Building Functionality into 4′-Hydrazone Derivatives of 2,2′:6′,2″-Terpyridine

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This article is dedicated to our friend and colleague *Jean-Claude Bünzli* on the occasion of his 65th birthday

The syntheses of the five 2,2′:6′,2″-terpyridine (tpy) ligands **5**–**9** functionalized in the 4′-position with a hydrazone substituent RR′C=N–NH (R = R′ = Me; R = H, R′ = 4-BrC_6H_4, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, or 3,5-$(MeO)_2C_6H_3$) are described. Protonation of the tpy domain of the ligands is facile. Solution behaviour has been studied by NMR and electronic spectroscopies. Representative structural data are presented for neutral and monoprotonated ligands, and illustrate that H-bonding involving the formal amine NH unit is a dominant structural motif in all cases.

Introduction. – There has been a long-standing interest in hydrazones and their metal complexes, largely through their applications in analytical chemistry [1][2], organic synthesis [3][4], biologically related areas [5–9] and sensors, optoelectronic and polymeric materials [10–17]. Hydrazone units attached to ligand scaffolds are relatively rigid spacers and have been incorporated into supramolecular assemblies including helical wires [18][19], grids [20–26], and coordination polymers containing interconnected metallomacrocycles [27]. The assembly of this last example depended upon the hydrazone unit acting as a nonlinear spacer, and upon the incorporation of a peripheral metal-binding domain, in this case, pyridine. We recently reported the family of 4′-substituted 2,2′:6′,2″-terpyridine (tpy) ligands **1**–**4** (*Fig. 1*), and described the effects that varying the R and R′ substituents had on their solution behaviour (in particular rotation about the $C_{pyridine}–N_{amine}$ bond) and packing interactions in the solid state [28]. The synthesis of these hydrazones was by the well-documented acid-catalysed condensation of a hydrazine (4′-hydrazino-2,2′:6′,2″-terpyridine or 4′-(1-methylhydrazino)-2,2′:6′,2″-terpyridine [29–31]) with an aldehyde or ketone. This methodology is readily adapted to the preparation of other 4′-hydrazone derivatives of tpy with pendant functionalities. We report here the synthesis of five new members of this series of compounds, along with solution behaviour and structural data for representative neutral and monoprotonated ligands.

Results. – The experimental strategy that we have previously established for the synthesis of 4′-hydrazone derivative **1** involves the reaction of 4′-hydrazino-2,2′:6′,2″-terpyridine with PhCHO in MeOH in the presence of a few drops of concentrated

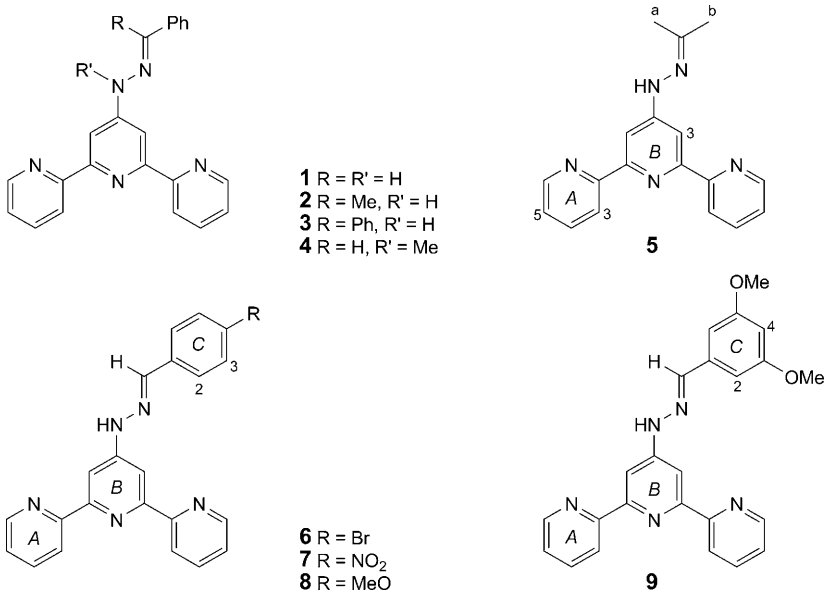

Fig. 1. *Structures of ligands* **1**–**9** *and atom labelling for NMR spectroscopic assignments*

H_2SO_4. This results in the formation of the bright yellow methyl sulfate salt of $[H_2\mathbf{1}]^{2+}$ (structurally confirmed for the chloride salt). Subsequent treatment of $[H_2\mathbf{1}][MeOSO_3]_2$ with $NaBF_4$ or K_2CO_3 results in the formation of $[H\mathbf{1}][BF_4]$ or **1**, respectively [28]. This same sequence of reactions has been used to isolate **2**–**4** and their mono- and diprotonated derivatives [28], as well as 4′-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,2′:6′,2″-terpyridine and its monoprotonated analogue [32]. The reaction of acetone with 4′-hydrazino-2,2′:6′,2″-terpyridine in MeOH in the presence of concentrated H_2SO_4 produced bright yellow $[H_2\mathbf{5}][MeOSO_3]_2$, formulated by analogy with the fully characterized diprotonated derivatives of compounds **1**–**4**. Treatment of $[H_2\mathbf{5}][MeOSO_3]_2$ with $NaBF_4$ led to the formation of $[H\mathbf{5}][BF_4]$, the electrospray mass spectrum (ESI-MS) of which showed peaks at *m*/*z* 304.1, 326.1, and 629.0 assigned to $[H\mathbf{5}]^+$, $[\mathbf{5}+Na]^+$, and $[(\mathbf{5})_2Na]^+$. In the ^{1}H-NMR spectrum, the signals assigned to H-atoms H_{A3} and H_{B3} are broad (*Fig. 2*,*a*), consistent with protonation restricting rotation about the C_{py}(ring *A*)–C_{py}(ring *B*) bonds. We have already presented a detailed study of the affects of protonation on the energy barriers to rotation about the C_{py}(ring *A*)–C_{py}(ring *B*) and C_{py}(ring *B*)–N_{amine} bonds [28].

Treatment of $[H_2\mathbf{5}][MeOSO_3]_2$ with K_2CO_3 gave **5** in good yield as an off-white solid. The ESI-MS exhibited a base peak at *m*/*z* 304.1 assigned to $[H\mathbf{5}]^+$. The ^{1}H- and ^{13}C-NMR spectra were fully assigned by 2D-techniques, the $H_{Me\text{-}a}$ and $H_{Me\text{-}b}$ signals being distinguished by the observation of a NOESY cross-peak between the signals for the NH and $H_{Me\text{-}a}$ H-atoms. The symmetrical appearance of the tpy region of the ^{1}H-NMR spectrum (*Fig. 2*,*b*) was evidence for there being free bond rotation about the C_{py}–N_{amine} bond on the NMR timescale, and the well-resolved signals for H_{B3} and H_{A3} confirmed that rotation about the C_{py}(ring *A*)–C_{py}(ring *B*) bonds was no longer

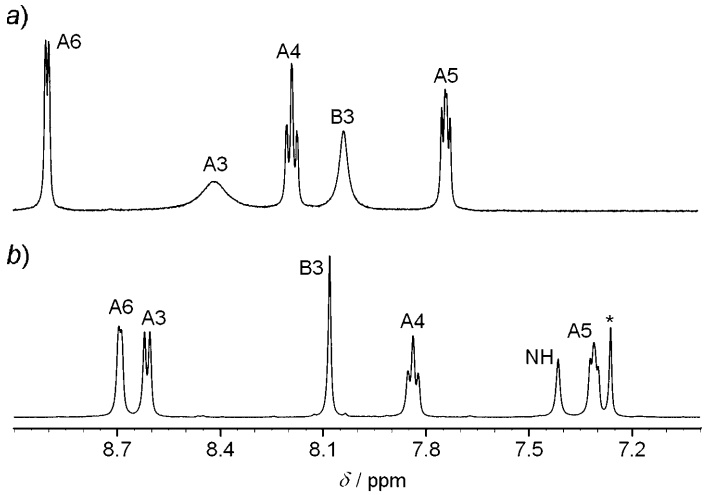

Fig. 2. *Part* (δ(H) 9.0–7.0) *of the room-temperature 500-MHz ^{1}H-NMR spectra of* a) *a* (D_6)DMSO *solution of [H***5***][BF$_4$], and* b) *a $CDCl_3$ solution of* **5** (* = residual solvent peak). For H-atom numbering, see *Fig. 1*.

