Synthesis, redox behaviour and X-ray structure of bis-TTF containing a pyridine unit as a potential building block in the construction of conducting magnetic materials

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The synthesis of singly and doubly bridged bis-TTF containing a 2,6-bis(methylthio)pyridine group as a linker and potentially usable as a ligand for paramagnetic transition metal complexes is reported. Cyclisation leading to doubly bridged bis-TTF has been achieved without using the high dilution technique generally employed in such cases. The redox behaviour of such precursors has been studied by cyclic voltammetry and square wave techniques. The crystal structure of one of these electron donors has been determined by X-ray diffraction showing a stacking arrangement of the TTF units.

Since the discovery of two coupled physical properties in a single organic material,[1] increasing interest in the search for new salts of the TTF (tetrathiafulvalene) type involving both electrical and magnetic behaviour has emerged[2–7] with the aim of creating more effective interactions between the conducting and magnetic networks.[8–10] Beside salts of TTF derivatives in which the magnetic units are introduced through the inorganic anions,[1–9] a second route consists of the use of TTF precursors covalently linked to either an organic radical[11–14] or to ligands able to coordinate paramagnetic transition metals.[10–15] In this context, we have planned to develop new building blocks for conducting-magnetic materials through a series of bis-TTF compounds (Scheme 1) in which the two TTF units are linked to each other by a spacer group containing a pyridine unit as a metal ligand.

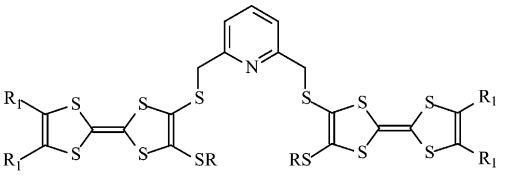
Synthesis

As shown in Scheme 2, the singly bridged bis-TTF compounds **1a–c** have been synthesised from the key intermediates of type **3**[16,17] by using the deprotection–realkylation methodology[18,19] developed by Becher and coworkers.[20] The pure compounds **1** were obtained in 45–57% yield after purification of the crude products by column chromatography (SiO_2/CH_2Cl_2) and crystallisation from CH_2Cl_2/CH_3OH.

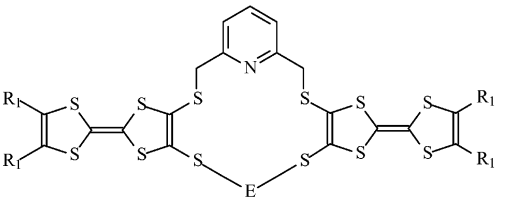
The doubly bridged derivatives (Scheme 3) could be prepared by using either route a or route b. Taking into account the low yield obtained in an attempt to synthesise **2c** ($< 20\%$) by using **1c** and 1,3-diiodopropane (route a), the macrocyclic bis-TTF **2b$_{1-3}$** and **2c** were prepared according to route b from compounds **4b$_1$**,[19] **4b$_2$**,[21] **4b$_3$**[22] and **4c**[18] respectively used as starting products. The two-step procedure giving rise to the desired cyclisation was carried out with success without the use of the sophisticated and awkward high dilution technique[22] generally employed to prevent the possibility of polymerisation.

The double deprotection of compounds **4** followed by cyclisation[21,22] by using 2,6-bis(halogenomethyl)pyridine (route b) afforded the expected compounds **2b–2c** in 40–72% yields. It is worth noting that the highest yield (**2b$_2$**: 72%) was surprisingly obtained by using 2,6-bis(chloromethyl)pyridine whereas lower yields (**2b$_1$**: 62%, **2b$_3$**: 50%, **2c**: 40%) were obtained when the dibromo derivative was used as an alkylating agent, despite the bromo group being considered a better leaving group than the chloro group.

