

Towards technomimetic spoked wheels: dynamic hexakis-heteroleptic coordination at a hexakis-terpyridine scaffold†

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The synthesis of hexakis-terpyridine **4** and an expedient approach to its dynamic hexakis-heteroleptic complexes are elaborated, the latter being readily accessible precursors for the construction of technomimetic molecular spoked wheels.

Technomimetic molecules are design based molecules emulating the macroscopic world on the molecular level. In this context, technomimetic molecules,¹ molecular machines,² metal helicates,³ six-leg molecules,⁴ wheelbarrows,⁵ and motors⁶ have recently received considerable interest. On the other hand, real-world spoked wheels have not found a major correspondence in the nanoscopic chemical world,⁷ *i.e.* molecular wheels with an axle unit, sturdy spokes and a circular rim, although the concept 'molecular wheel' is being employed in various associations in the literature.⁸ While a dazzling multi-step approach to a covalent D_{6h} spoked wheel has recently been realised by Höger *et al.*,⁷ a supramolecular strategy forcefully profiting from suitable preorganisation of building blocks to reduce the number of steps has not yet been elaborated. A supramolecular approach to a D_{4h} technomimetic spoked wheel has been reported previously by Sanders⁹ (not called a spoked wheel) and more recently by Lindsey and Holten (D_{3h}),¹⁰ but in both cases only an imperfect execution of a circular rim was achieved due to the low symmetry. Other notable approaches suffer from flexible spokes, thus generating floppy wheels.¹¹ Clearly, the construction of a supramolecular spoked wheel poses some major challenges due to the construction of a planar set of sturdy supporting spokes that have to be thoroughly linked by a circular rim. This will either require a macrocycle as a rim that is imposed on the spoke set (Fig. 1A), or it necessitates a directed macrocyclisation starting from preoriented rim elements (Fig. 1B). Being convinced of the latter strategy, we would like to report herein on an approach towards the construction of a supramolecular D_{6h} spoke set endowed with rim elements. Our approach emanates from a planar hexakis-terpyridine scaffold constituting the spoke set, which is equipped in a key step with phenanthrolines (rim elements) that are attached to the spokes via the HETTAP concept¹² (*heteroleptic terpyridine and phenanthroline complex formation*).¹³ For the finalisation of

a complete spoked wheel, thus only a covalent or coordinative linkage between the rim elements will be required.

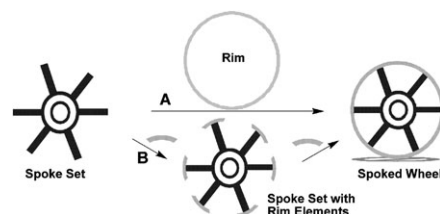


Fig. 1 Design of a technomimetic spoked wheel.

Chart 1 depicts phenanthrolines **1,2** and terpyridines **3,4** used as building blocks for the present study. Terpyridine **3** was purchased and used as received. Synthesis of compounds **1** and **2** was achieved using established protocols elaborated in our group.¹⁴ The presence of bulky alkylaryl groups at the 2,9-positions of the respective phenanthrolines **1,2** is essential to avoid formation of homoleptic complexes,¹⁵ thus guiding the reaction toward heteroleptic complexes with terpyridines.^{12,13}

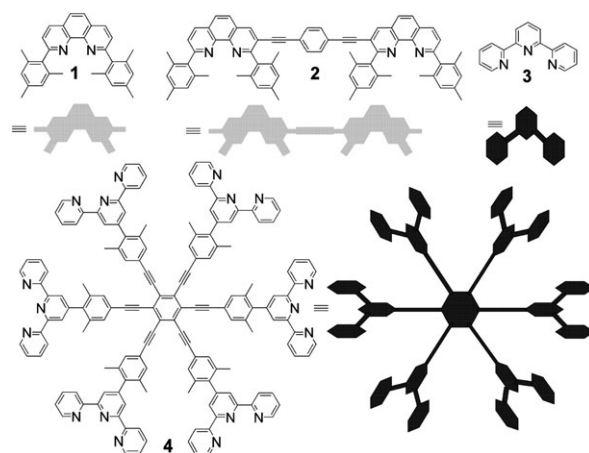


Chart 1 Compounds **1-4** and their cartoon representations.