restricted. Large pale yellow, X-ray-quality blocks of **5** were grown by slow evaporation of a $CDCl_3$ solution of the compound. The molecular structure of **5** is shown in *Fig. 3*, and selected bond parameters (which are unexceptional) are given in the caption. All the C- and N-atoms of the $Me_2C{=}NNH-$ (ring *B*) unit are within 0.2 Å of the least-squares plane through the 11 C- and N-atoms which comprise this unit. The tpy unit adopts the expected s-*trans*,s-*trans*-configuration, but one pyridine ring is twisted significantly out of the plane of the other two (angles between least squares planes of rings containing N(1) and N(2), and N(3) and N(2) are 17.94(3) and 1.42(4)°, resp.). The deviation from planarity is associated with the intermolecular interactions. Molecules associate in pairs by virtue of the H-bonds shown in *Fig. 4*,*a* ($N(4)H(1)\cdots N(1^i) = 2.75$, $N(4)\cdots N(1^i) = 3.570(1)$ Å, $N(4)-H(1)\cdots N(1^i) = 154°$; $C(7)H(71)\cdots N(1^i) = 2.75$, $C(7)\cdots N(1^i) = 3.580(1)$ Å, $N(4)-H(1)\cdots N(1^i) = 146°$; symmetry code, see *Fig. 4* caption). The centrosymmetric dimer forms a V-shaped motif, and these assemble into a herringbone architecture (*Fig. 4*,*b*), reminiscent of that adopted by compound **1** in the solid state [28].

The reaction of a slight excess of 4-bromobenzaldehyde, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde, or 3,5-dimethoxybenzaldehyde with 4′-hydrazino-2,2′:6′,2″-terpyridine in MeOH or EtOH (see *Exper. Part*) in the presence of a few drops of concentrated H_2SO_4 led to the bright yellow methyl sulfate or ethyl sulfate salts of $[H_2\mathbf{6}]^{2+}$, $[H_2\mathbf{7}]^{2+}$, $[H_2\mathbf{8}]^{2+}$, or $[H_2\mathbf{9}]^{2+}$. These compounds were difficult to fully characterize, and were typically used directly for the syntheses of the neutral ligands. In the case of $[H_2\mathbf{7}][EtOSO_3]_2$, an analytically pure sample was obtained. The ^{1}H-NMR spectrum in (D_6)DMSO solution showed two sets of Et signals, δ(H) 3.73 and 1.10, and δ(H) 3.44 and 1.06. The latter pair of signals was assigned to EtOH [33] and the former to the ethyl sulfate anion. The persistant appearance of EtOH can be explained by

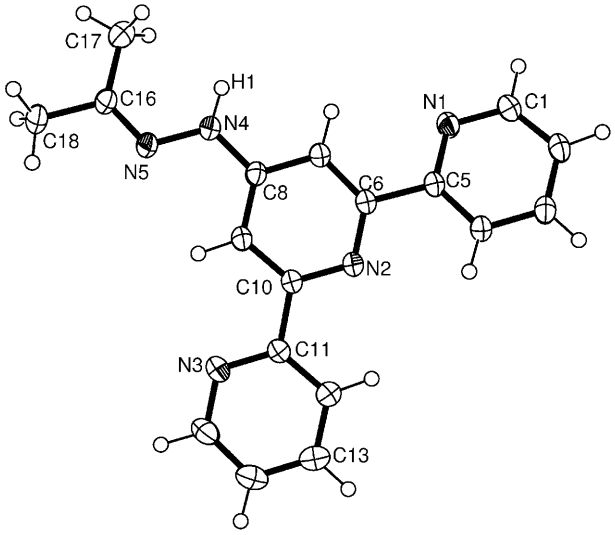

Fig. 3. *Molecular structure of* **5** *with thermal ellipsoids plotted at 50% probability level.* Selected bond parameters: N(5)–C(16) = 1.280(1), N(4)–N(5) = 1.3775(9), N(4)–C(8) = 1.3693(9), C(16)–C(17) = 1.496(1), C(16)–C(18) = 1.498(1) Å; N(5)–C(16)–C(17) = 124.77(7), N(5)–C(16)–C(18) = 117.18(8), C(17)–C(16)–C(18) = 118.05(8), N(4)–N(5)–C(16) = 116.87(7), N(5)–N(4)–C(8) = 119.41(6)°.

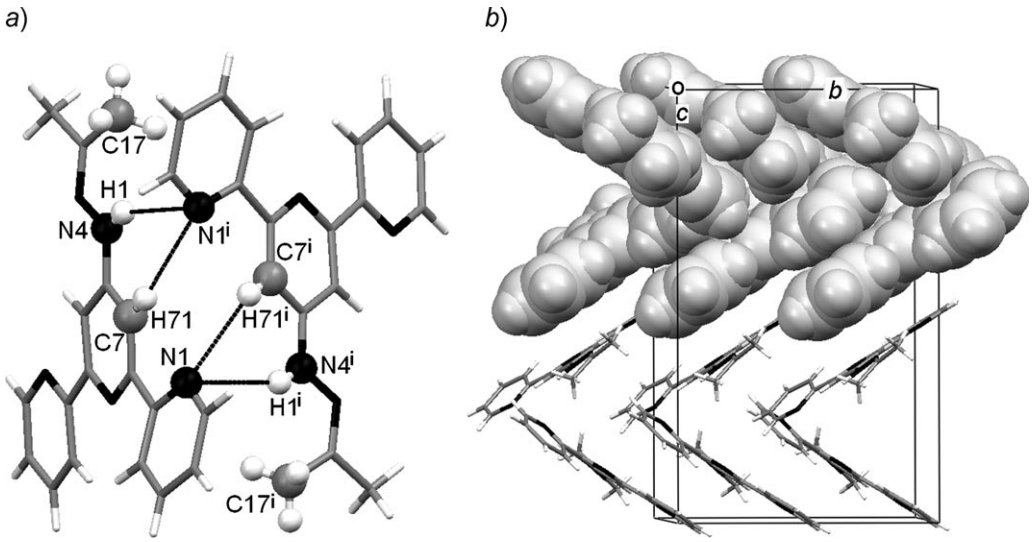

Fig. 4. a) *H-Bonded interactions between pairs of molecules of* **5** (symmetry code i = $-x$, y, $^3/_2 - z$). b) *Packing of dimeric motifs.* N-Atoms are shown in black.

hydrolysis of the anion by residual H_2O in the (D_6)DMSO solvent, and this phenomenon was consistently observed for methyl sulfate salts of $[H_2\mathbf{1}]^{2+}$, $[H_2\mathbf{2}]^{2+}$, $[H_2\mathbf{3}]^{2+}$, or $[H_2\mathbf{4}]^{2+}$ [28]. In the aromatic region of the spectrum of $[H_2\mathbf{7}][EtOSO_3]_2$, the

signal for H_{B3} was extremely broad, and that for H_{A3} appeared as a broadened *d* (see earlier discussion).

