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Preparation and structural properties of thiametacyclophanes having pyridine rings

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Various substituents have been introduced into the inner position of the dithia[3.3]metabenzenopyridinophanes (MPPs) and their conformational are evaluated by variable temperature ^{1}H NMR spectral measurements, IR measurements, computer calculation and X-ray structural analyses.

Keywords: metapyridinophanes, conformational properties, X-ray analyses

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Recently, weak interactions such as hydrogen-bonding, π–π interaction, charge-transfer, electrostatic interaction, *etc*. have been attracting great interest because they play very important roles *in vivo* and *in vitro*. On the other hand, conformational properties in the ring-shaped organic compounds are closely related to intra- and intermolecular weak interactions.[1,2] We have already discussed the conformational properties of substituted[3.3]metacyclophanes (MCPs) only in terms of bulkiness of the inner substituent.[3] We have also reported that the intra- and the intermolecular weak interactions play very important roles to regulate the crystal and the molecular structure in dithia[3.3]MCPs.[4]

We have also been investigating conformational properties in small- and medium-sized metacyclophane (MCP) compounds.[5] So far, the relationship between conformational properties of MCPs and the weak interactions has not well been understood. Vögtle *et al.* reported the preparation and conformational properties of dithia[3.3]MCPs in which no information about weak interactions in the system has appeared.[6] We report now on the preparation and structural properties of MPPs having one or two pyridine ring(s), since the pyridine nitrogen atom has the ability to be involved in hydrogen-bonding. ^{1}H NMR, FT-IR, UV measurement and X-ray structure analyses of the MPPs were employed in order to know the relationship between the structural properties and the intramolecular weak interactions in the MPPs.

Preparation of dithia[3.3]MPPs

2,11-Dithia[3.3]MPP[6] **3a**, 9-substituted 2,11-dithia[3.3]MPPs **3b–e** and 6,9-disubstituted 2,11-dithia[3.3]MPPs **3f–g** were prepared from the corresponding bis(halomethyl)arenes **1** and 2,6-bis(mercaptomethyl)pyridine **2** using the high-dilution method.[6] Reduction of nitroMPP **3c** with hydrogen in the presence of 10% Pd/C catalyst gave amino[3.3]MPP **3g** in *ca* 70% yield.

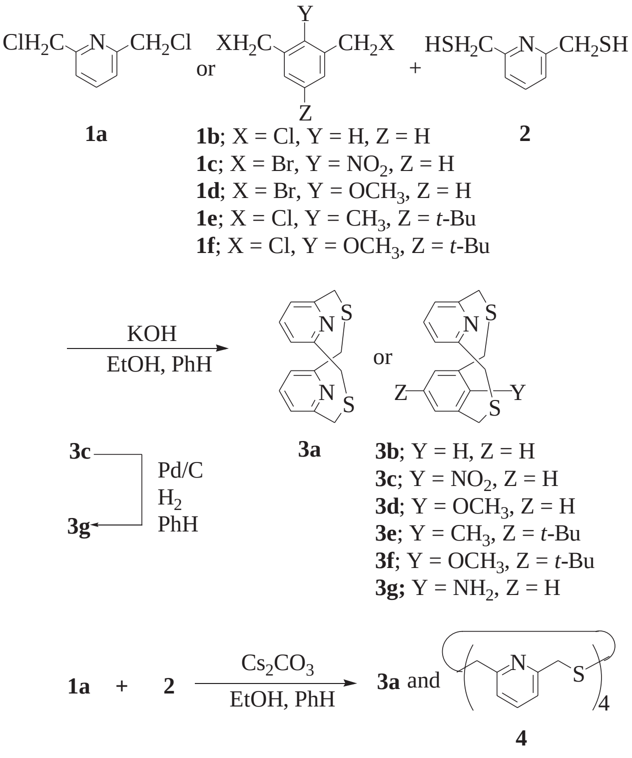
Interestingly, tetrathia[3^4]tetrametapyridinophane **4** can be obtained in low yield (20%) by using caesium carbonate instead of potassium hydroxide as a base (Scheme 1).