As a key building block constituting the axle and spokes unit, we designed the D_{6h} symmetric hexakis-terpyridine **4**. After the first synthesis of hexaethynylbenzene (**6**) in 1986 by Vollhardt,¹⁶ several derivatives of this interesting family of fully conjugated, rigid, quasi two-dimensional hydrocarbons have been prepared and studied,¹⁷ but so far not with 2,2':6',2''-terpyridines as terminal ligands.¹⁸

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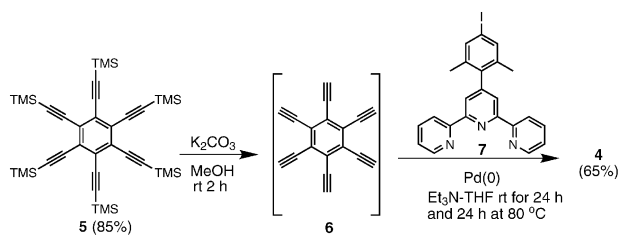


Fig. 2 Synthesis of **4**.

In Fig. 2, the synthesis of **4** is described. The first step involved the preparation of hexakis(trimethylsilylethynyl)benzene (**5**) via a Sonogashira coupling. Deprotection of **5** using K_2CO_3 in methanol led to hexaethynylbenzene (**6**).¹⁶ Since **6** was found to be very unstable, it was not purified for the ensuing step. The final transformation employed a Sonogashira coupling between **6** and **7**¹³ in the presence of Pd(0) and CuI as catalyst. For this step exclusion of oxygen was crucial, because traces thereof in the reaction mixture led to a notorious and inseparable mixture of products.

Compound **4** was characterised using standard organic techniques. As can be seen from the 1H and ^{13}C NMR spectra (ESI †), the methyl groups appeared as a single signal at 2.16 (1H) and 21.0 (^{13}C) ppm. In addition, the clean ESI-MS spectra of **4** and the experimental isotopic distribution for the protonated $4 + 3(H^+)$ (m/z 746.4 Da) and $4 + 2(H^+)$ (m/z 1119.1 Da) were in full agreement with the suggested structure.

Since it is well known that terpyridines can form bishomoleptic complexes in the presence of various metal ions,¹⁹ it was a challenging task to elaborate a hexakis-heteroleptic complex while avoiding any homoleptic ones. All initial efforts to react **1** and **4** with Zn^{2+} led to the formation of polymeric aggregates²⁰ as evidenced by a highly insoluble precipitate with only negligible amounts of the desired hexakis-heteroleptic complex being formed. Therefore, we turned our attention to the thermodynamically less stable copper(i) complexes,¹² also prepared via the HETTAP method,¹³ as use of copper(i) avoids formation of bishomoleptic octahedral terpyridine complexes. Thus, we were successful in preparing the Cu^+ complex **C1** which is a model for capping a spoke of ligand **4** with **1** as the rim element. Analogously, when phenanthrolines **1** or **2** were combined with terpyridine **4** in the presence of the appropriate amount of $[Cu(MeCN)_4]PF_6$ in dichloromethane, the dark red compounds **C2** and **C3** formed in virtually quantitative yield (Fig. 3). These assemblies were analysed by 1H NMR, ^{13}C NMR, IR, UV/Vis, ESI-MS and elemental analysis without the need for purification. They were found to be dynamic in nature, stable for several months and soluble in a variety of solvents like dichloromethane, acetonitrile, nitromethane, DMF, DMSO, etc.