The exchange of the $[MeOSO_3]^-$ or $[EtOSO_3]^-$ ion for $[BF_4]^-$ allowed the monoprotonated 4′-hydrazone derivatives of tpy to be isolated. This was confirmed by a structural determination of [H**9**][BF_4], single crystals of which were grown by slow evaporation of a MeOH/H_2O 10:1 solution of the compound. The structure of the $[H\mathbf{9}]^+$ cation is shown in *Fig. 5*. The s-*cis*,s-*cis*-conformation of the tpy unit is consistent with that observed in [H**1**][PF_6], [H**2**][BF_4], and [H**3**][MeOSO3] [28] but contrasts with the s-*cis*,s-*trans*-arrangement adopted by the $[Htpy]^+$ cations in [Htpy][CF_3SO_3] [34] and [Htpy][ReO_4] [35]. The difference appears to arise from the H-bonding ability of the NH H-atom in the hydrazone derivatives. In [H**9**][BF_4], the $[BF_4]^-$ anion is H-bonded to the H(4)N(4) unit (N(4)H(4)···F(1) = 1.95, N(4)···F(1) = 2.858(3) Å, N(4)–H(4)···F(1) = 169°), and there are supporting C–H···F interactions to the same anion (C(4)H(41)···F(2) = 2.53, C(4)···F(2) = 3.521(4) Å, C(4)–H(41)···F(2) = 166°; C(7)H(71)···F(2) = 2.26, C(7)···F(2) = 3.251(3) Å, C(7)–H(71)···F(2) = 166°). The latter nonclassical H-bonds are only switched on if the tpy unit is in an s-*cis*,s-*cis* conformation which results in the favourable NH···N H-bonds shown in *Fig. 5*. In the crystal lattice, the cations are organized in ribbon-like assemblies, supported by the nonclassical H-bonds shown in *Fig. 6*. The arene rings in one ribbon are π-stacked over the tpy domains of an adjacent ribbon (separation of 3.3 Å), and stacks of infinite ribbons assemble into a pleated sheet with the least-squares plane through one ribbon subtending an angle of 136° with the next.

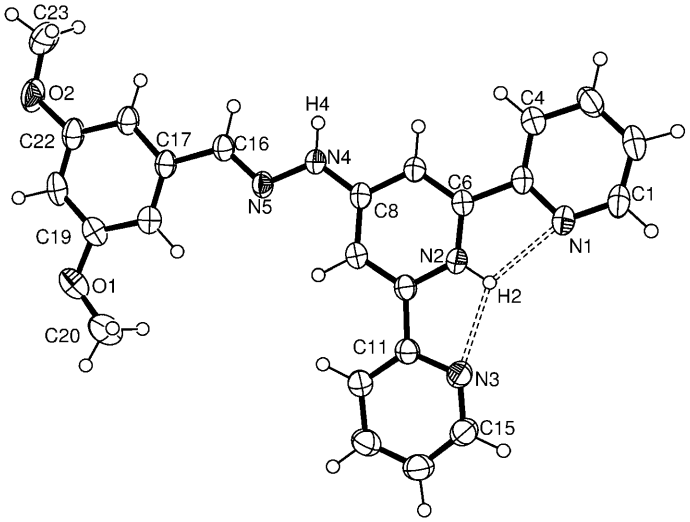

Fig. 5. *Molecular structure of [H**9**]⁺ in [H**9**][BF₄] with thermal ellipsoids plotted at 50% probability level.* Selected bond parameters: N(5)–C(16) = 1.284(3), N(4)–N(5) = 1.378(2), N(4)–C(8) = 1.346(3), C(16)–C(17) = 1.461(3), C(19)–O(1) = 1.360(3), C(20)–O(1) = 1.393(4), C(22)–O(2) = 1.365(3), C(23)–O(2) = 1.414(4) Å; N(5)–C(16)–C(17) = 121.9(2), N(4)–N(5)–C(16) = 114.1(2), N(5)–N(4)–C(8) = 120.5(2), C(20)–O(1)–C(19) = 118.6(2), C(23)–O(2)–C(22) = 118.4(2)°. H-Bonds: N(2)H(2)···N(1) = 2.23, N(2)···N(1) = 2.653(3) Å, N(2)–H(2)···N(1) = 107°; N(2)H(2)···N(3) = 2.25, N(2)···N(3) = 2.636(2) Å, N(2)–H(2)···N(3) = 105°.

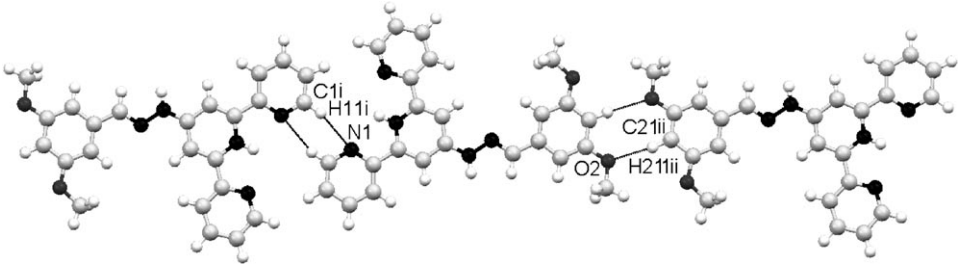

Fig. 6. *Ribbon assembly of [H**9**]$^+$ cations in [H**9**][BF$_4$]*. H-Bonds: O(2)···H(211^{ii})C(21^{ii}) = 2.44, O(2)···C(21^{ii})H(211^{ii}) = 3.425(4) Å, O(2)···C(21^{ii})–H(211^{ii}) = 163°; N(1)···H(11^{i})C(21^{i}) = 2.63, N(1)···C(21^{i}) = 3.555(4) Å, N(1)···H(11^{i})–C(21^{i}) = 153°. Symmetry codes: i = $-x$, $1-y$, $1-z$; ii = $1-x$, $1-y$, $1-z$.

Treatment of each of the methyl sulfate or ethyl sulfate salts of $[H_2\mathbf{6}]^{2+}$, $[H_2\mathbf{7}]^{2+}$, $[H_2\mathbf{8}]^{2+}$, or $[H_2\mathbf{9}]^{2+}$ with K_2CO_3 gave, after workup, neutral ligands **6**–**9** in moderate to good yields. All solution ^{1}H- and ^{13}C-NMR spectra were recorded in (D_6)DMSO and were assigned by 2D-techniques. The NMR spectroscopic characterization of these compounds is significantly easier than that of the protonated species since the spectra are well resolved at room temperature, with the exception of the signal for H-atom H_{B3} which is broad in all cases. This is consistent with hindered rotation about the C_{py}(ring *B*)–N_{amine} bond. For **6**, the ^{1}H-NMR spectrum was recorded in both (D_6)DMSO and $CDCl_3$. Whereas the signal for H_{B3} is broad in (D_6)DMSO, it is sharp in $CDCl_3$, indicating that the energy barrier to rotation about the C_{py}(ring *B*)–N_{amine} bond is lower in $CDCl_3$ than in (D_6)DMSO. The solvent dependence of the dynamic process can be attributed to H-bonding between a (D_6)DMSO and the NH in **6** which hinders bond rotation, an observation upon which we have previously commented with respect to compounds **1**–**3** [28]. Consistent with the environment of the NH being solvent dependent, the signal for this H-atom shifts from δ(H) 11.21 in (D_6)DMSO to 8.21 in $CDCl_3$. The chemical shift for the N=CH H-atom is also sensitive to solvent, appearing at δ(H) 7.64 in $CDCl_3$ and 8.02 in (D_6)DMSO. Other signals in the spectrum are little affected.