The identities of these small- and large-sized MPPs were confirmed by MS, elemental analyses, variable temperature ^{1}H NMR and IR spectra.

^{1}H NMR spectral properties

In the ^{1}H NMR spectra, bridged methylene protons of MPP **3a** appeared as only one sharp peak in $CDCl_3$ at 293 K.[6] On lowering the temperature to 213 K, two pairs of doublets for the bridge methylene protons were observed in MPP **3a**.

In contrast, MCP **4** seems to be more flexible than MPP **3a** because the bridge methylene protons were still observed as a singlet below 213 K. The NMR peaks of the bridge methylene protons of MPP **3b** show the same tendency: two sharp peaks are observed at 293K, and the bridge protons still appear as two singlets below 213 K (δ = 3.83 and 3.94 ppm). This can be explained by the fact that the two stable conformations of two bridged thiaethers of MPP **3b** exist and the one stable conformation can rapidly convert into the other, even in the low temperature region.



Scheme 1

On the other hand, MPPs **3c–d** exhibit quite different spectra from those of **3a**, **3b**, the bridge protons showing as two double doublets at 293 K. These data imply that the structures are rigid at room temperature, because the bulkiness of their inner substituent inhibits their conformational exchange. Such differences of the peak patterns and the coupling constants of their bridge protons of MPPs **3c–d** could be affected by the differences of their conformational stabilities and rigidity. It can be concluded that MPP **3a** and **3b** are more flexible than other MPPs.

In MPP **3g**, the chemical shifts of the NH_2 protons were observed at 4.75 ppm as a broad singlet. Outer aryl proton appeared in the same region (δ = 6.97 ppm) as that of MPP **3c** (δ = 6.95 ppm). Generally, the aryl protons of the aniline ring

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appear in a more upfield region than those of nitrobenzene. From these data, it can be assumed that the outer aryl proton is not affected by the ring current effect of the opposite pyridine ring in MPP **3g**. These results suggest that the conformation of MPP **3g** is not the "*syn*" structure but the "*anti*".

IR spectral properties

In the IR spectra, wavenumbers of symmetric and asymmetric stretching vibrations of the N–O bond in MPP **3c** appeared at 1433 cm^{-1} and 1350 cm^{-1}, respectively. The corresponding vibrations of the reference compound 2,6-dimethylnitrobenzene **5** were found to be at 1484 cm^{-1} and 1400 cm^{-1}, respectively. The frequencies for MPP **3c** are thus 51 and 50 cm^{-1} lower than those of **5**. This suggests that the N–O bonds strengths of MPP **3c** are weakened, a reasonable explanation being because the cationic character of the nitrogen atom is reduced by N–S electrostatic interaction. The large shifts to lower wavenumbers also strongly support the notion that N-S electrostatic interaction exists in MPP **3c**.

On the other hand, the wavenumbers of the symmetric and asymmetric stretching vibrations of the N–H bond in MPP **3g** appeared at 3361 cm^{-1} and 3306 cm^{-1}, respectively. The corresponding vibrations of the reference compound 2, 6-dimethylaniline **5** were at 3484 cm^{-1} and 3400 cm^{-1}. Values of MPP **3g** are 123 cm^{-1} and 94 cm^{-1} lower than those of **5**. The large shifts to lower wavenumbers strongly suggest that N–H hydrogen-bondings exist in MPP **3g**. In our recent paper,[4] the same IR spectral tendency was observed for the aminoMCP having a phenyl ring instead of the pyridine with a structure otherwise similar to MPP **3g**. That strong hydrogen-bondings exist between the two amino protons and the bridge sulfur atoms in the compound is also revealed by X-ray analysis. Therefore, we conclude that strong intramolecular hydrogen-bondings exist in the molecule of MPP **3g**.

