, $J = 6.6$ Hz, 6H, 2−CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$) $\delta = 178.1$ (2C, 2−CO_2−), 161.5 (2C, 2−CN_4−), 152.2, 137.4, 121.8, 53.7 (2C, 2−NCH_2−), 31.8, 29.3, 29.2, 29.1, 28.8, 26.3, 23.2, 22.6 (14C, 14−CH_2−, nonyl chains), 14.0 (2C, 2−CH_3). CHN: found C 48.47, H 6.25, N 17.14; requires C 47.78, H 6.15, N 18.57%.

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Crystallographic data will be deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 158011.

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