Single crystals of **6**·H_2O were grown by slow evaporation of a $CHCl_3$ solution of the compound. The compound crystallizes in space group $P-1$. The asymmetric unit contains two independent molecules which encapsulate two H_2O molecules within a H-bonded motif (*Fig. 7*); the O-attached H-atoms were located from the difference map. The tpy adopts the usual s-*trans*,s-*trans*-configuration, and the combination of two pyridine acceptors and two NH donors in a pair of ligands with the NH groups facing one another is ideally set up to host two H_2O molecules. One H_2O H-atom (H(101)) remains free to act as a H-bond donor to a similar motif stacked above the first one. The four aromatic rings in each molecule of **6** are not coplanar and deviate from a plane by between 13.3(1)° (angle between the least squares planes between rings containing atoms N(1) and N(2)) and 22.4(1)° (angle between rings containing N(7) and C(39)). The ((**6**)$_2$·2 H_2O) motifs align into parallel sheets, with the preferred orientations of the aromatic rings optimizing short intermolecular C–H···N, C–H···Br, and N···Br contacts (Br(1)···N(6^{ii}) = 3.417(3), Br(2)···N(3^{iii}) = 3.341(2) Å; symmetry codes:

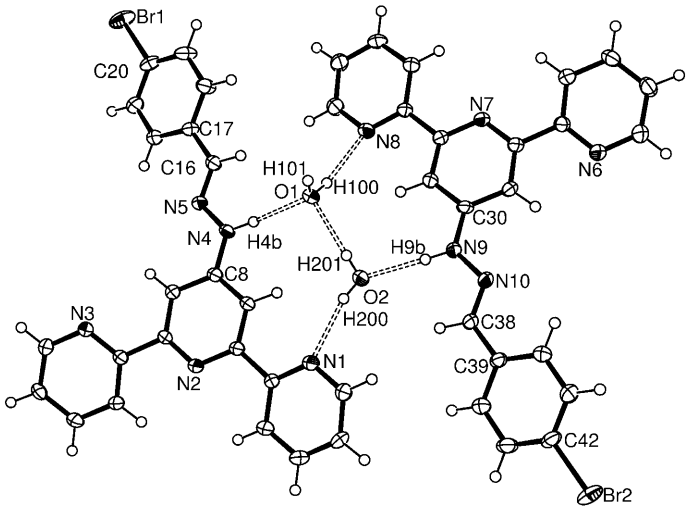

Fig. 7. *The asymmetric unit of the solid-state structure of* **6**·H_2O *with thermal ellipsoids plotted at 50% probability level.* Selected bond parameters: N(4)–C(8) = 1.376(3), N(9)–C(30) = 1.370(3), N(4)–N(5) = 1.362(3), N(9)–N(10) = 1.368(3), N(5)–C(16) = 1.291(3), N(10)–C(38) = 1.282(3), Br(1)–C(20) = 1.897(3), Br(2)–C(42) = 1.898(3) Å; N(5)–N(4)–C(8) = 121.8(2), C(16)–N(5)–N(4) = 114.1(2), N(10)–N(9)–C(30) = 122.5(2), C(38)–N(10)–N(9) = 113.6(2)°. H-Bonding: N(4)H(4)B···O(1) = 2.06, N(4)···O(1) = 2.930(3) Å, N(4)–H(4B)···O(1) = 170°; O(1)H(100)···N(8) = 2.16(4), O(1)···N(8) = 2.923(3) Å, O(1)–H(100)···N(8) = 160(4)°; O(2)H(201)···O(1) = 2.12(5), O(2)···O(1) = 2.904(3) Å, O(2)–H(201)···O(1) = 173(3)°; N(9)H(9B)···O(2) = 1.98, N(9)···O(2) = 2.855(3) Å, N(9)–H(9B)···O(2) = 178°; O(2)H(200)···N(1) = 2.11(2), O(2)···N(1) = 2.880(3) Å, O(2)–H(200)···N(1) = 165(4)°. Atom H(101) is H-bonded to an adjacent motif (see text): O(1)H(101)···N(3^i) = 2.11(4), O(1)···N(3^i) = 2.859(3) Å, O(1)–H(101)···N(3^i) = 157(3)°. Symmetry code i = $-x$, $1-y$, $1-z$.

ii = $-1+x$,$1+y$, z; iii = $1+x$, $-1+y$, z) both within and between the sheets. Short N···Br contacts stabilizing solid-state structures are not uncommon [36].

X-Ray-quality crystals of the NO_2 derivative **7** were grown by slow evaporation of a $CHCl_3$ solution of the compound. The asymmetric unit contains two independent molecules, one of which is shown in *Fig. 8*. Each molecule is close to planar. With the exception of the atoms of the NO_2 groups, the maximum deviation from the least-squares plane through one molecule is 0.24 Å, and 0.19 Å for the second. Each NO_2 unit is twisted only slightly out of the plane of the aromatic ring to which it is attached (3.2° for molecule A and 4.1° for B). The angle between the least-squares planes through the two independent molecules is 70.6°. Each molecule is involved in the same types of intermolecular interactions: $NH_{amine}\cdots O_{nitro}$ H-bonds and π-stacking of aromatic rings. The former is responsible for the assembly of planar ribbons which run parallel to the *b* axis, and the latter for the stacking of the ribbons into a herringbone assembly (*Fig. 9*).

In addition to our interest in using compounds **1**–**9** as ligands in supramolecular assemblies, the electronic spectroscopic properties of these phenylhydrazone derivatives are of interest in their own right. Like $[H_2\mathbf{1}][MeOSO_3]_2$, each of the methyl sulfate

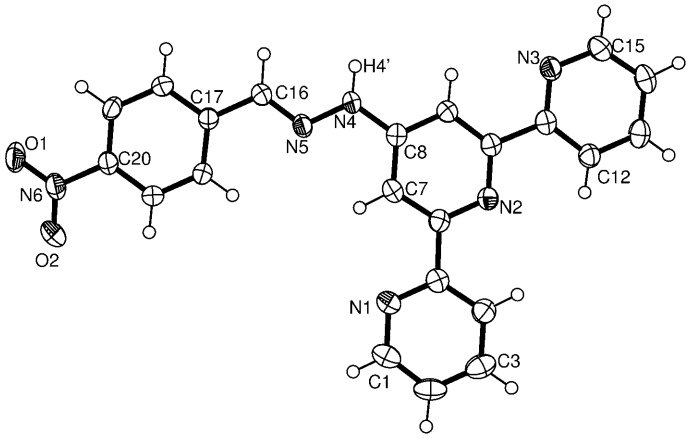

Fig. 8. *The structure of one of the two independent molecules* (A) *of* **7** *with thermal ellipsoids plotted at 50% probability level.* Selected bond parameters: N(4)–C(8) = 1.384(3), N(4)–N(5) = 1.358(3), N(5)–C(16) = 1.288(3), C(16)–C(17) = 1.463(3), O(1)–N(6) = 1.231(3), O(2)–N(6) = 1.219(3) Å; N(5)–N(4)–C(8) = 118.7(2), C(16)–N(5)–N(4) = 117.6(2), O(1)–N(6)–O(2) = 122.8(2)°. Bond parameters for the second molecule (B) are similar.

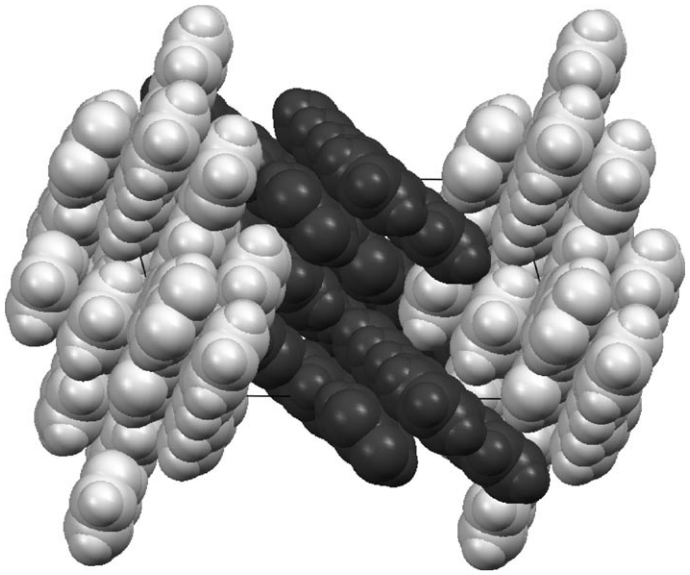

Fig. 9. *Packing of molecules of* **7**; *the unit cell is viewed down the* b *axis.* Crystallographically independent molecules A and B are shown in pale and dark grey, respectively.