X Ray structure analyses

In order to confirm the structures, we performed X-ray structural analyses of MPPs **3c**, **3d**, **3f**, **3g** and **4**. These molecular structures are shown in Figs 1, 2, 3, 4 and 5, respectively.

These crystal data were summarised in the experimental section and the selected bond lengths and angles are also listed in Tables 1–5. X-ray data of MPP **3b**, **3g** could not be obtained because the shapes of their crystals were not good.

The molecular structure of MPP **3c** having a nitro group on its inner position is shown in Fig. 1. Interestingly, the conformation "*syn*, boat-chair" is found to be unique to MPP **3c**. The distance between the nitrogen atom of the inner nitro group and the one bridge sulfur atom (3.19 Å) is much shorter than the sum of van der Waals radii of sulfur atom and nitrogen atom (*ca* 3.35 Å). This result strongly suggests the existence of intramolecular electrostatic interaction between the nitro atom (δ^+) of the inner NO$_2$ group and the one bridge sulfur atom (δ^-) in MPP **3c**. This N–S electrostatic interaction is indicated by dotted line in Fig. 1. It can be assumed that this interaction is responsible for the particular "*syn*, boat–chair" conformation.

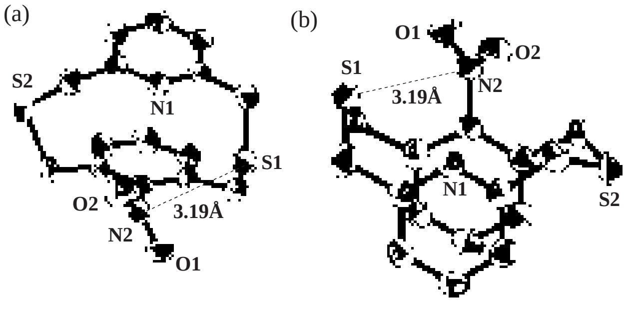

Fig. 1 Molecular structure of nitrodithia[3.3]MMP **3c**. Hydrogen atoms are omitted for clarity. Intramolecular N-S interaction is shown by dotted line. (a) Front view. (b) Top view.

Table 1 Selected bond lengths(Å) and bond angles(°) for **3c**

S(1)	C(1)		1.819(3)
S(1)	C(2)		1.817(3)
S(2)	C(8)		1.801(3)
S(2)	C(9)		1.811(3)
O(1)	N(2)		1.225(3)
O(2)	N(2)		1.219(3)
N(2)	C(9)		1.342(3)
N(1)	C(7)		1.335(3)
N(1)	C(3)		1.340(3)
N(2)	C(15)		1.471(3)
C(1)	S(1)	C(2)	104.5(1)
C(8)	S(2)	C(9)	103.5(2)
C(3)	N(1)	C(7)	118.0(2)
O(1)	N(2)	O(2)	123.6(2)
O(1)	N(2)	C(15)	117.1(2)
O(2)	N(2)	C(15)	119.3(2)

In the crystal, the conformation of MPP **3d** is also "*syn*, chair–chair". This implies that the inner methoxy group only works as the bulkiness substituent relevant to the steric hinderance between the methoxy group and the two side thiaether chains.

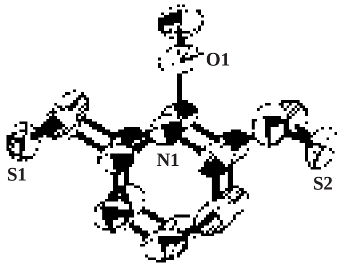

Fig. 2 Molecular structure of methoxydithia[3.3]MPP **3d** Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths(Å) and bond angles(°) for **3d**