Since it has been impossible so far to obtain single crystals, we have utilised spectroscopic techniques like ESI-MS, UV/Vis, NMR etc. to confirm the supramolecular structures. ESI-MS is one of the most important methods to elucidate the composition of metallo-supramolecular structures in solution.²¹ In our study, ESI-MS analysis provided conclusive evidence for the clean formation of the expected assemblies **C1–C3**. Fig. 4 displays the ESI-MS spectrum of **C3** as a representative example, showing the presence of four signals

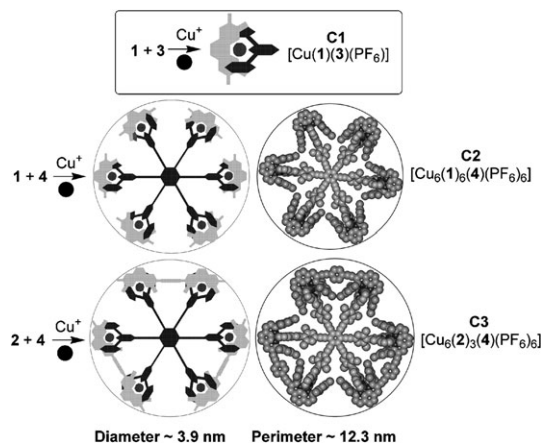


Fig. 3 Cartoon illustrations of **C1–C3** and computed structures of **C2** and **C3** (hydrogens are eliminated for clarity).

in the mass region $m/z = 200$ to 2000 , i.e. $[Cu_6(2)_3(4)]^{6+}$ (m/z 913.4 Da), $[Cu_6(2)_3(4)(PF_6)]^{5+}$ (m/z 1125.4 Da), $[Cu_6(2)_3(4)(PF_6)_2]^{4+}$ (m/z 1442.5 Da) and $[Cu_6(2)_3(4)(PF_6)_3]^{3+}$ (m/z 1972.2 Da). Notably, signals of the linear ligand **2** or of terpyridine **4** were not detectable. The experimental isotopic distributions (grey lines, for 4+ and 3+ charged species) were in good agreement with the calculated distributions (black lines). Similar results were also obtained for the assembly **C2** (ESI †), although it should be much more labile due to the presence of six mononuclear binding sites.

As can be seen from the 1H NMR spectra, the mesityl protons in **C1–C3** experienced a distinctive and diagnostic high field shift to ca. 6 ppm that is notably different from that in the free ligands (e.g. **1** in **C2** exhibits a shift of 6.22 ppm as compared to 6.96 ppm for the free ligand **1**, Fig. 5). Such a shift is typical for heteroleptic complex formation. Similar results were obtained for **C3** (6.24/6.15 ppm), but now the two mesityl units (in vs. out) have different environments in accordance with the overall structure (Fig. 3). Also the hexakis-terpyridine **4** experienced diagnostic shifts in the 1H NMR. In the free ligand, the methyl protons appeared as a single signal at 2.16 ppm (in $[D_2]$ dichloromethane, 25 °C, 400 MHz), while, upon complexation, the signal was shifted downfield, now emerging at 2.28 (in **C2**) and 2.42/2.22 ppm (in **C3**) (ESI †). This downfield shift is readily explained by the immersion of the methyl groups of **4** into the deshielding region of the mesityl rings of **1** and **2**. Likewise, the shifts of the methyls

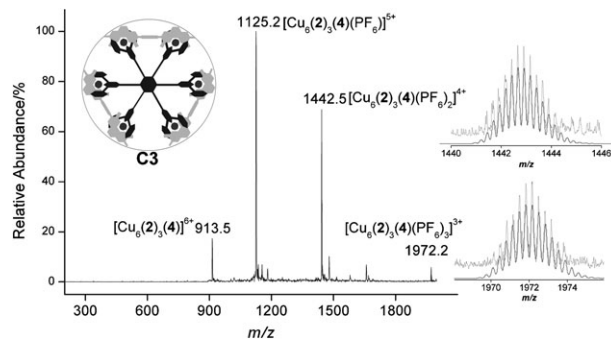


Fig. 4 ESI-MS spectra of **C3**.

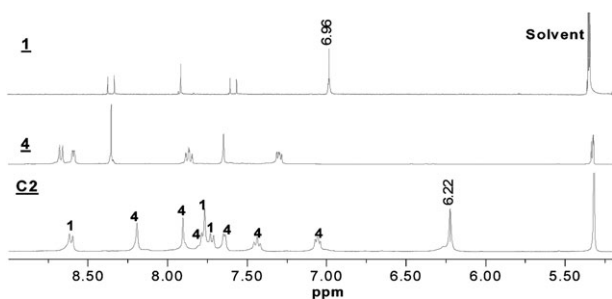


Fig. 5 ^1H NMR spectra of **1**, **4** and **C2** in CD_2Cl_2 .