or ethyl sulfate salts of $[H_2\mathbf{5}]^{2+}$, $[H_2\mathbf{6}]^{2+}$, $[H_2\mathbf{7}]^{2+}$, $[H_2\mathbf{8}]^{2+}$, or $[H_2\mathbf{9}]^{2+}$ is bright yellow, while the neutral hydrazones, with the exception of **7**, are off-white or pale yellow. The NO_2 derivative **7** is orange. The conversion of diprotonated to neutral ligands was carried out with K_2CO_3, but the addition of a stronger base such as KO*t*Bu results in the

deprotonation of the NH group. Compound **1** is the parent for the series of derivatives **6**–**9**, and titration of aqueous NaOH solution into a DMSO solution of $[H_2\mathbf{1}][MeO\text{-}SO_3]_2$ ($2.9 \cdot 10^{-5}$ mol dm^{-3}) is accompanied by a decrease in intensity of the absorption at 356 nm and a shift to 344 nm. If the base is changed to KO^{t}Bu, a new absorption appears at 459 nm when the base is present in excess, a consequence of the extended conjugation that is possible once the NH group is deprotonated. This is a general observation for compounds **1**, **6**, **8**, and **9**. Addition of excess KO^{t}Bu to a DMSO solution of orange **7** ($2.2 \cdot 10^{-5}$ mol dm^{-3}) results in the loss of the absorption at 400 nm and appearance of an absorption ($\varepsilon = 34000$ dm^3 mol^{-1} cm^{-1}) at 646 nm leading to an intense red colour consistent with extension of the π-system from the tpy to NO_2 domains once the NH group is deprotonated.

Conclusions. – We described the syntheses of five 2,2′:6′,2″-terpyridine ligands functionalized in the 4′-position with a hydrazone substituent RR′C=N–NH (R = R′ = Me (**5**); R = H, R′ = 4-BrC_6H_4 (**6**), 4-$O_2NC_6H_4$ (**7**), 4-$MeOC_6H_4$ (**8**), or 3,5-$(MeO)_2C_6H_3$ (**9**)). These extend our previously reported series of ligands in this family. Protonation of the tpy domain of **5**–**9** is facile, and the solution behaviour of the ligands was studied by NMR and electronic spectroscopies. In the solid state, the tpy domains in **5**, **6**·H_2O, and **7** adopt the expected s-*trans*,s-*trans*-conformation, while protonation causes a switch to an s-*cis*,s-*cis*-arrangement, exemplified in $[H\mathbf{9}][BF_4]$. In the solid state, H-bonding involving the NH unit is important in all the structures. In a future paper, we will report the synthesis, structures, and spectroscopic properties of homoleptic complexes of iron(II) and ruthenium(II) containing ligands **1**–**9**.

We thank the *Swiss National Science Foundation* and the University of Basel for financial support.

Experimental Part

General. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-DRX 500* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS: *Finnigan-MAT-LCQ* mass spectrometer; in *m*/*z* (rel. %).

*[H$_2$**5**][MeOSO$_3$]$_2$.* Acetone (0.5 ml, 7 mmol) was added to 4′-hydrazino-2,2′:6′,2″-terpyridine (0.20 g, 0.76 mmol) in hot MeOH. A few drops of conc. H_2SO_4 were added to the soln., and a yellow precipitate formed which dissolved within a few min. The soln. was heated under reflux for 3 h, and then cooled to r.t. At this stage, only a small amount of solid was present. The addition of Et_2O yielded a bright yellow, hygroscopic solid which was collected by filtration and washed with EtOH/Et_2O: $[H_2\mathbf{5}][MeOSO_3]_2$ (0.30 g, *ca.* 75%). Yellow solid. A pure sample was not obtained, and the compound was used without further purification.

*[H**5**][BF$_4$].* A sample of $[H_2\mathbf{5}][MeOSO_3]_2$ was dissolved in a minimum amount of hot H_2O, and a large excess of solid $NaBF_4$ was added. After stirring at r.t. for 1 h, a yellow-green solid formed which was collected and washed well with H_2O and cold EtOH. ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 10.94 (br., NH); 8.90 (*d*, *J* = 4.4, 2 H, H_{A6}); 8.41 (br., H_{A3}); 8.18 (*t*, *J* = 7.2, H_{A4}); 8.03 (br., 2 H, H_{B3}); 7.74 (*m*, 2 H, H_{A5}); 2.14 (*s*, Me); 2.08 (*s*, Me). ESI-MS: 304.1 ($[H\mathbf{5}]^+$; calc. 304.4), 326.1 ($[\mathbf{5} + Na]^+$; calc. 326.1), 629.0 ($[(\mathbf{5})_2 + Na]^+$; calc. 629.3).

Propane-2-one 2-([2,2′:6′,2″-Terpyridin]-4′-yl)hydrazone (**5**). $[H_2\mathbf{5}][MeOSO_3]_2$ (0.20 g, 0.38 mmol) was dissolved in H_2O (30 ml) and sat. aq. $KHCO_3$ soln. was added to give a colorless soln. This was extracted with $CHCl_3$ (4 × 100 ml), dried ($MgSO_4$), and the residue recrystallized from MeOH/$CHCl_3$: **5** (0.092 g, 79%). Off-white solid. ^{1}H-NMR (500 MHz, $CDCl_3$, 295K): 8.69 (*d*, *J* = 3.2, 2 H, H_{A6}); 8.61 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.10 (*s*, 2 H, H_{B3}); 7.83 (*t*, *J* = 7.7, 2 H, H_{A4}); 7.48 (*s*, NH); 7.31 (*dd*, *J* = 5.2, 5.8, 2 H, H_{A5}); 2.09 (*s*, Me_b); 1.88 (*s*, Me_a). ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 9.62 (*s*, NH); 8.68 (*ddd*, *J* = 4.6, 1.3,

0.6, 2 H, H_{A6}); 8.58 (*d*, *J* = 7.8, 2 H, H_{A3}); 8.16 (*s*, 2 H, H_{B3}); 7.96 (*td*, *J* = 7.7, 1.7, H_{A4}); 7.45 (*ddd*, *J* = 7.5, 4.8, 1.1, 2 H, H_{A5}); 2.03 (*s*, Me_b); 1.96 (*s*, Me_a). ^{13}C-NMR (125 MHz, $CDCl_3$, 295K): 156.7 ($C_{A2/B2}$); 156.2 ($C_{A2/B2}$); 153.32 (C_{B4}); 149.0 (C_{A6}); 146.5 (C=N); 136.8 (C_{A4}); 123.6 (C_{A5}); 121.4 (C_{A3}); 104.9 (C_{B3}); 25.3 ($C_{Me\text{-}b}$); 14.2 ($C_{Me\text{-}a}$). ^{13}C-NMR (125 MHz, (D_6)DMSO, 295 K): 155.8 (C_{A2}); 155.1 (C_{B2}); 153.7 (C_{B4}); 149.0 (C_{A6}); 147.6 (C=N); 137.1 (C_{A4}); 124.0 (C_{A5}); 120.6 (C_{A3}); 104.1 (C_{B3}); 25.1 ($C_{Me\text{-}b}$); 17.0 ($C_{Me\text{-}a}$). ESI-MS: 304.1 ([**5** + H]$^+$; calc. 304.4). Anal. calc. for $C_{18}H_{17}N_5 \cdot 0.33\ CH_3OH$: C 69.57, H 6.00, N 21.93; found: C 69.95, H 5.66, N 21.81.

*[H_2**6**][$MeOSO_3$]$_2$.* The 4-bromobenzaldehyde (0.15 g, 0.81 mmol) was added to 4′-hydrazino-2,2′:6′,2″-terpyridine (0.20 g, 0.76 mmol) in hot MeOH. A few drops of conc. H_2SO_4 were added, and a bright orange precipitate immediately formed. The suspension was heated under reflux for 3 h, then cooled to r.t. After cooling, a bright yellow precipitate had formed which was collected by filtration and washed with EtOH: [H_2**6**][$MeOSO_3$]$_2$ (0.36 g, *ca.* 55%). Yellow solid. The compound was used without further purification.