S(1)	C(1)		1.808(4)
S(1)	C(2)		1.815(4)
S(2)	C(9)		1.803(4)
S(2)	C(10)		1.805(3)
O(1)	C(8)		1.385(3)
O(1)	C(16)		1.422(4)
N(1)	C(11)		1.340(4)
N(1)	C(15)		1.336(4)
C(1)	S(1)	C(2)	102.3(2)
C(9)	S(2)	C(10)	102.0(2)
C(11)	N(1)	C(15)	118.5(2)
C(8)	O(1)	C(16)	113.6(2)

The molecular structures of *t*-butylated MPP **3f** and **3g** are also "*syn*, chair–chair". The bulkiness of the *t*-butyl group does not affect the conformation of the molecule. The angles between the aromatic rings having *t*-butyl group and the opposite pyridine rings are similar to those of the corresponding MPPs having no *t*-butyl group. These results mean that the angles between the two aromatic rings of MPPs **3f–g** are not affected by the bulkiness of the outer *t*-butyl group.

The single crystal of tetrathia[3^4]tetrametapyridinophane **4** was also investigated and the molecular structure was determined. The molecular structure is fixed and folded in the crystal but it can move freely in the solution. It is assumed that the molecule can include many acidic or cationic organic guests, and also coordinate to many metal ions. These properties of **4** as a host molecule are currently under investigation.

The structures of MPPs as determined by ^{1}H NMR or X-ray analysis are summarised in Table 6.

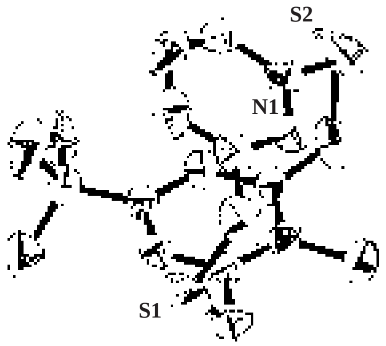

Fig. 3 Molecular structure of[3.3]MMP **3e**. Hydrogen atoms are omitted for clarity.

Table 3 Selected bond lengths(Å) and bond angles(°) for **3e**

S(1)	C(1)		1.810(8)
S(1)	C(2)		1.814(6)
S(2)	C(8)		1.811(7)
S(2)	C(9)		1.815(8)
N(1)	C(3)		1.344(7)
N(1)	C(7)		1.337(7)
C(1)	S(1)	C(2)	103.2(3)
C(8)	S(2)	C(9)	102.6(3)
C(3)	N(1)	C(7)	118.1(5)

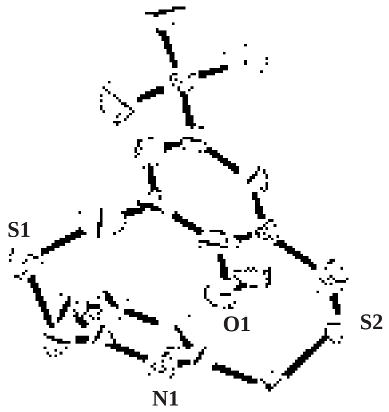

Fig. 4 Molecular structure of [3.3]MPP **3f**. Hydrogen atoms are omitted for clarity.

Table 4 Selected bond lengths(Å) and bond angles(°) for **3f**

S(1)	C(1)		1.799(3)
S(1)	C(2)		1.811(4)
S(2)	C(9)		1.811(3)
S(2)	C(10)		1.803(3)
O(1)	C(8)		1.388(3)
O(1)	C(16)		1.429(4)
N(1)	C(11)		1.340(3)
N(1)	C(15)		1.331(3)
C(1)	S(1)	C(2)	101.0(1)
C(9)	S(2)	C(10)	102.9(1)
C(11)	N(1)	C(15)	118.1(2)
C(8)	O(1)	C(16)	113.1(2)

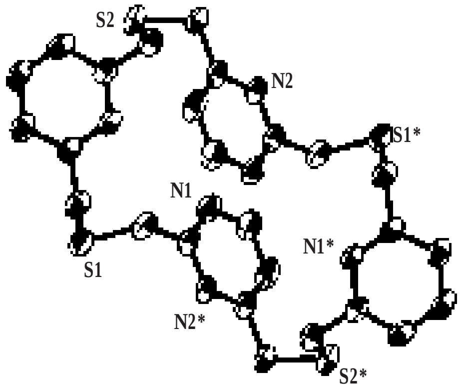

Fig. 5 Molecular structure of tetrathia[3^4]MCP **4**. Hydrogen atoms are omitted for clarity.