On the other hand, the synthesis of the macrocyclic bis-TTF **2d**, which contains two pyridine units as spacer groups, was carried out according to route a (Scheme 3) from precursor



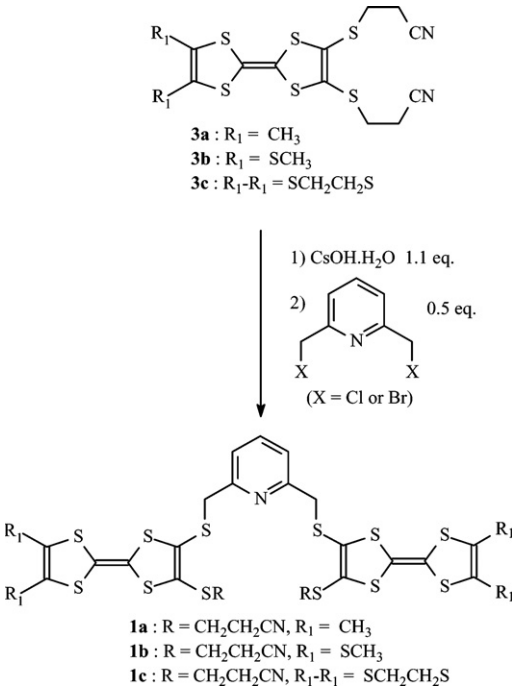
1a : R = CH_2CH_2CN, R_1 = CH_3
1b : R = CH_2CH_2CN, R_1 = SCH_3
1c : R = CH_2CH_2CN, R_1-R_1 = SCH_2CH_2S



2b$_1$: R_1 = SCH_3, E = CH_2CH_2
2b$_2$: R_1 = SCH_3, E = $CH_2CH_2CH_2$
2b$_3$: R_1 = SCH_3, E = $CH_2pC_6H_4CH_2$
2c : R_1-R_1 = SCH_2CH_2S, E = $CH_2CH_2CH_2$
2d : R_1 = SCH_3, E = $CH_2C_5H_3NCH_2$

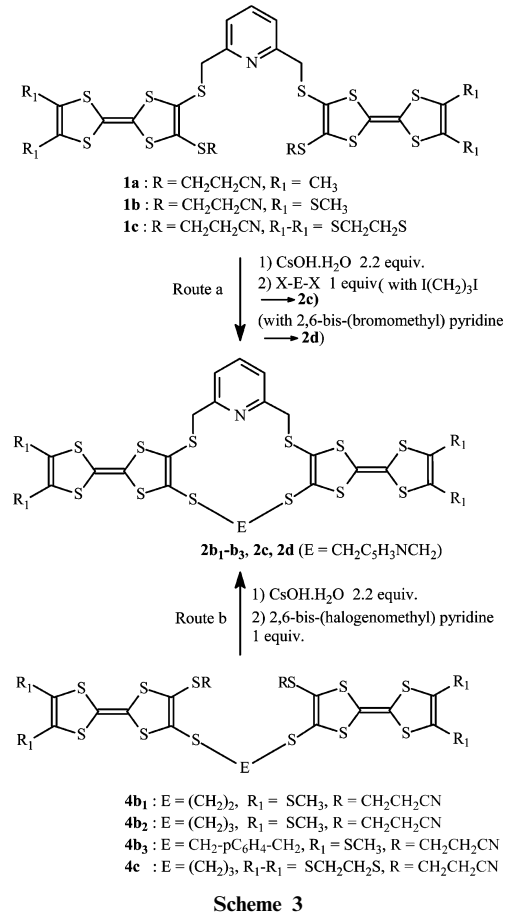
Scheme 1

 DOI: 10.1039/b208624g



Scheme 2

1b and 2,6-bis(bromomethyl)pyridine. The powder isolated (72% yield), which did not melt at temperatures higher than 265 °C, was found insoluble at room temperature in most usual organic solvents. Despite these results that we first believed were in favour of polymer formation, the mass spectrometry analysis (MALDI-TOF technique) indicated clearly the formation of the expected compound **2d** together with traces of the corresponding dimer containing four TTF units and four pyridine spacers. This side product was then eliminated by treating the crude powder by hot DMF.