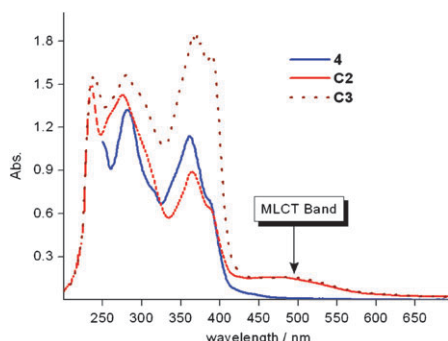


Fig. 6 UV/Vis absorption spectra of **4**, **C2** and **C3** (at 2.5×10^{-6} M) in dichloromethane at 25 °C.

in phenanthrolines **1** and **2** are instructive concerning the structure of the complexes. While ^1H NMR shifts of *p*- and *o*-methyls in free **1** show up at 2.33/2.05 ppm, those of **1** in complex **C2** are shifted to 1.85/1.54 ppm and similarly in complex **C1** to $\delta = 1.97/1.58$ ppm. For **C3** (1.96/1.94 and 1.45/1.43 ppm) the effect is even more pronounced.

UV/Vis absorption spectra can also be utilised for the characterisation of the assemblies. The absorption spectra of hexakis-terpyridine **4** and complexes **C2**, **C3** are shown in Fig. 6. The strong absorption bands at 250–400 nm correspond to typical ligand $\pi\text{-}\pi^*$ transitions,²² whereas the band at ~ 500 nm, definitely responsible for the red colour, was assigned to a metal-to-ligand-charge-transfer (MLCT) transition. For both assemblies, the MLCT bands were nearly identical, clearly indicative of extremely similar molecular environments at the metal centres. Moreover, these MLCT bands proved to be quite similar to those of analogous heteroleptic Cu^+ grid assemblies reported by our group.²³ The MLCT bands in the visible region at $\lambda_{\text{max}} = 479$ nm ($\epsilon_{\text{max}} = 63\,200\ \text{M}^{-1}\ \text{cm}^{-1}$) for **C2** and at 483 nm ($\epsilon_{\text{max}} = 62\,700\ \text{M}^{-1}\ \text{cm}^{-1}$) for **C3** represent six Cu^+ phenanthroline complex units. For comparison, MLCT bands in bis(2,2'-bipyridine) copper(i) complexes have typical $\epsilon_{\text{max}} = 6800\text{--}8500\ \text{M}^{-1}\ \text{cm}^{-1}$, while those for bisphenanthroline copper(i) complexes are in the range $3200\text{--}13\,200\ \text{M}^{-1}\ \text{cm}^{-1}$.²³

To gain some structural insight, we have performed MM⁺ computations (Hyperchem[®], Hypercube Inc.). Minimised space filling models of **C2** (other rotamers are also possible) and **C3** in Fig. 3 (*vide supra*) reveal a diameter and perimeter of 3.9 nm and 12.3 nm, respectively.

In conclusion, we present herein the first synthesis of the D_{6h} symmetric hexakis-terpyridine **4**, constituting our axle and

spoke set. Secondly, as a key step towards the construction of a spoked wheel we have achieved the selective formation of two multicomponent assemblies exhibiting dynamic hexakis-heteroleptic complexation. Thereby, rim elements have been attached onto the spokes, now being in place for a directed macrocyclisation. For final covalent linkages between the rim elements, however, we will need to introduce alkyne (for oxidative linkage) or alkene (for metathesis) groups in the appropriate positions of **1** (3,8-positions) and/or **2** (8,8'-positions). While this functionalisation is straightforward for **1**, the rotational flexibility in **C2** may also allow for an undesired inter 'supramolecular' coupling. Modification of **2** therefore may be more promising. Work along these lines is ongoing and hopefully will demonstrate the success of our strategy for the preparation of molecular spoked wheels as new technomimetic molecules.

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