Table 5 Selected bond lengths(Å) and bond angles(°) for **4**

S(1)	C(1)		1.816(3)
S(1)	C(14)		1.820(3)
S(2)	C(7)		1.819(2)
S(2)	C(8)		1.812(2)
N(1)	C(2)		1.337(3)
N(1)	C(6)		1.342(3)
N(2)	C(9)		1.342(3)
N(2)	C(13)		1.347(3)
C(1)	S(1)	C(14)	103.0(1)
C(7)	S(2)	C(8)	100.8(1)
C(2)	N(1)	C(6)	118.7(2)
C(9)	N(2)	C(13)	117.9(2)

Table 6 Summary of conformation of MPPs **3** determined by ^{1}H NMR data[a] and X-ray results[b]

Compound	Conformation		
	Bridge chains	Aromatic rings	Flexibility[c]
3b	Chair-chair	*Syn*	Flexible
3c	Boat-chair	*Syn*	Rigid
3d	Chair-chair	*Syn*	Rigid
3e	Chair-chair	*Syn*	Rigid
3f	Chair-chair	*Syn*	Rigid
3g	———	*Anti*	Rigid

Computer calculation for the molecular structure of MPP 3c

In computer calculation (PM3 level), the lowest energy structure of MPP **3c** is “chair–chair” conformation. When the lowest energy structure of MPP **3c** set to “boat-chair” conformation, the calculated length between the nitrogen atom of the NO_2 group and the one bridge sulfur atom (3.32 Å) is longer to the X-ray result (3.19 Å). This result also supports that the N–S electrostatic interaction exists in MPP **3c**. The results are summarised in Table 7.

Table 7 Distance between nitrogen atom of nitro group and a bridge sulfur atom in MPPs **3d** calculated by MOPAC PM3 level

	X-Ray result	Calculation	Sum of VDU radii
Distance	3.19Å	3.32Å	3.35Å
Conformation	Boat-chair	Chair-chair	———

[a] Most stable conformation

Conclusions

MPPs having various substituents on their inner or/and outer position(s) can be prepared, and the conformational properties of some MPPs in the crystals and in the solutions are studied by ^{1}H-NMR measurements and X-ray analyses.

It can also be presumed that the conformations of [3.3]MPPs are affected by not only the steric hindrance of the inner substituent and the electronic properties of the internal substituent but also the intramolecular weak interaction such as NH–S hydrogen-bonding or N–S electrostatic interaction.

It is also found that the outer bulky substituent does not affect the structures of the MPPs.

Experimental

All melting points were recorded on a Yanako hot-stage microscope apparatus. ^{1}H NMR spectra were recorded on a Nippon Densi α-500 spectrometer and a spectrometer in $CDCl_3$ or CD_3CN with Me_4Si as an internal reference. IR spectra were recorded on a Nippon Bunko JASCO IR-700 spectrometer. Mass spectra were obtained on a Nippon Densi JEOL-DX-300 spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300); the amounts of silica gel used were 5–50g.

Preparation of MPPs 3 except for 3g: typical procedure

A solution of 2,6-bis(halomethyl)arene **1** (7.00 mmol) and 3.00 g of 2,6-bis(mercaptomethyl)pyridine **2** (7.00 mmol) in benzene/ethanol (1:2) (300 cm^3) was added dropwise over period of 8 h from a Henshberg funnel with stirring to a refluxed solution of 2.25 g of KOH (40.0 mmol) in ethanol (1.0 dm^3) (high-dilution technique). After the addition, the reaction mixture was concentrated under reduced pressure to leave a residue which was extracted with dichloromethane. The extract was concentrated and the residue was chromatographed over silica gel using toluene as eluent, to give MPP **3**.