Scheme 3

Redox behaviour analysis

The redox characteristics of both singly bridged bis-TTF **1a–c** and macrocyclic bis-TTF **2b$_{1-3}$** and **2c** have been studied in $TBAPF_6/CH_2Cl_2$ solution by cyclic voltammetry (CV) and square wave (SQW) techniques (Pt electrodes *vs.* SCE). The CV measurements show reversible behaviour for all the compounds studied. The oxidation potential values (E_{ox}) are reported in Table 1 (SQW determinations).

As shown in Table 1, the E_{ox_1} values of compounds **1** are found in the same range as those of the electron donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) (614 mV) which provided until now the largest number of conducting and superconducting salts. Moreover it is worth noticing that the E_{ox_1} values of bis-TTF **1** are found in agreement with the electronic effects of the TTF units substituents.[18]

In addition, all these compounds **1** exhibit a three-wave SQW pattern as shown in Fig. 1 with compound **1a** taken as a model. As illustrated in Scheme 4, the relative intensities (1, 1, 2) of each wave suggest two successive one-electron redox processes (E_{ox_1}, E_{ox_2}) and one two-electron oxidation (E_{ox_3}). Despite the presence of two identical TTF units in compounds **1**, the flexibility of the spacer group can induce the formation of a π-dimer[23] involving a stabilising intermolecular interaction[24] which could be responsible for the splitting into the two single-electron waves observed at E_{ox_1} and E_{ox_2} respectively. Then, due to the repulsion between the two charged TTF units of the bis-radical cation, an open structure is formed and oxidised at E_{ox_3} into a bis-dication (Scheme 4).

Moreover it is worth noting that a similar result is observed for the macrocyclic compound **2d** which exhibits a more important splitting ($\Delta E = E_{ox_2} - E_{ox_1} = 166$ mV) between the two first waves ($E_{ox_1} = 506$ mV, $E_{ox_2} = 672$ mV) than in compounds of type **1** (**1a**: $\Delta E = 76$ mV). This result could be due both to the flexibility and to the same nature and length of the two spacer groups in **2d** allowing a better overlap of the two TTF units in the π-dimer formed at E_{ox_1}, inducing a more efficient stabilizing interaction.

In contrast, the partial rigidity of the doubly bridged bis-TTF **2b–2c** and the presence of two linkers of different nature and length must hinder the formation of the stabilising π-dimer discussed above for compounds **1**. As a result, a pattern involving only two two-electron waves is observed as illustrated in Fig. 2 (Scheme 5) for compound **2b$_3$**.

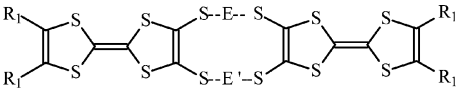
Crystal structure

The structure of compound **1b** obtained in solution as single crystals (red platelets) from a mixture of solvents (CH_2Cl_2/CH_3OH) was solved by X-ray diffraction.

The asymmetric unit of compound **1b** consists of one half pyridine ring covalently bonded *via* a $-CH_2-S-$ bridge to one substituted TTF moiety, two atoms of this ring (N1 and C13) being located on a twofold axis, yielding the whole molecule drawn in Fig. 3.

The two outer S–CH_3 groups (S6–C15 and S7–C14) are above the TTF mean plane while the two inner S–CH_2–CH_2–CN and S–CH_2–pyridine fragments (S8–C7–C8–C9–N2 and S1–C10–C11–C12–C13–C12^i–C11^i–N1) are below this plane. The angle between the pyridine ring and the TTF mean plane is 52.58(8)° and the angle between the two TTF fragments is 80.46(1)°. One TTF derivative stands below the pyridine plane, the second one is above, due to the presence of the twofold axis. Note that the S–CH_2–CH_2–CN fragment is

Table 1 Oxidation potential of singly bridged bis-TTF **1** and doubly bridged bis-TTF **2**.[E_{ox}/mV *vs.* SCE, with Pt electrodes in 0.1 M $TBAPF_6$/CH_2Cl_2 solution, scan rate 0.1 V s^{-1}]



(or in the singly bridged structures **1** : SR' R'S)