*[H**6**][BF_4].* A sample of [H_2**6**][$MeOSO_3$]$_2$ was dissolved in a minimum amount of hot H_2O, and $NaBF_4$ was added, and a yellow-green precipitate formed immediately. ESI-MS: 432.0 ([H**6**]$^+$; calc. 431.3). Anal. calc. for $C_{22}H_{17}BBrF_4N_5 \cdot 2.5\ H_2O$: C 46.92, H 3.94, N 12.44; found: C 47.18, H 3.78, N 12.53.

[C(E)]-4-Bromobenzaldehyde 2-([2,2′:6′,2″-Terpyridin]-4′-yl)hydrazone (**6**). [H_2**6**][$MeOSO_3$]$_2$ (0.20 g, 0.31 mmol) was dissolved in H_2O (10 ml), and sat. aq. $KHCO_3$ soln. (20 ml) was added. The resulting pale yellow suspension was extracted into CH_2Cl_2 (3 × 50 ml), and the yellow soln. was dried ($MgSO_4$). Evaporation gave **6** as a sticky yellow solid which was purified by column chromatography (short column, alumina, CH_2Cl_2/MeOH 99:1): **6** (0.051 g, 39%). Yellow needles. ^{1}H-NMR (500 MHz, $CDCl_3$, 295 K): 8.71 (*d*, *J* = 4.1, 2 H, H_{A6}); 8.61 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.21 (*s*, NH); 8.15 (*s*, 2 H, H_{B3}); 7.85 (*t*, *J* = 7.7, 2 H, H_{A4}); 7.64 (*s*, N=CH); 7.58 (*d*, *J* = 7.4, 2 H, H_{C2}); 7.50 (*d*, *J* = 7.4, 2 H, H_{C3}); 7.33 (*t*, *J* = 5.5, 2 H, H_{A5}). ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 11.21 (*s*, NH); 8.73 (*d*, *J* = 4.6, 2 H, H_{A6}); 8.61 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.15 (br. *s*, 2 H, H_{B3}); 8.02 (*s*, N=CH); 7.99 (*td*, *J* = 7.8, 1.7, 2 H, H_{A4}); 7.70 (*d*, 8.7, 2 H, H_{C2}); 7.67 (*d*, *J* = 8.7, 2 H, H_{C3}); 7.48 (*ddd*, *J* = 7.4, 4.9, 0.9, 2 H, H_{A5}). ^{13}C-NMR (125 MHz, $CDCl_3$, 295 K): 156.6 (C_{A2}); 152.3 (C_{B2}); 149.1 (C_{A6}); 139.0 (C=N); 137.0 (C_{A4}); 133.6 (C_{C1}); 131.9 (C_{C3}); 128.3 (C_{C2}); 123.9 (C_{A5}); 123.3 (C_{C4}); 121.6 (C_{A3}); 105.0 (C_{B3}). ^{13}C-NMR (125 MHz, (D_6)DMSO, 295 K): 155.6 ($C_{C2/B2}$) 155.5 ($C_{A2/B2}$); 152.5 (C_{B4}); 149.2 (C_{A6}); 139.5 (C=N); 137.2 (C_{A4}); 134.2 (C_{C1}); 131.8 (C_{C3}); 128.1 (C_{C2}); 124.2 (C_{A5}); 122.0 (C_{C4}); 120.7 (C_{A3}); 103.8 (C_{B3}). ESI-MS: 432.0 ([**6** + H]$^+$; calc. 432.1). Anal. calc. for $C_{22}H_{16}N_5Br \cdot 0.33\ H_2O$: C 60.57, H 3.85, N 16.05; found: C 60.77, H 3.86, N 15.61.

*[H_2**7**][$EtOSO_3$]$_2$.* The 4-nitrobenzaldehyde (0.15 g, 0.99 mmol) was added to 4′-hydrazino-2,2′:6′,2″-terpyridine (0.21 g, 0.80 mmol) in hot EtOH. A few drops of conc. H_2SO_4 were added, and a yellow-orange precipitate immediately formed. The suspension was heated under reflux for 3 h, then cooled to r.t. Filtration yielded a bright yellow powder which was washed with EtOH: [H_2**7**][$EtOSO_3$]$_2$ (0.43 g, 87%). ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 11.9 (br., NH); 8.82 (*d*, *J* = 4.1, 2 H, H_{A6}); 8.66 (br. *d*, *J* = 7.4, 2 H, H_{A3}); 8.34 (*d*, *J* = 8.8, 2 H, H_{C2}); 8.25 (*s*, N=CH); 8.17 (br., H_{B3}); 8.11 (*m*, 4 H, H_{C3+A4}); 7.63 (*m*, 2 H, H_{A5}); 3.73 (*q*, *J* = 7.13, MeCH_2, see text); 1.10 (*t*, *J* = 7.12, *Me*CH_2, see text). Anal. calc. for $C_{26}H_{26}N_6O_{10}S_2 \cdot H_2O$: C 46.98, H 4.25, N 12.64; found: C 46.97, H 4.12, N 12.61.

*[H**7**][BF_4].* [H_2**7**][$EtOSO_3$]$_2$ (0.20 g, 0.31 mmol) was dissolved in a minimum amount of hot H_2O, and excess $NaBF_4$ was added. The yellow-green solid that formed was collected by filtration and washed well with H_2O and cold EtOH: [H**7**][BF_4] (0.081 g, 54%). Yellow solid. ESI-MS: 397.1 ([H**7**]$^+$; calc. 397.2).

[C(E)]-4-Nitrobenzaldehyde 2-([2,2′:6′,2″-Terpyridin]-4′-yl)hydrazone (**7**). [H_2**7**][$EtOSO_3$]$_2$ (0.20 g, 0.31 mmol) was dissolved in H_2O (50 ml). Solid K_2CO_3 (5g) was added, and the suspension was extracted into CH_2Cl_2 (3 × 150 ml), washed with H_2O (2 × 250 ml), and dried ($MgSO_4$). The solvent was evaporated to give an orange powder which was recrystallized twice from EtOH/CH_2Cl_2: **7** (0.052 g, 41%). Orange needles. ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 11.52 (*s*, NH); 8.74 (*d*, *J* = 3.8, 2 H, H_{A6}); 8.62 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.33 (*d*, *J* = 8.8, 2 H, H_{C2}); 8.20 (br. *s*, 2 H, H_{B3}); 8.14 (*s*, HC=N); 8.00 (*m*, 4 H, H_{A4+C3}); 7.50 (*ddd*, *J* = 7.6, 4.9, 1.1, 2 H, H_{A5}). ^{13}C-NMR (125 MHz, (D_6)DMSO, 295 K): 155.7 ($C_{A2/B2}$); 155.4 ($C_{A2/B2}$); 152.2 (C_{B4}); 149.2 (C_{A6}); 147.0 (C_{C4}); 141.4 (C_{C1}); 138.2 (C=N); 137.3 (C_{A4}); 127.0 (C_{C2}); 124.3 ($C_{A5/C3}$); 124.2 ($C_{A5/C3}$); 120.8 (C_{A3}); 103.7 (C_{B3}). ESI-MS: 397.1 ([**7** + H]$^+$; calc. 397.4). Anal. calc. for $C_{22}H_{16}N_6O_2$: C 66.66, H 4.07, N 21.20; found: C 66.51, H 4.10, N 21.00.

*[H_2**8**]*[$MeOSO_3$]$_2$*. The 4-methoxybenzaldehyde (0.11 g, 0.81 mmol) was added to 4′-hydrazino-2,2′:6′,2″-terpyridine (0.20 g, 0.76 mmol) in hot MeOH. A few drops of conc. H_2SO_4 were added, resulting in the formation of an orange precipitate. The suspension was heated under reflux for 3 h, then cooled to r.t. [H_2**8**][$MeOSO_3$]$_2$ precipitated, was collected by filtration, washed with EtOH, and isolated as an orange powder (0.46 g, 99%). The compound was used without further purification.