2,11-Dithia[3.3]metapyridinophane (MPP) **3a**: colourless prisms (hexane) (420 mg, 22%); m.p. 230–235 °C; δ_H (400 MHz; $CDCl_3$) 3.99 (8H, s, bridged CH_2SCH_2), 6.95 (4H, d, aromatic, J = 7.6 Hz), 7.24 (2H, dd, aromatic, J = 7.6 Hz); *m/z* 274 (M$^+$). (Found; C, 61.6; H, 5.2; N, 10.4. $C_{14}H_{14}N_2S_2$ requires C, 61.3; H, 5.1; N, 10.2 %).

MPP **3b**: colourless needles (hexane) (380 mg, 20%); m.p. 176–178 °C; δ_H (400 MHz; $CDCl_3$) 3.83 (4H, s, bridged CH_2S), 3.94 (4H, s, bridged S CH_2), 6.88 (4H, d, bridged aromatic, J = 7.3Hz), 7.12 (1H, s, aromatic), 7.15 (2H, dd, aromatic, J = 7.3Hz); *m/z* 273 (M$^+$). (Found; C, 65.6; H, 5.6; N, 5.0. $C_{15}H_{15}NS_2$ requires C, 65.9; H, 5.5; N, 5.1%).

MPP **3c**: pale yellow prisms (dichloromethane-hexane) (550 mg, 25%); m.p. 165–167 °C; δ_H (500 MHz; $CDCl_3$) 3.50 (2H, d, bridged SCH_2, J = 13.7 Hz), 3.56 (2H, d, bridged CH_2S, J = 13.1 Hz), 3.81 (2H, d, bridged SCH_2, J = 13.7 Hz), 4.39 (2H, d, CH_2S, J = 13.1 Hz), 6.89 (1H, dd, aromatic, J = 7.5 Hz), 7.11 (2H, d, aromatic, J = 7.5 Hz), 7.14 (2H, d, aromatic, J = 2.4 Hz), 7.25 (2H, d, aromatic, J = 2.4 Hz); *m/z* 318 (M$^+$). (Found; C, 57.0; H, 4.5; N, 8.7. $C_{15}H_{14}N_2O_2S_2$ requires C, 56.6; H, 4.4; N, 8.8%).

MPP **3d**: colourless needles (hexane–dichloromethane) (504 mg, 24%); m.p. 110–112 °C; δ_H (400 MHz; $CDCl_3$) 3.42 (2H, d, bridged CH_2S, J = 14.0 Hz), 3.80 (2H, d, bridged SCH_2, J = 13.7 Hz), 4.04 (2H, d, bridged CH_2S, J = 14.0 Hz), 4.43 (2H, d, SCH_2, J = 13.7 Hz), 3.65 (3H, s, OMe), 6.63 (1H, dd, aromatic, J = 7.3Hz), 6.99 (1H, dd, aromatic, J = 7.4 Hz), 7.02 (2H, d, aromatic, J = 7.3Hz), 7.04 (2H, d, J = 7.4Hz); *m/z* 303 (M$^+$) (Found; C, 63.6; H, 5.3; N, 4.7. $C_{16}H_{17}NOS_2$ requires C, 63.3; H, 5.7; N, 4.6%).

MPP **3e**: colourless prisms (hexane) (1.54 g, 64%); m.p. 114–116 °C; δ_H (400 MHz; $CDCl_3$) 1.14 (9H, s, *t*-butyl), 1.58 (3H, s, Me), 3.59 (2H, d, bridged CH_2S, J = 13.6 Hz), 3.73 (2H, d, bridged SCH_2, J = 14.4 Hz), 3.90 (2H, d, bridged CH_2S, J = 13.6 Hz), 4.31 (2H, d, bridged SCH_2, J = 14.4 Hz), 6.86 (2H, d, aromatic, J = 7.6 Hz), 6.90 (2H, s, aromatic), 7.23 (1H, dd, aromatic, J = 7.6 Hz); *m/z* 343 (M$^+$). (Found; C, 70.0; H, 7.5; N, 4.0. $C_{20}H_{25}NS_2$ requires C, 69.9; H, 7.3; N, 4.1%).