Compound	R_1 or R_1–R_1	R′ or E′	E	E_{ox_1}	E_{ox_2}	$E_{ox_{3(2)}}$
1a	CH_3	CH_2CH_2CN	$CH_2C_5H_3NCH_2$	504	580	952
1c	SCH_2CH_2S	CH_2CH_2CN	$CH_2C_5H_3NCH_2$	604	696	995
1b	SCH_3	CH_2CH_2CN	$CH_2C_5H_3NCH_2$	616	668	962
2d	SCH_3	$CH_2C_5H_3NCH_2$	$CH_2C_5H_3NCH_2$	506	672	934
2c	SCH_2CH_2S	$(CH_2)_3$	$CH_2C_5H_3NCH_2$	588 (broad)		984
2b$_3$	SCH_3	CH_2-*p*-$C_6H_4CH_2$	$CH_2C_5H_3NCH_2$	604 (broad)		948
2b$_1$	SCH_3	$(CH_2)_2$	$CH_2C_5H_3NCH_2$	606		940
2b$_2$	SCH_3	$(CH_2)_3$	$CH_2C_5H_3NCH_2$	620 (broad)		956

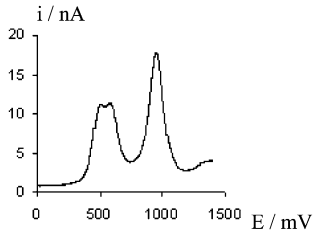
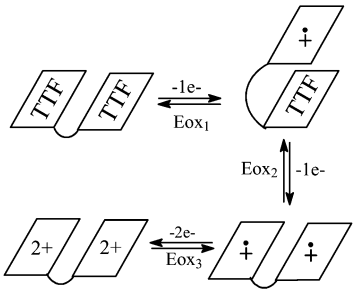


Fig. 1 SQW of compound **1a** on Pt in CH_2Cl_2 solution.



Scheme 4 Redox processes of compound **1a**.

located here and there from the pyridine ring, the distance between the N atom of the CN group and the pyridine mean plane is 3.5093(2) Å.

Fig. 4 shows the crystal packing of compound **1b**. We observe alternate layers of TTF and pyridine rings in the *bc* plane. Each pyridine ring is perpendicular to the *ac* plane. Along the *c* direction, two adjacent TTF fragments form an angle of 76.1°. The TTF fragments form infinite chains along the *b* direction (Fig. 4b), with the shortest S···S contacts as S4···S5 = 4.307(1) Å.

Conclusion

In this work we have prepared in 45–57% yield bis-TTF compounds **1a–c**, which form stacked structures, by the bis-thiolate deprotection–realkylation method. We have demonstrated that the conversion into doubly bridged bis-TTF **2** in 40–72% yield from singly linked bis-TTF **4b$_{1-3}$**, **4c** (route b), **1b** (route a) and 2,6-bis(halogenomethyl)pyridine could be achieved by cyclisation without using the awkward high dilution technique. The study of the electrochemical behaviour of these new series of bis-TTF π-donors has clearly shown a first oxidation wave involving a one-electron process for the flexible singly linked compounds **1a–c** and a two-electron oxidation (larger wave) for the more rigid macrocyclic bis-TTF **2b$_{1-3}$**, **2c**. For all the compounds of types **1** and **2**, the first oxidation potential (E_{ox_1}) displayed values close to that found for BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) indicating their quite good donating character. With compounds of type **1**, the potentiostatic technique used at $V_{constant} = E_{ox_1}$ could be the way to control the stoichiometry of their salts and possibly their conductivity. The synthesis of such salts is now under way.

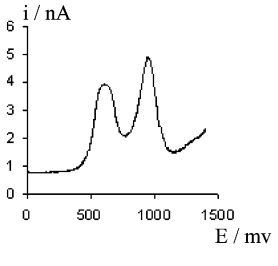


Fig. 2 SQW of compound **2b$_3$** on Pt in CH_2Cl_2 solution.