*[H**8**]BF_4*. A sample of [H_2**8**][$MeOSO_3$]$_2$ was dissolved in a minimum amount of hot H_2O. Addition of a large excess of solid $NaBF_4$ yielded a yellow precipitate. ESI-MS: 382.1 ([H**8**]$^+$; calc. 382.2). Anal. calc. for $C_{23}H_{20}BF_4N_5O \cdot 0.75\ H_2O$: C 57.22, H 4.49, N 14.51; found: C 57.33, H 4.32, N 14.51.

*[C(*E*)]-4-Methoxybenzaldehyde 2-([2,2′:6′,2″-Terpyridin]-4′-yl)hydrazone* (**8**). [H_2**8**][$MeOSO_3$]$_2$ (0.20 g, 0.33 mmol) was dissolved in hot H_2O (20 ml), and solid K_2CO_3 (5 g) was added, to give a milky suspension. CH_2Cl_2 (100 ml) was added, and the biphasic mixture was sonicated for 1 h. The aq. layer was extracted with CH_2Cl_2 (2 × 100 ml), the combined org. phase washed with H_2O (2 × 100 ml) and dried (Na_2SO_4), the solvent evaporated, and the residue purified by column chromatography (short column, alumina, CH_2Cl_2/MeOH 99:1): **8** (0.093 g, 74%). Pale yellow solid. ^{1}H-NMR (500 MHz, (D_6)DMSO, 295 K): 10.97 (*s*, NH); 8.72 (*d*, *J* = 4.4, 2 H, H_{A6}); 8.60 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.12 (*s*, 2 H, H_{B3}); 8.00 (*s*, HC=N); 7.98 (*t*, *J* = 7.5, 2 H, H_{A4}); 7.69 (*d*, *J* = 8.5, 2 H, H_{C2}); 7.48 (*dd*, *J* = 6.9, 5.4, 2 H, H_{A5}); 7.05 (*d*, *J* = 8.8, 2 H, H_{C3}); 3.81 (*s*, Me). ^{13}C-NMR (125 MHz, (D_6)DMSO 295 K): 160.1 (C_{C4}); 156.6 (C_{A2}); 156.4 (C_{B2}); 152.7 (C_{B4}); 149.1 (C_{A6}); 140.7 (C=N); 137.2 (C_{A4}); 127.8 (C_{C2}); 127.5 (C_{C1}); 124.1 (C_{A5}); 120.7 (C_{A3}); 114.4 (C_{C3}); 103.7 (C_{B3}); 55.3 (MeO). ESI-MS: 382.2 ([H**8**]$^+$; calc. 382.2). Anal. calc. for $C_{23}H_{19}N_5O \cdot 0.25\ H_2O$: C 71.58, H 5.09, N 18.15; found: C 71.60, H 5.19, N 17.84.

*[H_2**9**]*[$MeOSO_3$]$_2$*. The 3,5-dimethoxybenzaldehyde (0.15 g, 0.90 mmol) was added to 4′-hydrazino-2,2′:6′,2″-terpyridine (0.20 g, 0.76 mmol) in hot MeOH. A few drops of H_2SO_4 were added to the soln., and a bright yellow precipitate formed after a few seconds. The suspension was heated under reflux for 3 h and then cooled to r.t. [H_2**9**][$MeOSO_3$]$_2$ (0.30 g, *ca.* 62%) was isolated as a yellow powder, after filtration and washing with EtOH. The compound was used without further purification.

*[H**9**]*[BF_4]*. A sample of [H_2**9**][$MeOSO_3$]$_2$ was dissolved in a minimum amount of hot H_2O, and solid $NaBF_4$ was added. After stirring at r.t. for 1 h, a yellow-green solid had formed which was collected by filtration and washed well with H_2O and cold EtOH. ESI-MS: 412.1 ([H**9**]$^+$), 411.2, 434.4 ([**9** + Na^+]; calc. 434.2), 845.0 ([(**9**)$_2$ + Na^+]; calc. 845.3). Anal. calc. for $C_{24}H_{22}BF_4N_5O_2 \cdot 3\ H_2O$: C 52.19, H 4.93, N 12.68; found: C 52.44, H 4.20, N 12.60.

*[C(*E*)]-3,5-Dimethoxybenzaldehyde 2-([2,2′:6′,2″-Terpyridin]-4′-yl)hydrazone* (**9**). Solid K_2CO_3 (5 g) was added to a suspension of [H_2**9**][$MeOSO_3$]$_2$ (0.20 g, 31 mmol) in H_2O (50 ml). CH_2Cl_2 (100 ml) was added, and the mixture was sonicated for 1 h. The org. phase was washed with H_2O (2 × 100 ml) and dried ($MgSO_4$) and the solvent evaporated: **9** (0.11 g, 86%). Off-white powder. ^{1}H-NMR (500 MHz, (D_6)DMSO, 295K): 11.15 (*s*, NH); 8.73 (*d*, *J* = 4.1, 2 H, H_{A6}); 8.60 (*d*, *J* = 7.9, 2 H, H_{A3}); 8.15 (br. *s*, 2 H, H_{B3}); 7.98 (*t*, *J* = 7.7, 2 H, H_{A4}); 7.97 (*s*, HC=N); 7.47 (*dd*, *J* = 6.6, 5.4, 2 H, H_{A5}); 6.91 (*s*, 2 H, H_{C2}); 6.56 (*s*, 1 H, H_{C4}); 3.82 (*s*, 2 Me). ^{13}C-NMR (125 MHz, (D_6)DMSO, 295 K): 160.8 (C_{C2}); 155.5 (C_{A2+B2}); 152.6 (C_{B4}); 149.2 (C_{A6}); 140.5 (C=N); 137.2 (C_{A4}); 136.9 (C_{C1}); 124.2 (C_{A5}); 120.7 (C_{A3}); 104.4 (C_{A2}); 103.8 (C_{B3}); 100.7 (C_{C4}); 55.3 (MeO). ESI-MS: 412.2 ([H**9**]$^+$; calc. 412.2). Anal. calc. for $C_{24}H_{21}N_5O_2 \cdot 0.5\ CH_3OH$: C 68.83, H 5.42, N 16.38; found: C 68.56, H 5.40, N 16.06.

Crystal-Structure Determinations. General. Data were collected on a *Bruker-Nonius-Kappa-CCD* or *Stoe-IPDS* instrument; data reduction, solution, and refinement used the programs COLLECT [37], SIR92 [38], DENZO/SCALEPACK [39], and CRYSTALS [40], or *Stoe-IPDS* software [41] and SHELXL97 [42], structures were analysed by Mercury v. 2.2 [43]. ORTEP Diagrams were drawn with ORTEP-3 for Windows [44]. Crystallographic data were deposited with the *Cambridge Crystallographic Data Centre*, deposition numbers CCDC 726089 – 726092 for **5**, **6** · H_2O, **7**, and [H**9**][BF_4]. These data can be obtained free of charge *via* www.ccdc.ac.uk/data_request/cif.

Crystal Data of **5**. $C_{18}H_{17}N_5$, M_r 303.37, yellow block; monoclinic, space group *C*2/*c*; *a* = 12.200(2), *b* = 12.502(3), *c* = 20.658(4) Å, *β* = 91.55(3)°, *V* = 3149.9(11) Å^3, *Z* = 8, $D_{calc.}$ = 1.279 Mg m^{-3}; $\mu(MoK_\alpha)$ = 0.080 mm^{-1}, *T* 173 K, 6762 reflections collected. Refinement of 5339 reflections (208 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0511 (R_1 all data = 0.0593), wR_2 = 0.0570 (wR_2 all data = 0.0664), R_{int} = 0.065, g.o.f. = 1.0386.

Crystal Data of **6**·H_2O. $C_{22}H_{18}BrN_5O$, M_r 448.31, yellow block; triclinic, space group $P-1$; $a=11.147(2)$, $b=12.328(3)$, $c=15.273(3)$ Å, $\alpha=95.93(3)$, $\beta=102.46(3)$, $\gamma=104.38(3)^\circ$, $V=1957.7(8)$ Å^3, $Z=4$, $D_{calc.}=1.521$ Mg m^{-3}; $\mu(MoK_\alpha)=2.124$ mm^{-1}, T 200(2) K, 40694 reflections collected, merging $r=0.0927$. Refinement of 535 parameters with 9413 independent reflections against F^2 converged at final $R_1=0.0527$ (R_1 all data = 0.0669), $wR_2=0.1144$ (wR_2 all data = 0.1207), g.o.f. = 1.185.