MPP **3f**: colourless prisms (hexane) (553 mg, 22%); m.p. 166–168 °C; δ_H (400 MHz; $CDCl_3$) 1.13 (9H, s, *t*-butyl), 3.66 (3H, s, OMe), 3.41 (2H, d, bridged CH_2S, J = 13.6 Hz), 3.75 (2H, d, bridged SCH_2, J = 14.4 Hz), 3.92 (2H, d, bridged CH_2S,J = 13.6 Hz), 4.44 (2H, d, bridged SCH_2, J = 14.4 Hz), 6.91 (2H, d, aromatic, J = 7.7 Hz), 6.97 (2H, s, aromatic), 7.22 (1H, dd, aromatic, J = 7.7 Hz); *m/z* 359(M$^+$).(Found; C, 67.0; H, 7.1; N, 3.7. $C_{20}H_{25}NOS_2$ requires C, 66.8; H, 7.0; N, 3.9%).

Preparation of MPP 3g

10% Pd/C (100 mg) was added to a solution of MPP **3c** (96 mg, 0.30mmol) in benzene (50 cm^3). After hydrogen gas was introduced into the mixture with stirring for 2 h at r.t., the Pd/C was filtered off. The filtrate was evaporated under reduced pressure to leave the residue, which was recrystallised from hexane to give MPP **3g** (60 mg, 70%).

MPP **3g**: colourless prisms (hexane); m.p. 153–155 °C; ν_{max} (KBr)/cm^{-1} 3361, 3306 (NH_2); δ_H (400 MHz; $CDCl_3$) 4.73 (2H, broad s, NH_2), 3.52 (2H, d, bridged CH_2S, J = 13.7 Hz), 3.80 (2H, d, bridged CH_2S, J = 13.7 Hz), 3.93 (2H, d, bridged S CH_2, J = 14.3 Hz), 4.02 (2H, d, S CH_2, J = 14.3 Hz), 6.73 (1H, dd, aromatic, J = 7.5 Hz), 6.82 (2H, d, aromatic, J = 7.6 Hz), 6.93 (1H, d, aromatic, J = 7.5 Hz), 7.40 (1H, dd, aromatic, J = 7.6 Hz); *m/z* 288 (M$^+$). (Found; C, 62.5; H, 5.7; N, 9.9. $C_{15}H_{16}N_2S_2$ requires C, 62.5; H, 5.6; N, 9.7%).

Preparation of tetrathia[3^4]MPP 4

A solution of 2,6-bis(chloromethyl)pyridine **1a** (1.23 g, 7.00 mmol) and 2,6-bis(mercaptomethyl)-pyridine **2** (1.20 g, 7.00 mmol) in benzene/ethanol (1:2) (300 cm^3) was added dropwise over period of 8 h from a Henshberg funnel with stirring to a refluxing solution of Cs_2CO_3 (6.72 g, 40.0 mmol) in ethanol (800 cm^3) (high-dilution technique). After the addition, the reaction mixture was concentrated under reduced pressure to leave the residue, which was extracted with dichloromethane. The extract was concentrated and the residue was chromatographed over silica gel, using toluene as an eluent to give MPP **4** (380 mg, 20%).

MPP **4:** colourless prisms (hexane); m.p. 191–193 °C; δ_H (400 MHz; $CDCl_3$) 3.92 (16H, s, bridged CH_2S), 6.47 (4H, dd, aromatic, J = 7.6 Hz), 6.88 (8H, d, aromatic, J = 7.6 Hz), *m/z* 548 (M$^+$). (Found; C, 61.5; H, 5.2; N, 10.5. $C_{28}H_{28}N_4S_4$ requires C, 61.3; H, 5.1; N, 10.2%).