Experimental

All solvents were dried by standard methods and all commercial reagents used without purification. NMR spectra were recorded on a Bruker AC 200 instrument. FAB and MALDI-TOF mass spectra were recorded on a JEOL JMS-DX 300 spectrometer and a on a Bruker Biflex III type spectrometer respectively. Uncorrected melting points were measured on a 510 Buchi apparatus. Cyclic voltammetry and

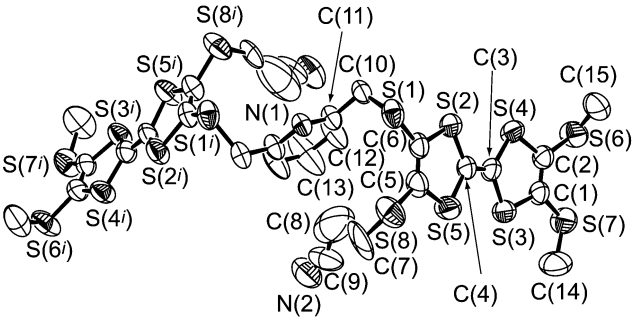
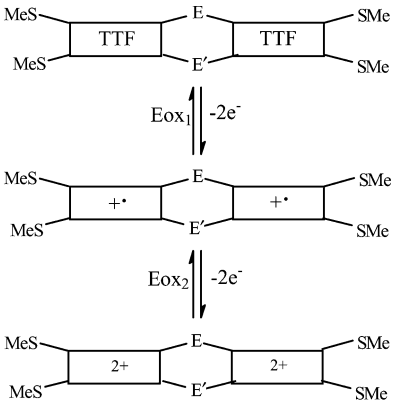


Fig. 3 ORTEP drawing for **1b** with a probability level of 50% and labelling scheme.



Scheme 5 Redox processes of compound $\mathbf{2b_3}$.

SQW measurements were carried out on a EG-G PAR-273 potentiostat/galvanostat.

Crystallographic data collection and structure determination

Single crystals of compound **1b** were mounted on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated MoK_α radiation source (λ = 0.71073 Å). Data collection was performed at room temperature. Effective absorption correction was performed (SCALEPACK[25]). Structures were solved with SHELXS-97[26] and refined with SHELXL-97[26] programs by full matrix least squares methods on F^2.

Crystallographic data are summarized in Table 2. CCDC reference number 192572. See http://www.rsc.org/suppdata/nj/b2/b208624g/ for crystallographic data in CIF or other electronic format.

Synthesis of singly bridged bis-TTF 1a–c

General procedure. To a solution of **3**[16,17] (0.5 mmol) in dry DMF (15 mL) was added dropwise under nitrogen a solution of $CsOH{\cdot}H_2O$ (0.55 mmol) in dry methanol (3 mL) over a period of 20 min, followed by stirring for 15 min after the addition. 2,6-Bis(halogenomethyl)pyridine (0.25 mmol) was then added under inert atmosphere to the reaction mixture. After addition followed by stirring for 15 min, 2,6-bis(halogenomethyl)pyridine (0.25 mmol) was added under inert atmosphere to the reaction mixture. After stirring for 12 h, and addition of CH_2Cl_2 (100 mL), the organic solution was washed with water (3 × 100 mL). After drying ($MgSO_4$) and removing the solvent, the residue was subjected to column chromatography (silica gel, CH_2Cl_2). Evaporation of the solvent *in vacuo* and crystallisation of the oil isolated from (CH_2Cl_2/CH_3OH) afforded **1** as an analytically (^{1}H-NMR, MS-FAB) pure powder.

Compound **1a**. Obtained from: **3a**[17] (200 mg, 0.497 mmol), $CsOH{\cdot}H_2O$ (91.81 mg, 0.547 mmol) and 2,6-bis(chloromethyl)pyridine (43.77 mg, 0.248 mmol).

1a: orange powder; yield: 89.40 mg (45%); mp 180–182 °C. ^{1}H NMR ($CDCl_3$): δ 1.95 (12H, s, CH_3); 2.49 (4H, t, J = 7.3 Hz, CH_2CN); 2.90 (4H, t, J = 7.3 Hz, CH_2S); 4.13 (4H, s, CH_2-pyridine-CH_2); 7.22 (2H, d, J = 7.9 Hz, H pyridine); 7.63 (1H, t, J = 7.6 Hz, H pyridine). MS (FAB): 801[M]$^+$. Anal. Calc. for $C_{29}H_{27}N_3S_{12}$: C 43.45, H 3.37; found C 43.68, H 3.38%.