Crystal Data of **7**. $C_{22}H_{16}N_6O_2$, M_r 396.41, orange block; monoclinic, space group $P2_1/c$; $a=19.617(4)$, $b=17.698(3)$, $c=11.301(2)$ Å, $\beta=105.66(3)^\circ$, $V=3777.9(12)$ Å^3, $Z=8$, $D_{calc.}=1.394$ Mg m^{-3}; $\mu(MoK_\alpha)=0.094$ mm^{-1}, T 223(2) K, 47531 reflections collected, merging $r=0.0699$. Refinement of 557 parameters with 6671 independent reflections against F^2 converged at final $R_1=0.0635$ (R_1 all data = 0.0851), $wR_2=0.1193$ (wR_2 all data = 0.1268), g.o.f. = 1.237.

*Crystal Data of [H***9***][BF*$_4$*]*. $C_{24}H_{22}BF_4N_5O_2$, M_r 499.27, colorless plate; monoclinic, space group $C2/c$; $a=32.0072(8)$, $b=7.0994(2)$, $c=25.6676(6)$ Å, $\beta=122.985(1)^\circ$, $V=4892.4(2)$ Å^3, $Z=8$, $D_{calc.}=1.356$ Mg m^{-3}; $\mu(MoK_\alpha)=0.109$ mm^{-1}, T 173 K, 5619 reflections collected. Refinement of 3282 reflections (326 parameters) with $I>1.8\sigma(I)$ converged at final $R_1=0.0564$ (R_1 all data = 0.0996), $wR_2=0.0654$ (wR_2 all data = 0.0916), $R_{int}=0.022$, g.o.f. = 1.1042.

REFERENCES

[1] M. Katyal, Y. Dutt, *Talanta* **1975**, *22*, 151.
[2] R. B. Singh, P. Jain, R. P. Singh, *Talanta* **1982**, *29*, 77.
[3] Y. Zhang, D. M. Wilson, *Sci. Synth.* **2004**, *27*, 723.
[4] S. Kim, J.-Y. Yoon, *Sci. Synth.* **2004**, *27*, 671.
[5] K. R. West, S. Otto, *Curr. Drug Discovery Technol.* **2005**, *2*, 123.
[6] C. A. M. Fraga, E. J. Barreiro, *Curr. Med. Chem*. **2006**, *13*, 167.
[7] S. Rollas, S. G. Küçükgüzel, *Molecules* **2007**, *12*, 1910.
[8] C. M. Armstrong, P. V. Bernhardt, P. Chin, D. R. Richardson, *Eur. J. Inorg. Chem*. **2003**, 1145.
[9] P. V. Bernhardt, P. Chin, P. C. Sharpe, D. R. Richardson, *Dalton Trans.* **2007**, 3232.
[10] J. V. Grazulevicius, *Polym. Adv. Technol.* **2006**, *17*, 694.
[11] R. U. A. Khan, O.-P. Kwon, A. Tapponnier, A. N. Rashid, P. Günter, *Adv. Funct. Mater.* **2006**, *16*, 180.
[12] C. Serbutoviez, C. Bosshard, G. Knöpfle, P. Wyss, P. Prêtre, P. Günter, K. Schenk, E. Solari, G. Chapuis, *Chem. Mater*. **1995**, *7*, 1198.
[13] D. Lupo, H. Ringsdorf, A. Schuster, M. Seitz, *J. Am. Chem. Soc*. **1994**, *116*, 10498.
[14] D. Saravanakumar, S. Devaraj, S. Iyyampillai, K. Mohandoss, M. Kandaswamy, *Tetrahedron Lett*. **2008**, *49*, 127.
[15] D. Millán, M. Domínguez, M. C. Rezende, *Dyes Pigm.* **2008**, *77*, 441.
[16] R. S. Becker, F. Chagneau, *J. Am. Chem. Soc*. **1992**, *114*, 1373.
[17] V. Getautis, J. V. Grazulevicius, M. Daskeviciene, T. Malinauskas, V. Jankauskas, J. Sidaravicius, A. Undzenas, *Eur. Polym. J.* **2007**, *43*, 3597.
[18] A.-M. Stadler, N. Kyritsakas, J.-M. Lehn, *Chem. Commun.* **2004**, 2024.
[19] A.-M. Stadler, N. Kyritsakas, G. Vaughan, J.-M. Lehn, *Chem. – Eur. J.* **2007**, *13*, 59.
[20] L. H. Uppadine, J.-P. Gisselbrecht, J.-M. Lehn, *Chem. Commun*. **2004**, 718.
[21] L. H. Uppadine, J.-M. Lehn, *Angew. Chem., Int. Ed.* **2004**, *43*, 240.
[22] M. Ruben, J.-M. Lehn, G. Vaughan, *Chem. Commun*. **2003**, 1338.
[23] F. Loiseau, F. Nastasi, A.-M. Stadler, S. Campagna, J.-M. Lehn, *Angew. Chem., Int. Ed.* **2007**, *46*, 6144.
[24] A.-M. Stadler, N. Kyritsakas, R. Graff, J.-M. Lehn, *Chem. – Eur. J.* **2006**, *12*, 4503.
[25] M. Barboiu, M. Ruben, G. Blasen, N. Kyritsakas, E. Chacko, M. Dutta, O. Radekovich, K. Lenton, D. J. R. Brook, J.-M. Lehn, *Eur. J. Inorg. Chem*. **2006**, 784.
[26] A.-M. Stadler, F. Puntoriero, S. Campagna, N. Kyritsakas, R. Welter, J.-M. Lehn, *Chem. – Eur. J.* **2005**, *11*, 3997.
[27] J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price, S. Schaffner, J. A. Zampese, *Dalton Trans.* **2008**, 6742.

[28] J. E. Beves, E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner, J. A. Zampese, *Eur. J. Org. Chem.* **2008**, 3569.
[29] G. Lowe, A. S. Droz, T. Vilaiven, G. W. Weaver, L. Tweedale, J. M. Pratt, P. Rock, V. Yardley, S. L. Croft, *J. Med. Chem.* **1999**, *42*, 999.
[30] G. Lowe, A. S. Droz, J. J. Park, G. W. Weaver, *Bioorg. Chem*. **1999**, *27*, 477.
[31] Z. Zhou, G. H. Sarova, S. Zhang, Z. Ou, F. T. Tat, K. M. Kadish, L. Echegoyen, D. M. Guldi, D. I. Schuster, S. R. Wilson, *Chem. – Eur. J.* **2006**, *12*, 4241.
[32] J. E. Beves, E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner, *Polyhedron* **2008**, *27*, 2395.
[33] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512.
[34] A. Hergold-Brundić, Z. Popović, D. Matković-Calogović, *Acta Crystallogr., Sect. C* **1996**, *52*, 3154.
[35] A. Kochel, *Acta Crystallogr., Sect. E* **2006**, *62*, m37.
[36] S. Berski, Z. Ciunik, K. Drabent, Z. Latajka, J. Panek, *J. Phys. Chem. B* **2004**, *108*, 12327, and refs. cit. therein.
[37] COLLECT Software, *Nonius BV*, 1997–2001.
[38] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr*. **1994**, *27*, 435.
[39] Z. Otwinowski and W. Minor, 'Methods in Enzymology', Vol. 276, Eds. C. W. Carter Jr., and R. M. Sweet, Academic Press, New York, 1997, p. 307.
[40] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487.
[41] IPDS Software v 1.26, *Stoe & Cie*, Darmstadt, Germany, 1996.
[42] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
[43] I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B*, **2002**, *58*, 389.
[44] L. J. Farrugia, *J. Appl. Crystallogr.*, **1997**, *30*, 565.

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