Crystal structure determinations of MPP 3c, 3d, 3f, 3g and 4

Crystal data for MPP **3c:** Recrystallised from benzene. $C_{15}H_{14}N_2O_2S_2$, M = 318.41, monoclinic, a = 9.212(1), b = 13.101(1), c = 12.351(1) Å, β = 114.97(1)°, U = 1454.7(3) Å^3, T = 293.2 K, space group $P2_1/n$ (no. 14), Z = 4, D_{calc} = 1.454 g/cm^3, μ(Mo-Kα) = 3.368 mm^{-1}, 2642 reflections measured, 2344 unique (R_{int} = 0.044) which were used in all calculations. The final $wR(F^2)$ was 0.137(all data).

Crystal data for MPP **3d:** Recrystallised from hexane. $C_{16}H_{17}NOS_2$, M = 303.45, triclinic, a = 8.0845(8), b = 9.139(1), c = 11.170(1) Å, α = 94.38(1), β = 106.297(10), γ = 104.501(9)°, U= 757.3(2)Å^3, T = 293.2 K, space group P-1 (no. 2), Z = 2, D_{calc} = 1.331 g/cm^3, μ(Mo-Kα) = 3.134 mm^{-1}, 2687 reflections measured, 2199 unique (R_{int} = 0.049) which were used in all calculations. The final $wR(F^2)$ was 0.165(all data).

Crystal data for MPP **3e:** Recrystallised from hexane. $C_{20}H_{25}NS_2$, M = 343.54, monoclinic, a = 9.614(4), b = 24.201(5), c = 16.136(5) d, β = 92.73(3)°, U = 3750(1) d^3, T = 293.2 K, space group $P2_1/a$ (no. 14), Z = 8, D_{calc} = 1.217 g/cm^3, μ(Mo-Kα) = 0.283 mm^{-1}, 8872 reflections measured, 4297 unique (R_{int} = 0.086) which were used in all calculations. The final $wR(F^2)$ was 0.223(all data).

Crystal data for MPP **3f:** Recrystallised from hexane. $C_{20}H_{25}NOS_2$, M =359.54, monoclinic, a = 11.425(1), b = 24.461(2), c = 14.623(1) Å, β = 108.490(7)°, U = 3875.9(6) Å^3, T = 293.2 K, space group $P2_1/c$ (no. 14), Z = 8, D_{calc} = 1.232 g/cm^3, μ(Mo-Kα) = 2.524 mm^{-1}, 7263 reflections measured, 5967 unique (R_{int} = 0.057) which were used in all calculations. The final $wR(F^2)$ was 0.152(all data).

Crystal data for MPP **4:** Recrystallised from hexane. $C_{28}H_{28}N_4S_4$, M = 548.80, triclinic, a = 8.285(1), b = 9.080(2), c = 10.086(1) Å, α = 112.55(1), β = 91.459(10), γ = 108.57(1)°, U = 654.8(2) Å^3, T = 293.2 K, space group P-1 (no. 2), Z = 1, D_{calc} = 1.392 g/cm^3, μ(Mo-Kα) = 3.527 mm^{-1}, 2322 reflections measured, 2154 unique (R_{int} = 0.044) which were used in all calculations. The final $wR(F^2)$ was 0.159(all data).

Intensity data for MPP **3c**, **3d**, **3e**, **3f** and **4** were collected on a Rigaku AFC7R diffractometer with graphite-monochromatised Mo-Kα radiation. These structures were solved with teXsan crystallographic software package of Molecular Structure Corporation.

CCDC reference numbers 165705 for **3c**, 175663 for **3d**, 165582 for **3e**, 167502 for **3f**, and 167501 for **4**, respectively.

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