Compound **1b**. Obtained from: **3b**[16] (200 mg, 0.429 mmol), $CsOH{\cdot}H_2O$ (79.28 mg, 0.472 mmol) and 2,6-bis(chloromethyl)pyridine (37.77 mg, 0.214 mmol).

1b: red crystals; yield: 113.32 mg (57%); mp 95–96 °C. ^{1}H NMR ($CDCl_3$): δ 2.43 (12H, s, SCH_3); 2.54 (4H, t, J = 7.6 Hz, CH_2CN); 2.93 (4H, t, J = 7.2 Hz, CH_2S); 4.14 (4H, s, CH_2-pyridine-CH_2); 7.21 (2H, d, J = 7.6 Hz, H pyridine); 7.66 (1H, t, J = 7.6 Hz, H pyridine). MS (FAB): 929 [M]$^+$. Anal. Calc. for $C_{29}H_{27}N_3S_{16}$: C 37.46, H 2.90; found C 37.02, H 2.04%.

Compound **1c**. Obtained from: **3c**[17] (500 mg, 1.070 mmol), $CsOH{\cdot}H_2O$ (199 mg, 1.18 mmol) and 2,6-bis(chloromethyl)-pyridine (94.96 mg, 0.538 mmol).

1c: red-brown powder; yield: 233.89 mg (47%); mp 149–151 °C. ^{1}H NMR ($CDCl_3$): δ 2.54 (4H, t, J = 7.5 Hz, CH_2CN); 2.91 (4H, t, J = 7.2 Hz, CH_2S); 3.29 (8H, s, SCH_2CH_2S); 4.14 (4H, s, CH_2-pyridine-CH_2); 7.21 (2H, d, J = 7.6 Hz, H pyridine); 7.65 (1H, t, J = 7.6 Hz, H pyridine). MS (FAB): 925 [M]$^+$. Anal. Calc. for $C_{29}H_{23}N_3S_{16}$: C 37.62, H 2.48; found C 37.83, H 2.55%.

Table 2 Crystallographic data

Empirical formula	$C_{29}H_{27}N_3S_{16}$
Formula weight	930.50
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	43.3630(16)
b/Å	5.8730(2)
c/Å	16.1730(8)
β/deg	100.367(2)
V/Å^3	4051.6(3)
Z	4
d_{cal}/g cm^{-3}	1.525
μ/mm^{-1}	0.881
λ(Mo Kα)/Å	0.71073
Theta range/deg	2.56/25.36
hkl range	−51, 52/−7, 6/−19, 19
Rflcns collected/ind.	6207/3700 [R(int) = 0.0337]
$R(F)$,[a] $wR(F)^b$, [I > 2σ(I)]	R_1 = 0.0647, ωR_2 = 0.1784 [2107]
$R(F)$,[a] $wR(F)^b$, [all data]	R_1 = 0.1155, ωR_2 = 0.2141
GOF in F^2	1.044

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$

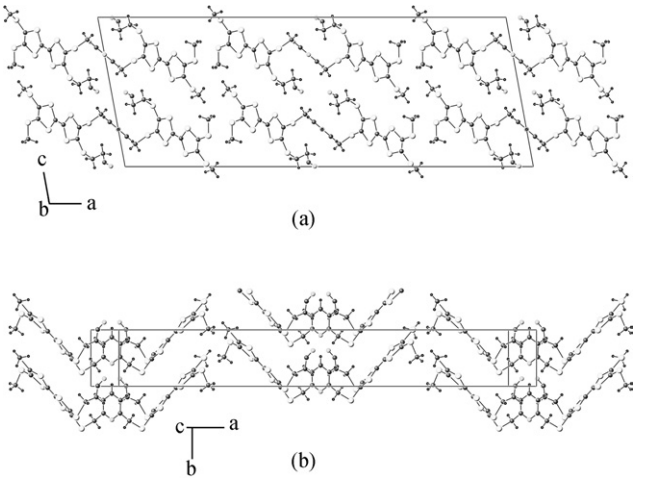


Fig. 4 (a) Projection of the crystal structure of **1b** in the *ac* plane, showing the layered structure. (b) Projection of the organic layer in the *ab* plane showing the overlap between the TTF fragments.

Synthesis of doubly bridged bis-TTF 2b–c, 2d

General procedure (route b). To a solution of **4**[18,19,21,22] (0.15 mmol) in dry DMF (25 mL) was added dropwise under nitrogen a solution of $CsOH{\cdot}H_2O$ (0.33 mmol) in dry methanol (5 mL) over a period of 10 min, followed by stirring for 25 min. 2,6-Bis(halogenomethyl)pyridine (0.15 mmol) was then added under inert atmosphere to the reaction mixture. Stirring was continued for an additional 2 h, and CH_2Cl_2 (100 mL) was

added to the reaction mixture. The organic solution was washed with water (3×80 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* affording a residue which was purified by column chromatography (silica gel, CH_2Cl_2). Evaporation of the solvent *in vacuo* and crystallisation of the oil isolated from (CH_2Cl_2/CH_3OH) afforded **2** as an analytically (^{1}H-NMR, MS-FAB) pure powder.

Compound **2b$_1$**. Obtained from: **4b$_1$**[19] (160 mg, 0.187 mmol), $CsOH{\cdot}H_2O$ (69.38 mg, 0.413 mmol) and 2,6-bis(bromomethyl)pyridine (49.75 mg, 0.187 mmol).

2b$_1$: orange-red powder; yield: 98.43 mg (62%); mp 180–181 °C. ^{1}H NMR ($CDCl_3$): δ 2.44 (12H, s, SCH_3); 2.77 (4H, s, SCH_2CH_2S); 4.03 (4H, s, CH_2-pyridine-CH_2); 7.05 (2H, d, $J = 7.6$ Hz, H pyridine); 7.57 (1H, t, $J = 7.6$ Hz, H pyridine). MS (MALDI): 849 $[M]^+$. Anal. Calc. for $C_{25}H_{23}NS_{16}$: C 35.33, H 2.71; found C 35.69, H 2.67%.

Compound **2b$_2$**. Obtained from: **4b$_2$**[21] (120 mg, 0.138 mmol), $CsOH{\cdot}H_2O$ (51.29 mg, 0.304 mmol) and 2,6-bis(chloromethyl)pyridine (24.40 mg, 0.138 mmol).

2b$_2$: brown powder; yield: 85.74 mg (72%); mp 80–81 °C. ^{1}H NMR ($CDCl_3$): δ 1.44 (2H, q, $J = 6.4$ Hz, CH_2); 2.43 (12H, s, SCH_3); 2.56 (4H, t, $J = 6.4$ Hz, CH_2S), 4.06 (4H, s, CH_2-pyridine-CH_2); 7.12 (2H, d, $J = 7.6$ Hz, H pyridine); 7.59 (1H, t, $J = 7.6$ Hz, H pyridine). MS (MALDI): 863 $[M]^+$. Anal. Calc. for $C_{26}H_{25}NS_{16}$: C 36.15, H 2.89; found C 36.21, H 2.92%.

Compound **2b$_3$**. Obtained from: **4b$_3$**[22] (160 mg, 0.172 mmol), $CsOH{\cdot}H_2O$ (63.69 mg, 0.379 mmol) and 2,6-bis(bromomethyl)pyridine (45.68 mg, 0.172 mmol).

2b$_3$: orange powder; yield: 79.55 mg (50%); mp 188–190 °C. ^{1}H NMR ($CDCl_3$): δ 2.44 (12H, s, SCH_3); 3.84 (4H, s, CH_2-pyridine-CH_2); 3.88 (4H, s, CH_2-phenyl-CH_2), 7.06 (2H, d, $J = 7.6$ Hz, H pyridine); 7.16 (4H, s, H phenyl); 7.54 (1H, t, $J = 7.6$ Hz, H pyridine). MS (MALDI): 925 $[M]^+$. Anal. Calc. for $C_{31}H_{27}NS_{16}$: C 40.21, H 2.92; found C 40.05, H 2.90%.

Compound **2c**. Obtained from: **4c**[18] (151 mg, 0.175 mmol), $CsOH{\cdot}H_2O$ (64.71 mg, 0.385 mmol) and 2,6-bis(bromomethyl)pyridine (46.41 mg, 0.175 mmol).

2c: brown powder; yield: 60.13 mg (40%); mp 157–159 °C. ^{1}H NMR ($CDCl_3$): δ 2.55 (4H, t, $J = 6.5$ Hz, CH_2S); 3.31 (8H, s, SCH_2CH_2S), 4.04 (4H, s, CH_2-pyridine-CH_2); 7.10 (2H, d, $J = 7.9$ Hz, H pyridine); 7.59 (1H, t, $J = 7.6$ Hz, H pyridine). MS (MALDI): 859 $[M]^+$. Anal. Calc. for $C_{26}H_{21}NS_{16}$: C 36.32, H 2.44; found C 36.23, H 2.51%.

Compound **2d** *(route a)*. To a solution of **1b** (126 mg, 0.135 mmol) in dry DMF (2 mL) was added dropwise under nitrogen a solution of $CsOH{\cdot}H_2O$ (50.11 mg, 0.298 mmol) in dry methanol (3 mL). After stirring for 30 min at room temperature, 2,6-bis(bromomethyl)pyridine (35.84 mg, 0.135 mmol) was added to the red-brown solution giving rise to the immediate formation of an orange-yellow precipitate. Stirring was continued for an additional 12 h. The precipitate was filtered off, washed with cold hexane, dried *in vacuo*: yield 90.1 mg (72%), and analysed by mass spectrometry (MALDI, dithranol–CH_2Cl_2): **2d**: 926 $[M]^+$ + impurity ($< 5\%$), dimer of **2d**: 1852 $[M]^+$. **2d** was then purified by partially dissolving the powder in hot DMF, filtering the suspension and precipitating the filtrate by cooling it at 0 °C. **2d** was finally isolated by filtration as an analytically pure sample as a yellow powder, yield: 87 mg (70%); mp > 265 °C. MS (MALDI-TOF): *m/z*: 926 $[M]^+$. Anal. Calc. for $C_{30}H_{26}N_2S_{16}$: C 38.87, H 2.80, N 3.02; found C 38.23, H 2.81, N 3.48%.

High dilution technique

Preparation of 2b$_2$. To a solution of **4b$_2$**[21] (117 mg, 0.135 mmol) in anhydrous DMF (25 mL) was added dropwise under nitrogen a solution of $CsOH{\cdot}H_2O$ (49.9 mg, 0.297 mmol) in anhydrous methanol (5 mL) over a period of 10 min. After an additional stirring of 1 h, this solution and a solution of 2,6-bis(chloromethyl)pyridine (23.78 mg, 0.135 mmol) in anhydrous DMF (30 mL) were added simultaneously (rate: 0.05 mL min^{-1}) under inert atmosphere at room temperature to anhydrous DMF (60 mL), using a infusionr pump. Stirring was continued for an additional 4 h, and CH_2Cl_2 (100 mL) was added to the reaction mixture. The organic solution was washed with water (3×80 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* affording a residue which was purified by column chromatography (silica gel, CH_2Cl_2). Evaporation of the solvent *in vacuo* and crystallisation of the oil isolated from CH_2Cl_2/CH_3OH afforded **2b$_2$** as a brown powder; yield: 65.24 mg (56%); mp 80–81 °C. ^{1}H NMR ($CDCl_3$): δ 1.44 (2H, q, $J = 6.4$ Hz, CH_2); 2.43 (12H, s, SCH_3); 2.56 (4H, t, $J = 6.4$ Hz, CH_2S), 4.06 (4H, s, CH_2-pyridine-CH_2); 7.12 (2H, d, $J = 7.6$ Hz, H pyridine); 7.59 (1H, t, $J = 7.6$ Hz, H pyridine).

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